

APPLICATIONS OF NEUTRON ACTIVATION ANALYSIS IN
SCIENTIFIC CRIME INVESTIGATION

A COMPREHENSIVE REPORT
COVERING THE SIX-YEAR PERIOD
MAY 1, 1962 THROUGH MAY 31, 1968

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PREVIOUS REPORTS IN THIS SERIES

- GA-5556 - May 1, 1962 - October 31, 1963
- GA-6152 - November 1, 1963 - October 31, 1964
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ABSTRACT

During the six-year period from May 1, 1962 through May 31, 1968, the Activation Analysis Group of Gulf General Atomic Incorporated vigorously addressed the possible forensic applications of thermal neutron activation analysis (INAA) and, to a lesser extent, other variations of activation analysis. The results of this effort, which was funded by the U. S. Atomic Energy Commission exclusively for over four years and together with the U. S. Department of Justice in later years, have been significant. A superior means of ascertaining whether a person has fired a gun and the nondestructive characterization of a wide variety of evidence materials through their major and trace element contents have been established as positive contributions of NAA in this program.

Not only has this work generally expanded the number of points by which evidence materials can be characterized, it has provided strong impetus to the establishment of the statistical accuracies with which statements about evidence materials can be made; and work is continuing to define relevant parameters in this connection. The consequence of the work has been a marked improvement in the quality of testimony that can be offered regarding the evidence materials investigated, and the continuing work will lead to further improvement.

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1. INTRODUCTION

This comprehensive report covers all of the work performed at Gulf General Atomic on the program of research "Applications of Neutron Activation Analysis in Scientific Crime Investigation" from the inception of the investigation (May 1, 1962) through May 31, 1968. During the 54-month period from May 1, 1962 through October 31, 1966, this study was funded entirely by the Division of Isotopes Development of the U. S. Atomic Energy Commission - at a level of about 1.3 man-years per year. The funding was for 50 months of this 54-month period, due to a 4-month gap in the funding (January 1 to April 30, 1966). During the subsequent 19-month period, from November 1, 1966 through May 31, 1968, the Office of Law Enforcement Assistance, of the U. S. Department of Justice assisted the Division of Isotopes Development (AEC) in the financial support. This increased support enabled the work to be carried out at an increased pace; namely, at a level of about 2.5 man-years for 12 months, with a 7-month gap in the funding - November 1, 1967 to May 31, 1968.

Four Annual Reports have been issued, covering most of the period included in the present comprehensive report:

1. GA-5556, by D. E. Bryan and V. P. Guinn, covering the period May 1, 1962 through October 31, 1963. ⁽¹⁾
2. GA-6152, by D. E. Bryan and V. P. Guinn, covering the period November 1, 1963 through October 31, 1964. ⁽²⁾
3. GA-7041, by D. E. Bryan, V. P. Guinn, and D. M. Settle, covering the period November 1, 1964 through December 31, 1965. ⁽³⁾
4. GA-8013, by V. P. Guinn, covering the period January 1, 1966 through October 31, 1966. ⁽⁴⁾

1.1 CRIMINALISTICS

Criminalistics may be simply defined as the field of scientific crime investigation, that is, it is a field of endeavor that involves the application of scientific methods to the particular problems of crime investigation. In practice, it normally consists of the scientific examination of physical evidence specimens associated with specific crimes. The criminalist usually endeavors to apply all the known scientific techniques that are available to him, and that he considers may provide useful results, to evidence specimens that he is examining in connection with a particular crime.

The arsenal of more-or-less conventional examinational or analytical techniques typically employed by a criminalist includes microscopy; photography; wet chemical analysis; emission spectrography; X-ray diffraction; atomic absorption; infra-red, visible, and ultra-violet spectrophotometry; gas chromatography; thin-layer chromatography; X-ray fluorescence; etc. In many crime investigation laboratories (city, county, state, federal), many of these techniques are available although only a few are equipped for all of them.

Criminalists are constantly seeking newer and more powerful techniques to help them in their work - techniques that can significantly supplement (or even replace) some of their conventional methods. Some of these newer methods of particular interest are: Electron microprobe spectroscopy, spark-source mass spectrometry, and neutron activation analysis. Very keen interest has been shown in the development, during the past few years, of the field of forensic activation analysis, i. e., activation analysis applied to the field of crime investigation. Some criminalists have been rather dubious of the potential practical value of forensic activation analysis; some have expressed a guarded optimism and "let's wait and see" attitude; some have gone so far as to state that this represents the first major step forward in the field of criminalistics in the last two decades.

A significant aspect of this investigation, from its inception, has been a close liaison with professional criminalists; with various city, county, state, and federal crime investigation laboratories; and with the principal professional societies in this field of study: the American Academy of Forensic Sciences, the Forensic Science Society (British), and the California Association of Criminalists, in particular. Every effort has been made to understand the main problems in the field of criminalistics, to learn the various conventional techniques that are used, and to present the results obtained in this investigation to members of the profession of criminalistics. This close liaison has proved to be very fruitful. It has been essential in the guidance of this study.

1.2 THE PRINCIPLE OF TRACE-ELEMENT CHARACTERIZATION

One of the fundamental principles of the field of criminalistics is the principle of trace-component characterization - especially developed and expounded by Professor Paul L. Kirk, Head of the Department of Criminalistics of the University of California (Berkeley) School of Criminology, and one of the world's leading criminalists. Basically, what this principle states is that: (1) specimens having a "common origin" will be closely similar, not only in their major- and minor-component composition, but also in their trace-component composition, whereas (2) specimens of a given type of material, but of different origins, although they may perhaps be similar in their major- and minor-component composition, will at least exhibit marked differences in their trace-component composition.

This principle is frequently applied in crime investigation work, typically to answer such questions as "Does this evidence specimen (e. g., a chip of paint, a speck of glass, a strand of hair, etc.), associated with the scene of this crime, have the same origin as this evidence specimen,

associated with this suspect?" Various analytical methods are employed to compare the composition (major, minor, and trace) of one evidence specimen with another. Some comparisons are based upon analysis for molecular constituents (e.g., gas chromatography, infra-red spectrophotometry, ultraviolet spectrophotometry), while others are based upon analysis for elemental constituents (e.g., emission spectroscopy, X-ray fluorescence, atomic absorption, activation analysis). Where the comparison is based upon the determination of elements, rather than molecular species, the principle of trace-component characterization becomes the principle of trace-element characterization.

Using one form of analytical technique or another, the principle of trace-component characterization has been applied very fruitfully by criminalists in the comparison of evidence specimens of many different types, e.g., soil, paint, glass, etc. In general, most criminalists seem to feel that this principle could be of much greater practical value if:

1. More trace components could be measured
2. Each detected component could be measured with high precision and accuracy
3. Even ultratrace impurities (< 1 ppb up to 1 ppm) could be detected
4. Many trace components could be measured in even a tiny specimen (even in the range of 1 μ g to 1 mg)
5. The method could be applied nondestructively
6. A broad background of data was available for the proper interpretation of the analytical data, in deciding whether a "common origin" was, or was not, indicated.

As will be developed more fully below, a high-flux thermal-neutron activation analysis (TNAA) provides by far the most powerful method yet

developed to extend the principle of trace-element characterization to greater usefulness, greater definition, and broader field of application.

1.3 ANALYSIS OF MINUTE SPECIMENS

The criminalist is also frequently faced with the problem of identifying the very nature of minute specimens of evidence materials – sometimes only microscopic specks. Is a tiny crystal of material one of the amphetamines, or some other dangerous drug or narcotic? Is a tiny speck of material a speck of paint, or glass, or bullet lead? In such instances, an analytical method of high absolute sensitivity (not necessarily high concentration sensitivity) is needed. Even with an extremely sensitive method, it may then only be possible to detect and measure the major components of such tiny samples – but this may suffice to identify the nature of the specimen. High-flux NAA will not aid in the identification of tiny specimens of drugs and narcotics, but can be of great help in the identification of minute specimens of gunshot residues, paint, glass, bullet lead, etc.

1.4 HIGH-FLUX THERMAL-NEUTRON ACTIVATION ANALYSIS

1.4.1 Brief Treatment of Theory

Since activation analysis, and particularly neutron activation analysis, has been thoroughly described in several books⁽⁵⁻⁷⁾ and many scientific papers, only a brief description is given here.

Activation analysis may be defined as a nuclear method of qualitative and quantitative elemental analysis. It is based upon nuclear reactions (bombardment and radioactive decay), rather than upon chemical reactions or electronic excitations. The method consists of two main steps: (1) irradiation (activation) of a sample, and (2) detection and measurement of induced radioactive species. In the first step, the sample is

bombarded with slow (thermal) neutrons, fast neutrons, energetic photons (gamma rays, bremsstrahlung), or energetic charged particles (e.g., protons, deuterons, ^3He ions, alpha particles), to make most of the elements present in the sample radioactive. In the second step, the activated sample is counted, either with or without one or more preceding radiochemical-separation steps, to detect and measure the induced activity or activities of interest.

Of the various types of activation analysis, by far the most generally powerful, most generally useful, and most fully developed is that involving activation with a high flux of thermal neutrons. Except for some brief studies involving photonuclear activation analysis (PNAA) and activation analysis with fast neutrons (FNAA), all of this investigation has involved the use of high-flux thermal-neutron activation analysis (TNAA). Thus, attention here will be devoted entirely to TNAA.

Thermal neutrons are defined as neutrons that are in thermal (kinetic-energy) equilibrium with their surroundings. At around room temperature ($\sim 20^\circ\text{C}$), this corresponds to an average neutron kinetic energy of about 0.025 electron volt (0.025 eV). Every stable nuclide is capable of capturing a thermal neutron, to form a nuclide of the same element (same Z), but now of one unit greater mass number:



For example, fluorine, which in nature consists entirely of ^{19}F , upon exposure to a flux of thermal neutrons, forms ^{20}F :



Such neutron-capture reactions are usually shown in abbreviated form - for example:



The γ shown in the above equations denotes the one or more "prompt" gamma-ray photons emitted almost immediately (usually within $\sim 10^{-12}$ second) after the capture event – by the excited compound nucleus, as it de-excites to its ground state. Prompt capture gamma rays are emitted regardless of whether the product nucleus is a stable nuclide or a radionuclide of the particular element. These are not the gamma rays that are detected and measured in the usual form of the TNAA method, since they would have to be measured during – rather than after – the irradiation, and this poses severe problems for sensitive detection.

If the (n, γ) product of a particular stable nuclide is merely another stable nuclide of that element, it is of no use in the normal TNAA technique. If, however, the (n, γ) product is a radionuclide of that element, with an appreciable half-life (in practice, anywhere from 0.1 second to several years), its subsequent radioactive decay can be detected and utilized for analytical calculations.

The readily-derived basic equation of TNAA is the simple and well-known one:

$$A_0 = N\phi\sigma S \quad , \quad (4)$$

where:

A_0 is the disintegration rate (in disintegrations per second, dps) of a particular radionuclide species formed in a sample by thermal-neutron capture, just at the end of an irradiation period of duration, t_i ,

N is the number of stable nuclei in the sample that can form this particular radionuclide, via thermal-neutron capture,

ϕ is the steady thermal-neutron flux to which the sample is exposed for a period of time, t_i , the units of ϕ being n/cm^2 -sec,

σ is the isotopic thermal-neutron capture cross section of the stable nuclide of interest, expressed in units of $cm^2/nucleus$, and

S is the saturation factor.

The saturation term, S, is a dimensionless quantity, whose magnitude only ranges between 0 (for $t_i = 0$) and 1 (for $t_i \rightarrow \infty$). It is related to the irradiation time, t_i , and the half-life, T, of the induced radionuclide species by the equation:

$$S = 1 - e^{-0.693 t_i / T} \quad (5)$$

With increasing values of t_i/T , S rapidly approaches the limiting value of 1, acquiring values of 1/2, 3/4, 7/8, 15/16, 31/32, etc., at t_i/T values of 1, 2, 3, 4, 5, etc.

The quantity, N, includes the unknown quantity sought in an analysis: w, the weight of a particular element in the sample. N is given by the equation,

$$N = w a N_A / AW \quad (6)$$

in which:

w is the mass of a particular element present in a sample (in grams),

a is the fractional isotopic abundance of the stable nuclide of that element that forms the detected and measured radionuclide by thermal-neutron capture,

N_A is Avogadro's number, i. e., 6.023×10^{23} atoms/gram-atom, and

AW is the chemical atomic weight of the element of interest.

A numerical example is instructive at this point. If a 1 mg sample of paint is activated for 30 minutes in a thermal-neutron flux of 10^{13} n/cm²-sec, and its ¹²²Sb activity is found to be 85 dps, just at the end of the irradiation, what is the concentration of antimony in the sample? By combining Eqs. 4 and 6, one obtains the equation:

$$w = A_o \cdot AW / \phi \sigma S a N_A \quad (7)$$

For antimony, $AW = 121.76$. The thermal-neutron capture cross section of ¹²¹Sb is 7.0 barns (i. e., 7.0×10^{-24} cm²/nucleus), ¹²¹Sb forming the detected and measured radionuclide, ¹²²Sb, via the ¹²¹Sb(n, γ) ¹²²Sb reaction. The fractional isotopic abundance of ¹²¹Sb, amongst the stable isotopes of antimony, is 0.5725 (57.25%). Since the half-life, T , of ¹²²Sb is 2.80 days, the value of S for a 30-minute irradiation period, t_i , is $1 - e^{-0.693 \times 0.5/2.80 \times 24}$, or 0.00515. The value of w , calculated from Eq. 7, is thus: $85 \times 121.76 / 10^{13} \times 7.0 \times 10^{-24} \times 5.15 \times 10^{-3} \times 0.5725 \times 6.023 \times 10^{23}$, or 8.3×10^{-8} g, i. e., 0.083 μ g Sb. The concentration of Sb in the small paint specimen is thus 83 ppm (i. e., 83 μ g/g), or 0.0083%.

In practice, one almost never determines absolute activities, in dps, but rather measures photopeak counts per second (or per minute) of a particular gamma-ray energy that is characteristic of the induced radionuclide of interest. The relationship between the measured photopeak cps and the radionuclide dps involves the decay scheme of the radionuclide and the photopeak efficiency of the detector for gamma rays of that particular energy, at the counting geometry employed. If one denotes the over-all fractional photopeak counting efficiency (for gamma rays of a particular energy, with a particular detector, at a specified counting geometry) by ϵ , and the fraction of the radionuclide disintegrations that result in the emission of a gamma-ray photon of that particular energy as f , then:

$$\text{photopeak cps} = \text{radionuclide dps} \times \epsilon f \quad . \quad (8)$$

In order not to be dependent upon literature or empirically-determined values for ϕ , σ , t_i , a , N_A , AW , ϵ , and f , one normally instead employs a comparator technique, in which a standard (known) sample of the element of interest is activated along with the unknown sample (or samples) – at exactly the same neutron flux, ϕ , for exactly the same period of time, t_i . Whatever the exact values may be for σ , a , N_A , and AW , they are exactly the same for sample and standard (providing suitable precautions are taken). Then, if Eq. 7 is written for both sample and standard, and one equation is divided by the other, the terms, AW , ϕ , σ , S , a , and N_A all cancel out, and one obtains the sample equation,

$$w(\text{sample})/w(\text{std}) = A_o(\text{sample})/A_o(\text{std}) \quad . \quad (9)$$

If one denotes the photopeak cps by A'_o , then,

$$A'_o = A_o \epsilon f \quad . \quad (10)$$

If this substitution is made in Eq. 9, one obtains the equation:

$$w(\text{sample})/w(\text{std}) = A'_o(\text{sample})/A'_o(\text{std}) \quad , \quad (11)$$

since, if sample and standard are counted under identical conditions, $\epsilon f(\text{sample}) = \epsilon f(\text{std})$. Equation 11 is not only true at time zero (i.e., just at the end of the irradiation), but also at any specified subsequent decay time, t :

$$w(\text{sample})/w(\text{std}) = A'_t(\text{sample})/A'_t(\text{std}) \quad , \quad (12)$$

since each induced radionuclide species decays away according to the first-order radioactive-decay equation,

$$A_t = A_o e^{-0.693 t/T} , \quad (13)$$

in which T is the half-life of the radionuclide species.

1.4.2 Sensitivities of Detection

Many of the important applications of high-flux TNAA that have developed, or are developing – in various fields, including that of criminalistics – depend upon the ultra-sensitive detection and quantitative measurement feature of the method, for a rather large number of elements. Just how sensitive the method is depends upon the particular element, the magnitude of the thermal-neutron flux available, how long an irradiation period one feels is reasonable (for those elements that form longer-lived radionuclide products), the detection efficiency of the available counting equipment, and the length of counting time one feels is reasonable (especially, again, for the longer-lived radionuclide products).

An illustrative table of sensitivities is presented in Table 1. These are calculated sensitivities, for an arbitrary – but quite reasonable – set of conditions. These conditions are: (1) a 1-hour (maximum) irradiation at a thermal-neutron flux of 10^{13} n/cm²-sec, and (2) direct gamma-ray spectrometry of the activated sample. In the gamma-ray spectrometry, a 3-in. x 3-in. solid NaI(Tl) scintillation detector, and a sample-to-detector face distance of 2 cm are assumed. Decay schemes are taken from the "Table of Isotopes,"⁽⁸⁾ and detector efficiencies and photofractions are taken from Heath's "Gamma-Ray Spectrum Catalogue".⁽⁹⁾ The minimum detectable net photopeak counting rates are arbitrarily taken as 1000 cpm (for half-lives less than one minute), 100 cpm (for half-lives

Table 1
CALCULATED LIMITS OF DETECTION FOR 70 ELEMENTS
VIA INSTRUMENTAL TNAA

(Thermal-neutron flux of 10^{13} n/cm²-sec for 1 hour,
NaI(Tl) gamma-ray spectrometry)

Element	(n, γ) Product	Half-Life	E _{γ} (MeV)	Photopeak (cpm/g)	Limit of Detection, (μ g)
F	F ²⁰	11.56s	1.63	1.0×10^{10}	1×10^{-2}
Ne	Ne ²³	37.6s	0.439	2.1×10^9	5×10^{-1}
Na	Na ²⁴	14.96h	1.369	1.9×10^{10}	5×10^{-4}
Mg	Mg ²⁷	9.46m	0.842	3.4×10^9	3×10^{-2}
Al	Al ²⁸	2.31m	1.780	1.1×10^{11}	9×10^{-4}
Si	Si ³¹	2.62h	1.26	$3. \times 10^5$	3×10^1
S	S ³⁷	5.07m	3.09	4.9×10^6	2×10^1
Cl	Cl ³⁸	37.29m	1.60	7.1×10^9	1×10^{-2}
Ar	Ar ⁴¹	1.83h	1.293	2.8×10^9	4×10^{-3}
K	K ⁴²	12.36h	1.524	2.6×10^8	4×10^{-2}
Ca	Ca ⁴⁹	8.8m	3.10	4.0×10^8	2×10^{-1}
Sc	Sc ^{46m}	19.5s	0.142	3×10^{12}	3×10^{-4}
Ti	Ti ⁵¹	5.79m	0.320	7.1×10^9	1×10^{-2}
V	V ⁵²	3.75m	1.434	1.3×10^{12}	8×10^{-5}
Cr	Cr ⁵¹	27.8d	0.320	6.9×10^7	1×10^{-1}
Mn	Mn ⁵⁶	2.576h	0.847	1.5×10^{12}	7×10^{-6}
Fe	Fe ⁵⁹	45.6d	1.095	4.0×10^5	2×10^1
Co	Co ^{60m}	10.47m	0.059	3×10^{12}	3×10^{-5}
Ni	Ni ⁶⁵	2.564h	1.481	2.3×10^8	4×10^{-2}
Cu	Cu ⁶⁴	12.80h	0.511(β^+)	1.8×10^{10}	5×10^{-4}
Zn	Zn ^{69m}	13.8h	0.439	7.1×10^8	1×10^{-2}
Ga	Ga ⁷²	14.12h	0.835	2.4×10^{10}	4×10^{-4}
Ge	Ge ⁷⁵	82m	0.265	6.3×10^9	2×10^{-3}
As	As ⁷⁶	26.4h	0.559	1.7×10^{10}	6×10^{-4}
Se	Se ^{81m}	56.8m	0.103	9.1×10^9	1×10^{-2}

Table 1 (Continued)

Element	(n, γ)Product	Half-Life	E _{γ} (MeV)	Photopeak (cpm/g)	Limit of Detection, (μ g)
Br	Br ⁸²	35.34h	0.554	1.3×10^{10}	8×10^{-4}
Kr	Kr ^{83m}	1.86h	0.033	3×10^{11}	3×10^{-5}
Rb	Rb ⁸⁸	17.8m	1.863	1.1×10^9	9×10^{-2}
Sr	Sr ^{87m}	2.83h	0.388	1.9×10^{10}	5×10^{-4}
Y	Y ^{90m}	3.1h	0.482	3×10^{10}	3×10^{-4}
Zr	Zr ⁹⁷	17.0h	0.747	3.4×10^7	3×10^{-1}
Nb	Nb ^{94m}	6.29m	0.042	3×10^{10}	3×10^{-3}
Mo	Mo ¹⁰¹	14.6m	0.191	1.1×10^{10}	9×10^{-3}
Ru	Ru ¹⁰⁵	4.44h	0.726	5.1×10^9	2×10^{-3}
Rh	Rh ^{104m}	4.41m	0.051	3.4×10^{12}	3×10^{-5}
Pd	Pd ^{109m}	4.69m	0.188	2.8×10^{10}	4×10^{-3}
Ag	Ag ¹¹⁰	24.4s	0.658	1.5×10^{13}	7×10^{-5}
Cd	Cd ^{111m}	48.6m	0.150	3.1×10^9	3×10^{-2}
In	In ^{116m₁}	54.0m	1.293	7.4×10^{12}	1×10^{-5}
Sn	Sn ^{123m}	39.5m	0.160	3.7×10^9	3×10^{-2}
Sb	Sb ¹²²	2.80d	0.564	7.7×10^9	1×10^{-3}
Te	Te ¹³¹	24.8m	0.150	2.8×10^{10}	4×10^{-3}
I	I ¹²⁸	24.99m	0.441	2.6×10^{11}	4×10^{-4}
Xe	Xe ^{135m}	15.6m	0.527	3×10^{10}	3×10^{-3}
Cs	Cs ^{134m}	2.895h	0.128	1.2×10^{11}	8×10^{-5}
Ba	Ba ¹³⁹	82.9m	0.166	5.7×10^{10}	2×10^{-4}
La	La ¹⁴⁰	40.22h	1.596	1.3×10^{10}	8×10^{-4}
Ce	Ce ¹⁴¹	32.5d	0.145	3.7×10^8	3×10^{-2}
Pr	Pr ¹⁴²	19.2h	1.57	1.6×10^9	6×10^{-3}
Nd	Nd ¹⁴⁹	1.8h	0.210	3×10^9	3×10^{-3}
Sm	Sm ¹⁵³	46.8h	0.103	1.6×10^{11}	6×10^{-5}
Eu	Eu ^{152m₁}	9.3h	0.963	8.3×10^{11}	1×10^{-5}
Gd	Gd ¹⁵⁹	18.0h	0.363	1.4×10^9	7×10^{-3}
Tb	Tb ¹⁶⁰	72.1d	0.966	7.1×10^7	1×10^{-1}
Dy	Dy ^{165m₁}	1.26m	0.108	6.6×10^{13}	2×10^{-6}
Ho	Ho ¹⁶⁶	26.9h	0.081	2.8×10^{11}	4×10^{-5}

Table 1 (Continued)

Element	(n, γ)Product	Half-Life	E_{γ} (MeV)	Photopeak (cpm/g)	Limit of Detection, (μ g)
Er	Er ¹⁷¹	7.52h	0.308	1.1×10^{10}	9×10^{-4}
Tm	Tm ¹⁷⁰	134d	0.084	3.4×10^8	3×10^{-2}
Yb	Yb ¹⁷⁷	1.9h	0.151	6.6×10^9	2×10^{-3}
Lu	Lu ^{176m}	3.69h	0.088	3×10^{11}	3×10^{-5}
Hf	Hf ^{180m}	5.5h	0.444	1.9×10^{11}	5×10^{-5}
Ta	Ta ^{182m}	16.5m	0.172	5.7×10^9	2×10^{-2}
W	W ¹⁸⁷	23.9h	0.686	3×10^{10}	3×10^{-4}
Re	Re ^{188m}	18.7m	0.106	8.3×10^{11}	1×10^{-4}
Os	Os ^{191m}	13.0h	0.074	3×10^{10}	3×10^{-4}
Ir	Ir ¹⁹⁴	17.4h	0.328	2.2×10^{11}	5×10^{-5}
Pt	Pt ¹⁹⁹	31m	0.075	3×10^{10}	3×10^{-3}
Au	Au ¹⁹⁸	2.697d	0.412	2.3×10^{11}	4×10^{-5}
Hg	Hg ^{197m}	24h	0.134	5.1×10^9	2×10^{-3}
Pb	Pb ^{207m}	0.80s	0.570	3×10^{10}	3×10^{-2}

between one minute and one hour), and 10 cpm (for half-lives longer than one hour). Most of these criteria are those selected some years ago in this Laboratory, by J. D. Buchanan.⁽¹⁰⁾ The values shown in Table 1 are taken, with slight modification, from the more-detailed compilation prepared by H. R. Lukens⁽¹¹⁾ of this Laboratory. For many elements, more than one (n, γ) product can be used for detection. In such cases, the one providing the most sensitive detection is given in Table 1. The sensitivity values of Table 1 are summarized in Table 2.

Table 1 reveals two main points: (1) high-flux instrumental TNAA provides anywhere from fairly sensitive to extremely sensitive detection for a large number (70) of elements, and (2) the sensitivity of detection (limit of detection) varies widely amongst these elements: ranging from as low as almost 10^{-6} μg , for a few ultra-sensitive elements, to as high as a few tens of μg , for a few rather insensitive elements. It should be noted that the limits of detection shown are approximately attainable in practice, under the stipulated irradiation and counting conditions, under "interference-free" conditions. In many actual analyses, interferences from other elements present are not appreciable – or can be suitably minimized by optimum selection of irradiation and decay times – and hence these interference-free limits of detection can be closely approached. In other actual analyses, interferences from other elements present will increase the attainable limits of detection for at least some of the elements of interest. Such interferences, of course, can be removed – if necessary – by radiochemical separations with carriers, then allowing one to attain interference-free limits of detection.

Most of the measurements conducted to date in this investigation have been carried out with the 250 kW TRIGA Mark I reactor – at thermal-neutron fluxes of 1.8×10^{12} n/cm²-sec (in the rotary specimen rack) or 2.5×10^{12} n/cm²-sec (in the pneumatic tube position), rather than at

Table 2
SUMMARY OF TABLE 1 SENSITIVITY VALUES

Calc. Limit of Detection, μg	Elements
$1 - 3 \times 10^{-6}$	Dy
$4 - 6 \times 10^{-6}$	
$7 - 9 \times 10^{-6}$	Mn
$1 - 3 \times 10^{-5}$	Co, Kr, Rh, In, Eu, Lu
$4 - 6 \times 10^{-5}$	Sm, Ho, Hf, Ir, Au
$7 - 9 \times 10^{-5}$	V, Ag, Cs
$1 - 3 \times 10^{-4}$	Sc, Y, Ba, W, Re, Os
$4 - 6 \times 10^{-4}$	Na, Cu, Ga, As, Sr, I
$7 - 9 \times 10^{-4}$	Al, Br, La, Er
$1 - 3 \times 10^{-3}$	Ge, Nb, Ru, Sb, Xe, Nd, Yb, Pt, Hg
$4 - 6 \times 10^{-3}$	Ar, Pd, Te, Pr
$7 - 9 \times 10^{-3}$	Mo, Gd
$1 - 3 \times 10^{-2}$	F, Mg, Cl, Ti, Zn, Se, Cd, Sn, Ce, Tm, Ta, Pb
$4 - 6 \times 10^{-2}$	K, Ni
$7 - 9 \times 10^{-2}$	Rb
$1 - 3 \times 10^{-1}$	Ca, Cr, Zr, Tb
$4 - 6 \times 10^{-1}$	Ne
$7 - 9 \times 10^{-1}$	
1 - 3	
4 - 6	
7 - 9	
$1 - 3 \times 10^1$	Si, S, Fe
Median $\sim 0.002 \mu\text{g}$	

10^{13} n/cm²-sec. For thermal-neutron fluxes of around 2×10^{12} n/cm²-sec, the limits of detection in the tables is about 0.002 μ g, so for a 1-hour irradiation at a thermal-neutron flux of 2×10^{12} n/cm²-sec, the median becomes about 0.01 μ g, with some elements detectable down to a level of about 10^{-5} μ g (e.g., Dy), and some rather insensitive ones detectable only down to a level of about 100 μ g (e.g., Si, S, Fe). Although the photo-peak cpm/g values of Table 1 are calculated values rather than experimental, many of them have been also determined experimentally at this Laboratory - see, for example, the publication by H. P. Yule.⁽¹²⁾ Almost all of the experimentally-determined sensitivities have been found to agree with the calculated sensitivities to within a factor of $\pm 2 - 3$.

These, of course, are not ultimate sensitivities, but most are quite adequate, or even more than adequate, for most analytical requirements. If in some cases one needs even more sensitivity, one has several possibilities available:

1. Use an even higher thermal-neutron flux (if available), and/or
2. Use an irradiation period longer than one hour (appreciably helpful only for those elements that form a detected and measured activity with a half life longer than an hour or two), and/or
3. Use a longer-than-normal counting period (also helpful only for the longer-lived induced activities).

Concentration sensitivity (as opposed to absolute sensitivity) can be improved by use of somewhat larger samples (e.g., 100 mg instead of 10 mg, providing that sufficient sample is available, and that there are no severe problems of thermal-neutron self-shielding in the larger samples). For a small number of elements, a better sensitivity can be achieved via NAA with fast neutrons (14 MeV or fission-spectrum), photonuclear activation

analysis, or charged-particle activation analysis. Each of these techniques, except CPAA, has been used in this investigation to provide improved sensitivities for certain elements – but only to a limited extent.

1.4.3 Nondestructive Instrumental Technique

Wherever it is applicable, the nondestructive – purely instrumental – form of the activation analysis method is usually preferred to the destructive, radiochemical-separation form of the method. Primarily, this preference is due to the economy in manpower effort. However, the nondestructive feature of the instrumental technique is also of importance in forensic studies of actual case evidence samples, since the evidence samples are thus preserved for possible introduction in court, or for subsequent further analysis or examination by other methods.

The instrumental technique is based upon multichannel gamma-ray spectrometry of activated samples (and standards) – including the characteristic X-rays emitted as a result of radioactive decay via electron capture (EC) and internal conversion (IC), as well as decay gamma rays and positron-annihilation radiation (0.511 MeV). Most of the earlier work in this field, and almost all of the gamma-ray spectrometry work carried out during the period of this investigation included in this report, has been conducted with thallium-activated sodium iodide (NaI(Tl)) scintillation detectors. More recently, an increasing amount of effort in this field is being carried out with lithium-drifted germanium semiconductor (Ge(Li)) detectors, which exhibit a much better energy resolution than do NaI(Tl) detectors – typically some 15 times better.

In gamma-ray spectrometry, any particular radionuclide of interest is identified via the location of one (or more) of its gamma-ray or X-ray "photopeaks", i. e., total-absorption peaks, in the observed pulse-height spectrum of the activated sample. Thus, the identification is based upon gamma-ray energies. If the photopeak of interest is symmetrical,

and of the proper width (full-width at half-maximum) for that gamma-ray energy and that particular detector, the identification is in most cases quite firm – especially with a high-resolution Ge(Li) detector. One then calculates the net photopeak counting rate (above the Compton continuum) for the sample, and also for the standard sample of that element, corrects both rates to the same decay time, and calculates the number of micrograms of that element in the sample, via the comparator equation. If desired, the μg value can be converted to a ppm value (μg of element per gram of sample) from the sample weight. From the counting statistics involved, one can also compute the standard deviation (σ) of the μg and ppm results. If sample and standard were not activated at the same thermal-neutron flux, or were irradiated for different periods of time, or were counted at different counting efficiencies, suitable normalization corrections must of course be made before inserting values into the comparator equation (Eqs. 11 or 12).

If the photopeak of interest is not due to gamma rays of only one energy, but consists of total-absorption pulses from gamma rays of two or three closely-similar energies, some additional steps must be taken. As mentioned above, in such instances, the photopeak will be: (1) too broad, and (2) usually asymmetrical. If the two or three components of the photopeak are due to radionuclides that have appreciably different half-lives, the various contributions can be unravelled by counting the sample at three or more decay times, and resolving the decay data. Also, one can often resolve such a complex peak into its components mathematically, via manual or computer calculations – or even by means of an analog device such as the DuPont Curve Resolver. These techniques of resolving a peak into its components are based upon treating the observed peak as a composite of two or more approximately Gaussian peaks (of somewhat different energies and different sizes). If all else fails, of course, one can resort to radiochemical separation with carriers.

Even if there is no overlapping-photopeak problem, the presence of high counting rates from gamma rays of higher energy than the photopeak of interest exerts an effect upon the instrumental limit of detection of the element of interest – by raising the Compton level upon which the photopeak is superimposed (thus worsening the counting statistics of the net photopeak counting rate). If optimization of irradiation and decay times is not of sufficient help, one can sometimes improve the counting statistics by: (1) using a thicker detector, or (2) employing a detector with a Compton-suppression anti-coincidence annulus. If the induced activity of interest emits gamma rays of two different energies in cascade, coincidence counting can also be helpful. Again, if all else fails, one can resort to radiochemical separation with carriers.

The instrumental technique is especially useful when one wishes to detect and measure as many elements in a sample as possible – rather than merely looking for one or a few specified elements. Such "scanning" analyses can, with some kinds of samples often encountered as evidence materials in forensic work, reveal many elements in a sample – even though the ones detected were not necessarily expected or looked for specifically. At Gulf General Atomic, a regular TNAA scanning procedure was developed for this type of situation. In this procedure, a sample is irradiated in the reactor for a 1-minute period, followed by gamma-ray spectrometry at one or two short decay times, then for a 30-minute period, followed by gamma-ray spectrometry at several longer decay times, and sometimes for an even longer period of time, followed by gamma-ray spectrometry at a few very long decay times. All of the resulting pulse-height data are then fed to the UNIVAC 1108 computer. Various computer programs developed at GGA then carry out various operations on the data. These include:

1. Searching the pulse-height data for all statistically-significant photopeaks,
2. Testing each peak for purity,
3. Resolving complex peaks into their components,
4. Computing the net photopeak counting rate of each detected peak,
5. Identifying each detected radionuclide via its gamma-ray energy (or energies),
6. Correcting all net photopeak counting rates to time zero (i. e. , at the end of the irradiation,
7. Computing μg and ppm values, and their respective standard deviations, for each element detected - by comparison with a library of pulse-height and yield data for all of the elements, previously obtained under the same irradiation and counting conditions,
8. Calculating a firm 3σ upper limit for the amount and concentration of each undetected element - from the counting statistics in the region of the spectra where each undetected photopeak should appear,
9. Printing out a list of "best" (most precise) μg and ppm values for each detected element, and their respective standard deviations, and the lowest upper limit established for each undetected element,
10. Plotting out each convolution-smoothed pulse-height spectrum, in semi-logarithmic form, with the unsmoothed original data points superimposed.

This multi-element scanning technique is of particular value when evidence samples are to be compared to establish the probability of "common origin", or of different origin. It is useful for comparisons of materials such as hair, paint, plastics, rubber, paper, bullet lead, oil, etc.

1.4.4 Destructive Radiochemical-Separation Technique

As mentioned earlier, this technique is, in general, less desirable than the purely-instrumental technique because it is more time consuming, and because it requires the destruction of the sample. However, in certain instances it must be employed, or is to be preferred to the instrumental technique. These instances include situations in which: (1) the element of interest forms, by (n, γ) reaction, a radionuclide that is either a pure β^- emitter (e.g., 14.28-day ^{32}P from phosphorus) or almost a pure β^- emitter (e.g., 2.62-hour ^{31}Si from silicon; ^{31}Si emits a gamma ray in only 0.07% of its β^- disintegrations), (2) gamma-ray detection is interfered with by one or more gamma rays of closely similar energy emitted by other activated elements in the sample, (3) gamma-ray detection is interfered with by an extremely high Compton level in the pulse-height spectrum, caused by higher energy gamma rays from one or more other radionuclides present in the activated sample, or (4) beta detection provides somewhat more sensitive detection than does gamma-ray detection. An example of Situation (3) is the TNAA determination of barium in gunshot-residue samples. The paraffin lifts remove gunshot-residue material from the skin, but also remove considerable NaCl, from perspiration. When the sample is activated in the reactor, the greatly predominant 14.96-hour ^{24}Na (1.369 MeV and 2.754 MeV gamma rays) and 37.29-minute ^{38}Cl (1.64 MeV and 2.170 MeV gamma rays) induced activities prevent one from instrumentally determining the much smaller amount of 82.9-minute ^{139}Ba activity (0.166 MeV gamma rays) present. Thus, one separates the ^{139}Ba activity chemically from the ^{24}Na , ^{38}Cl , and other activities, using ^{+2}Ba carrier - thus eliminating interferences prior to counting.

Briefly, radiochemical separations involve: (1) putting the activated sample into solution, along with a carrier amount of the element of

interest, (2) chemically equilibrating the induced activity of interest with the carrier, (3) chemically separating the element of interest, (4) checking the radiochemical purity of the separated activity, (5) counting the separated sample, and (6) measuring the chemical yield (i. e., the percentage recovery of the carrier). Dissolution of the sample can be accomplished in various ways, depending upon the matrix material, the amount of sample, and the element of interest. The various methods used include dry-ashing (with various oxidizing acids, such as HClO_4 , H_2SO_4 , HNO_3 , or aqua regia), and plasma-ashing - in each case ending up with an acidic solution. Chemical equilibration is usually achieved by refluxing the acidic sample solution, containing the carrier, or - in more difficult cases - alternately oxidizing and reducing the element of interest, usually in acid solution. Chemical separation of the element of interest can be achieved in various ways: by precipitation, volatilization, solvent extraction, ion exchange, etc. Radiochemical purity can be checked by counting the separated activity on a gamma-ray spectrometer, by beta counting with aluminum β^- absorbers of a few known thicknesses (to check the β^- E_{max}), and by counting at two or more decay times (to check the half-life). The chemical yield (recovery) can be determined by any of several ordinary analytical methods (gravimetric or volumetric determination, atomic absorption, spectrophotometry, etc.).

1.4.5 Precision and Accuracy

In general, at levels well above the limit of detection for any particular element, the amount of the element can be determined to a precision and absolute accuracy approaching $\pm 1\%$ of the value. In some instances, the precision can even be improved to a standard deviation of only $\pm$ a few tenths of a percent of the value, but this is not easy to achieve. The counting statistics alone require 10^6 counts to give a σ of $\pm 0.1\%$, even

with zero underlying Compton-continuum and background counts. Considering a more usual case, where perhaps only 10^4 counts are obtained in a given photopeak – and including other factors besides the counting statistics – a precision (1σ) of around $\pm 2-3\%$ of the value is more common. Under the proper analytical conditions, the absolute accuracy becomes essentially the same as the precision. Precisions and accuracies of $\pm 2-3\%$ of the value are quite sufficient for most analytical problems. By the very definition of the term, limit of detection, of course, the precision rapidly becomes markedly poorer as the value closely approaches the limit of detection. For almost all of the experimental values reported in this investigation, the standard deviation of the value – based only on the counting statistics – has also been calculated. With σ reported values greater than about 2% of the value, the counting statistics are the dominant factor in the over-all (but unknown) precision of the measured value – whereas, with σ reported values of $< 2\%$ of the value, the over-all precision may be somewhat poorer than the indicated σ value, since it is based only on the (in such cases, rather good) counting statistics.

2. ACTIVATION ANALYSIS FACILITIES AT GULF GENERAL ATOMIC

The conduct of an extensive and intensive investigation of possible fruitful applications of the neutron activation analysis method in the field of criminalistics requires the availability of high-caliber (1) nuclear reactor facilities, (2) counting equipment - especially NaI(Tl) and Ge(Li) multichannel gamma-ray spectrometers, (3) radiochemical separation facilities and procedures, and (4) computer facilities and computer programs, as well as a staff of highly experienced and competent radiochemists, especially skilled in the field of activation analysis. At least some of the staff must also be quite conversant with the field of criminalistics, with the conventional analytical methods already employed by criminalists, and with the relative merits of the activation analysis method compared with these other analytical methods.

In this section, the relevant physical facilities at GGA are described.

2.1 NUCLEAR REACTORS

Housed in a single building, next door to the GGA Activation Analysis Building, are three TRIGA research-type nuclear reactors: the Mark I, Mark F, and Mark III reactors. Almost all of the work carried out in this particular investigation has been conducted with the Mark I reactor, but some irradiations have employed the Mark F or the Mark III. All three are pool-type reactors.

2.1.1 TRIGA Mark I

This reactor can be operated at any desired steady power level up to 250 kW, and can be pulsed to any desired peak power level up to 1,000 MW. The principal relevant sample irradiation positions in this reactor are two pneumatic-tube termini, in vacant positions in the outermost ring (F ring) of fuel elements, and the 40-tube rotary specimen rack. At 250 kW steady-state operation, the thermal-neutron fluxes in the F ring and in the rotary rack are, respectively, 2.5×10^{12} n/cm²-sec and 1.8×10^{12} n/cm²-sec. The corresponding fast-neutron fluxes (> 10 keV) are, respectively, 5.3×10^{12} and 1.5×10^{12} n/cm²-sec. In a 1,000 MW pulse, the peak thermal- and fast-neutron fluxes in the F ring (pneumatic-tube) position attained are 1.0×10^{16} and 2.1×10^{16} n/cm²-sec, respectively, with a pulse full-width at half-maximum of 16 milliseconds (corresponding to nvt values of 1.7×10^{14} and 3.6×10^{14} n/cm², respectively).

The reactor core consists of 70-80 vertically-mounted fuel elements arranged in five concentric rings (lettered, starting with B for the first ring from the core center to F, the outermost ring). The central hole (sometimes called the A ring) is a "glory hole" irradiation position. The other rings contain the following number of positions: B(6), C(12), D(18), E(24), F(30), for a total of 90 positions (or 91, including the one A position). Some 70-80 of the positions are occupied by fuel elements, four by boron-loaded control rods, two (in the F ring) by pneumatic-tube termini, and the remaining positions are unoccupied, except by water. Of the four control rods, two or three are used for control during steady-state operation, and one (called a transient rod) is a pneumatically-driven rod used for pulse operation. The circular core is only about 18 inches in diameter, by 28 inches high. Each fuel element is 15 inches high by 1.4 inches diameter, and consists of an aluminum-clad rod of zirconium

(91.5%)-uranium (8.5%) alloy that has been hydrided to a 1/1 H/Zr atomic ratio. The uranium is enriched to 20% ^{235}U . Each 15-inch fuel rod has a 4-inch length of graphite at each end. The core is located in a pool of de-ionized water 6.5 feet in diameter by 20 feet deep (16 feet of water above the top of the core). An outside loop constantly runs the pool water through a heat exchanger and an ion-exchange column (continuously monitored for radioactivity).

The core is surrounded by an annulus of graphite, inside of which is an air cavity through which a rotary specimen rack moves. This rack contains 40 tubes, in which samples can be placed. Samples are loaded into these tubes (and unloaded) one at a time from the surface of the pool, via a vertical loading tube. Typically, each sample to be activated – sealed in its own small polyethylene vial – is placed inside a larger polystyrene tube (capsule), and then lowered into one of the 40 rotary rack tubes. The rack is then advanced one position and the next sample lowered into the next tube, etc. When all the samples to be irradiated have been placed in the rack (anywhere from 1 to 40), the rotation motor is started to rotate the rack around the reactor core at 1 rpm. The reactor is then quickly brought up to the desired power level (usually 250 kW), and run steadily for the desired period of time (usually 30 minutes; or 1, 2, or 4 hours). Only a few minutes are required to bring the reactor up to power, and it is shut off abruptly by "scramming". Loading and unloading the rotary rack require about one minute each, per capsule. During the unloading operation, each capsule is remotely monitored, for safety, as it reaches the surface of the pool. Because of the rack rotation, every sample position in the 40-tube rack is exposed to exactly the same average neutron flux, thus greatly facilitating NAA work.

The regular pneumatic tube has a transit time, in each direction, of 2.5 seconds, and requires that the sample vial be placed inside a larger,

thick-walled, polyethylene "rabbit". The pneumatic tube inlet and outlet are located in a counting room near the reactor, in the reactor building. Upon its return, the rabbit is automatically monitored, for safety. If it is safe to handle, it is opened, and the sample vial rapidly placed on top of a shielded 3-in. x 3-in. solid NaI(Tl) detector (or in the well of a 3-in. x 3-in. well-type NaI(Tl) detector), coupled to a 400-channel pulse-height analyzer – for a short counting period. Automatic precision timers measure the irradiation, decay, and counting times.

A newer and faster (0.5-second transit time) pneumatic tube is also used, where the induced activity (or activities) of interest is very short-lived. This tube also terminates in a vacant fuel-element position in the F ring of the TRIGA Mark I reactor core. With this faster pneumatic tube, no secondary containment is needed – the sample being placed in a small, thick-walled, polyethylene container, made in the GGA machine shop. As the activated sample leaves the reactor core, it passes a photocell which triggers a timer and turns on the pulse-height analyzer. The sample goes directly into the counter. The pulse-height analyzer can be operated in either a pulse-height or multichannel-scaling mode, as desired.

In some instances, a Ge(Li) detector is used in the pneumatic-tube measurements. Typically, the 2.5-second transfer system is used for measurements of induced activities with half-lives in the range of about 5 seconds to 10 minutes. The 0.5-second transfer system is used for measurements of induced activities with half-lives in the range of about 0.5 second to 5 seconds. Due to the appreciable enhancements of sensitivities attainable via high-intensity reactor pulses for very short-lived induced activities,⁽¹³⁻¹⁷⁾ the fast pneumatic tube is often used in conjunction with reactor-pulsing activations. A photograph of the Mark I TRIGA is shown in Fig. 1, a diagram of it in Fig. 2, and a view of the 2.5-second rabbit in-out position in Fig. 3.

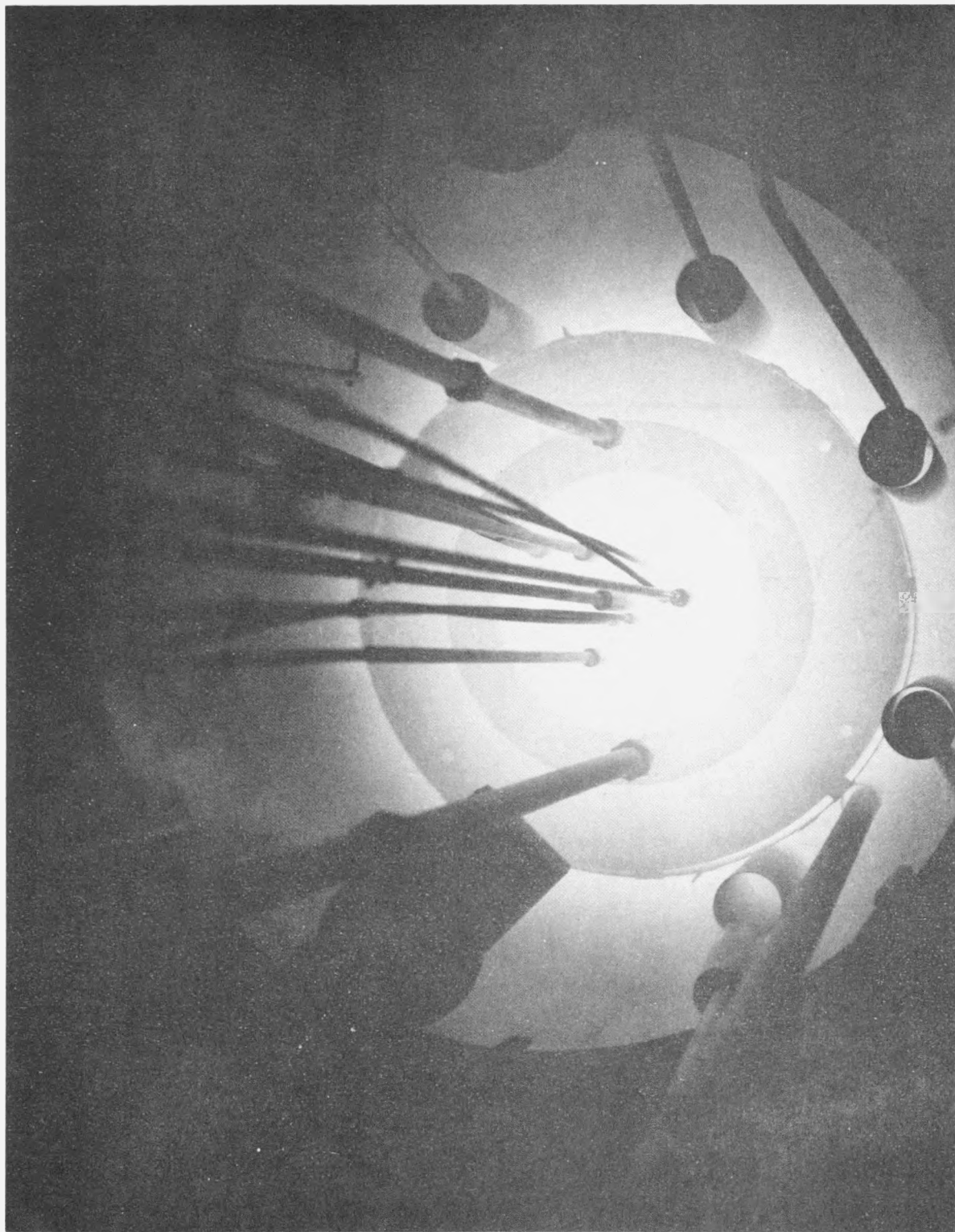
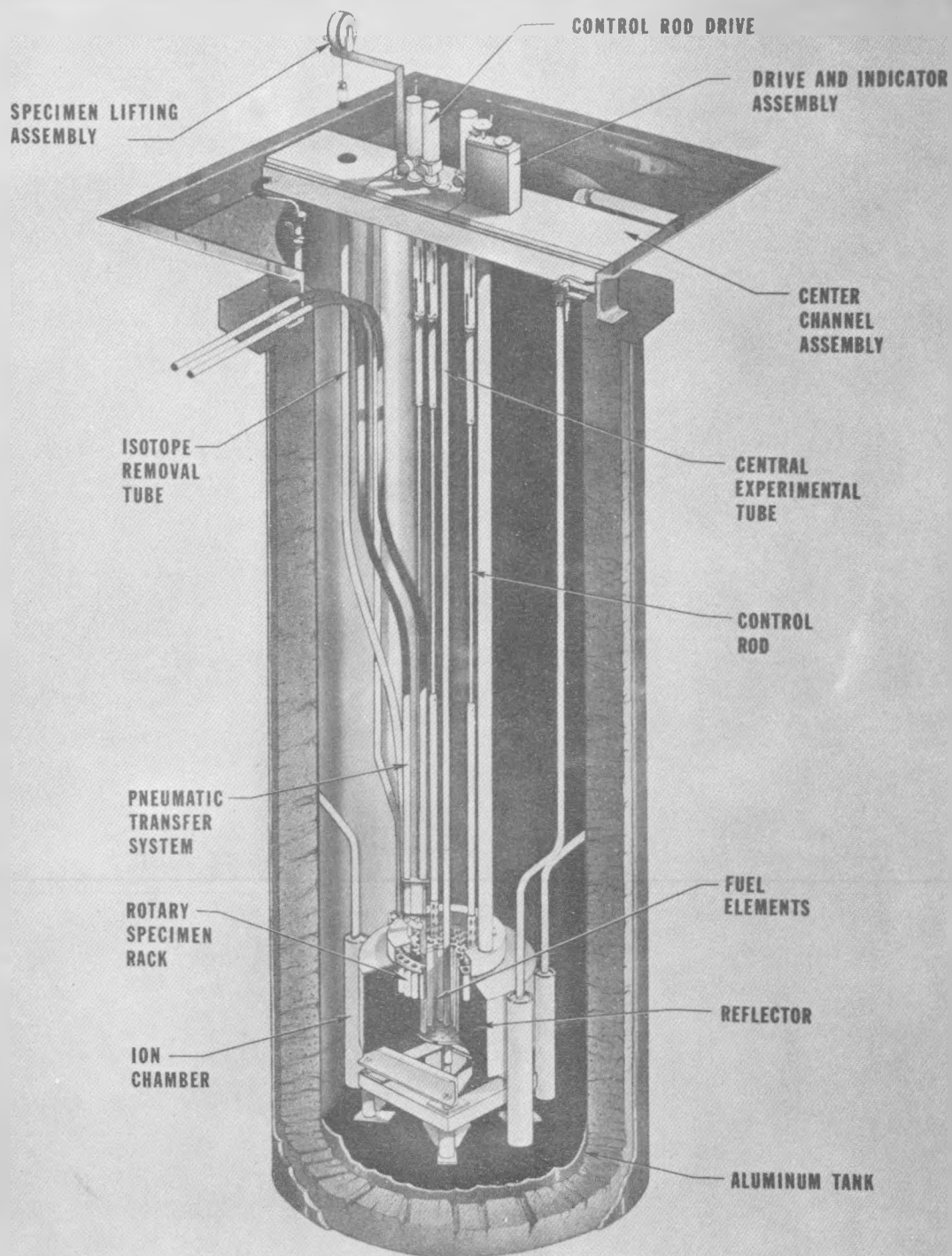


Fig. 1. TRIGA Mark I reactor



TRIGA MARK-I REACTOR

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

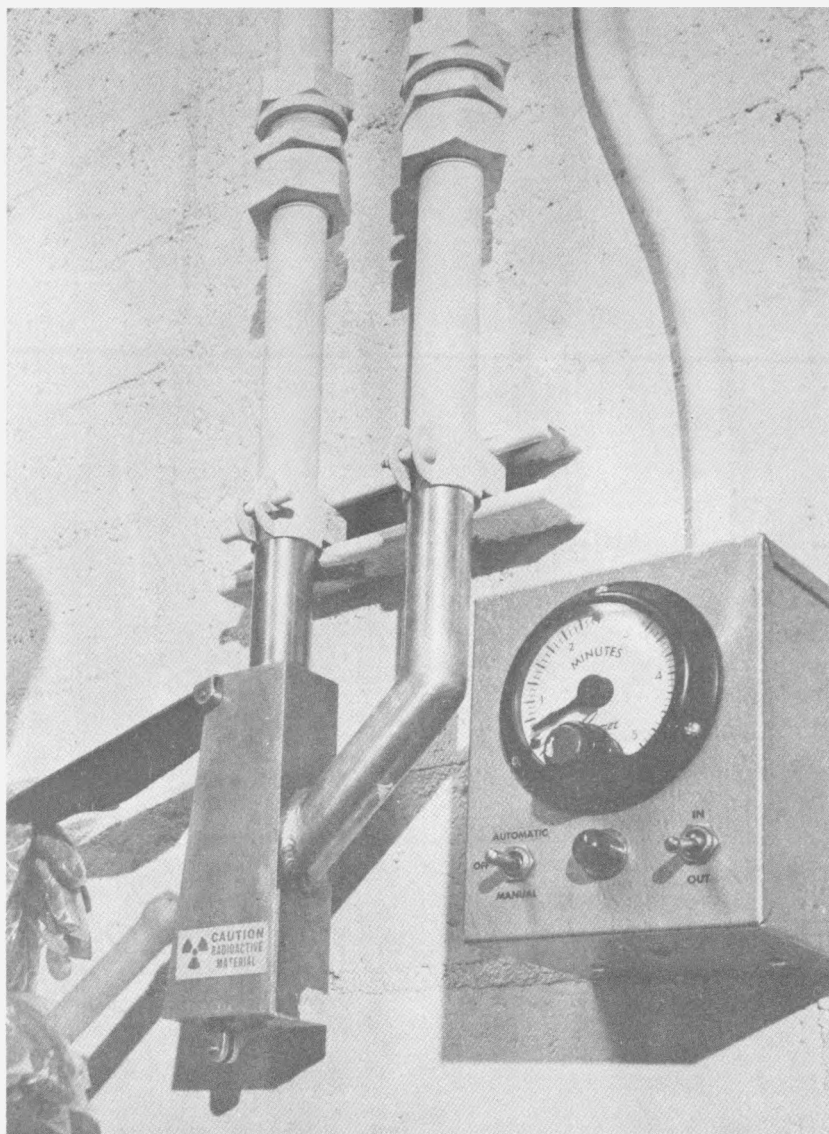


Fig. 3. Reactor pneumatic-tube system

2.1.2 TRIGA Mark F

This reactor is a somewhat larger and higher-powered version of the Mark I reactor. It contains one additional ring (the G ring) of fuel elements, the fuel elements are clad in stainless steel (instead of Al), the fuel elements have a higher H/Zr atomic ratio (1.7/1 instead of 1/1), and it does not contain a graphite reflector, rotary specimen rack, or pneumatic tubes. It can be operated at steady power levels of up to 1.5 MW, and can be pulsed to peak power levels of up to 6,400 MW. Samples can be lowered into vacant fuel-element positions, or into tubes located just outside the reactor core. The core is movable along a track, and is placed in a much larger, and somewhat deeper, pool of water.

