



GEOLOGICAL
SURVEY
OF
CANADA

DEPARTMENT OF ENERGY,
MINES AND RESOURCES

épreuve 11

This document was produced
by scanning the original publication.

Ce document est le produit d'une
numérisation par balayage
de la publication originale.

PAPER 67-37

ANALYSIS OF ROCKS AND MINERALS BY
ATOMIC ABSORPTION SPECTROSCOPY

Part 1. Determination of Magnesium,
Lithium, Zinc and Iron.

Sydney Abbey



GEOLOGICAL SURVEY
OF CANADA

PAPER 67-37

ANALYSIS OF ROCKS AND MINERALS BY
ATOMIC ABSORPTION SPECTROSCOPY

Part 1. Determination of Magnesium,
Lithium, Zinc and Iron.

Sydney Abbey

DEPARTMENT OF ENERGY, MINES AND RESOURCES

© Crown Copyrights reserved

Available by mail from the Queen's Printer, Ottawa,
from the Geological Survey of Canada,
601 Booth St., Ottawa
and at the following Canadian Government bookshops:

OTTAWA

Daly Building, Corner Mackenzie and Rideau

TORONTO

221 Yonge Street

MONTREAL

Æterna-Vie Building, 1182 St. Catherine St. West

WINNIPEG

Mall Center Bldg., 499 Portage Avenue

VANCOUVER

657 Granville Street

or through your bookseller

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

Price 75 cents Cat. No. M44-67-37

Price subject to change without notice

ROGER DUHAMEL, F.R.S.C.

Queen's Printer and Controller of Stationery
Ottawa, Canada

1967

CONTENTS

	Page
Abstract	v
Introduction	1
Principles of atomic absorption	1
Geological applications	3
Apparatus	4
Determinations of magnesium	4
Interferences	5
Atomic absorption measurements	6
Results and conclusions	7
Determination of lithium	7
Decomposition of the sample	8
Interferences	9
Atomic absorption technique	10
Results and conclusions	11
Determination of zinc	12
Decomposition of the sample	12
Effect of sample composition	12
Atomic absorption technique	13
Results and conclusions	14
High precision analysis-determination of magnesium and iron	14
Determination of iron	15
Determination of iron and magnesium in the same solution ...	16
Improvement in precision and accuracy	16
Results	17
Conclusions	18
Acknowledgments	19
References	19
Appendix I Operating procedure for magnesium determination	25
II Operating procedure for lithium determination	28
III Operating procedure for zinc determination	32
IV Operating procedure for determination of magnesium and iron in the same solution	34
Table I Comparison between atomic absorption and gravimetric results for magnesium	7
II Comparison between atomic absorption and other methods for lithium	11

	Page
Table III Comparison of results of determination of total iron by atomic absorption and titration	17
IV Recovery of magnesium and iron in synthetic biotite	18
V Results by atomic absorption and other methods	18

ABSTRACT

Following a brief description of the principles of atomic absorption spectroscopy, methods are described for determining magnesium and iron as major constituents, and zinc and lithium as minor constituents, in rocks and minerals. These methods not only serve to illustrate the potential sensitivity, precision and simplicity of this technique, but also to illustrate unexpected interferences and other limitations.

ANALYSIS OF ROCKS AND MINERALS BY ATOMIC ABSORPTION SPECTROSCOPY

Part 1 - Determination of magnesium, lithium, zinc and iron.

INTRODUCTION

Atomic absorption spectroscopy is one of the newest analytical techniques, the first report in the literature having appeared as recently as 1955 (Walsh, 1955). This technique was first considered for use in the Geological Survey of Canada as early as 1960, but commercial instrumentation was not very well developed at that time. Since then, at least ten different manufacturers have put atomic absorption equipment on the market - three American, three British, one German, one Italian, one Japanese and one Australian. At least three manufacturers offer models in more than one price range. So rapid has been the growth of the use of atomic absorption that it was estimated in the summer of 1966 (Kerber, 1966) that over 1,500 instruments were already in use in North America alone, over 90 per cent of which had been purchased in the preceding five years.

Principles of Atomic Absorption

Details of the principles of atomic absorption spectroscopy have been described in a multitude of references. The following outline gives only a general idea of the method, and shows how it differs from other forms of optical spectroscopy used in analyzing geological materials.

If a solution is sprayed into a flame, a portion of the solute is reduced to free atoms of its constituent elements. Some of those atoms will be further "excited" by the heat of the flame to the point where they will emit radiation of characteristic wavelengths - as in the familiar flame test for sodium. The vast majority of the free atoms are not excited by the flame, and are said to be in the "ground state". Such atoms are capable of absorbing incident energy at certain discrete wavelengths, known as "resonant wavelengths". Thus if light of a resonant wavelength of a particular element is passed through a flame into which a solution of a compound of that element is being sprayed, a fraction of that light will be absorbed by the ground state atoms of the element. Measurement of the fraction of light absorbed is the basis of atomic absorption spectroscopy.

In practice, the incident light is generally produced by a "hollow cathode" lamp, designed to emit the characteristic spectrum lines (which include the resonant wavelengths) of a particular element. The flame should

Manuscript received April 19, 1967.

be hot enough to decompose compounds of the element, thus providing free ground state atoms. However, the flame temperature should be such as to minimize excitation of the atoms to the point where a significant proportion of them will emit light of the same wavelength as the resonant line. The resonant line, originating in the hollow cathode lamp and reduced in intensity by the flame, is isolated by means of a prism or grating monochromator, and its intensity is measured by a photomultiplier tube.

In the ideal case, the concentration of the absorbing element is related to the fraction of light absorbed by Beer's Law:

$$c = k \log \frac{I_0}{I}$$

where c is the desired concentration,

I_0 is the intensity of incident light,

I is the intensity of transmitted light,

and k is a constant

Among commercially available instruments, points of difference may be found in the type of source lamps used, the design of the burner and sample aspirating system, the optical arrangement (including monochromator design, wavelength range, etc.) and the read-out system (meter, null-balance, digital, recorder, etc.).

Flame photometry is closely related to atomic absorption, and it might more properly be termed "atomic emission". In emission flame photometry, the intensity measured is that of the light emitted by excited atoms in the flame. Selectivity between elements in the sample depends mainly on the monochromator, which must discriminate between the spectrum lines of all of the elements in the flame. In atomic absorption, the source lamp provides the major basis of selectivity. An interrupter or pulsed power supply in the source, to which the alternating current detector circuit is tuned, eliminates the effect of continuous radiation from the flame. Thus the detection system deals with a relatively simple spectrum, and hence atomic absorption is much less subject to inter-element interferences than is emission flame photometry. Most of the commercially available atomic absorption instruments can be converted for use in flame photometry, if necessary.

The emission spectrograph operates on the same principle as the flame photometer. It differs from the latter mainly in two practical features. Firstly, the spectrograph can be used with solid samples, while both the flame photometer and the atomic absorption spectrophotometer can analyze only solutions. Secondly, the spectrograph, whether direct-reading or

photographic, can determine numerous elements simultaneously, whereas the other two techniques normally can handle only one at a time. However, at least one multi-channel instrument is commercially available, usable in both flame photometry and atomic absorption. In general, the spectrograph offers the advantage of speed and sensitivity, whereas atomic absorption is more precise, less expensive and less susceptible to interferences.

