

# Milestones in neutron activation analysis

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## Neutron activation analysis is an isotope specific analytical technique for the qualitative and quantitative determination of elemental content

P. Bode, J. J. M. de Goeij, *'Activation Analysis'*, Encyclopedia of Environmental Analysis and Remediation, J. Wiley & Sons, New York, 1998, ISBN 0-471-11708-0, pp 68–84

The method is based upon the conversion of stable atomic nuclei into radioactive nuclei by irradiation with neutrons

- and the subsequent detection of the gamma radiation emitted during the decay of these radioactive nuclei.

Activation by neutrons may result in radionuclides from all elements present in the sample, with sometimes strongly different production rates

## Brief outline:

- 1936: NAA first proposed
- 1950: First use of nuclear reactor in NAA, immediately followed by applications in geosciences and gradually in other areas (radiochemical separations needed)
- 1965: Instrumental NAA using Ge detectors: A major step forward.
- 1970-1985: “Golden age” of NAA:  
Successful applications in many fields of science and technology
- 1985-1995: NAA reached maturity: Few novel applications  
**Rapid development of alternative multi-element techniques**
- 1995-2010: **Decline in use of NAA in Europe and North America, mainly due to closing of research reactors**
- Present: Consolidation of NAA and further developments

## Pioneer papers in neutron activation analysis I:

### **1936: First example of NAA:**

G. Hevesy and H. Levy:

*Kgl. Danske Videnskab. Selskab, Mat.-Fys- Medd., 1936, 14, No. 5.*

Determination of dysprosium in yttrium oxide, using neutrons from a Ra-Be source.

### **1950: First application of a reactor as neutron source in NAA:**

H. Brown and E. Goldberg:

“The neutron pile as tool in quantitative analysis; The gallium and palladium content of iron meteorites”.

*Science 109, 347-353 (1949)*

Radiochemical separation of the product nuclides  $^{72}\text{Ga}$  and  $^{108}\text{Pd}$ .

Beta counting: Purity check by half-life based on repeated measurements.

## Pioneer papers in neutron activation analysis II:

### Determination of Small Quantities of Uranium in Rocks and Minerals by Radioactivation.

*A. A. Smales, Anal. Chem. 24, 1521 (1952)*

The determination of microgram amounts of uranium in minerals and rocks by neutron irradiation followed by radiochemical separation and measurement of the fission product barium-140 was described. The method has been applied to a number of different types of minerals containing as little as 0.0003% uranium in samples weighing less than 0.5 gram. Results show good agreement with those obtained on larger samples by accepted methods of analysis.

“The method may be of value where the available sample is small - in some examples of geological age determination on individual minerals separated from parent rocks”.

## Pioneer papers in neutron activation analysis III:

- E.A. Vincent and A.A. Smales:

“The determination of palladium and gold in igneous rocks by radioactivation analysis”.

*Geochim. Cosmochim. Acta* 9, 154-160 (1956).

- A.A. Smales, D. Mapper and G. Wood:

“The determination by radioactivation of small quantities of nickel, cobalt and copper in rocks, marine sediments and meteorites”.

*Analyst* 82, 75-88 (1957).

In these and other papers of the time the induced radionuclides had to be separated chemically from all other activities and measured by gross beta or gross gamma.

Early 1960s:

Introduction of the  
gamma spectrometer:

Sodium iodide detector coupled to multichannel analyzer.

INAA (Instrumental Neutron Activation Analysis) became possible.

Examples of papers:

R.A. Schmitt, R.H. Smith and G.G. Goles:

“Abundances of Na, Sc, Cr, Mn, Fe, Co, and Cu in 218 individual meteoritic chondrules via activation analysis”.

*Journal of Geophysical Research* 70, 2419-2444 (1965)

A.O. Brunfelt and E. Steinnes:

“Instrumental activation analysis of standard rocks”

*Geochimica et Cosmochimica Acta* 30, 921-928 (1966)

Late 1960s:

Sodium iodide detectors were replaced by germanium detectors for gamma spectrometry.

Examples of papers:

G.E. Gordon, K. Randle, G.G. Goles, J.B. Corliss, M.H. Beeson and S.S. Oxley:

“Instrumental activation analysis of standard rocks with high-resolution gamma-ray detectors”.

*Geochimica et Cosmochimica Acta* 32, 369-396 (1968)

A.O. Brunfelt and E. Steinnes:

“Instrumental activation analysis of silicate rocks with epithermal neutrons”.

