Recovery of Platinum Used in the Determination of Potash

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MANY reports have been made on the recovery of the platinum used in the Lindo-Gladding method for the analysis of potassium. Almost all of these direct the use of one of three reducing agents—i. e., hydrogen generated by a metal and hydrochloric acid (*4*, *8*), a boiling solution of sodium formate (*1*, *7*), or a boiling solution of ethyl alcohol (*5*, *6*). The first two methods introduce chemicals that will not volatilize at water-bath temperatures and may adhere to the platinum during the reduction process. The reduction with alcohol is slow and is said (*6*) to be due to the aldehyde content.

In a recent article (*2*), results of a questionnaire were reported which indicate that about 80 per cent of the analytical chemists are using zinc or aluminum in acid solution for the reduction of the chloroplatinates. The same report shows that 50 per cent are in doubt as to the purity of the recovered platinum. Because of dissatisfaction with recorded methods for this reduction, the authors have worked out a simple procedure that requires less attention, recovers almost 100 per cent of the platinum used, and produces a pure chloroplatinic acid.

Procedure

From the alcoholic wash solution obtained in the Lindo-Gladding procedure for potash determination, precipitate the chloroplatinic acid with excess ammonium chloride, using the method suggested by Haigh and Hall (*4*).

Into a 3-liter wide-mouthed bottle, introduce approximately 2000 cc. of distilled water and 25 cc. of 85 per cent formic acid. As the potassium determinations are completed, transfer the potassium and the ammonium chloroplatinates to the bottle, stopper loosely to keep out dust, and allow the mixture to stand at room temperature.

When it becomes necessary to prepare the chloroplatinic acid, decant off the colorless solution, and wash the residue with hot water until free from chlorides. Prepare the chloroplatinic acid in the usual way, by dissolving the platinum in nitrohydrochloric acid, removing the excess of the solvent on the boiling water bath, and diluting the pure chloroplatinic acid to a solution containing 10 per cent of platinum.

Discussion of the Method

The bottle for the reduction should be one with a wide mouth and sloping shoulders, so that the platinum can be easily removed.

If the asbestos in the Gooch crucible has been treated with aqua regia, all or any part of it may be transferred to the bottle along with the salt. In fact, this addition is advantageous, since the first platinum reduced settles on the asbestos in a finely divided form and, acting as a catalyst, hastens the reduction process.

It is unnecessary to dissolve the salts as they are added. Twenty-five cubic centimeters of the 85 per cent formic acid will reduce approximately 25 grams of the chloroplatinates at room temperature. After this amount of the salt has been added to the bottle, a new solution should be made. Although sodium formate (*1*, *7*) and buffered sodium formate (*3*) solutions have been used, the addition of an alkali is unnecessary for the reduction by formic acid, either in a cold or in a hot solution. In a cold solution, reduction of these salts will continue to pH 0.9.

Formic acid will reduce a saturated solution of the chloroplatinates in a few minutes at 100° C., but it requires from 3 to 5 days at room temperature. The form in which the platinum is deposited depends upon the temperature to which the solution is subjected. At high temperatures, sootlike platinum is deposited which adheres to the sides of the container. The reduction may be carried out at this temperature, for although a small amount of carbon always appears, it can be removed with the asbestos by filtration. From 23° to 40° C. metallic scales are produced which do not adhere to the sides of a clean container.

Since the platinum is not to be weighed, it is unnecessary to wash it with alcohol and, in fact, it is undesirable to do so. Reduced platinum in the presence of alcohol and exposed to air, such as in a Gooch crucible under suction, deflagrates with the production of finely divided carbon. This carbon is difficult to remove, and is one of the causes of the dark-colored impure chloroplatinic acid so often obtained.

After the reduced platinum and the asbestos have been washed free of impurities, they are transferred, without drying, to an evaporating dish. When the platinum has completely dissolved in the aqua regia, it is advantageous to allow the solution to stand overnight. Any sediment settles out and is filtered off along with the asbestos. The solution is then freed of nitric and hydrochloric acids in the usual way.

The authors have found three satisfactory methods for making the calculations to obtain a chloroplatinic acid solution contaning 10 per cent of platinum.

TABLE I. SPECIFIC GRAVITY OF CHLOROPLATINIC ACID CONTAINING 10 PER CENT OF PLATINUM

Sample number	I	II	III
Weight of platinum ignited to 1100° C.	5.5913	7.5105	4.7417
Dilution of H_2PtCl_6, cc.	55.90	75.10	47.40
Sp. gr. at 25° C. of diluted H_2PtCl_6 (containing 10% of platinum)	1.1553	1.1552	1.1551

As shown by Table I, the specific gravity of the required solution should be 1.1552 at 25° C. If the solution were diluted to 1.1550 specific gravity, it would contain 9.98 per cent of platinum; or to 1.1560, it would contain 10.05 per cent of platinum. Using the specific gravity of a more concentrated solution, calculations for the dilution may be made by alligation. This method requires the least time and work because it is unnecessary to dry and weigh the reduced platinum; moreover, it is just as accurate as calculating the dilution from the weight of pure platinum. Care must be taken, however, to remove all the hydrochloric acid before the specific gravity is determined.

TABLE II. ERROR IN CHLOROPLATINIC ACID IF PLATINUM IS DRIED AT 130° C.

Sample number	I	II	III
Weight of platinum			
A. Dried at 130° C.	5.6501	7.6005	6.5478
B. Ignited at 1100° C.	5.5913	7.5105	6.4732
Platinum in H_2PtCl_6 solution, %			
Calculated from A	9.89	9.88	9.88
Calculated from B	10.00	10.00	10.00

If calculations for making the chloroplatinic acid solution are to be made from the weight of the reduced platinum, it is unnecessary to dry the platinum at a temperature above 130° C.