The ordinary spectrophotometer or colorimeter is also related to the atomic absorption instrument in that it also measures the sample's absorption of incident light. However, the light source is then a continuous spectrum and the absorption spectrum is characterized by broad molecular bands rather than sharp lines. Selectivity depends mainly on the chemical treatment of the sample before photometry. In many cases where ordinary spectrophotometry requires isolation of the desired element by means of chemical separations, atomic absorption measurements can be made after little or no chemical treatment of the sample solution.

Atomic absorption is a versatile and useful analytical tool which has many advantages over other spectroscopic and chemical techniques, but it also has limitations. It will likely replace other techniques in many applications, but by no means in all.

GEOLOGICAL APPLICATIONS

Most of the published geological applications of atomic absorption spectroscopy have been concerned with the determination of base metals in ores, natural waters and mining and metallurgical process solutions (Belt, 1964a; Farrar, 1965; Fixman and Boughton, 1966). Relatively few reports have appeared on the determination of major and trace constituents in silicate rocks (Althaus, 1966; Belt, 1964b; Slavin, 1965; Trent and Slavin, 1964b). It is known, however, that several laboratories are actively developing schemes for complete silicate rock analysis in which atomic absorption plays a major role (Althaus, 1966); (McKay, 1966; Muysson, 1966; Shapiro, 1966, personal communications).

The four applications described below cover a range of analytical problems and illustrate some of the complexities encountered - not all of which were expected. Most of the work was done on aluminosilicates, and therefore sample decomposition was a problem. Many silicates leave insoluble residues, regardless of the technique used in dissolving the sample. In most cases it is necessary to establish whether or not the residue contains a significant portion of the desired element, and hence whether or not it is worthwhile to try to bring the residue into solution.

Apparatus

All of the work was done with a Techtron Model AA-3 Atomic Absorption Spectrophotometer, equipped with Atomic Spectral Lamps Pty., Ltd., hollow cathode lamps, a flat-topped 10-cm slot laminar flow burner, an R-136 photo-multiplier tube and a scale expander unit. A Varian G-10 Recorder was used in some of this work. Other types of equipment would probably be equally effective, with little or no modification to the methods.

Compressed air and acetylene were used throughout the work. Air pressure was maintained at 18 lb./sq. in., while acetylene flow rate was varied to attain the desired flame conditions.

Instrumental operating parameters were based on the manufacturer's instructions, and required few changes.

DETERMINATION OF MAGNESIUM

Magnesium determination presents problems in most schemes of silicate rock analysis. In the classical gravimetric scheme, magnesium is determined as the pyrophosphate only after most of the other major components have been separated. Thus all errors in the separation of the other elements tend to accumulate on this "end of the road" element. These errors become even worse where either calcium or magnesium greatly outweighs the other.

In most "rapid chemical" analytical schemes, magnesium is determined by the difference between two EDTA titrations: one for magnesium plus calcium, the other for calcium alone. Again, errors multiply as the ratio of Ca/Mg increases. At the Geological Survey of Canada, this problem was solved, in part, by the introduction of the "magon sulphonate" colorimetric method (Abbey and Maxwell, 1962) for small amounts of magnesium. However, that method did not eliminate the need to separate the R_2O_3 group, an operation which requires some compromise between speed and accuracy.

In the X-ray fluorescence scheme now in use, magnesium is the lightest element detectable, and results become less reliable as magnesium concentration diminishes.

Magnesium determination is one of the most common applications of atomic absorption spectroscopy. In this work, it was decided to apply it to an aliquot of the sample solution prepared for the chemical determination of sodium and phosphorus, two elements which cannot be determined by X-ray fluorescence under present conditions. The solution is prepared by digesting

the sample with HF and HCl, evaporating to dryness, and again evaporating to dryness after the addition of HCl alone. The residue is redissolved by the addition of a few drops of HCl and a small volume of water, and then made up to volume in a volumetric flask.

Interferences

As expected from perusal of the literature, the only interference observed was that caused by aluminum. In its usual concentrations in silicate rocks, aluminum substantially reduces the magnesium absorption.

This type of interference, referred to as "chemical", is one of those carried over to atomic absorption from flame emission photometry. The aluminate, silicate, sulphate and phosphate anions have such an effect on magnesium and the alkaline earths. It is believed to be the result of their forming compounds which are not completely decomposed in the flame, thus decreasing the concentration of free atoms of the metals.

In silicate rock analysis, silica is eliminated by volatilization as the fluoride, in decomposing the sample with HF. Concentrations of phosphate and sulphate in the final sample solution are generally too low to be significant - provided sulphuric acid is not used in the decomposition. The effect of aluminate is generally overcome by the addition of a "releasing agent" - a much higher concentration of another cation which preferentially combines with the anion, thus releasing the metal under study.

Lanthanum has become a favourite releasing agent for magnesium and the alkaline earths. Addition of "one per cent lanthanum" is used in several atomic absorption schemes for these and other elements in silicate rocks (e.g. Trent and Slavin, 1964a). Strontium has been used by others (David, 1960), and still others suggested the addition of both calcium and 8-hydroxyquinoline to release magnesium (Rubeska and Moldan, 1965).

An entirely different approach to the elimination of aluminum interference in the magnesium determination involves the use of a higher temperature flame (Nesbitt, 1966). A mixture of acetylene and nitrous oxide provides a combination of flame temperature and burning velocity that is suitable for use in a pre-mix, laminar flow burner. Use of such a flame serves to release free atoms of aluminum and other elements which form refractory compounds, and would otherwise not be amenable to determination by atomic absorption (Willis, 1965). Similarly, the temperature of the acetylene-nitrous oxide flame is sufficient to decompose magnesium aluminate, thus eliminating the aluminum interference in the magnesium determination. However, there are certain disadvantages in the use of that flame, among them being enhancement of "ionization interference" (see below in description of lithium method).

The calcium-hydroxyquinoline combination was tried in the present work, but results were not encouraging. The lanthanum addition was not tried, because it would have meant the use of large quantities of a relatively expensive reagent, and because it would have raised the total salt concentration of the sample solution to an undesirably high level - one per cent lanthanum corresponds to nearly two per cent lanthanum chloride.

Tests were run to establish the quantity of strontium required to "release" magnesium from the effect of aluminum. It was found that a strontium concentration of 500 ppm in 0.12N HCl was sufficient to release 0 to 2 ppm of magnesium from the effect of as much as 20 ppm of aluminum. Thus, in an aliquot containing 10 mg of sample, 0 to 2 per cent Mg (i. e. 0.0 to 3.3 per cent MgO) can be determined in the presence of as much as 38 per cent Al_2O_3 . If smaller aliquots are used - such as where the MgO content of the sample exceeds 3.3 per cent - even higher alumina contents can be tolerated in the sample.

Atomic Absorption Measurements

Operating parameters were essentially those recommended by the manufacturer. The magnesium hollow cathode lamp was operated at a current of 4 milliamperes. Acetylene flow was adjusted to provide a slightly reducing atmosphere in the flame, as shown by the presence of a barely visible luminous area immediately above the "inner cone" of the flame. Vertical adjustment of the burner was set in a position that permitted the light beam to pass through the luminous area. (Actually, slight changes in burner parameters have comparatively little effect on results, provided samples and standards are aspirated under identical conditions.)

Under these conditions, absorption sensitivity for magnesium is excessively high. Sensitivity can be diminished by reducing the length of the flame through which the beam is passed, by rotating the burner head through a small angle. This is done with a standard solution containing 1 ppm Mg in the flame. If the burner angle is set to give a transmittance reading between 45 and 50 per cent for that standard, convenient readings may be made in the range from 0 to 2 ppm Mg.

