ART. XL.—*On the Volumetric Estimation of Potassium as the Cobalti-nitrite*; by W. A. DRUSHEL.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxvi.]

THE use of sodium cobalti-nitrite for the qualitative detection of potassium is well known and its use as a quantitative reagent has been described by R. H. Adie and T. B. Wood,* whose results are fairly accurate and favorably comparable with results obtained by the platinic chloride gravimetric method. In the process worked out by these investigators a solution of a potassium salt containing the equivalent of 0·5 per cent to 1 per cent of K_2O is acidified with acetic acid and precipitated by an excess of sodium cobalti-nitrite. The mixture is allowed to stand at least a few hours, preferably over night, and is then filtered through a perforated crucible fitted with an asbestos felt. The precipitate is washed with 10 per cent acetic acid. According to Sutton it is important that the precipitation should be made in a solution containing the equivalent of 0·5 per cent to 1 per cent of K_2O, since in solutions of lower concentration the precipitate comes down in a condition in which it is apt to run through the filter in washing. The precipitate is then decomposed by boiling in dilute sodium hydroxide, and the cobalt is removed as the hydroxide by filtration. The nitrites, which are a measure of the potassium in the precipitate, are estimated by titrating with standard potassium permanganate. Adie and Wood found by analysis that the composition of the precipitated potassium salt is represented by the formula $K_2NaCo(NO_2)_6.H_2O$. According to their method a cubic centimeter of strictly $\frac{n}{10}$ potassium permanganate is equivalent to 0·000785 grm. K_2O.

The object of this investigation was to determine the best conditions for precipitating and filtering the potassium cobalti-nitrite, and to shorten the work of estimating the potassium by oxidizing directly with potassium permanganate without the preliminary decomposition of the precipitate and removal of cobalt recommended by Adie and Wood. In a series of preliminary experiments the precipitated cobalti-nitrite was oxidized by an excess of potassium permanganate, the excess of permanganate reduced by standard oxalic acid, and the remaining oxalic acid titrated to color. In this treatment trivalent cobalt is reduced to the bivalent condition, and from the formula of potassium sodium cobalti-nitrite it would appear that the oxygen thus made available should be equivalent to one-twelfth of that necessary to oxidize the nitrites. The results of these experiments are given in Table I.

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Portions of a potassium chloride solution of known strength were treated with an excess of sodium cobalti-nitrite* and filtered on perforated crucibles fitted with asbestos felts. The precipitates were first washed with a 10 per cent acetic acid solution, then once with water. In experiments 1 to 5 the precipitate was decomposed by boiling with sodium hydroxide and the nitrites estimated according to the method of Adie and Wood, giving the results in the second column of Table I. The cobaltic hydroxide filtered off on asbestos was reduced by heating nearly to boiling in a measured amount of standard oxalic acid containing a little sulphuric acid. The excess of oxalic acid was estimated by titrating with standard potassium permanganate, and from this the equivalent of the cobaltic hydroxide in terms of permanganate was found by subtraction, giving the results in the third column of the table. In experiments 6 to 10 the precipitated potassium salt together with the crucible and asbestos felt, after stirring the precipitate and felt loose from the crucible, was placed in a beaker containing a measured amount of standard permanganate, taking care to use an excess, diluted to about ten times its volume and heated nearly to boiling. After five to eight minutes, or when the manganese hydroxide formed gave the solution a dark color, it was acidified with 5^{cm^3} to 20^{cm^3} of sulphuric acid (1 : 7). After a few minutes a measured excess of standard oxalic acid was run in from a burette, the temperature being kept a little below the boiling point until the solution became clear, and then titrated to color with permanganate. The whole amount of permanganate used less the equivalent of the oxalic acid used is the amount necessary for the oxidation of the precipitate. The results are given in the fourth column.

TABLE I.

No.	K_2O taken grm.	$KMnO_4$ used in titration of nitrites after removal of cobaltic hydroxide cm^3.	$KMnO_4$ equivalent to cobaltic hydroxide cm^3.	$KMnO_4$ used in direct titration cm^3.
1.	0·0235	32·4	2·5	——
2.	0·0235	32·25	2·5	——
3.	0·0235	32·65	2·55	——
4.	0·0353	48·35	3·88	——
5.	0·0353	49·	3·95	——
6.	0·0235	——	——	30·
7.	0·0235	——	——	29·65
8.	0·0235	——	——	29·4
9.	0·0353	——	——	43·65
10.	0·0353	——	——	44·4

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* Prepared according to the directions given by Adie and Wood *loc. cit.*, also given in Sutton's Volumetric Analysis, 9th ed., p. 62.

