CANADA

DETERMINATION OF BERYLLIUM BY GAMMA-RAY ACTIVATION

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DETERMINATION OF BERYLLIUM BY GAMMA-RAY ACTIVATION

by

Hugh P. Dibbs*

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SYNOPSIS

An apparatus is described for the quantitative analysis of the beryllium content of powdered samples down to approximately 50 ppm of beryllium. The analytical technique is based upon the photoneutron reaction Be-9(γ, n)Be-8 and employs antimony-124 as the gamma source. A description is given also of a second apparatus for the qualitative screening of rock samples for beryllium content.

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DÉTERMINATION DU BÉRYLLIUM PAR ACTIVATION À L'AIDE DES RAYONS GAMMA

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Hugh P. Dibbs*

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RÉSUMÉ

Le présent bulletin décrit un dispositif qui sert à l'analyse quantitative de la teneur en béryllium d'échantillons pulvérises qui peuvent contenir aussi peu qu'environ 50 ppm de béryllium. Ce procédé analytique se fonde sur la réaction des photoneutrons Be-9(γ, n)Be-8 et utilise l'antimoine-124 comme source des rayons gamma. On trouve également dans ce bulletin la description d'un second dispositif servant au tamisage qualitatif d'échantillons rocheux pour en déterminer la teneur en béryllium.

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INTRODUCTION

Considerable interest has arisen in beryllium in recent years because of its favourable properties for high-temperature nuclear reactors and potential applications in other fields. This interest has led in turn to a need for rapid beryllium analysis, both in the field and in the laboratory. Standard wet chemical procedures for beryllium estimation are time-consuming and, for beryllium-containing ores, open to error because of interference from other elements, which may be present in the ore (1). A radiometric analytical technique which has gained wide acceptance, particularly in field work (2), is based upon the reaction

$$\text{Be-9} + \gamma \longrightarrow \text{Be-8} + \text{n}$$

Thus, by counting the neutrons emitted when a beryllium-containing sample is placed in a suitable gamma-ray flux, a measure of its beryllium content may be obtained. Several types of portable beryllium detectors based on this principle have been available commercially for use in the field for some time (3). However, because of the limitation on source strength and on suitable counting circuits imposed by the need for compactness and transportability on such equipment, the sensitivity and accuracy obtainable are not as high as would be desirable in a fixed installation for laboratory use. For this reason, apparatus has been designed and set up specifically for this purpose and is the subject of this report. It has

been used for the determination of the beryllium concentration of powdered samples down to about 50 ppm of beryllium. A second unit has also been constructed for a preliminary screening of rock samples to check for the presence of beryllium.

BASIS OF METHOD

The photoneutron threshold energy for the Be-9(γ, n)Be-8 reaction is 1.66 MeV. With the exception of deuterium, which has a (γ, n) threshold energy of 2.23 MeV, all other nuclides have threshold energies in excess of 5 MeV. This special property of beryllium, therefore, provides an unambiguous method of analysis, as long as the incident gamma energy is not too high. The source of gamma radiation may be an accelerator (4) or a radioactive isotope (3). For the latter case it is necessary that the source isotope be readily available in high specific activity, have a gamma energy greater than 1.66 MeV, and have a reasonably long half-life. Examination of the various gamma-emitting isotopes indicates that only antimony-124 fulfills these criteria: it has a half-life of 60.4 days and can be obtained with a specific activity of up to 2 c/g. Antimony-124 decays by a number of gamma emissions (5), with about 45% occurring at 1.692 MeV. Antimony-122 (half-life, 2.8 days) is formed simultaneously with antimony-124 during reactor irradiation, and also decays by a number of gamma emissions. The highest gamma energy of antimony-122 is below the 1.66 MeV threshold for the (γ, n) reaction, so that its presence does not increase the detection

efficiency for beryllium. However, antimony-122 does increase the gamma background, so the activated antimony source is allowed to decay for about a month before use, in which time the radiological hazard arising from antimony-122 is eliminated.

