

A Study of Methods for the Determination of Potassium in Fertilizer

by R. G. Hackman

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A senior thesis project of the University of Kansas

A STUDY OF METHODS FOR
THE DETERMINATION OF
POTASSIUM IN FERTILIZERS

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A Study of Methods for the Determination
of Potassium in Fertilizers,

By,

R. G. Hackman .

Presented to the Faculty
of the
School of Engineering
of the
University of Kansas.

In partial fulfillment of the requirements for the
degree of
BACHELOR of SCIENCE.

Lawrence, Kansas,
March fifteenth,
Nineteen Twelve.

Professor H. P. Gady,
Department of Chemistry,
University of Kansas.

Dear Sir:

I desire to submit the
following thesis entitled, A Study of the Methods
for the Determination of Potassium in Fertilizers.

Respectfully,

Bibliography.

- (I) Official and Provisional Methods of Analysis
 Association of official Agricultural Chemists.
 Bulletin 10 7 (Revised) Ppg. 11-12.
- (II) On the Determination of Potassium by the Cobalti
 Nitrite Method. By L. T. Bowser. The Jour, Ind.
 and Eng. Chemistry. Vol. 1. No. 12, ppg. 791-797.
- (III) Application of the Cobalti-Nitrite Method for the
 estimation of Potassium in Soils. By W. A. Drushel
 Amc. Journ. Sci. 26-3 29-32 and 24-433.
- (IV) Volumetric Determination of Potassium by the Cobalti-
 Nitrite Method. By O. M. Shedd.
 Chem. News, June 16, 1911. ppg. 282-284 and
 " " June 23, 1911. " 291-293.
- (V) Potash Tests in Commercial Fertilizers by
 J. E. Breckenridge. Jour. Ind. and Eng. Chemistry
 Vol. I, No. 12. ppg. 804-806 and ppg. 810-811.
- (VI) Potassium: Its Titrimetric Estimation in Small
 Amounts. By L. T. Bowser. The Jour. Am. Chem.
 Sac. Vol. 33- No. 11. ppg. 1752-1757.

- (VII) Potassium: Its Qualitative Detection as the
Cobalti-Nitrite. By L. T. Bowser. The Jour.
Amc. Chem. Soc. Vol. 33-No. 10. ppg. 1566-1569.
- (VIII) Sodium Cobalti-Nitrite Reagent. By Adie and
Wood. Jour. London Chem. Soc. Vol. 77. pg. 1076.

For the determination of potassium, there are at present, two practical methods, the platonic-chloride gravimetric method and the cobalti-nitrite volumetric method. Of these methods, the first is the one most generally used and perhaps the most reliable one at present. The second method however, has proven of enough importance to justify investigation by the Association of Official Agricultural Chemists.

In the determination of potassium in fertilizers, the platonic-chloride gravimetric method is the one recommended by the Association of Official Agricultural Chemists, after much investigation. The method as adopted by that body is given in Bulletin 107 (I).

The main objections to this method are its tediousness, the high cost of the reagents, and the uniformly low results given by it.

For some time sodium cobalti-nitrite has been used for the qualitative determination of potassium but Adie and Wood were the first to attempt to make use of this reagent in the quantitative determination of that salt. They worked out a method which gave only fairly accurate results. Later, and independently of each other, Bowser and Drushel experimented with this first

method in an effort to determine its accuracy. Bowers experiments were made with a view of determining if possible, the factors which caused the irregularities in the results obtained by Adie and Wood's method (II). Drushel worked out a modification of this method (III). The modified method adopted by him, was later investigated by Shedd (see IV).

Platenic-Chloride Method.

