GENERAL ATOMIC

DIVISION OF GENERAL DYNAMICS

GA-3491

APPLICATIONS OF NEUTRON-ACTIVATION ANALYSIS IN SCIENTIFIC CRIME DETECTION

QUARTERLY REPORT

FOR THE PERIOD ENDING JULY 31, 1962

Contract AT(04-3)-167
Project Agreement No. 15

U. S. Atomic Energy Commission

September 18, 1962

DISCLAIMER

GENERAL ATOMIC

DIVISION OF

GENERAL DYNAMICS

JOHN JAY HOPKINS LABORATORY FOR PURE AND APPLIED SCIENCE

P.O. BOX 608. SAN DIEGO 12. CALIFORNIA

GA-3491

APPLICATIONS OF NEUTRON-ACTIVATION ANALYSIS IN SCIENTIFIC CRIME DETECTION

QUARTERLY REPORT

FOR THE PERIOD ENDING JULY 31, 1962

Contract AT(04-3)-167
Project Agreement No. 15
U. S. Atomic Energy Commission

Work done by:

Sandra Bellanca
J. D. Buchanan
V. P. Guinn
J. C. Migliore
R. R. Ruch

Report written by:

V. P. Guinn

September 18, 1962

CONTENTS

Figures

Tables

I. INTRODUCTION

During 1961, the activation-analysis group at General Atomic became interested in the possible application of high-sensitivity neutron-activation-analysis techniques to the problems of scientific crime detection (criminalistics). Specifically, the possible application of these methods to the detection of gunpowder residues on the hands of suspects was considered. This led to a short exploratory study of the problem in cooperation with Mr. Ray H. Pinker, Chief Criminalist of the Los Angeles Police Department. The results were quite striking and encouraging.

A police officer fired a police revolver once, after which the backs of his hands were rinsed with very dilute nitric acid. He then fired the gun three times in succession, and the rinsing operation was repeated. Prior to these firings, blank rinsings were also carried out on both hands after they had been thoroughly washed. A retainer sample of the dilute nitric acid was also taken. The rinsings were then activated in the General Atomic TRIGA reactor at a flux of 1.8×10^{12} neutrons/sec-cm^2, and any induced radioactive Sb was radiochemically separated, with carrier Sb, for gamma-ray-spectrometer counting. Sb was looked for, specifically, since Sb_2S_3 is reportedly a component of all U. S. and most foreign revolver ammunition. The dilute nitric acid showed a blank of about 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). The rinse after one firing showed 0.12 μg Sb, or a net gain of 0.09 μg, and the rinse after three firings showed 0.23 μg Sb, or a net gain of 0.20 μg. These results were obtained from the gun hand (right hand in this case). The left-hand rinsings showed only the blank level of Sb (but did show Cu^{64} and Au^{198} activity from a gold ring the officer usually wore on his left hand). Sb was detected via the induced 2.8-d Sb^{122} activity. These very preliminary results were reported briefly by Mr. R. M. Watkins of General Atomic at the meeting of the California Association of Criminalists in San Francisco, October, 1961. The information was received with considerable interest by the criminalists at the meeting. A brief account of this work also appeared in the December, 1961, issue of Nucleonics.[1]

As a result of this encouraging beginning, further discussions were held with Mr. Ray Pinker. He felt that the whole area of characterization of very minute samples, and of trace impurities present in larger samples, of interest as possible material evidence in criminal cases would be a fruitful one for the application of activation-analysis techniques. In his

opinion, and that of General Atomic, in such areas activation analysis, because of its ultrasensitivity, might well extend conventional analytical techniques (wet chemical, spectrophotometric, emission spectrographic, and so on) to sample sizes and concentrations not otherwise analyzable. Since some work dealing with the application of activation analysis to the characterization of biological samples (hair, blood, opium) had already been reported by other investigators,[2-5] whereas virtually nothing had been reported on similar studies of nonbiological samples of forensic interest by this technique, it was decided to concentrate on the nonbiological-sample area. The following kinds of materials of possible interest were selected for a preliminary survey: plastics, paints, soils, papers, rubber, greases, inks, and metals. A proposal was made by General Atomic to the Division of Isotopes Development of the U. S. Atomic Energy Commission to investigate this area of criminalistics by means of activation-analysis techniques, working in cooperation with the Los Angeles Police Department. This proposal was favorably received, leading to the present research contract.

As is developed more fully in subsequent sections of this report, work carried out during the first three months of the contract period has been concentrated largely on the gunpowder-residue problem. However, an appreciable start has been made on the examination of commercial-plastic samples, and smaller preliminary efforts have been initiated on soils, greases, and inks.

II. FACILITIES EMPLOYED

Neutron activations of samples of interest have been carried out in both the 250-kw TRIGA Mark I and 1000-kw TRIGA Mark F reactors. For activations in the Mark I (shown in Figs. 1 and 2), a pneumatic tube was employed for irradiations in which very short-lived induced activities were involved (see Fig. 3), and the ("lazy susan") rotary specimen rack was used for irradiations involving induced activities of longer half lives. Activations in the Mark I have been carried out at thermal neutron fluxes of 1.8 to 2.8 $\times 10^{12}$ neutrons/sec-cm^2. In the Mark F reactor, samples were irradiated in a number of vertical sample tubes in the outer ring of the core--at thermal neutron fluxes of about 1×10^{13} neutrons/sec-cm^2. Activation periods have ranged from 30 sec (Mark I pneumatic tube) to 6 hr (Mark F).

Gamma-ray-spectrometer counting of activated samples has been carried out with several 3-in. by 3-in. NaI(Tl) crystals, of both the solid and the well types, shielded with 4 in. of lead. Three multichannel pulse-height analyzers (all of the transistorized type) have been employed: a Nuclear

