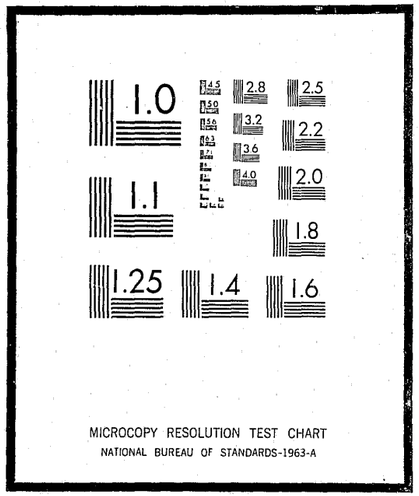

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APPLICATIONS OF SPARK SOURCE MASS SPECTROMETRY AND NEUTRON ACTIVATION ANALYSIS TO FORENSIC SCIENCE

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This report includes material taken from papers, theses, and oral presentations originating from our research groups over the past five years. Recognition should be directed to the graduate students who have worked on various phases of this project. They are (in chronological order): John P. Yurachek, Mark E. Mount, William H. Wadlin, Mary A. Ryan, Nick Alexandro, Linda D. Cooper, Gerardo G. Clemena, Gary S. Hoover, Donald A. Gregory, and Charles W. Magee.

I. TRACE ELEMENT ANALYSIS IN FORENSIC SCIENCES

Trace element analysis as a tool applicable to the forensic sciences has been widely acclaimed by practitioners of neutron activation analysis. International conferences on the subject of Forensic Activation Analysis were held in 1966 in San Diego, California and in 1972 in Glascow, Scotland. Excellent reviews of the subject have been written by Guinn,[1] Lyon and Miller,[2] Coleman,[3] Perkons[4] and Jervis.[5] Several court cases in which evidence analyzed by activation analysis has been presented are described by Lyon and Miller,[2] and Guinn[6] considers some of the difficulties which have arisen in presenting this type of evidence in court.

In general, there are three classes of investigations in which trace element analysis has been applied to the forensic sciences:

1) Characterization of a sample by its trace element profile.
2) Gunshot residue analysis.
3) Toxicological studies.

If a class of samples has a unique trace element profile, i.e., if the concentrations of the trace elements in the samples of a class are the same for all samples from that class and different from all other classes of samples, an analysis of the elemental profile should allow one to classify the samples. The trace element profile or "fingerprint" of evidence material could then be used to establish the origin of that material. The types of evidence material which are amenable to activation analysis include biological tissue, cloth fibers, paint, glass, soil, and tobacco. One type of biological material on which a considerable amount of effort has been spent and which illustrates the problems associated with fingerprinting evidence by trace element characterization is human hair. It is the type of sample which can often be collected at the scene of a crime against a person. Normally, there will be one or more suspects and the problem is that of matching the hair collected at the crime site against a sample taken from the suspect. To affect a match it must be shown that the two samples are identical and that there would be no other hair sample with the same characteristics. To say that there

is no other hair sample like the suspect's would require a knowledge of the hair characteristics of the entire population. Further, one would have to be assured that hair trace element pattern does not change with time or depend on the location of the body from whence it came. To investigate the variation among the population, three large scale surveys of head hair have been conducted by Perkons and Jervis,[7] Coleman, Cripps, Stinson and Scott,[8] and Bate and Dyer[9] each of whom have generated histograms of the concentrations or certain elements among the populations sampled. One of the most recent analyses of the variation of the trace element concentration from a single head was reported by Obrosnik, et al.[10] In this paper the authors make the point that if the variation in elemental concentrations from a single head is comparable to that observed between hairs taken from the heads of different individuals, then characterization becomes impossible. However, the distribution of a single element in the hair from one head is much narrower than the distribution of that element over the entire population, a fact which has lead to several statistical analysis approaches for predicting probabilities of a match between two individuals, mostly based on the original work by Parker.[11] Much of the evidence which has been presented in court has been based on Parker's work. Other difficulties attendant to hair analysis involve changes in hair composition with diet, changes with hair treatment, proper washing procedures and treatment after the sample has been collected, and the possibility of contamination during handling. Cornelis[12] calls hair forensic analysis by activation analysis the failure of a mission and Obrusnik, et al.[10] point out "the literature contains both optimistic and pessimistic prognoses of the possibility of hair charactertization." Guinn[6] also comments on the initial optimism that the detection of a large number of elements would somehow solve most of the unsolved problems of forensic science and urges caution to those in the analysis field. Guinn concludes that the method of forensic, as applied to "fingerprinting" evidence material will become a well accepted method, in the eyes of the law, where certain criteria are generally accepted and adhered to.

A second class of forensic problems to which trace element analysis has been applied is the detection of gunshot residues. Gunpowders and primers contain elements which are sprayed out of the muzzle and back through the chamber when a weapon is fired. A sample washed or swabbed from the skin of a suspect in the areas where the backflash would deposit and found to contain abnormal amounts of the elements in gunpowder can indicate that the suspect had fired a weapon. A sample taken from in front of a weapon, such as from a cloth sample around a bullet hole, can be analyzed to indicate whether the penetration is from a gun firing and determine the distance between the weapon and the target. The constituents of gunpowders and primers include antimony, barium, copper, and lead and traces of manganese, nickel, and zinc. The elements copper, manganese, nickel, and zinc are not useful as indicators specific for gunshot residue, since they are common elements for which background levels among the general population are high. Lead is not easily detectable by neutron activation analysis. Thus, most of the work associated with gunshot residue analysis has been based on the detection of the elements barium and antimony. The pioneering work was done by Guinn and associates at Gulf General Atomic [13] and eight papers involving analysis of gunshot residues were presented at the 1972 Glascow conference on Forensic Activation Analysis.[14] As is the case for fingerprinting general types of evidence, to show that a person has fired a gun and that the levels of antimony and barium on his hands are not present by chance or from occupational contamination, we must have a base of normal levels of these elements. A fairly large scale survey of hand blank backgrounds accompanied by a statistical approach to evaluate probabilities that a person has fired a weapon or not was done by Schlesinger, et al.[15] Because of the relatively narrow range of background levels of antimony and barium among the population, the analysis for these elements has promise for determining whether or not a suspect has fired a gun. This is true if the suspect can be sampled soon after the firing, i.e., if he has not washed his hands or rubbed the residue off. The test is certainly not without its problems. Some forensic analysts report that most of the samples submitted turn out to be inconclusive. More research is necessary.

The last class of forensic problems in which trace element analysis has been particularly successful has been in toxicological studies. Several of the classical poisons, such as arsenic and mercury, are easily detectable by neutron activation analysis. Probably the most widely publicized toxicological study was a study of Napolean's hair, which indicated high levels of arsenic in hair taken shortly after his death.[16,17] However, other authors are quick to point out that this does not offer conclusive proof that Napolean's death was caused by poisoning[2,5] since various medicines used in that day contained arsenic. One advantage to analyzing hair for arsenic is that the concentration variation along the length of the hair can be used to reveal the history of the poisoning.[18] This is an advantage unique to neutron activation analysis since the method has extreme sensitivity and thus only a small amount of sample is required for analysis. An extensive series of activation analyses for arsenic in hair was reported by Lenihan and Smith[19] who reported ranges in the normal population of 0.5 to 1.5 ppm in men and 0.1 to 1 ppm in women and that concentrations greater than 2.5 ppm were rare. Other investigations indicate that concentrations greater than about 3 ppm are abnormal.[5] However, as in other forensic investigations, the investigator must be careful to assure that measured high arsenic levels are not the result of accidental contamination (such as from fertilizers) rather than a deliberate poisoning attempt.

Whereas most of the trace element analysis that has been applied to forensic problems has been done by neutron activation analysis, other analysis techniques may be applicable. For example at the Glascow Conference, Barnes et al.[20] describe the use of charged particle induced X-ray analysis and discuss four applications to actual police problems. They conclude that the technique has promise but that considerable development remains to be done to put the technique on equal footing with other well developed analysis techniques. Atomic absorption is another analysis tool which is very sensitive for most elements. However, it suffers from the disadvantage of being selective for only one element per analysis. A fairly new analysis tool which has high and uniform sensitivity for most

all elements is the spark source mass spectrometer. Its application to samples of forensic interest and comparisons with instrumental neutron activation analysis is the subject of this report.

II. PRINCIPLES OF THE METHODS

A. Spark Source Mass Spectrometry (SSMS)

The application of mass spectrometers in analytical problems was suggested by J. J. Thomson as early as 1913, but it was not until 1940 that their usefulness was demonstrated in the analysis of multi-component hydrocarbon mixtures. Interest was focused on the determination of very small quantities of hydrocarbon impurities in soil gases for the purpose of oil prospecting and on monitoring gasoline refining streams.

The earlier ion sources, such as electron bombardment, thermal ionization, and gas discharge, restricted the application to only gases, liquids, organic solids, and several relatively volatile inorganic solids; this excluded non-volatile inorganic solids, such as metals, semiconductors, insulators, and others. Furthermore, ion species obtained from such low-energy sources were mainly molecular fragments. This thereby rendered elemental analysis infeasible.

In 1946, the mass spectrographic studies by Dempster[21] demonstrated that the use of spark source in mass spectrometry might be a very sensitive technique for the elemental trace analysis of non-volatile inorganic solids. A report by Shaw and Rall[22] in 1947 discussed a spark source mass spectrograph for analytical work similar to those in use today. A paper by Gorman, Jones, and Hipple[23] in 1951 reported a mass spectrometer which used an r-f spark source and an early form of electrical detection. Using standard samples, they demonstrated that the technique could be made quantitative.

The spectacular advances in solid state physics, technology, and chemistry 15-20 years ago, particularly in connection with the development of high purity semiconductor materials, created a great need for new analytical methods for the detection and measurement of trace impurities in solids. The growing awareness of the effects of trace impurities in the parts per million (ppm) to parts per billion (ppb) region in such physical properties as electrical, thermoelectrical, magnetic permeability, and ductility of metals was another stimulating

factor. These necessitated the revitalization of the spark source. In 1954, Hannay[24] designed and built a mass spectrograph using the Mattauch-Herzog geometry of double-focusing and equipped with a pulsed radio-frequency spark source. Using this instrument, Hannay and Ahearn[25] detected impurity concentrations as low as 0.1 ppm in semiconductors. This work marks the beginning of the application of r-f spark source mass spectrograph to trace analysis.

The appearance of commercial spark source mass spectrometers in 1958 provided greater momentum to the development of spark source mass spectrometry into an established analytical technique. It is now considered as a very valuable trace analysis technique due to its very broad applicability and extreme sensitivity.

Theory

Mass spectrometry is a technique which produces a beam of ions from a sample (solid, liquid, or gas), sorts out the resulting mixture of ions according to their mass-to-charge ratios, and provides output signals which are directly proportional to the relative abundance of each ionic species present. Accordingly, a mass spectrometer (see Figure 1) consists essentially of three components which must be highly evacuated. These components are:

1. The Ion Source

The objective of an ion source is to provide, with reasonable efficiency, an ion beam which is representative of the sample composition. There are several methods to produce ions from the sample, including: (a) electron bombardment, (b) thermal ionization, (c) ion bombardment, (d) field ionization, and (e) vacuum discharges. The vacuum radio-frequency spark source is grouped under the last method.

Since the ionizing energy available from an r-f spark source is much greater than the highest ionization potential of any element present, essentially uniform sensitivity is reported for all elements. It is particularly attractive for elemental trace analysis in providing a broad survey of all the trace elements present. Therefore, it was the one used in this study, and the following discussion will be restricted to this type of source.

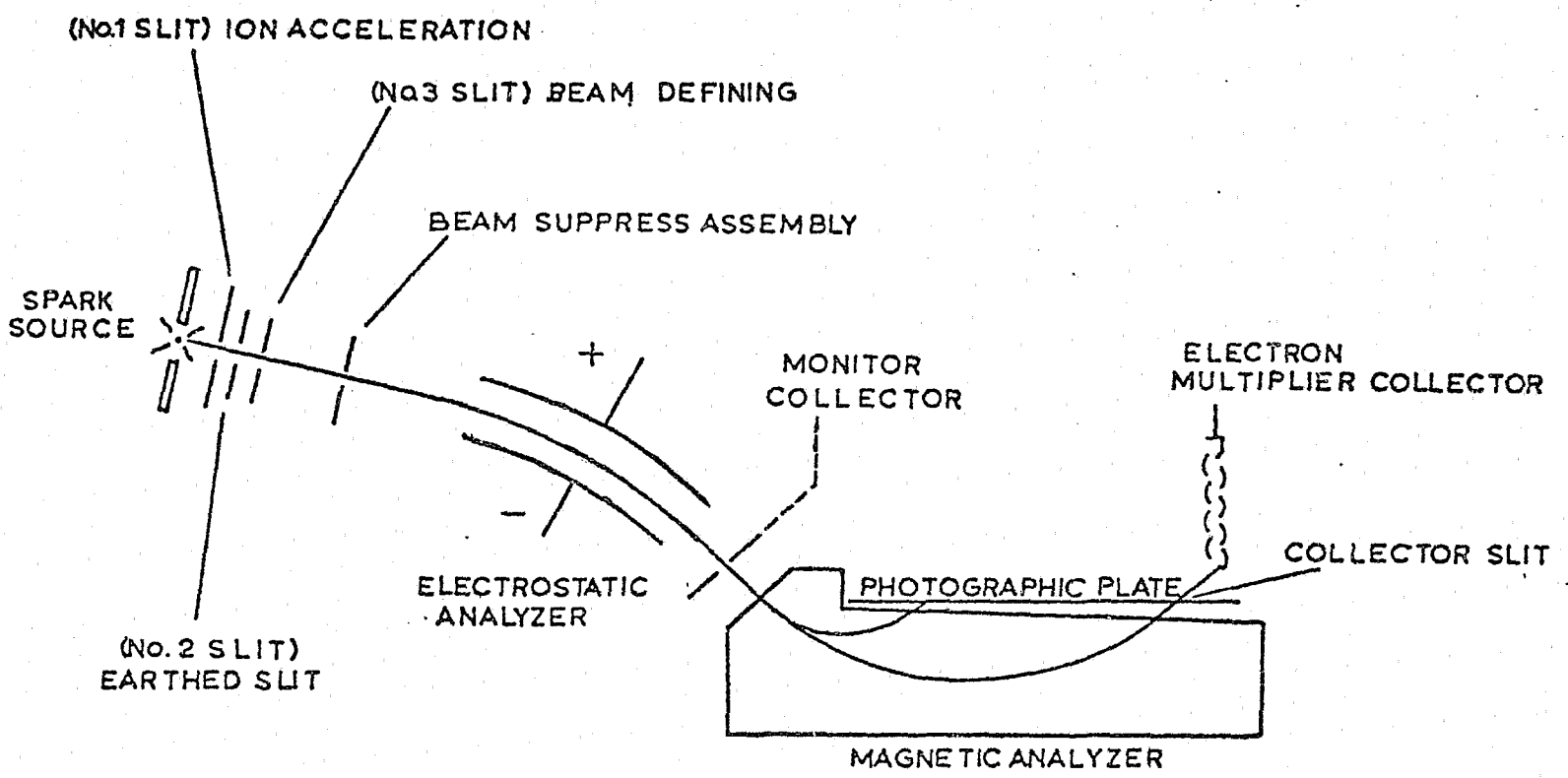

Figure 1. Schematic of MS-702 spark source mass spectrometer

In an evacuated source, a pulsed radio-frequency voltage of from 10 to 80 kv amplitude is applied between the electrodes of the sample material. The gap between the electrodes is approximately a few hundredths of a centimeter.

