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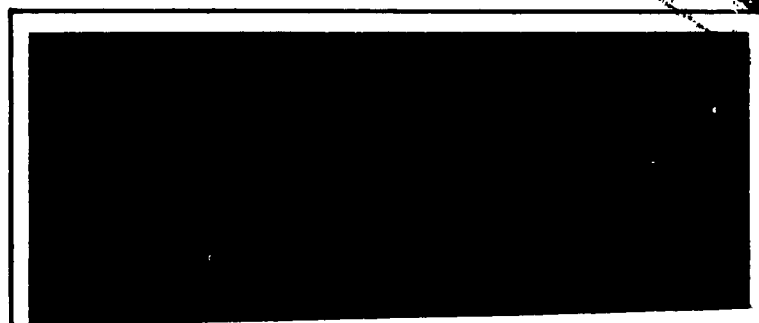


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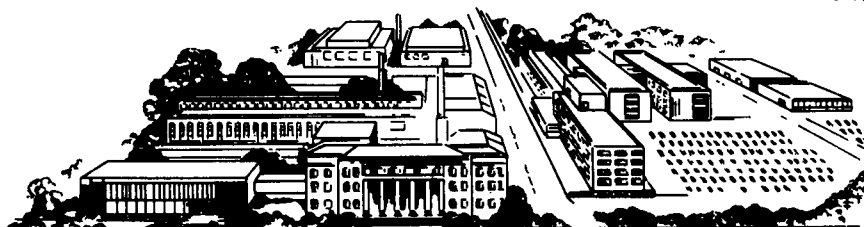


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(6) DEVELOPMENT OF ANALYTICAL TECHNIQUES
FOR THE DETERMINATION OF MINUTE
QUANTITIES OF SELECTED ELEMENTS
IN BERYLLIUM.

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ABSTRACT

↙ The work discussed in this report was principally in the areas of application of techniques developed to the analysis of beryllium material and in continuation of development of the mass-spectrographic and combustion-carbon analysis methods.

Studies were made of the effects of various sample etches and instrumental bake conditions on the determination of H, C, N, and O by mass spectrography. A sample preparation and flux combination was found which gave more uniform combustion-carbon values. ↗

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DEVELOPMENT OF ANALYTICAL TECHNIQUES FOR
THE DETERMINATION OF MINUTE QUANTITIES
OF SELECTED ELEMENTS IN BERYLLIUM

by

W. M. Henry

INTRODUCTION

This fourth bimonthly report on the research program to develop analytical techniques for the determination of minute quantities of selected elements in beryllium describes the effort during the period July 20 through September 20, 1964. The work discussed in this report was principally in the areas of (1) applying the various techniques developed under this program to the analysis of beryllium; (2) additional development efforts particularly in mass spectrography, emission spectrography and in carbon determination; and (3) continuation of building and assembling equipment for electron-beam cleaning of samples for mass-spectrographic analysis.

The total impurity content found in the SR Grade Pechiney beryllium was found to be approximately 13,000 ppm (see Table 1). The same grade of beryllium purchased from the same vendor about 1 year ago contained approximately 425 ppm of impurities. The high impurity content of this second lot of Pechiney beryllium precludes further extensive analytical effort directed towards its use as a secondary standard on this program on high-purity beryllium. Additional analytical work on this grade of beryllium will be carried out on the available material from the purer lot SR Grade Pechiney cast extruded rod.

Further investigations were carried out on the mass-spectrographic technique for the analysis of the important gas impurities in beryllium. These determinations of course require that surface concentrations of these elements be differentiated from their bulk concentration. The effectiveness of various sample etch treatments and sample bake procedures were studied. Also experimental trials were made using an electron-beam apparatus as a surface-cleaning technique. A full evaluation of the results of these studies is being deferred until a densitometer is available for reading the mass-spectrographic plates.

Effort on the determination of low amounts of carbon in beryllium by a combustion technique was directed towards finding suitable fluxes and combustion conditions to ensure complete burning of the sample. Smaller size samples were tried since it is believed that a mass-spectrometric readout of the combustion products can provide sensitivities considerably greater than obtained by conductometric readout.

TABLE 1. ANALYSIS OF SR GRADE PECHINEY VACUUM-CAST EXTRUDED ROD

Results given in ppm.

