

to bring each system to final equilibrium, and the solution then obtained contains only 2.080 grams CaSO_4 in a liter, from whichever side approached. The above sources of error should be guarded against in solubility work where the solubility is small. In attempting to approach the equilibrium from both sides, as is commonly done, it may happen that the point is *approached only from the supersaturated side*, as pointed out above.

If the bottom of an Erlenmeyer flask is covered with large particles or crystals of the solid, and the solvent rotated over these crystals by a motor-driven Schultz stirrer, none of the above difficulties will be encountered; further, the solution is always perfectly clear and free of particles, which is often a very considerable advantage. A supersaturated solution may also be rotated over the same crystals, and the equilibrium approached from both sides. By this method the solubility of gypsum from 0° to 100° has been determined by Hulett and Allen,¹ and the results in this paper show that the values obtained at that time, where the cleavage plane very largely predominated, are also the values for any plane of gypsum.

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October, 1904.

[CONTRIBUTIONS FROM THE BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE, NO. 57.]

THE ESTIMATION OF POTASH IN SOILS, PLANTS AND FERTILIZERS.

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Received November 2, 1904.

CONSIDERABLE interest has been displayed in improving standard methods for the estimation of potash in soils, plant substances and fertilizers during the past three or four years.²

It is now generally recognized that in the case of fertilizers, potash added in the form of salts is seldom entirely accounted for in the analysis of the completed mixtures, and this latter fact has led to much complaint from the manufacturers. It has been found

¹ This Journal, **24**, 667 (1902).

² *Chem. News*, **79**, pp. 135-136; *J. Chem. Soc. (London)*, **77**, 1076; *Stat. Spar. Agr. Ital.*, **33**, 454; *Ann. Chim. Anal. et. Appl.*, **5**, 289; *Ztschr. anal. Chem.*, **39**, 481; **40**, 385; **40**, 569; *Chem. Ztg.*, **26**, 1014; **28**, 210; **28**, 36; *Ztschr. angew. Chem.*, **15**, 1263; *Ztschr. anorg. Chem.*, **36**, 323; **36**, 325; this Journal, **25**, 416; **25**, 491; **26**, 297.

that low results are obtained both when organic matter is present in the mixed fertilizer and also when the mixture consists only of acid phosphates and of potash salts.¹

In the case of plant substances and of soils no particular complaint has been made as to the accuracy of the official methods, but the necessity of first removing iron, alumina, lime and phosphoric acid, and of washing thoroughly this precipitate in order to remove all potash from it, makes the estimation very tedious and slow. In addition to this, the use of, and the subsequent removal of, large quantities of reagents, certainly cannot add to the accuracy of the estimation. There has been good reason then, both from the standpoint of accuracy and of convenience, for the efforts to simplify and shorten the procedure in the estimation of potash in the above-mentioned materials.

In this effort it is unfortunate that more attention has not been given to the method proposed by Moore,² as in it many of the usual preliminary operations are omitted and the method is at once the simplest and the shortest and possesses apparently a high degree of accuracy. The method has been used on soils and plants in the Bureau of Chemistry by several independent workers with highly satisfactory results, and in presenting my own results with the original method, and with modifications of it, and in studying

¹ It is an open question how much of this potash which is insoluble in water should be regarded as available to plants, and it is to be doubted if it can be justly regarded as within the meaning of the law; most, if not all, state laws calling for "water-soluble potash."

