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MASTER

DETERMINATION OF BERYLLIUM
BY GAMMA ACTIVATION

C. A. Kienberger

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the **ATOMIC ENERGY COMMISSION** *under* **U. S. GOVERNMENT** Contract W-7405 eng 26

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OAK RIDGE Y-12 PLANT
P. O. Box Y
OAK RIDGE, TENNESSEE 37830

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DETERMINATION OF BERYLLIUM BY GAMMA ACTIVATION

C. A. Kienberger

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ABSTRACT

A short, precise, and economical method has been developed for determining the amount of beryllium in samples of beryllium metal, beryllium compounds, and beryllium oxide. The beryllium samples are prepared by dissolving them in a hydrofluoric acid solution or by compressing the powder in a stainless steel dish. The prepared samples are gamma activated with an antimony-124 source. The beryllium is determined by counting the neutrons produced and comparing the counting rate to that of a beryllium standard.

The precision of a single analysis, at the 95 percent confidence level, is ± 0.2 percent of the value. There is no significant bias in the analysis. An analysis can be made in about one-half hour.

CONTENTS

SUMMARY	5
INTRODUCTION	6
DEVELOPMENT OF THE PROCEDURE	7
Equipment and Gamma Source	7
Gamma Activation Source.	7
Beryllium Analyzer	7
Teflon Cups	8
Lucite Disc	8
Calibration Standards	8
Beryllium Metal Standard.	8
Beryllium Oxide Standard.	9
Preparation of Aqueous Solutions	10
Preparation of Powders	10
Gamma Activation of Samples.	11
Analyzer Calibration	11
Aqueous Solution Calibration Standards	12
Beryllium Metal Calibration Standards.	12
Beryllium Oxide Calibration Standards.	13
Calculations	13
Linear Relation	13
Proportional Equation.	14
Results.	14
Beryllium in Aqueous Solutions.	14
Beryllium in Powders.	15
REFERENCES	17
ACKNOWLEDGEMENTS.	19

SUMMARY

A gamma activation-photoneutron method has been developed at the Oak Ridge Y-12 Plant^(a) and used for determining beryllium in various samples of beryllium metal, beryllium compounds, and beryllium oxide. The beryllium is determined by activating an aqueous solution prepared by dissolving the beryllium sample in hydrofluoric acid, or by activating a powder compressed into a pellet in a stainless steel dish. The neutrons are counted with standard electronic counting equipment and helium-3 neutron detectors.

The analytical results are as follows:

1. The precision of a single analysis, at the 95 percent confidence level, is ± 0.2 percent of the value.
2. There is no significant bias in the method using either aqueous solutions or powders of similar composition.
3. The samples require a minimum amount of preparation. Analysis of an aqueous solution can be made in about one-half hour; that of a powder can be made in less time.

An instrument which positions the sample and container in the radiation field has been designed and is available. The precision of the measurements using this equipment was improved by designing special sample holders and containers for the beryllium sample.

(a) Operated for the US Atomic Energy Commission by the Union Carbide Corporation's Nuclear Division.

INTRODUCTION

The gamma activation-photoneutron method(1, 2) appeared to provide a technique for determining beryllium that would be rapid, reliable, and economical. The method has been utilized to detect and measure beryllium in geological samples,(3- 10) or processing samples,(11) and even in beryllium metal.(10, 12) The gamma activation-photoneutron reaction(4, 13- 15, 16) is summarized as follows:

The gamma, γ , is from Sb-124.

Instruments(3, 4, 6, 8- 10, 12, 15- 18) for applying the method have been described by many scientists.(11- 13, 16, 18- 20) They use a cylindrical arrangement with the antimony-124 source at the center surrounded by the sample, a lead sleeve, and a moderator containing boron trifluoride neutron detectors. However, this type of arrangement is not practical for the precise routine analysis of aqueous solutions and powders and for automation. A more practical technique for placing the samples in the gamma radiation field was needed so that the samples could be prepared in groups and immediately inserted into the gamma radiation field and removed without contaminating the sample holder or container.

DEVELOPMENT OF THE PROCEDURE

EQUIPMENT AND GAMMA SOURCE

Gamma Activation Source

The gamma source for the activation of the beryllium was prepared by sealing approximately 0.24 gram of antimony in a pure aluminum container (5/16" D x 1/4" L) and irradiating it in a neutron flux^(b) for about six days to produce a 500-millicurie antimony-124 source. The source was allowed to "cool" for two weeks, during which time practically all of the antimony-122 in the source decayed. The source is irradiated every six months.

