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TENTATIVE PROCEDURES
FOR THE
ANALYSIS OF BERYLLIUM METAL AND OXIDE

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by

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National Bureau of Standards
Washington, D.C.

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~~CONFIDENTIAL~~

As a result of a beryllium conference held at the National Bureau of Standards on December 5-6, 1948, a program was initiated to compile a set of procedures for the analysis of beryllium. The purpose was to adopt a standard procedure for an element in an effort to obtain more reliable determinations for some of the constituents and to obtain better agreement by the various cooperating laboratories.

The following laboratories have cooperated in the compilation of the methods and the analysis of the standard samples.

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The procedures have been selected on the basis of the results which have been obtained on the analysis of standard samples of beryllium. The tentative results on these samples have been compiled and are given in the Report A-2951 (HNS-0-101) entitled "Beryllium Analysis on Standard Samples HI, HF, HL, ST00, and 2035".

1. Silicon

The silicon is determined by the conventional gravimetric procedure. The beryllium metal is dissolved with sulfuric acid and the silica dehydrated by heating the solution to fumes of sulfur trioxide. The conventional method while satisfactory for concentrations above 1000 ppm Si is not very satisfactory for lesser concentrations. Brush utilized the colorimetric silico-molybdate method but obtained low results, presumably because the silicon was not brought completely into solution. The Massachusetts Institute of Technology Group made a further study of the colorimetric procedure.

The gravimetric procedure used at the National Bureau of Standards and the colorimetric procedure used at the Massachusetts Institute of Technology are outlined below. For the gravimetric procedure a 5 g sample is taken and after the removal of the silica the solution is reserved for the determination of aluminum, total beryllium, calcium, magnesium, iron, copper, and nickel.

Procedure (Gravimetric). A 5 g sample is transferred to a 500 ml Erlenmeyer flask, 120 ml of $\text{H}_2\text{SO}_4(1+1)$ is slowly added until the metal is dissolved, and the solution is heated to fumes of SO_3 for 30 minutes. The sides of the beaker are washed down with 50 ml of water. After cooling, 300 ml of H_2O and 20 ml of $\text{H}_2\text{SO}_4(1+1)$ are added and the solution heated until the salts have dissolved. The solution is then filtered through a Whatman No. 42 filter

paper into a dry weighed 500 ml volumetric flask, and the paper washed four times with hot H_2SO_4 (1+19) and three times with hot water.

The insoluble material is ignited in a platinum crucible at 1100°C and weighed. The SiO_2 in the residue is then volatilized with 5 drops of H_2SO_4 and a few ml of HF . The residue is ignited at 1100°C , weighed, and the silicon content of the sample computed.

Any residue is dissolved in H_2SO_4 (1+1) to be sure to bring all the beryllium in solution, adding the solution of the residue from the volatilization to the original filtrate in the 500 ml volumetric flask which is then diluted to the mark. The solution is mixed thoroughly, and the flask and its contents weighed. The total beryllium, calcium, magnesium, aluminum, iron, copper, and nickel are determined in the filtrate.

The following is a modification of the procedure of Boyle and Hughey⁽¹⁾ as used by the MIT Group.

Procedure (Colorimetric) A 2.5 g sample is placed in a 400 ml beaker, and to it is added 100 ml of H_2O containing 5 to 10 drops of H_2SO_4 , and then gradually sufficient HNO_3 to completely dissolve the metal. The solution is heated to boiling, and a little paper pulp is stirred into it. It is then filtered through a close filter paper, and the paper washed with hot H_2O . The

paper and insoluble material are ignited in a platinum crucible, and the residue fused with 1 g of fusion mixture (1 part borax to 4 parts sodium carbonate by weight). The melt is added to the acid solution of the metal which is then poured into a 250 ml volumetric flask, and the solution diluted to the mark and mixed well. A 25 ml aliquot (equivalent to 250 mg of sample) is pipetted into a 250 ml Vycor beaker.

The pH is adjusted to 3.7 to 4.0 by the addition of small portions of powdered ammonium carbonate (a pH of 2.5 will give comparable results and will reduce the amount of carbonate used), then 5 ml of 10% ammonium molybdate solution is added, and the pH is adjusted to 2.2 to 2.3 with 1 N HCl. After 5 minutes 25 ml of a 17% sodium sulfite solution is added which will produce at first a greenish and then a blue color with possible precipitation of beryllium. After allowing the solution to stand 10 minutes 10 ml of 40% ammonium tartrate solution is added which will redissolve any precipitated beryllium and give a clear blue solution. The solution is poured into a 100 ml volumetric flask, diluted to the mark with H_2O , mixed well, and allowed to stand for 1 to 5 hours. The optical density of this solution is determined in 1 cm cells, at 710 m μ compared against distilled water. To obtain the corrected optical density a blank is carried through the procedure on the reagents and the density of the blank is subtracted from that obtained of the sample. The Si content of the sample

4

solution is obtained from an optical density-concentration standard curve prepared as described below.

A stock solution containing 40 % Si per ml is prepared by fusing .0862 g of Standard Sample of glass sand No. 81 with 10 g of Na_2CO_3 , dissolving in water, and diluting to 1 liter. From this stock solution two solutions are prepared containing respectively 10 and 20 % Si per ml. From these solutions aliquots are taken containing respectively 10, 25, 50, 100, 200, 300, 400, and 500 % of Si in 250 Vycor beakers. The aliquots are diluted to 25 ml, 1 to 2 ml of HNO_3 is added to them, and the solutions heated to boiling. The solutions are then cooled, and the color is developed and measured as above. From the measurements obtained the optical density-concentration curve is constructed.

1. Boyle, A.J., and Hughey, V.V., Ind. and Eng. Chem. Anal. Ed., 15, 619 (1943)

2. Beryllium Assay

The method for the determination of total beryllium which was adopted was a sulfuric acid solution of the metal, removal of the silica, oxine separation of the aluminum, iron, etc., ammonium hydroxide precipitation of the beryllium, ignition of the precipitate at 1100°C, and correction for the silica present in the precipitate. To minimize weighing errors a weighed aliquot of a solution of the beryllium metal was taken.

Brush utilized a volumetric procedure but because of the dependence of the method upon a standard reference sample the method is subject to appreciable error. The method might be applicable and useful if an accurate standard were obtained.

The method outlined below is that used at the National Bureau of Standards and essentially the same as that used by Clifton.

Procedure (NBS) A 10 ml aliquot of the solution from the silica determination (see Silicon), equivalent to about 0.1 g of the beryllium metal, is pipetted into a weighed glass-stoppered bottle and the bottle and its contents weighed. The aliquot is then transferred to a 150 ml beaker containing 50 ml of 2 N NH_4Ac and the solution adjusted to a pH of 4.5 by the addition of H_2SO_4 or NH_4OH . Then 5 ml of 8-hydroxyquinoline (5% solution in 2 N HAc) is added, and the solution allowed to stand 18 hours and filtered through an S & S 589 filter paper. The precipitate is washed with cold water.

To the filtrate is added 10 ml of HNO_3 (1+1) and 20 ml of H_2SO_4 (1+1), and the solution evaporated on a steam bath. To the solution is added 150 ml of H_2O and it is boiled until the salts have dissolved. A slight excess of NH_4OH is added, the solution filtered through an S & S 589 paper, and the residue washed four times with a 2% NH_4NO_3 solution (slightly ammoniacal). The precipitate is ignited to constant weight at 1100°C in a 25 ml platinum crucible. The weighing is done quickly in the covered crucible and the crucible ~~over~~ over concentrated H_2SO_4 while cooling.

The BeO precipitate must be corrected for the SiO_2 present in it. The BeO is thoroughly moistened with 2 ml of cold water and 2 ml of H_2SO_4 , and the dissolved BeO transferred to a 250 ml beaker containing 100 ml of water and 10 ml of H_2SO_4 (1+1). The solution is heated to heavy fumes of SO_3 , cooled, diluted with 100 ml of H_2O , and heated until the salts have dissolved. The SiO_2 is filtered off on a Whatman No. 42 filter paper, washed with hot water, and ignited at 1100°C in a platinum crucible. The SiO_2 is volatilized with H_2SO_4 and HF and the residue re-ignited. The weight of the SiO_2 found is deducted from the weight of the BeO precipitate and the total beryllium present in the sample is computed.