2.1.3 TRIGA Mark III

This reactor is quite similar to the Mark F reactor, but is not equipped for pulsing. Whereas the Mark F reactor is largely used for high-intensity reactor pulsing experiments, the Mark III reactor is used entirely for long irradiations at a power level of 1.5 MW. In other research work at the Laboratory, the Mark III reactor is run steadily for periods of time as long as 1,000 hours (~ 42 days). In the criminalistics work, some samples have been activated in this reactor for periods as long as 100 hours (during one of the 1,000-hour runs), in vertical tubes placed just outside the reactor core. In the cores of the Mark F and Mark III reactors, thermal-neutron fluxes of up to several times 10^{13} n/cm²-sec are available for sample irradiations.

2.2 ELECTRON LINEAR ACCELERATORS

In some of the photonuclear activation analysis studies carried out in this investigation, GGA's two electron linear accelerators (Linacs) have been used. One of these machines accelerates electrons to energies

as high as 17 MeV; the other, up to 45 MeV. Both are high-current machines – the 45 MeV Linac providing a peak electron-beam power (at 25 MeV) of 12 kilowatts. For photonuclear activation analysis work, the electron beam (spread over a circular area of about one centimeter diameter) is stopped by a thick, water-cooled, tungsten "converter". This produces an intense bremsstrahlung (continuous X-rays) beam, heavily concentrated in the forward direction. The fractional conversion of electron energy to bremsstrahlung energy, and the degree of concentration in the forward direction, both increase with increasing electron energy. The bremsstrahlung energy distribution, except for a rising photon flux with increasing photon energy at the very low-energy end of the distribution (up to a few tenths of an MeV, caused by absorption of an appreciable fraction of the very low-energy bremsstrahlung photons in the tungsten converter), shows a rapidly-declining photon flux with increasing photon energy. The distribution extends all the way out to a photon energy equal to the energy of the electrons in the monoenergetic electron beam that is incident upon the tungsten converter. For example, approximately calculated for a thick tungsten converter, for a 12 kW 25 MeV electron beam, and for the forward 10° cone, the photons per second above the indicated energies are about:

<u>MeV</u>	<u>Photons/Second</u>
> 2	$1,000 \times 10^{12}$
> 4	460
> 6	280
> 8	190
> 10	96
> 12	72
> 14	48
> 16	34

<u>MeV</u>	<u>Photons/Second</u>
> 18	22×10^{12}
> 20	12
> 22	7.5
> 24	3.6



In front of the tungsten converter of either of the two Linacs, samples can be activated in either a pneumatic tube (for examination of short-lived induced activities) or in one of several multi-sample spinning racks. The pneumatic transfer system may be used with a short-distance tube into a nearby room in the Linac facility (transit time ~ 1 second), or with a longer-distance tube into the Activation Analysis Building (transit time ~ 8 seconds). Multi-sample spinning racks were constructed to allow one to simultaneously irradiate up to 6, 8, or 12 samples – in vertically-mounted sample vials. For irradiations at electron-beam energies above 20 MeV, aluminum sample vials are normally used – the sample later being transferred to an ordinary polyethylene vial for counting. At irradiation energies below about 20 MeV, polyethylene sample vials can be used, without the necessity of transferring after irradiation. Aluminum forms appreciable amounts of 6.37-second ^{26m}Al , via the $^{27}\text{Al}(\gamma, n)^{26m}\text{Al}$ reaction, and of 9.46-minute ^{27}Mg , via the $^{27}\text{Al}(\gamma, p)^{27}\text{Mg}$ reaction, at photon energies in the 20-25 MeV range. Above its 18.7 MeV threshold energy, carbon forms appreciable amounts of 20.34-minute ^{11}C , via the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction. At 25 MeV and 12 kW electron-beam power, a sample of carbon in the pneumatic-tube irradiation position is found experimentally to generate a 0.511 MeV photopeak counting rate of 3×10^8 counts per minute – calculated per gram of carbon, at the end of a 1-hour irradiation period.

2.3 COCKCROFT-WALTON 14 MeV NEUTRON GENERATORS

The Laboratory has three high-output, drift-tube type Cockcroft-Walton deuteron accelerators that are used for the generation of 14 MeV neutrons, via the ${}^3\text{H}(\text{d}, \text{n}){}^4\text{He}$ reaction. The oldest of these is a 1-milliampere D^+ beam, 150 kV, oil-diffusion pump Texas Nuclear Corporation accelerator, capable of producing 1×10^{11} 14 MeV neutrons/second (4 π yield) with a fresh, high-tritium target. It is housed in a ground-level shielded facility in the Linac area. The other two neutron generators are of a newer Texas Nuclear Corporation design, employ Vac-Ion pumps, operate at 150 kV with D^+ beam currents up to 2.5 milliamperes, and generate 3×10^{11} 14 MeV neutrons/second with a fresh, high-tritium target. These two generators are housed in a heavily-shielded underground bunker facility near the Activation Analysis Building. A photograph showing these two generators is presented in Fig. 4.

All three of these neutron generators have been used extensively for neutron activation analysis work – employing fast-neutron, rather than thermal-neutron, reactions – and including some forensic activation analysis studies involved in the research work of this contract. With a number of elements, useful detection sensitivities can be achieved via (n, n'), and/or (n, 2n), and/or (n, p), and/or (n, α) reactions in samples exposed for short periods of time to the $\sim 10^9$ n/cm²-sec fluxes of 14 MeV neutrons available from these generators. For a small number of elements, better sensitivities can be attained via 14 MeV-neutron activation at a 10^9 n/cm²-sec flux than can be attained by thermal-neutron activation at fluxes of 10^{12} - 10^{13} n/cm²-sec in one of the research reactors.

The two neutron generators in the underground bunker facility are equipped with a 1-second transit time pneumatic tube, and with a multi-sample spinning rack for use in longer irradiations. Because of the rather rapid decline in neutron output rate of the tritium targets, with operation

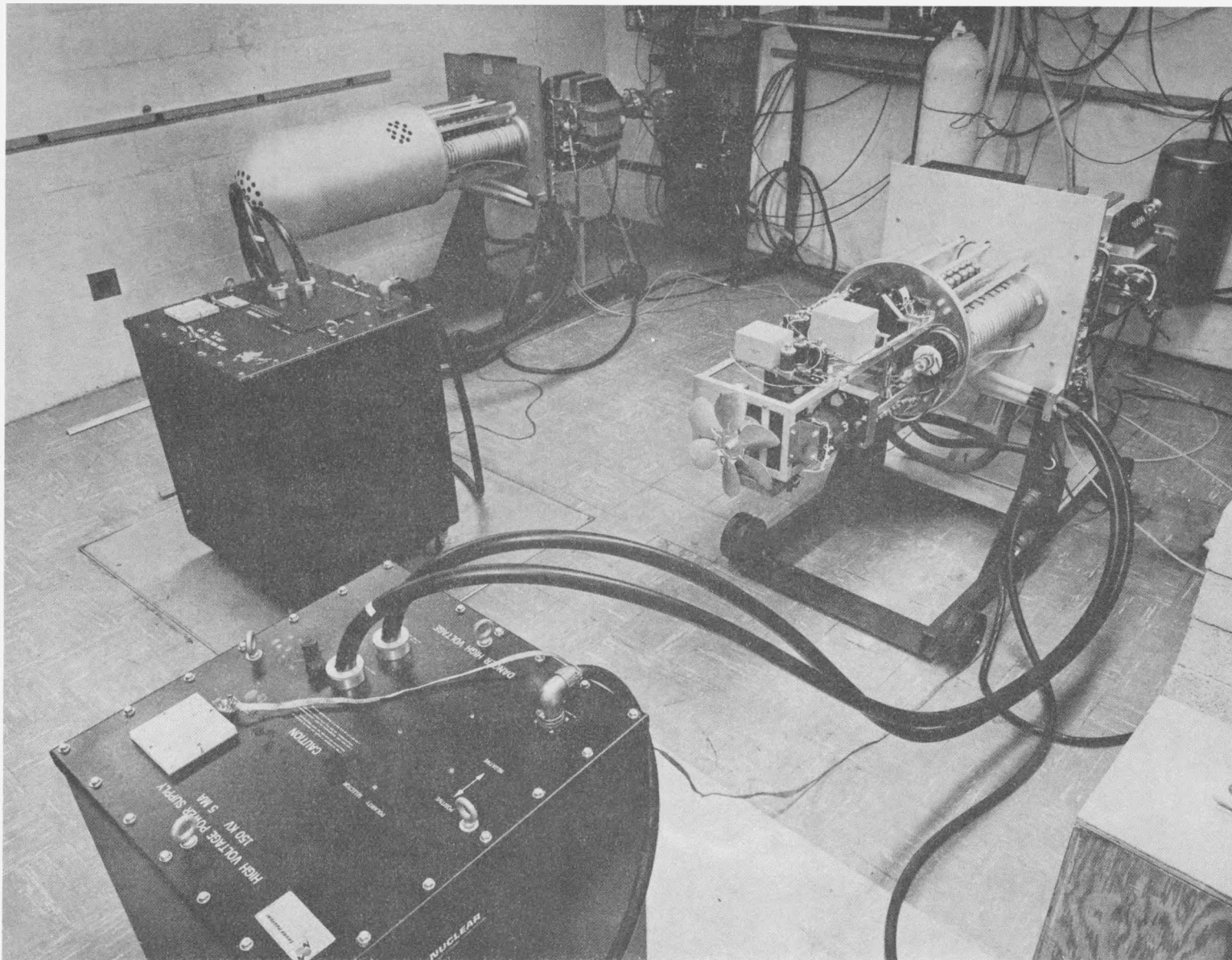


Fig. 4. Two high-output 14-MeV neutron generators at Gulf General Atomic

at high deuteron beam currents, the longest irradiations employed are usually only about 10 minutes.

2.4 NaI(Tl) MULTICHANNEL GAMMA-RAY SPECTROMETERS

Virtually all of the work carried out in this investigation involves the measurement of gamma-emitting induced activities, hence efficient gamma-ray detection equipment is essential in such work. Since a large fraction of the work carried out during the period covered by this report involved the purely-instrumental activation analysis of samples – looking for all elements that could be detected, rather than just for one or two selected elements – good provisions for performing gamma-ray spectrometry measurements on activated samples (as opposed to simple gross gamma-ray counting) are also essential. The Laboratory is very well equipped with NaI(Tl) multichannel gamma-ray spectrometers for such measurements, and a number of them have been utilized in the studies described in this report.

In the Activation Analysis Group at GGA, there are six multichannel pulse-height analyzers that are regularly used for activation analysis NaI(Tl) gamma-ray spectrometry measurements:

Four RIDL 400-channel analyzers
One TMC 400-channel analyzer
One TMC 100-channel analyzer.

Each of these analyzers is equipped with two NaI(Tl) detectors (a 3-in. x 3-in. solid crystal, and a 3-in. x 3-in. well-type crystal – each shielded by four inches of lead, lined with cadmium and copper), so that either type of NaI(Tl) detector can be used, as desired. For special cases, both larger (5-in. x 5-in.) and smaller (down to 1/2-in. thick) NaI(Tl) crystals are available for use with these analyzers. In some cases, γ - γ coincidence

measurements have been made on activated samples, using either a pair of 3-in. x 3-in. , or a pair of 5-in. x 5-in. NaI(Tl) crystals.

These gamma-ray spectrometers are equipped with various types of data-readout devices. Most are equipped with a paper-tape printer, a Mosely x-y precision plotter, and a small-cartridge fast magnetic-tape unit. Also, a Polaroid oscilloscope camera is frequently used to photograph the oscilloscope spectrum display. The four RIDL analyzers are also connected to an IBM punched-card readout unit. In most of the activation analysis work carried out by the Group, pulse-height data are automatically put onto punched cards with this unit, then processed on the Laboratory's UNIVAC 1108 computer. One of the RIDL analyzers is also tied to a punched-paper tape readout, coupled to a Teletype and Data Phone for transmission of raw pulse-height data over the telephone lines. Some of the analyzers are also equipped for operation in the multichannel-scaling mode. Figure 5 shows one of the NaI(Tl) spectrometers and the punched-card readout unit. Figure 6 shows the punched-paper tape Teletype unit.

In addition to the six multichannel NaI(Tl) gamma-ray spectrometry systems within the Activation Analysis Group (described above), there are a number of similar systems in other departments at the Laboratory (Chemistry Department, Linac Facility, etc.). These other systems were not used in the present investigation, but are always available as backup units, in case of analyzer breakdown or unusually heavy sample loads.

In addition to the multichannel analyzer NaI(Tl) systems, the Activation Analysis Group also has some single-channel analyzers and simple scalers, coupled to NaI(Tl) detectors. These are sometimes used for simple gamma-ray counting of radiochemically-separated induced activities.

2.5 Ge(Li) MULTICHANNEL GAMMA-RAY SPECTROMETERS

Several high-resolution Ge(Li) semiconductor detectors, coupled to pulse-height analyzers, have been used more recently in this

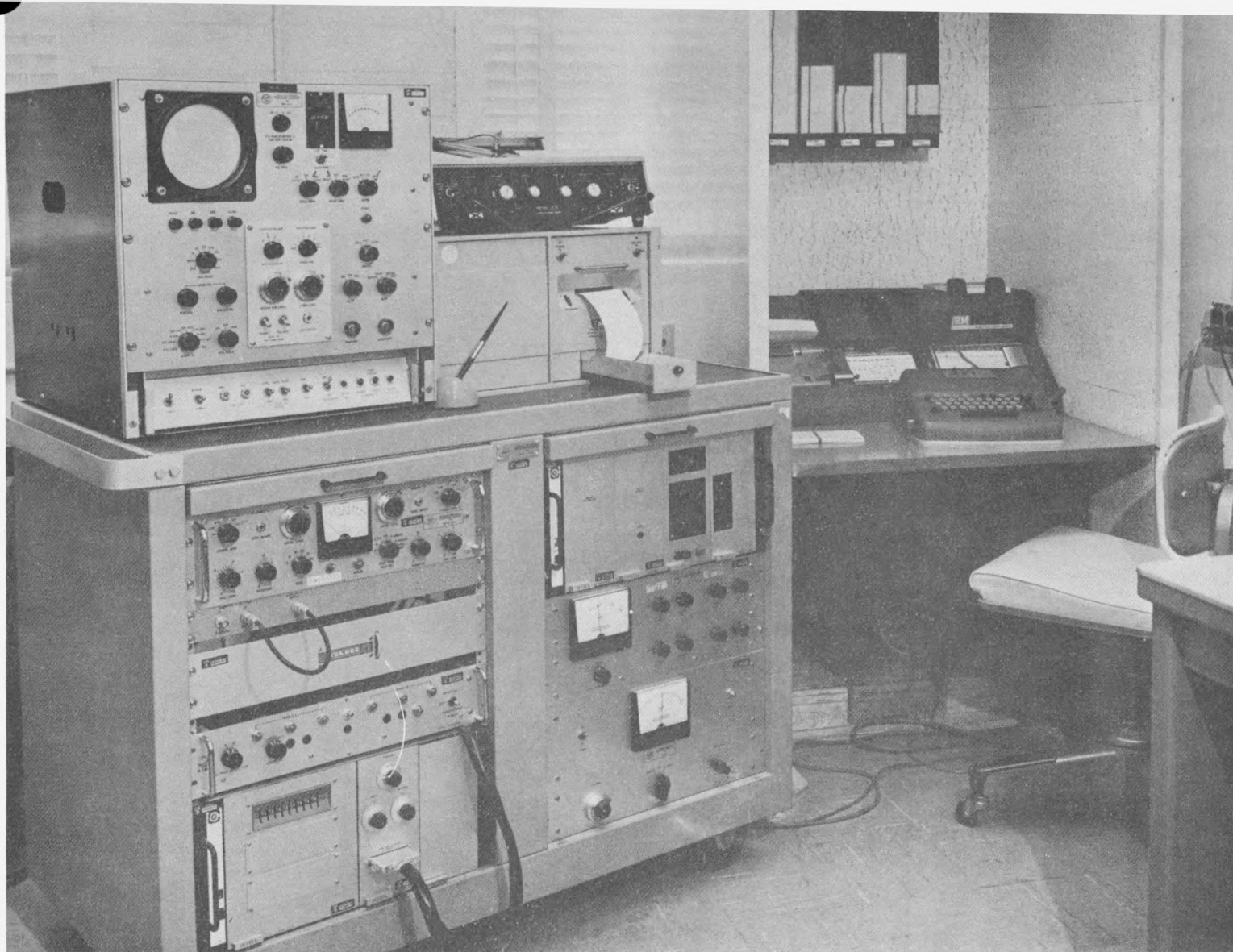


Fig. 5. NaI(Tl) 400-channel gamma-ray spectrometer with punched-card readout

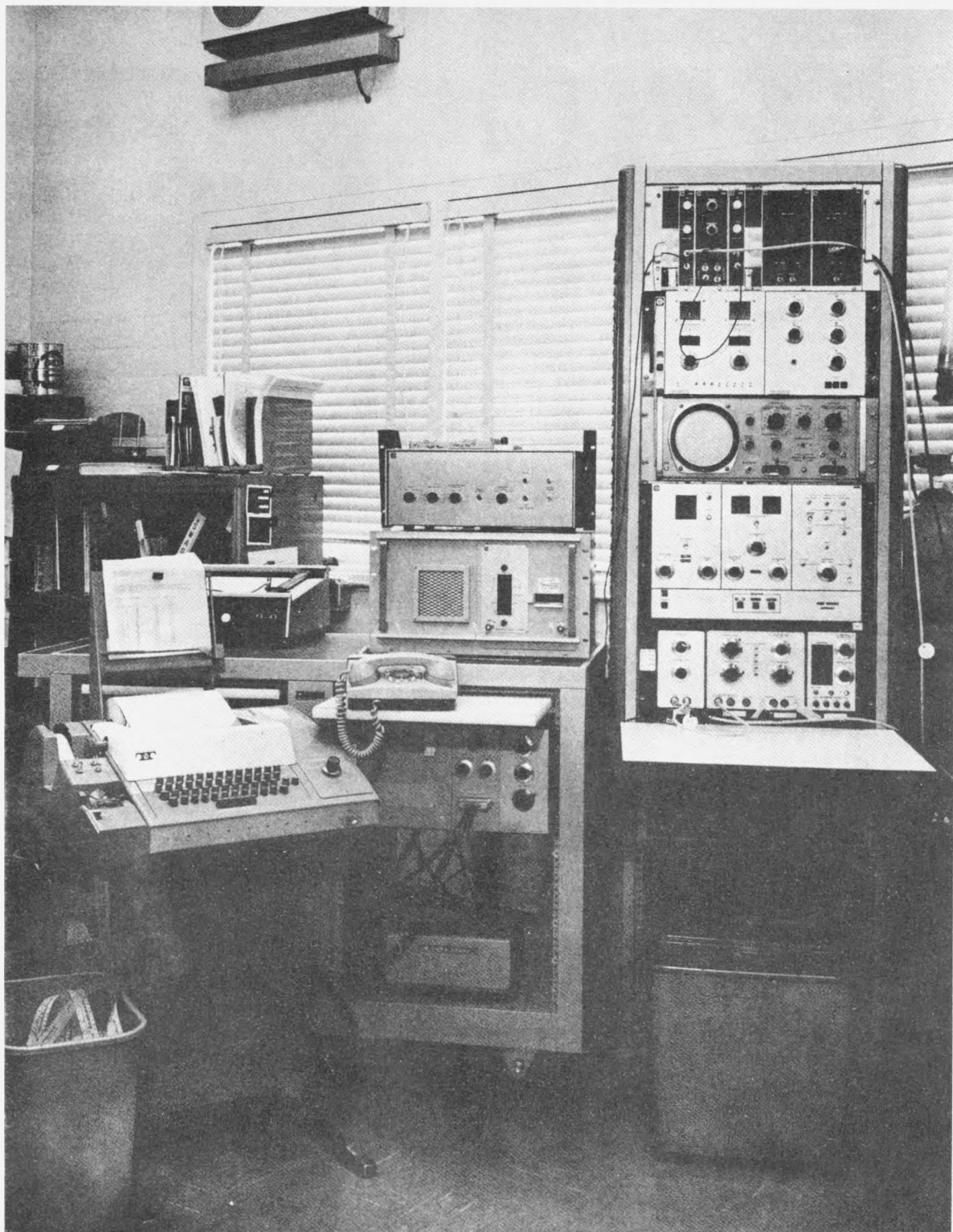


Fig. 6. NaI(Tl) 400-channel gamma-ray spectrometer with punched-paper tape teletype readout

investigation. Typically, these exhibit a 15-20 fold better energy resolution than that of a NaI(Tl) detector. However, because of the fact that only rather small Ge(Li) detectors are yet available, their detection efficiencies are markedly poorer than those of the usual 3-in. x 3-in. NaI(Tl) scintillation detector, especially with increasing gamma-ray energy. Even the largest one available at the Laboratory (45 cm^3), which is one of the largest sizes available commercially or that can be drifted in one's own laboratory, is small compared with the usual 3-in. x 3-in. NaI(Tl) crystal, which has a volume of 345 cm^3 .

The first Ge(Li) detector at the Laboratory was purchased several years ago, and had a volume of only 0.9 cm^3 . Later, this detector was replaced by a 15-cm^3 detector, which is still in use, and then this was supplemented by a 45-cm^3 detector. All three of these detectors are in the Chemistry Department, but have been used considerably by the Activation Analysis Group - in this investigation, as well as in other studies. The 15-cm^3 and 45-cm^3 Ge(Li) detectors are each coupled to a 4096-channel pulse-height analyzer. The 45-cm^3 detector system is directly coupled to a 4096-channel pulse-height analyzer. The 45-cm^3 detector system is directly coupled to a small computer, so that spectrum-analysis calculations are performed rapidly, in-place, giving "photopeak" cpm values for the various detected peaks almost immediately. The 15-cm^3 detector system has the usual magnetic-tape readout equipment - calculations then being made from the tape-recorded spectrum data on the Laboratory's UNIVAC 1108 computer.

Within the Activation Analysis Group itself, there are two additional Ge(Li) gamma-ray spectrometry systems. The first was purchased several years ago: a 4-cm^3 detector, coupled to a 400-channel pulse-height analyzer via a biased amplifier/pulse stretcher. Data are read out on a 20-channel/second printer. This unit is quite suitable if one

wishes only to examine the low-energy end of a gamma-ray spectrum with high resolution. Because of the small size of the detector, and the limited number of analyzer channels, however, it is not suitable for obtaining a wide pulse-height spectrum (e.g., 0-2 MeV) with either good resolution or good efficiency – in a single measurement. The second system was purchased near the end of the reporting period covered in this report, but is already being used extensively in this investigation, and in other activation analysis studies. It consists of a 34-cm³ Ge(Li) detector coupled to a Northern Scientific 4096-channel pulse-height analyzer and an Ampex magnetic tape output. This detector gives a resolution of 2.9 keV, a peak-to-Compton ratio of 16/1, and a detection efficiency of 4.0% (relative to a 3-in. x 3-in. NaI(Tl) detector) – for the 1.332 MeV gamma ray of ⁶⁰Co. Selected portions of a pulse-height spectrum can be printed out, if desired, on a 20-channel/second printer. Where the full 4096-channel spectrum is needed, the data are rapidly dumped onto the magnetic tape reel, for later processing on the Laboratory's UNIVAC 1108 computer.

All four of the currently used Ge(Li) spectrometry systems (two in the Chemistry Department and two in the Activation Analysis Group) are equipped with FET preamplifiers, precision amplifiers, precision high-voltage supplies, and either a gain stabilizer or a precision pulser. Of course, each detector is maintained at liquid nitrogen temperature at all times, and is shielded with lead. At present, plans are being made to couple the 34-cm³ detector to an automatic sample changer – thus extending its usefulness from the present ~ 40 hour/week limitation to 168 hours/week.

2.6 BETA-PARTICLE COUNTERS

Within the Activation Analysis Group, there are several conventional lead-shielded, thin-window Geiger-Müller and gas-flow proportional

counters. These are connected to scalers, and are used for beta counting of radiochemically-separated induced activities. Calibrated aluminum absorbers are used with these counters, to establish that the separated activity being counted has the correct beta-particle energy distribution. Quite a few additional beta counters are available, as backups, in the Chemistry Department. These include an anticoincidence-shielded Sharp low-background counter (background counting rate, 0.25 cpm), and one unit equipped with a large-capacity automatic sample changer.

2.7 RADIOCHEMICAL-SEPARATION LABORATORIES

The Activation Analysis Building contains one large and four small radiochemistry laboratories, used for radiochemical-separation work with activated samples. Some of these laboratories were used in this investigation for the radiochemical separation of ^{139}Ba and ^{122}Sb induced activities (with Ba and Sb carriers) in activated gunshot-residue and handblank paraffin-lift samples. Each of these laboratories is equipped with one or more chemical hoods (with filtered ducts), monitoring apparatus, lead-shielded radioactive storage areas, radioactive-waste storage vessels, and other apparatus typically used in moderate-level radiochemical laboratories. In the building, there is also a sample-preparation laboratory, in which no radioactive material is allowed. It is also used to store all of the standard and carrier solutions. This laboratory is next to the main counting room, which houses most of the gamma-ray spectrometry and beta counting equipment.

There are a number of additional radiochemical laboratories in the Chemistry Department, one of which is used at times by the Activation Analysis Group – the semi-hot laboratory, used for radiochemical separations of dangerously radioactive samples.

2.8 THE UNIVAC 1108 COMPUTER FACILITY

The Laboratory's central computer has been a UNIVAC 1108 computer for the past few years. It replaced an IBM 7044 computer, which in turn replaced an earlier IBM 7090 computer. Very early in this investigation, all calculations were performed manually (using only slide rules and desk calculators). Soon, however, computer programs were developed for making many of the necessary activation analysis calculations on the IBM 7090 and then the IBM 7044. With the advent of the more powerful UNIVAC 1108, the arsenal of activation analysis computer programs was developed considerably further. For the past few years, almost all of the calculations of the Activation Analysis Group, including those of this forensic activation analysis investigation, have been carried out on the UNIVAC 1108. The Group is no on-line with the computer, which is located in another building a few hundred yards away. Instead, punched-cards (data output from the NaI(Tl) gamma-ray spectrometers) and reels of magnetic tape (data output from the Ge(Li) gamma-ray spectrometers) are driven over to the computer facility several times a day. Results are usually obtained back during the same day, or on the following day.

From the gamma-ray spectrometry pulse-height data, the computer performs various calculations, as requested. These include: convolution data smoothing, peak searching, listing of gamma-ray energies detected and their respective radionuclides, calculation of net photopeak counting rates (and their standard deviations), decay corrections, weighted least-squares fitting, resolution of overlapping peaks, computation of μg and ppm values (and their standard deviations), half-life calculations, upper-limit calculations for nondetected elements, and plotting of smoothed pulse-height spectra along with the original data points.

3. GUNSHOT-RESIDUE STUDIES

3.1 BACKGROUND OF INITIATION OF THIS STUDY

During 1961, some informative discussions were held with Mr. Raymond H. Pinker, an eminent criminalist who was at that time Chief Criminalist of the very fine Los Angeles Police Department's Crime Investigation Laboratory. These discussions were aimed at assessing in what important areas of crime investigation work high-flux neutron activation analysis might possibly be of real value. Mr. Pinker suggested that there was a considerable need for a reliable method of detecting gunshot residues, and that if NAA could provide a usable method in this area, it would be making an important contribution to the field of criminalistics.

Mr. Pinker first explained that the older technique, variously referred to as the "paraffin test", "the paraffin-glove test", "the dermal nitrate test", and the "diphenylamine test", had been abundantly shown to be unreliable, was no longer accepted in most U. S. courts, and was now seldom used by good crime investigation laboratories. The method involved: (1) coating most of the back of the hand of a suspect in a shooting case (or of the victim in a questionable gunshot-suicide case) with molten paraffin, (2) reinforcing the paraffin "cast" or "glove" with a few layers of gauze as the cast is built up thicker, (3) peeling off the cast, after it has solidified, (4) pouring some diphenylamine-sulfuric acid solution on the concave inside surface of the cast (i. e., the surface that had been in contact with the skin), and (5) looking for blue specks imbedded in the paraffin. Thus, the dermal nitrate test is a color test for unburned or partially burned gunpowder, i. e., nitro compounds, which form a blue

product with the acidic diphenylamine reagent. In practice, it turns out that the test is not highly sensitive – not developing a detectable blue color with very tiny particles of gunpowder, it can apparently be interfered with in some cases by other material that may also be present on the back of a person's hand or in the perspiration, and the same color reaction can also be produced by various other nitrogen-containing compounds, such as fertilizers and urine, for example.

As Mr. Pinker then pointed out, a promising improved gunshot-residue detection method was developed by H. C. Harrison and R. Gilroy,⁽¹⁸⁾ at the University of Rhode Island, published in 1959. The Harrison and Gilroy technique also employed qualitative color reactions, but not with any gunpowder present on the back of the firing hand of a suspect, but instead with small traces of elements that originated as constituents of the cartridge primer: barium, antimony, and lead. Unfortunately, when various crime investigation laboratories attempted to use the Harrison and Gilroy method, they obtained very poor results. It appeared that at least one of the problems might be that the method was being used right at the limit of its sensitivity – the tiny amounts of these elements deposited on the back of the gunhand in a typical firing being very close to the limit of detection of the method. Since high-flux NAA is extremely sensitive for the detection of many elements, and is also quite quantitative, it definitely seemed worthwhile to see if these primer-residue elements could be reliably detected by high-flux NAA.

Some brief exploratory experiments conducted at General Atomic soon showed that this approach worked quite well for the detection and measurement of two of these primer-residue elements: barium and antimony. Since the NAA sensitivity for lead is rather poor, no effort was made to detect this third element. In these first exploratory experiments, the backs of both hands of a police officer were first rinsed with very

dilute nitric acid (after first washing his hands with ordinary soap and water), and the acid rinsings saved for analysis. The officer then fired a 0.38-caliber revolver once, firing with his right hand, and the rinsing procedure was followed again. He then fired the same gun three times in rapid succession, using his right hand again, and then both his hands were rinsed with dilute nitric acid. The various nitric acid rinsings were then each placed in a small polyethylene vial, sealed, and irradiated for 30 minutes in the 250 kW TRIGA Mark I reactor, at a thermal-neutron flux of 1.8×10^{12} n/cm²-sec. Because of all the NaCl in the perspiration that was rinsed along with the nitric acid solution, the principal induced radionuclides observable instrumentally (by NaI(Tl) multichannel gamma-ray spectrometry) were 14.96-hour ²⁴Na and 37.29-minute ³⁸Cl. The levels of these two radioactive species were so high that it was difficult to detect any other radionuclides possibly present, by a purely instrumental technique. Therefore, any radioactive antimony possibly present was separated from each sample, by means of chemical equilibration with nonradioactive carrier antimony (in solution), with precipitation of the antimony. When the various antimony precipitates, now free of contamination by ²⁴Na and ³⁸Cl were counted on the NaI(Tl) gamma-ray spectrometer, a noticeable photopeak appeared, at an energy of 0.564 MeV, in each case. This is the principal gamma ray emitted by 2.80-day ¹²²Sb. After measurement of the antimony yield (carrier recovery) in each case, the amounts of antimony present in each acid-rinse sample, normalized to 100% carrier recovery, were calculated. The antimony values found are shown below:

	Gross μ g Sb Found	
	Left Hand	Right Hand (Gunhand)
Handblank (before firing)	0.05	0.05
After one firing	0.05	0.12
After three firings	0.05	0.23

The nitric acid solution itself (before use) was similarly found to contain 0.03 μg Sb, in the amount used for hand washing. Thus, a true handblank Sb level for this particular officer, after a normal soap-and-water washing of his hands, was about 0.02 μg - on each of his hands, as removed from the back-of-the-hand area rinsed with acid solution. One firing of the 0.38-caliber revolver added approximately 0.07 μg of Sb to the removable antimony on the back of the gunhand, and added none to the back of the other hand. With three successive firings of the same weapon, the increase in removable Sb on the back of the gunhand (above the value corresponding to the reagent blank, 0.03 μg , and the clean-handblank, 0.02 μg) was about 0.18 μg .

Following these encouraging preliminary results, a somewhat more elaborate radiochemical-separation procedure was worked out - so that both 82.9-minute ^{139}Ba and 2.80-day ^{122}Sb could be efficiently and rapidly separated from neutron activated hand rinsings. A few additional exploratory 0.38-caliber revolver firings were conducted, with similar very dilute nitric acid rinsings of the back of the gunhand. These exploratory measurements revealed a slightly higher barium handblank value (ca. 0.10 μg Ba, versus ca. 0.02 μg Sb) and a considerably larger primer-residue amount, in a single firing (ca. 1.0 μg Ba, versus ca. 0.07 μg Sb), and a somewhat increased barium deposit with a triple firing.

The results of these early exploratory studies were presented at the October 1961, semi-annual meeting of the California Association of Criminalists, held in San Francisco, and were received with considerable interest. A short note on this initial study appeared in the December 1961 issue of Nucleonics.⁽¹⁹⁾ With these results, along with a number of ideas concerned with applying high-flux NAA to many other important kinds of evidence materials, as a basis, a research proposal to the Division of Isotopes Development (AEC) was prepared and submitted early in 1962.

A research contract was issued to General Atomic by DID for such an investigation, to commence on May 1, 1962. The initial contract was for one year, at a modest level of effort - about 1.3 man-years per year.

3.2 NEUTRON ACTIVATION DATA PERTAINING TO THE DETERMINATION OF BARIUM AND ANTIMONY

It is of interest to ascertain what kind of sensitivity should be attainable for the determination of these two particular elements, involved in the detection of gunshot residues, under practical NAA conditions routinely available at Gulf General Atomic. Although higher thermal-neutron fluxes are available in the 1.5 MW TRIGA Mark F and Mark III reactors at the Laboratory than are available in the 0.25 MW (250 kW) TRIGA Mark I reactor, the latter is better equipped, and more generally available, for routine NAA work. The TRIGA Mark I reactor is therefore used in most of the NAA work carried out at GGA, and has been used in most of the forensic activation analysis studies described in this report.

In the rotary specimen rack of the TRIGA Mark I reactor, operating at a power level of 250 kW, up to 40 samples can be activated simultaneously - all exposed to exactly the same average thermal-neutron flux: 1.8×10^{12} n/cm²-sec. In a 1-hour irradiation at this thermal-neutron flux, one can calculate from the known nuclear properties of barium and antimony, and the properties of their two principal (n, γ) products, 82.9-minute ¹³⁹Ba and 2.80-day ¹²²Sb the expected activity levels of these two products, per microgram of element. These parameters and resulting values are summarized below:

Element	Mass No.	% Abundance	Therm. -n Isotopic (n, γ) Cross Section in Barns	Product Radionuclide		Activity Level, in dps/ μ g	
				Mass No.	Half-Life	At Sat'n.	At t _i = 1 hr
Ba	¹³⁸ Ba	71.66	0.35	¹³⁹ Ba	82.9 m	2.0×10^3	7.8×10^2
Sb	¹²¹ Sb	57.25	6.5	¹²² Sb	2.80 d	3.3×10^4	3.4×10^2

The isotopic abundance values are taken from BNL-325, ⁽²⁰⁾ the cross sections from BNL-325 Supplement 2, ⁽²¹⁾ and the half-lives from the Sixth Edition of the "Table of Isotopes". ⁽⁸⁾

The next items to be considered are the decay schemes of ¹³⁹Ba and ¹²²Sb. From the Sixth Edition of the "Table of Isotopes", ⁽⁸⁾ it is seen that ¹³⁹Ba emits a β^- particle in every disintegration, and an unconverted 0.166 MeV gamma-ray photon in 23% of its disintegrations. Similarly, it is seen that ¹²²Sb emits a β^- particle in 97% of its disintegrations, and an unconverted 0.564 MeV gamma-ray photon in 66% of its disintegrations. Combining these values with those shown in the above table, one obtains (for a thermal-neutron flux of 1.8×10^{12} n/cm²-sec):

Radionuclide	β^- dps/ μ g Element		γ dps/ μ g Element (of Energy, E _{γ})		
	At Sat'n.	At t _i = 1 hr	At Sat'n.	At t _i = 1 hr	E _{γ} (in MeV)
¹³⁹ Ba	2.0×10^3	7.8×10^2	4.6×10^2	1.8×10^2	0.166
¹²² Sb	3.2×10^4	3.3×10^2	2.2×10^4	2.2×10^2	0.564

The next items of interest are the β^- and γ detection efficiencies for these two radionuclides, under typical counting conditions. The E_{max} values for the two predominant β^- particles of ¹³⁹Ba are 2.34 MeV (72%) and 2.17 MeV (27%). ⁽⁸⁾ For ¹²²Sb the E_{max} values for the three β^- particles are 1.97 MeV (30%), 1.41 MeV (63%), and 0.72 MeV (4%). For such fairly energetic β^- particles, using a thin-window Geiger-Müller or gas-proportional counter at close to 2 π counting geometry, one may assume an over-all β^- counting efficiency of about 40%. Using the gamma-ray detection efficiency values of Heath, ⁽⁹⁾ for a 3-in. x 3-in. solid NaI(Tl) crystal scintillation counter, at a sample-to-detector distance of 2 cm, the counting efficiency for the 0.166 MeV gamma rays of ¹³⁹Ba is seen to be 24%, and that for the 0.564 MeV gamma rays of ¹²²Sb is seen

to be 15%. Under these same conditions, Heath's⁽⁹⁾ photofractions, for these two gamma-ray energies, are, respectively, 0.95 and 0.59. Thus, again for a thermal-neutron flux of 1.8×10^{12} n/cm²-sec, and the counting conditions described above, one obtains the following expected counting rates, per microgram of element (and for the two specified gamma-ray energies):

Radionuclide	β^- cps/ μ g Element		γ cps/ μ g Element		γ Photopeak cps/ μ g Element	
	At Sat'n.	At $t_i = 1$ hr	At Sat'n.	At $t_i = 1$ hr	At Sat'n.	At $t_i = 1$ hr
¹³⁹ Ba	8.0×10^2	3.1×10^2	1.1×10^2	4.3×10^1	1.0×10^2	4.1×10^1
¹²² Sb	1.3×10^4	1.3×10^2	3.3×10^3	3.3×10^1	1.9×10^3	1.9×10^1

Although the expected β^- counting rates are seen to be somewhat higher than the expected corresponding gamma-ray counting rates, which in turn are somewhat higher than the expected corresponding gamma-ray photopeak counting rates, in practice it is most desirable to utilize the gamma-ray photopeak counting rates (as determined by counting with a NaI(Tl) multichannel gamma-ray spectrometer), even though the species (¹³⁹Ba or ¹²²Sb) has been radiochemically separated in supposedly uncontaminated form. Also, by using only the 0.564 MeV photopeak of ¹²²Sb, one avoids any appreciable difficulty in making any necessary decay corrections that can arise from the gamma rays of 60.4-day ¹²⁴Sb, which is also present to a significant degree, along with the 2.80-day ¹²²Sb.

If one arbitrarily assumes that the minimum gamma-ray photopeak counting rate that is still detectable with moderate precision is 10 cpm, converting the above photopeak cps values to cpm values, one estimates that a 1-hour irradiation at a thermal-neutron flux of 1.8×10^{12} n/cm²-sec should allow one to detect as little as $10/41 \times 60 = 0.0041$ μ g of Ba, and as little as $10/19 \times 60 = 0.0088$ μ g of Sb.

The above calculated sensitivities have also been checked experimentally. At a thermal-neutron flux of 1.8×10^{12} n/cm²-sec, a 1-hour irradiation is found experimentally to generate a 0.166 MeV ¹³⁹Ba photopeak counting rate of about 2.1×10^3 cpm/μg Ba, as compared with the calculated value of 2.5×10^3 . In the case of antimony, the experimental sensitivity is some 2.9 times better than the calculated sensitivity, probably due largely to three appreciable (n, γ) resonances of ¹²¹Sb (at neutron energies of 6.24 eV, 15.5 eV, and 29.7 eV). Thus, at a thermal-neutron flux of 1.8×10^{12} n/cm²-sec, a 1-hour irradiation is found to result in a 0.564 MeV ¹²²Sb photopeak counting rate of about 3.1×10^3 cpm/μg Sb, as compared with the calculated value of 1.1×10^3 cpm/μg Sb. The defined limits of detection (i. e., corresponding to 10 photopeak cpm), based upon the experimentally-determined, rather than calculated, sensitivities, become 0.0048 μg of Ba and 0.0032 μg of Sb. For only a 30-minute irradiation at the same flux, these values become 0.0086 μg of Ba and 0.0064 μg of Sb. In practice, the limits of detection are somewhat higher than these values, due to: (1) a less than 100% yield in the radiochemical separations, and (2) some decay prior to counting. Even so, with a typical practical limit of detection of about 0.01 μg for each element (using only a 30-minute irradiation at a thermal-neutron flux of 1.8×10^{12} n/cm²-sec), the sensitivities are quite adequate for the general gunshot-residue detection problem. If greater sensitivity were needed, it could readily be attained by: (1) using irradiation times much longer than 30 minutes (especially for Sb, since it forms a much longer-lived (n, γ) product than does Ba), and/or (2) using higher neutron fluxes, and/or (3) using longer-than-normal counting times.

3.3 THE RADIOCHEMICAL SEPARATION AND COUNTING OF ^{139}Ba AND ^{122}Sb

When the tiny particles of gunshot residue present on the back of the hand of a person who has recently fired a gun are removed – by essentially any means – other material present on the skin is also removed, at least to some degree. In particular, relatively considerable amounts of NaCl are removed. Thus, when the removed material is activated in the reactor and then promptly viewed with a gamma-ray spectrometer, the pulse-height spectrum is dominated by pulses from 37.29-minute ^{38}Cl (principal gamma rays: 1.60 MeV and 2.170 MeV; also producing a smaller sum peak at 3.77 MeV) and 14.96-hour ^{24}Na (principal gamma rays: 1.369 MeV and 2.754 MeV; also producing a sizeable sum peak at 4.123 MeV). These interfering activities completely obscure the detection and measurement of the much smaller levels of ^{139}Ba and ^{122}Sb , usually present. If one is willing to wait several days, until most of the ^{24}Na activity has decayed out (the shorter-lived ^{38}Cl activity of course decaying out much sooner), it is possible then to observe the ^{122}Sb activity instrumentally. Such delays are quite undesirable in actual case work, since an answer is generally needed as soon as possible. Also, as will be pointed out more fully later in this report, it is very important to measure both Ba and Sb, rather than only one of the two, and decay does not permit one to detect and measure the ^{139}Ba activity instrumentally – since its half-life (82.9 minutes) is in between that of ^{38}Cl (37.29 minutes) and that of ^{24}Na (14.96 hours).

Thus, a radiochemical separation of the two activities of interest, ^{139}Ba and ^{122}Sb , is needed. Initially, a radiochemical-separation procedure that separated out three activities – the ^{139}Ba and ^{122}Sb , and also 12.80-hour ^{64}Cu – was developed and used. This procedure was developed because it was thought initially that copper might also be a useful

indicator element in the detection of gunshot residues - small amounts of copper, from the cartridge case and primer case, possibly being also blown back onto the back of the gunhand in a firing. Some of the early gunshot-residue and handblank samples so analyzed (discussed in a later section of this report) soon showed, however, that copper was not as useful an indicator element as were barium and antimony. The radiochemical-separation procedure was therefore modified so as to only separate out the barium and antimony radionuclides, thus simplifying and speeding up the separations.

The resulting two-element separation procedure is briefly described here. The activated sample is placed in a beaker, along with about 15 ml of distilled water, 3.5 ml of concentrated HCl, 1 ml of concentrated HNO₃, about 100 mg of NaCl (as holdback carrier), and small amounts (1 ml each) of carrier solutions of Ba⁺², Sb⁺³, and Cu⁺² (20.0 mg each), and the mixture boiled for 10 minutes - to dissolve any particles present, and equilibrate any ¹³⁹Ba, ¹²²Sb, and ⁶⁴Cu present with their respective nonradioactive carriers. After cooling, the solution is poured into a 50 ml centrifuge tube. One ml of concentrated H₂SO₄ is added, and the solution is stirred to precipitate BaSO₄. The precipitate is centrifuged, filtered on a preweighed filter paper, washed with water and then with ethanol, dried at 110°C for 15 minutes, and weighed (thus determining the recovery of the Ba⁺² carrier). Cellophane tape is then placed over the precipitate, and the filter paper is carefully folded and placed in a 2-dram polyethylene vial - the sample then being counted for its ¹³⁹Ba activity in a well-type NaI(Tl) scintillation detector, coupled to a multichannel pulse-height analyzer. Copper is removed from the supernatant solution by adjusting the pH to 1.5-2.0 with NaOH solution, and extracting the copper by shaking with 5 ml of a CHCl₃ solution of dithizone (400 mg of dithizone in 100 ml CHCl₃) in a 150 ml separatory funnel.

The lower (CHCl_3) phase is discarded. The Sb^{+3} in the supernatant solution left from the BaSO_4 precipitation is precipitated as Sb_2S_3 , using about one gram of thioacetamide and heating. The precipitate is centrifuged, dissolved in about 10 ml of HCl solution, boiled for about 15 minutes (to remove H_2S), cooled, and diluted to about 30 ml. The free sulfur formed is centrifuged out. The supernate is transferred to a clean centrifuge tube, about 20 ml of water and 2 ml of chromous chloride solution (oxorbent) are added and stirred, and the tube is placed in a boiling water bath for 30 minutes. The solution is allowed to stand overnight to complete the precipitation and settling of elemental antimony, which is then transferred by means of a transfer pipette to a 2-dram polyethylene vial and counted for its ^{122}Sb activity in a well-type NaI(Tl) scintillation detector that is coupled to a multichannel pulse-height analyzer. The recovery of antimony carrier is determined by re-irradiation and comparing the resulting ^{122}Sb activity with that of a similarly activated and counted comparator standard.

3.4 METHODS OF REMOVING GUNSHOT RESIDUES FROM THE GUNHAND

In the preliminary studies described earlier in this report, the back of the gunhand was simply rinsed with a very dilute solution of nitric acid, to remove (hopefully) at least a significant fraction of any gunshot-residue material present. Shortly thereafter, a number of other possible means of removing gunshot residues from the skin were investigated briefly. These studies are described below.

First, a number of possible wiping materials were studied. These included absorbent cotton, cotton gauze, "Q-Tip" cotton, several kinds of filter paper, paper towels, Kleenex, polyurethane, cellulose, and plastic sponges. Samples of each were analyzed by means of instrumental thermal-neutron activation analysis. Each sample was irradiated for 30

minutes in the TRIGA Mark I reactor, at a thermal-neutron flux of 1.8×10^{12} n/cm²-sec, and then counted at several decay times on a 3-in. x 3-in. NaI(Tl) crystal multichannel gamma-ray spectrometer. All of these exhibited quite appreciable levels of a number of neutron-activatable elements that formed induced activities of medium to long half-life. Of these, the most acceptable was Whatman No. 42 filter paper. When this material was first washed with distilled water and alcohol, its level of activatable impurities was reduced even further (especially lowering the Na and Cl contents), making it quite suitable as a hand-wiping material.

Next, various liquids were studied, to ascertain whether some of these might be suitable as hand-rinsing liquids, or as moistening agents on Whatman No. 42 filter paper. The liquids studied included distilled water, 1% (and 2%) nitric acid, acetic acid, de-ionized water, paraffin oil, K & W waterless hand cleaner, alkyl-aryl sulfonate detergent, and an aerosol detergent. Samples of each were activated and counted in the same manner used on the samples of wiping materials (described above). Some of these liquids exhibited rather high levels of neutron-induced activities. Those showing the least induced activity were de-ionized water, 1% transistor-grade HNO₃, and paraffin oil.

Last, food-grade paraffin, as a possible residue-removal material, was studied. Activation and gamma-ray spectrometry showed this material to be the purest of all the materials studied.

Tests were then carried out to ascertain which of the various residue-removal techniques appeared to remove the most gunshot-residue material from the back of the gunhand, following a firing, and with the least complications. A number of persons, starting with clean hands, each fired a revolver once, using their right hand. Then, each person had both hands sampled by one of the following techniques:

1. Swabbing with filter paper moistened with de-ionized water
2. Swabbing with filter paper moistened with 1% HNO_3
3. Swabbing with filter paper moistened with 2% acetic acid
4. Swabbing with filter paper moistened with paraffin oil
5. Scrubbing with a clean nylon toothbrush moistened with de-ionized water
6. Scrubbing with a clean nylon toothbrush moistened with 1% HNO_3
7. Scrubbing with a clean nylon toothbrush moistened with 2% acetic acid
8. Coating with molten paraffin.

The results of these studies showed that a swabbing or scrubbing technique did not, in general, remove as much gunshot-residue material from the skin as did the paraffin. In a further search for possibly useful residue-removing materials, several kinds of tape (adhesive tapes, Scotch tape), and a stripping lacquer were analyzed. Although these were quite convenient to use, unfortunately each showed very high levels of induced activities, when activated in the reactor.

Following these exploratory studies, the paraffin-life procedure was adopted as the regular hand-sampling technique to be used in all the subsequent gunshot-residue work. Although not so convenient to apply, paraffin has the advantage of being readily available commercially in high purity, at a very low cost. In all subsequent work, each new batch of paraffin was routinely analyzed for barium and antimony, but only the barest traces were ever found – thus resulting in an essentially negligible paraffin blank correction.

The application technique finally adopted consists of melting pure paraffin in a clean porcelain evaporating dish, holding the temperature at about 120^o F, and then applying it to the desired region of the back of the hand (primarily the "thumb-web" area - discussed in the next section of this report), allowing the applied molten paraffin to cool and solidfy, peeling it off, and placing all of the removed paraffin in a labelled polyethylene vial - ready for neutron activation. The person applying the paraffin is required to wash his hands carefully first, and then put on thin disposable plastic gloves, before proceeding. The molten paraffin is allowed to flow off of a small clean paint brush onto the skin - rather than using a brushing or scrubbing motion - so that material is not transferred back to the dish of molten paraffin with repeated dippings of the brush into the dish. Naturally, a reasonably clean laboratory area must be used, and all materials employed must be free of barium or antimony. Measurements have shown that a second application of paraffin to a hand area, after the first lift has been peeled off, does not remove any significant additional amount of Ba or Sb.

Figures 7 and 8 show, respectively, the mode of application of the molten paraffin to the back of the hand, and the subsequent removal of the solidified paraffin. Several hundred special paraffin-life hand-sampling kits have been made up and distributed to various interested law enforcement agencies, during the past several years, at cost. Each kit contains high-purity paraffin, and all other necessary clean materials, a description of the procedure to be employed, and copies of Figs. 7 and 8. These kits are frequently employed for the sampling of the hands of suspects in shooting cases, and of victims in cases of questionable suicides.

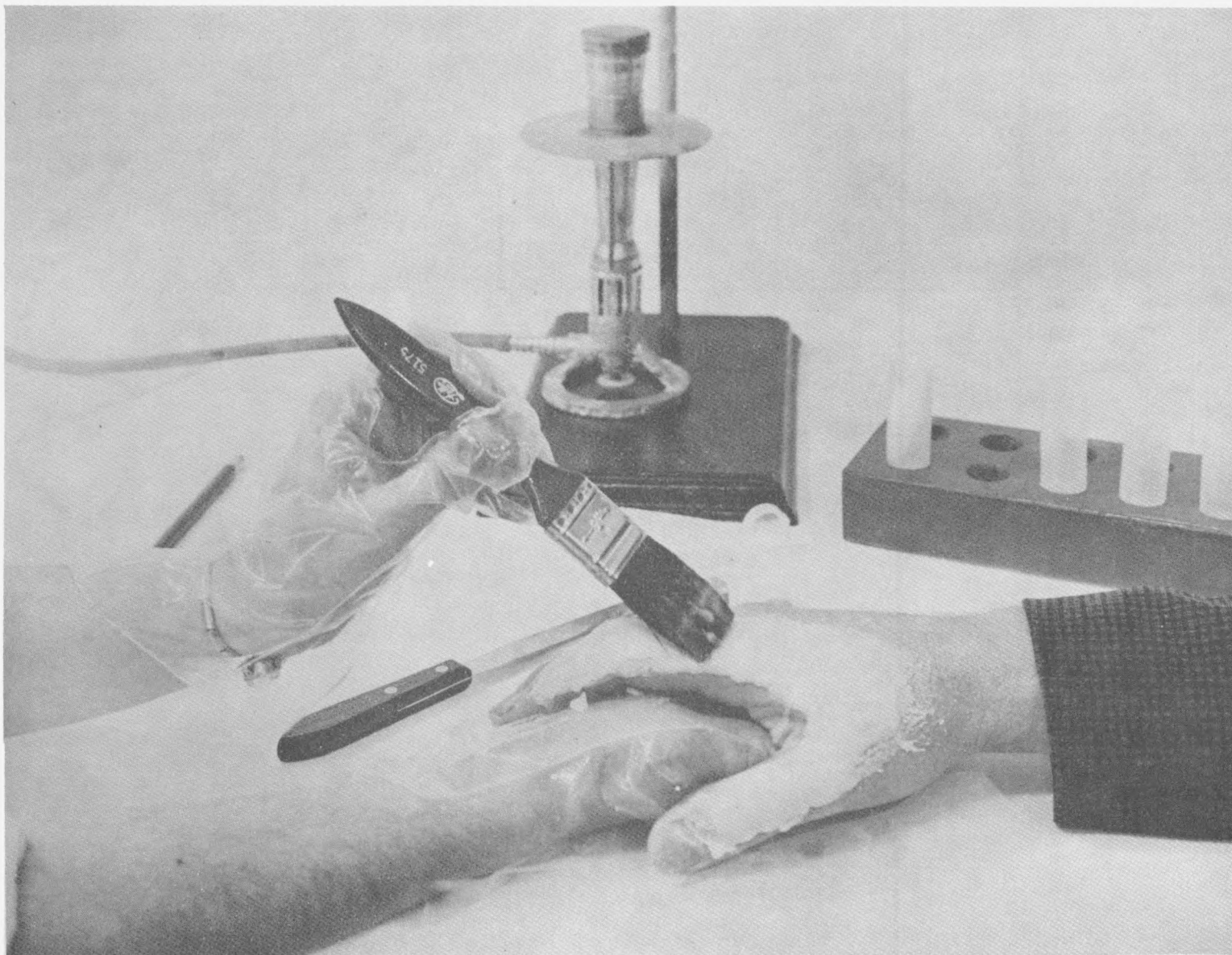


Fig. 7. Application of paraffin to the hand

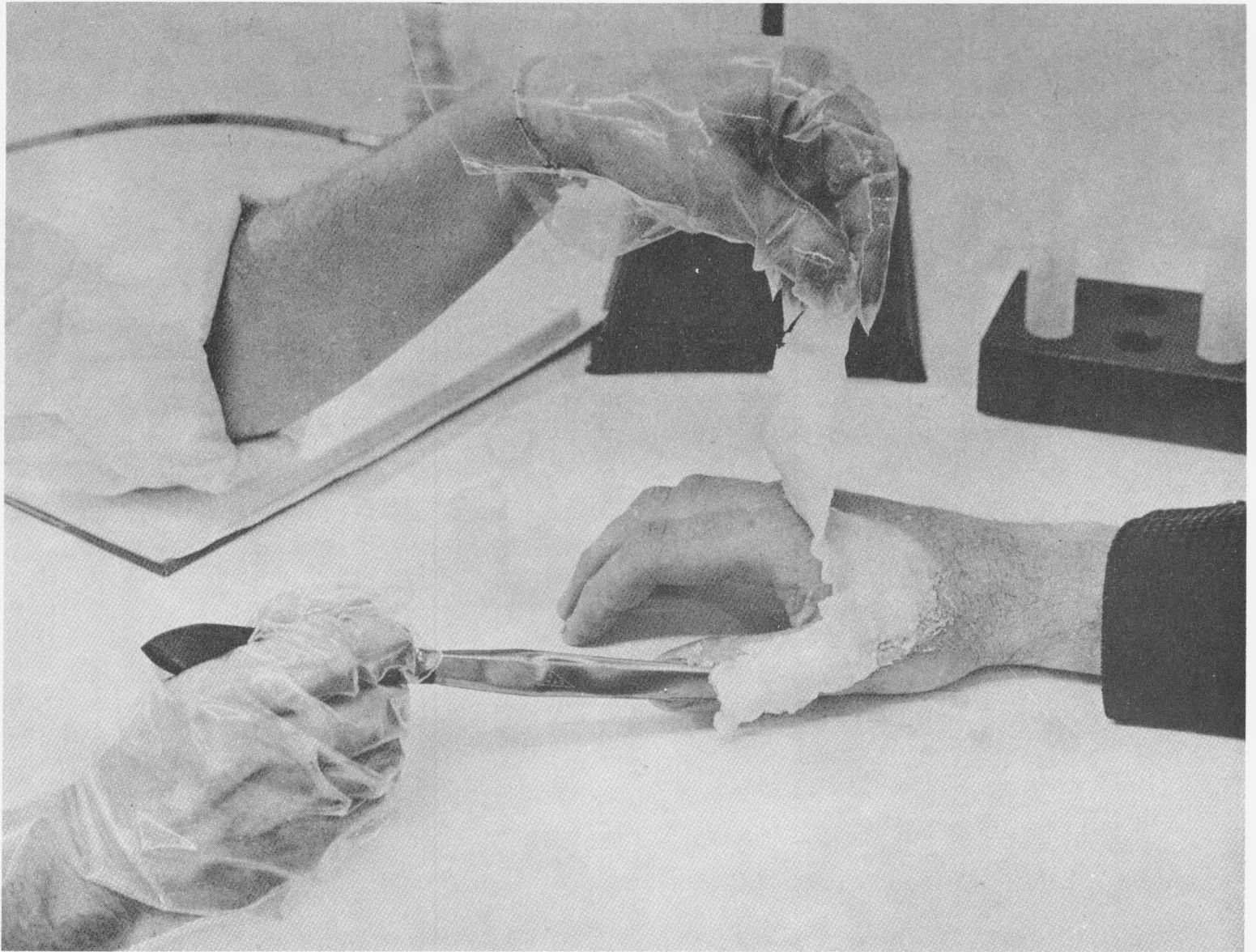


Fig. 8. Removal of paraffin lift

3.5 DISTRIBUTION OF GUNSHOT RESIDUES ON THE GUNHAND

Exploratory measurements were carried out early in the investigation to ascertain on which area of the gunhand there was a maximum deposition of gunshot residues. Test firings were conducted with the gunhand encased in a plastic glove - containing three moistened 2-in. -diam filter-paper discs - as shown in Fig. 9. The paper discs were placed in the "thumb-web" area, the back of the hand, and around the trigger finger, as can be seen in the figure. The use of plastic gloves was expected to eliminate the necessity of a post-irradiation radiochemical separation of the induced ^{139}Ba and ^{122}Sb activities, since the plastic prevented NaCl from perspiration reaching the filter-paper discs, but there were sufficient impurities in the filter paper that a radiochemical-separation procedure still had to be used.

