

~~SECRET~~

UNCLASSIFIED

THIS DOCUMENT CONSISTS OF 24 PAGES
NO. 6 OF 32 SERIES A



MASTER

FAIRCHILD ENGINE AND AIRPLANE CORPORATION

RESTRICTED DATA

ATOMIC ENERGY ACT OF 1946

SPECIFIC RESTRICTED DATA CLEARANCE REQUIRED

28323

METHODS FOR THE ANALYSIS
OF BERYLLIUM CARBIDE

PROJECT NC-A-70601

Report No. NEPA 940-SCR-40

DATE March 21, 1949

Prepared By

W. L. Bridges
W. L. Bridges

Approved By

V. P. Calkins
V. P. Calkins

E. S. Funston
E. S. Funston

S. A. Reed
S. A. Reed

UNCLASSIFIED

This document is
PUBLICLY RELEASABLE

Hugh Kinser
Authorizing Official
Date: 2/22/08

Classification cancelled (or changed to memo & instr. has 53-86 from)
by authority of Decl. Br. dtd 9-11-61
by J.C. Ridenour, date 11-29-61

NEPA DIVISION

OAK RIDGE, TENNESSEE

748 001

UNCLASSIFIED

~~SECRET~~

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

<u>Subject</u>	<u>Page</u>
Abstract	3
Introduction	4
<u>Experimental</u>	
Determination of Moisture	5
Determination of Carbon	5
(A) Free Carbon	7
(B) Combined Carbon	9
Determination of Beryllium Oxide	10
(A) By Differential Solubility Technique	10
(B) With Gaseous Halogens and Anhydrous Halogen Acids	15
Determination of Nitrogen	19
Determination of Iron	20
Determination of Silica	20
Determination of Total Beryllium	20
Determination of Free Beryllium Metal	20
<u>Procedures</u>	
Combined Carbon	21
Free Carbon	21
Nitrogen	21
Beryllium Oxide	22
Water	22
Free Beryllium	23
Silica	23
Iron	23
Total Beryllium	23
<u>Diagrams</u>	
Figure 1 - Apparatus For the Determination of Combined Carbon	11
Figure 2 - Apparatus For the Determination of Beryllium Oxide	17

ABSTRACT

Analytical methods are herein given for determining the composition and impurities of beryllium carbide. A summary of the experimental work leading to these procedures and supporting data are also presented. Analytical procedures for the determination of free and combined carbon, moisture, nitrogen, beryllium oxide, silica, iron, total beryllium, and beryllium metal are outlined. Diagrams of special apparatus used are included.

748 003

INTRODUCTION

Studies to determine the feasibility of beryllium carbide as a fuel rod component and moderator in a proposed NEPA reactor have required the development of analytical methods to ascertain its purity and composition.

Be₂C is usually prepared by one of the following methods: (1) by interaction of BeO and lampblack, or (2) by the combination of carbon and beryllium metal. High temperatures are required in either case. Major impurities introduced in its preparation are carbon, beryllium oxide, and beryllium metal; minor impurities are silica and iron. After exposure to air the compound may also contain varying amounts of nitrogen and moisture. After heating in air to temperatures above 700°C, the compound shows a decided increase in nitrogen and oxide.

The principal material tested in this laboratory was grade 46, mesh 200-325 Be₂C, manufactured by Fansteel Corporation from BeO and lampblack. A typical analysis of this material is:

Be ₂ C	80.13 %
C (free)	2.17
Be ₃ N ₂	1.97
BeO	9.30
H ₂ O (total)	6.40
Si	0.20
Fe	0.004
Total	100.17 %

748 004

EXPERIMENTAL

Determination of Moisture

Samples of Be_2C were dried in a stream of inert gas at $110^\circ\text{--}120^\circ\text{C}$ to determine the adsorbed moisture. Additional moisture, believed to be in a hydrated form, was also given off at higher temperatures. To test the possibility of the existence of the hydrated form, a sample of hydrated BeO was prepared by refluxing Be_2C in water for 22 hours. After portions of this material were dried at 120°C until no more water was lost, a sample was heated to various temperatures in a stream of dry argon. The following data were obtained on a sample of approximately 0.5 g.

TABLE I

Decomposition of Hydrated Beryllium Oxide
at Various Temperatures

<u>Time (Hour)</u>	<u>Temperature ($^\circ\text{C}$)</u>	<u>H_2O Lost (%)</u>
1	120	0.0
1	150-200	1.84
1	315	36.94
1	420	2.90
1	500	0.68
1	615	0.42

From the above data a possible formula for the hydrated oxide was found to be $\text{BeO}\cdot\text{H}_2\text{O}$. It is evident from the data in Table I that samples must be dried at higher temperatures to determine the total moisture. Additional tests showed that similar Be_2C samples lost all their water during a one-hour period at 700°C .

