RADIOMETRIC DETERMINATION OF POTASSIUM

IN SILICATES

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INTRODUCTION

Recent developments in the dating of rocks by the potassium-argon method have resulted in a renewed interest in analytical techniques for the determination of potassium in silicates. Replicate potassium-argon analyses yield A^{40}/K^{40} ratios with an average difference of about $\pm$ 3% (Baadsgaard, et. al., 1957; Long and Kulp, in press). Surprisingly enough the deviations are about equal for both the potassium analyses in which potassium is present in amounts usually from 5% to 10%, and for the argon analyses in which argon is present in amounts of a few p. p. m. or much less.

Winchester (1959) using a radioactive potassium tracer has found potassium yields during hydrofluoric-sulfuric acid digestion of silicate samples to be as low as 88% recovery. He also determined the potassium content of the standard M. I. T. biotite by neutron activation. The neutron activation results, which required no chemical treatment of the sample, were about 4% higher than the average of chemical determinations.

Experiments in this laboratory (Hedge, thesis research in progress) have confirmed Winchester's observation of occassionaly low potassium yields during silicate digestion. Furthermore, the low yields were found by Hedge to be the result of potassium loss, possibly by the physical process of transport on vapor droplets on a microscopic or submicroscopic scale. Russian workers (Levitskii, 1953) have found both potassium and sodium loss during acid digestion, and they have investigated the effect of the presence of different anions in solution on the extent of loss. The effect seems to be greater for sodium than for potassium. They conclude that the process resulting in loss is of a physical rather than a strictly chemical nature. A double crucible technique is now used in this laboratory to condense volatiles on an outer cooler surface, thus entrapping any escaping potassium.

Because of the difficulties encountered with chemical techniques for the analysis of potassium and the need for precise data, it may be of particular interest at this time to describe a radiometric method for potassium analysis which requires no chemical preparation. The method to be described was developed at Columbia University (Damon and Kulp, 1958, p. 435) and further tested in this laboratory. However, the technique has not heretofore been adequately described.

Radiometric Methods for Potassium Determination

The reader may refer elsewhere (Strominger, et. al., 1958) for the details of the decay scheme of radioactive potassium-40. Natural potassium contains about 119 micrograms of the radioactive isotope per gram of potassium. The radioactive isotope, potassium-40, decays with a half life of 1.3×10^9 years by both competitive beta emission and electron capture. The electron capture is followed by deexcitation resulting in the emission of a gamma ray of about 1.46 mev. energy. Out of every 100 transmuting K^{40} atoms, approximately 11 decay by electron capture to A^{40} followed promptly by gamma emission and approximately

89 decay by 1.33 mev. beta emission to Ca^{40}. Thus, for a pure potassium salt, measurement of either the beta ray activity or the gamma ray activity can be used to determine the potassium content. Gaudin and Panell (1948) used beta counting to determine potassium in sylvite. Damon (1950) has used the gamma transition for logging well cores. Wendt (1955) made use of the radiometric method for determining potassium underground in salt deposits. The radiometric method has also been applied to the rapid analysis of potassium in solution (Dresia and Beckmann, 1957).

The radiometric measurement of potassium in silicates is complicated by simultaneous beta and gamma emission from the uranium and thorium radio-active series. Serdyukova and Kapitanov (1958) overcame this difficulty by simultaneous radiometric determination of uranium, thorium, radium and po-tassium. This required the measurement of four parameters: (1) total alpha activity, (2) total beta activity, (3) total gamma activity, (4) selected pulse height analysis of a predetermined portion of the gamma ray spectrum. A set of four simultaneous equations were then solved for the four components. The method is complex, the various terms in the equation have both very large and very small coefficients and, as yet, this method has not been subjected to con-vincingly critical checks.

The method herein described is simpler and, as will be shown, it has been thoroughly checked against independent chemical analysis. The method involves alpha and beta counting of a powdered sample. The beta count may be taken with or without a 5 mil aluminum absorber to eliminate the soft beta particles from rubidium-87 (Rb^{87} interference is usually negligible). The beta count is then reduced by an empirical correction for the betas resulting from the uranium and thorium series. The alpha count, which is due only to the uranium and thorium series, determines the magnitude of this correction. The resulting beta count is compared with a standard sample of potassium to determine the potassium content.