Element	Mass Spectrographic	Emission	Chemical	Vacuum Fusion
C	1200		1240	
N	240		290	150
O	>5000			7800
F	40			
Na	50			
Mg	>1000	50		
Al	>1000	500	750	
Si	550	400		
P	5			
S	180		140	
Cl	35			
K	50			
Ca	290	5		
Sc	10			
Ti	85	70		
V	8	10		
Cr	230	100		
Mn	450	50	110	
Fe	1100	1400	1200	
Co	2	5		
Ni	200	120	195	
Cu	90	90		
Ga	6	5		
Br	1			
Mo	20	20		
Ag	15			
Sn	10			
Ba	5			
Pb	40	80		

EXPERIMENTAL WORK

Analysis of Beryllium Materials

An SR Grade cast extruded rod, designated Pechiney No. 2, was analyzed by several analytical methods. The results of this work are shown in Table 1. As stated above this particular rod contains considerably higher concentrations of impurities than one of a similar type obtained from the same vendor approximately 1 year ago. The mass-spectrographic values given represent an average of the values obtained by visual reading of the many photographic plates produced during experiments described in the following section of this report. The emission spectrographic values were obtained by use of argon-carrier, buffered d-c arc complete burn, and solution spark techniques. The chemical values were obtained by colorimetric methods and the sulfur and carbon values (included in Table 1 under chemical values) were obtained by combustion methods. All of the techniques used are described in earlier reports.

As evidenced by the values given in Table 1, general accord is obtained among the various methods of analysis with the exception of those for aluminum, calcium, and magnesium. For these elements the mass-spectrographic values appear to be high and further checking is needed to find why such a large discrepancy is obtained on these elements.

Mass-Spectrographic Studies

Electron-Beam Cleaning

The power supply has been constructed and found to be capable of its designed output rating - over 300 ma at 5000 v dc for the beam portion, and over 30 amp at about 10 v ac for the filament. As the schematic diagram Figure 1 shows, the polarity and/or ground can be reversed easily if such should be desirable for future experiments.

Rotary sample holders are being built to replace those presently used in the source chamber of the mass spectrograph. These will be used to rotate samples into position so that they can "see" the electron stream from the electron gun and be cleaned of surface contaminants. The electron gun purchased from Materials Research Corporation has been received. However, it is much too large to fit in the spectrograph source as it presently exists.

Pending completion of the rotary holders and possible modification of the MRC internal-bakeout electron gun, preliminary trials of the electron-beam cleaning were made in a crude glass vacuum chamber attached to an auxiliary vacuum system. The latter can provide a pressure below 10^{-3} torr (the limit of the McLeod and thermocouple gages) when trapped with liquid nitrogen. The glass chamber consisted of a section of tubing with a side arm which led to the vacuum system. In one end of the tube was a waxed-in copper wire holding a copper penny. The other end of the tube had waxed-in copper wires holding a projection lamp filament surrounded by a stainless steel cylinder, closed except for a 1/4 inch hole on the end facing the penny. The spacing between the end of the cylinder and the penny was from 1/4 to 1 inch.

