The Destruction of Platinum Crucibles Through the Ignition of Magnesium Ammonium Phosphate.

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Platinum is not oxidized in the air at any temperature, nor attacked by any single acid, yet there are many substances that attack and combine with it at comparatively low temperatures.

It sometimes happens that a platinum crucible is cracked or is fused through during the burning of the filter paper containing magnesium ammonium phosphate, or during the final ignition required to convert magnesium ammonium phosphate into magnesium pyrophosphate. This has again and again been a source of annoyance and expense to the phosphate analyst. The break down of the crucible is not due to invisible mechanical defects in the crucible, nor to the quality of the platinum or platinum alloy used in its construction. The cause of these occasional accidents is to be found in the reduction of the phosphate through incorrect procedure in burning or igniting the paper in connection with the precipitate, or, indirectly and less frequently, by failure to observe the well-established conditions for properly precipitating and washing magnesium ammonium phosphate.

The direction for the treatment of the magnesium ammonium phosphate residue given in the texts and handbooks, at the disposal of the writer, is by no means sufficient to enable the inexperienced operator to safely use a platinum vessel in this operation. The notes on the use and care of platinum ware, published by Baker & Co., Heraeus and other platinum smiths, do not suggest the possibility of a mishap from the ignition of magnesium ammonium phosphate in a platinum crucible. The notes furnished by the Baker Co. have long contained the statement: "Organic matter containing phosphorous should not be ignited in platinum dishes, as it affects the platinum seriously." This "serious affect" is the same as that noticed occasionally in connection with the ignition of magnesium ammonium phosphate in platinum crucibles, and is caused by the combination of reduced phosphorous with the platinum, forming platinum phosphide.

The reduced phosphorous unites with platinum even at a dull red heat (600° C.).

The external appearances of a crucible which has suffered such an attack are characteristic. Cracks of varying length appear, usually in the bottom, but sometimes in the sides; the fractured surfaces are distinctly crystalline; the edges of the fractures are usually raised and puffed and at times present unmistakable signs of fusion.

Reduced phosphorous, the immediate cause of the destruction of the crucible, may be accounted for by inquiry into the nature, the origin and the conditions governing the deportment of reducing agents which could act upon magnesium ammonium phosphate during the processes of incineration and ignition.

The reduction of the phosphate may be due to any or all of the following:

1. Carbon from the imperfectly ashed filter paper.

2. Ammonia liberated by heat from magnesium ammonium phosphate, or from sodium ammonium phosphate, or ammonium phosphate, which may be present in abnormal amount in the magnesium precipitate.

3. Hydrogen from the dissociation of ammonia at the high temperature, and also from the incomplete combustion zone of the gas flame by diffusion through the platinum crucible.‡

The reduction of magnesium pyrophosphate by carbon begins at 950° Cent. and becomes violent at 1,100 to 1,200° Cent.‡ The reduction by hydrogen begins somewhat below 900° Cent.‡ Dry ammonia gas passed over magnesium pyrophosphate heated to 950° Cent. yields phosphine and red phosphorous.‡ The destruction of the platinum vessel is most rapid when the residue contains free ammonium phosphate, which upon fusion yields most of its ammonia and meta-phosphoric acid. Ammonium phosphate heated in a covered platinum crucible to 700-800° Cent. causes complete destruction of the vessel. Holes appear in the bottom and sides, and the lid may fuse. The quantity of ammonia from the magnesium ammonium phosphate, which has been properly prepared, will prove destructive only under especially unfavorable conditions, e. g. very rapid heating of the phosphate to a high temperature.

Strict observance of the following summarized suggestions will insure the safety of the platinum crucible in the ignition of magnesium ammonium phosphate:

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1. Precipitate the magnesium with sodium hydrogen phosphate, or with ammonium sodium hydrogen phosphate, rather than with ammonium phosphate.

2. Do not neglect to wash the precipitate with water containing one-fourth its volume of conc. ammonium hydroxide until the washings show but a faint turbidity with silver nitrate acidified with nitric acid. If ammonium phosphate is present thorough washing is particularly important.

3. Remove the main portion of the residue from the paper before incinerating, or burn the paper with a small residue, in the crucible, over a very small Bunsen flame. This may be quickly accomplished in a draught produced by tilting the lid of the crucible. *Do not ignite strongly nor heat to the fusing point of the phosphate until the material in the crucible is white (carbon free).* If the ashing of the paper has been imperfect, allow the crucible to cool, moisten the residue with a few drops of conc. nitric acid, cover the crucible with the lid, carefully evaporate the acid and heat again in the Bunsen flame. The process must be repeated until the residue becomes white.

4. To the residue in the crucible add the main portion of the precipitate and heat in the Bunsen flame gently at first, or until the greater part of the ammonia has been expelled, then heat strongly in the blast flame until the material ceases to decrease in weight.