From the results of Table I it appears that the oxidizing value of the cobaltic hydroxide in terms of permanganate is nearly one-twelfth of that required for the oxidation of the nitrites, while the amount of permanganate necessary in the presence of the cobalt is nearly eleven-twelfths of that required for the oxidation of the nitrites after the removal of the cobalt. The factor used, therefore, in calculating the results from the direct titration should be twelve-elevenths of that given by Adie and Wood; that is, in titrating the precipitate without first separating the cobalt one cubic centimeter of strictly $\frac{n}{10}$ potassium permanganate is equivalent to 0·000856 grm. K_2O.

Unless the potassium salt solution is of the proper concentration the precipitate is very difficult to filter and wash, and shows a tendency to pass through the felt. By repeated experiments it was found that this difficulty as well as the necessity for allowing the precipitate to stand over night is avoided by evaporating the mixture nearly to dryness on the steam bath after adding the sodium cobalti-nitrite solution in considerable excess. Upon cooling the pasty residue it becomes hard and dry. It is then treated with cold water to dissolve the excess of sodium cobalti-nitrite, and the insoluble portion is collected on the filter. This precipitate may be freely washed with cold water without showing a tendency to pass through the filter, and is so insoluble that less than 0·5 of a milligram of the dried precipitate will dissolve in a liter of water at the room temperature during 24 hours standing with occasional shaking. This mode of treatment was found to work well and was used in all the subsequent experiments.

The method as worked out and used in all the experiments except those of Table I is as follows: The solution of a potassium salt, containing not more than 0·2 grm. K_2O and free from ammonium salt, was treated with a rather large excess of sodium cobalti-nitrite solution acidified with acetic acid, and evaporated to a pasty condition over the steam bath. It was then cooled and treated with 50^{cm^3} to 100^{cm^3} of cold water and stirred until the excess of sodium cobalti-nitrite was dissolved. It was allowed to settle and decanted through a perforated crucible fitted with an asbestos felt. The precipitate was washed two or three times by decantation, after which it was transferred to the crucible and thoroughly washed with cold water. In the meantime a measured excess of standard potassium permanganate was diluted to ten times its volume and heated nearly to boiling. Into this the precipitate and felt were transferred and stirred up, after which the crucible was also put into the solution, since particles of the precipitate stick persistently to the sides of the crucible. After the oxidation had proceeded five or six minutes manganese hydroxide separated out and the color of the solution darkened. At this point 5^{cm^3} to 25^{cm^3} of sulphuric acid (1:7) were added, and the solution, after stirring, was allowed to stand a few minutes. Then a measured amount of standard oxalic acid, containing 50^{cm^3} strong sulphuric acid per liter, was run in from a burette, taking care to add an excess. The temperature was maintained a little below the boiling point until the solution became colorless and the manganese hydroxide had completely dissolved. It was then titrated to color by permanganate in the usual manner. From the whole amount of permanganate used the permanganate equivalent of the oxalic acid used was subtracted and the remainder multiplied by the factor calculated for the strength of permanganate used, 0·000856 being the factor for strictly $\frac{n}{10}$ potassium permanganate.

To make the $\frac{n}{10}$ oxalic acid solution, exactly 7·1066 grm. of pure recrystallized ammonium oxalate were dissolved in about 700^{cm^3} of cold distilled water contained in a liter flask. To this solution were then added 50^{cm^3} of strong sulphuric acid. The contents of the flask were cooled to 15° C. and made up to the mark with distilled water. The potassium permanganate solution was made approximately decinormal and standardized in the usual way. This standard was checked by standardizing under conditions as nearly as possible like those under which the solution was used. A measured portion was diluted ten times, heated nearly to boiling, acidified with dilute sulphuric acid and allowed to stand a few minutes. It was then bleached with a measured amount of oxalic acid, using it in slight excess, and titrated to color. The two methods agreed very well, the difference in permanganate seldom being greater than one-tenth to two-tenths of a cubic centimeter in 25^{cm^2}.

TABLE II.

