with the apparent background in Figure 11*B* through *D*. Insets *E* and *F* correspond to the synthesis of a fully unidirectional discharge, emphasizing that the continual sampling resulting from sustained or increased unidirectional current does not cause a significant improvement in signal at the expense of background, except for the Al II lines which are intermediate in the production of Al I radiation from Al III parent species (*1*, *3*).

A more quantitative interpretation of the spectra in Figure 11 may be seen in Figures 12 and 13, where transmission measurements have been made on the resonance lines of the copper impurity in the aluminum alloy. It is clear that the maximum net line-to-background ratio for these lines during the entire series of discharge half-cycles monitored occurs when the shunted current is reduced to a level below 50 amperes but without polarity change. Here, the background intensity has been essentially reduced to scattered light and fog levels, and the signal may be integrated over the shunted current half-cycles for purposes of enhancement.

The above spectra are offered only as the most obvious examples of the control that may be exerted over the spectra observed in a free-air discharge. Their major significance from a spectrochemical viewpoint is that sample has been replenished in the observation zone between observation intervals and it was possible to sustain low-energy neutral-atom emission at the expense of background radiation, a situation not encountered in either a fully oscillatory or fully unidirectional system. The value of the source for basic studies has been previously illustrated (*1*).

ACKNOWLEDGMENT

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A New Method for Decomposition and Comprehensive Analysis of Silicates by Atomic Absorption Spectrometry

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Rapid decomposition of silicates is achieved in a specially designed vessel made of Teflon (Du Pont) without volatilization losses by hydrofluoric acid at 110 °C. A fluoboric–boric acids system was found to provide a favorable decomposition medium and a suitable salt-free single matrix system. Conditions were developed for sufficient inhibition of the hydrolytic decomposition rate of fluoboric acid. This matrix was found to diminish significantly or to eliminate entirely the chemical, ionization, matrix, and instrumental interferences for atomic absorption measurements. The system permits contamination-free sample handling in glass equipment, ensures sample solution stability, eliminates the need for closely matching the matrix constituents of the sample and standard solutions, contributes to signal stability, and to date provides an interference-free environment for the rapid and reliable atomic absorption spectrometric determinations of silicon, aluminum, titanium, and vanadium using a nitrous oxide–acetylene flame and for iron, calcium, magnesium, sodium, and potassium using an air–acetylene flame.

METHODS conventionally used to decompose igneous rocks are based on the use of acids or fusion approaches. The decomposition step using either of these procedures for atomic absorption measurements is known to present difficulties (*1*). Several authors successfully decomposed a number of silicates and refractory minerals by hydrofluoric acid in Teflon vessels but volatilization losses could not be entirely prevented because of Teflon's dimensional instability (*2–5*). The Teflon decomposition vessels described in the literature use stoppers, machine-tapered sealing areas, and bolts and screws for sealing (*3*, *4*). However, the stoppers tend to become loose after repeated use and cause low results (*6*). To prevent volatilization of the sample material being decomposed the tapered areas need frequent remachining or trimming off of extruding Teflon edges.

Fusion, in metal crucibles with fluxes such as carbonates, borates of sodium, potassium, or lithium may lead to incomplete attack of the sample as well as to the limited solubility of some metal ions in the particular flux environment and to losses caused by reduction and alloying. Such fusion agents furthermore preclude the determination of the particular cation used in the flux (*7*). In addition, fluxes are usually used in a ten to twenty fold excess over the sample weight. These undesirably high salt concentrations cause solution instability as well as high and fluctuating instrument background readings. Light scattering and/or molecular absorption phenomena which are known to exist in such environments are detrimental features in any analytical scheme which should

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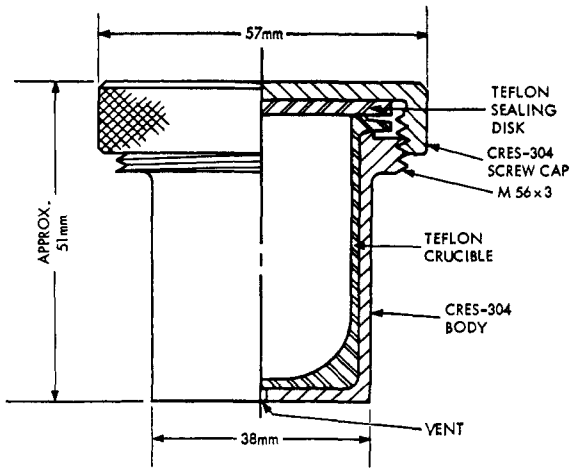

