

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]
GERMANIUM. V. EXTRACTION FROM GERMANIUM-BEARING ZINC OXIDE. DIRECT PREPARATION OF GERMANIUM DIOXIDE FREE FROM ARSENIC. DETECTION OF MINUTE AMOUNTS OF ARSENIC IN GERMANIUM DIOXIDE¹

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Introduction

In the methods for the extraction of germanium from germanium-bearing zinc oxide that have thus far been described,² the crude material was treated with hydrochloric acid, and germanium tetrachloride and arsenic trichloride were distilled together, or the distillation of the chloride solution was conducted in a current of chlorine which held back most or all of the arsenic.

In all three cases, the authors concentrated the germanium in the distillate by precipitating it with hydrogen sulfide as germanium disulfide, and then converted this sulfide to the dioxide, GeO_2 , by oxidation, usually with nitric acid. The dioxide was then further purified by processes more or less laborious.

The object of the present investigation was to develop a method that rapidly and completely would extract germanium from the crude zinc oxide, and that would yield directly, without the employment of hydrogen sulfide, a germanium dioxide of high purity.

Extraction of Germanium

The new method³ involves, (1) the solution of the crude zinc oxide in concd. hydrochloric acid, (2) the separation of the resulting germanium tetrachloride from the chlorides of the other elements present by column distillation, and (3) the concentration of the germanium tetrachloride by further distillations and its direct conversion to germanium dioxide.

A 12-liter, round-bottom Pyrex flask is charged with 2000 g. of germanium-bearing zinc oxide and is placed on an asbestos collar²⁰ over a wire gauze supported on a tripod. A rubber stopper carrying a 300cc. separatory funnel of cylindrical form, and a thin-walled glass tube 20 mm. in diameter and 90 cm. long, is inserted into the neck of the flask. A reflux condenser is connected to the upper end of the 20mm. tube by means of a rubber stopper. The water supply to the condenser is turned on, and 8200 cc. of

¹ This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by E. B. Johnson in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² (a) Buchanan, *J. Ind. Eng. Chem.*, **8**, 585 (1916); **9**, 661 (1917). (b) Müller, *THIS JOURNAL*, **43**, 1085 (1921). (c) Dennis and Papish, *ibid.*, **43**, 2131 (1921).

³ A brief résumé of this method was presented at the International Reunion of Chemists at Utrecht in June, 1922, and was published in the *Rec. trav. chim.*, **41**, 565 (1922).

hydrochloric acid, 10.6 *N*, is run into the flask through the separatory funnel, slowly at first and later quite rapidly. If the acid is added too quickly in the beginning, the heat of reaction between it and the oxide may cause the escape of acid through the condenser, with consequent loss of some germanium tetrachloride. The acid in the flask is then heated to boiling, and the heating is continued until practically all of the crude material has been dissolved. The flame is then turned off.

The stopper carrying the tube and condenser is removed from the neck of the flask, and is quickly replaced by one that is fitted with an inlet tube for chlorine and a Hempel distilling column of Pyrex glass, to the upper end of which is fused the still-head.

The distilling column *C*, Fig. 1, is 20 mm. in diameter and has a length of about 80 cm. It is filled with large glass beads 7 to 9 mm. in diameter, and is surrounded by a glass jacket-tube. To its upper end is fused the new form of still-head, *D, F, G, J*, which was devised by one of us (E. B. J.) while engaged in the fractional distillation of coal-tar naphthas at the Frankford Laboratory of the Barrett Company.⁴ This still-head yields excellent results even when operated at a much more rapid rate than the maximum speed that can be employed with a Hempel column or any other of the usual laboratory fractionating devices. A rubber stopper carrying a thermometer *E* is inserted in the open end of *D*, and an upright condenser *H* is attached by a rubber stopper to the tube *G*. A glass tube *N* joined to the upper end of the condenser is connected to a Friedrichs gas-washing bottle *O*, and a tube passes from this to the hood flue.

It is of advantage to grind the lower end of the condenser to a sharp angle to facilitate the flow of vapor and of condensate in opposite directions at this point. The Friedrichs gas-washing bottle is filled with water which will hydrolyze and thus stop any small amount of germanium tetrachloride that may be carried over by the chlorine when it leaves the condenser.

