Radiometric Determination of Small Amounts of Potassium

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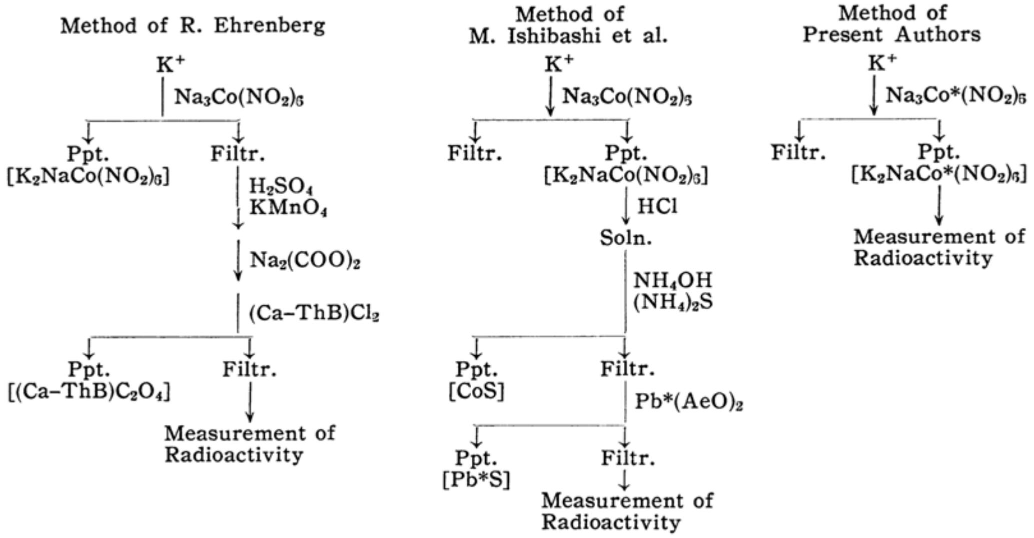
(Received May 29, 1953)

Sodium cobaltinitrite, the well-known reagent for both the gravimetric and the indirect colorimetric determinations of potassium⑴, was used in the radiometric determination of potassium by R. Ehrenberg⑵ and M. Ishibashi et al⑶. As it was difficult to obtain artificial radioactive substances, they were obliged to use natural radioactive indicators. Therefore, tedious chemical procedures were necessary before beginning the measurement of radioactivity. Their methods are schematically shown in Table I.

TABLE I SCHEMES OF RADIOMETRIC METHODS FOR POTASSIUM



In recent years, the artificial radio-isotope of cobalt (cobalt-60) is easily obtainable from the Atomic Energy Commission of U.S.A., so the present authors investigated a simplified radiometric determination of small amounts of potassium using radioactive sodium cobaltinitrite labelled with cobalt-60 as precipitant.

(1) Determination of (8∼0.3) mg. Potassium—Various amounts of the standard solution of recrystallised potassium chloride are taken and radioactive $K_2NaCo^*(NO_2)_6$ is precipitated according to the following procedure.

The relation between the relative intensity of the radioactivity of the precipitate and the amount of potassium taken is investigated.

(a) Preparation of the Radioactive Precipitant I—According to the usual method⑴,⑶ a solution of sodium cobaltinitrite labelled with cobalt-60, $Na_3Co^*(NO_2)_6$, is prepared as the precipitant.

First, the following two solutions are prepared.

Solution (A)	cobalt nitrate	21 g.
	cobalt-60 chloride	about 0.7 mc.
	water	42 cc.
	acetic acid	10.4 cc.
Solution (B)	sodium nitrite	100 g.
	water	150 cc.

Next, the solution (B) is added to the solution (A) and the nitrogen oxide formed by the double decomposition of the salts is expelled by passing the air through the combined solution. Any precipitate formed is filtered off and the filtrate which contains sodium cobaltinitrite labelled with cobalt-60 is used as the precipitant.