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Experimental Techniques for
alpha-beta Method

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The sample is washed in distilled water to eliminate surface contamination and then ground until the entire sample can be passed through an 80 mesh screen. It was found by trial and error that a sample ground to this fineness can be re-producibly packed to a high bulk density. Coarser samples can be used providing that they are carefully and tightly packed. An infinitely thick source is used to eliminate the dependence of alpha and beta count on sample packing and to give the highest possible count.

For beta counting, the sample is packed into a cylindrical planchette of inner dimensions 1.91 cm. in diameter and 0.47 cm. in depth. The sample thickness for silicates is approximately 650 mg./cm^2. The sample is then counted in a Volchok-Kulp (1955) low level beta counter with anti-coincidence ring and lead shielding. An Anton model 1007-T pancake geiger counter is used. The counting window is 2.86 cm. in diameter and 1.4 to 2 mg./cm^2 thick. The background of the counter averages 1.1 c.p.m.

Potassium dichromate was chosen as a counting standard (Bureau of Stan-dards chemical standard 136-A) because its density (2.69 g/cm^3) is about the same as the silicate unknowns and also because it is not deliquescent. The standard count is about 23 c.p.m. above background count shielded (5 mil Al), and about 30 c.p.m. unshielded. The standard contains 26.57% potassium. Thus 1% potassium is sufficient to approximately double the count over background count. This high sensitivity allows potassium to be determined in amounts down to 1 part per thousand.

An alpha counter modified after the type used by Kulp, Holland and Volchok (1952) is used. The counting tube is a 5 inch Dumont 6364 photomultiplier with a thin, continuous layer of Dupont No. 1101 phosphor on the face of the tube. Any other ZnS phosphor activated with silver will do. The background of the counter is about 35 c.p.h. A planchette 12.3 cm. in diameter and 2.4 mm. deep is

employed. A sample containing 1 p. p. m. uranium will approximately double the count over background count. The planchette is filled with dunite to obtain the background count both for beta and alpha counting. Dunite has about the lowest radioactivity of any natural material.

The equation for the potassium content of the unknown is as follows:

$$K_x = \frac{N_x}{N_s} \; K_s - CN_a$$

where K_x is the potassium content of the unknown and K_s is the potassium content of the standard; N_x, N_s and N_a are the beta count due to the unknown and standard and the alpha count respectively; C is the empirical correction factor for uranium and thorium series beta activity. It is 0.005% K per alpha per hour for unshielded samples and 0.004% for shielded samples. The uncertainty in C is approximately ± 0.0005. N_s must be determined separately for both shielded and unshielded samples. The correction for igneous rocks averages about 25% of the total equivalent potassium content. However, the correction for clean mineral separates is much less; for example, 10.97% for the M. I. T. biotite standard (B3203). This is a result of the well known fact that a large part of the uranium and thorium in igneous rocks is interstitially located, whereas separated and cleaned minerals have a much lower uranium and thorium content.

The effect of the presence of rubidium in the unshielded unknown is about the same as for potassium, i.e., 1% Rb is approximately equivalent in beta count to 1% K. The soft rubidium betas are completely eliminated by the 5 mil aluminum absorber.

RESULTS AND DISCUSSION

The alpha-beta radiometric method has been checked against various gravimetric methods as well as against flame photometry and the stable isotope dilution technique. The data for National Bureau of Standards Rock Standards and a Pb-Ba standard are shown in Table 1. Table 2 presents the results of a comparison of radiometric analyses and other methods for a number of silicate rocks and minerals.

The average difference of the radiometric values from other methods for samples containing greater than 1.5% potassium is approximately 2.7%. This is about equal to the average standard deviation computed from statistical considerations alone. On the other hand the error rises rapidly for samples containing less than 1.5% potassium. This is in part caused by counting errors but must also be due in large measure to the decreased accuracy of the comparison methods as well.

