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*THE USE OF FLAME PROCEDURES FOR THE  
ANALYSIS OF MINERALS, ORES, AND  
ELECTRIC FURNACE SLAGS*

*PART I: SAMPLE DISSOLUTION AND ATOMIC  
ABSORPTION PROCEDURES FOR USE IN THE  
DETERMINATION OF SILICON - A REVIEW*

R. J. GUEST

EXTRACTION METALLURGY DIVISION

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PART I: SAMPLE DISSOLUTION AND ATOMIC ABSORPTION  
PROCEDURES FOR USE IN THE DETERMINATION OF SILICON -  
A REVIEW

by

R. J. Guest\*

PREFACE

As the first report in a series on atomic absorption procedures for silicon, a literature review is presented with the intention of applying this information to the development of a general silicon procedure for use on a wide variety of sample material. In particular, the desired procedure should be applicable to most common types of ore as well as to electric furnace slags and associated materials. Several dissolution procedures are discussed as well as the effect on the procedure of such variables as interfering ions, sample matrices, solution stability, and some instrumental parameters.

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Utilisation des essais à la flamme pour l'analyse des minéraux,  
des minerais et des scories de fours électriques

Partie I: Dissolution de l'échantillon et méthodes de spectroscopie  
d'absorption utilisées pour le dosage de la silice

Revue

par

R. J. Guest\*

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Comme premier d'une série de rapports sur les méthodes de spectroscopie d'absorption utilisées pour le dosage de la silice, l'auteur présente une revue de la documentation existante afin d'utiliser ces renseignements pour le développement d'une méthode générale de dosage de la silice qui pourrait être utilisée pour une grande variété de substances. La méthode recherchée devrait s'appliquer plus particulièrement aux minerais des types les plus communs ainsi qu'aux scories des fours électriques et aux matériaux associés. L'auteur traite de plusieurs méthodes de dissolution ainsi que de l'effet sur ces méthodes de variables telles l'interférence d'ions, les matrices des échantillons, la stabilité des solutions ainsi que certains paramètres propres au matériel utilisé.

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## INTRODUCTION

The determination of silicon has traditionally been achieved by gravimetric or by spectrophotometric procedures. Both of these methods are subject to a number of problems which have been extensively discussed in the chemical literature. These problems are intensified on complex sample material, especially types containing high earth-acid content, and samples such as ilmenite and associated slag materials from high-temperature furnace work. Also, the gravimetric procedure is often long and tedious, especially if accurate results are required. For these reasons, then, a need has existed in many laboratories for a rapid, accurate procedure for silicon.

Although atomic absorption procedures for silicon are not very sensitive, their use on a wide variety of sample materials has received a considerable amount of attention. Two of the main advantages of atomic absorption methods are 1) analytical speed and 2) freedom from the effect of interferants, which, by eliminating the necessity for separations, also speeds up the method. However, it is still necessary to convert solid samples to solution form, which is often a time-consuming process. Accordingly, in analysing for silicon and/or a number of other elements, many workers have investigated rapid dissolution techniques such as simple acid attack and fusion procedures of various types, with the intention of saving time in analysis and obtaining a solution medium with a high interferant tolerance. In the case of silicon, the primary concern is to obtain a

medium in which the silicon will remain in a soluble form for an appreciable period of time. In order to achieve this, a variety of analytical approaches have been devised.

This paper attempts to summarize briefly the work done on 1) dissolution techniques preceding atomic absorption analysis, 2) procedures for maintaining silicon in a soluble form, and 3) the effect of interferants on results in various media. No attempt is made to provide an exhaustive summary of the prior literature on silicon determination using atomic absorption. Rather, the intention is to mention those points relevant to the analysis of sample types commonly encountered in our laboratory and, in particular, the analysis of ores, minerals, and high-temperature slags and associated materials. The purpose of the review is to categorize the important variables in the sample dissolution procedures required for silicon determination by atomic absorption in preparation for research on the method; this is the subject of other reports<sup>(48,49)</sup> in this series. It is presented here to provide background for the papers and to summarize the current state of the art.

