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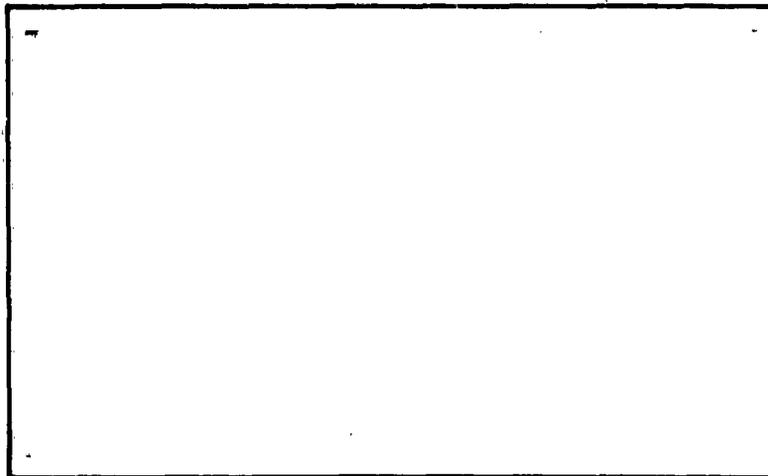
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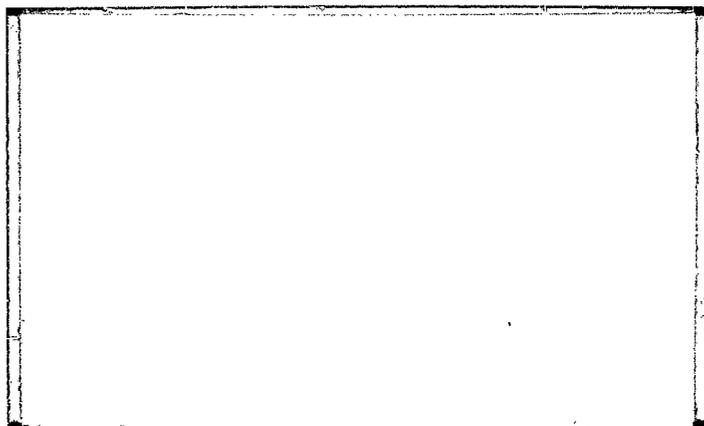
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WOOD AND FOREST PRODUCTS

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

July 22, 1963

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BATTELLE MEMORIAL INSTITUTE  
505 King Avenue  
Columbus 1, Ohio

### ABSTRACT

Development efforts were carried out on vacuum-spark mass spectrography, on activation oxygen analysis, and, to a lesser extent, on vacuum-fusion analysis, emission spectrography, chemical nitrogen analysis, and conductometric carbon analysis methods. The results of the efforts, together with analytical data and complete descriptions of the experimental work, are given. Mass spectrography provides for detection of metallic impurities at concentrations considerably less than 1 ppm and, with some additional standardization, with good accuracy. It is the only method investigated capable of detecting most nonmetallic elements at and below 1-ppm concentrations. However, problems of high blanks on carbon and hydrogen and insufficient standardization on oxygen and nitrogen make mass spectrography supplemented by gasometric and chemical methods for carbon, hydrogen, and possibly nitrogen and oxygen the most useful method for determining total minute traces of impurities in beryllium presently.

Resistivity measurements provide a rapid, economical method of evaluating the over-all purity of beryllium.

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

by

W. M. Henry

INTRODUCTION

The purpose of the work performed under Contract NOW 62-0629-c has been to furnish materials and services to develop analytical techniques for the determination of minute quantities, approximately 1 ppm and lower, of elements in beryllium metal. The elements of primary interest in this work were oxygen, hydrogen, nitrogen, carbon, iron, nickel, copper, aluminum, silicon, titanium, sodium, chromium, cobalt, manganese, vanadium, potassium, and sulfur. For this forward-looking materials-analysis program, the large number of elements, the concentration range of interest, and the anticipated difficulty of the individual impurity determination in respect to its relative estimated importance in affecting the final properties of the metal were the essential factors in selecting analytical methods for development. Consideration was also given to selection of methods on the bases of their over-all sample size and time requirements for complete analyses.

The methods chosen for most extensive investigation were spark-source mass spectrography and activation analysis. Lesser efforts in development were devoted to emission spectrography and carbon, sulfur, nitrogen, and vacuum-fusion analysis methods. The work on these latter methods was carried out largely to provide "backup" or reference determinations for the primary mass spectrographic and activation efforts and to ascertain the problems that might be encountered in extending the sensitivity of these other methods to the 1 ppm and lower concentration range.

The mass spectrographic work was directed toward the analysis of all of the impurities of interest, while the activation work was confined to the development of a sensitive technique for oxygen determination. As an additional reference for evaluating the validity of the mass spectrographic results, resistivity measurements were made on all of the beryllium materials. Although not an analytical method per se, resistivity data provide a rapid and independent means of evaluating the over-all purity of a metal. This report describes in detail the techniques used and the results obtained.

SUMMARY

The analytical method development program on the determination of minute quantities of impurities in beryllium is best summarized by dividing the work on the basis of metallic and nonmetallic impurity analyses.

Although most of the development work on this program was carried out on beryllium materials having impurity-element contents, especially of nonmetallics, in excess of the 1 ppm and lower level which was the aim of this program, analyses of the higher purity Franklin Institute materials as well as materials from Lawrence Radiation Laboratory (analyzed under a concurrent program) indicate that this low limit is a realistic one. Spark-source mass spectrography supplemented by vacuum-extraction hydrogen and conductometric carbon analyses represent the best over-all methods for the complete determination of minute amounts of impurities in beryllium. Additional standardization of the mass spectrographic method, especially for nonmetallic impurities, would be a useful step in establishing its accuracy.

Residual resistivity measurements made on 10 beryllium materials show good correlation with analysis and offer a rapid method of evaluating over-all impurity contents.

#### Metallic-Impurity Analysis

Spark-source mass spectrography has been shown to provide a sensitive and rapid method for the analysis of metallic-impurity elements. When only the metallic-impurity elements are being determined and samples are available of a size and shape favorable for the spark ionization, as many as six to eight sample runs are completed in an 8-hour working day. These are not maximum-sensitivity analyses but provide detections for most elements from 0.01 to 0.1 ppm atomic. Visual interpretation of the attendant mass spectrographic plates can be accomplished in approximately 1 hour for each sample run. The mass spectrographic results are obtained without the use of standards and are based on the assumption that the spark ionization and resultant isotopic detection is equal for all elements present in the sample. It is difficult to fully assess the accuracy of the mass spectrographic data because of the present lack of standards. However a comparison of mass spectrographic values with those obtained by emission spectrographic methods shows that, for most elements, the results check within at least a factor of two. On the basis of reproducibility obtained on repetitive runs on the same material, it is projected that, with adequate standards and if replicate runs are made, mass spectrographic accuracies of from 10 to 20 per cent could be obtained.

Certain emission spectrographic methods also provide detection of certain metallic impurities at or somewhat below the 1-ppm limit. However since this is nearly the limit of detection, the accuracy of these determinations, as based on repeatability runs, is exceedingly poor at these concentration levels.

In order to obtain reasonably repeatable results for metallic-impurity concentrations of 1 ppm and less using emission spectrographic methods, it was found useful to separate all or nearly all of the beryllium from the impurities in the sample and to carry out the analysis using a solution spark procedure. Using a 5-g beryllium sample and separating the beryllium from its impurities by evolution as the basic acetate, most metallic impurities can be determined simultaneously by the solution spark-emission method at or below the 1 ppm level. This method, while not yet entirely evaluated as to the completeness of recovery of the impurity contents and impaired by high blanks on certain elements, is a fairly rapid means of obtaining results for comparison with mass spectrographic results. Presently this concentrational spectrographic procedure can be carried out with an elapsed time of about 3 man-days.

## Nonmetallic Impurity Analysis

### Oxygen

Evaluation of the methods investigated as to their capability for the analysis of oxygen at and below 1 ppm is necessarily based on extrapolation, since the lowest-oxygen-content material thus far analyzed by Battelle's laboratory had an apparent concentration of about 55 ppm oxygen. Spark-source mass spectrography provides the only means of obtaining the desired sensitivity on bulk beryllium material. Apparent instrumental oxygen blanks due to atmospheric leakage as low as 1 ppm have been obtained thus far. Reasonably good agreement has been obtained between mass-spectrographic and vacuum-fusion data on relatively high-oxygen-content materials. However, accurate low-oxygen-content mass-spectrographic standards would be extremely useful. Even without these it is believed that reasonably good relative oxygen values are obtained by the mass spectrographic method.

The activation method investigated under this program, while providing possibly 1 to 10 ppm sensitivities for oxygen on finely divided samples, at present offers little capability for the analysis of low oxygen contents in bulk beryllium samples. The contamination encountered in reducing a bulk sample to a sufficiently low particle size and in obtaining a low-oxygen-content lithium source limits the usefulness of the method severely. Thus far little correlation has been obtained between analyses made on reduced-particle-size beryllium samples and their bulk oxygen contents.

Vacuum-fusion-analysis methods were not extensively investigated under this program. On the basis of the present experience, there appears to be little hope of extending the sensitivity of the method, as used, to 1-ppm oxygen-content materials unless perhaps an isotopic dilution technique were successfully employed.

### Carbon

A conductometric combustion method provides the best method for determining carbon in beryllium, but the sensitivity of the method is limited presently to 10 ppm. Extension of this sensitivity to 5 and possibly 1 ppm might be accomplished by modification of the technique. Little correlation has been obtained between mass spectrographic and conductometric carbon data. This is apparently due to the variable and unaccountable carbon blank obtained by the mass spectrographic method.

### Hydrogen

A vacuum-extraction procedure allows the determination of less than 1 ppm of hydrogen in beryllium. Again the mass spectrographic hydrogen blank is high, which this instance is probably due to the fact that, during construction, the instrument components were annealed for a prolonged length of time in a hydrogen atmosphere.

### Nitrogen

Spark-source mass spectrography provides detections for nitrogen at contents as low as 0.1 ppm and provides a ready method of determining relative nitrogen contents on materials. Additional correlation data or standardization is needed to evaluate the true accuracy of the method. A chemical Kjeldahl method is useful for nitrogen contents at about 10 ppm, and possibly could be extended to near a 1-ppm level by a reduction in the blank and the use of a larger sample size. Vacuum-fusion nitrogen values obtained with the oxygen determinations compare favorably with the chemical results. An isotopic dilution technique applied to these latter two methods might extend their sensitivities considerably.

### Sulfur

Considerable difficulty was encountered in developing a chemical method for the determination of low amounts of sulfur. On the basis of data obtained on sulfur in steel standards, the mass spectrographic technique appears valid and provides detection of sulfur in beryllium at 0.05-ppm concentrations.

## MATERIALS

The materials used for the investigative work were selected from among the highest purity beryllium materials available on a commercial or production scale. These were obtained in quantities from 75 grams to 1 pound each in order to provide sufficient amounts to subdivide and carry out developmental and experimental work using all of the analytical techniques being investigated and interrelate the analytical data obtained. Additionally, three lots of Franklin Institute zone-refined beryllium were obtained in very small but sufficient amounts for the solids mass-spectrographic analysis and electrical-resistivity measurements. The materials used are described in Table 1.

TABLE 1. BERYLLIUM MATERIALS USED IN PROGRAM

Designation	Description	Source
Berylco	Vacuum cast pieces of about 1/4 inch (UKAEA equivalent grade)	Beryllium Corporation of America
NMI	Ultrahigh-purity distilled metal	Nuclear Metals, Inc.
Pechiney	SR grade cast extruded rod	General Astrometals Corp.
Franklin	Zone-refined metal	Franklin Institute

A concurrent analysis assistance program carried out on Lawrence Radiation Laboratories high-purity beryllium materials, together with the Franklin Institute beryllium samples, provided materials more nearly representative of impurity contents at and below the 1-ppm level which was the objective of this program.

EXPERIMENTAL RESULTS

The analyses obtained on the three beryllium materials on which the major development work was carried out are given in the following tables. Detailed descriptions of the experimental work and procedures used for the analyses are given in the Experimental Work section of this report. Mass-spectrographic determinations were obtained on all of the elements of interest with the exception of hydrogen. A complete listing of all of the impurities found mass spectrographically in these three beryllium materials, as well as in the Franklin Institute materials, is given in a later section. The activation-analysis-method development was carried out as a nearly separate effort and was limited to the development of a sensitive method for determining oxygen.

The emission-spectrographic results given in Table 2 were obtained using a chemical-concentration solution-spark procedure for all elements except silicon. The silicon was determined by a carrier-burn method. For most elements the results obtained correlate within a factor of  $\pm 2$ .

