Overview of Neutron Activation Analysis

Borut Smodiš

Jozef Stefan Institute

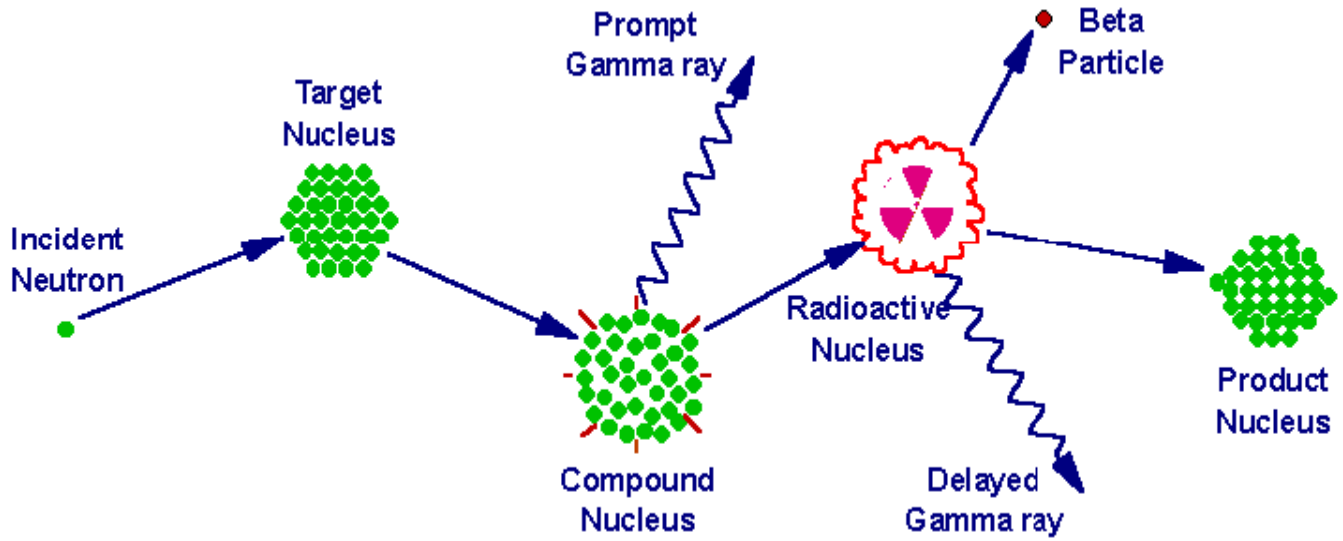
and

Jozef Stefan International Postgraduate School

Joint ICTP-IAEA Workshop on Nuclear Data for Neutron Dosimetry and Analytical Methods by Applying Research Reactors, 20 – 24 April 2015, ICTP – Miramare, Trieste, Italy

Overview of presentation

- Basic principles of NAA
- Analytical procedures
- Analytical characteristics
- Applications



NAA is a physical technique that is based on nuclear reactions. The sample becomes radioactive when neutrons react with the nuclei of the elements' atoms. Radioisotopes are formed and subsequently decay by emitting gamma rays that are unique in half-life and energy (identification). Gamma-ray intensity is proportional to the element content in the sample.

Neutron sources (1)

- **Radioisotopic neutron sources**
  - Two-component sources based on (α,n) reactions: α decay from ^{239}Pu, ^{241}Am, ^{210}Po then ^{9}Be(α,n)^{12}C
  - Two-component sources based on (γ,n) reactions: ^{24}Na, ^{124}Sb then ^{9}Be(γ,n)2 ^{4}He
  - Spontaneous fission sources, e.g. ^{252}Cf
- **Neutron generators**
  - 2.4 MeV neutrons D(d,n)^{3}He
  - 14-MeV neutrons D(t,n)^{4}He
- **Cyclotrons, e.g. d shot at Be target**

Neutron sources (2)

- **Spallation neutron sources e.g. heavy elements such as W, Pb, U irradiated with high-energy protons or other particles are spalled into two or more fragments and many neutrons are released**
- **Neutron reactors (mostly used, they allow for determinations using different neutron reactions – reactor neutron spectrum)**

Overview of NAA (1)

Promt gamma NAA (PGAA): prompt γ rays emitted by the excited intermediate nucleus are monitored.

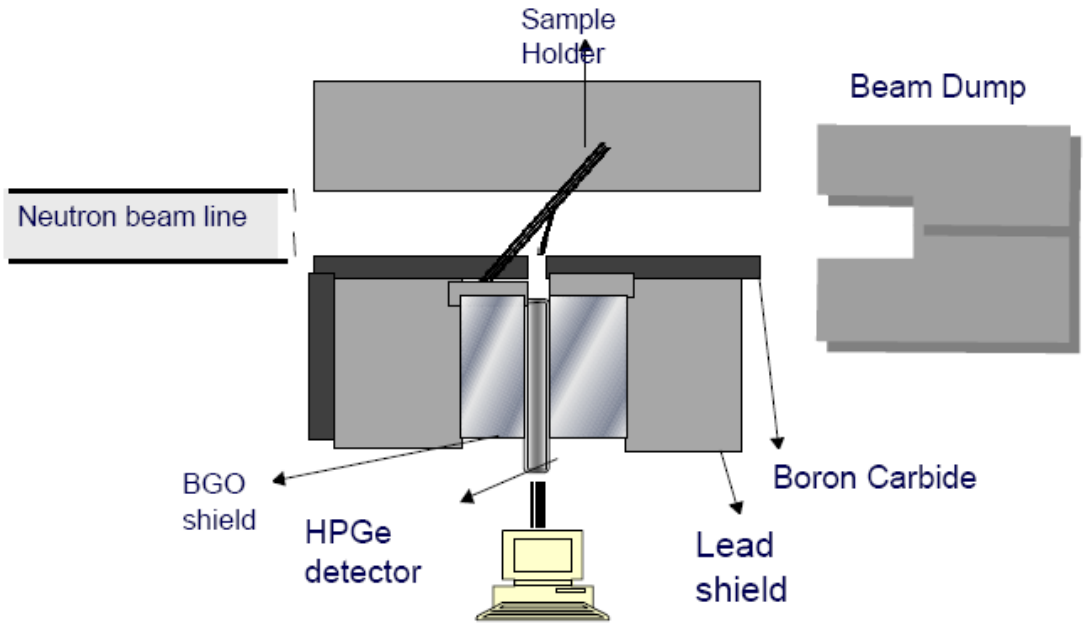
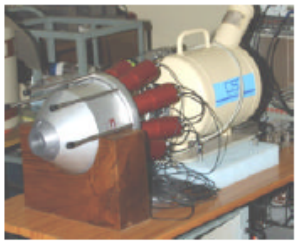


Fig.1 Schematic representation of the PGNAA set up



Overview of NAA (2)

Delayed gamma NAA (**NAA**): delayed γ radiation from the radioactive product is detected after activation.

Classification according to chemistry involved:

- **Instrumental NAA** (**INAA**): no chemical treatment of sample is involved.
- **Radiochemical NAA** (**RNAA**): chemical separations are done after irradiation to remove interferences or to concentrate the radionuclide of interest.
- **Chemical NAA** (**CNAA**): pre-irradiation chemical separations are employed.
- **Molecular activation analysis**: specific molecular components are determined.

Overview of NAA (3)

Classification according to energy of incoming neutrons:

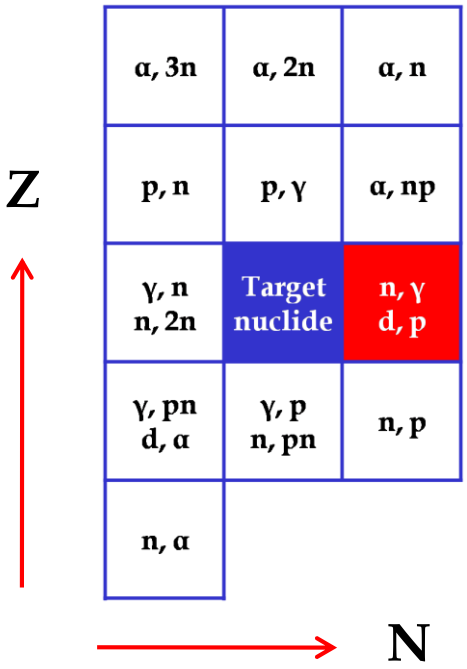
- **Thermal NAA** (**TNAA**): thermal ***n***: their velocity is low (≈ 2200 m/s) with mean energy of about 0.04 eV.
- **Epithermal NAA** (**ENAA**): epithermal ***n***: their energy is in the range of 0.1 – 1 eV. This type of NAA usually comprise also resonance ***n,*** that are in the range of 1 eV – 1 KeV.
- **Fast NAA** (**FNAA**): fast ***n***: their energy is > 0.5 MeV.
- **14-MeV INAA**: a form of FNAA based on reactions with 14-MeV neutrons that are produced by neutron generators.

Nuclear reactions

- **Neutron capture**

$$^{A}X(n, \gamma)^{A+1}X \rightarrow ^{A+1}Y$$

- **Treshold reactions**



$$^{A}X(n, 2n)^{A-1}X \rightarrow ^{A-1}Y$$

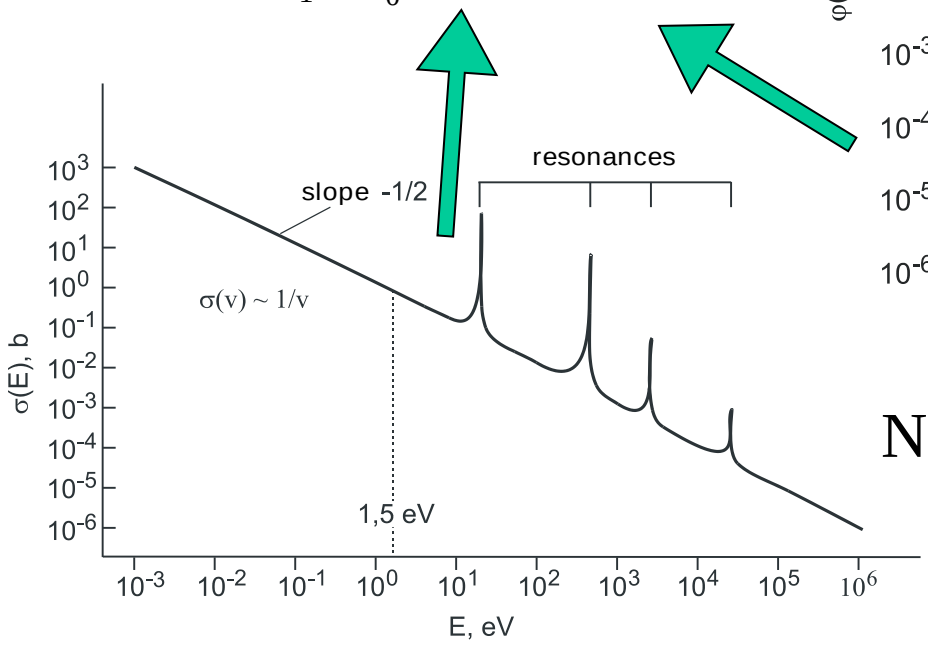
(n,p)

(n,α)

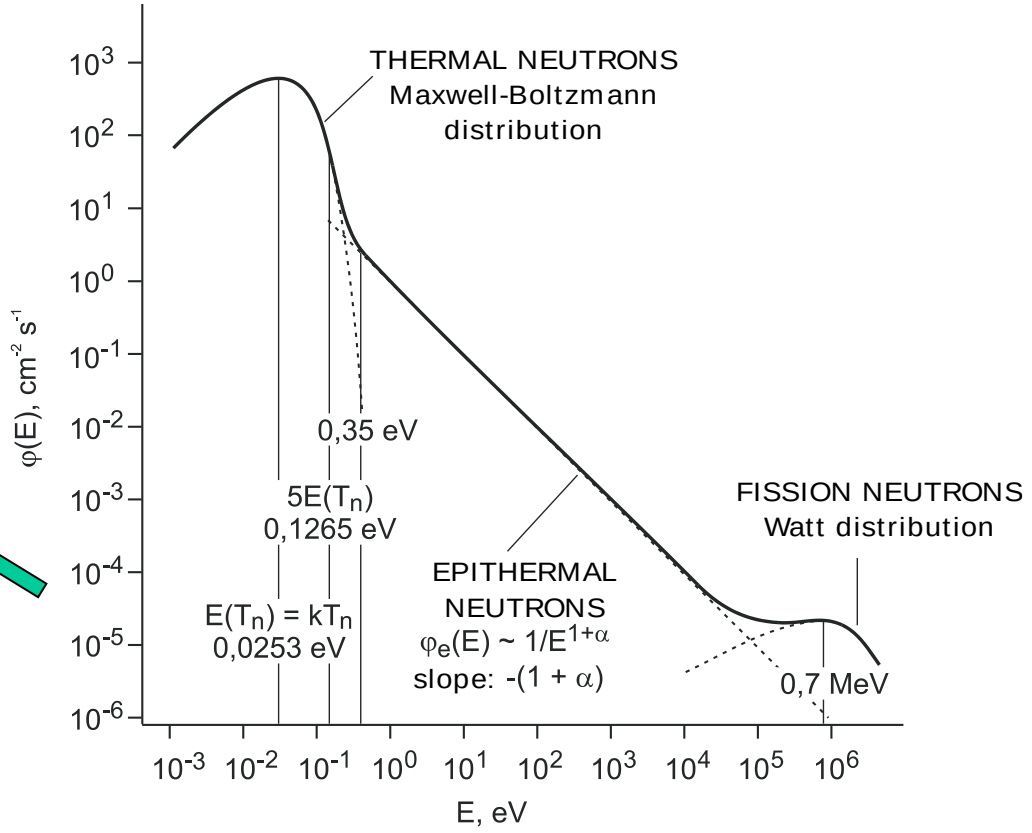
Activation via (n,γ) reaction

Specific reaction rate per target nuclide

$$R_X = \frac{R}{N_1} = \int_0^\infty \sigma(E)\,\varphi(E)\,dE$$



Cross-section vs. E



Neutron fluence rate distribution vs. E

The measured count rate (R) of the gamma rays from the decay of a specific isotope in the irradiated sample is related to the amount (n) of the original, stable isotope in the sample