In this paper, the precipitant thus prepared will be called the precipitant I.

(b) Procedure—According to the usual method⑴, radioactive potassium-sodium cobaltinitrite,

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1) R. Fresenius u. G. Jander, "Handbuch d. Analytischen Chemie", 3 Teil, Bd. Ia, Julius Springer, Berlin, 1940, p. 172.

2) R. Ehrenberg, *Microchem. Pregl Festschr.*, 61, (1929), *C.A.*, **24**, 2395; *Biochem. Z.*, **197**, 467 (1928), *C.A.*, **23**, 51.

3) M. Ishibashi and H. Kishi, *J. Chem. Soc. Japan*, **57**, 1039 (1936).

$K_2NaCo^*(NO_2)_6$ is precipitated by the precipitant described in (1, a). A definite amount of the standard solution of potassium chloride is poured slowly into a platinum or quartz crucible which contains 5 cc. radioactive precipitant I and 1 cc. of 1N nitric acid. Then some water is added until the total volume of the resultant solution amounts to 16 cc.

After standing over-night, the yellow precipitate of radioactive potassium-sodium cobaltinitrite is filtered on a glass filter and washed with about 20 cc. of 0.01N nitric acid and then with about 10 cc. of 95% alcohol. The washing solution is drained off by suction and the washed precipitate is dried at 110°C. in an air bath for about one hour. After cooling, the radioactivity of the precipitate on the glass filter is measured by a Geiger-Müller counter made by the Nuclear Instrument and Chemical Corporation, U.S.A.

The precipitate obtained from 3.145 mg. potassium is reserved as the standard of the radioactivity and the intensities of the activity of the precipitates obtained from the solutions containing various amounts of potassium are compared respectively with the standard. The relative intensity thus obtained is not affected by the decay of cobalt-60 or the daily variation of the sensitivity of the instrument for the measurement of radioactivity.

(c) Results—Results of the experiments are shown in Table II and Figure 1 and 2.

TABLE II RESULTS OF (1)

mg. K (Taken)	Relative Intensity of Radioactivity
7.863	2.27
6.291	1.82 1.98
4.718	1.58 1.47
3.145	1.00* 0.98
1.573	0.45 0.47 0.48 0.48
1.258	0.37 0.40
0.943	0.28 0.28
0.629	0.16 0.16
0.315	0.04 0.05

(*) Taken as the standard. The activity of the standard is about 1960 c/min. It shows slight variations according to the daily variation of the sensitivity of the counter.

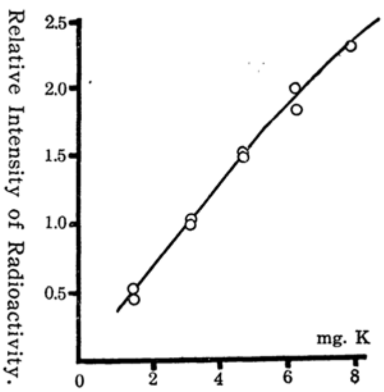

Fig. 1 Working curve of (1)

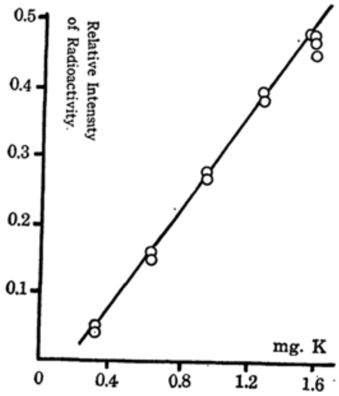

Fig. 2 Working curve of (1)

In Figures 1 and 2, the almost linear relationships between the relative radioactivities and the amounts of potassium taken are shown in a fairly wide range of amounts of potassium, so we conclude that we can determine the amounts of potassium radiometrically according to the above-mentioned procedure, using Figures 1 and 2 as working curves.

