APPARATUS FOR MANUFACTURE OF ARSENIC TRICHLORIDE

trace of arsenic trioxide. If opened when too hot, the sulfur residue is liable to take fire.

The charge of arsenic trioxide was divided into two parts in order to use agitation during as much of the process as possible. The first charge required about $1\frac{1}{2}$ hrs. to complete and the second charge about 3 hrs. The total time of operation was between $7\frac{1}{2}$ and 8 hrs.

Based on the amount of sulfur chloride used the yield was 93 per cent of product averaging 99 per cent pure.

The first distillate which was always colored was decolorized by redistilling with a small amount of arsenic trioxide.

This investigation was started under the Bureau of Mines at the American University Experiment Station and was continued under the Research Division of the Chemical Warfare Service.

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ORIGINAL PAPERS

THE DETERMINATION OF CADMIUM BY THE HYDROGEN SULFIDE METHOD

By EDWARD SCHRAMM

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I—INTRODUCTION

In the course of some coöperative work on the determination of small quantities of cadmium in brass it was found that varying results were obtained by several laboratories. A diversity of methods is in current use, most of which do not appear to have been tried out on materials of known composition.¹ The present work was accordingly undertaken with a view to developing a convenient and reliable procedure for this determination, and to ascertaining what degree of

¹ Two methods have been described in considerable detail in the second edition of Price and Meade, "Technical Analysis of Brass," pp. 229-233.

accuracy is to be expected. To accomplish these aims, analyses were made of brasses with cadmium additions and of salt mixtures of known composition. The hydrogen sulfide precipitation was chiefly employed for the necessary separations, and accordingly the work became primarily a study of the most suitable conditions for separating a small amount of cadmium from other metals by this method.

Structural brasses may contain, besides the principal constituents, copper and zinc, one per cent or more of tin, and varying quantities of lead, iron, manganese, arsenic, and other metals, which may have been added intentionally or introduced accidentally as impurities in the copper or zinc. Very little has been published on the determination of cadmium in brass, but its determination in spelter has been the subject of a

considerable amount of work, part of which will be briefly reviewed.

II—REVIEW OF LITERATURE

H. J. S. Sand¹ studied the electro-analytical separation of the metals by the graded potential method. The separation of cadmium from zinc was performed in acetate solutions containing free acetic acid.

J. J. Fox² separated cadmium from zinc as sulfide in the presence of trichloroacetic acid. This method is said to obviate the difficulty experienced in determining the proper concentration of mineral acid necessary for the complete precipitation of cadmium sulfide, uncontaminated with zinc sulfide, and to abolish the many solutions and reprecipitations necessary to purify the cadmium sulfide.

W. D. Treadwell and H. S. Guiterman³ found that the hydrogen sulfide separation gave better results in sulfuric than in hydrochloric acid solutions, less zinc being carried down. They recommended that the solution should be 4–5 *N* in sulfuric acid, and that hydrogen sulfide should be passed into the hot solution until it is cold. Treadwell and Guiterman also carried out the separation electrolytically, using oxalate or sulfate solutions; with the latter they found that 0.04 to 0.2 g. of cadmium could be separated from fifty times the amount of zinc.

E. J. Ericson⁴ separated cadmium from zinc by successive hydrogen sulfide precipitations in sulfuric and trichloroacetic acid solutions. The same author has described a separation of zinc from cadmium depending on the crystallization of zinc sulfate.⁵

W. Cooper⁶ dissolved 5 g. of zinc in dilute sulfuric acid and passed hydrogen sulfide into the cold solution. The precipitate was filtered off and dissolved in hydrochloric acid and bromine water, sulfuric acid was added, and the solution evaporated to the appearance of fumes. After filtering out any lead sulfate the process was repeated twice, and the cadmium was finally weighed as sulfide after drying at 100°.

A procedure commonly used in this country is the standard method of the American Society for Testing Materials.⁷ This consists briefly in dissolving 25 g. of drillings in dilute hydrochloric acid until nearly all the zinc has been dissolved. The residue, presumed to contain all the cadmium, is dissolved in nitric acid and evaporated with sulfuric acid to the appearance of fumes to remove the lead. The filtrate is diluted to 400 cc., 10 g. of ammonium chloride added, and hydrogen sulfide is passed in. It is occasionally necessary to start the precipitation of the cadmium sulfide by the addition of a drop or two of ammonia. The impure cadmium sulfide is filtered out by means of a Gooch crucible and is dissolved by boiling for 1½ hr. with 1 : 5 sulfuric acid. The solution is filtered, diluted to 300 cc., and the cadmium sulfide reprecipitated. This may be repeated a third time. The cad-

mium sulfide is dissolved in hot dilute hydrochloric acid (1 : 3), and finally converted to sulfate and weighed as such.

