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Chemistry

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DETERMINATION OF FREE, COMBINED, AND
ADSORBED CARBON IN BERYLLIUM

F. W. Postma, Jr.
G. E. Walden

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ABSTRACT

Carbon is contained in beryllium metal in three forms: combined, free, and adsorbed. To determine the amount of carbon contamination in beryllium, analytical methods are needed that can separate the carbon in its three forms and reveal the total amount of the element.

Combined carbon can be determined by converting the beryllium carbide to methane and sweeping the gas into a gas chromatograph; free carbon can be filtered from the dissolved beryllium sample, ignited to carbon dioxide, and the gas swept into a Leco conductometric cell containing barium hydroxide; and the adsorbed carbon (as CO_2 on the surface of the metal) can be separated from the beryllium by heating the sample in an inert atmosphere and sweeping the gas into the Leco instrument.

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SUMMARY

Total carbon was determined in beryllium directly by separately analyzing for combined, free, and adsorbed carbon.

The combined carbon (Be_2C) was converted to methane by the addition of dilute sulfuric acid:

and swept into a gas chromatograph for measurement.

The interstitial free carbon was filtered from the solution containing the dissolved sample, ignited to carbon dioxide, and swept for measurement into a Leco conductometric cell containing barium hydroxide solution:

The adsorbed carbon (CO_2 on the surface) was measured by heating the beryllium to 1025°C in an inert gas and sweeping the carbon dioxide into a Leco conductometric cell containing barium hydroxide solution.

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INTRODUCTION

Comparison of results from a beryllium sample analytical program, established to compare the performance of various analyses performed on beryllium metal samples, revealed discrepancies in the results obtained for carbon. These analyses were performed by induction-heated combustion of the beryllium along with iron and copper accelerators in a flowing oxygen atmosphere. Measurement of the evolved carbon dioxide was accomplished by either gravimetric or conductometric determinations. Although there were deviations in the analytical procedures, the principal deviation appeared to be the choice between New Brunswick Laboratory standard beryllium and National Bureau of Standards standard steel as a reference standard for the calibration of the instruments (Figure 1).

Figure 1. CALIBRATION CURVES FOR IRON AND BERYLLIUM STANDARDS ON THE LECO CARBON DETERMINATOR.

This investigation was performed in an effort to resolve the discrepancy. The basic approach was to provide an independent, direct analysis for carbon in beryllium that could be considered a referee method.

British atomic energy workers reported direct methods for determining free⁽¹⁾ and combined⁽²⁾ carbon in beryllium. Free (elemental) carbon was determined by dissolving the sample in dilute sulfuric acid, collecting the free carbon residue, igniting the residue to form carbon dioxide, and finally measuring the carbon dioxide gasometrically. For combined carbon, the evolved gases (hydrogen and methane) from the sulfuric acid dissolution were oxidized by copper oxide to water and carbon dioxide; the water was removed and the carbon dioxide was then measured gasometrically. These methods formed the starting point of the current investigation.

ANALYTICAL PROCEDURE

REAGENTS

The following reagents were used in performing this work: a copper ring accelerator (Leco 550-184), iron powder accelerator (Leco 501-78), acetone (reagent grade), bottled helium, Molecular Sieve (Grades 5A and 13X), bottled oxygen, sulfuric acid (both concentrated and 1:1 dilute), and calcium hydroxide solution (0.0032 M).

The calcium hydroxide solution was prepared at least one week before use according to the following procedure:

1. Bubble carbon dioxide-free air through 19 liters of distilled water for 8 hours.
2. Dissolve 20 grams of barium hydroxide ($\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$) in 500 milliliters of carbon dioxide-free water. Filter into 19 liters of carbon dioxide-free water prepared in Step 1.
3. Dissolve 2 grams of good gelatin in 500 milliliters of warm carbon dioxide-free water. Add 10 milliliters of 2-ethylhexanol (octyl alcohol).
4. Add this mixture to the solution, bring up to 20 liters with carbon dioxide-free water, stopper, and shake thoroughly. (3)

EQUIPMENT

Equipment used during the course of the investigation included the following items:

Crucible

A ceramic crucible designed for filtering (Leco 528-30). These crucibles are quite fragile and easily chipped if not handled carefully. The crucibles are prepared for use by placing in a Vycor evaporating dish and igniting in a muffle at 925°C for at least 8 hours (preferably overnight) to remove organic matter and to "condition" the crucibles. Ignited crucibles must always be handled with tongs. Remove the crucibles from the furnace, inspect for cracks, and transfer them to air-tight glass containers for storage. Defective crucibles with minor cracks may be used for blanks and standards.

Crucible Cover

Crucible-with-hole form (Leco 528-40), conditioned with the crucible.