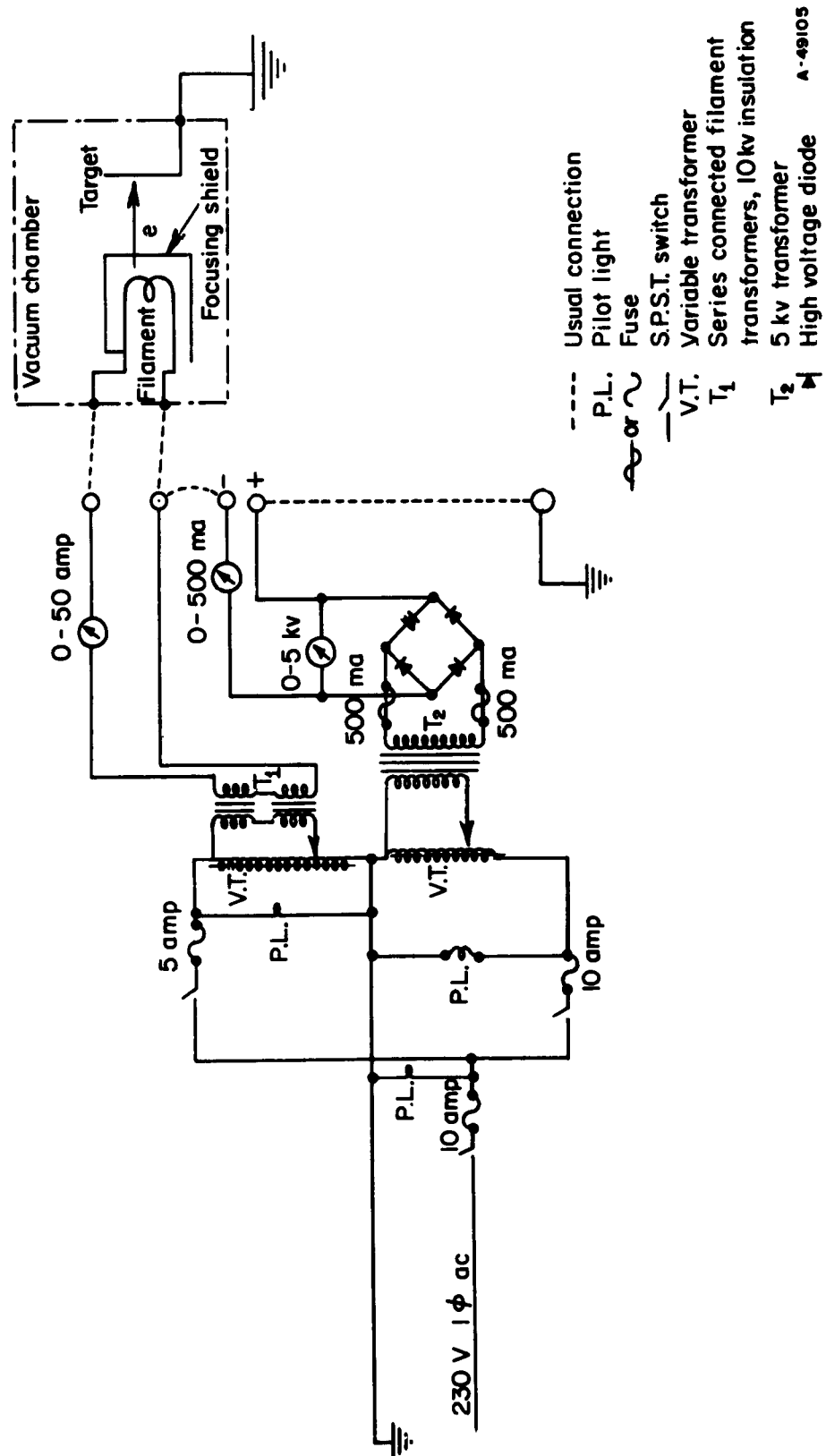


FIGURE 1. SCHEMATIC DIAGRAM OF ELECTRON-BEAM POWER SUPPLY

This relatively crude electron-beam system was tried on several materials and the following observations were made. After a few minutes of pumping the system, the pressure was about 10^{-3} torr. As the filament current was increased from 0 to about 13 amp the pressure rose to 5 to 10 torr, then slowly dropped as the filament and shield were outgassed. The high voltage was then slowly increased, the filament being negative with respect to the copper penny target. A very sudden rise in beam current usually occurred, blowing either the 500-ma fuses in the high-voltage supply, or the 10 amp-fuse in the primary of this supply. If the high voltage were turned up first and then the filament current used to control the beam current, a better control of the latter was obtained, but still an overload occurred frequently. Meanwhile, the pressure rose to as high as 200×10^{-3} torr; the overloads appeared as the pressure reached glow-discharge range. Finally, after many such attempts to get a stable beam current, the pressure would cease to rise excessively. With a beam current of 1-2 ma at 3000 v, the pressure would be more or less stable at about 20×10^{-3} torr. If the beam current was increased, it was possible to make the copper penny target red hot, but the pressure rose quite rapidly. No combination of filament current, beam current, and beam voltage was found that insured a steady beam and steady pressure.

The results of these experiments were disappointing. Starting with a comparatively new copper penny, it was quite black at the end of the experiment, indicating CuO contamination. Similar results were obtained with an old copper penny, a new steel washer, and a rusty washer. The inability to obtain a good vacuum, and the presence of waxed feedthrough connections may have contributed to the poor results.

A sample of the gas present in the vacuum chamber was obtained while the electron beam was operating. The analysis of this gas showed it to be mainly CO, with significant amounts of H₂, CO₂, and SO₂. Almost no H₂O, O₂, or N₂ were detected. Before additional experiments could be performed to verify these results, the filament burned out and further work was not attempted.

Further effort will be directed toward installing the electron-beam gun in the source section of the mass spectrograph and testing its sample-cleaning effectiveness in this system.