3. Calcium

The method which had been tentatively adopted is that of Clifton in which the calcium is precipitated as the sulfate in a 90% methanol solution followed by solution of the sulfate, precipitation as the oxalate, and the titration of the dissolved oxalate with permanganate. However, low results were obtained at the National Bureau of Standards utilizing this procedure. A study was therefore made to determine the feasibility of a sodium hydroxide separation. Inconsistent results were likewise obtained for low concentrations of calcium with this method.

Further investigation is desirable on the calcium determination particularly for low amounts. The agreement among the various laboratories has not been satisfactory.

The methods given below are the alkali separation procedure and the methanol separation.

Procedure (Alkali Separation) A 200 ml aliquot of the solution (equivalent to 2 g of beryllium metal) from which the silica has been removed (see Silicon) is evaporated to about 100 ml, cooled, and sufficient NaOH (1+3) is added to precipitate and redissolve the $\text{Be}(\text{OH})_2$. Then HCl is added, drop by drop with stirring, to produce a distinct uniform cloudiness causing a slight amount of $\text{Be}(\text{OH})_2$ to precipitate (the pH should be between 10.6 to 10.8, measured with a glass electrode).

The solution is filtered through a Gooch crucible containing a washed asbestos mat. Without washing, the precipitate is dissolved with 30 ml of hot HCl (1+4) and the crucible is washed three times with hot water. To the solution is added a slight excess of NH_4OH and the solution heated on a steam bath and filtered into a 400 ml beaker through an S & S 589 paper, washing the paper three times with a 2% NH_2NO_3 solution; the filtrate is evaporated to near dryness.

The precipitate is dissolved from the paper with 20 ml of hot HCl (1+1) and the paper washed three times with hot water. The filtrate is evaporated to a small volume and the $\text{Be}(\text{OH})_2$ again precipitated with a slight excess of NH_4OH . The solution is filtered through an S & S 589 filter paper into the 400 ml beaker containing the original filtrate from the first NH_4OH precipitation. The filtrate is evaporated to 100 ml. (If the first NH_4OH precipitate is small the reprecipitation with NH_4OH can be omitted.)

A few drops of methyl red is added to the NH_4OH filtrate, the solution heated to nearly boiling, and then 50 ml of a hot solution containing 1 g of ammonium oxalate is added. The solution is stirred, digested on a steam bath for 1 hour, allowed to stand overnight, and then filtered through a Whatman No. 42 filter paper into

a 400 ml beaker. The precipitate is washed four times with 0.25% ammonium oxalate solution, ignited at 1100°C to constant weight, cooled over H_2SO_4 , and weighed. The calcium content of the sample is computed from the value of the CaO obtained.

Procedure (Methanol Separation). A 2 g sample is dissolved in H_2SO_4 , the solution evaporated to as small a volume as possible without crystallization, and then to the hot solution is added 10 to 12 volumes of methanol. After 12 to 18 hours the precipitate, which may contain some beryllium, is filtered off, washed once with methanol, and dissolved from the filter with hot HCl (1+9) into the same beaker in which the precipitation was made.

The solution is diluted to 200 ml, NH_4OH added, and any beryllium which might be precipitated is filtered off. To the solution is added a few drops of methyl red indicator, 5 ml of HCl in excess, and then 50 ml of a warm ammonium oxalate solution containing 1 g of ammonium oxalate. The solution is heated to 70 to 80°C , and NH_4OH (1+1) is added dropwise with stirring until the color changes from red to yellow. The solution is allowed to stand without further heating for 1 hour and then filtered off in a Gooch, glass, or porcelain filter crucible. The crucible and precipitate are washed with small portions of cold water until the washings are chloride free, avoiding the use of more water than is really necessary. The precipitate

is dissolved by pouring 4 N sulfuric acid into the crucible (the sulfuric acid solution used should be tested for reducing substances with permanganate), allowing the acid to remain in the crucible for a minute or two before drawing it into the suction flask. (It is convenient to receive the acid solution directly in a 250 ml flask so that it will not be necessary to transfer the solution before the titration.) Solution of the calcium oxalate is hastened by stirring it in the liquid with a short stirring rod kept in the crucible. Drawing of the hot dilute sulfuric acid through the crucible is continued until all of the precipitate is dissolved. The solution is diluted with water until the sulfuric acid concentration is 1 to 1.5 N, heated to 80°C, and titrated slowly with 0.01 N KMnO_4 to the first pink tinge.

4. Magnesium

The conventional gravimetric method while unsuitable for low concentrations of magnesium gives good results for larger amounts. The procedure given below is the usual procedure following a calcium precipitation.

Procedure (NBS). The filtrate from the CaC_2O_4 (from alkali separation method) precipitation is evaporated to 100 ml, and cooled in ice. To the solution is added a few drops of methyl red, 5 ml of HCl, 10 ml of a 25% $(\text{NH}_4)_2\text{HPO}_4$ solution, and NH_4OH drop by drop to the methyl red endpoint. The solution is stirred for a few minutes, 5 ml of NH_4OH is added, and the solution is again stirred well.

The solution is allowed to stand overnight and filtered through a Whatman No. 42 filter paper. The precipitate is washed four times with cold NH_4OH (1+19), and then ignited at 1100°C to constant weight. The magnesium in the sample is computed from the weight of the $\text{Mg}_2\text{P}_2\text{O}_7$ obtained.

5. Aluminum

The colorimetric oxyquinolate procedure was adopted. The procedure is that used by the National Bureau of Standards and reported by Richmond and Rodden. (1)

Procedure (NBS). To 0.50 g of beryllium (or 1.39 g of beryllium oxide) in a 250 ml Erlenmeyer flask is added 15 ml of water, 2 ml of HNO_3 , and 15 ml of 70% HClO_4 , (a few ml at a time). After the reaction subsides, the solution is evaporated to fumes and then fumed at about 200°C for 15 minutes. (Beryllium oxides are covered and fumed about 30 minutes longer.) The sample is cooled, dissolved in water, and filtered through a No. 42 Whatman paper. Any residue obtained is saved for a separate analysis. The filtrate and washings are diluted to 200 ml and electrolyzed with a mercury cathode three inches in diameter at about 1.7 amperes for 30 minutes. The electrolyte is separated and diluted to volume. An aliquot, usually containing 50 ml of Be, is adjusted to pH 4.4 $\pm$ 0.2 in 50 ml by the addition of water and 4 N sodium acetate (272 g $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ in 300 ml water, filtered through a No. 40 Whatman paper). The pH is measured with a Beckman pH meter. The solution is extracted four times by shaking for 30 seconds with 10 ml of 0.1 M oxine in chloroform (14.4 g 8-hydroxyquinoline per liter of CHCl_3). The combined extracts are diluted to 0.04 M oxine with chloroform (U.S.P.), and about 25 ml is filtered through a No. 12 Whatman paper, to remove water. The transmittancy

of the filtered solution is measured against chloroform at 395 mμ using cylindrical cells 15 mm in diameter and a Coleman 10-S spectrophotometer.

An approximate blank correction, for the oxine and beryllium effects, is made by an empirical procedure in which the 5th extract of the sample is used as the blank for the - - 4th extracts of the sample.

The residue from the perchloric acid treatment is fused with 0.5 to 1.0 g sodium carbonate in a covered platinum crucible for 1 hour over a Meker burner. The cooled melt is digested with water and acidified with perchloric acid. The solution is then filtered, electrolyzed, and an aliquot analyzed colorimetrically as above.

- (1) Richmond, M.S. and Rodden, C.J., "Colorimetric Determination of Aluminum in Beryllium", M.B.S., A-2942, (June 1, 1947).

Additional Reference:

- (2) Gentry, C.H.R., and Sherrington, L.G., "The Analyst", 71, 432 (1946).

