

**RESEARCH ON ANALYTICAL METHODS FOR THE
DETERMINATION OF OXYGEN IN BERYLLIUM**

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FOREWORD

This report was prepared by Ledoux & Company, Inc., under USAF Contract No. AF 33(616)-6281. This contract was initiated under Project No. 7360, "Materials Analysis and Evaluation Techniques", Task No. 73615, "Compositional, Atomic and Molecular Analysis." The work was administered under the direction of the Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, with Mr. Charles D. Houston acting as project engineer.

This report covers work conducted from 1 March 1959 to 29 February 1960.

ABSTRACT

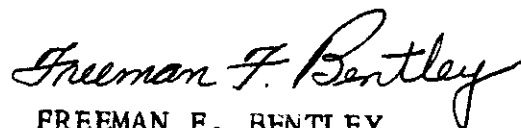
The inert gas fusion method is shown to be well suited for the determination of the total oxygen in beryllium metal. In order to release the oxygen from the very refractory beryllium oxide it is necessary to use a medium in which beryllium metal is soluble. Nickel was found to be the most suitable flux.

Among the methods based on differential solubility of beryllium, the bromine-methanol procedure was found superior. A limitation of the method is caused by the unspecificity of the reagent.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



FREEMAN F. BENTLEY
Chief, Analytical Branch
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THE DETERMINATION OF OXYGEN IN BERYLLIUM

I. Introduction

Methods for the determination of oxygen in beryllium have recently been reviewed and evaluated by Bradshaw (1).

(1) Vacuum Fusion Procedures - Gregory and Mapper (2) recommend the vacuum fusion approach using 50 mg or less of sample, a platinum bath and always maintaining a beryllium - platinum ratio of 1:50. Booth, Bryant and Parker (3), however, report that they were unable to duplicate the findings of Gregory and Mapper except in a limited number of instances. They obtained higher and more consistent results by adding platinum and powdered graphite before each sample. Runner (4) claims quantitative recoveries of oxygen by using a platinum flux technique, a comparatively low temperature and a beryllium - platinum ratio of about 1:10.

(2) Volatilization Procedures - Since beryllium oxide resists the attack of chlorine or hydrogen chloride, volatilization of beryllium chloride and treatment of the residual BeO has been made the basis of methods recommended by Rynasiewicz (5) White and Burke (6) and Osmond and Smales (7). These methods are essentially adaptations of methods successfully used for the determination of oxygen in zirconium or titanium involving either chlorine (8) or hydrogen chloride (9, 10). Because of the lower boiling point of zirconium tetrachloride (300°C) compared to beryllium chloride (520°C), the halogenation procedures appear less attractive for beryllium than for zirconium.

(3) Differential Solubility Procedures - Several methods have been suggested which are based on the solubility of beryllium metal and the insolubility of beryllium oxide in various reagents, such as dilute hydrochloric acid (5) copper sulfate (7) and bromine-methanol (11). Again these methods are essentially adaptations of earlier procedures designed for the determination of oxygen in aluminum (12, 13). Methods in this category will be discussed in some details in a later part of the report.

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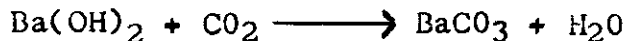
(4) Other procedures which have been considered for the determination of oxygen in beryllium are based on techniques involving isotopic dilution (14), radioactivation (7) and hydrogen evolution (15).

(5) Inert Gas Fusion Method - To our best knowledge, this approach which in principle goes back to the work of Smiley (16) has not yet been tested, although Bradshaw (1) lists it among the techniques which warrant investigation. In this method, metal oxides react at high temperature with graphite, thus forming carbon monoxide which is converted to carbon dioxide and measured in a capillary trap and manometer. A major portion of this report covers our investigation of the feasibility of this graphite fusion method (also referred to as the argon fusion method) to the determination of oxygen in beryllium using commercially available equipment.

