Determination of Potassium in Solids and Liquids by Measurement of the Gamma Activity of Naturally Radioactive Potassium-40

WAYNE G. HARRIS, WAYNE V. KESSLER, JOHN E. CHRISTIAN, and ELWYN D. SCHALL

Bionucleonics and Biochemistry Departments, Purdue University, Lafayette, Ind.

A method is described for the analysis of potassium in pure potassium salts and liquid fertilizers based on its gamma activity. The coefficient of variation for repeated measurements on the same sample was about 2% or less for samples with potassium concentrations of 5% or greater. This precision is based on a 2-minute sample counting time. The method cannot be applied to the analysis of all solid fertilizers since some of these contain a radioactive contaminant. The method is applicable to the routine analysis of samples with 5% or greater potassium contents, provided the samples have no radioactive contamination. The time required for analysis is about 10 minutes. Samples with less than 5% potassium could be analyzed by extending the counting time.

POTASSIUM possesses a natural source of radioactivity, K^{40}, with a half-life of 1.29×10^9 years. Potassium-40 decays by two modes, either of which may be used for radiometric analysis. The first mode is beta decay in which a 1.33 m.e.v. beta particle is emitted. This mode accounts for 89% of the decay of K^{40}. The second mode, accounting for 11% of the total decay, is electron capture followed by the emission of a 1.46 m.e.v. gamma ray (6). The beta activity can be measured efficiently with a Geiger-Muller counter, while the gamma activity can be measured efficiently with a scintillation counter.

There have been several reports of the analysis of potassium based on its beta activity (3, 7–9). Modifications of the conventional Geiger-Muller counter were used as the detector. A major limitation of this method was the long counting time usually required. Work here and in other laboratories has been reported (1, 4) or is in progress in which the gamma activity of potassium, measured with a scintillation counter, is used to determine the potassium content of large samples weighing about 25 to 300 pounds. This work prompted the present study in which the potassium contents of smaller samples were determined by measurement of their gamma activity. These measurements could provide a rapid and accurate method of analysis of potassium in bulk chemicals and fertilizers.

Solid and liquid standards containing different concentrations of potassium were prepared, and their gamma activities were measured. Regression equations relating the gamma activities to the potassium concentrations were calculated. The gamma activities of pure potassium compounds were measured

and their potassium contents determined by means of the regression equations. The measured potassium contents were compared with the actual potassium contents calculated from molecular formulas. Similarly, the potassium oxide contents of liquid fertilizers were measured and compared to those determined by chemical analysis.

Experimental

Counting Equipment and Calibration. The counter used was a 4-pi, large volume, liquid scintillation counter. Its design and operating characteristics have been reported (5). The counter was operated integrally with the base discriminator set so that all energies above 0.075 m.e.v. were detected. The counting efficiency based on the gamma emission of K^{40} was about 29%. Except where indicated, all counting data are based on 2-minute sample counts preceded and followed by 1-minute background counts. The average of the two background counts was used to determine the net sample counts. All counting data were corrected for variation in counter efficiency by use of a K^{40} standard.

The sample chamber of the counter measured 8 inches in length and $4^1/_4$ inches in diameter. Solid samples were placed in containers constructed of Coroflex, a flexible Kraft wrapping with a corrugated cardboard front and a 50-pound Kraft backing. Solutions were placed in metal cans with screw-cap closures. Both types of containers measured 8 inches in length and 4 inches in diameter. The weight adopted for solid samples was 1567 grams, and the volume for liquid samples was 1500 ml.

The counter was standardized for potassium measurements by use of standards with various concentrations of potassium. Solid standards were prepared by mixing the required amount of potassium chloride (Baker, A.R.) with sufficient granular sucrose to make 1567 grams. Standard solutions containing potassium chloride in sufficient distilled water to make 1500 ml. were prepared. Each of these standards was counted in the manner previously described.

Reproducibility and Background Depression Studies. The reproducibility of the counter was studied. For this study, the 10% standard potassium solution was counted every 30 minutes over a period of 12 hours.

The effects of sucrose and distilled water samples on the background were studied to determine whether or not a correction for background depression was necessary. A 1-minute count was taken with the sample chamber empty. This was followed by a 1-minute count with either a 1567-gram sucrose or a 1500-ml. distilled water sample in the chamber. This procedure was repeated 10 times consecutively for both the sucrose and the distilled water, and three replications were made for each.

Determination of Potassium in Pure Potassium Salts and in Fertilizers. Three potassium salts (Mallinkrodt, A.R.) were selected for radiometric analysis in their undiluted solid forms and five in aqueous solution. The salts counted in solid form were granular. A variety of solid and liquid N–P–K fertilizers were also selected for radiometric analysis. The fertilizers were counted in their undiluted forms. All samples were prepared in the manner used for the preparation of the standards.