*Analytica Chimica Acta* 48, 13-23 (1969)



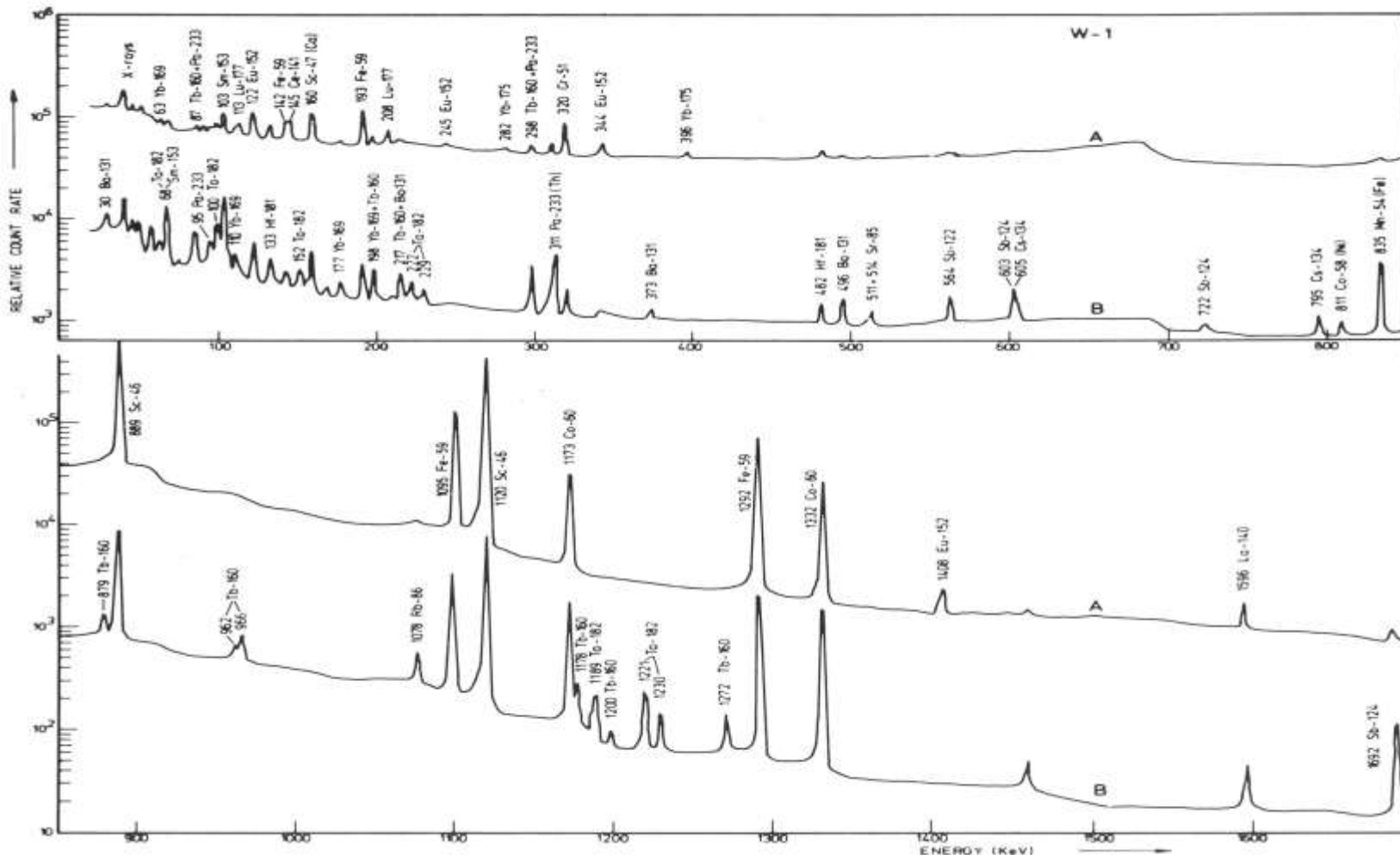
## Epithermal activation of rock samples:

### **Enhancement of radionuclides formed from a stable isotope with a high $I_0/\sigma_0$ ratio**

#### Advantages:

1. Improved detection limits by INAA:  
e.g. As, Br, Rb, Sr, Mo, Cd, Sb, I, Tb, Hf, Ta, Th, U
2. Reduction of high matrix activity;  
 $^{28}\text{Al}$ ,  $^{56}\text{Mn}$ ,  $^{24}\text{Na}$ ,  $^{140}\text{La}$ ,  $^{46}\text{Sc}$ ,  $^{59}\text{Fe}$ ,  $^{60}\text{Co}$
3. Reduction of fission product interference  
e.g. Mo  
( $^{235}\text{U}$  fission occurs essentially with thermal neutrons)

Gamma spectra of neutron activated rock sample 14 days after irradiation.  
 A. Total neutron spectrum; B. Epithermal (Cd cover).



