indications point to the formation of glyco-aldehyde which, already at 60°, goes over into a hexose sugar and reduces Benedict solution in the cold. Thus, paraldehyde, far from being a protection against sugar formation, itself, quite independent of the presence of carbon dioxide yields substances which reduce alkaline copper solutions. No evidence was obtained of the reduction of carbon dioxide itself to formaldehyde.

Summary and Conclusions

Unfortunately, in none of the work which has appeared on this subject have the experimental conditions and apparatus been described with the precision and care which the importance of the subject demands. In view of the fact that it was impossible to detect any reduction of carbon dioxide to formaldehyde by means of ultraviolet light, the only possible conclusion is that in those experiments in which a direct reduction of carbon dioxide to formaldehyde by means of ultraviolet light was reported, there existed certain essential conditions or factors not described in the publications or that there is some misinterpretation of experimental observations.

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[Contribution from the Laboratory of Analytical Chemistry, Princeton University]

THE SEPARATION OF TIN AND ARSENIC

By LeRoy W. McCay

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Introduction

When a moderately dilute hydrochloric or sulfuric acid solution of tin in the higher and arsenic in the lower state of oxidation is mixed with a little hydrofluoric acid and then treated with a current of hydrogen sulfide, arsenious sulfide is completely and alone precipitated.

The above observation was referred to in my paper on the "Separation of Tin and Antimony,"[1] also in the one on the "Analysis of Tin-Antimony Alloys,"[2] and N. Howell Furman[3] has utilized it in his scheme for the qualitative analysis of the tin group. The method of procedure is analogous to that employed in separating antimony from tin.

Experimental Part

The solution of the stannic and arsenious compounds, to which from 2 to 5 cc. of 48% hydrofluoric acid has been added, is brought at once into a large platinum dish, heated gently for a few minutes, cooled, diluted to

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[1] McCay, This Journal, **31**, 374 (1909).

[2] McCay, *ibid.*, **32**, 1244 (1910).

[3] Furman, *ibid.*, **40**, 902 (1918).

about 300 cc. and treated for half an hour with a rapid current of hydrogen sulfide. The gas is introduced into the solution through a platinum or paraffined glass tube, the piece of rubber tubing carrying the tube and joined with the gas generator being slung over the arm of a ring stand so that the tube hangs directly above the center of the dish, and can be raised or lowered until the end under the solution is about 1 cm. above the bottom of the dish. In the circumstances there is no splashing, little or no sulfide adheres to the dish and the tube serves as a convenient stirrer. The arsenious sulfide is collected in a Neubauer crucible, and the filtrate caught in a ceresin beaker[4] placed under a bell jar resting on a ground-glass plate and provided with the necessary adjustments for filtering by suction. It is well to cover the beaker with a paraffined clock glass having a hole in the center through which the lower end of the crucible support, which is also paraffined, passes. The precipitate is washed thoroughly with hydrogen sulfide water containing a little hydrochloric or sulfuric acid, and then with pure 95% alcohol to replace the acid and remove a small amount of sulfur. Sometimes it may be found necessary to wash the precipitate also with freshly distilled carbon disulfide. Since the alcoholic and carbon disulfide washings contain no tin, they are caught in a separate beaker and discarded. The arsenious sulfide is heated at 110° to constant weight.

If the original solution be a sulfuric acid one, the filtrate may be evaporated in platinum on the water-bath as far as possible, heated over a free flame until fumes of sulfuric anhydride are evolved, and the stannic sulfate hydrolyzed by pouring the residue into a large volume of water. After most of the free acid has been neutralized with ammonia, and the mixture allowed to stand for 12 hours, the stannic acid can be filtered off, washed, dried and ignited in a porcelain crucible in the ordinary way.[5] If, however, the solution contain hydrochloric acid a procedure due to Furman[6] is recommended. By means of a rapid current of carbon dioxide, or by heating in platinum, the hydrogen sulfide is expelled from the filtrate, and the latter poured into a Pyrex beaker containing an aqueous solution of boric acid(4–5 g. in 30 cc. of hot water). The free hydrofluoric acid as well as the stannic fluoride interacts at once with the boric acid, and completely on warming the solution, to form hydrofluoboric acid (HBF_4), and the liquid assumes the properties of an ordinary solution of a stannic salt. Since Furman has shown that the solution thus obtained

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[4] Ceresin beakers of 250 and 500cc. capacity were furnished me by the J. T. Baker Chemical Co. of Phillipsburg, N. J., as far back as 1910. They have been in use off and on ever since, and have given complete satisfaction. I recommend them highly as containers for all sorts of cold solutions of hydrofluoric acid and its salts.

