



**GEOLOGICAL  
SURVEY  
OF  
CANADA**

**DEPARTMENT OF ENERGY,  
MINES AND RESOURCES**

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**PAPER 68-20**

**ANALYSIS OF ROCKS AND MINERALS BY ATOMIC  
ABSORPTION SPECTROSCOPY  
PART 2. DETERMINATION OF TOTAL IRON, MAGNESIUM,  
CALCIUM, SODIUM AND POTASSIUM**

(Report and 5 tables)

**Sydney Abbey**



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#### ABSTRACT

A general method, developed earlier for the determination of magnesium and iron in rocks and minerals, is modified and extended to the determination of calcium, sodium and potassium, in most cases on the same solution. Possible adaptation of the method to a new precise scheme of analysis is discussed and possible future work indicated.



# ANALYSIS OF ROCKS AND MINERALS BY ATOMIC ABSORPTION SPECTROSCOPY

## Part 2 - Determination of Total Iron, Magnesium, Calcium, Sodium and Potassium

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### INTRODUCTION

In an earlier paper (Abbey, 1967) the application of atomic absorption spectroscopy in the determination of lithium and zinc as 'trace elements', and of magnesium and iron as major elements, in rocks and minerals was described. The lithium and zinc methods served to illustrate utilization of the sensitivity of atomic absorption spectroscopy. The analytical procedures for those metals were very similar, but lithium proved to be subject to many unpredictable interference effects from other components of the sample solution. Zinc was singularly free from such effects.

The combined magnesium-iron method showed that a high degree of precision and an astonishing economy of sample was possible using this technique. Thus the two elements could be determined quantitatively on an aliquot of the sample solution containing only 10 mg of sample. Even where duplicate absorption readings were taken for each of the elements determined, the quantity of sample solution consumed represented only 2-3 mg of the original sample.

The question then arose whether other elements could be determined on the same solution which is used to determine magnesium and iron. This paper shows how, with minor modifications, the procedure originally used to determine magnesium and iron can be extended to include calcium, sodium and potassium. Consideration is also given to possible future work on the determination of aluminum, manganese, barium, strontium, rubidium, cesium and possibly other metals.

### Acknowledgments

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### ATOMIC ABSORPTION COMPARED TO OTHER ROCK ANALYSIS TECHNIQUES

For many years, the analysis of rocks was based almost exclusively on what has come to be known as the 'classical' or 'conventional' methods. Despite the development of many new chemical and instrumental techniques, rock analysis continued to follow the tried and true ways. Many excellent analyses were produced, but these were more of a tribute to the skill of the analysts than to the scientific soundness of the methods.

Manuscript received 22 January, 1968.



The 'conventional' methods suffer from three disadvantages: (a) slowness; (b) only highly skilled operators can do the work; and (c) even the best of analysts can go wrong in applying established procedures to special samples to which they are not necessarily applicable. The last point is illustrated by published results of the determination of CaO in the United States Geological Survey standard dunite, DTS-1. Thus, the United States Geological Survey reported 0.00 and 0.03 per cent (Flanagan, 1967), whereas analysts at Pennsylvania State University reported 0.18 and 0.19 per cent (Goldich, Ingamells, Suhr, and Anderson, 1967).

The 1950s saw two major developments. First, there was the shocked surprise at the highly variable results reported on the standard granite and diabase, G-1 and W-1, by different analysts, most of whom were using essentially the same conventional methods. Then, there was the series of publications on the United States Geological Survey's 'rapid methods' (Shapiro and Brannock, 1952, 1956, 1962). These latter methods were based mainly on spectrophotometry, flame photometry and chelatometric titrations. Subsequently, other 'rapid methods' appeared, based on optical emission and X-ray fluorescence spectroscopy. Because all these methods emphasized speed, often at the expense of precision and accuracy, there has been a widespread impression that only the 'conventional' methods can produce accurate results.

Since Part 1 of this series (Abbey, 1967) appeared, several general schemes of rock analysis using atomic absorption have appeared in the literature (Galle and Angino, 1967; Belt, 1967; Shapiro, 1967). Although most of these schemes were intended for use as 'rapid' methods the present work was undertaken with the intention of working toward a precise scheme of analysis. Because of the essential simplicity of atomic absorption spectroscopy, it may be possible to abridge a precise scheme for use in 'rapid' work.

#### EXTENSION OF EXISTING METHOD

In the earlier magnesium-iron method, strontium was added to both standard and sample solutions, at a concentration of 500 ppm, where it served the dual purpose of releasing magnesium from the depressant effect of aluminum, and of removing an unexplained positive error in the iron determination. Inasmuch as the initial application of the magnesium method was as a check on low MgO values found by X-ray fluorescence, and because the MgO determination was done on a small aliquot of a sample solution prepared for sodium and phosphorus determination, the next step was to attempt to determine sodium by atomic absorption, on the same small aliquot. Further extension to the determination of calcium and potassium followed.

#### APPARATUS

The Techtron AA-3 Atomic Absorption Spectrophotometer was used as before, but with two modifications. Firstly, the Techtron Gas Control Unit was replaced by a similar Beckman Unit (designed for use with the Beckman Model 9200 Flame Photometer). Secondly, the recorder used was a Photovolt Linear/Log Varicord Model 43. This recorder gives linear read-out in absorbance, thereby

eliminating the necessity for conversion from transmittance, and simplifying base line corrections. Although linear absorbance may be read from 0.0 to 1.0, excessive noise was observed at absorbances over about 0.5. This effect is not surprising, because that portion of the absorbance scale, normally highly compressed, becomes unnaturally extended in a linear-absorbance readout system.