## METHOD REVIEWS

### A. Dissolution Procedures

#### 1. Acid Dissolution

Langmyhr and Graff<sup>(1)</sup> described the application of hydrofluoric acid to dissolve siliceous materials without loss of silicon tetrafluoride by the use of an excess of hydrofluoric acid in the cold. Other workers have described procedures using hydrofluoric acid with hydrochloric and nitric acids

to dissolve cast iron, and, with hydrochloric acid and hydrogen peroxide, to dissolve steel, cement, and aluminum alloys<sup>(2,3)</sup>. McAuliffe<sup>(4)</sup> used a combination of sulphuric acid with persulphate for dissolving cast iron and steel. Thormahlen and Frank<sup>(5)</sup> preferred a combination of sulphuric acid and hydrogen peroxide for niobium alloys, and hydrochloric and sulphuric acids together with hydrogen peroxide, for steels and bronze. Smith, Johnson and Soth<sup>(6)</sup> used a mixed-acid treatment, including hydrofluoric acid, followed by a sodium carbonate or sodium peroxide fusion of the insoluble residue, in analyzing for silicon in ferromanganese, silicomanganese, ferrochromium, and ferrosilicon. Sodium hydroxide and hydrogen peroxide, in a nickel or stainless steel crucible, have been used by Campbell<sup>(7)</sup> to dissolve aluminum alloys before determination of silicon.

Langmyhr and Paus<sup>(8-11)</sup> found that a hydrofluoric acid attack in a plastic beaker dissolved certain siliceous materials such as glass sand, as well as feldspar, cement, clinkers, raw mixes, and siliceous limestone. Capacho-Delgado and Manning<sup>(12)</sup> used a hydrochloric acid leach followed by a sodium carbonate fusion of the insoluble residue to dissolve cement. Reid et al.<sup>(13)</sup> used an acid attack in plastic bottles under pressure to dissolve slags and sinters before determination of silicon. Omang<sup>(14)</sup> used a combination of hydrochloric and hydrofluoric acids to dissolve bauxite. Phosphoric acid has been used by Lucas and Ruprecht<sup>(15)</sup> to dissolve chrome ore and chromium-magnesite.



## 2. Teflon Bomb Dissolution

In 1961, Ito<sup>(15)</sup> described a bomb technique for refractory minerals to precede the determination of ferrous iron and alkalies. He used a Teflon liner in a steel bomb, a temperature of 240°C, a mixture of sulphuric and hydrofluoric acids, and various digestion times. Langmyhr and Sveen<sup>(16)</sup>, using a similar bomb and a temperature of 250°, added hydrofluoric acid following addition of a little aqua regia as a wetting agent. They tested the dissolution of a number of the minerals found in silicate rocks and successfully dissolved many of them, including pyrite and chalcopyrite. In this latter paper, the fluoride was complexed with aluminum chloride before further handling. More recently, Bernas<sup>(17)</sup> described a modified bomb with which he used an effective temperature range of 110 to 170°C without causing undue stress on the Teflon liner. A calculated amount of boric acid was used to complex excess fluoride. Nine elements, including silicon, were analysed using atomic absorption procedures in samples of granite, diabase, and tektites. Also, it was found that the hydrofluoric-boric medium was beneficial from the standpoint of interference of contaminants in the various analyses. Langmyhr and Paus<sup>(18-21)</sup>, in a series of papers, described the use of a Teflon bomb, at temperatures of 110°C and higher, for the dissolution of bauxite, Certified iron ore and basic slag, and samples of pyrrhotite, chalcopyrite, and pyrite. The determination of a number of elements, including silicon, using atomic absorption procedures, was then done. These same authors have described a modified bomb using an

aluminum shell, a magnetic stirring facility, and a temperature regulator<sup>(22)</sup>.

### 3. Fusion Dissolution with Lithium Compounds

Fusion of silicate rocks and minerals with lithium metaborate was first reported by Ingamells<sup>(23)</sup> for silicate dissolution and has been used since by many other investigators to precede silicon determination using a variety of instrumental procedures. Suhr and Ingamells<sup>(24)</sup> described this dissolution technique for silicates. Ingamells<sup>(25)</sup> reported absorptiometric determination of silicon following lithium metaborate fusion. Van Loon and Parissis<sup>(26)</sup>, and Abbey<sup>(27)</sup> also used lithium metaborate fusion to decompose silicate rocks, while Medlin, Suhr and Bodkin<sup>(28)</sup> used the same flux for dissolving silicate rocks and minerals. In the above cases, the resulting sample solution was analysed for a number of elements, including silicon. For this fusion, platinum, graphite, or vitreous carbon crucibles may be used. Some of the above workers<sup>(25,26,28)</sup> used nitric, hydrochloric, or citric acid dissolution of the fusion melt while Abbey used a fluoborate medium to dissolve the melt and solubilize silicon.