The results of some illustrative single firings of two different kinds of cartridges (Peters and Western) in a 0.38-caliber revolver are shown in Table 3. After a firing, each paper disc was activated for 30 minutes in the reactor (1.8×10^{12} n/cm²-sec thermal-neutron flux) then heated in dilute HNO₃-HCl solution - along with Ba⁺², Sb⁺³, and Cu⁺² carriers - and the three induced activities radiochemically separated from other activities, and from one another, for counting on the NaI(Tl) gamma-ray spectrometer. As can be seen from Table 3, the largest amount of residue was found, in each case, on the trigger-finger patch, the next largest amount was found on the thumb-web patch, and the smallest amount was found on the back-of-the-hand patch. The large amount found on the trigger finger was later shown to be partially due to actual contact with the gun (the gun used in these test firings had not been rigorously cleaned).

Similar test-firing measurements (also with a 0.38-caliber revolver), using plastic gloves moistened in the same areas with paraffin oil -



Fig. 9. Plastic glove with moist filter paper patches for gunshot-residue distribution studies

instead of using water-moistened filter-paper discs – were also carried out. After each firing, each oil-coated area was carefully wiped with a small piece of filter paper, which was then activated, radiochemically separated, and counted as before. The results were quite similar to those found with the moist paper discs (shown in Table 3)

Table 3
DISTRIBUTION OF GUNSHOT-RESIDUE ELEMENTS ON THREE
AREAS OF THE GUNHAND AFTER SINGLE FIRINGS
(Plastic glove – moist filter-paper patch technique;
0.38-caliber revolver)

Ammunition	Hand Area	Ba	Sb	Cu
Peters	Trigger finger	4.3	1.1	2.4
	Thumb web	0.87	0.20	0.47
	Back of hand	0.94	0.19	0.28
Western	Trigger finger	3.3	0.37	4.2
	Thumb web	1.1	0.23	3.2
	Back of hand	0.68	0.06	0.37

It is of importance to note that the amounts of Ba and Sb found on the thumb-web paper discs are quite typical of the amounts found in paraffin lifts of the same hand area (again, with 0.38-caliber revolver firings). Since the moist paper discs should hold, and remove, essentially all the gunshot-residue material falling on them, this implies that the paraffin-lift technique is quite efficient for the removal of gunshot-residue material clinging to the skin.

3.6 SINGLE VERSUS MULTIPLE FIRINGS AND EFFECT OF GUN CALIBER

Some of the earliest measurements carried out indicated that, other factors being equal, the amount of detectable gunshot residue on the back of the gunhand increased with the number of successive firings of a particular gun. Three guns were used in these measurements: a 0.22-caliber revolver (with Western ammunition), a 0.38-caliber revolver (with Winchester ammunition), and a 0.45-caliber automatic (with Winchester ammunition). Each gun was fired 10 times (by 10 different persons), with a gunhand paraffin-life sampling after each firing; then each was fired three times in succession by two or more persons, with gunhand sampling after each three-shot sequence; and finally each gun was fired six times in succession by two persons, with sampling after each six-shot sequence. Each person firing had not fired a gun for at least several days prior to these firings, but also had not just recently washed his hands. Thus, the results obtained include small amounts of Ba and Sb possibly already on his hands before the firing. The three guns were not cleaned between firings. The results of these various firings are shown in Table 4.

The data shown in Table 4 provide the basis for two tentative conclusions:

1. The amount of Ba and Sb deposited increases with increasing caliber of weapon.
2. The amount of Ba and Sb deposited does not increase significantly with increasing number of firings (at least in the range of 1, 3, and 6 firings).

It had been assumed, on the basis of a few earlier random measurements (i. e., not under closely controlled conditions), that the amount of residue would increase with increasing number of firings of a given weapon. The

Table 4
EFFECT OF NUMBER OF FIRINGS UPON AMOUNT OF
GUNSHOT-RESIDUE ELEMENTS FOUND ON GUNHAND

No. of Shots	0.22-Cal. Revolver Western Ammo		0.38-Cal. Revolver Winchester Ammo		0.45-Cal. Automatic Winchester Ammo	
	$\mu\text{g Ba}$	$\mu\text{g Sb}$	$\mu\text{g Ba}$	$\mu\text{g Sb}$	$\mu\text{g Ba}$	$\mu\text{g Sb}$
One shot	0.46	0.07	1.16	0.24	7.7	1.56
	0.82	0.09	0.71	0.19	3.2	0.72
	0.21	0.07	1.12	0.29	5.1	0.60
	0.36	0.06	0.50	0.21	1.6	0.21
	0.44	0.08	0.53	0.14	5.2	0.62
	0.32	0.07	0.45	0.28	4.0	0.34
	0.22	0.07	0.40	0.20	6.5	0.82
	a	0.07	0.51	0.24	3.9	0.81
	0.32	0.05	0.95	0.30	5.5	1.32
	0.45	0.06	0.67	0.28	15.4	3.12
Mean:	0.40	0.07	0.70	0.24	5.8	1.01
Three shots	0.24	0.05	0.81	0.34	2.9	0.58
	0.46	0.14	0.86	0.57	8.3	1.5
			2.0	0.61		
			0.86	0.38		
	Mean:	0.35	0.10	1.14	0.47	5.6
Six shots	0.28	0.10	1.2	0.45	2.6	0.89
	0.35	0.24	0.81	0.37	0.95	0.18
	Mean:	0.32	0.17	1.02	0.41	1.8

^aSample spoiled during analysis.

data of Table 4, and subsequent data, indicate that any increase in deposit, if any, is quite small. It is now postulated that a firing, while depositing a fresh supply of residue, also shakes and/or blows off of the back of the hand most of the residue that is already there from a previous firing. The increase in residue with increasing weapon caliber, indicated by the data of Table 4, has been confirmed in many other measurements, described later in this report. However, this tendency can be reversed in some instances - as the result of other variables, such as the type of weapon, condition of the weapon, ammunition used, etc.

3.7 ORIGIN OF Ba AND Sb - IN CARTRIDGE PRIMERS

Although the paper of Harrison and Gilroy⁽¹⁸⁾ stated that Ba and Sb compounds were added as primer ingredients in U. S. ammunition, no information was provided on their typical amounts. In private conversations with Mr. Ray Pinker (then Chief Criminalist of the Los Angeles Police Department Crime Laboratory), it was learned that a typical primer might contain a total of about 25 milligrams of material, an unknown fraction of this consisting, typically, of $\text{Ba}(\text{NO}_3)_2$ and Sb_2S_3 . Some exploratory studies were therefore designed and carried out, to: (1) obtain some measure of the total amounts of Ba and Sb in commercial cartridge primers, and (2) see whether these amounts, or their ratio, differed appreciably amongst cartridges of different manufacture.

Five different brands of 0.38-caliber cartridges were studied, using a revolver. In each case, one firing was made with a cartridge from which the bullet and powder had been removed, but not the primer - the discharged material being collected on a clean 6-in. x 6-in. sheet of cleaned polyethylene held six inches in front of the gun muzzle. The collected total residue on the sheet was then analyzed for Ba and Sb via NAA, in each case. As can be seen from the data shown in Table 5,

Table 5
ANALYSIS OF PRIMER, MUZZLE-BLAST, AND CYLINDER-BLAST
PRODUCTS FROM FIVE 0.38-CALIBER AMMUNITIONS

Brand of Ammunition	Sample	μg of Elements Found			
		First Test		Second Test	
		Ba	Sb	Ba	Sb
Federal	Primer product	334.	100.	--	--
	Cylinder blast, inner	9.9	7.2	--	--
	Cylinder blast, outer	28.	1.1	--	--
	Muzzle blast, inner	9.8	8.2	--	--
	Muzzle blast, outer	17.4	10.1	--	--
Western	Primer product	246.	17.2	--	--
	Cylinder blast, inner	--	--	3.9	6.9
	Cylinder blast, outer	318.	16.9	43.	35.
	Muzzle blast, inner	4.5	6.2	12.	11.
	Muzzle blast, outer	4.1	7.1	15.	14.
Peters	Primer product	128.	38.	--	--
	Cylinder blast, inner	4.8	6.3	5.5	4.0
	Cylinder blast, outer	5.9	5.6	13.	9.0
	Muzzle blast, inner	9.9	4.8	13.3	6.7
	Muzzle blast, outer	12.	9.9	9.9	9.9
Remington	Primer product	49.	16.	--	--
	Cylinder blast, inner	5.3	4.4	3.3	3.4
	Cylinder blast, outer	9.8	6.5	5.3	5.1
	Muzzle blast, inner	18.	7.1	10.	3.8
	Muzzle blast, outer	9.5	7.5	20.	10.6
Winchester	Primer product	175.	168	--	--
	Cylinder blast, inner	3.3	6.3	4.3	6.9
	Cylinder blast, outer	2.2	4.7	17.	23.
	Muzzle blast, inner	15.	20.	21.	33.
	Muzzle blast, outer	8.7	16.	11.	25.

anywhere from 49 to 334 μg of Ba, and from 16 to 168 μg of Sb, were collected. These data confirm that Ba and Sb are present as appreciable constituents of the primers of these illustrative 0.38-caliber U. S. cartridges. In addition, one or two firings were carried out with each of these brands of 0.38-caliber cartridges, using whole cartridges – again collecting the residue ejected in the forward direction on a sheet of cleaned polyethylene held six inches in front of the gun muzzle. As shown in the diagram of Fig. 10, a dark-grey zone of deposit was observed around the hole made by the bullet, then a zone in which no residue was visible to the eye, and then a more diffuse light-grey outer zone of deposit. Each polyethylene sheet was then quartered, and samples of the inner zone (Zone 1 in Fig. 10) and the outer zone (Zone 2 in Fig. 10) analyzed for Ba and Sb by NAA. These results are also shown in Table 5. As seen in the table, the amounts of Ba so collected ranged from 4.5 μg to 21 μg (Zone 1) and from 4.1 μg to 20 μg (Zone 2). The Sb values ranged from 3.8 μg to 33 μg (Zone 1), and from 7.1 μg to 25 μg (Zone 2). The outer region (Zone 2), of course, covered a much larger area than the inner region (Zone 1), as can be seen from Fig. 10, so the deposit density ($\mu\text{g}/\text{cm}^2$) was greater in Zone 1. The intermediate region was not analyzed, although it no doubt contained appreciable amounts of Ba and Sb also – even though visual inspection indicated a lower deposit density than in either Zones 1 or 2.

Experiments were also carried out of "cylinder blast", using a similar polyethylene-sheet collector, by cutting a small hole in the center of a 6-in. x 6-in. sheet of cleaned polyethylene, and sliding this along the gun barrel to just in front of the cylinder. Even though the collector sheet was not out in front of the muzzle, in the direction of which most of the residue material is ejected, surprisingly large amounts of Ba and Sb were found on the polyethylene after each firing – probably the result of both leakage from the revolver and back-drifting of some of the material ejected

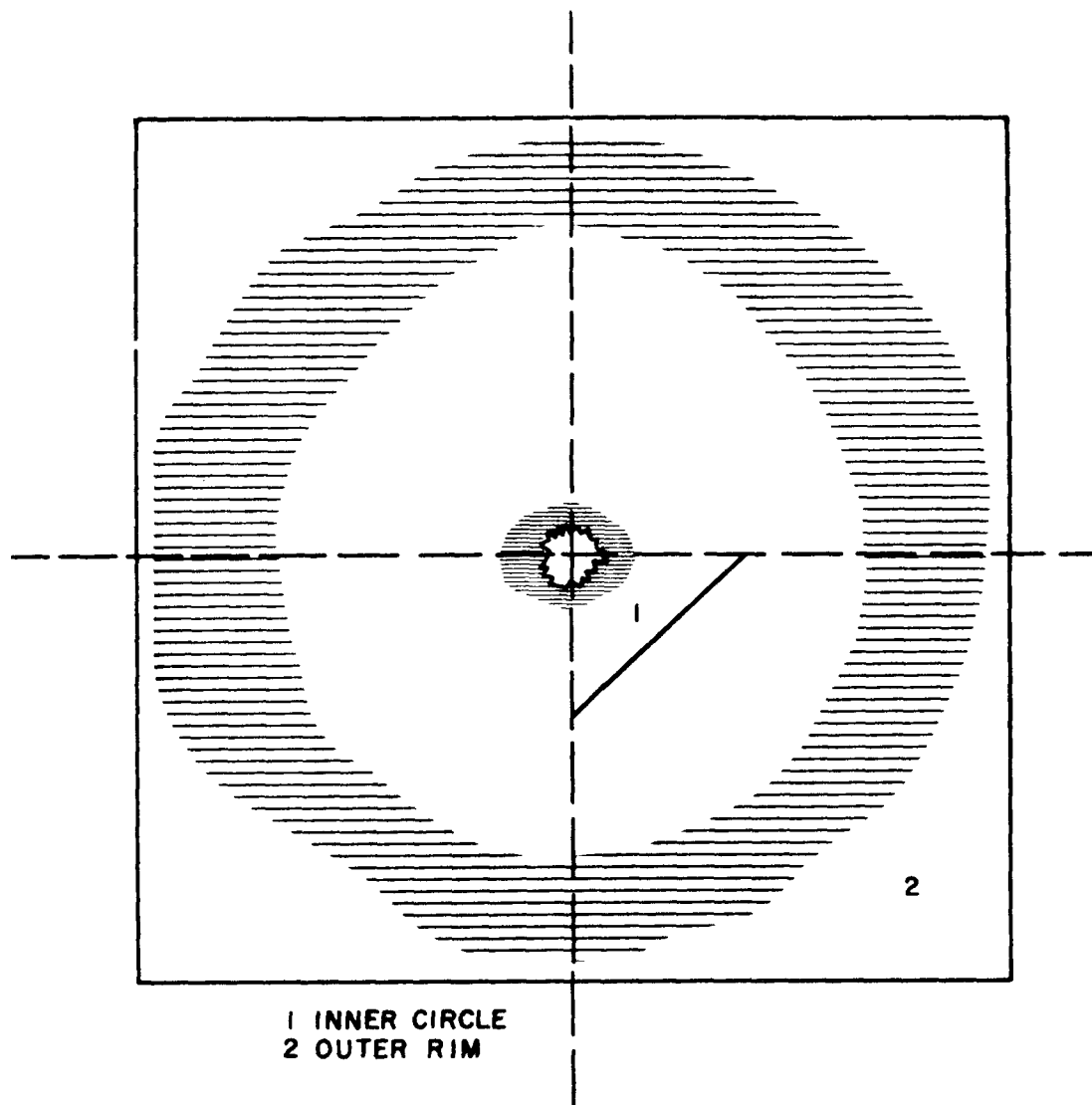


Fig. 10. Sampling of polyethylene sheet after muzzle blast

from the muzzle. The results of these experiments are also shown in Table 5. As in the case of the muzzle blasts, two rings of deposit were visually observable: an inner dark-gray ring (Zone 1), and an outer light-gray ring (Zone 2). As can be seen from Table 5, the Ba values found ranged from 3.3 μg to 9.9 μg (Zone 1), and from 2.2 μg to 318 μg (Zone 2). The corresponding Sb values ranged from 3.4 μg to 7.2 μg (Zone 1), and from 1.1 μg to 35 μg (Zone 2).

The cleaned polyethylene-sheet material itself was also analyzed for Ba and Sb (and Cu), and found to contain quite negligible levels of these elements. In a number of the firings in which muzzle-blast and "cylinder-blast" material was collected, the samples were also analyzed for copper. Values ranging from 0.4 μg Cu to 64 μg were found.

3.8 EFFECT OF WIND DIRECTION ON RESIDUE DEPOSITION

Exploratory studies were made of the effect of wind direction on the amount of residue deposited in test firings. A high-velocity fan was placed about five feet from the firing hand. The wind velocity at the gun position, measured by an Alnor Thermoanemometer, was 500 ± 100 linear feet per minute, in each case. In the tests, the fan was placed so as to blow from, respectively, the front of, the back of, the side of, and below the gun hand. For each wind direction, the 0.38-caliber revolver used was fired three times, using Winchester ammunition. The back of the gunhand was sampled with paraffin after each test, and analyzed for Ba and Sb by NAA as usual. The results are shown in Table 6.

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

Table 6
EFFECT OF WIND DIRECTION ON GUNSHOT-RESIDUE DEPOSITION

Wind Direction	μg of Residue Found on Gunhand	
	Ba	Sb
From front	0.62	0.26
From right side	0.38	0.19
From behind	0.21	0.13
From below	0.16	0.13

3.9 EFFECT OF WASHING THE HANDS AFTER FIRING

A test was made to determine the effect of washing the hands after firing a gun. The gunhand of an individual was sampled with paraffin before firing, and after he had fired a 0.38-caliber revolver six times and washed his hands (normal soap-and-water wash). Before firing, the amounts found on the back of his hand were 0.11 μg Ba and 0.01 μg Sb. After firing the gun and washing his hands, the amounts found on the back of his gunhand were 0.05 μg Ba and 0.01 μg Sb. Thus, as expected, it appears that normal washing of the hands destroys the evidence of a person having recently fired a gun.

3.10 RESIDUE PICKUP FROM THE HANDLING OF GUNS

It was of interest to ascertain whether the mere handling of uncleaned guns could leave residues on the hands. To explore this subject, the hands of a person who had handled several guns with both hands, but had not fired them, were sampled with paraffin, and the paraffin lifts then analyzed for Ba and Sb by the usual NAA procedure. The palm of the hand and the back of the hand were both sampled. As can be seen from Table 7, some pickup of residue from the uncleaned guns is evident - particularly on the palm of the hand.

Table 7
EFFECT OF EXTENSIVE HANDLING OF UNCLEANNED GUNS

Hand Area	μg of Elements Found	
	Ba	Sb
Back of right hand	0.49	0.30
Back of left hand	0.44	0.25
Palm of right hand	0.62	0.44
Palm of left hand	0.71	0.49

In a related exploratory study, three different uncleaned revolvers (0.22-, 0.38-, and 0.45-caliber) were swabbed with wet filter paper, and the swabbings then analyzed for Ba and Sb by the usual NAA procedure. The handle, barrel, and chamber areas of each gun were swabbed. The results are shown in Table 8. Obviously, uncleaned guns do have considerable residue material on their surfaces, some of which can be transferred to the hand (primarily to the palm) by mere handling of such guns.

Table 8
NEUTRON ACTIVATION ANALYSIS OF SWABBINGS OF
UNCLEANED GUNS

Revolver Caliber	Gun Surface Swabbed	μg of Elements Found	
		Ba	Sb
0.22	Handle	0.27	0.27
	Barrel and chamber	5.1	0.56
0.38	Handle	1.8	0.57
	Barrel and chamber	8.7	4.8
0.45	Handle	0.60	0.39
	Barrel and chamber	3.1	2.1

3.11 EXPLORATORY HANDBLANK MEASUREMENTS

Once barium and antimony, as primer constituents, had been shown to be deposited on the back of the gunhand in small amounts (but amounts readily measurable via high-flux NAA) in firings of handguns, it was important to ascertain whether one or both of these same indicator elements might be present on people's hands from sources other than the firing of a gun, e. g., from the materials encountered in their normal occupation.

The first exploratory study of occupational handblanks was carried out with the cooperation of the Los Angeles Police Department, thanks to the efforts of Mr. Ray Pinker, Chief Criminalist of the LAPD. He and his colleagues took paraffin lifts of 22 persons on the LAPD staff – persons such as secretaries, clerks, administrative personnel, laboratory personnel, etc. The sampling did not include anyone who had fired a gun within at least the previous several days. The sampling was done while the person was engaged in his or her normal occupation – not just after washing their hands. The paraffin lifts were analyzed at General Atomic by the usual NAA procedure. The results are shown in Table 9. It is seen that small, but quite measurable, amounts of barium were found on each hand of all 22 persons sampled. Considerably smaller amounts of antimony were found on the hands of quite a few of these people, but the amounts present were below the limit of detection (under the conditions employed) in slightly more than half the cases. As shown in Table 9, the handblank Ba values ranged from as low as $0.01\ \mu\text{g}$ to as high as $0.48\ \mu\text{g}$, with an average value of $0.13 \pm 0.11\ \mu\text{g}$ (1σ). Similarly, the handblank Sb values ranged from $<0.01\ \mu\text{g}$ up to $0.06\ \mu\text{g}$, with an average value of $0.015 \pm 0.012\ \mu\text{g}$ (1σ). In the averaging, lesser values were taken as actual values. The corresponding median handblank values were $0.09\ \mu\text{g}$ (Ba) and $<0.01\ \mu\text{g}$ (Sb). It was quite evident, even from the limited

Table 9
FIRST GROUP OF OCCUPATIONAL HANDBLANK MEASUREMENTS
(LAPD office and laboratory people)

Person No.	Hand	μg Found		Person No.	Hand	μg Found	
		Ba	Sb			Ba	Sb
1	R	0.14	0.06	12	R	0.15	<0.01
	L	0.22	0.06		L	0.07	<0.01
2	R	0.32	0.03	13	R	0.04	0.02
	L	0.19	0.01		L	0.01	<0.01
3	R	0.03	<0.01	14	R	0.22	<0.01
	L	0.04	<0.01		L	0.08	0.01
4	R	0.18	0.02	15	R	0.03	<0.01
	L	0.12	0.02		L	0.04	<0.01
5	R	0.48	0.01	16	R	0.09	<0.01
	L	0.44	0.01		L	0.08	0.03
6	R	0.18	<0.01	17	R	0.26	a
	L	0.32	<0.01		L	0.09	a
7	R	0.07	<0.01	18	R	0.11	<0.01
	L	0.02	<0.01		L	0.06	<0.01
8	R	0.07	<0.01	19	R	0.10	<0.01
	L	0.02	<0.01		L	0.08	<0.01
9	R	0.03	<0.01	20	R	0.26	0.02
	L	0.03	<0.01		L	0.13	0.01
10	R	0.17	0.03	21	R	0.15	<0.01
	L	0.06	<0.01		L	0.25	0.01
11	R	0.09	<0.01	22	R	0.09	<0.01
	L	0.07	<0.01		L	0.09	0.02

Maximum Ba 0.48 μg
Minimum Ba 0.01 μg
Average Ba 0.13 μg
Median Ba 0.09 μg

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

^a Sample spoiled during analysis.

number of test firings conducted at the time these first handblank measurements were made (e.g., values such as those shown in Table 4), that even a single firing of a revolver or automatic pistol usually deposited quite a bit larger amounts of Ba and Sb on the back of the gunhand than were likely to be already present from other sources.

Later, a second group of people (20) was studied. This group included eight additional occupations not included in the first group. The second group consisted mostly of people engaged in various occupations at General Atomic. Again, none of the people sampled had fired a gun within at least the previous several days. Again, also, each person was sampled while engaged in his or her normal occupation – not just after washing their hands. As seen in Table 10, the Ba values ranged from 0.045 μg to 4.70 μg , with a mean value of 0.63 μg and a median value of 0.26 μg . The Sb values ranged from < 0.004 μg to 0.383 μg , with a mean value of 0.051 μg and a median value of 0.023 μg . Clearly, a few occupations resulted in elevated handblank values, particularly of barium (e.g., automobile mechanics – presumably arising from Ba additives used in automobile greases that they handle).

A third group of people studied (15 persons) included a number of additional occupations. The conditions of sampling (paraffin lifts during normal occupational activities) and analysis (NAA) were the same as for the first two groups. The results obtained with these 15 additional persons are summarized in Table 11. The Ba values ranged from 0.080 μg up to 2.61 μg , with a mean value of 0.77 μg and a median value of 0.42 μg . The Sb values ranged from < 0.003 μg to 0.062 μg , with a mean value of 0.016 μg and a median value of 0.008 μg .

The fourth group of people studied (29 persons) included still other occupations. The results obtained are shown in Table 12. The Ba values are seen to range from 0.025 μg to 12.1 μg , with a mean value of 0.79 μg

Table 10

SECOND GROUP OF OCCUPATIONAL HANDBLANK MEASUREMENTS

Person No.	Occupation	Hand	μg Found		Person No.	Occupation	Hand	μg Found	
			Ba	Sb				Ba	Sb
23	Painter	R	0.453	<0.008	33	Automobile Mechanic	R	4.70	0.383
		L	0.385	<0.004			L	2.80	0.198
24	Painter	R	0.481	0.031	34	Watch Repairman	R	0.219	0.051
		L	0.303	<0.010			L	0.281	<0.006
25	Painter	R	0.795	a	35	Gardener	R	0.219	0.023
		L	0.472	0.031			L	0.267	0.018
26	Carpenter	R	0.310	0.090	36	Heating & air condi- tioning repairman	R	1.28	0.037
		L	0.290	0.065			L	1.18	0.074
27	Carpenter	R	0.404	0.058	37	Student, laboratory technician	R	0.116	0.012
		L	0.264	0.039			L	0.059	<0.005
28	Storekeeper	R	0.127	0.110	38	Student, laboratory technician	R	2.68	0.074
		L	0.181	0.135			L	0.346	0.023
29	Public accountant	R	0.091	<0.004	39	Photographer	R	0.220	0.069
		L	0.103	<0.004			L	0.257	0.069
30	Television technician	R	0.047	<0.004	40	Radioisotope technician	R	0.612	0.022
		L	0.057	<0.004			L	0.200	0.012
31	Secretary	R	0.137	0.011	41	Radioisotope technician	R	0.068	0.017
		L	0.068	<0.012			L	0.055	0.020
32	Automobile mechanic	R	1.78	0.051	42	Radioisotope technician	R	0.055	0.033
		L	2.78	0.174			L	0.045	<0.006
Maximum Ba			4.70 μg	Maximum Sb			0.383 μg		
Minimum Ba			0.045 μg	Minimum Sb			<0.004 μg		
Average Ba			0.63 μg	Average Sb			0.051 μg		
Median Ba			0.26 μg	Median Sb			0.023 μg		
^a Sample spoiled during analysis.									

^aSample spoiled during analysis.

Table 11
THIRD GROUP OF OCCUPATIONAL HANDBLANK MEASUREMENTS

Person No.	Occupation	Hand	μg Found	
			Ba	Sb
43	Chemist	R	0.119	0.011
		L	0.080	0.008
44	Plumber	R	1.65	0.018
		L	2.19	0.017
45	Plumber	R	0.481	0.052
		L	0.861	0.047
46	Electronic technician	R	0.147	0.024
		L	0.085	0.017
47	Secretary	R	0.208	0.004
		L	0.152	0.006
48	Graphic artist	R	0.362	0.006
		L	0.353	<0.003
49	Graphic artist	R	1.14	0.006
		L	2.61	0.005
50	Graphic artist	R	1.95	0.005
		L	1.57	0.014
51	Graphic artist	R	0.752	0.004
		L	0.360	0.006
52	Graphic artist	R	0.550	0.005
		L	0.509	<0.002
53	Graphic artist	R	0.483	0.002
		L	1.34	0.005
54	Graphic artist (supervisor)	R	0.241	0.009
		L	0.235	0.007

Table 11 (Continued)

Person No.	Occupation	Hand	μg Found		
			Ba	Sb	
55	Carpenter	R	0.214	0.062	
		L	0.182	0.021	
56	Mechanic	R	1.98	0.049	
		L	1.85	0.046	
57	Carpenter	R	0.340	0.017	
		L	0.231	0.017	
Maximum Ba			2.61 μg	Maximum Sb	0.062 μg
Minimum Ba			0.080 μg	Minimum Sb	<0.003 μg
Average Ba			0.77 μg	Average Sb	0.016 μg
Median Ba			0.42 μg	Median Sb	0.008 μg

Table 12

FOURTH GROUP OF OCCUPATIONAL HANDBLANK MEASUREMENTS

Person No.	Occupation	Hand	μg Found	
			Ba	Sb
58	Chauffeur	R	0.139	0.028
		L	0.152	0.021
59	Painter	R	0.481	0.029
		L	0.722	0.049
60	Electrician	R	0.508	0.054
		L	0.474	0.094
61	Maintenance man	R	0.228	0.022
		L	0.277	0.037
62	Maintenance man	R	1.21	0.180
		L	0.760	0.119
63	Painter	R	1.17	0.121
		L	1.51	0.070
64	Painter	R	0.918	0.027
		L	0.567	0.015
65	Draftsman	R	0.071	0.014
		L	0.086	0.008
66	Draftsman	R	0.135	0.009
		L	0.127	0.009
67	Draftsman	R	0.536	0.014
		L	0.470	0.007
68	Draftsman	R	0.171	0.034
		L	0.220	0.016
69	Draftsman	R	1.07	0.004
		L	1.64	0.004
70	Draftsman	R	0.159	0.081
		L	0.167	0.136

Table 12 (Continued)

Person No.	Occupation	Hand	μg Found	
			Ba	Sb
71	Draftsman	R	0.165	0.010
		L	0.373	0.031
72	Machinist	R	2.06	0.023
		L	1.94	0.015
73	Machinist	R	1.12	0.099
		L	1.26	0.127
74	Machinist	R	0.165	0.028
		L	0.345	0.026
75	Machinist	R	0.255	0.120
		L	0.318	0.598
76	Machinist	R	1.79	0.072
		L	1.99	0.098
77	Machinist	R	12.1	0.145
		L	5.28	0.128
78	Machinist	R	0.282	0.021
		L	0.440	0.036
79	Machinist	R	0.370	0.017
		L	0.204	0.021
80	Machinist	R	0.162	0.003
		L	0.154	0.003
81	Computer operator	R	0.102	0.008
		L	0.041	0.001
82	Computer operator	R	0.041	0.003
		L	0.071	0.003
83	Computer operator	R	0.032	0.002
		L	0.025	0.002
84	Computer operator	R	0.192	0.002
		L	0.168	0.005

Table 12 (Continued)

Person No.	Occupation	Hand	μg Found	
			Ba	Sb
85	Computer operator	R	0.045	<0.002
		L	0.032	<0.002
86	Computer operator	R	0.073	0.007
		L	0.082	<0.002
Maximum Ba	12.1 μg	Maximum Sb	0.598 μg	
Minimum Ba	0.025 μg	Minimum Sb	<0.002 μg	
Average Ba	0.79 μg	Average Sb	0.049 μg	
Median Ba	0.27 μg	Median Sb	0.024 μg	

and a median value of 0.27 μg . The Sb values ranged from $<0.002 \mu\text{g}$ to 0.598 μg , with a mean value of 0.049 μg and a median value of 0.024 μg .

The fifth group of people studied (11 persons) was the last group of people investigated during the period covered by this report - with respect to occupational handblank levels of Ba and Sb. This group included some additional occupations. The results are shown in Table 13. The Ba values are seen to range from $<0.005 \mu\text{g}$ to 0.200 μg , with a mean of 0.074 μg and a median of 0.060 μg . The Sb values ranged from $<0.001 \mu\text{g}$ to 0.024 μg , with a mean of 0.005 μg and a median of 0.003 μg .

The total number of people studied (in connection with handblank values) during this period of time was 97 - listed in Tables 9 through 13. The 30 occupations included among these 97 people are listed in Table 14. In Fig. 11, the 192 barium handblank values included in the five tables are presented in a logarithmic distribution form. It is evident that the values approximate a log-normal distribution. Figure 12 displays the corresponding 188 antimony handblank values in the same manner. In this case, the possible log-normal shape of the distribution histogram is compressed somewhat at the low-antimony end, because of the fairly numerous lesser values encountered - since each lesser value was treated as an actual value (even though some 26 early values, reported as $<0.01 \mu\text{g}$ Sb, were distributed proportionately among the three groups of values between 0.001 μg Sb and 0.01 μg Sb). From all the values listed, the median Ba value is found to be about 0.20 μg , and the median Sb value, about 0.010 μg .

Since it has been established that the firing of a handgun typically deposits quite measurable amounts of both Ba and Sb, and hence these two quantities are correlated with one another in firings, it was of interest to ascertain whether any Ba-Sb correlation could be detected in the handblank data. Figure 13 presents a plot of $\log_{10} (\mu\text{g Sb})$ versus $\log_{10} (\mu\text{g Ba})$

Table 13
FIFTH GROUP OF OCCUPATIONAL HANDBLANK MEASUREMENTS

Person No.	Occupation	Hand	μg Found	
			Ba	Sb
87	Nurse	L	0.048	0.002
88	Nurse	R	0.080	<0.002
		L	0.091	0.005
89	Nurse	R	0.026	0.003
		L	0.023	<0.001
90	Nurse	R	0.072	<0.001
		L	0.065	0.011
91	Nurse	R	0.027	<0.001
		L	<0.005	<0.002
92	Pathologist	R	0.086	<0.001
		L	0.105	0.010
93	Pathologist	R	0.041	0.003
		L	0.016	0.003
94	Pathologist	R	0.119	a
		L	0.159	0.005
95	Radiologist	R	0.200	0.002
		L	0.187	0.004
96	Surgeon	R	0.031	0.024
		L	0.048	0.010
97	Medical technician	R	0.054	<0.001

^aSample spoiled during analysis.

Maximum Ba	0.200 μg	Maximum Sb	0.024 μg
Minimum Ba	<0.005 μg	Minimum Sb	<0.001 μg
Average Ba	0.074 μg	Average Sb	0.005 μg
Median Ba	0.060 μg	Median Sb	0.003 μg

Table 14

THIRTY OCCUPATIONS INCLUDED AMONG THE 97 PERSONS
STUDIED IN HANDBLANK MEASUREMENTS

Clerks	Chemists
Secretaries	Plumbers
Painters	Electronic technicians
Carpenters	Graphic artists
Storekeepers	Chauffeurs
Public accountants	Electricians
TV technicians	Maintenance men
Auto mechanics	Draftsmen
Watch repairmen	Machinists
Gardeners	Computer operators
Heating repairmen	Nurses
Students	Pathologists
Lab technicians	Radiologists
Photographers	Surgeons
Radioisotope technicians	Medical technicians

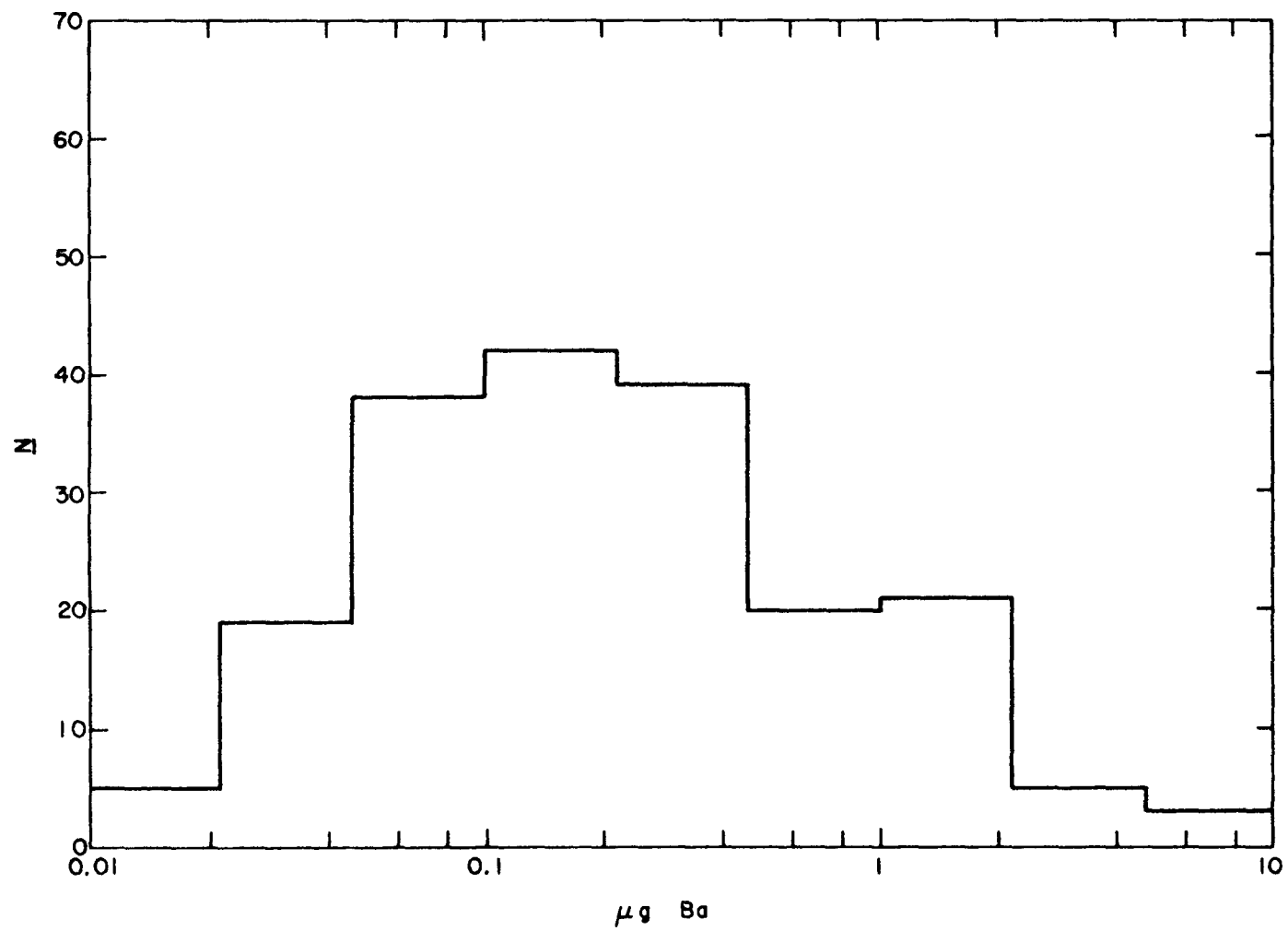


Fig. 11. ^{192}Ba handblank values from 97 persons in 30 different occupations

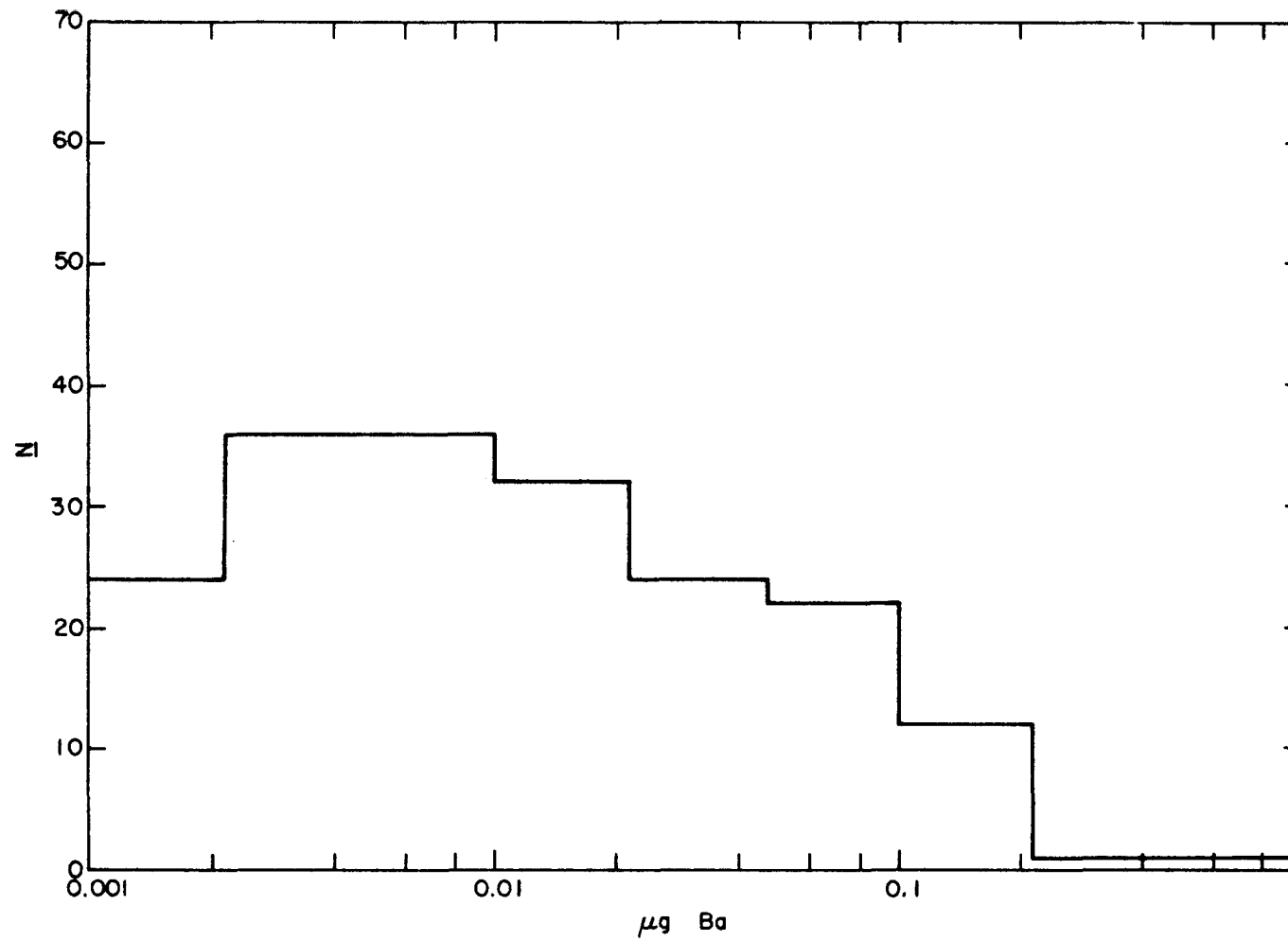


Fig. 12. 188-Antimony handblank values from 97 persons in 30 different occupations

for all of these handblank data. It is evident, by inspection, that the handblank data show very little correlation between the corresponding Sb and Ba values, although there is some evidence that a high Ba value is somewhat more likely to be associated with a high Sb value than with a low Sb value (and that a low Ba value is somewhat more likely to be associated with a low Sb value than with a high Sb value). If one takes the 139 handblank cases in which definite Ba and Sb values were obtained (i. e., excluding cases involving lesser values), and calculates the Sb/Ba ratio in each case, one obtains a mean value of 0.137 (shown as a dotted line in Fig. 13). However, the standard deviation of this ratio, calculated as the square root of 138, is ± 0.219 . It is thus apparent from this numerical approach, also, that the Ba-Sb correlation in handblank values, in general, is rather slight. This is, of course, not necessarily true for a few specific occupations which may normally involve some exposure to both of these elements.

3.12 SUMMARY OF GUNSHOT-RESIDUE MEASUREMENTS (HANDGUNS)

In Table 15, all of the gunshot-residue Ba and Sb values found in test firings, during the period covered by this report, are listed. Of the 144 test firings, 79 were made with 0.38-caliber revolvers, 32 with 0.45-caliber automatics, 16 with 0.22-caliber revolvers, 5 with 0.44-caliber revolvers, 5 with 9 mm automatics, and 3 with 0.22-caliber automatics. The table and its various footnotes, give further particulars. Below, some discussion and summary of the results obtained with the different caliber handguns are given.

3.12.1 0.45-Caliber Automatic Results

The mean values found in the 32 test firings were 3.60 μg Ba and 0.598 μg Sb. These mean values are, respectively, 6.9 times the average

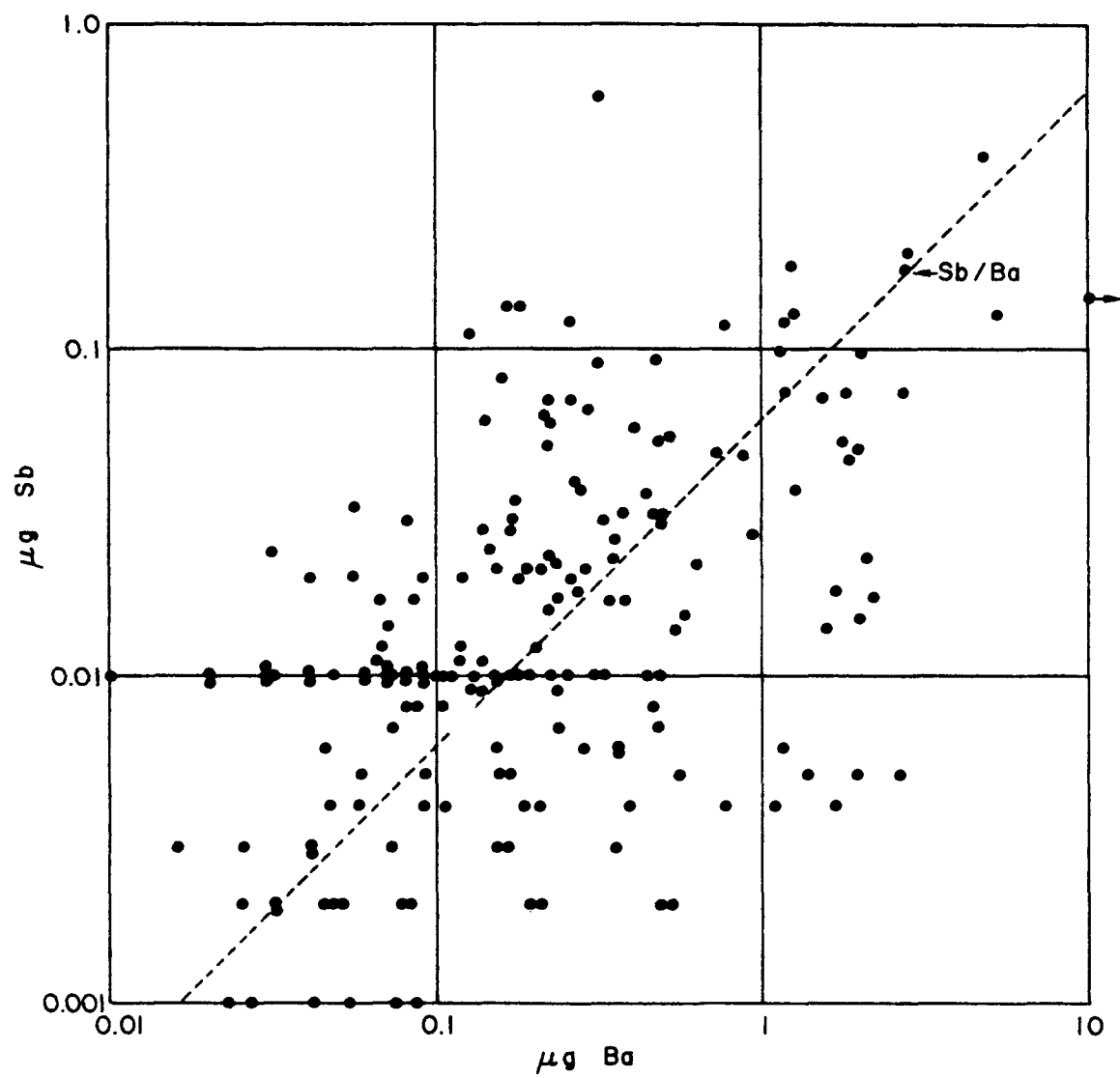


Fig. 13. Ba and Sb handblank values (139 pairs)

Table 15
 COMPILATION OF ALL GUNSHOT-RESIDUE VALUES OBTAINED
 DURING PERIOD REPORTED (HANDGUNS)

Firing Test No.	Weapon		Brand of Ammunition	No. of Firings	Firing Hand	μ g Elements Found	
	Type	Caliber				Ba	Sb
1	Rev.	38	Winch.	1	R	1.16	0.24
2	Rev.	38	Winch.	1	R	0.71	0.19
3	Rev.	38	Winch.	1	R	1.12	0.29
4	Rev.	38	Winch.	1	L	0.50	0.21
5	Rev.	38	Winch.	1	R	0.53	0.14
6	Rev.	38	Winch.	1	L	0.45	0.28
7	Rev.	38	Winch.	1	R	0.40	0.20
8	Rev.	38	Winch.	1	L	0.51	0.24
9	Rev.	38	Winch.	1	R	0.95	0.30
10	Rev.	38	Winch.	1	L	0.67	0.28
11	Rev.	22	West.	1	R	0.46	0.07
12	Rev.	22	West.	1	L	0.82	0.09
13	Rev.	22	West.	1	R	0.21	0.06
14	Rev.	22	West.	1	L	0.36	0.06
15	Rev.	22	West.	1	R	0.46	0.08
16	Rev.	22	West.	1	L	0.32	0.07
17	Rev.	22	West.	1	R	0.22	0.07
18	Rev.	22	West.	1	L	a	0.07
19	Rev.	22	West.	1	R	0.32	0.05
20	Rev.	22	West.	1	L	0.45	0.06
21	Auto.	45	Winch.	1	R	7.7	1.56
22	Auto.	45	Winch.	1	L	3.2	0.72
23	Auto.	45	Winch.	1	R	5.1	0.60
24	Auto.	45	Winch.	1	L	1.6	0.21
25	Auto.	45	Winch.	1	R	5.2	0.62

Table 15 (Continued)

Firing Test No.	Weapon		Brand of Ammunition	No. of Firings	Firing Hand	μg Elements Found	
	Type	Caliber				Ba	Sb
26	Auto.	45	Winch.	1	L	4.0	0.34
27	Auto.	45	Winch.	1	R	6.5	0.82
28	Auto.	45	Winch.	1	L	3.9	0.81
29	Auto.	45	Winch.	1	R	5.5	1.32
30	Auto.	45	Winch.	1	L	15.4	3.12
31	Rev.	38	Winch.	3	L	0.81	0.34
32	Rev.	38	Winch.	3	L	0.86	0.57
33	Rev.	38	Winch.	3	R	2.0	0.61
34	Rev.	38	Winch.	3	L	0.86	0.38
35	Rev.	38	Winch.	6	R	1.2	0.45
36	Rev.	38	Winch.	6	R	0.81	0.37
37	Rev.	22	West.	3	L	0.24	0.05
38	Rev.	22	West.	3	R	0.46	0.14
39	Rev.	22	West.	6	R	0.28	0.10
40	Rev.	22	West.	6	L	0.35	0.24
41	Auto.	45	Winch.	3	L	2.9	0.58
42	Auto.	45	Winch.	3	L	8.3	1.5
43	Auto.	45	Winch.	6	R	2.6	0.89
44	Auto.	45	Winch.	6	R	0.95	0.18
45	Rev.	38	Peters	1	--	1.44	0.62
46	Rev.	38	Peters	1	--	0.64	0.33
47	Rev.	38	Peters	1	--	0.96	0.26
48	Rev.	38	Peters	1	--	0.25	0.08
49	Rev.	38	Peters	1	--	0.85	0.30
50	Rev.	38	Peters	3	--	2.40	0.63
51	Rev.	38	Peters	3	--	1.54	0.58
52	Rev.	38	Peters	3	--	3.28	0.56
53	Rev.	38	Peters	3	--	1.73	0.29
54	Rev.	38	Peters	3	--	0.69	0.39
55	Rev.	38	-----	3	--	2.1	0.62
56	Rev.	38	-----	3	--	2.5	0.66

Table 15 (Continued)

Firing Test No.	Weapon		Brand of Ammunition	No. of Firings	Firing Hand	μg Elements Found	
	Type	Caliber				Ba	Sb
57	Rev.	38	----	3	--	0.97	0.39
58	Rev.	38	----	3	--	2.5	0.57
59	Rev.	38	Peters	1	--	0.88	0.11
60	Auto.	45	----	1	--	0.506	0.181
61	Auto.	45	----	1	--	0.789	0.146
62	Auto.	45	----	1	--	0.614	0.248
63	Auto.	45	----	1	--	0.504	0.140
64	Auto.	45	----	1	--	0.769	0.226
65	Auto.	45	----	1	--	1.39	0.414
66	Auto.	45	----	1	--	0.217	0.068
67	Auto.	45	----	1	--	1.81	0.627
68	Auto.	45	----	1	--	0.795	0.258
69	Auto.	45	----	1	--	0.460	0.098
70	Auto.	45	----	1	--	2.48	0.775
71	Auto.	45	----	1	--	2.40	0.553
72	Auto.	45	----	1	--	2.70	0.268
73	Auto.	45	----	1	--	0.769	0.237
74	Auto.	45	----	1	--	11.4	0.506
75	Auto.	45	----	1	--	3.20	0.297
76	Auto.	45	----	1	--	7.16	0.452
77	Auto.	45	----	1	--	4.29	0.353
78	Rev.	38	Reload	1	R	0.489	0.103
79	Rev.	38	Reload	1	L	0.423	0.128
80	Rev.	38	Reload	1	R	0.330	0.081
81	Rev.	38	Reload	1	L	0.459	0.247
82	Rev.	38	Reload	1	R	0.472	0.194
83	Rev.	38	Reload	1	L	0.205	0.045
84	Rev.	38	----	1	--	3.11	0.395
85	Rev.	38	----	1	--	0.633	0.117
86	Rev.	38	----	1	--	1.71	0.499

Table 15 (Continued)

Firing Test No.	Weapon		Brand of Ammunition	No. of Firings	Firing Hand	μ g Elements Found	
	Type	Caliber				Ba	Sb
87	Rev.	38	----	1	--	2.64	0.542
88	Rev.	38	----	1	--	1.74	0.334
89	Rev.	38	----	1	R	0.168	0.093
90	Rev.	38	----	1	R	0.514	0.398
91	Rev.	38	----	1	R	0.762	0.666
92	Rev.	38	Reload	1	R	2.75	0.678
93	Rev.	38	Reload	1	R	0.99	0.360
94	Rev.	38	Reload	1	R	0.67	0.163
95	Rev.	38	Reload	1	R	0.713	0.253
96	Rev.	38	Reload	1	R	0.252	0.067
97	Rev.	38	Reload	2	R	0.25	0.088
98	Rev.	38	Reload	2	R	0.303	0.096
99	Rev.	38	Reload	4	R	1.48	0.393
100	Rev.	38	Reload	4	R	2.11	0.791
101	Rev.	38	Fed.	1	R	0.480	0.179
102	Rev.	38	Fed.	1	R	4.18	2.23
103	Rev.	38	Fed.	1	R	2.48	1.31
104	Rev.	44	Magnum	1	R	1.49	0.259
105	Rev.	38	Fed.	1	R	1.94	0.595
106	Auto.	22	Fed. Long rifle	1	R	0.54	0.111
107	Auto.	22	Fed. Long rifle	1	R	1.25	0.242
108	Auto.	22	Fed. Long rifle	1	R	0.32	0.058
109	Auto.	25	----	1	R	7.26	1.26
110	Auto.	25	----	1	R	2.22	0.499
111	Auto.	25	----	1	R	8.46	0.561
112	Auto.	25	----	1	R	0.96	0.208
113	Rev.	22	Fed. Long rifle	1	R	0.71	0.072

Table 15 (Continued)

Firing Test No.	Weapon		Brand of Ammunition	No. of Firings	Firing Hand	μ g Elements Found	
	Type	Caliber				Ba	Sb
114	Rev.	22	Fed. Long rifle	1	L	0.195	0.033
115	Rev.	38	Fed.	1	R	0.305	0.113
116	Rev.	38	Fed.	1	R	0.208	0.063
117	Rev.	38	Fed.	1	R	1.09	0.182
118	Rev.	38	Fed.	1	R	0.383	0.156
119	Rev.	38	Fed.	1	R	0.61	0.217
120	Rev.	38	Reload	30	R	0.96	0.926
121	Rev.	38	Reload	30	R	0.97	0.282
122	Rev.	38	Reload	2	R	1.27	0.281
123	Rev.	38	Reload	30	R	1.83	0.604
124	Rev.	38	Reload	30	L	1.63	0.305
125	Rev.	38	Reload	2	R	0.540	0.242
126	Rev.	44	Rem. magnum	1	R	4.52	1.52
127	Rev.	44	Norma magnum	1	R	0.377	0.166
128	Auto.	9mm	Rem.	1	R	15.4	0.056
129	Auto.	9mm	Rem.	1	R	5.59	0.753
130	Auto.	9mm	Rem.	1	R	11.30	2.05
131	Auto.	9mm	Rem.	1	R	3.63	0.610
132	Auto.	9mm	Rem.	1	R	1.37	0.190
133	Rev.	44	Norma magnum	1	R	0.168	0.055
134	Rev.	44	Norma magnum	1	R	0.405	0.113
135	Rev.	38	Reload	1	R	1.04	0.314
136	Rev.	38	Reload	1	R	1.21	0.405
137	Rev.	38	Reload	1	R	1.13	0.334
138	Rev.	38	Reload	1	R	1.09	0.205
139	Rev.	38	Reload	1	R	0.71	0.167
140	Rev.	38	Military	1	L	12.7	4.17

Table 15 (Continued)

Firing Test No.	Weapon		Brand of Ammunition	No. of Firings	Firing Hand	μ g Elements Found	
	Type	Caliber				Ba	Sb
141	Rev.	38	Military	1	R	1.13	0.410
142	Rev.	38	Military	1	R	0.574	0.135
143	Rev.	38	Military	1	R	0.76	0.234
144	Rev.	38	Military	1	R	4.87	0.99

Abbreviations: Auto. = automatic
 Rev. = revolver
 Winch. = Winchester
 Rem. = Remington
 West. = Western
 Fed. = Federal
 R = right hand
 L = left hand
 * = sample spoiled during analysis
 -- = information not available

Notes: (1) Same gun used for tests 1-10, 31-36.
 (2) Same gun used for tests 11-20, 37-40.
 (3) Same gun used for tests 21-30, 41-44.
 (4) Same gun, same ammo, used for tests 55-58; 55 and 56 with dry hand -- 57 and 58 with moist hand.
 (5) Same gun, same ammo, used for tests 60-77.
 (6) Same person fired in tests 60-65, with gun wiped clean after each firing (started with clean hands and clean gun).
 (7) Same person fired in tests 66-71 (started with clean hands and clean gun, but gun not wiped clean between firings).
 (8) Same person fired in tests 72-77 (started with clean hands and clean gun, but gun not wiped clean between firings).

