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Neutron activation method in the analysis of environmental objects

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Abstract—Examing the possible methods of analysing the important environmental objects, the main role of nuclear - physical methods, including activation method using reactor neutrons have been marked. The main steps of analysis such as sample preparation, irradiation conditions, information processing and interpretation of results are discussed. Attentions are also paid on the necessity by using other analytical methods and on the programmatic coordination and widening international cooperation in the field of ecological investigations.

Keywords: neutron activation analysis; environmental objects; nuclear - physical methods.

1 Introduction

The tremendous technological progress of the world is leading to enhanced destructive action on the nature and bringing serious environmental changing. It is reflected by the condition of forests balancing oxygen between earth and atmosphere; ozone layer forming essential barrier for destructive ultraviolet radiations, pasture, fields, reservoirs suppliers of food material. Many countries, including Russia are paying much attention towards environmental protection, particularly Russian Academy of Sciences in its yearly meetings has discussed and worked out "Programme on biosphere and environmental investigations" (Marchuk, 1989).

2 Methodology

Overall problem of environmental protection can be formulated as essential working principle with man's interaction with natural biospheric processes. In this situation arises question concerning immediate study of anthropogenic factors, affecting the stability of biological systems and the ways of interaction of anthropogenic loads with these systems. This is an important environmental problem. The solution is linked with landshaft (continent on the whole), level of water (river, lake, ocean), air (atmosphere) and in general all natural systems represented in Fig. 1 (Valkovic, 1989).

Mainly the system affected by technogenic processes, transportation, population growth, also by natural evolutions like explosion of volcanoes, earthquake and so on. Such situation needs ecologically clear production and communal - domestic activities, problem concerning analytical control.

The main objects of analysis can be divided as follows: plants, cereals, soil, rocks, water,

sediments, atmospheric fall outs, aerosols, sewage water, agrochemicals, dust and gases. Most dangerous compounds are pesticides, freon, phenols, amides, oxides of sulphur and nitrogen, production of P, Sb, Cl, F and so on.

The elements influence mainly environment are grouped as in Table 1. Elements characterizing overall ecological situation - As, Be, Cl, Mn, Pb, Sb, Tl, V; as indicator elements, often introduces matter into ecologically important objects are Al, Ba, Fe, Zr, REE, toxic elements - As, Cd, Cr, Hg, Ni, Pb and others. Out of these, As, Hg, Pb and V are distinguished by their universal characteristics and fall in three separate elemental groups.

Estimation of above mentioned elements essentially determines the selections of the analytical methods. Generally, priority is given to chemical analysis and in the analysis of environmental objects, particularly other methods can be used(Zolatov, 1977), with low detection limit of $n \leqslant 10^{-5}\%$ order, small analysis error, high selectivity (particularly, in the analysis of biological products), minimum sample mass($\leqslant 10^{-3}$g), possibility of analysis in presence of high flux important for water and air sample analysis, instrumentation and automatization possibility and so on.

At present, to the large extent spectrophotometric (particularly, with new reagents), gas chromatography, mass spectrometric, atomic absorption, atomic emission with inductivcly coupled plasma and nuclear - physical methods fulfil the qualities and requisites of the analyses. Among above, activation analysis with neutrons is most important(Endman, 1987).

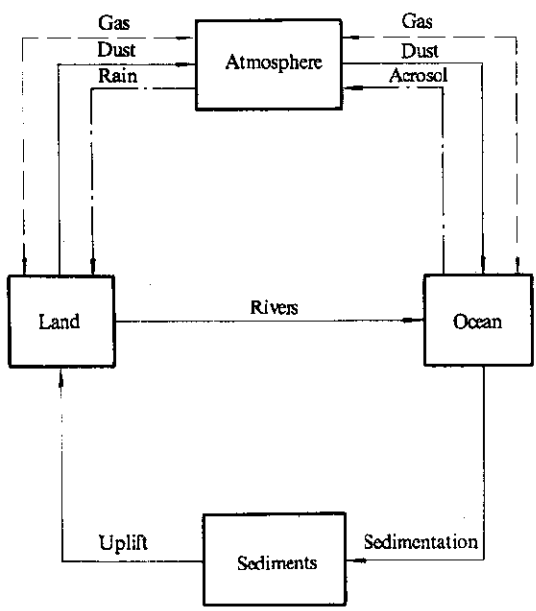

Fig. 1 Schematic representation of technogenic mutualexchange of matter in the nature

Great interest towards nuclear - physical methods has started at the end of 1970 and continued up to 1986 (particularly, in former USSR) till the Chernobyl Atomic Power Station acci-

dent. In USA, for example, this method mostly used in : 46% at universities, 27% at laboratories under government control, 16% at laboratories under industries, 11% at medical schools and hospitals. This means 24% in methodological processing and 76% in applied investigations. Out of them, 30% for industrialization, 20% for environmental studies, medicine and geochemistry (cosmochemistry and oceanology). For example, during 1950—1971 and 1976—1986 period 90% of analyses were carried out by neutron activation method, 5.5% by charged particle analysis and 4.5% by gamma activation method.