TABLE 2. METALLIC-IMPURITY ANALYSES

Element	Analyses, ppm						
	Berylco			Pechiney		NMI	
	Mass Spectro-graphic	Emission	Chemical	Mass Spectro-graphic	Emission	Mass Spectro-graphic	Emission
Na	2	--	--	10	--	<1.	--
Al	300	80	--	20	60	6.	10
Si	240	120	--	15	10	3.	10
K	<5	--	--	14	--	3.	--
Ti	460	440	--	4	1	3.	<1
Cr	25	25	--	3	3	0.6	<1
Mn	100	55	90	5	0.5	12.	12
Fe	360	330	--	50	20	15.	10
Co	0.5	<1	--	0.1	<1	<0.1	<1
Ni	50	25	--	25	10	0.4	1
Cu	High <sup>(a)</sup>	8	--	2	2	High <sup>(a)</sup>	2

(a) Mass-spectrographic sample was contaminated with copper during preparation.

Oxygen determinations were made on the materials using mass-spectrographic, vacuum-fusion, and activation techniques. The activation technique explored in this program entailed crushing the samples to a fine particle size in a helium purge box and then encapsulation to minimize atmospheric contamination prior to analysis. Portions of the crushed samples prepared in this way also were analyzed by vacuum fusion. Additionally, as described in the last bimonthly report, similar portions of the crushed samples as well as portions of bulk samples were submitted to three other laboratories for oxygen determination. The methods to be used by the other laboratories were inert-gas fusion, machine-source activation, and a Triga reaction  $O^{16}(n,p)N^{16}$  reaction. The results from these determinations are still pending.

The results on oxygen obtained in Battelle's laboratories are given in Table 3. From these limited results it appears that increasing the surface area of samples for analysis materially affects the oxygen results.

TABLE 3. OXYGEN ANALYSES

Method Used	Analyses, ppm					
	Berylco		Pechiney		NMI	
	Bulk	Fines	Bulk	Fines	Bulk	Fines
Mass spectrographic	550	--	100	--	65	--
Vacuum fusion	164	360	160	244	83	370
Activation $O^{16}$ (t,n) $F^{18}$ reaction	--	270	--	150	--	250

The results of nitrogen and carbon analyses are given in Tables 4 and 5, respectively. The nitrogen values obtained by the different analytical methods appear to be in fair agreement, while there appears to be little correlation between the mass-spectrographic and combustion-method results on carbon.

Sulfur analyses were made mass spectrographically and by several chemical techniques. A prolonged HCl etch of a mass spectrographic sample prior to analysis gave low results as compared with an unetched sample. The several results obtained are given in Table 6.

The hydrogen values obtained by a vacuum extraction technique given in Table 7 are the averages of three determinations for each sample. No attempt has been made thus far to obtain mass-spectrographic hydrogen analyses on these materials.

## EXPERIMENTAL WORK

### Solids Mass-Spectrographic Technique

E. R. Blosser

Three grades of beryllium metal were studied extensively by the mass-spectrographic technique for their impurity contents. The materials used were (1) a vacuum-cast material of United Kingdom Atomic Energy Authority equivalent purity (hereafter designated as UKAEA grade), (2) an ultrahigh-purity distilled material (hereafter designated as distilled grade), and (3) a Pechiney SR grade cast extruded rod. Three separate samplings and mass spectrographic runs were made on the UKAEA grade, four separate samplings and runs were made on the distilled grade, and one sampling and two runs on the Pechiney rod.

TABLE 4. NITROGEN ANALYSES

Method	Analyses, ppm		NMI
	Berylco	Pechiney	
Mass spectrographic	20	10	10
Vacuum fusion	24	30	<10
Kjeldahl	40	40	10

TABLE 5. CARBON ANALYSES

Method	Analyses, ppm		NMI
	Berylco	Pechiney	
Conductometric combustion	260	270	20
Mass spectrographic	400	90	60

TABLE 6. SULFUR ANALYSES

Method	Analyses, ppm		NMI
	Berylco	Pechiney	
Mass spectrographic	500(a) 12(b)	15	10
Combustion	500	--	<100
Titration	520	--	--

(a) Unetched sample.

(b) Sample etched in HCl for a considerable period prior to analysis.

TABLE 7. HYDROGEN ANALYSES

Hydrogen, ppm		
Berylco	Pechiney	NMI
10.4	5.4	6.6

Eleven series of exposures were made on these seven samples to study (1) effect of surface impurities on the bulk analysis; (2) variations in observed impurity levels as a function of repetitive sparking under constant conditions; (3) bulk impurity analysis; and (4) complex ions registering on the photographic plate. Additionally, to serve as a guide on the applicability of the method to beryllium containing impurities of the order of 1 ppm and less for many elements, three small rods of Franklin Institute's materials were analyzed as single runs. The results of these studies are reported below.

#### Effect of Surface Impurities on the Bulk Analysis

Because the high-voltage spark employed to ionize the elements present in the solid samples operates in a moderately high vacuum ( $10^{-6}$  to  $10^{-8}$  torr) in the mass spectrograph, it is quite small with respect both to power and to area covered. Sparking, and therefore ionization, occurs between the surfaces of the samples and consumes very little material. Although new material is exposed to the spark continually, the erosion over an entire analysis can consume as little as a few milligrams. Thus the short exposures necessary to determine larger traces of impurities may be made on only the first few layers of material. It becomes apparent that the surface composition will markedly influence the results obtained from the first few exposures of a new sample.

In Table 8 the ratios between surface and bulk elements are shown for both grades of material. A figure "10", for example, means that about 10 times as much of that element was detected in the first exposure (surface) than was detected in an identical exposure after additional sparking (bulk). These ratios are necessarily very approximate because, in many cases, the only suitable element line was too heavy to allow a good estimate of the ratio.

Apparently the distilled-grade samples were not washed as well following the etch as the UKAEA-grade samples. If this is true, then no conclusion can be drawn in respect to certain elements concerning the actual surface versus bulk impurities present in the sample as received; rather, the importance of very careful etching and rinsing, and perhaps pre-sparking, of the samples is demonstrated.

Some of the samples covered in this report were etched in approximately 1:5 HCl for about 1 minute, then rinsed by decantation a few times, again etched in dilute HCl, and rinsed many (at least ten) times in flowing deionized water. The samples were partially air dried and loaded into the spectrograph. It would be preferable if no etch were needed; however, the physical shape of the crystals as received dictated some cleaving or turning to produce samples which could be mounted in the spectrograph holders. The above etching procedure was intended to remove any contamination so introduced.

Following the suggestion of Dr. Bunshah of Lawrence Radiation Laboratory, samples analyzed after those described in Interim Report 4, the Pechiney sample and additional analyses of NMI and Berylco samples, were etched twice in dilute (1:50) HF using copious deionized-water rinses after each acid etch.

#### Homogeneity Study

One pair of samples of each material was sparked repeatedly under constant conditions to determine whether the impurity elements were of constant concentration in the

TABLE 8. APPROXIMATE RATIO BETWEEN SURFACE  
AND BULK IMPURITIES IN TWO  
BERYLLIUM SAMPLES<sup>(a)</sup>

Element	Distilled Grade	UKAEA Grade
B <sup>(b)</sup>	10.	3.
C	100.	3.
N	10.	10.
O	100.	100.
Na	3.	3.
Mg	10.	10.
Al	10.	3.
Si	10.	3.
P	10.	10.
S	10.	3.
Cl	100.	3.
K	10.	1.
Ca	100.	1.
Ti	10.	1.
V	N. D. <sup>(c)</sup>	1.
Cr	3.	1.
Mn	10.	3.
Fe	3.	1.
Co	N. D.	3.
Ni	10.	1.
Cu	100.	3.
Zn	10.	10.
Br	N. D.	1.
Zr	3.	1.
Ag	10.	10.
Cd	3.	3.
Sn	10.	10.
W	10.	0.3
Pb	10.	3.

(a) See Table 11 for instrumental parameters.

(b) May be  $\text{BeH}_2^+$ .

(c) N.D. = not detected with the exposure used.

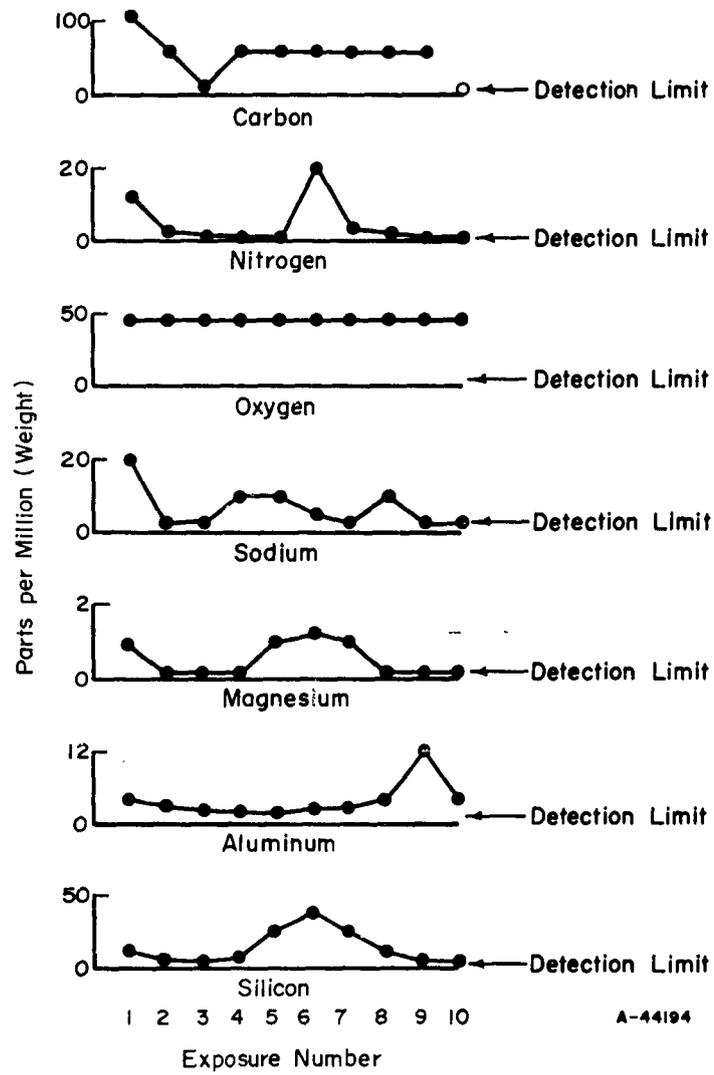


FIGURE 1. HOMOGENEITY STUDY OF DISTILLED-METAL-GRADE BERYLLIUM

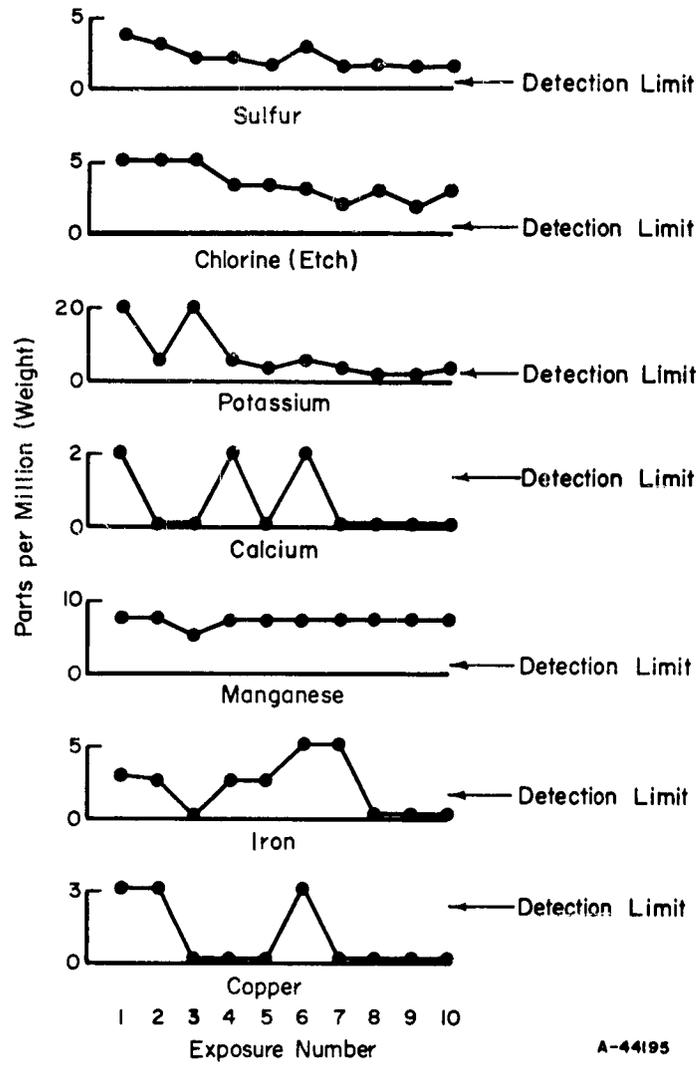


FIGURE 1. (CONTINUED)

small volume consumed by the spark. The sample electrodes used for the homogeneity study had been used immediately before for normal-graded series of exposures so that, presumably, only bulk impurities were seen during the homogeneity experiments. Figures 1 and 2 show the variations of the detectable elements in the two materials as a function of exposure. The exposures for the distilled-grade beryllium were 100 times heavier than those for the UKAEA-grade beryllium. Thus the distilled-grade group represents individual sampling using approximately 100 times as much material as for the UKAEA-grade group. The apparent inconsistencies in detection limits and numerical values are caused by having only one level of exposure to work with in each group; consequently the best element line under normal conditions was often either too light or too dark in these studies for optimum results.