Determination of Carbon

Methods for determining values for total, combined and free carbon

748 005

[REDACTED]

contained in Be_2C were studied. It was found that conventional combustion methods or adaptations thereof for carbon were not entirely suitable for Be_2C samples used. The grade 46 material, being of an extremely refractive nature, could not be directly burned in oxygen to quantitatively form CO_2 .

Since the decomposition temperature of Be_2C ($> 2100^\circ\text{C}$) prohibited direct ignition of the material, preliminary studies at NEPA were concerned with methods employing the use of fluxes at temperatures between 900° and 1400°C . The fluxes investigated were: litharge, tin, copper, cupric oxide, and electrolytic iron. A model A2-9 Burrell high temperature tube furnace fitted with high temperature McDanel tubes was used in the following tests.

Samples containing tin or a mixture of tin and electrolytic iron as flux reacted violently when introduced into the furnace at temperatures between 1100° - 1350°C and it was impossible to keep the material in the clay or porcelain boats. Litharge formed a lead glass with the material, causing the boats to fuse to and rupture the McDanel tubes. Copper, although somewhat better, failed to completely decompose the carbide and creeping was often evident. Cupric oxide, having a higher melting point than copper, gave smooth melts but did not bring about complete burning. Iron alone also gave smooth melts with a minimum of creep but results were still low. Representative data are given in Table II below. The total carbon value for this material was 34.2 percent.

TABLE II

Total Carbon Values Obtained by Combustion
At Various Temperatures

Weight of Be ₂ C	Flux	Time (hours)	Temperature (°C)	Total Carbon Found (%)
0.1100	None	1	900	2.83*
0.1044	None	1	1000	3.84
0.1106	None	17	1300	25.6
0.1021	Fe-2 g + Sn 0.2 g	1/2	1125	32.40
0.1022	Fe-2 g + Sn 0.2 g	3/4	1225	27.94
0.1019	Fe-3 g	1	1300	33.64
0.1057	Fe-3 g	1	1300	33.80
0.1091	Cu-3 g	1	1200	31.24
0.1031	CuO-1 g	1	1200	31.45
0.1065	CuO-1 g	1	1325	33.88
0.1062	CuO-2 g	3	1325	33.61
0.1025	CuO-2 g + 2 g Alundum **	2	1300	34.21

* This is approximate free carbon value.

** To protect combustion boats and increase wetting of sample by flux.

Further combustion studies were postponed in favor of results obtained by the methods outlined below.

(A) Determination of Free (graphitic) Carbon

Grade 46 Be₂C prepared by the interaction of BeO and lampblack usually contains 2-5 percent free carbon in the form of graphite. A literature survey compiled on analytical methods for determining free carbon in similar materials indicated that the preferred methods utilized the oxidation of this carbon to CO₂ in a stream of oxygen at suitable temperatures. The liberated CO₂ was in turn absorbed and weighed.

Therefore, similar methods were initiated in the NEPA laboratories for the determination of free carbon in Be₂C. A series of samples of grade 46 Be₂C were burned in a tube furnace in a stream of oxygen at various temperatures. One-hour test runs were made in the temperature range 820°- 960°C.

These data, as shown in Table III, were quite erratic. It was noted also that these values from combustion were consistently higher than those obtained by igniting the insoluble carbon residue from sulfuric acid decomposition of samples prior to total beryllium determinations. The difference in the values obtained by these two methods suggested the possibility of a slight breakdown of the Be_2C during combustion. This was proved to be the case, as may be seen from the data in Table IV.

TABLE III

Free Carbon Values Obtained by Combustion
at Various Temperatures

Weight of Sample (Gram)	Temperature ($^{\circ}\text{C}$)	Free Carbon (%)	% Free Carbon by Acid Insoluble Method
0.1417	815	2.83	2.22
0.1191	820	2.75	2.26
0.1241	820	2.35	2.20
0.1377	850	2.62	2.32
0.1042	850	2.62	*1.60
0.1151	910	2.94	*1.64
0.1076	920	3.17	*1.49
0.1275	950	2.89	
0.1171	950	2.75	
0.1423	960	2.88	
0.1801	960	3.00	

* These samples were extremely refractory and required prolonged fuming with H_2SO_4 to render them completely soluble. Some carbon was undoubtedly oxidized.

As shown above, values obtained by the sulfuric acid method, with the exception of those samples strongly fumed, were in good agreement. To eliminate the possibility of oxidizing the free carbon, hydrochloric acid was chosen to decompose later samples. Occasionally HCl failed to attack the last traces of BeO . However, this offered no disadvantage since the free carbon, along with the insolubles, could be filtered on a fritted crucible and dried to a constant weight. Ignition of this residue at 850°C completely removed

~~SECRET~~

the carbon and left the BeO unchanged. Since the loss of weight after ignition represents the free carbon content of the sample, traces of undissolved BeO do not interfere. Results of these determinations, using 1:1 HCl, are given in the table below.