The solid fertilizers could not be

Table I. Standardization of Counter for Potassium Solutions

Standard No.	Potassium, % W./V.	Gross Activity, C.P.M.	Net Activity, C.P.M.	Counting Error, %[a]
1	0.50	4656	519	12.81
2	1.00	4874	751	8.93
3	1.50	5343	1294	5.30
4	2.00	5923	1858	3.81
5	2.50	6256	2128	3.38
6	5.00	8532	4428	1.80
7	7.50	10587	6479	1.32
8	10.00	12654	8572	1.07
9	12.50	14874	10773	0.90
10	15.00	16880	12831	0.80
11	16.92[b]	18520	14464	0.73

[a] Based on the 2-minute counts used to determine the reported activities.
[b] Based on maximum solubility of potassium chloride in water at room temperature.

Table II. Standardization of Counter for Solid Potassium Samples

Standard No.	Potassium, % W./W.	Gross Activity, C.P.M.	Net Activity, C.P.M.	Counting Error, %[a]
1	5.00	8968	4954	1.63
2	10.00	13661	9666	0.97
3	15.00	17838	13908	0.75
4	20.00	22445	18539	0.62
5	25.00	27465	23569	0.53
6	30.00	32325	28356	0.48
7	35.00	36077	32236	0.44
8	40.00	40983	37060	0.40
9	45.00	45223	41263	0.38
10	50.00	50150	46262	0.36
11	52.44[b]	52599	48578	0.35

[a] Based on the 2-minute counts used to determine the reported activities.
[b] Based on % potassium in potassium chloride.

Table III. Radiometric Determination of Potassium in Pure Solid Potassium Salts

Salt	Actual K, Grams[a]	Av. Radiometric K, Grams[b]	Coeff. of Variation, %
Potassium acid phthalate	300.1	298.0	0.76
Potassium carbonate	886.6	890.5	0.19
Potassium chloride	821.7	819.1	0.14

[a] Calculated from potassium content of salt and sample weight.
[b] One sample of each salt was prepared for counting. Each sample was counted four times.

Table IV. Radiometric Determination of Potassium in Pure Potassium Salts in Solution

Salt	Actual K, Grams[a]	Av. Radiometric K, Grams[b]	Coeff. of Variation, %
Potassium acid phthalate	34.5	34.1	5.48
Potassium bromide	73.9	74.0	2.34
Potassium carbonate	118.8	117.2	1.74
Potassium chloride	225.0	225.3	0.44
Potassium iodide	94.2	93.5	0.91

[a], [b] Same as in Table III.

Table V. Determination of the Potassium Oxide Concentration of Liquid Fertilizers

Grade		STPB Method Av. K₂O, % w./w.[a]	STPB Method Coeff. of variation, %	Radiometric Method Av. K₂O, % w./w.[b]	Radiometric Method Coeff. of variation, %
7-9-6	(7-21-7)	6.20	0.83	6.34	2.00
4-5-9	(4-11-11)	10.71	0.16	11.08	1.23
8-4-7	(8-8-8)	8.18	0.89	8.08	2.48
4-4-8	(4-10-10)	10.14	0.10	10.41	1.15
4-5-9	(4-11-11)	11.24	0.58	11.15	1.12
8-4-7	(8-8-8)	8.13	0.44	8.10	1.27
8-11-0	(8-24-0)	1.69	1.15	1.51	2.56
12-3-5	(12-6-6)	8.92	0.29	9.01	1.11

[a] A stock solution was prepared for each fertilizer. Aliquots of this stock solution were titrated for six replications.
[b] One sample of each fertilizer was prepared for counting. All eight fertilizer samples were counted consecutively for six replications.

analyzed radiometrically since they contained a radioactive contaminant of high activity. Spectra run on a multichannel analyzer with a sodium iodide crystal tentatively identified the contaminant as uranium. The spectrum of a 16–21–0 (16–48–0) solid fertilizer showed this. Wilson *et al.* (9) and Russell (8) showed that traces of uranium are associated with rock phosphate from which the phosphorus content of the fertilizers is derived.

All the liquid fertilizer samples were analyzed by the sodium tetraphenylboron (STPB) method. The A.O.A.C. official method was used (2).

Results and Discussion

The data for the standardization of the counter for potassium measurements are given in Tables I and II. The regression equation for the standard potassium solutions in terms of per cent potassium was $0.001171 \times$ net activity $- 0.056$ with $r = 0.99$; that for the solid potassium standards was $0.001091 \times$ net activity $- 0.434$ with $r = 0.99$. The regression equations were used to calculate the potassium contents of the samples from their net activities.

An important consideration in radiometric analysis is the counting error. There was no problem with the solid standards and samples since they all contained a high potassium concentration. Figure 1 shows the relationship between the concentration of potassium in the standard potassium solutions and the counting error. A concentration of 4.5% or greater of potassium was needed to obtain a counting error of 2% or less with the counting procedure used. The potassium concentrations in the solutions analyzed were greater than 4.5% in all solutions except the potassium acid phthalate solution and the 8–11–0 (8–24–0) liquid fertilizer.

The counting error could be reduced by extending the counting time. For example, the counting error of the standard solution containing 2.00% potassium could be reduced to about 2% by using an 8-minute counting time. The counting error of the standard solution containing 1.00% potassium could be reduced to about 2% by using a 40-minute counting time.

