

## POTENTIOMETRIC AND VISUAL DETERMINATION OF POTASSIUM THROUGH COBALTNITRITE

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Potentiometric procedures for the assay of potassium with various reductants are described. Potassium in various samples is precipitated as dipotassium sodium cobaltinitrite [ $K_2NaCo(NO_2)_6$ ] with sodium cobaltinitrite [ $Na_3Co(NO_2)_6$ ] and this precipitate after treating with alkali was titrated potentiometrically with various reductants viz., iron(II) in 9-12M phosphoric acid, tin(II) in 2-5N hydrochloric acid, sodium thiosulphate in 0.5-2N hydrochloric acid and hydrazine sulphate in 0.5-1N hydrochloric acid. Potassium was also determined visually with iron(II), tin(II) and sodium thiosulphate in the same media using cacotheline, starch, ferroin, new methylene blue, azure A, azure C, methylene green and chloroform as indicators according to their applicability. The visual determination was also extended with Chloramine-T in 2-5N acetic acid using starch as indicator. Further, this method has been extended for the determination of potassium in fertilisers.

**Keywords:** Potassium; Cobaltinitrite; Potentiometry; Visual

### INTRODUCTION

SEVERAL methods of determination of potassium have been reported mostly involving the instrumental methods viz., nephelometric, gasometric, flame-photometric and spectrophotometric. The widely used flamephotometric method requires special apparatus, sensitive detectors, photomultipliers and suffers the disadvantage of the interference of other elements which is sometimes contradictory in the determination of potassium. For example, some workers have reported that sodium salts have either a slight or no effect on the determination of potassium (Schrenk & Glending 1955), whereas other sources indicate that the presence of sodium decrease the results for potassium (Parks *et al.*, 1948). Of the titrimetric methods, also the phosphotungstate method (Vanskyle & Reiben, 1944) and chloroplatinate method (Mohr, 1969) involve too many operations for the reduction of the precipitate and the usage of costly chemicals. In Sousa's method of determination of potassium, perchlorate is reduced to chlorine which is further precipitated by silvernitrate and the silverchloride precipitate is treated with tetracyanonickelate and the nickel ions are titrated with complexone-III. Because of the large number of operations, the method is less accurate. In the titanometric determination of potassium salt of a sulphonic acid (Wiggins & Wood, 1935) the errors are reported to be more i.e., 5-6 per cent due to aerial oxidation of titanous sulphate. In Curie's method (Curie, 1935)

the cobaltinitrite precipitate is directly treated with potassium iodide in HCl medium and the iodine liberated is titrated with thiosulphate. Even though the method is very simple, nitric oxide formed during the reaction is readily oxidised by atmospheric oxygen to liberate iodine from iodide.

The present method reported is simple and rapid as it does not involve gravimetric and instrumental operations, with chemicals easily available, stable and cheap in nature. In this method potassium is precipitated as dipotassium sodium cobaltinitrite and this precipitate is boiled with alkali, cooled and filtered. The filtrate containing nitrite is titrated with various reductants visually and potentiometrically and with chloramine-T visually. All these reductants are first titrated with  $\text{NaNO}_2$  and found to be giving accurate results in the said conditions.

## EXPERIMENTAL

### *Apparatus*

An Elico digital potentiometer (model LI-120) was used for all the potentiometric measurements along with a platinum electrode as an indicator electrode and a saturated calomel electrode as a reference electrode.

### *Reagents*

Solutions of (0.05N) iron(II) ammonium sulphate (in 1N sulphuric acid), tin(II) chloride (in 1N HCl), sodium thiosulphate, hydrazine sulphate and chloramine-T were prepared and standardised conventionally. 5 per cent solution of sodium cobaltinitrite was prepared in 2 per cent acetic acid. 0.5N NaOH and 10 per cent potassium iodide were prepared. Aqueous solutions of (0.1 per cent) new methylene blue, methylene green, ferroin, azure A, azure C, 0.2 per cent cocotheline and 1 per cent starch were prepared.

All other reagents used are of analar grade unless otherwise mentioned.

