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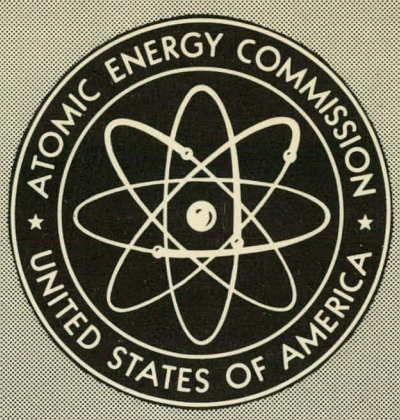

GA-6152

USE OF NEUTRON ACTIVATION ANALYSIS IN SCIENTIFIC CRIME DETECTION

Twelve Month Summary Report for the Period
November 1, 1963 — October 31, 1964

By
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V. P. Guinn

February 15, 1965

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for Pure and Applied Science
General Atomic Division
San Diego, California

UNITED STATES ATOMIC ENERGY COMMISSION • DIVISION OF TECHNICAL INFORMATION

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USE OF NEUTRON ACTIVATION ANALYSIS IN SCIENTIFIC CRIME DETECTION

12-MONTH SUMMARY REPORT FOR THE PERIOD NOVEMBER 1, 1963, THROUGH OCTOBER 31, 1964

Prepared under
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February 15, 1965

PREVIOUS REPORTS IN THIS SERIES

GA-3491—May, June, July, 1962

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GA-4297—February, March, April, 1963

GA-4576—May, June, July, 1963

GA-5556—May 1, 1962, through October 31, 1963

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I. INTRODUCTION

This is the second summary report on studies being carried out at General Atomic on the use of neutron activation analysis in the field of scientific crime detection (criminalistics), and covers the period from November 1, 1963, through October 31, 1964. The work done in the previous eighteen months (May 1, 1962, through October 31, 1963) is described in General Atomic Report GA-5556. This work is being carried out in close cooperation with Mr. Ray H. Pinker, Chief Criminalist of the Los Angeles Police Department.

There are several major objectives in this study. One is to develop a method to determine whether a person has recently fired a gun. This is a very important problem in the field of criminalistics, as no reliable method has been developed. The Gonzales test previously used involves the treating of a paraffin cast of the back of the hand with diphenylamine solution to detect nitrate traces from gunpowder. However, this test has been proven to be unreliable and is no longer accepted in most courts. Another major objective is to determine the feasibility of using neutron-activation analysis to characterize and identify various types of materials often found as physical evidence in criminal cases. Such materials have been analyzed and characterized by other analytical techniques (such as emission spectroscopy) for quite some time. Instrumental neutron-activation analysis, however, offers several advantages over other methods. First, for most elements it is more sensitive (if high neutron fluxes are used), thus allowing more elements to be detected in the samples and also enabling smaller samples to be analyzed. Second, an important advantage in criminalistics is that, in many cases, the samples can be satisfactorily analyzed by purely instrumental means, and thus the sample is not destroyed but is preserved for future presentation in court. Third, in some cases, the analyses are much more accurate. It is the purpose of this phase of the work to analyze various biological and nonbiological samples, such as paint, plastics, glass, hair, paper, etc., by purely instrumental means to determine if samples of the same type of material from different sources can be characterized by their elemental composition, including both major and minor constituents and, more important, trace element impurities.

During the first eighteen-month period, a method of detecting gunshot residues on the hands of persons firing a gun was developed to a considerable degree of accuracy. It involves the detection of traces of Ba and Sb coming from the primer portion of the cartridge. The residues are removed from

the hand by a paraffin cast, which is then activated and analyzed radiochemically. Test firings using several different types of pistols, as well as several different types of ammunition, were made. Single and multiple firings were carried out. In all cases, detectable gunshot residues were found on the hands of the persons doing the firing. Normal amounts of Ba and Sb on the hands of persons who had not recently fired a gun were also determined, and although found to be detectable were very small.

Various materials were analyzed by purely instrumental neutron-activation analysis. Such materials included automobile lubricating greases, plastics, rubber, paint, glass, soils, hair, fingernails, paper, ink, wood, and tobacco. In most cases, signficiant differences in the elemental composition of samples of the same type of material but from different sources were noted, and therefore samples were easily characterized. Several samples of evidence from actual cases were also analyzed.

During the one-year period ending October 31, 1964, studies of the deposition of gunshot residues on the hands and face of a person firing a rifle were initiated. In particular, a rifle of exactly the same type as the one used to assassinate President Kennedy was studied. The results showed that Ba and Sb traces are deposited on the hands and face when this rifle is fired. Paraffin casts from the hands of a number of gunshot suicide victims were analyzed for Ba and Sb. Very interesting results were obtained from these analyses. Work was also started on the feasibility of tagging gunpowder with trace amounts of elements especially suitable for detection by neutron-activation analysis. Test firings of cartridges tagged with Dy and Eu gave results which were quite promising.

A method of showing the comparison of samples in a manner which is easily visualized by nonscientists, such as members of a jury, has been developed. It allows the presentation of analytical results in court in a nonmathematical, but still scientifically sound, manner. The method involves the comparison of gamma-ray spectra of activated samples by plotting the normalized spectra of two or more samples on the same graph paper.

A number of samples of hair were analyzed, most of them being involved in actual criminal cases. However, in most cases, the results were inconclusive. The problems involved in the analysis of hair by neutron activation were evident in these studies.

Neutron-activation analysis as an analytical technique was successfully introduced into court for the first time in California. The case involved the analysis of blue and brown paints found on a tool allegedly used in an attempted burglary. The brown paint was matched with the paint on the door of the burglarized store, and the blue paint was matched with the paint from the suspect's automobile.

Several samples of paper were analyzed by purely instrumental means. The results show that different papers are quite different in composition and therefore easily characterized. The results also indicate that samples of the same paper from different batches are also distinguishable by means of neutron-activation analysis.

II. EQUIPMENT AND PERSONNEL

The irradiations of the samples were carried out primarily in the TRIGA Mark I reactor operated at 250 kw. Two irradiation positions were used. To determine short-lived activities, the pneumatic-tube transfer (rabbit) system was used. The thermal-neutron flux in the pneumatic-tube position is 4.3×10^{12} n/cm^2-sec. For longer irradiations, the rotary specimen rack, or "lazy susan," was used. Here, the thermal-neutron flux is 1.8×10^{12} n/cm^2-sec. In one case, the irradiation of the sample was done using a Cockcroft-Walton type neutron generator providing a fast (14 Mev) neutron flux of 10^8 n/cm^2-sec.

All counting of the samples was done with suitably shielded 3 in. by 3 in. NaI(Tl) scintillation crystals coupled to multichannel pulse-height analyzers. Both solid and well-type detectors were used, each shielded with 4 in. of lead.

The personnel actively engaged in this study during this period were primarily V. P. Guinn, D. E. Bryan, and Mrs. Dorothy M. Settle.

III. EXPERIMENTAL RESULTS

GUNSHOT-RESIDUE DETECTION

Various additional studies have been made on the detection of gunshot residues on the hands of persons who have recently fired a gun. The method used has been described previously (GA-5556) and involves the detection of Ba and Sb, which are found in the primers of most American and European firearm ammunition. When the gun is fired, residues from the gunpowder and primer fall on the hand. These residues (including Ba and Sb traces) are then removed by applying molten paraffin to the hand and allowing it to solidify to form a cast. This cast is removed, rolled up while still pliable, placed in a polyethylene vial, and irradiated in the TRIGA Mark I nuclear reactor. The Ba and Sb are detected by means of the 84-min Ba^{139} and 2.8-day Sb^{122} activities induced. These isotopes are separated radiochemically, using nonradioactive Ba and Sb as carriers, and are then counted by gamma-ray spectrometry using a well-type NaI(Tl) scintillation detector coupled to a multichannel pulse-height analyzer. Barium-139 has a gamma ray at 0.163 Mev, and Sb^{122} has a gamma ray at 0.56 Mev. The results are made quantitative through the use of comparator standards processed in an identical manner to the samples.

The normal hand blanks of Ba and Sb obtained earlier are given in Table 1.

Reproducibility of Deposition and Removal of Gunshot Residues

A series of experiments was performed to evaluate the reproducibility of the deposition of primer residues on the hand of a person firing a gun, and the removal of these residues by the paraffin technique. A .45-caliber automatic was used exclusively in these tests. Three sets of paraffin casts were taken. The first set was obtained in the following manner. A police officer thoroughly washed his hands and then fired the gun once. A cast was made of the thumb, thumb-web, and forefinger areas of his hand (one cast covering all points). He then washed his hands, the gun was wiped clean with a cleaning tissue, and another single firing was made. This procedure was repeated until six casts were made. The other two sets of six casts each were obtained in the same manner as the first, with the exception that the gun was not wiped clean after each firing. The casts were irradiated for 1 hr in a thermal-neutron flux

Table 1

NEUTRON ACTIVATION ANALYSIS OF RESIDUES FROM LEFT AND RIGHT HANDS OF INDIVIDUALS WHO HAD NOT RECENTLY FIRED A GUN

No.	Hand	μg Detected		Relative Amounts		No.	Hand	μg Detected		Relative Amounts	
		Ba	Sb	Ba	Sb			Ba	Sb	Ba	Sb
1	R	0.14	0.06	1.0	1.0	12	R	0.15	<0.01	2.1	1.0
	L	0.22	0.06	1.6	1.0		L	0.07	<0.01	1.0	1.0
2	R	0.32	0.03	1.7	3.0	13	R	0.04	0.02	4.0	>2.0
	L	0.19	0.01	1.0	1.0		L	0.01	<0.01	1.0	1.0
3	R	0.03	<0.01	1.0	1.0	14	R	0.22	<0.01	2.8	<1.0
	L	0.04	<0.01	1.3	1.0		L	0.08	0.01	1.0	1.0
4	R	0.18	0.02	1.5	1.0	15	R	0.03	<0.01	1.0	1.0
	L	0.12	0.02	1.0	1.0		L	0.04	<0.01	1.3	1.0
5	R	0.48	0.01	1.1	1.0	16	R	0.09	<0.01	1.1	<0.3
	L	0.44	0.01	1.0	1.0		L	0.08	0.03	1.0	1.0
6	R	0.18	<0.01	1.0	1.0	17	R	0.26	----	2.9	---
	L	0.32	<0.01	1.8	1.0		L	0.09	----	1.0	---
7	R	0.07	<0.01	3.5	1.0	18	R	0.11	<0.01	1.8	1.0
	L	0.02	<0.01	1.0	1.0		L	0.06	<0.01	1.0	1.0
8	R	0.07	<0.01	3.5	1.0	19	R	0.10	<0.01	1.2	1.0
	L	0.02	<0.01	1.0	1.0		L	0.08	<0.01	1.0	1.0
9	R	0.03	<0.01	1.0	1.0	20	R	0.26	0.02	2.0	2.0
	L	0.03	<0.01	1.0	1.0		L	0.13	0.01	1.0	1.0
10	R	0.17	0.03	2.8	>3.0	21	R	0.15	<0.01	1.0	1.0
	L	0.06	<0.01	1.0	1.0		L	0.25	0.01	1.7	>1.0
11	R	0.09	<0.01	1.3	1.0	22	R	0.09	<0.01	1.0	1.0
	L	0.07	<0.01	1.0	1.0		L	0.09	0.02	1.0	>2.0

Maximum Ba 0.48 μg
Average Ba 0.13 μg
Minimum Ba 0.01 μg

Maximum Sb 0.06 μg
Average Sb 0.015 μg
Minimum Sb <0.01 μg

of 1.8×10^{12} n/cm^2-sec. The induced Ba^{139} and Sb^{122} activities were then separated radiochemically and counted. The results are shown in Tables 2 and 3.

In the case where the gun was wiped clean before each firing, moderately reproducible results were obtained. The standard deviations of the Ba and Sb values were ±43% and ±45%, respectively. Only one cast, the last in this series, showed unusually high values.

When the gun was not wiped clean after each firing, the results were quite scattered and covered a wide range, except for the Sb values in the second set. The standard deviations in the Ba and Sb values for the first set of casts (gun not wiped) were ±74% and ±75%, respectively. For the second set of casts, the standard deviations of Ba and Sb were ±77% and ±30%, respectively. In every case, the Ba and Sb values seem to parallel each other, either being both high or both low in each individual firing. In virtually all cases, the Ba and Sb values were well above the levels found on the hands of persons who had not recently fired a gun (see Table 1).

This particular type of experiment, where several paraffin casts are made of the same hand, is complicated in that each successive cast becomes harder to remove than the previous one. This may be due to the removal of natural skin oils from the hand, and may have had some effect on the results that were obtained.

Rifle Studies

A study of the deposition of Ba and Sb on the hands and faces of persons who had recently fired a rifle was made. Previously, only revolvers and automatic pistols had been investigated in this study. The weapon used in these tests was a used 6.5 mm Mannlicher-Carcano rifle, of exactly the same type as the one used in the assassination of President Kennedy. The test firing and hand samplings were performed in a manner such that the conditions of the assassination were duplicated as nearly as possible. All of the persons who fired the rifle were right-handed, and the firings were performed in a room that had a door open to the outside; only a slight breeze was blowing at the time. The exact wind conditions at the time of the assassination were not known to us. The rifle had to be fired horizontally instead of at a slightly downward angle as in the assassination. The hands and cheeks of the persons doing the firings were not sampled until three to four hours after they had fired the rifle. During this time, they went about their normal activities, but they did not wash their hands or face. This was to duplicate, approximately, the time between the assassination and the obtaining by the Dallas police of paraffin casts from the hands and right cheek of Lee Harvey Oswald, the suspected assassin.

Table 2

REPRODUCIBILITY OF DEPOSITION AND REMOVAL OF RESIDUES ON HAND WHEN WEAPON[a] WIPED CLEAN BEFORE FIRING
(In μg)

	Ba	Sb
	0.506	0.181
	0.789	0.146
	0.614	0.248
	0.504	0.140
	0.769	0.226
	1.390	0.414
Avg.	0.762 ±0.331	0.226 ±0.101

[a] A .45 caliber automatic.

Table 3

REPRODUCIBILITY OF DEPOSITION AND REMOVAL OF RESIDUES ON HAND WHEN WEAPON[a] NOT WIPED CLEAN BEFORE FIRING
(In μg)

	First Run		Second Run	
	Ba	Sb	Ba	Sb
	0.216	0.068	2.70	0.268
	1.810	0.627	0.769	0.237
	0.795	0.258	11.4	0.506
	0.460	0.098	3.20	0.297
	2.480	0.775	7.16	0.452
	2.400	0.553	4.29	0.353
Avg.	1.360 ±1.000	0.396 ±0.295	4.92 ±3.80	0.352 ±0.105

[a] A .45-caliber automatic.

Two sets of casts were obtained. One set was first treated with diphenylamine solution, which is the old chemical test for gunpowder residues, and was the method used by the Dallas police on the Oswald casts. After chemical testing, the reagents were washed off the casts with distilled water. The other set of casts was not treated with diphenylamine. In each series, casts were made after one shot had been fired, and after three shots had been fired in rapid succession.

When obtaining casts to be used for the diphenylamine test, gauze is added to the cast to give it strength. Before analyzing these casts, a sample of the gauze used was irradiated in the reactor for 30 min at a thermal-neutron flux of 1.8×10^{12} n/cm^2-sec, and treated in the same manner as irradiated casts. Although the gauze did not dissolve during the post-irradiation radiochemical separation, appreciable amounts of Ba and Sb were detected. Levels corresponding to 0.46 ppm Ba and 0.044 ppm Sb in the gauze were obtained. Thus, since the weight of the gauze in each cast could not be determined, a blank correction could not be made and it was necessary to separate the paraffin from the gauze before irradiation. A clean spatula was used to cut the gauze from the paraffin which had contacted the skin.

The casts were irradiated for 2 hr in a thermal-neutron flux of 1.8×10^{12} n/cm^2-sec, and the Ba^{139} and Sb^{122} activities were separated radiochemically and counted. The results are shown in Tables 4 and 5.

The results of the analyses of the casts on which the diphenylamine test was not performed seem to indicate that detectable gunshot residues are deposited on both hands and both cheeks of persons firing this rifle. The levels of Ba and Sb found are all above the average on normal hands (see Table 1). The amounts of these elements present after three shots were fired were generally appreciably greater than those detected after only one firing. After three firings, the amounts of Ba and Sb found were above even the maximum values (0.48 μg Ba and 0.06 μg Sb) found on normal hands, the Ba value on the left cheek being the only exception. After one firing, only the Ba on the right hand and the Sb on the left cheek were above these maxima.

The Ba and Sb values obtained from the casts on which the diphenylamine test was performed are quite scattered. The Ba values are low, the only apparent exception being for the right hand of the person who fired three shots. This cast is the only one that gave a positive diphenylamine test (a test for nitrates). However, the levels of Sb on the casts were still well above normal levels, even after the casts were treated by the chemical test. It appears, therefore, that performing the diphenylamine test on the paraffin casts removes the Ba fairly completely but does not remove significant amounts of Sb.