## EXPERIMENTAL PROCEDURE

Whenever possible, readings were taken on solutions similar to those used in the determination of magnesium and iron - i. e. in the presence of sufficient perchlorate ion to correspond to the cations present, plus additional free hydrochloric acid to give an acidity of 0.12N. For each element, a calibration curve was drawn, using standard solutions of the element alone. It was found that for magnesium, iron, calcium, sodium and potassium, a concentration of 10 mg of sample per 100 ml made it possible to determine those elements in the concentration ranges found in most rocks. In some cases, it was necessary to rotate the burner head to reduce sensitivity; in others, the sample required further dilution. Only in the few cases where some of the elements under study were present in very low concentrations was it necessary to use a more concentrated sample solution.

### Inter-element Effects

David (1960) found it necessary to introduce 1,500 ppm of strontium to eliminate inter-element effects in the determination of sodium, potassium, calcium and magnesium in soils. In our samples, where those elements are generally present in higher concentrations than in soils, 500 ppm Sr was found sufficient to overcome interferences in the determination iron, magnesium and sodium in the presence of one another. However, need of a higher strontium concentration was indicated when attempts were made to determine calcium and potassium. The 1,500 ppm Sr concentration was found to be satisfactory for all solutions tested.

### Standard Solutions

A set of standard solutions was prepared, to serve the multiple purposes of: (a) calibration; (b) study of inter-element effects; (c) future extension of the method to include other elements.

A 'concentrated' standard solution was prepared for each element, containing the equivalent of 1,000 ppm of the oxide, sufficient perchlorate ion to correspond to the quantity of cation present, and 10 ml of concentrated hydrochloric acid per litre of final solution. One litre of each solution was prepared. Aluminum was weighed as the hydrated nitrate; iron and magnesium as the pure metals; calcium and manganese as the carbonates; sodium and potassium as the chlorides; titanium as the hydride; phosphorus as ammonium dihydrogen phosphate. In the case of titanium, a higher acidity was maintained in the concentrated standard solution, to prevent hydrolysis. Details of the preparation of these solutions are given in the Appendix.

TABLE I

Compositions of Standard Blend Solutions

Equivalent Percentages (in original samples)									
Blend No.	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO
R	17.5	2.0	0.5	1.0	2.0	5.0	0.15	0.05	0.05
S	20.0	4.0	1.0	2.0	10.0	2.0	0.30	0.10	0.20
T	25.0	3.0	1.5	5.0	5.0	9.0	0.50	0.40	0.15
U	15.0	6.0	3.0	10.0	1.0	3.0	1.50	0.30	0.05
V	12.5	27.5	5.0	15.0	3.0	1.0	2.50	0.50	0.50
W	10.0	9.0	10.0	20.0	0.5	0.5	1.00	0.20	0.10
X	2.0	40.0	15.0	1.5	0.3	0.1	0.05	0.05	0.80
Y	5.0	12.5	30.0	3.0	0.1	0.3	0.10	0.15	0.30
Z	1.0	19.0	50.0	0.5	0.2	0.2	0.20	0.10	0.15
RT	21.2 <sub>5</sub>	2.5	1.0	3.0	3.5	7.0	0.32 <sub>5</sub>	0.22 <sub>5</sub>	0.10
TU	20.0	4.5	2.2 <sub>5</sub>	7.5	3.0	6.0	1.00	0.35	0.10
YZ	3.0	15.7 <sub>5</sub>	40.0	1.7 <sub>5</sub>	0.1 <sub>5</sub>	0.2 <sub>5</sub>	0.15	0.12 <sub>5</sub>	0.22 <sub>5</sub>
RU	16.2 <sub>5</sub>	4.0	1.7 <sub>5</sub>	5.5	1.5	4.0	0.82 <sub>5</sub>	0.17 <sub>5</sub>	0.05

Using a microburette, volumes of each concentrated standard solution were measured out to give the desired weight for each 'concentrated standard blend', of the first nine compositions listed in Table I. When all of the desired quantities had been added to each blend, sufficient concentrated HCl was added to each to provide a final acidity of 0.12N after allowing for the HCl introduced with each component, and the solutions diluted to 200 ml. All solutions were transferred immediately to polyethylene bottles. The contents of each bottle were then equivalent to what would be obtained if a 200 mg sample of each composition shown in Table I were decomposed with HF, HNO<sub>3</sub> and HClO<sub>4</sub>, all excess acids removed by fuming to dryness, 2 ml HCl added, and the solution diluted to 200 ml. The compositions selected were designed to

cover the expected concentration range of each element, with the concentrations of the different elements in each blend combined in a manner which reflects typical rock compositions (Nockolds, 1954). The 'working level' standard blends were then prepared from the 'concentrated' standard blends in the same manner as a 'working level' sample solution is prepared from a 'concentrated' sample solution - by taking an aliquot representing 10 mg of sample, adding 10 ml of a 15,000 ppm Sr solution which is 1.2N in HCl, and diluting to 100 ml. The solutions thus produced must also be stored in polyethylene.

If extremes of composition require that the aliquot taken for preparation of the working level solution of a particular sample contain more or less than 10 mg of sample, the standard solutions can be treated in the same proportions. For example, in a dunite containing about 50 per cent MgO, only 2 mg of the original sample is present in 100 ml of the working level solution, representing a 2-ml aliquot of a concentrated sample solution which originally contained 200 mg of sample in 200 ml. Working level standards can then be prepared by taking aliquots of the same size from concentrated standard blends containing similar percentages of MgO.

Standard blends RT, TU, YZ and RU (Table I) were prepared only at the working level to fill in gaps in the concentrations of some of the elements. Thus the working level standard blend RT was prepared from 5 ml of concentrated standard blend R, and 5 ml of concentrated standard blend T, etc.

