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THE DETERMINATION OF TRACE AMOUNTS OF URANIUM BY NEUTRON ACTIVATION ANALYSIS

H. A. Mahlman
G. W. Leddicotte

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H A Mahlman
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ABSTRACT

The determination of trace concentrations of uranium in synthetic materials, ores, soils and water by neutron radioactivation analysis is described. The principles of the activation analysis method as applied to trace uranium determination, the processing of irradiated specimens, and some examples of the results obtained by this method of analysis are discussed in this paper.

I Introduction

A successful analytical method for any trace element determination should be (1) simple, (2) extremely sensitive, (3) adequately precise, (4) specific, and (5) free from interferences, especially from reagent blanks Most of the conventional methods of analysis for trace elements, i e., polarography, spectroscopy, fluorimetric, colorimetric, microgravimetric, microvolumetric, etc , do not always completely meet the aforementioned standards for a good analysis. However, more recently through the development of nuclear science, new analytical techniques have become available for the determination of trace quantities of many elements. Chief among these techniques is a method of analysis called "radioactivation analysis " This physical method is most often used in conjunction with chemical analysis and it is based on the measurement of the nuclear radiations (as either beta, gamma, or alpha radiation) from artificially radioactive isotopes which are induced in the stable isotopes of an element through interaction with the nuclear particles (neutrons, deuterons, etc) produced either in a chain-reacting pile or by a charged particle accelerator.

Radioactivation analysis is unique because it is extremely sensitive for most elements. It is also specific, i.e., other elements normally do not seriously interfere in the analysis because each induced radioactivity has its own particular decay constant and type of radiation neither of which are exactly duplicated in any other radionuclide. Contamination as experienced in most conventional methods of analysis is negligible unless present <u>before</u> nuclear bombardment It is almost always an analysis which is capable of giving results with a precision of ±10% or better.

The principles of radioactivation analysis have been aptly reviewed by Boyd[2] and Taylor and Havens[8] More recently Leddicotte and Reynolds[4,5]

have reported on the use of the Oak Ridge National Laboratory graphite reactor as an analytical tool for the analysis of trace concentrations of many elements by neutron bombardment and show that it is possible to determine trace quantities of at least sixty-five of the elements with sensitivities of detection ranging from 10^{-6} to 10^{-11} gram by this method

Neutron radioactivation analysis at ORNL has now been extended to include the analysis of low concentrations of uranium in synthetic solutions, ores, soils, and water. The ORNL graphite reactor was used as the source of neutrons and all of the data reported in this paper was obtained by the comparative method of analysis.

II. The Application of Neutron Radioactivation Analysis to Uranium Determination

a) Nuclear Data

The analysis of uranium by radioactivation analysis may be accomplished by the neutron bombardment of either U^{234} (0.0061%), U^{235} (0.72%), or U^{238} (99.274%). The reactions of these isotopes with the neutrons of the ORNL graphite reactor (or any other neutron source) are given in the following equations

1) $U^{234}\ (n,\gamma)\ U^{235}$
2) $U^{235}\ (n,\gamma)$ Fission Products
3) $U^{238}\ (n,\gamma)\ U^{239} \xrightarrow[23.5m]{\beta^-} Np^{239} \xrightarrow[2.33d]{\beta^-} Pu^{239}$

In reaction (1), the amount of U^{235} activity produced from U^{234} is negligible when short time bombardments are used because the half-life of U^{235} is of the order of 9×10^8 years.

