GEOLOGICAL SURVEY OF CANADA
BULLETIN 451

GEOANALYSIS 90

AN INTERNATIONAL SYMPOSIUM ON THE ANALYSIS OF GEOLOGICAL MATERIALS

Edited by G.E.M. Hall

1993

Natural Resources Canada
Ressources naturelles Canada

Canada

GEOLOGICAL SURVEY OF CANADA
BULLETIN 451

GEOANALYSIS 90

AN INTERNATIONAL SYMPOSIUM ON THE ANALYSIS OF GEOLOGICAL MATERIALS

1993

Available in Canada through authorized
bookstore agents and other bookstores

or by mail from

Canada Communication Group — Publishing
Ottawa, Canada K1A 0S9

and from

Geological Survey of Canada offices:

601 Booth Street
Ottawa, Canada K1A 0E8

3303-33rd Street N.W.,
Calgary, Alberta T2L 2A7

A deposit copy of this publication is also available for
reference in public libraries across Canada

Cat. No. M42-451E
ISBN 0-660-15347-5

Price subject to change without notice

CONTENTS

Papers presented at Geoanalysis 90/Rapports présentés à Geoanalysis 90

Workshop/Atelier:

Foreword

"GEOANALYSIS 90" was the inaugural conference of an international series of symposia focusing on the analysis of geological materials. Over 100 delegates from 17 countries gathered at the spectacular site of Grandview in the Ontario Muskoka Lakes district on the sunny afternoon of Sunday, June 3rd, 1990. For the next three and a half days, discussions centred on three major themes: geoanalytical methodology; geostandard reference materials; and geoanalysis in the Developing World.

The conference was organised by members of the Geological Survey of Canada (Gwendy E.M. Hall and Judy E. Vaive) and the Ontario Geological Survey (Chris Riddle and colleagues) in cooperation with the International Working Group on Geostandards, the U.N. Department of Technical Cooperation for Development, the Canadian Centre for Mineral and Energy Technology, and the Natural Sciences and Engineering Research Council of Canada.

In addition to the meeting at Grandview, a one day Laboratory Design Workshop was held in Toronto at the Ontario Geological Survey (OGS), under the direction of Chris Riddle. Laboratory tours were organised in both Toronto and Ottawa, and a two day field trip was conducted by Mike Easton of the OGS.

The symposium was opened by the keynote address on the status of geostandards given by K. Govindaraju (Centre de Recherches Petrographiques et Geochimiques), the editor of that invaluable journal, Geostandards Newsletter. Two lively and informal discussion sessions were prepared and lead by Phil J. Potts (Open University) and Jean Kane (then of the U.S. Gelogical Survey). Phil aroused debate on influences on the quality of geoanalytical data (published herein) while Jean sought the audience's opinions in the controversial area of the derivation of recommended values from compiled data. Xuejing Xie astounded the audience with his description of the very extensive geochemical mapping program in China and also led a discussion on recommendations of analytical methods for the international geochemical mapping project (IGCP 259). Formal papers took the form of oral or poster presentations.

An appreciation for the variety of subject matter presented can be gleaned from a perusal of all the abstracts accepted and listed in this volume. It is readily apparent that the time of the conference reflected activities worldwide in lowering detection limits for the precious metals and in continuing advancements in the application of ICP mass spectrometry to geological samples. It was interesting to gain insight into the state of geoanalysis in developing countries and into the different challenges encountered there; some of the papers in this volume discuss such issues. Seven papers presented at this conference on the subject of geostandards and quality control have been published in the April 1991 issue of Geostandards Newsletter; this volume reflects those submitted on analytical methodology.

The success of this meeting was indicated by the unanimous vote to instigate an international series entitled GEOANALYSIS, building upon the themes of the 1990 conference and aiming to attract in greater number our colleagues, the geochemists. At the memorable banquet on June 6th, the torch of Chairman for GEOANALYSIS 94 was passed to Doug Miles of the British Geological Survey. So we look forward to meeting again in some ancient Hall in Merry Old England...

Gwendy E.M. Hall
Geological Survey of Canada

Avant-propos

«GEOANALYSIS 90» a été la conférence inaugurale d'une série internationale de symposiums sur l'analyse de matériaux géologiques. Plus de 100 délégués de 17 pays se sont rassemblés sur le site grandiose de Grandview, dans la région des lacs Muskoka, en Ontario, par un après-midi ensoleillé, le dimanche 3 juin 1990. Pendant les trois jours et demi qui ont suivi, les discussions ont porté sur trois grands thèmes : la méthodologie géoanalytique; les étalons géologiques de référence; et la géoanalyse dans les pays en voie de développement.

La conférence a été organisée par des membres de la Commission géologique du Canada (Gwendy E.M. Hall et Judy E. Vaive) et de la Commission géologique de l'Ontario (Chris Riddle et ses collègues), en collaboration avec le Groupe de travail international sur les étalons géologiques, le Département de la coopération technique pour le développement à l'ONU, le Centre canadien de la technologie des minéraux et de l'énergie, et le Conseil de recherches en sciences naturelles et en génie du Canada.

En plus de la rencontre de Grandview, un atelier de conception en laboratoire d'une journée a eu lieu à Toronto à la Commission géologique de l'Ontario (CGO), sous la direction de Chris Riddle. Des visites de laboratoires ont été organisées à Toronto et à Ottawa, et une excursion de deux jours a été organisée par Mike Easton de la CGO.

Le symposium a débuté par le discours-programme sur la place actuelle des étalons géologiques prononcé par K. Govindaraju (Centre de Recherches Pétrographiques et Géochimiques), rédacteur en chef de l'importante revue intitulée *Geostandards Newsletter*. Deux séances de discussions informelles et animées ont été préparées et dirigées par Phil J. Potts (Open University) et Jean Kane (membre de l'*U.S. Geological Survey* à l'époque). M. Potts a lancé le débat sur les éléments qui influent sur la qualité des données géoanalytiques (publié dans le présent document), tandis que M^{me} Kane a sondé l'opinion de l'auditoire sur le sujet controversé du calcul des valeurs recommandées à partir de données compilées. Xuejing Xie a sidéré l'auditoire avec sa description du programme très poussé de cartographie géochimique en Chine et a aussi animé une discussion sur des méthodes analytiques recommandées pour le projet international de cartographie géochimique (PICG 259). Les communications officielles ont été faites sous la forme de présentations orales ou de présentations d'affiches.

On peut juger la diversité des sujets abordés à la lecture de tous les résumés acceptés et parus dans le présent document. Il en ressort immédiatement que la conférence a reflété les efforts en cours dans le monde pour abaisser les limites de détection des métaux précieux et continuer de réaliser des progrès dans l'application de la spectrométrie de masse avec plasma induit par haute fréquence (SM/PIHF) à des échantillons géologiques. Il a été intéressant d'être renseigné sur l'état de la géoanalyse dans les pays en voie de développement et sur les différents défis qu'ils ont à relever; certains exposés du présent document traitent de ces questions. Sept exposés sur les étalons géologiques et le contrôle de la qualité, présentés à la conférence, ont paru dans le numéro d'avril de *Geostandards Newsletter*; le présent document renferme ceux qui portent sur les méthodes analytiques.

Le vote unanime en faveur du lancement d'une série internationale intitulée *GEOANALYSIS*, qui exploite les thèmes de la conférence de 1990 et vise à attirer un plus grand nombre de nos collègues, les géochimistes, confirme le succès de cette rencontre. Lors du banquet mémorable du 6 juin, le flambeau de la présidence de GEOANALYSIS 94 a été remis à Doug Miles de la *British Geological Survey*. Au plaisir donc de vous revoir dans quelque lieu historique de cette bonne vieille Angleterre...

Gwendy E.M. Hall
Commission géologique du Canada

On the evaluation of rock reference materials

S. Abbey[1]

Abstract: The concentrations of numerous constituents must be evaluated in rock samples if they are to be used as reference materials. Because of varying degrees of specialized skills in earth science laboratories, the collaboration of many laboratories is required in order to establish reliable values.

Analytical data reported in such operations are highly variable. The number of constituents reported per sample varies from one laboratory to another. The number of values reported varies from one constituent to another. The reported values for each constituent are generally incoherent, often displaying skewed distributions. The problem, then, is how to deduce the most probably "true" concentration for each constituent.

Various computation schemes, based on medians, means and related measures, will be discussed. A new scheme, involving a combination of modes, will be proposed.

Résumé : Il faut évaluer les concentrations de nombreux constituants dans des échantillons de roche si l'on veut utiliser ces derniers comme matériaux de référence. Étant donné les divers degrés de compétences spéciales que l'on trouve dans les laboratoires des sciences de la Terre, il faut que plusieurs laboratoires collaborent afin d'établir des valeurs fiables.

Les résultats analytiques donnés par ces travaux sont très variables. Le nombre de constituants notés par échantillon varie d'un laboratoire à l'autre. Le nombre de valeurs notées varie d'un constituant à l'autre. Les valeurs citées pour chaque constituant ne sont en général pas uniformes et présentent souvent des distributions asymétriques. Comment alors déduire la concentration «vraie» la plus probable de chaque constituant?

L'auteur aborde diverses méthodes de calcul basées sur des médianes, des moyennes et des mesures connexes, et il propose une nouvelle méthode combinant les modes.

---

[1] Geological Survey of Canada, 601 Booth St., Ottawa, Ontario, K1A 0E8, Canada (Retired).

X-ray fluorescence determination of TiO_2 and other major oxides in Kahnooj Kerman ilmenite ore, KKI

Z. Akhavin Mohamadi[1]

Abstract: Titanium dioxide is the principal white pigment of commerce, and is used widely in the paint, paper, plastic, and ceramic industries. The aim of this project was to extract TiO_2 from ilmenite and consequently the ilmenite ore from the region Kahnooj of Kerman in Iran, was studied by X-ray fluorescence spectrometry. The concentration of titanium dioxide and other major oxides were determined by XRF and fusion of the sample. Details of this investigation will be described.

Résumé : Le dioxyde de titane, principal pigment blanc commercial, est largement utilisé dans la fabrication des peintures, des papiers, des plastiques et des céramiques. Le but de ce projet était d'extraire du TiO_2 à partir de l'ilménite. On a étudié par spectrométrie à fluorescence X le minerai d'ilménite en provenance de la région de Kahnooj de Kerman, en Iran. On a dosé le dioxyde de titane et d'autres oxydes majeurs par fluorescence X et par fusion de l'échantillon. On décrit les détails de cette étude.

---

[1] Materials and Energy Research Centre, P.O. Box 14155-4777, Tehran, Iran.

The analytical chemistry laboratory at the geophysics institute, Unam, Mexico

M.A. Armienta[1]

Abstract: The purpose of this work is to describe the stages, difficulties, and methodology in the establishment of a chemical laboratory for the analyses of geological materials (rocks and groundwaters) at the Geophysics Institute (UNAM, Mexico).

Starting from a basic laboratory substructure consisting basically of one colorimeter, one potentiometer, glassware, reagents, and one furnace, the objective was to implement a laboratory capable of obtaining good quality analyses with minimum expense. The results had to be adequate for use in the study of rock geochemistry, hydrogeochemistry, and quality of groundwaters.

The project is being developed in two stages. The first one is directed towards the quantification of major oxides in rocks and physicochemical parameters in waters. For that purpose, wet methods were developed using the existing equipment as well as one flame photometer, ion selective electrodes, and one oven. The methodology was based mainly on the "rapid methods" of rock analyses described by Riley (1958), and on the "Standard Methods for the Examination of Water and Wastewater" from APHA.

For rock analysis, special attention was paid to the decomposition procedure to avoid losses of elements, and in the silica and alumina measurement, to achieving good precipitation. A simple device for the FeO determination was developed. The methodology was tested with international standard rock samples.

For water analysis, modifications were carried out mainly in the alkalinity and sulfate determinations. Alkalinity was measured by volumetry using a mixture of bromcresol green and methyl orange as an indicator and heating the sample to expel the CO_2 at the end of titration. Sulphates were determined by a modified turbidimetric technique consisting of weighing exactly the $BaCl_2$ for a better control of the turbidity. The accuracy of the methodology was proven by analysis of the standard mineral water sample of the US EPA.

The second stage in the development of the laboratory has consisted of the establishment of techniques for the quantification of metallic contaminants in waters and trace elements in rocks. These analyses are actually in development using an atomic absorption spectrophotometer and a polarograph recently acquired by the laboratory.

Résumé : Dans le présent exposé, on décrit les étapes, les difficultés et les méthodes de mise sur pied d'un laboratoire de chimie pour l'analyse de matériaux géologiques (roches et eaux souterraines) à l'Institut de géophysique (UNAM, Mexique).

À partir d'une sous-structure fondamentale de laboratoire comprenant essentiellement un colorimètre, un potentiomètre, du matériel en verre, des réactifs et un four, l'objectif était de mettre sur pied un laboratoire capable de produire des analyses de bonne qualité au moindre coût. Les résultats devaient convenir à l'étude de la géochimie des roches, de l'hydrogéochimie et de la qualité des eaux souterraines.

Le projet se fait en deux étapes. La première vise à doser les oxydes majeurs des roches et à mesurer les paramètres physico-chimiques des eaux. À cette fin, on a élaboré des méthodes de dosage par voie humide avec le matériel existant et avec un photomètre de flamme, des électrodes pour ions spécifiques et un four. La méthode se fonde surtout sur les méthodes rapides d'analyse des roches décrites par Riley (1958), et sur les méthodes normalisées d'étude de l'eau et des eaux usées de l'APHA.

En ce qui concerne l'analyse des roches, on a surtout étudié la méthode de décomposition afin d'éviter les pertes d'éléments et, dans le cas du dosage de la silice et de l'alumine, d'obtenir une bonne précipitation. On a mis au point un dispositif simple de dosage de FeO, et l'on a éprouvé la méthode avec des étalons de roche internationaux.

Pour l'analyse de l'eau, on a apporté des modifications surtout au dosage de l'alcalinité et des sulfates. On a mesuré l'alcalinité par volumétrie en utilisant l'indicateur bromcrésol-vert-méthyl-orange et en chauffant l'échantillon pour en éliminer le CO_2 à la fin du titrage. On a dosé les sulfates par une technique turbidimétrique modifiée qui consiste à peser exactement le $BaCl_2$ pour mieux contrôler la turbidité. On a démontré l'exactitude de la méthode en analysant l'étalon d'eau minérale fourni par l'EPA des É-U.

La seconde étape de mise sur pied du laboratoire a consisté à établir des techniques de dosage des contaminants métalliques dans les eaux et des éléments traces dans les roches. On travaille actuellement à la mise au point de ces analyses à l'aide d'un spectrophotomètre d'absorption atomique et d'un polarographe dont le laboratoire s'est récemment doté.

Reference

Riley, J.P.
1958: The rapid analysis of silicate rocks and minerals; Analytica Chimica Acta, v. 19, p. 413-428.

---

[1] Instituto de Geoffsica, UNAM, Circuito Exterior, C.U. Coyoacan, Mexico, 04510, D.F.

Sampling and data evaluation of 13 rock samples for internal quality control

C. Backman[1] and J. Liukkonen[1]

Abstract: The Chemistry Laboratory of the Geological Survey of Finland (GSF) is responsible for the analytical services of the institute. The laboratory also serves customers outside the GSF. Analytical techniques include ICP, XRF, and AAS. For quality assurance purposes, the laboratory uses internationally certified reference samples, and for several decades has also used its own reference materials. Recently, a project was launched with the purpose of widening the choice of our reference materials and improving the reliability of results through reference to data from several laboratories.

The rock samples selected as reference material are listed in Table 1. Samples of about 300 kg each were collected from homogeneous outcrops and each sample was crushed.

Table 1

Sample	Rock Type	Sample	Rock Type
RS11	gabbro	RS91	fyllite
RS31	rapakivi granite	RS101	diorite
RS51	quartzite	RS111	granite
RS61	trondhjemite	RS121	peridotitic komatiite
RS71	diabase	RS131	basaltic komatiite
RS81	granite	RS211/RS212	serpentinite

About 50 kg of the sample was ground to powder, mixed, and packed into canisters and bottles. These were distributed to eight laboratories in the Nordic countries. During the project, six more participants joined in.

The mean value and coefficient of variation for the results from each laboratory were calculated. Each mean value was then treated as an analytical value, and values of central interest, such as the median, Gastwirth median, and dominant cluster (DC) mode, were calculated. Graphical presentation was made by means of cumulative frequency diagrams. For elements with more than about ten analytical values, the central values tend to be close together for normally distributed populations. The DC mode is then proposed as the recommended value. The major components are well represented, but fewer useful analytical values were submitted for trace elements.

The reference sample project has provided the laboratory with reference material for the future. Data collection is still taking place to increase the accuracy of the proposed values for the trace elements. It is emphasized, however, that the purpose of the project is to supplement international reference samples, not to replace them.

Résumé : Le laboratoire de chimie de la Commission géologique de la Finlande (CGF) est responsable des services d'analyse de l'institut. Il dessert aussi des clients de l'extérieur. Les techniques d'analyse utilisées comprennent le PIHF, la FX et la SAA. Afin de garantir la qualité, le laboratoire utilise des échantillons de référence certifiés internationalement et, pendant plusieurs décennies, il a aussi utilisé ses propres matériaux de référence. Récemment, on a lancé un projet visant à élargir le choix des matériaux de référence et à améliorer la fiabilité des résultats en les comparant aux données de plusieurs laboratoires.

Le tableau 1 donne les échantillons de roche choisis comme matériaux de référence. Des échantillons d'environ 300 kg chacun ont été prélevés dans des affleurements homogènes, et chaque échantillon a été broyé.

Environ 50 kg de l'échantillon ont été pulvérisés, mélangés et mis dans des boîtes métalliques et des bouteilles qui ont été distribuées à huit laboratoires dans les pays nordiques. Six autres participants se sont joints au groupe au cours du projet.

Tableau 1

Échantillon	Lithotype	Échantillon	Lithotype
RS11	gabbro	RS91	phyllade
RS31	rapakiwi	RS101	diorite
RS51	quartzite	RS111	granite
RS61	trondhjémite	RS121	komatiite péridotitique
RS71	diabase	RS131	komatiite basaltique
RS81	granite	RS211/RS212	serpentinite

On a calculé la valeur moyenne et le coefficient de variation des résultats de chaque laboratoire. On a ensuite traité chaque moyenne comme une valeur analytique et calculé les tendances centrales, comme la médiane, la médiane de Gastwirth et le mode de la grappe dominante (GD). La présentation graphique a été faite sous la forme de diagrammes de fréquences cumulées. Les tendances centrales sont plus rapprochées pour les éléments comportant plus d'environ dix valeurs analytiques que pour les populations à distribution normale. On propose donc le mode GD comme valeur recommandée. Les constituants majeurs sont bien représentés, mais un nombre moindre de valeurs analytiques utiles a été produit pour les éléments traces.

Le projet des échantillons de référence a permis au laboratoire d'obtenir des matériaux de référence pour des travaux futurs. On continue de recueillir des données en vue d'améliorer l'exactitude des valeurs proposées pour les éléments traces. Il est à noter toutefois que le projet a pour but de compléter les échantillons de référence internationaux, et non de les remplacer.

---

[1] Geological Survey of Finland, Betonimiehenkuja 4, SF-02150 Espoo, Finland.

Rare-earth element analysis of iron-formation reference samples by inductively coupled plasma mass spectrometry (ICP-MS)

V. Balaram[1]

Abstract: The currently available iron-formation reference samples, namely FER-1, FER-2, FER-3, and FER-4 from CCRMP, and IF-G from GIT-IWG are poorly characterized with respect to the rare-earth element (REE) concentrations. Certified data are not available for the majority of the REEs. An attempt is made to provide complete REE data on the above five reference samples using ICP-MS.

The analytical procedures for the determination of all REEs (La to Lu) in these samples by ICP-MS are described. ^{115}In is used as an internal standard to correct for any drift in the signal. The operating parameters of the instrument (VG PlasmaQuad) are presented. The matrix and other problems associated with the determination and the accuracies and precisions obtained are discussed. The data obtained are compared with available data in the literature and are found to compare favourably with the published data. Concentration values have been suggested in cases where certified data are not available.

Résumé : Les échantillons de référence actuellement disponibles qui proviennent de formations ferrifères, soit FER-1, FER-2, FER-3 et FER-4 du PCMR et IF-G du GIT-IWG, sont mal caractérisés quant à leurs concentrations de terres rares. On ne dispose d'aucune donnée certifiée pour la plupart des terres rares. On tente de produire par SM/PIHF un ensemble complet de données sur les terres rares pour les cinq échantillons de référence.

L'auteur décrit les méthodes de dosage par SM/PIHF de toutes les terres rares (La à Lu) dans ces échantillons. L'isotope ^{115}In est utilisé comme étalon interne pour corriger toute dérive du signal. L'auteur donne les paramètres de fonctionnement de l'instrument (VG PlasmaQuad) et analyse le problème de la matrice et d'autres problèmes d'évaluation, d'exactitude et de précision. Il compare les données obtenues aux données publiées et conclut qu'elles concordent bien. Il propose des valeurs des concentrations lorsque des données certifiées ne sont pas disponibles.

---

[1] National Geophysical Research Institute, Hyderabad – 500007, India.

A simple method for the chemical analysis of chromite

S. Biswas[1] and K. Satyanarayana[1]

Abstract: Complete and accurate chemical analysis of chromite ore is a matter of difficulty even if it is fused with a universally accepted flux (e.g. Na_2O_2). The basic problem is its incomplete fusion by most fluxes other than Na_2O_2, the availability of which is very scanty in the Indian market. Keeping this in consideration the authors have developed a simple new method of analysis of such ores without using Na_2O_2.

The method involves fusion of the ore first by Na_2CO_3 followed by extraction in hot dilute HNO_3. The residue thus obtained after filtration followed by ignition is fused with $K_2S_2O_7$. This pyrosulphate-fused material is extracted by boiling with dilute H_2SO_4 and mixed with the earlier filtrate. A clear solution of the completely fused ore is thus obtained which can be used for subsequent determination of Cr_2O_3, SiO_2, Al_2O_3, Fe_2O_3, MgO, etc. Detailed experimental procedure for every analysis is presented in the paper.

Samples of 18 beneficiation products and an original sample of a medium grade Indian chromite ore were analyzed and the results for Cr_2O_3 are tabulated. The head assays* calculated with these results are found to have negligible deviation from the original assay value. A set of six more samples of another chromite ore were analyzed simultaneously by fusing with Na_2O_2 and by this method and the results are tabulated for comparison. Some discussions have also been made to highlight the advantages of this method over the others.

$$*\text{head-assay} = \Sigma \frac{\text{Wt\%XAssay\%}}{100}$$

Résumé : Il est difficile de faire une analyse chimique complète et exacte du minerai de chromite même lorsque ce dernier est combiné à un fondant universel (p. ex. Na_2O_2). Le problème fondamental tient à sa fusion incomplète en présence de la plupart des fondants autres que le Na_2O_2, qui est très rare sur le marché indien. Par conséquent, les auteurs ont élaboré une nouvelle méthode simple d'analyse de ces minerais sans utiliser du Na_2O_2.

La méthode consiste à fondre le minerai d'abord avec du Na_2CO_3, puis à extraire le produit dans du HNO_3 dilué chaud. Le résidu obtenu après filtration, puis calcination, est fondu en présence de $K_2S_2O_7$. Ce matériau fondu au pyrosulfate est extrait par ébullition avec du H_2SO_4 dilué et mélangé au filtrat. On obtient ainsi une solution limpide du minerai complètement fondu, et cette solution peut servir ensuite à doser les matières suivantes : Cr_2O_3, SiO_2, Al_2O_3, Fe_2O_3, MgO, etc. L'exposé décrit une procédure expérimentale détaillée pour chaque analyse.

On a analysé des échantillons de 18 produits enrichis et un échantillon original d'un minerai indien de teneur moyenne en chromite, et l'on présente un tableau des résultats pour le Cr_2O_3. Les teneurs* du minerai de tête calculées à partir de ces résultats s'écartent peu des valeurs initiales. On a analysé simultanément un ensemble de six autres échantillons d'un autre minerai de chromite, en employant le procédé de fusion avec du Na_2O_2 et la méthode mentionnée ci-dessus, et l'on présente les résultats dans un tableau à des fins de comparaison. On ajoute certains commentaires pour montrer la supériorité de cette méthode par rapport aux autres.

$$*\text{teneur du minerai de tête} = \Sigma \frac{\text{\% poids X \% teneur}}{100}$$

---

[1] Ore Dressing Laboratory, Indian Bureau of Mines, Gorguntepalya, Bangalore-560022, India.

Determination of Pt, Pd, Rh, and Ru in rocks by NiS fire-assay followed by GF-AAS: instrumental drifts, interferences, and reliability

R. Boisvert[1], M. Bergeron[2], and J. Turcotte[1]

Abstract: PGEs (platinum group elements: platinum, palladium, rhodium, ruthenium, iridium, osmium) are commonly determined by nickel sulphide (NiS) fire-assay followed by neutron activation analysis. However, this approach meets serious difficulties with certain types of rock samples, particularly those rich in As, Sb, and Au, since these elements yield high dead times during counting. In order to avoid these problems we have used NiS fire-assay coupled to graphite furnace atomic absorption spectrometry (GF-AAS) for the measurement of Pt, Pd, Rh, and Ru in rocks.

We have examined: a) furnace operating conditions, b) choice of suitable solvent for analysis, c) possible interferences during GF-AAS analysis, and d) the reliability of the method through measurement of standard reference material SARM-7. Of these four parameters, the possibility of interferences was primarily investigated. Although numerous analytical procedures have been described in the literature dealing with PGE measurements by NiS fire-assay followed by GF-AAS, very few studies have been conducted on possible interferences between the precious metals themselves as well as those caused by elements present in the analytical solution (particularly Ni and Fe) and this at PGE concentrations in the order of a few parts per billion.

Results indicate that in order to obtain reliable results for Pt, Pd, Rh, and Ru, the furnace must be calibrated using solutions in which Ni concentrations are similar to those of the samples under analysis. This requires that Ni concentrations in samples be previously measured by flame AAS.

Résumé : Les EGP (éléments du groupe du platine : platine, palladium, rhodium, ruthénium, iridium, osmium) sont normalement soumis à l'analyse pyrognostique en présence de sulfure de nickel (NiS), puis à l'analyse par activation neutronique. Cette méthode pose toutefois de grandes difficultés pour certains types d'échantillons de roches, en particulier les roches riches en As, en Sb et en Au, car ces éléments produisent de longs temps morts durant le comptage. Pour éviter ces problèmes, les auteurs ont recouru à l'analyse pyrognostique avec NiS, couplée à la spectrométrie d'absorption atomique dans un four en graphite (SAA/FG) pour doser le platine, le palladium, le rhodium et le ruthénium dans les roches.

Ils ont examiné : a) les conditions d'exploitation du four, b) le choix d'un solvant approprié pour l'analyse, c) les interférences possibles pendant l'analyse SAA/FG, d) la fiabilité de la méthode, par analyses de l'étalon de référence SARM-7. De ces quatre paramètres, ils ont surtout examiné les interférences éventuelles. Même si de nombreux procédés analytiques sont décrits dans la documentation sur l'analyse pyrognostique des EGP avec NiS, suivie du procédé SAA/FG, très peu d'études traitent des interférences possibles créées par les métaux précieux eux-mêmes, ainsi que des interférences causées par les éléments présents dans la solution d'analyse (notamment Ni et Fe), à des concentrations des EGP de l'ordre de quelques ppb.

Les résultats indiquent que pour obtenir des valeurs fiables pour les éléments Pt, Pd, Rh et Ru, le four doit être étalonné au moyen de solutions dont les teneurs en Ni sont semblables à ceux des échantillons à l'étude. Pour cela, il faut que les teneurs en Ni des échantillons soient mesurés au préalable par spectrométrie d'absorption atomique par la flamme.

---

[1] Département de Chimie, Université Laval, Cité Universitaire, Québec (Québec) G1K 7P4.
[2] INRS-Géoressources, 2700 rue Einstein, case postale 7500, Sainte-Foy (Québec) G1V 4C7.

Automated analysis of geological and related materials by ICP-AES – a review of new developments

M. Borsier[1] and I.B. Brenner[2]

Abstract: In modern regional geochemical studies, major, minor, and trace element data are used to characterize petrogenetic processes, and evaluate chemical trends related to ore genesis. Thus effective sample preparation, calibration, instrumental analysis, and data interpretation are necessary if the sample population is large. In this presentation recent developments will be reviewed for automated computer-assisted multielement inductively coupled plasma analysis of diverse geochemical and environmental materials (rocks, soils, vegetation, and waters). Automated robotic sample decomposition and preconcentration devices allowing high sample throughput will be described. A systematic study of decomposition procedures was made and optimum protocols for various applications were established using discriminant and factor analysis. A dedicated interactive software package including integrated sample preparation cookbooks, calibration, and QC protocols using SRMs will be summarized. Spectral line databases will be demonstrated predicting spectral line interferences, facilitating optimum analyte line and background selection for a wide range of applications using simultaneous, sequential, and combination spectrometers. Emphasis will be placed on multivariant chemometric techniques for geochemical and environmental data interpretation. These include pattern recognition techniques (factor and discriminant analysis) and geochemical and geoenvironmental maps.

Résumé : Dans les récentes études de géochimie régionale, les données sur les éléments majeurs, mineurs et traces servent à caractériser les processus de pétrogenèse et à évaluer les tendances chimiques liées à la genèse des minerais. Il faut donc préparer efficacement les échantillons, les étalonner, en faire l'analyse instrumentale et interpréter les données lorsque la population d'échantillons est grande. Dans le présent exposé, les auteurs passent en revue les progrès récents en matière d'analyse multiéléments informatisée, par spectrométrie avec plasma induit par haute fréquence, de divers matériaux d'intérêt géochimique et environnemental (roches, sols, végétation et eaux). Ils décrivent des robots qui permettent de décomposer et de préconcentrer un grand nombre d'échantillons en peu de temps. Ils ont entrepris une étude systématique de la méthode de décomposition, et ils ont établi, par analyse discriminante et factorielle, des protocoles optimaux pour diverses applications. Ils présentent, sous la forme d'un résumé, un progiciel interactif spécialisé qui intègre les livres de recettes pour la préparation des échantillons, les étalonnages et les protocoles de contrôle de la qualité basés sur des étalons SRM. Ils font une démonstration des bases de données sur les raies spectrales, qui permettent de prévoir les interférences de raies spectrales et facilitent le choix des meilleurs fonds et raies caractérisant les produits analysés, dans le cadre d'une vaste gamme d'applications avec emploi de spectromètres disposés en parallèle, en série ou en mode combiné. Ils mettent l'accent sur l'utilisation des techniques de chimiométrie à plusieurs variables pour l'interprétation des données géochimiques et environnementales, notamment les techniques de reconnaissance des formes (analyses factorielle et discriminante) et les cartes géochimiques et géo-environnementales.

---

[1] Bureau Recherches Géologiques et Minières (BRGM), Orléans, France.

[2] Geological Survey of Israel, 30 Malkhe Israel Street, Jerusalem, 95501, Israel.

Current status of direct solids analysis of geological and related refractory materials by slurry injection (SI) and spark ablation (SA)

I.B. Brenner[1]

Abstract: The need to analyze geological materials by direct solids procedures is becoming more and more important especially in the field of mineral beneficiation, coal utilization, and other industrial applications. Currently these chemically resistant materials are analyzed by atomic spectrometries after time-consuming fusion and mixed acid dissolution techniques. Indeed for refractory silicates and composite materials it may not be possible to effect a complete dissolution of the sample. Hence an accurate, rapid, direct solid technique would improve sample throughput. In this presentation the current status of SI and SA ICP-AES are evaluated by analyzing a wide range of materials. For SI, rock, refractory, and coal (<5 μ m) slurries were nebulized into argon and mixed argon-oxygen and nitrogen ICPs in a Trassy-Mermet demountable torch using a high solids EBDON nebulizer. It will be shown that the addition of a molecular gas to the ICP increased excitation temperature and Ne and enhanced particle decomposition. In these plasmas the differences in the observation zones for various analytes in various materials are significantly reduced and the intensity-concentration relationships are improved. Quantitative data for SRM clays, coals, and alumina slurries will be presented. However SI-ICP analytical data for refractory materials are still inadequate due to particle-plasma interactions. Several new approaches for overcoming these setbacks will be discussed, in particular the application of internal references in the solution and in the solid phase to compensate for chemical effects in the transport system and the plasma itself.

SI performance will then be compared to GD (glow discharge)-ES and SA-ICP. SEM surface morphologies of the sputtered and ablated surfaces reveal that sample transport in GD-ES is mainly physical, and as a result the technique is free from the influence of mineralogical and chemical compositions, whereas in SA-ICP melting and sintering is responsible for selective volatilization resulting in significant bias of the analytical data. GD-ES is considered to be a very suitable technique for the analysis of these materials due to minimum interference effects, simple sample preparation, large dynamic range, superior precision, and accuracy.

Résumé : Il est de plus en plus nécessaire d'analyser les matériaux géologiques directement sous forme solide, surtout dans les domaines de l'enrichissement des minéraux et de l'utilisation des charbons, et dans d'autres applications industrielles. Actuellement, on analyse ces matériaux chimiquement neutres par spectrométrie atomique après des étapes laborieuses de fusion et de dissolution dans des solutions acides mixtes. En fait, il est parfois impossible de dissoudre complètement les échantillons de matériaux composites et de silicates réfractaires. Par conséquent, une technique précise, rapide et directe d'analyse des solides permettrait d'accélérer le traitement des échantillons. Dans le présent exposé, on évalue la place actuelle de la SE/PIHF avec injection de bouillie et ablation par étincelle, en analysant une vaste gamme de matériaux. Pour l'injection de bouillie, des suspensions de roche, de matériaux réfractaires et de charbon ($<5\ \mu$ m) ont été nébulisées en des plasmas induits par haute fréquence composés d'argon et d'un mélange d'argon/oxygène et d'azote, dans une torche démontable Trassy-Mermet, à l'aide d'un nébuliseur EBDON à rendement élevé en solides. Il est démontré que l'addition d'un gaz moléculaire dans le plasma induit par haute fréquence fait monter la température d'excitation du Ne et améliore la décomposition des particules. Dans ces plasmas, il y a réduction marquée des différences dans les zones d'observation de diverses substances à analyser venant de divers matériaux et amélioration des relations intensités-concentrations. On présente des données quantitatives sur des bouillies d'argiles, de charbons et d'alumine venant d'étalons de référence. Toutefois, les données analytiques fournies par les procédés d'analyse des matériaux réfractaires avec plasma induit par haute fréquence et injection de bouillie sont encore insuffisantes en raison d'interactions particules-plasma. On aborde plusieurs nouvelles solutions à ces problèmes, notamment l'introduction de références internes dans la solution et dans la phase solide pour compenser les effets chimiques dans le système de transport et dans le plasma lui-même.

On compare ensuite le rendement de l'injection de bouillie à la spectrométrie d'émission avec source à plasma par décharge continue et à la spectrométrie avec plasma induit par haute fréquence et ablation par étincelle. L'examen au microscope électronique à balayage de la morphologie des surfaces de nébulisation et d'ablation révèle que dans la spectrométrie d'émission avec source à plasma par décharge continue, le transport des échantillons est surtout physique. Par conséquent, cette technique ne subit pas l'influence des compositions minéralogique et chimique. Par contre, dans le procédé avec plasma induit par haute fréquence et ablation par étincelle, la fusion et le frittage causent la volatilisation sélective qui produit une importante erreur systématique dans les résultats analytiques. La spectrométrie d'émission avec source à plasma par décharge continue est considérée comme convenant très bien à l'analyse de ces matériaux, les interférences étant minimes, la préparation des échantillons simple, la plage dynamique étendue, et la précision et l'exactitude supérieures.

---

[1] Geological Survey of Israel, 30 Malkhe Israel St., Jerusalem, 95501, Israel.

Preconcentration by coprecipitation with gallium – a reappraisal

I.D. Brindle[1] and X.-C. Le[1]

Abstract: Coprecipitation with gallium has been described by Japanese workers as a method for the determination of trace elements in sea water by ICP-AES.

We have investigated this methodology to determine whether it can be applied to the determination of trace elements in surface and groundwaters. Our findings suggest that, in fact, gallium is unnecessary for this procedure. In fact, magnesium appears to be the agent that collects the trace elements. We shall report the results of our investigations into an alternate coprecipitation procedure. Determinations of germanium in surface and groundwaters have been determined by this procedure and range between <1 ng$\cdot$ L^{-1} and 17 ng$\cdot$ L^{-1}.

Résumé : Des chercheurs japonais ont décrit la coprécipitation avec le gallium comme une méthode de dosage par SE/PIHF des éléments traces dans l'eau de mer.

Les auteurs ont étudié cette méthode afin de déterminer si elle peut s'appliquer au dosage des eaux de surface et des eaux souterraines. Leurs résultats indiquent qu'en fait, le gallium n'est pas essentiel à la méthode. Le magnésium semble plutôt être l'agent qui capte les éléments traces. Les auteurs présentent les résultats de leurs recherches sur une autre méthode de coprécipitation. Le germanium a été dosé dans des eaux de surface et des eaux souterraines par cette méthode, et les valeurs obtenues se situent entre <1 et 17 ng$\cdot$ L^{-1}.

References

T. Akagi, K. Fuwa, and H. Haraguchi
1985: Simultaneous multi-element determination of trace metals in sea water by inductively-coupled plasma atomic emission spectrometry after coprecipitation with gallium; Analytica Chimica Acta, v. 177, p. 139-151.
T. Akagi and H. Haraguchi
1990: Simultaneous multi-element determination of trace metals using 10 mL of seawater by inductively coupled plasma atomic emission spectrometry with gallium coprecipitation and microsampling technique; Analytical Chemistry, v. 62, p. 81-85.

---

[1] Chemistry Department, Brock University, St. Catharines, Ontario, L2S 3A1, Canada.

Upgrading the chemical laboratory facilities of the Bangladesh geological survey and training of their staff in geochemical analysis

F.W. Brown[1]

Abstract: The USGS is assisting the Geological Survey of Bangladesh (GSB) in the modernization of its facilities. Some areas of upgrading include implementing programs in mineral exploration, geochemical analysis, geological mapping, engineering geology, geophysics, marine geology, groundwater, stratigraphy, geochemistry, drilling, and publications.

After a one-month visit to the GSB in July 1983, recommendations were made to upgrade the chemical laboratories. Suggestions included the acquisition of analytical instrumentation for support of GSB programs in mineral resources exploration. In 1986 and 1987, five GSB chemists were trained at the Branch of Geochemistry Laboratory in Reston, Virginia. The training consisted of the basic principles of rock and coal crushing, atomic absorption spectrometry, spectrophotometry, determination of the forms of sulphur, and fire-assay/atomic absorption techniques for the determination of gold, platinum, palladium, and rhodium. A follow-up visit in 1989 was made to GSB to ensure that modifications to their laboratories and rooms including the installation of fume hoods, had been completed. Also during this visit, time was spent working with the GSB chemists in familiarizing them with the newly acquired instrumentation, reviewing portions of the analytical procedures they learned during training at the USGS, and making additional recommendations for improvement of the laboratory facilities and operations.

The panel discussions will include the problems and successes encountered in making improvements to the laboratories, acquisition of instruments, chemicals, supplies, and the training of GSB chemists.

Résumé : L'USGS aide la Commission géologique du Bangladesh (CGB) à moderniser ses installations. Une partie des améliorations consiste à mettre sur pied des programmes de prospection minérale, d'analyse géochimique, de cartographie géologique, de géologie appliquée, de géophysique, de géologie marine, d'étude des eaux souterraines, de stratigraphie, de géochimie, de forage et de publication.

Après une visite d'un mois à la CGB en juillet 1983, les experts ont recommandé d'améliorer les laboratoires de chimie, notamment de faire l'acquisition d'instruments d'analyse à l'appui des programmes de prospection minérale de la CGB. En 1986 et 1987, cinq chimistes de la CGB ont été formés au laboratoire de la direction de la géochimie à Reston, en Virginie. Leur programme de formation a porté sur les principes fondamentaux du concassage de la roche et du charbon, et sur les principes de la spectrométrie d'absorption atomique, de la spectrophotométrie, de la détermination des formes du soufre et des techniques d'absorption atomique et d'analyse pyrognostique employées pour le dosage de l'or, du platine, du palladium et du rhodium. Une visite de suivi a été faite en 1989 à la CGB pour vérifier les modifications apportées aux laboratoires et aux salles, notamment l'installation de hottes. Pendant cette visite, on a passé du temps à familiariser les chimistes de la CGB avec les nouveaux instruments, à revoir des parties des procédés analytiques appris pendant le cours de formation à l'USGS et à faire des recommandations additionnelles quant à l'amélioration des installations et des procédés de laboratoire.

Les discussions en groupe porteront sur les problèmes et succès rencontrés lors de la modification des laboratoires, de l'acquisition des instruments, des produits chimiques et des fournitures, et de la formation des chimistes de la CGB.

---

[1] U.S. Geological Survey, 4200 University Dr., Anchorage, Alaska, 99508, U.S.A.

A new catalytic polarographic system for the determination of trace amounts of tungsten

D. Dan[1]

Abstract: A new catalytic polarographic system for the determination of trace amounts of tungsten is investigated. It was found that tungsten-MBT yields a sensitive catalytic hydrogen wave at -1.10V (vs. SCE) in strongly acid medium. The linear relationship occurs between the peak height and tungsten concentration over the range of 0.004-1.4 μ g/mL, in a solution of 0.9 M H_2SO_4-2% NaCl-0.01 μ g/mL MBT. The influence of foreign ions on the wave has been examined. The experiments show that the method is rapid, simple, sensitive, and has a wide linear range. The method has been applied to determine trace amounts of tungsten in six Chinese geochemical standard materials with satisfactory results without any separation. The mechanism of the polarogram has also been studied.

Résumé : Dans cet exposé, on examine un nouveau système polarographique catalytique permettant de doser des traces de tungstène. On constate que le tungstène MTB donne une onde hydrogène catalytique sensible à -1,10 V (vs électrode standard au calomel, SCE) dans un milieu fortement acide. La relation linéaire se manifeste entre le pic et la concentration de tungstène dans la gamme de 0,004 à 1,4 μ g/ml, dans une solution 0,9 M de H_2SO_4 - 2 % de NaCl - 0,01 μ g/ml de MBT. On a étudié l'influence d'ions étrangers sur l'onde. Les expériences montrent que la méthode est rapide, simple, sensible et a une application linéaire étendue. Elle a été appliquée avec des résultats satisfaisants au dosage de traces de tungstène dans six étalons géochimiques venant de la Chine, sans qu'il ait été nécessaire de procéder à une séparation. On a aussi étudié le mécanisme du polarogramme.

---

[1] Department of Applied Chemistry, Chengdu College of Geology, Chengdu, Sichuan, 610059, China.

Preconcentration-flow injection techniques for the analysis of geochemical samples by plasma spectrometry

N. De Silva[1], G.E.M. Hall[1], G. Gauthier[1], and J.C. Pelchat[1]

Abstract: Inductively Coupled Plasma Emission (ICP-ES) and Mass Spectrometry (ICP-MS) have evolved to be among the most popular and versatile analytical techniques available for multielement trace analysis, especially for geochemical applications. However, due to the complexity and wide range of composition of geochemical samples, one encounters serious physical, chemical, and spectroscopic interferences during the determination of trace quantities of analytes in the presence of high concentration of matrix elements resulting in significantly poorer detection limits and accuracy.

Immobilized ligands such as Chelex-100 can be used to remove the matrix components and to preconcentrate the trace analytes in order to improve the analytical figures of merit significantly. For routine application of preconcentration methods manual procedures are too cumbersome and generally require large volumes of samples and reagents. Analytical systems based on flow injection (FIA) can be used to automate these preconcentration and analysis procedures with much lower sample and reagent consumption. Strategies for optimization of hardware and data acquisition procedures in terms of the analytical figures of merit and the overall system efficiency by exploiting the advantages of both FIA and ICP spectrometry will be presented.

Résumé : La spectrométrie d'émission avec plasma induit par haute fréquence (SE/PIHF) et la spectrométrie de masse avec plasma induit par haute fréquence (SM/PIHF) font maintenant partie des techniques les plus répandues et les plus souples de dosage de plusieurs éléments traces, notamment à des fins géochimiques. Toutefois, étant donné la complexité et le vaste éventail de composition des échantillons géochimiques, de graves interférences physiques, chimiques et spectroscopiques se produisent pendant le dosage de traces de substances à analyser en présence de fortes concentrations d'éléments de la matrice, ce qui se traduit souvent par une exactitude et des limites de détection beaucoup moins élevées.

On peut utiliser des ligands immobilisés comme le Chelex-100 pour éliminer les constituants de la matrice et pour préconcentrer les substances à analyser présentes en traces, afin d'améliorer grandement les facteurs de qualité analytiques. Les procédés manuels de préconcentration couramment employés sont trop complexes et nécessitent en général de grandes quantités d'échantillons et de réactifs. On peut employer les systèmes de dosage basés sur la technique FIA pour automatiser ces méthodes de préconcentration et d'analyse, et ainsi consommer des quantités beaucoup plus faibles d'échantillons et de réactifs. Les auteurs décrivent des stratégies d'optimisation du matériel et des procédures de saisie des données en termes de facteurs de qualité analytiques et de rendement global des systèmes, lorsque les avantages de la technique FIA et de la spectrométrie avec PIHF sont exploités simultanément.

---

[1] Geological Survey of Canada, 601 Booth St., Ottawa, Ontario, K1A 0E8, Canada.

Determination of minor and trace elements in four Canadian iron-formation standard samples FeR-1, FeR-2, FeR-3, and FeR-4 by INAA, ICP-MS, and ICP-AES

P. Dulski[1] and J. Luck[2]

Abstract: Banded iron-formation recorded systematically the distribution of rare-earth elements (REEs) in the environment of ferruginous precipitation. Analyzing banded iron-formation therefore yields detailed information about both the source and the chemical conditions of deposition of REEs and iron. An international iron-formation reference sample would help to minimize the effect of analytical uncertainties (matrix effects, interelement interferences) and could be used as a basis for geochemical investigations of iron-formations.

The four Canadian iron-formation samples FeR-1, FeR-2, FeR-3, and FeR-4 are suitable for use as multielement comparators in the analysis of banded iron-formation. A first compilation of analytical data has been presented by Abbey et al. (1983) but the number of published data is small, especially for the REEs.

New data for some major, minor, and trace elements obtained by instrumental neutron activation analysis (INAA), inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES) will be presented. The analytical data obtained by those independent methods agree very well and might improve the available data. For example it can be shown that for Eu, which is used very often as a geochemical probe, in the FeR-1 standard 3.4 μ g/g might be the best value. The published value of 0.76 μ g/g could not be verified by INAA or ICP-MS.

Accuracy of the three methods is demonstrated by comparing the results of INAA, ICP-MS, and ICP-AES with the recommended values of the collaborative studies for the iron-formation sample IF-G and the Ailsa Craig granite AC-E.

Résumé : Les formations de fer rubanées ont enregistré systématiquement la distribution des terres rares dans les milieux de précipitation ferrugineuse. L'analyse des formations de fer rubanées renseigne donc sur la source et les conditions chimiques de dépôt des terres rares et du fer. Un échantillon de référence international provenant d'une formation ferrifère aiderait à minimiser l'effet des incertitudes analytiques (effets de matrice, interférences inter-éléments) et pourrait servir de base aux recherches géochimiques sur les formations ferrifères.

Les quatre échantillons de formations ferrifères canadiennes, soit FeR-1, FeR-2, FeR-3 et FeR-4, constituent des comparateurs multiéléments appropriés pour l'analyse des formations de fer rubanées. Abbey et al. (1983) ont présenté une première compilation de données analytiques, mais le nombre de données publiées est faible, surtout pour ce qui est des terres rares.

On présente de nouvelles données sur certains éléments majeurs, mineurs et traces qui ont été obtenues par analyse instrumentale par activation neutronique (AIAN), par spectrométrie de masse avec plasma induit par haute fréquence (SM/PIHF) et par spectroscopie d'émission avec plasma induit par haute fréquence (SE/PIHF). Les données analytiques obtenues par ces méthodes indépendantes concordent très bien et pourraient améliorer les données disponibles. Par exemple, on peut montrer que pour l'Eu, très souvent utilisé comme sonde géochimique, la valeur de 3,4 μ g/g relevée dans l'étalon FeR-1 pourrait être la meilleure obtenue. La valeur publiée de 0,76 μ g/g n'a pu être vérifiée par AIAN ni par SM/PIHF.

La précision des trois méthodes est établie par comparaison entre les résultats obtenus par AIAN, par SM/PIHF et par SE/PIHF et les valeurs recommandées citées dans les études conjointes sur l'échantillon IF-G de la formation ferrifère et sur le granite AC-E d'Ailsa Craig.

Reference

S. Abbey, C.R. McLeod, and L.-G. Wan
1983: FeR-1, FeR-2, FeR-3 and FeR-4. Four Canadian iron-formation samples prepared for use as reference materials, CANMET Report 83-19, 51 p.

---

[1] Hahn-Meitner-Institut Berlin GmbH, Berlin/FRG.
[2] SPECTRO Analytical Instruments, Kleve, Germany.

Preparation and certification of the new polish CRM: fine fly ash (CTA-FFA-1)

R. Dybczynski[1], H. Polkowska-Motrenko[1], Z. Samczynski[1], and Z. Szopa[1]

Abstract: About 60 kg of fine fly ash was collected from the third zone of electrofilters from the "Kozienice" power station. The material has a density of 2.53 $g \cdot cm^{-3}$ at a very fine mesh size (93% passed through the 0.06 mm sieve). The material was rotated for 16 h in a 110 L polyethylene (PE) drum placed in a specially constructed mixing device. Preliminary homogeneity checking was done by taking the samples from the drum at certain time intervals and analyzing them by XRF for their Y and Fe contents. After apportioning the material into PE containers, final homogeneity checking was performed by instrumental neutron activation analysis. Determination of Fe, Co, Cr, Cs, Sc, and Th in subsamples from six containers chosen at random, with analogous results for subsamples taken from a single container, revealed that the material can be considered homogeneous, at least for a sample size greater than or equal to 200 mg.

An international intercomparison brought together nearly 60 laboratories from 19 countries employing a variety of analytical techniques as: neutron activation analysis (NAA), atomic absorption spectrometry (AAS), atomic emission spectrometry (AES), X-ray fluorescence (XRF), mass spectrometry (MS), and others, with or without sample pretreatment and preconcentration or separation procedures. In total, about 3900 pieces of chemical data (over 950 laboratory means) on 65 elements were provided by participating laboratories. Evaluation of results was done by the method previously proposed by one of us with some recent refinements.

The procedure included the calculation of laboratory means, the use of four concurrent tests for outlier rejection (Dixon's, Grubbs's coefficient of skewness and coefficient of kurtosis), calculation of the overall mean and its confidence interval etc. Using a set of appropriate criteria formulated earlier with some recent modifications it was found that it will be possible to certify at least 30 elements and provide "information values" for at least a further ten. Observations on the performance of various analytical techniques and their contribution to the certification process are also presented.

Résumé : On a recueilli environ 60 kg de cendres volantes fines dans la troisième zone d'électrofiltres de la centrale «Kozienice». Le produit a une masse volumique de 2,53 $g \cdot cm^{-3}$ lorsque sa granulométrie est très fine (93 % traversant la maille de tamis de 0,06 mm). On a soumis le produit à une rotation pendant 16 h dans un cylindre de 110 L en polyéthylène (PE) qui était placé dans un dispositif mélangeur construit à cette fin. On a effectué une vérification préliminaire de l'homogénéité en prélevant des échantillons dans le cylindre à des intervalles de temps précis et en y dosant les éléments Y et Fe par fluorescence X. Après avoir réparti le produit dans des contenants en PE, on a vérifié l'homogénéité finale par analyse instrumentale par activation neutronique. Le dosage des éléments Fe, Co, Cr, Cs, Sc et Th dans des sous-échantillons provenant de six contenants choisis au hasard, les résultats étant analogues pour des sous-échantillons prélevés dans un seul contenant, a révélé que le produit peut être considéré comme homogène, du moins si la dimension de l'échantillon est supérieure ou égale à 200 mg.

Près de 60 laboratoires dans 19 pays ont participé à une comparaison à l'échelle internationale. Ces laboratoires ont employé une gamme de techniques d'analyse telles que l'analyse par activation neutronique, la spectrométrie d'absorption atomique, la spectrométrie d'émission atomique, la fluorescence X, la spectrométrie de masse et d'autres procédés, avec ou sans prétraitement et préconcentration ou séparation de l'échantillon. Au total, les laboratoires participants ont fourni environ 3 900 données chimiques individuelles (plus de 950 sont des moyennes des résultats obtenus en laboratoire) relatives à 65 éléments. On a évalué les résultats par la méthode antérieurement proposée par l'un des auteurs, avec quelques améliorations récentes.

Le procédé comprenait le calcul des moyennes des résultats obtenus en laboratoire, l'emploi de quatre essais simultanés permettant le rejet des valeurs aberrantes (coefficient de dissymétrie et coefficient d'aplatissement de Dixon, de Grubb), le calcul de la moyenne globale et de son coefficient de confiance, etc. En employant un ensemble de critères appropriés tels que formulés antérieurement mais avec quelques récentes modifications, on a constaté qu'il était possible de certifier au mois 30 éléments et de donner des «valeurs informatives» relatives à au moins 10 éléments additionnels. On présente également des observations sur le rendement de diverses techniques d'analyse et sur leur contribution au processus de certification.

Reference

Rajmund Dybczynski
1980: Comparison of the effectiveness of various procedures for the rejection of outlying results and assigning consensus values in interlaboratory programs involving determination of trace elements or radionuclides; Analytica Chimica Acta, v. 117, p. 53-70.

---

[1] Institute of Nuclear Chemistry & Technology, 03-195 Warsaw, ul. Dorodna 16, Poland.

Determination of elemental concentrations in nine CMEA rock and ore standards, in fired clay GHENT (FCG) and in NBS 98 plastic clay by instrumental neutron activation analysis

J.K. Frost[1]

Abstract: A wide variety of rock and mineral types are needed for use internationally as geological reference materials. More data, particularly for trace elements, are needed in the literature for many such existing reference materials. Concentration data for as many as 31 elements have been determined by instrumental thermal neutron activation analysis for nine European Community for Economic Development (CMEA) rock and ore standards. The standards analyzed were granite GM, granitoid 2B, black shale TS, monzonite MB, basalt BM, gabbro GV, nepheline syenite SNS-2, porphyry copper ore MrA, and lead-zinc ore OCrO.The Belgian Fired Clay Ghent FCG and the National Bureau of Standards Plastic Clay NBS 98 also were analyzed. Synthetic, multielement standards were used and USGS rock standards provided reference samples. Correction factors for uranium fission products on cerium and molybdenum and also less commonly encountered spectral interferences, such as those due to the 213 ppm tantalum in Granitoid 2B, were evaluated.

Résumé : Il faut une vaste gamme de types de roches et de minéraux comme matériaux de référence géologiques internationaux. Il faudra publier plus de données, notamment sur les éléments traces, pour un grand nombre de matériaux de référence existants. On a dosé un maximum de 31 éléments au moyen de l'analyse thermique instrumentale par activation neutronique dans neuf étalons de roche et de minerai envoyés par la Communauté européenne pour le développement économique (CMEA). On a analysé les étalons suivants : granite GM, granitoïde 2B, ampélite TS, monzonite MB, basalte BM, gabbro GV, syénite néphélinique SNS-2, minerai de cuivre porphyrique MrA et minerai de plomb et de zinc OCrO, ainsi que l'argile cuite de Belgique (Gand) et l'argile plastique NBS 98 du *National Bureau of Standards*. Des étalons multiéléments de synthèse ont été utilisés, et des étalons de roche de l'USGS ont servi d'échantillons de référence. On a évalué des facteurs de correction appliqués aux produits de fission de l'uranium dans le cérium et le molybdène, ainsi que des interférences spectrales moins courantes, comme celles causées par le tantale qui titrait 213 ppm dans le granitoïde 2B.

---

[1] Illinois State Geological Survey, 615 E. Peabody Drive, Champaign, Illinois, 61820, U.S.A.

Reference materials for environmental and geochemical analysis: past, present, and future

E.S. Gladney[1]

Abstract: Nearly forty years worth of data have been accumulated since the appearance of the original USGS G-1 and W-1 rock reference materials in 1950. Some NBS (now NIST) reference materials have an even longer history. My colleagues and I have collected over 110 000 individual data on a variety of USGS, CCRMP, and NBS materials. I will present an overall summary of the analytical developments that these data reveal in the geoanalytical and environmental communities, develop an assessment of the current state-of-the-art, and attempt to delve into the future needs of the analytical communities and the directions of the reference materials business.

Résumé : On accumule des données depuis près de quarante ans, soit depuis l'apparition des premiers matériaux de référence géologiques G-1 et W-1 de l'USGS en 1950. Certains matériaux de référence du NBS (maintenant le NIST) remontent même à plus loin. L'auteur et ses collègues ont recueilli plus de 110 000 données sur divers matériaux de l'USGS, du PCMRC et du NBS. L'auteur présente un résumé des progrès analytiques que ces données font ressortir dans les domaines de la géoanalyse et de l'environnement, évalue la situation actuelle, et tente de dégager les besoins futurs des chercheurs analystes et les orientations de l'industrie des matériaux de référence.

---

[1] Los Alamos National Laboratory, Group HSE-9, MS K-484, Los Alamos, New Mexico.

X-ray spectrometric analysis of five Chinese reference samples (GSR 1-5)

P.K. Govil[1]

Abstract: Ten major oxides and some selected trace elements: Zr, Y, Sr, Rb, Ba, V, Cr, Ni, Co, Zn, Cu, and Nb have been determined in five Chinese reference samples of granite GSR-1, andesite GSR-2, basalt GSR-3, sandstone GSR-4, and shale GSR-5 using a Philips PW 1400 XRF spectrometer having an on-line computer and software to correct for matrix effects. Few data are available in the literature on these Chinese standard samples and therefore, an attempt is made to provide usable values.

Fused beads using a mixture of lithium tetraborate, lithium metaborate, and lanthanum oxide in the ratio of 6:3:1 were prepared to determine major oxides. Pressed pellets with the backing of boric acid were used to determine trace elements. The sample pellets were prepared in triplicate and were analyzed ten times for major, minor, and trace elements.

XRF data were obtained with reference to the calibration curves prepared by using a large suite of international reference rock standards. Data on five Chinese standards are reported in this paper along with XRF methodology used for the analysis. The values obtained are in good agreement with the values reported by Xie and colleagues, the originators of the samples. The exception is for TiO_2 in major oxides where values are lower in almost all the standards.

Résumé : On a analysé dix oxydes majeurs et certains éléments traces (Zr, Y, Sr, Rb, Ba, V, Cr, Ni, Co, Zn, Cu et Nb) dans cinq échantillons de référence d'origine chinoise de granite (GSR - 1), d'andésite (GSR - 2), de basalte (GSR - 3), de grès (GSR - 4) et de shale (GSR - 5), avec un spectromètre à fluorescence X PW 1400 Philips relié en direct à un ordinateur et comportant un logiciel de correction des effets de matrice. La documentation renferme peu de données sur ces étalons d'origine chinoise, de sorte qu'on a tenté de produire des valeurs utilisables.

On a préparé des billes fondues constituées d'un mélange 6/3/1 de tétraborate de lithium, de métaborate de lithium et d'oxyde de lanthane pour le dosage des oxydes majeurs. Des granules pressés et de l'acide borique ont servi à doser les éléments traces. On a préparé les granules en triple exemplaire et dosé dix fois leurs éléments majeurs, mineurs et traces.

On a obtenu des données par fluorescence X pour les courbes d'étalonnage préparées à partir d'une vaste suite d'étalons de roche internationaux. On présente des données sur cinq étalons venant de Chine et l'on décrit la méthode d'analyse par fluorescence X. Les valeurs obtenues concordent avec celles de Xie et ses collègues, qui ont fourni les échantillons. L'exception est le TiO_2, pour lequel les valeurs sont plus faibles dans presque tous les étalons.

---

[1] National Geophysical Research Institute, Hyderabad-500007, India.

Granite and dolerite reference rock standards – preparation and evaluation

P.K. Govil[1] and S.M. Ahmad[1]

Abstract: Two reference rock standards, granite NGRI-G and dolerite NGRI-D, have been prepared to be used as reference samples for the chemical analysis of granite and dolerite rock samples using different instrumental methods of chemical analysis and for the calibration of instruments. The scarcity of and difficulties in obtaining international rock standards necessitated the preparation of some standards in our own country, especially in India where one of the best exposure of the rocks in the world is available. A program has been started in NGRI to prepare international reference rock standards. The granite was prepared in limited quantity and the preliminary data for major elements were published in the Journal of the Geological Society of India in 1986. The second dolerite sample (200 kg) was collected in 1987 from Osmania University campus, Hyderabad. The sample was found to be fine- to medium-grained dry dolerite dyke containing pyroxene, amphiboles, augite, plagioclase, etc. and showing no metamorphism. The sample was first subdivided using a hard steel jaw crusher and then finely powdered to -250 mesh size using a HERZOG grinding mill. The powdered sample was thoroughly mixed and stored in clean plastic bottles to supply different laboratories. The homogeneity test was performed and no significant evidence of inhomogeneity was observed by analysis of variance.

The sample was analyzed by different laboratories in India and abroad for major and trace elements. REE data were provided by the Bhabha Atomic Research Centre, in India; the Hahn Meitner Institute in W. Germany; NASA, U.S.A.; and ANRT, France. Replicate analysis at NGRI using spectrophotometry, AAS, XRF, and at other laboratories, has given us confidence in the results. The data received from different laboratories were treated as follows: (i) where 10 or more results are available the median, mean, and standard deviation are computed; or (ii) where fewer results are available for some elements, the decision as to whether or not to assign any usable value is made, based on the number of reported results, their degree of concurrence and the variety of analytical methods used. The assigned value is generally based on the median after the elimination of obvious outlines which should not constitute more than 10% of the data available. Usable values for all the major oxides, nine trace elements, and seven rare-earth elements for both standards are reported in this paper and the samples are now available for distribution.

Résumé : On a préparé deux étalons de roche de référence, le granite NGRI-G et la dolérite NGRI-D, à titre d'échantillons de référence pour l'analyse chimique d'échantillons de granite et de dolérite par différentes méthodes instrumentales et pour l'étalonnage d'instruments. La difficulté d'approvisionnement en étalons de roche internationaux et la rareté de ces étalons ont nécessité la préparation de certains étalons en l'Inde, où il existe l'un des meilleurs affleurements de ces roches au monde. Le NGRI a lancé un programme en vue de préparer des étalons de roche internationaux. On a préparé du granite en quantités limitées, et l'on a publié les données provisoires sur les éléments principaux en 1986 dans le *Journal of the Geological Society of India*. On a recueilli le deuxième échantillon de dolérite (200 kg) en 1987 sur le campus de l'Université Osmania, à Hyderabad. L'échantillon provenait d'un dyke de dolérite sèche à grain fin ou moyen qui contenait du pyroxène, des amphiboles, de l'augite, des plagioclases, etc. et ne présentait aucun indice de métamorphisme. On l'a d'abord concassé à l'aide d'un concasseur à mâchoires en acier dur, puis pulvérisé jusqu'à -250 mesh à l'aide d'un broyeur HERZOG. On a mélangé à fond l'échantillon pulvérulent, puis on l'a mis dans des bouteilles de plastique propres destinées à différents laboratoires. On a effectué l'essai d'homogénéité, et l'analyse de la variance n'a révélé aucune indication significative d'un manque d'homogénéité.

Différents laboratoires en Inde et à l'étranger ont dosé les éléments majeurs et les éléments traces de l'échantillon. Le Centre de recherches nucléaires de Bhabha (Inde), l'Institut Hahn Meitner (Allemagne de l'Ouest), la NASA (États-Unis) et l'ANRT (France) ont fourni des données sur les terres rares. Les analyses répétées par spectrophotométrie, par spectrométrie d'absorption atomique et par fluorescence X faites au NGRI et dans d'autres laboratoires donnent confiance dans la validité des résultats. Les données reçues de différents laboratoires ont été traitées comme suit : (i) pour les ensembles de dix résultats ou plus, la médiane, la moyenne et l'écart-type sont calculés; ou (ii) lorsque les résultats sont moins nombreux pour certains éléments, il faut décider s'il y a lieu d'attribuer une valeur utilisable basée sur le nombre de résultats rapportés, leur degré de concurrence et la variété des méthodes d'analyse utilisées. La valeur attribuée est en général basée sur la médiane après élimination des valeurs aberrantes qui ne doivent pas constituer plus de 10 % des données disponibles. Les auteurs donnent les valeurs utilisables pour tous les oxydes principaux, neuf éléments traces et sept terres rares contenus dans les deux étalons. Les échantillons sont maintenant prêts à être distribués.

---

[1] National Geophysical Research Institute, Hyderabad-500007, India.

Automated rock analysis for forty elements

K. Govindaraju[1]

Abstract: The "Centre de Recherches Pétrographiques et Géochimiques" has been involved in optical emission spectrochemical rock analysis for more than three decades. An enormous bottleneck in rock analysis laboratories is the preparation of samples. Automation of different steps involved in sample preparation schemes has been a constant subject of development in our production-oriented laboratory. This effort has been eased by the fact that all sample preparation schemes for the past three decades have been based on an initial lithium borate fusion with switch-over from solid analysis by arc/spark excitation to solution analysis in 1974 with the arrival of plasma excitation sources (microwave plasma, inductively coupled plasma). At present, a single solution prepared after an initial lithium borate fusion is used for the determination of over forty major, minor, and trace elements. All steps in the preparation scheme (weighings, fusion, acid dissolution, dilution, and preconcentration with ion-exchange columns for rare-earth elements, Sn, W, and Mo as well as for U and Th) have been either automated or robotized. Because of automation at all levels of analysis including that of running sample solutions with the spectrometer, high production of accurate rock analysis for forty elements has become routine at low cost.

Résumé : Le Centre de Recherches Pétrographiques et Géochimiques effectue depuis plus de trois décennies l'analyse des roches par spectrochimie d'émission optique. La préparation des échantillons de roche accapare considérablement les ressources des laboratoires d'analyse des roches. Au laboratoire du Centre, qui est axé sur la production, on cherche continuellement à perfectionner l'automatisation des différentes étapes de la préparation des échantillons. Cela est d'autant plus facile que depuis une trentaine d'années, tous les programmes de préparation des échantillons consistent d'abord à procéder à la fusion au borate de lithium, puis à analyser les solutions par des procédés employant des sources d'excitation de plasmas (procédés qui, avec l'introduction de plasma micro-onde et de plasma induit par haute fréquence, remplacent depuis 1974 l'analyse des solides par les procédés d'excitation arc/étincelle). Actuellement, une seule solution préparée après fusion initiale au borate de lithium sert à doser plus de quarante éléments majeurs, mineurs et traces. Toutes les étapes de la préparation (pesées, fusion, dissolution à l'acide, dilution et préconcentration au moyen de colonnes échangeuses d'ions dans le cas des terres rares, de Sn, de W, de Mo, d'U et de Th) ont été soit automatisées, soit robotisées. Grâce à l'automatisation de toutes les étapes d'analyse, y compris le passage des solutions de dosage dans le spectromètre, l'exécution rapide du dosage exact de quarante éléments des roches est devenue une opération courante peu coûteuse.

---

[1] CNRS, Centre de Recherches Pétrographiques et Géochimiques, B.P. 20, 54501 Vandoeuvre-les-Nancy, Cedex, France.

Are there still geostandards problems?

K. Govindaraju[1]

Abstract: In the mid-1970s, there was an uneasy feeling among specialists that something was wrong in the realm of geochemical reference samples. There was a great proliferation of "standard samples" with "recommended" or "certified" values. The blind use of these values, without any curiosity to ascertain their value (in both senses of the word) began to have repercussions on the quality of rock analysis. Among the solutions advanced for clarifying this chaotic situation, the inauguration of the Journal Geostandards Newsletter in 1977 turned out to be one of the actions in the right direction. That the term "geostandards" coined at that date has now become a "popular" word, points to the active role of the Journal as a "forum for exchange of ideas and information on geochemical reference samples". The geostandards problems which faced us at that period and the new ones which now arise today will be reviewed in the light of the progress made and to be made. Because progress in geochemical analysis is intimately tied up with progress in geostandards, an attempt will also be made to render geoanalysts more geostandard-conscious. In this connection, "Think Geostan" is a slogan that we wish to launch to set these problems in the limelight.

Résumé : Au milieu des années 1970, les spécialistes des échantillons de référence géochimiques se sont rendus compte de la confusion qui régnait dans ce domaine. Il y avait prolifération d'«étalons» ayant des valeurs «recommandées» ou «certifiées». L'utilisation aveugle de ces valeurs, sans aucune vérification de leur validité, a commencé à nuire à la qualité des analyses de roches. Parmi les solutions proposées pour corriger cette situation chaotique, l'inauguration en 1977 de la revue *Geostandards Newsletter* s'avère l'une des mesures judicieuses. La popularité actuelle du terme «étalons géochimiques» choisi à l'époque confirme le rôle actif qu'a joué la revue comme tribune d'échange d'idées et d'informations sur les échantillons de référence géochimiques. On examine les problèmes que posaient les étalons géochimiques à l'époque et les nouveaux problèmes qui surgissent maintenant, tout en tenant compte des progrès déjà réalisés et à réaliser. Comme tout progrès en analyse géochimique est étroitement lié aux progrès réalisés en matière d'étalons géochimiques, on tente aussi de sensibiliser davantage les géoanalystes au problème des étalons géochimiques. Dans ce contexte, «Pensons moyens de référence géochimique» est un slogan qu'on veut lancer pour attirer l'attention sur ces problèmes.

---

[1] CNRS, Centre de Recherches Pétrographiques et Géochimiques, B.P. 20, 54501 Vandoeuvre-les-Nancy, Cedex, France.

Evaluation of a rapid technique for the determination of precious metals in geological materials based on an aqua regia leach

C.J.B. Gowing[1] and P.J. Potts[1]

Abstract: Analysis of aqua regia extracts have been made by both graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS) with a view to developing a rapid, simple, and inexpensive technique for the determination of gold and the platinum-group elements (PGE) in exploration samples.

Although selective extraction by aqua regia is expected to leave the sample matrix largely unattacked, resultant solutions still contain high levels of Fe, Ni, Cu, Zn, Mg, and As, which produce significant interferences when the solutions are analyzed directly by GFAAS. To overcome these difficulties a simple solvent extraction procedure was investigated in which Au and the PGE are selectively complexed with triphenyl phosphine, then extracted from the aqueous phase into 1,2-dichloroethane. Results will be presented to demonstrate residual interference effects, the optimization of the furnace heating programme for organic solutions and the recovery efficiency of the solvent extraction process.

Routine direct analyses of diluted aqua regia solutions were found to be possible by ICP-MS. The procedures developed for the correction of drift effects and the calibration against aqueous standards will be described.

These procedures have been applied to:

a. a wide range of reference materials,

b. a series of samples that had been preanalyzed by nickel sulphide-fire assay,

c. two new chromitite reference samples, CHR-Pt+ and CHR-Bkg, in an appraisal of sample homogeneity.

Results will be presented to characterize the overall recovery efficiency of the aqua regia leach procedure and to assess the realistic capabilities of the technique for samples of varying matrix and PGE mineralogy.

Résumé : On a effectué l'analyse, par spectrométrie d'absorption atomique dans un four en graphite (SAA/FG) et par spectrométrie de masse avec plasma induit par haute fréquence (SM/PIHF), de produits extraits avec de l'eau régale dans le but de mettre au point une technique simple, rapide et peu coûteuse de dosage de l'or et des éléments du groupe du platine (EGP) dans les échantillons prélevés lors de la prospection.

Bien que l'extraction sélective à l'eau régale doive laisser la matrice de l'échantillon largement intacte, les solutions obtenues contiennent encore des taux élevés des éléments Fe, Ni, Cu, Zn, Mg et As qui produisent des interférences significatives lorsqu'on analyse les solutions directement par SAA/FG. Pour surmonter ces difficultés, on a étudié un procédé simple d'extraction par solvant, au cours duquel l'or et les EGP sont sélectivement complexés avec de la triphénylphosphine, puis extraits de la phase aqueuse dans du dichloroéthane-1-2. On présente les résultats afin de démontrer les interférences résiduelles, l'optimisation du programme de traitement des solutions organiques dans le four et le rendement du procédé d'extraction par solvant.

On a constaté qu'il était possible d'effectuer directement des analyses courantes de solutions diluées d'eau régale par la SM/PIHF. On décrit les procédés mis au point pour corriger les effets de dérive, et les procédés d'étalonnage en fonction d'étalons aqueux.

On a appliqué ces procédés :

a. à une large gamme de matériaux de référence,

b. à une série d'échantillons préalablement soumis à une analyse pyrognostique en présence de sulfure de nickel,

c. à deux nouveaux échantillons de référence de chromitite, CHR-Pt+ and CHR-Bkg, aux fins d'une évaluation de l'homogénéité des échantillons.

On présente les résultats de façon à caractériser le rendement global du procédé de lixiviation par l'eau régale et à évaluer de façon réaliste les possibilités d'appliquer cette méthode, à des échantillons dont la minéralogie de la matrice et les concentrations d'EGP sont variables.

---

[1] Department of Earth Sciences, The Open University, Walton Hall, Milton Keynes, Buckinghamshire, MK7 6AA, U.K.

Determination of stable isotope ratios by inductively coupled plasma mass spectrometry – impact on geological sciences

D.C. Gregoire[1]

Abstract: Inductively coupled plasma mass spectrometry (ICP-MS) is capable of measuring stable isotope ratios of most elements of the periodic table with a precision ranging from 0.1% to 0.5%. The relatively large sample throughput rate of ICP-MS now makes possible survey studies of stable isotope ratios in nature involving large numbers of samples. New applications of stable isotope ratios determined by ICP-MS are now emerging in the geological sciences and promise to have a great impact on petrogenic as well as exploration geochemistry studies. Discussed are isotope systems which are amenable to study by ICP-MS, methods employed for the determination of isotope ratios in geological materials, as well as specific examples of applications involving boron, osmium, silver, and bromine.

Résumé : La spectrométrie de masse avec plasma induit par haute fréquence (SM/PIHF) permet de mesurer les rapports d'isotopes stables de la plupart des éléments du tableau périodique avec une précision de 0,1 à 0,5 %. Le débit relativement élevé de traitement des échantillons par SM/PIHF permet maintenant de déterminer les rapports d'isotopes stables dans la nature pour un nombre élevé d'échantillons. Dans le domaine des sciences géologiques apparaissent de nouvelles applications des rapports d'isotopes stables établis par SM/PIHF, applications qui auront sans doute une profonde influence sur les études de pétrogenèse et les études géochimiques aux fins de prospection. On examine les systèmes isotopiques qui se prêtent à l'analyse par SM/PIHF, les méthodes employées pour déterminer les rapports isotopiques dans les matériaux géologiques, et des exemples précis d'applications portant sur le bore, l'osmium, l'argent et le brome.

---

[1] Geological Survey of Canada, 601 Booth St., Ottawa, Ontario, K1A 0E8, Canada.

Impact of ICP-MS on geoanalysis

G.E.M. Hall[1]

Abstract: The extremely variable composition of geological materials, particularly that of rocks and soils, poses an immense challenge to the accurate and precise multielement determination of trace and ultra-trace level constituents. Hence, it is not surprising that numerous geoanalytical laboratories leapt with both feet into ICP-MS in its early days, with promises of such features as simple spectra with few interferences, wide linear dynamic range, and detection limits in solution in the order of 0.01-0.1 ng• ml^{-1}. Inevitably, we have since learned to temper enthusiasm with caution, as fundamental and applied studies of matrix-induced interferences have evolved. However, new doors have been opened in geoanalysis by this technique whose ultimate power is yet to be fully exploited.

Undoubtedly two of the most significant achievements to date lie in the determination of two groups of elements: precious metals and the REEs. The collective determination of Au and the PGEs (Pt, Pd, Rh, Ru, Ir, Os) by commercial laboratories has been the sole domain of NAA. Application of ICP-MS in this field offers the advantages of superior sensitivity for Pt, Pd, and Ru and rapid turnaround time without the necessity of lengthy decay periods. This technique has also found a niche in the determination of Au, Pt, and Pd following Pb fire assay where previously ICP-AES and AAS have dominated. As in other applications the critical factor affecting detection limits is the purity of the reagents used, not the sensitivity of ICP-MS. Biogeochemical exploration for Pt and Pd has now become a practical tool, owing to the reasonable quantity of sample required to attain adequate detection levels. This technique now reigns supreme in its proven ability to determine all REEs down to 1 ng• g-1 if a separation step is incorporated into the procedure. This capability together with abundance level detection of high field strength elements (e.g. Nb, Hf, Ta) is greatly facilitating tectonic interpretation studies.

The application of surface and ground waters in geochemical exploration is yet to be thoroughly evaluated but the ability of ICP-MS to analyze waters directly and adequately for many trace elements assures it a key role. Research into the introduction of gaseous hydrides into the ICP mass spectrometer is currently active in an effort to improve detection limits over those offered by ICP-AES.

These comprise some of the accomplishments reviewed in this presentation. Progress in the use of alternative sample introduction techniques and calibration strategies is also discussed.

Résumé : La composition extrêmement variable des matériaux géologiques, notamment des roches et des sols, rend très difficile le dosage simultané et précis de plusieurs éléments traces et ultra-traces. Il n'est donc pas surprenant que de nombreux laboratoires de géoanalyse aient immédiatement adopté le procédé de SM/PIHF qui offrait des possibilités telles que des spectres simples avec peu d'interférences, une vaste plage dynamique linéaire et des limites de détection de l'ordre de 0,01 à 0,1 ng• ml^{-1} avec l'emploi de solutions. Inévitablement, on est devenu plus circonspect, les études fondamentales et appliquées des interférences causées par la matrice ayant progressé. Cependant, cette technique, dont les possibilités finales restent encore à exploiter pleinement, a ouvert de nouvelles perspectives dans le domaine de la géoanalyse.