### *Method*

*Precipitation of Potassium* — 0.03 to 0.04 gm of potassium sulphate was dissolved in 10 ml of water. 1 ml of 1N  $\text{HNO}_3$  was added followed by a freshly prepared solution of sodium cobaltinitrite, in excess. Now, the contents were mixed well and allowed to stand for 2 hours and filtered through a Gooch crucible and transferred the precipitate completely with the aid of 0.01N  $\text{HNO}_3$ . The filtrate is washed ten times with 2 ml portions 0.01N  $\text{HNO}_3$  and five times with 2 ml portions of 95 per cent EtOH. The precipitate is now boiled with 40 ml of 0.5N NaOH for 3 mts, cooled and filtered and filtrate containing—NITRITE—is collected. The residue was washed with water and the washings were added to the filtrate.

*Titration with Various Reductants* — The required volume of acid to give the optimum concentration near the end point (as given in Table I) was taken in the titration vessel through which Carbon dioxide was passed for 5 mts. (4 ml of KI is added for the titration with tin(II) and thiosulphate). Then a known volume of the reductant was added together with 0.2 ml of indicator solution (0.5 ml in the case of cocotheline

or 1ml for starch) and titrated with the nitrite solution, collected above, to a sharp colour change of the indicator. Alternatively, the indicator was omitted and titrated potentiometrically. The potentials attained steady values immediately in the beginning and after 30 seconds near the endpoint. Typical potentiometric curves are given in Fig. 1 and results are given in Tables II, III & IV.

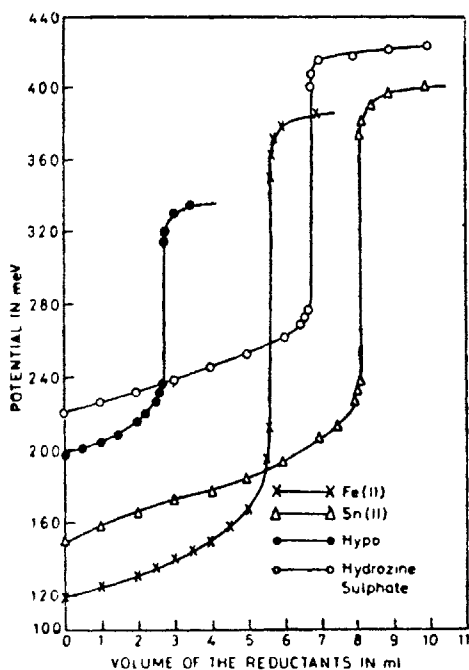


FIG. 1.

TABLE I

*Potentiometric and visual determination of cobaltinitrite with various reductants*

Reductant used	Endpoint detection	Medium of titration	Average error, %
Fe (II)	potentiometric	9-12M H <sub>3</sub> PO <sub>4</sub>	0.481
	indicators (1-6)	9-12M H <sub>3</sub> PO <sub>4</sub>	0.484
Sn (II)	potentiometric	2-5N HCl	0.138
	indicators (1, 3-7)	2-5N HCl	0.153
Thiosulphate	potentiometric	0.5-2N HCl	0.189
	indicators (7 & 8)	0.5-2N HCl	0.198
Hydrazine sulphate	potentiometric	0.5-1N HCl	0.354

1. cacoetheline 2. ferroin 3. new methylene blue 4. methylene green 5. azure A 6. azure C  
7. starch 8. chloroform

TABLE II

*Determination of NaNO<sub>2</sub> with tin(II) in presence of KI in 3N HCl using cacotheline as indicator*

Amount taken* (in mgs)	Amount found* (in mgs)	error %
15.12	15.05	0.46
45.37	45.47	0.22
60.50	60.60	0.16

\*average of three readings.