The platenic-chloride method as given in Bulletin 107 (I) and as used by a number of packing houses for the determination of potash in the fertilizers manufactured by them, is as follows: the sample for analysis is thoroughly mixed, quartered and requartered until a representative sample of sufficient size for grinding is obtained. This sample is ground in a mortar until it will pass through a 40 mesh sieve, after which it is thoroughly mixed. Next 10 grams are weighed out and transferred to a 500 cc graduated flask, 300 cc of water added and boiled for 30 minutes. Ammonium hydroxide and ammonium oxalate are added to the solution, which is then allowed to cool after which its volume is made up to 500 c.c. and thoroughly mixed. The solution is then filtered through a dry filter,

the filtrate being received in a dry flask. Fifty cc of this filtrate are withdrawn by means of a pipette and run into a platinum dish and then evaporated nearly to dryness on a water bath. One cc of dilute sulphuric acid is added and the evaporation continued to dryness. When all danger of spattering is over, the dish is heated over a free flame to full redness until the residue becomes perfectly white. This is then dissolved in hot water, a few drops of hydrochloric acid added and then an excess of the platinum-chloride reagent. (This reagent contains 1 gram of metallic platinum in every 10 cc of solution.). The contents of the dish are then evaporated on the water bath to a thick paste, taken up with 80% alcohol, and then filtered through a Gooch crucible fitted with an asbestos pad. The precipitate is washed with 80% alcohol until the washings are colorless, then with a solution of ammonium chloride to remove any impurities, and finally with 80% alcohol. The Gooch crucible and precipitate are then dried for 30 minutes in an oven at 100° c. after which it is weighed. The Gooch having been previously weighed, the difference in weight is the weight of the precipitated potassium chlor platinate. From the weight of this precipitate

the percentage of K_2O may be calculated.

This method is the one in general use but it is generally conceded that when used with fertilizers, it gives low results. In 1906, Mr. Breckenridge (V) made some experiments with this method to find, if possible, the source of error. He found that the length of time the solution, (after the addition of the ammonium hydroxide and ammonium oxalate) was allowed to stand before filtering affected the results. Solutions which are allowed to stand 2 weeks before filtering give the theoretical results, while those standing for 24 hours, give results from 25-50 % greater than those standing two hours only. At the same time he made experiments to determine what substances had the greatest effect on losing potash; he found that large amounts of iron and alumina, with even moderate amounts of the insoluble, had the most effect.

Cobalti-Nitrite Method.

Adie and Wood were the first to work out a method for the quantitative estimation of potash by means of the sodium cobalti-nitrite reagent. The method as worked out by them is as follows: Add 10 cc of the

cobalti-nitrite reagent and 1 cc of glacial acetic acid to 10 cc of the potash solution, allow to stand over night, filter the precipitate on a Gooch fitted with an asbestos pad, and wash with 10% acetic acid. The cobalt is precipitated by boiling the pad and precipitate with 2 or 3 cc of a 10% solution of sodium hydroxide, and filtered off along with the asbestos. The filtered solution is made up to 100 cc and aliquots of 20 cc are taken for titration with standard potassium permanganate. The solution is slowly acidified with dilute sulfuric acid and the potassium permanganate added until the pink color holds for a minute. According to this method, 1 cc of $\frac{N}{10}$ K. Mn O₄ is equal to 0.0007858 gram of K₂ O. The formula of the precipitated salt is K₂ Na Co (NO₂)₆.H₂ O.

The reagent used is prepared by the following method: 220 grams of sodium nitrite are dissolved in 400 cc of water, 113 grams of cobalt acetate are dissolved in 300 cc of water and 100 cc of glacial acetic acid. The solutions are filtered and mixed, and the evolved N O₂ evacuated by means of a filter pump. The solution is allowed to stand for 24 hours, filtered and made up to 1 liter.