Sans aucun doute, la réalisation actuelle la plus notable est le dosage de deux groupes d'éléments : les métaux précieux et les terres rares. Le dosage collectif de l'or et des éléments du groupe du platine (Pt, Pd, Rh, Ru, Ir, Os) par les laboratoires commerciaux s'est fait exclusivement par activation neutronique. Dans ce domaine, l'application du procédé SM/PIHF présente les avantages d'une sensibilité supérieure aux éléments Pt, Pd et Ru et d'un court délai d'exécution sans la nécessité de longues périodes de désintégration. Cette méthode a aussi trouvé comme application particulière le dosage de l'or, du platine et du palladium après l'analyse pyrognostique avec du plomb, dosage que l'on effectuait autrefois surtout par SE/PIHF et par SAA. Comme dans d'autres applications, le facteur critique qui influe sur la limite de détection est la pureté des réactifs utilisés, plutôt que la sensibilité de la SM/PIHF. La prospection biogéochimique du platine et du palladium est un outil pratique en raison de la quantité raisonnable d'échantillon requise pour atteindre des seuils de détection adéquats. Cette méthode surpasse maintenant toutes les autres, car il est prouvé qu'elle permet de doser toutes les terres rares jusqu'à 1 ng• g^{-1} si l'on intègre une étape de séparation au procédé. Cette faculté, combinée à la détermination de l'abondance des éléments décelables dans un champ à forte intensité (par ex. Nb, Hf, Ta), facilite grandement les études d'interprétation tectonique.

On n'a pas encore évalué en détail l'application de la prospection géochimique aux eaux de surface et aux eaux souterraines, mais la capacité de la SM/PIHF à doser directement et adéquatement dans ces eaux de nombreux éléments traces lui assure un rôle prépondérant. On poursuit actuellement des recherches sur l'introduction d'hydrures gazeux dans le spectromètre de masse/PIHF afin d'améliorer les limites de détection par rapport à celles de la SE/PIHF

Voilà quelques-unes des réalisations que passe en revue l'auteur. Il examine aussi les progrès réalisés dans l'emploi de nouvelles techniques d'introduction des échantillons et de nouvelles méthodes d'étalonnage.

---

[1] Geological Survey of Canada, 601 Booth Street, Ottawa, K1A 0E8, Canada.

Applications of a portable anodic stripping voltammeter in geoanalysis

G.E.M. Hall[1] and J.E. Vaive[1]

Abstract: To date the major use of the recently developed field-portable anodic stripping voltammeter, the PDV 2000 (Chemtronix, Australia), has been in environmental analysis, particularly in the determination of Pb. This instrument is battery-operated, weighs only 20 kg and, for most applications, does not require gases such as nitrogen for deaeration purposes. Studies at the Geological Survey of Canada (GSC) have shown the instrument to be suitable for the determination of base metals (Zn, Cu, Pb, Cd) in sediments, soils, and waters in remote locations. Investigation into its capability for the determination of Au is now in progress. Gold is extracted using an aqua regia or cyanide leach and various techniques to separate out possible electroactive interferences (e.g., Cu, Ag, Hg) are being evaluated. This paper presents a status report of the ongoing study into the capabilities of the PDV 2000 in geoanalysis.

Résumé : Jusqu'à présent, le voltampèremètre de redissolution anodique PDV 2000 (Chemtronix, Australie), transportable sur le terrain et récemment mis au point, a servi principalement aux analyses environnementales, notamment aux dosages du plomb. Cet instrument à piles ne pèse que 20 kg et, en général, ne nécessite pas l'emploi de gaz tels que l'azote à des fins de désaération. Des études entreprises à la Commission géologique du Canada ont montré que l'appareil peut servir au dosage de métaux communs (Zn, Cu, Pb, Cd) présents dans les sédiments, le sol et l'eau dans les régions éloignées. On examine actuellement ses capacités de dosage de l'or. On extrait l'or dans de l'eau régale or par le procédé de lixiviation par cyanuration, et l'on évalue divers autres procédés en vue de soustraire les interférences électroactives éventuelles (par ex. Cu, Ag, Hg). On présente l'état d'avancement des travaux en cours sur les possibilités du PDV 2000 en géoanalyse.

---

[1] Geological Survey of Canada, 601 Booth St., Ottawa, Ontario, K1A 0E8, Canada.

Comparison of the determination of Te by hydride generation ICP-MS and QT-AAS

G.E.M. Hall[1], K.N. De Silva[1], G. Gauthier[1], A.I. MacLaurin,
and J.C. Pelchat

Abstract: The determination of Te, along with other hydride-forming elements (As, Sb, Se, Bi), has traditionally been carried out at the Geological Survey of Canada by quartz tube atomic absorption spectrometry (QT-AAS). Samples are decomposed by an aqua regia leach or by the more 'total' $HF-HClO_4-HNO_3$ digestion in a sealed test-tube. The analytes are separated from possible interferences such as Cu and Ni by precipitation with $La(OH)_3$ and resolubilization in 4M HCl. However, 'mutual' interferences in the gas phase, from As especially, remain and degrade the low level detection of Te. For example, the presence of 1000 ppb in solution of As(V), Se(IV), and Bi(III) suppress the AA signal of 50 ppb Te by 17%, 40%, and 22%, respectively. This presents a major obstacle in ultra-trace analysis for Te in geological materials since its natural abundance is by far the lowest in this suite of elements (cf. the approximate abundance of Te at 1 ppb in igneous rocks with 2 ppm for As). Arsenic can be preferentially volatilized by evaporation in the presence of Br_2/H_2SO_4 and Se can be reduced to the noninterfering elemental state with KI; however, these procedures add complexity, time, and room for error in the sample preparation scheme.

The work presented here summarizes the preliminary investigation into the capabilities of hydride generation/ICP-MS in the low level detection of Te. This will eventually encompass the determination of all five hydride-forming elements by ICP-MS following phase-specific or total decompostion procedures.

Résumé : À la Commission géologique du Canada, on a traditionnellement effectué le dosage de tellure et d'autres éléments qui constituent des hydrures (As, Sb, Se, Bi) par spectrométrie d'absorption atomique en tubes de quartz (SAA/TQ). On décompose les échantillons par lixiviation avec de l'eau régale ou par digestion plus «complète» dans du $HF-HClO_4-HNO_3$ dans une éprouvette scellée. On sépare les produits à analyser des interférences éventuelles dues au Cu et au Ni, par précipitation avec du $La(OH)_3$ et resolubilisation dans une solution 4M de HCl. Cependant, les interférences «mutuelles» dans la phase gazeuse, causées surtout par l'arsenic, persistent et gênent la détection de faibles concentrations de tellure. Par exemple, la présence de 1 000 ppb dissoutes d'As(V), de Se(IV) et de Bi(III) supprime de 17 %, de 40 % et de 22 %, respectivement, le signal AA émis par 50 ppb de Te. Cela représente un important obstacle du point de vue du dosage d'ultratraces de tellure dans les matériaux géologiques, puisque l'abondance naturelle du tellure est de loin la plus faible dans cette suite d'éléments (l'abondance approximative du tellure se situant à 1 ppb dans les roches éruptives ayant 2 ppm d'As). On peut éliminer préférentiellement l'arsenic par volatilisation en présence de Br_2/H_2SO_4, et réduire le sélénium à l'état élémentaire, lequel ne peut créer d'interférences, avec du KI; cependant, ces procédés ajoutent de la complexité, prolongent le traitement et favorisent des erreurs dans le schéma de préparation des échantillons.

Les travaux présentés ici résument l'étude préliminaire des possibilités qu'offrent la génération d'hydrures et la SM/PIHF en vue de la détection de faibles concentrations de tellure. Cette étude devra en fin de compte englober le dosage par SM/PIHF de chacun des cinq éléments qui constituent des hydrures, après application soit de procédés spécifiques à une phase, soit de procédés de décomposition totale.

---

[1] Geological Survey of Canada, 601 Booth St., Ottawa, Ontario, K1A 0E8, Canada.

Commercial applications of neutron activation analysis

E.L. Hoffman[1]

Abstract: The theory behind instrumental neutron activation analysis (INAA) will be discussed. Various applications of INAA to exploration geochemistry will be described. The advantages and disadvantages of the technique will be shown and the role of INAA amidst other instrumental techniques described.

Cost, turnaround time, ultrasensitivity for certain elements, the nondestructive nature of analysis, and the high precision and accuracy of analyses have combined to make INAA an indispensable method for multielement analysis on virtually all geological matrices. Humus, vegetation, heavy minerals, lake bottom sediments, as well as rocks and soil analysis by INAA are some of the major applications of the method. As many as 60 elements can routinely and easily be determined by INAA.

Résumé : Dans cet exposé, on examine la théorie à la base de l'analyse instrumentale par activation neutronique (AIAN). On décrit diverses applications de l'AIAN à la prospection géochimique et l'on présente les avantages et les inconvénients de ce procédé et le rôle de l'AIAN par rapport à d'autres techniques instrumentales décrites.

En raison de son coût, des courts délais d'exécution, de son extrême sensibilité à certains éléments, de son caractère non destructif et de sa précision et de son exactitude élevées, l'AIAN est devenue une méthode indispensable pour le dosage simultané de plusieurs éléments dans pratiquement tous les types de matrices géologiques. L'analyse de l'humus, de la végétation, des minéraux lourds, des sédiments lacustres, des roches et du sol est une des principales applications de cette méthode. L'AIAN permet le dosage facile et courant de jusqu'à 60 éléments.

---

[1] Activation Laboratories Ltd., 1336 Sandhill Dr., Ancaster, Ontario, L9G 4V5, Canada.

New concepts and developments in reference materials for soil and vegetation analysis

M. Inhat[1]

Abstract: The nutritional and toxicological qualities of agricultural food crops and the associated soils are of concern with regard to nutrition, fertility, contamination, and erosion. For long term monitoring and other studies of chemical characteristics, incorporation of appropriate reference materials (RMs) into the analytical work is imperative. Although a moderate range of crop-based and some soil control materials are available for elemental analysis, quality control gaps are still evident, especially in the area of soil RMs certified for bioavailable or extractable elements. Developments and concepts applicable to the development of bioavailable element soil standards will be discussed. In addition, the latest progress in the development of several new crop-related reference materials to augment the current world repertoire of food and agricultural RMs will be presented.

Résumé : Les qualités nutritionnelles et les propriétés toxicologiques des cultures vivrières et les sols associés sont à étudier des points de vue de la valeur nutritionnelle des récoltes et de la fertilité, de la contamination et de l'érosion des sols en question. Pour la surveillance à long terme et les autres études des caractéristiques chimiques, il est essentiel d'intégrer les matériaux de référence appropriés aux travaux d'analyse. Bien que l'on dispose, à des fins d'analyse élémentaire, d'une gamme moyenne d'étalons de produits se rapportant aux cultures et de quelques étalons de sols, il y a encore de toute évidence des lacunes dans le contrôle de la qualité, notamment dans le domaine des matériaux de référence pédologiques certifiés pour ce qui est des éléments biodisponibles ou extractibles. On examine les détails et les notions applicables à l'élaboration d'étalons de sols comportant des éléments biodisponibles. En outre, on présente les derniers progrès réalisés dans la mise au point de plusieurs nouveaux matériaux de référence se rapportant aux cultures en vue d'accroître le répertoire mondial actuel de matériaux de référence alimentaires et agricoles.

---

[1] Land Resource Research Centre, Agriculture Canada, Ottawa, Ontario, K1A 0C6, Canada.

An alternative method of sample preparation for X-ray fluorescence analysis of rocks

G. Izquierdo[1] and M. Guevara[1]

Abstract: The present work deals with the adaptation of a method for sample preparation in the determination of the ten major elements in rocks, using a Siemens SRS 200 spectrometer. Initially the analysis was carried out employing lithium tetraborate glasses; due to the lack of materials such as platinum crucibles, furnaces, automatic polishing machines, and even reagents, we decided to look for another method of sample preparation. In order to reduce time and materials cost, compact discs made of high purity wax

and powdered rock were prepared, in such proportion to obtain a full and hard disc. So, depending on the composition of the rocks, it was necessary to increase the amount of wax, thereby resulting in the undesirable effect of high dilution of samples.

Another method tested was the preparation of discs from powdered cellulose and rock. This method was adopted since it offers some advantages such as low dilution and low cost; it is possible to determine all elements in the same pellet with a short preparation time. To prove the effectiveness of this method compared to that based on fusion, two series of the same geochemical reference standards were prepared both ways. Calibration curves were generated by least-squares linear regression. In order to evaluate the reproducibility of these two methods, duplicates of several samples were prepared, some being geochemical standards and others geological materials analyzed by different laboratories. Preliminary data show that accurate and precise results can be obtained by either of the two preparations. Additional analysis will be done to confirm that cellulose pellets do provide an alternative method of sample preparation for the XRF analysis of rocks.

Résumé : Le présent exposé porte sur la mise au point d'une méthode de préparation des échantillons en vue du dosage, au moyen d'un spectromètre Siemens SRS 200, des dix éléments majeurs trouvés dans les roches. Initialement, on effectuait l'analyse en employant des verres à base de tétraborate de lithium; or, en l'absence de matériel tel que les creusets en platine, les fours, les appareils de polissage automatiques et même les réactifs, les auteurs ont décidé de chercher une autre méthode de préparation des échantillons. Afin d'économiser temps et matériaux, ils ont préparé des disques compacts et durs à partir de cire très pure et de roche pulvérulente. Ainsi, en fonction de la composition des roches, il a fallu accroître la quantité de cire, ce qui a causé une dilution excessive des échantillons.

Une autre méthode essayée consistait à préparer des disques à partir de cellulose et de roche pulvérulentes. Les auteurs ont adopté cette méthode, car elle offre certains avantages comme une faible dilution et un coût peu élevé; en effet, il est possible de doser tous les éléments dans le même disque après un court temps de préparation. Pour démontrer que cette méthode est plus efficace que celle basée sur la fusion, les auteurs ont préparé deux séries des mêmes étalons géochimiques selon les deux procédés. Ils ont établi des courbes d'étalonnage par régression linéaire des moindres carrés. Pour évaluer la reproductibilité des résultats fournis par ces deux méthodes, ils ont préparé plusieurs échantillons en double, dont certains étalons géochimiques et certains matériaux géologiques analysés par différents laboratoires. Les données provisoires montrent que les résultats de l'une ou l'autre préparation peuvent être exacts et précis. D'autres analyses seront effectuées pour confirmer que les granules de cellulose constituent aussi des échantillons valables pour l'analyse des roches par fluorescence X.

---

[1] Instituto de Investigaciones Electricas, Interior Internado Palmira, Apartado Postal 475, 62000 Cuernava, Morelos, Mexico.

Application of plasma spectrometry (ICP-AES, ICP-MS) to the analysis of sediments: an evaluation study using standard reference materials

I. Jarvis[1] and K. Jarvis[2]

Abstract: Increased interest in the geochemistry of sedimentary samples by geologists and environmental scientists has led to the release of a range of new sedimentary standard reference materials (SSRM). Many of these standards, however, remain relatively poorly characterized when compared with established igneous rock reference materials.

Lack of characterization is a result of a number of factors, including: (a) sediments vary considerably in composition and most differ greatly from igneous rocks; (b) few geochemical laboratories specialize in sediment analysis, and therefore few have instruments which have been calibrated for this type of material;

(c) many trace elements occur at low levels in sediments, and consequently are difficult to determine by most routine analytical techniques; (d) many SSRMs have been released relatively recently and have not yet been characterized by a sufficiently large number of laboratories and/or techniques.

We have used a combination of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and ICP-mass spectrometry (ICP-MS) to study the compositions of a range of generally available SSRMs: Geological Survey of Japan (JSd-1, JSd-3 stream sediments; JCh-1 chert; JLk-1 lake sediment; JSl-1, JSl-2 slates; JDo-1 dolomite; JLs-1 limestone), National Institute of Standards and Technology, U.S.A. (1c argillaceous limestone; 88b dolomitic limestone), National Research Council of Canada (BCSS-1, MESS-1, PACS-1 marine sediments), United States Geological Survey (MAG-1 marine mud; SCo-1 Cody shale; SGR-1 Green River shale) and University of Liege (AWI-1 shale; CCH-1 limestone; DWA-1 dolomite; PRI-1 psammite; SBo-1 schist).

Samples were prepared in triplicate by three independent techniques: (1) fusion with lithium metaborate and digestion in dilute HNO_3; (2) digested in sealed microwave vessels using HF, HNO_3, and $HClO_4$ acids, evaporation, and dissolution in dilute HNO_3; and (3) grinding with agate beads in a $Na_4P_2O_7$ suspending agent. The first two preparations were analyzed by solution nebulization ICP-AES and ICP-MS; samples prepared by the third method were analyzed by slurry nebulization ICP-MS only.

The advantages and disadvantages of ICP-AES and ICP-MS for major and trace element analysis will be discussed, and procedures will be suggested for the routine determination of a wide range of elements in sedimentary materials by plasma spectrometry.

Résumé : Par suite de l'intérêt croissant manifesté pour la géochimie des échantillons de sédiments par les géologues et les scientifiques spécialistes de l'environnement, on a produit une gamme de nouveaux étalons de référence sédimentaires. Toutefois, bon nombre de ces étalons restent relativement mal caractérisés comparativement aux matériaux de référence reconnus constitués de roches ignées.

Cette caractérisation insuffisante est attribuable à plusieurs facteurs : (a) les sédiments ont une composition très variable et la plupart d'entre eux diffèrent grandement des roches ignées, (b) peu de laboratoires géochimiques se spécialisent dans l'analyse des sédiments, donc peu disposent d'appareils étalonnés en fonction de ce type de matériau, (c) de nombreux éléments traces sont présents en faibles teneurs dans les sédiments et ils sont donc difficiles à doser par les techniques d'analyse courantes, (d) de nombreux étalons de référence sédimentaires ont été mis en circulation assez récemment et n'ont pas encore été caractérisés par un nombre suffisant de laboratoires ou de méthodes.

Les auteurs ont combiné la spectroscopie d'émission atomique avec plasma induit par haute fréquence (SE/PIHF) et la spectrométrie de masse avec plasma induit par haute fréquence (SM/PIHF) pour étudier les compositions d'une gamme d'étalons de référence sédimentaires généralement disponibles et provenant de la Commission géologique du Japon (sédiments fluviatiles JSd-1, JSd-3, chert JCh-1, sédiment lacustre JLk-1, ardoises JSl-1, JSl-2, dolomie JDo-1, calcaire JLs-1), du *National Institute of Standards and Technology* aux É-U (calcaire argileux 1c, calcaire dolomitique 88b), du Conseil national de recherches du Canada (sédiments marins BCSS-1, MESS-1, PACS-1), de la *United States Geological Survey* (boue marine MAG-1, shale de Cody SCo-1, shale de Green River SGR-1) et de l'Université de Liège (shale AWI-1, calcaire CCH-1, dolomie DWA-1, psammite PRI-1, schiste SBo-1).

Ils ont préparé les échantillons en triple exemplaire selon trois techniques indépendantes : (1) fusion avec du métaborate de lithium et digestion dans du HNO_3 dilué, (2) digestion par du HF, du HNO_3, et du $HClO_4$ dans des récipients scellés pour traitement aux micro-ondes, évaporation et dissolution dans du HNO_3 dilué, (3) broyage avec des perles d'agate dans un agent de mise en suspension ($Na_4P_2O_7$). Les deux premières préparations ont été analysées par SE/PIHF et par SM/PIHF avec nébulisation d'une solution; les échantillons préparés selon la troisième méthode ont été analysés par SM/PIHF avec nébulisation d'une bouillie.

Les auteurs examinent les avantages et les désavantages de la SE/PIHF et de la SM/PIHF pour le dosage des éléments majeurs et des éléments traces, et ils suggèrent des procédés courants de dosage d'une large gamme d'éléments présents dans les matériaux sédimentaires, par spectrométrie avec plasma.

---

[1] School of Geological Sciences, Kingston Polytechnic, Penrhyn Road, Kingston upon Thames, Surrey, KT1 2EE, U.K.

[2] NERC ICP-MS Facility, Department of Geology, Royal Holloway & Bedford New College, Egham Hill, Egham, Surrey, TW20 OEX, U.K.

High dissolved solids and matrix effects in ICP-MS: methods towards improving determination limits for geoanalysis

K. Jarvis[1] and I. Jarvis[2]

Abstract: The excellent detection limits of inductively coupled plasma-mass spectrometry (ICP-MS) have brought the technique to the forefront of geoanalysis. For most elements, detection limits are typically <1 ng • mL^{-1} and this, combined with simple spectra and relative freedom from interferences (particularly for the heavier elements), offers the possibility for ultra-trace element determination in a wide range of geological materials. However, compromises must be made to minimize the effects of high total dissolved solids (TDS) or high concentrations of individual matrix elements. These compromises result in determination limits which, for many lighter elements, are comparable with those obtainable by ICP-AES.

We currently impose a limitation of ≈ 2000 µ g • mL^{-1} TDS on sample solutions. Above this level, significant analyte signal loss occurs over relatively short time-scales, and short-term precision is also impaired. In addition, a number of matrix effects, including analyte signal suppressions and enhancements, have been documented in solutions containing high concentrations (typically >1000 µ g • mL^{-1}) of a single matrix element.

The effects of high TDS and signal suppression are usually minimized by dilution of the sample solution, which then leads to increased limits of determination. A series of experiments has been carried out (primarily using shale and limestone standard reference materials), firstly to evaluate and minimize the effects of high dissolved solids in solution, and secondly to evaluate the particular problems associated with the analysis of sediments containing high concentrations of calcium (>20 wt.% Ca).

Previous work in our laboratory suggests that running times can be extended (before significant signal loss occurs) by replacing the standard 1.5 mm diameter torch injector tube with one of larger diameter. System optimization experiments have been carried out using a 3 mm diameter injector tube, not only to establish operating conditions which provide maximum sensitivity while minimizing interference effects, but also to examine the variation in analyte signal precision.

Analytical protocols developed during the study will be discussed, with particular reference to the improvement of routine analytical procedures for the ICP-MS determination of ultra-trace elements in sedimentary materials.

Résumé : En raison des excellentes limites de détection de la spectrométrie de masse avec plasma induit par haute fréquence (SM/PIHF), cette technique est devenue une méthode privilégiée de géoanalyse. Pour la plupart des éléments, les limites de détection sont typiquement de <1 ng • ml^{-1}; ces limites, les spectres simples et l'absence relative d'interférences (surtout dans le cas d'éléments lourds), offrent la possibilité de doser les éléments ultratraces dans une large gamme de matériaux géologiques. Cependant, on doit s'efforcer de trouver un moyen terme pour minimiser les effets des concentrations élevées de matières totales dissoutes (MTD) ou d'éléments de la matrice. On pourra ainsi établir des limites de dosage qui, pour de nombreux éléments légers, sont comparables à celles obtenues par le procédé de SE/PIHF.

On impose actuellement une limite d'environ 2 000 µ g • ml^{-1} de MTD pour les solutions de dosage. Lorsqu'on dépasse cette limite, il y a perte significative du signal venant de la substance à analyser sur un intervalle de temps relativement court et réduction de la précision à court terme. De plus, on a documenté un certain nombre d'effets de matrice, y compris la suppression et l'accentuation du signal venant de la substance à analyser, dans les solutions contenant des concentrations élevées (typiquement >1 000 µ g • ml^{-1}) d'ún seul élément de la matrice.

Habituellement, on réduit les effets des concentrations élevées de matières totales dissoutes et la suppression du signal en diluant la solution de dosage, ce qui accroît les limites de dosage. On a réalisé une série d'expériences (principalement sur des étalons de référence de shale et de calcaire), tout d'abord pour évaluer et minimiser les effets des concentrations élevées de matières dissoutes, puis pour évaluer les problèmes associés à l'analyse de sédiments contenant des concentrations élevées de calcium (>20 % de Ca en poids).

Les travaux de laboratoire portent à croire qu'il est possible de prolonger les temps d'exécution (avant qu'il y ait perte significative du signal) en remplaçant le tube d'injection standard de 1,5 mm de diamètre de la torche par un tube de plus grand diamètre. On a réalisé des expériences d'optimisation du système en employant un tube d'injection de 3 mm de diamètre et ce, non seulement pour établir des conditions de fonctionnement qui offrent une sensibilité maximale tout en minimisant les interférences, mais aussi pour examiner les variations de la précision du signal venant de la substance à analyser.

On examine les protocoles d'analyse élaborés au cours de l'étude, notamment l'amélioration des procédés analytiques courants de dosage par SM/PIHF d'éléments ultratraces dans les matériaux sédimentaires.

---

[1] NERC ICP-MS Facility, Department of Geology, Royal Holloway and Bedford New College, Egham Hill, Egham, Surrey, TW20 OEX, U.K.

[2] School of Geological Sciences, Kingston Polytechnic, Penrhyn Road, Kingston upon Thames, Surrey, KT1 2EE, U.K.

Review of literature (accepted, certified, concensus) values of standard reference materials with consideration of geochemical relationships

G.A. Jenner[1], H.P. Longerich[1], S.E. Jackson[1], and B.J. Fryer[1]

Abstract: There is an increasing number of rocks and minerals being made available to geochemists, for use as calibration standards and reference materials. Considerable effort is expended in compiling, analyzing, and distributing the analytical data collected on these materials. One aspect of the data evaluation, which is clearly neglected is consideration of the "geochemical" behaviour of the elements.

Geological processes most often follow a set of "rules", based upon crystallography, chemical bonding, and solid-liquid-gas equilibria, which maintain certain relationships between elements on primitive mantle normalized diagrams – integrating lanthanide, alkali metals, alkaline earth, Group IV, and Group V elements. It is possible to use these geochemical rules in evaluating data for the reference materials.

One of the advantages of ICP-MS is that it provides extensive coverage of many of the important geochemical groups. Use of this feature, in conjunction with knowledge of the "geochemistry" of the reference materials, makes it possible to evaluate not only the ICP-MS data, but the recommended values as well. We will present data, particularly for the newer USGS basalt standards, which clearly illustrate deficiencies in the literature data.

Résumé : Les géochimistes disposent de plus en plus de roches et de minéraux pouvant servir d'étalons et de matériaux de référence. Des efforts considérables sont déployés pour compiler, analyser et diffuser les données analytiques recueillies sur ces matériaux. Un aspect de l'évaluation des données qui est nettement négligé est l'étude du comportement «géochimique» des éléments.

Les processus géochimiques obéissent le plus souvent à un ensemble de «règles» basées sur la cristallographie, les liaisons chimiques et les équilibres solides-liquides-gaz, qui entretiennent certaines relations entre les éléments dans les diagrammes normalisés du manteau primitif, diagrammes intégrant les lanthanides, les métaux alcalins, les terres alcalines et les éléments des groupes IV et V. Il est possible d'utiliser ces règles géochimiques pour évaluer les données sur les matériaux de référence.

L'un des avantages de la SM/PIHF est qu'elle s'applique à un grand nombre de groupes géochimiques importants. Ce facteur, ajouté à la connaissance de la «géochimie» des matériaux de référence, permet d'évaluer non seulement les données de la SM/PIHF, mais aussi les valeurs recommandées. Les auteurs présentent des données, notamment sur les plus récents étalons de basalte de l'USGS, qui illustrent clairement les lacunes de la documentation.

---

[1] Department of Earth Sciences and Centre for Earth Resources Research, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X5, Canada

Use of geochemical reference standards in a quality control/quality assurance program

W.M. Johnson[1]

Abstract: A discussion is given of the role played by Geochemical Reference Standards in establishing and maintaining a Quality Control/Quality Assurance program in a commercial geochemical/assay laboratory. The discussion includes the development of internal standards and their certification with respect to internationally recognized standards. The discussion relates to standards used for geochemical trace analysis, ore grade assays and the analysis of concentrates for establishing the values of shipments. The source, preparation, and storage of the various types of internal standards developed is also covered.

Résumé : Le présent exposé porte sur le rôle joué par les étalons géochimiques dans l'établissement et le maintien d'un programme de contrôle et de garantie de la qualité dans un laboratoire commercial d'analyse géochimique. Il traite de la mise au point d'étalons internes et de leur certification par rapport aux étalons reconnus internationalement et, en particulier, des étalons utilisés pour le dosage géochimique des constituants présents en traces, le titrage des minerais et l'analyse des concentrés, aux fins de l'établissement de la valeur des produits expédiés. Il traite aussi de la source, de la préparation et de l'entreposage des divers types d'étalons internes mis au point.

---

[1] Bondar-Clegg & Co. Ltd., 5420 Canotek Rd., Ottawa, Ontario, K1J 8X5, Canada.

Derivation of recommended values from compilations: an opinion

J.S. Kane[1]

Abstract: In the July 1989 special issue of Geostandards Newsletter, Govindaraju indicated that a minimum of 40 analytical results, arrived at by at least four independent methods, are needed to derive working values or recommended concentrations, and that the working values are improved when derived from an even larger data set. To make the needed data more readily available, he suggests the desirability of annual updates for geochemical reference sample databases. It is the purpose of this opinion piece to comment on these issues.

First, the need for 40 or more analytical results to derive working values is a direct contradiction to the National Institute of Standards and Technology (NIST) approach in producing standard reference materials (SRMs). NIST certifies the elemental concentrations in SRMs, based on agreement between results from a minimum of three independent methods of analysis. Recently, the United States Geological Survey adopted a similar criterion in deriving recommended values for the shale reference sample, SDO-1 (1989).

Consensus values published by Gladney et al. (1987) do not differ significantly from original certified values, despite being based on as many as 50 independent results. Admittedly, the Gladney et al. (1987) compilation provides information on many elements not covered in the earlier certification program, and is, in this sense an improvement. However, the fact that consensus values for 19 elements in NBS coal SRM 1632, for example, are based on five or fewer literature values, and an additional 12 values are based on six to ten results, is itself a contradiction to the Govindaraju statement that 40 or more analyses are required for appropriate derivation of working values. It indicates the futility of annual updates to improve the quality of recommended concentrations, since even these few results were obtained only over twelve years.

Comparison of Flanagan's (1976 and 1984) original compilations for USGS geochemical reference samples with those published later by Gladney and Roelandts (1988a, b) similarly leads to the conclusions that 1) good working values can be derived from fewer than 40 laboratory results, providing all are obtained under stringent quality control, and 2) annual updates of compilations are likely to be redundant for all but a few elements.

Résumé : Dans le numéro spécial de juillet 1989 du *Geostandards Newsletter*, Govindaraju a indiqué qu'il fallait un minimum de 40 résultats analytiques fournis par au moins quatre méthodes indépendantes pour obtenir les valeurs de travail ou les concentrations recommandées, et que les valeurs de travail étaient meilleures lorsqu'elles provenaient d'un ensemble de données plus grand. Selon lui, pour faciliter l'accès aux données requises, il est souhaitable de mettre à jour annuellement les bases de données sur les échantillons de référence géochimiques. Le présent exposé examine ces détails.

Premièrement, la nécessité de disposer de 40 résultats d'analyse ou plus est en contradiction directe avec l'approche du *National Institute of Standards and Technology* (NIST) pour la production d'étalons de référence. Le NIST certifie les concentrations élémentaires dans les étalons de référence lorsqu'il y a concordance des résultats obtenus par au moins trois méthodes indépendantes d'analyse. Récemment, la *United States Geological Survey* (USGS) a adopté un critère semblable en vue d'établir des valeurs recommandées pour l'échantillon de référence de shale SDO-1 (1989).

Les valeurs de consensus, publiées par Gladney et al. (1987), ne diffèrent guère des valeurs certifiées originales, bien qu'elles soient basées sur un nombre aussi élevé que 50 résultats indépendants. En fait, la compilation de Gladney et al. (1987) renseigne sur de nombreux éléments non inclus dans le programme de certification antérieur et constitue à cet égard une amélioration. Toutefois, le fait que les valeurs de consensus, notamment pour 19 éléments de l'étalon de charbon SRM 1632 du NBS, soient fondées sur au plus cinq valeurs publiées et que 12 autres valeurs soient fondées sur entre six et dix résultats, contredit l'affirmation de Govindaraju selon laquelle on doit effectuer au moins 40 analyses pour obtenir des valeurs de travail acceptables. Cela indique l'inutilité de mises à jour annuelles pour améliorer la qualité des concentrations recommandées, car même ces quelques résultats n'ont été obtenus que sur une période de douze ans.

De même, l'étude comparative des compilations originales de Flanagan (1976 et 1984) pour des échantillons de référence géochimiques de l'USGS et des compilations publiées plus tard par Gladney et Roelandts (1988a, b) mène aux conclusions suivantes : (1) on peut obtenir de bonnes valeurs de travail à partir de moins de 40 résultats de laboratoire, pourvu qu'elles découlent toutes d'un étroit contrôle de la qualité, et (2) il est probable que la mise à jour annuelle des compilations est superflue pour presque tous les éléments.

References

E.S. Gladney, B.T. O'Malley, I. Roelandts, and T.E. Gills
1987: Standard reference materials: compilation of elemental concentration for NBS clinical, biological, geological and environmental standard reference materials; NBS Special Publication 260-111.

K. Govindaraju
1989: Compilation of working values and sample description for 272 geostandards; Geostandards Newsletter, Special Issue, v. 13, p. 1-113.

F.J. Flanagan (ed.)
1976: Description and analyses of eight new USGS rock standards; USGS Professional Paper 840, 192 p.

F.J. Flanagan
1984: Three USGS mafic rock reference samples, W-2, DNC-1, BIR-1; United States Geological Survey, Bulletin 1623, 54 p.
E.S. Gladney and I. Roelandts
1988a: 1987 compilation of elemental concentration data for USGS BHVO-1, MAG-1, QLO-1, RGM-1, SCo-1, SGR-1 and STM-1; Geostandards Newsletter, v. 12, p. 253-362.
1988b: 1987 compilation of concentration data for USGS BIR-1, DNC-1 and W-2; Geostandards Newsletter, v. 12, p. 63-118.

---

[1] U.S. Geological Survey, 12201 Sunrise Valley Drive, National Center MS923, Reston, Virginia, 22092, U.S.A., now at NIST, Gaithersburg, Maryland 20899.

Quality control and reference sample databases

J.S. Kane[1]

Abstract: A critical aspect of any quality control (QC)/quality assurance (QA) program is the definition of criteria for "satisfactory" performance of analytical methods. These criteria should address both expected accuracy and expected precision of the methods, as well as any variation in these figures of merit from one sample type to another.

It is reasonable to define the expected accuracy of a satisfactory method to be within the 95% confidence interval of the certified or recommended concentration for any reference sample. Then, using only such methods, any interlaboratory exercise involving analysis of reference samples would produce compilations from which little data would be rejected as outliers.

Perusal of the Canadian Certified Reference Materials Project (CCRMP) report for the characterization of the zinc sulphide ore KC-1 demonstrated this. Compilations for other geochemical reference samples, however, show a very different picture.

This has severe implications, since, for these materials generally, the compilations are used exclusively to derive recommended concentrations. The resulting "true" concentrations are therefore less well defined than they need to be, if reference sample analyses are to be useful in defining expected accuracy and satisfactory performance in QC programs.

There is a further concern in this regard as well. It must be supposed that we who are geoanalysts do our best work for participation in reference sample characterization programs. If, collectively, our best work evidences a lack of adequate quality control, what must the situation be in our routine geochemical exploration programs, where the requirements are presumably less stringent?

Résumé : Un détail critique de tout programme de contrôle de la qualité et de garantie de la qualité consiste à définir des critères de rendement «satisfaisant» des méthodes d'analyse. Ces critères devraient porter sur l'exactitude et la précision attendues des méthodes, ainsi que sur toute variation de ces paramètres d'un type d'échantillon à l'autre.

Il est raisonnable de définir l'exactitude prévue d'une méthode satisfaisante comme située dans l'intervalle de confiance de 95 % qui caractérise les concentrations certifiées ou recommandées pour tout échantillon de référence. Ainsi, toute recherche interlaboratoire visant à analyser des échantillons de référence par ces seules méthodes devrait produire des compilations dont peu de données seraient rejetées comme aberrantes.

L'examen du rapport sur le Projet canadien des matériaux de référence certifiés (PCMRC) l'a prouvé pour la caractérisation du minerai de sulfure de zinc KC-1. Les compilations relatives à d'autres échantillons de référence géochimiques donnent toutefois un tout autre résultat.

Cette situation a de graves répercussions, car pour la plupart de ces matériaux, les concentrations sont dérivées uniquement des compilations. Les concentrations «vraies» obtenues sont donc moins bien définies qu'elles ne devraient l'être si les analyses d'échantillons de référence doivent aider à définir l'exactitude prévue et le rendement satisfaisant dans le cadre des programmes de garantie de la qualité.

À cet égard, un autre problème se pose. Il faut partir du principe que les géochimistes font de leur mieux lorsqu'ils participent à des programmes de caractérisation des échantillons de référence. Si, collectivement, leurs meilleurs efforts manifestent un contrôle insuffisant de la qualité, quelle est alors la situation du point de vue des programmes courants de prospection géochimique, dont les exigences sont sans doute moins strictes?

---

[1] U.S. Geological Survey, 12201 Sunrise Valley Drive, National Center MS923, Reston, Virginia 22092, U.S.A., now at NIST, Gaithersburg, Maryland 20899, U.S.A.

Implications of sampling statistics in using slurry sample introduction for atomic spectrometric analysis of geochemical reference samples

J.S. Kane[1,2] and M.S. Epstein[1]

Abstract: A number of investigators have used slurry sample introduction for the atomic spectrometric analysis of a variety of materials. One advantage of the approach is that it reduces the sample preparation requirements for analysis. Additionally, slurry sample introduction eliminates the analytical errors due to incomplete decomposition. However, measurement precision for the technique is highly dependent on a homogeneous analyte distribution in the sample.

The expected analytical error from sampling can be calculated from grain size and mineral densities for analytes of inhomogeneous distribution, e.g., Cr as chromite in granites or dunites, Sn as cassiterite in granites, Zr as zircon in schists or granites, following the approach of Ingamells. We will present these calculations for a number of elements in specific geochemical and environmental reference samples where known mineralogy predicts inhomogeneous distribution.

Sampling constants can also be derived experimentally from the imprecision of analytical measurement. For slurry sample introduction, this imprecision should be greater for graphite furnace atomic absorption (GF-AAS) than for inductively coupled plasma atomic emission (ICP-AES) measurements, particularly when the analyte of interest is insoluble in the solvent phase of the slurry. Both GF-AAS and ICP-AES determinations of sampling constants will be made and compared to the calculated values.

The comparison will demonstrate the general acceptability of slurry sample introduction for atomic spectrometric analysis in reference sample characterization programs. It will also illustrate specific instances where the approach leads to unacceptable inaccuracies for best value estimations. Even in these instances, however, mineral speciation information frequently can be postulated from the data.

Résumé : Des chercheurs ont utilisé des échantillons sous la forme de bouillie pour analyser par spectrométrie atomique divers matériaux. Un avantage de cette méthode est qu'elle réduit les exigences de préparation des échantillons pour l'analyse. En outre, l'emploi de ces bouillies élimine les erreurs analytiques dues à une décomposition incomplète. Toutefois, la précision des mesures dépend étroitement d'une distribution homogène de la substance à analyser dans l'échantillon.

On peut calculer l'erreur d'échantillonnage prévue d'après le calibre et la densité des minéraux présents dans les produits à analyser de distribution hétérogène, par ex. Cr sous la forme de chromite dans les granites et les dunites, Sn sous la forme de cassitérite dans les granites, Zr sous la forme de zircon dans les schistes ou les granites, selon l'approche d'Ingamells. Les auteurs présentent ces calculs pour certains éléments contenus dans certains échantillons de référence géochimique et environnementale dont la minéralogie connue laisse prévoir une distribution hétérogène.

Il est possible également de dériver expérimentalement les constantes d'échantillonnage à partir de l'imprécision des mesures analytiques. Dans le cas d'un échantillon en bouillie, cette imprécision devrait être plus grande pour les mesures par spectrométrie d'absorption atomique dans un four en graphite

(SAA/FG) que pour les mesures par spectrométrie d'émission avec plasma induit par haute fréquence (SE/PIHF), surtout lorsque le produit à analyser est insoluble dans la phase qui correspond au solvant de la bouillie. On effectue des mesures des constantes d'échantillonnage par SAA/FG et par SE/PIHF, et l'on compare les résultats aux valeurs calculées.

L'étude comparative montre que l'introduction d'échantillons sous la forme de bouillie en vue de l'analyse par spectrométrie atomique est en général acceptable dans le cadre des programmes de caractérisation des échantillons de référence. Elle comporte aussi des exemples particuliers où ce procédé génère des inexactitudes inacceptables du point de vue des estimations de la meilleure valeur. Toutefois, même dans ces circonstances, on peut souvent déduire de ces données des renseignements sur la spéciation des minéraux.

---

[1] U.S. Geological Survey, 12201 Sunrise Valley Drive, National Center MS923, Reston, Virginia 22092, U.S.A.
[2] Now at NIST, Gaithersburg, Maryland 20899, U.S.A.

New selective reagents for the determination of platinum group elements and gold from geological materials

H.U. Kasper[1] and M. Schuster[1]

Abstract: Geochemical data on the siderophile platinum group elements in rock-generating differentiation processes of the upper mantle are still scarce, mainly due to analytical difficulties. Two major problems are to be solved for the determination of PGE and Au from ultrabasic rocks and chromite ores: (1) the quantitative decomposition of these materials, and (2) the separation of the extremely low contents of noble metals from the interfering matrices, followed by preconcentration.

Sample digestion was performed in PTFE lined high pressure decomposition vessels with a mixture H_2SO_4-HF-$HClO_4$ at temperatures up to 250°C and maximum pressure of 20 MPa over 48 hours. The resulting transparent sample solutions were tested with the new chelating agents N-acylthioureas from which N,N-diethyl-N′-benzoylthiourea (DEBT) yielded the best results. The PGE and Au chelates are extracted with isobutyl methyl ketone (IBMK). The high specificity and selectivity of DEBT for the noble metals and the excellent solubility of the chelates in IBMK enables considerable preconcentration factors of up to 50.

For the GFAAS determinations, IBMK offers optimal thermal decomposition performances and lowest nonspecific background absorption. Alternatively the DEBT chelates may be separated by TLC or HPLC with silica gel as stationary phase and solvents of moderate polarity. The elaborate decomposition and separation methods were used to analyze SARM-7, SARM-8, and some chromites from Greek ophiolite complexes. It is intended to apply these methods to the recently announced reference samples CHR-Pt^+ and CHR-Bkg.

Résumé : On dispose encore de peu de données géochimiques sur les éléments sidérophiles du groupe du platine présents lors des processus de différenciation du manteau supérieur qui produisent des roches, surtout en raison des difficultés que posent les analyses. Il faut résoudre deux grands problèmes afin de pouvoir doser les EGP et l'or présents dans les roches ultramafiques et les minerais de chromite : (1) la décomposition quantitative de ces matériaux et (ii) la séparation des teneurs extrêmement faibles de métaux nobles dans les matrices interférentes, puis la préconcentration de ces métaux.

On a réalisé la digestion des échantillons dans des récipients sous pression avec garniture de PTFE, dans un mélange de H_2SO_4-HF-$HClO_4$, à des températures atteignant 250°C et à une pression maximale de 20 MPa, pendant 48 heures. On a ensuite traité les solutions de dosage limpides ainsi obtenues avec les nouveaux chélateurs à N-acylthiourée, parmi lesquels le N,N-diéthyl-N′-benzoylthiourée (DEBT) a donné les meilleurs résultats. Les chélates d'EGP et d'or sont extraits dans l'isobutylméthylcétone (IBMK). La haute spécificité et la grande sélectivité de la DEBT vis-à-vis des métaux nobles, et l'excellente solubilité des chélates dans l'IBMK, permettent d'atteindre des facteurs de préconcentration considérables, allant jusqu'à 50.

Dans le cas des dosages par SAA/FG, l'IBMK donne la meilleure décomposition thermique et la plus faible absorption non spécifique de fond. Par ailleurs, les chélates traités à la DEBT peuvent être séparés par CCM ou par CLHP avec du gel de silice comme phase fixe et des solvants de polarité moyenne. On a employé des méthodes sophistiquées de décomposition et de séparation pour analyser SARM-7, SARM-8 et certaines chromites provenant de complexes ophiolitiques situés en Grèce. L'objectif est d'appliquer ces méthodes aux échantillons de référence récemment annoncés, CHR-Pt$^+$ et CHR-Bkg.

---

[1] Universitat zu Koln, Geologisches Institut Geochemisches Labor, Zulpicher Strasse 49, D-5000 Koeln 1, Germany.

A rapid method for the spectrophotometric determination of niobium in geological samples

B. Keshaven[1] and K.P. Krishna Prasad[1]

Abstract: A rapid method for the spectrophotometric determination of niobium at trace levels in geological samples is proposed. The method is based on the formation of a yellow coloured ternary niobium-thiocyanate-methotrimeprazine complex in 2µ to 5 M hydrochloric acid. The ternary complex which can be extracted into benzene exhibits an absorption maximum at 397 nm. Sandell's sensitivity of the reaction is 35 ng/cm^2 and the molar absorptivity is 2.64 x 10^4 L • mole^{-1} • cm^{-1}. Beer's law is valid over the niobium concentration range 0.2-3.5 µ g/mL. Maximum intensity is reached immediately after extraction and the absorbance readings remain stable for 24 hours.

The proposed method offers the advantages of sensitivity, selectivity, and reproducibility. The colour reaction is free from interferences due to many cations and anions which are usually encountered in the determination of niobium. Interferences due to iron can be masked by the addition of ascorbic acid. The method has been applied to the determination of niobium in columbite and other geological samples with good precision and accuracy.

Résumé : On propose une méthode spectrophotométrique rapide de dosage du niobium présent en traces dans des échantillons géologiques. Cette méthode se fonde sur la formation d'un complexe ternaire jaune de thiocyanate de niobium-méthotriméprazine dans de l'acide chlorhydrique de 2µ à 5M. Le complexe ternaire que l'on peut extraire dans du benzène présente un maximum d'absorption à 397 nm. La sensibilité de Sandell caractéristique de la réaction est de 35 ng/cm^2 et l'absorptivité molaire est de 2,64 x 10^4 L • mole^{-1} • cm^{-1}. La loi de Beer est valide dans la gamme de concentrations du niobium allant de 0,2 à 3,5 µ g/mL. L'intensité maximale est atteinte immédiatement après l'extraction, et les valeurs de l'absorbance restent stables pendant 24 heures.

La méthode proposée présente les avantages suivants : sensibilité, sélectivité et reproductibilité. La réaction de coloration est exempte des interférences dues aux nombreux cations et anions que l'on rencontre habituellement lors du dosage du niobium. Il est possible de masquer les interférences dues à la présence de fer par addition d'acide ascorbique. L'utilisation de cette méthode pour le dosage du niobium dans des échantillons de columbite et d'autres échantillons géologiques donne une précision et une exactitude élevées.

---

[1] Department of Postgraduate Studies and Research in Chemistry, University of Mysore, Mysore 570006, India.

The current status of geoanalysis at the IRMA

J. Li[1]

Abstract: The Institute of Rock and Mineral Analysis (IRMA) was founded in 1978 on the basis of the Beijing geological laboratory of the Chinese Ministry of Geology and Mineral Resources established in 1952. The institute itself is an exclusive research center of geoanalysis in China and takes full responsibilities for conducting: (1) development of new analytical techniques and methods for geoanalysis; (2) study, preparation, and analysis of geological reference materials; (3) analysis of complicated and difficult geological samples; and (4) technological services. IRMA now has a qualified staff of some 140 scientists and technicians and owns various analytical instruments for carrying out routine analysis and analytical method development. This talk will briefly present the current status of geoanalysis at the institute and the achievements of development research over the past years in the areas of arc source emission spectrometry, laser ablation ICP-ES, ICP-OES, ICP-MS, AAS, XRF as well as spectrophotometry and polarography.

Résumé : L'Institut d'analyse des roches et des minéraux a été fondé en 1978 à partir du laboratoire géologique du ministère chinois de la Géologie et des Ressources minérales, établi à Beijing en 1952. L'Institut proprement dit est un centre spécialisé de recherche géoanalytique en Chine qui a la pleine responsabilité : (1) de mettre au point de nouvelles techniques d'analyse et de géoanalyse; (2) d'étudier, de préparer et d'analyser des matériaux de référence géologiques; (3) d'analyser des échantillons géologiques complexes et difficiles à analyser; et (4) d'offrir des services techniques. Il est maintenant doté d'un personnel qualifié de quelque 140 scientifiques et techniciens, et possède divers instruments d'analyse destinés aux analyses courantes et à l'élaboration de méthodes analytiques. Dans cet exposé, on traite brièvement de la place actuelle de la géoanalyse à l'Institut et des succès des efforts de recherche de développement technique de ces dernières années dans les domaines de la spectrométrie d'émission avec source à arc, de la SE/PIHF avec ablation par laser, de la SE/PIHF, de la SM/PIHF, de la SAA, de la FX et enfin de la spectrophotométrie et de la polarographie.

---

[1] Institute of Rock and Mineral Analysis, Beijing, China.

Significance of the precise determination of trace element abundances by ICP-MS in continental flood basalts with specific reference to the Keweenawan and Siberian traps

P.C. Lightfoot[1] and W. Doherty[1]

Abstract: Inductively-coupled plasma mass spectrometry (ICP-MS) provides a fast and precise method for the routine determination of the rare-earth elements (REE), Rb, Sr, Y, Zr, Nb, Th, Ta, Hf, and U. Previous studies of flood basalt sequences have benefited from combined trace element and isotopic investigations, but determination of these elements by instrumental neutron activation analysis is both tedious and for many elements imprecise, whereas determinations by solid source mass spectrometry are very slow.

Of particular importance in studies of flood basalt petrogenesis is the ability to discriminate small changes in trace element ratios which have profound implications in petrogenetic modelling. We suggest that the ICP-MS method is capable of routinely determining all of these elements in basaltic rocks with a precision of 3%, or better, and suggest that the variations in ratios such as Th/Yb, Ta/Yb, Sm/Nd, La/Sm, Gd/Yb, and the magnitude of the Eu-anomaly in Keweenawan and Siberian trap basalts provide a basis for understanding the relative roles of crustal and mantle processes in flood basalt petrogenesis.

For example, the variations in La/Sm, Gd/Yb, and Sm/Nd through the sequence of 2200 m of 220 Ma old Siberian Trap lava flows at Noril'sk (USSR) provide a basis for a classification into six suites. Subtle variations in REE ratios through the upper 1700 m of basalt suggest that there was a progressive decline in the degree of crustal contamination upwards through the sequence.

Studies of the 2000 m of 1.1 Ga Keweenawan sequence exposed on the Black Bay Peninsula in Ontario provide a three-fold stratigraphic subdivision, and provide a basis for geochemical modelling.

Résumé : La spectrométrie de masse avec plasma induit par haute fréquence (SM/PIHF) est une méthode rapide et précise de dosage courant des terres rares et des éléments suivants : Rb, Sr, Y, Zr, Nb, Th, Ta, Hf et U. Des études antérieures de séquences de basaltes des plateaux ont comporté l'examen combiné d'isotopes et d'éléments traces, mais le dosage de ces éléments par l'analyse instrumentale par activation neutronique est laborieuse et, pour certains éléments, imprécise, tandis que les analyses faites sur des solides par spectrométrie de masse sont très lentes.

Dans les études de la pétrogenèse des basaltes des plateaux, il est particulièrement important de pouvoir distinguer les petites variations des rapports des éléments traces qui sont très importantes pour la modélisation pétrogénétique. Les auteurs estiment que la SM/PIHF permet le dosage courant de tous ces éléments dans les roches basaltiques à 3 % près, et que les variations de rapports tels que Th/Yb, Ta/Yb, Sm/Nd, La/Sm, Gd/Yb et la grandeur de l'anomalie en Eu dans les basaltes des plateaux de Keweenawan et de Sibérie constituent une base pour comprendre les rôles relatifs des processus qui ont lieu dans la lithosphère et le manteau lors de la pétrogenèse des basaltes des plateaux.

Par exemple, les variations de La/Sm, de Gd/Yb et de Sm/Nd dans les coulées de laves de Trap à Noril'sk, en Sibérie (URSS), constituent une base pour le classement des laves en six suites. Ces laves ont 2 200 m d'épaisseur et remontent à 220 ma. Les infimes variations des rapports des terres rares dans les 1 700 m supérieurs de basalte indiquent que le degré de contamination crustale a diminué progressivement vers le haut de la séquence.

Les études des 2 000 m de la séquence de Keweenawan, qui remonte à 1,1 ga et affleure dans la péninsule de Black Bay, en Ontario, ont permis de subdiviser la stratigraphie en trois parties et servent de fondement pour la modélisation géochimique.

---

[1] Geoscience Laboratories, Ontario Geological Survey, 77 Grenville Street, Toronto, Ontario, M5S 1B3, Canada.

Determination of trace elements in geological sample materials using ICP-MS

H.P. Longerich[1], S.E. Jackson[1], G.A. Jenner[1], and B.J. Fryer[1]

Abstract: The SCIEX Perkin-Elmer ICP mass spectrometer, which was installed in 1984 in the Department of Earth Sciences, has now been integrated into the department's elemental analysis facilities. ICP-MS is a routine analytical tool for many applications, determining trace elements in approximately 5000 samples per year. In rock matrices, it has been found especially suited to determining the heavier elements, from and including Rb to U. The major elements in rock samples along with the light trace elements Sc through Ga are determined using XRF or AAS. The trace elements Sc, Rb, Sr, Y, Zr, Nb, and Ba are determined by both XRF and ICP-MS thus serving as a quality control. Three ICP-MS packages are routinely available for elemental determinations including:

1. 33 trace elements: (Li, Be, Sc, Rb, Sr, Y, Zr, Nb, Mo, Cs, Ba, the lanthanides (La through Lu), Hf, Ta, W, Tl, Pb, Bi, Th, and U; in whole rock and mineral separate samples following an HF-HNO3 acid dissolution.
2. rare-earths and Th in rocks with a sodium peroxide sinter procedure, and
3. precious metals (Ru, Rh, Pd, Re, Os, Ir, Pt, and Au) following a NiS and Te precipitation collection.

Procedures for determining elements in fresh waters have been developed for application to geological programs. The water analysis includes several of the light elements in addition to a selection of heavier elements which are quantifiable in fresh surface and well waters. The long term precision and accuracy of the method will be demonstrated.

Résumé : Le spectromètre de masse/PIHF SCIEX de Perkin-Elmer, qui a été installé en 1984 au département des sciences de la Terre, est maintenant intégré aux installations de dosage des éléments dont dispose le département. La SM/PIHF est un outil courant d'analyse qui trouve de nombreuses applications et qui permet de doser les éléments traces dans environ 5 000 échantillons par année. Ce procédé est particulièrement efficace pour doser les éléments lourds, de Rb à U inclusivement, dans la matrice. Dans les échantillons de roches, les éléments majeurs et les éléments traces légers Sc à Ga sont dosés par FX ou par SAA. Les éléments traces Sc, Rb, Sr, Y, Zr, Nb et Ba sont dosés par FX et par SM/PIHF, ce qui permet un contrôle de la qualité. La SM/PIHF permet le dosage courant de trois groupes d'éléments :

1. 33 éléments traces : Li, Be, Sc, Rb, Sr, Y, Zr, Nb, Mo, Cs, Ba, les lanthanides (La à Lu), Hf, Ta, W, Tl, Pb, Bi, Th, U, dans des échantillons de roche totale et de constituants minéraux particuliers, après dissolution à l'acide HF-HNO3;
2. les terres rares et le thorium contenus dans les roches, après frittage avec du bioxyde de sodium;
3. les métaux précieux (Ru, Rh, Pd, Re, Os, Ir, Pt et Au) après leur collecte par précipitation en présence de NiS et de Te.

On a mis au point des méthodes de dosage des éléments dans l'eau douce pour les programmes de géologie. L'analyse de l'eau porte sur le dosage de plusieurs éléments légers et aussi d'une gamme d'éléments plus lourds qui sont mesurables dans les eaux douces de surface ou de puits. On démontrera que la méthode est précise et exacte à long terme.

---

[1] Department of Earth Sciences and Centre for Earth Resources Research, Memorial University of Newfoundland, St. John's, Newfoundland, A1C 5S7, Canada.

Determination of the isotope ratio ^{147}Sm/^{145}Nd, for application to isotope geology using ICP-MS

H.P. Longerich[1], S.E. Jackson[1], G.A. Jenner[1], and B.J. Fryer[1]

Abstract: The decay of ^{147}Sm to ^{143}Nd by alpha emission, with a half life of 106 000 000 000 years, is becoming increasingly important in geological isotopic studies. Knowledge of the isotope ratio of the daughter to a reference isotope (usually ^{143}Nd/^{144}Nd) requires attainment of precision (relative standard deviation less than 0.005%) much better than the ICP-MS is capable of, and is thus made using thermal ionization mass spectrometry (TIMS). However, the precision required for the isotope ratio of the parent to the reference, ^{147}Sm/^{144}Nd, is well within the capability of ICP-MS.

ICP-MS is used to make measurements of the intensity of two isotopes, ^{145}Nd and ^{147}Sm, in a fast peak jumping, data acquisition mode (0.05 seconds/isotope). The desired parameter (^{147}Sm/^{144}Nd) is calculated from the measured ratio (^{147}Sm/^{145}Nd), the known value of the ratio (^{145}Nd/^{144}Nd), and a factor which corrects for the instrumental measurement characteristics of mass discrimination, oxide formation, etc. The correction factor is obtained from measurements made on a standard solution prepared from high purity Nd and Sm metals. Using 225 second/isotope measurement times, relative standard deviations better than 0.5% are possible for samples with Sm greater than 6 ppm in the rock. Using ion-exchange procedures, solutions can be concentrated and better precisions obtained. Accuracy of the method will be demonstrated by comparison with results obtained by TIMS.

Résumé : La désintégration de ^{147}Sm en ^{143}Nd par émission alpha, avec une période de 106 ga, joue un rôle de plus en plus important dans les études géologiques basées sur des analyses isotopiques. La connaissance du rapport isotopique du produit de filiation en fonction d'un isotope de référence (habituellement ^{143}Nd/^{144}Nd) exige une précision (écart-type relatif de moins de 0,005 %) bien supérieure à celle que donne la SM/PIHF et qui n'est possible qu'avec la spectrométrie de masse avec thermo-ionisation. Cependant, la SM/PIHF est suffisamment précise pour fournir le rapport isotopique de l'isotope-parent en fonction de l'isotope de référence, ^{147}Sm/^{144}Nd.

La SM/PIHF permet de mesurer l'activité de deux isotopes, ^{145}Nd et ^{147}Sm, dans un mode de saisie de données à variation rapide de crêtes (0,05 seconde/isotope). On calcule le paramètre recherché (^{147}Sm/^{144}Nd) à partir du rapport mesuré (^{147}Sm/^{145}Nd), de la valeur connue du rapport ^{145}Nd/^{144}Nd et d'un facteur de correction des caractéristiques de mesure des instruments, notamment la discrimination de masse, la formation d'oxydes, etc. Le facteur de correction est basé sur des mesures provenant d'une solution étalon préparée à partir de Nd et de Sm métalliques très purs. En utilisant des temps de mesure de 225 secondes/isotope, il est possible d'obtenir un écart-type relatif de moins de 0,5 % pour des échantillons de roche titrant plus de 6 ppm de Sm. En utilisant des méthodes d'échange ionique, il est possible de concentrer les solutions et d'augmenter la précision. On démontrera la précision de la méthode par comparaison avec les résultats de la spectrométrie de masse avec thermo-ionisation.

---

[1] Department of Earth Sciences and Centre for Earth Resources Research, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X5, Canada.

RI-TOFMS analysis for trace elements in geological materials

W-Y. Ma[1], Q. Hui[1], K-L. Wen[1], X-Y. Xu[1], and D-Y. Chen[1]

Abstract: The direct and efficient detection of the concentration and the isotopic abundance of some trace elements, particularly the precious metals and the rare-earths, in geological materials is of great interest in geochemical exploration. This challenge has not been fully met using traditional techniques because of a lack of sensitivity. In recent years, a new method – Laser Resonance Ionization Time-Of-Flight Mass Spectrometry (RI-TOFMS) – has been investigated to solve this problem satisfactorily. The principal advantages are its high sensitivity and selectivity, as well as the possibility of direct analysis for trace constituents in various samples without appreciable matrix effects. We have been achieving the direct determination of Au and PGEs in geological materials with detection limits below 1 ppb; this work will be described.

Résumé : La détection directe et efficace de la concentration et de l'abondance isotopique de certains éléments traces, notamment des métaux précieux et des terres rares, dans les matériaux géologiques présente un grand intérêt pour la prospection géochimique. Jusqu'à présent, les procédés traditionnels n'ont pas entièrement permis d'atteindre ce but en raison de leur faible sensibilité. Ces dernières années, on a fait l'essai d'une nouvelle méthode – la spectrométrie de masse à temps de vol avec ionisation par résonance laser – pour bien résoudre ce problème. Les principaux avantages du procédé sont sa sensibilité et sa sélectivité élevées, de même que la possibilité de doser directement les constituants présents en traces dans

divers échantillons sans que la matrice ne produisent des effets notables. Les auteurs ont réussi à effectuer le dosage direct de l'or et des éléments du groupe du platine dans les matériaux géologiques avec des limites de détection inférieures à 1 ppb; ils décrivent ces recherches.

---

[1] Department of Physics, Tsinghua University, Beijing, China.

BANKAN – the batch of computer programs to accumulate and process elemental analyses of geological materials

K.V. Martynov[1]

Abstract: Having obtained an immense quantity of analytical data every geochemist needs a computer program to accumulate and process this information; BANKAN helps you in this purpose.

The bank of analyses consists of an unlimited quantity of informational blocks ("notes"). It is created as sequential mode file(s) on hard disk or diskette. Every "note" has an arbitrary structure (Table 1), determined by the user, and saved to file altogether with inputted data. The "note" consists of: 1) string variable – name of "sample"; 2) arrays of string variables ("lists") – descriptions of "sample"; 3) arrays of string variables – the names of analyzed "minerals"; 4) arrays of string variables – the names of analyzed "elements" in each "mineral"; 5) arrays of numeric variables – the means of element contents in "minerals" ("analyses").

Table 1. The structure of "note" from the bank of analyses

SAMPLE			
LIST 1	LIST 2	....	LIST I
DESCRIPTION 1.1 DESCRIPTION 1.2 .... DESCRIPTION 1.K	DESCRIPTION 2.1 DESCRIPTION 2.2	....	DESCRIPTION I.1 DESCRIPTION I.2 .... DESCRIPTION I.M
MINERAL 1			
ELEMENT 1	ELEMENT 2	....	ELEMENT N
ANALYSIS 1.1 ANALYSIS 1.2 .... ANALYSIS 1.P	ANALYSIS 2.1 ANALYSIS 2.2 .... ANALYSIS 2.P	....	ANALYSIS N.1 ANALYSIS N.2 .... ANALYSIS N.P
....	....	....	....
MINERAL R			
ELEMENT 1	ELEMENT 2	....	ELEMENT S
ANALYSIS 1.1 ANALYSIS 2.1 .... ANALYSIS 1.T	ANALYSIS 2.1 ANALYSIS 2.2 .... ANALYSIS 2.T	....	ANALYSIS S.1 ANALYSIS S.2 .... ANALYSIS S.T

BANKAN includes three BASIC-programs. The first one (INTO) is designed to create the "note" structure, i.e., to determine the quantity and dimensions of arrays ("list", "minerals", "elements"), and to name them. Besides that, this program is used to input data. The second program (SORT) helps to locate all "notes" having certain signs. These signs are the names of "lists" and their contents, the names of "minerals" and "elements". The third program (OUT) is employed to look through each "note" (sequentially or in the search regime, using the name of "sample"), to process the numeric data and to create a file(s) for printing. The processing of data includes: 1) the calculation of additional relationships (stoichiometric coefficients, mole fractions, etc.), which are determined by the user; 2) looking through "analyses" on a plot (up to 8 plots simultaneously), the axes of the plots are determined by the user; and 3) statistic processing. The last one includes calculations of the middle means, confidence intervals, standard deviations, variational coefficients, and the matrix of correlation coefficients. Statistic characteristics are calculated for Student's distribution with a confidence probability of 0.95. Initial and calculated data could be seen on a screen and saved to file(s) for printing as a convenient table.

The programs are suitable for BASIC-interpreters as well as for BASIC-compilers. Colour graphics are used in these programs. BANKAN's users have the possibility to keep in compatible form an immense quantity of analyses of geological samples and their descriptions.

Résumé : Après avoir obtenu une vaste quantité de données analytiques, tout géochimiste a besoin d'un programme informatique pour accumuler et traiter cette information. Voilà ce que permet BANKAN.

La banque d'analyses comporte une quantité illimitée de blocs d'information («notes»). On la constitue sous la forme de fichier(s) séquentiel(s) sur disque dur ou disquette. Chaque «note» a une structure arbitraire (tableau 1) déterminée par l'utilisateur et sauvegardée avec les données d'entrée. La «note» comprend 1) une variable chaîne – le nom de l'«échantillon»; 2) des tableaux de variables chaînes («listes») – les descriptions de l'«échantillon»; 3) des tableaux de variables chaînes – les noms des «minéraux» analysés; 4) des tableaux de variables chaînes – les noms des «éléments» analysés dans chaque «minéral»; 5) des tableaux de variables numériques – les moyennes des concentrations d'éléments dans les «minéraux» («analyses»).

Tableau 1. Structure de «Note» dans la banque d'analyses

ÉCHANTILLON			
LISTE 1	LISTE 2	....	LISTE I
DESCRIPTION 1.1 DESCRIPTION 1.2 .... DESCRIPTION 1.K	DESCRIPTION 2.1 DESCRIPTION 2.2	....	DESCRIPTION I.1 DESCRIPTION I.2 .... DESCRIPTION I.M
MINÉRAL 1			
ÉLÉMENT 1	ÉLÉMENT 2	....	ÉLÉMENT N
ANALYSE 1.1 ANALYSE 1.2 .... ANALYSE 1.P	ANALYSE 2.1 ANALYSE 2.2 .... ANALYSE 2.P	....	ANALYSE N.1 ANALYSE N.2 .... ANALYSE N.P
....	....	....	....
MINÉRAL R			
ÉLÉMENT 1	ÉLÉMENT 2	....	ÉLÉMENT S
ANALYSE 1.1 ANALYSE 2.1 .... ANALYSE 1.T	ANALYSE 2.1 ANALYSE 2.2 .... ANALYSE 2.T	....	ANALYSE S.1 ANALYSE S.2 .... ANALYSE S.T

BANKAN regroupe trois programmes BASIC. Le premier (INTO) est conçu pour créer la structure de «note», c'est-à-dire pour déterminer le nombre et les dimensions des tableaux («liste», «minéraux», «éléments») et les nommer. Il sert aussi à introduire les données. Le deuxième programme (SORT) aide à situer toutes les «notes» qui portent certains signes. Ces signes sont les noms des «listes» et de leur contenu, des «minéraux» et des «éléments». Le troisième programme (OUT) sert à scruter chaque «note» (séquentiellement ou en mode recherche, en utilisant le nom de l'«échantillon»), à traiter les données numériques et à créer un ou plusieurs fichiers à des fins d'impression. Le traitement des données comprend : 1) le calcul des relations additionnelles (coefficients stoechiométriques, fractions molaires, etc), que détermine l'utilisateur; 2) l'interprétation des «analyses» sur un diagramme (jusqu'à 8 diagrammes simultanément), les axes des diagrammes étant déterminés par l'utilisateur; et 3) le traitement statistique, qui comprend les calculs de la médiane, des intervalles de confiance, des écarts-types, des coefficients de variation et de la matrice des coefficients de corrélation. Les caractéristiques statistiques sont calculées pour une distribution de Student avec probabilité fiducielle de 0,95. On peut afficher sur écran les données initiales et les données calculées et les sauvegarder dans un ou plusieurs fichiers pour impression sous la forme pratique d'un tableau.

Les programmes conviennent aux interprètes et aux compilateurs du langage BASIC. Ces programmes utilisent le traitement graphique couleur. Les utilisateurs de BANKAN peuvent conserver sous une forme compatible un grand nombre d'analyses et de descriptions d'échantillons géologiques.

---

[1] Institute for Experimental Mineralogy, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

The reference samples block for EPMA

K.V. Martynov[1] and I.M. Romanenko[2]

Abstract: During the last thirty years considerable progress in the spatial elemental analysis of geological materials has been made with the development of such methods as X-ray spectral electron probe microanalysis (EPMA). However, as in any physically based method, EPMA needs standard reference samples to estimate the precision of the analytical data and to prepare calibrations.

Usually, the reference samples are matched to one type of matrix (e.g., rock-forming silicates, sulphides, and others), placing them in a common block. As this is not always convenient, we suggest the use of a universal reference samples block including all pure metals (stabilized at usual conditions), some metal oxides, and other simple and complex stoichiometric compounds. Most of them, with the exception of HgS and rock-forming minerals, are synthetic. The block is a bronze disk (24 mm diameter and 4 mm height) having 61 cells. Each cells has from 2 to 4 reference samples, totalling 206 samples. A qualitative composition of each sample has been determined using the scanning electron microscope JSM-35CF(JEOL) with an energy dispersive spectrometer LINK 860/500. Quantitative analysis has been determined using the microprobe Camebax-Microbeam.

Résumé : Depuis une trentaine d'années, on réalise des progrès considérables en analyse élémentaire spatiale des matériaux géologiques grâce à la mise au point de procédés tels que la microanalyse aux rayons X par sonde électronique. Cependant, comme pour toute autre méthode physique, il faut des étalons de référence afin de pouvoir estimer la précision des données analytiques et procéder à des étalonnages.

Habituellement, on fait correspondre les échantillons de référence à un type de matrice (par ex., silicates, sulfures et autres matières lithogénétiques) et on les place dans un bloc commun. Cette méthode n'étant pas toujours pratique, les auteurs proposent d'employer un bloc d'échantillons de référence universels composé de métaux purs (stabilisés dans des conditions normales), de certains oxydes métalliques et d'autres composés stoechiométriques simples et complexes. La plupart d'entre eux sont synthétiques, à l'exception du HgS et des minéraux naturels. Le bloc en question est un disque de bronze (24 mm de diamètre et 4 mm de hauteur) avec 61 cellules, chacune comportant de deux à quatre échantillons de référence; il y a 206 échantillons en tout. On a effectué une analyse qualitative de chaque échantillon au moyen d'un microscope électronique à balayage JSM-35CF(JEOL) et d'un spectromètre LINK 860/500 dispersif en énergie. On a effectué l'analyse quantitative au moyen d'une microsonde Camebax-Microbeam.

---

[1] Institute for Experimental Mineralogy, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

[2] Institute "Giprotzvetmetobrabotka", Moscow, U.S.S.R.

Regional geochemical mapping in the tropical environment: bedrock reflection of Precambrian volcanosedimentary sequences in B-horizon soil strata: case studies from Nigeria/West Africa

G. Matheis[1] and A. Utke[1]

Abstract: About one quarter of the Earth's land surface is covered by thick accumulations of lateritic soils, limiting the exposure of bedrock and leaving these regions the least explored. The most successful way to establish the badly needed geological and mineral inventories of these areas is the regional application of geochemical mapping, complemented by remote sensing and geophysics.

Although chemical weathering progresses rather quickly in the tropics, extensive leaching is nearly restricted to the major elements Mg, Ca, Na, K, and partly Si. Most of the trace elements, however, retain more or less their bedrock concentrations, i.e., lithologically determined concentration ranges of the bedrock are not overruled by the weathering processes.

In order to gain detailed information on the geochemical dispersion between the concealed bedrock and the uppermost soil horizons where sampling usually takes place (uppermost 60 cm of B-horizon), various orientation surveys were carried out in different climatic zones of Nigeria, ranging from the rain forest in the south to the dry Savannah in the north. The main lithological targets were late Proterozoic greenstone type associations which are host to Nigeria's gold resources and are equally important in revealing the Proterozoic geodynamic processes of the Nigerian basement complex.

Vertical dispersion was studied in auger drilled soil profiles. The regional distribution patterns cover selected areas over volcanosedimentary sequences, totally about 1000 km^2 at a sample density of one sample per square kilometre. Various selective leaching methods were applied to gain information on clay adsorbed, hydroxide adsorbed, and total geochemical dispersion.

A comparison of the resulting geochemical maps with the most detailed published maps at scale 1:250 000 clearly demonstrated the advantage of geochemical mapping in providing more detailed information as well as pointing out inaccuracies in the existing geological maps.

Résumé : Le quart environ des terres émergées sont recouvertes d'épais dépôts latéritiques qui réduisent l'étendue des affleurements du substratum rocheux, de sorte que ces régions sont parmi les moins explorées. Le moyen le plus efficace de dresser les inventaires géologiques et minéraux de ces régions, dont on a un besoin urgent, est d'en établir la cartographie géochimique régionale, complétée par des travaux de télédétection et de géophysique.

Même si l'altération chimique progresse assez rapidement sous les tropiques, la lixiviation poussée se limite surtout aux éléments majeurs (Mg, Ca, Na, K et en partie Si). Cependant, la plupart des éléments traces conservent plus ou moins les mêmes concentrations que dans le substratum rocheux, c'est-à-dire que dans le substratum rocheux, la gamme des concentrations qui est fonction de la lithologie n'est pas modifiée par les processus d'altération.

Pour obtenir de l'information détaillée sur la dispersion géochimique des éléments entre le substratum rocheux caché et les horizons de sol sommitaux où l'échantillonnage s'effectue normalement (les 60 premiers cm de l'horizon B), on a réalisé divers levés d'orientation dans différentes zones climatiques du Nigéria, allant de la forêt tropicale humide, dans le sud, à la savane sèche, dans le nord. Les principales cibles lithologiques étaient les associations de types roches vertes du Protérozoïque tardif qui sont le siège des ressources aurifères du Nigéria et, ce qui est également important, révèlent les processus géodynamiques du Protérozoïque qui ont formé le socle nigérien.

On a étudié la dispersion verticale dans des profils de sol creusés à la tarière. Les zones choisies de distribution régionale recouvrent des séquences volcano-sédimentaires et totalisent environ 1 000 km^2, la densité d'échantillonnage étant d'un échantillon au km^2. On a employé diverses méthodes de lixiviation sélective pour recueillir de l'information relative à l'adsorption sur les argiles, à l'adsorption sur les hydroxydes et à la dispersion géochimique totale.

L'étude comparative des cartes géochimiques produites et des cartes les plus détaillées, publiées à l'échelle de 1/250 000, montre clairement que la cartographie géochimique permet d'obtenir plus d'information détaillée et de relever les inexactitudes dans les cartes géologiques existantes.

---

[1] Technical University of Berlin, E Reuter Platz 1, Berlin 12, D1000, Germany.

Mobile field analysis for exploration and environmental geochemistry by AAS and IR: on-site evaluation of chemical and mineralogical properties

G. Matheis[1], H. Ganz[1], D. Kuster[1], and A. Utke[1]

Abstract: The evaluation of secondary geochemical dispersion patterns is equally important for application in both exploration and environmental geochemistry. Due to the rather complex chemical processes which overprint all weathering products, the application of selective leaching methods as well as detailed studies of the clay mineralogy are the basics of any sound interpretation.

Flame-AAS has been developed as the most versatile analytical tool in the evaluation of secondary geochemical dispersion patterns. The range of target elements which can be determined without difficulty even in a generator-powered mobile field laboratory covers a wide range of potential ore accumulations

either by the ore elements directly or via suitable pathfinder elements; similarly, AAS analysis is extremely helpful in geochemical mapping surveys under different climatic conditions as well as in environmental surveys.

The mineralogical and especially the clay composition of weathering products is critical in understanding chemical adsorption effects as the key to secondary dispersion. In contrast to X-ray diffraction, infrared (IR) spectroscopy provides a rapid and simple method to evaluate mineral compositions both qualitatively and quantitatively. Another advantage is the possibility to detect noncrystalline phases, the presence of water in a mineral and information on the nature of the silicate anion in the mineral structure. Sample preparation as well as instrumentation (220 V power supply, no cooling system) favour the application of both AAS and IR in mobile field laboratories in any climatic or logistical conditions.

Résumé : L'évaluation des schémas secondaires de dispersion géochimique est toute aussi importante en prospection géochimique qu'en géochimie environnementale. En raison des processus chimiques plutôt complexes qui se superposent à tous les produits d'altération, l'application de méthodes sélectives de lixiviation et les études détaillées de la minéralogie des argiles représentent les fondements de toute interprétation valable.

On mis au point le procédé de spectrométrie d'absorption atomique (SAA) par la flamme qui s'est avéré l'outil analytique le plus souple pour évaluer les schémas secondaires de dispersion géochimique. La gamme des éléments cibles que l'on peut doser sans difficulté même dans un laboratoire mobile de terrain à groupe électrogène couvre un large éventail de minéralisations potentielles constituées soit directement par les éléments du minerai, soit par des indicateurs géochimiques appropriés; également, l'analyse par SAA s'avère extrêmement utile lors des levés de cartographie géochimique dans différentes conditions climatiques et aussi lors des levés environnementaux.

Il est essentiel de connaître la composition des minéraux et notamment des argiles dans les produits d'altération afin de comprendre le rôle clé des effets de l'adsorption chimique dans la dispersion secondaire. Contrairement à la diffraction des rayons X, la spectroscopie infrarouge (IR) constitue une méthode simple et rapide d'évaluation à la fois qualitative et quantitative de la composition minérale. Un autre avantage est la possibilité de déceler des phases non cristallines, la présence d'eau dans un minéral et l'information sur la nature de l'anion silicate dans la structure du minéral. La préparation de l'échantillon ainsi que l'appareillage (alimentation électrique de 220 V, aucun système de refroidissement) facilitent l'exploitation des procédés SAA et IR dans les laboratoires mobiles de terrain, quelles que soient les conditions climatiques ou logistiques.

---

[1] Technical University of Berlin, E Reuter Platz 1, Berlin 12, D1000, Germany.

Characteristics of imaging sensor based spectrometer systems for high resolution ICP spectrometry of complex sample matrices

S. McGeorge[1]

Abstract: The detection of major, minor, and trace elements in geological samples using spectrochemical techniques can be complicated by several factors including sample preparation, sample introduction, matrix interferences operating in the sample transport and excitation regime, and spectral interferences due to the complex spectra produced by the sample. This paper will focus on the capabilities of high resolution spectrometer systems employing imaging detectors which record the emission spectra of several elements simultaneously.

