ESTIMATION OF POTASSIUM
BY THE COBALTINITRITE METHOD.

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The cobaltinitrite method for the estimation of potassium has been investigated by several workers of whom the following might be mentioned. Addie and Wood (*J.C.S.*, 1900, **77**, 1076) studied the method in detail and found that the precipitate of potassium-sodium cobaltinitrite obtained had the formula $K_2NaCo(NO_2)_6.H_2O$, and that potassium could be estimated gravimetrically or volumetrically either by weighing the precipitate as such or by determining the NO_2 in it by titration with standard permanganate. They also found that the results obtained by the cobaltinitrite method were just as accurate as those obtained by the perchlorate method for the estimation of potassium. Cunningham and Perkin (*J.C.S.*, 1909, **95**, 1568) observed in the course of their work on organic cobaltinitrites that the estimation of potassium as potassium-sodium cobaltinitrite was unsatisfactory as the precipitate could not be washed and filtered properly owing to its tendency to become colloidal on washing. Vürtheim (*Rec. trav. chim.*, 1921, **40**, 593) found that the formula of precipitated potassium-sodium cobaltinitrite was $K_{1.5}Na_{1.5}Co(NO_2)_6.nH_2O$, as had been previously suggested by Gilbert (*Z. anal. Chem.*, 1891, **38**, 184). This, however, was disproved by Bonneau (*Bull. Soc. Chim.*, 1929, **46**, 798) who at the same time confirmed the results obtained by Addie and Wood (*loc. cit.*) and showed that the number of water molecules attached to $K_2NaCo(NO_2)_6$ is usually one. According to him the composition of the precipitate depends on the ratio of the concentrations of sodium and potassium in the reaction mixture. Druschel (*Z. anorg. Chem.*, 1908, **56**, 223) effected some modifications in the procedure suggested by Addie and Wood (*loc. cit.*) and obtained satisfactory results by the volumetric method. On the other hand, Strecker and Junck (*Z. anal. Chem.*, 1923, **63**, 161) who carried out a comparative study of a number of methods of estimating potassium found that the precipitation of potassium as cobaltinitrite did not lead to concordant results, because, although the precipitation was complete, the composition of the precipitate varied considerably in different experiments. They therefore recommended the precipitation of potassium by addition of sodium cobaltinitrite and the subsequent determination of the potassium in the precipitate by the perchlorate method. Hamid (*Analyst*, 1926, **51**, 450) made some determinations of potassium by the cobaltinitrite as well as by the perchlorate method and found that the results obtained by the two methods were in satisfactory agreement.

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Wasselieef and Matwejeb (*Z. anal. Chem.*, 1930, **81**, 106) carried out a detailed study of the method on the basis of which they suggest a procedure for obtaining satisfactory results. In order to reduce the time necessary for the coagulation of the precipitate and thereby hasten the estimation of potassium, Grigoriev and Karol (*J. Chem. Ind.*, Moscow, 1931, **8**, 68: *cf. Chem. Abstr.*, 1931, 700) recommend the evaporation of the reaction mixture almost to dryness, diluting with water and filtering immediately.

This work was undertaken with a view to exploring the various sources of error and to determine the conditions necessary for getting accurate results. Trials were made of the various methods outlined above and it was found that the procedure recommended by Wasselieef and Matwejeb (*loc. cit.*) was the most reliable. This was the case, however, only when definite quantities of the reagents were employed, excess or deficit in the quantity of sodium nitrite added yielding results which were too high and too low respectively, if calculations were always based on the formula $K_2NaCo(NO_2)_6, H_2O$. We found that this was due to the fact that the number of water molecules in the precipitate was either $\frac{1}{2}$, 1, or 2 depending on the conditions of precipitation, all these three hydrates being quite stable at the temperature employed for drying, *viz.*, 100–110°. In order to overcome this complication we devised the method described in a later part of this paper and found it satisfactory.

EXPERIMENTAL.