As the potential across the two electrodes becomes sufficiently high, a spark discharge will take place, resulting in a region of negative resistance, and the potential across the electrode drops by several orders of magnitude. The spark is characterized by a short term high current flow, followed by a recovery of the original electrode potentials and current quenching. Some "whiskers" (projections of $\sim 1\ \mu$ that exist on any cathode surface) may vaporize and contribute cathode atoms to the interelectrode region, accompanied by emission of electrons from the cathode. Electron bombardment of the anode generates neutral atoms that are immediately ionized by the electron stream from the cathode. The neutral atoms from the cathode are also ionized by the electron stream. Furthermore, ions from the anode will bombard the cathode, causing sputtered neutral atoms and secondary electrons.

To summarize, during the spark, copious vaporization of electrode material occurs and the subsequent ionization by electrons in the discharge produces singly- and multiply-charged ions to form an ion beam which is generally representative of the sample composition.

This positive-ion beam is then accelerated by a high potential difference V, and injected into the analyzer. The kinetic energy, K, acquired by the ions is

$$K = \frac{1}{2} mv^2 = eV \qquad (1)$$

where m is the mass of ions, v is velocity, and e is unit charge.

2. The Analyzer System

If ions are emitted from a thermal or surface ionization source, the ion beam may have a negligible energy spread (~ 1 ev) and the ions can be easily sorted out according to their mass-to-charge ratios by

a magnetic field, but in the case of an r-f spark source, the ions produced have a very wide spread, approximately 2 kV. When the energy spread is so great that the electrostatic accelerator cannot make the initial energy variations negligible, ions of the same mass and charge may have different velocities and different radii in a magnetic analyzer. An energy filter (or, energy analyzer) is then required. Therefore, a combination of electrostatic and magnetic fields is necessary to achieve double-focusing in both energy and mass of the ions.

Most frequently used is the combination of a cylindrical condenser and a homogeneous magnetic sector field in tandem, i.e., the Mattauch-Herzog [26,27] geometry of double-focusing. This consists of a 31.8° electrostatic analyzer followed by a 90° magnetic sector analyzer.

(a) Electrostatic Analyzer

When ions are accelerated through a potential difference V and are then injected into a radial electrostatic field (a field generated by a voltage difference applied across the plates of a cylindrical condenser) of strength E (V/cm) the ions will describe a circular trajectory such that the centrifugal force is balanced by the acting electrostatic force,

$$\frac{mv^2}{r_e} = eE \qquad \text{or} \qquad r_e = \frac{mv^2}{eE} \tag{2}$$

where r_e is the radius of curvature. Replacing v by

$$v^2 = \frac{2eV}{m} \tag{3}$$

from Equation (1) one obtains

$$r_e = \frac{2V}{E} \tag{4}$$

This is a mass independent relationship, indicating that the electrostatic analyzer does not analyze mass. It does, however, analyze energy, since any variation in V results in a path of different radius. Therefore, ions of different energies will describe somewhat different trajectories

and form a kind of energy spectrum at the exit plane of the analyzer. If the narrow collimating slit is placed at the exit plane, ions having a kinetic energy between $e(V + \Delta V)$ and $e(V - \Delta V)$ will be passed through the slit, allowing the transmission of only ions having a fairly discrete energy range. This is illustrated in Figure 2. By this means, the magnetic analyzer then receives ions of essentially the same energy for subsequent high resolution based on mass-to-charge ratio.

(b) Magnetic Analyzer

As the monoenergetic ion beam from the electrostatic analyzer moves across a magnetic field of flux density B at right angles to the field, a force with a magnitude of Bev is exerted upon the ions of the beam. The ions, under the influence of this force whose magnitude is constant and whose direction is always at right angles to the velocity of the ions (left-hand rule), will describe a circular trajectory, and the force becomes balanced by the centripetal force, i.e.,

$$Bev = \frac{mv^2}{r_m} \tag{5}$$

and be rearranging

$$r_m = \frac{mv}{Be} \tag{6}$$

This indicates that a homogeneous magnetic field can be used to separate ions of different mass-to-charge ratios as long as their velocities (or kinetic energies) are uniform, which explains why the ion beam from an r-f source must be energy analyzed prior to the separation.

Now, from Equation (3)

$$v = \frac{2eV^{1/2}}{m} \tag{7}$$

we obtain

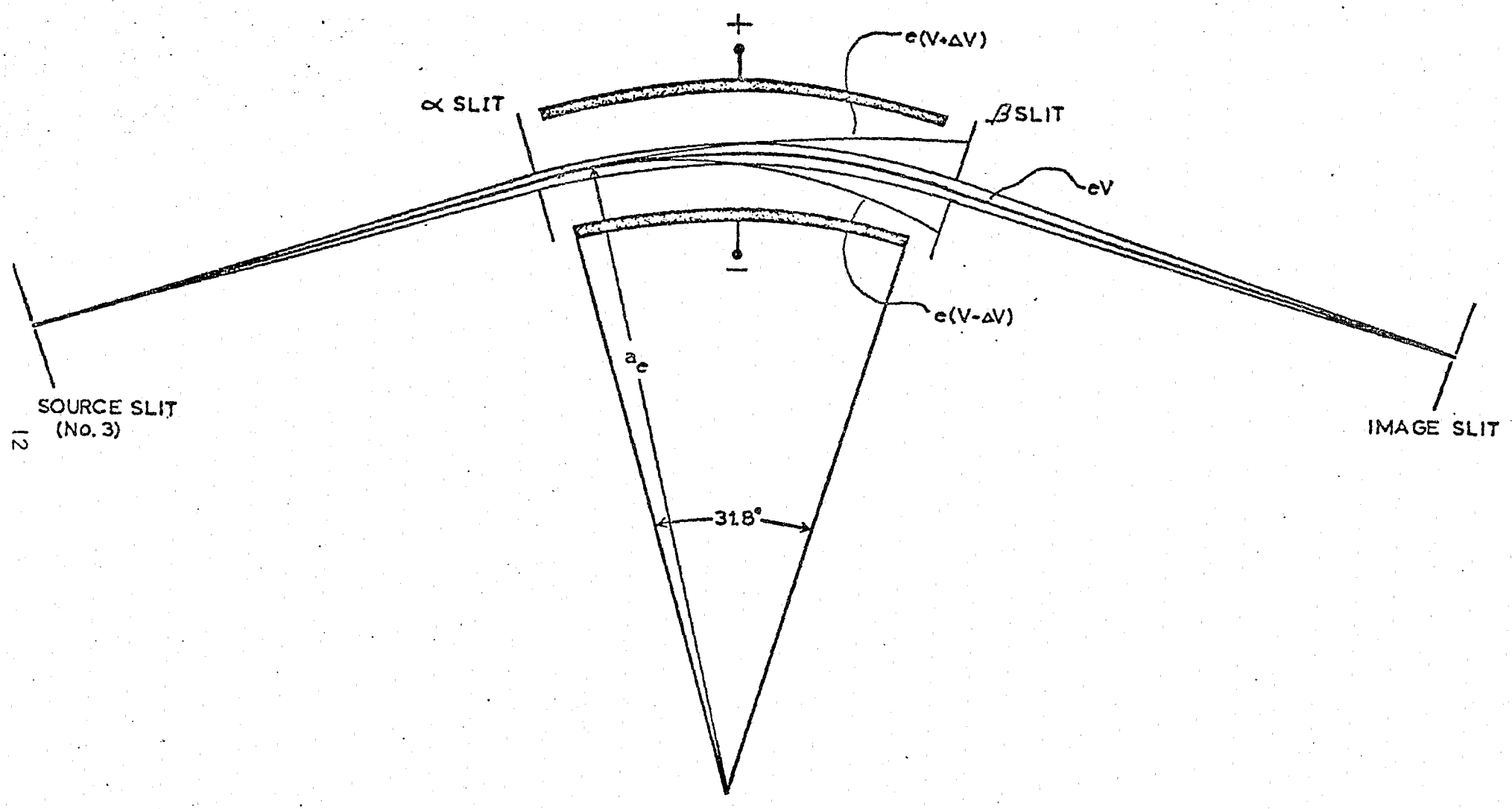

Figure 2. Electrostatic analyzer

$$r_m = \frac{2V}{B^2} \cdot \frac{m^{1/2}}{e} \qquad (8)$$

This suggests that for ions accelerated through the same potential, these of larger mass-to-charge ratio will have a larger radius or curvature. Thus, the ions of different charges and masses can be separated and yield a mass spectrum. This spectrum is recorded by a photoplate placed at the plane of the image curve which coincides with the exit boundary of the magnet. The mass range, in our particular instrument, covered in one exposure is m - 45 m, where m is the low mass detected.

3. Ion Detection Systems

Ions exiting the magnetic field must be detected with relatively high efficiency. In spark source mass spectrometry, where exclusively Mattauch-Herzog geometry is used, both photographic and electrical detection methods are used. Each has its advantages and disadvantages, which will be discussed in the following section.

(a) Photographic Detection

1) Advantages

The erratic nature of the ion beam makes the photographic (actually ion sensitive) plate a natural detector due to its good integrating qualities. In SSMS, exposures are not taken for specific times because of the fluctuating nature of the ion beam. Instead, the ion current collected at the monitor is integrated and used as the basis for photographic exposures.

The photographic plate has many advantages:

1) All elements are detected simultaneously. This is a distinct advantage when sparking very small samples or when samples such as surfaces and thin films are sparked. This is often done with a single spark, and the photographic plate is the only detector which can record all the data.

2) Photographic plates have good integrating properties while being insensitive to electrical noise. This was probably the reason plates were first chosen as ion detectors in SSMS.

3) Good resolution is also a quality of photographic plates. Spectral overlap arising from molecular ions and multiply charged ions is sometimes a problem in SSMS, and in practically all cases, the resolution obtainable with electrical detection techniques is not good enough to separate interferences from analytical lines. The photographic plate is the only means of obtaining high enough resolving power to eliminate these problems, and often there still is not enough resolution to solve all spectral overlap problems. Resolution by photographic detection is about 3000, with 10,000 obtainable by use of higher accelerating voltage and narrow slits.

4) The photographic plate also provides a compact permanent record of the analysis, which can be filed and re-examined years later if needed.

2) Disadvantages

Photographic detection techniques do suffer, however, from a number of serious disadvantages. These include the following:

1) There can be a considerable time delay between data collection and data reduction due to the need for development and evaluation of the plates. This can be a great inconvenience when trying to run and reduce the data from a large number of samples.

2) Another disadvantage is in the area of sensitivity. The photographic plate lacks a single ion detection capability; in fact, it takes approximately 4000 ions to make a barely discernable line. Sensitivity is also decreased by interference near the matrix lines due to secondary ion emission from the photographic emulsion. These ejected particles go back into the magnetic field where they again travel in circular trajectories eventually striking the plate, causing background fogging.

3) Photographic plates tend to create vacuum problems. They must be pre-pumped to remove the water from the emulsion before insertion into the analyzer. Even so, they still tend to raise the analyzer pressure somewhat, causing an increase in background on the plate (due to collisions of sample ions with residual gas molecules). Also, the fact that the plates must be inserted into the analyzer before the analysis creates the possibility for either mechanical failure or human error in

this process which involves breaking the integrity of the magnetic analyzer vacuum system.

4) Non-linearity of photographic plate response is also a serious problem. The response curve of blacking vs. numbers of ions is logarithmic. This relationship is only valid for a range in numbers of incident ions of about 30:1. Thus any comparison of ion populations of greater differences than this cannot be done with a single exposure. In practice, exposures are generally taken from 10^{-7} coulombs to 10^{-12} coulombs in steps of a factor of 3 (i.e., 100, 30, 10, 3, 1, etc.).

5) The most serious limitation of photographic techniques, however, is the general lack of truly quantitative results. Precisions and accuracies of the whole photographic process are on the order of ± 30%, this figure being contributed to by a number of factors. These include differences in emulsion sensitivity across the plate, as well as from one plate to another, variations incurred during the development process, errors introduced in reading the plates on the densitometer, and errors from the measurement of the length of exposure.

(b) Electrical Detection

Ions in SSMS may also be detected by electrical means, these being either a Faraday plate collector or a high gain electron multiplier. A brief comparison of electrical detection with photographic detection follows.

1) Advantages

The advantages of electrical detection correspond generally to the disadvantages of photographic detection.

1) With electrical detection one can see the readout response as it is being generated (in the peak switching mode) which allows the analyst to exclude obviously spurious values (for example, when the spark goes out), which are quite common in SSMS. This rapid data evaluation is also advantageous when trying to adjust machine parameters.

2) Rapid analysis time is also a positive factor in SSMS, with qualitative analysis for all elements possible in ten minutes using magnetic scanning.