Imaging sensors provide unique capabilities for the analyst when used to record spectral information. Several significant advantages include simultaneous background correction, flexible signal processing capabilities, and the ability to digitally record the sample spectrum for further review and postprocessing. One of the more interesting aspects of image processing is the potential for spectral evaluation by the computer system to detect possible spectral interference or complex background conditions.

The main theme of this paper will be the use of imaging detection systems for elemental analysis of complex sample matrices as found in the geochemical domain. Several problem sets will be presented along with techniques that can be used to provide analytical solutions.

Résumé : Plusieurs facteurs, notamment la préparation et l'introduction des échantillons, les interférences causées par la matrice durant le transport et l'excitation de l'échantillon et les interférences causées par les spectres complexes que produit l'échantillon, viennent parfois compliquer la détection, par des procédés spectrochimiques, des éléments majeurs, des éléments mineurs et des éléments traces dans les échantillons géologiques. Dans cet exposé, on examine principalement les possibilités qu'offrent les spectromètres à haute résolution munis de détecteurs imageurs qui enregistrent simultanément les spectres d'émission de plusieurs éléments.

Les capteurs-imageurs offrent à l'analyste des possibilités exceptionnelles pour ce qui est de l'enregistrement de l'information spectrale. Parmi les avantages notables, il y a la correction simultanée des valeurs de fond, la souplesse du traitement des signaux et la capacité d'enregistrer numériquement le spectre de l'échantillon à des fins d'examen ultérieur et de post-traitement. Un des détails les plus intéressants du traitement d'image est la possibilité d'évaluer les spectres par ordinateur afin de déceler les interférences spectrales éventuelles ou les conditions de fond complexes.

Dans cet exposé, on traite principalement des systèmes de détecteurs imageurs utilisés pour l'analyse élémentaire de matrices d'échantillon complexes comme celles que l'on rencontre dans le domaine géochimique. On présente plusieurs ensembles de problèmes ainsi que des techniques qui permettent d'obtenir des solutions analytiques.

---

[1] LECO Instruments Ltd./Analytical Spectroscopy Division, 5151 Everest Drive, Mississauga, Ontario, L4W 2R2, Canada.

An on-site method for measuring aluminium speciation in shallow well water samples from areas exposed to acid rain

J.C. Meranger[1], R.E. Lett[2], and T. Pickering[2]

Abstract: An on-site procedure involving filtration and ion exchange has been developed to study aluminium speciation in water samples from shallow wells. Immediately following collection samples are mixed continuously with Chelex 100 ion-exchange resin for eight hours. At intervals during the mixing cycle subsamples of the water are taken, filtered, preserved, and later analyzed for aluminium by graphite furnace atomic absorption spectrophotometry. The method has been applied to examine aluminium chemistry in water from selected shallow wells in rural areas of eastern Canada exposed to acid rain. Results show that in weakly acid water much of the aluminium remains in polymeric forms whereas more strongly acid (pH below 5.5) well waters contain predominantly monomeric, labile aluminium.

Résumé : On a élaboré un procédé *in situ* de filtration et d'échange d'ions pour étudier la spéciation de l'aluminium dans les échantillons d'eau recueillis dans des puits de faible profondeur. Immédiatement après leur collecte, on mélange les échantillons de façon continue avec de la résine échangeuse d'ions Chelex 100 pendant huit heures. À intervalles réguliers au cours du cycle de mélange, on prélève des sous-échantillons d'eau, on les filtre, on les conserve, puis on dose ensuite l'aluminium par spectrophotométrie d'absorption atomique dans un four en graphite. On a appliqué cette méthode à la chimie de l'aluminium dans de l'eau de puits peu profonds des zones rurales de l'est du Canada qui sont exposées aux pluies acides. Les résultats montrent que dans les eaux faiblement acides, une grande partie de l'aluminium reste sous forme polymère, tandis que les eaux de puits plus acides (pH inférieur à 5,5) contiennent surtout de l'aluminium monomère labile.

---

[1] Environmental Health Directorate Health and Welfare Canada, Tunney's Pasture, Ottawa, Ontario, K1A 0L2, Canada.
[2] Barringer Laboratories, 5735 McAdam Road, Mississauga, Ontario, L4Z 1N9, Canada.

Development and implementation of a comprehensive quality assurance programme for geochemical research

D.L. Miles[1]

Abstract: The British Geological Survey (BGS) is currently carrying out several separate research projects for a major funding agency which, early in 1988, insisted that all work be conducted under a single, comprehensive Quality Assurance (QA) Programme which the BGS would have to set up. The scope of the research involved is extensive, ranging from detailed chemical and mineralogical studies of fracture surfaces, through hydrogeochemical and microbiological studies, to geophysical surveying. Almost all the projects have a major geochemical component, and many rely heavily on analytical facilities, data, and hence quality control.

This paper describes the development of the QA Programme, its implementation, and the evolution of the associated documentation and audit procedures. Over and above all the usual features which would normally be thought of as constituting good analytical practice and formal Quality Control (QC), the procedures set out in the QA Programme provide assurance that QC is being achieved, and that a high level of traceability of both data and decisions exists. The Programme is monitored by a system of internal and external audits. Examples will be given of the application of QA to analysis by ICP-OES and ion chromatography, including the acquisition, validation, and archiving of data.

The success of any QA procedure depends very much on staff attitudes towards it. The varying reactions of scientific staff, project leaders and senior management to the BGS QA Programme at different times will be discussed, and its costs and benefits outlined.

Résumé : La *British Geological Survey* (BGS) entreprend actuellement plusieurs projets de recherche distincts pour un organisme de financement important qui, au début de 1988, insistait pour que tout le travail soit mené dans le cadre d'un même programme détaillé de garantie de la qualité, que devrait définir la BGS. Les recherches en cours ont une vaste portée et couvrent des études chimiques et minéralogiques exhaustives des surfaces de fracture, des levés géophysiques et des études hydrogéochimiques et microbiologiques. Presque tous les projets ont une composante géochimique importante, et la réalisation d'un grand nombre d'entre eux repose à un point important sur les installations d'analyse, les données analytiques et, par conséquent, sur les contrôles de la qualité.

Dans cet exposé, on décrit l'élaboration et la mise en oeuvre du programme de garantie de la qualité et l'évolution de la documentation et de la méthode de vérification connexes. Au-delà de toutes les caractéristiques usuelles qui normalement sont censées constituer une bonne méthodologie analytique et un contrôle de qualité formel, la méthode adoptée pour le programme de garantie de la qualité assure le contrôle de la qualité et la traçabilité des données et des décisions. Le suivi du programme se fait par un système de vérifications internes et externes. L'auteur fournit des exemples pour montrer comment la garantie de la qualité est appliquée à l'analyse par SE/PIHF et par chromatographie d'ions, notamment à la saisie, à la validation et à l'archivage des données.

Le succès de toute méthode de garantie de la qualité dépend largement de l'attitude du personnel vis-à-vis de cette méthode. L'auteur examine les réactions variées manifestées à diverses époques par le personnel scientifique, les chargés de projet et la haute direction à l'égard du programme de garantie de la qualité de la BGS, et il esquisse les avantages et les coûts de ce programme.

---

[1] British Geological Survey, Keyworth, Nottingham, NG12 5GG, U.K.

A new instrumental concept for multielement analysis of environmental materials – polyscan spectroanalyzers

Y. Nouri[1], Y. Lang[1], A. Lemarchand[1], and I.B. Brenner[2]

Abstract: The increasing constraints on the permissible levels of metals in the environment and the requirement that samples be analyzed for a wide range of trace and major elements (Si, P, S, and alkali elements) has resulted in the development of a versatile polychromator combining the speed and precision of a fixed channel instrument with the versatility of a sequential monochromator. The extended range of wavelength displacement of more than ± 1 nm on the Rowland Circle using a newly designed device called REST (Rowland Entrance Slit Translation) results in a substantial extension of the analytical program. It will be shown that for a 22 channel instrument, over 30 additional analytes can be determined with limits of detection that are generally within the criteria of the Environmental Protection Agency's approved methods. This facilitates cross checking of data for quality control which is critical in the monitoring program and extension of the list of elements to be determined. For the analysis of concentrated brines, the ability to select less sensitive spectral lines avoids sample dilution and reduces the cost of the spectrometer. Furthermore, the analyst is no longer restricted from applying spectral interference corrections if the interfering element is not in the fixed array. The interferent can be determined as a displacement from a primary channel. Analytical performance using conventional figures of merit (LODs, EIE effects, long and short term variations) will be described, with a 40 MHz generator. Data for a wide range of environmental materials, and natural and industrial brines will be presented.

Résumé : En raison des limites de plus en plus strictes sur les concentrations admissibles de métaux dans l'environnement et de la nécessité de doser une vaste gamme d'éléments traces et d'éléments majeurs (Si, P, S et éléments alcalins) dans les échantillons, on a mis au point un polychromateur alliant la vitesse et la précision d'un instrument à canal fixe à la souplesse d'un monochromateur séquentiel. Un nouveau dispositif appelé «REST» (Rowland Entrance Slit Translation) élargit de plus de ± 1 nm le domaine de déplacement en longueur d'onde du cercle de focalisation, ce qui permet d'accroître sensiblement la portée du programme d'analyse. On montre que, pour un instrument à 22 canaux, on peut analyser plus de 30 substances additionnelles à des limites de détection qui se situent en général dans les limites définies par l'EPA, ce qui facilite la contre-vérification des données destinées au contrôle de la qualité, essentiel au programme de surveillance, et l'augmentation de la liste des éléments à doser. Pour l'analyse des saumures concentrées, la possibilité de choisir des raies spectrales moins sensibles permet d'éviter la dilution des échantillons et de réduire le coût du spectromètre. En outre, l'analyste est désormais libre de corriger les interférences spectrales lorsque l'élément interférant ne fait pas partie de la série fixée. On peut déterminer cette interférence sous la forme d'un déplacement par rapport à un canal primaire. Les auteurs décrivent le rendement analytique exprimé en fonction des facteurs de mérite habituels (SD, effets EIE, variations à long et à court termes), à l'aide d'un générateur de 40 MHz. Ils présentent des données pour une vaste gamme de matériaux environnementaux et de saumures naturelles et industrielles.

---

[1] Jobin Yvon (ISA), 6 Olsen Av., Edison, New Jersey, 08820, U.S.A.
[2] Geological Survey of Israel, 30 Malkhe Israel Street, Jerusalem, 95501, Israel.

The challenges in managing a geoanalytical laboratory in Zimbabwe

E. Nyampingidza[1] and R.M. Tindwa[1]

Abstract: In Zimbabwe, most instruments and reagents required for analysis are imported, therefore an analytical laboratory is greatly affected by lack of foreign currency, as is any other establishment in the country. When the foreign currency is made available for such use, the waiting period for the importation of these vital requirements can be unbearable, from 6 months to 18 months or more for an instrument to be delivered. Meanwhile, both research and routine analytical work suffer. Although a great deal of import substitution is taking place, locally manufactured equipment is often of very poor quality and one would be correct to call them substandard (e.g., heating mantles, electric furnaces, etc.). The equipment breaks down so often that perhaps, in the long run, one would rather wait patiently for the imported items. Lack of modern instruments is a problem facing the whole country. Except for atomic absorption spectrophotometers, instruments such as the inductively coupled plasma emission spectrometer or the electron microprobe are obsolete. To acquire spare parts for such instruments becomes a mammoth task for any laboratory manager. Coupled with the shortage of instruments, is the shortage of well trained staff who can execute competently the tasks given to them and few technicians are trained to operate instruments such as the X-ray fluorescence spectrometer, the electron microprobe, or the scanning electron microscope. Service and repair of such instruments is still carried out by technicians from the respective parent companies who supply these instruments. This service is quite expensive, up to Z$1000 per day. These and many other problems make the whole job of managing a geoanalytical laboratory in Zimbabwe a bigger challenge to a chemist than most people realize. Despite all these setbacks, one is still expected to produce good, accurate results on international standards, since even a small developing country like Zimbabwe sells its minerals at the London Metal Exchange.

Résumé : Au Zimbabwe, où la plupart des instruments et des réactifs nécessaires à l'analyse sont importés, les laboratoires d'analyse, tout comme les autres établissements du pays, sont sérieusement affectés par la pénurie de devises étrangères. Une fois ces devises obtenues, la période d'attente pour l'importation de ces marchandises peut être insupportable, allant de 6 à 18 mois ou plus pour un instrument donné. Entre temps, la recherche et les analyses de routine en souffrent les conséquences. Même si des produits locaux remplacent une grande partie des importations, ils sont souvent de très piètre qualité, et l'on pourrait aisément dire qu'ils sont inférieurs à la norme (p. ex. chauffe-ballons, fours électriques, etc.). Le matériel tombe si souvent en panne qu'il est parfois préférable à long terme d'attendre patiemment la livraison des importations. La pénurie d'appareils modernes est un problème dont fait face le pays tout entier. À l'exception des spectrophotomètres d'absorption atomique, les instruments tels les spectromètres d'émission avec plasma induit par haute fréquence ou les sondes électroniques sont désuets. Acheter des pièces de rechange pour ces instruments est une tâche colossale pour les directeurs de laboratoire. S'ajoutent à la pénurie d'appareils un manque de personnel formé capable d'exécuter avec compétence les tâches qui lui sont confiées, et un nombre peu élevé de techniciens qui connaissent l'utilisation d'instruments tels que le spectromètre à fluorescence X, la microsonde électronique ou le microscope électronique à balayage. L'entretien et la réparation de ces instruments sont encore effectués par des techniciens des sociétés mères respectives qui fournissent les instruments. Cet entretien est très coûteux, pouvant atteindre 1 000 $ Z par jour. Ces problèmes entre autres font que, pour un chimiste, la gestion d'un laboratoire de géoanalyse au Zimbabwe est un défi plus difficile à relever que ne peuvent l'imaginer la plupart des gens. Malgré toutes

ces difficultés, on s'attend toujours à recevoir des résultats exacts et de bonne qualité, qui sont conformes aux normes internationales, car même un petit pays en voie de développement comme le Zimbabwe vend ses minéraux sur le marché de la Bourse des métaux de Londres.

---

[1] Zimbabwe Mining Development Corporation Management Services (Group Research Laboratories), P.O. Box 2370, Harare, Zimbabwe.

ICP emission spectroscopy with ultrasonic nebulization – application to waters and soils

D.D. Nygaard[1], F. Bulman[1], and T. Alavosus[1]

Abstract: Ultrasonic nebulization has been applied primarily to the analysis of relatively clean waters for purposes of environmental monitoring. In this application, it improves ICP detection limits by approximately an order of magnitude. In addition, accuracy and long term stability of the technique have been shown to be sufficient to meet quality control requirements such as those employed by the U.S. EPA Contract Laboratory Program. However, performance of ultrasonic nebulization is suspect on more complex samples. It is reputed to be more strongly affected by matrix variation than standard pneumatic nebulizers, and memory effects are reportedly more severe. This paper explores the possibility of expanding ultrasonic nebulization into soils analysis. It includes a systematic study of the effects caused by matrix elements and by acids used in sample preparations. Sensitivity enhancement is examined as a function of sample matrix, and memory effects are quantified.

Résumé : La nébulisation par ultrasons sert principalement à l'analyse d'eaux relativement pures à des fins de surveillance environnementale. Ce procédé permet d'améliorer les limites de détection du système PIHF d'environ un ordre de grandeur; en outre, son exactitude et sa stabilité à long terme sont suffisantes pour satisfaire aux exigences en matière de contrôle de la qualité comme celles du programme contractuel de laboratoire de l'EPA aux É-U. Toutefois, le rendement de la nébulisation par ultrasons est douteux dans le cas d'échantillons plus complexes. Il serait plus fortement influencé par la variation de la matrice que les nébuliseurs pneumatiques courants, et l'effet mémoire serait plus sérieux. Dans cet exposé, on examine la possibilité d'utiliser la nébulisation par ultrasons pour l'analyse des sols. On examine systématiquement les effets causés par les éléments de la matrice et par les acides utilisés pour la préparation des échantillons. On étudie l'accroissement de la sensibilité en fonction de la matrice de l'échantillon et l'on quantifie l'effet mémoire.

---

[1] Baird Corporation, 125 Middlesex Turnpike, Bedford, Maryland 01730, U.S.A.

Quantitative SIMS determination of REES in silicate minerals: choice of the standard for natural and glassy matrix

L. Ottolini[1], P. Bottazzi[1], and R. Vannucci[1,2]

Abstract: Several terrestrial minerals, most of them amphiboles, were analyzed by means of the secondary ion mass spectrometry (SIMS) technique for the rare-earth elements (REE). The present measurements were made with a Cameca IMS 4F ion microprobe, using a moderate energy filtering

(80 V offset from the maximum of the energy distribution, with an energy window of ~50 V), in order to eliminate complex ion interferences. The analyzed spectra were essentially free from molecular ions over the measured mass range. A peak deconvolution method was required, however, to separate the Eu signal from the BaO contribution, being still active at this offset. Quantitative determinations were carried out using relative sensitivity factors (RSF) calculated from natural mineral standards (RSFs$^{nat.}$) and the same minerals reduced to glass pellets (RSFs^{glass}). Such factors were successively compared with those calculated from synthetic geostandard glasses (NBS 612, NBS 610, NBS 614) and an ensemble of international silicate (mafic-ultramafic) rock standards fused in glasses. Differences in RSFs were shown, depending on crystalline structure and local inhomogeneities.

It is demonstrated that, even if the use of mineral standards for natural minerals and glassy standards for natural silicate melts is recommended in order to obtain a more accurate analysis, nevertheless a wide set of RSFs^{glass} could be tentatively applied in the analysis of silicates when suitable mineral standards are not available.

Résumé : On a analysé plusieurs minéraux terrestres, la plupart des amphiboles, par la spectrométrie de masse à émission ionique secondaire (SIMS) afin d'en doser les terres rares. On a effectué les mesures avec une microsonde ionique Cameca IMS 4F, en procédant à un filtrage énergétique modéré (décalage de 80 V à partir du maximum de distribution de l'énergie, avec une fenêtre énergétique d'environ 50 V), pour éliminer les interférences dues aux ions complexes. Les spectres analysés étaient essentiellement libres d'ions moléculaires pour la portée massique mesurée. Cependant, il a fallu employer une méthode de déconvolution des pics pour séparer le signal Eu de la contribution de BaO qui demeure actif à ce point de décalage. On a réalisé des dosages en utilisant des facteurs de sensibilité relative (RSF) calculés à partir d'étalons de minéraux naturels (RSF$^{nat.}$) et à partir des mêmes minéraux vitrifiés (RSF^{verre}). On a successivement comparé ces facteurs aux facteurs calculés pour des étalons géochimiques synthétiques (NBS 612, NBS 610, NBS 614) et pour un ensemble d'étalons internationaux de roches silicatées mafiques-ultramafiques vitrifiées. Les auteurs présentent les différences dans les facteurs de sensibilité relative en fonction de la structure cristalline et des inhomogénéités locales.

Les auteurs montrent que, même si on recommande d'utiliser des étalons minéraux pour les minéraux naturels et des étalons vitrifiés pour les bains silicatés naturels afin d'améliorer la précision des analyses, on pourrait aussi employer provisoirement un vaste ensemble de valeurs RSF^{verre} pour l'analyse des silicates quand on ne dispose pas d'étalons minéraux convenables.

---

[1] CNR – Centro di Studio per la Cristallografia Strutturale, Via Bassi 4, 27100 Pavia, Italy.
[2] Dipartimento di Scienze della Terra, Universita' di Pavia, Via Bassi 4, 27100 Pavia, Italy.

The rapid determination of the platinum group elements and gold with nickel sulphide fire assay and neutron activation analysis (NAA)

S.J. Parry[1] and M. Asif[1]

Abstract: Nickel sulphide fire assay is now a routine method of preseparating the platinum group elements (PGEs) and gold before their determination using AAS, ICP, NAA, or ICP-MS. In general there has been more effort devoted to the analytical techniques than to the preconcentration step. However, the main problems of analysis occur in the fusion and dissolution of the nickel sulphide button. The authors have been working on improving the fusion step, with the result that for most applications the technique can be straightforward and entirely free from reagent blank problems.

The major problem remaining has been the recovery of the elements, which is reproducible (81-83% PGE, 76% Au) but the losses are significant. The problem of losses may be avoided entirely if the nickel sulphide bead is analyzed directly. In the past the background effects have given very poor sensitivities when the bead was analyzed by NAA, but the improvements made by the authors to the fusion process have resulted in a sensitive technique for direct analysis of the bead.

We have developed a rapid and sensitive method which is sufficiently simple that large numbers of samples may be processed routinely, providing an inexpensive and reliable technique for determination of the PGEs. The validity of the method has been demonstrated using certified reference materials.

Résumé : L'analyse pyrognostique avec du sulfure de nickel est maintenant une méthode courante de préséparation des éléments du groupe du platine (EGP) ainsi que de l'or, avant leur dosage par SAA, par PIHF, par AAN ou par SM/PIHF. En général, on a consacré plus d'efforts aux techniques d'analyse qu'à la préconcentration. Toutefois, les principaux problèmes d'analyse surviennent lors de la fusion et de la dissolution du bouton de sulfure de nickel. Les auteurs ont cherché à améliorer la fusion et, maintenant, dans la plupart des applications, la technique est directe et entièrement exempte des problèmes posés par les solutions de l'essai à blanc.

Le problème principal qui reste à résoudre est celui de la récupération des éléments, qui est reproductible (entre 81 et 83 % d'EGP, 76 % d'Au), bien que les pertes soient importantes. On peut éviter entièrement le problème des pertes en analysant directement le bouton de sulfure de nickel. Par le passé, les effets de fond ont généré de très faibles sensibilités lorsque le bouton était analysé par activation neutronique, mais les améliorations apportées par les auteurs à la fusion ont permis de mettre au point une technique précise d'analyse directe de ce bouton.

Les auteurs ont mis au point une méthode rapide et précise qui est suffisamment simple pour traiter couramment un grand nombre d'échantillons tout en constituant une technique bon marché et fiable de dosage des EGP. Ils ont démontré la validité de la méthode à l'aide de matériaux de référence certifiés.

---

[1] Imperial College Reactor Centre, Silwood Park, Buckhurst Road, Ascot, Berkshire, SL5 7TE, U.K.

Objective evaluation of precision requirements for geochemical analysis using analysis of variance

M.H. Ramsey[1], M. Thompson[2], and M. Hale[1]

Abstract: The pursuit of high precision in geochemical analysis has no inherent limit. An appropriate analytical precision requirement can be set, however, by comparing the "analytical variance" with the two other sources of variance in geochemical data.

The purpose of a geochemical survey is to give a description of the geochemical variation of a region. This can be expressed in terms of the natural "geochemical variance" of the area. The information content is diminished by the two processes of measurement: the act of taking a sample adds a random error with "sampling variance"; and the act of chemical analysis adds another random error with "analytical variance".

In order to optimize the analytical variance for cost-effectiveness rather than simply to minimize it, all three variances must be estimated. This requires that the traditional analytical quality control scheme be extended to include the total measurement process, rather than only the "analytical" portion. Such a Total Analytical Quality Control Scheme (TAX) requires some duplication of field samples and the duplicate analysis of each field duplicate. The Analysis of Variance (ANOVA) is then used to separate the three components of the total variance.

For a clear description of the natural geochemical variance the combined sampling and analytical variances for the data should comprise, say not more than 20% of the total variance. If this figure is exceeded then these extraneous variances should be reduced. The decision as to whether this reduction requires

improved sampling variance or analysis variance can also be made from this ANOVA. As a general rule, the analytical variance should comprise not more than 5% of the total variance. If, on the other hand, the analytical variance is less than 0.5% of the total variance then needless expense has been incurred and the natural geochemical variation can be adequately described with less precise methods of analysis. Similar arguments can e applied to sampling variance.

For the analytical geochemist the combination of TAX and ANOVA can therefore provide a realistic target for analytical precision. For the field geochemist they provide a quantitative tool for the design of geochemical surveys. They allow the optimization of both sampling and chemical analysis for a given terrain to reveal geochemical patterns at minimal expense.

Résumé : La recherche de la précision élevée en analyse géochimique n'a pas de limite intrinsèque. On peut cependant établir une exigence appropriée en matière de précision de l'analyse en comparant la «variance analytique» aux deux autres sources de variance des données géochimiques.

Les levés géochimiques ont pour but de fournir une description des variations géochimiques d'une région. C'est ce que l'on peut représenter par la «variance géochimique» naturelle de la région. Les deux étapes de mesure réduisent la quantité d'information : le fait de prélever un échantillon ajoute une erreur aléatoire avec la «variance d'échantillonnage» et le fait de procéder à l'analyse chimique ajoute une autre erreur aléatoire avec la «variance analytique».

Pour optimiser la variance analytique en vue d'une plus grande rentabilité au lieu de tout simplement la minimiser, il faut estimer chacune des trois variances. Pour ce faire, il faut élargir le schéma traditionnel de contrôle de la qualité des analyses de façon à inclure tout le processus de mesure, plutôt que seulement la portion «analytique». Ce schéma de contrôle total de la qualité des analyses exige le prélèvement *in situ* d'échantillons répétés et l'analyse en double de chaque échantillon répété. L'analyse de variance sert alors à séparer les trois composantes de la variance totale.

Afin d'obtenir une description claire de la variance géochimique naturelle, il faut que pris ensemble, l'échantillonnage et les variances analytiques des données représentent au plus environ 20 % de la variance totale. Si l'on dépasse ce chiffre, il faut réduire les variances parasites. Cette analyse de variance permet aussi de décider s'il faut réduire les variances parasites en améliorant la variance d'échantillonnage ou la variance d'analyse. En règle générale, la variance analytique ne doit pas représenter plus de 5 % de la variance totale. Par contre, si la variance analytique est inférieure à 0,5 % de la variance totale, on aura alors encouru une dépense inutile et l'on pourra alors décrire la variation géochimique naturelle par des méthodes d'analyse moins précises. On peut appliquer des arguments semblables à la variance d'échantillonnage.

Pour le géochimiste analyste, le schéma de contrôle total de la qualité et l'analyse de variance mènent ensemble à un objectif réaliste de précision analytique. Pour le géochimiste de terrain, ils constituent un outil quantitatif de conception des levés géochimiques. Ils permettent d'optimiser l'échantillonnage et l'analyse chimique pour un terrain donné et de déterminer les schémas géochimiques avec un minimum de dépenses.

---

[1] Department of Geology, Imperial College, London, SW7 2BP, U.K.
[2] Department of Chemistry, Birkbeck College, Gordon House, 29 Gordon Square, London, WC1H OPP, U.K.

Matching analytical capabilities to client requirements

V.K. Rao

Abstract: In mineral exploration, the client requirements of geoanalysis are for the purpose of (i) locating the target areas and (ii) for detailed exploration. For the former, a vast number of samples are required to be analyzed as rapidly, accurately, and economically as possible for the principal elements. Simple chemical methods are being replaced by instrumental techniques like XRF, ICP, and AAS. For detailed exploration, drill core and exploratory mining samples are analyzed for the principal, rare, and deleterious elements. Elaborate chemical and spectral methods are employed to meet the requirements. Mineral analysis is carried out by XRD, DTA, and microscopic methods.

Résumé : En prospection minérale, l'analyse d'échantillons géologiques sert (i) à situer les zones cibles et (ii) à mener une exploration détaillée. Pour répondre à la première exigence, il faut recueillir un grand nombre d'échantillons et en doser les éléments principaux avec autant de rapidité, d'exactitude et d'économie que possible. On remplace les méthodes chimiques simples par des techniques automatisées telles que les procédés d'analyse instrumentale utilisant la fluorescence X, le plasma induit par haute fréquence et la spectrométrie d'absorption atomique. La prospection détaillée exige le dosage des éléments principaux, rares et parasites dans des carottes de forage et dans des échantillons recueillis au cours de travaux d'exploration minière. On emploie des méthodes chimiques et spectrales sophistiquées pour répondre aux exigences. On analyse les minéraux par diffraction de rayons X, par analyse thermique différentielle et par microscopie.

---

[1] Mineral Exploration Corporation Ltd., Seminary Hills, Nagpur-440006, India.

Determination of major, trace, and rare-earth elements in six Japanese rock standards

M.S. Rathi[1], P.P. Khanna[1], N.K. Saint[1], and P.K.R. Mukherjee[1]

Abstract: Six new Japanese geological reference materials (JA-2, JG-2, JG-1a, JP-1, JB-1a, and JF-1a) were analyzed for 28 elements (Si, Al, Ca, Mg, Na, K, Fe, Ti, Mn, P, Ba, Cu, Cr, Co, Ce, Dy, Li, La, Ni, Nb, Nd, Rb, Sr, V, Y, Yb, Zr, and Zn). Since these materials have been released only recently, the values reported for major as well as trace elemental concentrations are not well characterized (Govindraju, Geostandards Newsletter Special Issue, 1989). The analysis of the samples was carried out over a period of 30 days with at least ten repetitions each using different techniques like XRF (energy dispersive) ICP-AES, AAS, and flame photometry. Accuracy and precision in the analytical data were monitored using well established USGS, CRPG, and NBS certified rock standards. The results obtained for elements measured by more than one method were found to be consistent among themselves. In most of the cases our analytical data agree with the consensus values for these standards to within ± .5 to 3 relative per cent for major elements and ± 2 to 10 relative per cent for trace elements. The new values proposed in the present work, with few exceptions, are in good agreement with the values reported in literature and should be useful in a compilation of recommended values for these new standards.

Résumé : On a dosé 28 éléments (Si, Al, Ca, Mg, Na, K, Fe, Ti, Mn, P, Ba, Cu, Cr, Co, Ce, Dy, Li, La, Ni, Nb, Nd, Rb, Sr, V, Y, Yb, Zr et Zn) dans six nouveaux matériaux de référence géologiques provenant du Japon (JA-2, JG-2, JG-1a, JP-1, JB-1a et JF-1a). Comme elles sont relativement nouvelles, les valeurs citées pour les concentrations des éléments majeurs et des éléments traces ne sont pas encore bien caractérisées (Govindraju, Geostandards Newsletter Special Issue, 1989). On a analysé les échantillons sur une période de 30 jours en utilisant au moins dix exemplaires de chaque échantillon et diverses techniques telles que la fluorescence X (à dispersion d'énergie), la SE/PIHF, la SAA et la photométrie de flamme. On a surveillé l'exactitude et la précision des données analytiques en employant des matériaux de référence certifiés et reconnus de l'USGS, du CRPG et du NBS. Il y a eu concordance des résultats lorsqu'on a utilisé plus d'une méthode pour analyser le même élément. Dans la plupart des cas, les données analytiques concordent à entre ± 0,5 et 3 % près, pour les éléments majeurs, et à entre ± 2 et 10 % près, pour les éléments traces. À quelques exceptions près, les nouvelles valeurs proposées dans le présent exposé concordent bien avec les valeurs publiées et devraient s'avérer utiles aux fins d'une compilation des valeurs recommandées pour ces nouveaux étalons.

---

[1] Spectra Lab., Wadia Institute of Himalayan Geology, Dehra Dun, 248 001, India.

Optimization of the nickel sulphide fire-assay preconcentration procedure for platinum-group elements, gold, and silver in geological materials

T.D. Rice[1]

Abstract: Fire-assay preconcentration with a nickel sulphide collector is now widely used as a preliminary step in the determination of platinum-group elements (PGE) in geological materials by inductively-coupled plasma spectrometry (ICP-AES or ICP-MS), instrumental neutron activation analysis (INAA) or atomic absorption spectrometry (AAS).

In this laboratory a procedure is being developed which features:

- preparation of a 2.5 to 3.5 g nickel sulphide button after fusion of up to 30 g of sample for 1 hour in a covered ceramic crucible,
- maximizing the recovery of PGE, gold, and silver by including in the flux mixture magnesium, and about 75 mg of copper (as a powdered mixture of $CuSO_4 \cdot 5H_2O$ and technical-grade magnetite) and/or 12 mg of tellurium (as a 0.1% m/m mixture in quartz).

This procedure has so far been found to collect about 95% of the PGE in the reference pyroxenite SARM-7 and to fuse chromite samples completely if extra magnetite (9 g) is added to the flux.

Present work in this laboratory is aimed at establishing whether coprecipitation with tellurium after hydrochloric acid digestion of the powdered button enables quantitative recovery of silver as well as of PGE and gold.

Published data suggest that nickel sulphide may be highly carcinogenic. Hence skin contact with nickel sulphide, especially when powdered, is to be avoided. Laser ablation of small nickel sulphide buttons, followed by ICP-MS, deserves thorough study in the search for a safe, reliable and simple procedure for determining PGE, gold, and silver down to crustal abundance levels in geological materials.

Résumé : On emploie maintenant couramment la préconcentration par analyse pyrognostique avec un collecteur au sulfure de nickel comme étape préliminaire pour le dosage des éléments du groupe du platine (EGP) dans les matériaux géologiques par spectrométrie avec plasma induit par haute fréquence (SE/PIHF ou SM/PIHF), par analyse instrumentale par activation neutronique (AIAN), ou par spectrométrie d'absorption atomique (SAA).

Dans ce laboratoire, on élabore actuellement un procédé qui comprend :

- la préparation d'un bouton de sulfure de nickel de 2,5 à 3,5 g après la fusion d'un maximum de 30 g d'échantillon pendant une heure dans un creuset couvert en céramique;
- la meilleure récupération possible des EGP, de l'or et de l'argent par introduction, dans le fondant, de magnésium et d'environ 75 mg de cuivre (sous la forme d'un mélange pulvérulent de $CuSO_4 \cdot 5H_2O$ et de magnétite de qualité technique) ou de 12 mg de tellure (sous la forme d'un mélange de 0,1 % m/m dans du quartz).

Pour l'instant, on constate que ce procédé permet de recueillir environ 95 % des EGP dans la pyroxénite de référence SARM-7 et de faire fondre complètement les échantillons de chromite lorsqu'on ajoute de la magnétite (9 g) au fondant.

Les travaux en cours dans ce laboratoire visent à déterminer si la coprécipitation avec du tellure, après digestion du bouton pulvérulent par l'acide chlorhydrique, permet une récupération quantitative de l'argent, des EGP et de l'or.

Les données publiées portent à croire que le sulfure de nickel pourrait être fortement carcinogène. Il faut donc éviter tout contact cutané du sulfure de nickel, surtout lorsqu'il est en poudre. Il faudrait examiner en profondeur l'ablation par laser de petits boutons de sulfure de nickel, suivie de la SM/PIHF, en vue de trouver une méthode sûre, fiable et simple de doser, dans les matériaux géologiques, les EGP, l'or et l'argent à des teneurs aussi faibles que celles rencontrées dans la croûte terrestre.

---

[1] Department of Minerals and Energy, Mineral Resources Development Laboratory, P.O. Box 76, Lidcombe, N.S.W., 2141, Australia.

A quick separation of the rare-earth elements from some major matrix interferences prior to analysis by neutron activation

R. Robertson[1]

Abstract: Neutron activation analysis (NAA) plays a prominent role in the determination of the rare-earth elements in rocks and other geological matter. The method yields the most reliable data when used in conjunction with comprehensive chemical procedures which separate the REEs from interfering elements. Much work has been done in this area and much literature exists covering both pre- and post-irradiation separations.

The use of chemical separations to aid in the analysis is most attractive when time and cost are not factors in a particular project. In large research programs and in certain commercial situations, time and cost constraints militate against the use of exhaustive chemical procedures and in these situations the so-called instrumental NAA approach becomes more attractive.

As a compromise between the two positions, a very quick and easy separative method has been devised which removes the worst of the interferents at low cost. The method relies mainly upon the insolubility of the rare-earth fluorides in a solution containing hydrofluoric acid and upon the solubility of many interferents in the same situation. It is effective against uranium which may seriously interfere with the light REEs through fission reactions and against many elements such as manganese, sodium, and iron which typically interfere by producing high spectral backgrounds.

Detection limits are improved typically by a factor ranging from two to ten depending on element and sample matrix relative to the direct instrumental approach. The method is a good "leveller" with regard to sample matrix and is especially useful when the samples presented are complete unknowns where choices of sample size and irradiation and count timing are therefore difficult.

Résumé : L'analyse par activation neutronique (AAN) joue un rôle très important dans le dosage des terres rares que contiennent les roches et d'autres matériaux géologiques. Cette méthode donne les résultats les plus fiables lorsqu'elle est employée conjointement avec des procédés chimiques détaillés qui permettent de séparer les terres rares des éléments parasites. On a réalisé de nombreuses recherches dans ce domaine, et une abondante documentation couvre les séparations obtenues avant et après l'irradiation.

Il est particulièrement intéressant d'employer la séparation chimique pour faciliter l'analyse lorsque le temps et le coût n'entrent pas en ligne de compte dans un projet particulier. Dans les programmes de recherche de grande envergure et dans certaines situations commerciales, les contraintes de temps et les coûts empêchent l'emploi de méthodes chimiques exhaustives, et l'analyse instrumentale par activation neutronique devient alors plus intéressante.

On a trouvé un compromis entre ces deux solutions, à savoir une méthode de séparation très rapide et facile qui élimine les pires éléments parasites à faible coût. Cette méthode se fonde principalement sur l'insolubilité des fluorures des terres rares dans une solution contenant de l'acide fluorhydrique, et sur la solubilité de nombreux éléments parasites dans la même situation. Elle élimine efficacement les effets de l'uranium, qui peut sérieusement interférer avec les terres rares légères au cours des réactions de fission, et ceux de nombreux éléments tels que le manganèse, le sodium et le fer qui, typiquement, créent des interférences en générant des fonds spectraux prononcés.

On améliore typiquement les limites de détection d'un facteur de deux à dix selon les éléments et la matrice de l'échantillon, par rapport à la méthode instrumentale directe. La méthode constitue un bon compromis pour ce qui est de la matrice de l'échantillon et se révèle particulièrement utile lorsque les échantillons présentés sont complètement inconnus et qu'il est donc difficile de choisir leurs dimensions et les intervalles d'irradiation et de comptage.

---

[1] Becquerel Laboratories Inc., 6790 Kitimat Road, Unit 4, Mississauga, Ontario, L5N 5L9, Canada.

Rhenium as a neutron flux monitor in the neutron activation analysis of large mass geological samples for gold and other elements

R. Robertson[1] and D.C. Stuart[1]

Abstract: In recent years, some commercial laboratories have routinely determined gold and many other elements in large mass exploration samples using neutron activation analysis. The sample masses taken, typically in the range 5-50 g, are in keeping with the sample sizes traditionally used in fire assay.

In order to keep throughput high and irradiation costs low, it is common to irradiate 10 to 20 samples together in 5 cm diameter by 30 cm long bundles in positions at the periphery of reactor cores. In these positions, axial and radial neutron flux gradients and neutron spectrum variations must be well accounted for if good analytical data are to be produced. There are many properties desirable in a good neutron flux monitoring system for the above outlined purpose. This poster paper describes one system which has been found very effective in the analyses of hundreds of thousands of samples over a five year period.

The system is based on the use of the element rhenium incorporated in a self-adhesive label which is attached to each sample. The procedure used for rhenium doping of the carrier labels is outlined. Neutron flux profiles of irradiation positions as determined through activities induced in Re-185 and Re-187 in two different reactors in both thermal and epi-cadmium positions are presented. The responses of Re-185 and Re-187 are compared with the responses of over twenty elements of analytical interest, covering examples of elements whose activations are closely tracked by one or other of the rhenium isotopes with changing neutron spectrum shape, and examples of other elements whose activations are not so well tracked. The list of elements includes gold, antimony, arsenic, chromium, lanthanum, scandium, silver, sodium, tantalum, tungsten, uranium, thorium, and zinc.

The merits of simultaneous gamma counting of a rhenium flux monitor and associated sample with data acquisition into the same spectrum are discussed. The usefulness of this procedure in controlling sample counting geometry and rate related counting losses is indicated. Experience with the occurrence of rhenium in the samples themselves, which would tend to discourage simultaneous spectral acquisition, is also outlined.

Résumé : Depuis quelques années, certains laboratoires commerciaux ont recours régulièrement à l'activation neutronique pour doser l'or et de nombreux autres éléments dans de gros échantillons prélevés durant des travaux de prospection. Les échantillons prélevés pèsent habituellement entre 5 et 50 g, ce qui correspond à la masse des échantillons utilisés traditionnellement pour les essais pyrognostiques.

Afin de maintenir la capacité et de contenir les coûts de l'irradiation, il est courant d'irradier simultanément de 10 à 20 échantillons en paquets de 5 cm de diamètre et de 30 cm de longueur, à la périphérie du coeur d'un réacteur. Il faut donc bien tenir compte des gradients axial et radial du flux neutronique et des

variations du spectre neutronique afin d'obtenir de bonnes données analytiques. À cette fin, un bon système d'observation du flux neutronique devrait présenter de nombreuses propriétés. Dans cette communication affichée, on décrit un système qui s'est avéré très efficace pour analyser des centaines de milliers d'échantillons au cours d'une période de cinq ans.

Le système se fonde sur l'emploi de l'élément rhénium, qui est incorporé dans une étiquette autocollante fixée à chaque échantillon. On décrit brièvement le procédé de dopage au rhénium des étiquettes porteuses. On présente les profils des flux neutroniques des positions d'irradiation déterminés à partir de l'activité induite dans du ^{185}Re et du ^{187}Re dans deux réacteurs différents, en position thermique et en position épicadmique. On compare les réponses du ^{185}Re et du ^{187}Re à celles de plus de vingt éléments qu'il est intéressant d'analyser, y compris des exemples d'éléments dont l'activation est suivie de près par l'un ou l'autre des isotopes du rhénium ayant un spectre neutronique à configuration changeante, et des exemples d'autres éléments dont l'activation est moins bien suivie. La liste des éléments comprend l'or, l'antimoine, l'arsenic, le chrome, le lanthane, le scandium, l'argent, le sodium, le tantale, le tungstène, l'uranium, le thorium et le zinc.

On examine l'avantage d'effectuer en même temps le comptage, au moyen d'un moniteur du flux neutronique, des émissions gamma provenant du rhénium et de l'échantillon associé, et l'acquisition des données dans le même spectre. On indique l'utilité de ce procédé pour le contrôle de la géométrie du comptage de l'échantillon et des pertes de comptage liées au taux de comptage. On décrit aussi brièvement les essais dans lesquels le rhénium est présent dans les échantillons eux-mêmes, ce qui tend à décourager l'acquisition simultanée de spectres.

---

[1] Becquerel Laboratories Inc., 6790 Kitimat Road, Unit 4, Mississauga, Ontario, L5N 5L9, Canada.

Quantitative XRF analysis using the fundamental algorithm

R.M. Rousseau[1]

Abstract: In X-ray Fluorescence (XRF) analysis, one of the major problems to solve is the correction for matrix effects (absorption and enhancement). During the last three decades, one of the popular solutions proposed was the use of empirical influence coefficients (Lachance and Traill, 1966) which are numerical coefficients correcting for the effects of each matrix element on the analyte. These coefficients, that depend on the matrix composition, are calculated by a regression analysis of measured intensities and standard compositions. It will be shown that these empirical coefficients are not very accurate, depend on the composition of standards used, have a limited range of application, are sensitive to any experimental errors, and can be applied only to unknowns similar to the standards used. An easier and much more practical solution would be to calculate these influence coefficients from theory for any combination of elements and any experimental condition.

Sherman (1955) proposed a set of equations to calculate net X-ray intensities emitted by each element in a specimen of known composition when it is irradiated by a polychromatic X-ray beam. As proposed, these equations are not very useful to XRF analysts because intensities can be measured. There is therefore no need to calculate them. Furthermore, to calculate intensities the specimen's composition must be known whereas from the start this is precisely what is being sought.

Criss and Birks (1968) proposed the fundamental-parameters method, a new way to use Sherman's equations: the specimen composition is found by an iteration procedure that makes successively closer estimates of concentrations until the calculated intensities agree satisfactorily with the measured intensities.

Rousseau proposed a combination of the two worlds, fundamental parameters and influence coefficients, into a new approach which allows you to calculate theoretical influence coefficients inside of a new algorithm called the fundamental algorithm (Rousseau, 1984a, b). To calculate the composition of a specimen, a first estimate of composition must be calculated by iteration using the Claisse-Quintin algorithm. Then, from this estimated composition, the theoretical influence coefficients are calculated once only. Finally, with these coefficients used as constants, the final composition is obtained by applying an iteration process to the fundamental algorithm.

Theoretical influence coefficients are powerful tools to correct for matrix effects as long as a link exists for adapting the theory to the experimental reality, knowing full well that no theory accounts for all experimental variables. It will be shown that an appropriate calibration process can correct for all the imperfections of the theory and has as well, a few other major qualities that facilitate the work of the analyst.

The determination of sample compositions using the fundamental algorithm requires very complex calculations which must be done on a computer. A new computer program has then been written and it runs on any IBM-PC/XT/AT, PS/2 or compatible computer. It will be shown that it is a complete "off-line" program enclosing within itself all the steps necessary, after the collection of intensities by the XRF spectrometer, to calculate analytical composition: calculation of theoretical influence coefficients, calibration, reading of measured intensities, calculation of net intensities and concentrations of unknowns, print-out of analytical reports, and data transmission to or from an external computer.

Résumé : Un des principaux problèmes à résoudre lors de l'analyse par fluorescence X (FX) est la correction des effets de matrice (absorption et accentuation). Une des solutions populaires au problème préconisée depuis une trentaine d'années est l'emploi de coefficients empiriques d'influence (Lachance et Traill, 1966), ou coefficients numériques qui corrigent les effets de chaque élément de la matrice sur la substance analysée. On calcule ces coefficients, qui dépendent de la composition de la matrice, au moyen d'une analyse de régression des intensités mesurées et des compositions standard. On propose de démontrer que ces coefficients empiriques ne sont pas très précis, qu'ils dépendent de la composition des étalons utilisés, que leur champ d'application est limité, qu'ils sont sensibles à toute erreur expérimentale et qu'ils ne peuvent s'appliquer qu'à des substances inconnues qui ressemblent aux étalons utilisés. Il serait plus facile et beaucoup plus pratique de calculer théoriquement ces coefficients d'influence pour toute combinaison d'éléments et toute condition expérimentale.

Sherman (1955) a proposé un ensemble d'équations pour calculer les intensités nettes des rayons X émis par chaque élément dans un spécimen de composition connue lorsque ce spécimen est irradié par un faisceau polychromatique de rayons X. Ces équations telles que proposées ne sont pas très utiles aux analystes qui ont recours à la fluorescence X, car puisqu'il est possible de mesurer les intensités, il n'est pas nécessaire de les calculer. De plus, pour calculer les intensités, il faut d'abord connaître la composition de l'échantillon, ce qui est précisément ce que l'on cherche à faire.

En 1968, Criss et Birks (1968) ont proposé la méthode des paramètres fondamentaux, qui est une nouvelle façon d'utiliser les équations de Sherman : on trouve la composition du spécimen par un procédé d'itération qui donne des estimations de plus en plus rapprochées des concentrations, jusqu'à ce que les intensités calculées concordent suffisamment avec les intensités mesurées.

Rousseau a proposé de combiner les paramètres fondamentaux et les coefficients d'influence en une nouvelle méthode qui permet de calculer les coefficients d'influence théoriques à l'intérieur d'un nouvel algorithme appelé «algorithme fondamental» (Rousseau, 1984a, b). Pour calculer la composition d'un spécimen, il faut d'abord obtenir une première estimation de la composition par itération au moyen de l'algorithme de Claisse-Quintin. Ensuite, à partir de cette estimation de la composition, on ne calcule qu'une fois les coefficients d'influence théoriques. Enfin, ces coefficients étant considérés comme des constantes, on obtient la composition finale par application d'un procédé d'itération à l'algorithme fondamental.

Les coefficients d'influence théoriques s'avèrent très utiles pour corriger les effets de matrice pourvu qu'il soit possible d'adapter la théorie à la réalité expérimentale, car on sait pertinemment qu'aucune théorie ne rend compte de toutes les variables expérimentales. L'auteur montre qu'un procédé d'étalonnage convenable peut aider à corriger toutes les imperfections de la théorie, et il présente quelques autres qualités importantes qui facilitent le travail de l'analyste.

La détermination de la composition d'un échantillon par l'algorithme fondamental exige des calculs très complexes qu'il faut exécuter sur ordinateur. On a donc rédigé un nouveau programme machine que l'on peut utiliser sur n'importe quel ordinateur IBM-PC/XT/AT, PS/2 ou compatible. L'auteur montre qu'il s'agit d'un programme complet «autonome» qui englobe toutes les étapes nécessaires, après collecte des valeurs des intensités par le spectromètre FX, au calcul de la composition analytique : calcul des coefficients d'influence théoriques, étalonnage, lecture des intensités mesurées, calcul des intensités nettes et des concentrations des substances inconnues, sortie imprimée des rapports d'analyses et transmission des données en direction ou à partir d'un ordinateur extérieur.

References

Criss, J.W. and Birks, L.S.
1968: Calculation methods for fluorescent X-ray spectrometry – empirical coefficients vs. fundamental parameters; Analytical Chemistry, v. 40, p. 1080-1086.
Lachance, G.R. and Traill, R.J.
1966: A practical solution to the matrix problem in X-ray analysis; Canadian Journal of Spectroscopy, v. 11, p. 43-57.
Rousseau, R.M.
1984a: Fundamental algorithm between concentration and intensity in XRF analysis: 1 – Theory; X-ray Spectrometry, v. 13, p. 115-120.
1984b: Fundamental algorithm between concentration and intensity in XRF analysis: 2 – Practical application; X-ray Spectrometry, v. 13, p. 121-125.
Sherman, J.
1955: The theoretical derivation of fluorescent X-ray intensities from mixtures; Spectrochimica Acta, v. 7, p. 283-306.

---

[1] Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, K1A 0E8, Canada.

An expeditious wet-chemical scheme for silicate analysis using titrimetric determination of silica

I. Rubeska[1] and M. Huka[1]

Abstract: At the Geological Survey of Prague an expeditious procedure for the determination of silica has been developed and is currently used routinely. The procedure is based on sample decomposition using acids (HF + H_2SO_4), chemisorption of the evolving H_2SiF_6 on solid potassium nitrate and acidimetric titration of the HF released by hydrolysis of the resulting K_2SiF_6. The sample residue from this decomposition is dissolved, transferred to a PTFE beaker and HF is fumed off. The resulting solution is then used for the determination of other sample constituents either by chelatometry (high Al, Ca, Mg), AAS (Li, Na, K, Mn, Ti, low Al, Ca, Mg, Fe), spectrophotometry (P, high Fe) or ICP-ES (all of these).

For samples containing minerals not attacked by HF the sample solution is first filtered off, incinerated, and the insoluble residue fused with a mixture of Cs_2CO_3 and boric acid. After dissolution it is added to the sample solution and its SiO_2 content measured by AAS or ICP-ES. This silica amount is then added to that found by titration. The PTFE vessel assembly used for the sample decomposition and the procedure for Si will be described in detail. Results on international standard reference materials will be used to illustrate performance of the procedure. Examples of samples with unusual composition for which the procedure fails to give accurate results will be discussed.

The advantage of the procedure presented is that it is independent of reference samples with well established chemical composition and possesses the accuracy of wet-chemical procedures while considerably increasing the sample throughout. It may be applied with advantage particularly in laboratories where XRF spectrometry is not available.

Résumé : À la Commission géologique de Prague, on a mis au point un procédé rapide de dosage de la silice qui est maintenant employé de façon courante. Ce procédé se fonde sur la décomposition d'un échantillon dans des acides (HF + H_2SO_4), la chimisorption du H_2SiF_6 dégagé sur du nitrate de potassium solide, et le titrage acidimétrique du HF libéré par hydrolyse du K_2SiF_6 ainsi produit. On dissout le résidu d'échantillon produit par cette décomposition, on le transfère dans un becher en PTFE et on évacue le HF. La solution obtenue sert à doser les autres constituants de l'échantillon par chélatométrie (forte teneur en Al, Ca, Mg), par SAA (Li, Na, K, Mn, Ti, faible teneur en Al, Ca, Mg, Fe), par spectrophotométrie (P, forte teneur en Fe), ou par SE/PIHF (tous ces éléments).

Dans le cas d'échantillons contenant des minéraux qui ne sont pas attaqués par du HF, on filtre d'abord la solution de dosage, on calcine le produit obtenu et on fait fondre le résidu insoluble dans un mélange de Cs_2CO_3 et d'acide borique, puis on l'ajoute à la solution de dosage et l'on mesure son contenu en SiO_2, par SAA ou par SE/PIHF. On ajoute ensuite cette quantité de silice à celle qui a été déterminée par titrage. Les auteurs décrivent en détail le montage de récipients en PTFE employé pour effectuer la décomposition de l'échantillon et le procédé de dosage de Si. Il fournissent les résultats obtenus pour les étalons de référence internationaux afin d'illustrer le rendement de la méthode. Ils présentent des exemples d'échantillons de composition inhabituelle pour lesquels le procédé ne donne pas de résultats exacts.

La méthode présentée offre certains avantages; en effet, elle ne dépend pas des échantillons de référence de composition chimique bien établie, et elle est toute aussi précise que les procédés chimiques par voie humide, bien qu'elle augmente considérablement la vitesse d'analyse des échantillons. Elle est très utile, notamment dans les laboratoires où l'on n'utilise pas la spectrométrie par fluorescence X.

---

[1] Geological Survey of Prague, Malostranské Na'm. 19, 11821 Praha 1, Czechoslovakia.

Determination of the combined water (H_2O^+) in 41 geological reference samples by an infrared absorption method

R.J. Saikkonen[1]

Abstract: The combined water (H_2O^+) in 41 geological reference samples was determined by an infrared absorption method. After combustion at 1100°C without flux, samples were analyzed with the LECO° moisture analyzer RMC-100. In this method the dry sample is loaded into a resistance furnace, H_2O^+ is driven from the sample with nitrogen gas and is passed through the infrared cell, where water vapour absorbs IR energy at a specific wavelength. This wavelength is selectively passed through a filter to an IR sensor, where the concentration of H_2O^+ is detected as an energy level. The signal is amplified, rectified, and digitized. The data are sampled twice a second and after linear corrections the data are integrated to find the water concentration. The result is displayed as weight per cent.

The IR cell linearization was checked with rock standards and G-2, MRG-1, BE-N, PCC-1, and UB-N were used as the calibration standards. The method is capable of determining H_2O^+ at level 0.01 – 14% if the sample weight is 0.5 g. The sample calibration should be done at the start of each day and in-house reference samples should be analyzed periodically to confirm proper operation of the instrument. In routine work, where samples contain H_2O^+ at the level given above, the calibration of the instrument with one rock standard is sufficient.

The present results were in generally good agreement with published data. The coefficients of variation follow the general trend of large coefficients for samples containing the least amount of the constituent and of small coefficients for samples containing the greatest amount (BIR-1: $H_2O^+ = 0.10\%$, CV = 15%; BX-N: $H_2O^+ = 12.26\%$, CV = 2%). The detection limit, defined as three times the standard deviation of 20 blank determinations was 0.004% H_2O^+. The practical detection limit of the method is about 0.01% H_2O^+, and the time required for each determination is not more than 10 minutes.

Résumé : On a déterminé l'eau combinée (H_2O^+) dans 41 échantillons de référence géologiques par la méthode d'absorption dans l'infrarouge. Après combustion à 1 100°C sans fondant, les échantillons ont été analysés au moyen de l'analyseur d'humidité RMC-100 de LECO. Dans cette méthode, l'échantillon sec est chargé dans un four à résistance, l'eau combinée est éliminée de l'échantillon à l'aide d'azote gazeux et introduite dans la cellule infrarouge où la vapeur d'eau absorbe l'énergie infrarouge à une longueur d'onde précise. Cette longueur d'onde est filtrée avant d'atteindre un capteur IR, et la concentration de H_2O^+ est détectée sous la forme d'un niveau d'énergie. Le signal est amplifié, redressé et numérisé. Les données sont échantillonnées deux fois et, après correction linéaire, elles sont intégrées afin de déterminer la concentration d'eau. Le résultat est affiché en pourcentage massique.

On a vérifié la linéarisation de la cellule IR au moyen d'étalons de roche. Les étalons G-2, MRG-1, BE-N, PCC-1 et UB-N ont servi à des fins d'étalonnage. La méthode permet d'analyser le H_2O^+ dans la plage de 0,01 % à 14 % lorsque l'échantillon pèse 0,5 g. Il faudrait étalonner les échantillons en début de journée et analyser périodiquement les échantillons de référence internes pour confirmer le bon fonctionnement de l'instrument. Pour les analyses courantes, lorsque les échantillons contiennent H_2O^+ dans la plage donnée ci-dessus, il suffit d'étalonner l'instrument avec un seul étalon de roche.

Les résultats actuels concordent en général avec les données publiées. Les coefficients de variation obéissent à la tendance générale des coefficients élevés dans le cas d'échantillons qui contiennent la plus faible quantité du constituant, et à celle des coefficients faibles dans le cas d'échantillons qui en contiennent la quantité la plus élevée (BIR-1 : H_2O^+ = 0,10 %, CV = 15 % et BX-N : H_2O^+ = 12,26 %, CV = 2 %). La limite de détection, définie comme étant trois fois l'écart-type de 20 essais à blanc, est évaluée à 0,004 % de H_2O^+. La limite de détection pratique de cette méthode est d'environ 0,01 % de H_2O^+, et la durée de chaque dosage ne dépasse pas 10 minutes.

---

[1] Geological Survey of Finland, Betonimiehenkuja 4, SF-02150 Espoo, Finland.

Determination of gold and platinum-group elements in some candidate reference materials by GFAAS and ICP-MS

J.G. Sen Gupta[1] and D.C. Gregoire[1]

Abstract: The candidate reference material (5 g) was decomposed by heating with aqua regia and hydrofluoric acid followed by attack of the insoluble residue by fusion with sodium peroxide. The noble metals (osmium excepted) were co-precipitated with 5 mg added tellurium by reduction with stannous chloride. After filtration and dissolution of the precipitate in aqua regia followed by conversion to chlorides, the salts were dissolved in 2 mL of 1M hydrochloric acid. Gold, ruthenium, rhodium, palladium, iridium, and platinum were determined by graphite-furnace atomic-absorption spectrometry using 10-20 μl aliquots. To 1 mL aliquot of the sample solution, ^{101}Ru, ^{105}Pd, ^{193}Ir, and ^{194}Pt spikes were added, and after dilution to 5 mL, the unknown quantities of these elements were determined by isotope dilution inductively-coupled plasma mass spectrometry using solution nebulization. The data on gold and platinum-group elements, as obtained for several candidate geochemical reference materials and internal reference rocks, will be presented and compared with other values.

Résumé : On a décomposé le matériel de référence étudié (5 g) en le chauffant en présence d'eau régale et d'acide fluorhydrique, puis en faisant fondre le résidu insoluble par du bioxyde de sodium. On a coprécipité les métaux nobles (l'osmium excepté) et 5 mg de tellure par réduction avec du chlorure stanneux. Après filtration et dissolution du précipité dans de l'eau régale, puis conversion du produit en chlorures, on a dissous les sels dans 2 ml d'acide chlorhydrique 1M. On a dosé l'or, le ruthénium, le rhodium, le palladium, l'iridium et le platine par spectrométrie d'absorption atomique dans un four en graphite avec des parties aliquotes de 10-20 μl. On a ajouté à une aliquote de 1 ml de la solution de l'échantillon des pics de ^{101}Ru, ^{105}Pd, ^{193}Ir et ^{194}Pt et, après dilution à 5 ml, on a dosé les quantités inconnues de ces éléments par spectrométrie par dilution isotopique avec plasma induit par haute fréquence, en procédant à la nébulisation de la solution. On présente les données sur l'or et les éléments du groupe du platine obtenues pour plusieurs matériaux géochimiques de référence et pour des roches de référence internes, et l'on compare ces données à d'autres valeurs.

---

[1] Geological Survey of Canada, 601 Booth St., Ottawa, Ontario, K1A 0E8, Canada.

Recognition of mass spectral interferences in inductively coupled plasma mass spectrometry

Y. Shao[1] and G. Horlick[1]

Abstract: Inductively coupled plasma mass spectrometry (ICP-MS) is a relatively new technique for elemental analysis. Among its important analytical characteristics are high sensitivity, low detection limits, simple spectra, wide dynamic range, almost complete coverage of the Periodic Table, and the capability of providing element isotopic composition. The technique is rapidly evolving into a routine analytical tool for trace and ultra-trace elemental determinations. Research into both the fundamental and practical aspects of ICP-MS has resulted in a better understanding of the technique and has also revealed problems that remain to be overcome. One of the more serious problems is mass spectral interference in which the mass of an undesirable plasma species directly coincides with a mass of the element of interest. The sources of these undesirable species include basic plasma background species, interelement spectral overlaps, matrix induced molecular species, and argon-matrix related species. In part, because of the unit resolution of the quadrupole mass spectrometers used in ICP-MS, the resulting spectral overlaps are often difficult to even recognize.

As a first step in recognizing a spectral interference problem, analytical determinations should be made at more than one mass for elements that have two or more naturally occurring isotopes. If the results do not agree, then a spectral interference problem might be indicated. A powerful tool is to compare results and result discrepancies, sample by sample, with the sample composition of the suspected source of the spectral interferent. This can be effectively carried out using computer generated bar graphs. Two of the more problematic elements that can generate numerous spectral interference problems are S and Ca. Unfortunately, these two elements cannot readily be determined by ICP-MS. When these two elements are thought to be components of the sample matrix they should be independently determined using ICP atomic emission spectrometry. This complementary information, when compared to ICP-MS results by the bar graph method, can very effectively reveal spectral interference problems. The application of these approaches to spectral interference recognition will be illustrated for the analysis of ground water samples.

Résumé : La spectrométrie de masse avec plasma induit par haute fréquence (SM/PIHF) est une technique relativement nouvelle d'analyse élémentaire. Ses principales caractéristiques analytiques sont notamment une sensibilité élevée, des limites de détection faibles, des spectres simples, une plage dynamique large, une couverture presque complète du tableau périodique des éléments et une capacité de fournir la composition isotopique des éléments. Cette technique devient rapidement un outil courant de dosage des éléments traces et des éléments ultratraces. La recherche sur les aspects fondamentaux et pratiques de la SM/PIHF a permis de mieux comprendre cette technique et a révélé des problèmes qui restent à surmonter. L'un des plus sérieux est l'interférence liée au spectre de masse qui fait que la masse d'une espèce indésirable de plasma coïncide directement avec la masse de l'élément dosé. Les sources de ces espèces indésirables sont notamment les espèces de fond du plasma fondamental, le recouvrement des raies spectrales, les espèces moléculaires induites par la matrice et les espèces apparentées à la matrice d'argon. En partie à cause de la résolution unitaire des spectromètres de masse quadripôles employés en SM/PIHF, il est souvent difficile de même reconnaître le recouvrement des raies spectrales.

Pour reconnaître un problème d'interférence spectrale, il faut d'abord analyser plusieurs échantillons de masse différente lorsqu'il s'agit de doser des éléments qui possèdent au moins deux isotopes naturels. Si les résultats ne concordent pas, il peut y avoir un problème d'interférence spectrale. Un moyen efficace de détection consiste à comparer les résultats et les écarts, échantillon par échantillon, à la composition de la source probable de l'interférence spectrale. On peut y parvenir efficacement au moyen de diagrammes à barres produites par ordinateur. Deux des éléments plus gênants susceptibles de provoquer de nombreuses interférences spectrales sont le soufre et le calcium. Malheureusement, ces deux éléments ne se laissent pas facilement doser par SM/PIHF. Si l'on estime qu'ils sont des composants de la matrice de l'échantillon, il faut les doser indépendamment par spectrométrie d'émission atomique avec plasma induit par haute fréquence (SE/PIHF). Une fois comparée aux résultats de la SM/PIHF par la méthode du diagramme à barres, cette information complémentaire peut très bien révéler les interférences spectrales. On décrit l'utilisation de ces méthodes pour reconnaître les interférences spectrales lors de l'analyse des échantillons d'eaux souterraines.

---

[1] Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G 2G2, Canada.

Prompt gamma neutron activation analysis of SRMS at the McMaster Nuclear Reactor in 1990 and the future prospects

D.M. Shaw[1] and P.L.C. Smith[1]

Abstract: The 2 Mw McMaster Nuclear Reactor has operated a thermalized neutron beam with a dedicated prompt gamma neutron activation analysis (PGNAA) system for about six years, for determination mostly of B, but also for Gd, Sm, and H.

The horizontal neutron beam is filtered through silicon and sapphire, giving a flux of $6 \times 10^7 n \cdot cm^{-2} \cdot s^{-1}$ with a Cd ratio >100 at the sample position, 250 cm from the reactor core. Samples are irradiated in Teflon or polyethylene capsules which can hold up to 7 g of powder and gamma rays are received in an Aptec 12% efficient intrinsic Ge detector connected with standard multichannel counting equipment. The usual peaks are: B 478 keV, Gd 182 keV, Sm 334 and 439 keV, H 2223 keV. The blank signals from an empty capsule correspond to sensitivity limits of: B 0.4 μ g, Gd 0.2 μ g, Sm 0.4 μ g, H 100 μ g.

The system is calibrated using appropriate pure chemicals, deposited from solution in a base of silica powder. Precision is monitored by repeat measurements and averages 3-5% (1 standard deviation) for all four elements, except for concentrations near the detection limits. Accuracy is surveyed by including two or more SRMs in each analysis batch. In most cases our results of repeated analysis of many SRMs show agreement with results from other laboratories, using other methods.

If present plans can be carried out, the reactor will be retrofitted with a new core, using the so-called MAPLE design. This will increase the power to 12 Mw and, in addition, the enhanced thermal neutron flux will be generated using a methane cold source. The sensitivity of PGNAA will increase by several orders of magnitude.

Résumé : Le réacteur nucléaire de 2 Mw de McMaster emploie depuis environ six ans un faisceau de neutrons thermalisés avec système spécialisé d'analyse par activation neutronique aux photons gamma instantanés, principalement pour doser le bore, mais aussi pour doser le gadolinium, le samarium et l'hydrogène.

Le faisceau horizontal de neutrons est filtré avec du silicium et un saphir et produit un flux de $6 \times 10^7 n \cdot cm^{-2} \cdot s^{-1}$ avec un rapport cadmique supérieur à 100 à l'emplacement de l'échantillon, à 250 cm du coeur du réacteur. Les échantillons sont irradiés dans des capsules en téflon ou en polyéthylène qui peuvent contenir jusqu'à 7 g de poudre, et les rayons gamma parviennent à un détecteur Aptec intrinsèque de Ge dont l'efficacité est de 12 % et qui est relié à un appareil de comptage standard multicanal. Les pics habituels sont : B, 478 keV; Gd, 182 keV; Sm, 334 et 439 keV; H, 2 223 keV. Les signaux de l'essai à blanc réalisé avec une capsule vide correspondent à des limites de sensibilité de : B, 0,4 μ g; Gd, 0,2 μ g; Sm, 0,4 μ g; H, 100 μ g.

On étalonne le système au moyen de produits chimiques purs déposés en solution dans une base de poudre de silice. On surveille la précision en répétant les mesures. La précision moyenne est de 3 à 5 % (1 écart-type) pour chacun des quatre éléments, sauf lorsque les concentrations sont proches des limites de détection. On

étudie le degré d'exactitude en incluant au moins deux étalons de référence dans chaque lot analysé. Dans la plupart des cas, les résultats de l'analyse répétée de nombreux étalons de référence concordent avec les résultats d'autres laboratoires qui font appel à d'autres méthodes.

On prévoit actuellement l'installation d'un nouveau coeur dans le réacteur en utilisant le modèle MAPLE, ce qui devra augmenter la puissance à 12 Mw. En outre, la génération du flux de neutrons thermiques se fera à partir d'une source froide de méthane. La sensibilité de l'analyse par activation neutronique aux photons gamma instantanés augmentera de plusieurs ordres de grandeur.

---

[1] Department of Geology, McMaster University, Hamilton, Ontario, L8S 4M1, Canada.

The present and future of arc source emission spectrometry in China

R. Shen[1]

Abstract: The advantages of arc source emission spectrometry (AS-ES) are discussed in this paper and the intrinsic weakness of AS-ES and limitations of the arc source are reviewed. Some possible approaches for further development of AS-ES by means of theoretical study, method development, and instrument innovation, etc. are also discussed.

The principle characteristic of AS-ES is its high flexibility. This is due to the fractional distillation effect, by which elements of interest in the arc source can be selectively vaporized. The spectrum intensity to background ratio would be greatly increased by this method; coupled with proper excitation conditions, the detection limits of easily vaporized elements and refractory elements would be effectively lowered, the matrix effect and spectrum interferences could also be minimized. For geological powdered samples, the detection limits of such easily vaporized elements as Ag, As, Au, B, Bi, Cd, Cu, Ga, Ge, Hg, In, Li, Pb, Rb, Sb, Sn, Te, Tl, Zn, and such refractory elements as Ce, Hf, La, Mo, Nb, Sc, Ta, Th, Ti, V, W, Y, Zr are lower or equal to that of geochemical background values. Therefore, this method is superior to those such as ICP-ES, AAS, XRF, etc. with the exceptions of As and Hg. The detection limits of those elements with intermediate vaporization temperatures, such as Ba, Be, Co, Cr, Mn, Ni, Sr, and Yb are essentially equal to the methods mentioned above.

It should be pointed out that the stability of the arc discharge itself could be matched to various modern emission sources, but the analytical precision is mainly dependent upon the homogeneity of material to be analyzed entering the source. Therefore, it is still possible to obtain high analytical precision by selecting the proper analytical conditions. For example, the relative standard deviation (RSD) could be as good as 2% for the major elements in silicate rocks, soils, and refractory metal minerals; for trace elements, an RSD of about 5% is not difficult to achieve. Since AS-ES is capable of determining nearly 40 elements simultaneously, including some important 'indicator' elements for geochemical exploration, it should play an important role in analyzing samples collected in large regional reconnaissance programs. Matrix matching should be employed in the selection of calibration standards and accuracy improved by internal standardization.

Currently, studies to improve analysis by AS-ES should focus on: the creation of a stable arc plasma; understanding the functional mechanism of buffer and carrier distillation, and the diffusion mechanism of elements in the electrode; further perfecting some analytical methods which have already proven its usefulness; exploring the possibility of using multi-internal standardization weighted-compensation method and single-internal standardization coefficient compensation methods; and speeding up the development of computers in acquiring and processing signals.

Résumé : Dans le présent exposé, on examine les avantages et les faiblesses inhérentes de la spectrométrie d'émission avec source à arc (SE/SA) ainsi que les limitations de la source à arc. On examine aussi quelques possibilités de perfectionnement de la SE/SA par l'étude théorique, la mise au point de méthodes et de nouveaux appareils, etc.

La caractéristique principale de la SE/SA est sa grande souplesse qui est attribuée à l'effet de distillation fractionnée qui permet de vaporiser sélectivement les éléments intéressants de la source à arc. Cette méthode permet d'accroître considérablement le rapport de l'intensité du spectre et des valeurs de fond; alliée à des conditions d'excitation appropriées, elle contribuerait à baisser les limites de détection des éléments facilement vaporisés et des éléments réfractaires et à minimiser l'effet de matrice et les interférences spectrales. Dans le cas d'échantillons géologiques pulvérulents, les limites de détection d'éléments facilement vaporisés (p. ex. Ag, As, Au, B, Bi, Cd, Cu, Ga, Ge, Hg, In, Li, Pb, Rb, Sb, Sn, Te, Tl, Zn) et d'éléments réfractaires tels que Ce, Hf, La, Mo, Nb, Sc, Ta, Th, Ti, V, W, Y, Zr sont inférieures ou égales à celles des valeurs géochimiques de fond. Par conséquent, cette méthode est préférable à la SE/PIHF, à la SAA, à la FX, etc., sauf pour le dosage d'As et de Hg. À des températures de vaporisation intermédiaires, les limites de détection d'éléments tels que Ba, Be, Co, Cr, Mn, Ni, Sr et Yb sont essentiellement égales à celles des méthodes mentionnées ci-dessus.

Il faut préciser que la stabilité de la décharge en arc pourrait être adaptée à diverses sources d'émission modernes, mais que la précision analytique dépend principalement de l'homogénéité du matériau soumis à l'analyse et entrant dans la source. Par conséquent, il est toujours possible d'atteindre une précision analytique élevée en choisissant des conditions d'analyse appropriées. Par exemple, l'écart-type relatif pourrait atteindre 2 % pour les éléments majeurs des roches silicatées, des sols et des minéraux métalliques réfractaires; un écart-type relatif d'environ 5 % n'est pas difficile à atteindre pour les éléments traces. Puisque la SE/SA permet de doser simultanément presque 40 éléments, y compris certains indicateurs géochimiques importants, elle devrait jouer un rôle important dans l'analyse d'échantillons recueillis dans le cadre de programmes de reconnaissance régionale de grande envergure. Il faudrait assurer l'adaptation à la matrice lors de la sélection des normes d'étalonnage et l'amélioration de la précision au moyen d'une normalisation interne.

Actuellement, les études visant à améliorer l'analyse par SE/SA devraient porter sur la génération d'un plasma à arc stable; la connaissance du mécanisme de fonctionnement de la distillation du tampon et du porteur et du mécanisme de diffusion des éléments dans l'électrode; le perfectionnement de certaines méthodes d'analyse qui ont déjà fait leurs preuves; l'étude des possibilités d'utiliser la méthode de la compensation pondérée de la normalisation interne multiple et des méthodes de compensation du coefficient de normalisation interne unique; et la mise au point accélérée d'ordinateurs pour l'acquisition et le traitement des signaux.

---

[1] Applied Research Centre of Spectroscopy Instrumentation of China, University of Shijiazhuang, China.

Trace metal analysis – a comparison of atomic spectroscopic techniques

M.W. Tikkanen[1]

Abstract: This paper compares the performance characteristics of three routinely used methods for the determination of trace metal content in geochemical samples – Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Emission Spectroscopy (ICP-ES), and Direct Current Plasma Emission Spectroscopy (DCP-ES).

All three techniques have been shown to be capable of producing virtually any solution elemental analysis at acceptable levels of precision and accuracy. But 'real world' sample analyses, as with geochemical determinations, requires that other questions be answered, before determining which technique is the method of choice. Such considerations as sample preparation requirements, interference correction capabilities, speed, convenience, and cost must be considered. Examples of such considerations will be presented with specific application to trace metal determination in geochemical samples.

Résumé : Dans cet exposé, on compare les caractéristiques de rendement de trois méthodes courantes de dosage des métaux présents en traces dans des échantillons géochimiques : la spectrométrie d'absorption atomique (SAA), la spectroscopie d'émission avec plasma induit par haute fréquence (SE/PIHF) et la spectroscopie d'émission avec plasma à courant direct (SE/PCD).

On a démontré que ces trois techniques permettaient toutes d'effectuer pratiquement n'importe quelle analyse élémentaire d'une solution à des niveaux acceptables de précision et d'exactitude. Or, les analyses d'échantillons «réels», comme les dosages géochimiques, exigent que l'on réponde à d'autres questions avant de déterminer quelle est la méthode privilégiée. Il faut tenir compte de certaines considérations telles que les besoins de préparation de l'échantillon, la capacité de correction des interférences, la rapidité, la facilité d'emploi et le coût. On donne des exemples de ces considérations appliquées au dosage des métaux présents en traces dans les échantillons géochimiques.

---

[1] Fisons Instruments – ARL, 200 Cochrane Drive, Unit 6, Unionville, Ontario, L3R 8E8, Canada.

Is there an alternative to fire assay for the determination of platinum group elements?

M. Totland[1], I. Jarvis[1], and K. Jarvis[2]

Abstract: The platinum group elements (PGEs) Pt, Pd, Ru, Rh, Os, and Ir are found in nature heterogeneously distributed at ultratrace levels. They are, however, of major economic importance, being used as catalysts in the petroleum and chemical industries, as a raw material in the manufacture of electronic components and jewellery, and as a form of investment. Levels of a few $\mu g \cdot g^{-1}$ may be economic to recover, and consequently determinations of sub-$ng \cdot g^{-1}$ levels are required for geological studies.

Recent developments in analytical instrumentation, such as graphite furnace-atomic absorption spectroscopy, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and ICP-mass spectroscopy (ICP-MS), have encouraged a reassessment of methods for PGE determination. To analyze at the ultratrace levels present in natural materials, however, usually requires a preconcentration and/or separation step before final analysis.

Traditionally, fire assay has been used to concentrate PGEs in ores, collecting the noble metals in a lead, copper, or nickel sulphide button. This technique requires specialized equipment, large amounts of analytical reagents, and special procedures to avoid loss of volatile Os and Ru compounds. Additionally, analytical results are highly dependent on the assay conditions. Tellurium collection has also been used to separate and collect the PGEs, although this procedure is lengthy and isotope dilution is necessary to correct for incomplete co-precipitation. An alternative to Te collection is ion-exchange chromatography. The PGEs readily form anionic chloro-complexes enabling two approaches to ion exchange: (1) an anionic resin can be used and PGE species trapped on the resin, to be subsequently eluted and analyzed; or (2) a cationic resin can be used to remove the matrix elements, thereby allowing the analysis of concentrated solutions of PGEs.

This paper will present results from our research programme which aims to develop simplified procedures for the determination of the PGEs. A two-step dissolution will be discussed which combines a quick acid attack in sealed microwave vessels, followed by lithium borate fusion of the refractory minerals. Results for two types of ion-exchange resins will be presented (anionic resin, Dowex 1-X8, and cationic resin, Dowex 50W-X8), based on data obtained by ICP-AES and ICP-MS. Procedures will be evaluated using a range of PGE certified reference materials from South Africa (SARM-7) and Canada (PTA-1, PTC-1, PTM-1, and SU-1a).

Résumé : Dans la nature, les éléments du groupe du platine (EGP) (Pt, Pd, Ru, Rh, Os, et Ir) ont une distribution hétérogène et se rencontrent à l'état d'ultratraces. Ils ont toutefois une grande importance économique puisqu'on les utilise comme catalyseurs dans les industries pétrolière et chimique, comme matière première dans la fabrication de pièces électroniques et de bijoux, et à des fins d'investissement. Il peut être rentable de récupérer des concentrations de quelques $\mu g \cdot g^{-1}$ et, par conséquent, il faut réaliser des dosages à des concentrations inférieures au $ng \cdot g^{-1}$ pour les études géologiques.