Table 4

RESULTS OF RIFLE FIRINGS WHERE DIPHENYLAMINE TEST WAS NOT PERFORMED
(Element Values in μg Net)

Sample	Ba	Sb
Dan Miller (three firings)		
Left hand	0.511	0.083
Right hand	0.529	0.157
Left cheek	0.399	0.079
Right cheek	0.492	0.095
Ed Miller (one firing)		
Left hand	0.215	0.022
Right hand	0.596	0.028
Left cheek	0.300	0.104
Right cheek	0.144	0.037

NOTE: Subjects fired at 12:30 pm. Dan Miller casts were made at 3:30 pm. Ed Miller casts were made at 4:00 pm.

Table 5

RESULTS OF RIFLE FIRING WHERE DIPHENYLAMINE TEST WAS PERFORMED
(Element Values in μg Net)

Sample	Ba	Sb
Bingle (one firing)		
Left hand	0.144	0.088
Right hand	0.094	0.064
Left cheek	0.186	0.019
Right cheek	0.084	0.020
Howe (three firings)		
Left hand	0.075	0.095
Right hand[a]	0.341	0.051
Left cheek	0.148	0.066
Right cheek	0.091	0.028

NOTE: Subjects fired at 2:00 pm. Bingle casts taken at 4:30 pm. Howe casts taken at 4:45 pm.

[a]Only positive diphenylamine test.

As a result of these studies, the paraffin casts of the hands and right cheek of Lee Harvey Oswald were analyzed by neutron-activation analysis for Ba and Sb by the Federal Bureau of Investigation at Oak Ridge National Laboratory. The casts had been previously treated with diphenylamine by the Dallas police. As reported by the Warren Commission, the results were inconclusive--not because of failure of the activation analysis technique (which worked well), but rather because of earlier contamination of the casts, presumably by excessive handling.

The important casts in rifle studies are those of the cheeks. Large amounts of Ba and Sb on the cheeks would indicate that a rifle had been fired, as these elements would not be expected to be deposited on the cheeks when a revolver or pistol was fired, unless the revolver or pistol was held very close to the face, which is unlikely. The Kennedy assassination is an example of a case where unaltered casts of the cheeks (i.e., not chemically treated and not mishandled) would have been extremely important. It was alleged that the suspect, after firing the rifle, also fired a revolver (there were witnesses to the revolver firing by Oswald, which resulted in the death of Officer Tippett). Casts of the hands alone would indicate that a gun had been fired, but it could not be determined whether it was a rifle or a hand weapon. High levels of Ba and Sb on the cheeks would indicate that a rifle had been fired, regardless of whether a hand weapon had also been fired. The normal levels of Ba and Sb on the cheeks have not been determined, but there is no reason to suspect they should be higher than the normal levels on the hands.

Suicides

Paraffin casts from the left and right hands of a number of victims of gunshot suicides were analyzed for Ba and Sb. These casts were obtained through the cooperation of the Coroner's Offices of Los Angeles, San Diego, Orange, and San Mateo Counties (all in California). The purpose of this study was to evaluate this method of gunshot-residue detection in actual known cases which were uncontrolled, as opposed to controlled test firings in the laboratory, and to provide a basis for the interpretation of the results from unknown shooting cases (possible suicides or possible murders).

A total of seventeen cases were studied. Of these, two were not suicide victims, but were victims murdered by one of the suicides, and the remaining fifteen were known suicides. The results of the analyses are shown in Table 6.

By comparison of these results with the normal hand blanks (see Table 1), it is found that only one (No. 1) of the known suicides had both Ba and Sb above the normal maximum on one hand (the left hand) and below the normal maximum on the other hand. The values for both Ba and Sb

Table 6

NEUTRON ACTIVATION ANALYSIS OF PARAFFIN CASTS FROM HANDS OF KNOWN SUICIDE VICTIMS

No.	Description	Hand	μg Detected		Relative Amounts	
			Ba	Sb	Ba	Sb
1	.45 caliber Colt automatic	R	0.272	0.045	1.0	1.0
		L	0.921	0.350	3.4	7.8
2	.38 caliber Smith & Wesson revolver, one shot	R	0.071	0.025	1.0	1.0
		L	0.248	0.638	3.5	25.5
3	38 caliber Hy Hunter Derringer, one shot, left hand[a]	R	0.350	0.188	1.0	1.0
		L	1.32	1.33	3.8	7.1
4	.38 caliber Special, four shots, double homicide and suicide	R	11.65	2.21	4.5	5.9
		L	2.57	0.374	1.0	1.0
5	.38 caliber Colt Special snub nose	R	0.521	0.703	1.0	1.0
		L	4.71	8.83	9.0	12.5
6	.25 caliber automatic	R	1.09	0.060	1.0	1.0
		L	2.35	0.350	2.2	5.8
7	.38 caliber U.S. revolver, three shots, right handed[a]	R	0.937	0.654	1.7	5.5
		L	0.549	0.119	1.0	1.0
8	.38 caliber Special, one shot, right handed	R	1.29	0.767	1.0	1.0
		L	2.08	0.980	1.6	1.3
9	.22 caliber long rifle, one shot	R	0.410	0.023	1.0	1.0
		L	0.730	0.023	1.8	1.0
10	Shotgun	R	0.479	0.081	1.3	1.3
		L	0.356	0.061	1.0	1.0
11	.32 caliber Colt automatic, four shots	R	0.254	0.121	1.0	1.0
		L	0.362	0.135	1.4	1.1
12	Weapon unknown	R	0.355	0.053	1.3	0.78
		L	0.282	0.068	1.0	1.0
13	.38 caliber Ivar Johnson revolver, three shots	R	0.594	0.553	1.0	1.0
		L	0.809	0.517	1.4	0.93
14	7.65-mm Mauser rifle, one shot, right handed	R	0.009	≤0.01	1.0	---
		L	0.011	≤0.01	1.2	---
15	.357 caliber Smith & Wesson revolver	R	---	0.327	---	6.5
		L	---	0.050	---	1.0
16	Murder victim, shot once by No. 4	R	0.576	0.023	1.6	0.55
		L	0.363	0.042	1.0	1.0
17	Murder victim, shot once by No. 4	R	0.420	0.093	1.0	1.0
		L	0.512	0.042	1.2	0.45

[a] "Left (right) hand" indicates that it has been established that the gun was fired with the victim's left (right) hand; "left (right) handed" indicates that it has been established only that the victim was left (right) handed.

were above the normal average, however, on the right hand. The gun used in this case was a .45-caliber Colt automatic. One other case (No. 2) showed levels of Ba above the normal average but below the normal maximum on the left hand and below the normal average on the right hand. The left hand also showed an Sb level above the normal maximum, whereas the Sb level on the right hand was below the normal maximum (although above the normal average). This case involved one shot with a .38-caliber Smith & Wesson revolver. A third case (No. 3) gave a Ba level above the normal maximum on the left hand and below the normal maximum on the right hand. However, the amounts of Sb found on both hands were above the normal maximum. In this case, one shot was fired from a .38-caliber Hy Hunter Derringer with the left hand.

Four more cases (Nos. 4 through 7) gave values of Ba and Sb that were well above the normal hand maxima on both hands. Three cases involved .38-caliber revolvers and the fourth (No. 6) involved a .25-caliber automatic. In all seven of the above cases, the amounts of Ba and Sb found on one hand were much greater than those found on the other hand. These cases seem to show fairly definitely that a gun had been fired with one hand.

The interpretation of the results of case No. 8 is difficult. The gun was a .38-caliber revolver. The values of Ba and Sb found on both hands were far above the normal hand maxima. However, the differences in these values from one hand to the other were not very great. Also, this person was known to be right-handed and yet the larger amounts of both elements were found on the left hand. Such results could be obtained if both hands were used to hold the gun when it was fired. However, it is not known whether this was true in this particular case.

Two more cases involving pistols (Nos. 11 and 13) were studied. In No. 11, four shots were fired with a .32-caliber Colt automatic. The Ba values were above the normal average but below the normal maximum on both hands; the Sb values were both well above the normal hand maximum. However, the values for both of these elements did not differ greatly from one hand to the other. This also indicates that perhaps both hands were used to hold the gun. In No. 13, three shots were fired with a .38-caliber revolver. The Ba and Sb values on both hands were well above the normal hand maxima. As in No. 11, the values for these elements did not differ greatly from one hand to the other. Also, the hand which had the higher Ba content had the lower Sb content. This apparent inconsistency leads one to suspect that in this case the source of the Ba and Sb on the hands may not have been the gunshot residues, especially if only one hand was used.

The weapon used in case No. 12 is not known. All of the values obtained are above the normal hand averages, but only the Sb value on

the left hand is above the normal maximum. Here also, the hand having the larger Ba content had the lower Sb value.

Three suicides involving rifles were also studied (Case Nos. 9, 10, and 14). In the case where one shot was fired from a .22-caliber long rifle, the amount of Ba found on the left hand was above the normal hand maximum. The amount of Ba on the right hand was below this maximum. However, the amounts of Sb found on both hands were equal and well within the range of Sb found on normal hands. Case No. 10, involving a shotgun, showed levels of Ba and Sb on the right hand to be slightly higher than on the left hand. However, the amounts of Ba found on both hands are below the normal maximum, whereas both Sb values are above the normal maximum. Case No. 14 involved one shot with a 7.65 mm Mauser rifle. The amounts of Ba found on both hands are very low, and Sb was not detected on either hand. Suicide cases involving rifles are difficult to interpret, and the results obtained may not be as meaningful as those from suicides involving revolvers or pistols. When shooting oneself with a rifle, the rifle is, of course, not held in the normal firing position. Also, something other than the hand (such as a small stick or a string) may be used to push or pull the trigger.

Only partial results were obtained on the other known suicide (No. 15). Here, the body was partially decomposed when it was found and casts of the hands were taken. This resulted in an unusually high amount of Na and K contamination, which was not completely removed during the postirradiation radiochemical separation. The interferences from the Na^{24} and K^{42} therefore prevented the determination of Ba. The Sb, however, could be determined, and it was found that there was about six times as much on the right hand as on the left. The right hand value was well above the normal maximum, while the left hand value was below this maximum.

The casts from the hands of the two murder victims (Nos. 16 and 17), who had apparently not fired a gun, gave some interesting results. In both cases, the Ba and Sb values on both hands were above the normal hand averages, and three values were even above the normal hand maxima. However, in both cases the hand having the higher amount of Ba had the lower amount of Sb.

The results of these analyses seem to indicate that possibly three criteria are necessary to interpret the results obtained in unknown shooting cases, especially those involving pistols. First, the absolute amounts of Ba and Sb must be considered. It appears that values for at least one of the elements must be above the normal hand maximum and for the other must be above average (as in Case No. 2). It appears that having both Ba and Sb above the normal average is not sufficient, since blank No. 2 in Table 1 showed both Ba and Sb to be twice the normal averages on the right hand

although this person had not fired a gun recently. Second, it appears to be important to consider whether one of the hands has larger amounts of both Ba and Sb. This is shown in the cases of the two murder victims. Here, some of the values are above the normal hand maxima, but the larger amounts of both Ba and Sb were not found on the same hand. These two cases also indicate that more normal hand blanks may have to be determined and new averages and maxima for Ba and Sb on normal hands evaluated. Third, it may be necessary to consider the ratio of the amounts of Ba and Sb found on one hand to the amounts found on the other hand.

Four sets of casts from questionable suicide cases were also analyzed for Ba and Sb. The results are given in Table 7. One case (A) involved one or possibly two shots from a .22-caliber revolver. Although ten times as much Ba was found on the left hand as on the right hand, it was still below the normal hand average. The victim in this case was known to be right-handed. No Sb was detected on either hand. Previous test firings with a .22-caliber revolver indicate that small, but measurable, amounts of primer residues are deposited on the hand when such a gun is fired (see GA-4576, Table 2). Therefore, owing to the low values obtained in this case, it appears that this person had not recently fired a gun when the casts were taken. It was learned later, however, that the victim's hands may have been washed at the morgue prior to the taking of the paraffin casts.

Table 7

NEUTRON ACTIVATION ANALYSIS OF PARAFFIN CASTS FROM QUESTIONABLE GUNSHOT SUICIDE CASES

Case	Description	Hand	μg Detected		Relative Amounts	
			Ba	Sb	Ba	Sb
A	.22 caliber revolver--one, possibly two shots, right handed[a]	R	0.012	≤0.002	1.0	1.0
		L	0.123	≤0.002	10.2	1.0
B	.22 caliber Hi Standard automatic, right handed	R	0.124	≤0.004	2.2	≤0.36
		L	0.056	0.011	1.0	1.0
C	No details known	R	0.99	0.094	18.0	2.8
		L	0.055	0.034	1.0	1.0
D	.25 caliber Browning automatic, right hand of victim, left hand of suspect	V-R	0.88	0.699	----	---
		S-L	0.232	0.006	----	---

[a] "Left (right) hand" indicates that it has been established that the gun was fired with the victim's left (right) hand; "left (right) handed" indicates that it has been established only that the victim was left (right) handed.

Case B also gave results which failed to indicate that the victim had recently fired a gun. The values obtained for both Ba and Sb on both hands were below the normal hand averages. Also, Sb was not detected on the hand which had the higher Ba value (Sb was detected on the other hand). Therefore, it was possible to conclude that if this person had recently fired a gun, it certainly was not indicated by these analyses.

The results of case C appear to be quite positive. The values for both Ba and Sb found on the right hand were well above the normal hand maxima. The amounts of these elements found on the left hand were below these maxima, and the Ba value was even below the normal average. The type of gun used in this case is not known to us. It is possible, however, to conclude that the victim probably had fired a gun with his right hand.

A .25-caliber Browning automatic pistol was used in case D. The casts which were analyzed were from the right hand of the victim and the left hand of the suspect. Since casts were taken from only one hand of each person, the results could only be interpreted by comparison with normal hand blanks. Both Ba and Sb found on the right hand of the victim were well above the normal hand maxima. The amounts of these elements found on the suspect's left hand were well within the ranges found normally on hands. Therefore, it was concluded that the victim probably had fired a gun and that the suspect had not recently fired a gun, at least not with his left hand.

Results of an Actual Case

Two sets of paraffin casts from a shooting case (other than those previously cited) were analyzed for Ba and Sb. Casts were made of both hands of a woman (the suspect in this case) and her husband (the victim) in an attempt to determine whether murder was involved or whether the gun, a .32-caliber revolver, could have been accidentally discharged during a struggle, as the suspect contended. The results of the analyses are shown in Table 8. Although there was considerably more Ba on the woman's hands than on the man's, the values were well within the ranges of Ba and Sb found on the hands of persons who have not recently fired a gun. The amounts of these elements found on one hand were not greatly different from the amounts found on the other hand. Also, the hand having the larger amount of Ba had the smaller amount of Sb in both cases. Therefore, if either the suspect or the victim had recently fired a gun, it is not indicated by these tests, and it is impossible to conclude whether this was a murder or an accidental shooting. A time element (with opportunity for loss by rubbing) may be one reason that no significant amounts of Ba and Sb were detected. The victim was in surgery for about 3 hr before the casts were made of his hands. There was also a delay of 3 to 4 hr from the time of the shooting to the time the casts were

made of the suspect's hands. During this time interval, significant amounts of Ba and Sb could have been rubbed off both the victim's and the suspect's hands.

Table 8

NEUTRON ACTIVATION OF HAND RESIDUES FROM AN ACTUAL SHOOTING CASE
(Element Values in μg Net)

Sample	Ba	Sb
Man		
Right hand	0.056	0.014
Left hand	0.076	0.007
Woman		
Right hand	0.193	0.015
Left hand	0.115	0.016

Coding of Cartridge Gunpowder with Stable-element Tracers

Consideration has been given to the possibility of tagging gunpowder with traces of certain stipulated elements that are readily detectable by neutron-activation analysis. This concept has considerable merit because it would remove the dependence of the current method on the detection of two only moderately uncommon elements that are present in the primers of cartridges made in the United States. Also, Ba and Sb cannot be as sensitively detected as a number of other elements.

Calculations were made to select a series of elements possibly more suitable than Ba and Sb that could be introduced at trace levels in the gunpowder (rather than the primer) portion of the cartridges. Optimum elements should be uncommon, relatively nonvolatile elements that are very sensitively detected by neutron-activation analysis and produce gamma-emitting radioisotopes of moderate half lives. Ten elements appear to be particularly promising: Dy (Class I); Ho, In, and Lu (Class II); and Eu, Rh, Er, Ir, Re, and V (Class III). The Class I element (Dy) is most sensitively detected, being detectable down to levels of about 5×10^{-6} μg in even a 1-hr activation at a thermal-neutron flux of 1.8×10^{12} n/cm^2-sec. It forms 2.3-hr Dy^{165}. The Class II elements (Ho, In, and Lu) are somewhat less sensitively detected but are still detectable down to levels of about 5×10^{-5} to 1×10^{-4} μg. They form, respectively, 27-hr Ho^{166}, 54-min In^{116m}, and 3.7-hr Lu^{176}. The Class III elements (Eu, Rh, Er, Ir, Re, and V) are detectable down to levels of about 5×10^{-4} to 1×10^{-3} μg and form,

respectively, 9.3-hr Eu^{152m}, 4.4-min Rh^{104m}, 7.5-hr Er^{171}, 19-hr Ir^{194}, 17-hr Re^{188}, and 3.8-min V^{52}. The rather short half lives of Rh^{104m} and V^{52} would perhaps eliminate them from the list of most suitable elements. Five of the ten elements (Dy, In, Eu, Ir, and Re) are appreciably more sensitive to detection, after activation, by beta counting than by gamma-ray spectrometry. Since they would be radiochemically separated prior to counting, extra sensitivity could probably be achieved in practice by beta counting these elements after activation.