Allowing for the differences in scales in the two figures, it is apparent that the homogeneity in the distilled-grade metal is better than that of the UKAEA grade. This may well be because the exposures were 100 times more intense in the former. Nevertheless, in both samples there are variations of a factor of ten or more which can lead to serious errors. If these variations are in fact due to nonhomogeneity and not to some other variable, it would appear that longer exposures (which consume more material) are preferable to shorter ones. Ilford Q-1 plates, having less sensitive and perhaps more uniform emulsions, have been received but not evaluated. Use of these plates could be expected to result in less sensitivity to inhomogeneity in the sample, as well as to provide better spectral lines for densitometric purposes.

#### Analytical Results

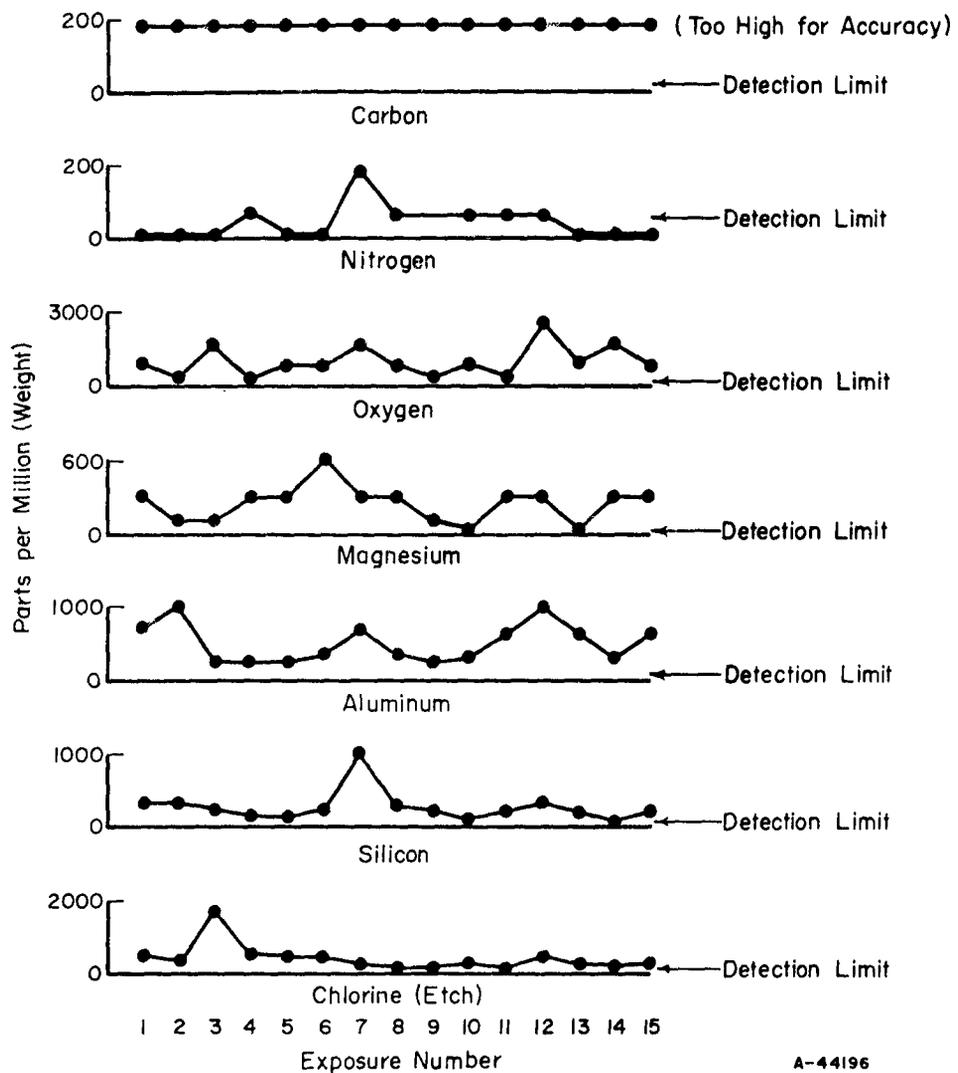
Table 9 summarizes the parts per million by weight of the elements detected in the six grades of beryllium. The Distilled-Metal and UKAEA values are an average of at least two separate analyses of different pieces of the materials, while the values for the other materials were obtained from single runs. Where an element did not appear to follow the general trend of increasing exposure, an estimate was made of its most probable value.

Elements were identified by their isotopic pattern, their exact mass as measured from known lines, or their presence at half-mass (doubly-ionized state) in the case of monoisotopic elements. Despite the multiplicity of complex ions of beryllium and beryllium plus another element detected on the photographic plate (see next section), the resolution of the spectrograph is ample in almost all cases to distinguish between these complexes and an element having the same nominal mass.

Estimates of the concentrations of the detected elements were made visually and no corrections for deviations from assumed equal ionizing efficiencies were made. The observed concentration of each element was calculated from the equation

$$\frac{E_s}{E_i} \times \frac{100}{I_i} \times \frac{W_i}{W_s} \times \frac{M_i}{1} \times 10^6 = \text{ppm (weight basis),}$$

where  $E_s$  is the "just visible" exposure for the  ${}^9\text{Be}^+$  line;  $E_i$  is the "just visible" exposure for an isotope line of the desired element;  $I_i$  is the per cent abundance of the element's isotope used for estimation;  $\frac{W_i}{W_s}$  is the ratio of the atomic weight of the desired element over the atomic weight of beryllium; and  $M_i$  is a multiply-charged factor, ranging from



A-44196

FIGURE 2. HOMOGENEITY STUDY OF UKAEA-GRADE BERYLLIUM

TABLE 9. ELEMENT CONCENTRATIONS IN BERYLLIUM MATERIALS AS DETERMINED BY MASS-SPECTROGRAPHIC ANALYSIS

Element	Approximate Concentration, ppm, Weight Basis					
	Distilled-Metal Grade	UKAEA Grade	Pechiney	Franklin SR-1	Franklin SR-6	Franklin SR-7
Li	<1.	<1.	<1.	<0.01	<0.01	<0.01
B	<0.05	<0.2	<0.05	<0.02	0.1	<0.02
C	60.	400.	90.	40.	40.	135.
N	10.	20.	10.	0.15	0.15	5.
O	65.	550.	100.	55.	135.	550.
F	--	<8.	<2.	1.	2.	<1.
Na	<1.	2.	10.	<1.	<2.5	0.15
Mg	3.	175.	20.	1.	<1.	<1.
Al	6.	300.	20.	<0.1	0.3	<0.1
Si	3.	240.	15.	3.	1.	3.
P	--	--	--	<0.03	<0.03	0.2
S	10.	500.	15.	<3.	3.	40.
K	3.	<5.	14.	4.	--	0.1
Ca	7.	12.	30.	0.1	0.5	<0.1
Ti	3.	460.	4.	<0.15	<0.15	<0.15
V	<0.05	3.	0.2	<0.05	<0.05	<0.05
Cr	0.6	25.	3.	<0.05	0.2	<0.05
Mn	12.	100.	5.	<0.06	2.	<0.06
Fe	15.	360.	50.	0.4	30.	2.
Co	<0.1	0.5	0.1	--	0.2	0.07
Ni	0.4	50.	25.	20.	20.	20.
Cu	--	--	2.	3.	3.	3.
Zn	1.3	4.	1.5	0.3	--	1.4
Ga	<0.05	<0.5	<0.05	<0.05	<0.05	<0.05
As	<0.05	0.2	<0.05	<0.05	<0.05	<0.05
Br	<0.05	0.7	<0.1	0.5	<0.1	0.2
Sr	<0.1	0.1	--	--	--	--
Zr	0.8	2.5	5.	--	--	--
Nb	<0.2	0.4	--	--	--	--
Mo	1.	1.	--	--	--	--
Ta	<3.	<0.2	<2.	<0.2	<0.2	<0.2
Pb	2.	5.	1.	--	--	--

3 to 30, used only when the analysis for an element is based on a doubly- or triply-charged line.

No correction was made for that fraction of the element occurring in multiply-charged lines when using singly-charged lines. Nor, in the case of oxygen, was a correction made for oxygen appearing in complexes. In both cases it was felt that the uncertainty caused by a lack of specific information regarding specific sensitivities of the impurity elements relative to beryllium would be greater than the above-mentioned corrections.

In the above equation relating exposures, isotopic abundances, and weight ratios to parts per million, the least easily established quantity is  $E_g$ , the "just visible" exposure of  ${}^9\text{Be}^+$ . The short (i. e.,  $10^{-12}$  coulomb and less) exposures are difficult to make with good accuracy because the noise level in the monitor circuit at the high gain setting required prevents an accurate measurement of the charge or exposure. Furthermore, even the smallest readable charge produces a line at  ${}^9\text{Be}^+$ , well above the visible level. It is therefore necessary to use densitometric readings and a photographic-plate response curve to establish the exposure at which this line would have been "just visible". No other densitometric measurements were made of other lines for the same reason (lack of sensitivity data) as mentioned above.

Experience with other materials, particularly iron, has shown that the manner in which these very short exposures are made is of utmost importance. For reasons not yet apparent, a series of short exposures may produce either sharp or quite diffuse lines. If the lines are sharp, a good estimation of  $E_g$  is possible; if the lines are diffuse, errors of 3 to 10 are introduced, even if total line width is considered. For this reason, it appears desirable to put a calibrating exposure of a known material on every plate; this is especially true for beryllium, which is monoisotopic and therefore offers no chance of direct, absolute plate calibration. For plate-calibration purposes, commercial gold with 0.03 weight per cent palladium has been tentatively chosen. Such a technique should at least make interplate comparisons valid and permit good use to be made of standardized beryllium samples.

### Complex Ions

As was mentioned earlier in this report, in the spark-ionized beryllium spectra, lines are present which correspond to complexes of beryllium, either with itself or with another element. A listing of these complex ions, all of which are singly charged, with their apparent abundance in atomic parts per million, is shown in Table 10.

It cannot be emphasized too strongly that these complex ions were observed only on the photographic plate and were not necessarily present as species in the samples. With a very high temperature existing in the spark gap, the beryllium and oxygen present in the sample may combine, recombine, or fragment in (at present) unpredictable ways. Considerably more work, beyond the scope of this contract, would be required to demonstrate the presence or absence of any or all of these complexes in the metal.

Evidence indicates that complex ions not representative of the sample are indeed produced in or by the spark. Gold, when sparked as two wires, shows no lines corresponding to  $\text{AuC}$  or  $\text{AuC}_2$ . However, a gold wire sparked with a carbon-containing sample produces lines of  $\text{AuC}$  and  $\text{AuC}_2$ ; similar results are obtained with tantalum and very likely with other metals.

