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I. INTRODUCTORY COMMENT

A. INTRODUCTION

§ 1. Definition

One of the newest and most promising techniques of forensic science is neutron activation analysis. The ability of this nuclear method to detect traces of elements in minute samples enables it to solve many problems of identification that have heretofore been considered hopeless. As shown in Figure 1, the process is essentially one whereby the material to be analyzed is first made radioactive—i.e., it is "charged" so that it will give off or emit radiation in the form of gamma rays. This radioactive sample is then exposed to a scintillation crystal; and every time a gamma ray from the radioactive material interacts with the crystal, it emits a flash of light, which is converted into an electrical pulse whose voltage is proportional to the energy of the gamma rays. An electronic device called a multichannel differential analyzer then sorts the electrical impulses into different energy groups and adds up the pulses in each group. The result is a graph shown on an oscilloscope screen (see Figure 5 in Appendix). The graph contains information related to the kind and amount of elements in

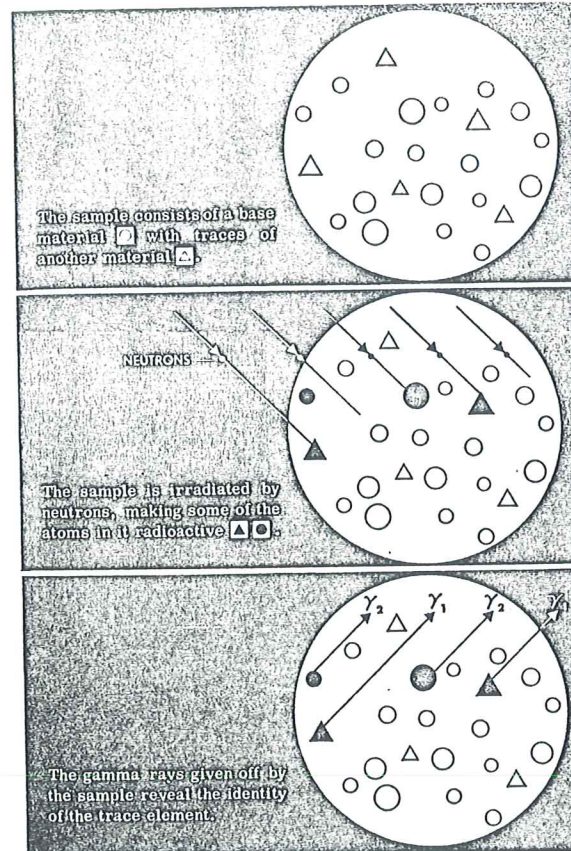


Figure 1. Illustration of How Activation Analysis Works. After being bombarded with neutrons, various elements in a sample material become radioactive, and by analyzing the energy of the emitted gamma rays, the different elements in the material can be identified and measured. (Reprinted from *Neutron Activation Analysis*, courtesy U. S. Atomic Energy Commission.)

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the radioactive sample and can be transcribed immediately or stored on magnetic tape or punched paper tapes for future reference.

These different stages of activation analysis can be seen in Figure 2.

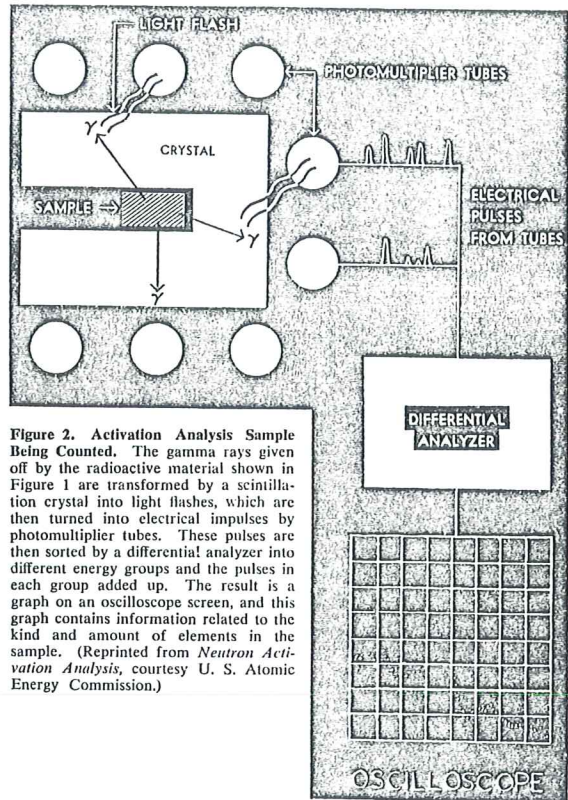


Figure 2. Activation Analysis Sample Being Counted. The gamma rays given off by the radioactive material shown in Figure 1 are transformed by a scintillation crystal into light flashes, which are then turned into electrical impulses by photomultiplier tubes. These pulses are then sorted by a differential analyzer into different energy groups and the pulses in each group added up. The result is a graph on an oscilloscope screen, and this graph contains information related to the kind and amount of elements in the sample. (Reprinted from *Neutron Activation Analysis*, courtesy U. S. Atomic Energy Commission.)

