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A NOTE ON THE DETECTION AND ESTIMATION OF COBALT IN PRESENCE OF NICKEL

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The methods to be described provide for the colorimetric detection of cobalt in the presence of 300 to 400 times its weight of nickel, and for the rapid and accurate colorimetric determination of 0.5 mg. (or 0.25 mg.) of cobalt in the presence of as much as 10 times its weight of nickel. Since nickel and cobalt are readily separated from other metallic ions, the method should prove useful, although, as will be detailed later, certain other cations give a reaction similar to that of cobalt.

The colorimetric reaction employed is the reduction by cobalt of arsenophosphotungstic acid in presence of cyanide whereby intensely blue tungstous acid is formed and the cobalt is oxidized to cobalticyanide. Under identical conditions nickel fails to reduce the complex tungstic acid reagent.

Solutions Required

1. **Reagent.**—The arsenophosphotungstic acid[1] is prepared by placing 100 g. of pure sodium tungstate in a liter pyrex flask and dissolving in about 600 cc. of water; 50 g. of pure arsenic acid (As_2O_5) is now added, followed by 25 cc. of 85% phosphoric acid and 20 cc. of concentrated hydrochloric acid, as condensing agent. The mixture is boiled for twenty minutes, cooled and diluted to one liter. The reagent appears to keep indefinitely.

2. **Sodium Cyanide.**—A 5% solution of sodium cyanide, to which 2 cc. of concentrated ammonia have been added per liter. This solution should be prepared fresh about every two months.

3. **The standard cobalt solution,** containing 0.5 mg. of cobalt in 10 cc. of solution, is prepared by dissolving in a liter of distilled water 1.25 g. of pure $CoCl_2 \cdot H_2O$, or 2.02 g. of $CoCl_2 \cdot 6H_2O$ or 2.47 g. of $Co(NO_3)_2 \cdot 6H_2O$. To obtain the standard, the solutions are diluted 1:10 before using.

For the qualitative detection of cobalt the following procedure is best. To 5 cc. of unknown solution in a test-tube add 2 cc. of the arsenophosphotungstic acid reagent, followed by 2 cc. of the 5% sodium cyanide; 0.01 mg. of cobalt gives immediately a recognizable blue color. Nickel, unless present in such concentration as to obscure a faint blue color by its dark green shade, does not interfere with this color test. Thus 0.01 mg. of cobalt can be detected in the presence of 2 or 3 mg. of nickel. Stannous tin, manganese, ferrous iron, mercurous mercury, copper and sulfide are interfering ions and must not be present. The fact that nickel does not react with the reagent permits the testing of nickel salts by this method for the presence of cobalt and iron as impurities. This qualitative test is made as follows. Add to 5 cc. of approximately 1% nickel salt, 3 cc. of reagent and enough 5% sodium cyanide just to redissolve the nickel cyanide that is first formed on the addition of the cyanide. An immediate blue or greenish-blue solution is formed if iron or cobalt is present.

The method for the estimation of cobalt in the presence of nickel is as follows.

[1] S. R. Benedict, *J. Biol. Chem.* **51**, 187 (1922).

To 10 cc. of approximately neutral cobalt solution containing about 0.5 mg. of cobalt, and also to 10 cc. of standard cobalt solution containing exactly 0.5 mg. of cobalt,[2] add 3 cc. of arsenophosphotungstic acid reagent. Invert once. Add 4 cc. of the cyanide solution from a buret. Invert both tubes once simultaneously. Compare the standard and unknown blue solutions in a colorimeter. For best results the colorimetric reading should be made from two to ten minutes after inversion of the tubes. The ratio of the reading of the standard to the reading of the unknown, multiplied by 0.5 gives the mg. of cobalt in 10 cc. of unknown solution. The colors obtained match exactly. No turbidity develops even after twenty-four hours of standing. Nickel does not interfere with this test except that if the 10 cc. of solution contains more than 5 mg. of nickel, nickel cyanide tends to be precipitated when the cyanide is added. If more cyanide is used (*i. e.*, 6–8 cc.), more nickel can be kept in solution, but the tendency to turbidity is increased. In the presence of up to 5 mg. of nickel, the readings are accurate to within about 1% (0.005 mg. of cobalt). The ions mentioned above which interfere with the qualitative reaction must be absent. There is another group of metallic ions which, although not giving the test directly, may interfere if present in appreciable amounts (*i. e.*, more than 4 or 5 times the concentration of cobalt) by yielding a turbid solution. This group includes NH_4, Mg, Ca, Sr, Ba, Sn, Sb, As, Cd, Bi, Pb, Ag. Finally, it should be noted that colored solutions of manganese and chromium obviously interfere with the proper color readings between standard and unknown.

The essential accuracy of this method was demonstrated by the determination of the cobalt present in pure cobalt solutions and in potassium cobaltinitrite precipitates (after converting the cobaltinitrite to a cobaltous salt by heating with *N* hydrochloric acid. The results obtained in a long series of determinations in the latter case showed a maximum deviation from the theoretical of 1.5%, with an average deviation of about 0.5%.

In conclusion the writer wishes to express his indebtedness to Professor S. R. Benedict, whose help has been essential to the completion of this work.

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SOME NEW EXPERIMENTS ON THE CHEMICAL EFFECTS OF X-RAYS AND THE ENERGY RELATIONS INVOLVED

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Although the photochemical action of x-radiation is of interest because of its possible significance in interpreting the physiological effects, very few studies in this field have been made until recently. Within the last two years, however, the oxidation of ferrous to ferric sulfate has been studied by Fricke and Morse,[1] oxyhemoglobin to methemoglobin by Fricke and Petersen,[2] the inversion of sugar by Reinhardt and Tucker,[3] and the

[2] If less than 0.5 mg. of cobalt is available, the volume of solution and of reagents used can be reduced correspondingly.

[1] Fricke and Morse, *Am. J. Roentgenology & Radium Therapy*, **18**, 426–430 (1927).

[2] Fricke and Petersen, *ibid.*, **17**, 611–620 (1927).

[3] Reinhardt and Tucker, *Radiology*, **12**, 151–153 (1928).