

DEPARTMENT OF ENERGY, MINES AND RESOURCES MINES BRANCH OTTAWA

THE USE OF FLAME PROCEDURES FOR THE ANALYSIS OF MINERALS, ORES, AND ELECTRIC FURNACE SLAGS PART II: DETERMINATION OF SILICON IN SULPHIDE AND SILICATE MINERALS AND THEIR MIXTURES

R. J. GUEST AND D. R. MACPHERSON

EXTRACTION METALLURGY DIVISION

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The Use of Flame Procedures for the Analysis of Minerals, Ores, and Electric Furnace Slags Part II: Determination of Silicon in Sulphide and Silicate Minerals and Their Mixtures

by

R. J. Guest* and D. R. MacPherson**

SUMMARY

This report, the second in a series of three, describes methods for the determination of silicon in typical sulphide and silicate minerals by atomic absorption spectrophotometry, using either hydrofluoric acid attack under pressure in a Teflon bomb or sodium peroxide fusion with subsequent controlled acidification. Both decomposition methods give silicon solutions which have excellent long-term stability and which are also suitable for the determination of other elements in the sample. The effects of various common contaminants carried through the whole procedure are described, and though, in general, satisfactory results are obtainable using pure silicon solutions as comparison standards, it is shown that the addition of an equivalent amount of the major contaminant present in the sample can give a significant gain in accuracy. The method is applicable to synthetic solutions and to specimen-grade minerals, separately and in mixtures, that represent most Canadian ores. Many types of sample materials, covering a range of silicon content from 0.1 to 45%, can be analysed with a considerable saving in time over gravimetric procedures. The average coefficient of variation found was 1.4%. Much of the deviation (of some 5%) from the gravimetric results can be attributed to the inaccuracies of that method.

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Direction des mines Bulletin technique TB 150

L'Utilisation du procédé à flamme pour l'analyse des minéraux, des minerais et des scories provenant du four électrique 2^e Partie: La Détermination du silicium dans les minéraux sulfurés et siliceux et leurs mélanges

par

R. J. Guest* et D. R. MacPherson**

Résumé

Dans ce rapport qui est le deuxième dans une série de trois, les auteurs décrivent les méthodes pour la détermination du silicium dans les minéraux sulfurés et siliceux typiques par la spectrophotométrie d'absorption atomique, utilisant soit l'acide fluorhydrique attaqué sous la pression dans une bombe Téflon soit la fusion du peroxyde de sodium avec l'acidification subséquente et contrôlée. Les deux méthodes de décomposition donnent des solutions de silicium qui ont une stabilité excellente de longue durée et qui sont aussi convenables pour la détermination d'autres éléments de l'échantillon. Les auteurs décrivent les effets d'impuretés communes et variées qui se trouvent à travers le procédé complet, et quoique en général les auteurs aient obtenu des résultats satisfaisants utilisant des solutions pures de silicium comme norme de comparaison, il est montré que l'addition d'un montant équivalent d'impurité majeure présente dans l'échantillon peut produire une amélioration significative dans la précision. La méthode est applicable aux solutions synthétiques et aux minéraux de grade-spécimen, séparément et dans les mélanges, qui représentent la plupart des minerais canadiens. Plusieurs genres de matériaux à échantillon, couvrant une gamme de teneur de silicium de 0.1 à 45% peuvent être analysés en gagnant beaucoup de temps avec les procédés gravimétriques. Le coefficient de variation était de 1.4%. Beaucoup de déviations (quelques-unes de 5%) des résultats gravimétriques peuvent être attribuées aux imprécisions de cette méthode.

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 Effect on Linearity of Silicon Response of Addition of Reagents to a Water Leach Following Sodium Peroxide Fusion

INTRODUCTION

In an earlier report⁽²⁴⁾, a review was presented of the work of a number of investigators on sample dissolution procedures, with and without subsequent determination of silicon using atomic absorption. A number of dissolution procedures were discussed, including Teflon bomb, lithium borate and other fusions, and hydrofluoric acid attack. The questions of solution stability and the effect of contaminants on atomic absorption results for silicon have given rise to some difference of opinion among investigators, and work reported on these subjects was also reviewed.

As a part of this paper, a description is given of work done on synthetic solutions to establish silicon solution stability and the effect of contaminants on silicon results and to aid in resolving some conflict of opinion on these subjects. Also, the application of dissolution and atomic absorption procedures to silicon determination in sulphide and silicate minerals and their mixtures has been done. It was felt that work on these types of sample material has received insufficient attention from investigators.

As a further part of this investigation, therefore, fourteen hand-picked minerals* were analysed both gravimetrically and by atomic absorption spectrophotometry. The individual minerals were chosen to cover all the most common ones normally encountered in typical silicate and sulphide gangue material.

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^{*}The minerals were provided by H. R. Steacy, Curator, Geological Survey of Canada.

Also, from the individual minerals, six mineral mixtures were made up, similar in composition to an Elliot Lake uranium ore, two copper ores, two flotation concentrates, and a mixture of feldspars, and these were analysed by the recommended atomicabsorption procedures. These mineral mixtures, prepared by combining sulphide and silicate minerals, were intended to represent a number of types of typical sample material which might be encountered here and elsewhere and to provide a measure of the effect of the interaction of the individual minerals on the procedure. The use of pure minerals simplified establishment of the silicon content of the complex mixtures because they were put together from simpler, more easily analysed components. Also, it was easier in this way to simulate a great number of different ores and to enable a mine analyst, who is familiar with . the mineralogy of his sample material, to derive useful information.

Two dissolution methods, Teflon bomb and sodium peroxide fusion procedures, were used throughout the investigation.

