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APPLICATIONS OF NUCLEAR SCIENCE IN CRIME INVESTIGATION

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INTRODUCTION

In forensic investigations the criminalist is called upon regularly to examine, analyze, and compare a variety of kinds of physical evidence that are involved in various kinds of criminal cases and to draw valid conclusions from these examinations that are relevant to the respective cases. The criminalist may be called upon to identify the nature of individual specimens (often very tiny) of possibly relevant materials collected at the scene of a crime, or from a suspect, to ascertain whether the specimens are particles or pieces of paint, metal of a certain type, bullet lead, glass, a dangerous drug or narcotic of a particular kind, blood, urine, semen, hair, a particular kind of fiber, safe insulation, grease, oil, soil, etc. Frequently the first step in such examinations is to conduct a series of physical measurements including visual and microscopic

examinations; for example measurements of density, refractive index, hardness, solubility in certain solvents, etc. Generally, nondestructive examination techniques are preferred, or at least ones that consume only a tiny portion of the evidence sample, so that such samples can be preserved for possible later presentation in court.

In most instances, however, a more comprehensive examination and comparison of evidence specimens is necessary in order to assess the evidentiary value of the various specimens collected in a particular criminal case. Usually, these further examinations involve quantitative analyses of samples, for certain specific elements or compounds, or for a large number of elements or compounds, so that specimens can be compared and probabilities of common origin can be estimated from the analytical results. In a large modern crime laboratory a staff of professionally trained criminalists has at their disposal quite an arsenal of analytical instruments for such analyses. These may include, for example, one or more optical spectrometers, emission spectrographs, atomic absorption and emission spectrophotometers, X-ray fluorescence spectrometers, and gas chromatographs.

In spite of the great usefulness of analyses carried out with such nonnuclear instruments, it is found that many kinds of physical evidence examinations and comparisons need even more powerful techniques, often used in conjunction with the more conventional techniques, if valid and useful conclusions are to be drawn concerning the relationships between the specimens, the crime, and the suspect or suspects. In recent years it has been shown that one nuclear technique, high flux neutron activation analysis (NAA), can be a powerful additional tool in the field of crime investigation. Although some other nuclear techniques such as radioisotope dilution, radiotracer methods, and gamma radiography have been of some use in forensic work, thus far it is only the NAA method that has been developed into a widely used nuclear method in the field of crime investigation. Quite recently, one conventional method of elemental analysis, X-ray fluorescence, has been greatly advanced by the use of radioisotopic sources and X-ray spectrometry utilizing Si(Li) or Ge(Li) detectors.

The Present Extent of Forensic Activation Analysis

As will be shown later, the NAA method only becomes a method of outstanding usefulness in the field of crime investigation if relatively high fluxes of thermal neutrons are available for the activation of evidence specimens—thermal neutron fluxes in the range of 10^{12}–10^{14} n/cm^{2}sec. In order to provide such high thermal neutron fluxes, it is essential that a research-type nuclear reactor be available. Since such reactors (100 kW to several MW) cost a few hundred thousand dollars or more, they are beyond the price range that can be considered by all but very large central crime laboratories. This fact, although a limitation to the wide, day-to-day usage of NAA in actual case work, has not deterred a very substantial degree of actual NAA case work; up to the present time, evidence specimens of a wide variety of types involved

in criminal (and some civil) cases have been analyzed by NAA in several thousands of cases, involving the analysis of approximately one hundred thousand evidence specimens, and the results of these analyses have been presented in court in hundreds of cases, particularly in the United States.

In the US the first laboratory to provide a regular forensic activation analysis service to law enforcement agencies and defense attorneys was the General Atomic Division of the General Dynamics Corporation in San Diego, California. Research in forensic activation analysis commenced there in late 1961, and case work started in late 1962. Through this service evidence samples involved in approximately one hundred cases have been analyzed and the results have been presented in US courts on a number of occasions.

The second group in the US to set up a regular forensic activation analysis operation was the US Treasury Department in Washington, DC. This work commenced in early 1963, and initially utilized the nearby Naval Research reactor. In early 1964 this group presented NAA results in court in the first two US court cases involving NAA results: US vs Anderson (New York, March 1964) and US vs Cornwell (Ohio, May 1964). The third US court case involved the group at General Atomic: California vs Woodard (California, July 1964). The Treasury Department group later switched to irradiations in the nearby National Bureau of Standards reactor. This group not only handles evidence specimens involved in cases concerning the Treasury Department, but also specimens from various other federal Departments and from many city, county, and state law enforcement agencies who request their assistance. This group continues to expand, and has employed NAA in the examinations of approximately one hundred thousand evidence samples involved in several thousand criminal cases. The group has presented NAA results in US courts on several hundred occasions.

The third US laboratory to form an activation analysis group for regular criminal case work was the laboratory of the Federal Bureau of Investigation, also located in Washington, DC. The FBI forensic activation analysis group commenced operations in early 1966, and initially also used the Naval Research Laboratory reactor, also switching later to the NBS reactor. The FBI group has utilized the NAA method for the analysis of thousands of evidence samples, involved in hundreds of criminal cases, and has frequently presented such results in US courts.

Other US groups have occasionally done some research in the field of forensic activation analysis, and/or become involved in one or a few court cases involving NAA results. However, until quite recently, only a few of these groups have developed continuing operations in connection with actual case work. These are groups at the University of Missouri in Columbia, the State University of New York in Buffalo, and the Georgia Institute of Technology in Atlanta, each of which provides some degree of forensic activation analysis service in its respective state.

A number of forensic activation analysis groups have also developed in law enforcement laboratories in several other countries: notably the Centre for

Forensic Sciences (Toronto, Canada), the Home Office Forensic Laboratory (Aldermaston, England), and the National Police Research Institute (Tokyo, Japan), plus some less fully organized groups in Argentina, Australia, Brazil, West Germany, and Thailand.

Early Development, and the 1966 and 1972 International Conferences

Aside from a few papers concerned with the neutron activation analysis of hair specimens for arsenic, in cases of suspected arsenic poisoning, which were published a few years earlier (1,2) or in the 1959 to 1962 period (3–7), the earliest publications concerning forensic activation analysis appeared during the period of 1959 to 1962. These publications presented forensic NAA research conducted in the laboratories of Jervis and colleagues in Toronto (8–11), of Leddicotte, Bate, and colleagues at the Oak Ridge National Laboratory (12–14), and of Guinn and colleagues at General Atomic (15). In this period, in particular, the NAA method was first applied to the multi-trace element characterization of human head hair and some other materials (8–14), and to the detection of gunshot residues (15).

During the period from 1963 to 1966, these same three groups conducted and published a considerable amount of further research in the field of forensic activation analysis. Also, a number of newer groups emerged. The status of the field was then well summarized in the 24 papers presented, from 5 countries, at the First International Conference on Forensic Activation Analysis (16) held at General Atomic in San Diego in 1966. At this conference, papers were presented on NAA studies of such evidence-type materials as hair, gunshot residues, paint, and glass.

In the six year period (1966–1972) following the First International Conference, much more forensic activation analysis research and case application work was conducted, more groups entered the field, and many more publications emerged. The studies of this period were then summarized at the Second International Conference on Forensic Activation Analysis (17) held in Glasgow, Scotland in 1972. The 34 papers presented at this conference, from 13 countries, covered studies of a wide range of evidence-type materials including hair, bone, gunshot residues, bullet lead, coins, whisky, safe insulation, soil, metals, glass, and fibers.

In early 1970, a forensic activation analysis bibliography (18) listed 135 publications in the field. By the end of 1971, the National Bureau of Standards activation analysis bibliography (19) listed 200 forensic activation analysis (FAA) publications. From 1964–1970 the results of several important large scale investigations, of several key evidence-type materials, were published: (*a*) the thesis of Perkons (20) in Canada on the FAA of human head hair, (*b*) a major report by Coleman et al (21) in England, also on the FAA of human head hair, and (*c*) a series of six approximately annual AEC reports (22–27) and a series of four special AEC reports (28–31) by Guinn et al at General Atomic. These special reports deal with the FAA of gunshot resi-

dues (28), paper (29), bullet lead (30), and paint (31). A large fraction of the published large scale background data on these five kinds of evidence materials, as analyzed by NAA, is contained in these publications by Perkons, Coleman et al, and Guinn et al.

RELEVANT FEATURES OF THE ACTIVATION ANALYSIS METHOD

Theory of the Method, and Techniques Used

The theory of the nuclear activation analysis method is well known, and hence will be treated only briefly here. Recent books and book chapters on the subject may be consulted if more detailed information is desired (32–36).

