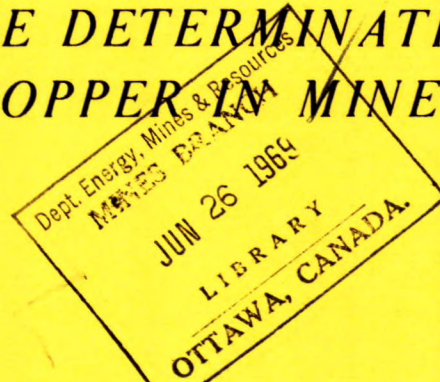




DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

*THE APPLICATION OF NEUTRON
ACTIVATION ANALYSIS TO
THE DETERMINATION OF
COPPER IN MINERALS*



H. P. DIBBS

MINERAL SCIENCES DIVISION

APRIL 1969

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THE APPLICATION OF NEUTRON ACTIVATION ANALYSIS
TO THE DETERMINATION OF COPPER IN MINERALS

by

H. P. Dibbs*

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ABSTRACT

An account is given of the application of neutron activation analysis to the rapid, non-destructive determination of copper in minerals, using a 14-MeV neutron source. Elements that interfere in the determination of copper by this method are given, together with the errors in the estimation of copper that result from the presence of varying amounts of these elements. The possible use of a compact "sealed-tube" 14-MeV neutron generator for the field assay of copper in minerals is discussed.

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Direction des mines

Rapport de recherches R 205

LA DÉTERMINATION DU CUIVRE DANS LES MINÉRAUX
À L'AIDE DE L'ACTIVATION PAR LES NEUTRONS

par

H. P. Dibbs*

RÉSUMÉ

On décrit l'application de la méthode d'analyse par activation aux neutrons d'une énergie de 14 MeV à la détermination rapide et non-destructive du cuivre dans les minéraux. On mentionne les éléments interférants, ainsi que les erreurs introduites par la présence de quantités variables de ces éléments. On discute aussi la possibilité d'utiliser sur le terrain une "source scellée" produisant des neutrons de 14 MeV pour la détermination en place du cuivre dans les minéraux.

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CONTENTS

| | <u>Page</u> |
|---|-------------|
| Abstract | i |
| Résumé | ii |
| Introduction | 1 |
| Basis of Neutron Activation Analysis | 2 |
| Laboratory Neutron Sources | 5 |
| Isotopic Sources | 5 |
| Machine Sources | 5 |
| Applications of Neutron Activation to Copper Determination | 7 |
| Induced Activities in Copper | 7 |
| 14-MeV Neutron Measurements | 8 |
| Neutron Attenuation | 10 |
| Gamma Attenuation | 10 |
| Interference | 13 |
| Conclusions | 21 |
| Acknowledgements | 24 |
| References | 24 |

FIGURES

| <u>No.</u> | <u>Page</u> |
|--|-------------|
| 1. 14-MeV Neutron Attenuation in Copper Ore | 11 |
| 2. Gamma-Ray Spectrum of Copper Ore Following Fast Neutron Irradiation | 12 |
| 3. Attenuation of 0.51-MeV Gamma Radiation in Copper Ore | 14 |
| 4. Increase in Cu-62 Activity with Increasing Thickness of Copper Ore Following 14-MeV Neutron Irradiation | 15 |

| <u>No.</u> | | <u>Page</u> |
|------------|--|-------------|
| 5. | The Relative Count-Rates for Various Elements Emitting 0.51-MeV Gamma Radiation .. | 18 |
| 6. | Error from Varying Fe and Cl Concentrations on Estimation of Copper Content | 19 |
| 7. | Error from Varying K and Zn Concentrations on Estimation of Copper Content | 20 |
| 8. | Decay Curve for a Cu/Zn Mixture (Zn/Cu, Weight Ratio 22:1) | 22 |

TABLES

| | | |
|----|--|----|
| 1. | Activity Build-Up Factors | 4 |
| 2. | Characteristics of Some One-Curie Isotopic Neutron Sources | 6 |
| 3. | Calculated Disintegration Rates for Neutron Activation of Copper with 14-MeV or Thermal Neutrons | 9 |
| 4. | List of Positron Emitters Produced by Fast-Neutron (n, 2n) Activation that could Cause Interference in Copper Determination .. | 17 |

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INTRODUCTION

Neutron activation analysis is now widely used in the laboratory as a routine analytical technique (1). Relatively little attention, however, has been given to the possible applications of neutron activation analysis to the mining industry (2), e.g. for rapid on-site logging of drill core in mineral exploration, or for grade control in mining operations (3). This lack of interest is rather surprising because the concentration levels of most elements of economic significance in mining operations are relatively high and are within the sensitivity range of analysis by commercially available, compact neutron sources. It was the aim of this feasibility study to investigate those advantages and limitations of neutron activation analysis that were relevant to the on-site determination of elements of economic significance in minerals. Copper was chosen as the element to be investigated; the reason for this choice being twofold. Firstly, from theoretical considerations to be discussed later, the sensitivity for copper determination should be high. Secondly, copper is economically very important, having the largest dollar value, after petroleum, in Canadian mineral production, representing 12.5% of the total value for all minerals (4).

This report gives a description of the techniques and of the background of neutron activation analysis, and the results of this feasibility study of the application of activation analysis to the determination of copper.

BASIS OF NEUTRON ACTIVATION ANALYSIS

Neutron activation analysis depends upon the fact that most elements become radioactive on neutron bombardment. The radioactive isotopes formed are unstable and decay to a stable ground state with the emission of beta and/or gamma radiation of characteristic energies and half-lives. These factors usually allow unambiguous characterization of the radioisotope and, hence, of its stable parent element. Although, in principle, neutron activation analysis is an absolute method for the determination of a given element, in practice a comparator technique is almost always used. Thus if a given element is being determined in a sample, a known weight of the same element is irradiated simultaneously with the sample (or separately under identical irradiation conditions) to act as a standard. A comparison of the activity induced in the known weight of the standard with that from the same isotope in the sample, gives a quantitative measure of the amount of the element in the sample. The method used for the determination of the amount of the radioisotope of interest depends on its activity level, on its radioactive-decay scheme, and on the presence of interfering radiation from the matrix. In many cases, particularly when the concentration of the element is relatively high, e. g. one or more percent, gamma-ray spectrometry may be used directly to count the irradiated sample, and to identify and to measure quantitatively the radioisotope of interest.

It is extremely important to note that neutron activation analysis differs from most conventional analytical methods in that it is based upon the interaction between a neutron and the target nucleus and is unaffected by the electron distribution around the nucleus. Neutron activation analysis is thus independent of the chemical (valence) or the physical state of the target element.

The amount of activity induced in an element by neutron irradiation depends upon four factors:

- (a) the number of atoms (N) of the target nuclide present
(i. e. $N = \frac{w \times A \times f}{W}$, where: w = weight of element, W = atomic weight of element, f = fractional abundance of target isotope, A = Avogadro's Number);
- (b) the flux of neutrons (F), in neutrons/cm²/sec, incident on the sample;
- (c) the cross section (σ) for the activation process { this is a measure of the probability of neutron-nucleus interaction and is in units of barns (10^{-24} cm²)};
- (d) the ratio of the time of irradiation (T), to the half-life of the product isotope ($T_{\frac{1}{2}}$).

