Bis-arylmercury Compounds.—The iodomercuri derivatives were precipitated from alcoholic solutions of the acetates and, without purification, were digested for several hours in alcohol with four moles of sodium iodide.[10] The substances were crystallized from chloroform. Diduryl mercury was prepared also by reduction of the acetate with sodium stannite.[7,11] The method was unsatisfactory because separation of the product from finely divided mercury was difficult.

Analyses.—Furter[12] demonstrated that mercury causes low analytical values for carbon. However, satisfactory carbon and hydrogen analyses of most of the mercury compounds were obtained by the semi-micro method with a Pregl universal filling in the combustion tube when precautions were taken. The substances were covered with cupric oxide and burned in an oxygen stream which had half the usual velocity. Silver foil was used in the tip of the combustion tube to collect free mercury. Silver was not very satisfactory for the purpose, but gold was not available.

Mercury analyses, in the absence of halogens, were made by titration with potassium thiocyanate after the organic material had been destroyed by hot concentrated nitric acid and permanganate.[13]

Summary

1. The mercuration of six polymethylbenzenes (mesitylene, pseudocumene, durene, isodurene, prehnitene and pentamethylbenzene) has been studied.

2. A number of related mercury derivatives have been prepared from each of the primary products of mercuration.

3. Twenty new organomercury compounds have been described.

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(10) Steinkopf and Baumeister, *Ann.*, **403**, 50 (1914); Whitmore, *et al.*, *loc. cit.*; Johns and Hixon, *J. Phys. Chem.*, **34**, 2218 (1930); THIS JOURNAL, **52**, 2820 (1930); **56**, 1333 (1934).

(11) Dimroth, *Ber.*, **35**, 2032, 2853 (1902); *ibid.*, **54**, 1504 (1921).

(12) Furter, *Mikrochem.*, **9**, 27 (1931); see also Hernler, *ibid.*, Pregl Festschrift, 154 (1929); Verdino, *ibid.*, **6**, 5 (1928); Grignard and Abelmann, *Bull. soc. chim.*, [4] **19**, 25 (1916).

(13) Tabern and Shelberg, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 401 (1932).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Organic Flocculating Agents in the Quantitative Precipitation of Zinc Sulfide[1]

BY JOHN R. CALDWELL AND HARVEY V. MOYER

Comprehensive reviews of proposed methods for the precipitation of zinc sulfide are to be found in the comparatively recent publications of Jeffreys and Swift,[2] J. N. Frers,[3] and Mayr.[4]

Practically all of the efforts made to obtain the precipitate in a suitable physical form are based on three general procedures: (a) precipitation from hot solution; (b) salting-out with a large excess of some neutral salt; (c) maintenance of a low *p*H value by means of buffers. It is a well-recognized fact that in the early stages of precipitation most sulfides exist as hydrosols, and the formation of an insoluble precipitate depends to a large extent on the rate of transformation from sol to flocculent state. This transformation may be promoted by the presence of finely divided solid matter as demonstrated by Kolthoff[5] and by Frers.[3]

Recently we have found that certain organic substances may be used to alter the nature of analytical precipitates.[6,7] It seemed quite probable that flocculation of colloidal zinc sulfide could be induced by a somewhat similar procedure. The coagulation of precipitates by means of small concentrations of organic substances has been reported frequently by colloid chemists. Contrary to the ordinary behavior, certain hydrophilic colloids such as agar-agar, gelatin, gum arabic, etc., will not stabilize suspensoid sols if present in minute traces, but will bring about complete and rapid flocculation. This phenomenon, called sensitization, has been known for many years, but apparently never before has been applied to analytical chemistry. A brief review of recent colloid literature furnished ample indication that this field offers attractive possibilities for further investigation.

Rossi and Scandallari[8] showed that minute quantities of gelatin brought about rapid coagulation of sulfur sols. Chaudhury[9] reported that sols of ferric hydroxide and arsenic trisulfide were sensitized and flocculated by methyl alcohol,

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(1) Presented before the Division of Physical and Inorganic Chemistry at the 89th meeting of the American Chemical Society, New York City, April 22 to 26, 1935.

(2) Jeffreys and Swift, THIS JOURNAL, **54**, 3219 (1932).

(3) J. N. Frers, *Z. anal. Chem.*, **95**, 1–36 (1933).

(4) Mayr, *ibid.*, **96**, 273 (1934).

(5) Kolthoff, *J. Phys. Chem.*, **36**, 549 (1932).

(6) Caldwell and Moyer, *Ind. Eng. Chem.*, *Anal. Ed.*, **7**, 38 (1935).

(7) Caldwell, THIS JOURNAL, **57**, 96 (1935).

(8) Rossi and Scandallari, *Ann. chim. appl.*, **23**, 67 (1933).

