

THE JOURNAL
OF THE
American Chemical Society

with which has been incorporated the

American Chemical Journal

(Founded by Ira Remsen)

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

GERMANIUM.¹ I. EXTRACTION FROM GERMANIUM-BEARING
ZINC OXIDE. NON-OCCURRENCE IN SAMARSKITE.

By L. M. DENNIS AND JACOB PAPISH.

Received June 25, 1921.

Material.

Argyrodite and canfieldite, which at present are the only minerals known to contain germanium as a definite constituent, are too rare to be regarded as sources of supply of the element. Bardet² examined various mineral waters spectroscopically and found that germanium was present in many of them. He succeeded in extracting 60 mg. of germanium dioxide from about 100 kilograms of residues, chiefly calcium carbonate, obtained in the manufacture of Vichy salts from the natural waters. This amount of germanium dioxide represented 250,000 liters of original Vichy water and corresponded to 0.00024 mg. of germanium dioxide per

¹ This article is based upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University by Jacob Papish in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Some details of manipulation and additional comments on the history of germanium have been omitted from this article. They will appear in an unabridged version to be published later in the *Zeitschrift für anorganische und allgemeine Chemie*.

² Bardet, *Compt. rend.*, **158**, 1278 (1914).

liter of water, a quantity too small to render these waters a practical source of supply of germanium. The extraction of germanium directly from blends, as has been carried out by Urbain, is a very expensive and tedious operation. The most promising source of the element at the present time is the concentrate from certain residues obtained in the smelting of American zinc ores. Buchanan³ reported that one such residue contained as much as 0.25 % of germanium dioxide. A large supply of this most valuable material was presented to the Department of Chemistry of Cornell University by the New Jersey Zinc Company and the present investigation, as well as others that will follow from this laboratory, would not have been possible except for the generous coöperation of this company. Concerning the origin of this material, Mr. W. M. Kelsey,⁴ Superintendent of the Palmerton plant of the New Jersey Zinc Company, states that it was obtained "by a fire concentration of certain residues produced in the ordinary process of smelting for zinc. The original ore was a mixture of high grade sulfides from the Wisconsin and Missouri fields, roughly in the ratio of two parts of Wisconsin ore to one part of Missouri ore."

Extraction of Germanium.

None of the various methods that were employed by Winkler for the extraction of germanium from argyrodite is adapted to the separation of the element from the germanium-bearing zinc oxide, because the association of elements in this latter material is quite different from that in argyrodite. Zinc oxide is, of course, present in preponderating amount and the concentrate further contains considerable quantities of lead, arsenic, and cadmium, and also traces of other elements, among them being indium, tin, and antimony.

Preliminary trials were made of a variety of possible methods of separation, but as none of these was found to be satisfactory, descriptions of them will not be given here. The procedure that was finally adopted is based upon the volatility of germanium tetrachloride, and is an elaboration of the method described by Buchanan.³ The essential features of this process consist in treating the crude zinc oxide with hydrochloric acid and then distilling the germanium tetrachloride in a current of chlorine. The chlorine maintains the arsenic in pentavalent form and thus prevents the distillation of arsenic trichloride with the germanium tetrachloride.

In the first trials of this method, portions of the crude zinc oxide of from 250 to 1000 g. each were treated with hydrochloric acid, chlorine gas was passed through the apparatus, and the mixture was heated to effect the distillation of the germanium tetrachloride. This gave a product substantially free from arsenic, but the necessity for long passage of large

³ Buchanan, *J. Ind. Eng. Chem.*, **8**, 585 (1916); **9**, 661 (1917).

⁴ Letter to L. M. Dennis, September 3, 1919.

amounts of chlorine through the apparatus rendered the procedure unsuited to the extraction of germanium on a large scale from several hundred pounds of the crude material. Browning and Scott⁵ substituted potassium permanganate, manganese dioxide, potassium chlorate, or potassium dichromate for chlorine. They used the method for the detection of germanium in very small samples that contained less than a gram of arsenic trioxide or pentoxide and not more than 5 mg. of germanium. But even so they found that when from 0.3 to 0.5 g. of As_2O_3 was used, some arsenic appeared in the distillate. It is apparently essential that if the formation of arsenic trichloride and its consequent appearance in the distillate are to be avoided, the concentration of chlorine must be high throughout the whole distillation.