In this method, as in others, a rough preliminary measurement is used to determine the concentration of standard solution that should be used for the analysis of each sample. In the final analysis, at least two readings are taken for each sample solution, each being preceded and followed by a reading on a standard solution of similar concentration. "Background" or "baseline" readings are taken, with water in the flame, between all other readings. Beer's Law was found to apply in all measurements made with magnesium in the range of 0-2 ppm in solution.

Details of the operating procedure are given in Appendix I.

Results and Conclusion

In Table I, results obtained by the proposed method are compared with those obtained by gravimetric determination as the pyrophosphate for a number of samples. For all of the samples containing less than 15 per cent MgO, results are in satisfactory agreement, although most of the atomic absorption values show a slight negative bias. With higher magnesium values, the negative bias is greater, possibly because of the large dilution factor.

Table I

Comparison Between Atomic Absorption and
Gravimetric Results for Magnesium

<u>Sample No.</u>	<u>MgO found (per cent)</u>	
	<u>AAS</u>	<u>Gravimetric</u>
14-65	0.74	0.75
19-65	0.96	0.98
15-65	1.47	1.52
18-65	3.45	3.45
A-75	6.48	6.51
A-13	10.45	10.42
A-62	16.4	16.7
1727-64	23.1	23.8
B-213	33.7	34.2
1090-64	35.2	35.6
16-65	43.6	44.0
17-65	49.5	50.2

The procedure outlined in Appendix I can give good results for MgO values under 15 per cent, in the rock types tested (granite, granodiorite, andesite, basalt, diabase, amphibolite). (For precise determination of higher magnesium contents, see Section on high precision analysis.)

DETERMINATION OF LITHIUM

Lithium, one of the "rarer" alkali metals, is seldom determined in the general analysis of geological materials. In classical analytical schemes, lithium generally follows sodium, and would indeed be reported as sodium in

the J. Lawrence Smith method. Chemical separation of lithium from sodium is tedious, slow, and not very quantitative. Thus it was not until the introduction of flame photometry that it was discovered that one of the standard samples issued by the U.S. National Bureau of Standards actually contained less sodium than reported earlier, the difference being due to the presence of lithium.

Lithium can be determined by flame photometry with good precision and fair sensitivity. Accuracy, as with many other flame photometric methods, depends largely on the means used to overcome interferences. In the Geological Survey of Canada laboratories, lithium has been determined on the Beckman DU Flame Spectrophotometer (with Spectral Energy Recording Adaptor) down to a concentration of 0.5 ppm in a solution containing 500 mg of sample per 100 ml, corresponding to 0.01 per cent (or 100 ppm) in the sample. This sensitivity could probably be improved somewhat by varying instrumental parameters. A more concentrated sample solution would be undesirable, because of the danger of clogging the capillary of the aspirator-burner. Because of possible interferences, it is advisable at first to determine the other components of the sample solution, in order that appropriate quantities of those elements may be added to the standard solutions. Preconcentration of the alkali metals as a group could serve both to minimize interferences and to improve sensitivity. However, such steps are rather lengthy, and there is some evidence that one such (Abbey and Maxwell, 1960) does not always give quantitative recovery of lithium.

There is very little in the literature on the determination of lithium by atomic absorption, and even less on application to geological materials. In our work, lithium determinations were required in a number of rock samples of widely varying composition, in which the concentration of that element was expected to be well below 100 ppm.

Decomposition of the Sample

In the determination of magnesium, the method of sample decomposition was governed by the fact that the determination was to be integrated with an existing analytical scheme. The HF-HCl decomposition, as used for magnesium (and sodium and phosphorus), leaves appreciable residual fluoride ion in solution, but the small aliquot used for the determination contains so little fluoride that there is no adverse effect. For the lithium determination, it was decided to use a more thorough method, one that would be applicable to the determination of many metals. More effective removal of fluoride requires fuming with a higher-boiling acid. Sulphuric acid was not favoured because of its known interference in the determination of several metals. Althaus (1966) has studied the effects of sulphuric acid in some detail, and has overcome some of those effects by rigorous control of the quantity of acid

used. However, his tests do not distinguish between the effect of free sulphuric acid and that of the sulphate ion. He makes no mention of perchloric acid, an obvious alternative.

The chemical procedure adopted in this work is one already in use for flame photometry (Abbey, 1965). The sample is digested with a mixture of hydrofluoric, nitric and perchloric acids, the excess acids being eliminated by fuming to dryness. The dry perchlorates are then redissolved in water containing a controlled quantity of HCl. Many samples leave some insoluble residue from this treatment, but only with one sample, a tungsten-bearing quartz vein material, was any lithium found in this residue and an unexpected effect was also observed in that case. The insoluble residue was fused with sodium carbonate, leached with water, and the leachate filtered. The residue on the filter paper was then dissolved in HCl and analyzed separately from the carbonate-bearing leachate. Chemical properties would suggest that the lithium would be found mainly in the carbonate solution, but tests revealed that most of it was in the HCl solution of the "carbonate-insoluble" residue.

Interferences

A common interference in both flame photometry and atomic absorption is the "ionization effect". In a flame containing an element such as lithium, an equilibrium exists, governing the relative proportions of the atoms of that element in the ground state and at the several possible levels of excitation. The presence of another easily-excited element in the same flame would upset the equilibrium by a redistribution of the excitation energy between the two elements. In atomic absorption, this would mean a greater population of ground-state atoms, and hence a stronger absorption signal for the element of interest when the interfering element is present.

Ionization interference from the relatively high concentrations of sodium and potassium might be expected in determining traces of lithium in rocks. In this work, however, tests revealed that the equivalent of 5 per cent sodium or potassium in a rock had no effect on the absorption signal of the equivalent of 50 ppm of lithium in the rock.

The concentration of free acid in the sample solution was found to have a marked effect on the lithium absorption signal. The normal working acidity was fixed at about 0.5 N in HCl. An increase in acidity to 1.0 N reduced the absorbance by about 10 per cent; a further increase to 3.0 N reduced the absorbance by 50 per cent.

Several actual "standard samples" (G-1, W-1 and the two standards of the Canadian Association for Applied Spectroscopy) were then put in solution, and analyzed by comparison with pure lithium standard solutions, all being adjusted to a uniform acidity. Results were persistently low. It was

then suspected that the total salt concentration in the sample solution might be responsible for the depressant effect, because there appeared to be a relationship between the magnitude of the negative bias and the overall composition of the sample. Assuming the compositions of the six new United States Geological Survey reference samples (granite, granodiorite, andesite, basalt, peridotite and dunite) to be a fair cross-section of silicate rock samples, calculations were made of the weight of perchlorate salts that would be obtained from the decomposition of one gram of each of those rocks. This weight was found to vary from about 1.5 g for granite to about 3 g for dunite.

Using pure salts (assumed to be free of lithium), three sets of synthetic mixtures were prepared, corresponding to the compositions of solutions resulting from the decomposition of the granite (G-2), the dunite (DTS-1) and of a mean of all six of the new United States Geological Survey reference samples. Within each set, the lithium concentration in solution was varied from 0.0 to 2.5 ppm (corresponding to 0 to 125 ppm lithium in the original rock), the normal working range of the method. Each of the synthetic solutions was then analyzed for lithium content, by comparison with pure lithium standard solutions.

