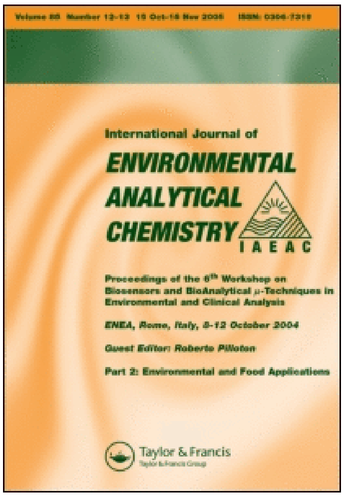

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Neutron Activation Analysis Applied to the Study of Elements Entering and Leaving a Coal-Fired Steam Plant

W. S. Lyon[a]; J. F. Emery[a]
[a] Analytical Chemistry Division, Oak Ridge National Laboratory, † Oak Ridge, Tennessee, U.S.A.

To cite this Article Lyon, W. S. and Emery, J. F.(1975) 'Neutron Activation Analysis Applied to the Study of Elements Entering and Leaving a Coal-Fired Steam Plant', International Journal of Environmental Analytical Chemistry, 4: 2, 125 — 133

To link to this Article: DOI: 10.1080/03067317508071108

URL: http://dx.doi.org/10.1080/03067317508071108

Intern. J. Environ. Anal. Chem., 1975, Vol. 4, pp. 125–133
© Gordon and Breach Science Publishers Ltd.
Printed in Great Britain

Neutron Activation Analysis Applied to the Study of Elements Entering and Leaving a Coal-Fired Steam Plant

W. S. LYON and J. F. EMERY

Analytical Chemistry Division, Oak Ridge National Laboratory,[†] *Oak Ridge, Tennessee 37830, U.S.A.*

(*Received June 17, 1973*)

KEY WORDS: neutron activation analysis, coal, trace elements, air pollution

Neutron activation analysis (NAA) is a highly sensitive non-destructive, multi-element technique useful for analyzing samples from many sources. Following irradiation of the sample with neutrons in a nuclear reactor, induced radioactivity in the isotopes present is measured with a Ge(Li) γ-ray spectrometer. Computer techniques are used to unfold γ-ray spectra and calculate concentrations.

The method has been applied to coal and ash samples from the Allen Steam Plant in Memphis, Tennessee. Twenty-nine elements have been identified, and a mass balance has been made to indicate the ultimate fate of these elements. Most are removed in either the precipitators or the bottom ash.

For the determination of the trace elemental constituents in environmental samples such as fly ash, coal, air particulates, etc., neutron activation analysis (NAA) has several important advantages. It is non-destructive, i.e., no sample preparation or dissolution is usually required, it is a multi-elemental technique, and it has quite high sensitivity. Although expensive equipment (primarily a nuclear reactor) is required, the cost per analysis can compare favorably with most other available methods, this cost being somewhere in

---

[†] ORNL is operated by Union Carbide for the U.S. Atomic Energy Commission. A portion of the work reported here was supported by the National Science Foundation under Interagency Agreement No. AEC 40-237-70 and NSF AG 398.

the range of $100 per sample. We will briefly review the fundamentals of activation analysis in part 1 of this paper, and then in part 2 describe some recent work concerned with determination of trace elements in coal and ash samples.

NEUTRON ACTIVATION ANALYSIS

Although neutron sources other than nuclear reactors can be used for activation, most practitioners use the reactor because of its higher neutron flux which results in greater sensitivity. When a sample is exposed to a neutron flux, a neutron may be captured by an isotope of an element to produce a radioisotope of that element with mass number 1 unit higher. The capture reaction is given by

$$A = Nf\sigma\left[1-\exp\frac{(-0.693t)}{t_{\frac{1}{2}}}\right] \tag{1}$$

where

A = activity of the induced radioisotope (sec^{-1})
N = # of atoms of target element
f = neutron flux ($n\ \text{cm}^{-2}\ \text{sec}^{-1}$)
σ = cross section of target nuclide (cm^2)
t = irradiation time in the reactor
$t_{\frac{1}{2}}$ = half life of induced radioisotope (in same units as t)

