SOME SOURCES OF ERROR IN OUR METHODS OF DETERMINING POTASH IN FERTILIZERS AND GERMAN POTASH SALTS.[1]

By N. Robinson, Reporter on Potash for the N. A. O. A. C. for 1893.

IN common with many others, the writer has for some time entertained the belief that none of our recognized or official methods for determining potash in fertilizers and potash salts were above criticism. The objections to our American official methods from German and other sources are entitled to the highest respect, and per contra, the grave doubts expressed in high quarters among chemists in this country, as to the validity of the superior claims made for the Anhalt or Stassfurt methods, determined the writer for his own satisfaction to undertake a series of experiments, to ascertain, if possible, the sources of error, if any should be found to exist, in the three best known and most widely used ways of potash determination; *viz.*, the official or Lindo-Gladding, the alternate, and the Stassfurt or Anhalt methods.

This series of experiments was begun over two years since, and has been prosecuted as time permitted from that period to the present. The writer is constrained to admit that he had at the beginning a very inadequate conception of the difficulties to be encountered in the solution of the problem, or the wide scope of inquiry which anything like an exhaustive study of the question involved.

The literature of the matter, while sufficiently voluminous on the general subject of potash determination, seemed to stop short at the very point where these inquiries must begin. Teschemacher and Smith, with the sanction of Fresenius and the apparent acquiescence of all the best German authorities, had declared that the removal of sulphuric acid was a *sine qua non* in all accurate potash estimations which, of course, at once excluded our chief American method from the list of "accurate" ones. Then came Zimmerman with a general and certainly rather formidable indictment of this same method. He charged that the

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ammonium-chloride solution was far from being a harmless and indifferent solvent of the miscellaneous impurities which are usually found in the potassium-platinochloride precipitate as obtained by the Lindo-Gladding method. Exact details were, however, wanting, or, at least not obtainable in any publication within the reach of the writer. Since then it is understood that one or two chemists in this country have undertaken investigations similar to those made by the writer, albeit the results of their work, perhaps from his somewhat isolated position, have failed to reach him.

It is with no little hesitancy, and he trusts with becoming modesty, that he is compelled to come into court with a general indictment against all our recognized or official methods of determining potash in fertilizers and potash salts. The writer does not make this sweeping charge lightly or without a full estimate of its gravity and of the overwhelming weight of authority which is likely at once to be marshalled against it. Methods of recognized value and almost universal acceptance are not dislodged without a struggle. The writer can only plead the evidence of the facts which he gives, and look patiently to the "calm judgment of the coming time" for the vindication of views which are presumably too radical for general acceptance, except as the result of extended and patient research at the hands of abler investigators than himself.

The First Count Against All Three Methods.—The first count in the indictment, and which is common to all our methods, comes from an obscure phenomenon, which so far as I am aware, has never been thoroughly investigated. For want of a better name I shall call it "The occlusion of potash salts by precipitates." Certain precipitates have long been known to manifest this peculiarity; but the bearing of this upon potash estimation seems somehow to have been overlooked. The fundamental fact is this. Many precipitates carry down potash salts and hold them so tenaciously that they cannot be washed out with hot water. All the precipitates thrown down in the customary working of our various official methods manifest more or less of this same tendency. Barium sulphate is probably the worst offender. Ferric and aluminic compounds are scarcely less chargeable with this occult species of chemical larceny, while calcium, magnesium, and the other salts of the alkali metals are by no means free from suspicion of at least a mild form of the same tendency to hide and hold potash.

The Lindo-Gladding Method.—According to the investigations of Zimmerman and others—investigations which the tabular estimates by the writer given below, seem to fully confirm, in addition to the above source of loss coming from the "occlusion" of potash in "precipitates," there are two other distinct and constant sources of error, with a number of casual and incidental ones, which may additionally vitiate results.

The first comes from the "alcohol washings" which, in the presence of the miscellaneous impurities nearly always found in the potassium platinochloride precipitate obtained by this method, result in the solution and consequent loss of the latter; and the second, from the fact that the solvent action of ammonium-chloride solution does not stop with the foreign salts which it is designed to remove; but that double decomposition often takes place. Potash is removed and ammonia substituted, involving the weighing of an impure potassium platinochloride, a portion of which is of different molecular weight. If we add to this the fact that calcium and magnesium sulphate, as well as ammonia, are not infrequently present in this same platinochloride, even when "washed to constant weight," we are certainly entitled to suspect the absolute correctness of all potash estimates made by the Lindo-Gladding method.