Fresenius⁶ states that when a mixture of sodium arsenate and conc. hydrochloric acid is distilled, small amounts of arsenic are volatilized. Mayrhofer⁷ in attempting to remove arsenical impurities from hydrochloric acid noticed that even when the acid was first treated with chlorine or when some pyrolusite was added to the acid and it was then distilled, small amounts of arsenic were always found in the distillate. Hehner⁸ distilled arsenic acid with strong hydrochloric acid and obtained comparatively large quantities of arsenic in the several fractions of the distillate. He states that "a similar result was obtained when potassium permanganate had been added before the beginning of the distillation, or, in other words, when the distillation was begun in the presence of chlorine."

In an investigation of the reaction between hydrogen sulfide and arsenic pentoxide in the presence of hydrochloric acid, Usher and Travers⁹ studied the reaction between arsenic pentoxide and hydrogen chloride in sealed tubes. They concluded that the reaction is that expressed by the equation $\text{As}_2\text{O}_5 + 10\text{HCl} \rightleftharpoons 2\text{AsCl}_3 + 2\text{Cl}_2 + 5\text{H}_2\text{O}$, the equilibrium shifting rapidly to the right with increasing concentration of hydrogen chloride.

These observations upon the reduction of arsenic pentoxide by conc. hydrochloric acid and volatilization of arsenic trichloride when such a mixture is distilled, have been sustained by the experimental evidence accumulated in this laboratory during the progress of the investigation here described. When potassium permanganate was added to the crude zinc oxide and this was then distilled with an excess of conc. hydrochloric acid, arsenic trichloride passed into the distillate. To maintain the concentration of chlorine, the procedure was modified by slowly running into the flask a solution of the potassium permanganate during the distillation with hydrochloric acid. It was found that the dilution of the acid soon rose to such an amount that the germanium tetrachloride instead of distilling off was hydrolyzed in the flask. To ascertain whether a mixture of sodium arsenate and sodium germanate, when distilled with an excess of conc. hydrochloric acid, would yield arsenic trichloride in the distillate, a mixture of the oxides of arsenic and germanium was fused with a slight excess of sodium peroxide, the fused mass was dissolved in water and the solution was heated to boiling. It was then cooled, and excess of hydrochloric acid was added and the liquid was distilled. The distillation gave a yellow precipitate with hydrogen sulfide which indi-

⁵ Browning and Scott, *Am. J. Sci.*, [4] **44**, 313 (1917); **46**, 663 (1918).

⁶ Fresenius, *Z. anal. Chem.*, **1**, 447 (1862).

⁷ Mayrhofer, *Ann.*, **158**, 326 (1872).

⁸ Hehner, *Analyst*, **27**, 268 (1902).

⁹ Usher and Travers, *J. Chem. Soc.*, **87**, 1370 (1905).

cated the presence of arsenic. In another experiment lead dioxide was used in place of sodium peroxide. Arsenic here also passed into the distillate. These experiments, as well as the observations of previous investigators, indicate that arsenic acid is reduced to arsenic trichloride during distillation with hydrochloric acid unless a high concentration of chlorine throughout the distillation is maintained.

To ascertain whether arsenic trioxide when dissolved in sodium hydroxide, saturated with chlorine, and then acidified with hydrochloric acid, would yield any arsenic trichloride when distilled in a current of chlorine, 5 g. of arsenic trioxide was dissolved in 20 cc. of a 30% solution of potassium hydroxide, this solution was saturated with chlorine, and then, without interrupting the current of chlorine, 190 cc. of pure conc. hydrochloric acid was added and the liquid was distilled. A Reitmaier-Stutzer bulb was used to prevent so far as possible the mechanical passage of some of the liquid into the distillate. Two fractions of 40 cc. each were obtained. Each of these was saturated with hydrogen sulfide. After 12 hours there separated a few small yellow particles that resembled sulfur. These were tested for arsenic by heating them with nitric acid, adding ferrous sulfate to reduce the nitric acid, then adding dil. sulfuric acid and warming the mixture to remove oxides of nitrogen, and finally subjecting the material to the "modified Gutzeit test."¹⁰ The reaction was allowed to proceed for 10 minutes but no discoloration of the crystal of silver nitrate was discernible.