² This Journal, 20, 342. The method is as follows: The material under examination is brought into solution in acid, ammonium salts, and organic matter destroyed with aqua regia and the excess of acid removed by several evaporations to dryness, care being taken to break up all nitrates with hydrochloric acid. Take up with water and a few drops of hydrochloric acid, filter and wash thoroughly. To the filtrate add a slight excess of chlorplatinic acid solution, and evaporate on the steam-bath nearly to dryness so that the salts solidify on cooling. (It is important that the evaporation is not carried to complete dryness as the dry iron and aluminum chlorides are exceedingly difficult to dissolve in acidified alcohol.) To the cooled mass add 15 to 25 cc. of acidified 90 per cent. alcohol, stir, and let stand several minutes, filter, wash with alcohol and ammonium chloride solution and dry in the usual manner. Dissolve the potassium chlorplatinic acid in hot water, evaporate, dry in water oven for one-half hour, and weigh. The acidulated alcohol is prepared by passing dry hydrochloric acid gas into cool 90 per cent. alcohol until 1 cc. of the alcohol neutralizes about 2.3 cc. of normal alkali.

its applicability to commercial fertilizers I only desire to redirect attention to a most excellent method which has apparently been overlooked.

In Table I are presented the results on 35 samples of soils by

TABLE I.—POTASH IN SOILS.

	Filtered on paper. Acid alcohol.			Filtered on Gooch crucible. Acid alcohol.	
	Official method. Per cent.	Moore method. Per cent.		Official method. Per cent.	Moore method. Per cent.
2134	0.39	0.42	2153	0.12	0.13
2135	0.27	0.27	2154	0.10	0.12
2136	0.18	0.18	2155	0.93	0.84
2137	0.52	0.54	2156	0.60	0.63
2138	0.41	0.40	2157	0.85	0.85
2139	0.23	0.24	2158	1.06	1.07
2140	0.14	0.12	2159	0.15	0.16
2141	0.27	0.34	2160	0.18	0.21
2142	0.29	0.27	2161	0.43	0.47
2143	0.29	0.27
Average	0.299	0.305		0.496	0.497
	Plain alcohol.			Plain alcohol.	
2144	0.44	0.42	2162	0.48	0.48
2145	0.48	0.50	2165	0.08	0.09
2146	0.47	0.47	2166	0.38	0.41
2147	0.50	0.48	2168	0.44	0.48
2149	0.44	0.42	2169	0.21	0.21
2150	0.60	0.62	2170	0.21	0.22
2151	0.78	0.82	2171	0.11	0.12
2152	0.67	0.66	2172	0.10	0.11
Average	0.547	0.548		0.25	0.265
General average	0.41	0.41		0.38	0.39

several different procedures. The results are given just as they were obtained in the regular routine of the laboratory; they were not repeated nor rejected. In some cases the differences are larger than they should be between duplicates, but as the average results are practically identical it seems fair to consider such differences as due to the analytical work rather than to the method itself.

The results are not noticeably different where the filtration and washing was done on paper rather than on the Gooch crucible, and under some conditions the use of paper presents certain advantages as the potassium chlorplatinat may be dissolved on the paper in order to separate it from foreign salts, and the solution evaporated, dried and weighed in platinum dishes. The combined

iron and aluminum oxides ranged from 5 to 25 per cent. in these samples. No particular advantage appears to result from the use of the acidified alcohol as recommended by Moore, at least where the amount of lime salts, more especially calcium sulphate, is not large. It would appear, therefore, that the simple method may be further simplified by substituting ordinary 90 per cent. alcohol for the acidified alcohol.

In reviewing the methods used and proposed for estimating potash in fertilizers¹ the writer suggested that the losses now occurring may be partly or entirely overcome by using the method of Moore, provided, of course, any potash is occluded in the ammonia and ammonium oxalate precipitate in the Lindo-Gladding method. The addition of other bases, as proposed by Hare in the lime-water method, appears to be unnecessary except for the purpose of saving the platinum dishes from the effects of igniting phosphates in the presence of organic matter.

In order to determine the applicability of the method to this class of materials several modifications were tried, the purpose of which was to destroy organic matter and ammonium salts in the most expeditious manner. These were destroyed both by aqua regia and by igniting in porcelain dishes, the potash being taken up afterward in distilled water and also in water acidified with hydrochloric acid. In all cases the results have been given corrected and uncorrected for the undissolved foreign salts. In cases where the ignited residue was taken up only in distilled water the impurities in the precipitate were sometimes considerable. Comparisons were also made of washing with plain alcohol and with acidified alcohol. The results are given in Table II.

