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NEUTRON ACTIVATION ANALYSIS APPLIED TO ENERGY AND ENVIRONMENT

W. S. Lyon
Analytical Chemistry Division
Post Office Box X
Oak Ridge National Laboratory*
Oak Ridge, Tennessee 37830

ABSTRACT

Neutron activation analysis has been applied to a number of problems concerned with energy production and the environment. Burning of fossil fuel, the search for new sources of uranium, possible presence of toxic elements in food and water, and the relationship of trace elements to cardiovascular disease are some of the problems in which neutron activation has been used.

INTRODUCTION

The use of the multielement analytical technique of neutron activation analysis has enabled researchers to gather information about the elemental composition of many materials. Such information is of increasing importance in understanding and attempting to solve the problems of the middle 1970's. Broadly stated, these are problems of energy and environment, each of which has for mankind an internal and external aspect. External energy requirements are met through consumption of fossil fuels and fissionable materials; internal energy requirements through food.

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The internal aspect of environmental problems--the effect of pollutants on living entities--dictates to a large extent external restraints (Figure 1). These restraints affect the technical, economic, and social aspects of energy production and use. The primary key to establishing the necessary restraints is measurement; following measurement of these pollutants comes evaluation and then finally control.

Instrumental neutron activation analysis (INAA) has been a major tool in making measurements of inorganic contaminants emitted to the environment; INAA has also been used to explore the health aspects of certain trace elements in living entities. These health studies not only attempt to find out what is harmful for man, but they also aim at ascertaining any beneficial effects of certain elements. Instrumental neutron activation analysis (INAA) has been used to determine trace element concentrations of fuel, food, water, plant material and biological tissue. In cereal and fertilizer production, neutron generators are now used to determine nitrogen content of the product. Thus, it is apparent that neutron activation analysis can provide information about many materials, processes, and products. Such information is helpful in understanding energy and environmental problems and in planning and controlling industrial activity.

Obviously it is impossible to cover every aspect of these problems in this paper. Rather instead I will attempt to discuss one of two examples from each category.

External Energy

Fission energy is still projected to provide a large fraction of the energy requirements of the U. S. by the Year 2000. There is a projected demand for U_3O_8 far in excess of known proved reserves at $8 per lb and

	Energy	Environment
External	Fossil Fuel →	SO_2, Ash, Particulates
	Fission Fuel →	Radioactivity
Internal	Food	Effect of Trace Elements in Food and H_2O on Living Organisms (+ or -). Effect of Organic Compounds (-).
	H_2O	

Figure 1. Problems of 1975 - 1980

under in the USA. Figures given in a recent talk by Alvin Weinberg, former Director of ORNL and now Director of the Institute for Energy Analysis, will serve to make the point although, as Weinberg admits, they may be a bit out-of-date. (1) He takes three reactor types and compares the 30-year U_3O_8 commitment (in tons) required with and without recycle:

	LWR	CANDU	HTGR
w/o	5400	4200	4500
w	3800	2200	2700

If one accepts present accounting that there is available 700,000-1,000,000 tons proved U_3O_8 reserves and divides this supply by the requirement per reactor, one quickly sees that the number of reactors that can be built is only a few hundred--nothing like the projected requirements of the old AEC. Thus the need for more uranium.

A National Uranium Resource Evaluation (NURE) Program is underway in the USA to search for uranium, and one aspect of it according to E. W. Grutt, Jr., Manager of ERDA's Grand Junction, Colorado office, is a program "for conducting regional hydrogeochemical and stream sediment surveys for uranium in the conterminous U. S. and Alaska" (2). A large sampling program is planned that will require analytical work to be performed on thousands of water and sediment samples. Most of these samples will contain uranium (if at all) at the ppb level; additionally, a multi-element analysis will be desired to look for certain "pathfinder" elements which are often indicative of uranium deposits. These pathfinder elements are Sc, V, Mo, and Th (3), but another 6 or 8 elements are also of interest. These will be determined by INAA, and results from sediment samples that are similar to those expected in the program are