II. The Inert Gas Fusion Method

1. Principle

Oxygen is extracted from the metal or alloy by a fusion resulting from induction heating in a graphite crucible in a stream of argon. The oxygen through the interaction with the graphite forms carbon monoxide which is oxidized to carbon dioxide by iodine pentoxide. The more complicated freeze-out manometric technique previously used by Smiley (16) has been replaced by a conductometric procedure capable of measuring accurately CO_2 . The carbon dioxide is absorbed by a dilute barium hydroxide solution. The amount of oxygen in the sample is determined by measuring the change in conductance of the absorbing solution and comparing this change against a standard curve. The basic reactions involved are as follows:



2. Equipment Available

The only commercially available equipment is that manufactured by the Laboratory Equipment Corporation. Their instruction manual #534-300 should be consulted for a detailed description of the equipment and for a suggested procedure suited for the determination of oxygen in titanium and zirconium. The main features of the equipment are outlined in Figure 1. The following additional information is of interest:

The power source for this unit is a Leco 1-1.5 kw 3.6 mc radio frequency generator necessitating the use of carbon black as insulating material. A report from another installation using a "homemade" apparatus (17), indicates that a different power source, such as the Lepel 2.5 kw 450 kc radio frequency generator, would allow the use of graphite insulation which is preferable to carbon black. The latter is more difficult to "blank out" and has a tendency to be blown into the graphite crucible when the flow of argon is increased.

The sample loading stopcock supplied with the original equipment is not well suited for the determination of oxygen in beryllium. It was apparently designed for accommodating 0.1 - 0.2 gram of titanium, zirconium and about 0.5 gram of uranium. The 9 mm bore hole of the stopcock holds less than 0.1 gram of beryllium metal thus making it impossible to analyze samples below 0.05% oxygen. Therefore, the original stopcock was replaced by us by a larger stopcock (20 mm bore hole) made of teflon and requiring no lubrication. Simultaneously, the ball joint connecting the stopcock was eliminated thus ensuring greater rigidity of the loading device. The size of the funnel was increased to allow the passage of larger sample weights and the funnel itself was suspended in the ball joint of the furnace tube.

Figure 2 shows a combined loading lock and storage tube which is well suited for introducing a number of samples of various weights into the graphite crucibles. This or a similar device (17) is a must when the oxygen content is 0.02% or below thus requiring sample weights of beryllium metal which cannot be accommodated by any stopcock-type loading device.

3. Development Procedure Applicable to Beryllium Metal

The only data found in the literature of interest for the development of an inert gas fusion procedure are based on experiments with the vacuum fusion system. It was shown (2) that, following the reaction $\text{BeO}_{\text{solid}} + \text{C}_{\text{solid}} = \text{CO}_{\text{gas}}$ and $\text{Be}_{\text{liquid}}$, the pressure of carbon monoxide in equilibrium with