$$R = n \Theta \gamma (\sigma \varphi_0 + I_0 \varphi_e) S D C \varepsilon$$

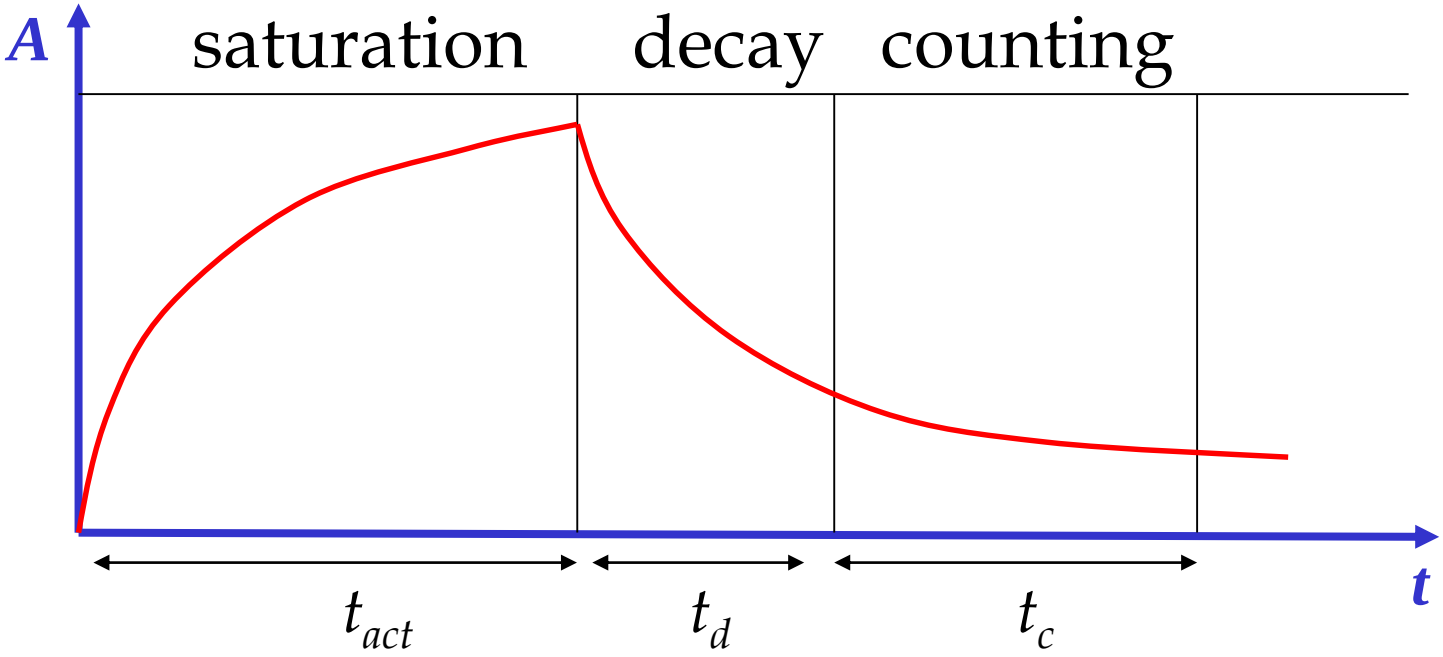
NAA classification according to standardisation:

- **Absolute**
- **Relative**
- **k_0**

$$W_{sam} = W_{std} \frac{R_{sam}}{R_{std}}$$

$$w_a = \frac{\left(\frac{N_p / t_m}{S D C} \right)_a}{A_{sp,m}} \frac{1}{k_{0,m}(a)} \frac{G_{th,m} f + G_{e,m} Q_{0,m}(\alpha)}{G_{th,a} f + G_{e,a} Q_{0,a}(\alpha)} \frac{\varepsilon_{p,m}}{\varepsilon_{p,a}}$$

S D C factors:



$$S = 1 - e^{-\lambda t_{act}} \qquad D = e^{-\lambda t_d} \qquad C = \frac{1 - e^{-\lambda t_c}}{\lambda t_c}$$

Mass fraction of analyte in sample, w_a:

$$w_a = \frac{\left(\frac{N_p}{SDCt_m m_{sample} coi}\right)_a}{\left(\frac{N_p}{SDCt_m m\, coi}\right)_m} \frac{1}{k_{0,m}(a)} \frac{\left[G_{th,m} f + G_{e,m} Q_{0,m}(\alpha)\right]\varepsilon_{p,m}}{\left[G_{th,a} f + G_{e,a} Q_{0,a}(\alpha)\right]\varepsilon_{p,a}}$$

$$k_0 = \frac{A_{sp} - (A_{sp})_{Cd}}{A^*_{sp} - (A^*_{sp})_{Cd}} \frac{\varepsilon^*}{\varepsilon} = \frac{A_{sp}}{A^*_{sp}} \frac{f + Q^*_0}{f + Q_0} \frac{\varepsilon^*}{\varepsilon} =$$

$$= \frac{M^* \theta P_\gamma \sigma_0}{M\ \theta^* P^*_\gamma \sigma^*_0}$$

$$Q_0(\alpha) = (Q_0 - 0.429)\overline{E}_r^{-\alpha} + \frac{0.429}{(2\alpha + 1)0.55^\alpha}$$

Nuclear research reactor TRIGA Mark II (250 kW)

- **Short and long irradiation in the CC:**

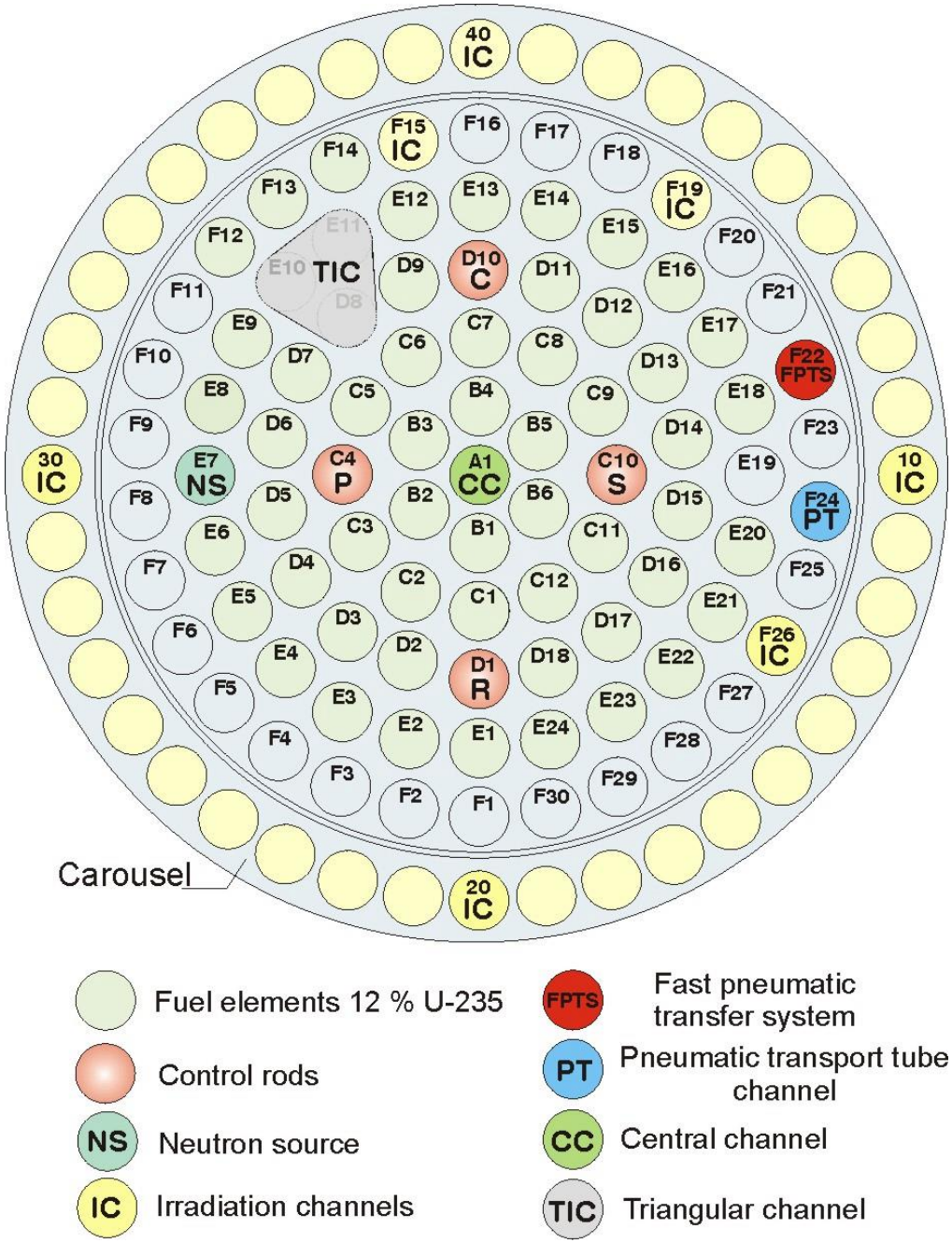
  $\varphi_{th} \sim 10 \cdot 10^{12}\ cm^{-2}\ s^{-1}$

- **Short irradiation in the PT and in the FPTS (up-to 30 min.)**

  $\varphi_{th} \sim 3.5 \cdot 10^{12}\ cm^{-2}\ s^{-1}$

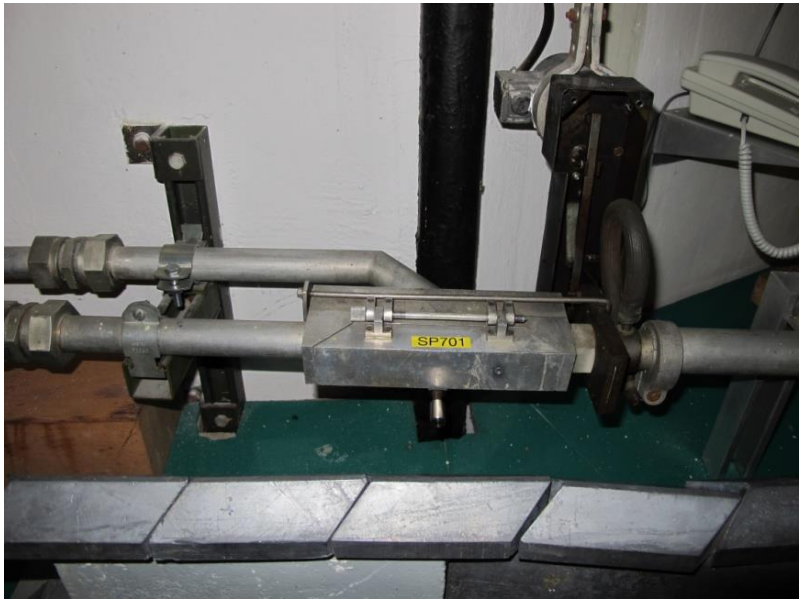
- **Long irradiation in the IC-40 (typically 20 hours)**

  $\varphi_{th} \sim 1.1 \cdot 10^{12}\ cm^{-2}\ s^{-1}$



Pneumatic system for loading and unloading samples for long irradiations, TRIGA Ljubljana

