Notes on the Determination of Chromium in the Presence of Iron, Aluminium, and Phosphoric Acid, with Perchloric Acid as Oxidising Agent

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RECENTLY we became interested in the determination of chromium in various paint-pigments, and certain results which we obtained led us to doubt the accuracy of methods depending on the oxidation of the chromic ion to chromate by means of sodium peroxide, particularly when reasonable amounts of iron were also present.

Järvinen (*Z. anal. Chem.*, 1928, **75**, 1), in a paper dealing with the determination and separation of chromium, iron, aluminium and phosphoric acid in presence of one another, describes in detail the results of his investigation of the various methods of oxidation of chromium to chromate, these methods including the use of sodium hypochlorite, sodium hypobromite, sodium peroxide, potassium permanganate and potassium persulphate, and his results pointed to the conclusion that the most efficient oxidising agent tried was sodium hypobromite.

Iron, aluminium, chromium and phosphoric acid are usually precipitated together in analytical work, and the correct determination of the chromium in such a mixture is a problem with which one is often confronted. Järvinen's method of attack on such a problem is as follows:—

> "The solution (about 100–200 ml.) containing iron, chromium, aluminium and phosphoric acid, is treated with 1 to 2 ml. bromine, and 2 *N* caustic soda solution added until a slight excess (about 10 ml.) is present. After standing for about a quarter of an hour, the precipitate is dissolved in the smallest possible quantity of hydrochloric acid, and the solution again made alkaline. After warming on the water-bath for some time, the mixture is acidified and diluted, and the bromine boiled off. Excess of 2 *N* ammonium phosphate solution is added, and the iron and aluminium precipitated as phosphates by the dropwise addition of concentrated ammonia solution, the whole being then diluted to a definite volume (500 ml.) and filtered. Two hundred-and-fifty ml. of the filtrate are acidified with sulphuric acid, potassium iodide solution is added, and the liberated iodine titrated with N/10 sodium thiosulphate solution. . . ."

We have investigated this method, using chromic solutions prepared by reducing known volumes of *N*/10 potassium dichromate solution with sulphurous acid in the presence of hydrochloric acid, together with known amounts of ferric chloride, aluminium chloride, and phosphoric acid. The results we obtained are given on p. 612 under the heading "Results obtained by Järvinen's Method."

In the first three experiments, where iron was absent, and where the oxidation took place in one phase, all the reactants being in solution, we obtained very satisfactory conversion of the reduced dichromate solution to chromate, but, in the remaining four, where iron was present, the results obtained were always low. These results are not altogether surprising in view of some statements made by Järvinen in his paper. He points out that when a solution of chromic chloride is neutralised with caustic soda solution, the precipitated hydroxide dissolves readily in excess of alkali, but if about the same quantity of ferric chloride is present, and an excess of alkali is added, the chromium hydroxide does not re-dissolve and the filtrate is colourless.

The chromium is held fast by the ferric hydroxide, and this fact may explain why chromium, in the presence of iron, is oxidised with greater difficulty.

Järvinen asserts that a double oxidation is necessary, and a modified double oxidation is actually carried out in his method, outlined above, but our results do not indicate that this ensures quantitative oxidation of the chromium to chromate when reasonable amounts of iron are also present.

Our attention was then directed to a method of oxidation of chromium proposed by Lichtin (*Ind. Eng. Chem., Anal., Ed.*, 1930, **2**, 126), in which all the reactants are in solution, and difficulties due to the presence of insoluble ferric compounds in suspension in the oxidation process are avoided.

The oxidising agent used is perchloric acid, which Lichtin used in the determination of chromium in chrome alum liquors and crystals, and further work on the use of this reagent has been carried out by Willard (*Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 88). We were unaware of Willard's work at the time we began our own, and, consequently, in our investigation have used Lichtin's technique, with modifications.

Lichtin and Willard disagree as to the mechanism of the oxidation, but Willard's explanation appears to be the more probable. He maintains that dilute perchloric acid, which, under ordinary conditions is extremely stable and is not affected by the ordinary reducing agents, on concentration to about 70 to 72 per cent. distils at about 203° C., a certain amount of decomposition taking place, thus: $4HClO_4 = 2Cl_2 + 7O_2 + 2H_2O$. The oxygen liberated under these conditions renders the concentrated acid an extremely powerful oxidising agent.

After carrying out oxidations of chromium to dichromate by means of perchloric acid, and removing iron and aluminium by precipitation as hydroxides, Lichtin determined the dichromate produced; the acidified dichromate solution was treated with potassium iodide solution, and the liberated iodine was titrated with standard sodium thiosulphate solution.

We have found that the dichromate produced in the oxidation is more accurately determined by Knop's method (*J. Amer. Chem. Soc.*, 1924, **46**, 263), which does not involve preliminary removal of iron and aluminium as hydroxides.

A known volume of a standard aqueous solution of chromic anhydride (A.R.), contained in an Erlenmeyer flask, was acidified with sulphuric acid (20 per cent.), and reduced by the passage of sulphur dioxide gas.

After the excess sulphur dioxide had been removed by boiling, 5 ml. of perchloric acid (A.R. 60 per cent. approx.) were added, and the solution was heated on the sand-bath, a small funnel, the stem of which had been removed, being placed in the neck of the conical flask to prevent loss by spurting. When the volume of the solution was considerably reduced by the heating, the oxidation to the orange dichromate took place almost instantaneously, after which the heating was continued for about five minutes.