Smales(7) and Seyfang and Smales(6) have recently reported on the application of radioactivation analysis to the determination of uranium in minerals and U^{235} in mixtures of naturally occurring uranium. They utilized reaction (2) and determined the U^{235} content of the sample by measuring the radioactivity of a certain fission product (Ba^{140}) produced in a predetermined time

of bombardment and processing

Reaction (3) has been the reaction used by the Activation Analyses Group, Analytical Chemistry Division, ORNL, to determine uranium by radioactivation analysis In this reaction, either the U^{239} activity, the Np^{239} daughter activity of U^{239}, or Pu^{239} can be used to determine the uranium concentration Since U^{239} decays with a half-life of 23 5 minutes, a rapid separation procedure is necessary However, this is not always conducive to an efficient separation of contaminating radioactivities produced from other elements appearing in the sample. Conversely, the formation of Pu^{239} from the Np^{239} by decay would take considerable time to obtain sufficient alpha activity for good sensitivity. Thus, the Np^{239} which decays with a half-life of 2.33 days offers a good radionuclide for a more elaborate separation procedure.

b) Determination of Np^{239} Radioactivity

Np^{239} as it decays emits both beta and gamma radiation It has seven gamma quanta(9) with an energy range of 0.057-0.50 Mev which can be conveniently detected by means of a gamma scintillation counter of the type described by Borkowski(1).

c) Comparative Method of Analysis

The amount of Np^{239} measured by γ counting is directly proportional to the amount of U^{238} in the sample If the sample and a comparative standard (a known weight of U_3O_8) are irradiated simultaneously in the same container and chemically processed and counted under similar conditions, then the amount of uranium in a sample can be calculated as follows

$$\frac{\text{Corrected count of } Np^{239} \text{ activity in sample}}{\text{Corrected count of } Np^{239} \text{ activity per unit weight of uranium in comparative std.}}$$

= weight of uranium in sample.

where the corrected count includes corrections for counter background and the unit weight of both sample and standard. Since the amount of Np^{239} formed is dependent upon the concentration of U^{238} present in the sample irradiated, it may be readily seen that alteration of the natural ratio of the uranium isotopes will cause bias results. The bias is limited on depleted uranium but may be serious where enriched uranium is under investigation.

The necessity of monitoring the flux of neutrons, which is usually a difficult quantity to measure or control, is eliminated by the use of the comparative sample

d) Neutron Source

The ORNL graphite reactor was used as the neutron source for all the work described here. The neutron flux of this reactor is about 10^{12} neutrons/cm^2/second

e) Self-Shadowing

The flux depressions at the center of the sample undergoing irradiation have been recognized. However, whenever solid samples are bombarded in quartz tubing of 4 mm internal diameter or when dilute aqueous solutions are bombarded in quartz ampoules, the self-shadowing effects are negligible. The presence of elements in the ore which have high cross sections, for example, gadolinium would have deleterious effects. Such a condition would result in a serious neutron flux attenuation in the sample and would necessitate a preirradiation separation of the uranium by some convenient quantitative method.

III. The Analysis of Samples Containing Uranium by Radioactivation Analysis

a) The Nuclear Bombardment of Sample

1) Solids

Weighed portions of the samples and standard are put into small quartz tubes three-fourths of an inch long x 6 mm in diameter (4 mm I.D.). The

tubes are capped either with a cork stopper wrapped in 2S aluminum and placed in the pneumatic "rabbit" of the pile The irradiation is carried out for a predetermined time, usually 16 hours After irradiation, the samples are allowed to decay about 4 hours and then chemically processed as described below. In our work with synthetics which had been processed by paper chromatographic techniques, the paper was conveniently bombarded in short pieces of quartz tubing whose openings were plugged by means of cork stoppers

2) Liquid and Semi-Liquid Samples

Aliquots of the sample were sealed in quartz ampoules of 12 mm I D x 54 mm long and the ampoules placed in a suitable bombardment container and bombarded for 16 hours. After bombardment, the ampoule is broken and an aliquot of the sample taken and processed by the separation procedure described below.

b) Chemical Separation

A chemical separation after neutron bombardment isolates the Np^{239} radioactivity to free it from all other radioactive species in the sample material Under normal conditions, a known amount of the natural inactive element as an "isotopic carrier" is added to the solutions of both the specimen and the comparison sample This "carrier" is then chemically processed to isolate it from other elements.