APPARATUS AND REAGENTS

Apparatus

Teflon bomb, model 4745, Parr Instrument Company, Moline, Illinois, U.S.A.

Zirconium crucibles, 45 ml

- Jarrell-Ash atomic absorption spectrophotometer, model 82-300, dual double-beam, fully compensated unit
- Techtron atomic absorption spectrophotometer, model AA-3, with model AA-5 burner-atomizer

Drying oven

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Plastic bottles, various sizes Volumetric flasks, various sizes Muffle furnace

Reagents

Hydrofluoric acid, concentrated.

Hydrochloric acid, concentrated.

Nitric acid, concentrated.

- Boric acid, reagent grade.
- Sodium peroxide, reagent grade.
- Sodium solution (peroxide, nitrate, or chloride) 5 % (W/V); store in plastic

Nitrous oxide cylinder

Acetylene cylinder

Standard silicon solution

Weigh out a portion of fused silica powder and take it into solution with either a Teflon bomb or a sodium peroxide fusion procedure. Treat the standard in the same manner as the samples, and as described later under <u>Dissolution</u> <u>Procedures</u>. This solution should contain between 200 and 500 ppm of silicon.

Take an aliquot of the main silicon solution, add enough hydrochloric acid to ensure that the final solution will be acid, and, enough of the sodium solution (see <u>Reagents</u>) to make the final sodium content about 6000 ppm. Dilute the solution to volume in an appropriate volumetric flask. If solutions of silicon plus contaminants are required, add the contaminant to the diluted silicon standard just before

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making up the standard to the mark in the volumetric flask.

The final dilution of the silicon solution should contain between 10 and 200 ppm silicon.

PROCEDURE

Dissolution Procedures

1. Teflon Bomb Procedure

Weigh out between 0.2 and 0.5 g of sample and transfer it into the Teflon container portion of the Teflon bomb. Add from 2 to 3 ml of aqua regia, as a wetting agent, then 3 ml of concentrated hydrofluoric acid. Cover the Teflon cup and enclose it in the metal shell, close the bomb, then make it hand-tight. Place the bomb in a drying oven set at 140°C and leave it for about 45 minutes. Cool the metal container to room temperature in a cold-water bath before loosening the metal screw-top. Remove the screw-top and the Teflon cup containing the sample, then transfer the sample to a plastic beaker. Wash out the Teflon cup with 20 ml of warm 14 % boric acid solution. Transfer the sample solution to a 100-ml volumetric flask and dilute to the mark with water. Mix, and transfer the solution to a plastic bottle as soon as possible for further dilution, for direct atomisation, or for storing*.

2. Sodium Peroxide Fusion

Weigh out between 0.5 and 2 g of sample into a zirconium crucible, add part of the sodium peroxide from a 5-g weighed

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^{*}In our experience, aluminum and silicon were slowly picked up from glass containers even in the presence of excess boric acid.

portion and mix intimately before covering with the remaining sodium peroxide. Cover the crucible with a zirconium cover and place it in a muffle furnace at between 600°C and 640°C for 30 minutes. Cool. Place the crucible and contents in a plastic beaker and add water gradually so that the reaction proceeds at a moderate rate, until the melt is leached from the crucible. Add concentrated hydrochloric acid to the beaker containing the crucible until the solution becomes acid and clears up. After addition of the acid has begun, add the entire amount at once because, otherwise, silicon will occasionally begin to come out of solution. Then add acid until the solution contains between 3 and 5 % hydrochloric acid; remove the crucible and rinse it with distilled water. Transfer the solution to an appropriate volumetric flask and dilute to the mark.

Atomic Absorption Procedure

Take an aliquot of the main sample solution and place it in an appropriate volumetric flask. Add enough of the sodium solution (see <u>Reagents</u>) so that the final dilution for atomisation contains about 6000 ppm in sodium, making sure that the sample solution remains well on the acid side by adding hydrochloric acid if necessary. Dilute to the mark with water. This solution should contain between 10 and 200 ppm of silicon.

Atomize the sample directly and, using the Jarrell Ash atomic absorption spectrophotometer, model $82-300^{(1)}$, compare readings with pure silicon standards which contain approximately the silicon content expected in the sample and which, preferably, span the sample content.

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Atomic Absorption Parameters with the Jarrell-Ash Dual Double-Beam Spectrophotometer, Model 82-300

Wavelength - 251.2 nm

Lamp current - 10 mA

Burner - Hetco total consumption, with laminar - flow head Burner height - 19 cm from the burner top to the bottom of

the burner holder

Range - variable

Slit - 100 and 150 microns

Fuel mixture - nitrous oxide and acetylene

Flame type - just luminous

Atomic Absorption Parameters with the Techtron Spectrophotometer, Model AA-3

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Wavelength - 251.5 nm

Lamp current - 12 mA

Burner - burner and atomizer assembly for the Model AA-5 with plain-slot and grooved burner-heads

Slit - 50 microns

Fuel mixture - nitrous oxide and acetylene

Flame type - just luminous

EXPERIMENTAL

Application of Atomic Absorption Procedures to Synthetic Solutions

Stability and Sensitivity Shown by Standard Silicon Solutions

Opinions are known to differ concerning the stability of silicon solutions in various media (2-7). Although the hydrofluoric-boric acid system is generally acknowledged to be satisfactory, a greater difference of opinion is found concerning silicon stability in mineral acid solution in the absence of hydrofluoric acid.