Beryllium Analyzer

The Sb-124 source is housed in the lead pig (9" OD x 12" H) of a commercially fabricated beryllium analyzer,^(c) seen in Figure 1. The pig has an inside cavity

Figure 1. BERYLLIUM ANALYZER.

(b) Irradiation was performed at the Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee.

(c) Fabricated by the Boulder Scientific Company, Boulder, Colorado.

that is 7 inches in diameter by 7 1/2 inches high. The container with the Sb-124 source is placed or screwed in a socket on the bottom inside the pig. A steel tray which holds the sample slides over the source. Above the tray there is a one-inch-thick lead disc and a plastic holder containing two neutron detectors.^(d) The detectors are cylindrical tubes (2" D x 10" L) containing He-3 at a pressure of six atmospheres. The two neutron detectors, or helium-filled tubes, are attached to a preamplifier, amplifier, and scaler. These items are the standard electronic components normally used for measuring or counting radiation. The beryllium analyzer is being automated by the attachment of an automatic sample changer which also operates the counting equipment. This automatic sample changer will be described in a later report (Y-1744).

Teflon Cups

The Teflon counting cups (2 1/2" D x 1" H) were machined with a bottom thickness of 0.1253 ± 0.0010 inch. The bottom of the cup was then sanded until the thickness was 0.1250 ± 0.0003 inch.

Lucite Disc

The Lucite discs ($\sim 23/24$ " D x 1/8" T) were machined in the shop so that they would press fit into the stainless steel dishes (1" OD x 5/16" H).^(e)

CALIBRATION STANDARDS

Beryllium Metal Standard

A beryllium metal standard (NBL F-224)^(f) was used to prepare metal powder and aqueous solution standards. The NBL F-224 standard had been analyzed eighteen times for beryllium by a gravimetric or titration method by each of five different laboratories (Union Carbide, Brush Beryllium, Kawecki Berylco, Dow, and Wyman-Gordon). The results were averaged, and the value assigned to the standard was 98.58 percent beryllium.

(d) Obtained from Reuter-Stokes Electronic Components, Inc, Cleveland, Ohio.

(e) Obtained from Tracerlab, a Division of Laboratory for Electronics, Inc, Waltham, Massachusetts.

(f) Obtained from the US Atomic Energy Commission, New Brunswick Laboratory, New Brunswick, New Jersey.

Beryllium Oxide Standard

A pure beryllium oxide powder (L-33)^(g) was analyzed for 45 elements. Table 1 reports the complete analysis. The cation impurities were assumed to be present as the oxide. The total quantity of impurities was then calculated to be 0.07 percent. This value leaves, by difference, a beryllium oxide content of 99.93 percent.

Table 1
IMPURITIES IN BERYLLIUM OXIDE POWDER
(Berylco, Type L-33)

Element	Amount (ppm)	Element	Amount (ppm)
Ag	< 4(1)	Mo	< 2.0
Al	35	N	2
As	2.0	Na	0.5
Au	< 0.2	Nb	1.5
B	2.6	Ni	3.5
Ba	0.7	P	15
Bi	< 0.2	Pb	5.0
C	56	Rb	< 0.4
Ca	15	S	17
Cd	< 2.0	Sb	1.0
Ce	< 0.2	Sc	< 0.5
Cl	26	Si	110
Co	20	Sn	1.2
Cr	1.5	Sr	< 0.4
Cs	< 0.2	Th	< 0.2
Cu	2.5	Ti	35
F	10	U	< 0.8
Fe	20	V	< 0.2
Hg	< 0.7	Y	< 0.3
K	0.2	Zn	0.5
La	< 0.2	Zr	20
Li	< 1	Total Measured Impurities	423.9
Mg	20	Total "Loss Than" Impurities	13.5
Mn	0.2		

(1) Less than (<) indicates the lower limit of detection.

(g) Obtained from the Kawecki Berylco Industries, Inc, Reading, Pennsylvania.

PREPARATION OF AQUEOUS SOLUTIONS

Aqueous samples are prepared by the following procedure:

1. Weigh approximately one gram of the beryllium sample to the nearest 0.1 milligram and transfer it to a Teflon bottle.^(h)
2. Add one to two milliliters of water and one or two drops of concentrated hydrofluoric acid to the bottle. Shake the contents of the bottle.
3. When the reaction subsides, add two or three drops more of hydrofluoric acid. Continue adding the acid dropwise until 10 milliliters of the acid have been added to the bottle.
4. Add five milliliters of concentrated nitric acid, then allow the solution to cool.
5. Place a Teflon counting cup on a precision balance and weigh it to the nearest centigram.
6. Pour the sample solution into the cup on the balance.
7. Wash the sides of the bottle down with about one milliliter of hydrofluoric acid, using a medicine dropper, then rinse the bottle three times with one to two milliliters of distilled water which is poured into the cup.
8. Add distilled water dropwise to the cup until a total of 30.00 grams of solution have been added to the cup.
9. Place a Teflon cap on the cup and tighten it without disturbing the solution.
10. After the solution in the cup is mixed by swirling, the sample is ready for gamma activation.

