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ACTIVATION ANALYSIS OF THE RARE EARTHS

H.W. KOHN
E.R. TOMPKINS

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ACTIVATION ANALYSIS OF THE RARE EARTHS

by

H. W. Kohn and E. R. Tompkins

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Abstract

Thermal neutron activation methods have been applied to the analysis of rare earths for contamination by other rare earths. By this procedure the presence of 0.63% samarium in cerium, 1.18% dysprosium in yttrium, 0.023% neodymium and 0.01% cerium in praseodymium, 0.03-0.3% cerium in lanthanum, and the purity of scandium have been determined. Mathematical relationships for use in these experimental procedures have been derived.

Introduction

The analysis of the rare earth group of elements has long been a difficult chemical or physical procedure. The precipitation of the rare earth group as oxalates or fluorides from acid solution provided a separation from most other elements, but the subsequent separation of one rare earth from another, heretofore accomplished by fractional recrystallizations, was a highly unsatisfactory procedure; the purity of the resulting compound always being subject to considerable doubt.

The preparation of rare earths of high purity by means of the ion-exchange column[1, 2] soon exhausted the usual chemical and physical procedures heretofore used as analytical methods. Spectrophotometric analysis could be used to detect as little as 0.3% of Pr in Nd[2]. The copper spark spectrographic analysis[3] of the rare earth group which had been used as a simple routine procedure at this laboratory was able to detect from 1.0-0.1% impurity[4], the limits being dependent on the individual species present and their relative amounts. Mass spectrographic techniques were able to detect 0.1% of one rare earth in another.

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1 Harris, D.H. and Tompkins, E.R., Ion Exchange as a Separations Method. II. Separation of Several Rare Earths of the Cerium Group (La, Ce, Pr and Nd), J.Am.Chem.Soc. 67 (1947).

2 Spedding, F.H., et al., A New Method for the Rapid Macroscopic Separation of the Rare Earths, J.Am.Chem.Soc. 67 (1947).

3 Frat, M., Nachtrieb, N.H., Tomkins, F.S., J. Optical Soc. of Am. 37, 279 (1947).

4 Rodden, C.J., J. Research, National Bureau of Standards 26, 517 (1941).

The general use of radiation techniques opened a new field in analytical chemistry and its application to the rare earth group was not a difficult matter. Ordinary radiochemical analysis, for example, of cerium in lanthanum[5], became a routine process. The general use of the ion exchange column permitted radiochemical separations of rare earths to be made often in a matter of hours[6]. Activation analysis, although applied to other elements[7, 8], had not yet been used for rare earth analysis.

In the activation analyses discussed in this paper, as opposed to radiochemical analyses, no attempt was made to separate the components after activation, but a study of the decay and absorption curves was made in an attempt to determine the components in the sample. This set certain limitations on the experiments, but in bypassing chemical separation of the rare earths (often a major undertaking), a great deal of convenience and simplicity was inherent in the analyses, as well as the added advantage of being able to detect short-lived activities. The procedure had the added advantage of allowing the principle component to act as a monitor. The requirements are simple: a

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5 Boldridge, W.F. and Hume, D.N., A Study of the Separation of Cerium by Iodate Precipitation and the Improved Radiochemical Determination of Cerium and Rare Earth Activities. CC-2845.

6 Ketelle, B.H. and Boyd, G.E., The Application of Ion-Exchange to the Separation of Yttrium Group Rare Earths, J.Am.Chem.Soc. 67, 2700 (1947).

7 Overman, R.T. and Clark, H.M., The Determination of Trace Amounts of Elements by Radioactivation Analysis. MonC-401.

8 Boyd, G.E., The Method of Activation Analysis. AECD-2507.

sample of high purity (since low purity samples yield extremely complicated curves which are difficult to analyze[7]), and a source of nuclear projectiles, such as a uranium reactor, a radium-beryllium pack or a cyclotron. It is preferred to have a source of slow neutrons whose flux is constant with respect to time to avoid reactions other than the n, γ type. The work described here was done at the Oak Ridge National Laboratory reactor which will be referred to in the remainder of this paper as the source of slow neutrons. For recording and measuring radioactivity, a Geiger-Müller bell type counter was used in these experiments, although ionization chambers have been used with success in similar work.

