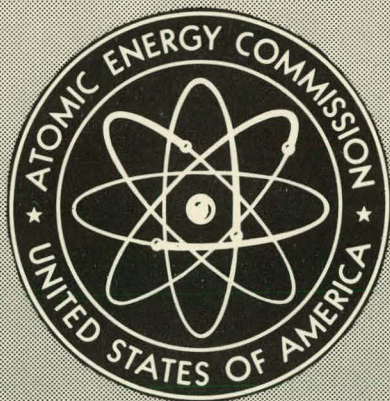


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GA - 5556

APPLICATION OF NEUTRON ACTIVATION ANALYSIS IN SCIENTIFIC CRIME DETECTION

18 - Month Summary Report for the Period May 1, 1962,
Through October 31, 1963

By
D. E. Bryan
V. P. Guinn

July 27, 1964

John Jay Hopkins Laboratory for Pure and Applied Science
General Atomic Division
San Diego, California

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DIVISION OF
GENERAL DYNAMICS

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CHEMISTRY
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**APPLICATION OF NEUTRON ACTIVATION ANALYSIS
IN SCIENTIFIC CRIME DETECTION**

18-MONTH SUMMARY REPORT

For the Period May 1, 1962, through October 31, 1963

Prepared under
Contract AT(04-3)-167
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U.S. Atomic Energy Commission

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July 27, 1964

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ABSTRACT

During the initial 18-month period of this investigation of applications of high-flux neutron activation analysis (NAA) in the field of scientific crime detection, many promising developments have evolved. A highly reliable NAA method has been devised for the detection of gunshot residues on the gunhand of a person who has recently fired a gun, based on the detection of microgram and submicrogram traces of barium and antimony deposited on the back of the gunhand from the detonation of the cartridge primer. A wide variety of manufactured products, such as automobile grease, automobile tire rubber, glass, paper, paint, and plastics, from different manufacturers of essentially the same product have been shown to display clearly recognizable differences in their minor-constituent and trace-level element contents. These findings have considerable potential application in the investigation of hit-and-run, burglary, and various other types of criminal cases. It has also been shown that numerous naturally occurring materials of forensic interest, such as soils and hair, also display characterizing differences in their trace-element compositions when examined by means of high-flux NAA. Emphasis has been placed, wherever possible, on the use of the purely instrumental, nondestructive form of NAA, based upon multichannel gamma-ray spectrometry of activated samples, since this technique is faster than the more detailed radiochemical-separation form of the method, it preserves the samples (for possible introduction in court), and its results lend themselves readily to graphical presentation in court.

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I. INTRODUCTION

In searching for possible fields of application in which the ultra-sensitivity of high-flux neutron activation analysis (NAA) might be especially useful, the field of criminalistics (scientific crime detection) loomed large as a possibility. During 1961, discussions were held on this subject with Mr. Ray H. Pinker, Chief Criminalist of the Los Angeles Police Department and a widely recognized authority in the field of criminalistics. The various kinds of physical evidence frequently encountered in criminal investigations were considered in relation to the potential value of an ultra-sensitive means of elemental analysis with such types of materials. These discussions quickly led to the conclusion that a great variety of such materials would be very promising candidates for a more sensitive method of elemental analysis than the methods presently available to the crime detection laboratory.

The tremendous detection sensitivity of neutron activation analysis offered two attractive possibilities: (1) the elemental analysis of samples too minute for analysis by the usual chemical and spectrographic methods, and (2) the detection of trace impurities in somewhat larger samples--traces which might characterize a sample sufficiently to establish its source or enable one to match it with another specimen suspected to have come from the same source. Of course, the very quantitative nature of the method was also appealing, and it was evident that wherever the purely instrumental, nondestructive form of the method could be employed, valuable physical evidence could be analyzed, yet still be preserved for presentation in court.

These discussions indicated many types of materials of forensic interest that might well be studied advantageously by neutron activation analysis. Those considered especially interesting and promising included gunshot residues, plastics, glass, paints, soils, paper, rubber, greases, inks, and metals. Emphasis was to be placed upon inorganic, or at least nonbiological, types of samples, since it was known that forensic studies on the characterization of hair by neutron activation analysis were being carried out by Professor R. E. Jervis in Canada and Dr. J. M. A. Lenihan in Scotland, as were studies on the characterization of narcotics at Oak Ridge National Laboratory.

As was originally planned, the work at General Atomic has been concentrated on studies with inorganic and nonbiological organic samples

of potential forensic importance, but it also has included some interesting investigations of hair, certain drugs (the amphetamines), pesticide residues, and poisons.

The first problem to be investigated at General Atomic was that of detecting gunshot residues on the gunhands of persons who had fired a revolver. Mr. Pinker made it clear that this was an outstanding unsolved problem in the field of criminalistics. Since antimony and barium were known to be present in the primers of all bullets made in the United States (and probably in almost all foreign ammunition), the possibility of detecting traces of these elements, blown onto the back of the gunhand during a firing, seemed an attractive possibility. Therefore, test firings of revolvers were carried out and swabs of the back of the gunhand of each person firing were activated at General Atomic in the 250-kw TRIGA Mark I reactor. The initial results were clear-cut and striking: even a single firing of a typical revolver deposited sufficient Sb and Ba on the gunhand to be readily detected by neutron activation analysis. The results of these initial gunshot residue analyses were reported at the October 1961 meeting of the California Association of Criminalists in San Francisco, where they were received with great interest. A note on this initial study appeared in the December 1961 issue of Nucleonics (page 74).

Since the application of the method in criminalistics was obviously very promising and of great potential public benefit, yet also vast in scope, assistance was sought in April 1962 from the Division of Isotopes Development of the U.S. Atomic Energy Commission, in the form of a research contract in this field. A research contract was issued to commence on May 1, 1962. The work carried out during the first 18 months of this research contract (May 1, 1962, through October 31, 1963) is the subject of this report. A large area of investigation has been explored, in some cases briefly, in other cases quite thoroughly. The results, to date, have been most encouraging and enlightening. In this investigation, the broad range of experience of the Activation Analysis Group at General Atomic in the analysis of samples of almost every possible description has been of great value in expediting the progress of the criminalistics research program, as has the large and versatile supply of irradiation and counting equipment already on hand.

As the criminalistics research program has progressed, the various radiochemists at General Atomic who are involved in the program have gradually acquired an appreciable knowledge and feel for the problems and techniques of the criminalist. Similarly, the many criminalists with whom the group now has frequent contact are acquiring an understanding of the activation analysis method, and an appreciation of what it can and cannot do in their field of interest. This cross-fertilization of disciplines is extremely valuable, and is essential to the future widespread use of the

technique in the field of criminalistics. As a part of this effort to acquaint criminalists with the method, the group has presented papers on this research at the semiannual meetings of the California Association of Criminalists--in October 1961 (San Francisco), October 1962 (Concord), May 1963 (Ventura), and October 1963 (San Mateo).^{*} In May 1962 the association met in San Diego and devoted half a day of its meeting to attending a series of talks on activation analysis and a tour of the laboratories at General Atomic.

From this increasing contact with professional criminalists have stemmed a gradually increasing number of requests by various law-enforcement agencies (local, state, and federal) to investigate specific cases for them by this technique. A number of such cases have been investigated, after careful initial screening by Mr. Pinker and ourselves to ensure that the suggested cases (1) were not amenable to conventional analytical methods, (2) looked susceptible to attack by means of neutron activation analysis, and (3) illustrated types of cases of wide occurrence and importance. In some cases the results were inconclusive; in others they were conclusive--indicating clearly either innocence or guilt of a particular suspect. In a number of instances the results were of distinct value to the investigating officers. In one case, plans were made to present the activation analysis data in court, but the suspect changed his plea to guilty so the case did not go to trial.

^{*} Although later than the period covered in this 18-month report, it may be remarked that papers have since been presented at the May 1964 (Long Beach) meeting. Also, invited papers were presented at the February 1963 and February 1964 national meetings of the American Academy of Forensic Sciences in Chicago.

II. EQUIPMENT AND PERSONNEL

EQUIPMENT

All of the equipment employed in this investigation was already on hand at General Atomic when this study was initiated or was acquired subsequently by General Atomic from its own funds. No equipment has been purchased with contract funds.

The principal relevant irradiation equipment available at General Atomic during the period described was the following: a 250-kw TRIGA Mark I nuclear reactor with pulse capability to 1000 Mw, a 1000-kw TRIGA Mark F nuclear reactor with pulse capability to 6500 Mw, a 45-Mev ARCO electron linear accelerator, and a Texas Nuclear Corporation 14-Mev neutron generator. Of these, the TRIGA Mark I reactor is used almost exclusively in this investigation. A photograph of the reactor, looking down through the water pool at the core, is shown in Fig. 1. A cutaway scale diagram of the reactor is shown in Fig. 2. The fluxes of neutrons of various energies at different locations in the reactor are shown in Table 1. The two most frequently used locations are (1) the rotary specimen rack, in which the thermal-neutron flux, at the normal 250-kw power level, is 1.8×10^{12} neutrons/cm²-sec, and (2) the pneumatic-transfer-tube terminus (in a vacant fuel-element position) in the outermost (F) ring of fuel elements, where the corresponding thermal-neutron flux is 4.3×10^{12} neutrons/cm²-sec. The pneumatic tube, shown in Fig. 3, has a transit time, from an adjacent counting room into the core or from the core to the counting room, of 2 sec. It is used for the activation of single samples where the induced activities of principal interest have half lives in the range of seconds to minutes. Irradiation times can be accurately preset with a timer. The rotary specimen rack enables one to activate, simultaneously and at identical fluxes, up to 40 samples (in the 40 tubes of the rack). It is used, of course, for longer irradiations (up to many hours), where one is primarily interested in longer-lived induced activities, i. e., radioisotopes with half lives of hours, days, or longer. The rotation of the rack around the core during the irradiation (1 rpm) evens out the neutron dose, so that each tube receives the same neutron dose--an extremely valuable feature if one wishes to activate many samples at the same time. Each of the 40 tubes can hold up to six of the small half-dram polyethylene sample vials (stacked vertically in a taller plastic tube which is mechanically lowered into or withdrawn from the rotary rack by means of a magnetic grapple device), so the total rack capacity is 240 sample vials. There is a small vertical flux gradient in the tubes, but this is known, and hence corrections can be readily made.

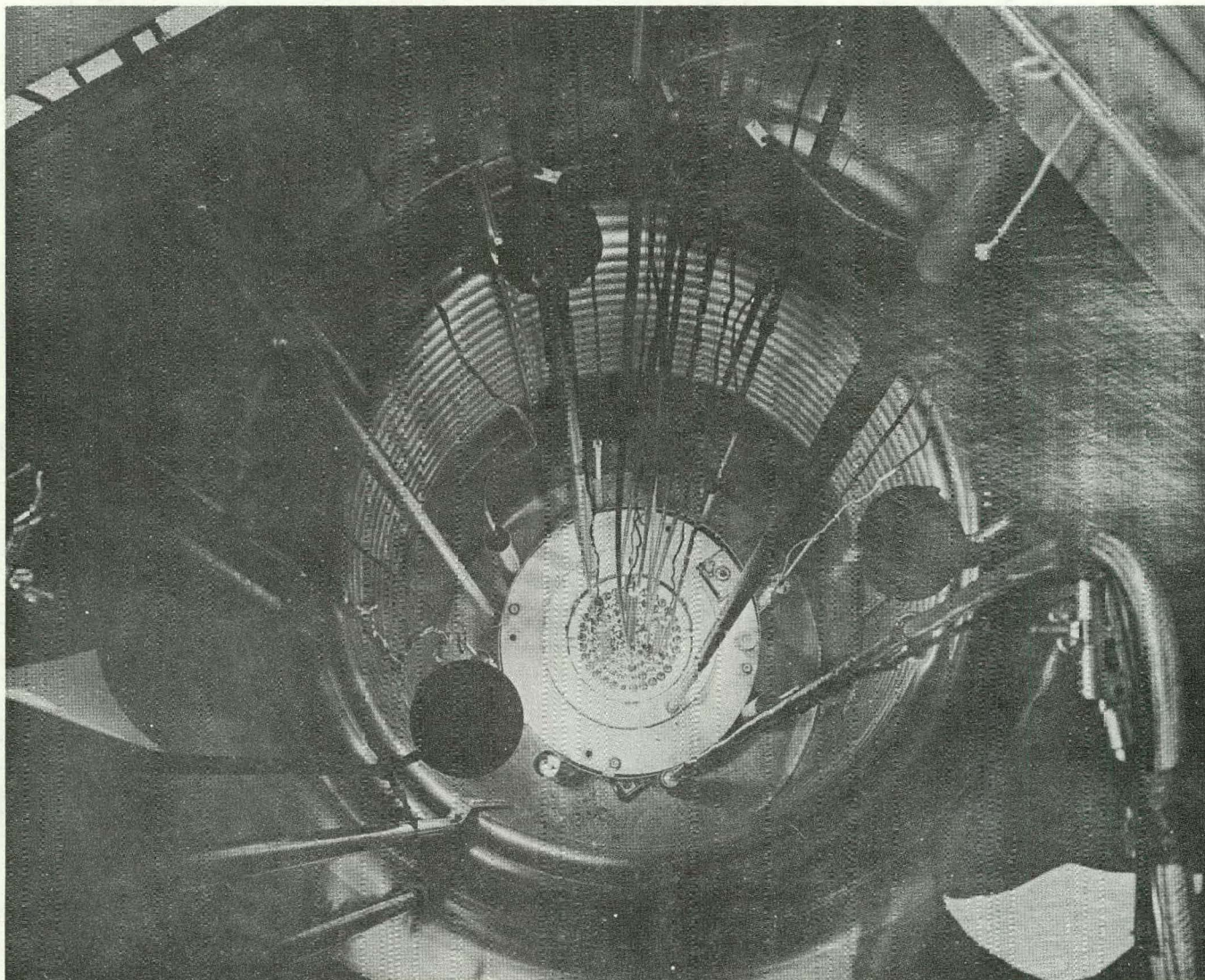


Fig. 1--The 250-kw TRIGA Mark I reactor

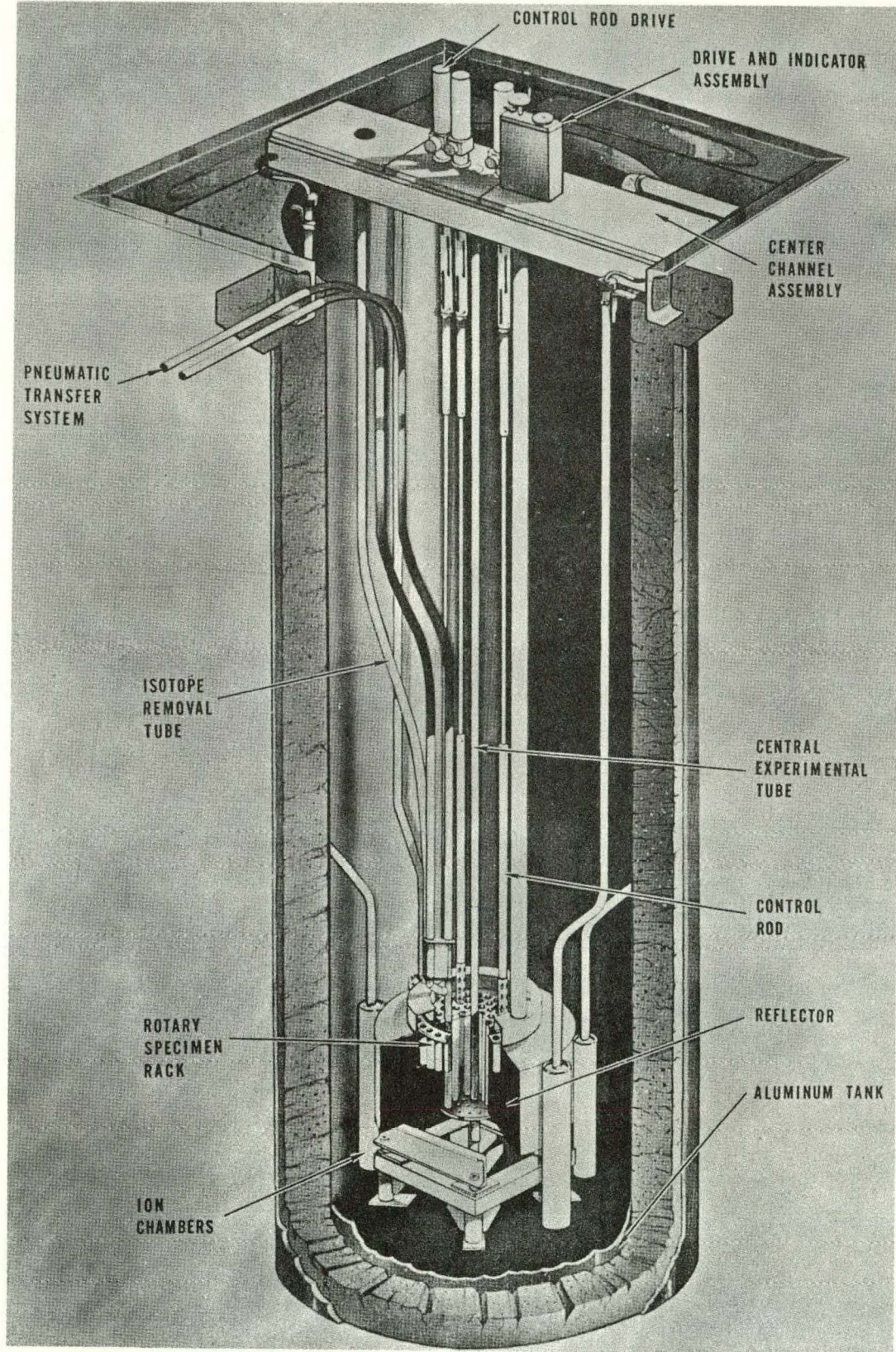


Fig. 2--Cutaway view of TRIGA Mark I reactor

Table 1
TRIGA MARK I NEUTRON FLUXES FOR STEADY-STATE
OPERATION AT 250 KW

Irradiation Position	Neutron Flux				
	Thermal	>10 kev	>1.35 Mev	>3.68 Mev	>6.1 Mev
Rotary specimen rack ("lazy susan")	1.8×10^{12}	1.5×10^{12}	1.8×10^{11}	2.5×10^{10}	4.0×10^9
Fuel-element ring D	4.9×10^{12}	9.0×10^{12}	2.3×10^{12}	4.1×10^{11}	6.2×10^{10}
Fuel-element ring F ("rabbit" terminus)	4.3×10^{12}	3.5×10^{12}	7.5×10^{11}	1.25×10^{11}	1.9×10^{10}
Reactor pool outside reflector	6.8×10^{11}	6.8×10^{10}	5.1×10^9	6.3×10^8	1.1×10^8

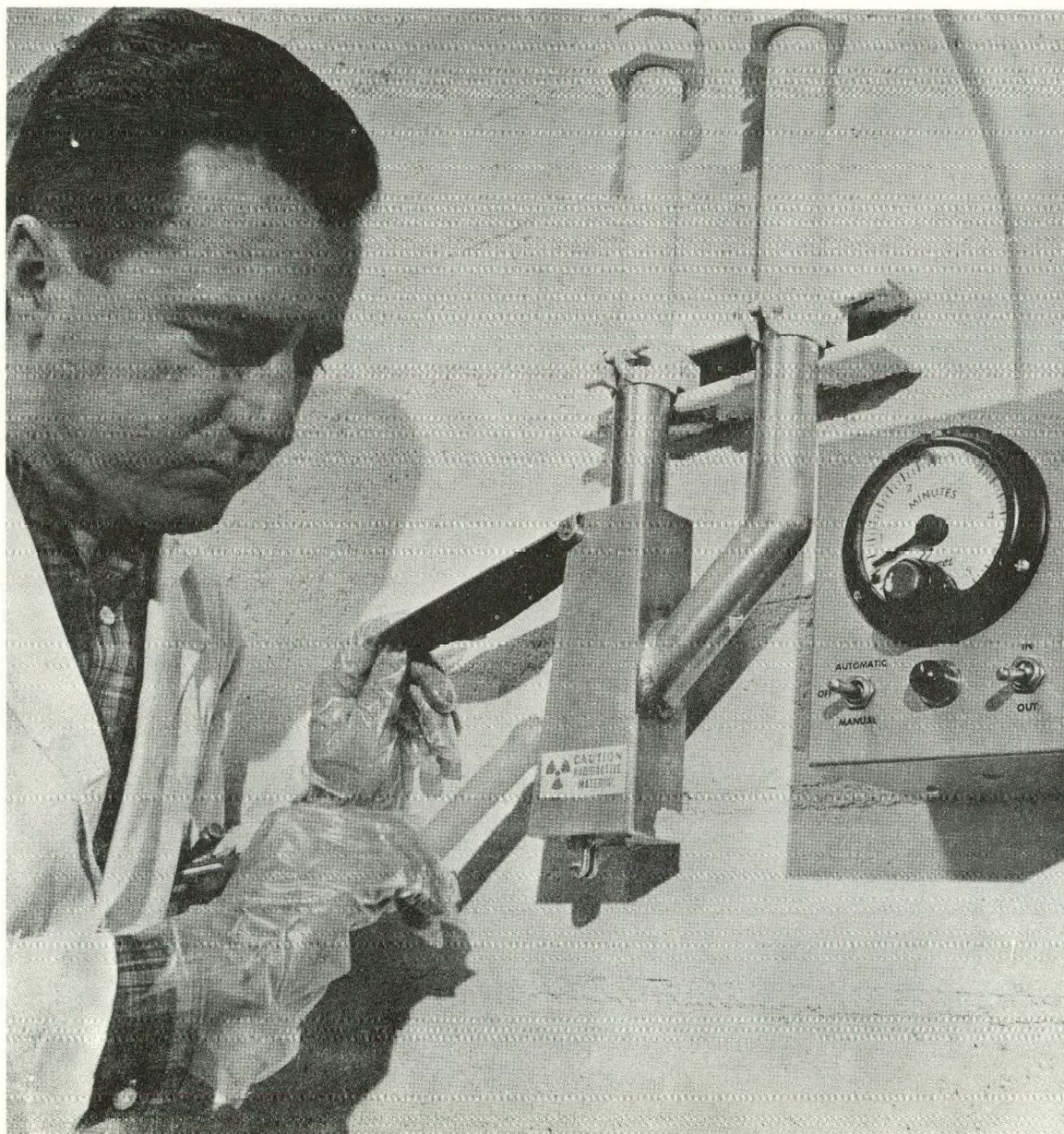


Fig. 3--Reactor pneumatic-tube system

Because of the intrinsic safety of the TRIGA reactor, resulting from its U-ZrH fuel elements, the reactor can also be safely and reproducibly pulsed, at roughly 5-minute intervals, to provide intense bursts of neutrons. For example, in a typical TRIGA Mark I pulse the main control rod is rapidly ejected, making the reactor appreciably supercritical. Within a few milliseconds it rises to a peak power of about one billion watts (TRIGA Mark F has been pulsed to over six billion watts), providing a peak total neutron flux, in the F-ring location, of 3.1×10^{16} n/cm²-sec. The pulse has, in this case, a full width at half height of about 18 millisec, thus giving an integrated nvt neutron dose in the pulse of 5.6×10^{14} . Such a pulse will generate 500 times as much 1-sec half-life activity and 5 times as much 10-sec half-life activity as can be produced by irradiation to saturation at the normal 250-kw steady operation level. The pulse is self-regulating, since the fuel elements quickly rise to temperatures of 400° to 500°C. Since the hydrogen content of the hydrided fuel elements provides a sizable fraction of the effective moderator in the system, fission neutrons moderated by collisions with such hot protons have sufficiently higher kinetic energies and fission U²³⁵ sufficiently more poorly (lower σ_f) that the system goes subcritical and the reactor shuts itself down.

The counting equipment used in this investigation consists of a number of multichannel pulse-height analyzers. These include a 100-channel RIDL tube-type unit, a 256-channel RCL tube-type unit, three 400-channel RIDL transistorized units, and a 400-channel TMC transistorized unit. Each analyzer has two different lead-shielded NaI(Tl) scintillation detectors which can be used with it, and a data printer. Most are also equipped with precision X-Y plotters, and three are equipped with magnetic-tape spectrum-stripping units. Several are equipped for choice of linear or semilogarithmic oscilloscope display, and two are equipped for multiscaler operation. A Polaroid oscilloscope camera is available for photographing the oscilloscope displays when desired. A view of the main spectrometry counting room is shown in Fig. 4.