Suction Flask

Two liters capacity and fitted with a rubber stopper that is drilled to accept the filtering crucibles.

Miscellaneous

Other items that were used included: aluminum foil (Alcoa, heavy duty, 2" x 4"), analyzer (conductometric carbon, Leco 515-000), analytical balance, beakers (50 and 150 mls), electrobalance (Cahn, Model RM), entrainment trap (to fit 250-ml Erlenmeyer flask), Erlenmeyer flask (250 mls), induction furnace (Leco 521-C), asbestos gloves, Kimwipes, rubber policeman, scoop (accelerator, Leco 503-32), hypodermic syringe (2.5 mls), and wash bottles (for wash water and acetone).

FREE CARBON

Sample Preparation

Caution: Anyone performing work involving beryllium or its compounds should be aware of the health hazards involved.⁽⁴⁾

Samples were prepared according to the procedure that follows:

1. Weigh out approximately one gram of beryllium (determine precise weight) and transfer the material to a 250-milliliter Erlenmeyer flask.
2. Wash the sample into the flask with acetone and place an entrainment trap in the mouth of the flask.
3. Add 60 milliliters of water, place the flask in a 70°C water bath, and add dropwise 25 milliliters of concentrated sulfuric acid.
4. Add dilute sulfuric acid (1:1) to the solution until a total volume of approximately 100 milliliters is obtained.
5. Cover the flask and trap with an inverted 50-milliliter beaker.
6. Digest the mixture for a minimum of five hours in a hot-water bath.

Filtration and Drying

Filtration and drying were accomplished by observing the following steps:

1. Wrap aluminum foil around the outside wall of a prepared crucible (handle the crucible with tongs). Allow a 1/2-inch overlap at the seam and a 1/2-inch

extension beyond the top and bottom of the crucible.

2. Wet the foil with water and insert the crucible into the rubber stopper opening by rotating and pushing so as to keep the foil overlap flat.
3. Insert the stopper into the suction flask and apply vacuum. Add water to the crucible. If air leakage is excessive around the foil, work the crucible down further into the stopper. When a satisfactory seal is obtained (some small leakage is expected), release the vacuum and wet the inside and outside crucible walls with acetone.
4. Remove the sample flask from the water bath and dry the outside with lint-free paper towel (Kimwipe).
5. Remove the 50-milliliter beaker. Wash the entrainment trap with water flowing into flask. Wash the inside walls of the flask with water, then wash the inside and outside walls of the flask with acetone.
6. Apply vacuum to the suction flask and crucible.
7. Grasp the flask at least one inch below its mouth and transfer the contents to the crucible using an acetone-washed stirring rod. Transfer at a rate that will prevent the crucible from becoming more than half full.
8. After all the sample solution has been transferred to the crucible, immediately wash the stirring rod and the inside walls of the flask with water and then acetone.
9. Transfer this solution to the crucible without the use of a stirring rod. Do not touch the flask to the crucible. With the flask still in position over the crucible, wash the outside one-inch portion at the lip with acetone, water, and then acetone; then wash the inside and finally the outside at the lip with acetone.
10. Hold the flask up to a light and inspect the bottom for evidence of adhering carbon particles. If necessary, rinse with warm water (60°C) and then with acetone. Any remaining particles can be loosened with a clean rubber policeman and water.
11. Wash the inside and outside crucible walls with water while the aluminum foil is still in contact with the crucible. Begin all washes on the rim of the crucible. Move around the crucible with the wash stream while moving slowly downward to the base.
12. Turn off the vacuum and remove the rubber stopper. Remove the crucible without touching it by hand.
13. Lift the aluminum foil at the seam (with the fingernail) and pull it away from

the crucible, then remove the crucible with tongs and place it in a 50-milliliter beaker and cover the beaker with an inverted 150-milliliter beaker. Finally, place the beaker arrangement in an oven at 150°C for a minimum of 1.25 hours.

Burning and Measurement

The procedure for performing the burning and measurement steps is similar to that suggested by Massey. (3)

1. Using asbestos gloves, remove the beaker containing the filtering crucible from the oven and add one scoop of powdered iron accelerator and one copper accelerator ring to the contents of the crucible. Place a crucible lid on the crucible.
2. Place the covered crucible on the furnace pedestal and raise it into the furnace.
3. Purge the system for three minutes, then set the coarse and fine controls for zero adjustment on the conductometric analyzer while the oxygen sweep gas is flowing.
4. Turn on the power to the induction furnace (plate current 260 ma) and burn the sample for three minutes.
5. Turn off the power and continue to sweep the gas through the conductometric cell for three minutes.
6. Exactly six minutes following the zero adjustment, balance the bridge and record the resistance setting.
7. Remove the sample crucible from the furnace and put fresh barium hydroxide solution into the conductometric cell for the next analysis.