III—GENERAL CONSIDERATIONS

Obviously none of the methods above outlined can be adopted as such for the determination of cadmium in brass because of the tin and the large amount of copper present. After the removal of these elements, any of the methods and especially the last, with certain modifications, may be taken as a guide to the further separation. The precipitation of the copper and cadmium together as sulfides followed by extraction with boiling dilute sulfuric acid has been employed by some analysts, but seemed a clumsy operation because of the great quantity of copper present. The best procedure therefore appeared to be the electrolytic separation of the copper from nitric acid solution, preceded by removal of the tin as metastannic acid. It is better to remove tin than lead at the start since the former is much more likely to contaminate the cadmium in subsequent operations. After the removal of the copper, the standard method of the American Society for Testing Materials was applied with certain changes in detail, and with the additional precaution of treating the cadmium sulfide with ammonium polysulfide before the final conversion to sulfate.

A brief consideration of the vital steps in the process outlined will assist in determining whether it will accomplish the desired separations, and in fixing suitable details.

We should not expect any deposition of cadmium during the electrolytic separation of the copper. With the very small concentrations of cadmium in question, a high potential would be required for its deposition under the most favorable conditions. It is well known that the concentration of nitric acid here employed (about 3 per cent) will prevent the separation of cadmium even from strong solutions. As an added precaution, the electrolysis should never be carried on long enough to cause much reduction of nitric acid, and should be stopped before all the copper is deposited.

The second vital step in the method is the precipitation of cadmium with hydrogen sulfide and its separation from zinc. In a solution of hydrogen sulfide¹ we have the following relation between the ions:

$$[H^+]^2 \times [S^{2-}] = K_2 = 1.1 \times 10^{-23}$$

The concentration of the sulfide ion is inversely proportional to the square of the concentration of the hydrogen ion. Now for the precipitation of cadmium sulfide to occur we must have

$$[Cd^{++}] \times [S^{2-}] > K_{CdS},$$

where K_{CdS} represents the solubility product constant of cadmium sulfide. Obviously, the larger the value of S^{2-} (hence the smaller the value of H^+), the smaller will be the concentration of Cd^{++} remaining in solution in equilibrium with the precipitated sulfide. If, however, the value of S^{2-} is made too large, the solubility product of zinc sulfide will be exceeded and we

¹ *J. Chem. Soc.*, **91-2**, 373-410; **93-4**, 1572-92.

² *Ibid.*, **91** (1907), 964-7.

³ *Z. anal. Chem.*, **52**, 459-70.

⁴ *Eng. Min. J.*, **87**, 1036.

⁵ *THIS JOURNAL*, **9** (1917), 670.

⁶ *Chem. News*, **110** (1914), 250-1.

⁷ *THIS JOURNAL*, **7** (1915), 547.

¹ Stieglitz, "Qualitative Analysis," **1**, 199, *et seq.*

shall fail to effect a separation. We therefore seek to regulate the acidity so as to permit cadmium but not zinc to come down. In the standard method for spelter (starting with a 25 g. sample) this is done by dilution to 300 or 400 cc. Now in diluting in this way, while we increase S^- we at the same time decrease Cd^{++} . It would therefore appear better to keep the solution as concentrated as possible in cadmium and regulate the acidity by other means than dilution. Moreover, since for a given hydrogen-ion concentration the concentration of cadmium in solution is fixed, the more dilute the solution the more cadmium will escape precipitation. To put the same proposition in another way—if we start with a 10 g. sample and precipitate in a volume of 100 cc., the percentage loss will be no greater than starting with 40 g. and precipitating in a volume of 400 cc.; provided the acidity is the same in both cases. By using a smaller sample, therefore, we should lose nothing in the ability to separate cadmium, avoid the trouble of removing the large amount of copper, and greatly simplify manipulations. With a 10 g. sample 0.01 per cent cadmium will give 0.0019 g. of cadmium sulfate which can be weighed with sufficient accuracy.

The third important question concerns the freedom from contamination of the cadmium sulfide, and the means taken to purify it. The repeated precipitations in regulated acid solution insure complete separation from zinc, iron, and manganese, while the boiling with dilute sulfuric acid accomplishes separation from small amounts of copper and lead not removed during electrolysis. Finally, the treatment with ammonium polysulfide removes any sulfides of tin, arsenic, or antimony which would not have much effect on the color of the precipitate. (This precaution appears in most cases unnecessary, since these elements can be separated in previous operations. If, however, a great amount of tin were originally present it is safer to adopt it.) It is considered by some that the alkaline sulfide treatment results in loss of cadmium, but Noyes¹ has shown in his "System of Qualitative Analysis" that it is possible to treat 300 mg. of cadmium sulfide with ammonium polysulfide and not find any cadmium in the filtrate. However, it must be recognized that cadmium sulfide has a tendency to go through the filter in the colloidal condition, but this can be avoided by adding ammonium chloride, as recommended by Noyes, and in carrying out the final precipitation in small volume. Under these conditions the cadmium sulfide does not go into the colloidal condition and can safely be treated with ammonium polysulfide.