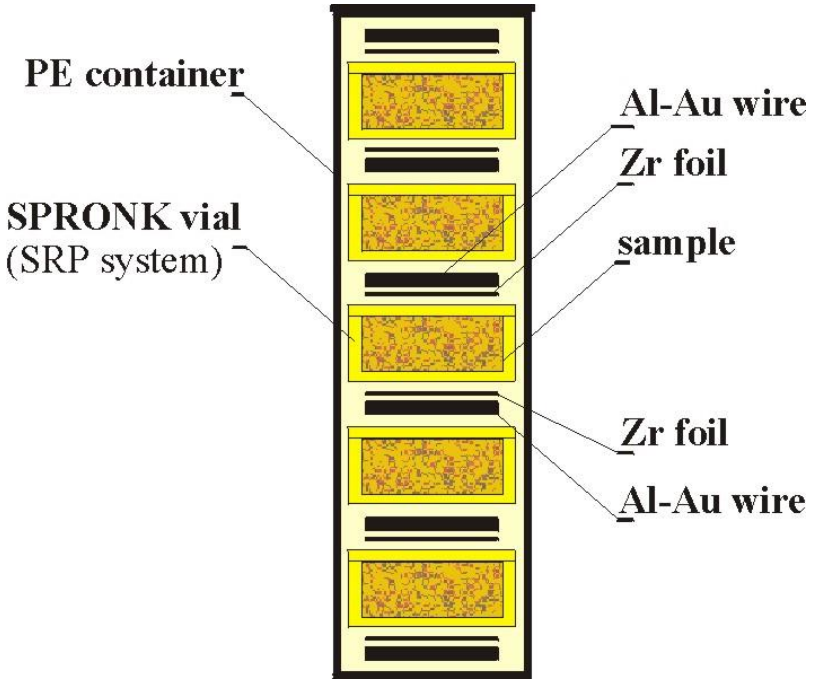
Pneumatic system for loading and unloading samples for short irradiations, TRIGA Ljubljana



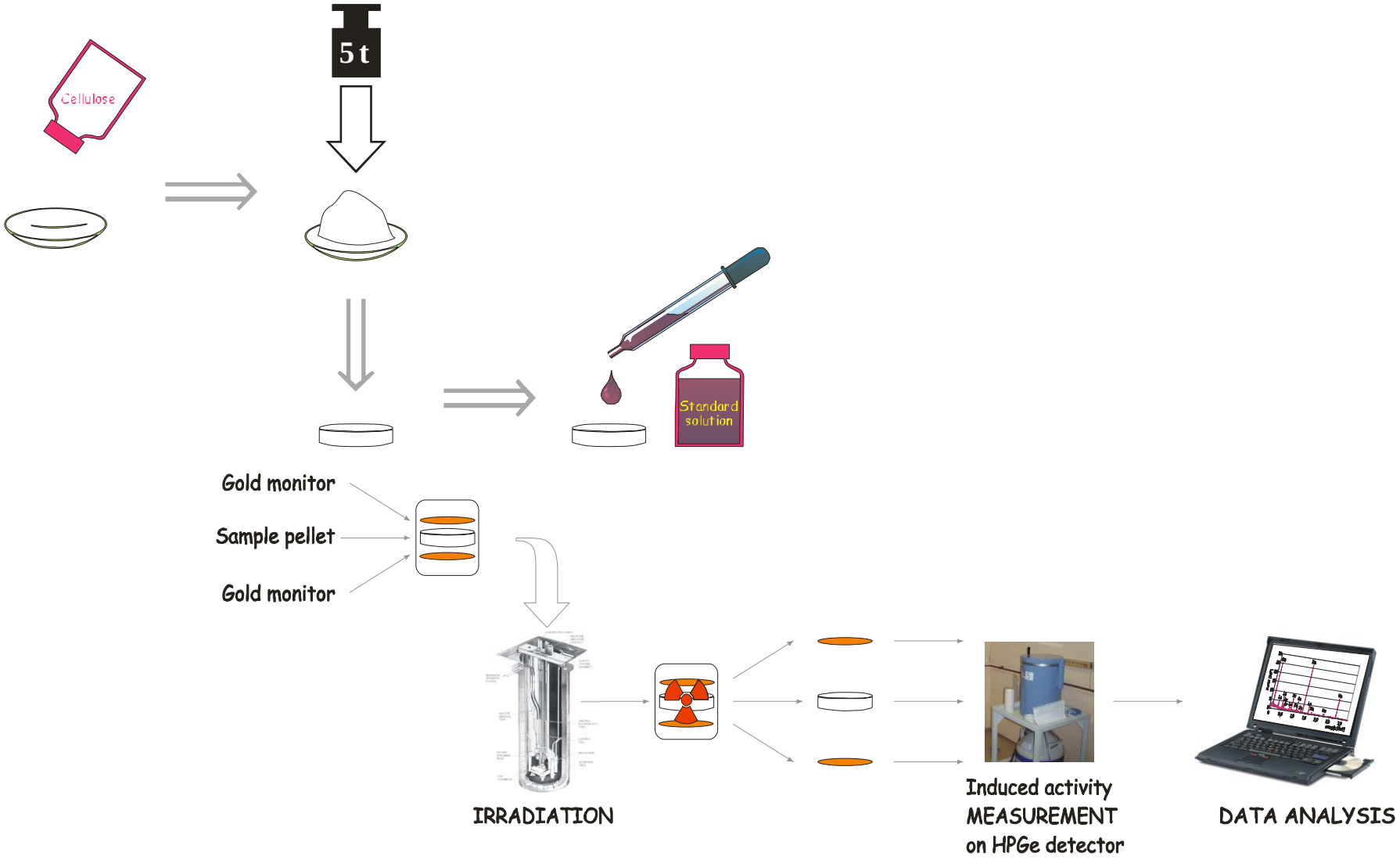
Samples are loaded into the core and received back via the station shown above
Left, the end station in the radiovhemical laboratory is shown.

Analytical procedure (1)

- Sample preparation
- Irradiation/activation
- Activity measurement
- Calculations

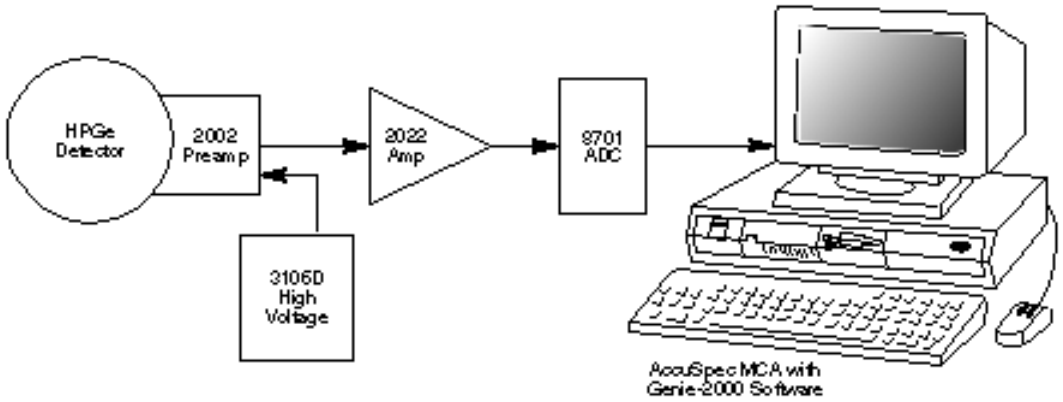


Analytical procedure (2)



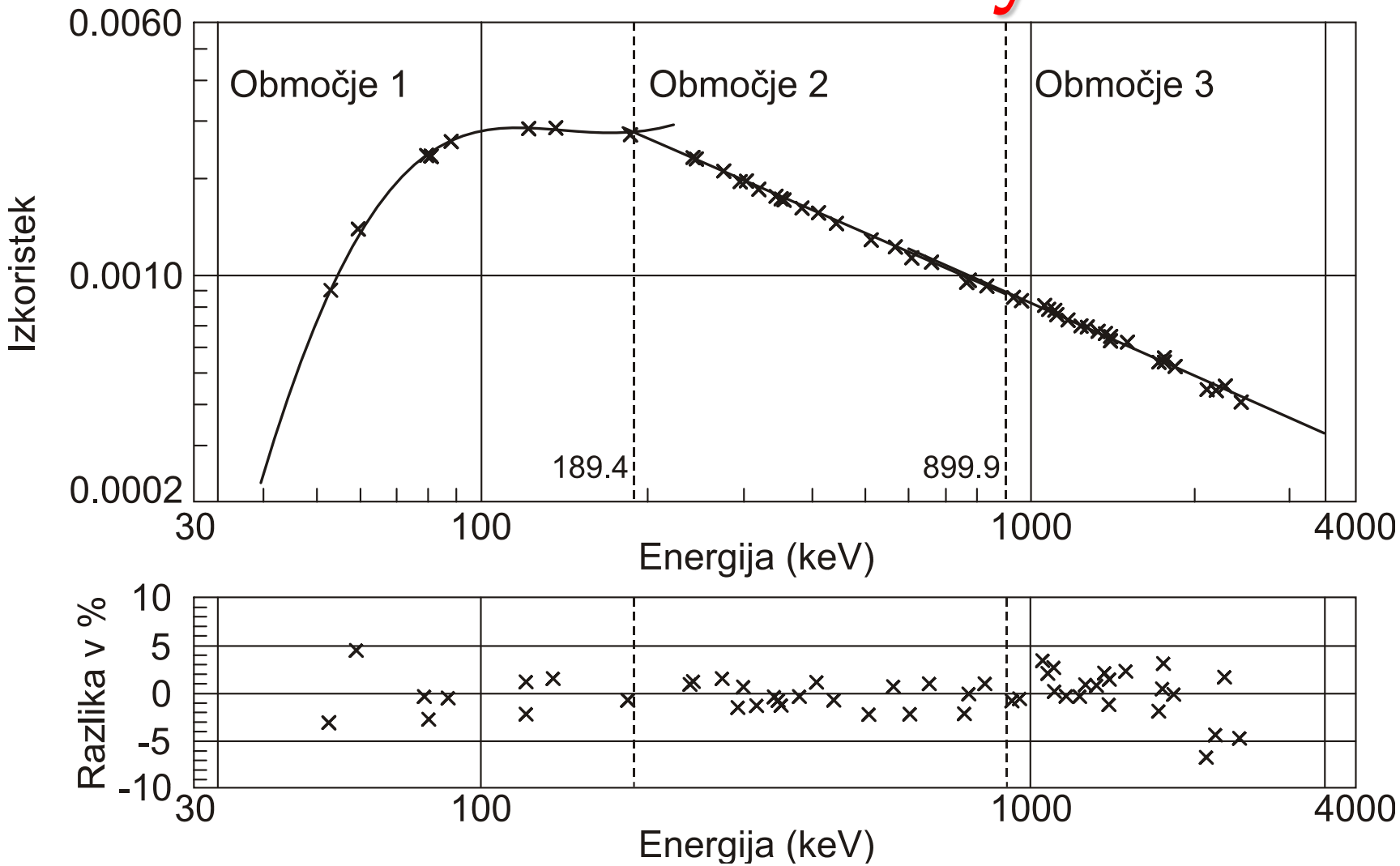
Analytical procedure (3)
Activity measurement

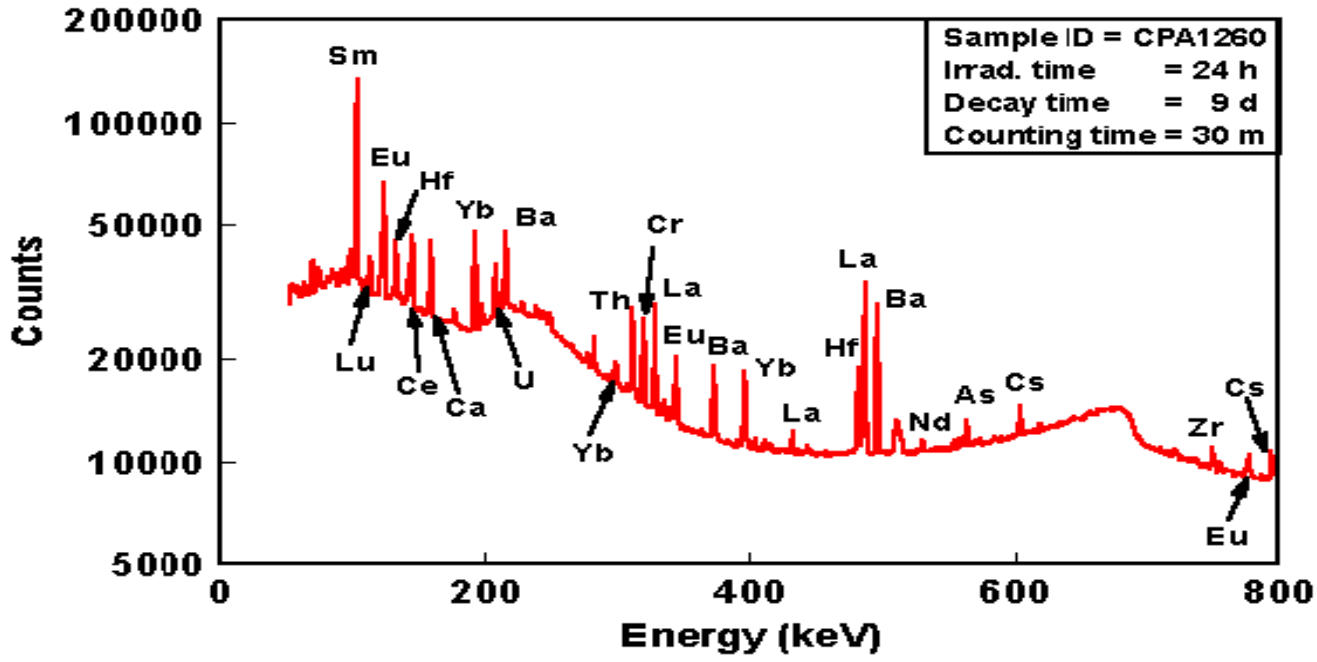
- **Gamma spectrometry using a Ge detector.**
- **Absolute efficiency calibration is needed in certain NAA modes.**