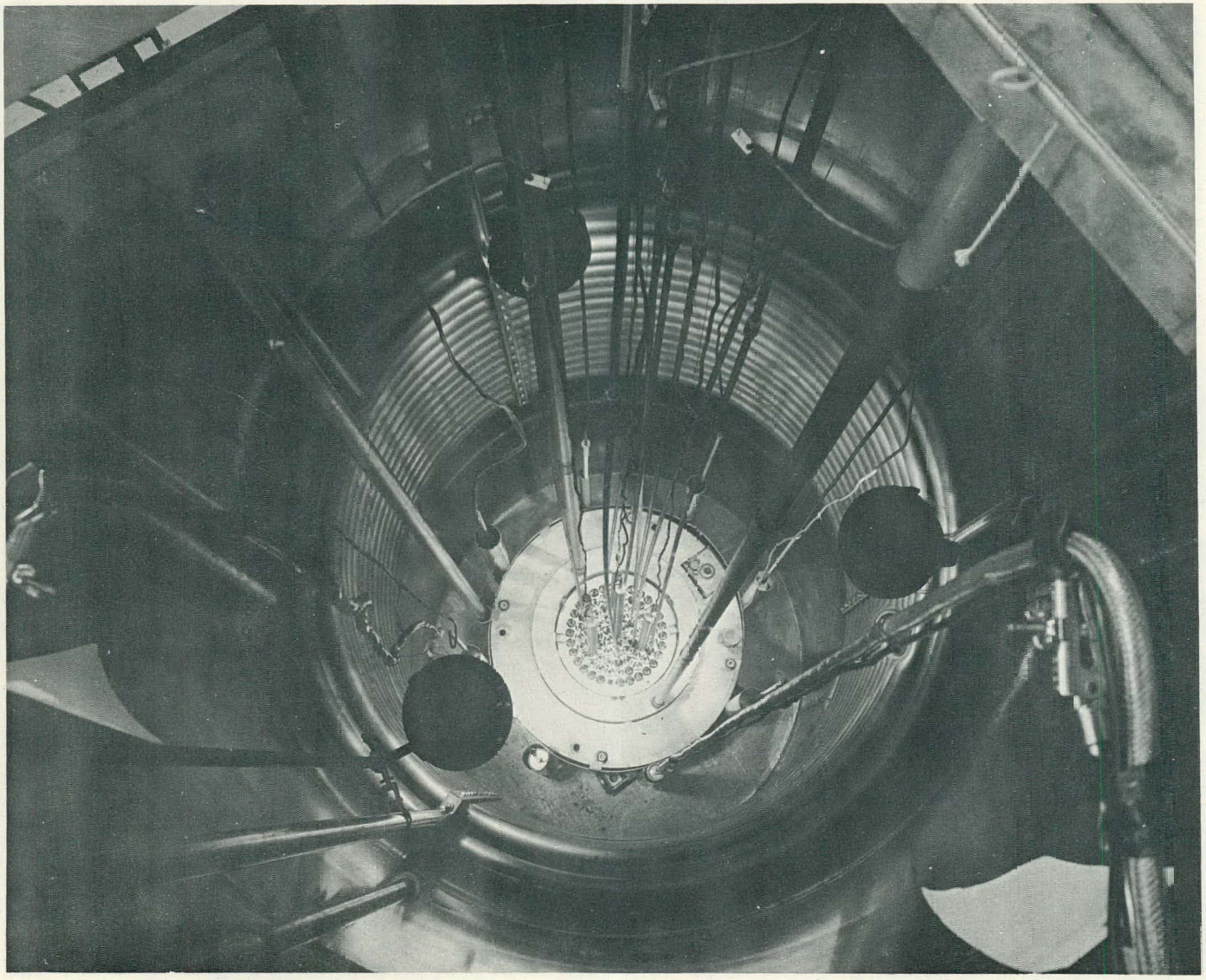

Fig. 1--The 250-kw TRIGA Mark I reactor

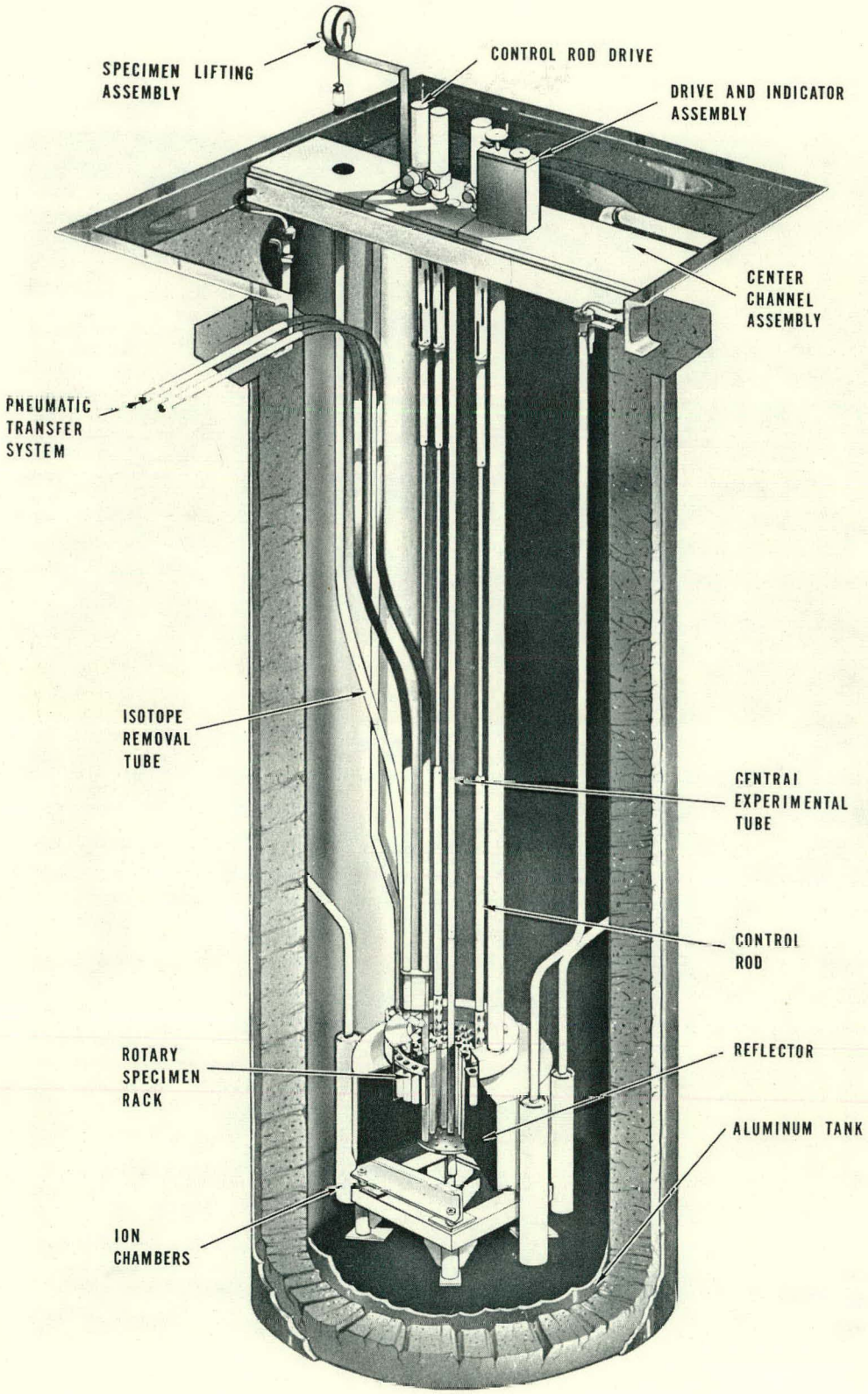

Fig. 2--Diagram of TRIGA Mark I reactor

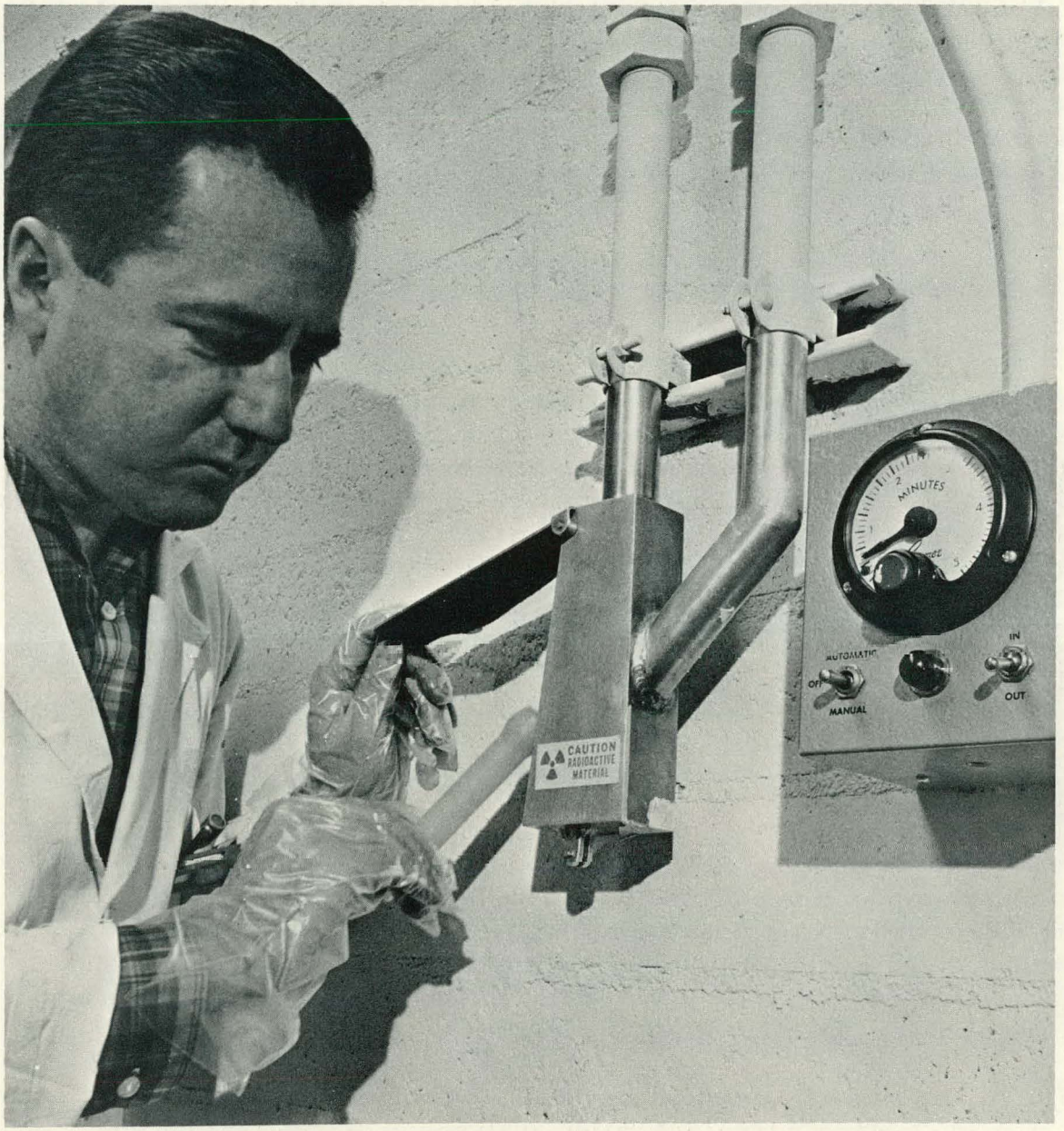

Fig. 3--Reactor pneumatic-tube system

Data 256-channel unit (see Fig. 4) and two RIDL 400-channel units (see Fig. 5). Analyses have been carried out both instrumentally and after radiochemical separations with carriers. Standard samples of the elements of interest have been irradiated simultaneously with the unknown samples or in duplicate runs, then processed and counted in the same way as the unknowns.

Sensitivities of detection for some 70 elements irradiated in the TRIGA Mark I reactor (flux of 1.8×10^{12} neutrons/sec-cm^2, maximum irradiation time of 1 hr)[6] are shown in Table 1.

III. PERSONNEL ENGAGED IN STUDY

During the quarter, the following chemists from the activation analysis group at General Atomic were actively engaged in the investigation: V. P. Guinn (Staff Member), J. D. Buchanan (Staff Associate), R. R. Ruch (Research Assistant), Sandra Bellanca (Research Assistant), and J. C. Migliore (Technician). Total manpower effort during this quarter was about 450 man-hours. During the second quarter, the same personnel will be engaged in the investigation, generally for somewhat higher percentages of their time.

IV. RESULTS OF STUDIES TO DATE

GUNPOWDER RESIDUES

According to the work of Harrison,[7] all, or virtually all, U. S. revolver ammunition contains Sb (as Sb_2S_3) in the primer portion of each cartridge, and most also contains $Ba(NO_3)_2$. The same appears to be true of most of the European ammunition studied by Harrison. With this information in mind, the early exploratory study, in which just radioantimony was looked for specifically, was carried out.

In the current investigation, both Sb and Ba are being determined in each sample--by neutron-activation analysis, with postirradiation radiochemical separations. No effort is being made to detect lead (probably also deposited as a residue from the lead part of the bullet), because the sensitivity of detection for lead is rather poor compared with that for Sb and Ba, and compared with the amounts of residue encountered on the hand. Our normal detection sensitivities (based on 1-hr activations at a thermal neutron flux of 1.8×10^{12} neutrons/sec-cm^2) for Sb, Ba, and Pb are 0.005 μg, 0.05 μg, and 10 μg, respectively. Since the amounts of each of these elements