Comparison of Etches on Apparent H, C, N, and O in Be

The object of these experiments was to determine what effect, if any, a variety of etching procedures has on the apparent concentration of H, C, N, and O in two grades of beryllium. One material was obtained as a sample for analysis on another contract and proved to be quite low in these elements by our mass-spectrographic analysis. The other was the Pechiney SR grade material which appears quite impure in these same elements.

Etch solutions were as follows:

- (1) Dilute HF, approximately 5-10 per cent HF in H₂O
- (2) Dilute H₂SO₄, 5.0 per cent by volume H₂SO₄ in H₂O
- (3) HF-HNO₃-H₂O, 1:5:5 by volume

- (4) $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4\text{-CrO}_3$, 45 ml H_3PO_4 , 2.7 ml H_2SO_4 , 5.3 g CrO_3
- (5) Dilute HCl, approximately 5-10 per cent HCl in H_2O .

With the exception of the H_2SO_4 and H_3PO_4 , all acids were Mallinckrodt "TransistAR" grade. The H_2SO_4 and H_3PO_4 were Du Pont Reagent grade, and the CrO_3 was Baker's Reagent A. C. S. grade. The water was demineralized. Etching was performed in a small glass beaker, except with those etches containing HF; these were done in a small polyethylene beaker. The $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4\text{-CrO}_3$ etch was done at 120 C for 20 seconds, the others for about 1 minute at room temperature. The same two electrodes of a particular material were used for all experiments.

The exposures were planned to be most useful when read using a densitometer (i. e., with the mass lines about midway on the gamma curve). Thus it is necessary to defer full evaluation of the plates until the densitometer is received.

The results of these visual readings are summarized in Table 2. Material "A" is the high-purity material; "B-1" and "B-2" are, respectively, samples taken from one-fourth and one-half the distance from one end of the Pechiney rod. Some values were obtained with the magnet strength reduced to get $^1\text{H}^+$, and therefore may not correspond exactly with normal analyses which are made at a higher magnet current, although a correction for the reduced sensitivity at reduced magnet current was made. In these experiments values were obtained on H, C, N, and O without the prior extensive pre-sparking as is normally used to obtain true analyses of these elements in a sample. This pre-sparking was omitted in order to get a better picture of the effects of various etches rather than analyses.

On the basis of these results it was concluded that no clear advantage lies with any etch, but that the $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4\text{-CrO}_3$ etch gives higher apparent oxygen values than the others. There being no apparent disadvantage to the HF- H_2O etch, it was continued as the usual etch in our beryllium work.

Comparison of Baking Procedure on Apparent H, C, N, and O in Be

As a continuation of the work described in our report dated June 24, 1964, the effect of baking and/or loading procedures was studied using the same two materials described above in this report. The techniques employed were the same as described in the June 24, 1964, report, and are briefly summarized below.

- (1) Long hot bake: the sample and source are baked overnight at about 150 C with no liquid nitrogen in the cold trap above the diffusion pump which pumps the source.
- (2) Long cold bake: the sample and source are baked overnight at 150 C with the above-mentioned cold trap filled with liquid nitrogen.
- (3) Short cold bake: same as long cold bake, except bake is concluded about 2-1/2-3 hours after start.
- (4) Helium-atmosphere loading: using a disposable "glove bag" filled with He to prevent contact of the source and samples with the air, the samples are scraped and loaded into a previously baked source.

TABLE 2. COMPARISON OF ETCHES ON APPARENT H, C, N, AND O CONCENTRATIONS

Material and Etch		Observed Concentration; ppm atomic basis			
		H	C	N	O
A	HF-H ₂ O	--(a)	30	1	30
A	HF-H ₂ O	--	4.3	0.2	5
A	H ₂ SO ₄ -H ₂ O	--	1.5	0.2	1.5
A	HF-HNO ₃ -H ₂ O	--	10	0.6	15
A	H ₃ PO ₄ -H ₂ SO ₄ -CrO ₃	--	11	0.5	50
A	H ₃ PO ₄ -H ₂ SO ₄ -CrO ₃	16	5	0.5	50
B-1	HF-H ₂ O	54	550	450	20,000
B-1	HF-H ₂ O	60	750	410	14,000
B-2	HF-H ₂ O	6.3	300	400	24,000
B-2	HF-H ₂ O	16	180	150	4,000
B-2	H ₂ SO ₄ -H ₂ O	13	700	725	24,000
B-1	HF-HNO ₃ -H ₂ O	30	510	280	16,000
B-2	HF-HNO ₃ -H ₂ O	6.3	440	350	20,000
B-2	H ₃ PO ₄ -H ₂ SO ₄ -CrO ₃	5.5	210	76	62,000
B-1	HCl-H ₂ O	20	315	265	25,000
B-2	HCl-H ₂ O	6.3	550	525	20,000

(a) Not in mass range.