Boar and Ingram<sup>(29)</sup> used a metaborate fusion for dissolving coal ash, and Omang<sup>(13)</sup> used a lithium carbonate-boric acid fusion for dissolving clay and soil extracts. The use of lithium tetraborate as a flux was described by Brown, McKay and Turek<sup>(30)</sup> who used a temperature of 1200°C and graphite crucibles for the fusion. Recently, Ingamells<sup>(31)</sup> reviewed

fusion techniques using lithium metaborate, pointing out some of the difficulties and how they could be avoided.

#### 4. Fusion Dissolution with Sodium Compounds

Fusion of samples with an alkaline flux such as sodium carbonate before acidification and dehydration of the silica, is a classical procedure for silica determination. The use of fusion techniques preceding an atomic absorption finish and using sodium compounds, alone or in combination with other compounds, is reported<sup>(38)</sup>, and fusions have also been used on the insoluble residue after acid attack of the sample<sup>(6,12)</sup>. A sodium hydroxide fusion in a nickel crucible was preferred by Katz<sup>(32)</sup> over a sodium carbonate fusion for attack on silicate rocks and minerals before atomic absorption spectroscopy. Sodium peroxide has been used in at least one investigation<sup>(6)</sup> to fuse the insoluble residue resulting from acid attack of ferrochromium.

Fusion with sodium peroxide in an iron or nickel crucible is a well-known dissolution procedure. Petretic<sup>(33)</sup> and Dinnin<sup>(34)</sup> used zirconium crucibles for this fusion, because considerably less contamination of the sample by the crucible takes place with this more resistant crucible material. However, Anibal<sup>(35)</sup> has pointed out some difficulties found in analyzing for chromium, phosphorus, and sulphur following sodium peroxide fusion in a zirconium crucible. Although this difficulty in chromium determination has been encountered in our laboratory also, the general fusion technique has been widely applied here for dissolving many materials because of its simplicity and great effectiveness on a wide variety of sample material.



## B. Interferants

### 1. Interfering Ions

The interference of other ions on the atomic absorption determination of silicon has been investigated by a number of workers and the literature reports a variety of findings. This is probably due not only to the different contaminant levels tested, but also to the different sample matrices and instrumental parameters used.

Langmyhr and Paus<sup>(8)</sup>, Van Loon and Parissis<sup>(26)</sup>, and Bernas<sup>(17)</sup> did not report any interferences for silicon at the contaminant levels they were using. Other investigators found that aluminum and certain other elements had an enhancement effect on silicon results. Omang<sup>(13)</sup> found a 7% enhancement, from aluminum in lithium carbonate-boric acid medium which could be removed by adding lanthanum or fluoride. Bowman and Willis<sup>(36)</sup> reported a 10% enhancement from aluminum either alone or in the presence of sodium, borate, and chloride. Boar and Ingram<sup>(29)</sup> also reported enhancement from aluminum but found the effect was constant beyond a certain aluminum level and could be masked by adding tartaric acid. Ferris, Jepson, and Shapland<sup>(37)</sup> found that aluminum and iron enhanced silicon results in the presence of phosphate, either alone or in combination. Katz<sup>(32)</sup> cut down the sample flow-rate to lessen the effect of interfering ions.

A detailed study of some interferences is reported by Price and Roos<sup>(2)</sup>. They added up to 3000 ppm of contaminant to silicon solutions and found enhancement from aluminum, iron, calcium, sodium, and vanadium, but phosphate suppressed silicon

results unless enough iron was present to complex it. These investigators found that the enhancement effect of the individual ions levelled off and that the combined enhancement effect of two or more ions tended to give the same overall enhancement. One effective technique suggested was to add sufficient of the interferant to samples and standards to compensate for the interference. Moderate amounts of sodium, however, were found to cause slight enhancement of silicon even in the presence of another element such as aluminum or vanadium. Price and Roos explain the enhancement of silicon absorption by the elements mentioned as suppression of the ionisation of silicon in the nitrous oxide-acetylene flame by the added elements. Because of these interferences, some workers preferred to use matched synthetic standards or to carry analysed samples along with the samples for comparison purposes (7,27,28,38,46,47).