TABLE IV
Free Carbon Values Obtained by the HCl Method

Weight of Sample (g)	Weight of Carbon (g)	Free Carbon (%)
0.2250	0.0050	2.22
0.2716	0.0060	2.21
0.2553	0.0055	2.15
0.2605	0.0055	2.11
0.2204	0.0047	2.13
0.2026	0.0043	2.12
0.5026	0.0107	2.12
0.5038	0.0111	2.20

(B) Determination of Combined Carbon

It is stated in Ephraim's Inorganic Chemistry* that methane is liberated from Be₂C upon treatment with solutions of mineral acids. Using this as a basis for further analytical measurements of combined carbon, a method was developed by which the liberated methane was quantitatively burned to CO₂ and weighed.

Samples of Be₂C were decomposed by boiling phosphoric acid. The evolved methane was swept by oxygen into a combustion tube which contained alternate layers of platinum, palladium, and cupric oxide as catalysts. The temperature of the tube was maintained at 850°C. The methane was thus quantitatively burned to CO₂, caught in ascarite, and weighed. Results obtained by this

* Fritz Ephraim, Inorganic Chemistry, 4th ed., p. 765, P. C. L. Thorne and E. R. Roberts, Interscience Publishers, Inc.

748 008
~~SECRET~~

method were in close agreement with calculated results for the samples and with values obtained by subtracting free carbon values from total carbon values obtained by separate measurements. Results from representative tests are given below. Figure I shows a detailed diagram of the apparatus used.

TABLE V

Combined Carbon Values Obtained by Burning
Methane After Acid Decomposition of Be_2C

Weight of Be_2C	Weight of CO_2 Formed	% Combined Carbon
0.0921	0.1075	31.85
0.1009	0.1185	32.05
0.1103	0.1295	32.04
0.1197	0.1408	32.10
0.1009	0.1182	31.97
0.0791	0.0925	31.91
0.0750	0.0880	32.02

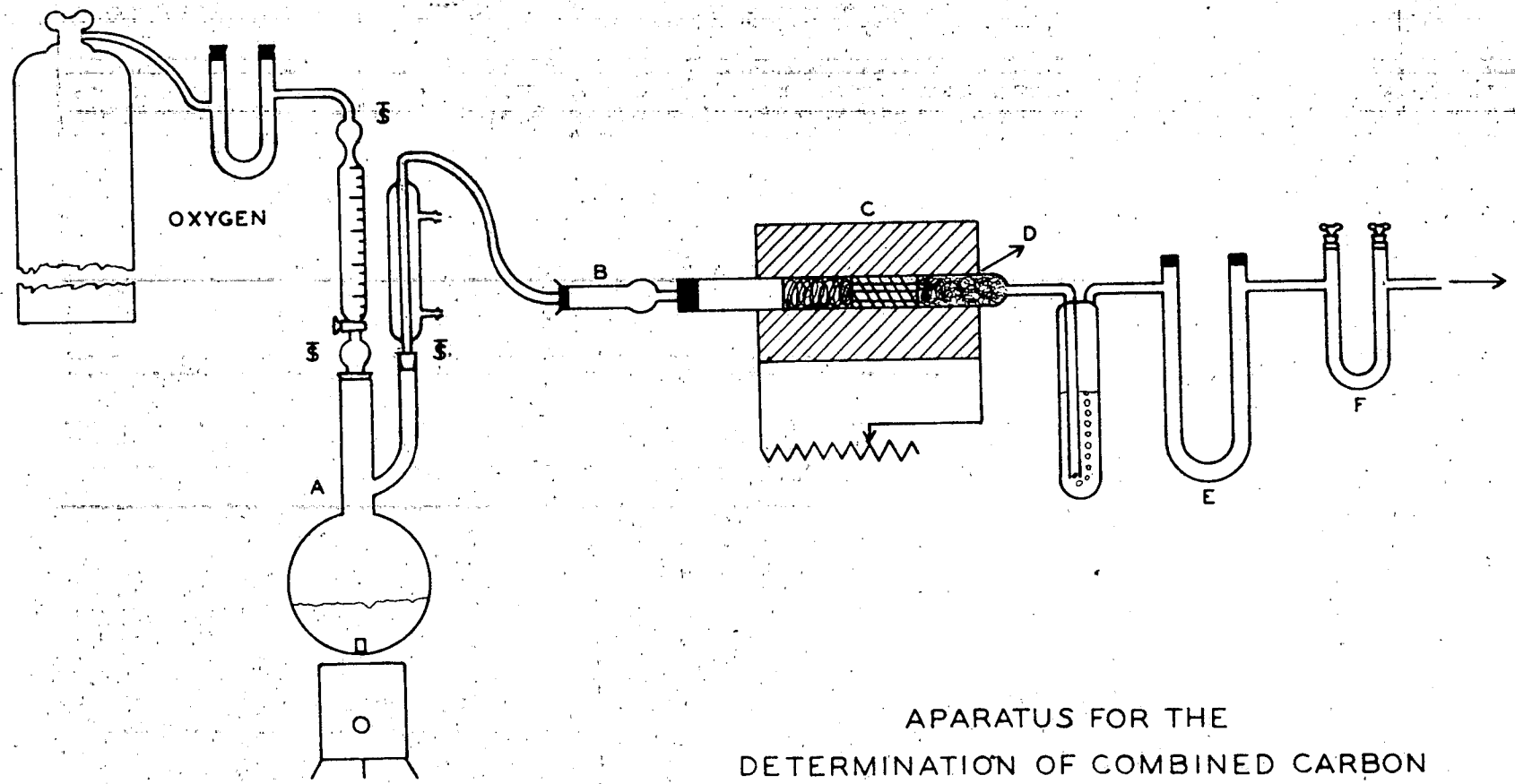
The flow rate during the above determinations was arbitrarily set at 95 cc/min. Lower oxygen flow rates produced explosive mixtures or incomplete burning of methane. The total analysis time in each case was three hours.