In an attempt to clarify this point, tests were carried out to establish the effect of ageing and dilution on the sensitivity and/or linearity found in using pure silicon solutions in a) hydrochloric acid, b) hydrochloric-hydrofluoricboric acid, and c) hydrofluoric-boric acid mediums. In a) and b) above, a sodium peroxide fusion was used to solubilize pure silica powder, whereas in c) above, a Teflon bomb procedure was used for this purpose. In all tests, the sodium content was normalized at between 3000 and 6000 ppm.

It was found that, following a sodium peroxide fusion and the addition of between 3 and 5 % excess of hydrochloric acid to its water leach, stability of a 400-ppm silicon solution was good for at least 4 weeks, with or without further dilution. The 400-ppm silicon solution, following the Teflon bomb procedure, was also stable for at least four weeks but, after fourfold dilution, it had deteriorated in strength by the fourth week by about 8 %.

The sensitivity obtained for atomic absorption readings after dissolution by bomb and fusion varied with the instrumental parameters and, especially, with the type of flame used. It was found that by using a barely luminous flame, the best combination of sensitivity and low flame background was obtained. A comparison of the sensitivity for silicon in hydrochloric acid and hydrofluoric-boric acid mediums, run at approximately the same time and with the same flame type and instrumental parameters, showed little difference in sensitivity.

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Satisfactory linearity was found for silicon absorption in hydrofluoric-boric acid medium after a bomb procedure at the normal 3 % (w/v) level and after dilutions of this solution. However, if the 3 % solution was concentrated (i.e. more $HF-H_3BO_3$ added), results became erratic and linearity was very poor in the 10 to 100-ppm working range of the procedure. In any event, as a matter of routine practice, it was more convenient to dilute the 3 % hydrofluoric-boric solution while preparing samples and their matching silicon standards.

Silicon standards in either hydrochloric acid or in hydrochloric-hydrofluoric-boric acid solution after a sodium peroxide fusion, showed satisfactory linearity. However, erratic results and loss of linearity ensued after adding hydrofluoric and boric acids to a silicon solution, in hydrochloric acid after a fusion, that had been allowed to stand for a few weeks (Figure 1). The results of these tests and of those in the preceding paragraph indicated that changes in the procedure could affect the type of silicon compound formed and, therefore, its behaviour in solution and in the flame.

Effects of Contaminants on Silicon Results

General Comments

The extent of element interference in the atomic absorption determination of silicon has been reported by a number of workers^(4,8,9,10,11). Some of the variances in their findings presumably reflect the effects of the different solution media used, as well as the different instrumental types and parameters used. Several investigators ^(9,12,13,14) have

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compensated for interference effects by running analysed standard samples with regular samples, for comparison purposes. This technique, though possible in some cases, is not always practical in our laboratory because of the wide variety of materials to be analysed. It was considered to be important, therefore, that the procedure permit comparison against puresilicon standards. Accordingly, synthetic solutions were tested to better ascertain the points at which common contaminants interfered with results.

Measured amounts of solutions of iron, titanium, potassium, copper, lead, aluminum, magnesium, calcium, and manganese were added alone and, at times, together to standard silicon solutions. The contaminants, in most instances, were put into solution with both Teflon bomb and sodium peroxide fusion procedures. Aliquots of these solutions in hydrochloric medium and/or hydrofluoric-boric medium were then combined with aliquots of a standard silicon solution. Sodium was present in all tests in different amounts. The amount of contaminant added represented the highest ratio of each contaminant to silicon found in the types of sample material encountered during this study.

Teflon Bomb Dissolution: HF-H3BO3 Medium

Results, as shown in Table 1, indicated that in the hydrofluoric-boric system following a Teflon bomb dissolution, most of the contaminants added did not cause recoveries to vary beyond experimental limits of \pm 5 %. However, large amounts of copper and lead caused serious enhancement which would necessitate addition of comparable amounts of the respective

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contaminants to the silicon comparison standards. None of the other elements except iron was present in this sample material in quantities comparable to copper and lead, therefore, comparably high contaminant:silicon ratios for the other elements were not tested.

Fusion Dissolution: HCl Medium

After fusing the silicon and the contaminant in sodium peroxide and dissolving the melt in hydrochloric acid, it was found that most of the elements added did not affect results beyond experimental limits. However, large amounts of iron, copper, and lead caused very high results (Table 2). It was clearly indicated that, if analysing samples containing preponderant amounts of these elements, the addition of the main contaminant to the standard silicon solutions would be required for the purpose of comparison with the sample.

Fusion Dissolution: HCl-HF-H3BO3 Medium

With the hydrofluoric-boric system following fusion dissolution, most of the contaminants added tended to cause high (apparent) silicon recoveries at lower levels of sodium content. This could be compensated for to a major extent by increasing the sodium content (Table 3). These tests, which were carried out using a Techtron Atomic Absorption spectrophotometer, Model AA3, encountered burner problems at these sodium levels, and especially beyond 12,000 ppm sodium, due to clogging of the burner slot, which necessitated frequent washing of the burner. This technique then, while usable when necessary, was not pursued further as it was not considered to be especially suitable for routine work.