Nuclear activation analysis is a method of quantitative elemental analysis based upon the nuclear activation of the chemical elements present in samples, followed by the detection, identification, and quantitative measurement of the induced radionuclides. Samples can be activated by bombardment with thermal neutrons, fast neutrons, energetic charged particles, or energetic photons, but activation with thermal neutrons, in the high flux of a research-type nuclear reactor, provides the best detection sensitivities for the largest number of elements, and is by far the most widely used form of the activation analysis method. Essentially all of the forensic activation analysis research and application studies carried out to date have utilized thermal neutron activation analysis, and hence this discussion is limited to the NAA method.

If a sample to be analyzed contains N nuclei of a particular mass number A and atomic number Z (e.g. ^{50}Ti), and is exposed to a steady flux ϕ of thermal neutrons for a time period t_i, it is readily shown that the disintegration rate of its (n,γ) product (if it is a radionuclide, as is the case for ^{51}Ti) just at the end of the irradiation (i.e. at decay time zero) is given by the equation:

$$-dN^*/dt = N\phi\,\sigma[1 - \exp(-0.693t_i/T)], \qquad 1.$$

in which σ is the isotopic thermal neutron (n,γ) cross section, in cm^2/nucleus, and T is the half-life of the product radionuclide (5.79 min in the case of ^{51}Ti), expressed in the same units as t_i. The activation of each stable nuclide of each element present in the sample follows this same equation, the various stable nuclides differing from one another, in general, quite widely in the size of their (n,γ) cross sections, and the various induced activities differing from one another, in general, quite widely in their half-lives. Also, very importantly, the various induced activities differ considerably from one another in the energies of their decay γ-ray photons (if they emit γ rays, as essentially all of the induced activities of forensic interest do).

The N term of equation 1 in turn is given by the equation $N = waN_A/\text{at wt}$, in which w is the mass (in grams) of the element present in the sample, a is the fractional isotopic abundance of the target nuclide amongst the stable nuclides

of that element (e.g. 5.25% of Ti atoms are ^{50}Ti atoms, so $a = 0.0525$), N_A is Avogadro's Number (6.023×10^{23}), and at wt is the chemical atomic weight of the element (e.g. 47.90 in the case of titanium).

The parenthetical expression in equation 1, $1 - \exp(-0.693t_i/T)$, is called the "saturation term." It is dimensionless, and ranges in magnitude only from 0 (for $t_i = 0$) to 1 (for $t_i/T \to \infty$). It rapidly and asymptotically approaches the limiting value of 1 with increasing values of t_i/T, acquiring values of 1/2, 3/4, 7/8, 15/16, 31/32 . . . at t_i/T values of 1, 2, 3, 4, 5. . . . The limiting value of 1 is due to the fact that, with very long irradiations (relative to T), a steady state is reached, in which previously formed radionuclei of that type are decaying at the same rate that new ones of that type are being formed.

The observed counting rate of a particular induced radionuclide species, just at the end of an irradiation, will depend on its disintegration rate, $(-dN^*/dt)$—usually written as its "activity," A_0, its decay scheme, and the counting detection efficiency, ϵ. Thus, its counting rate, A'_0, is equal to $A_0 f \epsilon$, in which, typically, f is the fraction of its decays in which a γ-ray photon of a particular energy is emitted, and ϵ is the photopeak detection efficiency of the counter (including the counting geometry) for γ rays of this energy. At any later decay time, t_d, of course $A = A_0 \exp(-0.693t_d/T)$, and $A' = A'_0 \exp(-0.693t_d/T)$.

Rather than use equation 1, per se, which would require accurate knowledge of the various values of ϕ, σ, t_i, T, a, at wt, and, in counting, the decay scheme and ϵ, a comparator technique is used which eliminates this difficulty. When samples are activated, standard samples of all the elements of interest are activated at the same time, and then counted under identical conditions (except at different decay times). If the equations are written for sample and standard, corrected to t_0, and one equation is divided by another, all of the above-mentioned terms, being identical for sample and standard, cancel out. This leaves the simple equation actually used:

$$A'_0 \text{ (sample)}/A'_0 \text{ (std)} = w \text{ (sample)}/w \text{ (std)}, \qquad 2.$$

or, for any later decay time, t, if all the counting data are corrected to the same decay time:

$$A'_t \text{ (sample)}/A'_t \text{ (std)} = w \text{ (sample)}/w \text{ (std)}. \qquad 3.$$

Typically, the A'_t values are the γ-ray photopeak counting rates of sample and standard, at the same decay time (usually of the major γ ray, or one of the major γ rays of the particular radionuclide being measured), w (std) is accurately known, and w (sample) is the only unknown quantity.

There are two general postirradiation techniques used in NAA: (*a*) the nondestructive, purely instrumental technique of direct γ-ray spectrometry of each activated sample and standard, and (*b*) the destructive technique, involving radiochemical separations prior to counting. With the exception of measurements made to detect gunshot residues, which involve the radio-

chemical separation technique, most of the FAA work published thus far has utilized the purely instrumental, nondestructive technique.

In instrumental NAA measurements, each sample and standard is activated in a thermal neutron flux for a selected length of time, and then, after an optimized decay period, each is counted on either a NaI(Tl) or Ge(Li) multichannel γ-ray spectrometer. Typically, in even a single irradiation and a count at just one decay time, virtually any kind of sample, including all the kinds of samples that are of importance in crime investigation, will produce a γ-ray pulse height spectrum that exhibits quite a number of photopeaks [with a large Ge(Li) detector, even as many as 70], which arise from the γ rays emitted by one or more radionuclides of each of the elements present in the sample that become significantly activated [again, in the case of a Ge(Li) detector, perhaps as many as 20–25 radionuclides, of as many as 10–15 elements, may be detectable in a single spectrum].

In FAA studies to establish probabilities of common origin (discussed more fully in a later section), it is important to detect and measure quantitatively as many elements in the samples as is reasonably possible. In such measurements, the samples are often activated for two or three different lengths of time, with γ-ray spectrometry measurements made on them at from one to three different decay times after each irradiation. Because of the wide range of half-lives of the various (n,γ) product radionuclides of use in NAA studies, ranging from seconds to even years, and the effect of half-life on the irradiation saturation term and the subsequent decay: (*a*) a short irradiation, followed rapidly by a short counting period, optimizes the detection of those elements that form short lived (n,γ) products (e.g. 11.56-sec ^{20}F), (*b*) a medium length irradiation, followed at a longer decay time by a somewhat longer counting period, optimizes the detection of elements that form radionuclides of medium half-life (e.g. 2.576-hr ^{56}Mn), and (*c*) a long irradiation, followed after a long decay time by a longer counting period, optimizes the detection of elements that form much longer lived radionuclides (e.g. 45.6-day ^{59}Fe).

In activation analysis measurements, the results are quite independent of the chemical form, or forms, of the element in the sample, and of its valence state(s). The choice of sample size is quite wide, ranging from micrograms to as much as ten grams, as desired, and depending upon how much sample is available. Using larger samples, when possible, often provides improved concentration limits of detection for the various elements present, since the absolute limits of detection, for a given set of irradiation and counting conditions, are nearly constant over this range of sample sizes. Thus, if a particular element has a limit of detection of 0.001 μg, its concentration limits of detection in samples weighing 1 μg, 1 mg, and 1 g are, respectively, 0.1%, 1 ppm, and 1 ppb.

Features Especially Important in Forensic Work

The three principal aspects of the NAA method that make it especially valuable in forensic analysis, in addition to its good precision and accuracy, are: (*a*) its extreme sensitivities of detection for a very large number of

elements, (*b*) its multi-element simultaneous detection capability, and (*c*) the nondestructive nature of the purely instrumental form of the method. Each of these particular features is discussed below.

LIMITS OF DETECTION In the absence of appreciable interferences, the limits of detection by instrumental NAA (i.e. based upon direct γ-ray spectrometry of the activated samples) range from 10^{-6} μg, for a few ultrasensitive elements, up to as high as 100μg, for a few rather insensitive elements, under rather typical NAA conditions, namely, a thermal neutron flux of 10^{13} n/cm^{2}sec, a maximum irradiation period of 1 hr, and detection with a standard 7.5 × 7.5 cm NaI(Tl) detector (coupled to a multichannel pulse height analyzer). The median sensitivity (interference–free limit of detection) for 71 elements is about 0.002 μg. The approximate instrumental limits of detection for these 71 elements are shown in Table 1. Essentially the only elements that are not sensitively detected by NAA under these conditions are H, He, Li, Be, B, C, N, O (the eight elements of lowest atomic number), and P, S, Tl, and Bi. It should be noted that even these twelve elements can also be sensitively detected by one or more of the related activation analysis techniques: NAA followed by radiochemical separations and counting, or activation with fast neutrons, charged particles, or energetic photons. All 71 sensitivities can be improved further by use of higher thermal neutron fluxes, and about half of them (those for elements that mainly form medium or long lived products) can be improved further by using longer irradiation times. The bases of the detection limits shown in Table 1 are described in references 35 and 36.