Determination of Beryllium Oxide

The determination of the beryllium oxide content of Be_2C was attacked in the following manner: (a) by the differential solubility method employing dilute mineral acids or solutions of slightly acidic salts, and (b) by removal of combined and free beryllium from the BeO by the action of elemental chlorine, bromine and iodine or anhydrous HCl and ammonia. Of the various methods tested only the action of elemental bromine was found to be successful.

(A) By experimentation Be_2C was found to be slightly soluble in certain organic salts as well as in its own salts, e.g., $\text{Be}(\text{NO}_3)_2$. This fact having been established, the preferential dissolution of Be_2C over BeO by solution of weakly acidic salts or dilute acids was investigated.

FIGURE I



APARATUS FOR THE DETERMINATION OF COMBINED CARBON

748 010

The salts chosen for the differential solubility tests were to serve a twofold purpose: they were to serve as complexing agents for the dissolved beryllium and to act as the solutioning medium. For this purpose the ammonium salts of formic and acetic acids were utilized. Solutions of 10 percent HCl and hydroxylammonium chloride were also tested. The latter compound was expected to give a more uniform acidity by virtue of its slow liberation of HCl in solution.

In each case 200 ml of a 10 percent solution of the reagent was refluxed with weighed portions of BeO, Be₂C or hydrated oxide. Several trials also contained CaCl₂, NH₄Cl, NaCl or Ca(NO₃)₂ as salting agents to lower the solubility of the BeO. After refluxing, each sample was tested for dissolved and/or insoluble BeO. Results from these experiments are tabulated below.

Preliminary experiments using 100 mg samples of Be₂C and various grades of BeO indicated that a 97-98 percent recovery of the oxide was possible after a two-hour refluxing period with 10 percent ammonium formate solution. Since the grade 46 Be₂C under investigation contained 5-10 percent BeO, part of which was in a hydrated form, it was necessary to ascertain the percentage recovery of both oxide forms for 5-10 mg quantities, as this amount more closely approached the analytical range. As shown in the following table, recoveries of BeO in this range dropped about 10 percent, while samples of BeO·(H₂O)_x were almost completely soluble. Additional tests employing salting agents increased BeO recoveries only to a slight degree.

748 011

TABLE VI

Results of Differential Solubility Tests
With Ammonium Formate

Sample No.	Material	Sample Weight (gram)	Reflux Time (hours)	Percent Soluble	Remarks
1	BeO	0.1133	3	2.91	Fluorescent Grade BeO
2	BeO	0.1275	3	2.90	"
3	BeO	0.0047	5	12.77	"
4	BeO	0.1053	3	1.99	BeO high fired at 1100°C for 50 hrs.
5	BeO	0.1116	4-1/2	2.96	"
5a	BeO	0.0056	3	8.93	BeO heated to 900°C for 5 hrs.
5b	BeO	0.0096	3	6.25	"
6	BeO	0.1073	4-1/2	0.47	BeO high-fired at 1400°C for 40 hrs.
7	BeO	0.0066	3	13.64	BeO prepared by heating hydrated oxide 5 hrs. at 900°C.
8	BeO(H ₂ O) _x	0.0047	5	75.00	Prepared by refluxing Grade 46 Be ₂ C With H ₂ O for 25 hrs.
8a	BeO(H ₂ O) _x	0.0098	24	93.22	"
8b	BeO(H ₂ O) _x	0.0145	28	97.70	"
9	BeO	0.1111	3	6.56	60g CaCl ₂ as salting agent.
10	BeO	0.1026	3	gained 1.36*	100g Ca(NO ₃) ₂ as salting agent.
11	BeO	0.1126	3	gained 3.91*	60g NH ₄ Cl as salting agent
12	BeO	0.1004	3	gained 2.39*	100g NaCl as salting agent
13	Be Metal	0.0055	3	54.55	
13a	Be Metal	0.1007	3	47.22	

