

# Major element rock analysis by X-ray fluorescence – a simple fusion method

Tim Padfield and Alan Gray

## Abstract

One part of powdered rock is mixed with seven parts by weight of anhydrous sodium tetraborate and 0.185 parts of anhydrous sodium carbonate. The mixture is melted in a gold plated platinum crucible over an Amal burner. The melt is stirred occasionally with a platinum wire. When it is homogeneous the melt is poured into the middle of a copper wire ring which rests on a hot stainless steel disc. The polished end of a cold aluminium cylinder is brought down to press out the molten blob to fill the ring. The chilled glass disc needs no annealing.

The disc is analysed for magnesium, aluminium, silicon, phosphorus, potassium, calcium, titanium, manganese and iron. The primary X-ray beam is generated by a silver target. Intensities of the  $K\alpha$  X-rays are measured. For most rocks no background measurements are necessary.

A vitreous enamel disc containing all the analysed elements is used as a permanent reference standard to record instrument drift. Synthetic standards are used to calibrate the instrument. The results are corrected to take account of absorption of the characteristic X-rays by the glass.

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# PHILIPS

## BULLETIN

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## Major Element Rock Analysis By X-ray Fluorescence - A Simple Fusion Method

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### SUMMARY

One part of powdered rock is mixed with seven parts by weight of anhydrous sodium tetraborate and 0.185 parts of anhydrous sodium carbonate. The mixture is melted in a gold plated platinum crucible over an Amal burner. The melt is stirred occasionally with a platinum wire. When it is homogeneous the melt is poured into the middle of a copper wire ring which rests on a hot stainless steel disc. The polished end of a cold aluminium cylinder is brought down to press out the molten blob to fill the ring. The chilled glass disc needs no annealing.

The disc is analysed for magnesium, aluminium, silicon, phosphorus, potassium, calcium titanium, manganese and iron. The primary X-ray beam is generated by a silver target. Intensities of the  $K\alpha$  X-rays are measured. For most rocks no background measurements are necessary.

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### INTRODUCTION

The analytical method described below was designed to suit an automatic X-ray spectrometer with punched tape output, operated by people with no analytical experience. The method treats all specimens alike and dispenses with those jobs that are not automated - such as changing the X-ray tube or deciding which is the most appropriate standard.

A fusion method is used for specimen preparation because this allows the use of a single calibration line to analyse rocks of widely

differing compositions. The dilution of the rock with flux reduces inter-element effect and the destruction of the minerals eliminates the unpredictable effects of mineralogy and particle size which prevent the analyst from taking full advantage of the high precision of X-ray spectrometry.

Many fusion methods for rock analysis have been published. We acknowledge particularly our debt to Norrish and Chappell (1967) from whose method we have developed the fusion process used in this analytical scheme.

### THE FLUX

The flux is anhydrous sodium tetraborate with two percent of sodium carbonate added to reduce the viscosity of the melt. The sodium oxideboric oxide system is described by Morey and Merwin (1936).

The choice of sodium tetraborate rather than the more commonly used lithium salt was influenced by the ready availability and low cost of high purity borax and by its higher X-ray absorption, making unnecessary the use of a heavy absorber.

The main defect of sodium tetraborate is its strong absorption of magnesium X-rays.

### THE FUSION MIXTURE

The choice of dilution factor is influenced by the incompatible demands of speed, precision, suppression of inter-element effects and limitation of the errors caused by impurities in the flux. On geochemical grounds we chose as the deciding factor a detection limit of 0.1% for magnesium oxide with a 200 second count time. For our instrument, a Philips PW 1212 spectrometer, this allowed a sevenfold dilution of the rock with flux. The fusion mixture is 0.4 g rock powder, 0.074 g anhydrous sodium carbonate and 2.77 g sodium tetraborate. Discs made with this mixture are about 2.8 cm diameter and 1.4 mm thick.

The mixture is loaded into a 25 ml gold plated platinum crucible in such a way that the rock powder, mixed with the sodium carbonate and with a portion of the sodium tetraborate is sandwiched between layers of pure sodium tetraborate powder.

A gold plated platinum crucible is used because the fusion mixture does not wet it. Other precious metal alloys share this essential property but some of these alloys are stiffer and tend to crack with misuse.

The loaded crucible is covered and heated, gently at first, over an Amal burner. The temperature is increased gradually over five minutes until the crucible is red hot. After this the lid is removed at intervals and the contents are stirred briefly with a short thin platinum wire bound to a 1 mm diameter wire of a furnace winding alloy such as Nichrome, which in turn is held in a brass pin vise.