The method of Adie and Wood gave very irregular results, so a series of determinations was made by Bowser (II) with a view to ascertaining the factors contributing to these irregularities. He found that most of the difficulty was due to the method of precipitation; the greater the dilution of the potash solution at the time of addition of the cobalti-nitrite reagent, the lower the results obtained. This he found to be due partly to the running of the precipitate through the filter; it was also thought probable that too great dilution causes a decomposition of the precipitated salt. After a number of determinations had been made he found that the best way to precipitate the potash was to evaporate the solution to 5 cc - 10 cc before the addition of the reagent. After considerable experimenting he finally worked out the following method: The potash solution is evaporated to 5 cc - 10 cc, on the water bath, 10 cc of reagent and 1 cc of glacial acetic acid added, and the mixture evaporated to pastiness of the water bath. After cooling, the residue is taken up with water and filtered on asbestos, washed with sufficient water to remove excess of reagent, and the asbestos and precipitate transferred to a beaker. An excess of standard

K Mn O_4 is now added and the contents of the beaker brought to boiling, 5 cc of dilute (1:1) $\text{H}_2 \text{SO}_4$ added, stirred for a few moments, then titrated with standard oxalic acid. Using this method Bowser found that 1 cc of $\frac{\text{N}}{10} \text{K Mn O}_4$ was equal to 0.0008573 gram $\text{K}_2 \text{O}$.

This method gave fairly accurate and regular results.

At about the same time that Bowser was carrying on his experiments, Drushel was also making a series of experiments with the cobalti-nitrite method of Adie and Wood (VIII). The method which he finally worked out is as follows: The potassium is precipitated as dipotassium-sodium-cobalti-nitrite by an excess of the reagent the mixture evaporated to pastiness on the water bath, the precipitate filtered on asbestos and oxidized by an excess of hot standard K Mn O_4 . This oxidation is accomplished by diluting a volume of standard K Mn O_4 to ten times its volume, and boiling, when the asbestos and precipitate are thrown in, and stirred up. After about five minutes the manganese hydroxide separates out, when 5-25 cc dilute $\text{H}_2 \text{SO}_4$ (1:7) are added, the solution stirred and allowed to stand for a few moments. Then the excess of permanganate is bleached by an excess of standard oxalic

acid, after which the solution is titrated back to color by means of the standard K Mn O_4 . The method of Bowser differs from this in that he restricts the volume of the potash solution to 5-10 cc on addition of reagent, and that he titrates directly for excess of K Mn O_4 , thereby saving considerable time.

O. M. Shedd (IV) later experimented with this method of Drushel and found that it was necessary to evaporate the potash solution to 5-10 cc before adding the reagent, in order to get accurate results. He found that a greater dilution caused a decomposition of the reagent, due to the increased time necessary for evaporation, and so prevented complete precipitation of the potash. He found also, that the precipitated salt is acted upon to some extent by water and acetic acid, so that it is imperative that an excess of reagent be present at the end of the evaporation, in order that accurate results may be obtained.

The work done by Shedd was on samples of fertilizers sent to him by the referee on potash, of the Association of Official Agricultural Chemists.

Experimental Part.

While working with fertilizers in the Swift and

Company laboratory in Kansas City, the following experiments with the platenic chloride method were carried out.

The first series of determinations was made to find if a longer period of boiling would give any higher results in potash. The samples used were the samples of fertilizer sent to the laboratory for analysis and were, for the most part, "Special Grain Fertilizers" and "Superphosphates." After grinding and mixing, 10 grams of each sample were weighed up, in duplicate, into 500 cc graduated flasks, 300 cc of water added and the contents of the flasks boiled. One flask was boiled for 45 minutes, the other for 30 minutes. After cooling the analysis was carried out by the method already given (I). The results of these determinations are given below.

No.	Time boiled.		Wt. of K_2PtCl_6 in gms.		Percentage of K_2O .	
	1	2	1	2	1	2
1	30 min.	45 min.	0.1072	0.1068	2.07	2.06
2	"	"	0.1204	0.1210	2.32	2.33
3	"	"	0.1140	0.1142	2.20	2.20
4	"	"	0.1135	0.1130	2.09	2.08
5	"	"	0.1204	0.1200	2.32	2.32
6	"	"	0.0862	0.0865	1.66	1.66
7	"	"	0.1121	0.1128	2.16	2.17
8	"	"	0.1182	0.1180	2.28	2.28
9	"	"	0.1010	0.1013	1.95	1.95

The conclusion drawn from these results was that 30 minutes boiling was sufficient for dissolving all of the water soluble potassium salts in the sample.