* These gains were due to adsorption of salting agents.

(continued)

Sample No.	Material	Sample Weight (gram)	Reflux Time (hours)	Percent Soluble	Remarks
14	Be ₂ C	0.1003	3	5.68	
15	Be ₂ C	0.0977	4-1/2	9.31	
15a	Be ₂ C	0.1048	4-1/2	20.50	
16	Be ₂ C	0.0045	3	15.56	Be ₂ C previously heated at 900°C for 5 hrs.
16a	Be ₂ C	0.0137	3	13.87	Be ₂ C previously heated at 900°C for 5 hrs.

Additional samples were tested for solubility effects using 10 percent solutions of ammonium acetate and hydroxylammonium chloride. These too were found to be unsuitable for quantitative estimation of BeO in Be₂C samples. Results from these tests are given in Table VII.

TABLE VII
Differential Solubility Tests
With Various Reagents

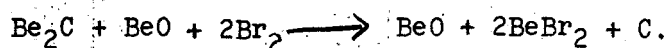
Sample No.	Weight of Sample (gram)	Reflux Time (hours)	Percent Soluble	Remarks
(10% Solution Ammonium Acetate)				
BeO	0.1062	6	2.17	
BeO	0.1105	6	6.06	Solutions adjusted to pH7 before refluxing
Be ₂ C	0.1012	6	93.60	
Be ₂ C	0.1103	6	96.20	
(10% Solution Hydroxylammonium Chloride)				
BeO	0.1068	2-3/4	9.08	
BeO	0.1009	2-3/4	8.33	
BeO	0.0927	2-3/4	9.73	
BeO	0.3285	2-1/2	2.43	BeO fired at 1100°C for 50 hrs.
(Solution Be(NO ₃) ₂ 1-1/2% by weight)				
BeO	0.1015	4-1/2	1.77	Solution adjusted to pH7 before refluxing
(10% HCl)				
BeO	0.0938	2-3/4	9.08	

(B) Attempts to quantitatively remove the combined beryllium and beryllium metal from BeO by the action of iodine, chlorine and anhydrous HCl at elevated temperatures were unsuccessful. Gaseous iodine in a sealed tube or under pressure in a steel bomb readily attacked the Be₂C; however, inherent difficulties encountered in separating the BeI₂ from the unreacted BeO prohibited quantitative work. The reaction of anhydrous ammonia to preferentially attack the Be₂C and metallic beryllium to form the more soluble nitride was found to be too slow for quantitative work.

Dried samples of grade 46 Be₂C were heated in a stream of anhydrous HCl at temperatures up to 1200°C. The reaction was initiated only after a temperature of 850°C was reached. No further reaction occurred at temperatures up to 1200°C. However, samples of fluorescent grade BeO were found to be appreciably attacked at a temperature of 950°C.

Gaseous chlorine was also found to readily attack Be₂C at 1000°C. The reaction was initiated at 600° ± 10°C and increased linearly with an increase in temperature for a period of 15 minutes, after which it slowly decreased. Examination of samples after chlorination indicated that the reaction had taken place only on the surface of the material. Dispersion of the sample in the reaction boat and other techniques to increase the surface area were unsuccessful. Samples of Be₂C mixed with lampblack as a filler to give greater surface exposure were not completely attacked after six-hour chlorination periods at 1000°C. On the other hand, samples of fluorescent grade BeO were readily attacked under these conditions.

Small amounts of BeO as an impurity of Be₂C can be quantitatively measured by the bromination technique. In addition to accurate BeO measurement, this method also enables the analyst to make a rapid estimation of the combined beryllium and total carbon contents of the material under investigation. In the absence of moisture the reaction may be represented as:



748 014

SECRET

The BeBr_2 , which is volatile at the reaction temperature, may be completely swept from the bromination tube with dry argon, leaving only unreacted BeO and carbon. The loss of weight during bromination represents the combined beryllium plus any water present. Ignition of the residue leaves BeO , while the weight loss from ignition represents the total carbon of the sample.