TABLE 10. APPARENT CONCENTRATION OF OBSERVED COMPLEX IONS

Complex Ion <sup>(a)</sup>	Line	Concentration, ppm (atomic)		Ratio, First to Second <sup>(b)</sup>
		Distilled Grade	UKAEA Grade	
Be	9	1,000,000.	1,000,000.	=
BeH	10	1.	4.	>>
Be <sub>2</sub>	18	40.	40.	=
Be <sub>2</sub> H <sup>(c)</sup>	19	0.4	1.	>
BeC	21	0.04	0.04	>
Be <sub>2</sub> H <sub>3</sub>	21	0.04	0.04	>
BeO <sup>(d,e)</sup>	25	0.12	1.	>
BeOH <sup>(d,e)</sup>	26	0.04	0.04	>
Be <sub>3</sub>	27	1.	4.	>
Be <sub>2</sub> O	34	0.4	4.	>
Be <sub>4</sub>	36	1.	1.	=
Be <sub>5</sub>	45	1.	1.	=
Be <sub>4</sub> O	52	0.4	0.4	>
Be <sub>6</sub>	54	0.4	1.	>
Be <sub>3</sub> O <sub>2</sub>	59	0.01	0.1	>
Be <sub>5</sub> O	61	0.01	0.04	=
Be <sub>7</sub>	63	0.1	0.4	=
Be <sub>4</sub> O <sub>2</sub>	68	0.01	0.1	>
Be <sub>6</sub> O	70	0.01	0.04	N. D. <sup>(f)</sup>
Be <sub>8</sub>	72	0.1	0.4	=
Be <sub>3</sub> O <sub>3</sub>	75	N. D. <sup>(g)</sup>	0.01	N. D.
Be <sub>5</sub> O <sub>2</sub>	77	N. D.	0.01	>
Be <sub>6</sub> C <sub>2</sub> <sup>(h)</sup>	78	N. D.	0.01	>
Be <sub>7</sub> O	79	N. D.	0.01	>
Be <sub>9</sub>	81	0.1	0.1	=
Be <sub>4</sub> O <sub>3</sub>	84	N. D.	0.04	>
Be <sub>8</sub> C <sup>(h)</sup>	84	N. D.	0.01	>
Be <sub>8</sub> O	88	0.01	0.04	N. D.
Be <sub>10</sub>	90	0.1	0.1	=
Be <sub>5</sub> O <sub>3</sub>	93	0.04	0.01	>
Be <sub>9</sub> O	97	N. D.	0.01	>
Be <sub>11</sub>	99	0.04	0.1	=
Be <sub>12</sub>	108	0.04	0.04	=
Be <sub>11</sub> O	115	N. D.	0.01	N. D.
Be <sub>13</sub>	117	0.01	0.04	N. D.
Be <sub>14</sub>	126	0.01	0.02	N. D.
Be <sub>15</sub>	135	0.01	0.02	N. D.
Be <sub>16</sub>	144	0.04	0.01	N. D.
Be <sub>17</sub>	153	0.01	0.01	N. D.
Be <sub>18</sub>	162	0.01	0.01	N. D.
Be <sub>19</sub>	171	0.01	0.01	N. D.
Be <sub>20</sub>	180	0.01	0.01	N. D.
Be <sub>21</sub>	189	0.01	N. D. <sup>(g)</sup>	N. D.

Footnotes appear on following page.

Footnotes for Table 10

- (a) All ions in this table are singly charged.
- (b) This ratio is an estimate of the ratio of intensities of the particular ion in two successive, identical exposures of a UKAEA-grade sample. The symbols  $\gg$ ,  $>$ ,  $\geq$ , and  $=$  mean, respectively, that on the photographic plate an ion appeared in the first exposure to be present in much greater, greater, somewhat greater, or equal concentration than in the second exposure.
- (c) May be fluorine.
- (d) Magnesium interferes.
- (e) Hydrocarbons may interfere.
- (f) N.D. in "ratio" column means not detected in the second exposure.
- (g) N.D. in this column means not detected.
- (h) Mass measurement does not confirm identification.

An interesting observation concerning complex ions was made when sparking beryllium samples as thin sheets rather than rods. The  $\text{Be}_n^+$  ions were less evident and ions corresponding to "n" greater than about 15 were not visible. This could suggest that thin sections present very short paths for ions before they leave the region of the solid sample, and that the length of the ion path is in some way a factor in  $\text{Be}_n^+$  ion formation. A similar effect of "short ion paths" has not been observed on other materials, perhaps because polymeric ions are not produced in such profusion by most other metals.

### Instrumental Parameters

Table 11 lists the exposure range and the setting of the spark circuit controls for the studies reported in Tables 8, 9, and 10 and Figures 1 and 2. Spark voltage is nominal, not measured, and is open-circuit voltage as estimated by the manufacturer. Repetition rate is the number of pulses per second the spark operates, and the pulse length is the time in microseconds for which it operates each pulse. The frequency of the spark is nominally constant at 0.5 megacycle. Thus, with settings of 40 kv, a repetition rate of 300, and a pulse length of 100, the half-megacycle spark is operating in pulses of 100 microseconds' duration 300 times a second at 40,000 volts open circuit. This corresponds to the spark discharging between the electrodes 3 per cent of the time.

The exposure range is given in units of a millimicrocoulomb ( $10^{-9}$  coulomb) charge as indicated by the integrator which intercepts about one-half of the total ion beam before it enters the magnetic analyzer section.

Following the practice suggested by several users of spark-source mass spectrographs, the pulse length is now being held constant and only the repetition rate of the spark is being varied between successive exposures. Particularly with elements easily ionized thermally, such as the alkali metals, this technique should give better accuracy.

Another change, or rather a point of special care, is to maintain as wide a spark gap as possible. This usually increases the ion yield, which is desirable, but far more importantly, it may improve accuracy. Work not yet published, but reported at the E-14 committee of ASTM in May, 1963, by Honig and Woolston of RCA indicates that the energy spread of ions produced in the spark can be varied and shifted by changing the spark gap. One of the most disturbing points is that not all elements behave in the same way with gap changes. At the same meeting, Professor Hintenberger of the Max Planck Institute, in a deliberate attempt to induce energy shifts, was able to make chromium content appear greater than the iron content in a stainless steel. Such evidence indicates that conditions prevailing in the spark gap must be closely controlled and reproduced if acceptable accuracy is to be obtained. In this connection, a note about sample configuration is in order. If a reasonable rate of ion production and a controlled spark gap are desired, the samples must be of a physical shape that minimizes shielding of the ion beam by the samples. For this reason sheets or square sections are preferable to large-diameter round rods. Sparking edge to edge or corner to corner may have the disadvantage of a very small sampling area, but shielding and excessively small spark gaps are minimized. Furthermore, a poorly shaped sample has required about 8 times as long to spark as a sharp-edged sample; in addition to the excessive manpower and equipment time involved for such a long sparking time, the limitation of magnet and electrostatic analyzer stability over an 8-hour period is far more severe than for 1 hour, and if the limitation is not met, a loss of resolution is inevitable.

TABLE 11. SPARK PARAMETERS USED IN OBTAINING THE RESULTS REPORTED

	<u>Open-Circuit Voltage, kv</u>	<u>Pulse Repetition Rate, per second</u>	<u>Pulse Length, 10<sup>-6</sup> second</u>	<u>Exposure Range, 10<sup>-9</sup> coulomb</u>
Table 8 (Surface versus bulk impurities)	40	300	100	100
Table 9(a) (Analytical results)	20-40	10-1000	25-200	0.0001 to 300
Table 10 (Complex ions)	40	300	100	100
Figure 1 (Homogeneity study of distilled grade)	40	300	25	10
Figure 2 (Homogeneity study of UKAEA grade)	30	300	200	0.1

(a) Voltage remained constant for any one plate. Other parameters were varied to suit the total charge required.

Activation Analysis

R. Ritzman and T. Ellemen

The activation technique used to determine the impurity oxygen content of beryllium metal is based upon the nuclear reaction of tritium ions (tritons) with oxygen atoms of mass 16 to produce the radioactive mass 18 isotope of fluorine. The emission of a neutron also accompanies this reaction which is commonly written in abbreviated notation as  $O^{16}(t,n)F^{18}$ . The product fluorine-18 isotope decays by positron emission and electron capture with a half-life of 112 minutes. The concentration of this isotope is determined by radioassay and used to calculate the concentration of oxygen in an irradiated sample.

The tritons are produced by the thermal-neutron bombardment of lithium, according to the reaction  $Li^6(n,t)He^4$ . The tritons (t) recoil from the reaction site with an energy of 2.75 Mev. Since thermal neutrons initiate the radioactivation process, a nuclear reactor with its relatively high thermal-neutron fluxes can be used for the irradiation. Lithium or one of its nonoxygenated compounds must surround the metal specimen whose oxygen content is to be determined so that the specimen surface is evenly bombarded by tritons. Also, a reference standard is usually carried through the determination with the specimen, to eliminate the need for difficult absolute measurements of the induced fluorine-18 activity. In principle this standard may be any convenient material which has a known oxygen content.

The range of 2.75 Mev tritons in beryllium metal, Atomic Number 4, is about 40 microns. Tritons of maximum energy occur only at the surface of the beryllium and the rate of energy loss per unit distance,  $\frac{dE}{dx}$ , increases slowly with decreasing triton energy or penetration distance below the surface. The cross section, which is a measure of the reaction probability, for the (t,n) reaction on oxygen-16 decreases rapidly with decreasing triton energy. (1, 2) (See Figure 3.) Therefore the reaction rate will be highest near the surface of the metal where the recoiling tritons are most energetic.

If the effect of decreasing reaction probability with decreasing triton energy is taken into consideration, as well as the fact that tritons enter a beryllium surface at all possible angles, it can be shown that 85 per cent of all triton-oxygen reactions occur in the top 10 microns of the beryllium surface. This is illustrated in Figure 4 where the relative reaction probability in arbitrary units is plotted versus the distance of triton penetration into beryllium. In deriving this curve, the simplifying assumption was made that the atomic number of the lithium bearing material was the same as that of beryllium.

There are several important consequences of the limited triton reaction range which affect the manner in which this technique must be used to determine oxygen in beryllium. For a given beryllium sample, the fraction of total oxygen in the specimen that is available for reaction with recoiling tritons depends upon the ratio of the reaction-zone volume to the total specimen volume. As this ratio approaches one, better sensitivities are obtained. The ratio is directly related to the surface area of the specimen. Since subdivision is an effective means of increasing the surface area of a specimen,

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(1) Jarmic, N., Phys. Rev., 98, 41 (1955).

(2) Sher, R., and Floyd, J. J., Phys. Rev., 102, 242 (1956).

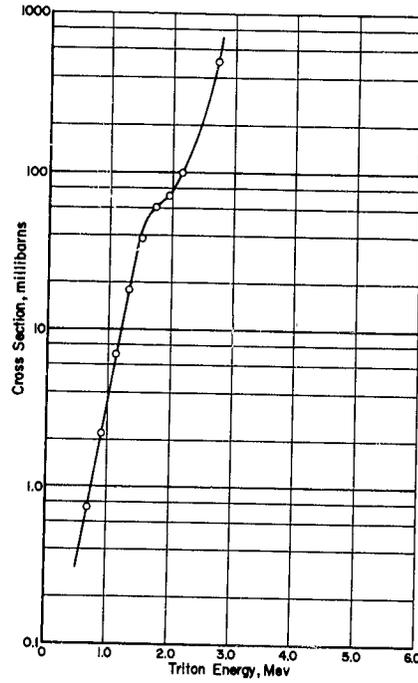


FIGURE 3. CROSS SECTION FOR THE REACTION  $O^{16}(t,n)F^{18}$  AS A FUNCTION OF THE TRITON ENERGY

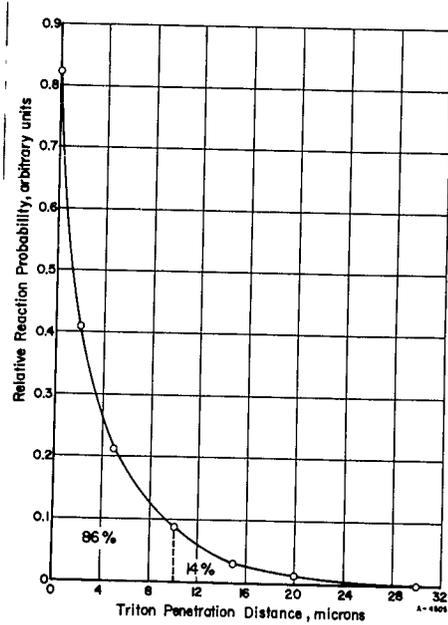


FIGURE 4. THE RELATIVE REACTION PROBABILITY OF TRITONS WITH OXYGEN IN BERYLLIUM AS A FUNCTION OF PENETRATION DISTANCE OF THE TRITONS

BATTELLE MEMORIAL INSTITUTE

oxygen determinations must be made on samples of crushed metal. Since surfaces can oxidize or absorb oxygen, care must be exercised to protect a crushed specimen from oxygen exposure until the radioactivation is completed. It is also desirable to maintain a narrow distribution of particle sizes in a particular sample so that the ratio of sensitive volume to total volume is accurately known.

Another important consideration is the selection of an oxygen standard material. The standard should have an effective atomic number near four; otherwise, the triton energy distribution in the standard and beryllium will be different. This results in a different reaction probability in each material which can be reconciled only by theory. It is also desirable to use standard material of the same particle size as the beryllium specimen to avoid corrections for differences in the ratio of reaction-zone volume to total volume, even though in principle this is a simple calculation for particles significantly larger than the recoil range.

The objective of this program was to investigate and develop the use of the triton recoil technique for the activation analysis of oxygen in pure beryllium metal. The sensitivity limits of the technique were evaluated, and its reproducibility and the possible sources of error were investigated. The oxygen content of several beryllium specimens was determined using the technique.

#### Experimental Techniques

Lithium fluoride was selected as the most satisfactory source for lithium-6. It is obtained commercially as the powder, and by heating in vacuum, the oxygen content can be reduced below 0.5 per cent. Neither the fluorine nor other common impurities in the salt cause production of interfering radioactivities during activation. In addition it is reasonably high melting and has an adequate water solubility of about 3 grams per liter.

Ammonium nitrate was used as the standard of known oxygen content. The effective atomic number of this compound is 4.66 and is available in crystalline form. The salt is easily dried, water soluble, and no radioisotopes are produced during irradiation which interfere with the determination of fluorine-18.