Some isotopes may produce no radioactive capture product, and for some the cross section (σ) may be so small that the method is not practical. Taking ^{59}Co as an example of a useful reaction, one can write

$$^{59}\text{Co}+n \rightarrow {}^{60}\text{Co}+\gamma$$

or

$$^{59}\text{Co}(n,\ \gamma)^{60}\text{Co} \tag{2}$$

^{60}Co is radioactive and decays to stable ^{60}Ni by beta decay followed by two γ-rays of known discrete energy. These γ-rays can be measured by use of a detector; lithium drifted Ge gives the highest resolution known at present for such measurements, and when ^{60}Co is counted with a Ge(Li) detector coupled to suitable electronic equipment—pre-amplifiers, amplifiers, and multi-channel analyzers—the γ-ray spectrum of ^{60}Co is observed as indicated in Figure 1. The decay scheme of ^{60}Co is shown to the left in Figure 1 and indicates that two γ-rays are found in equal amounts in the decay. These γ-ray photopeaks are seen in the spectrum with quite high resolution (2-3 kv full width at half maximum height). Thus the accurate measurement of the

γ-ray energy can be a qualitive identification of the radionuclide aided often by measurement of the half life—while the peak areas, when corrected for geometry, abundance of the γ-ray in the decay scheme, and radioactive decay—yield a quantitative measure of the radionuclide.

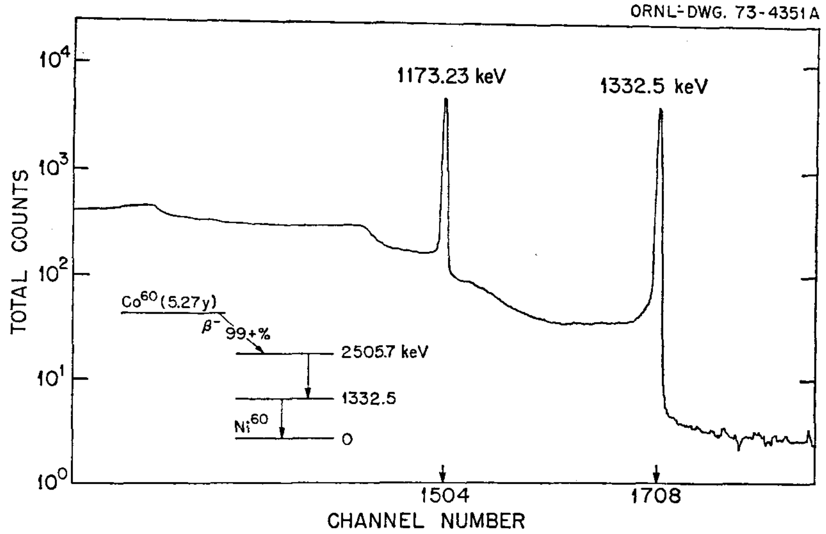

FIGURE 1 Gamma ray spectrum of ^{60}Co obtained with Ge(Li) spectrometer.

Figure 2 shows sensitivities for elements when irradiations are made at the ORNL High Flux Isotope Reactor (HFIR), where the flux is $\sim 5 \times 10^{14}$ cm^{-2} sec^{-1}, for a maximum time of 20 minutes.

Figure 2 indicates the high sensitivities obtainable for many elements by NAA; it also shows some elements for which NAA is not possible.

The Ge(Li) counting system used in non-destructive NAA requires several thousand channels of information storage and some type of data processing and read-out system. At ORNL we have a Nuclear Data 50-50 system interfaced to a PDP-15 computer. By use of computer programs developed here by J. F. Emery and F. F. Dyer,[1] we are able to process counting data obtained from Ge(Li) detectors, identify peaks, make nuclide assignments, and calculate A, the disintegration rate of the nuclide for use in Eq. 1. Flux monitors are irradiated with the samples, and from measurement of these we obtain f; since the irradiation time, half lives and cross sections are known, N the number of atoms of element present, can be calculated from Eq. 1. The weight of the determined elements is easily obtained from N, and this when divided by the weight of sample yields concentration (μg/g). The system has been checked by analyzing samples of coal and ash sent out by NBS for inter-