Table 15 (Continued)

- (9) In tests 78-83, 0.38 Special ammo was fired by three different men, in each case holding the gun with both hands; both hands of each man were then sampled.
- (10) In tests 84-88, five different persons each fired the same gun (a murder weapon in an actual case), using the same type of ammo used in a murder (0.38 Special).
- (11) In tests 89-91, three different persons each fired the same gun (a murder weapon) with 0.38 Special ammo.
- (12) Tests 92-144 were carried out at the San Diego County Sheriff's Office firing range; firings by various Deputy Sheriffs, with clean hands; both hands sampled after firing (only gunhand values reported in this Table).
- (13) 0.38 Special ammo was used in tests 92-103, 105, 115-125, and 135-144.
- (14) In tests 101-103 and 105, dysprosium-tagged primers were used.
- (15) In tests 115-119, holmium-tagged primers were used.
- (16) The 0.44-caliber revolver used in test 104 was a Smith & Wesson.
- (17) The 0.22-caliber automatic target pistol used in tests 106-108 was a Hi Standard.
- (18) The 0.25-caliber automatic pistol used in tests 109-112 was a Browning Junior Colt.
- (19) The 9mm automatic used in tests 128-132 was a Luger pistol.
- (20) The 0.22-caliber revolver used in tests 113 and 114 was a Smith & Wesson, with a 6-inch barrel.
- (21) The 0.44-caliber revolver used in tests 126, 127, 133, and 134 was a Smith & Wesson magnum, with a 5-inch barrel.
- (22) The same 0.38-caliber Special revolver was used in tests 135-144.

Ba handblank value ($0.523 \mu\text{g Ba}$) and 19 times the average Sb handblank value ($0.0316 \mu\text{g Sb}$) – obtained by averaging the handblank values found from the measurements of 97 persons listed in Tables 9 through 13. The 0.45-caliber Ba results (32 values) ranged from as low as $0.216 \mu\text{g}$ to as high as $15.4 \mu\text{g}$, with a median value of $2.65 \mu\text{g}$ (13 times the $0.20 \mu\text{g Ba}$ median handblank value). The 0.45-caliber Sb results ranged from as low as $0.068 \mu\text{g}$ to as high as $3.12 \mu\text{g}$, with a median value of $0.43 \mu\text{g}$ (43 times the $0.010 \mu\text{g Sb}$ median handblank value). The degree of overlap of the 0.45-caliber results with the handblank results is shown in Figs. 14 and 15 (Ba and Sb results, respectively).

3.12.2 0.44-Caliber Revolver Results

The mean values found in the five test firings were $1.39 \mu\text{g Ba}$ and $0.422 \mu\text{g Sb}$. These mean values are, respectively, only 2.7 times the average Ba handblank value, but 13 times the average Sb handblank value. The Ba values ranged from $0.168 \mu\text{g}$ to $4.52 \mu\text{g}$, and the Sb values ranged from $0.055 \mu\text{g}$ to $1.52 \mu\text{g}$.

3.12.3 0.38-Caliber Revolver Results

The mean values found in the 79 test firings were $1.31 \mu\text{g Ba}$ and $0.421 \mu\text{g Sb}$. These mean values are, respectively, only 2.5 times the average Ba handblank value, but 13 times the average Sb handblank value. The 0.38-caliber Ba results (79 values) ranged from as low as $0.168 \mu\text{g}$ to as high as $12.7 \mu\text{g}$, with a median value of $0.88 \mu\text{g}$ (4.4 times the median Ba handblank value). The corresponding Sb values ranged from as low as $0.045 \mu\text{g}$ to as high as $4.17 \mu\text{g}$, with a median value of $0.29 \mu\text{g}$ (29 times the median Sb handblank value). The degree of overlap of the 0.38-caliber results with the handblank results is shown in Figs. 16 and 17 (Ba and Sb results, respectively).

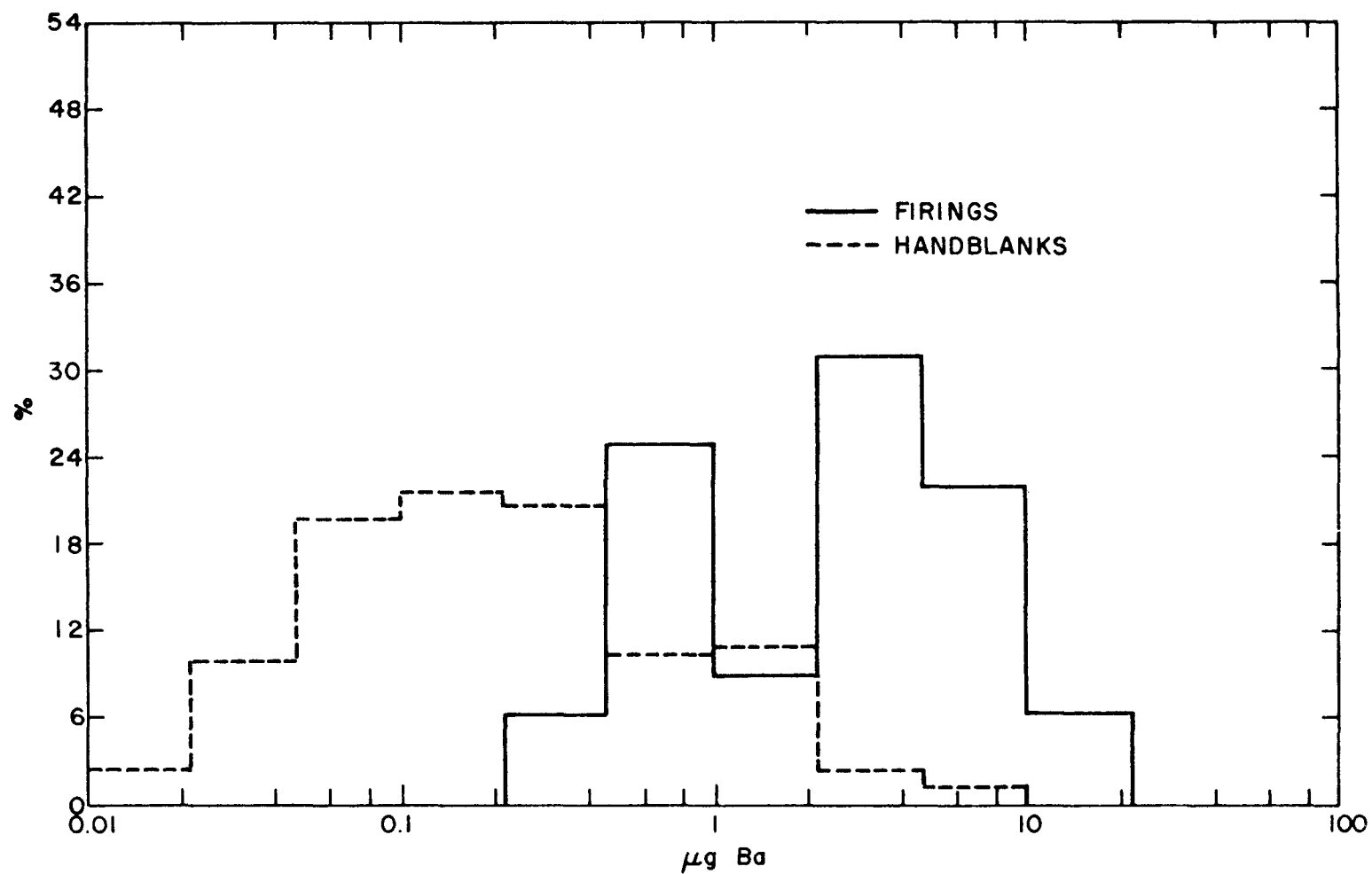


Fig. 14. Comparison of 32 firings of 0.45-caliber automatics with 192 handblank values for barium

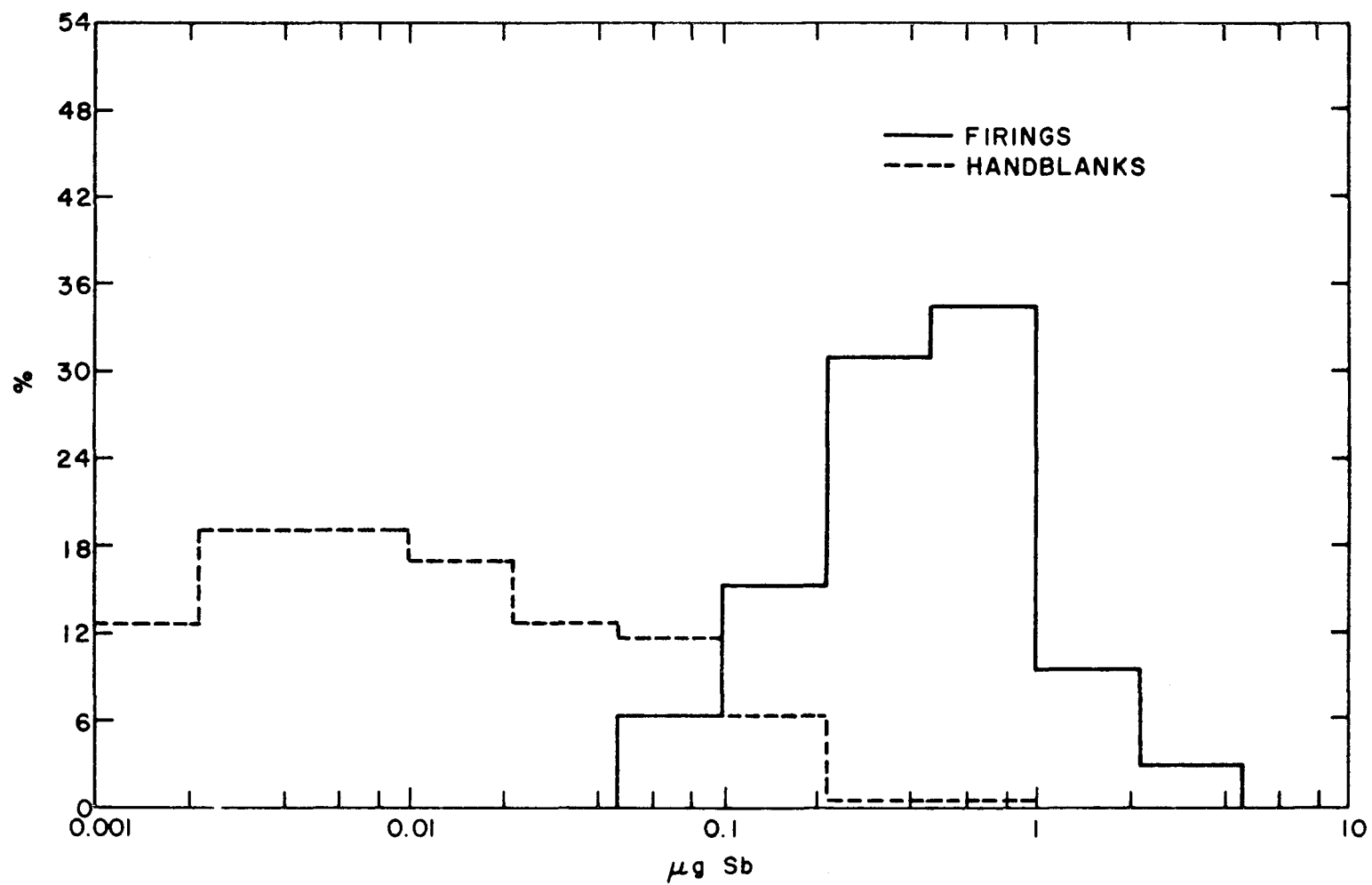


Fig. 15. Comparison of 32 firings of 0.45-caliber automatics with 188 handblank values for antimony

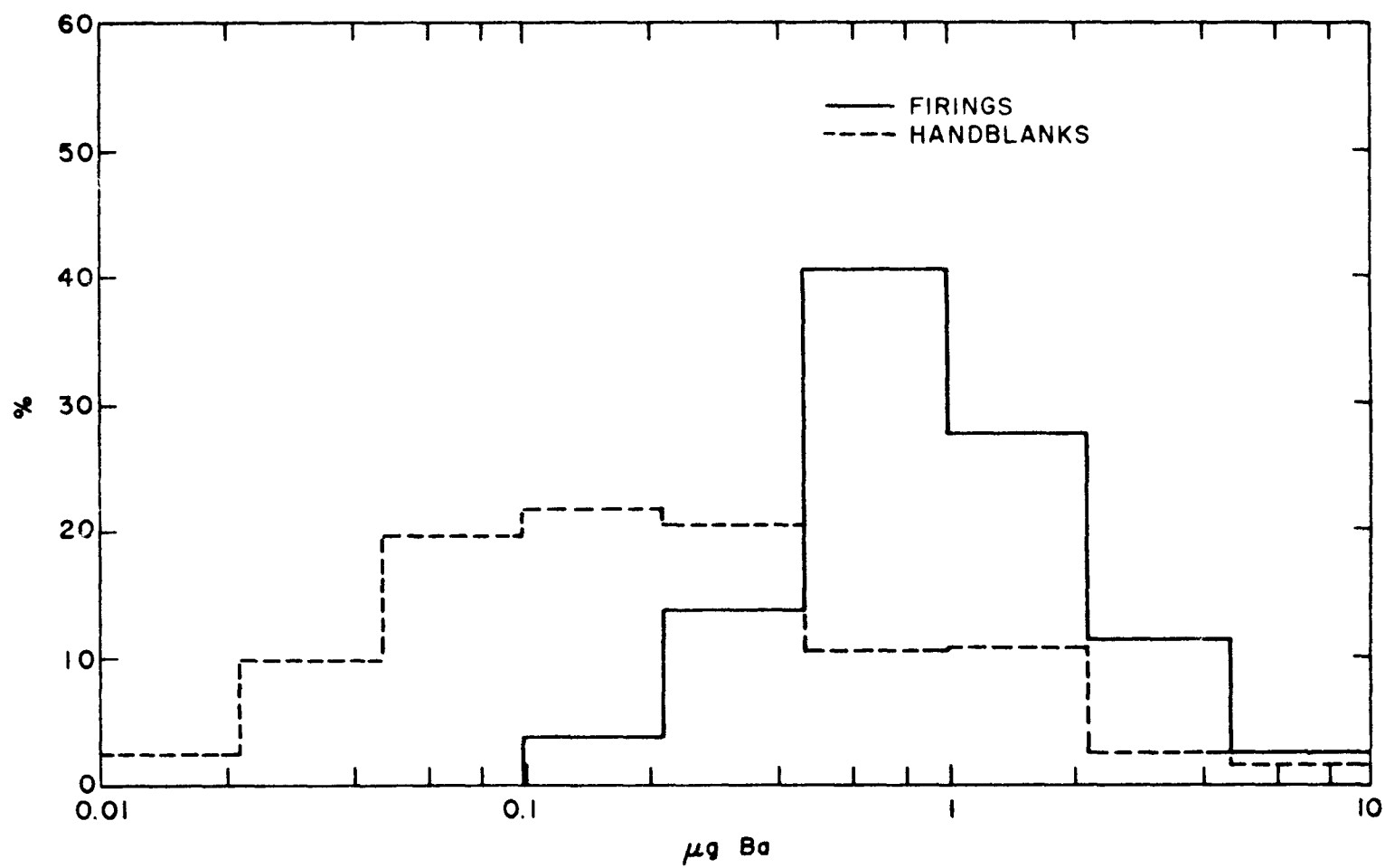


Fig. 16. Comparison of 79 firings of 0.38-caliber revolvers with 192 handblank values for barium

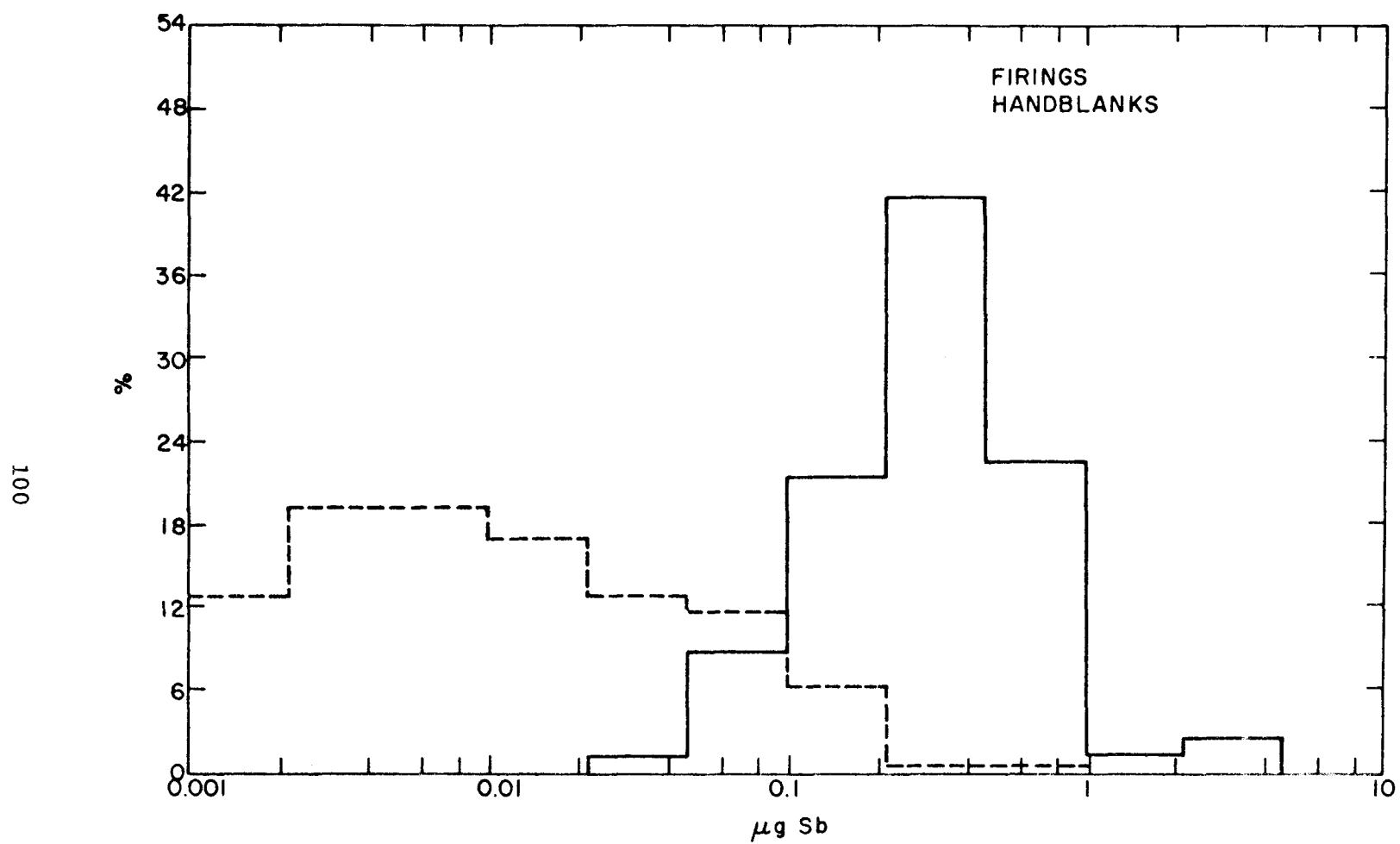


Fig. 17. Comparison of 79 firings of 0.38-caliber revolvers with 188 handblank values for antimony

3. 12. 4 0. 25-Caliber Automatic Results

The mean values found in the four test firings were 4. 72 μg Ba and 0. 632 μg Sb. These mean values are, respectively, 9 times the average Ba handblank value, and 20 times the average Sb handblank value. The Ba values ranged from 0. 96 μg to 8. 46 μg , and the Sb values ranged from 0. 208 μg to 1. 26 μg .

3. 12. 5 9-mm Automatic Results

The mean values found in the five test firings were 7. 47 μg Ba and 0. 732 μg Sb. These mean values are, respectively, 14 times the average Ba handblank value, and 23 times the average Sb handblank value. The Ba values ranged from 1. 37 μg to 15. 4 μg , and the Sb values ranged from 0. 056 μg to 2. 05 μg .

3. 12. 6 0. 22-Caliber Automatic Results

The mean values found in the three test firings were 0. 704 μg Ba and 0. 137 μg Sb. These mean values are, respectively, only 1. 3 times the average Ba handblank value, and 4. 3 times the average Sb handblank value. The Ba values ranged from 0. 32 μg to 1. 25 μg , and the Sb values ranged from 0. 058 μg to 0. 242 μg .

3. 12. 7 0. 22-Caliber Revolver Results

The mean values found in the 16 test firings were 0. 391 μg Ba and 0. 082 μg Sb. These mean values are, respectively, only 0. 75 times the average Ba handblank value, and only 2. 6 times the average Sb handblank value.

Although it is premature to draw very many conclusions, because of the limited amount of data thus far available, one tentative indication may be at least mentioned: the larger-caliber guns generally seem to deposit more residue than do the smaller-caliber guns. For example, in

the revolver firings, the mean Ba values in the firings of 0.44-, 0.38-, and 0.22-caliber guns were, respectively, 1.39 μg , 1.31 μg , and 0.391 μg , and the corresponding Sb mean values were 0.422 μg , 0.421 μg , and 0.082 μg . Similarly, in the firings of automatic pistols, the mean Ba values in the firings of 9 mm, 0.45-caliber, 0.25-caliber, and 0.22-caliber guns were, respectively, 7.47 μg , 3.60 μg , 4.72 μg , and 0.704 μg , and the corresponding Sb mean values were 0.732 μg , 0.598 μg , 0.632 μg , and 0.137 μg .

It is also of interest to note the $\bar{\text{Ba}}/\bar{\text{Sb}}$ ratios in the test firings of the various guns, as compared with the $\bar{\text{Ba}}/\bar{\text{Sb}}$ handblank ratio. If the handblank mean Ba value is divided by the corresponding mean Sb value, a Ba/Sb ratio of 16.5 is obtained (with wide scatter, as can be seen from Fig. 13). In all of the test-firing data, the $\bar{\text{Ba}}/\bar{\text{Sb}}$ ratio is quite a bit smaller, ranging from 3.12 (0.38-caliber revolver) to 10.2 (9 mm automatic). These ratios are not sharply defined – not only because of the numerous variables included even with a given caliber and type of gun (e.g., make and condition of gun, chamber fired – in the case of revolvers, brand of ammunition fired, wind direction and velocity, cartridge-to-cartridge variability of even a single brand of ammunition, reproducibility of the hand-area sampling technique, etc.), but also because in many cases they include varying amounts of Ba and Sb material already present on the hand before the test firing (i.e., handblank material).

As for the amount of gunshot-residue deposition, it may be noted that, whereas, of the ~ 190 Ba and Sb handblank values shown in Figs. 11 and 12, only 9% of the Ba values are $> 1.5 \mu\text{g}$ and only 7% of the Sb values are $> 0.1 \mu\text{g}$, in the case of the 32 firings of 0.45-caliber automatics (shown in Fig. 18), 66% of the Ba values are $> 1.5 \mu\text{g}$ and 94% of the Sb values are $> 0.1 \mu\text{g}$. Thus, the degree of overlap between the gunshot-residue values in 0.45-caliber automatic firings with handblank values is

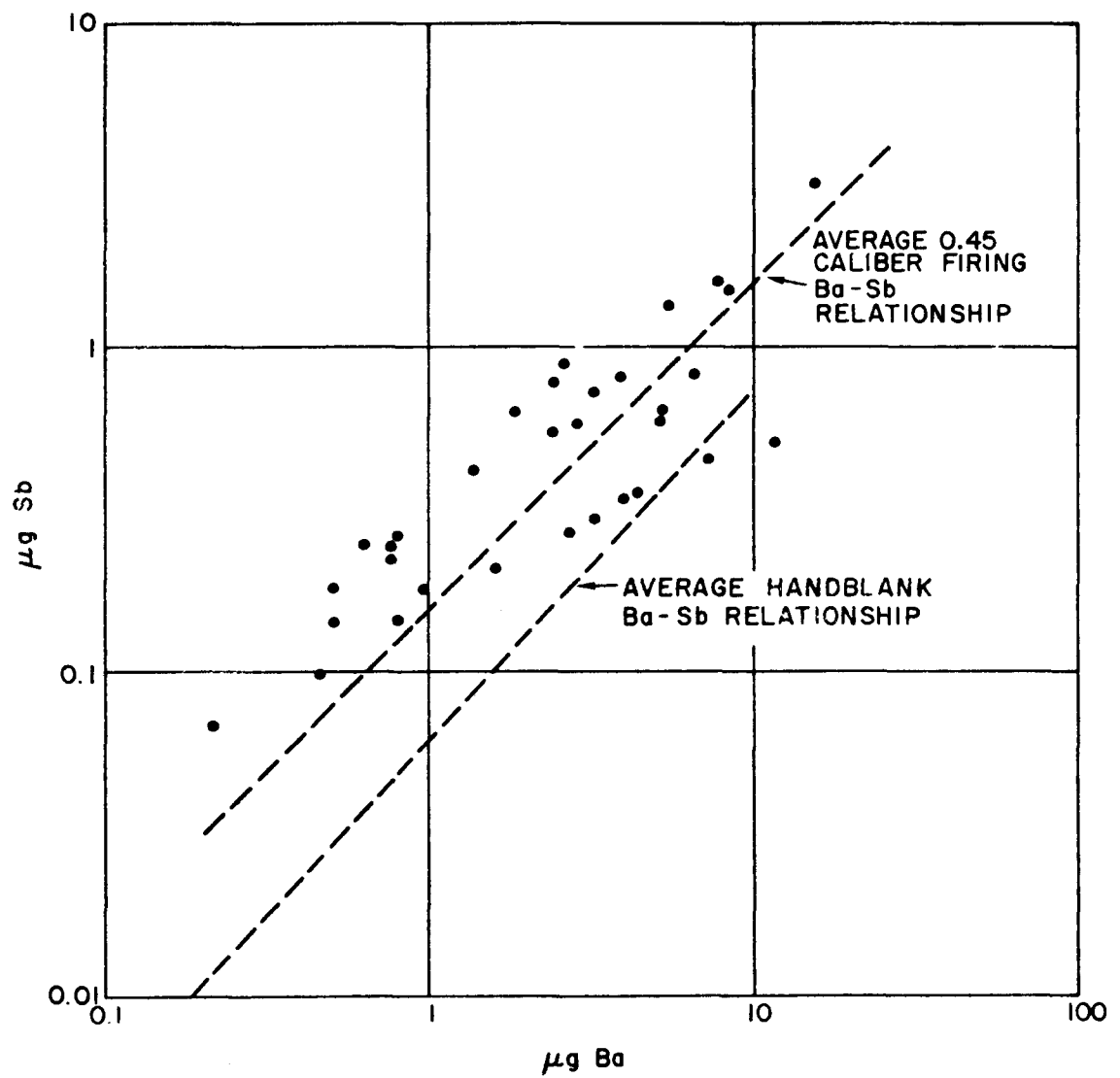


Fig. 18. Ba and Sb values from 32 firings of 0.45-caliber automatics

fairly small - particularly for antimony. In the case of the 79 firings of 0.38-caliber revolvers (shown in Fig. 19), only 27% of the Ba values are $> 1.5 \mu\text{g}$, but 90% of the Sb values are $> 0.1 \mu\text{g}$. Thus, in this case, the degree of overlap with handblank Ba values is considerable, but the degree of overlap with handblank Sb values is fairly small.

Whereas sufficient test firings have been made with 0.45-caliber automatics (32) and 0.38-caliber revolvers (79), to warrant some statistical analysis and interpretation, as presented above, the numbers of firings to date of other calibers of revolvers and automatics are insufficient to allow very much generalization. However, the results available for them, along with corresponding information on handblank values, and 0.38-caliber and 0.45-caliber firings, are summarized, from the same standpoint, in Table 16.

It is evident from the table that, in almost every case, the Sb value provides a better distinction between a firing value and a handblank value than does the Ba value. It is also evident, at least from the data presently accumulated, that it is very difficult to distinguish between a 0.22-caliber firing (especially revolvers) and a handblank value.

3.13 EXPERIMENTS WITH TAGGED CARTRIDGES

When a typical cartridge is fired in a gun, one might expect to possibly detect, on the back of the gunhand, traces of the inorganic elements: (1) Ba, Sb, and Pb (from lead styphnate) originating in the cartridge primer, (2) Cu from the primer casing, (3) Pb, Sb, and perhaps Cu (if a copper-jacketed bullet) from the bullet, and (4) Cu or Cu and Zn from the cartridge case, depending upon whether the cartridge case was made of copper or brass. Early in this investigation, attention was focussed on the detection and measurement of only Ba and Sb, since the sensitivity of detection by NAA is not very good for Pb, and Cu and Zn

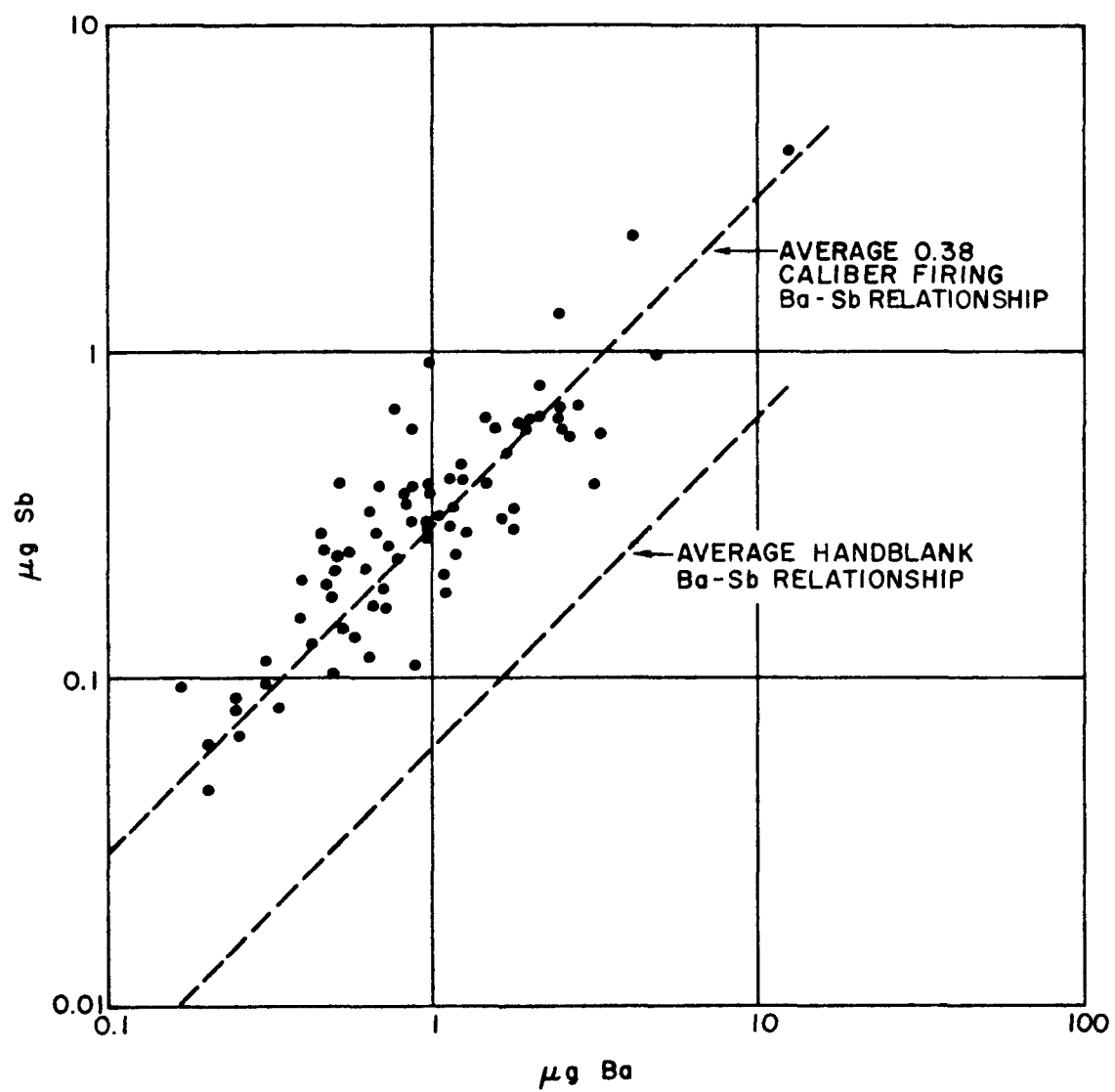


Fig. 19. Ba and Sb values from 79 firings of 0.38-caliber revolvers

Table 16
DEGREE OF OVERLAP OF FIRING VALUES WITH
HANDBLANK VALUES

Type	No. of Values	% of Ba Values > 1.5 μg	% of Sb Values > 0.1 μg
Handblanks	97 persons	9	7
0.45-automatics	32 firings	66	94
0.38-revolvers	79 firings	27	90
0.44-revolvers	5 firings	20	80
0.25-automatics	4 firings	75	100
9 mm-automatics	5 firings	80	80
0.22-revolvers	16 firings	0	19
0.22-automatics	3 firings	0	67

are rather common elements, frequently gotten onto the hands in many other ways besides firing a gun.

However, it was also recognized - after handblank measurements had been carried out on persons of quite a few occupations - that there were some occupations (though not a large number) in which high Ba hand-blanks could be expected, and even a few with appreciable handblank levels of both Ba and Sb. There are no doubt also a few occupations involving relatively high Sb handblank levels, but low Ba levels. This is not too surprising, since barium is the 19th most abundant element in the earth's crust (mean value, 250 ppm), whereas antimony is only the 58th most abundant element (~ 1 ppm). Of course, this is not a really valid comparison, since some relatively rare elements are of considerable use to man, and hence are mined, concentrated, and extensively used in manufactured products and jewelry - because of their desirable properties. For example, gold is only the 73rd most abundant element in the earth's crust (0.005 ppm), yet is used very extensively in jewelry - particularly on the hand (where, incidentally, it can often be detected in handblank samples, and in fingernail clippings). Similarly, silver is only the 67th most abundant element (0.1 ppm), and platinum is only the 72nd most abundant element (0.005 ppm), and yet both are used extensively in jewelry - silver also being used extensively in coins. Of the other elements to be expected in gunshot residues, their average abundances in the earth's crust are as follows: zinc (132 ppm; 23rd most abundant element), copper (70 ppm; 25th most abundant element), and lead (16 ppm; 36th most abundant element). Zinc, of course, is a major component of such common materials as paint, galvanized iron, and brass. Copper is commonly used in wire, screens, utensils, jewelry, and brass. Lead is less commonly used, but is a major component of most solders, and is used somewhat in plumbing pipes.

As an outgrowth of such considerations, the idea was developed of deliberately tagging the gunpowder or primer material used in cartridges with low levels of very uncommon elements - using those that can be detected with extremely good sensitivity by NAA. It was thought to be possible, as an aid to law enforcement, that different U. S. manufacturers of cartridges could tag their gunpowder (or primers) with different combinations of certain of these selected elements, also using a different combination for each different type of cartridge that each manufacturer produced. If technically and economically feasible, the use of such tagged cartridges would offer several benefits: (1) the determination of whether or not a suspect had recently fired a gun would be more definitive, (2) the analysis could also define the brand and caliber of the cartridge that had been fired, and (3) an instrumental, or at least a simpler radiochemical-separation procedure might be possible.

In order to test out this concept, quite a number of 0.38-caliber cartridges were prepared using the elements, dysprosium (Dy) and europium (Eu), in the cartridge cases and in the gunpowder, and the elements, dysprosium, holmium (Ho) and indium (In), in the primers. Various test firings were conducted with these tagged cartridges, followed by NAA determination of the tagging elements in paraffin lifts taken from the back of the gunhand of the various persons doing the firings. These studies, and the results obtained, are summarized below.

3.13.1 Exploratory Studies with Tagged Cartridge Cases

Fifteen tagged cartridges were prepared. In each instance, a small amount of aqueous solution, containing the desired amount of dissolved tracer, was applied to the inside of an empty, but primed 0.38-caliber cartridge case. The solution was allowed to dry thoroughly, and then the fifteen tagged cartridge cases were taken up to the Los Angeles Police Department's (LAPD) reloading facility, where the gunpowder and

bullet were added. The fifteen cartridges (three of each) contained, respectively, 1, 10, or 100 μg of dysprosium, or 10 or 100 μg of europium.

Each of the tagged cartridges was fired by a different person, at the LAPD indoor firing range. All of the cartridges containing Dy were fired in the same gun, in the order of increasing amount of Dy. A different gun was then used for the firing of the Eu-tagged cartridges. The cartridges containing 10 μg Eu each were fired in it before those containing 100 μg Eu each. Each person fired with his right hand, and paraffin handlifts were taken immediately after firing. A separate supply of paraffin, in a fresh container, as well as a new brush, were used for each paraffin handlift. Blank samples of paraffin were taken before and after each paraffin applications. The paraffin lifts, placed in polyethylene vials, were activated in the TRIGA Mark I reactor for one hour at a thermal-neutron flux of 1.8×10^{12} n/cm²-sec. After irradiation, the induced 139.2-minute Dy¹⁶⁵ and 9.3-hour Eu^{152 m1} activities were radiochemically separated, using the following procedure:

A known amount (about 10 mg) of the rare-earth carrier, about 20 mg of Ba carrier, and 25 ml of H₂O were placed in a 250-ml beaker. The irradiated paraffin lift was then added to the beaker, and the mixture was boiled for about five minutes. It was also stirred, to insure 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 H₂SO₄ was added to precipitate BaSO₄, which was centrifuged off and discarded. Concentrated NH₄OH was added to the supernate to precipitate the rare-earth hydroxide. After washing the precipitate with dilute NH₄OH, 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. 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 pulse-height analyzer. Dysprosium was detected by the 0.095 MeV gamma rays of Dy^{165} , and Eu by the 0.963 MeV gamma rays of $\text{Eu}^{152\text{m}_1}$.

With cartridges containing, respectively, 1, 10, and 100 μg Dy, the means of each group of three paraffin handlifts were 5.1×10^{-4} μg Dy, 3.2×10^{-3} μg Dy, and 3.5×10^{-2} μg Dy. These handlift values are in the ratio of 1.5/9.2/100, i. e., not greatly different from the ratios of the amounts present in the cartridges before firing (1/10/100). Of the amount of Dy present in a cartridge, an average of 0.039% of it was found on the back of the gunhand after a firing. In each 3-firing sequence, it was found that the amount of Dy deposited on the gunhand increased somewhat with each firing (with only one exception):

1 μg Dy	3.5×10^{-4} μg	$\rightarrow$	5.5×10^{-4} μg	$\rightarrow$	6.2×10^{-4} μg
10 μg Dy	0.71×10^{-3} μg	$\rightarrow$	1.0×10^{-3} μg	$\rightarrow$	7.8×10^{-3} μg
100 μg Dy	1.8×10^{-2} μg	$\rightarrow$	4.6×10^{-2} μg	$\rightarrow$	4.1×10^{-2} μg

This observation could be explained by: (1) buildup of Dy in the gun, with each firing, and/or (2) additional deposition of Dy on the hand from settling of particles in the air due to preceding firings. The second possibility seems more likely, since a different gun was used to fire the Eu-tagged

cartridges, and yet significant amounts of Dy (not added to those cartridges, and not present as a contaminant in the gun) were found in the paraffin handlifts taken after each firing of the Eu-tagged cartridges. With each 10 μg Eu-firing, the amount of Dy found in the resulting handlift was less than in the preceding one:

$$10 \mu\text{g Eu} \quad 2.7 \times 10^{-2} \mu\text{g Dy} \rightarrow 1.4 \times 10^{-3} \mu\text{g Dy} \rightarrow 7.3 \times 10^{-4} \mu\text{g Dy}.$$

In the subsequent 100 μg Eu firings, no Dy was found in the first two, and only a very small amount in the third firing:

$$100 \mu\text{g Eu} < 2.0 \times 10^{-4} \mu\text{g Dy} \rightarrow < 1.1 \times 10^{-4} \mu\text{g Dy} \rightarrow 9.5 \times 10^{-4} \mu\text{g Dy}.$$

Thus, it would appear that Dy drifting in the air of the firing room at the end of the three 100 μg Dy firings was still settling while the Eu-tagged cartridges were being fired, thus contaminating the hand of the firer with Dy. This settling apparently continued during the series of Eu firings, steadily diminishing in amount.

The Eu values found in the paraffin handlifts from the Eu firings were as follows:

$$\begin{array}{llllll} 10 \mu\text{g Eu} & 3.3 \times 10^{-4} \mu\text{g} & \rightarrow & 2.3 \times 10^{-4} \mu\text{g} & \rightarrow & 3.2 \times 10^{-4} \mu\text{g}. \\ 100 \mu\text{g Eu} & 8.7 \times 10^{-4} \mu\text{g} & \rightarrow & 2.7 \times 10^{-3} \mu\text{g} & \rightarrow & 3.8 \times 10^{-4} \mu\text{g}. \end{array}$$

These values give a mean value of only 0.0021% of the Eu fired being detected on the back of the gunhand (compared with 0.039% in the case of the Dy-tagged cartridges). The reason for this appreciable disagreement is not known. The paraffin used was not, itself, contaminated with Dy or Eu, since, of the five paraffin blank samples analyzed, no Eu could be found in them ($< 2.7 \times 10^{-6} \mu\text{g}$) and only a trace of Dy was found in one of them ($2.6 \times 10^{-4} \mu\text{g}$), the other four containing $< 2.1 \times 10^{-5} \mu\text{g Dy}$.

3. 13. 2 Studies with Tagged Gunpowder

Following the at least partially successful experiments with Dy- and Eu-tagged cartridge cases, further studies were conducted – this time tagging the gunpowder with Dy or Eu. Stock solutions of Dy and Eu were prepared at General Atomic, and then used by R. H. Pinker to tag gunpowder. The tagged gunpowder was then placed in 0.38-caliber cartridges at the LAPD cartridge-reloading facility. Cartridges containing, respectively, 5 μg Dy, 10 μg Dy, 5 μg Eu, and 10 μg Eu were prepared. This time, the various subsequent firings were conducted outdoors, where a slight breeze was blowing. A different gun was used in the Dy firing series than was used in the Eu series, and the Dy firing series was carried out first.

In the first series of test firings of cartridges in which the gunpowder was tagged with either 5 μg or 10 μg of the rare-earth element, the dysprosium results were somewhat confusing. For one thing, significant amounts of Dy were detected on the back of the gunhand of the person who fired an untagged cartridge at the very beginning of the series (16×10^{-4} μg Dy), and on the back of the gunhand of the person who fired an untagged cartridge at the end of the series (3.2×10^{-4} μg Dy). Secondly, in the firing of cartridges containing 5 μg Dy, there was wide scatter in the results, consecutive single firings depositing, respectively, 2.6×10^{-4} , 120×10^{-4} , and 4.2×10^{-4} μg Dy on the back of the gunhand. Two shots deposited 10×10^{-4} μg Dy. The results with the cartridges that each contained 10 μg Dy were slightly more consistent:

One shot: 7.0×10^{-4} , 1.9×10^{-4} , 6.9×10^{-4} μg Dy

Two shots: 13×10^{-4} , 11×10^{-4} μg Dy

Three shots: 24×10^{-4} , 140×10^{-4} μg Dy.

If one rejects the two extraordinarily large Dy values ($120 \times 10^{-4} \mu\text{g}$ and $140 \times 10^{-4} \mu\text{g}$), the mean deposit values per single shot become $3.9 \times 10^{-4} \mu\text{g}$ Dy for the 5 μg cartridges, and $6.0 \times 10^{-4} \mu\text{g}$ Dy for the 10 μg cartridges. The mean values correspond to 0.0078% and 0.0060% (respectively) of the amount of Dy present in a tagged cartridge being detected on the back of the gunhand after a firing.

In this series of firings, two spectators were present during the whole series of 18 firings: one standing five feet to the left, the other standing five feet to the right, of the firers. After the 18 firings of Dy-tagged cartridges the backs of both hands of these two spectators were sampled with paraffin, and the handlifts then analyzed for dysprosium as usual. The results obtained were as follows:

				<u>μg Dy Found</u>
Spectator,	18 shots,	left side,	right hand	3.8×10^{-4}
Spectator,	18 shots,	left side,	left hand	3.6×10^{-4}
Spectator,	18 shots,	right side,	right hand	30×10^{-4}
Spectator,	18 shots,	right side,	left hand	10×10^{-4}

These results would indicate that airborne particulate gunshot-residue material drifted more to the right of the firers than to the left – under the prevailing conditions. Dividing the mean amounts by 18, the spectator hand deposits turn out to be $0.21 \times 10^{-4} \mu\text{g}$ Dy and $1.1 \times 10^{-4} \mu\text{g}$ Dy, respectively, per firing.

In addition, one person – simulating a victim – stood slightly to one side, but five feet in front of the muzzle when two shots were fired with cartridges each tagged with 10 μg Dy. When the backs of both hands of this simulated victim were sampled and analyzed, $0.30 \times 10^{-4} \mu\text{g}$ Dy were found on his right hand, and $< 0.10 \times 10^{-4} \mu\text{g}$ Dy on his left hand. During this whole series of firings, four different batches of paraffin were

used: one for the hands of the firers of the 5 μg Dy cartridges, one for the hands of the firers of the 10 μg Dy cartridges, one for the hands of the spectators, and one for the hands of the simulated victim. After each batch of paraffin was almost used up, it was analyzed for Dy. The amounts of Dy detectable in an amount of paraffin comparable to that used in a handlift were, respectively, $< 0.14 \times 10^{-4}$, 0.47×10^{-4} , $< 0.30 \times 10^{-4}$, and $< 0.12 \times 10^{-4}$ μg . Thus, there is no evidence that the paraffin used became significantly contaminated with Dy during the sampling process.

After this series of firings with Dy-tagged cartridges, an exactly parallel series of firings was conducted with the Eu-tagged cartridges (fresh gun, but firings conducted on the same day as the Dy firings, at the same location). The results obtained were somewhat more consistent than those obtained in the series of firings of Dy-tagged cartridges. One shot with untagged ammunition, at the beginning of the Eu series, showed no detectable Eu ($< 0.06 \times 10^{-4}$ μg) in the paraffin handlift taken. At the end of the Eu series, another shot fired with untagged ammunition resulted in a small amount of Eu (1.9×10^{-4} μg) in the corresponding handlift - probably from Eu deposits inside and outside the gun from the preceding firings of Eu-tagged cartridges. Three single shots of 5 μg Eu cartridges gave handlift values of 0.85×10^{-4} , 0.61×10^{-4} , and 1.8×10^{-4} μg Eu, and two shots gave 4.9×10^{-4} μg Eu. Three single shots of 10 μg Eu cartridges gave handlift values of 3.3×10^{-4} , 1.5×10^{-4} , and 3.8×10^{-4} μg Eu, and two series of double firings gave 1.7×10^{-4} and 7.0×10^{-4} μg Eu. Two series of triple firings gave handlift values of 6.2×10^{-4} and 18×10^{-4} μg Eu. The 5 μg Eu results correspond to a mean hand deposit value of 1.6×10^{-4} μg Eu per firing (i. e., 0.0033% of the Eu in a cartridge falling on the back of the gunhand). The 10 μg Eu results correspond to a mean hand deposit value of 3.2×10^{-4} μg Eu per firing (i. e., 0.0032% of the Eu in a cartridge falling on the back of the gunhand).

In the Eu firing series, no Eu could be detected on the hands of the spectator who stood five feet to the left of the firer during the series of 18 firings of Eu-tagged cartridges: $< 0.24 \times 10^{-4} \mu\text{g Eu}$ (right hand) and $< 0.17 \times 10^{-4} \mu\text{g Eu}$ being the upper limits found. A little Eu was detected on the hands of the spectator who stood five feet to the right of the firer in this series of 18 firings: $1.2 \times 10^{-4} \mu\text{g Eu}$ (right hand) and $1.4 \times 10^{-4} \mu\text{g Eu}$ (left hand). No Eu could be found on the hands of the simulated victim who stood slightly to one side, five feet in front of the muzzle, when two $10 \mu\text{g Eu}$ cartridges were fired: $< 0.07 \times 10^{-4} \mu\text{g Eu}$ (right hand) and $< 0.08 \times 10^{-4} \mu\text{g Eu}$ (left hand) being the upper limits found. As in the case of the Dy series, no contamination of the paraffin supply during the sampling could be detected: the four paraffin samples taken showing $< 0.06 \times 10^{-4}$, $< 0.38 \times 10^{-4}$, $< 0.29 \times 10^{-4}$, and $< 0.31 \times 10^{-4} \mu\text{g Eu}$, respectively.

A second series of firings was also conducted, using cartridges with gunpowder tagged with either $10 \mu\text{g Dy}$ or $10 \mu\text{g Eu}$. The results obtained in this series were generally quite similar to those obtained in the preceding series. In general, reasonably consistent values were found — with an occasional anomalously high value. These values, coupled with those from the preceding series, indicate that, in a single firing of a cartridge containing gunpowder tagged with either Dy or Eu, about 0.004 (± 0.002)% of the tagging element present in the cartridge may be expected to deposit on the back of the gunhand area sampled.

One problem that plagued these studies with Dy- and Eu-tagged cartridges was a lanthanum-contamination, of unknown origin. The complete tables of results obtained in these two series of firings may be found in GA-7041, ⁽³⁾ pages 16-22.

3.13.3 Studies with Tagged Primers

Through the cooperation of Mr. Burton D. Munhall, of the Federal Cartridge Corporation, it was also possible to conduct firing studies with tagged primers. Sufficient Dy_2O_3 , Ho_2O_3 , and In_2O_3 were sent to the Federal Cartridge Corporation for them to tag three one-pound batches of their regular commercial primer mix with, respectively, the desired trace level of these three added tracer elements. They prepared Dy-tagged, Ho-tagged, and In-tagged primers from these materials, placed them in 0.38-caliber cartridges, and sent 75 of the tagged cartridges to General Atomic (25 of each type). Test firings of a number of these tagged cartridges were conducted, but only a few were conducted during the period covered in this report (the bulk of them being studied later), so discussion of the findings of the studies of cartridges containing tagged primers is deferred to the special report on gunshot-residue studies.

3.14 STUDIES WITH RIFLES AND SHOTGUNS

The great bulk of the experimental work on gunshot residues carried out during the period covered by this report was concerned with firings of handguns: revolvers, and automatic pistols of various types and calibers. However, some measurements were also made on gunshot residues produced by the firing of rifles and shotguns. These studies are described below.

3.14.1 Rifles

The first rifle measurements made were those on paraffin hand-lifts and facelifts (cheeks) after firings of a 6.5 mm Mannlicher-Carcano rifle. These measurements were made shortly after the assassination of President John F. Kennedy in Dallas, to ascertain whether: (1) this type of gun deposited significant amounts of Ba and Sb on the hands and face of

a firer, and (2) the diphenylamine-sulfuric acid "dermal nitrate" test, used by the Dallas Police Department for the examination of three paraffin casts (one of each hand and one of the right cheek) they took of the suspected assassin, Lee Harvey Oswald, removed any Ba and Sb residues from the inner surface of the paraffin. The single cheek cast was of special importance, since it was the only one of the three that might clearly indicate the firing of a rifle - known to have been the assassination weapon. Oswald was observed by witnesses, soon after the assassination, to fire a revolver - killing Officer Tippett. The revolver firing thus would have deposited Ba and Sb on the back of one of his hands - the gunhand. The cast from the other hand might also be of significance, if the Mannlicher-Carcano rifle deposited appreciable amounts of Ba and Sb on the nontrigger hand of the firer.

Since it was generally recognized that the dermal nitrate test was essentially useless, one of the authors of this report (V. P. Guinn) made efforts - through AEC channels - via telephone calls within hours after the assassination and the apprehension of Oswald, to reach the Dallas police and suggest that they take paraffin lifts of the hands and the cheeks of Oswald, for subsequent examination by neutron activation analysis for Ba and Sb. It was also suggested that these paraffin lifts not be chemically treated, since the dermal nitrate test was of no value anyway, and its use might remove any traces of Ba and Sb possibly present. Due to the turmoil existing at Dallas police headquarters during the hours following the assassination of President Kennedy and the apprehension of Oswald, it was not possible to get through to the Dallas police laboratory in time. Shortly after Oswald was brought in, they proceeded to take paraffin casts of the backs of each of his hands, and of his right cheek, and to test these via the chemical dermal nitrate procedure. As might have been expected, and as mentioned in the Warren Commission Report,⁽²²⁾ the results of their tests were inconclusive.

Nonetheless, it seemed possible that the diphenylamine-sulfuric acid solution might not have washed away all of the Ba and Sb possibly present on the inner surfaces of the Oswald casts, so experiments were conducted to check this point. In the meantime, of course, Oswald had been killed by Ruby.

Mr. Ray Pinker, of the Los Angeles Police Department, obtained a 6.5 mm Mannlicher-Carcano rifle, which was then used for test firings. All of the persons who fired the rifle were right-handed. 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 rifle had to be fired horizontally, instead of at a slightly downward angle. The hands and cheeks of the persons doing the firings were not sampled until 2-1/2 to 3-1/2 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 of paraffin casts by the Dallas police from the hands and right cheek of Oswald.

Two sets of casts were obtained. One set was first treated with diphenylamine-sulfuric acid solution (the dermal nitrate test). After the chemical testing, the reagents were washed off the casts with distilled water. The other set of casts was not treated chemically. In each set, casts were made (both hands, both cheeks) after one shot had been fired, and after three shots had been fired in rapid succession. Of the eight casts tested chemically, only one gave a clear-cut "positive" test for nitrates: this cast was from the back of the right hand (trigger hand) of the person who fired the rifle three times.

A clean spatula was then used to remove the inner-surface paraffin from each of the 16 casts (8 untreated casts and 8 chemically-treated casts). This was done to exclude the gauze used in building up the cast,

since analysis of the gauze showed that it contained small, but measurable, traces of Ba (0.46 ppm) and Sb (0.044 ppm). The 16 paraffin samples, placed in polyethylene vials, were then each activated for two hours in the reactor, in a thermal-neutron flux of 1.8×10^{12} n/cm²-sec. Several reactor runs were made, to allow time for each group of samples to be activated, radiochemically-separated, and counted before the next group of samples was processed. This was necessary because of the short half-life of ¹³⁹Ba (82.9 minutes). The resulting Ba and Sb values found are presented in Table 17.

A study of the values shown in Table 17 shows that firings of this rifle deposited quite measurable amounts of Ba and Sb on both hands and both cheeks of a firer – especially in the case of triple firing. In a single firing, the mean amount of Ba deposited (mean of all four areas sampled) was 0.314 µg, and the mean amount of Sb deposited was 0.048 µg. These mean values correspond to 2.4 times a mean handblank value of 0.13 µg Ba, and 3.2 times a mean handblank value of 0.015 µg Sb. After three firings, the mean deposit values rose to 0.483 µg Ba and 0.103 µg Sb, i. e., 3.7 times the mean Ba handblank level and 6.9 times the mean Sb handblank level. In the single firings, the amounts of deposit were in the ratio: left cheek > right hand > right cheek $\cong$ left hand, whereas, in the triple firings, the deposit values were in the ratio: right hand > right cheek $\cong$ left hand > left cheek.

