MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0361296 3

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

Cy 4

ORNL-2620
Chemistry-General

THE DETERMINATION OF TRACE ELEMENTS IN WATER BY NEUTRON ACTIVATION ANALYSIS

R. L. Blanchard
G. W. Leddicotte

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

Printed in USA. Price $2.25. Available from the

Office of Technical Services
Department of Commerce
Washington 25, D.C.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-2620
Chemistry-General

Contract No. W-7405-eng-26

Analytical Chemistry Division

THE DETERMINATION OF TRACE ELEMENTS IN WATER BY NEUTRON ACTIVATION ANALYSIS

R. L. Blanchard*
G. W. Leddicotte

DATE ISSUED

JUL 24 1959

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0361296 3

* U. S. Public Health Service on loan to Oak Ridge National Laboratory.

LIST OF FIGURES

Figure		Page
1	Qualitative Analysis, Chicago Drinking Water: Silver Chloride (AgCl) Group Precipitation	28
2	Qualitative Analysis, Chicago Drinking Water: Hydrogen Sulfide Group Precipitation	29
3	Qualitative Analysis, Chicago Drinking Water: Ammonium Hydroxide Group Precipitation	30
4	The Identification of Fluorine-18 in Distilled Water Irradiated for A 16-Hour Period	32
5	Qualitative Analysis, 16-Hour Irradiated Oak Ridge Water: Sodium Hydroxide Group Precipitation	34
6	Gamma Decay Studies, 16-Hour Irradiated Oak Ridge Water: Ammonium Hydroxide Group Precipitation (Decay Study Begun after the Short-lived Nuclides Had Decayed Out)	35
7	Qualitative Analysis, Chicago Drinking Water: Ammonium Sulfide Group Precipitation	36
8	Qualitative Analysis, Chicago Drinking Water: Ammonium Phosphate Group Precipitation	37
9	Qualitative Analysis, Chicago Drinking Water: Sodium (Soluble) Group Precipitation	39
10	The Magnesium-27 Gamma Spectra From Chicago Drinking Water	40
11	The Iodine-128 Gamma Spectra From Chicago Drinking Water	41
12	Chicago Drinking Water: The Determination of Argon	42
13	Beta Decay Studies, Chicago Water: Specific Silicon Separation Following a 16-Hour Irradiation Period	44
14	Si-31 Beta Absorption Measurements, 16-Hour Irradiated Chicago Water (Specific Silicon Separation)	45

LIST OF FIGURES (Continued)

Figure		Page
15	P-32 Beta Decay Studies, 2-Week Irradiated Chicago Water (Specific Phosphorus Separation)	46
16	P-32 Beta Absorption Measurements, Two-Week Irradiated Chicago Water (Specific Phosphorous Separation)	47
17	The Feather Plot of the Phosphorus-32 Beta Absorption Spectrum	48
18	Beta Decay Studies, Chicago Water: Specific Calcium Separation Following a Two Week Irradiation Period	50
19	Ca-45 Beta Absorption Measurements, Two-Week Irradiated Chicago Water (Specific Calcium Separation)	51
20	Qualitative Analysis, Two-Week Irradiated Chicago Water: Acid Sulfide Group Precipitation	52
21	Gamma Decay Studies, Two-Week Irradiated Chicago Water: Acid Sulfide Group Precipitation	53
22	Qualitative Analysis, Two-Week Irradiated Chicago Water: Ammonium Hydroxide Group Precipitation	54
23	A Gamma Spectrum Illustrating the Typical Characteristics	64

LIST OF TABLES

Table		Page
I	Nuclear Properties of Induced Radionuclides	10
II	The Separation of Various Elements by the Ion-Exchange Technique	13
III	Chemical Separation Scheme	16
IV	Carrier Solutions	17
V	Chemical Separation Scheme for Long-Lived Radionuclides	24
VI	Elements Determined in Water by Activation Analysis (Previously Determined by Conventional Chemical Analysis)	56
VII	Elements Determined in Water by Activation Analysis (Data by Conventional Chemical Means not Available)	57
VIII	Elements Determined in Water by Neutron Activation Analysis	59

TABLE OF CONTENTS

		Page
1.	INTRODUCTION	1
2.	PRINCIPLES OF NEUTRON ACTIVATION ANALYSIS	2
3.	SENSITIVITY OF THE TECHNIQUE	5
4.	ERRORS IN NEUTRON ACTIVATION ANALYSIS	7
5.	EXPERIMENTAL PROCEDURE	9
	A. Ion-Exchange Method	11
	B. Nondestructive Method	15
	C. Chemical Precipitation Method	15
	1. Magnesium	19
	2. Iodine	20
	3. Dissolved Gases	21
	4. Silicon	21
6.	RADIOACTIVE ASSAY TECHNIQUE EMPLOYED	25
7.	RESULTS OBTAINED BY NEUTRON ACTIVATION ANALYSIS	27
	A. Short-Lived Radionuclides	27
	B. Long-Lived Radionuclides (Chicago Water)	43
8.	SUMMARY AND CONCLUSION	58
9.	ACKNOWLEDGEMENTS	61
10.	APPENDIX A: Gamma Scintillation Spectrometry	62
11.	BIBLIOGRAPHY	67
12.	REFERENCES TO APPENDIX A	71

1. INTRODUCTION

Neutron activation anslysis is a sensitive and accurate technique for the determination of trace elements in many different types of sample materials. However, to date it has not been applied to the analysis of water. Thus, the purpose of the study reported herein was to investigate its application in water analysis with the thought in mind that, as neutron irradiation facilities become more widely available, the results would prove useful to sanitary engineers and geochemists.

Neutron activation analysis is a relatively new technique in analytical chemistry. As early as 1936, Hevesy and Levi determined dysprosium in impure yttrium by means of a thermal neutron irradiation,[1] and in 1938, Seaborg and Livingood determined Ga, Fe, Cu, P and S in the parts per million range by deuteron bombardment with the University of California cyclotron.[2] Since these early investigations, neutron activation analysis has found numerous applications in analytical chemistry,[3] and has been employed in the analysis of microgram and submicrogram concentrations of at least 70 of the elements.[4] Excellent review articles have been reported by Boyd[5] and Leddicotte and Reynolds.[4] Brooksbank[6] has shown that the activation analysis method is an accurate and precise analytical technique.

2. PRINCIPLES OF NEUTRON ACTIVATION ANALYSIS

Materials subjected to a neutron irradiation give rise to radioactive species of the same elements. The sample to be analyzed is placed in a homogeneous neutron flux for a period long enough to produce a measurable amount of radioactivity. The time the sample remains in the neutron flux will depend upon the "saturation factor" which is the ratio of the activity produced at time, t, compared to the activity which would be produced in an infinite time. The saturation factor may be expressed by Equation (1).[7]

$$S = 1 - e^{-\lambda t} \qquad (1)$$

where S is the "saturation factor", λ is the decay constant (equal to 0.693 divided by the half life of the induced radionuclide), and t is the irradiation time.

The quantity of radioactivity produced in a material during a neutron irradiation is dependent upon the criteria expressed in the relationship given by Equation (2):

$$A = \frac{f \cdot M \cdot \phi \cdot \sigma \cdot N_o \cdot S \cdot e^{-\lambda T}}{A_o} \qquad (2)$$

where A is the activity in disintegrations per second, f is the abundance of the stable parent isotope, M is the mass of the stable isotope in grams, ϕ is the effective thermal neutron flux in neutrons per square centimeter per second, σ is the atomic cross section for the interaction of the atoms of the parent isotope with neutrons, N_o is Avogadro's number, A_o is the atomic weight of the parent isotope, and S is the

"saturation factor". The decay of the radioactive material after irradiation is represented by the term $e^{-\lambda T}$, where λ is the decay constant as given above, and T is the time that has elapsed since the end of the irradiation. If the activity is known, the concentration of an element present in the sample can be obtained by solving for "M" in Equation (2).

The radioactivity produced by neutron reactions (most usually of the (n,γ) type)[4] is analyzed by radiation measuring instruments. From such measurements, the radiation energy (or energies) and the half life of the induced radionuclide can be determined with considerable accuracy. Since no two radionuclides have identical radiation energies and half lives, the radionuclide can be positively identified.[4]

Activation analysis may be made quantitative by either of two methods. The "absolute method" employs Equation (2) to calculate the mass of stable isotope present from the measured activity of the induced radioactive isotope. It can be seen that the neutron flux, the half-live, and the cross section must be known very accurately, and the activity be measured absolutely to obtain good results. However, neutron fluxes and the cross sections are not generally measured with accuracies better than 10%.[8,9] Furthermore, comparison of half-life tabulations[10] show discrepancies. Also the decay scheme, counting geometry, and crystal efficiency (in the case of gamma counting) must be known accurately to obtain the disintegration rate from the counting data.[11] Reynolds and Brooksbank[12] have shown that it is extremely

difficult to measure small amounts of activity absolutely, and the error in these measurements can be very large. Therefore, due to these many uncertainties, it is quite difficult to obtain dependable results by the absolute method.

Greater accuracy and precision can be obtained by the "comparator method" of analysis. Here a standard sample, containing a known quantity of the element or elements to be determined, is irradiated and processed simultaneously with the unknown. The activities of both are assayed in exactly the same manner, so the only counting corrections which have to be made are those for decay. The concentration of the element in the unknown is determined through comparison of its activity with that produced in the comparator.[4] The comparator method was used in this investigation. However, for trace element determinations in water on a routine basis, it may not be necessary to analyze a comparator sample with every unknown if the counting conditions remain constant and the neutron flux is closely monitored.

3. SENSITIVITY OF THE TECHNIQUE

The sensitivity of neutron activation analysis for some elements is as low as 10^{-11} gram.[4] Other elements cannot be detected at all. The factors which influence the sensitivity were indicated by Equation (2). These include:

1) The cross section or the probability for the neutron reaction to occur. The value is fixed for any one nuclide at a given neutron energy. Cross sections for fast neutrons are rarely much larger than the geometrical cross sections of nuclei (about 10^{-24} cm^2, or barn). Cross sections for slow or thermal neutrons will exceed this value.[13] Since the sensitivity for detection is proportional to the activation cross section, nuclides with large cross sections are more easily detected. Lead, for example, is not easily determined, since its cross section is only 4.5×10^{-4} barns.

2) The neutron flux, or the number of neutrons per unit area available for the irradiation. The sensitivity is proportional to the neutron flux, i.e., the greater the neutron flux, the greater the sensitivity The limits given by Leddicotte and Reynolds[4] can be greatly enhanced by irradiations at higher neutron fluxes.

3) The isotopic abundance of the parent nuclide, or the per cent abundance of the total stable element in nature. If an element has more than one stable isotope and the desired irradiation is produced from a neutron reaction on a stable isotope of low abundance, such as Iron-59 (0.33%), the sensitivity will be much less than if the stable isotope were 100% abundant.

4) The half-life of the induced radionuclide and the irradiation time also influence sensitivity. Since these two quantities determine the "saturation factor", it can be seen from Equation (1) that the shorter the half life and the longer the irradiation time, the greater the saturation factor. Maximum sensitivity occurs when the saturation factor is 1.0; however, in most cases, it is neither necessary nor practical to irradiate to saturation. As an example, if a radionuclide has a half life of 30 days, a 30 day irradiation would yield 50% maximum activity. Irradiation for an additional 30 days would only increase this to 75%. Thus, it is feasible to approach saturation in a reasonable time only if the radionuclide has a half life in the order of minutes or hours.

Due to the very short half lives of fluorine-20 (12 s) and boron-12 (0.027 s). radioactivity measurements essential for activation analysis are impossible on a routine basis unless elaborate equipment is available so that the sample can be ejected at a great speed from the reactor to the counting device.

5) The efficiency of radioactivity measurements. No counting device will detect and record every radioactive disintegration. Poor counting geometry will decrease the sensitivity of the method. Also, the crystal efficiency of a scintillation spectrometer decreases rapidly with increasing gamma energy.[11]

4. ERRORS IN NEUTRON ACTIVATION ANALYSIS

Neutron activation analysis is usually free from contamination errors common to most methods of trace element analysis.[4,5] Since the samples are not chemically treated before irradiation, the only possible means of contamination is through careless sample preparation or use of contaminated equipment or solutions.

Other errors may be classified as counting errors, radiochemical errors, and irradiation errors. Errors in beta counting include self-absorption, scattering, geometry, radioactive decay, background, and instrument failures.[14] The use of a comparator sample and correction for decay and background will minimize all errors except those of instrumental origin. The latter may be monitored by using a long-lived standard radioactive source for measuring counting reproducibility.[15]

In respect to possible errors in a radiochemical analysis, care should be exercised to assure that the ion species in the stable carriers exchange completely with their radioactive counterparts. Most often this means carrying them to the same valence state. Otherwise, the chemically separated product will not contain the same ratio of active to inactive element as the system.[14] Further, the chemical separation must be radiochemically pure. If not, extraneous activity might contaminate the separated fraction. This problem of purity may be reduced through use of gamma scintillation spectrometry.[16] In beta counting, radiochemical purity may be determined by decay and absorption measurements.[5,17]

Irradiation errors can originate if the sample material contains a nuclide having a high absorption cross section for neutrons.[6] The waters of interest in this investigation did not contain any of these materials in appreciable quantities. In general, if the sample is placed in the reactor so as to attain equal neutron irradiation from all directions, errors in irradiation are very small.

5. EXPERIMENTAL PROCEDURE

Water samples from seven grographical areas in the United States were used in this investigation. These samples were collected at random from drinking water taps in the cities listed below by sanitary engineers assigned to selected Public Health Service Regional Offices. The approximate date of sampling and the raw water source are given in the tabulation.

City	Date Collected	Water Source
Atlanta, Georgia	August, 1957	Chattahoochee River
Charlottesville, Virginia	August, 1957	Moorman's River, Ragged Mountain Watershed
Chicago, Illinois	August 15, 1957	Lake Michigan
Cincinnati, Ohio	June 26, 1957	Ohio River
Denver, Colorado	August 6, 1957	South Platte River, Blue River
New York, New York	August 8, 1957	Surface Water
Oak Ridge, Tennessee	September 25, 1957	Clinch River

Thirty milliliter aliquots of the samples collected were placed into polyethylene bottles* and irradiated in Hole 10 of the Oak Ridge National Laboratory Graphite Reactor. Hole 10 is a water-cooled irradiation facility with a temperature of about 40°C., making it possible to irradiate the sample in a liquid form. This eliminated the necessity for an evaporation step. Hole 10 is positioned in the reactor so that neutron bombardment will occur equally from all directions. The thermal neutron flux in this facility is approximately 6.5×10^{11} neutrons per square centimeter per second. A 16-hour

---

* Polyethylene does not become significantly radioactive when irradiated.

Table I
Nuclear Properties of Induced Radionuclides

Elements Detected	Stable Isotope(%)	Radioisotope Formed	Activation Cross Section (barns)	Half-life[a]	β^- (Mev)	γ (Mev)
Antimony	Sb-121 (57.25)	Sb-122 (n,γ)	6.0	2.80 d	1.41, 1.98, 0.74	0.56
	Sb-123 (42.75)	Sb-124 (n,γ)	2.5	60 d	0.61, 2.37	0.60, 0.65, 0.71, 1.67, 2.07
Argon	A-40 (99.6)	A-41 (n,γ)	0.53	1.83 h	1.2, 2.5	1.30
Arsenic	As-75 (100)	As-76 (n,γ)	4.1	26.6 h	2.97, 2.41, 1.76, 0.36	0.56, 0.64, 1.2, 1.4, 2.05, 1.8
Barium	Ba-138 (71.6)	Ba-139 (n,γ)	0.60	85.0 m	2.38, 2.22, 0.82	0.163
Bromine	Br-81 (49.5)	Br-82 (n,γ)	3.1	35.9 h	0.44	0.77, 0.55, 0.62, 1.03, 1.31, 1.47
Calcium	Ca-44 (2.07)	Ca-45 (n,γ)	0.69	164 d	0.25	- - - - - - - - - - - - - - - - - -
Chlorine	Cl-37 (24.47)	Cl-38 (n,γ)	0.56	37.5 m	4.8, 2.7, 1.1	1.60, 2.15
Copper	Cu-63 (69.1)	Cu-64 (n,γ)	4.1	12.82 h	EC, 0.57, β^+ (0.657)	1.35, (0.51, 1.02)[b]
Iodine	I-127 (100)	I-128 (n,γ)	6.7	25.0 m	2.12, 1.66, 1.12	0.45, 0.54
Iron	Fe-58 (0.31)	Fe-59 (n,γ)	0.98	45.1 d	0.462, 0.271, 1.56	1.10, 1.29, 0.191
Magnesium	Mg-26 (11.29)	Mg-27 (n,γ)	0.026	9.45 m	1.75, 1.59	0.84, 1.02
Manganese	Mn-55 (100)	Mn-56 (n,γ)	13.3	2.58 h	2.86, 1.05, 0.75	0.84, 1.81, 2.13
Oxygen	O-18 (0.204)	F-18 (p,n)[c]	0.2	1.87 h	0.649, β^+ (0.648)	(0.51, 1.02)[b]
Phosphorus	P-31 (100)	P-32 (n,γ)	0.21	14.3 d	1.70	- - - - - - - - - - - - - - - - - -
Potassium	K-41 (6.91)	K-42 (n,γ)	1.17	12.47 h	3.54, 1.98	1.53, 0.32
Rubidium	Rb-85 (72.2)	Rb-86 (n,γ)	0.82	18.6 d	1.76, 0.68	1.08
Silicon	Si-30 (3.12)	Si-31 (n,γ)	0.11	2.65 h	1.476	1.26 (0.07%)
Sodium	Na-23 (100)	Na-24 (n,γ)	0.53	15.0 h	1.39, 4.17	1.368, 2.754
Strontium	Sr-86 (9.87)	Sr-87^m (n,γ)	1.3	2.8 h	- - - - - - - - - - -	I.T., 0.388
Thorium	Th-232 (100)	Pa-233 (n,γ)[d]	7.0	27.4 d	0.23, 0.53	0.076, 0.105, 0.302, 0.41
Zinc	Zn-68 (18.6)	Zn-69^m (n,γ)	0.09	13.8 h	- - - - - - - - - - -	I.T., 0.436

[a] m denotes minutes, h denotes hours, and d denotes days.
[b] Annihilation gamma following positron emission.
[c] Origin: See reference 30.
[d] Origin: Daughter of Th^{233}(23.5m) produced by (n,γ) upon Th-232.

irradiation period was selected, since this period would produce sufficient activity to permit assay of most elements present in surface and drinking waters. The characteristic nuclear properties of the elements detected in this investigation are listed in Table I.

Because of the variety of elements in waters, radionuclides yielding gamma rays of many different energies are produced upon irradiation. When these gamma rays are analyzed with a scintillation spectrometer, many of the spectral peaks will be superimposed. This condition makes identification of the radionuclides very difficult and in most instances it is impossible to make a quantitative determination. Therefore, some type of radiochemical separation scheme must be employed to separate interfering nuclides so that single gamma spectral peaks can be resolved. Ion-exchange and precipitation techniques were used in this work. A general description of each application follows.

A) Radiochemical Separations by an Ion-Exchange Method

The adsorption of many elements at various HCl concentrations upon Dowex-1 ion-exchange resin has been determined by Kraus.[18] By applying these data, certain radiochemical separations in this investigation were performed by the following procedure:

1) Depending upon the degree of separation desired, the acidity of the irradiated water sample was adjusted to a specific HCl concentration, and passed through a 3/8-inch inside diameter glass column containing 2.5 grams of Dowex-1 resin (100-200 mesh, medium porosity, 33-39% moisture content) which had been equilibrated by a solution of the same HCl concentration. The flow rate through the column was approximately 1 milliliter per minute.

2) When all of the influent solution had been passed through the column, specific elements were removed from the resin by passing solutions of lesser HCl concentrations through the column. In this manner, nuclides which have approximately the same gamma energies may be separated so that full energy peak (photopeaks) interferences are minimized.