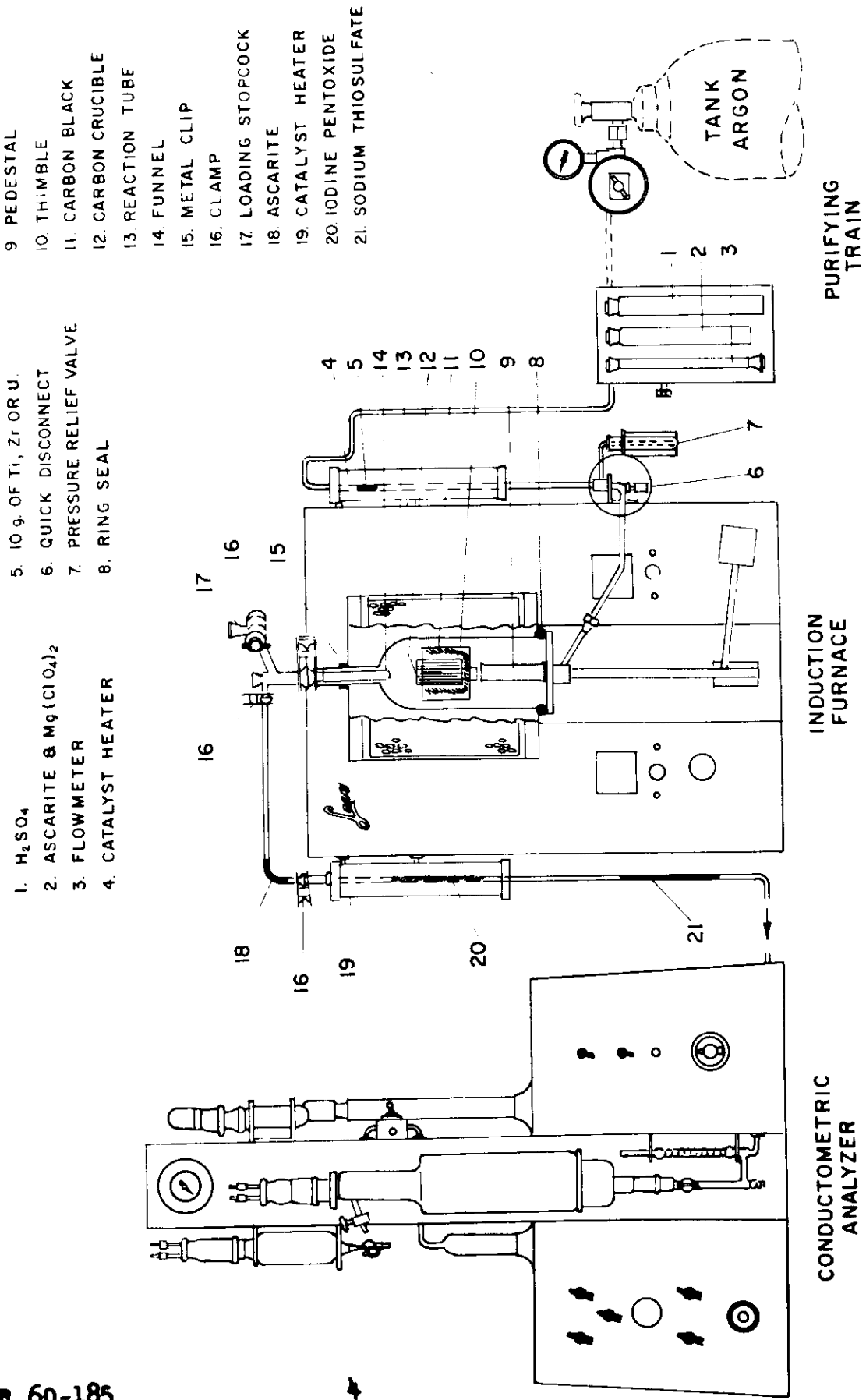


FIGURE 1. INERT GAS FUSION APPARATUS

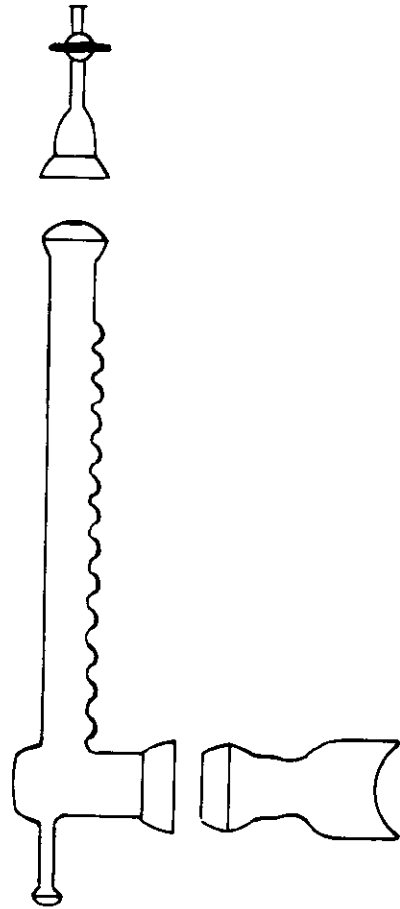


FIGURE 2. MODIFIED SAMPLE LOADING DEVICE

Beryllium oxide and graphite at 1860°C is 3.2×10^{-3} mm of mercury and that the rate of reduction of beryllium oxide by carbon alone is too slow for the vacuum fusion method. The use of a molten platinum bath speeds up the reaction by acting as a medium or solvent for bringing the beryllium oxide and graphite into intimate contact. However, at the temperature necessary for the reduction of beryllium oxide, the high vapor pressure of the metal (about 10 mm) leads to the evaporation of the latter with the inherent danger of chemisorption or "gettering".