IV—EXPERIMENTAL RESULTS

The first method used, based on the principles discussed above, was as follows:

Dissolve 10 g. of brass in 75 cc. of nitric acid (1:1) and boil for 30 min. Filter off the metastannic acid, dilute to 350 cc., add 10 cc. of sulfuric acid (1:1), and electrolyze till nearly all the copper is removed and the lead deposited on the anode as peroxide. The solution is then treated as in the standard method for spelter, except that precipitations are made in smaller volume, and that a final treatment with ammonium polysulfide is employed.

¹ *Technology Quarterly*, 19, 274.

To test the method, analyses were made of several brasses with and without additions of cadmium. The results are given in Table I.

SAMPLE No.	Cadmium Added Per cent	Cadmium Found Per cent	Added Cadmium Recovered Per cent
1.....	0.0	0.007	
	0.016	0.025	0.018
2.....	0.0	0.034	
	0.020	0.049	0.015

Determinations of cadmium on 10 samples of manganese bronze were carried out, the results ranging from 0 to 0.034 per cent. On several of these, duplicates were run and good checks obtained.

Some time after the experiments just described had been completed, the matter of cadmium determinations again came up, and the work was resumed in an effort, if possible, to simplify the manipulations. My attention was called to the complication caused by the presence of arsenic. In working on a sample containing 0.15 per cent arsenic and low in cadmium the original method was modified in several respects. In the first precipitation with hydrogen sulfide, ammonia was added till zinc began to come down. Only one treatment with 1:5 sulfuric acid was employed. The second precipitate of sulfides (containing much of the arsenic) was extracted with cold dilute hydrochloric acid (1:1), the arsenic sulfides remaining unattacked. After a third precipitation with hydrogen sulfide, the solution was evaporated to dryness with sulfuric acid and the first weighing of cadmium sulfate made directly. As a check in some cases the cadmium was again taken into solution, reprecipitated as sulfide, and the latter purified as before.

To test this modified procedure a mixture of salts was made up containing 6 g. of copper, 3.5 g. of zinc, and 0.1 g. each of tin, manganese, iron, lead, and arsenic. This mixture was run as a blank and with graded additions of cadmium. The results of these experiments are given in Table II and some analyses of brasses in Table III.

TABLE II—ANALYSES OF SALT MIXTURES CONTAINING Cu, Zn, Pb, Fe, Mn, As, AND Sn

Cadmium Added Per cent	Cadmium Found Per cent	Difference Per cent	
		Actual	Mean
0.00	...	...	0.000
0.01	0.008	—0.002	
0.01	0.013	+0.003	0.000
0.02	0.015	—0.005	
0.02	0.019	—0.001	—0.003
0.03	0.024	—0.006	
0.03	0.030	0.000	—0.003
0.04	0.035	—0.005	—0.005

TABLE III—ANALYSES OF BRASSES

MATERIAL	Cadmium Found Per cent
Arsenical Brass.....	0.013
	0.013
	0.014
Brass A.....	0.054
	0.057
Brass B.....	0.020
	0.019
Brass C.....	0.027
	0.022
Brass D.....	0.021
	0.022

The results in Table II on salt mixtures show that the values obtained are within 0.005 per cent of the true cadmium content and that they tend to be slightly

low rather than too high. This is what one would naturally expect, since there are a number of precipitations and filtrations, with opportunity in each operation for a slight loss of cadmium, by solution as well as by mechanical loss. Brasses can be run with at least the same degree of accuracy, since the salt mixtures used contained a greater proportion of possible interfering substances that is likely to be met with in an ordinary brass. Table III shows that excellent agreement can be obtained. As a final check, and to guard against the possibility of the results obtained being due to a balancing of errors, the cadmium sulfate residues from the salt mixtures, as well as from the brasses, were carefully examined. They were pure white and completely soluble in water. The combined solutions failed to give any test for interfering substances which could conceivably have been present.