A number of other elements (As, Au, Cu, Mn) are detectable down to suitable levels ($\leq 10^{-3}$ μg) but have been ruled out for this purpose because they are too common. Several other elements (La, Pd, Pr, Sm, W, Yb) have been omitted because they are detectable to suitable levels ($\leq 10^{-3}$ μg) only by beta counting. Another possible choice, Tc^{99}, was considered because it does not occur naturally, but was ruled out because its (n, γ) activation product, Tc^{100}, has a half life of only 16 sec.

For comparison with the above-mentioned sensitivities, the sensitivities for Ba and Sb after a 1-hr irradiation at 1.8×10^{12} n/cm^2-sec are 3×10^{-3} μg and 2×10^{-3} μg, respectively.

In the initial experimental investigation of this problem, two elements, Dy and Eu, were chosen as the tags. In this type of study, it was found desirable first to conduct some exploratory experiments, tagging the cartridges with a known amount of the particular rare-earth element to be surveyed. This would make it possible to determine the optimum amount of tagging element to be added to the cartridges, as well as to determine the fraction of the total powder charge that falls and is retained on the hand.

It was decided to prepare five different sets of cartridges containing the following tags: 1, 10, and 100 μg of Dy and 10 and 100 μg of Eu. It was then a question of deciding how best to add a known amount of the tag to the cartridge. The amount of the element to be added is so small that a homogeneous mixture would probably not be obtained by mixing a solid compound of the element with the gunpowder. Also, in order to accurately weigh the tagging element, a much larger quantity of gunpowder than would be used in these tests would be required. The possibility of using a solution of the element was also considered. A known amount of solution could be evaporated on a weighed amount of gunpowder. However, this was not done because it was feared that the solvent (water or an organic solvent) might change the ballistic properties of the gunpowder such that either of two possible extreme situations could occur: the powder might not ignite, resulting in a misfire, or the powder might explode violently rather than burn; this could blow the gun apart and cause serious injury to the person doing the firing. It should be pointed out that this is only a problem when tagging powder that has

already been manufactured and is not a problem if the tag is added during the manufacturing process.

For the initial tests, therefore, it was decided to tag the cartridge case rather than the gunpowder itself. A measured volume of a solution of known concentration of the element was evaporated on the inside of a primed .38-caliber cartridge case. The gunpowder and bullet were then added at the Los Angeles Police Department's cartridge reloading facility. Fifteen cartridges in all were prepared, the five different tags being contained in three cartridges each.

Each of the cartridges was fired by a different person. All of the cartridges containing Dy were fired in the same gun, in the order of increasing amount of Dy. A different gun was used for the Eu-tagged cartridges. The cartridges containing 10 μg Eu were fired before those containing 100 μg. Everyone fired with his right hand, and the casts were taken immediately after firing. When making the casts, care was taken to prevent contamination. A separate supply of paraffin in its own container, as well as a new brush, was used for each cast. Plastic gloves were worn at all times by the persons preparing the casts. Blank samples of paraffin were taken before and after the cast was applied.

The casts were irradiated in the TRIGA Mark I reactor for 1 hr at a thermal-neutron flux of 1.8×10^{12} n/cm^2-sec. After irradiation, the induced Dy^{165} and Eu^{152m} activities were separated radiochemically. The procedure used was as follows:

A known amount (about 10 mg) of the rare-earth carrier, about 20 mg of Ba carrier, and 25 ml of H_2O were placed in a 250-ml beaker. The irradiated cast was then added to the beaker, and the mixture was boiled for about 5 min. It was also stirred to ensure isotopic exchange with the carriers. The mixture was then swirled in an ice bath to solidify the paraffin phase, and the aqueous phase was transferred to a centrifuge tube. Concentrated H_2SO_4 was added to precipitate $BaSO_4$, which was centrifuged off and discarded. Concentrated NH_4OH was added to the supernate to precipitate the rare-earth hydroxide. After washing the precipitate with dilute NH_4OH, it was dissolved in 1 ml of 6N HCl and diluted to about 20 ml. Concentrated HF was then added to precipitate the rare-earth fluoride. This precipitate was washed with dilute HF and dissolved in 1 ml of saturated H_3BO_3 and 1 ml HNO_3. The solution was diluted to about 20 ml and then precipitation of the hydroxide and fluoride was repeated. The final fluoride precipitate was dissolved, and the solution was heated in a water bath until warm. Then 2 ml of saturated oxalic acid was added to precipitate the rare-earth oxalate. Heating was continued to assimilate the precipitate. Finally, the precipitate was filtered onto a preweighed filter paper and washed with H_2O, ethanol, and

ether. It was then dried in a desiccator, weighed, and mounted for counting in a well-type NaI(Tl) scintillation detector coupled to a multichannel gamma-ray spectrometer. Dysprosium was detected by the 0.094-Mev gamma ray of Dy^{165} and Eu by the 0.97-Mev gamma rays of Eu^{152m}. Figures 1 and 2 show spectra of Dy^{165} and Eu^{152m}, respectively.

The results of the analysis of the casts are shown in Table 9. In each case, the rare-earth element used to tag the cartridge was readily found on the hand of the person who fired the cartridge. On the average, the cartridges containing ten times more tagging element deposited about ten times more element on the hand. An increase in the amount of rare earth on the hand was also noted in each series of three cartridges, even though the amount of tagging element in each cartridge was the same. Also, Dy was detected on the hands of the persons firing the Eu-tagged cartridges, but the amount of Dy detected decreased with each firing. The reason for this has not been explained. Since different guns were used to fire the Dy- and Eu-tagged cartridges, this cannot be explained by residues remaining on the gun being blown off with the subsequent firings. Dysprosium settling from the air after the Dy firings and during the Eu firings may have been the cause of this anomaly.

Five of the paraffin blanks were also analyzed for Dy and Eu in the same manner as the casts. Each of the blanks was taken after the cast had been made. One blank was obtained for each of the five differently tagged cartridges (1, 10, 100 μg Dy; 10, 100 μg Eu). The results are shown in Table 10. Dysprosium was found in the paraffin used to make the cast after one of the cartridges tagged with 10 μg Eu was fired. The actual cast also contained an unusually high amount of Dy. All of the other blanks showed neither Dy nor Eu to be present. In general, these results indicate that the contamination of the paraffin by residues on the hand when making paraffin casts does not appear to be a problem.

Discussions have been held between Ray Pinker and representatives of the National Rifle Association and of the gunpowder manufacturing industry on the feasibility of tagging gunpowder during manufacture. Gunpowder manufacturers are very cooperative in aiding law enforcement, and they have said that there would be no technical problem involved in the tagging of the gunpowder with a particular rare-earth (or other) element. Also, the additional cost involved would be so small that it would not present a problem. It was also learned, however, that the manufacturers of the actual ammunition generally do not make their own gunpowder, but purchase it from powder manufacturers. A single powder manufacturer may supply the same type of gunpowder to several ammunition manufacturers. Therefore, to tag different makes of ammunition with different elements or combinations of elements would not be readily feasible from the standpoint of increased costs to the powder manufacturers, because they would have to make several different gunpowders (with different tags) rather than just one.

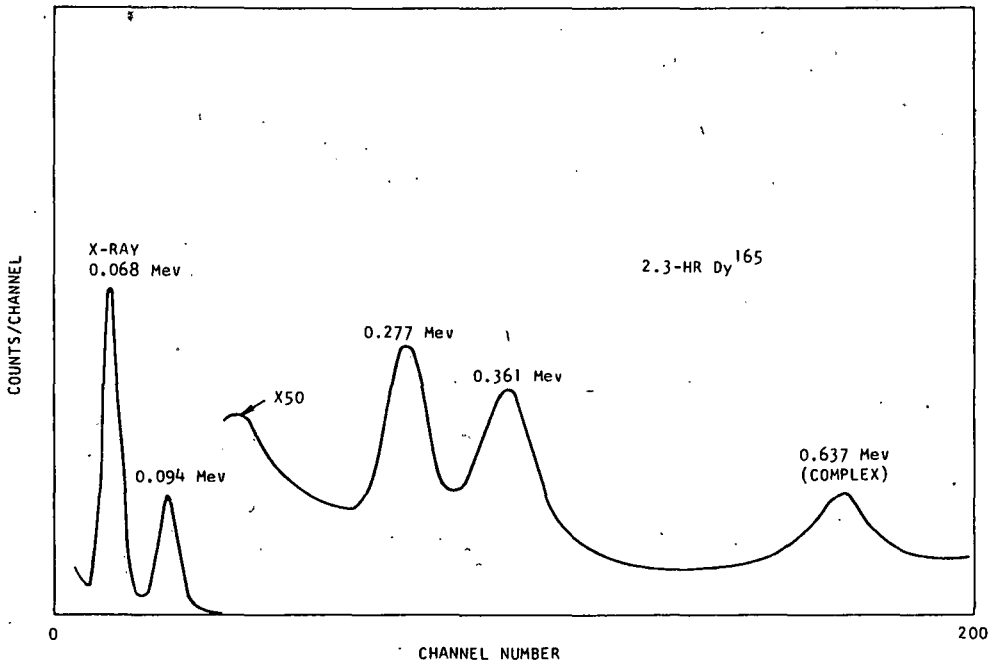

Fig. 1--Gamma-ray spectrum of 2.3-hour Dy^{165}

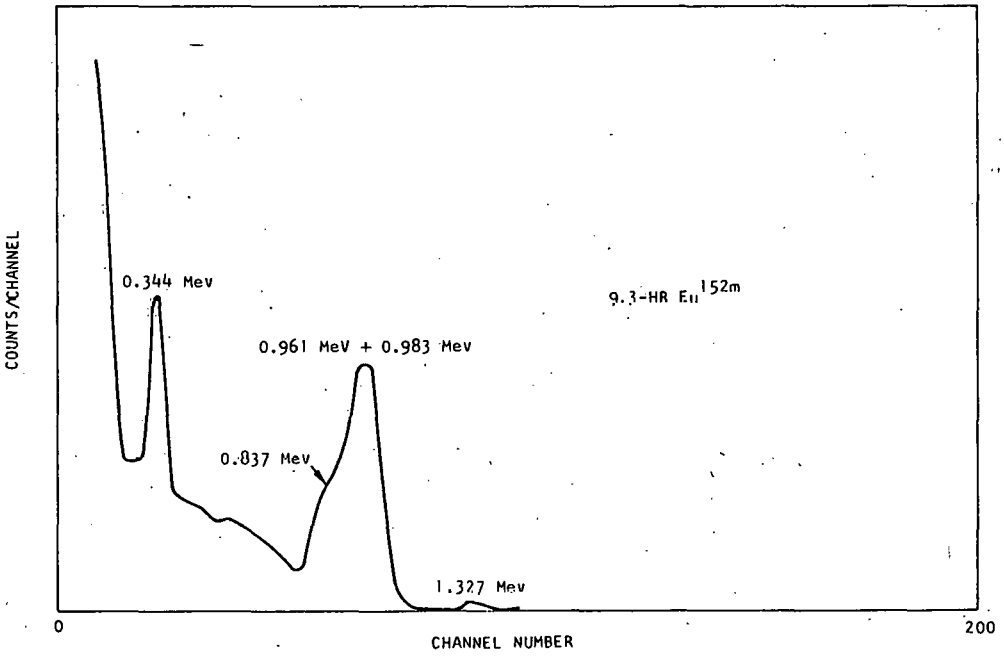

Fig. 2--Gamma-ray spectrum of 9.3-hour Eu^{152m}

Table 9

RESULTS OF FIRINGS WITH TAGGED CARTRIDGES

Tagged with	μg Dy		
1 μg Dy	3.54×10^{-4}	5.52×10^{-4}	6.21×10^{-4}
10 μg Dy	7.14×10^{-4}	1.05×10^{-3}	7.82×10^{-3}
100 μg Dy	1.76×10^{-2}	4.59×10^{-2}	4.11×10^{-2}
10 μg Eu	2.74×10^{-2}	1.35×10^{-3}	7.34×10^{-4}
100 μg Eu	$\leq1.95\times10^{-4}$	$\leq1.08\times10^{-4}$	9.46×10^{-4}
Tagged with	**μg Eu**		
10 μg Eu	3.30×10^{-4}	2.31×10^{-4}	3.20×10^{-4}
100 μg Eu	8.72×10^{-4}	2.66×10^{-3}	3.85×10^{-4}

Table 10

PARAFFIN BLANKS FROM TAGGED CARTRIDGE EXPERIMENT
(In ppm)

Tag	Dy	Eu
1 μg Dy	$\leq5.92\times10^{-6}$	----
10 μg Dy	$\leq2.09\times10^{-5}$	----
100 μg Dy	$\leq1.11\times10^{-5}$	----
10 μg Eu	2.55×10^{-4}	$\leq2.72\times10^{-6}$
100 μg Eu	$\leq1.09\times10^{-5}$	$\leq2.02\times10^{-6}$

Stripping Lacquer

A sample of stripping lacquer was analyzed to determine whether or not it would be suitable for removing gunshot residues from the hand. Unfortunately, the analysis revealed that the lacquer was a chlorine compound containing about 26% chlorine. The amount of 37.3-min Cl^{38} activity produced in a 30-min irradiation would prohibit immediate analysis for 84-min Ba^{139}, from the standpoint of radiation safety alone. This would not be a problem when analyzing for 2.80-day Sb^{122}, as the irradiated sample could be stored behind proper shielding for a day to allow the Cl^{38} activity to decay before beginning the analysis. Thus, because of its large chlorine content, this lacquer is not suitable for the removal of gunshot residues from the hand for immediate analysis for Ba by neutron-activation analysis.

TECHNIQUE FOR COMPARISON OF GAMMA-RAY SPECTRA

The majority of analyses involved in criminalistics concern the comparison of two or more samples to determine whether they may or may not be identical in origin. For instance, the object of the analysis is to determine whether material from the scene of a crime matches, in elemental composition, corresponding material connected with a suspect. Almost all such analyses are done instrumentally (i.e., nondestructively). In most instrumental activation analysis work, the photopeak areas of the various induced gamma-emitting activities are compared with those of standard samples of the elements. The samples and standards are all activated and counted in the same way, and numerical results expressed in percents or parts per million are obtained for each element detected. Usually, the standard deviation of each number, based on counting statistics, is also reported. However, this technique, in general, is not suitable for the presentation of results of analyses to nonscientists, such as jurors, judges, and lawyers. What is needed is a method that will clearly show similarities and differences between samples in a less mathematical, more pictorial, yet still scientifically sound manner.

A technique has been developed which appears to be effective. The samples are first given a short irradiation, usually of 1-min duration, and are all counted at exactly the same time after the irradiation and for the same length of time. The gamma-ray spectra that are obtained are stored on magnetic tape. The samples are then given a longer irradiation, usually for 1 hr, but in some cases as much as 10 hr, and are counted at various selected decay times. All of the samples are irradiated and counted under as nearly identical conditions as possible. Again, all spectra are stored on magnetic tape. The corresponding spectra are then

played back into the memory of the gamma-ray spectrometer, one at a time. At the same time, the spectra are normalized to the same sample weight by means of the variable multiplier of the magnetic tape unit, which permits multiplication of the spectra by any number greater than 0.001 in increments as small as 0.001. The corresponding normalized gamma-ray spectra (same irradiation, decay and counting times, and counting geometries) of the two samples to be compared are then plotted on the same sheet of graph paper with a precision x-y plotter, using a different stylus for each. If the samples are indeed identical, then the spectra should coincide with each other, within the statistical scatter of the points. Such close and extensive matching of the gamma-ray spectra is readily grasped by laymen, such as jurors, yet is scientifically sound and less time consuming than the more tedious quantitative comparisons with standards and calculations of standard deviation.

Several variations to the method were tried in order to determine which would be the most suitable. The plots were made in both the linear and logarithmic modes. It appeared that the linear plots gave, in general, a better comparison of the spectra. One spectrum was also subtracted from the spectrum with which it was being compared. If there were any qualitative or quantitative differences in the spectra, distinguishable peaks would remain after the subtraction. However, this method was completely unsatisfactory because of statistical considerations when subtracting two statistically uncertain numbers of about the same value. Another method was to multiply one spectrum by 1.0 and the other spectrum (already normalized) by 0.9 and 1.1, and then plot the three spectra. Ideally, the two plots of the same spectrum would bracket the other spectrum. However, this method has the disadvantage that it tends to complicate the presentation by having too many spectra plotted on the same paper. Also, it is best applicable to the comparison of only two samples. The method which appears to give the best presentation is the direct comparison of linear plots of the normalized spectra.