Since this is a unique procedure, it is of utmost importance that the directions given on page 22 be followed closely. The purification of argon and bromine is also of critical importance. To insure the absence of moisture, the system is swept at all times with purified argon. The best means of introducing bromine vapor into the equipment is by bubbling argon through the bromine itself. In this manner the argon is used as a vehicle for carrying the bromine vapor. It is important to raise the temperature after the bromination period to remove any entrapped BeBr_2 since this material is, upon contact with moist air, immediately hydrolyzed to BeO and HBr and causes a positive error in the oxide values. Values obtained for BeO by this method must be corrected if any silica is present in the samples, since it is not attacked by bromine under the conditions of this procedure. A diagram of suitable apparatus for the bromination of Be_2C is shown in Figure 2.

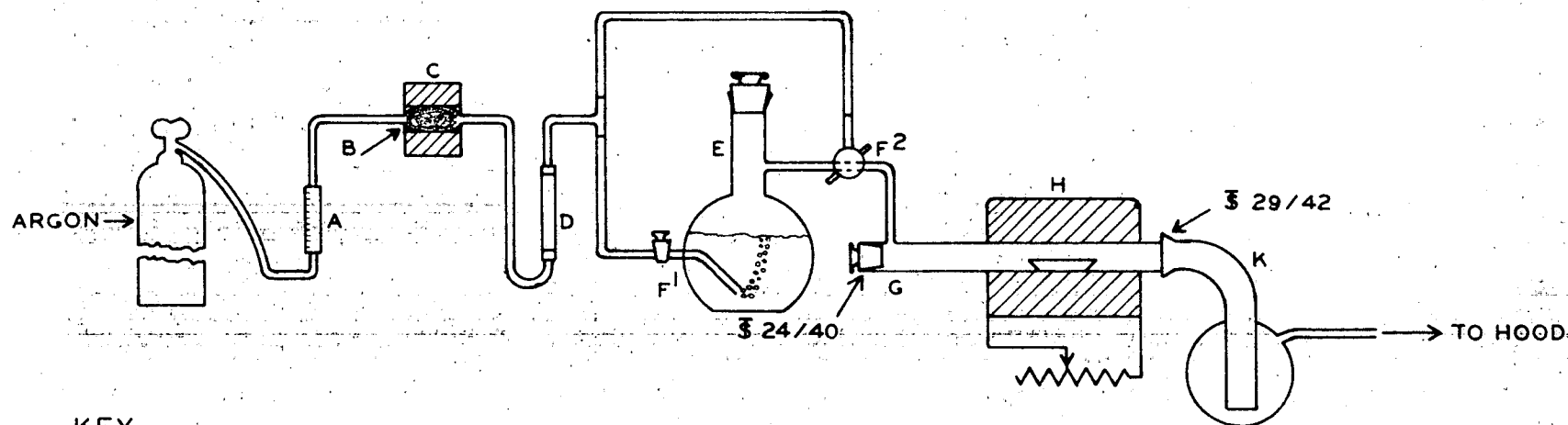
Studies of the effect of bromine at elevated temperatures on various types of combustion boats indicated that the following types could be suitably used: vitrosil, graphite, and platinum. Later studies using carbon boats with samples of BeO showed that a slight reaction took place between the graphite and BeO at brominating temperatures. In the following tests vitrosil boats were used in nearly every case.

A series of bromination tests was made on samples of fluorescent grade BeO to ascertain its stability in an atmosphere of bromine at temperatures from 750° to 1050°C . As indicated in the following table, the oxide is extremely stable at these temperatures.

748 015

SECRET

FIGURE 2



KEY

- A. FLOWMETER
- B. VYCOR TUBE CONTAINING COPPER TURNINGS
- C. PREHEATED FURNOCK
- D. P_2O_5 DRYING TUBE
- E. 500ML FLASK CONTAINING BROMINE & $AlBr_3$
- F¹ ONE WAY STOPCOCK
- F² TWO WAY STOPCOCK
- G. 1" VYCOR BROMINATION TUBE
- H. TUBE FURNACE
- K. $BeBr_2$ TRAP

APPARATUS FOR THE
DETERMINATION OF BeO IN Be_2C

748 016

TABLE VIII

Effect of Bromine on BeO at Various Temperatures

Temperature °C	BeO Taken mg	BeO Recovered mg	Loss Percent
750	10.5	10.5	0.0
800	9.0	9.0	0.0
850	8.7	8.7	0.0
900	11.2	10.9	97.3
1000	10.0	9.5	95.0
1050	11.1	9.5	85.6

Since it is shown by the above data that BeO is slightly attacked at 900°C, all later bromination studies were made between 825° and 850°C.