PREPARATION OF POWDERS

Powder preparation is accomplished by the following procedure:

(h) Obtained from J and H Berge, Inc, South Plainfield, New Jersey.

1. Grind the solid or chip metal samples and oxides to a fine powder and screen the powder through a US 100-mesh sieve.
2. Weigh approximately 1.5 grams of the powder to 0.1 milligram in a stainless steel dish.
3. Place a Lucite disc over the powder in the dish.
4. Next, position the dish containing the sample in the jaws of a hydraulic press.
5. Position a steel rod (1/2" D x 1/2" L) on the disc and operate the hydraulic press. (A pressure of about five tons is exerted on the steel rod which usually forces the disc down into the dish about the same distance, compressing the powder against the bottom of the dish to form a pellet. For very precise measurements, a metal gauge is used for each type of sample to stop the jaws of the press at exactly the same position for each sample, producing a constant sample or pellet thickness. The thickness of the gauge for oxides is approximately 0.225 inch).
6. Release the pressure. The sample is now ready for gamma activation.

GAMMA ACTIVATION OF SAMPLES

Standards of the same type of material as the samples are used for evaluating each sample. Thus, metal and oxide powder samples are compared to comparable standards. Activation is accomplished by the following procedure (the standards are activated and counted first):

1. Place the standard, or sample, in the sample holder or tray which is inserted into the lead pig. (The sample or standard is positioned just above and over the Sb-124 source.)
2. Count the standards and samples for five minutes.
3. Recount the standards after the samples have been counted or within a four-hour period of their original counting. (The average of the standard counts is used in the calculation.)

ANALYZER CALIBRATION

Several techniques were used for calibrating the beryllium analyzer and for calculating the beryllium content of a sample. The calibration standards were prepared as described in the sections that follow.

Aqueous Solution Calibration Standards

Samples of the beryllium metal standard (NBL F-224), ranging in weight from 200 to 1,600 milligrams, were weighed into Teflon bottles, dissolved, gamma activated, and counted according to the procedure previously outlined. The counting rates were plotted versus the milligrams of beryllium in the standards (Figure 2). The plot is a straight line, indicating that the amount (mgs) of beryllium content can be calculated using a linear equation or by a ratio of the counting rate of the sample to that of the standard. When a linear equation is used, standards are selected whose counting rates will bracket the counting rate of the sample. If the beryllium content is to be calculated by the ratio technique, a standard with a counting rate near that of the sample is selected and used.

Figure 2. COUNTING RATE OF BERYLLIUM STANDARDS.

Beryllium Metal Calibration Standards

The calibration standards for metal powder samples were prepared from the NBL F-224 metal standard. The standard was ground, like the sample, to a fine powder and screened through a US 100-mesh sieve. Approximately 1.6 and 1.4 grams of the standard material were placed in two separate stainless steel dishes and weighed to 0.1 milligram. A Lucite disc was placed over

each dish and pressed into the dish exactly as described for the samples. The standards were then ready for calibrating the beryllium analyzer.

Beryllium Oxide Calibration Standards

The calibration standards for beryllium oxide samples were prepared from pure beryllium oxide powder. Approximately 1.6 and 1.4 grams of the pure beryllium oxide powder were transferred into separate stainless steel dishes and weighed to 0.1 milligram. The standards were prepared by the procedure previously described for powder samples.

CALCULATIONS

Linear Relation

Counting rates of the high standards are averaged; those of the low standards are also averaged. When the counting rates of the high and low standards bracket those of the samples, the grams of beryllium in the sample are calculated as follows:

$$a = \frac{X_h - X_l}{Y_h - Y_l}, \text{ and}$$

$$b = X_h - aY_h,$$

where:

a represents the slope of the calibration equation,

X_h the grams of beryllium in the high standard,

X_l the grams of beryllium in the low standard,

Y_h the average counting rate for the high standard (corrected for background),

Y_l the average counting rate for the low standard (corrected for background), and

b the intercept of the calibration equation.