Fig. 4--Multichannel-analyzer system used in pneumatic-tube work

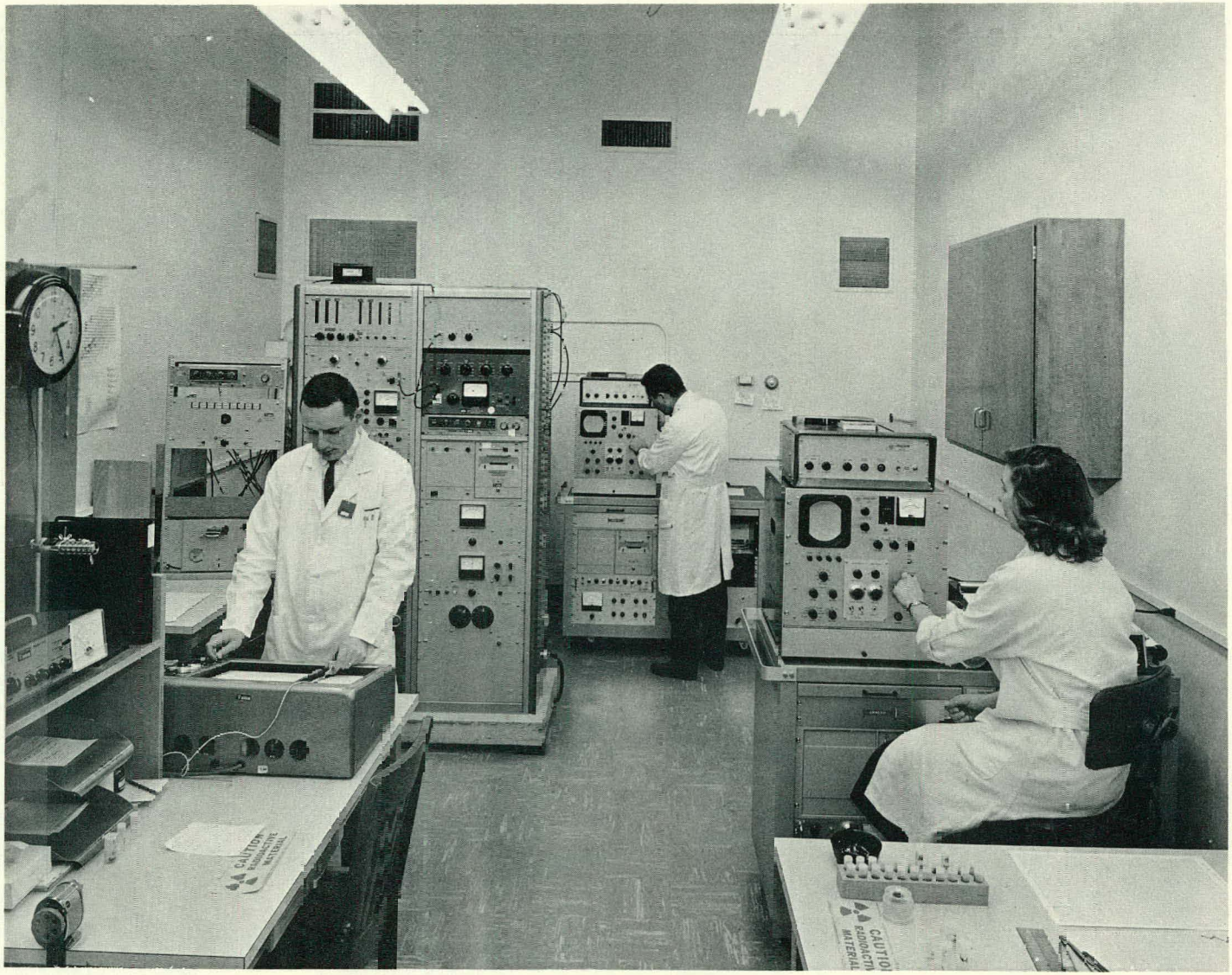

Fig 5--Main gamma-ray-spectrometry laboratory

Table 1

ESTIMATED DETECTION SENSITIVITIES FOR THERMAL NEUTRON FLUX OF 1.8×10^{12} NEUTRONS/SEC-CM^2 AND IRRADIATIONS OF ONE HOUR OR LESS

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				

deposited on the hand by a single firing of a revolver appear to be in the range of about 1 to 5 μg, the sensitivities for Sb and Ba are clearly quite sufficient, but that for Pb is inadequate. The induced Sb activity utilized is 2.8-d Sb^{122}, a β^-—γ emitter. The Ba activity utilized is 85-m Ba^{139}, also a β^-—γ emitter. The only potentially useful activity induced in Pb is 3.3-h Pb^{209}, a pure β emitter. Since bullet casings are usually of Cu or brass, and some bullets are Cu-coated, Cu residues on the hands are also of interest. Cu is normally detected down to levels of 0.001 μg via the 12.8-h Cu^{64} activity.

The over-all problem of detection of gunpowder residues has a number of interesting and important facets, each of which is under study or will be soon:

1. How may powder residues be most efficiently removed from the hand of a suspect--in a way that is compatible with activation-analysis requirements?
2. What are the detectable elements present in gunpowder residues from various ammunitions? What are the ratios of these elements in the residues from various ammunitions?
3. What is the distribution of powder residues on the hand after a firing? What factors affect this distribution? What is the total amount of deposit to be expected on the hand from a single firing under prescribed conditions? Does it build up linearly with additional firings?
4. For a given ammunition, how does the amount and distribution of powder residue depend upon the type of revolver used, and its condition?
5. What levels of Sb, Ba, and Cu are found on hands of persons who have not recently fired a gun?

Progress made to date on points 1, 2, and 3 is summarized below. Points 4 and 5 have not yet been studied.

Removal of Powder Residues

A number of possible means of removing gunpowder residues from the hands of a suspect were considered from the standpoint of efficiency and compatibility with the neutron-activation-analysis technique. These included (1) swabbing with water-moistened absorbent cotton, filter paper, Kleenex, sponge, or paper towel, (2) swabbing with wiping material soaked in mineral oil, (3) rinsing with dilute nitric acid, (4) rinsing with dilute acetic acid, (5) rinsing with detergent solution, and (6) wiping with a waterless hand cleaner.

In order to evaluate the possible application of the above techniques,

the various materials themselves were first checked for possible impurities or interferences. The results obtained on the various dry wiping media (absorbent cotton, filter paper, Kleenex, sponge, and paper towel) are shown in Table 2. The samples, selected and supplied by Mr. Pinker, were activated for 30 min at a thermal neutron flux of 1.8×10^{12} neutrons/sec-cm^2 and then transferred to fresh vials, following which their gamma-ray spectra were measured at intervals with a 3-in. by 3-in., solid NaI(Tl) crystal scintillation counter and a multichannel pulse-height analyzer (with a 1/4-in. polystyrene beta-particle absorber between the polyethylene sample vial and the crystal).

Table 2

ACTIVATION ANALYSIS OF DRY WIPING MEDIA

Material	Sample Wt. (g)	Elements Found (ppm)				
		Na	Cu	Sb	As	Others
Absorbent cotton	0.274	104	<5.0	<3.3	<4.5	1200 ppm K
Cotton gauze	0.502	163	<4	<1.3	<1.2	-----
"Q-Tip" cotton	0.021	360	<13	<4	<4	-----
Filter paper (qual.)	0.345	22	7.2	<0.8	<1.4	-----
Filter paper (quant.)	0.637	131	<2.7	<0.7	<1.0	-----
Filter paper (Whatman No. 42)	0.047	53	<0.6	<0.6	<0.4	-----
Filter paper (Whatman No. 42 washed with dist. water and alcohol)	0.047	22	<0.6	<0.6	<0.4	-----
Paper towel (acid-alcohol rinsed)		9	<1.3	-----	-----	-----
Kleenex (acid-alcohol rinsed)		17	2.1	-----	-----	-----
Polyurethane sponge		140	148	-----	-----	-----
Cellulose sponge (coarse)		105	68	-----	-----	-----
Cellulose sponge (fine)		170	109	-----	-----	Mn
Plastic sponge (white)		18	3.6	-----	-----	Mn, Au

Analyses of the various liquid removal media considered are summarized in Table 3. Activation and spectrometry procedures were carried out in the same fashion as for the dry media. Results of analyses of the waterless hand cleaners are also included in Table 3. Three samples

studied (alkyl aryl sulfonate detergent, Mac's waterless hand cleaner, and an aerosal detergent) were not completely analyzed because of the very high levels of Na^{24} generated in them by neutron activation.

Table 3

ACTIVATION ANALYSIS OF LIQUID MEDIA AND WATERLESS HAND CLEANERS

Material	Elements Found (ppm)		
	Na	Cu	Others
Distilled water	17	≤0.8	-----
1% nitric acid	31	2.6	-----
Acetic acid	54	11	-----
Demineralized distilled water	0.12	<0.007	<0.05 ppm Sb, <0.15 ppm Ba
Paraffin oil	0.77	<0.04	<0.08 ppm Sb, <0.15 ppm Ba
K & W waterless hand cleaner	20	≤4.5	Mn, K detected
El Pico waterless hand cleaner	122	≤3.7	Mn detected

From these studies it appears that swabbing the hand with washed Whatman No. 42 filter paper moistened with demineralized distilled water, with 1% transistor-grade HNO_3, or with paraffin oil offers attractive possibilities.

Elements Detected in Gunpowder Residues

In order to check on the presence of Sb, Ba, and Cu in powder residues from various revolver ammunitions, Mr. Pinker prepared a number of samples, which were then activated for 30 min in the TRIGA reactor (1.8×10^{12} neutrons/sec-cm^2 flux). The Sb, Ba, and Cu induced activities were then separated radiochemically with carriers.

Samples of primer products were prepared by removing primer from a number of bullets, igniting it in a crucible, and wrapping it in water-acetone-washed polyethylene sheet. Muzzle blast products (powder + primer) were caught on a 6-in. square of water-acetone-washed polyethylene sheet held 6 in. in front of the muzzle. In such cases, the bullet made a jagged hole in the center of the sheet. 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. Each square was cut into quadrants (see Fig. 6), and the inner and outer rings of one quadrant were examined