3) The sensitivity of electrical detection is very good, allowing the use of pulse counting techniques. This provides the ability to detect very low level ion beams, even single ions. This enhanced sensitivity, however, is mainly used to shorten the analysis time, because there are other factors which limit the absolute sensitivity to about one part per billion. The absolute sensitivity near a matrix peak is increased considerably using electrical methods, with detection limits down to 0.1 ppm[29] less than one mass unit away from the matrix.

4) When detecting ions electrically, one never has to open a valve into the magnetic analyzer; the detector is always ready for immediate use. This eliminates the possibility of vacuum problems sometimes associated with photographic plates.

5) The electron multiplier is an inherently linear device with very nearly linear output over three orders of magnitude as compared to a factor of thirty for the photographic plate. When in the scanning mode, this allows measurement of many elements of diverse concentration at a single multiplier gain.

6) The single most important advantage of electrical detection over photographic detection is the ability to obtain data with 5% to 10% precision on trace constituents. This cannot be done with photoplates, nor can photographic detection come near the precision of a less than 1% RSD obtainable with electrical detection on matrix and major components. Analysts using photographic methods have a difficult time measuring matrix lines due to the problems associated with taking the very short exposures needed for these high concentrations. With electrical detection, the multiplier gain can be lowered in response to high concentrations.

2) Disadvantages

Electrical detection of ion beams has the following disadvantages which may or may not be a serious problem depending on the type of sample being analyzed.

1) Electrical detectors are limited to sampling at one specific point in the focal plane. Thus, while one mass is being measured, data on all other masses is being lost. This method of non-simultaneous detection means that no two masses are ever measured under exactly the same conditions, a possible problem when accurately measuring isotopic ratios, or when the sample is very small.

2) Electrical detection techniques suffer from a lack of resolution, with resolving power usually about 500, with 1500 obtainable with very narrow source and collector slits. Low resolving power can be a serious difficulty when analyzing samples which tend to produce many molecular ions, such as ashed biological samples or silicate matrix samples. Here, interferences can not be resolved from analytical lines, and the data can, in some cases, differ markedly from actual sample composition.

Advantages as a Forensic Tool

Spark source mass spectrometry has several advantages over other trace element survey techniques, such as spectrographic emission.

1. Extreme Sensitivity

Detection limits for all elements are in the parts per billion (ppb) range, specific values depending upon exposure times. By use of a wide range of exposures, elements present at greatly variant concentration may be analyzed.

2. Response to Metal and Non-Metals

As opposed to emission spectroscopy or atomic absorption, all metals and non-metals may be determined by SSMS. This allows data collection from the halides, sulfur, phosporus, boron, etc.

3. Uniform Sensitivity

The high voltage spark produces very efficient ionization of all elements to essentially the same magnitude, providing the highly desirable situation in which all elements have approximately the same sensitivity, in sharp contrast to other analytical techniques.

4. Minimal Matrix Effect

Again, the high energy source produces a leveling effect to yield no great change in elemental sensitivity from one matrix to another.

It is thus obvious that SSMS has many critical advantages which should make it a powerful technique in the area of trace analysis. Limitation at present would include the considerable expense of the SSMS facilities and also the precision and accuracy of the method which are usually no better than ± 10-20%.

The application of this technique to forensic areas would basically involve utilization of the profusion of elemental data from SSMS for purposes of analysis, comparison, and identification. Normally, anywhere from 20-40 elements may be identified and quantitatively determined, even in rather pure materials. These elemental concentrations provide resultant profiles which are comprised of many sharp ionic peaks of varying area or peak height. The response of each individual isotope as well as the possible presence of multiply charged ions add additional reference points. Tabular comparison of computed concentrations is also done.

B. Instrumental Neutron Activation Analysis (INAA)

The first suggestion that elemental analysis can be accomplished by neutron activation is usually credited to Hevesy and Levi in 1936.[30] One of the first papers employing the technique was published in 1938 by Seaborg and Livingood.[31] Since then the field was developed to the point where several books have been written on the subject, notably those by Bowen and Gibbons,[32] Lyon[33] and Lenihan and Thompson.[34] As mentioned previously, two conferences have been held on the specific application of neutron activation analysis to forensic problems.

In principal, analysis by neutron activation is a simple procedure. A sample is irradiated in a neutron field and the produced radioactive nuclides are detected by suitable radiation counters. The elements comprising the sample are identified and quantified from the characteristics of the emitted radiations. Two characteristics of radioactive nuclides which can be easily measured and used to uniquely identify the

elements present are the energies of the emitted gamma rays and their decay rates. The sensitivity for detecting a given element depends on several factors:

a) Type of isotope produced--some elements will activate to produce isotopes which are pure beta particle emitters so that they will not be detected by gamma ray counting. Included in this class are such elements as hydrogen, helium, lithium, beryllium, carbon, and phosphorus.

b) Cross section--the cross section for capturing a neutron ranges over several orders of magnitude. For example, the cross section for the reaction $Pb^{208}(n,\gamma)Pb^{209}$ is 0.0005 barns and that for $Eu^{151}(n,\gamma)Eu^{152}$ is 5900 barns (all cross sections, decay schemes, etc. are taken from the Table of Isotopes).[35] Obviously, high cross section values mean good sensitivity.

c) Isotopic abundance--if the abundance of the isotope which activates is low then the sensitivity will be poor. For example, the isotopic abundance for $Fe^{58}(n,\gamma)Fe^{59}$ is 0.33% so that iron is not a particularly sensitive element to neutron activation analysis.

d) Half life--if the half life of the activated isotope is very short the transit time from the irradiation field to the gamma ray detectors must also be short. Several of the lighter elements are difficult to find by NAA because of short half lives, e.g., B^{12}: 0.020 sec; N^{16}: 7.35 sec; O^{19}: 29 sec; F^{20}: 11 sec; Ne^{23}: 38 sec. On the other hand, isotopes with long half lives will not activate to appreciable quantities in a reasonable irradiation time. Some examples of long half-lived isotopes for which the sensitivity can be increased by longer irradiations are Fe^{59}: 45.6 days; Co^{60}: 5.26 years; Zn^{65}: 245 days and Ag^{110m}: 255 days.

e) Gamma ray decay scheme--some isotopes emit numerous gamma rays which clutter up a spectrum and mask gammas from other isotopes, as for example Br^{82}, whereas other isotopes emit only a single gamma ray in a small percentage of the decays, e.g. Si^{31} emits a 1.26 MeV gamma ray in 0.07% of the disintegrations.

f) Equipment--the sensitivity is directly proportional to the neutron flux and to the efficiency of the gamma ray detectors.

With these factors in mind one can calculate sensitivities for all of the elements for a set of irradiation and counting conditions. Many authors have done this and have produced tables which include about two thirds of the elements and list detectable quantities in the range from picograms to micrograms. However, in publishing tables of this type one must be careful to note that the values represent interference free conditions. Very rarely does one have a truly interference free condition. If a major constituent of a sample activates readily, its decay products may mask out gamma rays from the minor constituents. A prime example of this problem is human body tissue which contains large amounts of sodium, chlorine, and bromine. These three elements have reasonably high sensitivities for detection by NAA so that trace quantities of other elements are hidden in the spectra. Thus, although interference free sensitivities may be calculated, the ultimate sensitivity depends also on the matrix material. The problem of the matrix effect may be minimized by post irradiation chemical separations. However, the selective nature of a chemical procedure limits the number of elements detected per sample run. Because of this limitation and because of the time involved in performing chemical separations the work reported here will be strictly instrumental neutron activation analysis.

III. EXPERIMENTAL

A. Spark Source Mass Spectrometry

Apparatus

Table I shows a summary of the equipment and experimental conditions used in the spark source mass spectrometric analysis.

The trace elements were determined using a Model 702 mass spectrometer manufactured by Associated Electrical Industries, Ltd., Manchester, England. This is a double focusing mass spectrometer employing a spark ionization source for the determination of impurities in solid materials. Several modifications were applied to the M.S. 702 used in this work, which increased the overall efficiency and performance of the instrument. The instrument's vacuum system was improved by adding two 25 l/s A.E.I. Triode Ion Pumps and one 120 l/s A.E.I. Triode Ion Pump. One of the 25 l/s ion pumps was attached to the source, while the analyzer region and the interspace were pumped by the 120 l/s ion pump and the other 25 l/s ion pump, respectively. The incorporation of ion pumps into the system is reported to reduce the risk of hydrocarbon contamination and make possible the attainment of lower analyzer pressures.

The source was equipped with electrode micromanipulators which enabled the operator to move both electrodes in the x, y, and z planes, thus permitting precise positioning of the electrodes and, in turn, the establishment of reproducible sparking conditions. The instrument was also equipped with an ion beam chopper which increased the precision and accuracy of the quantitative determination by minimizing the effects of inhomogeneity within the sample. The instrument is comprised of two large cubicles joined by an interconnecting bridge. The analyzer tube assembly, vacuum system, spark circuits, vacuum gauges, monitor collector and all operating controls are located in the Main Cubicle. The stabilized power supplies, amplifiers and other circuits are housed in the Electronics Cubicle.

Table I

SSMS EQUIPMENT AND EXPERIMENTAL CONDITIONS

Analysis Instrument	A.E.I. M.S. 702 Spark Source Mass Spectrometer with Electrical Detection
Other Equipment	Jarrell-Ash Model 23-100 Recording Microphotometer, Bristol Model 570 Dynamaster Recorder, Disc Chart Integrator Model 235A, Jarrell-Ash Model 3410 Processing Unit
Vacuum	Magnetic Analyzer 10^{-8} Electrostatic Analyzer 10^{-8} Source 5×10^{-6} (when sparking)
Spectrometer Parameters	Spark Voltage 30 kV Repetition Rate 300 pulses/second Spark Pulse Length 100 usec Electrostatic Analyzer 2 kV Accelerating Voltage 20 kV Primary Slit 0.002 mm Exposure Range 1×10^{-13} coulomb to 1×10^{-7} coulomb
Microphotometer Parameters	Slit 3 microns Occulter 1.2 mm Scanning Speed 1.0 mm/sec
Recorder Parameters	Response Time (Full Scale) 0.4 sec Range -0.05 to + 1.05 mV Chart Speed 2.5 inches/minute
Ion-Beam Chopper	Chopping Frequency 200 to 20,000 Hz Pulse Length 5 µsec
Detector	(a) 2 x 10 inch Ilford Q-2 thin glass photographic plate (b) Electron multiplier with DVM or recording readout
Developing Conditions for Plate Detection	Developing Eastman Kodak D-19 (1:1 ratio) at 20.0°C for 2 1/2 minutes under Wratten Series 1A safelight

Table I (continued)

Stop Bath	14% Acetic Acid solution for 30 sec
Fixing	Eastman Kodak Rapid Fixer with hardener for 3 minutes
Washing	Running water for 15 minutes, distilled-deionized water for 1 minute
Drying	Forced air for 15 minutes

The electrical detection was accomplished with a standard AEI system which interfaced to the MS 702. The system is too complex to describe here in detail but such is available in the literature.[29] Basically, the electrical system consists of an Allen type electron multiplier which can be read out by a DVM (Heath Model EU-805) or by a complete ratio scan as recorded on a Honeywell oscillographic recorder.

The photographic plates were developed in a Jarrell-Ash Model 3410 Processing Unit, and the interpretation of the mass spectra was carried out on a Jarrell-Ash Model 23-100 Recording Microdensitometer in conjunction with a Bristor Model 570 Dynamaster Recorder equipped with a Disc Chart Integrator Model 235A. This system permits precise measurement of the density of the mass spectra lines.

Reagents

Extreme purity is required for all reagents. Blanks should be shot to determine total reagent contribution in any case. Ultra Superior Purity graphite (Ultra Carbon Corporation, Bay City, Michigan) was used as a matrix with which certain samples were mixed for electrode preparation. A spectrographically pure standard yttrium oxide (Johnson, Matthey, and Co. Inc., London, England) was added as an internal standard. High purity acids (G. F. Smith Chemical Co., Columbus, Ohio and Suprapur, EM reagents Division, Brinkman Instruments Co., Westbury, N. Y.) were used for sample wet ashing.

Electrode Formation

A stainless steel moulding die (Associated Electrical Industries, Ltd., Manchester, England) was used to prepare electrodes from the homogeneous sample-matrix mixture. A small polyethylene slug is drilled to provide two shafts into which the mixture is added by means of special loading funnels. In the case of quite small samples, only the tips of the electrodes contained the sample, with pure graphite used for the remainder. The polyethylene slug is then pressed in the die at 10 tons pressure to form 10 mm x 1 mm electrodes.

Internal Standard

Yttrium was used as an internal standard because of its availability in a highly pure form, the considered improbability of its normal occurrence in the sample, and its monoisotopic nature. Standard yttrium solutions were prepared which were then used to dope the matrix to 100 ppmw yttrium by formation of a homogeneous slurry, drying, and Wig-L-Bugging to produce a stock quantity for mixing with the sample ash. Blanks were run on the matrices and standard.

Sample Preparation

Drying of the samples is done at 100°C in a laboratory oven. Organic base samples have been ashed by both low and high temperature dry ashing and also by wet ashing techniques using nitric and perchloric acids. Quartz apparatus is used for the ashing and subsequent preparation steps. The ash residue is mixed thoroughly with high purity graphite, transferred to a plastic vial containing a ball pestle, and shaken for 15 minutes on a Wig-L-Bug (Crescent Dental Mfg. Co., Chicago, Ill.) to achieve a homogeneous mixture. Specific sample preparation techniques will be described for hair and fingernails as representative materials of biological matrix. Similar techniques, at least certain aspects, would be suitable for other samples of interest, such as fibers, tobacco, drugs, and other organic base materials, and will not be repeated in later sections.

Sample Preparation for Hair

All tongs and forceps used for handling samples were Teflon coated. Glassware was washed with non-ionic detergent, rinsed, soaked in alcoholic solution of potassium hydroxide, and then rinsed with copious amounts of deionized distilled water.