Np^{239} while having a convenient half-life has the disadvantage of not having a stable isotope which can be used as an isotopic carrier. However, Fields(3) has shown that trace quantities of Neptunium-239can be carried on a non-isotopic carrier such as cerium. The basic chemistry involved in the present method of analysis for uranium by radioactivation analysis uses lanthanum as a carrier, however, the neptunium must be completely reduced and oxidized before a quantitative separation can be made by the procedure described below.

The Procedure

1. The soil and ore specimens were dissolved by digesting the irradiated material in a concentrated HNO_3, HF, $HClO_4$, and H_2SO_4 mixture. Additional HF is added if a residue of silica remains in the bottom of the crucible. The sample is concentrated to heavy sulfuric acid fumes, cooled and transferred to a 15 ml centrifuge tube The synthetic materials on paper chromatograms were treated with fuming HNO_3 to dissolve the paper and the hot solution diluted to a desired volume with water.

2 If a residue (sulfate salts) remains after transferring, centrifuge 5 minutes and wash the residue vigorously with 1 ml of 1 M HNO_3. Centrifugation should always be for the stipulated time and at full speed

3 Add 3 0 mg of La carrier, 250 λ of 5 M hydroxylamine hydrochloride and digest 5 minutes. Neutralize the solution cautiously with NH_4OH and add an excess to precipitate $La(OH)_3$. Centrifuge 5 minutes and discard supernate If an excessively large precipitate (ammonium sulfate) is present, wash with 1 ml of 1 M NH_4OH, centrifuge 5 minutes and discard the supernate

4. Dissolve the La hydroxide in 2 ml of 2 M HCl, add 1.0 mg of Sr carrier, 250λ of 5 M hydroxylamine hydrochloride and digest 5 minutes Make the solution 2 M in HF (about 100λ of conc HF per ml of solution), agitate well and digest 5 mins. Centrifuge and discard the supernate Wash the precipitate with 0.5 ml of 1 M HF-1 M HNO_3, centrifuge and discard the wash.

5 Dissolve the LaF_3 precipitate in a minimum of saturated H_3BO_3 and 6 M HNO_3 (usually 100 λ of each are sufficient). Add 200λml of 10% $KMnO_4$ solution, 100 λ of water, agitate well and digest 5 minutes Make 2 M in HF, agitate, digest 5 minutes and centrifuge Transfer the supernate to another centrifuge tube Wash the precipitate with 0 5 ml of 1 M HF-1 M HNO_3 solution and combine the wash with the supernate. Discard the precipitate.

6. To the supernate add 3.0 mg of La carrier and agitate, digest 5 minutes and centrifuge Add 3.0 mg of La carrier to the supernate, agitate and digest 5 minutes without disturbing the first precipitate on the bottom of the tube, then centrifuge and transfer the supernate to another tube Wash the precipitate with 0.5 ml of 1 M HF-1 M HNO_3 solution, centrifuge, and combine the wash with the supernate. Discard the precipitate.

7. To the supernate, add 250 λ of 5 M hydroxylamine hydrochloride, 1.0 mg of Zr carrier, agitate, and digest 5 minutes Add 3.0 mg of La carrier and make 2 M HF, agitate, digest 20 minutes, centrifuge and discard the supernate Wash the precipitate with 0 5 ml of 1 M HF-1 M HNO_3 solution, centrifuge and discard the wash solution

8. Slurry the precipitate in 100 λ of 1 M HNO_3 and transfer into a gamma scintillation tube by means of a transfer pipette Rinse the centrifuge cone with three 100 λ portions of 1 M HNO_3 and transfer the rinses into the gamma scintillation tube. Stopper the tube with a cork stopper and count the gamma activity. The standard sample of U_3O_8 is dissolved in HNO_3 and an aliquot of the solution processed under the same conditions as the specimen samples. As discussed previously the uranium content of the sample in question is determined by equating the ratio of the activities to the ratio of the concentrations.

c) Interferences in Chemical Separation

The interferences that can be attributed to the presence of radioactivities associated with thorium and the fission products is negligible if two or more lanthanum fluoride cycles are used to decontaminate the neptunium The only other experience with interferences was a chemical interference in which it was apparent that the sulfuric acid concentration was critical. Best results were obtained when this concentration was 1.25 M or less The initial NH_4OH precipitation, however, circumvented this difficulty completely. Phosphoric acid did

not interfere.