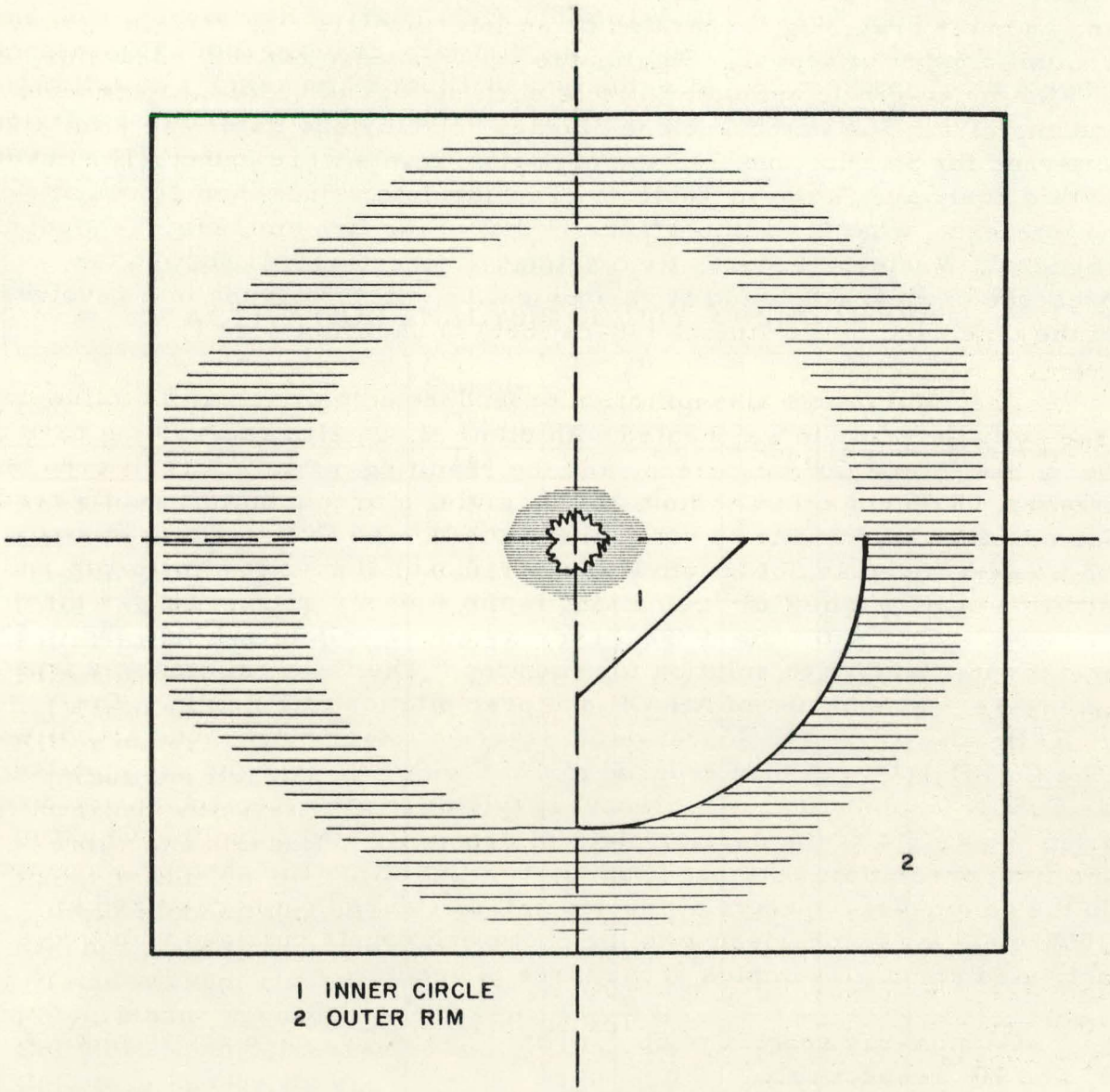

Fig. 6--Sampling of polyethylene sheet after muzzle blast

for Sb, Ba, and Cu by activation analysis. Cylinder blast products were collected by cutting a circular hole in the center of a 6-in. square of water-acetone-washed polyethylene sheet, sliding the sheet down the gun muzzle to just in front of the cylinder, then firing the gun. As in the case of the muzzle blast samples, two deposit rings were observed, an inner dark ring and an outer gray ring, separated by an intermediate ring containing only a small amount of deposit. Again, the squares were cut into quadrants, and the inner-circle and outer-circle portions of one quadrant were used in the analysis. The water-acetone-washed polyethylene itself was similarly analyzed for Sb, Ba, and Cu, and negligible levels were found. The results of this study are shown in Table 4. The absolute values themselves are of no interest. What is of importance is that of the five ammunitions studied (Federal, Western, Peters, Remington, Winchester), all showed the presence of Sb and Ba, and at various ratios. A photograph of a revolver of the type used in the studies (38-caliber) is shown in Fig. 7.

The radiochemical-separation procedure employed was as follows: The activated sample was heated with dilute HNO_3-HCl and ~20 mg each of Sb^{+3}, Ba^{+2}, and Cu^{+2} carriers, and the resulting mixture was filtered and washed. Sulfuric acid was then added, giving a precipitate of $BaSO_4$ ready for counting, and a filtrate containing $Sb^{+3(+5)}$ and Cu^{+2}. From this solution, Sb was extracted as $SbCl_5$ into ether (after oxidation to Sb^{+5} with Br_2 and addition of HCl), the Cu^{+2} remaining in the aqueous phase. Sb was then reduced to Sb^{+3} with ammoniacal hydroxylamine sulfate solution and to Sb metal with $CrCl_2$-HCl solution for counting. The Cu^{+2} solution was freed of any Fe^{+3} by addition of NH_4OH and precipitation of $Fe(OH)_3$. The $Fe(OH)_3$ also served to scavenge out traces of other extraneous activities. The $Cu(NH_3)_4^{+2}$ was then reduced to Cu^{+1} with HCl-SO_2 and precipitated as CuSCN for counting. The recovery (yield) of each element was computed from the weight of the carrier element originally added and the weight of the final precipitate obtained ($BaSO_4$, Sb, CuSCN). The photopeak counts in the gamma-ray spectra of the precipitates were then normalized to 100% yield for comparison with the photopeak counts obtained with the activated standard samples of the three elements.

Gamma-ray spectra of Sb^{122}, Ba^{139}, and Cu^{64} are shown in Figs. 8, 9, and 10, respectively.

Distribution of Powder Residues on the Hand

In studies of powder residues, it is important to establish the distribution of the residues on the various areas of the gun-firing hand. In the present work, a police officer of the Los Angeles Police Department donned on his gun hand a plastic glove having 2-in. circles of moist Whatman No. 42 filter paper on the thumb-web and back-of-hand positions and wrapped around the trigger finger (see Fig. 11). In two experiments, using a fresh

Table 4

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

Ammunition	Sample Type	Elements Found (μg)			Ba/Sb Ratio
		Sb	Ba	Cu	
Federal	Primer product	100	334	ND[a]	3.3
	Cylinder blast, inner	7.2	9.9	ND	1.4
	Cylinder blast, outer	1.1	28	ND	25
	Muzzle blast, inner	8.2	9.8	ND	1.2
	Muzzle blast, outer	10.1	17.4	ND	1.7
Western	Primer product	17.2	246	ND	14
	Cylinder blast, outer	16.9	318	5.1	19
	Muzzle blast, inner	6.2	4.5	2.3	0.73
	Muzzle blast, outer	7.1	4.1	3.4	0.58
Peters	Primer product	38	128	ND	3.4
	Cylinder blast, inner	6.3	4.8	1.1	0.76
	Cylinder blast, outer	5.6	5.9	0.8	1.1
	Muzzle blast, inner	4.8	9.9	0.5	2.1
	Muzzle blast, outer	9.9	12	1.7	1.2
Remington	Primer product	16	49	ND	3.1
	Cylinder blast, inner	4.4	5.3	0.4	1.2
	Cylinder blast, outer	6.5	9.8	1.4	1.5
	Muzzle blast, inner	7.1	18	1.4	2.5
	Muzzle blast, outer	7.5	9.5	1.4	1.3
Winchester	Primer product	168	175	ND	1.0
	Cylinder blast, inner	6.3	3.3	ND	0.52
	Cylinder blast, outer	4.7	2.2	ND	0.47
	Muzzle blast, inner	20	15	ND	0.75
	Muzzle blast, outer	16	8.7	ND	0.54

[a]ND = none detectable.