Virtually no sample of material is too small to be analyzed by activation analysis. A single hair, a shred of marijuana, or a fleck of automobile paint no larger than the period at the end of this sentence can be analyzed and correctly identified. Furthermore, activation analysis's high sensitivity allows quantitative measurement of elements in the parts per million and parts per billion range. For instance, if one thimbleful of arsenic poison were diluted in ten tankcars of water, the exact amount of arsenic present could be determined by activation analysis. In most cases the analysis is also nondestructive, so that material evidence may be preserved for presentation in court or saved for analysis by another method.

§ 2. Concept of Matter

In order to understand the principle of neutron activation analysis, it is important to have a fundamental, if highly simplified, grasp of the concept of matter as it is classified into elements—gold, arsenic, copper, nickel, and so forth.

The atom is the smallest known particle of any single element capable of independently existing by itself and yet still retaining the qualities that mark it as a specific element. Each atom is composed of a series of parts, interchangeable from one atom to the next, that revolve about its nucleus at tremendous speeds in an orderly manner, somewhat comparable to the movement of the solar system about the sun. The nucleus of the atom is composed of protons (particles possessing a positive charge of electricity) and neutrons (particles possessing no charge of electricity). Some distance away from the nucleus of the atom are the electrons (particles possessing a negative charge of electricity equal to, and opposite to, the positive charge of the proton). The electrons revolve about the nucleus of the atom and are firmly held in their course by the electric attraction generated from the nucleus of the atom.

The difference between any two elements—gold and tin for example—is the difference in the number of protons in the nucleus of each atom and is expressed as a specific atomic number. The atomic weight of any element is the sum total of the weights of the protons and neutrons in the nucleus of the atom. To gain a relative perspective of the difference in size between the atom and its nucleus, the atom may be compared to a structure possessing the size of a modern auditorium; its nucleus would be approximately

the size of a pea, suspended in the center of the auditorium in mid-air.

In 1932 Sir James Chadwick, in England, determined that the neutron, possessing no electrical charge, could penetrate the almost impenetrable force-field set up by the electrical attraction of the whirling electrons as they made billions of orbits per minute about the nucleus of the atom. Without examining in depth the scientific principles connected with this operation, it may be said that a technique was devised whereby a quantity of neutrons, expressed in the multitude of one million per second through every square centimeter, are fired at a controlled rate at a specific quantity of matter. This bombardment makes many of the atoms of the different elements present in a sample absorb neutrons, and alters their nuclear configuration. Such a neutron bombardment produces some unstable forms of the element called radioisotopes, which, since they are unstable, undergo "radioactive decay." This is an example of artificially induced radioactivity, as distinct from the natural radioactivity of such elements as uranium, thorium, and radium. The effect of this change (the creation of new isotopes by altering the nuclear balance of a particular atom) has allowed creation of more than one thousand radioisotopes from originally stable isotopes of the elements.

Radioisotopes, as they decay to more stable states, emit radiation principally as alpha particles and beta and gamma rays. The great penetrating power and characteristic energy of gamma rays make them best suited for identifying the non-radioactive form from which any particular radioisotope originated. It is the individuality of these gamma ray emissions, or "nuclear fingerprints," for particular elements that is the basis of activation analysis. In the most commonly used form of the technique, the gamma rays are measured (counted) with standard radiation detecting equipment after the sample has been made radioactive by inserting it into the core of a nuclear reactor. (See Figure 11 in the Proof and Figures 3 and 4, Appendix.)

§ 3. History and Development

The discovery of artificial radioactivity in 1933 by Frederic and Irene Curie-Joliot led almost immediately to the recognition of activation analysis as a valuable research tool. As early as 1936, G. Hevesy and H. Levi carried out the first activation analysis experiment. Progress from this point was rather slow, however,

as scientists awaited the development of the two basic components in any activation analysis facility—the neutron source and the radiation counting equipment.

It was only after World War II that nuclear research reactors, which are efficient high density sources of neutrons, became available. "Research" reactors should not be confused with the more widely known "power" reactors; the latter are designed to produce heat for conversion into electrical power. The energy from a power reactor could light a city, but the power output of a typical research reactor would be sufficient only to heat several hundred electric irons. Possessing the capability to conveniently irradiate samples, which power reactors commonly lack, research reactors are utilized as tools by industrial, university, and government laboratories active in nuclear research and development.

Coupled with the advances in research reactors has been the development of modern radiation detection and measuring equipment with a sensitivity unheard of only a few years ago. Thus, the stage has been set for the large scale utilization of activation analysis in numerous fields where it offers significant advantages.

§ 4. Basic Theory; Activation

The most useful neutrons for activation analysis travel with relatively low energy and are referred to as slow neutrons. Their probabilities for forming activation products are referred to as "slow neutron capture cross sections" and are expressed quantitatively in "barns." (The term "barn" is applied because it expresses the notion of a neutron "hitting the side of a barn," in this case an atom of a specific element.) Generally, but with certain distinct exceptions, the heavy elements have larger cross sections (higher barn values) for such capture than do lighter ones. Cobalt, with an atomic number of 27 and a cross section of 20 barns, is fairly easy to determine, while activation analysis sensitivities for light elements are relatively poor. Oxygen, for instance, whose atomic number is 8 and whose cross section for slow neutron capture is 0.0002 barns, is virtually impossible to determine by this method simply because the chances of hitting the oxygen atom with enough neutrons to make it sufficiently radioactive to be counted effectively are very low.