In the reproducibility study, the means of the gross sample, background, and net sample activities were 12,710; 4,005; and 8,705 c.p.m., respectively. The statistical counting error calculated from these mean values and based on the 2-minute counting time is 1.05%. The coefficient of variation of the net sample activities at the 30-minute intervals was 1.46%. These values indicate that the reproducibility of the counter over the 12-hour period was almost as good as the expected statistical counting error.

The sucrose and distilled water samples did not significantly affect the background of the counter. This was determined statistically using Student's "t" test. Thus, corrections for background depression by the samples counted were not necessary.

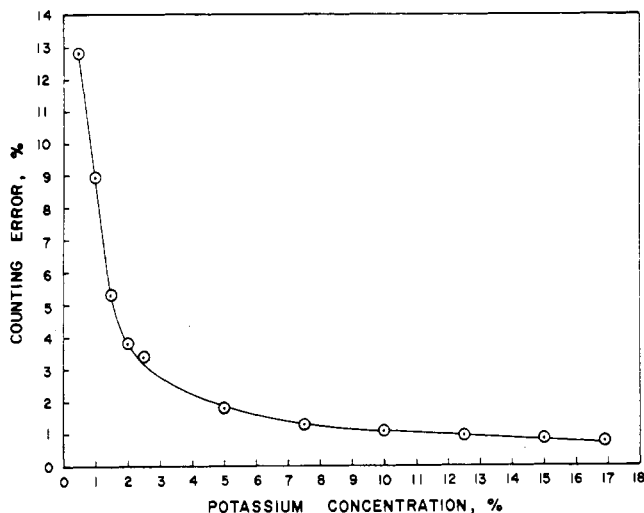The results for the determination of potassium in the potassium salts are

Figure 1. The relationship between the concentration of potassium in the standard potassium solutions and the counting error

given in Tables III and IV. The statistical counting errors ranged from 0.78 to 3.18% for the solutions and from 0.34 to 0.64% for the solids. The counting errors for the potassium acid phthalate both in solution and in solid form were the highest. The potassium contents of all samples except the potassium acid phthalate and potassium bromide in solution could be determined by the radiometric method with a coefficient of variation less than 2%. The two exceptions contained less than 5% potassium. In general, the coefficients of variation were just slightly higher than the statistical counting errors.

For both the solid samples and solutions, the potassium contents determined radiometrically scattered above and below the actual potassium contents. This scatter indicates that self-absorption of the gamma rays was negligible for the sample sizes used.

The results of the STPB and radiometric analyses of the liquid fertilizers reported in Table V show that the STPB method is more precise than the radiometric method under the conditions used. The highest average statistical counting error in the radiometric method was 4.88% for the 8–11–0 (8–24–0) fertilizer. Statistical counting errors for the other fertilizers all averaged 1.48% or less. The counting error was usually slightly less than the precision of the radiometric method for each fertilizer, indicating that the precision of the method could be increased by extending the counting time beyond 2 minutes.

For eight liquid fertilizers analyzed, the average absolute difference in the potassium oxide contents found by the STPB and the radiometric methods in six replications was 0.16% with a range of 0.03 to 0.37%. Equivalent results were obtained for five pure potassium salts in solution. This accuracy and

precision would be satisfactory for routine potassium analyses.

No sample preparation and no correction for self-absorption are required. A routine analysis of a liquid or solid would require about 10 minutes, and the method is adaptable to a continuous system type of analysis. A limitation of the method is its failure in the analysis of solid fertilizers due to the presence of a radioactive contaminant. This contaminant is in the phosphatic content, and may possibly be overcome by applying a correction based on the phosphatic content. Further study of the phosphatic component is required to ascertain whether or not the concentration of radioactive contaminant is proportional to the phosphatic content. The radioactive contamination problem would not be expected to be present in the majority of potassium-containing samples. Another restriction to the use of the method where limited sample size is available is the large sample required.

Literature Cited

(1) Anderson, E. C., Langham, W. H., Science 130, 713 (1959).
(2) Assoc. Offic. Agr. Chemists, Washington 4, D. C., "Official Methods of Analysis," 9th ed., p. 19, 1960.
(3) Barnes, R. B., Salley, D. J., Ind. Eng. Chem., Anal. Ed. 15, 4 (1943).
(4) Christian, J. E., Combs, L. W., Kessler, W. V., Science 140, 489 (1963).
(5) Dunavant, B. G., Christian, J. E., Intern. J. Appl. Radiation Isotopes 8, 223 (1960).
(6) Endt, P. M., Braams, C. M., Rev. Mod. Phys. 29, 735 (1957).
(7) Gaudin, A. M., Pannell, J. H., Anal. Chem. 20, 1154 (1948).
(8) Russell, O. J., Brit. J. Appl. Phys. 3, 47 (1952).
(9) Wilson, H. N., Lees, D. S., Broomfield, W., Analyst 76, 355 (1951).