Müller,¹¹ in a recent article upon the atomic weight of germanium, states "The chlorine—hydrochloric acid distillation process, though adequate for the removal of silica and tin, can hardly be accepted as a means of eliminating the last traces of arsenic from germanium compounds. Four redistillations of the chloride from hydrochloric acid solution in a stream of chlorine failed to remove the last of the arsenic." Careful perusal of his article fails to reveal experimental support for this statement. In fact, in his description of the purification of germanium, he remarks that the precipitation of redistilled germanium tetrachloride by hydrogen sulfide yielded a "snow-white germanium sulfide." The point is of importance, and the possible presence of arsenic in the distilled germanium tetrachloride will be followed carefully during further work in this laboratory.

To avoid the necessity for the use of the very large amounts of chlorine that would be called for if the germaniferous zinc oxide were directly distilled with hydrochloric acid in a current of chlorine for the separation of germanium, it was decided to distil germanium tetrachloride and arsenic trichloride together from the crude zinc oxide and thus to effect, as a first step, the separation of the germanium from the large amount of the zinc oxide that is present in the original material.

Apparatus.

The unit still consists of a round-bottom 5-liter Pyrex flask supported on an asbestos "collar"¹² 10 cm. high, the collar resting on an iron plate and this on a strong tripod. A 2-hole rubber stopper in the neck of the

¹⁰ Dennis and Whittelsey, "Qualitative Analysis," Ginn and Co., Revised Ed., p. 31.

¹¹ Müller, *THIS JOURNAL*, **43**, 1085 (1921).

¹² This device for heating glass or porcelain vessels that contain a mixture of liquid and solid materials has been in use in the Cornell Laboratory for several years. A

flask carries a bent glass tube for connection with a Liebig condenser, and through the other opening of the stopper is inserted a short glass tube through which the desired amount of conc. hydrochloric acid may be blown into the flask by air pressure from a large graduated bottle. After the acid has been driven into the flask in the actual operation, the glass tube is replaced by a solid glass plug. A bent glass tube is attached to the farther end of the condenser by means of a short piece of rubber tubing. This glass tube is about 10 mm. in diameter and reaches nearly to the bottom of a 4-liter bottle which serves as a receiver. The iron plate upon which the collar rests is heated with a large Meker burner, and to avoid loss of heat, the tripod is surrounded by sheets of asbestos board. The duration of each distillation is further shortened by covering the upper part of the flask with an asbestos jacket. This jacket is made by first covering that part of the flask which projects above the collar with a layer of moist filter paper. Asbestos felt which had been soaked in water is then laid upon the paper in over-lapping pieces and smoothed down to an even, continuous layer. Wet asbestos cement is then laid over the whole exterior of the jacket. The opening in the top of the jacket is made sufficiently large to permit of the removal of the cap from the flask. The cap is allowed to dry on the flask and is then removed and its lower edge and the upper rim are dipped in a solution of sodium silicate to stiffen them. The receiver stands in an earthenware jar.

Distillation.

One kilogram of the crude zinc oxide is introduced into the flask, water is placed in the receiver to such a depth as just to cover the end of the glass tube, and the earthenware jar in which the bottle stands is filled with cracked ice. Twenty-five hundred cc. of commercial conc. hydrochloric acid (1.18 sp. gr.) is next driven into the flask through the glass tube in the stopper, and the tube is then replaced by a solid glass plug. The heating of the flask is begun and continued until 2000 cc. of the distillate has collected, this amount having been shown spectroscopically to suffice for the recovery of all the germanium.