Samples of grade 46 Be₂C weighing approximately 0.1 g brominated for one hour at 825° to 850°C were found to be completely decomposed, leaving an oxide content of 9.3 percent. Attempts to shorten the period of bromination were limited to the fact that, as in early studies with HCl and chlorine, a surface reaction was taking place. Further tests proved that the period of bromination could be appreciably shortened by spreading the carbide sample on a layer of purified and preignited silica. With this modification a 30-minute bromination period proved to be sufficient.

A synthetic sample made by mixing grade 46 Be₂C with fluorescent grade BeO representing a total of 19.00 percent BeO was next subjected to a 30-minute bromination at 825°-850°C.

Data showing the results of these studies are tabulated in the following table.

TABLE IX

BeO Recoveries on Spiked Samples of Be₂C After
Thirty-Minute Bromination at 825°-850°C

Weight of Sample (gram)	Weight of Recovered Oxide (gram)	BeO Percent
0.1453	0.0275	18.93
0.1421	0.0268	18.86
0.1491	0.0283	18.98
0.1443	0.0274	19.01

Finally tests were made to prove that the bromination method gave quantitative results when the carbide samples contained beryllium nitride as an impurity. For these tests a sample of Be₃N₂ was prepared from Bureau of Standards analyzed beryllium metal by reaction with a mixture of anhydrous ammonia and nitrogen. Synthetic samples prepared from Be₂C and containing up to 20 percent Be₃N₂ were then brominated according to the procedure given above. A series of 5 runs indicated that the nitride was quantitatively attacked during a 30-minute bromination period and gave no interference to the BeO determination.

Determination of Nitrogen

As previously stated, samples of Be₂C heated in air at relatively high temperatures contained appreciable amounts of nitrogen. Specimens of impure beryllium carbide analyzed in the NEPA laboratories were found to contain from 1 to 14 percent Be₃N₂. The conventional Kjeldahl method using a 50 percent solution of sodium hydroxide was found to produce reliable results. If more refractory samples were encountered, fusion of the sample with a quantity of potassium hydroxide equivalent to 20 times the weight of the carbide could replace the caustic solution. The fusion was effected in an iron test tube. The evolved ammonia in either case was absorbed in a measured quantity of standard sulphuric acid and the ammonia determined by back titration with

[REDACTED]

standard base. Representative samples of grade 46 Be_2C analyzed by the Kjeldahl method were found to contain 1.01 percent nitrogen, which was equivalent to 1.98 percent Be_3N_2 . A portion of the grade 46 material was intimately mixed with a quantity of Be_3N_2 to make a synthetic sample which contained 7.75 percent Be_3N_2 . The analysis of 5 aliquots weighing approximately 250 mg each gave an average value of 7.76 percent Be_3N_2 .

Determination of Iron

Small quantities of iron as impurity in Be_2C are conveniently measured colorimetrically using alpha, alpha'-dipyridyl. Traces of iron are quantitatively separated from large amounts of beryllium by diethyl ether extraction in 6 N hydrochloric acid prior to the colorimetric measurement.

Determination of Silica

Silica may be determined in the BeO from the bromination method or in the ignited insolubles after solutioning samples with sulfuric acid. It is determined by loss of weight after fuming with hydrofluoric and sulfuric acids and re-ignition.

Determination of Total Beryllium

Beryllium is precipitated as the hydroxide with NH_4OH after decomposition of the sample in 1:1 sulfuric acid. The $\text{Be}(\text{OH})_2$ precipitate is ignited for 1-1/2 hours at 1000°C and weighed as BeO .

Determination of Free Beryllium Metal

Weighed quantities of Be_2C spiked with beryllium metal have been analyzed by decomposition in boiling H_3PO_4 and measuring the hydrogen liberated. Preliminary experiments have shown that hydrogen can be converted quantitatively to water in the presence of methane, which is also liberated by the acid, by passing it into a tube containing CuO heated to 310°C . The water is absorbed in magnesium perchlorate and weighed. Investigations using platinized asbestos at lower temperatures instead of the CuO are planned.

PROCEDURES

Combined Carbon

A diagram of the apparatus used for this determination is shown in Figure I.

An oxygen flow rate of 95 cc/min. is maintained throughout the determination.

A 0.1 g sample is weighed into a 2 ml beaker and placed in the dry reaction flask. Fifty ml of concentrated H₃PO₄ is added through the burette and the mixture is heated slowly to boiling. The reaction is continued with moderate boiling for 3 hours, after which the ascarite tube is disconnected and weighed.

Calculation:

$$\frac{\text{Wt. of CO}_2 \times 27.29}{\text{Wt. of sample}} = \% \text{ Combined Carbon}$$

Free Carbon

A 0.1-0.2 g sample of Be₂C is refluxed in 1:1 HCl until completely dissolved. The carbon and insolubles are filtered on a fritted crucible, dried at 110°C for one hour, and weighed. After ignition at 600°C for one hour the crucible is again weighed.