The second series of determinations was to determine if all of the water soluble potash was dissolved in any less than 30 minutes of boiling. The samples used were, as in the first series, those received in the laboratory, and were of the same character as those used in the first series of determinations. The samples were ground, mixed, 10 grams weighed up, in duplicate, into 500 cc graduated flasks, 300 cc of water added and the contents of the flasks boiled, the one for 30 minutes and the other for 20 minutes. After cooling the remainder of the determination was carried out according to the regular method.

No.	Time Boiled.		Wt. of K_2PtCl_6 in grams		Percentage K_2O	
	1	2	1	2	1	2
1	30 min.	20 min.	0.1210	0.1212	2.33	2.33
2	"	"	0.1229	0.1223	2.37	2.36
3	"	"	0.1206	0.1200	2.32	2.32
4	"	"	0.1012	0.1009	1.95	1.95
5	"	"	0.1100	0.1107	2.12	2.13
6	"	"	0.1271	0.1270	2.45	2.45
7	"	"	0.3389	0.3381	6.54	6.53

The conclusion drawn from these results was that 20 minutes of boiling was sufficient to dissolve all of the water soluble potash. However, the percentage of potash in these

fertilizers was small, so that it is possible with larger percentages, 20 minutes would be too short a time.

In the official method the directions are to allow the solution, after the addition of the ammonium hydroxide and ammonium oxalate, to cool before filtering. The next series of determinations made were to determine if the time of standing before filtering would cause any increase or decrease in the potash results. The samples used were of the same character as those used in the preceding determinations. After grinding and mixing, 10 grams of the sample were weighed, in duplicate, into a 500 cc graduated flask, 300 cc of water added, the contents of the flasks boiled for 30 minutes, ammonium hydroxide and ammonium oxalate added and the flasks set aside to cool. At the end of one hour, the volume of solution from one flask was made up to 500 cc mixed thoroughly and filtered through a dry filter. 50 cc of this filtrate were then drawn off by means of a pipette and the determination completed according to the official method. The other flask was allowed to stand for 24 hours before proceeding with the determination. The results are given below.

No.	Aliquot		Grams of K_2PtCl_6			Percentage of K_2O	
	1	2	1	2	2	1	2
1	1 hour	24 hours.	0.1166	0.1164		2.25	2.25
2	"	"	0.1135	0.1129		2.19	2.18
3	"	"	0.1107	0.1112		2.14	2.14
4	"	"	0.0530	0.0539		1.02	1.03
5	"	"	0.0848	0.0840		1.63	1.62
6	"	"	0.0927	0.0914		1.78	1.76
7	"	"	0.0958	0.0955		1.85	1.84
8	"	"	0.0131	0.0133		0.264	0.259

The conclusion drawn from these results was that the time of standing did not have an effect upon the percentage of potash. These results, however, do not agree with those obtained by Breckenridge (see V). He found that the time of standing materially affected the potash results. The difference may be due to the fact that he was working with higher percentage of potash.

The official directions are that the platinum dish containing the precipitate of potassium sulphate should be heated over a free flame at full red heat until the residue is perfectly white, and that no loss of potassium from volatilization need be apprehended from this. But the results obtained by this method were low, so the next series of determinations was made to determine if any of the potassium was lost in this manner. The samples of fertilizer were the same character as those used in the preceding determination. The official method was followed up to the point of heating the platinum dish, when one dish was heated over a free flame to full red heat and the other to a

dull red heat. From this point on, the official method was followed. The results of the determinations are given below.

No.	Wt. of K_2PtCl_6 in Grams		Percentage of K_2O	
	1 Low red	2 Full red	1	2
1	0.1109	0.1039	2.12	2.00
2	0.1427	0.1396	2.75	2.69
3	0.1280	0.1174	2.47	2.27
4	0.1058	0.1007	2.04	1.94
5	0.1111	0.1025	2.11	1.97
6	0.1098	0.1023	2.12	1.97
7	0.1669	0.1612	3.22	3.11
8	0.1025	0.0968	1.98	1.87
9	0.1102	0.1065	2.13	2.06
10	0.1215	0.1151	2.34	2.22

The conclusion drawn was that at a full red heat, the potassium sulphate was appreciably volatile.