6. Beryllium Oxide

The method adopted for the determination of beryllium oxide in beryllium metal is the volatilization of the beryllium metal with hydrogen chloride gas at a temperature of 600°C and the colorimetric determination of the beryllium in the residue with p-nitrobenzeazoborcinol.

The determination of beryllium oxide by volatilization of the beryllium metal with hydrogen chloride was initially carried out by Kulscar at the Brush Laboratories. The method was then utilized by the National Bureau of Standards with good results.

The following procedure is that of the National Bureau of Standards. The apparatus used is shown in Figure 1.

Procedure (NBS) A 0.2 g sample of the metal is accurately weighed in a small platinum boat (2.5 by 0.5 by 0.5 inches). The sample is placed in the Vycor volatilization tube, D, directly under the heating coil E. All connections are made air tight. The stopcocks on the drying tubes G_1 , G_2 , and G_3 are opened. Helium from tank L is passed through the system at a rate of one bubble per second at the outlet A. After 10 minutes, a Meker burner is placed under K, which contains copper turnings. The heating coil E is then turned on with a Variac adjusted to give a temperature of approximately 200°C. After 1 hour, the helium rate is cut to 1 bubble in 2 seconds at outlet A. The temperature inside D at E is raised to about 600°C. The stopcocks at G_2 and G_3

Figure 1.

HCl Volatilization Apparatus

- A. 1 liter beaker containing a strong sodium hydroxide solution.
- B. Pyrex tubing, 1 cm bore.
- C. 500 ml distilling flask, containing concentrated sulfuric acid.
- D. Vycor combustion tube, 25 x 31 x 750 mm.
- E. Heating coil, chromel "A" wire, B & S gauge 18, .040 in. dia., 0.406 ohms per foot, 100 turns spaced on the Vycor tube approximately 1.5 mm apart.
- F. Pyrex tubing, 4 mm bore.
- G₁, G₂, and G₃. Schwartz drying tubes, 150 mm phosphorous pentoxide.
- H. 250 ml cylindrical separatory funnel, glass stoppered and long stem, containing concentrated sulfuric acid.
- I. 500 ml filtering flask, containing sodium chloride dried at 120°C.
- K. Quartz combustion tube, with reduced end and side tube, 520 mm long, 17 mm bore, containing copper turnings.
- L. Helium tank.

are turned off and the stopcock to the thistle tube H, which contains concentrated H_2SO_4 is opened. The helium tank valve is now entirely closed. Concentrated H_2SO_4 is allowed to react with NaCl in flask I (predried at 120°C) to give a steady, rapid flow of HCl gas, which rate can be judged by the bubbling in flask C. Beaker A contains a strong solution of NaOH which absorbs the HCl gas and any BeCl_2 . Notice is taken of the time when the last bubble of H_2 evolved from outlet A and the flow of HCl gas is maintained for 1/2 hour longer. Some gentle heating of flask I may be necessary to maintain this flow of HCl, but excessive heating must be avoided. When the reaction is completed, the rubber stopper in the Vycor tube D, holding the glass tubing B is removed. Flask I is removed and its contents washed out with water. The rubber stopper in the Vycor tube D, holding the glass tubing F is removed and the platinum boat is carefully withdrawn from this end of the Vycor tube. The residue in the platinum boat is carefully brushed into a 50 ml platinum dish. The dish is placed over a Meker burner and the residue carefully ignited to free it of any carbon. After cooling the dish, the residue is moistened with 2 ml of concentrated H_2SO_4 . The dish is placed on a hot plate and fumed for about 1 minute. After cooling, about 5 ml of water is carefully added. If all the residue is not in solution, the sample is reheated gently on a hot plate until solution of the residue is complete. The solution is transferred to a 500 ml volumetric flask, made to volume and mixed thoroughly.

For analyses of the beryllium content, two 25 ml and one 50 ml aliquots are pipetted into 150 ml beakers (the aliquot should contain 10 to 100 γ Be). To each solution is added a few crystals of NH_4Cl and 1 ml (5 mg) of aluminum solution (31 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ per 500 ml). Concentrated NH_4OH is added drop by drop until the first permanent precipitate of $\text{Al}(\text{OH})_3$ is formed and then 3 drops in excess are added. The solutions are placed on a hot plate, heated nearly to a boil, and then filtered through 7 cm Whatman No. 42 filters. The hydroxide clinging to the sides of the beakers is washed back with about 15 ml of water and the precipitate on the papers is washed with this water. This process of washing the precipitate is repeated again. It is not necessary to transfer all the precipitate to the papers. After the filtrations and washings are completed, the filters are carefully removed, opened, and the precipitates washed back into their original beakers. Not over 30 ml of water should be required to entirely remove the precipitates from the papers. It is desirable to have good lighting available to observe that all precipitate is removed from the papers.

To each solution is added, from a buret, exactly 5.79 ml of 2 N NaOH . The samples are transferred to a hot plate, carefully boiled down to about 15 ml, cooled to room temperature, and transferred to 50 ml volumetric flasks which contain exactly 10 ml of 0.64 N boric acid solution

(39.6 g boric acid per liter water). About 15 ml of water is used for washing out the beakers, leaving room in the volumetric flasks for the addition of 6.00 ml of 0.025% p-nitrobenzeneazocresinol reagent (0.125 g in 500 ml of 0.1 N NaOH, the solution stirred for several hours, and filtered through Whatman No. 54 papers). After addition of the reagent, the solutions are made to volume, and thoroughly mixed. The solutions are poured into a clean dry 100 ml beaker and allowed to stand for 5 to 10 minutes. Any filter paper fibers will settle to the bottom. The solutions are then carefully decanted into the 20 mm cells and the transmittancies determined at 520 m μ using a Beckman spectrophotometer against a reagent blank. The reagent blank is prepared by diluting 5.70 ml of 2 N NaOH, 10 ml of 0.64 M boric acid, and 6.00 ml of 0.025% p-nitrobenzeneazocresinol reagent to 50 ml.

The amount of beryllium is obtained from a calibration curve prepared by taking 10, 20, 30, 40, 50, 60, 70, 80, 100, 120, and 140 μ of standard beryllium solution (1 g of N.B.S. Beryllium Standard 2686 dried at 120°C, dissolved in 10 ml of H₂SO₄, and diluted to 1000 ml; 27.74 ml of this solution is drawn from a buret and diluted to 1000 ml to give a solution of 20 μ Be per ml).

The calibration curve obtained does not obey Beer's law. For higher concentrations the optical densities are lower than those which would be obtained if Beer's Law were obeyed.

7. Boron

The method adopted is the distillation of the boron with methanol and the colorimetric determination with turmeric. In the procedure used at the National Bureau of Standards ⁽¹⁾ fluorine does not interfere; the method even being applicable to samples of beryllium fluoride.

The following method is that used at the National Bureau of Standards.

Procedure (NBS). In a 60 ml quartz distilling flask, A, (see Figure 2) is placed 0.25 g of metal shavings or powder and 0.5 ml of HNO_3 in 2 ml of water. Then 6 ml of HCl is placed in a quartz reagent tube, C, which has a pinhole bottom orifice; loss of acid is avoided by tilting the tube until its top has been closed with a stopper-airvent-pinch clamp assembly. The reagent tube and sample flask are connected to a quartz reflux tube, E, which has a 3 mm bottom orifice. A 4 l beaker of water at about 20°C is placed around the sample flask. Then the HCl is allowed to drop in slowly (about 5 seconds per drop initially). as soon as reaction starts 3 ml of water is put in the refluxer, to serve as a wash for gaseous products and as a reaction rate indicator. After all the HCl has been added and reaction nearly ceases, the solution is heated just to boiling for 10 minutes. The solution is cooled and removed from the refluxer.

(If the sample is in the form of pellets or solids a 1.50 g sample is placed in a 150 ml quartz flask with 15 ml of HNO_3 (1+4) and 10 ml of H_2O . The flask, reagent tube,

Figure 2

and refluxer

are connected and the water bath is placed around the sample flask. Then 36 ml of HCl is added slowly through the reagent tube. From 3 to 8 ml of H_2O is added through the refluxer during reaction. After all the HCl has been added and reaction nearly ceases, the solution is heated just to boiling for 15 minutes. The solution is cooled, removed from the refluxer and diluted to 69 ml. An 11.5 ml aliquot is taken for distillation.)