Table 1 Elements, characterizing ecological importance and their determination by activation methods

Element	Total pollution	Information about		Methods of analysis		
		pollution of matter	toxic materials	INAA	IGAA	CPAA
Al		*		+	−	
Ag		*			+	
As	*	*	*	+	+	
B	*			−	−	
Ba		*		+	+	
Be	*		*	−	−	
Br		*		+	−	+
C		*		−	−	+
Ca		*		+	+	+
Cd	*		*	+	+	+
Cl	*		*	+	+	
Co		*		+	+	
Cr	*		*	+	+	+
F	*	*		+	−	
Fe		*		+	+	+
Hg	*	*	*	+	+	
I		*		+	−	+
K		*		+	+	
Mn	*	*		+	+	
Na		*		+	+	
Ni	*	*	*	+	+	+
Pb	*	*	*	−	+	+
Rb		+		+	+	+
S	*			+	−	+
Sb	*	*		+	+	
Se	*		*	+	+	+
Sn		*		+	+	
Te	*		*	−	+	
V	*	*	*	+	+	+
Zn		*	*	+	+	+

INAA—Instrumental neutron activation analysis; IGAA—Instrumental gamma activation analysis; CPAA—charged particle activation analysis

In investigations, mostly neutron reactors (76%), accelerators (1.7%), isotopic sources (6%) are used. Most predominantly thermal neutrons (90%) are used. Nowadays, analysis by

epithermal neutrons has been decreased (6%). In many cases preference has given to isotopic sources with fluxes 10^{13}n/cm^2. s.

In neutron activation methods of analysis, 53% — instrumental analysis, 18.3% — radiochemical analysis, 8.4% — preconcentration of elements, 9.9% — prompt gamma radiation and 10.4% — slow and fast impulse neutrons of reactor are used. In recent years analysis by instrumental way has slowed down. Similar tendency is also observed in former Soviet Union from the conferences on neutron activation analysis and other nuclear physical methods. While distribution of neutron activation methods particularly, using reactor neutrons has many advantages. Important among them are availability of high neutron fluxes, simple way of sample irradiation and their analysis, high determinable selectivity with low detection limits and non-destructiveness of sample with small masses(in most cases).

Variety of analytical methods are as follows:

Analysis using very short lived isotopes (Grass, 1987). Good metrological determination characteristics (Table 2) obtained for F, V, Se, Rh elements. In fact, this method is completely automatized.

Table 2 Neutron activation determination of elements using short lived isotopes — $t_{1/2}<5$min

Elements	Radionuclide	Half life period, s	Detection limit, g
Li	^{8}Li	0.84	5×10^{-8}
B	^{12}B	0.022	0.213
N	^{16}N	7.13	1.7
O	^{19}O	26.9	3.6×10^{-3}
	$(n,p)^{16}$N	7.13	3.3
F	^{20}F	11.0	2.2×10^{-6}
	$(n,p)^{9}$O	26.9	1.2×10^{-5}
Ne	^{23}Ne	37.6	1.4×10^{-6}
Al	^{28}Al	2.24	2.0×10^{-8}
V	^{52}V	3.76	9.0×10^{-10}
Se	^{77m}Se	17.4	1.0×10^{-8}
Rb	^{86m}Rb	61.0	1.2×10^{-7}
Rh	^{104m}Rh	4.34	2.5×10^{-9}
	^{104}Rh	42.3	3.5×10^{-9}
Pb	^{207m}Pb	0.81	1.7

Notes: $t_{irradiation}$ = 5min or 1000 disintegrations/s, flux — 10^{13}n/cm^2. s and 10^{2}n/cm^2. s

Analysis using average life($t_{1/2}>1-2$d) and long lived ($t_{1/2}>20-100$d) radionuclides (this type of analysis is predominant in many experiments). It is seen from our obtained data (Table 3) that around 50 elements can be determined in this order of <n, 10^{-6}%.

Possibility of this method can be still widened by using Cd-and B-filters, i.e. by changing the energy spectrum of neutrons. Success of the method (particularly, radiochemical analysis)

depends on concentration and separation of elements. For this purpose, sorption, ion-exchange and extraction methods are used.