Nearly all rocks dissolve completely within five to twenty minutes, depending on their mineralogy.

### THE CASTING METHOD

After a final thorough stir the melt is brought to the lip of the crucible and then quickly poured out into the middle of a copper wire ring which lies on a stainless steel hotplate held at about 250°C.

The polished end of a cold aluminium cylinder is immediately brought down to press out the blob of molten glass to fill the ring. The chilled glass disc with its enclosing ring is removed to a cold surface. When it is cool the flash is chipped off. It is advisable to wear protective glasses when chipping off the surplus glass. No annealing is necessary. Occasionally a disc will crack but the wire ring holds the pieces together and the cracks have no effect on the analysis. Cracking is often diagnostic of incomplete fusion of the rock.

The analysed surface is that pressed by the aluminium block.

The wire rings are made by winding 1.2 mm

diameter copper wire in a tight spiral round a former of suitable size. The coil is removed and snipped into rings.

The various stages of the fusion and casting are illustrated in Fig. 1.

### CLEANING THE CRUCIBLE

The residue left after pouring is remelted with the crucible held horizontally. The melt will collect in two blobs on either side of the crucible rim. The crucible is removed from the flame and allowed to cool in a horizontal position. The two blobs can then be cracked off by gently

flexing the crucible.

If some small blobs are left inside the crucible a small amount of pure flux can be melted and swirled around. The flux is soluble in boiling water.

### REPRODUCIBILITY OF SPECIMEN PREPARATION

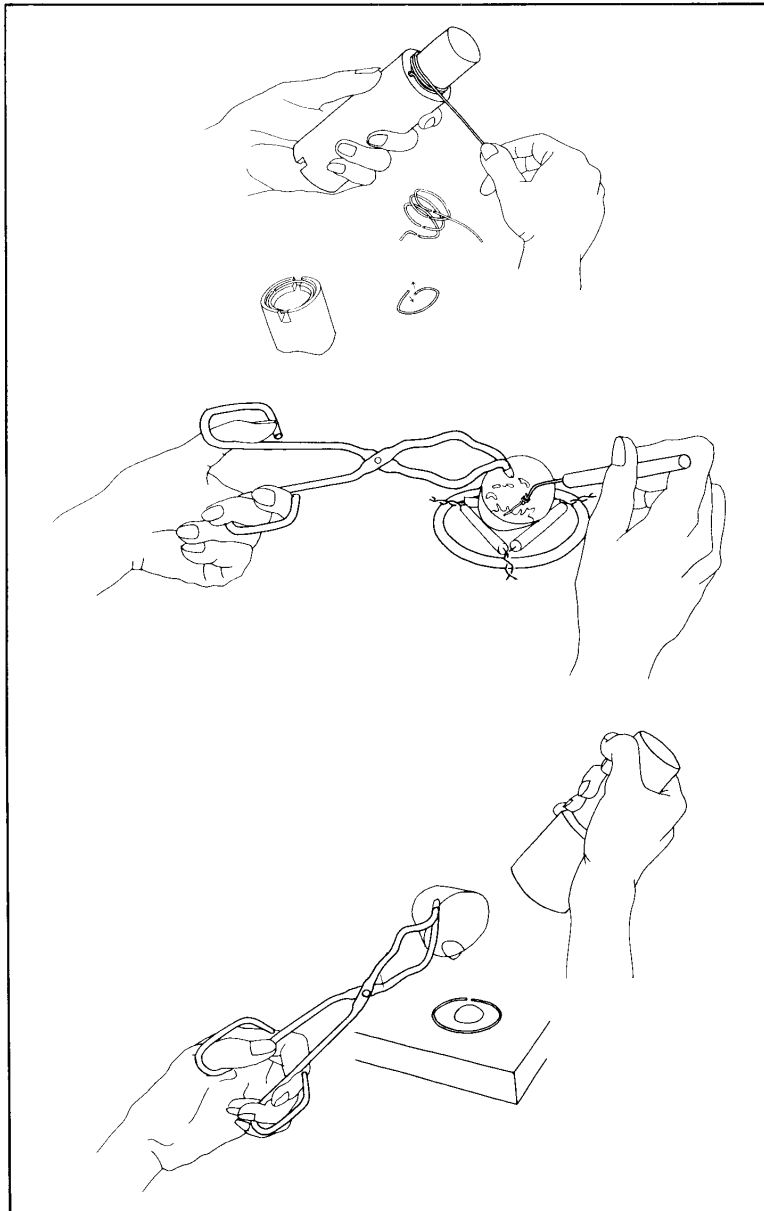
The reproducibility of the fusing and casting process has been tested with a variety of rocks. The relative standard deviation for silicon analysis of a granite (the most difficult common

rock type to fuse) is 0.3 percent. This measurement was made with stationary specimens although many spectrometers will spin the specimen during analysis.