(9) Chaudhury, *J. Phys. Chem.*, **32**, 1481 (1927).

ethyl alcohol, pyridine, urea and glycerol. Gelatin was used to flocculate sols of antimony trisulfide[10] while gum arabic had a similar effect on arsenic trisulfide and manganese dioxide sols.[11] Ghosh and Dhar[12] demonstrated that gelatin and tannin rapidly flocculated sols of ferric hydroxide and arsenic trisulfide. Weiser showed that certain organic compounds not only brought about rapid flocculation of arsenic trisulfide and ferric hydroxide sols, but also reduced the amount of adsorbed ions carried down by the precipitate.[13]

A review of the literature revealed that at least two attempts have been made to flocculate zinc sulfide precipitates by a mechanism similar to those just described. K. Bornemann[14] passed hydrogen sulfide into a zinc solution containing soldium bisulfite and buffered with ammonium acetate. He claimed that the colloidal sulfur formed in the reaction helped to coagulate the zinc sulfide. More recently, Hibbard,[15] in a procedure for the microdetermination of zinc as the sulfide, added talc to the solution in order to promote flocculation.

With the object of developing an improved method for precipitation of zinc sulfide, a systematic study was made of the effect of various hydrophilic colloids on the coagulation of the freshly formed precipitate.

Materials

Standard Zinc Solution.—Zinc ammonium sulfate was prepared by mixing concentrated solutions of C. P. ammonium sulfate and C. P. zinc sulfate. The zinc ammonium sulfate crystals which separated from solution were recrystallized twice. A solution was prepared containing approximately 5 mg. of zinc per ml. and was standardized by precipitating the zinc in 50 ml. as sulfide from a sulfate buffered solution according to the directions of Jeffreys and Swift[2] and also from chloroacetic acid–sodium acetate buffered solutions according to the procedure of Mayr.[4] In all cases the zinc sulfide was ignited to the oxide in an electric muffle at a temperature of 1000° as recommended by Hillebrand and Lundell.[16] The temperature of ignition was measured with a thermocouple. Of eight determinations, the extreme values were 0.3163 and 0.3155 g. of zinc oxide, the average being 0.3160 g.

Sulfates of Other Metals.—Reagent grade sulfates of nickel, cobalt and manganese were dissolved and filtered before use. Chromium, aluminum and iron were used in the form of their potassium alums.

Organic Materials, Gums, Soaps, etc.—No attempt was made to determine the purity of these materials and they were used without further treatment. Low-ash gelatin (0.03%) was purchased from the Eastman Kodak Co.

Experimental Work

Three hundred milliliters of a solution containing 0.25 g. of zinc as the sulfate and 6–8 g. of ammonium sulfate was used as the starting point for the tests. Two general plans were followed: (a) the substance to be tested was added to this solution and hydrogen sulfide passed in for fifteen to twenty minutes; (b) hydrogen sulfide was passed in for fifteen to twenty minutes and the test material was added slowly with stirring in the form of a dilute aqueous or alcoholic solution. Both methods were carried out at room temperature. Among the agents used were gelatin, agar-agar, gum ghatti, gum tragacanth, gum arabic, casein, egg albumin, sucrose, saponin, various soaps, and mixtures of these.

It was found that gelatin (0.5 to 2.0 mg.) and agar-agar (2 to 5 mg.) produced the desired effect. When added to the solution either before or after precipitation with hydrogen sulfide, these two agents caused instantaneous and complete flocculation of the zinc sulfide. Gelatin was chosen as the more suitable flocculating agent, because it can readily be obtained practically ash-free.

Further experimental work was carried out at higher dilutions and it was found that 0.05 mg. of gelatin would give a pronounced flocculation in volumes up to 500 ml. This is a dilution of one to ten million and the sensitivity is comparable to that of precipitin reactions with immune sera used in bacteriological work. If several milligrams of egg albumin was added to the solution before precipitation, the sensitivity of the gelatin was increased until it gave flocculation in dilutions of one:one hundred million.

Procedure for Quantitative Precipitation of Zinc Sulfide.—The procedure finally adopted for quantitative precipitation of zinc is based essentially on conventional methods. A solution free of chlorides, containing approximately 0.25 g. of zinc and 6 to 8 g. of ammonium sulfate is diluted to 250 to 300 ml. and made just acid to methyl orange. A rapid stream of hydrogen sulfide is passed through the solution for thirty minutes at room temperature. Five to 10 ml. of a 0.02% solution of gelatin is added with rapid stirring and the precipitate is allowed to settle. The most satisfactory gelatin for the purpose is a low-ash product containing less than 0.1% ash. A few drops of oil of wintergreen will preserve a dilute solution for several months. An instantaneous and complete flocculation of the colloidal precipitate takes place upon the addition of the gelatin, and if 10 to 20 mg. of gelatin is added, the flakes of precipitate are so large that they cling together and tend to slow up filtration. After fifteen minutes' standing, the supernatant liquid is practically clear, and may be decanted from the precipitate. The precipitate is easily washed by decantation and distilled water may be used as there is no peptizing action. In about 100 precipitations, a clear filtrate was always obtained when Schleicher and Schull blue-band filter paper was used.

The gelatin is adsorbed completely on the precipitate as shown by negative protein color tests on the filtrate.

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[10] Meneghetti, *Bull. soc. ital. biol. sper.*, **3**, 779 (1928).