Sodium iodide crystals of various sizes are used, ranging from very small, thin crystals (for optimum detection of low-energy X-rays and gamma rays with minimum interference from high-energy gamma rays) to 3-in. by 3-in. crystals (for good efficiency and good resolution of high-energy gamma rays). Both solid and well-type crystals are used, in the 2-in. by 2-in. and 3-in. by 3-in. sizes. Some of the 3-in. by 3-in. solid crystal counters are of the integral-line type, selected for high resolution and minimum counting-rate gain shift. Each of the larger crystal detectors is housed in a 4-in. -thick lead shield of moderate internal dimensions lined with thin layers of cadmium and copper (to absorb lead X-rays produced in the shield by interaction with sample gamma rays). Each of the solid crystals has a 1-cm-thick polystyrene cap for absorption of sample beta particles with minimum bremsstrahlung production. Also, each of the

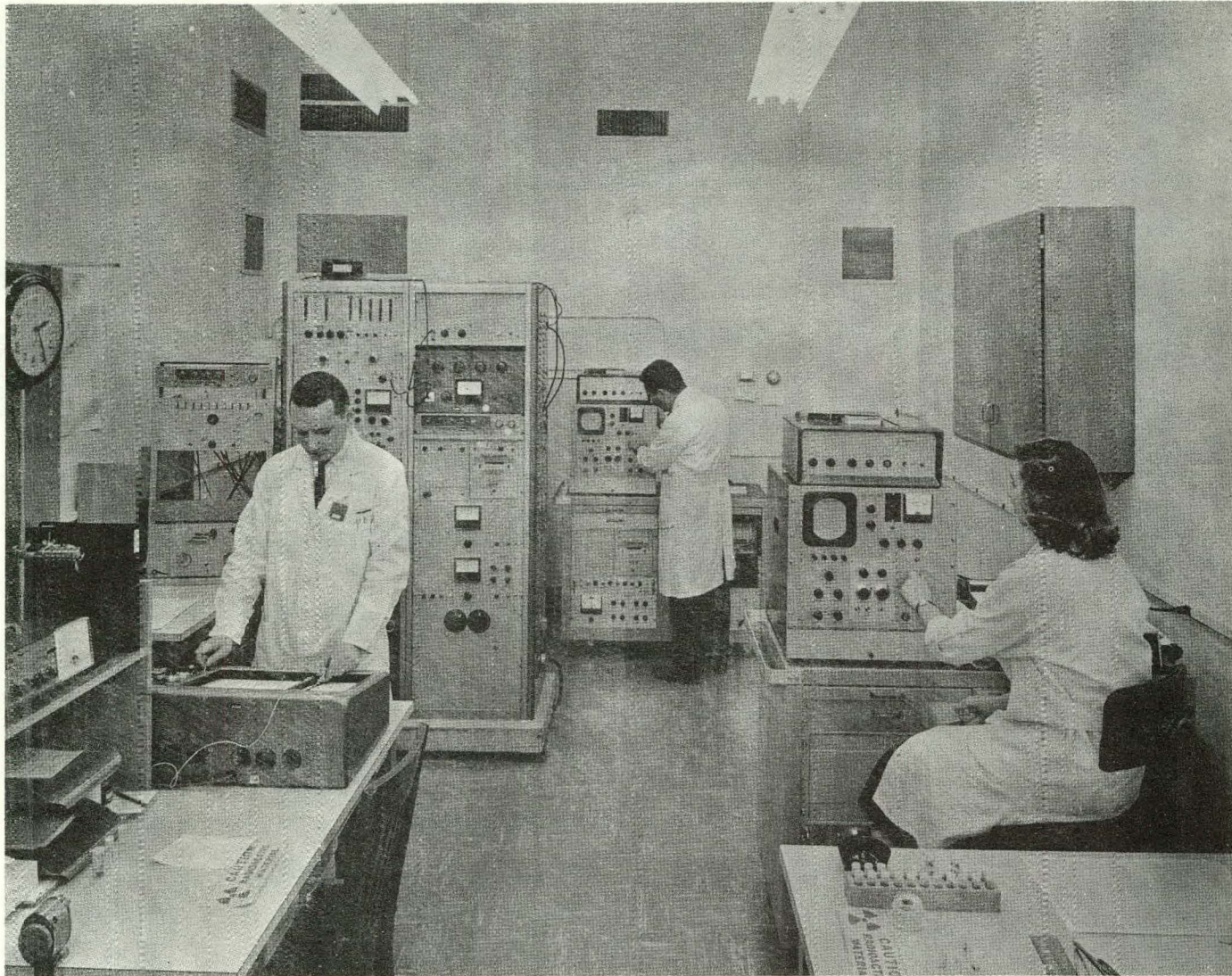


Fig. 4--Main gamma-ray-spectrometry laboratory

solid crystals has a rack, inside the shield and above the crystal, for counting of very active samples at reduced geometries (to avoid large dead times and appreciable counting-rate gain shifts).

In addition to the gamma-ray spectrometry equipment, a number of conventional shielded Geiger-Mueller and proportional counters are used for beta counting, and a Sharp Laboratories low-background (0.25 cpm) beta counter is used for very-low-activity samples. Beta counting is employed only for samples in which an induced beta-emitting activity has been radiochemically separated and purified first.

In addition to the irradiation and counting facilities mentioned above, the facilities include several radiochemistry laboratories (equipped with unshielded or shielded fume hoods), a sample preparation and standards room, and a number of the usual analytical balances, drying ovens, muffle furnaces, centrifuges, radiation monitors, etc.

Detection sensitivities for 69 elements, at the 1.8×10^{12} n/cm²-sec thermal-neutron flux in the rotary specimen rack of the 250-kw TRIGA Mark I reactor and irradiations of 1-hr maximum duration, are summarized in Table 2. In many cases, improved sensitivities are attainable by means of longer irradiations and longer counting periods.

PERSONNEL

Members of the General Atomic Activation Analysis Group who have participated to an appreciable extent in the criminalistics investigation during the period reported here include V. P. Guinn, J. D. Buchanan, R. R. Ruch, Sandra C. Bellanca, D. E. Bryan, and Dorothy M. Settle. All are professional radiochemists. In addition, a number of other radiochemists and technicians of the group have devoted lesser amounts of time to this study upon occasion, as needed. The total manpower effort during this 18-month period has amounted to approximately 27 man-months, i.e., about 1.5 man-years per year.

Table 2

ESTIMATED NEUTRON-ACTIVATION SENSITIVITIES FOR IRRADIATIONS OF 1 HR OR LESS
IN A THERMAL-NEUTRON FLUX OF 1.8×10^{12}

Element	Radionuclide Measured	Radiochemical Beta-ray Sensitivity (μg)	Instrumental Gamma-ray Sensitivity (μg)	Element	Radionuclide Measured	Radiochemical Beta-ray Sensitivity (μg)	Instrumental Gamma-ray Sensitivity (μg)
Ag	2.3-m Ag ¹⁰⁸	0.005	0.005	Na	15-h Na ²⁴	0.005	0.005
	24-s Ag ¹¹⁰	----	0.0001	Nb	6.6-m Nb ^{94m}	0.005	1
Al	2.3-m Al ²⁸	0.1	0.01	Nd	11.6-d Nd ¹⁴⁷	0.1	0.1
As	27-h As ⁷⁶	0.001	0.005	Ni	2.6-h Ni ⁶⁵	0.05	0.5
Au	2.7-d Au ¹⁹⁸	0.0005	0.0005	Os	31-h Os ¹⁹³	0.05	----
Ba	85-m Ba ¹³⁹	0.05	0.1	P	14.5-d P ³²	0.5	----
Bi	5.0-d Bi ²¹⁰	0.5	----	Pb	3.3-h Pb ²⁰⁹	10	----
Br	17.6-m Br ⁸⁰	0.005	0.005	Pd	4.8-m Pd ^{109m}	----	0.05
	36-h Br ⁸²	0.005	0.01		13.6-h Pd ¹⁰⁹	0.0005	5
Ca	8.8-m Ca ⁴⁹	1.0	5	Pr	19-h Pr ¹⁴²	0.0005	0.05
Cd	54-h Cd ¹¹⁵	0.05	0.5	Pt	31-m Pt ¹⁹⁹	0.05	0.1
Ce	32-d Ce ¹⁴¹	1	1		3.2-d Au ¹⁹⁹	0.1	0.1
	32-h Ce ¹⁴³	0.1	0.1	Rb	18.6-d Rb ⁸⁶	0.05	5
Cl	37-m Cl ³⁸	0.01	0.1	Re	91-h Re ¹⁸⁶	0.001	0.05
Co	10.3-m Co ^{60m}	0.005	0.1		17-h Re ¹⁸⁸	0.0005	0.001
	5.3-y Co ⁶⁰	0.5	0.5	Rh	4.4-m Rh ^{104m}	0.001	0.0005
Cr	27-d Cr ⁵¹	(no β)	1		4.2-s Rh ¹⁰⁴	----	0.01
Cs	2.2-y Cs ¹³⁴	0.5	0.5	Ru	40-d Ru ¹⁰³	0.5	1
Cu	12.8-h Cu ⁶⁴	0.001	0.001		4.5-h Ru ¹⁰⁵	0.01	0.05
	5.1-m Cu ⁶⁶	0.01	0.05	S	87-d S ³⁵	10	----
Dy	2.3-h Dy ¹⁶⁵	0.000001	0.000005		5.0-m S ³⁷	5	200
Er	9.4-d Er ¹⁶⁹	0.1	----	Sb	2.8-d Sb ¹²²	0.005	0.01
	7.5-h Er ¹⁷¹	0.001	0.001	Sc	84-d Sc ⁴⁶	0.01	0.05
Eu	9.3-h Eu ^{152m}	0.000005	0.0005	Se	120-d Se ⁷⁵	(no β)	5
F	11-s F ²⁰	----	1	Si	2.6-h Si ³¹	0.05	500
Fe	45-d Fe ⁵⁹	50	200	Sm	47-h Sm ¹⁵³	0.0005	0.005
Ga	14-h Ga ⁷²	0.005	0.005	Sn	9.5-m Sn ^{125m}	0.5	0.5
Gd	18-h Gd ¹⁵⁹	0.01	0.05	Sr	2.8-h Sr ^{87m}	0.005	0.005
Ge	82-m Ge ⁷⁵	0.005	0.05		64-d Sr ⁸⁵	50	50
	11-h Ge ⁷⁷	0.5	----	Ta	112-d Ta ¹⁸²	0.05	0.5
Hf	19-s Hf ^{179m}	----	1	Tb	72-d Tb ¹⁶⁰	0.05	0.1
Hg	65-h Hg ¹⁹⁷	(no β)	0.01	Te	25-m Te ¹³¹	0.05	0.05
Ho	27-h Ho ¹⁶⁶	0.0001	0.0001		8-d I ¹³¹	5	1
I	25-m I ¹²⁸	0.005	0.01	Th	27-d Pa ²³³	0.05	0.05
In	54-m In ^{116m}	0.00005	0.0001	Ti	5.8-m Ti ⁵¹	0.5	0.05
Ir	19-h Ir ¹⁹⁴	0.0001	0.001	Tm	127-d Tm ¹⁷⁰	0.01	0.1
K	12.5-h K ⁴²	0.05	0.5	U	2.3-d Np ²³⁹	0.005	0.005
La	40-h La ¹⁴⁰	0.001	0.005	V	3.8-m V ⁵²	0.005	0.001
Lu	3.7-h Lu ¹⁷⁶	0.00005	0.00005	W	24-h W ¹⁸⁷	0.001	0.005
	6.8-d Lu ¹⁷⁷	0.0005	0.005	Yb	4.2-d Yb ¹⁷⁵	0.001	0.01
Mg	9.5-m Mg ²⁷	0.5	0.5	Zn	14-h Zn ^{69m}	0.1	0.1
Mn	2.6-h Mn ⁵⁶	0.00005	0.00005	Zr	17-h Zr ⁹⁷	1	1
Mo	15-m Mo ¹⁰¹	0.1	5				
	67-h Mo ⁹⁹	0.5	0.1				

III. EXPERIMENTAL RESULTS

GUNSHOT RESIDUES

Early Exploratory Study

According to the work of Harrison and Gilroy, (1) all known U. S. and virtually all known European firearms ammunition contains antimony (as Sb_2S_3) in the cartridge primer, and most also contains barium (as $\text{Ba}(\text{NO}_3)_2$). On the basis of this information, an exploratory study of the detection of these elements in gunshot residues removed from the hand was carried out in 1961, in cooperation with Mr. Ray H. Pinker, Chief Criminalist of the Los Angeles Police Department.

A police officer fired a .38-caliber revolver once, and the backs of his hands were rinsed with very dilute nitric acid. The gun was then fired three times in rapid succession, and the officer's hands were again rinsed. His hands were also rinsed after they had been washed thoroughly but before firing the gun (these rinsings serving as blanks). A sample of the dilute nitric acid was also retained to serve as a reagent blank. The rinsings were then irradiated in a thermal-neutron flux of 1.8×10^{12} n/cm²-sec in the General Atomic TRIGA Mark I reactor. After the irradiation, any induced 2.8-day Sb^{122} activity was separated radiochemically, using non-radioactive Sb as a carrier. It was counted by gamma-ray spectrometry, using the 0.57-Mev gamma ray of 2.8-day Sb^{122} for indication of the Sb present. The dilute nitric acid showed a reagent blank of 0.03 μg Sb. The acid rinse before firing showed the presence of 0.05 μg Sb (of which 0.03 μg came from the nitric acid). After one firing, the rinse showed 0.12 μg Sb, a net gain of 0.09 μg (0.07 μg more than the 0.02 μg hand blank), and the rinse after three firings showed 0.23 μg Sb, a net gain of 0.20 μg (0.18 μg more than the 0.02 μg hand blank). These results were obtained from the gun hand (in this case the right hand). The left hand rinsings showed only the blank level of Sb.

Because of the encouraging results obtained in this exploratory study, an investigation was begun to determine both Ba and Sb in the gunshot residues on the hands of persons firing a gun. The type of gun used in most of the firings is shown in Fig. 5. Since cartridge cases are usually made of copper or brass, and since some bullets are copper-jacketed, it was originally thought that Cu residues on the hand would also be of interest. However, subsequent investigations showed that the Cu

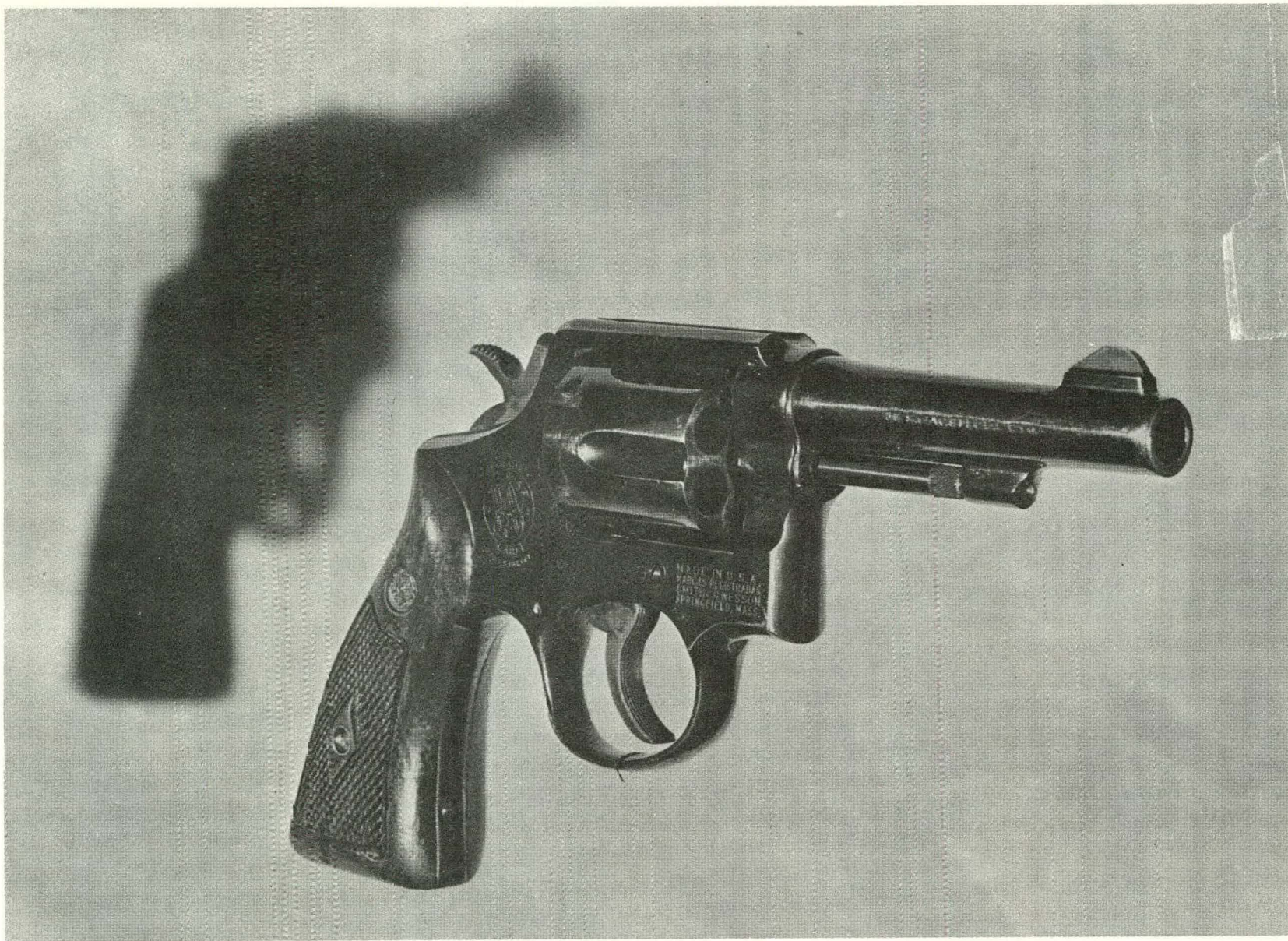


Fig. 5--Type of revolver used in gunshot-residue studies

content does not necessarily yield any useful results. Very erratic results were obtained, and it was also found that Cu hand-blank values were very erratic and often rather large. No attempt was made to detect lead on the hand, because of its rather poor NAA detection sensitivity compared with Ba and Sb and because the only potentially useful activity induced in lead is 3.3-hr Pb^{209} , a pure beta emitter. The detection sensitivities for Sb, Ba, and Pb are 0.005 μg , 0.05 μg , and 10 μg , respectively, based on a 1-hr irradiation in a thermal-neutron flux of 1.8×10^{12} n/cm²-sec and counting of the beta radiation after isolating the activity radiochemically (see Table 2). The induced Ba activity detected in these studies is 84-min Ba^{139} with a gamma ray at 0.163 Mev. Copper is detected by means of the induced 12.8-hr Cu^{64} activity, which produces 0.511-Mev positron annihilation radiation. Its detection sensitivity is 0.001 μg . Gamma-ray spectra of Ba^{139} , Sb^{122} , and Cu^{64} are shown in Figs. 6, 7, and 8.

Elements Detected in Gunshot Residues

A series of experiments was carried out to check the presence of Sb, Ba, and Cu in powder residues from various ammunitions. Samples of primer products were prepared by removing the primers from several cartridges, igniting them in crucibles, and wrapping the products in a water-acetone-washed polyethylene sheet. Muzzle-blast products (from both powder and primer) were caught on a 6-in. square of water-acetone-washed polyethylene sheet held 6 in. in front of the muzzle. A jagged hole was made in the center of the sheet by the bullet. This hole was surrounded by a dark ring of blast products, a region with very little deposit, and an outer ring that was lightly speckled with deposit (see Fig. 9). Each square was cut into quadrants, and the inner and outer rings of each quadrant were analyzed for Ba, Sb, and Cu. Cylinder-blast products were collected by cutting a hole in the center of a 6-in. square of water-acetone-washed polyethylene sheet, sliding the sheet down the gun barrel to just in front of the cylinder, and firing the gun. As in the case of the muzzle blasts, two rings of deposit were obtained: an inner dark ring and an outer gray ring, separated by an intermediate ring containing only a small amount of deposit. The sheet was then quartered, and the inner and outer rings were analyzed. A piece of the polyethylene sheet was analyzed as a blank and found to contain negligible amounts of Ba, Sb, and Cu. The blast deposits from five different brands of ammunition were analyzed. A check on the reproducibility of the amounts of Ba and Sb in the deposits was made with four of the ammunitions. The results are shown in Table 3. All of the ammunitions studied showed Ba and Sb to be present at various ratios. The reproducibility of the Ba/Sb ratios is fair, and this ratio might conceivably serve to identify the type of ammunition used in an actual shooting case.