Silicon is the only element in common rocks for which the imperfection of the preparation method seriously limits the accuracy of analysis. More complete data on precision is given in table 1. In general the two standard deviation confidence limit for specimen preparation is one percent of the amount of the element present. Silicon and aluminium results are low if the melt is not stirred immediately before casting. The discs may be stored for several months in small polythene zip fastened bags.\* They will deteriorate slowly through absorption of moisture and carbon dioxide from the air. Fingerprints cause a dramatic increase in the potassium and phosphorous results.

Fig. 1.

Illustrations of important points in the specimen preparation. Top: preparing the rings and testing them for size. Middle: stirring the melt. The sticky appearance of the melt indicates that fusion is incomplete. Bottom: the casting process.



### THE PERMANENT STANDARD

The instrument is calibrated by using synthetic standards to imitate a variety of typical rock compositions. These discs are chemically too unstable to use as monitors of instrument drift. A more robust secondary standard is permanently installed in the first of the four specimen holders of the spectrometer. All X-ray counts on the other three specimens are corrected for the instrument drift revealed by the count on this standard.

This secondary standard must be hard and resistant to the chemicals in sweat, soap and detergents. We use a thin layer of vitreous enamel recessed slightly within a copper disc. The ingredients for the enamel are given in table 2 which also includes a recipe for a base enamel suitable for spiking with trace elements. The components are well mixed and melted together at 1200°C in a gold plated platinum crucible. The melt is cooled, cracked out of the crucible, ground up and remelted. This process is performed twice. The final homogeneous glass is finely ground and spread thinly over the recess in the copper disc. The disc is heated over a gas burner until the enamel softens and adheres to the copper. Another layer of powder is applied and the heating is repeated until about half a millimetre of enamel has been deposited on the copper. A reference number may be embedded within the enamel by writing upon an intermediate layer with a suspension of titanium dioxide in water.

This standard is hard and very resistant to dilute acids and alkalis. Standards made in this laboratory have endured repeated handling and cleaning over two and a half years without any change in X-ray yield. The slight recessing of the enamel within the copper disc preserves the surface against abrasion.

The count rates from this standard should be high, to reduce the errors caused by counting statistics, but they should not be so high that the instrument responds differently to the signals from the standard and from a typical specimen. The standard recipe given in table 2 satisfies these requirements for the Philips PW 1212 spectrometer with a silver target operating at 1600 W (see table 4).

\* Obtainable from Supreme Plastics Co., Roeder House, Vale Road, LONDON, N.4.

TABLE 1

Precision of the calibration and of specimen preparation

	Repeated analysis of a single disc over a period of six months			Repeated fusion of a single rock powder (granite)			Detection limit 3s of background	Zero variation between extreme igneous compositions
	composition %	2s counting error	2s measured: (12 runs)	composition %	2s counting error	2s measured: (10 discs over 2 months)		
MgO	3	0.15	0.2	2	0.1	0.1	0.1	0.25
Al <sub>2</sub> O <sub>3</sub>	12	0.14	0.15	16	0.15	0.2	0.03	0.08
SiO <sub>2</sub>	51	0.23	0.3	60	0.2	0.6	0.02	0.07
P <sub>2</sub> O <sub>5</sub>	1	0.03	0.04	0.5	0.03	0.03	0.01	0.03
K <sub>2</sub> O	1	0.03	0.02	2.8	0.05	0.05	0.01	< 0.01
CaO	10	0.12	0.15	4.5	0.06	0.06	0.01	< 0.01
TiO <sub>2</sub>	2.5	0.02	0.03	1.5	0.02	0.03	0.01	< 0.01
MnO	1.5	0.02	0.02	0.1	0.004	0.005	0.005	< 0.01
Fe <sub>2</sub> O <sub>3</sub>	17	0.11	0.15	1.7	0.02	0.05	0.01	< 0.01