The samples represented mixtures of the commoner raw materials.

No.	
1759	Acid phosphate and
1761	“ “ “ cottonseed meal.
1762	“ “ “ muriate of potash.
1763	“ “ “ “ “ “ cottonseed meal and nitrate of soda.
2119	Peruvian guano.
2120	Mixed fertilizer.
2911	Acid phosphate and potash salts.
2912	Dissolved animal bone and potash salts.

¹ Proceedings Fifth International Congress of Applied Chemistry, Berlin, 1903.

TABLE II.—POTASH IN FERTILIZERS.

		Organic matter and NH_3 salts destroyed with $\text{HNO}_3 + \text{HCl}$.					Ignited in porcelain.			
		Acid alcohol.		Plain alcohol.			Dissolved in HCl .		Dissolved in H_2O .	
Official method.		$\text{K}_2\text{O} +$ undis. salts. Per cent.	Corrected K_2O . Per cent.	$\text{K}_2\text{O} +$ undis. salts. Per cent.	Corrected K_2O . Per cent.	Filt. on paper corrected. Per cent.	$\text{K}_2\text{O} +$ undis. salts. Per cent.	Corrected K_2O . Per cent.	$\text{K}_2\text{O} +$ undis. salts. Per cent.	Corrected K_2O . Per cent.
1759	4.98	5.10	5.01	5.25	5.17	5.31	4.96	4.92	4.84
1761	0.92	1.02	0.87	1.37	0.85	0.97	1.05	0.81	0.79
1762	0.70	0.68	0.62	0.99	0.67	0.87	0.92	1.43	0.79
1763	5.70	6.17	6.13	6.58	6.19	5.85	6.21	6.16	6.13	5.97
2119	3.88	4.00	3.96	3.74	3.71	3.92	3.47	3.44	3.50	3.49
2120	3.60	3.72	3.69	3.82	3.78	3.67	3.83	3.75	3.70	3.68
2911	3.96	4.04	3.99	4.01	3.83	2.09	2.08
2112	4.08	4.14	4.13	4.08	3.93	2.25	2.24

As a rule, the results are slightly higher by the Moore method than by the official method; this is only noticeably so in case of sample 1763. From this it would appear that the flocculent precipitate of iron and lime phosphate has but little to do with the low results usually obtained. It is to be noticed that only when the acid alcohol is used may the impurities contained in the platinum precipitate be neglected. Where plain alcohol is used it is usually necessary to dissolve the potassium chlorplatinite, wash, and reweigh the crucible to obtain the true weight of the potash.

It is obvious that after igniting the material it is not sufficient to treat it with water alone in order to dissolve the potash: such procedure does not always secure all the potash, some of it remaining undissolved, possibly in complex silicates or phosphosilicates, adhering to the dish. It was found that the potash so held could usually be readily recovered by dissolving the ignited material in the dish in dilute hydrochloric acid. This is not always true, however, the potash so held being dissolved but slowly in some instances, and while it appears that all potash may be recovered by prolonged treatment, I do not consider that this method has any advantages over the official method for regular fertilizer work, and further study was abandoned.

LEATHER AND PAPER LABORATORY.

NOTE.

An Explanation.—In the paper in the *American Geologist* on "The Dolomites of Eastern Iowa," which is abstracted in this Journal, 26, R 373, one fact should have been stated. The author had previously determined that if the silica in these dolomites is in the form of a silicate, it is of a class that can be decomposed by digestion and evaporation with hydrochloric acid. This was ascertained by obtaining concordant results when treating the dolomite powder with a "fusion mixture" of sodium-potassium carbonate, and again by digesting with hydrochloric acid, that is, by evaporating to dryness, stirring until a fine, dry powder results. The residue in each case was treated with pure hydrofluoric and sulphuric acids. Also the residues obtained by dissolving the powder with hydrochloric acid on the one hand, and from digesting with hydrochloric acid on the other, were shown to be silica by the