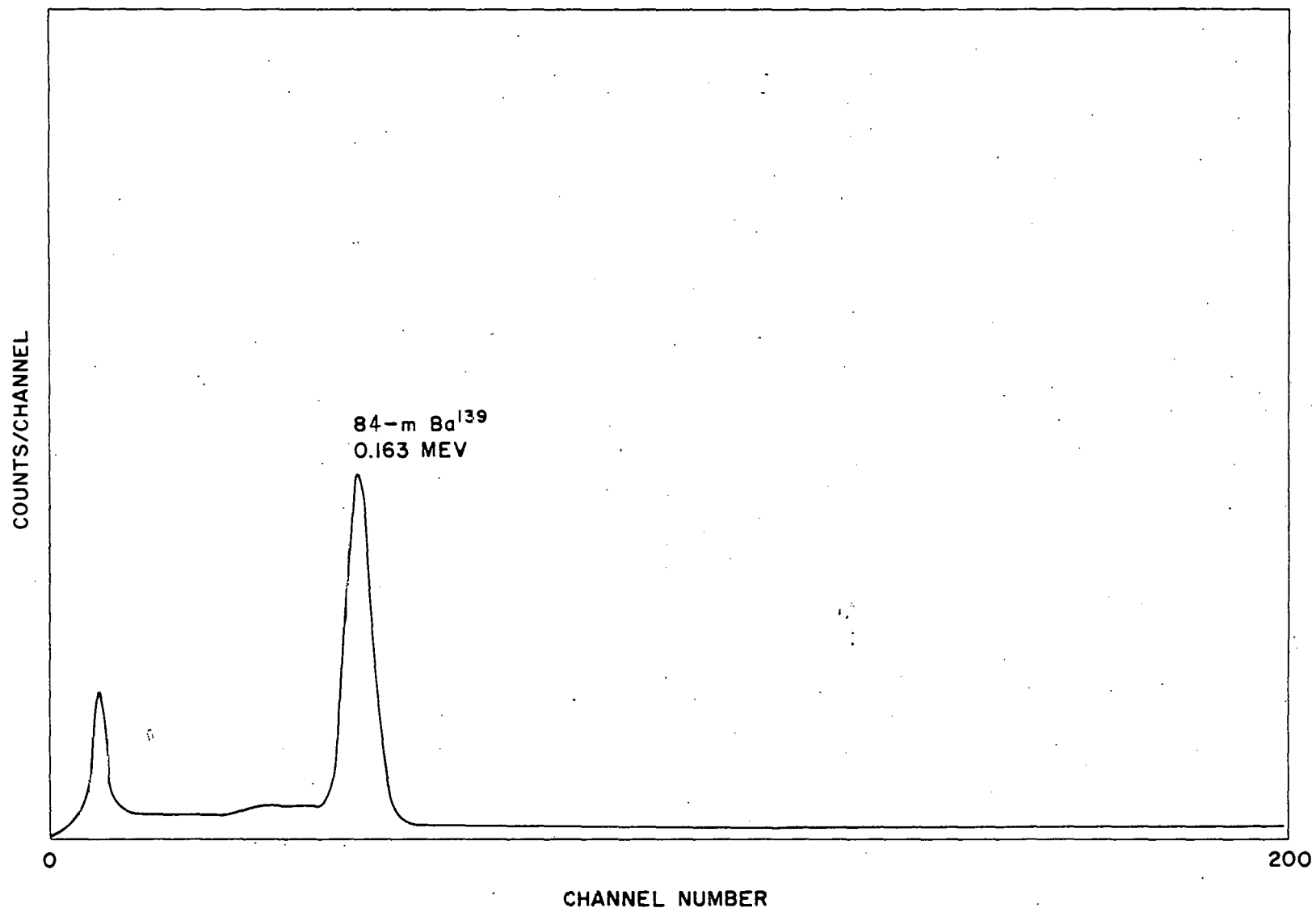


Fig. 6--Gamma-ray spectrum of 84-min Ba^{139}

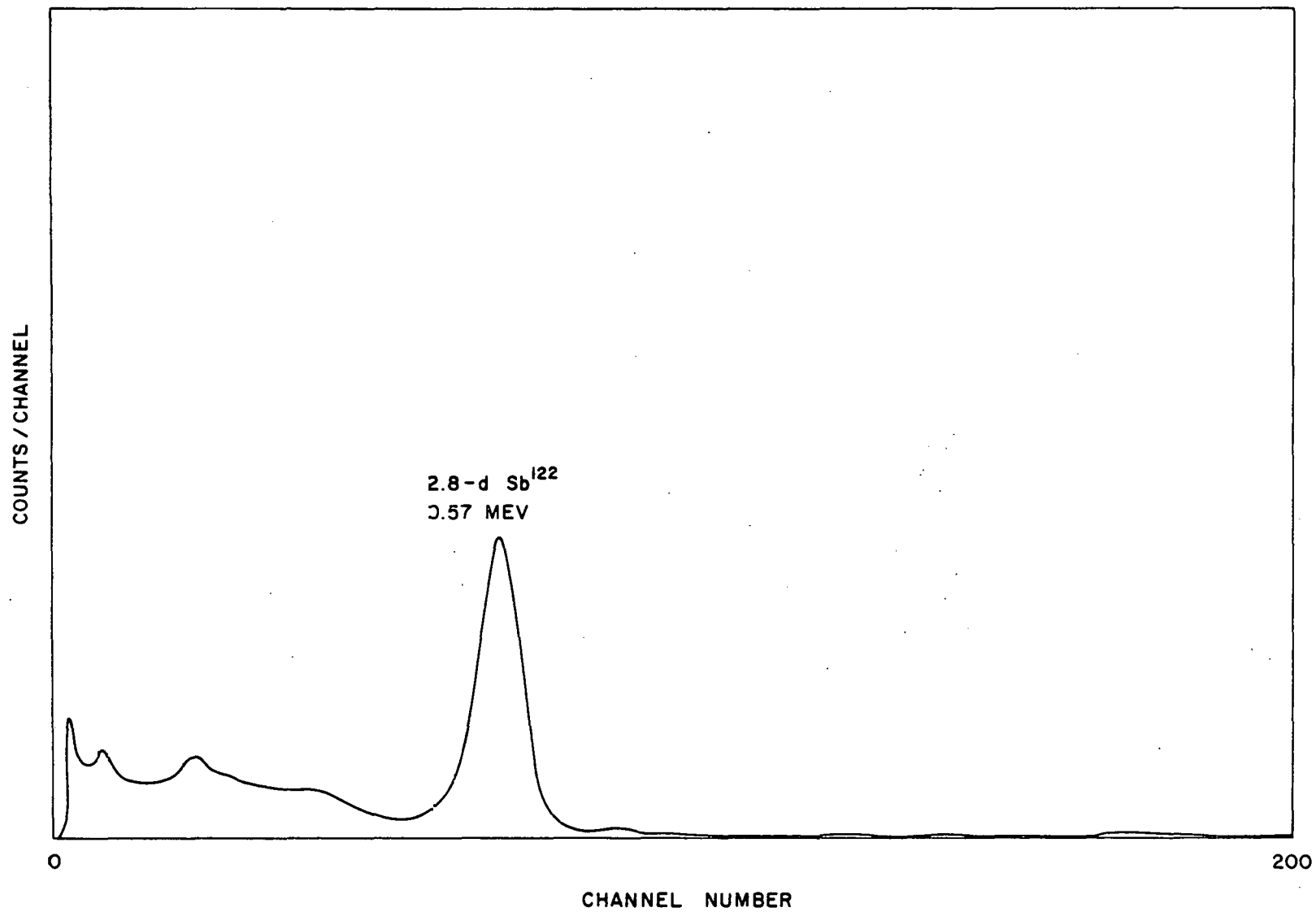


Fig. 7--Gamma-ray spectrum of 2.8-day Sb^{122}

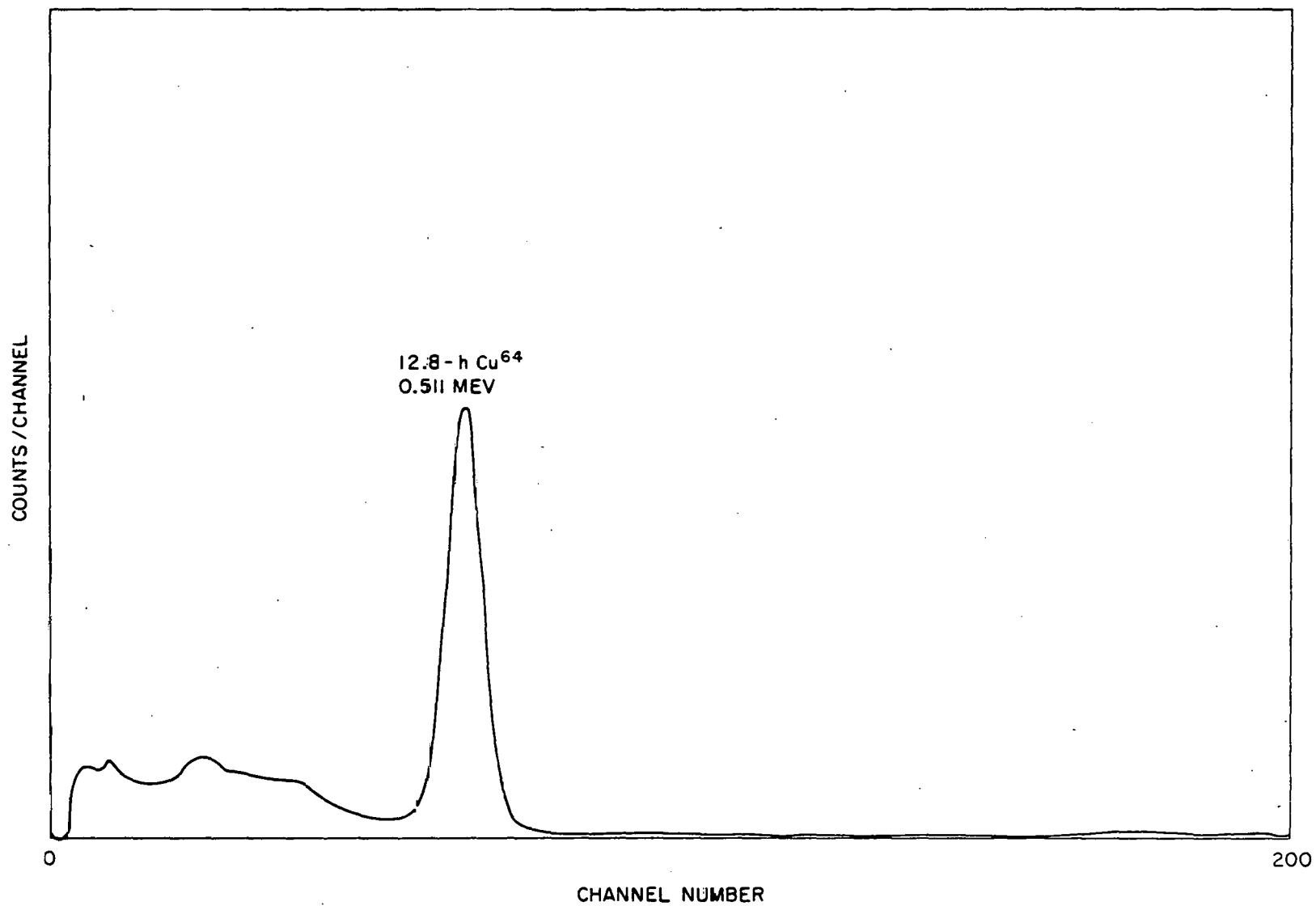


Fig. 8--Gamma-ray spectrum of 12.8-hr Cu^{64}

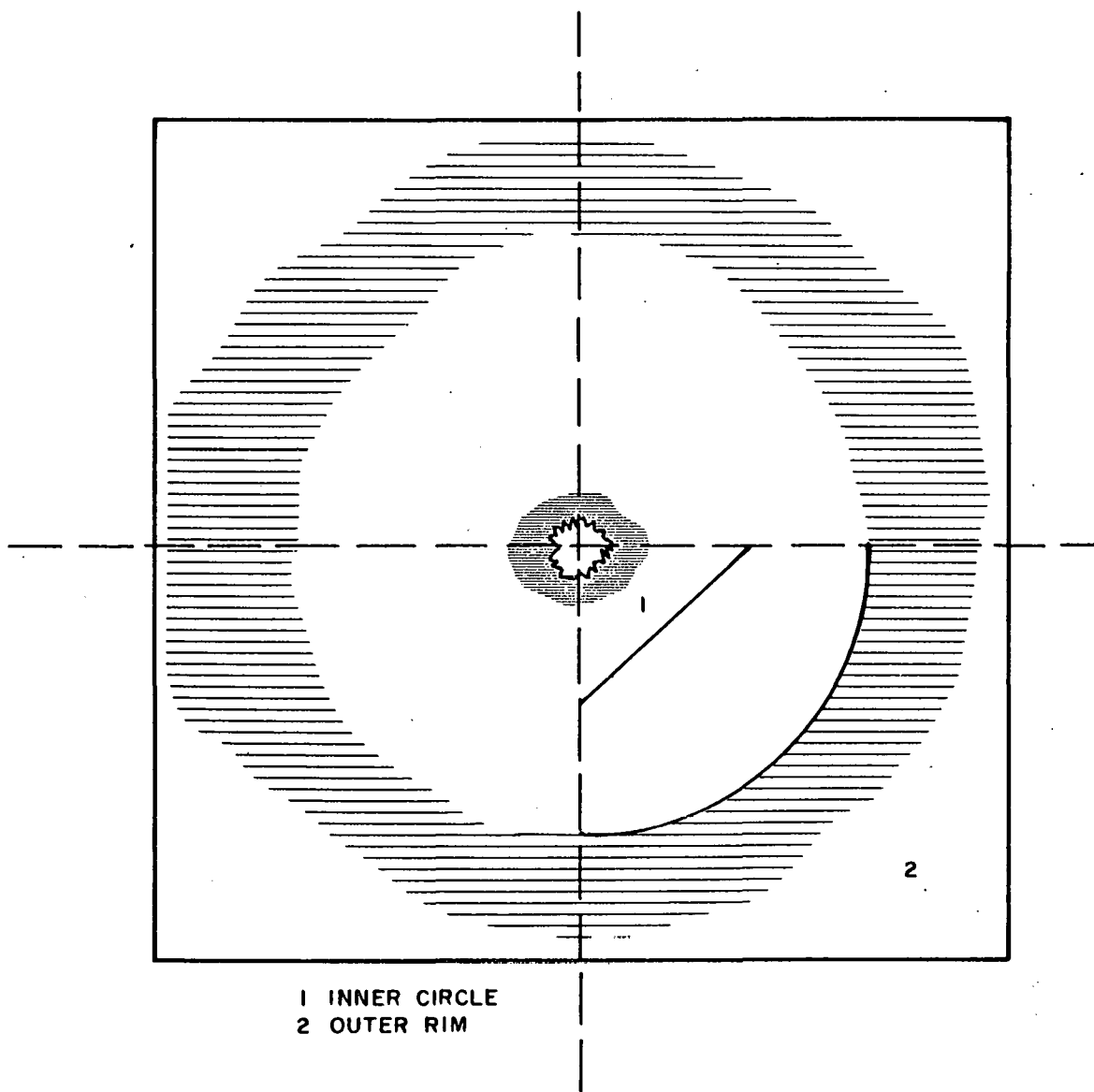


Fig. 9--Sampling of polyethylene sheet after muzzle blast

Table 3

ANALYSIS OF PRIMER, MUZZLE-BLAST, AND CYLINDER-BLAST PRODUCTS
FROM FIVE .38-CALIBER AMMUNITIONS

Brand	Sample	Elements Found, First Analysis (μg)			Elements Found, Second Analysis (μg)			Ba/Sb Ratio, First	Ba/Sb Ratio, Second
		Sb	Ba	Cu	Sb	Ba	Cu		
Federal	Primer product	100	334	---	----	----	----	3.3	----
	Cylinder blast, inner	7.2	9.9	---	----	----	----	1.4	----
	Cylinder blast, outer	1.1	28	---	----	----	----	25	----
	Muzzle blast, inner	8.2	9.8	---	----	----	----	1.2	----
	Muzzle blast, outer	10.1	17.4	---	----	----	----	1.7	----
Western	Primer product	17.2	246	---	----	----	----	14	----
	Cylinder blast, inner	----	----	---	6.9	3.9	3.5	----	0.57
	Cylinder blast, outer	16.9	318	5.1	35	43	64	19	1.2
	Muzzle blast, inner	6.2	4.5	2.3	11	12	6.7	0.73	0.92
	Muzzle blast, outer	7.1	4.1	3.4	14	15	10	0.58	1.1
Peters	Primer product	38	128	---	----	----	----	3.4	----
	Cylinder blast, inner	6.3	4.8	1.1	4.0	5.5	0.4	0.76	1.4
	Cylinder blast, outer	5.6	5.9	0.8	9.0	13	1.7	1.1	1.4
	Muzzle blast, inner	4.8	9.9	0.5	6.7	13.3	0.9	2.1	2.0
	Muzzle blast, outer	9.9	12	1.7	9.9	9.9	1.5	1.2	1.0
Remington	Primer product	16	49	---	----	----	----	3.1	----
	Cylinder blast, inner	4.4	5.3	0.4	3.4	3.3	0.6	1.2	1.0
	Cylinder blast, outer	6.5	9.8	1.4	5.1	5.3	1.4	1.5	1.0
	Muzzle blast, inner	7.1	18	1.4	3.8	10	0.5	2.5	2.7
	Muzzle blast, outer	7.5	9.5	1.4	10.6	20	1.5	1.3	1.9
Winchester	Primer product	168	175	---	----	----	----	1.0	----
	Cylinder blast, inner	6.3	3.3	---	6.9	4.3	----	0.52	0.62
	Cylinder blast, outer	4.7	2.2	---	23	17	1.1	0.47	0.74
	Muzzle blast, inner	20	15	---	33	21	2.9	0.75	0.64
	Muzzle blast, outer	16	8.7	---	25	11	2.9	0.54	0.44

Distribution of Gunshot Residues on Hand

Test firings were made to determine the distribution of the gunshot residues on the gun-firing hand. On his gun hand a police officer wore a plastic glove having 2-in. circles of moist filter paper on the thumb-web area, the back of the hand, and wrapped around the trigger finger, as shown in Fig. 10. A .38-caliber revolver was then fired once, using Peters ammunition. The experiment was repeated, using Western ammunition. The filter paper patches were then irradiated for 30 min in a thermal-neutron flux of 1.8×10^{12} n/cm²-sec. After irradiation the patches were heated in dilute HNO₃-HCl mixture with Ba, Sb, and Cu carriers present, and the three activities were separated radiochemically and counted with a multichannel gamma-ray spectrometer. The results of the analyses are shown in Table 4. In each case, the largest amount of residue was found on the trigger-finger patch, the next largest on the thumb-web patch, and the smallest on the back-of-the-hand patch. The large amount found on the trigger finger was later shown probably to be due to the fact that the finger actually touched the gun (and the gun had not been rigorously cleaned).

It is assumed that this technique provides essentially 100% collection of the powder residues impinging on the hand areas of interest. Thus, these results can be used as a basis for determining the efficiency of recovery of residues by removing them from the skin by other means.

An alternative method was also used to determine the amount of residue deposited on various areas of the hand. A police officer wore a plastic glove coated with paraffin oil in the thumb-web, back-of-hand, and trigger-finger areas, as well as on the palm of the hand. A .38-caliber revolver was then fired once with two different makes of ammunition. After firing, each oil-coated area was carefully wiped with a small piece of filter paper. The paper was then irradiated and analyzed as before. The results are shown in Table 5. The amount of residue recovered by this technique appears to be somewhat less than is recovered by the filter paper patch technique except for the back of the hand, where the two methods compare fairly well. The amount found on the palm appears to be low, considering the fact that the palm actually touches the gun.

Removal of Gunshot Residues

In order to carry out extensive studies of gunshot residues on the hand and to establish whether activation analysis can be of use in actual shooting cases, a reliable method of removing the residues from the hand had to be developed. The method should be efficient and simple, as well as being free of any contamination or interferences.

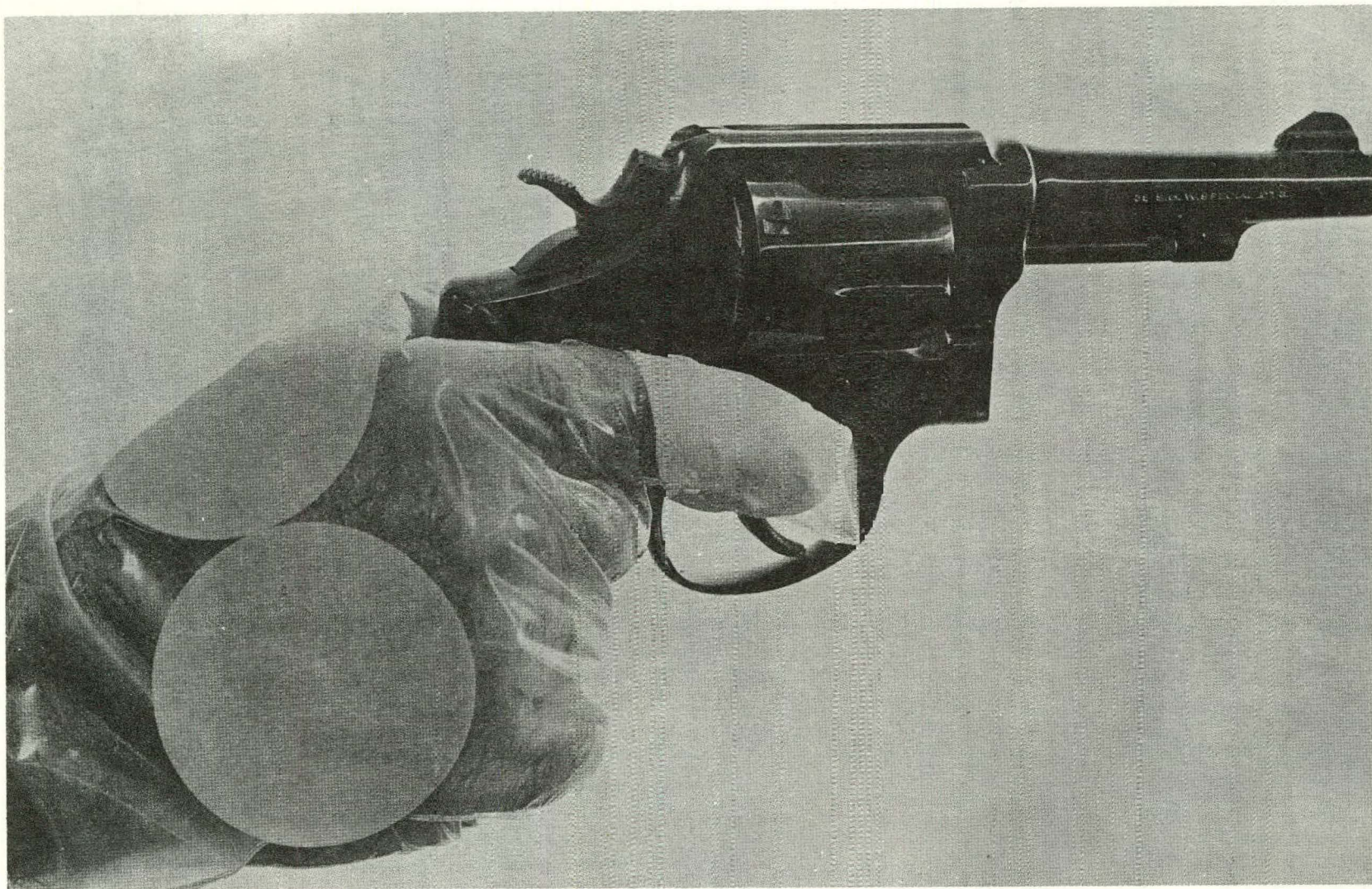


Fig. 10--Plastic glove with moist filter paper patches for gunshot-residue distribution studies

Table 4
DISTRIBUTION OF GUNSHOT RESIDUE ON THREE
AREAS OF GUN HAND
(Plastic glove-moist filter paper patch technique)

Ammunition	Hand Area	Elements Found (μg net)		
		Sb	Ba	Cu
Peters	Thumb web	0.18	0.74	0.47
	Trigger finger	1.1	4.2	2.4
	Back of hand	0.17	0.81	0.28
Western	Thumb web	0.21	0.96	3.2
	Trigger finger	0.35	3.2	4.2
	Back of hand	0.04	0.55	0.37

Table 5
DISTRIBUTION OF GUNSHOT RESIDUE ON FOUR AREAS
OF GUN HAND
(Plastic glove-paraffin oil technique)

Ammunition	Hand Area	Elements Found (μg net)		
		Sb	Ba	Cu
Peters	Thumb web	0.11	0.86	0.51
	Trigger finger	0.09	0.83	0.11
	Back of hand	0.05	0.66	0.17
	Palm	0.02	0.40	0.07
Western	Thumb web	0.21	0.55	2.4
	Trigger finger	0.16	2.2	1.7
	Back of hand	0.02	0.47	0.41
	Palm	0.08	0.40	0.76

Several possible dry wiping materials were analyzed by purely instrumental NAA means (i. e. , no radiochemical separations) to determine whether they would introduce any contamination or serious interferences if used to remove residues from the hand. Absorbent cotton, cotton gauze, "Q-tip" cotton, several filter papers, paper toweling, Kleenex, and polyurethane, cellulose, and plastic sponges were investigated. After irradiation for 30 min in the TRIGA reactor, the samples were counted with a 3-in. by 3-in. solid NaI(Tl) scintillation crystal coupled to a multi-channel gamma-ray spectrometer. Whatman No. 42 filter paper washed with distilled water and alcohol appeared to be the best from the standpoint of ease of handling and minimum of interferences.

Samples of distilled water, 1% nitric acid, acetic acid, deionized water, paraffin oil, K & W waterless hand cleaner, El Pico waterless hand cleaner, Mac's waterless hand cleaner, alkyl aryl sulfonate detergent, and an aerosol detergent were analyzed in the same manner as the dry material. The results indicated that the deionized water, 1% transistor grade HNO_3 , or paraffin oil would be best, from the purity standpoint, for removing residues from the hand.

The effectiveness of the removal of the residues from the hand by these various techniques was then investigated. A filter paper moistened with a 1% solution of nitric acid was wiped gently over the thumb webs, the backs of the hands, and the trigger fingers of eight persons who had fired a gun with the right hand. The swabbings from the left hand served as blanks. The filter papers were irradiated and analyzed radiochemically. The same procedure was tried using 2% nitric acid, 2% acetic acid, and 2% boric acid as the swabbing solution.

The hands were also scrubbed with these same four solutions using a clean nylon toothbrush. Five milliliters of the solution were used and the hand area was scrubbed for about 30 sec. The hand was then held over a porcelain dish and the solution was removed with a stream of acetone and analyzed.

The paraffin-test procedure was also tried. Casts were made by applying melted paraffin at a temperature of about 120°F to the thumb web, forefinger, and back of the hand with a brush. After cooling, the cast was peeled from the hand, irradiated, and analyzed radiochemically.

It was on the basis of these tests that it was decided to eliminate Cu as one of the elements being determined.

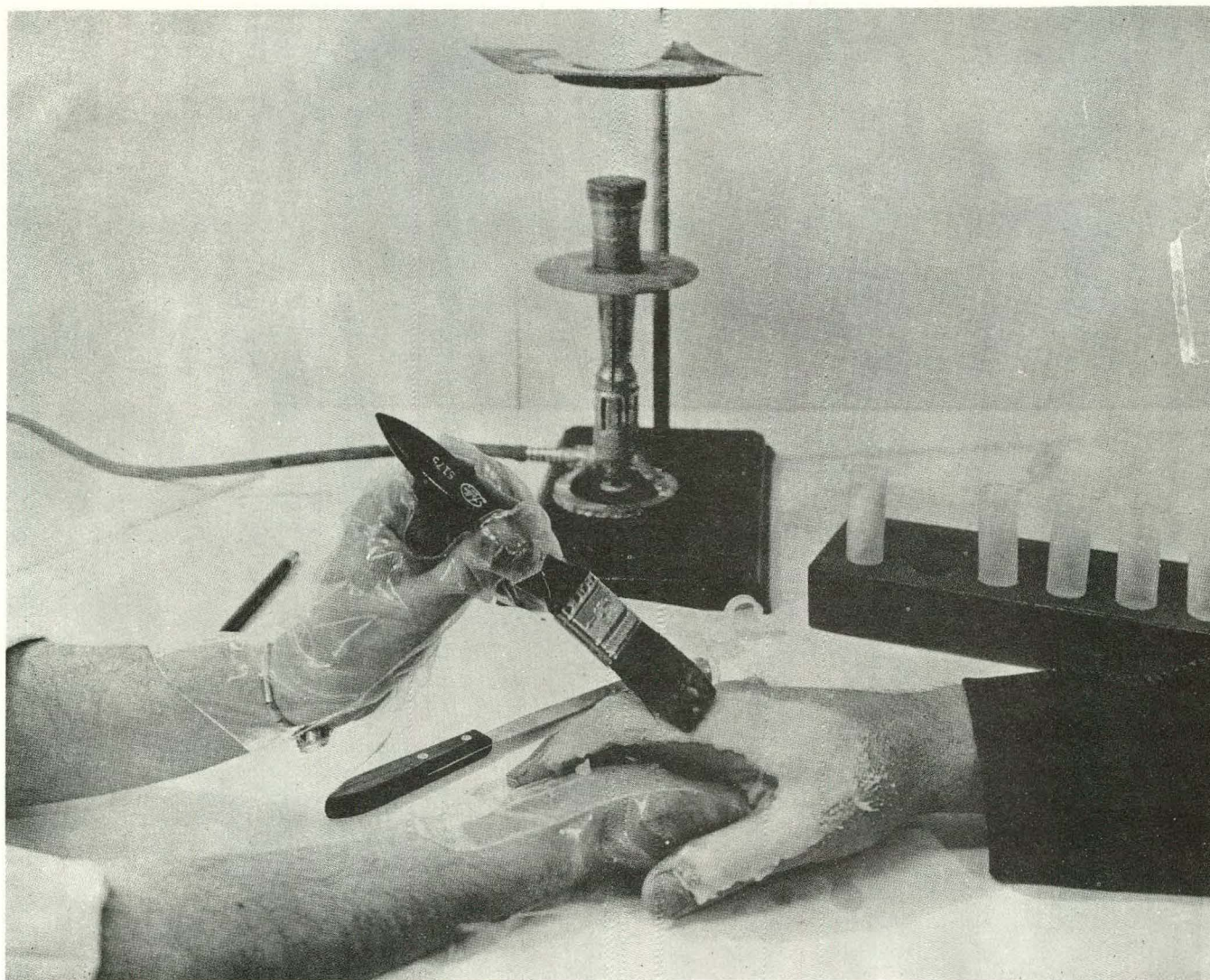
The results obtained from the filter paper swabbing indicate that little residue is removed from the hand by this technique. Also, this method has the disadvantage that the filter paper tends to crumble and a

portion of the sample may be lost. The scrubbing technique generally gave better results than the swabbing technique, but considerable manipulation, with possible loss of the sample, is a disadvantage. Another disadvantage with liquid scrubbing methods is that the liquids can drip onto areas of the hand which touched the gun, resulting in contamination of the sample. The paraffin technique, however, does not have these problems and appears to be effective in removing the residues from the hand. It has therefore been chosen as the best over-all method of residue removal. Paraffin has the additional advantages that the reagent has a very small or negligible blank and is easy to handle and that law enforcement agencies are already familiar with the technique involved, as it has been used in the old chemical test (diphenylamine test) for gunpowder residues. The detailed procedure follows.

