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MATRIC EFFECTS IN THE
DETERMINATION OF LEAD
BY ZEEMAN EFFECT ELECTROTHERMAL AAS

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Management Perspective

Our data base on the concentrations (and hence exposure levels) of trace metals in aquatic systems is imperfect because of the use of analytical procedures which do not have the required detection limits. When very sensitive procedures are used, such as graphite furnace AAS, there is often a greater effect of interferences which become analytically significant at the trace and ultratrace levels. Application of such procedures to complex samples, eg sediment extracts, also is prone to interference effects. It is therefore essential to study and wherever possible, eliminate or minimize such effects in order to obtain precise and accurate data on the environmental behaviour of toxic metal ions. This report has been prepared for the Colloquium Spectroscopicum Internationale, September 15-21, 1985, FRG, and is one example of the type of approach we have used to understand the nature of interferences in graphite furnace AAS.

Perspective - gestion

Notre base de données sur les concentrations (et par conséquent sur les niveaux d'exploitation) des métaux à l'état de traces dans les systèmes aquatiques est imparfaite parce que les formalités d'analyse appliquées n'ont pas les seuils de sensibilité voulus. Quand on emploie des moyens très sensibles comme le four d'atomisation muni de tubes en graphite en spectrophotométrie atomique, on ressent davantage l'effet des interférences qui influencent les analyses au moment de déterminer les traces et les ultratraces. L'application de ces formalités à des échantillons complexes, par exemple des extraits de sédiments, subit également l'effet des interférences. Il est donc essentiel d'étudier ces effets et, si possible, de les minimiser ou de les enrayer pour obtenir des données précises et exactes sur le comportement des ions métalliques toxiques dans l'environnement. Cette étude, dont un résumé sera présenté lors du Colloquium Spectroscopicum Internationale qui doit avoir lieu du 15 au 21 septembre 1985 en République fédérale d'Allemagne, est un exemple du type d'approche que nous avons employée pour comprendre la nature des interférences en spectrophotométrie d'absorption atomique dans le four d'atomisation muni de tubes de graphite.

Les effets de la substance de base sur la détermination du plomb en spectrophotométrie d'absorption atomique par l'effet Zeeman.

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ABSTRACT

The presence of metal salts in sample solutions creates many problems in graphite furnace AAS analyses. In this study the effects caused by chemical species most commonly encountered in solution [i.e. H^+, Na^+, Ca^{2+}, Mg^{2+}, NO_3^-, Cl^-, and SO_4^{2-}] have been examined in the determination of lead using a Hitachi 170-70 analyte-shifted Zeeman Effect Atomic Absorption Spectrophotometer. All species showed significant suppression of the Pb atomic absorption when present in high concentrations, except for H^+. Compared to the Pb signal in 0.16 mol/l HNO_3, 0.32 mol/l $MgCl_2$ (the matrix yielded by chemical extraction of exchangeable metal forms in soils, sediments and solid environmental materials) was found to be the most suppressive with 95% of the Pb signal lost. For the cations, the order of suppression was considered to be the result of vapour phase interferences. The anions studied separately, yielded the following order of suppression;-