Analytical procedure (4)

Ge detector efficiency curve




Sample ID = CPA1260
Irrad. time = 24 h
Decay time = 9 d
Counting time = 30 m
Counts
Energy (keV)
200000
100000
50000
20000
10000
5000
0
200
400
600
800
Sm
Eu
Hf
Yb
Ba
Cr
La
Th
Eu
Ba
Yb
La
Hf
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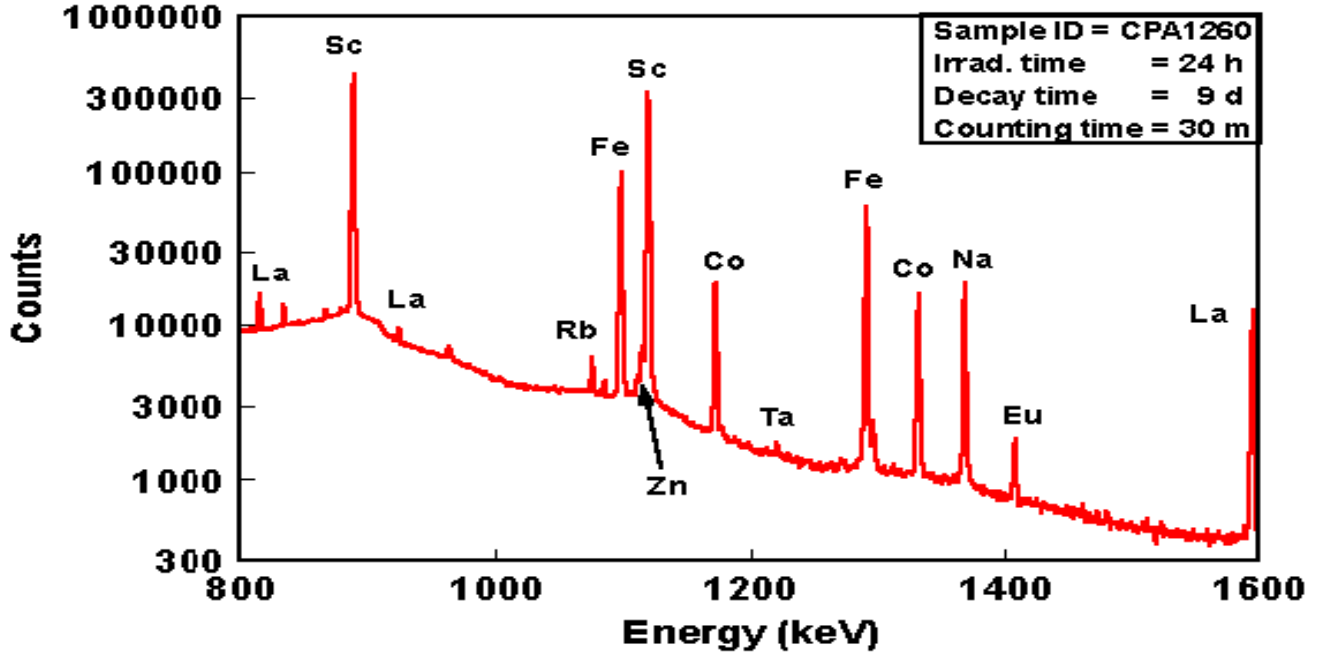
Ba
Nd
As
Cs
Zr
Cs
Eu
Lu
Ce
Ca
U
Yb


Sample ID = CPA1260
Irrad. time = 24 h
Decay time = 9 d
Counting time = 30 m
Counts
Energy (keV)
1000000
300000
100000
30000
10000
3000
1000
300
800
1000
1200
1400
1600
Sc
Sc
Fe
Fe
La
La
Co
Co
Na
La
Rb
Ta
Eu
Zn

Analytical procedure (5)
Calculations

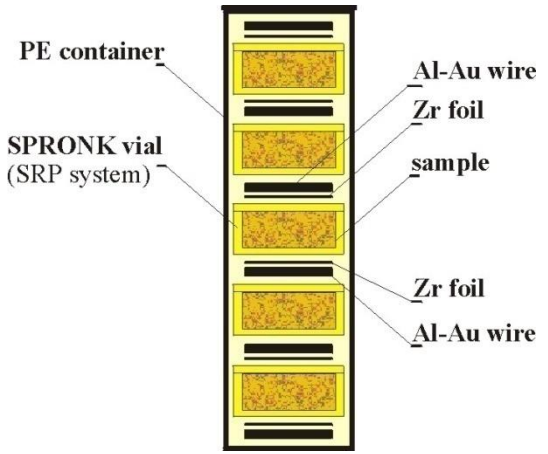
- Neutron spectra parameters (if needed).
- Gamma spectrometry parameters, e.g., efficiency, coincidences, etc. (if needed).
- Gamma-ray spectra evaluation (isotope identification, peak areas calculation).
- Calculation of element mass fraction(s).

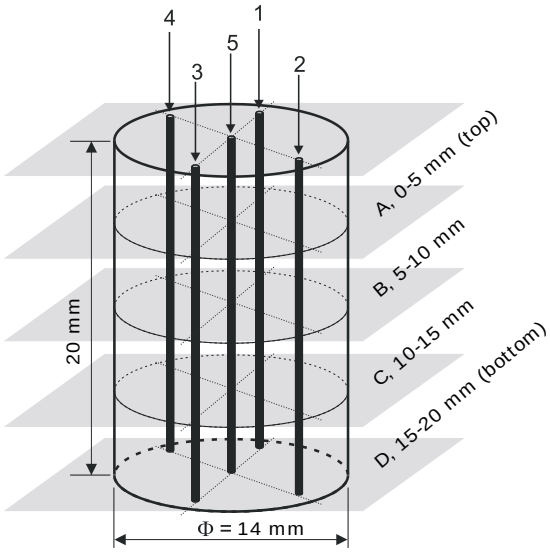
Uncertainties – sample preparation:

- Mass determination (sample, monitor – comparator)
- Moisture
- Purity, stoichiometry, content
- Isotopic abundance variation
- Blank (variation)

Uncertainties – irradiation:

- Geometry aspects
- Spectrum (f, α)
- Variations in time and space
- Self-shielding
- Reaction interferences
- Burn-up
- Volatilisation





Uncertainties – γ measurement:

- **Measurand loss, contamination, inhomogeneity**
- **Geometry differences**
- **Efficiency calibration**
- **True and random coincidences, dead time**
- **Self-attenuation**
- **Peak area determination and counting statistics**

Main characteristics of NAA

- Multi-element capability
- Sensitivity for many elements
- General good selectivity
- No effects of the chemical binding of the analyte element
- Absence/minimisation of the blank value
- Relatively minor matrix effects
- Ability to overcome inhomogeneities
- Possibility to use carriers after irradiation
- Good traceability
- Specific physical basis of the technique

Competitive role of NAA

- **Independent technique for QC and metrology purposes**
- **Ultra-trace levels of As, Au, Co, Cr, Cs, Hg, Mn, Mo, Ni, Rb, REE, Sb, Sc, Se, Th, U, V**
- **Long-lived NORM or artificial radionuclides ^{53}Mn, ^{99g}Tc, ^{129}I**
- **Combination with α-spectrometry for ^{238}U, ^{232}Th, ^{237}Np and ^{231}Pa**

Sensitvity (ng)	Elements
10^{-3}	Dy, Eu
10^{-3} - 10^{-2}	In, Lu, Mn
10^{-2} - 10^{-1}	Au, Ho, Ir, Re, Sm, W
10^{-1} - 1	Ag, Ar, As, Br, Cl, Co, Cs, Cu, Er, Ga, Hf, I, La, Sb, Sc, Se, Ta, Tb, Th, Tm, U, V, Yb
1 - 10	Al, Ba, Cd, Ce, Cr, Hg, Kr, Gd, Ge, Mo, Na, Nd, Ni, Os, Pd, Rb, Rh, Ru, Sr, Te, Zn, Zr
10 - 100	Bi, Ca, K, Mg, P, Pt, Si, Sn, Ti, Tl, Xe, Y
100 - 10^3	F, Fe, Nb, Ne
10^4	Pb, S

Optimisation of NAA (1)

Detection limit in units of mass fraction, m_D, is given by:

$$m_D = \frac{L_D}{K}$$

where L_D is the detection limit expressed by the signal magnitude (e.g., a number of counts in γ-ray spectrometry) and K is a calibration factor (a number of counts per mass unit) obtained in NAA by:

$$K = \frac{N_A \theta_a \gamma_a}{M_a} SDC\left(G_{th}\phi_0\sigma_{0,a} + G_{e,a}\phi_e I_{0,a}(\alpha)\varepsilon_{\gamma,a}Y_a\right)$$

The detection limit m_D can be decreased both by increasing K and decreasing L_D (e.g., background due to matrix activities, such as ^{24}Na, ^{42}K, ^{82}Br, ^{32}P in NAA of biological and environmental samples, interferences in γ-ray spectrometry, nuclear interference reactions, etc.) and by performing both.

Optimisation of NAA (2)

1. **Physical optimisation**
2. **Chemical optimisation (separation)**
    1. **After irradiation (blank-free, carriers, chemical yield; but: radiation burden, $T_{1/2}$)**
    2. **Prior to irradiation (no radiation burden, no time limitations, speciation; but: blank, risk of contamination, problems related to low concentrations and yield determination)**

Advantage factor (A. F.)

A. F. = (NA product A_2 (φ_{th}, φ_{epi}, φ_f, σ, I_0, T, t, η, ε) / (original activity ($A_1 = N_1 \times \lambda_1 \times \eta \times \varepsilon$))

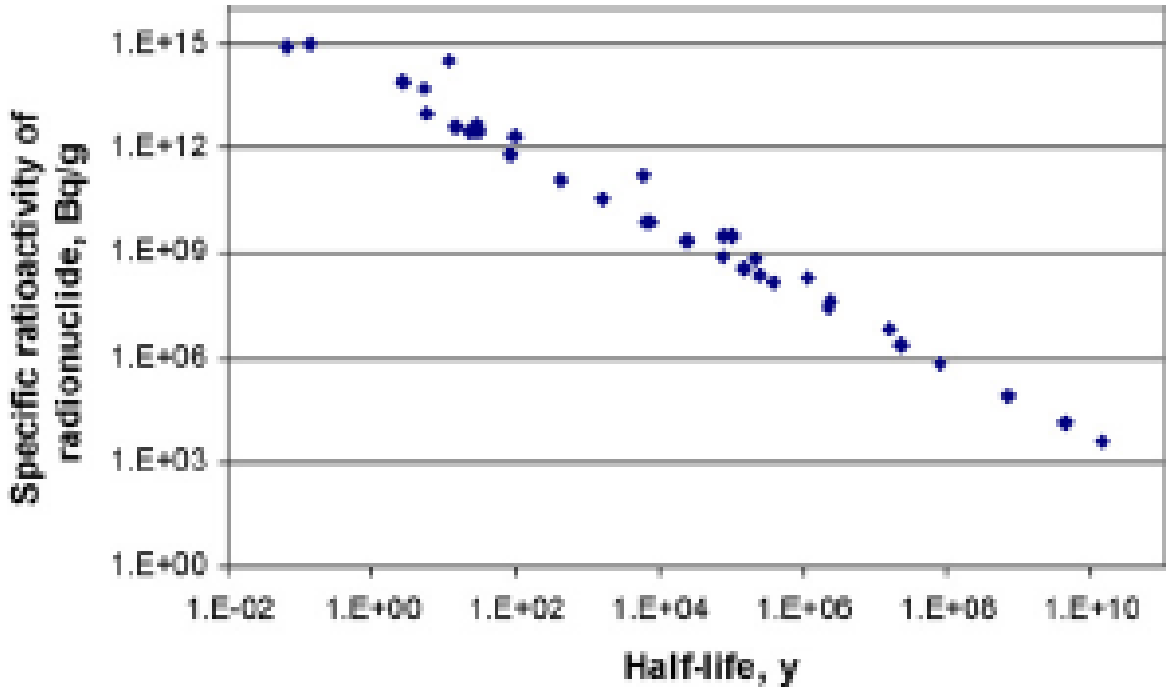


Fig. 1 – Plot of the specific radioactivity (Bq g^{-1}) vs. half-life of the radionuclides listed in Table 1.