To make the "activation" concept of the method more understandable, it is possible to compare the situation to a skeet shoot.

Every clay pigeon that is hit represents an atom that has been made radioactive and is, therefore, subject to detection by activation analysis. The number of radioactive atoms (clay pigeons hit) that will result from neutron irradiation of a given element is a function of:

(1) its neutron capture cross section as expressed in barns (the bigger the pigeon, the easier it is to hit, since elements with higher cross sections are easier to activate);

(2) the density or flux of bombarding neutrons (an air rifle bombardment would be analogous to a relatively low flux, while a shotgun blast would represent a higher flux of neutrons);

(3) the number of atoms of the element present in a unit volume of the sample (the more pigeons in the air at one time, the greater the chances of hitting them; many atoms of a particular element will be activated if it is present in a high concentration).

The person firing the gun could score only in a definite time period—say, one minute—and could count only those pigeons hit within a certain target area—one square yard, for example.

The basic equation for activation analysis may be simply expressed as follows:

$$N^+ = N \phi \sigma$$

where N^+ = the number of atoms activated per second in each cubic centimeter of the sample,

ϕ = the neutron flux, in neutrons per square centimeter per second,

σ = the neutron capture cross section, in square centimeters,

N = the number of atoms of the element in question present in each cubic centimeter of the sample.

§ 5. — Decay

Making an element radioactive, however, is not like turning out wooden croquet balls on a lathe. Once the wood is shaped into a sphere, it stays that way. Radioactivity is more like making soap bubbles: no sooner are radioisotopes created than they immediately begin to decay. The rate of decay is described in terms of a radioisotope's "half life." Half life is the period of time required for half the atoms of a radioisotope present to disintegrate. Man-

ganese 56, for example, has a half life of 2.6 hours: once made radioactive, it will take 2.6 hours for half the original radioactive atoms to decay. There will be one quarter of the original number of radioactive manganese 56 atoms left at the end of the second half life period, or 5.2 hours after irradiation; one eighth will remain after the third half life, and so on in a geometric progression toward zero. Gold 198 has a half life of 2.7 days and is well suited to determination by activation analysis. Silver 110, with a half life of only 24 seconds, decays so rapidly that there is not much time to count it after it is formed.

The counterpart of the previous equation for the creation of radioisotopes, then, is the equation for the decay of radioisotopes:

$$N^- = \lambda N^*$$

where λ = the radioactive decay constant, which is equal to 0.693 divided by the half life,

N^* = the number of radioactive atoms per cubic centimeter.

If new radioactive atoms are being created at a constant rate, their number will keep increasing until their rate of formation just equals their rate of decay. Usually, it takes such a long time to get to this point (which is called radioactive equilibrium) that the analyst settles for fewer radioactive atoms than he could get if he wished to pay for the additional irradiating neutrons. In effect, he activates a certain percentage of the total fraction of atoms available for activation within a sample, instead of all of them.

Of course, if the atom's half life is short, on the order of minutes, equilibrium can be reached rather easily. But then, by the time the irradiated sample has been transferred to the radiation analyzer, a large portion of the radioactive atoms of interest may have decayed. Therefore, some compromise between irradiation time and neutron flux level must be reached. Both time and flux cost money, so the analyst must choose the combination that costs the least and still does an adequate job.

§ 6. Sensitivity

Clearly, the most outstanding advantage of the activation analysis technique is the tremendous sensitivity offered in the determination of the composition of samples. When employing a high neutron density (flux) reactor, the method offers a median limit of detection for some 70 elements of about 0.05 micrograms (5/100,000,-

000 of a gram) or 5 parts per billion in a 10 gram sample. Some elements, such as dysprosium, are detectable to levels as low as one millionth of a microgram. The detection limits for many elements listed in Figure 3 can be pushed 10 to 100 times further if needed. Figure 4 shows that these sensitivity values are generally more than 1000 times better than those attainable by the emission spectrograph and other techniques commonly employed in establishing what elements make up samples of interest in forensic problems.

One hour irradiation at a thermal neutron flux of 2×10^{12} n/cm ² sec			
Limit of Measurement Element (micrograms)	Limit of Measurement Element (micrograms)	Limit of Measurement Element (micrograms)	Limit of Measurement Element (micrograms)
Aluminum 0.01	Indium 0.00005	Rhodium 0.0005	
Antimony 0.005	Iodine 0.005	Rubidium 0.05	
Argon 0.05	Iridium 0.0001	Ruthenium 0.01	
Arsenic 0.001	Iron 200	Samarium 0.0005	
Barium 0.05	Lanthanum 0.001	Scandium 0.01	
Bismuth 0.5	Lead 10	Selenium 0.01	
Bromine 0.005	Lithium 100	Silicon 0.05	
Cadmium 0.05	Lutecium 0.00005	Silver 0.0001	
Calcium 1	Magnesium 0.5	Sodium 0.005	
Cerium 0.1	Manganese 0.00005	Strontium 0.005	
Cesium 0.5	Mercury 0.01	Tantalum 0.05	
Chlorine 0.01	Molybdenum	Tellurium 0.05	
Chromium 1		Terbium 0.05	
Cobalt 0.005	Neodymium 0.1	Thallium 5.0	
Copper 0.001	Nickel 0.05	Thorium 0.05	
Dysprosium 0.000001	Niobium 0.005	Thulium 0.01	
Erbium 0.001	Osmium 0.05	Tin 0.5	
Europium 0.000005	Palladium 0.05	Titanium 0.05	
Fluorine 1	Phosphorus 0.5	Tungsten 0.001	
Gadolinium 0.01	Platinum 0.05	Uranium 0.005	
Gallium 0.005	Potassium 0.05	Vanadium 0.001	
Germanium 0.005	Praseodymium	Ytterbium 0.001	
Gold 0.0005		Zinc 0.1	
Hafnium 1	Rhenium 0.0005	Zirconium 1	
Holmium 0.0001			

