

NEUTRON ACTIVATION ANALYSIS AT THE ILLINOIS STATE GEOLOGICAL SURVEY

R. R. Ruch

## ABSTRACT

Neutron activation analysis, a relatively new analytical tool for determining the presence of trace and minor elements, has been added to Illinois State Geological Survey facilities.

The new technique has been applied to such Illinois materials as clays, coal and its ash, fluorspar, crude oil, limestone, chert, and argillaceous sediments. Water leached from sanitary landfills also has been analyzed for minor elements.

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## INTRODUCTION

Chemical analysis plays a very important part in the industrial development of Illinois mineral resources. The composition of a mineral or rock must be known before it can be evaluated for possible use as an industrial commodity, and close chemical control is necessary in the beneficiation of a crude ore to a concentrate and usable by-products.

Since 1931 the Illinois State Geological Survey has maintained a Section of Analytical Chemistry. Its primary role is to supply the chemical analyses required in the Survey's geological and mineral resource research projects. Because of this responsibility, the analytical staff must be alert to new and improved methods of chemical analyses and instrumentation.

Trace element analysis of geological materials is becoming important to basic and applied geological research and mineral resource development. For example, a knowledge of the trace vanadium content of crude oil is important in geochemical exploration for new oil resources. Especially sensitive analytical procedures are essential for the detection and determination of trace elements in the parts per million range, and in the Survey's new neutron activation analysis laboratories, such methods are being applied to Illinois mineral materials.

## NEUTRON ACTIVATION ANALYSIS

Neutron activation analysis, a quantitative analytical tool for the determination of trace elements, was introduced between 1936 and 1938 by two independent research teams, one led by G. von Hevesy and H. Levy, and the other by Glenn Seaborg and G. T. Livingood. The technique, although not fully developed until the early 1960's, is now universally accepted.

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Early in 1965, plans were begun for a program of neutron activation analysis in the Analytical Chemistry Section of the Illinois State Geological Survey. The opportunity for developing such a program came when the University of Illinois offered the Survey the use of its TRIGA MK II nuclear reactor for sample irradiations. Funds were allocated in the summer of 1966, and definite plans for the neutron activation laboratory were formulated.

In January 1967, laboratory alterations were completed and the necessary instruments installed. A 400-channel gamma-ray ( $\gamma$ -ray) spectrometer, NaI detector, and associated data retrieval systems were put into operation. In addition, a conventional chemical laboratory was altered to handle radioactive samples by the installation of a special hood equipped with a highcapacity blower and air filters. By June 1968 some 43 irradiations had been made with the University of Illinois TRIGA MK II nuclear reactor and used to analyze over 300 mineral and rock samples for trace elements (1 to 15 each).

# Theory of Activation Analysis

When an element is bombarded by nuclear particles (such as neutrons produced from a nuclear reactor) it will statistically permute to a different isotope, usually radioactive. The artificially formed radioactive isotope will then emit characteristic  $\gamma$ -radiation with a definite energy and half-life. The  $\gamma$ -radiation may be detected most conveniently by a  $\gamma$ -ray spectrometer (fig. 1). Such an instrument is capable of detecting and resolving  $\gamma$ -rays into discrete energy levels, which may be displayed as "gamma peaks" by a suitable recording instrument.

A typical  $\gamma$ -ray spectrum of Na<sup>24</sup> is shown in fig. 2. Either of the two main gamma peaks can be used to determine the amount of Na present by measurement of the area under it. If known chemical standards are processed in the same manner as the unknown sample and results compared, the amount of a particular element in a material may be quantitatively determined. In general, the technique is very sensitive, allowing as little as 1 part in a million of many elements to be detected in geologic materials.

A typical analysis involves the following steps. From 0.1 to 2 grams of ground, oven-dried material is accurately weighed and sealed in a polyethylene container. Appropriate chemical standards are weighed and similarly sealed. The sample and standards are then irradiated for periods up to 2 hours in the University of Illinois TRIGA MK II research reactor. Rotation of samples on a special "lazy Susan" rack in the reactor insures that samples and standards receive the same neutron flux. The samples and standards are removed from the reactor and the radiation of each is counted by the detector and their  $\gamma$ -peaks compared.

# Current Applications

The following tables illustrate the type of samples currently being analyzed, and the amounts and ranges of the various elements detected by neutron activation analysis.



Fig. 1 - Detection equipment used in neutron activation analysis of samples irradiated by the University of Illinois research reactor.



Fig. 2 - Gamma-ray spectrum of  $Na^{24}$ .

# Clays

Table 1 shows results obtained in a search for possible rare-earth elements in certain Illinois clays. As many as five or six rare earths have been detected in a single clay sample.

Element	ppm	Element	ppm
Lanthanum	37-48	Terbium	< 0.6
Scandium	16-23	Uranium	< 1
Dysprosium	2- 6	Thorium	<u>&lt;</u> 15
Samarium	6-10	Holmium	< 3
Europium	<2	Lutetium	< 1

TABLE 1 - TRACE ELEMENTS FOUND IN ILLINOIS CLAYS

Whole Coal and Ash of Whole Coal

Table 2 gives the determination of chlorine (Cl), sodium (Na), iron (Fe), manganese (Mn), lanthanum (La), scandium (Sc), and other elements in whole coal and whole coal ash. Macro, minor, and trace elements may be

detected by neutron activation analysis. Of special interest is the determination of low concentrations of chlorine (C1) in coal, which is difficult by other means.

