

acid gave 0.0475 carbon and 0.0254 sulphur, of which last 0.0036 was soluble in carbon disulphide. These figures indicate a similarity to quisteite, although the sulphur is lower.

*The Oxidation Products of the Ore.*—These are reported to cover the surface of the ground in the vicinity of the vein outcrop. The specimen examined by me resembles porous limonite in appearance. There was found in it by a rough partial analysis about 45V<sub>2</sub>O<sub>5</sub>, 14-15 Fe<sub>2</sub>O<sub>3</sub>, 15 H<sub>2</sub>O, 20 or more of siliceous gangue, nearly 1 of MoO<sub>3</sub> and a little SO<sub>3</sub>. Nickel is absent, or practically so. The material does not represent a single species, for it contains probably more than one vanadium compound, among them doubtless the minute micaceous scales, greenish sometimes, and sometimes yellowish, that may be seen with a lens.

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### THE NITROSO- $\beta$ -NAPHTHOL METHOD FOR THE QUALITATIVE SEPARATION OF NICKEL AND COBALT.

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The Nitroso- $\beta$ -naphthol method for the qualitative separation of nickel and cobalt is not a new one; and, in view of what has already been written on the subject, anything further may seem superfluous. However, this paper has two excuses to offer for its existence:

First—For the sake of those who are unacquainted with the method, it will aim to make the directions for the cobalt test more explicit than those usually given.

Second—It will present a method for determination of the nickel, which so far as the author knows is new.

The things this paper contains may be familiar to many; but for the sake of benefitting those who are still wandering in the dark, I shall brave the fear of repetition, and give them out for what they are worth.

*Cobalt.* Beginning at the point where the nickel and cobalt exist alone as sulphides after removal of zinc and manganese, we proceed as follows:—

Place paper and contents in a casserole, add 10 cc. dilute hydrochloric acid (1:4) and 1 cc. dilute nitric acid (1:3) and boil until only the paper and separated sulphur remain undissolved. Now filter, washing the paper slightly, return the filtrate to the casserole, and boil down to complete dryness, taking care to remove the casserole from the flame a little before this point is reached, so as not to overheat and render the residue insoluble. Take up with two or three drops of dilute hydrochloric acid and 10 cc. hot water, and add a solution of nitroso- $\beta$ -naphthol in slight excess. The cobalt comes down as a very bulky brick-red precipitate of cobalti-nitroso- $\beta$ -naphthol,  $\text{Co}(\text{C}_{10}\text{H}_6\text{ONO})_8$ . After stirring and allowing to stand a few minutes, filter, and confirm the presence of cobalt by means of the borax bead. Before testing for nickel, add a

few drops more nitroso- $\beta$ -naphthol to the filtrate to make sure that the cobalt is all removed, and of course filter off any precipitate that may be formed.

NOTES.—Hydrochloric acid in large quantities and nitric acid even in small quantities interfere with the precipitation of cobalt; hence the evaporation.

The solution of nitroso- $\beta$ -naphthol is made up as follows:—Weigh out 8 grams of the solid reagent, dissolve in 300 cc. cold glacial acetic acid, dilute with an equal volume of water, and filter. In this way is obtained a saturated solution in 50% acetic acid. For best results, the reagent should be made up as often as once a month, as it does not keep very well.

Owing to the bulkiness of the cobalt precipitate, we usually make up our unknowns with only a small amount of cobalt present (2 gm. crystallized cobalt nitrate per liter). Giving out about 5 cc. of such a solution in an unknown, only about 3 cc. nitroso- $\beta$ -naphthol solution will be required for complete precipitation. It is, however, by no means necessary to limit the quantity of the cobalt.

The test for cobalt, as above stated, has always given perfectly satisfactory results even with beginners, good tests for cobalt being obtained with certainty, when the quantity present was less than a milligram. Indeed, we have had difficulty in obtaining nickel salts of such purity that our students would not obtain a test for cobalt even when we did not intend it to be present.

*Nickel.* The main difficulty we have experienced with the method has rested with the test for nickel. In their usual form the directions for this test read as follows: "Make the filtrate from cobalt alkaline with ammonium hydroxide filter off the precipitated nitroso- $\beta$ -naphthol, and pass hydrogen sulphide. Confirm the presence of nickel by means of the borax bead."

So far as our experience goes, the test in this form has always been a failure. With our classes, failure became so common that the students lost all confidence in the method, and reported largely at random. We even made up our unknowns so that the amount of nickel exceeded that of cobalt ten to one (which only showed the weakness of the method and in no wise overcame it) and even then the number of failures was scarcely less. However, considering the shortness and simplicity of the method and its accuracy for the detection of cobalt, we determined not to give it up without some attempt at making it what it promised to be.

Thinking that possibly the nickel might be lost during the washing of the sulphides, as a result of oxidation and consequent solution, we investigated and found that the loss of nickel from this cause was not

worse than the loss of cobalt, which amounted to very little.

Next, we tested the solubility of nickel sulphide in the cold dilute (1:10) hydrochloric acid used to dissolve out zinc and manganese, but here again the loss was found to be very small.