In all cases, the final working level solutions, for samples or standards, contained 1,500 ppm Sr.

By preparing standard solutions in this manner, the number of solutions required is kept to a minimum, and there is less likelihood of mutual interferences being masked, as could occur where all components are in a constant ratio to one another (Shapiro, 1967). Considerable flexibility is also attained by preparing 'mixed' standards, such as RT, TU, etc. in Table I. It was also found convenient to prepare 100 ppm solutions of each oxide by taking 50 ml of the concentrated standard solution, adding 5 ml HCl, and diluting to 500 ml. Such solutions can be useful for making small additions of any desired element in the preparation of working level standard blends.

To facilitate identification, each type of standard solution was made up to a different volume: (a) the standard concentrates, each containing 1,000 ppm of a different oxide, in a volume of 1 litre; (b) the 100-ppm solutions of each oxide in 500-ml volumes; (c) the concentrated blends and sample solutions, each containing the equivalent of 200 mg of rock, in 200 ml; and (d) the working level solutions, each containing 10 mg equivalent of rock, in 100 ml. At that working level concentration, parts per million of a particular oxide in solution is numerically equal to the percentage of that oxide in the rock.

#### Tests for Interferences

Working level standard blends were prepared for the first nine compositions listed in Table I. The solutions were arranged in ascending order of iron content, the

atomic absorption spectrophotometer adjusted for iron determination, absorbance readings taken for all of the solutions, and absorbance plotted against iron concentration. Similarly, the solutions were arranged in ascending order of magnesium concentration and a magnesium calibration curve plotted. Similar calibrations were done for calcium, sodium and potassium.

In all cases, the resulting graph was a straight line or a smooth curve. Because all other components varied in a random manner as the desired component varied from minimum to maximum, it was concluded that the 1,500 ppm Sr present was sufficient to overcome all mutual interference effects.

### Potassium Problems

Potassium provided the greatest difficulty, partly as a result of weak emission by the potassium hollow cathode lamp, and partly because of the poor sensitivity of the photomultiplier tube at 7665 angstroms, the wavelength of the most sensitive potassium line.

When the potassium calibration was first plotted, a straight line relationship was observed. Some months later, the calibration graph was found to curve sharply toward the concentration axis, to such an extent that absorbance readings became unreliable for concentrations over about 5 ppm  $K_2O$ . Readings taken on several instruments, with hollow cathode lamps and photomultiplier tubes interchanged, revealed that most of the trouble was caused by the Hamamatsu R-213 photomultiplier, which was installed in our instrument after failure of the original Hamamatsu R-136 photomultiplier, which had given a linear calibration curve. R-136 tubes borrowed from other laboratories gave greatly superior sensitivity to that of the R-213, in some cases exceeding that obtained with the old R-136. However, it was not possible to restore the linear calibration.

### ANALYSIS OF 'STANDARD' SAMPLES

The six new reference samples issued by the United States Geological Survey (granite G-2, andesite AGV-1, peridotite PCC-1, dunite DTS-1, basalt BCR-1 and granodiorite GSP-1) were analyzed using the recommended procedure. The peridotite and dunite left black insoluble residues (probably chromite). These were separated by filtration, brought into solution by prolonged fuming with perchloric acid, and analyzed separately for iron, to provide a correction to the iron values found in the main solutions. On the same two samples, the high magnesium contents were determined on aliquots containing only 2 mg of sample, while the very low calcium and potassium contents were determined on aliquots containing 50 mg of sample. In the granodiorite sample, the relatively high potassium content lies in a region where the calibration curve is seriously flattened, if one works at the usual concentration of 10 mg of sample per 100 ml. Potassium was therefore determined in that sample using a solution containing only 5 mg of sample per 100 ml.

In Table II, results obtained by the proposed method are compared with those found by more conventional methods in our own laboratories, and also with

TABLE II  
Results Obtained on U. S. Geological Survey Reference Samples  
 (all in per cent)

Sample	Method	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
G - 2	AAS	2.65	0.79	2.03	3.98	4.57
	GSC	2.63	0.75	1.94	4.06	4.48
	PSU	2.72	0.75	2.03	4.05	4.50
	USGS	2.66	0.76	1.96	4.10	4.46
AGV-1	AAS	6.64	1.47	4.92	4.27	2.88
	GSC	6.71	1.52	5.05	4.27	2.95
	PSU	6.75	1.46	4.92	4.21	2.89
	USGS	6.64	1.50	4.90	4.24	2.86
PCC-1	AAS	8.39	43.18	0.56	0.00	0.00
	GSC	8.30	43.62	0.67	0.01	0.00
	PSU	8.15	43.22	0.55	0.00	0.00
	USGS	8.18	43.32	0.42	0.01	0.00
DTS-1	AAS	8.64	49.80	0.14	0.03	0.00
	GSC	8.58	49.91	0.27	0.01	0.01
	PSU	8.64	49.67	0.18	0.00	0.00
	USGS	8.64	49.82	0.02	0.04	0.00
BCR-1	AAS	13.32	3.52	6.89	3.31	1.70
	GSC	13.44	3.45	7.10	3.27	1.69
	PSU	13.47	3.41	6.98	3.23	1.68
	USGS	13.30	3.48	6.92	3.29	1.69
GSP-1	AAS	4.24	0.98	2.07	2.80	5.49
	GSC	4.26	0.98	2.04	2.72	5.58
	PSU	4.27	0.98	2.12	2.78	5.50
	USGS	4.25	0.98	2.06	2.80	5.50

Notes

- (1) AAS - proposed method  
 GSC - 'conventional' methods, our laboratories  
 PSU - Pennsylvania State University (see text)  
 USGS - U. S. Geological Survey (see text)
- (2) Fe<sub>2</sub>O<sub>3</sub> - total iron, calculated as Fe<sub>2</sub>O<sub>3</sub>

published values from Pennsylvania State University (Goldich, Ingamells, Suhr and Anderson, 1967) and the U. S. Geological Survey (Flanagan, 1967). The conventional methods used in the Geological Survey of Canada laboratories involved dichromate titration for total iron, classical gravimetry for magnesium and calcium, and flame photometry for sodium and potassium. The Pennsylvania State results are the recommended values of Goldich et al. The United States Geological Survey results are the means of the two 'conventional' analyses reported by Flanagan.