If a Ge(Li) detector is used instead of a NaI(Tl) detector, many of the 71 limits of detection shown in Table 1 remain about the same, and some are increased somewhat. However, the greatly superior energy resolution of the Ge(Li) detector more than compensates for its lower photopeak detection efficiencies for the higher energy γ rays when complicated multi-element samples are being analyzed. When short lived activities are to be measured (e.g. 0.80-sec ^{207m}Pb, 24.4-sec ^{110}Ag, 2.31-min ^{28}Al, 3.75-min ^{52}V, etc),

Table 1 Instrumental neutron activation analysis limits of detection for 71 elements[a]

μg Limit	Elements
10^{-6} to 10^{-5}	Mn, In, Eu, Dy
10^{-5} to 10^{-4}	V, Rh, Ag, Cs, Sm, Ho, Lu, Hf, Re, Ir, Au
10^{-4} to 10^{-3}	Na, Al, Sc, Co, Cu, Ga, As, Br, Kr, Sr, Pd, Sb, I, Ba, La, Er, W, U
10^{-3} to 10^{-2}	Cl, Ar, Ti, Zn, Ge, Se, Ru, Te, Pr, Gd, Yb, Pt, Hg, Th
10^{-2} to 10^{-1}	F, Mg, K, Cr, Ni, Rb, Mo, Cd, Sn, Xe, Ce, Nd, Tb, Tm, Ta, Os, Pb
0.1 to 1	Ne, Ca, Zr, Nb
1 to 10	
10 to 100	Si, S, Fe

[a]Conditions: 1-hr irradiation at a thermal neutron flux of 10^{13} n/cm^{2}sec, followed by NaI(Tl) γ-ray spectrometry. Interference-free basis.

samples and standards are activated and counted one at a time. However, for the measurement of longer lived species, many samples and standards can be activated simultaneously and then counted later one at a time. With a TRIGA reactor (37) the 40-tube rotary specimen rack is especially helpful, since up to 40 specimens can be activated simultaneously, all at exactly the same thermal neutron flux, thus avoiding the necessity of using flux monitors. With a reactor of highly reproducible flux, in multi-trace element comparison work it is not even necessary to activate elemental standards along with the samples if standards of all the elements of interest have previously been activated and counted under the same conditions, and all of the data stored for repeated use.

Processing of the γ-ray pulse height data is normally carried out with a computer. Each spectrum is rapidly transferred onto magnetic tape, later to be examined on the computer by routines for peak searching, photopeak energy calculations, net photopeak area calculations, radionuclide identifications, decay corrections, and comparisons with standards to obtain μg and ppm values for each detected element, along with the standard deviation of each value (based on the counting statistics). Overlapping peaks, which occur more frequently with NaI(Tl) spectra than with Ge(Li) spectra, can be resolved into their components by another computer subroutine. Computer routines are also available to provide a print-out of all the digital data, and/or a plot of the spectrum (either smoothed or unsmoothed), if desired.

In forensic studies, the excellent limits of detection for most elements, generally considerably lower than those of the more conventional elemental analysis methods available in most crime laboratories, allow one to effectively analyze samples too small to be analyzed by conventional methods (e.g. a tiny chip of paint or glass, or a single strand of hair), to detect and measure very small amounts of elements of particular interest (e.g. small amounts of Ba and Sb in gunshot residues), and to detect and measure the concentrations of numerous characterizing trace elements in sample comparisons regarding probability of common origin (e.g. specimens of hair, bullet lead, paint, glass, opium, paper, etc).

MULTI-ELEMENT CAPABILITY As mentioned earlier, the fact that many elements can be sensitively and simultaneously detected and measured by instrumental NAA makes the method especially valuable in trace element characterization comparisons of evidence samples.

NONDESTRUCTIVE CHARACTER OF INSTRUMENTAL FORM When the instrumental form of the NAA method is used, analytical results are obtained without destroying the evidence sample. This is important in forensic work, as the sample is thus preserved for possible later presentation in court, for re-analysis if such should be required, or for other kinds of measurements. Technically, the process of neutron activation changes the elemental composition of a sample somewhat, but, in practical terms, the change in composition is completely negligible in all but a few extreme cases. For example, if a

sample containing some amount of manganese is activated for 1 hr at a thermal neutron flux of 10^{13} n/cm²sec, only 0.000048% of the Mn nuclei present are converted, by (n,γ) reaction, to ^{56}Mn. The ^{56}Mn nuclei decay by β^- emission, with a half-life of 2.576 hr, to stable ^{56}Fe. Thus, after activation, the sample still contains 99.999952% of its original Mn. If the sample originally contained 10.00 ppm Mn and no Fe, it would later still contain 10.00 ppm Mn and now also a trace of Fe: 0.00048 ppm Fe (in the form of ^{56}Fe). Since (n,γ) activation of ^{56}Fe only forms stable ^{57}Fe, this tiny generation of ^{56}Fe from the decay of ^{56}Mn would not be detectable by NAA.

With many kinds of materials, activation with thermal neutrons does not visibly or measurably alter the appearance or physical properties of the materials (e.g. properties such as density, refractive index, melting point, solubility, etc). There are some kinds of materials of interest, however, which do change their appearance somewhat when irradiated for some length of time. For example, a colorless glass specimen may develop a distinct color. Long irradiations of organic samples can cause radiolysis physical damage. Thus a sample of human hair, if irradiated for 100 hr at a thermal neutron flux of 10^{13} n/cm²sec, becomes very brittle, the individual strands changing their appearance under the microscope and readily breaking down into short segments (38). However, the elemental composition of such samples is not detectably altered, so the method is still "nondestructive" in this respect.

TYPES OF FORENSIC ACTIVATION ANALYSIS APPLICATIONS

The applications of NAA to forensic problems may be classified into two main categories, discussed separately below: (*a*) those in which one or more evidence specimens are analyzed for one or a few specific elements of interest, and (*b*) those in which two or more evidence specimens of the same type are compared with respect to (especially) their trace element concentrations, in order to assess the probability that they have a common origin.

Single- or Few-Element Applications

The principal forensic examples of this type of application are the use of NAA to (*a*) detect the presence of gunshot residues (and two closely related kinds of applications), and (*b*) determine the presence in hair of toxic elements such as arsenic and mercury.

DETECTION OF GUNSHOT RESIDUES For a number of years the regular crime laboratory procedure for the detection of gunshot residues present on the back of the gunhand of a person who had recently fired a gun was the so-called "paraffin test," also known as the paraffin glove test and the dermal nitrate test. It consisted of applying molten paraffin to the back of each hand of a suspect or victim in a shooting case, building them up with layers of paraffin

and gauze, allowing them to solidify, peeling off the casts, and then treating the inner surface of the casts with an aqueous solution of diphenylamine and sulfuric acid. This reagent forms a blue color when in contact with particles of unburned or partially burned gunpowder, small amounts of which are deposited on the back of the gunhand when a handgun (revolver or automatic pistol) is fired. Unfortunately this test is only qualitative, its results are rather subjective in interpretation, it is not extremely sensitive, and the same blue color is also formed by many other common nitrogen compounds. It was therefore found to frequently give false negative results (in test or known firings), and to frequently give false positive results, from other materials on the hands of the person tested. For these reasons, the dermal nitrate test has for quite a few years been no longer used by most good crime laboratories.

In 1959, Harrison & Gilroy (39) published a new kind of test for gunshot residues based on spot color tests for traces of barium, antimony, and lead removed from the back of the gunhand. They pointed out that the primers of almost all US ammunition, and most foreign ammunition, contain multi-milligram amounts of barium nitrate, antimony sulfide, and lead styphnate, and hence traces of these three metallic elements should also be blown back onto the back of the gunhand in a firing. Many crime laboratories endeavored to use the Harrison-Gilroy procedure, but again with very poor results. The tests were only qualitative, the results subjective, the sensitivities borderline, and other metallic elements often gave similar results. The results were again all too often false positives or false negatives.

