

THE ANALYSIS OF RUBIDIUM IN LOW POTASSIUM THOLEIITES
BY XRF-SPECTROSCOPY

by

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February 1978

INTRODUCTION

The low Rb concentration of low potassium tholeiites (frequently below 5 ppm) makes the whole rock analysis of the element by XRF spectroscopy unfeasible. To overcome this, a simple separation of the alkalis followed by precipitation of the tetraphenylborates of K and Rb (Volborth, 1969) was used to prepare specimens compatible with the X-ray method. The method is based on the similar solution chemistry of the K and Rb ions.

A sample of known K content is dissolved in H_2SO_4/HF mixture and the silica separated as the tetrafluoride along with evaporation to dryness. The basic oxides are precipitated by saturation of the dissolved residue with calcium carbonate leaving the alkalis and Mg in solution (Hillebrand & Lundell, 1953). After filtration K and Rb are precipitated from the filtrate as the tetraphenylborates.

The precipitate is collected on a filter paper, fixed with cellulose resin and irradiated. The radiant intensities of K and Rb is compared with intensities from samples of known K/Rb ratio.

The method is not improved by strictly quantitative separation of the alkalis and quantitative collection of the precipitate, since the solution chemistry of K and Rb is sufficiently similar to preserve the K/Rb ratio of the sample throughout the procedure. Rb can simply be considered as impurity in the potassium tetraphenylboron precipitate. The quantity of sample used needs not to

be exactly known as long as the amount of K is sufficient for sample preparation (5-10 mg as K_2O). The K concentration of the sample has, however, to be known exactly, since the element serves as an internal standard and carrier for Rb through all steps of the analytical procedure.

The precision of the method is determined by counting statistics of the Rb-line and its background. Above 0.5 ppm Rb at intermediate K/Rb ratios relative standard deviation is better than 10 per cent. The accuracy of the method depends on standardization and accuracy of the K-determination. The analytical range of the method depends on the K/Rb ratio of the specimens and the quantity of K separated in the analytical procedure. Fig. 2 shows a calibration graph for the K/Rb ratios with a linear range between 100 and 1500. Although the method is interference free, it has to be noted that large monovalent ions such as Cs^{+1} , Tl^{+1} and NH_4^{+1} form insoluble tetraphenylborate. The presence of these ions in the filtrate containing the alkalis is of limited interest unless the method is to be extended to cover the analysis of Cs and Tl.

ANALYTICAL PROCEDURE

Separation

A sample of rock powder of known K concentration containing 5-10 mg K is placed in a 100 ml evaporating basin (teflon or platinum). Sulfuric acid (5 ml, 1:3) is added and the basin rotated to form a slurry of its content. Hydrofluoric acid (5 ml, 40%) is added with caution followed by evaporation to the fumes of sulfuric acid. The basin is cooled and additional 2 ml of hydrofluoric acid evaporated to fumes of sulfuric acid. The basin is cooled and 5 ml of nitric acid added and mixed with the residue.

The content of the basin is evaporated to dryness, cooled to room temperature and 50 ml water added. The residue is dissolved by boiling for 15 min. Precipitation of ferric hydroxide can occur at this stage, indicating effective removal of sulfuric acid in the last evaporation.

The solution is made basic to bromocresol green indicator by addition of calcium carbonate in suspension or as dry powder. The bulky precipitate is boiled for 10 min., allowed to settle and filtrated into 100 ml beaker through close textured filter paper and washed three times with 3 ml of water saturated with calcium carbonate.

The filtrate is acidified to the bromocresol green indicator with few drops of 12 M HCl. The filtrate is evaporated to approx. 25 ml and 1 ml 6 M HCl added.

The beaker is cooled in ice/water bath and 5 ml 5% solution of sodium tetrphenylborate added. The beaker is swirled few times to mix its contents and the tetrphenylborates of the heavy alkalis allowed to settle in the cool for half an hour.

Samples very low in K (less than 0.1%) are preferentially dissolved in two basins and their filtrates combined during the evaporation stage.

Specimen preparation

A close textured filter paper of proper size to fit the specimen holder of an X-ray spectrograph is placed on a fritted glass disc of the same size (Fig. 1). The disc is connected to a vacuum line and the filter paper washed with 2 ml water saturated with potassium tetraphenylboron.

The supernatant liquid of the tetraphenylboron precipitate is decanted and the remaining slurry transferred dropwise to the filter paper to form coating on its surface. The precipitate is washed by dropwise addition of 2 ml of the wash solution. The filter paper is transferred with caution to a dry sheet of porous paper and allowed to dry for an hour.

Few drops of thin cellulose resin is placed on a flat surface. The filter paper is transferred to the resin and allowed to absorb it until the coating on its surface is impregnated. This stage has to be carried out with utmost care since the coating is light and brittle and is easily flaked off the paper. The tetraphenylborates are very soluble in most organic liquids and form a resistant film on the paper when the impregnated resin is allowed to dry, whereupon the specimen is ready for analysis.