Table II is an example of separations which were obtained by passing 6 N and 12 N HCl solutions of the irradiated water through a Dowex-1 resin column. Table II also shows the separations that can be affected by using other solutions of various reduced HCl concentrations as eluting agents. In the study reported herein, the radionuclides in the effluent obtained with either the 6 N or 12 N HCl solution were further separated by use of solutions of reduced HCl concentrations (as shown in Table II).

Due to the high Compton scattering[19] from the large quantities of induced sodium-24 (15h) present, small amounts of barium-139 (85m) or strontium-87m (2.8h) radioactivity could not be detected in the elluents obtained when elutions were made with 6 N and 12 N HCl. Therefore, barium and strontium were separated from the effluent by adding appropriate carriers and precipitating them as sulfates with H_2SO_4.

Potassium-42 (12.47h) and/or rubidium-86 (18.6d) also present in these effluents were also masked by the 1.38 Mev peak of sodium-24 (Table I). These radioelements can be separated from sodium-24 in the following manner:[20]

Table II
The Separation of Various Elements by the Ion-Exchange Technique

6 M HCl					12 M HCl					
Elements Which Pass Through Column	Elements Which Adsorb on Dowex-1	Elements Eluted from Dowex-1 in			Elements Which Pass Through Column	Elements Which Adsorb on Dowex-1	Elements Eluted from Dowex-1 in			
		4 M HCl	2 M HCl	Elements Remaining on Dowex-1			6 M HCL	4 M HCl	2 M HCl	Elements Remaining on
Na	Cu		Cu		Na	Cu			Cu	
K	Zn			Zn	K	Zn				Zn
Rb	As	As			Rb	As		As		
Sr	Br			Br	Sr	Mn	Mn			
Ba					Ba	Hf	Hf			
Mn					Br					
Hf										

1) The effluent was 0.1 N in HCl, and carriers of Na, K, and Rb were added to it.

2) The solution was then cooled in an ice bath and stirred vigorously. While stirring, 4 ml of sodium tetraphenyl-boron reagent* was added dropwise to the solution (the tetraphenyl-boron reagent should not be added to a hot solution). The mixture was digested for 10 minutes and then centrifuged. The supernatant liquid was removed and analyzed for Na-24.

3) The K-Rb tetraphenyl-boron precipitate was dissolved in 2 ml of acetone. After adding 1 ml of 1 N HCl to the solution, Step 2 above was repeated. (This reprecipitation step produced larger crystals of K-Rb tetraphenyl-boron.)

4) The final tetraphenyl-boron precipitate was then transferred to a tared filter paper by use of suction and a Hirsch funnel. It was washed with alcohol and dried in an electric oven at 110° C. After drying, the precipitate and filter paper were placed in a 10 mm x 75 mm pyrex culture tube and the gamma radioactivity from K-42 and Rb-86 assayed by means of a gamma counter.

Although some significant information was gained by use of an ion-exchange separations method and it is the supplementary technique of

* This solution is prepared by dissolving 4 grams of sodium tetraphenyl-boron and 1 gram of $AlCl_3 \cdot 6H_2O$ in 100 ml of water. Add a few drops of phenolphthalein indicator solution and then add 6 M HaOH dropwise until the solution just turns red. Allow to stand several hours. Filter, dilute to 200 milliliters; store in cool location.

further separation by precipitation methods, it was not always possible to obtain complete separation in the elution process. Better separations might have been obtained by use of a very long column of resin and a slower flow rate for the elutriants. However, this would have been very time consuming and not practical as a routine procedure.

It is believed that an ion exchange technique is most applicable when only a small number of radioactive elements are present, because as the number of species present increases, the problem of proper group separations becomes much greater.

B) Nondestructive Method

Another method used was a nondestructive method. This technique, as the one above, is good only if few elements are present and if their half-lives differ considerably. The sample is irradiated and premitted to decay for a specific time. This enables all short-lived nuclides to decay out, leaving only the longer-lived nuclides to be analyzed by the scintillation spectrometer.

C) Radiochemical Separations by a Chemical Precipitation Method

The method which was used most in this investigation was that of chemical separation by precipitation. This technique provides very clean separations and permits more accurate determinations. In addition, any loss of radioactivity during chemical processing can be evaluated by measuring the loss of added carrier. Furthermore, this method is generally more rapid than the method involving ion-exchange.

Table III is a flow sheet of the chemical separation procedure. All water samples were first aerated in a hood to remove any dissolved radioactive gases. This step prevented unnecessary inhalation of

Table III
Chemical Separation Scheme

1) Add the radioactive sample to a 50 milliliter centrifuge tube. Aerate to remove radioactive gases. Acidify with HNO_3 and add Cl, Br, I, Cu, As, Fe, Y, Co, Mn, Zn, Ba, Sr, Ca, Na, and K carriers. Precipitate Cl, Br, and I with slight excess of Ag. Heat to coagulate the precipitate. Centrifuge.

2) Precipitate: AgCl, AgBr, AgI. Wash with water, filter, mount and count. Designate as the SILVER GROUP.

3) Supernate: Adjust acidity to 0.5 N HCl. Saturate with H_2S. Centrifuge.

4) Precipitate: CuS, As_2S_3. Wash with water, filter, mount and count. Designate as the ACID SULFIDE GROUP.

5) Supernate: Transfer to beaker. Add 1 ml conc. HCl. Boil until solution is clear. Oxidize Fe^{++} to Fe^{+++} by boiling with HNO_3. Cool solution and make 1:1 with conc. HCl. Neutralize with conc. NH_4OH to precipitate hydroxides. Centrifuge.

6) Precipitate: Fe + Y hydroxides. Wash with water, filter, mount and count. Designate as the HYDROXIDE GROUP.

7) Supernate: Saturate with H_2S. Centrifuge.

8) Precipitate: CoS, MnS, ZnS. Wash with water, filter, mount and count. Designate as the BASIC SULFIDE GROUP.

9) Supernate: Acidify solution with HCl. Boil to remove H_2S. Add $(NH_4)_2H(PO_4)$ and an excess of NH_4OH. Digest. Centrifuge.

10) Precipitate: Ca, Ba, and Sr phosphates. Wash, filter, mount and count. Designate as the ALKALINE GROUP.

11) Supernate: Soluble ions. Designate as the SOLUBLE GROUP.

Table IV

Carrier Solutions		
Element	Salt	Solvent
Arsenic	As_2O_3	dilute NaOH
Barium	$BaCl_2 \cdot 2H_2O$	H_2O
Bromine	KBr	H_2O
Calcium	$Ca(NO_3)_2 \cdot 4H_2O$	0.03 N HNO_3
Chlorine	NH_4Cl	H_2O
Cobalt	$Co(NO_3)_2 \cdot 6H_2O$	0.15 N HNO_3
Copper	$Cu(NO_3) \cdot H_2O$	0.03 N HNO_3
Iodine	KI	H_2O
Iron	$Fe(NO_3)_3 \cdot 9H_2O$	0.3 N HNO_3
Magnesium	$Mg(NO_3)_2 \cdot 6H_2O$	0.03 N HNO_3
Phosphorus	$(NH_4)_2PO_4$	H_2O
Potassium	KNO_3	H_2O
Rubidium	$RbNO_3$	0.3 N HNO_3
Silicon	Na_2SiO_3	H_2O
Sodium	$NaNO_3$	H_2O
Strontium	$Sr(NO_3)_2$	H_2O
Zinc	$Zn(NO_3)_2 \cdot 6H_2O$	H_2O

radioactive gases by personnel processing the samples and also prevented colloidal carry down of radioactive gases during subsequent radiochemical procedures. After aeration, each sample was acidified with nitric acid and a known quantity of approximately three milligrams of each stable elemental carrier was added. Table IV lists all of the carriers used in this investigation. The resulting solution was then processed to yield six different chemical groups. The chemical compounds produced from the elements normally present in each group are shown in Table III.

Further separation of each of the given chemical groups may be employed if identification or measurement is questionable. This is especially true for the soluble group. As stated above, the 1.38 Mev spectral peak of sodium-24 interfered with the spectral peaks of potassium-42 (1.51 Mev) and rubidium-86 (1.08 Mev). Separation of these elements may be accomplished with sodium tetraphenyl-boron as outlined above. However, the method used most frequently in this investigation was as follows:[21]

1) Add standard Na, K, and Rb carriers to the aliquot of sample used.

2) Add 2 ml of 70% perchloric acid and evaporate to dryness on a hot plate. Cool and redissolve in 2 or 3 ml of water and again evaporate to dryness. The salts are now in the perchlorate form.

3) Add 20 ml of a mixture of equal parts by volume of n-butyl alcohol and ethyl acetate (both anhydrous), digest near the boiling point for 2 to 3 minutes and cool. The sodium is in solution.

4) Repeat the separation by adding more sodium carrier and perchloric acid.

5) Collect the potassium and rubidium perchlorates on filter paper and count.

The most rapid method of separating sodium from potassium and rubidium is by precipitating the sodium with zinc uranyl acetate.[22] The only difficulty is that the uranium contributes activity to the sample. For obvious reasons, this is generally a bad practice. However, since the gamma activity of the uranium decay products is very low, they will not interfere with the gamma spectra of the other nuclides present.

In the Acid Sulfide Group both copper-64 and arsenic-76 are precipitated. Even though both radionuclides have energies of approximately 0.5 Mev (Table I), they do not have to be separated since their half-lives differ significantly, being 12.8 hours and 26.7 hours respectively. A simple decay measurement involving periodic counting indicates which radionuclide is present, or permits an estimate of relative amounts if both are present.

C. Specific Radiochemical Separation by Precipitation Methods

The techniques used above were not adequate for the determination of a few of the elements of interest in this study. Because of adverse nuclear, chemical, and physical properties, specific quantitative analyses had to be performed. These analyses included:

1. Magnesium: (determined as 9.5 min. Mg-27)

A 30 milliliter sample was irradiated for 10 minutes. Manganese-56 (2.58h) activity, produced by (n,γ) reactions with stable Mn-55, interfered with the use of the 0.84 Mev full energy

peak of magnesium-27 in the analysis. Therefore, the manganese was first removed by a specific decontamination step. The procedure employed was as follows:

a) Add standard magnesium carrier and manganese holdback carrier.

b) Make the solution about 1 M with H_2SO_4, add approximately one gram of $KBrO_3$ and boil for two or three minutes. (Insoluble MnO_2 precipitates under these conditions.)[23]

c) Centrifuge and decant.

d) Make supernate basic with NH_4OH and add NH_4Cl as a common ion to prevent the precipitation of $Mg(OH)_2$.

e) Add 1 ml of $(NH_4)_2HPO_4$ (~10 mg/ml), and let the solution stand for a few minutes.[24]

f) Centrifuge, filter and count.

The MnO_2 precipitate obtained in the decontamination step was analyzed by scintillation spectrometry and decay measurements. No magnesium-27 was detected, indicating that there was no loss of magnesium in the decontamination step.

The carrier and radiomanganese may also be separated from the magnesium by precipitation as a sulfide in a basic solution.[25] The magnesium will remain in solution.

2. Iodine: (determined as 25 min. I-128)

A 30 milliliter sample was irradiated for 30 minutes. The active solution was then added to a 125 ml separatory funnel along with iodine carrier, 10 ml of 2 M Na_2CO_3, 2 ml of 5% $NaClO_3$, 5 ml of conc. HNO_3, and 1 ml of 5 M hydroxylamine hydrochloride. The

iodine was then extracted into 15 ml of CCl_4[26] by manually agitating the flask. The phases were allowed to separate and the aqueous layer discarded.

To the CCl_4 phase, add 10 ml of water and $NaHSO_3$ dropwise until the solution clears. Extract and discard the CCl_4 layer.

Add 1 ml of 6 M HNO_3, heat to boiling and add 4 ml of 1 M $AgNO_3$ dropwise with stirring. Digest the AgI for a few minutes with gentle boiling and brisk stirring. Filter, and wash the precipitate with water, alcohol, and ether. The activity of the precipitate was then analyzed.

3. Dissolved Gases: (Argon-41)

A 30 ml water sample was irradiated for 16 hours and transferred to a round bottom flask. A 250 ml evacuated gas flask was fitted to the round bottom flask and the solution heated to approximately 50°C. for about 15 minutes. This will force the dissolved gases present in the water into the evacuated flask. The gamma activity present in the flask was then analyzed by scintillation spectrometry.[27]

4. Silicon: (determined as 2.65 hr silicon-31)

Silicon was not detected in the above determinations since all activities had been analyzed by scintillation spectrometry and the gamma-rays associated with silicon-31 are very weak (Table I). Therefore, a specific determination was performed by the procedure briefly described below. The radioactivity was analyzed by beta counting.

A 30 ml water sample was irradiated for 16 hours. Upon discharge from the reactor, 10 ml of 2 M $Al(NO_3)_3$ are added to the sample to complex any fluorine that may be present. Holdback solutions of Na, Ba, Sr. Ca, and Mn are added in addition to 20 mg of SiO_2 carrier. Fifteen milliliters of concentrated H_2SO_4 were added and the solution was boiled until the volume reached approximately 10 ml at which point the SiO_2 precipitates. The precipitate was washed with 35 ml of hot water and 5 ml of 86% H_3PO_4. The SiO_2 is then dissolved in 2 ml of 19 M NaOH by heating and vigorous stirring. The sample was then centrifuged, in case all precipitate did not dissolve, and the carrier and radiosilicon precipitated as silicic acid* with 15 ml. of saturated NH_4Cl.[28] The precipitate was then filtered on to an ashless filter paper and burned for 30 minutes at 1000°C. The residue is weighed and the activity counted.

Barium and strontium, if present, will precipitate as H_2SO_4 is added. When this occurs, the sample should be centrifuged and the precipitate removed before heating.

Certain elements upon irradiation yield nuclides with long half lives. These will not be detected by a 16 hour irradiation due to the small saturation factor. The elements phosphorus and calcium are of this group, since they are important in water analysis. These elements were determined by a special procedure.

---

* This is thought to be the compound which is formed, although it is questionable.

The number of samples which can be placed in Hole 10 of the ORNL Graphite Reactor was limited. The only other irradiation facility available was Hole 14 (~4.3 x 10^{11} n/cm/sec). However, here temperatures greater than 100°C. are reached. As a result, liquid samples could not be irradiated. Therefore, 100 ml of each water sample and a standard sample were evaporated to dryness and irradiated for two weeks. Upon removal, the samples were allowed to "cool" for two days to permit shorter lived nuclides to decay.

Table V is a flow sheet of the chemical separation scheme employed after the two week irradiation. Since the samples were in the reactor as a solid, aeration, in this case, was not necessary. The residue was dissolved in HNO_3, and 10 milligrams of carrier added. The chemical compounds produced from the elements present in each separated group are shown in Table V.

Table V

Chemical Separation Scheme for Long-Lived Radionuclides

1) Dissolve residue in 2 ml of conc. HNO_3. Heat if necessary.

2) Add Co, Ca, Cu, Fe, P, and Na carriers. Add 50 ml of Molybdic acid (Solution must be acid in HNO_3) and boil until solution is fully precipitated. Centrifuge.

3) Precipitate: (a) Wash $H_3PMo_{12}O_{40}$ ppt in dilute HNO_3. (b) Dissolve ppt in NH_4OH, make acid with HCl and add ~1 gm of citric acid. (c) Cool in ice bath and add 20 ml of magnesia mixture. (d) Add NH_4OH in excess, allow to cool, and filter through paper. (e) Mount and β^- count.

4) Supernate: Neutralize solution with NH_4OH and adjust to 0.3 M HCl. Saturate with H_2S and centrifuge.

5) Precipitate: (a) Wash CuS and As_2S_3 with hot H_2O. (b) Filter through paper, mount and γ count.

6) Supernate: Boil solution and add HNO_3 and Br_2H_2O until solution becomes clear. Add NH_4OH. Centrifuge.

7) Precipitate: (a) Dissolve $Fe(OH)_3$ and reprecipitate with NH_4OH. (b) Filter through paper, mount and γ count.

8) Supernate: Saturate with H_2S. Centrifuge

9) Precipitate: (a) Dissolve CoS in 6 M HNO_3 with heating. (b) Add $Br_2 \cdot H_2O$ to clear up the solution. (c) Reprecipitate the Co with 1 M KoH. (d) Filter, mount, and γ count.

10) Supernate: Add HCl and Br_2H_2O and heat to boiling until solution becomes clear. Add 10 ml of sat. $(NH_4)_2C_2O_4$, heat, and make basic with NH_4OH. Centrifuge.

11) Precipitate: (a) Wash CaC_2O_4 ppt in hot H_2O. (b) Filter, mount, and β^- count.

12) Supernate: Transfer aliquot to culture tube for γ counting.

6. RADIOACTIVITY ASSAY TECHNIQUES EMPLOYED

After each chemical separation, the sample was assayed by gross beta or gamma studies, beta absorption determinations and/or gamma spectral analysis. An interpretation of these data, together with knowledge of the chemistry of the particular separation, was used to identify the radionuclides in the sample.

Gross gamma studies were made utilizing a well-type scintillation detector coupled to a Model No. 101B research scaler manufactured by the Atomics Instrument Company, Cambridge, Massachusetts. A linear amplifier was included as an integral part of the scaler. The high voltage was obtained from a power supply also manufactured by the Atomics Instrument Company, Model No. 312. The detector was a NaI(Tl) crystal 2 inches in length and 2 inches in diameter with a central well 1.5 inches deep by 0.86 inches in diameter. The well contained an aluminum liner which acted as an absorber for the beta radiation emitted by the sample being analyzed. Also, a 3-inch lead shield surrounded the crystal detector to minimize background activity.

Gross beta decay and absorption studies were made by using a thin mica window Geiger-Mueller detector, type TGC-2, manufactured by Tracerlab, Inc., of Boston, Massachusetts. The detector was coupled to a Model No. Q-762 scaler, with scale of 64, manufactured by the Nuclear Instrument and Chemical Corporation of Chicago, Illinois. The high voltage supply was contained in the same chassis. A two inch cylindrical lead shield surrounded the detector and sample to minimize background activity. The beta absorption studies were made utilizing calibrated aluminum absorbers.

The gamma spectral analyses were performed with a multichannel gamma scintillation spectrometer[29] of the 20 channel type. The instrument, Model 520, Twenty-Channel Pulse Height Analyzer, was manufactured by the Atomics Instrument Company. The detector was either a solid, 3 x 3 inch, "thallium activated" sodium iodide crystal or a well-type crystal as described above. The pulses were differentiated and fed into twenty separate scalers, each having a scaling factor of 16. Controls were available for adjusting the channel widths and selecting the portion of the total spectrum to be recorded. Five settings of 20 channels each were necessary to cover the energy range 0.08 to 2.0 Mev. This range was most commonly used in this investigation. (See Appendix A for a discussion of Gamma Scintillation Spectrometry.)

Radioactive nuclides of known gamma energies were used for daily calibration of all instruments. For the gamma scintillation spectrometer, 30 year Cs-137 + Ba-137 (0.662 Mev) and the positron emitter 2.6 year Na-22 (1.28 Mev) were used. To measure counting reproducibility, the 30 year Cs-137 + Ba-137 was counted in the gross gamma counter and a UX_2 source in the beta counter each morning.

Samples for beta studies were placed on watch glasses fastened to cardboard mounts and covered with celophane. Samples for gamma studies were mounted in 10 x 75 millimeter pyrex culture tubes. These culture tubes were of the size which would fit into the well-type scintillation crystal.

7. RESULTS OBTAINED BY NEUTRON ACTIVATION ANALYSIS

A. Short-lived Radionuclides

Typical gamma spectra and decay data obtained in the group chemical separations on Chicago drinking water utilizing the 20-channel scintillation spectrometer are as follows.