Several serious difficulties were encountered. The determination of the minor component in rare earth mixtures is a matter of great difficulty. High activation purity was not always a guarantee of high chemical purity. The incompleteness and inaccuracy of present nuclear data limits the effectiveness of the results. Activation cross sections are known only to $\pm$ 20%. Ocasionally as unknown radiation is detected (Figure III). Reactions other than the n, γ type did not appear to interfere.

Theoretical

From a mixture of two inactive nuclei, (rare earths in this case), the relative activities after slow neutron activation may be derived as follows:

$$I_a = (1 - e^{-\lambda_a t})\, N_a\, F\, \sigma_a$$

Where I_a = radioactivity of the element a at zero time in disintegrations per second.

N_a = number of molecules of element a.

F = flux in neutrons/cm^2/sec.

σ_a = atomic activation cross section of a in cm^{-2}.

t = time of activation.

λ_a = decay constant of element a.

Similarly, $I_b = (1 - e^{-\lambda_b t})\, N_b\, F\, \sigma_b$ and

$$\frac{I_a = (1 - e^{-\lambda_a t})\, N_a\, \sigma_a}{I_b = (1 - e^{-\lambda_b t})\, N_b\, \sigma_b} \quad \text{as } t \text{ approaches zero}$$

$$\frac{I_a}{I_b}_{t \to 0} = \frac{\lambda_a}{\lambda_b} \cdot \frac{N_a}{N_b} \cdot \frac{\sigma_a}{\sigma_b} \quad \text{and} \quad \frac{N_a}{N_b} = \frac{I_a}{I_b} \cdot \frac{t_{\frac{1}{2}a}}{t_{\frac{1}{2}b}} \cdot \frac{\sigma_b}{\sigma_a}$$

If we now consider a short bombardment method to determine the short lived contaminant associated with a long lived constituent, the ratio $\frac{\sigma_b \; t_{\frac{1}{2}a}}{\sigma_a \; t_{\frac{1}{2}b}}$ is criterion of the value of of such an experiment (See Table I). The quantity $\frac{\sigma_b \; t_{\frac{1}{2}a}}{\sigma_a \; t_{\frac{1}{2}b}}$ is determined automatically by the half lives and cross section of any pair. For a short irradiation (we may define a short irradiation here as one in which the exposure time is short compared with the half lives) we can define $\frac{\sigma_b \; t_{\frac{1}{2}a}}{\sigma_a \; t_{\frac{1}{2}b}}$ as the molar ratio of the two components which will be present if the two radioactivities are initially present in equal amounts. Actual

determination of the ratio $\frac{I_a}{I_b}$ after neutron bombardment will give the ratio $\frac{N_a}{N_b}$ and from this $\frac{N_a}{N_b \quad N_b}$ can be calculated, giving the percent of a present in b.

Returning to the original ratio, $\frac{I_a}{I_b} \quad \frac{(1-e^{-\lambda at})\, N_a\, \sigma_a}{(1-e^{-\lambda bt})\, N_b\, \sigma_b}$ as t becomes large (i.e., is long compared to the half life of the components), $\frac{I_a}{I_{bt}} \quad \frac{N_a\ \sigma_a}{N_b\ \sigma_b}$, or merely the ratio of saturation activities. As the sample decays this becomes

$$\frac{I_{aT}}{I_{bT}} = \frac{N_a\ \sigma_a}{N_b\ \sigma_b} \quad \frac{e^{-\lambda aT}}{e^{-\lambda bT}} \quad \text{and Log} \quad \frac{I_a}{I_b} \ \frac{N_b}{N_a} \ \frac{\sigma_b}{\sigma_a} = T\,(\lambda b - \lambda_a)$$

where T is the time of decay. If substance a has a longer half life than substance b, the ratio $\frac{I_{aT}}{I_{bT}}$ at time T has no limiting value. We may now define a long irradiation method, one in which the principal component has a short half life (compared to the minor constituent) and is allowed to decay away so that the decay of the minor constituent may be observed. There are certain practical limitations to the determinations of this type set by sample size, neutron flux and time of exposure, and the ranges of the radioactivity recorder, but a calculation using the above formula will show the feasibility of any particular study and the lower limits shown by the absence of any appreciable long-lived activity.

In order to evaluate completely the accuracy and feasibility of an activation analysis, it became necessary to

have a criterion of the separability of the two activities as a function of amounts of activities initially present and the relation of their half lives and radiation characteristics. This problem was undertaken independently by Henry D. Zeldes and presented in "A Method of Analyzing Radioactive Decay Curves", ORNL-78[9]. The data appearing in Table II are calculated by application of this method of analysis to the data obtained.