As in the case of the experiments with etches, these experiments were designed to produce data best read with a densitometer. Therefore, the visual results reported below again represent less than optimum data. The material designation is the same as for Table 3. In all cases the samples were etched once in HF-H₂O, except for the He-atmosphere procedure, in which case the samples were scraped with a diamond lathe tool.

TABLE 3. COMPARISON OF BAKE PROCEDURES ON H, C, N, AND O IN Be

Material and Bake Procedure	Observed Concentration, ppm atomic basis			
	H	C	N	O
A Long hot	--	30	1	30
A Long hot	--	4.3	0.2	5
A Long cold	50	16	2.5	16
A Short cold	50	10	0.15	10
A He atmosphere	820	50	1.5	55
B-1 Long hot	54	550	450	20,000
B-1 Long hot	60	750	410	14,000
B-2 Long hot	6.3	300	400	24,000
B-2 Long hot	16	180	150	4,000
B-2 Long cold	170	350	300	12,500
B-2 He atmosphere	1700	500	65	4,200

Two observations may be made from these data. First, the He atmosphere appears to give very high hydrogen values. Hydrogen is read at m/e 1, so there can be no possible interference from He. Second, the low values obtained for oxygen in Be having a high oxygen content is consistent with the results found previously (see page 7, Bureau of Naval Weapons' report dated June 24, 1964). On the other hand, the He-atmosphere oxygen result found in the Be having low oxygen is the highest of any technique or etch. One possible explanation would be that any etch artificially enhances the oxygen content of the Be; thus the already high oxygen samples are left with a coating of some BeO compound. Conversely, lower oxygen samples do not have sufficient oxygen to build up such a layer. Scraping the sample may leave the surface quite representative of the bulk, thus accounting for the lower oxygen values in the higher-oxygen-content sample. During the He-atmosphere loading there is inevitably some residual oxygen in the bag which is picked up by the Be. In the high-oxygen-content sample, it is insignificant compared with the large amount already present; but in the pure sample, the pickup is large compared with that actually present.

The implication is that the addition or enhancement of oxygen affects a larger volume of sample than had been suspected. We have believed from the beginning of this work that surface effects played the most significant role in the determination of H, C, N, and O, but also had concluded that extensive sparking would largely eliminate the difficulty. This conclusion may still be valid, because in these experiments the elements H, C, N, and O were determined on exposures made after much less sparking

than is our usual practice. This was done so that a picture of the effect of bakes and etches could be obtained, rather than aiming for the best possible analysis of the material. Therefore, we again conclude that surface preparation is important, with the HF-H₂O etch being at least as good as any other tried; and that baking procedures are equally important, with the long hot bake being clearly superior to the He atmosphere for low-oxygen materials, and probably about comparable with both the long and short cold bakes.

Evaluation of the Depth Effect of Various Etches and Baking Procedures

A large number of photographic plates has been produced during the course of the experiments reported here and previously. These plates contain information concerning the decay of initially high values of H, C, N, and O to "normal" values, as a function of amount of sparking. The reduction of this information to usable data must await densitometric reading.

Emission-Spectrographic Studies

Work was continued on the use of an argon atmosphere coupled with a carrier-distillation method as an emission-spectrographic sample excitation technique. This work consisted mainly of analysis of beryllium materials and in modification of the argon-atmosphere excitation chamber. A rough sketch of the presently used chamber is given in Figure 2. As was shown in our previous bimonthly report of October 7, 1964,