The gamma spectral and decay data for the Silver Group, Figure 1, show gamma peak energies of 0.55, 0.77, 1.03, and 1.31 Mev which are characteristic of 35.9 hour bromine-82. This was confirmed by the decay study. Also, spectral peak energies of 1.60 and 2.16 Mev, appearing in Figure 2, which decay with a half life of about 36 minutes confirm the presence of 37.5 min. chlorine-38.

Figure 2, the spectral and decay data for the Acid Sulfide Group, shows a gamma spectral peak at 1.35 Mev, and an annihilation photon peak at 0.51 Mev which indicates the presence of copper-64. The 1.02 Mev spectral peak is a result of coincidence summing which occurs when both annihilation photons are counted simultaneously. This peak was not detected when a solid crystal was used. The decay study of the Acid Sulfide Group indicated a half life of about 13 hours, confirming the identity of 12.82 hr. Cu-64, and eliminating the possibility that 26.6 hr. arsenic-76 was also present.

Gamma spectral and decay studies of the Ammonium Hydroxide Group, Figure 3, indicates the possible presence of the positron emitter, 1.87 hr. fluorine-18. Fluorine-18 has been shown to originate from a (p,n) reaction on oxygen-18. These protons are "knock-on" protons produced from the water by fast fission neutrons and not by

UNCLASSIFIED
ORNL-LR-DWG. 28225B

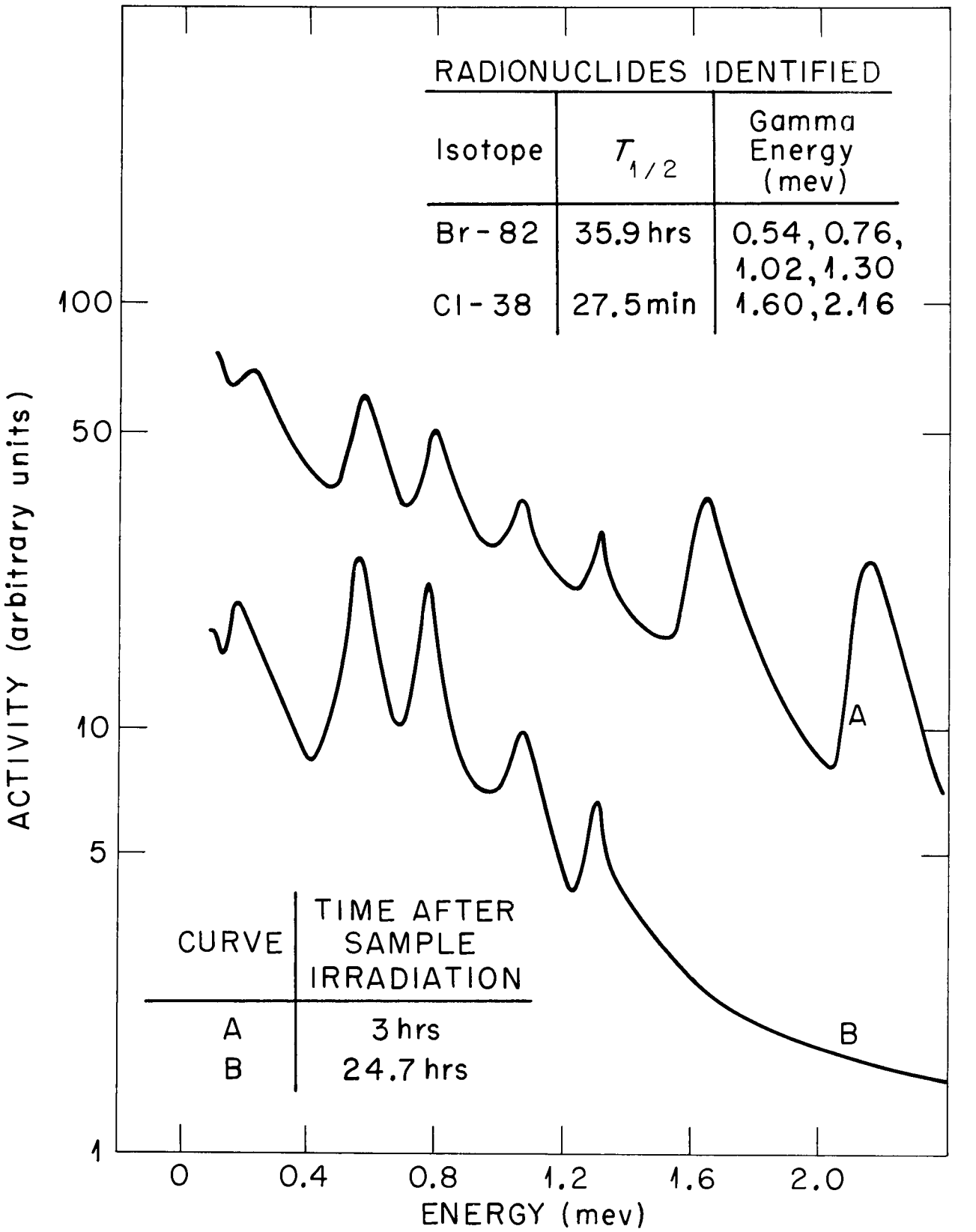

Figure 1

QUALITATIVE ANALYSIS, CHICAGO DRINKING WATER: SILVER CHLORIDE (AgCl) GROUP PRECIPITATION

UNCLASSIFIED
ORNL-LR-DWG.28226B

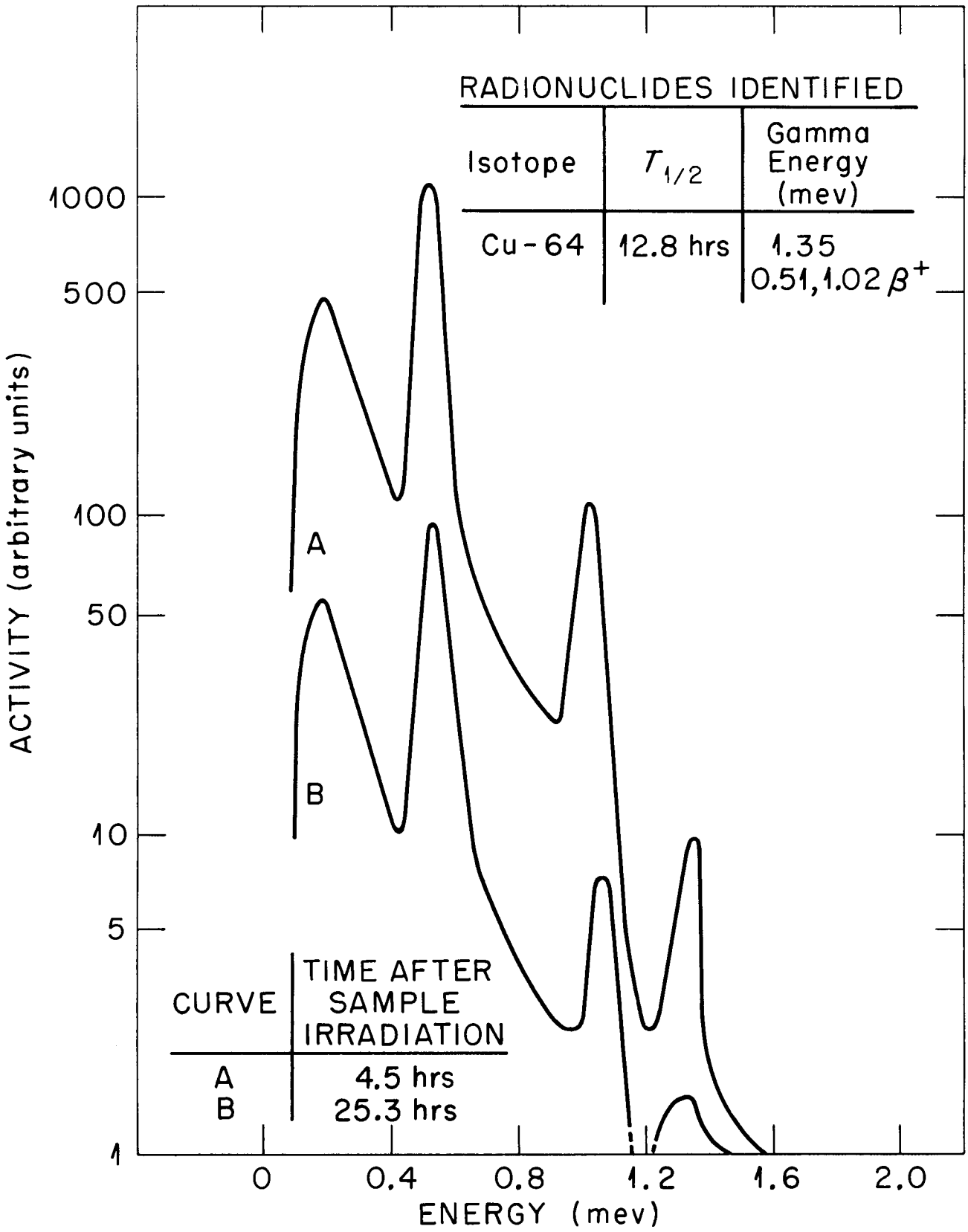

Figure 2

QUALITATIVE ANALYSIS, CHICAGO DRINKING WATER: HYDROGEN SULFIDE GROUP PRECIPITATION

UNCLASSIFIED
ORNL-LR-DWG. 28227B

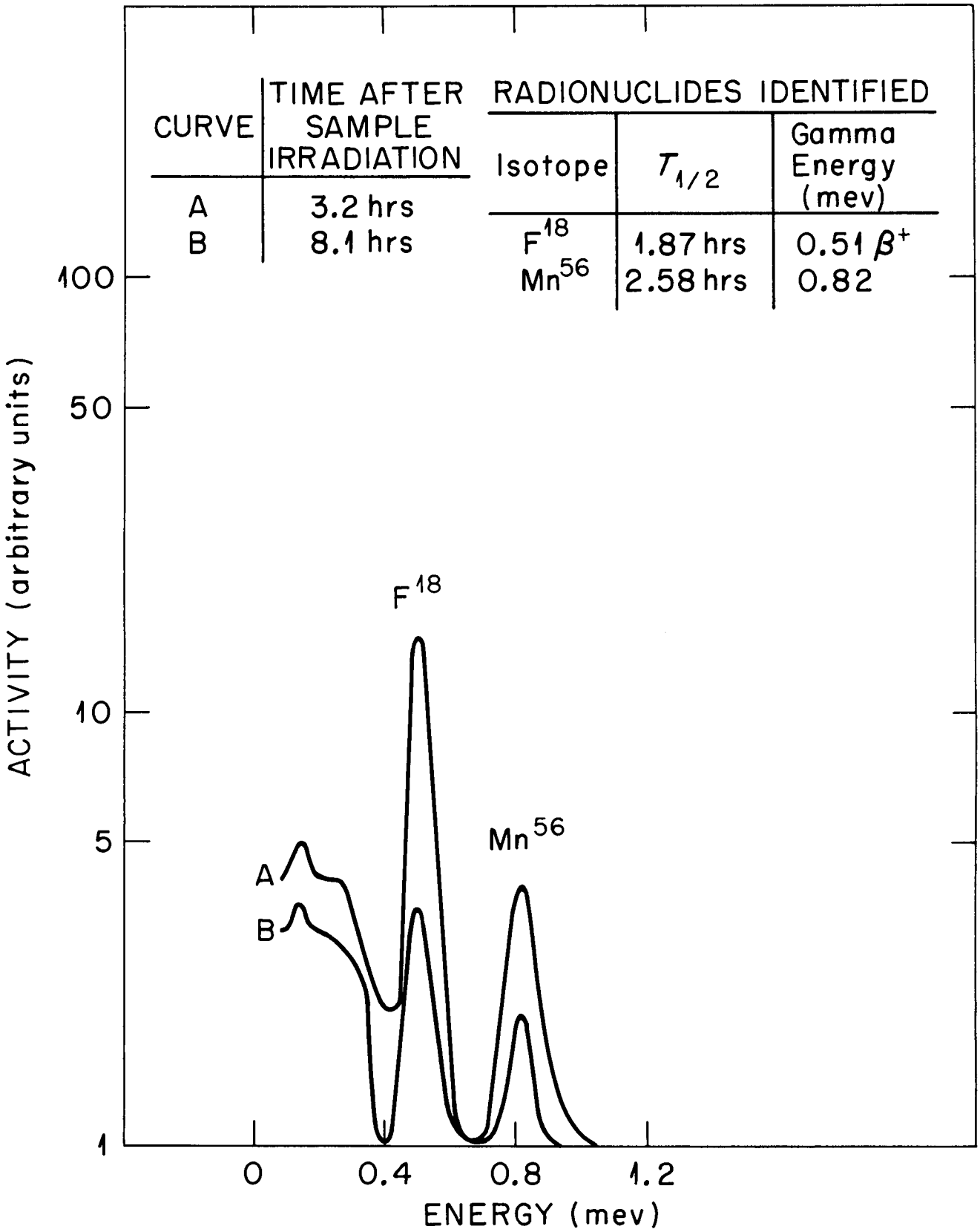

Figure 3
QUALITATIVE ANALYSIS, CHICAGO DRINKING WATER:
AMMONIUM HYDROXIDE GROUP PRECIPITATION

a $F^{19}(p,2n)F^{18}$ as might be expected.[29] The cross-section for the $O^{18}(p,n)F^{18}$ reaction for protons of 4 Mev energy has been reported to be 0.2 barn, and the threshold for the reaction being 2.56 Mev with a resonance maximum at 3.55 Mev.[30]

To gain additional confirmation of the presence of F-18, a 30 ml sample of distilled water was irradiated for 16 hours. Fluorine carrier was added in the form of HF and the solution distilled in the presence of H_2SO_4. The carrier and accompanying radiofluorine were then precipitated from the distillate as lanthanum fluoride. The precipitate was analyzed by means of the 20-channel scintillation spectrometer and the spectral data obtained are shown in Figure 4. The 0.51 and 1.02 Mev annihilation photon peaks decaying with a half life of 1.9 hours confirms the presence of the positron emitter, 1.87 hr F-18.* Fluorine precipitates with the Ammonium Hydroxide Group, because it forms a strong complex with iron.[31] Probably, at such small fluorine concentrations, there is an equilibrium between the complexes FeF^{++}, FeF_2^{+}, FeF_3, FeF_4^{-}, FeF_5^{-2}, and FeF_6^{-3}. Therefore, the fluorine is carried down with the iron by hydroxide precipitation.

---

* The production of fluorine-18 from oxygen-18 was useful in that it demonstrated the precision of the activation analysis technique. The average concentration of F-18 produced in the seven samples was 0.0563 ± 0.0012 microcuries per liter. Since it is generally concluded that the isotopic composition of water is relatively constant over wide geographical areas,[36] the precision obtained in the analysis of the seven samples was within ± 4%.

UNCLASSIFIED
ORNL-LR-DWG. 30303 A

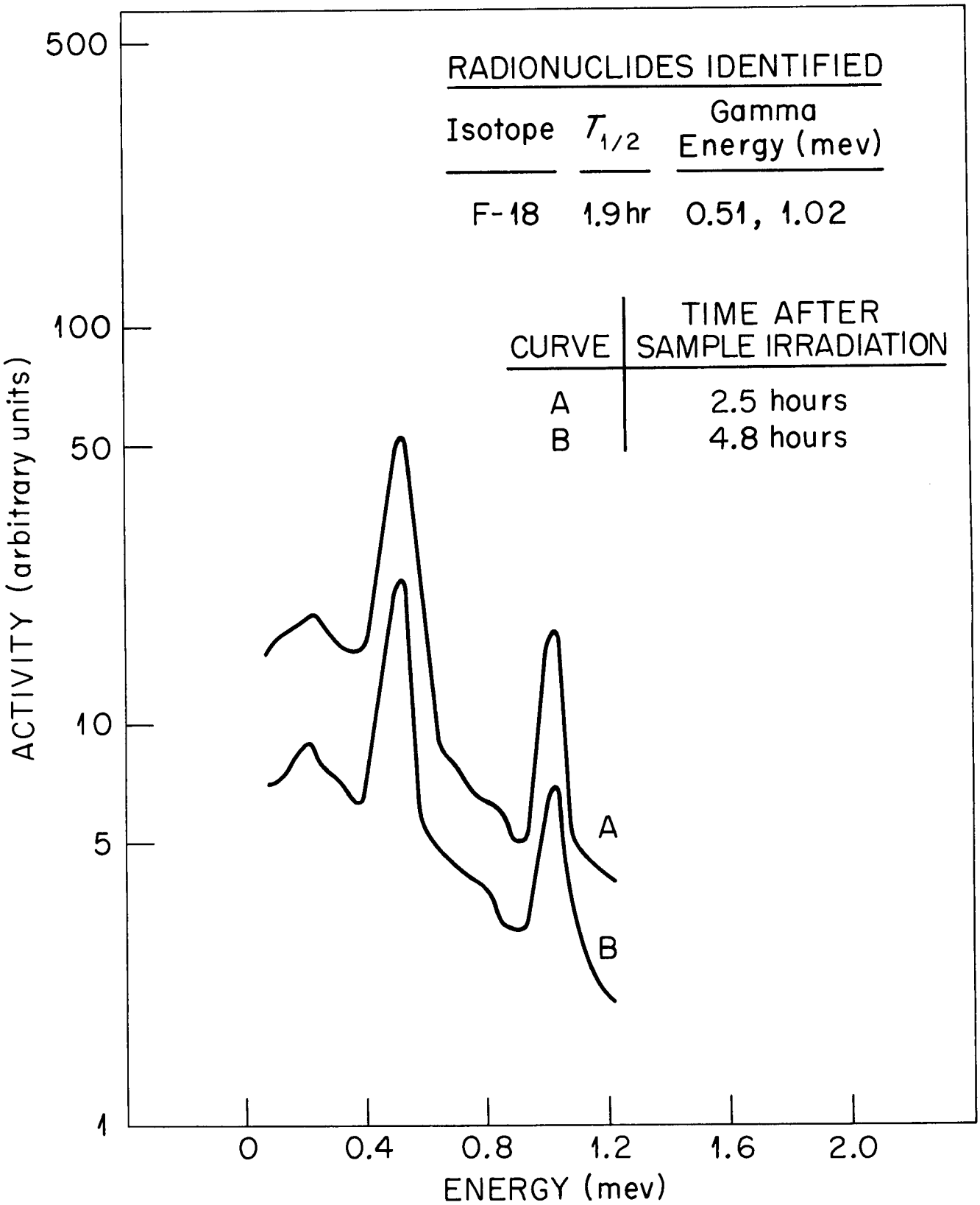

Figure 4

THE IDENTIFICATION OF FLOURINE-18 IN DISTILLED WATER IRRADIATED FOR A 16-HOUR PERIOD

With an irradiation period of 16 hours, the long half life of 45 days and the low activation cross-section limit the production of iron-59 in insufficient quantity for detection.

The 0.84 Mev spectral peak in Figure 3 indicated the presence of 2.58 manganese-56, which coprecipitated with the iron hydroxide.

All chemical groups of the seven water samples analyzed gave approximately the same gamma spectra except the Ammonium Hydroxide Group of the Oak Ridge sample. The spectral data, shown in Figure 5, are different from the hydroxide group spectra of the other samples in that they show gamma peaks at 0.11, 0.31, and 0.40 Mev. These decay with a half-life of approximately 26 days (see Figure 6). This has been identified as Pa-233.[32] This radionuclide is produced by a (n,γ) reaction on Th-232, forming Th-233 which has a half life of 23.3 minutes and decays into Pa-233 by beta and gamma emission.

The gamma spectral and decay studies of the Basic Sulfide Group, are shown in Figure 7. The 0.44 Mev peak is characteristic of 13.8 hour zinc-69^m, and the 0.84 Mev peak is characteristic of 2.58 hr manganese-56.

The gamma spectral data of the Ammonium Phosphate Group are shown in Figure 8. The 0.16 Mev spectral peak is characteristic of 85.0 min. Ba-139, and the 0.39 Mev peak is characteristic of the 2.8 hr Sr-87^m.