"collar" is made from asbestos board 3 to 6 mm. thick, a strip of the board of the desired width being first thoroughly wet with water, then bent into a circle and fastened at the over-lapping ends with iron or copper wire, and finally dried. The "collars" may of course be made of any desired diameter. The collar is placed upon an iron plate about 3 mm. thick and this plate rests in turn upon an iron tripod. If the collar is dipped in a dilute solution of sodium silicate, it becomes stiff when dry, and although somewhat brittle, its life is prolonged by this treatment. A glass flask or porcelain evaporator placed on one of these collars does not come into direct contact with the gas flames under the iron plate, and local heating that would result from the direct application of the flame to the container, which often causes the fracture of the vessel, is thus avoided. The collar is especially useful in the long digestion of a powdered mineral with acids.

The Precipitation of Germanium and Arsenic by Hydrogen Sulfide.

The acid distillate may now be treated with hydrogen sulfide in such manner as to precipitate all of the arsenic and germanium that are present, or the conditions may be so regulated as to cause the precipitation of arsenic trisulfide alone or mixed with only a very small amount of germanium sulfide. This last procedure was used by Winkler¹³ and is now being studied in this laboratory. The method that we have employed up to the present time involves the simultaneous precipitation of the sulfides of germanium and arsenic.

Successive distillates are poured into a 15-liter glass bottle until about 10 liters of the solution has been collected. Since the precipitation of germanium disulfide is most complete when the acid concentration is about 6 *N*, conc. sulfuric acid is slowly added to the contents of the bottle until the acidity is brought to about this point. The acid is run in from a separatory funnel that passes through one opening of a 2-hole rubber stopper inserted in the neck of the bottle. Loss of germanium tetrachloride that might be volatilized during the addition of the sulfuric acid is avoided by placing in the other opening of the stopper a short, bent delivery tube that dips into a liter of 6 *N* sulfuric acid that has been saturated with hydrogen sulfide. Washed hydrogen sulfide is now passed through this solution. Yellow sulfide of arsenic is first precipitated. White germanium disulfide next appears, and if the liquid is not agitated, this white sulfide separates as a distinct layer on the top of the yellow sulfide of arsenic. When precipitation is complete, the large bottle is stoppered and is allowed to stand for 24 hours. The contents of the bottle is then brought upon a filter and the sulfides are washed with the aid of suction with 3 *N* sulfuric acid that has been saturated with hydrogen sulfide.

The filtrate from the sulfides of germanium and arsenic is placed in a large bottle or in a tall, covered, glass cylinder and allowed to stand for 48 hours. At the end of this time a slight precipitate of the sulfides separates. The supernatant liquid is then siphoned off and the bottle or cylinder is filled with the filtrate from the next precipitation which is again allowed to stand for 48 hours. When a fairly large amount of the sulfides has accumulated in the vessel, it is brought upon a filter and washed as before. The amount of germanium that is recovered by this treatment averages about 2 mg. for every liter of filtrate.

From this point forward two different procedures have been followed. In the first of these the moist sulfides are dissolved in a 50% solution of sodium hydroxide with the aid of heat. Successive portions of the sulfides are added to this solution until a small amount is left undissolved.

¹³ Winkler, *J. prakt. Chem.*, **142**, 194 (1886).

This is then taken into solution by the addition of a little more of the concentrated solution of sodium hydroxide and then about 8 g. of solid sodium hydroxide is added to render the solution strongly alkaline which facilitates the later oxidation of the arsenic. This solution is then placed in a Pyrex flask which is provided with a rubber stopper that carries a delivery tube, a separatory funnel, and a glass tube that reaches nearly to the bottom of the flask. This last tube has a wider tube fused to its lower end to avoid stoppage. The flask is placed on an asbestos collar and is connected with a condenser and a receiver in the manner above described. Washed chlorine is then passed through the liquid in the flask to convert the arsenic to the pentavalent form. When the contents of the flask has been saturated with chlorine and the apparatus is filled with the gas, the speed of the flow of chlorine is lessened and conc. hydrochloric acid is run into the flask through the separatory funnel until the acid is in large excess. The flask is then heated and the germanium tetrachloride is distilled in a slow current of chlorine, the distillation being continued until half of the liquid in the flask has passed over.