The total vapor from the boiling liquid enters the bottom of the Hempel column and rising through this and the still-head, surrounds the thermometer *E*, and passes through the side-arm *F*, and up into the return condenser. This condenser is intended to completely condense the water, hydrochloric acid and germanium tetrachloride that may be in the vapor. The greater part of the chlorine passes through the condenser to the hood. The total condensate runs from the condenser to *I*, which at the beginning of the distillation is kept entirely closed by a rubber tube and pinchcock *L*. The condensate, therefore, collects and rises in the tube above *I* until the side arm *J* becomes

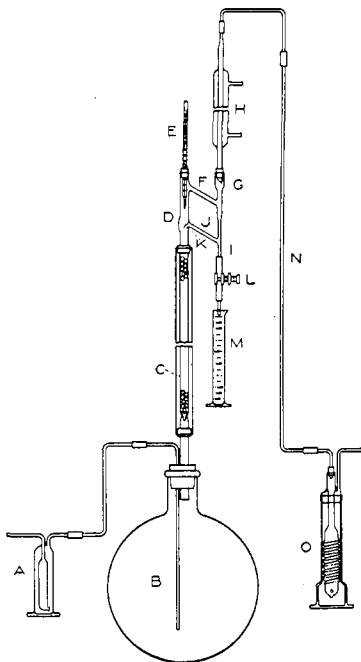


Fig. 1.—Apparatus.

⁴ I wish here to acknowledge my indebtedness to the director of that Laboratory, Dr. J. B. Hill, for furnishing materials and assistance for the construction of the first 3 laboratory still-heads of this type. It is planned to publish in a later paper a more complete discussion of this device showing the increase of efficiency in fractional distillation that results from its use. E. B. J.

filled and the liquid begins to drop back into the column from the tip *K* at the higher end of *J*. This return flow washes the vapor that is rising from the distillation flask. By now opening the pinchcock *L* to the required degree, any portion of the total flow of condensate may be taken off as distillate or forward-flow, while the remainder is returned as back-flow.

Germanium tetrachloride is a liquid boiling at $86^{\circ 5}$ and passes into the distillate together with hydrochloric acid and water. The proportion of hydrochloric acid and water in the distillate depends upon the acid concentration of the solution that is being distilled.

The current of chlorine is passed through the apparatus during the distillation to prevent the volatilization of arsenic as trichloride. Arsenic trichloride is a liquid boiling at $129^{\circ 6}$ and when a solution of this compound and germanium tetrachloride in hydrochloric acid is distilled, arsenic appears in the distillate. When, however, a current of chlorine is passed through the apparatus during the distillation, this distillate is found to be free from arsenic.

The chlorides of the other metals that are present in the crude zinc oxide are not volatile with water and hydrochloric acid.

Four of the assembled units described above may conveniently be operated at one time, and in this case chlorine may be supplied to the 4 stills from 2 cylinders, the gas from each cylinder passing through 2 distillation units in series. In case the series arrangement is followed, it is advisable to use 1-piece gas-washing bottles rather than those with ground neck between the cylinder of chlorine and the first distilling flask, because the back pressure at this point is high. It is not advisable to operate more than 2 of these stills in series.

When the distilling column has been set in place as described above, the burner under the flask is lighted, and passage of chlorine is begun at the same time. As soon as the liquid in the flask begins to boil, the heating of the flask is so adjusted that the column carries its maximum capacity for vapor flow without "flooding" or regurgitation. It will be observed at this point that chlorine is being absorbed very rapidly by the liquid in the flask. The forward-flow take-off at *L* is therefore kept closed, and all of the liquid resulting from the condensation of the vapor in the condenser is returned to the column until chlorination is complete. This point is indicated by the appearance of a greenish-yellow color due to dissolved chlorine in the gas-washing bottle beyond the condenser. When this point is reached, the flow of chlorine is adjusted to a rate that is slow enough to make it possible to distinguish separate bubbles as they pass through the first gas-washing bottle, but is just fast enough to make it impossible to count them. This rate is maintained throughout the distillation.

⁵ Dennis and Hance, *THIS JOURNAL*, **44**, 299 (1922).

⁶ Walden, *Z. physik. Chem.*, **43**, 420 (1903).