Experimental

The procedure used was to irradiate a small amount of the material in the Clinton Reactor for from 1-5 minutes when the short irradiation method was used and from 16 hours-1 wk. for the long method, then to spread a thin film of the oxide on scotch tape placed across a hole in an aluminum card, cover the sample and count in a bell type Geiger counter. Sample sizes varied from 200μg to 10 mg. and were chosen so that the observed activity would be approximately 10,000 counts per minute. The sample preparation after irradiation usually consumed from 2-3 minutes in the short irradiation tests and allowed the decay of components whose half lives were of the order of one minute to be followed.

Figure I shows the results of an early experiment with cerium oxide which was obtained from F. H. Spedding's group and purified by a recrystallization procedure. The decay curve shows a strong 24 minute activity due to 0.63% Sm. This was not

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9 Zeldes, Henry D., "A Method of Analyzing Radioactive Decay Curves", ORNL-78, June 15, 1948, p. 3.

detectable spectrographically and the α activity of the samarium was barely detectable (ca. twice background) in a thin plate of the powder. Figure II shows a similar experiment performed on yttrium purified by precipitation methods[10]. The dysprosium impurity was immediately evident and was later confirmed spectrographically. The 8 hour impurity was not immediately evident or confirmable, if present it was most probably Er^{171} or Eu^{152}. However, if erbium, the yttrium contained 34.6% Er, whereas if europium, the yttrium contained 0.028% Eu. The subsequent spectrographic data indicated that at least the bulk of the second impurity was europium. It was logical in this work to assume the absence of impurities other than rare earths.

The bulk of the work, however, was performed on column separated rare earths which were far purer than those heretofore described and which led to data not only difficult, but often impossible to interpret. Figure III, for example, shows typical data obtained for irradiated, column-purified Pr_6O_{11}. The growth of activity was obtained several times, and the half life of the daughter varied from 10-15 minutes depending on the amount of short lived neodymium impurity present (the neodymium impurity gives rise to a short lived 61 which compensates to an extent, for the growth). Mass spectrographic analysis did not show any appreciable amount of another praseodymium isotope, and the daughter producing activity was eventually removed from the early

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10 This and subsequent rare earths were supplied through the courtesy of D. H. Harris. The authors wish to express their appreciation for his cooperation.

fractions by exhaustive column purification. The long irradiation of praseodymium shown in Figure IV indicated the presence of both cerium and neodymium in amounts of 0.01 and 0.023% respectively.

Of particular interest was the purification of scandium[11] which finally gave a product which showed only two activities, an extremely short ($\sim$ 20 second) activity* and an 85 day activity. Analyzing the curve so obtained, we cannot expect to detect less than 10% of our impurity activity with a $\pm$ 20% error or 3 1/3% with a 40% error, if E^0 be considered 1%. The percentages of each of these, which then gives us the lower limit of impurities in the scandium are presented in Table II.

A final empirical check was made on the method by purposely contaminating La_2O_3 which had shown less than 0.008% Ce_2O_3 with 0.026, 0.175 and 0.35% Ce_2O_3 and subjecting to pile irradiation. The results shown in Figure V indicate close agreement $\pm$ 10% with the amount of added, although positive identification of Ce radiations in Sample 1 would be difficult.

Conclusion

An activation method for trace determination has been demonstrated. Mathematical relationships have been derived to demonstrate the feasibility of any such analysis and the limits of detectable impurity. A simple experimental procedure has been evolved. The results of analyses of samples of unknown and known composition are presented.

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11 Discussed in a separate paper by Harris, Tompkins and Kohn. (To be published.)

*Recent work by Goldhaber indicates that this is a scandium activity.

Where feasible, the use of chemical separations is to be preferred. The method will be capable of greater accuracy when the accuracy of existing nuclear data is improved.

Table I

Feasibility of a Slow Neutron Activation Analysis Showing Molar Ratio of B to A for a Short Bombardment and Equal Initial Activities. B = Lanthanum.