Results of these determinations were plotted as "apparent lithium found" against "lithium added". If there were no matrix effect, the resulting straight-line graphs would all have slopes of unity. The slopes actually observed were 0.90 for the granite-like set, 0.68 for the dunite-like set, and 0.74 for the "mean of six" set. These results suggest that the absorption signal is weakened with increasing total salt concentration in the sample solution, but that the depression is not directly proportional to the salt concentration. It may be that this effect is due to the increased viscosity of the more concentrated solutions, resulting in a reduced aspiration rate. However, observations with zinc (see below) cast some doubt on such an assumption.

For samples of unknown composition, it is necessary to run "standard addition" tests to establish the magnitude of the matrix depressant effect. Where large numbers of samples of similar composition are to be analyzed, a correction factor, established by doing standard addition tests on the first few samples, may then be applied to the remainder of the samples.

Atomic Absorption Technique

The label on the lithium hollow cathode lamp specified a maximum current of 6 milliamperes, somewhat lower than the 8 milliampere current recommended for lithium in the instruction manual for the instrument. After some experiments with varying currents, 5.5 milliamperes was finally chosen for the best combination of sensitivity and stability.

Absorption sensitivity of lithium was found to be significantly affected by changes in air- and fuel-flow rates in the flame. In the procedure adopted, while a lithium standard solution is being aspirated, air pressure is held at 18 lb./sq. in. and acetylene flow is varied, until conditions of maximum absorption are attained.

Lithium readings were found to be less stable than those for magnesium, but adequate stability can be obtained for trace analysis. Beer's Law is obeyed over the range of 0.0 to 2.5 ppm of Li in solution.

Details of the operating procedure are given in Appendix II.

Results and Conclusions

Lithium was determined on several "standard" samples. Results are given in Table II. Unfortunately, the actual compositions of the "standards" are not well established, so it is not possible to estimate the accuracy of this method.

Table II

Comparison Between Atomic Absorption and Other Methods for Lithium

Sample	Li found, ppm		
	This Method	Other Methods*	
		Range	"Recommended"
G-1	24	19-30	24
W-1	18	8-20	12
CAAS Syenite	109	80-200	126
CAAS Sulphide	14	10	10

* (Ahrens and Fleischer, 1960; Fleischer and Stevens, 1962; Webber, 1961, 1965).

The procedure outlined in Appendix II can be applied to many types of rocks, containing 5 to 125 ppm of lithium. For higher lithium contents, a more dilute sample solution is used, and the matrix effect is greatly diminished. Thus results on a lithium-bearing mica, obtained by atomic absorption without matrix correction, were in good agreement with those obtained by flame photometry.

DETERMINATION OF ZINC

Traces of zinc in rocks are generally determined colorimetrically by means of a reagent such as dithizone (Sandell, 1959). Dithizone is a group reagent for many of the heavy metals, masking agents and control of pH being required to make its reactions specific for a particular element. Further, the metal dithizonates must be extracted with a water-immiscible solvent before photometry. On the other hand, atomic absorption is particularly sensitive for zinc, measurements can be made in aqueous solution, and few interferences have been reported (Belt, 1964b). In our work, zinc determinations were required in a number of rocks of varying composition.

Decomposition of the Sample

The hydrofluoric-nitric-perchloric acid decomposition, as used for the lithium determination, was also applied in the determination of zinc. In the rock types tested, over 95 per cent of the zinc in each sample was found in the solution resulting from the acid treatment.

Where a small amount of zinc was actually detectable in the residue from the acid treatment, an unexpected effect was again observed - similar to that found with lithium. After the residue had been fused with sodium carbonate, the melt was leached with water and filtered. The residue from the filtration was dissolved in HCl, and the two solutions derived from the fusion were analyzed separately for zinc. All of the zinc was found in the HCl solution, none in the carbonate solution - again the opposite effect from what might be expected from chemical properties.

Effect of Sample Composition

On the basis of published data on the zinc determination, no interference was expected from the major components of the samples. As a check, "standard-addition" runs were done, as for lithium, using synthetic mixtures approximating the compositions of granite and dunite. Similar tests were made on "standard additions" to six representative samples (andesite, rhyolite, sericite schist, argillite, peridotite and aplite).

Plots of "apparent zinc found" against actual zinc added were straight lines in all cases, with slopes that departed from unity by no more than 3 per cent.

To determine the effect of varied acidity, aliquots of the six sample solutions were analyzed after the addition of varying quantities of HCl. Results showed no noticeable difference in zinc absorption between 0.25N and 1.5N in HCl.

The absence of matrix effects was not entirely unexpected, because the zinc content in most samples is higher, and the sensitivity of the method is superior, than is the case with lithium. The sample solution for zinc may therefore be less concentrated than that for lithium, and the corresponding concentration of salts lower. However, the absence of effects from variations in acidity was surprising.

The chemical preparation for zinc determination is simpler than that for lithium on three counts: (a) the insoluble residue from the acid decomposition may generally be ignored; (b) the filtrate from the separation of that residue need not be evaporated to dryness and redissolved in a controlled quantity of HCl; and (c) no additional manipulation is necessary to correct for matrix effects.

Atomic Absorption Technique

Operating parameters for the determination of zinc as given in the instruction manual - hollow cathode lamp current, slit width, etc. - were found to be satisfactory.

Absorption sensitivity is little affected by changes in flame composition. However, the absorption by the flame itself is appreciable, and is affected by variation in the air-acetylene ratio. To minimize that effect, it was decided to vary the acetylene flow, with water aspirating and air pressure held at 18 lb./sq. in. until conditions of maximum transmission are attained. The flame then transmits between 60 and 70 per cent of the incident light. This effect was not unexpected because the zinc line used is in the deep ultraviolet (2138 angstroms).

Stability of zinc readings is comparable to that with lithium. Beer's Law is obeyed only up to a concentration of about 1.5 ppm of Zn in solution. However, little error is introduced in analyzing solutions containing up to 2.5 ppm with the assumption that Beer's Law is obeyed, provided the zinc contents of sample and standard solutions are sufficiently close together.

Details of the operating procedure are given in Appendix III.

Results and Conclusions

No "standard samples" have been analyzed for zinc, mainly because of our limited supply of such material, and because of the uncertainty in the "recommended" zinc values.

Zinc may be determined in rock samples containing 5-250 ppm of that element. The method is extraordinarily free from interferences, either from other elements in the sample or from variations in free acidity. Almost all of the zinc in most of the samples tested can be brought into solution by treatment with hydrofluoric, nitric and perchloric acids, thus further simplifying the method.

HIGH PRECISION ANALYSIS - DETERMINATION OF MAGNESIUM AND IRON

Atomic absorption is generally regarded as highly sensitive, hence its widespread application in trace analysis. For elements such as magnesium and zinc, the combination of sensitivity and selectivity possible with atomic absorption gives it a decided advantage over many other techniques. With some elements, however, sensitivity is not as high as might be supposed - possibly because of the custom of expressing concentration in terms of "parts per million". To the casual reader, 'parts per million of solution' may be confused with 'parts per million of the sample'. Such confusion may be due, in part, to the fact that many applications of atomic absorption have occurred in fields where the sample is itself a liquid - e.g. body fluids, chemical process solutions, etc. With solid samples, such as rocks and minerals, if one gram of sample is brought into solution, it must be diluted, in general, to a volume of at least 50 ml. One part per million of a given element in such a solution would then correspond to 50 ppm in the solid sample.

