Neutron Activation Analysis in Scientific Crime Investigation

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Neutron activation analysis (NAA) is a nuclear method of qualitative and quantitative elemental analysis, applicable to the analysis of essentially all kinds of liquid or solid samples. Small samples are made radioactive by bombarding them with neutrons for a suitable length of time (t_i) and then counting them for a suitable period of time (t_c) following a suitable radioactive-decay period of time (t_d) with a germanium semiconductor gamma-ray detector coupled to a multi-channel pulse-height analyzer (i.e., a gamma-ray spectrometer). In order to achieve high detection efficiencies for the various detectable elements in a sample, the very high fluxes of thermal (i.e., slow) neutrons available in a research-type nuclear reactor are employed for the neutron-irradiation of samples and standards. The NAA method then has the desirable features of excellent detection sensitivities for a large number of elements; each of which can be firmly identified via the energies of the gamma-ray photons of its neutron-induced radioisotope (and the radioisotope half life), a high degree of accuracy, and excellent measurement precision. In the purely-instrumental form of the NAA method (INAA), the method is nondestructive. With a typical reactor neutron flux (10^{13} n $cm^{-2}s^{-1}$) and moderate irradiation and counting times, the NAA method can achieve lower limits of detection (LOD) in the range of 10^{-7} microgram (μg) to 10μg of an element for some 70 elements of the periodic system — how low depending on which element. A median LOD is around 10^{-3} μg (one nanogram), i.e., one part per million (ppm) in even a one-milligram sample.

Forensic NAA

Because of its great detection sensitivity, the NAA method has found important applications in many fields, e.g., medicine, biology, geochemistry, industry, art, and archaeology, environmental sciences — and forensic chemistry. Most of the currently-used applications of NAA in forensic chemistry originated during the period of 1962-1970 by the author and his colleagues in his former laboratory (General Atomic in San Diego, California) in an extensive study supported by the U.S. Atomic Energy Commission and the U.S. Department of Justice. Since 1970, the author and his students at the University of California at Irvine have extended the earlier studies further and added new ones.

The Detection of Gunshot Residue

The first of the earlier studies to be very successful was the development of a method for the detection of gunshot residue (GSR), e.g., on the back of the firing hand of a suspect in a shooting case. At the time, no satisfactory method for the detection of GSR was available — the old "paraffin test" having been long discarded because of its unreliability. The NAA test for the presence of GSR involves analyzing moistened swabs of the backs of the hands of a suspect for the elements barium (Ba) and antimony (Sb), typically present in the swab of the shooting hand in amounts of the order of 1 mg. They come from the presence of $Ba(NO_3)_2$ and Sb_2S_3 in the primers of almost all kinds of revolver, automatic pistol, and rifle cartridges, and shotgun shells, as major ingredients of the primers (except for 0.22-caliber cartridges, most brands of which do not contain both of these ingredients). In this application, the various hand swabs involved in a shooting case are activated in a nuclear reactor and the resulting radioisotopes, 84.6-minute Ba-139 and 2.70-day Sb-122, then radiochemically separated with non-radioactive Ba and Sb carriers before counting on a Ge gamma-ray spectrometer. Barium-139 emits a 166 keV γ-ray photon in its decays, and antimony-122 emits a 564 keV γ-ray photon in its decays. (keV is the abbreviation for one thousand electron volts of energy.)

The GSR application has been employed in many hundreds of gunshot homicide cases since about 1970 by the Federal Bureau of Investigation (FBI) Laboratory in Washington, D.C. A lesser, but substantial, number of such cases have been investigated by the author, plus some in other laboratories. The FBI Laboratory does such analyses for city, county, and state law enforcement agencies (but not for the defense) from all over the country who request such assistance. The results of such GSR analyses have been presented in court in hundreds of cases. Even though there are now three competitive, non-nuclear methods for the detection of GSR (flameless atomic absorption spectrophotometry, inductively-coupled plasma atomic emission spectroscopy, and scanning electron microscopy

with x-ray emission spectroscopy), the NAA method is still used considerably. These three competitive methods are usually abbreviated, respectively, as FAAS, ICP-AES, and SEM-XRE. All four methods have their own relative advantages and disadvantages.

Arsenic-in-Hair Measurements in Arsenic Poisoning Cases

For centuries, arsenic has often been used to poison individuals. With a massive ingestion of arsenic, if not vomited and if medical help is not quickly obtained, death can occur within hours or days. Such instances are known as acute arsenic poisoning. Since the symptoms are pronounced and death occurs rapidly, such deaths under suspicious circumstances are often diagnosed as acute arsenic poisoning; tests are run on urine, stomach contents, etc., and suicide or murder is ascribed as the cause of death. A less obvious form of arsenic poisoning, much more difficult to detect, is often used by a poisoner — chronic arsenic poisoning. In this form of murder by poison, the poisoner typically adds smaller amounts of arsenic (often in the form of arsenious oxide, As_2O_3) repeatedly to the food or drink of the victim. This produces sickness and weakens the body's resistance, but may not be fatal for perhaps weeks or months — and the symptoms are sufficiently non-specific that arsenic poisoning may not even be suspected. If death results under these conditions, it may be medically ascribed to other causes, no tests for arsenic are made, murder is not suspected, and the body is buried or cremated. In cases of chronic arsenic poisoning if death of the victim does not occur after one attempt (often involving a series of ingestions during a moderate period of time), the poisoner may try again — this time using a larger dose of arsenic and possibly causing death.