(2) Determination of (0.8∼0.16) mg. Potassium—The relation between the relative intensity of the radioactivity of the precipitate formed and the amount of potassium taken is investigated following the same procedure as described in (1, b), and using the precipitant having a stronger specific activity, which is prepared as follows.

For the measurement of radioactivity, the same standard as (1, b) is used.

(a) Preparation of Precipitant II—The precipitant II is prepared from the following two solutions, (C) and (D), in the same way as described in (1, a).

Solution (C)	cobalt nitrate	15 g.
	cobalt-60 chloride	about 4.5 mc.
	acetic acid	7.5 cc.
	water	30 cc.
Solution (D)	sodium nitrite	72 g.
	water	108 cc.

(b) Results—Results are summarized in Table III and the relation between the relative intensity of the radioactivity of the precipitate and the amount of potassium taken is shown in Figure 3. As seen in Figure 3, the deviation of each experiment is larger than in Figure 1 or 2. The working curve of Figure 3 is shaped S, while those of Figure 1 and 2 are almost linear.

TABLE III RESULTS OF (2)

mg. K (Taken)	Relative Intensity of Radioactivity	Mean
0.786	2.00 1.82 1.88 1.86	1.89
0.629	1.48 1.39 1.50 1.54 1.56	1.49
0.472	0.98 0.85 1.11 0.92	0.97
0.315	0.29 0.29 0.34	0.31
0.157	0.05 0.07 0.13 0.16	0.10

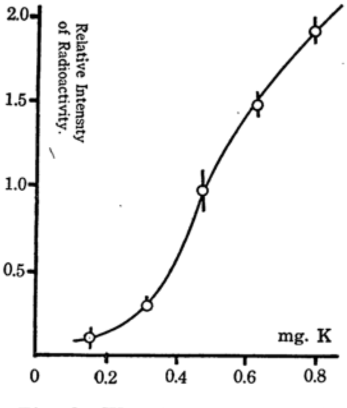

Fig. 3 Working curve of (2)

(c) Application of the Above Method to the Determination of Potassium in Silicate rocks—The determination of potassium contents in two kinds of andesite is tried by the above described radiometric method, combined with the method of J. Lawrence Smith for the isolation of alkali chlorides, using about 200 mg. of each sample. Comparison of the values thus obtained with those obtained by the usual gravimetric method as potassium chloroplatinate is shown in Table IV.

TABLE IV DETERMINATION OF POTASSIUM CONTENT OF ANDESITE

Sample	% K_2O obtained gravimetrically	% K_2O obtained radiometrically
(A)	0.46 0.40	0.39 0.39
(B)	0.40 0.33 0.37	0.32 0.32

(3) Determination of (0.126$\sim$0.0016) mg. Potassium—In the experiments for the minute quantities of potassium, the precipitation and the filteration must be done microchemically, and the precipitant with a much higher specific activity must be used. Further, cautions against the contamination by potassium from glass-wares must be taken.

(a) Standard Solution of Potassium Chloride—The stock solution which contains 1.5010 g. potassium chloride per litre is diluted just before use and a series of dilute standard solutions of potassium chloride is prepared.

(b) Preparation of Radioactive Precipitant III—The precipitant III is prepared from the following two solutions, (E) and (F), in the same way as described in (1, a) in a smaller scale.

Solution (E)	cobalt nitrate	1 g.
	cobalt-60 chloride	about 6.7 mc.
	acetic acid	0.5 cc.
	water	2 cc.
Solution (F)	sodium nitrite	4.8 g.
	water	72 cc.

(c) Procedure—Five drops of the precipitant III and one drop of 1N nitric acid are put into the platinum crucible which contains 0.5 cc. of standard solution of potassium chloride prepared as described in (3, a). After leaving it over-night, the precipitate formed is filtered off with a micro filter-tube[4] and washed with 0.5 cc. of 0.01N nitric acid and then three times with 0.7 cc. alcohol. The washed precipitate in the platinum crucible is dissolved in hot water. The solution is transferred to a glass dish through the filter-tube and evaporated up on a water bath.

