

## OTHER NUCLEAR TECHNIQUES

Recently some new techniques have come about by the marriage of atomic and nuclear methods. PIXE is an acronym for either proton or particle induced x-ray emission. Since the cross sections for x-ray emission in charged particle bombardments are quite high, the use of particle irradiation, usually protons, for analytical determination is quite feasible. A beam of protons,  $\alpha$ -particles or heavy ions passes through an irradiation chamber onto a target, typically a thin foil of carbon or plastic, upon which the sample to be analyzed has been deposited. Thick targets such as sections of organic tissue or powder compressed to a pellet may also be used. X-rays emitted by the sample pass through a thin window in the chamber and are detected by a silicon detector. The pulses from the detector are analyzed in a multichannel analyzer.

A typical spectrum consists of peaks corresponding to the K and L x-rays of the elements. Because for the heaviest elements cross-sections for K x-ray production are very small, L x-rays (as from lead) are used. The number of counts in a peak is a measure of the amount of the corresponding element in the sample. Since all the parameters determining the x-ray yield are either known or can be measured an absolute determination of the quantities of different elements in the sample is possible. Sensitivities approach those for INAA, and the method has found its greatest success in analyzing air particulate filters (11).

A number of workers have used the soft x-ray emission from synchrotrons to demonstrate x-ray fluorescence capabilities. Sparks and co-workers at ORNL have been leaders in this effort. Sparks (12) has shown that this technique gives greater sensitivity and higher signal/background ratio than PIXE. A laboratory for XRF at the National Light Source at Brookhaven National Laboratory is presently under design.

## CONCLUSION

This then is a brief overview of neutron activation analysis and its application. NAA gives high sensitivity multi-element capability. Another nuclear technique, PIXE is good for thin repetitive type samples. A new big machine technique is XRF using synchrotron radiation. All have their individual uses for the analytical radiochemist.

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PRACTICAL APPLICATIONS OF ACTIVATION ANALYSIS  
AND OTHER NUCLEAR TECHNIQUES\*

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PRACTICAL APPLICATIONS OF ACTIVATION ANALYSIS  
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ABSTRACT

Neutron activation analysis (NAA) is a versatile, sensitive multielement, usually nondestructive analytical technique used to determine elemental concentrations in a variety of materials. Samples are irradiated with neutrons in a nuclear reactor, removed, and for the nondestructive technique, the induced radioactivity measured. This measurement of  $\gamma$  rays emitted from specific radionuclides makes possible the quantitative determination of elements present. The method is described, advantages and disadvantages listed and a number of examples of its use given. Two other nuclear methods, particle induced x-ray emission and synchrotron produced x-ray fluorescence are also briefly discussed.

INTRODUCTION

Neutron activation analysis (NAA) is one of the most versatile, sensitive analytical techniques available for the determination of elements. It can be multielement and nondestructive, and can be used to analyze samples as small as a few micrograms. The analysis takes the general form of irradiation, counting and calculations.

METHOD

Samples, encapsulated in a suitable container, are placed in a nuclear reactor where they are exposed to a flux of neutrons. Neutrons interact with elements in the sample to produce radioactive isotopes. The basic activation analysis equation is given in equation 1.

$$A_0 = N\phi\sigma \left[ 1 - e^{-\left( \frac{0.693 t_i}{T_{1/2}} \right)} \right] \quad (1)$$

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Where






$A_0$	= disintegration rate of induced radionuclide at end of irradiation
$N$	= atoms of element irradiated
$\phi$	= neutron or particle flux
$\sigma$	= cross section of element
$t_i$	= irradiation time
$T_{1/2}$	= half-life of induced radionuclide: $\lambda = \frac{0.693}{T_{1/2}}$ = decay constant. $(1 - e^{-\lambda t_i})$ is often called $S$ , the saturation factor.