One of the most famous studies of arsenic poisoning conducted by the NAA of hair samples is that carried out on samples of Napoleon's hair, by Hamilton Smith. Taking samples of Napoleon's hair that had been cut at various times during the former emperor's exile on St. Helena (1815 to his death in 1821), Smith sectioned each sample into 3 mm lengths, activated them, and counted them for the presence of radioactive arsenic (26.3-hour arsenic-76). He found levels as high as 30 ppm As — compared with a normal level of only about 1 ppm As. The final conclusion of the studies (though erroneously reported by some journalists and writers as evidence that Napoleon was murdered by arsenic poisoning) was that Napoleon, a very sick man in exile, was being treated with arsenic-containing medicines in efforts to cure him, not kill him. At that time, such medicines were often used.

The author has analyzed hair samples in several cases of suspected chronic arsenic poisoning, including one rather publicized case that will go to trial soon. The procedure is to first obtain a bundle of 30-50 strands of head hair from the victim (surviving, just dead, or from an exhumed body, keeping the strands aligned, with the root ends together at one end. Second, the bundle of aligned hair strands is washed repeatedly with alternate washes of pure water and pure acetone — to remove any external contamination. Third, after allowing the washed bundle to air-dry overnight, the bundle is cut into consecutive 5 mm sections, with each section put into a separate small, labeled polyethylene vial, and each sample is accurately weighed, ready for analysis. Finally, the analytical samples are activated in the reactor for two hours, allowed to decay overnight, and then sequentially counted on a Ge gamma-ray spectrometer for 20 minutes each. From the spectrometer digital printouts, the size of the 559 keV γ-ray peak of As-76 of each sample is measured and compared with that of an arsenic standard, to calculate the amount of arsenic in each sample. Typically, each sample only weighs about 3 mg, so a 1 ppm As sample only contains about 3 nanograms of As, or a 100 ppm As sample contains about 300 ng of As (0.3 μg). In one case studied, the hair of one victim showed two broad concentration peaks along its length: over 120 ppm As near the root end, then down to around 1 ppm As, then another broad peak of about 40 ppm As, and then down to around 1 ppm As near the tip end. This showed, then, an earlier episode of arsenic ingestion (giving the 40 ppm As peak), later (i.e., more recently) followed by a larger ingestion (giving the 120 ppm As peak). The victim almost died, but his life was saved in the hospital. In the same case, the hair of another possible victim, whose body was exhumed, showed no evidence of arsenic poisoning — each hair section only showing the normal As level of around 1 ppm. Since human head hair grows at the rate of about 0.4 mm per day, a 5 mm length corresponds to a growth period of about 12 days. The body excretes some of its body burden of arsenic from the blood stream into the roots of the hair strands; as the hair grows, the hair strand is steadily extruded out of the hair follicle as the hair strand grows outward from the scalp.

Multi-Element Forensic Applications of NAA

In the field of forensic chemistry, there is a well-established "principle of trace-element comparison of evidence specimens as to probability of common, or non-common, origin." In the earlier forensic NAA studies at General Atomic, applications of this principle were explored with samples of known common origin and samples of known different origins of such evidence-type materials as bullet lead, paint, glass, and paper. In this short presentation only the bullet-lead applications (the most widely used) will be discussed. Applied to bullet-lead specimens, this principle states that two or more evidence specimens of bullet lead, carefully analyzed, will be indistinguishable from one another in their respective concentrations of all major, minor, and trace elements detected and measured in them — if all were produced from the same melt of lead. If they were not produced from the same melt of lead, they will exhibit significantly different concentrations of one or more of these elements. Some 80-90% of commercially-produced bullets are composed of antimony-hardened lead. In their manufacture, Sb is alloyed with the molten lead; upon solidification, the resulting lead is appreciably harder than straight lead. Various manufacturers employ various Sb concentrations in the various kinds of bullets that they produce, common Sb concentrations being 0.50, 0.75, 1.0, 1.25, 1.5, 2.0, on up to 4.0% by weight. The higher the Sb concentration, the harder the bullet. The other 10-20% of commercially - produced bullets are soft lead bullets, not alloyed with Sb. Since both soft and hardened lead bullets employ a good deal of recycled scrap lead (as well as virgin lead), some Sb is present in soft lead bullets also but only at quite low concentrations; e.g., in the range of about 1 to 1,000 ppm Sb (1 ppm = 0.0001%). Both soft lead and hardened lead bullets also contain low concentrations of Ag, As, and Cu — present as trace impurities in the lead. Silver is usually present only at levels in the range of about 1 to 100 ppm, whereas As and Cu usually each exhibit concentrations in the range of about 1-1000 ppm. In hardened bullets, the Sb concentration is regulated (to meet specifications) at close to the nominal value, but the other three trace impurity elements (and Sb also, in soft lead bullets) are not added deliberately and not regulated. Even when a manufacturer makes a series of production runs of the same kind of bullet — nominally all the same in composition — the levels of the trace elements vary from one melt of lead to the next. Thus, each melt of lead has its own elemental concentration pattern (sometimes referred to as its "signature" or "fingerprint").