HAIR ANALYSIS

Known Head Hair from Two Individuals

The initial studies of the sample-comparison technique were carried out using three samples of hair, two from the same person and the third from a different person. The samples were irradiated in the TRIGA Mark I reactor for 30 min in a thermal-neutron flux of 1.8×10^{12} n/cm^2-sec. They were then counted at several decay times under identical conditions. The weight-normalized spectra were plotted on the same graph paper, in both the linear and logarithmic modes. A linear representation is shown

in Fig. 3 and the corresponding logarithmic display is shown in Fig. 4. The two samples of hair from the same person gave spectra that were almost identical, although the ideal condition of exact superimposition (within counting statistics) of the two spectra was not obtained (one spectrum was slightly lower than the other by a constant factor). The spectrum of the third sample was quite different from the other two.

Hair Samples from American Academy of Forensic Sciences

Two sets of samples, each containing three hairs, were analyzed. The samples were prepared by the American Academy of Forensic Sciences as an identification problem for interested criminalists. Two of the hairs in each set had a common origin, and the third had a different origin. Each of the hairs was irradiated for 1 min and then counted immediately to determine the short-lived activities present. They were then irradiated for 2 hr and counted at various decay times. The normalized spectra comparing the three samples in the first set are shown in Fig. 5. Although no two spectra are exactly superimposed, it is obvious in this case which two hairs have a common origin. Two of the spectra are very similar, having Na^{24} as the predominant activity. The third spectrum is quite different, showing Cu^{64} as the predominant activity. The identification of the two identical hairs in the second set of samples was made by counting the samples four days after the irradiation. At this time, two of the samples showed 35.9-hr Br^{82} to be present (see Fig. 6). This isotope was barely detectable in the third sample. The results obtained agreed perfectly with the known origins of the samples (disclosed later by Mr. Ray Pinker).

Results of Actual Cases

Samples of hair from eleven actual criminal cases were analyzed by the comparison method. Each case is described individually. All irradiations were made in a thermal-neutron flux of 1.8×10^{12} n/cm^2-sec in the TRIGA Mark I reactor, and all counting was done with a multichannel gamma-ray spectrometer.

1. Thirteen samples of hair involved in a murder case were irradiated first for 1 min and then for 2 hr. Four of the samples were found at the scene of the crime, three were head, pubic, and body hair taken from a suspect when he was apprehended, and one was the victim's known head hair. The other five samples were head, pubic, leg, arm, and chest hair taken from the suspect seven months after his arrest. Seven of the hairs had been mounted in a sucrose solution on slides for microscopic examination. The analyses revealed that these hairs were contaminated with Hg, estimated to be about 0.5%. Washing the hairs five times with deionized water prior to irradiation failed to remove the Hg. A sample

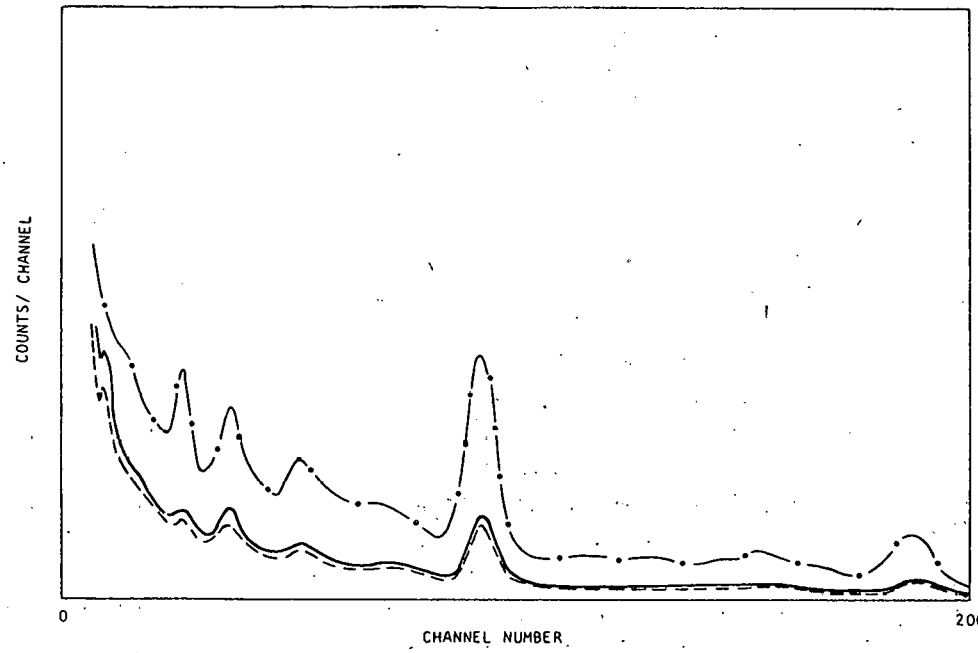

Fig. 3--Gamma-ray spectra comparing two head hairs from one person with a third head hair from another person (linear display)

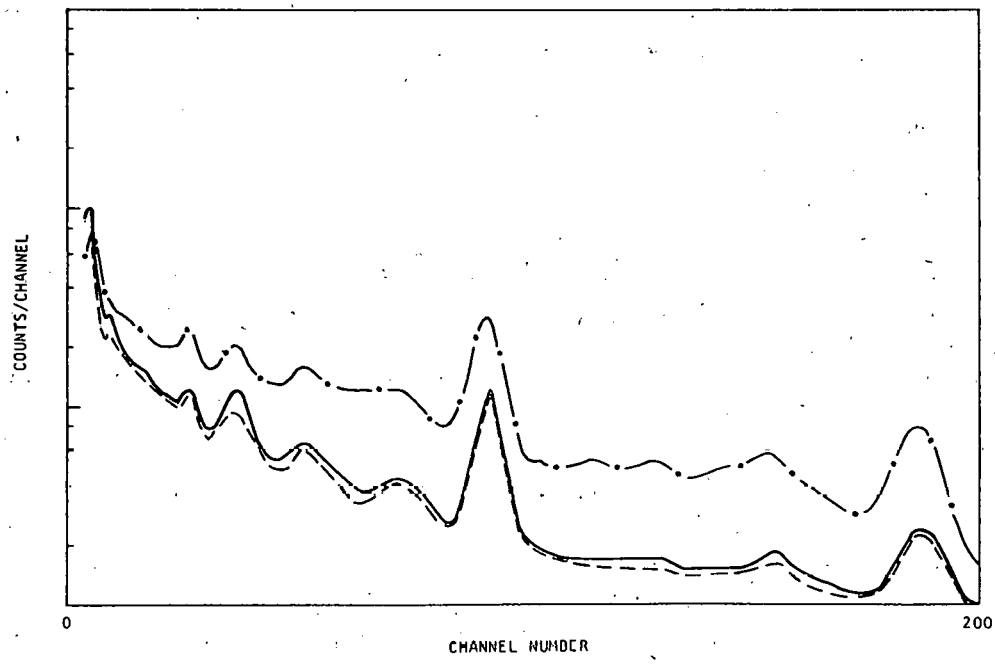

Fig. 4--Gamma-ray spectra comparing two head hairs from one person with a third head hair from another person (logarithmic display)

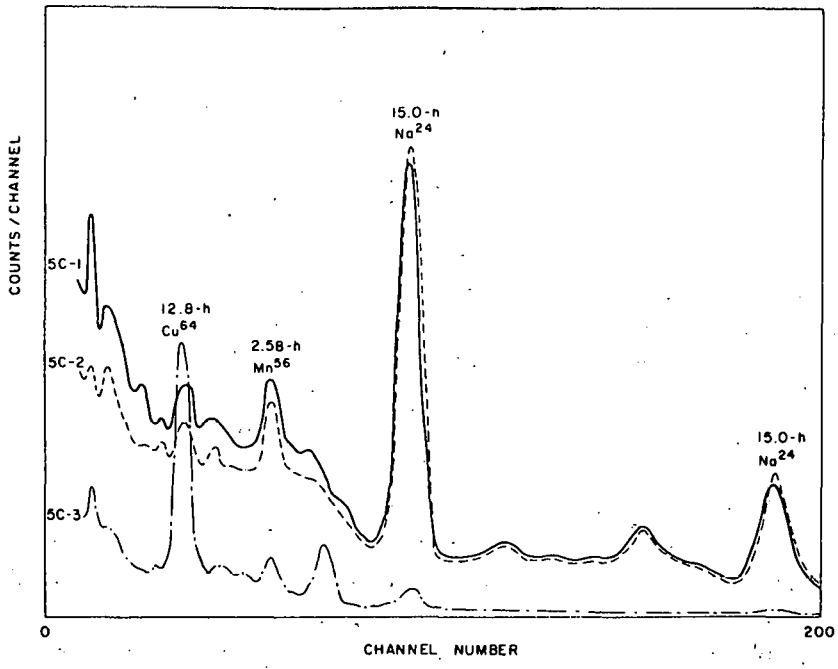

Fig. 5--Gamma-ray spectra comparing three samples of hair from first set of samples from American Academy of Forensic Sciences

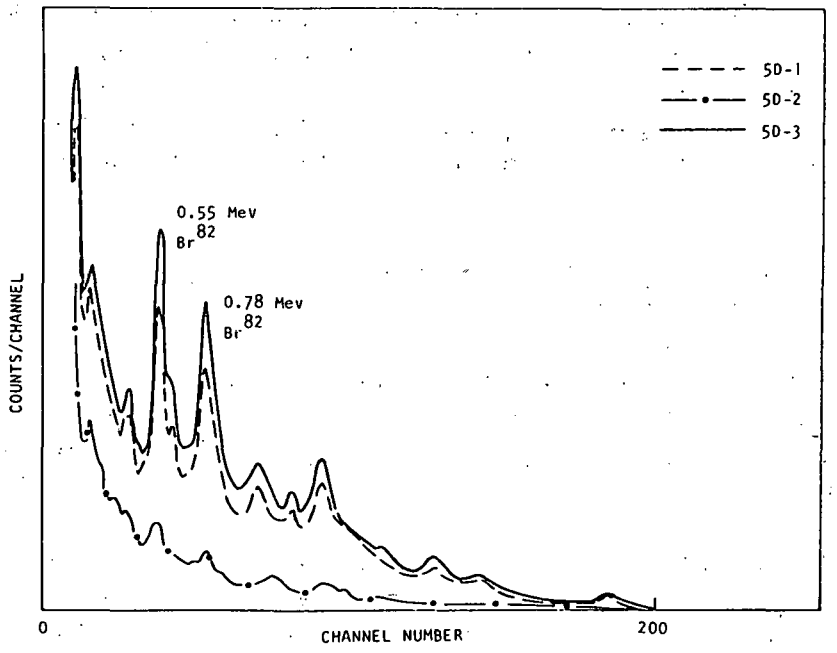

Fig. 6--Gamma-ray spectra comparing three samples of hair from second set of samples from American Academy of Forensic Sciences

of the mounting solution was also irradiated and found to contain Hg. Therefore, this was probably the source of the Hg contamination in the hair. The presence of the Hg severely limited the analysis by purely instrumental (nondestructive) means. The analyses did indicate, however, that one of the unknown hairs was similar to the arm hair from the suspect and that another unknown hair was similar to the suspect's head hair. Also, it was indicated from the analyses that the third unknown hair was not similar to any of the known hairs. However, because of the Hg contamination, these similarities and dissimilarities were not considered to be conclusive evidence of the origin of the unknown hairs.

2. Three samples of hair from a case involving the murder of a five-year-old girl were analyzed. The remains of the girl were found eight months after she had disappeared. Two of the hairs were found on the girl's body and were heavily encrusted with debris. The third sample was known hair from a suspect in the crime. The hairs were thoroughly washed with detergent, deionized water, and acetone, and were then irradiated for 1 min in the pneumatic-tube position and for 1 hr in the rotary specimen rack of the reactor. The samples were then counted at several decay times. One set of spectra, normalized to the same sample weight, comparing these samples is shown in Fig. 7. The analyses indicate that all three hairs are different in their elemental composition. The spectrum of the suspect's hair shows a peak at 0.51 Mev (probably due to Cu^{64}), which is absent from the two unknown hairs. Also, the two unknown hairs each have two peaks at about 0.15 Mev and 0.30 Mev, which were barely detectable in the suspect's hair. The two hairs found on the victim's body appeared to be different, since one had much more Mn than the other. It also contained much more Mn than the suspect's known hair.

There are two factors in this case which may have prevented a positive matching of these hairs. First, contamination of the samples may be a problem, since they were heavily encrusted with debris when found. The washing of the samples that was performed may not have been sufficient. Also, the eight-month time element involved here may be a significant factor, since the chemical composition of a person's hair changes with time.

3. Four hairs from another murder case were analyzed. Three hairs were unknown hairs and the fourth was a known hair. No further information concerning these hairs or the case was obtained from the police department involved. These samples, after being washed with deionized water, were irradiated for 1 hr and were counted at several decay times. As can be seen from the normalized spectra shown in Figs. 8 and 9, all of the hairs appear to be different. It is especially important that the known hair does not match any of the three unknown hairs.

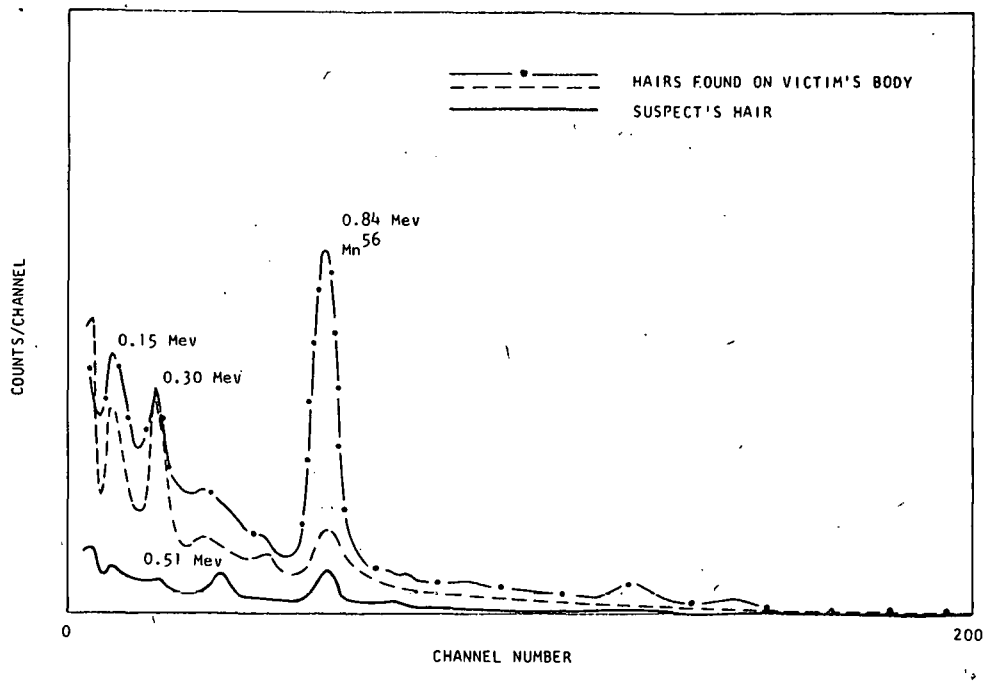

Fig. 7--Gamma-ray spectra comparing three hairs from an actual case involving the murder of a 5-yr old girl

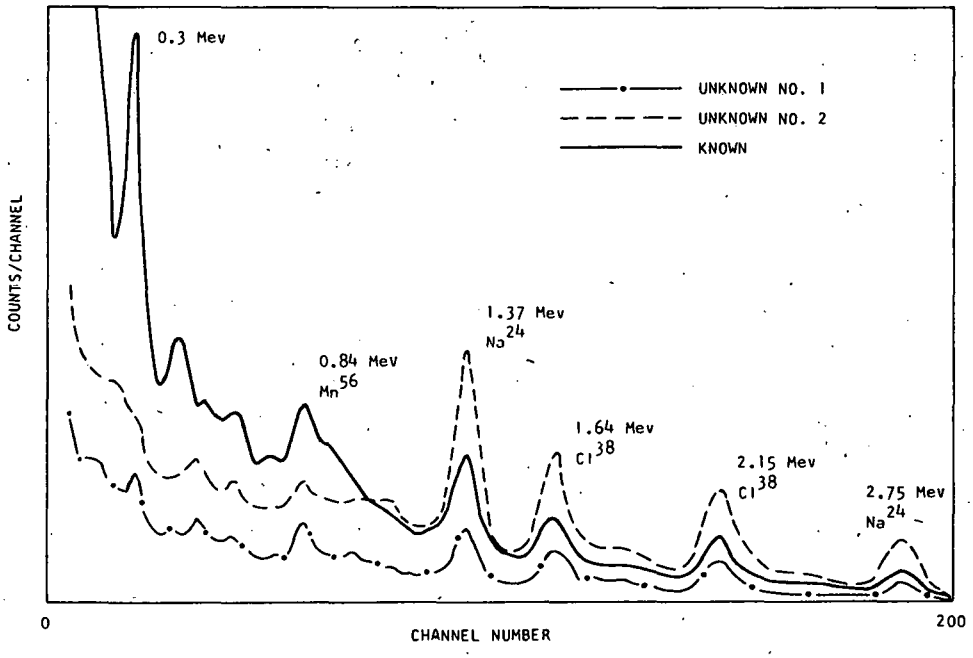

Fig. 8--Gamma-ray spectra comparing hair samples from a murder case

Therefore, it was concluded that all of these hairs probably had different origins.