Lithium fluoride was purified by heating at about 120 C for 20 hours under vacuum. The salt was stored in desiccators purged with helium until its encapsulation with beryllium. Ammonium nitrate was air dried at 110 C for 20 hours and also stored in a helium-purged desiccator until needed. Usually the salt was passed through standard sieves to obtain particle sizes corresponding to that of the beryllium. This sized material was then dried and stored.

All beryllium specimens were crushed in a helium-purged glove box. The equivalent of two to three box volumes of helium were passed before crushing was begun. The crushed metal was sized by sieving, the yield of particles of the desired size range being about 25 per cent of the starting mass of beryllium. Initially, about 0.5 gram of particles having an average diameter of 1840 microns was used in experiments. However, in most analyses requiring improved sensitivity, 0.25-gram particles, 505 microns in diameter were used. Two different types of irradiation containers were used for specimens: polyethylene bottles which could easily be heat sealed, and quartz vials which were more difficult to seal but became necessary after it was discovered that the plastic frequently softened and ruptured during irradiation. The beryllium particles

were thoroughly packed in lithium fluoride such that the weight of LiF was at least five times greater than that of beryllium. This assures an even triton flux throughout the specimens, as has been shown by Osmond and Smales<sup>(3)</sup>. In some cases the capsules were sealed off inside the purge box; in other instances the capsules were removed, placed under vacuum for 20 to 21 hours and then sealed off while still evacuated. Encapsulation of the ammonium nitrate standard, intimately mixed with lithium fluoride, followed the same procedures. The length of exposure of the materials to the purge-box atmosphere during crushing and capsule-loading operations varied from 2 to 3 hours. The degree of oxygen contamination present in the box over these periods was determined. Results of the gas-chromatographic analysis appear in Table 12. These results indicate exposure to several thousand parts per million of oxygen during sample preparation.

This level of contamination was also present in capsules that were sealed without evacuation.

TABLE 12. OXYGEN CONTENT OF HELIUM-PURGE-BOX ATMOSPHERE AS A FUNCTION OF PURGING TIME

Purge Time, hr	Crushed Beryllium Exposure Time, hr	Oxygen Content of Atmosphere, vol %
2	0	1.2
4	2	0.34
6	4	0.13

Following encapsulation, the specimens were irradiated at the Battelle Research Reactor for periods of 1 hour. This allowed production of about 30 per cent of the maximum possible fluorine-18 while limiting the production of interfering radioisotopes. Approximately 30 minutes after irradiation, the samples were recovered and the capsules subsequently opened. The beryllium particles were separated from the lithium fluoride powder using standard sieves. The metal particles were then rinsed with cold water to remove any LiF powder that may have adhered to them, washed with acetone, dried, and finally weighed. The residual oxygen content of purified lithium fluoride (0.2 per cent minimum) necessitates the above sequence of operations. If the lithium fluoride is allowed to accompany beryllium, the fluorine-18 activity produced in it will contribute significantly to the total amount radioassayed. It was assumed that the water rinse did not leach fluorine-18 activity from the beryllium particles. The wide range of oxygen contents that have been determined offers indirect evidence in support of this assumption.

After the beryllium particles were weighed they were dissolved in cool, dilute sulfuric acid. Dissolution normally required about 30 minutes. This was preparatory to making a steam-distillation separation of the radiofluoride using the method described by Osmond and Smales<sup>(3)</sup> and by Huckabay<sup>(4)</sup>. Separation was necessary since impurities in the beryllium, particularly manganese, resulted in the production of radioisotopes that interfered in the final radioassay of fluorine-18. The distillation required about 90 minutes to complete and yielded approximately 125 cc of distillate. The concentration of

(3) Osmond, R. G., and Smales, A. A., *Anal. Chim. Acta.*, **10**, 117 (1954).

(4) Huckabay, W. B., Welch, E. T., and Metler, A. V., *Anal. Chem.*, **19**, 154 (1947).

fluorine-18 was quite low in this solution, so a lead chlorofluoride precipitation was performed to concentrate the activity. Addition of a known weight of nonradioactive lithium fluoride prior to distillation allowed calculation of the chemical yield after the  $\text{PbClF}$  was weighed. Yields were generally good; varying between 60 and 90 per cent.

After the precipitate had been dried and weighed it was radioassayed by gamma-ray scintillation spectrometry. Since fluorine-18 decays by positron emission, and each positron, upon annihilation, gives rise to two 0.51-Mev gamma-ray quanta, the gamma-ray spectrum of the  $\text{PbClF}$  precipitate was recorded and the area under the 0.51-Mev photopeak was measured. Comparison of this area with that obtained from radioassay of the standard of known oxygen content, with corrections for differences in chemical yields, assay times, and weights of materials used, resulted directly in the oxygen content of the beryllium specimen.

The ammonium nitrate standard was prepared for assay by simply dissolving it in dilute acid, diluting to a known volume, and then removing an aliquot for counting. The ammonium nitrate was not separated from the lithium fluoride. Samples of the  $\text{LiF}$  that was packed around the beryllium particles were radioassayed to determine what fraction of the counting rate obtained for the standard mixture was due to the oxygen present in the lithium salt.

#### Analytical Results

The linearity of the activation technique was checked by irradiating samples of lithium fluoride mixed with different known amounts of oxygen in the form of ammonium nitrate. The results of this effort appear in Figure 5. The lower range of the determination was restricted by the oxygen content of  $\text{LiF}$  itself. The upper limit was restricted by dilution effects of excessive ammonium nitrate on the triton flux in the specimen. This effect is clearly illustrated in Figure 5 by the departure of the point at highest oxygen content from the linear curve. Osmond and Smales<sup>(3)</sup> reported similar data which indicate that the  $\text{LiF}$ /compound weight ratio must be greater than four to overcome this behavior. The other data in Figure 5 which conform to these conditions demonstrate the linearity of the technique within the limits of  $\pm 20$  per cent.

The reproducibility of the activation technique was also investigated. Here the method of sample preparation and encapsulation was held as nearly uniform as possible. Table 13 summarizes the results of four determinations of the oxygen content of Berylco metal in terms of parts per million oxygen. There is no obvious reason why the oxygen value obtained in Analysis 4 should have departed significantly from the others but this may reflect nonuniform oxygen concentrations in the bulk metal which was supplied for analysis. Considering this possibility, the activation method appears to offer a precision on the order of  $\pm 20$  to  $\pm 25$  per cent.

Early in the program it was recognized that the presence of high oxygen contamination in the lithium fluoride, which surrounds beryllium specimens, might produce erroneous results. The process need not be one of oxidation, but rather may result from the recoil of oxygen and/or fluorine-18 into the beryllium from the salt. These recoils would be produced by collisions or reactions of the impurity oxygen with bombarding tritons. To investigate this possibility one beryllium sample was packed in purified lithium fluoride (oxygen content = 0.2 per cent) while an identical sample was packed in lithium fluoride containing 5 weight per cent oxygen as benzoic acid. It was found that

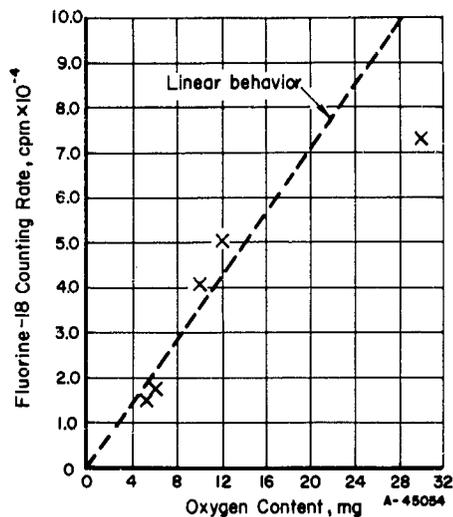


FIGURE 5. RESULTS OF THE LINEARITY CHECK OF THE ACTIVATION METHOD USING SAMPLES OF  $\text{LiF} + \text{NH}_4\text{NO}_3$

TABLE 13. REPRODUCIBILITY OF DETERMINATIONS OF OXYGEN CONTENT OF BERYLCO BERYLLIUM

Analysis	Oxygen Found, ppm	Deviation From Mean Value
1	270	+5
2	200	-65
3	190	-75
4	400	+135
Mean Value	265	$\pm 70$

the oxygen analysis for the beryllium sample that was packed in the highly oxygenated salt was a factor of two greater, i. e., actually 900 ppm compared to 400 ppm for the specimen packed in purified LiF. Since untreated reagent-grade lithium fluoride contains about 3 weight per cent oxygen, this experiment illustrates that, even with complete separation of metal and salt after radioactivation, the LiF must be purified prior to encapsulation to avoid this recoil effect.

During the course of the investigation it became apparent that special care must be taken to minimize the exposure of both beryllium and LiF to oxygen if the activation-analysis technique is to yield reliable values. Results obtained under varying exposure conditions and treatment illustrate the importance of this factor.

Table 14 summarizes oxygen contents obtained for beryllium and lithium fluoride as handling techniques were improved. Improvement consisted of continued reduction in sample-preparation time within a helium-purged atmosphere, followed in the final case (Analysis 4) by evacuation of the capsule atmosphere for a period of 20 hours before it was sealed. The evacuation step results in a significant lowering of the LiF oxygen content, which then minimizes errors introduced by the recoil effect discussed above. Improved techniques also appeared to reduce surface oxidation of the beryllium, since assay values decreased by a factor of four, while experiments in which the lithium fluoride contained 5 weight per cent oxygen showed only a factor of two increase in the beryllium-analysis values.

TABLE 14. EFFECT OF OXYGEN EXPOSURE ON THE ANALYSIS OF BERYLLIUM

Analysis	Measured Oxygen	
	Be, ppm	LiF, %
1	1020	3.2
2	810	3.0
3	440	1.1
4	270	0.41

Oxygen determinations were made on samples of beryllium metal supplied by three different sources using handling procedures which had previously given minimum oxygen-contamination results. Results of these analyses are given in Table 15. The errors assigned each value are based upon the precision determined for the Berylco metal.

TABLE 15. OXYGEN CONTENT OF BERYLLIUM SPECIMENS

Metal	Oxygen Content, ppm
Berylco	270 ± 70
NMI	250 ± 70
Pechiney	150 ± 40

### Evaluation of the Activation Technique

The ultimate sensitivity capability of the activation method for oxygen analysis is certainly less than 1 ppm, but practical limitations, which include the available neutron flux, limits on easily handled particle sizes, and the need for a rather lengthy radio-chemical separation, result in a more realistic sensitivity limit of about 10 ppm even on small-particle-size samples. Since the technique is sensitive only to oxygen which lies within 10 to 20 microns of the metal surface, specimens of larger surface area are required as the oxygen content becomes lower. This necessitates increased care in preparation of the metal for analysis. Oxygen-free atmospheres are mandatory and the materials which will contact the specimen, the source of lithium-6 in particular, should have an oxygen-impurity content approaching that of the beryllium itself. It is possible that the use of beryllium wafers sandwiched between lithium-metal sheets would meet these conditions. At oxygen levels of 50 ppm and above, the technique is relatively easily applied, assuming good control of specimen-handling conditions. Up to four determinations can be made per day with dual distillation equipment. With good control of experimental conditions, the technique would be particularly applicable in studies of surface-oxidation rates or for investigation of oxygen-concentration gradients near the metal's surface.

### Emission Spectrographic Methods

R. E. Heffelfinger

Several techniques were utilized for the spectrographic determination of impurities in beryllium, depending on the level of impurities. Table 16 gives the detection limits for selected elements by two carrier-distillation techniques, a solution-spark technique, and a barium fluoride-buffer method. This table also shows that, of these, the carrier technique is most useful for determining low amounts of impurities, while the solution and barium fluoride methods are useful for determinations of gross amounts of impurities.

TABLE 16. DETECTION LIMITS OF SELECTED IMPURITIES IN BERYLLIUM BY SEVERAL SPECTROGRAPHIC METHODS

Method	Element-Detection Limit, ppm																			
	Al	B	Ca	Cr	Co	Cu	Fe	Mg	Mn	Mo	Ni	Si	Zn	Ag	Pb	Ti	Sn	Zr	Na	V
Solution	100	50	10	100	50	10	50	10	50	100	50	--	500	10	--	100	--	100	50	100
BaF <sub>2</sub>	10	--	--	--	--	--	--	--	--	--	--	10	--	--	--	20	--	50	--	--
Carrier AgCl/Ga <sub>2</sub> O <sub>3</sub>	--	0.5	1	3	2	0.5	5	1	0.5	1	2	--	25	--	1	10	1	--	1	5
CuOHF carrier	--	0.5	--	--	--	--	--	--	--	--	--	1	--	--	--	--	--	--	--	--

While the carrier technique is capable of providing detections for many elements at the parts-per-million level, it is unsatisfactory for the determination of many other elements because of unknown purity of the base material in the spectrographic standards or because of inherent spectral insensitivities of some elements.