The solution to be distilled is adjusted to an **apparent** pH between 2 and 4 as indicated by alk-acid test paper. The method used for adjustment depends on the beryllium content of the solution. Thus for solutions containing 0.25 g of Be, which are highly buffered, the adjustment is usually made by a single addition of enough concentrated ammonia water (prepared by passing tank NH_3 into distilled water in quartz until 4.4 ± 0.4 ml is equivalent to 5 ml HCl, and stored in a refrigerator) to neutralize about 3.0 ml of HCl. This gives a gelatinous precipitate which is redissolved by standing, with occasional shaking at room temperature for 15 to 20 minutes. If the precipitate dissolves much faster or slower, more NH_3 or HCl (5 drops at a time) is added. If the solution contains only 0.10 g of Be, a single addition of NH_3 should give a precipitate which redissolves in 10 minutes. For unbuffered solutions, such as blanks, methyl red is used as a guide: NH_3 is added until the indicator turns yellow and the HCl is added to 2 drops in excess of the return of the red color (methyl red is destroyed if it is added to the initial, strongly acid solution; its addition

should be delayed until most of the excess acid has been neutralized).

During the ammonia addition, the sample should be cooled in an ice bath and mixed cautiously to avoid loss of boron in the heavy fumes. After the acidity adjustment has been completed any insoluble fumes in the sample flask, A, are blown out by means of a very gentle current of nitrogen. Then 25 ml of 10% CaCl_2 in methanol is added and the flask is connected to the still (see Figure 3) which has been provided with a 200 ml receiving dish (4.5 in. dia., #7 Amersil or Coors #4A porcelain dish) and a flask, B, containing 25 ml of redistilled methanol and a pellet of potassium or sodium hydroxide. The dish is supported in an enclosed water bath which consists of a 6 inch crystallizing dish with a plastic (Pittsburgh Plate Glass CR-39) cover, and is protected from the heat of the burners by a transite shield. The condenser tube passes through the hole in the center of the cover almost to the bottom of the receiving dish. Immediately after connection of the sample to the still, 5 ml of 0.1 N lime is added (through a second hole in the cover) to the receiving dish. Then the flasks A and B are immersed in beakers of hot water and heated gently so as to keep beaker at B at 80 to 82°C, and the beaker at A at 76 to 78°C. As the alcohol in flask B distills over, successive portions are added until a total of 125 ml has been added to flask B. The volume in flask A is maintained at about 35 ml by controlling the difference in temperature

SCALE
1 2 3 4
Centimeters

Figure 3

between the two beakers, and the depth to which the flasks are immersed in the water baths. After all the alcohol has been distilled from flask B, heating is discontinued, the stoppers in the flasks are loosened, and the end of the condenser tube is washed with 10 ml of water. Immediately, an extra 5 ml of lime is added to the distillate and the solution is evaporated to dryness on the steam bath.

The dry sample is ready to be analyzed colorimetrically (if necessary it can be stored satisfactorily in a desiccator containing a small dish of NaOH pellets and sealed with vaseline). For analysis, the dry sample is removed from the steam bath and cooled to room temperature. Then 2 ml of dilute oxalic-hydrochloric acid reagent (80 g $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ dissolved in 540 ml H_2O , 320 ml $\text{C}_2\text{H}_5\text{OH}$, and 100 ml HCl) is added. The dish is manipulated so as to bring the reagent into contact with all the lime. Then 2 ml of turmeric extract (1 g of turmeric stirred with 95% ethanol for 2 to 3 hours and the solution filtered through boron-free paper and stored in the dark) is added and the dish is swirled until all reagents are mixed thoroughly. Each of these reagents is added rapidly from a coarse tipped pipet. The dish is placed in a water bath containing enough water to just float the dish which is kept at $55 \pm 1^\circ\text{C}$ until the sample is just dry and then for 30 or 45 minutes longer. The dish is removed from the bath and cooled. With the aid of a rubber tipped stirring rod the precipitate is extracted with 90% ethanol added in 5 to 8 ml

portions. The extracts are poured into a 25 ml graduate, diluted to 25 ml with 90% ethanol, mixed, and filtered through a dry 11 cm No. 42 paper. The transmittancy of the solution is determined using as a reference the blank obtained by carrying 5 ml of lime through the procedure, beginning with evaporation on the steam bath. Known amounts of boric acid (0.5 to 1.5 % of boron) plus 5 ml of 0.1 N lime each, are carried through the color development with each group of samples. The transmittancies are measured with a Coleman 10-S spectrophotometer at 540 mμ. The boron content of the test solution is obtained from a transmittancy concentration curve and then is corrected for a solution blank which is run through all steps of the procedure except that no beryllium sample is used.

A correction is also made for the average loss in the solution, neutralization, and distillation step. This is determined by analyzing samples both alone and with added amounts of boron.

- (1) Martinez, Z., Norris, J.M., Richmond, M.S.,
"Determination of Boron in Beryllium and Its
Compounds", N.B.S., A-2943 (June 1947).

8. Cadmium

The dithizone-polarographic method ⁽¹⁾ has been found to be applicable for the determination of cadmium in beryllium metal in concentrations down to 0.2 ppm of cadmium. The mercury electrolysis-distillation-polarographic method gave poor recoveries for low concentrations ⁽¹⁾ of cadmium.

The dithizone-polarographic method is given below.

Procedure (NBS) In a 250 ml Erlenmeyer flask is placed 3 g of sample, 10 ml of water, and 4 drops of H_2SO_4 (1+1). The flask is covered with a stemless (or short-stem) funnel and placed in a pan of cold water. From a dropping funnel 66 ml of HNO_3 (2+1) is added through the funnel to the sample at a rate of 3 seconds per drop; then 15 ml of HNO_3 is poured in. After the reaction slows down the flask is heated cautiously on a low temperature hot plate until the reaction is complete. The speed of reaction increases rapidly with increase in temperature and the sample may boil over if it is warmed before most of the metal has dissolved. It is desirable to have within reach an extra container of cold water in which to nearly immerse the flask and thus bring the reaction under control if necessary. After the reaction appears complete, the flask is uncovered and the solution is heated nearly to boiling for 15 to 30 minutes (to insure maximum reaction, and to remove gases), cooled, filtered

through a 9cm Whatman No. 42 paper and washed. The filtrate is ready for the extraction step unless it contains much lead.

If the filtrate contains more than 100 γ of lead most of it is removed by electrolysis as follows. The filtrate is adjusted to about 150 ml of 0.5% HNO_3 solution by the addition of 21 ml of 45% NaOH (453 g of NaOH dissolved in 897 ml of H_2O and filtered through a 15 cm Whatman No. 54 paper), cooled, and then electrolyzed at about 3 to 4 V (0.1 to 0.4 amps.) and stirred overnight using platinum gauze electrodes. The electrolyzed solution is separated quickly from the electrodes before the current is turned off, and the electrodes are not washed. (Between samples the electrodes may be cleaned easily by treatment with HNO_3 .) The solution is heated near boiling to remove gaseous electrolytic products, and after cooling is ready for the extraction step.

To the filtrate or electrolyzed solution from the above, in a 500 or 600 ml Erlenmeyer flask, is added 1 ml (depending upon the type of sample) of dithizone-extracted 25% sodium tartrate at a pH of 9 (purified by extracting with 0.05% dithizone in CHCl_3 , extracting the excess dithizone with CHCl_3 , filtering, and storing in the dark) and approximately 5 ml excess of 45% NaOH (a total of 131 ml is required for the filtrate or 110 ml for the electrolyzed solution). The solution is mixed and cooled

simultaneously by swirling the flask under running water. The flask is then placed in a pan of water and swirled occasionally until the beryllium hydroxide adhering to the flask is dissolved. The practically clear solution obtained is transferred to a 500 ml separatory funnel containing a few ml of CHCl_3 , which reduces seepage of the sample solution into the stem of the funnel. The solution, diluted to about 300 ml, is then extracted with filtered 0.05% dithizone in CHCl_3 , using a 100 ml portion and then several 50 ml portions, continuing until two (brown) green extracts are obtained. Each portion is shaken with the sample for 60 seconds.