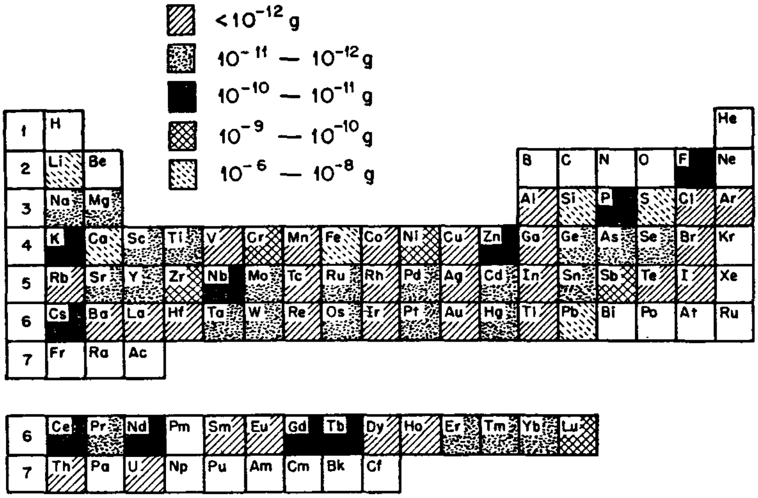

FIGURE 2 Sensitivities with NAA for elements at high flux isotope reactor (HFIR).

laboratory comparison; our agreement with average values has been satisfactory. By using combinations of short and long irradiation and decay times, twenty or more elements have been determined on a number of samples. In the work described in Part 2, below, analytical data have been obtained by spark-source mass spectrometry (SSMS), NAA, and in the case of Hg, atomic absorption spectrometry. Agreement between these methods has been quite gratifying.

APPLICATION OF NAA TO STEAM PLANT STUDIES

Much of the data handling capability described above was developed during the preliminary stages of a program designed to measure the trace element balance through a coal fired steam plant. The Thomas A. Allen Plant at Memphis, Tennessee, was chosen for this study and a sampling team from the Tennessee Valley Authority (TVA), in cooperation with N. Bolton, Industrial Hygienist at ORNL, spent one week sampling during late January, 1972. The Allen Plant is equipped with cyclone furnaces, new electrostatic precipitators, and thus represents a highly efficient combustion and clean-up system. Operation of the plant was held constant at 83% capacity—240 MW. Five different samplings were made, each on a different day; each sampling included coal (C), bottom ash or slag tank (ST), precipitator inlet (PI), and precipitator outlet (PO). The sampling train is shown schematically in Figure 3. The sample collectors are standard alundum thimbles about 5″ long. These were tared,

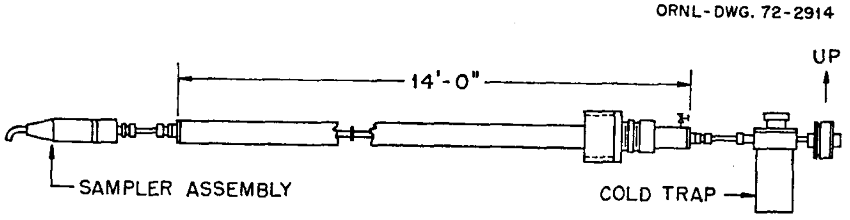

FIGURE 3 Sampler train used in plant sampling.

placed in the sample train, used for isokinetic sampling, then reweighed. Because of the small size of the fly ash particles and the porous nature of the thimble, some of the material was trapped in the thimble and thus unavailable for analysis. This was particularly true of the stack and precipitator outlet samples which were small samples of small particles. The thimbles were backed up with filters and cold traps; these were assayed for Hg by use of flameless atomic absorption (FAA), but little was found. We are unable to account for most of the Hg from analysis of the particulates, so we assume it is in the gas phase. Later samplings performed using ICl traps confirmed the presence of Hg in quantities that appear to make up this deficit. The FAA method was checked by both NAA and SSMS and found to give excellent reproducibility and accuracy.