As a starting point, the following physical and chemical properties derived from previous vacuum fusion experiments, were therefore taken into consideration. The melting point of beryllium is $1350 \pm 20^\circ\text{C}$, its boiling point is 2970°C , and the vapor pressure at 1950°C is almost 10^{-2} atmospheres. At this temperature, the graphite reduction of refractory beryllium oxide is very slow. A platinum bath does not sufficiently increase the rate of reaction between the beryllium oxide and the graphite to allow the operations to be carried out at a temperature where the vapor pressure of the beryllium metal could be disregarded.

Preliminary tests carried out in our laboratory indicated that for the inert gas fusion procedure platinum was even less suited than for the vacuum fusion technique. In order to achieve an optimum reaction rate between beryllium oxide and graphite, temperatures of about 2600°C are required which lead to excessive evaporation of beryllium and prohibitive "gettering".

The next metal investigated was copper. Its potential use was indicated by the availability of a commercial copper beryllium master alloy containing up to 3.5% of beryllium. When portions of this alloy with a known oxygen content were introduced into the hot graphite crucible, reaction of the oxide with graphite was immediate and without any apparent "gettering". On the other hand, when beryllium was introduced into a bath of molten copper, difficulties were encountered, in as much as the first determination usually yielded the full oxygen content while subsequent runs indicated an increasing loss of oxygen. Apparently, beryllium metal vaporizes before it has a chance to dissolve in the molten copper and before the oxide reacts with the graphite.

When the copper was introduced into the crucible simultaneously with the beryllium, thus acting as a flux, the precision of the results improved markedly. It was frequently possible to obtain as many as six determinations before the oxygen recovery decreased significantly. Copper, however, is unable to combine with more than 3.5% weight per cent of beryllium, thus requiring about 30 parts of copper for each part of beryllium. This makes copper virtually useless for beryllium metal with an oxygen content below 0.05% since a minimum of 0.25 grams of beryllium and 7.5 grams of copper would be required to provide sufficient sensitivity for the conductometric measurement.

Our search for a better flux material finally led to nickel. While other metals were found to be superior to nickel as far as their alloying affinity towards beryllium is concerned (beryllium and zirconium for instance, form well defined alloys with a ratio of about 1:1) they could not be obtained with a sufficiently low oxygen content to be useful as flux material. Some of the potential alloying constituents need platinum to release their own oxygen content.

Nickel looks attractive as a flux for several reasons. It can be obtained with a very low oxygen content (<10 ppm), its melting point of 1455°C is fairly close to that of beryllium (1350°C) and its boiling point of 2900°C is virtually the same as that of beryllium (2970°C). A nickel-beryllium alloy containing up to 15% of beryllium is formed during the fusion step. This alloy apparently effectively reduces the volatilization of the beryllium. It was found advantageous to continue using copper for wrapping the beryllium, since many samples are submitted for analysis in powder or flake form which is unsuited for direct introduction into the graphite crucible. Copper foil with a very low oxygen content (<10 ppm) is used, and the resulting monel-like nickel alloy is able to dissolve up to 17% of beryllium.

4. Procedure

Apparatus: See Figures 1 and 2 and comment on changes.

Reagents:

- (a) Ascarite (20 - 30 mesh)
- (b) Magnesium Perchlorate (anhydrous)
- (c) Sulfuric Acid (Sp. Gr. 1.84)
- (d) Gelatine (U.S.P.)
- (e) Sodium Thiosulfate (coarse reagent grade)
- (f) 2-Ethyl-1-Hexanol

- (g) 1,1,2-Trichloroethylene (Reagent grade)
- (h) Acetone (Reagent grade)
- (i) Lead Oxide (PbO) or silver oxide Ag₂O (Reagent grade)
- (j) Titanium Sponge
- (k) Iodine Pentoxide (coarse reagent grade)
- (l) Copper 1.5 in. 2 mil foil. Clean with HCl, trichloroethylene and acetone.
- (m) Nickel --- sheet 15 mil. Clean with HCl trichloroethylene and acetone.
- (n) Tin foil
- (o) Graphite crucibles, United Carbon Products #PE-5-20-58 or Leco #534-314. The capacity of Leco crucibles for holding molten sample can be increased by decreasing the wall thickness of the crucible.
- (p) Carbon Black, Leco Special
- (q) Barium Hydroxide Solution. Approximately one week before needed, prepare the barium hydroxide solution as follows:

Bubble carbon dioxide free air through 17 liters of distilled water in an 18 liter flask for 45 minutes. Dissolve 15 grams of barium hydroxide Ba(OH)₂·8H₂O in 500 ml of water, freed of CO₂ by boiling, and filter into the 17 liters of water. Dissolve 2 grams of gelatine in 500 ml of warm carbon dioxide free water. Add 5 ml of 2-ethyl-1 hexanol. Add this solution to the barium hydroxide solution, stopper and mix by bubbling carbon dioxide free air through the solution.

(a) Starting the Conductometric Analyzer

About 30 minutes before starting the initial operation, turn on the constant temperature bath switch. Fill the standard cell with Ba(OH)₂, drain and refill several times. Finally fill to a little below the top of the water jacket. With the furnace closed and the sample loading device open to the air, adjust the argon flow with the needle valve on the purifying train until the flow meter on the purifying train reads 0.5 liters min. Close the sample loading device, apply pressure on the Ba(OH)₂ solution and fill the measuring cell.

(b) Preparation of Crucible

The graphite crucibles used for the analysis are "floated" in a bed of Leco "special" carbon black contained in a quartz thimble. Fill the thimble about three-quarters full with carbon black and insert the graphite crucible so that its top is at the same level as the thimble top. Re-use the same charge of carbon

black each time the thimble is packed. Tap the crucible assembly lightly one or twice to remove air pockets in the carbon black. Remove any carbon inside the crucible proper and with a bent glass tube blow out any fine carbon black which may have fallen into the crucible. Place the entire assembly on the pedestal and raise it into the reaction tube with the furnace in the off position.

(c) Blank Rate of Apparatus

Turn on the catalyst furnace switch about 30 minutes before use. Maintain the argon flow on the purifying train at 0.5 liters per minute by use of the needle valve, leaving the loading device in the load or open position. Allow the argon to flow for 5 minutes before turning on the catalyst heaters. Turn on the water supply, furnace filament and the high voltage supply to the generator. Advance the variable temperature control on the generator to heat the crucible assembly. Advance this setting by 100 milliamperes on the plate current at one minute intervals until the maximum heat is obtained. Maintain this temperature of approximately 2700°C for 10 minutes, then turn off the high voltage and cool the crucible. Obtain the blank rate of the apparatus by turning on the high-voltage switch and adjusting the current to 700 milliamperes. Maintain this temperature setting for one and a half minutes and follow with a five and a half minute flush of the system by the argon. Follow this procedure until a blank of at most 1.5 ohm for the 7 minute period is obtained.

(d) Blank Rate of Flux

Transfer 0.4 gram of copper foil and 1 gram of nickel, both previously cleaned with hydrochloric acid then rinsed in succession with 1,1,2-trichlorethylene and acetone, to the sample loading device. Repeat the cycle previously described. The flux blank should not exceed 0.5 ohm, particularly when samples of a low oxygen content are analyzed.

(e) Preparation of Standard Curve

Prepare copper foil packages (100 mg) containing either silver oxide or lead oxide (PbO) containing between 100 and 400% of oxygen. Introduce the foil packages individually into the sample loading stopcock. If the multiple sample loading device is used, a number of packages can be introduced at the same time. Adjust the stopcock in such a way that argon will flush out any CO₂ and O₂ from the loading device. Adjust the variable temperature control knob to bring the plate current to 700 m.a. and allow the graphite crucible to stabilize in temperature. Turn the loading stopcock to lock position to allow argon to flow