The larger part of the germanium tetrachloride passes over between 90° and 100° . Instead of collecting the germanium tetrachloride as such from this distillation, some water is placed in the receiver to hydrolyze the compound. The resulting hydrated germanium dioxide is pure white in color. If any of the oily tetrachloride is seen to collect under the layer of liquid on the bottom of the receiver during the distillation, it is an indication that the concentration of hydrochloric acid in the receiver is so high as to repress the hydrolysis of the germanium tetrachloride. In such case more water is poured into the receiver. When half of the liquid in the flask has passed over, the receiver is removed and a fresh receiver containing some water is put in its place. A volume of conc. hydrochloric acid equal to the volume of the liquid that has distilled over is now run into the flask through the separatory funnel and the distillation is continued. When half of the liquid now in the flask has distilled over, most of the germanium tetrachloride has usually passed into the distillate, but it was found that complete separation of that element as the tetrachloride is effected only by many repetitions of the distillation.

The hydrated germanium dioxide is now collected on a small disk of filter paper supported by a Witt plate in a large funnel and is washed first with dil. sulfuric acid and then with small portions of cold water. It is transferred to an evaporating dish and is dried in an air bath at a temperature of 110° . Photographs of the arc spectra of various portions of this material showed that the germanium dioxide contained traces of sodium, calcium, and iron. Fractional precipitation of a solution of a sample of the dioxide by hydrogen sulfide failed to disclose the presence of arsenic.

Germanium in the filtrate and washings from the hydrolyzed germanium dioxide is recovered by precipitation with hydrogen sulfide.

To free the germanium dioxide from the traces of impurities noted above, it is dissolved in a slight excess of sodium hydroxide with the aid of heat, the solution is treated with chlorine in the manner above described, hydrochloric acid is added, and the germanium tetrachloride is again distilled in a current of chlorine and is hydrolyzed as before.

The above method for the separation of germanium and arsenic gives quite satisfactory results in respect to the completeness of the recovery of the germanium, but it is open to the following objections.

The precipitate of the mixed sulfides contains a preponderating amount of arsenious sulfide. This necessitates the use of large quantities of sodium hydroxide, chlorine, and hydrochloric acid, and greatly lengthens the time of treatment with chlorine. Again, the addition of hydrochloric acid to the chlorinated solution of the mixed sulfides in sodium hydroxide reprecipitates a part of the sulfides, and the conversion of the germanium in this precipitate into the volatile germanium tetrachloride by the action of hydrochloric acid and chlorine proceeds very slowly. Furthermore, a large amount of arsenic in the precipitate causes the appearance of some of that element in the distillate even though the current of chlorine through the apparatus is not interrupted during the distillation. This fact necessitates a second precipitation of the sulfides of germanium and arsenic and a redistillation in chlorine in order to free the germanium completely from arsenic.

It is evident that these difficulties would largely be obviated if the greater part of the arsenic could be separated from the germanium before distillation in chlorine. Preliminary experiments indicated that this separation could be accomplished by roasting the dried sulfides in air and this led to the development of the second procedure for the treatment of the mixed sulfides which is as follows.

If the mixed sulfides of germanium and arsenic are to be roasted, it is, of course, essential that the sulfide precipitate be washed free from chlorides before the roasting to avoid loss of germanium through volatilization of germanium tetrachloride. To this end the washing of the sulfides with 3 *N* sulfuric acid is continued until the chlorides are completely removed. The absence of chlorides in the wash-water is ascertained by adding cadmium nitrate to a portion of the liquid to precipitate the hydrogen sulfide, filtering off the precipitate, and then adding silver nitrate to the filtrate. The washed sulfides are transferred to a large evaporating dish and are dried in an air-bath at 110°.