In common with other nuclear processes, a definite cross-section may be ascribed to the (γ, n) reaction. It is fortunate that in the case of beryllium the cross-section - energy curve goes through a maximum of 1.35×10^{-3} barns at the antimony-124 energy (6).

The neutrons produced in the (γ, n) reaction, using an antimony-124 source, have an energy of about 30 keV. For detection purposes, it is convenient to have them at thermal energies (0.025 eV). This is readily achieved by surrounding the source with a layer of a suitable moderator, such as paraffin wax. The neutron counters used in this work were boron trifluoride gas-filled proportional counters. These were preferred to boron-loaded zinc sulphide scintillation counters because the latter have poor discriminating power in a high gamma field (7). The sensitivity of the system is essentially proportional to the source strength, which is limited mainly by shielding and irradiation conditions.

APPARATUS

The requirements for a beryllium assay unit using this technique are a suitably shielded antimony-124 source, surrounded by sufficient moderator to slow down the neutrons produced to thermal

energies, and a means of introducing the sample for assay without prolonged exposure of the operator to a high radiation field. Figure 1 is a diagram of the unit which was built for the assay of powdered samples with these principles in mind. It consists essentially of a lead castle into which an annular container, loaded with the powder for analysis, is lowered. For measurements, the antimony-124 source, which is located at the bottom of the movable inner tube, is raised into the assay position. Additional shielding is provided by a 4-in. lead plug in this tube and also by a 1-in.-thick, movable lead collar around the top of the castle. A 2-in.-thick lead wall was also placed in front of the unit to provide additional shielding for the operator. A locating bar ensures that the antimony source is always raised to the same position with respect to the annular container. Counting is performed by three boron trifluoride neutron counters (Chalk River type BP 24), suitably connected to a high-voltage supply and a scaler. The whole unit has been mounted on casters to permit movement from one location to another within the building.

Using a 240-mc antimony-124 source, the following radiation fields (in mr/hr) were measured around the unit (Table 1).