Les perfectionnements récents des techniques d'analyse comme la spectroscopie d'absorption atomique avec un four en graphite, la spectroscopie d'émission atomique avec plasma induit par haute fréquence (SE/PIHF) et la spectroscopie de masse avec plasma induit par haute fréquence SM/PIHF) ont encouragé la réévaluation des méthodes de dosage des EGP. Toutefois, pour doser les concentrations ultratraces que l'on rencontre dans les matériaux naturels, on doit habituellement procéder à une étape de préconcentration ou de séparation avant d'entreprendre le dosage final.

On a traditionnellement employé l'analyse pyrognostique pour concentrer les EGP dans les minerais, en recueillant les métaux nobles dans un bouton de sulfure de plomb, de cuivre ou de nickel. Cette technique exige un matériel spécialisé, de grandes quantités de réactifs pour l'analyse et des procédés spéciaux permettant d'éviter les pertes de composés volatils d'osmium et de ruthénium. En outre, les résultats dépendent fortement des conditions de l'analyse. On a également eu recours au captage du tellure pour séparer et recueillir les EGP, bien que ce procédé soit long et qu'il faille procéder à la dilution isotopique pour remédier à la coprécipitation incomplète. Au lieu du captage du tellure, on peut employer la chromatographie d'échange d'ions. Les EGP forment facilement des chloro-complexes anioniques qui permettent deux procédés d'échange ionique : (1) on peut employer une résine anionique et piéger les espèces d'EGP sur la résine, puis procéder à leur élution et à leur analyse; ou (2) on peut employer une résine cationique pour éliminer les éléments de la matrice et pouvoir ensuite analyser les solutions concentrées d'EGP.

Dans cet exposé, les auteurs présentent les résultats de leur programme de recherche, qui vise la mise au point de procédés simplifiés de dosage des EGP. Ils examinent la dissolution en deux étapes, qui combine une attaque acide rapide dans des récipients scellés pour traitement aux micro-ondes et la fusion des minéraux réfractaires dans du borate de lithium. Ils donnent les résultats obtenus par SE/PIHF et par SM/PIHF avec deux types de résines échangeuses d'ions (résine anionique Dowex 1-X8 et résine cationique Dowex 50W-X8). Ils évaluent les procédés en utilisant une gamme de matériaux de référence certifiés constitués d'EGP et provenant de l'Afrique du Sud (SARM-7) et du Canada (PTA-1, PTC-1, PTM-1 et SU-1a).

---

[1] School of Geological Sciences, Kingston Polytechnic, Penrhyn Road, Kingston upon Thames, Surrey, KT1 2EE, U.K.
[2] NERC ICP-MS Facility, Department of Geology, Royal Holloway and Bedford New College, Egham Hill, Egham, Surrey, TW20 OEX, U.K.

Analysis of standard reference materials for thallium, gallium and indium

J.E. Vaive[1] and G.E.M. Hall[1]

Abstract: At present, there are few methods available for the determination of Tl, Ga, and In in geological materials at or below the average crustal abundance level. A method capable of determination down to 10 ppb for all three elements has been developed at the Geological Survey of Canada. The samples are decomposed using a multiacid ($HCl-HF-HClO_4-HNO_3$) 'total' decomposition procedure, extracted in a suitable form into MIBK and analyzed by graphite furnace atomic absorption spectrometry. Palladium is used as a matrix modifier to remove gas phase interferences which would result in significantly higher detection limits.

This methodology was evaluated by the analysis of international standard reference materials and results presented here compare favourably with accepted values.

Résumé : Il existe actuellement peu de méthodes permettant le dosage des éléments Tl, Ga et In dans des matériaux géologiques à une teneur égale ou inférieure à leur teneur moyenne dans la croûte terrestre. À la Commission géologique du Canada, on a élaboré une méthode capable de doser aussi peu que 10 ppb de chacun de ces trois éléments. On décompose les échantillons par un procédé de décomposition «totale» en présence de plusieurs acides simultanément ($\mathrm{HCl\text{-}HF\text{-}HClO_4\text{-}HNO_3}$), on les soumet sous une forme appropriée à une extraction dans la MIBK, puis on les analyse par spectrométrie d'absorption atomique dans un four en graphite. Le palladium sert de modificateur de la matrice et permet d'éliminer les interférences dues aux phases gazeuses qui élèveraient de façon significative les limites de détection.

On a évalué cette méthodologie par analyse d'étalons de référence internationaux, et les résultats présentés ici sont assez proches des valeurs acceptées.

---

[1] Geological Survey of Canada, 601 Booth St., Ottawa, Ontario, K1A 0E8, Canada.

A versatile method for analysis of oxide ore samples by energy dispersive X-ray fluorescence (ED-XRF)

P.C. Webb[1], P.J. Potts[1], and J.S. Watson[1]

Abstract: A simple modification of a method used routinely for analyzing silicate rocks enables the accurate determination of major elements in a range of oxide ore samples. Samples are prepared as glass discs by adding an equal weight of pure quartz to the sample before fusion with a lithium metaborate/tetraborate flux. Actual proportions are 1:1:12 of sample:quartz:flux. The added quartz serves to: i) assist in the dissolution of refractory oxides, ii) promote the formation of stable glass discs using a flux normally appropriate for silicate rocks, and iii) convert the matrix to mimic that of a silicate rock so that routine methods used for calibrating silicate samples are applicable with only minor modification. Furthermore, the effective dilution of the ore constituents reduces the magnitude of matrix corrections which can be severe in samples of unusual composition.

To calibrate for high levels of ore components, routine silicate calibrations (1:6 dilution) require extending with additional ore reference samples (1:1:12 dilution). Only the ore samples require addition of quartz, and a numeric correction must be applied to the composition data to take the added 50 wt.% SiO_2 into account. One consequence of the higher dilution is that precision errors and detection limits for ore samples are greater than for corresponding silicate analysis, but this problem can be reduced by extending count times.

These procedures have been applied to a range of oxide (i.e. nonsulphide ores of Cr, Mn, and Fe) ore reference samples with determinations by ED-XRF analysis. The calibrations produced give good agreement between expected and regressed values of major elements across a wide compositional range, demonstrating the versatility of the method. Additional data are presented for major elements in a number of ore reference materials for which matrix compositions are not well characterized. These data should be of value to analysts needing to assess matrix effects and instrumental interferences before selecting the most appropriate conditions for analysis.

Résumé : En apportant une simple modification à une méthode couramment employée pour analyser des roches silicatées, on peut doser avec précision les éléments majeurs dans une gamme d'échantillons de minerai oxydé. On prépare les échantillons sous la forme de disques de verre en ajoutant une masse égale de quartz pur à l'échantillon avant sa fusion avec un fondant de métaborate/tétraborate de lithium. Les proportions réelles sont 1/1/12 d'échantillon/quartz/fondant. Le quartz ajouté sert i) à favoriser la dissolution des oxydes réfractaires, ii) à faciliter la formation des disques de verre stable avec un fondant qui convient normalement aux roches silicatées, et iii) à convertir la matrice de façon à ce qu'elle imite celle d'une roche silicatée afin de pouvoir utiliser des méthodes courantes d'étalonnage des échantillons de silicates avec seulement quelques modifications mineures. De plus, la dilution effective des constituants du minerai réduit l'importance des corrections relatives à la matrice, qui peuvent être considérables dans les échantillons de composition inhabituelle.

Pour étalonner en vue de concentrations élevées de constituants des minerais, en plus de l'étalonnage courant des silicates (dilution 1/6), il faut introduire des échantillons de minerais de référence (dilution 1/1/12). Seuls les échantillons de minerai exigent l'addition de quartz, et il faut apporter une correction numérique aux données sur la composition pour tenir compte du pourcentage massique (50 %) de SiO_2 ajouté. Cette dilution plus élevée fait que les erreurs de fidélité et les limites de détection sont plus élevées pour les échantillons de minerai que pour l'analyse correspondante des silicates, mais on peut pallier ce problème en prolongeant la période de comptage.

On a appliqué ces procédés à une gamme d'échantillons d'oxydes de référence (c.-à- d. de minerais non sulfurés de Cr, de Mn et de Fe), les dosages étant effectués par fluorescence X à dispersion d'énergie. À en juger par les étalonnages ainsi réalisés, les valeurs prévues concordent bien avec les valeurs de régression des éléments majeurs dans une vaste gamme de compositions, ce qui atteste la souplesse de la méthode. Les auteurs présentent des données additionnelles sur les éléments majeurs dans un certain nombre de minerais de référence pour lesquels la composition de la matrice est insuffisamment caractérisée. Ces données devraient s'avérer utiles pour les analystes qui doivent évaluer les effets de matrice et les interférences causées par l'appareillage avant de sélectionner les conditions convenant le mieux à l'analyse.

---

[1] The Open University, Department of Earth Sciences, Walton Hall, Milton Keynes, MK7 6AA, U.K.

Analytical requirements in international geochemical mapping

X. Xie[1]

Abstract: The history of the development of geochemical exploration has been closely connected with the progress of geoanalysis techniques and instrumentation. The application of spectrographic methods and the development of sensitive colorimetric methods in analyzing geological materials provided the necessary background for the birth of this new exploration method. The use of atomic absorption spectometry highlighted local and semi-regional scale geochemical exploration in the whole world. Regional and national geochemical mapping became established only when automatic instruments with multielement analysis capability became available (e.g., the XRF spectrometer, the ICP emission spectrometer, and the neutron activation facility).

International geochemical mapping is the inevitable outcome in the trend of development of geochemical exploration. But its analytical requirements possess some marked differences with its earlier stages due to its international or global nature.

ELEMENTS DETERMINED: Elements determined in existing regional or national geochemical mapping projects have been highly diversified. They should be unified in the International Mapping Program (IGCP 259), but flexibility must be allowed. To solve this problem, the elements will be grouped into six packages and analysis can be made in sequence in these packages according the facility and capability of different laboratories.

DETECTION LIMITS: Detection limits of trace and ultratrace elements should be lowered below their crustal abundance in order to make the geochemical maps of these elements much more informative than before. A proposed list of detection limits is given.

ACCURACY: Accuracy is the long-time neglected item in geochemical exploration analysis, because the exploration geochemist has been mainly interested in looking for the relative contrast of anomalous values with background values. But in International Geochemical Mapping, the interlaboratory bias must be reduced to a minimum to make the data globally comparable. This could be done by developing unified procedures for selecting optimum methods, and for routine monitoring of the data quality. Primary and secondary standard samples have to be prepared and used in these procedures.

Résumé : L'évolution de la prospection géochimique a été étroitement liée à l'évolution des techniques et des appareils de géoanalyse. L'application de méthodes spectrographiques et la mise au point de méthodes colorimétriques sensibles pour le dosage des matériaux géologiques ont fourni les bases de cette nouvelle méthode de prospection. L'emploi de la spectrométrie d'absorption atomique a mis en évidence dans le monde entier l'importance de la prospection géochimique locale et semi-régionale. La cartographie géochimique à l'échelle régionale ou nationale n'est devenue courante qu'une fois mis au point des instruments automatiques capables de doser simultanément plusieurs éléments (par ex., le spectromètre à fluorescence X, le spectromètre d'émission à plasma induit par haute fréquence et l'analyseur à activation neutronique).

La cartographie géochimique à l'échelle internationale est le résultat inévitable des progrès réalisés en prospection géochimique. Toutefois, en raison de son caractère international ou global, les exigences analytiques actuelles de cette science présentent certaines différences marquées par rapport aux exigences analytiques initiales.

ÉLÉMENTS DÉTERMINÉS : Les éléments déterminés lors de la réalisation des projets existants de cartographie géochimique régionale ou nationale sont très variés. On prévoit les unifier dans le cadre du Programme international de cartographie géochimique (PICG 259), mais il faudrait garder une certaine marge de souplesse. Pour résoudre ce problème, on entend regrouper les éléments en six ensembles; on pourra alors analyser séquentiellement ces ensembles selon les installations et les capacités des divers laboratoires.

LIMITES DE DÉTECTION : Il faudrait abaisser les limites de détection des éléments traces et ultratraces au-dessous de leur teneur dans la croûte afin d'accroître la valeur informative des cartes géochimiques de ces éléments. L'auteur donne une liste des limites de détection proposées.

EXACTITUDE : L'exactitude a été longuement négligée en prospection géochimique, car le géochimiste prospecteur cherchait principalement à déceler les anomalies par rapport aux valeurs de fond. Or, dans le Programme international de cartographie géochimique, il faudra minimiser le biais interlaboratoire afin de pouvoir comparer les données globalement. On peut y parvenir en mettant au point des procédés uniformisés permettant de sélectionner les méthodes optimales et de surveiller régulièrement la qualité des données. Il faudra préparer des étalons primaires et secondaires et les utiliser dans ces procédés.

---

[1] Institute of Geophysical and Geochemical Exploration, Langfang, Hebei 102849, P.R. China.

Solid sample introduction by laser ablation for inductively coupled plasma emission spectrometry

Z. Xu[1]

Abstract: The introduction of powdered geological solid samples by laser ablation for analysis by inductively coupled plasma emission spectrometry (ICP-ES) is studied.

The fundamental principles of laser ablation, the phenomenon of the transportation of the aerosol (ablation particulate material), and the application of ICP-ES are investigated.

Three modes of laser ablation are applied in this work.

1. A Nd YAG laser is used, which can be operated either in the free running or Q switched mode (pulse duration 8 ns and irradiance larger than 10^{11} W•cm^{-2}) at repetition rate of 1-20 Hz. The accuracy and precision of the data produced in the Q switched mode are superior than the free running mode, achieving good detection limits, but the results for Zr are low. We have observed that the structure of the refractory mineral, zircon, could not be destroyed by the laser beam and vaporized completely. If the sample is pretreated by chemical means, good results will then be obtained.

2. A dual laser beam ablation system is used, combining both the CO_2 laser and Nd YAG laser in Q switched mode to ablate the sample sequentially. Sample is mixed with some chemical fluxing reagents, fused by the CO_2 laser at first and then ablated (vaporized) by the YAG Q switched laser in the same chamber. We obtained good analytical results for Zr, but the orifice of the ICP torch may be clogged by the salts of chemical reagents.
3. Now we use a YAG laser with an acoustic optic Q switch to ablate the sample. This system appears to achieve the best results and its future looks promising.

Résumé : Dans cet exposé, l'auteur traite de l'introduction, par ablation par laser, d'échantillons géologiques solides pulvérulents aux fins de l'analyse par spectrométrie d'émission avec plasma induit par haute fréquence (SE/PIHF).

Il examine les principes fondamentaux de l'ablation par laser, le phénomène du transport de l'aérosol (matière particulaire générée par ablation) et l'application de la SE/PIHF.

Il décrit trois modes d'ablation par laser.

1. Un laser YAG-néodyme est utilisé en mode relaxé ou en mode déclenché (impulsions d'une durée de 8 ns et flux lumineux supérieur à 10^{11} W• cm^2) à une fréquence de répétition de 1 à 20 Hz. L'exactitude et la précision des données produites en mode déclenché sont supérieures à celles obtenues en mode relaxé, donnant ainsi de bonnes limites de détection, mais les résultats relatifs au Zr sont médiocres. La structure du zircon, minéral réfractaire, ne peut être détruite par le faisceau laser, donc vaporisée complètement. Lorsque l'échantillon subit un prétraitement chimique, les résultats sont bons.
2. Un système double d'ablation par laser, combinant le laser à CO_2 et le laser YAG-néodyme en mode déclenché, est utilisé pour réaliser l'ablation séquentielle de l'échantillon. L'échantillon est mélangé à des fondants chimiques, liquéfié par le laser à CO_2, puis vaporisé (ablation) dans la même chambre par le laser YAG-néodyme en mode déclenché. Les résultats analytiques sont bons pour le Zr, mais les sels des réactifs chimiques peuvent obstruer la buse du chalumeau PIHF.
3. Un laser YAG muni d'un Q-switch acoustico-optique sert maintenant à réaliser l'ablation de l'échantillon. Ce système semble donner les meilleurs résultats et son avenir est prometteur.

---

[1] Nanjing Laboratory of Rock and Mineral Research, Ministry of Geology and Mineral Resources, Nanjing, China.

Applications of inductively coupled plasma mass spectrometry (ICP-MS) to geoanalysis

N. Yin[1]

Abstract: ICP-MS has received special attention from geoanalysts due to its unique features, namely, high detection power, simple spectra, and rapid isotopic ratio capability. However, real-world geoanalysis has shown that there are certain limitations preventing this technique from giving full play to its advantages. These limitations, in many cases, relate to sampler orifice clogging with relatively low dissolved solids and signal suppression/enhancement in the presence of relatively low contents of matrix elements. Moreover, sample dissolution procedures conventionally used also pose limitations on achieving the best possible analytical results. A VG PlasmaQuad system was installed in the Institute of Rock and Mineral Analysis in 1986 and is now in routine use for geoanalysis. This talk will summarize geoanalytical applications which have been developed at this institute and present analytical data of trace elements and lead isotopic ratios for various geological samples and standard reference materials.

Résumé : La SM/PIHF a suscité un intérêt particulier chez les géoanalystes à cause de ses caractéristiques uniques, notamment son pouvoir de détection élevé, ses spectres simples et la rapidité d'établissement des rapports isotopiques. Toutefois, la géoanalyse comporte de toute évidence certaines limites qui empêchent d'en tirer pleinement avantage. Ces limites sont le plus souvent dues à l'obturation de la buse de l'échantillonneur par des solides mal dissous et à la suppression ou à l'amplification du signal en présence de quantités relativement faibles d'éléments de la matrice. En outre, la méthode courante de dissolution des échantillons impose aussi des limites quant à l'obtention des meilleurs résultats analytiques possibles. Un système VG PlasmaQuad a été installé à l'Institut d'analyse des roches et des minéraux en 1986; il sert maintenant à faire les géoanalyses courantes. Dans cet exposé, on résume les applications géoanalytiques qui ont été mises au point à l'Institut et l'on présente des données analytiques sur les éléments traces et les rapports isotopiques du plomb dans divers échantillons et étalons géologiques.

---

[1] Institute of Rock and Mineral Analysis, Beijing, China.

The determination of major and trace elements in geological materials samples by XRF

Q. Zhai[1]

Abstract: Eight major elements and 14 traces have been determined by pressed pellet XRF using an ARL 8680 SIM/SEQ X-ray spectrometer. Samples are ground to less than 200 mesh and pressed into pellets using a paraffin-boric acid mixture as adhesive. Corrections are made for overlapping spectra on Ba, Y, Zn, and Th; the Compton scattered line is used as internal standard to improve accuracy. Matrix effects are corrected for by the use of the Traill-LaChance equation or the Lucas-Tooth equation. Analysis of the pressed rock or sediment powder pellet for 22 elements requires about nine minutes of machine time; 130 samples can be analyzed in 24 hours. Tables 1 and 2 show the accuracy and precision, respectively, obtained by this method.

Résumé : On a dosé huit éléments majeurs et 14 éléments traces en soumettant des granules pressés à la spectrométrie par fluorescence X au moyen d'un spectromètre à rayons X ARL 8680 SIM/SEQ. On broie les échantillons jusqu'à moins de 200 mesh, puis on les comprime en granules en employant un mélange de paraffine et d'acide borique comme liant. On effectue une correction pour tenir compte des spectres se recouvrant partiellement sur Ba, Y, Zn et Th; la ligne diffusée Compton sert d'étalon interne pour améliorer l'exactitude des mesures. On corrige les effets de matrice en employant l'équation de Traill-LaChance ou l'équation de Lucas-Tooth. Le dosage de 22 éléments dans des granules pressés de roche ou de sédiment exige environ neuf minutes d'utilisation du spectromètre; 130 échantillons peuvent être analysés en 24 heures. Les tableaux 1 et 2 montrent l'exactitude et la précision, respectivement, données par cette méthode.

---

[1] Test center of Geology and minerals of Yunnan, China.

Table 1. Comparison of results with recommended values for standard reference materials

Element or oxide	GSR-5		GSS-3		GSD-6	
	This method	Recommended value	This method	Recommended value	This method	Recommended value
(%)						
MgO	1.92	2.03	0.61	0.58	3.02	2.98
Al_2O_3	18.32	18.82	12.73	12.25	13.97	14.17
SiO_2	60.26	59.28	73.25	74.65	62.22	61.22
K_2O	4.33	4.18	2.93	3.06	2.39	2.43
CaO	0.69	0.59	1.27	1.20	3.86	3.85
Na_2O	0.32	0.35	2.80	2.70	2.17	2.32
Fe_2O_3	7.64	7.58	2.21	2.00	5.68	5.85
(ppm)						
P	660	700	307	320	969	1064
Ti	208	202	2207	2220	4433	4640
Mn	183	175	362	310	923	970
V	93	86	43.6	36.6	130	142
Cr	101	96	38.6	32	174	190
Zn	54	54	28.8	30.4	134	144
Nb	18.2	15	9.2	9.7	13.7	12
Y	30	26	15.2	15.3	26	20.2
Rb	209	202	79	85	110	107
Sr	97	90	371	380	273	266
Zr	105	95	230	250	171	170
Th	10.0	13	7.6	6.0	8.8	9.0
La			20	21	34	39
Pb	9.2	8.5	25.4	26.4	22.9	27
Ba	460	450	1022	1230	304	330

Table 2. Precision of XRF-pressed pellet method

Element or oxide	GSD-12			GSS-2		
	This method (n=10)	Recommended value	Coefficient of variation (%)	This method (n=10)	Recommended value	Coefficient of variation (%)
(%)						
MgO	0.45	0.44	0.84	1.26	1.05	1.03
Al_2O_3	9.65	9.36	0.17	10.41	10.31	0.11
SiO_2	76.42	77.27	0.01	74.03	73.34	0.2
K_2O	2.84	2.92	0.17	2.62	2.54	0.43
CaO	1.01	1.16	0.19	2.42	2.37	0.05
Na_2O	0.48	0.44	0.78	1.88	1.62	0.11
Fe_2O_3	4.75	4.87	0.23	3.62	3.53	0.11
(ppm)						
P	213	238	0.99	431	440	1.35
Ti	1613	1510	0.04	2685	2700	0.28
Mn	1329	1420	0.40	582	513	0.63
V	49.2	46	2.69	66	61.5	3.94
Cr	41	35.4	4.53	54	47	6.68
Zn	509	497	0.86	42.1	42	4.25
Nb	17.1	15.6	6.90	26.7	26.7	4.41
Y	35	30	6.62	20.9	22	9.03
Rb	282	270	1.17	86	88	2.82
Sr	24.2	24.2	7.43	196	187	1.16
Zr	245	235	1.67	190	217	0.91
Ta	19.9	21.5	3.01	15.5	16.5	9.27
La	32.5	33	7.80	144	160	5.97
Pb	291	286	0.31	16.2	21	9.16
Ba	220	206	2.49	916	930	1.63

Tableau 1. Comparaison des résultats et des valeurs recommandées pour les étalons de référence

Élément or oxyde	GSR-5		GSS-3		GSD-6	
	Cette méthode	Valeur recommandée	Cette méthode	Valeur recommandée	Cette méthode	Valeur recommandée
(%)						
MgO	1.92	2.03	0.61	0.58	3.02	2.98
Al_2O_3	18.32	18.82	12.73	12.25	13.97	14.17
SiO_2	60.26	59.28	73.25	74.65	62.22	61.22
K_2O	4.33	4.18	2.93	3.06	2.39	2.43
CaO	0.69	0.59	1.27	1.20	3.86	3.85
Na_2O	0.32	0.35	2.80	2.70	2.17	2.32
Fe_2O_3	7.64	7.58	2.21	2.00	5.68	5.85
(ppm)						
P	660	700	307	320	969	1064
Ti	208	202	2207	2220	4433	4640
Mn	183	175	362	310	923	970
V	93	86	43.6	36.6	130	142
Cr	101	96	38.6	32	174	190
Zn	54	54	28.8	30.4	134	144
Nb	18.2	15	9.2	9.7	13.7	12
Y	30	26	15.2	15.3	26	20.2
Rb	209	202	79	85	110	107
Sr	97	90	371	380	273	266
Zr	105	95	230	250	171	170
Th	10.0	13	7.6	6.0	8.8	9.0
La			20	21	34	39
Pb	9.2	8.5	25.4	26.4	22.9	27
Ba	460	450	1022	1230	304	330

Tableau 2. Précision de l'analyse par spectrométrie FX de granules pressés

Élément or oxyde	GSD-12			GSS-2		
	Cette méthode (n=10)	Valeur recommandée	Coefficient de variation (%)	Cette méthode (n=10)	Valeur recommandée	Coefficient de variation (%)
(%)						
MgO	0.45	0.44	0.84	1.26	1.05	1.03
Al_2O_3	9.65	9.36	0.17	10.41	10.31	0.11
SiO_2	76.42	77.27	0.01	74.03	73.34	0.2
K_2O	2.84	2.92	0.17	2.62	2.54	0.43
CaO	1.01	1.16	0.19	2.42	2.37	0.05
Na_2O	0.48	0.44	0.78	1.88	1.62	0.11
Fe_2O_3	4.75	4.87	0.23	3.62	3.53	0.11
(ppm)						
P	213	238	0.99	431	440	1.35
Ti	1613	1510	0.04	2685	2700	0.28
Mn	1329	1420	0.40	582	513	0.63
V	49.2	46	2.69	66	61.5	3.94
Cr	41	35.4	4.53	54	47	6.68
Zn	509	497	0.86	42.1	42	4.25
Nb	17.1	15.6	6.90	26.7	26.7	4.41
Y	35	30	6.62	20.9	22	9.03
Rb	282	270	1.17	86	88	2.82
Sr	24.2	24.2	7.43	196	187	1.16
Zr	245	235	1.67	190	217	0.91
Ta	19.9	21.5	3.01	15.5	16.5	9.27
La	32.5	33	7.80	144	160	5.97
Pb	291	286	0.31	16.2	21	9.16
Ba	220	206	2.49	916	930	1.63

Discussion of mineral standard reference samples tests in EPMA

Y. Zhang[1], S. Wang[2], L. Yang[1], and X. Meng[1]

Abstract: Standard reference samples of minerals of natural origin in EPMA must have a degree of homogeneity in chemical composition at about the micrometer (µm) scale of spatial resolution and possess excellent stability in electron beam bombardment.

This paper has evolved from work on the development of mineral standard reference samples for electron microprobe mineral analysis and discusses: homogeneity testing and stability testing using the electron microprobe; certification of chemical composition; and the statement of uncertainty in certified values. The process of assessing homogeneity and the criteria used in selecting suitable standards are discussed in this paper.

Résumé : Les étalons de référence de minéraux naturels qui sont utilisés dans l'analyse par microsonde électronique doivent avoir une composition chimique relativement homogène à une échelle de résolution spatiale de l'ordre du micromètre (µm) et posséder une excellente stabilité en présence d'un bombardement électronique.

Cet exposé est le produit de recherches sur la mise au point d'étalons minéraux utilisés pour l'analyse de minéraux par microsonde électronique. Les auteurs examinent les essais d'homogénéité et de stabilité effectués avec la microsonde électronique, la certification de la composition chimique et l'expression de l'incertitude des valeurs certifiées. Ils décrivent le processus d'évaluation de l'homogénéité et les critères de sélection d'étalons acceptables.

---

[1] Yunnan Provincial Central Lab., Ministry of Geology and Mineral Resources, Dashiba, Kunming, 650218, P.R. China.
[2] Institute of Multipurpose Utilization of Mineral Resources, Ministry of Geology and Mineral Resources, Emei, P.R. China.

The Analytical Chemistry Laboratory at the Geophysics Institute, UNAM, Mexico

M.A. Armienta[1], F. Juárez[1], and A. Aguayo[1]

Abstract: The establishment of a chemical laboratory for the analyses of geological materials (rocks and groundwaters) at the Geophysics Institute (UNAM, Mexico) is described.

The objective was to establish a laboratory capable of obtaining good quality analyses with minimum expense. The results had to be adequate to use in the study of rock geochemistry, hydrogeochemistry, and quality of groundwaters.

The project is being developed in two stages. The first is to design methods for the quantification of major element oxides in rocks and physicochemical parameters in waters. For that purpose, wet methods were developed. The second stage in the development of the laboratory has consisted of the establishment of a technique for the quantification of metallic contaminants in waters and trace elements in rocks. These analyses are in development using an atomic absorption spectrophotometer and a polarograph recently acquired by the laboratory.

Résumé : Dans cet exposé, on décrit l'établissement d'un laboratoire de chimie pour l'analyse de matériaux géologiques (roches et eaux souterraines) à l'Institut de géophysique (UNAM, Mexique).

Il s'agissait d'établir un laboratoire pouvant fournir des analyses de qualité à moindres frais. Les résultats devaient convenir aux études de la géochimie des roches, aux études hydrogéochimiques et aux études de la qualité des eaux souterraines.

On réalise actuellement le projet en deux étapes. La première consiste à concevoir des méthodes de dosage des éléments majeurs oxydés contenus dans les roches et de quantification des paramètres physico-chimiques dans les eaux souterraines. À cette fin, on a élaboré des méthodes d'analyse par voie humide. La seconde étape de l'établissement du laboratoire a consisté à mettre sur pied une technique de dosage des contaminants métalliques présents dans les eaux souterraines et des éléments traces présents dans les roches. Ces analyses sont en voie de mise au point et seront effectuées avec un spectrophotomètre d'absorption atomique et un polarographe récemment acquis par le laboratoire.

---

[1] Instituto de Geofisica, UNAM, México, Circuito Exterior, C.U., México 04510, D.F.

INTRODUCTION

Geochemistry is an important field of the earth sciences, requiring accurate chemical analyses of geological samples. Equipment for analyzing these kinds of materials is available but it tends to be very expensive. Developing nations, particularly Latin-American countries, are now in a bad economic situation. Moreover, the percentage of the GNP assigned to research and education is very low, making it difficult for educational institutions to acquire instruments like ICP emission spectrometers or XRF. It is indeed necessary for these countries to independently carry out their own rock geochemistry, hydrochemical, and contamination studies. The challenge then is to obtain the analytical results required with the available equipment (not very sophisticated) and with minimum expense.

Various research groups at the Geophysics Institute of the National University of Mexico, five years ago, faced the challenge of establishing a chemistry laboratory capable of carrying out analyses for geochemical, hydrochemical, and contamination research. In view of the limited resources, the implementation of the laboratory was planned in two stages: the first for major element oxide quantification in rocks and principal ions in waters; and the second for trace analysis in rocks and inorganic contaminants (mainly heavy metals) in water. The analytical methodology was adapted from wet techniques, in view of the available equipment and the types of rocks and water samples to be analyzed.

The laboratory was initiated with the basic substructure of a common analytical chemistry laboratory, consisting mainly of lab ware, reagents, ovens, furnaces, hot plates, and magnetic stirrers. For the first stage, the equipment acquired consisted of a pH meter, a colorimeter, a potentiometer with specific electrodes, a flame photometer, a conductivity meter, and an analytical balance. For the second stage, an atomic absorption (AA) spectrophotometer and a polarograph were added.

ROCK ANALYSIS

Prior to analysis, the rock samples were washed with deionized water, dried under infrared light, crushed in a jaw crusher, and divided in four parts. One of those parts is ground in a ceramic grinder to -100 mesh, and split again in four parts. Finally, a portion of 5 g is ground by hand in an agate mortar.

The powdered rock is divided in four portions: the first for the determination of H_2O^- and L.O.I.; the second for the determination of SiO_2, Al_2O_3, MgO, CaO; the third for the quantification of Fe, MnO, P_2O_5, TiO_2, Na_2O, K_2O; and the last one for the determination of FeO.

Silica is determined gravimetrically taking advantage of its insolubility in strong acids. A known amount of the rock powder is fused together with Na_2CO_3 and K_2CO_3, treated with dilute HCl, and filtered twice. The precipitate is heated to 950°C until the filter is completely charred, and the solid is weighed. Finally the residue is treated with water, H_2SO_4 and HF, evaporated to dryness until all the SiF_4 is volatilized and weighed again. The difference in weight corresponds to the SiO_2 content. This determination takes about 32 hours. For the cleaning of the platinum crucibles it is advisable to fill them with $KHSO_4$ and fuse. This procedure is a modification of Hillebrand and Lundell (1953) and Vogel (1960).

L.O.I. and H_2O^- are also determined by gravimetry, heating to 1000°C and 110°C for one and two hours, respectively.

For the determination of P_2O_5, MnO, K_2O, Na_2O, TiO_2, and total Fe, 1 g of the powdered sample is treated with $HClO_4$ and HF, evaporated slowly to near dryness in a Teflon beaker and dissolved with dilute $HClO_4$. In order to obtain a total dissolution without loss of the analyzed species, it is important to stop the heating in the right point, just when the solid residue can be separated from the bottom of the beaker, avoiding excessive drying. Different aliquots of this solution are taken for the quantification of the various oxides.

Phosphorus and titanium are determined by colorimetry: P through the formation of a yellow complex of phosphomolybdate; and Ti by treatment of an aliquot of the rock solution with $BeSO_4$ and H_2O_2 in acid medium. In the latter determination, it is important to prepare the Ti standard very carefully. A weighed powder of TiO_2 is added to a platinum crucible, mixed with $K_2S_2O_7$, covered and heated in the furnace to 700°C, until a yellow and transparent liquid is obtained. The solution is allowed to cool and solidify, then it is dissolved with H_2SO_4 (10%) and heated gently over a hot plate until dissolution (Obregón, 1973).

Manganese and total Fe are also determined by colorimetry. Manganese is quantified by its oxidation to permanganate with KIO_4, and Fe by the formation of a red complex with ortho-phenanthrolin at a pH between 3.5 and 5.0, in a 1:10 dilution of the rock solution. (Energlyn and Brealey, 1971; Ringbom, 1979; Sandell, 1959).

Sodium and potassium are determined by flame photometry, using rock standards to obtain the calibration curve.

For the determination of ferrous iron, to 0.5 g of a finely ground sample (finer than -180 mesh), HF and then H_2SO_4 are added and thoroughly mixed in a Teflon beaker. The beaker is then covered with parafilm and heated over a hot plate to 200°C, until a white cloud free of rock powder is formed in the bottom. The beaker is then immersed in a solution of boric and sulphuric acids, and finally the Fe^{2+} is quantified by titration with $KMnO_4$.

The determination of Al_2O_3, CaO, and MgO is performed in the filtered liquid that results from the SiO_2 analysis. For the Al_2O_3 quantification, an aliquot of the filtered solution is heated until boiling, NH_4Cl is added, and the solution is heated again. Next, a 1:1 solution of NH_4OH is added while agitating until no more precipitate is formed. The solution is heated again for 1 minute, taking care that the pH must be kept between 7 and 8, avoiding in this way a further dissolution of the aluminum hydroxide. The precipitate is filtered, maintaining the funnel and the solution over a water bath. Then it is washed with a NH_4NO_3 solution, keeping it wet and controlling the pH as before. The filter with the precipitate is placed in a weighed crucible and heated slowly to 1100°C, then allowed to stand until cool and weighed again. The residue consists of Al_2O_3, Fe_2O_3, TiO_2, and P_2O_5 (Ringbom, 1979).

The MgO determination is made by titration with EDTA; Ca^{2+} and Mg^{2+} are quantified together. Twenty-five millilitres of the solution resulting from the Al_2O_3 determination is passed through activated charcoal to remove the colour, the pH is adjusted to 9.2 with ammonia solution, and titrated using black eryochrome T as indicator.

CaO is determined volumetrically. A solution consisting of NH_3, citric acid, ammonium oxalate, NH_4Cl, urea, and water, is added to an aliquot of the filtered liquid from the SiO_2 determination. This is heated to gentle boiling for an hour. A few drops of NH_3 are then added and the precipitate is filtrated through Millipore membrane filter. The filter with the solid is immersed in an H_2SO_4 solution and the Ca titrated with $KMnO_4$ (Kirschenbaum, 1983; Riley, 1958).

The methods for the analysis of rocks have been tested with geostandard rocks. Table 1 shows some results obtained by other authors and by the Analytical Chemistry Laboratory with the above procedures, in two standard rocks and one sample.

WATER ANALYSIS

Chemical analyses of groundwater are performed by different standard methods.

Sulphates are determined by a modified turbidimetric technique based on APHA (1975), consisting of a precise weighing of the amount of $BaCl_2$, which varies for low and high levels of $SO_4$2-, to increase the reproducibility of the SO_4 quantification by means of a better control of the turbidity. Bicarbonates are measured by titration using a mixture of methyl red and bromocresol green as indicator, and heating the sample at the end of the titration for the displacement of the CO_2 in order to obtain a more accurate end point.

Table 1. Analysis of 2 standard samples (SY-2 and NIM-P) and one rock by the described procedures. Values in per cent.

	SY-2		NIM-P		J 2.2	
Constituent	a	b	a	c	a	d
SiO_2	59.65	60.09	50.98	51.10	55.77	55.49
Al_2O_3	12.22	12.07	4.37	4.18	16.10	15.61
TiO_2	0.15	0.16	0.19	0.20	0.68	0.72
CaO	7.59	7.98	2.53	2.66	7.38	7.94
MgO	2.65	2.69	24.90	25.33	7.79	7.77
MnO	0.34	0.32	0.21	0.22	0.13	0.11
Na_2O	4.20	4.34	0.36	0.37	3.25	3.36
K_2O	4.40	4.47	0.10	0.09	1.28	1.29
P_2O_5	0.43	0.43	0.02	0.02	0.20	0.19
Fe_2O_3	2.33	2.44	0.98	1.02	2.81	1.85*
FeO	3.77	3.60	10.11	10.59	3.78	5.25*
L.O.I.	0.95	-	0.35	-	1.02	1.1

a) Obtained with this methodology
b) Reported by Abbey, 1981
c) Reported by Steele and Hansen, 1979
d) Reported by A. Saunders using XRF at Leicester University, England, 1986
* $Fe_2O_3/FeO = 0.2$

Iron, B, NO_3-, and SiO_2 are determined by colorimetry, with a Carl Zeiss PM2 DL spectrophotometer. Iron is quantified through the formation of the red complex with o-phenanthrolin, and extraction with isopropyl-ether to eliminate the interference due to complex formation. Boron is determined by its reaction with carminic acid in concentrated sulphuric acid which gives a bluish red or blue colour when concentrations over 1 mg/L of B are present. Boron may also be quantified by the potentiometric method adding mannitol to the sample and titrating with NaOH. The chosen method depends on the B concentration in the sample. For the determination of nitrates, the sample is dried, then the remaining solids are treated with phenoldisulphonic acid and neutralized with NH_4OH until a yellow colour is obtained. Silica is determined by the formation of molybdosilicic acid at a pH of 1.1, which when reduced with 1-amino-2-hydroxy-naphtalin-4-sulphonic acid gives a blue colour, that obeys Beer law between 0.05 to 1 mg/L SiO_2 at 790 mm, with an optic path of 1 cm.

Magnesium and calcium concentrations are obtained through the complexometric titration with EDTA. Although the standard technique establishes a fixed amount of NH_4OH for adjusting the pH, when dealing with complex samples it is better to add small amounts of the hydroxide until pH 9.2 is reached, avoiding in this way the formation of ammonia complexes.

Chloride, fluoride, and ammonia are determined potentiometrically with selective electrodes. For the Cl^- quantification, the sample is measured after adjusting the ionic strength. The F^- determination is made in a sample treated with a solution of glacial acetic acid, NaCl, sodium citrate, and NaOH. In this way F is decomplexed and the ionic strength is buffered (Frant and Ross, 1968). Ammonia is measured with a gas sensitive electrode; by increasing the pH with NaOH, the determination of ammonium in this way is also possible. The measurements are made with an Orion Research Ionalyzer 407A.

Na+ and K+ are directly measured with a Perkin Elmer Coleman 51 flame photometer. $LiNO_3$ is added to the standards and the samples as a radiation buffer.

These water analysis methods have been applied to the analysis of a standard sample from the EPA (Table 2).

The second stage of the laboratory development was initiated with the acquisition of an AA spectrophotometer. This equipment was chosen because of its moderate price, the availability of good maintenance services and the simple infrastructure that it requires. According to the Institute priorities, it has been first used for the determination of heavy metals in groundwaters.

The concentrations of Fe, Cu, Cr_{tot}, Zn, and Pb have been determined using AAS. For the determination of Fe, the sample is heated with HCl and HNO_3 before the quantification. The determination of total Cr by AAS is made after the sample has been digested with acids and treated with NH_4Cl in order to avoid interferences from Fe, Ni, Co, and Mg.

Table 2. Analysis of the US EPA standard water sample. Values in ppm.

Constituent	These methods	U.S. EPA 95% confidence level
Calcium	20.19	17.5-22.2
Magnesium	4.89	4.18-5.62
Alkalinity	24.31	21.3-28.0
Sulphate	19.68	16.3-23.1
Chloride	54.00	44.6-57.4
Fluoride	0.97	0.89-1.09
pH	6.00	5.91-6.11

In order to differentiate oxidation states in a direct way, an inexpensive polarograph was purchased. The determination of Cd(II), Ni(II), Pb(II), Zn(II), and Cu(II) is made by DC polarography. The sample is first treated with H_2SO_4, then with HNO_3, and finally neutralized with NH_3. With this treatment, a differentiated curve is obtained for each metal in the following order: Cu, Pb, Cd, Ni, and Zn, using a Sargent Welch 3001 Polarograph. Cr(VI) is determined using NaOH (0.1 M) as the supporting electrolyte. Although the minimum detectable amount is still rather high, approximately 5×10^{-4} M, this method allows the differentiation of oxidation states in a straightforward way.

The next step in the development of the laboratory will be to use AAS for rock analysis, mainly for trace quantification, and to determine Hg and As in waters using the hydride generator.

QUALITY CONTROL

In order to assure and improve the analytical quality, an internal program of control has been developed. The program covers the following aspects: a) adequate purity of the reagents and a thorough cleaning of the labware; b) periodic maintenance of the equipment; c) periodic calibration of the analytical balance; d) microcomputer programs for the calculation of individual determinations; e) ionic balance for each water sample and comparison between measured and calculated total dissolved solids, also using a computer program; f) summation of the major oxides to 100%, g) analysis of international rock standards every ten samples; h) analysis of the EPA mineral water sample; i) interlaboratory comparison of analytical results for the same samples; j) analysis every five samples, of two *in house* reference samples, one made from a basalt that outcrops at the UNAM, and other from a rhyolite that outcrops in San Luis Potosí.

CONCLUSIONS

The philosophy of the laboratory involves the idea that every sample must be analyzed according to its specificity, trying as much as possible to substitute the lack of expensive equipment with methodology based on sound chemical principles. Every method must be understood, so its application is made with the knowledge of the objectives of every step of the analysis. In this way it is possible to prevent the errors that may result from a blind application of the methodology, without taking into account other species that may react with the analyte, colour, turbidity, formation of nondesirable products during the analysis, etc.

With the above described procedures, adequate results have been obtained in various geochemical studies. For instance, in the contamination study of groundwaters of San Luis Potosí; in the geochemical monitoring of active volcanoes like the Tacaná and Colima; and in tectonic and petrogenetic studies, such as the research concerning the formation of the Chapala lake, and the genesis of the isla Isabel Nayarit (De la Cruz-Reyna et al., 1989; Cabral-Cano et al., in press; Carrillo and Armienta, 1989).

ACKNOWLEDGMENTS

The authors thank Mrs. Selma Campos for the drawing.

REFERENCES

Abbey, S.
1981: The search for "best values", a study of three Canadian rocks; Geostandards Newsletter, v. 5, p. 13-26.
APHA (American Public Health Association)
1975: Standard methods for the examination of water and wastewater; American Public Health Association, 874 p.
Cabral-Cano, E., Armienta-Hernández, M.A., and Urrutia-Fucugauchi, J.
in press: Reconocimiento Geológico y Paleomagnético en la Isla Isabel, Nayarit, México; Geofísica.
Carrillo, J.J. and Armienta, M.A.
1989: Diferenciación de la Contaminación Inorgánica en las Aguas Subterráneas del Valle de la Ciudad de San Luis Potosí, S.L.P., México; Geofísica Internacional, v. 28-4, p. 763-783.
De la Cruz-Reyna S., Armienta, M.A., Zamora, V., and Juárez, F.
1989: Chemical changes in spring waters at Tacaná volcano, Chiapas, Mexico: a possible precursor of the May 1986 seismic crisis and phreatic explosion; Journal of Volcanology and Geothermal Research, v. 38, p. 345-353.
Energlyn, T.L. and Brealey, L.
1971: Analytical use of the beryllium fluoride complex; Analytical Chemistry, v. 23, p. 351-353.
Frant, M.S. and Ross, J.W., Jr.
1968: Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water supplies; Analytical Chemistry, v. 40, p. 1169-1171.
Hillebrand, W.F. and Lundell, G.E.F.
1953: Applied inorganic analysis; John Wiley, 1034 p.
Kirschenbaum, H.
1983: The classical chemical analysis of silicate rocks – the old and the new; United States Geological Survey, Bulletin 1547.
Obregón, A.P.
1973: Métodos de Análisis Químico de Rocas y Materiales Similares; Instituto de Geología UNAM, 52 p.
Riley, J.P.
1958: The rapid analysis of silicate rocks and minerals; Analytica Chimica Acta, v. 19, p. 413-428.
Ringbom, A.
1979: Formación de Complejos en Química Analítica; Alhambra, 458 p.
Sandell, E.B.
1959: Colorimetric determination of traces of metals; Interscience, 1032 p.
Steele, T.W. and Hansen, R.G.
1979: Major element data (1966-1978) for the six "Nimroc" reference samples; Geostandards Newsletter, v. 3, p. 135-172.
Vogel, A.I.
1960: Química Analítica Cuantitativa; Kapelusz, v. 1, 812 p.

A new catalytic polarographic system for the determination of trace amounts of tungsten and its application in geoanalysis

Dezhong Dan[1] and Jun Re[1]

Abstract: A new catalytic polarographic system for the determination of trace amounts of tungsten is described. It is found that tungsten-MBT (2-mercaptobenzothiazole) gives a sensitive catalytic hydrogen wave at -1.10 V (vs. SCE) in strongly acid medium. The linear relationship occurs between peak height and tungsten concentration over the range of 0.004-1.4 μ g/mL W in a solution of 0.9 M H_2SO_4- 2% NaCl-0.01 μ g/mL MBT. The influence of foreign ions on the wave has been examined. The experiments show that the method is rapid, simple, sensitive, and has a wide linear range. The method is suitable for the analysis of samples in a wide variety of matrices, and has been applied to determining trace amounts of tungsten in six Chinese stream-sediment reference standard materials with satisfactory results without any separation. The relative error found is from 3.7% to 13.7%. The properties of the catalytic polarographic wave have been investigated.

Résumé : Dans cet exposé, on décrit un nouveau système polarographique catalytique permettant de doser des traces de tungstène. On constate que le tungstène MBT (2-mercaptobenzothiazole) donne une onde hydrogène catalytique sensible à -1,10 V (vs. électrode standard au calomel, SCE) dans un milieu fortement acide. La relation linéaire se manifeste entre le pic et la concentration du tungstène dans la gamme de 0,004 à 1,4 μ g/ml W dans une solution 0,9 M de H_2SO_4 - 2 % de NaCl - 0,01 μ g/ml de MBT. On a étudié l'influence d'ions étrangers sur l'onde. Les expériences montrent que la méthode est rapide, simple, sensible et a une vaste application linéaire. Elle convient à l'analyse d'échantillons dans une grande variété de matrices et a été appliquée avec des résultats satisfaisants au dosage de traces de tungstène dans six étalons de référence composés de sédiments fluviatiles originaires de Chine, sans qu'il ait été nécessaire de procéder à une séparation. L'erreur relative trouvée se situe entre 3,7 % et 13,7 %. On a étudié les propriétés de l'onde polarographique catalytique.

---

[1] Department of Applied Chemistry, Chengdu College of Geology, Chengdu, Sichuan 610059, P.R. China.

INTRODUCTION

The determination of W by catalytic polarography was first described by Deng (1963) and since then several catalytic polarographic systems have been used widely in many laboratories in China and become a reliable routine analytical technique (Shu, 1984).

This paper describes a new catalytic polarographic method for the determination of W. We found 2-mercaptobenzothiazole (MBT) to be an excellent reagent for the determination of W by linear sweep polarography (LSP). Toropova et al. (1977) reported on the polarographic behaviour of MBT in strongly acid medium. It can give a sensitive and well-defined catalytic hydrogen wave in a solution of 0.9 M H_2SO_4-2% NaCl. The peak height is enhanced by addition of trace amounts of W. MBT can be used for the determination of W by LSP with good analytical results. The influence of various factors on the catalytic wave, the interference of foreign ions with the wave and the characteristics of the wave have been investigated in this paper. Any interference is eliminated by fuming with sulphuric acid. The procedure has been successfully used for the determination of W in geochemical reference standard materials.

EXPERIMENTAL

Reagents

All the chemicals used were of analytical-reagent grade.

MBT: AR grade (The Third Reagent Factory of Shanghai), 100 µ g/mL without further purification.

Tungsten stock solution: 2 mg/mL W. Weigh out 3.5885 g $Na_2WO_4 \cdot 2H_2O$, dissolve with de-ionized water, add about 50 mg NaOH, and dilute to 1000 mL with de-ionized water. Working solutions were prepared from the W stock solution.

Apparatus

A Model JP-1A oscillopolarograph (Chengu Instrumental Factory, China) was used. For derivative polarography the typical parameters employed were: drop time 7 s scan rate 250 mV/sec, scan range from -0.8 V to -1.3 V, mercury head 55 cm, and mercury flow rate 0.5 mg/sec. The three electrode system comprised a dropping mercury electrode (DME), platinum counter-electrode, and saturated calomel electrode (SCE) as reference. All potentials were referred to the SCE. The electrolytic cell was a 10 mL beaker.

Procedures

To the W standard solution in a 25 mL test tube, add 2.5 mL of H_2SO_4 (1+1), 2.5 mL of 20% NaCl, 0.25 mL of 1 µ g/mL MBT solution in turn, dilute to volume with de-ionized water, and let stand for about 30 min. Record the derivative linear sweep polarogram from -0.8 V to -1.3 V (vs. SCE). The polarogram of W-MBT is shown in Figure 1.

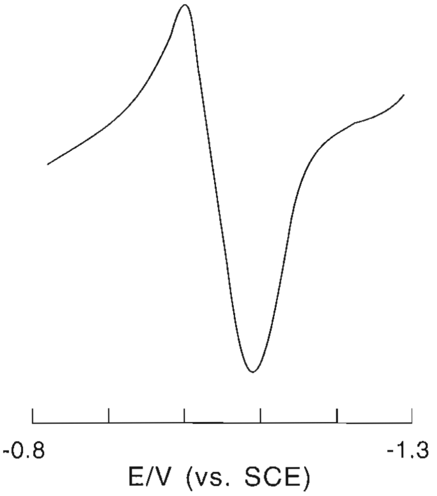


Figure 1. Derivative polarogram. System: 0.9 M H_2SO_4 – 2% NaCl – 0.01 µ g/mL MBT – 0.5 ug W.

Analysis

Weigh 0.1000-0.2500 g of sample or geochemical standard into a 50 mL crucible, add 10 mL of hydrochloric acid, and heat gently on hot-plate. Add 3 mL of nitric acid, 5 mL of hydrofluoric acid, 2 mL of perchloric acid, and heat continuously. Evaporate the solution to dryness until no more fumes are evolved. Cool, add 1 mL of hydrochloric acid (1+1) to dissolve the moist residue, then transfer to a 25 mL beaker. Wash the crucible wall with de-ionized water. Add 2 mL of sulphuric acid (1+1), heat the solution until the yellow colour disappears, transfer the solution to a 25 mL standard flask and dilute to volume with 5% sodium hydroxide. Allow the solution to clear. Take a 10 mL aliquot of the transparent solution into a 25 mL test tube, add various reagents in accordance with the procedure described previously and dilute to known volume. Stand for half an hour prior to determination.

Calibration graph

Add 2 mL of sulphuric acid (1+1) to a W standard solution (to cover the concentration range 0.004-1.4 µ g/mL). Evaporate the solution to fuming for 2 minutes. Cool, dilute to the volume of 25 mL with 5% sodium hydroxide solution and mix. Take a 10 mL aliquot of solution into a 25 mL test tube and add 3.2 mL H_2SO_4 (1+1). Proceed with the analysis as described above.

RESULTS AND DISCUSSION

Optimum conditions for the catalytic system

Tungsten gives a sensitive catalytic wave at about -1.10 V (vs. SCE) in MBT of acidic medium by LSP. The following acids were examined: sulphuric, hydrochloric, phosphoric, and perchloric. The peak potentials vary with acid species. A well-defined peak was obtained in sulphuric acid; furthermore, the peak height was stable in 0.9 M to 2 M H_2SO_4 solution. The peak's shape changes at higher pH and the wave disappears at pH>5.

If there was not enough supporting electrolyte, it would be difficult to obtain a stable catalytic wave. For practical purposes, KCl, NaCl, and NH_4Cl solutions were used, and of these, NaCl was preferred because the sensitivity of wave was reasonably high and the height did not change over the 2% to 10% NaCl (Fig. 2).

MBT can give a background current increasing with concentration. Figure 3 compares the current generated by W and that due to the background. The experiment showed 0.01 μ g/mL MBT was appropriate to obtain reasonable sensitivity and a small background, together with a wide linear range for W. To sum up, the optimum composition of catalytic system was found to be 0.9 M H_2SO_4, 2% NaCl, and 0.01 μ g/mL MBT.

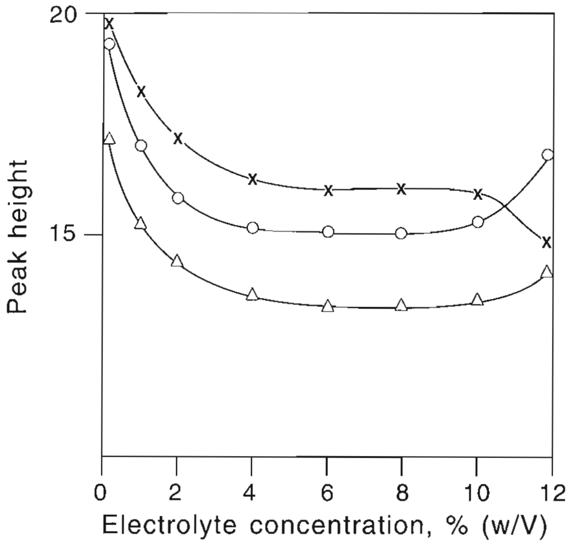


Figure 2. Effect of supporting electrolytes on the peak height. System: 0.9 M H_2SO_4 – 0.01 μ g/mL MBT – 0.5 μ g W. Electrolyte: o NaCl Δ KCl x NH_4Cl.

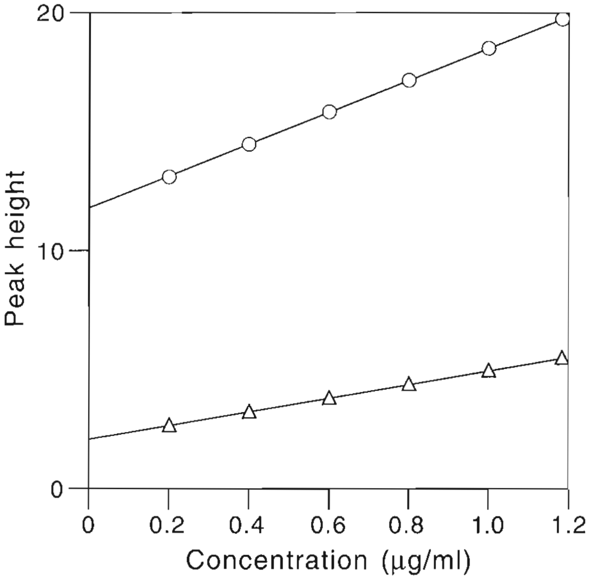


Figure 3. Comparison between W current and MBT background. System: o 0.9 M H_2SO_4 – 2% NaCl – 0.01 μ g/mL MBT – W ($X10^{-1}$). Background: Δ 0.9 M H_2SO_4 – 2% NaCl – MBT ($X10^{-2}$).

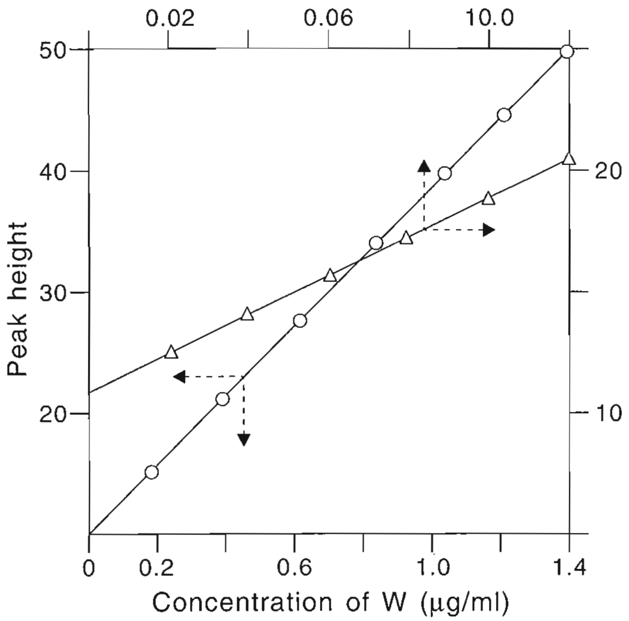


Figure 4. Calibration graphs from 0.02 to 1.4 μ g/mL W.

Effect of standing time

For the prepared solutions, the peak height decreased slightly within half an hour, and remained unchanged for one day.

Peak height as a function of concentration

The dependence of the current on concentration is shown in Figure 4. A linear relationship occurs between peak height and W concentration over the range of 0.004-1.4 μ g/mL.

Study of the characteristics of the catalytic wave

The peak height changes with temperature (T) over the range 5°C to 55°C (Fig. 5). The temperature coefficient is positive (about 7.1%/1°C) at T<30°C and negative (about -6%/1°C) at T>40°C. The peak height is constant over the range 30°C to 40°C. The behaviour for the background current is similar to that of the W catalytic wave.

The effects of anionic, cationic, and non-ionic surfactants on peak current were examined. The peak height was not affected by the presence of 0.1% KI. It was found that the peak height was considerably decreased by the addition of 1-2 drops of surfactants such as sodium lauryl sulphate (0.1%), gelatin (0.1%), tetrabutyl ammonium iodide (0.01%), Triton X-100 (0.01%) into the medium used. The peak height was increased greatly by the presence of 0.01% polyvinylalcohol (PVA). The mechanism for the enhancement effect of PVA was not clear.

The effect of mercury pressure on the wave was also investigated. The peak height was proportional to the height of mercury head.

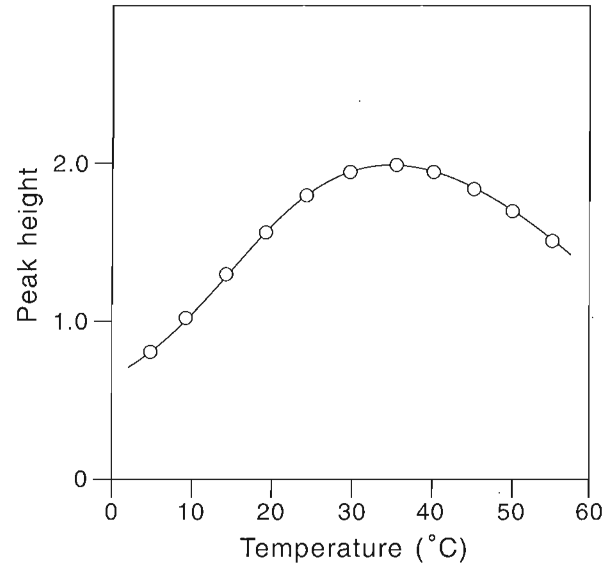


Figure 5. Effect of temperature on peak height. System: 0.9 M H_2SO_4 – 2% NaCl – 0.01 μ g/mL MBT – 0.5 μ g/mL W.

Table 1. The effect of foreign ions

Ions (X)	Maximum concentration ratio tolerated X/W
alkali metals and alkali-earth metals	no interference
Fe^{3+}, Cu^{2+}, Bi^{3+}, Sb^{3+}, Ga^{3+}, Cd^{2+}, Pt^{4+}	500-800
Co^{2+}, Ti^{4+}, Os^{8+}, Ta^{5+}, Mo^{6+}, Se^{4+}, Ag^{+}, Ni^{2+}, Zn^{2+}	40-80
V^{5+}, Te^{4+}, In^{3+}, Ge^{4+}, Mn^{2+}, Hg^{2+}	1-5
As^{3+}, Ru^{3+}, Rh^{3+}, Au^{3+}, Pb^{2+}, Cr^{3+}	interfere seriously

Table 2. Determination of W in six Chinese stream-sediment reference standard materials (in ppm)

Sample	Recommended value	This method (mean n=3)	Relative error (%)
GSD-2	24.4 ± 2.7	23.5	3.7
GSD-3	2.9 ± 0.7	3.3	13.7
GSD-4	2.5 ± 0.8	2.3	8
GSD-5	3.2 ± 0.6	3.4	6.2
GSD-6	25 ± 3	26	4
GSD-8	1.95 ± 0.44	1.78	8.7

The above experimental results indicated that the catalytic wave had evident adsorption characteristics. Hydrogen bubbles can be observed at the surface of the dropping mercury electrode, if large amounts of MBT or W were present in the system. It was clear that the catalytic current was due to the catalytic discharge of H^+ ions. On the basis of these observations, it may be deduced that MBT can yield a hydrogen catalytic wave. The effect of catalysis would be enhanced by addition of W.

The effect of foreign ions

Under the experimental conditions, more than 40 ions were examined for possible interference in the determina-tion of W by LSP. The experimental results showed that the system had good selectivity (Table 1). Most common metal ions had little effect. Only As^{3+}, Ru^{3+}, Au^{3+}, Pb^{2+}, and Cr^{3+} interfered seriously; some ions caused the shape of the wave to change while other ions made the wave split. It was interesting that all interferences were found to be negative. Anions did not interfere in the determination of W, with the exception of NO_3^-. Prior separation was unnecessary because the sample preparation procedure eliminates interference.

Results of sample analysis

Six Chinese stream-sediment reference standard materials (GSD-2 to GSD-8) were analyzed by this method. These samples have been used throughout China as primary-control standards for the trace-element analysis of geological exploration samples. They are well homogenized and have a particle size of less than 200 mesh. The results of this study are compared with the "recommended values" by Chinese laboratories, using about 20 independent analytical techniques (Chinese Academy of Metrology, unpub. report, 1985). The results are listed in Table 2. It is clear that the proposed procedure is acceptable for geoanalysis.

ACKNOWLEDGMENTS

We are grateful of Mr. Peifan Xu for his help with the experimental work.

REFERENCES

Chinese Academy of Metrology
1985: Catalogue on standard materials of People's Republic of China.
Deng, J.
1963: Catalytic polarographic analysis of ultra amount tungsten; Huaxue Shijie, v. 17, p. 565-566.
Shu, B.
1984: Catalytic polarographic determination of trace amount of tungsten; Fenxi Huaxue, v. 12, p. 331-334.
Toropova, V.F., Budnikov, G.K., Medyantseva, E.P., and Frolova, V.P.
1977: Study of catalytic hydrogen currents in 2-mercaptobenzothiazole solution in the presence of cobalt (II) ions; Zhurnal Obshchei Khimii, v. 47, p. 154-156.

Determination of fourteen major and minor elements in different geological materials by X-ray fluorescence

Li Guohui[1]

Abstract: An X-ray fluorescence (XRF) method has been developed for the determination of Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe, Ba, Sr, Rb, and Zn in different geological materials including silicates, carbonates, iron ores, clays, bauxites, and peridotites, using a series of geological reference materials and fusion. The interelement effect is corrected by using the theoretical alpha coefficient and Rh Ka line Compton scattered radiation as internal standard. The precision and accuracy obtained are excellent.

Résumé : On a élaboré une méthode basée sur la fluorescence X pour doser certains éléments (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe, Ba, Sr, Rb et Zn) dans divers matériaux géologiques, notamment des silicates, des carbonates, des minerais de fer, des argiles, des bauxites et des péridotites, en employant une série de matériaux géologiques de référence et le procédé de fusion. On corrige l'effet interélément au moyen du coefficient alpha théorique en utilisant comme étalon interne la diffusion Compton sur la ligne Rh Ka. La précision et l'exactitude des résultats obtenus sont excellentes.

---

[1] Institute of Geophysical and Geochemical Exploration, Ministry of Geology and Mineral Resources, Langfang, Hebei 102849, P.R. China.

INTRODUCTION

The high productivity and excellent accuracy and precision obtained for the determination of major and minor elements by XRF have established it as a reliable and commonly used method in the analysis of silicate rocks (Lee and McConchie, 1982; Raschka et al., 1982; Diao et al., 1983; Li et al., 1986; Xu et al., 1986; Ji et al., 1986). However, the existing method does not sufficiently meet the demand of analysis of a large variety of geological materials of different composition and with a wider range of element content. In this paper, I present a new method based upon XRF for the determination of 14 elements, namely Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe, Sr, Rb, Zn, and Ba, in various kinds of geological materials, such as silicates, carbonates, iron ores, clays, bauxites, and peridotites.

THE FUSION UNIT

In our laboratory, the fusion unit AAG-50 from Germany (Richard Schoeps KG, GmbH & Co.) is used. During operation, some small fusion beads can easily adhere to the upper wall of the Pt-Au alloy (95% Pt, 5% Au) crucible; the percentage of material lost to the walls is dependent upon the sample matrix. It is difficult to shake the beads into the molten mass. This limitation can be overcome by modification of the fusion unit, the AAG-50. An electromagnetic valve has been installed on the air tube controlling the crucible holder, together with a slant-range-altitude switch on the operating panel for control. When the supply power is off, the electromagnetic valve is closed, the gas tube is shut and the crucible holder is closed. When the supply power is on, compressed air is released from the gas tube through the electromagnetic valve and the crucible holder moves toward both sides, making it possible to remove the crucible. The molten mass is then swirled throughout the crucible, thus gathering the separated beads near the top of the wall.

PREPARATION OF THE GLASS DISC

Lithium tetraborate is used as flux, lithium nitrate as oxidizing agent, and a small amount of lithium bromate to increase the liquidity of the molten substance.

The process of preparation of the glass disc is as follows:

- Dry the -200 mesh sample and lithium tetraborate in oven at 105°C.
- Weigh 0.7000 g of sample and 5.600 g of lithium tetraborate int the Pt-Au alloy crucible; mix the sample and flux carefully with a glass rod.
- Add a solution containing of 25 mg of lithium bromate and 300 mg of lithium nitrate per millilitre of water, and dry the contents in an oven.
- Put the crucible on the AAG-50 fusion unit. Use liquified petroleum gas as fuel and oxygen to support combustion. Adjust the flame temperature to 1200-1250°C. Put the crucible lid on and prefuse 2.4 for min. Remove the lid and swirl the contents over the flame. Replace the crucible on the fusion unit and fuse for 8 min. (the crucible is under constant agitation).

Pour the high temperature molten substance into the Pt-Au casting mould previously heated to 800°C. After cooling, the glass disc can be released easily from the mould. Label these discs and put them into a desiccator to await analysis.

REFERENCE MATERIALS

A large number of reference materials should be used to develop an analytical procedure feasible for a variety of geological samples with different composition. The consultation ranges of the set of reference materials should be wide enough for all the elements to be determined, and the content intervals for each element among the reference materials should be more or less uniform. Fifty-five standards were used in this study, including the series GSD 1-12, GSR 1-12, GSS 1-8 and other international reference materials. The range of elemental contents in the reference materials are shown in Table 1.

CORRECTION FOR INSTRUMENTAL DRIFT

Standardization is needed to correct for instrumental drift; a control sample performs this function. The intensity of the analytical line of the element to be determined in the control is given as Is and is stored on a computer disk. The intensities of the analytical line of the elements to be determined in the reference materials are used to construct the calibration curve. When analyzing an unknown sample, the control is also analyzed. The intensity of the analytical line of the element to be measured in the control is Im, and the intensity calibration coefficients α =Is/Im. The intensity of the unknown sample is multiplied by the calibration coefficient α, giving the calibrated intensity.

It can be seen that the control must contain all the elements to be determined, as well as all the interfering elements. Each element in the control should be present at sufficient concentration to minimize the counting errors. Further, the

Table 1. Concentration ranges in the reference materials

Oxide	Range, %	Oxide	Range, %
Na_2O	0.081 - 13.38	TiO_2	0.005 - 7.000
MgO	0.08 - 45.74	MnO	0.062 - 2.250
Al_2O_3	0.08 - 70.00	Fe_2O_3	0.09 - 70.00
SiO_2	1.00 - 96.00	SrO	0.001 - 0.140
P_2O_3	0.005 - 0.460	Rb_2O	0.005 - 0.360
K_2O	0.01 - 12.81	BaO	0.005 - 0.400
CaO	0.04 - 68.00	ZnO	0.0015 - 0.130

physical and chemical properties of the control must be stable. The composition of the control, prepared from synthetic reagents, is given in Table 2.

INSTRUMENT AND OPERATING CONDITIONS

A Rigaku Model 3080 E2 XRF spectrometer equipped with an end window Rh-target X-ray tube, an automatic sample exchanger with 24 positions, M243 computer, DF-151A software, and fusion unit AAG-50 (Richard Schoeps KG, GmbH & Co.) were used.

Table 2. Composition of the control sample

Oxide	Concentration, %	Oxide	Concentration, %
Na_2O	10.00	TiO_2	2.00
MgO	10.00	MnO	0.50
Al_2O_3	15.00	Fe_2O_3	6.00
SiO_2	42.00	BaO	0.50
P_2O_5	0.50	SrO	0.20
K_2O	5.00	Rb_2O	0.20
CaO	7.00	ZnO	0.20

The elements determined by the method have a wide concentration range (e.g., SiO_2: 1-96%). In order to obtain not only a high counting rate and good peak-to-background ratio for elements present at ion levels, but also to achieve good accuracy for the major constituents, the measurement conditions for each element have been carefully selected. Table 3 lists the operations used.

MATRIX EFFECT CORRECTION

Although samples were fused with lithium tetraborate to eliminate particle and heterogeneity effects, matrix effects still remained. The interelement effects were corrected for using the theoretical alpha coefficients. These equations of DATAFLEX-151A software (Rigaku Industrial Corporation, Japan, 1984) were applied:

$$x_i = a_k I_i 2 + b_k I_i + c_k \text{ (or } b_k I_i + c_k) \qquad (1)$$

where x_i is calibration curve calculation standard value (chemical analysis value or presumed reference value $x_i = w_i/(1 + K + \Sigma A_i F_{i\,j}))$;

I_i is the X-ray intensity (or internal standard ratio value);

a_k, b_k, c_k are calibration curve constants (the letter "k" corresponds to the calibration curve No. L, M, H in the calibration curve selection);

$$W_i = x_i (1 + K + \Sigma A_j F_{ij}) + \Sigma \beta_j F_{ij} + \Sigma D_j k F_{ij} F_i k + c \qquad (2)$$

where W_i is the matrix calculation standard value (chemical analysis value);

Table 3. Operative conditions

Spectral line	Crystal	2θ angle		Counting time(s)		Detector	Pulse height analyzer	Overlap spectral	Detection limit (% oxide)
		Spectral line	Background	Spectral line	Background				
NaKα	TLAP	55.165	58.50	100	40	F-PC	7-35		0.0332
MgKα	TLAP	48.275	48.00	100	40	F-PC	7-35		0.046
AlKα	PET	144.67	140.00	40	40	F-PC	7-35		0.0062
SiKα	RX4	144.67	140.00	40	20	F-PC	7-35		0.01
P Kα	GE	141.15	144.00	20	10	F-PC	10-35		0.0044
K Kα	PET	50.65	54.00	20	10	F-PC	7-35		0.01
CaKα	LIF200	113.28	110.00	40	20	F-PC	10-35		0.0058
TiKα	LIF200	86.25	88.50	40	20	F-PC	10-30		0.0030
MnKα	LIF200	63.00	64.50	20	10	F-PC	10-35		0.0012
FeKα	LIF200	57.54	55.00	40	10	SC	7-35		0.0061
SrKα	LIF200	25.13	24.00	40	20	SC	7-35		0.0005
RbKα	LIF200	26.59	29.70	40	20	SC	7-35		0.0010
BaLα 1	LIF200	87.22	88.00	40	20	F-PC	10-30	TiKa	0.0023
ZnKα	LIF200	41.79	42.79	40	20	SC	7-35		0.0005
RhKαc	LIF200	18.84		20		SC	7-35		

*Path-vacuum; Collimator-coarse; Applied voltage and current to X-ray tube: 50kV, 50mA

Table 4. Alpha coefficients of eliminated loss ignition (LOI)

Analyte	matrix constituents									
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
Na_2O	0.066	0.086	0.100	0.111	0.119	0.142	0.163	0.201	0.304	0.321
MgO	0.309	0.099	0.107	0.119	0.127	0.145	0.166	0.204	0.309	0.326
Al_2O_3	0.310	0.347	0.125	0.128	0.137	0.148	0.167	0.206	0.313	0.330
SiO_2	0.311	0.349	0.386	0.154	0.153	0.148	0.170	0.208	0.316	0.333
P_2O_5	0.313	0.351	0.387	0.422	0.189	0.151	0.172	0.209	0.320	0.338
K_2O	0.310	0.349	0.388	0.424	0.476	0.295	0.170	0.183	0.260	0.278
CaO	0.313	0.352	0.391	0.423	0.480	1.400	0.328	0.202	0.268	0.383
TiO_2	0.311	0.350	0.391	0.429	0.480	1.414	1.393	0.403	0.264	0.272
MnO	0.304	0.343	0.384	0.422	0.475	1.421	1.402	1.515	0.699	0.605
Fe_2O_3	0.309	0.347	0.389	0.428	0.481	1.433	1.416	1.531	0.709	0.725

fused disc : 0.7000 g sample +5.600 g $Li_2B_4O_7$
target : Rh, 50kv
geometry : 63,40 degree

Table 5. Results of 10 separate analyses of GSR 2

Oxide	Average value of determination (n=10), %	Standard deviation, %	Coefficient of variation, %
Na_2O	3.97	0.033	0.83
MgO	1.69	0.016	0.94
Al_2O_3	16.23	0.052	0.32
SiO_2	60.73	0.147	0.24
P_2O_5	0.2360	0.0027	1.12
K_2O	1.85	0.032	1.70
CaO	5.20	0.008	0.16
TiO_2	0.5148	0.0029	0.57
MnO	0.0723	0.0011	1.55
Fe_2O_3	4.87	0.009	0.19
SrO	0.0942	0.0003	0.28
ZnO	0.0082	0.0003	3.07
Rb_2O	0.0063	0.0008	12.4
BaO	0.1010	0.0101	10.0

X_i is the uncorrected quantitative analysis value;

F_{ij}, F_{jk} are intensities of coexisting elements (j, k);

K, A, B, D, C are matrix correction constants.

The theoretical alpha (i.e., A_j in the equation (2) is calculated by using X-ray tube spectrum distribution and other parameters (Lachance, 1979; Rousseau, 1984) and then is transformed into the alpha coefficient of eliminated loss on ignition (LOI) through equation (3) (Hua, 1984; see Table 4).

$$\alpha^{LOI}_{ij} = (\alpha^{i}_{ij} - \alpha^{i}_{iLOI})/(1 + \alpha^{i}_{iLOI}) \qquad (3)$$

where α^{LOI}_{ij} is the alpha coefficient of element j of eliminated LOI to element i;

α^{i}_{ij} is the alpha coefficient of element j of eliminated LOI to element i;

α^{i}_{iLOI} is the alpha coefficient of element i of eliminated LOI to element i.

DETECTION LIMIT, PRECISION, AND ACCURACY

Detection limit (DL) for each element is calculated by equation (4):

$$DL = 3/2 \cdot \frac{\sqrt{I_b}}{M \sqrt{T}} \qquad (4)$$

where M is the count rate for unit concentration;

I_b is the background count rate;

T is the total count rate.

The results are listed in Table 3.

Ten glass discs from the sample GSR 2 were prepared and measured using the operating conditions in Table 3. The standard deviation and coefficient of variation obtained are given in Table 5, where it can be seen that this method achieves excellent precision. The accuracy of this method was studied by analyzing standard reference materials from different sources. The analytical results are listed in Tables 6 and 7. It is evident that the results of this method are in good agreement with the certified values of these standard reference materials.

Table 6. Results for standard reference materials by the proposed XRF method, with comparison to recommended values. All data in per cent.

	DT-N[c]		STM-1[d]		FK-N[c]		SY-2[e]		JG-1[f]		GXR-1[d]	
	a	b	a	b	a	b	a	b	a	b	a	b
Na_2O	0.16	0.04	9.30	8.95	2.68	2.58	4.35	4.34	3.50	3.39	0.18	0.11
MgO	0.06	0.04	0.08	0.10		0.01	2.62	2.70	0.71	0.74	0.49	0.36
Al_2O_3	58.76	59.20	18.32	18.44	18.66	18.61	11.93	12.12	14.10	14.20	6.74	6.81
SiO_2	37.17	36.45	59.34	59.66	65.34	65.02	59.63	60.10	72.23	72.30	48.85	48.61
P_2O_5	0.072	0.09	0.16	0.16	0.01	0.02	0.43	0.43	0.093	0.097	0.149	0.141
K_2O	0.13	0.12	4.25	4.25	13.08	12.81	4.44	4.48	3.95	3.95	0.05	0.06
CaO	0.06	0.04	1.11	1.09	0.14	0.11	7.79	7.98	2.15	2.18	1.26	1.24
TiO_2	1.35	1.40	0.14	0.13	0.02	0.02	0.14	0.14	0.27	0.26	0.06	0.06
MnO	0.006	0.003	0.22	0.22			0.32	0.32	0.061	0.063	0.12	0.11
Fe_2O_3	0.60	0.66	5.21	5.20	0.10	0.09	6.26	6.28	2.09	2.14	36.16	35.71
SrO	0.0035		0.0815	0.0828	0.0044	0.0046	0.0310	0.0325	0.0210	0.0218	0.0295	0.0319
Rb_2O	0.0025		0.0131	0.0136			0.0241	0.0246	0.0198	0.0201	0.0047	
ZnO	0.0033		0.0299	0.0250			0.0311	0.0245	0.0045	0.0051	0.078	0.087
BaO	0.0231		0.0558	0.0625			0.0400	0.0514	0.0435	0.0516	0.073	0.068

c: Association Nationale de la Recherche Technique
d: United States Geological Survey
e: Canadian Certified Reference Materials Project
f: Geological Survey of Japan
a: determined value b: certified values

Table 7. Results for standard reference materials by the proposed XRF method, with comparison to recommended values. All data in per cent.