$$SO_4^{2-} > NO_3^- \gg Cl^-.$$
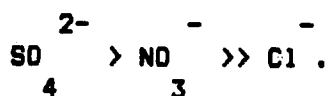
RÉSUMÉ

En spectrophotométrie d'absorption atomique, la présence de sels métalliques dans les échantillons occasionne de nombreux problèmes lors des analyses au four d'atomisation muni de tubes de graphite. Dans la présente étude, on a examiné les effets qu'ont sur la détermination du plomb les espèces chimiques que l'on rencontre le plus souvent en solution (H^+, Na^+, Ca^{++}, Mg^{++}, NO_3^-, CI^- et SO_4), à l'aide d'un spectrophotomètre d'absorption atomique Hitachi 170-70 doté d'un système de correction par l'effet Zeeman. Dans toutes les espèces, sauf l'H^+, on a constaté une diminution considérable de l'absorption atomique du Pb quand il existait en concentrations élevées. À comparer au signal du Pb dans 0,16 mol/l HNO_3, 0,32 mol/l $MgCl_2$, c'est dans la substance de base obtenue par l'extraction chimique des genres métalliques dans les sols, les sédiments et les matières solides dans l'environnement que l'on a constaté la plus grande diminution du signal Pb, soit 95 p. 100. Pour ce qui est des cations, l'ordre d'élimination est fonction des interférences en phase vapeur. Les anions étudiés séparément ont produit l'ordre d'élimination qui suit :

$$SO_4 \longrightarrow NO_3^- \gg CI^-$$

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INTRODUCTION

Demands on electrothermal atomization AAS (ETA-AAS) as a means of offering improved accuracy and precision in the determination of trace and ultratrace amounts of many elements, has generated interest in ways other than the use of the deuterium arc for background correction, especially in the presence of complex or unusual matrices. Even with improvements in sensitivity and background correction capability, ETA-AAS as an absolute method of analysis is not yet a reality because of gaps in knowledge of the physicochemical processes that occur in graphite furnace atomizers. Recurring problems include variations in sensitivity of successive measurements even with the same furnace, a marked and often unpredictable dependence of sensitivity due to conditions of measurement (for example heating mode, position of the sample in the furnace, gas flow rate etc.) and effects of the chemical form of the compound introduced and of the other constituents of the sample on sensitivity (L'vov, 1978). This report describes a study of changes in sensitivity and the interferences encountered in determining lead in a variety of matrices using a Hitachi Zeeman Effect AAS. The cations and anions studied were Na^+, Ca^{2+}, Mg^{2+}, NO_3^-, Cl^- and SO_4^{2-}. The anticipated result was the proper selection of instrumental parameters for the determination of lead in sequential

chemical extracts of suspended and bottom sediments. Such extraction
procedures are widely used in soil science (eg Jackson, 1958; Chapman,
1965) and in geochemical studies of metal ion availability (eg Gibbs,
1977; Tessier et al, 1979). Exchangeable and specifically-sorbed metal
forms are of particular interest because they represent the fraction of the
total metal content which is most readily available. Usually, these forms
are extracted by solutions containing high concentrations (0.32 mol/l) of
$MgCl_2$ and NaOAc. In concurrent work with a D.C. Argon Plasma Atomic
Emission spectrometer, we have found that the high background associated
with measurements at the most intense emission line for lead seriously
impairs the analytical usefulness of emission determinations in such
complex matrices. A further benefit of this study is a better
understanding of matrix interferences caused by high salt concentrations
which affect the precision and accuracy of the direct determination of lead
in whole blood, blood plasma and urine for rapid screening of populations.

MATERIALS AND METHODS

A Hitachi Model 170-70 Zeeman Effect Atomic Absorption Spectrophotometer
and a Hitachi Model 056 Chart Recorder were used. The instrument
incorporates a permanent magnet positioned transversely about the furnace
in conjunction with a quartz prism rotating at a frequency of 38.85 Hz. The
prism is used to alternately polarize the resonance line in a direction

horizontal or parallel to the magnetic field and vertical or perpendicular to the magnetic field before it passes through the furnace. The Zeeman effect is produced in the furnace by the constant homogenous magnetic field of 10.6 kB on the atomic vapour. Pyrolytically coated graphite cuvettes and a sample volume of 10 ul were used throughout this investigation. The 283.3 nm resonance line was produced by a Westinghouse hollow cathode lamp operated at half the maximum current recommended by the manufacturer. The sheathing gas flow rate was 3.0 ml/min of Ultra High Purity Argon (Linde). Ashing and atomizing conditions were established by preparing ash/atomize curves as suggested by Price (1979). The temperature programme used was as follows:-

Dry: Ramp mode; room temperature to ca 325 C at 0.6 Amp/sec.