Food-grade paraffin is rinsed with deionized water and acetone, melted, and heated to about 120°F in a clean porcelain dish. A small brush, which has been cleaned with deionized water and allowed to dry, is used to apply the melted paraffin to the hand, as shown in Fig. 11. In general, a flowing application is best, and the cast is built up with repeated applications to a thickness of about 1/8 in. so that it will be strong enough to remove in one piece after solidification. Care must be taken that the cast does not touch the areas normally in direct contact with the gun. The cast is removed by peeling it off the hand (see Fig. 12) and is stored in a clean polyethylene bag or folded and placed directly in a clean irradiation vial. Plastic gloves are worn at all times when handling the casts.

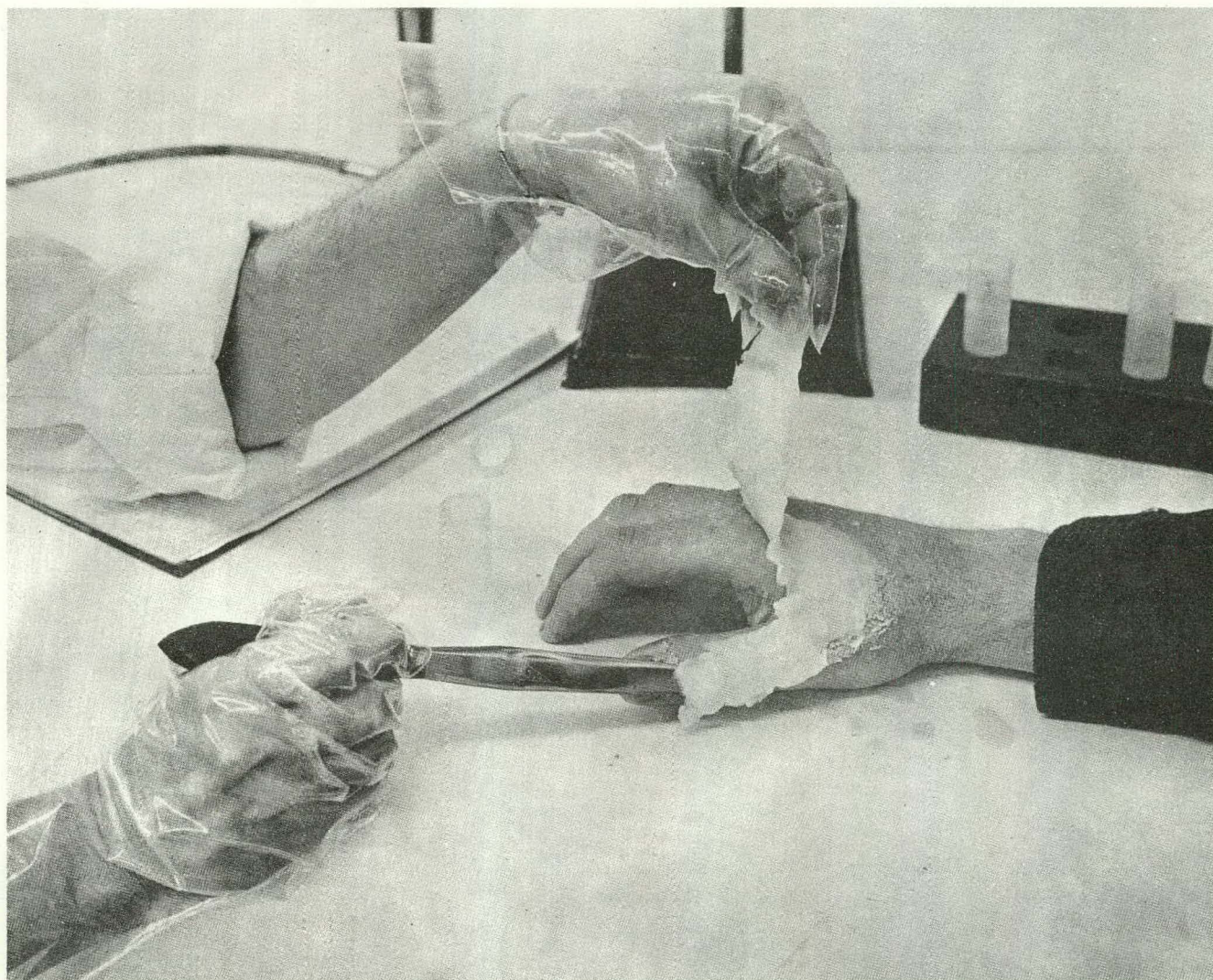
The cast is irradiated for 1 hr in a thermal-neutron flux of $1.8 \times 10^{12} \text{ n/cm}^2\text{-sec}$ in the rotary specimen rack of the TRIGA Mark I reactor. After irradiation, the sample is placed in a 250-ml beaker containing known amounts of Sb^{+3} and Ba^{+2} carrier (~20 mg each), 30 ml of water, 5 ml of concentrated HCl, and 1 ml of concentrated HNO_3 . The mixture is boiled for about 5 min. The two phases (paraffin and aqueous) are stirred to ensure adequate contact and complete isotopic exchange with the carriers. The mixture is then swirled in an ice bath to solidify the paraffin phase. The aqueous layer is poured into a 40-ml centrifuge tube containing Na^+ , K^+ , Mn^{++} , and Cl^- as holdback carriers. Two milliliters of concentrated H_2SO_4 are added, and the solution is stirred to precipitate BaSO_4 . The precipitate is centrifuged, filtered onto a preweighed filter paper, washed with water and ethanol, dried at 110°C for 15 min, and weighed. Cellophane tape is then placed over the precipitate, and the filter paper is carefully folded and placed in a 2-dram polyethylene vial and counted for Ba^{139} activity, using a well-type NaI(Tl) scintillation crystal coupled to a multi-channel gamma-ray spectrometer.

The Sb^{+3} in the supernatant solution is precipitated as Sb_2S_3 , using about 1 g of thioacetamide and heating. The precipitate is centrifuged and



T-27716

Fig. 11--Application of paraffin to the hand



T-27717

Fig. 12--Removal of paraffin cast

dissolved in about 10 ml of HCl, boiled for about 15 min to remove the H_2S , cooled, and diluted to about 30 ml. The free sulfur formed is centrifuged out and 10 ml of CrCl_2 solution (Oxorbant) are added to the supernatant. After heating, Sb will precipitate as the metal. The Sb is centrifuged, filtered, washed with water and ethanol, dried, and weighed. The sample is prepared for counting in a manner identical to that used for the BaSO_4 precipitate. The Sb^{122} activity is counted in a well-type crystal after a decay period of about three days to reduce the interference from any 12.8-hr Cu^{64} present. Any contribution from Cu^{64} remaining at this time is subtracted out of the spectrum by spectrum stripping. The measurements are made quantitative through the use of comparator standards treated in the same way as the samples.

Control Study

In order to interpret the data obtained after firing a gun, the normal levels of Ba and Sb found on the hand must be determined. Both hands of 22 persons who had not recently fired a gun were sampled. The results are shown in Table 6. The right hands averaged $0.15\text{ }\mu\text{g Ba}$ and $0.016\text{ }\mu\text{g Sb}$, and the left hands averaged $0.11\text{ }\mu\text{g Ba}$ and $0.014\text{ }\mu\text{g Sb}$. The range of values found for Ba was $0.01\text{ }\mu\text{g}$ to $0.48\text{ }\mu\text{g}$ and for Sb was <0.01 to $0.06\text{ }\mu\text{g}$. The left- and right-hand values do not differ significantly.

Single and Multiple Firings Using Same Gun and Ammunition

The residue deposited on the hand by single and multiple firings was determined for .38- and .22-caliber revolvers and for a .45-caliber automatic. The same gun and make of ammunition were used for all firings in a series. The results of the single firings are given in Table 7 and the results of the multiple firings are shown in Table 8. Firing was done using both left and right hands. The results are net values corrected for reagent blank and an average normal hand content.

The results of the single firings definitely indicate, in all cases, a deposition of Ba and Sb on the hand, increasing with increasing caliber of the weapon used. However, the values obtained are quite scattered, indicating that the deposition on and/or removal of the deposit from the hand may not be reproducible, or that perhaps there are differences in the individual cartridges from the same manufacturer.

The amount of deposit does not appear to increase linearly with the number of firings. One possible explanation is that additional blasts blow or shake off some of the previous deposit. It is possible that an "equilibrium" occurs in which a layer of residue is blown off while another is applied. It would appear, then, that one cannot generally tell from such measurements how many times a gun has been fired.

Table 6
NEUTRON ACTIVATION ANALYSIS OF RESIDUES
FROM LEFT AND RIGHT HANDS OF INDIVIDUALS
WHO HAD NOT RECENTLY FIRED A REVOLVER
(Element values in μg , net)

Right Hand		Left Hand	
Ba	Sb	Ba	Sb
0.14	0.06	0.22	0.06
0.32	0.03	0.19	0.01
0.03	<0.01	0.04	<0.01
0.18	0.02	0.12	0.02
0.48	0.01	0.44	0.01
0.18	<0.01	0.32	<0.01
0.07	<0.01	0.02	<0.01
0.03	<0.01	0.03	<0.01
0.17	<0.01	0.06	<0.01
0.09	0.03	0.07	<0.01
0.15	<0.01	0.07	<0.01
0.04	0.02	0.01	0.01
0.22	<0.01	0.08	0.01
0.03	<0.01	0.04	<0.01
0.09	<0.01	0.08	0.03
0.26	<0.01	0.09	0.02
0.11	<0.01	0.06	<0.01
0.10	<0.01	0.08	<0.01
0.26	<0.01	0.13	<0.01
0.15	0.02	0.25	0.01
0.09	<0.01	0.09	0.01
Avg 0.15 ± 0.11	0.016 ± 0.012	0.11 ± 0.11	0.014 ± 0.012

Table 7

NEUTRON ACTIVATION ANALYSIS OF HAND RESIDUES FROM
SINGLE FIRINGS USING SAME GUN AND AMMUNITION
(Element values in μg , net)

.38-caliber Revolver, Winchester Ammunition		.22-caliber Revolver, Western Ammunition		.45-caliber Automatic, Winchester Ammunition	
Ba	Sb	Ba	Sb	Ba	Sb
1.03 (R)	0.22 (R)	0.33 (R)	0.05 (R)	7.6 (R)	1.54 (R)
0.58 (R)	0.17 (R)	0.69 (L)	0.07 (L)	3.1 (L)	0.70 (L)
0.99 (R)	0.27 (R)	0.08 (R)	0.04 (R)	5.0 (R)	0.58 (R)
0.37 (L)	0.19 (L)	0.23 (L)	0.04 (L)	1.5 (L)	0.19 (L)
0.40 (R)	0.12 (R)	0.33 (R)	0.06 (R)	5.1 (R)	0.60 (R)
0.32 (L)	0.26 (L)	0.19 (L)	0.05 (L)	3.9 (L)	0.32 (L)
0.27 (R)	0.18 (R)	0.09 (R)	0.05 (R)	6.4 (R)	0.80 (R)
0.38 (L)	0.22 (L)	---	0.05 (L)	3.8 (L)	0.79 (L)
0.82 (R)	0.28 (R)	0.19 (R)	0.03 (R)	5.4 (R)	1.30 (R)
0.54 (L)	0.26 (L)	0.32 (L)	0.04 (L)	15.3 (L)	3.10 (L)
Over-all Average: Ba, 0.57 $\pm$ 0.27 Sb, 0.22 $\pm$ 0.05		Over-all Average: Ba, 0.27 $\pm$ 0.18 Sb, 0.05 $\pm$ 0.01		Over-all Average: Ba, 5.7 $\pm$ 3.8 Sb, 0.99 $\pm$ 0.84	
Right-hand Average: Ba, 0.68 $\pm$ 0.31 Sb, 0.21 $\pm$ 0.06		Right-hand Average: Ba, 0.20 $\pm$ 0.12 Sb, 0.05 $\pm$ 0.01		Right-hand Average: Ba, 5.9 $\pm$ 1.1 Sb, 0.96 $\pm$ 0.44	
Left-hand Average: Ba, 0.40 $\pm$ 0.09 Sb, 0.21 $\pm$ 0.04		Left-hand Average: Ba, 0.36 $\pm$ 0.23 Sb, 0.05 $\pm$ 0.01		Left-hand Average: Ba, 5.5 $\pm$ 5.5 Sb, 1.02 $\pm$ 1.19	

Single and Multiple Firings Using Different Guns but Same Ammunition

Five different .38-caliber revolvers were fired once and three times using the same ammunition (Peters). The results, shown in Table 9, have been corrected for reagent blank and an average normal hand content.

Single firings using different guns gave slightly higher standard deviation values than single firings using the same gun. The multiple firings using different guns gave about the same standard deviation values for Sb as did those using the same gun, but the Ba standard deviation values are lower. Multiple firings with different guns show some increase in deposit over single firings, but the relationship again is not linear.

Effect of Wind Direction

Using an upright high-velocity fan placed about 5 ft from the firing hand, a .38-caliber revolver was fired in a wind of 500 ± 100 linear feet per minute (measured by an Alnor Thermoanemometer). The fan was moved so that it blew from in front of, from the back of, from the side of, and from below the gun hand. Three shots were fired, using Winchester ammunition, for each wind direction. The results, corrected for reagent blank and an average normal hand content, are shown in Table 10.

It appears from these results that wind from the front tends to blow the blast products back across the hand, increasing the amount of deposit. Wind from the back or below appears to blow the blast products away from the hand, resulting in very small deposits of residue. A wind from the side also appears to reduce the amount of deposit on the hand.

Effect of Wet and Dry Hands

Identical firings were made with a .38-caliber revolver, except that the amount of moisture on the gun hand was varied. One person's hands were wiped dry with a paper towel, while the other person left his hands completely wet. Each fired the gun three times, and paraffin casts were made of their hands. The results of the analyses are shown in Table 11. From these results, it appears that moisture on the hands does not have any pronounced effects on the deposition of gunshot residues on the hand.

Effect of Washing Hands after Firing

A test was made to determine the effect of washing the hands after firing a gun. The gun hand of an individual was sampled before firing and after he had fired a .38-caliber revolver six times and washed his hands. The Ba value before firing was $0.11 \mu\text{g}$ and after firing and

Table 8

NEUTRON ACTIVATION ANALYSIS OF HAND RESIDUES FROM
MULTIPLE FIRINGS USING SAME GUN AND AMMUNITION
(Element values in $\mu\text{g, net}$)

.38-caliber Revolver, Winchester Ammunition		.22-caliber Revolver, Western Ammunition		.45-caliber Automatic, Winchester Ammunition	
Ba	Sb	Ba	Sb	Ba	Sb
Three Firings					
0.68 (L)	0.32 (L)	0.11 (L)	0.03 (L)	2.8 (L)	0.56 (L)
0.73 (L)	0.55 (L)	0.33 (R)	0.12 (R)	8.2 (L)	1.5 (L)
1.9 (R)	0.59 (R)				
0.73 (L)	0.36 (L)				
Avg 1.01	0.45	0.22	0.08	5.5	1.0
± 0.89	± 0.13	± 0.16	± 0.06	± 3.3	± 0.6
Six Firings					
1.1 (R)	0.43 (R)	0.15 (R)	0.08 (R)	2.5 (R)	0.87 (R)
0.68 (R)	0.35 (R)	0.22 (L)	0.22 (L)	0.82 (R)	0.16 (R)
Avg 0.89	0.39	0.19	0.15	1.7	0.51
± 0.29	± 0.05	± 0.05	± 0.10	± 1.1	± 0.36

Table 9

NEUTRON ACTIVATION ANALYSIS OF HAND RESIDUES
FROM SINGLE AND MULTIPLE FIRINGS USING
DIFFERENT GUNS BUT SAME AMMUNITION
(Element values in $\mu\text{g, net}$)

One Firing		Three Firings	
Ba	Sb	Ba	Sb
1.31	0.60	2.27	0.61
0.51	0.31	1.41	0.56
0.83	0.24	3.15	0.54
0.12	0.06	1.60	0.27
0.72	0.28	0.56	0.37
Avg 0.70	0.30	1.79	0.49
± 0.43	± 0.19	± 0.96	± 0.14

washing was $0.05 \mu\text{g}$. The corresponding Sb values were $0.01 \mu\text{g}$ and $0.01 \mu\text{g}$. Thus, as expected, it appears that normal washing of the hands destroys the evidence of having fired a gun.

Effect of Handling Guns

In the study of gunshot residues, it is important to determine the amounts of Ba and Sb which can be picked up by handling guns without actually firing them. Casts were taken of the backs, as well as the palms, of the hands of a person who had handled several guns over a period of time but had not fired any of them. The results are shown in Table 12. A definite increase over the normal levels is indicated. As would be expected, the palms pick up a considerable amount of Ba and Sb.

Various guns were swabbed with a wet filter paper to determine what levels of Ba and Sb could be removed. The handle, the barrel, and the chamber area of the gun were each sampled. The results, shown in Table 13, indicate that significant amounts of Ba and Sb can be transferred just by handling the gun, especially if the chamber area is touched.

Results of an Actual Case

Five paraffin casts from an actual shooting case were analyzed for Ba and Sb. Two of the casts were from the victim (but, unfortunately, after his hands had been washed), two were from the suspect, and one was from a person in the laboratory who fired once with the confiscated .38-caliber revolver. There was a strong possibility that suicide, rather than murder, was involved. The results of the analyses of these casts are shown in Table 14.

The values of Ba and Sb from the hands of the suspect and the victim fall well within the statistical limits for normal hands. The fact that the victim's hands were washed destroyed the possibility of determining whether or not he had fired a gun. Therefore, no conclusion could be drawn in this case. The control firing appears to agree with the results obtained earlier using .38-caliber Peters ammunition.

Gunshot Residues on Gloves

A pair of gloves, possibly worn by a suspect in a shooting case, was submitted for gunshot residue analysis. The palm, web, and forefinger of each glove were gently rubbed with filter paper moistened with 2% HNO_3 . The six samples, plus a reagent blank, were irradiated for 30 min in a thermal-neutron flux of $1.8 \pm 10^{12} \text{ n/cm}^2\text{-sec}$ and analyzed radiochemically for Ba and Sb. No Sb ($\leq 0.01 \mu\text{g}$) was detected in any of the samples, but small amounts of Ba were found on each glove (palm 0.72 and $0.89 \mu\text{g}$,

Table 10

EFFECT OF WIND DIRECTION ON RESIDUE DEPOSIT
(Element values in μg , net)

Wind Direction	Ba	Sb
From front	0.49	0.24
From right side	0.25	0.17
From behind	0.08	0.11
From below	0.03	0.11

Table 11

EFFECT OF DRY AND WET HANDS ON AMOUNT
OF DEPOSIT
(Element values in μg , net)

Dry Hands		Wet Hands	
Ba	Sb	Ba	Sb
2.0	0.60	0.84	0.37
2.4	0.64	2.4	0.55

Table 12

EFFECT OF HANDLING GUNS EXTENSIVELY
(Element values in μg , net)

Hand Area	Ba	Sb
Right hand, dorsal	0.36	0.28
Left hand, dorsal	0.31	0.23
Right palm	0.49	0.42
Left palm	0.58	0.47

Table 13
 NEUTRON ACTIVATION ANALYSIS OF SWABBINGS
 FROM VARIOUS GUNS
 (Element values in μg , net)

Caliber	Area	Ba	Sb
.22	Handle	0.27	0.27
.22	Barrel and chamber	5.1	0.56
.38	Handle	1.8	0.57
.38	Barrel and chamber	8.7	4.8
.45	Handle	0.60	0.39
.45	Barrel and chamber	3.1	2.1

Table 14
 RESULTS OF ANALYSIS OF PARAFFIN CAST
 FROM ACTUAL SHOOTING CASE
 (Element values in μg , net)

Sample	Ba	Sb
Victim (L)	0.24	0.01
Victim (R)	0.29	0.01
Suspect (L)	0.17	0.05
Suspect (R)	0.04	0.03
Control (R)	0.75	0.09

web 0.22 and 0.27 μg , forefinger 0.56 and 0.35 μg). The fact that the gloves had been handled so much and wiped with a moist cloth prior to being received prevented a good evaluation.

AUTOMOBILE GREASES

The characterization of greases is of importance in hit-and-run cases, where a small smear of grease from the underside of the automobile may be left on the clothing or body of the victim or on the grass or weeds in an adjacent field if the car veered off the road before being driven on.

Thirteen samples of clean grease, obtained from garages and service stations in the Los Angeles and San Diego areas, were analyzed by purely instrumental NAA techniques. The samples were first irradiated for 30 sec in a flux of 4.3×10^{12} n/cm²-sec (pneumatic-tube position of the TRIGA Mark I reactor) and were immediately counted by gamma-ray spectrometry for induced short-lived activities. They were then irradiated for 30 min in the rotary specimen rack of the reactor (1.8×10^{12} n/cm²-sec flux) and counted at several decay times. A typical spectrum obtained is shown in Fig. 13. The results are shown in Table 15. A total of eleven elements were detected in the thirteen samples. Calcium was a sizable constituent (0.1% to 1.0%) in six of the greases. Barium was a major constituent (4.6%) in one grease, and zinc (5%) in another. The other elements were present in amounts generally ranging from 0.07 to 250 ppm. Sodium (1500 ppm) was the only element detected in one sample. All of the samples studied, including three different grades from the same oil company, showed wide differences in their composition, both qualitatively and quantitatively.

The study on clean greases shows that they can be characterized very well. However, in actual cases the grease sample will most likely not be clean but will contain a certain amount of dirt and dust. It would be desirable, therefore, to separate the dirt from the grease so that both could be studied separately.

A number of solvent-separation techniques were explored in an attempt to devise a satisfactory method of separating dirty grease samples into a clean grease phase and a dirt (solid particulate) phase. Solvents tried included benzene, toluene, xylene, cyclohexane, ethanol, ether, petroleum ether, hexane, heptane, acetone, carbon tetrachloride, chloroform, and a mixture of alcohol-hexane-acetone. Of these, hexane appeared to work best, as it dissolved the grease, dispersed some of the grease additive material, and left the dirt particles unaffected.

A sample of a green-colored grease, manufactured by Tidewater Oil Company, was irradiated for 30 min in a flux of 1.8×10^{12} n/cm²-sec.