Figure 3. Activation Analysis Sensitivities. The detection limits of many elements listed here can actually be pushed 10 to 100 times further if needed.

In addition to this, the precision offered by activation analysis for trace contamination is superior to that offered by competing techniques. (Precision is the degree of reproducibility, among several independent measurements, of the same true value under

specified conditions.) When dealing with concentrations well above the lowest limits of detection, precisions of \pm (plus or minus) 3% of the value are commonly attainable. This compares with \pm 50% to 100% in trace level determinations with the emission spectrograph.

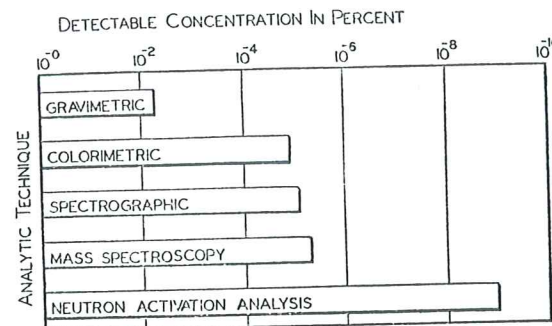


Figure 4. Comparison of Neutron Activation Analysis Sensitivity With That Offered by Other Analytic Methods. The sensitivity of activation analysis varies with the neutron flux level, the time of irradiation, the energy of the bombarding neutrons, and the particular element being analyzed.

B. FORENSIC APPLICATION

§ 7. A Case Study

Despite consistent and categorical denials by the United States Treasury Department, rumors once circulated for two decades that a few copper pennies actually had been minted by the Treasury in 1943. (It will be remembered that in 1943 iron alloy or "white" pennies were issued in order to conserve copper for defense purposes.) A private coin collector confronted the Treasury with what he claimed to be authentic copper pennies that had been turned out by the Mint in 1943 and insisted that his claim either be disproved or substantiated.

First a careful examination indicated that the coins had been turned out by standard U.S. Mint dies, and that the dates "1943" had not been tampered with in any way. The next problem was to learn exactly what the coins were made of. In using any ordinary method of chemical analysis, the collector's coins would have

been damaged in the process. Obviously another solution had to be found, and activation analysis was suggested. One of the coins was placed in a sealed vial, which was then placed in a nuclear reactor to be made radioactive. The part of the reactor that the coin occupied was kept essentially at room temperature so that the coin was unharmed. After being activated, the coin was removed from the reactor and transferred to a gamma ray analyzer.

As the radioactive coin emitted the telltale gamma rays, the spectrum that was plotted across the screen of the analyzer oscilloscope showed that the coin was authentic. Not only had it been turned out by a U.S. Mint stamping machine, but it was made of the Mint's 1942 copper alloy. The private collector really had the fabled 1943 copper pennies that numismatists had dreamed about for twenty years. It was the presence of identical amounts of the same trace elements in 1942 pennies and the collector's 1943 penny that solved the case. From this evidence, authorities speculated that some 1942 copper blanks were hidden away by a person inside the Mint when it was announced that copper was not to be used in 1943 pennies. Once the 1943 dies were turning out coins, the unmarked 1942 copper blanks probably were slipped through the stamping machine and smuggled out of the plant.

This particular case illustrates two of the method's three most outstanding features: nondestructive testing and trace element determination. Although a relatively large sample was used in this case, it would have been possible to analyze a pinhead-sized sample had it been necessary to do so.

§ 8. In Criminal Cases

Numerous investigators have demonstrated the feasibility of using activation analysis in the field of crime detection. In an interesting study of hair characterization, R.E. Jervis and his co-workers have reported on the determination of arsenic in biological samples.¹ The use of activation analysis in shooting cases has been explored under the direction of V. P. Guinn.² J. M. A. Lenihan

1. Macintosh, W. D. and Jervis, R. E.: *The Determination of Arsenic in Biological Materials*. Atomic Energy of Canada, Ltd. Report No. AECL-1083, August 1960.

2. Guinn, V. P.: *Neutron Activation Analysis in Scientific Crime Detection—Some Recent Developments*. *Journal of Forensic Sciences*, Vol. 9, p. 19, Jan. 1964. (First presented at meeting of American Academy of Forensic Sciences, Feb. 1963.)

and his group have detailed various clinical applications of activation analysis.³ It was this last-named Scottish team of scientists who determined the presence of arsenic in Napoleon's hair,⁴ giving rise to the suspicion that he may have been slowly poisoned.

