

## A Modification of the Volumetric Cobaltinitrite Method for Potassium Estimation, not Requiring Alcohol as Wash Liquid

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A modification of the volumetric cobaltinitrite method of potassium estimation has been described. Washing the precipitate with 10% acetic acid, followed by 2.5% sodium sulphate has been demonstrated to be a satisfactory substitute for alcohol washing, thus eliminating the use of alcohol, which is usually costly. The applicability of the method to a wide range of potassium concentrations in fertiliser material has been tried, as also to soils representing different important soil groups and regarding a wide range of potassium contents. It is suggested that by employing this modified method it is possible to dispense with the use of the costly material, alcohol.

Of the several methods available for potassium estimation, the cobaltinitrite method of precipitating potassium as potassium sodium cobaltinitrite offers several advantages, it being rapid, economical and adaptable to semi-micro-techniques; the solubility of the precipitate in water is low when compared to other precipitates containing potassium. Further, in the cobaltinitrite method, prior removal of organic matter and ammonium salts alone is necessary. In spite of being simpler and more economical than most other methods, the common cobaltinitrite methods are still dependent upon alcohol as wash liquid. In this paper procedural details have been worked out for a volumetric cobaltinitrite method giving accurate results in potassium estimation in fertiliser and soils, but eliminating the necessity for alcohol washing.

### MATERIAL AND METHODS

#### a. Formulation of procedural details for proposed method

A solution of A.R. potassium chloride containing 0.6232 g KCl in 500 ml of water (Standard) was used for finding out the relative accuracy of different procedures involved in the volumetric cobaltinitrite method, using the following reagents.

Reagents: A: Fifty g of cobaltous nitrate (crystalline) dissolved and made up, with 12.5 ml of glacial acetic acid, to 500 ml.

B: Three hundred g of sodium nitrite dissolved and made up, with 12.5 ml of glacial acetic acid, to 500 ml.

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TABLE I. Formulation of suitable procedural details for method of potassium determination  
Theoretical value : 0.6232 g KCl/500 ml.

Without Evaporation of sample plus precipitant		With evaporation of sample plus precipitant	
Without	With	Without	With
Acetic acid and sodium sulphate washing	Acetic acid and sodium sulphate washing	Acetic acid and sodium sulphate washing	Acetic acid sodium sulphate washing
Addition of Precipitate after H <sub>2</sub> SO <sub>4</sub> before H <sub>2</sub> SO <sub>4</sub>	Addition of Precipitate after H <sub>2</sub> SO <sub>4</sub> before H <sub>2</sub> SO <sub>4</sub>	Addition of Precipitate after H <sub>2</sub> SO <sub>4</sub> before H <sub>2</sub> SO <sub>4</sub>	Addition of Precipitate after H <sub>2</sub> SO <sub>4</sub> before H <sub>2</sub> SO <sub>4</sub>
Estimated value : (g KCl/500 ml)			
0.7069	0.7036	0.7010	0.6589
Difference from theoretical value			
+13.75	+12.90	+12.48	+5.73
		0.6735	0.6497
		+8.04	+4.26
			0.6628
			+6.35
			-1.41

Equal volumes of reagents A and B above are mixed and allowed to settle for 2 days, and the clear, sediment free solution used as precipitant for potassium estimation.

The strength of the precipitant obtained from the above reagents is roughly 7%, and is sufficient to buffer out considerable differences in Na concentrations of test solution. The present method was tested at room temperature (about 30°C) and found to be satisfactory.

**Wash liquids:** Solutions of acetic acid (5 and 10%) and sodium sulphate (2.5%)

The relative accuracy of different procedures like (1) evaporation of test solution after addition to precipitant (Drushel, 1907) (2) without evaporation of the solution (Lewis and Marmoy, 1933) (3) Washing the precipitate of potassium sodium cobaltinitrite with 10

per cent acetic acid and 2.5 per cent sodium sulphate (Mitscherlich *et al*, 1912; Lewis and Marmoy, 1933), (4) Washing precipitate with water alone, was tested. The above procedures were further tested for the relative efficiency of adding the precipitate to the standard KMnO<sub>4</sub> solution before or after addition of sulphuric acid.

