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IDENTIFICATION AND COMPARISON OF PHYSICAL EVIDENCE
FOR LAW ENFORCEMENT PURPOSES BY NEUTRON ACTIVATION ANALYSIS

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Abstract

A feasibility study has been conducted on the application of activation analysis to forensic chemistry. Test portions of automobile paint finish, soot, and soil samples have been irradiated in the ORNL Graphite Reactor and the induced gamma radioactivity of each specimen measured with a gamma scintillation spectrometer. Spectral decay curves of the radionuclides in the various specimens classified the materials as to origin. This nondestructive technique is particularly suitable for the analysis of evidence samples that must be maintained in its "as-is" state.

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Very often the forensic scientist is called upon to examine physical evidence obtained at the scene of the crime. Although many physical and chemical techniques⁽¹⁻⁴⁾ are available, some types of evidence cannot be characterized by these methods of analysis. This is especially true when the available evidence is extremely small (a few milligrams). Also, organic compounds of considerable purity used as evidence is difficult to compare even though the most sensitive instrumental techniques are employed. Therefore, the use of radioactivation analysis as a specific analytical tool for the determination of elemental composition and trace impurities in many types of enforcement samples should provide an excellent technique for obtaining additional court evidence.

This study was initiated to determine the feasibility of radioactivation analysis in law enforcement work. The objects of this work were to show (1) that samples of physical evidence can be compared or differentiated from each other by neutron activation; (2) that differences in the individual constituents can be employed to compare these samples; and (3) the relationship between some of the constituents, used in comparing samples in question with those of known origin.

The principles and techniques used in activation analysis are described in Appendix A. The references given in Appendix A have been chosen so that further information about the possibilities of the very sensitive and specific method of neutron activation analysis may be obtained.

Experimental

In the experiments conducted in this study, portions of each test sample were irradiated in the ORNL Graphite Reactor for predetermined time

intervals. Immediately following the neutron irradiation, each specimen was mounted and its induced-gamma radioactivity measured with a gamma scintillation spectrometer. After an appropriate decay interval, the samples were recounted and the data plotted as spectral decay curves. From these data the various specimens were compared to determine if they are identical to or different from each other.

Six black automobile finishes were neutron irradiated for different time intervals and assayed nondestructively by gamma scintillation spectrometry. From the gamma spectral measurements, it was possible to observe five distinct groups, with two samples appearing to be identical. In addition, soil and soot samples from a typical law enforcement case were irradiated in the same manner and the radionuclides compared by gamma spectrometry. The measurements made at various decay periods show that the soot samples appear to have the same origin. Similar results were obtained for the soil samples. From the information that appears below, it is believed that the determination of the elemental composition of a sample by the activation analysis method may be successfully employed to compare and, in some cases, identify physical evidence.

A. Black Automobile Finishes

In the initial study, each finish was irradiated at a neutron flux of 8×10^{11} n/cm²/sec for one hour and allowed to decay approximately 30 minutes before the gamma spectrometer measurements. Figures 1 - 6 show

the results of this work. Then, radioactivity measurements were recorded at different time intervals and the gamma spectral data were used to determine the half-lives of the induced radioactivity. This decay technique was employed as an aid in positive identification of the observed radioactivity emitted from the neutron-induced radionuclides. In effect, the gamma radiations reassured as photopeaks at discrete gamma energies and the subsequent loss of individual photopeaks by radioactive decay are indicative of a specific radionuclide that has resulted from an irradiation of a stable trace element in the specimen with neutrons. These characteristics can be interpreted as a "fingerprint" of the element, since no two neutron-induced radionuclides have exactly the same gamma-ray energy and half-life. (See Table 1). An identification of the gamma-ray photopeaks presented in Figures 1 - 6 show that these radionuclides result from the neutron activation of trace manganese, barium, copper, and sodium in the various sample specimens. Because each of these radionuclides have short-half-lives (Table 1), the radioactivity had to be measured soon after reactor discharge. The quantities of sample used in this work were representative of what might be obtained in enforcement cases. In this initial analysis, the weights of each specimen tested ranged from about 1 to 10 milligrams. In later studies, the specimen sizes ranged from 2 to 20 milligrams.

After each specimen was irradiated for 1 hour and the radioactivity measurements made of the short half-lived radionuclides, it was allowed to decay for 1 day. Then, each sample was reirradiated for an additional 140 hours to build up sufficient radioactivity of longer-lived radionuclides. Following this later irradiation, each specimen was allowed to

TABLE I
NUCLEAR DATA

Stable Element	Neutron-Induced Radio-Nuclide	$T_{1/2}$	Gamma Radiations, Mev	Other Methods of Production****
Ba ¹³⁰	Ba ¹³¹	11.6 d	0.12, 0.21, 0.37, 0.49, others	Ba ¹³² (n,2n)Ba ¹³¹
Ba ¹³⁸	Ba ¹³⁹	85 m	0.16	La ¹³⁹ (n,p)Ba ¹³⁹
Cr ⁵⁰	Cr ⁵¹	27 d	0.31	Fe ⁵⁴ (n, α)Cr ⁵¹ Cr ⁵² (n,2n)Cr ⁵¹
Co ⁵⁹	Co ⁶⁰	5.27 y	1.17, 1.33	Ni ⁶⁰ (n,p)Co ⁶⁰ Cu ⁶³ (n, α)Co ⁶⁰
Cu ⁶³	Cu ⁶⁴	12.8 h	0.51*, 1.34	Zn ⁶⁴ (n,p)Cu ⁶⁴ Cu ⁶⁵ (n,2n)Cu ⁶⁴
La ¹³⁹	La ¹⁴⁰	40.2 h	0.32, 0.49, 0.80, 1.59	Ce ¹⁴⁰ (n,p)La ¹⁴⁰
Mn ⁵⁵	Mn ⁵⁶	2.58 m	0.845, 1.82	Fe ⁵⁵ (n,p)Mn ⁵⁵
Na ²³	Na ²⁴	15.0 h	1.37, 2.75	Mg ²⁴ (n,p)Na ²⁴ Al ²⁷ (n, α)Na ²⁴
Sc ⁴⁵	Sc ⁴⁶	85 d	0.89, 1.11	Ti ⁴⁶ (n,p)Sc ⁴⁶
Th ^{232**}	Pa ²³³	27.4 d	0.32, 0.095	
U ^{238***}	Np ²³⁹	2.35 d	0.105, 0.22, 0.28	
Zn ⁶⁴	Zn ⁶⁵	285 d	0.51*, 1.12	Zn ⁶⁶ (n,2n)Zn ⁶⁵
Zn ⁶⁸	Zn ⁶⁹	13.8 h	0.44	Ge ⁷² (n, α)Zn ⁶⁹ Zn ⁷⁰ (n,2n)Zn ⁶⁹

* Annihilation radiation.

** $\text{Th}^{232}(\text{n},\gamma)\text{Th}^{233}$ ($T_{1/2}$; 23 min.) $\text{Th}^{233}(\beta,\gamma)\text{Pa}^{233}$.