The dried sulfides consist of from 78 to 90% of arsenious sulfide, the remainder being germanium disulfide and moisture, together with small quantities of sulfur and sulfuric acid. These dry, crude sulfides are placed in shallow iron dishes and are roasted in a muffle furnace at a tempera-

ture not to exceed 500°. This removes the greater part of the arsenic.

Up to 500° there is no loss of germanium, as shown by examining spectrographically the sublimate on a sheet of aluminum placed above the iron dish. At slightly above 600° there is a 30% and at 800–900° about a 90% loss of the germanium.

Each of three 100g. samples of the dried, crude sulfides yielded, on roasting, about 24 g. of the germaniferous residue. The actual decrease in the amount of arsenic was, however, greater than this difference of weight indicates, because of the formation of a considerable amount of iron oxide during the roasting. The extent of the removal of arsenic was approximately ascertained by determining the amount of arsenic in an unroasted sample and in that sample after roasting. Before roasting, the material contained 78.2%, and after roasting, 5.52% of arsenic calculated as the trisulfide, As_2S_3 . These results indicate that somewhat over 90% of the arsenic is removed by this treatment.

The germanium in this residue is extracted by dissolving the finely pulverized material in a 50% solution of sodium hydroxide, chlorinating the solution, adding two parts by weight of conc. hydrochloric acid to every one part by weight of the roasted residue, and distilling. Usually, this completely removes the germanium and no more than faint traces of arsenic are found in the distillate. The resulting hydrated germanium dioxide is freed from the last traces of arsenic by dissolving it in sodium hydroxide, chlorinating the solution, and again distilling with hydrochloric acid in a current of chlorine.

This procedure of first roasting the mixed sulfides to remove the greater part of the arsenic and then distilling the germanium tetrachloride from the residue is superior to the first method of directly distilling the germanium tetrachloride from the mixed sulfides in that the consumption of materials is less, the time needed for the distillation is much shorter, and the separation from arsenic is more complete. It possesses, however, one drawback, the necessity of washing the mixed sulfides free from chlorides before roasting. If a small sample of the sulfides be washed with 3 *N* sulfuric acid that has been saturated with hydrogen sulfide, chlorides can be removed quite completely and the filtrate is free from detectable amounts of germanium, but it was found that when this method was used on a large scale, repeated washing with 3 *N* sulfuric acid yields eventually a milky filtrate which slowly deposits white germanium sulfide when its acidity is brought up to 6 *N*. 5 *N* sulfuric acid saturated with hydrogen sulfide was substituted for the 3 *N* acid. This gave a clear filtrate from which no appreciable amount of germanium sulfide separated on standing, but the removal of the chlorides was very slow. Attempts to wash the precipitated sulfides with 5 *N* sulfuric acid by decantation led to no satisfactory results.

Either of the above processes yields a very pure germanium dioxide. The first gives a somewhat higher yield and the second procedure is considerably shorter. The precipitation of arsenic trisulfide substantially free from germanium sulfide from weakly acid solutions is now being studied in the hope that a procedure superior to either of those above described may be developed.

The Determination of Germanium.

To gage the efficiency of the extraction of the germanium from the crude material, it was necessary to develop a method for the quantitative determination of germanium. The procedure that was finally adopted is based directly upon the method of extraction that has already been described.

A weighed quantity, 20 to 100 g., of the germaniferous zinc oxide that had been dried at 110° is ground into a paste with water and is then poured into a flask that contains a solution of sodium hydroxide. These three substances are used in the proportions of 1 part of sodium hydroxide, 2 parts of the crude zinc oxide, and 5 parts of water. The flask is provided with a 3-hole rubber stopper through which are inserted a glass tube that reaches almost to the bottom of the flask, a small Vigreux distilling column, and a small separatory funnel. To the side arm of the Vigreux tube is fused a Liebig condenser, and a glass adapter is fused to the further end of the condenser. The receiver consists of an Erlenmeyer flask that is provided with a 2-hole rubber stopper. Through one of these holes passes the glass adapter which reaches to within a few millimeters of the bottom of the flask. A delivery tube is inserted through the other hole of the stopper and this tube is connected with a second Erlenmeyer flask. Water is placed in the first Erlenmeyer flask to a depth of 3 cm. and the second flask is half filled with water. The second flask serves as a check upon the completeness of the stoppage of germanium chloride in the first receiver. If any germanium is later found to have passed into the second flask, the determination is rejected. Both flasks are placed in a trough containing ice water.