Inspection of equation indicates that the amount of  $A$  produced (and hence the sensitivity of any activation analysis) is a linear function of the amount of element to be determined, the flux, and the cross section. The half-life, present in the exponential term, determines the irradiation time: obviously activities with short half-lives may be impractical for use. Neutron fluxes presently available range from  $10^{11}$  to  $10^{15}$  n cm<sup>-2</sup> sec<sup>-1</sup>. Cross sections of most thermal neutron capture reactions vary from 0.1 to  $100 \times 10^{-24}$  cm<sup>2</sup> (0.1 to 100 barns). Based on a flux of  $10^{14}$ , irradiation time of  $0.5 T_{1/2}$  or 1 week, whichever is shorter, and a reasonable counting procedure, concentrations of a number of elements determinable by activation analysis are shown in Figure 1. These values may be either raised or lowered, depending on what interferences may be present in the sample. The important point is that the sensitivity is quite good for a number of important elements. Nuclear reactors are the main source of neutrons of fluxes above  $10^9$  n cm<sup>-2</sup> sec<sup>-1</sup>.

Three basic methods are used in applying activation analysis: single element comparator, multielement comparator, and multielement absolute. The latter is usually referred to as instrumental neutron activation analysis (INAA). The single element comparator technique is the simplest and oldest. It is now mainly used only for elements in very low concentrations. One merely irradiates a sample and a standard (comparator) containing a known weight of the element sought and then compares the activity induced in each under standard radioactivity counting conditions. Almost always chemical separations are performed so as to isolate the desired radioelement in standard and sample from the interferences. The radiochemical separation technique usually follows these steps:

1. Dissolution of sample (and standard).
2. Addition of a known weight of carrier to both sample and standard (i.e., a nonradioactive species of the radioelement sought), followed by complete mixing and interchange.

FIG. 1. Sensitivities for Elements by Neutron Activation.

-  < 0.002  $\mu$ g
-  0.02 - 0.002  $\mu$ g
-  0.2 - 0.02  $\mu$ g
-  2 - 0.2  $\mu$ g
-  > 2  $\mu$ g

1	H																		He
2	Li	Be											B	C	N	O	F		Ne
3	Na	Mg											Al	Si	P	S	Cl		Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br		Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I		Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At		Em
7	Fr	Ra	Ac																

8	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
9	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf					

3. Separation, isolation, and determination of weight (yield) of carrier element in both sample and standard.
4. Counting of sample and standard, correction for yield through Step 3, and comparison of corrected count of sample and standard to determine amount of element in sample.

The multielement comparator technique begins like the single element method: irradiation of sample and known standards of the elements to be sought. However, an instrumental, nondestructive counting technique is generally used and individual radioelements are compared in sample and standard.

The instrumental neutron activation analysis technique requires the use of no elemental comparators; one irradiates the sample and simultaneously determines the neutron flux. Then equation 1 is used, with nuclear constants such as cross sections and half-lives being inserted along with the known irradiation times.  $A_0$ , the disintegration rate, must be obtained experimentally. INAA is seen to be simplest as far as manipulation is concerned, but the most sophisticated relative to equipment required, for one must be able to quantitatively measure each radionuclide in the sample. Measurement is thus seen to be the heart of present-day INAA.

Continuing with the procedure, when the irradiation is completed the sample is removed from its irradiation container and placed at a defined geometry, i.e., one for which efficiencies are known, next to a GeLi solid state detector. GeLi must be kept at liquid nitrogen temperature; consequently, one usually finds the detector at the end of a cold finger arrangement that dips into a Dewar flask. This detector is electronically coupled to a multichannel analyzer, which is a device capable of sorting the various voltage pulses obtained from the detector system into energy increments. When electromagnetic radiation (gamma and x-rays) interacts with the GeLi detector, the interacting gamma ray may lose all, part, or none of its energy in it. Interactions of the first type are called photoelectric events, and result in pulses whose size is proportional to the original gamma ray energy. Interactions of the second type are termed Compton interactions and result in a distribution of pulses up to some maximum that is less than the full gamma ray energy. Thus, in a multichannel analyzer system photoelectric events should appear as a single line spectrum; actually, statistical considerations cause the gamma ray photopeak to appear with a resolution of about 2 keV. Since most gamma rays of interest in nuclear analysis range from 50 keV to 2500 keV (2.5 MeV) this resolution is adequate to completely resolve most mixtures. Gamma ray interactions from the Compton process merely appear as a broad continuum; upon this continuum the photopeak is superimposed.

## MEASUREMENT

Most radioactive nuclides produced by neutron capture decay by emission of a beta particle followed by one or more gamma rays; the energies and half-lives of these gamma rays uniquely characterize each radionuclide. Thus, if one is able to differentiate and quantitatively measure a gamma photopeak from a particular radionuclide, and if one can then calculate the disintegration rate,  $A_0$ , of that radionuclide, one can insert this value of  $A$  into equation 1 to solve for  $N$  the number of atoms of target element. Let us examine this process using cobalt as a target element.