Due to the short irradiation time with respect to the long half life of calcium-45 and the small isotopic abundance of calcium-44, the quantity of radioactivity from calcium-45 produced would be insufficient for detection.

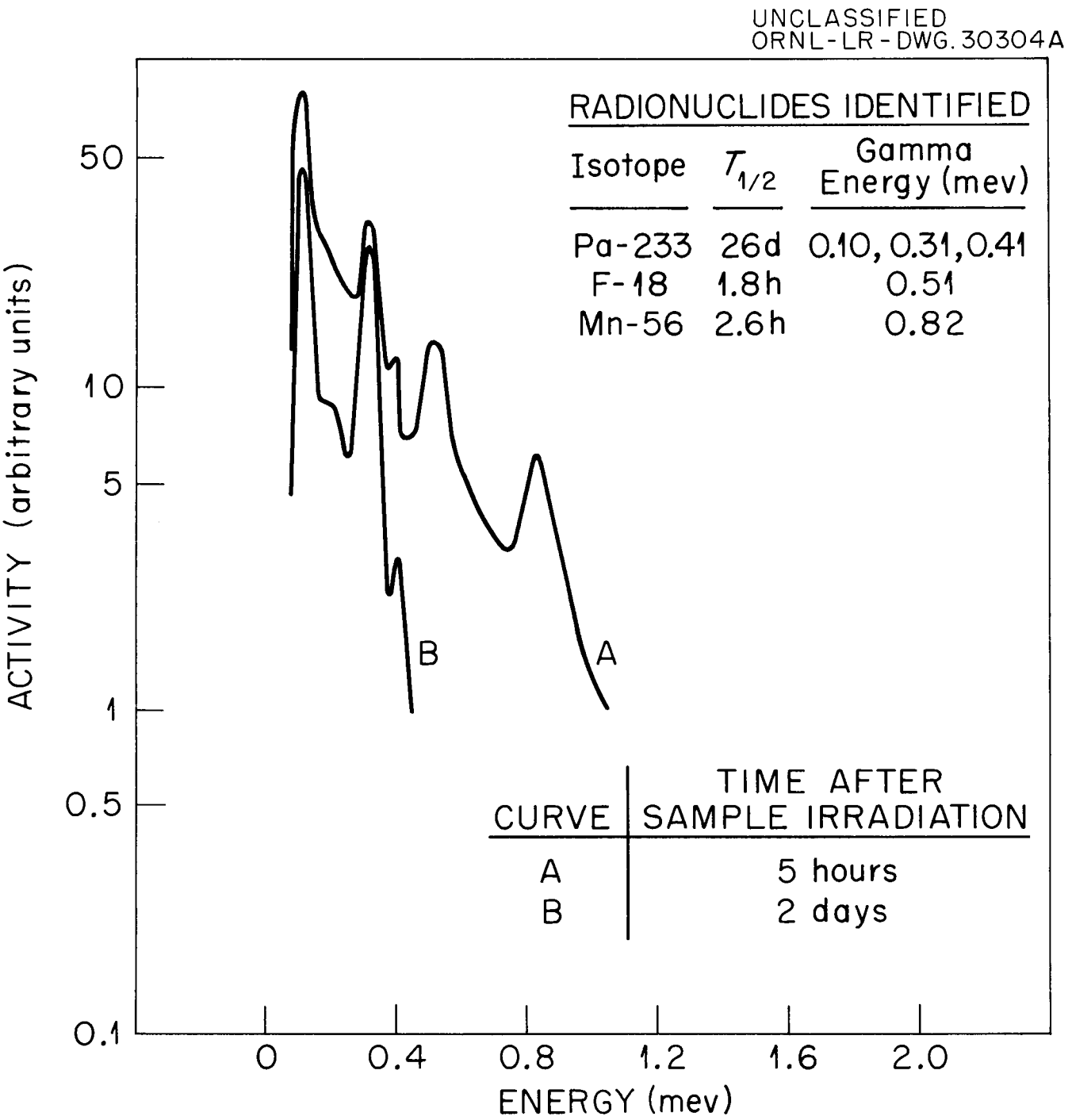

Figure 5
QUALITATIVE ANALYSIS,
16-HOUR IRRADIATED OAK RIDGE WATER:
SODIUM HYDROXIDE GROUP PRECIPITATION

UNCLASSIFIED
ORNL-LR-DWG. 30305A

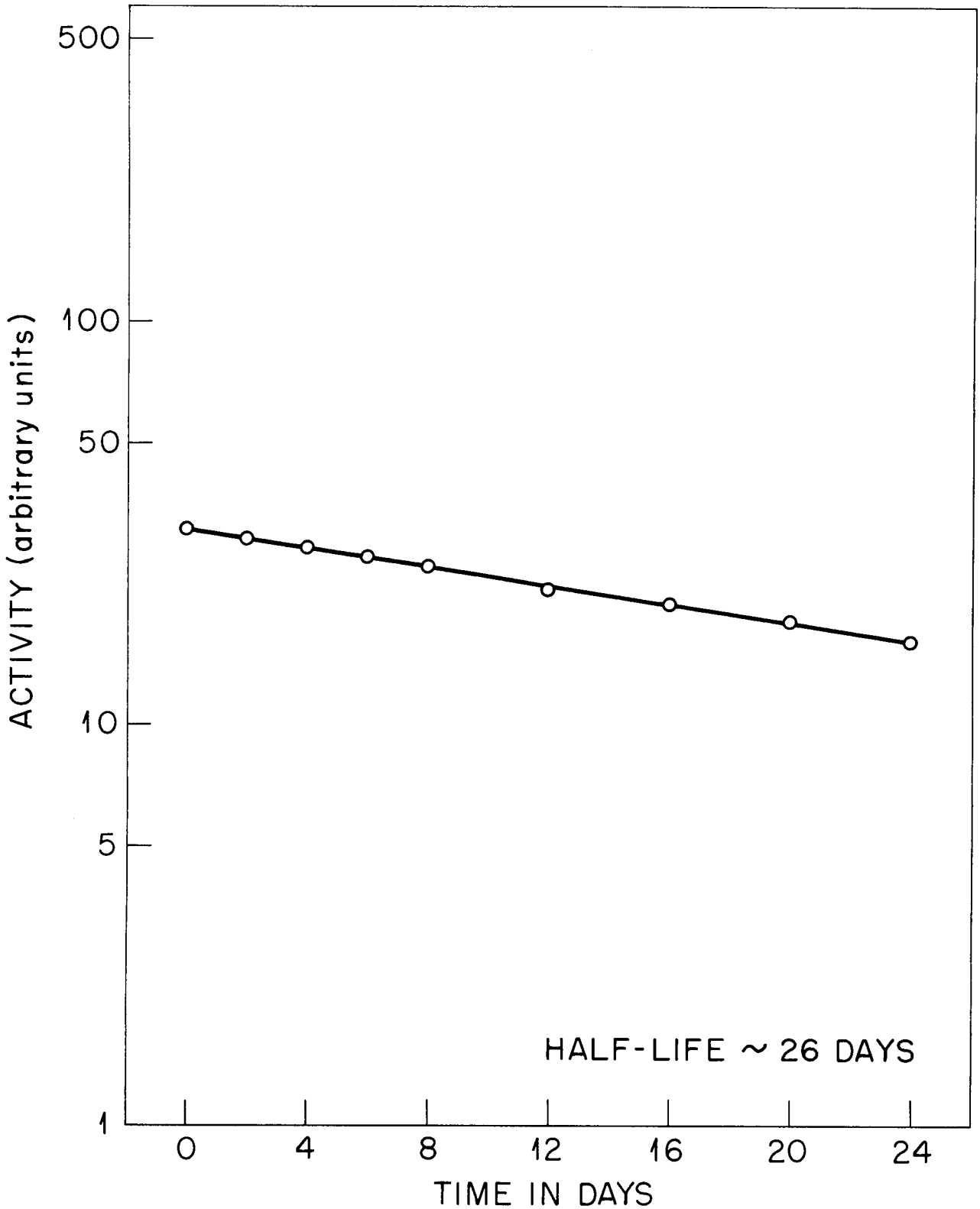

Figure 6
GAMMA DECAY STUDIES, 16-HOUR IRRADIATED OAK RIDGE WATER: AMMONIUM HYDROXIDE GROUP PRECIPITATION (Decay Study Begun after the Short-lived Nuclides Had Decayed Out)

UNCLASSIFIED
ORNL-LR-DWG. 28228B

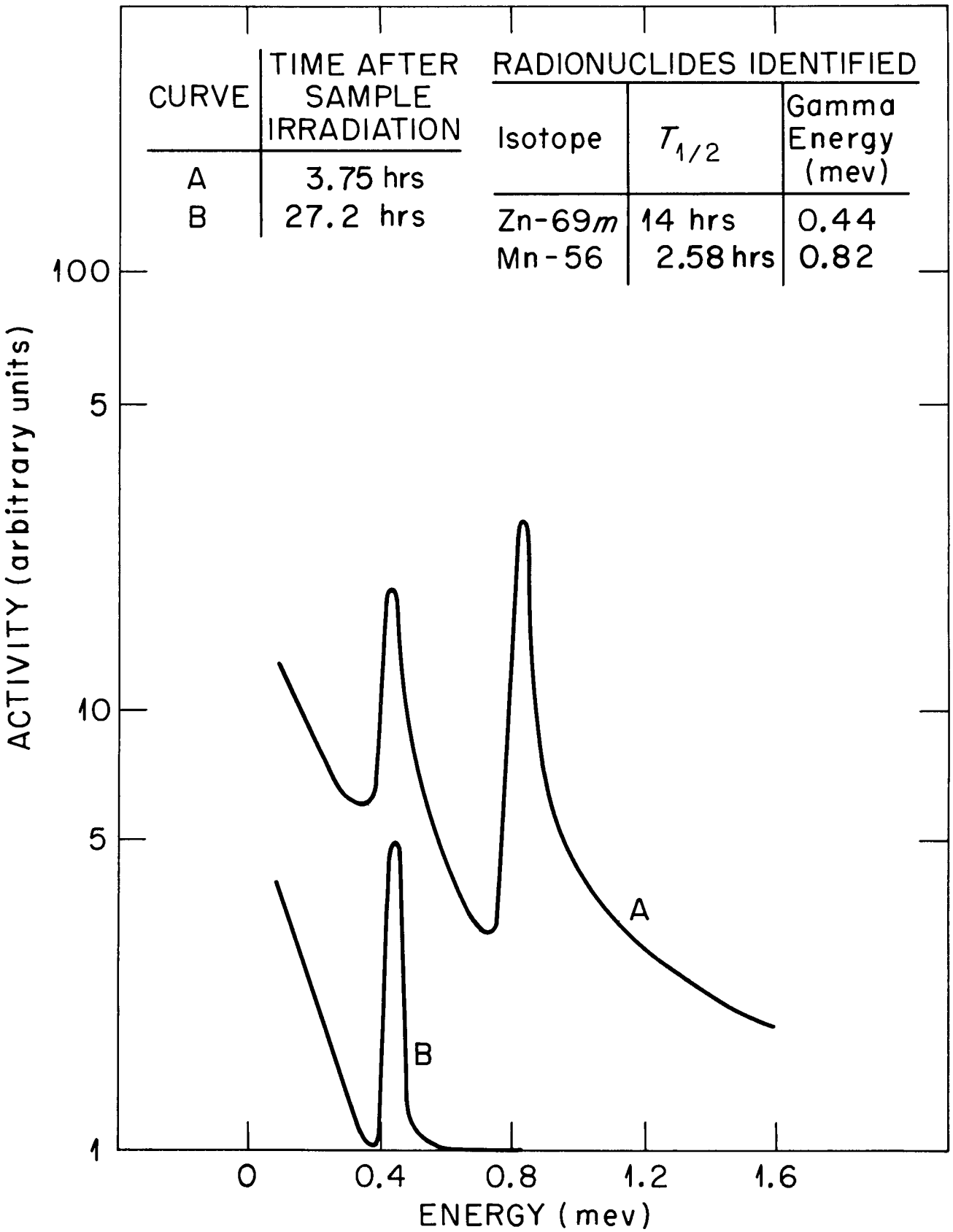

Figure 7
QUALITATIVE ANALYSIS, CHICAGO DRINKING WATER:
AMMONIUM SULFIDE GROUP PRECIPITATION

UNCLASSIFIED
ORNL-LR-DWG.28229B

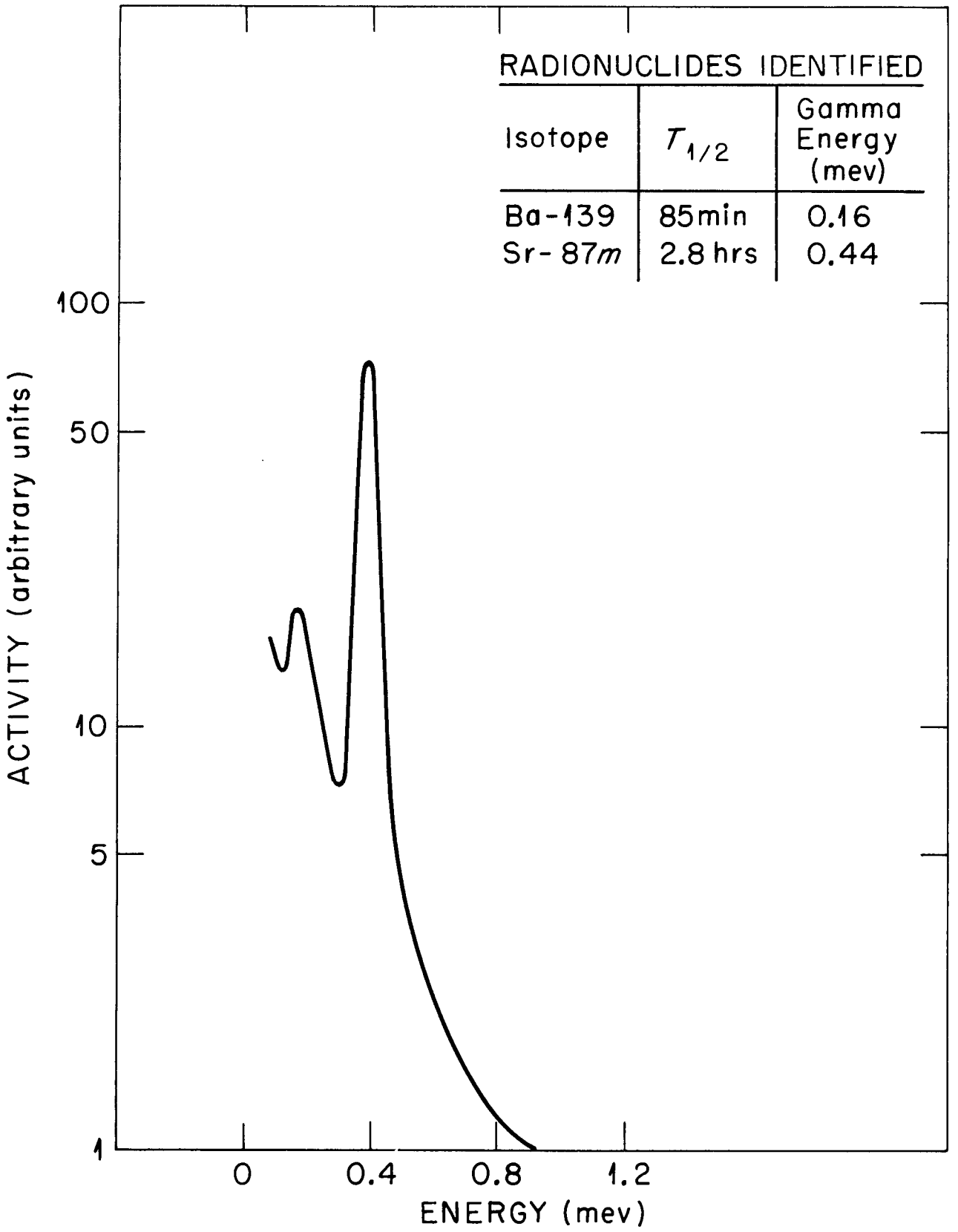

Figure 8
QUALITATIVE ANALYSIS, CHICAGO DRINKING WATER :
AMMONIUM PHOSPHATE GROUP PRECIPITATION

Gamma spectral and decay studies of the Soluble Group are shown in Figure 9. The photopeaks at 1.37 and 2.75 Mev (Curve A and B) indicate the presence of 15 hr sodium-24. The two peaks at 1.73 and 2.24 Mev are escape peaks due to pair production from the 2.75 Mev gamma-ray. The decay data confirmed the presence of sodium-24.

Without additional chemical separation, only Na-24 is detected in the Soluble Group. But, by separating the sodium from this group by one of the methods given earlier, other spectral peaks are resolved. Gamma spectral data of the separated portion of the Soluble Group are shown as the dotted curve in the lower portion of Figure 9. The spectral peak at 1.08 Mev is characteristic of 18.6 day rubidium-86 and the spectral peak at 1.50 Mev indicate the presence of 12.47 hr potassium-42. Decay studies confirm these conclusions.

After a specific separation for magnesium and iodine, the radioactivity was analyzed by scintillation spectrometry and the spectra obtained are shown in Figures 10 and 11 respectively. In Figure 10 the 0.84 and 1.02 Mev spectral peaks which decay with a half life of 9.5 min confirm the presence of 9.45 min magnesium-27. If the manganese-56 were not completely removed, the 0.84 Mev peak would decay with a slightly longer half life than that indicated. In Figure 11 the 0.44 Mev spectral peak which decays with a half life of 25 minutes confirms the presence of 25 min iodine-128. The shoulder on the receeding side of the 0.44 Mev peak is probably due to the weak 0.54 Mev gamma-ray of I-128 which was inadequately resolved by the instrument.

