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The k0-method of NAA: role of reference materials

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The k_0-method of NAA: Optimization at the JSI, Slovenia

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Introduction

- k_0-standardization method of NAA was launched in the 1970s
- **SINGCOMP** program: 1987 written for VAX
- **KAYZERO/SOLCOI** program: 1994, 1996, 2003 written for **DOS** and in 2004 written for **Windows**
- KAYZERO library - 144 nuclides (68 elements)
- k_0-NAA became widespread as a practical analytical tool used to analyse different sample matrices

The k_0-method of NAA

The k_0-standardization method in its basic form assumes:

– known burn-up factor,

– constant irradiation conditions,

– well known neutron spectral parameters in particular irradiation channels,

– known neutron fluence gradients,

– absolutely calibrated an HPGe detector,

– calibrated counting geometry and

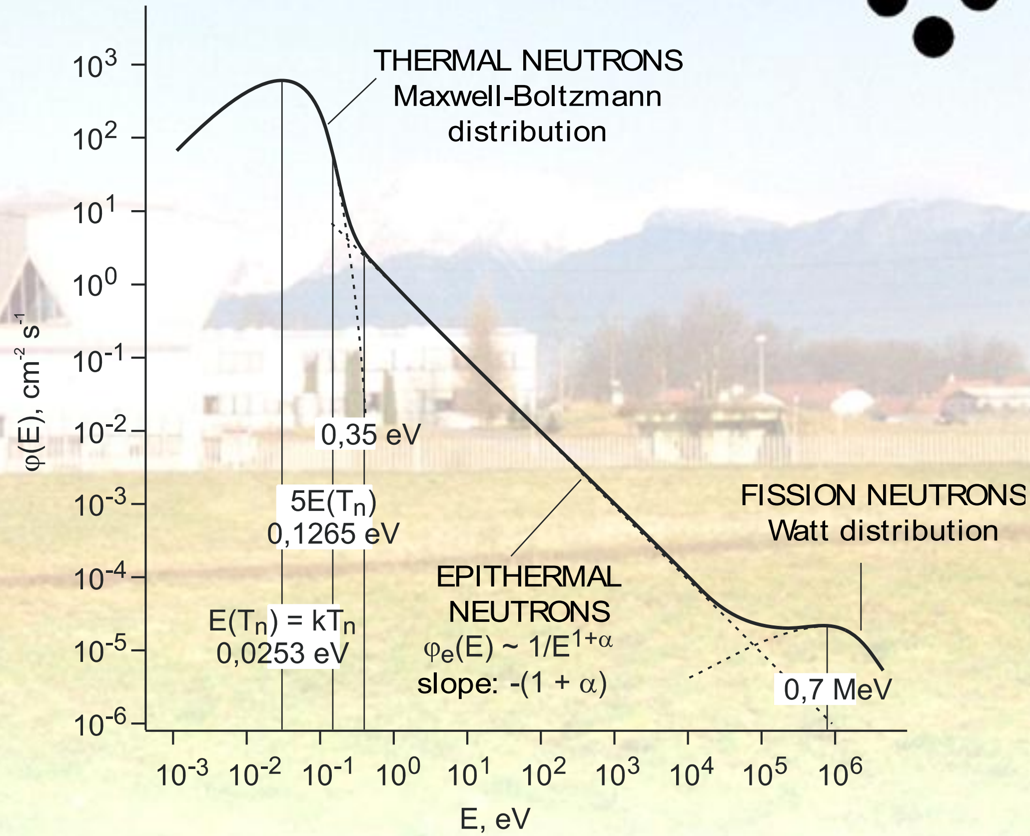
– negligible neutron self-shielding.

! which may not always be the case !