From the above preliminary experiment (Table-I) it was found that the following procedure was the best and capable of giving the most accurate values, and hence it was followed in the rest of the investigations reported here.

**Procedure:** The test material from which ammonium salts had been removed by evaporation and ignition was dissolved in water and evaporated to dryness in a round bottom potash basin. To the dry residue obtained 10 to 20 ml (depending upon the K content) of the precipitating mixture mentioned above

was added. The mixture was evaporated to dryness on a water bath; on 10 ml of 10 per cent acetic acid was added, stirred and allowed to stand for half an hour; 10 ml of water was then added and the contents left to stand overnight.

The solution containing the cobaltinitrite precipitate was filtered through the asbestos mat prepared fresh, using gentle suction and the precipitate washed three times, by decantation with 5 per cent acetic acid. It was then washed 10 times, with 5 ml. lots of 2.5 per cent sodium sulphate solution, allowing the wash liquid to drain through completely each time.

In a 500 ml conical flask 25.0 ml (or suitable volume) of 0.1 N  $\text{KMnO}_4$  were taken, 100 ml water added and heated to *just below boiling point* (*The solution should not boil*). The asbestos mat containing the precipitate was added to the permanganate solution and shaken vigorously for half a minute to disintegrate the asbestos.

Then 10 ml of conc.  $\text{H}_2\text{SO}_4$  was added in 2 ml lots, shaking well after each addition. The contents were allowed to stand for 10 minutes and 25.0 ml of 0.1 N oxalic acid was added. The solution was heated again just to boiling, preventing bumping by occasional shaking, and titrated against 0.1 N  $\text{KMnO}_4$  to faint pink end point.

1 ml 0.1 N  $\text{KMnO}_4$  = 0.0008564 g  $\text{K}_2\text{O}$  (Theoretical factor)

b. Suitability of proposed method to varying potassium concentrations (Table II)

Solutions containing different amounts of potassium were taken and potassium estimated by the procedure arrived at in the previous section. Over a range of KCl weights of about 2.5 to 28.8 mg. quite good estimates of potassium were capable of being obtained by the use of the proposed method.

c. Fertiliser material

(1) Estimation with variation in amount of fertiliser sample pre-

TABLE II. Suitability of proposed method of potassium estimation to varying potassium amounts. Theoretical value : 0.6232 g KCl/500 ml

Weight of KCl in aliquot taken (Approx.) mgm.	2.5	6.3	10.0	13.8	17.5	21.3	25.0	28.8
Estimated values Using Milne's factor (g KCl/500 ml)	0.5919	0.6313	0.6001	0.6098	0.6201	0.6190	0.6017	0.6034
Difference from theoretical value (%)	-5.02	+1.49	-3.80	-2.15	-0.50	-0.68	-3.45	-3.18
							Mean : 1.72	
Estimated values using theoretical factor (g KCl/500 ml)	0.6106	0.6513	0.6191	0.6292	0.6398	0.6387	0.6209	0.6226
Difference from theoretical value (%)	-2.02	+4.51	-0.66	+0.96	+2.67	+2.49	-0.37	-0.10
							Mean : 1.72	

TABLE III. Potassium estimations with variation in amount in sample present in unit volume

Sample : Potassium sulphate (C.P.) : (K<sub>2</sub>O = 52.05%) (Percentages of K<sub>2</sub>O)

a. Low concentration series

Lot No.	Concentration of K <sub>2</sub> SO <sub>4</sub> (ppm)	Aliquot 1	No. 2	
1	50	51.6	50.6	Difference between estimated and actual K <sub>2</sub> O contents expressed as percentage on actual value (d): -1.41 Mean 51.31
2	100	51.4	52.2	
3	200	50.6	50.2	
4	400	52.3	50.6	
5	500	52.6	52.3	
6	1000	49.9	51.4	
	Mean	51.40	51.21	51.31
	Variability %	1.48	± 1.42	1.45
	C.V. %	1.81	1.55	