Small samples (e.g., 10-20 milligrams) cut from evidence specimens of bullet lead can be analyzed by INAA for their silver contents via a rapid procedure in which the silver is measured via the 658 keV γ-ray peak of 24.6-second Ag-110. Using a longer reactor irradiation, Sb is measured via the 564 keV γ-ray peak of 2.70-day Sb-122; As via the 657 keV peak of 26.3-hour As-76; and Cu via the 511 keV peak of 12.7-hour Cu-64.

The INAA method has been used by the author for the analysis of bullet-lead evidence specimens in about 100 gunshot homicide cases and by the FBI Laboratory in perhaps a thousand or more such cases. Typically, samples of fragments of a fatal bullet or of a mashed bullet — recovered at autopsy from the body of a victim are compared with samples of unfired bullets associated with one or more suspects in a shooting case (e.g., from unfired cartridges in his gun or from other unfired cartridges in his possession). Such an INAA comparison for four elements can ascertain whether or not the fatal bullet and any of the unfired bullets were produced from the same melt (batch) of lead. If there is a perfect "match" between two or more specimens, however, it cannot prove that the bullets came from the same original manufacturer's box of cartridges, since one melt of lead will produce a very large number of indistinguishable bullets, enough to fill a large number of boxes of cartridges. For example, neglecting any losses along the way, one ton (2,000 pounds) of lead can produce 93,400 identical 150-grain lead bullets (1 gram = 15.432 grains). This is enough to fill some 1,870 boxes of 50 cartridges each.

The President Kennedy Assassination.

Among the many gunshot homicide cases in which the author has analyzed bullet-lead evidence specimens by INAA, some of the better known cases are the SLA shootout (Symbionese Liberation Army, the kidnappers of Patty Hearst) in Los Angeles, the murder of Argentine heavyweight fighter Oscar Bonavena in Nevada, and the assassination of President John F. Kennedy in Dallas. In this short presentation, only the President Kennedy assassination will be discussed.

As most people know, President Kennedy was shot and killed in Dallas on November 22, 1963. The subsequent Warren Commission investigation of the assassination, as summarized in their 1964

report, stated the conclusion that the assassin was Lee Harvey Oswald (himself killed by Jack Ruby some 48 hours later) and that he probably acted alone. Many people were skeptical of the Warren Commission findings and many books were written on the subject. The FBI conducted the investigation for the Warren Commission. The findings were quite conclusive on various points: (1) the two copper-jacketed bullets (one broken into two large pieces) recovered from Governor Connally's hospital stretcher intact and the two large pieces found in the limousine were fired from Oswald's recovered 6.5 mm Mannlicher-Carcano rifle, (2) he fired three shots, one of which missed the limousine, (3) the President was first hit in the back, the bullet exiting at his throat — a painful, but not lethal wound, (4) the President was then hit in the back of the head causing massive brain damage, the fatal wound, and (5) Governor Connally (sitting in a jump seat in front of the President) was struck in the back, the bullet then exiting his chest, breaking bones in his right wrist, and finally (allegedly) imbedding itself slightly in his left thigh, then falling out onto his stretcher.

The FBI Laboratory analyzed samples of the various bullet-lead evidence specimens first by emission spectroscopy (a qualitative method that produced no useful results) and then by neutron activation analysis. Unfortunately, this was their first experience with NAA, and their results were also inconclusive — the objective being to ascertain whether more than two bullets were represented among the various specimens.

In an effort to settle the controversy over the Warren Commission findings, the U.S. House of Representatives in 1977 established a Select Committee on Assassinations to conduct an independent examination of all the evidence in the case. The Select Committee asked the author to reanalyze all of the bullet-lead evidence specimens by INAA and he did so. The specimens were flown out to California from the National Archives by a man from the Archives. During a period of three days the author examined and sampled the specimens and then analyzed them for Sb, Ag, Cu, and As (though no arsenic was detectable in any of them). This time the results were quite conclusive: all of the specimens were of one or the other of two, and only two, compositions. The largest difference between the two groups of specimens was in their Sb concentration: one group (the Connally stretcher bullet and fragments from Connally's wrist) averaged 815 ± 25 ppm Sb, whereas the other group (fragments from President Kennedy's brain and one large fragment and various small fragments found in the limousine averaged only 622 ± 20 ppm Sb. The two groups of specimens also differed significantly in their Ag and Cu concentrations. In 1978, the author presented his findings before the Select Committee, in Washington, D.C.

In 1986, London Weekend Television produced an excellent 5-hour documentary film entitled, *On Trial, Lee Harvey Oswald*, in which the author testified at the mock trial.