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TABLE 1

:

Effect of Contaminants on Silicon Results by Atomic Absorption After Teflon Bomb Dissolution; HF-H₃BO₃ Medium

| Silicon Present ppm Si | Contaminant* and Amount Present ppm | R atio of Silicon to Contaminant | Silicon Found ppm Si | Deviation % |
|------------------------------|---|---|----------------------------|----------------|
| 100 | 3000 Fe | 1:30 | 99.1 | - 0.9 |
| 50 | 3000 Fe | 1:60 | 50.0 | 0.0 |
| 100 | 1500 Ti | 1:15 | 100.3 | + 0.3 |
| 50 | 1500 Ti | 1:30 | 49.6 | - 0.8 |
| 100 | 700 Al | 1:7 | 96.8 | - 3.2 |
| 50 | 700 Al | 1:14 | 52.0 | + 4.0 |
| 100 | 430 Mg | 1:4 | 100.3 | + 0.3 |
| 50 | 430 Mg | 1:9 | 50.8 | + 1.6 |
| 100 | 285 Ca | 1:3 | 99.4 | - 0.6 |
| 50 | 285 Ca | 1:6 | 51.1 | + 2.2 |
| 50 | 200 Mn | 1:4 | 97.8 | - 2.2 |
| 100 | 200 Mn | 1:2 | 97.8 | - 2.2 |
| 20 | 5800 Pb | 1:290 | 33.5 | +67.5 |
| 20 | 12,000 Pb | 1:600 | 31.4 | +57.0 |
| 100 | 200 К | 1:2 | 93.5 | - 6.5 |
| 50 | 200 К | 1:4 | 48.4 | - 3.2 |
| 48 | 4400 Cu** | 1:90 | 60.6 | +26.3 |
| 24 | 2400 Fe + 2200 Cu | l:100 Fe: 90 Cu | 27.7 | +15.4 |
| 100 | 50 Al + 20 Ca | 1:0.5 Al: 0.2 Ca | 100.0 | 0.0 |
| 100 | 430 Fe + 215 Ti +100 Al + 60 Mg + 40 Ca + 30 Mn + 30 K | - | 99.8 | - 0.2 |

*From 3000 to 5000 ppm sodium present except where noted.
**No sodium added.

TABLE 2

Effect of Contaminants on Silicon Results by Atomic Absorption After Sodium Peroxide Fusion; HCl Medium

| Silicon Present ppm Si | Contaminant* and Amount Present ppm | Ratio of Silicon to Contaminant | Silicon Found ppm Si | Deviation % |
|------------------------------|---|---------------------------------------|----------------------------|-----------------------|
| 100 50 50 | 3000 Fe 3000 Fe 6500 Fe | 1:30 1:60 1:130 | 100.00 53.0 60.3 | 0.0 + 6.0 +12.1 |
| 100 50 | 1500 Ti 2000 Ti | 1:15 1:40 | 100.2 51.9 | + 0.2 + 3.8 |
| 100 50 | 700 Al 1000 Al | 1:7 1:20 | 101.0 49.6 | + 1.0 - 0.8 |
| 100 50 | 430 Mg 600 Mg | 1:4 1:12 | 100.8 49.0 | + 0.8 - 2.0 |
| 100 50 | 285 Ca 430 Ca | 1:3 1:9 | 99.8 50.5 | - 0.2 + 1.0 |
| 100 | 200 Mn | 1:2 | 100.2 | + 0.2 |
| 20 | 12,000 Pb | 1:600 | 30.4 | +52.0 |
| 100 50 | 200 K 300 K | 1:2 1:6 | 100.0 50.0 | 0.0 0.0 |
| 100 | 50 Al + 20 Ca | 1:0.5 Al: 0.2Ca | 100.5 | + 0.5 |
| 48 | 4400 Cu | 1:90 | 61.5 | +28.1 |
| 24 | 2200 Cu + 2400 Fe | 1:90 Cu: 100 Fe | 28.2 | +17.5 |
| 100 | 430 Fe + 215 Ti +100 Al + 60 Mg + 40 Ca + 30 Mn + 30 K | - | 99.6 | - 0.4 |

*From 3000 to 6000 ppm sodium present.

Application of the Procedures to Sulphide and Silicate Minerals and their Mixtures

In the literature on atomic absorption procedures, relatively little has been reported on pure minerals, especially on mineral mixtures. Dissolution techniques for minerals by means of a Teflon bomb were reported by Ito⁽¹⁵⁾, by Langmyhr and Sveen⁽¹⁶⁾, and by Langmyhr and Paus⁽¹⁷⁾. These investigators did not report silicon results. Langmyhr and Paus⁽²⁵⁾ decomposed a soda feldspar and nepheline syenite with hydrofluoric acid in plastic containers before determining a number of elements, including silicon, by atomic absorption. Medlin, Suhr, and Bodkin⁽⁷⁾ used a lithium metaborate fusion to decompose a number of minerals preceding the determination of silicon and other elements by atomic absorption.

Of the dissolution procedures considered for use, the two used for the work on contaminants, described on pages 9 and 10 and under PROCEDURE, were chosen: a Teflon bomb procedure and a sodium peroxide fusion in a zirconium crucible ^(18,19). Although this latter procedure has apparently received little attention for sample dissolution preceding atomic absorption analysis, it was chosen as an alternative to the Teflon bomb procedure because of our familiarity with it, its simplicity, and known effectiveness on difficultly-soluble sample material.

These two dissolution procedures combined several desirable features in that they were rapid, readily adaptable to control work, effective for dissolving different sample materials, and materials required for them were either at hand or were readily available.

