*Cobalt.*—For these tests a solution of cobalt nitrate was used. The reagent was sodium hydroxide.

| | |
|---|---|
| 5 cc. = 25.0 mg. Co | Heavy precipitate (blue becoming a dirty orange), coagulates and settles on boiling |
| 5 cc. = 5.0 mg. Co | Heavy precipitate |
| 5 cc. = 2.5 mg. Co | Slight precipitate |
| 5 cc. = 1.0 mg. Co | Slight precipitate |
| 5 cc. = 0.5 mg. Co | Very slight precipitate |
| 5 cc. = 0.25 mg. Co | Faint precipitate |
| 5 cc. = 0.125 mg. Co | Faint precipitate |
| 5 cc. = 0.06 mg. Co | Limit. |

Not less than 0.25 mg. can be seen in the cold. The limit test shows a concentration of one part in 80,000.

*Manganese.*—The following results were obtained with a solution of manganese chloride. In each test a slight excess of ammonia was added and the mixture boiled.

| | |
|---|---|
| 5 cc. = 25.0 mg. Mn | Heavy precipitate (orange) |
| 5 cc. = 5.0 mg. Mn | Heavy precipitate (red-brown) |
| 5 cc. = 2.5 mg. Mn | Medium sized precipitate |
| 5 cc. = 1.0 mg. Mn | Slight precipitate (dark red) |
| 5 cc. = 0.5 mg. Mn | Slight precipitate (black) |
| 5 cc. = 0.25 mg. Mn | Slight precipitate (black) |
| 5 cc. = 0.12 mg. Mn | Faint precipitate (black) |
| 5 cc. = 0.06 mg. Mn | Faint precipitate (black) |
| 5 cc. = 0.03 mg. Mn | Limit |

With sodium hydroxide as reagent, the same results were obtained. With 5.0 mg. and less, the precipitate appears like a coloration before boiling.

The limit test shows a delicacy of one part in 170,000.

*Magnesium.*—A solution of magnesium sulfate was used in these tests with sodium hydroxide as the precipitant.

| | |
|---|---|
| 5 cc. = 25.0 mg. Mg | Heavy gelatinous precipitate |
| 5 cc. = 5.0 mg. Mg | Heavy gelatinous precipitate |
| 5 cc. = 2.5 mg. Mg | Heavy gelatinous precipitate |
| 5 cc. = 1.0 mg. Mg | Slight precipitate |
| 5 cc. = 0.5 mg. Mg | Limit |

The limit test shows a delicacy of one part in 10,000.

---

# THE COBALTINITRITE METHOD OF DETERMINING POTASSIUM.

By F. H. MacDougall.

Received May 24, 1912.

In the usual way of determining potassium by the cobaltinitrite method, the yellow precipitate, supposed to have the composition represented by the formula $K_2NaCo(NO_2)_6.xH_2O$, is boiled with excess of 0.1 *N* $KMnO_4$ for several minutes, dilute sulfuric acid is added, then oxalic acid and finally 0.1 *N* $KMnO_4$ until the end point is reached. In this process the oxidation of the nitrite by the permanganate takes place in alkalin solution and the permanganate is first reduced to manganese dioxide. This manganese dioxide usually interacts but slowly with the oxalic acid subsequently added, since the reaction mixture is so dilute. The author decided to test the advisability of adding dilute sulfuric acid to the yellow precipitate before oxidizing with permanganate and obtained some results that may be of interest.

The yellow precipitate dissolves so slowly in dilute sulfuric acid that loss of nitrous acid or of oxides of nitrogen need not be feared. As a matter of fact, more permanganate is required when the oxidation is carried out in acid solution than when the regular method is followed. This is shown by the results presented in the following table. The last column gives the ratio of the amounts of permanganate used in the two methods. This ratio is seen to be very approximately 12 : 11. A study of the reactions that take place during the oxidation of the cobaltinitrite soon led to an explanation of this ratio.