Each extract is added to a second 500 ml separatory funnel containing 70 ml of 0.1 HCl , mixing 10 to 15 seconds after each addition, and a final shaking of 60 seconds after the last addition. Then the CHCl_3 layer is discarded and the aqueous layer is washed with two 5 ml portions of CHCl_3 . The last one is allowed to separate for about 15 to 30 minutes. The CHCl_3 wash is discarded and the aqueous layer is poured into a 150 ml beaker. The flask is rinsed 3 times, first with about 10 ml of HCl (1+10), and then with two 5 to 10 portions of water. Each rinse is poured into the sample. Then 1 ml of HNO_3 is added and the solution is concentrated by evaporation without boiling. After evaporation to about 25 ml, the solution is transferred to a 50 ml beaker,

a few drops of HNO_3 and 1 ml of 70% HClO_4 are added, and the solution is evaporated to fumes. It is then heated at about 200°C until no fumes are visible. The sample is cooled, taken up with a little water, a few drops of HNO_3 , and 1 ml of HClO_4 , and evaporated and fumed again as above.

The walls of the beaker are then washed down with about 2 ml of water, and two drops of filtered 0.01% methyl orange (aqueous) are added. The acidity is adjusted to a pH of about 3 to 4 by dropwise addition of 0.05 N and 0.01 N NaOH or 0.01 N HClO_4 , as needed. Then 3 ml of 0.24 N NaClO_4 reagent (475 ml of H_2O , 11 ml of 45% NaOH , and 10 ml of 70% HClO_4 mixed and adjusted with HClO_4 to a pH 3.5) is added and the solution is evaporated to dryness; it is permissible to continue the heating as much as 30 seconds after the residue looks dry. The residue is allowed to cool (if desired, it may be stored in a desiccator at this stage) and then taken up with 1 ml of H_2O . It is allowed to stand at room temperature for 5 minutes. Then 0.5 ml of 0.02% gelatin is added, and the solution mixed and poured into the polarographic cell, which contains mercury for the anode. Oxygen is removed with a stream of oxygen-free nitrogen which is passed through the solution for 1 minute and then over the solution while the polarogram is made.

- (1) Richmond, E.B. "Determination of Cadmium in Beryllium Metal", *ANAL. A-1948* (November 1947)

9. Carbon

The determination of carbon by combustion in a stream of oxygen and subsequent weighing of the resulting carbon dioxide has been studied by Lais and Reed.⁽¹⁾

The primary difficulty has been obtaining a complete combustion. Using a bed of sand, complete combustion at 1200°C was obtained with the addition of as little as 0.1 g of copper for 1 to 2 g of beryllium metal.

The procedure gave consistent values for the carbon with blanks of about 0.5 ng. Porcelain boats which were used are not too satisfactory because they are attacked by the slag and tend to crack and freeze to the combustion tube. Boats of other refractory material, such as chrome refractory are suggested for study.

The procedure which is given is that of Lais and Reed.⁽¹⁾

Procedure (MIT) The combustion-tube shown in Figure 4 is heated to 1200°C and oxygen is passed through the train at the rate of 300 ml/minute at a pressure of 2 in. of Hg until the ascarite bulb is at constant weight. The bottom of the porcelain boat, 5" long by 1/2" wide, is lined with 7 g of calcined sand, 1 to 2 g of beryllium metal chips is evenly distributed over the layer of sand, 0.1 to 0.2 g of copper is placed on the beryllium metal and concentrated in one spot (the copper is not effective if it is distributed over the surface of the beryllium

Fig. 1

metal), and then a layer of 7 g of calcined sand is placed over the metal (see Figure 8).

The boat is placed in the hot zone of the combustion tube and, with the stopper in place, the oxygen is passed through the system. After 2 to 10 minutes the metal starts to burn, the burning taking about 10 to 30 seconds. During the burning period the pressure drops and the flow of oxygen is increased to maintain a pressure of 2 in. of Hg.

After the completion of the combustion the flow of oxygen is maintained at the same pressure for 5 to 10 minutes. The ascarite bulb is then removed and weighed. A blank (usually about 0.5 mg) with only sand and copper in the boat is run before and after each sample.

- (1) Zeis, A.M. and Read, E.B., "Determination of Carbon in Beryllium Metal", MIT, M-4078 (July 1947).

Figure 5

10. Chlorine

The distillation of the chloride followed by nephelometric determination has been adopted as the standard procedure for concentrations of chloride less than 1000 ppm. The conventional gravimetric procedure is suitable for larger concentrations.

The National Bureau of Standards Group is investigating the possibility of determining the chloride nephelometrically directly in the presence of beryllium.

The following procedure is that used at the Iowa State Laboratory and is a modification of the method described by Wexler.⁽¹⁾ The apparatus used is shown in Figure 6. It must be thoroughly cleaned with cleaning solution, tap water, distilled water, and finally with redistilled chloride-free water. All reagents should be prepared with redistilled water.

Procedure (Iowa State). After sweeping the chloride apparatus thoroughly with steam from redistilled water, about 1 g sample is carefully introduced into the reaction flask and 20 ml of HNO_3 containing 10 to 15 drops of H_2SiF_6 (1+50) is placed in the dropping funnel. Twenty-five ml of 0.05 M Na_2CO_3 solution (5.30 g of Na_2CO_3 per liter) is used in the receiving vessel to catch the evolved HCl . The tip of the condenser tube should extend just below the surface of the Na_2CO_3 solution. Air (purified over soda-lime) is blown through the apparatus so as to cause a flow of one bubble per second in the receiver. Dust is excluded by covering the receiving vessel with a piece of filter paper torn to fit the condenser tube and cover the opening. Then the HNO_3 is cautiously dripped onto the beryllium sample. The reaction flask may be heated with a low flame to aid in

dissolving the last of the sample. When solution has been effected, the distillation flask is surrounded with a salt bath (7% NaNO_3 , 40% NaNO_2 , and 53% KNO_3) and the salt bath heated until a temperature of 300°C is reached. This temperature is maintained until the beryllium nitrate is converted to the oxide. At this point the horizontal portion of the condenser tube is heated to drive over the last droplets of moisture which have collected there. While the reaction flask is cooling 20 ml of H_2SO_4 is slowly run into the reaction flask. After the beryllium oxide has dissolved the temperature of the salt bath is maintained at $150 \pm 50^\circ\text{C}$ for at least one half hour. At the end of this time, the air flow is increased to about 2 bubbles per second in the receiving vessel. Distillation is continued until the volume of the distillate reaches 50 to 55 ml. A close watch on the air flow is necessary in order to avoid suckbacks. At the end of the distillation, the horizontal portion of the condenser tube is heated to drive over the last drops of moisture. The receiver is lowered, and the tube allowed to drain.

The distillate from the sample is transferred to a 100 ml glass stoppered graduated cylinder. At this time a comparison standard is made up by adding 25 ml of 0.05 N of Na_2CO_3 , 4 ml of HNO_3 (1+1), V ml (usually 4 ml) of the standard KCl solution (a stock solution is prepared by dissolving G grams, about 1 g, of KCl in 2000 ml of water; 10 ml of this solution is diluted to 1 liter) and (11-V) ml of redistilled water to another 100 ml glass stoppered graduated cylinder. An apparatus blank is also included in every set of runs. This apparatus blank is made by placing the same amount (V ml) of the

standard KCl solution as was used in preparing the comparison standard in the apparatus and distilling it in the same manner that a sample is distilled. The distillate from the apparatus blank is also placed in a 100 ml glass stoppered graduated cylinder. Ten ml of 0.01 N AgNO_3 solution (1.70 g AgNO_3 per liter) is added to each of the cylinders and after shaking (each the same way and the same number of times) they are placed in a $40 \pm 5^\circ\text{C}$ thermostated bath for 1/2 hour. After removal and cooling to room temperature, the volumes are recorded and the turbidities of the apparatus blank and of the sample are compared with the turbidity of the comparison standard within 45 minutes.

