

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA.]

A SEPARATION OF GERMANIUM AND ARSENIC.

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In a recent publication on the atomic weight of germanium,¹ the author has called attention to the difficulties experienced in removing the last traces of arsenic from germanium. The distillation process from aqueous hydrochloric acid in the presence of chlorine which has been recommended did not give sufficiently accurate results as the distillate was at no time free from small quantities of arsenic.

Careful regulation of the temperature and maintenance of a low concentration of hydrochloric acid will give a distillate almost free from arsenic, but under these conditions the volatilization of the germanium is very slow or incomplete.

As the distillation from hydrochloric acid completely separates germanium from all metals and semi-metals other than arsenic, the complete removal of the latter element is all that is needed for the accurate analysis of germanium-bearing material.

A study of the relative physiological action of the derivatives of arsenic and germanium made necessary the detection and separation of small quantities of arsenic in the presence of large quantities of germanium.

Germanium dioxide was found to be non-toxic, and solutions of the same substance, when introduced subcutaneously, show a marked erythropoietic action.² It may be of interest to note that the peculiar likeness of germanium to arsenic, especially the solubility of the dioxide, suggested the study of its physiological action and that its non-toxicity links it with the non-poisonous oxides in its periodic group. In working up some 300 g. of impure germanium dioxide a separation of these closely associated elements has been found possible through a difference in their behavior toward hydrogen sulfide in presence of hydrofluoric acid.

The purpose of this paper is to describe this method.

Experimental.

The germanium dioxide employed was some of the material used in the recent determination of the atomic weight of germanium. It was necessarily free from arsenic and other impurities

Approximately 5 g. of germanium dioxide was fused in platinum with sufficient sodium carbonate to form the normal sodium salt, the melt was dissolved in water, made up to 1 liter and the exact concentration of the solution determined by taking the mean of three analyses of 50cc.

¹ Müller, *THIS JOURNAL*, **43**, 1085 (1921).

² Details to appear in *J. Exp. Med.*, **35**, Feb. (1922).

samples. One liter of this solution contained 4.9640 g. of the dioxide. Dilution of this solution (A) to 0.1 and 0.01 concentration gave Solutions B and C respectively.

The arsenic trioxide was prepared by fractionation and resublimation of the nearly pure oxide. The standard arsenic trioxide solution was prepared like that for germanium and the concentration determined by three determinations of the trioxide as magnesium pyro-arsenate. One liter of this solution contained 4.8506 g. of arsenic trioxide. Dilution of this solution (A) to 0.1 and 0.01 concentration gave Solutions B and C respectively.

Definite portions of these solutions, in quantities shown in the table, were introduced by pipet into platinum dishes and after addition of hydrofluoric acid the solutions were saturated with hydrogen sulfide.

The hydrofluoric acid used was carefully examined and found free from iron, arsenic, silica and all metals precipitated by hydrogen sulfide.

The precipitated sulfide of arsenic was in each case filtered through filter paper in a platinum funnel upon which the sulfide was washed, first with hydrofluoric acid saturated with hydrogen sulfide and then with pure water until the washings were approximately neutral. The sulfide was then removed from the paper by dil. ammonium hydroxide and the solution evaporated in quartz. Pure conc. nitric acid was added and after evaporation of the excess of acid the arsenic was determined in the usual manner as magnesium pyro-arsenate. Porcelain Gooch crucibles with asbestos mats were employed. The acid filtrates containing the germanium, which were collected in platinum dishes, were treated with 10 cc. of pure conc. sulfuric acid and evaporated upon water-baths until nearly all of the hydrofluoric acid was expelled. The residual acid was then more strongly heated until the fuming of the residual sulfuric acid just began. When much germanium was present the dioxide tended to separate in an adherent layer on the bottom of the dish, but after diluting with water and making alkaline with ammonium hydroxide the whole was easily transferred to a glass vessel. The solution was then neutralized by addition of hydrochloric acid and sufficient excess of concentrated acid added to bring the concentration of free acid to 15–20% by weight. Hydrogen sulfide passed through this solution gave all the germanium as sulfide.

Care was taken, of course, to wash the germanium sulfide with strongly acidulated wash-water which had been thoroughly saturated with hydrogen sulfide, finishing the washing with very little cold water saturated under pressure with the same gas. The germanium was weighed as dioxide. Frequent treatment of the slowly ignited sulfide with pure nitric acid and subsequent evaporation and ignition were carried out to constant weight.