through the I_2O_5 , $Na_2S_2O_3$ and the conductometric cell. Close the inlet stopcock on the conductometric unit. Fill the conductometric adsorption cell with $Ba(OH)_2$. Allow the lines on the oscilloscope to become stable. Drop the sample from the loading stopcock into the crucible and start a stopwatch. Alternatively, use a magnetic sample manipulator if the multiple sample loading device (Figure 2) is used. The oscilloscope lines should not spread more than 0.5 ohms in the first 30 seconds. Oxygen will be detected in 40-60 seconds as noted by the movement of the lines on the oscilloscope. At exactly one and a half minutes from the time the stopwatch was started, shut the furnace off. Flush for exactly five and a half minutes and balance the bridge and take the reading of the resistance duodial. Repeat for each of the standards. Correct the resistance reading in ohms for the standards for the apparatus blank and plot the corrected readings versus the known oxygen content of the standards (in micrograms) on linear co-ordinate paper. The graph should be a straight line up to 400 . Check the curve daily with at least two calibration standards.

(f) Health Safety Precautions

Observe all health physics requirements for beryllium!! The following precaution should always be observed. When opening the exit stopcock to allow the escape of argon, attach a glass tube in such a way as to permit the gas to pass through water.

(g) Preparation and Analysis of Samples

To analyze solid samples, cut off pieces with a hacksaw, file or sand the surface and degrease with 1,1,2-trichloroethylene and rinse in acetone. Allow to dry, then weigh. No sample preparation is possible for beryllium powder or flake.

Wrap into a 1.5 inch sheet of copper foil 0.25 grams of beryllium, if the oxygen content is between 0.01 to 0.1%. Use a 0.1 gram sample for an oxygen content from 0.1 to 0.4% and 0.05 gram for the 1% oxygen range. Add to this nickel to the extent of 10 times the weight of the beryllium and introduce into the sample loading device. If a 0.25 gram sample is used the multiple sample loading device (Figure 2) must be used. Adjust the stopcock in such a way that argon will flush out any CO_2 and O_2 from the loading device. From this point on follow the instructions given in the preceding chapter (Preparation of Standard Curve).

(h) Calculations

$$\text{ppm O}_2 = \frac{A}{B}$$

Where A = micrograms of oxygen read from curve and corrected for apparatus and reagent blank.

B = sample weight in grams.

5. Results

No standard samples as such were available. Substitute "standards" were prepared by mixing varying proportions of samples I and II. Sample I was a beryllium powder with an oxygen content of 1.07%, as determined by the bromine-methanol method and 1.03% by the HCl volatilization procedure. Sample II was a vacuum melted beryllium sample with an oxygen content below 100 ppm as indicated by the fact that a 2 gram sample yielded no weighable residue by the bromine-methanol method and that a 0.25 gram sample treated by the above suggested procedure did not yield more CO₂ than the combined apparatus and flux blank.

Table I

Results Obtained by the Proposed Procedure

<u>Oxygen Present</u>	<u>Oxygen Found</u>	<u>Oxygen Present</u>	<u>Oxygen Found</u>
1.05%	0.97%	0.05%	0.04%
1.05	1.02	0.05	0.038
1.05	0.99	0.05	0.052
1.05	1.10	0.05	0.060
0.30	0.33	0.025	0.029
0.30	0.32	0.025	0.018
0.30	0.27	0.87	0.85
0.30	0.30	0.87	0.90
0.12	0.10	0.62	0.65
0.12	0.13	0.62	0.58
0.12	0.09	0.24	0.25
0.12	0.11	0.24	0.25
* 0.78	0.80		
* 0.78	0.76		
* 0.92	0.92		
* 0.97	0.97		

*Beryllium Zirconium Alloy. Comparison with HCl volatilization method.

6. Discussion:

The results in Table 1 would indicate that the method is valid within the range tested. It is difficult to extend the method to a much lower oxygen level because the weight requirements both for sample and flux are such that the graphite crucible could not hold more than two runs. The results in Table 1 do not tell the whole story. They do not show how many determinations failed when the furnace was not operating at full efficiency or when for other often unexplainable reasons results suddenly dropped off. Failure is indicated when duplicate determinations disagree widely. When this happens it is our practice immediately to introduce a standard of lead or silver oxide. If the standard also fails, it is time to change the graphite crucible and replace the carbon black. The question may be asked how many determinations can be carried out in the same crucible before the system fails. This depends largely on sample weights which in turn are controlled by the oxygen content of the sample. Often it was possible to carry out up to ten determinations in the same crucible. On the other hand at times it was necessary to change the crucible after three or four determinations.