The forward-flow take-off is now opened to such an extent that the volume of distillate drawn off at *L* is half that of the condensate returned to the column through *K*. This adjustment is maintained during the distillation, and is checked at frequent intervals by comparing the number of drops falling into the receiver *M* below *I* over a given time with the number falling back from the tip of *K* into the tube *D*.

The distillate is collected in 100cc. portions. If the volume and concentration of the acid used in the charge bear the proper relation to the quantity of crude material taken, water that contains a small amount of chlorine will begin to run off when *L* is opened and the thermometer will indicate 100°.

When, however, 100 cc., or at most 200 cc., of water has distilled through *L*, germanium will begin to appear in the distillate. If the chlorine in a sample of the first portion of the distillate is reduced by hydrogen sulfide, and the sample is titrated with alkali, using methyl orange as indicator, the solution will be found to be about 0.02 *N* in acidity, but it contains no germanium. This acidity is quite constant during the distillation of the first 100–200 cc. and is probably due to the hydrochloric acid that is formed when the chlorine in the distillate is reduced with hydrogen sulfide in order to prevent its bleaching the indicator, and not to hydrochloric acid that passes over from the flask. This view is supported by the fact that if the conditions prescribed for the distillation are carefully adhered to, but the use of chlorine is omitted, water that contains so little acid that it will not affect methyl orange may first be distilled.

After the distillation has proceeded for a short time, a frost-like deposit of germanium dioxide begins to appear in the lower part of the tube *C*. This is due to the hydrolysis of germanium tetrachloride that is now beginning to pass up into the tube. At the same time, hydrochloric acid begins to pass over into the distillate. The appearance of the deposit of germanium dioxide in *C* serves as a warning that germanium will soon be found in the distillate. The acid concentration of the distillate steadily rises during this period, and the constant-boiling mixture of water and hydrochloric acid is approached from the low acid side. The thermometer begins to rise, and when the distillation is not interrupted this rise is continued until the boiling point of the constant-boiling mixture for the prevailing atmospheric pressure is reached. During this rise in acid concentration the deposit of germanium dioxide in the column gradually extends upward and disappears from the lower part of the column because it is redissolved and reconverted to the chloride by the more highly concentrated hydrochloric acid that is now passing off. As soon as the deposit of germanium dioxide appears in the distilling column, successive samples of 10 cc. each of the distillate are collected and each is reduced by hydrogen sulfide and titrated with alkali, using methyl orange as

indicator. When the acid concentration of the samples is found to have reached 0.05 *N*, the collection of the distillate for its germanium contents is begun. The concentration of the hydrochloric acid during this early period of distillation rises so rapidly that it is not safe to cut in on an indication of the thermometer. After the collection of the distillate for germanium is begun, no further tests of the acid concentration of the distillate are made, and the liquid is collected until the white deposit of germanium dioxide has entirely disappeared from the column.

All of the distillates thus obtained from 4 simultaneous distillations are poured into a 12-liter, round-bottom, Pyrex flask. The volume of the distillate collected for its germanium contents from each distilling flask up to this point varies from 400 to 600 cc. Each distillation is continued still further and two fractions of 100 cc. each are run off from each still and are held while a third fraction of like volume is distilled and is tested for germanium by means of hydrogen sulfide. This last fraction will usually yield no appreciable precipitate of germanium disulfide. When such is the case, the distillation is stopped and the residue in the flask is discarded. The two preceding 100cc. fractions are then tested in turn with hydrogen sulfide, and if germanium is present, the precipitated disulfide is dissolved in a small volume of a warm, 10% solution of sodium hydroxide and this solution is then added to the combined distillates in the 12-liter flask. Some germanium dioxide usually separates on cooling in the receivers that have been used for collecting the major portion of distillates, and some of this adheres to the walls of the receiver when the liquid is transferred to the large flask. This material is recovered by dissolving it in a few cubic centimeters of a 10% solution of sodium hydroxide and this solution is added to the main portion of the distillate.