Preparation of standards

Solutions of spec. pure K and Rb compounds are prepared and stock solutions of known K/Rb ratio prepared. In most cases K/Rb ratio between 200 and 1500 covers the analytical range. Aliquots of the stock standard solutions containing proper amount of K are carried through the procedure in order to eliminate reagent impurities.

The K compound used to prepare standard solution have to be tested for its Rb impurities by analysing its tetraphenylboron at the ultimate sensitivity of the X-ray equipment used.

Counting techniques

The specimens are irradiated in vacuo using tungsten X-ray tube. The $K-K_{\alpha}$ line is resolved on PET analysing crystal (or its equivalent) and counted twice for 20 sec using flow counter and pulse height discrimination. Background correction proves to be of limited value for the K analysis. The $Rb-K_{\alpha}$ line is resolved on LiF analysing crystal and counted twice for 100 sec with scintillation counter using pulse height discrimination. The Rb radiant intensity measured is corrected for background radiation by counting the radiant intensity one degree (two theta) on either side of the Rb line. This background value is corrected for the intensity slope of the continuous radiation from pure K tetraphenylboron and subtracted from the radiant intensity measured for the Rb line.

The measured intensity of K and the net intensity of Rb are normalized to a reference sample measured along with all batches of unknown samples and standards. A stable reference sample can be prepared by fusing sodium tetraborate containing proper amounts of K and Rb to a glass disc fitting into the specimen holder of the spectrograph.

The ratio of the normalized intensities of K and Rb are plotted against the known K/Rb ratio of the standards. The resulting calibration line (Fig. 2) is used to compute the K/Rb ratio of the unknowns or their Rb concentration.

In table I, column A, Rb-values obtained by single run on few reference samples are listed. Column B shows the values compiled by Flanagan (1973).

REFERENCES

- Flanagan, F.J., 1973. 1972 values for the international geochemical reference samples. *Geochim. Cosmochim. Acta* 37, pp. 1189-1201.
- Hillebrand, W.F. & Lundell, G.E.F., 1953. *Applied Inorganic Analysis*. John Wiley & Sons, Inc., New York.
- Volborth A., 1969. *Elemental Analysis in Geochemistry*. Elsevier, New York.

TABLE I

| | A | B |
|--------|-----|------|
| G-2 | 168 | 168 |
| AGV-1 | 67 | 67 |
| BCR-1 | 45 | 46.6 |
| GM | 264 | 250 |
| BM | 6.8 | 12 |
| BHUO-1 | 9.9 | |

TEXT TO FIGURES

Fig. 1. Filter assembly for specimen preparation.

Fig. 2. Calibration curve showing the normalized K/Rb count ratio plotted against the K/Rb ratio of standard samples. The linear range extends to K/Rb = 1500.

The analyses were performed on Philips 1540 vacuum spectrograph using W-tube at 30 kV, 15 mA for K and 50 kV, 20 mA for Rb.