Cobalt 59 undergoes neutron capture to produce two products: 10-min  $^{60m}\text{Co}$  and 5.27 year  $^{60}\text{Co}$ . If one waits for an hour or so after the irradiation of a sample of pure cobalt powder, the 10-min  $^{60m}\text{Co}$  will have all decayed and only the 5.27-year activity will remain. Figure 2 shows a portion of the gamma ray spectrum of  $^{60}\text{Co}$  taken with a GeLi detector: in the lower left-hand corner of the figure, the decay scheme of  $^{60}\text{Co}$  is given. This decay scheme shows that  $^{60}\text{Co}$  decays by negative beta particle emission to a 2.505 MeV excited state of the product daughter nucleus ( $^{60}\text{Ni}$ ). From this level it de-excites by emission of a 1.1732 MeV gamma ray followed by a 1.3325 MeV gamma ray. These gamma rays produce photoelectron interactions in a GeLi detector that result in a gamma ray spectrum such as that shown in the figure. This spectrum is obtained by coupling the GeLi through a preamplifier, amplifier, multichannel analyzer, and readout device.

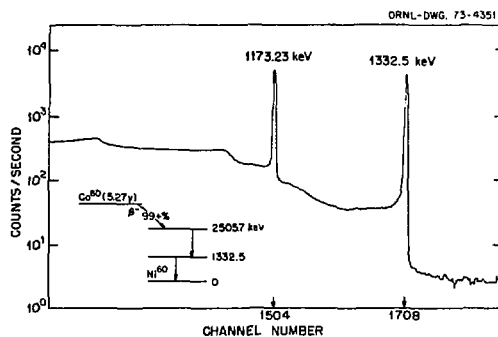


FIG. 2. Decay scheme and GeLi spectrum of 5.27 y  $^{60}\text{Co}$ .



In the INAA technique many elements are activated and many radionuclides are formed. The gamma ray spectra obtained under analysis conditions are consequently much more detailed than that of pure  $^{60}\text{Co}$ . Figure 3 shows a typical gamma ray spectrum

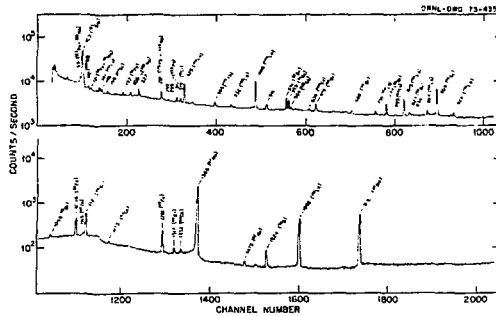


FIG. 3. Typical GeLi  $\gamma$ -ray spectrum. Coal Sample.

obtained from irradiation of a sample of coal. These data were obtained using a GeLi detector coupled to a minicomputer interfaced to a 4096 multichannel analyzer. Data obtained from the GeLi detector are stored in the analyzer memory, and from an energy calibration of the detector system, one can obtain the exact energy of each gamma ray photopeak; this enables positive identification of the radionuclide to be made. The integrated area of each photopeak can then be used to determine the quantitative amount of the radionuclide present. To do this one must have an empirical calibration curve of the detector made at the particular geometry (physical position) used in measuring the sample. This calibration is made using the following equation for  $E_\gamma$  the gamma efficiency

$$E_\gamma = \frac{N_p}{A_0 I_\gamma} \quad (2)$$

where  $N_p$  is the integrated value of a known energy gamma ray photopeak obtained by counting a known disintegration rate standard (obtained, for example from NBS),  $I_\gamma$  is the gamma ray branching, and  $A_0$  is the disintegration rate. If one has the efficiency vs. energy curve, one can then determine the disintegration rate of any radionuclide ( $A_0$ ) that has a measured identified gamma ray photopeak.

It is needed for each  $\gamma$  ray measured and is tabulated in most tables of nuclear data. The peak searching, identification, integration, and calculation of  $A_0$  are all carried out in the minicomputer using efficiencies obtained experimentally.