	GSR-1[c]		GSR-2[c]		GSR-3[c]		GSR-4[c]		GSR-5[c]		GSR-6[c]	
	a	b	a	b	a	b	a	b	a	b	a	b
Na_2O	2.89	3.13	3.93	3.86	3.31	3.38	0.03	0.061	0.25	0.35	0.15	(0.081)
MgO	0.41	0.42	1.69	1.72	7.85	7.77	0.10	0.082	2.01	2.01	5.42	5.19
Al_2O_3	13.30	13.40	16.21	16.17	13.73	13.83	3.35	3.52	18.96	18.82	5.08	5.03
SiO_2	72.68	72.83	60.71	60.62	44.52	44.64	90.50	90.36	59.58	59.23	15.78	15.60
P_2O_6	0.086	0.093	0.24	0.23	0.95	0.95	0.22	0.22	0.16	0.16	0.054	0.052
K_2O	4.97	5.01	1.85	1.89	2.29	2.32	0.65	0.65	4.31	4.16	0.78	0.78
CaO	1.57	1.55	5.18	5.20	8.84	8.81	0.28	0.30	0.60	0.60	35.93	35.67
TiO_2	0.29	0.29	0.52	0.52	2.32	2.36	0.27	0.26	0.66	0.66	0.33	0.33
MnO	0.052	0.06	0.07	0.08	0.16	0.17	0.022	0.022	0.015	0.02	0.05	0.06
Fe_2O_3	2.09	2.04	4.87	4.90	13.31	13.40	3.23	3.22	7.68	7.60	2.42	2.52
SrO	0.0127	0.0127	0.0943	0.0922	0.125	0.1289	0.0067	0.0067	0.0108	0.0106	0.1099	0.1064
Rb_2O	0.515	0.0514	0.0064	0.0042	0.0037	0.0039	0.0041	0.0032	0.0221	0.0235	0.0035	0.0041
ZnO	0.0030	0.0027	0.0072	0.0072	0.0150	0.0148	0.0017	0.0020	0.0061	0.0054	0.0050	0.0052
BaO	0.0338	0.0368	0.1019	0.1139	0.0637	0.0581	0.0120	0.0161	0.047	0.0502	0.0100	0.0133

c: Institute of Geophysical and Geochemical Exploration, People's Republic of China
a: determined values b: certified values

CONCLUSION

An XRF spectrometric method has been developed for the determination of Si, Al, Fe, Ca, Mg, Na, P, Mn, Ti, K, Ba, Sr, Rb and Zn in a variety of geological materials with different composition, including silicates, carbonatites, iron ores, clay, bauxite, peridotites, etc. The precision and accuracy achieved with this efficient method have been shown to be good.

REFERENCES

Diao, G.N., Cheng, P.T., Li, J.Z., and Liu, Z.M.
1983: Calculation of theoretical alpha coefficients in X-Ray fluorescence spectrometry and its application to analysis of silicate rock; Analytical Chemistry (in Chinese), v. 1, p. 45-48.
Hua, Y.N.
1984: Transformation of theoretical alpha coefficients in X-Ray fluorescence spectrometry; Analytical Chemistry (in Chinese), v. 12, p. 258-265.
Ji, A., Tao, GY., Shen, M.F., and Yuan, N.E.
1986: A new attempt for combination of fundamental parameter method and empirical influence coefficient method; Spectroscopy and Spectral Analysis (in Chinese), v. 3(1), p. 38-42.
Lachance, G.R.
1979: The family of alpha coefficients in X-Ray fluorescence analysis; X-ray Spectrometry, v. 8, p. 190-195.
Lee, R.F. and McConchie, D.R.
1982: Comprehensive major and trace element analysis of geological material by X-ray fluorescence using low dilution fusion; X-Ray Spectrometry, v. 11, p. 55-63.
Li, G.H., Liu, D.H., and Su, Y.L.
1986: X-Ray fluorescence quantitative determination of Fe, Mn, Ti, Ca, P, Si, Al, Mg, S, Sr, Rb and Ba in silicates; Geophysical and Geochemical Exploration (in Chinese), v. 10, p. 60-65.
Raschka, H., Lodziak, J., Li, G.H., Liang, D.A., and Zhang, B.Y.
1982: Determination of Fe, Mn, Ti, Ca, K, S, P, Si, Al, Mg and Na in silicates by X-Ray spectrometry; Analytical Chemistry (in Chinese), v. 10, p. 609-611.
Rigaku Industrial Corporation
1984: DATAFLEX-151A, data processing operating manual.
Rousseau, R.M.
1984: Fundamental algorithm between concentration and intensity in XRF analysis; X-ray Spectrometry, v. 13(3), p. 115-125.
Xu, J.R., Wu, Z.H., Li, C., and Li, Q.H.
1986: XRF determination of 30 major and trace elements in silicate samples by fusion method; Rock and Mineral Analysis (in Chinese), v. 5(3), p. 201-206.

An expeditious wet chemical analysis of silicate rocks

M. Huka[1] and I. Rubeska[1]

Abstract: A procedure for silicate rock analysis after acid decomposition is described. Using a special PTFE vessel assembly, the SiF_4 evolved during decomposition is sorbed on KNO_3 as K_2SiF_6. After hydrolysis, the HF is titrated with NaOH to determine the SiO_2 content in the sample. The sample residue after acid decomposition is dissolved and used for the determination of the remaining elements by chelatometry, spectrophotometry, and AAS.

Résumé : Dans cet exposé, on décrit un procédé d'analyse des roches silicatées après leur décomposition en présence d'acide. Dans un ensemble spécial de récipients en PTFE, le SiF_4 produit par la décomposition est adsorbé sur du KNO_3 et donne du K_2SiF_6. Après l'hydrolyse, on titre le HF avec du NaOH pour doser le SiO_2 contenu dans l'échantillon. On dissout ensuite le résidu d'échantillon après décomposition de l'échantillon par l'acide, puis on l'emploie pour doser les éléments restants par chélatométrie, spectrophotométrie et SAA.

---

[1] Geological Survey of Prague, Malos transké, Na'm. 19, 11821 Praha 1, Czechoslovakia.

INTRODUCTION

Determination of the bulk chemical composition of rocks and other silicate materials will always constitute a major and important part of geoanalytical laboratories' workload. The number of samples required for analysis is, in general, increasing and in order to cope with this task, analysts try to apply automated instrumental methods. Among these, X-ray fluorescence (XRF) spectrometry is being used commonly for what is generally called "silicate analysis". This comprises the determination of all major and minor metallic elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Li, Na, K), P, and S. The analysis is usually completed by determining LOI and possibly some other constituents like divalent Fe, S, C, F, constitutional water, etc. Such an approach requires not only an XRF spectrometer but also reference samples of well established chemical composition.

If such samples are not available, a possible way to cope with the requirement of an increased sample throughput is to simplify the necessary decomposition procedure and to speed up wet chemical determinations of individual elements. Modern analytical wet chemistry has indeed succeeded in the latter to a considerable extent. By introducing selective chelatometric titrations with EDTA or spectrophotometric and atomic absorption spectrometry (AAS) determinations of individual elements directly from the sample stock solution, the time required for analysis has become a fraction of that needed previously using classical methods.

The most time- and labour-consuming procedure remaining is the gravimetric determination of silica, SiO_2. This involves precipitation of silicic acid by dehydration, filtration, multiple washings, ignition of the resulting precipitate, and possibly fuming off the precipitated silicic acid with HF and repeated weighing.

Decomposition of silicates by HF has the advantage that silica is simultaneously separated from the sample matrix by volatilization. If the evolving gaseous products of HF with silicic acid were quantitatively trapped, SiF_4 could be determined, e.g., by acidometric titration and the sample residue used for the determination of all other elements. Such a procedure would not require any expensive instrumentation, would not need reference samples, and would be competitive in sample throughput with instrumental methods such as XRF spectrometry.

Establishment of a successful procedure based on this principle would require clarification of the following points:

1. conditions under which SiF4 is quantitatively released from the reacting solution,
2. suitable reagents for efficient sorption of SiF4, and
3. quantitation of the sorbed SiF4.

EXPERIMENTAL

Preliminary experiments have shown that solid crystalline KNO_3 is an efficient absorber but that without the presence of HF, SiF_4 alone is virtually not absorbed. A quantitative sorption of SiF_4 on KNO_3 requires either the presence of HF vapours, in which case it is probably sorbed directly as H_2SiF_4 (Remy, 1957), or a preliminary formation of KHF_2 which results from sorption of the prevalently dimeric $(HF)_2$ on KNO_3. SiF_4 then may react according to the equation

$$2KHF_2(s) + SiF_4(g) = K_2SiF_6(s) + 2HF\ (g)$$

Any excess KHF_2 formed is subsequently again removed by vapours of HNO_3 which is a stronger acid than HF and which volatilizes with HF during the sample decomposition. Since HNO_3 is a weaker acid than H_2SiF_6, HF is not released from the potassium fluosilicate.

However, if HNO_3 cannot release HF from K_2SiF_6 formed in the sorbent, neither should it be capable of releasing it from K_2SiF_6 which eventually crystallizes in the solution during decomposition. It was indeed confirmed experimentally that, with increasing content of K in the sample, the amount of SiO_2 found decreased. To release SiF_4 from the fluosilicates completely, a stronger acid, either $HClO_4$ or H_2SO_4, must be added to the solution.

Perchloric acid releases HF from the K_2SiF_6 in the solution but its vapours remove it also from the sorbent, thus causing low Si values to be found. Evidently any fluosilicic acid liberated by $HClO_4$, which starts to evaporate only once all HF from the sample has been vapourized and no more HF vapours are present, will undergo dissociation and the SiF_4 is not absorbed any more.

For the decomposition of K_2SO_4 may be used instead of $HClO_4$. It is strong enough to decompose fluosilicates in the solution but, due to its high boiling point (338°C), conditions may be set so that H_2SO_4 does not evaporate during the sample decomposition and displace HF from the potassium fluosilicate in the sorbent.

This sequence of processes and reactions dictates the composition of the mixture of acids for the decomposition and the temperatures used. The acid mixture used for decomposition thus includes HF, HNO_3, and a small amount of H_2SO_4. The temperature of the decomposition vessel at the bottom should be below 200°C to prevent any vapourization of H_2SO_4 but above 120°C at the top to prevent any condensation of HF (b.p. 120°C) and/or HNO_3 (b.p 120.5°C) acids in the sorbent. Such conditions may be achieved by setting the hot plate temperature to 200°C and placing a radiative heater with infra-red IR bulbs above the hot plate.

Decomposition

For decomposition a special vessel must be used to trap the evolving gases containing SiF_4. The vessel assembly made from PTFE is shown on Figure 1. It consists of a decomposition vessel which has an upper rim with a larger diameter to fit tightly into a covering bell. The rim has four groves on the top and on the sides. These form channels enabling acid fumes to leave the vessel when the decomposition vessel, with the lid on, is inserted into the covering bell. The whole unit is placed centrally into the sorption vessel and the sorbent placed around it.

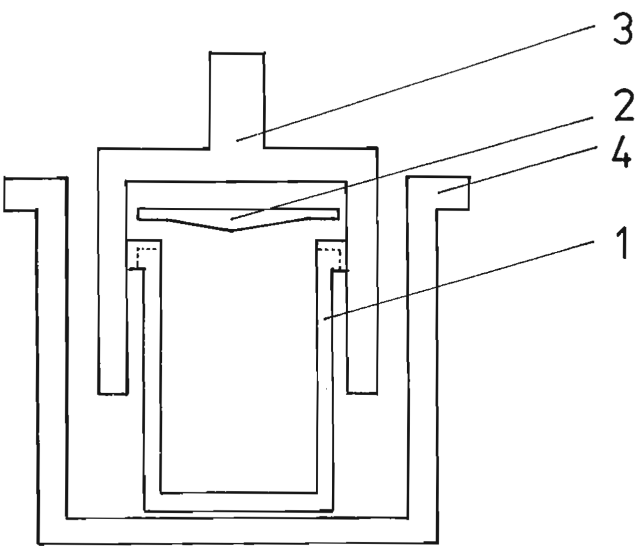


Figure 1. Vessel assembly for acid decomposition and sorption of SiF_4. 1-decomposition vessel; 2-lid (partly lifted); 3-covering bell (vessel not fully inserted); 4-sorption vessel.

All fumes leaving the decomposition vessel are forced by the covering bell to stream down, enter the sorption vessel at the bottom and then pass through the sorbent layer. To keep the sorbing KNO_3 porous, it is mixed with $KClO_4$ in a ratio of 2:1.

To 200 mg of sample in the decomposition vessel, 0.5 mL of distilled water and 4 mL of acid mixture composed of 12 parts HF, 12 parts HNO_3 and 1 part H_2SO_4 are added. The whole vessel assembly is placed in openings drilled in an Al block which is heated on a hot plate to 200°C. The vessel assembly is inserted at about 140°C, the temperature is raised to 200°C and, after 2 hours, the decomposition is complete.

Hydrolysis of potassium fluosilicate

After cooling down, the assembly is removed from the heating block, the sorbent mixture is moistened with distilled water so that it sticks to the covering bell and thus may be easily transferred into a 600 mL beaker. The covering bell and the decomposition vessel are rinsed with a saturated KNO_3 solution. The decomposition vessel is then partly retracted from the covering bell, rinsed with a minimum amount of H_2O, then completely removed and placed aside for further treatment of the sample residue. Water is used for rinsing at this stage to reduce the danger of contamination with K. Some of the salts in the beaker must stay undissolved so that a saturated KNO_3 solution is always present to prevent hydrolysis of the K_2SiF_6.

Any possible traces of acids that might have condensed in the sorbent are first neutralized by titration on phenolphtalein. This requires normally one to three drops only. Then 500 mL of distilled water are added and the solution is heated to boiling in order to hydrolyze all K_2SiF_6 according to the reaction

$$K_2SiF_6 + 3H_2O = 6HF + K_2SiO_3$$

Titration of HF

Titration of the HF should proceed with the solution still hot since high temperature favours dissociation of the fluosilicic anion and accelerates establishment of equilibria. Titration by NaOH with visual indication is used, though in principle potentiometric indication should also be possible. The change in pH decreases with the amount of Si present. At high Si content, the starting pH is higher and the final pH lower due to the buffering effect of potassium silicate (Fig. 2).

The equivalence point is around pH 7, for which cresol red should be optimal. However, the colour change of cresol red is extended over a large pH range starting at pH 6.8, with a change to orange and reaching full red at about 7.5. With this indicator a back-drifting of the colour change was also observed, probably due to residual unhydrolyzed fluosilicate. It is therefore advantageous to slightly "over-titrate" using phenolphtalein to the slightest pink colouration, indicating a pH of 8.2. At low Si content, the pH change goes well up above this value so that the error is negligible, while for high Si content it secures a slight excess of NaOH which is necessary to complete hydrolysis of the last traces of K_2SiF_6. The indication to the slightest pink colour requires some experience and it is recommended to try a few titrations before applying the procedure to "real" samples.

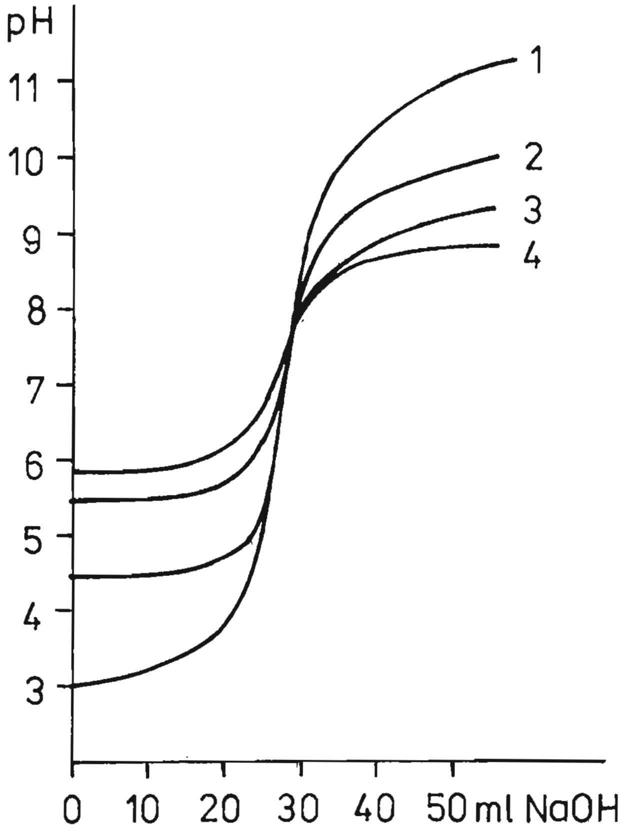


Figure 2. Titration curves of HF in presence of increasing K_2SiO_3 corresponding to: 1-no SiO_2, 2-20%, 3-60%, 4-95% SiO_2.

The NaOH solution for titration has a concentration of 0.2663M, so that 1 mL corresponds to 4 mg of 2% of SiO_2 in the sample. The factor of the titrant is checked on 0.2 M H_2SO_4 and on a sample with a well established SiO_2 content. The latter corrects also for any possible traces of Si in the KNO_3 and $HClO_4$ salts used which are only technical grade.

PRECISION AND ACCURACY

Precision of the procedure was estimated from analyses of 15 samples with SiO_2 contents between 45 and 76%. Each analysis was repeated five times. The standard deviation found was 0.15% SiO_2.

Accuracy was tested on 26 rock SRMs with SiO_2 contents between 39% (MRG-1) and 73% (RGM-1). The results were compared with recommended values published in the Special Issue of Geostandards Newsletter, 1989. The described procedure gave results with an average positive error of 0.186% SiO_2 and a standard deviation of 0.198%. A histogram of the differences is presented (Fig. 3).

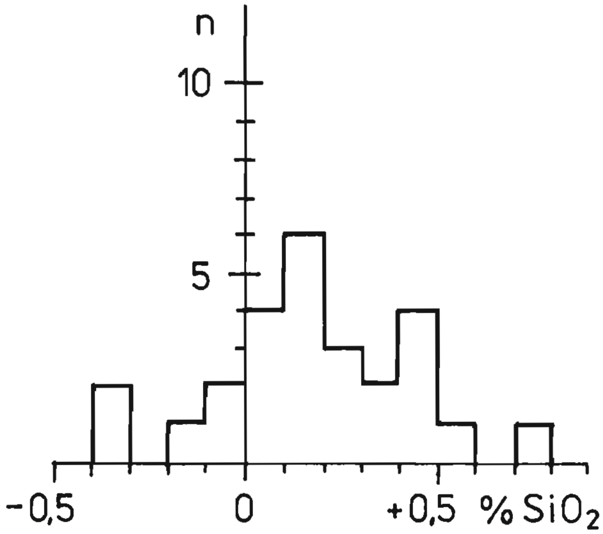


Figure 3. Histogram of differences between "found" and "recommended" values of SiO_2 in 26 SRMs. $\Delta x = 0.186\%$ SiO_2, $s_x = 0.198\%$ SiO_2.

TREATMENT OF THE SAMPLE RESIDUE

The sample residue in the decomposition vessel may be used for the determination of other elements. Further treatment depends clearly on the procedure used. The treatment described below is suited for a combination of AAS, chelatometric titration, and spectrophotometry, as used in our laboratory.

The sample residue is first dissolved with dilute HCl, transferred to a PTFE beaker and the HF is fumed off by adding boric and nitric acids. If the sample contains organic matter, $HClO_4$ is also added to remove any colouration which might interfere with the spectrophotometric measurements. At this stage it is important to note whether any insoluble residue is present. If not, after fuming to dryness, 10 mL of a mixture containing 2.5 mL H_2SO_4 + 2g Cs_2CO_3 in 100 mL HCl (1+1) are added and the sample is transferred to a 100 mL volumetric flask and filled up to the mark with distilled water. If an insoluble residue is present, the sample is dissolved in 5 mL HCl (1+1) and filtered into a 100 mL volumetric flask. The filter is incinerated and fused with 0.35 g of a mixture of $H_3BO_3 + Cs_2CO_3$ (3 + 4). The resulting melt is dissolved in 5 mL of HCl (1+1) containing 0.25 mL of H_2SO_4 and added to the sample solution in the volumetric flask. Both procedures ensure the same composition of the final solution. The Cs salt added acts as an ionization buffer for the AAS measurements.

Elements measured by AAS include Li, Na, K, Mn, Ti, and low Al, Fe, Mg, Ca, and possibly also Si in samples which had an insoluble residue. Because of the presence of sulphate anions in the sample solutions, the alkaline earth elements must be measured with a $C_2H_2 - N_2O$ flame. Even in this flame, sulphates have a slight depressive effect on Al, Ti, Ca, and Mg. In the presence of boric acid, the depressive effect levels off above 500 mg H_2SO_4 and remains constant to at least 1000 mg. The content of sulphates is easily kept within these limits.

High Al, Ca, and Mg are determined by chelatometry with EDTA, high Fe by spectrophotometry with sulphosalicylic acid and all P with the molybdenum blue method. The procedures are described in *Methods of Chemical Analysis of the Geological Survey Prague (D. Weiss, unpub. report, 1983).*

CONCLUDING REMARKS

The procedure presented has been used in our laboratory for several years with very good results. Two chemists may carry out the decomposition of 50 samples per day plus the titrations of Si and Al. One chemist performs the spectrophotometric determinations of P and high Fe and another chemist all the AAS determinations. Thus, four chemists can analyze about 200 samples per week. The procedure is highly expeditious, comparable to XRF spectrometry. It offers an alternative method of silicate analyses suitable for smaller laboratories where an XRF spectrometer is not available. The investment costs for the necessary equipment are only a fraction of the price of an XRF spectrometer. A further advantage is that the resulting sample stock solution contains no, or very little, flux and may be used for the determination of a number of trace elements by AAS or inductively coupled plasma spectrometry.

REFERENCE

Remy, H.
1957: Lehrbuch der anorganischen Chemie, Vol. 1, Akademische Verlagsgesellschaft Geest & Portig, Leipzig, 866 p.

Implications of sampling statistics in using slurry sample introduction for atomic absorption spectrometric analysis of geochemical reference samples

Jean S. Kane[1] and Zhen, Xu[1]

Abstract: A number of investigators have used slurry sample introduction for the atomic absorption spectrometric analysis of a variety of materials. A unique application of the method, however, is evaluation of the degree of homogeneity of reference samples. For geochemical samples, the expected analytical error attributable to subsampling from mineral mixtures can be calculated from grain size and component mineral densities, following the approach of Ingamells. This paper presents these calculations for a number of elements in specific geochemical reference samples for which known mineralogy predicts inhomogeneous distribution of analytes. Measurements are made for Cr in the reference dunite, DTS-1, and for a number of elements in the certified reference sulphide ore, MP-1a, at two different subsample weights, using slurry atomization atomic absorption spectrometry. The experimental and calculated sampling parameters are compared, and the feasibility of using the slurry technique for establishing homogeneities and sampling constants of geochemical reference samples is demonstrated.

Résumé : Plusieurs chercheurs ont employé l'introduction d'échantillons en bouillie lors de l'analyse spectrométrique par absorption atomique de divers matériaux. Cette méthode trouve cependant un emploi particulier dans l'évaluation du degré d'homogénéité des échantillons de référence. Dans le cas d'échantillons géochimiques, on peut calculer l'erreur analytique prévue, attribuable au sous-échantillonnage de mélanges minéraux, d'après la granulométrie et la densité des composants minéraux, en suivant le procédé d'Ingamells. Dans cet exposé, on présente ces calculs pour plusieurs éléments trouvés dans certains échantillons de référence géochimiques dont la minéralogie connue laisse prévoir une distribution hétérogène des éléments dosés. On a dosé Cr dans la dunite de référence (DTS-1) ainsi que divers éléments présents dans le minerai sulfuré certifié (MP-1a), en prenant deux sous-échantillons de masse différente et en utilisant la spectrométrie d'absorption atomique avec atomisation de bouillies. On compare les paramètres d'échantillonnage expérimentaux et calculés, et l'on démontre la possibilité d'utiliser la technique des bouillies pour établir les homogénéités et les constantes d'échantillonnage des échantillons de référence géochimiques.

---

[1] National Institute of Standards and Technology, Gaithersburg, Maryland, 20889, U.S.A.

INTRODUCTION

Considerable interest has been shown in recent years on using some form of solid sampling (Routh and Tikkanen, 1987; Thompson and Walsh, 1989), such as: slurry (Fuller et al., 1981; Wilkinson et al., 1982; Ebdon and Parry, 1987; Williams et al., 1987; Miller-Ihli, 1988; Epstein et al., 1989); direct insertion (Schlemmer and Welz, 1987; Carnrick et al., 1986; Brown et al., 1987; Baxter and Frech, 1987); and laser ablation (Hale et al., 1984; Gray, 1985) in atomic spectrometry. A critical concern in using any of these methods is sample homogeneity.

The literature on the use of direct insertion and slurry sample introduction for homogeneity studies of reference samples by graphite furnace atomic absorption spectrometry (GF-AAS) has generally focused on biological samples, either plant, animal tissue, or food materials (Mohl et al., 1987; Stoeppler et al., 1985; Miller-Ihli, 1988). Measurement-to-measurement precision of sample slurries compared to that of calibration solutions at approximately the same concentration has been interpreted to imply homogeneity or inhomogeneity at small sample sizes. Little comment has appeared in these reports, however, about the actual partitioning of the analyte(s) between different sample components, e.g., carbohydrates, fats, proteins, etc., or about the ratio of analyte concentrations in the bulk sample to that in those components which concentrate the analyte. The ratio between concentrations in the high and low concentration components, however, is inferred from the overall range of individual results (Stoeppler et al., 1985), to be smaller than in geochemical samples.

In contrast, a great deal is known about such partitioning in geochemical samples. Ores are, quite simply, inhomogeneous mixtures of mineral species highly enriched in a particular analyte and a gangue material containing that analyte at much lower concentrations, or possibly devoid of it altogether. Inhomogeneities in rocks are equally serious; they differ from those in ores only with respect to the mineral/bulk analyte concentration ratio, which is higher for rocks than for ores of similar speciation.

Solid sample analysis is hardly new, as solids, not solutions, are analyzed using such long-standing techniques as neutron activation analysis (NAA) (Baedecker and McKown, 1987; Potts, 1987), X-ray fluorescence (XRF) (Johnson and King, 1987; Potts, 1987; Taggart et al., 1987), and DC arc atomic emission spectrometry (AES) (Golightly et al., 1987; Potts, 1987). The concerns about how inhomogeneity will affect analytical results are minimized for NAA and XRF, as subsamples of 0.5 g or larger are used for analysis. However, for DC arc AES, which typically employs 10-15 mg subsamples, the concerns are substantial (Ondrick and Suhr, 1969). The case of chromite in G-1 (Ingamells and Switzer, 1973; Ingamells and Pitard, 1986) summarized below, is illustrative.

Slurry nebulization into the inductively coupled plasma (ICP) for either atomic emission (AES) or mass spectrographic (MS) measurement, direct insertion and slurry atomization in the graphite furnace for AAS analysis, and laser ablation sample introduction for ICP-AES and ICP-MS measurement all use subsample sizes which are potentially a factor of 100 or more smaller than the DC arc subsample. Using these techniques, errors in analysis due to inhomogeneity will be magnified beyond those previously identified for DC arc AES analyses.

Calculations following the Ingamells and Pitard (1986) approach are presented to estimate the magnitude of these errors, and to indicate the minimum number of replicate subsamples which must be analyzed in order to have confidence that inhomogeneities will be identified. Experimental data for homogeneity studies of two geochemical reference samples using slurry atomization GF-AAS are also presented, and compared to the results predicted by the sampling model calculations.

It is important to note that we are discussing subsample homogeneity within a single bottle split of reference sample, as distributed. Most of the homogeneity evaluation previously done for U.S. Geological Survey (USGS) geochemical reference samples (GRMs) (e.g., Flanagan, 1976) focused instead on between bottle variation, assuming that 0.015 g subsamples were taken from all bottles for replicate AES analysis.

SAMPLING THEORY CALCULATIONS FOR KNOWN REFERENCE SAMPLE INHOMOGENEITIES

Chromite in G-1

Experimentally, Ingamells and Switzer (1973) found 105 grains of chromite remaining undecomposed after acid digestion, first with hydrofluoric acid and then with sulphuric and boric acids, of a single 21 g split of the USGS reference granite, G-1. The residual grains were collected, counted, and identified mineralogically using X-ray diffraction and

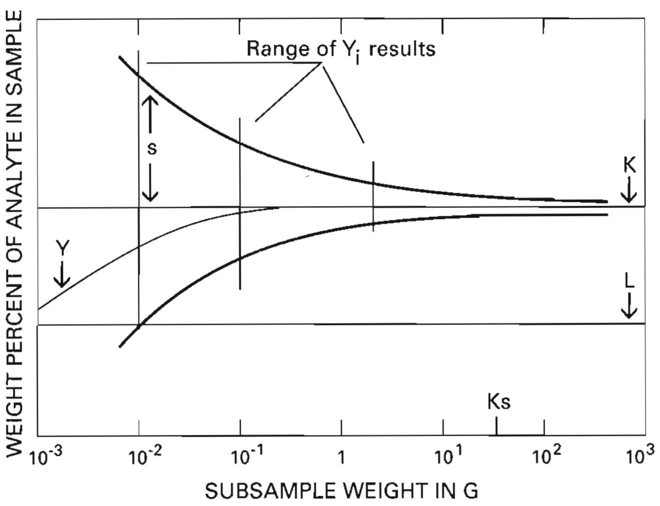


Figure 1. Theoretical sampling diagram; Y,K,Y,L as defined by/for equation 2; S as defined by equation 5; Ks as defined by equation 6.

emission spectrometry. Experimentally, the average number of grains per subsample, z, of chromite in G-1 was found to be five grains per gram. Most of these grains just passed a 170 mesh screen (screen opening, 0.01 cm or 100 μ m), giving chromite in G-1 an effective grain size of 0.01 cm.

Calculations based on these experimental results and on sampling theory have been applied to the occurrence of chromite in G-1 (Ingamells and Switzer, 1973; Ingamells and Pitard, 1986). The average number of grains, z, of chromite which would occur in G-1 subsamples of any size, can be calculated, using equation (1). The most probable chromium assay, Y, for the analysis of these subsamples is calculated according to equation (2).

$$z = (K-L)w/Hd_H\mu^3 \qquad (1)$$

$$Y = (K - (K-L))/(2z + 1) \qquad (2)$$

where K = correct elemental assay for the bulk sample; the certified or recommended concentration

H= elemental assay of the mineral species
L= elemental assay of the gangue
w= subsample weight
d_H= density of the mineral species
μ = estimated grain dimension, volume assumes cubical grain

Except for L and μ, the above variables are known. L is estimated either from the lowest result obtained for analysis of subsamples likely to be free of mineral grains, i.e. $P_{n=0} > 0.8$ (equation 3 below), or from acid soluble fraction of analyte in cases of refractory minerals.

μ is estimated to be the screen opening of a screen passing $\geq 90\%$ of the sample.

The probability of encountering a given number, n, of chromite grains, including n=0, in an individual subsample is given by equation (3), and the distribution of n in replicate subsamples of G-1 will approximate the Poisson distribution (Ingamells and Switzer, 1973; Ingamells and Pitard, 1986).

$$P_n = (z^n e^{-z})/n! \qquad (3)$$

The contribution c_H of a single grain to the analytical result Y_i of that same subsample is given by equation (4).

$$c_H = \frac{Hd_H\mu^3}{w} \qquad (4)$$

and for H>>L,

$$c_H \simeq c \qquad (4a)$$

since $c = \dfrac{c_H\,(H-L)}{H}$, by definition.

The standard deviation for replicate determinations of n will be the square root of z, based on Poisson statistics. For a sufficiently large number of replicates, the average of all experimental results Y_i, will approach Y as a limit with a standard deviation given by equation (5).

$$s = c\sqrt{z} \simeq c_H\sqrt{z} \qquad (5)$$

so that the 95% confidence interval of Y will be $Y - 2\sqrt{z\,c}$ to $Y + 2\sqrt{z\,c}$. At subsample weights where sampling error is small, Y approaches K as a limit, while at sample sizes for which z approaches zero, Y approaches L (see Fig. 1). Note the dependence of all of these parameters on both subsample weight and assumed grain size.

The final sampling theory calculation, given by equation (6), defines the sampling constant K_s, the subsample weight which must be taken for subsampling error to be no more than 1% relative. The constant can also be arrived at experimentally, from the standard deviation, s, of replicate determinations of Y_i, according to equation (7).

$$K_s = \frac{10^4\,(H-L)\,(K-L)\,\mu^3 d_H}{K^2} \qquad (6)$$

$$K_s = \frac{10^4 s^2 w}{K^2} \qquad (7)$$

Note that, unlike the other sampling parameters, K_s (equation 6) varies only with the cube of grain size, while the dominant functional relationship for z, Y, C_H, and s is with subsample weight. Table 1 lists all calculated parameters (equations 1-6) for chromite in G-1 at 10 mg and 0.10 mg subsample weights. These represent the Ingamells DC arc example subsample weight and the weight for a potential GF-AAS slurry subsample, as discussed below.

Previous slurry work (Miller-Ihli, 1988; Epstein et al., 1989) has shown that measurement precision is dependent on the degree of analyte dissolution in the slurry solvent. Where such dissolution occurs, effective subsample weight for the analysis is related in complex fashion to weight taken for

Table 1. Sampling parameters for Cr as chromite in USGS G-1

Given:

K % Cr	0.0020
H % Cr	46.00
L % Cr	0.0008
d_H g• cm^{-3}	4.5
u cm	0.010

Using equations 1-6, calculated for subsample weight

	10 mg*	0.10 mg**
z	0.0579	0.000579
Y %Cr	0.0009	0.0008
$P_{n=0}$	0.944	0.999
$P_{n=1}$	0.055	0.0006
$P_{n=2}$	0.0016	1.7×10^{-7}
c_H %Cr	0.0207	2.07
s %Cr	0.0050	0.050
K_s g	621	621

* 10 mg sample corresponds to the Ingamells dc arc AES example

** 0.10 mg sample corresponds to injection of 10 μL of a 1% w/v slurry for GFAAS analysis slurry preparation which dissolves in the slurry solution, not the much smaller weight actually injected into the graphite furnace or plasma during analysis. For example, 1 mL of a 1% weight/volume slurry is prepared, and repetitively, 10 μ L of slurry are injected into the graphite furnace for analysis. If no portion of the analyte-bearing species dissolves in the slurry medium, the effective subsample taken for each measurement is 0.1 mg. If on the other hand, the analyte present is totally leached from the solid into the slurry liquid, the effective subsample weight for each measurement is 10 mg.

Table 2. Sampling parameters for Cr as chromite in USGS DTS-1 and USGS PCC-1

	USGS DTS-1		USGS PCC-1	
Given:				
K %Cr	0.4000		0.2700	
H %Cr	46.00		46.00	
L %Cr	0.130		0.100	
d_H g• cm^{-3}	4.5		4.5	
u cm	0.0074		0.007	
Using equations 1-6, calculated for subsample weight				
	10 mg	0.10 mg	10 mg	0.10 mg
z	13	0.13	8.2	0.082
Y %Cr	0.39	0.186	0.26	0.124
$P_{n=0}$	2.2 x 10^{-6}	0.877	2.7 x 10^{-4}	0.921
$P_{n=1}$	2.8 x 10^{-5}	0.114	2.2 x 10^{-3}	0.076
$P_{n=2}$	1.8 x 10^{-4}	0.008	9.1 x 10^{-3}	0.003
c_H %Cr	0.0207	2.07	0.0207	2.07
s %Cr	0.0475	0.745	0.0377	0.377
K_s g	1.41	1.41	1.95	1.95

The sampling calculations for slurry atomization were made on the assumption that chromite is largely insoluble in the slurry solvent, so that effective sample size will be 0.1 mg. The resulting values of Y and $P_n \neq 0$ indicate that, for any reasonable number ($n \leq 100$) of GF-AAS measurements with slurry sample introduction, G-1 will appear to be homogeneous with respect to Cr even at the 0.1 mg subsample weight, and to have an apparent Cr concentration of 0.0008% Cr. Both conclusions are erroneous, if Ingamells and Switzer's (1973) detection of chromite in G-1 is typical of the bulk sample, and not unique to the one split on which they performed their study.

Chromite in DTS-1 and PCC-1

The dunite DTS-1 and the peridotite PCC-1 provide similar case studies for inhomogeneities due to chromite occurrences, with more favourable Poisson statistics, because of their considerably higher chromite contents (Flanagan, 1976). For these two reference samples, z = 1300 grains/g, and 820 grains/g, respectively. However, the 10 μ L furnace aliquots of a 1% weight/volume slurry contain only z = 0.26 and z = 0.16 grains, respectively, and Poisson statistics show probabilities of finding no chromite grains in the furnace injection sample volume to be 88% for DTS-1, and 92% for PCC-1. These calculations indicate the need for no fewer than 50 furnace analyses in detecting the known inhomogeneity (see Table 2).

Table 3. Sampling calculations for cassiterite and zircon mineralization in a number of geochemical reference samples

Ref.	Sn/MAN-1 Govindaraju, 1980	Zr/GSP-1	Zr/G-1	Zr/G-2	Zr/SDC-1
		<------ Flanagan, 1976 ------>			
Given:					
K %	0.105	0.05	0.021	0.03	0.029
H %	78.6	49.77	49.77	49.77	49.77
L %	0.007	0.01	0.005	0.005	0.010
d_H g• cm^{-3}	6.8	4.69	4.69	4.69	4.69
u cm	0.0074	0.0074	0.0149	0.0074	0.0074
w g	0.0001	0.0001	0.0001	0.0001	0.0001
Calculated:					
z	0.0045	0.0052	0.0021	0.0021	0.020
Y %	0.0072	0.0104	0.0051	0.0063	0.0107
$P_{n=0}$	0.956	0.995	0.998	0.974	0.980
$P_{n=1}$	0.0043	0.005	0.0021	0.026	0.0196
$P_{n=2}$	0.001	1.3x10^{-5}	2.1x10^{-6}	0.0003	0.0002
c_H %	2.17	0.946	7.72	0.946	0.946
s %	0.460	0.305	0.193	0.154	0.134
K_s g	19.3	15.0	85	26	21

Similar calculations were undertaken for Sn occurring as cassiterite in the CRPG granite MA-N (Govindaraju, 1980), and for Zr occurring in zircon in GSP-1, G-1, G-2, and SDC-1 (Flanagan, 1976). Cassiterite and zircon, like chromite, are insoluble in the slurry medium, so effective subsample weight for each measurement is limited to that contained in the injected slurry volume. For all of these examples, it appears necessary to make several hundred measurements to detect the inhomogeneity of the material, and arrive at analyses which are not severely biased low, as shown in Table 3.

The difficulty in demonstrating inhomogeneities with reasonable solid sampling experiments is due first to the extremes in concentrations between the two components of the sample, mineral grain and gangue, and second, to the very small weight or volume per cent of the mineralizing species in sample. Chromium in chromite is 46%, while in G-1 the over-all Cr concentration is 20 $\mu g \cdot g^{-1}$, and in the gangue it is 8 $\mu g \cdot g^{-1}$, based on a 2.6 x 10^{-3} weight per cent of chromite in G-1. Similarly Sn in cassiterite is 78.6%, while in MA-N it is 0.105%, and in the MA-N bulk matrix it is approximately 70 $\mu g \cdot g^{-1}$, based on measurement of acid soluble Sn. Cassiterite is 1.3 x 10^{-1} weight per cent in MA-N.

Sulphide minerals in MP-1a

Similar sampling calculations for the Canadian Certified Reference Materials Project (CCRMP) sulphide ore MP-1a (Steger, 1984) showed that sample inhomogeneities would be readily detectable at sample weights close to those typical of slurry atomization using 50 or fewer replicate measurements.

MP-1a is a Zn-Sn-Pb-Cu sulphide ore consisting of approximately 30% sphalerite, with cassiterite, stannite, galena, and chalcopyrite occurrences of 0.5-2.0%. Arsenopyrite, molybdenite, argentite, wolframite, and other mineral species are also present in smaller amounts. Indium and cadmium, whose concentrations are certified, occur as substituents for Zn in sphalerite. Bismuth presumably occurs as native Bi, as reported for the similar reference ore, MP-1 (Faye, 1972). Table 4 summarizes the speciation and the sampling calculations for the four analytes, As, Cu, In, Bi, determined experimentally in this study.

EXPERIMENTAL

Instrumentation

Determinations were made on a Perkin Elmer* Model Zeeman 5100 PC atomic absorption spectrometer equipped with an HGA 600 graphite furnace atomizer. Sample introduction was performed with the AS-60 autosampler which had an ultrasonic probe mixer synchronized to mix suspended particles just prior to sampling.

Injection volume is programmable using the AS-60; it varied between 10 μL and 20 μL, as a function of element. The graphite furnace used maximum power heating for atomization of the slurry from L'vov platforms in pyrolytically coated graphite tubes. Peak area measurements were used for all determinations. Additional measurements for DTS-1 only were made using simultaneous multielement

Table 4. Mineralogical composition of MP-1a

Mineral	Weight per cent of mineral in MP-1a	K_s for principal analyte(s) of mineral	
Sphalerite	31.1	Zn	0.057g
		In	0.375
		Cd	0.177
Galena	4.8	Pb	0.583
Chalcopyrite	4.1	Cu	0.39
Arsenopyrite	3.8	As	1.34
(Native Bismuth	<0.5)	Bi	>50.

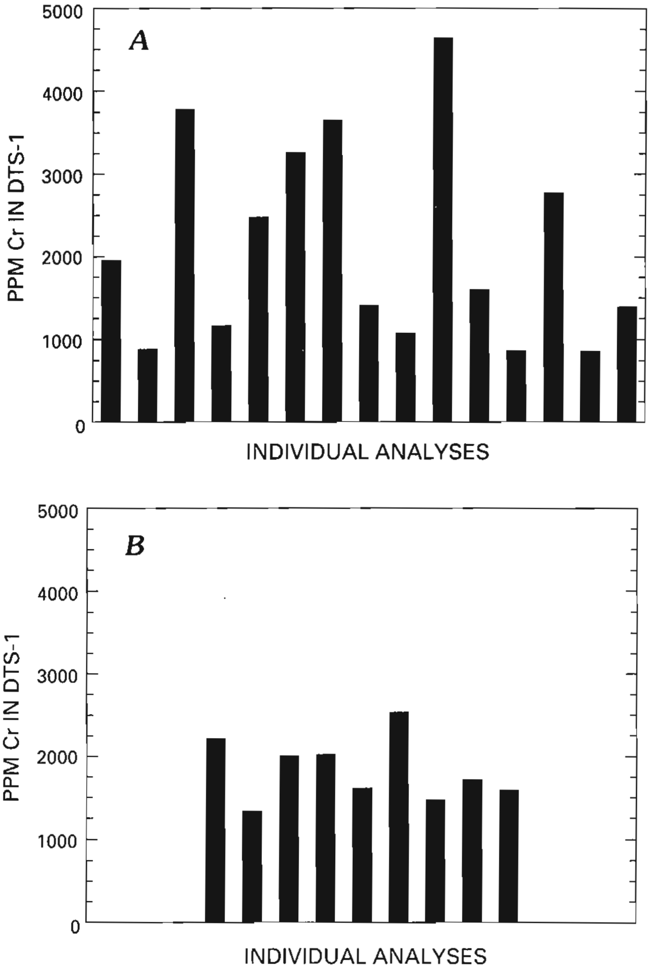


Figure 2. Individual analytical results for Cr in DTS-1 at two different slurry concentrations. **A.** 0.114 mg• mL^{-1}; **B.** 10 mg• mL^{-1}.

---

* Use of trade names is for identification purposes only and does not imply endorsement by the USGS.

Table 5. Grain count and relative sampling error for 20 μ L injection volume

Mesh size	Number of grains for range of densities granite-cassiterite	Relative uncertainty in per cent due to sampling
170	29 ± 5.4 - 71 ± 8.4	19 - 12
325	344 ± 18 - 836 ± 29	5.2 - 3.5

atomic absorption with continuum source (SIMAAC) instrumentation equipped with a Perkin Elmer HGA 400 graphite furnace and a dedicated DEC PDP-11/34 minicomputer (Kane, 1987).

Slurry preparation

When using the Zeeman AAS with an autosampler/ultrasonic mixer, ~1%-2% weight/volume slurry samples were prepared by accurately weighing solid directly into polyethylene autosampler cups on an electronic balance with an accuracy of ± 0.01 mg. A 1 mL aliquot of diluent solution containing 5% nitric acid and 0.04% Triton X-100 was pipetted directly into the autosampler cup. For more dilute slurries, samples were weighed into polyethylene sample bottles and appropriate volumes of diluent were added. The bottles were capped and shaken vigorously to suspend the solid before pipetting 1 mL of the slurries into autosampler cups. For SIMAAC analyses, slurries were prepared by weighing sample and diluent into polyethylene bottles, capping, and shaking 30 minutes in a laboratory shaker, before pipetting the first aliquot into the furnace. The bottle was recapped and manually shaken between all successive furnace injections.

USGS and CCRMP reference samples were analyzed on an "as received" basis. Corrections for moisture were not made. Standards were prepared from NIST SRM spectrometric solutions or other commercial standards certified in weight/volume (mg/mL) units by dilution with the slurry diluent solution.

RESULTS AND DISCUSSION

Cr in DTS-1

Figures 2A and 2B plot individual results for analyses of DTS-1 slurries at two different sample weight/slurry volume ratios, 0.01% w/v and 1.0% w/v. The first (0.01% w/v) slurry (Fig. 2A) contained 0.1 mg• mL^{-1} of sample, in order to use the conventional AAS wavelength within its linear calibration range. Calculations indicated that only gangue concentrations should be measured, as the average grain count per furnace aliquot was <0.01 grains. That proved not to be the case. For simplicity, the calculations assumed a constant grain size just equivalent to the -200 mesh screen dimension which passed 94% of the DTS-1 powder (Flanagan, 1976), a grain size similar to that reported by Ingamells and Switzer (1973) for G-1. The lowest Y_i measured, 800 μ g• g^{-1}, was low, and the average assay for 15 replicates of 2115 μ g• g^{-1} was high, in

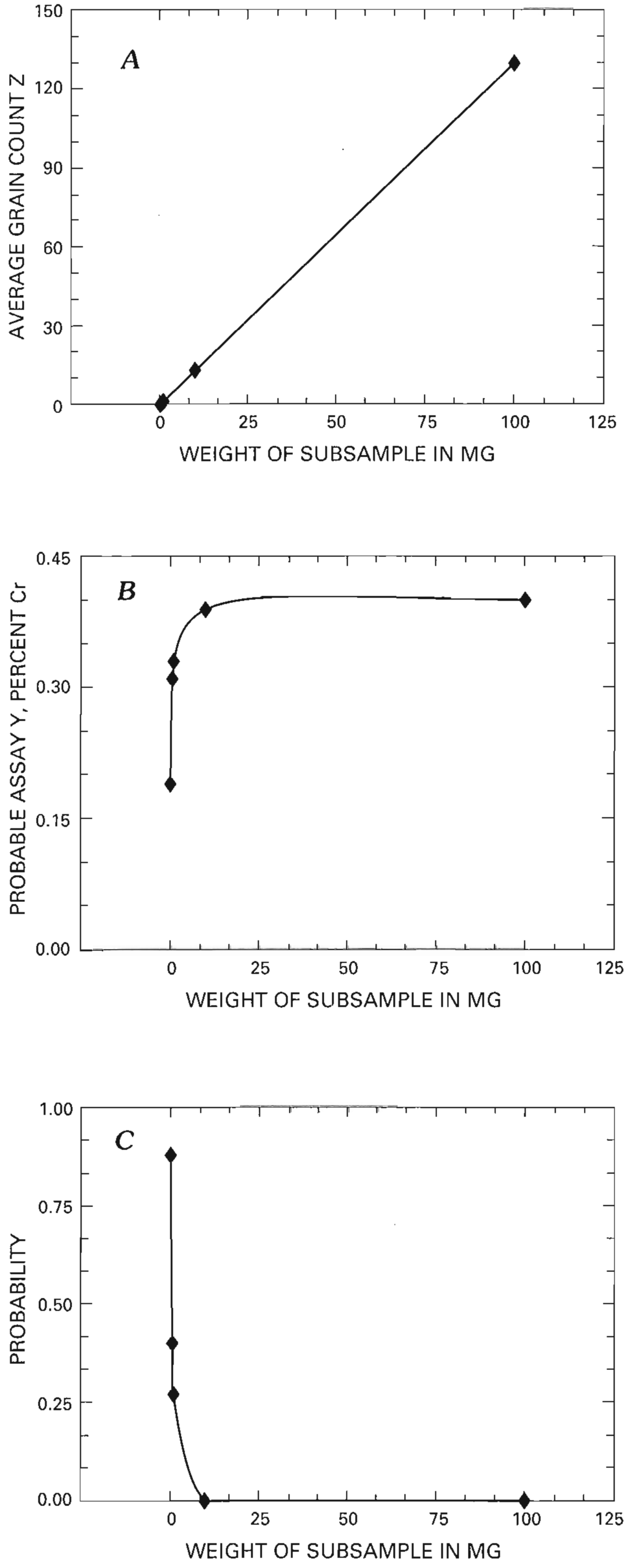


Figure 3. Sampling parameters for chromite in USGS DTS-1 as a function of subsample weight. **A.** Z, average grain count. **B.** Y, most probable chromium assay. **C.** probability that subsample will contain no grains of mineral species.

comparison to the estimated gangue concentration L of 1300 $\mu g \cdot g^{-1}$ used for calculations. Based on the average chromite grain count for chromite at the weight taken, both were expected to approximate L. Additionally, precision of the measurement was unexpectedly poor, in view of the expectation that gangue concentration would not be subject to subsampling imprecision.

Several factors account for the discrepancy between expected and observed results. First, the sample size used was so small that even the gangue concentration measurement was subject to sampling errors, as shown in Table 5. Additionally, there is less than 1% leaching of Cr from solid into the slurry medium, so dissolution does not significantly increase effective sample size over the solid weight contained in the injection volume. Finally, grain sizes are apparently widely distributed over a range of sizes below 200 mesh, rather than constant at 74 μ m. The probability of encountering mineral grains in the furnace would increase substantially at smaller grain sizes. Taking this into account would increase z and Y, while decreasing c_H (Fig. 3A-C) relative to values in Table 2. The experimental results are therefore in reasonable agreement with theoretical values, once an assumption of a distribution of grain sizes from -200 to $\leq$ -350 mesh (74 μ m to $\leq$ 44 μ m) is made.

The second (1.0% w/v) slurry contained 10 $mg \cdot mL^{-1}$, required use of the SIMAAC instrument extended calibration range (Kane, 1987; Harnly and O'Haver, 1981), and led to an average determination of Cr in DTS-1 of 1873 ± 343 $\mu g \cdot g^{-1}$, based on 12 replicates (Fig. 2B). The lowest result of 1200 $\mu g \cdot g^{-1}$ approximates the gangue concentration L estimated from acid decompositions of DTS-1. The standard deviation for the average analysis is equivalent to ± 2 grains

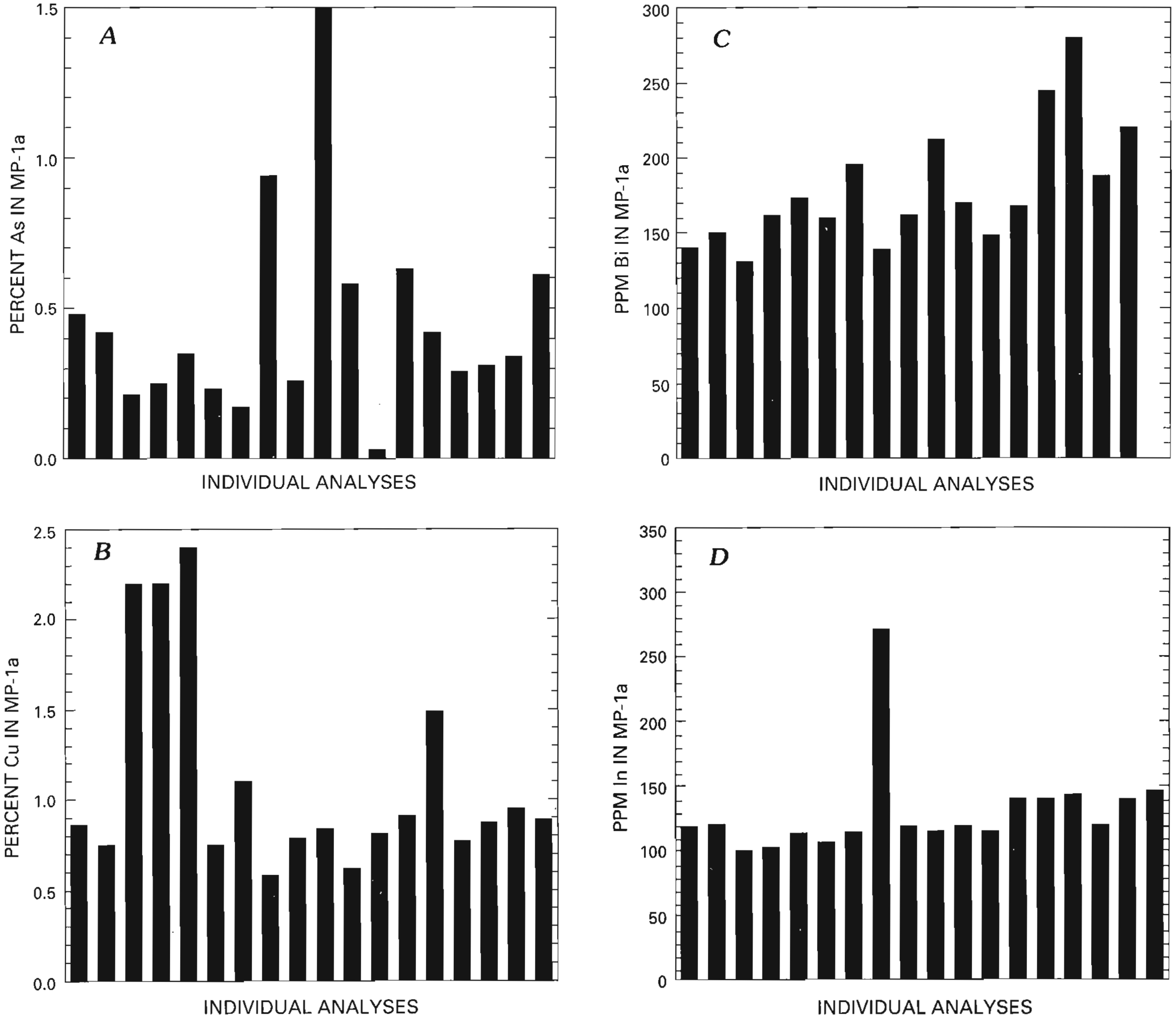


Figure 4. Individual analytical results for slurries of CANMET MP-1a. **A** - Cu; **B** - As; **C** - In; **D** - Bi.

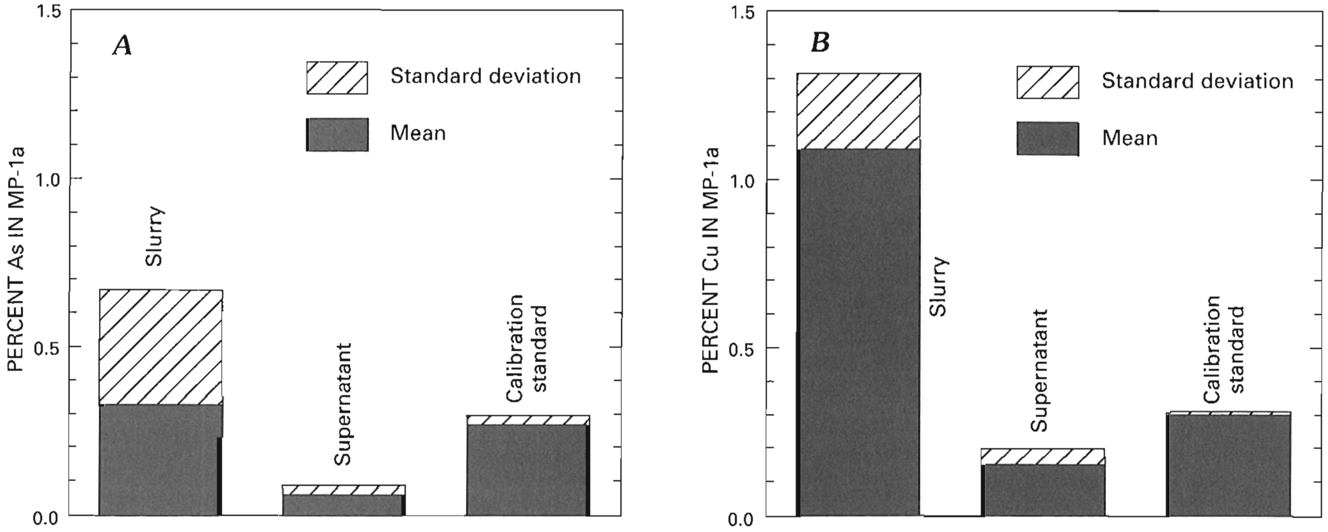


Figure 5. Averaged analytical results for slurries of CANMET MP-1a, 3.5 x 10^{-5} mL^{-1}, their supernatants, and calibration standards. **A.** Cu; **B.** As.

Table 6. Experimental K_S based on MP-1a analyses

	K_s, g	Measured MP-1a Concentration wt %		number of injections	wt/vol*
As	0.21	0.326 ± 0.336	slurry	9	0.64 mg/20 mL
	0.093	0.178 ± 0.225		12	
	0.32	0.459 ± 0.420		12	
	0.13	0.499 ± 0.027		12	
		0.061 ± 0.025	supernatant	6	
Cu	0.033	1.09 ± 0.23	slurry	9	
	0.22	1.15 ± 0.68		12	
	0.023	0.94 ± 0.19		12	
		0.154 ± 0.046	supernatant	6	
Bi	0.084	0.0092 ± 0.0049	slurry	9	0.98 mg/mL
	0.0035	0.0144 ± 0.0053		12	1.53
	0.0029	0.0151 ± 0.0012		12	1.25
	0.029	0.0162 ± 0.0010		12	1.29
In	0.016	0.0240 ± 0.0036	slurry	9	0.98
	0.039	0.0163 ± 0.0024		12	1.53
	0.025	0.0196 ± 0.0041		12	1.25
	0.023	0.0199 ± 0.0036		12	1.49

*As prepared. The sample weight used for all calculated K_s is based on 15-20% dissolution in the slurry medium, as measured for Cu and As.

of 74 µm dimension. Since the probability of finding even one 74 µm grain in the furnace aliquot is <0.001, the uncertainty must be attributed to the presence of considerably smaller grains contained in the actual furnace injection volume.

Sulfide minerals in MP-1a

Slurries of 1 mg• mL^{-1} had to be used for the determination of In and Bi in MP-1a, and of 3 x 10^{-5} mg• mL^{-1} for As and Cu, because of the very high concentration of analyte in the ore, and the difficulty of calibrating the instrument at such atypical concentrations for furnace AAS analysis. Partial solubility of all sulphide minerals increased the effective subsample weights over those based on solid in the slurry injection volume. Inhomogeneities were clearly identified (Fig. 4A-4D), actual sample weights estimated from supernatant analyte concentrations (Fig. 5A-5B), and experimental sampling constants were calculated using equation 7 (Table 6) for the analytes, assuming a uniform 74 µm grain size for all minerals. Constants calculated theoretically from equation 6 for that and other grain sizes are plotted in Figure 6. A range of grain sizes below 200 mesh rather than a uniform grain size of 74 µm is sufficient to account for the differences between experimental and theoretical values, as had been noted previously for DTS-1.

CONCLUSIONS

The data demonstrate the usefulness of slurry atomization in assessing homogeneity, and developing sampling constants experimentally for reference sample measurements. Extreme care in selection of subsample size must be exercised to ensure that a reasonable fraction of the subsamples analyzed contain mineral grains in addition to unmineralized sample material. But with that concern in mind, the technique greatly enhances our ability to define, as Engels and Ingamells (1977) suggested many years ago, the sampling characteristics of reference sample materials.

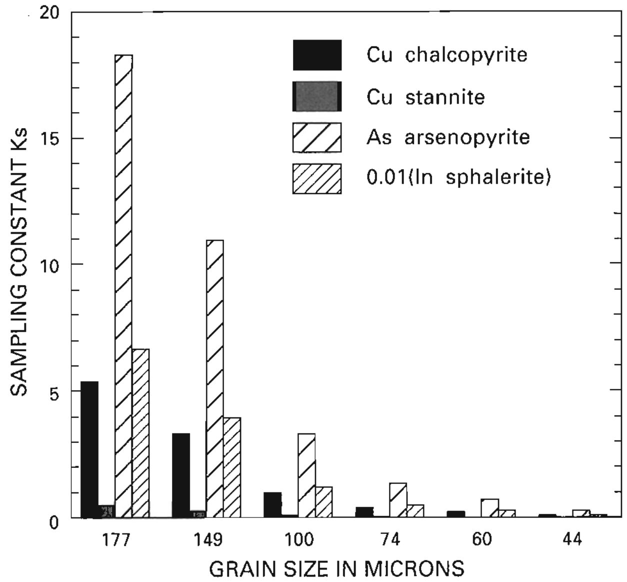


Figure 6. Sampling constants K_S for Cu, As, In, Bi in CANMET MP-1a as a function of grain size.

REFERENCES

Baedecker, P.A. and McKown, D.M.
1987: Instrumental neutron activation analysis of geological samples; in Methods for Geochemical Analysis, (ed.) P.A. Baedecker; p. H1-H14.

Baxter, D.C. and Frech, W.
1987: Analysis of solid samples by graphite furnace atomic emission spectrometry; Fresenius Zeitschrift fur Analytishe Chemie, v. 328, p. 324-329.

Brown, A.A., Lee, M., Küllemer, G., and Rosopulo, A.
1987: Solid sampling in graphite furnace atomic absorption spectrometry; Fresenius Zeitschrift fur Analytishe Chemie, v. 328, p. 354-358.

Carnrick, G.R., Lumas, B.K., and Barnett, W.B.
1986: Analysis of solid samples by graphite furnace atomic absorption spectrometry using Zeeman background correction; Journal of Analytical Atomic Spectrometry, v. 1, p. 443-447.

Ebdon, L. and Parry, H.G.M.
1987: Direct atomic spectrometric analysis by slurry atomisation Part 2. Elimination of interferences in the determination of arsenic in whole coal by electrothermal atomisation atomic absorption spectrometry; Journal of Analytical Atomic Spectrometry, v. 2, p. 131-134.

Engels, J.C. and Ingamells, C.O.
1977: Geostandards- A new approach to their production and use; Geostandards Newsletter, v. 1, p. 51-60.

Epstein, M.S., Carnrick, G.R., Slavin, W., and Miller-Ihli, N.J.
1989: Automated slurry sample introduction for analysis of a river sediment by graphite furnace atomic absorption spectrometry; Analytical Chemistry, v. 61, p. 1414-1419.

Faye, G.H.
1972: Zinc-Tin-Copper-Lead ore, MP-1: its characterization and preparation for use as a standard reference material; Energy, Mines and Resources, Canada, Technical Bulletin TB155, 57 p.

Flanagan, F.J.
1976: Descriptions and analyses of eight new USGS rock standards; United States Geological Survey, Professional Paper 840, 192 p.

Fuller, C.W., Hutton, R.C., and Preston, B.
1981: Comparison of flame, electrothermal, and inductively coupled plasma atomic emission techniques for the direct analysis of slurries; Analyst, v. 106, p. 913-920.

Golightly, D.W., Dorrzapf, A.F. Jr., Mays, R.E., Fries, T.L., and Conklin, N.M.
1987: Analysis of geological materials by direct-current arc emission spectrography and spectrometry; in Methods for Geochemical Analysis, (ed.) P.A. Baedecker, p. A1-A13.

Govindaraju, K.
1980: Report (1980) on three GIT-IWG rock reference samples: Anorthosite from Greenland, AN-G; Basalte d'Essey-la-Cote, BE-N; Granite de Beauvoir, MA-N; Geostandards Newsletter, v. 4, p. 49-138.

Gray, A.L.
1985: Solid sample introduction by laser ablation for inductively coupled plasma source mass spectrometry; Analyst, v. 110, p. 551-556.

Hale, M., Thompson, M., and Wheatley, M.R.
1984: Laser ablation of stream-sediment pebble coatings for simultaneous multi-element analysis in geochemical exploration; Journal of Geochemical Exploration, v. 21, p. 361-371.

Harnly, J.M. and O'Haver, T.C.
1981: Extension of analytical calibration curves in atomic absorption spectrometry; Analytical Chemistry, v. 53, p. 1291-1298.

Ingamells, C.O. and Pitard, F.F.
1986: Applied Geochemical Analysis; New York, John Wiley & Sons, p. 1-84.

Ingamells, C.O. and Switzer, P.
1973: A proposed sampling constant for use in geochemical analysis; Talanta, v. 29, p. 547-568.

Johnson, R.G. and King, B.-S.W.
1987: Energy-dispersive X-ray fluorescence spectrometry; in Methods for Geochemical Analysis, (ed.) P.A. Baedecker, p. F1-F5.

Kane, J.S.
1987: The US Geological Survey instrument for simultaneous multielement atomic absorption spectrometry; United States Geological Survey, Open File Report 87-604, 71 p.

Miller-Ihli, N.J.
1988: Slurry sample preparation for simultaneous multielement graphite furnace atomic absorption spectrometry; Journal of Analytical Atomic Spectrometry, v. 3, p. 73-81.

Mohl, C., Grobecker, K.H., and Stoeppler, M.
1987: Homogeneity studies in reference materials with Zeeman solid sampling GFAAS; Fresenius Zeitschrift fur Analytishe Chemie, v. 328, p. 413-418.

Ondrick, C.W. and Suhr, N.H.
1969: Error and the spectrographic analysis of graywacke samples; Chemical Geology, v. 4, p. 429.

Potts, P.J.
1987: A Handbook of Silicate Rock Analysis; Glasgow, Blackie & Son, Ltd., p. 71-105, 226-325, 399-439.

Routh, M.W. and Tikkanen, M.W.
1987: Introduction of solids into plasmas; in Inductively Coupled Plasmas in Analytical Atomic Spectrometry, (ed.) A. Montaser and D.W. Golightly; New York, VCH Publishers, Inc., p. 431-486.

Schlemmer, G. and Welz, B.
1987: Determination of heavy metals in environmental reference materials using solid sampling graphite furnace AAS; Fresenius Zeitschrift fur Analytishe Chemie, v. 328, p. 405-409.

Steger, H.F.
1984: Certified Reference Materials; Energy, Mines and Resources Canada, Report 84-14E, 32 p.

Stoeppler, M., Kurfurst, U., and Grobecker, K.H.
1985: Investigations on the analysis of heavy metals in solids by direct Zeeman atomic absorption spectroscopy V. The homogeneity factor as a criterion for pulverized solid samples; Fresenius Zeitschrift fur Analytishe Chemie, v. 322, p. 687-691.

Taggart, J.E. Jr., Lindsay, J.R., Scott, B.A., Vivit, D.V., Bartel, A.J., and Stewart, K.C.
1987: Analysis of geologic materials by wavelength-dispersive X-ray fluorescence spectrometry; in Methods for Geochemical Analysis, (ed.) P.A. Baedecker, p. E1-E19.

Thompson, M. and Walsh, J.N.
1989: Handbook of Inductively Coupled Plasma Spectrometry; Glasgow, Blackie & Son, Ltd., p. 183-200.

Wilkinson, J.R., Ebdon, L., and Jackson, K.W.
1982: Determination of volatile trace metals in coal by analytical atomic spectroscopy; Analytical Proceedings, v. 19, p. 305-307.

Williams, J.G., Gray, A.L., Norman, P., and Ebdon, L.
1987: Feasibility of solid sample introduction by slurry nebulisation for inductively coupled plasma mass spectrometry; Journal of Analytical Atomic Spectrometry, v. 2, p. 469-472.

New selective reagents for the determination of platinum group elements and gold from geological materials

H.U. Kasper[1] and M. Schuster[2]

Abstract: Geochemical data on the siderophile platinum group elements in rock-generating differentiation processes of the upper mantle are still scarce, mainly due to analytical difficulties. Two major problems are to be solved for the determination of the platinum group elements and Au from ultramafic rocks and chromite ores: (i) the quantitative decomposition of these materials, and (ii) the separation of the extremely low contents of noble metals from the interfering matrices, followed by preconcentration.

Sample digestion was performed in PTFE-lined high pressure decomposition vessels with a mixture of H_2SO_4-HF-$HClO_4$ at temperatures up to 250°C and maximum pressure of 20 MPa over more than 48 hours. The PGEs are then chelated with the new agents N-acylthioureas, of which N,N-diethyl-N'- benzoylthiourea (DEBT) yields the best results. The PGE and Au chelates are extracted into isobutyl methyl ketone (IBMK). The high specificity and selectivity of DEBT for the noble metals and the excellent solubility of the chelates in IBMK enables considerable preconcentration factors of up to 200.

Alternatively the DEBT chelates may be separated by high performance liquid chromatography (HPLC) or with silica gel as stationary phase and solvents of moderate polarity, or by solid phase extraction. The elaborate decomposition and separation methods were used to analyze SARM-7, SARM-8, and some chromites from Greek ophiolite complexes.

Résumé : On dispose encore de peu de données géochimiques sur les éléments sidérophiles du groupe du platine présents lors des processus de différenciation du manteau supérieur qui produisent des roches, surtout en raison des difficultés que posent les analyses. Il faut résoudre deux grands problèmes afin de pouvoir doser les EGP et l'or présents dans les roches ultramafiques et les minerais de chromite : (i) la décomposition quantitative de ces matériaux et (ii) la séparation des teneurs extrêmement faibles de métaux nobles dans les matrices interférentes, puis la préconcentration de ces métaux.

On a réalisé la digestion des échantillons dans des récipients sous pression avec garniture de PTFE, dans un mélange de H_2SO_4-HF-$HClO_4$, à des températures atteignant 250 °C et à une pression maximale de 20 MPa, pendant plus de 48 heures. On a ensuite procédé à la chélation des EGP avec les nouveaux chélateurs à N-acylthiourée, parmi lesquels la N,N-diéthyle-N'-benzoylthiourée (DEBT) a donné les meilleurs résultats. Les chélates d'EGP et d'or sont extraits dans l'isobutylméthylcétone (IBMK). La haute spécificité et la grande sélectivité de la DEBT vis-à-vis des métaux nobles, et l'excellente solubilité des chélates dans l'IBMK, permettent d'atteindre des facteurs de préconcentration considérables, allant jusqu'à 200.

Par ailleurs, on peut séparer les chélates de DEBT par chromatographie liquide à haute performance (CLHP) ou avec un gel de silice servant de phase stationnaire et avec des solvants de polarité moyenne, ou par extraction en phase solide. On a employé des méthodes complexes de décomposition et de séparation pour analyser SARM-7, SARM-8 et quelques chromites provenant de complexes ophiolitiques situés en Grèce.

---

[1] Geologisches Institut der Universität zu Köln, Zülpicherstr. 49 4000 Köln 1.

[2] Institut für Anorganische Chemie der J.W. Goethe – Universität, Niederurseler Hang, 6000 Frankfurt/Main 50, Germany.

INTRODUCTION

The geochemistry of the platinum group elements (PGEs) is not well understood, mainly due to analytical difficulties (Parthé and Crocket, 1978; Riddle, Vander Voet, and Doherty, 1988). We have only a small database concerning the behaviour of the highly siderophile PGEs during rock generating differentiation processes in the upper mantle. Moreover, we possess little information on the position of these elements either in the silicate matrix or in the crystal lattice of the different minerals (Wilson, 1989; Rösler, 1981). Analysis for the PGEs is also becoming important in the environmental field; for example in soil and vegetation near roadsides contaminated by Pt emitted from catalysts used in automobiles.

Of the instrumental methods of analysis, instrumental neutron activation analysis (INAA), flame atomic absorption spectrometry (AAS), and graphite furnace AAS (GFAAS), the last achieves the lowest detection limits, except for Ir (Potts, 1978; Sen Gupta, 1989). In addition GFAAS is at present a low cost analytical method with regard to instrumentation as well as consumables such as inert gas, reagents, and graphite tubes. Likewise HPLC and more recently the solid phase extraction (SPE) can be an economic alternative as well (König et al., 1989; Kasper et al., 1989).

Two major problems exist in determining PGEs in mafic and ultramafic rocks and especially in the associated chromites: (i) the decomposition of the material, and (ii) the low concentration levels which inevitably necessitate the separation of the matrix. The lack of adequate standard reference materials (rocks and ores) is a serious concern. Only a few reference materials are available (e.g., SARM-7 and SARM-8, and the Canadian standards PTA-1, PTM-1, and PTC-1) and of these, only SARM-7 is a natural magmatic rock. The amelioration of this situation by new standard reference materials such as CHR-Pt+ and CHR-Bkg is welcome (Potts and Govindaraju, 1989).

DIGESTION

The digestion of chromite-bearing ultramafic rocks, and in particular the digestion of the two chromitites CHR-Pt+ and CHR-Bkg, has been a challenge. Riddle et al. (1988) stated that fire assay methods can result in low recoveries for such matrices. We were successful in decomposing chromites with two methods only: (a) fusion with a mixture of Na_2O_2 and NaOH in Ni crucibles, and (b) acid digestion under high pressure with a mixture of HF, H_2SO_4, and $HClO_4$ (Kasper et al., 1989; Kasper and Aslanidis, 1989).

The fusion is inconvenient because both the handling of the reagents and the fusion itself are dangerous. Moreover, the matrix becomes concentrated in Ni salts and the necessary critical pH adjustment is difficult. Best results have been obtained with the acid digestion under pressure. Despite difficulties in digesting some materials (e.g., CHR-Bkg), this method offers two essential advantages: it is one step procedure and the loss of volatile elements (e.g., Os, Ru) minimized.

To accomplish this digestion, system II produced by Berghof, Eningen was used (Fig. 1). This system allows temperatures up to 250°C and pressures up to 20 MPa. Temperatures higher than 210°C increase gas diffusion excessively leading to contamination and corrosion. An

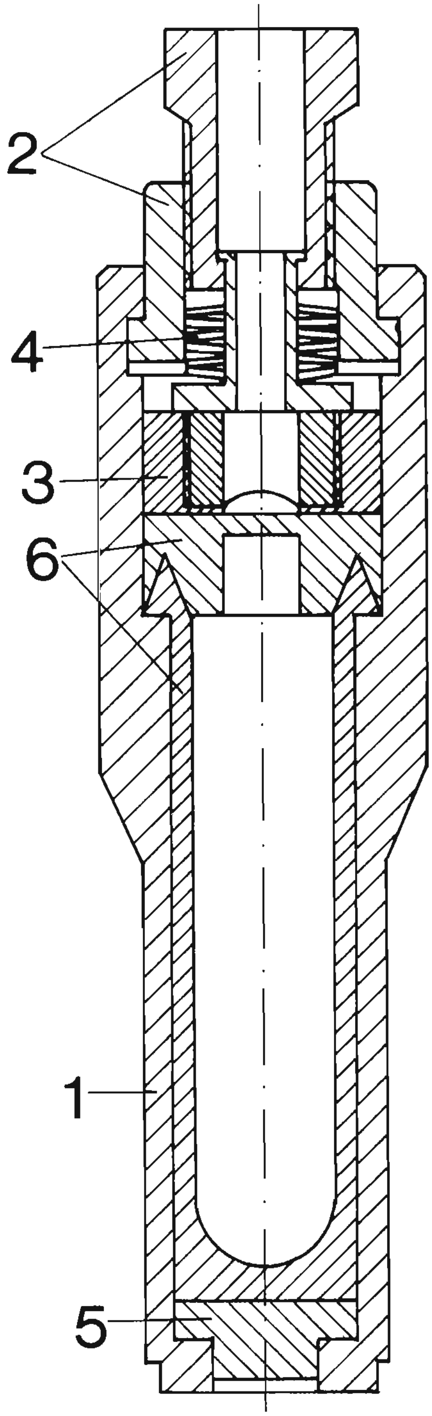


Figure 1. Pressure digestion system II (Berghof, Eningen). General and schematic view: 1-pressure vessel; 2-bayonett quick lock device; 3-pressure cap with rupture disc; 4-springs; 5-base plate; 6-PTFE liner with cap (25 and 50 mL).

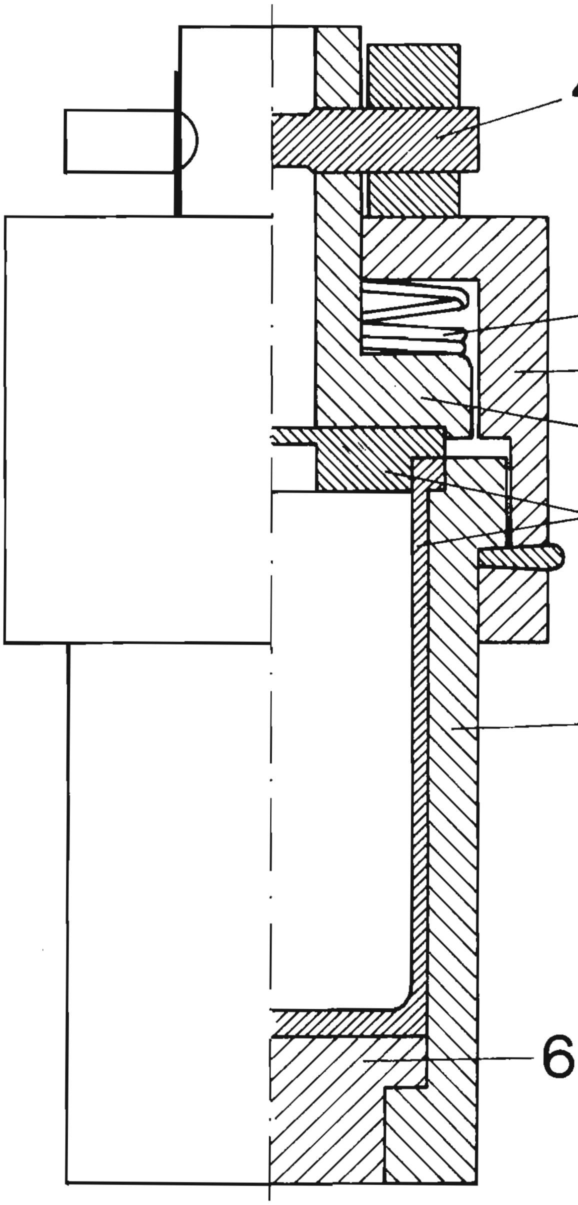


Figure 2. Pressure digestion system IV (Berghof, Eningen). General and schematic view: 1-pressure vessel; 2-bayonett quick lock device; 3-pressure valve with outlet; 4-tension bolt; 5-springs; 6-base plate; 7-PTFE liner with cap (100 mL).

existing aluminum protection is useful but does not avoid diffusion. Instead of using a heating block, we preferred a heating oven which facilitates precise temperature control.