Before giving tabulated results the writer may be pardoned for outlining in the briefest manner, the methods used in the work. In all cases, precipitates were washed with hot water until some time after any cloudiness was perceptible in the filtrate, either with barium chloride or silver nitrate. Potash was recovered from precipitates thrown down by ammonia and ammonium oxalate by re-solution and reprecipitation, and from barium sulphate by boiling the filter and its contents twice in dilute hydrochloric acid. The recovery of the potash from the ammonium-chloride washings seems to present the greatest practical difficulty. The ordinary method of volatilizing the ammonium salts over an open Bunsen flame involved so much loss of potash that no reliance could be placed on the results. Fair work was done by exposing the well-dried material in a thin layer, in a shallow flat-bottomed platinum capsule on a portion of the sand-bath where the heat could be kept at the lowest vaporizing temperature of ammonium chloride, and consuming five or six hours in the operation. Another method involving several evaporations, incinerations, and filtrations with a slight loss of potash, was to add to the washings enough sulphuric acid to change all bases into sulphates, with appropriate subsequent treatment. The recovery of the potash from the "alcohol washings" seemed to present no special difficulty.

A word as to the factor of correction used for the potash already present in the ammonium-chloride solution. In my first experiments I assumed that the amount of potash present could be correctly estimated "by difference," by simply subtracting the weight of the undissolved portion from the five grams of potassium platinochloride first placed in the 500 cc. of the washing-fluid. The factor, 0.000195 per cc. thus obtained was used until recently without a suspicion of its inaccuracy. Some inexplicably discordant results led to a careful review of the whole matter. Analytical determinations showed that nearly twice as much potash was present in my ammonium-chloride solution as I had supposed. On carefully carrying out the official directions with another lot of this ammonium-chloride solution, I found that the potassium platinochloride had done something else besides "settle over night." Mutual decomposition had taken place. The ammonium-chloride solution was found to contain about as much potash in the form of chloride as platinochloride. The undissolved portion was a mixture of potassium platinochloride and ammonium platinochloride. The final amount as ascertained by several analytical determinations of the solution actually used, was potash corresponding to 0.00039 potassium platinochloride to the cubic centimeter, and the work as now given is corrected by that factor.

Still another factor of correction, small in all probability but still necessary for exact work, may be casually referred to. It is more than doubtful whether the potassium platinochloride precipitate obtained by the Lindo-Gladding method—in spite of all its numerous "washings"—is ever strictly chemically pure. My observations indicate that, in addition to ammonium platinochloride, calcium and magnesium sulphate, and sometimes other impurities, are almost certain to be present. In the limited time at my disposal, I was unable to devise any satisfactory plan for the estimation of these impurities, and the tabulated results are, therefore, given without this correction.

In regard to the last example given (No. 6), which was from the "mixed potash sample" sent out to chemists in this country and Europe, it may be said that the quantity taken, ¼ gram, is too small for accurate work, as every error is, of course, quadrupled in the final result. These estimates were the last made, and lack of material prevented the employment of a larger quantity. As the results tally fairly well, however, with the work of others, they are given for what they are worth.

It will be observed that the "alternate" method is to a certain extent liable to the same objection as the Lindo-Gladding. Most of the loss here comes from the "occlusion" of potash in the barium sulphate. How seriously this affects the final estimate may be seen from the tabulated results given below.

A large amount of work done in the same line of investigation is omitted, but all leading substantially to the same results.

The six examples given are, indeed, selected from some twenty that were more or less fully carried out. Those taken are those in which the amount of loss by washings and precipitates is the lowest. In the course of the work some very anomalous results were obtained. In one case as high as thirty-four milligrams of potassium platinochloride were recovered from a barium sulphate precipitate weighing only 320 milligrams, and from which boiling water had ceased to dissolve out any more potash. Faulty manipulation may in some way have affected the result; but I think that any chemist who attempts to wade through the mass of work that I have gone over, and to unravel the singularly tangled skein of surface or molecular forces which govern the behavior of potash salts in the presence of barium sulphate and other precipitates, will meet with a good many surprises. He will find first of all, that the accredited statement of most chemical authorities that potash salts are not carried down by barium sulphate in acid solutions, is altogether a fallacy. He will find that the amount carried down is subject to wide variations, and that, too, under conditions seemingly identical. He will probably come at last to the conclusion that this whole subject of the occlusion of potash salts by precipitates needs thorough and exhaustive investigation; and that until it is done and the losses resulting therefrom are eliminated, we must write "doubtful" after every potash determination made by processes involving this very obscure but very positive source of error.