The radioactivity of the residue in the glass dish is measured with Lauritsen electroscope, made by the Scientific Research Institute, Tokyo. For the measurement of radioactivity, an arbitrarily selected specimen is used as the standard and the ratio of the intensities of the radioactivity of each specimen and the standard is calculated.

(d) Results—Results are shown in Table V and Figure 6. The relation between the relative intensity of the measured radioactivity and the amount of potassium is linear, so that the quantitative determination of the minute amounts of potassium can be carried out in the procedure described in (3, c).

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[4] E. Beryl Daw, "Quantitative Organic Microanalysis", J. & A. Churchill Ltd., 1937, p. 96,

TABLE V RESULTS OF (3)

mg. K (Taken)	Relative Intensity of Radioactivity
0.0000	0.003
	0.003
0.0016	0.004
	0.005
0.0047	0.023
	0.025
0.0094	0.052
	0.061
0.0236	0.14
	0.12
0.0394	0.23
	0.24
0.0630	0.36
	0.36
0.1260	0.69
	0.70

The activity of the standard is about 347 div./min. It shows slight variations according to the daily variation of the sensitivity of the electroscope.

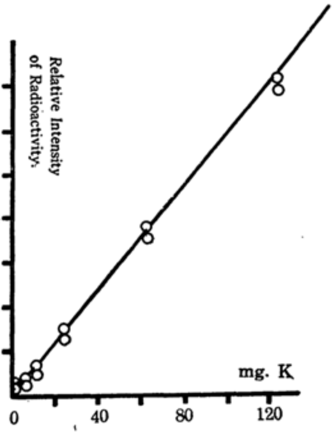

Fig. IV Working curve of (3)

(e) Applications of the Above Method—(i) The potassium contents of two samples of silicate rocks; andesite found in Kurofuyama, ASAMA[5] and the standard sample of diabase sent from the U. S. Geological Survey, W-I[6], are determined according to the following procedure:

About 20 mg. of the powdered sample is treated according to the J. Lawrence Smith method to obtain the total alkali chlorides. The chlorides are dissolved in a little water and treated as (3, c). A platinum or quartz crucible is used as a microbeaker and all filtrations are done with a micro filtertube.

In Table VI, the values thus obtained are compared with those obtained by the usual method. The coincidences are fairly good and we conclude that this method will be effective for the microdetermination of potassium in silicate rocks.

TABLE VI DETERMINATION OF POTASSIUM CONTENT OF SILICATE ROCKS

Sample	% K_2O obtained gravimetrically	% K_2O obtained radiometrically
Andesite (Kurofuyama)	0.85*	0.54
		1.07***
Standard Sample of Diabase	0.78**	0.77***
		0.88***

(*) Value given by I. Iwasaki.
(**) Value reported from our laboratory.
(***) Value obtained by the extrapolation of the working curve.

(ii) The potassium content of the tap water which is supplied to our laboratory is determined in our micro-radiometric method.

The procedure is as follows: About ten grams of the tap water is taken in a platinum crucible and evaporated to about 0.5 cc. on a water bath. After cooling, the evaporate is treated as described in (3, c).

The determinations are done with 10 g. and 15 g. of the water, and potassium with the concentrations of 0.083 and 0.087 millimole per litre are obtained respectively. Although the presence of ammonium ion disturbs the determination, the ammonium content of the sample is estimated to be 0.006 millimole per litre by the colorimetric method, so that our value for potassium should be reliable.

The authors wish to express their sincere thanks to Prof. Sinnosuke Matuura for the facilities accorded to them during this investigation, to Prof. Iwaji Iwasaki for providing samples of andesite and to Mr. N. Kokubu for determining the ammonium content of the tap water.

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[5] I. Iwasaki, *J. Chem. Soc. Japan*, **57**, 1324 (1936).

[6] W. G. Schlecht, *Anal. Chem.*, **23**, 1568 (1951).