The slag tank presented a problem since ash is accumulated for 4 hours and then flushed out with H_2O. Grab samples were taken, but of course no accurate weights were obtained for the total amount dumped. We calculate the mass balance, therefore, by taking total input as weight of coal per minute × % ash. Output consists of precipitator inlet (calculated by multiplying the g/cu ft obtained in the thimble sampling by the total cu ft/min passing through), and slag tank (calculated at the difference between the above two quantities).

Samples of coal and ash were encapsulated in rabbits (sample carriers transported rapidly through the reactor in a pneumatic tube), irradiated in the reactor, and then removed from the rabbit for counting. Typical γ-ray spectra obtained are shown for coal (Figure IV) and fly ash (Figure V). From such data the values in Table I were calculated. The left side of Table I presents the concentration ($\mu g/g$) of each element found in coal, ST, PI, and PO. The right side shows the mass flow ($g\ min^{-1}$) calculated from these data and the % imbalance. This imbalance is in general on the negative side, and for some volatile elements is quite large. We believe there is a possibility that the systematically low results are due to failure to sample precipitator blow-by; the unusually large imbalances on volatile elements such as As may be due to failure to adequately sample the gas phase. Additional work is

TABLE I

Elemental concentrations and mass balance obtained by use of NAA

	Concentration (μg/g unless otherwise indicated)				Mass flow (g/min)				
Element	Coal	S.T.[b]	P.I.[c]	P.O.[d]	Coal	S.T.	P.I.	Imbalance (%)[a]	P.O.
Ag	<2–5		<2		<6		<0.10		
Al	1.06%	6.6%	6.9%	3.5%	1.3×10^4	7.2×10^3	3.4×10^3	−18	68
As	3.8	0.5	46	50	4.7	0.05	2.2	−52	0.097
Ba	79	600			99	66			
Br	2.0	<0.5	<5	10	2.5	<0.05	<0.24		0.019
Ca	0.38%	2.7%	1.4%	0.49%	0.47×10^4	3.0×10^3	6.8×10^2	−22	9.5
Cl	355		<5–50	1000	460		<0.24–2.4		1.9
Cr	21	180	356	300	26	20	17	42	0.59
Cs	1.5	8	21	4	1.9	0.88	1.02	0	0.0078
Eu	0.17	1.4	1.8		0.21	0.15	0.09	14	
Fe	1.3%	10.1%	9.3%	23.5%	1.6×10^4	1.1×10^4	4.5×10^3	−3.1	4.6×10^2
Hf	3.0				3.7				
K	0.22%	0.95%	1.65%	1.28%	0.27×10^4	1.0×10^3	8.0×10^2	−33	25
La	5.0	42	32		6.3	4.6	1.5	−3.2	
Mg	0.17%	0.41%	0.55%	0.88%	0.21×10^4	4.5×10^2	2.7×10^2	−66	17
Mn	54	418	323	550	67	46	16	−7.5	1.1
Mo	20				25				
Na	0.069%	0.32%	0.7%	0.28%	860	3.5×10^2	3.4×10^2	−20	5.5
Rb	19.4	100	<120		24.3	11	<5.8		
S	5.1%			10.5%	6.4×10^4				2.0×10^2
Sc	3.2	22	25	10	4.0	2.4	1.2	−10	0.019

TABLE I (continued)

Element	Concentration (μg/g unless otherwise indicated)				Mass flow (g/min)				
	Coal	S.T.	P.I.	P.O.	Coal	S.T.	P.I.	Imbalance (%)	P.O.
Se	3.2	14	< 32–48	760	4.0	1.5	< 1.5–2.3		1.4
Sm	1				1.3				
Ta	< 1	2	1.3		< 1.3	0.22	0.06		
Th	3	20	18		3.7	2.2	0.87	−17	
U	1.67	14	17	7	2.09	1.5	0.83	11	
V	21	125	200	63	26	14	9.7	−8.8	0.12
W	< 5				< 6.3				

[a] Imbalance $= \dfrac{\text{S.T.}+\text{P.I.}-\text{coal}}{\text{coal}} \times 100.$

[b] Slag tank.

[c] Precipitator inlet.

[d] Precipitator outlet.