The acid digestion of common silicate rocks containing small quantities of spinels and the chelation procedure were performed in the digestion system IV (Kasper, 1985) of Berghof, Eningen (Fig. 2).

Table 1 shows the decomposition conditions for rocks and chromite ores. Special conditions were necessary for the new chromitites (CHR-Pt+ and CHR-Bkg. For a 0.5 g sample, the maximum amount tested, decomposition time was 72 hours for CHR-Pt+ and 168 hours for CHR-Bkg after further grinding of the sample in an agate mortar. For CHR-Bkg, a small residue was still present, despite the lengthy digestion time and varying the acid mixture. None of the initial minerals of CHR-Bkg could be identified in this residue by X-ray diffraction. It was not possible to digest 5-10 g of sample, as requested for trace elements in the two chromitites (Potts and Govindaraju, 1989).

After digestion a dark green-yellowish transparent solution was obtained, which was transferred to a PTFE beaker and evaporated to dryness. The residue was dissolved in 20 mL diluted HCl (1:9) and brought to volume in a 100 mL volumetric flask. The PGEs and gold were determined from aliquots of this solution.

SEPARATION AND PRECONCENTRATION OF PGEs

The PGEs can be separated by (i) an ion exchange column and elution with thiourea; and (ii) precipitation with tellurium in the presence of ascorbic acid (Kasper et al., 1989). Both methods yield good results, but are laborious. However, N-acylthioureas are easily modified (Douglass and Dains, 1934; König et al., 1985; Schuster, 1986). It is possible to change the extraction properties by introducing fluorescent molecular groups. The new chelating agent N,N-diethyl-N'-benzoylthiourea (DEBT) is a highly specific ligand for PGEs and Au; it will be available soon commercially. Synthesis and recrystallization from an ethanolic solution is performed after Douglass and Dains (1934) by König et al. (1985). DEBT is very stable as either a solid or in solution over a long period of time. The elements chelated by DEBT at pH about 1 comprise Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au.

Table 1. Digestion conditions for ultramafic rocks and chromite ores

Sample	Chromite	°C	Time	Weight	Reagents[1]
Pyroxenite	<1 weight %	180	8 h	max. 3g	H_2O
Chromite ore	10-20 weight %	180	12 h	max. 2g	HF
Chromite ore	20-50 weight %	200	16 h	max. 2g	H_2SO_4
Chromite ore	50-70 weight %	210	24 h	max. 1g	$HClO_4$
Chromite ore	>70 weight %	210	48 h	max. 1g	

[1] Variable quantities

Two applications were investigated: the use of DEBT in combination with GFAAS determination; and its use in thin layer chromatography. The reaction between the ligand and a metal is given in Figure 3.

Separation and preconcentration procedure

The digested sample is transferred to a 100 mL volumetric flask and an aliquot of this solution (e.g., 20 mL) is pipetted in the PTFE liner of the digestion system II or IV, and the container filled up with water to a volume of about 50 mL. The pH is adjusted to 1 with NaOH. In accordance with the PGE content, 5 to 200 µL of DEBT are added to this solution. The chelation is performed under pressure at a maximum of 120°C. In a volumetric flask, the complexed PGEs are extracted, after thoroughly mixing, first with 5 mL of IBMK and then with 1 mL of IBMK using a pipette. The combined IBMK extract is evaporated to dryness and the residue dissolved in a definite volume of diluted HCl (e.g., 1 mL). This solution contains the analyte at a 20 times concentration. Figure 4 presents a schematic representation of the procedure.

Some elements (e.g., Ir) can be determined directly from this solution; others require dilution. If the final volume is less than 1 mL, often necessary, then the 25 mL PTFE liner of digestion system II should be used. Thus one can achieve, at best, a preconcentration of up to 200 fold.

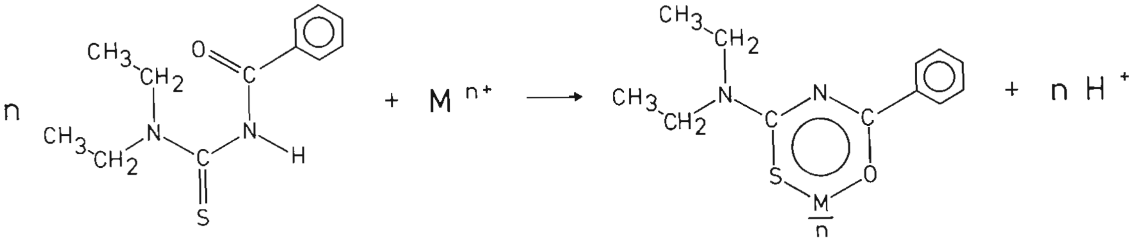


Figure 3. Reaction of N,N-diethyl-N'-benzoylthiourea (n=1,2,3) with a metal.

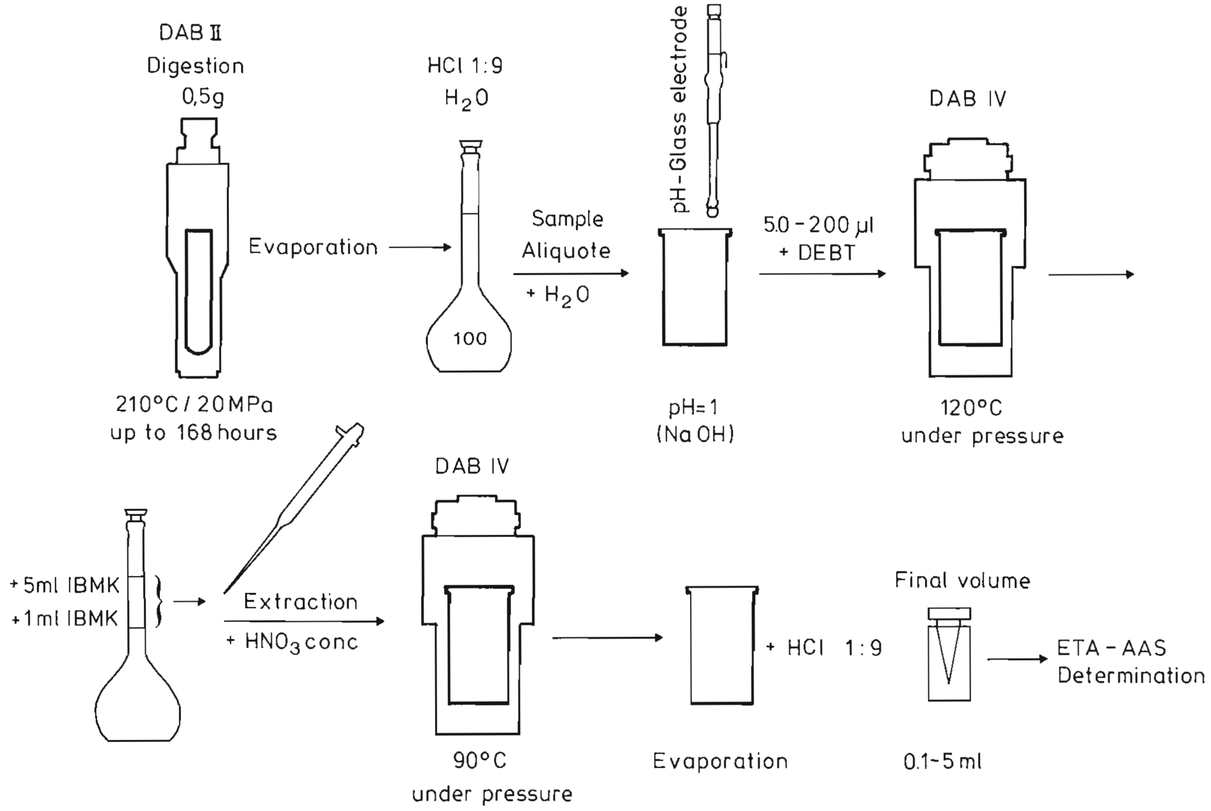


Figure 4. Schematic representation of the separation and preconcentration procedure.

Initially the final volume used for determination was the IBMK fraction (Kasper et al., 1989). We have added the last two steps because: (a) exact measuring of the IBMK, due to its physical properties is extremely difficult, even with glass pipettes; (b) full recuperation is also not possible due to the pH dependent solubility of the IBMK in the sample solution; (c) any further dilution step (also with IBMK) has the same imprecision; and (d) DEBT, especially in excess, considerably increases the background absorption (Fig. 5b).

The analyte in Figure 5 is in a 50 µ L aliquot of a 10 times preconcentrated solution diluted with water to 1 mL. In the recording of Figure 5a there is no DEBT present, due to the decomposition step with nitric acid. In Figure 5b we added 5 µ L of 0.1 M DEBT and in Figure 5c, 5 µ L of IBMK as matrix modifier. The influence on the background is evident. Clearly DEBT should not be added in excess. The same signals were seen for the other PGEs. It was not possible to use standard additions considering the substantial matrix modifying effect of Pd.

DETERMINATION OF PGEs BY HPLC

An outstanding feature of HPLC is the small volume of sample solution (less than 5 mL) needed for one determination. To aliquots of sample solution (e.g., 0.5 mL CHR-Pt+, 10 mL CHR-Bkg) from the 100 mL volumetric flask, which were brought to pH 4 and stabilized with 1 mL of standard phosphate buffer, are added 200 µ L of DEBT (ethanolic solution, 0.1 M). This mixture is heated for 30 minutes at 90°C. After cooling to room temperature, the extraction is performed with toluene.

The HPTLC conditions are after König et al. (1989) and are as follows: stationary phase: HPTLC plates with silica gel K 60 (Merck); mobile phase chloroform (Lichrosolv, Merck);

Table 2. Determination of four PGEs in different geological materials

	µg/g			
Sample	Pt	Pd	Ir	Au
SARM-7	3.80	1.49	0.081	0.29
SARM-8	2.70	0.078	-	-
GR-6 Chromite ore	2.0	0.008	-	0.008
GR-7 Chromite ore	2.85	0.010	-	0.017
LS-1 Fe-Ni-Laterite	1.90	0.007	-	0.013
CHR-Pt +	16-21	74-101	<0.5	1.9-2.6

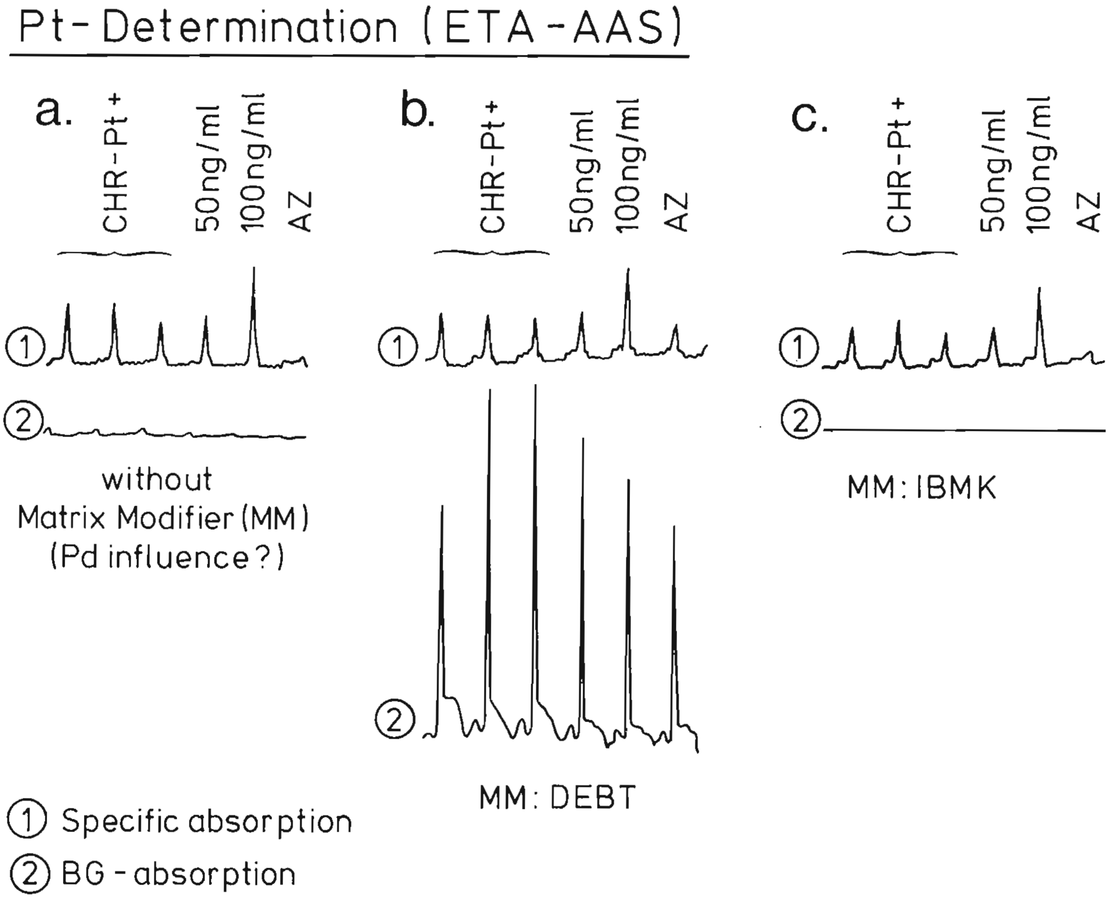


Figure 5. The influence of DEBT and IBMK on the determination of Pt by GFAAS.

relative humidity 20%; migration distance 4 cm; development: Camag chamber, sandwich procedure; ultraviolet detection at 275 nm. The peaks due to DEBT, Pd, and Pt are well separated.

DISCUSSION AND RESULTS

The use of the chelating agent DEBT in analysis for the PGEs offers several advantages when compared to PGE separation by ion chromatography or by precipitation with tellurium (Sen Gupta, 1989; Kasper et al., 1989). Considering the small amount of ligand as well as the easy and rapid extraction of the DEBT chelates (with IBMK for GFAAS or with $CHCl_3$ or C_7H_8 for HPTLC) the proposed separation and preconcentration is an economic and time-saving procedure.

In Table 2 are presented selected results for SARM-7, SARM-8, two chromite ores, and a Fe-Ni-laterite from a Greek ophiolite complex, and preliminary values for CHR-Pt+.

REFERENCES

Douglass, I.B. and Dains, F.B.
1934: Derivatives of benzoyl and furoyl isothiocyanates. Some derivatives of benzoyl and furoyl isothiocyanates and their use in synthesizing heterocyclic compounds; Journal of the American Chemical Society, v. 56, p. 719-721.

Kasper, H.U.
1985: Ein neues Druckaufschlubgefäb mit Tefloneinsatz für anorganische Proben mit silicatischer Matrix; Fresenius Zeitschrift für Analytische Chemie, v. 320, p. 55.

Kasper, H.U. and Aslanidis, P.
1989: New digestion procedures for ultrabasic rocks and chromite ores for the determination of platinum group elements (PGE) by ETA-AAS; Terra Abstracts, v. 1, p. 53-54.

Kasper, H.U., Aslanidis, P., und Schuster, M.
1989: Die Bestimmung der Elemente der Platin-Gruppe (EPG) aus ultrabasischen Gesteinen und Chromiterzen nach Extraktion und Präkonzentration; in 5 Colloquium Atomspektrometrische Spurenanalytik, Hg. B. Welz, Bodenseewerk Perkin-Elmer, p. 449-456.

König, K.H., Schuster, M., Schneeweis, G., and Steinbrech, B.
1989: Zur Chromatographie von Metallchelaten. XIV. Dünnschicht-Chromatographie von N,N-Dialkyl-N'-benzoylthioharnstoff-Chelaten; Fresenius Zeitschrift für Analytische Chemie, v. 319, p. 66-69.

König, K.H., Schuster, M., Steinbrech, B., Schneeweis, G., und Schlodder, R.
1985: N,N-Dialkyl-N'-benzoylthioharnstoffe als selektive Extraktionsmittel zur Abtrennung und Anreicherung von Platinmetallen; Fresenius Zeitschrift für Analytische Chemie, v. 321, p. 457-460.

Parthé, E. and Crocket, J.H.
1978: Platinum metals; in Handbook of Geochemistry, (ed.) K.H. Wedepohl, II-5, Springer.

Potts, P.J.
1978: A handbook of silicate rock analysis; Blackie, 622 p.

Potts, P.J. and Govindaraju, K.
1989: Call for analysis, Chromites CHR-Pt+ and CHR-Bkg – two new platinum-group element reference samples; Geostandards Newsletter, v. 13, p. 193.

Riddle, C., Vander Voet, A., and Doherty, W.
1988: Rock analysis using inductively coupled plasma mass spectrometry: a review; Geostandards Newsletter, v. 12, p. 203-234.

Rösler, H.J.
1981: Lehrbuch der Mineralogie; Deutscher verlag für Grundstoffindustrie, 833 p.

Schuster, M.
1986: N,N-Dialkyl-N'-benzoylthioharnstoffe und strukturanaloge (Se, O)-, (O, O)- und (S, S)-1, 3 dichalkogenliganden für die Extraktion und Chromatographie von Metallen; Inaugural-Dissertation Universität Frankfurt/Main, 207 p.

Sen Gupta, J.G.
1989: Determination of trace and ultra-trace amounts of noble metals in geological and related materials by graphite atomic-absorption spectrometry after separation by ion-exchange or co-precipitation with tellurium; Talanta, v. 36, p. 651-656.

Wilson, M.
1989: Igneous petrology; Unwyn Hyman, 466 p.

Determination of $^{147}Sm/^{144}Nd$ isotope ratios in geological materials using inductively coupled plasma-mass spectrometry (ICP-MS)

Henry P. Longerich[1]

Abstract: The isotope ratio $^{147}Sm/^{144}Nd$ has been determined in 12 geological reference materials using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). A fast (50 ms) peak jumping sequence of ^{147}Sm and ^{146}Nd is used with calibration to an external Sm/Nd standard solution. Using 120 s data acquisition times for each isotope, the relative standard deviation (RSD) of the ratio is a function of the Sm concentration in the rock, and varies from 0.2% (at 109 ppm Sm) to 1% (at 1 ppm Sm). The values determined in this study compared to literature values for all materials are better than 6%. For the best measured reference materials W-1, BHVO-1, and BCR-1 the relative difference in the isotope ratio is better than 0.6%.

Résumé : On a déterminé le rapport isotopique $^{147}Sm/^{144}Nd$ dans 12 matériaux géologiques de référence, par spectrométrie de masse avec plasma induit par haute fréquence (SM/PIHF). On emploie une séquence à variation de crête rapide (50 ms) de ^{147}Sm et ^{146}Nd, en même temps qu'un étalonnage par rapport à une solution étalon externe de Sm/Nd. Si les durées d'acquisition des données sont égales à 120 s pour chaque isotope, l'écart-type relatif du rapport est fonction de la concentration de Sm dans la roche, et varie de 0,2 % (à 109 ppm Sm) à 1 % (à 1 ppm de Sm). Les valeurs déterminées au cours de cette étude, comparées aux valeurs qui figurent dans la documentation pour tous le matériaux, sont meilleures que 6 %. Dans le cas des matériaux de référence le mieux mesurés, W-1, BHVO-1 et BCR-1, la différence relative du rapport isotopique est meilleure que 0,6 %.

---

[1] Department of Earth Sciences and Centre for Earth Resources Research, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X5, Canada.

INTRODUCTION

Neodymium isotope geochemistry, based on the slow decay ($t_{1/2}$ = 106 Ga) of ^{147}Sm to ^{143}Nd by alpha emission, is an increasingly important tool in geological studies (DePaolo, 1988). The crucial isotope ratios to determine are the daughter/reference ratio (^{143}Nd/^{144}Nd) and the parent/reference ratio (^{147}Sm/^{144}Nd). The precision required for the determination of ^{143}Nd/^{144}Nd is generally in the range 0.0005%-0.002% (Potts, 1987), a level of precision which cannot economically be obtained using ICP-MS instrumentation. Determination of the parent/reference ratio (^{147}Sm/^{144}Nd), where less stringent precision requirements are adequate due to the larger range over which this ratio varies (Potts, 1987), is feasible using ICP-MS (Longerich et al., 1990). Compared to the usual technique of determining ^{147}Sm/^{144}Nd, i.e. isotope dilution thermal ionization mass spectrometry (ID-TIMS), the ICP-MS technique involves considerably simpler sample preparation, and requires less time per determination. This paper expands upon the brief introduction to the determination of Sm/Nd isotope ratios made in Longerich et al. (1990), and provides complete documentation of the methodology and a detailed analysis of error. The results presented for ^{147}Sm/^{144}Nd in 12 geological reference materials verify the potential usefulness of this technique.

EXPERIMENTAL

Instrumentation

Data were acquired using a SCIEX ELAN model 250 inductively coupled plasma-mass spectrometer. The instrument and the ancillary equipment installed in our laboratory is described in Longerich et al. (1986). Operating conditions were essentially unchanged from those reported in Longerich et al. (1990). Sample uptake was controlled using a peristaltic pump at 0.9 mL• min^{-1}. The nebulizer gas was optimized daily to produce 100 000 counts• s^{-1} in a solution containing 100 ppb of the monoisotopic Cs, with the oxide/element ratio, ThO/Th, less than 10%. The plasma gas was set to 13 L• min^{-1} and the auxiliary at 1 L• min^{-1}. Applied RF power was 1.2 kW with a reflected power of less than 5 W.

Sample preparation

Samples (0.1 g) were dissolved on a hot plate in screw-top 15 mL Teflon containers (Savillex) with 1 mL HF and 1 mL HNO_3 (Jenner et al., 1990). After one week the containers were opened and the contents evaporated to dryness. The samples were then taken into solution using 2-3 mL of 8 M HNO_3, and evaporated to dryness. Finally the sample was dissolved in 2-3 mL of 8 M HNO_3, allowed to warm on a hot-plate for 2 hours (in closed container), transferred to a 125 mL bottle, and diluted with distilled deionized water to a final weight of approximately 100 g. For isotope ratio determination, the accurate weights of the sample and the final dilution are not required. A single ICP-MS determination of the Sm/Nd ratio requires only 10 g of the final solution, allowing replicate determinations of the Sm/Nd ratio and a sufficient solution aliquot for determination of the radiogenic daughter ratio (^{143}Nd/^{144}Nd) using TIMS, following separation of Nd from Sm and the matrix. Along with the reference materials, three reagent blanks were prepared, none of which contained detectable quantities of either Nd or Sm.

Standards

High purity, accurately preweighed quantities of elemental Nd and Sm (Ames Laboratory, Ames, Iowa) were dissolved individually in high purity acid and distilled deionized water. From these two standard solutions, a stock solution containing 330 ppm of Sm and 555 ppm of Nd was prepared solely for ICP-MS determination of Sm/Nd ratios. For use, this stock solution was diluted approximately 500-fold, producing a solution which was introduced into the ICP at a Sm concentration of 0.8 ppm and Nd concentration of 1.3 ppm in 0.2 M HNO_3. This solution produced ion count rates of approximately 200 000 ions• s^{-1} for ^{146}Nd (isotopic abundance = 17.18%) and 100 000 ions• s^{-1} for ^{147}Sm (isotopic abundance = 15.00%). It should be noted that any change of concentration of either the stock Sm/Nd or the diluted solution due to evaporation does not affect the Sm/Nd ratio, an important advantage over methods which determine absolute Sm and Nd concentrations separately and subsequently calculate the ratio. Using the molecular weights of Sm (150.36) and Nd (144.24), the isotopic abundances of ^{147}Sm (15.00%) and ^{146}Nd (17.18%), and the ^{146}Nd/^{144}Nd ratio of 0.7219 (used by most isotope geochemists), the ^{147}Sm/^{144}Nd ratio of the standard solutions was calculated to be 0.3590 and ^{147}Sm/^{146}Nd was 0.4973. To monitor the possible interference of Ba oxides and hydroxides, a 1 ppm solution of Ba prepared from SPEX plasma grade powders (SPEX Industries, Metuchen, N.J., U.S.A.) was also analyzed.

Data acquisition sequence

Data were acquired using the SCIEX supplied software using "Low" resolution, the "Elemental" scanning mode, 1 measurement/peak, and the "Multichannel" measurement mode. The "measurement time" was set to 120 s, one "repeat", with a "dwell time" of 50 ms. Low resolution, where the peak width at 10% peak height was set to 1 mass unit, gives optimum sensitivity with negligible peak overlap. The use of 1 measurement per peak minimizes peak overlap, in comparison with the use of additional off-peak centre measurements. The dwell time was chosen as the minimum integer number (50) of ms with a length equal to an integer number (3) of cycles of the 60 Hz (1/60 s = 16 2/3 ms) line frequency, a well known source of noise in all instruments operating from 60 Hz AC lines (Belchamber and Horlick, 1982). The software thus counts each isotope for 50 ms, in a "peak-jumping" acquisition sequence, continuing until a total "measurement time" of 120 s was reached for each isotope.

In this study three isotopes were determined (^{137}Ba, ^{146}Nd, ^{147}Sm), for a total acquisition time of 6 min plus a few seconds of overhead. The isotope of Ba was measured to monitor the magnitude of the interference of the poly-atomic ions $^{130}Ba^{16}O$ on ^{146}Nd and $^{130}Ba^{16}O^{1}H$ on ^{147}Sm. The expected interference of these two poly-atomic ions was minimal as the abundance of the ^{130}Ba isotope is only 0.1%, BaO/Ba was 0.26%, and BaOH/Ba was 0.11%. The contribution of the Ba molecular ions was not statistically detectable using the 1 ppm Ba solution standard (equivalent to 1000 ppm of Ba in a rock).

An automated run consisted of 75 test-tubes contained in the Sciex supplied ISCO ISIS autosampler. Each test-tube contained approximately 10 mL of solution. Following the data acquisition time for each tube, a flush time (aspiration of a dilute nitric acid solution) of 3.5 min was used, followed by a 1.5 min sample delay (aspiration of the subsequent sample prior to data acquisition). The total run time was approximately 14 hours. The sequence of tubes which was introduced into the ICP was the Ba standard, the Sm/Nd standard, a calibration blank (0.2 M HNO_3), followed by 3 sample solutions. This 6 tube sequence was repeated 12 times, followed by a concluding set of the Ba standard, the Sm/Nd standard, and the calibration blank. In a 14 hour run, each of 18 preparations was analyzed twice. On a subsequent day the run was repeated, thus each preparation was analyzed four times.

Following data acquisition, the summary data file was stored in a ELAN data communications file and later transmitted via data communications software to a DOS ASCII file, for use with IBM compatible software and hardware. The ASCII file was then "parsed" into a Lotus 123 spread sheet, where all data reduction took place. The mean of all 13 calibration blanks was first subtracted from all data. As mentioned, the interference of the Ba poly-atomic ions was statistically negligible, and thus no correction was made. The $^{147}Sm/^{146}Nd$ isotope ratio for the Sm/Nd standards and samples were calculated as ratios of the background corrected ion intensities. The $^{147}Sm/^{146}Nd$ isotope ratio for all Sm/Nd standards was then linearly interpolated with time and a correction factor (ratio of the $^{147}Sm/^{146}Nd$ in the standard (0.4973) relative to the measured $^{147}Sm/^{146}Nd$ of the interpolated standard) calculated for each sample. This correction factor is different from unity for 2 reasons: mass discrimination (the change in molar sensitivity with mass); and differing degrees of formation of the singly charged ions (Houk, 1985), partially due to the higher degree of oxide formation of Nd (4%) compared to that of Sm (0.7%). As the magnitude of the correction changes throughout a run, it is necessary that the data acquisition protocol uses frequent recalibration. This data acquisition sequence is analogous to that used in gas source stable isotope mass spectrometers, which sequentially acquire data from both sample and standard and then correct the measured sample ratio to the known ratio of the standard. Finally, the corrected sample $^{147}Sm/^{146}Nd$ isotopic ratio (measured multiplied by the correction factor) was converted to the desired $^{147}Sm/^{144}Nd$ by multiplying by the accepted ratio of $^{146}Nd/^{144}Nd$, 0.7219.

Results

Results of the analysis of a set of 12 selected geological reference materials are presented in Table 1. The selected materials have $^{147}Sm/^{144}Nd$ ratios covering a large range from a low of 0.08 (G-2, a light rare-earth element enriched granite) to a high of 0.30 (BIR-1, a light rare-earth element depleted basalt). There were four repeat determinations of each solution, and for three geological reference materials (BIR-1, W-1, and JB-1a), determinations were made on duplicate sample preparations, thus the number of determinations is 8 for these reference materials.

Precision

Almost all rock and mineral samples contain concentrations of Nd which are greater than those of Sm. A typical Type I carbonaceous chondrite has a Nd concentration of 0.711 ppm, and a lower Sm concentration of 0.231 ppm (Taylor and McLennan, 1985), a Nd(ppm)/Sm(ppm) ratio of 3. Also the isotopic abundance of ^{147}Sm is slightly less (15%) than that of ^{146}Nd (17%). Thus, in almost all geological samples, the count rate of the Sm isotope (^{147}Sm) is less than the count rate of Nd (^{146}Nd), and the errors in the ratio are determined predominately by the error in the determination of ^{147}Sm. Hence, the following discussion considers errors in the ratio as a function of the concentration of Sm.

The determined RSD in the $^{147}Sm/^{144}Nd$ ratio (Table 1) ranges from a low of 0.2% for SY-3, the material with the highest concentration of Sm (109 ppm) to a high of 1.0% for BIR-1, the sample with the lowest concentration of Sm (1 ppm). In Table 1, the RSD calculated from Poisson counting statistics alone is also given. The sigma ratio in Table 1 is the ratio of the measured RSD divided by the Poisson counting statistic RSD, which has a mean value of 1.55. These data are shown in Figure 1, where BIR-1 with the lowest concentration of Sm (1.07 ppm) is shown to have the largest error, while SY-3 with the highest concentration of Sm (109 ppm) has the smallest error. To a reasonable goodness of fit, the total error is approximately 1.55 times the counting statistics error. This sigma ratio of 1.55 is close to that obtained in our laboratory using our modified standard addition trace element trace analysis procedure (Longerich et al., 1990), where for 38 analyses of SY-2 in 38 runs using separate dissolutions and 10 s determination times, the RSD of the $^{147}Sm/^{144}Nd$ ratio was 1.2%, 1.6 times the Poisson RSD of 0.8%.

An analysis of variance of the difference between duplicate preparations (BIR-1, W-1, and JB-1a) showed no significant differences, t-test equal to 0.79, 0.01, and 1.06, respectively. There is no significant difference for the separate digestion, not unexpectedly, as isotope ratios are relatively insensitive to sampling error, to incomplete dissolution, and to sample loss during preparation.

It is recognized that the precision could be improved if the measurement time of ^{146}Nd were decreased, with a corresponding increase in the measurement time of ^{147}Sm. At the limit of doubling the acquisition time for ^{147}Sm, the maximum possible improvement in the error of measurement of the ^{147}Sm intensity would be obtained. Neglecting the small contribution from the background, and from the standardization, this would result in a reduction in the RSD of the ^{147}Sm intensity by the inverse of the square root of 2 (0.71), from 1.78% to 1.26% (Fig. 2). Thus, the maximum

Table 1. Values for the $^{147}Sm/^{144}Nd$ ratio in 12 standard reference materials

			$^{147}Sm/^{144}Nd$							
Sample	Sm ppm	Nd ppm	literature	mean determined	rel. dif.	RSD determined	RSD Poisson	sigma ratio	t test	n
BIR-1 (basalt)	1.07	2.19	0.2954	0.2792	-5.7%	1.0%	1.0%	1.1	-15.9	8
DNC-1 (diabase)	1.38	4.9	0.1703	0.1784	4.7%	0.4%	0.7%	0.6	22.5	4
W-1 (diabase)	3.68	14.6	0.1524	0.1521	-0.2%	0.6%	0.5%	1.2	-0.9	8
JB-1a (basalt)	5	27	0.1120	0.1165	4.0%	0.5%	0.4%	1.3	21.2	8
JG-1a (granodiorite)	4.5	19.7	0.1381	0.1350	-2.3%	0.4%	0.4%	1.0	-11.0	4
AGV-1 (andesite)	5.9	33	0.1081	0.1098	1.6%	0.3%	0.4%	0.8	10.6	4
BHVO-1 (basalt)	6.2	25.2	0.1488	0.1496	0.6%	0.7%	0.4%	2.0	1.6	4
BCR-1 (basalt)	6.59	28.8	0.1384	0.1388	0.3%	0.3%	0.3%	0.8	2.5	4
G-2 (granite)	7.2	55	0.0792	0.0810	2.3%	0.7%	0.3%	2.2	6.4	4
JG-2 (granite)	7.2	24	0.1814	0.1862	2.6%	0.9%	0.3%	2.8	5.5	4
SY-2 (syenite)	16.1	73	0.1334	0.1266	-5.2%	0.3%	0.2%	1.4	-37.4	4
SY-3 (syenite)	109	670	0.0984	0.1022	3.8%	0.2%	0.1%	3.2	30.1	4
mean								1.55		

Compiled values for the concentrations of Sm and Nd in the table are taken from Govindaraju (1989), except for the values for JG-1a which are from Ando et al. (1989), and for BIR-1 which are from Jochum et al. (1988). Literature values for the ratio, $^{147}Sm/^{144}Nd$, are calculated from the tabulated values of the elemental concentration of Sm and Nd. The values of "rel. diff." are the relative difference (determined-literature). The uncertainties are relative standard deviations "RSD" of a single 6 min determination. The sigma ratio is the ratio of the standard deviation between samples (determined) and the standard deviation due to Poisson counting statistics alone. To compare the difference between literature and determined values of $^{147}Sm/^{144}Nd$ the statistical t-test value is given; see text for further interpertation. The number of determinations (n) is 4 or 8.

possible reduction in the RSD of the ratio obtained by using unequal data acquisition times for ^{147}Sm and ^{146}Nd would be to 71% of the RSD obtained using equal data acquisition times. The actual reduction in the RSD must be less since this reduction neglects the accompanying increase in the RSD of the Sm intensity as the Sm data acquisition time is decreased. In any rock sample, the improvement will be less, as the acquisition time for ^{146}Nd cannot be reduced close to zero.

In Figure 2, the Poisson RSD for the Sm/Nd ratio is shown as a function of Nd data acquisition times of 0 to 240 s, with the constraint that the sum of the data acquisition time for Nd and Sm is 240 s. Also shown is the RSD for the Sm intensity and the RSD for the Nd intensity. These data were calculated using a model in which the operating conditions and data acquisition sequence of this study are used, with a background of 10 counts• s^{-1}. The contribution of the small error due to the calibration is neglected. The Nd and Sm concentrations are that of a sample with typical chondritic concentrations (Sm = 0.231 ppm and Nd = 0.711 ppm). The RSD of the isotope ratio using equal data acquisition times for Sm and Nd of 120 s is 1.97%. The minimum RSD (1.86%) of the Sm/Nd ratio occurs when the data acquisition time for Nd is decreased to 78 s with a corresponding increase in that of Sm to 162 s, an insignificant improvement over that from equal data acquisition times of 120 s. At what might be thought to be the optimum acquisition time, where the RSD of Sm (1.39%) equals the RSD of Nd (Nd data acquisition time of 46 s), results in an RSD of the ratio of 1.97%, the same as obtained using equal data acquisition times of 120 s.

The predicted RSD for the determination of the $^{147}Sm/^{144}Nd$ isotope ratio is shown in Figure 3, using 120 s per isotope data acquisition, and a sigma ratio of 1.55 for samples with Sm concentrations from 1 ppm to 16 ppm. The error is 1.4% for a sample containing 1 ppm Sm, decreasing asymptotically with increasing Sm concentration to 0.3% at a Sm concentration of 16 ppm. The model uses a Sm/Nd ratio equal to that of a chondrite, and thus overestimates the total error for a light rare-earth element enriched sample. The model assumes our standard operating conditions (1000 cps/ppb for a monoisotopic rare-earth element), a background of 10 counts• s^{-1}, and a sample solution containing 1 g rock per kg of solution (i.e. a dilution factor of 1000).

Accuracy

Accuracy is much more difficult to assess than precision due to the lack of high precision published values for the concentrations of Sm and Nd in geological reference materials. Further, there are few published values for $^{147}Sm/^{144}Nd$ isotope ratios in geological reference materials. As well, there is a limited amount of data on the uncertainties of the available compiled concentration values.

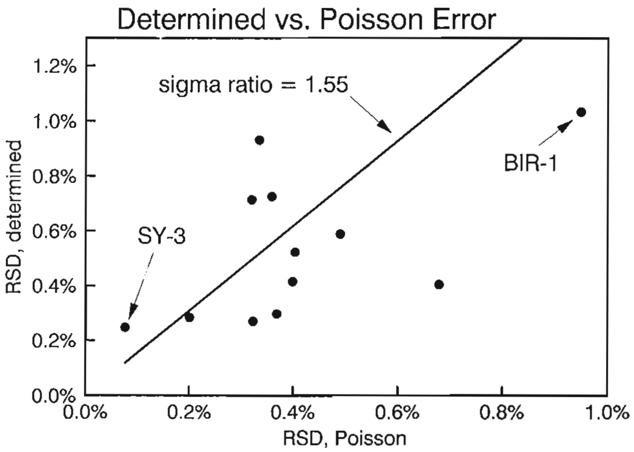


Figure 1. Determined versus Poisson RSD for the determination of the $^{147}Sm/^{144}Nd$ ratio. Data was obtained using a data acquisition time of 120 s for each isotope (^{146}Nd and ^{147}Sm). The solid line indicates a determined error which is 1.55 times the error (sigma ratio = 1.55) due to Poisson counting statistics only.

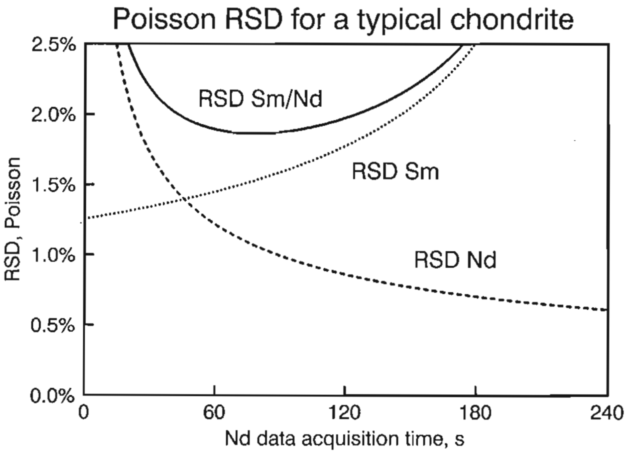


Figure 2. Poisson RSD for the determination of Sm/Nd, Sm, and Nd in a rock having concentrations of a typical chondrite. The RSD is presented as a function of the data acquisition time of Nd from 0 to 240 s, while the total data acquisition time for Sm plus Nd is held constant at 240 s.

The USGS reference material BCR-1 is, in this author's opinion, probably the best characterized material produced by the geological community, as testified by the 151 page compilation report of Gladney et al. (1990) devoted entirely to this material. Gladney et al. (1990) reported a BCR-1 consensus value for Sm (6.59 ± 0.12 ppm) and Nd (28.8 ± 0.5 ppm), which, using the laws for propagation of error, gives a relative error of 2.5% for the $^{147}Sm/^{144}Nd$ ratio. Gladney et al. (1990) also gave a more precise value for $^{147}Sm/^{144}Nd$ based upon a compilation of five reports using IDMS of 0.1371 ± 0.0013 (0.9%). For comparison, the results of this study (Table 1) for a single determination of $^{147}Sm/^{144}Nd$ in BCR-1 give an RSD of 0.3%.

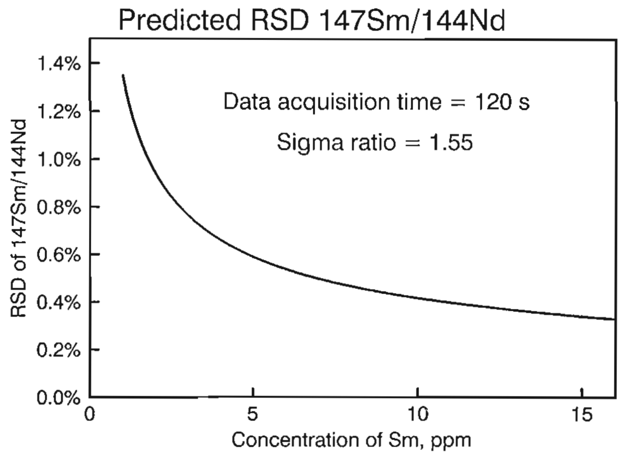


Figure 3. Predicted RSD of the $^{147}Sm/^{144}Nd$ isotope ratio versus the concentration of Sm. Data is for one measurement using a data acquisition time of 120 s for each isotope (^{146}Nd and ^{147}Sm). The predicted error is calculated as 1.55 times the error (sigma ratio = 1.55) due to Poisson (counting) statistics only.

Gladney et al. (1983) have produced a similar compilation for 11 USGS reference materials, including the materials AGV-1, G-2, and W-1, which were analyzed in this study. Using the uncertainties for the Sm and Nd values given by Gladney et al. (1983), the relative uncertainties for $^{147}Sm/^{144}Nd$ are 17% for AGV-1 and G-2, with a higher uncertainty of 22% for W-1. A later compilation by Gladney and Roelandts (1990) give data for three Canadian Certified Reference Material Project (CCRMP) materials including SY-2 and SY-3. Using the uncertainties for the Sm and Nd values given by Gladney and Roelandts (1990), the relative uncertainties are 16% for SY-2 and 26% for SY-3. For comparison this study reports RSDs (Table 1) between 0.2% and 0.7% for this set of five reference materials.

For other reference materials, some idea of the uncertainty in the compiled values can be obtained from inspection of the number of significant figures to which the compiled data is expressed (Govindaraju, 1989). Inspection of the compiled values of Table 1 shows a worst case in the value of 5 ppm Sm in JB-1a which, based upon the number of significant figures stated, implies an uncertainty of 0.5 ppm (relative error = 10%). While this is the worst case of the data in Table 1, even the value of 73 ppm for the concentration of Nd in SY-2 implies an error of 0.5 (relative error = 0.7%) compared to the RSD determined for the isotope ratio of 0.3%.

The relative difference between this method and literature values for $^{147}Sm/^{144}Nd$ for a wide range of sample types is, however, within a limited range of from -6% to 5% (Table 1), while the ratio itself, $^{147}Sm/^{144}Nd$, varies over a wide range from 0.08 to 0.30. The student's t-test is calculated and shown in Table 1 for the difference between the literature and the determined value of $^{147}Sm/^{144}Nd$. The absolute value of the t-test is less than 3 (3 standard deviations of the difference) for the well-characterized USGS samples W-1, BHVO-1, and BCR-1 (cf. Jenner et al., 1990). Thus, for these well-characterized geological reference materials there is no significant difference between the results of this study and those in the literature. For the remaining materials there is a significant difference between the literature and the values determined in this study (cf. Jenner et al., 1990). While there is a statistically significant difference between the literature and this study, the absolute value of the relative difference is less than 6%, a typical error in absolute concentrations determinations.

CONCLUSIONS

Using fast sequential data acquisition to determine the isotope ratio, $^{147}Sm/^{144}Nd$, with correction for instrumental effects, including mass discrimination and degree of formation of the singly charged ion, and the drift in these effects by frequent recalibration, it has been demonstrated here that ICP-MS can be a powerful tool for application in isotope geochemistry. The determination of $^{147}Sm/^{144}Nd$ ratios using ICP-MS will be most useful for studies on Palaeozoic and younger samples characterized by Sm concentrations greater than 5 ppm. For example, most sedimentary and granitic samples (Taylor and McLennan, 1985) fulfil this requirement. Regional Nd isotopic tracing studies on such rocks are useful to constrain providence, to estimate crustal recycling, and provide model ages (DePaolo, 1988).

The errors for samples with Sm concentrations less than 5 ppm are higher than those tolerated for most applications. However, a rare-earth element ion-exchange group separation (Longerich et al., 1990) can easily be used to concentrate these elements ten-fold, while reducing the matrix concentration to a level which can be tolerated by ICP-MS (total dissolved solids less than 300 ppm). With this sample preparation procedure, the errors can be reduced and useful determinations can be made on samples with Sm concentrations less than 5 ppm. The errors presented in this paper are the uncertainties of a single 6 min analysis. Error can be reduced by making replicate measurements. For example, by obtaining four replicates, the error can be reduced by 2 (the square root of 4) which places the determined error for many samples into a useful range, making the technique applicable for a far wider variety of rock types.

Effort by the geoanalytical community is needed to establish accurate values for the concentrations of all the rare-earth elements, especially Sm and Nd, and Sm/Nd isotope ratios in geological reference materials with certified accuracies better than 1%, for a set of rocks with concentrations of Sm as low as 1 ppm. The development of ICP-MS techniques has made the compiled values of the concentrations of many trace elements in geological reference materials at concentrations levels in the low parts per million range inadequate.

ACKNOWLEDGMENTS

The samples and standards were meticulously prepared by P. Horan, and the ICP-MS data acquisition was carried out by S. Jackson. Discussions with and a careful reading by G. Jenner and B. Fryer are acknowledged. Financial support was obtained from NSERC in the form of a major installation grant, which made possible the original purchase of instrumentation, and the continuing support of the operation of the facility through an NSERC infrastructure grant. Further support was obtained from NSERC in the form of an operating grant to the author and an NSERC infrastructure grant in support of the radiogenic facilities at Memorial. The generous support of Memorial University is also acknowledged.

REFERENCES

Ando, A., Kamioka, H., Terashima, S., and Itoh, S.
1989: 1988 values for GSJ rock reference samples, "Igneous rock series"; Geochemical Journal; v. 23, p. 143-148.

Belchamber, R.M. and Horlick, G.
1982: Noise-power spectra of optical and acoustic emission signals from an inductively coupled plasma; Spectrochemica Acta, v. 37B, p. 17-27.

DePaolo, D.J.
1988: Neodymium isotope geochemistry: an introduction; Springer-Verlag, Berlin, 187 p.

Gladney, E.S. and Roelandts, I.
1990: 1988 compilation of elemental concentrations for CCRMP reference rock samples SY-2, SY-3, and MRG-1; Geostandards Newsletter, v. 14, p. 373-458.

Gladney, E.S., Burns, C.E., and Roelandts, I.
1983: 1982 compilation of elemental concentrations in eleven United States Geological Survey rock standards; Geostandards Newsletter, v. 7, p. 3-226.

Gladney, E.S., Jones, E.A., Nickell, E.J., and Roelandts, I.
1990: 1988 compilation of elemental concentrations data for USGS basalt BCR-1; Geostandards Newsletter, v. 14, p. 209-359.

Govindaraju, K.
1989: 1989 compilation of working values and sample description for 272 geostandards; Geostandards Newsletter, v. 13, p. 11-38.

Houk, R.S.
1985: Mass Spectrometry of Inductively Coupled Plasmas; Analytical Chemistry, v. 58, p. 97A-105A.

Jenner, G.A., Longerich, H.P., Jackson, S.E., and Fryer, B.J.
1990: ICP-MS – a powerful tool for high-precision trace-element analysis in Earth sciences: evidence from analysis of selected U.S.G.S. reference samples; Chemical Geology, v. 83, p. 133-148.

Jochum, K.P., Seufert, H.M., Midinet-Best, S., Rettmann, E., Schonberger, K., and Zimmer, M.
1988: Multi-element analysis by isotope dilution-spark source mass spectrometry (ID-SSMS); Fresenius, Zeitschrift fuer Analytische Chemie, v. 331, p. 104-110.

Longerich, H.P., Jenner, J.A., Fryer, B.J., and Jackson, S.E.
1990: Inductively coupled plasma-mass spectrometric analysis of geological samples: a critical evaluation based on case studies; Chemical Geology, v. 83, p. 105-118.

Longerich, H.P., Strong, D.F.S., and Kantipuly, C.J.
1986: Progress in evaluation of instrumental and other parameters affecting chemical and isotopic analysis by inductively coupled plasma-mass spectrometry (ICP-MS); Canadian Journal of Spectroscopy, v. 31, p. 111-121.

Potts, P.J.
1987: A Handbook of Silicate Rock Analysis; Blackie, Glasgow and London, 622 p.; p. 531.

Taylor, S.R. and McLennan, S.M.
1985: The continental crust: its composition and evolution; Blackwell, Oxford, 312 p.

A rapid field method for the determination of gold in rocks and soils

Y. Lu[1]

Abstract: Extraction of Au is performed at room temperature using a mixture of thiourea, sulphuric acid, hydrogen peroxide, and ammonium fluoride. Polyurethane foam loaded with active charcoal is used to separate Au from solution. After ashing and extraction of Au into buffer solution, 0.05 mL of TMK (Thio Micher's ketone) is added and the Au is extracted into a small organic solvent drop for analysis by colorimetry. The method is rapid, simple, and sensitive. The range of determination of Au is from 1 ppb to 10 ppm. Forty determinations can be made in one working day.

Résumé : On réalise l'extraction de l'or à la température ambiante avec un mélange de thiourée, d'acide sulfurique, de peroxyde d'hydrogène et de fluorure d'ammonium. On emploie de la mousse de polyuréthane chargée de charbon actif pour séparer l'or d'une solution. Après réduction en cendres, et extraction de l'or dans une solution tampon, on ajoute 0,05 ml of TMK (thiocétone de Michler) et l'on extrait l'or dans une gouttelette de solvant organique que l'on soumet à une analyse colorimétrique. Cette méthode est rapide, simple et sensible. Le dosage de l'or s'effectue dans la gamme de 1 ppb à 10 ppm. On peut effectuer quarante dosages en une seule journée de travail.

---

[1] Institute of Geophysical and Geochemical Exploration, Langfang, Hebei 102849, P.R. China.

INTRODUCTION

Geochemical exploration for Au has achieved great success recently in China: during the implementation of China's national geochemical mapping project (Xie et al., 1989), thousands of significant regional Au anomalies were delineated. After follow-up and detailed geochemical and geological surveys, more than 300 new Au occurrences were found, many of which are developing into workable mines. A variety of rapid field methods have been developed by Chinese workers for field determination of Au in samples collected during follow-up of the regional Au anomalies and detailed geochemical surveys. The methods developed by Jiang (unpub. report, 1986) using hot aqua regia attack in closed vessels, polyurethane foam or sulphydryl cotton preconcentration, and TMK colorimetry achieve a detection limit of 4-5 ppb. Although closed vessels were used, the irritating odour from aqua regia during operation under field conditions could not be avoided. Interference of As, Sb, Bi, and Hg in complex mineralized samples is also a problem. This paper describes an alternative attack using thiourea in order to avoid these disadvantages.

EXPERIMENTAL

Reagents

1. TMK (Thio Micher's ketone), 0.02%.

20 mg of TMK is dissolved in 100 mL of a mixed solvent (80% absolute alcohol + 10% of octylamine + 10% tributylphosphate). Pour into a brown bottle wrapped with black paper and store in a dark place. This is diluted to 0.002% of TMK when used.

2. Standard Au solution.

Stock solution: 100 μ g/mL (in 10% aqua regia). Working solution: 100 ng/mL (in 1% aqua regia).

3. Buffer solution: pH 3.5 HOAc, NaOAc.
4. Mixed masking agent.

Dissolve 2 g of EDTA-Na$_2$, 1 g of NaF, 5 g of urea in water and dilute to 100 mL.

5. Standard ferric chloride solution: 1 mg/mL FeCl$_3$.
6. Potassium chloride: 20% (w/V) aqueous solution.
7. Thiourea-sulphuric acid mixture.

Prepare 20% sulphuric acid. After cooling, add thiourea by 7% (w/V), stir and mix well.

8. "OP" solution, 2% (w/V).

2 mL of polyethylene glycol octyplunyl ether is dissolved in water and diluted to 100 mL.

Apparatus

1. Water bath.
2. Electric heater (1.5 kW).
3. Alcohol burner.
4. Polyethylene bottle (150 mL).
5. Porcelain crucible, 5 or 10 mL.

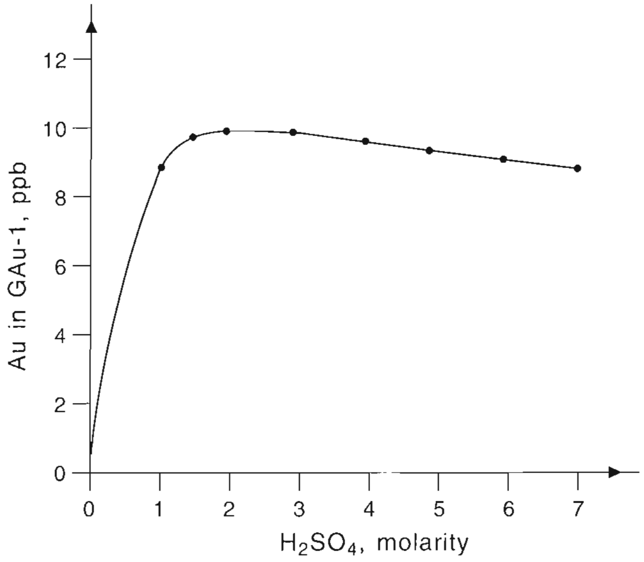


Figure 1. Effect of sulphuric acid concentration on the extraction Au by thiourea.

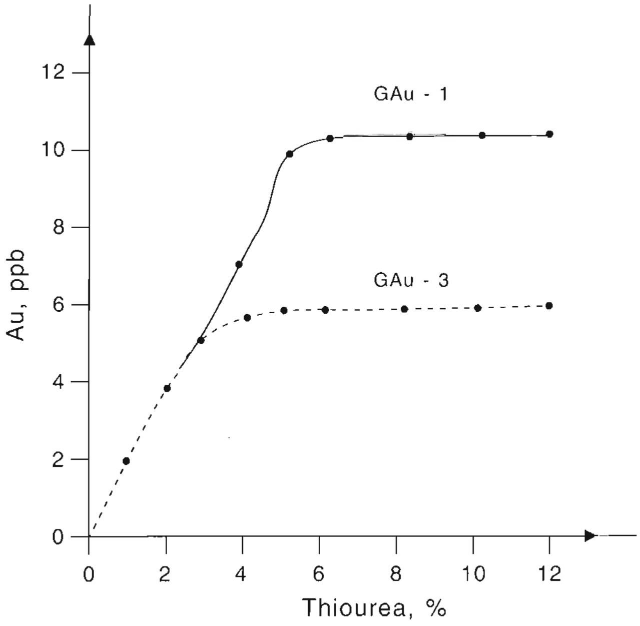


Figure 2. Effect of thiourea concentration on the determination of Au in standard samples, GAu-1 and GAu-3.

Preparation activated charcoal loaded polyurethane foam

1. Preliminary treatment.

Cut the foamed polyurethane to 1.5x1x1.5 cm pieces (about 0.15 g each). After washing, soak them into 0.5 M HNO_3 for 12 h. After washing with water, dry at room temperature. Soak them with acetone (the volume will increase by two folds), and squeeze (the original volume is restored).

2. Grind activated charcoal to 200 mesh, and put it into a plastic vessel.
3. Put (1) into (2). Rub and squeeze the small pieces by hand and soak in water. Extract the foam piece and shake off excess charcoal. Dry for use. The activated charcoal load is about 20 mg per piece.

Procedure

Weigh out 10 g of sample into a polyethylene bottle, wet with a little water, add 2 g of ammonium hydrogen fluoride, 25 mL of thiourea-sulphuric acid mixture, and 5 drops of hydrogen peroxide. Shake the bottle to disperse the sample well. Stand at least 2 h, and shake 2-3 times during standing (stir with a plastic rod if the sample adheres the bottom). Dilute to about 100 mL, add a piece of polyurethane foam and turn the lid tightly, shake for 30 min. Pick out the foam piece, wash with water, and squeeze to dryness. Wrap it with a piece of qualitative filter paper and put it into a porcelain crucible. Add 3 mL of alcohol, heat on an electric heater and ash it, igniting on a burner until the black carbon disappears. Cool, add 2 drops of 20% KCl, 2 drops of ferric chloride solution (0.1 mg of Fe), 2 mL of 2:1 HCl, and 2 mL of 30% H_2O_2. Stand 3-5 min. Evaporate to dryness on a water bath. Add 2 drops of mixed washing agent and 2 drops of absolute alcohol. Shake well and stand for 5 min. Add 0.05 mL of 0.002% TMK and 3 drops of water. Add 2 drops of water after micro-beads appear. Rotate the crucible carefully to merge the micro-beads together. Compare the colour of bead formed visually with the standard series. If the amount of Au is higher than 40 ppb, 0.05 mL of 0.02% TMK should be added.

Standard series

Measure 0, 10, 20, 30, 40,... 2000 ng of Au into plastic bottles. Carry out the above procedure. For 10 g of sample, the Au concentration is equal to 0, 1, 2,... 20 ppb respectively. For 40 ppb, 0.02% TMK is used; above 100 ppb, 0.1 mL of 0.02% TMK is used.

DISCUSSION

Conditions for cold extraction of Au by thiourea

Experiments by the author showed that 15-20% H_2SO_4 (about 3 M) is appropriate for the efficient extraction of Au by thiourea (Fig. 1). Higher concentrations of H_2SO_4 yield low results. This can be explained by the free sulphur formed due to the increased rate of oxidation of thiourea. Sample particles may be occluded by free sulphur and protected from further attack by thiourea. Figure 2 shows the effect of the concentration of thiourea upon the extraction of Au from samples. Complete or consistent extraction can be achieved when the concentration of thiourea is more than 5%.

Table 1 shows that complete extraction of Au from samples can be obtained if the extraction is proceeded for 2 hr. If the particle size is greater than 74 µm, the sample should sit overnight. Hydrogen peroxide is used as the oxidizing agent to accelerate the dissolution of Au by thiourea. In acid solution the following reaction may occur:

$$2Au + 4(NH_2)2CS + H_2O_2 + 2H \rightarrow 2Au\,[(NH_2)2CS]_2 + 2H_2O$$

Hydrogen peroxide must not be added too early or in excess, otherwise free sulphur will be formed due to the increased rate of oxidation of thiourea. It is appropriate to added H_2O_2 separately after the addition of thiourea-H_2O_4 solution. Five drops of 30% H_2O_2 may be sufficient. The addition of fluoride facilitates the dissolution of Au by thiourea.

Preconcentration

Polyurethane foam has been used successfully for the concentration of negative Au complex ions from solution (Luo et al., 1980). However, incomplete absorption is obtained for the Au-thiourea positive complex, $Au(N_2H_4CS)_2$ (Table 2). The use of tributyl phosphate loaded polyurethane foam raises the percentage of preconcentration

Table 1. Effect of standing time on the extraction of Au

	Sample 1				Sample 2			
	certified value	this method			certified	this method		
standing 2 h	13	10	11	10	5	5	6	5
standing 28 h	13	10	12	12	5	5	6	6

Table 2. Preconcentration of the Au-thiourea complex positive ion by unloaded polyurethane foam in different acidic media

	HCl (5%)	$HClO_4$ (5%)	H_2SO_4 (5%)
added Au (ng)	50	50	50
found Au (ng)	35,23,28	29,36,33	29,38,35
Au recovery (%)	46-70	58-72	58-76

Table 3. Preconcentration of Au-thiourea complex positive ion by activated charcoal loaded polyurethane foam in 5% H_2SO_4

added gold (ng)	2.5	5.0	10.0	20.0	50.0	100	500
found gold (ng)	2.4	4.9	11.0	19.0	49.0	101	490
	2.6	5.5	10.5	20.5	51	98	490
	2.6	6.0	9.0	22.0	52	95	480
Au recovery (%)	96-104	98-110	90-110	95-110	98-103	95-101	96-98

Table 4. Results of the determination of Au in standard samples by the proposed method

Sample	Au, certified ppb	This method ppb					mean ppb	RSD %
GAu-1	13	8	8	7	9	10	8.4	15.5
GAu-5	3.2	2.5	3.0	3.0	4.0	4.0	3.3	20.3
GAu-6	25.4	19	20	18	21	23	20.2	9.5

RSD: Relative standard deviation

of $Au(N_2H_4CS)_2$ to 98% (Braun and Farag, 1973a, b), but it is difficult for further operation especially in field conditions. The author used activated charcoal (-200 mesh) loaded polyurethane foam to achieve satisfactory preconcentration (Table 3). It is easy to prepare and to ignite to ash after preconcentration.

Determination of Au

For obtaining a very low detection limit of Au in TMK colorimetry, the microanalysis technique of Shen et al. (1988) is used, with modification for field conditions. Colour development proceeds in a small crucible; only 0.05 mL of 0.002% TMK solution is added. The coloured floating drop formed is compared with a series of colour standards. If organic matter, As, Sr, and Sb are present in high amounts, the samples must be ignited first: 100 mg As or Bi, 20 mg Hg or 50 mg Pb will produce a positive interference of 1 ppb Au, 10 mg Sb will cause a blue tint to the drop formed. If, after ignition of the sample, significant amounts of As and Sb still remain, 2 drops of 20% ammonium fluoride are added to the ash, which is then dried and ignited to volatilize the interfering elements.

RESULTS

Standard samples for Au determination (Yan and Wang, 1986) GAu-1, GAu-5, and GAu-6 were analyzed using the field method. The results are comparable with the certified Au values of these standards. One hundred eighty-six samples were analyzed by the field method and also by graphite furnace atomic absorption spectrometry. Some of the data are listed on Table 4 for comparison.

CONCLUSION

A rapid field method for the determination of Au in rocks, soils, and other surface materials has been developed with a detection limit of 1 ppb. The method has been used to determine Au in several thousand samples in China and will become a powerful tool for geochemical reconnaissance and follow-up surveys.

REFERENCES

Braun, J. and Farag, A.B.

1973a: Reversed-phase foam chromatography chemical enrichment and separation of gold in the TBP-thiourea-perchloric acid system; Analytica Chimica Acta, v. 65, p. 115-126.

1973b: The recovery of gold from thiourea solution with open-cell polyurethane foams; Analytica Chimica Acta, v. 66, p. 419-426.

Luo, D., Zhou, L., Du, J., Liu, X., and Liming

1980: Determination of gold by AAS after using thiourea to de-absorp gold enriched by polyurethane foam; Analytical Chemistry, v. 8(1), p. 77-79 (in Chinese).

Shen, S., Qui, W., Li, P., and Zhou, X.

1988: Micro-ball colorimetric determination of trace gold; Analytical Chemistry, v. 16(2), p. 153-155 (in Chinese).

Xie, X., Sun, H., and Ren, T.

1989: Regional Geochemistry-National Reconnaissance Project in China; Journal of Geochemical Exploration, v. 33, p. 1-9.

Yan, M. and Wang, C.

1986: Development of Geochemical standard samples of trace gold; Geophysical and Geochemical Exploration, v. 10(3), p. 233-236 (in Chinese).

An on-site method for measuring aluminum speciation in shallow well water samples from areas exposed to acid deposition

J.C. Meranger[1], R.E. Lett[2], and T. Pickering[2]

Abstract: An on-site procedure involving filtration and ion exchange has been developed to study aluminum speciation in water samples collected from shallow wells. Immediately following collection the samples are mixed continuously with Chelex 100 ion exchange resin for eight hours. At intervals during the mixing cycle subsamples of the water are taken, preserved with acid, and later analyzed for aluminum by graphite furnace atomic absorption spectrophotometry. The method has been applied to an examination of Al chemistry in the water from shallow wells in rural areas of eastern Canada where there is evidence of exposure to the impact of acid deposition. The results show that in weakly acid wells much of the Al remains in polymeric form whereas in more strongly acid waters (below pH 5.8) the Al is predominantly in an easily extractable monomeric form.

Résumé : On a élaboré un procédé *in situ* de filtration et d'échange d'ions, pour étudier la spéciation de l'aluminium dans des échantillons d'eau recueillis dans des puits de faible profondeur. Immédiatement après leur collecte, on mélange les échantillons de façon continue avec de la résine échangeuse d'ions Chelex 100 pendant huit heures. À intervalles réguliers au cours du cycle de mélange, on recueille des sous-échantillons d'eau, que l'on conserve avec de l'acide et dont on dose ensuite l'aluminium par spectrophotométrie d'absorption atomique dans un four en graphite. On a appliqué cette méthode à la chimie de l'aluminium dans l'eau de puits peu profonds des zones rurales de l'est du Canada, où existent des indices d'une exposition aux effets de dépôts acides. Les résultats montrent que dans les puits faiblement acides, une grande partie de l'aluminium reste sous forme polymère, tandis que dans les eaux plus fortement acides (pH inférieur à 5,8), l'aluminium apparaît principalement sous une forme monomère facilement extractible.

---

[1] Environmental Health Directorate, Health and Welfare Canada, Tunney's Pasture, Ottawa, Ontario, K1A 0L2, Canada.
[2] Barringer Laboratories, 5735 McAdam Road, Mississauga, Ontario, L4Z 1N9, Canada.

INTRODUCTION

Increased aluminum levels in North American and Scandinavian lakes have been attributed to the impact of atmospheric acid deposition ("acid rain") on soil within lake catchment basins. High levels of dissolved aluminum are toxic to freshwater fish (Robinson and Deano, 1986) and the accelerated aluminum depletion from soil may also be a factor in forest decline. The aquatic chemistry of aluminum is complex and the extent of toxicity depends not only on the actual concentration, but also on the relative abundance of the different physical and chemical forms. There is considerable literature on the behaviour of aluminum during the weathering of geological materials in areas exposed to acid deposition (Bache, 1986; Johnson et al., 1981). Several analytical schemes have been developed to measure the abundance of various chemical forms of aluminum in natural waters. For example, Loescher (1984) used dialysis in conjunction with extraction with 8-hydroxyquinoline isobutyl ketone to distinguish monomeric, monomeric-organic, and less labile aluminum forms. Driscoll (1984) and Campbell et al. (1983) employed an ion exchange resin as a means of partitioning aluminum forms. Andelman and Miller (1986) used Chelex 100 ion exchange resin to distinguish between rapidly exchangeable aluminum (absorbed in 1-4 hours), slowly exchangeable aluminum (absorbed in 4-24 hours), and inert aluminum (unabsorbed after 24 hours).

One problem associated with these partitioning methods is the unavoidable change in the aluminum chemistry which can occur if there is a lengthy delay between sample collection and analysis. Loescher (1984) avoided this problem by performing the extractions within four hours of taking the sample. Water chemistry investigations in remote areas where several days may separate collection from extraction and analysis require that a modified protocol be used if results of these studies are to be reliable. A partitioning method, based on the technique used by Andelman and Miller (1986), was therefore developed. The procedure involved extraction of aluminum with Chelex 100 ion exchange resin over an eight hour period, preservation of aluminum with acid and laboratory analysis of these solutions by graphite furnace atomic absorption spectrophotometry (GFAAS). A description of the method and its application to the analysis of shallow (dug) well drinking water samples from Nova Scotia are given in this paper.

ALUMINUM EXTRACTION METHOD

Before extractions were begun, a batch of Chelex 100 resin (Bio-Rad Laboratories, 50-100 mesh) was equilibrated at pH 6.0 with a solution containing Mg and Ca concentrations similar to those found in the Nova Scotia shallow well waters by Meranger and Gladwell (1986). The general water sampling and extraction procedure involved preparation of eight 100 mL polycarbonate bottles each containing 1 g of the prepared Chelex 100 resin. The polycarbonate bottles, tubes and other equipment were soaked in nitric acid and rinsed several times in distilled, deionized water. Aluminum values were than obtained on the deionized water rinses using GFAAS under the conditions outlined below. All values were below the detection level of 0.001 mg/L Al. At each site, a 5 mL portion of the raw drinking water was transferred directly to a clean polycarbonate tube with 150 μL of ultrapure nitric acid. A second 5 mL portion of the water was filtered through a 0.4 μm nuclepore filter into a polycarbonate tube and acidified with ultrapure nitric acid. These two samples were designed to provide total and dissolved Al concentration at "zero time" in the extraction cycle. A 100 mL portion of the water was transferred to a Chelex resin charged polycarbonate bottle. The bottle was then inserted in a rotating mixer installed in the field vehicle and the mixing cycle started. After one hour the mixing was interrupted, the bottle removed and a 5 mL portion transferred to a polycarbonate tube with 150 μL of ultrapure nitric acid. The mixing was restarted and further samples were taken and preserved at four and eight hours from the start of the cycle. Using this extraction system, four to six water samples could be extracted and treated each day. After the samples had been returned to the laboratory, 350 μL of hydrogen peroxide were added to each tube. In addition to the resin extracted samples, an unfiltered, unacidified water sample was taken for determination of pH, anions, and alkalinity. Unfiltered, acidified and filtered (0.45 μm), acidified samples were also collected at each site for analysis of metals. All samples were maintained at 4°C between the field and the laboratory.

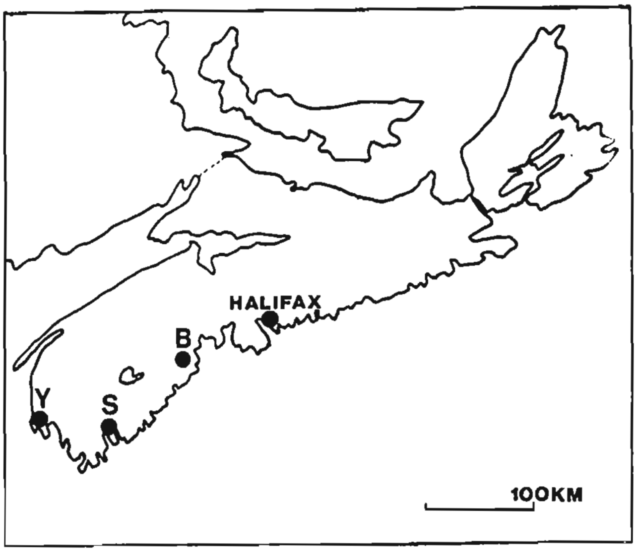
FIELD APPLICATION

The method was applied to a study of shallow (dug) well water chemistry in the area around Shelburne and Yarmouth, Nova Scotia (Fig. 1). Five private drinking wells were sampled near Yarmouth and three near Shelburne. At each well samples were taken from the faucet in the home after the system had been flushed for three to five minutes. The two areas have similar bedrock and surficial geology.

Bedrock of the Shelburne area consists of Cambrian slates and younger granite partially concealed beneath a granite-quartzite, sandy glacial till and partially by glacial outwash deposits. Well drained, acid soils developed from the glacial deposits support a mixed evergreen-broadleaf forest growth. Areas of wetland are common along stream valleys. Bedrock of the Yarmouth survey area consists of Ordovician slates and volcanic rocks in contact with younger granites and covered by an older, silty, reddish brown glacial deposit and a younger, more sandy glacial deposit (Beaver River Till). These deposits have been moulded in drumlin land forms by the advancing ice. The area is partly cultivated with stands of mixed hardwood-softwood timber.

SAMPLE ANALYSIS

In addition to Al, the filtered and unfiltered water samples were analyzed for 28 other elements, alkalinity, dissolved organic carbon, and pH. Table 1 summarizes the analytical



NOVA SCOTIA SAMPLING SITES
Y - YARMOUTH
S - SHELBURNE
B - BRIDGEWATER

Figure 1. Nova Scotia sampling sites. Y-Yarmouth, S-Shelburne, B-Bridgewater.

methods employed for each parameter and the detection levels obtained. The techniques and parameters identified in Table 1 are described below.

ICP-ES (inductively coupled argon plasma-emission spectroscopy)

A 1:20 preconcentration of the water sample was obtained by evaporation on a sand bath at approximately 98°C, followed by analysis for metals by ICP-ES using an Applied Research Laboratories QA-137 spectrometer.

GFAAS (graphite furnace AAS)

Raw water samples were analyzed for Pd and Al by GFAAS using a Varian Model AA-475 fitted with a Perkin Elmer HGA-20 graphite furnace. Background correction was used for Pb and Al. Operating wave lengths were Pb-217 nm, Al-309.1 nm. For Pb, the dry time was 30 s at 125°C, the char time was 30 s at 500°C, and the atomize time was 10 s at 2700°C. For Al the dry time was 40 s at 200°C, the char time was 40 s at 1400°C, and the atomize time was 10 s at 2400°C followed by a 90 s cool down time.

IC (ion chromatography)

Raw water samples were analyzed for anions using a Dionex Model 2110i ion chromatograph with chemical suppression. Sodium carbonate-bicarbonate was used as the eluent solution.

DOC (dissolved organic carbon)

The filtered, raw samples were analyzed for DOC by automated colorimetry using a Chemlab Mark III colorimeter with an in-house manifold. The sample was first acidified and inorganic carbon sparged. The sample was then passed through a UV digester followed by a dialyser. The carbon dioxide evolved was dialysed into 50 mL of buffer solution (containing 5.0 g/L Na_2CO_3 and 2.5 g/L borax, adjusted to pH 9.45 with 0.1 N NaOH or H_2SO_4 + 1 mL 0.1% g/v phenolphthalein solution). The carbon content was measured as indicated by the colour change in the solution (when diluted to 2 L).

ALK (alkalinity and pH)

The alkalinity of the sample was measured by fixed endpoint titration to pH 4.5 using a Brinkmann Model 686/1 Titroprocessor. The pH of the sample was measured before

Table 1. Analytical methods employed in the study

Parameter	Method	Detection level (mg/L)
Alkalinity	ALK	
Al	GFAAS	0.001
Ag	ICAP	0.0005
B	ICAP	0.005
Ba	ICAP	0.0005
Be	ICAP	0.00005
Ca	ICAP	0.005
Cd	ICAP	0.0005
Cl	IC	0.01
Co	ICAP	0.005
Cr	ICAP	0.001
Cu	ICAP	0.001
Fe	ICAP	0.001
F	IC	0.01
K	ICAP	0.03
Mg	ICAP	0.001
Mn	ICAP	0.001
Mo	ICAP	0.02
Na	ICAP	0.05
Ni	ICAP	0.005
NO_3	IC	0.02
P	ICAP	0.05
Pb	GFAAS	0.001
Si	ICAP	0.01
Sr	ICAP	0.0005
SO_4	IC	0.02
Th	ICAP	0.005
DOC	COL	0.01
Ti	ICAP	0.0005
V	ICAP	0.0005
Zn	ICAP	0.001
Zr	ICAP	0.002
pH	ALK	

the titration which is carried out using standardized H_2SO_4 at concentrations ranging from 0.002 N to 0.01 N depending on the alkalinity levels expected in the sample.

RESULTS AND DISCUSSION

Prior to field application, the extraction method was tested in the laboratory using "synthetic" water of composition similar to that determined in Nova Scotia shallow wells (average 11.3 mg/L Ca, 2.5 mg/L Mg, pH 6.0) with the addition of 50 µg/L, 100 µg/L, and 500 µg/L Al spikes. Analysis of solutions removed at 1, 4, 8, and 24 hours from the start of the mixing cycle revealed that the resin extracted over 90% of the total Al in the first hour. The pH changed from 6.0 to 6.4 after 24 hours. The extraction profile for the 500 µg/L Al spike is identified as curve "A" in Figure 2. A second, identical experiment was carried out with the 500 µg/L Al spike, but with the addition of a 10 mg/L humic acid solution. This curve is identified as "B" in Figure 2.

Analytical data for the eight wells are shown in Table 2. The Yarmouth well waters (1-5) are generally harder and more alkaline than the Shelburne waters (6-8). This difference may reflect the finer texture and higher slate content of the glacial deposits in the Yarmouth area compared to the more sandy Shelburne overburden. The majority of Cd, Co, and Cr values are below detection level. Some of the water samples, especially in the Shelburne area, have high Cu content, probably as a result of leaching from the water distribution systems. The higher pH and hardness of the Yarmouth waters was reflected in the lower filtered Al concentrations compared to the total Al. Extraction profiles for Al with Chelex 100 resin (Fig. 2) reveal that more than 60% of the Al remains in solution after one hour in the Yarmouth waters (numbers 1, 2, 3, and 5), and more than 30% remains after 8 hours. In the Shelburne waters (6-8), however, over 60% of the Al is removed after one hour and over 80% after 8 hours. The Shelburne waters clearly have a much higher rapidly extractable Al content (exchanged in less than one hour) than do the Yarmouth waters. This difference can probably be explained by the lower pH and buffering capacity of the Shelburne shallow well waters.

Analytical data quality is shown by the results of GFAAS obtained by calibration curves (routine method) and by standard addition (Table 3). In Table 4 the results of duplicate extractions of Al from well water 1 are displayed.

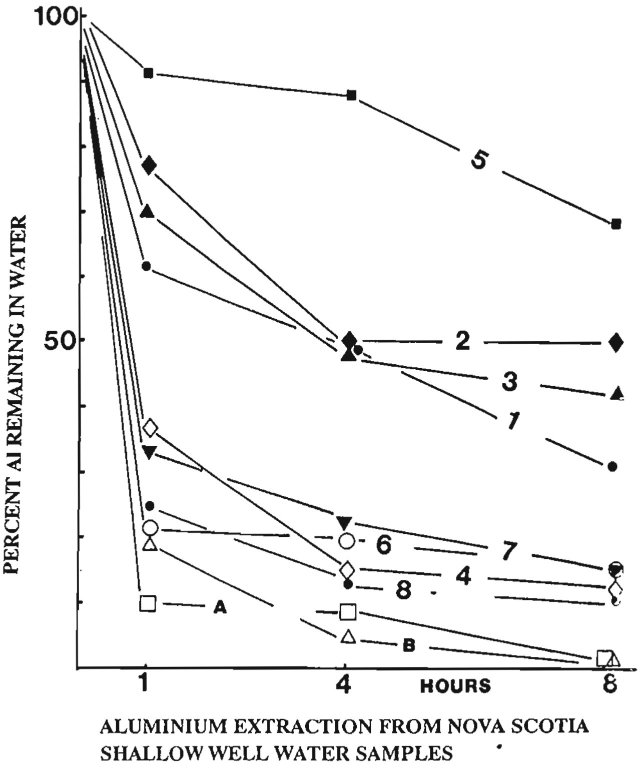


Figure 2. Aluminum extraction from Nova Scotia shallow well water samples.