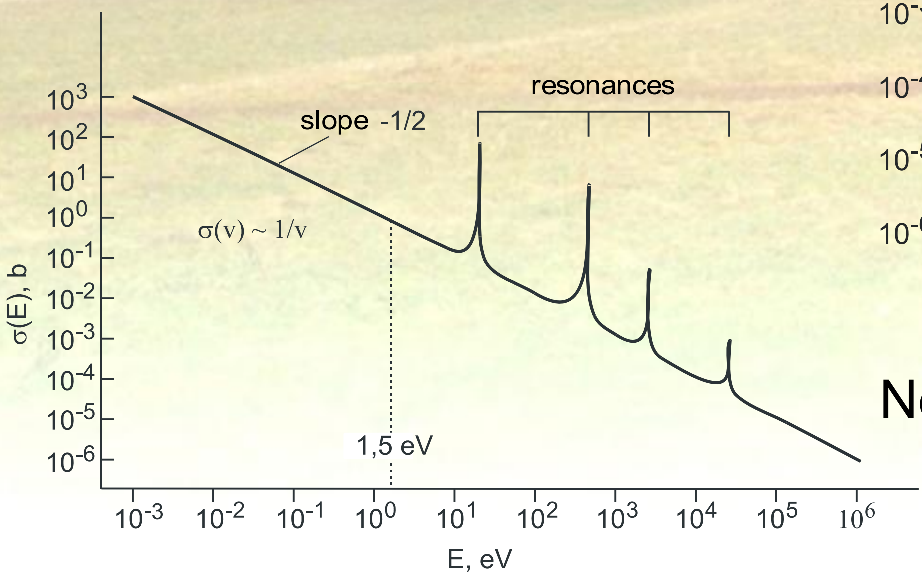
(n,γ) reaction rate

Specific reaction rate per target nuclide

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



Neutron fluence rate distribution vs. E



Cross-section vs. E ($\sigma(\nu) \sim 1/\nu$)

k_0-standardization: KAYZERO/SOLCOI

Thermal and epithermal activation

$$\rho_a = \frac{\left(\dfrac{N_p / t_m}{S\,D\,C\,w}\right)_a}{\left(\dfrac{N_p / t_m}{S\,D\,C\,w}\right)_{Au}} \frac{1}{k_{0,Au}(a)} \frac{G_{th,Au}\,f + G_{e,Au}\,Q_{0,Au}(\alpha)}{G_{th,a}\,f + G_{e,a}\,Q_{0,a}(\alpha)} \frac{\varepsilon_{p,Au}}{\varepsilon_{p,a}}$$

Only epithermal activation

$$\rho_a = \frac{\left[\left(\dfrac{N_p / t_m}{S\,D\,C\,w}\right)_{Cd}\right]_a}{\left[\left(\dfrac{N_p / t_m}{S\,D\,C\,w}\right)_{Cd}\right]_{Au}} \frac{1}{k_{0,Au}(a)} \frac{F_{Cd,Au}\,G_{e,Au}\,Q_{0,Au}(\alpha)}{F_{Cd,a}\,G_{e,a}\,Q_{0,a}(\alpha)} \frac{\varepsilon_{p,Au}}{\varepsilon_{p,a}}$$