The preparation of sample prior to analysis consisted of three steps. These were:

(a) Washing of Sample

Each hair sample was washed in a 100 ml polyethylene bottle with 50 ml of 1% solution of non-ionic detergent for removal of surface

contaminant. The bottle was shaken in a mechanical shaker for 30 minutes. Upon completion of the washing, the sample was transferred to a polyethylene filter crucible and rinsed with a total of 500 ml of deionized water to remove the detergent. The cleaned sample was transferred to a 100 ml beaker, covered with a watch glass, and dried overnight at 110°C.

(b) Digestion of Sample

A 50-mg portion of the dried sample was weighed to the nearest 0.0001 gm in a 10 ml quartz Erlenmeyer flask. The digestion was started by adding 1 ml of concentrated nitric acid to the Erlenmeyer flask containing the sample and allowed to stand for a few hours covered by an inverted 50-ml beaker (heating immediately after the addition of acid could cause excessive foaming). During this period, the mixture was swirled occasionally. The mixture was then heated slowly on a hotplate and, maintained at about 180°C until it became colorless. The excess perchloric acid was driven off by heating the solution at approximately 200°C to a moist residue.

(c) Preparation of Sample Electrodes

The moist residue was dissolved by addition of 2 ml of a 5 µg/ml standard yttrium solution. Several drops of deionized distilled water were used to wash the standard yttrium solution from the neck and sides of the Erlenmeyer flask. The solution was carefully swirled to insure homogeneity and then slightly warmed for easy mixing with graphite powder. One-ml portions of this solution were added to 20 mg of pure graphite in a quartz crucible, stirred with a fine-tipped glass rod forming a homogeneous slurry, which was dried under an infra-red lamp after each addition. After all the sample solution was added and dried, the graphite residue was transferred to a 25 x 12.5 mm polyethylene vial and shaken in a Wig-L-Bug for five minutes.

It would require approximately 100 milligrams of the graphite residue to prepare two full sized electrodes of 1 1/4 mm diameter and 10 mm long. However, the amount of graphite residue available was only approximately 20 milligrams, which necessitated the tipping out of the residue on support electrodes of pure graphite. This was achieved by placing in

each hole of a polyethylene plug, with the aid of a filler guide, half of the graphite residue, on top of which enough pure graphite was packed in to fill the hole. The plug was inserted into the molding die which was then compressed in a heavy duty laboratory press at 10 tons per square inch to form the electrodes for analysis.

B. Instrumental Neutron Activation Analysis

Three items are necessary to do instrumental neutron activation analysis: intense neutron flux, a good resolution high efficiency detector, and detector readout. Intense thermal neutron fluxes are available at most reactor facilities with values in the range 10^{12}-10^{14} neutrons/cm^2-sec. These reactors are located at national laboratories, universities, and in a few industrial centers. There are approximately 30 reactors in the United States from which reactor time can purchased at sites which would hardly justify construction of a new reactor for a forensic laboratory.

The irradiations in this report were done in the University of Virginia Reactor in a nominal activating flux of 3×10^{13} neutrons/cm^2-sec. Large lithium drifted germanium detectors (GeLi) with very good efficiencies and with resolutions in the range of 1.5 to 5 keV. Much of the later work in this report was done with a Hershaw detector with 2.5 keV resolution for the 1.332 MeV Go-60 gamma ray and a 10% efficiency as compared with NaI. The earlier analyses were done with a 3" x 3" NaI crystal and some of the intermediate work with a smaller GeLi crystal than that used later. Multichannel analyzers which will interpret the pulse output from the detector and provide a graphic display may be obtained from one of several vendors. It is desirable to have about 4000 channels of analyzing capability to fully utilize the superior resolution of today's GeLi detectors. The work reported here used a Nuclear Data 2200 system.

To do an instrumental analysis which will allow the detection of many elements, it is generally necessary to expose the sample to a short and a long irradiation. The short irradiation will induce the shorter lived activities which can then be counted without much interference from the longer lived species. In this work most of the short irradiations were for 5 minutes and the samples taken to a counter for analysis within 5 minutes. A later count was taken approximately 20 minutes after the completion of the irradiation. The short lived isotopes which have been detected in the forensic samples in this study are listed in the first part of Table 2. A long irradiation, one to two hours, in a neutron flux of 3×10^{13} neutrons/cm^2-sec, followed by a count after several days and one after one or two weeks decay can detect those elements listed in the second half of Table 2. This list does not include all elements detectable by NAA but only those reported in this study. Many practitioners of NAA will use longer irradiations, up to several days, and longer waits before the final count. We believe that for most forensic samples there is an advantage to having results as soon as possible, thus all irradiations were limited to two hours. Further, after long irradiations, many samples will suffer severe radiation damage and therefore lose the integrity and usefulness for presentation in court.

The cross sections listed in Table 2 are from the Table of Isotopes (35) and are good numbers for estimating the sensitivity of NAA and for calculating approximate values of elemental concentrations after an irradiation. The most accurate way of doing NAA is to prepare standards to irradiate under the same conditions as the sample of interest. The standard should contain all of the elements which will be analyzed in the approximate concentrations as in the sample. Further, the standard and sample should be of the same size and geometry. This procedure eliminates the errors involved in knowledge of the neutron flux, activation cross section, isotope decay scheme, and detector counting efficiency. A less accurate procedure, but one which eliminates the problem of making standards for each run, is to irradiate standards and adjust the procedure for reducing the data from multichannel output so as to match known concentration in the standard. The parameters which can be adjusted most easily are the

Table 2

ISOTOPES PRODUCED BY NEUTRON IRRADIATION

Isotope	Half-Life	Cross Section Barns	Isotopic Abundance of Parent %	Gamma Ray Energy Used in Analysis MeV
Short Irradiation				
Al^{28}	2.31 min	0.235	100	1.780
V^{52}	3.75	4.9	99.75	1.434
S^{37}	5.07	0.14	0.014	3.09
Cu^{66}	5.1	2.3	30.9	1.039
Tl^{51}	5.79	0.14	5.34	0.36
Ca^{49}	8.8	1.1	0.185	3.10
Mg^{27}	9.46	0.027	11.29	1.013
Br^{80}	17.6 min	8.5	50.5	0.618
Cl^{38}	37.3	0.4	24.5	1.64
Ba^{139}	82.9	0.4	71.7	0.166
Mn^{56}	2.58 hr	13.3	100	0.847;1811
Long Irradiation				
K^{42}	12.36 hr	1.2	6.77	1.524
Cu^{64}	12.80 hr	4.5	69.1	0.511 (β^+)
Zn^{69m}	13.8 hr	0.1	18.56	0.439
Na^{24}	14.96 hr	0.53	100	1.369;2.754
W^{187}	23.9 hr	40	28.4	0.479;0.686
As^{76}	26.4 hr	4.5	100	0.559;0.657
Br^{82}	35.3 hr	3.0	49.48	0.777;0.698
La^{140}	40.2 hr	8.9	99.9	0.4871;1.596
Cd^{115}	53.5 hr	1.1	28.86	0.53
Au^{198}	2.7 da	98.8	100	0.412
Sb^{122}	2.8 da	6.1	57.2	0.364
Ca^{47}	4.5 da	0.3	0.0033	1.308
Rb^{86}	18.7 da	1.0	72.15	1.078
Cr^{51}	27.8 da	17	4.31	0.320
Fe^{59}	45.6 da	1.1	0.31	1.095;1.292
Hg^{203}	46.9 da	4	28.8	0.279

activation cross section and the gamma ray branching ratios. The program can then be used to analyze unknown samples as long as a neutron flux monitor is irradiated with each sample. The standards should be irradiated periodically to monitor for system changes, such as changes in the irradiating flux energy spectrum. Samples with certified concentrations of many elements are available from the National Bureau of Standards. Some particularly useful ones are

SRM 608-619	Glass
SRM 1571	Orchard Leaves
SRM 1577	Bovine Liver

It should be emphasized that this procedure is not the most accurate and should not be used where the highest precision is required, e.g. when attempting to match samples as having a common origin.

IV. RELATIVE MERITS OF NAA AND SSMS FOR FORENSIC SAMPLES

To form a basis for comparing the two techniques we must first establish criteria which are based on the nature of forensic samples. These criteria are:

1) Number of elements which may be detected - The more elements which can be found in a sample, the better the chance of establishing its origin.

2) Precision of the results - The greater the precision with which the concentrations of individual elements may be determined, the better the chance of establishing the origin of the sample.

3) Sample size - Often samples found at the scene of a crime are very small, e.g., a single hair or a chip of paint.

4) Time required for analysis - It is advantageous to have results of the analysis in a short time.

5) Preservation of sample - If the sample is to be used as evidence in court, it should be preserved.

Direct comparisons of the two analysis techniques, NAA and SSMS, can only be made for each type of sample. Such comparisons are discussed in the appendices to this report. However, some general statements can be made. The sensitivities for determining elemental concentrations by SSMS are essentially the same for all elements, whereas they range over several orders of magnitude for NAA. Thus, more elements may be detected by SSMS than by NAA. The wide range in sensitivity by NAA leads to interference problems for samples in which the major constituents of the sample activate readily, and thus reduces the number of trace elements which may be detected. Molecular interferences are a problem with SSMS analyses, particularly in organic samples. This source of interference is usually eliminated by ashing the sample before analysis. However, inorganic molecular interferences, such as oxides, may remain a problem.

Very precise work can be done by NAA if accurate standards are prepared and irradiated with the samples. For instrumental activation analysis in which procedures are checked periodically the precision is

probably no better than 10%. The accuracy of the SSMS method depends on the readout mode. Density measurements of photographic plates give results with a net experimental error of approximately 30%. With electronic integration readout, this error may be reduced to approximately 5%, although only with close control of parameters.

The minimum amount of sample required for the SSMS is several milligrams, particularly if it is a sample which must be ashed before analysis to reduce the organic content. NAA can be performed on a much smaller sample, i.e., a few tenths of a milligram. However, one must be careful when making comparisons of this type, since the smaller the sample which is being analyzed the smaller is the number of trace elements which will be detected.

The results from a SSMS analysis can be obtained within 12-24 hours, even for those samples requiring pretreatment. The sample can be usually prepared, ashed, and analyzed in the spectrometer within one day. To obtain the maximum amount of information by NAA a sample should be exposed to two irradiations, a short and a long one. This implies that a period of several days to several weeks must elapse before the full results can be made available.

A sample to be analyzed by NAA requires no preparation, other than cleaning and encapsulation, before being irradiated. If the irradiations are not so long that the sample suffers irradiation damage, it is preserved and may at a later time be presented as evidence in the courts. By the very nature of sparking a sample in the SSMS, at least part of it is destroyed.

In many ways the two analysis techniques complement each other. The high sensitivity of NAA for certain elements, such as gold and manganese, allows it to detect these elements in lower concentrations and with a greater degree of precision than the SSMS. The uniform sensitivity of SSMS will find more elements than NAA and in particular those elements which are not amenable to analysis by NAA, lead and boron, to name two. Each of the two techniques has certain interference problems, molecular interferences in SSMS and matrix effects in NAA. Because they are

different types of interference, one technique can be used to resolve questions of interpretation by the other technique. Since essentially no sample preparation is required for NAA, it can be used as a check of the preparation procedures involved with use of the SSMS.

In summary SSMS analysis is quicker and allows determination of more elements with uniform sensitivity. INAA has greater sensitivity for certain elements, requires less sample and sample preparation, and has a history of acceptability in the courts.

V. SUMMARY EXAMPLES OF SAMPLE TREATMENT AND RESULTS

In this section, ten (10) different sample types or categories are summarized briefly in regards to their study by SSMS and/or INAA. Specific comments are offered concerning methodology and forensic application; representative data are also shown.

Certain sample types were more amenable to study by one of the two techniques than the other. The summantions will reflect this fact by their discussion, sample preparation, and resultant data.

A. Human Hair

1. Introduction

The forensic use of a human hair as a chemical "fingerprint", specific and unique to each individual, appeared very promising in the early 1960's. Overenthusiastic response by early proponents suggested that even a single hair could act as an identifier by its trace element composition. The development of this early work by INAA and the subsequent caveats from its most noted researchers have been described in an interesting book by Thorwald.[36] Much effort has since followed in the study of hair, mainly by INAA.[9,7]

Most of the effort in our study has been with the use of SSMS for hair analysis because (a) no previous work had been reported by this technique for hair and (b) the greater number of elements which may be determined by SSMS offered more reference points for fingerprint comparison.

2. Sample Treatment

The samples are all prepared in the Chemistry Laboratory in a clean environment to eliminate analysis errors arising from differences in sample treatment which might occur if separate samples were prepared in two laboratories. Hair samples are cleaned by washing for one hour in a one percent non-ionic detergent solution,[37] rinsing with one liter de-ionized water, and dried at 100°C. Several strands of hair are placed in polyethylene vials that have been cleaned in a detergent solution,

de-ionized water and acetone and sent to the reactor for irradiation. The samples are irradiated in a thermal neutron flux of 3×10^{13} $n \cdot cm^{-2} \cdot sec^{-1}$ for periods of 10 minutes and 2 hours. The samples are removed from their polyethylene vials and are counted throughout their decay with times as short as 3 minutes. The activities are determined by peak area integration and least squares fitting to the decay curves. The 10 minute irradiation is used to detect aluminum, bromine, chlorine, magnesium (by stripping the 0.64 MeV decay curve) and the presence of sulfur and calcium. The 5.07 minute ^{37}S activity decays by emission of a 3.09 MeV gamma ray in 90% of its disintegrations and the 8.8 minute ^{49}Ca isotope emits a 3.10 MeV gamma ray in 89% of its disintegrations and a 4.1 MeV gamma ray in 10%.[35] The 4.12 MeV ^{24}Na sum peak interferes with the latter gamma ray making it difficult to separate the sulfur from the calcium activity with a NaI crystal.

The four hour irradiation is counted over several days and used to calculate concentrations of copper, gold, manganese, sodium and zinc.

For analysis by the mass spectrometer hair samples of about 0.1-0.5 g of a gram have been used. These are minced by chopping with a stainless steel scalpel and mixed to provide a homogeneous representative sample. The hair is then ashed in a muffle furnace at 450°C overnight to eliminate background hydrocarbon spectra. The ash is then mixed with a suitable matrix for shaping into an electrode for analysis. Both high purity silver (99.999+%) and USP grade graphite (Ultracarbon Corp.) have been used. The powdered silver is much easier to handle, forms much more stable electrodes and sparks more profusely. However, the trace element contamination is significantly higher than for graphite and the silver also suffers from a larger powder particle size than graphite which made the preparation of homogeneous electrodes difficult.