From the Ba and Sb results obtained on the casts that had first been tested chemically for indication of nitrates, it is evident that the diphenylamine-sulfuric acid solution (followed later by a water rinse) washed away essentially all of the Ba present. Thus, the four single-firing samples showed a mean value of only 0.127 µg Ba (compared with a mean value of 0.314 µg Ba on the untreated single-firing casts), and the four triple-firing samples showed a similarly low mean value of only

Table 17
GUNSHOT-RESIDUE VALUES FROM FIRINGS OF A
6.5 mm MANNLICHER-CARCANO RIFLE

Series	Firer	No. of Firings	Area Sampled	μg Ba Found	μg Sb Found
Casts not chemically treated before analysis	EM	1	Left Hand	0.215	0.022
			Right Hand	0.596	0.028
			Left Cheek	0.300	0.104
			Right Cheek	0.144	0.037
	DM	3	Left Hand	0.511	0.083
			Right Hand	0.529	0.157
			Left Cheek	0.399	0.079
			Right Cheek	0.492	0.095
Casts tested for dermal nitrates before analysis	B	1	Left Hand	0.144	0.088
			Right Hand	0.094	0.064
			Left Cheek	0.186	0.019
			Right Cheek	0.084	0.020
	H	3	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

^a Only cast of the eight tested that gave a positive diphenylamine test.

0.164 μg Ba (compared with a mean value of 0.483 μg Ba on the untreated triple-firing casts). However, the results indicate only a partial loss of Sb from the chemical treatment. Thus, the mean Sb value for the four single-firing chemically-treated samples was 0.048 μg (the same as the mean Sb value found on the untreated single-firing samples), and the mean Sb value for the four triple-firing chemically-treated samples was 0.060 μg (58% of the mean Sb value found on the untreated triple-firing samples).

These results were then transmitted to the FBI Laboratory, in Washington, D. C. (who now had custody of the three Oswald paraffin casts), with the recommendation that the inner surfaces of the casts be analyzed – particularly for antimony – by neutron activation analysis. It was pointed out that there might still be sufficient Sb left on the chemically-treated paraffin casts of Oswald's right cheek and left hand to indicate that he had fired a rifle not long before he was sampled – if, indeed, he had fired a rifle and had not washed during the intervening time. The complete General Atomic neutron activation/radiochemical separation/counting procedure was also supplied to the FBI. We also offered to conduct the analysis for them, in their presence, if desired – and assured them that due security would be maintained. They, however, elected to keep the matter within the confines of government laboratories. Since at that time the FBI had neither the facilities nor the appropriately trained personnel to conduct NAA measurements on the casts, they took them to the Oak Ridge National Laboratory – where the samples were carefully analyzed for Ba and Sb by an experienced ORNL activation analyst, in the presence of one of the members of the FBI Laboratory staff, using the General Atomic procedure.

The results obtained on the three Oswald casts were not released until the Warren Commission Report⁽²²⁾ was published. As reported there, they found significant levels of Ba and Sb on all three of the Oswald casts, but both in paraffin samples removed from the outer surface and the inner

surface of each cast. The presence of Ba and Sb on the outer surface of each cast indicated that the casts had been contaminated – probably by indiscriminate handling in Dallas by various persons – before they were analyzed for Ba and Sb. Thus, there was no way to draw any useful conclusions from the results.

Although the General Atomic Mannlicher-Carcano rifle studies did not turn out to be of any help in the Kennedy assassination investigation (because the paraffin casts of Oswald were first chemically treated, and then apparently contaminated by handling), they did indicate that at least this particular type of rifle did deposit small, but significant, amounts of Ba and Sb on both hands and both cheeks of a person who fired the rifle.

Subsequently, some additional rifle-firing studies were carried out with other types of rifles. The first such additional rifle series was one involving three single firings of a 30.06 rifle (by three different persons). After each firing, both hands and both cheeks of the firer were sampled with paraffin. The paraffin lifts were analyzed for Ba and Sb by NAA, with radiochemical separations, by the usual procedure. The results are shown in Table 18. All of the Ba values are seen to be fairly close to a normal Ba handblank value ($0.13 \mu\text{g Ba}$) – ranging only from 0.45 to 2.7 times the normal handblank value. However, only one of the Sb values was less than a normal Sb handblank value ($0.015 \mu\text{g Sb}$), the rest ranging from 2.3 to 20 times the normal handblank value – even excluding the anomalously high $3.47 \mu\text{g Sb}$ value found on the left cheek of firer No. 3. In general, the largest deposits of Ba and Sb, from single firings of this rifle, were found on the hands (both right and left) of the firer. Excluding the suspect high value of $3.47 \mu\text{g Sb}$, it would appear that firings of this rifle deposited very little material on either cheek of a firer.

Table 18
GUNSHOT-RESIDUE RESULTS FROM THREE SINGLE FIRINGS
OF A 30.06 RIFLE

Person No.	Area Sampled	$\mu\text{g Ba}$	$\mu\text{g Sb}$
1	Left Hand	0.354	0.133
	Right Hand	0.226	0.058
	Left Cheek	0.095	<0.005
	Right Cheek	0.186	0.034
2	Left Hand	0.184	0.040
	Right Hand	0.185	0.051
	Left Cheek	0.058	0.034
	Right Cheek	0.069	0.075
3	Left Hand	0.277	0.300
	Right Hand	0.295	0.248
	Left Cheek	0.124	3.47
	Right Cheek	0.222	0.155

Another rifle firing study was conducted with a British 0.303-caliber rifle. Seven different people each fired this rifle once, and both hands and both cheeks of each firer were sampled with paraffin after firing. The results are shown in Table 19. In general, the results show a negligible amount of deposit on the cheeks of the firer, but a significant amount of deposit on the hands (particularly on the firing hand). Thus, the average firing cheek Ba value was $0.120 \mu\text{g}$ – compared with a typical Ba handblank value of $0.13 \mu\text{g}$, and the average firing cheek Sb value was $0.033 \mu\text{g}$ – compared with a typical Sb handblank value of $0.015 \mu\text{g}$. However, the average firing Ba value for the hands was $0.278 \mu\text{g}$ (2.1 times a typical Ba handblank value), and the average firing Sb value for the hands was $0.125 \mu\text{g}$ (8.3 times a typical Sb handblank value). The hand values are of more significance if the values for the firing hand, and those for the nonfiring hand, are treated separately. In general, the firing hand received more deposit than did the nonfiring hand. Thus, the mean Ba and Sb values found for the firing hand were $0.384 \mu\text{g}$ Ba (3.0 times the usual Ba handblank value) and $0.191 \mu\text{g}$ Sb (13 times the usual Sb handblank value) – whereas, for the nonfiring hand, the corresponding values were $0.172 \mu\text{g}$ Ba (only 1.3 times the usual Ba handblank value) and $0.059 \mu\text{g}$ Sb (3.9 times the usual Sb handblank value).

3.14.2 Shotguns

Two exploratory shotgun firings were also carried out, using a 12-gauge shotgun. Two persons each fired the shotgun once, and both hands and both cheeks of each firer were then sampled with paraffin. In both cases, appreciable amounts of Ba and Sb were found on both hands of the firer, but only small amounts on the cheeks. Thus the mean values found on the hands were $0.721 \mu\text{g}$ Ba (5.5 times a typical Ba handblank value) and $0.283 \mu\text{g}$ Sb (19 times a typical Sb handblank value) – whereas

Table 19
GUNSHOT-RESIDUE RESULTS FROM SEVEN SINGLE
FIRINGS OF A BRITISH 0.303-CALIBER RIFLE

Person No.	Area Sampled	$\mu\text{g Ba}$	$\mu\text{g Sb}$
1	Left Hand	0.365	0.062
	Right Hand	0.130	0.023
	Left Cheek	0.062	0.020
	Right Cheek	0.068	0.006
2	Left Hand	0.321	0.061
	Right Hand	0.444	0.304
	Left Cheek	0.090	0.029
	Right Cheek	0.102	0.031
3	Left Hand	0.098	0.019
	Right Hand	0.173	0.038
	Left Cheek	0.265	0.002
	Right Cheek	0.142	0.010
4	Left Hand	0.477	-----
	Right Hand	0.193	0.045
	Left Cheek	0.205	0.053
	Right Cheek	0.118	0.048
5	Left Hand	0.151	-----
	Right Hand	0.157	0.031
	Left Cheek	0.107	0.012
	Right Cheek	0.156	0.012
6	Left Hand	0.265	0.209
	Right Hand	0.052	0.049
	Left Cheek	0.060	0.090
	Right Cheek	0.090	0.095
7	Left Hand	0.807	0.504
	Right Hand	0.259	0.155
	Left Cheek	0.091	0.016
	Right Cheek	0.125	0.040

the corresponding mean values found on the cheeks of the firers were only 0.154 μg Ba (1.2 times a typical Ba handblank value) and 0.029 μg Sb (1.9 times a typical Sb handblank value).

In connection with possible face deposits from firings of rifles or shotguns, a few "faceblank" measurements were made. Both cheeks of three laboratory technicians were sampled with paraffin. The mean Ba value found was 0.098 μg (versus a typical handblank value of 0.13 μg), and the mean Sb value found was 0.010 μg (versus a typical handblank value of 0.015 μg).

3.15 MISCELLANEOUS OTHER GUNSHOT-RESIDUE STUDIES

A number of miscellaneous studies on gunshot residues were carried out during this six-year period, but are not considered to be of sufficient importance to be included in the present report. These miscellaneous small-scale studies include those on residue samples from questionable suicides, and murder and assault cases; residues on gloves; the effect of hand moisture on retention of residues; findings of a gyrojet gun; firings of blank cartridges; smokers versus nonsmokers relative to handblank levels (no difference found); antimony from the lighting of matches; and barium in automobile greases. These brief studies of miscellaneous side issues are described in the four "annual" reports (Refs. 1-4).

4. PAINT STUDIES

4.1 INTRODUCTION

Paint is frequently encountered as evidence material in the investigation of accidents and crimes. It may exist as specks transferred from one object to another, as from a window casing to a prying tool or from an automobile to an object struck by that automobile. It is of prime importance in the distinction between genuine and forged paintings. In all investigations involving paint samples it is necessary to obtain analytical information regarding the samples.

In most criminal cases the analyst is confronted with two constraints: (1) the amount of evidence sample is small, and (2) the sample should be preserved for submission as evidence. Neither of these constraints present difficulty to the useful application of neutron activation analysis (NAA). Hence, work was undertaken to disclose the applicability of NAA to paint characterization and identification.

The work was initiated with a series of small experiments, and, based upon the encouraging results derived therefrom, a larger study was carried out to define statistical probabilities relevant to paint identification with NAA.

4.2 EXPERIMENTAL

Neutron activation analysis was carried out by activation with the Gulf General Atomic TRIGA Mark I nuclear reactor and subsequent examination of the gamma rays from the activated specimen by multichannel gamma-ray spectrometry.

The samples were irradiated for a short period of time (≤ 1 minute) in a pneumatic tube position at a thermal neutron flux of 2.8×10^{12} n/cm²-sec and/or for a longer period (≥ 30 minutes) in a rotary specimen rack at a thermal neutron flux of 1.8×10^{12} n/cm²-sec. The fission spectrum neutron fluxes in these two positions were 2.5×10^{12} n/cm²-sec and 1.5×10^{12} n/cm²-sec, respectively.

Generally the samples were counted for a few minutes, or less, subsequent to a short irradiation, while they were counted for longer times after longer intervals from the end of the irradiations in the rotary specimen rack. The gamma-ray spectrometer which we used consisted of a 3-in. -diam by 3-in. long NaI(Tl) counter coupled to a 400-channel pulse-height analyzer.

Multiple samples of each of five different colored automobile paints from a single manufacturer were analyzed instrumentally by irradiating aliquots for 30 seconds and 60 minutes and subsequently obtaining gamma-ray spectra.⁽¹⁾ Although paints of a given color were scarcely different to the eye, the NAA data revealed sharp distinctions, as can be seen in Table 20.

The uniformity of a single automobile paint within a can and between two cans of the same paint was examined and found to be fairly good,⁽¹⁾ as shown in Table 21.

Ten samples of light blue, automobile touch-up enamels, six from one manufacturer and virtually indistinguishable by color, were subjected to NAA with short (1 minute) and long (60 minutes) irradiations.⁽²⁾ All samples were found to have different elemental concentrations, as shown in Table 22.

Eight random, nonconsecutive batches of Sinclair off-white paint (No. 1929) were analyzed in duplicate with 1-minute and 30-minute irradiations.⁽³⁾ The ten elements, Ti, Al, Mn, In, Zn, Na, La, Sb, Sm, and Co were observed in each sample, and the concentrations are given in Table 23.

Table 20
NAA RESULTS FOR AUTOMOBILE PAINTS

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

Table 21

PAINT UNIFORMITY, RED AUTOMOBILE PAINT
NO. 4403-LH

Sample		Elements (ppm)			
Can	Aliquot	Na	Mn	Al	Br
1	1	168	238	7.1	266
2	1	178	289	7.4	267
	2	181	284	6.9	276
	3	181	265	7.5	278
	4	175	268	7.0	251

Table 22

NAA RESULTS FOR BLUE, AUTOMOBILE TOUCH-UP ENAMELS

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 23

NAA RESULTS FOR SINCLAIR PAINT NO. 1929

Batch No.	Run	Ti (%)	Al (ppm)	Mn (ppm)	In (ppm)	Zn (%)	Na (ppm)	La (ppm)	Sb (ppm)	Sm (ppm)	Co (ppm)
78808	1	12.6	978	10.5	0.369	1.56	120	12.9	62.1	2.11	124
	2	12.8	962	9.93	0.347	1.44	123	11.7	69.0	2.17	123
	Av	12.7	970	10.2	0.358	1.50	122	12.3	65.6	2.14	124
78988	1	11.7	824	10.5	0.378	1.57	193	13.0	55.6	1.88	91.7
	2	12.8	866	10.6	0.374	1.53	191	10.6	68.3	1.97	83.7
	Av	12.2	845	10.6	0.376	1.55	192	11.8	62.0	1.92	87.7
79320	1	12.3	750	9.93	0.104	1.49	113	11.4	55.2	1.34	101
	2	11.9	741	9.69	0.128	1.46	109	9.32	58.9	1.45	88.9
	Av	12.1	746	9.81	0.116	1.48	111	10.4	57.0	1.40	95.0
79864	1	12.9	843	10.5	0.137	1.55	132	8.72	60.7	1.44	76.5
	2	12.4	859	10.4	0.176	1.54	139	8.94	62.4	1.74	86.7
	Av	12.6	851	10.4	0.156	1.54	136	8.83	61.6	1.59	81.6
80044	1	12.4	762	10.4	0.363	1.54	98.3	10.3	66.8	1.46	178
	2	12.9	730	10.3	0.351	1.53	94.6	8.86	69.0	1.77	186
	Av	12.6	746	10.4	0.357	1.54	96.4	9.60	67.9	1.62	182
80528	1	12.2	942	10.4	0.105	1.49	126	5.70	68.9	1.05	93.7
	2	12.4	991	10.5	0.126	1.53	134	5.75	75.9	1.25	102
	Av	12.3	966	10.4	0.116	1.51	130	5.72	72.4	1.15	97.8
80804	1	12.6	1147	9.89	0.248	1.66	102	10.2	65.4	1.20	107
	2	12.2	1098	9.66	0.268	1.57	102	8.21	67.9	1.47	94.1
	Av	12.4	1122	9.78	0.258	1.62	102	9.20	66.6	1.33	101
81865	1	12.0	795	10.5	0.517	1.52	126	9.49	70.1	1.17	116
	2	12.6	820	10.2	0.507	1.37	117	9.17	76.4	1.39	121
	Av	12.3	808	10.4	0.512	1.44	122	9.33	73.2	1.28	118

Thirty-two different kinds of house paint were studied by painting onto glass plates, allowing to dry thoroughly, then subjecting small scrapings of each kind of paint to both a short and long irradiation-count cycle. The following elements were discerned among the various paints: Na, Al, Cl, K, Ca, Ti, Cr, Mn, Co, Cu, Zn, As, Br, Sr, Mo, Sb, Ba, La, Sm, Ta, and Hg. The radioisotopic analytical indicators generated by activation and used to identify and quantitate these elements are given in Table 24. The analytical results are given in Table 25.

4.3 DISCUSSION

Although the experiments did not provide sufficient data for the formulation of highly sophisticated probability statements, they were highly instructive. For example, it is obvious that the uniformity of results degrades from intra-can samples to inter-can samples of a given batch, to inter-batch samples of a given paint, to different paints, in that order.

It is of considerable interest to understand the probabilities of: (1) differentiating between different paints of a given color, (2) differentiating between different batches of the same paint, (3) differentiating between or identifying samples of a given batch of paint taken from different cans, and (4) identifying two samples of paint taken from a common can. This understanding is furthered by the data presented in the experimental section above.

4.3.1 Paints of a Single Kind

Based on the variances of the four elements determined in the red automobile paint (see Table 21), it may be assumed that in at least 90% of the samples from a given can the concentrations of the four elements (Na, Mn, Al, and Br) will not deviate more than 8% from the average values.

Table 24

ANALYTICAL INDICATORS USED IN PAINT ANALYSES

Element	Indicator			Element	Indicator		
	Isotope	Half-Life	Principal Gamma Rays (MeV)		Isotope	Half-Life	Principal Gamma Rays (MeV)
Na	Na ²⁴	15 h	1.37, 2.75	As	As ⁷⁶	26.4 h	0.559, 0.66, 1.22
Al	Al ²⁸	2.3 m	1.78	Br	Br ⁸²	35.9 h	0.777, 0.55, 0.62
Cl	Cl ³⁸	37.3 m	1.59, 2.16	Sr	Sr ^{87m}	2.8 h	0.388
K	K ⁴²	1.25 h	1.53	Mo	Mo ⁹⁹	66 h	0.142, 0.741
Ca	Ca ⁴⁹	8.8 m	3.10	Sb	Sb ¹²²	2.8 d	0.564
Ti	Ti ⁵¹	5.79 m	0.32	Ba	Ba ¹³⁹	84 m	0.165
Cr	Cr ⁵¹	27.8 d	0.32	La	La ¹⁴⁰	40.2 h	1.60, 0.490, 0.32
Mn	Mn ⁵⁶	2.58 h	0.847, 1.81, 2.11	Sm	Sm ¹⁵³	47.1 h	0.103
Co	Co ⁶⁰	5.24 y	1.17, 1.33	Ta	Ta ¹⁸²	115 d	1.122, 1.222, 1.18
Cu	Cu ⁶⁴	12.8 h	0.511, 1.34	Hg	Hg ¹⁹⁷	65 h	0.077
Zn	Zn ^{69m}	13.8 h	0.439				

Table 25
NAA RESULTS OF 32 PAINT SAMPLES

Sample No.	Paint Brand	Color Designation	Concentration (ppm)																				
			Ti	Al	Mn	Cl	Zn	Na	Sm	Co	Ca	K	Cu	Hg	As	Ta	La	Br	Cr	Mo	Sb	Ba	Sr
1	Sears Roebuck	Antique White	225,000	5,670	2.62	806	2,340	145	0.386	410	<1,100	<270	<4.6	--	--	--	--	--	<480	<160	<3.9	<25	<7.6
2		Horizon Blue	129,000	4,080	3.48	44.1	1,240	105	<0.74	600	35,500	55.9	107	--	--	--	--	--	226	<120	<5.0	<19	<5.8
3		Frosty Pink	230,000	6,760	2.24	<8.4	2,880	159	<0.72	611	<1,300	<120	<2.6	--	--	--	--	--	328	<120	3.03	<17	<6.3
4		Heritage Brown	2,610	1,080	85.7	<36	<470	117	<0.86	742	50,100	<290	28.2	--	--	--	--	--	<570	<140	<5.3	1,260	<23
5		Sunshine Yellow	185,000	4,570	3.82	9,730	13,200	180	<0.81	380	<1,500	1,780	<5.0	--	--	--	--	--	8,290	<130	<3.1	<55	<17
6		Spring Green	206,000	6,200	7.26	544	1,640	143	<1.1	463	<1,500	<260	109	--	--	--	--	--	410	<180	<7.4	<42	<19
7		Cherry Red	<440	834	135	<49	<610	215	<3.5	675	<820	<360	<8.8	--	--	--	--	--	<530	16,400	<5.5	<150	4,58
8		Snowwhite	224,000	6,500	1.58	<7.3	2,560	165	<0.65	403	<1,100	<98	<2.3	--	--	--	--	--	<260	<110	4.71	<13	<4.
9	Sherwin-	Racer Blue	46,400	1,620	12.9	1,850	<150	118	<0.61	593	6,100	--	1,140	--	--	--	<2.0	<47	--	--	--	--	--
10	Williams	Peacock	13,100	5,130	9.07	2,780	<720	67.1	<1.6	339	<1,300	--	798	--	--	--	<3.4	1,420	--	--	--	--	--
11	(Kem Hi-	Fire Orange	46,900	1,680	12.8	1,809	<200	35.9	<0.39	827	5,530	--	<3.2	--	--	--	<1.2	<6.4	--	--	--	--	--
12	Gloss	Summer Sky	151,000	5,230	3.56	99.1	<390	96.5	<0.91	258	<920	--	53.8	--	--	--	<2.3	<18	--	--	--	--	--
13	Enamels)	Flat Black	<2,900	78,600	22.5	2,000	<760	315	2.29	406	<13,000	--	<12	--	--	--	3.76	<23	--	--	--	--	--
14		Chinese Red	12,100	1,330	22.0	7,030	<360	56.1	<0.66	648	<1,800	--	<6.2	--	--	--	<2.3	<12	--	--	--	--	--
15		Dragon Green	98,100	3,970	11.6	6,220	9,510	56.9	<3.8	266	<2,000	--	<29	--	--	--	<9.0	953	--	--	--	--	--
16		Bonnett Green	206,000	6,820	3.56	469	<210	57.1	<0.47	382	<1,100	--	25.1	--	--	--	<1.2	<8.0	--	--	--	--	--
17	Du Pont	Scotch Gray	102,000	3,170	4.05	<6.4	11,200	405	<0.47	179	41,900	--	<2.3	51.4	<6.2	<16	<1.6	--	<130	--	<2.2	--	--
18	(Duco Gloss	Oyster White	89,400	3,730	3.34	<4.9	10,100	19.4	<0.62	187	<320	--	<2.1	<26	<4.8	<19	<0.91	--	<210	--	<1.7	--	--
19	Enamels)	Light Ivory	135,000	3,750	3.35	<6.1	10,300	61.0	<0.80	159	<350	--	<2.5	<34	<6.8	14.8	<1.6	--	<290	--	<2.4	--	--
20		Mission Ivory	87,600	3,810	3.01	<4.9	9,740	3,100	<0.64	227	<300	--	<2.2	<27	6.27	<21	<1.1	--	<240	--	<2.1	--	--
21	Colorama	Skyline Blue	112,000	4,610	39.3	<15	<480	351	<0.79	1,090	9,290	--	31.6	<34	41.8	<28	<2.9	--	6,030	--	<3.7	--	--
22	(Super Yacht	Sabor	143,000	4,630	3.43	518	<220	287	<0.68	518	<570	--	<2.9	<29	39.2	<21	<2.5	--	7,550	--	<2.9	--	--
23	Enamels)	Shrimp Coral	125,000	4,270	12.2	<10	<310	226	<0.73	1,040	7,740	--	<3.7	<31	43.6	<33	<2.7	--	995	--	<3.3	--	--
24		Appleblossom	115,000	4,490	1.38	<6.3	843	223	<0.56	1,000	<450	--	<1.9	<24	<6.6	<26	<2.1	--	<250	--	3.36	--	--
25		Driftwood	130,000	4,090	283	<37	<490	194	<0.95	755	<400	--	<8.4	<40	<15	9.82	<3.2	--	<430	--	32.1	--	--
26	Pittsburgh	Stratosphere Blue	64,200	4,460	16.9	<30	4,410	4,170	<1.9	350	136,000	--	<11	<82	<34	<26	<8.4	--	<450	--	126	--	--
27	(Satinhide	Blue Jade	96,100	1,600	141	833	4,440	116	1.57	144	119,000	--	(a)	<40	<22	<20	8.68	--	<310	--	92.6	--	--
28	Enamels)	Frosted Mint	74,800	968	139	<21	1,970	120	1.61	116	155,000	--	<5.7	<24	<10	<12	9.84	--	<210	--	44.2	--	--
29		Sea Mist	93,200	1,120	149	<23	1,420	122	1.53	144	174,000	--	<6.1	<27	<11	<15	13.9	--	<240	--	35.2	--	--
30		Sunny Yellow	95,400	1,180	153	<27	2,040	102	2.81	142	194,000	--	<7.2	<33	<13	<39	16.9	--	1,070	--	37.4	--	--
31	Sherwin-	Flasher Yellow	96,900	4,010	3.93	59.2	<230	60.6	<0.6	362	<480	--	(a)	<25	<13	<20	<1.2	--	280	--	46.0	--	--
32	Williams	Basket Brown	10,600	782	97.4	<23	<370	143	<0.6	722	28,400	--	73.9	<26	<13	<29	<2.0	--	<270	--	<4.7	--	--

(a) Copper was detected but could not be quantitatively measured.

Similarly, based on the duplicate analyses of Sinclair paint 1929 (see Table 23), the 90% confidence levels are as follows:

<u>Element</u>	<u>Relative Deviation, %</u>	<u>Element</u>	<u>Relative Deviation, %</u>	<u>Element</u>	<u>Relative Deviation, %</u>
Ti	7	Na	7	In	26
Al	5	Co	13	La	21
Mn	4	Zn	10	Sb	18

The aggregate values of elemental concentration for all samples of Sinclair paint 1929 were used to compute similar 90% confidence levels for interbatch samples, and these are as follows:

<u>Element</u>	<u>Relative Deviation, %</u>	<u>Element</u>	<u>Relative Deviation, %</u>	<u>Element</u>	<u>Relative Deviation, %</u>
Ti	3.0	Na	37	In	77
Al	22.6	Co	45	La	32
Mn	4.6	Zn	5.1	Sb	28

The foregoing indicates that little differentiation between different batches of a given paint can be obtained from the determination of Ti, Mn, and Zn, but that the other elements can be useful for this purpose. In other words, the elements Al, Na, Co, In, La, and Sb provide six points of comparison with which to evaluate whether two samples of a given paint come from a common batch or from different batches.

4.3.2 Different Kinds of Paint

The most useful set of data with respect to the comparison of different kinds of paints is given in Table 25, which gives both more samples and elements determined than Table 20. Among the elements reported in the 32 samples, the elements Ti, Mn, Al, Na, and Co are found in nearly

every sample, and these elements will be treated as primary comparison points in the following discussion. The other elements will be used as supplementary points of comparison.

Comparison of the 32 samples with respect to concentrations of the primary comparison points is facilitated by a coded sequence of concentration ranges. Each range must be sufficiently large to comfortably encompass the variations within a given batch of paint. The larger the range can be made in this sense without excessively limiting the number of useful ranges, the more useful the concentration codes will be. With these considerations in mind the codes given in Table 26 were devised for comparison purposes.

With the codes specified in Table 26, the concentrations for the five primary elements in Table 25 can be expressed in letter patterns. These patterns ordered first by Ti concentration, and next, in order, by Mn, Al, Na, and Co concentrations given in Table 27.

Only two of the 32 paints are described by the same letter pattern in Table 27. These are samples Nos. 29 and 30. Referring to the more definitive descriptions of these two samples given in Table 25, we see that they are differentiable on the basis of color. They are also distinguishable by their different zinc concentrations.

The letter code pattern method of comparing elemental concentrations of samples is very convenient, and provides a simple, if unsophisticated, means of quickly comparing samples. The same approach applied to the Sinclair paint number 1929 (Table 23) shows that sample No. 4 and sample No. 6 have the same primary letter codes, but the two samples are differentiable by the concentrations of the rare earth elements. The same statement can be made for samples Nos. 1 and 8. All other samples have different primary letter code patterns.

Table 26
CONCENTRATION CODES

Code	Elements and Concentration Ranges				
	Ti (thousands of ppm)	Mn (ppm)	Al (thousands of ppm)	Na (ppm)	Co (ppm)
A	<1	1-2.1	0.7-1	<31	100-150
B	1-40	2.1-4.6	1-1.5	31-47	150-230
C	4-80	4.6-10	1.5-2.3	47-70	230-310
D	80-120	10-21	2.3-4.7	70-100	310-470
E	120-160	21-46	4.7-7.0	100-150	470-700
F	160-200	46-100	7.0-10	150-230	700-1000
G	200-240	100-210	>10	230-310	1000-1500
H	>240	210-400		310-470	>1500
I		>400		>470	

Table 27
LETTER PATTERNS FOR 32 DIFFERENT PAINTS

Sample No.	Element					Sample No.	Element				
	Ti	Mn	Al	Na	Co		Ti	Mn	Al	Na	Co
13	A	E	G	H	D	21	D	E	D	H	G
6	A	G	A	F	E	29	D	G	B	E	A
10	B	C	E	C	D	30	D	G	B	E	A
14	B	E	B	C	E	27	D	G	C	E	A
32	B	F	A	E	F	19	E	B	D	C	B
4	B	F	B	E	F	2	E	B	D	E	E
11	C	D	C	B	F	22	E	B	D	G	E
9	C	D	C	F	E	12	E	B	E	D	C
26	C	D	D	I	D	23	E	D	D	F	G
28	C	G	A	E	A	25	E	H	D	F	F
24	D	A	D	F	G	5	F	B	D	F	D
18	D	B	D	A	B	7	G	A	E	F	D
31	D	B	D	C	D	16	G	B	E	C	D
17	D	B	D	H	B	1	G	B	E	E	D
20	D	B	D	I	B	3	G	B	E	F	E
15	D	D	D	C	C	8	G	C	E	E	D

4.4 CONCLUSION

The foregoing work has enabled the preliminary definitions of variations to be expected among concentrations of elements in a given batch of paint. These have been used as a basis for defining significant differences in elemental concentrations, which in turn have been used to assign meaningful concentration ranges of five elements to be used as primary comparison points. These ranges, coded by letters to ease comparisons, were found to provide a swift means to single out possible matching pairs of samples.

Among 32 different paints, no two had the same trace element patterns, although a supplementary identification point was required to differentiate between one pair of paints (ignoring color differences). Also, it was possible to distinguish between eight different batches of the same kind of paint on the basis of trace element concentrations (again using supplementary trace element identification points in two cases).

In view of the foregoing, it is apparent that NAA is a simple and powerful method for comparing paint samples. Different kinds of paints and different batches of paints of a given kind of paint can be distinguished using difference definitions within which samples from a given batch of paint appear identical. It remains to be determined, however, just how small the probabilities are of either having two samples of the same batch appear to be different or two different paints appear to be the same.

5. PAPER

5.1 INTRODUCTION

Inasmuch as paper ranks among the more common evidence materials in criminalistics, a study was made to assess the degree to which NAA could augment normal laboratory procedures for characterizing and identifying this material. This seemed promising since, whereas the more usual tests depend on physical characteristics (water-marks, mold or press marks, cut or torn edges, microscopic fiber properties, density, color, and strength), NAA yields an elemental analysis that comprises an entirely new set of identity parameters.

As in the studies of other materials described in this report, the activation of samples was carried out with the Gulf General Atomic TRIGA Mark I nuclear reactor at thermal neutron fluxes of 1.8×10^{12} n/cm²-sec and 2.8×10^{12} n/cm²-sec in rotary specimen rack and pneumatic tube positions, respectively. All induced radioactivity measurements were carried out with a 3-in. -diam by 3-in. -long NaI(Tl) counter coupled to a multichannel pulse-height analyzer.

5.2 EXPERIMENTAL AND RESULTS

5.2.1 Initial Studies

Initial studies consisted of the examination of eight samples of white paper. ⁽¹⁾ One set of samples were irradiated for 15 seconds and counted immediately, and another set was irradiated for 60 minutes and counted at several decay times during an eight day period. The gamma-ray spectra were interpreted with respect to the concentrations of eight elements, and the results are given in Table 28.

Table 28
CONCENTRATIONS OF ELEMENTS IN PAPER (ppm)

Sample	Na	Cl	Cu	Sb	Mn	Sc	La	Al
Small Scratch Pad	186	970	11	6.8	1.1	≤0.8	≤ 4.2	3530
Report Sheet ^a	221	1230	18	≤2.0	6.5	≤1.2	≤13.0	13200
Letterhead ^a	407	532	≤10	≤2.5	1.2	≤0.8	≤ 4.8	1400
Memo Sheet ^a	330	1050	≤14	4.9	2.9	1.9	≤ 8.6	18400
Eagle "A" Trojan Bond	336	543	≤ 9	≤1.2	4.5	≤0.7	≤ 4.7	5460
Eagle Trojan Onion Skin	352	980	≤12	≤3.1	1.2	≤1.6	≤13.0	6650
Large Scratch Pad	106	1550	15	≤1.6	3.6	3.2	12.0	28900
Manuscript (ISA Form B3-20)	264	1470	≤10	≤1.3	3.8	1.8	11.0	21600

^a Standard GD/GA stock

A number of samples of paper were obtained from the U. S. Treasury Department wherein there exists significant interest in paper characterization. Duplicate samples of the same paper from the same batch, plus, in some cases, samples of the same paper from two different batches were submitted. Analyses of these samples via the short irradiation regimen gave results shown in Table 29.⁽²⁾

Another set of samples, consisting of two samples of paper, two counterfeit bills, and seven pigments were received from the Treasury Department for analysis, in order to study the possibility of identifying pigments used in counterfeiting.⁽³⁾ The samples were processed by the short irradiation regimen; and, when no measurable activity remained, the paper samples and new portions of each pigment were processed by the longer irradiation regimen. The results are summarized in Table 30.

Some quantitative values for several of the elements observed in the set of inks, counterfeit bills, and papers are given in Table 31, in the same order.

5.2.2 Larger Study of Bond Paper

A set of 120 samples of white bond paper was obtained from nine manufacturers. The set comprised 40 different grades of paper, including opaque papers, which have a relatively large proportion of fillers. This set of papers is described in Table 32, and it is enumerated in Table 33.

To expedite this study, three portions were removed from each sample. A fragment weighing approximately 50 mg was irradiated for exactly one minute in the pneumatic transfer system and counted for exactly one minute (live time) after being transferred to an unirradiated vial. Counting was begun one minute after the end of the irradiation.

Both the second and third portions, weighing about 30 mg and one gram, respectively, were packed in the same vial and irradiated for two hours in the rotary specimen rack of the nuclear reactor. The samples

Table 29

CONCENTRATION OF ELEMENTS IN BOND PAPER (ppm)

Sample	Al	Ti ($\times 10^4$)	Cl
Gilbert Lancaster Bond, 100% rag. Batch 1	2714	1.9	146
Gilbert Lancaster Bond, 100% rag. Batch 1	2630	1.9	226
Gilbert Lancaster Bond, 100% rag. Batch 2	1790	2.2	214
Gilbert Radiance Bond, 75% rag. Batch 1	2400	1.4	326
Gilbert Radiance Bond, 75% rag. Batch 1	2060	1.1	194
Gilbert Bond, 25% rag. Batch 1	5459	1.1	370
Gilbert Bond, 25% rag. Batch 1	5600	0.8	290
Gilbert Bond, 25% rag. Batch 2	10323	2.0	557
Gilbert Opaque Bond, 100% sulph. Batch 1	6161	1.8	624
Gilbert Opaque Bond, 100% sulph. Batch 1	5051	1.3	559
Gilbert Opaque Bond, 100% sulph. Batch 2	9228	2.6	490
Gilbert Cardinal Bond, 100% sulph. Batch 1	13182	0.37	543
Gilbert Cardinal Bond, 100% sulph. Batch 1	13693	≤ 0.16	565
Eagle A Cupon Bond, 100% rag. Batch 1	2172	1.4	192
Eagle A Cupon Bond, 100% rag. Batch 1	1970	1.3	138
Eagle Agawam Bond, 100% rag. Batch 1	4169	2.0	220
Eagle Agawam Bond, 100% rag. Batch 1	4168	1.9	174
Eagle Agawam Bond, 50% rag. Batch 1	6913	0.94	502
Eagle Agawam Bond, 50% rag. Batch 1	5885	0.67	493
Eagle Trojan Bond, 25% rag. Batch 1	6237	0.77	558
Eagle Trojan Bond, 25% rag. Batch 1	5601	0.77	435
Eagle Trojan Bond, 25% rag. Batch 2	2575	0.45	478
Eagle Translucent Bond, 100% sulph. Batch 1	498	≤ 0.03	216
Eagle Translucent Bond, 100% sulph. Batch 1	506	≤ 0.03	285
Eagle Translucent Bond, 100% sulph. Batch 2	1007	≤ 0.04	240
Eagle Quality Bond, 100% sulph. Batch 1	12363	0.84	593
Eagle Quality Bond, 100% sulph. Batch 1	12614	0.76	724

Table 30
ELEMENTS OBSERVED IN PAPERS AND PIGMENTS

Sample	Na	Al	Ti	V	Cr	Mn	Fe	Co	Cu	Sb	Te	R. E. ^a
1. Holland Ink, Emerald Green	x	x		x					x		x	x
2. Interchem. Corporation, Everyday Med. Blue	x	x		x	x	x		x	x			
3. Midwest Printers Supply, Yellow Lake 42560	x	x		x	x	x			x			
4. Midwest Printers Supply, Niagara 58937	x	x		x					x			x
5. Midwest Printers Supply, Quickset Cornflower 54252	x	x		x	x				x		x	
6. Davidson Non Skin Black					x		x					
7. Letter Press and Litho Inks, Emerald Green 2729	x	x		x		x		x	x	x		
8. Counterfiet Bill No. 1 RJL-2-29-64	x	x	x	x	x		x		x			x
9. Counterfiet Bill No. 2 RJL-2-29-64	x	x	x	x	x		x		x			x
10. Warren Silkote Offset Paper	x	x	x	x	x				x			
11. Victor Bond Paper	x	x	x	x					x	x		x

^aUsual rare earths observed were La, Ce, Er, and/or Sm.

Table 31
ELEMENTS FOUND IN PAPER AND PIGMENTS

Sample	Element (ppm)				
	Ti	Cr	Fe	Sb	Co
1					
2		366 ± 55			322 ± 48
3		4883 ± 732			
4					
5					
6		81 ± 12	3283 ± 492		
7					156 ± 23
8	750 ± 150	53 ± 8			
9	750 ± 150	49 ± 7			
10	2300 ± 450	25 ± 4			
11	100 ± 16			1.13 ± 0.17	

Table 32
CHARACTER OF SAMPLES

Manufacturer	Total Samples	Number of Different Grades Represented		
		100% Rag	Part Wood Fiber	Opaque
1	14	1	4	1
2	14	1	4	1
3	30	1	4	2
4	12		2	
5	8	1	1	
6	10	1	3	1
7	6	1	2	
8	16	2		
9	10	1	4	2
	120	(9	24	7) = 40

Table 33
120 PAPER SAMPLES

Sample Ref. No.	Source	Type
HLS-1	Fox River	Anniversary Bond
2	"	Anniversary Bond
3	"	National Bank Bond
4	"	English Bond
5	"	English Bond
6	"	Fox River Bond
7	"	Fox River Bond
8	"	Fox River Bond
9	"	Fox River Bond
10	"	Fox River Opaque
11	"	Fox River Opaque
12	"	Fox River Opaque
13	"	Fox River Laid
14	"	Fox River Laid
15	Gilbert Paper	Lancaster
16	"	Lancaster
17	"	Lancaster
18	"	Lancaster
19	"	75% Radiance Bond
20	"	75% Radiance Bond
21	"	25% Gilbert Bond
22	"	25% Gilbert Bond
23	"	Gilbert Opaque Bond
24	"	Gilbert Opaque Bond
25	"	25% Gilbert Superese
26	"	25% Gilbert Superese
27	"	25% Gilbert Envelope Bond
28	"	25% Gilbert Envelope Bond
29	Writing Plover	Permanized Parchment
30	"	Permanized Parchment
31	"	Permanized Parchment
32	"	Permanized Parchment
33	"	Cold Springs Bond
34	"	Cold Springs Bond
35	"	Cold Springs Bond
36	"	Cold Springs Bond
37	"	Artesian Bond
38	"	Artesian Bond

Table 33 (Continued)

Sample Ref. No.	Source	Type
39	Writing Plover	Artesian Bond
40	"	Artesian Bond
41	"	Artesian Bond Opaque
42	"	Artesian Bond Opaque
43	"	Erasable Plover Bond No. 20
44	"	Erasable Plover Bond No. 20
45	"	Erasable Plover Bond No. 20
46	"	Erasable Plover Bond No. 20
47	"	Plover Bond
48	"	Plover Bond
49	"	Plover Bond
50	"	Plover Bond
51	"	Plover Bond Opaque
52	"	Plover Bond Opaque
53	"	Plover Bond Opaque
54	"	Plover Bond Opaque
55	"	Plover Bond Opaque
56	"	Plover Bond Opaque
57	"	Plover Bond Opaque
58	"	Plover Bond Opaque
59	Parsons Paper	Edgemont Bond
60	"	Edgemont Bond
61	"	Edgemont Bond
62	"	Edgemont Bond
63	"	Parson's Bond
64	"	Parson's Bond
65	"	Parson's Bond
66	"	Parson's Bond
67	Rising Paper	Rising Parchment
68	"	Rising Parchment
69	"	Rising Parchment
70	"	Rising Parchment
71	"	Rising Bond
72	"	Rising Bond
73	"	Rising Bond
74	"	Rising Bond

Table 33 (Continued)

Sample Ref. No.	Source	Type
75	Valley Paper	Valley Congress Bond
76	"	Valley Congress Bond
77	"	Valley Forge Bond
78	"	Valley Forge Bond
79	"	Edgeworth Bond
80	"	Edgeworth Bond
81	"	Raceway Bond
82	"	Raceway Bond
83	"	Realopak Densor Fifty
84	"	Realopak Densor Fifty
85	Brown Co.	Coupon Bond
86	"	Coupon Bond
87	"	Contract Bond
88	"	Contract Bond
89	"	Trojan Bond
90	"	Trojan Bond
91	Crane & Co.	Crane's Bond
92	"	Crane's Bond
93	"	Crane's Bond
94	"	Crane's Bond
95	"	Crane's Bond
96	"	Crane's Bond
97	"	Crane's Crest
98	"	Crane's Crest
99	"	Crane's Crest
100	"	Crane's Crest
101	"	Crane's Crest
102	"	Crane's Crest
103	"	Crane's Crest
104	"	Crane's Crest
105	"	Crane's Crest
106	"	Crane's Crest
107	Byron-Weston	Old Hampshire Bond
108	"	50% Winchester Bond
109	"	25% Weston's Bond
110	"	25% Weston's Bond
111	"	25% Weston Opaque Bond
112	"	25% Rag Merit Bond
113	"	25% Rag Merit Bond

Table 33 (Continued)

Sample Ref. No.	Source	Type
114	Byron-Weston	25% Merit Opaque Bond
115	"	25% Merit Opaque Bond
116	"	25% Research Bond
117	Parsons Paper	Parson's Bond
118	"	Parson's Bond
119	"	Edgemont Bond
120	"	Edgemont Bond

were transferred to two separate vials after irradiation. The smaller portion was counted after about a one-hour delay and again after a 24-hour delay. The larger portion was counted routinely on the eighth day after irradiation. Some samples, however, were followed with many additional counts to verify half-lives or to permit a long-lived component to be quantitated more accurately. Some samples were last counted 25 days after irradiation. Much smaller specimens can be successfully analyzed if longer irradiation times are employed.

The data were processed by a standard procedure for survey work at this laboratory. The digital output of the pulse-height analyzers was placed on data-processing cards. A computer program was employed to prepare plots from the cards. Figures 20, 21, and 22 were traced from some of these plots. A second computer program used the cards to locate the energy of each major peak and calculate its area. From this information, the element responsible for each peak could be identified. A third program made appropriate calculations for sample weight, radioactive decay, and other parameters, and printed the amount present for each element identified and an estimate of the precision of the analysis. In these figures, the radionuclide and gamma-ray energy (in keV) associated with each major photopeak is indicated. The analytical results are given in Table 34.

Table 35 presents the pertinent data for the radionuclides and elements discovered in these samples. Titanium, aluminum and calcium were quantitated from data obtained following the 1-minute irradiation. Sodium, manganese and chlorine were quantitated from the counts obtained one hour after irradiation. Sodium-24 was the major activity present from the first to the sixth day after irradiation for almost all samples, and was probably the direct cause for the low frequency with which gold and lanthanum were detected. The other elements were quantitated from

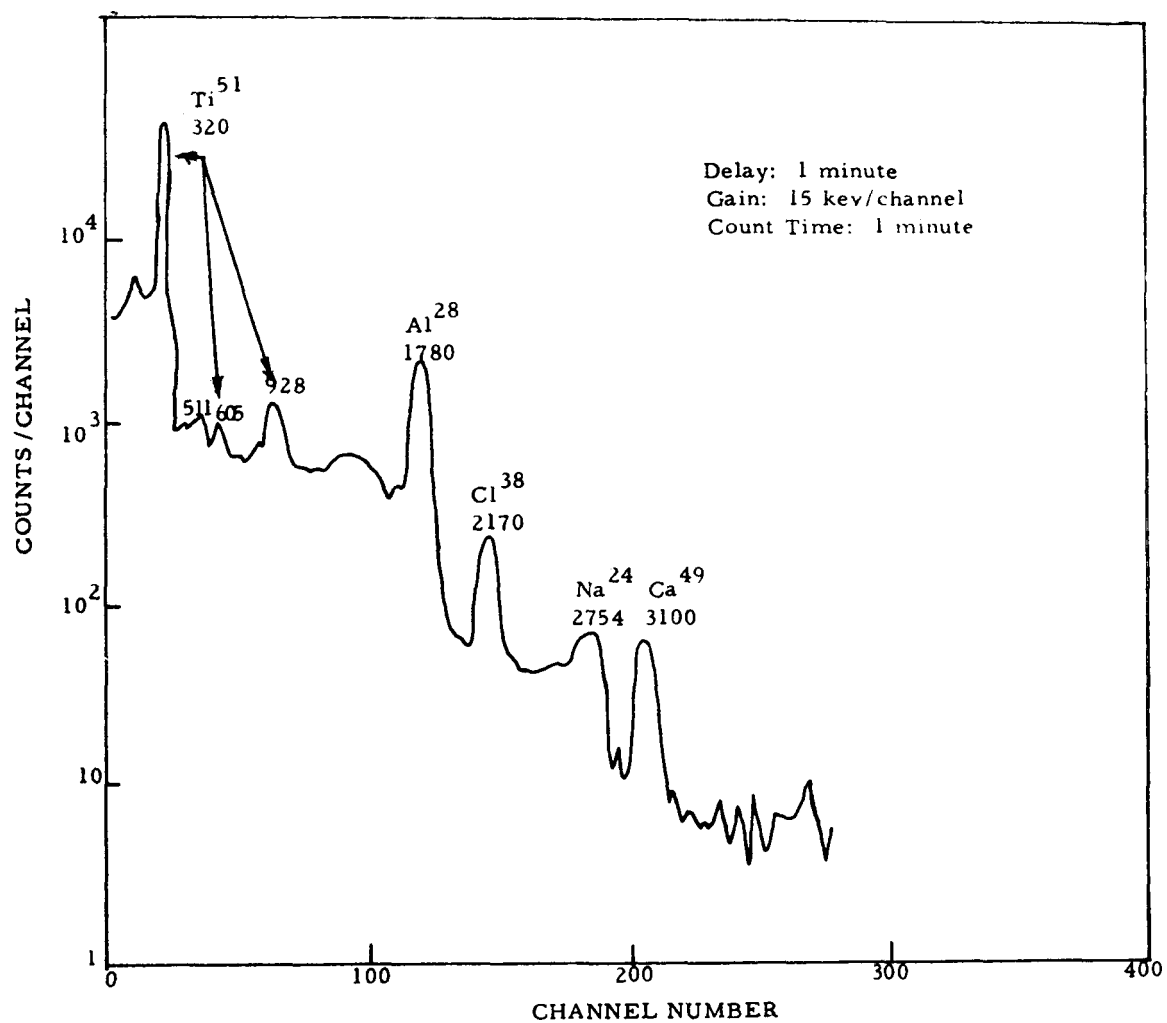


Fig. 20. Gamma-ray spectrum of paper sample; one-minute irradiation

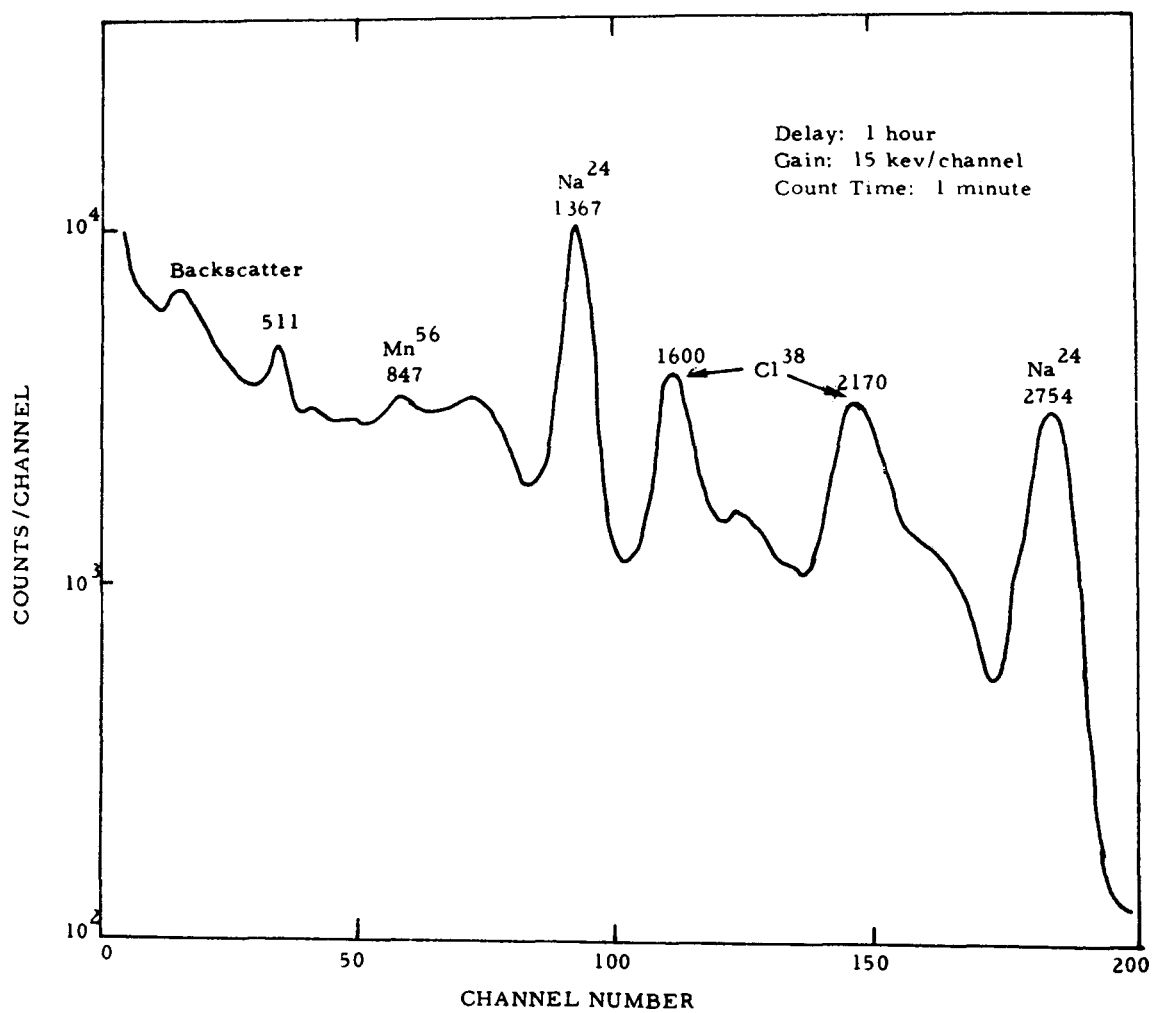


Fig. 21. Gamma-ray spectrum of paper sample; one-hour irradiation

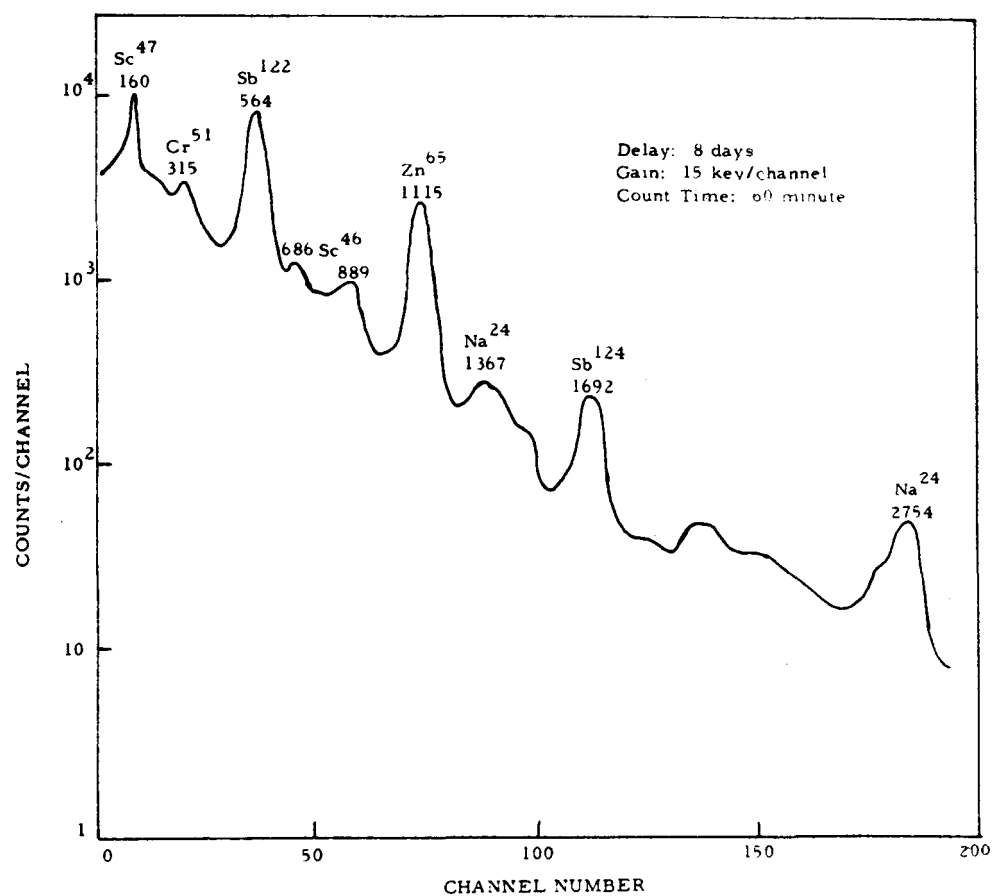


Fig. 22. Gamma-ray spectrum of paper sample; long-lived nuclides

Table 34

ANALYSIS OF 120 PAPERS; ELEMENTAL CONCENTRATIONS (ppm)

Sample	Ti	Al	Ca	Na	Mn	Cl	Cr	Sb	Zn	Ta
1	3100	34	2900	110	3.4	190			64.0	0.41
2	3000	27	3100	84	3.0	110			54.0	0.34
3	2700	17	2200	210	2.8	300	0.71		39.0	
4	3400	200	2800	290	1.1	660		0.60		
5	3200	130	2300	290	1.0	670		0.58	9.0	
6	2400	150	3300	180	0.58	460		0.16	7.1	
7	2100	160	2800	240	0.90	580		0.25	6.4	
8	2000	280	3200	250	0.14	640		0.24	9.2	
9	1800	110	2700	260	1.2	540		0.26	6.8	
10	15000	44	2100	210	1.2	560		2.0	11.0	
11	16000	82	2400	210	1.1	490		2.3	13.0	
12	7800	52	1400	200	0.77	480		1.1	13.0	
13	2500	170	3900	210	1.2	610				
14	3200	98	3100	210	1.0	600		0.62	9.4	
15	3700	600	790	230	1.6	200	2.9	1.0	87.0	
16	4500	260	1100	100	2.2	48	3.0	0.96	87.0	
17	3800	410	620	72	2.0	100	2.5	0.96	92.0	
18	4600	590	760	180	1.8	90	2.2	0.88	89.0	
19	7300	1100	450	200	1.9	125	0.14	0.42		
20	8700	1600	500	400	2.2	76			10.0	
21	≤10000	13000	≤5700	290	1.1	340	17.0	0.12		
22	≤10000	12000	≤6400	360	0.95	380	20.0	0.10		
23	11000	9100	≤4700	380	0.79	170		0.50		
24	14000	10000	≤6900	430	0.71	330		0.17		
25	8300	2700	1400	530	1.1			22.0		
26	13000	4800	1300	490	1.1			77.0		
27	≤22000	19000	≤23000	550	0.91		23.0			
28	≤23000	19000	≤27000	590	1.3		1.6			
29	6800	2100	≤550	640	7.6		1.4	0.78		1.1
30	6600	2100	≤450	540	7.4					0.14
31	4500	2200	≤460	580	6.1					0.10
32	9800	2200	≤480	290	6.7		1.3			0.27
33	7400	1700	≤4400	290	3.2		0.44	0.023		0.64
34	7400	1700	≤270	550	3.3		0.86	0.38		
35	10000	2600	≤450	560	7.6	100	2.4	0.44		
36	7600	2200	<490	580	22.0		2.8	0.53		0.88

Table 34 (Continued)

Sample	Ti	Al	Ca	Na	Mn	Cl	Cr	Sb	Zn	Ta
37	6900	2200	<520	890	19.0	410	1.8	0.31		0.74
38	6300	2000	<390	1200	18.0	370	1.3	0.22		1.2
39	5400	1600	<360	730	14.0	610	0.17			0.41
40	3900	1600	<370	770	15.0	270	1.1			0.81
41	14000	1700	<420	840	15.0	380		0.70		0.85
42	11000	1500	<400	1000	28.0	670		0.67		1.5
43	7900	1900	<480	680	28.0	500		1.5		
44	8600	2100	<530	2100	27.0			1.6		1.4
45	6900	1400	<370	2100	28.0	540		1.6		0.97
46	7900	1600	<420	2400	57.0			1.8		1.2
47	4600	4800	<1300	2500	14.0		7.6			
48	4600	4900	<1300	800	14.0		8.0			
49	1100	4500	<1200	730	14.0	1180	7.2			
50	260	4100	<940	720	16.0	790	5.9			
51	8900	1200	<480	680	18.0	900				1.1
52	18000	2000	<560	670	18.0	910				1.9
53	16000	2000	<470	610	15.0	670				2.0
54	14000	1600	<330	1000	15.0					1.4
55	6600	740	<340	660	20.0					0.72
56	7300	800	<200	530	18.0	190	1.0			0.79
57	15000	1200	<320	570	8.1					1.9
58	9100	1400	<390	520	8.1					2.0
59	6000	2000	<510	1400	8.1		2.6	1.2		
60	6100	2000	<590	1400	8.2		2.6	1.2		
61	5600	1800	<390	1600	6.7		2.3	1.0		
62	5300	1800	<440	13000	6.1		2.1	1.3		
63	7500	2000	<580	820	3.0			1.5		
64	5000	2000	<450	780	2.9			1.4		
65	8800	1700	<300	1100	2.0		1.4	2.1		
66	8200	1700	<490	1100	3.0		2.2	2.2		
67	15000	2800	<690	520	2.3		2.0	2.2		
68	15000	2900	<580	460	1.9			2.6		
69	14000	2600	<1100	930	2.7		2.7	2.1		
70	14000	2600	<1100	420	1.1	1100	1.8		74.0	
71	<3700	2400	4800	150	1.1	460		4.1	130.0	
72	<4000	3300	2600	160	0.77	520		5.2		

Table 34 (Continued)

Sample	Ti	Al	Ca	Na	Mn	Cl	Cr	Sb	Zn	Ta
73	<5700	2200	2800	340	0.98	520		3.1		
74	<4400	3000	3200	360	0.83	520		3.8		
75	<5600	5400	<2900	290	1.3	150	6.9			
76	<5800	5600	<2300	260	1.1	160	6.4			
77	<13000	12000	<4700	310	1.8	360	20.0			
78	<14000	14000	<3700	300	1.9	350	21.0			
79	<14000	14000	<6600	330	2.0	500	15.0			
80	<14000	14000	<5000	310	2.0	430	22.0			
81	<10000	9900	<2800	500	1.3	500	14.0			
82	<9900	9500	1600	470	1.4	420	14.0			
83	<6900	6500	<1300	220	1.4		8.0			
84	<6500	6000	<900	220	1.5	150	9.7			
85	1500	830	<280	430	2.4	430	3.5	1.1	53.0	
86	1600	960	<360	340	2.7	300	5.1	2.5	76.0	
87	3400	1900	<300	270	1.5	240		5.1	21.0	
88	3600	1200	<420	290	1.8	220	0.87	4.2	51.0	
89	7900	3000	<790	770	2.6	31		12.0		
90	9300	3400	<860	700	2.5			14.0		
91	<2100	1800	<380	130	0.58	120		0.93	67.0	
92	<2100	1800	<430	170	0.40	190	0.97	0.40	73.0	
93	<2300	2100	<510	150	0.59	20	2.5	0.19	160.0	
94	<2300	1900	<580	190	0.44	13	2.0	0.15	120.0	
95	<1700	2000	<590	140	0.56	130	1.6	0.09	140.0	
96	<1700	1900	<520	200	0.36	40	3.3		130.0	
97	<1900	2300	<590	120	0.42	91		0.47	79.0	
98	<1900	2100	<620	170	0.46	57		0.37	85.0	
99	<1500	2100	1500	170	0.56	84	2.3	2.3	110.0	
100	<1300	2000	1200	150	0.41		2.2	0.62	140.0	
101	<1600	1900	<680	160	0.68	130	2.3	0.44	120.0	
102	<1800	2200	<570	150	0.38		2.4	1.2	130.0	
103	<1200	1900	<530	160	0.63	280	2.2	0.050	110.0	
104	<1300	2000	<520	170	0.44	420	2.4	0.14	120.0	
105	<1800	2000	<410	130	0.34	110	2.6	0.14	98.0	
106	<1600	1800	<410	230	0.64	600	1.7	0.13	80.0	
107	6800	1800	930							
108	4000	1300	550	320	0.73	910	3.2	0.58	83.0	

Table 34 (Continued)

Sample	Ti	Al	Ca	Na	Mn	Cl	Cr	Sb	Zn	Ta
109	3400	3000	<1100	300	0.79	1100		0.60	5.5	
110	a	a	a	260	0.61	1200		2.0		
111	10000	980	<390	430	0.83	1200		1.7		
112	8800	1200	<440	380	0.97	1200		0.64		
113	4600	2600	<900	330	0.95	1200		0.78		
114	7800	900	<330	400	0.80	1400		1.4		
115	9800	940	<400	320	0.80	1100		1.6		
116	3100	3000	<1200	310	0.75	1200		0.63		
117	7100	2100	<610	360	1.5	1100		0.98		
118	6300	1800	<250	420	1.2	950		1.4		
119	5500	2000	<580	400	1.3					
120	5100	1800	<500	380	1.3					

^aValue not determined

Table 35

RADIONUCLIDES DETECTED IN PAPER SAMPLES

Radionuclide	Half Life (Minutes)	Gamma-Ray Energy Used for Quantitation (keV)	Smallest Amount of Element Detected (ppm)	Largest Amount of Element Detected (ppm)	% of Samples in Which the Element Was Detected
⁵¹ Ti	5.8	320.0	1100.0	17,600.0	78.0
²⁸ Al	2.3	1779.0	17.0	19,700.0	100.0
⁴⁹ Ca	8.8	3083.0	360.0	27,100.0	21.0
⁵⁶ Mn	154.0	847.0	0.33	57.0	100.0
²⁴ Na	900.0	1367.0	83.0	2,540.0	100.0
³⁸ Cl	37.3	1642.0	13.0	1,440.0	70.0
¹⁸² Ta	166,000.0	1100-1200	0.14	2.05	19.0
⁶⁵ Zn	353,000.0	1115.0	5.5	222.0	35.0
¹²² Sb	4,030.0	564.0	0.02	77.0	70.0
¹²⁴ Sb	86,800.0	603.0			
⁵¹ Cr	40,000.0	320.0	0.43	23.0	51.0
¹⁹⁸ Au	3,870.0	412.0	0.0002	0.02	5.0
¹⁴⁰ La	2,420.0	1596.0	0.03	3.51	17.0

data accumulated on or after the eighth day following irradiation. Scandium-46 was detected in 91% of the samples analyzed. Since this isotope can be produced from titanium by the $^{46}\text{Ti}(n,p)^{46}\text{Sc}$ reaction, and was found at levels approximating the known yield from that reaction, it was not included in the present study.