Isotope	Half Life	Atomic Cross Section	Where B=La $\frac{\sigma B\ t_{\frac{1}{2}}a}{\sigma a\ b_{\frac{1}{2}}B}$
La^{139}	40 hours	8.4	1
Ce^{141}	28 days	$\frac{0.4^{*}}{0.089}$	$\frac{35.3}{189.0}$
Ce^{143}	33 hours	0.12	57.8
Pr^{142}	19.2 hours	10	0.4
Nd^{147}	11.1 days	0.26	206
Nd^{149}	1.8 hours	0.165	2.29
Sm^{153}	46 hours	36.6	0.254
Sm^{155}	25 min.	1.23	0.071
Eu^{152}	9.2 hours	678	0.0285
Eu^{154}	5-8 years	391	30.6
Gd^{159}	17.9 hours	0.125	30
Gd^{161}	3.6 min.	0.181	693
Tb^{160}	72 days	100	3.62
Tb^{160}	3.9 hours	10.7	0.0766
Dy^{165}	140 min.	715.0	0.000685
Ho^{166}	27 hours	59.6	0.095
Er^{171}	$7\frac{1}{2}$ hours	0.27	5.84
Tm^{170}	125 days	126	5.0
Yb^{169}	33 days	11.0	15.1
Yb^{175}	102 hours	0.5	40.8
Yb^{177}	2.4 hours	0.93	5.42
Lu^{176}	3.7 hours	15.9	0.0504
Lu^{177}	6.6 days	91	0.37
Y^{90}	61 hours	1.24	10.3
Sc^{46}	85 days	22	19.5

*Depending on which value of cross section is used.

Table II

Lower Limits of Impurities in Scandium

Element (A)	$T\frac{1}{2}$	%A/% Sc(20% error)	%A/% Sc(40% error)
Y^{90}	61 hrs.	5.27	1.42
Lu^{176}	3.7 hrs.	0.026	0.009
Lu^{177}	6.6 days	0.19	0.06
Yb^{177}	2.4 hrs.	2.74	0.91
Er^{169}	$7\frac{1}{2}$ hrs.	2.8	0.93
Ho^{166}	27 hrs.	0.48	0.12
Dy^{165}	2.5 hrs.	0.00035	0.00012
Tb^{160}	3.9 hrs.	0.039	0.013
Gd^{159}	17.9 hrs.	11.2	3.40
Eu^{152}	9.2 hrs.	0.145	0.048
Sm^{155}	25 min.	0.036	0.013

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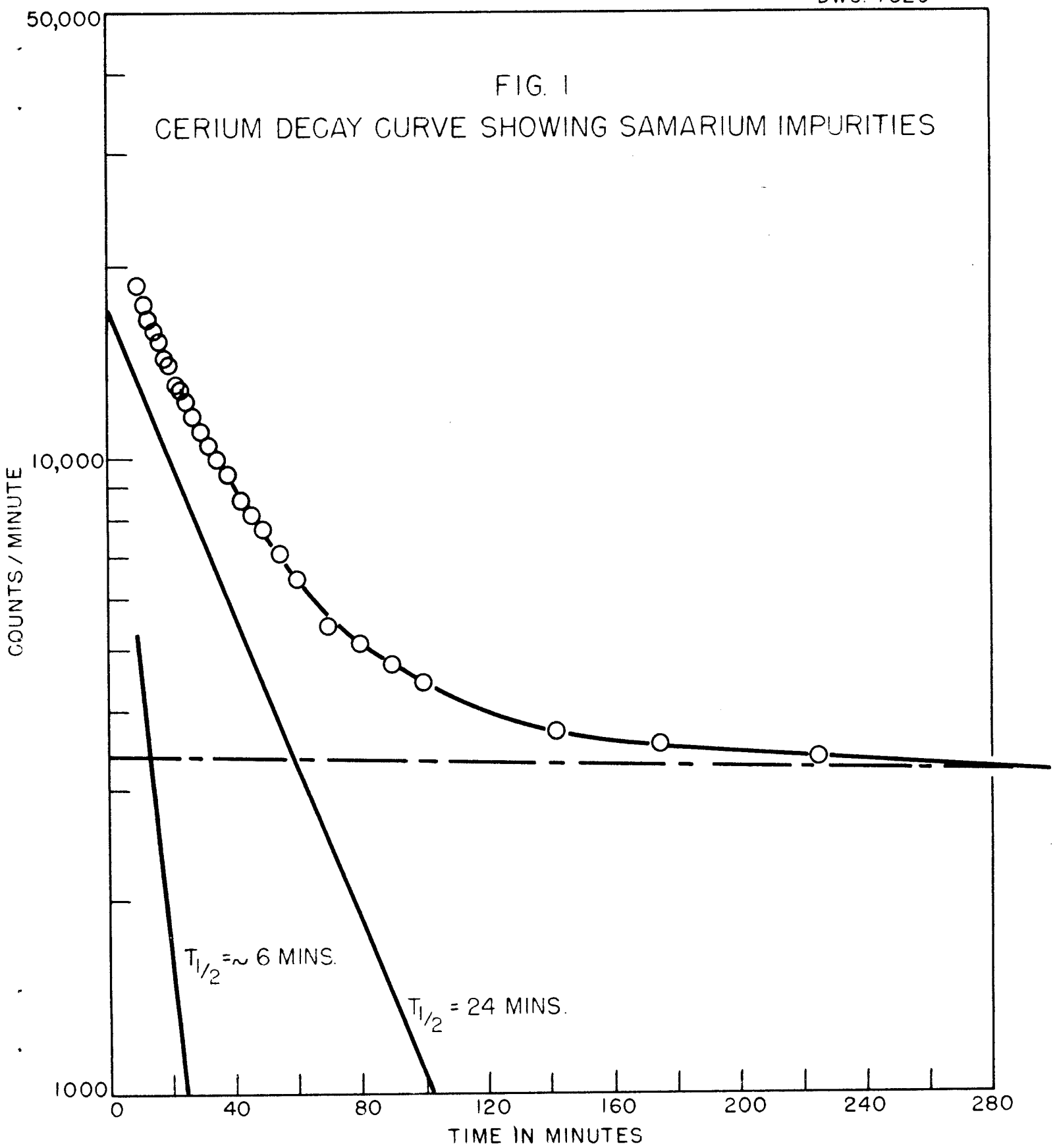

