ANALYSIS OF NASHVILLE AIR POLLUTION VIA NEUTRON ACTIVATION ANALYSIS

R. F. CARLTON AND A. LEHMAN, JR.
Middle Tennessee State University
Murfreesboro, Tennessee

ABSTRACT

By use of NAA, five elements have been determined in a sample of Nashville air pollution. The gamma ray analysis has been carried out using both NaI and Ge(Li) detectors. The sensitivity of this method of analysis is discussed as well as some of the problems which one might encounter in such an analysis.
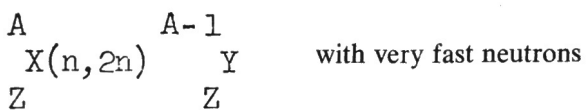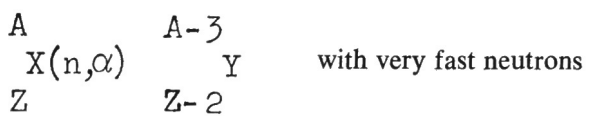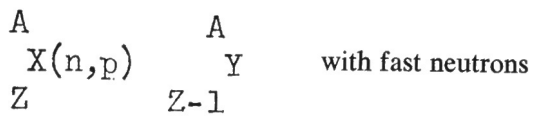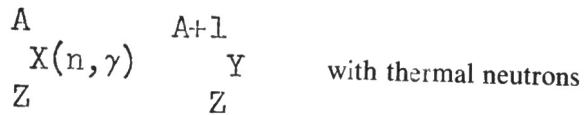
INTRODUCTION

The location of a source of pollution may require the analysis of a number of samples each day, and a rapid determination of the components of the matrix is essential. The usual procedure followed in locating a source of pollution is to bracket an area with several sampling stations and to move these stations until they converge upon the source. In a large city this may involve as many as sixteen samples each day.

The matrix, which in the case of air pollution can be collected on a filter paper, may contain as little as 1 mg of pollutant since 75% of the sample is normally composed of carbon, hydrogen and oxygen. In the present experiment the sample weight was nominally 25 mg, leaving approximately 6 mg of pollutant, and these pollution samples were obtained on days of relatively high pollution index. Samples taken on some days may therefore weigh less than 5 mg. One can then see that the analysis of air pollution may involve trace element determinations.

The above requirements for air pollution analysis eliminate many of the standard chemical methods of analysis completely. Those chemical methods which are not completely eliminated are generally too time consuming or lack the required sensitivity. The sensitivities of the various methods of analysis are shown in Figure 1 where it can be seen that neutron activation analysis (NAA) is the superior method. Since elaborate sample preparation is unnecessary, this method is also desirable from the standpoint of the time required.

NAA involves the bombardment of an unknown matrix with neutrons in an effort to produce radioactive isotopes of the constituent elements which in turn emit beta or gamma radiation with energies and half lives which are characteristic of the decaying nucleus. A knowledge of these characteristics is most helpful in determining the components of the matrix. In many cases an accurate determination of the energies of the emitted radiation is sufficient to allow an unambiguous determination. When this is not the case, half life measurements will usually remove the ambiguity.

When an element X is bombarded with a beam of neutrons, four types of possible reactions are

$$^{A}_{Z}X(n,\gamma)\,^{A+1}_{Z}Y \qquad \text{with thermal neutrons}$$

$$^{A}_{Z}X(n,p)\,^{A}_{Z-1}Y \qquad \text{with fast neutrons}$$

$$^{A}_{Z}X(n,\alpha)\,^{A-3}_{Z-2}Y \qquad \text{with very fast neutrons}$$

$$^{A}_{Z}X(n,2n)\,^{A-1}_{Z}Y \qquad \text{with very fast neutrons}$$

where the notation is the usual shorthand for nuclear reactions.

It should be noted that other particles can be used in activation, but neutrons are generally favored because of their higher reaction probability with most elements, the deeper sample penetration obtainable in the absence of any Coulomb interaction with the sample and because of the availability of neutron sources.

For NAA to be possible the reaction product Y formed in the irradiation process must be unstable and subsequently decay into another element in the case of beta emission or to another excited state of the reaction product Y in the case of gamma emission. It is by studying these secondary emissions that one determines the constituents of the matrix. If we have a flux of Φ neutrons/cm²-sec incident upon N_X target nuclei of type x, the rate of formation of a stable reaction product Y will be given by

$$\frac{dN_Y}{dt} = N_X\sigma\Phi \qquad (1)$$

where σ is the activation cross section or probability in cm². If on the other hand the reaction product is unstable with a decay possibility λ, the nuclei of the type Y will be decaying during the irradiation process and the above expression will be modified to

$$\frac{dN_Y}{dt} = N_X\sigma\Phi - \lambda N_Y \qquad (2)$$

where the decay probability λ is related to the half life $t_{1/2}$ by $\lambda = .693/t_{1/2}$. The number of atoms of type Y remaining after a time t equal to the irradiation time is obtained by intergrating eq. 2. The result, assuming that $N_Y = O$ at $t = O$ yields

$$N_Y = \frac{N_X \, \sigma \phi}{\lambda} \, (1-e^{-\lambda t}). \qquad (3)$$

The activity of A_0 to be expected at the end of the irradiation period is then given by

$$A_0 \equiv \lambda N_Y = N_X \sigma \phi \, (1-e^{-\lambda t}). \qquad (4)$$

The quantity in parentheses is referred to as the saturation factor S and is important when considering the variation of the irradiation period for the purpose of inhibiting the formation of radioactive species of differing half life.