In 1961, R. H. Pinker, the head of the Los Angeles City Crime Laboratory, with members of the General Atomic activation analysis group, decided to see if NAA would be capable of detecting the presence of two of these primer residues (Ba and Sb) in gunshot residues removed from the back of the gunhand after a firing. The third primer metallic element, Pb, was known to be rather insensitive to NAA, so it was not included. After initial successful exploratory tests at General Atomic, a lengthy systematic study was carried out, and a considerable background of data obtained and published (22–28) following earlier preliminary publications (15,40,41). After testing a number of methods for removal of gunshot residues from the back of the gunhand, a paraffin handlift procedure was selected as the most satisfactory. It involves application of a thin layer of high purity molten paraffin to the area included by the thumb web, back of the thumb, and back of the index (trigger) finger, allowing it to solidify, peeling it off, and pressing it down into a polyethylene vial, ready for activation in the reactor. Even a 30-min activation at a thermal neutron flux of 10^{12} n/cm^{2}sec provides quite adequate sensitivity for the detection and measurement of Ba and Sb, giving limits of detection of about 0.005 μg Ba (via the 166-keV γ ray of 82.9-min ^{139}Ba) and about 0.001 μg Sb (via the 564-keV γ ray of 2.80-day ^{122}Sb), using NaI(Tl) γ-ray spectrometry. These limits of detection are 100 to 1000 times lower than typical gunshot residue amounts.

Since the handlifts not only remove (generally invisible) particles of gunshot residues from the skin, but also considerable amounts of NaCl (from perspiration) and other materials, a postirradiation radiochemical separation is necessary if both Ba and Sb are to be determined, as is highly desirable. (Some workers have relied solely on the Sb levels, in which case a radiochemical separation is not necessary, the principal interfering induced activity, 14.96-hr ^{24}Na, decaying out sufficiently in a 3-day period to allow the detection of 2.80-day ^{122}Sb purely instrumentally). The radiochemical separation procedure developed by the General Atomic group, and widely used by many workers, involves: (*a*) boiling the activated paraffin handlift in a solution of dilute nitric and hydrochoric acids, some NaCl holdback carrier, and known carrier amounts of Ba^{2+} and Sb^{3+}, and (*b*) precipitating the Ba^{2+} as $BaSO_4$ and the Sb^{3+} as Sb_2S_3, after first removing any Cu^{2+} present by extraction of its dithizone complex in chloroform, at a pH of 1.5–2.0, followed by dissolution of the Sb_2S_3 in HCl and reprecipitation of the antimony as metallic Sb by reduction with $CrCl_2$ solution. The two precipitates, $BaSO_4$ and Sb, are counted separately on a NaI(Tl) γ-ray spectrometer. Barium and antimony standards are activated, precipitated, and counted in exactly the same manner. The carrier recoveries are determined by weighing the washed and dried $BaSO_4$, and by reactivation of the Sb. The ^{139}Ba and ^{122}Sb photopeak counting rates of the various samples irradiated at the same time are then corrected to the same decay time, normalized to 100% carrier recovery, and compared with the corresponding values for the standards to provide μg values for Ba and Sb in each sample analyzed. Details of the procedure may be found on pages 53–55 of reference 26. If NaI(Tl) γ-ray spectrometry is employed, it is very important that any induced 12.80-hr ^{64}Cu activity be removed, since otherwise this activity will contaminate the separated ^{122}Sb and will cause erroneously high apparent Sb values. With a NaI(Tl) detector, the 511-keV positron annihilation peak of ^{64}Cu overlaps with the 564-keV γ-ray peak of ^{122}Sb. This difficulty can be removed by either using instead a Ge(Li) detector, with its perhaps 20-fold better energy resolution, or by allowing a decay period of about three days, during which the ^{64}Cu activity will decrease considerably relative to the ^{122}Sb activity. Some groups prefer to use a moistened cotton swab for removal of any possible gunshot residues from the hand of a suspect, instead of the more tedious paraffin handlift procedure. In general, however, the Ba blank value for such cotton swabs can be appreciable and variable, whereas both the Ba and Sb blank values of the paraffin used in such work are quite negligible.

Recently, Rudzitis et al (42) have modified the regular radiochemical separation procedure somewhat, employed 7.2-yr ^{133}Ba and 60.4-day ^{124}Sb as internal standards (to measure carrier recoveries), and employed Ge(Li) γ-ray spectrometry after activation, with excellent results. A quite similar approach has been used by McFarland & McLain (43), using 7.2-yr ^{133}Ba and 2.71-yr ^{125}Sb as internal standards for the measurement of carrier recoveries.

Borra et al (44) have shown that many kinds of paraffin candles can be used, dropwise, to build up a suitable paraffin handlift. Scott et al (45) have shown that the individual Sb containing residue particles can be detected visually by autoradiography of activated handlifts.

The results of the extensive NAA gunshot residue study at General Atomic, plus corroborative and/or extending more recent results of other workers, may be summarized briefly as follows:

(*a*) Virtually all types and brands of US ammunition (with a few 0.22 caliber cartridge exceptions) contain both Ba and Sb in their primers.

(*b*) In the firing of a handgun, and to a lesser extent in the firing of a rifle or shotgun, measurable amounts of Ba and Sb are deposited, in particulate form, in a small area on the back of the gunhand.

(*c*) The amounts of Ba and Sb deposited in a particular firing depend upon many factors such as weapon caliber, type, condition, and barrel length; brand of ammunition used; chamber fired (in the case of a revolver); wind direction and velocity; and angle of firing.

(*d*) Multiple firings of a gun deposit very little more retained residue on the gunhand than a single firing, additional amounts apparently being offset by blowing off of some of the deposit laid down in preceding firings.

(*e*) Mere handling of a gun (unless its grip surfaces have first been carefully cleaned) transfers measurable amounts of Ba and Sb, from earlier firings, onto the palm of the hand.

(*f*) Gunshot residue is only loosely bound to the skin, is readily removed in even a single light washing of the hands, and gradually disappears, even without washing, in a matter of hours.

(*g*) Numerous uncontrolled variables result in an appreciable scatter of the Ba and Sb gunhand values even when the same weapon is fired repeatedly with the same brand of ammunition, with hand sampling between each firing.

(*h*) In general, the typical amounts of Ba and Sb found, deposited on the back of the gunhand in single firings, increase in the sequence: 0.22 caliber revolvers (0.39 μg Ba, 0.08 μg Sb), 0.22 caliber automatic pistols (0.70 μg Ba, 0.14 μg Sb), 0.38 caliber revolvers (1.3 μg Ba, 0.42 μg Sb), 0.44 caliber revolvers (1.4 μg Ba, 0.42 μg Sb), 0.45 caliber automatic pistols (3.6 μg Ba, 0.60 μg Sb), 0.25 caliber automatic pistols (4.7 μg Ba, 0.63 μg Sb), and 9 mm automatic pistols (7.5 μg Ba, 0.73 μg Sb).

(*i*) "Handblank" values for Ba and Sb (on the hands of persons of many occupations, who have not recently fired a gun) are generally much lower than the above average gunshot residue values, averaging 0.13 μg Ba and 0.015 μg Sb, but the variabilities cause some overlap, particularly in the case of 0.22 caliber firings, and there are a few occupations that often give considerably higher than average Ba handblank values, even fewer that give high Sb handblank values, and very few that give both elevated Ba and Sb handblank values.

(*j*) In actual case work it is vital to sample the hands of the suspect(s) and the victim (in the case of possible suicide) in any shooting case as soon as possible; to sample both hands of each person involved; to carefully avoid any contamination of the samples; and, if the weapon and fired or unfired ammunition are recovered, test firings, hand samplings, and analyses should be carried out with it and the same brand of ammunition.

With reference to the forensic interpretation of the various Ba and Sb values found in a particular case, two approaches have been developed: (*a*) a bivariate normal (BVN) statistical treatment, developed by Hackleman, and (*b*) a simpler "bin-type" statistical treatment, developed by Lukens. Both are described in reference 28. The BVN treatment assumes that the gunshot residue Ba and Sb values each follow a log normal distribution, which is somewhat of an approximation. The bin-type treatment does not make any assumption as to the nature of the distributions.

Gunshot residue results from NAA measurements have now been presented in court, especially in the US, on many occasions. The method is used extensively by both the FBI and Treasury laboratories. In almost all cases, the results, when presented in court, are interpreted only in a qualitative way—the expert witness testifying, for example, that "the results (for Ba and Sb) are indicative of the presence of gunshot residues." In only a few instances has an expert witness in court given a probability of firing, based upon the case results and the large scale statistical reference base of firing and hand-blank data of reference 28. Some court cases have involved the presentation of NAA data on residues from firings of shotguns or rifles, although the background of comparison test firing data is far smaller for such firings than it is for revolvers and automatic pistols.