The amount of chloride in the sample is computed from the following relationships

$$K = \frac{2.375 G V V_b R_s}{V_s R_b}$$

$$X = \frac{2.375 G V V_u R_s}{V_s R_u}$$

$$\text{and } \text{ppm Cl} = \frac{X + 2.375 G V - K}{W}$$

Where G = the grams of KCl in 2 l of standard KCl solution, V = the volume in ml of standard KCl used in the comparison standard, V_b = the volume from the apparatus blank, V_u = the volume from the sample, R_b = the reading of the cup containing the apparatus blank, R_s = the reading from the cup containing the comparison standard, R_u = the reading of the cup containing the sample, and W = the weight of the sample in grams.

(1) Wexler, S., CG-358, (December 15, 1942).

11. Chromium

The diphenylcarbazide method used by the Battelle and the Argonne laboratories has been adopted as the standard procedure. While the agreement between the two laboratories using the procedure is fairly good, the agreement with the spectrographic values is poor. No other laboratory has reported results using the chemical method.

The following procedures are those used at the Argonne Laboratory and at Battelle. Chromium is oxidized to the hexavalent state by potassium permanganate in an acid medium. The resulting chromium (VI) reacts with S-diphenylcarbazide in a solution approximately 0.25 N in sulfuric acid to form a reddish purple colored complex of unknown composition. The color of this complex obeys Beer's Law.

Procedure (Argonne) A one to two gram sample of the metal is dissolved in a minimum amount of H_2SO_4 , and the solution is cooled, transferred to a 100 ml volumetric flask, and diluted to volume. A suitably sized aliquot (containing 1 to 20% of Cr) is transferred to a 100 ml beaker, 2 ml of H_2SO_4 is added, and the solution is gently heated to fumes of SO_3 . (This step is necessary to destroy the small amount of organic matter which is present in some

of the standard samples and which would interfere later in the oxidation of the chromium using permanganate.) The sample is cooled and the excess of H_2SO_4 is exactly neutralized with 6 N NaOH using a Fisher Titrimeter to detect the neutralization point of the reaction. (A Fisher Titrimeter is used to detect the endpoint since it was found that if phenolphthalein is used the small amount of organic matter thus introduced interferes with the oxidation of the chromium by the permanganate.) The solution is acidified by the addition of 0.4 ml of H_2SO_4 and then 0.1 N KMnO_4 is added dropwise until the solution is distinctly pink. The solution is boiled for two minutes and then small amounts of sodium azide are added until the pink color of the permanganate is discharged. In order to remove the hydrazoic acid the solution is boiled for another minute after which time the solution is transferred to a 50 ml volumetric flask and cooled in an ice bath. One ml of 1% alcoholic solution of S-diphenylcarbazide is added, the solution is diluted to volume, and the percent transmittency is read on a spectrophotometer at 540 m μ using a blank on the reagents as a reference solution. The concentration of chromium in the aliquot is obtained from a previously prepared transmittency-concentration curve.

Procedure (Battelle). A 1.0 g sample is dissolved in 12 ml of H_2SO_4 (1+1). The solution is diluted to 250 ml, boiled, 10 ml of 0.25% AgNO_3 solution and 10 ml of 10% $(\text{NH}_4)_2\text{S}_2\text{O}_8$ are added, and the boiling is continued vigorously for a minimum of 30 minutes. The solution is cooled, transferred to a 250 ml volumetric flask (any insoluble matter should be removed) and diluted with water almost to the mark. Two ml of 0.5% diphenylcarbazide (in equal parts of water and acetone) is added and the solution diluted to the mark. The solution is then mixed and the density is read at 545 m μ using a Beckman spectrophotometer and a 0.015 slit.

Results are calculated by means of additional standards from the following relation:

$$D_2 = \frac{D_1}{C} (C+A)$$

where D_1 is the optical density before addition of a small amount of Cr, D_2 is the optical density after the addition, C is the concentration of the unknown and A is the concentration of the known Cr which is added.

12. Copper

The colorimetric dithizone method has been adopted for the determination of copper in beryllium. At a pH of 1 the only possible interfering elements are silver, gold, mercury, and palladium which can be neglected in the analyses of beryllium samples. The mixed-color method which is used is quicker and more reproducible than the mono-color method.

The following procedure is that used at the National Bureau of Standards.

Procedure (NBS). A 100 ml aliquot of the filtrate from the silica determination (equivalent to 1 g of the beryllium sample) is taken and the solution evaporated to about 90 ml, adjusted to a pH of 1 with NH_4OH or H_2SO_4 , and diluted to 100 ml (the pH will not be appreciably affected). Copper and nickel are determined on aliquots of this solution.

An aliquot of the above solution (usually about 0.25 g of beryllium) containing about 25 of copper is pipetted into a separatory funnel. To this is added, if necessary, H_2SO_4 at a pH of 1 to make the volume 25 ml, and from a buret, 15.0 ml of a 0.005% CCl_4 solution of dithizone. The solution is shaken vigorously for two minutes, the layers allowed to separate, and the organic layer drawn off into a 50 ml volumetric flask, transferring the organic layer quantitatively by washing the solution with small

portions of CCl_4 . The organic layer is then made to 50 ml by the addition of CCl_4 and mixed well.

About 25 ml of the dithizone extract is filtered through a filter paper into a small dry glass-stoppered Erlenmeyer flask and the transmittancy of the solution measured on a Beckman spectrophotometer at 515 m μ , using a 1 to 2 m μ bandwidth and 2 cm cells, against a blank carried through the procedure.

The copper concentration is determined by reference to a standard curve prepared from readings obtained by taking 0, 5, 10, 15, 20, and 25 $\%$ of copper (a stock solution is prepared by dissolving 1 g of pure Cu metal in 25 ml of H_2SO_4 and 10 ml of HNO_3 and diluting to 1 liter; 5 ml of the stock solution is diluted to 1 liter to give a standard solution containing 5 $\%$ Cu/ml) in about 25 ml of 0.1 N HCl, extracting the copper, and determining the percent transmittancy of the extracts as previously described.

Since the standard curve obtained is dependent upon the strength of the dithizone solution used for the extractions, the strength of the solution should be checked from time to time to determine the reliability of the standard curve. This is done by measuring the 0.005% dithizone solution against CCl_4 . Tests indicate that the 0.005% dithizone solution is stable over a long period of time if it is kept in a dark place.

13. Fluorine

The pyrohydrolytic procedure as used at Iowa State College has been adopted as the standard procedure for the fluorine determination. Under the conditions of the procedure it was found that the fluoride if present as magnesium fluoride was 94% hydrolyzed.⁽¹⁾ The pyrohydrolytic method for the determination of fluoride has been treated in detail by Harf and Cline.⁽²⁾

The procedure is outlined below. The apparatus used is similar to that shown in Figure 7.

Procedure (ISC). The furnaces are heated to 700 to 800°C and steam is passed through the apparatus at a rate of 0.5 g per minute. This rate corresponds to a setting of 80 volts on the variable transformer that regulates the temperature of the water heater. The tip of the condenser should not dip beneath the surface of water in the silver dish receiver. A sample of beryllium, containing from 0.5 to 40 of fluorine (usually about 2 g), is weighed into a platinum foil boat and inserted in the platinum reaction tube of the pyrohydrolysis apparatus. A steam rate of 0.5 g per minute is maintained until the vigorous evolution of hydrogen has subsided and it is then increased to 5 g per minute and maintained at this rate until a total of 35 ml of distillate has been collected. This rate corresponds to a setting of 120 volts on the

Figure 7

- A - 2 liter bottle filled with distilled H_2O .
- B - 500 ml Florence Type wash bottle.
- C - Fisher Electric Heater, 550 watt.
- D - 500 ml Florence Type wash bottle.
- E - Condenser, part of platinum tube.
- F - Platinum reduction tube.
- G - Electric Furnace
800° - 900°C
- H - Glass condenser.