### Discussion

With few exceptions, the results obtained by the proposed method are in good agreement with those obtained by other methods and in other laboratories.

The iron value on PCC-1, as obtained by the proposed method, appears to be high. This is not surprising in view of the extra pains that must be taken in obtaining reliable iron results on a sample of this type. Goldich et al. (1967) reported that values of 8.15 and 8.29 were found by 'conventional' rock analysis, but they do not explain why the former value was favored in their final tabulation. By contrast, the close agreement obtained on DTS-1 comes as a pleasant surprise.

The calcium values on DTS-1 (and to a lesser extent on PCC-1) provide the most striking discrepancies, and serve to underline the pitfalls that can occur even in conventional analytical methods. In another analysis, done by atomic absorption in our laboratory, but by an inexperienced analyst, 0.59 per cent CaO was found in PCC-1, and 0.26 per cent in DTS-1. In still another case, the two samples were carried through a conventional analytical scheme to a point just beyond the separation of the  $R_2O_3$  group. Magnesium ammonium phosphate was then precipitated, carrying the calcium with it. The precipitate was ignited, fused with sodium carbonate, leached with water and filtered. The residue on the filter was dissolved in HCl and analyzed for calcium by atomic absorption. These operations, performed by an experienced analyst, yielded 0.52 per cent CaO in PCC-1 and 0.18 per cent in DTS-1. All of these values, combined with those of Goldich et al., cast considerable doubt on the low results obtained by the United States Geological Survey.

The sodium result on G-2 is low. However, in an earlier analysis, 4.05 per cent  $Na_2O$  was found. The 3.98 value is reported here because it was obtained on the same solution which produced most of the other results in Table II.

The potassium result on G-2 is high. In another analysis, done before the old R-136 photomultiplier tube failed, a value of 4.50 per cent  $K_2O$  was found. Again, the 4.57 value is reported because it was obtained on the same solution which produced most of the other results in Table II.

### A POSSIBLE NEW SCHEME FOR PRECISE ROCK ANALYSIS

In the light of the problems outlined in the preceding section and in view of recent experience with conventional rock analysis, a new, simplified scheme for precise rock analysis becomes possible. Designed to reduce both the time and quantity

of sample required without sacrificing accuracy, the scheme could take the following form:

(a) A 0.8-g sample is fused with sodium carbonate in the usual way. Silica is removed by a single dehydration with HCl. (Substitution of perchloric for hydrochloric might be time-saving at this point). Two small aliquots are taken from the filtrate - one to determine residual silica that escaped dehydration, using a molybdenum blue method; the other to determine phosphorus, also by a molybdenum blue method. The  $R_2O_3$  is precipitated in the usual way, filtered, ignited and weighed. After re-resolution by means of pyrosulphate fusion, titanium is determined photometrically (preferably using titron), and any manganese that may have been carried down with the  $R_2O_3$  is determined photometrically by periodate oxidation.

(b) A 0.5-g sample is decomposed by a somewhat scaled-up version of the procedure outlined in the appendix to this paper. The resulting solution is made up to 500 ml, and a 10-ml aliquot taken to determine magnesium, calcium, potassium, sodium, and possibly total iron by atomic absorption. Meanwhile HCl is eliminated by evaporating a large aliquot of the 500-ml solution with sulphuric acid, and total manganese can then be determined photometrically. Other aliquots of the same master solution could also be used to determine phosphorus and titanium, instead of doing those determinations on the 'main portion', as outlined in (a) above.

(c) Water, carbon dioxide and ferrous iron would be determined as usual, total iron being done on the same solution as ferrous iron, if it is not done by atomic absorption.

#### SUGGESTIONS FOR FURTHER WORK

From this paper and Abbey (1967) it is clear that atomic absorption spectroscopy can serve two main purposes in a rock and mineral analysis laboratory: (i) as a major time-saving component of a precise scheme of analysis; (ii) to facilitate determination of certain trace elements.

By introducing certain short-cuts in the proposed precise scheme of analysis it is possible to use atomic absorption as a major component of a scheme of rapid analysis (cf. Shapiro, 1967).

Of the other major constituents of rocks, it would appear that aluminum and manganese should lend themselves to determination by this method. Aluminum, which forms refractory oxides in the flame, requires the hotter acetylene - nitrous oxide flame to reduce its atoms to the ground state. Sensitivity is such that it will probably require a more concentrated sample solution - possibly the 100 mg/100 ml solution produced in dissolving the sample. Possible interferences will require investigation although little difficulty is expected. Manganese can be determined readily with the ordinary air-acetylene flame. It would probably be necessary to use the more concentrated solution in this case, not because of limited sensitivity, but because the manganese concentration in most rocks is so low. There is some doubt whether the use of atomic absorption would be more time-saving than the periodate photometric method for manganese.



If the aluminum determination can be applied without difficulty, the possible new scheme for precise analysis could be further simplified by elimination the precipitation of the  $R_2O_3$  group.