DETERMINATION OF FIRING DISTANCE A closely related application is that of using NAA to determine the pattern of gunshot residue deposited on a surface in front of the gun muzzle, rather than in the back direction, on the gunhand of the firer, in order to estimate the distance between the gun muzzle and the victim (e.g. his shirt front) when the firing took place. Somewhat analogous to the case of the old paraffin dermal nitrate test, the rather similar Walker test (46) has some shortcomings. In the Walker test the surface to be examined for the presence of gunshot material is pressed against a sheet of paper that has been impregnated with a solution of sulfanilic acid and α-naphthylamine. The reaction of this reagent with unburned or partially burned gunpowder particles produces an orange red color. By means of similar tests made in test firings of the weapon and ammunition involved, at various firing distances, the pattern comparison can indicate the approximate firing distance at which the victim was shot. Unfortunately, the Walker test is not accurate beyond distances of two to at most three feet. In many cases of questionable suicides by shooting, it is important to be able to estimate firing distances well beyond two or three feet.

In Germany, in 1963, Baumgaertner et al (47) showed that improved firing distance determinations could be made by neutron activation of the residue material, followed by counting of the radioactive antimony per unit area as a function of radial distance from the bullet hole, again compared with similar measurements made on samples from test firings of the gun and ammunition at various firing distances. In a series of studies in Canada, Krishnan (48–50) extended this approach, initially measuring both 2.80-day ^{122}Sb and 12.80-hr ^{64}Cu by NAA with radiochemical separations. He found that the concentration of these deposited elements falls off rapidly with increasing distance out from the bullet hole, and that firing distances up to about 5 ft can be estimated with reasonable accuracy and precision. The Sb results proved to be the more reliable, and they can be obtained by purely instrumental NAA, after a few days decay. The Sb comes from both the primer and the bullet lead, which in most cases contains from 0.1 to 3% Sb, added as a hardening agent. The Cu comes from ablation of the cartridge case and the primer case, and, in the case of copper jacketed bullets, the bullet itself. X-radiography shows that the deposits also contain specks of lead, especially from unjacketed bullets, but probably some also coming from the primer. Krishnan (51) has also employed autoradiography on activated samples of cloth, in the region of a bullet hole, to estimate firing distances, approximately, at shorter distances. The autoradiographic technique, which mainly detects ^{122}Sb, has also been used quite recently in Germany by Schmitz (52), and in Canada by Gislason & Pate (53). In the work of Menke et al (54) in Germany, firing distance curves were obtained by NAA and rapid counting of the 4.2-min ^{122m}Sb and 0.80-sec ^{207m}Pb activities, and in some cases by means of a longer irradiation, radiochemical separations, and counting of the 2.80-day ^{122}Sb and 82.9-min ^{139}Ba activities. Their maximum measurable firing distance (with a 0.22 caliber rifle) was 2 m.

IDENTIFICATION OF BULLET HOLES Another type of FAA application that is closely related to the NAA detection of gunshot residues, and the NAA determination of firing distance, is that of determining whether a hole or slit in some type of material (e.g. cloth, wood, flesh, etc) was caused by a bullet. It should be noted that a bullet hole in many kinds of materials does not always look anything like a circular hole; for example, passage of a bullet through a loosely woven fabric usually merely results in a slit that almost returns to the original fiber alignment configuration. At very short firing distances, other analytical methods, or X-radiography (looking for specks of lead), can often determine whether a hole was caused by a bullet. However, at longer firing distances these other methods are not sufficiently sensitive to make such determinations. The much better sensitivity of reactor flux NAA, for the elements of interest, has proved to be very useful in extending the conventional methods to much greater firing distances.

The first NAA studies devoted to the identification of bullet holes were those published in 1967 by Krishnan (48) and by Schlesinger et al (55,56).

These first studies were followed by additional studies by Krishnan & Nicol (57) and by Krishnan (51). The technique developed is to activate either a small section of the material that includes the suspected bullet hole, or material swabbed from the suspected bullet hole, and then determine whether significant amounts of activities from elements associated with firings are detectable. The elements of interest are Ba, Sb, and Pb (from primers), Cu (from Cu jacketed bullets and from the cartridge case and the primer case), Sb and Pb (from the bullet), and perhaps Zn (from brass cartridge cases). In the work of Schlesinger et al (55,56), it was possible to measure microgram amounts of Cu and Sb by instrumental NAA in bullet holes made in leather and other materials. By an indirect method they were also able to determine Pb—by preparing special test bullets which contained indium alloyed with the Pb. They did not observe any Ba or Zn activities, but might have been able to if they had carried out radiochemical separations before their NaI(Tl) γ-ray spectrometry. They noted that a copper jacketed bullet rubbed off more Cu and less Pb in a bullet hole, whereas an unjacketed lead bullet rubbed off more Pb and less Cu.

DETECTION OF TOXIC ELEMENTS IN HAIR As was cited earlier, the first applications of NAA in the field of crime investigation involved the detection and measurement of one toxic element, arsenic, in specimens of human head hair (1–7). In cases of chronic arsenic poisoning, that is, cases in which sublethal doses of arsenic are administered to an individual at various times, eventually, in some cases, accumulating sufficiently in the body to cause death, the body endeavors to excrete as much of the arsenic as possible, and excretion into hair is one of the pathways. Since a strand of growing hair grows from the follicle (root) end fairly steadily (typically, about 0.3 mm/day, i.e. about 10 cm/year for human head hair), and the excreted As enters the hair strand from the blood stream through the follicle, it is found that the As level varies along the length of a growing hair strand in a pattern that is related to the magnitude and time spacing of the various administered doses of As. If a large amount of hair is available for analysis, the As contents of sections taken at various distances from the root ends can be detected and measured by regular chemical analysis methods. However, if only a small amount of hair is available, perhaps only a single strand, and if it is necessary to section it into 1-mm (~ 3-day growth) pieces, a much more sensitive analytical method, such as reactor flux NAA, is needed. Another toxic element excreted into hair is mercury, which also can be sensitively detected by NAA.

In a fascinating study in Scotland, Smith and co-workers (5, 7, 58) analyzed a number of samples of Napoleon's hair, taken during the last five years of his life and including samples taken just after his death, for arsenic. Careful analysis of 1-mm sections (by reactor irradiation followed by radiochemical separation of the induced 26.4-hr ^{76}As activity and β^- counting) enabled them to plot As profiles along the hair lengths, and estimate the approximate dates when As was administered to Napoleon, presumably by his various physi-

cians, as medicines, in efforts to cure him of his many illnesses. In some regions of his hair, As levels as high as 40 ppm were found—compared with normal levels of about 1 ppm.

A number of other workers have used the NAA method for forensic measurements of As in hair: Atalla et al (59) in Brazil; Baró et al (60) in Argentina; Erickson (61) in Canada; Krishnan & Erickson (62) in Canada; Wyttenbach et al (63) in Switzerland; and Jervis et al (9) in Canada. Additional As in hair studies in Scotland have also been published by Smith (64) and by Smith & Lenihan (65). Complications in the determination of As in hair have been pointed out by Lima (66), and by van den Berg et al (67) in The Netherlands.

Multi-Element Trace Characterization Applications

An even broader field of application of NAA to forensic problems is that in which two or more evidence specimens of a particular type, involved in a given crime, are compared with one another via their elemental compositions (and especially their trace element compositions), in order to assess the probability that they have a common origin; for example, to answer such questions as: Did this sample of hair, found at the scene of a murder, come from this person —the suspect? Or: Is this speck of paint, found in the pants' cuff of the suspect, of the same brand and production batch as paint on a jimmied door frame, in a burglary case? This is not a new principle, but rather is an extension of the principle of trace component characterization, to assess the probability of common origin, that has been used to various degrees in crime investigation work for many years. For example, it has long been common practice to compare paint specimens by means of their elemental compositions, as measured by emission spectrography, and more recently, to compare various liquids, such as "moonshine" whisky, by means of gas liquid chromatography. The application of NAA to such specimen comparisons has in many instances provided much more information on trace element levels than was possible before (and data on more trace elements in a given specimen), more precise results than are provided by emission spectrography, and a nondestructive analysis. It has also led to a more mathematical, statistical approach for the treatment of the data, to establish actual numerical probabilities of common origin.

The NAA method has been applied fairly extensively to the problem of the trace element characterization of such important kinds of evidence materials as human head hair, bullet lead, paint, and glass. Each of these kinds of application studies is discussed in moderate detail below. Similar, but much less extensive NAA studies have also been carried out on a variety of other kinds of relevant materials such as marijuana, opium, heroin, paper, soils, adhesive tapes, etc. These are discussed only very briefly below.