d) Measurement and Identification of the Separated Np^{239}

A slurry of the La + Np^{239} fluoride precipitate was placed in a small pyrex culture tube and measured by means of a gamma scintillation counter. In the experimental work, identification was made by aluminum absorption studies of the beta radiations and a decay, or half-life, study. Examples of these are given in Figures 1 and 2, respectively

e) Sensitivity of Detection

Such factors as the number of neutron particles bombarding the material, the length of irradiation, "self-shadowing," self-absorption, time for chemical separation, the efficiency of measuring the separated radioactivity reflect upon the sensitivity attainable by radioactivation Experimentally, it has been shown that it is possible to attain a practical sensitivity of detection for uranium of the order of 10^{-10} gram with a probable error of no more than ±10%

IV. Results

a) Reproducibility

As already stated above, the precision of analysis for uranium is ±10% or better. The individual results reported in Tables I through III specifically show the standard deviation for each set of determinations

b) Determination of Uranium in Synthetics

One of the earliest applications of the method of radioactivation analysis was concerned with the determination of series of synthetic uranium samples eluted through a paper chromatography strip The method of handling the samples before irradiation has been described. The samples were then irradiated for about 62 hours and processed by the procedure given in this report Typical data obtained on this type of material is shown in Table I

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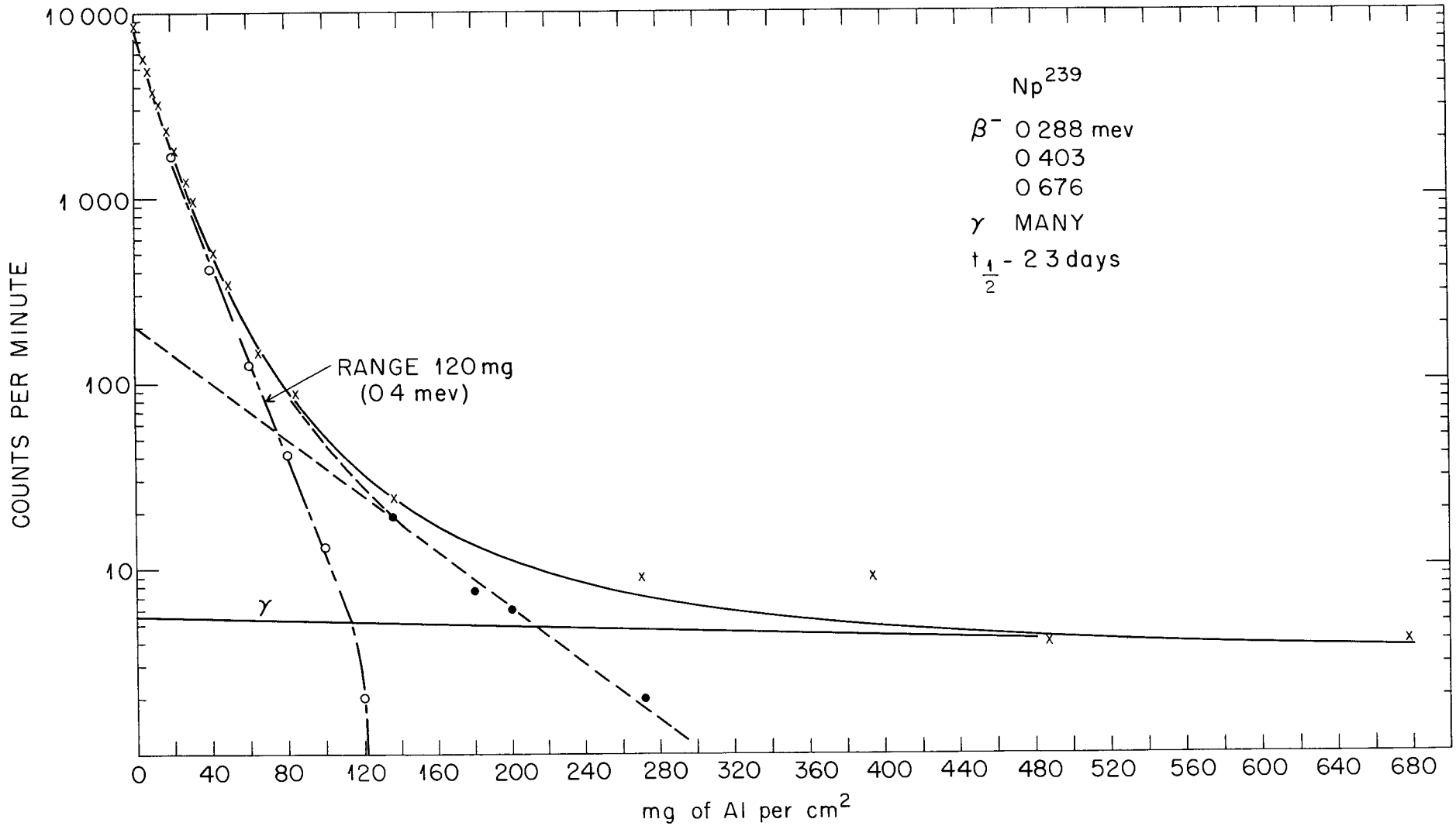