Figure 7

SCALE: 1cm = 4cm

The distillate is transferred to a 50 ml Nessler tube, 2.0 ml of 0.05 N HCl and 1.0 ml of 0.1% indicator solution (0.1000 g of sodium alizarin sulfonate is dissolved in 1 liter of distilled water), are added, and the solution diluted to the mark with redistilled water. This solution is titrated with 0.0004 N $\text{Th}(\text{NO}_3)_4$ (5.52 g of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ is dissolved in enough water to make 1 liter of stock solution; the 0.004 N solution is prepared by diluting 10 ml of the stock solution to 1 liter) to a pink endpoint. A reference solution is prepared by adding 40 ml of redistilled water, 1.0 ml of the indicator solution, and 2.0 ml of 0.05 N HCl to a 50 ml Nessler tube and diluting to the mark with redistilled water. A volume of 0.004 N $\text{Th}(\text{NO}_3)_4$ equal to that required by the sample is added to the reference solution. The reference solution is now titrated with a standard NaF solution (2.211 g of NaF is dissolved in enough water to make 1 liter of stock solution which is stored in a wax or rubber bottle; the standard solution containing 10 $\mu\text{F}/\text{ml}$ is prepared by diluting 10 ml of the stock solution to 1 liter) until the color matches that of the endpoint of the sample. The amount of NaF added is a measure of the quantity of fluoride in the sample.

The concentration of fluoride in the sample is computed from the following:

$$\text{ppm F} = \frac{(\text{ml of Std. NaF}) (10)}{\text{wt. of sample in grams}}$$

- (1) Bank, C.V., and Krause, D.P., "The Study of the Hydrolysis of Refractory Magnesium Fluoride", Iowa State College (February 1947).
- (2) Warf, J.C., and Cline, W.D., "Pyrohydrolysis in the Analysis of Fluoride and Other Halides", Iowa State College, CO 2723 (September 1945).

14. Iron

The colorimetric 1,10-phenanthroline method has been adopted for the determination of iron in beryllium metal. The agreement between the laboratories employing the method is good.

The following procedures are those used at the National Bureau of Standards and at the Iowa State College and are essentially identical.

Procedure (NBS) An aliquot of the filtrate from the silica determination (usually 0.1 to 0.25 g) containing 100 to 150 γ of iron is pipetted into a 150 ml beaker. The volume is diluted to about 75 ml, 1 ml of 10% $\text{NH}_2\text{OH} \cdot \text{HCl}$ and 10 ml of 0.1% 1,10-phenanthroline solution are added to it, and the pH adjusted to 3.5 with NH_4OH using a Beckman pH meter. The solution is then made to 100 ml and the transmittancy measured on a Beckman spectrophotometer at 515 m μ , using 2 cm cells and a 1 to 2 m μ bandwidth, against a reagent blank carried through the procedure.

The iron concentration is determined from a standard calibration curve prepared from readings obtained as follows. Six 0.25 g samples of BeO , No. 2686, are dissolved in 2 ml H_2SO_4 and 5 ml H_2O , and the solutions diluted to 20 ml. To the solutions are then added from a buret respectively, 0, 5, 10, 15, 20, and 25 ml of standard iron solution (1 g of electrolytic iron is dissolved in 50 ml of H_2SO_4 (1+1) and the solution diluted to 1 liter; 10 ml of this solution

is diluted to 1 liter to give the standard solution of 10 % Fe/ml). The solutions are diluted to about 75 ml, the color developed, and the transmittancies measured as given above for the samples.

Procedure (ISC) A standard curve is prepared as follows. Solutions containing 0, 20, 40, 60, 80, 100, 120, 140, 160, 180, and 200 % of iron per 100 ml are prepared by placing 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20 ml of the standard iron solution (containing 10 % of iron per ml prepared by dissolving 20 mg of pure iron wire in a minimum amount of HCl and diluting the resulting solution to 1000 ml) in a series of eleven 100 ml volumetric flasks. One ml of 10% $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution and 10 ml of 0.1% 1,10-phenanthroline solution are added to each of the flasks. The pH of each solution is adjusted to 3 to 5 with NH_4OH and HCl, followed by dilution to the 100 ml mark with distilled water. These solutions are, one at a time, placed in a 1 cm cuvette and their transmittancies determined with a spectrophotometer.

One gram samples of beryllium are cautiously dissolved in 25 ml of HCl (1+1) and 2 ml of HNO_3 . The solutions are evaporated to near dryness, quantitatively transferred to 100 ml volumetric flasks, and diluted to the calibration mark. Suitable aliquots are taken (20 ml aliquots suitable

for iron concentrations from 200 ppm to 800 ppm) and transferred to 100 ml volumetric flasks. These aliquots are diluted to about 50 ml. One ml of 10% $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution and 10 ml of 0.1% 1,10-phenanthroline solution are added to each diluted aliquot. The pH of each solution is adjusted to 3 to 5 with NH_4OH and HCl , followed by dilution to the 100 ml mark with distilled water. The samples are compared against a reagent blank prepared as above. Samples may be centrifuged after color development and dilution if necessary.

15. Lead

Argonne has determined lead in beryllium polarographically, taking the sample in solution with hydrochloric acid and making no separation. Clifton has used the electrolytic separation of the lead as lead dioxide and then colorimetrically determined the lead as the dithizonate. The Clifton procedure gives high results.

The Argonne direct polarographic procedure seems to give satisfactory results, however, a colorimetric procedure is desirable, because of the unavailability of a polarograph by some laboratories. The National Bureau of Standards have successfully adopted the colorimetric dithizonate procedure utilizing a sulfate separation with strontium as a carrier.
(1)

The following is the polarographic procedure used at Argonne. The dithizonate procedure is being written and will be made available later.

Procedure (Argonne). Two grams of beryllium metal are dissolved by slowly adding 30 ml of HCl to the sample. (Distilled water may be added to control the rate of reaction.) The solution is diluted to 100 ml with distilled water and introduced into a polarographic cell. The cell is immersed in a constant temperature water bath kept at 25° C. Purified nitrogen is bubbled through the solution for 15 to 20 minutes. A Heyrovsky Polarograph, Model XI is used at a sensitivity of 5, with a total bridge voltage of 1.5 volts. It was found convenient to start the analysis with the Applied Potential Scale set at 0.1. With a saturated calomel reference electrode, the half wave potential for

Pb occurred at about - 0.4 volts. The diffusion current is measured and the Pb concentration read from a curve plotting diffusion currents or wave heights against concentration. The curve is produced by duplicating the conditions of the actual analysis with known amounts of Pb, prepared by adding Pb solutions containing a 2 g of lead-free beryllium metal dissolved with 30 ml of HCl all diluted to 100 ml.

1. Eberle, A. R., and Petretich, G. J., "The Dithionite Determination of Lead in Beryllium," NBS, A-2952 (December, 1947).

16. Manganese

The conventional colorimetric periodate-permanganate method has been adopted as the standard procedure for the determination of manganese in beryllium metal. All the cooperating laboratories used this procedure and the agreement obtained on the analysis of the standard samples has been good.

The following procedure is that used at the National Bureau of Standards.

Procedure (NBS) To a 1 g sample in a 400 ml beaker is added about 10 ml of H_2O and then very carefully 10 ml of H_2SO_4 (1+1). After the reaction has subsided the sides of the beaker are washed with water and then 40 ml of H_2SO_4 (1+1) is added. The solution is heated until all the metal has reacted, and then evaporated to fumes of SO_3 . The solution is cooled, 40 ml of H_2O is added to it, and it is then heated until all the salts have dissolved. After cooling to room temperature it is filtered through a Whatman No. 40 filter paper into a 250 ml beaker, and the paper washed with 25 ml of H_2O . To the filtrate is added 0.5 g of KIO_4 , and it is boiled for at least 5 minutes. After complete oxidation, the solution is cooled, transferred to a 100 ml volumetric flask, made to volume, and mixed thoroughly.