If the third 100cc. fraction shows any appreciable amount of germanium when tested with hydrogen sulfide, the distillation is of course continued and further fractions of 100 cc. each are tested until the last one is found to be practically free from germanium. In testing for the presence of germanium by means of hydrogen sulfide, a faint opalescence will be obtained. This is due to the sulfur that is formed by the reaction of the hydrogen sulfide and the small amount of chlorine that is always present in the distillate. If any considerable amount of germanium is present, the bulky character of the precipitate of germanium disulfide renders it easy to distinguish that compound from liberated sulfur. When the germanium in the test fraction is quite small in amount, it is necessary to pass hydrogen sulfide through the solution for from 30 to 45 minutes before precipitation of the germanium disulfide begins. It differs greatly in this respect from arsenic, for when arsenic is present in the distillate, its precipitation begins very soon after the passage of hydrogen sulfide is begun.

The time required for the distillation in a current of chlorine as described above, if the flow of vapor is kept at the maximum which the column will safely handle and $\frac{2}{3}$ of the distillate is returned to the column, is about 1 hour per 100 cc. of distillate drawn off. If 200 cc. of water is distilled before the germanium appears in the distillate, the total distillation will require from 10 to 12 hours, allowing about 90 minutes for heating the contents of the distillation flask to boiling. The distillation may be interrupted at any point and taken up again later.

This first distillation with column and still-head completely separates germanium from arsenic and concentrates the germanium at the same time. Any arsenic trichloride that may be volatilized in the distillation flask is converted to the pentoxide by contact in the vapor phase with chlorine and water vapor in the column and is washed back by the return-flow.

The distillate obtained in this first distillation, taken over the whole of the running, is a mixture of hydrochloric acid, water and germanium tetrachloride which is saturated with chlorine for the temperature at which it leaves the still-head. Since this temperature is close to the boiling point of the mixture, the amount of the chlorine that it contains is very small. The germanium tetrachloride is next larger in amount. The principal constituent, however, is water or hydrochloric acid, and during the early part of the distillation may be one or the other, depending on the relative amounts of these two components in the still charge.

If, after the solution of the oxides in the acid, the resultant concentration of hydrochloric acid is above that of the constant-boiling mixture of water and acid for the prevailing atmospheric pressure, the early portions of the distillate will be relatively high in hydrochloric acid and low in water. The acid concentration will after a time begin to decrease, however, as the distillation goes on, and the constant-boiling mixture will be approached from the high acid side. If, on the other hand, the reaction between the oxides and acid results in a concentration of hydrochloric acid in the still charge below that of the constant-boiling mixture, the early portions of the distillate will be relatively low in hydrochloric acid and high in water, but the acid concentration will after a time begin to increase as the distillation goes on, and the constant-boiling value will be approached from the low acid side.

If the still-head or fractionating device used in such a distillation were perfectly efficient, we should have in each of these cases only 2 products and no intermediate concentrations. In the first case, that of the higher acid concentration, these products would be hydrogen chloride and the constant-boiling mixture. In the second case, that of the lower acid concentration, these products would be water and the constant-boiling mixture, and the change between them would not be gradual, but abrupt.

In the first case, germanium tetrachloride, if present, would be expected to come over between the 2 products, hydrogen chloride and the constant-boiling mixture, because its boiling point is 86°, and that of the constant-boiling mixture is about 107°. This expectation is borne out in practice, for it is found that even in a simple distillation, where no column is used, very nearly all of the germanium chloride has passed over into the distillate when the vapor temperature has reached 107°.

In the second case, in which the resultant concentration of hydrochloric acid in the still charge after the reaction is below that of the constant-boiling mixture for the prevailing atmospheric pressure, it is also true that germanium tetrachloride is the intermediate product. From a consideration of the boiling points alone, it might be thought that the order of the products obtained in this case would be germanium chloride 86°, water 100°, and the constant-boiling mixture 107°. Germanium tetrachloride, however, like aluminum trichloride on the one hand and phosphorus pentachloride on the other, hydrolyzes in the presence of water or water vapor giving the oxide and hydrochloric acid. This germanium dioxide may, by the addition of strong hydrochloric acid and the application of heat, be re-converted to the chloride. We, therefore, have to deal here, not only in the distillation flask, but at every point in the column as well, with an equilibrium between germanium tetrachloride, water, germanium dioxide and hydrochloric acid: $\text{GeCl}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{GeO}_2 + 4\text{HCl}$.