#### ADVANTAGES AND DISADVANTAGES

Some of the principal advantages of NAA are listed below:

1. Nondestructive
2. Minimum sample preparation and follow up
3. Very sensitive (ppb)
4. Multi-element
5. Low cost per element

Some of the disadvantages are:

1. Sample size limitations due to reactor and irradiation container
2. Irradiation time
3. Radioactive interferences
4. Sometimes chemical separations are required.
5. Nuclear property limitations
  - self-shadowing
  - interference reactions
  - interference in assay
6. Some elements (primarily low Z) cannot be determined.

One very obvious limitation not mentioned but implicit is the need for a reactor and a laboratory with sophisticated equipment. Figure 4 shows the schematic of the ORNL facility in

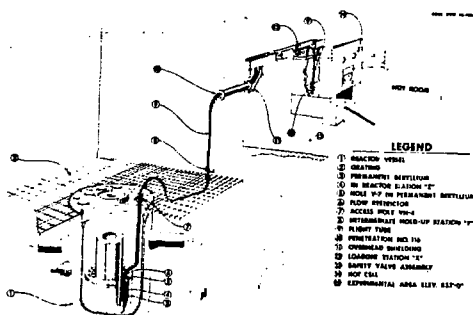


FIG. 4. Schematic of activation analysis facility at ORNL High Flux Isotope Reactor (HFIR).

the HFIR. Such installations are expensive to build, staff and to operate. NAA competes with a number of other analytical techniques. Three of the more popular are inductively coupled plasma atomic emission spectroscopy (ICP-AES), spark source mass spectrometry (SSMS) and atomic absorption spectroscopy (AA). Sensitivities for a number of elements using these techniques are shown in Table 1. Each of these techniques has its own advantages and disadvantages. The ICP-AES method requires the sample to be solubilized, SSMS as a multielement technique has only an accuracy of about  $\pm 50\%$ , and AA is not a multielement method, but is quite accurate and inexpensive for large replicate single element determination.

The previous discussion coupled with the data in Table 1 lends support to our assertion that NAA is the best and most versatile multielement method presently available.

Mention should be made of the 14 MeV neutron generator. This low flux ( $10^7$  n  $\text{cm}^{-2}$   $\text{sec}^{-1}$ ) device is primarily useful to analyze for oxygen and nitrogen. It enjoyed a vogue some fifteen years ago, but is now used only for some specialized applications. For this reason no further mention of generators will be made.

#### APPLICATIONS OF NAA

NAA has been applied to such a diversity of problems that to discuss even one example from each field of application would require almost a book in itself. Consequently several reviews that list applications, articles and books about NAA are listed in the references (1,2). In this paper only a few examples will be discussed so as to give a perspective on application.

1. **Materials Analysis.** There are many reports in the literature concerning the determination of trace element content of high priority metals and alloys. NAA is ideally suited for many of these analyses because it is only necessary to take a small piece of the sample, irradiate it and then count it. In some instances, however, separations are necessary to remove interferences. Beurton et al. (3) describe such a technique for trace elements in aluminum and its ores. After irradiation the samples are etched with  $4M$  NaOH, weighed, and then dissolved in an appropriate medium. A number of different groups of elements are delineated, and each group is treated differently. Ion exchange on DOWEX 1, DOWEX 50, and  $\text{Sb}_2\text{O}_5$  is the primary separation scheme. Some groups are further separated by distillation, or solvent extraction. About 30 elements were determined, and results for some elements showed concentrations at levels of 0.002 ppm.