The calibration equation is:

$$M = ax + b,$$

where:

M represents the grams of beryllium in the sample aliquot, and

x the sample counting rate (corrected for background).

The weight of beryllium is divided by the sample weight to obtain the grams of beryllium per gram of sample.

The calculations were made on an Underwood-Olivette computer.

Proportional Equation

When the counting rate of the sample is not bracketed by two standards, the counting rate of the sample is compared to that of a standard having approximately the same counting rate. The calculation is as follows:

$$\text{gms Be/gm of Sample} = \frac{(\text{Counting Rate of Sample/gm}) \times (\text{Be in Standard})}{\text{Counting Rate/gm of Calibration Standard}}.$$

RESULTS

Beryllium in Aqueous Solutions

The described method was used to determine the beryllium in New Brunswick Laboratory (NBL) "powder" (Standard F-226) and the NBL "chip" (Standard F-227). The standards were dissolved in an aqueous solution and compared by the described method to an aqueous solution of the NBL standard (Standard F-224). The results are reported in Table 2.

As reported, the precision of a single analysis, at the 95 percent confidence level, is ± 0.19 percent of the value. The mean of the results is not significantly different from that obtained by other laboratories using either a gravimetric or volumetric method, as Table 3 points out. There appears to be no significant bias in the method. The determination of beryllium in the metal or oxide sample can be made in about one-half hour.

Table 2
ACTIVATION ANALYSIS OF NBL BERYLLIUM STANDARDS

Sample Number	Beryllium in the NBL Standards (%)	
	NBL F-226	NBL F-227
1	98.57	98.64
2	98.42	98.54
3	98.57	98.54
4	98.59	98.61
5	98.53	98.65
6	98.61	98.55
7	98.40	98.51
8	98.66	98.48
9	98.56	98.44
10	98.50	98.53
11	98.41	98.52
12	98.56	98.58
13	98.56	98.51
14	98.50	98.54
15	98.42	98.48
16	98.44	98.37
17	98.51	98.59
18	98.75	98.80
Mean	98.53	98.55
Precision of a Single Analysis	$\pm 0.19\%$ (at the 95% confidence level)	

Table 3
LABORATORY COMPARISON OF BERYLLIUM RESULTS IN NBL STANDARDS

Laboratory	Beryllium in the NBL Standards (%)	
	NBL F-226	NBL F-227
Union Carbide (Y-12 Plant), Gamma Activation	98.53	98.55
Union Carbide (Y-12 Plant), Gravimetric	98.46	98.59
General Astrometals	98.46	98.48
Brush Beryllium	98.44	98.44
Kawecki Berylco	98.42	98.35
Dow (Rocky Flats)	98.49	98.44
Wyman-Gordon	98.45	98.37
Mean	98.46	98.45

Beryllium in Powders

The NBL F-224, F-226, and F-227 metal standards were converted to beryllium oxide by pyrohydrolysis and ignited at 1,300° C. Each oxide standard was ground to a fine powder and screened. The counting rates obtained by activation

were compared to those of the Berylco beryllium oxide powder standard (L-33). Assuming the beryllium in the Berylco powder to be 36.007 weight percent ($36.032 \times 99.93\%$), the beryllium content of the metal samples was calculated from a ratio of their counting rates to the percentages of beryllium in them (Table 4).

Table 4
BERYLLIUM CONTENT OF NBL METAL STANDARDS
BASED ON PURE BERYLLIUM OXIDE POWDER

Sample Number	NBL F-224 (%)	NBL F-226 (%)	NBL F-227 (%)
1	98.53	98.44	98.37
2	98.57	98.45	98.42
3	98.63	98.40	98.57
4	98.49	98.58	98.60
5	98.65	98.54	98.44
6	98.47	98.50	98.36
7	98.69	98.65	98.40
8	98.67	98.62	98.48
Mean	98.59	98.52	98.46
Precision of a Single Analysis	$\pm 0.19 (\pm 0.2\%)$	$\pm 0.22 (\pm 0.2\%)$	$\pm 0.21 (\pm 0.2\%)$

As reported, the precision of a single analysis, at the 95 percent confidence level, was ± 0.2 percent of the value. There was no significant bias in the analysis provided the powders had very similar compositions and particle sizes so that they occupied the same volume. The same weight of the sample and standard should occupy approximately the same volume after compressing the two in separate stainless steel dishes. Adjustments in the pressure exerted on the powders and guides to stop the jaws of the hydraulic press at the same place with each pressing helped produce the same volume for each sample and standard. The same volume must be maintained to eliminate inaccuracies.

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