[5] Fresenius, "Quantitative Chemical Analysis," John Wiley and Sons, New York, **1904**, vol. I, p. 406.

[6] Ref. 3, p. 900.

has practically no action on good glass, its evaporation to a volume of about 250 cc. may be effected in the beaker. The tin is now precipitated with hydrogen sulfide and the stannic sulfide, after standing for 10 or 12 hours, is filtered off, washed thoroughly with water containing ammonium nitrate and then with pure 95% alcohol until all traces of boric acid are removed, dried and converted into the oxide by roasting.[7] According to Furman[8] the best method for separating the tin from a hydrofluoric acid solution to which boric acid has been added is that of Kling and Lassieur.[9] The reagent employed by them is cupferron. A freshly prepared aqueous solution of this compound precipitates the tin completely from such a solution in the form of a white, curdy mass. The latter soon becomes crystalline; it can be crushed to a coarse powder with the end of a glass rod, and so obtained in a form which is easy to filter off and wash. On ignition in a current of air the compound is converted into pure stannic oxide.

Solution of Arsenious Oxide.—5.1070 g. of arsenious oxide was dried to constant weight at 105°, dissolved in warm sodium hydroxide solution, the latter was acidified with hydrochloric acid and the liquid diluted at 20° to a liter; 20 cc. of this solution contains, theoretically, 0.1021 g. of arsenic trioxide, or 0.0773 g. of arsenic. The arsenic in 20 cc. was determined in duplicate by precipitating it with hydrogen sulfide as the trisulfide, washing the sulfide first with hydrogen sulfide water containing a little hydrochloric acid, and finally with alcohol. Found: (a) 0.1274 g. of As_2S_3 = 0.0776 g. of As; (b) 0.1268 g. of As_2S_3 = 0.0773 g. of As; av., 0.0774 g. of As.

Solution of Stannic Chloride.—15.5115 g. of crystallized stannic chloride was dissolved in water strongly acidified with hydrochloric acid,

TABLE I

DETERMINATION OF ARSENIC IN THE PRESENCE OF TIN

Expt.	As_2O_3 solution Cc.	$SnCl_4$ solution Cc.	HCl conc. Cc.	HF Cc.	As found as As_2S_3 G.	As taken G.
1	20	10	10	4	0.0772	0.0774
2	10	10	8	3	.0388	.0387
3	5	10	10	4	.0196	.0194
4	7	10	10	4	.0274	.0272
5	25	10	10	4	.0968	.0968
6[a]	25	25	10	7	.0968	.0968
7	20	25	..	7	.0772	.0774
8	5	25	..	7	.0196	.0194
9	25	10	..	4	.0097	.0097

[a] The first weight of the As_2S_3 being a little high, the precipitate was soaked in freshly distilled carbon disulfide, washed with alcohol, dried and reweighed.

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[7] Ref. 5, p. 407.

[8] Private communication.

[9] Kling and Lassieur, *Compt. rend.*, **170,** 1112 (1920).

and the solution was diluted at 20° to a liter. The tin in 25 cc. of the solution was determined in duplicate, (a) by precipitating it with ammonia and ammonium nitrate, and strongly igniting the stannic acid,[10] and (b) by precipitating it with hydrogen sulfide and roasting the stannic sulfide, the resulting stannic oxide being ignited to constant weight in the presence of ammonium carbonate. Found: (a) 0.1683 g. of SnO_2 = 0.1326 g. of Sn; (b) 0.1684 g. of SnO_2 = 0.1327 g. of Sn. The volumes of the standard solutions and of the acids, as shown in the table, were pipetted into the large platinum dish, the mixture in each case was warmed, diluted to about 300 cc. and hydrogen sulfide introduced as above directed.