While neutron activation is a reliable and proven method of scientific crime detection, it is not yet extensively employed by forensic chemists.⁵ Probably the principal reason for this is that police, criminalists, and lawyers are not fully informed about the capabilities of the method. Also, the equipment needed is very expensive (a nuclear reactor costs \$150,000 to \$250,000), and only highly skilled personnel can perform the task; thus, it is not practical for a police crime laboratory to set up its own activation analysis facility.

Several nuclear laboratories perform activation analyses on a service basis and utilize airmail service for shipment of samples when necessary.⁶ With the growth of these services, criminalists and others interested in applying activation analysis to their problems can readily make use of the technique without buying their own equipment.

§ 9. — Firearms Identification

Some of the first work in the United States on the application of activation analysis in scientific crime detection was directed toward developing an improved technique for the identification

3. Lenihan, J. M. A. and Smith, H.: *Clinical Applications of Activation Analysis*. Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Vol. 26, United Nations, Geneva, 1958, pp. 238-241.

4. Forshufvud, S., Smith, H. and Wassen, A.: *Arsenic Content of Napoleon's Hair Probably Taken Immediately After His Death*. *Nature*, Vol. 192, pp. 103-105, 1961.

5. A program of applications of activation analysis in forensic science, sponsored by the United States Atomic Energy Commission, is being carried out by the Los Angeles Police Department Crime Laboratory and the General Atomic Division of General Dynamics Corporation in San Diego, California. Inquiries concerning forensic applications of activation analysis may be sent to Director, Division of Isotopes Development, U. S. Atomic Energy Commission, Washington, D. C., or to Mr. Ray Pinker, Chief Criminalist of the Los Angeles Police Department Crime Laboratory, who is coordinating the selection of samples used in this study.

6. General Dynamics's General Atomic Division, San Diego, California; Union Carbide, Nuclear Division, Tuxedo Park, New York; and the Western New York Nuclear Research Center, Buffalo, New York.

of suspects in shooting cases.⁷ This work is based on detection of abnormally high concentrations of barium and antimony on the hands of suspects. (Both barium and antimony are used in primer compositions for all domestic and most foreign revolver ammunition.)

Quantities of barium and antimony as low as one billionth of a gram may be positively identified by using activation analysis. This offers a considerable improvement over the old "paraffin test" or the colorimetric reagent approach suggested by H. C. Harrison in dealing with this type of problem.⁸ It has been demonstrated that the levels of barium and antimony which result from firing a revolver are significantly higher than those which result from lighting safety matches or handling other common sources of these elements.

The following figures illustrate a typical example of the results that were achieved by employing this technique in an actual case.

	Antimony Deposited on Hand Antimony Detected in Sample (After Correcting for Blank)	
Reagent blank	0.03 micrograms
Before shooting	0.05 micrograms	0.02 micrograms
After one shot	0.12 micrograms	0.09 micrograms
After three shots	0.23 micrograms	0.20 micrograms

It is interesting to note that activation analysis is so sensitive that it has been possible to determine that a suspect normally wore a gold ring, based on the identification of submicrogram traces of gold and copper in hand wipings that were being analyzed for primer residues.⁹

The samples are taken in essentially the same way as in the old paraffin test. After removal from the hands of a suspect, the solid paraffin is irradiated to activate traces of barium and antimony that will have been deposited on the suspect's hands if he has fired a revolver. In this case, the irradiated sample must be dissolved and radiochemical separations (for an explanation of radiochemical separation, see § 27, *infra*) employed due to inter-

7. Neutron Activation Analysis: New Tool Against Crime. *Nucleonics*, 1961, Vol. 19, No. 12, p. 74.

8. Harrison, H. C. and Gilroy, R.: *Firearm Discharge Residues*. *Journal of Forensic Sciences*, Vol. 4, No. 2, p. 184, 1959.

9. Guinn, V. P.: *Applications of Neutron Activation Analysis in Scientific Crime Detection*. General Atomic Report No. GA-3491, Sept. 18, 1962.

ference with the gamma spectra of interest resulting from the relatively large quantities of sodium and chlorine that are commonly associated with samples that have come in contact with the skin. (See Figure 6, Appendix.)

In the Warren Commission Report, as published to date, it is mentioned that activation analysis was employed by the FBI on the paraffin cast taken of Oswald's cheek by the Dallas police in the investigation of the death of President Kennedy. Antimony was found by this work in large enough quantities on the inner surface of the cast to indicate the probable firing of a rifle. An activation analysis test was also made by the FBI on the outer or rear surface of the cast. Surprisingly, this also showed a high antimony level, which was probably due to improper handling of the cast after it was taken. Activation analysis was therefore inconclusive in this instance. (See the *Warren Commission Report on the Assassination of President John F. Kennedy*, 1964, p. 562.)

One of the most imaginative and useful ideas for applications of activation analysis tagging has been made by Dr. Paul C. Aebbersold of the United States Atomic Energy Commission. He has suggested that all small arms ammunition that is manufactured in the United States be tagged with different amounts of exotic elements that offer high activation analysis sensitivities. If this were done, it would be possible not only to simplify identification procedures, but also to determine what type of ammunition was used.