Table 3 Elemental detection limits obtained by neutron activation method

Element	Det. limit. g.	Element	Det. limit. g.	Element	Det. limit. g.	Element	Det. limit. g.
Cl	10^{-8}	Na	10^{-11}	Ca	10^{-6}	Sc	10^{-13}
Mn	10^{-11}	K	10^{-10}	Sn	10^{-8}	Cr	10^{-9}
Ni	10^{-7}	Cu	10^{-8}	Ba	10^{-6}	Fe	10^{-7}
Eu	10^{-11}	Zn	10^{-8}	Ce	10^{-9}	Co	10^{-10}
Dy	10^{-11}	Ga	10^{-10}	Nd	10^{-8}	Rb	10^{-9}
Er	10^{-10}	As	10^{-9}	Yb	10^{-10}	Zr	10^{-8}
		Br	10^{-9}	Lu	10^{-11}	Ag	10^{-8}
		La	10^{-10}	Au	10^{-10}	Sb	10^{-8}
		Pr	10^{-8}	U(Np)	10^{-10}	Cs	10^{-9}
		Sm	10^{-10}			Tb	10^{-9}
		Gd	10^{-9}			Tm	10^{-9}
		Ho	10^{-9}			Hf	10^{-10}
		W	10^{-10}			Ta	10^{-10}
		Os	10^{-10}			Hg	10^{-10}
		Ir	10^{-11}			Th(Pa)	10^{-10}

Notes: Flux 1.2×10^{-3}n. cm^{-2}. s^{-1}, tirradiation $-^{20}$h, $t_{cooling}-<1$, 1—2, 7—14 and 30days

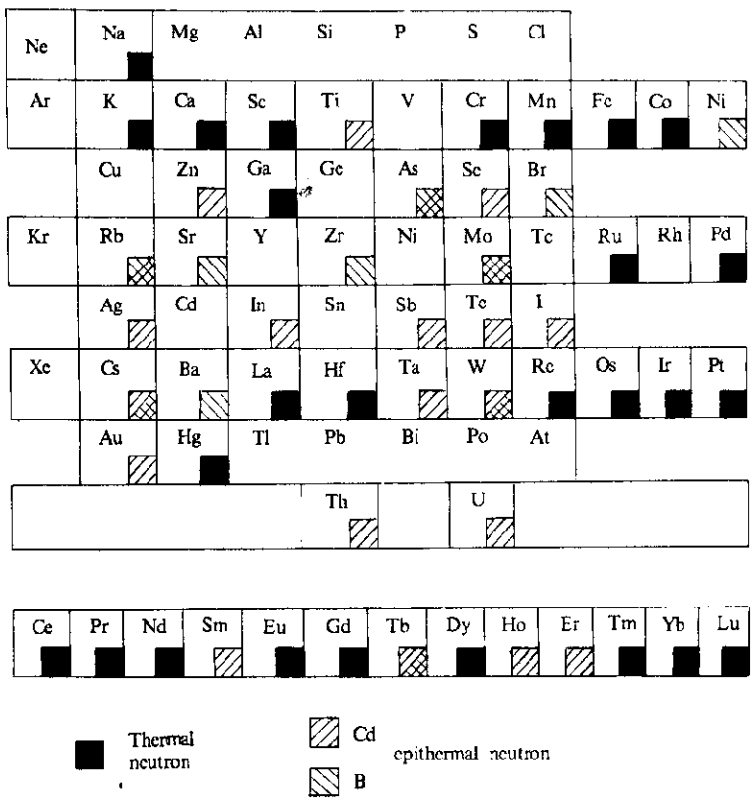

Fig. 2 Preferential neutron spectra used in elemental determination

Analyses using neutron sources ^{252}Cf, ^{124}Sb-Be and others are important and very useful, particularly in field investigations such as constructing mobile laboratories. In this way up to 55 elements can be determined with elemental contents of order $(10-100)\times10^{-4}\%$ (Table 4).

Table 4 Neutron activation determination of elements using radioactive sources ^{252}Cf

Elements	Detection limit, $10^{-4}\%$
Eu, Dy	10^{-3}
Mn, In, Ir, Au, Lu, Ho, Sm, Re	$10^{-3}-10^{-2}$
Na, Sc, Co, Ga, Br, Ag, Sb, Cs, La, Tm, Yb, Ta, W, As, Se	$10^{-2}-10^{-1}$
K, Cr, Y, Cu, Cd, Ce, Nd, Gd, Tb, Er, Hg, Hf, Ge, Sr	$10^{-1}-1$
Cl, Zn, Mo, Ru, Rh, Pd, Ba, Os, F, Mg, Al	1—10
Mg, Al, Ti, Ni, Sn, Rh, Y	10—100
Ca, Fe, Zr	100—1000

Analysis using fast neutrons (energy 14 mV) of generators.