4. Four samples of hair from a rape case were analyzed. One of the samples was a short curly hair found on the bed of the victim and was compared with known head hair from a suspect in the crime. The other two samples compared were long hairs found loose on the back of the suspect's neck (apparently not the suspect's own hair) and known head hair from the victim. Thus, there are two ways to possibly link the suspect to this crime: by matching his hair with that found on the bed, and by matching the victim's hair with those found loose on the suspect. These hairs, after being washed, were irradiated for 1 min and counted immediately to determine the short-lived activities induced. They were then irradiated for 1 hr and counted at several decay times. The normalized spectra comparing the short hairs (see Fig. 10) showed that they were very similar in many respects, both qualitatively and quantitatively. However, discrepancies, particularly in the amount of Au present, prevented the positive identification of these two hairs as being common in origin. Sufficient data were not available to say whether differences in the amounts of certain elements could or could not be found in hairs known to be from the same person. A similar situation developed in the case of the two long hairs. Again, the normalized spectra were very similar. However, as shown in Fig. 11, the amount of Au present varied. The short irradiation also revealed a difference in the amount of Al present in these two samples. Owing to these quantitative discrepancies, it could not be concluded that the two short hairs or the two long hairs were of common origin. Figure 12 shows the victim's known hair compared with the suspect's known hair. As can be seen, they are vastly different.

5. Six samples from another case were analyzed. This case involved the possible sexual assault by the suspect on a seven-month-old child. Two of the samples were found on two different diapers which had been used while the mother was absent and at which time the child was in the care of the suspect. These samples were each subdivided into two additional samples. The hairs from one of the diapers were divided into long hairs and short hairs. Only two hairs were found on the other diaper, and they were analyzed separately. The other four samples were head and pubic hairs from the suspect, and the head and pubic hairs from the victim's mother. The samples were irradiated for 1 hr and were counted at several decay times. Two hairs showed no major qualitative or quantitative differences. These were the long hairs found on one of the diapers and the known head hair of the suspect. All other samples showed some qualitative and quantitative differences. The analysis of these two matching hairs was continued by irradiating them for 2 min and counting immediately. There were no apparent differences in the

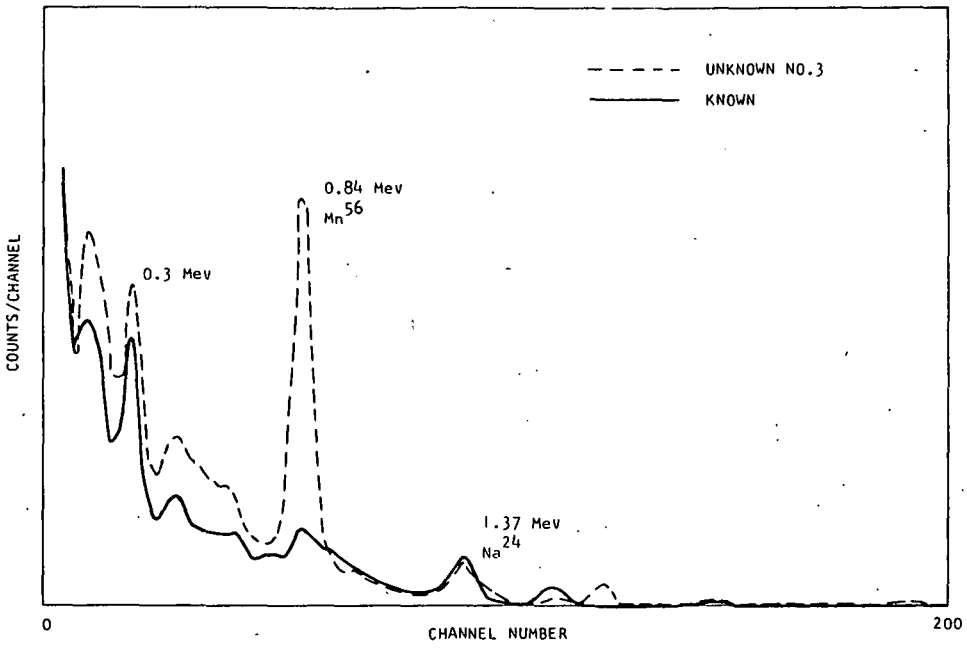

Fig. 9--Gamma-ray spectra comparing hair samples from a murder case

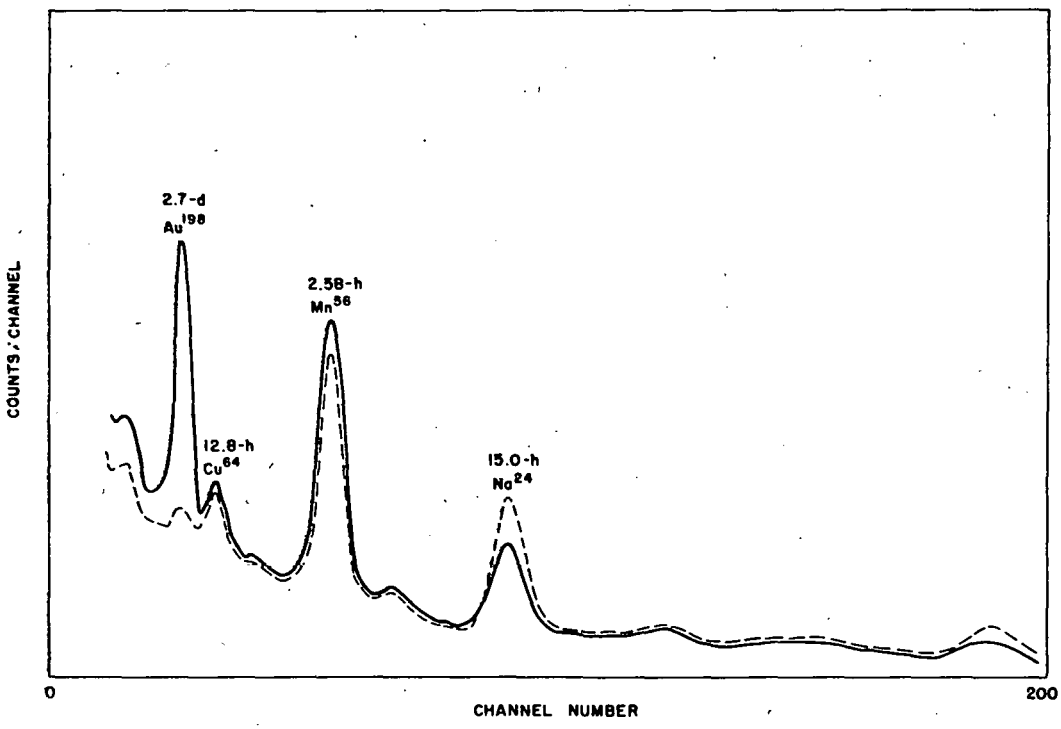

Fig. 10--Gamma-ray spectra comparing short hairs from a rape case

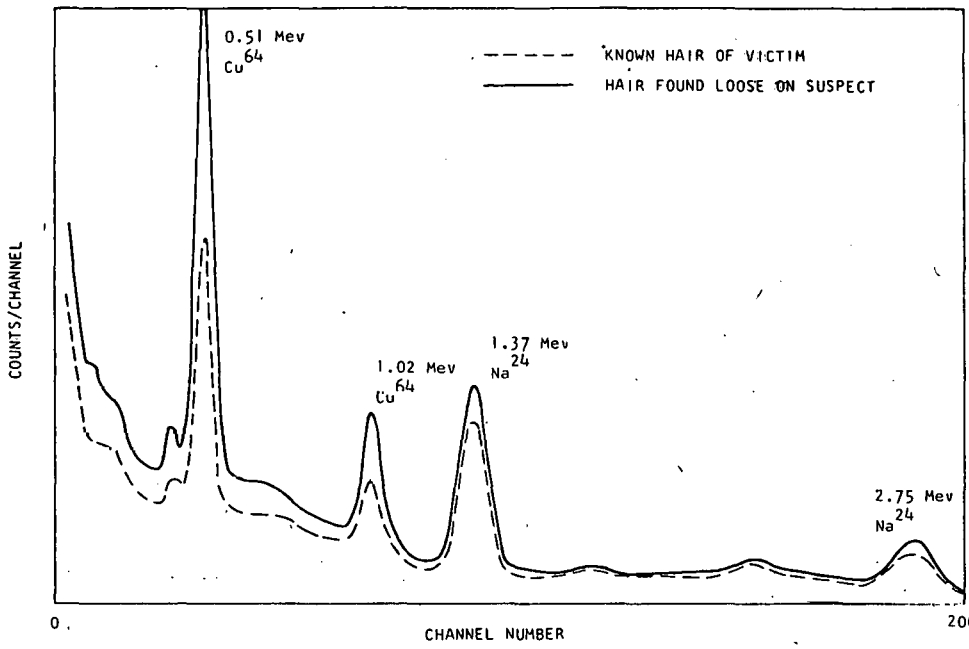

Fig. 11--Gamma-ray spectra comparing long hairs from a rape case

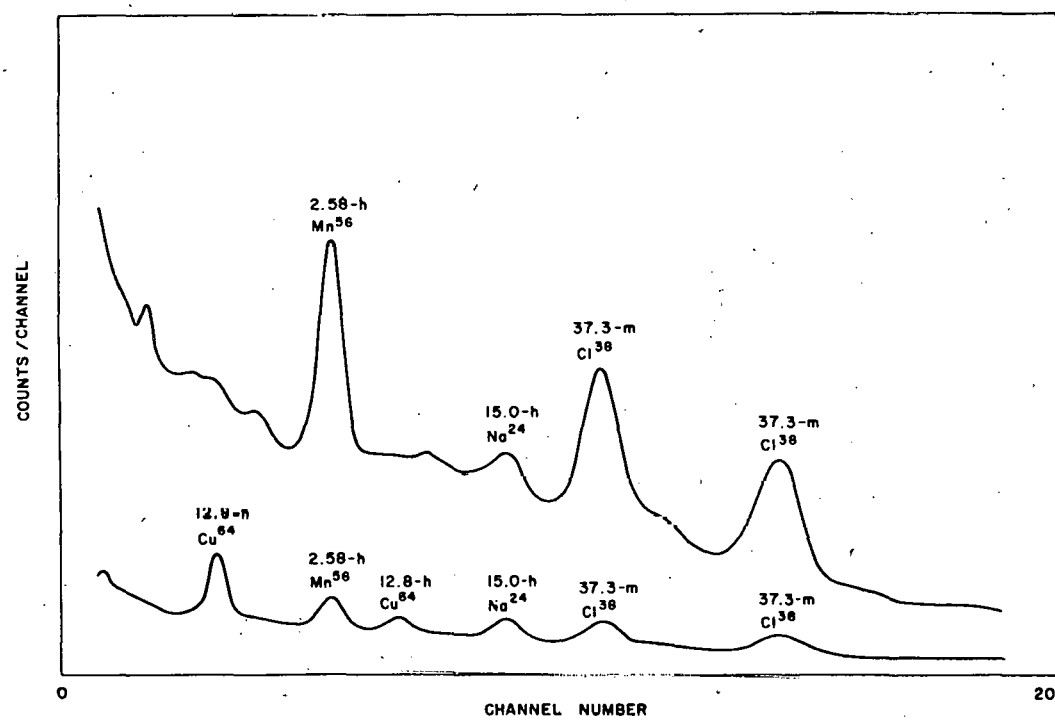

Fig. 12--Gamma-ray spectra comparing victim's known hair with suspect's known hair in a rape case

short-lived activities induced in these samples. These two hairs were then irradiated for approximately 6 hr (with the reactor operating intermittently). Again, counting the samples after several days' decay showed no apparent differences in their composition. Figure 13 shows one of the sets of spectra obtained for these two samples. The spectra have been normalized to the same sample weight. Since no differences were found in these hairs, it was possible to conclude that, with a high probability, the hair found on the diaper was the suspect's head hair. The suspect, however, confessed after the analyses were performed, so this evidence was not presented in court. This case represents the most conclusive comparison analysis of hair yet performed in these studies.

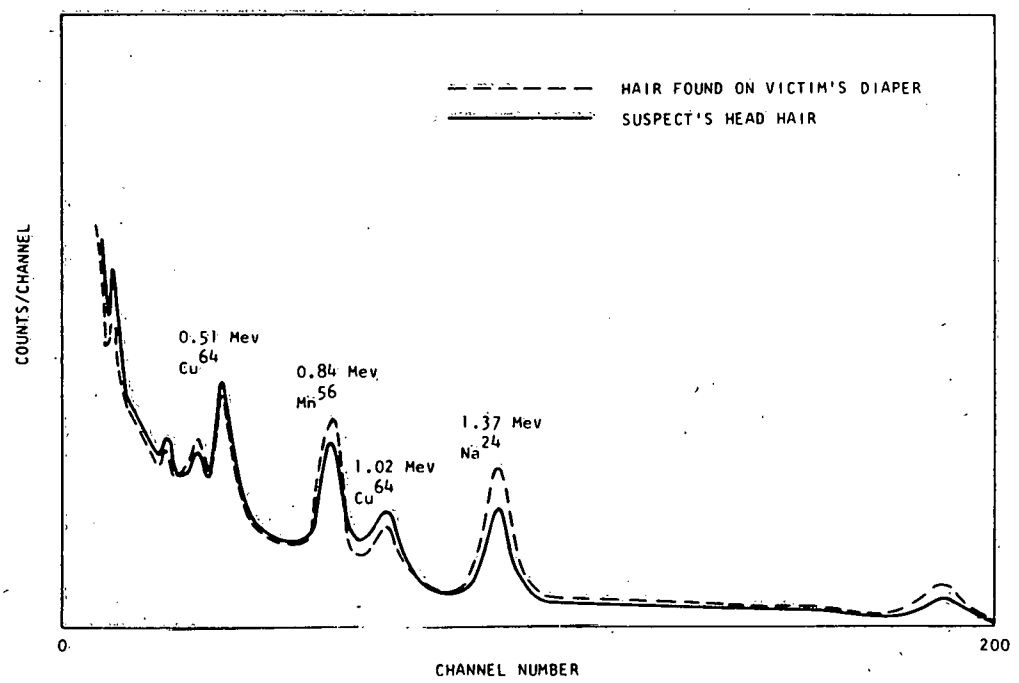

Fig. 13--Gamma-ray spectra comparing two samples of hair from a child assult case

6. Seven samples in another case were analyzed. Four of the samples were head, pubic, and left and right axillary hair removed from the body of a female murder victim. The other three hairs were found in a truck. It was the purpose of the investigation to determine if the hairs found in the truck were those of the victim. This would indicate that the victim had been in the truck, which is what the police department involved wanted to determine. A 1-min irradiation followed by immediate counting

revealed sizable differences in the amount of Al present in the unknown and known samples. The samples were then given a 1-hr irradiation. Again, the samples showed some differences in their elemental composition, especially in the amount of Mn present. Therefore, it seems probable that the hairs found in the truck were not the victim's hair.

7. Three samples of hair from a kidnap-murder case were submitted for analysis. Although a suspect had been apprehended, there was insufficient evidence to bring him to trial, and the case had been open for nearly two years. Two of the hairs were unknown hairs and were unfortunately mounted in a 50% sucrose solution for microscopic examination. The third hair was the suspect's hair and was not mounted. A 1-hr irradiation of these hairs revealed the presence of a large amount of Hg, presumably the result of contamination from the sucrose solution, in the hairs which had been mounted. Because of this Hg interference, no further work was done on these samples.

8. Five hair samples from a rape-murder case were analyzed. The victim in this case was a six-year-old girl. One of the samples was unknown hair found in the front seat of the vehicle suspected of being the place where the crime was committed. Another sample was unknown hair found on the body of the victim. The other three samples were known head hair of the victim and known head and pubic hair of the suspect in the crime. The police criminalist involved in this case had stated that the evidence is very strong that the unknown hairs are in fact the suspect's pubic hairs. Microscopically, the unknown hairs are indistinguishable from the suspect's pubic hair. The suspect has now confessed.

Counting the samples immediately after a 1-min irradiation revealed that Al^{28} was the only short-lived activity induced in these samples. Aluminum was present in about equal concentrations in all of the samples. The samples were then irradiated for a total of approximately 10.5 hr (with the reactor operating intermittently). They were counted 1 hr, 24 hr, 4 days, and 2 weeks after the irradiation ended. The quantitative comparison of the spectra obtained showed that no two samples were exactly alike. Figures 14 and 15 show the comparison of the suspect's pubic hair with both of the unknown hairs. The suspect's known pubic hair contained more Au than any of the other samples. Also, the amounts of Mn and Na seemed to vary from one sample to another. Bromine was detected in the victim's head hair but not in any of the others. Chromium was detected in the suspect's head hair but not in any of the others. Although the police department involved identified both unknown hairs as probably being the suspect's pubic hair, the quantitative differences obtained by neutron-activation analysis failed to confirm their conclusion.