§ 10. — Narcotics

Activation analysis work at Oak Ridge National Laboratory has shown that the country of origin of narcotics can be ascertained, based on trace levels of various elements absorbed by the growing plants from local ground waters.¹⁰

§ 11. — Soil

In the first instance of activation analysis evidence being accepted in a court in the United States, it was shown that illicit whiskey seized on a truck in one state had been transported from a still in

10. White, J. C. and Lyon, W. S.: *Nuclear and Radiochemical Analysis*. Oak Ridge National Laboratory Report No. ORNL-3397, pp. 71-112, Dec. 31, 1962.

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posed to neutron bombardment, it is placed next to a high speed X-ray film, and the radioactive atoms of the mineral pigments take their own photograph.¹⁶

Activation analysis is extremely valuable in authenticating some metal objects that may have been counterfeited. A counterfeiter may go to the expense of using real gold, silver, or other precious metals in duplicating ancient coins. If these supposedly ancient coins were analyzed for their trace element composition and were checked against known coins of the same type, it would be quite simple to establish whether or not they were bona fide. Work of this type has been done successfully by a division of the U. S. Treasury Department.

C. PROCEDURES AND TECHNIQUES

§ 21. Masking Effects

Sometimes the general sample material (matrix) has a dominant gamma ray spectrum of its own that masks less dominant spectra. In such cases, the only hope for meaningful activation analysis comparison of apparently similar items depends on a careful selection of irradiation time and decay period prior to counting in order to minimize the interferences from the matrix. New computer codes are being written to simplify the solution of the spectra masking problems via a multiple spectra stripping approach. At the moment, however, interfering spectra from matrix activation remains the single largest limitation in the effective utilization of activation analysis.

When even spectrum stripping (see § 26, *infra*) fails to help significantly in freeing the desired spectra from masking, the analyst must resort to the destructive radiochemical technique for successful activation analysis work. This method is limited in scope to a few elements per analysis due to the necessity of employing non-radioactive carriers in the separation of activities of interest. In addition, the analyst must know which elements are "of interest" in order to add the proper carriers. This also limits the applicability of the technique.

When the radioisotope that the analyst is trying to determine has an extremely short half life, on the order of a few minutes or less,

16. Seaborg, Glenn T.: *Science and the Humanities: A New Level of Symbiosis*. Science, 1964, Vol. 144, pp. 1200, 1201.

it is pointless to use radiochemical separations. By the time the carriers can be added to the sample, the radioisotopes would have decayed to such an extent that there would be practically nothing left to count.

A dispute that one radiochemist was asked to settle is a classic example of hopelessly overwhelming interference and contamination problems. In arranging for the cremation of a deceased relative, the family had specified and paid for an expensive mahogany coffin. Afterward, they suspected that in the actual cremation, a cheap pine coffin had been purposely substituted by the funeral director. Approaching the radiochemist with an urn containing the remains of the deceased, they asked him to employ activation analysis in the settlement of their case by determining the presence of certain elements that are commonly associated with mahogany. When confronted with this conglomeration of ash material and unknown contaminants, the radiochemist refused even to attempt an analysis.

§ 22. Sample Collection

Samples are usually irradiated in an "as received" condition in order to avoid possible contamination with foreign material. From this standpoint, it is critical that a "blank" be obtained for all solvents, paper, or other materials coming into contact with the samples from the time they are collected until the irradiation step. (In activation analysis a blank is an unused portion of material similar to that which comes in contact with the sample prior to irradiation. Because the blank may contain naturally occurring traces of the sought element, it is necessary to analyze it, and then subtract the quantity found from that determined in the sample.)

When paraffin casts are employed in sample collection (as in an effort to detect primer residues in shooting cases), both hands should be treated identically; and a piece of the unused paraffin should be preserved in a polyethylene container as a blank. The importance of collecting blanks was demonstrated in one case where a group of scientists was performing an analysis for antimony to determine the presence of primer residues on the hands of a suspect in a shooting. They found large quantities of this element present in a paraffin cast, but activation analysis performed on a blank sample of the same material showed that it too was badly contaminated with antimony. Further checking pinpointed the container that had been used for holding the paraffin supply as the

source of the antimony. Since the cast obviously had picked up antimony from the container, the presence of this element in the sample proved nothing, and thus the tests were inconclusive.

Since activation analysis is so extremely sensitive to trace level contamination, it is suggested that clean polyethylene gloves be worn while collecting samples or handling materials that are to be analyzed. Prior to use, sample containers should be rinsed with distilled water, followed by "analytical reagent" grade acetone or ethyl alcohol.

§ 23. Sample Preparation

Classically, the neutron flux distribution of all reactors is uneven. When comparing materials in an effort to show similarities in elemental composition, precautions must be taken to establish the same geometry in each of the small polyethylene vials that are commonly used to contain the samples. This insures that all materials "see" the same neutron level and are thus activated to the same extent. In terms of the skeet shoot analogy (see § 4, supra), the spray of bullets (neutrons) fired at the clay pigeons (atoms to be activated) is somewhat uneven. Even two identical pigeons would have different chances of being hit. Since two pigeons, or two samples, cannot occupy the same space at the same time, the radiochemist must do the next best thing—treat them as much alike as possible.

The type of nuclear reactor being used at General Atomic in the United States Atomic Energy Commission study of activation analysis in forensic science has its "core," or neutron source (Uranium-235), in the center. All the samples are placed around the core in a rotating specimen rack, often referred to as a "lazy Susan" (after the familiar rotating relish dish). During irradiation, the samples are all exposed to the same neutron bombardment on a horizontal plane.