FIGURE 1
ABSORPTION OF Np^{239} BETA RADIATIONS IN ALUMINUM

[redacted]

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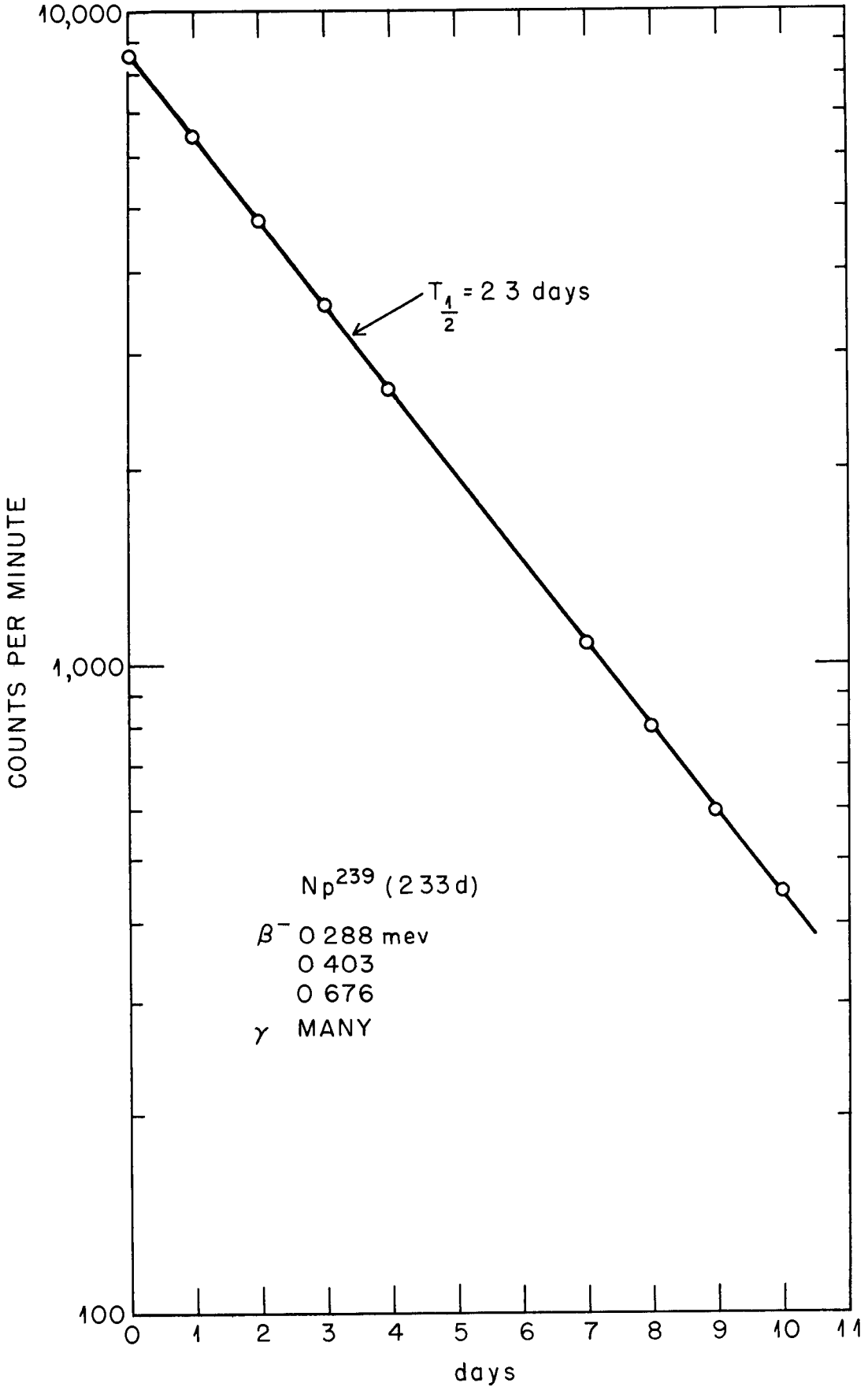