E. Steinnnes: "Epithermal activation analysis of geological material".

In "Activation Analysis in Geochemistry and Cosmochemistry", pp. 113-128. Oslo 1971

# Elements particularly favorable for determination in coal and coal ashes by epithermal activation analysis

(J.J. Rowe and E. Steinnes, *J. Radioanal. Chem.* 37(1977)849)

H	Improvement 5-20 times																He
Li	Be	Improvement 20-100 times										B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Example of a multi-element scheme used for analysis of [lunar rocks](#):

A.O. Brunfelt and E. Steinnes:

“A neutron activation scheme developed for the determination of 42 elements in lunar material”. *Talanta* 18 (1971) 1197-1208.

Combination of instrumental and radiochemical NAA using thermal and epithermal neutrons

Total sample consumption: 420 mg

Experiment	Neutrons	Irradiation time	Delay	ND/RC	Detector	Sample weight (mg)
A	Total	30 sec	no	ND	Ge(Li)	10
B	Total	5 min	2 hr	ND	Ge(Li)	Sample from A
C	Epithermal	2 d	3-5 d	ND	Ge(Li)	100 mg
D	Total	1 d	5 d	ND	Ge(Li)	Sample from C
E	Total	15 min	20 min	RC	NaI, Ge(Li)	50
F	Total	20 hr	30 hr	RC	NaI, Ge(Li)	50 mg
G	Total	7 d	7 d	RC	NAI, Ge(Li)	200 mg
						Total: 420 mg

ND: Non-destructive; RC: Radiochemical separations

# Elements determined in lunar rocks and soils by the Norwegian group

Neutron activation scheme for the determination of 42 elements in lunar material

*Instrumental, thermal activation*  
*Instrumental, epithermal activation*  
 Radiochemical separation

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
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Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
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## INAA in air pollution studies:

*Multi-element analysis of aerosols and related materials: Up to 44 elements*

R. Dams, J.A. Robbins, K.A. Rahn and J.W. Winchester:

Nondestructive neutron activation analysis of air pollution particulates.

*Analytical Chemistry* 42, 961-866(1970)

J.J. Rowe and E. Steinnes:

Instrumental neutron activation analysis of coal and fly ash with thermal and epithermal neutrons. *Journal of Radioanalytical Chemistry* 37, 849-857(1977).

R.R. Greenberg, W.H. Zoller and G.E. Gordon:

Composition and size distribution of particles released in refuse incineration.

*Environmental Science and Technology* 12, 566-573 (1978)

W. Maenhaut, W.A. Zoller, R.A. Duce and G.L. Hoffman:

Concentrations and size distribution of particulate trace elements in the South Polar atmosphere. *Journal of Geophysical Research* 84, 2421-2431 (1979)

E. Steinnes:

Atmospheric deposition of heavy metals in Norway studied by the analysis of moss samples using neutron activation analysis and atomic absorption spectrometry.

*Journal of Radioanalytical Chemistry* 58 (1980) 387-391.

**1970-1985: “Golden age” of NAA:  
Successful applications in many fields of science**

- “Contamination-free” studies of trace elements in medicine and biology
- Ultra-trace concentrations of trace elements in high-purity materials
- Tracing origin of archaeological samples by their trace element distribution
- Certification of analytical reference materials for element contents
- Concentrations and chemical speciation of trace elements in water
- Determination of platinum-group metals after fire-assay pre-concentration
- Lanthanide distributions in nature

J. Versieck and R. Cornelis:

Normal levels of trace elements in human blood plasma or serum. *Analytica Chimica Acta* 116(1980)217-254

### Examples of literature values

Plasma or serum **chromium** concentration (ng/mL)