It seems evident that with proper safeguards the proposed method is superior to other procedures in the range under investigation.

III. Chemical Solution Techniques

Methods for the determination of oxygen in beryllium metal surveyed in the introduction of this report, are based on the fact that beryllium oxide is insoluble while beryllium metal is easily dissolved by certain solvents. The most attractive looking solvent is bromine-ethanol which previously had been used by Werner (13) for the determination of aluminum oxide. It should be always remembered that methods in this category do not provide beryllium oxide figures but merely the total amount of oxygen attached to beryllium, and, or other cations. The methods therefore are valid only if beryllium is the only cation. If other cations are present and the residue is weighed, differences in the conversion factors will make a gravimetric finish highly uncertain. If, on the other hand, the residue is analyzed for beryllium only the possible presence of other oxides

is disregarded and the final result represents only the BeO content but not the total amount of oxygen. Even greater difficulties must be expected if the sample contains intentional additions of boride, carbide or nitride. While Eberle and Werner (11) cite experimental proof for the non-interference of beryllium carbide in the methanol-bromine procedure, we found that beryllium carbide remained in the residue leading to erroneous oxygen results. Even greater difficulties are encountered with beryllium alloys most of which are not soluble in the solvents suggested in the past or examined in connection with this investigation.

The most attractive looking solvent for the determination of oxygen in beryllium metal is bromine-methanol. The method involving bromine-methanol is easy to manipulate and results are not significantly affected by a small water content of the alcohol ($H_2O > 0.25\%$) (11). Eberle and Werner have investigated this procedure extensively and have added an extra treatment with methanol-hydrochloric acid thus ensuring the solution of unreacted metal which has been coated with a thin layer of oxide. We prefer to analyze the residue photometrically by the aluminon method which is easier to manipulate.

1. The Bromine Methanol Procedure

2. Apparatus and Reagents:

- (a) Spectrophotometer - Beckman Model DU. 1 cm cells.
- (b) Platinum crucibles.
- (c) Methanol ($H_2O < 0.1\%$)
- (d) Methanol-hydrochloric acid, prepare fresh. Dilute 50 ml of hydrochloric acid with methanol to 500 ml.
- (e) Wash solution. Add 5 ml of hydrochloric acid to 500 ml of methanol.
- (f) Standard Beryllium solution. 1 ml = 0.05 mg. Dissolve 0.05 gram of high purity beryllium in 10 ml of 6N hydrochloric and dilute with water to exactly 1 liter.
- (g) Aluminon - Buffer Composition solution. Transfer 500 grams of ammonium acetate to a 2 liter beaker. Add 80 ml of glacial acetic acid and 1000 ml of water and stir until dissolution is complete. Filter if necessary. Dissolve 1.000 gram of Eastman Kodak aluminon in 50 ml of H_2O and add to the buffer solution. Dissolve 3 grams of benzoic acid in 20 ml of methanol and add to the buffer solution while stirring. Dilute the mixture to 2 liters. Transfer 10 grams of gelatine into 250 ml of water in a 400 ml beaker. Place

the beaker on a boiling water bath and allow to remain, with occasional stirring, until the gelatine has dissolved completely. Pour the warm gelatine solution into 500 ml of distilled water while stirring. Cool to room temperature, dilute to 1 liter and mix. Transfer the aluminon and gelatine solutions to a 4 liter bottle, mix well and store in a cool, dark place.

(h) E.D.T.A. solution. 2.5% of disodium salt.

3. Procedure - Gravimetric

Weigh 0.5 to 1 gram of the sample into a 300 ml Erlenmeyer flask. Add 20 ml of methanol and in small additions, 100 ml of methanol containing 6 ml of bromine. After the action subsides, add 50 ml of methanol hydrochloric acid and swirl occasionally to ensure complete reaction.