In the present procedure a one to one mixture of USP graphite-hair ash is mixed with a Teflon spatula and transferred to vial on a mechanical mixer where it is homogenized for 20 minutes. A portion of the mixture is "tipped out" in a stainless steel die using a polyethylene plug to eliminate contamination. Graphite is placed on top of the tip mixture and electrodes formed at 10-20 tons pressure.

The electrode is sparked in the mass spectrometer for a series of graded exposures. For photographic detection, the plate is read by a densitometer and the data analyzed by computer. A similar background run is made using an electrode prepared in the same manner without the addition of the hair ash. Calibration is performed by analyzing a sample of the minced, homogenized hair by atomic absorption for one element, usually copper or by using yttrium as an internal standard. The analysis program then (1) calculates and plots a calibration curve for the photo plate to correct for variation in response with exposure, (2) corrects data to this calibration, (3) corrects for background exposure, (4) corrects for isotopic abundance of each element, (5) correlates exposure differences, (6) corrects for atomic weight ratio between element and standard, (7) corrects for the mass response of the photo plate, (8) corrects for the area of the selected line, (9) compares these corrections to a standard calibration element and computes concentrations and (10) prints the results in parts per million by weight.

Hair samples may also be analyzed by the electrical detection readout system, employing a galvanometer recorder to display isotopic lines. Peak heights taken from the scans are compared to an internal standard for elemental analysis.

3. Results and Discussion

Several different hair samples have been run by spark source mass spectrometry and compared to activation analysis runs. Some typical results on hairs from the same person and prepared in the same manner are shown in Table A-I, which lists the concentrations by weight of 22 elements detected by mass spectrometry and 8 elements by neutron activation analysis with a NaI crystal. The agreement is reasonable with the exception of manganese and there is the possibility of a hydrocarbon interference in the mass spectrometer data. This interference may also affect the titanium and barium results.

The advantages of neutron activation analysis to the forensic scientist in characterizing evidence material have often been listed.

Table A-1

ANALYSIS OF HAIR

Element	SSMS	NAA
Aluminum	41	25
Magnesium	262	180
Silicon	146	--
Chlorine	--	230
Phosphorus	141	--
Sodium	199	170
Calcium	1754	--
Manganese	16	1.5
Bromine	1.3	4.5
Chromium	7.7	--
Titanium	87	--
Nickel	2.6	--
Cobalt	4.5	--
Zinc	367	81
Arsenic	2.2	--
Strontium	37	--
Molybdenum	0.82	--
Tin	71	--
Iodine	0.95	--
Barium	111	--
Tungsten	4.4	--
Lead	67	--
Gold	--	0.40
Copper	22.6	9.6

Coleman, et al.[38] list 12 elements they have used to characterize hair and Perkons[39] lists 20 elements that he finds using a NaI scintillation crystal, and 23 elements[40] using a GeLi detector. These were obtained from long irradiations in a high flux reactor and long decay times. We list 8 elements that can be detected from single stands of hair with delays between the irradiation and final analysis of about one week. The mass spectrometer gives quantitative information for at least 22 elements in hair, with an analysis time of less than two days, i.e., if a hair sample is received one day, it can be ashed overnight and the complete analysis done the following day. On the other hand the spark source mass spectrometer does not preserve the hair, it is destroyed when sparked, and it requires a larger quantity than the activation analysis.

We have shown[41] that hair batches (100 mg) can be statistically distinguished, based on their trace element content. However, this is not to suggest that single hairs are equally distinctive. Studies in our laboratories[37] have shown that variables such as sample washing may have a very large effect on trace element constituents. Our present conviction is that it is extremely risky to use a single hair as an identifier for an individual.

B. Blood and Human Tissues

1. Introduction

Trace element analysis of these samples are of possible forensic interest, but not normally in the sense of identification or fingerprinting. Instead, the police laboratory may wish to examine such biological samples as blood, serum, urine, fingernails, or various autopsy tissue from a toxicological standpoint. Materials such as arsenic, lead or cadmium may appear in these sample types and present difficult analytical problems. SSMS and INAA were used to examine several such cases.

2. Sample Types

(a) Blood Serum

The homeostatic nature of blood and serum maintains a remarkably even elemental distribution for a group of normal subjects which was

studied. The variations were often found to be within the uncertainty of the technique, ± 20%. However, in subjects who are not normals, data have been reported showing a more significant change in elemental concentrations. Thus, the technique could be of forensic interest depending upon the manner in which the subject became abnormal.

Blood samples were drawn into sterilized polyethylene syringes and transferred to acid-cleaned glass tubes. After clotting, the samples were centrifuged and the serum separated. Two mls of serum was mixed with 100 mg of graphite and the mixture dried, then ashed in a muffle furnace at 475°C. In addition to removing organic species, ashing also serves to concentrate the elements in the sample, thereby increasing the sensitivity of the method and allowing clear detection and determination of elements present in such low concentration in the serum that they might be undetected or at least not quantitatively determined otherwise.

Table B-I shows SSMS data from six normal subjects for eleven elements for which comparison literature values are available. Values determined by atomic absorption are probably the most reliable standard of comparison, and normal values for serum Mg, Fe, Cu, Zn, and Ca have been rather well established by this method. The spark source mass spectrometer Mg values are somewhat lower than the accepted normals, but the values for Fe, Cu, Zn, and Ca agree well with the established levels. Furthermore, the mass spectrometric values for these four elements in sample V agree very closely with specific normal ranges determined over a ten month period in our laboratories by atomic absorption for subject V.

Most of the elements in Table B-I other than Fe, Cu, Ca, Zn, and Mg are difficult, and in some cases impossible, to determine by atomic absorption. Iodine, being a non-metal, cannot be determined, and elements such as Mo, Co, and Ba, which are present at very low levels, require tedious preconcentration methods to arrive at reasonable working levels. Aluminum forms refractory compounds in the flame, and is, therefore quite difficult to analyze by atomic absorption, unless high temperature flames are used. Emission spectroscopy has been used to determine serum concentration of Al, Co, Mo, and Ba, but not without involved sample preparation

Table B-I

SPARK-SOURCE MASS SPECTROMETRIC ANALYSIS OF HUMAN BLOOD SERUM FROM SIX DIFFERENT SUBJECTS
(values in ppm by weight)

Element	I	II	III	IV	V	VI	Lit. Values	Method
Mg	9.5	13	6.7	13	14	7.2	18-27	AA[a]
							18.1-22.8	AA
							13	NAA[b]
Al	0.26	1.6	0.44	0.20	0.34	0.60	0.40	ES[c]
Ca	127	92	104	147	133	135	90-110	AA
							85-105	AA
							39	NAA
Mn	0.18	0.55	0.30	0.51	0.46	0.90	0.15	AA
							0.013	ES
							0.0043	NAA
Fe	1.2	1.9	1.1	3.7	1.7	1.9	0.5-2.0	AA
							0.65-1.75	AA
							1.71	ES
Co	0.08	0.24	0.09	0.24	0.20	0.17	0.061-0.063	ES
Cu	1.3	1.6	1.9	1.3	1.9	1.4	0.70-1.65	AA
							0.5-1.5	AA
							1.20	AA
							1.10	ES
							0.85	NAA
Zn	0.36	0.79	0.74	0.67	0.97	0.61	0.6-1.5	AA
							0.8-1.6	AA
							1.30	ES
							0.93	NAA
Mo	0.093	0.13	0.11	(d)	0.19	0.11	0.34	ES
I	0.061	(d)	0.144	(d)	(d)	(d)	0.050-0.120	
Ba	(e)	(e)	(e)	0.017	0.029	0.031	0.071	ES
							0.066	NAA

[a] atomic absorption
[b] neutron activation analysis
[c] emission spectrography
[d] interference
[e] barely detectable

procedures. In contrast, spark-source mass spectrometric analysis requires only dry ashing and preparation of electrodes.

INAA measurements in blood or serum are subject to interference from the high sodium, chlorine and bromine levels in this and other biological samples. Therefore, little INAA work was expended on these sample types.

(b) Fingernails

This sample was also studied as an indicator of excess metal intake. Like hair, fingernails store and concentrate toxic metals such as arsenic.

The sample preparation is very similar to that for hair. The organic material must be removed by oxidation.

The presence of approximately 30 different trace elements has been detected and quantitated in these nail samples, as shown in Table B-2. It is interesting that the elements found in fingernails are essentially the same as those found in human hair,[41] indicating similarity in the qualitative compositions of these two epidermal tissues. Further examination of the tabulated results revealed that the quantitative composition of the trace elements also overlaps, to an extent, those found in human hair. For example, zinc ranges of 14-280 µg/g and 62-360 µg/g were found in hair and nails respectively. For copper, a range of 31-98 µg/g was found in hair, overlapping with 17-64 µg/g range in nails. Several other elemental examples could also be drawn. These similarities in the qualitative and quantitative compositions of the two tissues may be due to the fact that both contain significant quantities of keratin, providing a certain like affinity for the metabolites in human blood.

The blank spaces in Table B-2 represent lack of detection in those cases. Some of the high values for silicon possibly reflect pickup from the quartz ware in which the sample was prepared. This was not observed in the blanks, however. The aluminum values also look very high compared to data we had observed on hair, but no source of contamination could be found.

Table B-2

TRACE ELEMENT SURVEY ANALYSIS OF 17 FINGERNAIL SAMPLES BY SPARK SOURCE MASS SPECTROMETRY

Donor	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*
Age	*1 mth*	*1 yr*	*1½ yr*	*1½ yr*	*4½ yr*	*24 yr*	*25 yr*	*26 yr*	*27 yr*	*27 yr*	*27 yr*	*28 yr*	*30 yr*	*34 yr*	*38 yr*	*55 yr*	*58 yr*
Sex	*F*	*M*	*F*	*M*	*F*	*F*	*F*	*F*	*M*	*M*	*M*	*M*	*M*	*M*	*M*	*F*	*F*
Bi						0.89	1.8										
Pb	21	64	28	5.3	14	12	3.7	1.7	24	13	11	14	4.7	7.2	6.7	1.7	1.8
Ce							0.27							0.34		1.2	
La							0.17		7.2					0.25		0.51	
Ba	11	8.8	8.4	1.5	43	5.3	6.8	2.0	10	4.5	2.0	2.4	5.8	2.8	5.3	3.3	4.8
Cs									6.6								
Sb									5.9	0.75							
Sn	2.5	13	7.1		14	3.8	2.3	6.6		4.5	43	11	2.9	2.1	8.3	58	0.63
Cd			7.9								2.6		2.0	0.99			
Ag	1.6	3.4	2.8	0.76			0.34				1.0	1.1				0.43	
Mo	5.2	3.5	5.0	3.3	19	3.4	7.5			6.8			2.1	2.7		4.6	4.4
Zr		2.1	1.9			0.64	0.28			0.80			1.1	0.44			0.47
Sr						0.78					0.60		0.86		0.58	0.43	
Rb											1.9	1.4				2.9	
Se				1.7		20	16		15		0.83	3.0	9.1	1.7			4.1
As	2.2	1.3	0.67	0.37	1.3	1.9	0.24		2.7	2.2	0.48	0.51	0.20	0.71	1.4	0.16	0.45
Ge				0.87		1.5	1.2			11	1.6	0.77	1.5	1.0	11	0.48	1.8
Zn	300	187	139	152	142	62	217	151	240	360	190	160	160	120	120	120	150
Cu	15	70	72	41	36	27	17	22	64	28	59	27	30	25	19	43	22
Ni*	24	21	11	40	8.0	24	7.0	4.3	12	8.8	13	5.2	7.3	8.1	3.2	1.8	6.6
Fe	28	27	180	60	69	64	21	37	88	160	74	130	44	92	160	56	62
Mn	4.2	5.7	3.6	0.58	3.0		0.21		2.0	1.5	1.2	1.3		1.2	2.2	1.3	1.3
Cr	11	9.1	9.3	6.9	3.6	5.2	3.0	7.0	5.3	13	3.4	4.5	10	2.8	5.0	2.4	4.9
Ca	930	1,000	1,060	550	420	640	450	1,030	1,600	1,200	1,600	1,020	1,400	690	1,300	480	1,100
K	3,500	990	2,040	2,500	1,950	4,800	2,000	817	9,900	950	5,400	3,400	4,200	2,900	2,400	2,200	7,400
P	42	300	480	90	140	78	61	92	570	140	390	260	240	200	230	24	150
Si**	1,600	300	890	310	710	96	83	150	200	110	280	74	80	95	120	70	150
Al*	290	180	270	79	390	53	16	50	110	260	130	42	37	75	150	58	90
Mg	94	77	160	190	80	59	11	150	270	380	170	100	160	59	140	29	140
Na	3,300	1,300	1,100	1,200	3,300	1,500	760	720	5,900	590	580	1,200	2,800	850	2,100	2,100	420

* Possible unresolved interference
** Likely pickup from quartz ware

Typical comparisons between SSMS and INAA are shown in Table B-3.

(c) Tissues

Autopsy tissues or biopsies of patients may also be of analytical importance to the forensic laboratory. In particular, tissues which tend to store and concentrate metals are of interest in detecting possible poisonings. Liver, kidney, and brain tissues are all of interest from this standpoint.

The tissues can be treated and prepared for analysis in a similar manner to the hair and fingernails. For SSMS, the organic material must be removed. Often, the inorganic residue is 5% or less of the original tissue.

In general, SSMS allows the analysis of more elements than INAA, although possibly not to as accurate an extent. For possible poisonings, however, the highest accuracy is not normally necessary. Of importance, is whether an abnormally high level of the toxic element is present.