TABLE 2

Vitreous enamel components, parts by weight

	SiO <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	TiO <sub>2</sub>	LiF	BaCO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	LiPO <sub>4</sub>	MnCO <sub>3</sub>
Major element enamel	50	20	5	7	3	3	4	7	5	5	3	2	0.5
Base for trace enamel	50	16	7	13	10	6	(Trace elements: 0.003 g to 1 g of base)						

## THE CHOICE OF TARGET

A silver target is very convenient for rock analysis. The reasons for this are illustrated in Fig. 2. The silver L spectrum provides very good excitation of the elements which most need it - chlorine, sulphur and phosphorus. Excitation of silicon and aluminium is good, magnesium is moderately well excited but the heavier elements, potassium to iron are poorly excited. For these last elements a sufficiently high count rate is given by all common rocks. The poor excitation of calcium is a great advantage because it reduces the interference of calcium K $\beta$  with phosphorus K $\alpha$ . 50% CaO in a rock adds only 0.03% to the true P<sub>2</sub>O<sub>5</sub> concentration under the analytical conditions described below. The poor excitation of potassium results in low excitation of potassium K radiation from the KAP crystal. The performance on magnesium is inferior to that of a chromium target.

Fig. 2 shows that the silver L $\alpha$  gives second order interference on aluminium K $\alpha$  and the silver L $\gamma$  interferes with silicon K $\alpha$ . Both these interferences can be removed by careful discriminator setting. The silver L almost coincides with chlorine K $\alpha$  but does not cause serious interference.

The silver target also gives good excitation of the K spectra of the elements arsenic to molybdenum and of the L spectra of lead to uranium. In this region the peak to background ratio, though not the absolute count rate, is superior to that given by a tungsten target.

## INSTRUMENT OPERATING CONDITIONS

1. Generator voltage and current. The operating conditions, 44 mA at 36 KV are chosen to give the maximum efficiency for magnesium analysis.
2. Diffracting crystals. The KAP crystal covers

the range of elements from magnesium to chlorine and the LiF 200 crystal covers the other elements. A LiF 220 crystal is used for iron but this is merely a convenient way of reducing the count rate - not an analytical necessity.

3. Detector. A gas flow proportional detector is used. The gas is 10% methane, 90% argon. The wire is 24  $\mu$ m diameter stainless steel and the window material is 3.75  $\mu$ m aluminised polyethylene terephthalate. The resolution for iron K $\alpha$  is at best 17% and is allowed to deteriorate to 21% before changing the wire.

4. Discriminator settings. The detector resolution is shown for each element in Fig. 2 and in table 4. The discriminator upper limit is set to eliminate as much as possible of the scattered silver spectrum and the potassium fluorescence. The lower limit is only critical for some elements. It is set to exclude the feeble escape peak of calcium K $\beta$  interfering with phosphorus K $\alpha$ . A narrow window increases the peak to background ratio for magnesium and a wide, unsymmetrical window is needed to accommodate the lower silicon pulse voltage distribution from the standard.

Three different discriminator settings are used in this method. The standard Philips PW 1212 spectrometer is limited to one discriminator setting in automatic operation. A universal setting with a lower limit at 2 and an upper limit at 7 gives fairly good results.

## CALIBRATION

Synthetic standards are used for calibration. The starting chemicals are the pure oxides of iron, titanium, silicon, aluminium and magnesium, the carbonates of sodium, calcium and potassium, disodium hydrogen phosphate and potassium permanganate.

The calibration is built up around a synthetic

mixture which represents the average composition of the rocks which we analyse. For this composition the effect of X-ray absorption is ignored.

For each element a calibration equation is set up, of the form:

$$\text{concentration} = -B + \text{count}/P + (\text{count})^2 \times C$$

B is the approximate background count expressed as a concentration, P is the count per percent for a fixed count time and C is initially zero.

Other standards of different compositions are then measured. For each element the net peak count is corrected for absorption by multiplying it by the ratio of its mass absorption coefficient to the mass absorption coefficient of the central standard. Corrected counts from a variety of standards are used to refine the calibration.

Fig. 2. A simplified voltage distribution of pulses leaving the detector pre-amplifier plotted against  $n\lambda$  (escape peaks are omitted). The area covered by horizontal lines represents the silver L spectrum scattered by specimen and crystal and the potassium K spectrum generated within the KAP crystal. The striped lozenges represent lines from the silver target. Only the K $\alpha$  lines of the elements in the specimen are shown.