In order to provide a method which would avoid some of the inadequacies of the previously mentioned methods and determine as many elements as possible, work was directed toward developing a method which would utilize a separation of impurities from the beryllium prior to spectrographic analysis.

#### Development of Separation-of-Impurities Method

Beryllium has been separated from its impurities by extracting the beryllium in the form of basic beryllium acetate [ $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$ ] with chloroform.<sup>(5)</sup> The separation by the chloroform extraction is about 95 per cent complete. For example, on a 5-gram sample, 0.25 gram of beryllium in terms of metal would remain after extraction. This is a concentration factor of 20.

In this program it was desirable to utilize a solution-spark technique, which was judged to be the most precise spectrographic technique available for this type sample. As can be seen in Table 16, the detection limits for the majority of elements is of the order of 50 ppm when beryllium is analyzed by a solution-spark spectrographic technique. Applying the concentration factor of 20 obtainable by a chloroform extraction of beryllium, this would indicate that the extracted sample could be analyzed by solution spark to a lower limit of the order of 2 to 3 ppm — not 1 ppm as stated as an objective of this program.

Inasmuch as the boiling point of basic beryllium acetate is low, it was decided to try a thermal evolution of the beryllium. It was found that 2 to 5 grams of the basic acetate could be evolved almost completely at 200 to 250 C under a gas hot plate in a period of 4 to 6 hours.

The basis for this "concentrational" method is to remove by vapor evolution the beryllium as the basic acetate, dissolve the residue in acid, and subject the resulting solution to spectrographic analysis. By using the technique, 5 grams of beryllium can be evolved and the residue dissolved and held in solution in a total volume of 5 milliliters. This is effectively a hundredfold concentration factor over the usual solution-spark methods and permits detections of the order of 1 ppm (based on original matrix metal) and less, as shown in Table 17.

TABLE 17. DETECTION LIMITS OF IMPURITIES IN BERYLLIUM BY A CHEMICAL-SPECTROGRAPHIC METHOD

Element-Detection Limit, ppm																			
Al	B	Ca	Cr	Co	Cu	Fe	Mg	Mn	Mo	Ni	Si	Zn	Ag	Pb	Ti	Sn	Zr	Na	V
1	--	--	2	3	0.5	1	1	1	1	2	--	50	0.5	3	0.5	3	0.5	--	1

A measure of the precision and accuracy of this concentrational method is given in Table 18, which reports recovery data. These data were obtained by adding impurity elements at known levels to a previously analyzed sample of high-purity beryllium. The concentration of a given element in the "spiked" sample should equal the sum of the amount added and the amount already present.

(5) Karabash, A. G., Peizalaen, Sh. I., Slyusarcva, R. L., and Lipatova, V. M., J. Anal. Chem. U.S.S.R., 14 (1) (January-February, 1959).

TABLE 18. RECOVERY DATA OF SOLUTION CONCENTRATIONAL METHOD

	Element, ppm										
	Cr	Co	Fe	Mg	Mn	Mo	Ni	Sn	Zr	Cu	Ti
Present	--	--	4	--	5	--	0.5	--	--	--	--
Added	4	4	4	4	4	4	4	4	--	--	--
Total	4	4	8	4	9	4	4.5	4	--	--	--
Recovered	3	3	7	3	11	4	3	16	--	--	--
Present	10	--	10	5	15	--	--	--	5	--	--
Added	10	--	10	10	20	10	10	--	10	10	--
Total	20	--	20	15	35	10	10	--	15	10	--
Recovered	20	--	20	10	50	13	8	--	13	20	--
Direct Solution	Analysis	--	330	106	55	--	--	--	--	--	440
Solution Concentration	Analysis	--	350	80	60	--	--	--	--	--	400

The recovery was also checked by analyzing an impure sample of beryllium by a solution-spark method and then analyzing a 0.2-gram portion of the same sample by the concentrational technique. These data also are given in Table 18.

The specific procedure used is as follows: In a 600-milliliter beaker, 5 grams of beryllium sample is dissolved using 200 milliliters of 6N HCl plus 20 milliliters of concentrated HNO<sub>3</sub>; 0.5 milligrams of niobium is added for an internal standard and the solution is evaporated to a sirupy consistency. The solution is thereafter taken to sirupy consistency after each of three additions of 100 milliliters of HNO<sub>3</sub> to obtain beryllium nitrate. The beryllium nitrate sirup is diluted to 100 milliliters with water, and ammonium hydroxide is added to precipitate the sample as the hydroxide. (The ammonium hydroxide used was prepared by dissolving ammonia gas in water contained in polyethylene bottles.) The hydroxide is dried and ignited at 500 C to obtain beryllium oxide and to drive off the ammonium nitrate. The oxide is then dissolved in 400 milliliters of glacial acetic acid to form the basic beryllium acetate, [Be<sub>4</sub>O(CH<sub>3</sub>COO)<sub>6</sub>]. The solution is evaporated to dryness and transferred to a platinum dish which is then heated to drive off the beryllium as the basic acetate. The residue, which consists of the sample impurities, is dissolved in 1 milliliter of H<sub>2</sub>SO<sub>4</sub> and 2 to 3 milliliters of HNO<sub>3</sub> and transferred to the beaker in which the original sample was dissolved. The solution is then evaporated to fumes of H<sub>2</sub>SO<sub>4</sub> and cooled; 1 milliliter each of HNO<sub>3</sub> and HCl and 2 milliliters of H<sub>2</sub>O are added and the solution is analyzed spectrographically.

The final solution of impurities is in a volume of 5 milliliters which corresponds to the original sample weight of 5 grams. The concentration of an element in solution will therefore correspond exactly to the concentration of that element based on the original sample. Standards are made to include the expected impurity elements or elements for which detection data are desired in the range of 0.3 to 100 ppm. It is common in this laboratory to change the concentration of an element from one standard to the next by a factor of 2 or 3. Typical concentration of an element in a set of standards would be 0.3, 1, 3, 10, 30, 100 ppm. The standards also contain 20 per cent H<sub>2</sub>SO<sub>4</sub> and the internal standard element in the concentration in which it was added to the original beryllium specimen. In this experiment niobium was added at the level of 100 ppm. Finally, the

standards are put through the same procedure as is the sample for analysis, adding the same amounts of reagents, drying down and bringing back to the final volume so that the blank level in the standard will be similar to the blank level in the standards. Loss of an element by mechanical accident such as spattering will also tend to be equalized between sample and standard.

The solution is analyzed spectrographically by a solution-spark technique according to the conditions in Table 19.

TABLE 19: SPECTROGRAPHIC CONDITIONS OF ANALYSIS OF SOLUTION OF IMPURITIES FROM BERYLLIUM

Spectrograph	ARL 1.5 meter grating
Film	SA 1
Electrode System	Upper - graphite 1/4 rod pointed to 30 per cent included angle rounded to 1/16-inch radius Lower - Lucite cup electrode
Power	150-v primary, 15,000 v secondary, 5.7 amp rf
Inductance	410 $\mu$ h
Capacitance	0.007 $\mu$ f
Breaks Per Half Cycle (Mechanically Interrupted)	2
Prespark	10 sec
Exposure	50 sec
Development	D19, 3 min

The recovery data indicates that this method is, in general, valid. However, more data are needed. More elements should be tested for recovery, a precision study should be made, and a good means for collecting the beryllium basic acetate distillate should be worked out.

#### Vacuum-Fusion Analysis

M. W. Mallett

An attempt was made to analyze high-purity beryllium for oxygen by the exact method of Booth and Parker, Anal. Chem., 84, 546-548 (1959). However, the analyses

obtained on 50-milligram samples showed 100 per cent uncertainty. Consequently the method was altered to use four individual 50 milligram sample portions, each with its own 70 milligram wrapper of tin, dropped in rapid succession into the platinum bath. Except for increasing the sample weight fourfold in this special way the analysis was made in the prescribed manner. The results obtained are given in Table 20 together with attendant nitrogen values.

TABLE 20. MODIFIED BOOTH AND PARKER  
METHOD WITH UKAEA GRADE  
BERYLLIUM

Sample Weight, gram	Oxygen, ppm	Nitrogen, ppm
0.222	157	17
0.210	132	26
0.196	176	33
0.191	164	20
0.193	157	22
0.198	181	31
0.209	151	17
0.188	192	25
Average:	164	24
Standard Deviation:	19	8
Oxygen Coefficient of Variation: 12 per cent		

Further modification of the method was tried. Five analyses were made with a 70 Pt:30 Sn (eutectic) bath. A minimum Pt:Be ratio of 30:1 was maintained. Samples each consisted of four 50-milligram pieces of UKAEA grade beryllium. Results ranged from 109 to 187 ppm oxygen with a standard deviation of 31 ppm and a coefficient of variation of 23 per cent. These poorer results seem to confirm the observation of Still that tin should be of little help in the analysis because of its low solubility for beryllium.

A platinum bath (33 Pt:1 Be) was tried. All tin was excluded from the bath and from addition as a sample wrapper. Results (72, 73, and 83 ppm) were low compared with the average of 164 ppm oxygen shown in Table 20. This seemed to show that, although relatively high tin contents are detrimental, the small tin additions recommended by Booth and Parker are essential to complete oxygen removal.

Three exploratory analyses of the same metal were made with an iron bath at 1650 C. The results of 17, 43, and 48 ppm oxygen were extremely low, so nothing further was done with this approach.

Six more analyses were made by the Booth and Parker method, except that the samples (UKAEA grade) consisted of one piece of beryllium weighing about 200 milligrams as compared with the four 50-milligram pieces of Battelle's modified technique. Although the average result was 154 ppm, the coefficient of variation was 40 per cent. This erratic behavior was largely absent when the composite sample (see Table 20) was used.

Two additional materials were analyzed by the modified (composite sample) technique to serve as reference values for these materials in massive form for comparison with mass spectrographic values and with results obtained for the same metals when powdered for use in the activation-analysis method. The results obtained for oxygen are given in Table 21 together with attendant nitrogen results.

TABLE 21. VACUUM-FUSION OXYGEN AND NITROGEN ANALYSES

Material	Oxygen, ppm	Nitrogen, ppm
NMI distilled metal	77	3
	86	<5
	86	4
Average:	83	<10
Pechiney SR cast rod	132	26
	157	44
	190	21
Average:	160	30

Samples of three grades of beryllium were pulverized in the same manner and in the same equipment as was used for preparing samples for activation analysis. The powder material was held under argon in sealed containers until analyzed. The analyses are given in Table 22. It is seen that the comminution process has caused an increase of from about 100 to 200 ppm in the amount of oxygen found. From the limited number of analyses made, it appears that the increase bears no relationship to the original amount of oxygen found.

TABLE 22. VACUUM-FUSION ANALYSIS OF BERYLLIUM POWDERS AS PREPARED FOR ACTIVATION ANALYSIS

Material(a)	Oxygen, ppm
NMI distilled grade	353
	418
	319
Pechiney	256
	231
UKAEA grade	270
	360
	452

(a) Samples consisted of 200 milligrams of powder wrapped in one piece of tin foil.

Hydrogen Analysis

M. W. Mallett

Three grades of beryllium were analyzed by a method designed specifically for determination of hydrogen. The method consists of dissolving the beryllium sample in a copper bath at 1100 C under vacuum and collecting the evolved gases. The beryllium content of the melt is limited to a maximum of 12 weight per cent. After a 20-minute extraction, the gases are oxidized by passing over hot CuO. This converts the hydrogen to water vapor which is removed from the low-pressure collection system by freezing out in a trap cooled by a stirred Dry Ice-acetone mixture. The volume of hydrogen is calculated from the drop in pressure in the calibrated volume of the system.

Samples in massive form were analyzed with the following results shown in Table 23. At present the occasional high hydrogen values for the NMI and UKAEA grade materials can be accounted for only by heterogeneity. It is not known whether the excess hydrogen is occluded or derived from a surface contaminant.

TABLE 23. ANALYSIS OF HYDROGEN CONTENT OF BERYLLIUM

Material	Sample Weight, grams	Hydrogen <sup>(a)</sup> , ppm
NMI	1.016	3.3
	0.752	4.1
	1.195	12.5
Pechiney	1.144	4.2
	0.780	6.6
	1.178	5.5
Berylco	0.941	8.3
	1.060	6.5
	1.008	16.5

(a) The precision of the analysis is  $\pm 0.5$  ppm for a 1-gram sample.

Chemical Nitrogen Analysis

D. Chase and F. Huber

Nitrogen in beryllium was determined chemically by use of a modified Kjeldahl technique. The apparatus used is mostly conventional laboratory equipment, the two most important items being Parmas-Wagner still assembly using an electric steam generator and a steaming rack. All digestion and titration vessels are steamed out on the steaming rack before use. The procedure used for the analysis is as given below.