Nuclear reaction involved	A.F.
$^{238}U\ (n, \gamma)\ ^{239}U$	7.0×10^{6}
$^{238}U\ (n, \gamma)\ ^{239}U\ (\beta^{-})\ ^{239}Np$	8.0×10^{5}
$^{232}Th\ (n, \gamma)\ ^{233}Th\ (\beta^{-})\ ^{233}Pa$	4.0×10^{5}
$^{230}Th\ (n, \gamma)\ ^{231}Th$	27
$^{237}Np\ (n, \gamma)\ ^{238}Np$	640
$^{231}Pa\ (n, \gamma)\ ^{232}Pa$	106

Major fields of applications of NAA

Geological mapping

Environmental monitoring

Health related studies

Trace contaminants in high purity materials

Industrial quality control

Occupational health studies

Paleo-climate studies in ice cores

Forensic applications

Certification of reference materials

Halogen analysis in hydrocarbons

Metabolic studies in animals and humans

Trace elements in agriculture and food industry

Main trends in NAA

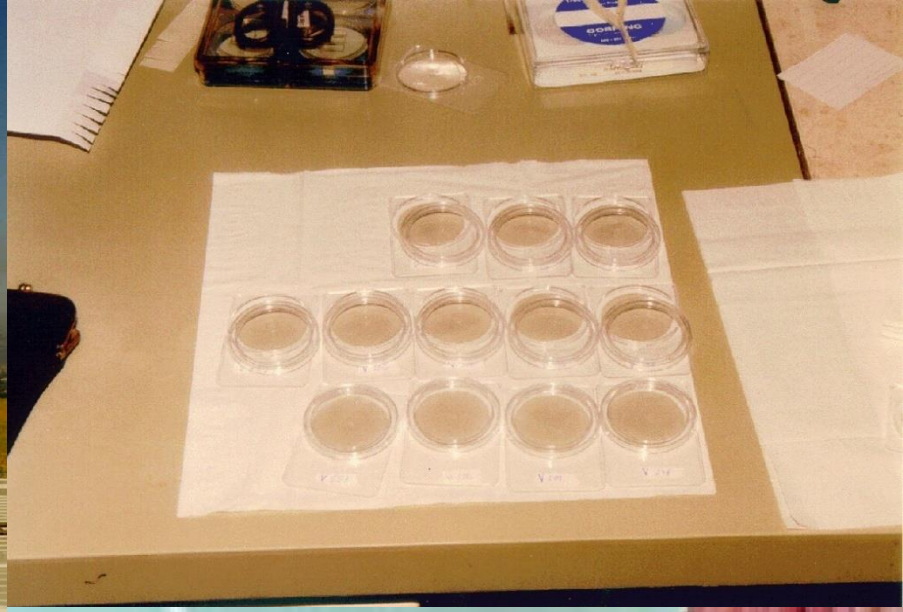
- PGNAA
- NAA using advanced instrumentation
- Large samples NAA
- Small samples NAA
- Automated NAA
- NAA for halides in organic pollutants

NAA applications

- Routine quality control, trace level contaminants and panoramic elemental characterisation
- Matrices that are not suited for other analytical methods
- Alternative procedure that expands and verifies results obtained by other analytical techniques

Example applications (1)

- Archaeology: fingerprinting of obsidian artifacts
- Biochemistry and epidemiology: Se, V in human tissues and fluids
- Environmental restoration: actinides and REE, U, large samples, plastics
- Forensic: gunshot residues, bullet lead, glass, paint, hair (JFK); Napoleon's hair
- Geological science: high Ir content in limestone deposits from Italy and Denmark – dinosaurus extinction



Example applications (2)

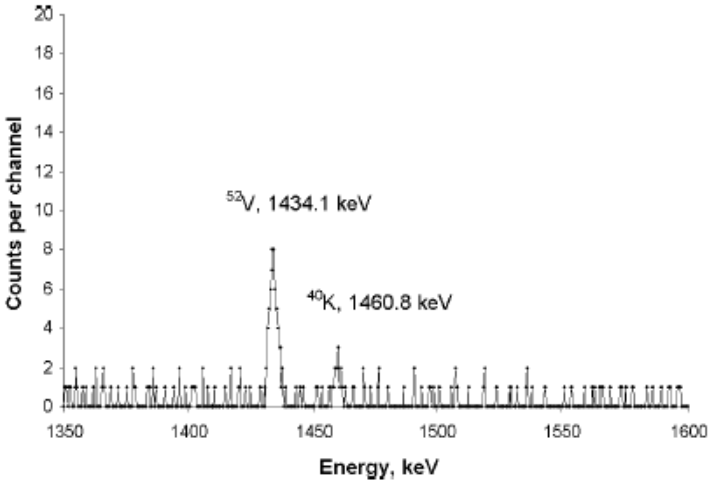
- Semiconductor materials and other high purity materials: sources of contamination
- Soil science: Stable activable tracers, e.g. Br
- Pharmaceutical materials: ultra-trace impurities

Example of RCNAA

Determination of V in blood

^{52}V was separated from 250 mg of freeze dried blood, irradiated for 12 min in flux of 5x10^{12} n cm^{-2} s^{-1} and counted for 7 min in a well type HPGe detector

Value found: 23 ± 14 pg/mL

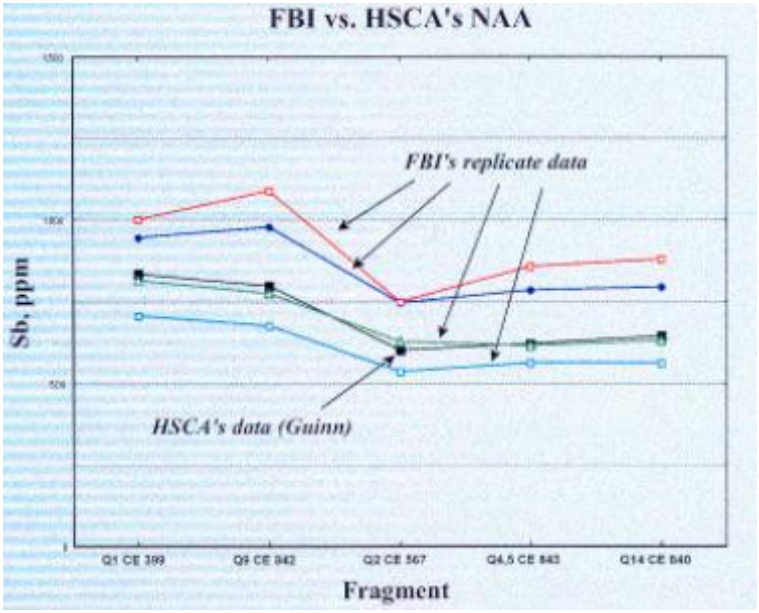


Example 1

NAA and the JFK assassination (K.A. Rahn, L.M. Sturdivan, 2004)

JFK assassination in 1963, FBI investigation in 1964 and V. P. Guinn performed NAA in 1977

Results confirmed that only two bullets hit the victim

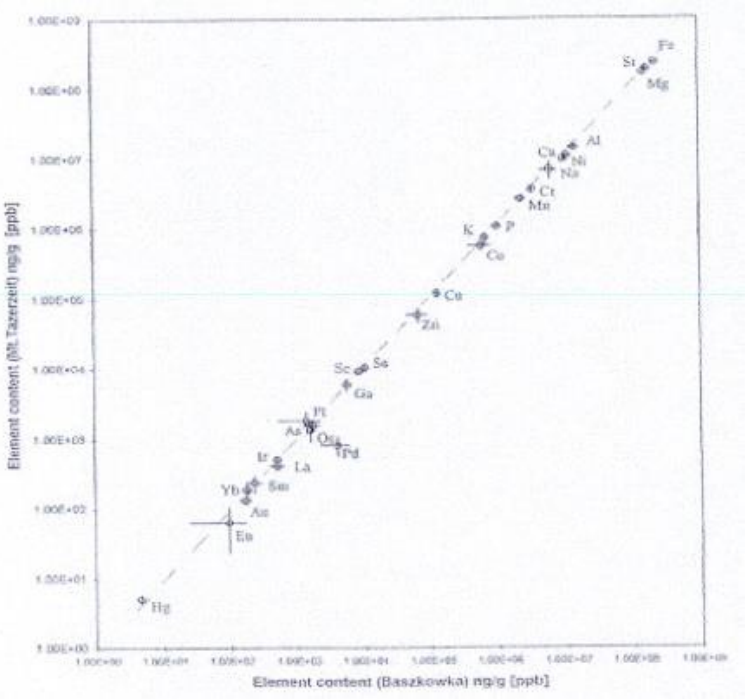


Example 2

Analysis of extraterrestrial material such as moon rock or a meteorite

Two different meteorites fallen in 1935 and 1991 showed identical composition as determined by NAA; R = 0.998

It could be proved that both materials belonged to a common parent body



Example 3

Two strands of Napoleon's hair (0.1722 m and 0.2151 mg, respectively) were analys using INAA

Being a multi element technique, As, Cr, Hg, Sb and Zn could be determined simultaneously

Results suggested that As poisoning was not the major reason for Napoleon's death

Table 1. Elemental concentrations of arsenic, mercury and three more trace components in the samples of Napoleon's hair (see text for uncertainty evaluation)

	Elemental concentration in ppm	
Element	Hair-1	Hair-2
As	1.85 ± 0.11	3.05 ± 0.18
Cr	7.65*	10.5 ± 1.9
Hg	1.84*	3.98 ± 0.29
Sb	4.47 ± 0.27	4.32 ± 0.38
Zn	35*	58 ± 13

Example 4

Heterogeneous material such as waste or scraps that are difficult to homogenise can be analysrd by large sample NAA

1 kg of waste was analysed using the k_0 standardisation and compared with results obtained following homogenisation

Silarly, Cd in plastics and shredded computer waste was determined in 1.5 kg samples

Determination of EOX in fatty tissue

Organic compounds that contain Cl, Br or I substances

Lunde (1972) determined Br in marine oils using NAA

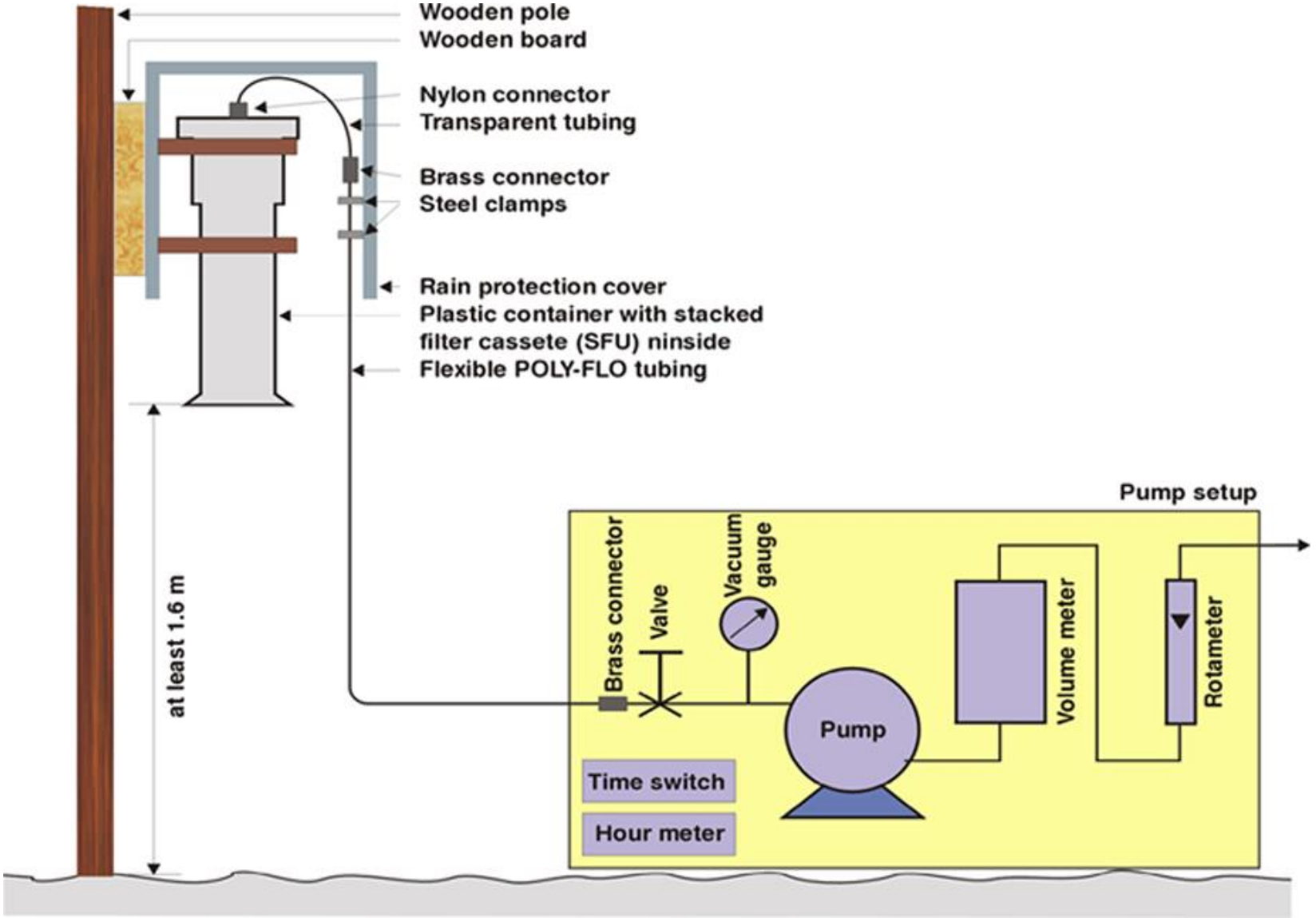
Lunde and Steinnes (1975), Gether *et al.* (1979) determined EOX in fish oils using INAA