C. Cloth Fibers

1. Introduction

A type of evidence material often found at the scene of a violent crime agairst a person is a scrap of cloth. A certain amount of identification of cloth fibers can be done with a microscope, i.e. color, weave, nature of fiber, etc. Once this preliminary identification has been done, analysis of the trace element profile can be further used to match similar looking samples. It is not feasible to consider collecting a large background of trace element profiles for all fibers, as has been done for hair samples, because of the many types of fibers, the many treatment and dying processes, and the change in fiber characteristics with wear and laundering procedures. A comprehensive study by activation analysis of some fibers and the effects of wear on wool sweaters is reported by Bush, et al.[42]

2. Sample Preparation

The samples chosen for a comparative study were artificial fibers obtained from E. I. duPont Company of Richmond, Virginia. These were

Table B-3

ANALYSIS OF NAIL CLIPPINGS

(Patient C)

Elemental Concentrations ppm

Element	Nail Clippings SSMS	Nail Clippings NAA
Pb	6.7	--
Au	--	--
Ba	5.3	--
Sb	--	--
Sn	8.3	--
Sr	0.58	--
Br	--	--
As	1.4	--
Ge	11	--
Zn	120	--
Cu	19	18
Ni	3.2	--
Fe	160	--
Mn	2.2	.65
Cr		
Tl	2.8	--
Sc	--	--
Ca	1300	--
K	2400	8500
S	1800	--
P	230	--
Si	120	--
Al	150	230
Mg	140	--
Na	2100	1700

pure fibers which had not been dyed or processed into cloth. The samples treated by NAA were irradiated and counted with no sample preparation. Those analyzed by the SSMS were ashed and combined with graphite to form an electrode in the usual manner.

3. Results and Discussion

Table C-I shows a comparison of data obtained from Nylon and Nomex samples by SSMS and NAA. There are very obvious gross differences between the two samples which point out the ease of distinguishing between the two materials. Discussions with a chemist at duPont revealed that certain of these elements are added intentionally to control certain features of the fibers. For example, copper and iron fall into this category and are generally the only elements for which duPont analyzes. These two alone would make any identification studies open to low confidence. Iodine is also of interest. Potassium iodide is used in the manufacture of nylon, so potassium and iodine are expected to be present in rather large concentrations. However, the iodine is not detectable by the SSMS because it is driven off in the ashing process but is detectable by NAA since no preirradiation sample preparation is used.

A longer irradiation and counts after several week decay of processed cloth samples indicated the presence of additional longer lived isotopes. In these samples, the number of elements detectable by INAA ranged from 8 to 14, however, it must be remembered that a wait time of one to two weeks is required. The ability to monitor 10-20 elements by either technique, INAA or SSMS gives the forensic analyist many "fingerprint" marks to go by. The differences in trace element concentration which result from the methods used to manufacture the fibers and process the cloths can be useful if an adequate number of comparison samples is available.

D. Tobacco

1. Introduction

In one of the earlier reports of the General Atomics forensic activation analysis group[43] duplicate samples of tobacco from different brands

Table C-I

ANALYSIS OF NYLON AND NOMEX FIBERS

	Nylon I		Nylon II		Nomex	
ELEMENT	SSMS	NAA	SSMS	NAA	SSMS	NAA
Pb	0.61		1.15		1.20	
Ba	2.16		2.07		1.10	
Zn	2.27		2.30		6.10	
Ni	0.66		0.56		1.60	
Mn	0.26	0.37	0.30	0.45	0.37	1.76
Cr	3.00		2.22		0.98	
Ca	19.8		14.4		790	
K	2640*	1105	1310	947	527	819
Na		15.7		14.0	660	558
S	23.6*		5.70		35	
Si	31.1*		10.3		22	
Al	10.6	6.6	9.9	7.6	26	
P	0.37		0.51		1.2	
Cu	74.0	58.1	69.7	47.8	15	27
Fe	10.1		9.1		35	
Cl		240		253		2204
I		1144		1200		
Au						0.42

*possible interference

of cigarettes were irradiated and counted with a NaI detector. Concentrations of Na, K, Br, Mn, and Sc were calculated for all brands and four other elements were positively identified or indicated to be present in some samples. The authors conclude that NAA for the identification of tobacco does not appear to be very promising because agreement between duplicate samples is only fair and tobacco from different brands does not seem to vary greatly.

Later activation analysis work by Nadkarni and Ehmann[44] and by Jenkins et al.[45] with high resolution GeLi detectors have reported 14 and 10 elements respectively in tobacco and its products. These investigations did not involve chemical separations but did include long irradiation periods and long wait times.

2. Sample Preparation

Samples of tobacco were taken at random from several packs of cigarettes. The tobacco of a given brand was mixed and separated into samples for NAA and SSMS analysis. The NAA samples were irradiated directly, that to be analyzed by the SSMS was ashed, mixed with graphite and formed into an electrode in the usual manner.

3. Results and Discussion

The results of a typical analysis are shown in Table D-I. It is clear from this table that many more elements can be analyzed for by the SSMS with ease and that the two techniques complement each other. The elements Br and Cl are not readily quantified by the SSMS because of interferences and because of the losses of these elements during the ashing process. There are some evident discrepancies in the table and discrepancies between replicate runs by one technique of samples from the same batch. It is believed that these discrepancies are real and represent the lack of homogeniety of the sample. Other authors[44] report large standard deviations, 10-20% for 5 elements and 30-50% for three others, for replicate analyses on a given type of cigarette. This wide variation in the concentrations of so many elements in tobacco and its products makes it very difficult to fingerprint cigarettes by their trace element profiles, even with improved techniques.

Table D-I

ANALYSIS OF COMMERCIAL CIGARETTE TOBACCOS

Element	Salem		Marlboro		Kent No. 1		Kent No. 2	
	SSMS	NAA	SSMS	NAA	SSMS	NAA	SSMS	NAA
Pb	8.1		7.5		34		8.8	
Ba	94		50		320		56	
Br	--*	162	--*	152	--*	171	--*	164
Cl	--*	7425	--*	7054	--*	8100	--*	10200
Sr	82		58		290		120	
Zn	55		79		71		110	
Cu	81	46	77	40	23	79	177	79
Ni	4.8		7.4		6.5		11	
Fe	460		180		930		890	
Cr	6.3		2.6		5.4		--*	
Ca	3100		10000		--*		26000	
K	25000	10975	76000	43000	--*	52000	35000	48765
P	--*		2100		6100		560	
Si	2300		250		972		2800	
Al	850		200		2400		990	
Mg	3200		3600		14000		2700	
Na	770	430	307	805	15000	576	350	924
Mn	150	180	250	170	200	164	381	229
S	--*		2.4		11.		741	

*Interference

E. Glass

1. Introduction

A large scale survey of trace element concentrations in glass from England has been done by Coleman[46,47] and co-workers who analyzed 539 samples of broken window panes collected from the scenes of fires in England and Wales. Using group chemical separations and sodium iodide crystals they analyzed for 21 elements by NAA with a combination of short and long neutron exposures. They have used the statistical approach suggested by Parker[11] to examine the correlation of the various elements and conclude that eleven elements (aluminum, arsenic, barium, calcium, hafnium, manganese, sodium, rubidium, antimony, scandium, and strontium) are sufficiently uncorrelated to be used as indicators. They have run test cases on mixed samples which were successful in discovering those samples from a common origin and state that their study indicates that multi-element analysis is a discriminating method of comparing glass fragments.

2. Sample Preparation

Two different types of glass were obtained for these comparative studies. One was a common bottle glass, the other a common plate glass. Small fragments of each were taken and pulverized to prepare identical samples for analysis by the two methods. The powder in a polyethylene vial was run directly by NAA, while the non-conducting nature of the sample dictated its mixture with a suitable matrix for analysis by SSMS. High purity graphite was found to be satisfactory as a matrix. Mixed in a 1 part glass to 2 part graphite ratio, the resulting electrode sparked well and produced a vigorous ion flux.

3. Results and Discussion

Some typical results are shown in Table E-1. As is the case for other samples, the number of elements readily found by SSMS is about twice the number found by NAA under the conditions imposed. With longer irradiations and longer wait times more of the longer lived isotopes reported by Coleman could also be detected. However, it should be noted that glass

Table E-1

ANALYSIS OF GLASS
(values given in ug/g)

Element	Bottle Glass		Plate Glass	
	SSMS	NAA	SSMS	NAA
Na	17,200	17,770	1,450	59,135
Mg	Int.	--	51,600	--
K	20,000	25,700	8,070	20,171
Ca	315,000	--	130,000	--
Ti	926	--	793	--
Cr	6,800	--	3,760	--
Mn	132	143	150	197
Fe	3,540	2,000	4,120	2,000
Ni	Int.	--	154	--
Cu	65	Int.	105	Int.
As	210	31.3	66	46
Sr	1,000	--	800	--
Zr	441	--	633	--
Ba	12,600	4,156	764	3,622
Pb	103	--	115	--
Al	45,400	78,800	34,000	81,900

is not an ideal matrix for doing multi-element instrumental NAA because of the large amounts of sodium, potassium, iron and silicon. The sodium and potassium will activate fairly readily and mask many of the short lived isotopes. Iron is not particularly sensitive to analysis by NAA but its presence in large quantities will mask some of the longer lived isotopes. Silicon does not activate readily and is not reported here, however, it is known to be a major constituent of glass. The reaction $Si^{28}(n,p)Al^{28}$ is induced by fast neutrons and the gamma ray detector cannot distinguish Al^{28} produced from Si from Al^{28} produced by the reaction $Al^{27}(n,\gamma)Al^{28}$. This probably is the reason why the aluminum values reported by NAA are so much higher than those reported by SSMS. One must be careful of this type of interference in situations where the matrix can produce significant amounts of activity by fast neutron activation.

The National Bureau of Standards has made available since 1970 standard reference materials SRM 610 through 619, trace elements in glass. These should be used as standards for all glass analyses.

F. Metals

1. Introduction

Metal samples are of broad interest to forensic laboratories. The elemental composition of metal samples, such as bullet lead, may be used to attempt a matching of a bullet fragment to a known manufacturer.[48] As another example, stolen copper wire may have an impurity distribution of trace elements which will provide a comparison to a questioned source.

INAA is not particularly useful at analysis of common metals because many metals have large activation mass sections. For example copper has two stable isotopes, Cu^{63} and Cu^{65}, which have cross sections at 4.5 and 2.3 barns respectively for forming an activation product. The radioactive isotope Cu^{64} has a 12.8 hour halflife and Cu^{66} a 5.1 minute halflife. Thus the spectrum from a short irradiation will be dominated by the Cu^{66} and that from a long irradiation by Cu^{64} making it virtually impossible to detect the presence of trace elements in copper by INAA. Although iron does not activate readily it is difficult to find many trace elements

in stainless steel because of the presence of manganese, chromium, tungsten and cobalt. Even the analysis of bullet lead by INAA is complicated by large amounts of antimony.[15] However, SSMS with its uniform sensitivity is particularly well suited for the analysis and identification of metals.

No significant sample treatment is necessary, other than surface cleaning. The mass spectra provides convenient "fingerprints" for qualitative comparison. The addition of quantitative analysis for each element is an even better check, of course.

2. Sample Preparation

Reagents. Electrodes, 1 mm x 10 mm, were prepared from standard aluminum and copper rods (Johnson, Matthey, and Co., Inc., London, England) and from NBS stainless steel rods. High purity acids (G. F. Smith Chemical Co., Columbus, Ohio) were used for a cleansing etch before prespark.

3. Results and Discussion

The range of elements which can be determined by SSMS is shown in Table F-1. The copper sample shows many impurities at the parts per million level and below. Most of these are accidental inclusions resulting from the source of ore, processing, etc. Different batches even from the same company may show significant differences.

Quantitative results are shown in Tables F-2 and F-3 for metal standards analyzed against other known metal standards. The use of such standards allows the concentrations of elements in unknown metal samples to be determined. A dual electrode holder system was used so that the standard and unknown could be analyzed close together in time.

Dual Electrode Mount. The designed holder for the dual electrode pair is made from stainless steel and tantalum. Tantalum is used for the shields and clamps, those parts surrounding the spark discharge. Tantalum tension springs are used to mount compacted samples to avoid breakage, while set screws are preferred to hold metal samples securely. The design allows use of the standard AEI electrode holder support. A broad shield

Table F-1

QUALITATIVE IDENTIFICATION RESULTS OF ELEMENTS FOUND IN A COPPER SAMPLE BY SSMS

Element	Identification by Mass No.(s)	Element	Identification by Mass No.(s)
Beryllium	9	Selenium	76,77,78,80,82
Boron	10,11	Bromine	79,81
Carbon	12,13	Strontium	86,87,88
Nitrogen	14	Zirconium	90,91,92,94
Oxygen	16	Niobium	93
Sodium	23	Molybdenum	92,94,95,96,97,98,100
Magnesium	24,25,26	Silver	107,109
Aluminum	27	Cadmium	110,111,112,113,114
Silicon	28,29,30	Indium	115
Phosphorous	31	Tin	116,118,120
Chlorine	35,37	Antimony	121,123
Potassium	39	Tellurium	126,128,130
Calcium	40	Barium	134,135,136,137,138
Titanium	47,48	Tantalum	182
Vanadium	51	Gold	197
Chromium	52,53	Mercury	198,199,200,201,202,204
Manganese	55	Lead	204,206,207,208
Iron	54,56	Bismuth	209
Cobalt	59		
Nickel	58,60		
Copper	63,65		
Zinc	64,66,68		
Arsenic	75		

on one holder extends between the two electrode pairs and prevents direct deposition of material from one set onto the other while sparking. Geometry of the holders is such that when one pair is sparking, the other pair is sufficiently separated to prevent sparking.

Analytical Results. Tables F-2 and F-3 show data obtained on two different sample types using the dual electrode pair arrangement. Integrations were taken in the order shown under each element. Analyte integrations were alternated with those of the standard for repetitive comparison. The data are from consecutive analyses of the two materials and represent truly typical obtained data. Precision difficulties may appear more often in the compacted samples if extreme care is not taken in the preparation. The small amount of sample consumed puts severe demands on sample homogeneity.