The results obtained agree in a very gratifying way with the amounts actually present.

Determination of Both Arsenic and Tin.—(1) From 20 cc. of arsenic trioxide, 25 cc. of stannic chloride and 7 cc. of hydrofluoric acid (etc.), 0.1272 g. of arsenic trisulfide was obtained, equivalent to 0.0775 g. of arsenic, as compared with 0.0774 g. taken. The filtrate, free from hydrogen sulfide, was poured into a Pyrex beaker containing about 5 g. of boric acid dissolved in hot water, the liquid was stirred, evaporated to the required volume, cooled and hydrogen sulfide passed into it for half an hour. After standing overnight the stannic sulfide was treated as above directed; 0.1688 g. of stannic oxide was obtained, equivalent to 0.1330 g. of tin, as compared with 0.1327 g. taken. (2) From 20 cc. of arsenic trioxide, 10 cc. of stannic chloride, 5 cc. of conc. hydrochloric acid and 4 cc. of hydrofluoric acid, etc., 0.1269 g. of arsenic trisulfide, equivalent to 0.0772 g. of arsenic and 0.0667 g. of stannic oxide equivalent to 0.0526 g. of tin were obtained as compared with 0.0774 g. and 0.0531 g., respectively, taken.

The following are the results of some further separations which I made quite recently, and with freshly prepared and carefully standardized solutions. The method of procedure was the same as that already described.

TABLE II

SEPARATION OF ARSENIC AND TIN

As taken G.	As found G.	Sn taken G.	Sn found G.
0.1016	0.1020	0.1377	0.1375
.1016	.1018	.1377	.1375
.1016	.1018	.1377	.1372

The method is well adapted for separating both trivalent arsenic and trivalent antimony from quadrivalent tin when all three are present in a solution. To obtain a solution containing the 3 elements *in their proper states of oxidation* it is only necessary, in the case of an alloy, to cover the

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[10] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, New York, 1908, vol. II, p. 174.

finely divided material with about 10 cc. of conc. sulfuric acid,[11] and boil the acid gently for from 15 to 20 minutes, or, in case of a mixture of the sulfides, to drop a bit of sulfur somewhat larger than a pea on the surface of the acid and then heat it to boiling and continue to boil it for from 15 to 20 minutes. The sulfur dioxide generated reduces any arsenic and antimony present in the higher to the lower states of oxidation, while the stannic sulfate,[12] into which the tin is converted by the hot acid, remains unaffected.

By the method here described, lead, mercury, copper, bismuth and cadmium can be separated quantitatively from tin,[13] and some qualitative experiments seem to prove that the reaction may be employed for separating divalent from quadrivalent tin and trivalent from quinquivalent antimony.

I wish to express my warmest thanks to my friend and former assistant, Mr. Louis B. Dobie, to whom I am indebted for most of the quantitative determinations given in this paper.

Summary

From a moderately dilute hydrochloric or sulfuric acid solution of trivalent arsenic and quadrivalent tin containing a relatively small amount of hydrofluoric acid hydrogen sulfide precipitates the arsenic completely and free from tin. The reaction serves as an accurate and convenient means for the quantitative separation of the 2 elements.

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[11] Fresenius, "Qualitative Chemical Analysis," John Wiley and Sons, New York, **1921**, p. 328.

[12] This behavior of tin toward hot, conc. sulfuric acid does not seem to be generally known, for Mellor ("Modern Inorganic Chemistry," **1912**, p. 789), Alexander Smith ("General Inorganic Chemistry," **1906**, p. 694), v. Richter-Klinger ("Lehrbuch der anorganischen Chemie," **1914**, p. 541) and other eminent text-book writers state plainly that *stannous* sulfate is the product of the reaction. My own experience has been that excess of boiling, conc. sulfuric acid converts tin so completely into stannic sulfate that not a trace of stannous sulfate can be detected in the resulting solution.

[13] Arthur A. Noyes showed as far back as 1904 that the method may be employed for the qualitative separation of Cu, Bi, Se and Te from Sn^{IV} and W^{VI}. See "A System of Qualitative Analysis including nearly all the Metallic Elements," *Technolog. Quart.*, **17**, pp. 216 and 221 (1904).