Figure 1. Decomposition vessel

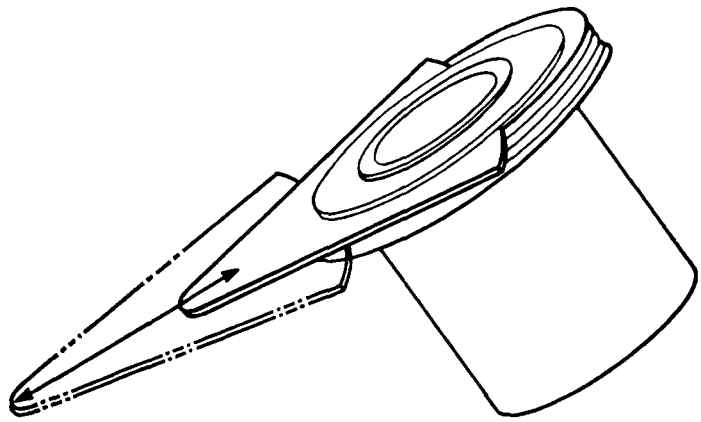

Figure 2. Decomposition vessel with spout

ultimately also cover the determination of trace constituents (*8, 9*).

Atomic absorption spectrometry is finding increasing use in geochemical analysis, and procedures for the determination of some of the major and minor constituents were published (*10–14*) and summarized in a recent monograph (*15*). Developments since the introduction of the nitrous oxide–acetylene flame (*16–18*), used for the determination of refractory elements, have made it possible to include the major and minor constituents into a scheme for the analysis of silicates.

However, when dealing with such complex systems, the overall efficiency of the technique is considerably diminished by the number of interfering factors which have to be considered and the time consuming remedies which must be introduced. At best, these consist of either chemically separating the interfering species or adding various releasing, compensating, and/or complexing agents to samples and standards alike. In all the approaches described to date, silica is removed to facilitate the determinations of alkaline earth metals and lanthanum is added as an interfering buffer to eliminate or diminish the interference caused by aluminum. To eliminate ionization effects in the alkali metals determination, a salt having a higher ionization potential has to be added. In extreme situations, it becomes necessary to match the matrix composition of the unknown and standards so closely that standard rock samples have to be used for calibration graphs to correct for the most frequently occurring interelemental and ionization interferences (*11*).

The purpose of the present investigation was to develop a comprehensive but simple analytical scheme for determining all the major and minor constituents in silicates of tektite type composition where atomic absorption spectrometry is applicable. Furthermore, the analysis of extraterrestrial materials is also envisaged within this context—for example, such requirements on lunar samples may include areas which at present cannot be gauged, but may well prove useful by using this technique.

The parameters investigated were: the design of a decomposition vessel which would reliably prevent the losses through volatilization of potentially volatile constituents, reduction and alloying, and contamination of sample solution; the development of an acid-type decomposition system; and the conversion of the sample solution into a matrix from which all the determinations could be carried out directly without any further treatment.

The analysis of small size samples for as many constituents as possible directly from a single sample solution and eliminating the need for separation and/or concentration steps were considerations envisaged in the development of the present scheme. Although effective extractants with high selectivity for both single elements or groups of elements are available, the complex nature and the often unsuspected varying composition of the investigated material tend to preclude the use of any separative step. The pH adjustments in buffered media of sample solutions create problems of solution stability—*i.e.*, precipitation and subsequent coprecipitation. The coexistence of more than one valency state of many multivalent elements in these systems require that the one preferential valency configuration be sought to achieve optimized extraction conditions. The complexities involved, both analytical and manipulative, are implied in this brief outline.