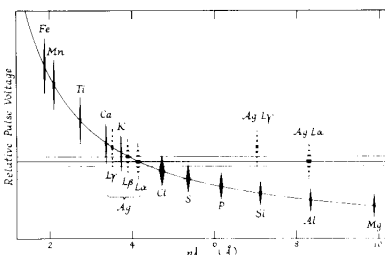


TABLE 3

Performance of the absorption correction and analyses of U.S.G.S. standard rocks. Low magnesium results are corrected for background variation.

Central standard composition	Synthetic mixtures: The concentration is followed by the error of the X-ray analysis. Average of two discs.											U.S.G.S. standards (average of 2 discs)							
	G 2	GSP 1	AGV 1	BCR 1	PCC 1	DTS 1													
SiO <sub>2</sub>	57	40	-0.3	46	0	90	-0.1	20	-0.3	10	-0.1	10	+0.02	69.2	67.4	59.3	54.3	42.0	40.4
TiO <sub>2</sub>	2	0	0	1	+0.01	0.5	+0.02	0	0	0	0	0	+0.01	0.50	0.67	1.08	2.30	0.01	0.01
Al <sub>2</sub> O <sub>3</sub>	15	2	+0.02	25	0	3	-0.04	8	+0.05	60	-0.2	5	+0.02	15.2	15.0	17.0	13.6	0.8	0.30
Fe <sub>2</sub> O <sub>3</sub>	9	8	-0.03	10	+0.1	3	-0.1	15	-0.1	20	-0.05	5	-0.14	2.62	4.21	6.69	13.4	8.27	8.76
MnO	0	0	0	0	0	0	0	0	0	0.7	+0.05	0	+0.01	0.03	0.38	0.10	0.19	0.13	0.13
MgO	7	50	0	1	-0.07	1	+0.04	20	+0.4	4	+0.1	80	-0.5	0.8	1.0	1.5	3.6	43.6	49.7
CaO	7	0	+0.02	10	-0.04	2	+0.02	20	0	5	+0.05	0	+0.05	1.93	2.05	4.97	7.01	0.56	0.14
K <sub>2</sub> O	3	0	0	7	-0.1	0.5	0	0	0	0.4	+0.04	0	0	4.42	5.49	2.94	1.72	0.00	0.00
P <sub>2</sub> O <sub>5</sub>	0	0	0	0	+0.01	0	-0.03	10	-0.15	0	0	0	-0.01	0.11	0.26	0.49	0.37	0.00	0.00

TABLE 4

Instrument operating conditions, Philips PW 1212 spectrometer

Oxide	Collimator	Crystal	Resolution %	Discriminator Limits	Count time seconds	Count per percent	Count on standard
MgO	Coarse	KAP	36	3	7	200	40000
Al <sub>2</sub> O <sub>3</sub>			33	3	7		200000
SiO <sub>2</sub>			29	2.2	7		2000000
P <sub>2</sub> O <sub>5</sub>	Fine		26	3.25	6.75		25000
K <sub>2</sub> O		LiF 200	21	3	7	20	80000
CaO			21	3	7		60000
TiO <sub>2</sub>			19	3	7		100000
MnO			17	3.25	6.75		40000
Fe <sub>2</sub> O <sub>3</sub>		LiF 220	17	3	7		15000

Accurate zero points are found by using a set of standards from which each element in turn is omitted. Only the silicon, calcium and iron calibrations require the constant C.

When specimens of unknown composition are analysed an approximate composition is found from the calibration equation. The difference from 100% is attributed arbitrarily to sodium oxide and then the mass absorption coefficient of the glass is calculated for each characteristic X-ray. The concentration is then multiplied by the ratio of the specimen absorption coefficient to the central standard absorption coefficient. This improved result is refined by a second absorption correction.

The validity of this simplified absorption correction which ignores absorption of the primary beam, is demonstrated by the results from synthetic mixtures quoted in table 3.

The accuracy of the method is shown by the analyses of the USGS standards also given in table 3.

Rocks of unusual composition can be matched by synthetic mixtures to test whether further slight corrections are necessary. Such rocks may also need a measured background. The purity of each batch of flux should be tested by making a disc from the flux alone.