	K_2O taken	K_2O found		Error in K_2O	
No.	As KCl grm.	Gravimetrically grm.	Volumetrically grm.	Gravimetrically grm.	Volumetrically grm.
1.	0·0237	0·0240	0·0238	0·0003 +	0·0001 +
2.	0·0237	0·0243	0·0242	0·0006 +	0·0005 +
3.	0·0354	0·0359	0·0355	0·0004 +	0·0000 ±
4.	0·0474	0·0478	0·0471	0·0004 +	0·0003 —
5.	0·0048	0·0048	0·0050	0·0000 ±	0·0002 +
6.	0·0024	0·0024	0·0023	0·0000 ±	0·0001 —
7.	0·0005	-----	0·0006	--------	0·0001 +
8.	0 0015	-----	0·0017	--------	0·0002 +
9.	0·0355	-----	0·0355	--------	0·0000 ±

In the first six experiments of this series the precipitate was dried at 115° C. and weighed. It was then treated with permanganate by the method previously described. Experiments 6, 7 and 8 show that very small amounts of potassium may be estimated with a fair degree of accuracy.

In Table III the effect of the presence of members of the calcium group was investigated. Calcium and magnesium apparently do not interfere, while barium and strontium tend to give high results.

TABLE III.

	$CaCl_2$	$MgCl_2$,	$BaCl_2$, taken	$Sr(NO_3)_2$	K_2O taken	K_2O found	Error
	grm.	grm.	grm.	grm.	grm.	grm.	grm.
1.	0·2000	0·2000	------	------	0·0005	0·0007	0·0002+
2.	0·3000	0·5000	------	------	0·0237	0·0234	0·0003—
3.	0·5000	1·0000	------	------	0·0829	0·0824	0·0005—
4.	0·5000	1·0000	------	0·5000	0·0711	0·0737	0·0026+
5.	0·5000	1·0000	0·5000	0·5000	0·0474	0·0493	0·0019+
6.	0·5000	1·0000	0·5000	------	0·0237	0·0251	0·0014+
7.	0·5000	1·0000	------	------	0·0711	0·0713	0·0002+

The method may also be used in the presence of phosphoric acid and is therefore applicable to the estimation of K_2O in fertilizers. In Table IV are the results obtained in nine fertilizers by the platinic chloride method and the cobalti-nitrite volumetric method. In columns one and two are the duplicate results obtained by two analysts of the Connecticut Agricultural Experiment Station, and in column three are the results by the volumetric method. The water-soluble phosphoric acid present in these samples is given in the fourth column.

TABLE IV.

K_2O in Mixed Fertilizers.

	K_2O by platinum chloride method		K_2O by vol. cobalti-nitrite meth.	Water-soluble P_2O_5 in sample
No.	per cent	per cent	per cent	per cent
1.	5·22	5·18	5·18	4·16
2.	6·53	6·56	6·56	3·10
3.	2·23	2·24	2·24	7·82
4.	8 68	8·64	8 78	0·94
5.	6·37	6·42	6·38	6·62
6.	6·08	6·13	6·13	5·61
7.	4·08	4·02	4·02	3·15
8.	4·62	4·66	4·67	2·43
9.	1·68	1·67	1·77	6·03

Ten grams of the fertilizer were placed in a 500^{cm^3} flask and 300^{cm^3} of water were added. The contents were boiled for 30 minutes and ammonia water was added to slight alkalinity. Enough ammonium oxalate was added to precipitate all the calcium and, after cooling, the solution was made up to the mark on the neck of the flask and well shaken. The solution was then filtered through a dry filter into a dry flask. Two 50^{cm^3} portions of the filtrate were transferred with a pipette to platinum dishes, one portion being used for the gravimetric estimation by the platinum chloride method and the other for the volumetric estimation by the cobalti-nitrite method. After evaporating these portions to half their volume over the steam bath, 1^{cm^3} sulphuric acid (1 :1) was added and the evaporation was continued as far as possible over the steam bath, and finally over a low flame. After the danger of spattering was over the flame was increased and the charred organic matter was burned off, finally, over the blast lamp. The potassium sulphate was dissolved by adding a little water and heating over the steam bath, and the potassium was estimated as previously described.

The volumetric method may be summed up thus: The potassium is precipitated as potassium sodium cobalti-nitrite by an excess of sodium cobalti-nitrite and the mixture is evaporated on the steam bath. The precipitate is separated by filtration through asbestos and oxidized by hot standard potassium permanganate. The excess of permanganate is bleached by an excess of standard oxalic acid and the solution is then titrated to color by permanganate. The amount of potassium oxide is found by multiplying the oxygen value of the amount of potassium permanganate used by the factor 1·09.

This method has the advantages over the platinum chloride method that no expensive reagents are used and that the time required for a determination is materially reduced. The method is considerably shorter than that of Adie and Wood and does not require the potassium solution to be of any definite concentration to work well.

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