The development of an acid decomposition system should eliminate the need to use salt fluxes thus overcoming difficulties and disadvantages of the decomposition step encountered at present. However, an acids system useful for the determination of silica requires the presence of hydrofluoric acid which would lead to contamination problems in glass volumetric ware. As plastic volumetric flasks are not available yet, and attempts to use polypropylene pipets were unsatisfactory, it became necessary to investigate and develop an environment which would prevent contamination and at the same time prove advantageous when applied to atomic absorption measurements.

The matrix environment should significantly diminish or entirely eliminate chemical, ionization, matrix, and possibly instrumental interferences. Ideally, the use of such a single matrix system should substitute for the manyfold modes of correcting media presently in use. Furthermore, it should make it possible to determine a given constituent by comparison with standards only, thereby eliminating the need to use either different reagents to overcome the various types of inter-

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Table I. Instrumental Settings and Analytical Conditions for Atomic Absorption Measurements

Element	Si	Fe	Al	Ti	V[a]	Ca	Mg	K	Na
Source type	HBT[b]	SCT[c]	SCT	SCT	SCT	MSCT[d]	MSCT	ADL[e]	ADL
Wavelength, Å	2516	3720	3093	3643	3184	4227	2852	7665	5890
Recorder Expansion	1	3	1	3–10	10–30	3	1	3–10	3
Noise suppression	2–3	2–3	1	2–3	2–3	2	1	2–3	2
Calibration graph concentration limits, ppm	100–200	5–20	20–50	1–6	0.5–3.0	1–5[f]	0.5–2.0[g]	0.3–1.0[h]	0.4–1.2[i]

[a] Sample weight 300 mg.
[b] High brightness tube.
[c] Shielded cathode tube.
[d] Multielement shielded cathode tube.
[e] Arc discharge lamp.
[f] Sample dilutions: 1:4 or 1:10.
[g] Sample dilutions: 1:1 or 1:4.
[h] Sample dilution: 1:10 or 1:100.
[i] Sample dilution: 1:10.

Table II. Preparation of Standard Stock Solutions

Element	Source	Medium	Concentration, ppm
Silicon	SiO_2	HBF_4–H_3BO_3	1,000
Iron	Fe wire	HCl	1,000
Aluminum	Al wire	HCl	1,000
Titanium	TiO_2	$KHSO_4$–H_2SO_4	1,800
Vanadium	V_2O_5	HCl	140
Calcium	$CaCO_3$	HCl	500
Magnesium	MgO	HCl	1,000
Sodium	NaCl	H_2O	1,000
Potassium	KCl	H_2O	700

ferences or of having to match sample and standards with respect to the other matrix constituents.

The above requirements were met by developing the fluoboric–boric acids matrix. Such a system has not previously been considered within the context of silicate analysis, nor has it been evaluated as a possibly favorable matrix for atomic absorption measurements. The medium was found attractive because it does not introduce any cationic salts to the sample solution. It permits volume measurements in calibrated glass containers without contamination to any analytically significant degree. It was found to contribute to signal stability. The significant feature is the system's ability to compensate for interelemental effects and thus to eliminate interference phenomena. To date, it facilitates the direct determinations of nine elements.

EXPERIMENTAL

Decomposition Vessel. The construction materials used, the components, and the main features of the vessel for which a United States patent is pending are illustrated in Figures 1 and 2.

The Teflon–Teflon contact area, dimensionally optimized between the crucible's rim and a Teflon sealing disk, provides a simple and effective means of sealing when the metal cup with the inserted Teflon disk is manually screwed onto the crucible's metal body. The fact that quantitative decomposition is achieved within 30–40 minutes at a temperature as low as 110 °C suggests that the pressure build up within the crucible accounts for the speed with which disintegration of the compact silicate lattice takes place. The vessel does not undergo dimensional changes which would interfere with its reliable, continuous, and leak proof operation. The Teflon pouring spout, which is snapped to the peripheral sides of the crucible's rim, prevents any contact between the highly corrosive sample solution and the metallic parts, and facilitates quantitative transfer of the decomposed sample solution.

