anogen held by them can be determined approximately from the data in series 12 and 13.

Generally, with impure solutions, the results of titration by this method are more accurate than those obtained by the ordinary Liebig method; with pure solutions the results are practically identical, and in nearly all cases the end-reaction is sharper and an estimation can be more rapidly carried out.

108 grams silver, or 170 grams silver nitrate correspond to 52 grams cyanogen or 130 grams potassium cyanide.

The standard silver solution used may be, with advantage, quite dilute; preferably not over twentieth normal, or one-half per cent. silver.

For technical purposes it is common to take 1.305 grams silver nitrate crystals per 100 cc. of water, when each cc. corresponds to one centigram of potassium cyanide (or four milligrams of cyanogen); or, taking samples of ten cc. each, one cc. of standard silver solution used represents one-tenth of one per cent. potassium cyanide in the liquid tested.

If prepared by dissolving the weighed metal it is not generally necessary to expel all acid. Satisfactory results have also been obtained by using a standard ammoniacal silver solution, made by dissolving pure silver in commercial nitric acid, and adding a slight excess of ammonia.

QUALITATIVE SEPARATIONS WITH SODIUM NITRITE IN ABSENCE OF PHOSPHATES, ETC.[1]

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IF a solution of sodium nitrite be added to a solution of ferrous sulphate, the ferrous sulphate solution at first turns a deep brown, and in a short time a greenish brown flocculent precipitate forms, which gradually changes to a fine yellow precipitate, and at the same time a copious evolution of nitrous fumes takes place. If there is a small amount of free acid present in the ferrous sulphate solution, the yellow precipitate occurs almost immediately, and more rapidly still if heated.

A. Peccini and M. Zuco[2] obtained a precipitate similar to this, but used barium nitrite instead of sodium nitrite. Barium

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[1] Read at the meeting of the New York Section, March 5, 1897.

[2] *J. Chem. Soc.*, **50**, 448.

sulphate was the first pecipitated, and the liquid turned brown. Finally an ochre-colored powder separated accompanied by an evolution of nitric oxide. From a quantitative determination of the nitric oxide evolved, the authors considered the precipitate to be a basic ferric nitrate. However, in my investigation, no test has been found for the nitric acid in the precipitate when precipitated with sodium nitrite.

If a ferric salt be used instead of a ferrous, as ferric chloride, the solution at first turns deep red, and evolution of nitrous fumes occurs almost immediately, with the formation of a dark brown precipitate. As with the ferrous sulphate, a small amount of free acid and heat aids the precipitation. If treated in this way the iron will be completely precipitated in a few minutes, and when the heat is withdrawn, the precipitate quickly settles to the bottom of the containing vessel, leaving the solution perfectly clear above.

This precipitate was investigated by L. Pesci,[1] who considered it to be the dimeta ferric hydroxide, $Fe_2O_2(OH)_2$. In precipitating it he excluded air, and obtained a brown precipitate, soluble in water, from which solution it was again reprecipitated by strong nitric acid, but dissolved in excess of acid. In precipitating it without excluding the air, the precipitate was apparently as insoluble in water as that produced with ammonium or sodium hydroxide.

Observing the above reactions, I thought it would be of interest to see what effect sodium nitrite had upon salts of other metals of the iron and chromium group, and have obtained the following results: Of the common elements of the iron and chromium groups, iron, aluminum and chromium are completely precipitated by sodium nitrite, if the solution is boiled for a short time, while cobalt nickel, zinc and manganese are unaffected, if a small amount of free acid is present in the solution of the salts. At first neutral solutions were used, in which case small amounts of cobalt, nickel, zinc and manganese were sometimes precipitated. But this never occurred when a few drops of hydrochloric acid were first added. In the cold, iron and some of the cobalt are precipitated (the cobalt being precipitated as the double nitrite of cobalt and sodium), while

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[1] *J. Chem. Soc.*, *1888*, 1252.

chromium and aluminium do not come down until heated nearly to the boiling-point.

It was my next endeavor to ascertain whether the iron and chromium precipitate carried down with it any zinc, as is the case when precipitated with sodium hydroxide or ammonia. Qualitative experiments were here used instead of quantitative, as perhaps should have been done, but the results justify me in believing that at least no more than inappreciable quantities of zinc are carried down by the iron and chromium.

Various proportions of iron and chromium were added in small amounts of zinc solution and precipitated, the zinc always showing plainly in the filtrate. Twenty parts of ferric and chromic chloride were mixed with one part of zinc nitrate and the solution so diluted that it contained one part of zinc nitrate iron, to 5000 of solution, and then precipitated with sodium nitrite; grams zinc was easily detected in the filtrate Equal amounts of chromium and zinc salts were mixed together, about two each, and precipitated with sodium nitrite; the precipitate was washed until the washings gave no test for zinc, then dissolved in hydrochloric acid; diluted and reprecipitated with barium carbonate, and filtered, the barium removed from the filtrate and the filtrate evaporated to forty cc., when a test was made for zinc with negative results. Tests were also made with iron and manganese. Equal quantities of manganous sulphate and ferric chloride were added together, precipitated and washed, and the precipitate tested for manganese with the sodium carbonate bead with negative results, showing that the separation is more complete than with barium carbonate. After these preliminary experiments, various mixtures of the salts of the iron and chromium groups were analyzed and the results were found as accurate, and in the case of iron and manganese, more accurate than with barium carbonate, and much more expeditious.

In case iron is present it is better to precipitate the iron in the ferrous state, as it gives a precipitate that is less bulky and gelatinous than the ferric iron, and therefore can be washed more quickly.

In a later paper I hope to give favorable results with the use of alkali nitrites in qualitative separations in the presence of phosphates, etc., as well as in quantitative separations.

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