ADSORBED CARBON

Sample Preparation

Samples were prepared according to the procedure that follows.

1. Weigh out approximately one gram of beryllium (determine precise weight) and transfer the material to a prepared crucible.
2. Add one scoop of powdered iron accelerator and one copper accelerator ring to the contents. Place a crucible lid on the crucible.
3. Place the crucible in the cold furnace and purge the system with helium for ten minutes.

4. Set the course and fine controls for zero adjustment on the conductometric analyzer while the helium sweep gas is flowing and then immediately heat the sample for six minutes.
5. Exactly six minutes following the zero adjustment, balance the bridge and record the resistance setting.
6. Remove the sample crucible from the furnace and put fresh barium hydroxide solution into the conductometric cell for the next analysis.

FREE AND ADSORBED CARBON

Calibration

Calibration of the Leco conductometric cell was achieved by transferring aliquots of spectrographically pure graphite (ranging in mass from 20 to 250 micrograms) to previously blanked crucibles and burning the graphite according to the procedure given in the Burning and Measurement section (Page 14). The values of the resistance obtained were used to plot a standard curve of resistance as a function of the number of micrograms of carbon (Figure 2).

Figure 2. CALIBRATION CURVE FOR FREE AND ADSORBED CARBON USING SPECTROGRAPHIC GRADE CARBON STANDARD.

Blanks

Blanks were obtained by carrying prepared crucibles through the entire procedure with the omission of the sample. This work was repeated until two consecutive blanks agreed within ± 0.06 ohm.

Calculations for the Calibration

To calculate the amount of free or adsorbed carbon, observe the following mathematical steps:

1. Sample Resistance (ohms) - Blank Resistance (ohms) = Net Sample Resistance (ohms).
2. Refer the net sample resistance to the calibration curve (Figure 2) to obtain the quantity of carbon (μ gs) in the aliquot.
3. The amount of carbon in the entire sample can be obtained by the following proportion:

$$\frac{\mu\text{gs C}}{\text{Weight of Sample (gms)}} = \frac{\mu\text{gs C}}{\text{Grams of Sample}}$$

COMBINED CARBON

Sample Preparation

Samples were prepared according to the procedure that follows.

1. Weigh out approximately one gram (determine precise weight) of beryllium and transfer the material to a 250-milliliter Erlenmeyer flask.
2. Connect the flask to a gas train leading to the chromatograph.
3. Place a liquid nitrogen trap around a 13X Molecular Sieve trap in the gas train just preceding the chromatograph.
4. With the helium-sweep gas above the solution in a separatory funnel, add dropwise dilute sulfuric acid to the sample as required to limit the dissolution to a slow gas evolution rate.
5. After complete dissolution of the sample, warm the Type 13X Molecular Sieve trap to room temperature and sweep the methane into the chromatograph. The Molecular Sieve used in the chromatograph is Type 5A.

6. From the chromatogram, calculate the area under the curve for the methane peak:

$$A = \text{Peak Height} \times \text{Width at } 1/2 \text{ Height.}$$

Calibration

To calibrate the chromatograph for the combined carbon determination, observe the following procedure:

1. Place a liquid nitrogen cold trap around the 13X Molecular Sieve trap and begin the helium sweep gas.
2. Inject 0.5 milliliter of methane through the rubber hose carrying the helium sweep gas from the reaction flask to the 13X Molecular Sieve trap.
3. After five minutes, warm the 13X Molecular Sieve trap to room temperature and sweep the methane into the chromatograph for measurement.
4. Repeat Steps 1 - 3 for other volumes of methane through 2.5 milliliters.

Calculations for the Calibration

To calculate the amount of combined carbon, observe the following mathematical steps:

1. Convert the volume of methane used at room temperature and pressure to micrograms of carbon by the following equation:

$$\mu\text{gs C} = V \left(\frac{273}{T} \times \frac{P}{760} \times \frac{12}{22.4} \right) = 0.1924 V \frac{P}{T},$$

where:

V represents the volume of methane (in microliters) at room temperature and pressure,

P the room pressure (in torr), and

T the room temperature (in ° K).

2. The area under the curve obtained on the chromatograph is obtained by measuring the peak height and the width at one half the peak height and multiplying these two values.
3. Plot the curve area against the weight of carbon to obtain the standard curve (Figure 3).