As a matter of fact, it was found that in this first column distillation the germanium tetrachloride is hydrolyzed by the high concentration of water in the vapor entering the column and is converted to germanium dioxide and hydrochloric acid. The latter with more water forms the constant-boiling mixture. Germanium dioxide is non-volatile. These two products are less volatile than water and, therefore, water first passes over during the distillation, and germanium tetrachloride does not appear in the distillate until a point is reached during the change from water to the constant-boiling mixture at which the acid concentration of the distillate becomes high enough to prevent complete hydrolysis of the germanium tetrachloride in the column.

The use of the column and still-head accelerates the passage of germanium tetrachloride into the distillate, and thus yields a product that is very much more concentrated in respect to germanium than could be obtained in a simple distillation.

By this first distillation the germanium that was present in the 8 kg. of crude material that was charged into these stills is concentrated in a solution that need not be more than 2500 cc. in volume and that is free from the other metals which were present in the original material, including arsenic. The combined distillates from the 4 stills will contain some-

what more than 20 g. of germanium calculated as the dioxide, and the distillation has thus concentrated the germanium from 1 part in 400 of the crude material to nearly 4 parts in 400 of the solution.

Preparation of Pure Germanium Dioxide

The concentration of the germanium tetrachloride in the distillate must, however, be very considerably increased before the compound can be hydrolyzed to yield a large proportion of germanium dioxide in solid form.

The next step in this concentration consists in the distillation of the combined distillates under such conditions as will remove a considerable portion of the water that is present, without the passage of germanium tetrachloride into the distillate. To this end, the large flask containing the combined distillates is provided with a column and still-head identical with those used in the first distillation, and the liquid is distilled, this time without the use of chlorine, until the frost-like deposit of germanium dioxide appears in the lowest part of the column *C*. If the ratio of distillate drawn off at *L* to condensate returned through *J* is held at 2 : 1 during this operation, from 1400 to 1500 cc. of water can be distilled without loss of germanium. This raises the concentration of germanium in the residual liquid in the distilling flask to 8 parts in 400, and this solution will now have a volume of about 1000 cc. and will consist of approximately 4 *N* hydrochloric acid containing an amount of germanium tetrachloride equivalent to about 20 g. of germanium dioxide. To this is now added a second quantity of distillate and alkaline washings measuring about 2500 cc. obtained from a second series of first distillations of 4 more charges of crude material of 2 kg. each, and the second distillation of these combined liquids is repeated in the manner above described.

The residue of approximately 2000 cc. of 4 *N* hydrochloric acid containing an amount of germanium chloride equivalent to about 40 g. of the dioxide is now subjected to the third and final distillation in which the germanium tetrachloride is concentrated still further and is hydrolyzed to the dioxide. Before beginning this final distillation, concd. hydrochloric acid in amount sufficient to bring the acidity to 8 *N* is added to the solution. The distillation flask is then placed on an asbestos collar over a wire gauze supported on a tripod, and there is inserted into the neck a rubber stopper carrying a short, empty, Hempel tube whose side arm is connected to a Liebig condenser. The opening in the top of the Hempel tube is closed during the distillation with a rubber stopper which may carry a thermometer if desired. The further end of the condenser is connected by means of a rubber stopper to a bent adapter which carries the condensate to the bottom of a 1500cc. Erlenmeyer flask. This flask contains 600 cc. of distilled water which is kept cold by a bath of ice and water that surrounds it.

The solution in the flask is then heated to boiling by means of a triple burner. Germanium tetrachloride begins to distil as an oily liquid, heavier than water, which falls in very small drops from the end of the condenser. After a time, larger drops of a water-hydrochloric acid mixture are observed to fall from the condenser along with the smaller ones. The drops of the 2 liquids do not coalesce, but they frequently fall together, the smaller drop of the tetrachloride adhering to the larger one of the acid. The distillation is continued at a slow rate until these small separate drops of germanium tetrachloride can no longer be seen, and is then prolonged beyond this point at the same rate for 1 hour.