At last we turned our attention to the final filtrate in which hydrogen sulphide had failed to give a precipitate of nickel sulphide when nickel salts were known to be present in the original solution. We thought that perhaps the organic matter left in the solution was preventing the precipitation, but were surprised to find that this filtrate contained no nickel. The cause of the difficulty was now plain: In making the solution alkaline, and filtering off the precipitate of nitroso- $\beta$ -naphthol, we were removing from the solution large quantities of nickel, the amount removed depending upon the excess of nitroso- $\beta$ -naphthol.

What we needed, then, was a method by which we could remove the nitroso- $\beta$ -naphthol, so that the solution might be made alkaline for precipitation of nickel without removing the nickel. The method most easily worked out seemed to be the common one for removal of organic matter, viz:— oxidation by means of sulphuric and nitric acids. Trial proved the method to be quick, easy and always successful. Best of all, it did not interfere in any way with the subsequent test for nickel.

The details of this process, as we apply it, and of the final test for nickel are as follows:—

To the filtrate from cobalt add 5 cc. of dilute sulphuric acid (1:5) and 1 cc. of nitric acid (1:3), and boil down in a casserole until dense white fumes of sulphur trioxide are evolved. If a dark color still remains, cool somewhat, add two or three drops more of nitric acid and again heat until fumes of sulphur trioxide appear. By this time all organic matter should be removed and the solution should be colored only yellow at most. Cool now completely, cautiously add 5 cc. water and a piece of litmus paper, and then drop in ammonium hydroxide with constant stirring until the paper is distinctly blue, but avoiding an excess. Now remove the paper, transfer the solution to a test tube, and pass hydrogen sulphide. A black precipitate is probably nickel. Confirm by means of the borax bead.

NOTE.—If through careless work the cobalt is not all removed in its proper place, the excess will appear with the nickel; or, if no nickel is present, in place of the nickel. However, we have never seen enough cobalt carried over to obscure the bead test for nickel, where that element was present; and, on the other hand, in absence of nickel, the bead test never fails to disclose the identity of the small amount of cobalt sometimes carried over. If the work is carefully done, no cobalt will ever be carried over, as its removal by this process is quantitative.

We have been using this method for the nickel determination long enough to discover the weak points, if there were any, and are perfectly satisfied with the results. Failure on the part of our students is a very rare thing, although we have greatly cut down the amount of nickel in our unknowns. I think we are safe in saying that the test for nickel is fully as delicate as that for cobalt; and the ease and rapidity with which it is carried out make it the best method, in our estimation, we have ever used.

### ON PRECIPITATED SULPHUR.<sup>1</sup>

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*Historical.*—Ever since, in the year of 1848, Deville<sup>2</sup> first discovered amorphous sulphur and Selmi<sup>3</sup> found the same substance in flowers of sulphur, many chemists have studied its occurrence and its properties. St. Claire Deville<sup>4</sup> examined numerous specimens of commercial flowers of sulphur and found that the percentage of the insoluble amorphous modification varied from 11.3-23.4 per cent. In roll sulphur he found 2.9-7.3 per cent. of sulphur insoluble in carbon disulphide. Deville<sup>5</sup> was the first to notice that the sudden cooling of melted sulphur gave sulphur insoluble in carbon disulphide. After sudden cooling of sulphur from 230° Berthelot's<sup>6</sup> method of measurement<sup>7</sup> gave 60 per cent. of the amorphous variety. After pouring the hot sulphur into ether his method of extraction gave 70 per cent. After heating the sulphur with a small quantity of iodine and cooling suddenly in water, the method used seemed to indicate the presence of as much as 80 per cent. of amorphous sulphur.<sup>8</sup>

Berthelot<sup>9</sup> also prepared amorphous sulphur by precipitation from various compounds of sulphur by means of acids and other reagents. He says<sup>10</sup> "In general the kind of sulphur disengaged is independent of the agent used for precipitating, provided it is not an alkali or an oxidizing

<sup>1</sup> The work upon this paper was carried on simultaneously with that published by Smith, Holmes and Hall, *Journal of the American Chemical Society*, **27**, 797, 979, and was read in abstract by Alexander Smith on June 30, 1906, at Ithaca, N. Y., before the American Chemical Society.

<sup>2</sup> *Pharm. Centr.*, **1848**, 200; Graham Otto's "Lehrbuch," **1**, 53S.

<sup>3</sup> Graham Otto's "Lehrbuch," **1**, 539.

<sup>4</sup> Graham Otto's "Lehrbuch," **1**, 539.

<sup>5</sup> *Compt. rend.*, **26**, 119; Ostwald's "Lehrbuch," **2**, 2, 55f.

<sup>6</sup> *J. pr. Chem.*, **71**, 360.

<sup>7</sup> In the experiments referred to, Berthelot did not allow the precipitated sulphur to harden, but extracted the viscous mass with carbon disulphide immediately. It is evident that much of the sulphur could not come in contact with the solvent, and hence a high percentage of amorphous sulphur would be indicated.

<sup>8</sup> *Compt. rend.*, **56**, 39.

<sup>9</sup> *Ann.* (3) **49**, 430.

<sup>10</sup> *loc. cit.* p. 444.