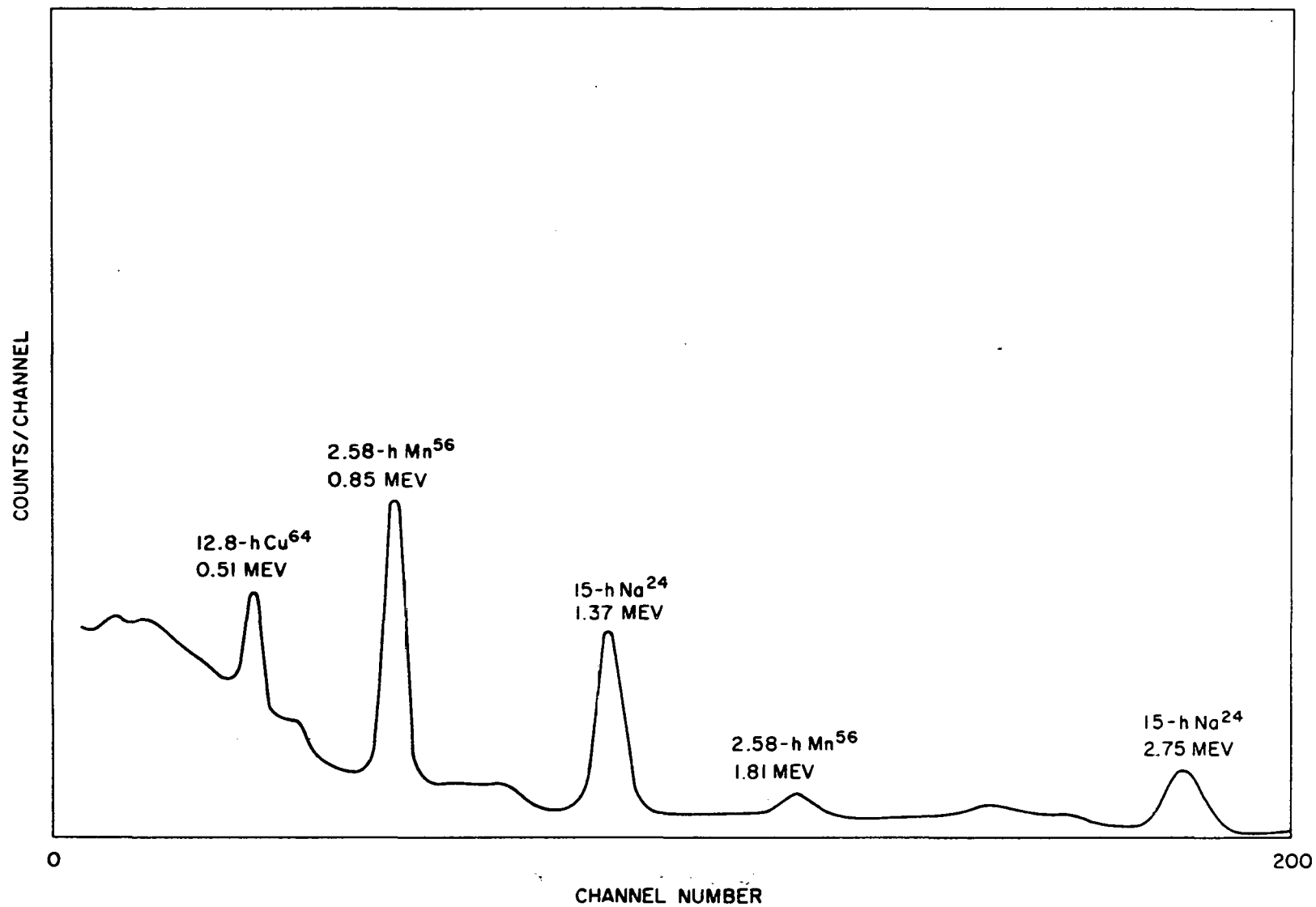


Fig. 13--Gamma-ray spectrum of a neutron-activated chassis-lubricating grease

Table 15

ELEMENTS DETECTED IN THIRTEEN LUBRICATING GREASES
(Element values in ppm)

Sample	Na	Al	Cl	Ca	V	Mn	Zn	As	Br	Mo	Ba
Wilshire	25	120	---	240	----	0.4	----	1.1	---	1	-----
Mobil	4	4	8	6500	0.23	0.2	----	1.0	---	--	17
Standard	160	80	---	2200	1.9	2.9	----	---	3.2	--	-----
Shell	50	25	70	1100	----	---	----	---	---	---	-----
Union	7	2.5	2.5	----	130	---	----	---	---	--	4.6×10^4
LAPD (Lube Specialties)	60	240	240	4200	----	0.4	----	---	---	11	-----
Signal	30	13	---	2700	1.7	0.3	----	0.2	---	--	-----
Texaco	1500	----	---	----	----	---	----	---	---	---	-----
Douglas	10	19	28	250	----	0.2	----	---	---	--	340
Richfield	10	6	---	190	0.9	0.07	----	---	---	--	15
Tidewater	12	30	---	730	----	0.09	5×10^4	---	---	--	-----
Seaside (Tidewater)	80	20	---	9600	----	0.6	----	---	---	--	-----
GA Garage (Tidewater)	16	250	---	800	----	---	----	---	---	--	-----

After irradiation the grease was shaken with hexane, and the hexane phase was shaken with several portions of deionized water. Then 10 ml of the hexane layer was taken for counting. The results, compared with a hexane solution of a similar amount of the same grease but which was not shaken with water, are shown in Table 16. It appears that shaking a hexane solution of the grease with water tends to extract some Na, Cl, and Mn from the grease into the aqueous phase but does not tend to extract the Zn.

Using the same Tidewater grease, a comparison was made between the results of a preirradiation separation and a postirradiation separation. Three samples of dirty grease were dissolved in 20 ml of hexane. The solution was then washed three times with water. The hexane phase was then irradiated and counted. Another sample of the same dirty grease was first irradiated and then separated as described above. A sample of clean grease was also irradiated, dissolved in hexane, and counted. The results are shown in Table 17. The three identical samples (1, 2, and 3) show fairly good reproducibility, with the exception of the low Mn value in sample 1. The Mn and Cl values are higher in the preirradiation-separated samples than in the postirradiation-separated samples, but the Na and Zn values are consistent. The Na and Al values are considerably lower in all of the samples which were separated than in the untreated grease, but the Cl and Mn values are consistent.

The same procedure used with the green grease was used with a brown Tidewater grease. The results are shown in Table 18. Only Na and Al were determined in this sample because the large amount of Na^{24} activity obscured any other radioactive species which might have been present. The Na values appear to be consistent throughout, but the Al values are somewhat erratic.

A green Standard Oil Company grease was also studied, using both preirradiation and postirradiation separations. In this case, however, when hexane and water were used, an emulsion was formed which was difficult to break. Addition of alcohol to the hexane removed this difficulty. The grease samples, both irradiated and nonirradiated, were shaken with 20 ml of hexane and 10 ml of alcohol, and then 20 ml of water was added and the mixture was again shaken. The aqueous-alcohol layer was then removed, 10 ml of alcohol was added to the hexane layer, and the mixture was shaken. Water was again shaken with the hexane-alcohol mixture, and the aqueous-alcohol layer was removed and discarded. This procedure was repeated once more. Finally, 10 ml of the hexane solution of the irradiated sample was taken for counting, and 10 ml of the hexane solution of the nonirradiated sample was irradiated and counted. The results are shown in Table 19. The separation procedure removes a large fraction of the Na from the grease as well as a considerable amount of the Ca.

Table 16
GREASE-DIRT SEPARATIONS WITH HEXANE-WATER

Sample ^a	Elements (ppm)			
	Na	Cl	Mn	Zn ^b
A	69	76	0.31	1.0
B	50	62	0.14	1.0
C	52	66	0.31	0.9
D	41	57	0.11	1.2

^a Sample designations:

- A, Clean grease dissolved in 10 ml hexane.
- B, Clean grease dissolved in 20 ml hexane, washed once with 20 ml H₂O, 10 ml hexane phase counted.
- C, Dirty grease dispersed in 20 ml hexane, washed three times with 20 ml H₂O; 10 ml hexane phase counted.

D, Same as B, except three water washings.

^b Relative values only.

Table 17

PREIRRADIATION AND POSTIRRADIATION SEPARATIONS
OF GREEN TIDEWATER GREASE

Sample ^a	Elements (ppm)				
	Na	Cl	Mn	Zn	Al
1	41	73	0.20	139	--
2	41	58	0.39	132	28
3	38	69	0.43	145	23
4	44	36	0.12	137	--
5	69	76	0.31	---	43

^a Sample designation:

1, 2, 3, Dirty grease, preirradiation separation.

4, Dirty grease, postirradiation separation.

5, Clean grease, no separation.

Table 18

PREIRRADIATION AND POSTIRRADIATION SEPARATION
OF BROWN TIDEWATER GREASE

Sample ^a	Elements (ppm)	
	Na	Al
1	7800	1900
2	----	2600
3	7900	1600
4	8200	2600
5	8100	----
6	7400	----
7	8400	----

^a Sample designation:

1, 2, 3, Dirty grease, preirradiation separation.

4, Clean grease, preirradiation separation.

5, 6, Dirty grease, postirradiation separation.

7, Clean grease, no separation.

Table 19

PREIRRADIATION AND POSTIRRADIATION SEPARATION
OF GREEN STANDARD OIL GREASE

Sample ^a	Elements (ppm)					
	Na	Cl	Mn	Al	Br	Ca
1	240	420	4.6	390	27	24,000
2	190	410	4.2	390	27	33,000
3	270	280	7.0	---	22	---
4	3900	---	---	---	--	66,000

^a Sample designation:

- 1, 2, Dirty grease, preirradiation separation.
- 3, Dirty grease, postirradiation separation.
- 4, Clean grease, no separation.

A degreasing solvent, trichlorethylene, was tried as a solvent for nine different clean grease samples. In every case a thick, gummy-appearing suspension was formed. It was found, however, that if glacial-acetic acid was added, this suspension would dissolve. With a mixture of trichlorethylene and glacial acetic acid, four of the greases dissolved completely, but a small granular residue remained for the other five. In one case this residue was water-soluble. No solvent was found which would dissolve the other residues, although several solvents were tried. Samples of these greases were irradiated for 30 min and were then dissolved in the trichlorethylene-acetic acid mixture, centrifuged, washed thoroughly with the solvent, and filtered. In each case a significant amount of the induced activities remained with the residue.

A hot-filtration method was also tried, but was unsuccessful.

The main problem with these separations is that the greases are so different that a method which is satisfactory for one grease will fail completely when used with another. A method which is universal for all greases is yet to be developed.

COMMERCIAL PLASTICS

Plastics, as they are used in a very large number of objects, are frequently of interest in criminal cases, and it is desirable to be able to identify a piece of plastic as to its origin.

Virtually all commercial plastics are polymerized hydrocarbons (e. g., polyethylene, polypropylene, polystyrene) or polymerized C-H-O compounds (e. g., lucite, nylon, cellulose acetate). A few contain either F (teflon), Cl (polyvinyl chloride), or N (cellulose nitrate) as one of the major constituents. The detection of F, Cl, N, or O in the plastic by neutron activation analysis will identify it as to type (C and H are not detected by this method). Identification of the trace impurities in the plastic may identify the manufacturing process used, or even the manufacturer, and possibly the batch from which the particular sample came.

Twenty different plastic samples (see Table 20) were analyzed by purely instrumental NAA means. They were first irradiated for 30 sec in a thermal-neutron flux of 4.3×10^{12} n/cm²-sec and immediately counted. They were then irradiated for 30 min in a thermal-neutron flux of 1.8×10^{12} n/cm²-sec and counted at several decay times, ranging from one hour to several weeks after the irradiation.

A total of thirteen different elements were detected at trace levels in the twenty samples. The amounts of these elements, shown in Table 21,

Table 20

IDENTIFICATION OF PLASTIC SAMPLES

Sample	Type	Trade Name	Manufacturer
1	Acetal	Delrin 500	Dupont
2	Acrylic	Lucite 140	Dupont
3	Cellulose acetate	Tenite 043-A	Eastman
4	Cellulose acetate butyrate	Tenite 205-A	Eastman
5	Cellulose propionate	Tenite 306-A	Eastman
6	Fluorocarbon	Teflon-1	Dupont
7	Polyamide (nylon)	Zytel 101	Dupont
8	Polyethylene	Tenite 860-A	Eastman
9	Polyethylene	DYNH-1	Union Carbide
10	Polyethylene	617	Allied Chemical
11	Polypropylene	Escon 104	Enjay
12	Polypropylene	Tenite Polypropylene	Eastman
13	Polystyrene	SMD-3500	Union Carbide
14	Acetonitrile-butadiene-styrene	Kralastic-B	U. S. Rubber
15	Acetonitrile-butadiene-styrene	Kralastic-MM	U. S. Rubber
16	Vinyl	VND-9970	Union Carbide
17	Phenolic	BMG-5000	Union Carbide
18 ^a	Unknown	Unknown	Guide
19	Polyurethane	Unknown	Unknown
20 ^b	Polyvinyl chloride	Unknown	Unknown

^aPiece of automobile taillight.^bPiece of a street-marking cone.

Table 21

NEUTRON ACTIVATION ANALYSIS OF COMMERCIAL PLASTICS
(Element values in ppm)

Sample ^a	Na	Al	Cl	Mn	Cu	Cd	Ba	Ti	Sb	Br	Zn	As	Au
1	2	1	--	0.26	0.4	----	----	----	-	---	----	----	----
2	10	--	8	----	----	----	----	----	-	---	----	----	----
3	3	3	--	----	----	2800	620	----	-	---	----	----	----
4	3	3	--	0.14	----	3000	2800	----	-	---	----	----	----
5	10	80	6	0.05	----	----	----	8×10 ⁴	5	---	----	----	----
6 ^b	25	--	--	----	----	----	----	----	-	---	----	----	----
7	0.2	--	3	0.05	----	----	----	----	-	---	----	----	----
8	0.4	--	3	----	----	----	----	----	-	0.2	----	----	----
9	0.3	--	0.3	----	----	----	----	----	-	---	----	----	----
10	0.9	3	2	0.1	----	----	----	----	-	0.1	----	----	----
11	1	6	14	0.1	0.08	----	----	----	-	---	18	0.06	----
12	0.04	15	3	0.03	----	----	----	----	-	---	----	----	----
13	0.6	0.3	0.3	0.05	----	----	----	----	-	---	----	----	----
14	170	2	--	----	25	----	----	----	-	---	1200	----	----
15	190	3	--	----	30	----	----	----	-	---	----	----	----
16	4	--	2.3×10 ⁵	----	70	----	----	----	-	---	----	----	----
17	150	50	390	1	25	----	----	----	-	---	----	----	----
18	4	2	10	0.06	----	----	----	----	-	---	----	----	0.06
19	170	15	130	0.6	210	----	----	----	-	---	----	----	----
20	500	--	3×10 ⁵	----	----	----	----	----	-	---	700	----	----

^aSee Table 20.^bFluorine also detected as a major constituent.

clearly indicate that all of the samples studied differed greatly, both qualitatively and quantitatively, in their elemental composition and are thus easily characterized and identified. A typical gamma-ray spectrum of an irradiated plastic sample is shown in Fig. 14.

The above measurements were made on rather large samples (0.5 to 3.0 g). In criminal cases, however, very small samples are often encountered, and the problem of sample inhomogeneity must be considered. In a preliminary investigation of this problem, four small (25 to 50 mg) samples of each of two different plastics were analyzed by irradiating for 30 min and counting. The results, shown in Table 22, are relative values, not absolute values. They indicate that one sample is quite homogeneous with respect to all four elements but that the other sample varies somewhat in its Mn and Au contents, while its Na and Cl contents are consistent.

RUBBER

Nine different samples of automobile tire rubber were analyzed by purely instrumental NAA means. A single sample of each rubber was irradiated for 30 sec in a thermal-neutron flux of 4.3×10^{12} n/cm²-sec and immediately counted. For intercomparison of the samples, and also to check on the homogeneity of each sample, duplicate samples of each rubber were irradiated for 30 min in a thermal-neutron flux of 1.8×10^{12} n/cm²-sec and counted. The elements detected and their estimated concentrations are shown in Table 23. A typical spectrum is shown in Fig 15.

All of the samples showed the presence of Al, Na, Cl, Mn, and Zn. Sulfur was detected in four samples, and titanium in one. Antimony was positively detected in one of the samples and may also have been present in four of the other samples, but the apparent peak at about 0.57 Mev was not resolved from the 0.51-Mev annihilation radiation peak from Zn⁶⁵. The various rubber samples all appear to be different from one another.

The results of the duplicate determinations generally agree to within about $\pm 10\%$, and therefore no significant inhomogeneity is indicated.

Four small rubber samples from an actual case were analyzed instrumentally. Two samples were obtained at the scene of a crime and were thought to be from the heel and sole of a shoe. The other two samples were obtained from the heel and sole of a shoe of a suspect in the crime. The samples were not weighed, to avoid the possibility of losing the tiny evidence samples in the process.

The samples were irradiated for 30 min in the reactor. Counting the samples showed Na, Cl, Mn, and Zn to be present. The results are

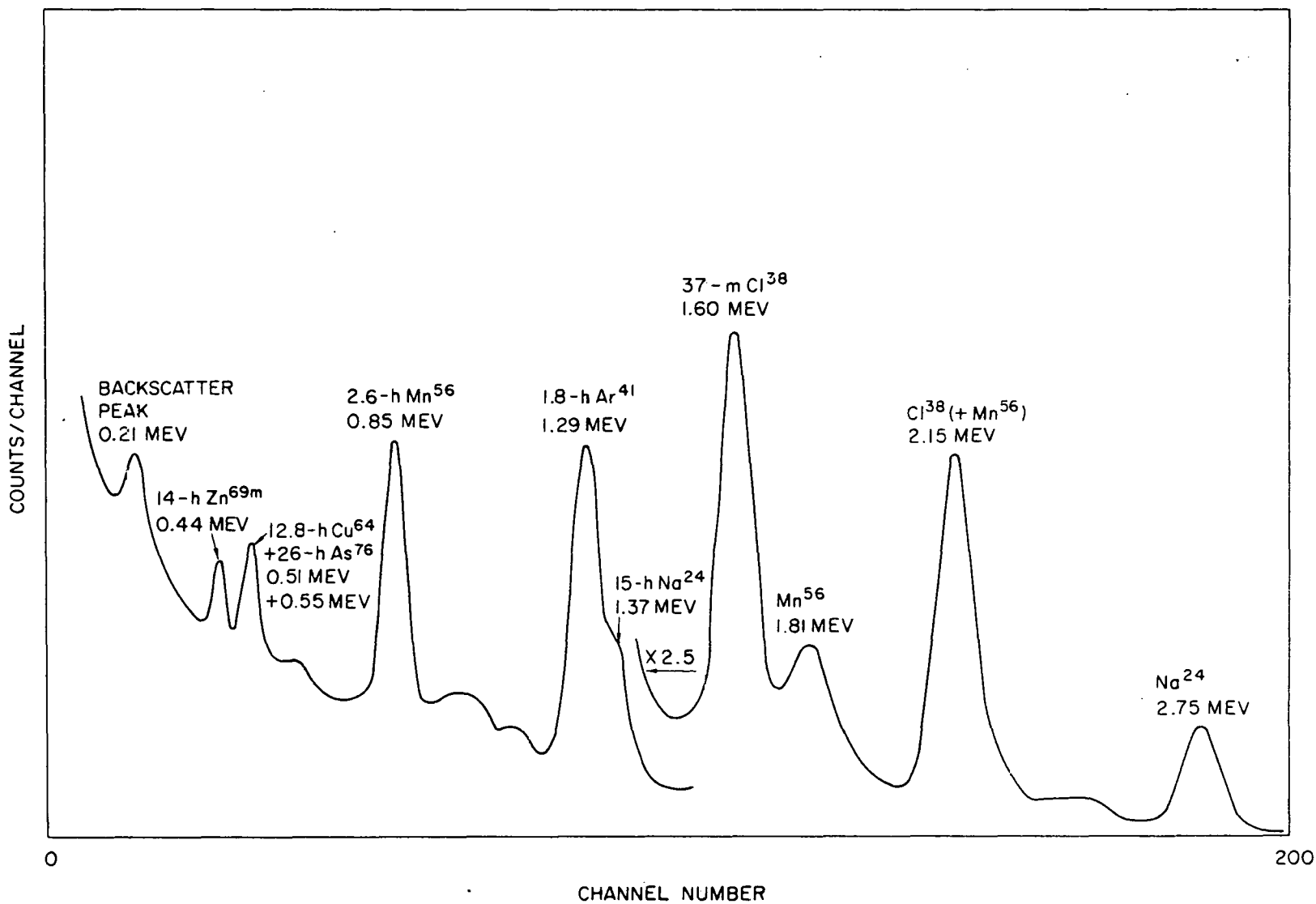


Fig. 14--Gamma-ray spectrum of an irradiated commercial plastic

Table 22
STUDY OF HOMOGENEITY OF TWO PLASTIC SAMPLES

	Relative Concentrations			
Enjay Polypropylene (11)	Cl	Mn	Zn	Na
1	44	96	44	32
2	44	104	39	27
3	40	97	35	28
4	43	102	40	24
Average	43±2	100±4	40±5	28±3
Guide Red Taillight (18)	Cl	Mn	Au	Na
1	21	51	7	38
2	20	30	8	37
3	18	44	7	40
4	19	28	23	34
Average	19±2	38±12	12±8	37±3

Table 23

NEUTRON ACTIVATION ANALYSIS OF AUTOMOBILE TIRE RUBBER

Sample	Concentrations of Elements Detected (ppm)					
	Al	Na	Cl	Mn	Zn	Other
U.S. Royal	780	1,620	1,980	6.3	12,900	S, 9×10^4
		1,760	2,180	6.7	14,400	
General	3,800	2,300	3,140	3.8	16,500	
		2,120	3,160	3.6	14,100	
Fisk	3,100	1,470	2,500	7.8	22,300	
		1,550	2,720	7.8	21,800	
Goodyear No. 1	2,400	2,200	3,690	11.5	17,000	S, 8×10^4
		2,000	3,180	9.3	16,700	
Goodyear No. 2	250	1,790	4,350	8.0	13,000	S, 7×10^4
		1,750	3,920	6.8	13,300	
Atlas	330	2,000	2,920	2.5	19,200	Ti, 1.2×10^4
		2,050	2,370	3.2	20,400	
Firestone-Phoenix (Germany)	480	540	840	2.3	21,800	Sb, 100
		490	840	2.3	21,700	
Firestone (domestic)	1,360	2,000	3,300	4.6	15,300	
		2,140	3,650	5.6	14,500	
Interstate Rubber	310	520	560	7.2	14,200	S, 2×10^5
		500	580	5.4	15,100	

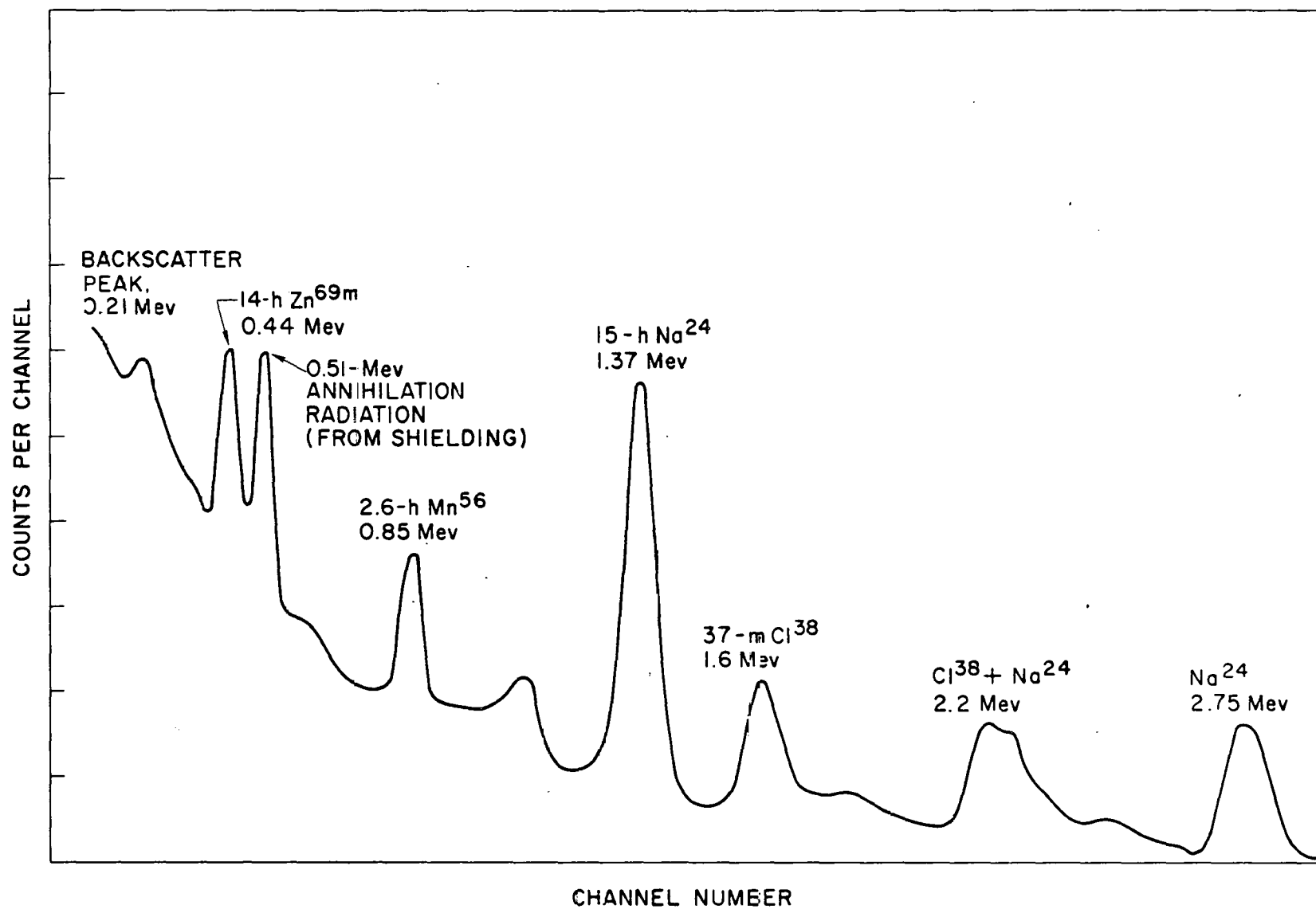


Fig. 15--Gamma-ray spectrum of an irradiated automobile-tire rubber

shown in Table 24. These values represent the relative amounts of the same element in each sample and not the relative amounts of the different elements in the same sample. For better comparison, the ratios of the relative amounts of each element in the evidence samples and the known samples were calculated and are shown in Table 25. Although there are similarities in the relative amounts of the elements detected in the samples, there are also significant quantitative differences. Therefore, no conclusion as to the source of the two evidence samples could be made. The differences could have been due to inhomogeneous samples or contamination.