In the past strontium and barium have been determined in the Geological Survey's laboratories by means of flame photometry, after chemical isolation of the alkaline earth group. Such a procedure suffers from two drawbacks - possible incomplete recovery in the chemical steps, and limited sensitivity for barium in flame photometry. There is good reason to believe that these elements can be determined by atomic absorption (using the acetylene - nitrous oxide flame) with adequate sensitivity, and without preliminary chemical separations.

Rubidium and cesium have also been determined by flame photometry, in this case using the neutral sulphate solution obtained for potassium determination by the 'ignition-leach' method (Abbey and Maxwell, 1960). The sensitivity of such a method is limited, even if the sample solution is concentrated by evaporation. There is also some uncertainty about the completeness of recovery in the leaching operation. Atomic absorption sensitivity for these elements would appear adequate, but difficulties are foreseen. Firstly, both have their most sensitive lines in the near infrared, where photomultiplier sensitivity is limited. Secondly, hollow cathode lamps for these elements have insufficient emission, and the less stable Osram discharge lamps must be used. In one test, done in the laboratory of an instrument distributor, it was found that a major proportion of the light emitted from a cesium Osram lamp at the apparent peak wavelength of 8520 A was due to the second order emission spectrum of the filler gas, with resulting poor sensitivity for cesium absorption. Further work will be necessary.

Capacho - Delgado and Manning (1967) report the determination by atomic absorption of silicon and titanium (among other elements). Their precision for silicon is only fair in the 20 per cent  $SiO_2$  range in cements, and it is doubtful whether the method would be applicable to the higher silica contents in rocks. Titanium appears a little more promising, but again there is some doubt whether atomic absorption offers much advantage over photometric methods.

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APPENDIX

Operating Procedures

Special Reagents

1. Strontium Solution (15,000 ppm Sr)

Weigh 50.5 g of strontium carbonate into a 2-litre beaker. Cover with 400-500 ml of water. Cover the beaker, move cover slightly aside, and add concentrated HCl in small portions, until a total of 255 ml has been added. When the reaction finally subsides, rinse down the watch glass and beaker walls with water, and heat to boiling to expel carbon dioxide. Cool, dilute to 2 litres in a volumetric flask and transfer to a polyethylene bottle.

2. Standard Aluminum Solution (1,000 ppm  $\text{Al}_2\text{O}_3$ )

Weigh 7.360 g  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (e. g. Fisher Certified A-586) into a 250-ml silica beaker. Dissolve in about 30 ml of water, add 20 ml HCl, cover, and boil until no further oxides of nitrogen are evolved. Evaporate to dryness on a steam bath. Redissolve in 20 ml HCl (1:1), heat to boiling, then evaporate nearly to dryness on the steam bath. Add 5 ml HCl, 5 ml  $\text{HClO}_4$ , and about 50 ml water. Warm to dissolve, cool and dilute to 1 litre in a volumetric flask. Store in polyethylene. If this solution is to be used for aluminum determination, evaporate an aliquot to dryness in a tared platinum crucible, on a steam bath. Add 2 ml  $\text{H}_2\text{SO}_4$  (1:1), evaporate twice to  $\text{SO}_3$  fumes, then continue until all fumes are expelled. Transfer to a cold muffle furnace and gradually raise temperature to decompose the sulphate. Finally, ignite over a Meker burner and weigh as  $\text{Al}_2\text{O}_3$ .

3. Standard Iron Solution (1,000 ppm  $\text{Fe}_2\text{O}_3$ )

Weigh 0.6994 pure iron (e. g. G. Frederick Smith electrolytic, ignited in moist hydrogen) into a 250-ml silica beaker. Add about 10 ml water and 5 ml  $\text{HClO}_4$ . Warm gently to dissolve, then evaporate twice to fumes, finally continuing heating until no further fumes are evolved. Add 10 ml HCl and about 10 ml water, swirl to dissolve, and evaporate to dryness. Add 10 ml HCl and sufficient water to dissolve. Make up to 1 litre in a volumetric flask and store in polyethylene. Standardization is not required if sufficiently pure iron was used.

4. Standard Magnesium Solution (1,000 ppm MgO)

Weigh 0.6032 g pure magnesium (e. g. Dominion Magnesium 99.95 per cent grade) into a 250-ml plastic or silica beaker. Cover with water and add 4 ml  $\text{HClO}_4$  and 10 ml HCl. When solution is complete, dilute to 1 litre in a volumetric flask. Store in polyethylene. Standardization is not required if sufficiently pure magnesium was used.

5. Standard Calcium Solution (1,000 ppm CaO)

Weigh 1.7848 g oven-dried  $\text{CaCO}_3$  (ACS Reagent Grade, low in alkalis, e. g. Baker Analyzed 1294) into a 250-ml silica beaker. Add about 20 ml of water and cover the beaker. Slip cover slightly aside and add, in small portions, 3 ml  $\text{HClO}_4$  and 5 ml HCl. When reaction is complete, rinse down cover and beaker walls and heat to boiling to expel carbon dioxide. Allow to cool, add 5 ml HCl and dilute to 1 litre in a volumetric flask. Store in polyethylene. Standardization is not required if sufficiently pure calcium carbonate was used.

6. Standard Sodium Solution (1,000 ppm  $\text{Na}_2\text{O}$ )

Weigh 1.8858 g oven-dried NaCl (ACS Reagent Grade) into a 250-ml plastic or silica beaker. Dissolve in about 20 ml of water. Add 3 ml  $\text{HClO}_4$  and 7 ml HCl. Dilute to 1 litre in a volumetric flask and store in polyethylene. Standardization is not required.

7. Standard Potassium Solution (1,000 ppm  $\text{K}_2\text{O}$ )

Weigh 1.5845 g oven-dried KCl (ACS Reagent Grade) into a 250-ml plastic or silica beaker. Dissolve in about 20 ml of water. Add 2 ml  $\text{HClO}_4$  and 10 ml HCl. Dilute to 1 litre in a volumetric flask and store in polyethylene. Standardization is not required.