When the distillation is finally stopped, 2 liquid layers and a white solid are found in the receiver. The solid is germanium dioxide that has resulted from the partial hydrolysis of the germanium tetrachloride that has distilled. The lower, oily liquid layer consists of that part of the germanium tetrachloride which has not yet been hydrolyzed. The upper liquid layer, which constitutes the greater part of the distillate, contains hydrochloric acid and water with some dissolved germanium tetrachloride that has not been hydrolyzed, and some dissolved germanium dioxide. The hydrolysis of the germanium tetrachloride in the receiver is retarded because most of the germanium chloride and most of the water are in separate, immiscible layers and each layer contains considerable hydrochloric acid. Some water is, therefore, added to the material in the receiver, and the latter is taken out of the ice-bath and is shaken at intervals, while it is warming to room temperature, until the oily layer disappears and a further quantity of solid germanium dioxide separates. The supernatant liquid is now homogeneous. In order to insure that hydrolysis and precipitation are as nearly complete as is practicable, the acidity of the supernatant liquid is reduced to 3 *N* by dilution with the proper amount of water, and the flask is allowed to stand overnight. During this interval, equilibrium is reached in the hydrolysis reaction, and the precipitation of that quantity of germanium dioxide which exceeds the amount required for saturation of the solution is completed. The solid, white dioxide is then filtered on a Witt plate, using a disc of filter paper, and is washed with cold, distilled water until only a faint test for chlorides can be obtained in the wash water. The wash water is added to the filtrate. It is almost impossible to remove hydrochloric acid completely from large quantities of the dioxide by washing with water without using excessive amounts of water, which would dissolve appreciable quantities of the compound. One part of germanium dioxide dissolves in 247 parts of water at 20°. The washed dioxide is dried in the funnel at 110°, and is then transferred to a porcelain crucible and ignited over a Méker burner. This is the final product of the whole process.

The germanium dioxide adhering to the sides of the funnel and the disc

of filter paper is dissolved and washed off with a small amount of 10% solution of sodium hydroxide and this is added to the filtrate and wash water.

If there has been no loss of germanium throughout the whole process either through fault inherent in the procedure or through careless handling, all of the germanium that was charged to the stills in the first distillation in the form of the original crude material should now reappear either as (1) a residue in the last distilling flask, or (2) solid germanium dioxide, or (3) the dissolved germanium dioxide in the filtrate and wash water from (2).

The completeness of the recovery of the germanium was ascertained as follows.

The crude material was analyzed by the method of Dennis and Papish^{2c} and was found to contain 0.262% of germanium dioxide. Eight charges of 2 kg. each of this material would therefore contain 41.9 g. of germanium dioxide. The distribution of this dioxide among the 3 products resulting from the process was as follows.

	(1) In last dist. flask	(2) Solid	(3) In filtr. and wash Water fr. (2)	Total
GeO ₂ , g.	0.1	34.6	6.8	41.5
% of total GeO ₂	0.2	82.6	16.2	99.0

In continuous operation, both (1) and (3) are returned to the process in the running of the next set of charges. The residue in the distilling flask (1) is brought up to 10.6 *N* in acid by the addition of concd. hydrochloric acid, and this solution is added with further hydrochloric acid to the crude material in the first distillation. The filtrate and wash water in (3) are added to the contents of the distillation flask before the third distillation is begun and just before the adjustment of the acid concentration of that charge to 8 *N*.

Detection of Arsenic in Germanium Dioxide

Careful examination was made of different lots of germanium dioxide prepared by this process to ascertain its purity and particularly its freedom from arsenic. Four lots were thus examined, the first being that of 34.6 g. mentioned in the preceding tabulation, which we will designate Lot I, and 3 other lots, II, 302 g., III, 212 g. and IV, 237 g.

Müller^{2b} has stated that the chlorine-hydrochloric acid distillation of material containing germanium and arsenic does not yield germanium that is free from arsenic. He later described⁷ a method for the determination of arsenic in the presence of germanium which he states gives accurate results when only 0.01% of arsenic is present. Müller's test was first applied to a solution containing 0.0002 g. of arsenic trioxide and

⁷ Müller, *THIS JOURNAL*, 43, 2549 (1921).

0.4000 g. of germanium dioxide. A distinct precipitate of arsenic sulfide was obtained. The test was then used upon Lots I to IV of germanium dioxide and no evidence of the presence of arsenic was observed in any case. This demonstrates that germanium dioxide prepared by the chlorine-hydrochloric acid distillation in the manner earlier described in this article appears to contain less than 0.01% of arsenic when tested by Müller's method.