Table 2. Nova Scotia shallow well water data*

Sample	Al*	Al	C	ALK	pH	Cu	Pb	Hard.	SO_4	NO_3	Fe	Zn
1	114	140	4.9	32	5.8	80	2	98	39	67	68	18
2	22	29	1.2	60	6.8	128	2	67	11	13	14	884
3	62	92	2.4	53	6.6	416	10	55	8	1	195	25
4	16	22	0.8	25	6.0	241	8	47	28	22	451	34
5	14	21	1.3	51	6.4	6	<1	50	16	1	3250	578
6	59	60	1.3	16	5.7	689	2	13	4	1	286	42
7	102	137	0.8	14	5.7	46	2	13	6	<1	1740	129
8	44	49	1.1	11	5.6	391	5	56	17	19	244	181

*Al, Cu, Fe, Pb, Zn in ug/L; Hardness, SO_4, NO_3 in C & ALK in mg/L
Al* - filtered (0.4 µm) sample

Table 3. Aluminum determined by calibration curve (Al-C) and by standard addition (Al-S). Concentrations in μg/L.

Site Number	Al-C	Al-S
1	140	135
3	90	96
5	21	20
7	137	140

Table 4. Duplicate extractions on the site 1 well water (Al in μg/L)

Time (h)	Al-extract.1	Al-extract.1 (repeat)
0	140	141
1	86	93
4	68	65
8	42	51

CONCLUSIONS

1. A procedure based on sample filtration, extraction with Chelex 100 resin, and residual sample preservation enables Al partitioning into readily extractable, moderately extractable, and inert forms in well water samples collected in remote areas where several days may separate sampling and laboratory analysis.
2. Applied to the examination of Al chemistry in the water from five shallow wells near Yarmouth and three wells near Shelburne, Nova Scotia, the method reveals a much higher amount of dissolved (less than 0.45 μm size) and readily extractable Al (monomeric forms) in water where pH is less than 5.8.

REFERENCES

Andelman, J.B. and Miller, J.R.
1986: The impact of acid rain on aluminum species in streams; WHO-CCIW Water Quality Bulletin, v. 11 (1), p. 19-25.

Bache, B.W.
1986: Aluminum mobilization in soils and waters; Journal of the Geological Society, London, v. 143, p. 699-706.

Campbell, G.C., Bisson, M., Bougie, R., Tessier, A., and Villeneuve, J.P.
1983: Speciation of aluminum in acid fresh waters; Analytical Chemistry, v. 55, p. 2245-2252.

Driscoll, C.T.
1984: A procedure for the fractionation of aqueous aluminum in dilute acid waters; International Journal of Environmental Analytical Chemistry, v. 16, p. 267-283.

Johnson, N.M., Driscoll, C.F., Eaton, J.S., Likens, G.F., and McDowell, W.H.
1981: "Acid Rain", dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire; Ceochemica et Cosmochima Acta, v. 45, p. 1421-1437.

Loescher, B.
1984: Aluminum speciation procedure pinpoints causes of acid rain in lakes; Canadian Research, March 1984, p. 43-44.

Meranger, J.C. and Gladwell, D.R.
1986: Application of conceptual model to assessing the impact of acid rain on drinking water quality; WHO-CCIW Water Quality Bulletin, v. 11, no. 1, p. 26-33.

Robinson, J.W. and Deano, P.M.
1986: Acid Rain: The effect of pH, aluminum and leaf decomposition product on fish survival; American Laboratory, March 1986, p. 17-26.

The challenges in managing a geoanalytical laboratory in Zimbabwe

E. Nyampingidza[1] and R.M. Tindwa[1]

Abstract: In Zimbabwe, with most of the instruments and reagents required for analysis being imported, an analytical laboratory, like any other establishment in the country, is greatly affected by lack of foreign currency. When the foreign currency is obtained, the waiting period for the importation of an instrument can be from 6 to 18 months or more. Meanwhile, both research and routine analytical work suffer. The instruments available in most cases are obsolete and replacements are either too late in coming or never come at all because nobody produces them any more. Lack of instruments is a problem facing the whole country. The other problem is the shortage of well trained staff who can competently execute the tasks given to them. These and many other problems make the job of managing a geoanalytical laboratory in Zimbabwe a bigger challenge to a chemist than the analysis itself.

Résumé : Au Zimbabwe, où la plupart des instruments et des réactifs nécessaires à l'analyse sont importés, les laboratoires d'analyse, comme tous les autres établissements du pays, sont sérieusement affectés par la pénurie de devises étrangères. Une fois ces devises obtenues, l'importation d'un appareil peut prendre de 6 à 18 mois, sinon plus. Entre temps, la recherche et les analyses de routine en souffrent les conséquences. Dans la plupart des cas, les instruments disponibles sont trop anciens et les appareils de remplacement mettent trop de temps à arriver ou n'arrivent jamais parce qu'ils ne sont plus fabriqués. La pénurie d'appareils est un problème auquel doit faire face le pays tout entier. L'autre problème est le manque de personnel bien formé, capable d'exécuter avec compétence les tâches qui lui sont confiées. Ces problèmes entre autres font que pour un chimiste, la gestion d'un laboratoire de géoanalyse au Zimbabwe est un plus grand défi que l'analyse elle-même.

---

[1] Z.M.D.C. Group Research Laboratories, P.O. Box 2370, Harare, Zimbabwe.

INTRODUCTION

Zimbabwe is a developing country situated in the southern part of Africa with Zambia, Mozambique, South Africa, and Botswana as its immediate neighbours. The two most important foreign currency earners are agricultural exports and metals such as gold, nickel, ferro-chrome, copper, etc. This inevitably makes the agricultural and mining sectors of Zimbabwe the most crucial industries for sustaining the country's economy. In turn, this also means that the role played by a geoanalytical laboratory in the mining industry should not be underestimated. The role of a geoanalytical laboratory in establishing new mining ventures through tireless analysis of exploratory samples, monitoring the quality of export minerals and developing mineral dressing processes for Zimbabwean ores needs to be emphasized. Some of these laboratories are the Government Department of Metallurgy, Bindura Nickel Corporation Analytical Laboratory (Anglo-American Corporation), Geo-Met, Zimbabwe Mining Development Corporation (Z.M.D.C.) Group Research Laboratories, the Institute of Mining Research (University of Zimbabwe), and RIO-TINTO's analytical laboratories at Eiffel Flats in Kadoma.

The major problems arise from lack of foreign currency to buy new instruments or spare parts for the existing ones, reagents, and other consumables. Reagents such as hydrochloric, sulphuric, nitric, hydrofluoric, and perchloric acids which form the basis of most geochemical analysis in any laboratory are all imported, as are most apparatus like separating funnels, pyrex beakers, electrodes, etc. Although companies like Glassblowing Industries are trying to make as much glassware as possible locally, they too are affected, inevitably, by unavailability of foreign currency. Not only does lack of foreign currency affect the acquisition of instruments and reagents, it also affects subscriptions to relevant journals. Few journals are subscribed to by different organizations. The University Library, which is the biggest library in the country, has few journals which are relevant for geo-analytical work, while Chemical Abstracts were last received in 1986. This, therefore, results in inadequate literature sources.

As if this was not enough, geoanalysis is greatly affected by lack of experienced trained staff to run these establishments. At present "fresh" graduates from universities and colleges are being employed in such establishments but they require a lot of training before they become confident in their work. The main body of this paper will deal with the problems individually.

REAGENTS/APPARATUS

The reagents commonly used in an analytical laboratory such as sulphuric, perchloric, nitric, hydrochloric, and hydrofluoric acids and many others are all imported from Chemicals Houses abroad such as BDH (British Drug House), Fluka (Switzerland), and Riedil-Dihaen (West Germany). This importation is done either directly by a laboratory or through local companies such as Protea Medical, McDonald Scientific (Pvt.) Ltd., or Tinto Industries. These companies actually share the foreign currency allocation among themselves for the same commodity (e.g., acids). When the companies are really short of foreign exchange, they normally ask the clients to apply for the foreign currency from the Reserve Bank of Zimbabwe – the application takes so long to be approved or is rejected. Another difficulty is faced when trying to acquire items like platinum crucibles. Suppose one has old crucibles which one can actually exchange for new ones and pay the difference in cash with companies such as Johnson Matthey and Co. Ltd. in South Africa, then clearance is needed from the Reserve Bank of Zimbabwe so that the old crucibles can be sent out of Zimbabwe. Here the argument a chemist has to put forward to convince these officers is, in itself, a mammoth task considering that these are non-scientific personnel unfamiliar with the requirements of a laboratory. The only alternative is to sell them to jeweller shops and to order new crucibles and inevitably wait until they arrive. The problem of waiting for so long is aggravated by virtue of Zimbabwe being a land-locked country. This therefore makes it difficult for any laboratory manager to operate within budget since by the time the goods arrive, the original price quoted may have changed due to fluctuations in exchange rates or due to an increase in the price.

INSTRUMENTS

The most common instrument used in any geoanalytical laboratory in Zimbabwe is an atomic absorption spectrophotometer (AAS). At Z.M.D.C. Group Research Laboratory we have three, a comfortable number by local standards. Most of the routine work is done by AAS or atomic emission spectroscopy (AES). However, since these instruments are all imported too, there are some inherent problems. Some of the instruments, although imported through local agencies, have poor back-up service. When anything goes wrong with the instrument, the local supplier is often found lacking in the quality of services provided. Very few qualified technicians are employed in these companies and the turn-over rate is high.

Besides the AA spectrophotometers, a few other instruments are relevant to geoanalytical work. These are based on X-ray fluorescence (XRF), X-ray diffraction (XRD), inductively coupled plasma/AES, and the electron microprobe. Besides the problem of having only one or two people trained to use these instruments, it is very expensive to maintain them. For example, when the ICP at Kamative breaks down, a technician can be flown in from South Africa at a cost of about Z$1000 per day plus expenses. When the XRF unit (Model: Siemens SNR 200 sequential XRF spectrometer) at the Institute of Mining Research (University of Zimbabwe) breaks down, a technician has to be flown in from South Africa too.

Simple problems like replacing broken parts or ordering spare parts turn out to be mammoth tasks since one has to go through the ritual of getting foreign currency for all the parts no matter how small BUT also one faces the problem of trying to get spare parts for an obsolete piece of equipment. As a developing country, we are inevitably so behind in technology that some of the laboratories carry very old instruments that could have been long sent to the "museum" in an industrialized country.

The XRF analyzer, though one of the fastest techniques for comprehensive chemical analysis in geochemical samples, is out of reach to most people, mainly because of the expense involved. The Institute of Mining Research charges Z$60 for a qualitative analysis (orscan) and interpretation per sample, Z$50 for an XRD scan with interpretation, Z$70 for the use of microprobe per hour.

Because of the scarcity of instruments, one takes it upon oneself to try and keep in touch with other chemists or directors of geoanalytical laboratories in case one needs to use their instruments. When working in a geoanalytical laboratory in Zimbabwe, one cannot afford to isolate oneself. Borrowing of items from other laboratories is common otherwise there would be a lot of discontinuity in the day to day analytical work.

THE QUALITY OF PERSONNEL

Although the country does have quite a number of chemistry graduates and qualified technicians, there is a shortage of qualified and experienced personnel to work in the geoanalytical laboratories. Before 1980, a lot of young Zimbabweans emigrated abroad for further studies. Soon after Independence the country was flooded with "fresh" graduates from universities and technical colleges; among these were chemists and technicians. Most of them have never worked before which means in-house training cannot be avoided. Most chemists, therefore, are employed first as trainee chemists. Normally the training period varies from one organization to the other (12 to 24 months). While this might sound simple and straight-forward, the challenge facing a laboratory manager in this case is whether or not he can keep his trained staff.

Because of lack of experienced staff, companies have resorted to "poaching" staff from each other and hence recruitment for new staff is almost a continuous process. There is a general trend of staff leaving the government establishments and joining the private sector.

Inevitably, the quality of chemists or technicians in a geoanalytical laboratory, or any other laboratory for that matter, also affects the quality of results reported by that laboratory.

QUALITY OF RESULTS

One of the most challenging tasks for any laboratory manager running a geoanalytical laboratory in Zimbabwe is to design a set of methods that are specific to our geological samples. However, method development is affected by limited literature sources and prohibitive prices for reagents. For example, in 1987, a kilogram of toluene 3-4 dithiol could cost as much as Z$36 000 (quotation obtained from Protea Chemicals Ltd.). Toluene 3-4 dithiol is recommended for the complexing of Mo and W prior to analysis by UV-Vis. Spectrophotometry. This therefore means that, like the instruments, method development, indirectly, is also affected by the limited foreign currency allocation. Because of the hardships faced in acquiring reagents, one is faced with the challenge of designing methods that are not only economic but reliable. For example, if the literature states that 25 mL of hydrofluoric acid (HF) are added, one has to try and add 10 mL of HF and compare the result to that obtained after using 25 mL of HF. Thus, the method used for sample preparation inevitably affects the quality of results obtained.

At Z.M.D.C. Research Laboratories, the use of internationally certified reference materials gives us a guideline as to how good our methods of digestion are and our ability to use AA spectrometry. We have reference materials from the International Working Group (Paris), the United States Department of the Interior (Geochemistry Department), and the British Geological Survey.

In 1988, Z.M.D.C. Research Laboratories participated in the interlaboratory study of six geochemical exploration reference materials from the United States Department of Interior. Such work does indeed help us compare our results with international laboratories and it gives us more confidence in our work. However, within Zimbabwe itself, it is difficult to achieve two or more laboratories producing results in good agreement. Tables 1 and 2 are examples of such results.

Such results are quite confusing to the client, not knowing which result is correct. Generally such deviations can arise if the method of digesting the samples differed and also if different instruments were used for the final analysis of the prepared samples. As mentioned before, although AA spectrometry is a rapid method of analyzing geological samples, it lacks sensitivity for elements such as Ta, Nb, and

Table 1. Comparison of results obtained by Zimbabwean laboratories*

Sample no. and type	Laboratory	ppm		
		Pt	Au	Pd
1 Rock Sample	A	ND	0.24	0.08
	B	3.2	trace	1.6
	C	0.62	ND	0.06
2 Rock Sample	A	ND	0.10	0.08
	B	11.5	ND	2.8
	C	0.56	ND	0.06
3 Rock Sample	A	ND	0.22	0.10
	B	5.8	ND	1.00
	C	0.18	ND	0.10
4 Rock Sample	A	ND	0.20	0.15
	B	6.4	ND	1.20
	C	0.36	ND	0.06
5 Rock Sample	A	ND	0.22	0.13
	B	3.8	ND	0.80
	C	0.48	0.1	0.06

*From presentation by L. Siziba (Acting Group Chief Geologist with Z.M.D.C.), Dec. 1989.

Table 2. Comparison of results obtained by Zimbabwean laboratories*

Laboratory no.	Sample no.	%	
		Pb	Zn
X	1	1.36	0.5
Y	"	1.30	0.5
Z	"	1.20	0.5
X	2	0.20	0.25
Y	"	0.15	0.5*
Z	"	0.15	0.20
X	3	2.69*	1.0
Y	"	1.30	1.0
Z	"	1.20	0.5*
X	4	4.6	0.5*
Y	"	4.3	1.0
Z	"	4.35	1.0

*Month end report by an assistant chemist with Z.M.D.C., September, 1986.

W. An ICP emission spectrometer is clearly required to augment our laboratory, to improve not only capabilities but also efficiency.

CONCLUSION

It can be summarized, therefore, that a geoanalytical laboratory in Zimbabwe is affected by lack of foreign currency which in turn results in limited literature sources, limited choice of instruments, and slow method development. Also, lack of experienced staff affects the progress of work in any such laboratory. Nevertheless, the work achieved in these laboratories should not be belittled or underestimated as they are playing a vital role in the mining industry which in turn is a major foreign currency earner for the country.

Efforts are made endlessly to keep up to date with activities in similar establishments by, for example, reading Geostandards Newsletter. Although the techniques described in this Journal are too advanced for a laboratory such as ours, there is no replacement for knowledge and this provides us with an excellent vehicle for learning.

Quantitative SIMS analyses of REEs in silicate minerals: choice of the standard for natural and glassy matrix

L. Ottolini[1], P. Bottazzi[1], and R. Vannucci[1,2]

Abstract: Five silicate samples – three hornblendes and two kaersutites – were chosen to test the empirical approach to calibration curves (working curves) and relative sensitivity factors in the quantitation of rare-earth elements (REE) in amphiboles, by means of Secondary Ion Mass Spectrometry (SIMS).

The measurements were carried out with a Cameca IMS 4F ion microprobe, using a moderate energy filtering (-80 V offset), from the maximum of the energy distribution, with an energy window of 25 eV, in order to eliminate complex ion interferences.

One of the two kaersutites, investigated both as a crystal mineral and a fused glass pellet, did not reveal evident systematic effects due to matrix structure; La and Ce seemed to ionize better in glass (crystal/glass intensity ratios ranging from 0.90 to 0.91), an opposite trend occurring for heavy REEs (e.g., 1.06 for Dy and 1.11 for Yb). The tested inhomogeneity of the other samples prevented the addition of more experimental data and no simple explanation seems available at this point.

Relative sensitivity factors from our present investigation were successively compared with those calculated from an ensemble of mafic-ultramafic international rock standards fused in glasses (differences are about 18% for Nd and Sm, 2% for Eu), and with those obtained from natural minerals, namely clinopyroxene and garnet (differences of 23% for Sm and <1% for Er).

It is concluded that relative sensitivity factors from fused glasses of amphiboles can be employed in the REE analysis of natural amphiboles (which are naturally more inhomogeneous). They could also be tentatively used in the analysis of silicates, over a wide compositional range, especially for heavy REEs, when suitable standards are not available.

Résumé : On a choisi cinq échantillons de silicates, dont trois hornblendes et deux kaersutites, pour éprouver la méthode empirique des courbes d'étalonnage (courbes de fonctionnement) et les facteurs de sensibilité relative lors du dosage des terres rares dans les amphiboles par spectrométrie de masse à émission ionique secondaire (SIMS).

On a effectué les mesures avec une microsonde ionique Cameca IMS 4F, en procédant à un filtrage énergétique modéré (décalage -80 V), à partir du maximum de distribution de l'énergie, avec une fenêtre énergétique de 25 eV, pour éliminer les interférences dues aux ions complexes.

L'une des deux kaersutites, étudiée à la fois sous forme cristalline et sous forme de granule vitrifié, n'a pas montré d'effets systématiques résultant de la structure de la matrice : La et Ce ont apparemment subi une ionisation plus poussée dans le verre (rapports d'intensité cristal/verre compris entre 0,90 et 0,91), contrairement aux terres rares lourdes (par ex., 1,06 pour Dy et 1,11 pour Yb). Le manque d'homogénéité des autres échantillons, révélé par les essais, a empêché de recueillir davantage de données expérimentales et, pour l'instant, on ne dispose d'aucune explication simple.

On a successivement comparé les facteurs de sensibilité relative déduits de la présente étude, à ceux calculés à partir d'un ensemble d'étalons de référence internationaux de roches silicatées mafiques-ultramafiques vitrifiés (les différences sont d'environ 18 % pour Nd et Sm, 2 % pour Eu), et à ceux obtenus à partir de minéraux naturels, notamment des clinopyroxènes et des grenats (différences de 23 % pour Sm et % pour Er).

On en conclut que les facteurs de sensibilité relative, tels que déduits des spécimens d'amphibole vitrifiés, peuvent servir lors du dosage des terres rares dans les amphiboles naturelles (qui par nature sont moins homogènes). On pourrait aussi chercher à les employer pour l'analyse des silicates dans une vaste gamme de compositions, surtout pour doser les terres rares lourdes, quand on ne dispose pas d'étalons convenables.

---

[1] CNR – Centro di Studio per la Cristallochimica e la Cristallografia, Via Bassi 4, 27100 Pavia, Italy.
[2] Dipartimento di Scienze della Terra, Universita' di Pavia, Via Bassi 4, 27100 Pavia, Italy.

INTRODUCTION

The extreme sensitivity of Secondary Ion Mass Spectrometry (SIMS) for elements at trace levels has increased the attention and interest of geochemists towards quantitation; the ability to acquire secondary ion intensities at any mass number has stressed the necessity to design a procedure to convert intensities into concentrations.

The SIMS technique requires an ion primary beam to produce ions, characteristic of the sample surface composition. The secondary ion intensity, I_S, measured at the detector, relative to an isotopic constituent, may be expressed in principle by the formula:

$$I_S = I_P \, S \, \beta C f \qquad (1)$$

where I_P is the primary ion intensity; S is the sputter yield; β, the degree of ionization; C, the fractional atomic concentration; and f, a transmission factor. The complexity of the sputtering-ionization process, affected by many factors, such as the matrix surface properties, the crystal orientation in crystalline samples, and the difficulty to accurately measure instrumental transmission, make equation (1) practically unusable in every day analysis.

Among the semi-theoretical models proposed, the local thermal equilibrium model (LTE)(Andersen and Hinthorne, 1973), which assumes the formation of a dense plasma in the sample sputtering region, allows semiquantitative analysis by employing internal standards, by which both the plasma temperature and electron density are determined. Since it does not take into account the interelement effects in the matrix, it fails to some extent in complex samples, yielding less accuracy than empirical methods which rely upon proper standards. Such analytical procedures are usually based on calibration curves (working curves) or on the use of relative sensitivity factors (RSF) (McHugh, 1975), defined as follows:

$$\mathrm{RSF}\,(X/R) = \frac{(I_X / C_X \eta_X)}{(I_R / C_R \eta_R)} \qquad (2)$$

where I is the intensity measured for an atomic ion; C is the atomic concentration; η, the isotopic abundance of the species measured; X, the element of interest; and R the reference element of the same sample, generally chosen as a matrix element. Through the use of equation (2), instrumental factors are taken into account and do not need to be measured or calculated separately if standards and unknowns are analyzed in the same experimental configuration. Tuning, spot size (Meyer, 1979; Bradley et al., 1975) as well as the energy of secondary ions (Riedel and Duesterhoeft, 1984), and the width of the energy window of the electrostatic analyzer (Gries and Ruedenauer, 1975) all cause variation in sensitivity factors and, for this reason, they should be kept as constant as possible. The calibration standards must be very close in composition to the samples in major and minor elements, with a wide compositional range for the trace elements under investigation.

The aim of the present work was:

i) to construct high quality working curves for a number of trace elements, i.e., REEs sputtered from silicate minerals such as amphiboles (for which SIMS quantitation is generally prevented by the scarce availability of homogeneous natural standards);

ii) to determine eventual structural matrix effects on secondary ion yields by investigating the samples as crystal minerals and as fused glasses; and

iii) to compare the relative sensitivity factors so obtained with those previously determined from rock standard glasses and other silicate minerals such as garnets and pyroxenes (Bottazzi et al., 1990).

STANDARDS AND MATRIX EFFECTS

The necessity to use matrix-matched standards, as much as possible, is due to the existence of matrix effects. Generally speaking, a "matrix effect" is defined as "a variation in an analytical signal for an impurity element, not in direct proportion to concentration, but loosely associated with a change in the concentration of major constituents" (Deline, 1979). According to Deline (1979), variations in the secondary ion yield can concern:

a) different elements contained in a single matrix;

b) a single element sputtered from different matrices;

c) different elements sputtered from different matrices.

While for case a), it was possible (Andersen and Hinthorne, 1972) to find a dependence of the relative atomic ion yields on the ionization potential of the elements in a single matrix, case b), also known as the "SIMS matrix effect", is still the least known of the ion yield phenomena. In spite of the use of primary ion species, such as oxygen and cesium, to enhance ion yields, secondary ion intensity is found to vary by many orders of magnitude from one matrix to another (Deline, 1979).

As Shimizu (1985) pointed out, the matrix effects occur among different mineral groups, qualitatively similar to b), and even within a given mineral group as the composition of the solid solution varies (Shimizu et al., 1978).

STANDARDIZATION

The characterization of samples as standards is an expensive and time consuming task. The need for an independent artifact-free reference method, which can be used to calibrate SIMS standards, is obvious. Bulk analytical techniques such as neutron activation analysis (NAA), inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence (XRF), generally employed for minor and trace constituents, are useful to provide average information relative to a given sample volume. Other techniques, such as electron probe

X-ray microanalysis, provide in situ information, but they do not possess enough sensitivity to detect elements at trace levels.

According to Newbury and Simons (1984), a complete characterization of samples as SIMS standards may necessitate employing multiple analytical techniques, including SIMS itself to test lateral and in-depth homogeneity, while a bulk technique should provide an independent measure of concentration. The major characteristics of a suitable standard for SIMS are summarized as follows (Newbury and Simons, 1984):

1. the composition should be homogeneous, both laterally and in-depth, since the sample volume eroded during the analysis may be quite shallow;
2. the composition should not be significantly altered during ion bombardment by effects such as migration; and
3. the composition should be stable over a long period of time.

In some cases, instead of crystalline standards obtained from natural minerals, it is advisable to use artificial glass standards (Steel et al., 1981; Marinenko, 1982), which generally may be made homogeneous on the micrometer scale, are present in only one phase which is noncrystalline, and are generally oxygen saturated.

The choice of glass standards instead of crystalline ones may be done only after checking that the sensitivity factors are not significantly affected by structural matrix effects or by taking into account eventual systematic differences (Ray and Hart, 1982).

Table 1. Chemical compositions of major (weight per cent) and rare-earth (ppm by weight) elements of analyzed amphiboles

	JW83	JW87	JW88	KK	KSS
SiO_2	46.84	45.89	47.22	40.37	40.27
TiO_2	1.17	1.45	1.08	4.38	5.36
Al_2O_3	6.60	6.38	5.09	14.90	13.76
Fe_2O_3	2.89	2.96	4.71	3.30	-
FeO	13.68	14.22	13.26	7.95	17.02
MnO	0.48	0.68	0.73	0.09	-
MgO	12.21	11.62	11.78	12.80	9.87
CaO	10.92	10.73	10.28	10.30	10.36
Na_2O	1.08	1.23	1.31	2.60	2.91
K_2O	0.38	0.55	0.36	2.05	1.17
La	5.7	15.3	27.4	5.0	21.0
Ce	22.4	61.6	107.0	15.9	67.0
Nd	28.0	71.8	127.0	15.2	56.0
Sm	9.8	23.9	42.2	4.4	15.0
Eu	2.0	2.48	2.7	1.57	3.45
Gd	11.4	29.6	56.3	4.15	9.9
Dy	13.8	34.3	62.7	2.15	8.9
Er	8.8	22.4	39.0	0.696	4.6
Yb	9.0	22.4	36.8	0.362	4.7

INTERFERENCES AND QUANTITATION

Due to the existence of matrix effects, secondary ion intensities are generally not linearly related to concentrations. In any valid quantitative empirical procedure, it is desirable to construct well defined curves, intersecting the origin, since the accuracy in constructing them will qualify all successive investigations.

A further difficulty in analyzing minerals and rocks is due to the existence of interfering complex ions (molecules, oxides, hydroxides, and hydrides) and multicharged ions in mass spectra, which can mask the actual content of trace elements in the sample. There are basically two methods for removing spurious interferences: high mass resolution and energy filtering, both of which, nevertheless result in large losses of ion intensities (Reed and Smith, 1985; Shimizu, 1978; Shimizu and Hart, 1982; Zinner and Crozaz, 1986). For ion masses greater than 60 a.m.u., the energy filtering technique is generally preferred. As molecular and monoatomic ions possess different energy distributions at high energies, the discrimination can be carried out by analyzing only high energy ions, which are basically monoatomic ions.

EXPERIMENTAL

Five natural silicate minerals, three of them hornblendes (hornblendes from Uasilau-Yau Yau Intrusive Complex, New Britain, Papua New Guinea, hereafter JW83, JW87, JW88) and two kaersutites (Kakanui and Soda Springs, hereafter KK and KSS, respectively) were chosen to test the empirical approach to relative sensitivity factors in the quantitation of REEs. In Table 1, chemical compositions of major and trace elements are reported. REE distribution patterns are shown in Figure 1.

In the JW samples major elements were determined by XRF, flame photometry (Na_2O), and titration (FeO); REE determinations were carried out by ICP-MS (Whalen, 1985; N.D. MacRae, pers. comm., 1989). REE values in KK were

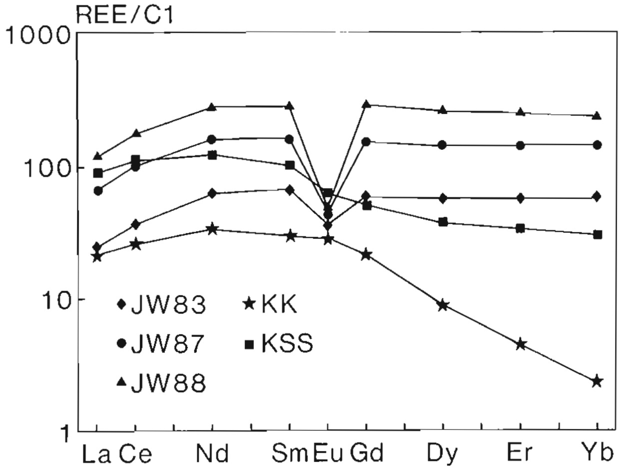


Figure 1. Abundances of REEs in investigated amphiboles, normalized to chondrite values.

obtained by isotopic dilution mass spectrometry and NAA (Philpotts et al., 1972; Mason and Allen, 1973) while those in KSS were produced by INAA (F.A. Caporuscio, pers. comm., 1989).

The selection of mineral grains from hornblendes was carried out at the optical microscope. A portion of each specimen was coarsely ground and any foreign material removed. The homogeneity of major and minor elements was tested by electron probe X-ray microanalysis in random positions inside the selected grains. As these grains were shown to be chemically zoned, they were melted in a Pt crucible at about 1500°C for 1 hour and a glass of the three was produced by pouring into a stainless steel mould (MacRae, 1987).

KSS grains were derived by a single megacryst which revealed an extremely homogeneous composition (within 2% for major and <4% for most REEs) after random SEM and SIMS analyses. It was chosen among all of the samples as a suitable standard to be investigated both as a crystalline and a glassy matrix, in order to detect eventual structural matrix effects. For this reason, part of the split was used to obtain glass beads by fusing in air small amounts (≤ 10 mg) of its mineral powder on a Pt-Rh strip heater, without introduction of flux (Nicholls, 1974) and then subsequently examined under the optical microscope to test the final homogeneity.

The scarce amount of KK prevented the preparation of an equivalent glass button and therefore it was analyzed only as a crystal mineral. All the selected grains and glasses were embedded in resin, polished and gold-coated (~ 40 nm thickness).

A Cameca IMS 4F ion microprobe, installed at Centro di Studio per la Cristallochimica e la Cristallografia (CSCC) in Pavia, was employed. A primary beam of O^- ions at 12.5 kV accelerating voltage was used to sputter a 30x40 µm diameter sample area. According to the energy filtering technique (Shimizu et al., 1978), positive monoatomic secondary ions were collected under a voltage offset of -80 V with respect to + 4.5 kV sample voltage, with a ±25 eV energy band width, and focused by a 150 µm imaged field static transfer optics. Entrance and exit slits were completely open for maximum transmission.

REE signals at masses ^{139}La, ^{140}Ce, ^{146}Nd, ^{149}Sm, ^{163}Dy, ^{167}Er, and ^{174}Yb were collected. In order to separate the Eu signal from the BaO contribution, the ion intensities at masses 151 and 153 were detected. A computing correction, according to a peak stripping procedure, was applied to the signals at masses 156, 158, 161, and 162, to discriminate the Gd signal from Dy, NdO, and CeO contributions. ^{30}Si was chosen as internal standard.

Counting times ranged from 2 s for $^{30}Si^+$ ions to 20 s for all REEs, over five cycles. Background was measured at 174.5 a.m.u. and was generally negligible. Ion intensities corrected for isotopic abundance were normalized with respect to Si intensity and plotted versus REE atomic concentrations, ratioed to the atomic concentration of Si. Calibration curves constructed with a linear regression procedure of Y on X (intensity on concentration) show regression coefficients ranging from 0.994 (for Eu) to 0.999 (for Nd). The representative points of the analyzed samples and their respective working curves are reported in Figure 2 for all REEs. Due to the tested inhomogeneity of the three JW hornblendes, the calibration curves were constructed using SIMS data obtained from glass buttons. For the sample KSS concerns, the data used in the fit were derived from measurements of the crystalline sample.

RESULTS AND DISCUSSION

A few remarks are necessary:

- In the fit procedure for Ce, Nd, Dy, Gd, Er, Yb, experimental data from JW88 were discarded; for these elements, some scatter occurs. Among the three JW samples, JW88 (from a quartz-granodiorite; Whalen, 1985), was shown to be the least homogeneous white JW83 (from a diorite; Whalen, 1985) was the most homogeneous. Furthermore, REE concentration bulk values in JW88 glass were probably affected by the presence of small accessory phases (almost always ilmenite) as inclusions.
- Due to uncertainties introduced by the peak stripping procedure for the Eu signal and due to the fact that all the investigated samples were characterized by almost the same Eu concentration, linear regression was carried out by imposing a zero intercept for the straight line.
- For Gd, error propagation from the peak stripping procedure is probably the major factor responsible for the high standard deviation values (21%).

Calibration curves for all the REEs show nearly identical slopes, with an intercept close to zero. Error bars for intensity ratios are twice their standard deviations. Curves from amphiboles are plotted with our SIMS data from acidic rock standards (Bottazzi et al., 1990): GA, AC-E, NIM-S, G-2, and RGM-1 (Govindaraju, 1989). We pointed out (Bottazzi et al., 1990) that all data from acidic rocks are generally rather scattered. The reasons are due both to compositional matrix effects (high silica contents, above 63%; Shimizu, 1986) and small scale inhomogeneities.

Our SIMS data from the international standard NBS-612 are also shown. It is a synthetic glass, with a support matrix composition of 72% SiO_2, 12% CaO, 14% Na_2O, and 2% Al_2O_3 (by weight), to which 61 elements have been added at a nominal level of 50 ppm (by weight). Concentration values are taken from U.S. National Bureau of Standards certification (1982).

Such a fit procedure seems to be valid over a wide compositional range, considering also the agreement with the extrapolated working curves (Fig. 3) from mafic-ultramafic rock standards (DR-N, AN-G, NIM-N, NIM-P, DNC-1, W-2; Bottazzi et al., 1990). Compilation data are taken from Govindaraju (1989). As a comparison, experimental data from MNAG are given (pyrope megacryst in Kimberlite, Monastery mine, South Africa; REE concentrations, obtained by isotopic dilution mass spectrometry, were kindly provided by N. Shimizu, pers. comm., 1989).

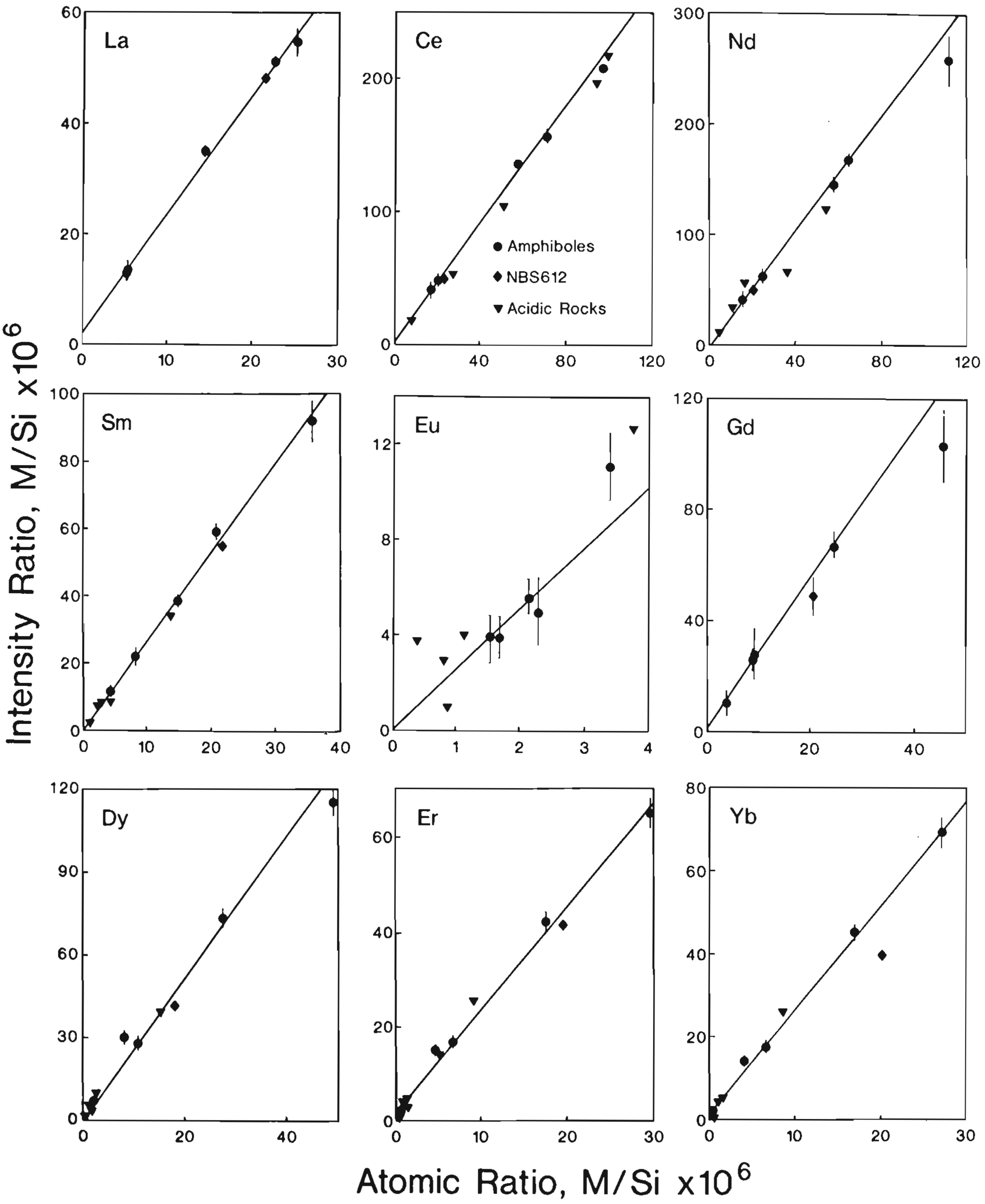


Figure 2. Calibration curves: intensity versus atomic concentration (normalized to Si) from amphiboles. The representative points are reported in lin-lin scale 10^6 units. Data are relative to 10-12 measurements. NBS-612 data are shown as a comparison. When present, data from acidic rocks (Bottazzi et al., 1990) are also reported.

In Table 2, relative sensitivity factors, as derived by the equation:

$$\frac{I^{REE}}{I^{si}} = \frac{1}{RSF}\,\frac{C^{REE}}{C^{si}} \qquad (3)$$

from samples here investigated, A, are shown and compared with those, B, obtained from mafic-ultramafic rock samples (Bottazzi et al., 1990); with those, C, from standards of natural garnets and pyroxenes (MNAG; KH1 augite megacryst, Kilbourne Hole, New Mexico: REE determination by NAA, Irving and Frey, 1984); KAUG augite megacryst, Kakanui, New Zealand: REE determination by isotopic dilution mass spectrometry and NAA (Philpotts et al., 1972; Mason and Allen, 1973); and finally, with those, D, from four silicate synthetic glasses (Drake and Weill, 1972).

We conclude the following:

- The agreement among the four sets of RSFs is quite good. Some discrepancies are represented by RSFs for Ce and Nd from standards of natural garnets and pyroxenes (set C), for which satisfactory explanations cannot be furnished at present. Moreover, the differences in RSFs for Eu can be attributed to the stripping technique corrections applied only for sets A and B.
- Maximum variation of RSFs of mafic-ultramafic rocks (set B) with respect to RSFs of amphiboles (set A) is found to be about 18% for Nd and Sm whereas the minimum variation is 2% for Eu.
- Maximum variation of RSFs of garnets and pyroxenes (set C) with respect to RSFs of amphiboles is 23% for Sm whereas the minimum variation is <1% for Er.

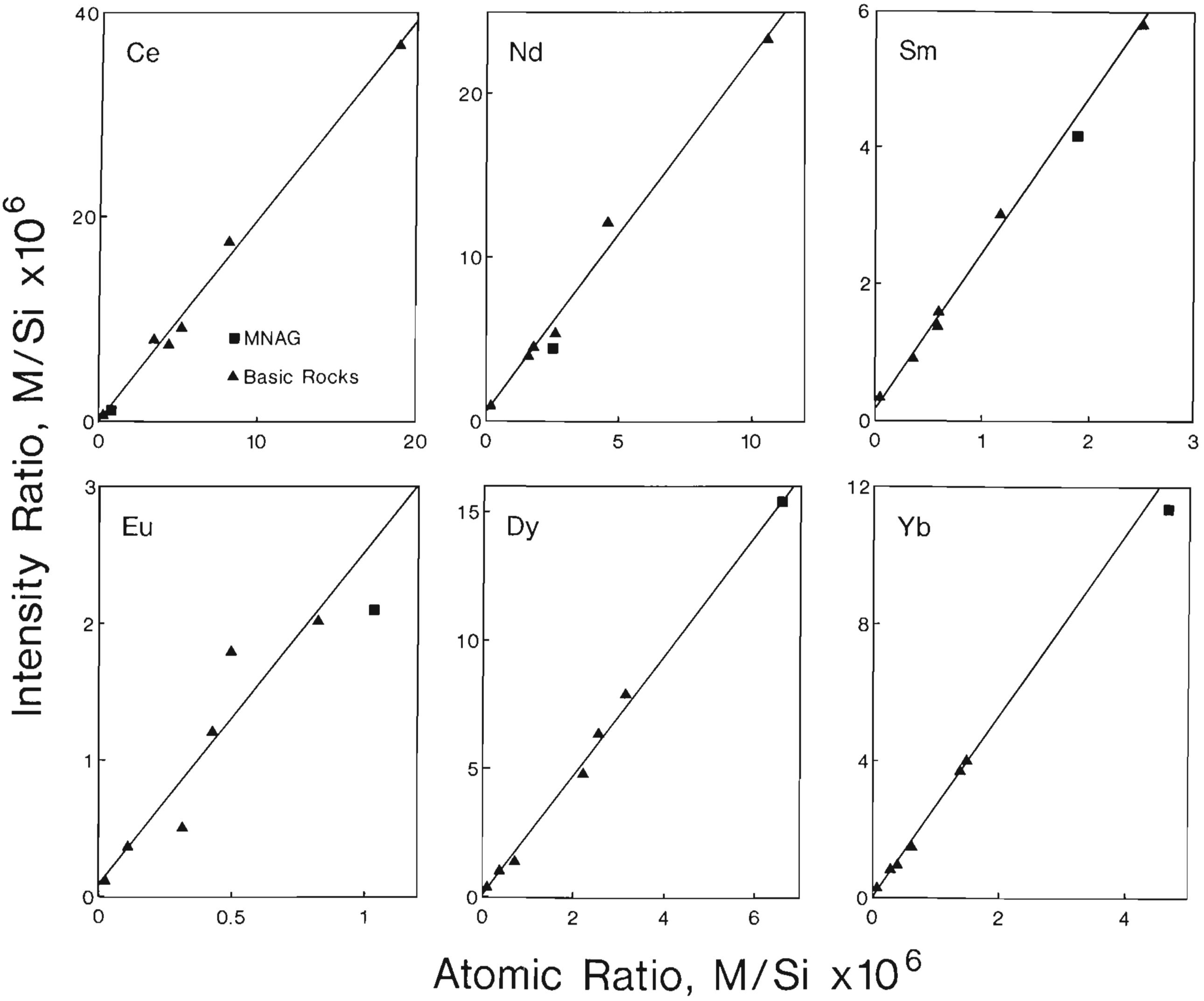


Figure 3. Calibration curves: intensity versus atomic concentration (normalized to Si) from basic rocks (Bottazzi et al., 1990). The representative points are reported in lin-lin scale 10^6 units. MNAG data are also shown as a comparison.

- The comparison between the sets A and D must consider the different matrices involved (26.96% SiO_2 (by weight); 30.52% Al_2O_3; 25.16% CaO; 4% for all REE oxides in the 4 synthetic glasses investigated).
- Finally, we acknowledge the fact that all these samples have been analyzed over the time span of one year.

In Table 3, crystal/glass intensity ratios from KSS are reported. These values were obtained by analyzing sequentially crystal->glass->crystal, repeatedly several times within a day, after checking before every analysis, primary ion intensities, focusing conditions of the spot and magnetic field calibration.

La and Ce seem preferentially to ionize in the glass structure rather than in the crystalline one; the contrary is true from Eu to heavier masses. Previous investigations, carried out on both glass and crystalline matrix of different silicates, may be summarized as follows:

1. For Na, Mg, Al, Ca, Ti, Sr, Sc, and Cr, ions were sputtered from clinopyroxenes more readily than from glasses of all the same composition. The intensity ratio (glass/crystal) varies from 0.55 to 0.9 (Ray and Hart, 1982). For this reason, Ray and Hart warned about the use of glass calibration standards for the analysis of crystalline materials.
2. For certain elements (Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Sr, Y, Zr, and Nb), Muir et al. (1987) found no remarkable systematic differences in a comparative study of ion intensities from crystal, glass, and ceramic of the same composition (titanite), by both the Specimen Isolation technique (Nesbitt et al., 1986) and conventional energy filtering.
3. Secondary ion intensities of REE/^{30}Si, from an augite crystal mineral, were marginally lower than from the equivalent fused glass (MacRae, 1987). Due to the higher values of standard deviations for the crystalline sample than for the fused glass, MacRae (1987) concluded that any differences in ion yields, due to matrix structure, should be considered within the statistics of analysis.
4. On the basis of Meyer's experience (1979), glasses prepared from Lake Co. plagioclase gave results similar to those in crystalline material. According to Meyer, "apparently the primary ion beam establishes a damaged boundary layer at the surface of the sample, from which sputtered atoms are ejected. Atoms sputtered have no memory of crystallinity of surface. For this reason glass standards are satisfactory to analyse minerals."

In our case, a simple explanation does not justify such evidence. The tested inhomogeneities of the three hornblendes (JW83, JW87, JW88) and the scarce amount of KK prevented the acquisition of more experimental data and no simple model seems available at this point.

Table 2. Relative sensitivity factors (RSFs)

	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb
A	.464	.449	.390	.380	.391	.368	.390	.459	.398
B	-	.510	.462	.449	.399	-	.429	.402	.376
C	-	.842	.583	.467	.514*	-	.456	.456	.464
D	.398	.456	.346	.303	.280*	.338	.382	.418	.367

* stripping technique not applied.

A: RSFs from present work (amphiboles);
B: RSFs from glasses of ultramafic-mafic rocks;
C: RSFs from standards of natural garnets and pyroxenes;
D: RSFs from silicate synthetic glasses.

Table 3. Crystal to glass intensity ratios from Soda Springs Kaersutite, KSS

	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb
A	0.90	0.91	0.98	1.00	1.05	-	1.06	1.04	1.11
B	1.1%	1.4%	1.7%	2.0%	6.2%	12.2%	3.2%	3.9%	3.8%
C	2.0%	5.0%	3.9%	6.0%	6.6%	14.6%	5.3%	2.4%	4.3%

A: $\dfrac{\text{Intensity REE}^{+}/\text{Si}^{+}\text{ for crystal}}{\text{Intensity REE}^{+}/\text{Si}^{+}\text{ for glass}}$
B: standard deviation (%) relative to crystal;
C: standard deviation (%) relative to glass.

Our conclusions are that relative sensitivity factors from fused glasses could be employed in the analysis of natural amphiboles, which are naturally more inhomogeneous.

Even if the use of mineral standards of the same composition as the unknowns is recommended in order to obtain a more accurate analysis, the factors from amphiboles could also be tentatively used in the analysis of silicates, over a wide compositional range, especially for the determination of HREEs, when suitable standards are not available.

ACKNOWLEDGMENTS

The authors are grateful to N.D. MacRae to have generously provided JW hornblendes and for fruitful discussion. N. Shimizu is thanked for comments on the early version of the manuscript and for the precious standards KK, MNAG, KH1, and KAUG. Synthetic silicate glasses were kindly furnished by E. Zinner. The authors are also indebted to F. Caporuscio who provided kaersutite Soda Springs and unpublished data. Finally M. Palenzona is thanked for his technical assistance and sample preparation.

REFERENCES

Andersen, C.A. and Hinthorne, J.R.
1972: Ion Microprobe Mass Analyzer; Science, v. 175, p. 853-860.
1973: Thermodynamic approach to the quantitative interpretation of sputtered ion mass spectra; Analytical Chemistry, v. 45, p. 1421-1438.

Bottazzi, P., Ottolini, L., and Vannucci, R.
1990: Quantitative SIMS Analysis of Rare Earth Elements in Mafic-Ultramafic Rock Samples; in SIMS VII Proceedings, (ed.) A. Benninghoven, C.A. Evans, K.D. McKeegan, H.A. Storms, and H.W. Werner; John Wiley & Sons, p. 413-416.

Bradley, J.G., Jerome, D., and Evans, C.A. Jr.
1975: A comparison of mass spectra from three ion probes; Secondary Ion Mass Spectrometry, NBS Special Publication 427, p. 69-77.

Deline, V.R.
1979: Factors influencing secondary ion yields; in SIMS II Proceedings, (ed.) A. Benninghoven, C.A. Evans Jr., R.A. Powell, R. Shimizu, and H.A. Storms; Springer Verlag, p. 48-52.

Drake, M.J. and Weill, D.F.
1972: New rare earth element standards for electron microprobe analysis; Chemical Geology, v. 10, p. 179-181.

Govindaraju, K.
1989: 1989 Compilation of working values and sample description for 272 geostandards; Geostandards Newsletter, v. XIII, Special Issue, p. 1-113.

Gries, W.H. and Ruedenauer, F.G.
1975: SGAE Ber. n. 2430.

Irving, A.J. and Frey, F.A.
1984: Trace element abundances in megacrysts and their host basalts: constraints on partition coefficients and megacryst genesis; Geochimica et Cosmochimica Acta, v. 48, p. 1201-1221.

MacRae, N.D.
1987: Quantitative analysis of REEs by SIMS; American Mineralogist, v. 72, p. 1263-1268.

Marinenko, R.B.
1982: Preparation and characterization of K-411 and K-412 mineral glasses for microanalysis: SRM 470; United States National Bureau of Standards, Special Publication (Washington), p. 260-274.

Mason, B. and Allen, R.O.
1973: Minor and trace elements in augite, hornblende and pyrope megacryst from Kakanui, New Zealand; New Zealand Journal of Geology and Geophysics, v. 16, p. 935-947.

McHugh, J.A.
1975: Empirical quantitation procedures in SIMS; in Secondary Ion Mass Spectrometry, (ed.) K.F.J. Heinrich and D.E. Newbury; United States National Bureau of Standards, Special Publication no. 427 (Washington), p. 129-134.

Meyer, C. Jr.
1979: Trace element analysis of silicates by ion microprobe; in SIMS II Proceedings, (ed.) A. Benninghoven, C.A. Evans Jr., R.A. Powell, R. Shimizu, and H.A. Storms; Springer Verlag, p. 67-69.

Muir, I.J., Bancroft, G.M., and Metson, J.B.
1987: A comparison of conventional and specimen isolation filtering techniques for the SIMS analyses of geological materials; International Journal of Mass Spectrometry and Ion Processes, v. 75, p. 159-170.

Nesbitt, H.W., Metson, J.B., and Bancroft, G.M.
1986: Quantitative major- and trace-element whole-rock analyses by secondary-ion mass spectrometry using the specimen isolation technique; Chemical Geology, v. 55, p. 139-160.

Newbury, D.E. and Simons, D.
1984: The role of standards in secondary ion mass spectrometry; in SIMS IV Proceedings, (ed.) A. Benninghoven, J. Okano, R. Shimizu, and H.W. Werner; Springer Verlag, p. 101-106.

Nicholls, J.A.
1974: A direct fusion method of preparing silicate rock glasses for energy-dispersive electron microprobe analysis; Chemical Geology, v. 14, p. 151-157.

Philpotts, J.A., Schnetzler, C.C., and Thomas, H.H.
1972: Petrogenetic implications of some new geochemical data on eclogite and ultrabasic inclusions; Geochimica et Cosmochimica Acta, v. 36, p. 1131-1166.

Ray, G. and Hart, S.R.
1982: Quantitative analysis of silicates by ion microprobe; International Journal Mass Spectrometry and Ion Physics, v. 44, p. 231-255.

Reed, S.J.B. and Smith, D.G.W.
1985: Ion probe determination of rare earth elements in merrillite and apatite in chondrites; Earth Planetary Science and Letters, v. 72, p. 238- 244.

Riedel, M. and Duesterhoeft, H.
1984: Energy distribution of positive secondary ions from pure elements and amorphous alloys; in SIMS IV Proceedings, (ed.) A. Benninghoven, J. Okano, R. Shimizu, and H.W. Werner; Springer Verlag, p.73-75.

Shimizu, N.
1978: Analysis of the zoned plagioclase of different magmatic environments: a preliminary ion-microprobe study; Earth Planetary Science and Letters, v. 39, p. 398-406.
1985: Silicon-induced enhancement of secondary ion emission in silicates: a study of the matrix effects; in SIMS V Proceedings, (ed.) A. Benninghoven, R.J. Colton, D.J. Simons, and H.W. Werner; Springer Verlag, p. 45-47.
1986: Silicon-induced enhancement in secondary ion emission from silicates; International Journal of Mass Spectrometry and Ion Processes, v. 69, p. 325-338.

Shimizu, N. and Hart, S.R.
1982: Isotope fractionation in secondary ion mass spectrometry; Journal of Applied Physics, v. 53, p. 1303-1311.

Shimizu, N., Semet, M., and Allegre, C.J.
1978: Geochemical applications of quantitative ion-microprobe analysis; Geochimica et Cosmochimica Acta, v. 42, p. 1321-1334.

Steel, E., Newbury, D., and Pella, P.
1981: Analytical Electron Microscopy; San Francisco Press, p. 65.

U.S. National Bureau of Standards
1982: Certificate of Analysis Standard Reference Material 612; Trace Elements in a Glass Matrix; United States National Bureau of Standards, Washington D.C.

Whalen, J.B.
1985: Geochemistry of an island-arc plutonic suite: the Uasilau-Yau Yau Intrusive Complex, New Britain, P.N.G.; Journal of Petrology, v. 26, p. 603-632.

Zinner, E. and Crozaz, G.
1986: A method for the quantitative measurements of rare earth elements in the ion microprobe; International Journal of Mass Spectrometry and Ion Processes, v. 69, p. 17-38.

Preliminary investigations into small nickel sulphide button preconcentration of platinum group elements, gold, and silver in geological materials

T. Denis Rice[1] and Helen M. Waldron[2]

Abstract: A procedure is described for preconcentrating platinum group elements (PGE), gold and silver in a small nickel sulphide button (2.5-3.5 g) by fusion of up to 30 g of sample for one hour at 1000°C in a covered ceramic crucible. A single fusion by this procedure of the reference pyroxenite SARM-7 has been found to collect about 98% of the total measured PGEs. With chromite samples, this procedure gives a uniform, fluid slag if the flux contains magnetic iron oxide (9 g) plus extra borax and soda ash. Inclusion of magnesium oxide in the flux appears to give a higher recovery of platinum in SARM-7. Addition of aluminium powder (1 g) to the flux did not increase the recovery of gold in SARM-7. Possible enhancement of gold recovery by inclusion of, for example, copper (75 mg) and/or tellurium (2 mg) in the flux requires further investigation.

Digestion of pulverized buttons in a covered, spoutless beaker with 30 mL of concentrated HCl for 16 hours on a boiling water bath is likely to result in appreciable solubilization losses of palladium, iridium, gold, and probably platinum. Such losses can be avoided either by coprecipitating precious metals with tellurium or by limiting the digestion time to three hours.

Subsequent treatment of the filtered residue for a neutron activation or spectrometric finish is described. Suggestions are made for further work on the small NiS button procedure.

Résumé : On décrit un procédé de préconcentration des éléments du groupe du platine (EGP), de l'or et de l'argent dans un petit bouton de sulfure de nickel (de 2,5 à 3,5 g), par fusion d'un maximum de 30 g d'échantillon pendant une heure, à 1 000 °C, dans un creuset couvert en céramique. On a constaté qu'une seule opération de fusion de la pyroxénite de référence SARM-7 permettait de recueillir environ 98 % des EGP totaux mesurés. Dans le cas des échantillons de chromite, ce procédé donne un laitier fluide uniforme, à condition que le fondant contienne de l'oxyde ferroferrique (9 g) et aussi un peu de borax et de carbonate de sodium. En introduisant de l'oxyde de magnésium dans le fondant, on a pu atteindre un taux plus élevé de récupération du platine dans l'échantillon SARM-7. En ajoutant de la poudre d'aluminium (1 g) au fondant, on n'a pas amélioré le taux de récupération de l'or dans l'échantillon SARM-7. Il faudrait étudier plus en détail la possibilité d'augmenter le taux de récupération de l'or en introduisant par exemple du cuivre (75 mg), du tellure (2 mg), ou les deux, dans le fondant.

Il est probable que la digestion par 30 ml de HCl concentré pendant 16 heures dans un bain-marie, de boutons pulvérisés placés dans un verre gradué sans bec, cause des pertes appréciables par solubilisation du palladium, de l'iridium, de l'or et sans doute du platine. On peut éviter ces pertes, soit en coprécipitant les métaux précieux avec du tellure, soit en limitant le temps de digestion à 3 heures.

On décrit le traitement ultérieur du résidu filtré en vue de son analyse par activation neutronique ou de son analyse spectrométrique. On suggère de poursuivre les recherches sur le procédé consistant à utiliser un petit bouton de NiS.

---

[1] Department of Minerals and Energy, Mineral Resources Development Laboratory, P.O. Box 76, Lidcombe, N.S.W., 2141, Australia.

[2] Becquerel Laboratories Pty. Ltd., P.O. Box 93, Menai, N.S.W., 2234, Australia.

INTRODUCTION

Fire-assay preconcentration with a nickel sulphide collector is now widely used as a preliminary step in the determination of platinum group elements (PGE) in geological materials by instrumental neutron activation analysis (INAA), inductively coupled plasma spectrometry (ICP-AES or ICP-MS), or atomic absorption spectrometry (AAS). The procedure of Robert et al. (1971), subsequently used with an INAA finish by Hoffman et al. (1978), involved preparation of a 25 g NiS button requiring 400 mL of hydrochloric acid for its dissolution. The work of Kuznetzov et al. (1974) suggested that a much smaller button would suffice. Asif and Parry (1989) have recently shown that small NiS buttons of mass down to less than 1 g (made from 0.5 g of nickel) collected PGEs and Au in the reference pyroxenite SARM-7 (Steele et al., 1975) as efficiently as a large button (made from 10 g of Ni). These authors have discussed the advantages of small buttons and their findings complement those described in this paper.

The present work is aimed at developing a reliable NiS small button procedure applicable to a wide range of samples and which maximizes recovery of precious metals in the residue for INAA and in the solution for AAS, ICP-AES, or ICP-MS. The soda ash to borax ratio of fluxes used in the present study was 1:2 (Robert et al., 1971) rather than 2:1 (Kuznetzov et al., 1974; Myasoedova et al., 1985).

The possibility of improved precious metal recovery (especially that of Au) in the NiS button by addition of the following substances was investigated in the present study:

Magnesium oxide (10 g) so that the slag would more closely resemble an ultrabasic magma.

Copper (75 mg). Lenahan and Murray-Smith (1986) have advised the addition of a small amount of Cu to the flux so as to increase the recovery of Au.

Aluminium powder (1 g). Kallmann and Maul (1983) have reported good but not completely satisfactory Au recovery when Al powder as well as Cu oxide are in the flux.

Tellurium (2 mg). Tellurium has a high affinity for precious metals and a Te sulphide fire-assay preconcentration procedure has been studied (Shazali et al., 1988). Tellurium addition is not feasible when INAA is to follow, because of serious interference of Te on Pt determination by INAA.

EXPERIMENTAL

Equipment

Conventional fire-assay facilities including a Lindberg electric assay furnace (maximum operating temperature 1290°C), 450 mL ceramic crucibles (Type A) and ceramic lids (Duraboard, thickness 10 mm, diameter 110 mm); crucibles and lids were obtained from Mathews Industrial Products Pty. Ltd., Osborne Park, Western Australia.

Buttons and slags were pulverized in a small chrome steel grinding head (Model No. Chrome 3, maximum sample mass 10 g, Rocklabs Ltd., Auckland, New Zealand) and a medium-sized chrome steel grinding head (Rocklabs Model No. Chrome 2), respectively.

Pulverized buttons were decomposed in 200 mL tall-form Berzelius beakers (without a pouring spout; Crown Corning Cat. No. 1040-200) covered with suitable watchglasses.

PGE residues were separated with the aid of a Millipore filtration apparatus (Cat. No. XX15 04700) and Millipore type HVLP 04700 (for INAA) or acid-decomposable type HAWP 04700 membrane filters, pore size 0.45 m, diameter 47 mm.

INAA was carried out by Becquerel Laboratories Pty. Ltd. at the ANSTO (HIFAR) irradiation facilities, Lucas Heights, N.S.W., with conditions similar to those of Hoffman et al. (1978). Rhodium determination was not possible because of the unavailability of on-site reactor counting facilities.

An Instrumentation Laboratory Model IL 251 instrument was used for air-acetylene flame atomic absorption measurements.

Reagents

Custom-made NiS fire-assay flux mixtures are available commercially and very reasonably priced (e.g., from Sigma Chemicals, Balcatta, Western Australia). Sigma Chemicals 'nickel carbonate', approximately $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$, 47-49% Ni, labelled as low in PGEs, was used in this study.

Copper addition to the flux was via a milled copper sulphate pentahydrate (15.0 g)/technical grade magnetic iron oxide (55.5 g) mixture.

Tellurium addition to the flux was via a milled mixture of 0.1% weight/weight Te in (mainly) quartz. This mixture was conveniently prepared by dissolving 50.0 mg of Te granules in a tared 7 mL glass vial with 2 mL of warm aqua regia, evaporating to dryness, weighing the vial plus dry residue (tellurous acid) and pulverizing in a chrome steel grinding head the vial plus residue along with 50 g (minus the mass of vial plus residue) of quartz.

Calibration standard solutions

All calibration standard solutions were prepared gravimetrically. Individual analyte standard solutions (500.0 μg/g) were prepared from Johnson Matthey Specpure compounds in 10% weight/volume HCl, except for Ag which was prepared from Ag metal as a 200.0 μ g/g solution in 5% weight/volume HNO_3. Flame AAS calibration solutions were prepared in the range 0-10 g/g for Ag, Au, Pd, Rh, and 0-50 g/g for Pt in a 40% volume/volume aqueous solution of HCl containing 1% weight/volume uranium as releasing agent (Royal and Mallett, 1978) with the aid of polyethylene dispensing bottles (Rice, 1978), Pasteur pipettes, and a Sartorius A200S electronic 4-place balance; these solutions were matrix-matched with the sample solutions.

Fire assay procedure

1. To a 20 x 25 cm plastic freezer bag supported in a 450 mL ceramic crucible, add:

   35 g of soda ash (55 g for chromite),

   70 g of fused borax (110 g for chromite),

   5.40 g of '$NiCO_3$' (7.00 g for chromite),

   1.83 g of sulphur (2.42 g for chromite),

   10 g of quartz powder (20 g for chromite),

   and, for chromite only, 9 g of magnetic iron oxide.

NOTE: As discussed in the text, the following additional flux components were investigated in the present study:

   10 g of MgO,

   1.0 or 3.0 g of Al powder,

   1.40 g of Cu sulphate/Fe oxide mixture containing 5.4% Cu,

   and, 2.00 g of 0.1% weight/weight Te in quartz (not when INAA is to follow).

   Alternatively, add to the bag the appropriate amount of bulk premixed flux.

2. If not using premixed flux, carefully remove the bag from the crucible, seal the bag by hand and carefully mix its contents.
3. Weigh to the nearest 0.01 g between 10 and 30 g of the finely powdered and homogenized sample. Transfer it to the flux mixture in the bag. Again seal bag and carefully mix its contents. In a batch of fusions, include at least one blank consisting of flux mixture only.
4. Cover the crucible with a ceramic lid and transfer it to a 1000°C assay furnace.
5. One hour after the furnace again reaches 1000°C, typically 1 3/4 hours after loading a batch of eight crucibles, remove the crucible, detach the lid, and pour the crucible contents into an iron mould.
6. Allow the mould to cool for 30-60 minutes and separate the button from the slag. Place the button in a tared, covered 200 mL tall-form, spoutless beaker. If necessary, keep the slag for further treatment which involves:

   (a) crushing for 3 minutes in a chrome steel grinding head;

   (b) mixing with 5 g of soda ash, 8 g of borax, 4.50 g of '$NiCO_3$', 1.55 g of S, and, if added in Step 1 above, the same amounts as in Step 1 of Al powder, 5.4% Cu mixture, and 0.1% Te in quartz;

   (c) preparing a second button by fusing this mixture in its original covered crucible for 1 1/4 hours in a furnace preheated to 1000°C and proceeding as above.

NOTES: (i) Typical button masses are between 2.8 and 3.5 g for the first fusion and between 1.8 and 2.8 g for the second fusion; (ii) For chromite and chromite blank initial fusions only, extra '$NiCO_3$' and S are added to prevent a lowering of button mass caused by the added Fe oxide.

7. Weigh the button plus beaker before and after pulverizing the button for 45 seconds in a small chrome steel grinding head. Use a small camel hair brush to facilitate transfer of pulverized material to the beaker.

NOTE: Losses during pulverizing and transfer of pulverized material have been found to be between 10 and 15 mg.

SAFETY NOTE: Handle the pulverized material in a suitably ventilated hood. Although NiS would only be a carcinogenic hazard if inhaled or ingested, avoidance of skin contact with the pulverized material is recommended. Recent information on the toxicology of NiS is available (Worksafe Australia, 1988; Morgan, 1989).

Dissolution of the button for INAA

1. In a fume cupboard, add 30 mL of concentrated HCl to the beaker containing the pulverized button. Immediately cover the beaker with its watchglass and leave it on the smallest hole of a boiling water bath in a fume cupboard for 3 hours.
2. Remove the beaker from the water bath, wash down the watchglass and sides of the beaker with water, and stir the contents with a glass rod. Allow the PGE sulphides to settle and cool for about 1 hour.
3. Filter the solutions in a fume cupboard through a Millipore type HVLP filter. Wash out the beaker once with cold 20% (volume/volume) HCl and then with water. Wash the membrane filter containing the PGE sulphides at least five times with water to remove all traces of Ni.
4. Remove the top section of the filtration apparatus and, with the vacuum still on, carefully wash the circumference of the filter with a fine jet of water, to ensure that Ni is washed off the edge of the filter that was covered by the top section of the filtration apparatus.
5. Place the filter plus residue on a watchglass and let dry for at least one hour at room temperature.
6. Fold the filter into a quarter circle, carefully so as to retain any loosely adhering residue. Place the folded filter in a numbered 30 x 40 mm polyethylene bag – with the curved edge on the left when the bag is viewed on its numbered side. Heat-seal the bag in readiness for INAA.

Dissolution of the button for AAS, ICP-AES and ICP-MS

The two procedures recommended are:

Procedure A, which is similar to that for INAA with a 3 hour boiling water bath digestion. Silver is mostly lost in the filtrate.

Procedure B, which involves coprecipitation of precious metals with Te (Oumo and Nieboer, 1979), after a 3 hour or an overnight (16 hour) boiling water bath digestion. At least 98% of the Ag has been found to be recovered in the precipitate. This procedure involves a single filtration, unlike the procedure of Shazali et al. (1987) which involves two filtrations.

PROCEDURE A

1. Follow the dissolution procedure for INAA as far as the end of the filtration and washing, except use a Millipore HAWP acid-decomposable membrane filter.
2. Return the washed filter plus residue to the beaker. Add 10 mL of aqua regia, cover the beaker, and heat gently for about one hour to dissolve the filter and the precipitate.
3. Allow the beaker to cool somewhat, wash down its underside and the sides of the beaker with water and add 1 mL of 2% (mass/volume) sodium chloride solution (Sen Gupta, 1989).
4. Evaporate to dryness on a low hot-plate. Add 5 mL of concentrated HNO_3, digest covered on a low hot-plate to destroy residual organic matter from the filter. Remove cover, wash down with water as above, and evaporate to dryness.
5. Allow to cool, add 5 mL of aqua regia, cover and heat gently for about 15 minutes. Remove cover, wash down with water as before, and again evaporate slowly to dryness.

NOTE: The mass of residue is typically 0.03 g. This can readily be measured with for example a Sartorius A200S electronic balance.

6. Add a suitable mass of a suitable acidic solvent to the residue; for example, for measurement of PGEs, Au and Ag by flame AAS, 5.00 g of an aqueous solution containing 40% (volume/volume) HCl and 1% (mass/volume) U as uranyl nitrate.
7. Cover the beaker and occasionally swirl for about 20 minutes after the residue has completely dissolved. Transfer the solution to a suitable plastic screw-capped glass vial with an efficient seal, such as Mallinckrodt Cat. No. SB45C and SU85C, capacities 7 mL and 32 mL, respectively. Set aside for spectrometric measurements.

PROCEDURE B

1. Follow the dissolution procedure for INAA as far as the end of the 3 hour digestion on the water bath.

NOTE: This digestion can be prolonged to 16-20 hours if convenient, since any dissolved precious metals will be reprecipitated with Te.

2. Remove the beaker from the water bath, wash down the cover and sides with water, stir the contents with a glass rod, add 2.0 mL of 1 mg Te per mL solution (Sen Gupta, 1989) and adjust volume with water to about 90 mL. Cover the beaker and again place it on the boiling water bath.
3. Have ready a 15% solution of stannous chloride in 2M HCl freshly prepared by dissolving 15 g of $SnCl_2 \cdot 2H_2O$ with 20 mL of hot concentrated HCl, cooling and diluting with water to 100 mL (Shazali et al., 1987).
4. Remove cover from beaker on water bath, add 10 mL of 15% stannous chloride solution slowly and with stirring. Wash down the stirrer with water and digest the covered beaker on the water bath for 30 minutes after which time the precipitate has coagulated.
5. Remove beaker from water bath and filter, while still warm to hot, as in Procedure A. Wash with cold 20% (volume/volume) HCl.

NOTE: Testing of many filtrates in the present study by reprecipitation after adding more Te and stannous chloride has shown that at least 98% of the Rh, Pd, Ag, Pt, and Au present is recovered in the first precipitate.

6. Return the filter plus residue to the 200 mL beaker and prepare the solution by adding 10 mL of aqua regia, and so forth, as in Procedure A.

RESULTS AND DISCUSSION

In the present study, the above fire-assay procedure has been investigated mainly for the reference pyroxenite SARM-7 with the aid of an INAA finish. At a late stage of the present study, coprecipitation with Te (Procedure B) was investigated for SARM-7 and for the proposed reference chromite CHR-Pt+ (International Working Group "Geostandards", 1989) with the aid of a flame AAS finish.

INAA sensitivity and blank values

Table 1 gives INAA detection limits in this and other studies after NiS preconcentration of 30 g samples, as well as detection limits for other instrumental finishes. Blank values in this study were below the INAA detection limit, except the Au blank which was typically 0.6 ppb.

Covering the crucible and MgO addition

To maintain the size of the button from fusions in uncovered crucibles, it was found necessary to increase the amounts of '$NiCO_3$' and S in the flux by 11%. Table 2 is a summary of the results of a combined investigation of covering the crucible and of MgO addition; for this particular experiment, it was decided to add an extra 15 g of quartz when no MgO was added, to increase further the acidity of the slag. Each result in Table 2 is the sum of INAA analyses of: the first fusion button; the filtrate after HCl digestion of this button (Shazali et al., 1987); and buttons from two refusions of the slag. Table 2 shows that with MgO addition the first fusion button collects at least 98% of the Pd, Ir, and Pt; without MgO addition and with a more acidic slag, this percentage tends to be slightly lower (at least 96%). (All such percentages given in this paper are percentages of the total measured analyte concentration in a particular subsample taken for analysis.)

In a radioactive tracer study of the procedure of Robert et al. (1971), Dixon et al. (1975) found somewhat lower PGE recoveries in the first button, e.g. 88% for Pt.

Table 2 shows results obtained with covered crucibles to be generally higher. The MgO addition appears to enhance Pt recovery – however it cannot be explained why the Pd, Pt, and Au results in the third row of Table 2 are higher than the certificate

Table 1. Detection limits for precious metals in geological materials after nickel sulphide preconcentration of 30 g samples

	Detection limit, ppb							
	Ru	Rh	Pd	Ag	Os	Ir	Pt	Au
Flame AAS[a]	-	10	5	10	-	-	50	5
Furnace AAS[b]	-	0.3	0.3	0.1	-	-	0.7	0.3
INAA[c]	5	-	5	-	3	0.1	5	0.3
INAA[d]	3	1	5	-	2	0.1	5	0.1
INAA[e]	-	-	5	-	-	-	5	1
ICP-MS[e,f]	0.5-1	0.5-1	0.5-1	-	-	0.5	0.5-1	1

[a] Concentrations giving 0.002 absorbance in the present study, with the final solution being 5.0 g of 40% (volume/volume) HCl, 1% (mass/volume) U.

[b] Concentrations giving 0.010 absorbance; inferred from Hall et al. (1987).

[c] Present study.

[d] Hoffman et al. (1978).

[e] Hall and Bonham-Carter (1988).

[f] Herring et al. (1988).

Table 2. Results for SARM-7 (15 g) with and without covered crucibles and MgO addition

	ppb					
Fusion conditions	Ru	Pd	Os	Ir	Pt	Au
No MgO, 25 g quartz, covered crucible	380	1680 (98.1)[a]	60	72.3 (96.1)[a]	3490 (97.3)[a]	301 (94)[a]
No MgO, 25 g quartz, uncovered crucible	270	1605 (97.2)	47	63.9 (96.2)	3240 (95.8)	323 (99)
10 g MgO, 10 g quartz covered crucible	400	1710 (98.5)	63	74.1 (98.1)	4240 (98.9)	446 (87)
10 g MgO, 10 g quartz, uncovered crucible	340	1585 (99.0)	60	74.5 (98.8)	3750 (98.7)	271 (99)
Certificate values[b]	430 ±57	1530 ±32	63 ±7	74 ±12	3740 ±45	310 ±15

[a] Figures in brackets are the percentages of the total measured amount of an element recovered in the first NiS fusion. Low INAA sensitivity prevented calculation of such percentage recoveries for Ru and Os.

[b] Steele et al. (1975).

values. On the basis of these results, it was decided to include MgO in the flux, and to cover the crucibles for all subsequent work described in this paper. The results in Table 3, obtained about six months after those in Table 2, are a duplicate set for the third row of results in Table 2; it is noteworthy that the Pt and Au results in Table 3 agree with the certificate values.

Boiling water bath digestion time

In Step 1 of the INAA button dissolution procedure, effervescence ceases after 1-2 hours of digestion on the boiling water bath. However cooling and filtration after this cessation of visible reaction was found to give INAA detection limits for Pd, Pt, and Ru 5-10 times higher than those shown in Table 1 for the present study, probably because of the presence of As and Sb. Table 3 indicates that these latter elements had sufficiently dissolved after a 3 hour digestion for INAA sensitivity to be restored. Tables 3 and 4 show that solubilization losses of Pd, Au, Ir, and probably Pt can occur after a 16 hour digestion; and that such losses are negligible after a 3 hour digestion. Filtrates were analyzed after Te coprecipitation (Shazali et al, 1987); the presence of Te prevented the INAA determination of Pt. Hydrogen sulphide has to be present if solubilization losses of some PGEs are to be prevented (Kuznetzov et al., 1974) and, in the present study, the smell of H_2S was detectable in the cooled beaker after a 3 hour digestion but not after a 16 hour digestion.

Use of ‘$NiCO_3$’

Ni powder (Hoffman et al., 1978) was used for the analyses reported in Tables 3 and 4 because of the temporary unavailability of ‘$NiCO_3$’. Tables 3 and 4 show PGE recoveries in the first fusion button to be 90-95% as opposed to about 98% observed when ‘$NiCO_3$’ was used during study of MgO addition (see above). The observed greater PGE collection efficiency of NiS when ‘$NiCO_3$’ is used rather than Ni metal may be due to the particle size of the ‘$NiCO_3$’ powder being lower than that of the Ni metal powder.

Table 3. Results for SARM-7: 15 g subsample, MgO in flux, covered crucible, 3 hour hot HCl (30 mL) digestion of 3 g NiS buttons

	ppb					
	Ru	Pd	Os	Ir	Pt	Au
1st fusion button:	340	1630	51	67.0	3500	276
Filtrate:	<12	<10	<5	<0.1	-	3
1st slag refusion button:	16	109	<4	3.8	220	27
Filtrate:	<13	<10	<5	<0.1	-	<2
2nd slag refusion button:	<10	26	<3	0.7	20	10
Filtrate:	<13	<10	<5	<0.1	-	<2
Total:	360	1765	51	71.5	3740	316

Table 4. Results for SARM-7: as in Table 3, except the HCl digestion which was for 16 hours

	ppb					
	Ru	Pd	Os	Ir	Pt	Au
1st fusion button:	370	990	60	66.0	2800	135
Filtrate:	<13	430	<5	2.8	-	80
1st slag refusion button:	24	78	<3	4.4	194	4
Filtrate:	<15	23	<5	0.2	-	16
2nd slag refusion button:	-	-	-	-	-	-
Filtrate:	-	-	-	-	-	-
Total:	394	1520	60	73.4	2990	235

Aluminum powder addition

Duplicate fusions in covered crucibles of 15 g of SARM-7 (containing about 15 mg of Cu), without added Cu or Te but with 1.0 g of Al powder added, gave by INAA 0.20 and 0.21 ppm Au – appreciably lower than the certificate value of 0.310± 0.015 ppm. A single analysis in an uncovered crucible in the presence of 3.0 g of Al powder gave 0.25 ppm. These three results were obtained at the same time as the results in Table 2 and include the amount of Au recovered from the filtrate and the slag (in each case totalling 0.03 ppm); they are unexplainably lower than the Au results in Table 2. (The flux for the first of the duplicate fusions contained no MgO and 25 g of quartz (Table 2); the flux for the other two fusions with added Al contained 10 g of MgO and 10 g of quartz.) The effect on Au recovery of adding extra Cu (say 75 mg) in the presence of Al powder was not investigated in the present study.