#### ANALYSIS OF ROCKS CONTAINING VOLATILE COMPONENTS

Carbonate rocks and rocks with a high combined water content are analysed by dissolving the rock in the usual way. The crucible with its charge is then cooled and the weight loss is measured. Sodium tetraborate is added to compensate for this weight loss and the crucible

charge is reheated, mixed and cast in the usual way.

The absorption correction must be altered so that the difference between the total of measured oxide concentration and 100% is attributed to sodium tetraborate.

#### ANALYTICAL PROCEDURE

The instrument operating conditions are given in table 4.

Conditions common to all elements are the silver target operated at 44 mA and 36 KV, a vacuum path for all X-rays and a gas flow proportional detector. A potentiometer geared to the spectrometer maintains a constant peak pulse voltage for every element and the discriminator settings listed in table 4 refer to a peak pulse voltage of 5.

The X-ray intensity of the K line of each element in the specimen is measured and corrected for the instrument drift measured by the enamel disc. No background measurement is necessary unless the rock composition varies greatly from the central standard or very small quantities of an element are to be measured.

The count time is divided into two sessions so that the instrument stability can be checked. In effect the entire analysis is performed twice.

A computer program compares the drift corrected counts on each cycle and prints the number of times the square root of the average count divides into the difference between the two. If this number exceeds 5 there is a high probability that the analysis will err outside the limits imposed by counting statistics. This precaution has proved useful in detecting intermittent sources of interference and machine error.

Since all the abundant rock forming elements except sodium are analysed in a single run the punched tape output of counts can be processed automatically to give absorption corrected concentrations.

#### ANALYSIS OF OTHER LIGHT ELEMENTS IN ROCKS

Sodium can be analysed by using a flux consisting of six parts by weight of lithium tetraborate with one part of lithium fluoride, 0.8 g of rock are fused with 1.6 g of this flux and cast in the usual way. The X-ray yield is about 700 counts per percent per 200 seconds. The inter element effects are greater than with the usual fusion. Furthermore since only one element is analysed an automatic absorption correction is not possible. In this laboratory therefore sodium is analysed by flame photometry.

Sulphur is lost from the fusion when it is performed over a flame. Under the oxidising conditions in an electric furnace sulphur is retained in the melt. The X-ray yield is 7500 counts per percent per 100 sec.

Chlorine is steadily lost from the melt under all conditions.

The KAP crystal is not ideal for analysing chlorine and sulphur because of the potassium fluorescence. Recently a rubidium hydrogen phthalate crystal has been introduced which greatly improves the spectrometer performance for these elements.

Chromium can be analysed in the glass discs although excitation by the silver target is poor. The yield is 300 counts per percent per 20 seconds and the detection limit for this count time is 0.07%. Rocks containing abundant chromite are difficult to fuse but even pure chromites can be dissolved by increasing the sodium carbonate concentration in the flux and fusing in a furnace at 1250°C. A suitable mixture is 0.3 g chromite, 0.8 g Na<sub>2</sub>CO<sub>3</sub> and 3.4 g Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. Mixtures with a greater concentration of sodium carbonate will not form a glass.

#### REFERENCES

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G.W. Morey and H.E. Merwin, (1936) Phase Equilibrium Relationships in the Binary System, Sodium oxide-Boric oxide, J. Am. Chem. Soc., 58, 2248-2254.

**Addendum to Philips Analytical Equipment Bulletin FS35**

**Major element rock analysis by X-ray fluorescence. T. Padfield & A. Gray.**

Errors and omissions:

1. The flux recommended for sodium analysis gives off toxic fumes when heated.
2. The crucible is a 5% gold-95% platinum alloy.
3. A minimum dilution of seven parts of flux to one of rock is necessary to ensure that limestone forms a homogeneous glass.
4. Additional data, for carbonate rocks, to add to table 3:

SiO <sub>2</sub>	1.5	-0.03	5	-0.15
TiO <sub>2</sub>	0	0	0	-0.01
Al <sub>2</sub> O <sub>3</sub>	1.7	-0.05*	1.7	+0.03
Fe <sub>2</sub> O <sub>3</sub>	1	-0.04	2	-0.05*
MnO	0	0	0	0
MgO	20	-0.1*	0	0*
CaO	30	-0.2	50	-0.2
K <sub>2</sub> O	0	0	0	0
P <sub>2</sub> O <sub>5</sub>	0	0	0	+0.03

\* Corrected for background variation

5. Acknowledgements. We are grateful for help from Dr. G. Hornung, Mr. C.R. Neary and Mr. D. Greenbaum.