TABLE.

| | | Cc. of $KMnO_4$. | | | | |
|---|---|---|---|---|---|---|
| Material used. | K. calc. | Regular method. | | Author's method. | | Ratio. |
| C. P. KCl........... | 0.01694 | 23.91 | | 26.02 | | 1.088 |
| Fertilizer........... | ....... | 15.71 | 15.76 | 17.09 | 17.18 | 1.090 |
| | | 15.80 | | 17.28 | | |
| | | 15.77 | | 17.16 | | |

The assumed formula for the yellow precipitate is $K_2NaCo(NO_2)_6$ or $2KNO_2.NaNO_2.Co(NO_2)_3$. To oxidize this to nitrates would require 12 oxidizing units (one oxidizing unit being equivalent to O/2), were it not that cobalt changes from a valence of three to a valence of two, so that 11 oxidizing units are required. Accordingly, we have the following series: $2K = K_2NaCo(NO_2)_6 = 11\ O/2$. From this, 1 cc. of 0.1 *N* oxidizer is equivalent to 0.0007111 gram K or 0.0008564 gram $K_2O$. These are the factors to be used when the regular method is adopted. In acid solution, however, trivalent cobalt is not an active oxidizer. It is evident, at least, that it will not oxidize nitrous acid, since it is in acid solution that nitrous acid oxidizes divalent to trivalent cobalt. Accordingly in sulfuric acid solution the cobaltic salt formed must change to the cobaltous salt with evolution of free oxygen. In this case, then, we have the series: $2K = K_2NaCo(NO_2)_6 = 12\ O/2$, and 1 cc. of 0.1 *N* oxidizer will be equivalent to 0.0006518 gram K or 0.0007850 gram $K_2O$. We thus see that if sulfuric acid is added to the yellow salt before the permanganate, the amount of permanganate required will be greater than in the regular method in the proportion of 12 to 11.

Referring now to the table, we note that $23.91 \times 12/11 = 26.08$ and that 15.76 × 12/11 = 17.19 instead of 26.02 and 17.18, respectively. In the case of the determination with pure potassium chloride, the calculated quantity of potassium was 0.01694, that obtained by the regular method 23.91 × 0.0007111 = 0.01700, and that obtained by the author's modification 26.02 × 0.0006518 = 0.01696.

## Summary.

In this paper are given the results of some experiments on a modification of the cobaltinitrite method of determining potassium. Cobaltic cobalt is shown to be unable to oxidize nitrites in sulfuric acid solution under the conditions of the described method.

UNIVERSITY OF CALGARY,
CALGARY, ALBERTA, CANADA.

## NOTE.

*The Asserted Explosivity of Uranyl Nitrate.*—Under the title "Explosionsfähigkeit von salpetersaurem Uran" some interesting observations have been recently published by Ivanov.[1] This author saw crystals, supposed to be of uranyl nitrate, and which on analysis gave the correct percentage of uranium, that would explode on slight friction or even spontaneously. He appears inclined to assume that there was some connection, not definitly specified, between the explosivity of the salt and the radioactivity of uranium.

It would hardly be worth while to seriously combat so improbable a theory, which is both so vague and so unsupported, unless it were possible to offer an explanation of the facts, which if not demonstrated, at least rests on *some* evidence.

A number of years ago I made several involuntary observations on explosive uranyl "nitrate," of which the following are a part: A portion of about 40 grams of uranyl "nitrate" which had been recently made in the laboratory by me, was left at the close of the day's work in a porcelain bowl on a laboratory table, in order to give the smell of ether which still hung about it a chance to evaporate. In the morning it was discovered that the salt had exploded during the night. Fragments of the porcelain dish were embedded in the wood of a cupboard six or eight feet away and scattered all over the floor, a heavy bell jar quite two feet away was destroyed; in short, the explosion had been pretty sharp but not exactly violent, as there was no hole through the bench where the dish had stood. Another, much smaller portion of the same lot had been put in a desiccator and was found intact, in its glass dish. It was safely transferred. Then, when an attempt was made to scrape off the small quantity which stuck to the dish, a succession of flashes of flame resulted, similar to the sparks sometimes given out when a safety match is

---

[1] *Chem. Ztg.*, **36**, 297 (1912).