## 2. Other Interferants

Marks and Welcher<sup>(39)</sup> studied the effect of inter-element interferences on aluminum, titanium, nickel, and chromium absorbances with the nitrous oxide-acetylene flame and evaluated the effects of flame and instrumental variables on results. They concluded that the magnitude of cation interferences is affected primarily by the burner height during measurement, the fuel:oxidant ratio, and the concentration of analyte in the salt matrix. Many of the observed interferences could be lessened by proper selection of operating parameters. They found that salt vaporisation effects were the most critical in determining interference effects.

In the determination of silicon and other elements, a number of workers have reported burner and other problems when working with highly salted solutions. Bowman and Willis<sup>(36)</sup> found clogging of the burner slot from working with highly salted solutions (> 2%); and, Lucas and Ruprecht<sup>(14)</sup> reported burner clogging from working with phosphoric solutions unless a special wide-slot burner was used. Campbell<sup>(7)</sup> advised matching the salt content of standards and samples closely and stated that the salt content should be kept below 2%, preferably below 0.5%, to avoid burner problems. Galloway and Reid<sup>(38)</sup> reported difficulties with carbon build-up on the burner slot while analysing for silicon or aluminum in a fuel-rich flame.

In a study of the effect of burner temperature on atomic absorption spectroscopy using the nitrous oxide flame, Goguel<sup>(40)</sup> reported, in the determination of silicon, the formation of a crust on the sides of the burner slot while using a grooved burner (Techtron). This caused high background noise and extensive baseline drift. Apparently, silica, which had precipitated in the slot, slowly vaporised into the flame. This effect did not happen with the plain-slot burner, although the grooved burner prevented the build-up of carbon much more efficiently than the plain-slot burner.

### C. Stability of Silicon Solutions

A variety of claims have been made about the stability of the silicon solutions in various media. Van Loon and Parissis<sup>(41)</sup>



found that the addition of calcium improved the stability of a standard silicon solution. Omang<sup>(13)</sup> found that, following fusion of the silicon standard with sodium carbonate, a stable solution could be obtained without the addition of calcium. Lucas and Ruprecht<sup>(14)</sup> found a phosphate solution of silicon stable for at least 2 years. Bernas<sup>(17)</sup> observed that a hydrofluoric-boric acid solution of silicon following bomb dissolution showed no precipitation for at least four weeks. Some other investigators reported results to the contrary. Galloway and Reid<sup>(38)</sup>, and Reid et al.<sup>(47)</sup> reported an ageing effect with synthetic standard silicon solutions. Suhr and Ingamells<sup>(24)</sup> reported a shelf-life of about three days for a nitric acid solution of a metaborate fusion melt of silicon. Medlin, Suhr and Bodkin<sup>(28)</sup> recommended doing silicon analysis as soon as possible after lithium metaborate fusion and nitric acid dissolution of the melt. Brown, MacKay, and Turek<sup>(30)</sup> found standard silicon solutions to be stable for at least 11 months following lithium tetraborate fusion at a high temperature for an extended time (1200°C for 1 hour). By comparison, a standard silicon solution, following lithium metaborate fusion at a lower temperature and for a shorter time (950°C for 10 to 15 minutes), deteriorated by about 15% in 11 months.

#### D. Extraction Techniques

A number of papers have described the indirect determination of silicon after the extraction of its heteropoly-molybdo acid with the acids of phosphorus and arsenic<sup>(42,43,44,45)</sup>. The three elements may then be separated selectively by solvent

extraction and determined individually. The twelve molybdate ions associated with each silicate ion are determined, to increase the sensitivity of the procedure.

#### SUMMARY

Work done by a number of investigators on decomposition procedures, for a variety of sample material, preparatory to the determination of silicon and several other elements has been reviewed, and important variables in the sample dissolution procedures required for silicon determination have been categorized.

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