Analysis of Mixed Fertilizers containing Bone, Blood, Etc., together with the sample of Mixed Potash Salts sent out by the "Reporter" by the Lindo-Gladding Method with estimates of losses of Potash in precipitates and "washings." Made at the Florida State Laboratory, Norman Robinson, Analyst.

Mixed Fertilizer.	Amt. of material used in grams.	Weight of K_2PtCl_6 by Lindo-Gladding Method.	Weight of K_2PtCl_6 recovered from precip. by Am. and Am. Ox.	Weight of K_2PtCl_6 recovered from first alcohol washing.	Weight of K_2PtCl_6 recovered from washing with NH_4Cl solution with 2nd alcohol W.	Total weight of K_2PtCl_6 recovered from all sources.	Percentage of K_2O by Lindo-Gladding Method.	Percentage with losses added.	Percentage of loss.
1—With Bone, Etc.	½	0.3263	0.0030	0.0041	0.0051	0.0122	12.60	13.07	0.475
2—With Bone, Etc.	1	0.4040	0.0041	0.0034	0.0061	0.0136	7.80	8.06	0.26
3—With Bone, Etc.	1	0.2433	0.0031	0.0021	0.0033	0.0085	4.70	4.86	0.16
4—With Bone, Etc.	1	0.2114	0.0028	0.0031	0.0053	0.0112	4.10	4.32	0.22
5—With Phos. R'k.	½	0.3160	0.0084	0.0033	0.0018	0.0135	12.20	12.72	0.52
6—Mixed Potash Salts.	¼	0.4884	0.0031	0.0042	0.0022	0.0095	37.70	38.43	0.73
Average loss to each 1 per cent. of potash estimated by Lindo-Gladding method.									0.029

Analysis of same by the "Alternate" Method with Similar Estimates of Losses in Precipitates and Washings.

	Amount taken in grams.	K_2PtCl_6 by alternate method.	K_2PtCl_6 recovered from Am. and Am. Ox. precipitate.	K_2PtCl_6 recovered from $BaSo_4$ precipitate.	K_2PtCl_6 from alcohol washings.	Total K_2PtCl_6 recovered.	Per cent. of K_2O by alternate method.	Per cent. with losses added.	Per cent of loss.
1—................	½	0.3268	0.0021	0.0061	0.0024	0.0106	12.63	13.04	0.41
2—................	1	0.3989	0.0015	0.0083	0.0036	0.0124	7.70	7.94	0.24
3—................	1	0.2331	0.0024	0.0063	0.0024	0.0111	4.50	4.70	0.21
4—................	1	0.2072	0.0010	0.0064	0.0033	0.0107	4.00	4.21	0.21
5—................	½	0.3056	0.0022	0.0073	0.0031	0.0126	11.80	12.29	0.49
6—................	¼	0.4896	0.0015	0.0044	0.0038	0.0097	37.81	38.56	0.75
Average loss to each 1 per cent. of K_2O estimated by Alternate method.									0.29

The Stassfurt or Anhalt Method.—As our German friends are naturally very partial to the Stassfurt method of determining potash in potash salts, the writer was led to make some tests to determine whether the same or similar objections could be urged against it as are believed to lie against our American methods. Concerning this plan of estimating potash, it may be said that it is not likely to be popular until one acquires considerable facility in its use. The accurate precipitation of the sulphuric acid is pretty certain to give trouble at first. If, however, the precipitation be made in a vigorously boiling solution, this difficulty vanishes. The barium sulphate is then heavy and crystalline, and settles like so much sand. After considerable experience in its use the writer has come to prefer this German method to any other from the fact that it involves less manipulation, gives an unusually clean precipitate of potassium platinochloride, and generally requires less alcohol for washing. The writer is convinced, however that it is chargeable with the same essential defect as the Lindo-Gladding and the alternate methods. It does not estimate all the potash present. The barium sulphate manifests the same peculiarity here as elsewhere.