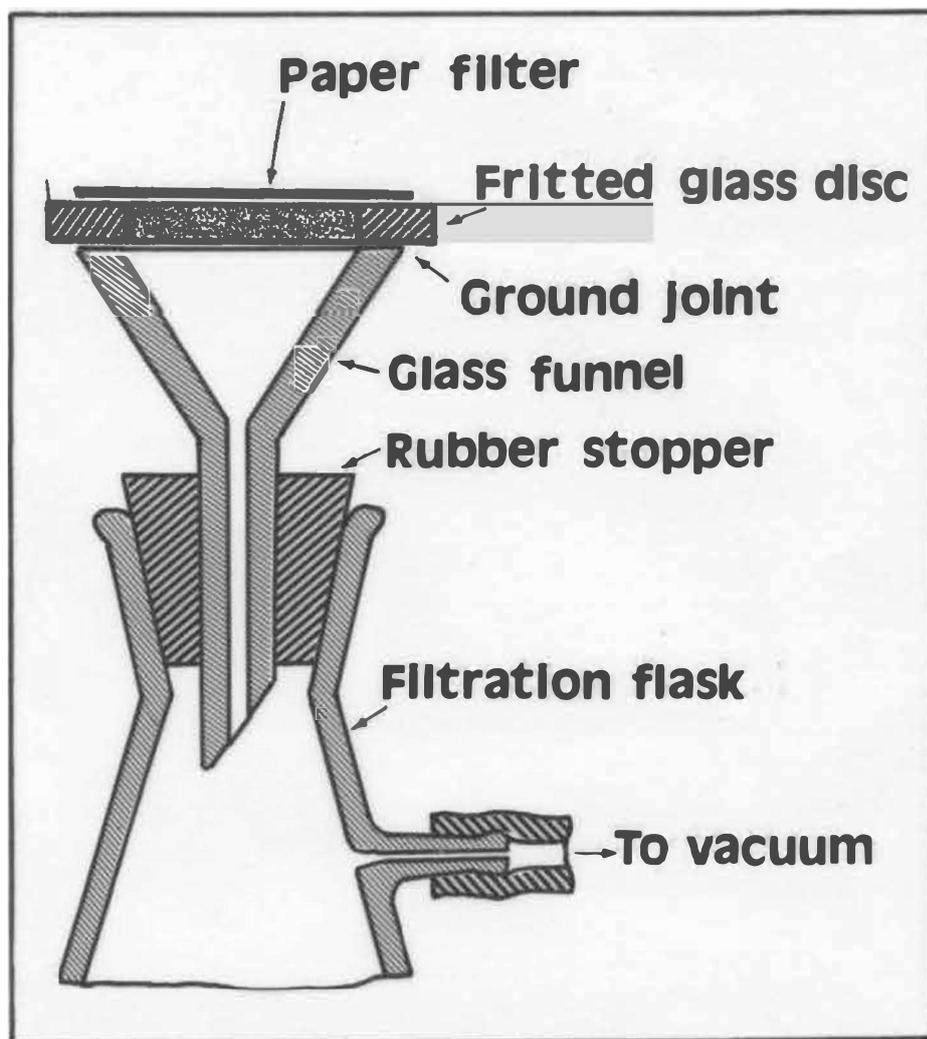


FIG1

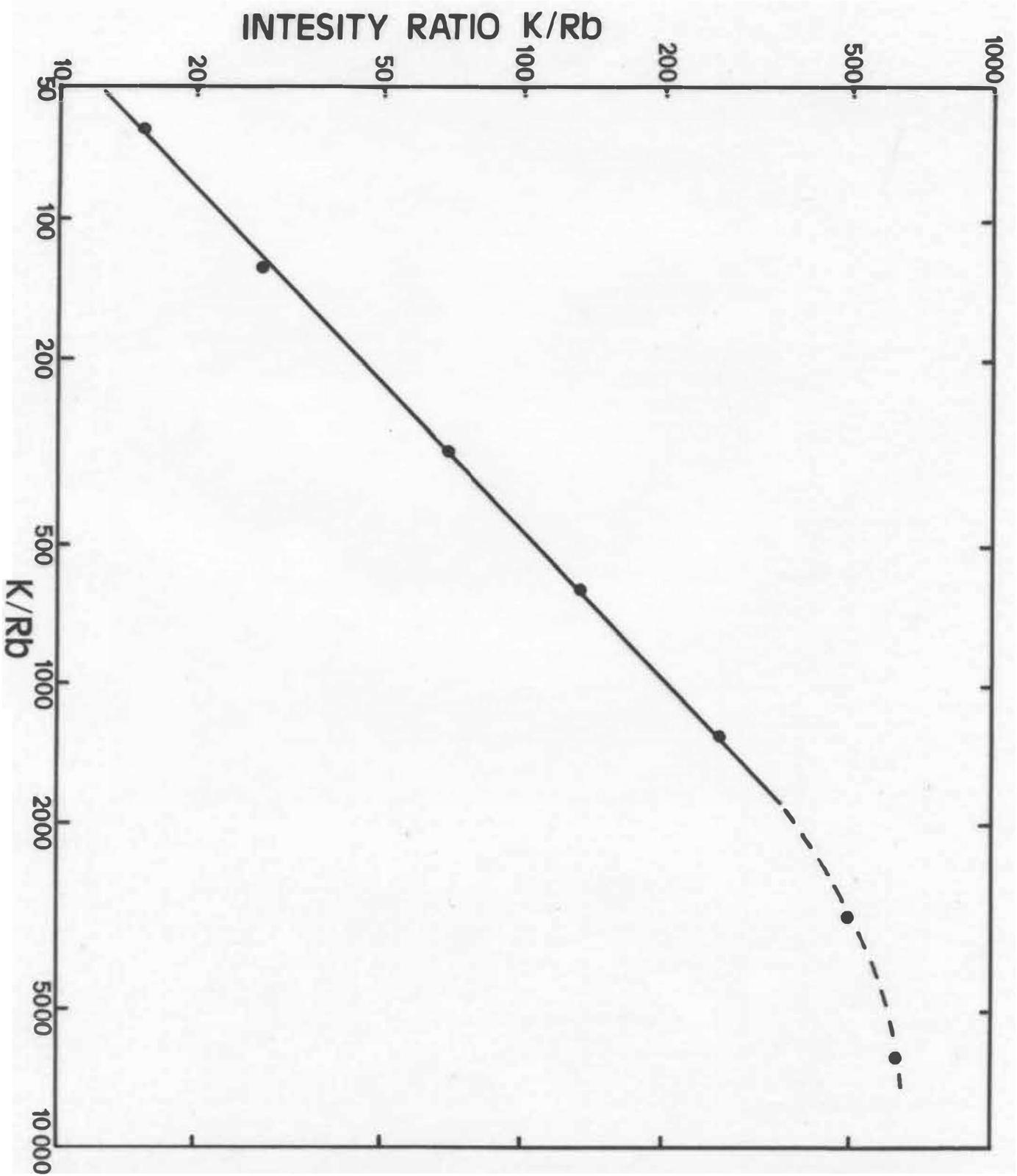


FIG 2