### Procedure

Weigh a 0.5-gram sample of beryllium, preferably in the form of chips or turnings, into a 50-milliliter beaker, and cover with 10 milliliters of deionized water. Cautiously add 1:1 hydrochloric acid until the sample is completely dissolved. Transfer sample solution to the Parmas-Wagner still washing with three small portions of water. Add 25 milliliters NaOH solution (prepared by dissolving 340 grams of NaOH in 1000 milliliters of H<sub>2</sub>O, adding 0.5 gram of Devarda's alloy, and boiling until the volume is about 900 milliliters). Distill and collect the condensate in a 50-milliliter conical flask containing 5 drops of mixed indicator solution (0.0166 gram of methyl red and 0.0834 gram of bromcresol green in 100 milliliters of neutral ethanol) and 10 milliliters of 0.16 per cent boric acid solution (prepared by dilution of 4 per cent stock solution). Adjust heat input to the still so that a 10-milliliter volume of condensate is collected in a 5-minute interval. Titrate the collected ammonia with 0.007 N HCl.

### Extension of Sensitivity

The above procedure is adequate for nitrogen in beryllium concentrations of about  $\pm 10$  ppm. It is believed that this could be readily extended to  $\pm 5$  ppm by overcoming the problem of a high blank. The blank is derived both from reagents used in the analysis and from nitrogen-containing gases, especially ammonia, in the laboratory atmosphere condensing or occluding in the laboratory ware or sample solution. Purifying the reagents, carefully cleaning the apparatus and laboratory ware, and carrying out the sample dissolution rapidly in a nitrogen-low room atmosphere can minimize the blank problem. Fortunately the acid-digestion time required for beryllium is quite low. The use of a larger sample size also should aid in improving sensitivity. However, due to the voluminous precipitate formed in the still, this requires a change in the present apparatus.

If the blank problem were minimized, extension of the technique to  $\pm 1$  ppm would become largely a problem of accurately determining the end point. For this, the titration step could be supplanted by a more sensitive method such as Nessler's method, conductivity measurement, or an isotopic dilution measurement.

### Combustion Carbon Analysis

D. Chase and F. Huber

A Leco conductometric apparatus is used for the carbon determinations and the analysis is carried out in the following way. If cleaning is required, the sample is solvent washed three times using ethyl alcohol, followed by three washings with ethyl ether, and then dried. A 0.3 to 0.5-gram sample in the form of small particles such as turnings, millings, or coarse powder is weighed into a combustion crucible which has been preignited at 900 C for at least 2 hours. The flux used consists of approximately 1 gram of Leco iron, 1.2 grams of pure granular lead and 1 gram of Leco tin accelerator. After running, the completeness of combustion is checked by crushing the sample and examining the powder under low power magnification. If combustion is found to be incomplete, the results of the run are discarded. The main problem encountered in analyzing high-purity beryllium is to obtain quantitative combustion on a large enough sample to provide

good detection limits and to avoid too violent a reaction. The presently used flux, a mixture of tin, lead and iron, in most cases gives complete combustions and precisions of  $\pm 10$  ppm on 0.3 to 0.5-gram samples. However the reaction mixture fouls the combustion tube rapidly.

#### Improved Flux

It is believed that the combustion technique can be improved in the following ways so as to obtain other precisions of  $\pm 5$  ppm or possibly even  $\pm 1$  ppm.

The iron presently being used in the flux to "load" the furnace induction coil has a carbon content of up to 50 ppm, which in view of the comparatively small sample, amplifies the blank problem considerably. A supply of zone-refined iron drawn to a fine diameter and snipped into small lengths should provide a suitable coil load and a much lower blank. The use of copper or other metal in combination with iron and/or lead and tin might provide for complete combustion of a larger sample.

The very rapid and occasionally violent sample combustion, which is a problem both for safety and possibly in ensuring a complete sample burn, might be overcome by the use of a more dilute oxygen flow.

The sensitivity of the detection in the apparatus possibly could be increased by reducing the concentration of the barium hydroxide in the absorption cell.

#### Residual-Resistivity Measurements

R. Bate

Resistivity measurements have long been recognized by workers in various areas of metal physics as a means of evaluating the over-all purity of metals. Their utility arises from the fact that dissolved impurities introduce an additional component of resistivity which is nearly independent of temperature and is proportional to the concentration of solute atoms of a particular type (for small concentrations).

In metals of reasonable purity, at ordinary temperatures, this component of resistivity, called the residual resistivity,  $\rho_r$ , is much smaller than the thermal or ideal resistivity,  $\rho_i$ , which is temperature dependent and is an intrinsic property of the metal, independent of purity. However, at very low temperatures, near 0°K, the ideal resistivity becomes very small and the resistivity is dominated by the residual component.

#### Resistivity Ratios

The assumption that the two resistivity components discussed above are additive is the basis of Matthiessen's Rule:

$$\rho(T) = \rho_i(T) + \rho_r, \quad (1)$$

where  $\rho(T)$  is the specific resistivity of the metal measured at the temperature T (in degrees Kelvin).

The ideal resistivity of most metals is negligible compared to the residual resistivity at the boiling point of liquid helium (4.2°K), and this assumption is certainly true for beryllium of attainable purity (see the subsequent discussion of detection limits). Thus from Equation (1) we have:

$$\rho(4.2^\circ\text{K}) = \rho_r, \quad (2)$$

so that the residual resistivity can be determined by measuring the specific resistivity with the sample immersed in boiling liquid helium. Since the residual resistivity is roughly proportional to the concentration of dissolved impurities,\* this measurement gives an indication of purity. However, the use of the resistivity value itself is inconvenient because of anisotropy effects and the necessity of knowing the exact geometry and dimensions of the sample. In practice, it is better to determine the ratio of the resistivity at room temperature (~300°K) to that at 4.2°K, since the determination requires only voltage and current measurements. From Equations (1) and (2) we have:

$$\frac{\rho(300^\circ\text{K})}{\rho(4.2^\circ\text{K})} = \frac{\rho_i(300^\circ\text{K}) + \rho_r}{\rho_r}, \quad (3)$$

and rearranging,

$$\frac{\rho(300^\circ\text{K})}{\rho(4.2^\circ\text{K})} - 1 = \frac{\rho_i(300^\circ\text{K})}{\rho_r}. \quad (4)$$

If the resistance ratio, which is the first term on the left side of Equation (4) is large compared to unity, then it is inversely proportional to the residual resistivity.

#### Experimental Technique

The measurements were made by a standard potentiometric technique, using a Leeds & Northrup type K-3 potentiometer.

The specimen and a calibrated standard resistor were connected in series and fed by a Kepco Model SC-18-4M power supply operating in the constant-current mode.

Potential probes were provided at both the specimen and the standard resistor, and the potentiometer was connected by appropriate switching alternately to one or the other set of probes. Voltage readings were taken for both polarities of current to cancel any Seebeck potentials which might have been present due to temperature gradients in the system.

These measurements were made first at room temperature, and then with the specimen immersed in a liquid helium bath, yielding the desired resistance ratio,  $\rho(300^\circ\text{K})/\rho(4.2^\circ\text{K})$ .

To conserve liquid helium, the specimen holder was designed to fit in standard storage dewars manufactured by Supairco. These dewars have spherical inner chambers

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\*Actually, the relationship is  $\rho_r = c_1\gamma_1 + c_2\gamma_2 + \dots$  where  $c_i$  is the concentration of atoms of the  $i^{\text{th}}$  impurity and  $\gamma_i$  is the specific contribution of the  $i^{\text{th}}$  dissolved impurity.

of various diameters, depending on the capacity, which ranges from 15 to 50 liters. The inside diameter of the neck on all sizes is 0.6 inch.

The specimen holder is a 3-foot length of 1/2-inch red fiber rod machined to accommodate sample contacts and leads. Details of the construction are shown in Figure 6.

This dip type of measurement has proven to be quite economical, as very little helium is boiled off during the dip, the largest loss occurring from the normal boil-off rate of the dewar, which is approximately 0.3 liter per day.

The main source of error in the measurement is the small magnitude of specimen potentials at 4.2°K, usually of the order of 5 to 50 microvolts. The potentiometer has a resolution of about 0.1 microvolt, while residual errors may be of the order of 0.2 microvolt. Thus it is advantageous to use as large a current as possible without causing rapid boil-off of helium due to excessive dissipation in the specimen. It is also necessary that specimen cross sections be small to provide measurable signals. The specimens used were in some cases machined down to appropriate size. A typical sample of square cross section would measure .040 inch on a side and 3/4 inch in length. Typical probe spacing would be 0.4 inch.

### Results and Discussion

The results of resistance-ratio measurements are listed in Table 24. The samples indicated by (a) were investigated under another program but have been included here to demonstrate more fully the correlation between resistance ratio and purity. The results taken from this table are presented graphically in Figure 7, in which the resistance ratio minus one is plotted (on a log-log plot) against the total impurity concentration (in ppm atomic) determined from the mass-spectrographic data. Inspection of Equation (4) reveals that, if the residual resistivity is proportional to the total impurity concentration, then the experimental points on this plot should lie on a straight line with slope -1. Since different impurities contribute differently to the resistivity and since all of the impurities may not be in solution, this relationship will not be satisfied exactly. However, inspection of Figure 7 reveals that a line of slope -1 can be drawn which relates the resistance ratio to the total impurity content within a factor of two for nearly every sample tested.

TABLE 24. RESULTS OF RESISTANCE-RATIO MEASUREMENTS ON  
SELECTED BERYLLIUM SAMPLES

Sample	$\rho(300^\circ\text{K})/\rho(4.2^\circ\text{K})$	Total Impurities, ppm atomic
UKAEA grade-berylco	6.2	1150
Distilled metal grade-NMI	122	154
SR-1-Franklin	121	68
S-7-Franklin	53	440
LRL-Cast-2 <sup>(a)</sup>	34	247
LRL-Cast-3 <sup>(a)</sup>	29	560
LRL-Distilled-4 <sup>(a)</sup>	62	187
LRL-Distilled-5 <sup>(a)</sup>	207	42
LRL-Distilled-6 <sup>(a)</sup>	172	67
Pechiney SR grade	69	169

(a) Work done under another contract.