The transmittancy of the solution is measured on a Beckman Spectrophotometer at 525 mμ against H₂O using a 1 to 2 mμ bandwidth and 2 cm cells. The manganese content of the sample is determined from a standard calibration curve prepared from readings obtained by taking 0, 5, 10, 15, 20, 25, and 30 ml of standard manganese solution (0.2877 g of KMnO₄ dissolved in 1000 ml; 100 ml of this solution is diluted to 1000 ml to give the standard solution containing 10 γ Mn/ml) and carrying the standards through the procedure.

17. Nickel

The Argonne Laboratory found that the direct colorimetric determination of nickel in beryllium by oxidation of the dimethylglyoxime complex gave high results compared to their spectrographic values. The National Bureau of Standards likewise got high results employing the direct colorimetric determination, presumably due to the interference of copper, manganese, and iron in the samples. However, by first separating the nickel dimethylglyoxime with chloroform favorable agreement was obtained with spectrographic results. No other laboratories determined nickel chemically. The Massachusetts Institute of Technology Group is working on the extraction of the nickel dimethylglyoxime with chloroform, and the colorimetric determination of the nickel with sodium diethyldithio-carbonate and extraction with benzene.

The following procedure is that used at the National Bureau of Standards. While the interference due to copper is slight it is nevertheless desirable to remove the copper.

Procedure (NBS) An aliquot of the solution used in the analysis of copper and previously adjusted to a pH of 1 (see the procedure for the determination of copper) is extracted with dithizone to remove the copper, and with carbon tetrachloride to remove the dithizone. The solution

is then heated slightly to remove the carbon tetrachloride.

To the solution is added 5 ml of CHCl_3 and 5 ml of ammonium citrate. The solution is mixed well and 5 to 6 ml of NH_4OH is added to it and it is again mixed well. Then 3 ml of 1% dimethylglyoxime solution is added and the nickel extracted by shaking vigorously for one minute. The CHCl_3 layer is drawn off into a 60 ml separatory funnel containing 10 ml of 0.5 N HCl. The funnel tip is washed out with about 5 ml of CHCl_3 , catching the wash solution in the separatory funnel. The beryllium solution is again extracted with 5 ml of CHCl_3 and the extracts combined.

The CHCl_3 extracts are shaken vigorously with the acid for one minute, the CHCl_3 layer is drawn off, the funnel tip dried with a piece of filter paper, and the acid layer transferred to a 25 ml volumetric flask, washing the funnel twice with 5 ml portions of distilled water. To the acid solution is added saturated bromine water, drop by drop, until it is colored, and the bromine color finally discharged by the addition of NH_4OH , drop by drop. Then 3 to 5 drops of NH_4OH in excess and 0.5 ml of 1% dimethylglyoxime is added, and the solution made to volume and mixed thoroughly.

The transmittancy of the solution is measured at 450 m μ with a Beckman spectrophotometer using 2 cm cells against water or a reagent blank if the reagents are

contaminated with traces of nickel. The readings are made within 15 minutes.

The concentration of nickel is determined by reference to a standard calibration curve prepared from readings obtained by taking 0, 5, 10, 15, 20, and 25 γ of nickel (a stock solution is prepared by dissolving 1 g of Ni with HNO_3 (1+1) and diluting to 1 liter; 5 ml of the stock solution is diluted to 1 liter to give the standard solution containing 5 γ Ni/ ml) in about 25 ml of 0.1 N HCl, and carrying the standards through the procedure described above.

18. Nitrogen

The procedure adopted for the determination of nitrogen in beryllium is solution of the metal with Hydrochloric acid and determination of the nitrogen by the conventional Kjeldahl method. The agreement between the various laboratories utilizing the procedure is quite good.

The following procedures are those used at the National Bureau of Standards and at Battelle.

The apparatus used by the National Bureau of Standards is a slightly modified Parnas and Wagner micro-Kjeldahl distillation apparatus ⁽¹⁾ shown in Figure 8.

Procedure (NBS) A 1 g sample in a micro-Kjeldahl flask is dissolved with 15 ml of HCl added 0.5 ml at a time. While the sample is dissolving the distillation apparatus is thoroughly steamed out. When the apparatus has cooled somewhat from the steaming, 40 ml of 50% NaOH is washed into the distillation flask D, through C. Then 5 ml of 2% H_3BO_3 and 4 drops of mixed indicator (5 parts of Bromocresol green and 1 part of 0.1% alcoholic methyl red) is added to the receiver F. The tip of the level condenser E is placed under the boric acid indicator.

Figure 8

After the sample is in solution, the contents of the flask are boiled for 5 minutes, and then quantitatively transferred to the distillation flask D through the funnel C. All the connections are closed, a flame is applied to the steam generator A, and the distillation is allowed to proceed for 3 minutes, the time starting when the condensation of water is observed in B. At the end of the 3 minutes the receiver flask F is lowered so that the condenser tip is above the liquid level and the distillation is continued for 1 minute longer. The tip of the condenser is rinsed and the contents of the receiving flask are titrated with 0.01 N HCl to a faint pink tinge. A reagent blank is prepared as above.

Procedure (Battelle) A 0.5 g sample of beryllium is placed in a micro-Kjeldahl flask. A 75 cm by 0.8 cm rubber stoppered air condenser is inserted into the neck of the flask. While cooling the bulb of the flask in ice, 17 ml of HCl is cautiously poured onto the sample and when the vigorous reaction has subsided the contents of the flask are transferred to a hot water bath to complete the digestion. The contents are then transferred to a Pregl-Parnas-Wagner micro-Kjeldahl distillation apparatus and 25 ml of NaOH solution (specific gravity 1.23) is added to the solution of the sample. The solution is then distilled into about 7 ml of 0.114% (w/v) boric acid solution

and the distillate titrated with 0.007 N H_2SO_4 against an indicator prepared by dissolving 0.0166 g of methyl red and 0.0834 of Bromocresol green in 100 ml of ethanol.

- (1) Friedrich, A. "Mikroanalyse", pp 75-84
Franz Deuticke, Leipzig und Wien, 1933.

19. Water

Water has been found in beryllium metal samples presumably tied up with the beryllium oxide of the metal. The water is determined by ignition of the sample and absorption of the liberated water in Anhydron.

The following procedure is that utilized at the National Bureau of Standards. The apparatus for the determination is shown in Figure 9.

Procedure (NBS) During a series of analyses and especially after the train is newly assembled, or after alterations or replacements have been made in the system, blanks are run to insure complete freedom from sources of water. In determining the blanks an empty porcelain boat, 3 by 0.5 by 0.5 inches, is inserted into the combustion tube G to point H. The platinum shield H is heated with a Meker burner (850 to 900°C inside the tube), the heaters D and I are maintained at about 700°C, and helium is passed through the system for 1 to 2 hours, the Friedrich absorption tube K being removed from the train. The Friedrich absorption tube is then weighed and inserted in the train. After 1 hour the tube is reweighed and the blank determined. The system should be swept with helium until a blank of 0.2 mg or less is obtained.

After the blank has been determined, the Friedrich tube is kept in the balance or desiccator while the sample

Figure 9

Determination of Water

- A - Flask containing H_2SO_4 .
- B - Two liter safety bottle.
- C - U - tube containing Anhydrous.
- D - Electric furnace heated to 700°C .
- E - H_2SO_4 bubble counter.
- F - U - tube filled with Ascarite and Anhydrous.
- G - Vycor combustion tube, 50 cm in length, 1 cm in diameter, filled with CuO .
- H - Platinum foil, 2 inches in length.
- I - Electric furnace heated to 700°C .
- K - Friedrich micro-absorption tube containing Anhydrous.
- L - Drying tube containing glass beads covered with H_2SO_4 .

Figure 9

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is weighed. About 1 g of beryllium metal is placed into the porcelain boat. The Friedrich tube is inserted into the train and the boat is placed into the combustion tube. The sample is kept in the system for 1 hour, helium being swept through it at the same rate as for the blank determinations. The Friedrich tube is then removed from the train, cooled, and weighed.

The water content of the beryllium is determined from the gain in weight of the Friedrich tube correcting for the blank.