shown in Table 1. These data were obtained by irradiating a few hundred milligrams of the sample at a flux of ∿5 x 10^{13} n cm^{-2} sec^{-1} in the Oak Ridge Research Reactor (ORR) for periods ranging from a few seconds to several minutes. The irradiated samples were counted on a gamma ray spectrometer system consisting of a high resolution Ge(Li) gamma ray detector and a minicomputer interfaced to a 4096 multichannel analyzer. A Computer Program MONSTR (4) was used for peak resolution and identification. The program gives excellent precision and accuracy, but the low concentrations of some of the radionuclides produced require long counting times. Thus the time for counting is the rate determining step. Probably no more than four samples a day can be run, since each sample may require counting at several decay intervals.

Not so slow, however, is the delayed neutron method for uranium determination. One merely evaporates an aliquot of the solution (or in some instances, uses the liquid solution itself) in the rabbit, irradiates for about 1 minute, removes the rabbit and waits 20 seconds or so to allow 4 sec ^{17}N, a delayed neutron emitter, to decay, and then counts the delayed neutrons with BF_3 counters (Figure 2). Standards are run and counted in the usual comparator manner. These delayed neutrons arise from several short-lived fission products with half-lives ranging up to about 55 seconds. Interferences are other fissionable nuclides, Th at concentrations greater than 10^3 of U (in our reactor flux spectrum; this will be much less in a more thermalized spectrum), and neutrons produced by (gamma, n) reactions. The latter come from high energy gamma rays and are usually not a great problem. The gamma sensitivity of the neutron counters can be a problem but usually isn't. The sensitivity for U in our ORR facility is about

Table 1. Results on Sediment Samples Obtained by NAA

(μg/gram unless % sign given)

Sample Sediment	Al	Sb	As	Ba	Br	Ca	Ce	Cs	Cl	Cr	Co	Ga	Hf	Fe	La
	%					%								%	
1	7.92	0.48	6.0	253	2.6	0.11	100	4.9	<100	104		20	13	5.8	46
2	5.31	0.57	6.3	280	3.6	0.16	99	3.3	<100	91		15	17	4.8	42
3	4.04	0.44	5.3	300	3.9	1.87	85	3.5	<100	39	14	6.4	18	3.0	34
4	3.82	0.40	6.0	300	3.2	1.27	81	3.3	<100	46	16	6.6	18	3.0	33
5	3.80	1.50	100	300	2.5	2.22	82	3.8	<100	42	17	11	15	4.0	32
6	4.65	0.83	8.8	300	2.8	0.82	107	4.0	<100	62	16	8.8	18	3.4	46
7	6.26	0.74	11	600	3.7	0.4	106	6.0	<100	76	22	18	14	4.8	54
8	2.35	1.0	12	500	3.9	0.15	108	6.0	<200	93	17	16	16	4.6	52
9	1.45	0.37	5.3	<100	1.2	0.22	28	<2	41	60		3.6	20	1.3	19

Sample NURE Sediment	Mg	Mn	K	Rb	Sm	Sc	Se	Na	Sr	Ta	Th	Ti	W	U	V
	%		%												
1	1.13	700	2.4	163	3.9	17	<10	370	-	1.3	10	4380	2.3	10.6	72
2	0.71	1210	1.25	111	4	14	<10	370	-	1.5	10	4270	2.9	12	47
3	0.59	630	1.0		5.4	11	<10	1500	-	1.3	4	4240	1.4	3.1	50
4	0.53	590	1.12		5.1	10	<10	1550	-	1.2	4	4170	1.56	2.94	48
5	0.64	735	1.3		5.2	12	<10	1580	-	1.3	4	3330	3.6	3.17	63
6	0.87	1330	1.2	109	6.6	13	<10	1500	-	1.4	4	4290	<5	3.6	54
7	0.82	2180	1.3	147	8.0	18	<10	1360	-	1.5	5	4130	2.0	3.82	76
8	0.71	2100	1.3	146	8.0	18	<10	1370	-	1.4	5	2790	2.1	3.64	41
9	0.19	153	0.4	23	2.4	4	<10	190	-	0.5	2	2240	1.1	2.54	20

10 ppb; and since one is interested in U at ~1 ppb, there is a requirement on water samples for evaporation-concentration, or concentration by some other method. We have under development a quick ion-exchange resin method to concentrate uranium. It is conceivable that several hundred thousand such samples will be run in the next few years.