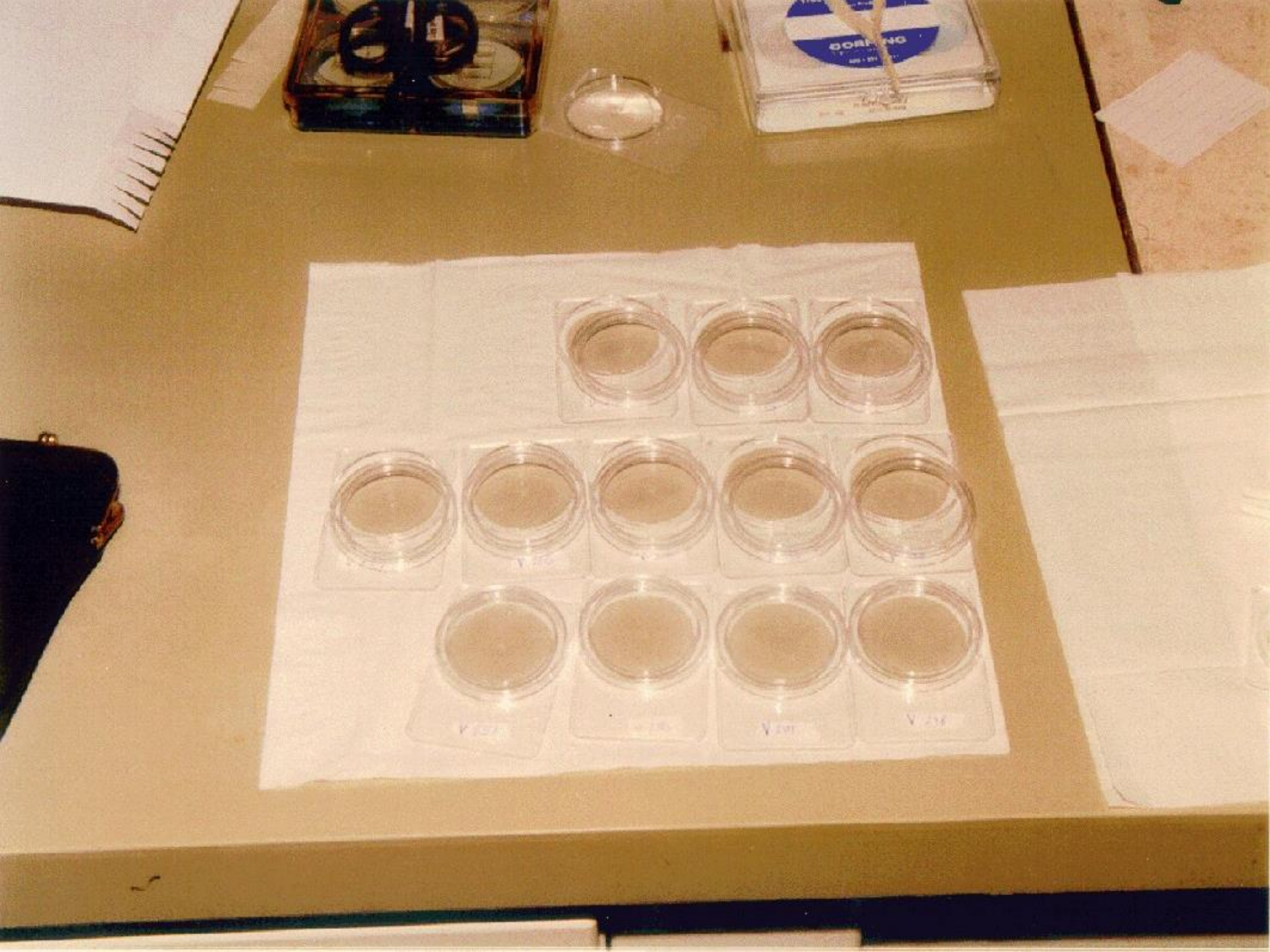
Newsome *et al.* (1993) determined EOCl in fish lipid by INAA at the Dalhousie SLOWPOKE reactor

Comparison of total EOCl (NAA) and total PCB and Chlorinated Pesticides (GC-MS) in Fish Samples from the Great Lakes

Fish Species	PCB + OC, ppm lipid	NAA, ppm	Unaccounted, %
Bass	28.4	138	79.5
Bullhead	4.1	87.1	95.3
Carp	1.1	73.4	98.5
Eel	6.2	44.3	86.0
Herring	6.7	93.4	92.8
Perch	3.6	130	97.2
Smelt	1.5	108	98.6
Trout	6.4	98.1	93.2

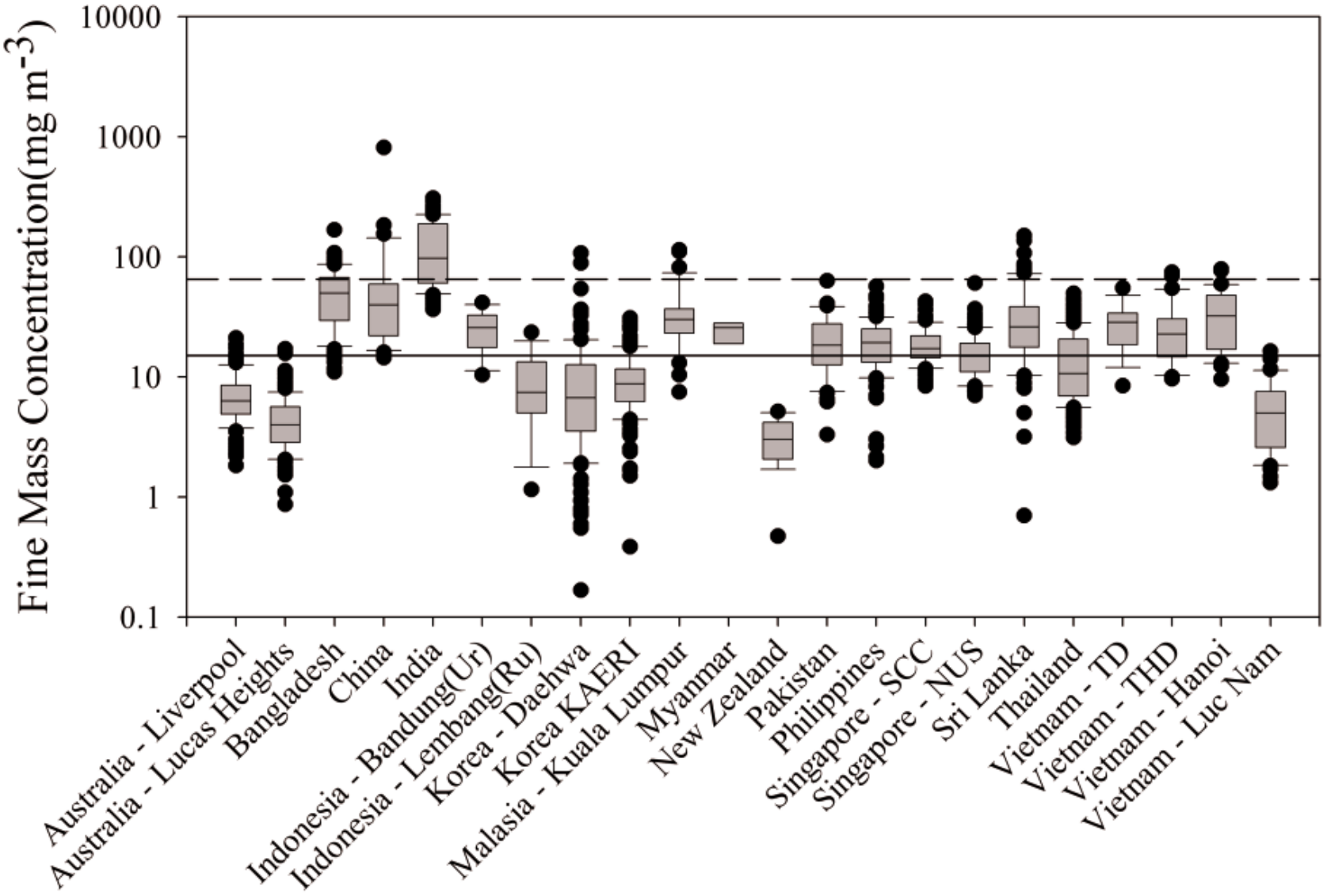
Gent stacked filter unit PM_{10} sampler