SENSITIVITY

The sensitivity of NAA, which is an indication of the minimum amount of an isotope which must be present in order to be detected, is determined by considering eq. 4. Here the activity is expressed in terms of the number of target nuclei, the neutron flux and the cross section for neutron capture by the isotope in question. The minimum activity which will permit the detection of a radionuclide depends on the half life of the same. This is due to the fact that short lived elements are only present for a short period of time, and in order to yield a sufficient number of counts for identification, the initial activity must be high. An arbitrary but reasonable criterion for the counting rate C as a function of half life is

$$t_{\frac{1}{2}} < 1m \quad : \quad C \geq 10^3 \text{ cpm}$$

$$1 m < t_{\frac{1}{2}} < 1 \, hr \quad : \quad C \geq 10^2 \text{ cpm}$$

$$t_{\frac{1}{2}} > 1 \, hr \quad : \quad C \geq 10^1 \text{ cpm}.$$

It is seen from equation 4 that the sensitivity will be greatest for those elements which have high neutron capture cross sections. However, these numbers are fixed by nature and therefore the sensitivity of NAA in detecting a given element is determined primarily by the neutron flux available. It thus becomes apparent that the nuclear reactor would be the most satisfactory source of neutrons from the standpoint of sensitivity. This is not the case from the standpoint of cost, and for many applications, the sensitivity attainable with the reactor is not necessary. For such applications there are neutron generators producing fluxes of 10^9 n/cm²-sec. available for under $25,000.

The ^{52}Cr (n,p) ^{52}V reaction serves to illustrate the relationship between the sensitivity and the factors discussed above. We are interested in determining the smallest amount of ^{52}Cr which can be detected using a neutron flux of 10^9 n/cm²-sec., a flux which is well within the capabilities of the neutron generator mentioned above. The decay scheme of the reaction product ^{52}V reveals a half life of 3.76 m, the primary mode of de-excitation resulting in a beta ray and a subsequent 1.43 MeV gamma ray.

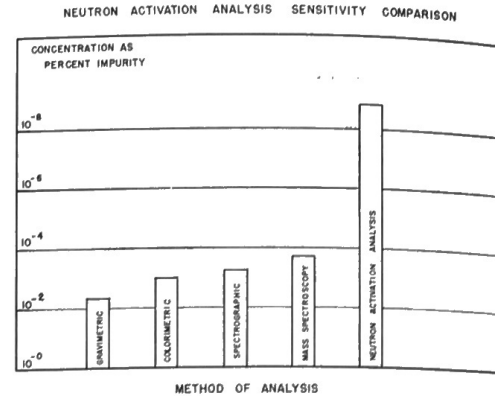NEUTRON ACTIVATION ANALYSIS SENSITIVITY COMPARISON

Figure 1: A comparison of the sensitivity of neutron activation analysis with standard chemical methods of analysis.

The half life suggests that a count rate of at least 100 cpm will be necessary for detection. The cross section for the capture of a neutron by ^{52}Cr is $\sigma = 80$ mb. For a typical detection system only approximately 3.5% of the ^{52}V disintegrations will result in a full energy photo-peak pulse from the detector. Hence, the activity of the radionuclide must be greater than 100 cpm. Solving eq. 4 for N_X in grams therefore yields

$$N_X = .05 \text{ mg}$$

for the minimum amount of ^{52}Cr necessary for detection. Similar calculations for other elements yield the sensitivities shown in Table I. The Table assumes an irradiation time of 5 m for all the elements.

Table I: Sensitivity of NAA for various elements assuming a 14 MeV neutron flux of 10^9 n/cm²-sec and an irradiation time of 5 m.

LIMIT OF DETECTION (in mg)	ELEMENT
0.001-0.003	Pr
0.004-0.009	Cu, Ga, Ba, Ce
0.01 -0.03	Si, P, Sc, Rb, Zr, Pd
0.04 -0.09	Al, V, Cr, Ag, Cd, Sb, Hf, Pb
0.1 -0.3	N, F, Mg, Mn, Fe, Zn, Ge
	Mo, Sn, Te, Sm
0.4 -0.9	Na, K, Co, Sr, Nb, Cs, Ta
1 -3	O, Ti, As, In, La, Nd, Eu
	Gd, Er, Pt
4 -9	Ni, I
10 -30	Cl, Ru, Tb, Dy
40 -90	S, Ca

SAMPLE COLLECTION AND PREPARATION

Due to the high sensitivity of NAA, special care should be exercised in acquiring the sample and preparing it for irradiation in order to prevent contamination. Often it is possible to add sufficient sodium to the sample from a touch of the hand to introduce error in the analysis. The samples of air pollution analyzed in this experiment were obtained from the metro government of Nashville, Tennessee, after having been collected at the sampling station at Eighth Avenue South and Broadway on 8" x 10" fiber glass filter papers which were attached to a suction pump. The average weight of pollution on each filter paper was 25 mg as determined by the office in charge of air pollution in Nashville. Due to the number of filter papers (8) used in obtaining the sample to be analyzed, it was not possible to place filter papers and pollution in the container used for irradiation. Hence, the filters were subjected to an extraction process using a soxhlet extractor and three solvents ranging from non polar to very polar (petroleum ether, acetone, water). The resulting solution was then evaporated and placed in a sample holder, which is often referred to as a rabbit.