[11] A. S. Mennon, *Kolloid-Z.*, **38**, 242 (1926).

[12] Ghosh and Dhar, *ibid.*, **41**, 229 (1927).

[13] Weiser, *J. Phys. Chem.*, **28**, 1253 (1924).

[14] K. Bornemann, *Z. anorg. Chem.*, **82**, 216 (1913).

[15] P. L. Hibbard, *Ind. Eng. Chem., Anal. Ed.*, **6**, 423 (1934).

[16] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929.

It was found that this quantity of gelatin (1 to 2 mg.) does not interfere with the ferrocyanide volumetric determination of zinc.

If iron is present, it is better to wash with hydrogen sulfide water to keep the iron in a reduced state.

Quantitative Experiments.—Fifty milliliters of standard zinc solution, equivalent to 0.3160 g. of zinc oxide, precipitated according to the procedure outlined above, gave this weight of zinc oxide after ignition at 1000° with deviations of +0.6, −0.3, −0.4, +0.1, +0.3 mg.

Separation of Zinc from Iron, Nickel, Cobalt, Manganese, Aluminum, Chromium.—Table I summarizes the results obtained when zinc sulfide was precipitated in the presence of other metals. In each case, the precipitate was ignited to the oxide and analyzed for the contaminating metal. The iron was reduced with sulfur dioxide and the sulfur dioxide removed with carbon dioxide before saturation with hydrogen sulfide. This step was necessary, as the *p*H of the solution allows the formation of a small amount of ferric hydroxide before reduction of iron by hydrogen sulfide is complete. Iron in the ignited precipitate was determined colorimetrically as ferric thiocyanate. Manganese was determined colorimetrically as permanganate after oxidation with potassium periodate. Nickel was determined with dimethylglyoxime. Cobalt was determined colorimetrically by dissolving the precipitate in concentrated hydrochloric acid and comparing with standards prepared in the same way. For aluminum and chromium, the precipitate was dissolved in hydrochloric acid and the solution made just basic to methyl red with ammonia. No precipitate appeared with aluminum, and a trace of precipitate was formed with chromium.

TABLE I

PRECIPITATION IN PRESENCE OF OTHER METALS

Volume 250 to 300 ml. containing 6 to 8 g. of $(NH_4)_2SO_4$. Zinc equivalent to 0.3160 g. of ZnO, and 0.25 g. of other metal present.

Other metal	Other metal in ZnO ppt., mg.	Ignited ppt., g.	Dev. from std., g.
Ni	Less than 0.1	0.3157	−0.0003
	Less than .1	.3157	− .0003
Mn	0.1	.3164	+ .0004
	.1	.3158	− .0002
Al	Less than 0.1	.3163	+ .0003
	Less than .1	.3160	± .0000
Co	5.8	.3236	+ .0076
	7.0	.3258	+ .0098
Cr	0.1	.3162	+ .0002
	.1	.3159	− .0001
Fe	.3	.3166	+ .0006
	.2	.3164	+ .0004

If zinc sulfide is precipitated in the presence of small concentrations of certain aldehydes, practically no cobalt is carried down. A new separation of zinc and cobalt based on this principle will be described in a later paper.

As a final test of the method, zinc ore No. 2a from the Bureau of Standards was analyzed according to the procedure outlined by Lord and Demorest.[17] The only departures from the original procedure were a reprecipitation of cadmium sulfide, and the use of 2 mg. of gelatin as a flocculating agent. The average of four determinations was 30.45% of zinc, while the value given by the Bureau was 30.53%.

Precipitation in Solution Buffered with Chloroacetic Acid–Sodium Acetate.—When it is necessary to precipitate zinc in the presence of alkaline earth metals, it is not permissible to use a sulfate buffer. Mayr[4] has proposed a chloroacetic acid–sodium acetate buffer for this purpose. It is also possible to make a separation from iron without preliminary reduction, as the *p*H is sufficiently low (2.8) to hold ferric iron in solution. Excellent results were obtained when this method was used together with flocculation by gelatin. Mayr recommends a wash solution consisting of the diluted buffer saturated with hydrogen sulfide, but when the precipitate has been flocculated by 1–2 mg. of gelatin, distilled water may be used and no peptization occurs. Satisfactory separations from all metals but cobalt were obtained.

Other Applications.—Further applications of this principle are now being investigated, and preliminary experiments on the precipitation of other sulfides, ammonium phosphomolybdate, certain fluorides, and the hydrous oxides indicate a promising field for future research.

Summary

A new method for flocculating certain colloidal precipitates is proposed. It has been found that gelatin (0.5 to 2 mg.) and agar-agar (2 to 5 mg.) will produce instantaneous and complete flocculation of 0.3 g. zinc sulfide in 300 ml. of solution. Precipitations are made at room temperature, and the solution may be filtered within fifteen minutes after precipitation. Satisfactory separations from all metals but cobalt are obtained, and the precipitate may be washed with cold distilled water.

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[17] Lord and Demorest, "Metallurgical Analysis," McGraw-Hill Book Company, Inc., New York, 1924.