High precision is another potentially useful characteristic of atomic absorption, as is suggested by the first six results in Table I. An opportunity to examine this aspect presented itself in connection with a study of the mutual substitution of magnesium and iron in biotites, involving as little as 50 to 100 mg of material for some of the samples. Atomic absorption readily suggested itself for magnesium determination, and the possibility of determining iron as well in the same solution appeared worthy of study. The problem resolved itself into three phases: (a) determination of iron, (b) conditions for determining iron and magnesium in the same solution, and (c) how to improve precision and accuracy.

Determination of Iron

Twelve samples of biotite were put in solution by the hydrofluoric-nitric-perchloric acid treatment (all decomposed completely). Atomic absorption was used to determine iron in aliquots of the sample solutions, by comparison with standard iron solutions to which no other elements had been added - i. e. assuming no matrix effects. Other aliquots of the same solutions were analyzed for iron by reduction with stannous chloride and potentiometric titration with dichromate. The atomic absorption results showed a positive bias, relative to the titrimetric values, of about 12 per cent of the amount present.

Similar tests on the new United States Geological Survey reference samples gave atomic absorption values for iron showing a positive bias of one to six per cent of the amount present. Earlier published work on iron determination had reported either no apparent interferences, negative bias, or relatively erratic results (Sprague, 1963; Trent and Slavin, 1964a, 1964b). A study of the general composition of the samples involved in this work indicated a possible correlation between the positive bias for iron and the concentrations of sodium, potassium and calcium in the samples. Thus biotites, containing about 7 per cent potassium, showed a 12 per cent bias; basalt with about 3 per cent sodium, 1 per cent potassium and 5 per cent calcium showed a 6 per cent bias; and dunite, containing less than 1 per cent of sodium, potassium and calcium combined, showed a bias of only 1 per cent.

The positive bias for iron, apparently related to the presence of easily ionized metals, suggested that an "ionization effect" was responsible. Such a conclusion, however, does not appear justified in the case of iron, an element less readily ionized than lithium, which showed no ionization interference from very much higher concentrations of the other alkali metals. Ionization interference, where it does occur, can be eliminated by adding a large excess of an easily ionized metal to both sample and standard solutions, using the radiation buffer principle as in flame photometry. It was then decided to attempt to use strontium, as an "ionization buffer" for iron, because it was already in use as a "releasing agent" for magnesium. It was found that the presence of 500 ppm of Sr in both sample and standard solutions effectively eliminated the positive bias in the iron results.

An attempt was also made to determine iron by means of a "high intensity" hollow-cathode lamp (Sullivan and Walsh, 1965). In such lamps, the line spectrum of the desired element is greatly enhanced, relative to the spectra of the inert filler gases and the continuous background. Readings with such a lamp proved to be too erratic for high-precision use, although there was some evidence that the positive bias effect was not present.

To sum up, iron apparently behaves as though it were subject to ionization interference, and the interference is eliminated by the usual remedy for ionization effects, although this explanation is improbable, according

to accepted theory. Further, the apparent absence of the interference when the high-intensity lamp was used suggests that some other explanation is necessary.

Operating conditions for iron were as recommended in the instruction manual. Sensitivity was found to be better than expected from the manual, and relatively independent of flame conditions, but the acetylene flow was adjusted to the maximum possible without the appearance of a luminous area, with air pressure maintained at 18 lb./sq. in.

Determination of Iron and Magnesium in the Same Solution

With strontium serving the twofold purpose of eliminating different interferences for iron and magnesium, it would be convenient to be able to determine the two elements in one solution, representing a fixed dilution of the sample. Using the most sensitive iron line, the working range is about 0-10 ppm of Fe in solution, corresponding to 0-28 per cent Fe_2O_3 (total iron calculated as Fe_2O_3) for a 5-mg sample aliquot in a 100-ml volume, a convenient range for biotites. At that dilution, however, the existing magnesium procedure, covering 0-2 ppm of Mg would correspond to 0.0-6.6 per cent MgO in the sample, which is low for biotites. By rotating the burner head through a slightly larger angle it was possible to extend the magnesium range to 0-6 ppm in solution, or 0-20 per cent MgO in the sample. Simple tests revealed that Beer's Law is still valid at the higher magnesium concentrations, and that the 500 ppm of Sr present is adequate to release the higher magnesium content from the masking effect of the amount of aluminum likely to be present in biotites.

Improvement in Precision and Accuracy

Two points of interest emerged from an examination of means for improving precision and accuracy.

Firstly, the atomizer and burner assembly must be dismantled and cleaned at frequent intervals. Although the system is normally flushed with water between all readings and at the end of each run, there are several locations where acidic residues can accumulate, causing corrosion, possible restriction of sample flow, and possible cross-contamination.

Secondly, aspiration rates must be uniform. In normal operation, solutions are aspirated by immersing the flexible capillary tube of the aspirator in the sample solution, generally contained in a 100-ml volumetric flask. From a full flask, this involves raising the sample solution through a 5-cm head. For a nearly empty flask, this head becomes about 15 cm. Tests revealed that the difference in absorbance reading for the same solution under the two conditions amounted to about one per cent - a small but

significant difference for precision work. To eliminate this effect, samples are aspirated from graduated 20-ml beakers. The beakers are filled to about one or two millimetres above the 15-ml mark, and are refilled when the level goes below the 10-ml mark. By setting the beaker on a block when taking readings, it is possible to maintain a head between solution level and atomizer which remains between 9 and 10 cm.

Details of the operating procedure are given in Appendix IV.

Results

Table III shows results for iron compared with titrimetric values, the two determinations being done on separate aliquots of the same solution of each sample. Although the agreement is not as good as required for accurate work, it is good enough for most practical purposes. As a further check, both iron and magnesium were determined on two synthetic solutions, approximating the compositions of two biotites. Results (Table IV) are calculated as percentage of the relevant oxide in the hypothetical synthetic sample. Finally, the six new United States Geological Survey reference samples were analyzed for both elements. In the case of the peridotite and the dunite, the preponderance of magnesium over iron made it impractical to determine both at the same sample dilution. Further, the presence of a small amount of chromite in those two samples required a peroxide sinter of the insoluble residue from the hydrofluoric-nitric-perchloric treatment to ensure full recovery of iron. Results are given in Table V.

Table III

Comparison of Results of Determination of Total Iron
by Atomic Absorption and Titration

Sample	<u>Total Iron Found (expressed as Fe₂O₃), per cent</u>	
<u>No.</u>	<u>AA</u>	<u>Titration</u>
1	22.28	22.36
2	23.04	22.71
3	20.59	20.84
4	17.68	17.85
5	19.79	20.36
6	19.73	19.45
7	18.27	18.49
8	19.21	19.41
9	21.62	21.68
10	19.62	19.81
11	23.73	23.98
12	20.73	20.72

Table IV

Recovery of Magnesium and Iron in "Synthetic Biotite"

Sample No.	<u>MgO, per cent</u>		<u>Fe₂O₃, per cent</u>	
	<u>Taken</u>	<u>Found</u>	<u>Taken</u>	<u>Found</u>
A	8.73	8.80	21.45	21.60
B	3.48	3.47	28.60	28.49

Conclusions

Magnesium and iron can be determined in rocks and minerals by atomic absorption, with a precision and accuracy approaching that of classical analysis, and very much more rapidly. Strontium addition serves to eliminate interference effects with both metals. For samples in which magnesium is not too preponderant, the two metals can be determined on the same dilution of the sample solution. Because the aliquot used normally contains 5 mg or less of the sample, the sample size required for analysis is limited mainly by the accuracy with which the original material can be weighed.