B A T T E L L E M E M O R I A L I N S T I T U T E

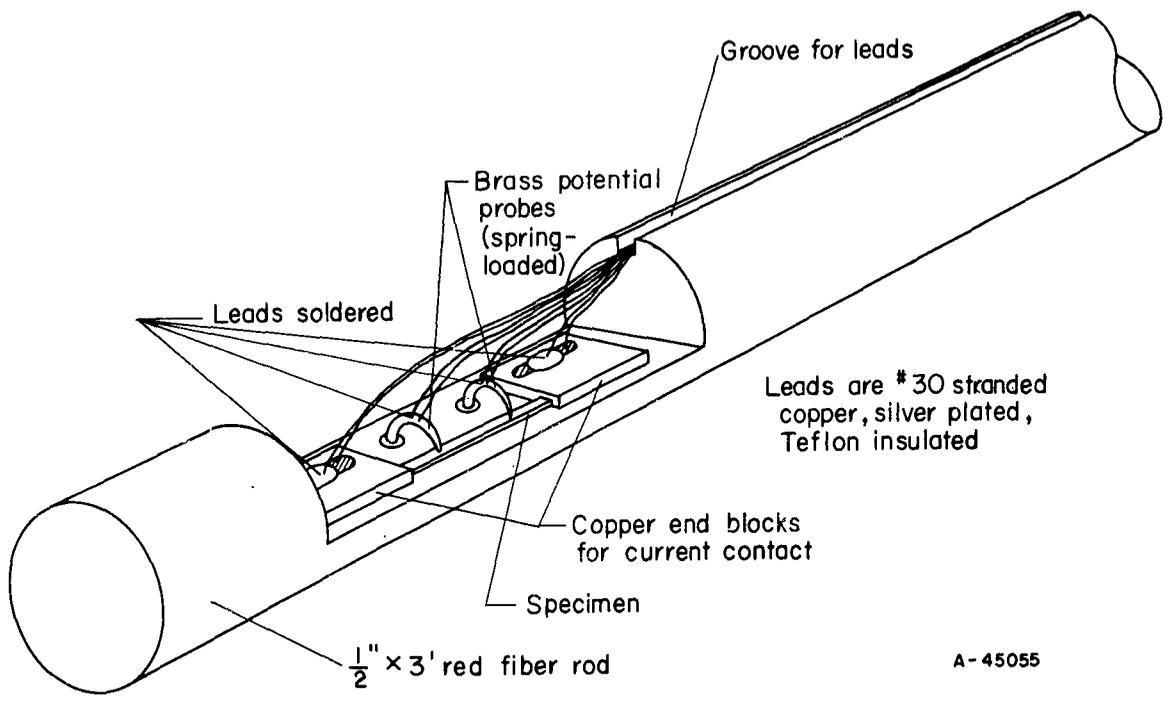


FIGURE 6. DETAIL OF SAMPLE HOLDER

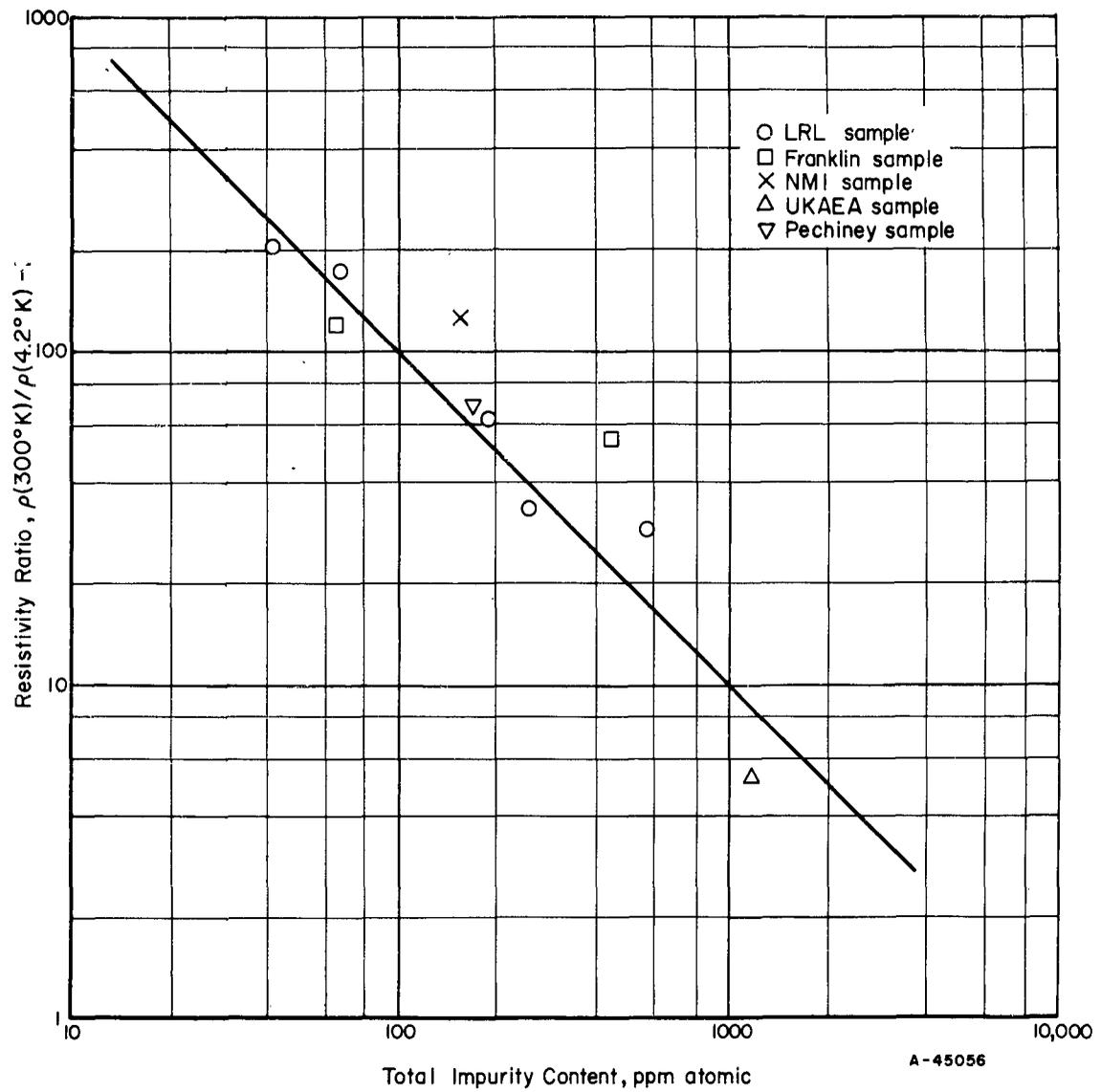


FIGURE 7. CORRELATION OF RESISTIVITY RATIO WITH IMPURITY CONTENT FOR SEVERAL BERYLLIUM SAMPLES

Thus we can conclude that there is a definite correlation between the resistance ratio and the general impurity level in beryllium samples coming from a number of different sources. This confirms the hypothesis that residual-resistivity measurements can be used as a rapid method of determining roughly the over-all level of purity.

Resistivity measurements were also made on some of the samples at the temperature of boiling liquid nitrogen (77°K), and their  $\rho(300^\circ\text{K})/\rho(77^\circ\text{K})$  were ratios calculated. This ratio can be mathematically related to the ratio  $\rho(300^\circ\text{K})/\rho(4.2^\circ\text{K})$ .

The relationship between these two ratios, is:

$$\frac{\rho(300^\circ\text{K})}{\rho(4.2^\circ\text{K})} = \frac{\rho(300^\circ\text{K})/\rho(77^\circ\text{K}) - 1}{1 - C \rho(300^\circ\text{K})/\rho(77^\circ\text{K})} + 1, \quad (5)$$

where  $C = \rho_i(77^\circ\text{K})/\rho_i(300^\circ\text{K})$  is a constant which is independent of purity if Matthiessen's rule is obeyed. The constant  $C$  can be determined from the data on samples for which both ratios were determined, and then Equation (5) can be used to construct a curve which gives the relationship between the two ratios. Comparison of the data on several samples gives a value of 0.0112 for  $C$ , and the curve relating the two ratios is exhibited in Figure 8. Examination of this curve reveals that measurement of the nitrogen temperature-resistance ratio,  $\rho(300^\circ\text{K})/\rho(77^\circ\text{K})$ , is sufficient to determine the helium temperature-resistance ratio with reasonable accuracy for the levels of purity normally encountered. This is very significant, because liquid nitrogen is easy to obtain and to store for long periods and costs about twenty times less per liter than does liquid helium. Thus, it appears that measurements of  $\rho(300^\circ\text{K})/\rho(77^\circ\text{K})$  could be employed very economically as a rough indication of over-all purity.

#### Detection Limits

One of the biggest advantages of resistance-ratio measurements for detection of impurities is the extreme sensitivity to small concentrations of solute when measurements are made at 4.2°K. A fundamental limitation on the sensitivity would occur when the impurity concentration became small enough that the residual resistivity was less than the ideal resistivity at 4.2°K. Approximate calculations indicate that a sufficient degree of purity for this to occur in beryllium is not likely to be achieved ( $\sim 10^{-3}$  ppb), although such a situation can arise in other metals. Another limitation is due to the residual resistivity introduced by lattice defects. This is a point which deserves further investigation in the case of beryllium.

In addition, practical problems in measurement by the techniques employed here will arise as higher purities are attained, because of the necessity of measuring small voltages. However, an eddy current technique which circumvents this difficulty is available at Battelle. The evidence obtained so far indicates that resistivity ratios can be used as rough indicators of purity in the 10 to 100 ppm range and can very likely be extended into the 0.1 to 10 ppm range without any difficulty.

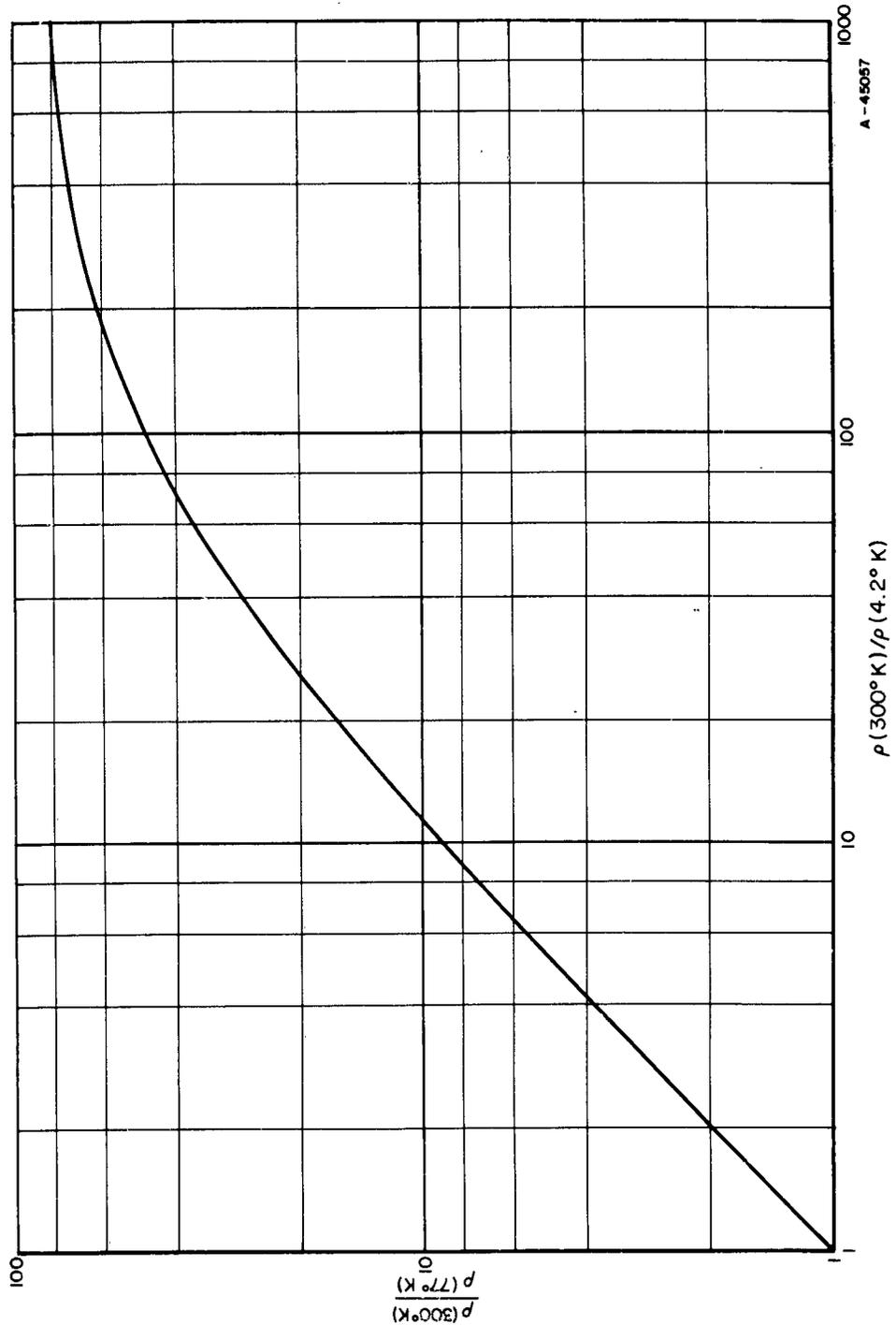


FIGURE 8. RELATION BETWEEN NITROGEN TEMPERATURE AND HELIUM TEMPERATURE RESISTANCE RATIOS FOR BERYLLIUM

FUTURE WORK RECOMMENDATIONS

The accuracy of determination of metallic impurities by mass spectrography should be investigated further by more standardization and, if found necessary, sensitivity factors should be applied. The precision of determination and the utility of replicate runs should be established.

Most needed is greater accuracy for the determination of low concentrations of oxygen and carbon. For oxygen, at least four techniques appear promising and should be investigated.

- (1) Mass-spectrographic samples could be acid etched in an atmosphere containing a known  $O^{18}-O^{16}$  ratio and then placed in the source section of the mass spectrograph and subjected to surface-cleaning techniques, including the high voltage spark and argon ion bombardment. Subsequent mass spectrographic analyses should show the extent of the cleaning operation.
- (2) Efforts could be made to prepare oxygen standards for mass spectrography by melting beryllium metal in an evacuated system containing only a known ratio of  $O^{18}-O^{16}$  atmosphere. The resultant metal could be analyzed both by spark mass-spectrographic and by vacuum fusion-gas mass-spectrometric analysis methods.
- (3) Possibly more readily done, beryllium metal could be ignited to the oxide, again in a known  $O^{18}-O^{16}$  atmosphere and the resultant oxide used as a diluent to prepare a series of standards to investigate the mass spectrographic technique.
- (4) An isotopic dilution technique could be applied to the vacuum-fusion method both to investigate the extent, if any, of regettering during the release of the gas and to extend the sensitivity of the method.

Consideration should be given to the possibility of simultaneously investigating these techniques for the nitrogen determination.

Work on carbon analysis that should prove of value would include (1) endeavoring to find and eliminate or minimize the source of the mass-spectrographic carbon blank; (2) developing an isotopic dilution vacuum fusion method; (3) and endeavoring to extend the sensitivity and accuracy of the conductometric method by (a) developing a flux which would permit use of a larger sample, (b) use of a less rich oxygen combustion atmosphere to attain a more stable and complete burn, (c) increasing the sensitivity of the final readout by use of a more dilute solution; and (d) using purer reagents to lower the blank.

Much of the work outlined here would represent a continuation, with extensions, of the present program.

WMH/slp