These factors are related (5) by the equation

$$\frac{dN}{dt} = NF\sigma \left(1 - \exp - \frac{0.693 T}{T_{\frac{1}{2}}} \right), \quad \dots \quad (\text{Eq. 1})$$

where $\frac{dN}{dt}$ is the disintegration rate (the rate of decay to a stable ground state), in disintegrations per second, of the product isotope at the end of the irradiation time. For the calculation of the amount of induced activity that may be determined by gamma-ray counting, the decay scheme of the radioisotope has to be known to determine what fraction of the nuclei (D_{γ}) decay by gamma emission. D_{γ} can range from 0-1 for different isotopes (6). Thus Equation (1) for gamma-ray counting becomes

$$\left(\frac{dN}{dt} \right)_{\gamma} = NF\sigma \left(1 - \exp - \frac{0.693 T}{T_{\frac{1}{2}}} \right) D_{\gamma}. \quad \dots \quad (\text{Eq. 2})$$

For analytical purposes it is desirable to have the value of the disintegration rate as high as possible. From Equations (1) or (2) it will be seen that the disintegration rate is a linear function of the number of atoms, N, of the target nuclide and of the neutron flux, F, and also depends

on the exponential factor $\left(1 - \exp - \frac{0.693 T}{T_{\frac{1}{2}}}\right)$, which is called the "build-up" factor. The values of the build-up factor for various ratios of irradiation time to half-life are given in Table 1.

TABLE 1
Activity Build-Up Factors

| $T/T_{\frac{1}{2}}$ | $\left(1 - \exp - \frac{0.693 T}{T_{\frac{1}{2}}}\right)$ |
|---------------------|---|
| 0.2 | 0.13 |
| 0.5 | 0.29 |
| 0.75 | 0.41 |
| 1.0 | 0.5 |
| 2.0 | 0.75 |
| 3.0 | 0.875 |
| 4.0 | 0.94 |

The remaining factors in Equation (2) are the activation cross section, σ , and the gamma-decay factor, D_{γ} . Both σ and D_{γ} are fundamental nuclear properties and vary widely from nuclide to nuclide. In addition, the activation cross section is dependent on the incident neutron energy. As will be discussed later in the section on neutron sources, two types of neutron source, producing neutrons of widely different energies, are available for laboratory use. These neutrons are termed thermal neutrons (energy, 0.025 eV) and fast neutrons (energy, 14 MeV). As a very general rule, σ decreases with increase in neutron energy. From a knowledge of the numerical values of the terms in Equation (2), it is possible to calculate the kind of analytical sensitivities to be expected in the determination of various elements (using gamma-ray counting) employing either different types of neutron sources or different nuclear reactions.

LABORATORY NEUTRON SOURCES

There are two types of low-flux neutron sources available at reasonable cost (\$20,000 - \$30,000) for routine laboratory use, viz., isotopic sources and machine sources. Each type of source has its own particular advantages and limitations. Although nuclear reactors have very high neutron fluxes, they are not considered here because of their high cost and limited availability.

Isotopic Sources

Isotopic sources produce neutrons either by a nuclear reaction based on the interaction of radiation emitted by the decaying isotope with a target element, or by neutrons emitted in the isotope's decay scheme. Table 2 lists some isotopic neutron sources, together with their neutron outputs and neutron energies. It should be noted that the most frequent use of these sources is for thermal-neutron activation, which involves moderating the primary neutrons, normally with hydrogenous material.

The neutron output of an isotopic source is continuous and reliable, decreasing with the half-life of the radioisotope responsible for the neutron-production reaction. These characteristics are excellent for on-line applications. The sources are also essentially maintenance-free. However, isotopic sources do pose transport problems because of the relatively massive radiation shielding that is always required around them.

Machine Sources

The other type of laboratory neutron source, the machine source (or neutron generator as it is commonly called), is based on the principle of the Cockroft-Walton positive-ion accelerator and has been commercially available for about the last decade. Neutron generators produce neutrons by accelerating a beam of positive deuterium-ions (H-2) through 100,000 -

TABLE 2
Characteristics of Some One-Curie Isotopic Neutron Sources

| Source | Neutron-Production Reaction | Half-Life | Average Neutron Energy | Yield, n/sec/curie |
|-----------|-----------------------------|-----------|------------------------|--------------------|
| Sb-124/Be | (γ , n) | 60d | 24 keV | 1.6×10^6 |
| Po-210/Be | (α , n) | 138.4d | 4.3 MeV | 5×10^5 |
| Po-210/F | (α , n) | 138.4d | 1.2 MeV | 1.5×10^5 |
| Cm-244/Be | (α , n) | 17.6y | 4 MeV | 3×10^6 |
| Cf-252 | Spontaneous Fission | 2.6y | 2.3 MeV | 4.4×10^9 |

150,000 volts and causing the deuterium ions to interact with a tritium-containing target (H-3) to give the reaction



Both deuterium and tritium are isotopes of hydrogen, tritium being radioactive with a half-life of 12.6 years. The neutrons produced by the reaction in Equation 3 are essentially monoenergetic, with an energy of 14 MeV.

Until recently, neutron generators of reasonable output were physically bulky, required installation in a large shielded room (18 feet by 15 feet), and were in no sense portable. The lifetime of the tritium target for neutron production at full output (2×10^{11} n/sec) was also only a few hours. A full description of the installation and operation of this type of generator is given elsewhere (7).

Recently, as a result of major design changes, a new generation of 14-MeV neutron generators has become available ("sealed-tube" generators), which are much more compact than the original "pumped" neutron generators. These sealed-tube generators are typically about 2 feet long by 6 inches in diameter (8), and one such unit (Philips, Eindhoven, Netherlands) has a

guaranteed lifetime of 500 hours at full neutron output (2×10^{10} n/sec).

The neutron-producing tube now represents a portable high-output 14-MeV neutron source. Fast neutron shielding for personnel protection (consisting of three-four feet of hydrogenous material) is, of course, required around the generator during operation. There is no radiation hazard when the generator is not in operation.

APPLICATIONS OF NEUTRON ACTIVATION TO COPPER DETERMINATION

Induced Activities in Copper

Naturally-occurring copper consists of two stable isotopes, Cu-63 and Cu-65, that have relative isotopic abundances of 69.09% and 30.91% respectively. Assuming that neutron activation analysis is to be used for the rapid determination of copper, employing either a thermal-neutron or a fast-neutron source, the following two thermal-neutron reactions (Equations 4 and 5) and one fast-neutron reaction (Equation 6) are potentially useful.



An appreciation of the relative analytical sensitivities to be expected from the above reactions may be obtained from calculations using Equations 1 and 2. For the purpose of these calculations the following assumptions were made:

- (1) one gram of copper is irradiated;
- (2) the neutron flux available is 10^8 n/cm²/sec;
- (3) the irradiation time is one minute;
- (4) there is a decay time of five minutes between the end of the irradiation and the counting of the induced copper-activity. This

time was chosen to allow for the decay of possible short-lived activities that may be induced in the matrix.