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TABLE 3

Effect of Contaminants on Silicon Results by Atomic Absorption After Sodium Peroxide Fusion; HCl-HF-H3BO3 Medium, and with Varying Amounts of Sodium

| Silicon | HF-H3BO3 | Contaminant | | Amount | t of Sodiu | um Added · | - ppm Na | |
|-------------------|-----------|--|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| Present ppm Si | Present 8 | and Amount Present ppm | 6,000 Found ppm Si | 12,000 Found ppm Si | 18,000 Found ppm Si | 21,000 Found ppm Si | 24,000 Found ppm Si | 27,000 Found ppm Si |
| 23.3 46.7 | 0.75 3 | 750 Fe 1500 Fe | 26.2 | 25.0 50.2 | 22.8 - | 24.6 - | 23.7 | 23.5 - |
| 23.3 46.7 | 0.75 3 | 450 Ti 900 Ti | 24.3 | 25.0 48.1 | 22.5 | 23.5 | 24.0 | 24.6 |
| 23.3 46.7 | 0.75 3 | 130 A1 265 Al | 25.9 | 23.5 46.7 | 23.3 | 23.3 | 23.6 | 23.3 |
| 23.3 46.7 | 0.75 3 | 90 Mg 180 Mg | 25.3 | 23.5 47.7 | 21.4 | 23.6 | 23.5 | 23.9 |
| 23.3 46.7 | 0.75 3 | 180 Ca 360 Ca | 27.1 | 29.6 47.2 | 26.0 · _ | 23.5 | 23.8 | 23.5 |
| 23.3 | 0.75 | 150 Fe 90 Ti 26 Al 18 Mg 36 Ca | 26.9 | 25.0 | 23.2 | - | 23.8 | _ |

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The chosen procedure should provide a solution matrix which does not interfere, does not enhance, but preferably diminishes the effects of contaminants on atomic absorption results; which provides silicon in a soluble and stable form suitable for atomization; and which permits the determination of other elements besides silicon in the same solution.

Bernas⁽²⁾ has reported that the above requirements are met with the hydrofluoric-boric acid medium resulting from the Teflon bomb procedure. Also, he calculated the amount of boric acid necessary to complex the fluoride and recommended that the solution be transferred to plastic within two hours instead of being left in glass.

Less is known, however, about the flame behaviour of the solution after acidification of the water leach of a sodium peroxide fusion but it has been reported to be beneficial to add sodium as an ionization suppressant before silicon determination $(^{8,20})$. For this reason, therefore, and because of the results found earlier on synthetic solutions (see previous section), it was anticipated that this medium would be suitable for atomization purposes.

Individual Minerals

Decomposition of the Minerals

Teflon bomb and sodium peroxide fusion procedures were applied to the fourteen hand-picked minerals selected for this work. The minerals chosen were considered to be the most common constituents of the type of silicate and sulphide gangue minerals in the rock-types commonly encountered here. By using

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pure minerals, it was believed to be easier to simulate a great number of different ores by mixing a comparatively small number of samples. The composition of these minerals may be seen in Table 4.

It was found that all of the minerals could be dissolved in a sodium peroxide fusion. However, with a Teflon bomb dissolution, some residue remained from the pyrite sample, although each of the other minerals was completely soluble. Smaller amounts of pyrite, if mixed with other minerals, went completely into solution in the bomb procedure (see <u>Mineral</u> <u>Mixtures</u>). In the case of galena, a white precipitate, believed to be lead sulphate, came down in the solution left standing after both dissolution procedures.

In the peroxide fusion, it was found important to prevent the fusion temperature from going much higher than the 640°C normally used. Otherwise, some fine white precipitate appeared in the acid solution after fusion of some of the minerals. This indicated refractory compounds, believed to be zirconia, formed due to attack by the sodium peroxide on the zirconium crucible, which could contain some silicon.

Comparison of Atomic Absorption Results with Chemical Results

All of the samples were analysed for silicon by atomic absorption procedures after both Teflon bomb and fusion dissolutions. The silicon results obtained gravimetrically and by atomic absorption were compared and the deviation was calculated. It was difficult to obtain consistent gravimetric

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TABLE 4

Composition of the Minerals Analysed for Silicon Using Atomic Absorption and Chemical Procedures

| · · · · · · · · · · · · · · · · · · · | | M | ineral | . Com | posit | ion (| Appro | xima | te % |) |
|--|---|-----|--------|-------|-------|-------|----------|------|------|-------|
| Mineral Type | Source of Mineral . | Si | ' Al | Ca | Mg | Fe | Na | K | S | Other |
| Amphibole (Var: Hornblende) -Metasilicate of Na, Ca, Mg, Al, Fe | Faraday Mine, Bancroft, Ont. | 20 | 5 | 7 | 9 | 12 | - | - | - | - |
| Biotite -Silicate of Fe, Mg, K, Al | Douglas, Ont. | 18 | 6 | - | 10 | 15 | - | - | - | - |
| Chalcopyrite -Sulphide of Cu, Fe | Temagami, P.Q. | 0.4 | <0.1 | - | - | 33 | - | - | 31 | 30 |
| Pyroxene -Metasilicate of Ca, Mg, Fe | Sandy Creek, New Otter Lake, P.Q. | 25 | <0.1 | 18 | 11 | 3 | - | - | - | - |
| Feldspar -(Var: Labradorite) | Tabor Island, Coast of Labrador | 25 | 14 | 7 | - | - | - | - | - | - |
| Oligoclase -Feldspar, Albite and Anorthite Blend | Kragero, Norway | 30 | 12 | 2 | - | - | - | - | - | - |
| Feldspar (Var: Albite) Disilicate | Villeneuve, P.Q. | 30 | 12 | - | - | _ | - | - | - | - |
| Feldspar (Var: Microcline) | Back Mine, Buckingham Area,P.Q. | 30 | 12 | - | - | _ | - | - | - | - |
| Muscovite -Hydrous Silicate | Purdy Mine, Eau Claire, Ont. | 20 | 15 | - | - | - | - | - | - | - |
| Serpentine . -Hydrous Silicate | Portland Township, P.Q. | 20 | <0.1 | - | 25 | - | - | - | - | - |
| Talc | Madoc, Ont. | 28 | <0.1 | - | 17 | - | - | - | _ | — |
| Galena | Keno Hill, Yukon | 0.1 | - | - | - | - | - | - | 13 | 87 Pb |
| Pyrite -Sulphide of Fe | Ambasaguas, Spain | 0.9 | <0.1 | - | ÷ | 46 | - | - | 53 | - |
| Quartz | Lyndhurst, Ont. | 46 | <0.1 | - | - | 1 | <u> </u> | - | | <0.1 |

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results on several of the samples, and this made comparison of results more difficult than had been anticipated.