"A" NON-OPERATING SOURCE POSITION
"B" OPERATING SOURCE POSITION

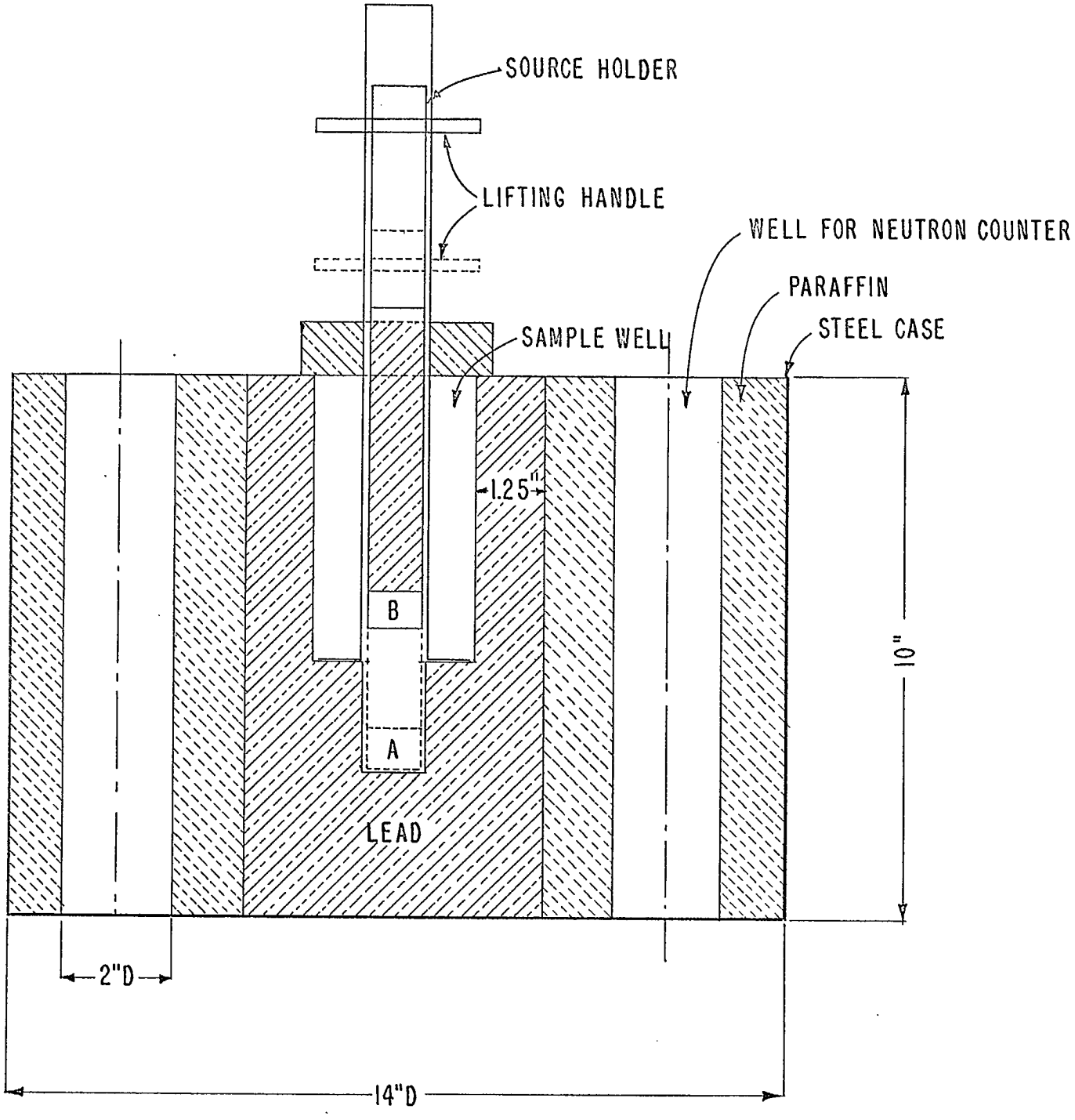

FIGURE 1. SOURCE ASSEMBLY FOR BERYLLIUM ASSAY.

TABLE 1

Radiation Fields Around Beryllium Assay Unit (in mr/hr)

	Source Down	Source in Assay Position
At the counting equipment (8 ft away)	0	0
Directly in front of unit	5	9
On top of unit	9	100

The only occasion when the operator may be exposed to relatively high fields is while raising the source for measurements. However, as this operation takes no more than 2 to 3 seconds, the integrated dose received while changing samples is extremely low.

For the assay of many rock samples it is not convenient to pulverize the sample for analysis and one desires to know only if the rock contains beryllium or not. To accommodate this type of sample, the apparatus shown in Figure 2 was constructed. It consists of a lead container with a well in which an antimony-124 source is located. The lead container in turn is at the centre of a larger container filled with paraffin wax. For measurements, the lead cover over the antimony source is pulled back along guide rails and the sample on platform A is brought over the source. Counting is performed with one large neutron counter (Chalk River type BP11B) lying parallel to the guide rails on top of the outer wax