Fig. 7--Type of revolver (38-caliber) used in studies

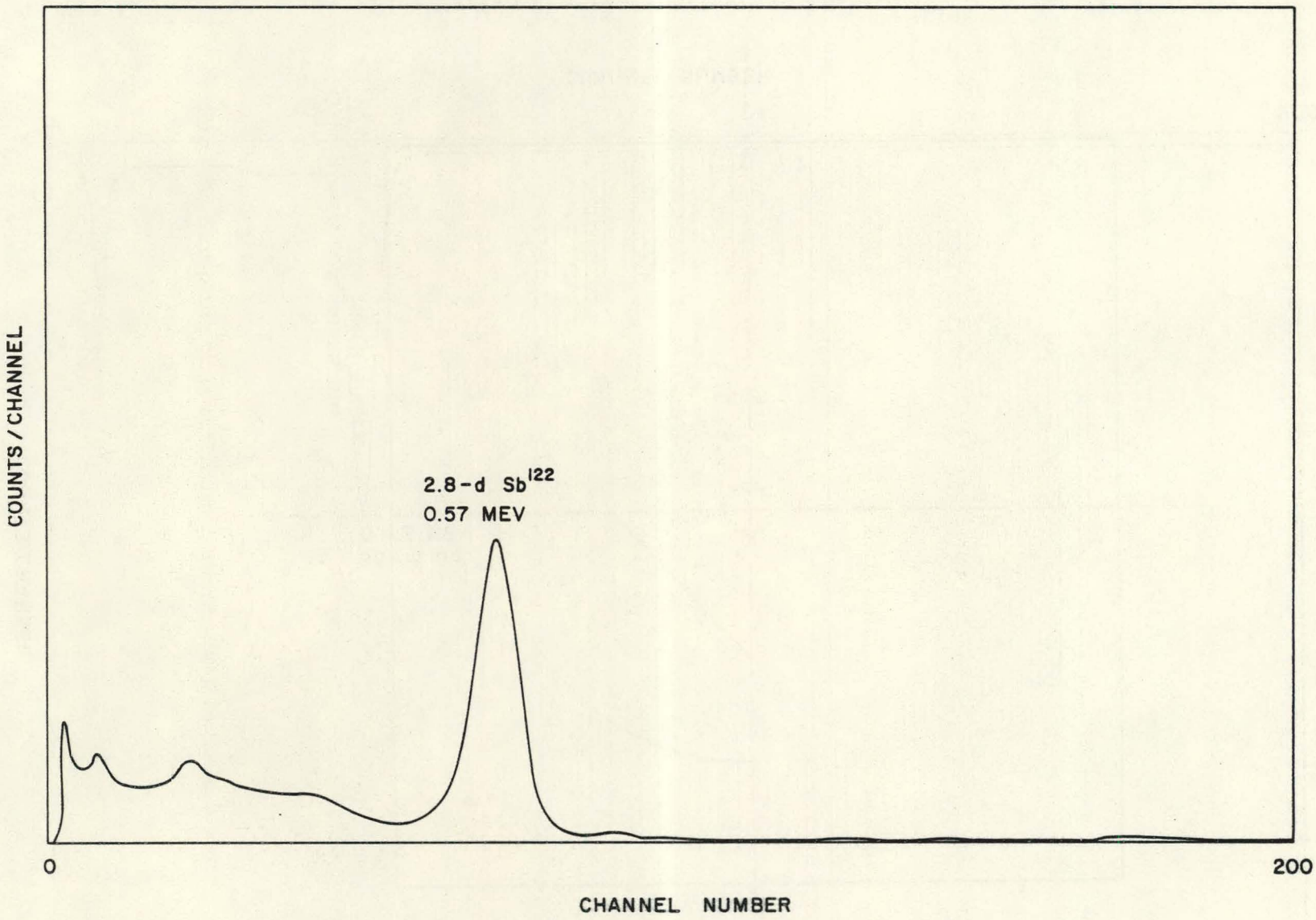

Fig. 8--Gamma-ray spectrum of 2.8-d Sb^{122}

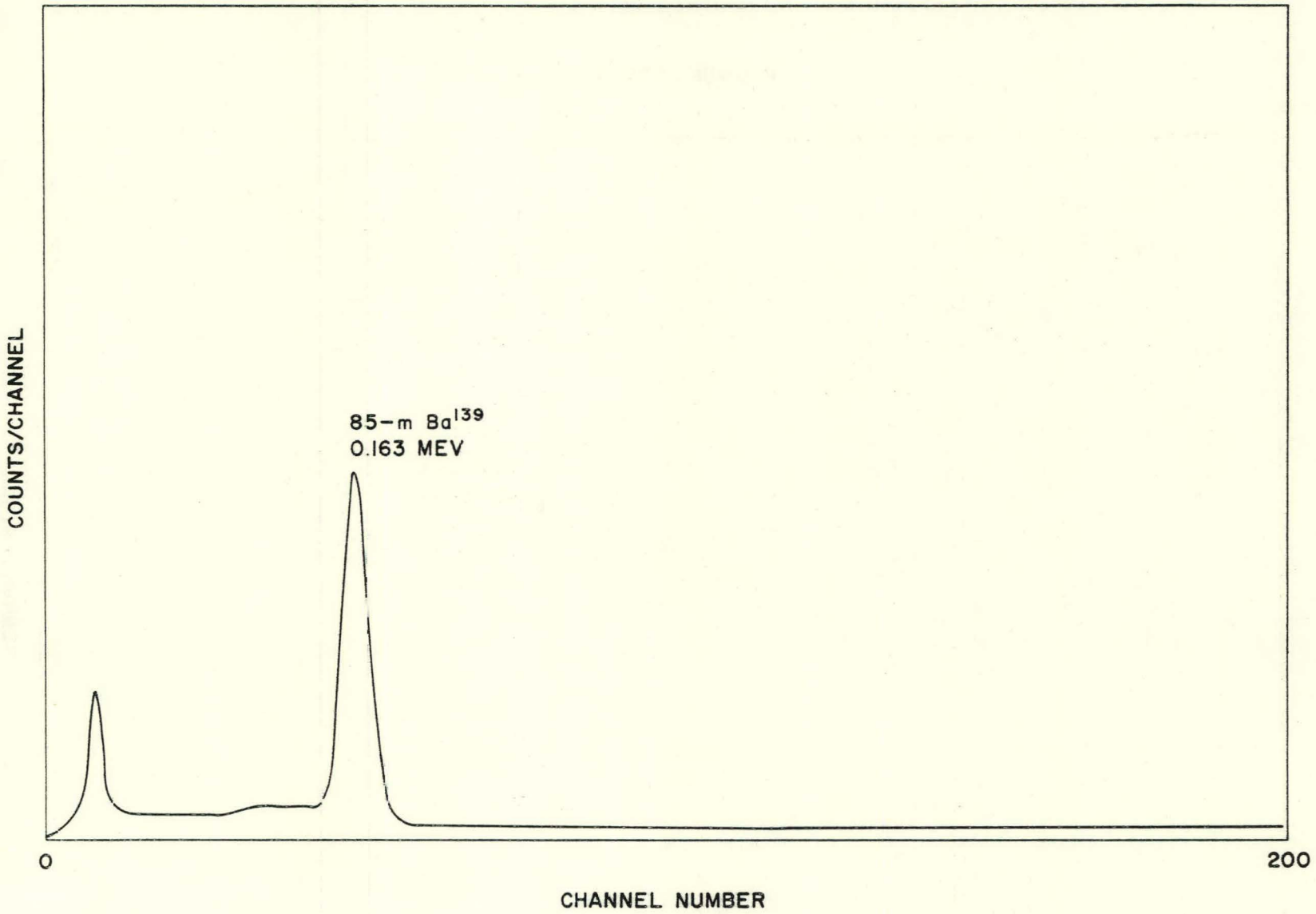

Fig. 9--Gamma-ray spectrum of 85-m Ba^{139}

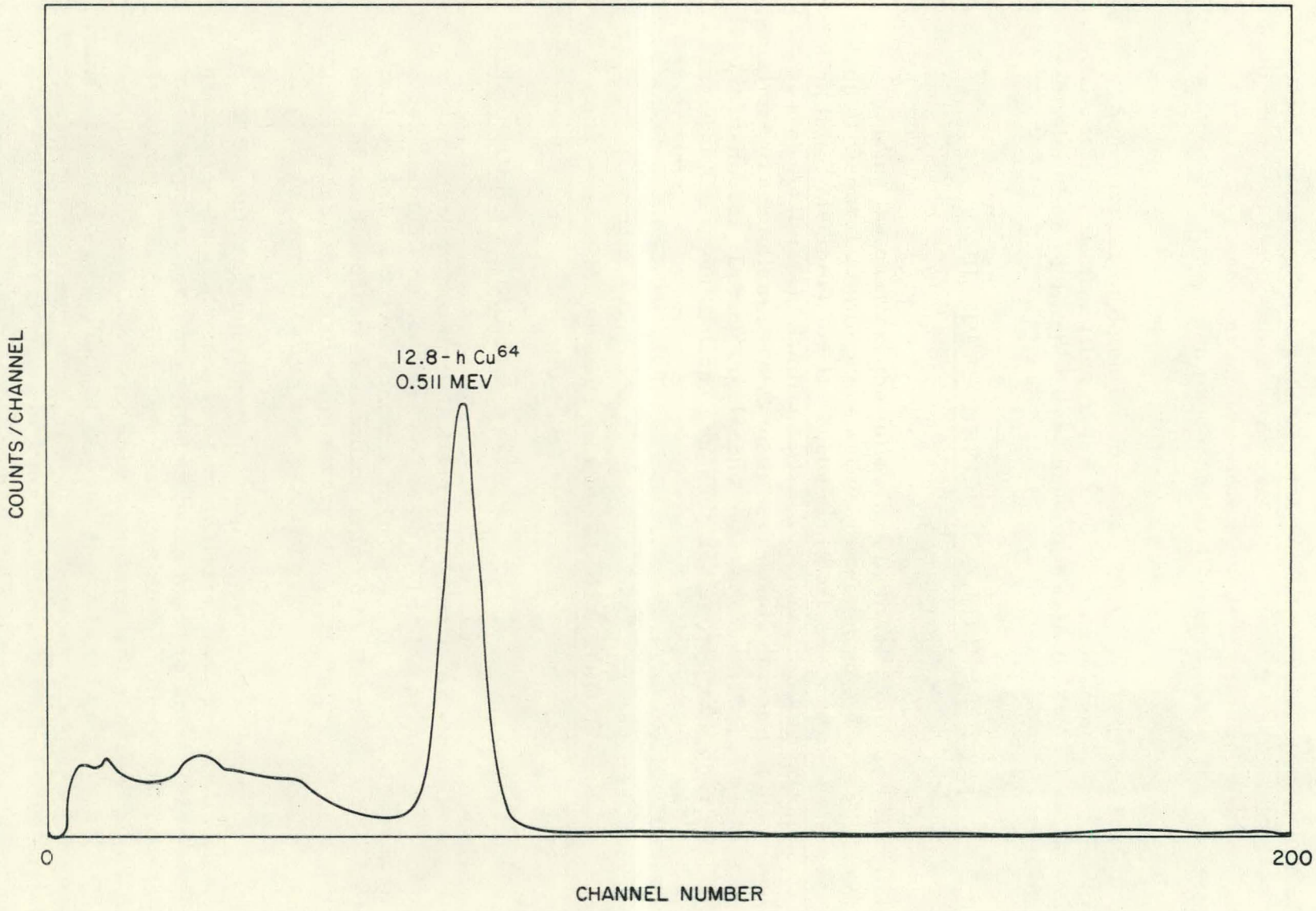

Fig. 10--Gamma-ray spectrum of 12.8-h Cu^{64}

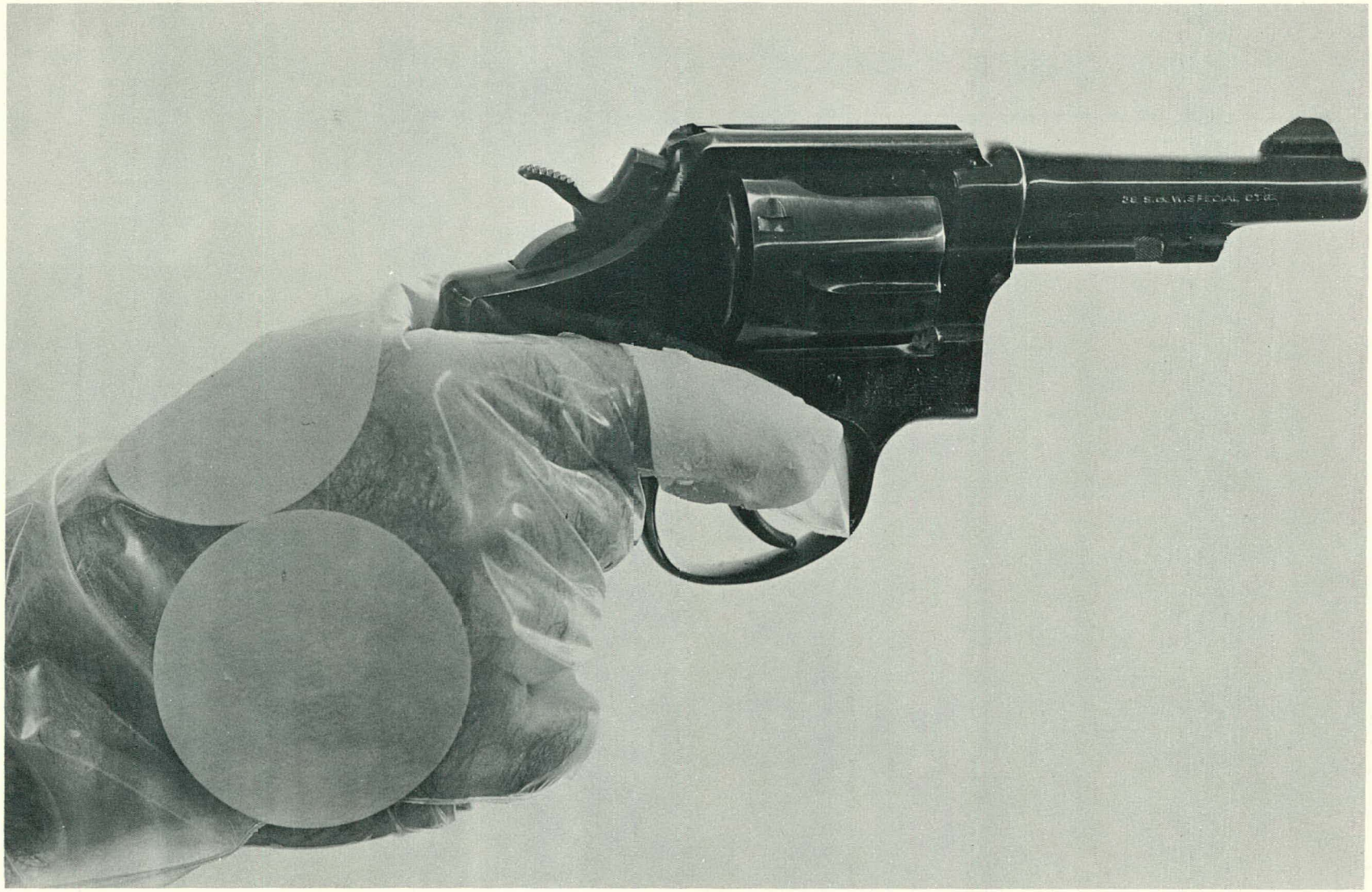

Fig. 11--Plastic glove with moist filter-paper patches for powder-residue distribution studies

plastic glove and fresh moist patches each time, he fired a 38-caliber revolver once with Peters ammunition and once with Western ammunition. The six patches were activated in the TRIGA reactor for 30 min, heated in the presence of dilute HNO_3-HCl for 10 to 15 min, with carrier Sb, Ba, and Cu, and the three elements of interest then separated chemically (yield determined), and counted on a multichannel gamma-ray spectrometer. With each ammunition, the total amounts collected (sum on all three areas) in one firing were about 1 μg Sb, 5 μg Ba, and 5 μg Cu. 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 detailed results are shown in Table 5. The values in Table 5 are net values, already corrected for the filter-paper blank (average of four determinations: <0.02 μg Sb, ≤0.10 μg Ba, 0.34 μg Cu).