The potassium salts employed in the investigation were either purified for the purpose or were pure analytical preparations of Kahlbaum. The procedure required to be followed in order to get accurate results was experimentally worked out and found to be as follows. Known quantities of the potassium salt were dissolved in 5 c.c. of water, acidified with 1–2 c.c. of acetic acid and the required quantities of sodium nitrite (50 per cent. solution) and cobalt sulphate (25 per cent. solution) were added. The mixture was then heated on a water-bath for about 5′, and then kept aside to settle for about 16 hours. It was then filtered through a weighed gooch crucible, the precipitate being washed with 50–75 c.c. of cold water, first by decantation and then on the filter. The precipitate was dried at 110° to constant weight. From the weight of the precipitate obtained, the quantity of potassium was calculated assuming that the precipitate had the formula $K_2NaCo(NO_2)_6, H_2O$. The results obtained by employing this procedure are given in Table I.

Equal quantities of the solutions of sodium nitrite (50 per cent.) and cobalt sulphate (25 per cent.) were always added, the quantities employed in the analysis of 0·05, 0·1, 0·2, 0·3, 0·5 and 1·0 g. of potassium nitrate being 1, 2-3, 6-7, 10-11, 15-17 and 25-27 c.c. respectively of each solution.

TABLE I.

KNO$_3$ taken g.	found g.	Error per cent.	KNO$_3$ taken g.	found g.	Error per cent.	KNO$_3$ taken g.	found g.	Error per cent.
0·0500	0·0497	−0·6	0·2000	0·2006	+0·3	0·5000	0·4980	−0·4
,,	0·0499	−0·2	,,	0·2002	+0·1	,,	0·4970	−0·6
,,	0·0498	−0·4	,,	0·1992	−0·4	,,	0·5015	+0·3
,,	0·0502	+0·4	,,	0·1994	−0·3	,,	0·5020	+0·4
0·1000	0·1005	+0·5	,,	0·2010	+0·5	,,	0·4995	−0·1
,,	0·0993	−0·7	,,	0·1996	−0·2	1·0000	1·0030	+0·3
,,	0·1003	+0·3	0·3000	0·2997	−0·1	,,	0·9962	−0·4
,,	0·1007	+0·7	,,	0·3009	+0·3	,,	0·9952	−0·5
,,	0·0999	−0·1	,,	0·2994	−0·2	,,	1·0030	+0·3
,,	0·0999	−0·1	,,	0·2994	−0·2	,,	0·9922	−0·8
			,,	0·3010	+0·3	,,	0·9992	−0·1

It is seen from Table I that all the results given are accurate to within 1 per cent. This, however, was found to be the case only when the specified quantities of the reagents were added. Addition of the proper quantity of cobalt sulphate but different quantities of the sodium nitrite reagent led to inaccurate results as is shown in Table II.

The results given in Table II indicate that addition of a smaller quantity of reagent than that required (3 c.c. for 0·1 g. and 7 c.c. for 0·2 g. KNO$_3$) yields results which are low whereas addition of excess leads to results which are high. Similar variations in the quantity of cobalt sulphate employed were found to have no effect on the accuracy of the determinations. Since it was found that the low results shown in Table II were not due to incomplete precipitation, it was thought that they were due to formation of precipitates other than K$_2$NaCo(NO$_2$)$_6$, H$_2$O. Hence a close study of these precipitates was undertaken by collecting them in sufficient quantities and analysing them. Of the various precipitates collected and analysed, only three will be mentioned here as the others were probably only mixtures of these in various proportions. The three types were those which yielded values for potassium which were (a) accurate, (b) 2 per cent. too low, and (c) 4 per cent. too high respectively when calculated on the basis of the formula

TABLE II.

KNO₃ taken g.	NaNO₂ added c.c.	KNO₃ found g.	Error per cent.	KNO₃ taken g.	NaNO₂ added c.c.	KNO₃ found g.	Error per cent.
0·1000	2	0·0992	−0·8	0·2000	4	0·1928	−3·6
,,	3	0·0998	−0·2	,,	4·5	0·1940	−3·0
,,	4	0·1017	+1·7	,,	5	0·1958	−2·1
,,	5	0·1020	+2·0	,,	5·5	0·1970	−1·5
,,	6	0·1023	+2·3	,,	6	0·1982	−0·9
				,,	6·5	0·1984	−0·8
					7	0·1990	−0·5
					7·5	0·2016	+0·8
					8	0·2036	+1·8
					9	0·2058	+2·9

$K_2NaCo(NO_2)_6, H_2O$. The analysis of the precipitates consisted in the estimation of potassium, sodium, cobalt, "NO_2", and water by the methods given below.