PAINT

Seventeen samples of five different colors of DuPont automobile paint were analyzed instrumentally by irradiating them in the reactor for 30 sec and 60 min, respectively. Although the paints of one color had a different manufacturer's identification number, they appeared almost identical in color to the eye. The results of the analyses are shown in Table 26 and a typical spectrum is shown in Fig. 16. As seen from the table, all of the paints are definitely different.

Analytical results for four samples of red paint (No. 4403-LH) from the same can, as well as one sample of this same paint from a different can, are compared in Table 27. The results show good reproducibility, even in the samples from different cans.

In a study of an actual case, samples of paint from a vending machine were analyzed for possible comparison with paint found on a tool possibly used to jimmy the machine in a burglary. The paints were a red enamel and a white undercoat. Irradiations for 1 min and 30 min, respectively, revealed the presence of six elements. The red enamel contained 14% Mn, 2% Cr, 1.4% Na, and 0.2% Sb, and the white paint contained 30% Ti, 4% Al, and 0.07% Na. The results were of value to the investigating officers.

GLASS

Samples of nine different kinds of laboratory glass were analyzed instrumentally. After irradiation for 30 min in the reactor, the samples were counted at various decay times for up to three weeks. The results, in Table 28, show differences in the composition of the different glasses. A typical gamma-ray spectrum obtained is shown in Fig. 17.

Samples of automobile headlight and windshield glass were also irradiated and counted in a preliminary study. The samples appeared to be different, although no quantitative measurements were made.

Table 24

RELATIVE AMOUNTS OF EACH ELEMENT DETECTED IN
RUBBER SAMPLES FROM ACTUAL CASE
(Values are in different arbitrary units for each element)

Sample	Na	Cl	Mn	Zn
Suspected sole	1.26	0.95	6.2	0.18
Suspected heel	0.45	0.21	0.72	<0.08
Known sole	25	23	98	6.0
Known heel	60	<6	176	7.5

Table 25

RATIOS OF RELATIVE AMOUNTS OF ELEMENTS DETECTED
IN RUBBER SAMPLES FROM ACTUAL CASE

Sample Ratio	Na	Cl	Mn	Zn
Suspected sole:known sole	0.050	0.041	0.063	0.030
Suspected heel:known heel	0.0075	<0.03	0.0041	<0.011

Table 26

NEUTRON ACTIVATION ANALYSIS OF DUPONT AUTOMOBILE PAINT

Color	Color Number	Composition (ppm)								
		Na	Mn	Cl	Al	Cu	Ti	Br	Zn	Cr
Red	2931-LH	1,820	15,880	---	----	---	----	---	---	17,730
	4387-LH	857	6,140	---	----	---	----	---	---	29,210
	4034-LH	4,230	23,700	---	----	---	----	4,300	---	----
	4403-LH	168	238	---	7.1	---	----	226	---	----
	4260-LH	2,100	31,140	---	----	1,950	----	---	---	----
Beige	2928-L	92	5.1	175	7,800	---	2.4×10^5	---	2,390	----
	4026-L	51	2.2	96	7,100	---	2.4×10^5	---	1,314	----
	4401	80	10.9	235	7,700	---	1.9×10^5	---	2,410	----
Green	2940	215	6.8	5,340	5,100	629	1.1×10^4	---	---	----
	4029	113	13.0	1,800	3,600	168	1.9×10^4	---	---	----
	4142	409	12.1	6,640	4,300	774	4.8×10^3	---	---	----
Black	88-L (Lucite)	25	3.6	172	46	320	----	---	---	----
	44 (lacquer)	61	2.1	95	20	893	----	---	---	----
	93-005 (enamel)	555	1,080	---	----	---	----	---	---	----
Blue	2925-L	128	6.2	532	1.6×10^4	175	----	---	---	----
	4250-L	331	9.8	779	3.1×10^4	414	----	---	---	----
	4251-LH	352	10.1	3,920	2.4×10^4	303	----	---	---	----

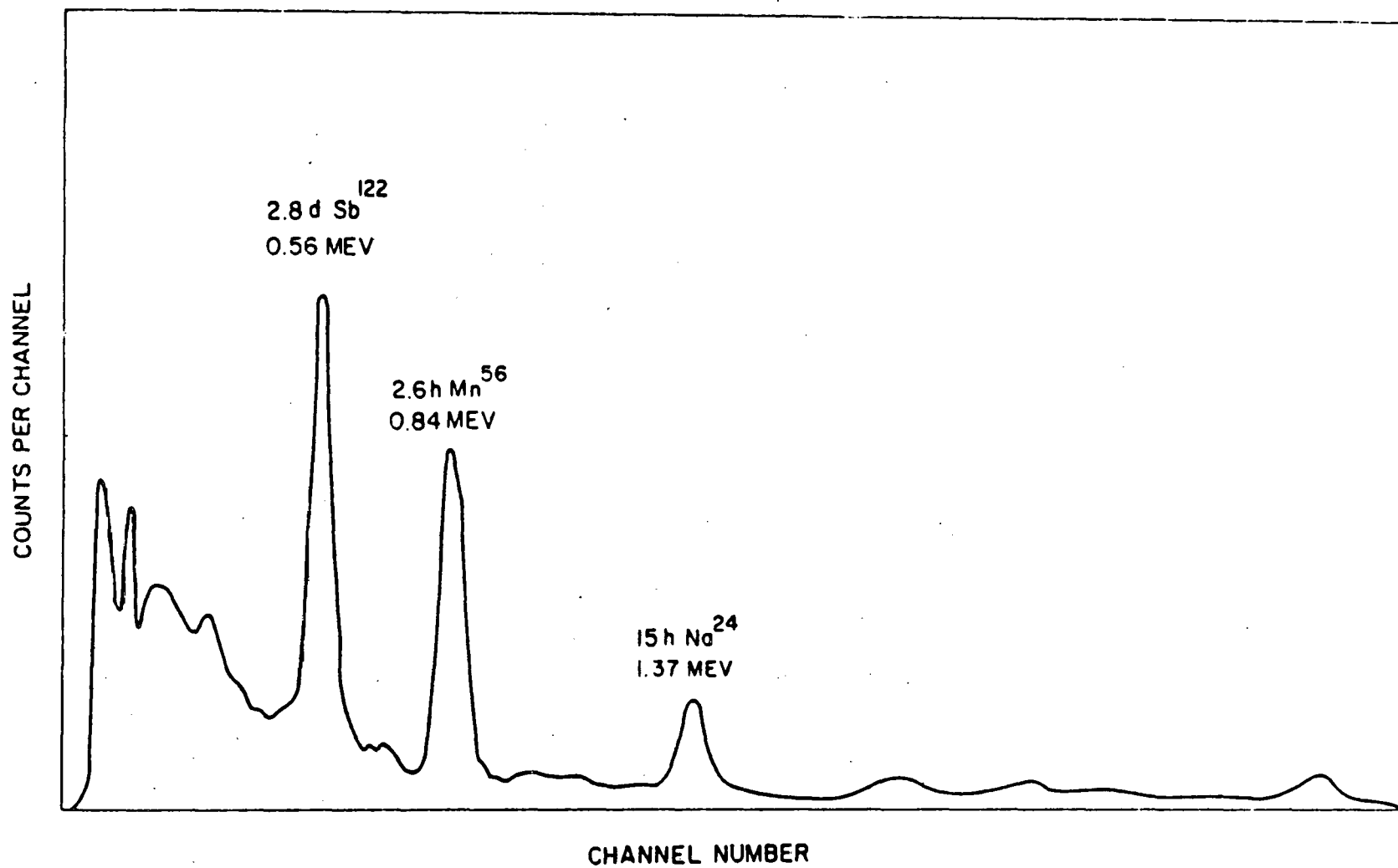


Fig. 16--Gamma-ray spectrum of a neutron-activated automobile paint

Table 27
COMPARISON OF FIVE SAMPLES OF
SAME PAINT
(Element values in ppm)

Sample	Na	Mn	Al	Br
Can 1	168	238	7.1	266
Can 2				
A	178	289	7.4	267
B	181	284	6.9	276
C	181	265	7.5	278
D	175	268	7.0	251

Table 28
ANALYSIS OF LABORATORY GLASS SAMPLES
(Element values in ppm)

Sample	Sc	Hf	Na	Ba	Zr	Sb
Centrifuge tube	0.06	7	1.6×10^4	-----	750	--
Beaker	0.08	16	1.3×10^4	-----	1400	--
Large bottle	-----	--	1.0×10^4	2.6×10^4	-----	--
Small bottle	-----	--	1.0×10^5	1.9×10^4	-----	--
Glass bead	0.27	--	1.2×10^5	-----	-----	--
Stirring rod	0.09	11	2.2×10^4	-----	850	--
Funnel	0.04	8	1.2×10^4	-----	480	--
Watch glass	-----	--	8×10^4	-----	-----	73
Transfer pipette	-----	--	1.1×10^5	2.4×10^4	-----	--

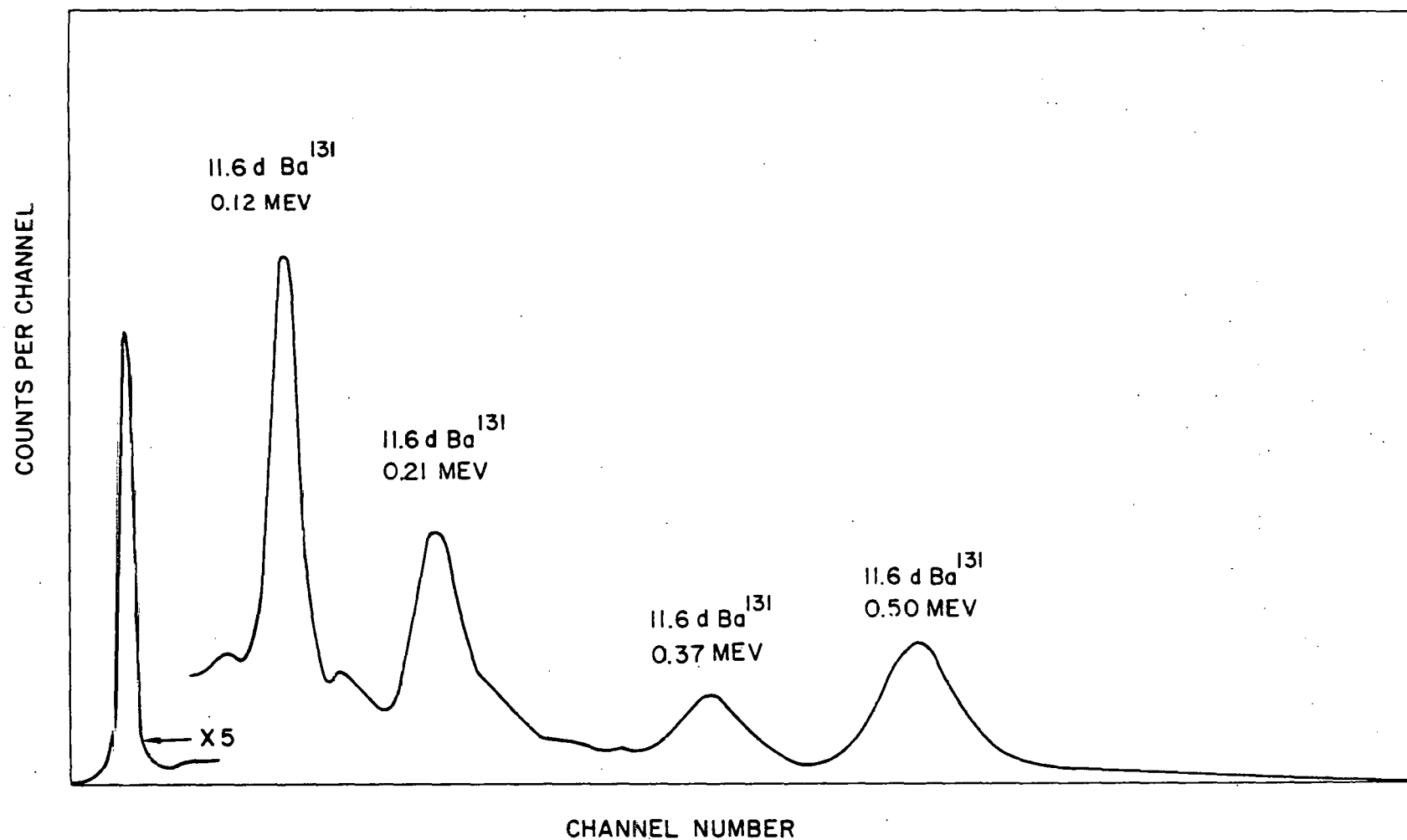


Fig. 17--Gamma-ray spectrum of a neutron-activated glass sample

SOILS

In many criminal cases it is often necessary to compare samples of soil. As an example, a suspect may be linked to a crime if dirt found on his shoes is identical to the soil at the scene of the crime. A preliminary study on the characterization of soil samples by neutron activation analysis was therefore carried out.

Small samples of four different local soils were irradiated for 30 min in a thermal-neutron flux of 1.8×10^{12} n/cm²-sec. After irradiation, small portions of each sample (because of the high initial activity level) were counted shortly after the end of the irradiation and also 24 hr later. The total sample was then counted at various decay times for three weeks. All samples were analyzed in duplicate. Five elements were positively identified and their concentrations in each sample are shown in Table 29. A typical gamma-ray spectrum is shown in Fig. 18. Cobalt and/or iron were also detected but were not measured quantitatively. Irradiation for 30 sec, immediately followed by counting of the sample, showed only the presence of 2.3-min Al²⁸ and 6.6-min Al²⁹, produced by the fast-neutron (n,p) reactions on Si²⁸ and Si²⁹, respectively. These activities obscured the detection of other short-lived activities possibly present.

The results show a wide variation in the amounts of Na and Mn in duplicate samples of the same soil. This is probably due to sample inhomogeneity. Therefore, experiments were carried out to see if different sampling procedures would improve the results. Six large samples (~1.5 g) of the same soil were irradiated for 30 min in the reactor and after several days' decay were counted at various times for two weeks. The concentrations of Na, La, Sc, Cr, and Co were estimated and are shown in Table 30. With the exception of one of the Cr values, the results are seen to be quite reproducible.

Two more samples of the same soil, each containing a small stone, were also analyzed to determine the effect of larger particles on the elemental composition of the soil samples. The results, also shown in Table 30, show some variation in Na and Co content from the other samples, but the La, Sc, and Cr values agree fairly well.

The soils were also sifted to remove particles which might contain extraordinary concentrations of one element in preference to another. Each of five different soils was sifted through a No. 30 and a No. 60 Harshaw sieve. Three ranges of particle sizes were thus obtained and separated. Triplicate samples of each of the three sizes of one of the soils were irradiated for 30 min in the reactor. The results of these analyses are shown in Table 31. The smallest particles show considerable variation in composition, whereas the larger particles are more homogeneous.

Table 29
ANALYSIS OF FOUR DIFFERENT SOILS
(Element values in ppm)

Sample	Na	Mn	Sc	La	Cr
1	13,300	1,020	8.8	35	15
	15,100	7,710	6.4	28	12
2	7,600	490	7.5	32	13
	12,100	1,030	6.6	46	11
3	11,200	930	10.1	37	10.8
	11,600	4,700	9.3	39	10.7
4	84,000	1,290	8.3	108	14
	33,100	680	9.1	109	19

Table 30
REPLICATE ANALYSES OF LARGE SAMPLES OF SOIL
(Element values in ppm)

Sample (same soil)	Na	La	Sc	Co	Cr
A	14,000	20	9.3	9.6	159
B	15,000	19	10.0	10.8	138
C	15,700	20	9.1	9.8	146
D	15,300	17	9.0	9.6	138
E	14,500	18	9.5	9.5	238
F	13,900	18	8.9	9.2	135
G ^a	15,000	22	9.7	5.7	166
H ^a	17,100	29	10.0	7.2	130

^aSamples contain ~5 mg stone.

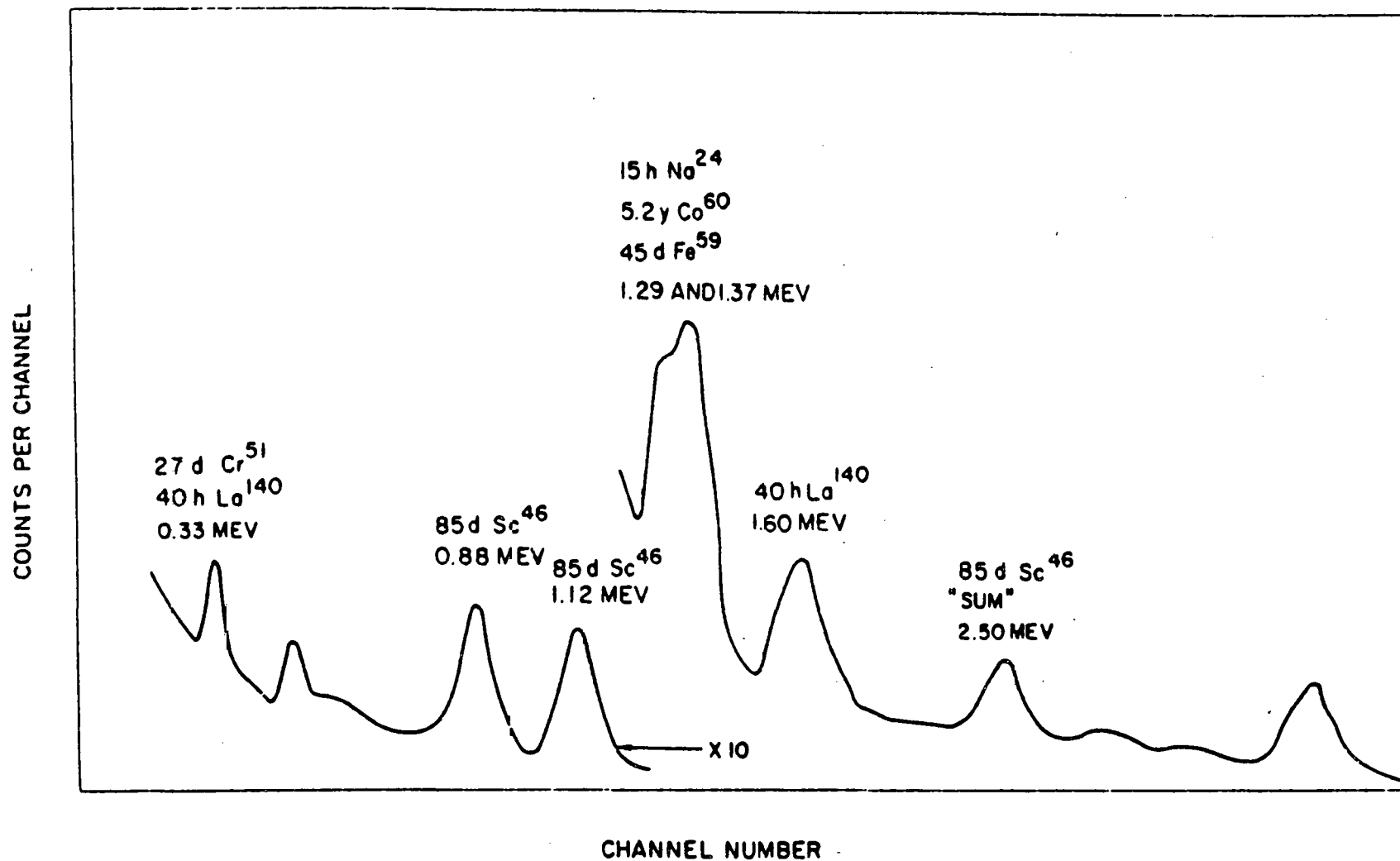


Fig. 18--Gamma-ray spectrum of a neutron-activated soil sample

Table 31
ANALYSIS OF DIFFERENT PARTICLE SIZES OF SAME SOIL
(Element values in ppm)

Particle Size (in.)	Sample	Na	La	Sc	Co	Cr
>0.0234	1	1620	21	74	9.1	118
	2	1330	18	59	9.9	154
	3	1480	16	72	10.4	124
<0.0234 but >0.0098	4	1380	23	81	10.1	110
	5	1390	18	82	11.7	101
	6	1220	15	89	5	108
<0.0098	7	1960	36	14.9	12.9	239
	8	2000	34	13.5	22	1149
	9	1970	--	41	13.9	276

Duplicate samples of each of the three sizes of the remaining four soils were irradiated for 1 hr. The results are shown in Table 32 and leave some doubt as to the reliability of the sifting method to obtain homogeneity in soils.

Three small blue rock particles from an actual murder case were analyzed. Sample 3 was removed from a bit of dirt attached to a brick (the murder weapon), sample 2 was removed from the soil in a local brickyard (near where the suspect lived, and from where it was suspected the murder-weapon brick was obtained), and sample 1 was a small rock particle of similar color selected at random from a location near the brickyard but not from near any stack of bricks.

Irradiation for 30 sec and immediate counting showed only the presence of Al^{28} activity. A 30-min irradiation showed the presence of Na, Mn, and Co. The samples were then irradiated in the 1000-kw TRIGA Mark F reactor for 6 hr at a thermal-neutron flux of about 10^{13} n/cm²-sec and then counted at various decay times. The results showed the presence of Sc and Cr, in addition to the Mn, Na, and Co.

The relative amounts of the five elements found are shown in Table 33. In each case, the amount of the element found in sample 2 was taken as unity. In the case of Co, none was found in samples 2 and 3, so the statistical upper limit of the possible Co content of sample 2 was taken as unity. Cobalt was found in sample 1, and the amount is shown as a multiple of the unit value taken as the upper limit of the Co content of sample 2.

Samples 2 and 3 are virtually identical in composition with regard to all five elements. Sample 1 is reasonably similar in its Na, Mn, and Cr contents, but differs from samples 2 and 3 in its Sc and Co contents. These results were so striking that plans were made to introduce them in court when the case came to trial. However, so much other evidence against the suspect was available that the District Attorney decided not to use the NAA results in court (since their use would involve additional effort to explain the method, etc.). The case did come to trial, and the defendant was found guilty of murder. Had the NAA results been introduced in this very strong case, it would have been the first U.S. court case in which NAA evidence was introduced.

PAPER

Eight different samples of white paper were irradiated for 60 min in the reactor. They were then counted by gamma-ray spectrometry at several decay times during a period of eight days. The samples were also

Table 32

ANALYSIS OF DIFFERENT PARTICLE SIZES OF FOUR
DIFFERENT SOIL SAMPLES
(Element values in ppm)

Sample	Particle Size (in.)	Na	Sc	Cr	Co
1	>0.0234	9,000	2.9	91	5
		8,300	3.8	129	9
	<0.0234 but >0.0098	11,700	4.1	95	15
		11,200	5.0	110	8
	<0.0098	20,800	10.1	256	16
		17,300	9.8	243	18
2	>0.0234	9,100	7.1	71	8
		9,600	2.7	152	9
	<0.0234 but >0.0098	10,300	5.6	90	10
		11,800	5.5	113	12
	<0.0098	16,100	12.5	258	28
		15,700	12.1	251	23
3	>0.0234	12,300	7.1	119	10
		13,500	8.8	135	15
	<0.0234 but >0.0098	10,100	7.9	95	8.8
		10,500	7.4	93	5.6
	<0.0098	15,900	19.0	352	19
		15,300	18.3	330	28
4	>0.0234	14,600	10.4	248	16
		14,200	9.2	184	17
	<0.0234 but >0.0098	12,800	6.6	135	12
		13,100	6.8	137	12
	<0.0098	18,900	7.1	207	14
		18,300	7.1	185	15

irradiated for 15 sec and counted immediately. The results are shown in Table 34. It is evident from these results that different samples of white paper differ in composition.

INK

Since it is important to identify inks nondestructively on printed or written documents, the five inks studied were all on samples of the same paper and were analyzed nondestructively. The paper used was a 3 cm by 10 cm piece of General Atomic letterhead stationery watermarked "Gilbert Resource Bond, 50% Cotton Fibre, U.S.A." The ink sample was prepared by writing the type of ink used on the paper; e. g., "Black Ballpoint Ink" was written on the paper in black ballpoint ink. The inks studied in addition to the black ballpoint were a blue ballpoint, Parker Superchrome blue-black, Schaeffer's Skrip permanent jet black, and Schaeffer's Skrip washable black.

The samples and a paper blank were irradiated, and gamma-ray spectra were obtained at several decay times after the irradiation. In every case the ink-paper samples gave exactly the same spectrum as the blank paper. It appears, therefore, that there is not much hope for the nondestructive identification of ink printed or written on paper. It may, however, be feasible to study ink by removing it from the paper, but this in turn destroys the sample.

HAIR

At the request of a sheriff's office of a county in a nearby state, the analysis of a number of hair samples involved in a murder case was undertaken. All of the hairs were washed with deionized water and were then irradiated for 1 min, 60 min, and 6.8 hr, respectively, in the reactor. Counting the samples showed the presence of Na, Cl, Mn, Au, and Cr in some or all of the samples. The results are shown in Table 35.