Table 5

DISTRIBUTION OF POWDER RESIDUE ON THREE AREAS OF THE GUN HAND
(Plastic Glove/Moist Filter-paper Patch Technique)

Ammunition	Hand Area	Elements Found (net) (μg)		
		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

It is felt that this technique provides essentially 100% collection of powder residue impinging on the hand areas of maximum interest. The results obtained in test firings of this type thus can provide a means of measuring the recovery achieved by other methods of removal of residues from the hand.

In a different attempt at determining the amounts of residue deposited on various hand areas, the policeman firing the gun wore a plastic glove coated with paraffin oil in the same three areas, plus an area on the palm of the hand. Again, the 38-caliber revolver was fired only once with each kind of ammunition. After each firing, the four oil-coated areas were wiped carefully with a small piece of Whatman No. 42 filter paper, activated,

and analyzed for Sb, Ba, and Cu by means of radiochemical separations with carriers, and multichannel gamma-ray spectrometer counting. As can be seen from the data in Table 6, the deposit on the palm of the hand was rather small, and the over-all recovery of residue in the other three areas was only about half that found by the moist-filter-paper patch technique.

Table 6

DISTRIBUTION OF POWDER RESIDUE ON FOUR AREAS OF THE GUN HAND
(Plastic Glove/Paraffin Oil Technique)

Ammunition	Hand Area	Elements Found (net) (μg)		
		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 of hand	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 of hand	0.08	0.40	0.76

COMMERCIAL PLASTICS

The widespread use of plastics for so many kinds of objects makes this type of material one of frequent interest in criminal cases. Identification of the origin of plastic pieces from a broken automobile tail light in a hit-and-run case is an obvious example.

Virtually all plastics used commercially are polymerized hydrocarbons, containing only C and H as main constituents (e. g., polyethylene, polypropylene, polystyrene), or polymerized C-H-O compounds (e. g., Lucite (polymethyl methacrylate), nylon, cellulose acetate). A few contain C, H, and either F (Teflon), Cl (polyvinyl chloride), or N (cellulose nitrate). With the C-H and C-H-O types, identification is possible by means of quantitative measurement of the amounts of catalyst residues present in the finished polymer, or of other impurities introduced in the manufacture of the plastic. F, Cl, N, and O are, of course, also readily determined by neutron-activation analysis (N and O by fast neutrons). Their presence in major amounts quickly establishes the general type of polymer. Identification of trace

impurities in these polymers may also identify the manufacturing process used, or even the particular manufacturer or user, and possibly the particular batch.

Because of the lack of matrix activation of C-H and C-H-O (N) polymers by thermal neutrons, such plastics offer an ideal case for characterization of impurity levels by purely instrumental, nondestructive neutron-activation analysis. A series of 19 commercial plastics, collected by Mr. Pinker, were therefore surveyed by the instrumental method. The results are summarized below.

In order to look for short-lived induced activities, 0.5-g samples were activated for 30 sec in half-dram polyethylene vials, at a thermal neutron flux of 2.8×10^{12} neutrons/sec-cm^2, then removed from the reactor by means of the pneumatic tube, transferred rapidly to fresh vials, and counted with a multichannel gamma-ray spectrometer. Such analyses were, of course, carried out one sample at a time. Standard samples of the elements found were activated and counted under the same conditions.

For detection of longer-lived induced activities, 2- to 3-g samples, contained in 2-dram polyvials, were activated for 30 min in the rotating lazy susan of the reactor at a thermal neutron flux of 1.8×10^{12} neutrons/sec-cm^2 and then transferred to fresh vials. Each sample was then counted on a multichannel gamma-ray spectrometer at a variety of decay times, ranging from 1 hr to several weeks. Standard samples of each of the elements detected were similarly activated and counted.

In the 19 samples studied, a total of 13 different trace elements were detected: Na, Al, Cl, Mn, Cu, Cd, Ba, Ti, Sb, Br, Zn, As, Au. The results are summarized in Table 7. A representative spectrum is shown in Fig. 12.

Although most of the samples were colorless and clear (or translucent or opaque white), some were orange (sample 3), red (samples 4 and 18), black (samples 14 and 17), yellow (sample 15), or light blue (sample 19). Some samples may contain fillers or dyes. In the case of Teflon (sample 6), the F detected is, of course, a major constituent of the tetrafluoroethylene polymer. Similarly, in the case of the vinyl sample (16), the chlorine detected is a major constituent of the polyvinyl chloride.

The maximum number of trace elements detected in a single sample (sample 11, Enjay polypropylene) was seven: Na, Al, Cl, Mn, Cu, Zn, As. The minimum number detected was one: Na in sample 6, Teflon. In this case, however, the large F activity may have obscured the presence of additional induced activities otherwise detectable. Three samples showed only two trace elements detectable under these conditions: Na-Cl and Na-Cu,

Table 7

ACTIVATION ANALYSIS OF 19 COMMERCIAL PLASTICS

Sample No.	Type	Trade Name	Manufacturer	Elements Found (ppm)
1	Acetal	Delrin 500	DuPont	Na(2), Al(1), Mn(0.26), Cu(0.4)
2	Acrylic	Lucite 140	DuPont	Na(10), Cl(8)
3	Cellulose acetate	Tenite 043-A	Eastman	Na(3), Al(3), Cd(2800), Ba(620)
4	Cellulose acetate butyrate	Tenite 205-A	Eastman	Na(3), Al(3), Mn(0.14), Cd(3000), Ba(2800)
5	Cellulose propionate	Tenite 306-A	Eastman	Na(10), Al(80), Cl(6), Mn(0.05), Ti(80,000), Sb(5)
6	Fluorocarbon	Teflon 1	DuPont	Na(25), F(major const.)
7	Polyamide (nylon)	Zytel 101	DuPont	Na(0.2), Cl(3), Mn(0.05)
8	Polyethylene	Tenite 860-A	Eastman	Na(0.4), Cl(3), Br(0.2)
9	Polyethylene	DYNH-1	Union Carbide	Na(0.3), Cl(0.8)
10	Polyethylene	617	Allied Chemical	Na(0.9), Al(3), Cl(2), Mn(0.1), Br(0.1)
11	Polypropylene	Escon 104	Enjay	Na(1), Al(6), Cl(14), Mn(0.1), Cu(0.08), Zn(18), As(0.06)
12	Polypropylene	Tenite Polypropylene	Eastman	Na(0.4), Al(15), Cl(3), Mn(0.03)
13	Polystyrene	SMD-3500	Union Carbide	Na(0.6), Al(0.3), Cl(0.8), Mn(0.05)
14	Acetonitrile-butadiene-styrene	Kralastic-B	U.S. Rubber	Na(170), Al(2), Cu(25), Zn(1200)
15	Acetonitrile-butadiene-styrene	Kralastic-MM	U.S. Rubber	Na(190), Al(3), Cu(30)
16	Vinyl	VND-9970	Union Carbide	Na(4), Cl(230,000), Cu(70)
17	Phenolic	BMG-5000	Union Carbide	Na(150), Al(50), Cl(390), Mn(1), Cu(25)
18[a]	Unknown	Unknown	Guide	Na(4), Al(2), Cl(10), Mn(0.06), Au(0.06)
19	Polyurethane	Unknown	Unknown	Na(170), Al(15), Cl(130), Mn(0.6), Cu(210)

[a]This sample is a piece of an automobile taillight.