As shown in Table 5, gravimetric and atomic absorption results showed an average deviation of less than 5% for all samples, including those at both extremes of the procedural range. On two samples which were low in silicon, galena, and chalcopyrite, the ratio of major contaminant to silicon was as high as 600 to 1. In these cases, the results obtained were corrected by adding the major contaminant to the standard, otherwise results would be high. Following this procedural step, agreement with gravimetric results was considered to be satisfactory at this low silicon level.

Discrepancies were found, however, between atomic absorption and gravimetric results on the feldspar (labradorite) and amphibole samples. As the contaminant present in these samples was well below the amount previously found to cause interference in the atomic absorption procedure, this lack of agreement was surprising. In an attempt to resolve the greater of these discrepancies, a synthetic sample was prepared to simulate the composition of the feldspar (labradorite). Also, as will be shown in Table 7, a mixture of minerals was made up to approximate the chemical composition of the same feldspar. In both cases, no difficulties were found with the atomic absorption procedures on these prepared samples.

The amphibole and feldspar samples were submitted for fluorine analysis by neutron activation, with 1.46% fluorine being found in the amphibole sample but less than 0.05% in

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the feldspar. This could account for the lower gravimetric result on the amphibole because no precautions were taken in the chemical procedure to prevent premature loss of silicon tetrafluoride. However, the cause of the disagreement between atomic absorption and gravimetric results on the feldspar (labradorite) sample has not been established.

Precision Found for the Atomic Absorption

The precision of the two atomic absorption procedures was calculated using the method of Dean and Dixon⁽²¹⁾, and Bauer⁽²²⁾. In each case, a single sample weighing each of feldspar, muscovite, and quartz was taken, with five individual sets of atomic absorption measurements being made, representing two readings in each case. It was intended that, as the sample was carefully mixed and completely in solution, the precision found would be a measure of the reproducibility of the instrumental and flame conditions. The latter variable, in particular, was difficult to reproduce without elaborate gas control equipment, and it was considered to be the largest single factor affecting the precision found. The coefficient of variation obtained following the Teflon bomb procedure averaged 1.2%, compared with 1.5% obtained following the fusion procedure (Table 6).

Mineral Mixtures

Decomposition of Mineral Mixtures

Six mineral mixtures of the composition shown in Table 7 were prepared and were put into complete solution using both the Teflon bomb and the fusion dissolution procedures. The solutions of the mixtures remained clear during the analyses.

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| Mineral | Silicon Found | Silicon Fo | ound by A.A. Si | Deviation of AA Results from Chemical Results - % | | |
|---------------------------|---|----------------------------|-----------------------|--|----------------|--|
| | & Si | Teflon Bomb Dissolution | Fusion Dissolution | Bamb | Fusion | |
| Amphibole (Hornblende) | 19.6 ^a | .21.7 | 21.0 | + 10.7 | + 7.1 | |
| Biotite | 18.1 ^b | 18.3 | 18.55 | + 1.1 | + 2.5 | |
| Chalcopyrite | 0.31 ^b | 0.34 ^g | 0.35 ^g | + 10. | + 13. | |
| Pyroxene | 24.5 ^C | 24.0 | 25.15 | 2.0 | + 2.7 | |
| Feldspar (Labradorite) | 25.2 ^a | 28.9 | 29.1 | + 14.7 | + 15.5 | |
| Oligoclase | 28.8 ^a | 29.2 | 29.5 | + 1.5 | + 2.4 | |
| Feldspar (Albite) | 29.9 ^a | 30.95 | 30.3 | + 3.5 | + 1.4 | |
| Feldspar (Microcline) | 29.95 ^a | 30.6 | 30.55 | + 2.2 | + 2.0 | |
| Muscovite | 20.8 ^a | 20.55 | 21.9 | + 1.2 | + 5.1 | |
| Serpentine | 19.3 ^b | 19.05 | 19.35 | - 1.2 | + 0.4 | |
| Talc | 28.15 ^C | 28.3 | 28.7 | + 0.5 | + 1.95 | |
| Galena | 0.10 ^d | 0.11 ^h | 0.116 ^h | + 10. | + 16. | |
| Pyrite | 0.94 ^b | 0.935 | 0.935 | - 0.5 | - 0.5 | |
| Quartz | 45.5 ^{b,e,} 46.0(by diff.) ^f | 47.4 47.4 | 47.3 47.3 | + 4.1 + 2.8 | + 3.9 + 2.5 | |

TABLE 5

Comparison of Atomic Absorption Results with Chemical Results on Common Minerals

a - Multi-acid attack to perchloric fumes, followed by Na_2CO_3 fusion of the insoluble residue, then a single dehydration with perchloric acid.

b - Multi-acid attack, single perchloric dehydration.

c - Multi-acid attack to sulphuric fumes, then Na_2CO_3 fusion of the insoluble residue, followed by a double dehydration with hydrochloric acid.

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- d Multi-acid attack to perchloric fumes, then digestion of the insoluble residue with ammonium acetate solution (range of results was 0.12 to 0.09 % Si).
- e Multi-acid attack to perchloric fumes, Na_2CO_3 fusion of the insoluble residue, then double dehydration with $HClO_4$.
- f Value obtained by subtracting impurities found in the mineral.
- g Corrected value to compensate for Cu and Fe present (0.40 % without correction).
- h Corrected value to compensate for Pb present (0.17% without correction).