TABLE III

*Visual determination of potassium (as K<sub>2</sub>O) by titrating potassium cobaltinitrite*

Sample	Amount taken as K <sub>2</sub> O (mgs)	Amount found as K <sub>2</sub> O (mgs)*			
		Fe(II)	Sn(II)	Hypo	Ch-T
KCl	52.84	52.63	52.90	52.75	52.82
K <sub>2</sub> SO <sub>4</sub>	75.90	76.10	75.82	75.39	75.82
KH <sub>2</sub> PO <sub>4</sub>	35.62	35.10	35.55	35.55	35.57
Mureite of potash	56.74	56.80	56.71	56.82	56.84
N P K fertiliser	25.76	25.70	25.81	25.69	25.84

\*average of three readings.

TABLE IV

*Potentiometric determination of potassium (as K<sub>2</sub>O) by titrating potassium cobaltinitrite*

Sample	Amount taken as K <sub>2</sub> O (mgs)	Amount found as K <sub>2</sub> O (mgs)*			
		Fe(II)	Sn(II)	Hypo	Hydrazine
KCl	52.75	52.52	52.70	53.05	52.68
K <sub>2</sub> SO <sub>4</sub>	75.20	75.02	75.52	76.00	75.69
KH <sub>2</sub> PO <sub>4</sub>	35.17	35.39	35.08	34.85	35.38
Mureite of potash	56.36	56.38	56.49	56.17	56.41
N P K fertiliser	24.84	24.80	24.91	24.86	24.86

\*average of three readings.

*Titration with Chloramine-T* — 10ml of the nitrite solution, 25ml of chloramine-T and 5ml of acetic acid were kept in the titration vessel till the white densed fumes disappeared. Dilute to 50 ml and the excess chloramine-T was back titrated iodometrically. Typical results are given in Table III.

*Application to NPK Fertiliser and Mureite of Potash (Chloride Form)* — A known amount of the sample was weighed accurately and dissolved in water and filtered,

if necessary. The filtrate was collected and 5 to 10ml of formaldehyde was added, if the sample contains ammonia. Now the procedure is followed as given above. The potassium in the sample was determined by sulphanilic acid method (cf. Fiat Microfilm PBL 17692, Suppl. S.2; IG Analysenvorschrift No. 18.) and the results were compared.

### RESULTS AND DISCUSSION

The precipitation of potassium solutions with sodium cobaltinitrite reagent under the experimental conditions given above gives a quantitative yield of dipotassium sodium cobaltinitrite. Precipitation is made in acetic acid solution with a reagent prepared by mixing a solution of cobaltinitrite or acetate in dilute acetic acid and of sodiumnitrite in water. There is some evidence that the composition of the precipitate will vary from the formula given above. If the precipitation is made from a nitric acid solution by a solution of trisodium cobaltinitrite, the crystalline precipitate invariably has the composition  $[K_2Na(Co(NO_2)_6)] H_2O$  (Cf. Vogel, 1969). Acidification with dilute nitric acid tends to prevent decomposition of nitrite.

The method gives accurate results with a sharp colour change for all the indicators. By separate experiments, it is determined that iron(II) needs a medium of 8–12M phosphoric acid with an optimum concentration of 10M. The reaction between tin(II) and nitrite in presence of KI in 2–5N HCl using cacotheline as indicator is studied by the authors and found to be giving quantitative results and some results are given in Table II. When starch is used as indicator for tin(II) and hypo, the appearance of starch-iodine blue colour is taken as the endpoint.

In the titrations the nitrite solution is taken in the burette and the tip of the burette should be dipped just below the surface of the titrand. If not, low values may occur. The passage of carbon dioxide in iodometric methods, also, will prevent aerial oxidation of nitric oxide, and so the liberation of iodine due to aerial oxidation of nitric oxide can be stopped.

The sample solution should be free from mineral acids which will decompose the reagent. For the same reason, salts of trivalent iron, aluminium and other elements should be absent which are liable to become hydrolysed. There should not be oxidising agents and reducing agents or even traces of iodides. The salts of Mg, Ca do not interfere in the precipitation in a considerable manner.

The solution of formaldehyde will prevent the interference of ammonia, if any, in the precipitation of potassium, by complexing it as formamide. The method is least expensive and is applicable even in the presence of sulphates and phosphates and in this respect it has the distinct advantage over chloroplatinate and perchlorate methods where they do interfere.

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