Figure 12 is the gamma spectral and decay data obtained from the dissolved gas separation. The spectral peak at 1.30 Mev which

UNCLASSIFIED
ORNL-LR-DWG. 28230B

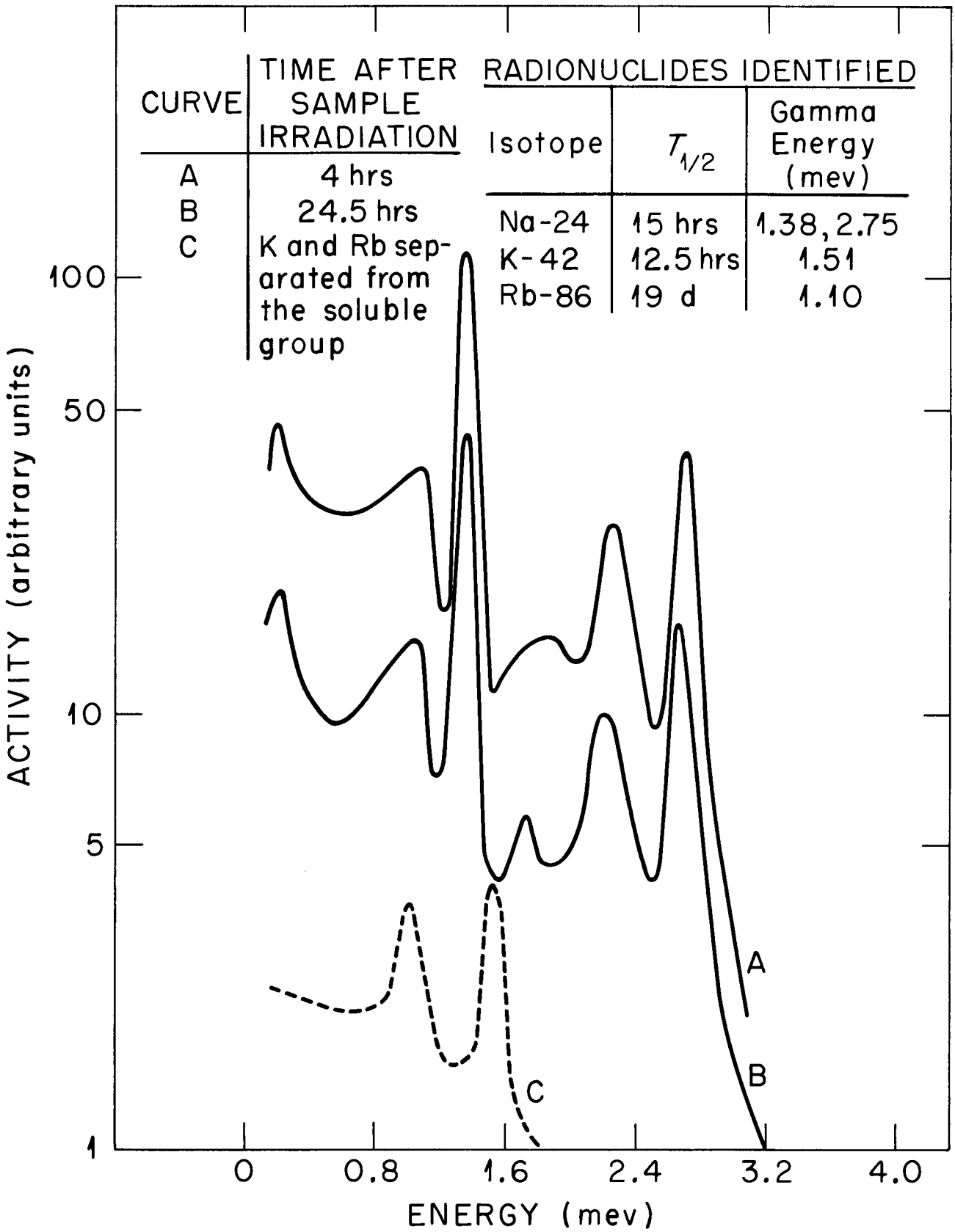

Figure 9
QUALITATIVE ANALYSIS, CHICAGO DRINKING WATER: SODIUM (SOLUBLE) GROUP PRECIPITATION

UNCLASSIFIED
ORNL-LR-DWG. 28232B

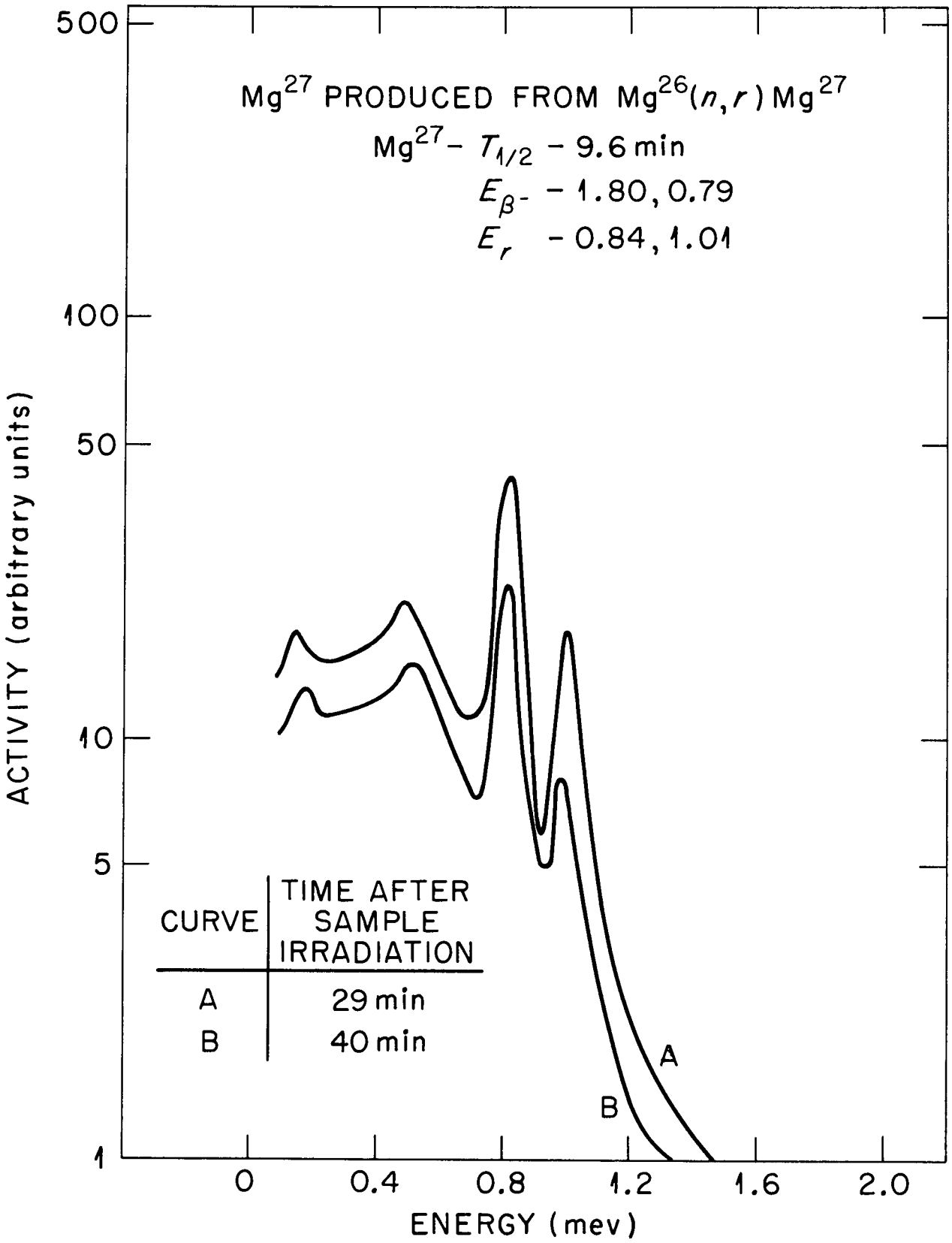

Figure 10
THE MAGNESIUM - 27 GAMMA SPECTRA
FROM CHICAGO DRINKING WATER

UNCLASSIFIED
ORNL-LR-DWG. 28233B

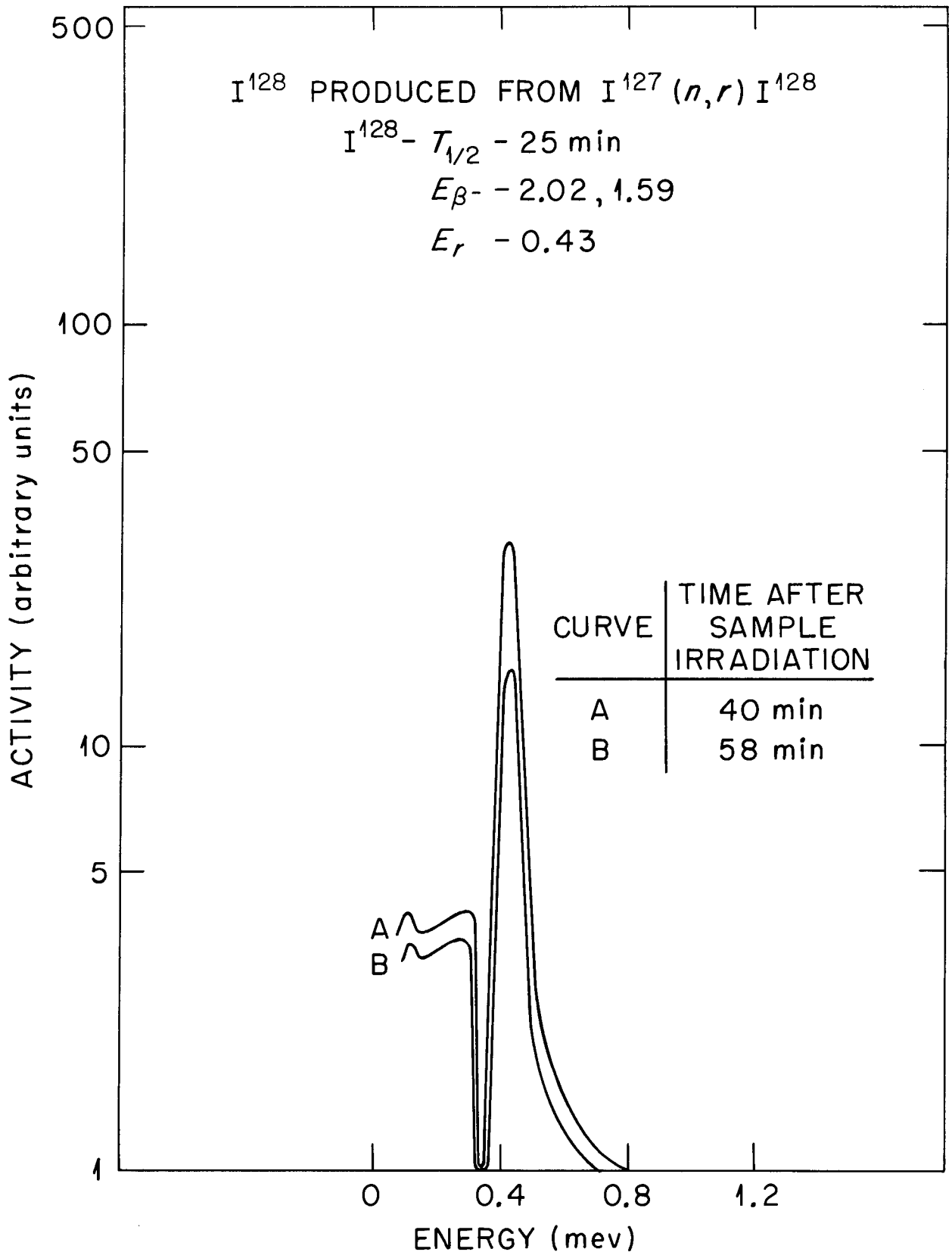

Figure 11

THE IODINE-128 GAMMA SPECTRA FROM CHICAGO DRINKING WATER

UNCLASSIFIED
ORNL-LR-DWG. 28231B

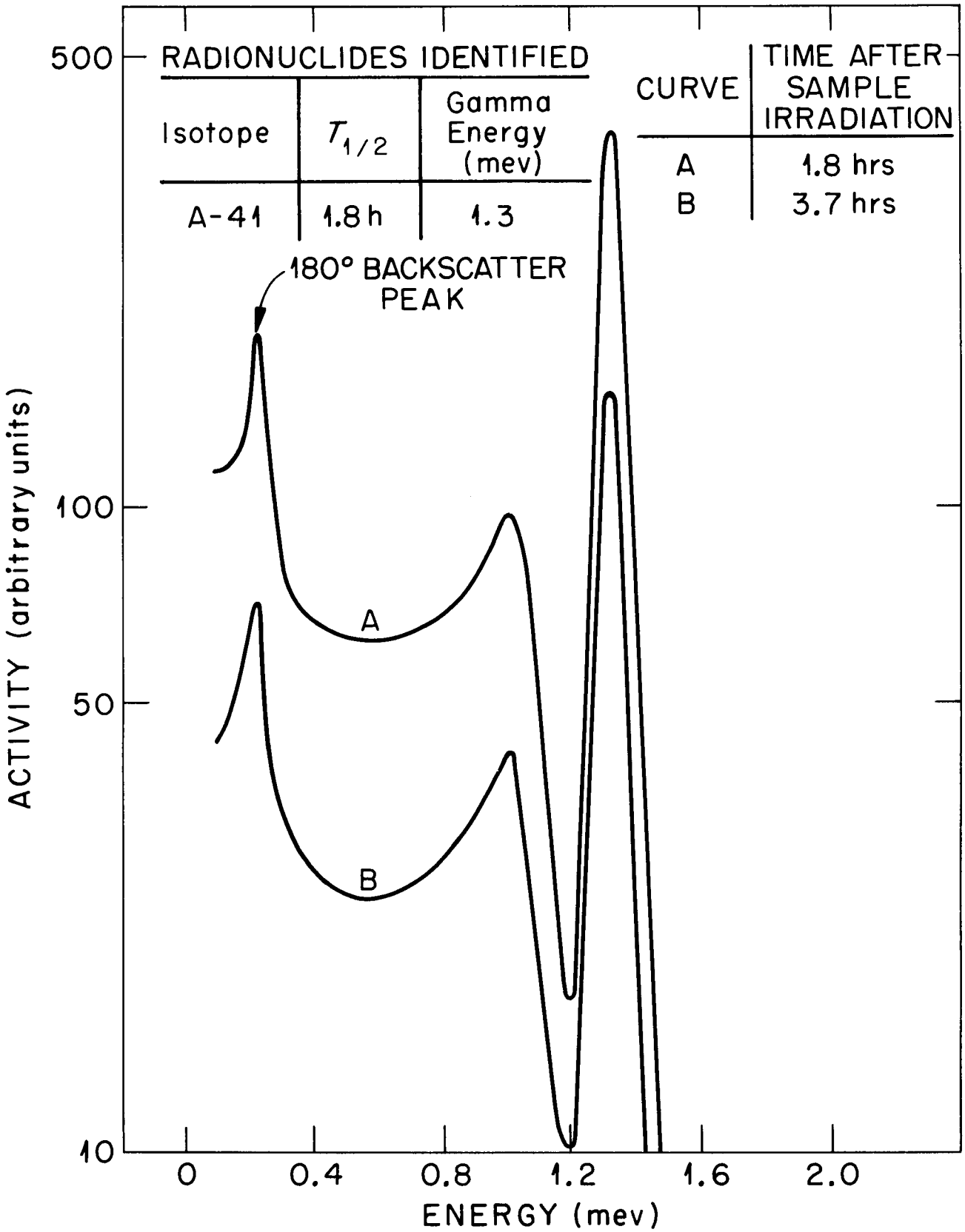

Figure 12
CHICAGO DRINKING WATER: THE DETERMINATION OF ARGON

decays with a half life of 1.8 hours is characteristic of 1.83 hr argon-41. The two peaks which appear at 0.22 Mev and 1.00 Mev are attributed to 180° backscatter and accented Compton shoulder. This was confirmed both by applying Equations (5) and (6) and noting that the decay of these two peaks was identical to that of the 1.30 Mev peak of argon-41.

After the specific separation for silicon was completed, the radioactivity of the precipitate was analyzed in the beta instrument described previously in this paper. Beta decay and absorption studies for the Chicago water are shown in Figures 13 and 14 respectively. In Figure 13 the decay data produces a straight line indicating the presence of only one radioactive constituent decaying with a half life of 2.6 hours. Figure 14 indicates a half-thickness of 86 mg/cm^2 of aluminum which corresponds to a beta energy of 1.47 Mev.[32] This, along with the chemistry, confirms the presence of 2.65 hour silicon-31.

B. Long-Lived Radionuclides (Chicago Water)

Figures 15 and 16 show the beta decay and absorption studies for the phosphorus separation of the 2 week irradiated Chicago drinking water. Analysis of the absorption data by the "Feather Method"[33] indicates an apparent maximum beta particle range of 784 mg/cm^2 which corresponds to an energy of 1.7 Mev (Figure 17).

Phosphorus-32 is not only produced from phosphorus-31 by a (n,γ) reaction, but is also produced from sulfur-32 by a (n,p) reaction. Therefore, if sulfur is present in the original solution, the concentration of phosphorus-32 obtained will be greater than the true concentration of phosphorus in the sample. This value can be corrected