*** $\text{U}^{238}(\text{n},\gamma)\text{U}^{239}$ ($T_{1/2}$; 23 min.) $\text{U}^{239}(\beta,\gamma)\text{Np}^{239}$.

**** These reactions may be omitted due to the very low cross-section and high neutron threshold of the reactions.

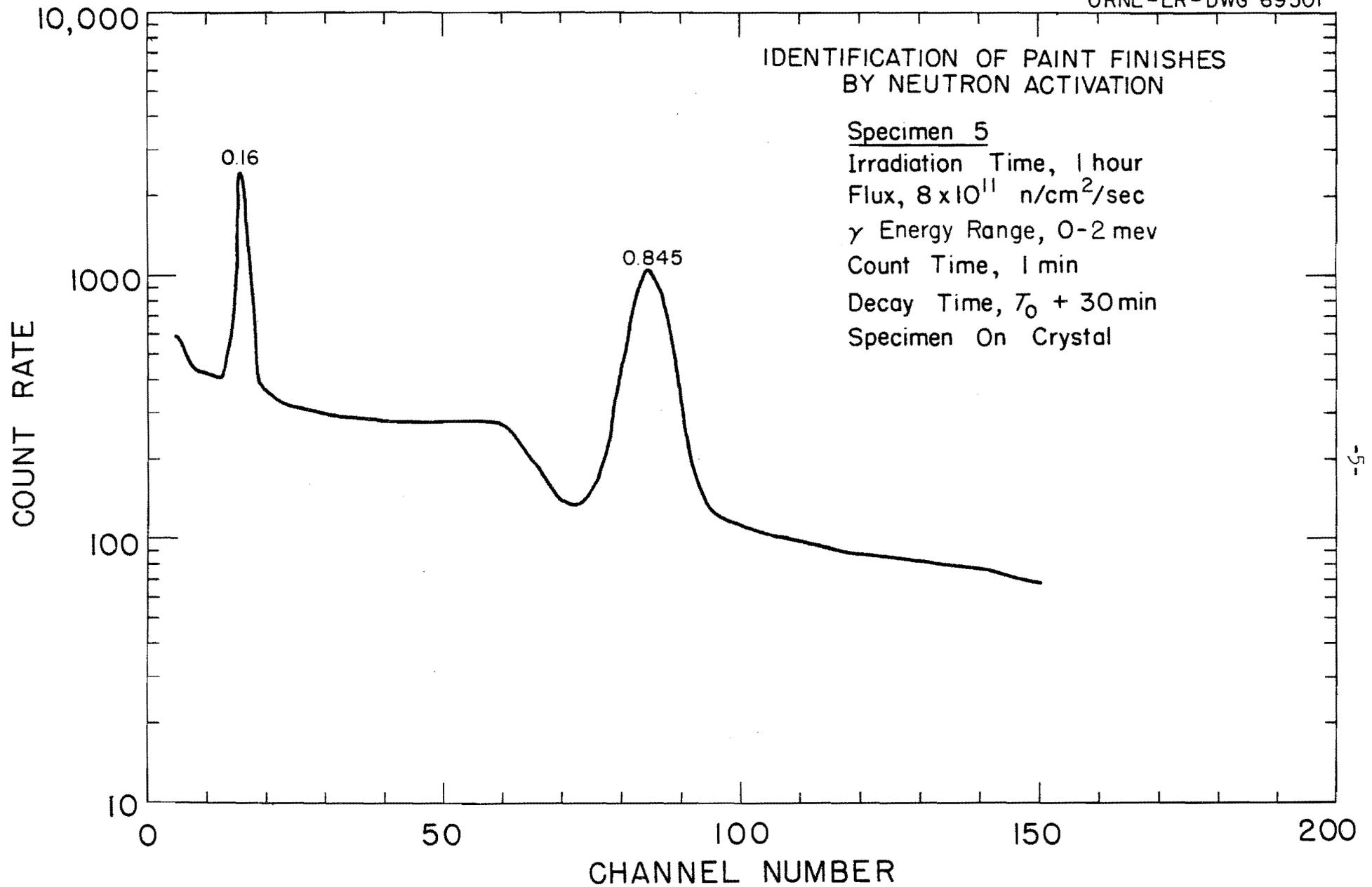


FIGURE 1

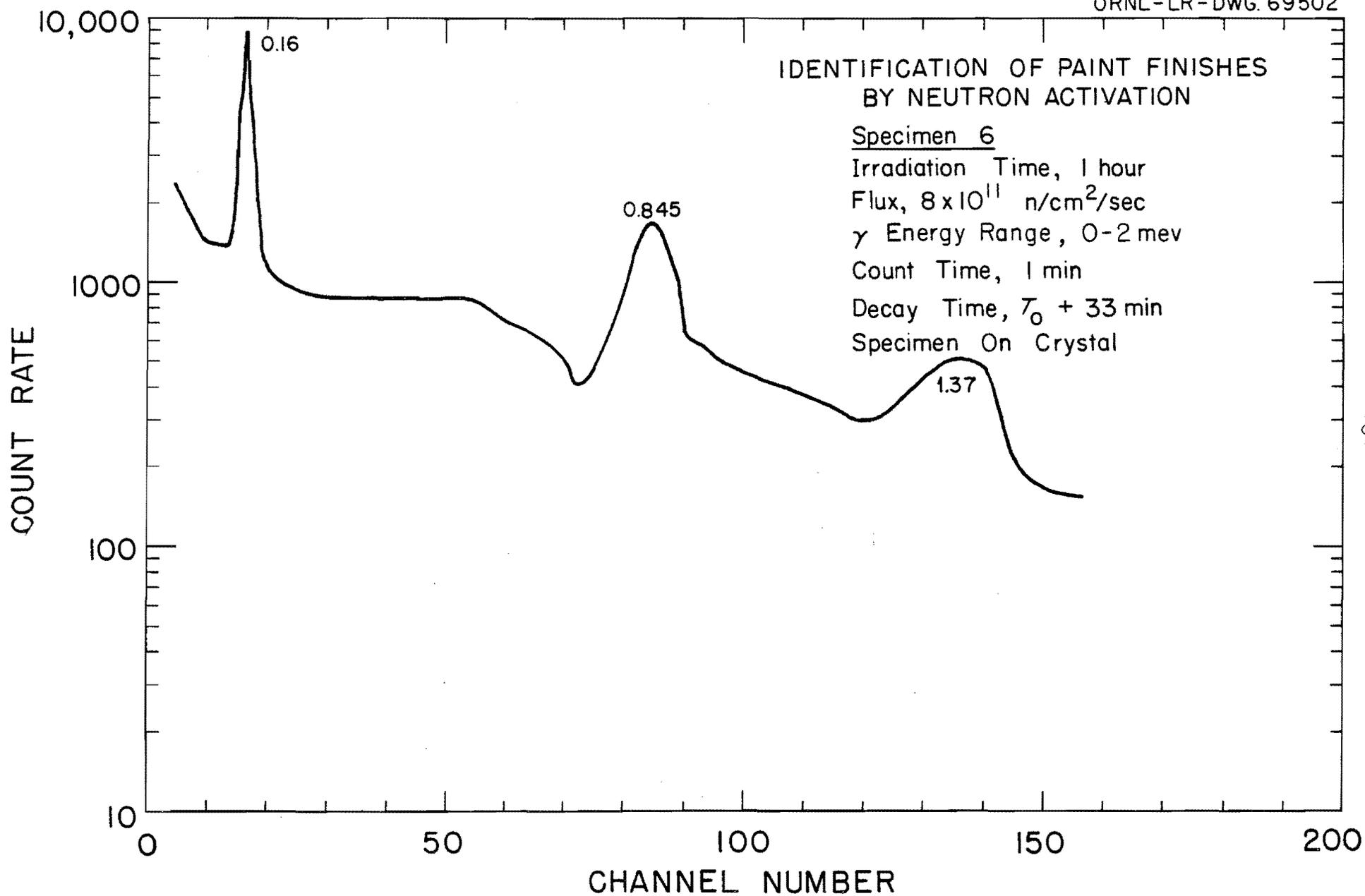


FIGURE 2

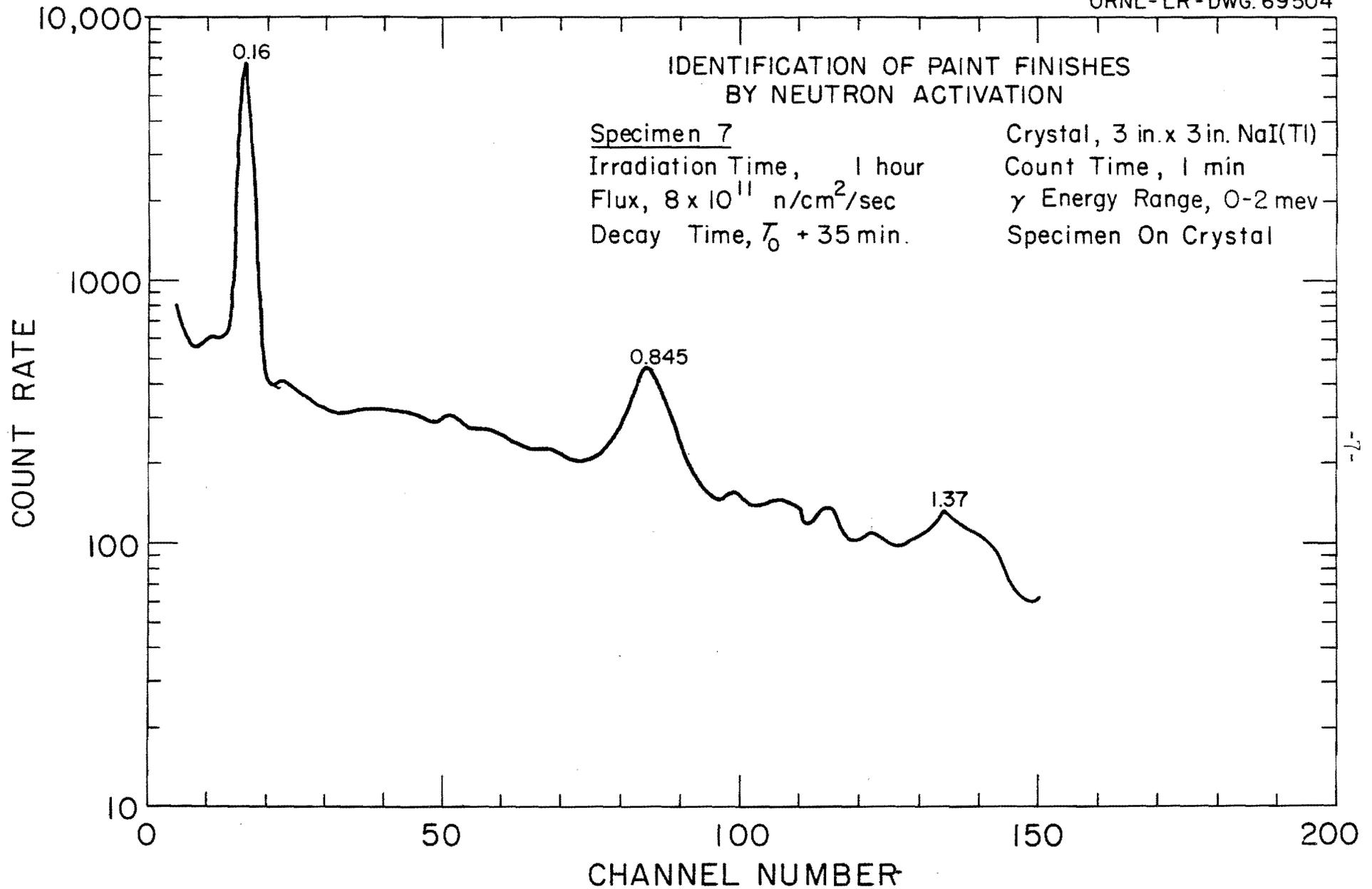


FIGURE 3

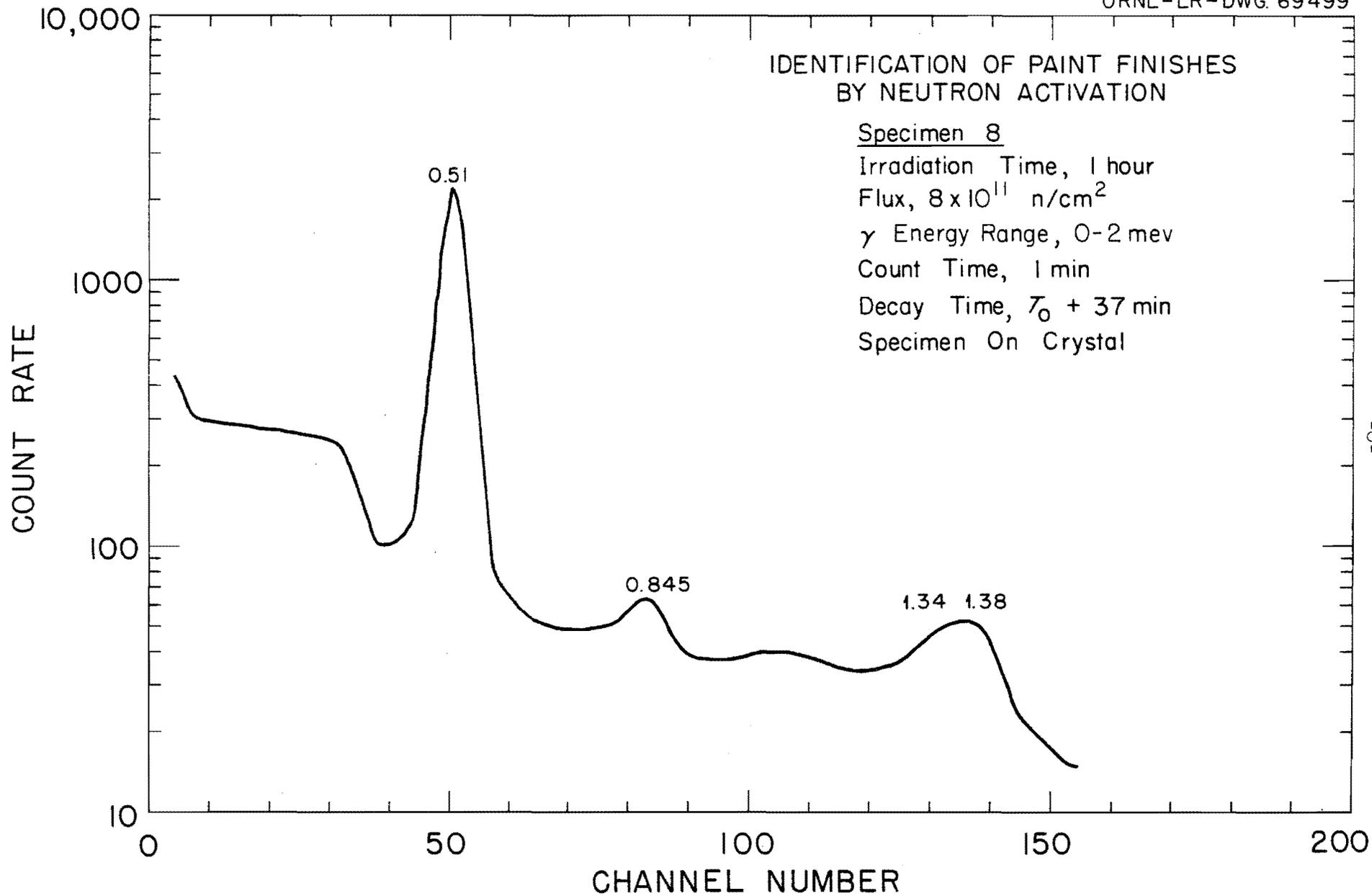


FIGURE 4

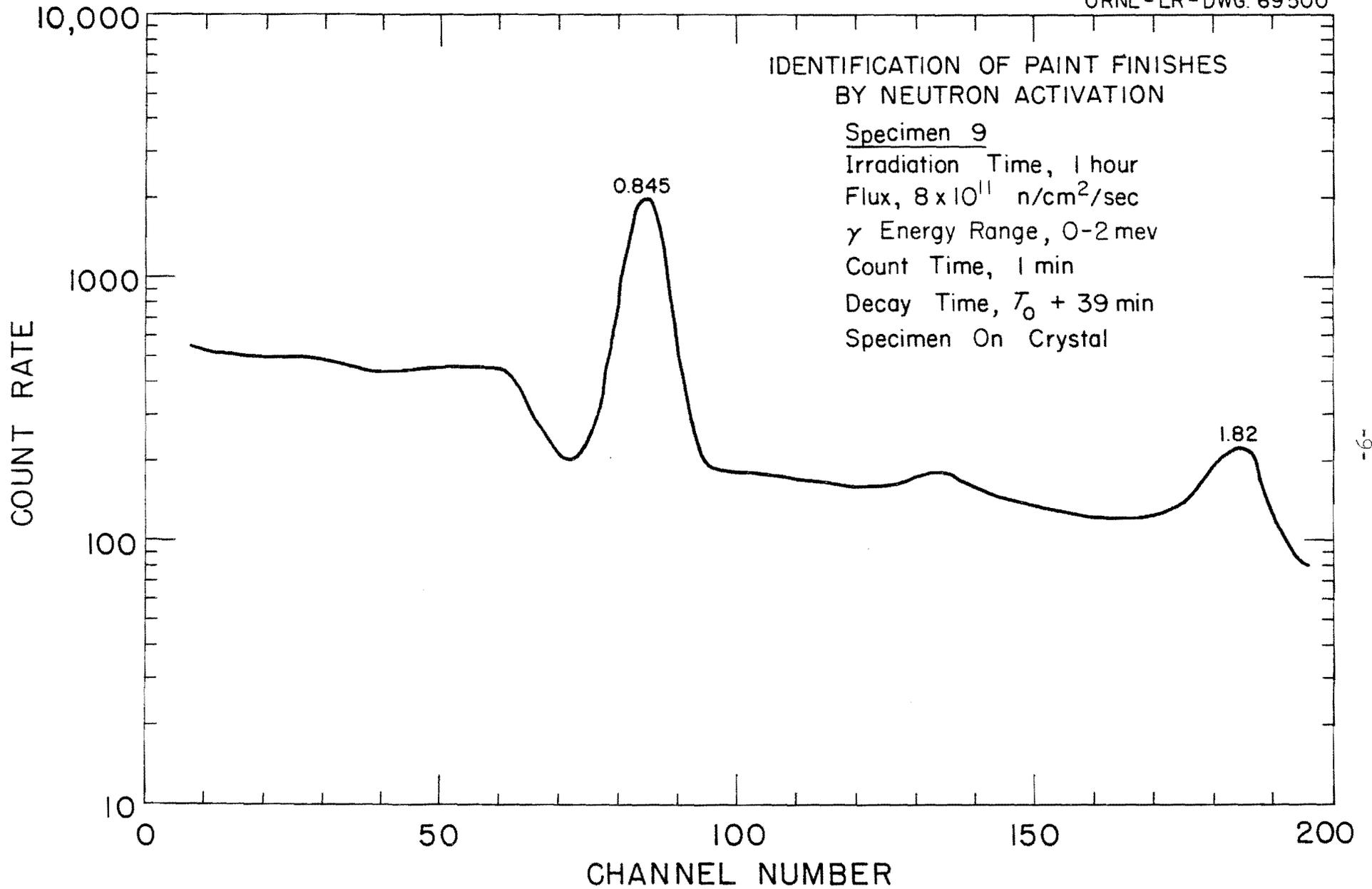


FIGURE 5

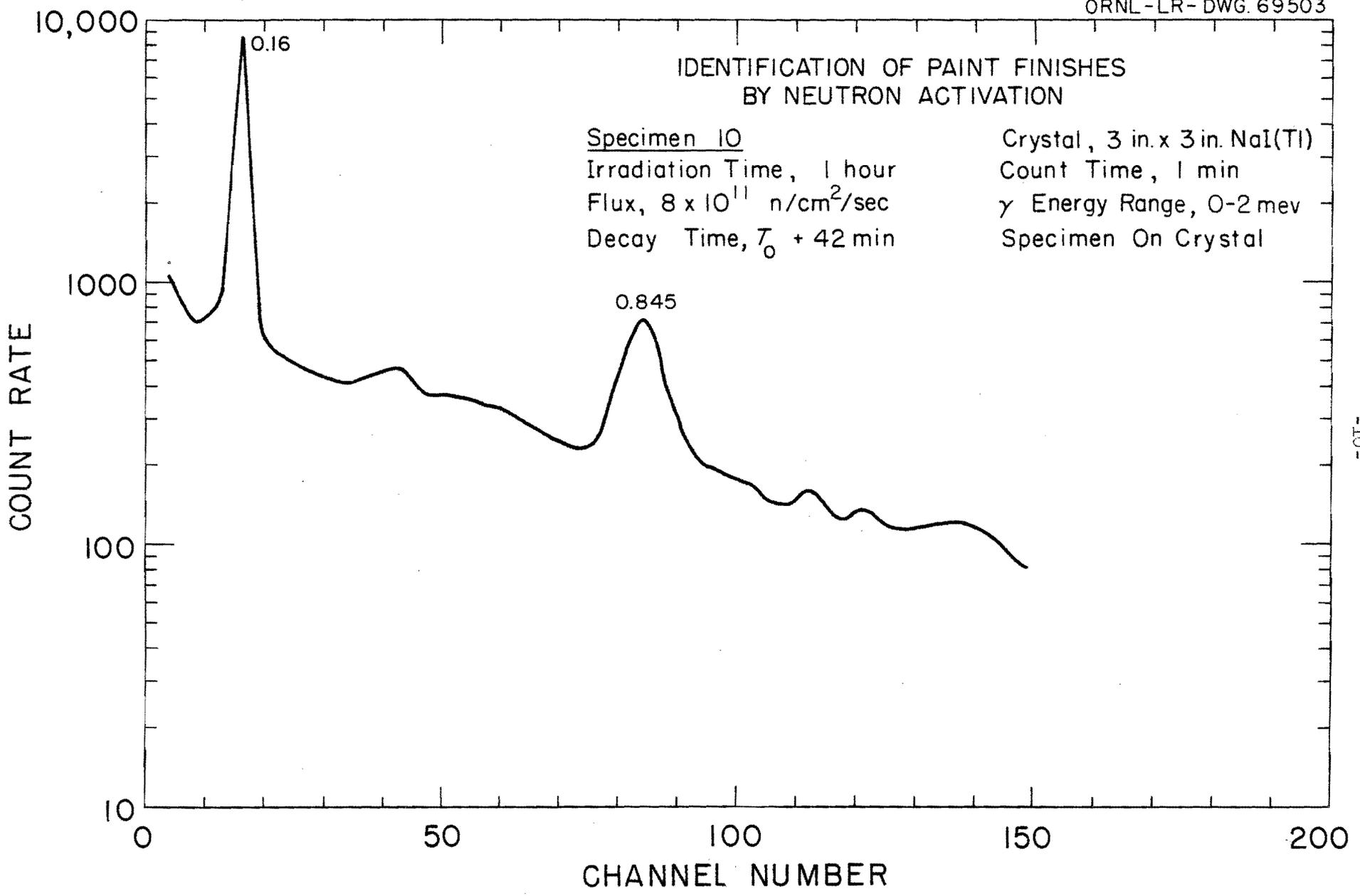


FIGURE 6

decay for about 6 hours before radioactivity measurements were made. This decay time was long enough to allow the short half-lived radionuclides in each sample to decay sufficiently so that radionuclides of longer half-lives could be more easily detected and determined. After these measurements, the samples were allowed to decay, with occasional radioactivity measurements, until the spectra of the induced radionuclide began to show strongly the longer-lived radionuclides. This decay period was for 30 hours.

The specimen was again analyzed by gamma spectrometry, and the spectral data recorded. Additional data were recorded 7 days following reactor discharge, and these gamma-spectral curves are shown in Figures 7 - 14. These curves record the decay of the shorter half-lived radionuclides (the last spectrum "C" in each Figure). Table II lists the stable elements found in the finishes. Also, the relative amount of each radioactive species present may be compared from the spectral data. Apparent peak-height ratios for Ba¹³⁹ to Mn⁵⁶ and Ba¹³¹ to Zn⁶⁵ are also given in Table II. Since all the samples were irradiated in the same neutron flux, the photo-peak heights (radioactivity) for specific radionuclides in one sample may be compared to those found for the same radionuclides in another sample to show the relative abundance of one trace element to another. The intensity of these ratios can be used to identify or selectively separate similar sample materials.