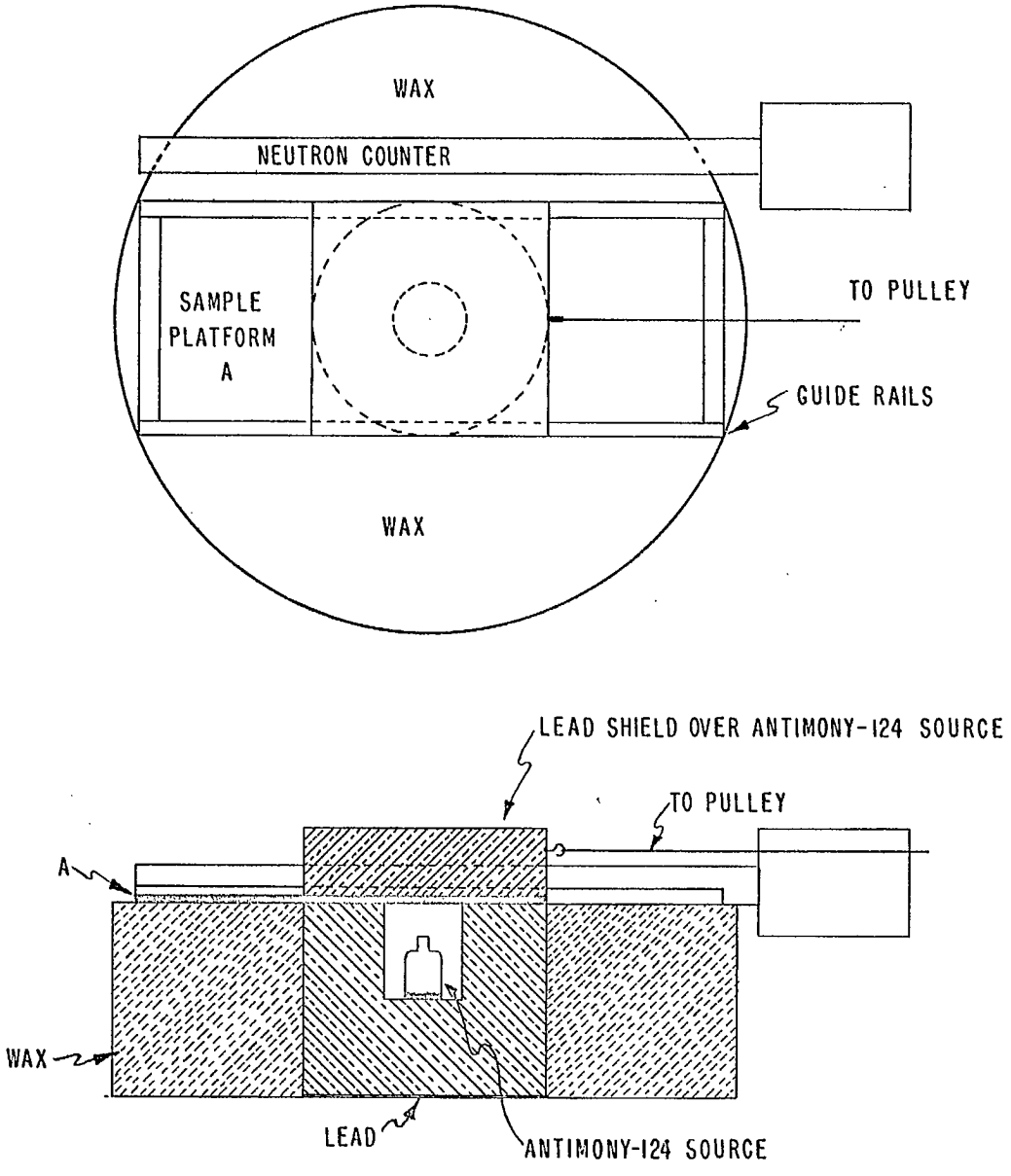

FIGURE 2. ROCK ASSAY UNIT.

container. The neutron counter is surrounded by paraffin wax, and a paraffin neutron reflector wall was also placed opposite the counter to increase the detection sensitivity. This apparatus is not intended to provide a quantitative measure of beryllium content, since this would obviously depend on obtaining samples of a reproducible geometrical shape. It does, however, provide an initial screening of samples to indicate if they contain sufficient beryllium to warrant more detailed examination. Since the radiation shielding is not as heavy in this case as with the powdered sample assay unit, a maximum source strength of 30 mc of antimony-124 was used with this unit.