		Chlorine (%)	Sodium (%)	Iron (%)	Manganese (ppm)	Lanthanum (ppm)	Scandium (ppm)
Whole coal (14 samp	les)	0.01-0.3	6 0.02-0.1	2 0.45-2.3	16 <del>-</del> 120	1-16	1.3-2.2
Coal Ash f (9 sampl	rom whole comes)	al <0.013	0.08-1.2	7.5-15.0	290-840	9 <b>-7</b> 0	7.7-24.0
Other elem	ents in coal	ash (upper 1	imits), in j	percent:			
	Copper	<0.02	Arsenic	<0.01	Zinc	<0.1	
	Cermanium	<0.03	Bromine	<0.001	Uranium	<u>&lt;</u> 0.006	
	Antimony	<0.001	Gallium	<0.001	Chromium	<u>&lt;</u> 0.03	

TABLE 2 - TRACE ELEMENTS IN COAL AND COAL ASH

# Fluorspar

The results of fluorspar analysis for rare-earth and other possible color-producing ions are shown in table 3. Many trace elements may be quanti-tatively determined at one time.

Element	ppm	Element	ppm
Scandium	<0.04-0.60	Sodium	<b>5-1</b> 88
Europium	0.17-1.5	Manganese	<0.1-<1.2
Dysprosium	0.2-9.4	Cobalt	<0.2-<0.8
Samarium	0.2-4.1	Chromium	<1 -<10
Copper	1 -113		

TABLE	3	-	TRACE	ELEMENTS	IN	FLUORSPAR	(CaFa
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# Crude Oil

Illinois crude oil has been analyzed for trace elements (table 4). Of particular interest is the vanadium (V) content, which may be used as a geochemical prospecting tool.

Element	ppm	Element	ppm
Vanadium	0.1 <b>1-3</b> .8	Arsenic	<0.07
Copper	0.17-0.55	Antimony	<0.05
Sodium	0.15-0.22	Gallium	<0.03
Chlorine	2.3	Bromine	<0.3
Sulfur	1.1 x 10 <sup>4</sup>	Manganese	<0.005

TABLE 4 - TRACE ELEMENTS IN ILLINOIS CRUDE OIL

#### Limestone

Various kinds of limestone have been analyzed for the elements listed in table 5. Multiple determinations can be made in limestone because of its low background contribution after irradiation.

TABLE	5	-	TRACE	elements	IN	ILLINOIS	LIMESTONE	(CaCO <sub>3</sub> )
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(in parts per million)

Chlorine	Sodium	Bromine	Mercury	Manganese
<0.5-219	2-20	<0.03-2	<0.4	6-14

Argillaceous Sediments

Clays, shales, and muds can be assayed for various trace and minor elements (table 6). Excess sodium (Na) present seriously interferes with the determination of many other elements that would be detectable in its absence.

TABLE 6 - TRACE AND MINOR ELEMENTS IN ILLINOIS ARGILLACEOUS SEDIMENTS

Element	ppm	Element	ppm
Cobalt	13- 50	Sodium	3 x 10 <sup>3</sup> - 1.6 x 10 <sup>4</sup>
Manganese	180-1390	Dysprosium	<u>≤</u> 5
Scandium	15- 37	Bromine	<7
Lanthanum	10- 63	Lutetium	<0.3
Chromium	118- 289	Europium	<0.5

Sanitary Landfill Leachate

Leachate from sanitary landfills has been analyzed for certain undesirable elements (table 7). Neutron activation analysis can detect low amounts of selenium (Se) and bromine (Br), among other elements.

TABLE 7 - TRACE AND MINOR ELEMENTS IN SANITARY LANDFILL LEACHATE

(in parts per million)

Bromine	Sodium	Chlorine	Manganese	Selenium
	_	· · · ·		
<0.1-15	7-875	2-1150	0.01-0.1	<0.1

## Chert

An interesting archeological project is underway involving the orgin of the chert used in Indian artifacts. Results to date are shown in table 8 comparing trace elements found in the artifacts with trace elements detected in samples of chert from the area where the artifacts were found. The manganese (Mn) content differs widely between the two cherts and may indicate that the chert used in the artifacts was from a different source.

TABLE 8 - TRACE ELEMENTS IN CHERT AND CHERT ARTIFACTS

#### (in parts per million)

Manganese	Sodium	Gold	Lanthanum	Scandium
		CHERT		
13-269 (30-100)	52-415	<0.002-0.13	1.1-1.2	0.5-0.8
		CHERT ARTIFA	CTS	
0.5-12 (.3)	83-321	<0.002-0.15	0.4-3.1	0.3-0.7

## Other Materials

Other geological and metallurgical materials such as fly ash, mica concentrates, sandstone, shale, sand, salt, and zirconium oxide have been analyzed for individual elements, which are in table 9. Determinations of these elements were specifically requested, but it is certainly possible to extend this list.

Material	Trace element	ppm
Fly ash	Eu	<0.3
Mica concentrates	Cs	<14
Zirconium oxide	Sr	1.3 x 10 <sup>3</sup>
Sandstone and shale	e Au	<0.02 to <0.18
Sand concentrates	La	2 x 10 <sup>3</sup> - 4 x 10 <sup>3</sup>
Sodium chloride	Br	$1 \times 10^1 - 6 \times 10^3$

TABLE 9 - OTHER MATERIALS ANALYZED

#### SUMMARY AND FUTURE CONSIDERATIONS

The results of the analyses made at the Survey demonstrate the general usefulness and versatility of neutron activation analysis. Most results were obtained with an instrumental approach involving no chemical separations. Many additional elements can be determined by activation analysis when a radiochemical separation is made. This involves dissolution and special chemical techniques coupled with the available instrumentation.

In the future many more elements will be added to those reported here, and additional procedures will be developed and employed where needed. Activation analysis will contribute much to the geological knowledge of Illinois natural resources by making possible new kinds of determinations which were formerly either difficult or required excessive time.

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<sup>\*</sup> Out of print