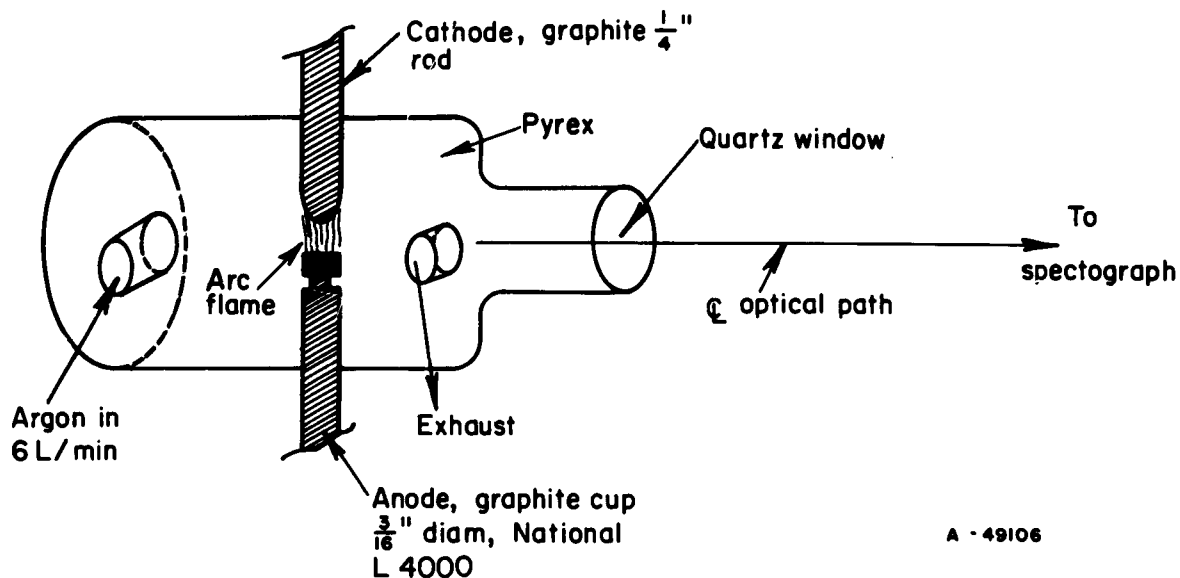


FIGURE 2. LINE DRAWING OF THE ARC CHAMBER

this technique provides greatly enhanced sensitivities in determining impurity elements in beryllium. The sensitivity of the method - 1 ppm or less for many elements - is such that a series of lower-impurity-concentration standards should be prepared in order to utilize the technique effectively on very pure materials. It is anticipated that zone-refined Pechiney SR Grade vacuum-cast extruded rod will provide material of the desired purity.

Carbon Determination

Calculations and some preliminary trials show that, by coupling the combustion and gas train of the Leco Conductometric Carbon Determinator with a mass-spectrometric readout of the carbon-containing gases ensuing from combustion, about 0.1 ppm of carbon can be determined in 0.1 gram of sample. For this reason efforts were discontinued, at least temporarily, to develop combustion conditions and attendant fluxes that would accommodate large samples of beryllium and thereby permit increased sensitivity on carbon determinations. Instead the work on carbon determination was directed toward obtaining complete and uniform combustion of smaller size beryllium samples. Considerable experimentation with various sample sizes and flux materials showed that a 0.3-gram sample with 1 gram of iron, 1 gram of tin, and 1.5 grams of lead gave fairly good results. With this combination the resulting combustion residue generally contained no visibly intact pieces of beryllium and the carbon values obtained on samples were higher and more uniform, indicating more complete combustion. Although this procedure gave occasionally erratic results, the combination appeared satisfactory and the erratic results were attributed to inhomogeneous samples of beryllium.

Continued investigation showed that fairly finely divided samples provided even more uniform carbon values. It was found also that substituting pure copper rings for the lead and decreasing the sample size somewhat gave very uniform melts and, more important, uniform carbon values. The combustion mixture now in use consists of 0.25 gram of finely divided beryllium, 1.0 grams of pure iron, 1.0 grams of pure tin, and 1 copper ring (Leco Corporation, 0.5 gram).

FUTURE WORK

The determination of impurities in zone-refined Pechiney beryllium will be carried out using all of the applicable techniques developed thus far on the program and, to the extent that sample is available, similar work will be carried out on the lot of SR Grade of Pechiney beryllium which had been obtained 1 year ago.

Efforts will be continued on the development of an electron-beam-cleaning procedure for mass-spectrographic analysis. On installation of the recording densitometer, work will be begun to re-evaluate many of the hundred or more mass-spectrographic plates now on hand.

The doping of beryllium with O17 experiments will be completed and evaluation of the recovery and distribution of the doped metal will be started.

Experimental work will be continued to find optimum conditions for combusting beryllium to obtain accurate low-carbon-content determinations. This experimental work will include readout of the combusted gases with a mass spectrometer.

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