ON THE ESTIMATION OF POTASH.*

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The standard method of estimating potash consists in evaporating the solution, which must contain the potash in the form of chloride, with excess of $PtCl_4$ solution, nearly to dryness, washing the residue with strong alcohol, and weighing as K_2PtCl_6. A strongly advocated modification of the above is the method of Tatlock, the main feature of which is a preliminary washing with 2 or 3 c. c. of a strong platinum solution and final washing with alcohol. This method has the great advantage of estimating potash directly, whether in the form of chloride, sulphate, or nitrate.

In all the published experiments on the standard method we find a tendency to high results. Even when chemically pure KCl and NaCl are used without a mixture of other salts, and when the platinum solution has been refined to the utmost purity, this tendency to excess is recognized. Thus Fresenius, in order to insure removal of all NaCl after washing with alcohol, recommends washing with a few c. c. of water and recovery of any dissolved potash salt from the washings. The committee of the British Association finds that in case the platinum solution is in large excess the results are 5 to 6 per cent. too high, and this even when chemically pure KCl alone is employed. It is manifest that in many cases of commercial analyses where the contents of potash are unknown this large excess and consequent error cannot be avoided.

Again, it has been found that even when the platinum solution gives, in a blank experiment, a residue perfectly soluble in alcohol, it may, from presence of certain impurities, give results far too high when working with chemically pure KCl. When, then, to the above considerations we add the conditions under which the process is used in commercial analysis, especially in fertilizer work, and the difficulty of removing all sulphuric acid, nitric acid, organic matter, lime, salts, etc., and obtaining a solution containing nothing but pure KCl and NaCl, the greater tendency to error is at once evident.

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*Reprinted from the Proceedings of the Association of Official Agricultural Chemists, Sept. 1 and 2, 1885.

On the other hand, the fact that in Tatlock's method the potash can be estimated directly without removal of sulphuric or nitric acids is a strong argument in favor of its use, and were it not for the one objection—that there is a loss varying from 0 to .5 per cent.—we should certainly prefer it to the standard method.

The labor and great care required to make an accurate potash estimation by the standard method in fertilizer analysis has led to an examination of a method proposed by Lindo,* which seems to possess all the advantages of Tatlock's method, and at the same time to be free from a tendency to low results.

Lindo made 10 analyses of a mixture of KCl with 25 per cent. $MgSO_4$ and 10 per cent. NaCl. This mixture was evaporated with excess of platinum solution and the precipitate washed thoroughly with alcohol as usual, until all platinum salts except the potash salt has been removed. A half saturated water solution of NH_4Cl was shaken in a bottle with K_2PtCl_6 till saturated with the latter. This salt is very slightly soluble in the NH_4Cl solution and only a trifling amount is taken up. This solution was used to dissolve out any Na_2SO_4 or sodium chloride from the precipitate. A final washing with alcohol removed all NH_4Cl, and the Gooch crucible contained only pure K_2PtCl_6. His results were as follows:

KCl taken.	Weight of precipitate.	KCl obtained.
0. 46239	1. 5148	100. 11
0. 40915	1. 3404	100. 02
0. 42510	1. 3920	100. 07
0. 41477	1. 3597	100. 18
0. 45149	1. 4797	100. 16
0. 48252	1. 5805	100. 10
0. 44488	1. 4552	99. 96
0. 48679	1. 4244	99. 66
0. 48062	1. 4050	99. 71
0. 41726	1. 3649	99. 96
		99. 99

This proposed method was submitted to the following investigation:

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* Chemical News, xliv., p. 130, note.

Chemically pure KCl was obtained by recrystallizing chemically pure $KClO_3$, and fusing to convert it to KCl. 0.25835 grms., of this KCl gave 0.4967 grms. AgCl, equal to 0.25836 grms. KCl. 5 c. c. of the platinum solution employed evaporated to dryness, dissolved perfectly in 90 per cent. alcohol. A solution of KCl in water was now made. By weighing this solution, the KCl employed in all subsequent experiments was very accurately determined. Using KCl alone, Lindo's method gave the following results :

KCl taken.	Weight of precipitate.	KCl obtained.
(1)....0. 24618	0. 80650	100. 11%
(2)....0. 12752	0. 41770	100. 06%
(3)....0. 12395	0. 40550	99. 98%

These analyses show that there is no tendency to loss by this method.