To obtain more exact evidence as to the presence of arsenic and of other metals as well in the various lots of germanium dioxide, recourse was had to spectroscopic examination of Lots, II, III and IV. This examination was kindly made for us by Dr. J. Papish, Instructor in Chemical Spectroscopy in this Department, who reports his findings as follows.

"The spectroscopic tests for arsenic were made with a Hilger E-4 Quartz Spectrograph. The procedure was that described in a previous paper.⁸ It was first established experimentally that the arsenic lines of wave length 2349.88 and 2288.18 Å. persist even when as small a quantity as 0.005 mg. of arsenic is placed on the positive electrode, and that these lines disappear when this quantity of arsenic is halved.

"In testing the various preparations for arsenic, 0.5 g. of the substance was placed in the crater of the lower, positive electrode.

"In Lot II the spectrograms showed the two most persistent lines in the ultra-violet characteristic of arsenic, but the quantity of arsenic here present was estimated to be less than 1 part in 100,000 parts of the dioxide. A small amount of iron was present in this sample.

"In the spectrograms of Lot III the half-gram sample of germanium dioxide did not show the two most persistent lines of arsenic, from which it could be concluded that the quantity of arsenic present is certainly less than 0.005 mg., and probably less than 0.0025 mg., which would mean that in this sample the arsenic was probably below 1 part in 200,000. The spectrogram showed the presence of a trace of iron in this lot.

"The spectrograms of the fourth lot of germanium dioxide did not show either of the two persistent lines of arsenic nor were the lines of iron of greater intensity than the very faint lines of this element from the iron in the electrodes themselves. This last preparation, therefore, contained either no arsenic, or an amount considerably less than 1 part in 200,000 of germanium dioxide, and iron was either absent or, if present, its amount was less than the sensitivity of the quartz spectrograph for iron. This sensitivity for iron is not known at present, but estimating its value from the quantity of iron that may be detected with the use of a spectrograph employing glass prisms and lenses, it may be placed at an amount far less than one part per 100,000."

The greater purity of Lot IV as compared with the earlier lots is doubtless to be ascribed to improved technique. After one has gained experience with the process, this high purity of the product should be attainable in every case.

Summary

A new method for the extraction of germanium from crude zinc oxide⁹ is described. Like the earlier published methods for the extraction of

⁸ Germanium II. *Z. anorg. Chem.*, **122**, 262 (1922).

⁹ Supplied by the New Jersey Zinc Company.

germanium from this material, this new method is based upon the volatility of germanium tetrachloride, but it is superior to the earlier methods in that it eliminates the necessity for the use of hydrogen sulfide and concentrates germanium by successive distillations with the aid of a column still of new design.

Ninety-nine per cent. of the germanium in the crude material is recovered. Of this, 83% is obtained directly as germanium dioxide, and the remaining 16% is recovered indirectly by the return of the material to later runs.

The germanium dioxide produced by this method is of exceptional purity. Spectroscopic examination of the material indicated that it contained less than 0.001% of iron and less than 0.0005% of arsenic.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, DAIRY DIVISION, UNITED STATES
DEPARTMENT OF AGRICULTURE]

THE DETERMINATION OF MUCIC ACID¹

BY E. O. WHITTIER

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In the course of an investigation on the products of oxidation of certain sugars, it became necessary to determine mucic and oxalic acids in the same solution. The use of potassium permanganate was thought of immediately but, since both acids are oxidizable and are not quantitatively separable from each other, it was evident that a differential method was needed. Since considerable amounts of other substances, both oxidizing and reducing, were present, the problem was further complicated.

It is frequently stated that mucic acid is entirely insoluble in water.² Beilstein's *Handbuch*³ states its solubility in water as 1 to 300 at 14°. In the preparation of mucic acid, it is separated and purified by making use of its slight solubility. It appears to be somewhat more soluble in the presence of certain other substances in solution. The calcium salt is stated to be insoluble in water, but soluble in acetic acid.⁴

The temperature at which potassium permanganate reacts with various substances in solution with acid is known to depend on the nature of the substances themselves. The temperature and speed of decolorization were determined roughly for a number of acids that are known to be

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² Richter, "Organische Chemie," Friedrich Cohen, 1909, vol. 1, p. 718.

³ Beilstein, "Handbuch der organischen Chemie," Julius Springer, 1921, vol. III, p. 582.

⁴ Hagen, *Ann.*, 64, 349 (1847).