It is needless to add that molybdic acid may be substituted for tungstic acid in all these bodies, and very likely columbic and tantalic oxides may be introduced for vanadic, arsenic and phosphoric oxides, and also with them, thus opening up a new and extensive class or group of acids which we hope to study as time permits.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 62.]

A NEW QUALITATIVE TEST FOR COBALT.

BY J. L. DANZIGER.

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THE following test, if carried out properly, will serve to detect the presence of cobalt, in a solution containing 1 part of cobalt, in 500,000 parts of water, provided the solution is colorless or but slightly colored, which can readily be obtained by dilution.

To about 5 cc. of the solution, acid with hydrochloric acid, in a test-tube, there is added solid ammonium thioacetate, CH_3COSNH_4, a few drops of stannous chloride solution, and an equal volume of amyl alcohol, or a mixture of acetone and ether or of alcohol and ether; the whole is well shaken and allowed to separate. If any cobalt is present, the upper layer will be colored blue, the intensity of the color depending on the amount of cobalt present. Solid ammonium thioacetate is added to prevent dilution of the solution, since water destroys the blue color. Stannous chloride is added to reduce any iron present, since ferric iron gives a deep red coloration, as with ammonium thiocyanate. Amyl alcohol, a mixture of acetone and ether or of alcohol and ether, is added to diminish the dissociation and extract the color produced by the undissociated cobalt salt. Amyl alcohol was found to be the most efficient, but is objectionable on account of its disagreeable odor.

In order to ascertain to what compound the color was due, a large amount was prepared by the addition of a saturated solution of ammonium thioacetate to a saturated solution of cobalt chloride, the solution extracted with a mixture of acetone and ether, and the ethereal solution evaporated.

After trying a great number of solvents, it was found impossible to crystallize the substance; so it was washed free from impurities, and its formula deduced from the ratio of cobalt, ammonium, and sulphur present as follows:

About 1 gram of the substance was dissolved in water, an excess of potassium hydroxide added, and the ammonia distilled into a known excess of standard acid, the excess of acid being determined by standard alkali.

The residue in the flask, consisting of cobalt sulphide, potassium sulphide, etc., formed by the decomposing action of the hot strong alkali, was diluted and filtered. The precipitate was treated with a large excess of fuming nitric acid, to oxidize the sulphur, the excess of nitric acid boiled out and the cobalt twice precipitated with potassium hydroxide, dissolved in nitric acid and precipitated as cobalt ammonium phosphate, as described by Dakin[1], except that alcohol was added to render the precipitation complete, and finally weighed as cobalt pyrophosphate, $Co_2P_2O_7$.

The first filtrate from the cobalt, containing sulphides, was oxidized with fuming nitric acid, combined with the other filtrates and the sulphur precipitated as barium sulphate, ignited and weighed.

The analysis was run in duplicate, the results being:

			Molecular ratios.		
	Gram.	Gram.	I.	II.	Average.
NH_4	0.06625	0.07965	1.96	2.03	1.99
S	0.23650	0.27970	3.95	4.01	3.98
Co	0.11000	0.12866	1.00	1.00	1.00

These ratios approximate 2:4:1, and correspond to the formula $(CH_3COS)_2Co.2CH_3COSNH_4$.

A number of tests were made to compare the sensitiveness of the test with the thiocyanate test proposed by Vogel[2] and described by Treadwell.[3]

Several solutions of cobalt chloride were prepared, of dilutions varying from 1:5,000 to 1:50,000. To equal amounts of each of these solutions, quantities of ammonium thiocyanate and of ammonium thioacetate, sufficient to saturate them, were added, and

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[1] *Chem. News*, Jan. 25, 1901, p. 37.

[2] *Ber. d. chem. Ges.*, **12**, 2314 (1879).

[3] *Ztschr. anorg. Chem.*, Jan., 1901, p. 108.

then an equal volume of amyl alcohol. The colors of the upper layers were then compared, and were found to be of equal intensity for each dilution. The thiocyanate test was found to be much more sensitive than Treadwell claimed.

Attention is called to the fact that the double ammonium cobalt thioacetate has 2 molecules of ammonium thioacetate to 1 of cobalt thioacetate; this is analogous to the double ammonium cobalt thiocyanate.

QUANTITATIVE LABORATORY,
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A NOTE ON THE VOLUMETRIC DETERMINATION OF COPPER.

BY S. W. PARR.

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THE volumetric method for copper recently described,[1] wherein the cuprous thiocyanate is titrated directly with permanganate, first in the alkaline and then in the acid condition, is found at times to give an unsatisfactory end reaction. This seems to be due to an incomplete oxidation of the cuprous hydroxide by the permanganate, the latter acting somewhat slowly under the conditions described. Upon acidifying, therefore, any copper remaining in the cuprous condition reverts to the cuprous thiocyanate and in this form is slowly acted upon by the permanganate; hence the occasional indefiniteness at the end.

This difficulty is very easily overcome by the following slight modification: The washed precipitate of cuprous thiocyanate and the asbestos pulp having been returned to the beaker, there is added 10 cc. of a 10 per cent. solution of potassium hydroxide, followed by 10 cc. of ammonia (sp. gr. 0.96) then, without delay, the titration is begun with the standard permanganate solution, continuing until, upon warming, the green color of the supernatant liquid remains. The heating should not be prolonged, 45° to 55° being quite sufficient. Add now a sight excess of permanganate equal to one-third or one-fourth of the quantity needed to produce the permanent green coloration. Allow the mixture to stand for five

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[1] This Journal, 22, 685.