To test the method applied to the estimation of potash in the form of sulphate, chemically pure K_2SO_4 was employed, using an excess of platinum solution and several c. c. of HCl. The results were as follows :

K_2SO_4 taken.	Weight of precipitate.	K_2SO_4 obtained.
(1)....0. 12539	0. 8580	100. 95%
(2)....0. 13228	9. 3790	102. 81%
(3)....0. 49785	1. 4148	101. 45%

These results show that with HCl alone added the ppt is not pure K_2PtCl_6. It may be that the presence of free H_2SO_4 causes the error. To test this an amount of NaCl about equal to the K_2SO_4 was added in the following experiments, thus avoiding presence of free H_2SO_4 :

K_2SO_4 taken.	Weight of precipitate.	K_2SO_4 obtained.
(1)...0. 134977	0. 3782	100. 01%
(2)...0. 121427	0. 3415	100. 16%
(3)...0. 122500	0. 3429	99. 95%

The method was now applied to the estimation of potash in superphosphate, using the following mixture: To 60 parts of an acid phosphate were added 10 parts each of the following salts: $NaNO_3$, $NaCl$, $MgSO_4$ and $(NH_4)_2SO_4$. A blank experiment, using 1 grm. of this mixture, gave 0.08 per cent. potash. This amount was deducted in subsequent experiments.

Experiment 1: 1 grm. +0.07484 grm. KCl, containing 0.0478 grm. K_2O, gave 0.2464 grm. K_2PtCl_6. Taken, 4.78 per cent.; obtained, 4.75 per cent.

Experiment 2: 1 grm.+0.02748 grm. K_2SO_4, containing 0.01485 grm. K_2O, gave 0.01486 grm. K_2O; taken, 1.485 per cent.; obtained, 1.486 per cent.

A second mixture, which was received from Dr. E. H. Jenkins, and which contained 12.62 per cent. K_2O by composition, gave by this method 12.61 per cent., 12.56 per cent., 12.63 per cent.

These very satisfactory results as regards accuracy, taken in connection with the far easier manipulation, have led to the adoption of the following scheme for the estimation of potash in fertilizers:

(1) *Superphosphates.*—Boil 10 grms. of the fertilizer with 300 c. c. of water for ten minutes. Cool the solution, add ammonia in slight excess, thus precipitating all phosphate of lime, oxide of iron, and alumina, etc., make up to 500 c. c., mix thoroughly, and filter through a dry filter; take 50 c. c., corresponding to 1 grm., evaporate nearly to dryness, add 1 c. c. of dilute H_2SO_4 (1 to 1), and evaporate to dryness and ignite to whiteness. As all the potash is in form of sulphate, no loss need be apprehended by volatilization of potash, and a full red heat must be used until the residue is perfectly white. This residue is dissolved in hot water plus a few drops of HCl; 1 c. c. of a solution of pure $NaCl$ (containing 20 grms. $NaCl$ to the litre) and an excess of platinum solution (2 c. c.) are now added, and the whole evaporated as usual. The precipitate is washed thoroughly with alcohol by decantation and on filter, as usual. The washing should be continued even after the filtrate is colorless. Ten c. c. of the NH_4Cl solution prepared as above are now run through the filter. These 10 c. c. will contain the bulk of the impurities, and are thrown away. A fresh portion of 10 c. c. NH_4Cl is now run through the filter several times (5 or 6). The

filter is then washed thoroughly with chemically pure alcohol, dried, and weighed as usual. The platinum solution used contains 1 grm. metallic platinum in every 10 c. c.

(2) *Muriates of potash.*—In the analysis of these salts an aliquot portion containing 0.500 grm. is evaporated with 10 c. c. platinum solution plus a few drops of HCl, and washed as before.

(3) *Sulphate of potash, kainite, etc.*—In the analysis of these salts an aliquot portion containing 0.500 grm. is taken, 0.250 grm. of NaCl added, plus a few drops of HCl, and the whole evaporated with 15 c. c. platinum solution. In this case special care must be taken, in the washing with alcohol, to remove all the double chloride of platinum and sodium. The washing should be continued for some time after the filtrate is colorless. 25 c. c. of the NH_4Cl solution are employed instead of 10 c. c., and the second 25 c. c. poured *through at least six times to remove all sulphates and* chlorides. Wash finally with alcohol, dry, and weigh as usual.

A single experiment attempting to estimate potash directly in nitrate of potash did not yield satisfactory results. In such cases it may be necessary to first evaporate to dryness with HCl and then proceed as in analysis of muriates.

To test the solubility of K_2PtCl_6 in the NH_4Cl solution prepared as above, 3.13 grms. of finely pulverized K_2PtCl_6 were digested with 200 c. c. of the NH_4Cl solution and filtered through a Gooch crucible. The loss was found to be 0.0002 grm.

Wherever the standard method of estimating potash is employed, the washing of the precipitate of K_2PtCl_6 with the NH_4Cl solution would undoubtedly be a valuable addition to the present process.

To prepare the washing solution of NH_4CL, place in a bottle 500 c. c. H_2O, 100 grms. NH_4Cl ; shake till dissolved. Now pulverize 5 or 10 grms. of K_2PtCl_4, put in the bottle, and shake at intervals for six or eight hours ; let settle over night ; then filter off liquid into a second bottle. The first bottle is then ready for a preparation of a fresh supply when needed.