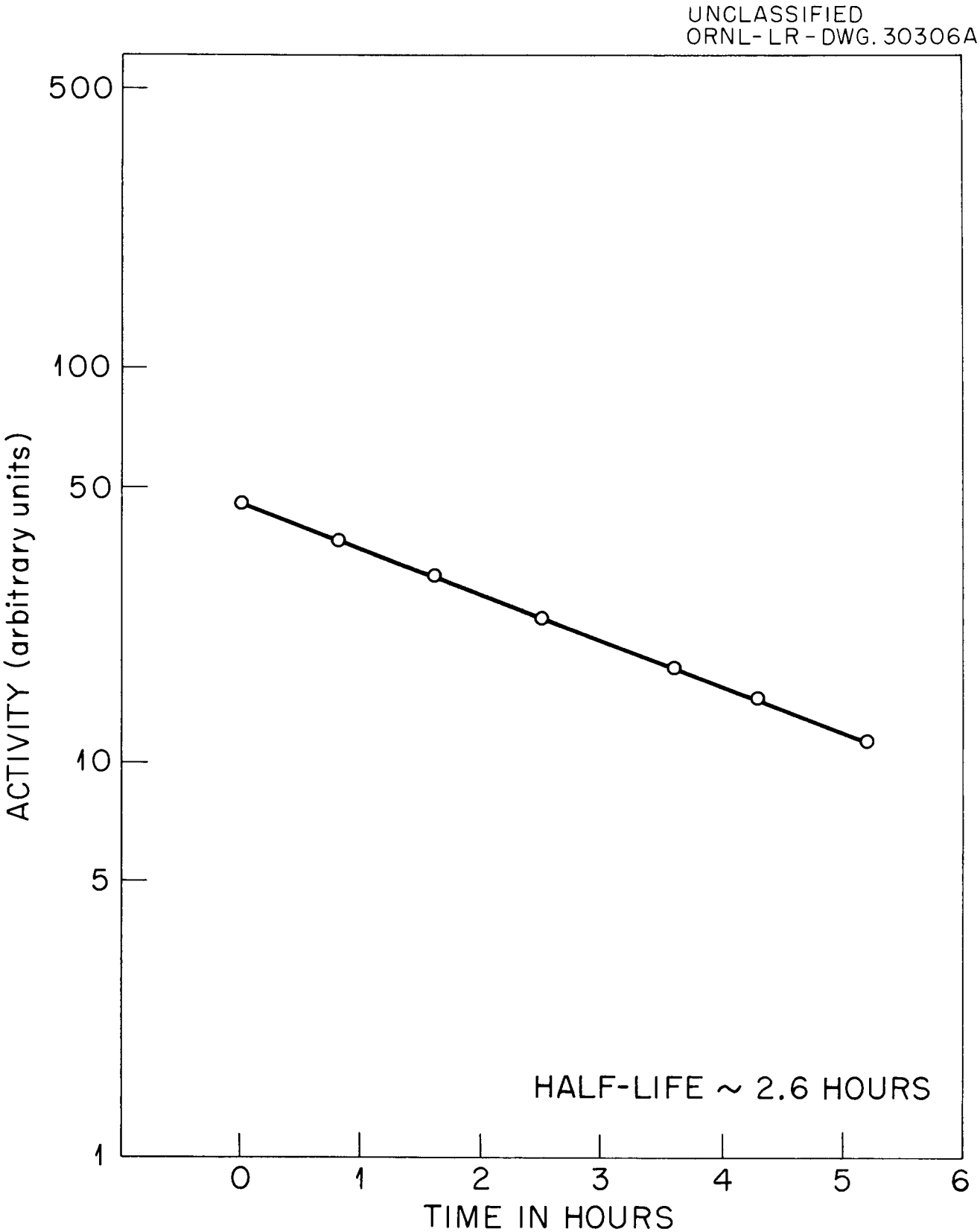

Figure 13

BETA DECAY STUDIES, CHICAGO WATER: SPECIFIC SILICON SEPARATION FOLLOWING A 16-HOUR IRRADIATION PERIOD

UNCLASSIFIED
ORNL-LR-DWG. 30307A

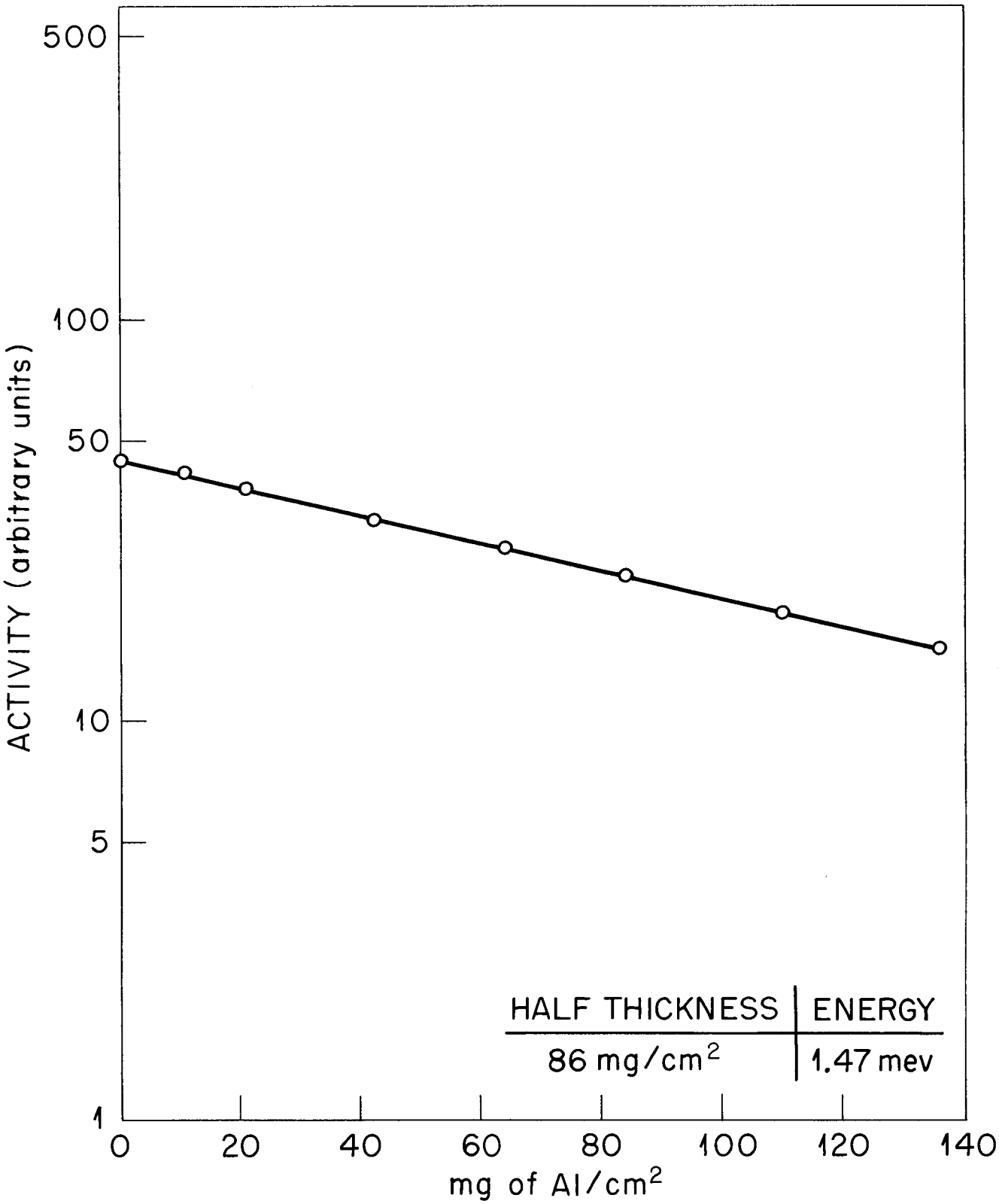

Figure 14

Si^{31} BETA ABSORPTION MEASUREMENTS, 16-HOUR IRRADIATED CHICAGO WATER

(Specific Silicon Separation)

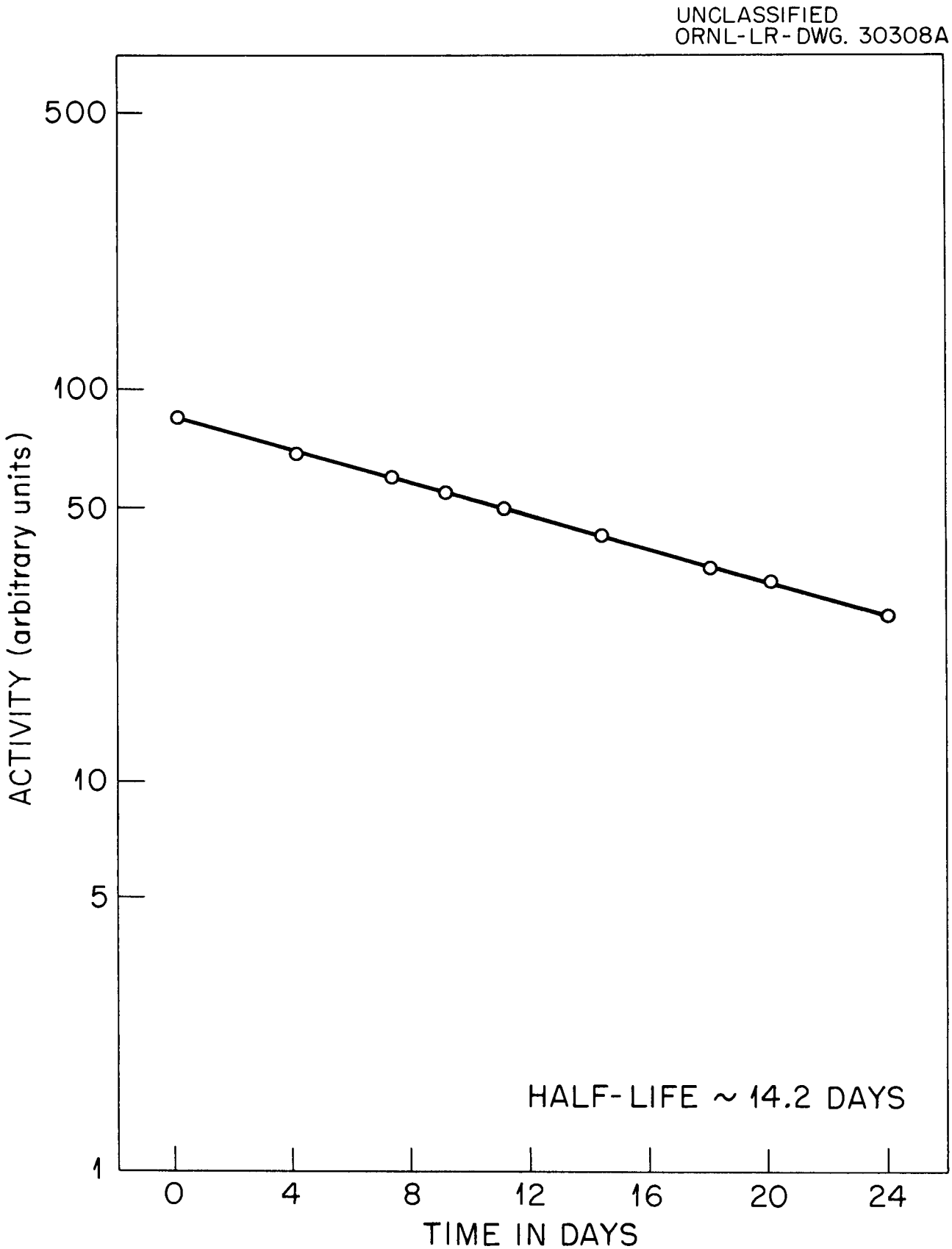

Figure 15

P^{32} BETA DECAY STUDIES, 2-WEEK IRRADIATED CHICAGO WATER
(Specific Phosphorus Separation)

UNCLASSIFIED
ORNL-LR-DWG. 30309A

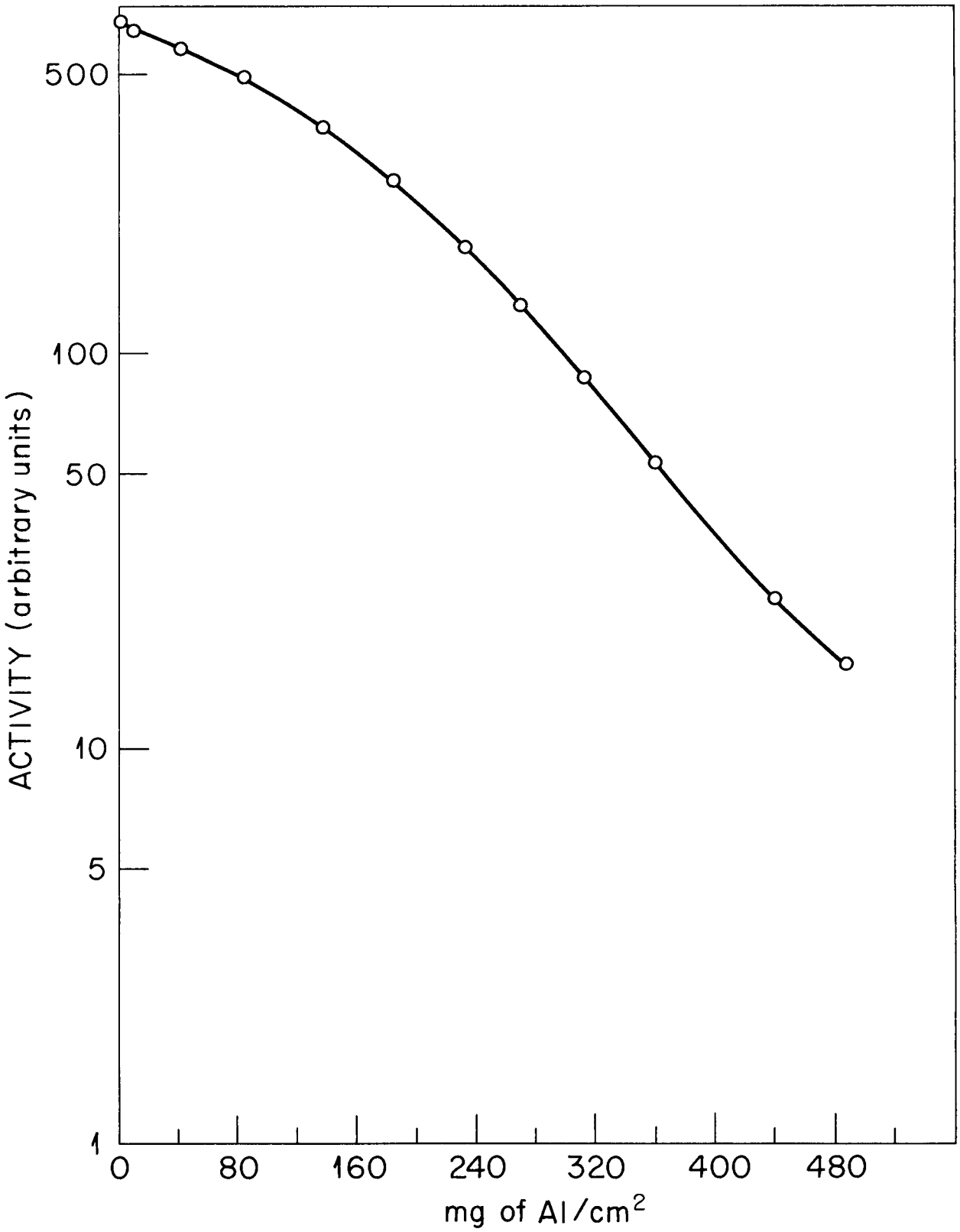

Figure 16

P^{32} BETA ABSORPTION MEASUREMENTS, TWO-WEEK IRRADIATED CHICAGO WATER
(Specific Phosphorous Separation)

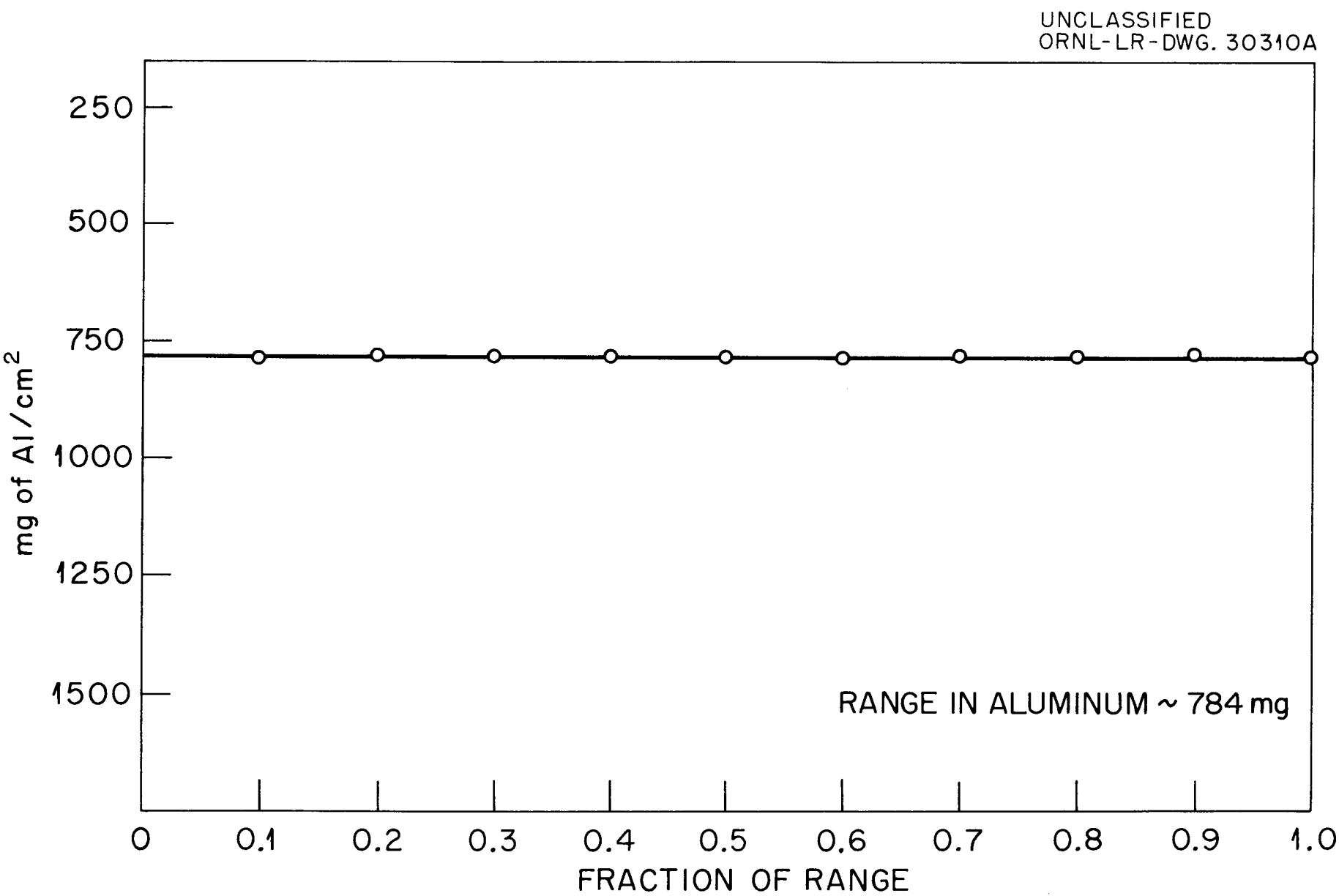

Figure 17

THE FEATHER PLOT OF THE PHOSPHORUS-32 BETA ABSORPTION SPECTRUM

by measuring the quantity of phosphorus-32 produced from a sulfur standard. This value is then subtracted from the original value to obtain the corrected phosphorus concentration.

The decay and absorption data obtained from the calcium separation of the Chicago sample, Figures 18 and 19 respectively, show the presence of a 160 day component having a beta energy of 0.25 Mev. This confirms the presence of 164 day calcium-45.

Figure 20 presents the gamma spectral data obtained for the Acid Sulfide Group. These spectra show peaks at 0.56 Mev which decay with a half life of approximately 3 days, and peaks at 1.60 Mev which have a much longer half life. Decay data, Figure 21, indicate two components, one with a half life of 2.8 days and the other with a half life of 54 days. This is characteristic of 2.8 d antimony-122 and 60 day antimony-124 respectively.

Gamma spectral data obtained from the Ammonium Hydroxide separation of Chicago water are presented in Figure 22. The only spectral peak appears at 0.16 Mev which decays with a half life of approximately 3 days. This is characteristic of 3.4 day scandium-47. As the calcium group of this separation scheme also contained the 0.16 Mev component upon decaying for a few days, it was concluded that the scandium-47 was produced from the beta decay of 4.7 day calcium-47 and not from titanium-47 by a (n,p) reaction. This same 0.16 Mev peak was also identified in the standard calcium and iron hydroxide groups of the comparator sample which further confirms that scandium-47 is the daughter of Ca-47 and not a product of a neutron reaction on Ti-47.

