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THE COLORIMETRIC DETERMINATION OF MINUTE AMOUNTS OF CADMIUM

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Cadmium is becoming increasingly an industrial hazard both in the primary smelting of ore and in such secondary uses as cadmium plating. The need for an accurate method for the determination of minute amounts of the metal is apparent both in the analysis of ores and in toxicological investigation of the substance. Although many methods for the microscopical detection of cadmium have been developed, none of these is particularly applicable to quantitative use. The blue color which is developed when resorcinol is added to solutions of cadmium salts[1] is far less intense than that developed by zinc, is subject to vagaries and is seriously affected by other metals which yield the same color. Breyer[2] determined small amounts of cadmium in the dry way by volatilizing cadmium and measuring the depth of yellow color of the sulfide deposited on a glass tube. The most promising method is that of Hessel,[3] who employed the yellow color of the sulfide in solutions as a means of determining cadmium quantitatively in amounts of 2 to 10 milligrams in organic material. These various methods and several of the microscopic methods were investigated in an attempt to develop a method for cadmium analysis, accurate for small quantities and particularly in organic material.

Experimental

In the initial experiments it was found that extremely dilute solutions of cadmium salts, which under ordinary light develop only a faintly yellow coloration with hydrogen sulfide water, give a pronounced bright yellow appearance under a quartz mercury vapor lamp. In concentrations of less than 0.1 mg./50 cc. of cadmium, differences in the yellow color of the sulfide become indistinguishable in ordinary light, while under the mercury arc the yellow color is perceptible in concentrations as low as 0.01 mg./50 cc., so that differentiation may be made with experience between solutions of this volume varying but 0.01 mg. of cadmium in amount. If we assume a lower limit of twice this value, however, that is, of 0.02 mg./50 cc., this represents a delicacy of 1:2,500,000, whereas Hessel found with his method a delicacy of but 1:70,000.

Since cadmium and its salts are so volatile, ashing in the ordinary way is out of the question. Nitric acid ashing with the addition of a small

[1] M. Lavoye, *J. Pharm. Belg.*, **3**, 889 (1921).

[2] F. G. Breyer, *Comm. 8th Inter. Cong. Applied Chem.*, **25**, 1–5 (1912).

[3] G. Hessel, *Biochem. Z.*, **177**, 146 (1926).

amount of sulfuric acid gives good results and in the case of animal tissues is most conveniently effected by slow oxidation in conical beakers at a low heat on an electric hot-plate. As cadmium sulfide is much more insoluble in acid than zinc sulfide, it is possible to separate the two readily when the zinc is not present in greater amount than that found in animal tissues. In order to insure complete separation of the cadmium as sulfide, copper may be added as an entraining medium. Copper was chosen because it is normally present in animal tissues and because the coloration of cadmium sulfide may be produced in the presence of copper without interference merely by the addition of potassium cyanide. The disagreeable tendency of cadmium sulfide to pass into the colloidal condition when it is washed is readily overcome by the addition of a drop of 5% aluminum chloride solution in the initial stage of separation.

Using the method outlined below, various analyses were made of organic material to which known amounts of cadmium had been added. Cadmium in amounts varying from 0.40 to 1.00 mg. was added in each case to 100 g. of muscle and the material oxidized. The cadmium was separated and read as the sulfide, comparison being made with cadmium standards prepared in an exactly similar manner. Readings were made by two observers on separate aliquot portions of the separated cadmium chloride obtained in the course of analysis. The results are shown in the following table. The error in these analyses ranged from zero to 0.09 mg. and averaged 0.04 mg.

TABLE I

RESULTS OF EXPERIMENTS

Number	Amount present, mg. of Cd	Readings P.		F.	Amount found, mg. of Cd	Error
1	0.50	0.10	0.08	0.08	0.43	0.07
2	1.00	.20	.15	.20	.91	.09
3	1.00	.20	.17	.20	.95	.05
4	1.00	.20	.17	.18	.91	.09
5	0.40	.08	.08	.08	.40	.00
6	.60	.10	.11	.11	.53	.07
7	.50	.10	.08	.10	.47	.03
8	.80	.15	.15	.15	.75	.05
9	1.00	.20	.18	.19	.95	.05
10	1.00	.20	.18	.20	.97	.03
11	0.90	.18	.13	.18	.81	.09
12	.80	.16	.14	.17	.79	.01
13	.50	.09	.08	.10	.45	.05
14	1.00	.20	.15	.20	.92	.08
15	1.00	.20	.15	.20	.92	.08
16	0.50	.10	.09	.10	.49	.01
17	1.00	.20	.20	.20	1.00	.00
18	1.00	.20	.20	.20	1.00	.00
19	1.00	.20	.20	.20	1.00	.00
20	1.00	.20	.20	.20	1.00	.00
					Average	0.04

Method of Analysis

Add sufficient concentrated nitric acid to the organic material to cover it and heat it very gently at first. After the solid material has dissolved, add 10 cc. of concentrated sulfuric acid and occasionally add small amounts of nitric acid until oxidation is complete and then heat until fumes of sulfur trioxide are freely given off. Dilute to 75 cc. and add the equivalent of 0.5 mg. of copper and 2 g. of sodium citrate. Neutralize the acid solution for the first precipitation with ammonia (rather than potassium hydroxide, as this avoids precipitation of potassium sulfate from the cooling solution) and adjust the concentration of hydrogen ion to approximately 10^{-3} by means of the indicators thymol blue and brom chlor phenol blue. Pass hydrogen sulfide into the resulting solution for five to ten minutes, add one drop of 5% aluminum chloride solution and allow the solution to stand for six to twelve hours. Filter, dissolve the precipitate in nitric acid and hydrochloric acid and carefully evaporate to dryness. Repeat the precipitation as sulfide twice more, omitting the addition of sodium citrate the last time and adjusting the hydrogen-ion concentration to 10^{-2} by means of dilute potassium hydroxide. Carefully evaporate the final solution of chloride to dryness, dissolve it in water and make up to a convenient exact volume in a volumetric flask. An aliquot portion of this solution is used in a Nessler tube for the final reading. To each tube add five drops of 10% potassium cyanide, distilled water and finally 5 cc. of hydrogen sulfide water. Mix thoroughly and compare under a flood of ultraviolet light with standards similarly prepared. The solution should exhibit a bright, clear yellow color under the mercury arc. Dark or turbid solutions usually indicate incomplete removal of iron. Traces of lead although not usually present in animal tissues are usually found in the reagents and must be removed.[4] The reagents are usually free from cadmium. The comparison tubes and the standard tubes should be prepared at the same time, as there is a notable deepening in tone when they are allowed to stand overnight. In doubtful cases, however, it is sometimes advantageous to allow the tubes to stand for a few hours before reading.

Conclusion

A colorimetric method for the determination of minute amounts of cadmium is described in which advantage is taken of the intensification of color of the sulfide under ultraviolet rays. A sensitivity of 1:2,500,000 is thus obtained and an accuracy attained of 4% in the analysis of material containing from 0.40 to 1.00 mg. of cadmium in 100 g. of organic material.

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[4] L. T. Fairhall, *J. Biol. Chem.*, **57**, 461 (1923).