FIGURE 2

DECAY OF NEPTUNIUM 239

TABLE I

Determination of Uranium in Synthetics by Neutron Activation Analysis

Uranium Found	Uranium Taken
0.33 microgram	0.34 microgram
0.31	Fluorimetric Analysis
0.33	0.29 micrograms
0.32	Difference with Amount Taken 15%
0.36	
0.34	
0.35	
0.35	
0.30	
0.30	
0.33 - Mean	
2 70% - Std Deviation	
3 5% - Difference with Amounts Taken	

c) Determination of Uranium in Phosphate Ores

A series of samples (Bartow clays) were analyzed by irradiating at least duplicate portions of about 0.025 gram of the material for a period of no longer than 62 hours in the graphite reactor After the irradiation, the samples were put into solution and processed by the procedure described. The results obtained are reported in Table II.

TABLE II

Determination of Uranium in Phosphate Ores

Sample	#1	#2	#3	#4
	345 µg/gm	171 µg/gm	288 µg/gm	172 µg/gm
	325	161	261	164
	385	171	262	158
	342	161	275	149
	336	158	249	148
	316	168	256	180
	368	158	271	166
	315	163	240	164
	346	160		
	366	174		
	341	166		
	357	169		
Mean	345 µg/gm	165 µg/gm	263 µg/gm	163 µg/gm
Std Deviation	20.8 µg	5 5 µg	15.3 µg	10.8 µg
σ	6.0%	3.3%	5.8%	6.6%
Fluorimeter Results	210 µg/gm	160 µg/gm	250 µg/gm	160 µg/gm

d) Determination of Uranium in Soils and Water

A series of soil and water samples were analyzed by irradiating duplicate portions of the material for a period of no longer than 62 hours in the graphite reactor After the irradiation the samples were processed by the procedure described elsewhere. The results obtained are reported in Table III

TABLE III

Determination of Uranium in Soils and Waters by Neutron Activation Analysis

Sample	Uranium Concentration
1	69.7, 68.2 μg/gram
2	48.3, 51.1
3	84.0, 80.0

CONCLUSIONS

From the results reported, it is felt that the method of neutron radioactivation analysis is quite capable of being a specific, sensitive and precise method of analysis for uranium in a variety of materials. The degree of sensitivity attained by the particular nuclear reaction used in the analyses described in this paper is better than the sensitivities associated with present conventional methods for determining uranium Comparison of the activation analysis results with the results obtained by conventional methods show that the method of analysis is precise Although the precision and accuracy of this determination has been arbitrarily set at ±10%, it has been found to be much better than that value.

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