UNCLASSIFIED
ORNL-LR-DWG. 30311A

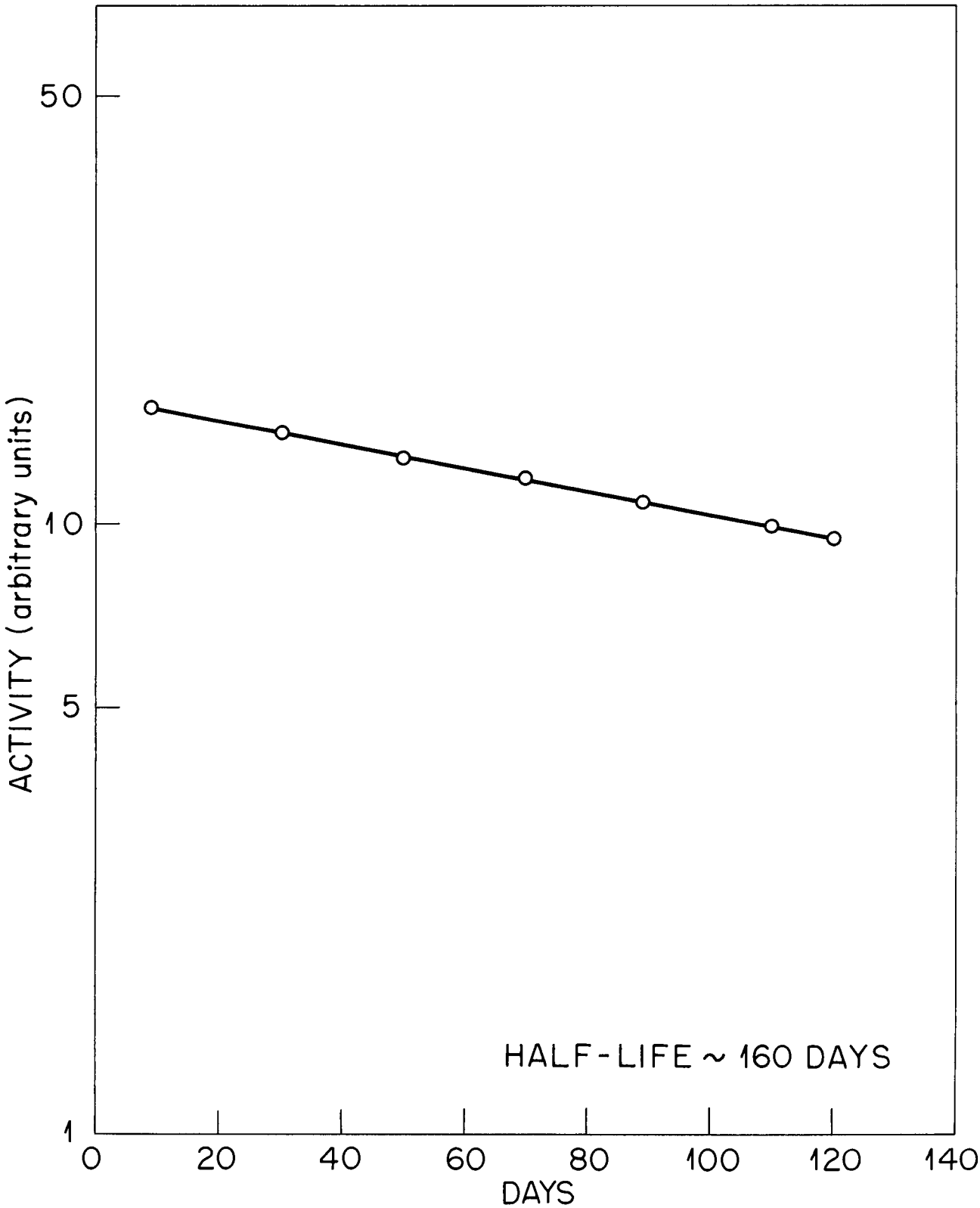

Figure 18
BETA DECAY STUDIES, CHICAGO WATER: SPECIFIC CALCIUM SEPARATION FOLLOWING A TWO WEEK IRRADIATION PERIOD

UNCLASSIFIED
ORNL-LR-DWG. 30312 A

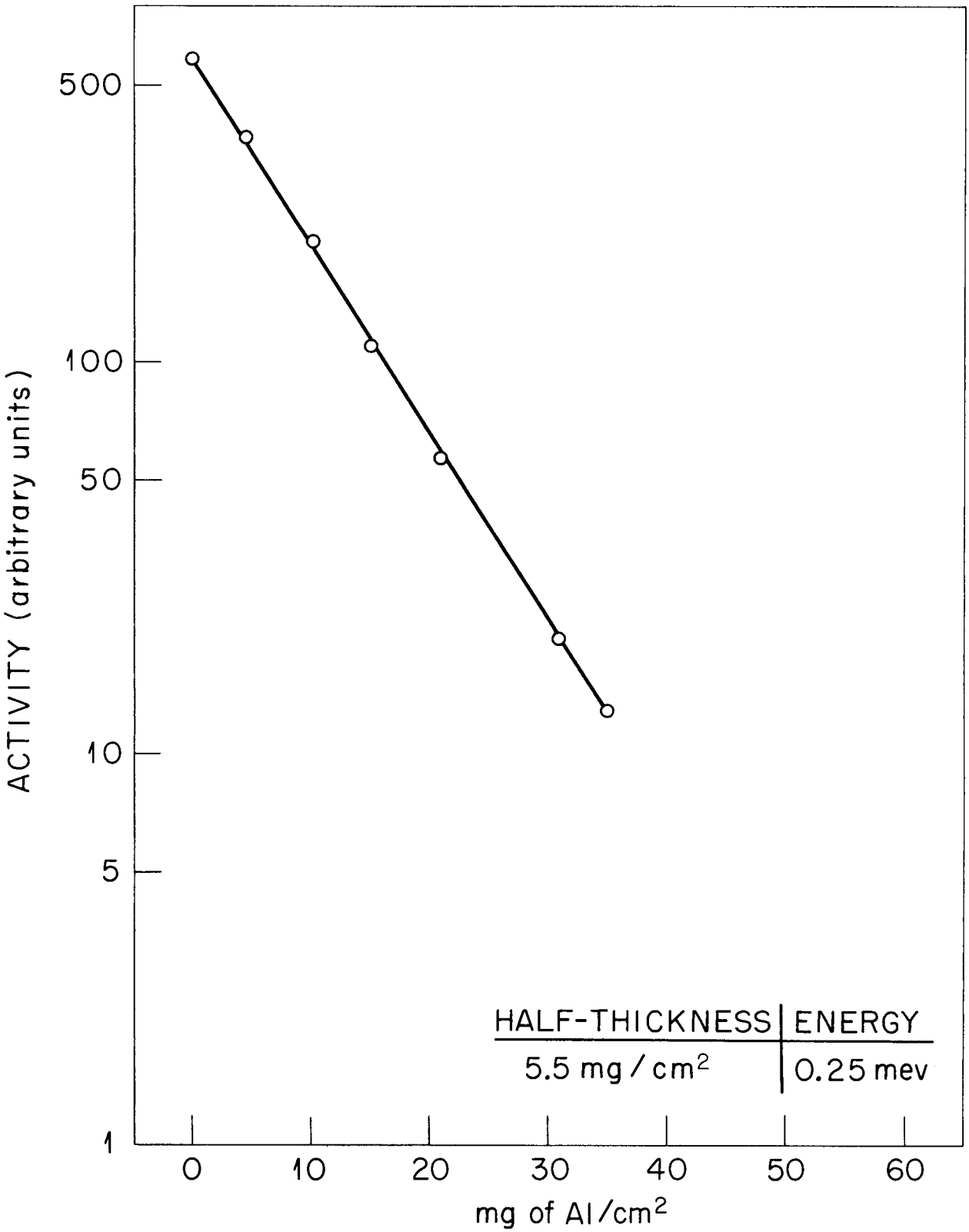

Figure 19

Ca^{45} BETA ABSORPTION MEASUREMENTS, TWO WEEK IRRADIATED CHICAGO WATER

(Specific Calcium Separation)

UNCLASSIFIED
ORNL-LR-DWG. 30313A

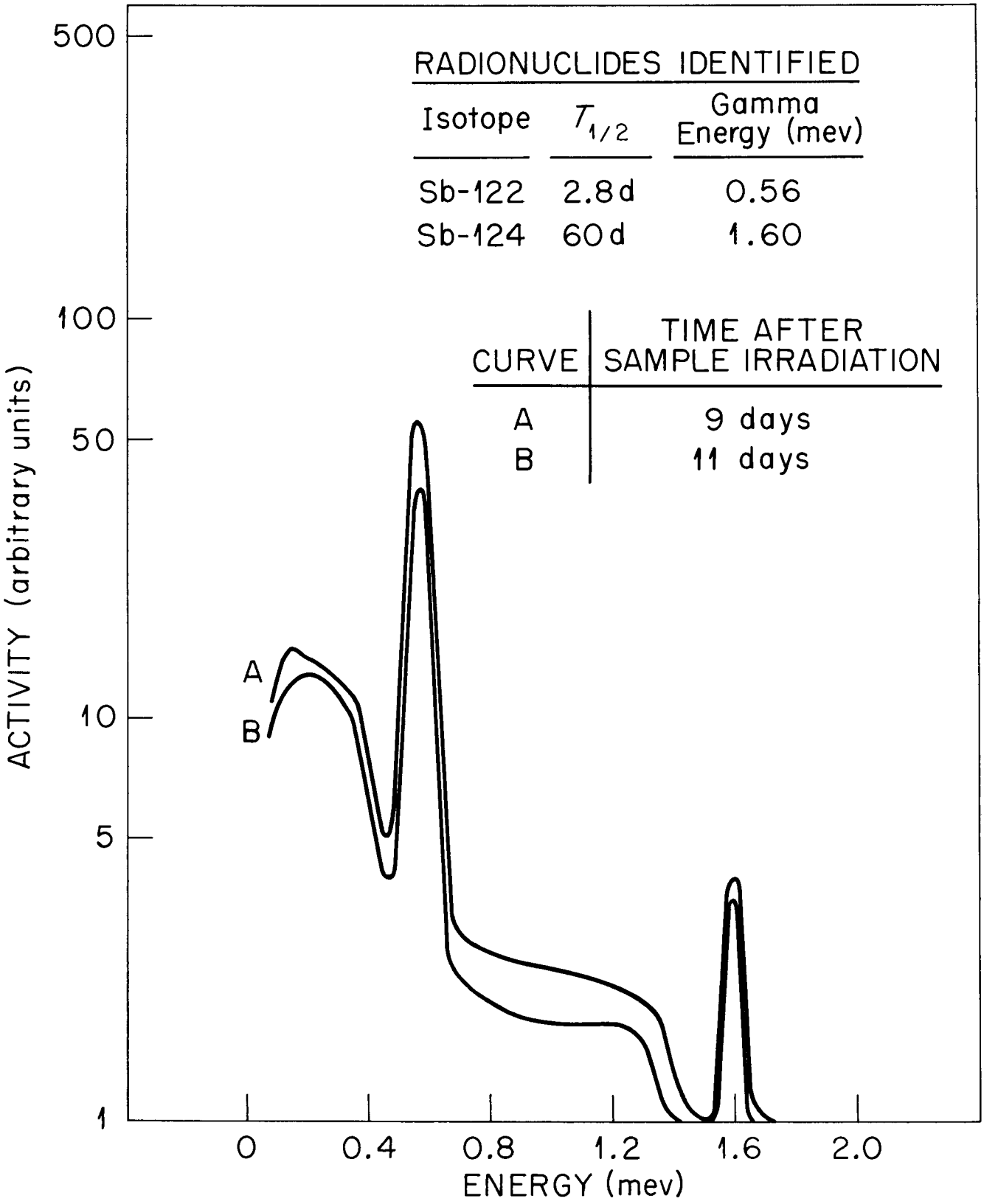

Figure 20
QUALITATIVE ANALYSIS,
TWO-WEEK IRRADIATED CHICAGO WATER:
ACID SULFIDE GROUP PRECIPITATION

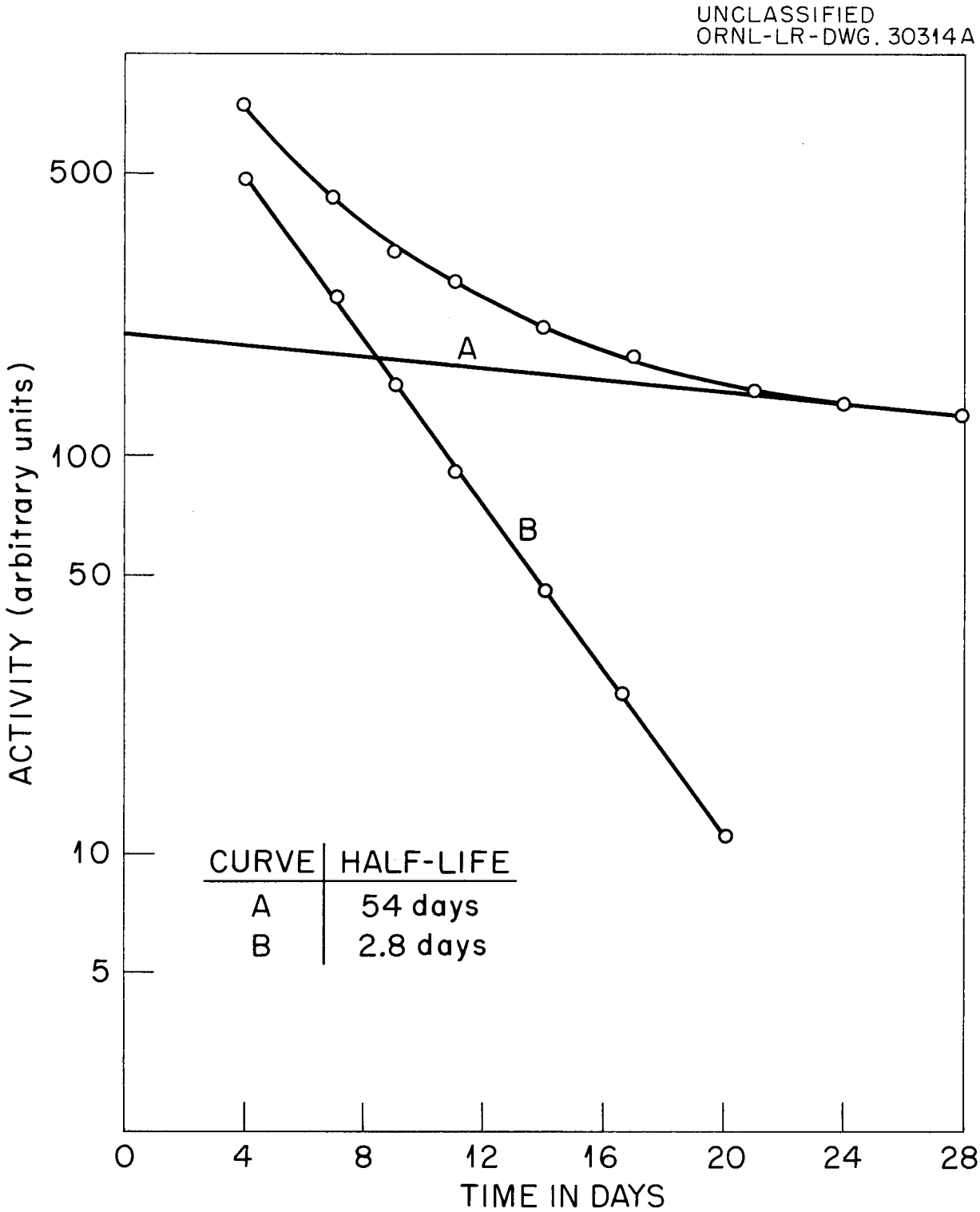

Figure 21
GAMMA DECAY STUDIES, TWO-WEEK IRRADIATED CHICAGO WATER: ACID SULFIDE GROUP PRECIPITATION

UNCLASSIFIED
ORNL-LR-DWG. 30315A

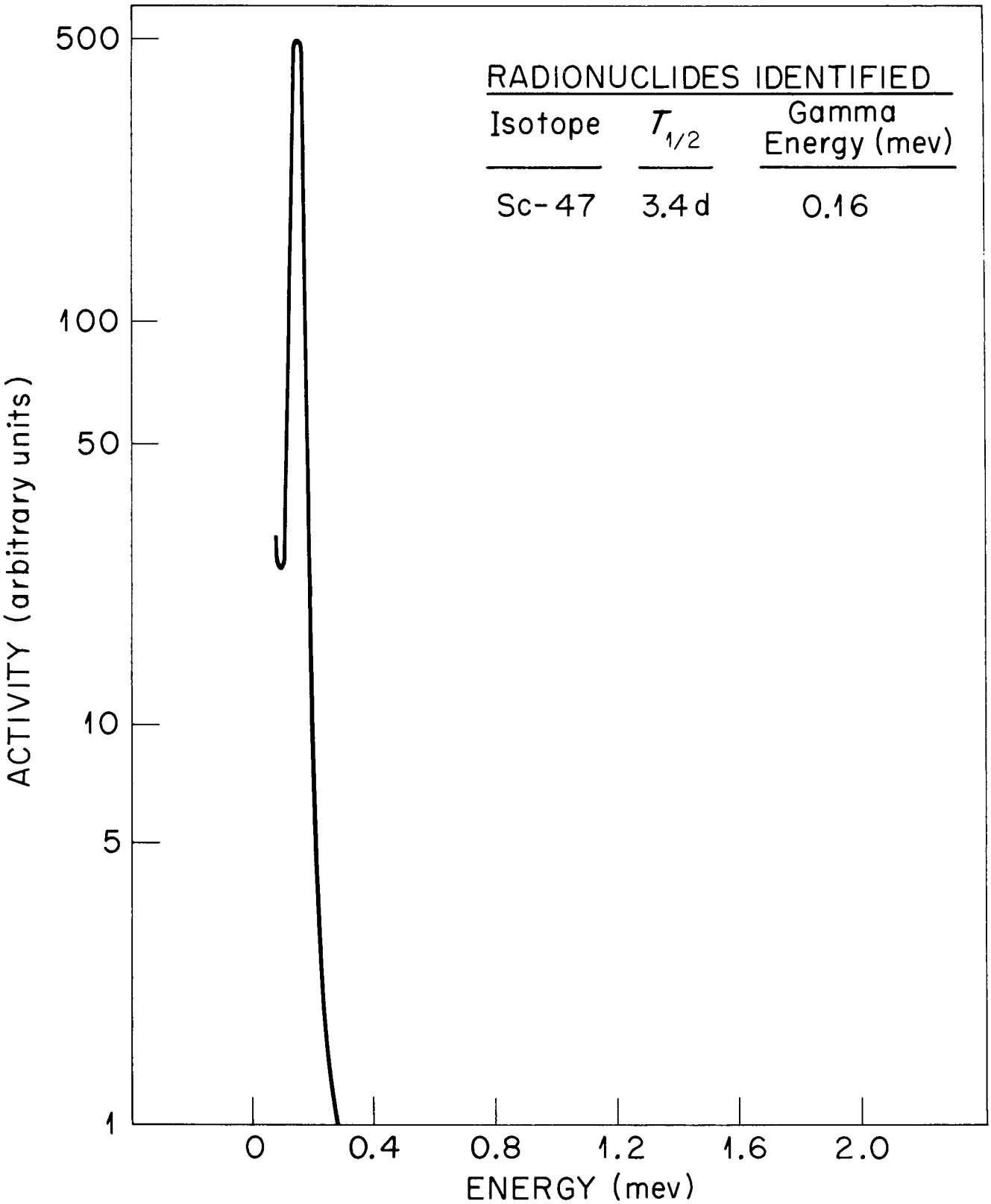

Figure 22

QUALITATIVE ANALYSIS,
TWO-WEEK IRRADIATED CHICAGO WATER:
AMMONIUM HYDROXIDE GROUP PRECIPITATION

Only a very small quantity of radioactivity was detected in the basic sulfide separation. The activity present was thought to be due to either 245 day Zn-65, since zinc was previously detected with a 16 hour irradiation period as $Zn-69^m$, or possibly 72 day Co-58 produced from a (n,p) reaction upon Ni-58. However, the activity present was not sufficient to obtain a conclusive confirmation. In the soluble portion remaining at the end of the separation scheme, only 15 hour Na-24 was detected as time did not permit further study of this fraction.

Table VI lists the neutron activation analysis results obtained for the elements usually assayed for by conventional methods. For comparison, Table VI also includes typical results of the Chicago water analysis obtained by conventional chemical techniques.[34]

Table VII lists the quantitative results for other elements detected by neutron activation analysis, but which had not been reported by conventional chemical analysis. Argon-41 is denoted only as being present, since the amount present is uncertain due to the procedure used for the dissolved gas separation.

Quantitative results were also obtained by the absolute method of analysis which employs Equation (2). The difference in the results obtained by these two methods ranged from 6% to 33%. It is reasonable to conclude, therefore, if accuracy were not too important in a specific analysis, the absolute method could be employed.

Table VI
Elements Determined in Water By Activation Analysis*
(Previously determined by Conventional Chemical Analysis)

Element	Conventional Analysis of Chicago, Illinois Water	Neutron Activation Analysis						
		Chicago, Illinois	Oak Ridge, Tennessee	Cincinnati, Ohio	New York, New York	Denver, Colorado	Atlanta, Georgia	Charlottesville, Virginia
Ca	40.2	34.6	36.0	63.3	8.5	23.5	11.6	12.3
Cl	7.0	6.6	3.1	5.1	6.7	20.8	12.0	12.1
Cu	0.004	0.004	0.003	0.010	0.005	0.017	0.003	0.007
Mg	9.5	20.7	2.8	3.6	5.0	4.5	1.1	8.5
P	0.002	0.004	0.005	0.029	0.0031	0.011	0.0017	0.014
K	2.50	1.9	1.4	3.6	0.67	2.1	0.72	0.53
SiO_2	2.1	1.85	1.70	4.25	3.8	4.2	6.6	1.70
Na	4.40	6.5	6.4	1.6	1.6	21.2	3.8	4.0
Sr	0.48	0.29	0.38	0.61	0.10	1.23	0.14	0.08
Zn	0.023	0.028	<0.01	<0.01	0.047	<0.01	<0.01	0.038

* Concentrations given in parts per million.

Table VII
Elements Determined in Water by Activation Analysis*
(Data by Conventional Chemical Means Not Available)

Element	Chicago, Illinois	Oak Ridge, Tennessee	Cincinnati, Ohio	Denver, Colorado	New York, New York	Atlanta, Georgia	Charlottesville, Virginia
Sb	0.030	0.030	0.016	0.023	0.040	0.057	0.044
A	**	**	**	**	**	**	**
As	<0.00002	0.00002	<0.00002	<0.00002	<0.00002	<0.00002	<0.00002
Ba	0.010	0.021	<0.005	<0.005	0.006	0.005	<0.005
Br	0.32	0.18	0.12	0.18	0.07	0.17	0.05
I	0.027	0.002	0.027	0.007	0.004	0.027	0.018
Mn	0.0004	0.0014	0.0026	0.0098	0.0049	0.0028	0.040
Rb	0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
Th	<0.001	0.021	<0.001	<0.001	<0.001	<0.001	<0.001

* Concentration given in parts per million.