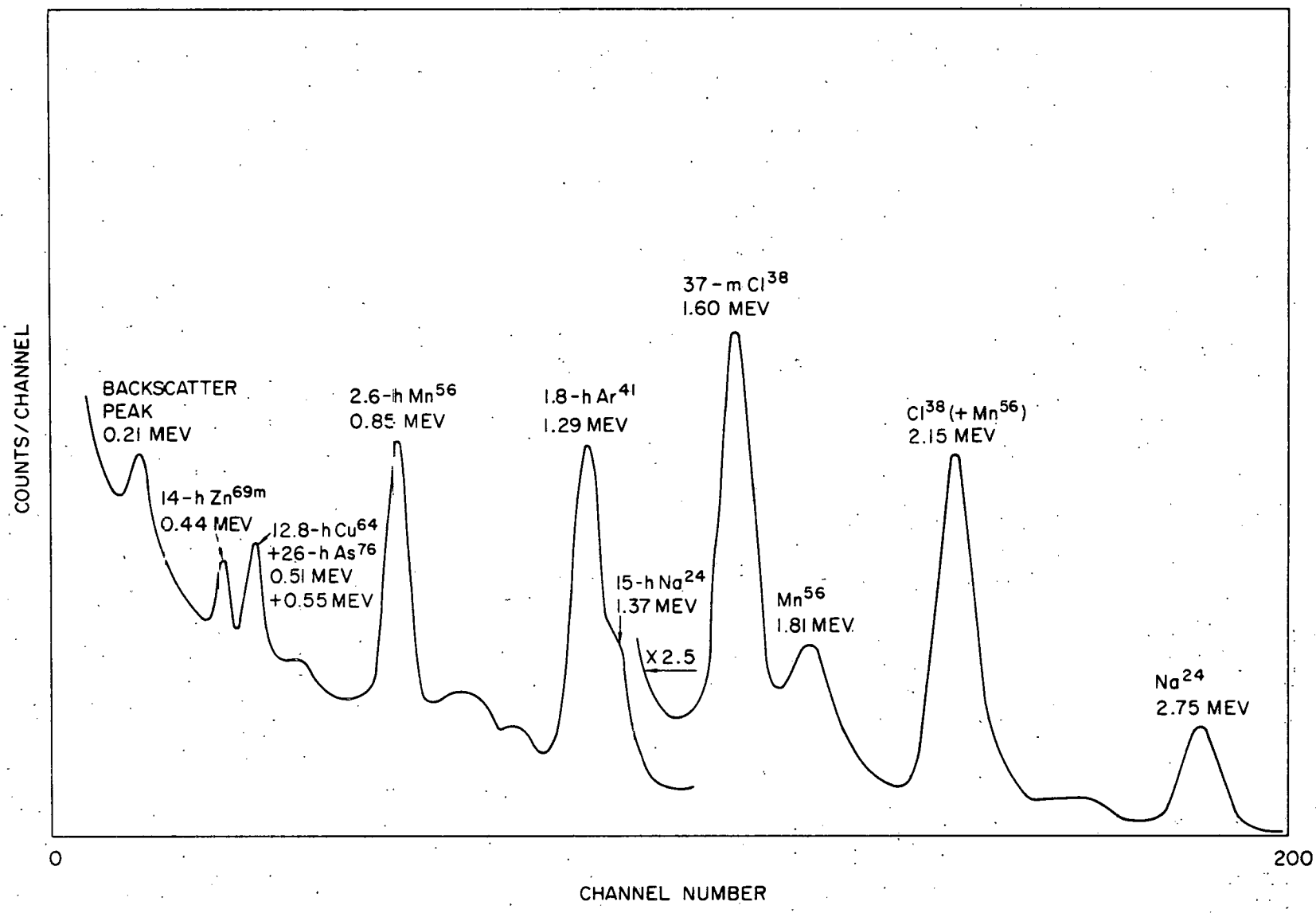

Fig. 12--Gamma-ray spectrum of an activated commercial-plastic sample

the Na-Cu sample also showing Cl as a major constituent (vinyl). Three samples showed the presence of only three trace elements: Na-Cl-Mn, Na-Cl-Br, Na-Al-Cu. Five samples showed the presence of four trace elements: Na-Al-Mn-Cu, Na-Al-Cd-Ba, Na-Al-Cl-Mn, Na-Al-Cl-Mn, Na-Al-Cu-Zn. Five samples showed the presence of five trace elements: Na-Al-Mn-Cd-Ba, Na-Al-Cl-Mn-Br, Na-Al-Cl-Mn-Cu, Na-Al-Cl-Mn-Au, Na-Al-Cl-Mn-Cu. One sample showed the presence of six trace elements: Na-Al-Cl-Mn-Ti-Sb.

The most commonly encountered trace elements were Na (found in all 19 samples, but at levels ranging from 0.2 to 190 ppm); Cl (found in 12 samples, at levels, excluding vinyl, from 0.8 to 390 ppm); Al (in 13 samples, at levels of 0.3 to 80 ppm); Mn (in 11 samples, at levels of 0.03 to 1 ppm); and Cu (in 7 samples, at levels of 0.08 to 210 ppm). Ti and Sb were found only in one sample (sample 5, Eastman cellulose propionate). As was found only in one sample (sample 11, Enjay polypropylene), and Au was found only in one sample (sample 18, Guide red automobile tail light plastic). Cd and Ba were found only in two samples (samples 3 and 4, Eastman cellulose acetate and cellulose acetate butyrate). Br was found only in two samples (samples 8 and 10, Eastman and Allied Chemical polyethylenes), and Zn was found only in two samples (samples 11 and 14, Enjay polypropylene and U. S. Rubber acetonitrile-butadiene-styrene).

From this preliminary survey, it would appear that a given sample of plastic might be identified as to manufacturer by a combination of conventional tests (ultraviolet absorption, infrared absorption, C-H combustion) and activation analysis with fast neutrons (to determine N and O and perhaps F) and thermal neutrons (to determine major constituents such as F and Cl and trace impurities). Many more commercial plastics will be examined soon.

To expedite the measurements, the samples examined in this survey were rather large (0.5 to 3 g). In criminal cases, however, very minute samples are often encountered. Although the sensitivity of neutron-activation analysis may still be adequate with such small samples, the problem of sample homogeneity must be considered. In a preliminary examination of this aspect of the problem, rather small (25 to 50 mg) quadruplicate samples of two of the 19 samples (11, Enjay polypropylene, and 18, Guide red tail light plastic) were analyzed as before (30-min activation at 1.8×10^{12} neutrons/sec-cm^2). In the case of the Enjay polypropylene samples, the relative (not absolute) values of Cl, Mn, Zn, and Na, expressed in arbitrary units, are shown in Table 8. For the case of the Guide plastic (sample 18), the relative values of Cl, Mn, Au, and Na are also shown in Table 8, again in arbitrary units (the numbers are only intercomparable for a given element in a particular plastic--not for different elements in the same plastic or for the same element in the two different plastics). The (±) value after

each value is the standard deviation, based on counting statistics only. The (±) value of each mean is the standard deviation of the mean, based on the spread of the four values averaged.

Table 8

STUDY OF HOMOGENEITY OF TWO PLASTICS

Plastic	Sample Wt. (mg)	Relative Concentrations			
		Cl	Mn	Zn	Na
No. 11 (Enjay polypropylene)	32.9	44±3	96±6	44±4	32±3
	25.4	44±4	104±6	39±4	27±3
	26.6	40±5	97±6	35±4	28±3
	28.5	43±5	102±6	40±4	24±3
		mean 43±2	100±4	40±5	28±3
		Cl	Mn	Au	Na
No. 18 (Guide red plastic taillight)	30.8	21±3	51±5	7±3	38±3
	49.6	20±2	30±4	8±2	37±3
	44.8	18±3	44±4	7±2	40±3
	28.0	19±4	28±3	23±2	34±3
		mean 19±2	38±12	12±8	37±3

As can be seen from Table 8, the four samples of Enjay polypropylene appear identical, within statistical error, in all four elemental components. The four samples of Guide red plastic appear identical with respect to their contents of Na and Cl, but show significant scatter in their contents of Mn and Au. The plastic homogeneity problem will be investigated further.

SOILS

The area of trace and major-constituent element characterization of soils has not yet been explored systematically in this investigation. However, a very interesting specific case was studied at the request of Mr. Pinker and of Mr. Wayne Burgess, Criminalist with the San Diego Police Department. This study consisted in the characterization of three very small (0.4- to 2.9-mg) rock particles involved in a current local murder case. All of the samples showed a characteristic blue color.

The samples were given a short (30-sec) activation, one at a time, in the 2.8×10^{12} neutrons/sec-cm^2 pneumatic-tube location in the reactor, followed by rapid gamma-ray spectrometry. A very large Al^{28} activity was produced in each of the samples, blocking detection of any other short-lived activities. Presumably, this activity was generated by slow-neutron activation of Al and fast-neutron activation of Si (via $Si^{28}(n, p) Al^{28}$). With a longer (30-min) irradiation at a flux of 1.8×10^{12} neutrons/sec-cm^2, and a decay period to eliminate the Al^{28} activity (2.3-min half life), gamma-ray spectrometry at several decay times revealed the presence of Na and Mn in each sample, and of Co in one of the samples. Finally, the samples were given a 6-hr irradiation at a 1-Mw reactor power level (flux of $\sim 10^{13}$ neutrons/sec-cm^2), followed by gamma-ray spectrometry at various decay times. In this manner, the additional elements Cr and Sc were found (besides the Na, Mn, and Co previously detected).

The relative amounts of Sc, Co, Cr, Na, and Mn found in the three samples are shown in Table 9. In each case, the amount of the element found in sample 2 is taken as unity, and the amounts of that element found in the other two samples are shown as multiples of the unit value found in sample 2. In the case of Co, no trace was detectable in samples 2 and 3, so the statistical upper limit of the possible Co content of sample 2 was taken as unity. Co was definitely found in sample 1, and the amount is shown as a multiple of the unit value taken as the upper limit of the possible Co level of sample 2.

Table 9

ANALYSIS OF THREE ROCK PARTICLES INVOLVED IN A CURRENT MURDER CASE

Sample No.	Sample Wt. (mg)	Relative Contents[a]				
		Sc	Co	Cr	Na	Mn
1	2.870	5.5	215	2.4	0.8	1.9
2	0.582	1.0	1.0[b]	1.0	1.0	1.0
3	0.411	1.1	2.0[b]	1.0	1.1	1.0

[a] Sample No. 2 = 1.0.
[b] Upper limit (none detected).

It will be noted that samples 2 and 3 are virtually identical in composition with regard to all five elements detected. Sample 1 is reasonably similar in its contents of Na, Mn, and Cr, but is much richer in Co (100- to

200-fold) and considerably richer in Sc (5-fold) than the other two. Sample 3 was removed from a bit of dirt attached to a brick that was used as the murder weapon and left at the scene of the crime. Sample 2 was removed from the soil in a local brickyard, just at the location of a brick that had been removed (possibly the murder weapon). Sample 1 was a larger bluish rock selected at random from a location somewhere near the brickyard, but not from under any stack of bricks. Thus, in this case, activation analysis established the probable identity of the source of the unusual blue particles found on the murder weapon and of the similar blue particles found in a local brickyard, just at the spot where a similar brick had been removed. The suspect, already tied closely to the crime by several other independent lines of evidence, lived in a shack at the brickyard. The nonidentity of a similar-appearing bluish rock was also established by activation analysis.

A systematic investigation of the possibility of the characterization of small soil and rock samples by activation analysis will be initiated soon.

GREASES

Characterization of greases is of importance in hit-and-run cases, in which a small smear of grease from the underside of the hit-and-run car may be left on the body or clothing of the victim, or upon grass or weeds in an adjacent field if the hit-and-run car veered off the road before being driven on. Such grease may have a considerable accumulation of dust and dirt in it, picked up over a period of time. Thus, if the suspected car is found, it may be possible to show that grease on its underside is identical in nature, and in dirt impurity, to grease found at the scene of the crime. Often the latter material is available only in very minute quantity; hence highly sensitive detection is needed.

In the preliminary study of greases carried out during this first quarter, six commercial automobile greases (Wilshire, Mobil, Standard, Shell, Union, Los Angeles Police Department) supplied by Mr. Pinker were studied. Samples (0.3 to 1.0 g) were activated for 30 sec in the TRIGA Mark I pneumatic-tube position (2.8×10^{12} neutrons/sec-cm^2 flux), and the gamma-ray spectra of the induced activities were determined promptly after irradiation. The samples were also given a 30-min activation in the TRIGA Mark I lazy susan (1.8×10^{12} neutrons/sec-cm^2 flux), and gamma-ray spectra were then obtained at several decay times. In the six samples, 11 elements were detected altogether: Na, Al, Cl, Ca, V, Mn, Cu, As, Br, Mo, Ba. The results are summarized in Table 10, and a representative gamma-ray spectrum of an activated chassis-lubricant sample is shown in Fig. 13. Ca was a sizeable constituent (0.1% to 0.6%) in four of the greases, and Ba was a major constituent (4.6%) in one. The other elements appeared generally as trace impurities (0.2 to 240 ppm). It is of interest to note that the six greases differed widely in their elemental constituents.