FIG. 1
CERIUM DECAY CURVE SHOWING SAMARIUM IMPURITIES

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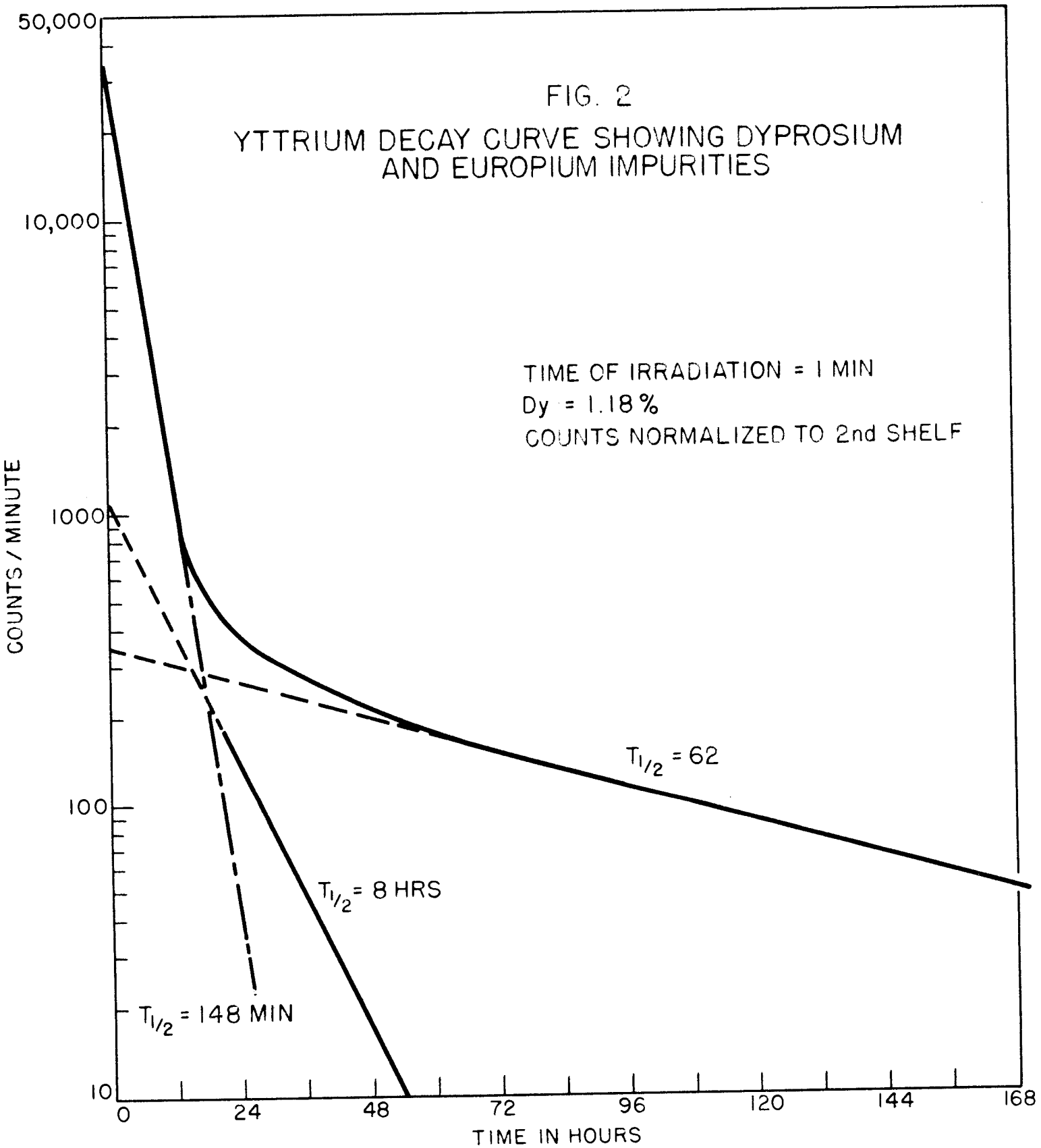