Instrument. Atomic absorption measurements were carried out on a Perkin-Elmer 303 unit with a Servo-riter Texas Instrument recorder attachment. The instrumental conditions are summarized in Table I.

Reagents. The standard stock solutions for calibration graphs were prepared from Johnson, Matthey & Co., Ltd. Specpure reagents. Their preparation is summarized in Table II. The standard stock solution for silicon was prepared by weighing 0.2139 gram silicon dioxide into a 50-ml polystyrene Spex vial, then 4 ml distilled water and 3.0 ml (48%) hydrofluoric acid were added. The vial was closed by a polyethylene cap, left standing until dissolution was completed, and cooled to ambient temperature. Then, 2.8 grams boric acid were added, its dissolution aided by a Teflon stirring rod. The solution was diluted to 40 ml, transferred into a 100-ml volumetric flask and diluted to mark, then stored in a polyethylene container. The standard stock solution for titanium was prepared by fusing titanium dioxide with potassium hydrogen sulfate and dissolving the melt in diluted sulfuric acid. All standard stock solutions were further diluted to conform to the concentration limits set forth in Table I.

Each of the standard solutions for silicon, iron, aluminum, titanium, vanadium, and magnesium used for calibration graphs or for bracketing contained 3.0 ml hydrofluoric acid (48%) and 2.8 grams boric acid per 100 ml. Standards for calcium contained 0.75 ml hydrofluoric acid (48%) and 0.70 grams boric acid per 100 ml. The standard solutions for sodium and potassium were diluted with distilled water only.

Boric acid was of 99.99+ certified purity. Other reagents were of certified analytical grade.

The following silicate materials, which were analyzed by the United States Geological Survey and for which established values are available, were used: granite G-1; diabase W-1; Philippinite P_0-300, a naturally occurring tektite and Australite 191 BU 2, a synthetic tektite prepared by the Corning Glass Co.

Procedure. The decomposition and reaction steps are carried out in a hood.

DECOMPOSITION. Transfer 50 mg (300 mg for vanadium) of a representative −150-mesh size sample portion into the Teflon decomposition vessel. Add 0.5 ml aqua regia as a wetting agent, making certain that the sample has become thoroughly wetted. Then add 3.0 ml hydrofluoric acid (48%) and close the vessel by hand tightening the screw cap containing the Teflon sealing disk. Place the crucible, without tilting, into a drying oven for 30–40 minutes at 110 °C. Then let cool to ambient temperature.

Table III. Results for Granite, Diabase, and Tektite Samples

Element, %	Sample	Granite G-1	Diabase W-1	Australite	Philippinite
Silicon	present[a]	33.84	24.52	35.40	33.56
	found	33.6(2)[b]	24.6(2)	35.3(3)	34.0(2)
	rel error	−0.71	+0.33	−0.30	−1.3
Iron	present	1.36	7.78	3.81	3.66
	found	1.32(3)	7.52(2)	3.83(2)	3.65(3)
	rel error	−3.0	−3.5	+0.52	−0.27
Aluminum	present	7.56	7.97	6.00	7.06
	found	7.67(2)	7.84	6.08	7.08(2)
	rel error	+1.4	−1.6	+1.3	+0.28
Titanium	present	0.156	0.650	0.300	0.456
	found	0.15	0.62	0.31	0.45
	rel error	−4.0	−4.8	+3.3	−1.3
Vanadium	present	0.0021	0.024	0.0007 0.0004	0.011
	found		0.023		0.0097
	rel error		−4.3		−13.4
Calcium	present	0.986	7.83	1.90	2.10
	found	0.98(3)	7.60	1.84	2.10
	rel error	−0.10	−3.0	−3.2	0.0
Magnesium	present	0.247	3.99	0.91	1.42
	found	0.24	3.84(2)	0.92	1.42
	rel error	−2.9	−3.9	+1.1	0.0
Sodium	present	2.45	1.54	0.786	0.987
	found	2.51(2)	1.56(3)	0.78(3)	1.00(3)
	rel error	+2.0	+1.3	−0.8	−1.4
Potassium	present	4.55	0.531	1.56	2.00
	found	4.48(4)	0.527(2)	1.54(5)	2.04(4)
	rel error	−1.6	−0.8	−1.3	+2.0

[a] Values established by the United States Geological Survey.
[b] Figures in brackets indicate the number of replicates from independent sample portions.