b. High concentration series

Lot No.	Concentration K <sub>2</sub> SO <sub>4</sub> (ppm)	Aliquot 1	No. 2	
1	250	52.1	51.7	Difference % (d): -0.16  Mean 51.96
2	500	53.1	50.1	
3	1000	50.9	52.2	
4	2000	52.2	52.1	
5	4000	53.1	53.7	
6	5000	50.1	52.2	
	Mean	51.92	52.00	51.96
	Variability %	± 1.81	± 1.38	1.60
	C.V. %	2.12	2.01	

sent in unit volume (Table III). Concentrations of K<sub>2</sub>SO<sub>4</sub> ranging from 50 to 5000 ppm were prepared and the potassium estimated in duplicate aliquots by the proposed method. The results were considered under two series, low and high concentration, with some overlaps for comparison. Variability percentage worked out for the data by summing up the deviations from the mean for the values, ignoring the sign, taking the average of these deviations, and expressing it as a percentage for the two series was practically the same (1.45 and 1.38, respectively) while the percentage difference from the actual value for the high concentration series (-0.15) was considerably lower than that for the low concentration series (-1.41).

(2) Repeated potassium estimations with same concentration of fertiliser (Table IV). To determine

TABLE IV. Repeated potassium estimations with same concentration sample: Potassium sulphate (C.P.) (K<sub>2</sub>O : 52.05%) (percentages of K<sub>2</sub>O)

a. Low concentration series

Aliquot No.	K <sub>2</sub> SO <sub>4</sub> (ppm)	100	250	500	
1.		52.2	51.7	52.3	Mean 51.67 51.78 51.28 Variability % ± 1.31 ± 1.38 ± 1.47 ± 1.39 C.V. % 1.53 1.61 1.71 Difference % (d) -0.75 -0.52 -1.20 0.25
2.		52.0	52.2	52.0	
3.		52.3	51.1	51.9	
4.		52.2	52.4	51.0	
5.		50.1	50.4	50.2	
6.		51.2	52.9	50.3	
	Mean	51.67	51.78	51.28	
	Variability %	± 1.31	± 1.38	± 1.47	± 1.39
	C.V. %	1.53	1.61	1.71	
	Difference % (d)	-0.75	-0.52	-1.20	0.25

b. High concentration series

Aliquot No.	K <sub>2</sub> SO <sub>4</sub> (ppm)	1000 (A)	1000 (B)	5000	
1.		51.4	51.9	53.0	
2.		52.3	52.9	53.0	
3.		52.3	53.1	51.7	
4.		51.6	52.3	51.5	
5.		52.7	51.9	52.2	
6.		52.3	53.0	52.2	
Mean					
Mean		52.08	52.52	52.12	
Variability %					
		±0.75	±0.92	±0.67	0.78
C.V. %					
		0.86	0.96	0.91	
Difference % (d):					
		+0.06	+0.90	+0.13	0.36

Mean Variability % for all values above : ± 1.09  
 Mean difference % (d) for all values in tables 3 & 4 : 0.65

the repeatability of the potassium determinations at different concentrations,

potassium was estimated by the proposed method six times for each concentration examining two series, low and high. The mean variability percentage for the high concentration series (0.78) was considerably lower than that for the low concentration series (1.39). Similarly the percentage difference from actual value for the high concentration series (0.36) was considerably lower than for the low concentration series (0.85).

d. Soils

1) Potassium estimation by proposed method in representative soils. (Table V) : Twelve soil samples representing the major soil groups of Tamil Nadu, viz., red, black, alluvial and lateritic, were collected and total potassium determined in the hydrochloro-

TABLE V. Potassium estimation by original and proposed methods in representative soils of Tamil Nadu

