ON THE PREPARATION OF AMMONIUM CITRATE SOLUTION.

By Rudolf de Roode.

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MANY times in preparing a solution of ammonium citrate, I have observed a fact which seems to indicate that the preparation of a strictly neutral solution is an extremely simple matter. If some citric acid is treated with ten per cent. ammonia until dissolved, the solution becomes quite hot, and if it is now diluted to nearly the proper specific gravity, made decidedly alkaline with ammonia, and allowed to stand over night in an open dish, it will be found in the morning to be strictly neutral.

Being warm and in an open dish the excess of ammonia escapes completely, leaving it neutral. For the last four or five times which I have had occasion to prepare an ammonium citrate solution, I have observed this fact and each time have found it unnecessary to alter the neutrality in the least degree. I find it very convenient. I also find it advantageous to add a small quantity of salicylic acid to the solution (about one gr. for five liters of solution is sufficient). This is added before neutralization, so that the salicylic acid is also neutralized by the ammonia. The salicylic acid prevents the growth of fungus in the solution and it remains unchanged a long time. Some solution six months old when used in fertilizer work, gave results practically identical with those obtained by the use of a freshly prepared solution.

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THE DETERMINATION OF POTASH IN MANURES.

By W. E. Garrigues.

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THE following method for the determination of potash in fertilizers, has been in use in the writer's laboratory for some months, and in view of its ease, quickness, and comparative accuracy is believed to be a decided improvement on that of Lindo-Gladding.

It depends upon: 1. The ignition of the material with sulphuric acid, thereby converting all potash present, to sulphate, if not already in that form, and at the same time expelling any ammonia and organic matter. 2. Precipitation of the sulphuric acid with barium chloride. 3. Precipitation of the excess of barium, together with other earthy bases, by sodium carbonate. 4. Evaporation of the filtrate with platinic chloride as usual.

The process entails but one filtration and evaporation and with due precaution the final precipitate of potassium platinochloride is obtained practically chemically pure.

The analysis: Ten grams of the sample are weighed into a platinum dish and worked into a paste with concentrated sulphuric acid. The rod is wiped with a small piece of filter paper, which is added to the sample, and the whole ignited, raising the heat gradually and finishing with a blast until the residue is white, or red if much iron be present.

The contents of the dish are now scraped out into a porcelain mortar and ground to a fine powder, a little hot water is added, washing out the dish at the same time, and the mass triturated for a few minutes. It is next washed into a 500 cc. flask and boiled with 250 cc. of water for half an hour, when a ten per cent. solution of barium chloride is run in five cc. at a time and boiling after each addition, until no further precipitation is visible.

Add a single drop of phenolphthalein solution and sodium carbonate, drop by drop, until a faint permanent rose color is obtained. Boil for a minute, set aside to cool, and make up to the mark. Filter through a dry paper and measure out fifty cc. of the filtrate = one gram of sample. Add hydrochloric acid to slight acid reaction, as shown by the disappearance of the rose color, and evaporate on a water-bath with platinic chloride. Wash the precipitate with alcohol, sp. gr. 0.848 (= eighty per cent. by weight), dry at 100° C., and weigh. For potash salts, the ignition with sulphuric acid is omitted.

Remarks: 1. The sulphuric acid must be added cautiously as fertilizers containing chlorides and nitrates react somewhat violently, endangering loss of the assay. 2. It is important that the ignited mass be very finely pulverized, otherwise the calcium sulphate, most of which remains insoluble, will mechanically enclose the potassium sulphate and prevent its complete solution. 3. An excess of sodium carbonate is not permissible as double decomposition with the precipitated barium sulphate may take place, leaving sodium sulphate in solution and rendering erroneously high results. 4. It is recommended to turn the flame under the bath below boiling temperature when the solution has evaporated to small bulk. In case it then goes to hard dryness, no harm is done, while, if the bath be boiling, it is necessary to keep a close watch lest this occur. 5. For the filtration and weighing, a Gooch crucible, fitted with a single disk of filter paper, leaves nothing to be desired.

This method was first adopted as a safe one, on its favorable showing when checked against the Lindo-Gladding, and has since proven in the writer's hands very much more concordant than the latter. Since the publication of Mr. Norman Robinson's criticism of several well-known methods of potash determination (This JOURNAL, **16**, 364), the writer has made a more careful investigation of the value of this process, comparing it with two others and incidentally confirming some of Mr. Robinson's work.