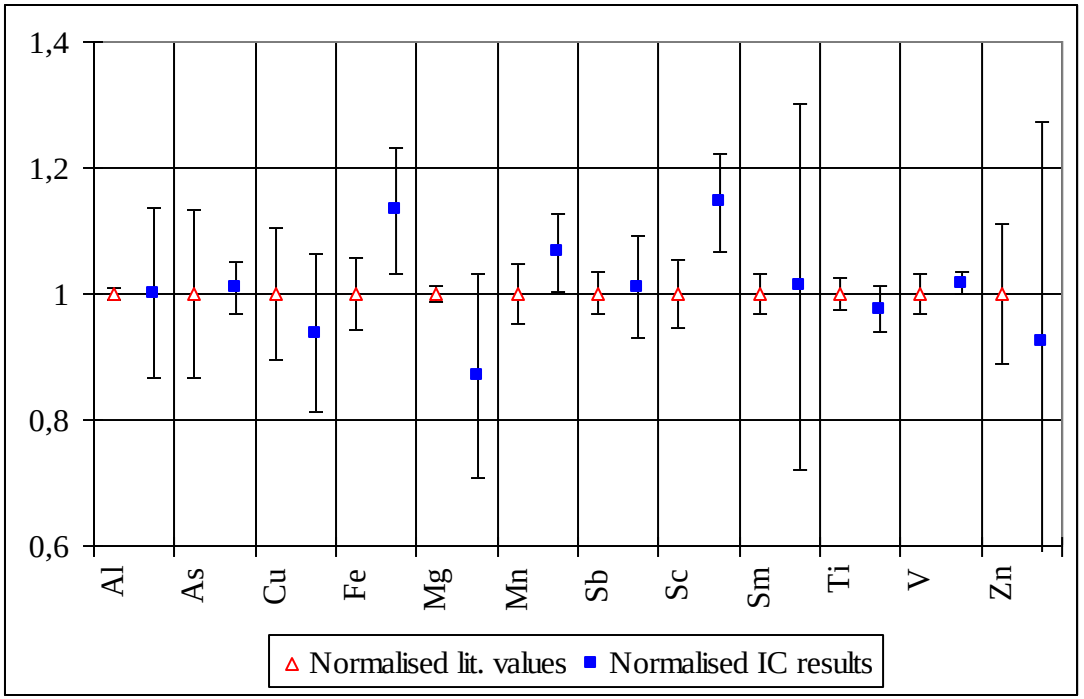




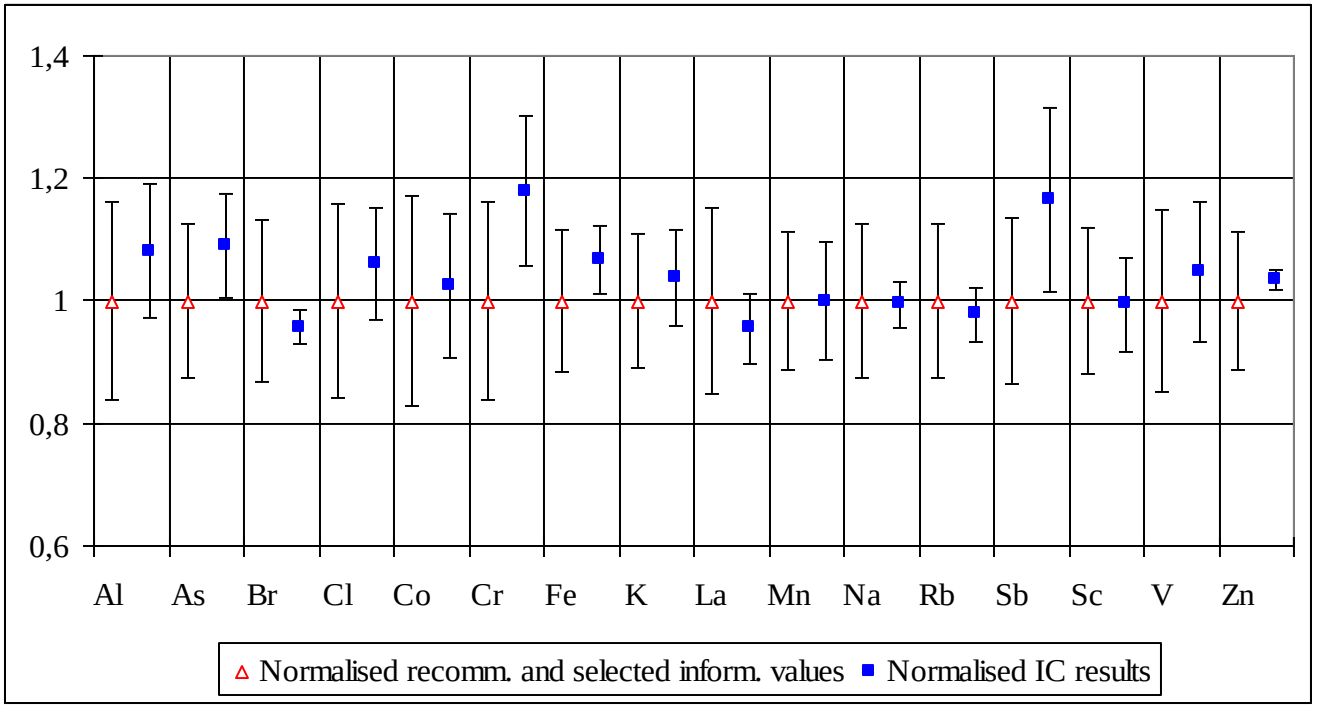
Gent SFUs world distribution

Results obtained by Gent SFUs



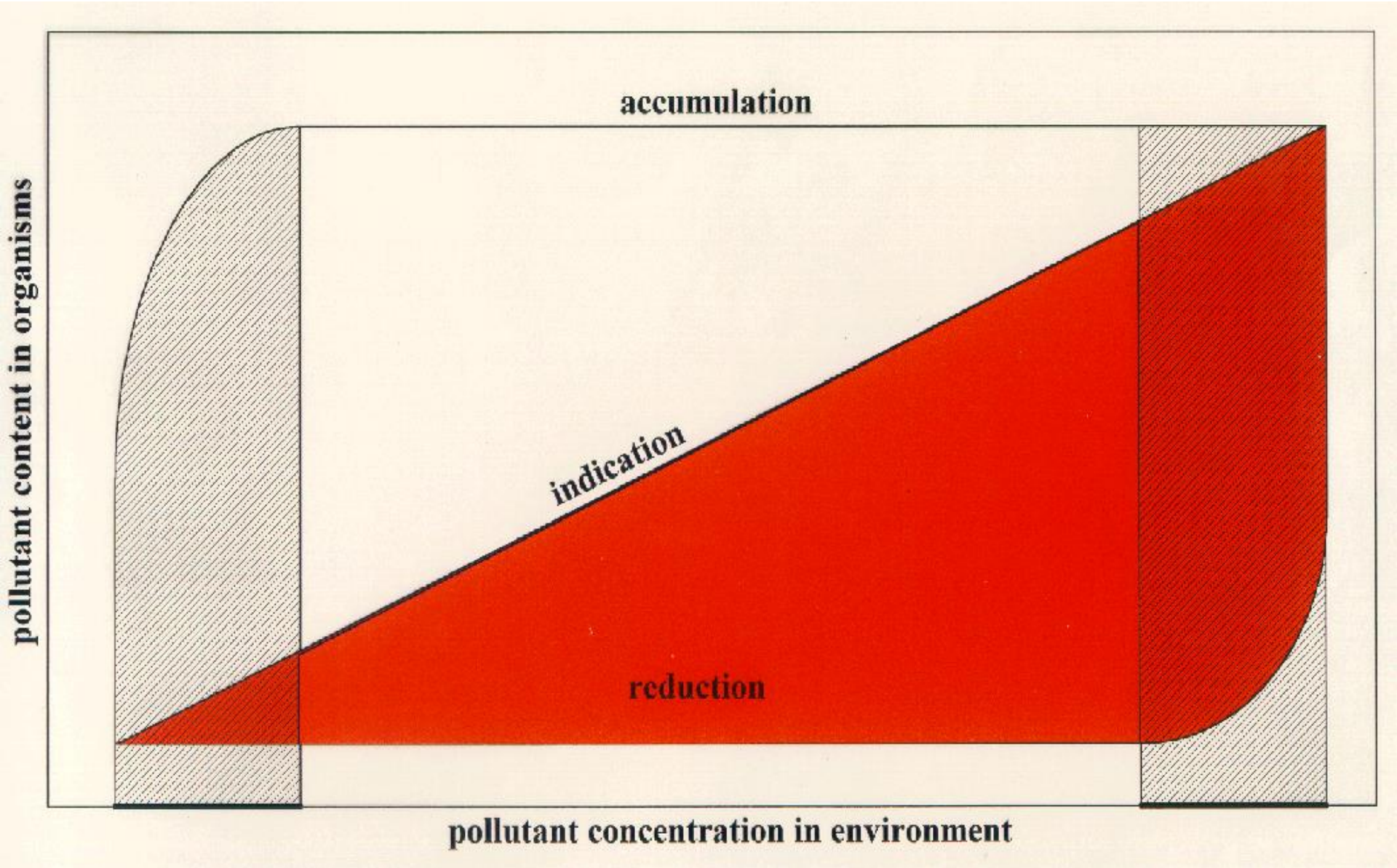


INAA means in filters loaded with urban dust. The error bars for the intercomparison results are expressed as standard deviations of the laboratory means.



INAA means in lichen material. The error bars for the intercomparison results are standard deviations of the laboratory means.

Biomonitoring air pollution



Biomonitoring organisms

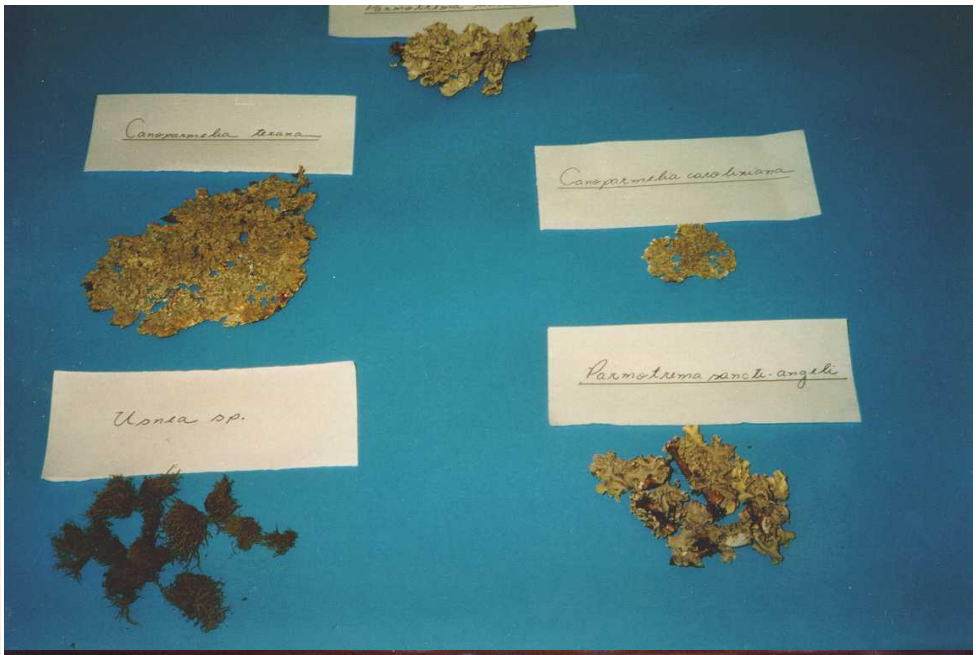
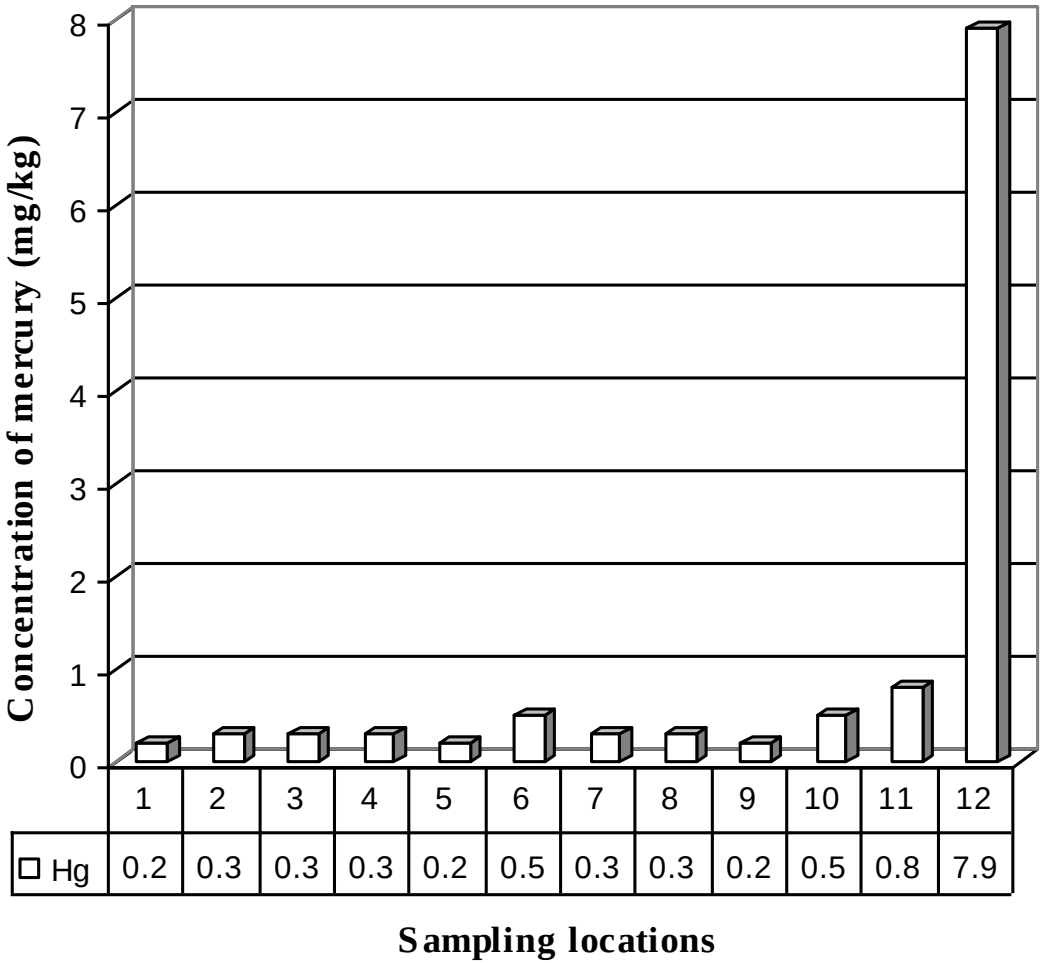


Fig 2a. Variations in the concentration of Hg in lichen samples

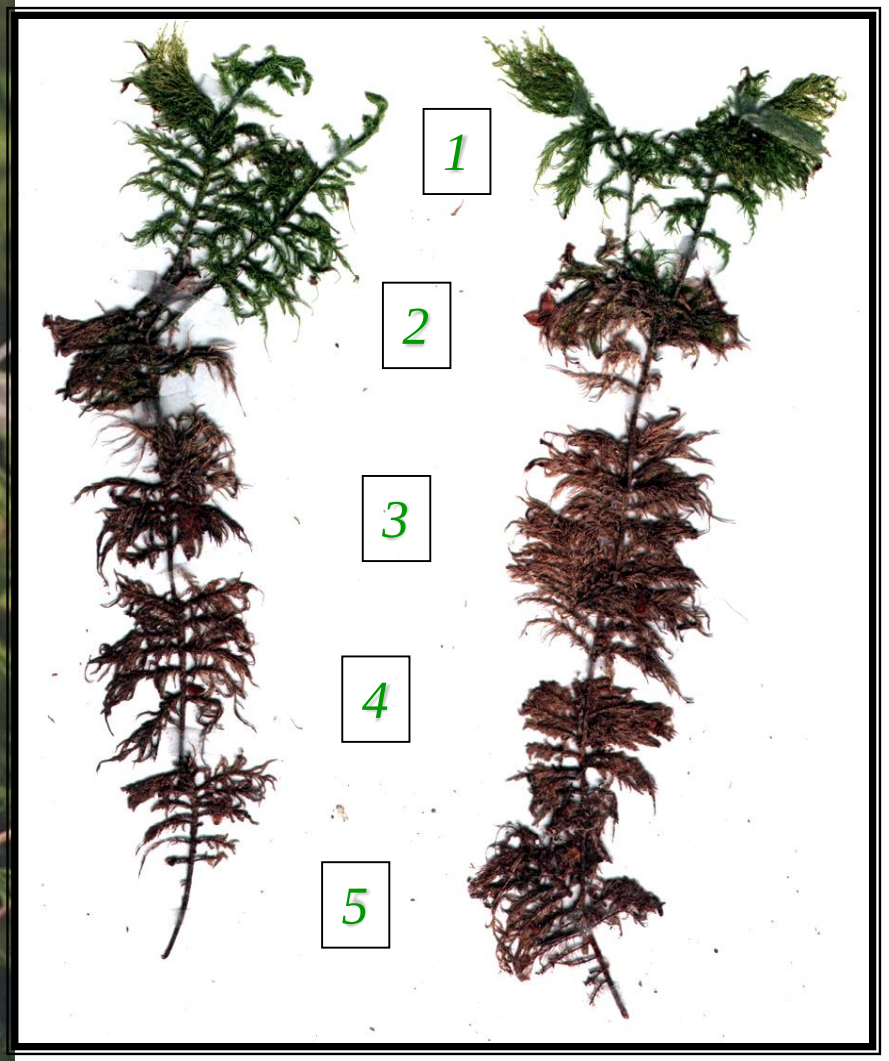
Sampling Locations at Kodaikanal

1. Berijam
2. Pillar Rock
3. Cap view point
4. Upper Lake view
5. Near Kodai lake
6. Botanical Garden
7. Coackers walk
8. Manjikal Raod
9. Khil Bhumi
10. Mercury scrap yard wall
11. St. Mary Church
12. Thermometer Factory