The results do not seem to lead to any firm conclusions as to the origin of the hairs found on the body of the victim or of the hairs found on the suspect. The case, however, is a good example to illustrate the complexities involved in the identification of hair. Samples 4-1 through 4-5 are all of the loose hairs recovered from the victim at the scene of the murder and were separated as follows: 4-1 consisted of four thin, short hairs; 4-2 consisted of four thick, short hairs; 4-3 consisted of one thick, dark, long hair; 4-4 consisted of two thick, brown, long hairs; and 4-5 consisted of one long hair. These could have come from a variety of sources, including the victim, the murderer, other persons, and possibly

Table 33
ANALYSIS OF SMALL BLUE ROCK PARTICLES

Sample	Relative Content				
	Sc	Co	Cr	Na	Mn
1	5.5	215	2.4	0.8	1.9
2	1.0	1.0 ^a	1.0	1.0	1.0
3	1.1	2.0 ^a	1.0	1.1	1.0

^aUpper limits (none detected).

Table 34
ANALYSIS OF SAMPLES OF WHITE PAPER
(Element values in ppm)

Sample	Na	Cl	Cu	Sb	Mn	Sc	La	Al
Small scratch pad	186	970	11	6.8	1.1	≤0.8	≤4.2	3,530
GD/GA report sheet	221	1,230	18	≤2.0	6.5	≤1.2	≤13	13,200
GD/GA letterhead	407	532	≤10	≤2.5	1.2	≤0.8	≤4.8	1,400
GD/GA memo sheet	330	1,050	≤14	4.9	2.9	1.9	≤8.6	18,400
Eagle "A" Trojan Bond	336	543	≤9	≤1.2	4.5	≤0.7	≤4.7	5,760
Eagle Trojan onion skin	352	980	≤12	≤3.1	1.2	≤1.6	≤13	6,650
Large scratch pad	106	1,550	15	≤1.6	3.6	3.2	12	28,900
Manuscript (ISA)Form B3-20	264	1,470	≤10	≤1.3	3.8	1.8	11	21,600

Table 35
 ACTIVATION ANALYSIS OF HAIR SAMPLES FROM
 A MURDER CASE
 (Element values in ppm)

Sample	Sample Description	Na	Cl	Mn	Au	Cr
1	Found on suspect	3,800	4,100	≤5.8	≤0.09	≤53
2	Found on suspect	390	1,800	12	≤9.8	≤55
3	Found on suspect	1,300	5,100	≤3.6	0.40	≤57
4-1	Found on victim	2,100	3,400	8.4	1.73	≤38
4-2	Found on victim	2,800	4,000	6.6	≤0.16	≤40
4-3	Found on victim	1,300	660	≤2	≤0.48	1570
4-4	Found on victim	3,700	4,100	≤5.6	≤0.12	≤40
4-5	Found on victim	1,800	2,500	≤4.4	≤0.30	≤89
5	Victim's head hair	980	780	5.0	0.33	≤23
6	Victim's pubic hair	1,020	2,700	≤2.3	0.16	≤34
I-A	Suspect's head hair	650	3,200	2.8	≤0.20	≤32
II-A	Suspect's body hair	750	1,800	≤1.5	≤0.15	≤51
III-A	Suspect's pubic hair	1,060	2,800	≤2.0	≤0.04	≤14

animals. The time element also introduces some difficulties. Samples 1, 2, and 3 were obtained from the suspect when he was arrested, about two months after the murder. Samples IA, IIA, and IIIA were obtained from him five months after the murder and after he had spent three months in jail. Three of the hairs in the 4-1 through 4-5 series are known to have been taken from the right hand of the victim and would have been significant. Unfortunately, the investigating officers mixed these hairs with the other hairs found at the scene of the crime. Sample 4-3, which showed a large amount of Cr, was tentatively identified as animal hair, possibly from a dog.

Samples 1 and 4-4 were irradiated for 23.6 hr at a thermal-neutron flux of 1.0×10^{13} n/cm²-sec in the Materials Testing Reactor at Idaho Falls, Idaho. Counting of the samples for detection of long-lived induced activities showed the presence of 74.4-day Ir¹⁹² in both samples. However, the concentration of this element in sample 1 was ten times that in sample 4-4. No conclusions could therefore be drawn in this case.

FINGERNAILS

An unusual series of fingernail samples was analyzed. The samples were thumbnail clippings taken by one member of the Los Angeles Police Department at regular monthly intervals for the past eight years. Not all of the samples were analyzed, but only nine representative ones, which were obtained at yearly intervals. In addition, fingernail samples were taken from each of two other persons and were labeled "JM" and "LR".

After being washed with deionized water and acetone, the samples were irradiated for 30 sec and 30 min, respectively, to determine the short- and long-lived activities produced. The concentration of each element detected is shown in Table 36, and a typical spectrum is shown in Fig. 19. These results show that the concentrations of the elements found in the fingernails of the same person varied significantly over the 8-yr period. The concentrations found for the other two individuals are generally in the same range as those of the "police" samples. The range of concentrations of a particular element found for one individual over the 8-yr period is as great or greater than the range of concentrations found for the other two persons' fingernails. This shows that it is desirable to obtain biological samples, such as fingernails, from suspects as soon after the crime as possible if a good identification is to be made.

ARSENIC POISON

Hair and fingernail clippings from an individual having symptoms resembling arsenic poisoning were analyzed radiochemically for arsenic.

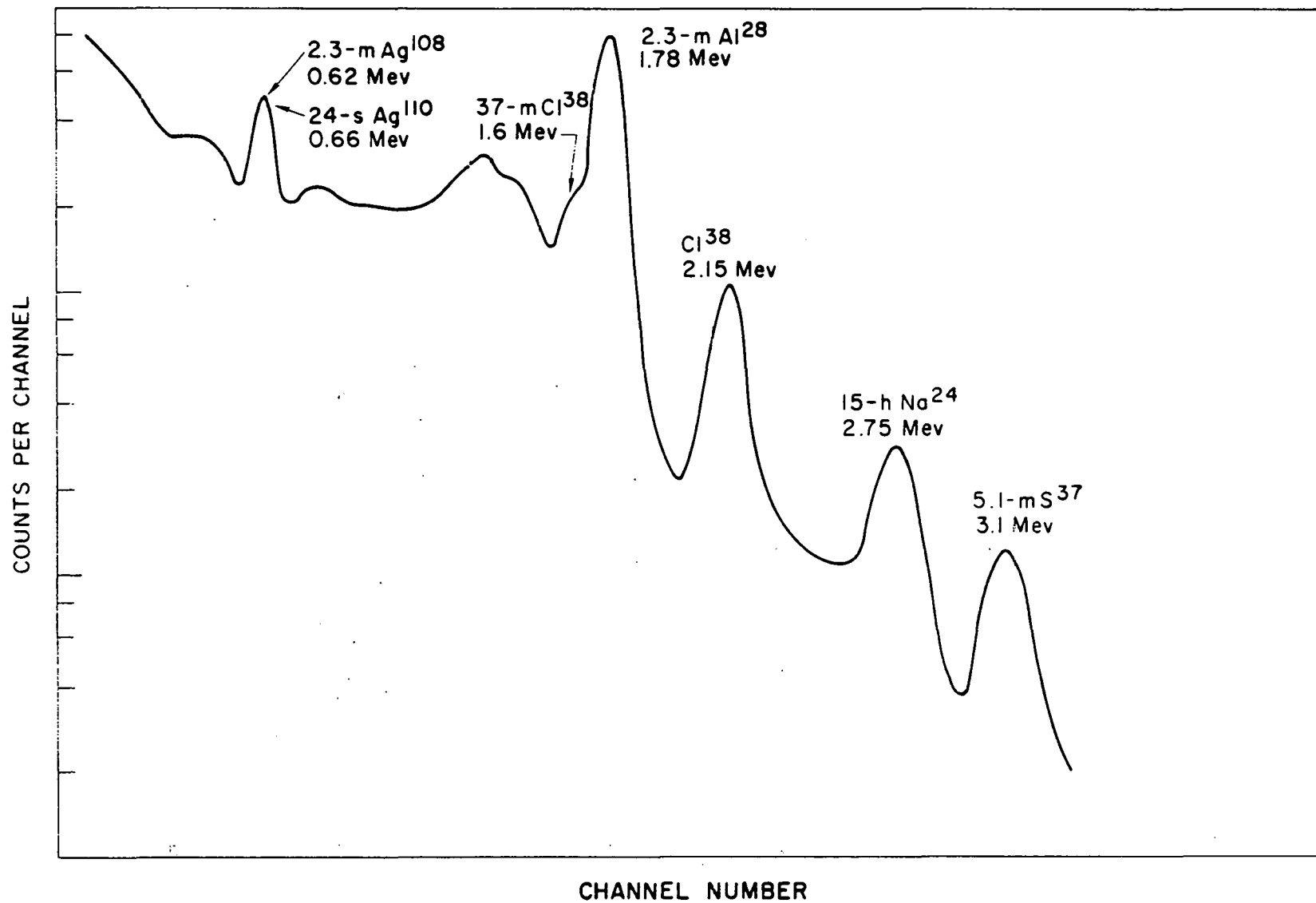


Fig. 19--Gamma-ray spectrum of a neutron-activated thumbnail clipping

The two samples, along with an arsenic standard, were irradiated for 1 hr in a thermal-neutron flux of 1.8×10^{12} n/cm²-sec.

After irradiation each sample was rinsed several times with acetone, then with water, and again with acetone. They were dissolved in the presence of As carrier, using a mixture of H₂SO₄ and HNO₃. The As was radiochemically purified by adding HI, extracting the AsI₃ formed into chloroform, washing the extract with a HCl-HI mixture, and back-extracting into dilute H₂SO₄. Arsenic metal was then precipitated by reduction with CrCl₂, and the precipitate was filtered, dried, weighed, and mounted for counting. The As standard was treated similarly, with the omission of the extraction steps.

The samples and the standard were counted for 26.5-hr As⁷⁶ activity, using a low-background end-window beta proportional counter. The activity was verified as being As⁷⁶ by absorption and decay measurements. The analyses revealed the presence of 0.041 ± 0.002 ppm As in the hair and 0.14 ± 0.01 ppm As in the fingernails.

The As concentration found in the hair may be compared with the concentrations found by Lenihan and Smith⁽²⁾ in the hair of 606 persons. Their findings are summarized in Table 37. Szep⁽³⁾ reported As levels of from 0.27 to 0.77 ppm in normal hair and from 1.5 to 5.2 ppm in fingernails. Smales and Pate⁽⁴⁾ found a range of from 0.51 to 2.1 ppm As in normal hair and from 0.82 to 3.5 ppm As in normal fingernails. On the basis of these findings, it is possible to conclude that no As poisoning is indicated in this case, since the levels found in both the hair and the fingernails are well below the maximum concentrations found in normal hair and nails.

WOOD

Eight different kinds of wood (redwood, Douglas fir, cedar, birch, mahogany, ash, oak, and pine) were analyzed to determine the feasibility of the use of neutron activation analysis for the identification of wood samples. Each sample was irradiated for 1 hr in the reactor and then counted by gamma-ray spectrometry. Six elements were detected and their concentrations are shown in Table 38. A typical gamma-ray spectrum is shown in Fig. 20. The results show that there is considerable difference in the wood samples studied.

Five different samples of the same piece of wood (pine) were also analyzed. The results, in Table 39, show that the same wood, or different areas of the same piece of wood, can vary significantly in composition.

Table 36
ACTIVATION ANALYSIS OF THUMBNAIL CLIPPINGS
(Element values in ppm)

Sample	Year Taken	Na	Al	Cl	Mn	Cu	Ag	Au
Police	1954	440	53	780	0.6	12	11	0.63
Police	1955	790	160	1,650	2.7	12	5	1.25
Police	1956	340	72	690	0.6	9	5	0.41
Police	1957	650	87	1,230	0.5	22	5	0.42
Police	1958	710	145	1,230	0.9	27	21	1.8
Police	1959	1,340	76	3,300	0.4	25	6	0.72
Police	1960	650	80	1,350	0.3	12	3.6	1.32
Police	1961	440	87	910	0.3	16	6.8	1.08
Police	1962	370	49	940	0.5	14	19	0.60
LR	1962	950	110	3,180	1.0	17	3.5	0.57
JM	1962	300	114	1,310	1.0	9	2	0.14

Table 37
ARSENIC CONCENTRATIONS IN THE HAIR OF 606 PERSONS
(Data from Ref. 2)

	Arsenic Concentration (ppm)				
	0-0.49	0.5-0.99	1.0-1.49	1.5-2.49	>2.49
Number of cases	219	230	79	44	34
Percentage of cases	36	38	13	7	6

Table 38

ACTIVATION ANALYSIS OF WOOD SAMPLES
(Element values in ppm)

Sample	Mn	K	Al	Cl	Na	Cu
Redwood	60	≤310	32	≤169	209	≤2
Douglas fir	67	≤84	108	≤51	20	1
Cedar	2	824	48	238	65	2
Birch	23	385	6	≤108	8	2
Mahogany	3	≤1,360	16	845	340	≤3
Ash	2	2,290	14	352	221	440
Oak	8	2,100	8	≤144	93	10
Pine	55	624	77	≤165	16	3

Table 39

ACTIVATION ANALYSIS OF PINE WOOD
(Element values in ppm)

Sample ^a	Mn	K	Al	Na	Cu
1	55	624	77	16	1
2	45	443	11	82	≤1
3	48	516	23	43	≤1
3A	48	462	--	27	≤1
11	61	563	24	47	4

^aSamples 1, 2, and 3 are from the same 8-ft board--1 and 3 from opposite ends and 2 from the middle. Samples 3 and 3A are from the same area. Sample 11 is from a different board.

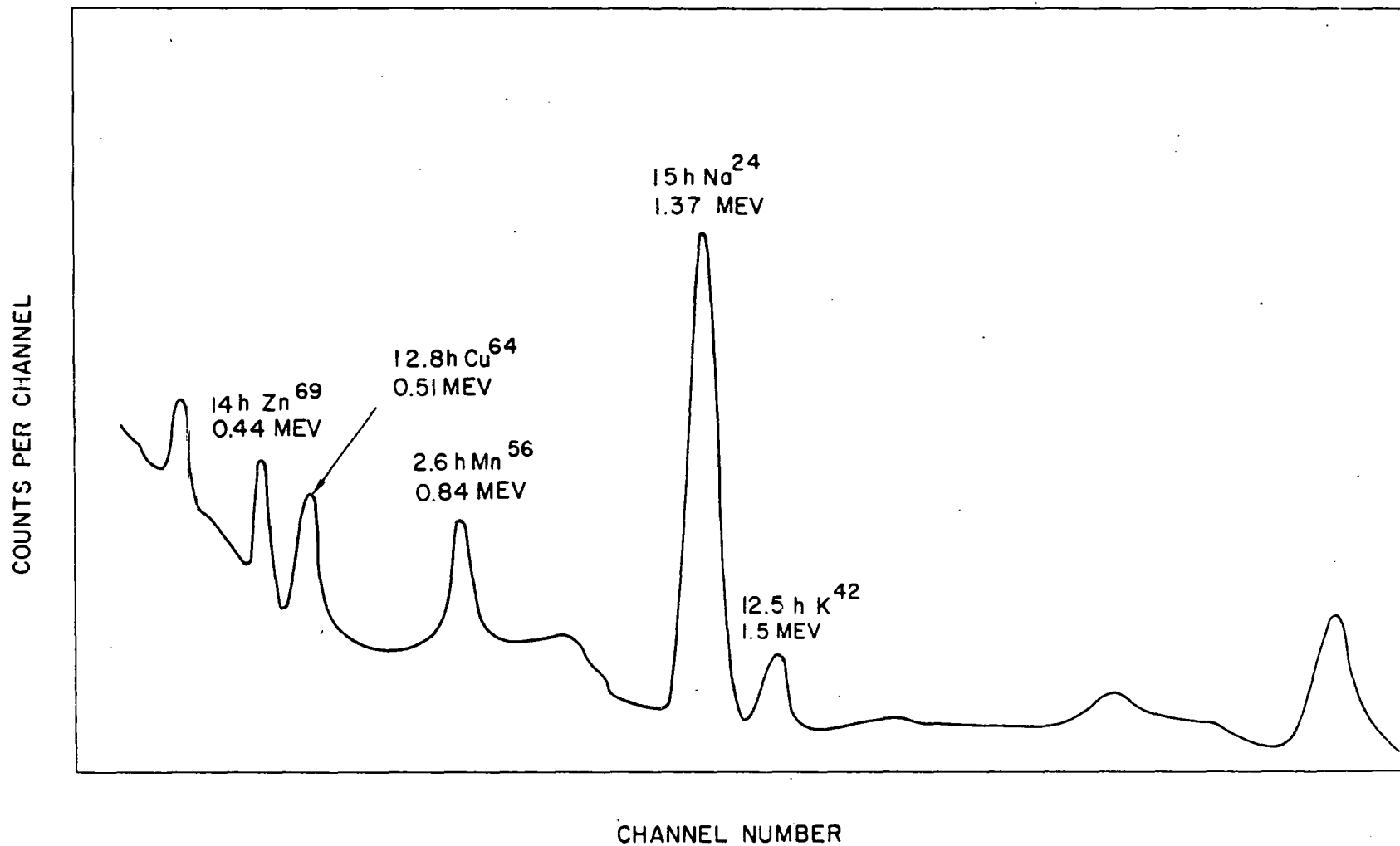


Fig. 20--Gamma-ray spectrum of a neutron-activated wood sample

TOBACCO

Duplicate samples of tobacco from six different brands of cigarettes, as well as samples of the same brand but from different packs, were irradiated for 30 min and counted instrumentally. The results, shown in Table 40, are estimates of the Na, K, Br, and Sc concentrations found. In most samples, Cr, Zn, Co, and Fe were either positively identified or indicated to be present but were not quantitatively measured. The agreement between duplicate samples is, in general, only fair. Also, tobacco from different brands of cigarettes does not seem to vary greatly. Based on these limited results, the use of neutron activation analysis for the identification of tobacco does not appear to be very promising.

DRUGS

As a method of determining the source of manufacture of drugs seized in illicit traffic, neutron activation analyses were performed on amphetamine tablets from eleven different drug manufacturers. Each sample was irradiated for 30 sec to determine the short-lived species and for 30 min to determine the longer-lived activities induced. The results, in Table 41, show that all of the drugs studied are quite different in trace-element composition and are easily distinguishable from one another.

SEDIMENT POLLUTION OF RIVERS

A study carried out at the request of the U.S. Army Corps of Engineers involved the determination of which of several steel mills was primarily responsible for the formation of large deposits of sediment in a river. This area of the river is under the jurisdiction of the Corps of Engineers and must be dredged out by them. Each steel company denied that it was a main contributor to the sediment buildup in the river. Tides and currents make it impossible to tell for sure which sediment accumulation comes from any particular mill. Ordinary chemical analyses showed only the major and minor constituents of the sediments (e.g., Si, Al, Fe, Ca, Mg, Na, and Mn), and these, with the exception of Na and Mn, do not show significant differences among the effluents from the several mills or among the sediment deposits removed from various parts of the river.

Three different sediment samples (42, 48, and 61) and two different sewer water samples (69 and 70) were taken from the river at various locations and analyzed, sample 42 being analyzed in triplicate. The water samples were filtered, and the solids collected were dried, weighed, and irradiated. The sediment samples were also dried and weighed before irradiation. A short (15 sec) and two long (30 min and 6.8 hr) irradiations

Table 40
NEUTRON ACTIVATION ANALYSIS OF CIGARETTE
TOBACCO SAMPLES
(Element values in ppm)

Brand	Na	K	Br	Mn	Sc
Salem (pack 1)	282	53,000	139	460	0.085
	882	41,000	136	---	0.12
Salem (pack 2)	263	43,000	147	420	0.12
	297	46,000	157	---	0.13
Kent	716	49,000	134	500	0.22
	524	51,000	169	---	0.20
Viceroy (pack 1)	408	38,000	150	430	0.20
	342	42,000	266	---	0.40
Viceroy (pack 2)	342	42,000	126	400	0.11
	414	45,000	126	---	0.09
Lucky Strike	346	40,000	96	720	0.12
	418	41,000	100	---	0.21
Pall Mall	414	40,000	159	390	0.21
	402	39,000	142	---	0.13
Newport	447	47,000	276	440	0.28
	446	47,000	259	---	0.20

Table 41

NEUTRON ACTIVATION ANALYSIS OF AMPHETAMINE SAMPLES

Sample	Na (ppm)	Cl (ppm)	Mn (ppm)	K (ppm)	Al (ppm)	Ca (rel)	Mg (rel)
1	226	~219	~5.7	---	31	1.000	---
2	200	----	1.98	---	63	≤ 0.002	0.201
3	62	41	≤ 0.18	310	4.0	≤ 0.002	---
4	179	~246	~2.16	---	137	≤ 0.002	0.369
5	350	170	0.32	---	89	0.305	0.315
6	545	~5500	~1.6	---	235	≤ 0.002	0.318
7	332	~227	7.3	---	368	≤ 0.002	1.000
8	106	----	~21.9	---	83	0.644	0.147
9	429	~490	4.6	---	281	0.574	---
10	169	740	1.9	---	252	≤ 0.002	0.253
11	108	≤ 34	1.38	---	90	≤ 0.002	0.274

were made on each sample. The amounts of the elements detected are shown in Table 42. Aluminum was also detected but was not determined quantitatively. Considerable variation in the elemental compositions of the various samples was shown to exist. The agreement among the three portions of sample 42 is good. Therefore, the analysis of more samples might make it possible to determine which steel mills are major contributors to certain large sediment deposits in the river. Further work could not be undertaken, however, because of insufficient time and funds.

OIL POLLUTION OF HARBORS

This study was requested by the U.S. Bureau of Customs to help them identify the source of oil pollution of harbor waters. Samples of such pollution are skimmed from the surface of the water and are therefore contaminated with salt water, which must be removed before analysis. Sixteen samples of pure fuel oils and sixteen samples of these same oils mixed with salt water were received for analysis.

To determine how washing the oils affects their composition, a number of the pure oils were washed several times with hot deionized water and analyzed instrumentally. Samples of the same oils which were not washed were analyzed at the same time. The results are shown in Table 43. The values given for Sb and As require some further explanation. Both As and Sb have a photopeak at 0.56 Mev and, because of the small size of the peak obtained with these samples, accurate half-life measurements could not be made to identify the activity. The spectrum shown in Fig. 21 will help illustrate this problem. The value given for As is the maximum concentration of this element present if the entire 0.56-Mev peak was due to 26.5-hr As⁷⁶. The Sb values were obtained by counting the same sample eight days later and assuming the remaining 0.56-Mev peak was due entirely to 2.8-day Sb¹²². These maximum possible concentrations of As and Sb are represented by ($\leq$) values. When no 0.56-Mev peak was obtained after eight days' decay, upper limits using three standard deviations, based on counting statistics, were calculated and are shown in the table as ($<$) values. This problem of Sb and As could, of course, be resolved if radiochemical separations were employed.

The results indicate that washing the oil removes some of the Na and Mn. The values for the other elements indicate a possible lack of homogeneity in the samples (washed samples contained more of a particular element in some cases than did unwashed samples).