Table V

Results by Atomic Absorption and Other Methods
(U. S. G. S. rocks)

Sample No.	<u>MgO found, per cent</u>		<u>Fe₂O₃ found, per cent</u>		
	<u>AA</u>	<u>Gravimetric</u>	<u>AA</u>	<u>Titrimetric</u>	<u>Colorimetric</u>
14-65	0.73	0.75	2.65	2.63	2.70
15-65	1.53	1.70 1.54 1.52	6.69	6.49 6.52 6.71	6.53
16-65	43.75	43.95	8.05	8.49	
17-65	50.51	50.18	8.40	8.58	8.32
18-65	3.40	3.47 3.45	13.17	13.10 13.44	13.17
19-65	0.96	0.98	4.19	4.26	4.21

ACKNOWLEDGMENTS

The author expresses his thanks to G.A. Hunt, R. J. Guest, J. C. Hole and D. J. Charette, of the Mines Branch, for the use of their instruments and the loan of an iron hollow cathode lamp; to G. Pleizier for assistance in the development of the procedure for zinc; to E. Froese for initially suggesting determining both magnesium and iron on the same solution by atomic absorption; and to J. A. Maxwell and J. J. Lynch for critically reviewing the manuscript.

REFERENCES

- Abbey, Sydney
1965: Determination of potassium, sodium and calcium in feldspars; Can. Mineralogist, vol. 8, pp. 347-353.
- Abbey, Sydney, and Maxwell, J. A.
1960: Determination of potassium in micas; Chem. Canada, vol. 12, No. 9, pp. 37-41.
- 1962: Photometric determination of small amounts of magnesium in rocks; Anal. Chim. Acta, vol. 27, pp. 233-240.
- Ahrens, L. H., and Fleischer, Michael
1960: Report on trace constituents in granite G-1 and diabase W-1; U.S. Geol. Surv., Bull. 1113, pp. 83-111.
- Althaus, Egon
1966: Die Atom-Absorptions-Spektralphotometrie - ein neues Hilfsmittel zur Mineralanalyse; N. Jahrb. Mineral., vol. 1966, pp. 259-280.
- Belt, C. B., Jr.
1964a: Determination of copper and zinc in bayer process liquor; Atom. Abs. Newsletter, No. 19, pp. 7-9.
- 1964b: Atomic absorption spectrophotometry and the analysis of silicate rocks for copper and zinc; Econ. Geol., vol. 59, pp. 240-258.
- Canadian Association for Applied Spectroscopy
1961: Report of nonmetallic standards committee of C. A. A. S.; Appl. Spectroscopy, vol. 15, pp. 159-161.

- David, D. J.
1960: Determination of exchangeable sodium, potassium, calcium and magnesium in soils by atomic absorption spectrophotometry; Analyst, vol. 85, pp. 495-503.
- Farrar, B.
1965: Determination of copper and zinc in ore samples and lead-base alloys; Atom. Abs. Newsletter, vol. 4, pp. 325-327.
- Fixman, M., and Boughton, L.
1966: Mineral assay for silver, zinc and cadmium by atomic absorption; Atom. Abs. Newsletter, vol. 5, p. 33.
- Fleischer, Michael, and Stevens, R. E.
1962: Summary of new data on rock samples G-1 and W-1; Geochim. Cosmochim. Acta, vol. 26, pp. 525-543.
- Kerber, J. D.
1966: Atomic absorption spectroscopy; 49th Chem. Conference, Chem. Inst. Can., Saskatoon.
- Nesbitt, R. W.
1966: Determination of magnesium in silicates by atomic absorption spectroscopy; Anal. Chim. Acta, vol. 35, pp. 413-420.
- Rubeska, I., and Moldan, B.
1965: Determination of magnesium in silicate and carbonate rocks by atomic absorption spectrophotometry; Acta Chimica Acad. Sci. Hung., vol. 44, pp. 367-371.
- Sandell, E. B.
1959: Colorimetric determination of traces of metals, 3rd ed., Interscience, pp. 955-956.
- Slavin, Walter
1965: Application of atomic absorption to geochemical prospecting and mining; Atom. Abs. Newsletter, vol. 4, pp. 243-254.
- Sprague, Sabina
1963: Cement analysis; Atom. Abs. Newsletter, No. 14, pp. 9-11.
- Sullivan, J. V., and Walsh, A.
1965: High intensity hollow-cathode lamps; Spectrochim. Acta, vol. 21, pp. 721-730.

Trent, Dorothy, and Slavin, Walter

1964a: Determination of the major metals in granitic and diabase rocks by atomic absorption spectrophotometry; Atom. Abs. Newsletter, No. 19, pp. 1-6.

1964b: Determination of various metals in silicate samples by atomic absorption spectrophotometry; Atom. Abs. Newsletter, vol. 3, pp. 118-125.

Walsh, A.

1955: The application of atomic absorption spectra to chemical analysis; Spectrochim. Acta, vol. 7, pp. 108-117.

Webber, G.R.

1965: Second report on analytical data for C.A.A.S. syenite and sulphide standards; Geochim. Cosmochim. Acta, vol. 29, pp. 229-248.

Willis, J.B.

1965: Nitrous oxide-acetylene flame in atomic absorption spectroscopy; Nature, vol. 207, pp. 715-716.

APPENDICES I-IV

Operating Procedures

Appendix I

Operating Procedure for Magnesium Determination

Special Reagents

1. Standard Magnesium Solution (10 ppm Mg)

Prepare by diluting a more concentrated solution, prepared from pure magnesium metal. The final solution should contain about 10 ml free HCl per litre.

2. Strontium Solution (5,000 ppm Sr)

Weigh 8.43 g of strontium carbonate into a 2-litre beaker. Cover with water and dissolve by the gradual addition of 110 ml of concentrated HCl. Boil free of carbon dioxide, cool and dilute to 1 litre in a volumetric flask.

Sample Treatment

For precise work, decompose a 100-mg sample by the HF-nitric-perchloric procedure described in Appendix II.

Alternatively, for rapid control work, the sample may be decomposed by evaporating to dryness in a Teflon dish, first with 5 ml concentrated nitric acid, then with 5 ml of concentrated HCl and 5 ml HF together, and finally with 5 ml of concentrated HCl alone. In either case, the final residue is dissolved by the addition of 0.5-1.0 ml of concentrated HCl and 20-25 ml of water, and heating. Insoluble matter may generally be ignored. Make up to volume in a 100-ml volumetric flask. For samples containing less than 3 per cent MgO, transfer a 10-ml aliquot (corresponding to 10 mg of sample) to another 100-ml volumetric flask. (For samples containing 3-6 per cent, use 5 ml, for those from 6 to 15 per cent, use 2 ml.) Add 10 ml of strontium solution and dilute to volume.

Atomic Absorption Measurements

The following instructions are intended for use with the Techtron AA-3 Atomic Absorption Spectrophotometer. Modifications will be necessary with other instruments.

At least 30 minutes in advance, turn on the magnesium hollow-cathode lamp in "stand-by" at 2 milliamperes current. About 5 minutes before use, switch to a regulated modulated current of 4 milliamperes. Turn on acetylene and compressed air, light the burner, and adjust compressed air pressure to

18 lb./sq. in. With water aspirating, adjust acetylene flow to give a faintly luminous zone just above the inner blue "cone" of the flame.