Ash: Step Mode; 20 sec at 60 Amp, ca 600 C.

Atomize: Ramp Mode; to 220 Amp, ca 2400 C at 32 Amp/sec.

Lead standards were prepared by serial dilution of 1000 ug/ml stock solution supplied by Fisher Scientific Co Ltd. Acids were obtained from G. Frederick Smith Co. and were doubly distilled in vycor and stored in teflon bottles. All other chemicals were reagent grade quality. All data points reported in this study were obtained by averaging six replicates of each standard/sample with corrresponding peak height measurements in millimetres.

RESULTS

Effect of Nitrate, Chloride and Sulfate.

The reference matrix used was 0.16 mol/l nitric acid as this in accordance
with common practice for the determination of lead.   Calibration curves of
10, 20, 30, 40 and 50 ug/l were run in 0.16 mol/l hydrochloric acid and
0.16 mol/l sulfuric acid as well as in the same concentration of nitric
acid. Linear regression analysis was done on the data and applying a
t-test at the 95% confidence interval on the slopes of the three curves
confirmed that there was a significant difference in the slope of the
sulfuric acid curve relative to the other two acid matrices. In order to
determine whether the suppression of the lead atomic absorption signal was
caused by the presence of sulfate or the increased hydrogen ion
concentration, a 30 ug/l lead standard was run in a range of concentrations
of the three acid matrices. The peak heights of all the measurements are
expressed as percent of that obtained for the 30 ug/l standard in 0.16
mol/l nitric acid This experimental design also permitted an assessment of
the effect of anionic concentration on the lead atomic absorption signal.
Thus in Fig 1, concentration of acid is plotted against percent peak height
relative to 0.16 mol/l nitric acid.   Interestingly, with increasing
hydrogen ion concentration, both the nitric acid and sulfuric acid matrices

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showed marked suppression of the lead signal. This effect was not observed for hydrochloric acid and the suppression was found to be about 17% relative to the peak measured for 0.16 mol/l nitric acid. Examination of Fig 1 suggests that the principal cause of the suppression is the presence of anions. The order of suppression is sulfate > nitrate >> chloride. Note that the common practice of using 0.16 mol/l nitric acid still results in a slightly better sensitivity relative to hydrochloric acid at least for the instrumental settings employed here.

Effect_of_sodium,_magnesium_and_calcium.

The chloride, nitrate and sulfate salts of the three cations were studied at the 0.32 mol/l concentration because the sequential extraction procedure used by us results in such an extract. Calcium sulfate was not used because of its insolubility. As before the percent peak height relative to a blank corrected spike of 30 ug/l lead is reported (Table 1). Apart from magnesium chloride, the results show that the nitrate salts are least suppressive and the sulfate salts seriously impair the sensitivity of the lead signal. Magnesium nitrate is essentially non-suppressive and this finding is consistent with the use of this compound as a matrix modifier for the direct determination of trace metals in seawater (Brobenski et al, 1984). The role of the cation is relatively unimportant in comparison with the effect of the anions. The severe suppressive effect of 0.32 mol/l magnesium chloride is anomalous. Indeed, the results for the chlorides do indicate some role played by the cation in that there is a marked

difference in the behaviour of lead in the presence of the calcium and magnesium salts at constant chloride concentration.

DISCUSSION

The results obtained indicate that the lead atomic absorption signal is very sensitive to small changes in matrix composition which suggests that changes in the mechanism of production of free atoms has occurred. The ideal mechanism for production of the free atomic population involves the decomposition of the analyte element to its oxide. Reduction of the metal oxide in the presence of the furnace then produces the free atoms necessary for absorption measurements. The desired formation of the metal oxide is due to the fact that such oxides are thermally stable compounds and provide a more reproducible means of producing free atom populations (L'vov, 1978). The fact that the Pb signal is suppressed in the majority of the cases under consideration here suggests that other mechanisms may be taking place in the furnace during atomization causing the interferences that have been noted. Mechanisms by which these interferences occur have been postulated by Hageman et al (1979) and are classified in two broad groups; vapour phase type interferences and solid phase interferences. Vapour phase interferences are considered to be caused by inadequate heat delivery to the analyte as it moves out of the furnace. This results in recombination of the analyte atoms with interfering species or complete dissociation of the compounds containing the analyte species, therefore reducing the absorption of the analyte. Inadequate heat delivery to the analyte species