Further precautions are taken to make sure that samples are exposed to the same flux in a vertical plane. All containers of similar material are filled to the same height so that the volume of liquid samples will be identical—i.e., all two-thirds full or all one-half full, not some half full and others two-thirds or three-quarters full. Different hairs, strips of metal, or coins should be placed either all vertically or all horizontally.

Reference standards for particular elements are made up as dilute aqueous solutions of high purity chemical reagents and are irradiated at the same time as the samples under study. These standards, contained in vials of the same size as the samples, may be diluted so that they will be the same height as the material in the sample vials; this eliminates the necessity of applying corrections for vertical neutron flux gradients in the irradiation positions. Such corrections may be quite significant, and it is important that they be avoided. If a radiochemist were looking for traces of antimony and barium in a primer residue analysis, he would irradiate a known amount of antimony and barium, along with samples of the paraffin cast in question. Should the spectra for antimony and barium appear in the paraffin samples, he would then compare them with spectra of the known standards in order to determine the exact amounts of each element present in the paraffin sample.

§ 24. The Reactor and Irradiation

In the study being carried on at General Atomic, a TRIGA (Training, Research, Isotope-Production, General Atomic—see Figure 10) nuclear reactor is used in activation analysis. This type of reactor has a high neutron flux (2×10^{12} neutrons per square centimeter per second) and possesses the unique feature of a rotating specimen rack, which offers a definite advantage for activation analysis. For the determination of elements whose activation products have half lives of approximately ten minutes or less, irradiations are usually performed using pneumatic transfer or "rabbit" systems to transport samples to and from the neutron sources. Samples travel the forty foot distance from the core of the reactor to the counting equipment in the laboratory in only two seconds. With a pneumatic transfer system, irradiation periods can be controlled manually, or an automatic timer can be set to give a predetermined irradiation period.

For short-lived radioisotopes, irradiation periods of approximately one half life are generally selected. When longer-lived isotopes are being determined, and speed in handling the samples is less critical, a standard length of irradiation of thirty minutes to one hour is employed. Although a gain in sensitivity is achieved with longer irradiation times, practical considerations usually rule out exposure over one hour in duration. This time period in a reactor, as shown in Figure 3, § 6, permits very good sensitivity for a broad range of elements.

When a general scanning type analysis is necessary to look for clues to the similarity of materials that may have had a common origin, both long and short irradiation times are employed. The measurement of activation products takes place after various periods of decay following irradiation.

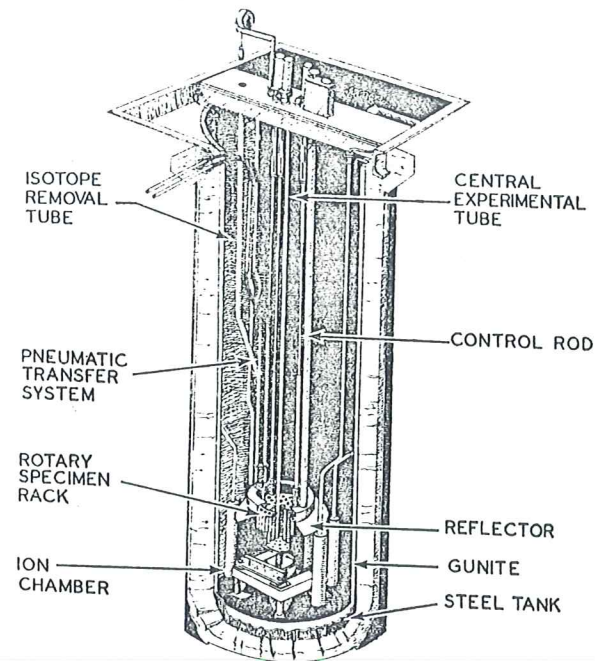


Figure 10. Diagram of TRIGA Mark I Nuclear Reactor. This illustration shows the reactor's many working parts, including the rotary specimen rack and pneumatic transfer system. The source of neutrons in the core, or cylindrical area surrounded by the rotary specimen rack. (See Figures 1 and 2, Appendix.)

§ 25. Purely Instrumental Technique

The simplest and fastest approach to activation analysis involves measurement of the induced radioactive isotopes in the sample

without any postirradiation treatment. The sample is simply transferred from its irradiation vial to a clean, nonradioactive container for counting. This prevents any possible contribution to the activity spectrum from constituents of the original sample container that was also exposed to neutron bombardment. Radioisotopes in the sample are then counted. No "wet chemistry" is used, but only the basic steps of activation followed by counting and gamma ray spectra analysis.

Because the instrumental activation analysis technique employs gamma ray measurement, or spectrometry, in determining the sample's induced activity, the technique is confined to the determination of those elements that form gamma emitting radioisotopes under neutron bombardment. Elements, such as bismuth and phosphorus, that have no detectable gamma rays associated with their common activation products cannot be determined by using the purely instrumental method of activation analysis.

As pointed out earlier, the constituents of the matrix (or material in which the sought trace elements are embedded) may have such dominant spectra of their own that they obscure or mask the trace elements. For example, the large sodium content of a common glass sample will mask the spectra of shorter-lived induced activation products such as aluminum, vanadium, and titanium that may be present in the glass in much lower concentrations.