General Comments on Gravimetric Procedures

Method b was not satisfactory on amphibole, pyroxene, the feldspars, muscovite, talc, and galena nor was Method c satisfactory for analyzing amphibole, the feldspars, and muscovite in that results were low and/or erratic, as were results from using a direct sodium carbonate fusion followed by a double dehydration with hydrochloric or perchloric acids.

TABLE 6

Precision of Atomic Absorption Results for Silicon on Some Common Minerals

| | | Individual | | Precision Found | | | |
|----------------|---------------------|--|---------------------------|-------------------------------|----------------------------------|---|--|
| Sample Type | Sample Treatment | Determinations Using Atomic Absorption % Si | Average Result % Si | Standard Deviation S.D. | Coefficient of Variation % | 95% Confidence Limits for Average Result | |
| Feldspar | Teflon Bomb | 28.65, 28.35 28.35, 27.95 28.3 | 28.3 | ± 0.30 | ± 1.06 | ± 0.37 | |
| Feldspar | Fusion | 28.6, 28.25, 28.3, 28.85 28.6 | 28.5 | ± 0.26 | ± 0.90 | ± 0.32 | |
| Muscovite | Teflon Bomb | 20.55, 20.7, 20.0, 20.5 21.0 | 20.55 | ± 0.43 | ± 2.09 | ± 0.53 | |
| Muscovite | Fusion | 22.15, 22.1, 21.95, 20.9, 22.2 | 21.9 | ± 0.56 | ± 2.56 | ± 0.69 | |
| Quartz | Teflon Bomb | 47.25, 47.5. 47.2, 47.6 47.35 | 47.4 | ± 0.17 | ± 0.36 | ± 0.21 | |
| Quartz | Fusion | 47.9, 47.05, 47.75, 46.75, 46.9 | 47.3 | ± 0.495 | ± 1.05 | ± 0.60 | |

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| Mineral | | | | Element Pre | sent - % | | |
|----------------|------|----|-------|-------------|----------|-----|-----|
| Mixture # | Si | Al | Ca | Mg | Fe | Cu | Pb |
| 1 ^a | 40.4 | 2 | < 1 | < 1 | 3-4 | _ | - |
| 2 ^b | 27.4 | 6 | < 1 | 2-3 | 7-8 | 3 | - |
| 3 ^C | 24.4 | 3 | 1 | 1-2 | 15-20 | 1-2 | - |
| 4 ^d | 9.56 | 3 | < 1 | < 1 | 23-27 | 6 | 9 |
| 5 ^e | 3.43 | 1 | < 1 | < 1 | 20-25 | 12 | 26 |
| 6 ^f | 25.9 | 10 | 0.5-1 | 0.2-0.5 | 1-2 | - | - 1 |

TABLE 7

Composition of the Mineral Mixtures Prepared for Silicon Determination

- a Elliot Lake Uranium Ore (80% quartz, 13% muscovite, 5% pyrite, 1% oligoclase, and 1% biotite).
- b High-copper ore (50% feldspar (albite), 20% quartz, 10% chalcopyrite, 5% pyrite, 5% amphibole, 5% biotite, and 5% serpentine).
- c Low-copper ore
 (20% Feldspar (microcline), 30% quartz, 30% pyrite, 5% talc, 5% chalcopyrite,
 5% pyroxene, and 5% oligoclase).
- d Flotation concentrate
 (40% pyrite, 20% chalcopyrite, 10% galena, and 30% feldspar (microcline)).
- e Flotation concentrate

(20% pyrite, 40% chalcopyrite, 30% galena and 10% feldspar (microcline)).

f - Feldspar (labradorite)

(25% pyroxene, 50% oligoclase and 5% muscovite).

After 10 days, however, a precipitate, which appeared to be siliceous, became apparent in the hydrochloric acid solution of the fused Mixtures #1 and #4 and in the solution from Teflon bomb dissolution of Mixture #4.

Comparison of Atomic Absorption with Chemical Results

Silicon results found on the sample mixtures were compared with calculated silicon values for the mixtures, as determined both by atomic absorption and by gravimetric analyses on the individual minerals making up the sample. The deviation found, as calculated for atomic absorption results versus both atomic absorption and gravimetric results on the individual minerals, was considered acceptable in that it was within 2%. The satisfactory agreement, between the atomic absorption results on the mineral mixtures and on individual minerals, indicated that the interaction of the minerals did not affect results (Table 8).

DISCUSSION

Dissolution

Neither of the recommended dissolution procedures showed a clear superiority over the other, because each had certain advantages. Between them, they offered an effective attack upon any of the mineral and mineral mixtures described here, and upon the ores, slags, and other sample material described in Part III of this series (to follow).

The Teflon bomb procedure showed a small superiority in accuracy and precision over the fusion procedure. The behaviour of its solution in the flame was at least as good