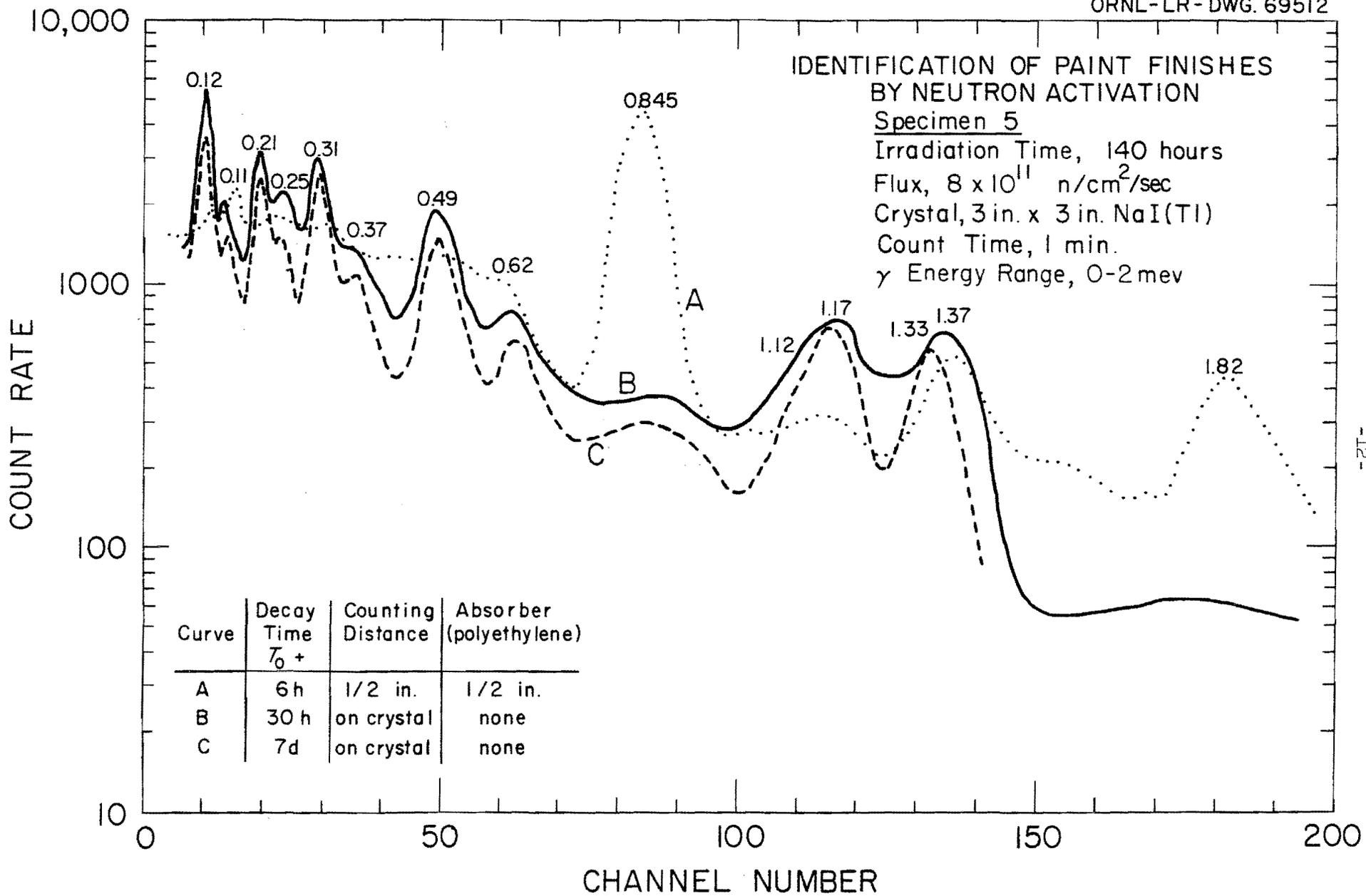


FIGURE 7

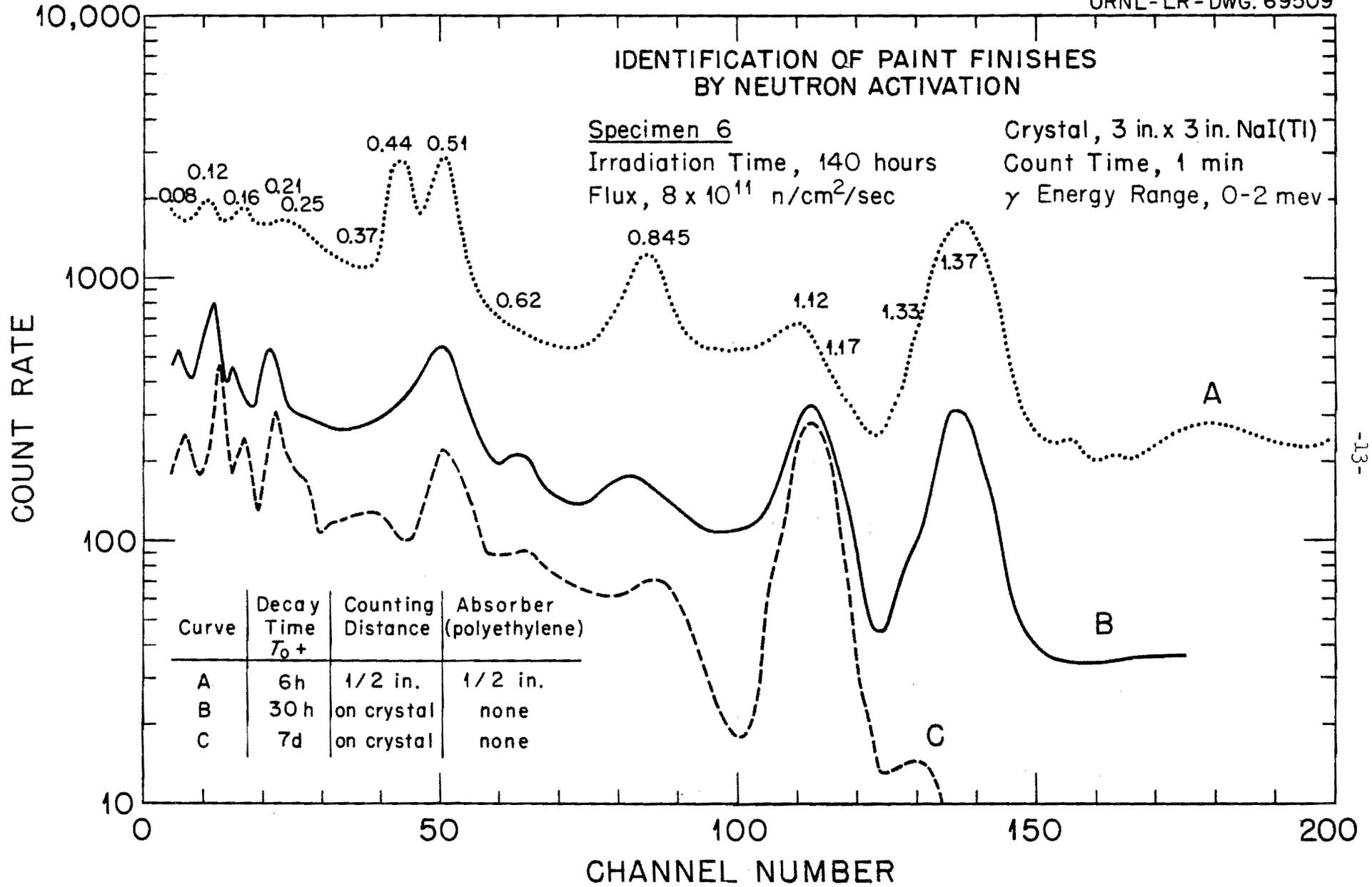


FIGURE 8

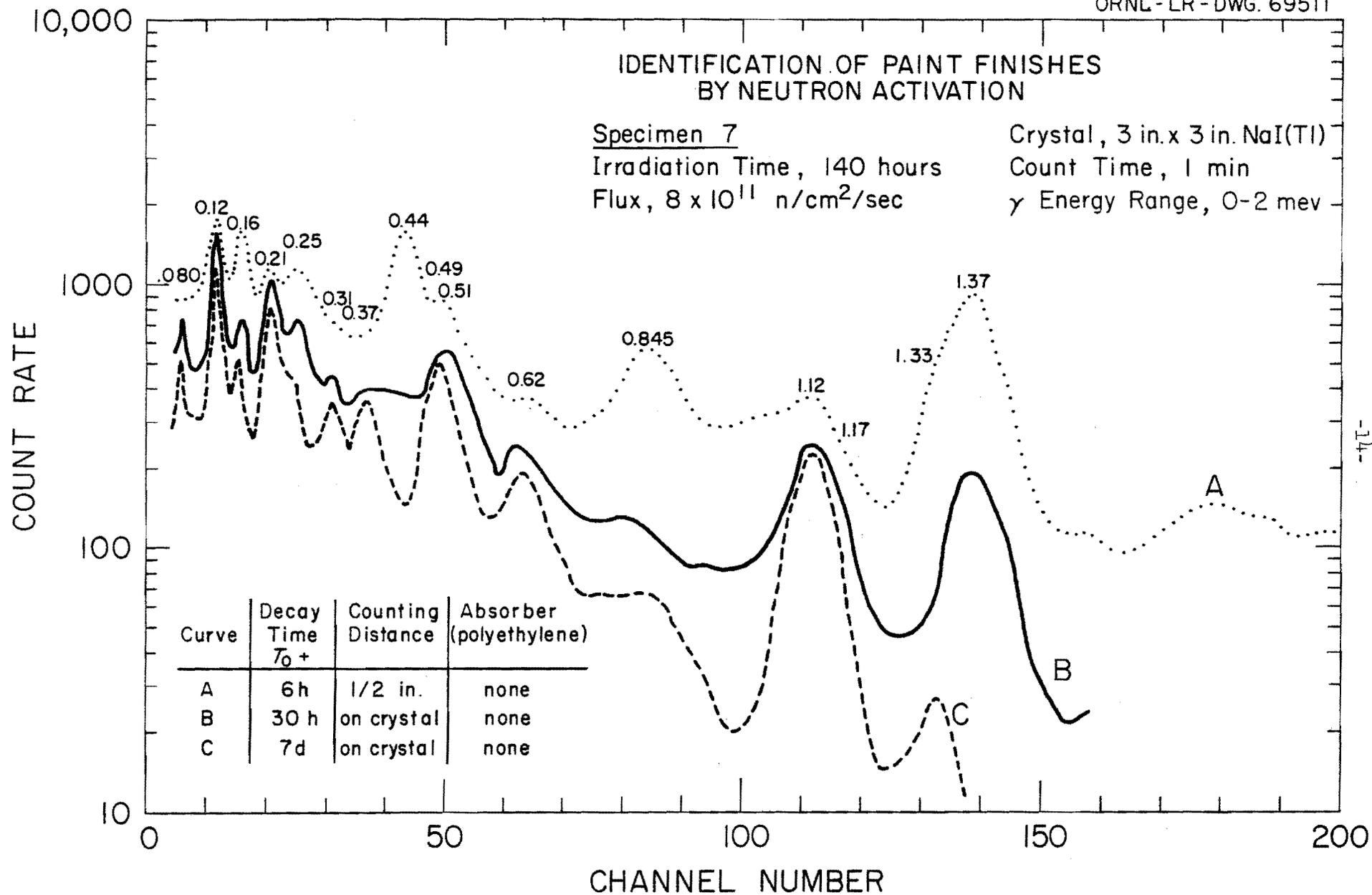


FIGURE 9

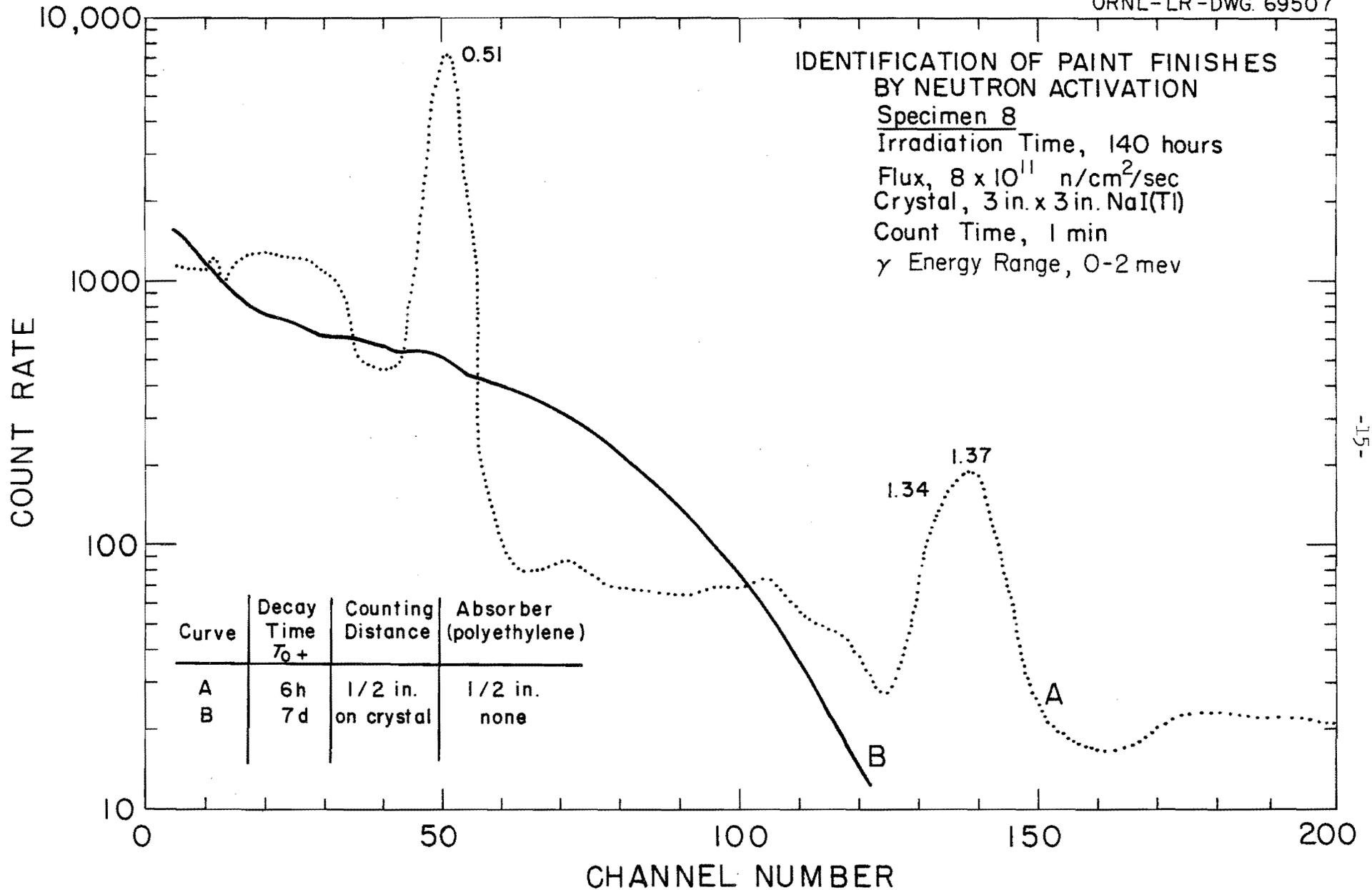


FIGURE 10

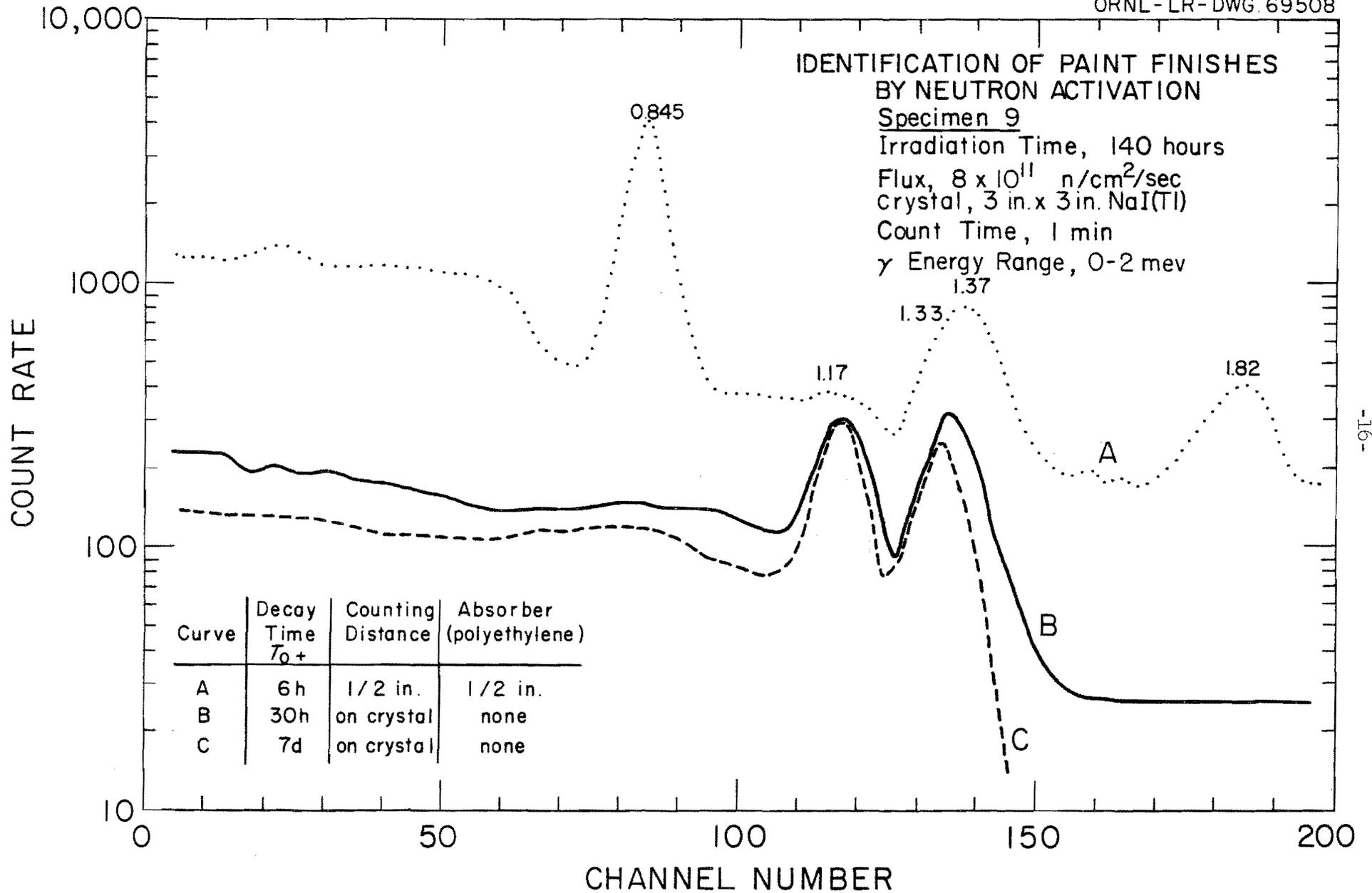


FIGURE 11

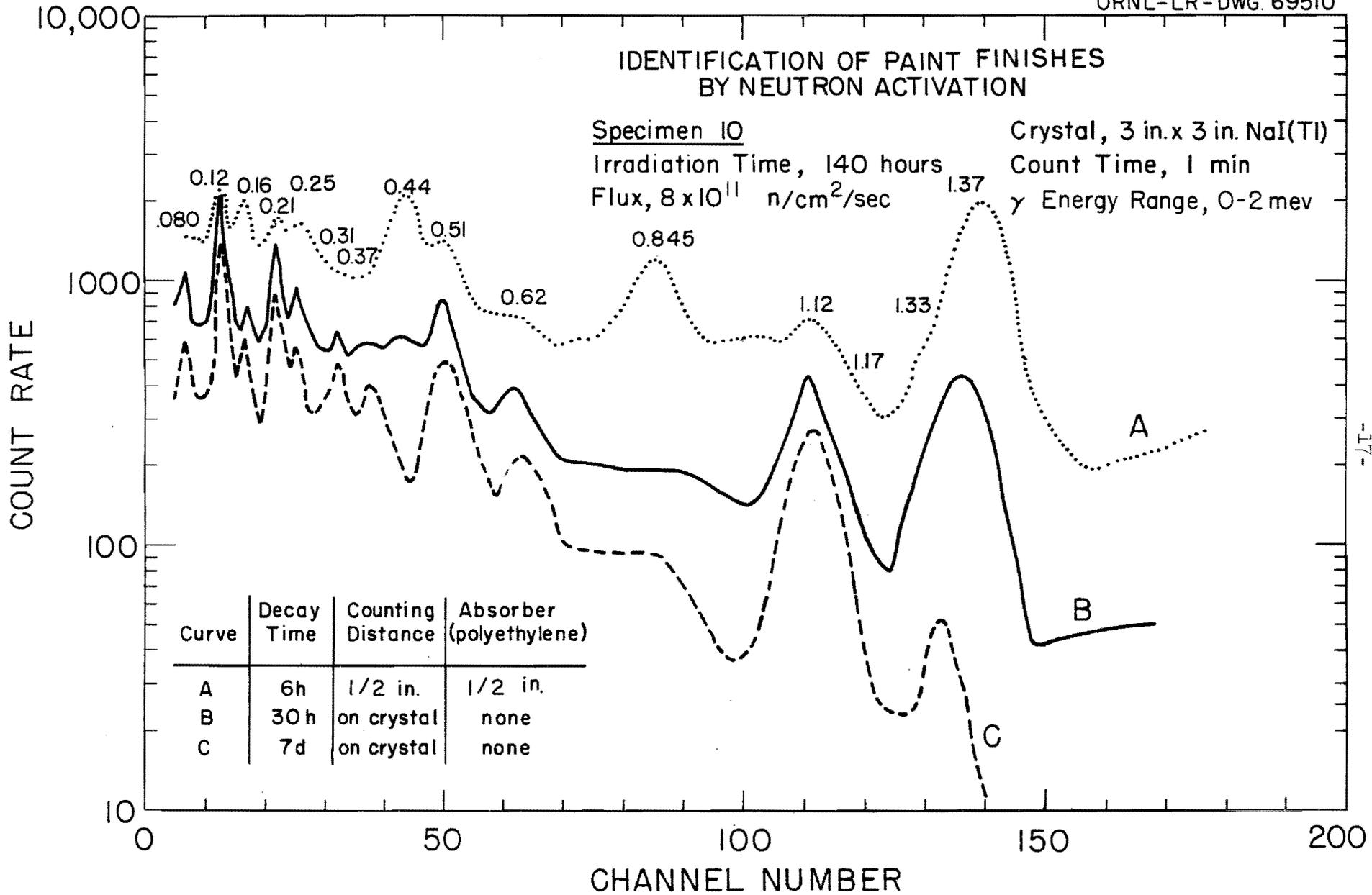


FIGURE 12

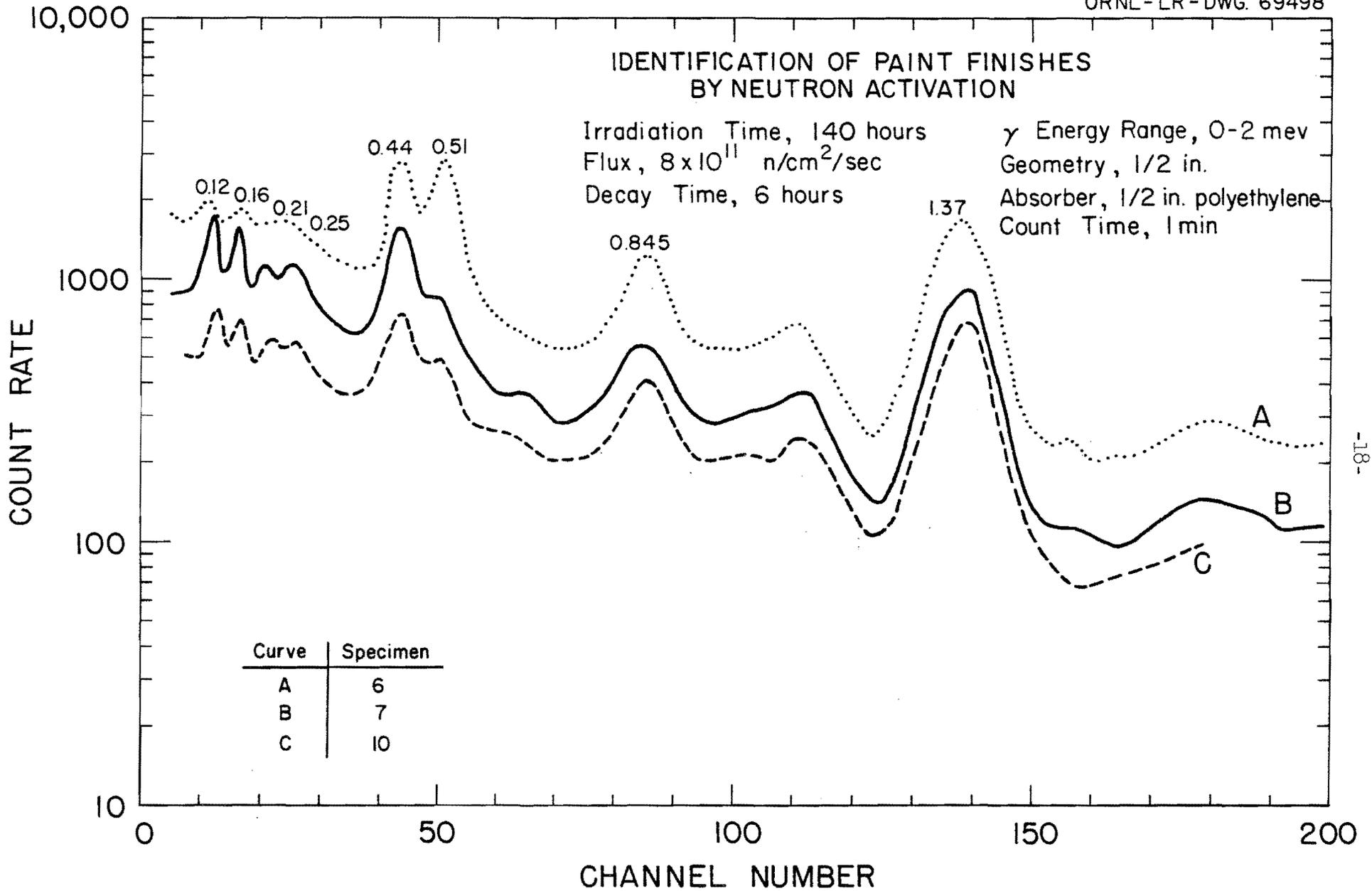


FIGURE 13

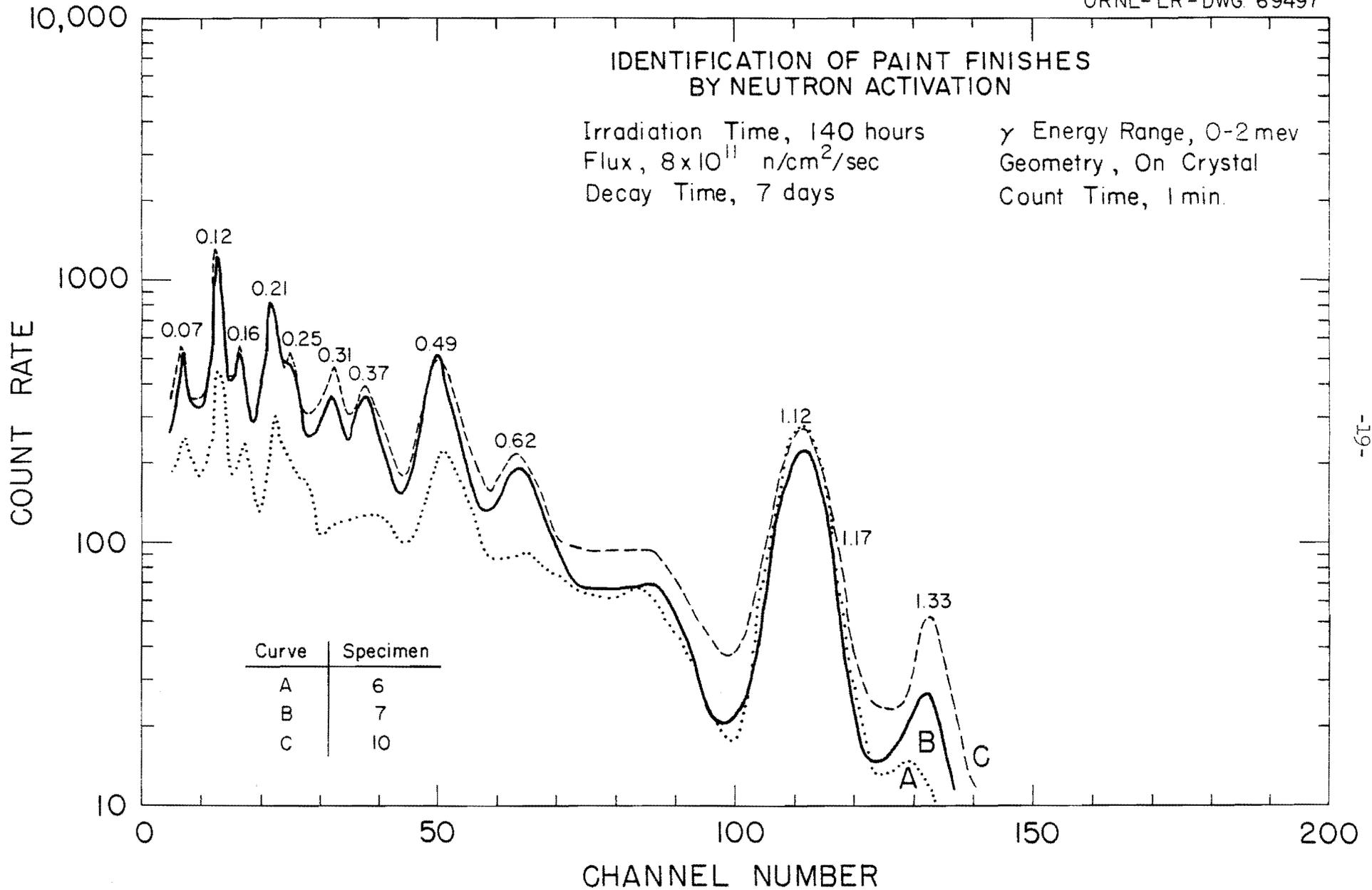


FIGURE 14

TABLE II

ELEMENTS FOUND IN AUTOMOBILE PAINT FINISHES

<u>Paint</u>	<u>Mn</u>	<u>Ba</u>	<u>Zn</u>	<u>Co</u>	<u>Na</u>	<u>Cu</u>	<u>Cr</u>	<u>P</u>	<u>Ba¹³⁹/Mn⁵⁶</u>	<u>Ba¹³¹/Zn⁶⁵</u>
5	P	P	P	P	P		P		2	1.5
6	P	P	P	X	P	X			4	5
7	P	P	P	D	P	X			10	
8					P	P		P		
9	P			P	P					
10	P	P	P	D	P	X			10	5

P = elements definitely present.

X = possible but not definite.

D = detected as present but at limit of detection.

B. Soot and Soil Samples

The soot and soil specimens were treated in the same manner as the paint samples. However, the data shown in Figures 15 - 20 were obtained after a longer decay time to allow a more complex mixture of short-lived radionuclides, to decay away and leave longer-lived radionuclides for gamma spectral measurements.

Discussion

A. The Automobile Finishes

It can be expected that paint will have a homogeneous composition due to the manufacturer's control of the various components used to reproduce colors and textures. In effect, each paint is composed of color agents of very fine particulates that have a controlled particle size and that are homogeneously blended together in a binder material. Thus, two chips of paint from the same product, when neutron irradiated, would have very similar gamma-ray spectrum with the gamma-ray photo-peaks relative to each other. A comparison of these gamma-ray spectra makes it possible to identify paint specimens. For example, Figures 1 - 6 were obtained after a one-hour neutron irradiation and a 30 - 40 minute decay interval. By comparing these spectra, it becomes rather evident that finishes 8 and 9 contain radionuclides of copper and manganese, respectively, which distinguish them from the other specimens. The other four finishes show barium and manganese. Thus, by comparing the relative peak heights (Table II) of Ba¹³⁹ (85 m) and Mn⁵⁶ (2.6 h), these finishes may be tentatively separated into three distinct types. Paints 7 and 10 appear to have identical Ba/Mn ratios. Paint 5 and 6 have significantly different Ba/Mn ratios.