External Environment

An external environmental effect of energy production is the ash resulting from coal combustion. Neutron activation analysis was the principle analytical technique used in the trace element study at the coal-fired Allen Steam Plant in Memphis, Tennessee. Samples of coal bottom ash (slag tank), precipitator inlet ash, and precipitator outlet ash were irradiated, gamma ray spectra obtained, and elemental constituents identified and quantified. Figure 3 is a typical gamma ray spectrum obtained from an irradiation of fly ash. These values were then used to calculate a balance of trace elements into and out of the plant. In addition, the effect of the effluent particulates was studied by analyzing soil and moss up to 20 miles north and south of the plant. These studies of ash, soil, and moss have been reported in part elsewhere (for example (6)). Table 2 shows typical results from one study. The important conclusion that emerged was that the use of high efficiency precipitators such as those at Allen, reduces the output of fly ash to the status of only a minor nuisance. Our results from the soil and moss analyses showed no effects of the fly ash.

Internal Energy

The highly industrialized society of the U. S. seems to go from crisis to crisis--many of which involve real or imagined threats to

Table 2. Trace Element Flows Through a Coal-Fired Power Plant

Element	Element Flows g/min			Imbalance Per Cent	Atmospheric Discharge g/min
	Coal	Slag	Inlet Fly Ash		
Al	15,340	8,620	6,720	0	30
As	6.5	1.5	8.1	+48	0.2
Ba	96	42	55	+ 1	0.3
Br	5.4	0.2	0.3	-90	∿6
Ca	6,380	3,880	2,360	- 2	10
Ce	12.1	7.1	6.2	+10	.04
Cl	1,340	8	15	-98	∿1,300
Co	4.3	1.8	2.9	+ 9	.02
Cr	26	13	22	+33	0.3
Cs	1.6	0.6	1.0	0	0.01
Eu	0.15	0.09	0.09	+20	0.0005
Fe	15,950	9,440	8,940	+16	60
Ga	6.6	0.4	6.0	- 3	
Hf	0.59	0.39	0.30	+17	.002
K	2,260	1,330	1,480	+24	9
La	5.6	3.5	3.0	+16	0.02
Mg	1,780	1,040	780	+ 2	
Mn	49.7	24.9	22.0	- 6	0.2
Na	1,020	420	750	+15	4
Ni	23	7	16	0	
Rb	22.8	8.6	11.5	-12	0.07
Sb	0.74	0.05	0.89	+27	0.2
Sc	3.2	1.8	1.9	+16	0.01
Se	3.2	0.0	1.8	-22	0.4
Si	33,960	19,300	14,480	- 1	
Sm	1.47	0.69	0.78	0	0.003
Ta	0.16	0.08	0.10	+12	.0007
Th	3.1	1.3	1.5	-10	0.01
Ti	740	340	440	+ 5	4
U	3.20	1.26	2.22	+ 8	
V	41.9	21.9	32.5	+30	0.4

personal health through contamination of food or water. A few years ago mercury was found in a number of lakes and streams, and this touched off a massive analytical program to look for Hg in food and water. Neutron activation analysis is a useful tool for Hg determinations since it measures total Hg--both inorganic and organic. Additionally, contamination of the sample through laboratory operations is minimized because the sample can be irradiated with no prior handling. Table 3 shows some data obtained in our laboratory on wheat and other food stuffs (7). These data illuminate two points: (1) NAA is quite sensitive--note the range of results from 0.5 μg/gram down to 0.007. (2) There was only a minor Hg problem with wheat and flour, but certain tuna fishes were quite contaminated. We have also looked for other toxic elements in H_2O and food; As, Se, Zn, for example. Unfortunately, for two of the most dangerous elements, Cd and Pb, the sensitivity of NAA is very poor. But the method has been used as a check and calibration for other techniques such as mass spectrometry.