The results of these calculations are shown in Table 3 (Columns 8 and 10), together with the nuclear data upon which the calculations were based. It will be seen that $(dN/dT)_\gamma$ for the fast-neutron reaction in Equation 6 offers better sensitivity than either of the two thermal-neutron reactions (Equations 4 and 5). An additional factor in favour of the reaction in Equation 6, that is not apparent in these calculations, is that this reaction has one of the highest fast-neutron cross sections of any nuclide (9). This relatively high fast-neutron cross section of copper-63, compared to other elements, means that the formation of possible interfering activities from other elements in the matrix is minimized. Such a relative statement is not true for the thermal-neutron activation of copper, since many other elements have much higher thermal-neutron-activation cross sections than copper (9), which can lead to possible matrix interference and neutron adsorption.

14-MeV NEUTRON MEASUREMENTS

Since the calculated sensitivities given in Table 3, and the other factors just discussed, indicate good sensitivity for copper estimation by fast neutron activation, a series of 14-MeV neutron measurements were made on powdered copper ore (assaying 1.44% copper, from Opemiska Copper Mines (Quebec), Limited) to determine the attenuation of neutrons by the ore during activation, and the self-adsorption of gamma radiation within the ore during counting. These two factors, viz. neutron attenuation and gamma adsorption, are extremely important in non-destructive neutron activation analysis, because together they govern the effective sample volume that may be analysed. Thus a large neutron-penetration depth in the ore is of limited value if the gamma radiation being counted from induced activity in the ore has a much smaller penetration depth.

TABLE 3

Calculated Disintegration Rates for Neutron Activation of Copper with 14-MeV or Thermal Neutrons

| Target Isotope | % Abundance | F or T (a) | σ (barns) | Reaction | Half-Life | Gamma Energy (MeV) (b) | $\left(\frac{dN}{dt}\right)_{(c)}$ | D_{γ} | $\left(\frac{dN}{dt}\right)_{\gamma} (c)$ |
|----------------|-------------|------------|------------------|------------------------|-----------|-------------------------------|------------------------------------|--------------|---|
| Cu-63 | 69.09 | F | 0.5 | Cu63(n, 2n)Cu62 | 9.8 min | 0.51; others of low intensity | 1.6×10^4 | 0.98 | 1.54×10^4 |
| Cu-63 | 69.09 | T | 4.5 | Cu63(n, γ)Cu64 | 12.8 hr | 0.51 | 2.65×10^3 | 0.19 | 5.3×10^2 |
| Cu-65 | 30.91 | T | 2.3 | Cu65(n, γ)Cu66 | 5.1 min | 1.04 | 4.25×10^4 | 0.09 | 3.8×10^3 |

(a) F or T refers to 14-MeV or thermal neutron activation.

(b) 0.51-MeV gamma radiation arises from positron annihilation (see page 13).

(c) Disintegration rate per gram of copper after a five-minute decay.

Measurements were also made to determine the amount of interference produced, in the non-destructive determination of copper, by gamma-emitting isotopes decaying with the same energy as copper-62, that could be formed from other elements that might be present in copper-containing ore.

These measurements were made with a Texas Nuclear Model 150-IHV neutron generator and associated equipment previously described (7).

Neutron Attenuation

In order to measure the decrease in induced copper activity in copper ore as a function of distance from the generator target, a number of plastic Petri dishes (dimensions; 9 cm in diameter, 1.5 cm thick) were each filled with approximately 100 g of the powdered ore and were placed in series against the target of the generator (inset diagram, Figure 1). Following a one-minute neutron irradiation and a minimum decay time of five minutes, each of the dishes was counted individually on top of a 3 x 3-inch NaI (Tl) scintillation detector using a 100-channel gamma-ray spectrometer to measure the gamma-ray spectrum from each sample. For each sample the counts for the 0.51-MeV gamma radiation, see Figure 2 for a typical spectrum, were then corrected to a decay time of five minutes from the end of the irradiation, and the amount of induced copper-62 activity per unit weight of copper in the sample was calculated. This activity is shown as a function of distance from the generator target in Figure 1. The induced activity decreases in an almost exponential manner with distance; a ten-fold decrease in activity occurring at ~7 cm from the target.

Gamma Attenuation

A similar experiment to the neutron-attenuation measurements was made to determine the adsorption of 0.51-MeV gamma radiation within the sample. In this experiment a few grams of pure copper were irradiated to produce a copper-62 source. This source was mounted at a fixed distance (~15 cm) above the NaI (Tl) detector and increasing thicknesses of copper