Estimation of sodium and potassium.—A known quantity of the precipitate was ignited in a porcelain crucible and the mass digested with water when black oxide of cobalt separated and the alkali salts went into solution. It was then filtered and the residue thoroughly washed with hot water. The filtrate was then evaporated in a silica dish and the sodium and potassium weighed together as chlorides. Potassium was then estimated by the perchlorate method and the sodium obtained by difference.

Cobalt.—About 1·5 g. of the substance was dissolved in sulphuric acid (1 : 4) and the oxides of nitrogen driven off by boiling. The solution was first neutralised with dilute ammonia after which 5 g. of ammonium sulphate and 50–60 c.c. of conc. ammonia were added. This solution was electrolysed employing a current-density of 0·5–0·7 Amp./sq.dm., and an E.M.F. of 2·8–3 volts. The cylindrical platinum gauze cathode was rotated by an electrically driven motor, the speed of which could be varied from 100–2000 revolutions per minute. It was found that the period necessary for the complete deposition of cobalt was considerably shortened by the addition of some sodium bisulphite (0·2–0·4 g.) as suggested by Brophy (*Ind. Eng. Chem. Anal.*, 1931, **3**, 363).

NO₂.—This estimation was always done by the permanganate oxidation method, and in some cases also by the nitrometer method due to Dumas. In the former method the substance (0·2 g.) was boiled with sodium hydroxide (30 c.c. 10 per cent. sol.), and the cobalt hydroxide which separated was filtered off. The filtrate and washings were diluted with water to about 400 c.c., acidified with sulphuric acid and titrated with N/10 KMnO₄. As this procedure leads to low results owing to loss of oxides of nitrogen during the process of neutralization with sulphuric acid, it was modified as follows. To the filtrate and washings containing the nitrite, N/10 KMnO₄ was added in such a quantity as was insufficient by about 1 c.c. to effect complete oxidation. It was then acidified with sulphuric acid and the titration completed with N/10 KMnO₄. The results obtained by this method were in good agreement with those obtained by the method of Dumas.

Water.—Owing to the low water content of the precipitates analysed, fairly large samples (1·5 g.) had to be employed. The weighed sample was kept in a porcelain boat in a combustion tube connected at one end with a carbon dioxide Kipp's apparatus through drying vessels containing sulphuric acid and phosphorus pentoxide. Freshly reduced copper gauze was kept heated at the other end of the combustion tube in order to reduce the oxides of nitrogen given off by the substance on heating. The water vapour evolved was collected and weighed in a calcium chloride U tube which was protected from atmospheric moisture by suitable guard tubes. The substance was introduced into the combustion tube after the apparatus had been thoroughly dried in a stream of dry carbon dioxide. All the precautions usual in such determinations were duly observed.

The results of analyses of the various precipitates are assembled together in Table III, each result being the mean of three or four concordant determinations.

TABLE III.

	K	Na	Co	NO₂	H₂O
Ppt. which yielded low results ..	17·7	5·5	13·1	61·9	1·8
K₂NaCo(NO₂)₆, ½ H₂O requires ..	17·6	5·2	13·2	62·0	2·0
Ppt. which yielded accurate results ..	16·9	5·3	13·1	60·8	3·8
K₂NaCo(NO₂)₆,H₂O requires ..	17·2	5·1	13·0	60·8	3·9
Ppt. which yielded high results ..	16·6	4·9	12·8	58·8	6·9
K₂NaCo(NO₂)₆, 2H₂O requires ..	16·6	4·9	12·8	58·6	7·2