In beginning the distillation a dish containing cracked ice is brought up under the distilling flask, and the apparatus is filled with chlorine which indicates that the contents of the flask has been saturated with the gas. Pure, conc. hydrochloric acid is next slowly introduced through the separatory funnel in amount sufficient to neutralize the sodium hydroxide that was originally employed and, in addition, to equal twice the weight of the crude zinc oxide that is being used. The passage of chlorine and the cooling of the flask are continued during the addition of the acid. When all of the acid has been introduced, the dish of cracked ice is replaced by an asbestos collar and the contents of the flask is then heated

in the manner already described. When $\frac{1}{2}$ of the liquid has distilled over, an equal volume of conc. hydrochloric acid is run into the flask and the distillation is continued until $\frac{1}{2}$ of the liquid has again passed over. The addition of hydrochloric acid and distillation of $\frac{1}{2}$ of the liquid are once more repeated. The heating is then stopped and the two receivers are disconnected. Sulfuric acid is added to the contents of each to bring the acidity to 6 *N*, the flasks standing in ice during the addition of the acid. The liquid in each flask is then saturated with hydrogen sulfide and the flasks are stoppered and set aside for 24 hours. If the passage of the chlorine through the apparatus during the distillation has been slow, and if the receivers have been kept well cooled with ice, no germanium tetrachloride will pass over into the second receiver. A precipitate will, however, appear in the second flask because of the liberation of sulfur through the interaction of chlorine and hydrogen sulfide. The precipitate is tested spectrographically to ascertain whether it is free from germanium. If it is not, the determination is rejected. The precipitated germanium disulfide in the first flask is brought upon an ashless filter paper and the small amount of precipitate that adheres to the walls of the flask is loosened by means of a rubber "policeman" and brought upon the filter by rinsing with 3 *N* sulfuric acid that has been saturated with hydrogen sulfide. The whole precipitate is now washed with this liquid until the chlorides are removed. The germanium disulfide is then washed with alcohol to remove the sulfuric acid and is next dried. The bulk of the precipitate is removed from the filter and placed in a weighed porcelain crucible. It is moistened with nitric acid (1:1), the crucible is gently heated until the liquid has been driven off, is then allowed to cool, and conc. nitric acid is added. This is also driven off by gentle heating and the crucible is finally heated to dull redness.

Germanium dioxide that has been dried at 110° still contains an appreciable amount of water. Experiments performed in this laboratory by Miss K. M. Tressler, which will be described in a later article, have shown that complete dehydration is secured only when the dioxide is heated to 900°.

The filter paper is incinerated over a second weighed crucible. The product is black, due to the formation of some germanous oxide caused by the reduction of the germanium dioxide by the carbon of the paper. This is oxidized to the dioxide by treatment with nitric acid.

The filtrate from the precipitation of the germanium disulfide is set aside for 48 hours and the precipitate that then appears is treated in the same manner as the first precipitate. The sum of the weight of the dioxide in the two crucibles less the weight of the ash of the two filter papers gives the weight of the germanium calculated as dioxide that is present in the original sample.

Although no great accuracy is claimed for the method as thus far developed, two determinations in duplicate of the germanium in different samples of the crude zinc oxide gave concordant results.

Sample I.	I.	II.
Weight of sample, g.	50	75
GeO ₂ found, g.	0.1235	0.1860
GeO ₂ , %	0.247	0.248
Sample II.		
Weight of sample, g.	50	100
GeO ₂ found, g.	0.0950	0.1885
GeO ₂ , %	0.19	0.188

The completeness of the recovery of germanium from the crude zinc oxide by the method of extraction above described is evidenced by the fact that from a series of runs in which a total of about 10.7 kilograms of Sample I of the undried, crude oxide was used, 25.936 g. of pure germanium dioxide was obtained.