MATRIX REACTION AND DETERMINATION. Unscrew the lid, insert the spout, and transfer the decomposed sample solution with the aid of 4–6 ml distilled water from a wash bottle into a 50-ml polystyrene Spex vial. Take care to transfer quantitatively any precipitated metal fluorides which may have formed. The volume should not exceed 10 ml. Add 2.8 grams of boric acid and stir with a Teflon stirring rod to dissolve the boric acid and hasten the slightly exothermic reaction. Add 5–10 ml of distilled water. Any precipitated metal fluorides will dissolve at this stage and upon further dilution to about 40 ml a clear homogeneous sample solution results. Transfer to a 100-ml volumetric flask, adjust to volume, and store in a polyethylene container. The sample solution should not remain in the glass container for longer than two hours.

Determine all the constituents from this solution or, if necessary, dilute further with a glass pipet to conform to the concentration ranges given in Table I. Aspirate the sample solutions and the standards for silicon, aluminum, titanium, vanadium, calcium, and magnesium into a nitrous oxide–acetylene flame and for iron, potassium, and sodium into the air–acetylene flame. Calculate the concentrations from a calibration graph or by narrow range bracketing.

Run blank determinations on reagents used in the decomposition step when determining sodium and potassium.

RESULTS AND DISCUSSION

The method was tested by analyzing the four silicate rock standards which were treated as unknowns. The results for granite, diabase, and tektite samples summarized in Table III agree with established values to within 1.3% relative or better for the major constituents and 4.0% relative or better for the minor constituents. The high overall reliability achieved shows that this simplified method for silicate analysis provides satisfactory accuracy. Despite the fact that no separative steps were introduced, it will be noted that no interelemental intereferences for any of the determined elements were observed. The results for vanadium in the granite G-1 and Australite samples are missing because the aqueous matrix used did not provide sufficient sensitivity for the determinations. The results clearly indicate that the presence of the major refractory forming constituents, silicon, aluminum, and titanium, have no detrimental effects on the determinations of the alkaline earth and alkali metals, nor are interelemental effects, usually caused by the presence of the alkali metals, apparent. Furthermore, the quantitative recovery of silicon demonstrates the leak proof operation of the decomposition vessel for no volatilization losses of silicon occurred.

Information is scarce on the extent of interelemental interferences for some of the discussed elements in systems of similar complexity. Table III also shows the concentration limits within which each element was determined and also those concentration ranges which had no effect on the determination of other elements in the sample.

Although the decomposition method was used for silicates of the diabase and granite types, the applicability of the technique to the decomposition of silicious materials containing appreciably high concentrations of organic matter has not been evaluated.

It has been reported (*2*, *4*) that higher temperatures are needed to decompose some refractory compounds. The present vessel has been used up to 170°C for the decomposition of titanium diboride, niobium diboride, and silicon nitride (*19*) and should also be applicable to the decomposition of most of the refractory minerals associated with silicate rocks.

Matrix System (HBF_4–H_3BO_3–Ionic Constituents of a Silicate). A two-step exothermic reaction is involved in

(19) B. Bernas, unpublished data, NASA Tech Brief, 68-10104, March 1968.

the formation of fluoboric acid from hydrofluoric and boric acids:

$$H_3BO_3 + 3\ HF \rightleftharpoons HBF_3OH + 2\ H_2O \quad (1)$$

$$HBF_3OH + HF \rightleftharpoons HBF_4 + H_2O \quad (2)$$

Fluoboric acid hydrolyzes in a stepwise manner to hydroxyfluoborate ions: BF_3OH^-; $BF_2(OH)_2^-$; $BF(OH)_3^-$ and H_3BO_3, with hydrofluoric acid as a coproduct of each step (*20*, *21*). The HF–H_3BO_3–HBF_4 system has been extensively studied and the extent to which the parameters of the concentrations of hydrofluoric and boric acids, the dilution, and the temperature affect the rate and equilibrium conditions of hydrolysis, have been discussed (*22*). Hydrogen as well as calcium ions are known to contribute to the increase in the rate of hydrolysis, and other multivalent cations are assumed to behave in a similar manner (*23*). However, conflicting statements appear in the literature as to the rate of attack on glass. Therefore, it became necessary to investigate whether conditions could be established which would arrest or inhibit for a sufficiently long period of time the hydrolytic decomposition process of fluoboric acid to an analytically acceptable limit in presence of the ionic constituents of a silicate rock.