This method is more prospective in the determination of O, Si, Al. U. S. A geological survey's investigations of rock samples (including soil and other objects) are given in Fig. 3. The 10 analysis covered 20 different methods with largest number of elements determined with concentration level of order $<n$, $10^{-4}\%$ (40 elements) done by neutron activation analysis. These are Ta, Th, Y, U, REE, noble elements, As, Sb, V and others (Baodker, 1987).

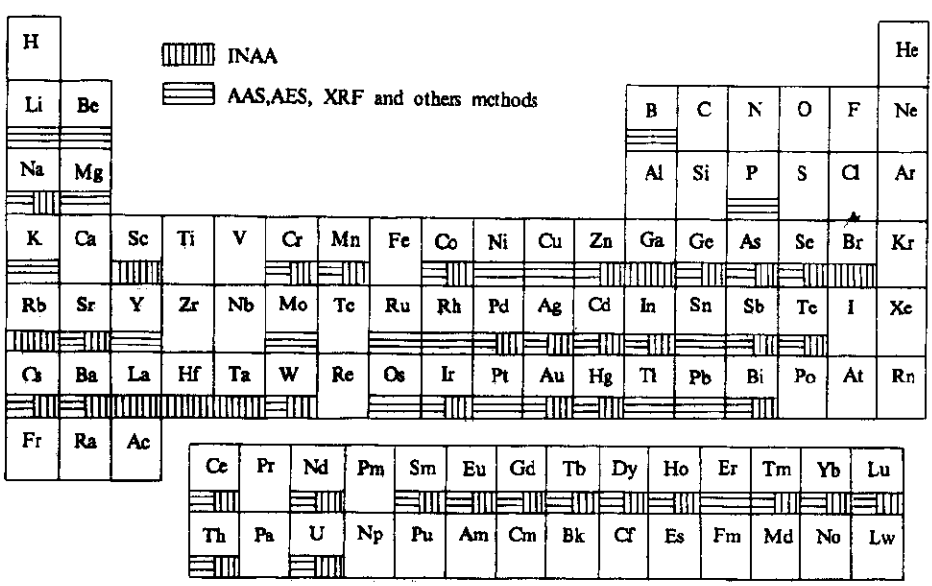

Fig. 3 Methods of analysis, used in elemental determination in rocks (and soil) in the order of $n\times10^{-4}\%$

Using neutron activation method and also analysis by gamma quanta radiations and changed particles in determination of ecologically important elements (Vandecasteele, 1988) were earlier mentioned above. As such it is necessary to stress the prospectivity of their use in the analysis of natural samples, environmental objects and industrial materials, additionally also their combination with these methods, for example of atomic absorption.

In recent years, X-ray fluorescence methods, mainly X-rays produced by the interaction of gamma quanta of radioisotope sources (for example, ^{55}Fe, ^{57}Co, ^{109}Cd and ^{241}Am) and synchronized radiation given new way to X-ray fluorescence analysis (Bareshew, 1986).

Neutron activation methods like other nuclear-physical methods developed at nuclear centres, such as basis for linear accelerators, betatrons, microtrons, cyclotron, generators, reactor and so on. Every investigation centre of the former USSR has developed and applied above methods, particularly in the analyses of mangenese concrets, sediments, ores, soil, water, petroleum products, biological samples, agricultural products and other environmental objects.

Certain example will be mentioned (principally methodology) the application of neutron activation analysis in the Vernadsky Institute partialy reflects the tendency of their use in the country at the present time. It will be assessed sequentially by considering the main parts of the analysis.

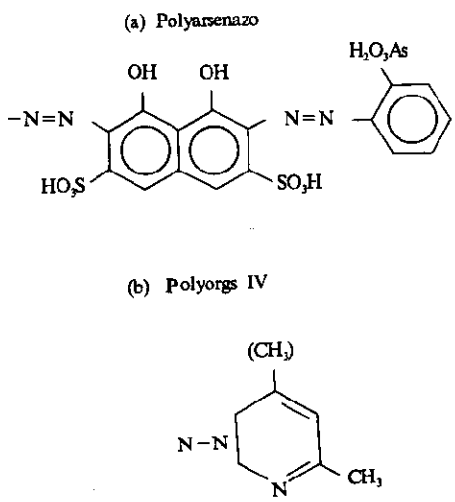

Fig. 4 Sorbents used in concentration of REE(a) and noble metals(b)

3 Sample preparation

Different varieties of objects are chosen for neutron activation analysis, preferably in soil form. Plant and plankton samples are usually dried and ashed, aerosol samples are analyzed along with filters, natural water samples are evaporated or carried other chemical concentration method of analysis of elements. The weight of sample are 1mg to 1g. Samples are prepared by ashing, acid digestion and using microwave ashing system, particularly in the analysis of food materials, concrets, chromates and ores.