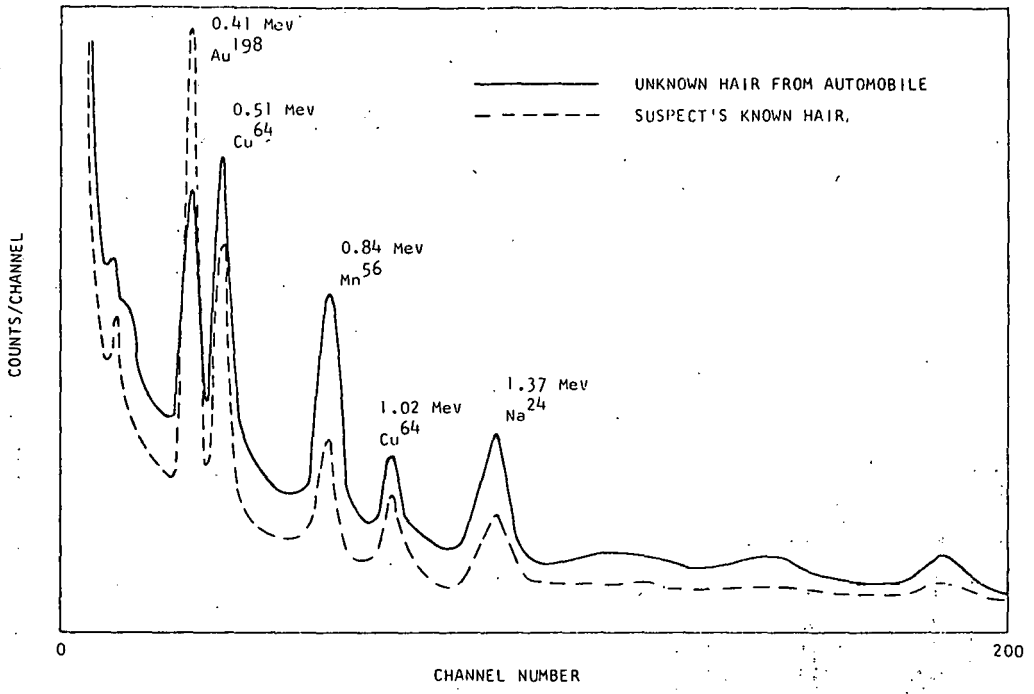

Fig. 14--Gamma-ray spectra comparing hair samples from a rape-murder case

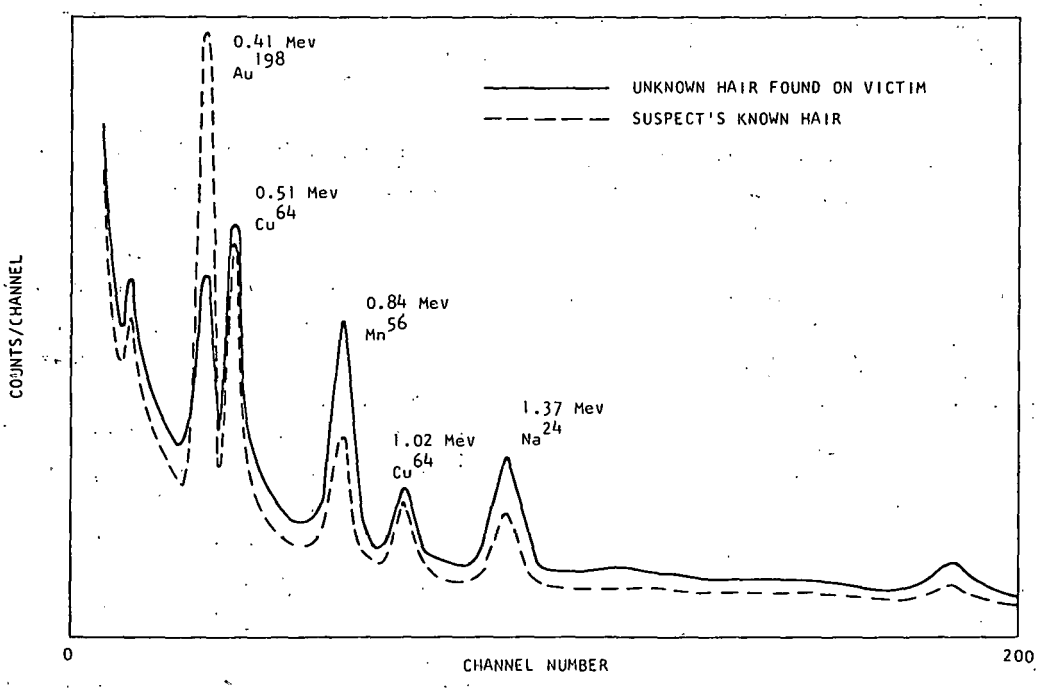

Fig. 15--Gamma-ray spectra comparing hair samples from a rape-murder case

Figure 16 shows a comparison between the known head and known pubic hair of the suspect. As can be seen from these normalized spectra, hair from different parts of the same person's body may differ appreciably in elemental composition (in agreement with Jervis' findings).

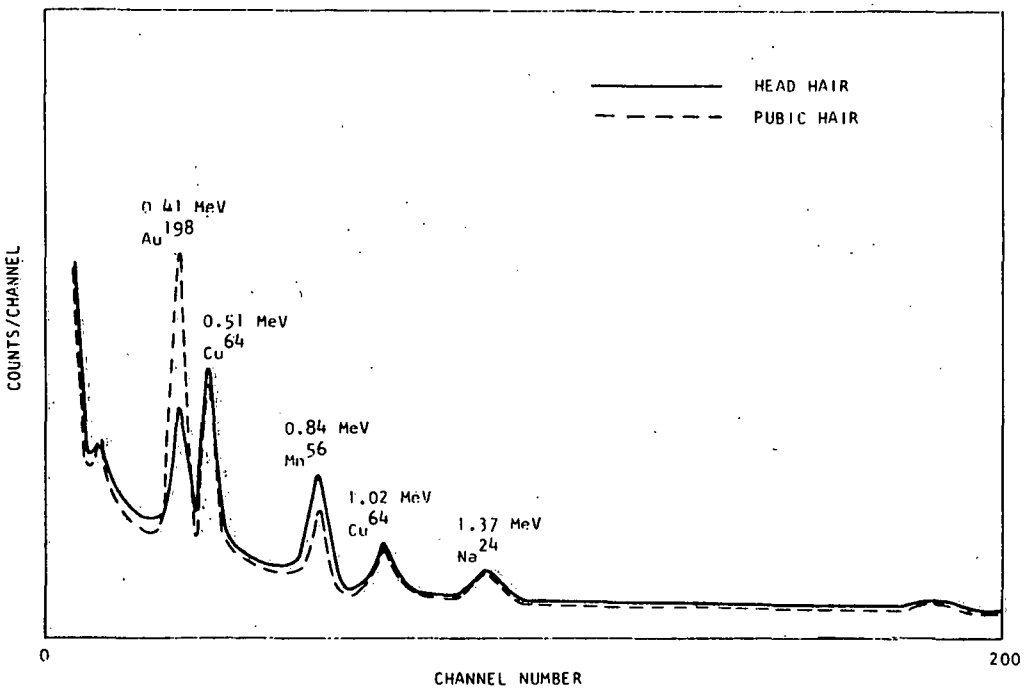

Fig. 16--Gamma-ray spectra comparing known head and pubic hairs of suspect in a rape-murder case

9. Three samples of hair obtained from the scene of an apparent double murder were analyzed. One sample was removed from a plastic hair band on one of the bodies, another sample was removed from the skull of the second body, and the third sample was taken from a mass of hair found between the two bodies. The purpose of the analyses was to determine if the mass of hair was from one of the victims or possibly from a third party. The hairs were washed with acetone and water and were then irradiated for 1 min and for 1 hr. They were counted at several decay times. The results indicate that the hair removed from the first body is very probably of different origin from the mass of hair found between the bodies, as both qualitative and quantitative differences were noted. There were no qualitative differences noted between the hairs found on the second body and the mass of hair, the same five elements being detected in each. Three of these elements, Al, Cu, and Cr, were present in equal concentrations in each sample. However, the mass of

hair found between the bodies contained about three times as much Mn and about twice as much Na as the hair removed from the second body. Therefore, it is probable that these two samples are also of different origin, unless unremoved contamination affected the results.

10. A sample of known hair from a murder victim was compared with hair found in the car belonging to the suspect. After washing these hairs with water and acetone, they were irradiated for approximately 9 hr in the reactor (with the reactor operating intermittently). They were then counted at several decay times. Sizable quantitative differences were noted in these samples. In addition to the differences in the amounts of Mn and Na, shown in Fig. 17, other spectra showed that the amounts of Au present also differed. Figure 18, obtained after several days' decay, shows qualitative differences in these two samples. Therefore, it was possible to conclude with high probability that these two samples are of different origins.

11. A number of hair samples from a double murder and rape case were analyzed. Three of the hairs were pubic hairs removed from one of the victims at the morgue, three more were hairs picked from the victim's coat lining, and three other hairs were picked from different garments belonging to the prime suspect. Known hairs of the suspect were not taken. The samples were all washed with deionized water and acetone. They were irradiated for 1 min and immediately counted. Then they were irradiated for 1 hr and counted at several decay times. The victim's pubic hairs were compared with the hair removed from her coat and also with the hair removed from the various garments of the suspect. Each of the hairs removed from the victim's coat was also compared with each of the hairs from the suspect's clothes. Comparison of the normalized spectra showed that the victim's pubic hairs were different from the hairs from her coat and from the hairs from the suspect's clothes. It was interesting to note that the victim's pubic hair contained a rather large amount of iodine. Each of the hairs found on the victim's coat lining was also different from each of the hairs taken from the suspect's clothes.

Three more samples of hair were received in connection with this case. One sample was the known head hair of one of the victims. The second sample was a head hair found in a suitcase belonging to a second suspect. The third hair was found on a sweater belonging to a third suspect. These hairs were washed, irradiated, and counted. It was found that one of the unknown hairs was quite different from the victim's known hair. The other unknown hair, however, was very similar qualitatively to the victim's head hair. However, there were quantitative differences apparent which prevented the identification of this unknown hair as the victim's head hair.

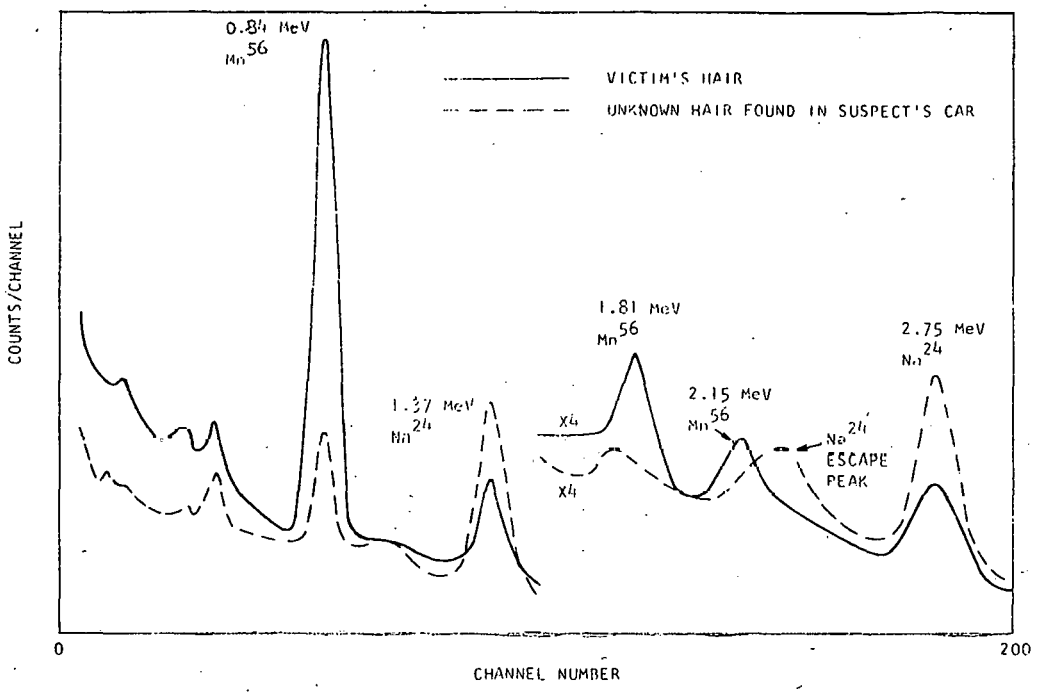

Fig. 17--Gamma-ray spectra comparing two hairs from a murder case

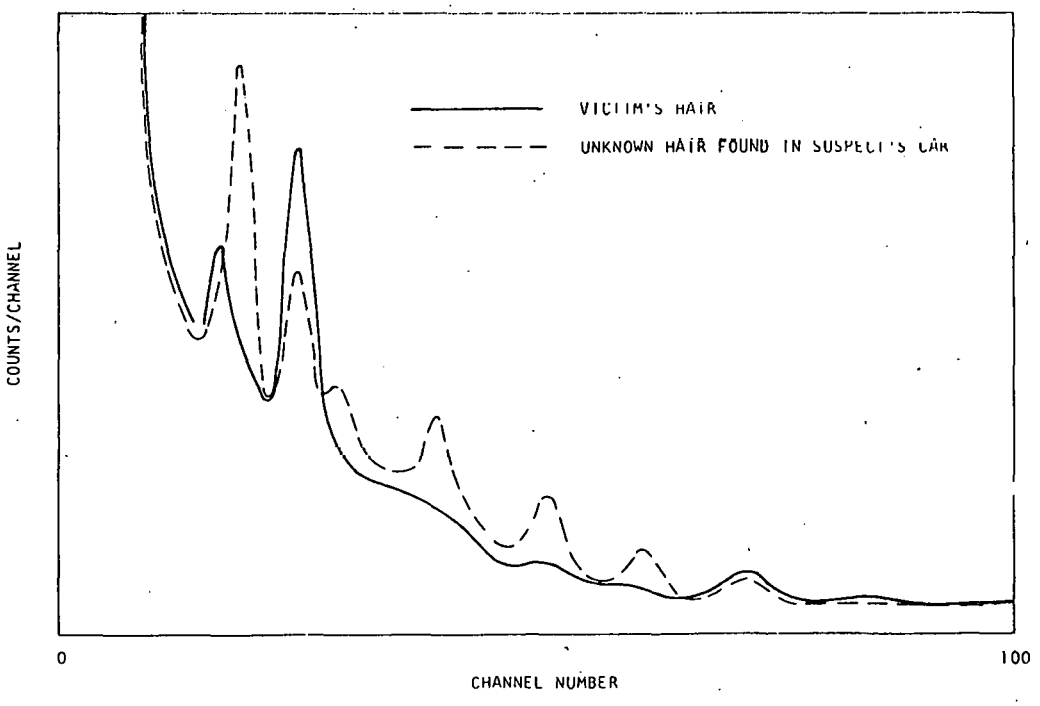

Fig. 18--Gamma-ray spectra comparing two hairs from a murder case

Of the eleven actual hair cases studied, only one yielded positive results (i.e., all spectra for one hair were virtually identical to the spectra of the other hair obtained under the same conditions). In most other cases, the spectra of the hairs being compared were quite similar in many respects, but they also showed some differences, primarily in the amounts of one or more elements present. One of the problems connected with the analysis of hair, of course, is the proper cleaning of the sample. The present method of cleaning the hair consists of rinsing with acetone and then soaking in deionized water. The hairs are then rinsed several times with deionized water, and finally rinsed again with acetone. This procedure, however, may not completely remove all external contamination, which, of course, would then give erroneous results. The sample cleaning problem has been investigated thoroughly by L. C. Bate of Oak Ridge National Laboratory. His results also reveal the difficulty of the problem. However, another, and probably more serious, problem deals with sample inhomogeneity. The composition of hair may change with time. Also, hair goes through cycles, some hairs actually growing while others are in a dormant state. This could very possibly lead to differences in composition of different hairs on one person's head. This would not be a serious problem if large composite samples of hair were being analyzed, as more representative and homogeneous samples would be obtained. However, in the majority of actual cases involving hair identification, one is concerned with very small amounts of hair, sometimes only single short strands. Here, sample inhomogeneity can be a serious problem. It appears that if meaningful results are to be obtained from the analysis of hair from actual cases, more work will have to be done to determine what limits of variability in the amounts of certain elements in the hair can be tolerated when making a decision as to whether two hairs are identical or not.