8. Standard Titanium Solution (1,000 ppm  $\text{TiO}_2$ )

Weigh 0.6500 g  $\text{TiH}_4$  (Metal Hydrides high purity grade) into a 250-ml silica beaker. In another silica beaker, heat 100 ml HCl (1:1) to boiling. Add the titanium hydride carefully, in small portions, to the boiling acid. When hydrogen evolution ceases, add 30 per cent hydrogen peroxide, dropwise, with caution, until the purple colour is completely discharged. Add 4 ml  $\text{HClO}_4$  and 155 ml HCl. Heat to boiling and boil until oxygen evolution ceases. Cool and dilute to 1 litre in a volumetric flask. Store in polyethylene. If this solution is to be used for titanium determination, evaporate an aliquot in a tared platinum crucible, after adding 2 ml  $\text{H}_2\text{SO}_4$  (1:1). Take to fumes twice, finally heating until no further fumes are evolved. Transfer to a cold muffle furnace and gradually raise temperature to decompose the sulphate. Finally, ignite over a Meker burner and weigh as  $\text{TiO}_2$ .

9. Standard Phosphorus Solution (1,000 ppm  $\text{P}_2\text{O}_5$ )

Weigh 1.8607 g  $(\text{NH}_4)_2 \text{HPO}_4$  (ACS Reagent Grade) into a 250-ml plastic or silica beaker. Dissolve in about 20 ml of water. Add 10 ml HCl and dilute to 1 litre in a volumetric flask. Store in polyethylene. Standardization is not required.

10. Standard Manganese Solution (1,000 ppm MnO)

Weigh into a 250-ml silica beaker sufficient  $\text{MnCO}_3$  to contain the equivalent of 1 g of MnO (e. g. 1.6880 g of Fisher M-85, lot 705452, assay 45.9 per cent Mn).

TABLE III

Volumes of 1,000 ppm oxide concentrates required  
to make 200 ml of each concentrated standard blend

Blend No.	ml 1,000 ppm oxide standard									HCl ml
	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	
R	35.0	4.0	1.0	2.0	4.0	10.0	0.3	0.1	0.1	1.40
S	40.0	8.0	2.0	4.0	20.0	4.0	0.6	0.2	0.4	1.10
T	50.0	6.0	3.0	10.0	10.0	18.0	1.0	0.8	0.3	0.85
U	30.0	12.0	6.0	20.0	2.0	6.0	3.0	0.6	0.1	0.65
V	25.0	55.0	10.0	30.0	6.0	2.0	5.0	1.0	1.0	0.00
W	20.0	18.0	20.0	40.0	1.0	1.0	2.0	0.4	0.2	0.60
X	4.0	80.0	30.0	3.0	0.6	0.2	0.1	0.1	1.6	0.80
Y	10.0	25.0	60.0	6.0	0.2	0.6	0.2	0.3	0.6	0.95
Z	2.0	38.0	100.0	1.0	0.4	0.4	0.4	0.2	0.3	0.50

Add about 20 ml of water and cover the beaker. Slip cover slightly aside and add, in small portions, 2.5 ml HClO<sub>4</sub> and 5 ml HCl. When reaction is complete, rinse down cover and beaker walls. Add 30 per cent hydrogen peroxide, dropwise, with caution, and swirl to dissolve any suspended matter. Heat to boiling to expel oxygen and carbon dioxide. Allow to cool, add 5 ml HCl and dilute to 1 litre in a volumetric flask. Store in polyethylene. If this solution is to be used for manganese determination (in samples containing over 2 per cent MnO), standardization by a titrimetric method may be necessary.

11 to 19. Diluted Metal Standard Solutions (100 ppm oxides)

For each of solutions 2 to 7 inclusive, and 9 to 10 inclusive, pipette 50 ml into a 550-ml volumetric flask. Add 4.5 ml HCl, dilute to volume and store in polyethylene. If a similar titanium solution is required, it should be similarly prepared immediately before use.

#### Concentrated Standard Blends (100 mg sample equivalent per 100 ml)

Into a series of 200-ml volumetric flasks labelled R, S, T, U, V, W, X, Y and Z, measure the volumes of 1,000-ppm oxide standards (i. e. solutions 2-10 inclusive) indicated in Table III. To each, add the volume of concentrated HCl indicated in the table. Dilute to volume and store in polyethylene.

#### Working Level Standard Blends (10 mg sample equivalent per 100 ml)

For each of the concentrated standard blends, pipette 10 ml into a 100-ml volumetric flask. Add 10 ml of the 15,000 ppm Sr solution and dilute to volume. Store in polyethylene.

#### Mixed Working Level Standard Blends

Where necessary to prepare a mixed blend, such as RT in Table I, pipette into a 100-ml volumetric flask 5 ml of concentrated standard blend R and 5 ml concentrated standard blend T. Add 10 ml of the 15,000 ppm Sr solution and dilute to volume. Store in polyethylene. The concentration of each element in this solution will be the mean of its concentrations in the two standard blends from which it is derived.

#### Special Working Level Standard Blends

Where extremes of composition indicate that a particular determination must be done on a working level solution containing a weight of sample other than 10 mg per 100 ml, the aliquot of the concentrated standard blend may be varied at will, each ml volume of the aliquot corresponding to 1 mg of sample, provided the final volume is always 100 ml, and that 10 ml of the 15,000 ppm Sr solution is always present.