Advantages of Dual Electrode Pairs. The quantitative analysis difficulties with SSMS in the past are well-known. Electrical detection and integration now allow quantitative respectability for SSMS, but our experience has been that extremely close parameter control is necessary. It is not at all unusual to see integration changes of 30-50% with slight changes in electrode alignment and shielding. Changes in magnet current, acceleration-ESA voltages or vacuum conditions may also produce time dependent differences. With dual electrode holders, the time between sampling of the standard and analyte is quite small and rechecks of any particular element vs. the standard can be made at any time before the total analysis is completed. In our laboratory, this has resulted in more precise and accurate data than using a standard pair to take integrations for a series of elements, followed by breaking vacuum, replacement with the analyte pair, and then obtaining integration values for each element in the analytical sample. This is not to suggest that accurate and precise data cannot be obtained by the conventional single electrode pair approach,

Table F-2

ANALYSIS OF NBS 444 STEEL VS. NBS 442 AS A STANDARD, USING THE DUAL ELECTRODE HOLDERS

Trial	V, ppm	Cr, %	Mn, %	Co, ppm	Ni, %	Cu, ppm
1	1043	19.1	4.75	2340	9.84	2510
2	1043	19.8	4.57	2340	9.96	2510
3	1043	19.2	4.64	2300	9.84	2480
4	1000	20.1	4.61	2340	10.01	2480
5	1043	20.0	4.68	2320	9.70	2480
6					9.70	
Av	1034	19.7	4.65	2320	9.85	2495
NBS cert.	1200[a]	20.5	4.62	2200[b]	10.1	2400[c]
Rel error	14%	3.9%	0.75%	5.9%	2.5%	0.4%

[a]Certified as 0.12%
[b]Certified as 0.22%
[c]Certified as 0.24%

Table F-3

ANALYSIS OF JOHNSON-MATTHEY CB-4 COPPER VS. CB-0 AS A STANDARD
(values in ppm, by weight)

Trial	Mn	Fe	Co	Ni
1	16.7	26.5	17.4	24.7
2	16.5	25.7	17.4	23.6
3	16.5	25.5	17.0	23.6
4	16.0	25.7	16.7	23.6
Av	16.3	25.8	17.1	23.9
J.-M. cert.	15	29	18	26
Rel error	9.3%	10.8%	5.0%	9.6%

but data can be obtained more rapidly with the dual-electrode holders and, of greater significance, more frequent cross checks can be made between sample and standard.

G. Art Objects

1. Introduction

Mr. Tom Chase of the Freer Gallery of Art, Washington, D. C., pointed out an interesting potential use of SSMS in the analytical examination of many different types of art objects. Trace element profiling of these materials may aid in authentication (and detection of bogus items) when a catalog of data is built up for genuine objects of a particular period.

After visiting the Freer Gallery, several ancient chinese bronzes were made available for analysis. The metal objects are ideal samples for SSMS, where many elements may be determined. Ceramics and pottery ware are also of potential interest in examining the pigment materials and the clay itself for elemental constituents.

2. Sample Treatment

The basic approach for preparation and cleaning is similar to that described for metals. However, the sampling of possibly precious art objects may provide only a few drillings or chips which must then be compacted into an electrode form or tipped out on some suitable matrix. For the results described here, sufficient material was available to form an entire set of electrodes.

3. Results and Discussion

Table G-I shows the elemental analyses of two different chinese bronzes. A first problem is the selection of a suitable standard. The closest available standard was the National Bureau of Standards SRM No. 63, which was then used for all three samples.

The greatest problem encountered in such work is the lack of suitable homogeneity in the samples. Sampling in one portion of the object may not produce the same results as a sample taken from an adjacent portion. These limitations should be recognized in attempting to use the analytical data for authentication purposes.

Table G-I

ANALYSIS OF ANCIENT CHINESE BRONZES BY SSMS

Element	Bronze 1	Bronze 2
Ag	0.027	0.185
Al	0.023	0.002
As	0.050	0.346
Bi	0.004	0.004
Br	0.004	ND
Ca	0.081	INT
Cl	0.030	0.001
Cr	0.048	0.010
Fe	0.055	0.199
K	0.012	INT
Mg	0.007	0.0005
Mn	0.0008	0.0005
Na	0.020	0.001
Pb	0.341	0.184
S	0.020	0.074
Sb	0.007	0.166
Se	0.004	ND
Si	0.090	0.022
Ti	0.001	ND
V	0.002	0.0002
Zn	0.006	0.002

H. Narcotics and Drugs

1. Introduction

Our approach to these materials has been completely different from the conventional drug analysis. Essentially all of these techniques are designed to examine the organic constituents of narcotics and drugs (for identification, purity, etc.); our interest is in the inorganic constituents, with the thought of developing a "fingerprint" spectrum from the data. This could be of value in the following ways:

(1) Point of origin (growth site) might be determined by relating the trace elements in such as marihuana with the soil where it was grown. Under a BNDD license, we have done studies of domestic and non-domestic marihuana samples which indicate vast differences. The large number of elements available by SSMS allow many data points for comparison.

(2) For batch preparations, such as hashish, the successive treatment steps create specific trace element residues which are striking. The final dried product may be influenced by (a) the composition of the original marihuana plant, (b) the purity (or lack of it) of extracting agents involved in the processing, and (c) containers used for the mixing, extracting, and drying. The many synthesis steps provide more opportunity for unique identification than even natural distribution of the elements.

SSMS and NAA can detect extremely small concentrations of elements which may be picked up from these steps and possibly relate a specific hash sample to a specific batch or a batch utensil which may contribute identifying elements. For example, a recent industrial residue run in our laboratory by SSMS for another firm showed a distribution of elements that pointed out a stainless steel vessel as the corrosion source. As unstandardized as hashish preparations appear to be, significant differences may be found.

2. Sample Preparation

These organic based samples require treatment in a similar manner to that described for the hair or tissue samples.

3. Results and Discussion

Little attention has been given to the inorganic constituents of drugs and narcotics. Bate and Pro[49] examined several drugs, looking at various trace elements by NAA. Reynolds, et al.[50] used NAA to study the source of a drug from its elemental concentrations. Schlesinger and co-workers[51] reported on the characterization of tranquilizers and heroin by NAA.

We were aware of no work by SSMS in this respect. The greater versatility of SSMS, with its ready detection of more elements than NAA, makes it of particular interest to apply to these studies. The greater amount of elemental data again provides more reference points for comparison.

Table H-1 shows representative data by SSMS for three marijuana samples, two domestic and one foreign. Significant differences are shown even between the two domestic varieties; the Korean sample exhibits an even greater divergence.

Table H-2 shows a SSMS comparison between three different types of narcotics samples. Very high levels of certain elements are found in hashish, probably as a result of contact with various preparation ware.

INAA data for four different hashish samples are shown in Table H-3. Aluminum and iron are again noted to be very high. The background preparation of these samples is unknown, as would normally be the case. To our knowledge, no extensive tabulation of trace metal constituents of narcotics samples has been done. Obviously, extensive analysis would be required of domestic and non-domestic samples to determine the overall variation in trace element content.

As an interesting side product of our research, we have found some hashish samples to contain unacceptable quantities of toxic elements, such as lead. The user may be in more danger at times from the hidden inorganic impurities than the organic active components.

Table H-I

Analysis of Three Different Marijuana Samples by SSMS.
(values in ppm)

Element	Marijuana I	Marijuana II	Korean Marijuana
Pb	1.6	8.2	6.6
Ce	--	--	4.9
La	0.49	--	2.1
Ba	24	56	480
Sr	92	110	570
Rb	22	74	60
Zn	30	71	59
Cu	6.3	19	18
Fe	580	340	1,100
Mn	330	860	380
Tl	97	32	310
F	10	6.5	22
B	110	71	53
Al	650	141	3,800
Mg	4,000	8,200	9,900
Ca	> 1%	> 1%	> 1%
K	> 1%	> 1%	> 1%
P	5,400	6,800	3,300
Si	> 1%	> 1%	> 1%
Na	1,700	(88?)	1,600
Sc	--	--	9.4

Co, Ni, Cr - not calculated due to inferences

Br, Cl, S - variable ashing losses

Table H-2

Analysis of Controlled Substances by SSMS.
(values in ppm)

Element	Marihuana	Hashish	Opium
Pb	4.1	21.7	57.9
La	0.92	6.2	ND
Ba	43.9	38.8	25.6
Sr	71.9	120	46.6
Rb	28.1	71.3	41.9
Br	7.7	66.0	63.0
Zn	79.9	27.3	73.6
Cu	11.4	23.2	4.6
Co	3.7	0.9	Int.
Ni	0.75	ND	Int.
Cr	3.6	18.6	3.0
Fe	149	16,000	5,330
Mn	430	422	52.5
F	12.4	3.4	36.3
B	54.4	--	--
Ca	Major	Major	6,400
K	Major	Major	Major
P	6,800	1,740	5,440
Al	110	24,000	7,060
Mg	8,160	3,840	1,870
Na	28.1	890	1,080
Ce	ND	10.2	1.5
Cs	ND	ND	1.2
Sn	ND	ND	290
Ag	ND	3.6	3.9
Nb	ND	ND	1.3
Zr	ND	23.1	19.0
As	ND	6.2	4.0
Ga	ND	8.7	4.5
V	ND	33.0	7.0
Tl	ND	1,940	283
Sc	ND	2.3	0.8

Table H-3

Analysis of Hashish by NAA
(ppm) by weight of leaf

Element	Hash 1	Hash 2	Hash 3	Hash 4
V	5±1	33±3	8±2	18±3
Br	39±3	25±1	31±1	42±2
Cl	1,420±80	1,800±200	2,850±150	1,250±250
Na	900±300	800±50	900±200	1,500±500
Mn	250±30	420±40	900±50	300±30
Al	1,900±100	12,000±1,000	6,200±300	10,000±1,000
La	4±.5	5.5±.5	3.8±1	6.4±1
Au	~.15	<.1	~.4	<.1
K	1.2%	2.5%	2.5%	2%
Sb	2±16%	1.5±20%	8±12%	11±10%
Co	2.1±14%	6.8±8%	5.3±17%	6.6±10%
Fe	1,200±12%	7,000±5%	4,000±17%	7,000±5.5%
Sc	<1	5±2%	3±3%	5±2%
Cr	7±24%	38±12%	14±30%	35±12%

I. Gun Shot Residues

1. Introduction

One popular application of NAA to the forensic science has been in the analysis for gunshot residue. If a person fires a hand gun, there will be a certain amount of powder backflash which may be detectable by NAA. Normally a lift will be taken from a suspect's hand using a paraffin cast or dilute acid wash and the lift irradiated and analyzed for barium and antimony. These two elements are known constituents of gun powder and bullet primers, are readily detectable by NAA, and are not commonly found in significant quantities on human skin. This technique was first used by Ruch, Guinn, and Pinker[52] and reported by Guinn and his co-workers at General Atomics in several publications. One of the latest G. A. reports is by Schlesinger, et al.,[13] in which the results of many firings are reported and a statistical analysis performed based on the determination of two elements. Coleman[3] has also reported similar gunshot residue analysis done in England. Three papers on the subject were presented at the First Forensic Activation Analysis Conference[53] and six at the Second.[14]

2. Sample Preparation

Paraffin casts are taken from the hand by painting a thin layer of hot paraffin on the back of the hand with a new nylon paint brush. The area sampled includes the thumb, the thumb webbing, the back of the hand near the trigger finger and the top of the trigger finger. The cast is peeled off with tweezers and stored in a plastic bag. For NAA the cast is placed in an irradiation vial and irradiated for 20 minutes with a barium and antimony standard. With a high resolution GeLi detector the 0.166 MeV gamma ray from the 82.9 minute isotope Ba^{139} and the 0.564 MeV gamma ray from the 2.8 day isotope Sb^{122} are detectable after a one hour wait, which is necessary to reduce the chlorine interference. The casts to be analyzed by the SSMS were ashed in a muffle furnace and the ash mixed with graphite to be formed into an electrode.

Table I-1

Barium and Antimony Content of Paraffin Lifts
After Firing 0.38 Pistol

Sample	Barium Micrograms	Antimony Micrograms	Lead Micrograms
	NAA Results		
T4F	1.63	1.17	N.D.
W4F	2.12	9.60	N.D.
G4F	5.08	5.30	N.D.
K4F	1.91	6.58	N.D.
	SSMS Results		
W31	1.4	1.1	11
W32	1.7	0.23	9.3
T3	0.71	0.57	4.6
T5	0.27	N.D.	1.2
A3	0.86	1.4	2.9
	Blank Values--No Gunshot		
	SSMS Results		
WR1	0.67	5.8	0.94
LW	0.12	0.17	N.D.
WR2	N.D.	N.D.	N.D.
MR	0.66	N.D.	N.D.
ML	N.D.	N.D.	N.D.

Table I-2

Analysis of Gunshot Residue
Dilute Acid Lifts

Sample (1)	Barium Micrograms	Antimony Micrograms
	SSMS Results	
NT3	6.74	2.92
NA2	3.94	1.18
NT2	23.55	1.89
NW2	3.88	1.76
AA	2.86	0.49
AT	1.32	4.89
	NAA Results	
NK2	4.14	0.81
NW3 (2)	2.01	1.52
NA3 (2)	2.43	1.12
NG3 (2)	0.81	1.31
NG2 (3)	5.05	--

(1) Sample notation N-nitric acid, A-acetic acid, second letter is persons code, number is number of times fired.

(2) Sample taken with cotton swipe.

(3) Rinse sample not evaporated down. Fraction of sample used, Sb not detectable.

Table I-3

Analysis of Gunshot Residue
Dilute Acid Lifts

SSMS Results - Elements Other than Ba and Sb
Micrograms

Sample	Code	Pb	Cu	Zn	As	Mn	Se	Ag	Te	Ga
43-a	NT3	127.0	28.3	153.8		1.1				
b	NA2	27.5	6.9	87.7	67.3	7.6	184.6	11.2	23.3	
c	NT2	145.6	52.0	111.7		2.5				
d	NW2	25.0	46.5	35.6		1.2				
e	AA	1194.9	2.6	over	0.5	1.2				9.1
f	AT	10.3	24.3	77.7		1.9				

prominent in the spark source spectra. Lead, which cannot easily be detected by NAA, is clearly present in large quantities and is a suitable third element which could be used in conjunction with barium and antimony to characterize the firing of a hand gun. Copper, zinc and manganese are also present in higher quantities than in the blanks but they may not be useful in characterizing a weapons firing. Since they are fairly common elements, there is a wide variation in the amounts of these elements on the hands of the general public.