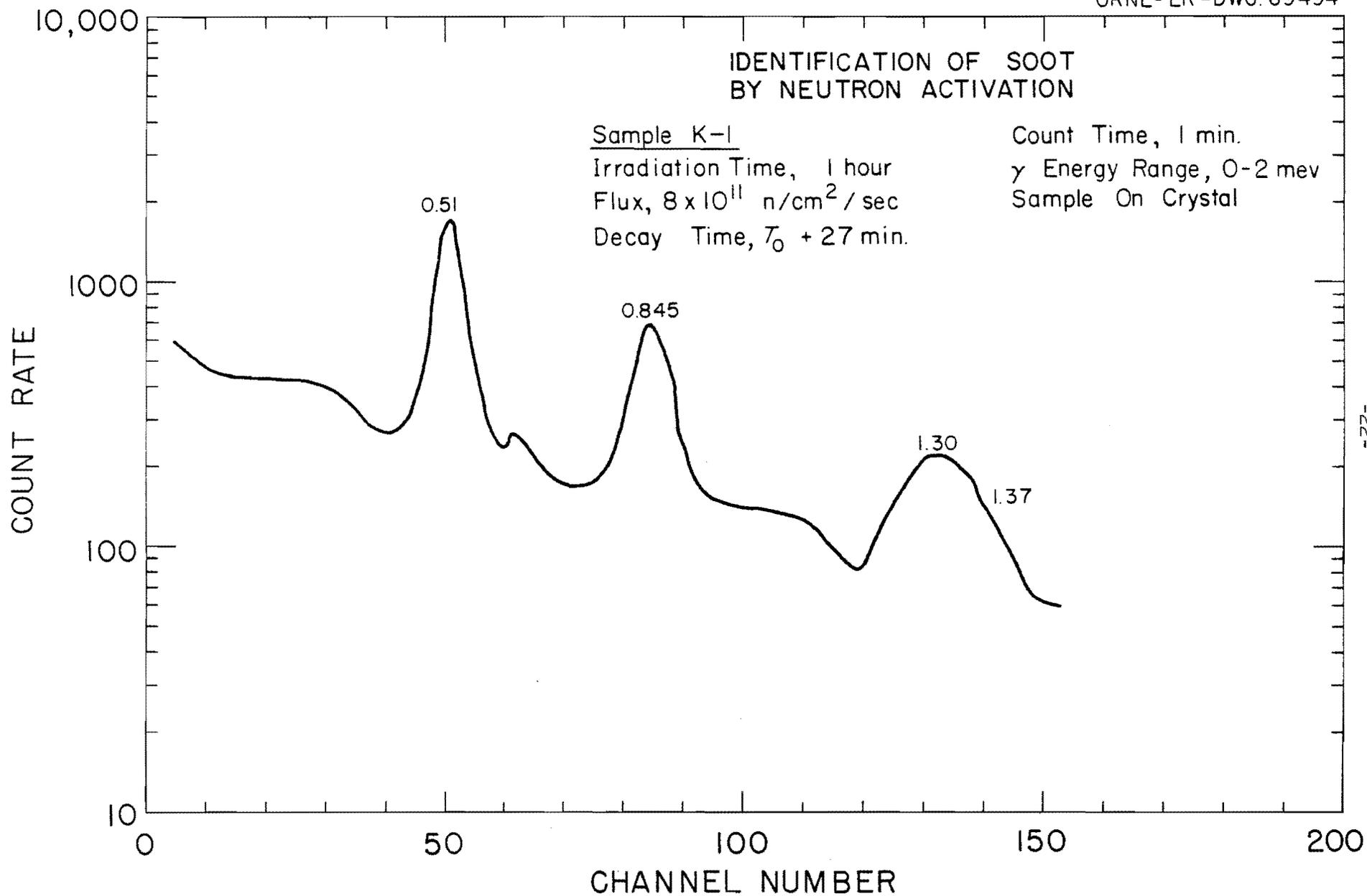


FIGURE 15

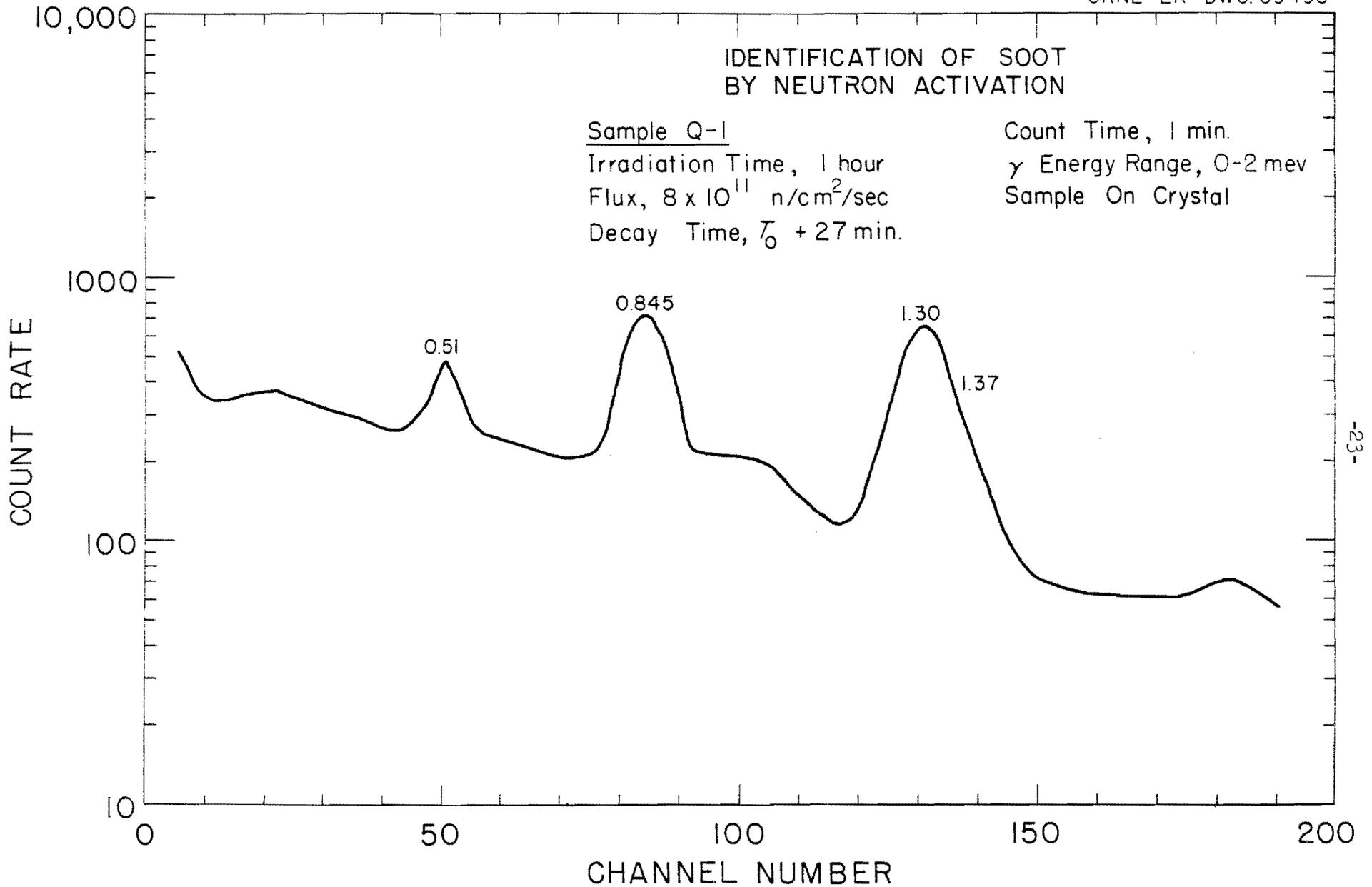


FIGURE 16

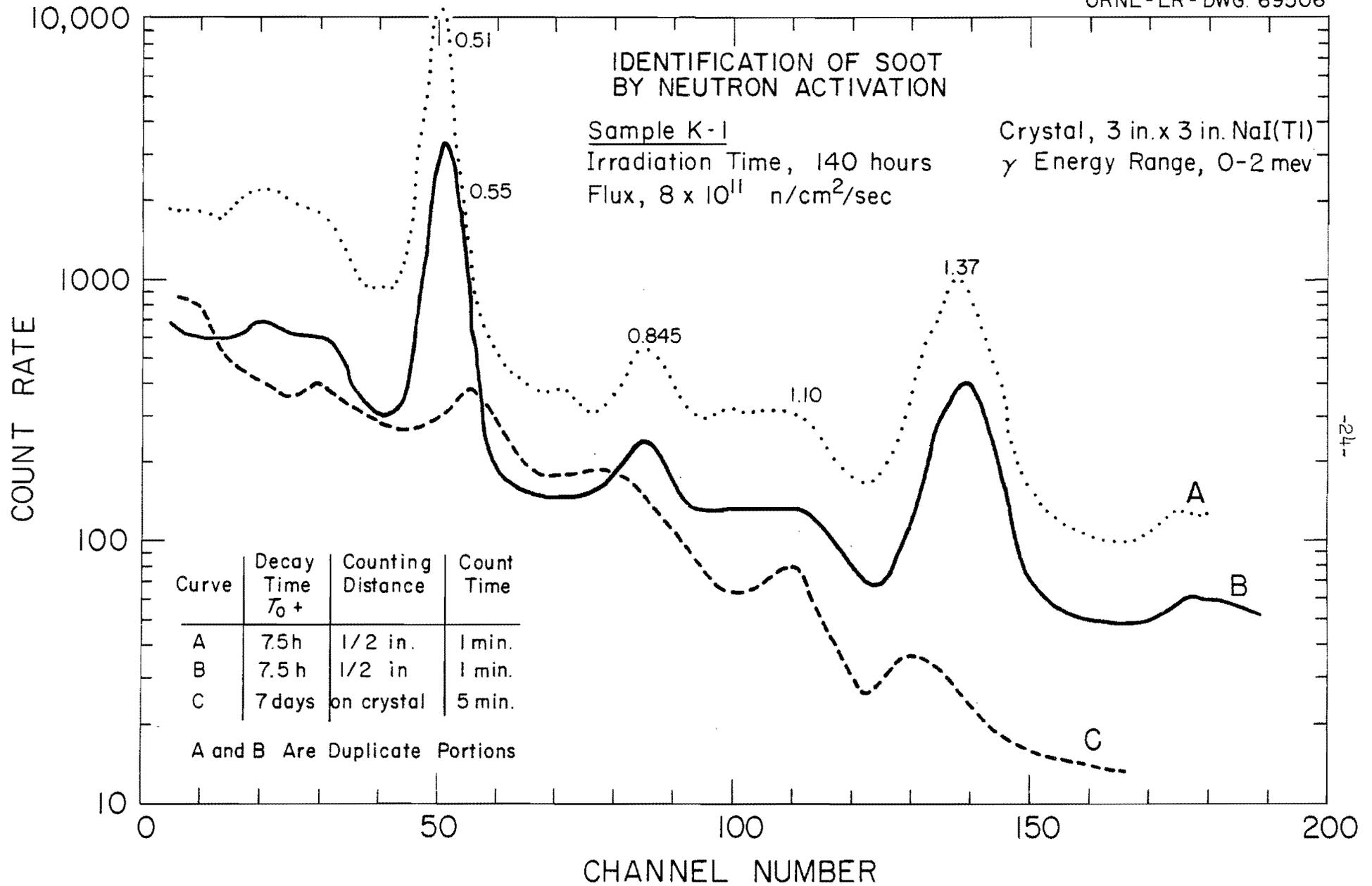


FIGURE 17

-24-

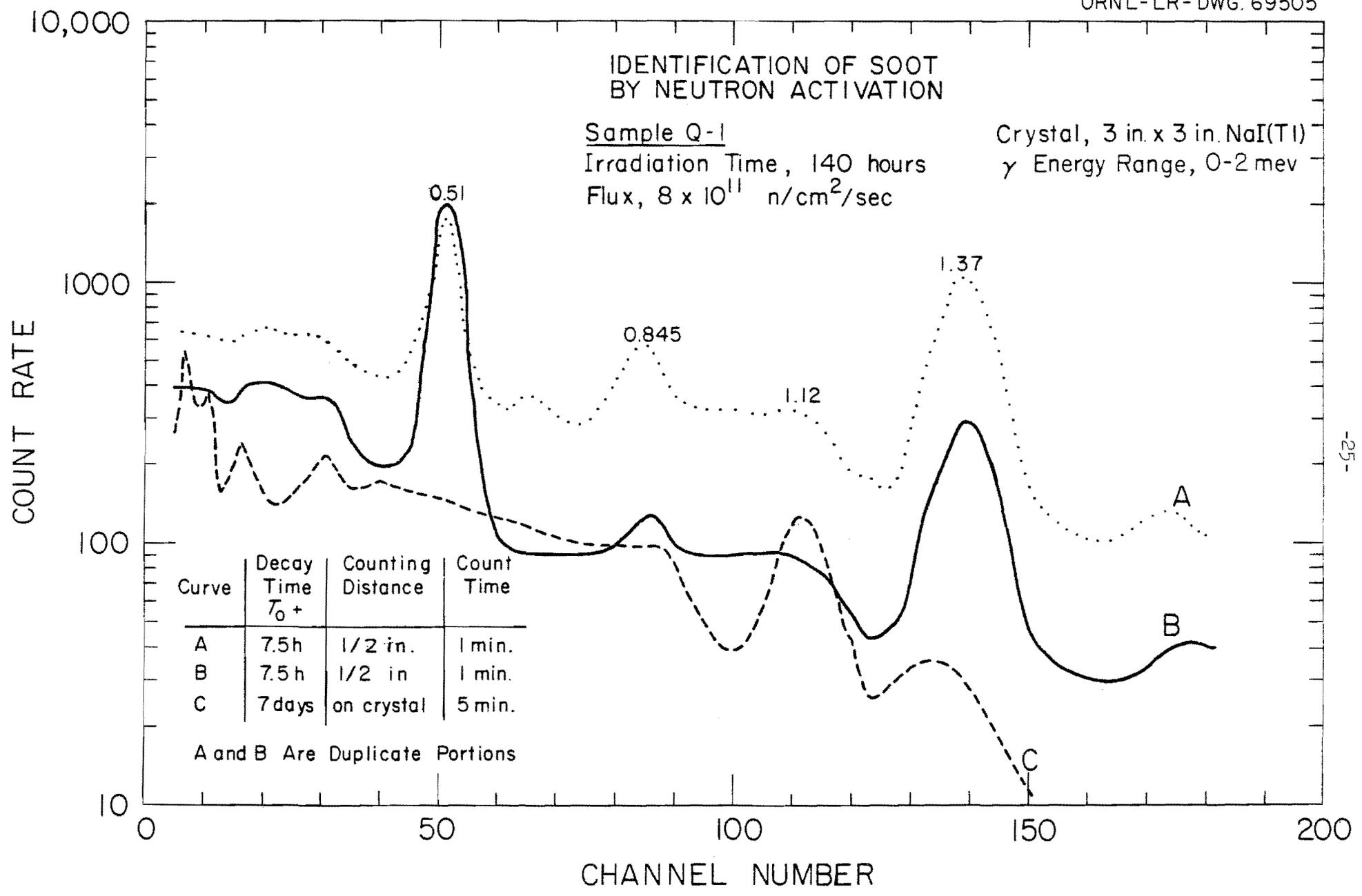


FIGURE 18

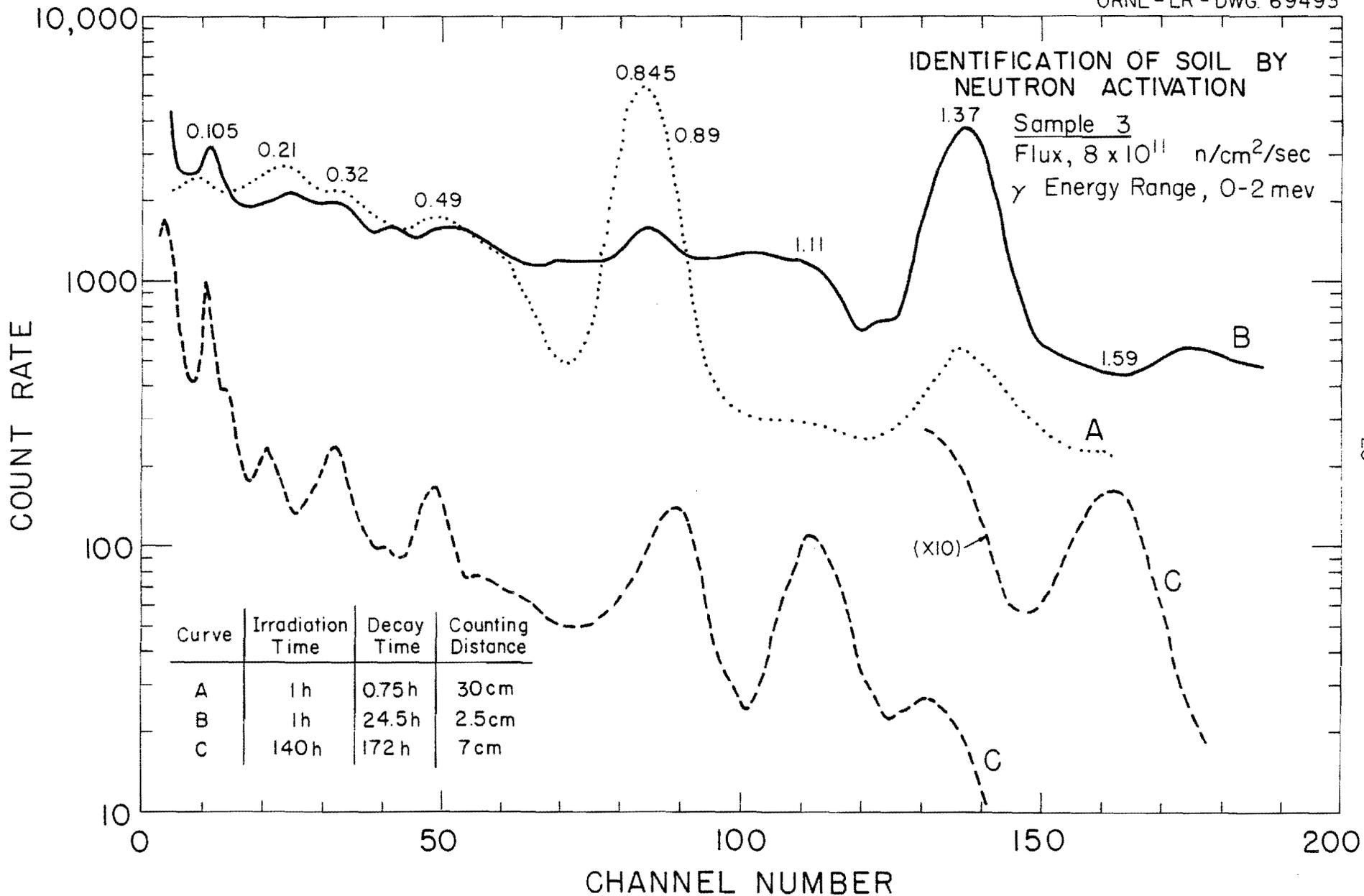


FIGURE 19

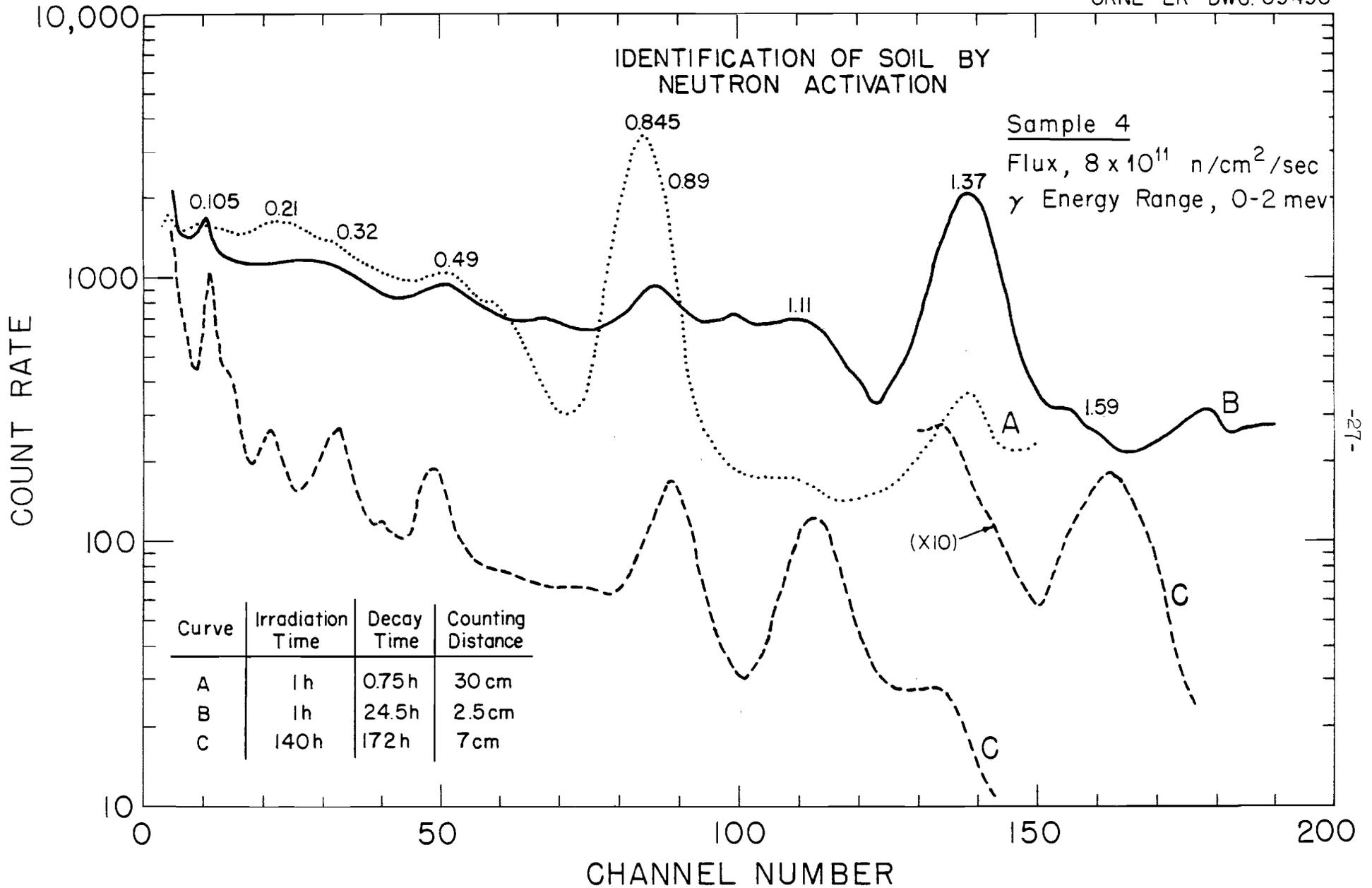


FIGURE 20

Following the 140-hour irradiation, the spectra were recorded after (1) a 6-hour decay, (2) a 30-hour decay, and (3) a 7-day decay (See Figures 7 - 12). In comparing these gamma spectra, it is also observed that finishes 8 and 9 are distinctly different from each other and from the other paint samples. Finish 8 has Cu^{64} (12.8 h) as the only apparent radionuclide after irradiation, but after a weeks decay, only a Bremsstrahlung from beta emission is remaining. After the manganese and sodium had decayed away, Co^{60} was predominant in sample 9. In comparison of sample 5 with the other paints, it is noted that considerable Co^{60} is present, and Zn^{65} can be detected. The other three similar finishes show larger quantities of Zn^{65} present with a trace of Co^{60} . Finish 5 also has a large gamma peak at 0.31 Mev (Cr^{51}), and this peak is very small or absent in the other specimens. Thus, finish 5 may be distinguished from finish 6, 7, and 10. Finish 6 is similar to finish 7 and 10, but the absence of two gamma peaks at 0.31 and 0.37 Mev along with a different ratio of Zn (1.12 Mev) and Ba^{131} (0.12 Mev) indicate that it is not identical with finishes 8 and 10. The gamma spectra of the 140-hour irradiation specimens of finishes 6, 7, and 10, after a 6-hour decay (Figure 13), and after a 7-day decay (Figure 12), further compare these three specimens.

In the comparison of the gamma spectra of finishes 7 and 10 for both the 1-hour and the 140-hour irradiations, it can be noted that their spectra are always identical; hence, it is believed that they are identical finishes.

B. Soot and Soil Samples

The radioactivation analysis data observed for the soot and soil specimens offer some possibilities for identifying origin of the materials. However, it should be noted that after 1-hour irradiation and about 30-minute decay, the gamma spectral curves (Figures 15 and 16) show the soot samples contain the same radioelements, but in different concentrations (as can be seen from the difference in the relative peak heights). The radioelements present in these samples, after a 1-hour irradiation, were copper-64, manganese-56, and sodium-24.

After 140-hours irradiation of duplicate portions of the soot samples and a 7.5 hour decay, each portion was again analyzed. From the relative peak heights displayed by Curves A and B in Figures 17 - 18, it is possible to conclude that sample (Soot K-1) is homogeneous and the other is nonhomogeneous (Soot Q-1). A comparison of the relative peak heights at 0.51 Mev and 0.84 Mev (Cu^{64} and Mn^{56}) indicates that it is not homogeneous. Curve C on the same figures was prepared after a 7-day decay; the duplicate samples were counted together in order to have enough radioactivity to measure. Sample K-1 contained P^{32} and Sb^{124} , and sample Q-1 contained mostly Zn^{65} . From these data, it has been concluded that this difference is either due to the nonhomogeneity of the samples or that the samples have originated from two separate places.

The soil samples were analyzed in a similar manner. The original data taken after 45-minutes decay; the only radioactivity observed at this time was 2.6 h Mn^{56} (Curve "A" in Figures 19 and 20). The spectra designated as B in these Figures were prepared after a 24.5-hour decay showing that the Mn^{56} has almost decayed out leaving only Na^{24} (14.97 h)

present. Curve "C" in these figures was prepared after one week's neutron irradiation and a week's decay. At this decay time, Na^{24} would have decayed away almost completely so that each spectrum would be composed of only long-half-lived components having half-lives greater than 15 hours. The comparison of these spectra from each soil indicates that the soils are very similar in composition since their gamma spectra are identical.

Conclusions

From the foregoing study, it can be concluded that activation analysis is a useful technique for the forensic scientist. The six black automobile finishes investigated have been easily separated into five distinct groups by the trace elements present. By applying this analytical technique, it may be possible to separate other paints which cannot be differentiated by the more conventional methods. The experiments on the soil and soot specimens show that similar possibilities exist for other law enforcement materials.

From this study a new approach is attained in the identification of physical evidence for law enforcement. The practicality of the technique can be enhanced by using very short irradiation periods followed by a gamma-spectral measurement within seconds after the irradiation so that it is possible to observe the induced radioactivity of very short half-lived radioelements. The results of this study have all been obtained by nondestructive methods so that the samples are still in the same state as when received and may be used in further tests, if necessary.