The principle of trace element characterization, with respect to probability of common origin, basically states simply that two specimens of the same general kind of material may well have closely similar major element and minor element compositions, but will differ quite significantly in their trace

element levels if they do not have a common origin, whereas they will also be closely similar in their trace element levels if they do have a common origin. The principle applies to both natural and manufactured materials.

HAIR The first application of NAA to the problem of trace element characterization of an important evidence type material was concerned with human head hair. This application was pioneered by Jervis and co-workers, particularly Perkons, in Canada (9, 11, 20, 68–72). In his PhD thesis, Perkons (20) presented quantitative instrumental NAA data for 20 elements found in specimens of human head hair from some 770 persons. The samples were not single strands of hair, but instead each sample was a bundle of many strands obtained from a particular person. The hair samples were each given a simple washing with solvents (water, alcohol, acetone) prior to irradiation to remove as much as possible of any adhering external contaminants (dust, grease, etc) and water-soluble contaminants (perspiration, etc), but hopefully not extracting significant amounts of any of the internally bound trace elements.

In this extensive study, Perkons detected and measured, in toto, the 20 elements Na, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Ag, Sb, Cs, La, Au, and Hg. Whereas some elements were found in all or nearly all the hair samples, but generally at a wide variety of concentrations, many of the elements were found in only a fraction of the samples. In 99% of the samples, 12 or more elements could be detected and measured. Since the activated samples had to be transported quite a distance from the reactor to his laboratory in Toronto, the shortest lived induced activity that could be detected was 2.56-hr ^{65}Ni. Each sample received an activation of about 50 hr at a thermal neutron flux of about 10^{13} n/cm^2 sec, and then was counted on a NaI(Tl) 200-channel γ-ray spectrometer. Calculations of the ppm values were carried out on a computer via a weighted least-squares spectrum fitting program and comparisons with the corresponding counting rates of similarly activated and counted elemental standards.

Perkons' concentration frequency histograms for each element exhibit variously skewed semigaussian shapes—for some elements severely skewed, for others moderately skewed. For a number of the elements, a log concentration frequency plot is more nearly gaussian. Depending upon the element, the range of concentration found amongst the ~770 persons whose hair was analyzed was anywhere from 10-fold to nearly 1000-fold. For example, Perkons' data for zinc are presented in summary form in Table 2. Omitting two extremely high Zn values, his remaining 763 Zn values ranged from as low as 10 ppm to as high as 3040 ppm, a range of over 300-fold. The most probable value was ~450 ppm, and the median value was ~600 ppm.

In addition to his multi-element study of bundles of hair strands from some 770 individuals, Perkons also conducted smaller scale studies of the hair of twins and of members of the same family, of selenium workers, and of persons fed silver in their diet. In general, he found that the hair of one member of a set of twins was considerably more similar to that of his or her twin than

would be expected purely statistically from the overall population. However, considerable differences in a number of elements were observed, even in these extreme cases. Among members of a given family living together, there were also some similarities, but much less pronounced than in the case of twins. Hair of workers in a selenium mine was definitely higher in its Se content than for many other persons, but not strikingly higher. The hair of persons fed a silver supplement in their diet did show increased Ag concentrations, but again not strikingly higher. His measurements also showed that prolonged soaking of hair specimens in distilled water, or in his water-alcohol-acetone washing liquid, would alter the concentrations of some elements appreciably and others very little. Some methods of hair treatment (shampooing with detergents, bleaching, dyeing) were also found to alter some element concentrations appreciably and others very little. Perkons also found measurable, but not large, correlations between the concentrations of some elements in hair and the sex of the individual, and with the natural color of the hair. He also found that some pairs of elements exhibited concentrations that were somewhat correlated with one another. Taking into account all of these variables, Perkons estimated that if two bundles of hair matched one another fairly closely in the levels of all of the elements detected, and 10 to 15 elements were detected and measured, the probability of an accidental match was only, at most, 10^{-6}–10^{-8}. That is, the number of persons having a given modal hair composition (with a reasonable range allowed for each element concentration) ranges from about one person in a million (for modal concentrations of 10 elements) to about one person in 100 million (for modal concentrations of 15 elements). Perkons concluded that the eight most significant elements for NAA hair matching were Zn, Mn, Cu, As, Se, Ag, Fe, and Co. He considered five others to be possibly useful elements: Au, Br, Sr, La, and Hg, and seven others to be appreciably less significant: Na, Cr, Ni, Ga, Rb, Sb, and Cs.

The findings of Jervis and Perkons created considerable interest among forensic scientists because (*a*) hair is frequently found as physical evidence

Table 2 Perkons' NAA values for zinc in the head hair of 763 persons[a]

ppm Zn	% of Persons	ppm Zn	% of Persons
0–200	8.4	1600–1800	2.2
200–400	17.5	1800–2000	1.0
400–600	24.0	2000–2200	1.2
600–800	18.2	2200–2400	0.2
800–1000	12.7	2400–2600	0.6
1000–1200	7.5	2600–2800	0.3
1200–1400	3.8	2800–3000	0.1
1400–1600	2.2	3000–3200	0.2

[a]Tabulated from data contained in reference 20.

at the scene of crimes of violence, such as murders and rapes which involved a struggle, (*b*) no other method was available to assess the probability that the hair of a suspect in such a case matched that found at the scene of the crime, and (*c*) their results indicated that NAA could provide extremely high probabilities of common origin if indeed two specimens of head hair were really from the same person. It should be noted that essentially the only other method of comparing hair specimens that had shown any promise of forensic usefulness at all was that of microscopic examination, in which hair specimens are compared as to average diameter, number of scales per centimeter, scale shapes, appearance of the medulla, etc. Such measurements can often show that two specimens did not come from the same person, but essentially complete microscopic matching of two specimens by no means proves that they are from the same person. It merely means that they might be from the same person. (Microscopic examination is of value to determine whether the hair is human or animal hair, and, if human, whether it is head, body, or pubic hair).

Stimulated by the findings of Jervis and Perkons, a number of other groups embarked on NAA studies of hair. In England, Coleman et al (21, 73) performed instrumental NAA measurements on samples of head hair from about 800 individuals from throughout England and Wales. Their procedure differed in some respects from that used by Perkons: (*a*) samples were cleaned by refluxing with diethyl ether, rather than by washing with water, alcohol, and acetone, (*b*) each sample was given two different reactor irradiations, 30 min at a thermal neutron flux of 4×10^{12} n/cm^2 sec, followed by a 10-min count after a decay period of 20 min; and 4 to 5 days at the same flux, followed by counting after decay periods of 1, 5, and 12 days. The shorter irradiation period/shorter decay period enabled them to detect and measure some elements in hair that form short lived (n, γ) products (e.g. 37.29-min^{38} Cl, 24.99-min^{128} I, and 8.8-min^{49} Ca) that were not detected in the work of Perkons. They also used NaI(Tl) γ-ray spectrometry, and a least-squares computer program. In all, they measured the levels of 12 elements in all the samples (Na, Cl, Mn, Br, I, Cu, Au, Hg, Cr, Zn, Sb, and Ca), as well as three other elements in some of the samples (Se, Ag, and Ba). Coleman et al found that their data for these 12 elements could be represented quite well by log normal distributions. They also found that there were small, but statistically significant, differences for most elements between the distribution for males and that for females. Due mainly to the different population studied, and the different hair cleaning procedure used, the mean value and spread of the population distribution curve, for each element, differed appreciably from the corresponding values obtained by Perkons for those elements measured in both studies. In both the studies of Coleman et al and Perkons, the measurement precision on an individual sample was generally much better than the inter- or intra-person variability.

Coleman et al (21, 73) also conducted a limited study of the variability of hair elemental composition among individual strands of hairs taken from the

head of a given individual. These measurements showed that the strand-to-strand variation in the elemental composition of the hair from any one person was quite appreciable. Although the inter-person relative standard deviation for manganese was about ±103%, the intra-person relative standard deviation was only about ±30%. For zinc, the difference between the two values was less: ±39% for the inter-person σ_{rel} and ±20% for the intra-person σ_{rel}. Since, in many criminal cases, individual strands of hair, rather than bundles of hair strands, must be compared, these results pointed out that the statistical interpretation of NAA hair data obtained in actual case work would often be appreciably more complicated, and less conclusive, than was indicated by Perkons and Jervis. Since human head hairs weigh only in the range of about 0.02–0.2 mg/cm, even the high sensitivity of high flux NAA is strained if a short single strand of hair must be analyzed for many elements. Since the long reactor irradiation then necessary destroys the physical characteristics of the hair, any microscopic examination must be done first, taking care not to use one of the commercial mounting media that can contaminate the sample.