In several preliminary experiments the delicacy of the reaction of hydrogen sulfide upon hydrofluoric acid solution of arsenic trioxide was determined. It was found that as little as 0.0002 g. of arsenious oxide will be deposited as a visible precipitate from a solution containing 100 cc. of water and 50 cc. of 48% hydrofluoric acid and that this reaction may best be carried out in the cold.

A blank experiment was made with a solution containing 10 g. of germanium dioxide converted to fluoride in the presence of the 2NaF equivalent and 50 cc. of hydrofluoric acid and 300 cc. of water. Hydrogen sulfide had no effect upon this solution. The introduction of less than 0.001 g. of arsenic trioxide into a similar germanium solution gave all of the arsenic as sulfide after saturation with hydrogen sulfide. It was therefore concluded that the delicacy of this reaction for arsenic is not measurably influenced by large quantities of germanium fluoride, fluo-germanic acid or the alkali salts of the latter.

The following table shows the results of eight analyses of mixtures of the oxides of germanium and arsenic. Numbers 8 and 9 are especially significant insofar as they show the possibility of separating 0.02 to 0.01% of arsenic from germanium compounds.

TABLE I.
SEPARATION OF GERMANIUM AND ARSENIC.

Analysis.	Germanium dioxide present. G.	Arsenic trioxide present. G.	Germanium dioxide found. G.	Arsenic trioxide found. G.	Conc. hydrofluoric acid in solution (48%). Cc.	Total volume of solution. Cc.
1	0.2482	0.2425	0.2479	0.2420	50	150
2	0.2482	0.0243	0.2483	0.0234	50	100
3	0.2482	0.0024	0.2484	0.0040	50	150
4	0.2482	0.0005	0.2487	0.0004	30	110
5	0.0049	0.4851	0.0057	0.4841	55	160
6	0.0010	0.4851	0.0011	0.4839	51	152
7	10.0006	0.0020	not determined	0.0017	50	350
8	10.0002	0.0010	not determined	0.0010	50	150

Summary and Conclusion.

1. Hydrogen sulfide is without action upon solutions of fluo-germanic acid and the alkali salts of this acid.
2. Arsenic and germanium can be quantitatively separated by the action of hydrogen sulfide upon a solution of their oxides in the presence of a large excess of hydrofluoric acid.
3. The separation is sufficiently accurate to determine as little as 0.01% of arsenic in germanium compounds.
4. The method is especially useful in connection with the preparation of pure germanium compounds, as the fractional crystallization of the

double fluoride can thus be avoided and the operation carried out in small volume. The precipitation of the arsenic sulfide is complete and rapid in the cold.

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THE CO-PRECIPITATION OF VANADIC ACID WITH AMMONIUM PHOSPHOMOLYBDATE.¹

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1. Introduction.

In 1912 there was developed in this laboratory a method for the determination of vanadium in which this element was separated from other materials by co-precipitation with ammonium phosphomolybdate. In the paper³ describing this method no details of the mechanism of this reaction were given. The purpose of the present paper is to discuss an investigation of the mechanism of the co-precipitation of vanadic acid with the ammonium phosphomolybdate in order to define better the conditions upon which the success of the procedure as an analytical method depends and, incidentally, to throw light upon the formation of vanado-phosphomolybdates and to indicate that a simple relation exists among the many members of this class of so-called "complexes."

The method, as published, is in brief outline as follows. The hot nitric acid solution containing the vanadium as vanadic acid is nearly neutralized with ammonium hydroxide, and phosphorus (as sodium phosphate) is added in an amount at least ten times that of the vanadium suspected to be present. The phosphorus is then precipitated as ammonium phosphomolybdate and the resulting precipitate is washed with ammonium hydrogen sulfate solution. Finally, the vanadium is determined by dissolving the precipitate in conc. sulfuric acid, reducing with hydrogen peroxide, and titrating with permanganate. Except for the changes of conditions made necessary in order to study the problem advantageously, this general method was adhered to in all the experiments that follow.

2. Preliminary Study.

It was mentioned in the former paper that the color of the ammonium

¹ Published by permission of the Director of the Bureau of Standards.

² The experimental work reported in this paper was carried out in 1912. Publication of the results has been delayed on account of the resignation of the authors since that time.

³ "A Rapid Method for the Determination of Vanadium in Steels, Ores, etc., based on its Quantitative Inclusion by the Phosphomolybdate Precipitate." *Bur. Standards, Tech. Paper*, 8. J. R. Cain and J. C. Hostetter, *J. Ind. Eng. Chem.*, 4, 250 (1912).