Copper and Tellurium addition

After the analyses reported in Tables 2-4 had been carried out, it was decided, in view of the low Au results, to include 75 mg of Cu in the flux. This much Cu incorporated into a 2.5 g button would not be sufficient to either impede the acid decomposition of the button or interfere in subsequent INAA. Kuznetzov et al. (1974) advised against the preparation of buttons containing more than 10% Cu.

Table 5. Retention of Pd, Pt and Au in the slag for 10 g of chromite CHR-Pt+ after triple NiS fusion

	CHR-Pt+: results by Pb/Ag collection/AAS[a]	Amount retained in CHR-Pt+ slag after triple NiS fusion[b]	
	ppm	ppm	% of total
Pd	(81.8, 4.9) 86.7	1.4	1.6
Pt	(56.3, 2.3) 58.6	0.5	0.9 (1.6)[d]
Au	(4.34, 0.31) 4.65[c]	0.26	5.6 (4.2)[d]

[a] Flux (for a 10-g subsample) consisted of 30 g of soda ash, 40 g of borax, 20 g of quartz, 80 g of litharge, 3.0 g of flour, 3.5 g of calcium fluoride, 5.0 g of magnetic Fe oxide, 1.40 g of Cu sulphate/magnetic Fe oxide containing 5.4% Cu, and 12 mg of Ag. A second Pb button was prepared in the same crucible after milling the slag, adding 50 g of litharge, 3.0 g of flour, and 3 mg of Ag and fusing as before. Results in brackets are for the first and second Pb buttons.

[b] Flux contained 75 mg of Cu and 2 mg of Te. After three NiS fusions, the slag was pulverized, mixed with 80 g of litharge, 5.0 g of flour, and 3 mg of Ag, and fused in the same covered crucible for 45 minutes at 1000°C.

[c] This result is close to 4.80 ppm Au, obtained for CHR-Pt+ in the present study by INAA without fire-assay preconcentration.

[d] The figures in brackets are from the radioactive tracer study of Dixon et al. (1975) and are the average percentages remaining the slag after a double NiS fusion by the procedure of Robert et al. (1971).

It was also decided at the same time to study the effect of adding 2 mg of Te to the flux with or without added Cu. This investigation is incomplete; the only results so far obtained (by Te coprecipitation (Procedure B) and a flame AAS finish, for SARM-7 and the chromite CHR-Pt+) were low because of unidentified PGE-containing precipitates in the measurement solutions. This precipitation was due to one or both of the following:

(i) The final solvent was 40% HCl/1% U as uranyl acetate instead of the preferred but temporarily unavailable uranyl nitrate.

(ii) An organic residue remained because of decomposition of the filter with aqua regia alone rather than, as described in Procedure A, aqua regia followed by nitric acid.

Despite this setback, the following points can be made from the results so far obtained:

- Addition of Fe oxide to the chromite flux gave a uniform, fluid slag. However this slag (after a single NiS fusion) appeared to retain 10-15% of the total measured precious metals – appreciably higher than about 2% observed in this study for SARM-7.
- Conventional Pb collection fire assay/AAS results in Table 5 show that appreciable amounts of Pd, Pt, and especially Au remained in the slag after preparation of three NiS buttons for the one 10 g portion of the chromite CHR-Pt+. The radioactive tracer study of Dixon et al. (1975) showed similar losses of Pt and Au to the slag after preparation of two NiS buttons by the procedure of Robert et al. (1971), without any sample added to the flux.

SUMMARY

In conclusion, the small NiS button procedure merits further study along the following lines:

1. Development of a flux for maximum precious-metal collection efficiency especially for difficult samples such as chromite, and perhaps sometimes resorting to the use, instead of borax, of the more expensive lithium tetraborate (Borthick and Naldrett, 1984; Robert, 1987; Asif and Parry, 1989). The present study has not conclusively established the need for MgO addition; however such addition has been found to give a nonhygroscopic, easily milled slag. A multiple-additive flux containing for example 10 g of MgO, 1.0 g of Al powder, 75 mg of Cu, and 2 mg of Te is worthy of study.
2. Because use of a crucible lid is inconvenient, investigation of whether it can be omitted if the flux/sample mixture (transferred to the crucible from a suitable plastic mixing jar) is covered by a mixture, conducive to a highly reductive fusion, of for example 17.5 g of soda ash, 35 g of borax, and 2 g of graphite powder. The masses of soda ash and borax in the flux would be decreased by the above amounts and the cover mixture would 'wash out' the mixing jar.

3. Measurement by ICP-MS in order to assess the applicability of the proposed procedure to a wide range of samples, with particular attention to difficulties with Os determination (Date et al., 1987).
4. In view of the carcinogenic properties of powdered NiS, and in order to simplify the procedure, investigation of laser ablation ICP-MS for determining precious metals in small NiS buttons.

REFERENCES

Asif, M. and Parry, S.J.
1989: Elimination of reagent blank problems in the fire-assay preconcentration of the platinum-group elements and gold with a nickel sulfide bead of less than one gram mass; Analyst, v. 114, p. 1057-1059.

Borthick, A.A. and Naldrett, A.J.
1984: Neutron activation analysis for platinum metals and gold in chromitites; Analytical Letters, v. 17(A4), p. 265-275.

Date, A.R., Davis, A., and Cheung, Y.Y.
1987: The potential of fire assay and inductively coupled plasma source mass spectrometry for the determination of platinum-group elements in geological materials; Analyst, v. 112, p. 1217-1222.

Dixon, K., Jones, E.A., Rasmussen, S., and Robert, R.V.D.
1975: The efficiency of the fire-assay procedure with nickel sulfide as the collector in the determination of platinum, silver, gold, and iridium; National Institute for Metallurgy, South Africa, Report No. 1714, 15 p.

Hall, G.E.M. and Bonham-Carter, G.F.
1988: Review of methods to determine gold, platinum and palladium in production-oriented laboratories, with application of a statistical procedure to test for bias; Journal of Geochemical Exploration, v. 30, p. 255-286.

Hall, G.E.M., De Silva, K.N., Pelchat, J.C., and Vaive, J.
1987: Advances in analytical methods based on atomic absorption spectrometry in the Geochemistry Laboratories of the Geological Survey of Canada; in Current Research, Part A; Geological Survey of Canada, Paper 87-1A, p. 477-484.

Herring, D.P., Price, B.D., and Staunton, W.P.
1988: Platinum group metal analysis – an overview; in Bulletin 8; Australian Institute of Geoscientists, p. 87-94.

Hoffman, E.L., Naldrett, A.J., Van Loon, J.C., Hancock, R.G.V., and Manson, A.
1978: The determination of all the platinum-group elements and gold in rocks and ore by neutron activation analysis after preconcentration by a nickel sulfide fire-assay technique on large samples; Analytica Chimica Acta, v. 102, p. 157-166.

International Working Group "Geostandards"
1989: Chromites CHR-Pt+ and CHR-Bkg – two new platinum-group element reference samples; Geostandards Newsletter, v. 13, p. 193.

Kallmann, S. and Maul, C.
1983: Reference analysis of precious metal sweeps and related materials; Talanta, v. 30, p. 21-39.

Kuznetzov, A.P., Kukushkin, Y.N., and Makarov, D.F.
1974: Use of nickel matte as a collector for the noble metals in analysis of poor materials; Zhurnal Analiticheskoi Khimii, v. 24, p. 2155-2160.

Lenahan, W.C. and Murray-Smith, R. de L.
1986: The determination of the platinum-group elements; in Assay and analytical practice in the South African mining industry; South African Institute of Mining and Metallurgy, Monograph Series M6, p. 507-553.

Morgan, L.G.
1989: Nickel toxicology; Environmental Geochemistry and Health, v. 11, p. 75-76.

Myasoedova, G.V., Antokol'skaya, I.I., and Savvin, S.B.
1985: New chelating agents for noble metals; Talanta, v. 32, p. 1105-1112.

Oumo, P.R. and Nieboer, E.
1979: Determination of microgram amounts of precious metals using X-ray fluorescence spectrometry; Analyst, v. 104, p. 1037-1049.

Rice, T.D.
1978: Polyethylene dispensing bottles – a gravimetric alternative to volumetric ware; Analytica Chimica Acta, v. 97, p. 213-217.

Robert, R.V.D.
1987: The use of lithium tetraborate in the fire-assay procedure with nickel sulfide as the collector; Mintek Report No. M324, 9 p.

Royal, S.J. and Mallett, R.C.
1978: Handbook of the interference effects encountered in atomic absorption spectrophotometry at the National Institute for Metallurgy, South Africa (printed and distributed by Varian Techtron Pty. Ltd., Australia) 74 p.

Robert, R.V.D., Van Wyk, E., and Palmer, R.
1971: Concentration of the noble metals by a fire-assay technique using nickel sulfide as the collector; National Institute for Metallurgy, South Africa, Report No. 1371, 15 p.

Sen Gupta, J.
1989: Determination of trace and ultra-trace amounts of noble metals in geological and related materials by graphite-furnace atomic-absorption spectrometry after separation by ion-exchange or coprecipitation with tellurium; Talanta, v. 36, p. 651-656.

Shazali, I., Van't Dack, L., and Gijbels, R.
1987: Determination of precious metals in ores and rocks by thermal neutron activation/gamma spectrometry after preconcentration by nickel sulfide fire assay and coprecipitation with tellurium; Analytica Chimica Acta, v. 196, p. 49-58.
1988: Preconcentration of precious metals by tellurium sulfide fire assay followed by instrumental neutron activation analysis; in Geoplatinum 87, p. 29-42.

Steele, T.W., Levin, J., and Copelowitz, I.
1975: Preparation and certification of a reference sample of a precious-metal ore; National Institute for Metallurgy, South Africa, Report No. 1696, 50 p.

Worksafe Australia
1988: Draft exposure standards for atmospheric contaminants in the occupational environment; Australian Government Publishing Service, Canberra, 120 p.

Rapid separation of the rare-earth elements from some matrix interferences prior to analysis by neutron activation

R. Robertson[1] and Donald D. Burgess[1]

Abstract: A simple procedure for pre-irradiation treatment of samples in the determination of rare-earth elements by neutron activation analysis (NAA) is described. Matrix elements are extracted from samples at room temperature using a mixture of hydrofluoric, nitric, and hydrochloric acids. The remaining solids are retained for NAA. Manganese, uranium, iron, and tantalum are removed effectively while other elements including sodium are partially removed. Thorium is not extracted. The treatment reduces interferences and improves detection limits.

Résumé : Dans cet exposé, on décrit un procédé simple de traitement d'échantillons par pré-irradiation, en vue du dosage des terres rares par activation neutronique. On extrait des échantillons les éléments de la matrice à la température ambiante en employant un mélange d'acides fluorhydrique, nitrique et chlorhydrique. On recueille le résidu solide pour le soumettre à l'analyse par activation neutronique. On retire efficacement le manganèse, l'uranium, le fer et le tantale, alors que les autres éléments, y compris le sodium, ne sont que partiellement enlevés. On n'extrait pas le thorium. Le traitement réduit les interférences et améliore les limites de détection.

---

[1] Becquerel Laboratories Ltd., 6790 Kitimat Rd., Unit 4, Mississauga, Ontario, L5N 5L9, Canada.

INTRODUCTION

The determination of the rare-earth elements (REE) by neutron activation analysis (NAA) can be rendered complicated by the sample matrix in several ways. Radioactivities due to matrix elements may cause interference by peak overlap or through fission reactions. The overall radioactivity due to the matrix may be so high that spectrometers cannot tolerate the resulting count rate. This can prevent the determination of elements giving short-lived isotopes and delay the measurement of others, with the consequent loss of sensitivity. While these problems can sometimes be overcome by the adjustment of procedures, such adjustment is undesirable in the analysis of large numbers of samples.

The aim of this study is to develop a rapid, inexpensive method for reducing the effect of the sample matrix on the determination of the REEs in geological matrices. The approach taken is a simple chemical removal of matrix elements from samples prior to irradiation, leaving REEs in a solid form.

Previously reported methods for pre-irradiation separation of the REEs have employed precipitation (Massart and Hoste, 1968; Abdel-Rassoul et al., 1971; Randa, 1976), solvent extraction (Saiki, 1989), or liquid chromatography (Gorsky et al., 1989). Samples were dissolved by fusion, acid attack, or a combination of these with the objective of dissolving the REEs. In most cases, the procedures reported were complex, and in all cases they were time-consuming.

In this study, a simple acid attack was employed to remove as much matrix material as possible under the chosen conditions. No attempt was made to dissolve samples completely or to place the REEs in solution.

PROCEDURE

Samples of crushed rock, soil, and sediment weighing approximately 500 mg were placed in 13 mL polypropylene tubes fitted with an O-ring cap. Yttrium (1 mg) and calcium (10 mg) were added in solution to act as carriers for the REEs.

Aliquots of 10 mL of a mixed acid solution (40% hydrofluoric acid, 40% distilled water, 10% hydrochloric acid, and 10% nitric acid) were added to the tubes. All acids were reagent grade. The caps were firmly applied and the tubes were agitated overnight.

The tubes were centrifuged for 2 minutes and the supernatant solution discarded. The remaining solids were washed with 10 mL of distilled water, the centrifuging was repeated, and the wash liquid was discarded.

The washed solids were transferred to a 0.45 μm membrane filter (Millipore HVLP 047 00) using 10-20 mL of 1% aqueous ammonium hydroxide. The filters were folded in quarters, placed in polyethylene bags and dried overnight at approximately 90°C. The filters were heat-sealed and packaged with rhenium flux monitors for irradiation.

The nominal NAA procedure was as follows: a) (Dy, Er, Ho) 1 min. irradiation with epithermal neutrons at $2E+10\ n\cdot cm^{-2}\cdot s^{-1}$ followed after 4 h by counting for 10 min.; b) (Gd, Pr, La, Sm, Yb, U) reirradiation for 15 min. with thermal neutrons at $2E+12\ n\cdot cm^{-2}\cdot s^{-1}$ followed after 6 days by counting for 1 h; and c) (Tm, Nd, Tb, Ce, Lu, Eu, Th) counting for 1 h after a further 7 day decay.

Irradiations were carried out at the McMaster Nuclear Reactor (Ontario, Canada). Gamma ray spectrometry was done using an intrinsic Ge detector (Aptec Engineering, 15% relative efficiency) resolution?, a Nuclear Data ND591 linear amplifier, a Nuclear Data ND581 ADC, and a Nuclear Data ND66 multichannel analyzer. Spectrum analysis and data reduction were done using software written by the authors.

Standard reference materials were used as trial samples. These included LKSD-2 (lake sediment), SO-2 (soil), SARM-1 (granite), SY-2 (syenite), and SY-3 (syenite).

CHEMICAL YIELD

Table 1 shows the observed chemical yields for the REEs and some matrix elements. Where possible, this was computed as the ratio of results for extracted and unextracted samples. Literature values were used when a result could not be

Table 1. Chemical yields (%)

Sample	La	Ce	Nd	Sm	Eu	Tb
LKSD-2	93	97	107	93	93	99
SARM-1	95	94	105	94	105	93
SO-2	98	100	102	100	100	90
SY-2	100	98	96	99	95	99
SY-3	96	96	95	103	91	95
	Dy	Ho	Er	Tm	Yb	Lu
LKSD-2	101	69	---	117	91	102
SARM-1	93	91	84	79	94	99
SO-2	92	78	---	82	95	94
SY-2	102	90	104	80	99	108
SY-3	104	108	103	91	95	109
	Th	U	Na	Mn	Fe	Hf
LKSD-2	99	7	41	4	6	59
SARM-1	100	5	6	1	<4	26
SO-2	92	15	25	5	4	70
SY-2	99	3	41	8	6	23
SY-3	98	9	42	8	8	---
	Ta	Sc	Sb	As		
LKSD-2	---	40	26	6		
SARM-1	35	28	21	3		
SO-2	<20	27	58	17		
SY-2	---	66	61	<6		
SY-3	<20	68	77	<10		

obtained for unextracted samples. The recovery of the REEs ranged from 80 to 117% and is satisfactory for routine analysis. Thorium is also completely recovered.

The matrix elements examined are removed to varying degrees. It is important to note that the degree of removal varies with sample type.

REDUCTION OF MATRIX ACTIVITY

In geological matrices, the most important matrix elements in the determination of the REEs are Mn, Sc, and Na. Manganese can give rise to high activities in the determination of Dy, which yields a radioisotope of similar half-life. Such high matrix activity can raise detection limits by delaying counting (with consequent decay of Dy activity) and by increasing the Compton continuum of gamma ray spectra. In this work, Er and Ho were determined together with Dy and were therefore also susceptible to problems due to Mn activity. Extraction of samples gave good removal of Mn (see Table 1). This improved detection limits (see Table 3 below) and permitted longer irradiation time which further improved detection limits.

Matrix activity due to Na affected the remaining REEs, which were determined using thermal neutrons. The removal of Na, however, was disappointing and varied widely among sample types. For a single type of sample, however, extraction was consistent. Experiments in which samples were mixed with the acid solution and heated overnight at approximately 70°C showed no improvement in Na removal. Where Na was

Table 2. Detection limits (ppm) for matched conditions

Sample	Dir.	Ext.	Dir.	Ext.	Dir.	Ext.	Dir.	Ext.
Ti,Td	La 15,6		Ce 15,13		Pr 15,6		Nd 15,13	
LKSD-2	0.34	0.36	3.8	3.2	17	18	11	11
SARM-1	0.38	0.32	3.8	3.6	19	15	12	12
SO-2	0.27	0.27	2.8	2.9	14	14	7	10
SY-2	0.46	0.39	7.3	5.8	20	19	10	16
SY-3	1.10	1.40	14.0	11.0	47	59	33	27
Ti,Td	Sm 15,6		Eu 15,13		Gd 15,6		Tb 15,13	
LSD-2	0.06	0.06	0.16	0.14	120	120	0.39	0.22
SARM-1	0.06	0.06	0.15	0.16	120	110	0.19	0.13
SO-2	0.05	0.06	0.10	0.12	95	92	0.33	0.19
SY-2	0.10	0.07	0.18	0.14	200	130	0.36	0.22
SY-3	0.21	0.18	0.65	0.49	470	460	0.58	0.38
Ti,Td	Dy* 1,4 (hr)		Ho* 1,4 (hr)		Er* 1,4 (hr)		Tm 15,13	
LKSD-2	1.9	0.72	2.3	1.10	18	7.4	0.67	0.66
SARM-1	1.4	0.74	1.6	0.98	11	4.7	0.73	0.72
SO-2	1.7	0.85	1.9	0.99	15	6.3	0.48	0.62
SY-2	3.5	1.28	3.5	1.34	20	10.0	1.20	1.00
SY-3	4.0	2.07	4.1	2.07	27	12.0	2.30	1.80
Ti,Td	Yb 15,6		Lu 15,13					
LKSD-2	0.12	0.13	0.09	0.07				
SARM-1	0.12	0.12	0.07	0.07				
SO-2	0.10	0.11	0.07	0.06				
SY-2	0.14	0.14	0.13	0.10				
SY-3	0.38	0.46	0.26	0.19				

*epithermal irradiation
Ti: irradiation time (min.), Td: decay time (days)
Dir.: direct (unexpected), Ext.: extracted

Table 3. Detection limits (ppm) for varied conditions (Ext.: extracted, Dir.: direct (unextracted))

A) Change in Irradiation Time

	Dy			Er			Ho		
	Ext.	Ext.	Dir.	Ext.	Ext.	Dir.	Ext.	Ext.	Dir.
Ti	5	1	1	5	1	1	5	1	1
LKSD-2	0.53	0.72	1.9	3.6	7.4	18	0.54	1.10	2.3
SARM-1	0.46	0.74	1.4	1.9	4.7	11	0.44	0.98	1.6
SO-2	0.47	0.85	1.7	2.6	6.3	15	0.46	0.99	1.9
SY-2	0.59	1.28	3.5	4.1	10.3	28	0.62	1.34	3.5
SY-3	1.00	2.07	4.0	5.6	11.8	27	0.62	2.07	4.1
Decay time: 4 hr; Ti: irradiation time (min.)									

B) Change in Decay Time

	Gd			Pr			La		
	Ext.	Ext.	Dir.	Ext.	Ext.	Dir.	Ext.	Ext.	Dir.
Td	3.5	5.75	6.75	3.5	5.75	6.75	3.5	5.75	6.75
SARM-1	29	89	253	4.2	12	38	0.29	0.30	0.54
SO-2	31	79	200	5.9	12	29	0.36	0.26	0.39
Irradiation time: 15 min.; Td: decay time (days)									

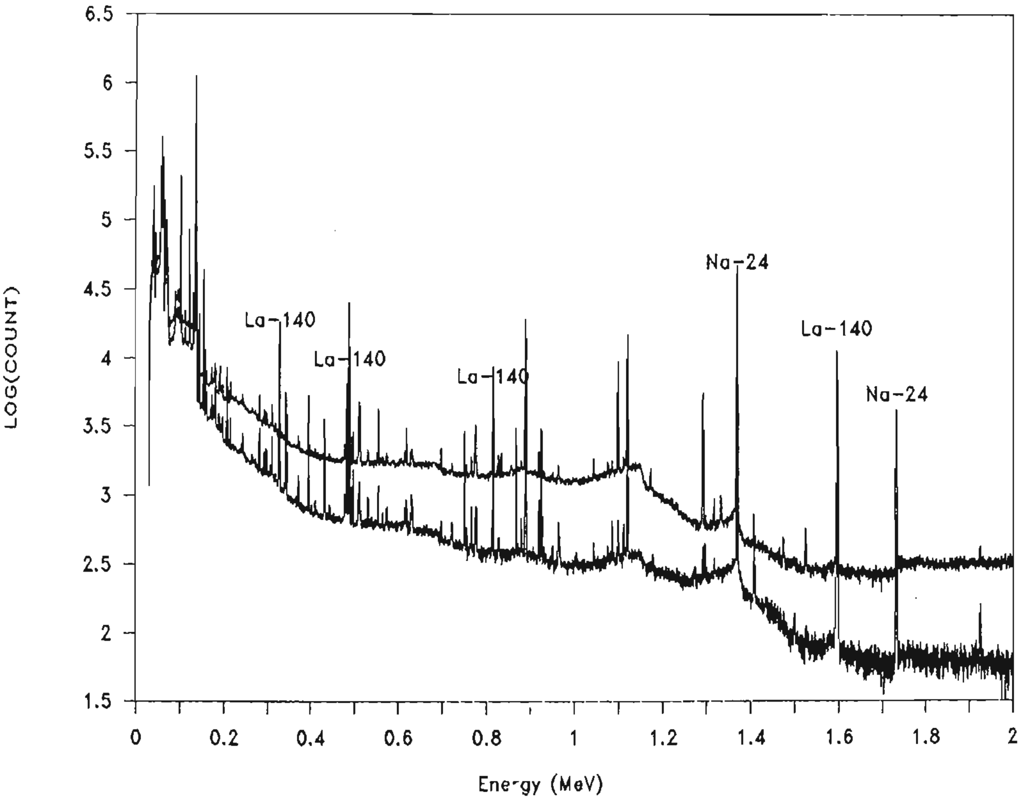


Figure 1. Comparison of Baseline Shapes. Sample: SO-2.

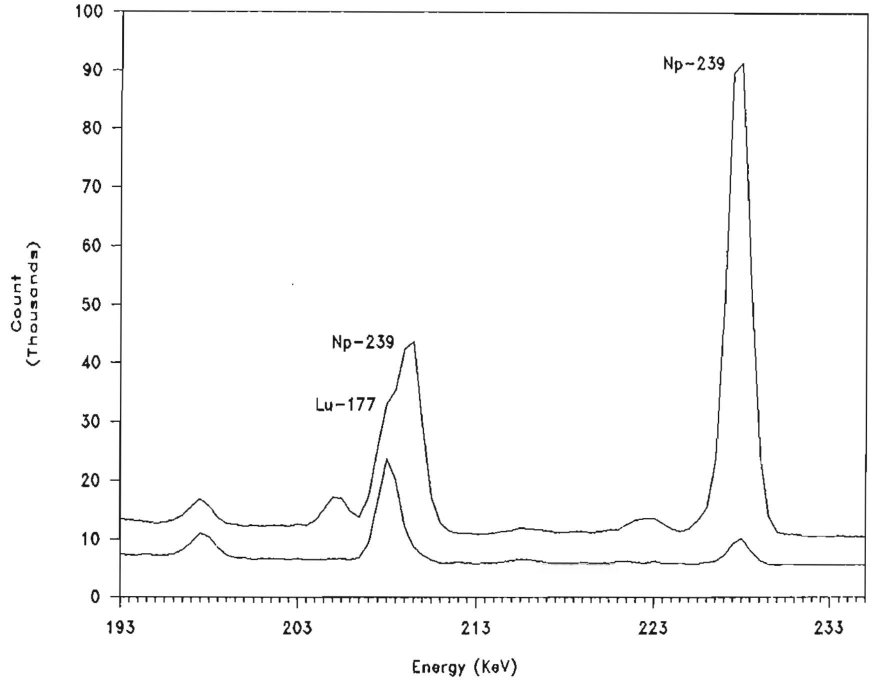
largely removed, it was possible to carry out counting at shorter decay times (see Table 3), improving detection limits for the shorter-lived rare-earth activities due to Gd, Pr, and La.

DETECTION LIMITS

Detection limits were computed for 95% confidence using the definition of Currie (1968). Detection limits in units of counts were converted to units of ppm using the same computation as was used for analyte values, taking account of the effect of interference corrections. It should be noted that detection limits in units of analyte level depend on both the uncertainty of the blank, here the spectral baseline, and the measurement sensitivity. In radiation measurement, the uncertainty of the baseline depends on its magnitude due to Poisson counting statistics. Results are shown in Table 2 for the measurement of extracted and unextracted samples under similar irradiation and decay times. Table 3 gives results for variation of these times.

Figure 2.

Interference Reduction. Sample: SY-2; Np-239 is produced by U.



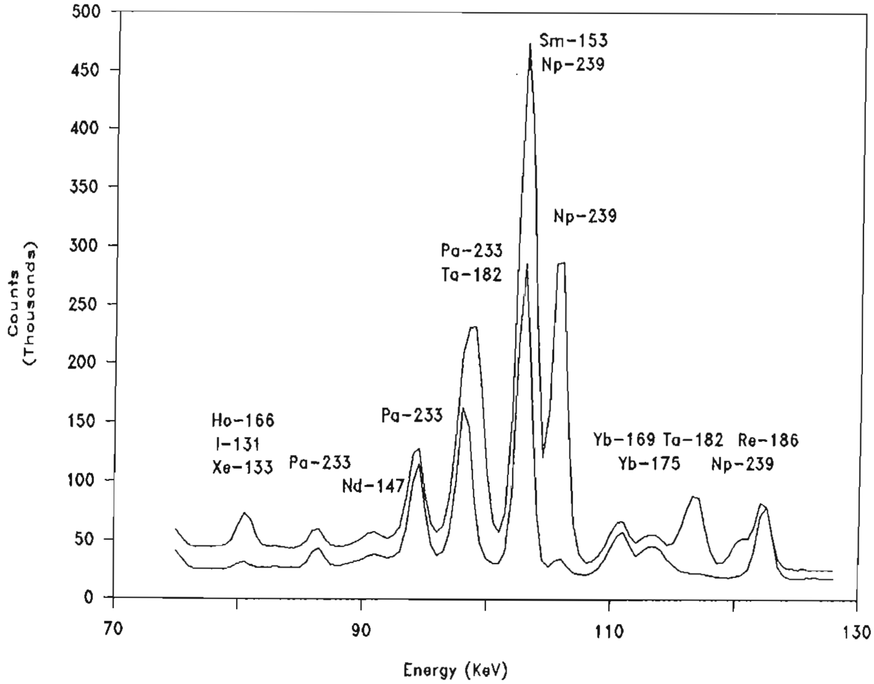


Figure 3.

Interference Reduction. Sample: SY-2; Pa-233 is produced by Th; Np-239, I-131 and Xe-133 are produced by U.

When matched conditions were considered, extraction gave improvement in detection limits only for Dy, Er, and Ho (removal of Mn), and for Tb (removal of Na). The detection limits after extraction were approximately half those observed without extraction. This change was due only to the reduction of the baseline, as the only change in procedure was the extraction step. The remaining REEs showed no improvement in detectability due to extraction. As shown in Figure 1, reduction in Na content affected the shape of the baseline most strongly between about 0.8 and 1.2 MeV. Only Tb was determined using a peak in this region. Figure 1 also shows that the baseline shape is strongly affected by peaks due to La-140, which are present at several energies. This indicates that the detection limits for several REEs depend on the amount of La present. All these observations indicate that the extraction procedure described here gives limited improvement in detectability due to baseline reduction alone.

The reduction of matrix activity permits the use of procedures that would not be possible with unprocessed samples. Irradiations can be lengthened, decays can be shortened, or both. The effect is to increase the specific activity of indicator isotopes at the time of counting and therefore increase the measurement sensitivity. If the increase in sensitivity more than offsets any increase in baseline height, and if count rates are not excessive, detection limits are improved. Table 3 demonstrates this point. In the experiments carried out here, detection limits were improved by factors of from two to almost ten. If improvement is desired for long-lived indicator isotopes, however, irradiation time must be lengthened as reduction in decay time has little effect on sensitivity.

INTERFERENCE REDUCTION

Interference in the determination of the REEs by NAA occurs chiefly as a result of peak overlap in gamma ray spectra and of fission reactions, mostly due to U, that produce the isotope being measured or isotopes that give peak overlap. Peak overlap and fission interferences can in many cases be corrected by computation, but these corrections degrade the precision of the final result.

Figure 2 demonstrates the reduction obtained by acid extraction in the Np-239 activity due to U and the reduction of the interference on the peak used to determine Lu. Figure 3 shows the very useful reduction in spectral complexity below about 120 KeV that results from the removal of U and Ta. The direct and partial peak overlaps of Np-239 on the peak used to determine Sm are greatly reduced and the interferences on the Ho peak by I-131 and Xe-133 due to fission are decreased. Removal of Ta simplifies computation of the area of the Sm peak.

Removal of U also reduces fission contributions to the isotopes used to determine Ce, Nd, and La.

RUGGEDNESS

An important benefit of pre-irradiation extraction is that samples become more similar at the time of counting. Large differences in levels of Mn, U, and other elements among samples are then less likely to demand modification of routine operating procedures or to cause undetected errors. This expedites the efficient analysis of large numbers of samples.

CONCLUSIONS

A simple pre-irradiation extraction of samples with mixed acids can provide useful improvements in the determination of the REEs by NAA. The removal of Mn and U is especially beneficial. Desirable further developments would be the removal of Th and the more effective removal of Na. The procedure described is rapid and suitable for the processing of large numbers of samples.

REFERENCES

Abdel-Rassoul, A.A., Herpers, U., and Herr, W.
1971: Improved techniques for separation and determination of rare-earth elements in extraterrestrial material; in Activation Analysis in Geochemistry and Cosmochemistry, (ed.) A.O. Brunfelt and E. Steinnes; Universetetsforlaget, Oslo.

Currie, L.A.
1968: Limits for qualitative detection and quantitative determination; Analytical Chemistry, v. 43, p. 586-595.

Gorsky, B., Korotkin, Yu. S., and Kosyakov, V.N.
1989: Selective concentration of the lanthanides with simultaneous purification from scandium; Journal of Radioanalytical and Nuclear Chemistry, v. 135, p. 27-37.

Massart, D.L. and Hoste, J.
1968: Activation analysis of rare earths; Analytica Chimica Acta, v. 42, p. 7-14.

Randa, Z.
1976: Routine neutron activation determination of REE in rocks and similar materials by pre-activation group separation; Radiochemical and Radioanalytical Letters, v. 24, p. 177-188.

Saiki, M.
1989: Solvent extraction studies using tetracycline as a complexing agent; Journal of Radioanalytical and Nuclear Chemistry, v. 130, p. 111-119.

Advantages of the fundamental algorithm in quantitative XRF analysis

Richard M. Rousseau[1]

Abstract: A modern theoretical method using the Fundamental Algorithm to correct for matrix effects in X-ray fluorescence (XRF) analysis is described. This powerful quantitative method combines the practical flexibility of influence coefficient concepts and the theoretical exactness of the fundamental parameter technique. This method is in full agreement with the treatment of the physics as proposed by Sherman and can be applied to the analysis of any sample type. It offers the maximum of accuracy limited only by the quality of sample preparation. The special calibration procedure associated with the Fundamental Algorithm is explained. This procedure allows the matching of theoretical formalism to experimental data of each individual laboratory. Finally and obviously, this approach requires a computer program to be applied. Some important guidelines are given to help XRF analysts to select the XRF program appropriate to their needs.

Résumé : Dans cet exposé, on décrit une méthode théorique moderne fondée sur l'emploi de l'algorithme fondamental pour corriger les effets de matrice lors de l'analyse par fluorescence X (FX). Cette méthode quantitative efficace combine la souplesse pratique des concepts de coefficient d'influence et l'exactitude théorique de la technique des paramètres fondamentaux. Elle concorde entièrement avec le traitement physique tel que proposé par Sherman et convient à l'analyse de tous les types d'échantillons. Elle présente la précision la plus grande, seulement limitée par la qualité de la préparation des échantillons. On explique le procédé spécial d'étalonnage associé à l'algorithme fondamental. Ce procédé permet d'accorder le formalisme théorique avec les données expérimentales fournies par chacun des laboratoires. Finalement, de toute évidence, cette méthode exige l'emploi d'un programme informatique. On présente quelques lignes directrices importantes qui aideront les analystes à sélectionner le programme FX leur convenant.

---

[1] Geological Survey of Canada, 601 Booth St., Ottawa, Ontario, K1A 0E8, Canada.

INTRODUCTION

In quantitative XRF analysis, one of the major problems to solve is the correction for matrix effects (absorption and enhancement). During the last three decades, many solutions have been proposed to this problem, but two methods in particular are more popular than any of the others. The first popular solution to have been proposed uses empirical influence coefficients which are numerical coefficients correcting for the effects of each matrix element on the analyte (Lachance and Traill, 1966). These coefficients, which depend on the matrix composition, are calculated by a regression analysis of measured intensities and standard compositions.

The other popular solution to correct for matrix effects was proposed by Criss and Birks (1968). Their method, called "Fundamental Parameters", is an application of the equations derived by Sherman (1955). These equations allow one to calculate theoretical net X-ray intensities emitted by each element from a specimen of known composition when it is irradiated by a polychromatic X-ray beam.

The advantages and disadvantages of both of the above procedures will be explained. To eliminate their respective disadvantages, Rousseau (1984) proposed a new approach which combines the practical flexibility of the influence coefficient concepts and the theoretical exactness of the fundamental parameter technique. This new approach allows one to calculate theoretical influence coefficients within a new algorithm called the Fundamental Algorithm. It is this third solution which will be explained in the present paper.

The special calibration procedure associated with the Fundamental Algorithm will also be explained. This procedure allows the matching of theoretical formalism to experimental data of each individual laboratory. Finally and obviously, the application of this approach requires a computer program. Some important guidelines will be given to help XRF analysts to select the XRF program appropriate to their needs.

EMPIRICAL INFLUENCE COEFFICIENTS

Empirical influence coefficients are based on the empirical observation that the magnitude of matrix effects (absorption and enhancement) of any element j on analyte i, in a given specimen, can be quantified by an influence coefficient a_{ij}. Lachance and Traill (1966) were among the first to apply influence coefficients to practical analytical applications, by proposing an equation of the form:

$$C_i = R_i \ (1 + \Sigma_j a_{ij} C_j) \qquad (1)$$

where R_i is the intensity of analyte i in the specimen relative to the intensity of the pure analyte i; C_i and C_j are respectively concentrations of analyte i and of element j.

Empirical coefficients for matrix effect corrections can easily be obtained by multiple regression methods using measured intensities and standard compositions, which cover the analyte concentration ranges of interest. The success of empirical coefficients depends on the availability of standards that closely match the compositions of the unknowns. As the number of analytes increases, so must the number of standards required. In fact, to avoid any divergent solutions of the respective simultaneous equations, it is recommended to use at least 2N standards, where N is the number of elements to determine.

The great advantage of empirical coefficients is that they only have to be calculated once, and without the need to resort to complex theory. Their use is quite simple and practical. It is the best approach to use when one has to analyze nonhomogeneous specimens or when it is not possible to eliminate problems such as particle size or mineralogical effects. In other words, empirical coefficients can tolerate less meticulous sample preparation. There is also no need for standards to total close to 100%.

On the other hand, the preparation and measurement of an adequate number of reliable standards could be long and tedious and can easily yield empirical coefficients that are often not very accurate and have no physical meaning. This statistical approach is sensitive to any experimental errors in the data and the calculated coefficients can only be applied to unknowns of composition similar to those of the standards used. In other words, empirical coefficients are likely to be inaccurate if applied over extended composition ranges and consequently their range of application is limited.

An easier and much more practical solution to these problems is to compute theoretical coefficients. They can be calculated for any combination of elements and any experimental conditions, within a few seconds! The use of empirical coefficients, with all their potential problems, must then be limited as much as possible.

FUNDAMENTAL PARAMETERS

Sherman (1955) prophetically proposed mathematical equations allowing one to calculate net intensities of every analyte in a specimen as a function of the composition. At that time, these equations did not become widely used for the following reasons:

- First, XRF analysts do not need to calculate intensities, which can be measured, but they do want to calculate the composition of unknowns. Furthermore, in order to calculate intensities, the specimen's composition must be known when it is, of course, an unknown prior to the analysis.
- Second, algebraic operations cannot produce explicit equations allowing the calculation of concentrations C_1, C_2, ..., C_N as a function of corresponding measured intensities. In other words, inversion of Sherman's equations is impossible.
- Finally, in 1955, no computer was powerful enough to calculate the composition of multielement specimens.

To resolve these problems Criss and Birks (1968) proposed a method called "Fundamental Parameters". With this method a first estimate of concentrations is evaluated from measured intensities. This estimate of composition is used to calculate a new set of intensities from which a revised estimate of composition is then calculated. This procedure is iterated until the difference between compositions of two consecutive cycles is insignificant.

The great advantage of this method is its theoretical exactness. However, although this method has been improved by many researchers since its publication, the original proposed method nevertheless suffers from the following weaknesses: to be able to use this method, a first approximation of the specimen composition is absolutely necessary. Frequently, however, a poor first approximation is generated from measured intensities because such intensities have been strongly modified by the matrix. To improve the first approximation, concentrations are normalized during the procedure of calculation. This must be avoided if accurate results are required, and its use is not recommended. The proposed calibration procedure is also somewhat ambiguous and inefficient and its range of application is limited also. Speed of calculation is very slow because the complex part of the equations are calculated for each iteration and many such iterations are required since the first approximation of the composition is often very far from the final composition.

THE THIRD SOLUTION

The fundamental parameter approach proposed by Criss and Birks (1968) is an application of the equations derived by Sherman. By simply manipulating these same equations and by doing absolutely no approximation at all during the process of derivation, Rousseau (1984) deduced new theoretical expressions for multielement influence coefficients in which the correction for both absorption and enhancement effects are clearly and accurately defined. They are used in the Fundamental Algorithm

$$C_i = R_i \frac{1 + \Sigma_j \alpha_{ij} C_j}{1 + \Sigma_j \rho_{ij} C_j} \qquad (2)$$

where α_{ij} and ρ_{ij} are the multielement coefficients correcting for absorption and enhancement, respectively. These are calculated by means of equations (9) and (10) in Rousseau (1984). The Fundamental Algorithm can be applied to any type of sample of any composition. An experimental verification of this method done by Rousseau and Bouchard (1986) on different types of alloys confirms the accuracy and versatility of the method.

To determine the composition of each specimen, a first estimate of the composition is calculated using the Claisse-Quintin algorithm (Claisse and Quintin, 1967; Rousseau and Claisse, 1974; Rousseau, 1989):

$$C_i = R_i\,[1 + \Sigma_j\,(a_{ij} + a_{ijj}\,C_M)\,C_j + \Sigma_j\,\Sigma_k\,a_{ijk}\,C_j\,C_k] \qquad (3)$$

where C_M is the concentration of the total matrix and a_{ij}, a_{ijj}, and a_{ijk} are binary influence coefficients. Then, from this estimated composition, all α_{ij} and ρ_{ij} coefficients, the complex part of Sherman's equations, are calculated once only. With these calculated coefficients now used as constants, the final composition of the specimen (and a more accurate one) is calculated by applying an iteration procedure to the Fundamental Algorithm.

The Fundamental Algorithm method has the following clear advantages:

- Since the numerator of the equation (2) corrects for all the absorption effects of the matrix on the analyte and since the denominator corrects for all the enhancement effects, the shape of equation (2) makes it much easier to understand the physical principles behind the complex equations of Sherman.
- Empirical coefficients are no longer required. The fundamental algorithm uses theoretical influence coefficients that are in full agreement with the treatment of the physics as proposed by Sherman. This method also uses a fully theoretical approach to calculate all the required parameters. For example, the method uses equations proposed by Pella et al. (1985) to calculate up to 350 different intensities of the incident spectrum emitted by the X-ray tube. It uses data of Heinrich (1986) to calculate mass absorption coefficients by a method proposed by Springer and Nolan (1976). It also uses modern values of X-ray fluorescence yields (Bambinek et al., 1972; Hanke et al., 1985) and Coster-Kronig transition probabilities (Schreiber and Wims, 1982).
- Normalization of calculated concentrations is no longer required. Since the complex part of Sherman's equations is calculated once only, the calculation time is greatly reduced.

CALIBRATION

The calibration procedure associated with the fundamental algorithm will not be explained here in full detail, that having been described in a preceding paper (Rousseau, 1989a). However, the most important features will be recalled.

The calibration procedure is based on the simple relation

$$\frac{I_i}{I_{iStd}} = m_i\ R_i \qquad (4)$$

The left hand term is the MEASURED relative intensity defined as the ratio of the net intensity of the analyte i in the specimen to the net intensity of the analyte i in any standard. In the right hand term, R_i is the relative intensity CALCULATED by the inverted algorithm (2) and m_i is the slope of the calibration curve. The R_i intensities are calculated for all the standards on hand and their I_i and $I_{i\,Std}$ intensities are measured. Then, if the MEASURED relative intensities $I_i / I_{i\,Std}$ (Y-axis) are plotted as a function of the CALCULATED relative intensities R_i (X-axis), it gives a straight line of slope equal to m_i.

With this approach, we are comparing two similar variables, i.e. calculated and measured relative intensities. If for example, $I_{i\,Std}$ is the measured intensity emitted by the pure analyte i, we get a straight line at 45°, i.e. $m_i = 1.0$. However, the slope might be slightly different from 1.0 depending on how well the theory matches the measured data. But one thing is certain: the slope is the link which allows one to adapt the theory (R_i) to each spectrometer and makes truly meaningful the equal sign in equation (4). Once the slope m_i of the calibration curve of the analyte i is determined, the concentrations C_i of the unknown are calculated from a combination of equations (2) and (4):

$$C_i = \frac{1}{m_i} \cdot \frac{I_i}{I_{iStd}} \cdot \frac{1 + \Sigma_j \alpha_{ij} C_j}{1 + \Sigma_j \rho_{ij} C_j} \qquad (5)$$

Another consequence of the fact that the calibration curve compares two similar variables, is that the slope is independent of the composition of the standards used. Consequently, the standards do not have to be similar to the unknowns and very few standards are necessary (as few as one).

Pure analytes are not required because their intensities are directly calculated from the slope of the calibration curves. But if some are available, they are handled as any other standard.

The calibration curves can be extrapolated by a factor of two or three, thus protecting the analyst from errors which would otherwise result when the specimen concentrations exceed the calibration range.

GUIDELINES FOR SELECTING NEW XRF SOFTWARE

Some new computer programs have been written to perform quantitative XRF analysis incorporating the most modern correction methods. A good example of one such program is the one called CiROU (Rousseau, 1989b). It can be run on any IBM-PC/XT/AT, PS/2 or compatible computer. It is a complete "off-line" program enclosing within itself all the steps necessary, after the collection of intensities by the XRF spectrometer, to calculate analytical composition: calculation of theoretical influence coefficients, a clearly defined and efficient calibration procedure with graphics output, the ability to read measured intensities, calculation of net intensities and concentrations of unknowns, print-out of analytical reports and data transmission to or from an external computer.

Other commercial XRF programs (Bilbrey et al., 1988) are also available and some important guidelines are given here to help users to select the appropriate XRF program corresponding to theirs needs:

- Does it run on any IBM or compatible personal computers?
- Have the programmers experience of working in an XRF laboratory? Recently...?
- Whether full details of the method used are available?
- To minimize keystrokes, does it propose previously entered data as default?
- Does it recommend the use of calibration standards similar to the unknowns? If the answer is yes, throw it away!
- Does it include calibration graphics output?
- Does it normalize concentrations during their calculation? If so, discard it!
- Does it include corrections for dilution, volatile, unmeasured components, and L.O.I.?
- Does it allow data editing and report printing?
- For a given computer, how long does it take to calculate the composition of a specimen of 10 elements?
- Is the computer interface really user friendly?
- Is after-sale support readily available?
- Is the price too high?

CONCLUSION

We strongly believe that the performance of the fundamental parameter method has been improved by incorporating the concept of influence coefficients into the fundamental algorithm. If, for some, the fundamental parameter method is a limit, for us, it has been the starting point, all the while remaining faithful to the principles of theoretical physics. The method offers the maximum of accuracy limited only by the quality of sample preparation.

There is no longer any need for empirical coefficients. The theoretical multielement coefficients can be calculated from an estimate of the composition of each specimen and then used in the fundamental algorithm to obtain a more accurate composition of this specimen.

The proposed calibration procedure offers many advantages compared to the traditional calibration of intensities versus concentrations; it increases the accuracy of XRF analysis and facilitates the work of the analyst.

Without computer programs, theoretical coefficients cannot be calculated. Some high quality ones are already available, making empirical and approximate methods less and less popular, especially when the performance of microcomputers increases every year while their cost decreases more and more.

REFERENCES

Bambinek, W., Crasemann, B., Fink, R.W., Freund, H.U, Mark, H., Swift, C.D, Price, R.E., and Rao, P.V.
1972: X-ray fluorescence yields, Auger, and Coster-Kronig Transition Probabilities; Reviews of Modern Physics, v. 44, p. 716-813.

Bilbrey, D.B., Bogart, G.R., Leyden, D.E., and Harding, A.R.
1988: Comparison of fundamental parameters programs for quantitative X-ray fluorescence spectrometry; X-ray Spectrometry, v. 17, p. 63-73.

Claisse, F. and Quintin, M.

1967: Generalization of the Lachance-Traill method for the correction of the matrix effect in X-ray fluorescence analysis; Canadian Journal of Spectroscopy, v. 12, p. 129-134.

Criss, J.W. and Birks, L.S.

1968: Calculation methods for fluorescent X-ray spectrometry – Empirical coefficients vs. fundamental parameters; Analytical Chemistry, v. 40, p. 1080-1086.

Hanke, W., Wernisch, J., and Pohn, C.

1985: Fluorescence yields, ω_K ($12 \leq 7 \leq 42$), and ω_{L3} ($38 \leq 7 \leq 79$), from a comparison of literature and experiments (SEM); X-ray Spectrometry, v. 14, p. 43-47.

Heinrich, K.F.J.

1986: Mass absorption coefficients for electron probe microanalysis; 11th International Congress on X-ray Optics and Microanalysis, August 1986, London, Ontario, p. 67-119.

Lachance, G.R. and Traill, R.J.

1966: A practical solution to the matrix problem in X-ray analysis; Canadian Journal of Spectroscopy, v. 11, p. 43-57.

Pella, P.A., Feng, F., and Small, J.A.

1985: An analytical algorithm for calculation of spectral distributions of X-ray tubes for quantitative X-ray fluorescence analysis; X-ray Spectrometry, v. 14, p. 125-135.

Rousseau, R.M.

1984a: Fundamental algorithm between concentration and intensity in XRF analysis: 1 – Theory; X-ray Spectrometry, v. 13, p. 115-120.

Rousseau, R.M. (cont'd.)

1984b: Fundamental algorithm between concentration and intensity in XRF analysis: 2 – Practical application; X-ray Spectrometry, v. 13, p. 121-125.

1989a: Painless XRF analysis using new generation computer programs; Advances in X-ray Analysis, v. 32, p. 77-82.

1989b: Concepts of influence coefficients in XRF analysis and calibration; Advances in X-ray Analysis, v. 32, p. 69-75.

Rousseau, R.M. and Bouchard, M.

1986: Fundamental Algorithm between concentration and intensity in XRF analysis: 3 – Experimental verification; X-ray Spectrometry, v. 15, p. 207-215.

Rousseau, R.M. and Claisse, F.

1974: Theoretical Alpha Coefficients for the Claisse-Quintin relation for X-ray spectrochemical analysis; X-ray Spectrometry, v. 3, p. 31-36.

Schreiber, T.P. and Wims, A.M.

1982: Relative intensity factors for K, L and M shell X-ray lines; X-ray Spectrometry, v. 11, p. 42-45.

Sherman, J.

1955: The theoretical derivation of fluorescent X-ray intensities from mixtures; Spectrochimica Acta, v. 7, p. 283-306.

Springer, G. and Nolan, B.

1976: Mathematical expression for the evaluation of X-ray emission and critical absorption energies, and of mass absorption coefficients; Canadian Journal of Spectroscopy, v. 21, p. 134-138.

The present and future of arc source emission spectrometry (AS-ES) in China

Ruiping Shen[1]

Abstract: Detection limits, analytical precision, and accuracy of "old" arc source emission spectrometry (AS-ES) are reviewed and compared with some modern spectrochemical methods. While emphasizing the strong points of AS-ES and its unique capabilities for some analytical tasks, the inherent weak points and limitations are also pointed out. Some basic approaches towards further development of AS-ES, outlined in this paper, should result in establishing its continuing role in both routine and research-oriented analysis.

Résumé : Dans cet exposé, on examine les limites de détection, la précision de l'analyse et l'exactitude de l'ancienne méthode de spectrométrie d'émission avec source à arc (SE/SA), et on les compare à celles de quelques méthodes spectrochimiques modernes. Tout en insistant sur les points forts de la méthode SE/SA et sur ses possibilités uniques quant à certains travaux d'analyse, on indique aussi ses limitations et ses points faibles inhérents. Les efforts fondamentaux de perfectionnement du procédé SE/SA, tels qu'esquissés dans le présent exposé, devraient permettre d'établir son rôle continu à la fois en analyse courante et en analyse orientée vers la recherche.

---

[1] Applied Research Centre of Spectroscopical Instrumentation of China, University of Shijiazhang, China.

INTRODUCTION

There are several reasons which encourage the author to raise the issue and to emphasize the possibility and indeed, the necessity of further development of "old" arc source emission spectrometry (AS-ES). There are at least 2000 laboratories in China where AS-ES is still being used as a routine analytical tool. Among them, about 1000 are geological laboratories with the responsibility of analyzing geochemical exploration samples. China is a developing country and consequently it is almost impossible to outfit such a large number of laboratories with modern expensive equipment in a short period of time. Although there are some inherent weaknesses in AS-ES analysis, there are also a number of strong points which make the technique attractive. Moreover, it has some unique capabilities which have not been fully exploited in research-oriented studies.

DETECTION LIMITS, PRECISION, AND ACCURACY OF AS-ES

The flexibility of the arc source is demonstrated in 'fractional distillation' which allows the analyte of interest to be vaporized under controlled conditions. The signal to background ratio can be greatly enhanced by this fractional distillation effect and, with the appropriate excitation conditions, detection limits can be lowered substantially. When Scribner and Mullin (1946) discovered the carrier distillation method in 1946, detection limits with spectral analysis were dramatically reduced from 10^{-3} -10^{-4}% to 10^{-5} -10^{-6}%. Since then, detection limits have been further lowered and, more importantly, the analytical precision and accuracy improved, leading to a wide range of applications. Today, detection limits for the volatile elements by AS-ES remain superior to those by ICP-ES, AAS, and XRF, though inferior to atomic fluorescence spectrometry (AFS) for As and Hg. Detection limits for elements of intermediate volatility are in the order of 1 ppm. Only for those elements with strong ion lines (such as Be and some rare-earth elements) are detection limits inferior to those by ICP-ES. For refractory elements, the arc concentration method can be used to improve their detection limits significantly to levels such as: Nb – 0.3 ppm; Ta – 0.5 ppm; Hf – 0.1 ppm; Mo – 0.3 ppm; W – 0.5 ppm; and Th – 1 ppm. The advantage of this method is significant compared with various modern spectrochemical analysis methods (Shen, 1964). Figure 1 compares typical detection limits by AS-ES with those by other instrumental techniques.

The precision of measurement by AS-ES depends upon the stability of the arc source, commonly agreed to be better than 2%. The overall precision is dependent upon the operative conditions used and hence the skill of the analyst. We have achieved relative standard deviations (RSD) in the range 1.8-3.2% for refractory elements in mono-minerals (Shen, 1983). A comprehensive package designed more recently to determine 37 elements achieved RSDs in the range

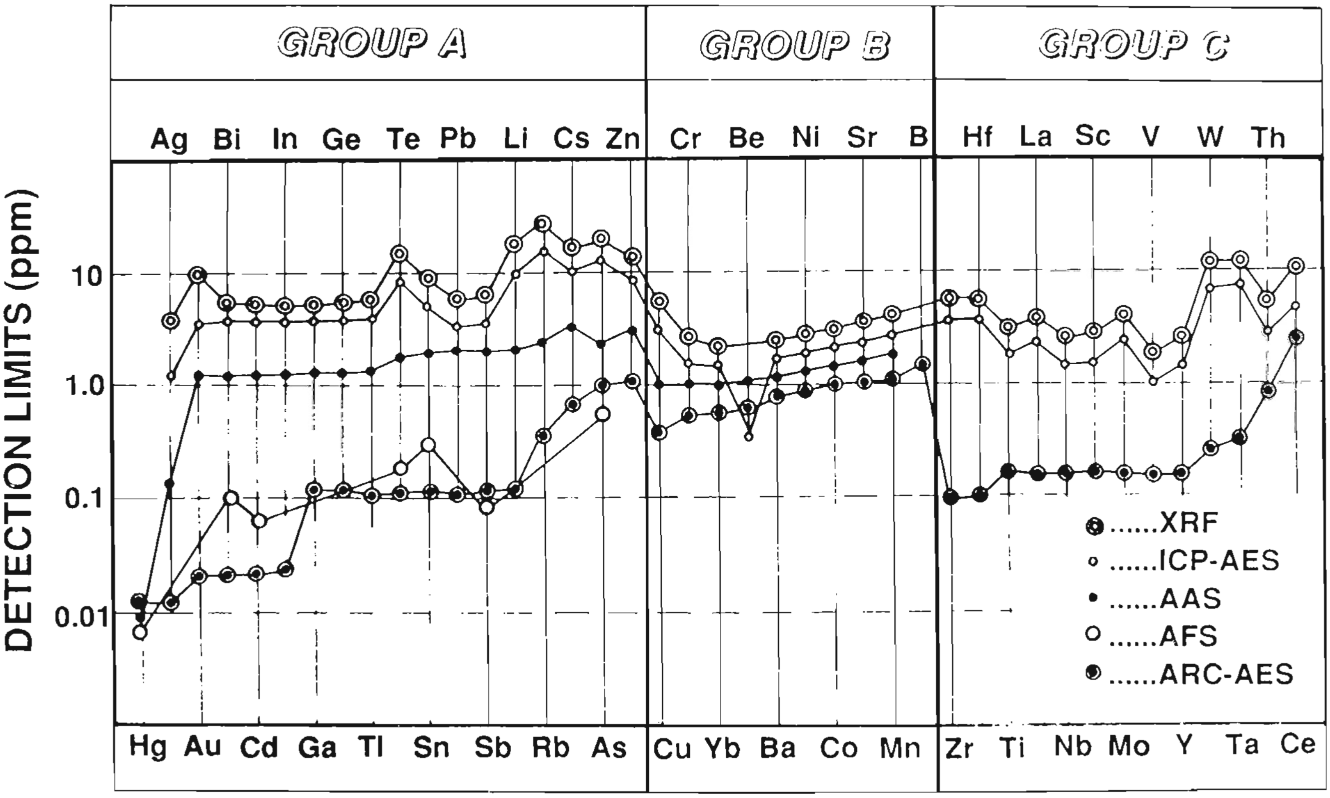


Figure 1. Comparison of detection limits by AS-ES (labelled ARC-AES) with those reported using ICP-AES, AAS, XRF, and AFS.

3-5% for one third of the elements, 5-10% for most of the remaining, and only one or two elements exhibited RSDs in the range 10-15% (Shen, 1989). Values obtained for precision using different analytical methods are shown in Table 1.

The accuracy attainable by AS-ES is indicated in a comparison with recommended values for the GSD (sediments) and GXR (rocks) series of standard reference materials (Table 2). Overall, agreement for the seven elements listed is well within 30%. It is well known that the limiting factor in the accuracy achieved by AS-ES is the effect of sample matrix on the processes of vaporization, excitation, and absorption. Either mat?? the matrix of the sample and calibration standard or employing high dilution can be chosen to ensure good accuracy. Internal standards (e.g., Ta-W; Nb-Hf; Zr-Mo) can be selected experimentally. We have found replicate analyses for the major elements in mono-minerals (e.g., Nb, Ta in niobites, tantalites; Zr, Hf in zircons; REEs in their minerals) to agree within 5%. Accuracy in the range 5-10% has been obtained for elements of intermediate volatility using internal standardization, for example in the determination of Fe, Mn, Cr, Ni, Co, V, B, Ba, Sr, and Be. Matrix effects are significant for volatile elements such as P, Se, Te, As, Sb, Ge, Sn, and Zn which have high excitation energies; this is less important for elements such as Pb, Ga, In, Tl, Bi, Cd, Li, Rb, and Cs. For the former group, matrix interference can easily lead to 100% error and therefore careful matching with standards is mandatory.

ANALYTICAL FIGURES OF MERIT

The advantages of AS-ES are as follows:

1. The arc source generator is easy to operate and to maintain. Cost is low.
2. Powdered samples can be analyzed directly without chemical pretreatment, of environmental benefit and low cost.
3. Adequate detection limits are achieved for over 40 elements.
4. No special gases (e.g., argon) are required.
5. Levels of contamination are minimal.

Thus, AS-ES is used in China to efficiently analyze tens of thousands of geochemical samples annually, in a semi-quantitative mode. The author has found AS-ES to be particularly advantageous in another application: in mineral analysis, of the study of the state of the element, mineralogical composition, and particle size distribution (Shen, 1976, 1977a, b, 1983). The author has studied over 50 different types of mineral deposits, leading to a comprehensive evaluation of the deposits and building a framework for accurate and predictive modelling. Such studies have included: (1) correlation curves for U and Zr in uraninite and for Cu and Ag in chalcopyrite; (2) particle size distribution of Au in the mesothermal alteration zone at the Shandong gold deposit; and (3) the ratio of Au to Ag in different types of gold deposits.

Table 1. Precision typical of AS-ES using various analytical methods

Analytical method	Element	Precision (RSD %)	Test conc.
Specially designed-covered electrode	As	5.2	0.001
	Bi	3.7	0.00003
	Cd	3.8	0.00001
	Ga	5.6	0.001
	Ge	5.1	0.00005
	Hg	6.6	0.001
	In	3.2	0.00001
	Pb	3.8	0.001
	Sb	4.8	0.0001
	Sn	3.4	0.0003
	Tl	6	0.0001
	Zn	4.8	0.001
	Mn	5.2	0.01
	Cu	8	0.003
	Co	7.5	0.001
	Cr	7.8	0.005
	Ni	6.7	0.01
	Ba	10	0.03
	Be	8.9	0.0003
	B	6.9	0.005
	Sr	5.8	0.01
	Fe	5.9	3
	Yb	8.2	0.0003
	Li	5	0.005
	Sc	3.3	0.001
	Ce	9.1	0.01
	La	5.9	0.005
	Y	4	0.0005
	V	8.7	0.01
	Ti	7.7	0.3
	Nb	6.9	0.001
	Mo	7.5	0.001
	W	4.4	0.001
	Zr	6.3	0.03
Direct burning	Nb	1.9	70
	Ta	2.6	50
	Zr	3.2	60
	Hf	2.3	20
	La	3	30
	Ce	2.5	40
	Th	3.2	50
Arc concentration	Nb	3.8	0.01
	Ta	6.3	0.01
	Zr	3.5	0.01
	Hf	3.5	0.005
	La	4.8	0.0125
	Ce	3.6	0.025
	Th	4.5	0.01
Carrier distillation	Hg	6.8	0.00001
	Ga	4.5	0.001
	Ge	4.2	0.0003
	Te	6	0.0005
	Au	10	0.0003
Averaged		5.4	

Table 2. Results (in ppm) for standard reference materials by AS-ES

Sample	This method	Recommended value	This method	Recommended value	This method	Recommended value	This method	Recommended value	This method	Recommended value	This method	Recommended value	This method	Recommended value
	As		Bi		Co		Cr		Pb		Zn		Zr	
GSD-1	3.0	2.0 ± 0.2	0.55	0.66 ± 0.09	21.9	20.6 ± 1.3	183	195 ± 5	23.0	24.5 ± 1.5	72.0	79.2 ± 3.5	324	314 ± 15
GSD-2	8.1	6.4 ± 0.3	1.5	1.6 ± 0.1	3.6	2.8 ± 0.3	12.0	12.5 ± 2.1	26.3	30.8 ± 2.2	63.1	43.8 ± 2.6	502	462 ± 19
GSD-3	21.7	17.6 ± 1.0	0.79	0.81 ± 0.12	11.0	12.0 ± 0.07	87.3	87.3 ± 3.0	40.3	50.6 ± 1.3	67.6	52.1 ± 2.1	236	221 ± 10
GSD-4	18.7	19.7 ± 1.0	0.52	0.67 ± 0.10	19.5	18.2 ± 0.9	67.5	81.0 ± 3.1	29.9	30.9 ± 2.1	101	102 ± 6	212	190 ± 8
GSD-5	75.6	73.8 ± 3.5	2.0	2.4 ± 0.2	19.5	19.3 ± 1.1	60.9	69.6 ± 2.8	103	113 ± 4	271	241 ± 8	220	218 ± 8
GSD-6	12.0	13.4 ± 0.6	5.5	5.0 ± 0.4	28.5	24.7 ± 1.0	181	192 ± 8	31.3	28.5 ± 1.9	152	143 ± 4	175	171 ± 6
GSD-7	82.3	82.6 ± 3.8	0.67	0.68 ± 0.11	22.8	21.0 ± 0.9	116	122 ± 4	343	350 ± 8	261	238 ± 7	170	163 ± 6
GSD-8	2.7	2.5 ± 0.2	0.18	0.20 ± 0.03	3.6	3.7 ± 0.2	6.7	7.3 ± 0.2	21.1	21.3 ± 1.2	63.7	43.6 ± 1.6	515	494 ± 29
GXR-1	326	460 ± 30	1750		7.9	9.3 ± 1.1	8.1	10 ± 2	732	670 ± 20	717	740 ± 110	30.6	66 ± 20
GXR-2	29.4	31 ± 5	0.58		7.5	9 ± 2	34.8	37 ± 10	500	615 ± 15	577	500 ± 60	292	200 ± 40
GXR-3	4370	4000 ± 450	1.2		48.0	48 ± 5	16.9	19 ± 1	13.5	15 ± 2	226	220 ± 70	112	<200
GXR-4	97.9	98 ± 10	18.7		14.4	16 ± 2	59.1	64 ± 10	24.2		75.0	64 ± 10	221	200 ± 40
GXR-5	12.1	12 ± 3	0.30		29.1	30 ± 8	106	100 ± 5	11.6	22 ± 2	55.0	50 ± 5	189	140 ± 20
GXR-6	231	340 ± 30	0.23		11.2	14 ± 3	93.1	96 ± 10	72.2	110 ± 10	135	120 ± 20	141	106 ± 8

LIMITATIONS OF AS-ES

As mentioned above, most analytical methods as AS-ES rely on matrix matching to achieve good accuracy. This is challenging in the field of geoanalysis where the composition of samples varies widely and standard reference materials are not always in adequate supply. In the electrode-cavity method, the line intensity of an element is a function of time and the spectra are complex. The availability of a direct reading spectrometer would greatly improve the present efficiency now obtained with the photo-plate spectrographic instrument.

PROSPECTS FOR AS-ES

Research activities directed towards gaining an improved understanding of the precesses taking place in AS-ES and towards more versatile and efficient instrumentation have been few as scientists in the developed countries and more recently in China have adopted the modern techniques such as ICP-ES and AFS. However, effort in several areas could well lead to a "re-birth" of AS-ES. For example, a systematic protocol to select optimum operating conditions for the most stable plasma (and automation thereof) would lessen the dependence on operator skills. Further improvements in the figures of merit would undoubtedly result from fundamental studies of vaporization and diffusion processes, mechanisms of carriers and buffers, and so on. The application of modern computer technology is badly needed to acquire and process data. A new type of direct reader based on photographic plates would eliminate many hours of tedious manipulation. With these accomplishments, AS-ES will continue to occupy its rightful place among the array of analytical techniques at our disposal today.

REFERENCES

Scribner, B. and Mullin, H.J.
1946: The carrier-distillation method for spectrographic analysis and its application to the analysis of uranium-based materials; Journal of Research of the National Bureau of Standards, v. 37, p. 379-390.

Shen, R.P.
1964: The function and application of spectrochemical analysis by arc concentration technique; in Symposium Proceedings of the Annual National Meeting for the test and analysis of rare elements in China, Published by the National Sciences and Technology Committee, p. 198-203 (in Chinese).
1976: Fundamental principles of the spectrographic method for quantitative determination of minerals; Geochimica, v. 4, p. 251-261 (in Chinese).
1977a: Experimental practice of the spectrographic method for quantitative determination of minerals; Geochimica, v. 1, p. 47-58 (in Chinese).
1977b: Practical application of mineral quantitative spectrographic analysis; Geochimica, v. 3, p. 194-198 (in Chinese).
1983: Spectrochemical Analysis of Rare Elements and Related Minerals; Publishing House of Science and Technology of Jiangshu (in Chinese), Volume 2.
1989: Simultaneous determination of 37 elements in geochemical samples by spectrographic method using specially designed covered electrode; Journal of Geochemical Exploration, v. 33, p. 215-236.

Perspectives on the development of geoanalytical techniques

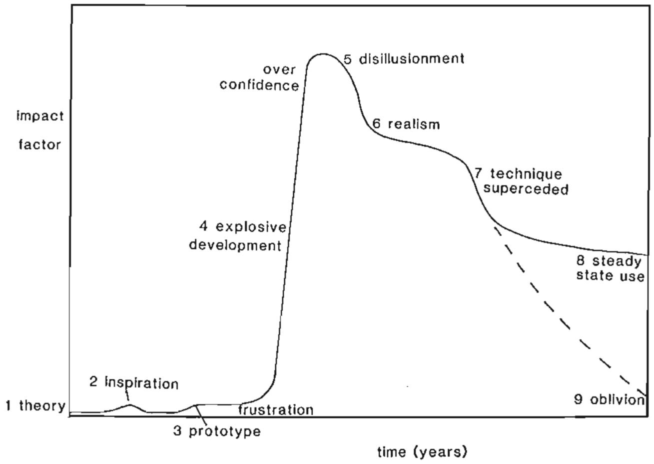
Philip J. Potts[1]

INTRODUCTION

In many fields of activity, the lessons of history are often the only sensible way of predicting future developments. The purpose of this paper is to evaluate whether such criteria can be applied to the evolutionary development of selected geoanalytical techniques. In particular, a comparison is made of a number of techniques commonly employed for the analysis of geological samples to suggest that almost all follow a similar evolutionary pattern which can, therefore, be used to predict the future analytical impact of any one technique. This concept will be applied specifically to atomic absorption spectrometry (AAS), X-ray fluorescence analysis (XRF), instrumental neutron activation analysis (INAA), inductively coupled plasma – atomic emission spectrometry (ICP-AES) and ICP – mass spectrometry (ICP-MS). The particular features that may influence the future development of these techniques is summarized.

EVOLUTION HYPOTHESIS

The hypothesis expounded here is that almost all geoanalytical techniques follow the same evolutionary development pattern in terms of their perceived analytical importance as a function of time. This evolution diagram is shown in general form in Figure 1 and plots the 'analytical impact' of a technique against time (in years). In this diagram, neither axis is scaled. Indeed, it is expected that notional scales may vary from technique to technique. However, the overall form of this diagram, together with the tendency of techniques to evolve from left to right in Figure 1, is a characteristic of almost all instrumental procedures. It must be stressed that 'analytical impact' is not specifically defined, but should be regarded as an indicator of the esteem with which a technique is held, related to both the analytical productivity of that technique and the interpretational value placed on these data.



The stages in this evolution diagram may be summarized as follows (numbered paragraphs correspond to those marked on Figure 1).

THEORY

The theoretical basis of almost all geoanalytical techniques has been understood at least since the dawn of the modern physical sciences in the eighteenth and nineteenth centuries. However, due to the lack of appropriate instrumental technology or ignorance of a critical missing link, the techniques listed above have only been applied to quantitative geoanalysis within the last thirty years or so.

Inspiration

In the course of (perhaps) speculative physical investigations, instrumentation is constructed that appears to yield an analytical useful signal. Although such investigations may arouse some interest (often in the theoretical origin of the associated phenomenon), results may be judged to be impractical in a routine quantitative sense due to contemporary deficiencies in instrumental technology and indeed the work may lapse into obscurity.

Prototype

With further developments in analytical technology, and often given the single-minded conviction of one or two investigators, the practical quantitative capabilities of a technique are demonstrated. Following construction of prototype instrumentation, accompanied by persistent lobbying of the scientific community by papers presented at international conferences, some analytical interest is aroused. However, considerable frustration can accompany this phase

---

[1] Department of Earth Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, U.K.

of development, arising from the difficulty in convincing instrument manufacturers of the commercial viability of the technique.

Explosive development

With the demonstration of the unique analytical advantages of a technique together with the appearance on the market of commercial instrumentation, an explosion of interest is likely to occur. Rivalry will be encountered between competing research groups involved in (a) refining the instrumentation, (b) studies of the physical basis of measurements, and (c) applications to a diverse range of sample types. This phase in the evolution diagram always appears to be accompanied by a degree of self-delusion in which over-optimistic claims are made of sensitivity, detection limits, and freedom from interference effects.

Disillusionment

Inevitably, this unjustifiable over-confidence leads to some disillusionment as unsustainable claims are discredited. The realization that interference effects may be significant leads to a reduction in the analytical impact of a technique from its pinnacle of expectation.

Realism

However, further evaluation of performance in practical applications leads to a realistic appreciation of the performance of the technique. In this productive phase, data from the technique may initiate new areas of geochemical study leading to new discoveries that were beyond the capabilities of previous techniques. An example would be the rapid development of rare-earth element geochemistry following the widespread application of INAA in the late 1960s.

Technique superseded

Inevitably, advances in instrumental technology and further research endeavour leads to the development of competitive analytical techniques, the superior analytical performance of which causes a decline in the 'analytical impact' of the technique in question. Thus to some degree, the impact of INAA has been reduced by the competing analytical capabilities of ICP-AES and now ICP-MS. Two outcomes may result:

Steady-state use

The technique achieves a state of analytical 'maturity' in which particular analytical characteristics are perceived to possess advantages, even against more modern developments.

Obscurity

Alternatively, the performance of the technique may be seen to be substantially inferior to more recently developed procedures so that in the extreme, its use declines to the point of being of historical interest only.

STATUS OF CURRENT GEOANALYTICAL TECHNIQUES

Having outlined the features of this evolutionary life-cycle, it is appropriate to assess the status of the commonly used techniques referred to above. It must be emphasized that this assessment depends not only on personal prejudice, but also on the application in which a technique is used. The following perspective is made, therefore, from the point of view of a research-oriented laboratory where the quality of data in terms of accuracy, precision, and detection limit are at least as important as cost and sample throughput rate. This assessment is not necessary valid for commercial, exploration, or production-orientated laboratories where other criteria will predominate.

The suggested stage of development of contemporary techniques is marked on Figure 2. The status assigned to individual techniques in this figure may be justified as follows, starting first with the more 'mature' techniques:

Steady-state use: It is proposed that both XRF and INAA have found a useful niche in geochemical research laboratories. XRF is a technique that offers data of the highest precision (second only isotope dilution mass spectrometry procedures) not only in the determination of the major elements, but also a range of geochemically important trace elements including Rb, Sr, Y, Zr, Nb. Though possessing some analytical limitations, INAA is highly effective in the determination of selected rare-earth elements (REE) as well as other elements that pose difficulties in solution chemistry by other techniques (e.g. Ta, Hf, Th).

Obscurity: Conversely, 'classical' wet chemical techniques have now almost disappeared from the analytical repertoire for routine major element determinations in many instrumentally oriented laboratories (although admittedly retaining some element specific applications, e.g. Fe(II)). Similarly, apart from geochemical reconnaissance laboratories, the traditional form of spark source optical emission spectrometry (OES-ss) has long since been superseded, often by more modern forms of atomic emission instrumentation (note, however, the recent in applying isotope dilution calibration procedures to this technique).

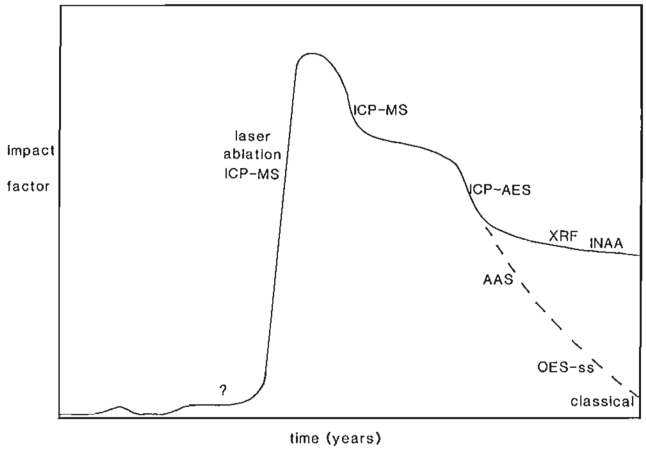


Table 1. Standing and potential of current routine methods of analysis

Advantage	Disadvantage	Research potential
AAS Very high element specificity. Low costs	Single element capability.	Development of simultaneous multi-element capability.
XRF Very high analytical precision. Solid samples.	Calibration is matrix dependent and requires reliable reference sample data.	Development of versatile (and standardized?) calibration procedures.
INAA High sensitivity for some elements with a 'difficult' solution chemistry (e.g. Ta, Hf, Th). Solid samples.	Requires a reactor. Some radiological hazard.	Potential of radiochemical separation procedures fully exploited?
ICP-AES High sensitivity including some low atomic number elements.	Precision not as good as XRF. Line overlap interferences. Chemical separations necessary (e.g. REE).	Wider adoption of precision enhancement procedures. Further developments in miniturized, low blank, separation procedures.
ICP-MS Potentially the 'universal' trace element technique. Detection limitation is the analytical blank.	Precision not as good as XRF. Problems with the quantitative dissolution of resistant minerals.	Instrumental developments to achieve high precision and greater tolerance to dissolved salts. 'Universal' dissolution techniques.

In the present classification, atomic absorption spectrometry presents something of an enigma. Although AAS is now rarely used in routine multielement analysis, having declined from the pre-eminent position it occupied in the early 1960s, such instrumentation is widely available in geochemical laboratories. Furthermore, AAS has a secure role in complementing ICP-AES in the determination of selected trace elements (e.g. Rb) that cannot be detected with sufficient sensitivity by the latter technique. Perhaps AAS is unusual in having moved in a reverse manner on the evolutionary diagram in recent years by improving its analytical impact factor rating.

Technique superseded: It is proposed that ICP-AES is a technique that is currently being eclipsed by the wide-spread application of ICP-MS. Many (but not all) of the capabilities of emission instrumentation are out-performed by ICP-MS (though at a substantially higher outlay in terms of capital cost).

Realism: ICP-MS itself has now passed through the stage of disillusionment since sufficient work has established a realistic assessment of instrument capabilities that is leading to the widespread application of such data.

Explosive interest: One technique that is currently the subject of widespread interest in the development of both instrumental capabilities and analytical applications is laser ablation ICP-MS. Although such instrumentation may find specialized applications in research laboratories interested in direct micro-analysis of solid samples, the impact factor of this technique must surely rise significantly in the next few years.

Inspiration/prototype: Techniques that lie to the left hand side of Figure 2 (i.e. '?') fall in the area of speculation. However, much interest has been shown in the potential of atomic fluorescence spectrometry, laser applications in both mass spectrometry (e.g. RIMS) and optical emission and the trace element capabilities of synchrotron X-ray fluorescence facilities.

FUTURE DEVELOPMENTS

Following this review of the evolution of the more common analytical techniques, it is appropriate to speculate on the directions in which these procedures may develop in forth-coming years. A summary of those advantages and disadvantages perceived to be most important in defining the analytical role of these techniques is listed in Table 1. Together with these analytical characteristics, proposals are also made in Table 1 of areas in which future research and development activities may be profitably expended to extend analytical capabilities. As with all predictions, time alone will decide the validity of these observations!

ACKNOWLEDGMENT

This paper is based on a workshop 'Analytical Methodology' held at 'Geoanalysis 90', Huntsville, Canada, June 1990 and the contribution of individuals who attended this workshop is gratefully acknowledged.

AUTHOR INDEX