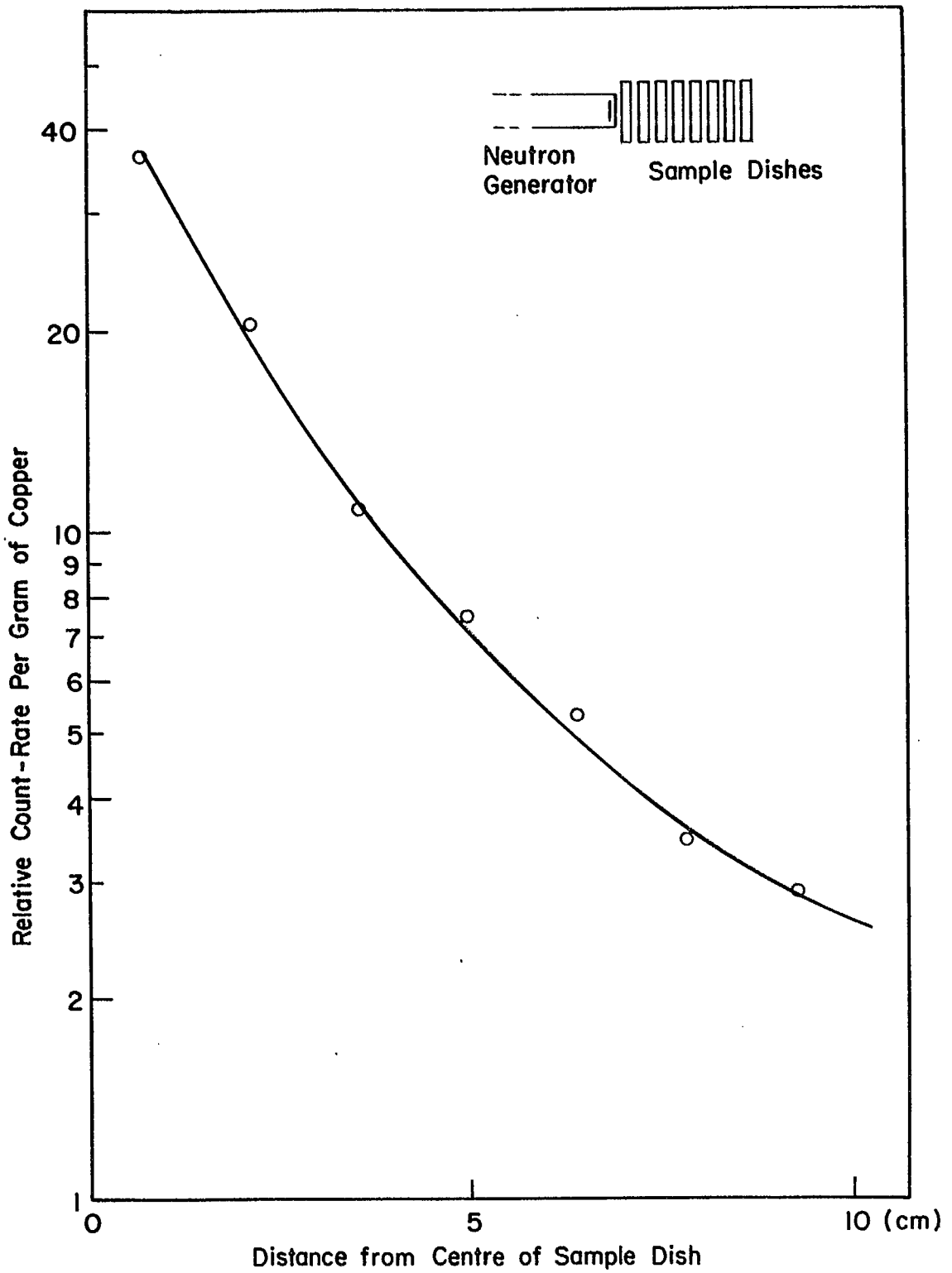


FIGURE 1

14-MeV NEUTRON ATTENUATION IN COPPER ORE
(Inset diagram shows irradiation geometry)

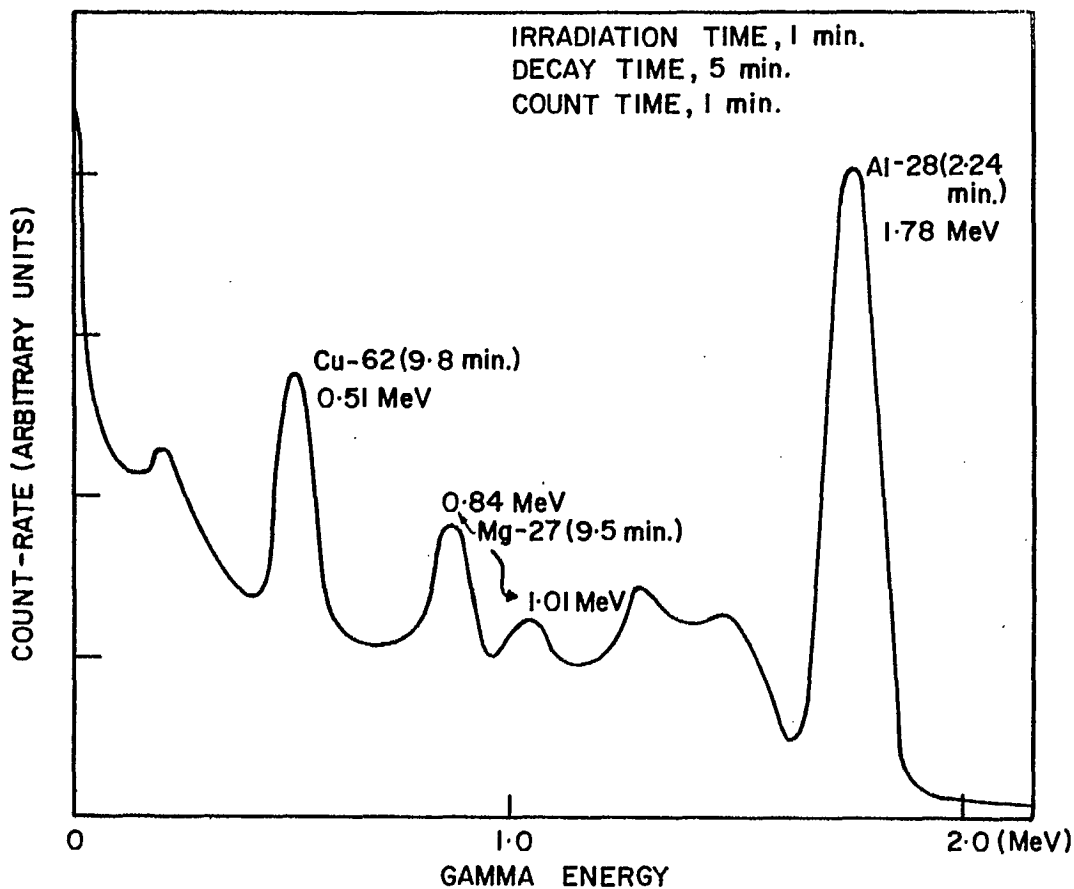


FIGURE 2
GAMMA-RAY SPECTRUM OF COPPER ORE FOLLOWING
FAST NEUTRON IRRADIATION

ore were interposed between the source and the detector. The decrease in copper-62 activity (after suitable correction for decay during the series of measurements) as a function of the thickness of the copper ore is given in Figure 3. As may be expected, the adsorption of the gamma radiation is exponential, corresponding to a linear adsorption coefficient of 0.11 cm^{-1} , with a three-fold decrease in activity occurring at 9 cm.

In comparing the data in Figures 1 and 3 it is interesting to note that the limiting factor in the volume determination of copper is not the self-adsorption of gamma radiation within the sample, but rather the attenuation of neutrons as the sample thickness increases. The effective thickness of copper ore that is accessible to measurement using fast neutron-activation analysis was obtained by placing successive thicknesses of powdered samples, irradiated as for the neutron penetration test, on top of the NaI (Tl) scintillation detector. The results, given in Figure 4, indicate that an effective thickness of ~ 9 cm was available for measurement.

Interference

The determination, by gamma-ray spectrometry, of the amount of a particular gamma-emitting isotope in an irradiated sample is subject to error if other gamma-emitting isotopes of the same energy are present in the sample. In the measurement of copper-62, the 0.51-MeV gamma ray is counted. This gamma ray arises from the initial nuclear-decay process of copper-62 in which a positron (positive electron) is emitted from the copper-62 nucleus. The lifetime of the positron is extremely short and it is "annihilated" by an electron, resulting in two 0.51-MeV photons (the sum of the rest masses of an electron and positron) being emitted in nearly opposite directions (10). Although only one of the 0.51-MeV gamma rays is available for measurement with a single detector, coincidence counting methods can be used; this allows both gamma photons to be measured. In this technique, two NaI (Tl) scintillation detectors are mounted 180° apart with the positron-emitting source between them. The counting circuit is