In the study by Coleman et al (21, 73) another aspect of hair comparisons by instrumental NAA was also investigated in a limited way: the change in the hair composition of a particular individual with time. Hair samples were obtained from six persons at one to two week intervals over a period of seven months, and these hair bundle samples were cleaned and analyzed by their regular procedure. The results showed that the head hair elemental composition of any one individual generally changed relatively little during a period of one to three weeks, but changed quite markedly over a period of several months. These findings pointed out an additional difficulty in the application of NAA to the comparison of hair specimens involved in actual case work: if hair specimens found at the scene of a crime were to be compared with hair of a suspect, the comparison sample from the suspect would have to be obtained not more than at most about three weeks after the time the crime took place. Otherwise, the combined factors of possible dietary changes, changes in environmental contamination of the hair (that which became sufficiently bound to the hair that it could not be removed by the washing procedure used prior to analysis), and changes resulting from shampooing, bleaching, dyeing, etc would in general change the elemental composition of the hair of the suspect so much that it could no longer be matched with the hair found at the crime scene even if, in fact, the crime scene hair was his.

Another aspect of hair comparisons that had been largely ignored in both the Canadian and English studies was the fact that the hair strands on the head of any one person, at any given time, have different growth histories, and hence probably appreciably different elemental compositions. In a simplified fashion, one may say that the hairs on a person's head fall into three classes: (*a*) growing hairs, (*b*) hairs that have ceased to grow, but are still firmly attached to the scalp, and (*c*) hairs that have not only ceased to grow, but which also have shrivelled roots and are about to fall out. This aspect of hair growth cycles was discussed in detail by Kerr (74). If, in a struggle, a clump

of hair is pulled out, it will generally contain strands of all three types. However, those strands that readily fall out, or are removed by very light brushing or combing, will be mainly those of the third class. As pointed out by Guinn (75), for proper comparisons of hair samples, only samples of the same class should be compared with one another, i.e. living hairs with living hairs, or dead hairs with dead hairs. With hair specimens to which the root is still attached, microscopic examination will show whether the hair was a growing hair (or had only recently stopped growing) at the time it was removed from the scalp, then showing a full bulbous root. If the hair sample had ceased growing for some time before it was removed from the scalp, its root bulb will be quite shrivelled. Guinn (75) also pointed out that, for proper comparison, hair specimens of equal length (and hence representing approximately equal time periods), measured from the root end, should be compared with one another. It should be remarked that, once a hair specimen has been obtained, it can be stored for long periods of time with no further change in its elemental composition, if stored properly.

During the period from 1965 to 1973, various other smaller scale studies of various aspects of NAA hair comparisons have been published, and many conflicting opinions expressed. Many have concentrated on the problems introduced by various sources of external contamination of hair (59, 66, 67, 76–81). Since the principal component of hair is the protein keratin, which is a good ion exchange material, contamination from external solutions can be appreciable. Other studies contain additional useful information on other aspects (82–85). Several NAA studies of the variation of element concentration along lengths of individual strands of hair have shown that they can sometimes be quite marked (86–89). An excellent statistical approach to the interpretation of multi-element NAA data involved in the comparison of forensic specimens (especially hair) has been developed by Parker (90, 91). Data obtained from the NAA examination of hair specimens have been introduced in US courts on a number of occasions with mixed success. In the earlier cases, when not all of the complications involved in hair comparisons were adequately realized, unjustified conclusions were sometimes drawn from the data. More recently, forensic scientists have been more cautious in their use of NAA results from hair comparisons, and in the firmness of their conclusions when presented in court. A number of both good and bad examples of NAA results on hair (and some other evidence materials), as presented and interpreted in various US court cases, have been described by Guinn (92). Karjala (93) has presented a very good legal summary of US court cases that have involved NAA results obtained on evidence samples of hair and numerous other kinds of materials. As yet, only a few NAA measurements have been published on human pubic hair, often involved as physical evidence in rape cases.

To summarize the situation regarding the FAA comparison of hair specimens involved in criminal cases, it may be stated that, although numerous complications have greatly diminished the initial enthusiasm for this application of NAA, it can still be very useful in cases involving specimens that are ob-

tained from a suspect (or suspects) fairly soon after a crime was committed, in the absence of significant intervening contamination. It can also often be useful in determining whether hair found in a suspect's automobile came from the victim of an attack or murder. If comparable lengths (measured from the scalp end) of comparable hairs (all living hairs, or all dead hairs) are washed identically and then analyzed under conditions such that a sizable number of elements can be detected and measured quantitatively, it is possible to deduce fairly reliable probabilities of common origin. Such probability estimates should take into account the intra-person strand-to-strand variability of the individual's hair, and the large scale data available on inter-person variations in the concentrations of the various elements in human head hair. The problem is appreciably simplified if one can legitimately analyze a whole clump of hair, rather than individual strands, as in cases in which a murder victim has pulled out a clump of hair from the murderer, or in which a clump of the hair of the victim of a hit and run accident is found adhering to the bumper of a suspect's automobile. If a suspect is apprehended almost immediately after a crime, it is sometimes useful to compare his hair with hair at the crime scene, by NAA, without washing the samples prior to irradiation. The external contaminants in such instances may help, rather than hinder a comparison, and may be linked to the suspect's occupation (81). At present there are not sufficient background data to allow one to draw supportable conclusions regarding common origin from data on pubic hair specimens. Unfortunately, only a fraction of the criminal cases involving evidence specimens of hair meet the criteria necessary for the full utilization of the NAA method.

OTHER BIOLOGICAL MATERIALS Just as the factors of heredity, diet, and environmental exposure affect the trace element composition of human head hair, resulting in the possibility of human individualization by means of the trace element composition of his or her hair, at a particular time, or the possibility of establishing a common origin for two or more specimens of human head hair, via a detailed NAA comparison, so, at least in principle, many other biological materials encountered as physical evidence in crimes should show analogous variations in their trace element concentrations.

To date NAA has been applied from the forensic viewpoint to only a few other such biological materials, and in only relatively small scale studies. Some of the NAA studies on hair, such as that by Perkons (20), have also included some measurements on human fingernails. Some studies have been conducted on samples of raw opium, (94, 95), as well as a brief study of samples of marijuana (24). None of these studies has been extensive enough to allow useful probabilities of common origin to be calculated in actual case work when two or more specimens of one of these three kinds of materials are compared via instrumental NAA. The results do indicate, however, that fingernail trace element variations rather similar to hair trace element variations do occur, although for any given person the head hair composition is appreciably different from the fingernail composition. Similarly, specimens of

opium and marijuana that are grown in different areas of a country, or of the world, show considerable variation in their trace element compositions, as might be expected from the fact that they have grown in a variety of kinds of soil, water, and degree of sunlight.

Although soil is predominantly an inorganic, rather than an organic, material, it may be included for discussion in this section inasmuch as it is natural, rather than manufactured. Some instrumental NAA studies have been carried out on soil samples from different geographical regions in the US (96–98). They reveal, not unexpectedly, that many elements can be detected and measured, in even quite small samples of soil, by a combination of instrumental NAA and atomic absorption (96, 97), or by a combination of instrumental NAA and NAA with radiochemical separations (78), and that wide ranges are found for each element among different samples of soil. However, it is also found that, even in a given micro location, there are wide vertical and lateral variations in the levels of many of the trace elements. These variations make the application of elemental analysis methods of rather little use in actual case work. In spite of this difficulty, one group has presented NAA results on soil specimens, and conclusions based on such results, in US courts on a number of occasions.

MANUFACTURED MATERIALS Published results of NAA studies of a number of kinds of manufactured materials of forensic interest show that, in general, the trace element compositions of specimens of a given type can be used to estimate probabilities of common origin when two or more evidence specimens in a case, of the same type, are compared with one another. However, in general, "common origin" is here usually limited to establishing the probability that the specimens were made by the same manufacturer, or by the same manufacturer in a particular manufacturing plant, or by the same manufacturer in a particular production batch—depending upon the extent of comparative background information that is available. To date, only a few such manufactured materials have been studied sufficiently to provide even a limited basis for such probability estimates in actual case work: paint, bullet lead, and glass.