** Presence indicated.

8. SUMMARY AND CONCLUSIONS

Neutron activation analysis was applied to seven water samples from selected geographical areas in the United States. The technique proved adequate for the identification and measurement of nineteen different elements (See Table VIII) ranging in concentrations from 0.00002 to 63.3 ppm. Irradiations were conducted in the Oak Ridge Graphite Reactor, gamma spectrometry serving as the principal tool for identification and measurement of specific induced radionuclides.

The degree of chemical separation required for a given sample depended upon the element being determined and the variety of constituents present. It was possible to determine chlorine, sodium, and argon on the sample as irradiated. Most other elements required separation. Ion exchange and precipitation were investigated and the latter proved most generally satisfactory. For certain of the elements, a general chemical separation was adequate. Others required specific procedures. A summary of the elements identified, time of irradiation and analytical procedure is given in Table VIII.

From the results reported in Table VIII, it is believed that neutron activation analysis can be a valuable tool for sanitary engineers and geochemists in water studies. The technique is specific in that each induced radionuclide decays with its own characteristic radiation and half life. It is sensitive in that concentrations as small as 10^{-11} gram of some elements can be determined with an accuracy of $\pm$ 5% or better.[4]

The precision acquired by neutron activation analysis was also demonstrated by the production of fluorine-18 from oxygen-18. The

Table VIII
Elements Determined in Water By Neutron Activation Analysis

Element	Irradiation Period	Nuclide Produced	Separation Technique	Counting Procedure
A	2 h	A^{41}	None	γS
Cl	1 h	Cl^{38}	None	γS
	16 h	Cl^{38}	General	γS
Na	16 h	Na^{24}	None	γS
	16 h	Na^{24}	General	γS
As	16 h		General	γS
Ba	16 h		General	γS
Br	16 h		General	γS
Cu	16 h		General	γS
Mn	16 h		General	γS
Sb	16 h		General	γS
Sr	16 h		General	γS
Th	16 h		General	γS
Zn	16 h		General	γS
I	16 h		Specific	γS
K	16 h		Specific	γS
Mg	16 h	Mg^{27}	Specific	γS
Rb	16 h		Specific	γS
Si	16 h		Specific	β^-
Ca	2 w		Specific	β^-
P	2 w		Specific	β^-

average quantity of fluorine-18 produced from the seven analyzed water samples was 0.0563 ± 0.0012 microcuries per liter. Since it is generally concluded that the isotopic composition of water is quite constant over a wide geographical area,[35] the precision obtained in the analysis of the seven samples was within 4%.

The study reported herein was limited to elements yielding radionuclides with half lives ranging from minutes to days. Location of counting equipment nearer irradiation facilities would permit determinations involving radionuclides of much shorter half lives, thus, widening the range of elements suitable for analysis.

9. ACKNOWLEDGEMENT

The authors of this paper would like to express their appreciation to S. A. Reynolds for his aid in helping to analyze selected gamma spectra obtained in this investigation. Appreciation is also due to Mrs. Nelle Tuck for assisting in performing the analyses.

10. APPENDIX A: Gamma Scintillation Spectrometry

In order to understand and interpret correctly the gamma spectra obtained from a scintillation spectrometer in this paper it is first necessary to understand the gamma reactions taking place in the NaI(Tl) crystal detector.

A gamma-ray interacting with the crystal loses its energy in one or more steps by exciting the electronic states of the atoms composing the crystal. As the atoms return to unexcited states, light is emitted the quantity being proportional to the amount of energy absorbed from the gamma photon. The light falls on a photo-cathode, initiating a current pulse proportional to its intensity. The photomultiplier amplifies the pulse which is then differentiated and recorded after passing through a preamplifier, a linear amplifier circuit, and a discriminator.[1]

The various characteristics of gamma spectra originate from the manner in which the gamma photons lose their energy in the crystal. This loss of energy can be accredited to the photoelectric effect, Compton scattering, or pair production.[2]

When the photoelectric effect takes place, all of the gamma energy is transferred to an electron, and the electron is removed from the atom with a kinetic energy very nearly equal to that of the gamma ray. In losing its kinetic energy by collisions with other electrons, the ejected electron excites these atoms and produces flashes of light and is ultimately slowed to rest. For a photoelectric interaction, the instrument will record a gamma-ray energy equal to

$$E_\beta = E_\gamma - W \qquad (3)$$

where E_β is the kinetic energy of the electron, E_γ is the initial gamma energy, and W is the work function which is equal to the binding energy of the electron. The energy E_β is very nearly equal to E_γ, since the binding energy of an electron is very small compared to the energy of photons. The "photopeak" created by this reaction is the spectral peak normally used in the identification of gamma emitting nuclides and is labeled "A" in Figure 23.

The second mechanism by which a gamma-ray may lose energy is by the Compton scattering. This occurs when a gamma photon "collides" with an electron and transfers only a fraction of its energy, the fractional amount depending upon the angle through which the photon is scattered. Such interactions may be described by Equation (4)

$$E_\beta = \frac{E_\gamma}{1 + \frac{m_o c^2}{E_\gamma(1-\cos\theta)}}. \qquad (4)$$

where E_β is the energy of the recoil electron, E_γ is the energy of the incident gamma-ray, $m_o c^2$ is the rest energy of the electron, and θ is the angle through which the photon is scattered after collision.

Subsequent to Compton scattering, a photon may be absorbed in a photoelectric interaction or undergo additional Compton efents. If the photon is completely absorbed within the crystal, the pulse recorded by the instrument will fall beneath the photoelectric peak. If, however, the photon excapes from the crystal after being scattered, a pulse representing a lower energy will be recorded. (See Compton slatter region, marked "C" in the spectrum of Figure 23.)

UNCLASSIFIED
ORNL-LR-DWG.30302A

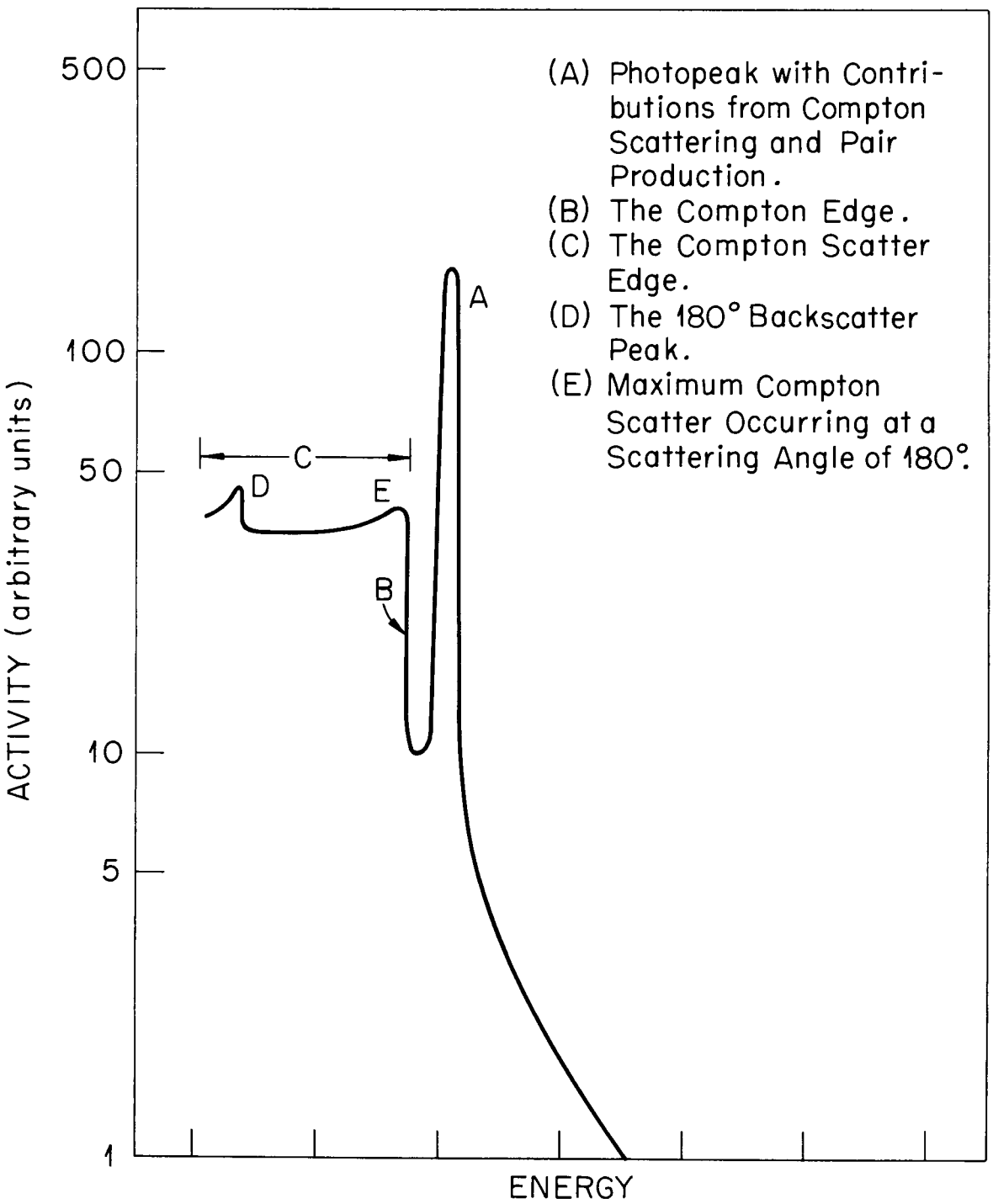

Figure 23

A GAMMA SPECTRUM ILLUSTRATING THE TYPICAL CHARACTERISTICS

The amount of energy which can be transferred to an electron by a single Compton scatter process is a maximum when the angle of scatter is 180°. That is, the electron recoils straight forward and the photon is scattered straight back. If the photon is scattered out of the crystal after such a collision process, the energy recorded by the instrument will be degraded from the photopeak and the pulse will fall under region "B" on the spectrum of Figure 23.

The large dip in the spectrum immediately before the photopeak is termed the "Compton Shoulder." The energy of the Compton Shoulder can be derived from Equation (4) by substituting 180° for θ, and solving for the energy of the recoiling electron, E_{max}. This equation becomes

$$E_{max} = \frac{E_{\gamma}}{\left(1 + \frac{m_0 c^2}{2E_{\gamma}}\right)}. \qquad (5)$$

It can be shown by the Klein-Nishina Equation[3] that the cross-section, or probability, for a Compton scatter process increases with the angle and becomes a maximum as the angle of the scatter reaches 180°. This explains the slight peak at region "E" on the gamma spectrum of Figure 23.

The region marked "D" in Figure 23 is called the "180° backscatter peak." This peak results from photoelectric absorptions of gamma photons previously scattered 180°. The energy of this peak is

$$E_{bsc} = E_{\gamma} - E_{max}, \qquad (6)$$

where E_{bsc} is the energy of the backscattered photon entering the crystal.[4]

The third process in which a photon can lose energy is by pair production. In the presence of a near-by nucleus, a photon possessing an energy greater than 1.02 Mev can form two particles, an electron, and a positron. These particles possess a kinetic energy equal to E_γ - 1.02 Mev, which they lose through their collisions with electrons. As the kinetic energy of the positron approaches zero, it annihilates with an electron to produce two photons, each having an energy of 0.51 Mev. If all of these processes are detected by the instrument, the gamma energy will be recorded beneath the photopeak. But, if one of the 0.51 Mev photons escapes, a peak will appear on the gamma spectrum at an energy of 0.51 Mev less than the photopeak energy. If both 0.51 Mev photons escape from the crystal, a spectral peak will appear at an energy of 1.02 Mev less than the photopeak energy. The peaks are called "escape peaks" and are shown very clearly at energies of 1.73 and 2.24 Mev in the Na-24 spectrum of Figure 9.

Another phenomenon occurring generally when a well-type crystal is employed, is "coincidence summing," or what is sometimes called "pile up" or "build up."[5] That is, if two different photons enter the crystal and react at exactly the same time, the photo-cathode will "see" both flashes of light as one and will produce a false peak which can create some uncertainty if not understood and interpreted correctly. In a solid crystal coincidence summing is considerably reduced.

11. BIBLIOGRAPHY

1. Hevesy, G. and Levi, H., Kgl. Kanski Videniskab. Selskab, Mat.-fys. Medd., 14, No. 5 (1936).

2. Seaborg, G. T. and Livingood, J. J., J. Am. Chem. Soc., 60, 1748 (1938).

3. Leddicotte, G. W., Nucleonics 14, No. 5, 46 (1956).

4. Leddicotte, G. W. and Reynolds, S. A., Nucleonics 8, No. 3, 62, (1951).

5. Boyd, G. E., Anal. Chem. 21, 335, (1949).

6. Brooksbank, W. A., ORNL-2226 (1956).

7. Friedlander, G. and Kennedy, J. W., Nuclear and Radiochemistry, John Wiley and Sons, Inc., New York, pp. 132-134 (1955).

8. Brooksbank, W. A., "Flux Measurements in Hole 10, ORNL Graphite Reactor," Preliminary Progress Report WAB-15a, Issued July 21, 1955.

9. Hughes, D. J. and Harvey, J. A., BNL-325 (1955).

10. Hollander, J. M., Perlman, I., and Seaborg, G. T., Rev. Mod. Phys. 25, 469 (1953).

11. Siegbahn, K., Beta- and Gamma-Ray Spectroscopy, North Holland Publishing Company, Amsterdam, pp. 151-155 (1955).

12. Reynolds, S. A. and Brooksbank, W. A., Nucleonics 11, No. 11, 46, (1953).

13. Friedlander, G. and Kennedy, J. W., Nuclear and Radiochemistry, John Wiley and Sons, Inc., New York, pp. 60-63 (1955).

14. Plumb, R. C. and Lewis, J. E., Nucleonics 13, No. 8, 42 (1955).

15. Brooksbank, W. A., Leddicotte, G. W., and Reynolds, S. A., Anal. Chem. 28, 1033 (1956).

16. Kahn, B. and Lyon, W. S., Nucleonics 11, No. 11, 61 (1953).

17. Smales' A. A., Atomics 4, No. 3, 55 (1953).

18. Kraus, K. A. and Nelson, F., "Anion Exchange Studies of the Fission Products," from the proceedings of the International Conference of the Peaceful Uses of Atomic Energy, Vol. 7, p. 113 (1955).

19. Crasemann, B. and Easterday, H., Nucleonics 14, No. 6, 63 (1956).

20. Gloss, G. H., Chemist Analyst 42, 50 (1953).

21. Lundell, G. E. F. and Hoffman, J. I., "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, pp. 651-654 (1953).

22. Ibid. p. 666.

23. Scott, W. W., "Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York, pp. 559-560, (1925).

24. Ibid, pp. 532-534.

25. Lundell, G. E. F. and Hoffman, J. I., "Outline of Methods of Chemical Analysis," John Wiley and Sons, Inc., London, p. 104 (1938).

26. Oak Ridge Master Analytical Manual, Method No. 2 21391, "Iodine Activity in Aqueous and Organic Solutions," TID-7015, (Section-2) (1957).

27. Emery, J. F. and Leddicotte, G. W., ORNL-CF-57-11-41 (1957).

28. Lundell, G. E., Bright, H. A., and Hoffman, J. I., "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, pp. 671-682 (1953).

29. Heath, R. L., A.E.C. Research and Development Report, IDO-16213 (1956).

30. Du Bridge, L. A., Barns, S. W., Bush, J. H., and Strain, C. V., Phys. Rev. 53, 447 (1938).

31. Didgen, N. W. and Rollefson, G. K., J. Am. Chem. Soc. 71, 2600 (1949).

32. Reynolds, S. A., personal communication (1957).

33. Friedlander, G. and Kennedy, J. W., Nuclear and Radiochemistry, John Wiley and Sons, Inc., New York, p. 200, (1955).

34. Poston, H. W., personal communication (1957).

35. de Laguna, W., personal communication (1958).

12. REFERENCES TO APPENDIX A

1. Jordon, W. H., and Bell, P. R., Nucleonics 5, No. 4, 30 (1949).

2. Kaplan, I., "Nuclear Physics," Addison Wesley Publishing Company, Inc., Cambridge, pp. 328-343 (1955).

3. Klein, O. and Nishina, Y., Z. Physik 52, 853 (1929).

4. Crasemann, G. and Esterday, H., Nucleonics 14, No. 6, 63 (1956).

5. Siegbahn, K., "Beta- and Gamma-Ray Spectroscopy," North Holland Publishing Company, Amsterdam, p. 157 (1955).

ORNL-2620
Chemistry-General
TID-4500 (14th ed.)

INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Reactor Experimental Engineering Library
7-26. Laboratory Records Department
27. Laboratory Records ORNL R. C.
28. A. M. Weinberg
29. L. B. Emlet (K-25)
30. J. P. Murray (Y-12)
31. J. A. Swartout
32. E. H. Taylor
33. E. D. Shipley
34. M. L. Nelson
35. M. T. Kelley
36. C. P. Keim
37. W. H. Jordan
38. R. R. Dickison
39. F. L. Culler
40. S. C. Lind
41. A. H. Snell
42. A. Hollaender
43. K. Z. Morgan
44. T. A. Lincoln
45. A. S. Householder
46. R. S. Livingston
47. D. S. Billington
48. C. E. Winters
49. H. E. Seagren
50. D. Phillips
51. J. A. Lane
52. M. J. Skinner
53. G. E. Boyd
54. C. L. Burros
55. J. H. Cooper
56. L. T. Corbin
57. C. Feldman
58. D. J. Fisher
59. P. M. Reyling
60. U. Koskela
61. W. R. Laing
62. C. E. Lamb
63. D. E. LaValle
64. G. W. Leddicotte
65. S. A. Reynolds
66. P. F. Thomason
67. T. E. Willmarth
68. G. R. Wilson
69. E. I. Wyatt
70. L. J. Brady
71. H. P. House
72. J. R. Lund
73. E. C. Lynn
74. O. Menis
75. A. S. Meyer, Jr.
76. C. D. Susano
77. C. K. Talbott
78. W. F. Vaughan
79. J. C. White
80. H. P. Raaen
81. J. A. Norris
82. D. L. Manning
83. T. C. Rains
84. A. E. Cameron
85. K. E. Cowser
86. F. Parker
87. W. J. Lacy
88. D. N. Hume (consultant)
89. N. H. Furman (consultant)
90. C. E. Larson (consultant)
91. L. L. Merritt (consultant)
92. H. A. Laitinen (consultant)
93. G. Friedlander (consultant)
94. ORNL - Y-12 Technical Library Document Reference Section

EXTERNAL DISTRIBUTION

95-115. R. A. Taft Sanitary Engineering Center, Cincinnati (1 copy to D. W. Moeller)
116-135. R. L. Blanchard, U.S. Public Health Service, Salt Lake City, Utah
136-140. U. S. Public Health Service, Washington, D.C. (Terrill)
141. Regional Engineer, Public Health Service, Region 2, Room 1200, 42 Broadway, New York 4, N.Y.
142. Regional Engineer, Public Health Service, Region 3, 700 E. Jefferson St., Charlottesville, Va.
143. Regional Engineer, Public Health Service, Region 4, Room 164, 50 Seventh St., N.W., Atlanta 24, Ga.
144. Regional Engineer, Public Health Service, Region 5, 69 W. Washington St., Room 200, Chicago 2, Ill.
145. Regional Engineer, Public Health Service, Region 8, Room 525, New Customs House, 19th and Stout Streets, Denver 2, Colo.
146. C. E. Miller, Physics Research Division, Armour Research Foundation, 10 W. 35th St., Chicago 16, Ill.
147. Division of Research and Development, AEC, ORO
148-709. Given distribution as shown in TID-4500 (14th ed.) under Chemistry-General category (75 copies - OTS)