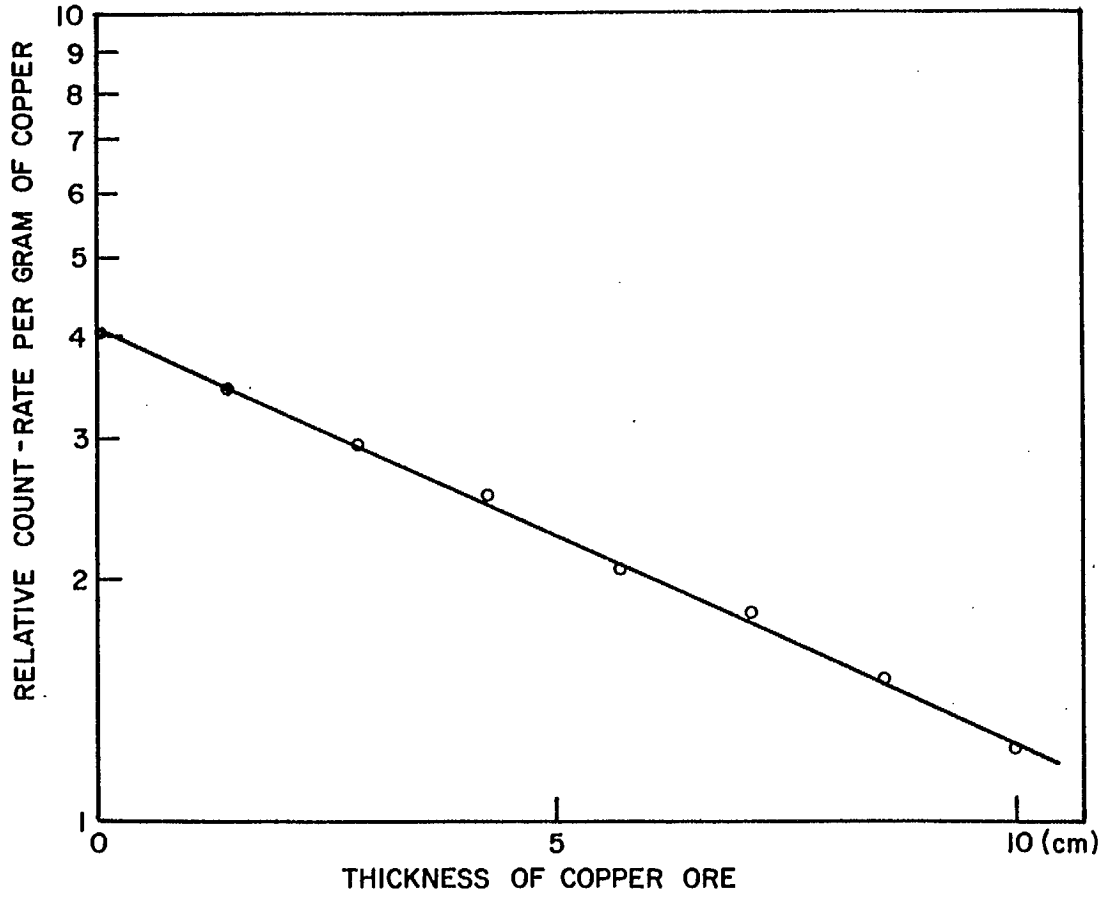


FIGURE 3
ATTENUATION OF 0.51-MeV GAMMA RADIATION IN COPPER ORE

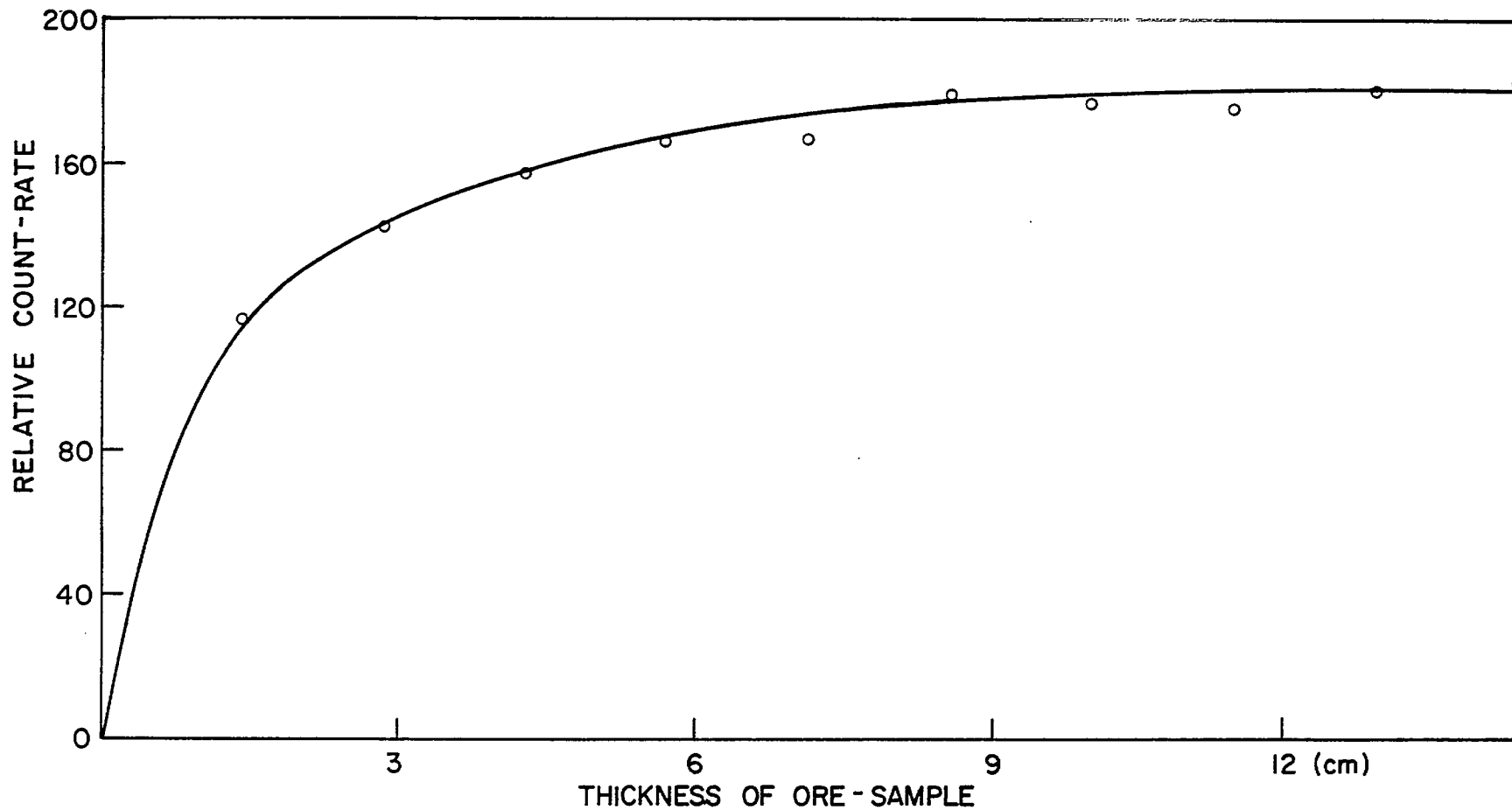


FIGURE 4
INCREASE IN Cu-62 ACTIVITY WITH INCREASING THICKNESS OF COPPER ORE
FOLLOWING 14-MeV NEUTRON IRRADIATION

arranged so that a count is recorded only if a signal (resulting from a 0.51-MeV photon) is received simultaneously in both detectors. Thus, apart from a small number of random coincidences, this technique can be made specific to nuclides emitting positrons (11).