It was thought most satisfactory to operate on samples of known composition, and with this end in view several, representing the usual variety met with in commerce, were prepared. In each case the potash "occluded" by the various precipitates was determined after washing until no reaction with silver nitrate was visible. To facilitate comparison all the figures are given in per cent. potassium oxide.

Nature of Sample.	Calculated content potassium oxide.	Found by Lindo. Gladding.	Recovered from precipitates.	Found by Stassfurt.	Recovered from precipitatcs.	Found by Garrigues.	Recovered from precipitates.
Complete Fertilizer; containing K_2SO_4.	5.40	5.16	0.20			5.17	0.09
		5.28	0.11			5.19	0.12
						5.25	0.09
						5.28	0.17
Complete Fertilizer containing KCl.	6.31	6.12	0.15			6.22	0.08
		6.09	0.14			6.14	0.12
Mixed salts $KCl+CaCl_2+MgSO_4$.	63.17	63.19	0.12	62.85	0.19	62.75	0.18
		62.74	0.15	62.80	0.17	62.95	0.15

The figures under the headings of the three methods do not include the per cent. recovered from precipitates. In the Stassfurt method the quantity of barium chloride necessary was calculated and exactly added, so that no doubt need exist as to the potassium platinochloride obtained having been contaminated with sulphates on an excess of barium chloride. In one case the total return by the Lindo-Gladding method was apparently more than was present, due no doubt to a slight contamination with calcium sulphate. It should be remarked that no corrections were made for the volume occupied by the precipitates in the flasks. The factor used in calculating the double chloride to potassium oxide was 0.193.

The writer is frank to acknowledge that frequently the Lindo-Gladding method has given him very discordant results. This has been especially noticeable in fertilizers containing liberal amounts of potash. An aggravated case of the kind was a return in triplicate of 10.16–11.37–12.75. The writer's method gave 12.73–12.76 and an experiment station working on the same sample found 13.10. Two other instances of disagreeing duplicates by the Lindo-Gladding process are 4.76–5.07, and 6.10–6.54.

It is difficult to give any satisfactory reason for these discrepancies, as they are probably due to a multiplicity of causes. The writer has always felt the re-solution of the ignited potassium sulphate in water to be an unsatisfactory step and this alone sufficed to make the adoption of a new method desirable to him, the official alternate method being too tedious for ordinary use.

It is suggested that the material differences among chemists working by the Lindo-Gladding method, may be, in part, due to the varying strength of the alcohol-wash. The official directions, though they mention eighty per cent., do not lay sufficient stress on this point. If ninety, or even eighty-seven, be used in the second washing, ammonium chloride is precipitated with consequently higher returns.

In conclusion, while it is plain the method here proposed does not, in common with those now in use, return quite all the potash, it is seemingly less accurate than none and certainly less discordant than the Lindo-Gladding, besides being more satisfactory to work, and quicker. It obviates the no small difficulty of precipitating all the sulphuric acid without adding an excess of barium chloride in the Stassfurt, and avoids the tedious evaporations and filtrations entailed by the alternate. Against all these advantages there has appeared so far only one disadvantage: the necessity of using a greater quantity of platinic chloride.

THE RAPID AND ACCURATE ANALYSIS OF BONE-BLACK.[1]

BY W. D. HORNE, PH.D.

SEVERAL years' experience in the analysis of bone-black have led me to the adoption of the following method for attaining accurate results with comparative rapidity.

In new char, bought from the dealer, the determination of moisture is of importance, being frequently limited by contract to three per cent.

In char, in constant use in sugar refineries, the moisture in the revivified sample is of no importance under usual conditions.

The moisture is determined by heating two grams of the unground char for two hours in a hot air-bath at 140° C. It can be weighed between watch-glasses held by a clip to prevent absorption of moisture.

A convenient way of estimating calcium carbonate is with Lunge's nitrometer, using mercury. Two grams of the finely pulverized sample are introduced into a two-ounce Erlenmeyer flask and moistened with three cc. of a saturated solution of mercuric chloride, the tube of ten cc. of hydrochloric acid (sp. gr. = 1.12) introduced and the flask closed with a rubber stopper, which, with a short glass tube and a rubber tube, is hung to the tube of the three-way cock. By tipping the acid out upon the char and properly manipulating the stop-cock the carbon dioxide is liberated, collected, and measured. Any hydrogen sulphide given off is absorbed by the mercuric chloride. Corrections are made for temperature and atmospheric pressure.

For the determination of carbon, iron, calcium sulphate, and insoluble ash, one portion is used. In preparing the sample

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[1] Read before the New York Section, November 9, 1894.