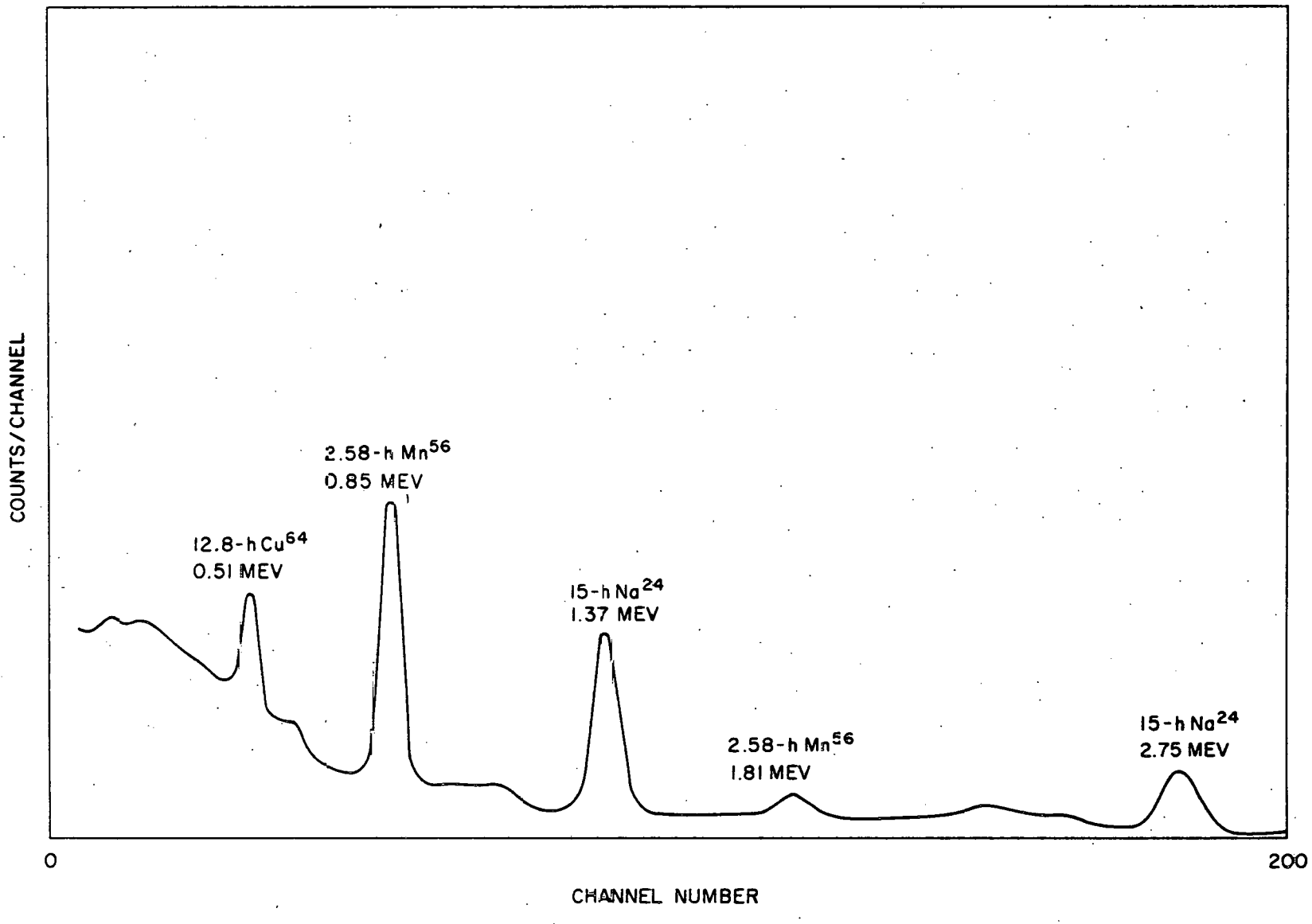

Fig. 13--Gamma-ray spectrum of an activated commercial-chassis-lubricant sample

Table 10

ELEMENTS DETECTED IN SIX COMMERCIAL AUTOMOBILE GREASES
(In ppm)

Element	Grease					
	Wilshire	Mobil	Standard	Shell	Union	L. A. P. D.
Na	25	4	160	50	7	60
Al	120	4	80	25	2.5	240
Cl	-----	8	-----	70	2.5	240
Ca	240	6,500	2,200	1,100	-----	4,200
V	-----	0.23	1.9	-----	130	-----
Mn	0.4	0.2	2.9	-----	-----	0.4
Cu	-----	-----	30	-----	-----	-----
As	1.1	1.0	-----	-----	-----	-----
Br	-----	-----	3.2	-----	-----	-----
Mo	≤ 1	-----	-----	-----	-----	11
Ba	-----	17	-----	-----	46,000	-----

Many more commercial greases will soon be studied instrumentally. Also, dirty grease samples from the undersides of cars will be investigated.

INKS

One very difficult problem is the identification of ink on written or printed documents. This problem is especially difficult if the sample must be analyzed nondestructively, since activation of impurities in the paper may tend to swamp the small amounts of activities generated in the ink. Nevertheless, work has begun on this problem.

Five different inks were investigated, all as writing on a single type of writing paper. The inks were black ballpoint, blue ballpoint, Parker Superchrome blue-black, Schaeffer's Skrip permanent jet black, and Schaeffer's Skrip washable black. The paper used was General Atomic letterhead stationery, watermarked "Gilbert Resource Bond, 50% Cotton Fibre, U. S. A." A 3-cm by 10-cm piece of this paper, weighing 0.23 g, was used for each specimen. Each ink sample consisted of the ink identification written on the strip of paper, e. g., "Black Ballpoint Ink" written on the strip of paper with black ballpoint ink.

The samples, including a blank strip of paper, were irradiated in a thermal neutron flux of 1.8×10^{12} neutrons/sec-cm^2. Gamma-ray spectra of the activated samples were then obtained at several decay times. The

ink-paper samples showed exactly the same gamma-ray spectra as the blank paper itself. Five elements were detected: 510 ppm Cl, 80 ppm Na, 17 ppm Cu, 5 ppm Mn, and 4 ppm Sb. A few other low-energy gamma-ray peaks (0.05 to 0.16 Mev) were observed, but not identified.

This discouraging start was not unexpected. Some further studies of inks will be conducted before any conclusion is reached that the identification of ink by activation analysis is definitely hopeless. Some inks will be studied per se, i.e., not on paper, to see if they do contain characteristic trace impurities that could be useful in identification studies. If they do, efforts will be made to analyze the inks after removal from the paper. Even though this would destroy a sample, there are cases in which enough sample is available so that destruction of a portion of it would be acceptable. Mr. David A. Crown of the San Francisco Identification Laboratory of the U. S. Postal Inspection Service has expressed a strong interest in this problem, and has offered to assist us in this study in any way that he can.

OTHER MATERIALS

As has been already discussed, five types of materials of interest as forms of material evidence in criminal cases have been explored at least in a preliminary fashion to date: gunpowder residues, commercial plastics, soils, greases, and inks. Five other materials of significance will ultimately be investigated (as mentioned in the original contract proposal): glass, paints, papers, rubber, and metals. Studies of the five materials already under investigation will, of course, be extended much further. Mr. Pinker has now collected a considerable variety of automobile-tire rubber samples (natural and synthetic), which are to be investigated soon.

V. ADDITIONAL ACTIVITIES

Relevant literature on the subject of the application of neutron-activation analysis to crime detection has been collected, including several books on criminalistics, journal articles by Jervis, Lenihan, and others, and back issues of the Journal of Forensic Sciences. Numerous discussions have been held with Mr. Pinker in Los Angeles and in San Diego, and by telephone. Several discussions have also been held with Mr. Burgess of the San Diego Police Department crime laboratory. An all-day seminar on applications of neutron-activation analysis to problems of scientific crime detection was held at General Atomic on May 26, 1962, for some 40 members of the California Association of Criminalists, as an extra day of their annual meeting. Lectures on activation analysis and its applications were given by members of the General Atomic activation-analysis group in the

morning, and an inspection of the TRIGA reactor, radiochemical laboratories, and gamma-ray-spectrometry laboratories was made in the afternoon, with several demonstrations of actual analyses. The seminar was very well received by the criminalists attending.

An article describing portions of the present study appeared in the June 22, 1962, issue of Time Magazine (page 48). A paper by R. R. Ruch, V. P. Guinn, and R. H. Pinker entitled "Detection of Gunpowder Residues by Neutron Activation Analysis" has been accepted for presentation at the November 26-28, 1962, American Nuclear Society meeting in Washington, D. C. (at the special Symposium on Forensic Science Applications of Radioisotopes).

At the invitation of Mr. J. Edgar Hoover, a discussion on the subject of neutron-activation-analysis applications in criminalistics was held with the FBI in Washington, D. C., in April, with Mr. Heilman, Mr. Gallagher, Dr. White, and Dr. Guinn of General Atomic in attendance. Mr. Heilman also attended the General Atomic-sponsored April 30, 1962, Symposium on New Developments in Activation Analysis, in Newark, New Jersey, after which he participated in a discussion of the subject with Professor Robert E. Jervis of the University of Toronto (who spoke at the Symposium on Applications of Activation Analysis in the Field of Scientific Crime Detection), Mr. John C. Dempsey (AEC-DID), and Dr. Guinn. At a similar symposium in Baton Rouge, Louisiana, on May 4, 1962, Dr. Guinn spoke on the same subject. Captain Albert H. Pethick of the Connecticut Department of State Police has expressed an interest in the present study and has asked to be kept informed of progress. Mr. William H. Parker, Chief of the Los Angeles Police Department, visited General Atomic in May and inspected the work in progress on this study.

REFERENCES

1. "Neutron-Activation Analysis: New Tool Against Crime," Nucleonics, Vol. 19, No. 12, 1961, p. 74.
2. Jervis, R. E., "Neutron Radioactivation Helps Solve Crime," Can. Nuclear Technol., Vol. 4, 1962, p. 21.
3. Mackintosh, W. D., and R. E. Jervis, The Determination of Arsenic in Biological Materials, Atomic Energy of Canada Limited, Report CRDC-958, August, 1960.
4. Lenihan, J. M. A., and H. Smith, "Clinical Applications of Activation Analysis," Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Vol. 26, United Nations, Geneva, 1958, p. 238.
5. Leddicotte, G. W., private communication.

6. Buchanan, J. D., "Activation Analysis with a TRIGA Reactor," Proceedings of the 1961 International Conference on Modern Trends in Activation Analysis, Texas A & M College, p. 72.

7. Harrison, H. C., and R. Gilroy, "Firearm Discharge Residues," J. Forensic Sci., Vol. 4, No. 2, 1959, p. 184.