Figure 3 shows that conditions exist where the sample solution becomes contaminated by not more than 0.1 mg silicon at the end of two hours in the presence of 2.8 grams of boric acid per 100 ml. This is an excess of 119% or 0.246*M* of free boric acid over stoichiometric requirements of Reactions 1 and 2. Under these conditions, the concentration of fluoboric acid is 0.207*M*. The presence of the sample's constituents were not considered in these calculations. The presence of aqua regia (curve *b*) and the sample's constituents (curve *c*) also contribute to some extent to the suppression of the fluoboric acid hydrolysis as indicated by lower contamination effects.

It can thus be concluded that in the presence of an excess of boric acid the hydrolytic decomposition of fluoboric acid is suppressed for a period of at least two hours and during this period only analytically insignificant contamination occurs.

This new approach was found to be a satisfactory solution to problems of decomposition, dissolution of any insoluble fluoride salts which may have precipitated, and sample solution stability. The matrix was found to keep the sample solution from causing colloidal precipitation of silica, and no other type of precipitation was observed over a period of four weeks. The same was valid for the diluted standard solutions.

The system's positive environmental effects upon atomic absorption measurements can be summarized as follows: The acid matrix was found to eliminate the need for releasing, compensating, or complexing agents, or for closely matching the matrix composition to that of the unknown sample. The fact that no cations were introduced by reagents was found to contribute to signal stability of the atomic absorption measurements and to a decrease in instrumental background readings, a significant point when contemplating the use of this matrix for accurate trace elements determinations.

As a result of this effort, the analyst is brought closer to the use of single element standards in the analysis of complex materials.

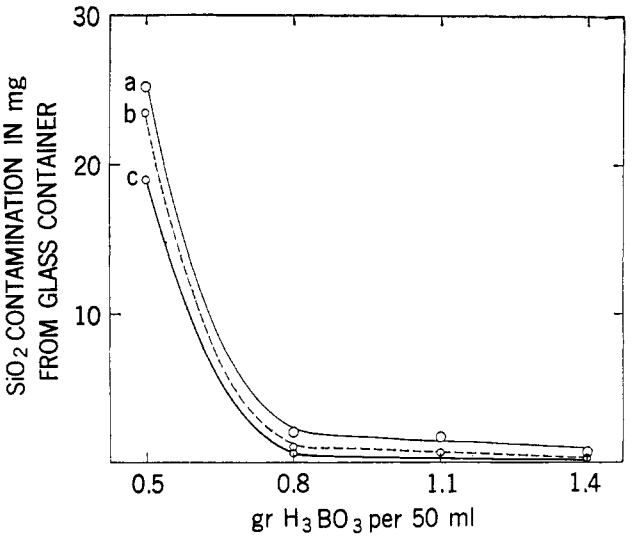

Figure 3. Influence of boric acid upon inhibition of fluoboric acid hydrolysis in the system (HBF_4–H_3BO_3–H^+–ionic constituents of silicate)

Experimental conditions: All test solutions contained 1.5 ml hydrofluoric acid (48%); volume, 50 ml; residence time, 2 hours; temperature, ambient; concentration of fluoboric acid, 0.207*M*; concentration of free boric acid, 0.246*M*.

Curve *a*: HBF_4–H_3BO_3–borosilicate glass
Curve *b*: HBF_4–H_3BO_3–0.25 ml aqua regia–borosilicate glass
Curve *c*: HBF_4–H_3BO_3–0.25 ml aqua regia–ionic species from 50 mg of a decomposed silicate–borosilicate glass

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