Where it is necessary to change only one component of a working level standard blend, this can be done by using the 100 ppm oxide standards. Thus in preparing, say, working level standard R, by adding 1 ml of the 100 ppm  $K_2O$  solution before dilution to volume, the resulting solution (which could be called R + 1K) would contain the equivalent of 6.0 per cent  $K_2O$ , instead of the 5 per cent in R, while all of the other components would be at the same concentration as they are in R.

#### Operating Parameters

Table IV gives the instrument settings for the various concentration ranges for each oxide. The 'burner angle' is the angle between the optic axis of the light beam and the burner slot. The size of the angle for a particular analysis is established by aspirating a standard solution containing the desired component at the maximum concentration of the working range, and rotating the burner to give an absorbance reading of about 0.5.

TABLE IV

Instrument Settings

Component	H. C. Current mA	Range		Sample mg per 100 ml	Burner angle *	Slit microns	Wave- length A
		% in sample	ppm in solution				
Fe <sub>2</sub> O <sub>3</sub>	10	0-15	0-15	10	zero	25	2483
		10-40	10-40	10	small		
MgO	4	0-3	0-3	10	small	50	2852
		3-15	3-15	10	large		
		5-30	2-15	5	large		
		15-50	3-10	2	large		
CaO	10	0.0-3.0	0-15	50	zero	25	4227
		1-10	1-10	10	zero		
		5-20	5-20	10	small		
Na <sub>2</sub> O	5	0.0-0.3	0.0-0.3	10	zero	50	5889
		0.3-10.0	0.3-10.0	10	moderate		
K <sub>2</sub> O	5	0.0-1.0	0.0-5.0	50	zero	300	7665
		1.0-5.0	1.0-5.0	10	zero		
		5.0-9.0	2.5-4.5	5	zero		

\*See text

Compressed air pressure of 18 psi, and acetylene at 7.5 psi are used for all five determinations. The needle valve at the side of the gas control unit is adjusted with a screwdriver, with gas pressures set as above, to give a very faint, barely visible luminous area immediately above the 'inner core' of the flame, with no liquid aspirating. When water is aspirated, the luminous area should become distinctly visible as a series of 'waves' spreading toward both ends from the centre of the burner.

With the flame adjusted, set the burner level as high as possible without obstructing the flame. The same setting is used for all five determinations.

For maximum precision, all readings are taken on solutions aspirating from graduated 20-ml Pyrex beakers, containing between 9 and 17 ml of solution.

### Calibration

#### (1) Fe<sub>2</sub>O<sub>3</sub>

Arrange the following working level standards in order of increasing iron content: R-T-S-U-W-Y-Z. With conditions set for 0-15 per cent Fe<sub>2</sub>O<sub>3</sub>, take readings on all of the solutions, in the order given. Repeat the readings in the reverse order. By using the recorder in the linear-absorbance mode, the base-line correction can be easily made by subtracting the mean of the water readings before and after each peak reading, to give net absorbance readings. Determine the mean absorbance for each standard solution, and plot absorbance against Fe<sub>2</sub>O<sub>3</sub> concentration.

With conditions adjusted for the 10-40 per cent Fe<sub>2</sub>O<sub>3</sub> range, use the standards W-Y-Z-V-X, and proceed exactly as in the preceding paragraph.

#### (2) MgO

Set conditions for 0-3 per cent MgO, use standards R-S-T-U, and proceed as for Fe<sub>2</sub>O<sub>3</sub>. With conditions set for 3-15 per cent MgO, proceed with standards U-V-W-X. With conditions set for 15-50 per cent MgO, use standards W-X-Y-Z.

#### (3) CaO

Set conditions for 0.0 to 3.0 per cent CaO, and proceed with standards Z-R-X-S-Y. In this case, because of the measurable calcium content of the strontium solution, readings should be taken also on a blank (or O standard) containing only 10 ml of the 15,000 ppm Sr solution in 100 ml. The mean net absorbance for the O standard must be subtracted from the mean net absorbance of each of the standard solutions before plotting the calibration.

Set conditions for 1 to 10 per cent CaO, and proceed with standards O-R-X-S-Y-T-U. Finally, set conditions for 5 to 20 per cent CaO, and proceed with standards O-T-U-V-W. Correction for absorbance of the O standard must be applied in all cases.



(4) Na<sub>2</sub>O

Set conditions for 0.0 to 0.3 per cent Na<sub>2</sub>O, and proceed with standards O-Y-Z-X-W. Set conditions for 0.3 to 10.0 per cent Na<sub>2</sub>O, and proceed with standards O-X-W-U-R-V-T-S. Correction for the O standard will probably be required in the lower range and possibly also in the higher range.

(5) K<sub>2</sub>O

Set conditions for 0.0 to 1.0 per cent K<sub>2</sub>O, and proceed with standards O-X-Z-Y-W-V. Set conditions for 1.0 to 5.0 per cent K<sub>2</sub>O, but in this case, it will be necessary to prepare mixed standards, because of the non-linearity of the potassium calibration curve. For the 1.0 to 5.0 per cent K<sub>2</sub>O range, use W-V-S-U-RU-R-TU. Set conditions for 5.0 to 9.0 per cent K<sub>2</sub>O, and proceed with standards RU-R-TU-RT-T. Correction for the O standard may be necessary, but only for the lowest readings.

Sample Treatment

Accurately weigh 200 mg of sample into a 100-ml platinum or Teflon dish. Moisten with water and add 10 ml HNO<sub>3</sub> 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 HNO<sub>3</sub>, rinse down the walls of the dish with a little water and again evaporate to dryness.

Add 2 ml HClO<sub>4</sub>, 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 or crucible.

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 (1:99) and warm to dissolve salts. Filter, if necessary, through a 7-cm Whatman No. 42 paper, and wash with warm HCl (1:99). (If there is any reason to suspect the presence of one of the desired elements in the residue, it must be brought into solution by some suitable method and checked for the presence of those elements).