From a previous dissolved sample of the mixed German potash salts sent out by the reporter, 200 cc. was taken, corresponding to five grams of material, precipitated as accurately as possible with barium chloride and made after cooling to 251.25 cc., and after vigorous shaking set aside for a few hours to secure the complete subsidence of the barium sulphate. (The volume of the latter was determined at 1.25 cc. by calculation from the barium chloride used and confirmed by subsequent weighing.) Ten cc. accurately measured of the clear solution corresponding to one-fifth gram gave 0.392 of potassium platinochloride × 5 = 1.960 or 37.84 per cent., which closely approximate the average of the estimates made by German chemists; as much of the remaining liquid as could be moved without disturbing the precipitate was now poured off into a clean, dry beaker, and the precipitate with portions of this same solution was washed into an accurately calibrated fifty cc. measuring cylinder and again allowed to settle. After three hours the precipitate with the mingled solution occupied a volume of sixteen cc. and did not seem inclined to go any lower. The clear liquid was now taken out with a pipette until exactly 21.25 cc. remained. The whole was now poured upon a dry nine cm. Schleicher and Schüll filter and exactly ten cc. filtered off and rejected. This of course left ten cc. of the solution and 1.25 cc. of the barium sulphate. The filter was repeatedly washed with hot water until no reaction was observable with silver nitrate. This last ten cc. of solution with the washings gave 0.4276 of potassium platinochloride or 22.6 mgms. more than the first ten cc. of solution examined, showing that this amount of potash was held up or occluded by the barium sulphate in a form that boiling water would remove. The filter with its precipitate was then boiled twice in twenty-five cc. dilute hydrochloric acid (one to five). In this way forty-four mgms. more potassium platinochloride were obtained. The total amount of potassium platinochloride recovered from the barium-sulphate precipitate was 66.6 mgms. or 0.01288 to each gram of substance $=$ 0.247 per cent., or nearly one-fourth of one per cent. Other tests of the same material in smaller quantity gave considerably higher results, but as great care was taken to secure accuracy in every stage of the process, it is believed that the above fairly indicates the average loss where this particular material is estimated by the Stassfurt method. Much more extended investigations are required before any confident statements can be made as to the average loss from occluded potash when this method is employed.

Several other determinations exceeded this estimate. The instance given was carried out with special care. Full details of the methods used will be furnished to any one interested in the matter and perhaps not unfairly represents the average loss from this source.

In conclusion, it may be urged that, even conceding that there are some inherent defects in all our methods, since they are generally recognized and understood, and give fairly accurate results; anything looking towards a change is ill-timed and unwise. But what are we to consider "fairly accurate results?" As reporter on potash for the current year, the writer is compelled to echo an altogether too familiar refrain. We come up here and, year after year, sing the same old tune. It is just as full of discord this year as it was last year and the year before that. To the question "How much potash?" working upon identically the same sample, New Hampshire says 12.13 per cent., New Jersey 12.76, New York and Maine 12.94, and North Carolina 13.08 per cent. and 13.22 per cent. Now here is a difference of considerably more than one per cent. in the same material, and that too, scattered along the whole gamut of rising estimates. Can these be considered "fairly accurate results?"

If we turn to our German friends, we find more unanimity but by no means complete agreement. Their answers to the same questions range from 13.10 per cent. to 13.44 per cent. Now who in this "confusion" of chemical tongues, has given us the right answer? Even on the face of it, is there not enough to suggest that there may be something wrong with the chemistry, as well as the chemists?

Notwithstanding the views and tabulated determinations above given, your reporter has no changes in existing methods to suggest. He only desires that the investigations he has outlined shall be submitted to careful re-examination, especially the "occlusion" of potash salts in precipitates, and that the relation of this as yet obscure phenomenon, to potash determination (a source of the error to which, so far as he is aware, the writer has now for the first time directed attention), should be made the subject of thorough investigation and review. If his conclusions are confirmed, changes are sure to come. Until then it seems the wiser course to adhere to existing methods.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—NO. 4.]

GANTTER'S PROCESS FOR DETERMINING THE IODINE FIGURE OF FATS.

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F. Gantter, (*Ztschr. anal. Chem.*, **32**, 178 and 181) proposes a new method of determining the iodine figure of fats and oils in which he uses carbon tetrachloride as a solvent for both the fat and iodine and uses no mercuric chloride as in the Hübl pro-