APPENDIX A

Radioactivation Analysis

The method of radioactivation analysis^(5,6,7) involves the irradiation of the sample being investigated in a nuclear reactor or in some apparatus capable of producing nuclear particles. Through interactions between nuclear particles and stable nuclei, radioactive isotopes of the element being determined are produced. A typical example of such a reaction is that wherein a neutron interacts with Cl^{37} , a stable isotope of chlorine, to produce the radioisotope Cl^{38} .



This reaction can be abbreviated to



Cl^{38} decays with a half-life of 37 m to stable A^{38} , emitting beta and gamma radiations as it decays. The decay properties, i.e., half-life and the energies of the emitted radiations, establish the radioisotope's identity and can then be used to determine the quantity of the stable source element.

Neutron radioactivation analysis is the most used method of radioactivation analysis.⁽⁵⁾ At least 70 of the elements can react with neutrons having an energy of 0.026, i.e., slow, or thermal, neutrons, to produce radionuclides that are usable in completing a radioactivation analysis. The half-lives of these radionuclides vary from the order of a few tenths of a second to several years. The radiation energies these radionuclides emit as they decay also vary.

The amount of radioactivity exhibited by a radionuclide at the end of a nuclear particle interaction is given by the equation

$$A = f \sigma_{ac} NS \quad (3)$$

where A = the amount of radioactivity, as disintegrations per second,

f = the number of nuclear particles (flux) bombarding the nuclei in the sample, as particles/cm²/sec,

σ_{ac} = the "activation" cross-section for the nuclear reaction, barns, 10⁻²⁴ cm² per target atom,

N = the number of target atoms,

S = 1 - e^{-λt} = the "saturation factor" or the ratio of the amount of radioactivity produced in time, t, the deviation of irradiation in seconds, so that produced in an infinite time, λ = the radioactivity decay constant for the radionuclide formed, based upon the relationship λ = 0.693/t_{1/2}.

Since the rate of radioactivity formation is constant and the number of target atoms do not change during the irradiation, equation 3 can be rearranged to give an equation for the determination of the amount of element.

$$W = \frac{AM}{(6.02 \times 10^{23})(f)(\theta)(S)(D)\sigma_{ac}} \quad (4)$$

In this equation, W = weight of element in grams; M = the atomic weight of the stable element; θ = the abundance of the particular isotope of the stable element reacting with the nuclear particle source; and D = e^{-λt} = a factor for the decay of the radionuclide; where T = the decay time (in seconds) from the end of the irradiation to the time of the radioactivity measurement.

From these equations, it can be seen that the amount of radioactivity produced (and, therefore, high sensitivity) is chiefly influenced by the number of nuclear particles available for bombarding the stable nuclei and the activation cross-section of the nuclear reaction. The half-life of the induced radionuclide, and the length of irradiation are minor influences.

Radioactivation Analysis Methods

Any nuclear particle-neutrons, protons, deuterons, alphas, and gammas - capable of entering into an interaction with the nuclei of an element can be used to initiate a radioactivation analysis. However, it is significant to note that the use of all other particles, except neutrons, has been limited. Several reasons can be cited for explaining this lack of usage. For example, the heat dissipated within the chamber of an accelerator like a cyclotron as well as the small area of the charged particle beam available for activation have minimized the use of such devices for radioactivation analysis. Another difficulty with the use of charged particle accelerators is that many different nuclear reactions can occur simultaneously during an irradiation so that competitive reactions greatly influence the ease with which an element can be determined. Another factor in favor of neutron radioactivation analysis is that, after 1950, nuclear reactor facilities became more readily available to most researchers and the rigid requirements of sample type and sample sizes that could be irradiated were relaxed. In addition, newer reactors have provided much more intense neutron sources. Likewise, the development of techniques for inserting neutron producing targets into

Van de Graaff accelerators have contributed to the increased use of neutron radioactivation analysis. The simple neutron capture reactions, n,γ , are the most used neutron reactions in activation analysis;^(5,8) however, other types of neutron reactions, such as n,p and n,α , may yield significant quantities of radionuclides.