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| | | | | | TADLE 6 | | | | | |
|------------|----|--------|------------|-----|----------|---------|----|----------|---------|----------|
| Comparison | of | Atomic | Absorption | and | Chemical | Results | on | Prepared | Mineral | Mixtures |

| Mineral* | Silicon I | Present** | Silio by . | on Found A.A.*** | Deviation - A.A. vs Calculated Results | | | | |
|--------------|----------------------|-----------------------------|---------------|---------------------|---|-----------|-------------|--|--|
| Mixture # | A.A. Average % Si | Gravimetric Average-% Si | Bomb %_Si | Fusion % Si | Previous Result for Comparison | Bomb % | Fusion % | | |
| 1 | 41.2 | 40.0 | 40.45 | 40.05 | AA | - 1.7 | - 2.7 | | |
| | | | | | Grav. | + 1.0 | + 0.05 | | |
| 2 | 27.8 | 27.2 | 27.6 | 27.3 | AA | - 0.79 | - 1.9 | | |
| | | | | | Grav. | + 1.4 | + 0.29 | | |
| 3 | 24.7 | 24.2 | 24.4 | 24.25 | AA | - 1.4 | - 2.0 | | |
| | | | | | Grav. | + 0.99 | + 0.37 | | |
| 4 | 9.65 | 9.43 | 9.65 | 9.97 | AA | 0.0 | + 3.3 | | |
| | | - | | | Grav. | + 2.3 | + 5.7 | | |
| 5 | 3.46 | 3.34 | 3.40 | 3.55 | AA | - 1.7 | + 2.6 | | |
| | | | | | Grav. | + 1.8 | + 6.3 | | |
| 6 | 26.1 | 25.7 | 25.8 | 26.1 | AA | - 1.3 | 0.0 | | |
| | | | | | Grav. | + 0.27 | + 1.4 | | |

* For sample composition see Table 7
 ** Calculated silicon content based on a) the average of atomic absorption results, and b) gravimetric results, found on the individual minerals making up the sample.
 ***Based on two sets of readings from one sample weighing.

as the solution following the fusion procedure. The effects of contaminants on results after either dissolution procedure were comparable. An advantage of the bomb dissolution procedure over most others would be its suitability for silicon determination in samples containing fluorine.

Among advantages found for the fusion procedure were its greater flexibility in allowing a choice of sample size and its effectiveness on certain sample material which was difficult to dissolve by other procedures. With the Teflon bomb procedure, samples heavier than 0.5 g were difficult to dissolve and certain refractory samples were harder to dissolve than by the fusion procedure.

Stability

Our observation was that the stabilities of the silicon standard solutions and of the sample solutions, could be affected by - the type of dissolution procedure used and its resultant solution medium, its acid strength, its ageing time, the amount of silicon and other elements present, and the manner of handling during the procedure. After long standing, samples and pure silicon standards sometimes behaved differently. It was our experience, however, that if the procedures described here had been followed, pure silicon solutions normally remained stable for several weeks and that, generally, samples behaved in a similar manner.

Effect of Interferents

When using the Jarrell Ash spectrophotometer and burner-atomizer system, the use of comparison solutions of

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contaminants plus standards was not normally required. In some cases, however, in which the ratio of contaminant to silicon was unusually high, the addition of one or more major contaminants to the silicon standards served to correct for any effect from this source. This latter technique could be considered to be a good general safety measure because the effect of contaminants varied with flame changes and these changes should be as accurately reflected as possible. It would be expected, therefore, that the closer the matching of standard and sample, the greater the improvement in accuracy and precision. For most work, however, the procedural addition of the major contaminant to the standard could be eliminated. In such cases, the saving in time realized from measuring against pure standards, particularly if the composition of the sample were unknown, would be very advantageous.

The presence of sodium has been reported to cause an enhancement of the absorption of silicon and this can be beneficial, if controlled, because its effect levels-off at higher sodium content levels. Its function has been explained in terms of suppression of silicon ionization. The low ionization potential of sodium causes an increase in the absorption of the other elements, if the latter are ionized less easily in the flame type being used ⁽⁸⁾. A working level of about 6000 ppm of sodium in the final solution for atomization was found to be beneficial for use following both dissolution procedures as this amount was both effective and convenient. The use of much higher amounts of sodium than this caused burner-clogging that necessitated

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frequent washing of the burner. With the recommended procedure, the Jarrell Ash burner required scraping three or four times an hour but washing of the burner was not required for at least two hours.

General Comment

A major advantage of the recommended atomic absorption procedures over gravimetric methods was in the saving of analysis time. When analysing for silicon gravimetrically, especially difficult sample material (feldspars, amphibole, muscovite, galena, chalcopyrite, and pyroxene), the analysis time was several times longer than by using the atomic absorption procedures. Also, a number of different analytical approaches had to be made in applying the gravimetric method in order to obtain acceptable accuracy and precision on the series of minerals analysed. This finding is in agreement with that of Hillebrand (23) and many other investigators, who have discussed extensively the problems which may be encountered in gravimetrically analysing minerals and ores for silicon. By comparison, the same atomic absorption procedures were used on all the minerals and their mixtures, except galena and chalcopyrite for which simple modifications of major-contaminant addition to the comparison standard were made.

The usable range of the atomic absorption procedure was wide, with samples containing between 0.1 and 45% silicon being analysed. It was found that 0.1% is close to the lower limit of the described atomic absorption procedure and that special techniques such as solvent extraction would be necessary to extend its range to lower levels.

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CONCLUSIONS

The two dissolution procedures described are satisfactory for use preceding the atomic absorption determination of silicon and give solutions that have excellent long-term stability with respect to silicon and which are suitable for the determination of other constituents of the samples. The applicability of the given operating parameters for the atomic absorption procedure is confirmed for comparable highly salted solutions that contain contaminants. Adequate results will normally be obtained from using comparison standards prepared from pure silicon, but a significant gain in accuracy can be realized, even in moderately complex materials, by: using comparison standards adjusted to contain comparable amounts of the predominant contaminant.

The method is generally applicable to mineral specimens or mixtures typical of sulphide ores and tailings. Silicon contents between 0.1 and 45 per cent can be determined at between one fifth and one third of the cost of gravimetric procedures and with comparable, or better, accuracy. The precision, expressed as the relative standard deviation, is about 1.5%, and the average deviation from the gravimetric results is less than 5%, much of which can be attributed to errors in the gravimetric method.

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