Wash the content of the flask into a 250 ml beaker with methanol. Add filter pulp, filter through a 9 cm Whatman #42 filter paper and wash thoroughly with the wash solution (1% HCl in methanol) until the yellow color is completely removed. Ignite the residue in a tared platinum crucible and weigh as BeO. If the weight is more than 5 mg calculate directly to oxygen. $\text{Weight of BeO} \times 0.6394 = \text{weight of oxygen in sample.}$

For smaller weights of BeO proceed as follows. Add to the platinum crucible 2 ml of hydrofluoric acid and 1 ml of perchloric acid. Heat to complete solution then evaporate to near dryness. Dissolve the residue in water and transfer the solution to a 25 ml volumetric flask.

4. Photometric Determination

Transfer 0, 1, 2, 4 and 6 ml of the standard beryllium solution (1 ml = 0.05 mg of Be) to 100 ml volumetric flasks. Also transfer aliquots of the sample solution covering the same range (0.05 to 0.3 mg) to 100 ml flasks. Add 2 ml of EDTA solution and 15 ml of aluminon buffer composite solution, mixing well between additions. Dilute to the mark and mix without delay. Immediately, transfer portions of the solutions to the 1 cm absorption cells and allow to stand away from direct sunlight for exactly half an hour from the time of the addition of the aluminon buffer composite solution.

Measure the absorbance of the solutions at 515 m μ using the solution containing no beryllium as a reference. Plot the absorbance versus concentration of the standards and calculate the oxygen content of the sample as follows:

$$\% \text{ Oxygen} = \frac{\text{gram of beryllium in bromine insoluble} \times 1.774 \times 100}{\text{gram of sample}}$$

5. Discussion:

In our opinion, no useful purpose is served in analyzing the bromine insoluble residue by a photometric procedure as long as the residue can be accurately weighed. A photometric determination will provide only the answer as to the BeO content of the insoluble residue. It does not reveal impurities such as SiO₂ and Al₂O₃. If the total oxygen content is required there is no other alternative but to submit the residue to a complete analysis in order to provide proper conversion factors.

6. Results:

No standard samples were available. Our practice of mixing a high oxygen beryllium powder with a low oxygen beryllium metal (valuable for the inert gas fusion procedure) was not practical for the solution techniques because of the different rates of reaction. Results always compare favorably with the HCl volatilization technique which is not altogether surprising since both procedures probably leave identical residues, possibly containing Al₂O₃, SiO₂, ZrO₂.

7. Other Halogen - Alcohol Mixtures

Solvents consisting of methanol, ethanol, propanol and butanol containing either iodine or bromine were tested for their suitability for a differential solubility procedure. Our conclusion is that methanol is the best alcohol and bromine is superior to iodine.

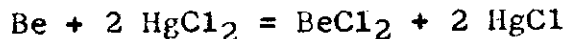
8. Other Solvents

Copper sulfate was investigated as a solvent. The solution of beryllium metal in copper sulfate causes the formation of an equivalent amount of copper metal which makes it difficult to decide when the reaction is finished.

Similarly, the solution of beryllium in mercuric chloride yields an unwieldy large precipitate consisting of mercurous chloride and mercury. For awhile, efforts were concentrated on entraining the insoluble BeO in mercurous chloride which then

could be removed by ignition. However, we were unable to remove quantitatively soluble beryllium salts by washing.

In a somewhat related procedure, we attempted to develop a procedure based on the following reaction.



Our aim was to collect the insoluble HgCl. However, it was discovered that some of the beryllium reduced a fraction of the mercuric chloride to metallic mercury.

The determination of oxygen based on the insolubility of BeO in dilute hydrochloric acid was found unreliable. High results were obtained when the treatment with HCl was kept to a minimum. Low results were frequently recorded when the treatment with HCl was extended.

In conclusion, we feel that of the differential solubility procedures the bromine-methanol method is superior.

IV. Conclusion

With slightly modified commercially available equipment it is possible to determine oxygen in beryllium metal with fairly good accuracy by the inert gas fusion procedure using nickel as a flux.

The bromine methanol procedure is well suited for the determination of BeO. Results, however, are of questionable value when the sample contains other metal oxides.

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