An examination of a list of positron-emitting isotopes produced by fast-neutron activation (7) indicates that a number of elements can be activated under the irradiation and counting constraints specified for copper activation, (one minute irradiation, five minutes decay and one minute count) and may cause interference in the determination of copper if they are present in significant amounts. These elements, their activation reactions, and the half-lives of the product isotopes are given in Table 4.

Experimental measurements have been made of the amount of interference that would be caused in the determination of copper, by the elements listed in Table 4, by comparing the 0.51-MeV counts obtained from suitable compounds of these interfering elements, to the 0.51-MeV counts obtained from a copper standard. The samples were packed in 7-ml polyethylene vials and were irradiated using a pneumatic transfer system. The irradiation and counting conditions were: 1 minute irradiation, 5 minutes decay and 1 minute count. The results obtained (Figure 5) are plotted on a double-logarithmic relative scale of count rate versus the weight of element and are normalized to one count/gram of copper. It will be seen that, on an equal-weight basis, copper gives at least a ten-times greater count-rate than any of the interfering elements.

Figures 6 and 7 show some of the same data, given in Figure 5, presented in a different form. In these Figures, the ratio of the weight of the interfering element to the weight of copper is plotted against the percentage error that would result if all the measured counts from a mixture of copper and the interfering element were assumed to arise from the decay of copper-62. It should be noted that all interference results in an "apparent" higher value of copper in a sample than is in fact present. For example,

TABLE 4

List of Positron Emitters Produced by Fast-Neutron (n, 2n) Activation that could Cause
Interference in Copper Determination

| Target Nuclide | Isotopic Abundance (%) | Product Isotope | Half-Life | Positron Emission (%) | Other Gamma Energies (MeV) |
|----------------|------------------------|--------------------|-----------|-----------------------|---------------------------------|
| P-31 | 100 | P-30 | 2.53 min | 100 | --- |
| K-39 | 98.08 | K-38 | 7.7 min | 100 | 2.16 (100%) |
| Fe-54 | 5.82 | Fe-53 | 9.0 min | 98 | 0.38 (32%) |
| N-14 | 99.63 | N-13 | 10 min | 100 | --- |
| Sb-121 | 57.25 | Sb-120 | 15.7 min | 43 | 1.17 (1.3%) |
| Cl-35 | 75.53 | Cl-34 ^m | 32.4 min | 50 | 1.17(12%), 2.12(38%), 3.3(12%) |
| Zn-64 | 48.89 | Zn-63 | 38.1 min | 93 | 0.67(8%), 0.962(6%), 1.42(0.9%) |