The sixteen pairs of oil samples were then compared. Both the pure oils and the oils mixed with salt water were washed several times with hot deionized water and analyzed instrumentally. The results are shown in

Table 42

ACTIVATION ANALYSIS OF SEDIMENT AND WATER SAMPLES

Sample	Elements in Dried Material (ppm)							
	Mn	Na	Sb	Cr	Cu	La	Sc	Fe (%)
42-A	3,260	4,300	14	250	87	18	6.0	~18
42-B	3,090	3,960	14.8	314	87	19	7.5	~23
42-C	2,770	3,410	12.6	230	76	14	5.5	~17
48	5,000	1,600	42	930	210	17	≤5.6	~32
61	3,500	3,400	41	500	320	15	6.5	~20
69	8,500	270	121	1,180	1,050	≤8	≤3.0	~58
70	3,300	200	77	590	650	≤6	≤3.1	~42

Table 43

NEUTRON ACTIVATION ANALYSES OF WASHED AND
UNWASHED PURE OIL SAMPLES
(Element values in ppm)

[illegible]

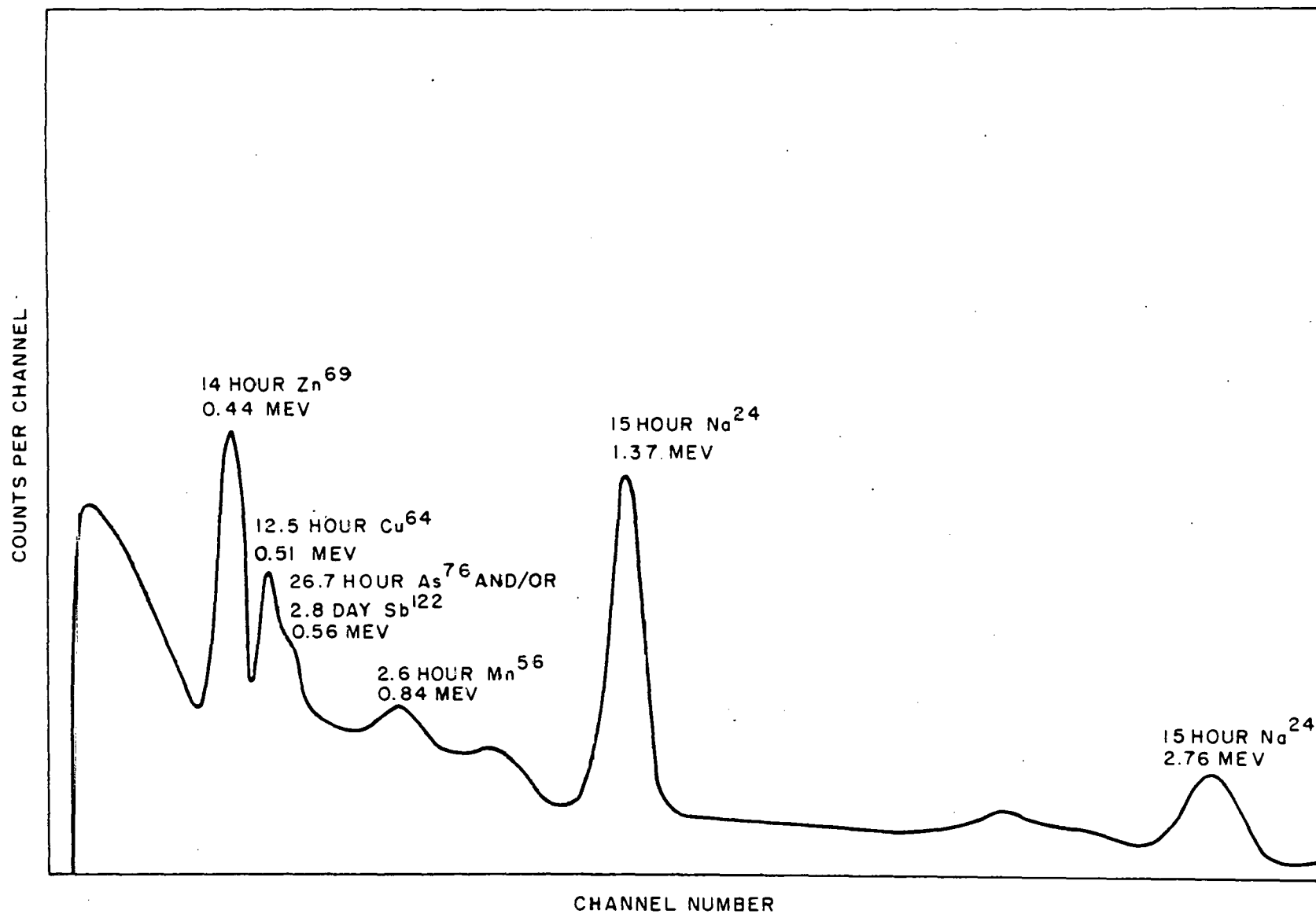


Fig. 21--Gamma-ray spectrum of a neutron-activated oil sample

Table 44. Again, ($\leq$) values are maximum possible concentrations calculated when a photopeak was obtained but was not positively identified, and ($<$) values are statistical upper limits calculated when no photopeak was observed.

Although there are discrepancies in the apparent composition of the same oils (one mixed with salt water, the other clean), generally speaking, it appears that two oils from different sources can be distinguished and that oils from the same source can be matched fairly well.

RICE WHISKY

Three samples of "bootleg" rice whisky confiscated by the Internal Revenue Service, U.S. Treasury Department, were analyzed instrumentally. They were irradiated for 30 min in a thermal-neutron flux of 1.8×10^{12} n/cm²-sec and then counted by gamma-ray spectrometry. Samples of the same whisky were also irradiated for 1 min and counted immediately, to determine the short-lived activities induced. Sodium and copper were detected in all three samples, and aluminum was detected in one. The amounts are shown in Table 45.

The residues obtained by evaporating large volumes of these three whiskies were also analyzed instrumentally. These samples were also irradiated for 1 min and 30 min. Sodium, copper, chlorine, and aluminum were detected in the residues. However, because of the indeterminate amount of moisture in the residues, quantitative measurements could not be made. Qualitatively, however, samples 1 and 2 appeared to be almost identical, whereas sample 3 was decidedly different. Gamma-ray spectra of each residue are shown in Figs. 22, 23, and 24. Samples 1 and 2 had relatively large amounts of Cu, whereas sample 3 showed little Cu but much more Al than samples 1 and 2. It appeared, on the basis of the analyses of the whiskies and their residues, that samples 1 and 2 were very similar and could have a common origin, whereas the origin of sample 3 was probably different from that of samples 1 and 2. This information proved to be of value to the Internal Revenue Service.

Table 44

NEUTRON ACTIVATION ANALYSES OF WASHED OIL SAMPLES
(Element values in ppm)

Sample ^a	V	Mn	Na	Cu	As	Sb	Co
1A	17.5	≤0.304	35	≤1.24	≤0.19	≤0.10	0.92
1B	17.5	≤0.279	30	≤1.59	≤0.18	≤0.06	0.93
2A	175	0.043	7.9	<0.5	≤0.09	≤0.07	0.39
2B	200	0.033	9.4	<0.6	≤0.16	≤0.14	0.36
3A	220	0.020	1.69	<0.3	≤0.10	≤0.08	0.62
3B	230	0.023	1.27	<0.3	≤0.12	≤0.10	0.45
4A	470	0.077	44	≤0.11	<2	<2	0.41
4B	325	0.43	58	≤0.06	<2	<2	0.40
5A	77.6	≤0.368	108	≤4.40	≤0.51	≤0.98	1.84
5B	68.2	≤0.580	166	≤6.30	≤0.72	≤0.08	1.66
6A	170	0.011	2.12	<0.18	≤0.10	≤0.08	<0.07
6B	174	0.007	1.75	0.162	≤0.05	≤0.06	0.15
7A	3.8	0.002	0.36	0.02	≤0.02	≤0.01	0.08
7B	1.8	0.001	0.11	0.04	≤0.02	≤0.02	<0.06
8A	865	≤0.186	38	≤1.37	≤0.23	0.26	0.13
8B	825	≤0.341	94	≤0.134	≤0.35	0.24	<0.07
9A	91	≤0.388	25.0	≤0.75	≤0.13	≤0.09	0.40
9B	76	≤0.378	30.5	≤0.90	≤0.16	≤0.05	0.54
10A	250	≤0.244	19.0	≤0.88	≤0.14	<0.04	0.40
10B	274	≤0.216	26.1	≤0.99	≤0.14	≤0.11	0.56
11A	126	≤0.226	7.0	≤0.59	≤0.06	<0.08	0.23
11B	134	≤0.517	5.2	≤0.90	≤0.13	≤0.10	0.23
12A	284	0.08	12.4	≤1.28	≤0.16	≤0.06	0.25
12B	273	0.14	27.0	≤1.01	≤0.11	≤0.06	0.21
13A	292	≤0.276	85	≤2.12	≤0.28	≤0.06	0.35
13B	325	≤0.145	82	≤1.66	≤0.11	≤0.04	0.42
14A	208	0.07	6.3	≤0.71	≤0.17	≤0.02	0.21
14B	207	0.15	7.7	<0.87	≤0.18	≤0.14	0.35
15A	152	0.24	32	≤0.93	≤0.12	≤0.07	0.57
15B	146	0.23	40	≤1.29	<0.08	≤0.04	0.54
16A	57.5	0.113	13.3	≤1.74	≤0.45	≤0.03	<0.08
16B	56.2	0.101	9.6	≤1.86	≤0.41	<0.04	<0.07

^aSamples designated "A" are pure oils; samples designated "B" were originally mixed with salt water.

Table 45
NEUTRON ACTIVATION ANALYSES OF
CONFISCATED RICE WHISKY
(Element values in ppm)

Sample	Cu	Na	Al
1	0.57	1.26	<0.04
2	0.48	1.26	<0.04
3	0.12	1.38	0.16

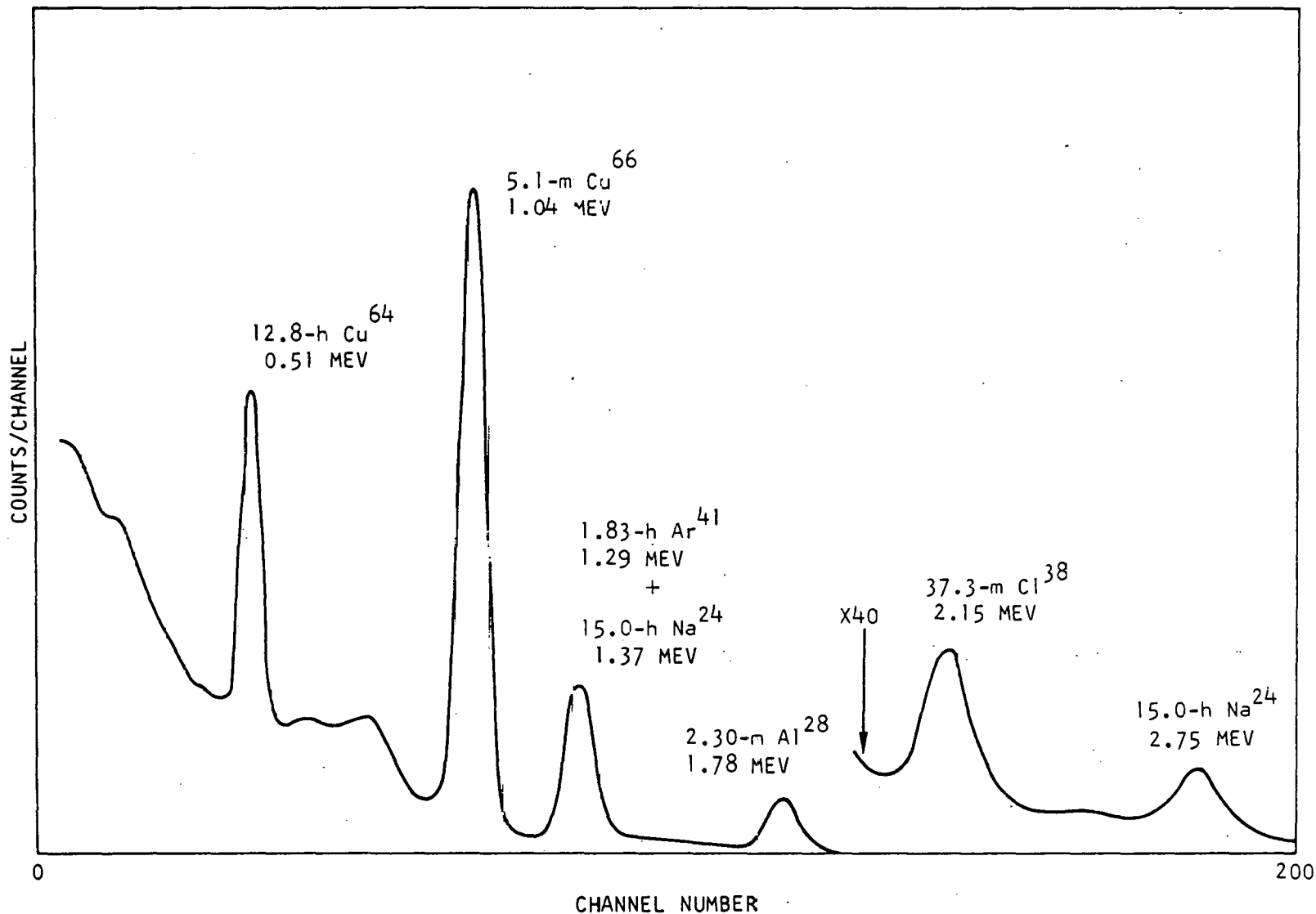


Fig. 22--Gamma-ray spectrum of neutron-activated residue of rice whisky, sample 1

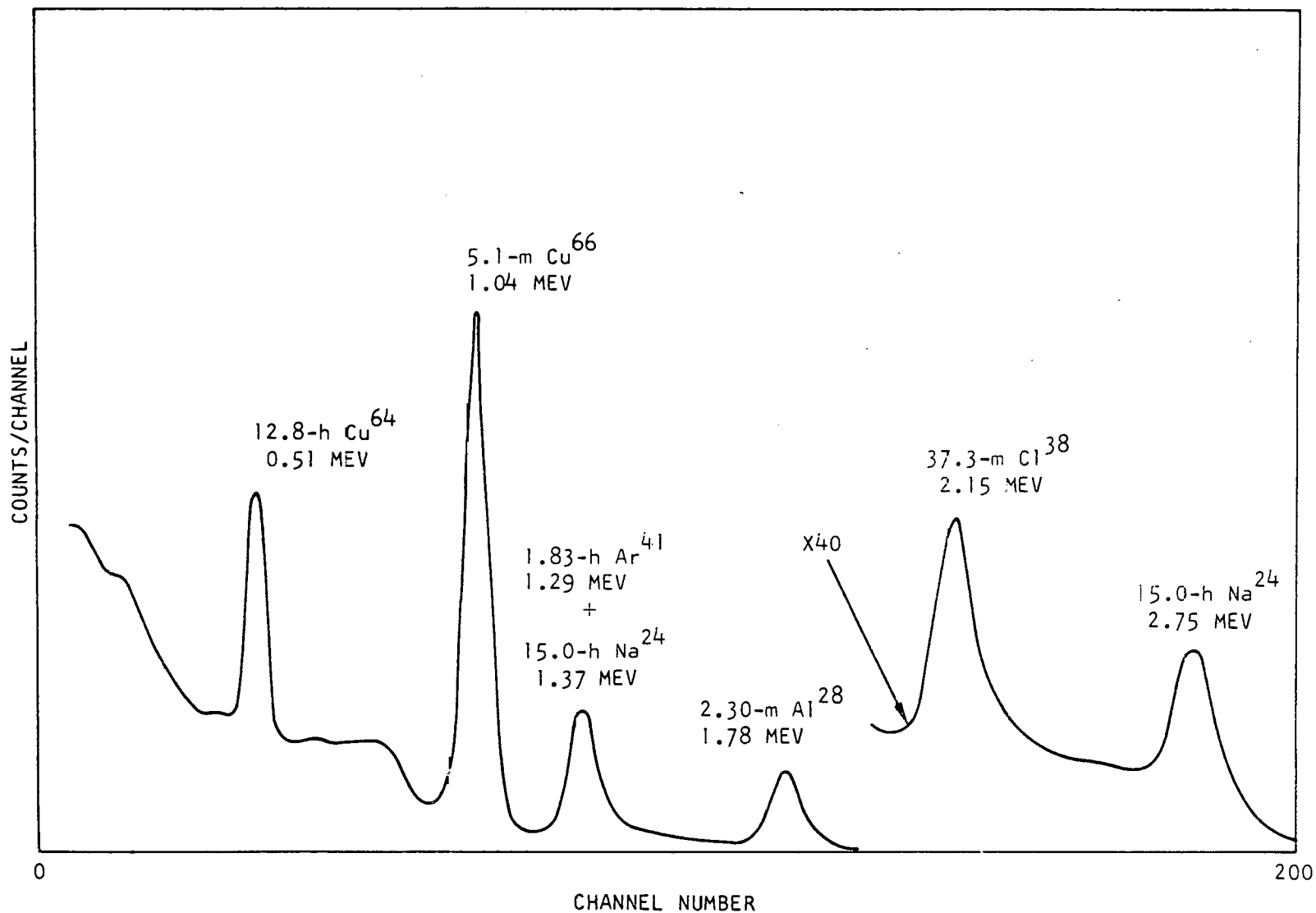


Fig. 23--Gamma-ray spectrum of neutron-activated residue of rice whisky, sample 2

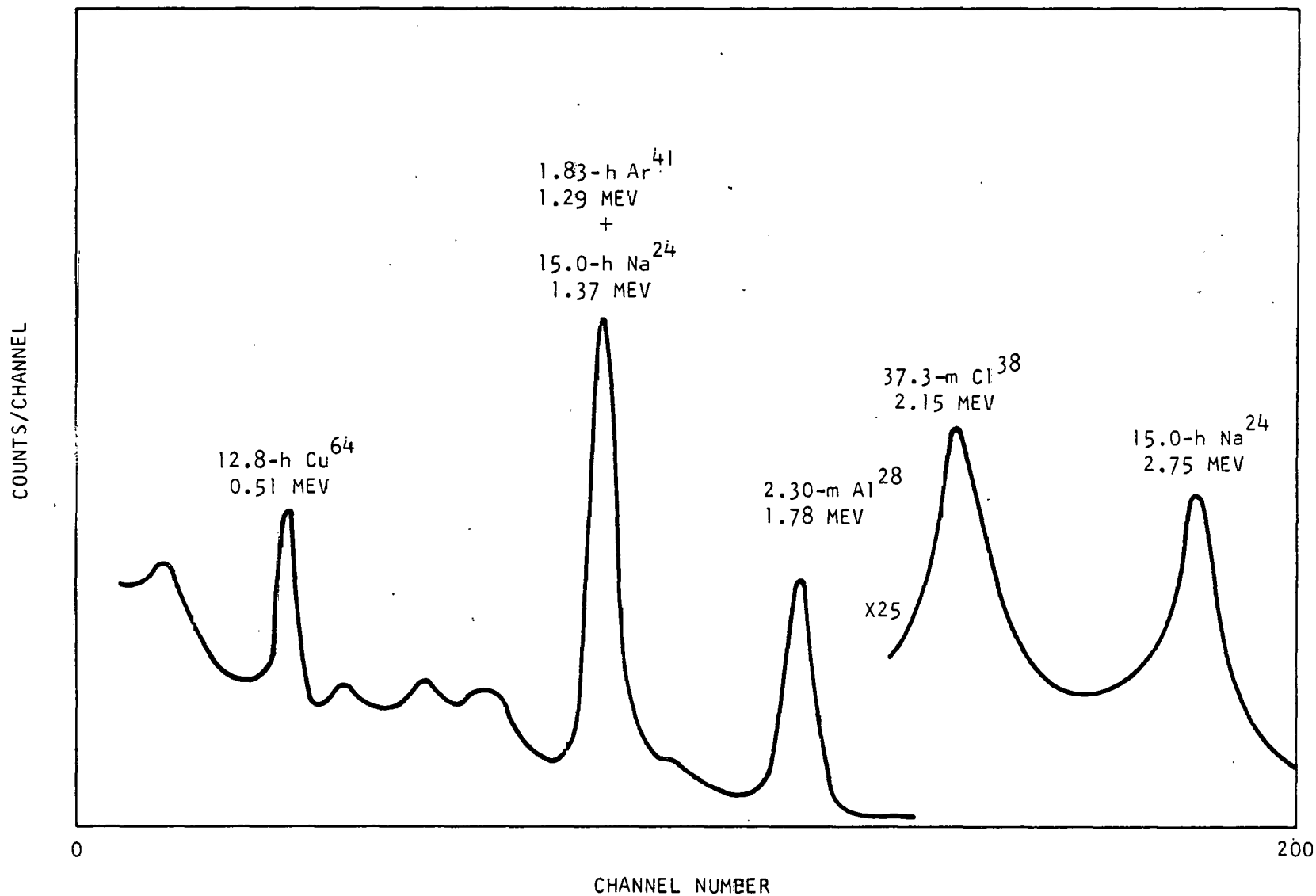


Fig. 24--Gamma-ray spectrum of neutron-activated residue of rice whisky, sample 3

IV. DISCUSSION AND CONCLUSIONS

The results of the studies carried out during this 18-month period appear to justify a number of conclusions:

1. High-flux neutron activation analysis does indeed have wide potentialities for fruitful application in the field of criminalistics.
2. With its great sensitivity it can analyze samples of forensic importance that are too tiny to be analyzed by the conventional methods normally available to the criminalist.
3. By means of its ability to determine even parts per billion levels of impurities, the method enables one to match two samples of a material (typically one from the crime scene and one from a suspect) and establish whether they have a common origin (this has been shown to be feasible with samples of soil, tire rubber, automobile grease, plastics, paper, glass, and hair).
4. The method can often be applied in its purely instrumental, non-destructive form, thus preserving evidence samples for possible presentation in court--a valuable asset.
5. A far more reliable method than the old, outmoded chemical test for determining the presence of gunshot residues on the gunhand of a person who has recently fired a gun is now available; it is based on the neutron activation analysis determination of microgram and submicrogram amounts of Sb and Ba deposited on the back of the gunhand during a firing from the Sb and Ba compounds used in cartridge primers.
6. The method of neutron activation analysis has been shown to be of practical value in the investigation of a number of actual cases of various types, involving various kinds of evidence materials.
7. The method has been sufficiently established, for application with certain materials in certain kinds of cases, that it is now ready, in such instances, for courtroom presentation.*

* Although it did not occur during the period herein reported, it should be noted that as of the time of writing, one case investigated by the General Atomic group has gone to court, the NAA data (on paint samples in an attempted burglary case) being presented on July 3, 1964, by D. E. Bryan; they were accepted, and a verdict of guilty was obtained on July 7, 1964.

8. The work has led, as hoped, to many new ideas in the criminalistics field for further investigation, some of which have since been implemented.
9. Efforts to familiarize professional criminalists with the potentialities and areas of practical application of NAA, through discussions at General Atomic and elsewhere and at meetings of the California Association of Criminalists and the American Academy of Forensic Sciences, and through published papers, have been quite successful. As a result, many criminalists (especially in California but also many in such agencies as the Federal Bureau of Investigation, the Internal Revenue Service, the U.S. Post Office Department, and the Food and Drug Administration) have become cognizant of its potentialities and are following the General Atomic work closely.

V. PAPERS PRESENTED AND PUBLISHED

Papers on the criminalistics studies at General Atomic presented at scientific meetings during the period May 1, 1962, through October 31, 1963, included the following:

1. General summary of work, by V. P. Guinn, at the May 26, 1962, conference and facility tour of General Atomic by the California Association of Criminalists (CAC), during their Spring 1962 semiannual meeting, in San Diego.
2. Paper on "NAA in Scientific Crime Detection," by V. P. Guinn, at the May 4, 1962, Symposium on New Developments in Activation Analysis, held at Louisiana State University.
3. Paper on "Detection of Gunshot Residues by NAA," by R. R. Ruch, R. H. Pinker, and V. P. Guinn, presented by R. R. Ruch at the October 25-26, 1962, semiannual meeting of the CAC, in Concord, California.
4. Paper on "Trace Element Characterization of Commercial Plastics and Greases by NAA," by J. D. Buchanan, R. H. Pinker, and V. P. Guinn, presented by R. R. Ruch at the October 1962 CAC meeting in Concord, California.
5. Paper on General Atomic NAA criminalistics work presented by V. P. Guinn at the October 29, 1962, conference on NAA in criminalistics organized by Dr. J. M. A. Lenihan, Glasgow, Scotland.
6. Paper on "Detection of Gunpowder Residues by NAA," by R. R. Ruch, V. P. Guinn, and R. H. Pinker, presented by V. P. Guinn at the criminalistics symposium session at the November 1962 national meeting of the American Nuclear Society, Washington, D.C.
7. Paper on new General Atomic criminalistics work presented by V. P. Guinn at the May 1963 meeting of the CAC in Ventura, California.
8. Paper on "NAA in Scientific Crime Detection--Some Recent Developments," by R. R. Ruch, J. D. Buchanan, R. H. Pinker,

V. P. Guinn, and Sandra C. Bellanca, presented by R. R. Ruch at the February 1963 national meeting of the American Academy of Forensic Sciences, in Chicago.

9. Paper on "Activation Analysis as Applied to Law Enforcement Problems," presented by R. R. Ruch at the 47th Annual Conference, California State Division, International Association for Identification, June 19-21, 1963, Las Vegas, Nevada.
10. Paper on "New Applications of NAA to Criminalistics," by R. R. Ruch, Sandra B. Madigan, and V. P. Guinn, presented by V. P. Guinn at the National Meeting of the Society for Applied Spectroscopy, San Diego, October 14-18, 1963.
11. Paper on progress of General Atomic criminalistics work presented by V. P. Guinn at the October 1963 semiannual meeting of the CAC, in San Mateo, California.

Prior to this period, R. M. Watkins presented a brief account of the earliest General Atomic NAA studies on gunshot residue determinations at the October 1961 semiannual meeting of the CAC. (As of this writing, in the months just following the end of the 18-month period reported herein additional papers have been presented, by various members of the group, at the February 1964 National Meeting of the American Academy of Forensic Sciences in Chicago and at the May 1964 semiannual meeting of the CAC in Long Beach, California.)

Papers published or accepted for publication include a short note in Nucleonics (December 1961), a paper (No. 8 above) in the January 1964 issue of the Journal of Forensic Sciences, a paper (No. 6 above) accepted for publication in Nuclear Science and Engineering, and a chapter entitled "Non-Biological Applications of NAA in Forensic Studies," by V. P. Guinn, for Methods of Forensic Science, Volume III (edited by A. S. Curry, Interscience, in press). In addition, the criminalistics papers presented by the General Atomic group have formed the basis for a large number of newspaper and magazine articles that have appeared, including one in Time magazine.

The work carried out during the first five quarters of this 18-month period has been reported in General Atomic Reports GA-3491, GA-3664, GA-4041, GA-4297, and GA-4576 (the sixth quarter is included in this 18-month summary).

ACKNOWLEDGMENTS

The advice and suggestions of the eminent criminalist Mr. Ray H. Pinker have been of invaluable help in the study. The very considerable help of Mr. Wayne Burgess, Chief Criminalist of the San Diego Police Department, has also been of great value.

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