5.3 DISCUSSION

From the initial and relatively small studies, it was apparent that fairly large number of elements were observable in paper, and that the concentration variations were greatest among different papers. Also, it was seen that concentration variations from batch to batch of a given paper, while not as great as among different papers, were greater than the variations from a given batch.

It was also observed that the trace elements within a paper would dominate those of the comparatively small amount of ink on a printed paper to the point that essentially no signal from the ink was observable.

The larger study of 120 papers gave more definitive information, and the results warrant detailed interpretation and discussion. The first aspect to be treated will be paper production methods, after which the results of the NAA work will be treated.

5.3.1 Production of Bond Papers

Visits were made to two companies that supplied samples for this study. Some information which bears on the observed variability of elemental concentration in paper was obtained, and is presented in this section.

Paper-making is essentially a continuous, as distinguished from a batch, process. While the terms "lot" or "batch" are used in the industry and this report, in reality the smallest unit of production is the production

run. This encompasses all of the uninterrupted production of a given grade of paper by a single paper-making machine.

Batches of raw materials are mixed in one or more large tanks for each paper-making machine, but this new material is constantly mixed with reclaimed material from other stages of the paper-making process. This recycling of material must have a profound effect on the variability of the finished product, especially at the beginning and end of a production run.

For example, trimmings from the edges of rolls and defective paper are routinely recycled into batches of raw material. Similarly, uncompacted material lost through the fine screen on which the paper is formed is trapped on a filter and intermittently returned to the machine.

As a result of this recycling of material and of slight differences in the physical properties of the raw materials, adjustments are continuously made to the nominal formula for a particular grade of paper. Also, adjustments are routinely made in the operating parameters of the paper-making machine. The total effect of these changes may result in differences in the elemental composition of paper produced in a single production run. Significant differences in elemental composition were certainly observed in this study.

One final observation made during these plant visits should be included here in reference to the interleaving of papers in a boxed ream. While it is not significant in this study, due to the fact that samples were obtained from known production runs, it should certainly be borne in mind when examining paper samples from actual cases.

Rolls from the paper-making machine are trimmed and split into half-rolls. These half-rolls are marked "left" or "right" to identify the side of the paper-making machine on which they were formed. Paper-making machines habitually produce paper slightly thicker on one side of

the roll than the other. These half-rolls are placed on a machine which slits and cuts the paper into finished sheets. Machines used to form 8-1/2 in. x 11 in. sheets can hold as many as six half-rolls, but can be operated with only a single half-roll mounted. The usual practice is to mount as many "right" as "left" half rolls so that the weight of all the boxed reams are equal. Paper is graded by the weight of a ream. To aid in equalizing these weights, the cutting machine interleaves sheets from each of the half-rolls mounted. If six such rolls are mounted, every seventh sheet in a ream will have come from the same half-roll.

It is common practice in the industry to produce slightly more paper than is required in each production run. The excess is stored. When that grade of paper is produced again, the stored rolls from previous production are used.

This presents a problem to the person who is asked to examine a sheet of paper to determine if it is "the same as" one or more other sheets. It is apparent from the foregoing discussion that two sheets of paper could differ in significant respects and yet still be "the same as" the other in that they were both obtained from the same boxed ream. Unless profound differences are found, only if a significant number of sheets are available for comparison can an unequivocal statement be made as to the common origin of such samples.

5.3.2 NAA Results from Larger Study

In view of the manner in which bond paper of a single kind from a single manufacturer is assembled into packages of cut sheets, it is clear that different production runs within a time span of several weeks may each contribute to a given package of paper. Therefore, in examining the analytical data, the data obtained from each of the forty kinds of paper should be averaged (production runs did not exceed several weeks separation for any kind from a given manufacturer). These averages are given

in Table 36. Among those elements most frequently observed the average relative standard deviations within the samples of a given manufacturer and kind were as follows:

Ti $\pm$ 33%	Ca $\pm$ 22%	Mn $\pm$ 33%	Cr $\pm$ 70%
Al $\pm$ 27%	Na $\pm$ 35%	Cl $\pm$ 41%	Sb $\pm$ 68% .

Inasmuch as the values within the various groups have considerably less spread than the spread of all values for the 40 sample sets, the sets were ordered in accordance with Al concentration ranges. Within each Al concentration range the sets were ordered with respect to the sequential precedence and concentrations of Ti, Na, Mn, Cl, Ca, Cr, and Sb. The concentration ranges chosen for this purpose are suitably large with respect to the aforementioned standard deviations. The concentration ranges and their letter designations are given in Table 37. The ordered sets of samples are shown in Table 38; in this table undetermined values (denoted, x) are ranked last. The sequence of letters for each kind of paper forms a letter code.

It is of considerable interest that the letter codes for the various kinds of papers are all different, except for the two Valley papers of ranks 38 and 39. This is an indication that papers can be characterized with fairly high confidence levels by their elemental constituents. However, the data at hand do not permit definitive statements regarding the relevant statistics because of the limited number of manufacturers represented in the sample and the number of letter codes that are similar, although not identical.

There does not seem to be a clear cut distinction between papers of one manufacturer and another, except that the Fox River papers occur in the first six ranks of Table 38.

Table 36
AVERAGE CONCENTRATIONS FOR EACH KIND OF PAPER (ppm)

Sample	Ti	Al	Ca	Na	Mn	Cl	Cr	Sb	Zn	Ta
Fox River 1, 2	3050	30	3000	97	3.2	150			52.0	0.38
3	2200	17	2200	210	2.8	300	0.71		39.0	
4, 5	3300	165	2550	290	1.1	670		0.59		
6-9	2080	175	3000	233	0.71	555		0.23	7.4	
10-12	12900	59	1970	207	1.0	510		1.8	12.0	
13, 14	2850	134	3500	210	1.1	605				
Gilbert 15-18	4150	465	818	146	1.9	109	2.7	0.95	89.0	
19, 20	8000	1350	475	300	2.1	100				
21, 22		12500		325	1.0	360	19.0	0.11		
23, 24	12500	9500		405	0.75	250		34.0		
25, 26	10650	3750	1350	510	1.1					
27, 28		19000		570	1.1		12.0			
Plover 29-32	6930	2200		510	7.0					0.4
33-36	8100	2100		500	9.2		1.6	0.35		
37-40	5700	1850		900	17.0	420	1.1			0.79
41, 42	12500	1600		920	24.0	525		0.69		1.2
43-46	7800	1750		1800	35.0			1.7		
47-50	2640	4600		1190	15.0		7.2			
51-58	11900	13700		660	15.0					1.5
Parson 59-62, 119, 120	5600	1900		1060	5.3					
63-66, 117, 118	7200	1900		760	2.3			1.6		
Rising 67-70	14500	2700		580	2.0			3.2		
71-74		2700	3600	250	9.2	510		4.1		
Valley 75, 76		5500		275	1.2	155	6.7			
77, 78		13000		305	1.9	355	21.0			
79, 80		14000		320	2.0	465	18.0			
81, 82		9700		485	1.4	460	14.0			
83, 84		6250		220	1.5		8.9			
Brown 85, 86	1550	895		385	2.6	365	4.3	1.8	65.0	
87, 88	3500	1550		280	1.7	230		4.7	36.0	
89, 90	8600	3200		735	2.6			13.0		

Table 36 (Continued)

Sample	Ti	Al	Ca	Na	Mn	Cl	Cr	Sb	Zn	Ta
Crane 91-96		1900		160	0.49	86	1.7	0.29	115.0	
97-106		2030		161	0.49	222	2.3	0.59	97.0	
Weston 107	6800	1800	930							
108	4000	1330	550							
109, 110	3400	3000		280	0.70	1150		1.3		
111	10000	980		430	0.83	1200		1.7		
112, 113	6700	1900		355	0.96	1200		0.71		
114, 115	8800	920		360	0.80	1250		1.5		
116	3100	3000		310	0.75	1200		0.63		

Table 37
CONCENTRATION RANGES FOR ORDERING SAMPLES

Element	Range, in hundreds of ppm								
	A	B	C	D	E	F	G	H	I
Al	0.1-1	1-2	2-4	4-8	8-16	16-32	36-64	64-128	>128
Ti	10-20	20-40	40-80	80-120	120-240				
Na	0.1-1	1-2	2-4	4-8	8-16	16-32			
Mn	0.004-0.008	0.008-0.016	0.016-0.032	0.032-0.064	0.064-0.128	0.128-0.256	0.256-0.512		
Cl	0.6-1.2	1.2-2.4	2.4-4.8	4.8-9.6	9.6-19.2				
Ca	4-8	8-16	16-32	32-64					
Cr	0.005-0.01	0.01-0.02	0.02-0.04	0.04-0.08	0.08-0.16	0.16-0.32			
Sb	0.002-0.004	0.004-0.008	0.008-0.016	0.016-0.032	0.032-0.064	0.064-0.128	0.128-0.256	0.256-0.512	

Table 38

SAMPLES ORDERED BY ELEMENTAL CONCENTRATION RANGES^a

Rank	Samples	Al	Ti	Na	Mn	Cl	Ca	Cr	Sb
1	Fox River 1, 2	A	B	A	D	B	C	X	X
2	Fox River 3	A	B	C	C	C	C	A	X
3	Fox River 10-12	A	E	C	B	D	C	X	D
4	Fox River 6-9	B	B	C	A	D	C	X	A
5	Fox River 4, 5	B	B	C	B	D	C	X	B
6	Fox River 13, 14	B	B	C	B	D	D	X	X
7	Gilbert 15-18	D	C	B	C	A	B	C	C
8	Brown 85, 86	E	A	C	C	C	X	D	D
9	Brown 87, 88	E	B	C	C	B	X	X	E
10	Weston 108	E	C	A	X	X	X	X	X
11	Gilbert 19, 20	E	D	C	C	A	A	X	X
12	Weston 111	E	D	D	B	E	X	X	D
13	Weston 116	F	B	C	A	E	X	X	B
14	Weston 109, 110	F	B	C	A	E	X	X	C
15	Weston 112, 113	F	C	C	B	E	X	X	B
16	Parson 63-66, 117, 118	F	C	D	C	X	X	X	D
17	Plover 29-32	F	C	D	E	X	X	X	X
18	Parson 56-62, 119, 120	F	C	E	D	X	X	X	X
19	Plover 37, 40	F	C	E	F	C	X	B	X
20	Plover 43-46	F	C	F	G	X	X	X	D
21	Weston 107	F	C	X	X	X	B	X	X
22	Weston 114, 115	F	D	C	B	E	X	X	C
23	Plover 33, 36	F	D	D	E	X	X	B	A
24	Rising 67-70	F	E	D	C	X	X	X	E
25	Plover 41, 42	F	E	E	F	D	X	X	B
26	Crane 91-96	F	X	B	A	A	X	B	A

Table 38 (Continued)

Rank	Samples	Al	Ti	Na	Mn	Cl	Ca	Cr	Sb
31	Brown 89, 90	G	D	D	C	X	X	X	G
32	Valley 75, 76	G	X	C	B	B	X	D	X
33	Valley 83, 84	G	X	C	B	X	X	E	X
34	Gilbert 23, 24	H	E	D	A	C	X	X	H
35	Gilbert 21, 22	H	X	C	B	C	X	F	A
36	Valley 81, 82	H	X	D	B	C	X	E	X
37	Plover 51, 58	I	E	D	F	X	X	X	X
38	Valley 77, 78	I	X	C	C	C	X	F	X
39	Valley 79, 80	I	X	C	C	C	X	F	X
40	Gilbert 27, 28	I	X	D	B	X	X	E	X

^aX denotes value not determined.

Table 39
INSTRUMENTAL ACTIVATION ANALYSIS OF A VARIETY OF BULLET LEADS

Bullet	Sample Wt., mg	Concentrations of Elements Observed ^a				
		Sb, %	Sn, %	Ag, ppm	Cu, ppm	Al, ppm
0.45 Cal., reloader's semi-wad- cutter, Krasne's Sporting Goods	11.1	1.0	0.56			15.0
0.45 Cal., reloader's semi-wad- cutter, Hensley & Gibbs	12.0	2.8				10.0
0.22 Cal., pellet, Crossman	9.7	<0.02		39		
0.30-'06 Cal., Remington, 150 gr, Brass point	18.4	1.2			400	12.0
0.22 Cal., Hornet, Hornady, 50 gr.	10.1	3.5				5.4
0.308 Cal., Sierra, 150 gr., Spitzer	21.4	3.1	0.21			5.3
0.30 Cal., Nosler, 150 gr., Partition Spitzer						
Upper Section	28.0	2.2			120	5.2
Lower Section	16.7	2.1				7.8
0.38 Cal., reloader's semi-wad- cutter, Hensley & Gibbs	23.2	4.4	0.34			75.0
0.45 Cal., Military	30.8	<0.007				11.0
Shot from Remington-Peters 12 gauge shot-shell	81.4	1.0				0.92
0.38 Cal., Federal	54.2	1.89				

^a Analytical Indicators:

For: Sb, Sb¹²², 2.8 day half-life, 0.564 MeV gamma ray; Sn, Sn^{125m}, 9.5 min. half-life, 0.325 MeV gamma ray; Ag, Ag¹¹⁰, 24 sec. half-life, 0.658 MeV gamma ray; Cu, Cu⁶⁴, 12.8 hour half-life, 0.511 MeV gamma ray; Al, Al²⁸, 2.3 min. half-life, 1.78 MeV gamma ray.

It is well known that titanium dioxide, clays, and powdered limestone are used as "fillers", "opacifiers", or "whiteners" in paper manufacture. Examination of Tables 29 and 36 shows that, while various kinds of papers have little elemental correlation, opaque quality papers tend to have high concentrations of Ti. Thus an expectation that some correlation between kinds of paper and elemental composition might exist, a correlation imposed by the necessities of manufacture, is borne out in part.

From the results of this study, which indicate the useful role of NAA in paper characterization, it may be said that further work is warranted to fully define the elemental characteristics of the population of the more important kinds of paper. The kinds of paper utilized for documents would be of particular interest, for example. In addition, it is recommended that, for each kind of paper, comparisons of ash with unburned paper be carried out. Also, future work should be performed with the use of a Ge(Li) detector to examine the irradiated samples in order to maximize the amount of information obtained.

6. BULLET LEAD STUDIES

6.1 INTRODUCTION

The identification of bullets is of major interest in criminalistics. The primary technique applied to this end has been the examination of striations imposed on the bullet by the gun during firing. A bullet in evidence will be compared with one fired from a weapon that is linked to a suspect. If the two bullets have matching striations, then the evidence bullet may be considered as linked to the suspect. Unfortunately, a bullet fired in the field often undergoes such severe encounters that the markings are obliterated for all practical purposes. Sometimes the bullet is even fragmented. With the possibility in mind that NAA (Neutron Activation Analysis) might provide a means of definitively comparing spent bullet with unfired bullets in a suspect's weapon, which would be particularly useful where markings on the spent bullet (or fragment) were absent, the study described herein was initiated.

The possibility that other potential uses for the NAA characterization of bullets could exist augmented the initial consideration. For example, in cases where the weapon involved in a shooting incident could not be found, it could be of interest to compare an evidence bullet with unfired bullets found in the possession of a suspect. Or, as a corollary, in cases where a multiplicity of weapons were fired it would be of interest to compare certain spent bullets with unfired bullets found in selected weapons.

6.2 EXPERIMENTAL

The examination of bullets by NAA involved the exposure of weighed bullet lead slices of uniform thickness to neutron bombardment in the Gulf General Atomic TRIGA Mark I nuclear reactor for purposes of generating radioactive analytical indicator radioisotopes from the elemental constituents of the samples. In some experiments the irradiation was carried out for ≤ 1 minute at a thermal neutron flux of 2.8×10^{12} n/cm²-sec, and the irradiated samples were examined by multichannel gamma-ray spectrometry within a few minutes after termination of the irradiation. In other experiments irradiations were carried out for 30 minutes at a thermal neutron flux of 1.8×10^{12} n/cm²-sec, and the irradiated samples were counted at longer decay times.

Examination of irradiated specimens by counting was carried out with 3-in. x 3-in. NaI(Tl) detectors coupled to multichannel pulse-height analyzers, particularly in the early phases of the work. Later, Ge(Li) detectors were used so that indicator radioisotopes giving rise to gamma rays of similar energy could be distinguished and quantitated.

In initial experiments tabulated photopeak yield values (in photopeak counts per minute per gram of element)⁽¹⁾ were used to obtain elemental yield values from the quantitized photopeaks.

Once it became clear which elemental constituents of bullet lead were of most interest in this study, weighed comparator standards of these elements were irradiated and measured with, and in identical manner to, the samples. Thus, concentrations of key elements in the samples were derived by comparison of appropriate, quantitized photopeaks in the sample and comparator spectra.

Clean polyethylene vials were used to contain the samples and standards during irradiation and counting. Usually the samples, which were solid pieces, were transferred to unirradiated vials for counting in order to dispel Ar⁴¹ and avoid vial blanks.

Small samples (10-100 mg slices) of bullet leads from a variety of bullets were irradiated for 15 seconds, and counted for one minute with a NaI(Tl) detector beginning at one minute after the end of the irradiation. A number of elements were quantitatively determined from the intensities of observed photopeaks, and the results are given in Table 39.

Lead samples from a few of the foregoing bullets were examined by emission spectroscopy to ascertain the degree to which this method and NAA complement one another. The emission spectroscopy results are given in Table 40.

The initial gamma-ray spectra of irradiated, antimony-containing lead sample were fairly complex in the 0.50-0.70 MeV region, which rendered the determination of silver by means of the 24-second isotope, ^{110}Ag ($E_{\gamma} = 0.658$ MeV), somewhat difficult. This is illustrated in Fig. 23.

It was ascertained that the complexity in the 0.50-0.70 MeV region was due to the production of a short-lived antimony isotope by irradiating a 1.2 mg portion of antimony metal for 15 seconds at a thermal neutron flux of 2.8×10^{12} n/cm²-sec and measuring its gamma-ray spectra starting at 0.5 minute and 4.75 minutes after the irradiation. The initial spectrum, shown in Fig. 24 has 0.51 MeV and "0.62" MeV peaks similar to those in Fig. 23. The later spectrum (in Fig. 2) shows that the responsible isotope is short-lived; the 0.564 MeV photopeak of 2.8 day ^{122}Sb is visible in the later spectrum.

The short-lived radioisotopes generated from antimony by neutron activation include 3.5 minute $^{122\text{m}}\text{Sb}$, which has gamma rays of 0.061 MeV (50% yield) and 0.075 MeV (17% yield). The weak gamma rays of $^{122\text{m}}\text{Sb}$ are shown as a composite peak in both Fig. 23 and 24. The irradiation of ^{121}Sb (99% enriched, obtained from Oak Ridge National Laboratory) produced $^{122\text{m}}\text{Sb}$, as shown by the spectra in Fig. 25. The

Table 40

EMISSION SPECTROSCOPIC ANALYSES OF BULLET LEAD

Bullet	Sb, %	Sn, %	Ag ppm	Cu ppm	Bi ppm	Fe ppm
0.45 Cal., reloaders semi-wad-cutter Krasne's Sporting Goods	1.0	<0.2	10	40	200	100
0.45 Cal., reloaders semi-wad-cutter Hensley & Fibbs	>1.0	0.04	20	80	400	100
0.30-'06 Cal., Remington, 150 gr. Brass Point	1.0	<0.006	20	800	600	60
0.45 Cal., Military	<0.008	<0.006	10	40	800	40

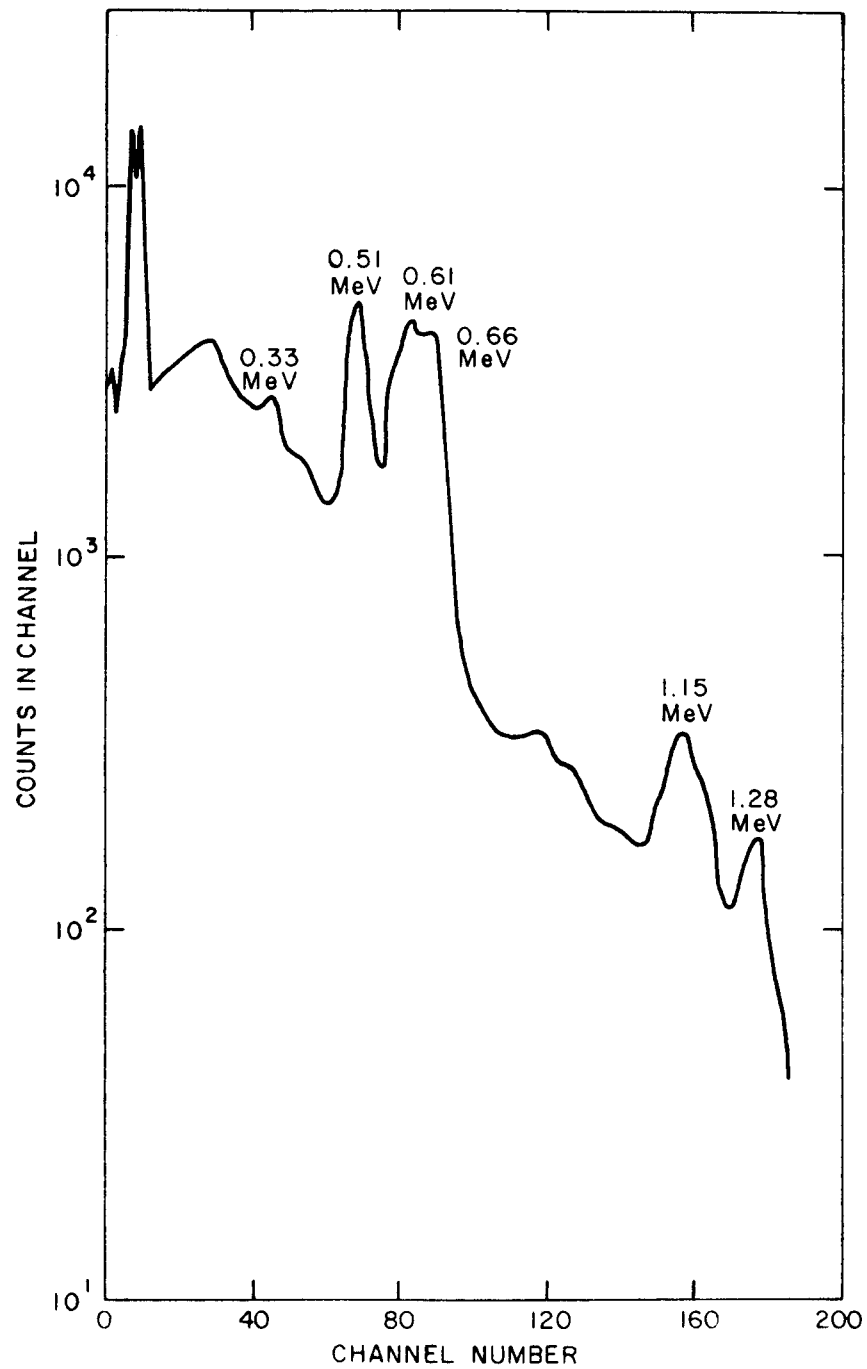


Fig. 23. Gamma-ray spectrum from activated lead from Sierra .30-caliber Spitzer

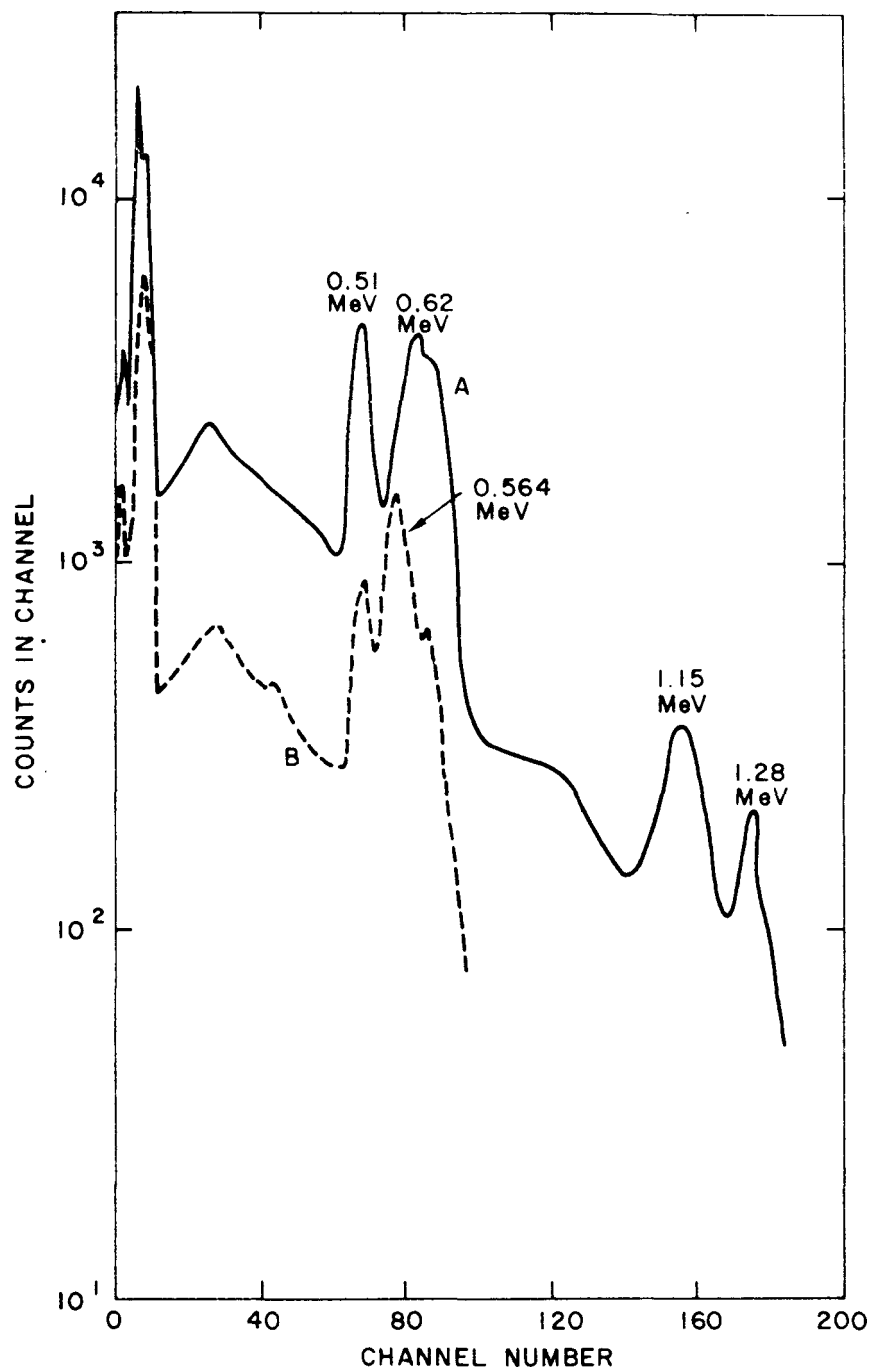


Fig. 24. Gamma-ray spectrum of activated Sb

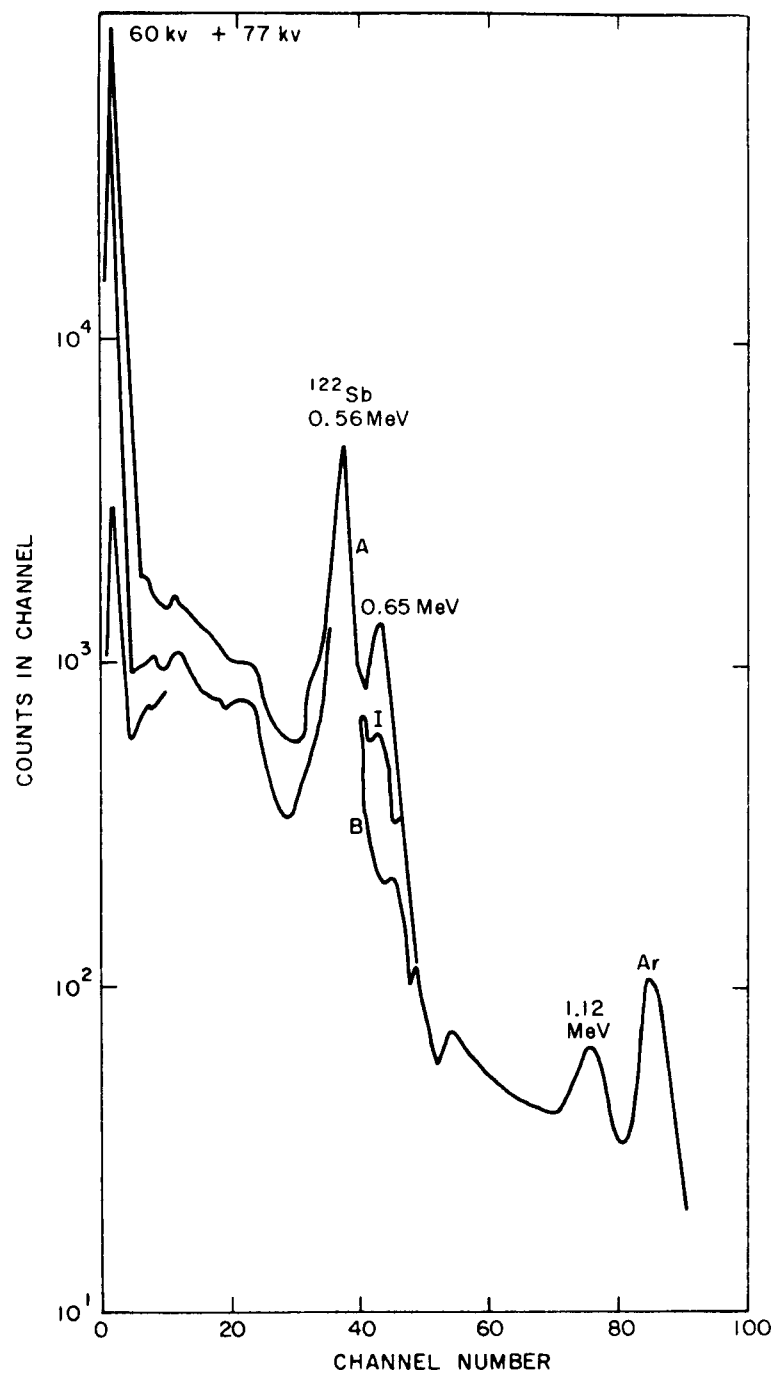


Fig. 25. Gamma-ray spectrum of activated Sb-121

composite 0.061 MeV - 0.075 MeV peak is clearly seen, and the 0.564 MeV photopeak from 2.8 day ^{122}Sb is in evidence, also.

Another short-lived isotope is 1.3 minute $^{124\text{m}}\text{Sb}$, which emits gamma rays of 0.505 MeV (20% yield), 0.603 MeV (20% yield), and 0.644 MeV (20% yield). Spectra of this isotope were obtained subsequent to the irradiation of ^{123}Sb (99% enriched, from ORNL) as shown in Fig. 26.

The 0.505-MeV peak and the composite 0.603 MeV plus 0.644-MeV peak which are clearly shown in Fig. 4, show that the $^{124\text{m}}\text{Sb}$ is responsible for the complexity of the 0.5-0.7 MeV region of Fig. 23.

The data obtained from the measurements of irradiated, enriched ^{121}Sb and ^{123}Sb indicated the photopeak intensities of the short-lived antimony isotopes shown in Table 41.

Elucidation of the 0.50-0.70 MeV region of spectra from activated antimony has made it possible to avoid excessive errors in the computation of silver when a strong 0.66-MeV peak, due to 24-second ^{110}Ag , is observed. The 0.66-MeV peak in Fig. 23 is evidence of the presence of ^{110}Ag activity; but it is a fairly weak peak - therefore, a silver concentration was not computed in this case.

An examination of 18 bullets obtained from the Bureau of Criminal Identification and Investigation (CII) laboratory of the California State Department of Justice was carried out. All bullets were 0.38-caliber (either Smith and Wesson or Colt New Police), but no two bullets were alike with respect to all of the following: manufacturers: S&W variant, Colt N.P. variant, case, jacket, and lot. These bullets were examined initially with respect to antimony concentration to further study the variation of this element in bullets known to be different from one another. However, at a later time the silver and arsenic contents were examined. A Ge(Li) detector (3 c. c.) was used for the measurement of arsenic (to be discussed later). A summary of the findings is given in Table 42.

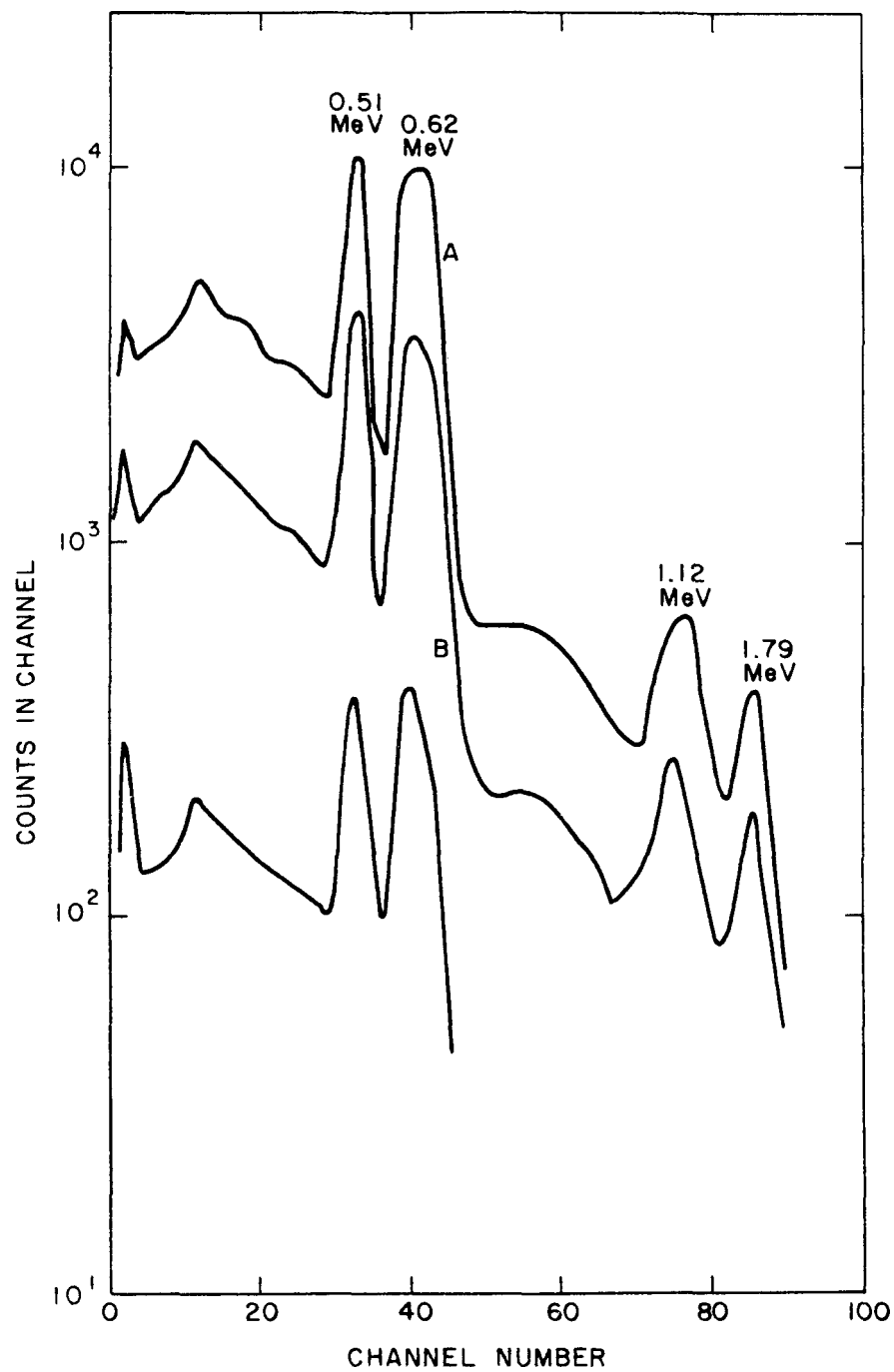


Fig. 26. Gamma-ray spectrum of activated Sb-123

Table 41
Sb ^{122m} AND Sb ^{124m}₁ PHOTOPeAK INTENSITIES

Target Isotope	Product Isotope	Half-Life	Observed Photopeak (MeV)	Integrated Photopeak Intensity CPM/g ^a
Sb ¹²¹	Sb ^{122m}	3.5 m	0.061 + 0.075	2.1 x 10 ⁸
Sb ¹²³	Sb ^{124m} ₁	1.3 m	0.505	6.2 x 10 ⁷
			0.603 + 0.644	1.2 x 10 ⁸

^aCorrected to specific activity in natural, un-enriched, antimony at the end of a 15-second irradiation at a thermal-neutron flux of 2.8×10^{12} n/cm²-sec. Sample on 0.5-in. plastic cap on 3-in. x 3-in. NaI(Tl) solid counter.

Table 42
ANTIMONY, SILVER, AND ARSENIC IN EIGHTEEN
0.38-CALIBER BULLETS

Type of Bullet	Sb, %	Ag ppm	As ppm
U. S. Cartridge Co.			
S & W	<0.003	86.5	< 0.45
C. N. P.	1.55	0.67	< 23.0
Union Metallic Cartridge Co. (UMIC), S & W	0.082	2.20	2.2
Remington-UMC,			
S & W (non-crimp)	0.013	2.64	27.0
S & W (crimp)	1.76	4.1	< 32.0
C. N. P.	2.07	8.8	< 39.0
Peters			
S & S (Lot B25A67NK)	1.94	7.6	< 35.0
C. N. P.	2.99	0.77	<100.0
Remington-Peters,			
S & W	0.92	3.6	< 12.0
C. N. P. (Index 7138)	0.87	3.1	< 15.0
Western,			
S & W (Jacketed, Steel Case)	3.00	2.6	< 72.0
S & W (Jacketed, Brass Case)	0.044	11.5	< 2.2
Winchester,			
S & W (Brass Case)	0.076	16.0	167.0
S & W (Steel Case)	3.09	4.9	< 66.0
C. N. P. (Crimp)	1.38	0.56	< 24.0
C. N. P. (Non-crimp)	1.47	0.56	< 25.0
C. N. P. (No. W38CNP)	1.55	3.9	< 24.0
C. N. P. (Lot L747)	1.23	1.8	31.2

From the foregoing experiments it seemed possible that instrumental activation analysis can differentiate between bullets that are not from the same batch of lead. However, it was necessary to examine bullets from a given batch of lead, and even individual bullets, for uniformity of composition - especially with respect to antimony concentration - in order to ascertain that compositional differences are not due to batch inhomogeneity.

A rod of bullet lead, which contained a nominal 1-1/2% w Sb, was sampled from the exterior to the interior. Two groups of samples were obtained - a group of eight samples weighing from 62.3 to 113.2 mg each and a group of 12 weighing from 7.20 to 27.60 mg each. The samples were activated for 30 minutes, allowed to decay for eight hours, and measured by a multichannel gamma-ray spectrometer (using a 3-in. x 3-in. NaI(Tl) detector). The net ^{122}Sb photopeak (0.564 MeV) cpm per milligram of each sample is given in Table 43. The average of the first eight samples is 5450 cpm/mg with a standard deviation of 3.85% of the value. The average of samples 9 through 20 is 5505 cpm/mg with a standard deviation of 2.50% of the value. The average of all 20 samples is 5483 cpm/mg with a standard deviation of $\pm 3.00\%$ of the value.

In a second test of bullet uniformity, a Remington 0.38-caliber bullet was sampled from the side to the center and processed in the same manner as the Norma bullet lead. The results are given in Table 44. The average net counts per minute in the ^{122}Sb peak per milligram of lead was 1123.3 cpm/mg, and the standard deviation was 2.85% of the value. A Western and a Federal 0.38-caliber bullet were also examined in the same fashion. All of the intra-uniformity experiments are summarized in Table 45.

A multiplicity of bullets from each of a number of boxes of bullets were sampled. The coating (grease, copper, and/or bronze) was removed

Table 43
UNIFORMITY OF NORMA BULLET LEAD ROD

	Sample	Wt., mg	Peak Net CPM/mg
Exterior	1	88.35	5140
↓	2	52.6	5721
↓	3	73.6	5363
↓	4	113.2	5235
↓	5	62.3	5560
↓	6	92.7	5359
↓	7	62.3	5545
Center	8	63.7	5681
↓	9	13.15	5346
Exterior	10	19.15	5428
↓	11	8.00	5573
↓	12	11.65	5561
↓	13	15.35	5651
↓	14	26.70	5461
↓	15	11.45	5522
↓	16	20.50	5288
↓	17	7.20	5700
↓	18	27.60	5332
↓	19	18.45	5650
Center	20	10.40	5547

Table 44
UNIFORMITY OF REMINGTON 0.38 CALIBER BULLET

	Sample	Wt. , mg	Peak Net CPM/mg
Exterior	1	15.6	1142.1
	2	28.7	1069.6
	3	48.4	1149.8
	4	47.8	1085.5
	5	97.3	1155.1
↓	6	103.0	1162.1
to	7	36.4	1162.1
	8	80.5	1108.4
	9	55.0	1103.6
	10	103.1	1139.1
	11	98.4	1078.5
↓	12	50.1	1124.2
Center			

Table 45
COUNT RATE DATA OBTAINED FROM MULTIPLE SAMPLES FROM
SINGLE BULLETS (0.38-Cal.) AND A BULLET WIRE (0.22-Cal.)

Sample	Specific Activity, cpm/mg, of Individual Samples ^a				
	Norma (Wire) Section 1	Norma (Wire) Section 2	Remington (Bullet)	Western (Bullet)	Federal (Bullet)
1 (outermost)	5140	5346	1142.1	1138	1,070
2	5721	5428	1069.6	1200	1,054
3	5363	5573	1149.8	1195	1,005
4	5235	5561	1085.5	1195	999
5	5560	5651	1155.1	1185	1,040
6	5359	5461	1162.1	1155	1,040
7	5545	5522	1162.1	1195	1,033
8	5681 (Center)	5288	1108.4	1150	1,060
9		5700	1103.6	1195	995
10		5332	1139.1	1163 (Center)	1,043 (Center)
11		5650	1078.5		
12		5547 (Center)	1124.2 (Center)		
Avg.	5450	5505	1123.2	1177.1	1,033.9
σ , % of value	± 3.85	± 2.50	± 2.85	± 1.98	± 2.36

^a Net cpm in the Sb¹²² 0.564 MeV photopeak per mg of sample. Inasmuch as different counters and geometries were used, the average specific activities cannot be used to judge the relative Sb concentrations; e.g., from Table , Avg. Sb in 0.38 Western was 2.59%, while Avg. Sb in 0.38 Remington was 0.85%.

from each bullet with organic solvent and weak nitric acid, and bullets were washed with water and dried before sampling. Again the emphasis was placed on the examination of antimony concentration; however, two brands of 0.22-caliber bullets that had similar antimony concentrations were examined for trace elements. Results are given in Table 46.

A 3 c.c. Ge(Li) detector was found to be able to measure As in the presence of Sb, provided the Sb/As ratio was not too great. The radioisotopic analytical indicator for As is 26.5 hour ^{76}As , which emits a 0.559-MeV gamma ray. Thus only 0.005 MeV separates the energy of the ^{76}As gamma ray from that of 2.8 day ^{122}Sb ($E_{\gamma} = 0.564$ MeV). Nevertheless, the Ge(Li) detector was capable of resolving the two gamma rays, as shown in Fig. 27. This figure shows the gamma-ray spectrum obtained from a 99.6 mg portion of lead from a 0.22-caliber bullet (Sears) that had been irradiated for 30 minutes and counted for 10 minutes (at two hours after the irradiation) with the 3 c.c. Ge(Li) detector. Examination of five bullets from the same box (Sears, 0.22-caliber) showed that the arsenic content was 285 ± 40 ppm. A Peters 0.22-caliber bullet had 345 ppm As, a Western 0.22-caliber bullet had 78 ppm As, an Imperial 0.22-caliber bullet had < 4 ppm As, and a Lapua 0.22-caliber bullet had < 5 ppm As.

6.3 DISCUSSION

Antimony concentrations, which were the chief focus of the work, have been found to be very uniform within a single bullet (Table 45) and between bullets from the same box of bullets, excepting perhaps the Peters 0.22-caliber bullets (Table 46). The usual standard deviation of the antimony concentration within either a single bullet or within a box of bullets is about $\pm 3\%$ of the concentration value. It is worthy of note, from Tables 43 and 44, that, because of the thickness uniformity of bullet slices, the antimony-122 photopeak specific activity was essentially independent of sample weight over a wide range of sample weights.

Table 46
BULLET-TO-BULLET UNIFORMITY EXPERIMENTS

Bullets	No. of Samples from a Single Box	Sb, % w ^a	Other Elements
Lapua, 0.22-cal. L.R. matchgrade	50	1.22 ± 0.04	1.04% Sn, 1.09 ppm Al
Sears, 0.22-cal. short	20	1.26 ± 0.03	0.18% Sn, 1.25 ppm Al
Imperial, 0.22-cal. short	20	0.99 ± 0.04	
Peters, 0.22-cal. short	20	0.87 ± 0.08	
Remington, 0.22-cal. short	20	0.85 ± 0.04	
Remington, 0.38 S & W	10	0.85 ± 0.02	
Western, 0.38 S & W	10	2.59 ± 0.10	

^a The plus-or-minus values represent one standard deviation determined from counting statistics only.

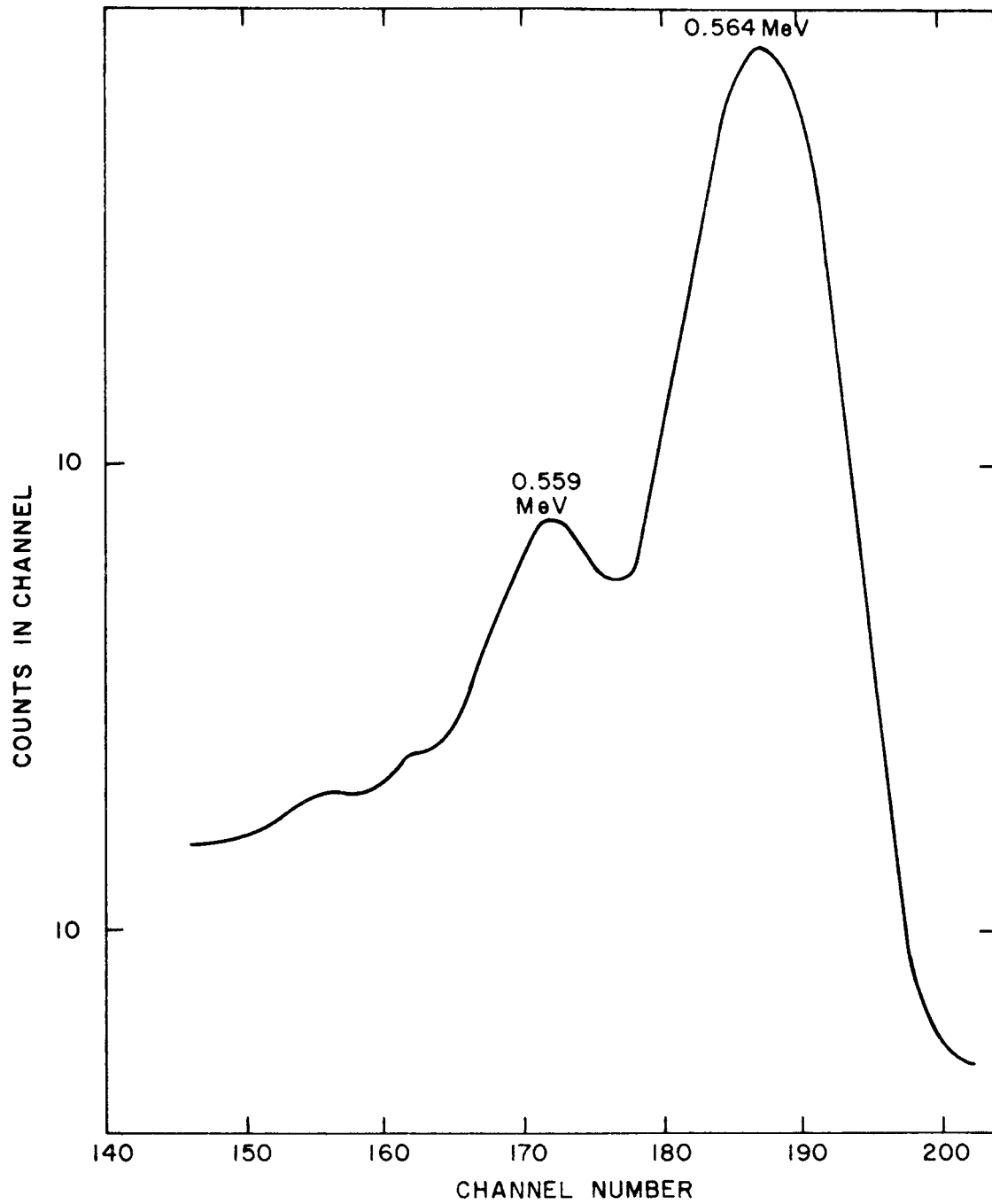


Fig. 27. Gamma-ray spectrum of activated Sears 0.22-caliber bullet lead

Among the bullets listed in Tables 39, 42, and 46 a majority have a distinctive antimony concentration. However, in some cases there is an overlap of values within the usual $\pm 3\%$ relative standard deviation: (1) a Remington-Peters 0.38-caliber bullet and a Remington 0.38-caliber bullet were found to contain 0.85% and 0.87% w antimony, respectively; (2) the Peters and Remington 0.22-caliber bullets were found to contain 0.87% and 0.85% w antimony, respectively; (3) the Lapua and Sears 0.22-caliber bullets contained 1.22% and 1.26% w antimony, respectively; (4) a U. S. Cartridge Company and a Winchester 0.38-caliber bullet each contained 1.55% w antimony, and (5) a Peters and a Western 0.38-caliber bullet each contained very close to 3.0% w antimony. In cases (3), (4), and (5), however, the bullets could be distinguished from one another on the basis of trace-element constituents, while in cases (1) and (2) sufficient trace-element information has not yet been gathered to determine if the pairs can be distinguished.