Procedure of Analysis

Activation analysis can be used as both a qualitative and quantitative technique. The usual procedure followed in a radioactivation analysis consists of (1) sample irradiation, (2) post-irradiation processing, (3) radioactivity measurements, and (4) the identification of the induced radionuclide. More specific details about these steps are presented below. A quantitative analysis for the amount of any stable element present in the sample can be accomplished by irradiating a standard or comparator sample with the unknown sample. The standard contains a known quantity of the element being determined and is processed in the same manner as the unknown sample. A direct comparison of the radioactivity in each sample makes it possible to determine the stable element concentration in the unknown. This relationship is as follows:

$$\frac{W \text{ in unknown}}{W \text{ in comparator}} = \frac{A \text{ in unknown}}{A \text{ in comparator}} \quad (5)$$

Corrections for chemical yield (if a radiochemical separation is made), radioactive decay, and sample weights must be considered in Equation 5.

The following information is more specific for the applications cited in this report.

1. Irradiation of Samples: In the method of analysis followed in these applications cited here, all of the samples were irradiated in a neutron flux of 8×10^{11} n/cm²/sec. Each sample was placed in a small polyethylene vial for the irradiation. Varied periods of irradiation were used; no irradiation exceeded 150 hours.

2. Post-Irradiation Processing of Samples: Two techniques of analyzing the irradiated samples can be followed. One involves a direct, or nondestructive measurement of the sample's radioactivity by means of a gamma scintillation spectrometer.⁽⁶⁾ The other technique involves the use of a radiochemical analysis.⁽⁸⁾ In this technique, the sample is usually dissolved in a mineral acid and a known amount of stable element added as a "carrier" to the solution. An isotopic exchange of the radioactive species with the stable element makes it possible to carry the radionuclide through chemical manipulations. Precipitation, solvent extraction, ion exchange, distillation, etc., techniques may be used in this radiochemical processing.

3. Radioactivity Measurements: Gamma scintillation spectrometers of the 20- and 200-channel types are most frequently used to make a radioactivity measurement.⁽⁶⁾ A solid, 3 x 3-inch NaI (thallium-activated) crystal served as the detector for the gamma radiations. Decay measurements assisted in identifying the radionuclides.

Advantages and Limitations

The results obtained in the development of radioactivation analysis indicate that activation analysis is extremely sensitive for many elements and possesses limits of measurement for many elements that are far below

the range of other chemical and physical methods of analysis. For instance, neutron fluxes of 8×10^{11} n/cm²/sec give a range from 0.00001 to 10 ppm for at least 70 of the elements. Increased neutron fluxes, i.e., greater than 10^{13} n/cm²/sec, will greatly enhance the limits of measurement obtainable by neutron radioactivation.

Radioactivation analysis is a very specific method of analysis in that the radionuclides of an element produced by a nuclear particle reaction disintegrates in a manner unique only to that radioactive species. The characteristic half-life of the radionuclide and the type of radiations emitted in its decay are never exactly duplicated by any other radionuclide product so that it is possible to identify and measure the radioactivity of interest without too much difficulty.

Radioactivation analysis is also greatly favored because of its almost complete freedom from spurious contamination that is most common with other analytical methods. Contamination is not a serious problem in radioactivation analysis unless the trace element is added to the sample in some manner before the nuclear particle irradiation; contamination in very high orders of magnitude can be tolerated after the irradiation without seriously affecting the analysis.

The limitations of radioactivation analysis have been recognized.⁽⁸⁾ These may be tabulated as being physical, chemical, and nuclear. The limitations established in this evaluation also apply for all methods of radioactivation analysis regardless of the type of nuclear particle used. The size of the irradiation facility available for irradiation and its temperature levels are usually considered as physical limitations. Generally, the irradiation facilities will vary with the type of nuclear-

particle-producer available. For example, in the nuclear reactors at Oak Ridge National Laboratory (ORNL), at least 12 different types of containers are used to irradiate sample materials. These include 1-dram glass or plastic vials, metal cans, plastic cartridges, and polyethylene bottles (maximum size, 8-ounce). Similarly, the thermal temperature within each facility will vary, and, in most instances, only solid samples can be irradiated. However, in one of the reactors at ORNL it has been possible to use a water-cooled facility to irradiate gaseous, liquid, and solid samples. The temperature in this facility normally is about 40° C.

With regard to chemical limitations, any experimenter using radiochemical separation methods for the isolation of a desired radioelement recognizes the need for obtaining a radiochemically pure radionuclide, i.e., a radionuclide free of radioactive contaminants, to use in completing an analysis. Examples of many radiochemical separation methods are cited throughout the literature on radioactivation analysis.

Nuclear Limitations must always be considered in the type of sample being analyzed. Most sample materials when analyzed have been found to be virtually transparent to any impinging nuclear particle. However, in those instances where the sample containing a relatively large amount of some neutron-absorbing material with a high cross-section, a nuclear particle flux attenuation or slowing down of the particles as they pass through the sample can result in a lower production of radioactivity than should be expected, since the inner atoms of the sample are exposed to a lower nuclear particle flux than the atoms on the outer layers of the samples. Appreciable absorption or self-shielding can be minimized

either (1) by analyzing a smaller sample, or (2) by diluting the sample material with a low cross-section diluent, or (3) by using comparator samples made up to contain a known amount of the element being analyzed for in a mixture containing an amount of the nuclear particle absorbing material equal to that contained in the unknown sample, or (4) by correcting for self-shielding by means of a suitable calibration curve.

Another limitation sometimes encountered in radioactivation analysis is imposed by the production of the same radionuclide by some other type of nuclear reaction or by a second nuclear particle reaction upon the stable decay product of the radionuclide produced in the original nuclear reaction. In these situations, it is possible to circumvent these limitations by special techniques. The trace element may be separated by chemical means prior to irradiation and the separated material subsequently activated by irradiation or a nuclear particle source essentially free of nuclear particles capable of producing the unwanted nuclear reactions can be used for irradiating the sample or a differential counting technique can be utilized. For example, thallium sulfide has been used as a carrier agent for manganese-55 in order to determine microgram amounts of manganese in iron. The radioactivity produced by the primary particle reaction $\text{Mn}^{55}(\text{n},\gamma)\text{Mn}^{56}$ is greatly distorted by the Mn^{56} radioactivity produced by the fast neutron reaction $\text{Fe}^{56}(\text{n},\text{p})\text{Mn}^{56}$. Thus, by putting the unknown sample into solution, adding a known amount of thallium as a carrier agent, subsequently precipitating the thallium plus manganese as a sulfide and then irradiating the separated sulfide in a neutron flux for several hours, it was possible to determine the manganese

content of the iron sample. Following the irradiation, the Mn^{56} was separated by a radiochemical analysis method. Similar precipitation techniques must be used if phosphorus is to be determined in silicon and its compounds. Long irradiation periods are required in a radioactivation analysis for P^{31} and appreciable amounts of P^{32} (14.3 d) can be produced by the radioactivation of the stable P^{31} formed from the decay of Si^{31} (2.6 h) produced in the activation of Si^{30} by the neutron reaction $\text{Si}^{30}(\text{n},\gamma)\text{Si}^{31}$.

Examples of the production of the same radionuclide by another nuclear reaction can be had in determining microgram amounts of sodium in aluminum. The primary nuclear reaction is $\text{Na}^{23}(\text{n},\gamma)\text{Na}^{24}$; however, Na^{24} (15 h) is also produced by the fast neutron reaction $\text{Al}^{27}(\text{n},\alpha)\text{Na}^{24}$.

As a further example of another nuclear limitation, it is known that whenever microgram amounts of arsenic are being determined in germanium and germanium tetrachloride by the thermal neutron reaction $\text{As}^{75}(\text{n},\gamma)\text{As}^{76}$, compensation must be made for the production as As^{77} (40 h) by the neutron $\text{Ge}^{76}(\text{n},\gamma)\text{Ge}^{77} \xrightarrow[\beta^-, \gamma]{12 \text{ h}} \text{As}^{77}$. This difficulty has been resolved by using differential counting techniques involving beta and gamma counting to measure the radiations being emitted by the two arsenic isotopes.

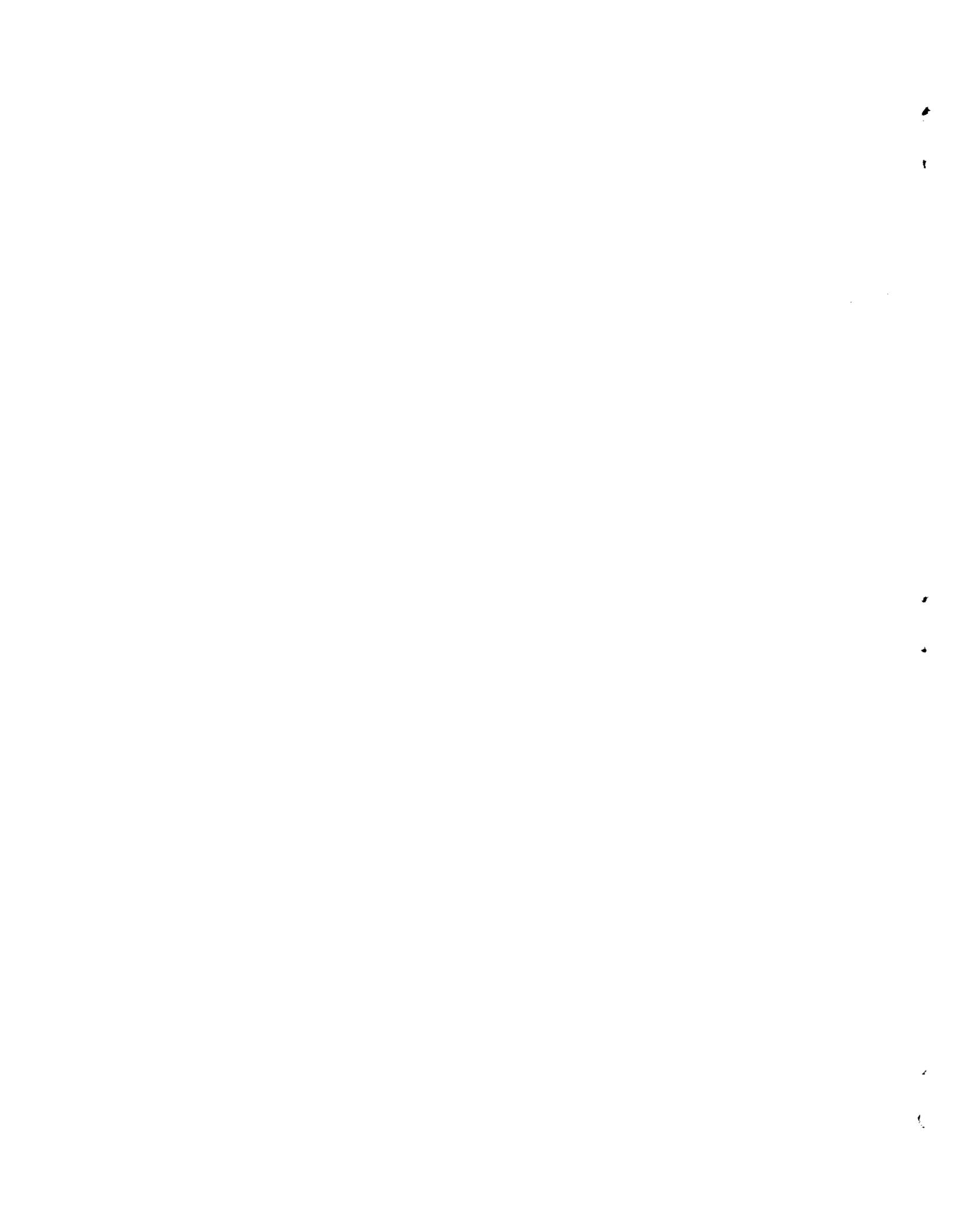
As these examples show, it is possible to overcome most of the problems based upon nuclear limitations. The analyst can best assist in this by carefully studying the requirements for each analysis and using techniques and adaptations whereby practical applications can be made of the methods of radioactivation analysis.

The chief significance of the use of neutron activation analysis is that it can be utilized for measuring trace elements, either in conjunction with or independently of more conventional methods of analysis. Activation analysis can be used in the analysis of many diverse materials and it is apparent that much information can be obtained in relation to trace element behaviors; none of which can be determined easily by any other analytical method. One of its most distinctive features, namely, is that trace contaminants in reagents used in the analysis do not cause difficulty in activation, makes it possible for radioactivation analysis to be a valuable method in calibration of reference samples used as standards for other chemical analysis methods.

It is to be expected that a radioactivation analysis program can be a part of any analytical chemistry laboratory, because many reactors of various types are now in operation and could be used as convenient nuclear particle sources. Likewise, usable sources of nuclear particles can be obtained from nuclear generators already on the market or being developed. Also, laboratory requirements for physical equipment and radioactivity measurement devices are not rigid even if the laboratory is some distance from a reactor. Thus, radioactivation analysis, especially with neutrons, can rapidly achieve an important place in the analytical chemistry necessary for use in many research areas.

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