Taking the data as a whole, there is no evidence of a systematic difference between the different methods. However, as mentioned previously, in individual cases systematic errors do appear to be present. For example, the M. I. T. standard biotite has been analyzed six times in this laboratory by the flame photometric method using a lithium internal standard. In the first three analyses, the digestion was carried out in a covered platinum crucible using hydrofluoric and perchloric acids and a temperature of approximately 100°C. The vapor from these digestions was passed through a polyethylene funnel and tubing into a water trap and a small, but measurable, amount of potassium was found to have collected in the cool water. The experiment was repeated without sample for a blank check and in this case, no potassium was detected. Three more replicate M. I. T. standard biotite samples were run placing the platinum crucible inside a larger, covered nickel crucible to condense the less volatile vapors. The lids of the nickel crucibles were sufficiently good radiators to keep them at a temperature below 45°C. Salts containing potassium collected on the under side of the lids of the nickel crucibles. However, potassium could no longer be detected in the water trap. The salts from the lids of the nickel crucibles were returned to the original solutions and, in this manner, three values averaging 7.80% potassium were obtained. The average of the three single crucible results was 7.40%.

The alpha-beta radiometric method for potassium determination is simple and requires a minimum of labor when compared with chemical methods. The most laborious step is the sample preparation, whereas the packing of samples in the planchettes requires the most care. The method has the added advantage that it requires no wet chemistry and does not destroy the sample. One disadvantage is that the correction factor C assumes radioactive equilibrium within the uranium and thorium series and normal ratios of uranium and thorium (U/Th~3). It may be of interest to consider extreme hypothetical cases involving failure of these assumptions. For example, consider the very improbable case in which a granite has lost its entire content of radon and its decay products. For an otherwise typical granite with a potassium content of 4.00% and a 25% correction for uranium and thorium betas, the error caused by this disequilibrium would result in an apparent potassium content of 3.88% or a -3% error. In the second, highly improbable, hypothetical case assume that the above granite contains no thorium and that the entire alpha count is from the uranium series. In this case, the apparent potassium content would be 3.96% or a -1.6% error. Thus the maximum uncertainty introduced by CN_a is about 3% for granite and about 1% for pure potassium bearing minerals such as biotite and perthite. It should be pointed out that the alpha activity determination is a useful geochemical parameter in its own right because both uranium and thorium tend to be concentrated in felsic magmas and residual fluids.

In conclusion, it may be stated that alpha-beta radiometric method for determining potassium has been found to be very reliable and apparently as precise as the methods used for comparison.

ACKNOWLEDGEMENT

TABLE I

Radiometric K Measurements for National Bureau of
Standards Rock Standards

Sample Description	Radiometric Determination		Gravimetric Determination
	without Al absorber %(K+Rb)	with Al absorber %K	(Nat'l. Bur. of Stds.) % (K+Rb)
Chelmsford granite	4.61	4.47	4.61
Pb-Ba glass	6.90	----	6.91
Milford granite	3.39	----	3.32
Gabbro-diorite	1.53		1.29
Columbia R. basalt	0.88} 1.07}	0.88	0.82
Triassic diabase	0.46		0.48

TABLE 2

Comparison of K Analyses by Counting and Other Methods

Sample description	Radiometric method %K	Comparison method %K
Black Hills feldspar	11.8	11.8 (L)
McKinney feldspar	11.7	11.0 (G)
Brown Derby feldspar	11.1	10.4 (L)
Wind River Canyon feldspar	9.65	9.39 (G)
M.I.T. Standard Biotite	7.71	7.40 (f.p.s.) 7.80 (f.p.d.)
Lake Kivu leucitite	4.83	5.20 (i.d.)
Cat Mt. rhyolite	4.24	4.41 (f.p.s.)
Wilburforce antiperthite	3.39	3.73 (L)
Atascosa Mts. basalt	1.04	0.98 (f.p.s.)
Beryl Mt., N.H. beryl	0.35	0.39 (L) 0.42 (G)
Hawaiian Olivine basalt	0.24	0.35 (i.d.)
Stillwater plagioclase	0.17	0.12 (i.d.)

L= determined by Ledoux and Co. using a wet chemical method (Kallman, 1956).

G= Analyzed in the University of Minnesota Rock Analysis Laboratory by the L. Lawrence Smith fusion method (Goldich and Osland, 1956).

i.d. = isotope dilution analysis by P. W. Gast (1957), Lamont Geological Observatory, Columbia University.

f.p.s. = flame photometric analysis in this laboratory using internal lithium standard (Hedge, 1959).

f.p.d. = analyzed as above using double crucible technique.

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