Comparison of Head Hairs from One Person

In a preliminary study, four single strands of hair from the head of one person were analyzed. The samples were all obtained at the same time by combing the hair and recovering the loose hairs from the comb. They were all washed with deionized water and acetone and irradiated for 1 hr in a thermal-neutron flux of 1.8×10^{12} n/cm^2-sec. They were then counted at several decay times by gamma-ray spectrometry. Normalized spectra comparing each of three of the hairs with the fourth hair are shown in Fig. 19. In one case the spectra compare very favorably, whereas in the other two cases definite differences in the spectra are noted. In one case, no parts of the two spectra are superimposed, leading one to suspect that the hairs were actually different. In another case, the spectra agreed very nicely, except that Cr was detected in one of the hairs and not in the other. A qualitative difference such as this in hairs involved in an actual case would be sufficient at the present time to

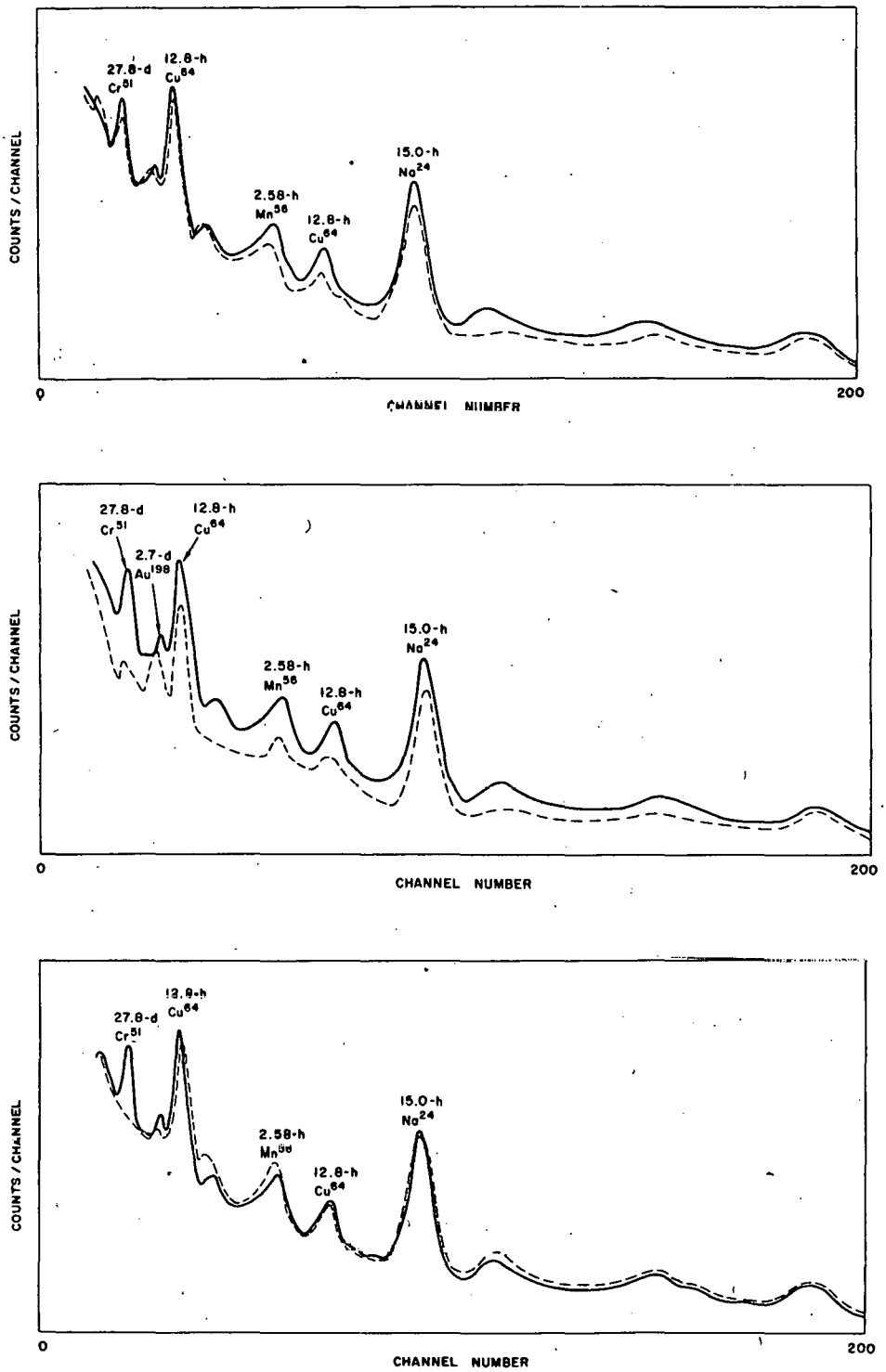

Fig. 19--Gamma-ray spectra comparing samples of known head hair from the same person

prevent the conclusion that the two samples are of common origin, yet it is known that these two hairs were from the same person and were obtained at the same time and in the same manner. These very preliminary analyses of single strands of hair seem definitely to indicate that inhomogeneity is a problem when comparing such samples. More work on the comparison of hairs is indicated before useful interpretations of the results of actual cases can be made.

Animal Hair

A preliminary study was made of the feasibility of using neutron-activation analysis for the identification of animal hair. In this study, hairs from ten cats were analyzed. The hairs from three of the cats were subdivided into light and dark hairs, making a total of thirteen samples. The samples were all washed with a mixture of 2/3 ether and 1/3 ethanol, followed by deionized water, and finally acetone. They were then irradiated for 1 min in a thermal-neutron flux of 4.3×10^{12} n/cm^2-sec and were immediately counted for the short-lived activities induced. The results showed that Al was present in varying amounts in all of the samples and that Cl was present in eleven of the samples. These were the only short-lived activities induced by the 1-min irradiation. Quantitative calculations were not made, since no standards were irradiated in this exploratory investigation.

The samples were also irradiated for 1 hr in a thermal-neutron flux of 1.8×10^{12} n/cm^2-sec and were counted by gamma-ray spectrometry at several decay times. This revealed the presence of large amounts of Na in all of the samples and varying amounts of Mn in ten samples. Chlorine was again detected in all but two of the samples. No other elements were detected. Semiquantitative estimates of the amounts of Na and Mn present are shown in Table 11. These results show that the hairs from the ten cats in general show little qualitative differences. However, there are some considerable quantitative differences. The Mn levels varied from ≤ 0.24 ppm to 23 ppm, a 100-fold range, and Na levels varied from 310 ppm to 5200 ppm, a 17-fold range. Also, as shown in Table 11, the light and dark hairs from the same cat varied appreciably in their Mn and Na values. On the basis of this preliminary study, it appears to be possible to characterize cat hair by quantitative comparison of the samples. However, since only four elements were detected, the number of points for comparison is small. More work needs to be done on this problem, and especially a study on the variability in the composition of hairs from the same animal is indicated.

Table 11

ESTIMATED CONCENTRATIONS OF Na AND Mn
IN THE HAIR OF TEN CATS

Sample	Mn (ppm)	Na (ppm)
1	$\leq$0.32	2600
2 light	1.3	4100
2 dark	0.90	2500
3	0.84	1700
4 light	1.7	1900
4 dark	2.0	1300
5	23	2300
6 buff	0.69	310
6 light	2.4	1300
7	0.37	5200
8	0.77	1300
9	0.24	600
10	0.58	3200

PAINT ANALYSIS

San Mateo County, California, Court Case

On July 3, 1964, the use of neutron-activation analysis for the analysis and comparison of evidence samples was accepted by a California State trial court. This was the first time activation analysis is known to have been introduced in a California court (or any state court), and the first time activation analysis performed at General Atomic had been introduced in court. Neutron-activation analysis had been accepted as evidence in two Federal trial courts in two cases a few months earlier. The analyses in the two Federal cases were performed by the Internal Revenue Service. The California case involved the analysis of very small samples of paint.

On October 25, 1963, a burglary of a store in South San Francisco was attempted. The burglar tried to jimmy the back door of the store. In doing so, he set off a silent burglar alarm that sounded at the police station. The police responded, and when they arrived they found a man standing near the store; however, he was not caught actually trying to jimmy the door. On the ground nearby, the police found an automobile

tire lug wrench. A search of the nearby car belonging to the man found at the scene revealed that the tire lug wrench was missing from his car. This person was taken into custody as a suspect in the attempted burglary, and the lug wrench was taken to the San Mateo County Sheriff's Department Crime Laboratory for further examination.

The Sheriff's Department criminalist, upon examination of the wrench, found some brown paint on the wedge end. This paint appeared to be very similar to the paint on the jimmied store door. The examination also revealed that there was some light blue paint embedded in some tar material on the wrench. This blue paint appeared to be very similar to the blue paint of the suspect's automobile. The wrench itself was painted dark blue. The tiny pieces of light blue and brown paints were removed from the lug wrench by the Sheriff's Department criminalist and were submitted for analysis, together with known samples of brown paint from the door and blue paint from the suspect's car. The known paint from the car was recovered from the trunk, and was also embedded in some tar material.

The blue paints were washed with benzene to remove the tar, dried gently, and then rinsed with deionized water. The four samples, ranging in weight from 0.036 mg to 1.61 mg, were irradiated for 1 min in a thermal-neutron flux of 4.3×10^{12} n/cm^2-sec and were counted immediately. This revealed the presence of Al and Ti in all four samples. The samples were then irradiated for 1 hr in a thermal-neutron flux of 1.8×10^{12} n/cm^2-sec and were counted at various decay times during a period of about one week. Three additional elements (Mn, Cu, and Na) were detected in each of the blue paints, and five additional elements (Mn, Na, Sb, Zn, and In) were detected in each of the brown paints. The results are shown in Tables 12 and 13. The results for the elements are given in terms of counts per minute in the gamma-ray photopeak per milligram of sample, corrected for decay to the end of the irradiation, when no comparator standard was irradiated. No detectable long-lived activities were induced in the blue paints by a 1-hr irradiation, and 2.80-day Sb^{122} was the only long-lived activity detected in the brown paints.

Although the amounts of Mn, Na, and Cu found in the blue paints agree very closely, different amounts of Ti and Al were reported. These values, however, were not as reliable as those reported for the other elements. This was because the analysis for Al and Ti was performed using the pneumatic-tube transfer system. During transfer, the sample, consisting of very tiny flakes of the paint, acquired a charge of static electricity, which caused the sample to cling to the sides of the polyethylene irradiation vial. This resulted in the samples being counted at different geometries on the solid scintillation crystal. By comparing the positions

of the two paints in the vials, it was anticipated that the Al and Ti results for the paint taken from the wrench should be somewhat low. A correction based on an approximation of the geometric difference in fact brought the results for one paint very close to those obtained for the other paint.

Table 12

NEUTRON ACTIVATION ANALYSIS OF BLUE AUTOMOBILE PAINT FROM SAN MATEO CASE

	Ti (%)	Al (%)	Na (ppm)	Cu (ppm)	Mn (ppm)
Paint from lug wrench	7.51	0.671	194	1110	11.4
Paint from suspect's car	9.11	0.925	215	1240	11.6

Table 13

NEUTRON ACTIVATION ANALYSIS OF BROWN PAINT FROM SAN MATEO CASE

	Ti (%)	Al (%)	Mn (ppm)	Na (cpm/mg)	Sb (cpm/mg)	Zn (cpm/mg)	In (cpm/mg)
Paint from lug wrench	8.8	0.32	604	4,840	2,740	9,210	38,600
Paint from jimmied door	9.9	0.23	535	3,690	2,810	10,200	36,500

The values obtained for the brown paints also showed some small differences. This was possibly due to contamination of the brown paint with the dark blue paint of the wrench itself. This dark blue paint was found to contain a rather large amount of Mn. Also, when such small samples are analyzed, any inhomogeneity in the paint could lead to variations in the amounts of each element detected.

An important point is that no element was detected in one paint of one color that was not detected in the other paint of the same color, and at almost the same concentration. If such were not the case, this would immediately indicate that the two paints had different sources (if suitably cleaned).

The results of these analyses appear to be quite decisive. The successful matching of the two brown paints links the tool to the crime, and the matching of the blue paints links the tool to the suspect's car (or to a car painted with the same brand of paint as the suspect's car). It was decided to try to introduce these results as evidence at the trial.

After two postponements, the trial finally took place early in July, 1964. On July 3, 1964, the activation analysis evidence was introduced and accepted in court. In the testimony, it was stated that it was 99.97% probable that the blue paints were identical in type, and 99.999% probable that the brown paints were identical in type. This was a rough but fairly conservative estimate, calculated as follows. Partially on the basis of previous experience in the analysis of paint samples, it was estimated that if a particular element is detected in two paint samples, the concentrations being within ±30% of each other, the probability that they are not of the same brand of paint would be about 1/5. If n elements were detected and met the above criterion, then the probability that the paints were different would be only about $(1/5)^n$, assuming all of the elements were independent of each other. Since the same five elements were detected in each of the blue paint samples, at very similar levels, the probability that they were different (based on the above assumptions) is $(1/5)^5$ or approximately 1/3000. This corresponds to a probability of 99.97% that they were identical paints. Similarly, for the brown paints, the probability that they were different is $(1/5)^7$ or about 1/100,000, since seven elements were detected. This corresponds to a probability of 99.999% that they were the same. The paint on the wrench was the only real physical evidence against the defendant, all other evidence being circumstantial. The jury found the defendant guilty and he was put on probation.

In an attempt to obtain further evidence linking the suspect to this crime, a sample of the tar material found on the lug wrench was analyzed, together with a similar sample of tar obtained from the trunk of the car. However, because of the large amount of dirt embedded in these tars, the results were of little value. Filtered benzene solutions of these tars were also analyzed, but because of the impurities in the benzene, these results were also of little value.

Blue Automobile Paint

Ten samples of light-blue automobile paints were analyzed. (Samples of automobile paints of different colors had been analyzed previously, and the results are reported in GA-4576.) All of the paints were touch-up enamels. Six of the paints were from the same manufacturer and were virtually indistinguishable from one another by color. The samples were irradiated for 1 min in a thermal-neutron flux of 4.3×10^{12} n/cm^2-sec

and were immediately counted by gamma-ray spectrometry. They were then irradiated for 1 hr in a thermal-neutron flux of 1.8×10^{12} n/cm^2-sec and were counted at various decay times over a period of several days. The results are shown in Table 14. Four elements (Ti, Al, Na, and Mn) were found in all ten paints; nine of the paints also contained Cu. Zinc was found in eight of the paints and Co in three. One paint contained Cr and another contained As. The paints from different manufacturers were found to be very different in composition, both qualitatively and quantitatively. In paints from the same manufacturer, but of different types, the same elements were present in each, but the amounts of these elements varied considerably from sample to sample. Thus, all ten paints were found to be different in composition and therefore distinguishable from one another. They were also different from the two blue paints involved in the San Mateo County court case.

PAPER ANALYSIS

A number of samples of paper were submitted by the U. S. Treasury Department to determine whether it would be feasible to use neutron-activation analysis to characterize and identify paper samples of different types or brands. The identification and tracing of counterfeit currency and other documents is an important problem for the Treasury Department. The samples consisted of different types of papers from two different manufacturers. Duplicate samples of the same paper (from the same batch) were submitted, as well as samples of the same paper but from different batches (labeled "run A" and "run B").

The samples were first irradiated for 30 sec in a thermal-neutron flux of 4.3×10^{12} n/cm^2-sec and were counted immediately by gamma-ray spectrometry to determine the short-lived activities induced. Aluminum and Cl were detected in all of the samples, and Ti was found in most of them. The amounts of these elements found are shown in Table 15. The samples were then irradiated for 1 hr in a thermal-neutron flux of 1.8×10^{12} n/cm^2-sec and counted by gamma-ray spectrometry at several decay times over a period of several days. This revealed the presence of a number of long-lived activities in the samples. Many of these activities have not yet been positively identified.