Those bullets for which upper limits of antimony concentration are reported can all be distinguished on the basis of trace-element information.

It can be seen from the foregoing that 32 out of the 36 bullets can be distinguished on the basis of antimony plus trace-element information, while 26 of the 36 bullets have distinctive antimony concentrations. Thus, while it can be said with confidence that bullets with different antimony concentrations have different origins, the present data indicate that there is a 28% chance that whole bullets with the same antimony level may have a different origin, and (tentatively) that there is a 11% chance that whole bullets with the same antimony and currently-detected trace-element levels may have a different origin. The latter, tentative estimate may be revised as additional trace-element data are gathered.

If the caliber of bullet cannot be determined, as when the sample consists of a bullet fragment, the foregoing overlapping cases number (1)

and number (2) become a group of four indistinguishable bullets on the basis of antimony level, and in the absence of sufficient trace-element data. Similarly, a 0.30-caliber Remington rifle bullet and a 0.38-caliber Winchester bullet join the two bullets of overlapping case number (3), although the available trace-element information makes it possible to distinguish between the bullets in this group. Also, a 0.38-caliber Winchester bullet with 3.09% w antimony and a 0.30-caliber Sierra bullet with 3.10% w antimony overlap with respect to antimony, but can be distinguished by virtue of the large tin concentration in the latter.

The work has established a strong basis upon which to judge a lack of commonality between bullets or bullet fragments with different antimony levels. Also, the consistency of antimony concentration that has been found in single bullets and among bullets of common lot origin is an important factor in establishing commonality between bullets or bullet fragments. However, it is clear that additional background information is needed - with respect to the consistency of trace-element levels in bullet lead of common origin, and the differences of levels that may exist between bullet leads of different origin - in order to improve the confidence in conclusions derived from bullets or bullet fragments that have similar antimony levels.

7. EXPLORATORY STUDIES OF OTHER EVIDENCE-TYPE MATERIALS

In addition to the major study of gunshot residues, and the fairly extensive studies of paint, paper, and bullet lead conducted during this six-year period, small, to fairly extensive NAA studies were also carried out on a great variety of other kinds of materials that are frequently encountered as evidence in criminal cases. These studies are discussed in the following sections.

7.1 HAIR

A number of small studies were carried out on the trace elements detectable in hair via instrumental NAA. These were far smaller in scope and less intensive than the excellent earlier large-scale NAA hair studies of R. E. Jervis,⁽²³⁾ in Canada, or of the equally good and also large-scale NAA hair studies carried out later by R. F. Coleman,⁽²⁴⁾ in England. However, the General Atomic studies did bring out some useful points not recognized earlier – and confirmed or underscored some of the earlier findings of Jervis.

7.1.1 Hair-Washing Methods

In the studies reported here, two different kinds of hair-washing techniques were investigated: one involved alternate washings of the hair specimens with acetone and distilled, deionized water – the other involved alternate washings with selected detergents and high-purity water. In accord with the findings of L. C. Bate,⁽²⁵⁾ it was found that each different washing procedure resulted in a different degree of removal of various

elements from hair specimens of a given source. Also, with fixed washing solvents, the degree of removal of some elements increased appreciably with increased washing time. From these exploratory studies, it became evident that any sharp distinction between "intrinsic" hair elements and "external contamination" elements was not feasible. In most of the subsequent measurements on hair a carefully reproduced, mild, washing procedure was employed - using alternate brief washings with acetone and high-purity water, at room temperature.

7. 1. 2 Elements Detectable in Short Irradiations

Most of the hair studies employed only rather mild reactor irradiation conditions (one to a few hours at a thermal-neutron flux of about 2×10^{12} n/cm²-sec), compared with the much more severe irradiation conditions (50 hours at 1×10^{13} n/cm²-sec flux) used by Jervis. ⁽²³⁾ With these milder irradiation conditions, the hair specimens suffered very little radiation damage - as opposed to the very severe radiation damage caused by reactor irradiations of the nvt used by Jervis. On the other hand, such mild irradiation conditions do not result in as large a number of detected elements in hair specimens. In the Canadian work, for example, a total of some 20 elements were detectable instrumentally in samples of human head hair - with from 8 to 12 elements typically detectable in a single sample of hair. Under the milder irradiation conditions employed in our studies, only a total of 10 elements were detected instrumentally (Na, Cl, Mn, Au, Cu, Br, Al, Cr, Zn, and Hg) - with only from 5 to 7 elements usually detectable in any given sample. Part of this difference is also attributable to the fact that we used smaller samples (typically, 10-fold smaller) than those used in the Canadian work. In order to be of value in actual criminal cases, it is important that the method be applicable to even very small samples of hair, e. g., to single

strands perhaps only a few centimeters long, since in actual cases one usually must work with individual single strands of hair - rather than with large, multi-strand, samples.

In the list shown above of the ten elements detected in human head hair samples, two are of particular interest: Al and Cl, since these elements were not detected in the Canadian studies. The reason they were not detected in their work was that they could not count their activated samples until many hours after the end of an irradiation, because their laboratory was of the order of a hundred miles from the reactor. The half-lives of the (n, γ) products of aluminum and chlorine are, respectively, only 2.31 minutes (^{28}Al) and 37.3 minutes (^{38}Cl). In the British work, ⁽²⁴⁾ Cl was detected in hair specimens, but not Al. In the British work, the first counting measurements on the activated samples were made 20 minutes after the end of an irradiation, so an ample amount of ^{38}Cl activity still remained, but the ^{28}Al activity was decayed down to undetectable levels. In the General Atomic work, a short (one-minute) pneumatic-tube irradiation of each sample was first carried out, followed by a one-minute count on the NaI(Tl) multichannel gamma-ray spectrometer, after a one-minute decay period. Aluminum and chlorine were thus detected. Following the longer irradiation, with counting typically started after a one-hour decay period, ^{38}Cl was again detected (along with several other longer-lived induced activities), but the ^{28}Al activity had decayed out.

7.1.3 Intra-Person Hair Trace-Element Variability

Some measurements were also made to assess the degree of variation, in trace-element composition, that typically exists among various individual strands of each hair taken from any particular person at the same time. The work of others, ^(23, 24) has shown that considerable

intra-person variation does exist, but the number of persons studied in this respect is still rather small compared with the large-scale studies of intra-person variation that have been made. In the General Atomic work, as one example, two single strands of hair from one person were compared, via instrumental NAA, with one strand of hair from another person. In this instance, only a 30-minute irradiation at a thermal-neutron flux of 1.8×10^{12} n/cm²-sec was used. The samples were treated identically in every respect: washing, irradiation, and counting. Illustrative pulse-height spectra of the three specimens, measured at approximately the same decay time (several hours) and normalized to the same sample weight, are shown in Fig. 28. Only three elements show up clearly in these spectra - gold via 2.70-day ¹⁹⁸Au ($E_{\gamma} = 0.412$ MeV), bromine via 35.3-hour ⁸²Br (major E_{γ} 's at 0.554 MeV and 0.777 MeV), and sodium via 15.0-hour ²⁴Na (E_{γ} 's at 1.37 MeV and 2.75 MeV). Although all three of these elements appear in all three of the spectra, it is evident that much smaller amounts are present in the two samples from the same person (the two lower, almost identical, spectra) than in the other sample, from a different person (the higher spectrum in the figure). Close examination of the two nearly identical spectra, however, show significant quantitative differences, i. e., the two samples from the same person, although quite similar in their levels of Au, Br, and Na, are not identical in these levels.

In another hair comparison study, two sets of head-hair samples, each containing three hairs, were investigated. These samples were prepared by the American Academy of Forensic Sciences as an identification problem for interested criminalists, and were transmitted to General Atomic by Mr. Raymond H. Pinker, as test unknowns. Two of the hairs in each set were stated to be from the same person, with the third hair being from a different person. Each of the hairs was activated for one minute, and then counted immediately - for the detection of short-lived

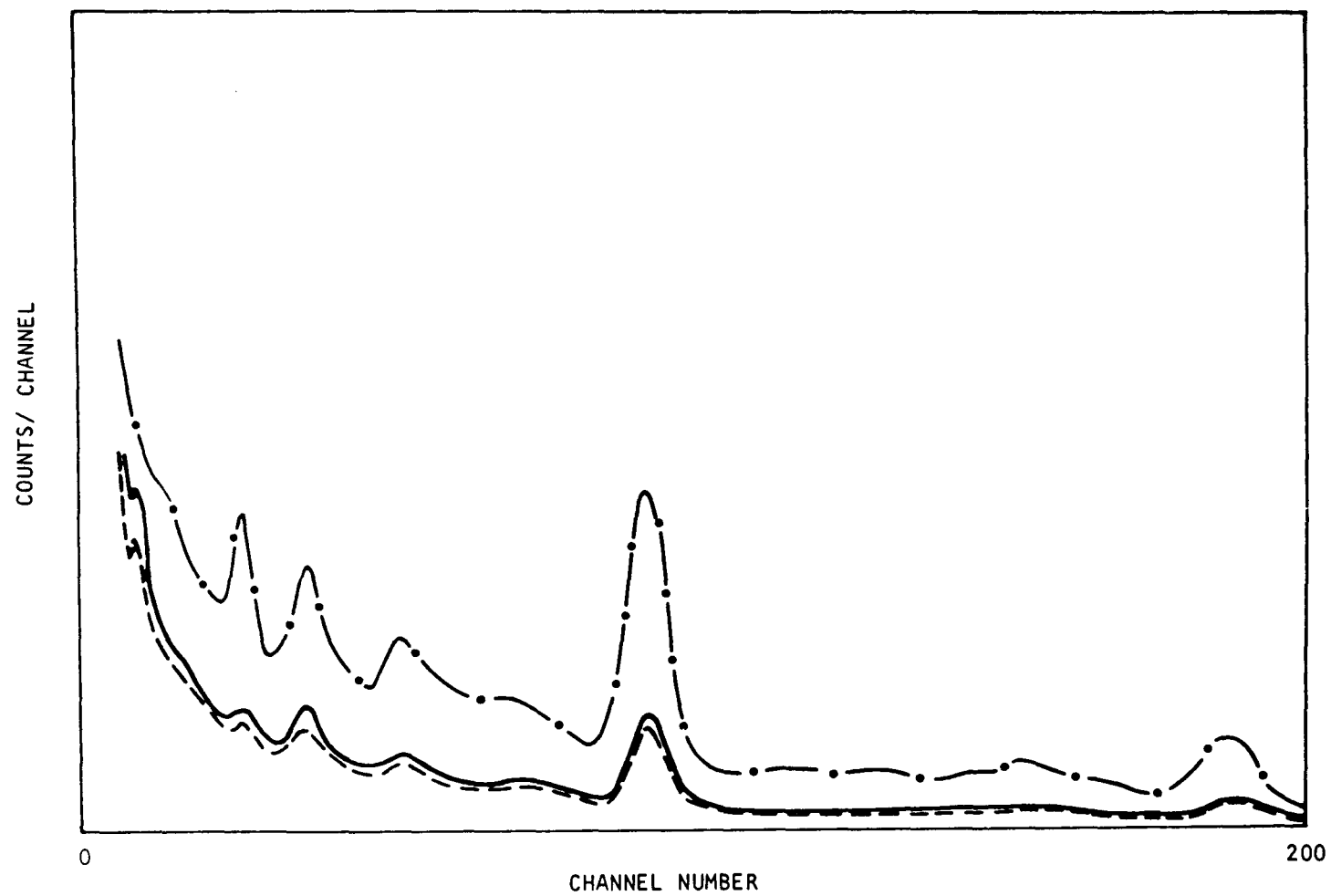


Fig. 28. Gamma-ray spectra comparing two head hairs from one person with a third hair from another person

induced activities. Then, they were activated for two hours, and counted at various decay times. Altogether, six elements were detected. The pulse-height spectra of the three hair specimens of Set 1, normalized to the same sample weight, are shown in Fig. 29. These spectra were obtained at approximately the same decay time - a few hours after the two-hour irradiation. It is quite evident that the two samples, 5C-1 and 5C-2 (giving the two higher spectra in the figure), are quite similar to one another - and quite different from sample 5C-3. Similarly, the pulse-height spectra of the three hair specimens of Set 2, normalized to the same sample weight, are shown in Fig. 30. These spectra were obtained four days after the two-hour irradiation. It is evident that the two samples, 5D-1 and 5D-3 (giving the two higher spectra in the figure), are quite similar to one another - and quite different from sample 5D-2. The conclusions reached from the NAA examination of these various hair samples proved to be entirely correct. Whereas, in each case, it was easily possible to select the two hairs coming from the same person, it is quite evident from the spectra shown in Figs. 29 and 30 that the two strands from the same person showed appreciable differences from one another - illustrating the significant intra-person variability in hair trace-element composition (which, however, is in general much less than the inter-person variability).

In a third series of measurements concerned with the intra-person human head hair trace-element variability, four loose head hairs (obtained by combing) from one person were individually analyzed by instrumental NAA. First, each strand was washed with acetone and deionized water (each strand treated identically), air-dried, and weighed. They were then all activated in the reactor for one hour (at a thermal-neutron flux of 1.8×10^{12} n/cm²-sec), and then counted at several decay times on a NaI(Tl) multichannel gamma-ray spectrometer. A number of elements

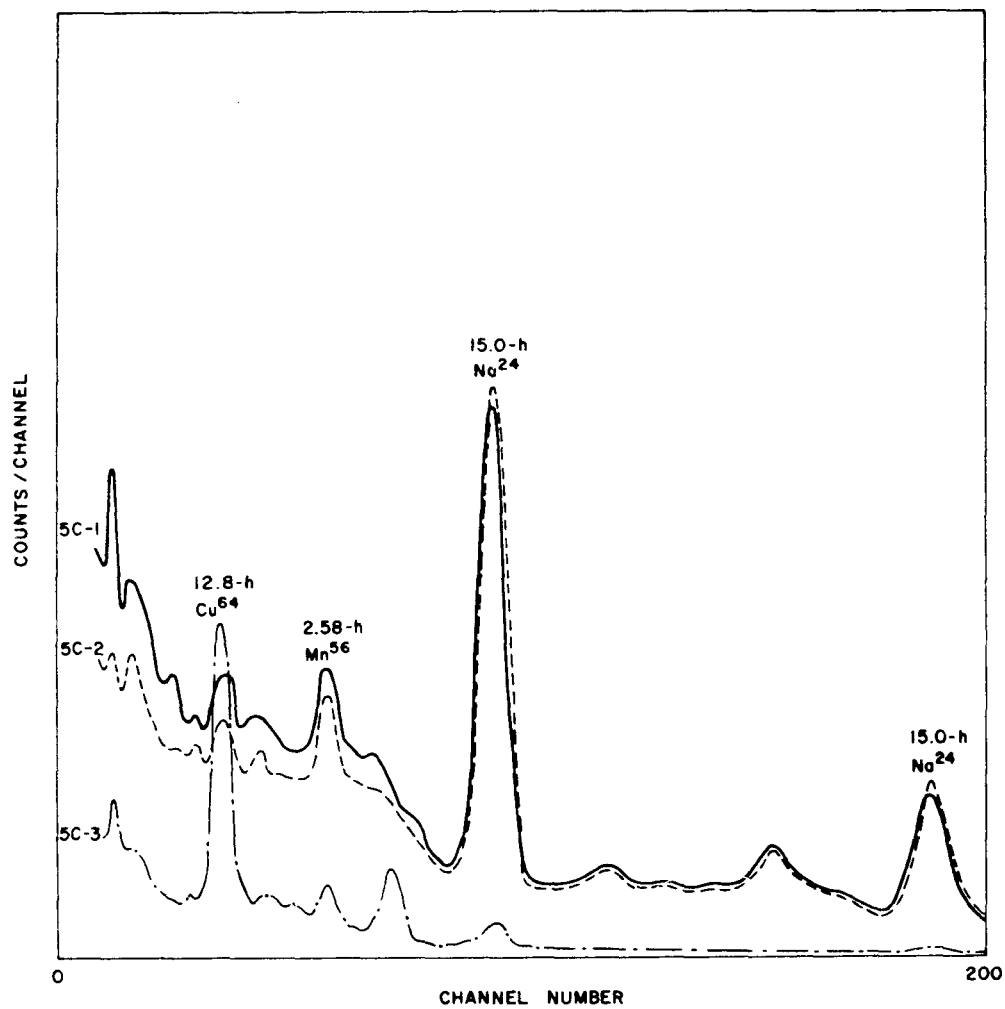


Fig. 29. Gamma-ray spectra comparing three samples of hair from first set of samples from American Academy of Forensic Sciences

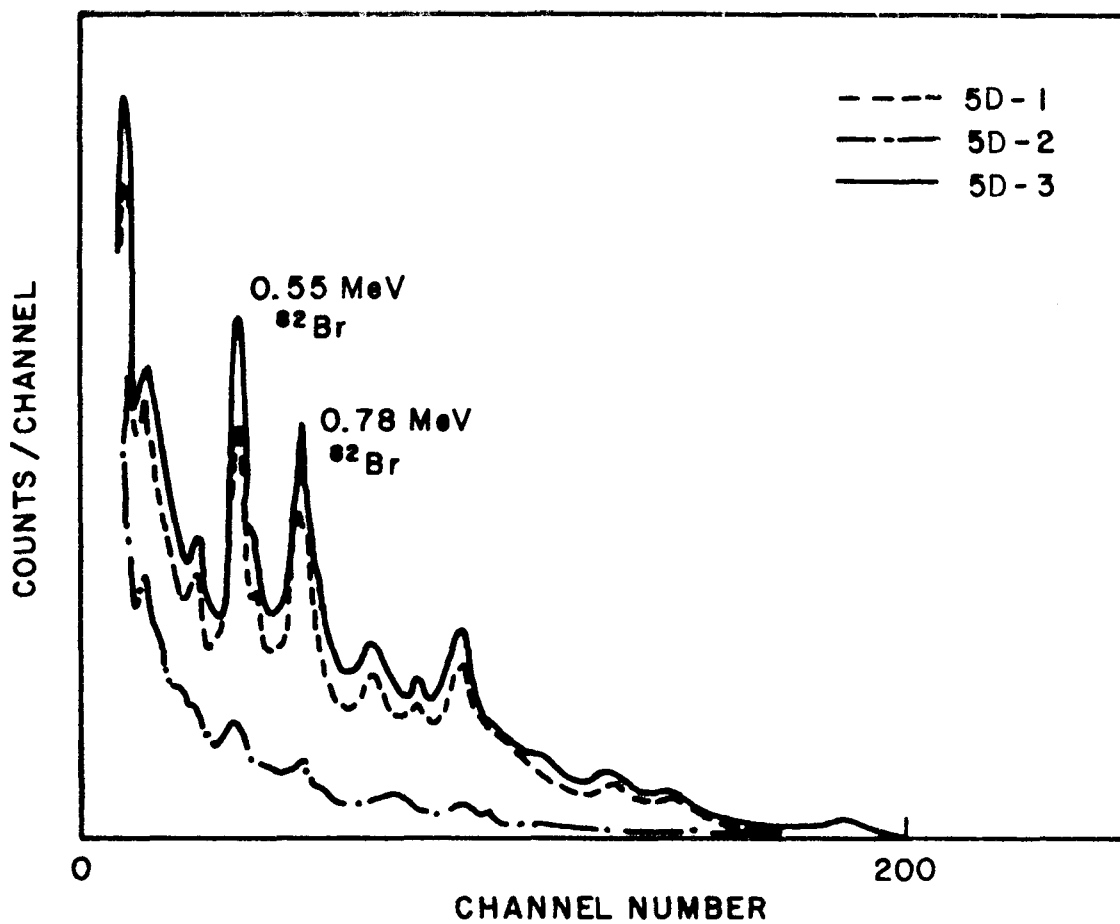


Fig. 30. Gamma-ray spectra comparing three samples of hair from second set of samples from American Academy of Forensic Sciences

were detected, particularly Cr, Au, Cu, Mn, and Na. Weight-normalized pulse-height spectra, obtained at about the same decay time (several hours), are shown in Fig. 31. In the figure, the spectra of three of the specimens are each compared with that of the fourth specimen. As can be seen, the first specimen compared very closely with the fourth specimen, the second showed the same elements as the fourth specimen - but with considerable quantitative differences, and the third compared very closely with the fourth specimen - except for one element, chromium.

7.1.4 Analysis of the Coleman Intercomparison Hair Sample

R. F. Coleman, of the Atomic Weapons Research Establishment at Aldermaston, England, distributed hair specimens to a number of laboratories interested in the forensic activation analysis of hair. The samples distributed were aliquots of a large sample of hair from a 12-year old girl. He suggested that each laboratory use its own favored washing, activation, counting, and calculational procedures - and that each laboratory analyze six bulk samples (three washed, and three unwashed) and also several washed and unwashed individual strands.

At General Atomic, six bulk samples (three washed, three unwashed) and 13 single-strand samples (6 washed, 7 unwashed) were analyzed. The washing procedure used consisted of shaking with acetone, then three times with distilled-deionized water, then once more with acetone - followed by air drying and weighing. Each specimen was irradiated for one minute in the pneumatic-tube position of the 250 kW TRIGA Mark I reactor (at a thermal-neutron flux of 2.5×10^{12} n/cm²-sec), and then counted for one minute, after a one-minute decay period, on a solid 3-in. x 3-in. NaI(Tl) detector - coupled to a 400-channel pulse-height analyzer. A half-inch plastic beta-particle absorber was placed between the sample vial and the top of the NaI(Tl) crystal. Later, each bulk sample

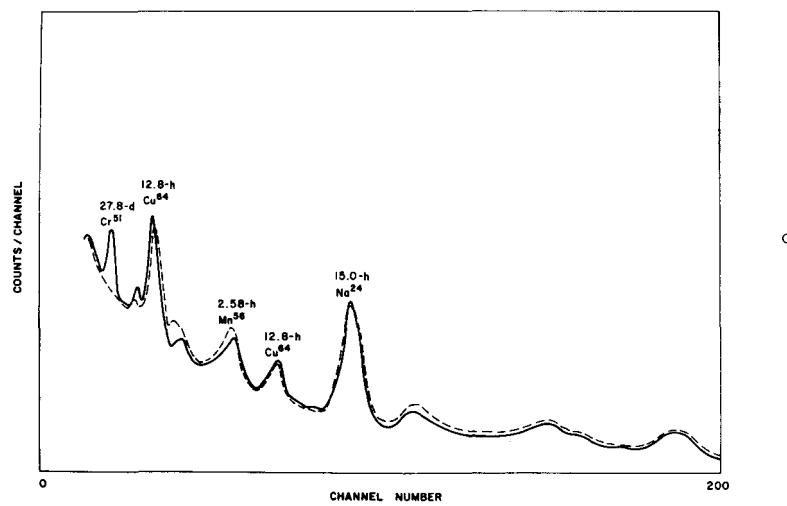
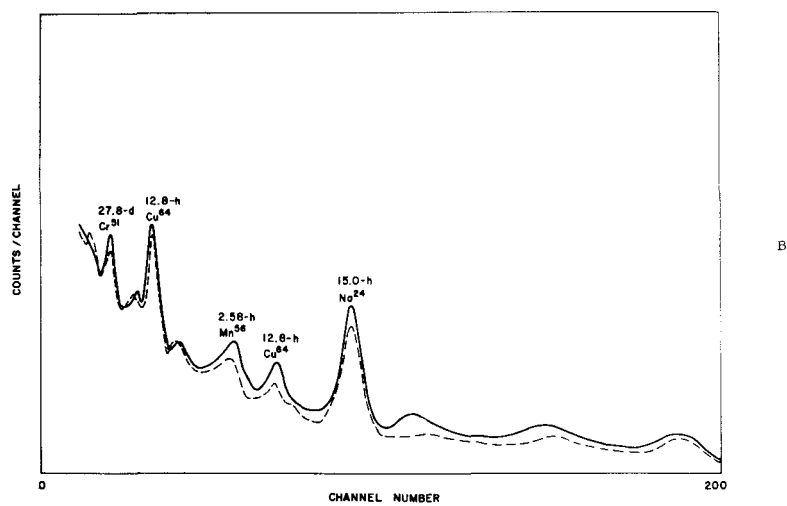
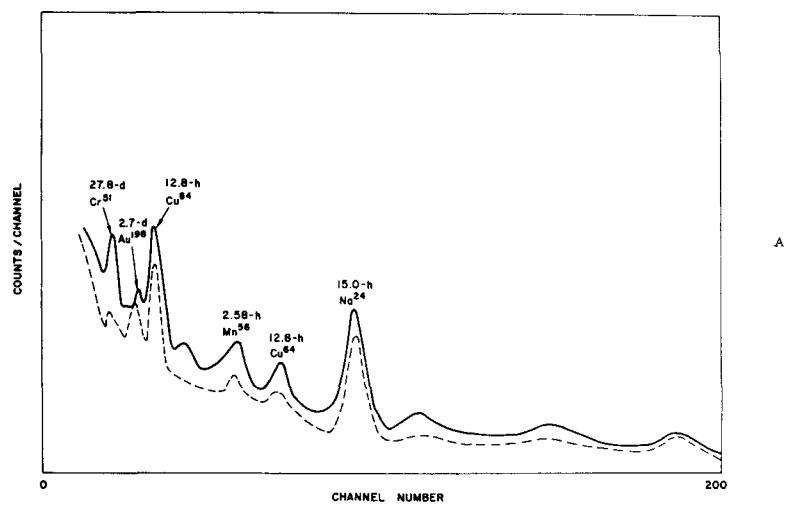


Fig. 31. Gamma-ray spectra comparing samples of known head hair from the same person

was irradiated for one hour, and each single-strand sample for two hours, in the rotary specimen rack of the reactor, at a thermal-neutron flux of 1.8×10^{12} n/cm²-sec. After these longer irradiations, the three washed bulk samples and the six washed single-strand samples were washed further by shaking once with a detergent solution (alconox), three times with deionized water, and finally once with acetone. Each of the samples was then counted under the same conditions used after the pneumatic-tube irradiations, but now at decay times of one hour, one day, and eight days. At the various decay times, progressively longer counting periods were employed. Quantitative calculations were based on yield data for the various detected elements accumulated earlier, with any necessary flux, irradiation-time, and decay-time corrections. The calculations, based on net photopeak areas, were performed on the IBM-7044 computer.

With such relatively mild irradiation conditions (which caused only negligible radiation damage to the hair specimens), it was only possible to detect six elements (Al, Cu, Mn, Cl, Na, and Zn) in even the unwashed bulk samples. Except for Na, these same elements were also detected in the washed bulk samples. Five of these elements (Al, Cu, Mn, Cl, and Na) were detected in each of the unwashed single-strand specimens, and the first four (but not Na) in each of the washed single-strand specimens. Zinc was detected in two of the unwashed, and one of the washed, single-strand specimens. All of the results are presented in Tables 47 and 48, except upper-limit values calculated for the bulk unwashed samples, for Br, Au, Hg, Sb, and As, which are shown in Table 49.

Several observations may be noted from the results obtained on the bulk samples (Table 47). One is that the results for each element are fairly reproducible, when such large samples (32-40 mg, with a mean of 36 mg) are used. Thus, the relative standard deviations of the mean values for the three unwashed bulk samples were only $\pm 14\%$ (Al), $\pm 11\%$

Table 47

RESULTS OF THE NEUTRON ACTIVATION ANALYSIS OF BULK
HAIR SAMPLES (COLEMAN MATERIAL)
(Element Values in ppm)

Weight (mg)	Al	Cu	Mn	Cl	Na	Zn
<u>Unwashed</u>						
35.27	28.2±0.8	54.5±0.7	0.72±0.02	73.1±2.8	64.1±0.6	285±13
38.88	24.9±0.8	45.1±0.6	0.70±0.02	53.7±2.6	45.3±0.5	264±14
33.64	22.1±0.8	54.7±0.6	0.67±0.02	56.3±2.8	39.8±0.5	289±14
Average	25.1±3.6	51.4±5.7	0.70±0.03	61.0±11.5	49.7±14.4	279±15
<u>Washed</u>						
39.87	9.8±0.6	53.2±0.5	0.30±0.01	18.3±1.0	<0.88	293±14
36.58	12.5±0.7	59.2±0.5	0.30±0.01	14.3±1.1	<0.92	292±13
31.71	13.3±0.7	52.4±0.5	0.29±0.01	10.8±1.1	<0.92	269±14
Average	11.9±2.1	54.9±4.0	0.30±0.01	14.5±4.4		285±14

Table 48

RESULTS OF THE NEUTRON ACTIVATION ANALYSIS OF SINGLE STRANDS
OF HAIR (COLEMAN MATERIAL)
(Element values in ppm)

Weight (mg)	Al	Cu	Mn	Cl	Na	Zn
<u>Unwashed</u>						
0.597	21.1±4.9	59.6±2.2	0.79±0.07	92.0±14	13.8±1.3	1880±770
0.607	30.5±5.3	66.2±2.3	0.78±0.09	163±27	65.0±2.5	675±330
0.758	30.6±5.3	38.6±1.5	0.86±0.08	267±36	129±3	<1100
0.648	7.72±4.70	68.3±2.1	0.60±0.05	106±9	37.9±2.0	<1400
0.693	50.2±6.0	49.6±2.1	1.0±0.1	139±12	63.0±2.3	<1300
0.814	11.2±3.2	56.7±1.6	0.81±0.06	106±15	43.8±1.8	<1100
0.569	38.6±6.1	49.9±2.1	0.86±0.07	167±29	76.9±3.4	<1400
Average	27.1±15.7	55.6±11.0	0.81±0.15	149±65	61.3±42.6	
<u>Washed</u>						
0.579	24.0±4.7	50.9±1.6	0.39±0.04	52.5±4.6	≤62	<1000
0.746	20.2±3.8	49.3±1.4	0.31±0.03	39.8±5.0	≤48	<850
0.491	15.2±4.5	61.1±1.9	0.44±0.05	35.0±11.0	≤73	<1200
0.625	18.9±4.8	44.6±1.7	0.32±0.05	41.5±5.7	≤58	<1100
0.860	33.0±4.5	56.2±1.6	0.32±0.03	49.8±5.8	≤42	<970
0.786	9.29±3.10	63.3±1.6	0.33±0.04	49.8±8.8	≤46	611±370
Average	20.1±9.4	54.2±7.4	0.35±0.05	44.7±6.9		

Table 49

COLEMAN HAIR INTERCOMPARISON RESULTS
(Unwashed Bulk Samples)

Element	Mean Value in ppm, for () Labs	Range of Values from all Labs	GA Mean Value	$\Delta GA/\sigma$
Al	36 ± 16 (3)	25 to 55	25	-0.69
Cu	83 ± 28 (6)	51 to 110	51	-1.14
Mn	0.88 ± 0.28 (5)	0.5 to 1.2	0.70	-0.64
Cl	110 ± 34 (4)	61 to 130	61	-1.50
Na	78 ± 37 (5)	50 to 140	50	-0.76
Zn	390 ± 110 (6)	280 to 600	280	-1.00
			Mean:	-0.95
		Range of Values Except GA < Value		
Br	1.2 ± 0.3 (3)	1.0 to 1.5	< 9	---
Au	0.4 ± 0.6 (3)	0.04 to 1.1	< 0.08	---
I	2.9 ± 2.8 (3)	1.3 to 6.2	---	---
Hg	19 ± 9 (3)	8 to 24	< 13	---
V	0.23 (1)	---	---	---
Ca	3700 (1)	---	---	---
Sb	0.50 ± 0.14 (2)	0.4 to 0.6	< 2	---
As	0.20 ± 0.14 (2)	0.1 to 0.3	< 8	---

(Cu), $\pm 4\%$ (Mn), $\pm 19\%$ (Cl), $\pm 29\%$ (Na), and $\pm 5\%$ (Zn). Similar relative standard deviations were obtained for the three washed bulk samples: $\pm 18\%$ (Al), $\pm 7\%$ (Cu), $\pm 3\%$ (Mn), $\pm 30\%$ (Cl), and $\pm 5\%$ (Zn). Secondly, it may be noted that the washing of the bulk samples essentially did not change the Cu mean value (51 ± 6 ppm unwashed; 55 ± 4 ppm washed), nor the Zn mean value (279 ± 15 ppm unwashed; 285 ± 14 ppm washed) – but lowered the Al mean value appreciably (25 ± 4 ppm unwashed; 12 ± 2 ppm washed), the Mn mean value appreciably (0.70 ± 0.03 ppm unwashed; 0.30 ± 0.01 ppm washed), the Cl mean value markedly (61 ± 11 ppm unwashed; 14 ± 4 ppm washed), and the Na mean value tremendously (50 ± 14 ppm unwashed; < 0.9 ppm washed).

From Table 48 (single-strand results), it may be seen that mean values for Al (27 ± 16 ppm single; 25 ± 4 ppm bulk), Cu (56 ± 11 ppm single; 51 ± 6 ppm bulk), Mn (0.81 ± 0.15 ppm single; 0.70 ± 0.03 ppm bulk), and Na (61 ± 43 ppm single; 50 ± 14 ppm bulk) agree reasonably well, when the single-strand mean values are compared with the bulk values for the unwashed samples. For Cl, the agreement is not as good (150 ± 65 ppm single; 61 ± 12 ppm bulk), and Zn was not detected in enough of the single strands to allow one to make a meaningful comparison. As shown in Table 48, the weights of the single-strand samples were in the range of 0.5-0.9 mg (mean = 0.67 mg), i. e., about 1/54 the mean weight of the bulk samples. With such small samples, the individual standard deviations (calculated from the counting statistics) were larger than for the corresponding large bulk samples, and the standard deviations of the mean values were also larger – as mentioned above.

It is of interest to compare the General Atomic results on the unwashed bulk samples with those of the five other laboratories that participated in this intercomparison study. From the preliminary results reported by R. F. Coleman (private communication), the values shown in

Table 49 were derived. It is seen that, although all of the six General Atomic mean values are within 0.64 to 1.50 standard deviations of the mean values for the reporting laboratories 3 to 6, all of the General Atomic values are on the low side. This is probably the result of error in the neutron flux values – in correcting the hair results to the neutron flux used in the earlier element-yield determinations. This discrepancy, however, does not affect the relative values given in Tables 47 and 48, but only the absolute values.

Of the six participating laboratories, General Atomic reported values on the unwashed bulk samples for six elements (Al, Cu, Mn, Cl, Na, Zn), another U. S. laboratory reported values for 10 elements (Al, Cu, Mn, Cl, Na, Zn, Br, Au, I, V), a third U. S. laboratory gave results for seven elements (Al, Cu, Mn, Na, Zn, Au, Hg), one British laboratory gave results for 11 elements (Cu, Mn, Cl, Na, Zn, Br, Au, I, Hg, Ca, Sb), one Scottish laboratory gave values for five elements (Cu, Zn, Hg, Sb, As), and one Brazillian laboratory reported results for eight elements (Cu, Mn, Cl, Na, Zn, Br, I, As).

It is more difficult to compare the results of the various participating laboratories on the washed hair samples, since various washing procedures were used. However, some comments are apropos, and these are summarized in Table 50. In this table, the percentage retention of each element, after washing, is shown – for the bulk hair samples – compared with the mean concentration found before washing. It is evident that the different washing procedures used varied widely in their degrees of removal (Coleman's ether reflux method generally removing very little), and that the various elements were removed to widely different degrees. In general, Na and Cl were washed out rather effectively; Cu and I were washed out very little; the remaining elements in between.

As expected, the spread of values obtained on single-strand specimens was larger, in any given laboratory, than the spread of values obtained on the bulk samples.

Table 50
COLEMAN HAIR INTERCOMPARISON RESULTS -
EFFECT OF WASHING ON BULK SAMPLES

Element	Mean % Retention after Washing for () Labs	Range of % Retention Values	GA % Retention	Coleman % Retention
Al	31 (2)	14 to 48	48	--
Cu	97 (5)	74 to 119	108	81
Mn	76 (5)	43 to 154	43	77
Cl	45 (4)	23 to 97	23	97
Na	20 (5)	0 to 91	<2	91
Zn	79 (5)	8 to 106	102	91
Br	70 (3)	52 to 92	---	92
Au	65 (3)	39 to 85	---	85
I	91 (3)	82 to 108	---	84
Hg	54 (2)	37 to 70	---	70
V	33 (1)	---	---	--
Ca	96 (1)	---	---	96
Sb	91 (1)	---	---	91
As	86 (1)	---	---	--

7.1.5 Other Work on Hair

Details regarding some actual case studies involving hair specimens, and short exploratory studies on animal hairs (cat), pubic hair, and the microscope mounting media often used in hair examinations, may be found in the General Atomic reports GA-5556 (pages 63, 65, 66),⁽¹⁾ GA-6152 (pages 24-42),⁽²⁾ GA-7041 (page 31),⁽³⁾ and GA-8013 (pages 38 and 41).⁽⁴⁾

7.2 AUTOMOBILE GREASES

The characterization of greases is of importance in hit-and-run cases, where a small smear of grease from the underside of the automobile may be left on the clothing or body of the victim, or on the grass or weeds in an adjacent field if the car veered off the road before being driven on. An exploratory instrumental NAA study of various commercial automobile chassis lubricants was therefore carried out.

Thirteen samples of different unused commercial greases, obtained from garages and service stations in the Los Angeles and San Diego areas, were analyzed. Each sample was given a short (30-second) irradiation at a thermal-neutron flux of 2.5×10^{12} n/cm²-sec, and a longer (30-minute) irradiation at a flux of 1.8×10^{12} n/cm²-sec. Sodium-iodide multichannel pulse-height spectra were obtained on each activated sample at a number of decay times. In toto, 11 elements were thus detected - in any given sample ranging from as few as one element to as many as eight elements, with a median of six. The results obtained are shown in Table 51. It is evident that wide differences in major-, minor-, and trace-element composition were observed among these 13 greases, even in this cursory study.

The high levels of Ca, Ba, or Zn found in some of the greases are due to the metal soaps (e.g., stearates) added in the manufacture of most

Table 51
ELEMENTS DETECTED IN THIRTEEN LUBRICATING GREASES
(Element values in ppm)

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

commercial greases. These high levels tend to obscure the detection of a number of trace elements present that would otherwise be detectable, instrumentally, via NAA. However, with longer irradiations, followed by Ge(Li) gamma-ray spectrometry measurements at longer decay times, the instrumental method should be able to detect and measure a satisfactorily large number of elements in small evidence samples of grease, to distinguish specimens of different brands and match specimens of the same brand.

Since the greases encountered in typical criminal cases (e. g., hit-and-run cases) are usually considerably contaminated with dust, such specimens might be examined in two different ways: (1) as received, or (2) after separation of the grease phase from the suspended dust particles. A number of unsuccessful attempts were made to devise solvent separation schemes for removing dust material from dirty grease samples, without altering the elemental composition of the grease itself. Details of these efforts may be found in the General Atomic report GA-5556 (pages 36-43).⁽¹⁾

7.3 COMMERCIAL PLASTICS

In some instances, broken plastic objects are encountered as physical evidence in criminal cases. Examples are broken automobile tail lights, combs, eyeglass frames, etc. It was therefore considered worthwhile to conduct a small-scale exploratory instrumental NAA study of a modest variety of commercially available plastics - to ascertain whether plastics of different manufacture do exhibit a wide variation in their trace-element compositions.

Virtually all commercial plastics are polymerized hydrocarbons (e. g., polyethylene, polypropylene, polystyrene, butadiene) or polymerized C-H-O compounds (e. g., lucite, cellulose acetate, phenol-formaldehyde). These would be expected to lend themselves quite well to the

general approach of trace-element characterization via instrumental neutron activation analysis – since reactor neutrons do not detectably activate carbon or hydrogen, and produce only a small amount of very short-lived induced activities in oxygen (a little 29.1-second ^{19}O , from the $^{18}\text{O}(\text{n}, \gamma)^{19}\text{O}$ thermal-neutron reaction, and a little 7.14-second ^{16}N , from the $^{16}\text{O}(\text{n}, \text{p})^{16}\text{N}$ fast-neutron reaction – plus negligible levels of 123-second ^{15}O , from the $^{16}\text{O}(\text{n}, 2\text{n})^{15}\text{O}$ fast-neutron reaction; 4.16-second ^{17}N from the $^{17}\text{O}(\text{n}, \text{p})^{17}\text{N}$ fast-neutron reaction; 0.63-second ^{18}N , from the $^{18}\text{O}(\text{n}, \text{p})^{18}\text{N}$ fast-neutron reaction; and 2.5-second ^{15}C , from the $^{18}\text{O}(\text{n}, \alpha)^{15}\text{C}$ fast-neutron reaction).

Some commercial plastics also contain certain other elements as major constituents, e.g., F (teflon), Cl (polyvinyl chloride), or N (polyurethane, acetonitrill polymer, nylon, cellulose nitrate). Thus, instrumental NAA detection of major-constituent levels of O, F, Cl, or N can help classify the type of plastic – fluorine being detected and measured via the 1.63 MeV gamma rays of its thermal-neutron product, 11.56-second ^{20}F , chlorine via the 1.60 MeV and 2.170 MeV gamma rays of its thermal-neutron product, 37.29-minute ^{38}Cl , and nitrogen via the 0.511 MeV positron-annihilation radiation of its fast-neutron product, 9.96-minute ^{13}N . Major constituent levels of oxygen are detectable and measurable best via either the 0.197 MeV and 1.37 MeV gamma rays of its thermal-neutron product, 29.1-second ^{19}O , or the 6.13 MeV gamma rays of its fast-neutron product, 7.14-second ^{16}N . However, it must be noted that high levels of fluorine will also produce significant levels of ^{19}O and ^{16}N activities – via, respectively, the $^{19}\text{F}(\text{n}, \text{p})^{19}\text{O}$ and $^{19}\text{F}(\text{n}, \alpha)^{16}\text{N}$ fast-neutron reactions. If the instrumental NAA examination of a plastic does not indicate the presence of major-constituent levels of O, F, Cl, or N, the plastic may be considered to be one of the hydrocarbon type.

In this exploratory study, 20 different commercial plastic samples, of various types and manufacturing sources, were examined briefly by

instrumental NAA. Samples of each (0.5 to 3 g) were first irradiated for 30 seconds at a thermal-neutron flux of 2.5×10^{12} n/cm²-sec (pneumatic-tube position), and then counted briefly, starting about 20-30 seconds after the end of the irradiation, on a 400-channel NaI(Tl) gamma-ray spectrometer. Then, groups of the samples were activated for 30 minutes at a thermal-neutron flux of 1.8×10^{12} n/cm²-sec (rotary-rack position), following which each activated sample was similarly counted at several decay times - ranging from one hour to several weeks after the irradiation. In these 20 samples, a total of 13 elements were detected and measured (Na, Al, Cl, Mn, Cu, Cd, Ba, Ti, Sb, Br, Zn, As, Au). Activities due to oxygen and/or nitrogen, and/or fluorine were also observed in some samples - but not measured. Most of the elements detected were present at levels of a few hundred ppm (100 ppm = 0.01%) or lower, except for the two polyvinyl chloride samples, in which the chlorine levels were of course very high ($2.3-3.0 \times 10^5$ ppm, i.e., 23-30%), the sample of cellulose propionate, in which the titanium level was very high (~8%), and a few samples in which Cd, Ba or Zn were present as minor constituents, at the 0.1-0.3% levels. Fluorine was detected, of course, as a major constituent of the teflon sample. The complete results are shown in Table 52, and the various samples are described in Table 53. The number of elements detected in any one sample ranged from only two to as high as seven, with a median of four.

The most frequently detected elements were Na (found in all 20 samples, but at levels ranging all the way from 0.04 ppm up to 500 ppm), Cl (found in 14 samples, at levels from 0.8 ppm to 390 ppm - besides the 23-30% levels in the two polyvinyl chloride samples), Al (found in 13 samples, at levels from 0.3 ppm to 80 ppm), Mn (found in 11 samples, at levels from 0.03 ppm to 1 ppm), and Cu (found in seven samples, at levels from 0.08 ppm to 210 ppm). It is of interest to note that the three

Table 52
NEUTRON ACTIVATION ANALYSIS OF COMMERCIAL PLASTICS
(Element values in ppm)

Sample ^a	Na	Al	Cl	Mn	Cu	Cd	Ba	Ti	Sb	Br	Zn	As	Au
1	2	1	--	0.26	0.4	----	----	----	-	----	----	----	----
2	10	--	8	----	----	----	----	----	-	----	----	----	----
3	3	3	--	----	----	2800	620	----	-	----	----	----	----
4	3	3	--	0.14	----	3000	2800	----	-	----	----	----	----
5	10	80	6	0.05	----	----	----	8×10 ⁴	5	----	----	----	----
6 ^b	25	--	--	----	----	----	----	----	-	----	----	----	----
7	0.2	--	3	0.05	----	----	----	----	-	----	----	----	----
8	0.4	--	3	----	----	----	----	----	-	0.2	----	----	----
9	0.3	--	0.8	----	----	----	----	----	-	----	----	----	----
10	0.9	3	2	0.1	----	----	----	----	-	0.1	----	----	----
11	1	6	14	0.1	0.08	----	----	----	-	----	18	0.06	----
12	0.04	15	3	0.03	----	----	----	----	-	----	----	----	----
13	0.6	0.3	0.8	0.05	----	----	----	----	-	----	----	----	----
14	170	2	--	----	25	----	----	----	-	----	1200	----	----
15	190	3	--	----	30	----	----	----	-	----	----	----	----
16	4	--	2.3×10 ⁵	----	70	----	----	----	-	----	----	----	----
17	150	50	390	1	25	----	----	----	-	----	----	----	----
18	4	2	10	0.06	----	----	----	----	-	----	----	----	0.06
19	170	15	130	0.6	210	----	----	----	-	----	----	----	----
20	500	--	3×10 ⁵	----	----	----	----	----	-	----	700	----	----

^aThe nature of these samples is shown in Table 53.

^bFluorine also detected as a major constituent.

Table 53
IDENTIFICATION OF PLASTIC SAMPLES

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

^aPiece of automobile taillight.

^bPiece of a street-marking cone.

polyethylene samples, made by three different companies (samples 8, 9, and 10 in Table 52), were exceptionally pure, and noticeably similar, yet still showed quite significant differences in their Na, Al, Cl, Mn, and Br levels. Similarly, the two polypropylene samples, made by two different companies (samples 11 and 12 in Table 52), were quite pure and fairly similar, yet showed considerable differences in their levels of Na, Al, Cl, Mn, Cu, Zn, and As.

Since fairly large samples (0.5 to 3 g) were used in the above measurements, it was also thought worthwhile to analyze some much smaller samples - more of the size that might be encountered as evidence specimens in criminal cases. Some measure of the homogeneity or heterogeneity of such materials was also desired. Hence, four 25-50 mg samples of each of two of the plastics studied earlier (number 11 - a polypropylene, and number 18 - a red plastic taillight material) were briefly analyzed. The results (shown on a relative basis only) are given in Table 54 with the partial exceptions of the Mn and Au levels in sample 18, these two materials are seen to be reasonably homogeneous in the levels of the elements measured, at the 25-50 mg sample level.

From even these limited-scale results, it is evident that there is considerable promise that the principle of trace-element characterization can be applied to specimens of plastic materials.

7.4 RUBBER

Rubber fragments - especially from automobile tires - are sometimes encountered as physical evidence in criminal cases, such as in hit-and-run cases. An exploratory instrumental NAA study of automobile tire rubbers was therefore conducted. Samples of nine different commercial brands of automobile tires were first activated one at a time, for 30 seconds each, in a thermal-neutron flux of 2.5×10^{12} n/cm²-sec

Table 54
STUDY OF HOMOGENEITY OF TWO PLASTIC SAMPLES

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

(pneumatic-tube position), followed rapidly by NaI(Tl) multichannel gamma-ray spectrometry. In these measurements, Al was detected and measured in all nine samples, S in four of them, and Ti in one of them (via, respectively, the (n, γ) products, 2.31-minute ^{28}Al - 1.780 MeV gamma ray; 5.07-minute ^{37}S - 3.09 MeV gamma ray; and 5.79-minute ^{51}Ti - 0.320 MeV gamma ray). Duplicate specimens of each were then activated, at the same time, for 30 minutes in a thermal-neutron flux of $1.8 \times 10^{12} \text{ n/cm}^2\text{-sec}$ (rotary-rack position) - following which they were similarly counted at several decay times. Via the longer-lived induced activities thus produced and detected, a total of five additional elements were found (Na, Cl, Mn, Zn, and Sb). All of the results obtained on these nine different samples of automobile tire rubber are shown in Table 55. From the values shown in the table, it is evident that these tire samples are quite reasonably homogeneous.

Although Al, Na, Cl, Mn, and Zn were detected and measured in all nine samples, the range of concentrations found was quite appreciable for each element, i. e., Al ranged from as low as 250 ppm (Goodyear No. 2) to as high as 3,800 ppm (General); Na ranged from as low as ~ 500 ppm to as high as $\sim 2,200$ ppm; Cl ranged from 570 ppm to $\sim 4,000$ ppm; Mn ranged from 2.3 ppm to ~ 10 ppm; and Zn ranged from 13,000 ppm (1.3%) to $\sim 22,000$ ppm (2.2%).

Again, the exploratory results obtained indicate considerable promise for the applicability of instrumental NAA trace-element characterization to actual evidence samples of tire rubber.

7.5 GLASS

Glass of various types (e. g., automobile windshield and headlight glass, window glass, spectacle glass, etc.) is quite frequently encountered as physical evidence in criminal cases - such as cases of breaking and

Table 55

NEUTRON ACTIVATION ANALYSIS OF AUTOMOBILE TIRE RUBBER

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

entering, hit-and-run, assault, etc. In this investigation, a modest number of specimens of several different types of glass, and specimens of the same type of glass but produced by different manufacturers were analyzed by means of instrumental activation analysis. First, the usual reactor thermal-neutron activation analysis was taken. Because of the very high levels of 14.96-hour ^{24}Na (1.369 MeV and 2.754 MeV gamma rays) produced in essentially all of the glass samples, very few elements could be detected – and these only ones that generate quite long-lived (n, γ) products, still detectable after perhaps a 10-day decay period, needed for almost complete decay of the induced ^{24}Na activity. In an effort to circumvent the ^{24}Na large interference problem, a number of glass samples were analyzed via photonuclear activation analysis, using the large electron linear accelerator. The ^{24}Na interference was greatly reduced, but this advantage was largely offset by the poor sensitivities obtainable, with available photon fluxes, via the photonuclear activation method. In addition, some Pyrex samples were analyzed for boron, via activation analysis with reactor fast neutrons and detection of the very high-energy β^- particles of 0.841-second ^8Li (formed by the $^{11}\text{B}(\text{n}, \alpha)^8\text{Li}$ fast-neutron reaction) with a Cerenkov detector. In these samples, and in nonboron glass specimens, the major constituent, oxygen, was also detected and measured – via Cerenkov detector measurement of the very high-energy β^- particles of 7.14-second ^{16}N (formed by the $^{16}\text{O}(\text{n}, \text{p})^{16}\text{N}$ fast-neutron reaction). In these experiments, a new high-speed (0.5-second transit time) pneumatic tube was employed, along with small, specially made polyethylene sample containers which went directly into the counter assembly.

In general, these attempts at instrumental activation analysis of glass specimens were not very fruitful – relatively few elements were unambiguously and accurately detectable, at least under the limited

conditions employed. Longer irradiations, plus Ge(Li) gamma-ray spectrometry, would be more effective, but neither of these approaches were feasible when most of these studies of glass specimens were conducted. Only a short summary of the results on glass will be presented here, rather than presenting a detailed account.

With thermal-neutron activation, a total of 11 elements were detected in glass samples: Na, Sc, Hf, Ba, Zr, Sb, Fe, Cr, Zn, Co, and As. However, many of these elements were detected in only one or a few specimens of glass, and many were barely detectable and not accurately measurable. With reactor fast neutrons, as mentioned above, the major constituent, oxygen, was detected and accurately measured - and boron (in the range of 7-11%) was detected and measured in Pyrex glass. In the photonuclear activation analysis measurements on glass, a modest number of photopeaks were observed, at various decay times, in the NaI(Tl) pulse-height spectra, but only a few were clearly identified: a 0.511 MeV β^+ annihilation peak largely due to 2.62-year ^{22}Na (confirmed by the detection of the 1.275 MeV gamma-ray peak of ^{22}Na), from the $^{23}\text{Na}(\gamma, n)^{22}\text{Na}$ reaction; the 1.369 MeV and 2.754 MeV gamma-ray peaks of 14.96-hour ^{24}Na , probably formed by the $^{25}\text{Mg}(\gamma, p)^{24}\text{Na}$ reaction, and the 0.388 MeV gamma-ray peak of 2.83-hour $^{87\text{m}}\text{Sr}$, probably produced by the $^{88}\text{Sr}(\gamma, n)^{87\text{m}}\text{Sr}$ reaction.

Details of the thermal-neutron glass activation work may be found in General Atomic reports GA-5556 (pages 51, 55, 56)⁽¹⁾ and GA-8013 (pages 32-37).⁽⁴⁾ The photonuclear activation analysis studies on glass are described in General Atomic report GA-8013 (pages 35 and 37),⁽⁴⁾ and the reactor fast-neutron activation measurements are described in the monthly report for December 1966 (GACD-6153).

7.6 SOIL

Soil (and related materials, such as dust and mud) is frequently encountered as physical evidence in criminal cases. It obviously possesses one complication, as compared with most other kinds of physical evidence – that of considerable heterogeneity. Exploratory instrumental NAA studies were conducted to investigate the possible usefulness of elemental analysis of small soil samples, such as might be encountered as evidence material.

In the first exploratory study of soils, small samples of four different local soils were irradiated for 30 minutes in a thermal-neutron flux of 1.8×10^{12} n/cm²-sec. These samples were then so radioactive that small aliquots of each had to be taken for counting, in order to keep the multichannel analyzer deadtime down to a reasonably low level while counting the aliquots at the usual counting geometry. The aliquots were counted shortly after the end of the irradiation, and also 24 hours later. The total sample was then, in each case, counted at several longer decay times during the next three weeks. All samples were analyzed in duplicate and counting was performed on the usual lead-shielded 3-in. x 3-in. solid NaI(Tl) 400-channel gamma-ray spectrometer. The results obtained are shown in Table 56. As indicated, five elements were clearly detected and measured: Na, Mn, Sc, La, and Cr. Cobalt and/or iron were also detected but not measured quantitatively. The samples were also each initially activated for 30 seconds in the reactor pneumatic-tube position, but the only induced activities detected were 2.31-minute ²⁸Al ($E_{\gamma} = 1.780$ MeV) and 6.6-minute ²⁹Al ($E_{\gamma} = 1.28$ MeV). These are the fast-neutron products of the major-constituent element, silicon – via the ²⁸Si(n,p)²⁸Al and ²⁹Si(n,p)²⁹Al reactions. These induced activities were present at such high levels that they obscured the possible detection of other short-lived induced activities.

Table 56
ANALYSIS OF FOUR DIFFERENT SOILS
(Element values in ppm)

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

From the table, it is evident that the samples were quite heterogeneous – the agreement between duplicate samples being generally quite poor for Na and Mn (determined from the small aliquots), although considerably better for Sc, La, and Cr (determined from the larger total samples).

In order to estimate the sample size necessary to obtain good reproducibility (by averaging out the smaller-scale heterogeneity), six large samples (~ 1.5 g) of one selected soil were irradiated for 30 minutes at 1.8×10^{12} n/cm²-sec thermal-neutron flux, and then counted on the NaI(Tl) gamma-ray spectrometer at several decay times during a two-week decay period, starting several days after the end of the irradiation. The results obtained are shown in Table 57. It is apparent that the reproducibility obtained with soil samples as large as 1.5 grams is quite good: all of the replicate results agreeing quite well with the others for that element (for each of the five elements detected and measured – Na, La, Sc, Co, and Cr), with the exception of one anomalously high Cr value, 238 ppm.

Additional NAA measurements on soil samples, somewhat inconclusive, were conducted on portions of various particle sizes (obtained by screening with standard screens) of several soils. The details of these measurements may be found in General Atomic report GA-5556 (pages 57-61).⁽¹⁾

7.7 INK

The trace-element characterization instrumental NAA studies conducted on paper specimens have been discussed in an earlier section of this report (in Section 5). A much less extensive study was made of a closely-related type of evidence material – ink, important in document cases, counterfeiting cases, and in cases involving supposed suicide notes, extortion notes, ransom notes, etc. These exploratory studies of inks are described below.