is believed to be caused by excessive concentrations of matrix components allowing numerous energy transfer sites to exist in the same environment as that of the analyte atoms. Solid phase interferences describe situations where differing volatilities of the analyte occur because of the chemical form and thermal stability of the analyte. In this instance less stable forms of the analyte may be volatilized earlier than the appearance temperature expected producing enhancement of the absorption signal or a double peak. In light of the above, the results of this study appear to be consistent with vapour phase type interferences as the principal cause of the suppression observed which is consonant with the observations of Fuller (1977) and Slavin et al (1984). However, we did not observe char losses which have been suggested by the latter workers as contributing to the interferences caused by $MgCl_2$ perhaps because of the very severe suppression caused by this compound - the peak height during atomic absorption was 0.83mm (s.d. = 0.35). Further support for this conclusion is provided by L'vov (1979) who suggested that chemical interference effects resulting from an excess of chlorides in a sample come about by the formation of a relatively volatile chloride whose dissociation in the gas phase is incomplete. Also implied here is that the suppression of the Pb atomic absorption (as a monotonic entity) decreases with an increase in the dissociation energies of the monochlorides that are formed in the furnace. Dissociation energies of the monochlorides of Na, Ca and Mg are 410, 398 and 318 kJ/mol respectively. Although this trend correlates with the result for $MgCl_2$, there is a discrepancy with the observations for Ca and Na. This discrepancy appears to be related to the cation as in the case

of the nitrates, Na causes greater suppression than Ca. The work done in this study lends support to the view that interferences caused by high concentrations of alkali and alkaline earth metal salts are very complex in nature. Thus, it would be expected that prediction of suppressive effects in samples containing mixtures of these compounds would be very difficult. Clearly, the application of the analyte-shifted Zeeman Effect is, by itself, an insufficient means of background compensation. Preliminary work using a microprocessor-controlled furnace with peak area integration and very fast heating rates (standard features in the Hitachi 180-80) indicates that background absorbances can be minimized without loss of analyticall sensitivity.

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Table 1. Effect of hydrogen ion and anion
concentration (in mol/l) on peak height of 30 ug Pb / l
relative to 0.16 mol/l HNO .
                                3

Concentration	HNO$_3$	HCl	H$_2$SO$_4$
0.16	100%	85%	59%
0.32	88%	88%	53%
0.48	68%	87%	not done
0.80	66%	83%	42%
1.60	38%	78%	33%
2.40	35%	80%	not done
3.20	38%	83%	27%

Table 2.　Effect of alkali and alkaline earth salts at
the 0.32 mol/l level on the atomic absorption signal of 30 ug/l of Pb
relative to 0.16 mol/l HNO_3 .