It was intended to carry out determinations adding an excess of dilute sulphuric acid just before the complete evaporation of the filtrate in the platinum dish, to see whether this would prevent the volatilization of the precipitate when heated to a full red heat. But was unable to carry out these determinations.

It was planned to make a comparison of the results obtained by the platonic chloride method and the cobalti-nitrite method, by making a series of determinations with the cobalti-nitrite method, upon samples of fertilizer which had been previously analyzed for potash by the

gravimetric platonic-chloride method. But these samples of fertilizer were not procurable. However, a series of determinations was made with the cobalti-nitrite method, using a solution of chemically pure potassium chloride. In the first determinations a solution containing 1 gram of potassium chloride per 500 cc of solution was used and a solution of permanganate which was $\frac{N}{20.6}$ and of which 1 cc was equivalent to 0.000416 gram K_2O . Later a new potash solution containing 5 grams of potassium-chloride per 500 cc of solution and a new permanganate solution, which was $\frac{N}{11.4}$, were made.

In the first series of determinations, 10 cc of potash solution or an equivalent of 0.01264 gram K_2O , were transferred, by means of a pipette, to a 300 cc beaker and evaporated to about 2 cc - 3 cc, when 10 cc of a mixture of equal parts alcohol and glacial acetic acid, called acid-alcohol, were added then 10 cc of the reagent. The reagent was prepared according to the method given by Adie and Wood (VIII). The beaker was allowed to stand for about an hour, when the precipitate was filtered on a Gooch, asbestos pad and washed with a 20% solution of acetic acid, to remove any excess of reagent. The

asbestos felt and precipitate were then washed back into the same beaker, an excess of standard permanganate added, the mixture boiled for a few moments, 1 cc of dilute sulphuric acid (1:1) added and titrated against standard oxalic acid.

No.	cc.s KMnO ₄	Theory K ₂ O	Found K ₂ O	Percentage K ₂ O.
1	15.82	0.01264	0.0065912	52.14
2	18.63	0.01264	0.00775008	69.22
3	22.30	0.01264	0.0092768	73.39
4	19.21	0.01264	0.00799136	63.22

According to Bowser (II) 1 cc of $\frac{N}{10}$ K Mn O₄ = 0.0008573 gram K₂O. These 1 cc of $\frac{N}{20.6}$ K Mn O₄ = 0.000416 gram K₂O.

The results of these determinations were due to the fineness of the precipitate, which ran through the filter, and probably somewhat to the reagent, which was not prepared correctly, as discovered later.

A second set of determinations was run, using the same potash solution, reagent, and K Mn O₄. In this set, 10 cc of potash solution were transferred, by means of a pipette, to a 300 cc beaker, 10 cc of reagent and 10 cc of acid-alcohol were added directly. The beaker was allowed to stand for an hour when the precipitate was filtered and titrated as in the first set of determinations. The lowness of the results in this case were due

to the same causes as in the first set.

No.	cc's. K Mn O ₄	Theory K ₂ O	Found K ₂ O	Percentage K ₂ O
1	18.14	0.01264	0.00754624	59.70
2	17.04	0.01264	0.00708864	56.08
3	19.63	0.01264	0.00816608	64.60
4	19.92	0.01264	0.00828672	65.55

Two determinations were made in the same manner as the second set, except that the potash solution was evaporated to dryness before adding the reagent and acid-alcohol. It was impossible to filter the precipitate.

A third series of determinations was made in the same manner, except that the precipitate was allowed to stand over night before filtering. It was thought that perhaps standing would cause the precipitate to become more crystalline. But the results would seem to indicate that standing does not improve the condition of the precipitate much.