NEUTRON IRRADIATION

The source of neutrons in this experiment was a Cockcroft-Walton positive ion accelerator and a tritium target. Deuterium ions were accelerated to an energy of 170 keV before impinging on the tritium target. The subsequent T(d,n)^{3}He reaction resulted in a neutron flux of 10^9n/cm²-sec. A rapid transfer system transported the sample into the neutron beam and returned the sample for counting after the desired irradiation.

In order to detect short lived radiation that might be present, initial irradiation times were kept short, thus inhibiting the growth of long lived components of the sample. Irradiation times were then progressively increased in order to selectively look for components of increasing half life. After the irradiation time was increased, there was a time lapse between termination of the irradiation and the beginning of counting which was sufficient to allow the short lived components to die out of the spectrum.

DETECTION SYSTEM

The counting was accomplished with the electronic system shown in Figure 2. An attempt was made to use a 3" x 3" NaI detector with a resolution of 6%, but the spectrum was sufficiently complex to require the use of a higher resolution de-
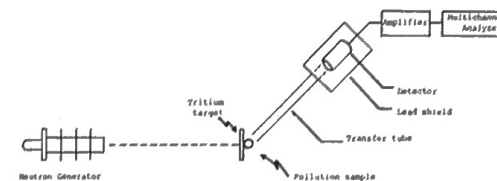

Figure 2: Schematic diagram of the equipment involved in the experiment.

dector in order to identify all the peaks in the spectrum. A planar Ge(Li) detector with a resolution of 3 keV for the 1.33 MeV line and peak-to-Compton ratio of 13 was used to obtain the spectra for analysis. The superior resolution of the Ge(Li) detector is shown in Figure 3, where a typical spectrum from each detector is presented. In order to reduce background gamma radiation the detector was surrounded by 4" of lead.

SAMPLE ANALYSIS

In analyzing the data obtained, first consideration was given to the energies of the various peaks, and the results for the peaks in Figure 3 are shown in Table
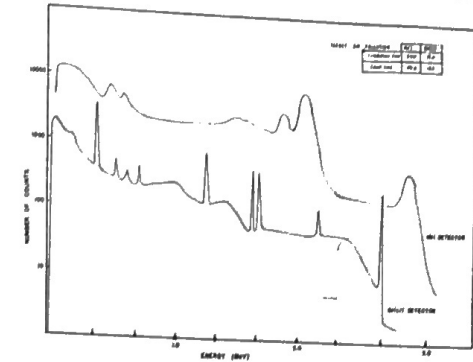

Figure 3: Typical spectra from a sample of irradiated air pollution, showing the improved resolution of the Ge(Li) detector.

II along with the reaction product which gives rise to the observed radiation. The sources were assigned primarily on the basis of the energy of the gamma radiation. This analysis served as a good example of the difficulty that can often arise when energy and half life considerations are not sufficient in making an elemental determination. The difficulty here lay in the fact that two of the radioactive reaction products, ^{24}Na and ^{28}Al, can each be produced by three of the four reactions listed above, i.e. the radiation from ^{24}Na can be due to the presence of ^{23}Na, ^{24}Mg or ^{27}Al in the sample while the radiation from ^{28}Al may be due to ^{31}P, ^{28}Si or ^{27}Al in the sample. In order to decide which of these are actually present, consideration must

Table II. Energies of the γ-rays resulting from the neutron activation of air pollution, together with the reaction products which could give rise to the radiation.

Channel Number	Computed Energy (MeV)	Assigned Energy (MeV)	Source
170	0.511	0.511	Annihilation
204	0.658	0.660	^{62}Cu
246	0.839	0.843	^{27}Mg
366	1.360	1.370	^{24}Na
449	1.721	1.730	2.75 MeV double escape
460	1.767	1.780	^{28}Al
566	2.225	2.239	2.75 MeV single escape
683	2.732	2.750	^{24}Na

be given to the cross section of each of the reactions, the relative intensities of the peaks and the percentage abundance of the element in question. Also, the presence or absence of other peaks which should not or should be in the spectrum can be used to eliminate some of the possibilities. On the basis of the considerations mentioned above, it was found that ^{31}P, ^{24}Mg, ^{27}Al, ^{62}Cu and ^{28}Si were the components of the air pollution which could be detected by this method. No attempt was made to determine the amount of each component in the sample, though this is now in progress.