Transfer the filtrate to a 200-ml volumetric flask, using HCl (1:99) for all rinsings. Dilute to volume, using the same acid, and transfer to a polyethylene bottle.

Pipette 10 ml of the sample solution into a 100-ml volumetric flask. Add 10 ml of the 15,000 ppm Sr solution, dilute to volume with water and transfer to a

polyethylene bottle. (If the concentration of any component is known to fall outside the limits suitable for analysis at this sample concentration level, as given in Table IV, suitably more concentrated or diluted working level solutions should also be prepared, remembering to keep the strontium concentration of every final solution at the 1,500 ppm level).

### Preliminary Analysis

If the approximate iron content in a series of samples is known, select a standard working level solution containing iron at about the average expected concentration. If the iron content is not known, use a standard about midway in the concentration range. Take a single reading for the standard and for each sample solution. Use the calibration curve to find a first approximation of the  $\text{Fe}_2\text{O}_3$  content of each sample, applying the necessary correction if the standard reading does not fall on the curve.

Repeat the above operations for the other four elements - magnesium, calcium, sodium and potassium. If any element in any sample lies outside the concentration range for the original settings, repeat the readings for that element after taking a larger or smaller aliquot, as required, from the original concentrated sample solution, and/or change the burner angle. A similar change must be made in the size of aliquot taken from the concentrated standard blend to make up the working level standard used for comparison.

Example: In analyzing the six samples reported in Table I, the preliminary analysis was done by first comparing readings on standard U (Table I) with readings for each of the components in each sample. The standard and sample solutions were all at the normal working level equivalent - i. e. 10 mg sample per 100 ml. Settings used gave working ranges of 0-15 per cent  $\text{Fe}_2\text{O}_3$ , 0-3 per cent MgO, 1-10 per cent CaO, 0.3-10.0 per cent  $\text{Na}_2\text{O}$  and 1-5 per cent  $\text{K}_2\text{O}$ .

Under these conditions,  $\text{Fe}_2\text{O}_3$  values fell within the range for all of the samples; MgO only for G-2, AGV-1 and GSP-1; CaO and  $\text{Na}_2\text{O}$  for all but PCC-1 and DTS-1;  $\text{K}_2\text{O}$  for G-2, AGV-1 and BCR-1.

For MgO in BCR-1, the burner angle was then increased somewhat, and a new comparison reading taken against standard U. For MgO in PCC-1 and DTS-1, the initial readings were so high that it was found necessary to prepare new working solutions of the samples, using only 2 mg of sample (i. e. 2 ml of the original sample solution) per 100 ml, and to compare readings against a similarly diluted solution of standard Z (Table I).

For CaO and  $\text{K}_2\text{O}$  in PCC-1 and DTS-1, the preliminary readings were repeated on new solutions containing 50 mg of sample per 100 ml, compared with readings on standard Z at the same concentration level. For  $\text{K}_2\text{O}$  in GSP-1, preliminary readings were repeated, using a new solution containing 5 mg of sample per 100 ml, compared to a similarly diluted solution of standard R.

For Na<sub>2</sub>O, preliminary readings on PCC-1 and DTS-1 were repeated on the solutions containing 10 mg of sample per 100 ml, but the burner angle was reduced to zero, and comparison made with a similar solution of standard Y (Table I).

(Such wide variation in solution concentrations and instrument settings will not be necessary where samples are analyzed in batches of more uniform composition than are the six United States Geological Survey reference samples).

### Final Analysis

For each determination in each sample solution, select two standard solutions, one containing a little less than the approximate amount of the desired component found in the preliminary analysis, the other a little more. Each sample must be analyzed against standards at the same dilution level, and all final solutions must contain 1,500 ppm Sr. As an example, the standards used for analyzing the six United States Geological Survey reference samples are given in Table V.

For each determination, take readings in the sequence L-a-H-a-L, where L represents the 'low' standard, H the 'high' standard and a the sample.

$$\text{Then } C_a = C_L + \frac{A_a - A_L}{A_H - A_L} \cdot (C_H - C_L)$$

where

- C<sub>a</sub> = concentration in the sample
- C<sub>L</sub> = concentration in the low standard
- C<sub>H</sub> = concentration in the high standard
- A<sub>a</sub> = absorbance of the sample
- A<sub>L</sub> = absorbance of the low standard
- A<sub>H</sub> = absorbance of the high standard

(Note: All corrections (e. g. base-line variations, etc.) must be applied to absorbances before calculating concentrations).

Two values for C<sub>a</sub> can be calculated, corresponding to the two readings of A<sub>a</sub>, but the A<sub>L</sub> used in each case should be the reading closest to that on the standard. Report the mean of the two calculated values. (If there is a large discrepancy between the two readings of A<sub>a</sub> that is not compensated by a corresponding change in A<sub>L</sub> - or vice versa - additional readings should be taken to obtain consistent values).

TABLE V

Standard Solutions Used in Final Analysis of U. S. G. S. Samples

	<u>Fe<sub>2</sub>O<sub>3</sub></u>	<u>MgO</u>	<u>CaO</u>	<u>Na<sub>2</sub>O</u>	<u>K<sub>2</sub>O</u>
G-2	R - T	R - S	YZ - S	V - T	RU - R
AGV-1	U - W	S - T	Y - T	V - T	S - U
PCC-1	U - W	YZ - Z	Z - R	O - Y	O - X
DTS-1	U - W	YZ - Z	O - Z	O - Y	O - X
BCR-1	Y - YZ	U - V	T - TU	V - RT	V - S
GSP-1	S - TU	R - S	S - Y	R - V	R - TU