Authors, year	Anal. technique	Mean	St. dev.	Range
Monacelli et al., 1956	OES	185	-	82-308
Niedermeier et al., 1962	OES	55	-	10-390
Feldman et al., 1967	AAS	30	-	11-66
Savory et al., 1972	GC	13.5	-	2.7-24
Behne and Diel, 1972	NAA	10.3	6.2	
Salvadeo et al., 1979	AAS	8.2	2.4	
Hambidge, 1974	OES	3.1		
Pekarek et al., 1974	AAS	1.62	0.31	
Grafflage et al., 1974	AAS	0.73	0.45	
Kasperek et al., 1979	NAA	0.45	0.15	
Kayne et al., 1978	AAS	0.14		
<b>Versieck et al., 1978</b>	NAA	0.160	0.083	0.038–0.35

Data from J. Versieck and R. Cornelis: Normal levels of trace elements in human blood plasma or serum, *Anal. Chim. Acta* 116 (1980) 217-254

The erroneously high values may be due to:

- A. Contamination during sample handling and analysis
- B. Contamination during sampling



## Certification of analytical reference materials for element contents

NAA plays an important role in certification of element contents in analytical reference materials:

1. Accepted reference values for US Geological Survey rock standards. depend strongly on values obtained by NAA.
2. NAA is one out of 3-4 **physically independent** analytical techniques used regularly by US National Institute of Standards and Technology (NIST), IAEA and other organizations certifying reference materials for determination of trace elements.
3. In the European program for studying atmospheric deposition of metals based on collection and analysis of moss samples (cfr. next talk) three moss reference samples were produced and analyzed by the participants prior to the program, and recommended values were issued. (cfr. E. Steinnes et al., *Accreditation and Quality Assurance* (1997) 243-249)

## Technical developments affecting INAA 1970-1990:

- Improvement of coaxial Ge detectors (resolution and volume)
- Improvement of computer routines for spectrum resolution

These improvements have had a positive effect on the quality of measurements and improved determination limits,  
- but no strong impact on novel developments in NAA per se.

- Introduction of low-energy photon detectors
- Compton suppression systems

These developments have shown some promise, but have had little if any general influence on the progress in NAA

## Techniques for trace element determination

Technique	Introduced	Detection limit (ng)
NAA	1950	0.05 – 10000
*AAS, flame	1965	10-1000
**AAS, electrothermal	1970	1-100
**ICPMS, quadrupole	1985	1-50
**ICPMS, sector field	1995	0.1-5

AAS and ICPMS require sample in solution

AAS is a single element technique

ICPMS is a multielement-technique

# Observed determination limits for sector-field ICPMS (nanograms)

Conditions:

**1-gram sample** decomposed with 5 ml 14M HNO<sub>3</sub>

Diluted to 50 ml

H																	He
Li 10	Be 2											B 30	C	N	O	F	Ne
Na 3000	Mg 100											Al 0.07	Si 1300	P 100	S 3000	Cl 30000	Ar
K 2000	Ca 3000	Sc 1	Ti 7	V 1	Cr 2	Mn 2	Fe 7	Co 1	Ni 4	Cu 7	Zn 10	Ga 2	Ge 7	As 3	Se 50	Br 1000	Kr
Rb 0.4	Sr 10	Y 0.1	Zr 2	Nb 1	Mo 7	Tc	Ru 1	Rh 0.2	Pd 20	Ag 0.7	Cd 0.7	In 0.2	Sn 3	Sb 0.8	Te 30	I	Xe
Cs 0.2	Ba 4	La 0.7	Hf	Ta	W 1	Re	Os	Ir	Pt 2	Au 0.07	Hg 0.3	Tl 0.1	Pb 0.7	Bi 0.3	Po	At	Rn
Fr	Ra	Ac															

Ce 0.07	Pr 0.1	Nd 3	Pm	Sm 0.2	Eu 0.7	Gd 17	Tb 0.08	Dy 0.7	Ho 0.1	Er 0.1	Tm 0.2	Yb 0.1	Lu 0.03
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Th 0.2	Pa	U 0.08	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
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Theoretical detection limits for NAA (nanograms):

Irradiation time:

Neutron flux:  $2 \times 10^{13}$  n cm<sup>-2</sup> sec<sup>-1</sup>

Induced activity: 40 dps

Radiochemical separation

H																
Li	Be											B	C	N	O	F
Na	Mg											Al	Si	P	S	Cl
0.1	10											0.5	10	0.5	200	0.5
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
1	100	0.5	50	0.2	10	0.005	100	0.1	0.5	0.05	1	0.05	1	0.05	0.1	0.05
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
0.01	1	0.1	5	5	0.5		1	0.5	0.1	1	1	0.002	5	0.05	1	0.05
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
0.5	1	0.02	0.2	0.05	0.05	0.02	0.5	0.005	2	0.5	0.5	10	50	5		
Fr	Ra	Ac														

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
0.1	0.5	2		0.01	.0005	5	0.05	0.001	0.005	0.2	0.05	0.05	0.005

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
0.02		0.1											

# Observed determination limits for sector-field ICPMS (nanograms)

Conditions:

**1-gram sample** decomposed with 5 ml 14M HNO<sub>3</sub>

Diluted to 50 ml

H																	He
Li 10	Be 2											B 30	C	N	O	F	Ne
Na 3000	Mg 100											Al 0.07	Si 1300	P 100	S 3000	Cl 30000	Ar
K 2000	Ca 3000	Sc 1	Ti 7	V 1	Cr 2	Mn 2	Fe 7	Co 1	Ni 4	Cu 7	Zn 10	Ga 2	Ge 7	As 3	Se 50	Br 1000	Kr
Rb 0.4	Sr 10	Y 0.1	Zr 2	Nb 1	Mo 7	Tc	Ru 1	Rh 0.2	Pd 20	Ag 0.7	Cd 0.7	In 0.2	Sn 3	Sb 0.8	Te 30	I	Xe
Cs 0.2	Ba 4	La 0.7	Hf	Ta	W 1	Re	Os	Ir	Pt 2	Au 0.07	Hg 0.3	Tl 0.1	Pb 0.7	Bi 0.3	Po	At	Rn
Fr	Ra	Ac															

Ce 0.07	Pr 0.1	Nd 3	Pm	Sm 0.2	Eu 0.7	Gd 17	Tb 0.08	Dy 0.7	Ho 0.1	Er 0.1	Tm 0.2	Yb 0.1	Lu 0.03
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Th 0.2	Pa	U 0.08	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
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“Relative” versus “absolute” activation analysis:

- For a long time the quantification of element content in NAA was based on comparison with standards of the elements irradiated together with the samples to be analyzed (“**Relative method**”).
- But the amount of an element in the sample can be calculated in principle, provided that you know the following:
  - a. Thermal and epithermal neutron flux in the irradiation position
  - b. Thermal neutron activation cross-section and resonance activation integral of the target nuclide
  - c. Decay scheme of the product radionuclide
  - d. Efficiency of your detector system for the gamma-ray selected

In principle, therefore, it is possible to replace the element standards with a single flux monitor

## Important papers in the development of “absolute” NAA:

F. Girardi, G. Guzzi and J. Pauly:

“Reactor neutron activation analysis by the single comparator method”.  
*Anal. Chem.* 37, 1085-1092 (1965)

A. Simonits, F. De Corte and J. Hoste:

“Single comparator methods in reactor neutron activation analysis”.  
*J. Radioanal. Chem.* 24, 31-46 (1975)

R.R. Greenberg, P. Bode and E.A. De Nadai Fernandes:

“Neutron activation analysis: A primary method of measurement”.  
*Spectrochimica Acta Part B* 66, 193-241(2011)