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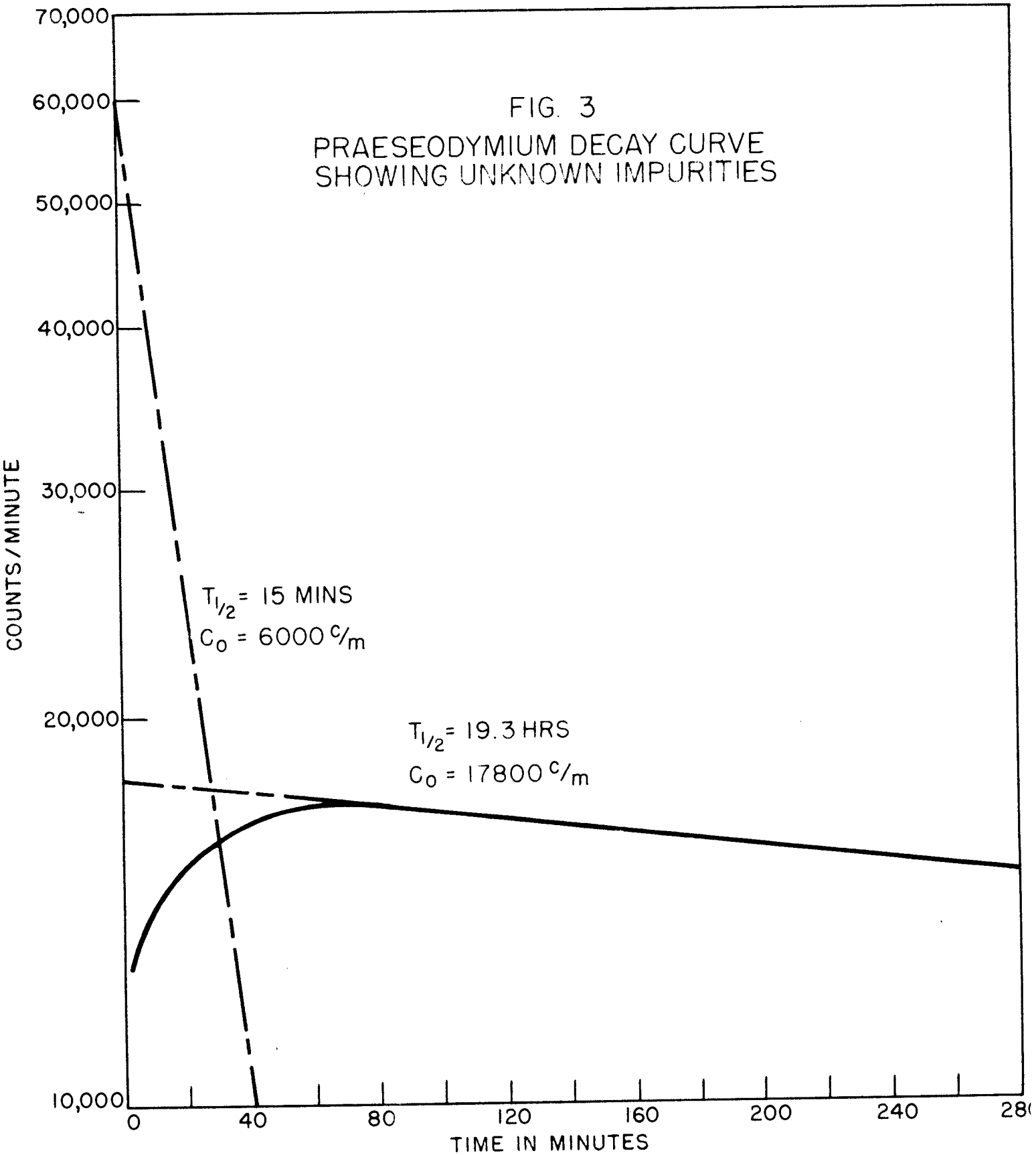