The results given in Table III indicate that whereas the precipitate which yields accurate results corresponds to the formula $K_2NaCo(NO_2)_6, H_2O$, those which gave low and high results correspond to $K_2NaCo(NO_2)_6, \frac{1}{2}H_2O$ and $K_2NaCO(NO_2)_6, 2H_2O$ respectively. It is evident therefore that incorrect results would be obtained if the precipitate is always assumed to have the formula $K_2NaCo(NO_2)_6, H_2O$. It has been shown already (Table II) that correct results can be obtained, i.e., potassium precipitated as $K_2NaCo(NO_2)_6, H_2O$ only when the quantities of reagents added, strictly correspond to the quantity of potassium present in the solution. It therefore appeared to us that the accurate estimation of the potassium content of a mixture could be carried out as follows. The sample is brought into solution and assuming that it consists almost entirely of a salt of potassium the corresponding quantities of reagents are added, the details of the procedure being as outlined on p. 3. From the weight of the precipitate obtained, the potassium content of the mixture is calculated, and as this value is about 5 per cent. too high, the actual potassium content of the mixture is arrived at approximately. So, another lot of the mixture is weighed out, brought into solution and such quantities of the reagents are added as correspond to the potassium content deduced as mentioned above and the determination carried out as described already. In case, however, the stock of mixture is insufficient for several analyses, the precipitate obtained in the preliminary estimation in which excess of the reagents were added can be utilised in place of a fresh lot of mixture as follows. The precipitate is dissolved in hydrochloric acid (5 p.c.), the excess of acid expelled by evaporating the solution to dryness, and the residue taken up with water and filtered. Since the potassium content of the filtrate is known approximately, it is relatively simple to carry out the determination by the procedure described earlier. The results of some determinations carried out by this modified procedure are given in Table IV.

All the results shown in Table IV are accurate to within 1 per cent. thus indicating that the procedure outlined above is reliable. Parallel estimation of potassium in some mixtures was then conducted by this method as well as by the perchlorate method as recommended by Treadwell (*Analytical Chemistry*, II, 1930, 64). The results obtained are given in Table V, and it can be seen that they are in fair agreement.

The next point studied was the solubility of potassium-sodium cobaltinitrite in water at different temperatures. A weighed quantity (2 g.) of the substance was added to 100 c.c. of water contained in a round bottomed flask which was kept in a water bath maintained at the desired temperature $\pm 1°$. The contents of the flask were stirred vigorously for about two hours after which it was filtered through a weighed gooch crucible and the solid collected was weighed. This

TABLE IV.

Mixture	KNO₃ per cent.	Actual per cent.	Error per cent.
$KNO_3 + MgO$	66·8	66·7	−0·2
,,	66·9	66·7	−0·3
,,	50·3	50·0	+0·6
$KNO_3 + NaCl$	66·8	66·7	+0·3
,,	49·9	50·0	−0·2
$KNO_3 + Na_2HPO_4$	49·8	50·0	−0·4
,,	49·7	50·0	−0·6
$KNO_3 + NaCl + Fe_2O_3 + Al_2O_3 + SiO_2 + CaO + MgO$	33·2	33·3	−0·3
,,	33·3	33·3	0·0
,,	33·5	33·3	+0·6
,,	22·4	22·3	+0·5
,,	22·4	22·3	+0·5
,,	10·25	10·16	+0·9
,,	10·15	10·16	−0·1

TABLE V.

KNO₃ actually present ..	22·30	22·30	10·76	10·76	per cent.
KNO₃ found by cobaltinitrite method	22·44	22·47	10·82	10·83	,,
KNO₃ found by perchlorate method	22·49	22·40	10·85	10·86	,,

weight when deducted from the weight of the solid originally taken gave the quantity of the solid which went into solution. In some cases a control determination of this quantity was made by evaporating the filtrate to dryness in a small silica dish and weighing the solid recovered. Measurements of solubility could not be made at temperatures exceeding 60° as the precipitate decomposed during the experiments at those temperatures. Attempts were not made to obtain very accurate figures as the solubility was found to be small. The results obtained are given in the table below.

TABLE VI.

Temperature	20	25	30	40	50
Solubility in mg. per 100 c.c. of water	1	3	9	21	60

It should be noted that the data shown above were obtained by stirring the substance vigorously for two hours in water at the required temperature. In actual estimations of potassium, however, the precipitate was in contact with water at 25–30° for not more than 20–30 minutes, and it was found that the solubility of the precipitate under such conditions was negligible.

SUMMARY.

Precipitates of potassium-sodium cobaltinitrite obtained under varying conditions were analysed and found to belong to three classes (a) $K_2NaCo(NO_2)_6,H_2O$, (b) $K_2NaCo(NO_2)_6,\frac{1}{2}H_2O$, and (c) $K_2NaCo(NO_2)_6,2H_2O$. Since it is assumed that the precipitate obtained is (a) serious errors arise whenever (b) or (c) is present. A procedure has been suggested by which the precipitation of potassium as (a) can be ensured and accurate results obtained.

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