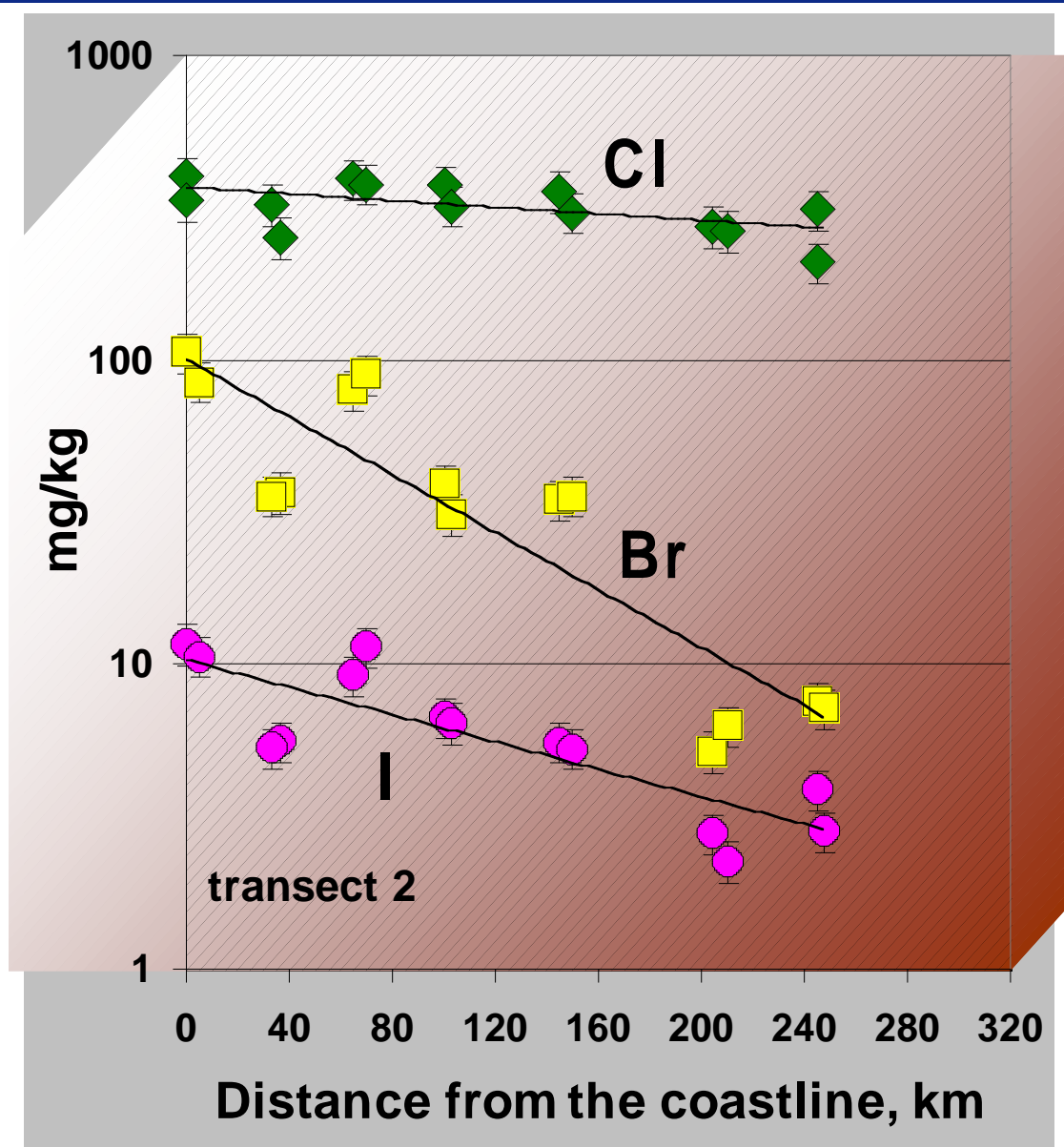
Activation analysis remains an important resource for society

### Recommendations for the future:

1. In order to maintain and further develop the capabilities of NAA, 5-10 “Centers of Excellence” should be established worldwide.
2. Dubna is an obvious candidate for one of those centers.
3. These centers should form an international network ensuring coordination, collaboration, and mutual progress regardless of the political situation worldwide and in the host countries.

## Examples of future tasks in NAA:

- Studies of extraterrestrial material (micrometeorites, samples from Mars, etc.).
- Examinations of all kinds of aerosols.
- Research on elements where NAA offers particular advantages
  - a. Halogens (Cl, Br, I)
  - b. Noble metals (Ag, Au, Ru, Rh, Pd, Ir, Pt)
  - c. Other elements where NAA has superb determination limits (In, Sb, ..)
- Standardization and certification of analytical reference materials
- Non-destructive analysis of
  - a. Particularly valuable samples
  - b. Samples to be further investigated by “destructive” methods
  - c. Investigations related to nanoparticles (?)



**Halogens in surface soil in northern Norway  
(Frontasyeva and Steinnes, 2005)**

## Specific advice to the Dubna NAA group:

- Look for project where the NAA competence may complement or strengthen the specific competence of other techniques
- Develop your competence in chemistry. You may need it before you know!
- Always consider the specific and unique neutron spectrum of the Dubna reactor (resonance and fast neutrons), which may place you in a better position than other NAA laboratories for specific analytical tasks.