Figure 20 shows one pair of normalized spectra comparing two samples of the same paper from the same batch. These spectra were exactly superimposed (within counting statistics) and the two spectra are indicated by the round and square data points, respectively. Generally, the spectra obtained at other decay times also agreed very closely with one another. However, when different batches of the same paper were compared, some differences were apparent in the spectra. An example

Table 14

NEUTRON ACTIVATION ANALYSIS OF TEN BLUE AUTOMOBILE PAINTS

Sample	Ti (%)	Al (%)	Na (ppm)	Cu (ppm)	Mn (ppm)	Zn^{65} (cpm/mg)	Co^{60} (cpm/mg)	Also Detected
Pactra Soft Spray 'Namel, Sky Blue S-22	24.2	0.386	193	≤11.8	171	≤0.76	13.5	As
Ferro-Bond Enamel, Baby Blue	18.6	0.255	112	102	1.59	43.8	7.4	--
Pittsburgh Waterspar Enamel, Bonnett Blue	19.6	0.343	230	85.5	258	17.8	≤3.35	--
Pactra Soft Spray 'Namel, Sea Blue 18	15.3	0.214	285	71.6	566	≤0.74	11.3	Cr
Dupli-Color Touch Up, Casmere Blue No. 2	8.00	0.078	59.4	274	6.03	3.52	≤0.32	--
Dupli-Color Touch Up, 1961 General Motors Acrylic	11.3	0.138	73.2	131	2.36	8.14	≤0.26	--
Dupli-Color Touch Up, 1962 General Motors Acrylic	11.8	0.144	48.2	94.6	0.89	5.49	≤0.32	--
Dupli-Color Touch Up, Wedgewood Blue	15.3	0.171	83.0	158	2.62	11.1	≤0.43	--
Dupli-Color Touch Up, 1961 Chrysler Corp.	10.8	0.155	71.1	160	0.74	6.76	≤0.38	--
Dupli-Color Touch Up, Azure Blue	7.57	0.067	40.8	161	4.60	3.60	≤0.53	--

Table 15

NEUTRON ACTIVATION ANALYSIS OF PAPER SAMPLES
(Results, in ppm, for Al, Ti, and Cl only)

Sample	Al	Ti($\times 10^4$)	Cl
Gilbert Lancaster bond, 100% rag, run A	2,714	1.9	146
Gilbert Lancaster bond, 100% rag, run A	2,630	1.9	226
Gilbert Lancaster bond, 100% rag, run B	1,790	2.2	214
Gilbert Radiance bond, 75% rag, run A	2,400	1.4	326
Gilbert Radiance bond, 75% rag, run A	2,060	1.1	194
Gilbert bond, 25% rag, run A	5,459	1.1	370
Gilbert bond, 25% rag, run A	5,600	0.8	290
Gilbert bond, 25% rag, run B	10,323	2.0	557
Gilbert opaque bond, 100% sulph., run A	6,161	1.8	624
Gilbert opaque bond, 100% sulph., run A	5,051	1.3	559
Gilbert opaque bond, 100% sulph., run B	9,228	2.6	490
Gilbert Cardinal bond, 100% sulph., run A	13,182	0.37	543
Gilbert Cardinal bond, 100% sulph., run A	13,693	$\leq$0.16	565
Eagle A Cupon bond, 100% rag, run A	2,172	1.4	192
Eagle A Cupon bond, 100% rag, run A	1,970	1.3	138
Eagle A Agawam bond, 100% rag, run A	4,169	2.0	220
Eagle A Agawam bond, 100% rag, run A	4,168	1.9	174
Eagle A Acceptance bond, 50% rag, run A	6,913	0.94	502
Eagle A Acceptance bond, 50% rag, run A	5,885	0.67	493
Eagle A Trojan bond, 25% rag, run A	6,237	0.77	558
Eagle A Trojan bond, 25% rag, run A	5,601	0.77	435
Eagle A Trojan bond, 25% rag, run B	2,575	0.45	478
Eagle A translucent bond, 100% sulph., run A	498	$\leq$0.03	216
Eagle A translucent bond, 100% sulph., run A	506	$\leq$0.03	285
Eagle A translucent bond, 100% sulph., run B	1,007	$\leq$0.04	240
Eagle A Quality bond, 100% sulph., run A	12,363	0.84	593
Eagle A Quality bond, 100% sulph., run A	12,614	0.76	724

of a quantitative difference obtained is shown in Fig. 21. Spectra obtained after several days' decay also showed qualitative differences in the samples. Samples of different papers were found, in general, to be quite different from one another, both qualitatively and quantitatively. A typical pair of spectra, comparing a 100% rag with a 100% sulphite paper, is shown in Fig. 22. Thus, it appears, on the basis of these results, that the comparison and characterization of paper is very promising. It may also be feasible to identify paper as to batch, in addition to manufacturer and type.

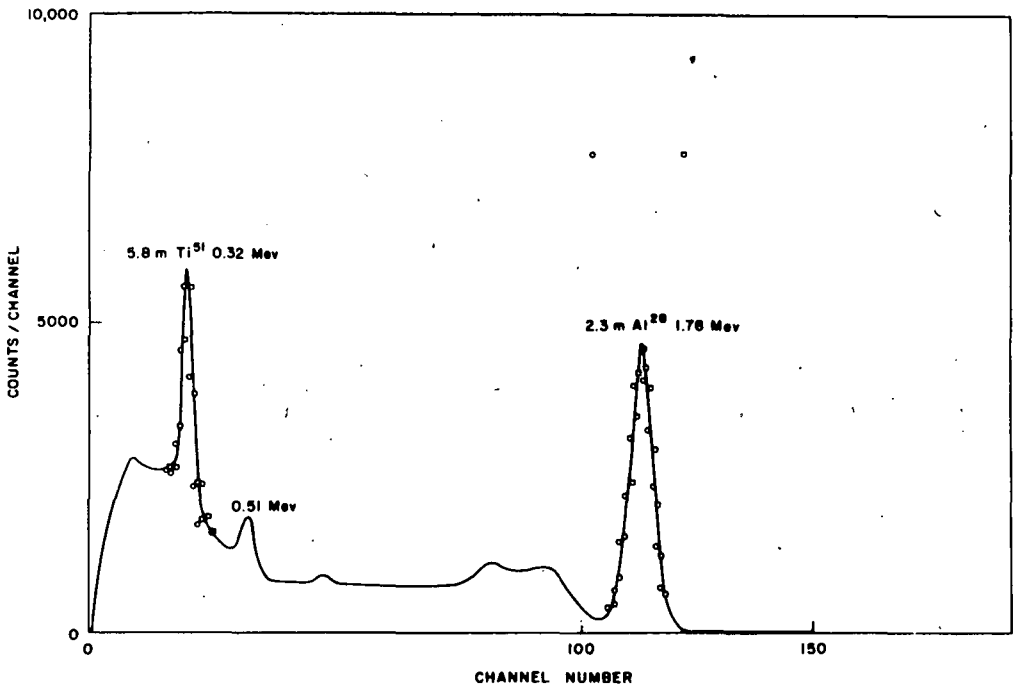

Fig. 20--Gamma-ray spectra comparing two samples of the same paper from the same batch (30-sec irradiation, 100% rag)

FLUORINE IN SAMPLES OF DOG TISSUE

Samples of the liver, stomach, kidneys, bone, and muscle tissue of a dog, as well as the contents of the dog's stomach, were analyzed for fluorine. It was suspected that this dog had been poisoned by sodium fluoracetate in an outbreak of animal poisonings in a midwestern state. The samples, together with a fluorine standard, were irradiated for 5 min in a fast (14 Mev) neutron flux of about 10^8 n/cm^2-sec, using a Cockcroft-Walton type neutron generator. After a period of about 2 hr, to allow for the decay of 10.0-min N^{13} produced by the $N^{14}(n, 2n)N^{13}$ reaction, the samples were counted for 110.2-min F^{18} via the 0.511-Mev positron-annihilation radiation peak. The reaction utilized was the $F^{19}(n, 2n)F^{18}$

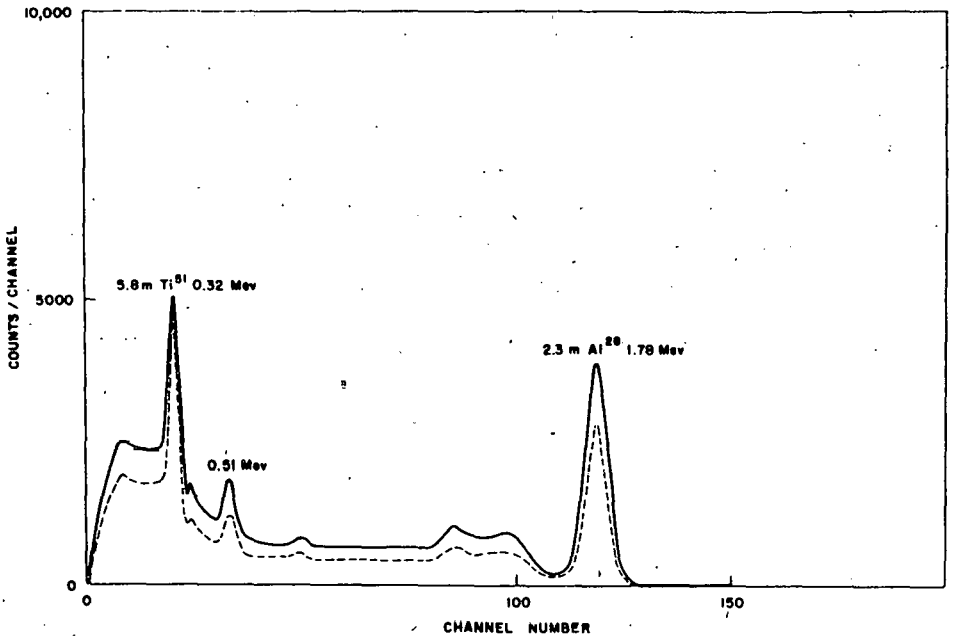

Fig. 21--Gamma-ray spectra comparing two samples of the same paper from different batches (30-sec irradiation, 100% rag)

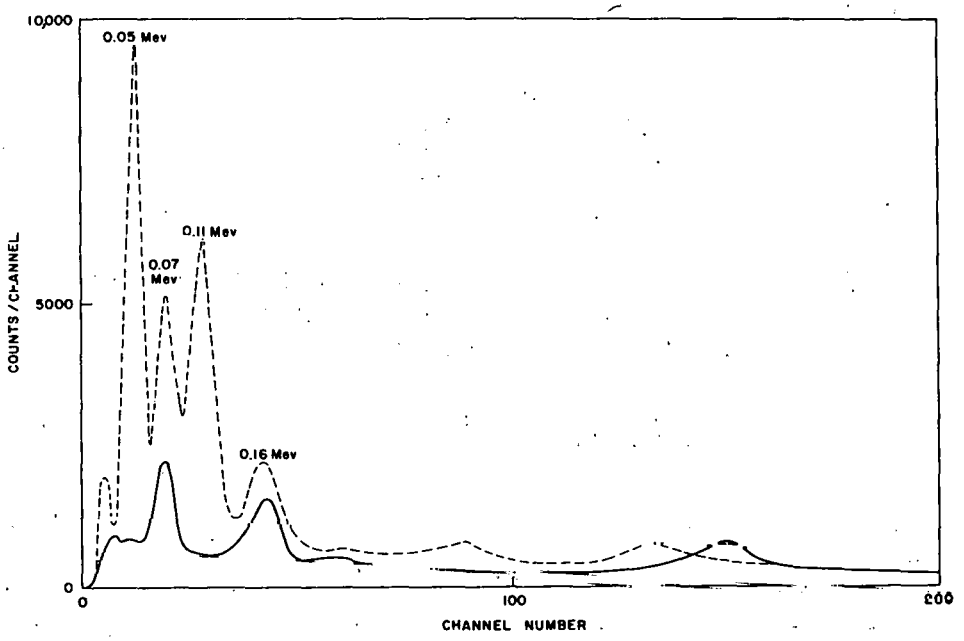

Fig. 22--Gamma-ray spectra comparing two different types of paper (60-min irradiation, 100% rag versus 100% sulph)

reaction. No fluorine was found in any of the tissue samples, but 137 ppm fluorine was found in the contents of the stomach. The 0.511-Mev peak obtained was verified as being from F^{18} by half-life measurements. These results were transmitted to the crime laboratory involved for their interpretation and use.

ARSENIC IN SKIN

A sample of skin was submitted by a West Coast physician for an arsenic determination. The sample was from a patient who, it was suspected, had received a large dose of arsenic through medication over a period of several years. Although there is no criminal action involved here, this analysis was of interest because similar cases may arise in the future involving arsenic poisoning in a crime.

The sample was irradiated for 30 min in the reactor at a thermal-neutron flux of 1.8×10^{12} n/cm^2-sec. After a decay period of about four days (to allow the 15-hr Na^{24} activity to decay), the sample was counted in a well-type scintillation crystal. Sodium-24 was still the principal apparent activity present, and no sign of an 0.561-Mev gamma-ray photopeak from 26.4-hr As^{76} was detected. Magnetic-tape spectrum stripping of the Na^{24} interference still failed to reveal any As^{76} peak. Although no As was detected, a firm upper limit (99.9% confidence level) of ≤ 0.53 ppm was established. The normal As content of human skin is not known, but the limit given is well within the range found by Lenihan in normal human hair and fingernails.

IV. DISCUSSION AND CONCLUSIONS

The gunshot-residue detection method has been refined and extended considerably. Although not infallible, it is far more reliable than the old chemical test--the dermal nitrate "paraffin" test with diphenylamine. In most firings of revolvers and automatic pistols the amounts of Ba and Sb (from the cartridge primer) found on the back of the gun hand are larger than even the largest amounts found thus far on hand blanks (hands of persons who have not recently fired a weapon). In almost all cases, the amounts of Ba and Sb deposited in a firing are larger than the blank average values. The amounts found increase considerably with increasing caliber of the weapon, and increase somewhat with increasing numbers of firings. The paraffin method is a fairly good method for removing residues from the hand, and a good radiochemical-separation procedure is available for the postirradiation isolation of the induced 2.80-day Sb^{122} and 84-min Ba^{139} (with Sb and Ba carriers), prior to counting. Only one rifle study has been carried out, and that was with a 6.5 mm Mannlicher-Carcano Italian rifle of the type used in the Dallas assassination. This study revealed that this type of weapon deposited clearly detectable amounts of both Ba and Sb on both hands and both cheeks of the person firing it, that the diphenylamine procedure was ineffective in detecting residues from the firings, and that the diphenylamine solution washed the traces of Ba off of the paraffin rather effectively, but did not appreciably remove the Sb. Further studies with rifles and shotguns are planned. The cartridge gunpowder-coding idea has been successfully explored, using low levels of Dy and Eu in the gunpowder followed by neutron-activation analysis of the hand residues. This idea is very promising and will be pursued further.

Our experience with the neutron-activation analysis (NAA) characterization of hair samples has been rather disappointing--as has been the case with several other groups who have investigated this problem. There does not seem to be much doubt that hairs from different individuals differ quite considerably in their trace-element compositions, as revealed by high-flux instrumental NAA. However, the problem of proper cleaning of the hair prior to analysis is a formidable one. Until a suitable cleaning method is devised, the results of NAA measurements on hair samples are in most cases not conclusive. There are also other problems in hair analysis not yet solved. In the future, less work will be devoted to the study of hair samples, at least until some new and useful leads arise.

Paint samples have been shown to be excellent candidates for sensitive comparison by means of instrumental NAA. Different brands of paint,

even of the same type and apparent color, have been shown to differ widely in their elemental composition. Even very tiny samples (in the μg to mg range), too minute to be analyzed adequately by other analytical methods, have been analyzed quite successfully by NAA. The San Mateo case (the first NAA paint case in the United States, the first non-Federal NAA case in the United States, and the first NAA case in California) was a very good example of the power and usefulness of the method.

Paper samples have also been shown to be especially suitable to characterization by high-flux instrumental NAA. Earlier studies in this investigation had revealed this to be the case, and this is now confirmed in the study of 27 paper samples submitted by the U.S. Treasury Department. Extension of this phase of the work should be of real value to the Treasury Department.

During the past year, considerable progress has been made in making scientific crime investigators in this Country and abroad aware of the nature and the power (and also limitations) of the NAA method in forensic work. This has been accomplished through presentation of papers by our group at meetings of criminalists, publication of papers on our work in journals, and correspondence and numerous discussions with criminalists.

V. ACKNOWLEDGMENTS

This work has been carried out with the excellent and close cooperation of Mr. Ray H. Pinker, Chief Criminalist of the Los Angeles Police Department. Also, Mr. Wayne Burgess, Criminalist of the San Diego Police Department, has been very interested in this work, and his cooperation has been very valuable. We would also like to express our appreciation and thanks to the Coronor's Offices of Los Angeles County, San Diego County, and San Mateo County.

VI. PAPERS PRESENTED AND PUBLISHED

An invited paper entitled "Neutron Activation Analysis in Criminalistic Studies," by V. P. Guinn and R. R. Ruch, was presented at the Sixteenth Annual Meeting of the American Academy of Forensic Sciences in Chicago (February 27-29, 1964).

The Twenty-Third Semiannual Seminar of the California Association of Criminalists, held in Long Beach, California, May 22-23, 1964, was attended by V. P. Guinn, D. E. Bryan, and Dorothy M. Settle. Invited papers were presented by V. P. Guinn on "Recent Developments in the Detection of Gunshot Residues by Neutron Activation Analysis," and by D. E. Bryan on "Studies of Paints and Hairs by Neutron Activation Analysis."

At the Twenty-Fourth Semiannual Seminar of the California Association of Criminalists in Oakland, California, October 22-23, 1964, invited papers were presented by Dorothy M. Settle on "Neutron Activation Analysis Characterization of Paper Samples," and by D. E. Bryan on "Presentation of Neutron Activation Analysis Data in Court--The San Mateo Paint Case."

A chapter entitled "Non-Biological Applications of Neutron Activation Analysis in Forensic Studies," by V. P. Guinn, was published in Methods of Forensic Science, Vol. III, edited by A. S. Curry (Interscience Publishers, 1964).

A paper entitled "Recent Developments in the Application of Neutron Activation Analysis Techniques to Forensic Problems," by V. P. Guinn, was published in the October 1964 issue of the Journal of the Forensic Science Society (British), Vol. 2, No. 4, pp. 184-191.

A paper entitled "Neutron Activation Analysis in Scientific Crime Detection--Some Recent Developments," by R. R. Ruch, J. D. Buchanan, V. P. Guinn, Sandra C. Bellanca, and R. H. Pinker, was published in the Journal of Forensic Sciences, Vol. 9, pp. 119-133 (January, 1964).

A paper entitled "Activation Analysis in Forensic Science" was presented by V. P. Guinn at the Glasgow Conference on Recent Advances in Activation Analysis (August 27-28, 1964).

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