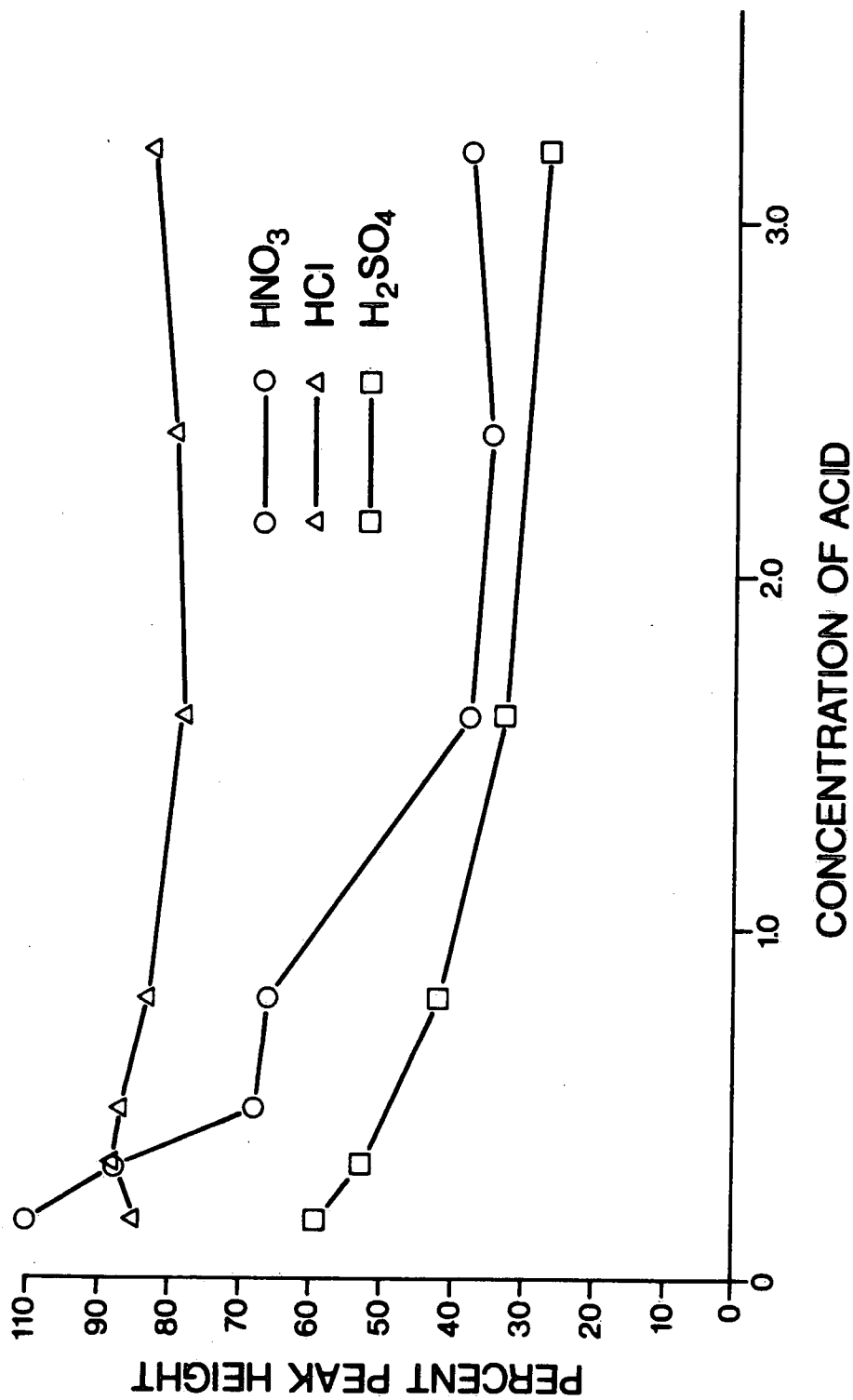| Compound	% peak height relative to 0.16 mol/l HNO_3
$NaNO_3$	62.8　(s= 7.0)
$Ca(NO_3)_2$	71.7　(s= 2.5)
$Mg(NO_3)_2$	91.1　(s= 9.2)
$NaCl$	27.7　(s= 4.5)
$CaCl_2$	42.6　(s= 3.0)
$MgCl_2$	5.0　(s= 2.1)
Na_2SO_4	22.4　(s= 6.7)
$MgSO_4$	13.0　(s= 2.6)

FIGURE 1. EFFECT OF MINERAL ACID CONCENTRATION ON THE PERCENT PEAK HEIGHT OF 30 μg/L Pb RELATIVE TO 0.16 mol/L HNO$_3$