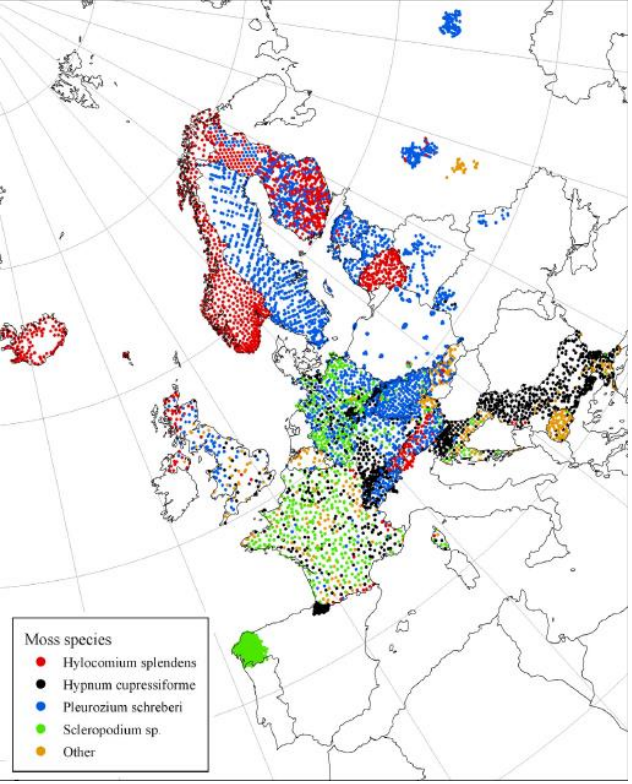


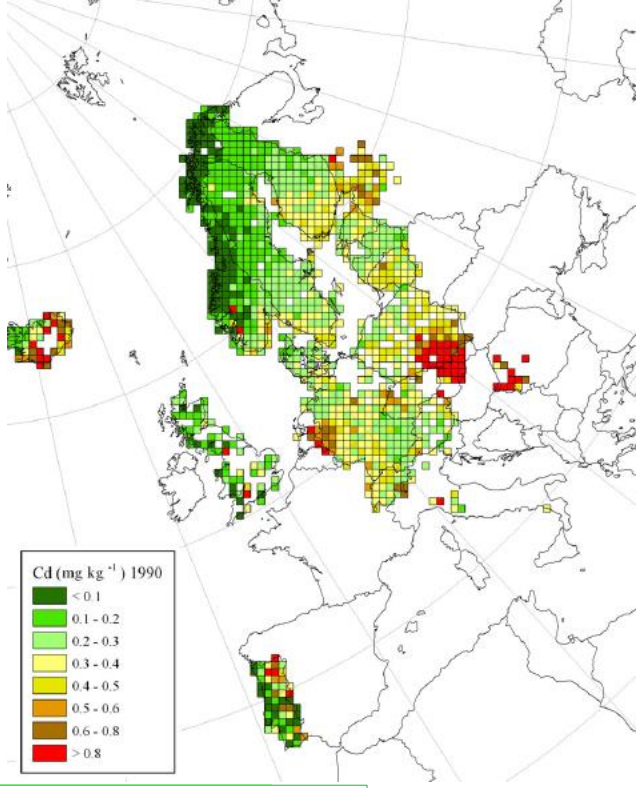
Biomonitoring:

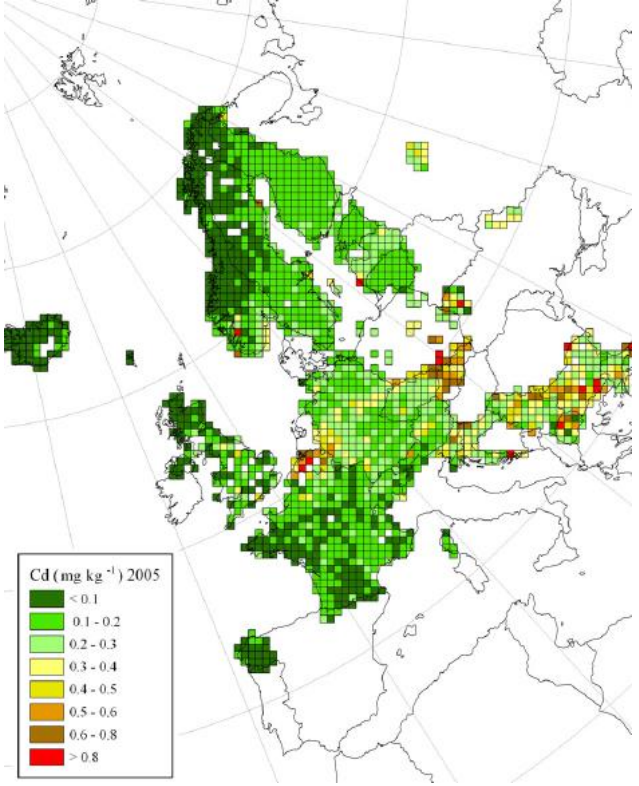
Hylocomium splendens

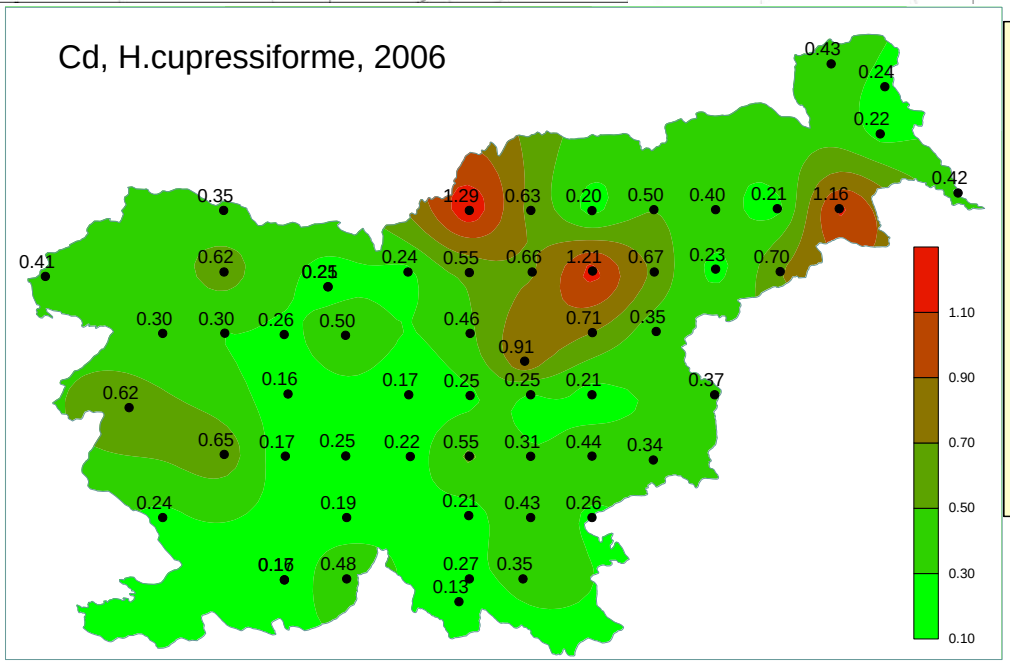


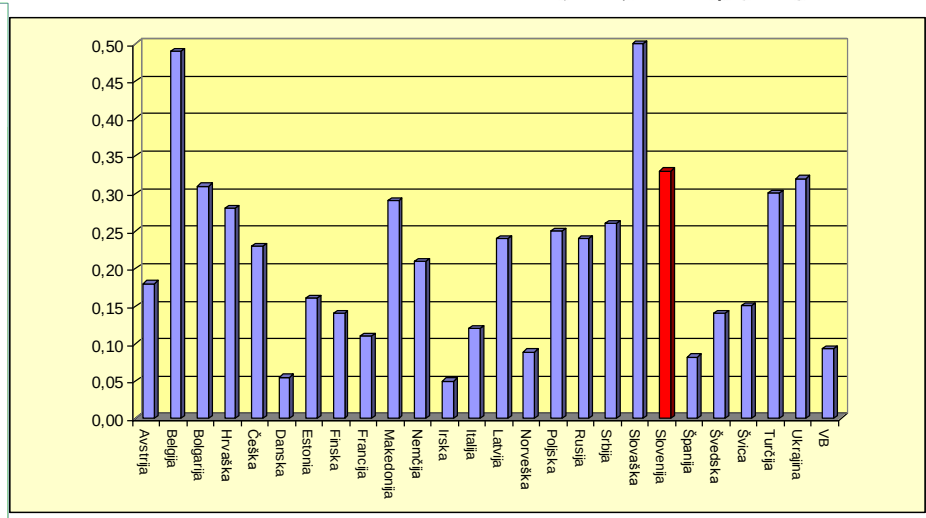
Moss annual segments


Moss species
Hylocomium splendens
Hypnum cupressiforme
Pleurozium schreberi
Scleropodium sp.
Other


Cd (mg kg⁻¹) 1990
< 0.1
0.1 - 0.2
0.2 - 0.3
0.3 - 0.4
0.4 - 0.5
0.5 - 0.6
0.6 - 0.8
> 0.8


Cd (mg kg⁻¹) 2005
< 0.1
0.1 - 0.2
0.2 - 0.3
0.3 - 0.4
0.4 - 0.5
0.5 - 0.6
0.6 - 0.8
> 0.8


Cd, H.cupressiforme, 2006
0.43
0.24
0.22
0.42
0.35
1.29
0.63
0.20
0.50
0.40
0.21
1.16
0.41
0.62
0.24
0.55
0.66
1.21
0.67
0.23
0.70
0.30
0.30
0.26
0.50
0.46
0.71
0.35
0.91
0.16
0.17
0.25
0.25
0.21
0.37
0.62
0.65
0.17
0.25
0.22
0.55
0.31
0.44
0.34
0.24
0.19
0.21
0.43
0.26
0.48
0.27
0.35
0.13
1.10
0.90
0.70
0.50
0.30
0.10


0,50
0,45
0,40
0,35
0,30
0,25
0,20
0,15
0,10
0,05
0,00
Avstrija
Belgija
Bolgarija
Hrvaška
Češka
Danska
Estonia
Finska
Francija
Makedonija
Nemčija
Irska
Italija
Latvija
Norveška
Poljska
Rusija
Srbija
Slovaška
Slovenija
Španija
Švedska
Švica
Turčija
Ukrajina
VB

Example applications (3)

- **Industrial applications**
  - **Polymers, resins, adhesives, and organic solids to measure for trace metals, trace catalyst residues, or to verify known inorganic elemental constituents**
  - **Fine chemicals, solvents, and organic liquids to determine the presence of trace catalyst residues, ultra trace-impurities, or to verify known inorganic constituents**
  - **Catalysts – such as automotive, oil refining, and commodity chemical catalysts to determine trace-impurities, and to verify known inorganic elemental constituents, particularly precious metals.**

Example applications (4)

- **Verification of measurements results (QA/QC)**
  - **CRMs**
  - **As an independent method**
  - **For “difficult” materials, e.g. BAM glass, W metal, SiC, Al alloy**

Sectors where NAA is advantageous (IAEA)

- Bulk elemental composition of materials difficult to dissolve or where elements may get lost during dissolution
- Samples for which other methods have difficulties due to matrix effects or absence of suitable calibrants
- Analysis requiring a high degree of accuracy
- Sample analysis of very inhomogeneous materials
- Samples where element concentrations vary over orders of magnitude
- Very low level element analysis where contamination risk during digestion is high

IAEA examples of industrial NAA applications (1)

- Analysis of trace oxygen in steel (14 MeV neutrons)
- Determination of Cl in steel and nuclear materials
- Hydrogen analysis by PGNAA
- Halogens and metals in plastics and rubber
- Analysis of refractory or insoluble materials, e.g AlN, SI_3N_4 or W
- Impurities in nano-materials, e.g. carbon nano tubes etc.

IAEA examples of industrial NAA applications (2)

- Bulk analysis in the semi conductor industry (quartz, graphite…)
- ^{129}I in environmental materials
- Precious metals in minerals, catalysts or waste, etc…
- Organohalogens, POPs, etc. after chemical separation in environmental samples
- Airborne particulate matter on filters, etc…

Conclusions (1)

- Nuclear principles and well-known physics allow for high accuracy (candidate CRMs, inter-validation of other analytical methods, verification of dissolution steps)
- Almost freedom from analytical blank (high pure materials, low quantities)
- Ability to analyse large quantities (waste-streams)

Conclusions (2)

- Ability to analyse large series of solid samples which are individually different (large-scale ecological studies)
- Ability to analyse samples with very resistant matrices (glass, ceramic materials)
- Radiochemical mode for analysis of extremely low concentrations (biomedical applications)