For preconcentration of elements in radiochemical methods, the sorbents are used such as polyorgs, tertiary amines, polyarsenazo-N (Fig. 4). The microfine assay and coupling simultaneous dissolution and separation of elemental groups (Fig. 5).

4 Irradiation

Various irradiation regimes, cooling, activity measurements of samples are chosen according to automatization of the method and energy spectrum of neutron (while using Cd- or B-filter). This gives idea how to plan experiment and to get better metrological characteristics, for example, detection limit which accounts in increasing the preferential factor.

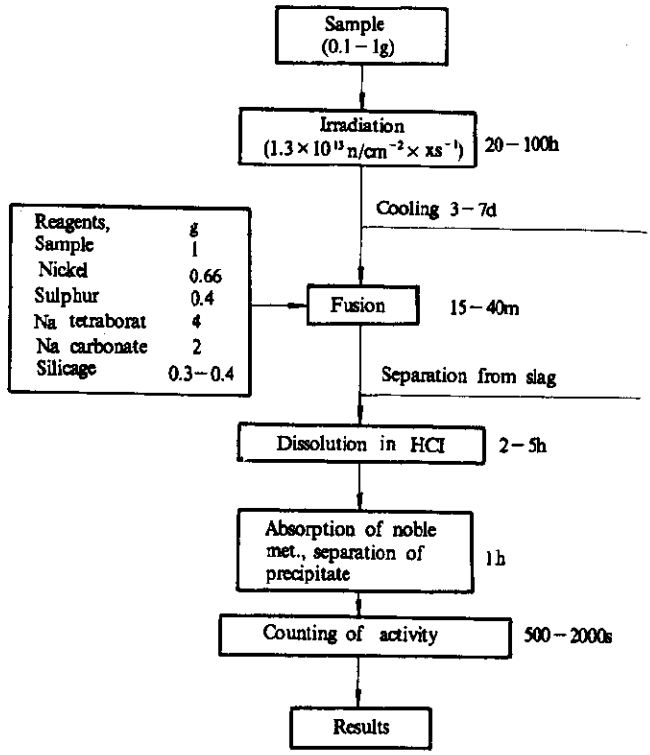

Fig. 5 Schematic representation of microfine assay neutron activation analysis

5 Information processing

Decoding multicomponent gamma spectra of radionuclides, calculation of elements contents, correction of interfering reactions and isotopes are carried out with the help of automatization of the method using programmes such as KROKO, OBRAZ and ASPRO (Shubina, 1989).

6 Interpretation and verification of results

Comparison method, in which the obtained data of samples are compared to that of standards, simultaneous analysis is widely used. Exactness of analysis and background comparison are used in methods such as X-ray fluorescence and atomic emission inductively coupled plasma. Normalization method in which the obtained values are divided by the contents of elements, is used in chondrites, clays or soils and so on. All this explains anamolous distribution of elements, accounting sources of their entrance and transfer into matter. On the whole, such complex approach allowed to determine 25 – 45 elements in a single sample with a detection limit of $(1-100)\times10^{-4}\%$ (Kolesov, 1988).

Many concrete ecological problems have been solved by us using neutron activation analysis. Correct way of determinating chemical composition of sample, pollution level of objects, determination of quantity (in large amount) introducing matter and then the ways and possibilities of improving ecosystem with the help of specialists is important for an analyst.

7 Conclusion

It is now apparent that the neutron activation method has been sufficiently developed and is fairly universal. Nevertheless has the potential to be used for increasing the number of standard sample contents, elaborates sample and universal schemes for mass analyses of samples and group isolation of elements, widespread use of high intensive neutron sources of type ^{252}Cf, and for the constructing (including ^{124}Sb - Be, ^{109}Cd, ^{57}Co) mobile measuring complex.

Realizing these possibilities , and especially combining with other analytical methods, the role of neutron activation analysis in the studies of natural and environmental samples composition can be further increased. Furthermore, the solution of the problem of ecological protection depends largely upon the coordinated research programme and widening international cooperation.

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