Table 57
 REPLICATE ANALYSES OF LARGE SAMPLES OF SOIL
 (Element values in ppm)

Sample (same soil)	Na	La	Sc	Co	Cr
A	14,000	20	9.3	9.6	159
B	15,000	19	10.0	10.8	138
C	15,700	20	9.1	9.8	146
D	15,300	17	9.0	9.6	138
E	14,500	18	9.5	9.5	238
F	13,900	18	8.9	9.2	135

In general, it would be highly desirable if the elemental composition of even a small ink specimen could be obtained nondestructively – in-situ on a paper specimen. To quickly ascertain whether this might be possible, the first samples of ink examined via instrumental NAA were analyzed in-situ on paper specimens. Five inks were examined, each written on a 3 cm x 3 cm piece of U. S. business stationery bond paper (50% cotton fibre). In each case, the writing consisted of the name of the ink, written out, i. e., "Black Ballpoint Ink", "Blue Ballpoint Ink", "Parker Superchrome Blue-Black Ink", Schaeffer Skrip Permanent Jet Black Ink", and "Schaeffer Skrip Washable Black Ink". The samples, and a blank sample of the same bond paper, were each folded up, placed in separate polyethylene vials, and activated in the reactor for 30 minutes at a thermal-neutron flux of 1.8×10^{12} n/cm²-sec. Unfortunately, the subsequent NaI(Tl) multichannel gamma-ray spectrometry measurements on the activated samples showed no detectable differences in the pulse-height spectra between the blank paper sample and any of the five paper specimens that were written on with ink. The activated samples were quite radioactive, exhibiting a number of induced radionuclide species, but all of the activities (within the precisions of the counting statistics) were the result of neutron activation of elements present in the paper itself. Any additional amounts of these same induced activities, or any activities from other elements, due to the small mass of ink present were simply too small to show up in the presence of the high levels of various activities induced in the paper itself (e. g., 14.96-hour ²⁴Na, 37.29-minute ³⁸Cl, 2.576-hour ⁵⁶Mn, 2.31-minute ²⁸Al, 12.80-hour ⁶⁴Cu, 2.80-day ¹²²Sb, 83.9-day ⁴⁶Sc, and 40.22-hour ¹⁴⁰La).

Next, it was decided to investigate inks themselves (or ink pigments), and paper that was very heavily inked (e. g., a dollar bill). Some interesting samples for this purpose were supplied by the U. S. Treasury

Department. They consisted of seven ink pigments, two counterfeit U. S. one-dollar bills, and two kinds of paper of the type that is sometimes used in the preparation of counterfeit bills.

The essential findings from the study of the inks, counterfeit bills, and papers have been given in Tables 30 and 31, and it was previously mentioned that the ability to discriminate between the paper and the ink of a counterfeit bill was not proven.

7.8 WOOD

Splinters of wood are often encountered as evidence specimens in criminal cases. For example, it may be important to ascertain, if possible, whether a splinter of wood found in the clothing of a suspect came from a door frame or window frame that was jimmied in a burglary case - or whether a splinter of wood found adhering to the automobile of a suspect came from a fence or telephone pole struck a glancing blow by a fleeing automobile. In some instances, a morphological comparison is successful, i. e., if a splinter associated with a suspect exactly matches, in size and detailed shape, an area at the scene of a crime where a splinter of wood was broken off. More often, however, a shape comparison is not feasible or is inconclusive. Therefore, it was thought that a trace-element NAA comparison of wood specimens might be productive.

In an exploratory study, small specimens of eight different kinds of wood (redwood, Douglas fir, cedar, birch, mahogany, ash, oak, and pine) were activated for one hour in the rotary specimen rack of the reactor (thermal-neutron flux = 1.8×10^{12} n/cm²-sec), and then counted at decay times of a few minutes and about one hour on a 3-in. x 3-in. solid NaI(Tl) crystal 400-channel gamma-ray spectrometer. In this cursory examination, six elements (Mn, K, Al, Cl, Na, and Cu) were detected and measured in almost every specimen. As may be seen from the ppm

results, shown in Table 58, the levels of these six elements varied widely among the samples of the eight different kinds of wood. Thus, Mn ranged from 2 ppm to 67 ppm, K from <310 ppm to 2290 ppm, Al from 6 ppm to 108 ppm, Cl from <51 ppm to 845 ppm, Na from 8 ppm to 340 ppm, and Cu from 1 ppm to 440 ppm.

These results were encouraging, as being indicative of possibly large differences in elemental composition at least among wood specimens of different species. However, it was suspected that sample variability in composition, due to its heterogeneous structure, might be a severe problem. To check this possibility, four specimens were taken from one 8-foot long pine board, and one from a different, but similar, 8-foot pine board. Samples 1, 2, and 3 were taken, respectively, from one end, the middle, and the other end of one of the boards – and sample 3A was taken very close to the location of sample 3. Sample 11 was taken from the second pine board. The five specimens were activated and counted in the same fashion as the eight wood samples discussed above. The same six elements were detected, and five of them were measured quantitatively, as shown in Table 59. Although the four specimens from the one pine board are much more similar in elemental composition than were the specimens of eight different kinds of wood, some appreciable differences – even in a single board – are apparent. The Mn, K, and Cu values do not show much spread, but the Al content is seen to range from 11 ppm up to 77 ppm, and the Na content from 16 ppm up to 82 ppm. The two adjacent specimens, samples 3 and 3A, are more closely alike in composition. Except for the higher Cu value (4 ppm), the levels of the elements found in the second pine board (Mn, K, Al, Na) are seen to be quite similar to those found in the first pine board.

These exploratory results, while not ruling out the possibility of useful trace-element NAA comparisons of wood specimens in certain

Table 58
ACTIVATION ANALYSIS OF WOOD SAMPLES
(Element values in ppm)

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

Table 59
ACTIVATION ANALYSIS OF PINE WOOD
(Element values in ppm)

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

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

instances, in actual case work, were not felt to be sufficiently promising to warrant a more extended investigation, at least for the present.

7.9 AMPHETAMINES

Various kinds of dangerous drugs, such as the amphetamines, are frequently found as physical evidence in criminal cases. Sometimes these are legitimately produced drugs, sometimes they are counterfeit products. Often, the brand and brand authenticity can be established by means of physical parameters such as weight, color, size, shape, and microscopic examination of the brand die marking. When such verification is not possible, or is inconclusive, comparison of specimens of possibly similar origin (manufacture) via measurement of their chemical composition (compounds and/or elements) can be quite valuable.

In order to ascertain whether or not a simple instrumental NAA examination of amphetamine tablets might be illuminating, tablets produced by eleven different drug manufacturers were analyzed by thermal-neutron activation in the reactor (using 30-second and 30-minute irradiations), followed by NaI(Tl) multichannel gamma-ray spectrometry at a few decay times. The results are shown in Table 60. In this brief study, seven elements were detected in some or all of the eleven amphetamine samples (Na, Cl, Mn, K, Al, Ca, and Mg). Measured ppm values are given for all except Ca and Mg, for which only relative values are given. With the exception of potassium, which was detected in only one sample, these elements were observed in all, or almost all, of the eleven samples. Their ranges were quite wide, however. Thus, the Na levels ranged from 62 ppm to 545 ppm, Cl from < 34 ppm to ~ 5400 ppm, Mn from < 0.18 ppm to ~ 22 ppm, Al from 4 ppm to 368 ppm, Ca (relative from < 0.002 to 1, and Mg (relative) from 0.147 to 1. Of the amphetamine samples from eleven different manufacturers, no two were alike - i. e., each

Table 60

NEUTRON ACTIVATION ANALYSIS OF AMPHETAMINE SAMPLES

Sample	Na (ppm)	Cl (ppm)	Mn (ppm)	K (ppm)	Al (ppm)	Ca (rel)	Mg (rel)
1	226	~219	~5.7	---	31	1.000	---
2	200	----	1.98	---	63	≤0.002	0.201
3	62	41	≤0.18	310	4.0	≤0.002	---
4	179	~246	~2.16	---	137	≤0.002	0.369
5	350	170	0.32	---	89	0.305	0.315
6	545	~5500	~1.6	---	235	≤0.002	0.318
7	332	~227	7.3	---	368	≤0.002	1.000
8	106	----	~22.0	---	83	0.644	0.147
9	429	~490	4.6	---	281	0.574	---
10	169	740	1.9	---	252	≤0.002	0.253
11	108	≤34	1.38	---	90	≤0.002	0.274

could be distinguished from the other ten on the basis of even a brief instrumental NAA examination.

It is felt that these exploratory results show great promise for a more thorough and more modern instrumental NAA technique for the trace-element characterization of amphetamine samples (and probably of other kinds of dangerous drugs, too) of different origins. Particularly, using longer irradiation and decay times, and Ge(Li) gamma-ray spectrometry, a much larger number of characterizing trace elements could be detected and measured in such samples. It is felt that this possibility definitely should be pursued further.

7.10 ILLICIT WHISKEYS

At the request of the Internal Revenue Service, six samples of illicit whiskey were analyzed for lead via instrumental photonuclear activation analysis. The samples (and an aqueous Pb standard) were irradiated for one hour with bremsstrahlung produced with 25 MeV Linac electrons (impinging on a tungsten converter). After a 3-day decay period, the activated samples were counted on a NaI(Tl) multichannel gamma-ray spectrometer. In all of the samples except one, high levels of lead were observed - via the 0.279 MeV gamma ray of 52.1-hour ^{203}Pb , generated in the specimens by the $^{204}\text{Pb}(\gamma, n)^{203}\text{Pb}$ reaction. The $\mu\text{g Pb/liter}$ values found are shown in Table 61. They are seen to range from none detectable (in Sample 4) to 4,080 $\mu\text{g Pb/liter}$ (~ 4 ppm) in Sample 5, up to as high as 79,000 $\mu\text{g Pb/liter}$ (~ 80 ppm) in Sample 3. The photonuclear activation analysis values are seen to agree very well with the lead values found by the IRS group, using a colorimetric procedure.

Table 61
ANALYSIS OF MOONSHINE WHISKEY FOR LEAD

Sample	$\mu\text{g Pb/liter}$	
	Colorimetry, IRS	Photonuclear Activation Analysis, GA
1	10,700	$10,100 \pm 1,900$
2	28,300	$27,500 \pm 1,600$
3	86,400	$79,000 \pm 7,600$
4	None detectable	None detectable
5	5,060	$4,080 \pm 380$
6	16,400	$14,700 \pm 2,800$

7.11 MARIJUANA

A group of 22 samples of marijuana, containing possibly one or more subgroup of samples in which the samples of each subgroup had a common origin - in that they came from the same region - were analyzed by instrumental NAA. Initially, 30-second and 30-minute activations of leaf samples in the reactor, followed by NaI(Tl) multichannel gamma-ray spectrometry, revealed that six elements were readily detected in all 22 samples of marijuana: Mn, Na, K, Cl, Al, and Br. However, there were quite considerable quantitative differences. For example, the pulse-height spectra of two of the marijuana leaf samples (normalized to the same sample weight) obtained under these different irradiation time/decay time conditions are compared in Fig. 32. One sample was of known origin. The other sample was of unknown origin - but possibly of the same origin as the known. It is quite apparent that these two samples are markedly different, quantitatively, in their elemental compositions, and hence probably of different origins. Since marijuana is sometimes diluted with parsley before marketing, some similar NAA measurements were carried out on local parsley. Although five of the six elements detected, under comparable conditions, in marijuana were also detected in the parsley (Mn, Na, K, Cl, Al), the quantitative differences were such that the parsley sample was quite measurably different in its elemental composition from any of the 22 marijuana samples. However, these measurements point out the difficulties that one would encounter in trying to establish that seized parsley-diluted marijuana contained marijuana of a particular origin, where undiluted known marijuana was the material available for comparison.

Another difficulty encountered in marijuana comparisons in which the possibility of common origin is being investigated is the extreme heterogeneity of the bulk material. The usual distributed marijuana

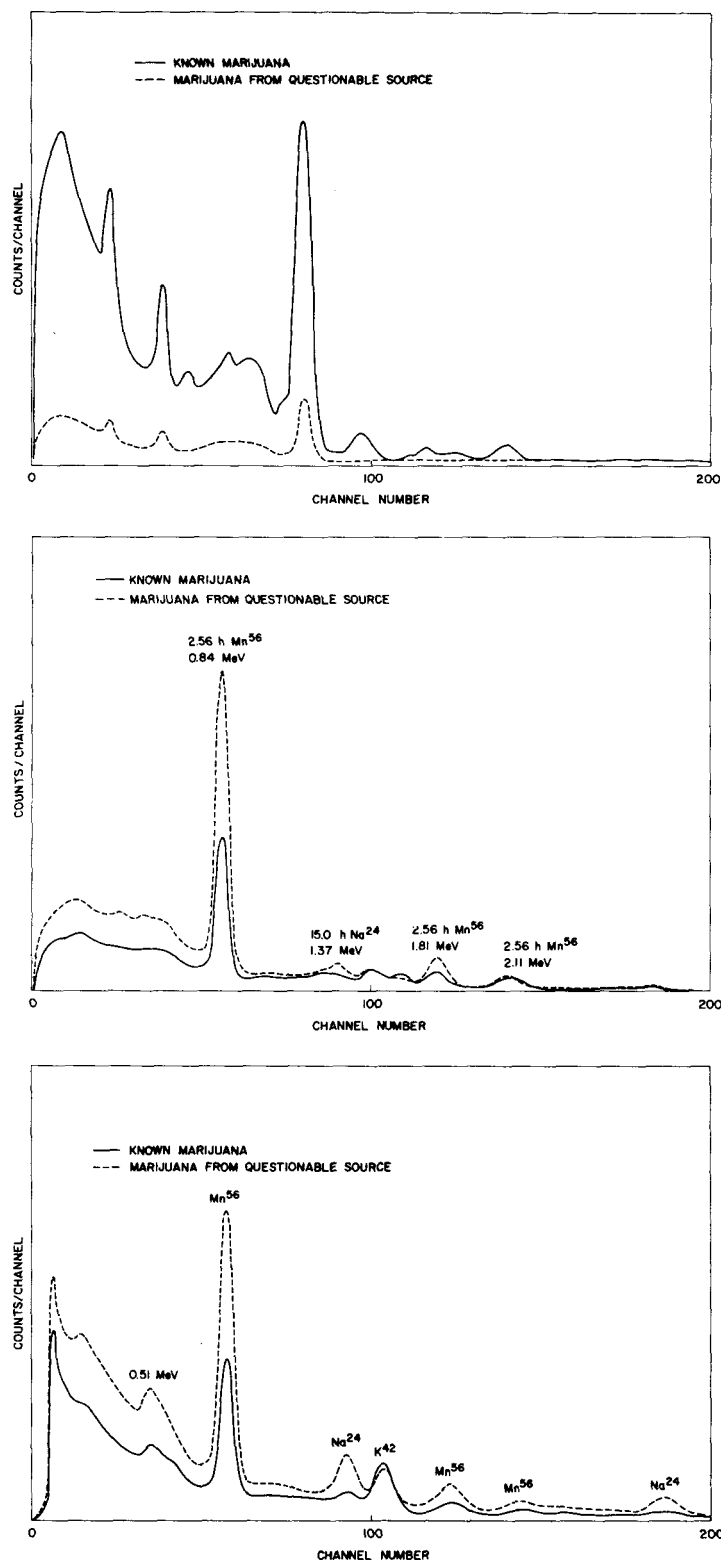


Fig. 32. Gamma-ray spectra comparing samples of known marijuana and marijuana from an unknown source

contains varying proportions of leaves, stalks, and seeds. Unless considerable care is taken, and a fairly large sample is taken, reproducibility of sampling is very poor. Alternatively, one might separate the material into piles of its three components, and then compare one sample of seeds with a second sample of seeds, or leaves with leaves, or stalks with stalks – rather than compare the more heterogeneous bulk samples themselves. In Fig. 33, a photograph is shown of seeds, stalks, and leaves separated from one sample of marijuana. These separated specimens were also activated and counted, and found to differ markedly from one another in their elemental compositions (as might well be expected). Illustrative NaI(Tl) pulse-height spectra of the three materials, following a 30-minute reactor irradiation, and an 8-hour decay period (spectra normalized to the same sample weight) are shown in Fig. 34. The differences in elemental composition of these three materials, all separated from one sample of marijuana from one locality, are quite apparent.

In the measurements conducted on the 22 bulk marijuana samples, measurements at longer decay resulted in the detection and measurement of three additional elements (Cr, Fe, and Sc) bringing the total number of elements detected in the samples to nine. In spite of the heterogeneity problems mentioned earlier, two pairs of samples agreed to within about $\pm 10\%$ in their concentrations of all nine elements, and five other pairs matched that closely in their levels of 8 out of the 9 elements. It seems likely that all seven of these pairs of samples had a common origin within each pair, i. e., they represented marijuana samples of seven different origins. The remaining eight samples exhibited elemental compositions appreciably different from one another – and different from any of the seven matched pairs of samples. On the other hand, some of the elements detected do not appear to vary significantly with the origin of the marijuana, since five of the nine detected elements were found at almost the same concentrations in all 22 samples.

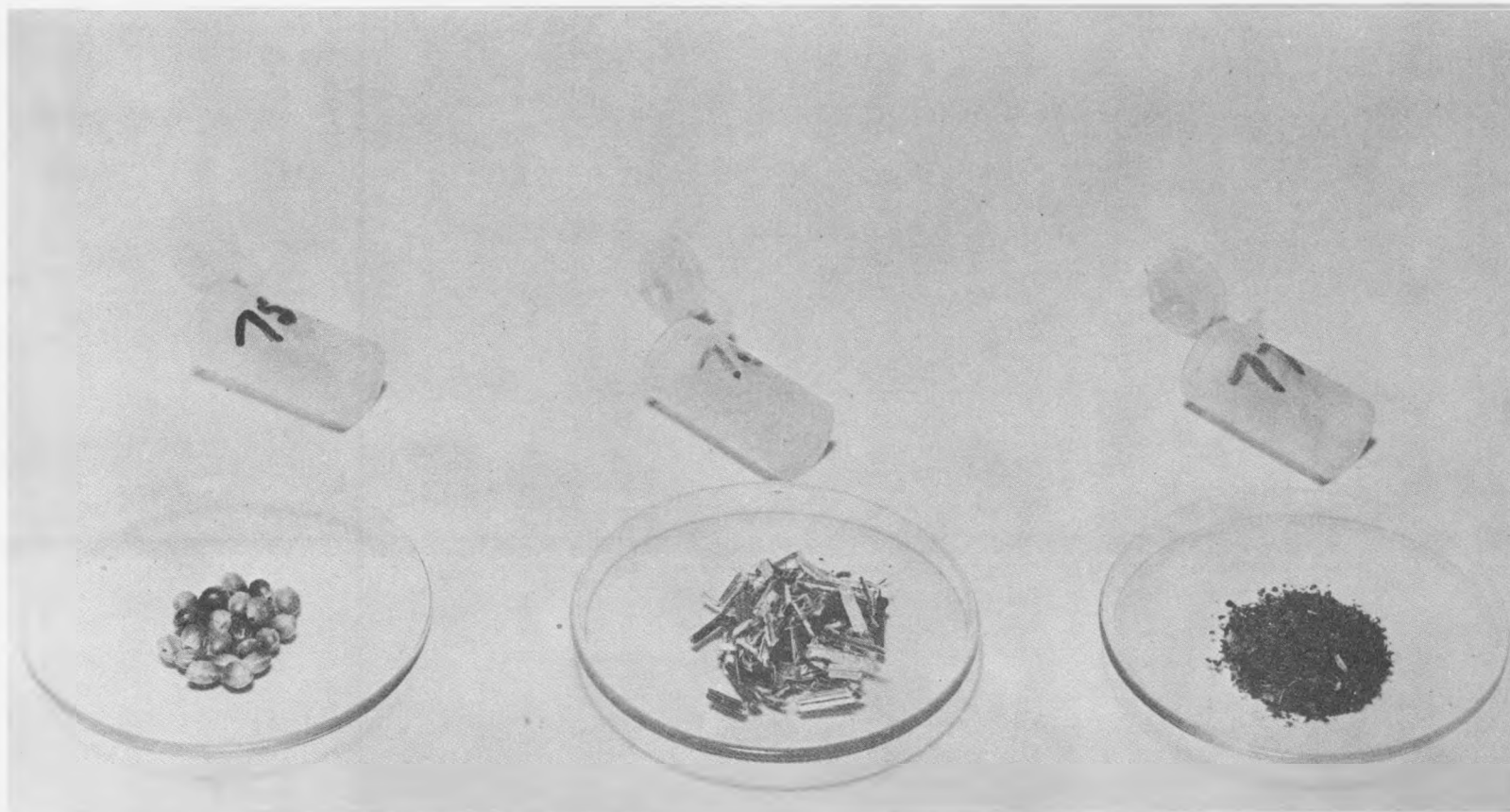


Fig. 33. Seeds, stalks, and leaves taken from the same sample of marijuana

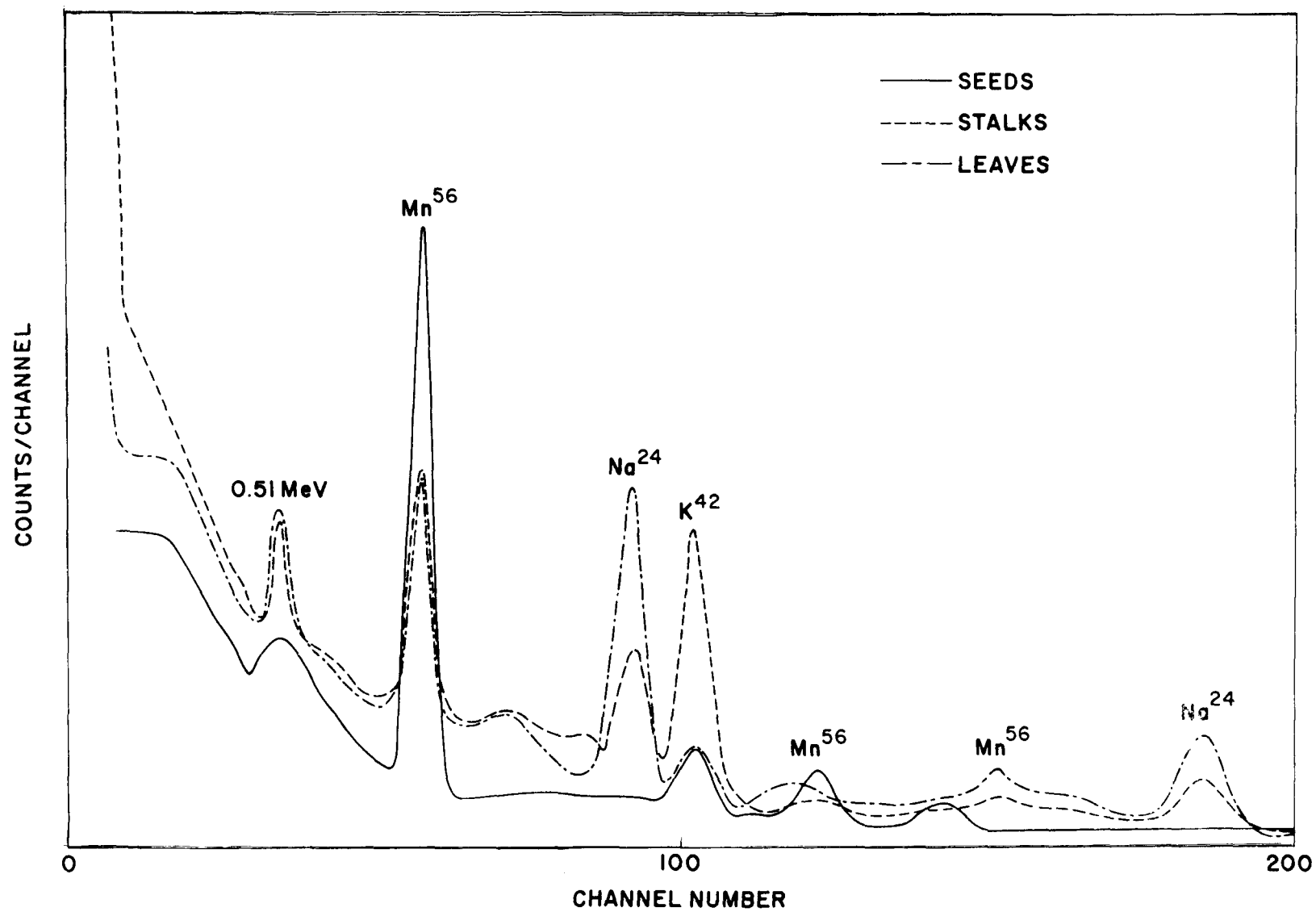


Fig. 34. Comparison of gamma-ray spectra from seeds, stalks, and leaves of known marijuana

The exploratory results obtained on marijuana seem very promising, and indicate the desirability of conducting a much more extensive study of the possibilities of trace-element characterization of such samples via instrumental NAA (especially if longer irradiations and Ge(Li) gamma-ray spectrometry are employed).

7.12 OIL SLICKS ON WATERWAYS

At the request of the U. S. Bureau of Customs, an exploratory study was made of the possibility of identifying the source of an oil slick found on river, harbor, or coastal waterways - via instrumental NAA trace-element characterization. They supplied 32 fuel oil samples: 16 different pure fuel oils, and the same 16 oils mixed with salt water.

Since an oil slick sample would typically be appreciably emulsified with the water in which it was in contact (including sea water), some suitable means of removing the emulsified water, without changing the elemental composition of the oil itself, was needed. Simple repeated washings with hot de-ionized water, with centrifugation between each washing, seemed an obvious good possibility, and so was tested. Six of the pure fuel oil samples were analyzed as received, as well as after several washings with hot de-ionized water - to ascertain whether such washing produced any significant changes in the elemental compositions of the oils. The samples were activated in the reactor for 30 seconds, and for 30 minutes, in each case followed by NaI(Tl) multichannel gamma-ray spectrometry measurements at a few appropriate decay times. The results obtained are shown in Table 62. The elements, Na, Mn, V, Cu, and Co were detected and measured in some or most of the samples, and Sb and/or As were detected in many of them (with the NaI(Tl) detector, the ~ 0.56 MeV peak observed in most of the pulse-height spectra could not be resolved into peaks due to ^{76}As and ^{122}Sb , and not enough decay

Table 62
NEUTRON ACTIVATION ANALYSES OF WASHED AND
UNWASHED PURE FUEL OIL SAMPLES
(Element values in ppm)

Sample	Na	Mn	V	Cu	Sb	As	Co
2A unwashed	10.7	0.037	314	1.7	<0.035	≤0.11	-----
2A washed	4.8	0.023	416	2.3	≤0.022	≤0.05	-----
3A unwashed	1.09	0.017	-----	1.8	≤0.069	≤0.07	-----
3A washed	0.61	0.013	-----	4.0	≤0.24	≤0.30	-----
4A unwashed	69	0.139	403	2.6	≤0.064	≤0.04	-----
4A washed	62	0.190	384	2.3	≤0.030	≤0.04	-----
5A unwashed	236	0.26	70	-----	-----	-----	-----
5A washed	170	0.23	72	-----	-----	-----	-----
6A unwashed	-----	-----	120	2.0	<0.18	≤0.03	0.20
6A washed	-----	-----	129	1.1	<0.04	≤0.06	0.21
7A unwashed	-----	-----	1.59	0.63	<0.04	≤0.11	<0.03
7A washed	-----	-----	1.88	0.38	≤0.03	≤0.09	0.08

data were available to untangle them on the basis of their half-lives, so only $<$ upper limits for each element are shown in the table; if no 0.56 MeV peak could be detected after eight days decay, a $<$ upper limit figure for Sb is shown. Of these elements, only one (Na) appears to be somewhat lowered by the water-washing procedure.

Since this water-washing procedure appeared to work fairly well, it was then used on all 32 samples – the 16 pure fuel oils, and the 16 corresponding oils contaminated with salt water. The washed samples were then activated and counted as before, with the results shown in Table 63. Two points are evident from inspection of the data presented in the table: (1) after the water-washing procedure, each pure fuel oil closely resembles the corresponding oil that had been contaminated with salt water, and (2) the 16 different fuel oils (whether originally uncontaminated or contaminated with salt water) show markedly different trace-element compositions, no two being sufficiently alike to cause a mistaken identification. The vanadium levels are seen to range all the way from 1.8 ppm up to 865 ppm, the Mn levels from 0.001 ppm to 0.43 ppm, the Na levels from 0.11 ppm to 166 ppm, and the Co levels from $<$ 0.06 ppm up to 1.84 ppm.

These very promising results caused us to recommend that a much more detailed and larger-scale study of the possibilities of instrumental NAA trace-element characterization of oil slicks (both crude oils and fuel oils) be conducted. Unfortunately, at the time these exploratory studies were made (1963), there was not sufficient concern about the problem of pollution of our waterways by oil to generate any support for an expanded study of the method. (Note: much later, in 1969, interest in such an approach had developed, and the authors then undertook a larger-scale, more detailed and advanced study that has fully confirmed the expectations from the earlier exploratory study, and has advanced the method much further.)

Table 63
NEUTRON ACTIVATION ANALYSES OF WASHED OIL SAMPLES
(Element values in ppm)

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

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

7. 13 MISCELLANEOUS OTHER MATERIALS

A number of other kinds of evidence-type materials were also investigated by instrumental NAA at various times in the course of this 6-year study. These studies, however, were too brief to warrant inclusion in the present report, but are referenced below to the "annual" reports in which they are described.

Measurements on fingernails are described in GA-5556 (pages 66-69).⁽¹⁾ A brief study of cigarette tobacco of various brands is described in GA-5556 (pages 72-73).⁽¹⁾ Measurements on sediment samples involved in a river pollution problem are described in GA-5556 (pages 72-76).⁽¹⁾ A short study of a few samples of rice whisky, conducted for the Internal Revenue Service, is described in GA-5556 (pages 79-84).⁽¹⁾ Some measurements on rope specimens involved in an actual case are described in GA-7041 (pages 44 and 48).⁽³⁾

8. OTHER ACTIVITIES

8.1 THE FILM, "THE NUCLEAR WITNESS"

A related activity of considerable interest and importance (although carried out under a separate contract with the Division of Isotopes Development, AEC), was the production, in late 1965, of a 28-minute color-sound 16-mm film entitled, "The Nuclear Witness - Activation Analysis in Crime Investigation". The script, prepared by V. P. Guinn, was based largely on several illustrative actual criminal cases investigated by NAA techniques by the General Atomic group. Filming was done by McNamara Productions (Hollywood). Besides various members of the General Atomic Activation Analysis Group, the cast includes numerous deputy sheriffs from the San Diego County Sheriff's Office, four San Diego Deputy District Attorneys, one City of San Diego Municipal Judge, one State of California Bureau of Narcotics investigator, and one member of the Internal Revenue Service's forensic activation analysis group (M. J. Pro). The excellent cooperation of all these people is gratefully acknowledged.

The film has been very well received, and is still in considerable demand. It received a "Chris" award in the annual Columbus, Ohio film festival, and has been used for the past several years by the FBI and the U. S. Treasury Department in their agent training programs. It is also used extensively by numerous other law enforcement agencies in the U. S. and abroad.

8.2 THE FIRST INTERNATIONAL CONFERENCE ON FORENSIC ACTIVATION ANALYSIS

During September 19-21, 1966, the First International Conference on Forensic Activation Analysis was held at the General Atomic laboratories. It was organized by the General Atomic Activation Analysis Group, and was co-sponsored by General Atomic, the Division of Isotopes Development (AEC), and the California Association of Criminalists. It was attended by some 120 persons, about two-thirds of whom were law-enforcement personnel (criminalists, coroners, investigators, sheriffs, chiefs of police, district attorneys, and members of a number of state and federal law-enforcement agencies), the others being nuclear scientists. The attendees (including the speakers) were from 24 states, the District of Columbia, and nine countries (Australia, Brazil, Canada, England, France, India, Japan, Scotland, and the United States).

Session I was entitled "Introduction to Forensic Activation Analysis" and was chaired by Dr. Constantine J. Maletskos (Department of Legal Medicine, Harvard University). During this session, the following papers were presented:

1. "The Introduction of New Scientific Methods in Court, " by Dr. C. J. Maletskos (Harvard University).
2. "Neutron Activation Analysis and Its Forensic Applications, " by Dr. Vincent P. Guinn (General Atomic).
3. "Some Criminalistics Problems, and Neutron Activation Analysis, " by Professor Paul L. Kirk (Department of Criminology, University of California, Berkeley).
4. "Organization and Equipment of an Activation Analysis Laboratory, " by Dr. John M. A. Lenihan (Western Regional Hospital Board, Glasgow, Scotland).

5. "Early Forensic Neutron Activation Analysis Studies at the Oak Ridge National Laboratory, " by Professor George W. Leddicotte (Nuclear Engineering Department, University of Missouri).
6. "Application of Special Counting Techniques to Forensic Problems, " by Dr. Morris A. Wahlgren (Argonne National Laboratory).
7. "Forensic Applications of Neutron Activation Analysis, " by Mr. Maynard J. Pro (U. S. Treasury Department, Washington, D. C.).

Session II was entitled "Forensic Activation Analysis of Various Evidence Materials" and was chaired by Dr. George J. Rotariu (USAEC Division of Isotopes Development). During this session, the following papers were presented:

8. "The Role of the Division of Isotopes Development, USAEC, in Aiding the Development of Forensic Activation Analysis, " by Dr. George J. Rotariu (DID-AEC).
9. "Revelation of Internal Structure of Paintings through Neutron Activation Autoradiography, " by Dr. Edward V. Sayre (Brookhaven National Laboratory).
10. "The Comparison of Paint Samples by Neutron Activation Analysis, " by Mr. Donald E. Bryan (General Atomic).
11. "Preliminary Evaluation of the Value of Trace Analysis in the Identification of Glass Fragments, " by Mr. Ronald F. Coleman (United Kingdom Atomic Energy Authority, Aldermaston, England).
12. "Neutron Activation and Photonuclear Activation Analysis of Glass Samples, " by Mrs. Dorothy M. Settle (General Atomic).
13. "The Determination of Traces of Barium and Antimony in Gunshot Residues by Activation Analysis, " by Dr. Vincent P. Guinn (General Atomic).

14. "Distance Determination of Gunshot Firings by Neutron Activation Analysis," by Dr. S. S. Krishnan (Attorney General's Laboratory, Toronto, Canada).
15. "Bullet Residue Transference to Various Materials," by Mr. Howard L. Schlesinger* (U. S. Treasury Department, Washington, D. C.).

Session III was entitled "Neutron Activation Analysis of Hair" and was chaired by Inspector F. Michael Kerr (Royal Canadian Mounted Police Crime Detection Laboratory, Ottawa, Canada). During this session, the following papers were presented:

16. "Chairman's Remarks," by Inspector F. Michael Kerr (RCMP, Ottawa, Canada).
17. "The Trace Element Content of Human Head Hair in England and Wales, and the Application of Forensic Science," by Mr. Ronald F. Coleman (United Kingdom Atomic Energy Authority, Aldermaston, England).
18. "Individualization of Human Head Hair," by Dr. Auseklis K. Perkons (Attorney General's Laboratory, Ottawa, Canada).
19. "Neutron Activation Analysis of Some Hair Samples as Evidence for an Australian Court," by Dr. Lloyd E. Smythe (Australian Atomic Energy Commission Research Establishment, Lucas Heights, Australia).
20. "The Use of Hair Trace Elements in Forensic Applications," by Mr. Lamont C. Bate (Oak Ridge National Laboratory).
21. "Exogenous Contamination of Hair by Capillary Action of Arsenic Solutions," by Dr. Fausto W. Lima (Instituto de Energia Atomica, Sao Paulo, Brazil).

* Since April 1967, a member of the Activation Analysis Group at General Atomic.

22. "Arsenic in Hair, " by Mr. Norman E. Erickson (Attorney General's Laboratory, Ottawa, Canada).
23. "The Value of Neutron Activation Analysis Hair Comparisons in Forensic Investigations - a Critique, " by Professor Robert E. Jervis (Department of Chemistry, University of Toronto, Toronto, Canada).
24. "Activation Analysis in Forensic Science Using Radiochemical Separations, " by Dr. Hamilton Smith (Department of Forensic Medicine, University of Glasgow, Scotland).

These 24 technical presentations by the principal researchers in the field of forensic activation analysis were summarized in the "Abstracts" issued to all attendees at the start of the Conference. Conference attendees also received a list of all the U. S. court cases (the first on March 16, 1964; the most recent on August 10, 1966) in which NAA results had been successfully introduced. This list was compiled by Dr. V. P. Guinn (General Atomic) and Mr. M. J. Pro (U. S. Treasury Department). Each attendee at the Conference also received a special gunshot-residue sampling kit, with photographs and instructions for proper use. Later, attendees received a comprehensive bibliography of references to published papers and reports on forensic activation analysis, and a copy of the 314-page Conference Proceedings, both prepared by V. P. Guinn.

The Conference also included a number of forensic activation analysis demonstrations, a mock trial, a showing of the film, "The Nuclear Witness", and a tour of the General Atomic laboratories. The Conference was very well received by both law enforcement and nuclear science attendees. The speakers included everyone from the U. S. and abroad who had contributed significantly to the development of the field of forensic activation analysis up to the time of the Conference (financial assistance from the Division of Isotopes Development, AEC, to help defray the travel

expenses of the Conference speakers from abroad, and from U. S. universities, is most gratefully acknowledged; motel accommodations and local transportation for the speakers were provided by General Atomic). The Second International Conference on Forensic Activation Analysis is tentatively scheduled to be held in Glasgow, Scotland, in 1971. Plans for it are being developed by the co-chairman, Dr. John Lenihan and Dr. Hamilton Smith.

8.3 THE FORENSIC ACTIVATION ANALYSIS COORDINATING GROUP

On the day following the International Conference (September 22, 1966), an Advanced Seminar on Forensic Activation Analysis was held in San Diego by the Conference speakers and session chairmen. Near the close of this seminar, it was decided to form an informal, international Forensic Activation Analysis Coordinating Group which would have the following principal objectives:

1. To encourage the sound development of forensic activation analysis.
2. To help develop standardized, thoroughly tested and approved techniques.
3. To discourage premature use of partially developed applications in actual case work and in courtroom presentations.
4. To foster closer cooperation with professional criminalists.
5. To rapidly disseminate new information, techniques, papers, and reports among all workers in this field.

Membership in this informal group is open to anyone working in the field of forensic activation analysis.

The initial Executive Committee of the group consists of Mr. R. F. Coleman (representing the United Kingdom and Europe), Dr. S. S. Krishnan

(representing Canada), Dr. F. W. Lima (representing Central and South America), Dr. L. E. Smythe (representing Australia and New Zealand), and Dr. V. P. Guinn, Dr. C. J. Maletskos, and Mr. M. J. Pro (jointly representing the United States). The initial Chairman of the Executive Committee is Dr. Guinn, who will also represent Japan. Some work to further the objectives of the group has already been initiated by Dr. Maletskos and Dr. Guinn.

8.4 THE GENERAL ATOMIC NON-PROFIT FORENSIC ACTIVATION ANALYSIS SERVICE

General Atomic's nonprofit Forensic Activation Analysis Service was formed early in 1965. This service is now being periodically utilized by a number of law-enforcement agencies around the country. Some of these agencies have procured the special gunshot-residue sampling kits supplied by General Atomic. Proper taking of gunshot-residue samples costs almost nothing, and the paraffin lifts, stored in labelled and capped bottles or vials, can be kept indefinitely for possible later analysis for Ba and Sb by NAA. All law-enforcement agencies are therefore being urged to take paraffin lifts of both hands of each gunshot victim or suspect in all apparent suicide and murder gunshot cases.

8.5 PAPERS AND REPORTS PRESENTED AND/OR PUBLISHED

During the six-year period covered by this report, various members of the General Atomic Activation Analysis Group presented a very large number of papers, talks, and lectures, covering various aspects of the investigation, before meetings of various groups and organizations. Many of the papers presented were subsequently published in various journals. Below, a short digest (far from complete) is given of the various oral presentations, and then the various published papers and reports are listed (excluding published abstracts).

1. Oral Presentations on Forensic Activation Analysis
(a Partial Listing)

- a. Research papers (one to four) were presented at each of the twelve of the Semi-Annual Seminars of the California Association of Criminalists that were held during this six-year period.
- b. A paper was presented by V. P. Guinn at a one-day conference on forensic activation analysis (FAA) held in Glasgow, Scotland, in October 1962 (conference organized by Dr. John Lenihan to coincide with a visit in Glasgow by Dr. Guinn).
- c. Papers were presented at four national meetings of the American Nuclear Society (in 1962, 1964, 1966, and 1967).
- d. V. P. Guinn presented a paper on FAA at the Glasgow Conference on Recent Advances in Activation Analysis, and a lecture on FAA in the NATO-sponsored Post-graduate Course in Activation Analysis, both held in Glasgow, Scotland, in August 1964.
- e. A paper was presented at the Second International Conference on Modern Trends in Activation Analysis, held at Texas A & M University in April 1965, and another paper at the follow-on Advanced Seminar on Activation Analysis, held at General Atomic immediately following the Texas A & M conference.
- f. Papers were presented at the 1963, 1964, 1967, and 1968 annual meetings of the American Academy of Forensic Sciences (three papers at the 1968 meeting).
- g. Invited papers were presented at three national meetings of the International Association for Identification (in 1963, 1965, and 1967).
- h. V. P. Guinn presented an invited paper at the 7th Japan Conference on Radioisotopes (Tokyo, May 1966).

- i. Two papers were presented at the First National Symposium on Law Enforcement Science and Technology (Chicago, March 1967).
- j. V. P. Guinn gave an invited lecture at Interpol Headquarters (St. Cloud, France, May 1967).
- k. An FAA paper was presented at the IAEA Symposium on Nuclear Activation Techniques in the Life Sciences (Amsterdam, May 1967).
- l. V. P. Guinn lectured on FAA in the Oak Ridge Associated Universities Activation Analysis courses in June 1966 and June 1967.
- m. Papers were presented at national meetings of the Society for Applied Spectroscopy in October 1963 and June 1966 (2 pages).
- n. V. P. Guinn was invited by the National District Attorney's Association to speak at their 1965 national meeting (Mackinaw Island, Michigan), and at the subsequent regional meetings in Kansas City, San Francisco, and Philadelphia, and these presentations were very well received.
- o. Four papers were presented at the First International Conference on Forensic Activation Analysis (San Diego, September 1966).
- p. In August 1966, V. P. Guinn gave invited papers at the annual meeting of the American Society of Questioned Document Examiners (New York City), at the 4th International Meeting in Forensic Medicine (Copenhagen), and at the 2nd International Meeting in Questioned Documents (Copenhagen).
- q. V. P. Guinn was a guest lecturer in the Bureau of Drug Abuse Controls' 1966 and 1967 State and Local Crime Laboratory Chemists School.
- r. V. P. Guinn presented the invited lecture on FAA at the National Symposium on Science and Criminal Justice, in Washington, D. C., June 1966 - organized by the Department of Justice.

- s. Lectures on FAA were also presented at numerous meetings of county and state sections of such organizations as the American Society for Industrial Security (2), Investigators Associations (2), District Attorneys Association (3), Check Investigators Association (1), Peace Officers Association (1), the American Nuclear Society (4), at five universities, and at several local meetings of service organizations (Rotary, Kiwanis, Lions).

The above partial listing of forensic activation analysis oral presentations (principal papers, seminars, lectures, talks) by members of the General Atomic Activation Analysis Group totals some 78 presentations.

2. Published Papers and Reports on Forensic Activation Analysis

- a. R. R. Ruch, V. P. Guinn, and R. H. Pinker, "Detection of Gunpowder Residues by Neutron Activation Analysis," Transactions of the American Nuclear Society 5 (1962) 282.
- b. D. E. Bryan and V. P. Guinn, "Applications of Neutron Activation Analysis in Scientific Crime Detection." General Atomic Report GA-5556, covering the period May 1, 1962 through October 31, 1963 (89 pages).
- c. V. P. Guinn, "Recent Developments in the Application of Neutron Activation Analysis Techniques to Forensic Problems," Journal of the Forensic Science Society 4 (1964) 184-191.
- d. D. E. Bryan and V. P. Guinn, "A Method of Comparing Gamma-Ray Spectra for the Presentation of Activation Analysis Results in Court," Transactions of the American Nuclear Society 7 (1964) 329.
- e. V. P. Guinn, "Non-Biological Applications of Neutron Activation Analysis in Forensic Studies," chapter in Methods of Forensic Science. Vol. 3, edited by A. S. Curry (Interscience Publishers, London, 1964), 47-68.

- f. R. R. Ruch, J. D. Buchanan, R. H. Pinker, V. P. Guinn, and S. C. Bellanca, "Neutron Activation Analysis in Scientific Crime Detection - Some Recent Developments, " Journal of Forensic Sciences 9 (1964) 119-133.
- g. R. R. Ruch, V. P. Guinn, and R. H. Pinker, "Detection of Gunpowder Residues by Neutron Activation Analysis, " Nuclear Science and Engineering 20 (1964) 381-385.
- h. D. E. Bryan and V. P. Guinn, "Use of Neutron Activation Analysis in Scientific Crime Detection, " General Atomic Report GA-6152, covering the period November 1, 1963 through October 31, 1964 (56 pages).
- i. D. E. Bryan, V. P. Guinn, and D. M. Settle, "New Developments in the Application of Neutron Activation Analysis to Problems in Scientific Crime Detection, " in the Proceedings of the 1965 International Conference on Modern Trends in Activation Analysis (Texas A & M University, 1965) 140-145.
- j. V. P. Guinn, "Forensic Applications of Activation Analysis, " chapter in Activation Analysis - Principles and Applications, edited by J. M. A. Lenihan and S. J. Thomson (Academic Press, London, 1965) 125-127.
- k. D. E. Bryan, V. P. Guinn, and D. M. Settle, "Applications of Neutron Activation Analysis in Scientific Crime Detection, " General Atomic Report GA-7041, covering the period November 1, 1964 through December 31, 1965 (54 pages).
- l. V. P. Guinn, "New Developments in the Application of Activation Analysis to Problems of Crime Investigation, " in the Proceedings of the 7th Japan Conference on Radioisotopes (Japan Atomic Industrial Forum, Tokyo, 1966) 563-569.

- m. V. P. Guinn (Editor), Proceedings of the First International Conference on Forensic Activation Analysis (General Atomic, San Diego, 1966) (314 pages).
- n. D. E. Bryan, "The Comparison of Paint Samples by Neutron Activation Analysis," in the Proceedings of the First International Conference on Forensic Activation Analysis (General Atomic, San Diego, 1966) 133-144.
- o. D. E. Bryan and V. P. Guinn, "Forensic Activation Analysis - Trace-Level Elements in Commercial Paints," Transactions of the American Nuclear Society 9 (1966) 589.
- p. V. P. Guinn, "The Determination of Traces of Barium and Antimony in Gunshot Residues by Activation Analysis," in the Proceedings of the First International Conference on Forensic Activation Analysis (General Atomic, San Diego, 1966) 161-176.
- q. V. P. Guinn, "Applications of Neutron Activation Analysis in Scientific Crime Detection," General Atomic Report GA-8013, covering the period January 1, 1966 through October 31, 1966 (62 pages).
- r. D. M. Settle, "Neutron Activation and Photonuclear Activation Analysis of Glass Samples," in the Proceedings of the First International Conference on Forensic Activation Analysis (General Atomic, San Diego, 1966) 147-160.
- s. V. P. Guinn, "Neutron Activation Analysis and Its Forensic Applications," in the Proceedings of the First International Conference on Forensic Activation Analysis (General Atomic, San Diego, 1966) 7-39.
- t. H. R. Lukens and V. P. Guinn, "Neutron Activation Analysis of Bullet Lead," Transactions of the American Nuclear Society 10 (1967) 66-67.
- u. D. E. Bryan, V. P. Guinn, and D. M. Settle, "Activation Analysis of Biological Samples of Forensic Interest," in Nuclear Activation Techniques in the Life Sciences (International Atomic Energy Agency, Amsterdam Symposium, 1967) 681-694.

- v. V. P. Guinn, "A State-of-the-Art Report on Forensic Activation Analysis, " in Law Enforcement Science and Technology, Volume 1, edited by S. A. Yefsky (Academic Press, 1967) 371-377.
- w. V. P. Guinn and R. H. Pinker, "The World-Wide Status of Forensic Activation Analysis, " General Atomic Report GA-7688 (1967) (24 pages).
- x. D. E. Bryan, V. P. Guinn, and D. M. Settle, "High-Flux Neutron Activation Analysis as an Investigative Tool in the Field of Criminalistics, " in Law Enforcement Science and Technology. Volume 1, edited by S. A. Yefsky (Academic Press, 1967) 371-377.
- y. H. R. Lukens, "Forensic Activation Analysis: Bullet Lead, " Transactions of the American Nuclear Society, 11 (1968) 80-81.
- z. V. P. Guinn, "The Current Status of Forensic Activation Analysis, " Transactions of the American Nuclear Society, 11 (1968) 78-79.

8.6 LIAISON WITH LAW ENFORCEMENT AGENCIES AND SOCIETIES

In efforts to learn the problems and techniques of the field of criminalistics, and to disseminate information to criminalists on the progress of this research in forensic activation analysis, the following groups were visited by V. P. Guinn:

CID Laboratory at Fort Gordon, Georgia
 CID Laboratory at Camp Zama, Japan
 CID Laboratory at Frankfurt, Germany
 CID Headquarters in Washington, D. C.
 Naval Intelligence Headquarters in Washington, D. C.
 U. S. Secret Service, Washington, D. C.
 State of California CII Laboratory, Sacramento, California
 Department of Criminalistics, University of California, Berkeley, California

IRS Laboratory, Washington, D. C. (on numerous occasions)

FBI Laboratory, Washington, D. C. (on several occasions)

Interpol Headquarters, St. Cloud, France

John Jay College of Criminal Justice, New York City

Forensic Science Department, Georgetown University,
Washington, D. C.

New York City Police Department Crime Laboratory

Philadelphia Police Department Crime Laboratory

Los Angeles Police Department Crime Laboratory

Bureau of Drug Abuse Control, Washington, D. C.

Also, as mentioned earlier, close liaison was established with the American Academy of Forensic Sciences (of which V. P. Guinn is a Fellow, and H. L. Schlesinger is a member), the California Association of Criminalists (of which V. P. Guinn is a member), the International Association for Identification, the National District Attorney's Association, and the American Society of Questioned Document Examiners.

9. SUMMARY

The present work clearly demonstrates that activation analysis, particularly TNAA (thermal neutron activation analysis) is a useful tool for the examination of a wide variety of evidence materials. At the very least it can provide useful data in supplement to those data acquired by more conventional means, and strong indications suggest that it will completely replace certain conventional techniques.

Unlike the discredited dermal nitrate method for testing whether or not a person had discharged a firearm (a test scarcely better than tossing a coin to indicate guilt or innocence), TNAA has been shown to provide a high degree of reliability for detecting gunshot residues. Considerable progress has been made to establish a basis from which to define the statistics of handblank values and gunshot residue values related to the TNAA test. This work continues, and when completed it will permit the criminalist to make definitive statements regarding the conclusions that can be derived from any given TNAA gunshot residue data.

Examination of elemental concentrations of paint and paper by TNAA has been shown to provide an excellent basis from which to judge whether or not two samples of apparently "identical" material could have come from the same manufacturer and production batch. Observed elemental concentrations, when divided into letter-coded ranges appreciably larger than the ranges of variability within a given batch, were found to have significant differences among ~ 40 batches of each material.

The use of TNAA to examine bullets has been shown to have potentially useful application, especially since there is a major probability that bullets of different origin can be discerned on the basis of antimony concentration alone.

As in the case of gunshot residue studies, work has continued on paint, paper, and bullets to enlarge the basis from which statistical inferences regarding individual applications of TNAA data.

Examination of hair by TNAA has given indications of potential usefulness. However, environmental contamination and the transient nature of some elements in hair impose difficulties for which completely satisfactory solutions have yet to be found.

Activation analysis has shown promise as a means of examining evidence samples of oil, grease, marijuana, amphetamine, whiskey, wood, and soil, also. The last two materials, neither of which have the desired attribute of homogeneity, require great care in sampling. Thus, the suspected source of an evidence splinter sample must be sampled immediately adjacent to the area from which the splinter came from in order to obtain a meaningful comparison.

Related activities in the field included actual case work in which activation analysis was used for the examination of evidence samples, the production of a film that described the application of the method, and dissemination of information regarding the work via papers, lectures, reports, and participation conferences (including organization of the first International Conference on Forensic Activation Analysis).

The experimental findings of the work described are of great value, of course. However, the full value of the method for examining evidence material will be realized when the trace elements and their concentrations among the population of that material have been fully defined. It will then be possible to give accurate statements concerning the probabilities of "identity" or "difference" of two samples by comparing the results of their examination by activation analysis. This will make it possible to give testimony of the highest quality.

REFERENCES

1. D. E. Bryan and V. P. Guinn, "Applications of Activation Analysis in Scientific Crime Detection," USAEC Report GA-5556, General Dynamics Corporation, General Atomic Division (May 1962 through October 1963).
2. D. E. Bryan and V. P. Guinn, "Use of Activation Analysis in Scientific Crime Detection," USAEC Report GA-6152, General Dynamics Corporation, General Atomic Division (November 1963 through October 1964).
3. D. E. Bryan, V. P. Guinn and D. M. Settle, "Applications of Neutron Activation Analysis in Scientific Crime Detection," USAEC Report GA-7041, General Dynamics Corporation, General Atomic Division (November 1964 through December 1965).
4. V. P. Guinn, "Applications of Neutron Activation Analysis in Scientific Crime Detection," USAEC Report GA-8013, General Dynamics Corporation, General Atomic Division (January 1966 through October 1966).
5. H. J. M. Bowen and D. Gibbons, Radioactivation Analysis (Clarendon Press, Oxford, 1963).
6. W. S. Lyon (Editor), Guide to Activation Analysis (D. Van Nostrand Co., New York, 1964).
7. J. M. A. Lenihan and S. J. Thomson (Editors), Activation Analysis -- Principles and Applications (Academic Press, New York, 1965).
8. C. M. Lederer, J. M. Hollander, I. Perlman (Editors), Table of Isotopes, Sixth Edition (John Wiley & Sons, New York, 1967).
9. R. L. Heath, Scintillation Spectrometry Gamma-ray Spectrum Catalogue, IDO-16880-1 and -2, 2nd Ed., 1964.

10. J. D. Buchanan, "Activation Analysis with a TRIGA Reactor, " Proceedings of the 1961 International Conference on Modern Trends in Activation Analysis (Texas A&M University, 1961), p. 72. Also GA-2662.
11. H. R. Lukens, "Estimated Photopeak Specific Activities in Reactor Irradiations, " USAEC Report GA-5073 (Excerpt), General Dynamics Corporation, General Atomic Division (1964).
12. H. P. Yule, "Experimental Reactor Thermal-Neutron Activation Analysis Sensitivities, " Anal. Chem. 37 (1964) p. 129.
13. H. P. Yule and V. P. Guinn, "Enhancement of Neutron Activation Analysis Sensitivities by Use of Reactor Pulses: Experimental Results for 13 Elements, " Radiochemical Methods of Analysis 2 (IAEA, Vienna, 1964), p. 111.
14. H. R. Lukens, H. P. Yule and V. P. Guinn, "Reactor Pulsing in Activation Analysis, " Nucl. Instr. and Methods 33 (1965) p. 273.
15. V. P. Guinn, "Neutron Activation Analysis with Reactor Pulses, " chapter in Activation Analysis -- Principles and Applications, edited by J. M. A. Lenihan and S. J. Thompson (Academic Press, New York, 1965) p. 69.
16. H. R. Lukens and J. K. MacKenzie, "Utilization of Reactor Pulses and Sub-Second Half Lives in Neutron Activation Analysis, " Trans. Amer. Nucl. Soc. 10 (1967) p. 85.
17. H. R. Lukens, "A Neutron Activation Analysis Method for the Determination of Be, Li, B, F, and Pb, " J. of Radioanalytical Chem., Vol. 1 (1968) pp. 349-354.
18. H. C. Harrison and R. Gilroy, "Firearms Discharge Residues, " J. Forensic Science 4, 1 (1959) pp. 184-199.
19. Nucleonics, 19 (12) (1961), p. 74.
20. D. J. Hughes and R. B. Schwartz, "Neutron Cross Sections, " BNL-325, 2nd Edition, 1958.
21. D. J. Hughes, B. A. Magurno, and M. K. Brussell, "Neutron Cross Sections, " BNL-325, 2nd Edition, Supplement No. 1, 1960.

22. Report of the President's Commission on the Assassination of President Kennedy, U. S. Government Printing Office, Washington, D. C. (1964) 816 pages.
23. R. E. Jervis, A. K. Perkons, W. D. Mackintosh, and M. F. Kerr, "Activation Analysis in Forensic Investigation, " Proceedings of the 1961 International Conference on Modern Trends in Activation Analysis (Texas A&M University, College Station, Texas, 1961), pp. 107-113.
24. R. F. Coleman, F. H. Cripps, A. Stimson and H. D. Scott, "The Trace Element Content of Human Head Hair in England and Wales and the Application to Forensic Science, " Atom. No. 123 (January 1967) pp. 12-22.
25. L. C. Bate, "Adsorption and Elution of Trace Elements on Human Hair, " International Journal of Applied Radiation and Isotopes 17 (1966) pp. 417-423.