As shown in Table II, the chloroplatinic acid solution calculated from the weight of the platinum dried at 130° C. would contain slightly less than the usual 10 per cent of platinum. Since an excess of chloroplatinic acid, sufficient to compensate for this difference, is always used for precipitation of the potassium chloroplatinate, this slight error is negligible.

Dilution of the chloroplatinic acid may be made from the weight of the recovered chloroplatinic acid crystals. Because of the variable amounts of water of crystallization and the hygroscopic nature of chloroplatinic acid, this method is the least satisfactory. Usually, the solution will contain from 9.8 to 10.2 per cent of platinum.

Since the chloroplatinic acid need not contain exactly 10 per cent of platinum, any of these methods will produce the desired solution sufficiently accurately for all practical purposes.

Summary

The prevalent methods for the recovery of chloroplatinic acid from the chloroplatinates obtained in the Lindo-Gladding procedure for the analysis of potassium require much attention and frequently give an impure product. The use of formic acid at room temperature for the reducing agent saves much effort and gives a platinum from which pure chloroplatinic acid is always recovered. Except for the addition of the chloroplatinates as they are obtained, this reduction process requires no attention after the formic acid solution is prepared.

The chloroplatinic acid solution containing 10 per cent of platinum can be made most efficiently and accurately by diluting the recovered chloroplatinic acid to a solution having the specific gravity of 1.1552 at 25° C.

Unless the platinum is to be ignited sufficiently to oxidize all the carbon present, it should not be washed with alcohol and dried by suction. With this treatment the platinum often deflagrates, finely divided carbon is produced, and a dark-colored impure chloroplatinic acid results.

Formic acid reduction, at room temperature, yields a platinum which does not adhere to the sides of a clean container. Unless the longer time required for the reduction is a deterring factor, this process is suitable for those analyses in which the potassium is calculated from the weight of the platinum reduced from the potassium chloroplatinate.

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Ash Determination in Cereal and Other Vegetable Materials

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The author has used for some time a very satisfactory method for ash determination in cereal products.

The determination of ash in such materials as wheat flour is ordinarily a long and often unsatisfactory procedure. If the combustion takes place in an electric or gas muffle at low red heat, often 12 hours or more are necessary. At higher temperatures, fusion of the ash, especially of the ash of spring wheat flours, causes occasional occlusion of carbon which can be oxidized only with great difficulty at high heat. The ash of wheat flour is acid in reaction and consists mainly of acid phosphates of potassium, etc. Many methods have been proposed, using added calcium salt solutions, but the hygroscopic character of the calcium compounds and their absorption of carbon dioxide have caused difficulties by the increase in weight which takes place even when the ash is promptly weighed. Organic salts of magnesium added in the form of solutions have been proposed, but in some cases the solutions have been spoiled by mold growths, and with water solutions considerable time is lost by the necessity of drying before beginning the combustion. Working and Anderson (*1*) proposed the use of a 70 per cent alcoholic solution of magnesium nitrate. Independently the author found that magnesium nitrate was the best of the magnesium salts, as it is not subject to mold growth, its oxygen content helps in the oxidation of the flour, and it contributes no carbon to the combustion.

After considering a number of solvents, carbitol (monoethyl ether of diethylene glycol) was adopted. It has a moderately high boiling point, a low vapor pressure, good solvent action on magnesium nitrate, low viscosity, and very rapid penetrating or wetting power for even the finest milled flours; burns away quickly without sputtering and, in the proportions suggested, leaves a light, fluffy, nonhygroscopic, white ash.

It may be added to the flour from a pipet or by some other appliance capable of dispensing small amounts accurately. The 2-ml. dispensing pipet holding 1 liter, made by the Scientific Glass Apparatus Company, Bloomfield, N. J., has been found very accurate and useful. The apparatus preserves the solution without loss or concentration by evaporation of the solvent and consequent inaccuracy.

Following this method 6.358 grams of magnesium nitrate, $Mg(NO_3)_2.6H_2O$, are weighed into a 1-liter measuring flask. The nitrate is dissolved in carbitol by shaking and finally made up to the mark. For patent and straight grade flours, exactly 2 grams are weighed out in a weighed porcelain, silica, or platinum crucible or ignition capsule of approximately 8-ml. capacity, and 2 ml. of the solution are added to the flour. For clear flours, 1 gram of flour is used; for lower grades, 0.75 gram. The solution is added to the crucible, allowing about 0.25 minute for the solution to drain, then the tip of the dispenser is touched to the inner edge of the crucible. The crucible is placed over a Meker or Fisher burner and the gas ignited for about 10 seconds or until the contents of the crucible begin to burn. The gas is then turned off and the carbitol allowed to burn away quietly. After the flame has flickered out, the burner is again lit and the flour allowed to burn, or it may be placed in the muffle for 1 to 2 hours at bright orange heat. It yields a white or faintly grayish ash.

Before using a new lot of the nitrate solution, the yield of magnesium oxide is determined by weighing an empty crucible, adding 2 ml. of solution, allowing the carbitol to burn off, then strongly igniting until the residue is white. After cooling, the crucible is weighed. The weight of magnesium oxide obtained (which is calculated for 2 mg.) is subtracted from each determination.

Duplicates agree accurately with each other and in comparisons with flours ashed without addition of solution, the results usually check within 0.002 per cent.

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