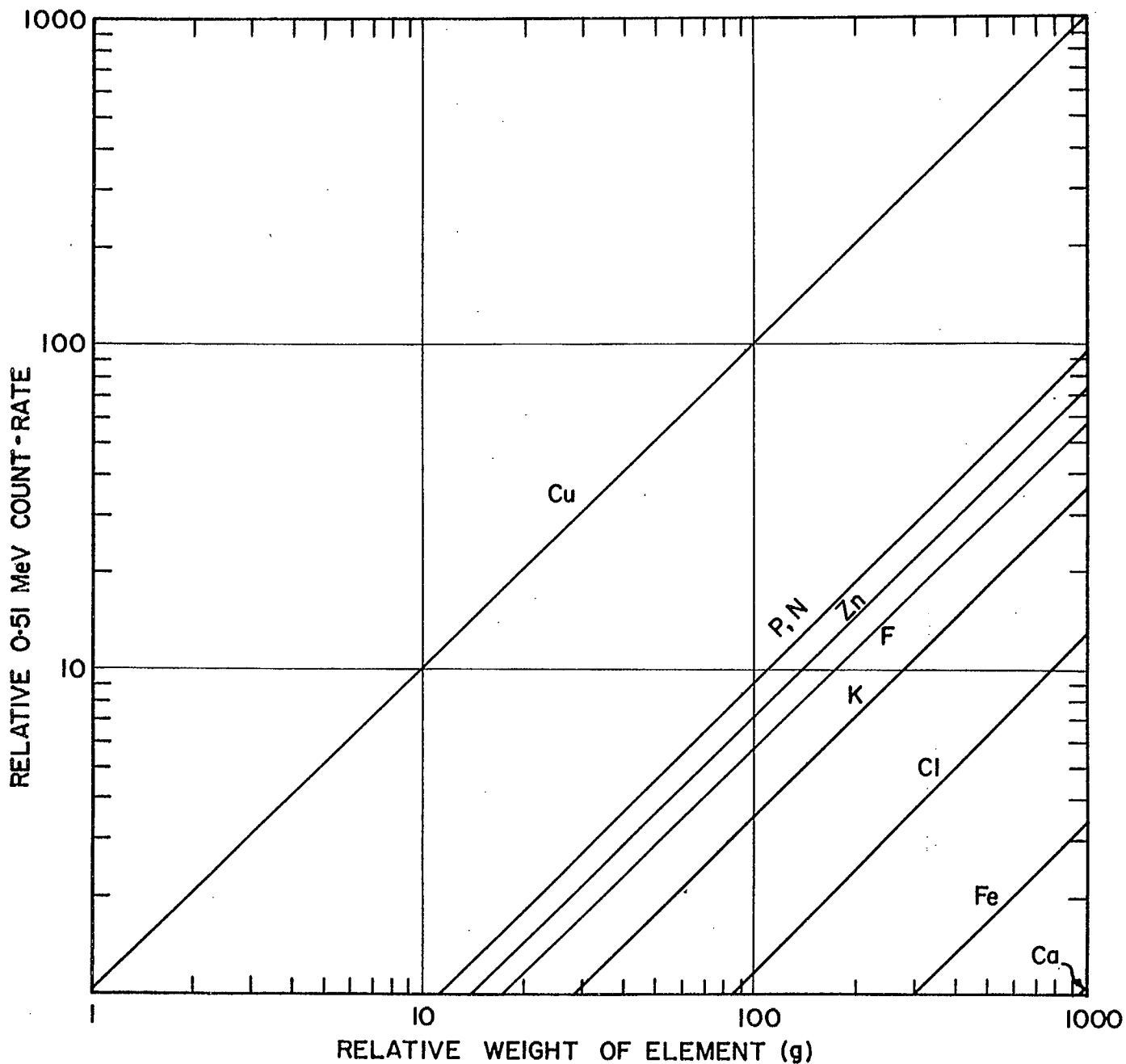


FIGURE 5
THE RELATIVE COUNT-RATES FOR VARIOUS ELEMENTS
EMITTING 0.51-MeV GAMMA RADIATION

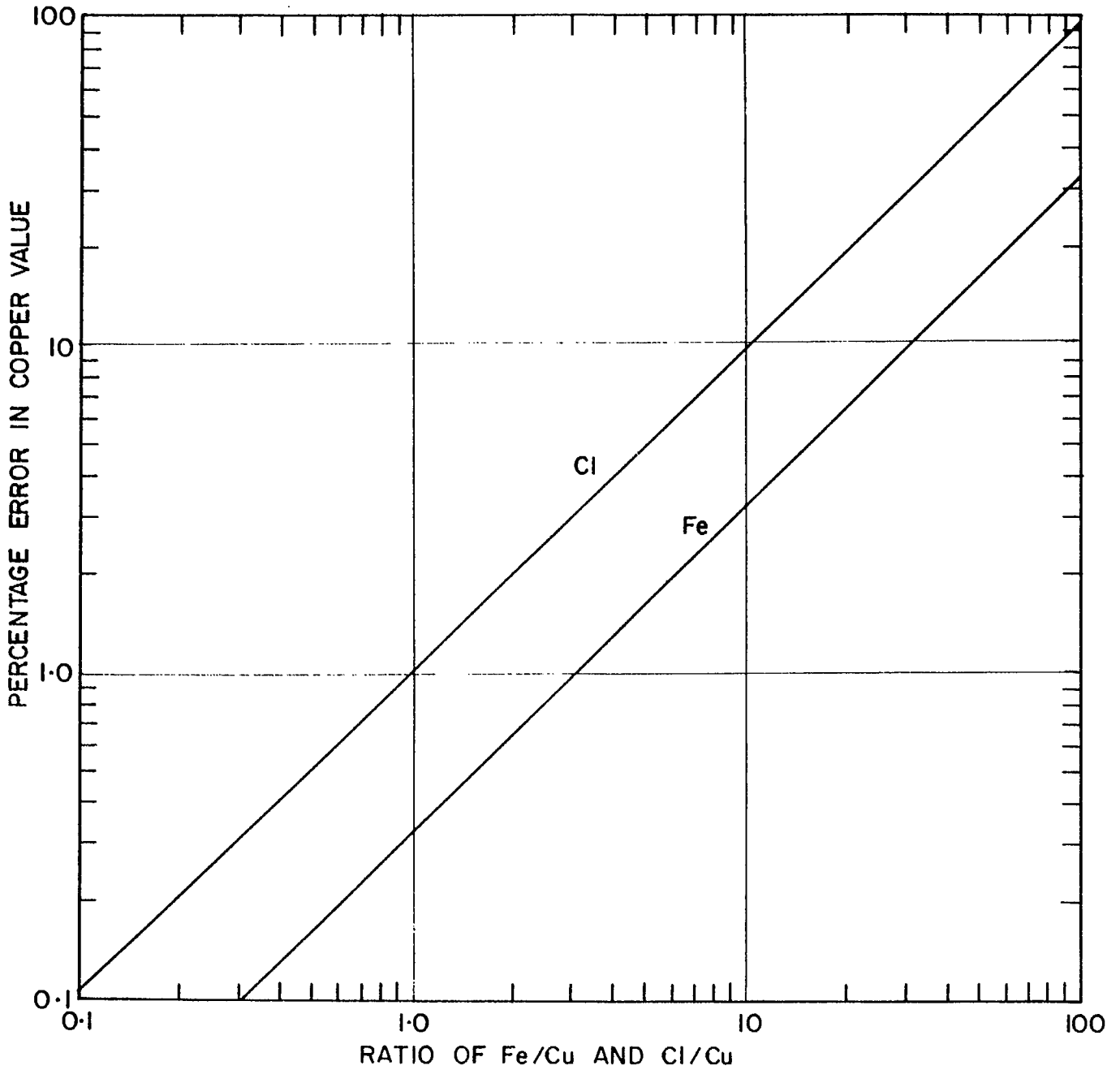


FIGURE 6
ERROR FROM VARYING Fe AND Cl CONCENTRATIONS ON
ESTIMATION OF COPPER CONTENT

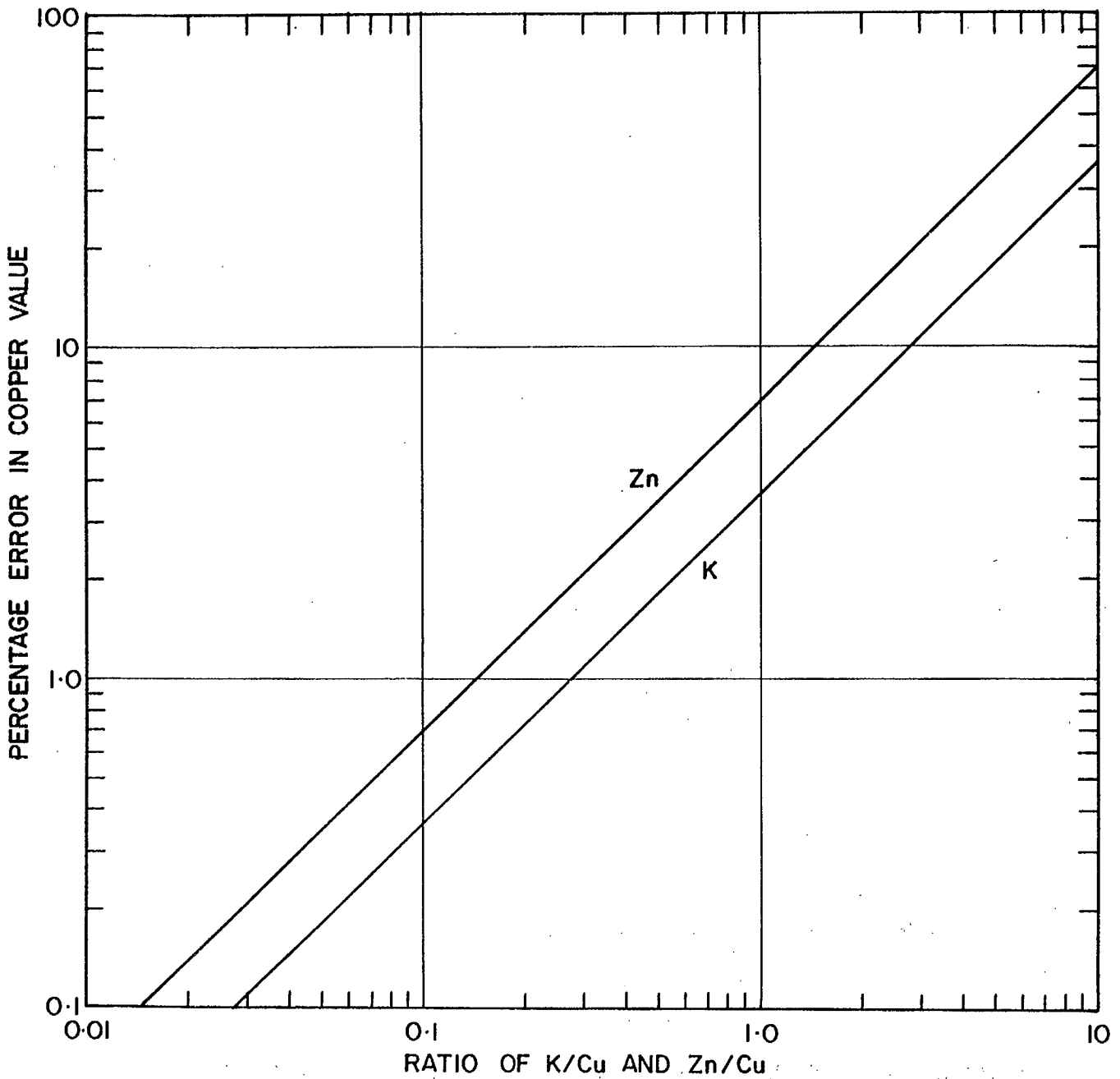


FIGURE 7
ERROR FROM VARYING K AND Zn CONCENTRATIONS ON
ESTIMATION OF COPPER CONTENT

considering the iron data in Figure 6, a weight ratio of Fe:Cu of 10:1 would result in a copper reading that is too high by 3% of its actual value, i. e. 1% Cu would appear as 1.03% Cu. Similarly, because of iron interference, the apparent amount of copper determined in a hypothetical sample containing 1% copper (as chalcopyrite) in a pure pyrite matrix would be 1.14% copper. Thus, in practice, it may be concluded that interference from the presence of iron does not present a significant error in copper determinations.