CALIBRATION AND MEASUREMENT

The assay of beryllium by the (γ, n) method provides only a relative measure of the total amount of beryllium exposed. In order to obtain an absolute value, it is necessary to calibrate the equipment with powder samples of known beryllium content. For this purpose, three synthetic reference standards were prepared, containing a known weight of Analar BeO intimately mixed with powdered silica sand. Because of the extremely high toxicity of BeO, these reference standards were compared with a secondary standard (Sample "D"), a high-grade beryl ore, which was then used as an operating standard. The calibration results obtained are given in Table 2.

TABLE 2

Calibration Results of the Beryllium Assay Unit

Standard	% BeO in Standard	% BeO in "D"
1	3.316	12.96
2	8.09	12.98
3	11.04	12.82

The average value for the BeO concentration in Sample D is 12.92%, which is the value used in all subsequent standardizations of the equipment.

For an actual measurement, the sample container is filled to the top with the powder under investigation. The count-rate obtained, after background corrections, is then compared with that found for the same volume of the beryl reference standard. The percentage of BeO in the sample is given by:

$$\text{\% BeO in sample} = \text{\% BeO in standard} \times \frac{\text{Net count rate for sample/unit weight}}{\text{Net count rate for standard/unit weight}}$$

Because of the relatively short half-life of antimony-124 (60.4 days), calibration of the equipment is required at least once per day to correct for source decay. Sample containers of three different sizes (capacities 100 ml, 50 ml and 15 ml respectively) were used, depending on the volume of sample available. Samples of less than 15 ml in volume were diluted with silica sand or other inactive powder.

The background was approximately 25 c.p.m. for a 240-mc antimony-124 source and arises mainly from cosmic radiation and a "pile-up" of gamma pulses (8). The latter contribution may be minimized to some extent by suitable pulse discrimination. Thus, although an increase in the strength of the antimony-124 source will lead to an increase in the neutron count obtained, it also increases the background, so that the overall increase in sensitivity obtained is not quite a direct function of the source strength. This is shown in Table 3. However, the ultimate sensitivity, expressed by the figure of merit $S^2/_B$, increased considerably as the source strength was raised.

TABLE 3

Influence of Source Strength on Sensitivity

Sb-124 Activity	Background (B), c.p.m. (scale of 256)	Net Count Rate (S) 155 g "D" Standard, c.p.m. (scale of 256)	Figure of Merit, $S^2/_B \times 10^3$
30 mc	0.022	5.09	1.17
240 mc	0.082	38.9	18.5

If it is assumed that a minimum signal-to-background ratio ($S/_B$) of 3:2 is required for analysis, the 240-mc source will detect approximately 50 ppm of beryllium, using the largest sample container (100 ml).

As the (γ, n) reaction is specific to beryllium in practice,

it would be expected that the count-rate obtained, for a given antimony-124 source, would be a linear function of the beryllium concentration. This is confirmed in Figure 3, where the count-rate obtained from a series of synthetic samples is plotted against their known BeO contents.

A series of beryllium-containing samples, which had been analysed for beryllium content by the (γ, n) method, was also submitted for chemical analysis. The results obtained are shown in Table 4.

TABLE 4

Comparison of Chemical and (γ, n) Analysis for Beryllium

Sample	Chemical (% BeO)	γ, n (% BeO)
A	12.45	13.2
B	0.52	0.52
C	6.25	6.94
D	12.5	12.92

It will be seen that although agreement between the two methods is reasonably good, the chemical results tend to be lower than those determined by the (γ, n) method. In view of the good internal consistency of the (γ, n) technique, it is felt that this discrepancy could arise from losses in the chemical determination.