FIG. 3
PRAESEODYMIUM DECAY CURVE
SHOWING UNKNOWN IMPURITIES

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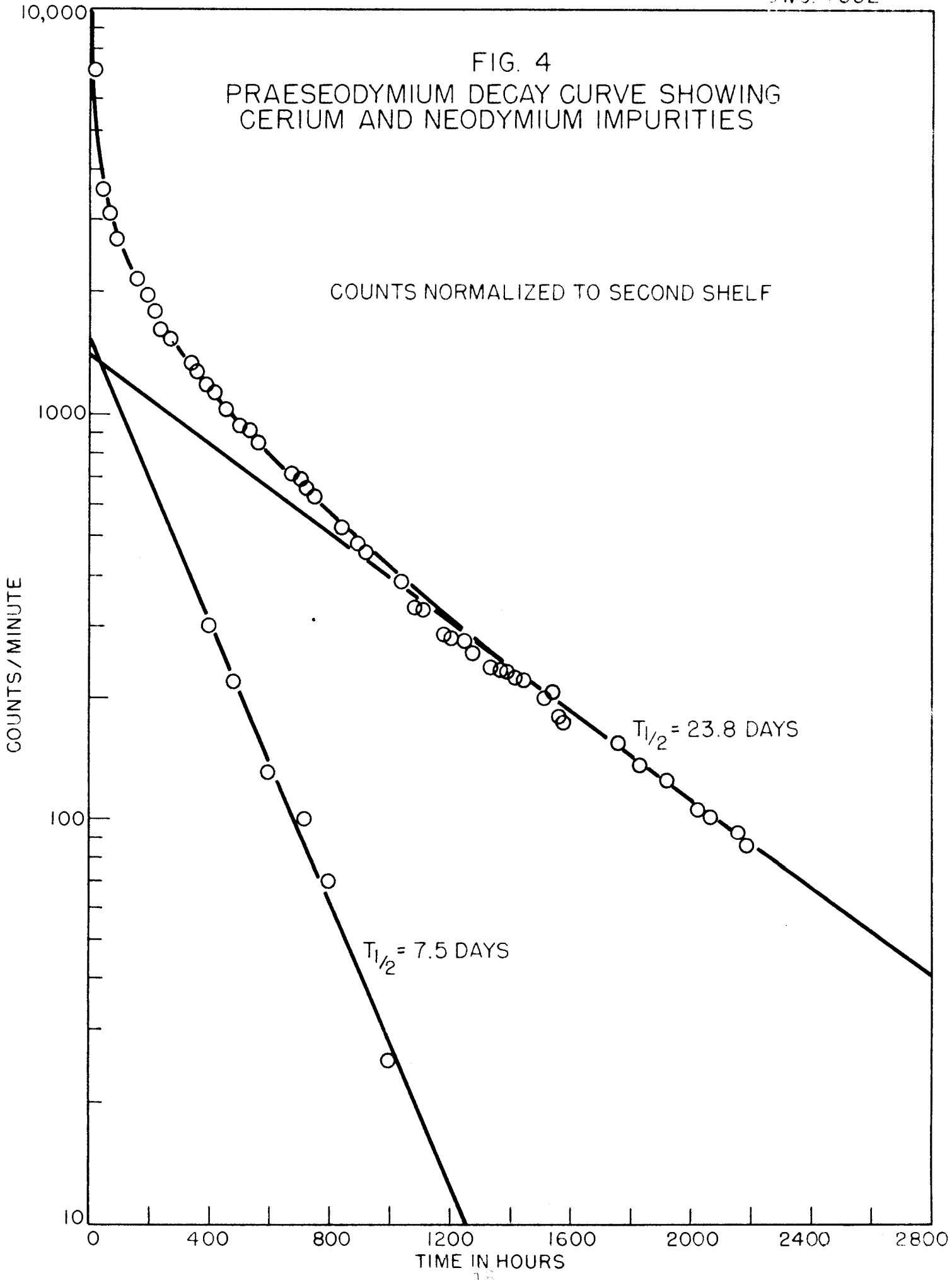