Table 1  
ELEMENTAL SENSITIVITIES  
BY SEVERAL TECHNIQUES

Element	Sensitivity (nanograms/gram)			
	NAA <sup>1</sup>	AA <sup>2</sup>	ICP-AES <sup>3</sup>	SSMS <sup>1</sup>
Ag	0.1	2	0.7	0.2
Al	1	20	0.6	0.02
As	0.5	20	3	0.06
Au	0.05	10	-	0.02
B	-	2,000	1	0.01
Bz	10	10	0.1	0.2
Be	-	2	0.01	0.008
Bi	-	3	8	0.2
Ca	500	1	1.6	0.03
Cd	20	2	0.1	0.03
Ce	10	-	-	0.1
Cl	0.1	-	-	0.4
Co	0.9	10	2	0.05
Cr	200	3	0.4	0.05
Cu	0.2	1	0.06	0.06
F	0.1	-	-	0.05
Fe	40 x 10 <sup>3</sup>	10	0.5	0.05
Ga	0.4	100	5	0.09
Ge	2	200	10	0.2
Hg	2	200	20	0.06
K	40	1	1.0	0.03
Mg	50	1	1.5	0.03
Mn	0.005	2	0.02	0.05
Mo	30	600	2	0.3
Na	0.9	0.2	7	0.02
Nb	100	200	9	0.8
Ni	50	2	0.5	0.7
P	-	100 x 10 <sup>3</sup>	8	0.03
Pb	-	10	2	0.3
Pt	5	100	-	0.5
S	20 x 10 <sup>3</sup>	-	0.2	0.03
Sb	10	40	4	0.2
Sc	50	20	0.4	0.04
Se	50	100	2	0.1
Si	20 x 10 <sup>3</sup>	20	1	0.03
Sn	20	20	3	0.3
Sr	0.9	2	0.04	0.09
Te	9	50	4	0.3
Th	10	-	8	0.2
Ti	10	50	0.6	0.5
Tl	-	20	4	0.2
U	0.4	30 x 10 <sup>3</sup>	25	0.2
V	0.1	50	0.6	0.04
W	0.7	1 x 10 <sup>3</sup>	3	-
Y	1 x 10 <sup>3</sup>	100	0.1	-
Zn	20	1	0.2	0.1
Zr	200	1 x 10 <sup>3</sup>	0.7	0.1

(1) G.H. Morrison in Elemental Analysis of Biological Materials, IAE Technical Reports Series 197, p. 222 (1980).

(2) G. F. Kirkbright, Ibid, p. 155.

(3) W. J. Haas, V. A. Fassel, Ibid, p. 170.

2. Air Pollution Studies. Air filters are another type of sample quite amenable to INAA. Samples are usually collected on low background filters (organics, for example) loaded into irradiated rabbits and counted at various intervals. The work by Dams et al. (4) is typical. In a different study Oakes et al. (5) sampled grass alongside highways and determined bromine by irradiation and counting. An interesting result of the study was that elevated levels of bromine occur at distances of 30 and 60 meters away from the highway.
  
3. Biological and Medical Studies. Perhaps the main difficulty in performing NAA on human tissue and blood samples is the interference seen from radioactive  $^{24}\text{Na}$ . In biological samples  $^{82}\text{Br}$  and phosphorous-32 may also present difficulties, the latter being formed either from  $^{32}\text{S}$  (n,p)  $^{32}\text{P}$  or  $^{31}\text{P}$  (n,  $\gamma$ )  $^{32}\text{P}$ . P. F. Girardi (6) developed the use of an  $\text{Sb}_2\text{O}_5$  column to remove  $^{24}\text{Na}$ ; amazing enough a solution passed through this column deposits only Na; the other elements in solution remain essentially unchanged and pass through. Maziere et al. (7) describe a method for separating P, Na, and Br from biological matrices through distillation followed by the use of an  $\text{Sb}_2\text{O}_5$  column. Their data show that the detection limit for many elements in serum and liver samples can be lowered a factor of ten over the non-destructive values. G. F. Clemente (8) studied trace element pathways in the Italian population. He measured trace elements in food, drinking water and air, and then attempted to measure excretion of these same elements. He also analyzed blood and hair samples from his subjects and attempted to set up a mass balance. The results indicate that many elements, Sc, Cr, Fe, Zn, Se, Rb, Sb, Cs, are essentially all excreted, but very small amounts of Fe, Co, Zn, Se, Rb and Cs are found in the blood. Some of these elements are also seen in hair, but elucidation of the source and time interval over which the element was accumulated is not clear-cut. The whole question of normal levels of trace elements in blood and serum is important but still unknown.

The effect of certain metals on the lungs has been studied by a number of workers; typical is work of Porritt et al. (9) who measured tungsten in very small lung biopsy samples at below 1  $\mu\text{g/g}$  levels. Other organs such as liver, kidney, brain, muscle, etc. from human, animal, fish and fowl have also been studied. An interesting experiment reported from Germany by Bratter et al. (10) studied the distribution of trace elements in skeletons from ancient humans. Samples were taken from the iliac crest of the hip bone and a separation was made of collagen and inorganics. Twenty-five elements were determined and the biological variation obtained. The latter ranged from 35% to 220%, and the authors suggest these data might be used as background data to estimate modern pollution contribution.