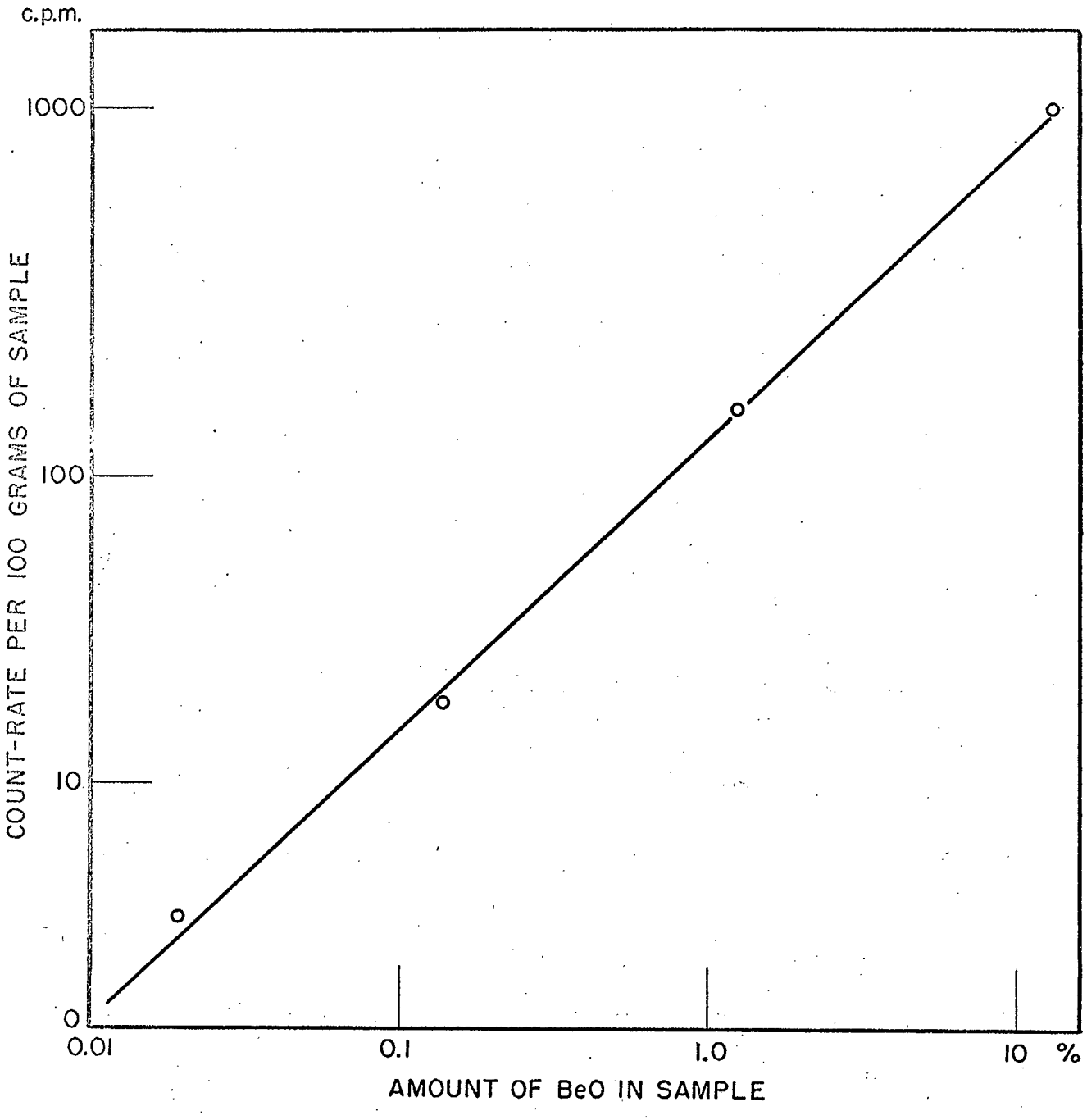

FIGURE 3. DEPENDENCE OF COUNT-RATE ON BeO CONCENTRATION.

CONCLUSIONS

The accurate analysis of beryllium, over a wide range of concentration, is possible by the (γ, n) technique. The method is straightforward and non-destructive and the measurement may be made with a minimum of attention on the part of the operator. Higher sensitivities than those quoted in the present report may be achieved by the use of a more active antimony-124 source, using greater lead shielding and more neutron counters. A disadvantage of the method is that the relatively short half-life of antimony-124 entails periodic source replacement if the highest sensitivity is to be maintained.

ACKNOWLEDGMENTS

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