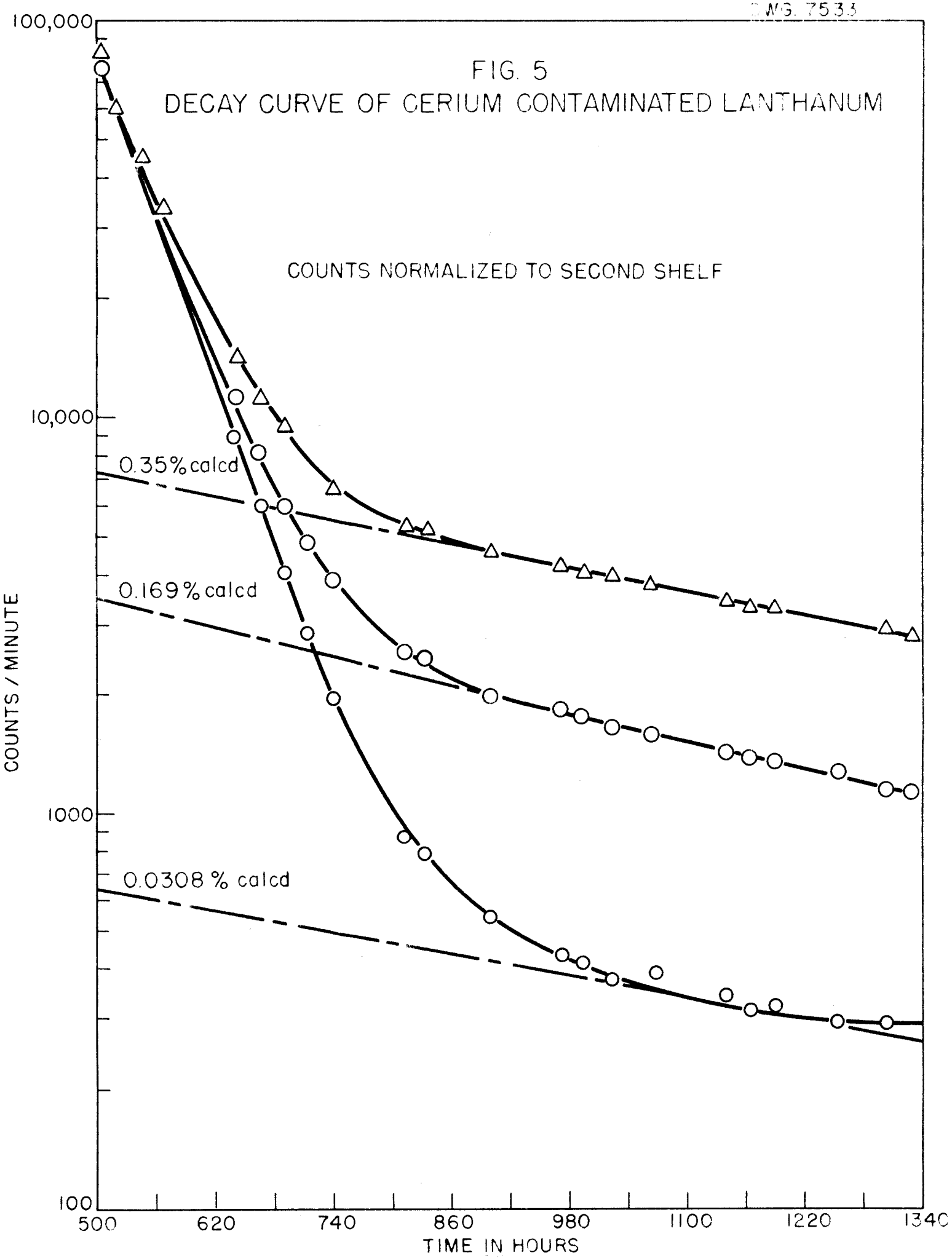

FIG. 5
DECAY CURVE OF CERIUM CONTAMINATED LANTHANUM