Another type of gunshot residue sample analyzed is the area around a bullet hole. In some cases in which there is a penetration, as for example, through cloth or tissue, the question is raised as to whether the hole was made by a bullet or some other objects, such as a knife.

The sample available for analysis was a flesh wound about one centimeter thick and four or five centimeters square. Samples of tissue were cut from the entrance and from the exit of the wound and from the top and back surface of the tissue near the edge as controls. The sample to be analyzed by NAA was activated for three minutes with the reactor at power of one megawatt and then counted for the 83-minute Ba-139 isotope. They were later irradiated for two hours and counted after a 21-day wait to detect the two antimony isotopes. The spectrum from the long irradiation was dominated by the antimony so that no other elements other than zinc were found.

The tissue samples for the spark source were ashed overnight, mixed with spec-pure graphite to form an electrode and sparked. The results as shown in Table I-4 show abnormal amounts of many of the heavy elements. The high lead concentrations in the wound entrace almost completely blackened the plate. The high concentrations of all of the elements listed, even in the controls, is probably the effect of redistribution in the formalin solution in which the sample had been stored. The disagreement between the two analysis methods at the wound exit is probably a sampling difference caused by the jagged characteristic of the wound.

It is clear from this table that the spark source is the preferable technique for this type of analysis. NAA can detect only a small number

Table I-4

Analysis of Gunshot-Wound Skin Tissues

Micrograms/Gram of Dry Weight

Sample	Entrance Control SSMS	Entrance Control NAA	Wound Entrance SSMS	Wound Entrance NAA	Exit Control SSMS	Exit Control NAA	Wound Exit SSMS	Wound Exit NAA
Bi	ND		31		ND		ND	
Pb	47		65,600		84		890	
Ba	1.7	ND	210	262	6.8	ND	34	442
Sb	ND	1.89	100	132	ND	3.85	0.69	83
Sn	ND		380		0.39		4.7	
Cd	ND		41		ND		2.0	
Ag	ND		2.2		ND		ND	
Sr	2.6		26		1.5		1.7	
Zn	11	ND	250	189	31	ND	45	188
Cu	4.3		120		47		22	
Ni	--				13		20	
Fe	29		460		78		970	
Mn	--				1.1		4.9	
Cr	--				4.0		11.0	

of elements and some of the major constituents in bullets, such as lead, tin, and iron either are not detectable by NAA or can be found only with long irradiations or special techniques. Also, the time factor can be significant. Because of the nature of radioactive decay, waits of several days are necessary for shorter lived isotopes to decay.

J. Toxicological Studies

1. Introduction

Several of the classical metal poisons, such as arsenic and mercury, have a high sensitivity for detection by NAA. There have been many papers written on arsenic concentrations in normal hair, hair subjected to external contamination from various industrial processes, and hair from persons allegedly poisoned. Most of this work is well summarized in the proceedings of the two International Conferences on Forensic Activation Analysis.[14,53] Much of the earlier arsenic analyses were done with a chemical separation, selective for arsenic, which is necessary when counting is done with a NaI crystal because of the interference of the Br-82 gammas. With a high resolution GeLi detector the 0.559 MeV As line can be separated from the 0.555 MeV Br line and the 0.657 As gamma can be detected with no chemical separation if the arsenic level is above normal. An extensive series of activation analyses for arsenic in hair of people from the British Isles was reported by Lenihan and Smith[19] who reported ranges in the normal population of 0.5 to 1.5 ppm in men and 0.1 to 1 ppm in women and that concentrations greater than 2.5 ppm were rare. Jervis[5] reports studies indicating that normal concentrations of arsenic in hair range from 0.2 to 3 ppm and concentrations greater than this are rarely found. This upper limit of 3 ppm has been found to be about the lowest concentration of arsenic that can be detected by instrumental neutron activation analysis. Concentrations in hair from poisoned persons are higher than this and are readily detectable.

Certain elements other than arsenic are of forensic interest due to their toxic nature. It also happens that these particular elements present difficult analytical problems at times. For example, lead, mercury, arsenic, and selenium are all toxic and potentially lethal. Each

can be difficult to analyze at trace levels. One of the prime advantages of SSMS over NAA is that all of these can be analyzed simultaneously, along with certain other hazardous elements, such as beryllium and cadmium. Still, problems can exist in the spark discharge. Mercury, being rather volatile, may be lost from the samples. Arsenic and selenium may also show some loss under certain conditions.

2. Sample Preparation

Hair samples for analysis of metal poisons are taken and either irradiated directly or ashed and mixed with pure graphite to be sparked in the SSMS. Normally there is an ample amount of sample to facilitate the analysis.

3. Results and Discussion

A typical set of comparative data for a patient from the University of Virginia Hospital whose hair was found to contain an abnormal amount of arsenic is listed here.

NAA hair unwashed	29 ppm As by weight
NAA hair washed	24 ppm As by weight
SSMS hair washed	12 ppm As by weight.

In this case the hair was cleaned with a dilute detergent solution, acetone and demineralized water. Since the cleaning procedure appeared not to alter the measured arsenic concentration, later hair samples were not cleaned. The difference in the results between NAA and SSMS may result from either of two causes: a) A large hair sample was analyzed so the difference may be a true difference arising from the nonhomogeneous sample representing different growth periods or b) some volatile arsenic compounds may have been lost during the ashing process.

One case in which high arsenic levels were determined is an interesting study, which illustrates precautions which must be taken to obtain a proper sample. A patient was admitted to the University Hospital with all of the symptoms of a massive dose of arsenic. Hair clippings were taken and analyzed with two standard samples from the reactor staff as a comparison. The gamma ray spectrum of the patient's hair showed only

a slight trace of arsenic, approximately 2 ppm which is at the lower limit of detectability and the upper range of normal levels. This was inconsistent with the medical findings and mystifying to the attending physicians. Approximately a week later a larger hair sample was clipped from the patient with care taken to include newly grown hair close to the scalp. Part of this sample was sent to be analyzed in the spark source laboratory and the other part carefully cut into two sections, one part from the neighborhood of the scalp and the other from the tip ends. The sample investigated by the spark source included the entire length of hair and had a concentration of 60 ppm of arsenic, the highest levels of arsenic seen in this lab. No other heavy metals were seen, indicating arsenic as the toxic element. The other two sections of hair, analyzed by neutron activation, showed only a small trace of arsenic in the tip ends but a very large clearly defined arsenic peak in the sample taken close to the scalp as shown in Figure J-1. This indicates that the patient probably received one large dose rather than a long term chronic exposure. In such cases one must be careful about drawing conlusions from hair clippings taken too soon and be careful to obtain representative samples of the entire hair length.

As a follow up on this case, fish samples and fertilizer were analyzed by NAA for arsenic. The patient was especially fond of fish that he caught in his private pond and was the only one in the family to eat them. Shortly before becoming sick, he had spread a load of commercial fertilizer on his garden on a windy day so both the fish and fertilizer were suspect. The fish did not evidence abnormal arsenic concentration, however, the arsenic in the fertilizer was clearly evident in the gamma ray spectra as shown on Figure J-1.

To study other toxic elements and possible arsenic losses during the ashing process more carefully, simulate samples containing lead (as a relatively stable reference), mercury, arsenic, and selenium were prepared. The first decision required was that of proper matrix. High purity graphite is generally used in our laboratories, so that was first examined. Results showed that all of the elements except mercury stayed in the electrode

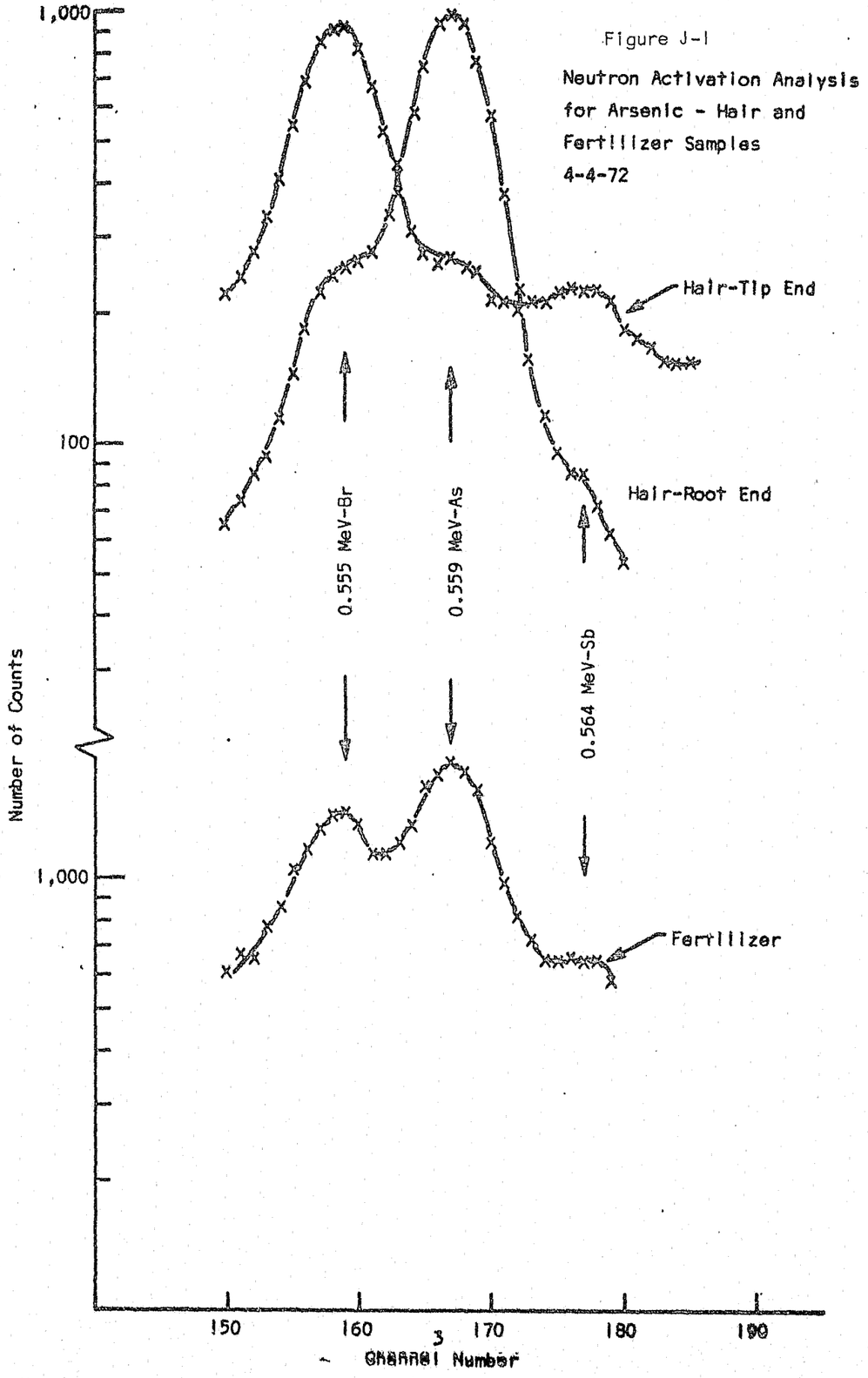

Figure J-1

Neutron Activation Analysis for Arsenic - Hair and Fertilizer Samples 4-4-72

during the spark discharge. Subsequent comparison with silver as a matrix element showed that mercury was not evolved from the electrode, an effect attributed to the amalgamation properties of silver. Closer inspection, however, indicated that a heating effect was probably the cause of the difference. On rerunning the two matrices, increasingly severe spark conditions were imposed which in turn gradually raised the temperature of the electrodes. Normally, the silver electrode allows milder conditions than the graphite, thus running at a lower temperature. In this controlled test, however, where the temperatures were essentially the same for each matrix, mercury loss occurred for each at the same high spark conditions. Thus, mercury loss is not negated by the silver matrix, as this points out. What is important seems to be low spark conditions to prevent heating of the electrode.

The other elements, arsenic, selenium, and lead, did not show any observable vaporization loss, even at high spark conditions. Thus, in running any forensic SSMS analysis where the presence of mercury is suspected, low spark conditions should be maintained. A pulse length of 100 usec and a pulse repetition rate of 100 seem to work conveniently.

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THESES, PAPERS, AND PUBLICATIONS ARISING FROM PROJECT

A. Theses

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B. Papers Presented

1. "Comparison of Activation Analysis and Spark Source Mass Spectrometry for Forensic Applications," presented at the 1968 International Conference on Modern Trends in Activation Analysis, Oct. 7-11, 1968.

2. "Factors Affecting Trace Analysis by Spark Source Mass Spectroscopy," Southeastern Meeting, American Chemical Society, Tallahassee, Florida, December 1968.

3. "Comparisons of Neutron Activation Analysis and Spark Source Mass Spectroscopy," 13th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tennessee, October 1969.

4. "Effect of Spark Position in Spark Source Mass Spectroscopy," Southeastern Meeting, American Chemical Society, Richmond, Virginia, November 1969.

5. "Trace Elemental Analysis of Blood Serum by Spark Source Mass Spectroscopy," Southeastern Meeting, American Chemical Society, Richmond, Virginia, November 1969.

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11. "Determination of Trace Elements in Biological Materials by Spark Source Mass Spectroscopy," Mass Spectrometry Symposium, Middle Atlantic Regional Meeting, American Chemical Society, Baltimore, Maryland, February 4, 1971.

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22. "Gap Width as a Critical Parameter in Spark Source Mass Spectrometry," American Society for Mass Spectrometry, Dallas, Texas, June 6, 1972.

23. "An Automated Gap Control Unit for Spark Source Mass Spectrometry," Solids Workshop, American Society for Mass Spectrometry, Dallas, Texas, June 8, 1972.

24. "Survey Analysis of Drugs and Narcotics by Spark Source Mass Spectrometry," Solids Workshop, American Society for Mass Spectrometry, Dallas, Texas, June 8, 1972.

25. "The Multichannel Analyzer as a Spectra Accumulator in Spark Source Mass Spectrometry," American Society for Mass Spectrometry, San Francisco, California, May 1973.

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1. "Comparison of Activation Analysis and Spark Source Mass Spectrometry for Forensic Applications," Modern Trends in Activation Analysis, NBS Special Publ. 312, 283-287 (1969).

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