Adjust wavelength to the magnesium peak at 2852 angstroms, leaving at point of maximum response. Use a 50 micron slit.

With COARSE GAIN at maximum and FINE GAIN near maximum adjust W. M. A. read-out to near 100, using H. T. ADJ., followed by fine adjustment with FINE GAIN. Close the slit opening and adjust the zero reading. Re-expose the slit and readjust the 100 reading if necessary.

With water aspirating, set the burner to the highest possible position without permitting the inner cone to impede the light beam. With a magnesium standard (preferably 0.5 ppm - see below) aspirating, set the lateral adjustment of the burner to a position of maximum absorption. The lateral adjustment should require no further change in going from one element to another. The vertical adjustment may require change for some elements.

With water aspirating, readjust meter reading to 100, if necessary; with the 1.0 ppm magnesium standard aspirating, rotate burner head to give a reading between 45 and 50.

Using the 1.0 ppm standard, take a rough reading for each sample. Select a standard as close as possible in magnesium content to each sample. For each sample, take readings in the sequence: O-s-O-x-O-s-O-x-O-s-O, where O is water, s the standard and x the sample. Before proceeding to the next sample, check the wavelength for peak response, and also readjust the zero if necessary. (These readings may be taken from the meter, or with a recorder.)

Calculation

Convert all readings to absorbance. From each absorbance reading, subtract the mean of the immediately preceding, and immediately following, water absorbance, to give "net absorbance".

Because the calibration curve is a straight line, concentration is directly proportional to absorbance. Calculate the apparent concentration for each net absorbance reading on each sample, using the standard readings preceding and following the sample reading. Determine the mean of the four apparent concentrations thus obtained.

If the four calculated values are not in close agreement, further readings should be taken.

Convert ppm Mg in solution to per cent Mg in the sample. (With 10 mg of sample in 100 ml of solution, these values are numerically equal.) Finally, convert per cent Mg to per cent MgO.

Calibration

Into five 100-ml volumetric flasks, measure 0, 5, 10, 15 and 20 ml of standard magnesium solution. Add 10 ml strontium solution to each and dilute to volume. These solutions will then contain 0.0, 0.5, 1.0, 1.5 and 2.0 ppm Mg.

Adjust the instrument as outlined above and take readings on the standards, first in ascending order of magnesium content, then in descending order. Take a reading with water aspirating before and after each reading on a standard.

Calculate net absorbances as above and plot mean net absorbance against ppm Mg. These should fall on a straight line.

Because it is not possible to assure that operating parameters are always identical, the calibration curve cannot be used for accurate analysis. It is drawn only to assure that Beer's Law is obeyed and for establishing a first approximation of magnesium content in unknown samples. Final analysis must always be done by comparison with standard solutions, as described above.

Appendix II

Operating Procedure for Lithium Determination

Special Reagents

1. Standard Lithium Solution (10 ppm Li)

Prepare by diluting a more concentrated solution, prepared from lithium carbonate and HCl.

Sample Treatment

Weigh 0.5 g sample into a 100-ml platinum or Teflon dish. Moisten with water and add 10 ml concentrated nitric acid and 5 ml HF.

Cover and heat on a steam bath to decompose.

Rinse off and remove cover. Evaporate to dryness on the steam bath.

Add 5 ml concentrated nitric acid, rinse down the walls of the dish with a little water and again evaporate to dryness.

Add 2 ml 70 per cent perchloric acid, rinse down the walls and swirl to dissolve soluble matter. If the analysis was begun in a Teflon dish, transfer now to a platinum dish.

Evaporate on a sand bath to perchloric fumes.

Rinse down the walls and again evaporate, but continue until no further fumes are evolved.

Add 20 ml HCl (1:19) cover and warm to dissolve salts. Filter on a 7-cm Whatman No. 42 paper, receiving filtrate in a 100-ml beaker. Wash with warm HCl (1:19), followed by two washes with water.

Further treatment will vary with the nature of the sample:

- (a) If the matrix correction factor is unknown, treat the filtrate according to the standard addition method.
- (b) If the correction factor has been established by running a number of similar samples by the standard addition method, use the direct method and apply the correction factor.
- (c) If there is reason to suspect the presence of lithium in the insoluble residue, it must also be analyzed, using the fusion method (see below).

Atomic Absorption Measurements

The lithium hollow-cathode lamp is warmed in "stand-by" at 3.5 milliamperes, and run for analysis at a regulated modulated current of 5.5 milliamperes. The wavelength is 6708 angstroms and the slit width 100 microns. The burner is used with the slot parallel to the light beam.

With the flame ignited and air pressure at 18 lb./sq. in., adjust acetylene flow to give maximum absorption, with a 1 ppm Li standard in the flame. If necessary, adjust vertical and lateral flame position for maximum absorption.

Other details of instrumental operation are as given in Appendix I.

Standard Addition Method

Measure the volume of the filtrate in a graduated cylinder and dilute to the next multiple of 5 ml. Measure two portions, each $\frac{2}{5}$ of the volume, into 50-ml beakers. Add 1.00 ml of the 10 ppm Li standard solution to one of the beakers.

Evaporate both to dryness.

Redissolve each by warming with 8 ml of HCl (1:19). Make each up to 10 ml in volumetric flasks. The two solutions thus obtained represent the sample solution and the sample solution with 1 ppm Li added.

Obtain a first approximation of the lithium concentration of the sample solution by comparison with any standard lithium solution. Knowing that the other solution contains 1 ppm Li more than the sample solution, select standard solutions to match each of those solutions as closely as possible.

Take readings in the sequence O-Sx-O-X-O-Sx-O-X-O-Sx-O-Sy-O-Y-O-Sy-O-Y-O-Sy, where O is water, X is the sample solution, Y the sample solution with 1 ppm Li added and Sx and Sy are respectively the standard solutions similar in composition to X and Y.

Calculate net absorbances for X and Y, as in Appendix I. Assuming that concentration is directly proportional to absorbance calculate "apparent concentrations" for each net absorbance value of each unknown, using both the preceding and following standard readings. Determine the four apparent concentrations thus obtained for each unknown solution.

Then, the true concentration, Tx, of the sample solution is given by

$$T_x = \frac{A_x}{A_y - A_x}$$

where A_x = apparent concentration of sample solution;
 A_y = apparent concentration of sample solution to which 1 ppm
Li has been added.

Multiply T_x by the dilution factor to get ppm Li in the original sample. (For $\frac{2}{5}$ of 0.5 g in a final volume of 10 ml, dilution factor is 50.)

Direct Method

Evaporate the filtrate to dryness.

Redissolve by warming with 20 ml HCl (1:19). Make up to 25 ml in a volumetric flask.

Determine the apparent concentration of the sample solution as above. Calculate the true concentration by multiplying apparent concentration by a factor,

$$F = \frac{1}{A_y - A_x}$$

where A_y and A_x have the same meaning as in the standard addition method. The actual factor used should be the mean of those obtained in analyzing a number of samples of similar composition, using the standard addition method.

Fusion Method

Transfer the filter and residue to a 10-ml platinum crucible and ignite to destroy the paper.

Mix the cooled residue with 0.5 g sodium carbonate and fuse for 15 minutes.