The Non-Occurrence of Germanium in Samarskite.

Khrushchov¹⁴ has stated that he had found germanium in American samarskite. This statement was published in the form of a report in the *Journal of the Russian Physical-Chemical Society*.¹⁵ Literally translated it reads as follows.

"K. D. Khrushchov reports about finding germanium in columbium and tantalum minerals. American samarskite was heated in a 300g. platinum crucible for the purpose of comminuting the samarskite. After three heatings, the platinum was altered to such an extent that the crucible crumbled to a powder. On dissolving the platinum, a residue was obtained which resembled silica, but it was fairly difficultly soluble in hydrofluoric acid. Assuming the gelatinous sediment to be germanium dioxide, the reporter found that it was changed very easily by hydrogen to the black powder of germanium. Traces of germanium were also found in tantalite, fergusonite, columbite, gadolinite and in other minerals. American samarskite contains up to 1.5% of germanium. In view of the rarity of argyrodite the reporter calls attention to samarskite as an important source of germanium."

Lincio¹⁶ failed to find evidence of the presence of germanium in samarskite. After the method for determining germanium that has been described in the preceding pages had been developed, the question of the occurrence of the element in American samarskite was taken up in this laboratory. Two hundred g. of finely-ground, selected samarskite was

¹⁴ Khrushchov, *J. Russ. Phys. Chem. Soc.*, [1] **24**, 30 (1892).

¹⁵ We are indebted to the Library of Congress for a pen copy of this report. The translation here given was made by one of us (J. P.).

¹⁶ Lincio, *Zentr. Min.*, **1904**, 142.

fused with 1200 g. of potassium hydrogen sulfate. The fused mass was extracted with water and the residue, which contained a small quantity of undecomposed samarskite, was mixed with more potassium hydrogen sulfate and was fused and extracted with water as before. The two water extracts were combined and were evaporated to dryness.

The insoluble residue from the fusion was moistened with nitric acid and was then introduced into a Pyrex flask of 500cc. capacity. Two hundred cc. of hydrochloric acid was added and the mixture was subjected to distillation until 150 cc. of distillate had passed over. The distillate was saturated with hydrogen sulfide and was allowed to stand for 24 hours. The very slight precipitate that formed was collected on a small filter and was dried. The photograph of the arc spectrum of this material failed to show the presence of germanium.

The residue obtained from the water extracts of the fused material was moistened with nitric acid, and was introduced into a flask of 3 liters capacity. Fifteen hundred cc. of conc. hydrochloric acid was added and the mixture was distilled until about 600 cc. had passed over. Five hundred cc. of hydrochloric acid was then run into the flask and a second distillate of 400 cc. was obtained. The two distillates were united, were saturated with hydrogen sulfide and were allowed to stand for 24 hours. The slight precipitate that separated showed no spectrographic evidence of the presence of germanium.

Khrushchov's report is by no means convincing. He obtained a gelatinous residue which he assumed to be germanium dioxide, but he gives no reasons for this assumption and it is difficult to imagine what his reasons might have been. The fact that the material was darkened when heated in hydrogen might indicate the presence of a variety of compounds other than germanium dioxide. Moreover, it is probable that when he dissolved the platinum, he used aqua regia for this purpose. If he did so, all of the germanium would probably have been lost through volatilization of the germanium tetrachloride. It seems evident, therefore, that Khrushchov's experimental work does not justify his statement that samarskite contains germanium, and the results obtained by Lincio and in this laboratory would seem to show that that mineral does not carry detectable amounts of the element.

Summary.

This article contains (1) the details of an experimental study of the extraction of germanium from germanium-bearing zinc oxide, and the preparation of pure germanium dioxide; (2) a description of a method for the determination of germanium; (3) the details of an examination of American samarskite which showed that the mineral does not contain germanium in an amount detectable by means of the spectroscope.

ITHACA, NEW YORK.