The most significant interference in the determination of copper is from the presence of zinc (Figure 5), which has a high sensitivity in fast-neutron activation analysis (7) and which is also frequently associated in nature with copper-containing minerals (12). The relative concentrations of copper and zinc can be determined in an irradiated Cu-Zn mixture, by following the decay of the irradiated mixture as a function of time and utilizing the difference in the half-lives of copper-62 and zinc-63 (Cu-62, 9.8 minutes; Zn-63, 38.1 minutes) to resolve the decay curve into its two components (Figure 8). However, such a procedure is relatively cumbersome and is subject to error in the presence of any additional positron emitters. Also, as approximately 75% of the copper ore milled in Canada is reported to be zinc-free (12), the application of fast-neutron activation to copper estimation is not seriously impaired if only zinc-free copper ore is examined.

CONCLUSIONS

Recent developments in the design of fast-neutron generators have resulted in the commercial availability of compact, long-lived generators of high neutron output. The application of this type of neutron source to the "in-situ" determination of copper, either at a drilling site or in a mine-control laboratory, appears feasible, and offers a number of advantages over conventional analytical techniques, viz.:

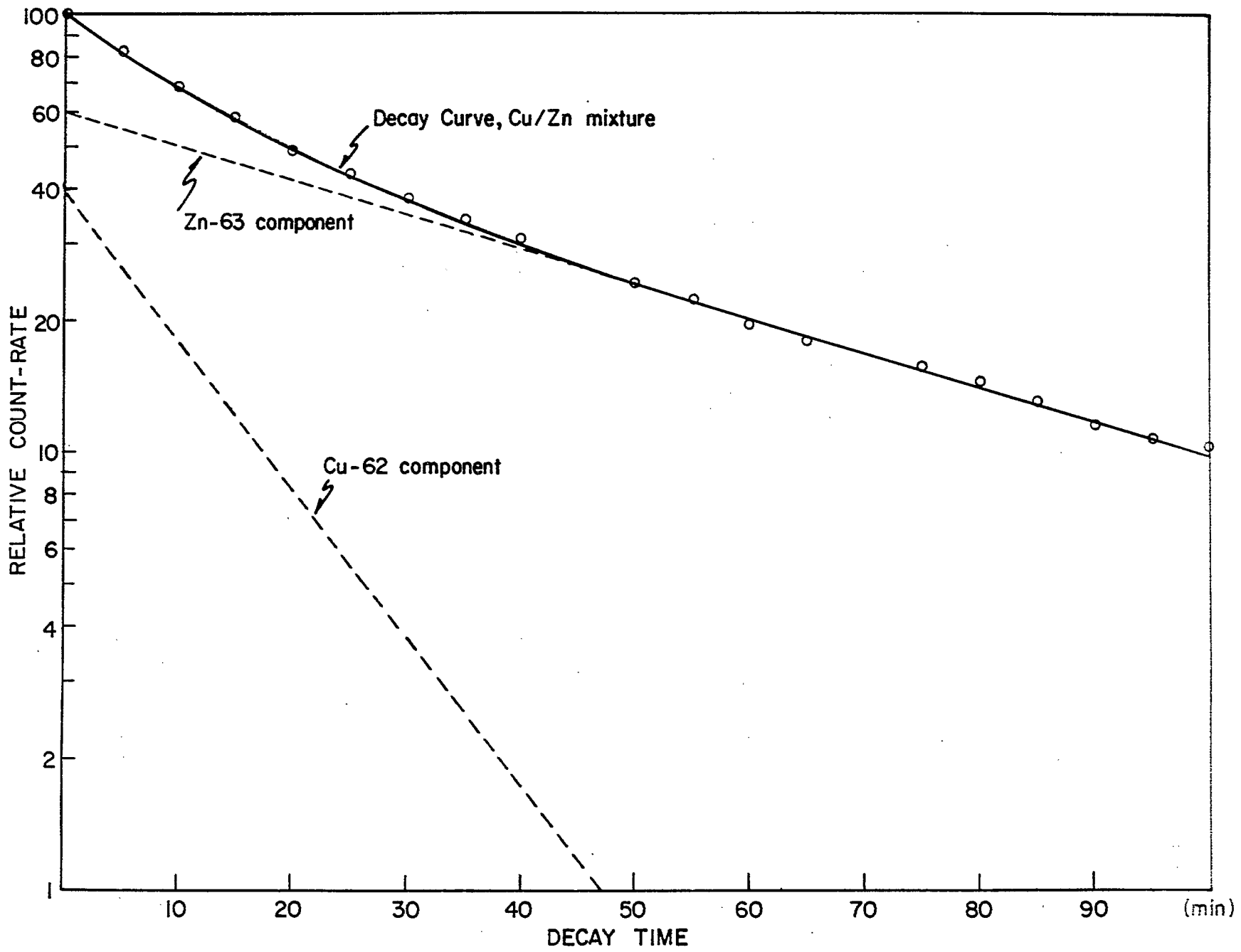


FIGURE 8
 DECAY CURVE FOR A Cu/Zn MIXTURE (Zn/Cu, WEIGHT RATIO 22:1)

- a) the determination is rapid and non-destructive and may be completed in less than ten minutes;
- b) the method may be used with samples having a variety of physical shapes, e.g. drill core or powder, the only constraint being that a copper-containing standard of similar geometry to the sample be used as a reference standard. Thus, in principle, it is possible to determine the copper content of the total volume of a drill core without the need for splitting, crushing and sampling, at a rate of at least one inch per minute;
- c) a large volume (up to $\sim 500 \text{ cm}^3$) of powdered mineral may be used in the determination, which greatly simplifies the problem of obtaining a representative sample (13) for analysis;
- d) since neutron activation analysis is a volume measurement, sample preparation is not such a critical factor as it is in chemical techniques, in which the constituents of interest have to be liberated, either in the grinding process or in the chemical assay, or in X-ray fluorescence methods where only the surface layer of a sample is analysed;
- e) the total copper content of the sample is measured, independent of its chemical state.

In order to translate these advantages into a viable field unit, appropriate shielding of the neutron source and a transfer system for the controlled irradiation and counting of numerous samples must be developed.

Finally, it should be noted that, although this discussion has been restricted to the determination of copper, fast-neutron activation may also be applied to other systems, e.g. the determination of zinc in essentially copper-free minerals or the determination of silicon in iron oxide (14), with similar advantages to those listed above.

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