The flask was removed and allowed to cool, about 100 ml. of water were added, and the solution was boiled until any free chlorine was removed. The cooled solution was diluted to 150 ml., and an excess of $N/10$ ferrous ammonium sulphate solution was added, this excess being determined by titration with $N/10$ potassium dichromate solution, diphenylamine being used as internal indicator (Knop, *loc. cit.*).

The experiment was repeated with the addition of known amounts of ferric sulphate, aluminium sulphate and phosphoric acid, very satisfactory results being obtained, as indicated by those given under the heading "Results obtained by the use of the modification of Lichtin's Method," Experiments 8 to 14 (p. 612).

There are two results, however, which call for comment, and these are given under Experiment 14.

In this case the aqueous solution of the chromic anhydride was reduced in the presence of 2 ml. of concentrated hydrochloric acid, instead of 2 ml. of dilute sulphuric acid solution, so that the final oxidation was carried out in the presence of chloride. The perchloric acid vapour was definitely yellow in colour, and the presence of volatile chromium compounds in the vapour was proved by carrying out a similar oxidation in a round-bottomed flask to which a glass condenser was attached by means of a ground-glass joint, the drawn-out tube of the condenser

RESULTS OBTAINED BY JÄRVINEN'S METHOD

	Added	Found N/10 potassium dichromate solution ml.
1	20·0 ml. of N/10 potassium dichromate solution	20·02
2	20·0 ml. of N/10 potassium dichromate solution 0·04 grm. of aluminium	20·00
3	20·0 ml. of N/10 potassium dichromate solution 0·04 grm. of aluminium 0·05 grm. of phosphoric acid	19·97
4	20·0 ml. of N/10 of potassium dichromate 0·04 grm. of iron	18·47
5	20·0 ml. of N/10 potassium dichromate 0·04 grm. of iron 0·05 grm. of phosphoric acid	18·57
6	20·0 ml. of N/10 potassium dichromate 0·04 grm. of iron 0·04 grm. of aluminium	17·5
7	20·0 ml. of N/10 potassium dichromate 0·04 grm. of iron 0·04 grm. of aluminium 0·05 grm. of phosphoric acid	17·82

RESULTS OBTAINED BY A MODIFICATION OF LICHTIN'S METHOD

8	(*a*) 19·97 ml. of N/10 dichromate (*b*) 19·97 ml. of N/10 ,,	(*a*) 19·96 ml. of N/10 dichromate (*b*) 19·94 ,, ,, ,, ,,
9	19·97 ml. of ,, ,, 0·036 grm. of aluminium	19·97 ,, ,, ,, ,,
10	19·97 ml. of N/10 dichromate 0·035 grm. of iron	19·91 ,, ,, ,, ,,
11	19·97 ml. of N/10 dichromate 0·31 grm. of phosphoric acid	19·94 ,, ,, ,, ,,
12	19·97 ml. of N/10 dichromate 0·035 grm. of iron 0·036 grm. of aluminium	19·95 ,, ,, ,, ,,
13	19·97 ml. of N/10 dichromate 0·035 grm. of iron 0·036 grm. of aluminium 0·31 grm. of phosphoric acid	19·94 ,, ,, ,, ,,
14	(*a*) 19·97 ml. of N/10 dichromate (*b*) 19·97 ,, ,, ,, ,,	(*a*) 19·57 ,, ,, ,, ,, (*b*) 18·93 ,, ,, ,, ,,

dipping into about 10 ml. of water contained in a small beaker. When the oxidation was complete the condenser was washed down with water, and the washings were added to the contents of the receiver.

This aqueous solution was rendered faintly ammoniacal, then just acid with acetic acid and evaporated to a small bulk. The evaporated solution gave the reaction for silver chromate when tested with aqueous silver nitrate solution, and the reaction for lead chromate with aqueous lead acetate solution. A further portion, when treated with hydrogen peroxide, sulphuric acid and ether, gave the characteristic blue oxidation-product of chromium, soluble in the ether.

There is little doubt, therefore, that this behaviour is due to the production of volatile chromyl chloride when perchloric acid oxidations of chromium are carried out in the presence of chlorides, and, in our opinion, chlorides should be excluded from such oxidations.

The behaviour of manganese is interesting. Our experience is that manganese, in reasonable quantity, gives rise to a higher oxide of manganese which interferes in the final titration of the dichromate, and, when considerable quantities of manganese are present, it is probably best to separate the bulk of this element by the preliminary isolation of the hydroxides of iron, aluminium and chromium, etc., with ammonia before proceeding to the perchloric acid oxidation.

There are several very interesting applications of this perchloric acid oxidation process. Such substances as ferrochrome are readily attacked by perchloric acid, and we have determined the chromium in such alloys by direct oxidation with perchloric acid, the dichromate produced being titrated by Knop's method.

Such refractory substances as chrome-iron ore may be disintegrated by fusion with potassium bisulphate in a silica crucible, in accordance with Schoeller's technique; the melt is leached with dilute acid, and metals precipitated by hydrogen sulphide are removed, and, after oxidation of the iron with dilute nitric acid, the mixed hydroxides of iron, aluminium and chromium are precipitated with ammonia. The hydroxides are filtered off, washed with water, and dissolved in dilute perchloric acid solution, and this solution is evaporated until oxidation of the chromium takes place, the dichromate produced being subsequently determined by Knop's method.

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