Calculation:

$$\frac{\text{Wt. loss on ignition} \times 100}{\text{Wt. of sample}} = \% \text{ Free Carbon}$$

Nitrogen

A 0.2 g sample is digested with 100 ml 50 percent NaOH for one hour. The evolved ammonia is caught in 25 ml 0.1 N H₂SO₄. The acid is back-titrated with 0.1 N NaOH using methyl red indicator.

Calculation:

$$\frac{2.752 (\text{ml H}_2\text{SO}_4 \times N \text{ H}_2\text{SO}_4 - \text{ml NaOH} \times N \text{ NaOH})}{\text{Wt. of sample}} = \% \text{ Be}_3\text{N}_2$$

Beryllium Oxide

A diagram of the apparatus used for this determination is shown in Figure 2.

The system is swept with dry argon (150 cc/min.) throughout the determination.

Line a 4" vitrosil boat with purified SiO₂ to a depth of 1/4". Spread evenly over the surface of the silica a 0.2 g sample of beryllium carbide. Place the boat in the cold bromination tube and raise the temperature rapidly to 820°C. Brominate* the sample for 30 minutes. After the tube is swept free of Br₂, raise the temperature to 900°-950°C and sweep for another 30 minutes. Cool, remove the sample and weigh. Place the boat in a muffle furnace at 900°C for one hour. Cool in a desiccator and again weigh.

Calculations:

$$(a) \frac{(\text{Wt. of Sample}) - (\text{Wt. loss during bromination})}{\text{Wt. of Sample}} \times 100 = \% \text{ Combined Be}$$

$$(b) \frac{\text{Wt. loss on ignition}}{\text{Wt. of original sample}} \times 100 = \% \text{ Total Carbon}$$

$$(c) \frac{\text{Wt. of oxide}}{\text{Wt. of original sample}} \times 100 = \% \text{ Beryllium Oxide}$$

Hydrated Beryllium Oxide

Hydrated beryllium oxide is calculated from the value obtained for water of hydration. The BeO equivalent of the calculated hydrate should of course be subtracted from the BeO as determined above.

Calculation:

$$\frac{\text{Wt. of water of hydration}}{\text{Wt. of sample}} \times 2.2389 \times 100 = \% \text{ BeO} \cdot \text{H}_2\text{O}$$

Water

(a) Adsorbed: A 0.5 g sample is dried at 110°-120°C for one hour in a stream of dry argon. The evolved water is caught in Mg(ClO₄)₂ and weighed.

* The bromine must be anhydrous. The addition of 5 g of anhydrous AlBr₃ per pound of bromine was found to be satisfactory for the purpose.

(b) Water of Hydration: The sample used in the above determination is again dried in a stream of dry argon for one hour at 700°C. The water is collected as above and weighed.

The sum of these two values represents the total water in the sample.

Free Beryllium (Preliminary procedure)

A suitable apparatus for decomposing the sample is shown in Figure 1. The evolved gases, after drying, are passed into a pyrex tube, containing CuO, which is heated to 310° ± 2°C. Hydrogen is quantitatively converted to water while the methane passes through the system unaffected. The water is absorbed in Mg(ClO₄)₂ and weighed.

Calculation:

$$\frac{\text{Wt. of H}_2\text{O} \times 0.5007 \times 100}{\text{Wt. of Sample}} = \% \text{ Be metal}$$

Silica, Iron and Total Beryllium


Silica, and total beryllium are determined by conventional methods found in most analytical texts or reference works. Outlines for these measurements are therefore unnecessary.

After the iron is separated from beryllium by diethyl ether extraction it is measured spectrophotometrically using alpha, alpha'-dipyridyl. A discussion of this procedure may be found in:

Industrial and Engineering Chemistry (Analytical Edition) 14, 862,
(1942) by M. L. Mass and M. G. Mellon.


UNCLASSIFIEDDISTRIBUTION

R. E. Adams
W.N. Becker
E. S. Bettis
V. P. Calkins
J. F. Coneybear
K. C. Cooper
D. D. Cowen (3)
R. L. Echols
F. Franklin
G. H. Giboney
J. V. Hewitt
A. Kalitinsky
W. J. Koshuba (2)
A. Mason
D. E. Meitzler
A. J. Miller
A. O. Mooneyham
W. B. Seaver
W. A. Selle
G. R. Shepherd
G. Simmons, Jr. (G. S. Knopf)
Main Library
Materials Library
W. K. Anderson
W. E. Browning
G. Cremer
S. A. Reed
C. E. Teeter, Jr.
Battelle Memorial Institute


UNCLASSIFIED