No.	cc. KMn O ₄	Theory K ₂ O	Found K ₂ O	Percentage K ₂ O
1	9.83	0.00632	0.004099	64.70
2	10.15	0.00632	0.0042224	66.81
3	12.65	0.00632	0.0052624	83.26
4	9.22	0.00632	0.00383556	60.68
5	11.10	0.00632	0.0046176	73.06
6	11.28	0.00632	0.00469248	74.24

It was observed that the potassium precipitate was soluble in hot water. In the next series of determinations the procedure was the same as in the preceeding

set, up to the point of titration. After washing the precipitate free from excess of the reagent the asbestos pad and precipitate were washed into the same beaker, the precipitate dissolved in hot water, dilute H_2SO_4 added and the solution titrated directly to color with permanganate. The results from these determinations are lower than the preceeding ones. This is possibly due to decomposition of the precipitate.

No.	cc's . K Mn O ₄	Theory K ₂ O.	Found K ₂ O	Percentage K ₂ O.
1	9.52	0.00632	0.00396032	62.65
2	10.03	0.00632	0.00417248	66.01
3	9.12	0.00632	0.00379392	60.03
4	9.26	0.00632	0.00385216	60.95

As all of these determinations gave low results, due in part, at least, to the running through the filter of the precipitate, some new asbestos was obtained. New reagent was prepared, as the old was thought to have some influence on the low results.

In the following determinations the method of Drushel as modified by Shedd (IV) was used. It was as follows:
 1 cc of potash solution was added to a 500 cc casserole.
 10 cc of reagent and 1 cc of glacial acetic acid were added and the mixture evaporated on a water bath until the contents of the casserole were firm and dry on cool-

ing. This residue was then taken up with cold water, 2 or 3 drops of glacial acetic acid having been added, filtered on asbestos, washed with cold water until the excess of reagent was removed, the asbestos pad and precipitate washed into the casserole, an excess of standard K Mn O_4 added, the mixture heated to boiling, 5 cc of dilute $\text{H}_2 \text{SO}_4$ (1:1) added, stirred a few moments, and then bleached with an excess of standard oxalic acid. The solution was then titrated to color with standard permanganate. In these determinations a new permanganate solution was used. It was $\frac{N}{11.4}$ so that 1 cc was equal to 0.000752 gram K_2O .

In this series of determinations, No's. 13, 14 and 15 were made in beakers of 300 cc capacity instead of the 500 cc casseroles as recommended by Shedd. The results compare favorably with those obtained with the casserole.

The high results of No's. 4, 5 and 6 were due to the asbestos which had not been washed and which contained some reducing substance. The results of these determinations are given below.

No.	cc. K Mn O ₄	Theory K ₂ O.	Found K ₂ O	Percentage K ₂ O.
1	8.54	0.00632	0.00642208	101.49
2	8.53	0.00632	0.00641456	101.44
3	8.43	0.00632	0.00633936	100.30
4	9.37	0.00632	0.00704624	111.49
5	8.97	0.00632	0.00674544	106.73
6	9.61	0.00632	0.00722672	114.34
7	8.68	0.00632	0.00652736	103.27
8	8.50	0.00632	0.00639200	101.12
9	8.45	0.00632	0.00635440	100.54
10	8.51	0.00632	0.00639952	101.10
11	8.39	0.00632	0.00630928	99.83
12	8.46	0.00632	0.00636944	100.78
13	8.50	0.00632	0.00639200	101.13
14	8.44	0.00632	0.00634688	100.42
15	8.46	0.00632	0.00636192	100.66

It is possible that the uniform high results were due to the fact that more or less fumes of ammonia were present in the atmosphere of the laboratory all the time the experiments were being carried out.

The conclusion drawn from these determinations was that by using the method as outlined by Shedd, and employing due care, the cobalti-nitrite method should give results on fertilizers which would compare favorably with the results obtained by the platonic-chloride method.

In conclusion, I desire to thank Professor Cady for the many valuable suggestions made by him, during the course of the determinations.

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