The procedure for determination of cadmium in brass as finally adopted is as follows:

Dissolve 10 g. in 75 cc. of nitric acid (1:1). Boil the solution $\frac{1}{2}$ hr. and filter off metastannic acid. Dilute to 350 cc. which should bring the concentration of nitric acid to about 3 per cent. Add 10 cc. of sulfuric acid (1:1) and electrolyze with a current of 4 amp., using rotating anode, until the copper is nearly all removed, which should take about $2\frac{1}{2}$ hrs. Siphon off the electrolyte, add another 10 cc. of sulfuric acid, and evaporate over night nearly to dryness. Dissolve in 100 cc. of water, neutralize with ammonia, add 5 cc. of 1:1 sulfuric acid, pass hydrogen sulfide into the cold solution 30 min. until the sulfides settle. Add ammonia until zinc begins to come down and pass in hydrogen sulfide 30 min. more. Filter, using water containing ammonium chloride and hydrogen sulfide to wash the precipitate out of the beaker. Boil the precipitate 15 min. with 20 cc. of 1:5 sulfuric acid, maintaining the volume by adding water occasionally. Filter and wash, keeping the volume down to 50 cc. Add 5 cc. of strong ammonium hydroxide, pass in hydrogen sulfide $\frac{1}{2}$ hr., adding ammonia until the cadmium begins to come down. Filter and treat the precipitate with a little cold hydrochloric acid (1:1). Neutralize the solution with ammonia and add 5 cc. of 1:5 sulfuric acid, keeping the volume down to about 30 cc. Pass in hydrogen sulfide as before and add ammonia to start the precipitation of the cadmium. Filter, dissolve the cadmium sulfide on the filter in a little 1:1 hydrochloric acid. Collect the solution in a weighed platinum or porcelain dish, add 1 cc. of sulfuric acid, evaporate to fumes, and add a little concentrated nitric acid. Evaporate carefully to dryness and finally weigh as sulfate. If there is any possibility of the presence of tin, dissolve the cadmium sulfate in 25 cc. of water and 5 cc. of 1:5 sulfuric acid and reprecipitate with hydrogen sulfide, adding a little ammonium chloride to the solution. Let the sulfide settle, decant through a filter, add a little ammonium polysulfide and ammonium chloride to the precipitate in the beaker, warm for several minutes, and pour through the filter. If there is any turbidity, refilter until the solution comes through clear. Finally dissolve the cadmium sulfide in hydrochloric acid and proceed as before with the evaporation and weighing.

In conclusion, it will be well to call attention to certain possible sources of error and important precautions to be observed. Because of the mass of salts present, the first precipitation with hydrogen sulfide must be made in a somewhat larger volume than the later precipitations, *i. e.*, under less favorable conditions. Two means are taken to counteract this. A small part of the copper is allowed to remain in solu-

tion after electrolyzing and the copper sulfide precipitated tends to act as a carrier and bring down the cadmium. In addition the acidity is reduced so as to permit the precipitation of part of the zinc, under which condition the solubility of cadmium sulfide is greatly lowered. In later precipitations the volume of solution is so small that the cadmium sulfide forms readily, and the acidity can be so regulated as to effect a separation from zinc without any great proportion of the cadmium remaining in solution. It may sometimes happen, however, if the concentration of hydrogen ion is too small, that some zinc will come down with the third precipitate of cadmium sulfide. This can usually be detected by the color of the precipitate or by the appearance of the cadmium sulfate residue, and when it occurs a fourth precipitation must be made.

Finally, it must be remembered that cadmium sulfide is insoluble in a solution containing 2 or 3 per cent sulfuric acid only when the solution is saturated with hydrogen sulfide. Such solutions, however, are unstable and if allowed to stand in an open beaker, gradually lose their hydrogen sulfide. As a result of the removal of the sulfide ion the solubility product of cadmium sulfide is no longer exceeded, the reaction is reversed, and finally all of the cadmium goes back into solution. On the other hand, if insufficient time is allowed, the cadmium sulfide remains in a colloidal condition and runs through the filter. As pointed out above, the presence of ammonium salts tends to coagulate the sulfide, which can be successfully filtered under the conditions described. If any runs through, a second filtration will suffice to retain it. In case it is desired to allow the precipitate to stand, the solution must be placed in a tightly stoppered vessel or in communication with a hydrogen sulfide reservoir so that equilibrium may be established between the solution and a definite pressure of the gas.

It is doubtless through neglect to consider one or several of the conditions dwelt on in this paper that low results for cadmium have been sometimes reported.

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THE DETERMINATION OF PHOSPHORUS IN VANADIUM STEELS, FERROVANADIUM, NON-VANADIUM STEELS, AND PIG IRON

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I—METHOD FOR STEEL CONTAINING VANADIUM UP TO 2.6 PER CENT

Ibbotson and Brearley, in 1902,¹ recommended that phosphorus be precipitated from the *reduced* solution of vanadium, using ferrous sulfate as a reducing agent, claiming thereby to aid in the precipitation of phosphorus when vanadium is present.

Cain and Tucker, in 1913,² recommended that the vanadium present be reduced with ferrous sulfate and sulfurous acid for the same purpose.

¹ "Analysis of Steel Works Materials."

² THIS JOURNAL, 5 (1913), 647.