§ 26. — Spectrum Stripping

The problem of overlapping spectra of different elements has been greatly reduced with the widespread use of "spectrum stripping." This technique allows the subtraction of masking gamma spectra that result from major constituents in the sample. A library of standard spectra may be maintained and used by a skilled analyst in the elimination of such interferences. This permits determination of those elements whose identifying gamma "fingerprint" might otherwise have been hidden by the overwhelming spectra of major constituents. It is these minor constituents that are often critically important in establishing the similarity or dissimilarity of materials.

This situation might be better explained by use of an analogy. The analyst's task is like that of a person who is trying to pick out the few people at a large cocktail party who are whispering in Spanish (they represent a trace element). The other people in the

room are shouting in Russian, English, French, and Chinese (representing the matrix interferences that are masking the trace element). This person would first play a recorded message in Russian that would request all those who are speaking Russian to be quiet. (A standard spectrum is used to "strip" away an interference.) Repeating the message from recordings in English, French, and Chinese, he would eventually get everyone to be quiet except the Spanish-speaking people he is trying to find. Thus, as long as the radiochemist can follow the routine procedure of stripping away interferences through the use of his standard spectra, he can perform activation analysis by the relatively simple instrumental technique.

§ 27. Radiochemical Technique

When spectra of interest are masked beyond hope of separation through the purely instrumental technique, the analyst may resort to postirradiation chemical techniques in order to separate particular activation products from the bulk of the masking activity. This approach involves the addition of an amount of the element being determined in a *nonradioactive* form, which acts as a "carrier" for the radioactive atoms formed during the neutron irradiation and permits their separation.

To resume the analogy of the multilingual cocktail party, what would happen if everyone had had too much to drink and refused to be quiet? The recorded messages would be completely ineffective (the overlapping spectra could not be stripped away). One practical solution would be to send into the crowd a small group of mute people who understood only Spanish (representing the "carrier," or nonradioactive portion of the sought trace element). After circulating through the crowd for some time, they would hear the people who are speaking in Spanish, mix with them, and lead them out of the group. (The carrier unites with the sought trace elements, and they are "separated" from the group or matrix.)

In the final step only the original radioactive atoms are counted. It would make no difference how much nonradioactive barium, for example, were added to an activated sample in order to separate the traces of activated barium from the matrix. Only the barium originally present would show up when the separated barium was counted. In terms of the analogy, only the Spanish-speaking people led out of the cocktail party would be able to communicate

with the person seeking them, not the mute persons who had been sent in to get them.

Because the sample must be dissolved for the radiochemical work, this procedure is suggested only when there is an excess of material available for analysis or when this is the only way to achieve the desired results.

§ 28. Radioactive Counting

What is involved in counting a radioactive sample? As shown in Figure 2, the sample, after being irradiated, is placed near a gamma ray detector, an electronic device that records the numbers and energies of the gamma rays emitted by the sample. Next a multichannel differential analyzer sorts out the gamma rays by their energies and adds them up by energy group. The resulting spectrum is displayed on an oscilloscope screen. Counting is common to both the purely instrumental technique and to that involving radiochemical separations.

The gamma spectrum itself is simply a plot of the energy of the gamma rays being emitted by the sample versus the number of gamma rays recorded. The energy scale is usually divided into 100 or more different energy increments, each one forming a point employed in establishing the spectrum pattern, and this spectrum pattern can be printed on graph paper at the time of the analysis. As a matter of convenience the analyst may have the analyzer store the information on punched paper or magnetic tape until the end of the day and then print out all the accumulated spectra at one time. The printed spectra is the documentation of analytical work that may be presented as evidence in court.

Two hairs from the same person, or materials of like origin, should have essentially the same gamma ray spectra when irradiated and counted under the same conditions; nonidentical, though similar materials, such as hairs from different people (see § 13, supra), will exhibit slight differences in their gamma ray spectra, based on the presence of small variations in their trace element composition acquired through exposure to different environments in the course of their dissimilar histories. Thus activation analysis, as a "nuclear fingerprinting" technique, offers a great potential to the criminalist in establishing the identity of material evidence.

§ 29. Calculations

Since both samples and standards are irradiated under similar

conditions, the concentration of an element in the sample, compared to its concentration in the standard, is directly proportional to the intensity, or peak height, of the gamma ray spectra. Usually a single prominent peak is selected and used in a comparison to establish the concentration of a given element in a sample under study. If the radioactivity of the samples and standards are measured at different times, a correction for radioactive decay must be made.

D. REFERENCES

§ 30. Technical References

These references described a basic library of works in the field and are of value to both the plaintiff and the defense attorney in the presentation of a case involving neutron activation analysis.

The expert witness should be referred to these to refresh his memory of technical data in order to prepare himself to give testimony on direct examination and to anticipate cross-examination.

The use of this material for the cross-examination of an opposing expert can be invaluable as an index to the expert's familiarity with his field, to refute the expert's competency, and to destroy the weight of his testimony. Under proper circumstances, selected material can be used directly in cross-examination. For examples of this use, see 7 POF MEDICAL BOOKS AS USED IN CROSS-EXAMINATION p. 645.

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