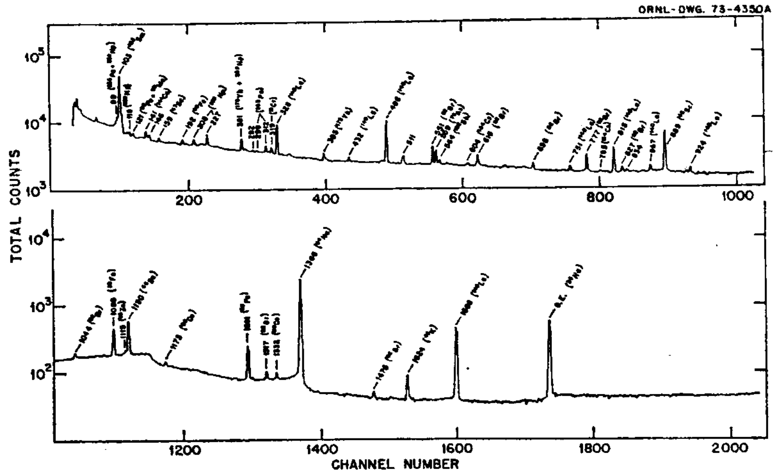

FIGURE 4 Gamma ray spectrum of irradiated coal sample.

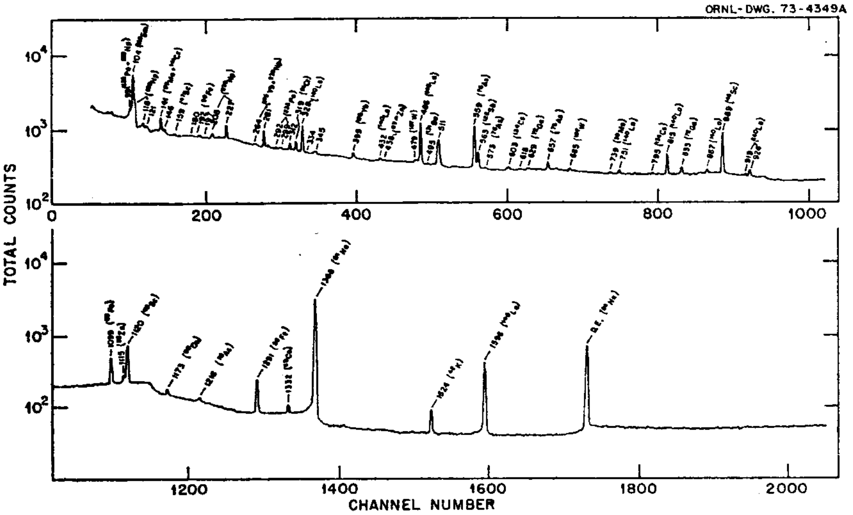

FIGURE 5 Gamma ray spectrum of irradiated ash sample.

contemplated with the Memphis plant, and particular attention this time will be paid to sampling the gas phase. Besides the previously mentioned ICl solution traps for Hg it may be possible to use sodium acetate and/or hydroxylamine hydrochloride solutions to trap Se, As and perhaps other elements. Use of these solutions will require use of chemical separations.

CONCLUSIONS AND FUTURE WORK

Use of neutron activation analysis has enabled preliminary elemental balance on 29 elements at the Allen Steam Plant to be obtained. Future plans include resampling and reanalysis for those elements for which there are poor or no results. Additional studies will be made to try to correlate elemental concentrations with particle size. Air sampling will be employed in the latter study.

Because of the high efficiency of the precipitators at the Allen Plant, little environmental impact is to be expected from the stack effluent for most of the elements so far studied. The volatiles may be the exception to this statement and it is to this problem that major future efforts will be devoted.

We acknowledge the assistance of N. Bolton, the TVA sampling crew under John Lytel, and Bill Fulkerson who helped interpret the data.

This paper was originally presented at the Third Annual Symposium on Recent Advances in the Analytical Chemistry of Pollutants, May 14–16, 1973, at Athens, GA.

References

1. F. F. Dyer and L. C. Bate in "Applications of Nuclear Data in Science and Technology," I. A. E. A., Vienna (1973), in press.