Figure 3. CALIBRATION CURVE FOR COMBINED CARBON AND BERYLLIUM. (1 ml $\text{CH}_4 = 480 \mu\text{gs C}$)

Calculations for the Amount of Combined Carbon

To determine the amount of combined carbon in the beryllium sample, divide the weight of carbon obtained from the standard curve by the sample weight, thus:

$$\frac{\mu\text{gs Carbon}}{\text{Grams of Sample}} = \text{ppm C.}$$

DISCUSSION

Carbon in beryllium was considered to be present in one or more of three forms: free or elemental carbon interstitially bound; combined carbon as beryllium carbide, and/or carbon dioxide adsorbed on the surface. Free carbon was determined in the residue

remaining after dissolution of the beryllium sample in sulfuric acid. The residue was collected in preblanked porous Leco crucibles, washed with water, and dried. Carbon in the residue was converted to carbon dioxide by ignition in a flowing stream of oxygen, using a Leco furnace.⁽³⁾ The carbon dioxide was swept from the furnace into the barium hydroxide conductivity cell where the change in conductance of the solution resulting from the precipitation of barium carbonate served as a measure of the free carbon in the sample.

A study was made of the effects of sample size and reaction time for the metal-dissolution step on the free-carbon analysis. As seen by the decrease in carbon (from Be₂C) with increased time on the one-gram samples (Table 1), the dissolution was found to be dependent on sample size when digestion times of less than five hours were used.

Table 1
EFFECTS OF SAMPLE SIZE AND BOILING
TIMES ON FREE CARBON ANALYSIS

Boiling Time			
Three Hours		Five Hours	
0.5 Gram Sample (ppm)	1.0 Gram Sample (ppm)	1.0 Gram Sample (ppm)	2.0 Gram Sample (ppm)
93	117	107	110
164	178	115	116
85		86	122
104			
102			
145			
133			

The dissolution temperature was not critical. After the initial surge of heat, caused by the dissolution of the major portion of the beryllium, the flask containing the solution could be placed on a hot plate. However, it was necessary to give close attention to the sample to prevent boiling and excessive frothing and to keep the solution level adequate as a safeguard against bumping and drying out. It was found that more efficient use could be made of the analyst's time if the dissolution did not require attention (eg, this time could then be used for burning residues). For this reason, the water bath was chosen. Seventy degrees centigrade was found to give the fastest dissolution rate without excessive loss of water from the bath.

Adsorbed carbon was obtained by heating the sample in an inert atmosphere while sweeping the released carbon dioxide from the sample into the conductometric cell for measurement. Table 2 summarizes the results obtained from two samples.

Table 2
ADSORBED CARBON AS CARBON DIOXIDE

Run	Resistance (ohm)			Carbon Content (µgs)	Weight of Sample (gm)	Carbon Concentration (ppm C as CO ₂)
	Specimen	Blank	Net			
<u>Berylco 100</u>						
1	0.40	0.25	0.15	2.3	0.5001	4.6
2	0.50	0.20	0.30	5.0	0.5001	10.0
3	0.70	0.20	0.50	7.2	0.5000	14.4
4	0.50	0.20	0.30	5.0	0.5001	10.0
<u>Brush 866</u>						
1	0.65	0.15	0.50	7.2	0.5001	14.4
2	0.55	0.18	0.37	5.2	0.5001	10.4
3	0.60	0.20	0.40	5.6	0.5000	11.2
4	0.55	0.20	0.35	5.1	0.5001	10.2

The combined carbon was obtained by dissolving the beryllium in dilute sulfuric acid to give:

The methane was swept into a gas chromatograph for measurement. Helium was used as the sweep gas. Table 3 gives a summary of the results obtained from two samples for all three types of carbon.

At one point during this work, beryllium carbide was studied briefly. Difficulty was encountered in placing the specimen in the flask for dissolution, due to the static charge on the flask. It was found that by wrapping the flask completely with a wet Kimwipe and wearing wet cotton gloves, the sample could be placed in the flask with no charge effect.

Table 3
SUMMARY OF CARBON RESULTS FROM TEST SAMPLES

	Combined Carbon (ppm)	Free Carbon (ppm)	Adsorbed Carbon (ppm)	Total Carbon	
				Summation (ppm)	Mean(1) (ppm)
<u>Berylco 100</u>					
	1011	133	4.6		
	978	127	10.0		
	998	121	14.4		
		129	10.0		
		104			
		105			
Mean $\pm$ LE	996 $\pm$ 31	120 $\pm$ 13	9.8 $\pm$ 5	1126 $\pm$ 49	1220 $\pm$ 120
<u>Brush 866</u>					
	1066	107	14.4		
	1067	115	10.4		
	1104	86	11.2		
		122			
		116			
		110			
Mean $\pm$ LE	1079 $\pm$ 31	110 $\pm$ 12	12.0 $\pm$ 3	1201 $\pm$ 46	1160 $\pm$ 88

(1) Values obtained by conventional combustion-heating techniques.

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REFERENCES

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