Internal Environment

The International Atomic Energy Agency (IAEA) and the World Health Organization (WHO) have for the past five years jointly coordinated investigations at an international level on the role possibly played by stable trace elements in the etiology of cardiovascular diseases. A coordinated group of 12 analysts in 9 Member States has commenced work on two separate but related autopsy projects: (1) a study of trace elements (principally Cd, Cr, Cu, Se and Zn) in relation to ischaemic heart disease, and (2) a study of Cd and Zn in human kidney and liver in relation to arterial hypertension.

Table 3. Mercury Found in Wheat and Flour

Sample	µg Hg/gram Sample
Wheat (1)	0.007
Wheat (2)	0.014
Wheat (3)	0.016
Flour (1)	0.010
Flour (2)	0.005
Flour (3)	0.008
Tuna Fish (1)	0.52
Tuna Fish (2)	0.31
Tuna Fish (3)	0.13
Tuna Fish (4)	0.41

The analytical problems posed by these projects include some which test the limits of present-day analytical technology. Some of the trace elements of interest occur in tissues in concentrations of only a few parts in 10^9 and are therefore extremely difficult to determine with accuracy. The analytical methodology in project 1 is further complicated by the requirement to analyse as many elements as possible in samples which, for practical reasons, are often limited in size to a gram or so. Neutron activation analysis is the primary technique used in these studies, since it is a multielement, highly sensitive method. We at Oak Ridge have collaborated with physicians and other scientists at Vanderbilt University, Nashville, Tennessee on this project (8). These biomedical people have prepared samples of human heart, heart muscle, liver and kidney for analysis; then activation analyses were performed at ORNL. No definite conclusions can yet be made concerning the relationship of trace elements and disease, since the data are sent to the WHO-IAEA for correlation and interpretation. We have checked our methods by analyzing on NBS Bovine Liver Standard. Table 4 compares our results with those reported by NBS; as can be seen agreement is quite good.

One other collaborative venture with Vanderbilt should be mentioned. Several years ago during the mercury scare, we began a study of the elemental content in placentas for residents of Nashville, as an index of the trace or pollutant element exposure to the mother and the human fetus. The data provided information of the base trace element levels for a large normal population from this geographical area. No evidence of abnormal trace pollutant levels were detected. Mercury was an element of considerable interest here, particularly the transfer of mercury across

Table 4. Summary of Analyses on NBS Standard (SRM 1577) Bovine Liver

Element	NBS Values (ppm)	Vanderbilt (ppm)	ORNL (ppm)
K	9700 ± 600	---	9480 ± 290
Na	2430 ± 130	---	2570 ± 220
Fe	270 ± 20	331 ± 23	293 ± 12
Zn	130 ± 10	160 ± 19	139 ± 6
Rb	18.3 ± 1.0	23.3 ± 2.6	19.9 ± 0.8
Mn	10.3 ± 1.0	---	9.42 ± 0.41
Se	1.1 ± 0.1	1.00 ± 0.33	1.23 ± 0.20
Cl	2600	---	1880 ± 80
Co	0.18	0.225 ± 0.017	---
Mg	605	---	517 ± 57
Mo	3.2	---	2.5 ± 0.2
Cr	---	0.49 ± 0.19	1.57 ± 0.40
Br	---	---	7.35 ± 0.33
Al	---	---	7.0 ± 1.3
V	---	---	<.0ᵥ
Pb	0.34 ± 0.08	0.262 ± 0.014	---
Cd	0.27 ± 0.04	0.283 ± 0.026	---
Hg	0.016 ± 0.002	0.041 ± 0.010	---

the placenta. Again the results were negative (9).

Conclusion

There are numerous applications of neutron activation analysis and other nuclear techniques to problems of energy and environment. These few examples discussed here are representative of the projects we have been involved in at ORNL. There are other laboratories in all parts of the world where activation analysis work is underway. Surely it is one of the most versatile and useful analytical techniques in use today.

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