Locality	Soil group	Total K <sub>2</sub> O percentage				Difference from original method %
		Original method	Proposed method			
			I	II	Mean	
Keramadaï	Black	0.353	0.371	0.362	0.367	3.91
Sirugamani	Black Alluvial	0.539	0.509	0.521	0.515	4.53
Aduthurai	-do-	0.702	0.685	0.692	0.689	1.92
Kovilpatti	Red	0.251	0.262	0.241	0.252	0.24
Paramathi	-do-	0.311	0.301	0.312	0.306	1.54
Vezhappadi	-do-	0.403	0.413	0.418	0.416	3.21
Madurai	-do-	0.628	0.609	0.617	0.613	2.34
Nagercoil	-do-	0.643	0.602	0.601	0.602	6.44
Gingee	-do-	0.689	0.700	0.691	0.696	0.99
Kodaikanal	laterite	0.401	0.398	0.388	0.393	1.99
Gudalur	-do-	0.561	0.601	0.553	0.577	2.89
Coonoor	-do-	0.817	0.852	0.802	0.827	1.20
Mean						2.60

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TABLE VI. Repeated potassium estimations with sample (Soils) (Percentages of total K<sub>2</sub>O)

Locality	Karamadai	Madurai	Nagercoil	Coonoor	
Soil Group :	Black	Red	Red	Laterite	
Lot No.					
1.	0.372	0.618	0.643	0.853	
2.	0.361	0.614	0.602	0.801	
3.	0.376	0.654	0.593	0.795	
4.	0.364	0.605	0.623	0.799	
5.	0.351	0.632	0.606	0.855	
Mean	0.3648	0.6246	0.5134	0.8206	Mean
Variability %	±2.02	±2.36	±2.56	±3.26	2.55
C.V. %	2.40	3.74	3.87	3.34	
K <sub>2</sub> O % by original method	0.353	0.628	3.643	0.817	
Difference from original method %	+3.29	-0.56	-4.63	+0.43	2.23

ric acid extracts of these samples by the proposed method. The estimations were performed in duplicate and compared with the corresponding values obtained with the original cobaltinitrite method. The values for K<sub>2</sub>O content according to the original method ranged from 0.251 to 0.817 per cent in these soils, thus, covering a fairly wide range of potassium contents. The mean difference from the values for the original method, taking all 12 soils together worked out to 2.60 per cent.

2) Repeated potassium estimations with same soil sample (Table VI): In four representative soils K was estimated 5 times and the variability percentage and CV worked out. The potassium contents were also determined by the original cobaltinitrite method for comparison. The mean variability percentage came to 2.55 for all the four soils taken together, and the mean dif-

ference from original method also to a comparable figure (2.23%).

## RESULTS AND DISCUSSION

The suitability of the modified volumetric cobaltinitrite method for potassium determination has been established in the foregoing sections. The reproducibility of the method and its applicability to a wide range of potassium concentrations usually met with in fertiliser and soil analysis has been demonstrated. In the case of soils the method has been compared with the original volumetric cobaltinitrite method also, and has been found to compare quite well. There are indications that the reproducibility of the method and agreement with theoretical value are better for higher concentrations of potassium in fertiliser material, suggesting the better suitability of the method for higher potassium concentrations. In solutions containing low amounts of

potassium larger aliquots may be taken to increase the amounts of potassium estimated in order to ensure higher accuracy. Under the conditions of the experiment described the theoretical factor for potassium estimation was better than Milne's arbitrary factor.

The range of potassium concentrations over which the method was satisfactory was quite wide. In the case of  $K_2SO_4$ , quite satisfactory results were obtained for concentrations between 50 and 5000 ppm. This would indicate the applicability of the method to a wide range of potassium concentrations.

In the case of soils, the variability percentage (2.55) and difference from original method (2.60%) were understandably higher than for the fertiliser material examined (1.09 for variability percentage and 0.65% for difference from actual value). This was evidently due to the known heterogeneity of the soil samples as contrasted to the fertiliser samples. The first two authors of this paper obtained variability percen-

tage values of 2.1 and 2.3 respectively for Walkle-Black organic carbon values and values for organic carbon estimated by a rapid and simple method devised by them. Contrasted to this chemical estimations in homogeneous material usually register variability percentages of about 0.5. It is also known that soil heterogeneity itself can bring about a variability percentage of about 2.0. Considering these, and making allowance for inherent soil heterogeneity, which increases with content of coarse particles, it can be concluded that the variability percentage obtained in the case of the proposed potassium estimation method applied to soil is satisfactory.

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