Paint In a moderately large scale instrumental NAA study of common types of paints, both fresh paints and specimens removed from a variety of common painted objects (automobiles, houses, furniture, etc), the General Atomic group analyzed a few hundred paint specimens of different origins, plus many replicate determinations and analyses of samples of the same manufacturer but from different production batches (26, 31). Both NaI(Tl) and Ge(Li) γ-ray spectrometry measurements were used. The maximum number of elements detected and measured in any one paint specimen was 25, and the average number was 15. Altogether, 37 elements were detected in one or more samples: Na, Mg, Al, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Br, Sr, Mo, Ag, Cd, In, Sb, I, Ba, La, Ce, Sm, Eu, Dy, Lu, Hf, Ta, W, Au,

Hg. Many of these elements were found only at trace levels, whereas some (Na, Al, Cl, K, Ca, Ti, Cr, Fe, Cu, Zn, Br, Mo, Sb, Ba) were found in some samples at major or minor levels, and in others only at trace levels.

In the later stage of this study (31), the results were presented for 37 elements found in 156 paint specimens removed from a great variety of painted objects. The results were grouped into five color classes, and the concentration levels were classified within each color class, for each element, into 20 concentration bins (three logarithmically equal bins per decade of concentration) represented by letter codes ranging from *A* (< 0.21 ppm) through *T* (210,000–460,000 ppm). This bin coding approach is used in a sample comparison technique based upon combinatorial statistics, and appears to work very well to establish probabilities that two paint specimens of a given color are of the same manufacturer, or even of the same production batch. An earlier effort, based upon a multivariate normal statistics approach, turned out to be less accurate (as well as more complicated), because most of the elemental concentration/frequency distributions for paints turned out not to be log normal. Due to the fact that many elements appear in some paints as major constituents, in others as minor constituents, and in others as trace constituents, many of the frequency distributions exhibit two or even three peaks, and many also are skewed, even when plotted logarithmically. This report (31) contains a wealth of information on the elemental compositions of paints, on the pigment, filler, and extender sources of the elements frequently found in paints as major constituents, on element/element correlations in paints, and on the statistical approach to comparing paint specimens.

Other accounts of smaller scale FAA studies of paints have been published by Aufroix et al (99), Bryan (100), Snow et al (101), Wyttenbach (102), and Snow & Washington (103). The NAA method has also been used to examine paint specks removed from paintings of questioned authenticity, for example, by Keisch (104), Miller et al (105), Houtman & Turkstra (106), and Lux et al (107). Sayre (108) has used neutron activation autoradiography in the authentication of paintings.

Bullet lead Another material of forensic interest that has been studied fairly extensively by means of instrumental NAA is bullet lead. The General Atomic group analyzed several hundred bullets, of various types, calibers, and manufacturer sources, as well as many groups of bullets from individual boxes of cartridges, and from individual production batches. All of this work is described in reference 30. It was found in this study that the number of minor and trace elements that can be detected and measured by instrumental NAA in small samples of bullet lead is much smaller than the number of elements that can be found in such materials as hair or paint. The reason for this is the high levels of antimony activities generated in most samples of bullet lead by (n, γ) activation. Almost all brands of bullet lead contain antimony, alloyed with the lead by the manufacturers or suppliers as a hardening agent. Depending upon the manufacturer and the type of bullet, the Sb

concentration usually lies in the range of 0.1–3.2%. Homecast reload bullet leads sometimes even include Sb levels as high as 8%. When samples containing appreciable concentrations of Sb are activated with thermal neutrons, high levels of 2.80-day ^{122}Sb and 60.4-day ^{124}Sb are generated, each of which emits gamma rays of a number of energies, in the range from 564–2088 keV. These high levels of activity make it rather difficult to detect activities due to traces of very many additional elements. However, the Sb concentration itself proves to be a fairly effective means of deciding whether two specimens of bullet lead do not have a common origin. Measurement of the levels of a few additional elements that can be detected, e.g. Al, Cu, As, Ag, Sn, can lead to at best only a moderately strong probability of common origin. Unfortunately, many bullets have Sb concentrations in the range of 0.7–0.8%, and the levels of Cu and As are appreciably correlated with the Sb levels.

In this study it was also ascertained that the bullet lead composition was usually quite constant (*a*) at various points within a given bullet, and (*b*) amongst various bullets taken from a single box of cartridges.

In criminal investigation work, it is often important to establish whether or not bullet fragments involved in a case match whole bullets also involved in the case as to type, caliber, manufacturer, and even batch. At present, the NAA method gives the best promise of becoming a practical method for such cases, but it appears that radiochemical separations may be required in most cases in order to detect and measure the levels of a larger number of elements if reasonably high probabilities of common origin are to be attained. The purely instrumental NAA approach can readily indicate that two specimens do not have a common origin, but it cannot yet establish very high probabilities of common origin.

The General Atomic bullet lead studies have also been reported by Lukens & Guinn (109). The Sb levels in bullet leads have also been studied in Japan by Isono et al (110). By employing longer irradiations at higher thermal neutron fluxes (10^{14} n/cm^{2}sec), radiochemical separations to remove most of the induced ^{122}Sb and ^{124}Sb activities, and Ge(Li) γ-ray spectrometry, Guy & Pate (111, 112) were able to detect and measure the levels of not only Sb, As, and Cu in various bullet lead specimens, but also in some or many cases the levels of Ag, Au, Cr, Te, and Zn. They also analyzed bullet jacket materials, finding the elements Zn, Sb, Au, and Ag via instrumental NAA. Bullet lead NAA results have been presented in US courts in some cases.

Glass Following exploratory instrumental FAA studies of glass by Settle (113), in which 11 elements (Na, Sc, Cr, Fe, Co, Zn, As, Zr, Sb, Ba, and Hf) could be detected via NaI(Tl) γ-ray spectrometry, and some additional elements by means of photonuclear activation analysis by Coleman (114) and by Coleman & Wood (115), Goode et al (116), in England, embarked upon a very careful large scale FAA study of window glass fragments collected in England and Wales. They have reported their findings (117, 118) from the

analysis of 540 such samples. They employed an automated radiochemical separation procedure, following reactor activation, and NaI(Tl) γ-ray spectrometry of the six separated groups of elements. They present concentration/frequency histograms for 22 elements: Na, Mg, Al, Ca, Sc, Cr, Mn, Fe, Co, As, Rb, Sr, Sb, Cs, Ba, La, Sm, Eu, Yb, Hf, Th, and U. Examples of the FAA of glass specimens involved in actual criminal cases have been reported by Coleman & Weston (119), and by Schmitt & Smith (120).

Other materials Forensic activation analysis studies of several other kinds of manufactured or processed materials that are of forensic interest have also been reported, but mostly only small scale studies. These include studies of (*a*) paper, by Lukens et al (29)—a moderately large scale study, and by Brunelle et al (121); (*b*) adhesive tape, by Scott et al (122); (*c*) safe insulation, by Evans et al (123); (*d*) synthetic fibers, by Vogt & Hashii (124); (*e*) illicit whisky, by Hoffman et al (125), Pro et al (126), and Lima et al (127); (*f*) various kinds of drugs, by Bate & Pro (128), Reynolds et al (129), Schlesinger et al (130), and Tuckerman et al (131); and (*g*) crude oils and residual oils, in this case a large scale study carried out at General Atomic, from the standpoint of identification of the source of oil pollution of waterways, and reported by Bryan et al (132), Lukens et al (133), and Guinn et al (134).

Those interested in learning more about conventional criminalistics methods are referred to the book by Kirk (135). The book by Thorwald (136) is a fascinating account of the development and early case applications of many forensic methods, including NAA.

SUMMARY

The high sensitivity of detection of high flux neutron activation analysis for a large number of elements, the nondestructive nature of the instrumental form of the method, and the good measurement precisions and accuracies attainable with the method make it a potentially very powerful and useful tool in the field of scientific crime investigation. Very tiny evidence specimens can be analyzed effectively, and numerous characterizing trace elements can be detected and measured in evidence specimens to facilitate their comparison as to probability of common origin. Most of the development of the field of forensic activation analysis has occurred in only about the last ten years, and it appears to be steadily growing. Although in a sense yet in its infancy, it has already been used in the investigation of evidence samples involved in several thousand criminal cases, and FAA results have been presented in court in hundreds of cases. Crime investigation laboratories in several countries of the world are now using the method quite regularly in cases of selected types. The most fully developed applications of the method thus far are in the detection of gunshot residues, and in the comparison of evidence specimens of paint, hair, glass, and bullet lead, although much more development work is

needed in even these areas of application. The advent of the Ge(Li) detector has increased the power of the FAA method even further, as has the development of good statistical methods for the proper interpretation of FAA data. Both the research and case application aspects of the field involve interesting interrelationships of the radiochemist, the criminalist, and members of the legal profession.

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