Add 5 ml water and 3-4 drops 95 per cent ethanol to the cooled fusion, cover and warm to disintegrate the melt. Start a blank at this point by weighing 0.5 g sodium carbonate into a 20-ml beaker, adding water and alcohol, covering and warming as with the sample.

Filter on a 5.5-cm Whatman No. 42 paper, receiving filtrate in a 100-ml beaker. Wash with warm sodium carbonate solution (5 g per 500 ml). Evaporate the sample filtrate, if necessary, and make up to 25 ml in a volumetric flask. (Save the residue.)

Measure the volume of the blank solution in a graduated cylinder and dilute to the next multiple of 5 ml. Measure two portions, each $\frac{2}{5}$ of the volume,

into 50-ml beakers. Add 1.00 ml of the 10 ppm Li standard solution to one of the beakers. Evaporate to about 5 ml, and make up both to 10 ml in volumetric flasks.

Determine "apparent lithium concentration" in sample, blank and "spiked blank", as above. Calculate true concentrations by multiplying apparent concentrations by a factor,

$$G = \frac{1}{B_y - B_x}$$

where B_x = apparent concentration of the blank;

B_y = apparent concentration of the blank to which 1 ppm Li has been added.

If B_x is not zero, it must be subtracted from the concentration of the sample solution as a blank correction.

Finally, dissolve the residue on the small filter paper by passing through it repeated portions of HCl (1:19), warmed in the platinum crucible in which the fusion was done. Wash the filter paper several times with additional warm HCl (1:19) and evaporate the resulting solution to dryness.

Dissolve the residue by warming with 20 ml HCl (1:19) and make up to 25 ml in a volumetric flask. Determine the lithium concentration as above. No correction factor is necessary because the salt concentration is relatively low.

Calibration

Into six 100-ml volumetric flasks, measure 0, 5, 10, 15, 20 and 25 ml of standard lithium solution. Add 4 ml concentrated HCl to each and dilute to volume. This gives a series of standards containing 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 ppm Li.

Using the operating conditions for lithium determination, plot a calibration curve as described in Appendix I. This curve should be a straight line.

The same limitations on the use of this curve apply as in the case of magnesium, the effect of flame conditions being more marked with lithium.

Appendix III

Operating Procedure for Zinc Determination

Special Reagents

1. Standard Zinc Solution (10 ppm Zn)

Prepare by diluting a more concentrated solution, prepared from zinc metal and HCl.

Sample Treatment

Proceed exactly as outlined in Appendix II, as far as the filtration and washing.

Discard the filter and residue. Evaporate the filtrate, if necessary to about 40 ml. Make up to 50 ml in a volumetric flask.

(If there is any reason to suspect the presence of zinc in the residue, it should be analyzed as in the fusion method in Appendix II).

Atomic Absorption Measurements

The zinc hollow-cathode lamp is warmed in "stand-by" at 3 milliamperes, and run for analysis at a regulated modulated current of 6 milliamperes. The wavelength is 2138 angstroms and the slit width 300 microns. The burner is used with the slot parallel to the light beam.

With the flame ignited and air pressure at 18 lb./sq. in., adjust acetylene flow to give maximum transmission, with water in the flame. If necessary, adjust vertical and lateral flame position for maximum absorption, with a 1-ppm Zn standard in the flame.

Other details of instrumental operation, calculation, etc., are similar to those in Appendix I.

Calibration

Into six 100-ml volumetric flasks, measure 0, 5, 10, 15, 20 and 25 ml of standard zinc solution. Add 2 ml concentrated HCl to each and dilute to volume. This gives a series of standards containing 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 ppm Zn.

Using the operating conditions for zinc determination, plot a calibration curve as described in Appendix I. This curve should be a straight line over more than half its length. The curve may be assumed to be straight, in obtaining a first approximation of the zinc content of unknown samples. In the final analysis, very little error is introduced by assuming that the calibration curve is linear, provided the sample and standard are sufficiently close together in zinc content.

Appendix IV

Operating Procedure for Determination of Magnesium and Iron in the Same Solution

Special Reagents

1. Standard Iron Solution (50 ppm Fe)

Prepare by diluting a more concentrated solution prepared from pure iron and HCl, oxidized by addition of a little nitric acid while the solution is hot.

2, 3. Standard Magnesium Solution and Strontium Solution

These are the same as described in Appendix I.

Sample Treatment

Decompose 100 mg sample as outlined in Appendix II. If there is any residue, it may contain significant amounts of iron, in which case it must be brought into solution by fusion with sodium carbonate or sintering with sodium peroxide. In either case, the product is leached with water and filtered. All of the iron should then be in the residue on the filter. The filtrate from the fusion may then be discarded and the residue dissolved in warm dilute HCl. The resulting solution may be analyzed for iron in the same way as the main sample solution. In most cases, all of the magnesium and most of the iron will be found in the solution resulting from the initial attack on the sample.

The main sample solution is diluted to volume in a volumetric flask of convenient size, to permit taking an aliquot containing 0.0-1.5 mg of Fe. The magnesium content of the aliquot should be under 0.2 mg, but it may be as high as 0.6 mg, if the magnesium determination is done with the burner head turned through a greater angle than in Appendix I.

The aliquot is transferred to a 100-ml volumetric flask, 10 ml of the strontium solution added, and the solution diluted to volume. For samples in which magnesium is present in much higher concentrations than iron, it may not be possible to determine both elements at the same dilution. In such a case, the same quantity of strontium must be present in the solutions used for both determinations.

Atomic Absorption Measurements

Magnesium is determined under the same conditions as in Appendix I, except that if the higher concentration range is used, the burner head must be rotated through an angle that will cause a 3 ppm Mg standard to read about 50 per cent transmittance.

The iron hollow-cathode lamp is warmed in "stand-by" at 5 milliamperes and run for analysis at a regulated modulated current of 10 milliamperes. The wavelength is 2483 angstroms and the slit width 25 microns. The burner is used with the slot parallel to the light beam.

With the flame ignited, water aspirating, and air pressure at 18 lb./sq. in., adjust acetylene flow to give the faintly luminous zone, as used for magnesium determination, but then reduce acetylene flow until the luminous zone just disappears. If necessary, adjust vertical and lateral flame position for maximum absorption, with a 5 ppm Fe standard aspirating.

For maximum precision, the sample and standard solutions should be aspirated from 20-ml graduated beakers, in which the level of the solution is kept within the range of about 8 to 17 ml. Also, the aspirator and burner assembly must be dismantled and cleaned at frequent intervals.

Other operating details are similar to those in Appendix I.

Calibration

Into six 100-ml volumetric flasks, measure 0, 5, 10, 15, 20 and 25 ml standard iron solution and 0, 4, 8, 12, 16 and 20 ml standard magnesium solution. Add 10 ml strontium solution to each and dilute to volume. These solutions will then contain 0.0, 2.5, 5.0, 7.5, 10.0 and 12.5 ppm Fe and 0.0, 0.4, 0.8, 1.2, 1.6 and 2.0 ppm Mg respectively. If the higher magnesium range is to be used, the volumes of standard magnesium solution will be 0, 10, 20, 30, 40 and 50 ml, and the final magnesium concentration in the standards will be 0, 1, 2, 3, 4 and 5 ppm.

The calibration curves for both magnesium and iron should be straight lines, but their usefulness is limited, as outlined in earlier Appendices. For final analysis, a single standard solution may be prepared for both iron and magnesium in each sample.