Activation-decay scheme in the k_0-method of NAA

Type	Activation-decay scheme
I	$1 \xrightarrow[\sigma_0,\, I_0]{n,\gamma} 2 \xrightarrow{\lambda_2}$ [e.g. $^{75}As\ (n,\gamma)\ ^{76}As$]
IIa	$1 \xrightarrow[\sigma_0,\, I_0]{n,\gamma} 2 \xrightarrow{F_2,\lambda_2} 3 \xrightarrow{\lambda_3}$ [e.g. ^{101}Tc from $^{100}Mo\ (n,\gamma)$]
IIb	Special case: $\lambda_2 >> \lambda_3$ and $D_2 = 0$ [e.g. ^{233}Pa from $^{232}Th\ (n,\gamma)$]
IIc	Special case: $\lambda_2 < \lambda_3$ and $D_3 = 0$
IId	Special case: measurement of the 140.5 keV line of $^{99}Mo/^{99m}Tc$ [from $^{98}Mo\ (n,\gamma)$]
IIIa	$1 \xrightarrow[\sigma_0,\, I_0]{n,\gamma} 2 \xrightarrow{F_2,\lambda_2} 3 \xrightarrow{F_3,\lambda_3} 4 \xrightarrow{\lambda_4}$; $2 \xrightarrow{F_{24},\lambda_2} 4$ [e.g. ^{97}Nb from $^{96}Zr\ (n,\gamma)$]
IIIb	Special case: $F_{24} = 0$
IIIc	Special case: $\lambda_3 >> \lambda_2$ and λ_4, $D_3 = 0$ $F_3 = 1,\ F_2 + F_{24} = 1$ [e.g. ^{105}Rh from $^{104}Ru\ (n,\gamma)$]
IVa	$1 \xrightarrow[n,\gamma]{\sigma_0^m,\, I_0^m} 2$; $1 \xrightarrow[n,\gamma]{\sigma_0^g,\, I_0^g} 3$; $2 \xrightarrow{F_2,\lambda_2} 3$; $3 \xrightarrow{\lambda_3}$ [e.g. ^{80}Br from $^{79}Br\ (n,\gamma)$]
IVb	Special case: $\lambda_2 >> \lambda_3$ and $D_2 = 0$ [e.g. ^{60}Co from $^{59}Co\ (n,\gamma)$]
IVc	Special case: $\lambda_2 < \lambda_3$ and $D_3 = 0$
Va	$1 \xrightarrow[n,\gamma]{\sigma_0^m,\, I_0^m} 2$; $1 \xrightarrow[n,\gamma]{\sigma_0^g,\, I_0^g} 3$; $2 \xrightarrow{F_2,\lambda_2} 3 \xrightarrow{F_3,\lambda_3} 4 \xrightarrow{\lambda_4}$
Vb	Special case: $\lambda_4 << \lambda_2$ and λ_3 [e.g. ^{199}Au from $^{198}Au\ (n,\gamma)$]
Vc	Special case: $\lambda_3 << \lambda_2$ and λ_4, $D_2 = D_4 = 0$ [e.g. ^{113m}In from $^{112}Sn\ (n,\gamma)$]
VI	Special case: ^{124}Sb [from $^{123}Sb\ (n,\gamma)$] after long decay time $(D_2 = D_3 = 0)$ $1 \xrightarrow[n,\gamma]{\sigma_0^{m_2},\, I_0^{m_2}}\ ^{124m_2}Sb\ (T_{1/2} = 20.2\ min)$ $\downarrow \lambda_2, F_2 = 1$ $1 \xrightarrow[n,\gamma]{\sigma_0^{m_1},\, I_0^{m_1}}\ ^{124m_1}Sb\ (T_{1/2} = 93\ s)$ $\downarrow \lambda_3, F_3 = 0.75$ $1 \xrightarrow[n,\gamma]{\sigma_0^{g},\, I_0^{g}}\ ^{124}Sb\ (T_{1/2} = 60.2\ d)$ $\downarrow \lambda_4$
VIIa	$1 \xrightarrow[n,\gamma]{\sigma_0^m,\, I_0^m} 2$; $1 \xrightarrow[n,\gamma]{\sigma_0^g,\, I_0^g} 3$; $2 \xrightarrow{F_{24},\lambda_2} 4$; $2 \xrightarrow{F_2,\lambda_2} 3$; $3 \xrightarrow{F_3,\lambda_3} 4$; $4 \xrightarrow{\lambda_4}$
VIIb	Special case: $F_2 = 0$ [e.g. ^{125}Sb from $^{124}Sn\ (n,\gamma)$]
VIII	$1 \xrightarrow[n,\gamma]{\sigma_0^m,\, I_0^m} 2$; $1 \xrightarrow[n,\gamma]{\sigma_0^g,\, I_0^g} 3$; $2 \xrightarrow{F_{25},\lambda_2} 5$; $2 \xrightarrow{F_{24},\lambda_2} 4$; $3 \xrightarrow{F_3,\lambda_3} 4$; $3 \xrightarrow{F_{35},\lambda_3} 5$; $4 \xrightarrow{F_4,\lambda_4} 5 \xrightarrow{\lambda_5}$ [e.g. ^{117}In from $^{116}Cd\ (n,\gamma)$]

Nuclear research reactor
TRIGA Mark II (250 kW)

- Short and long irradiation in the CC:

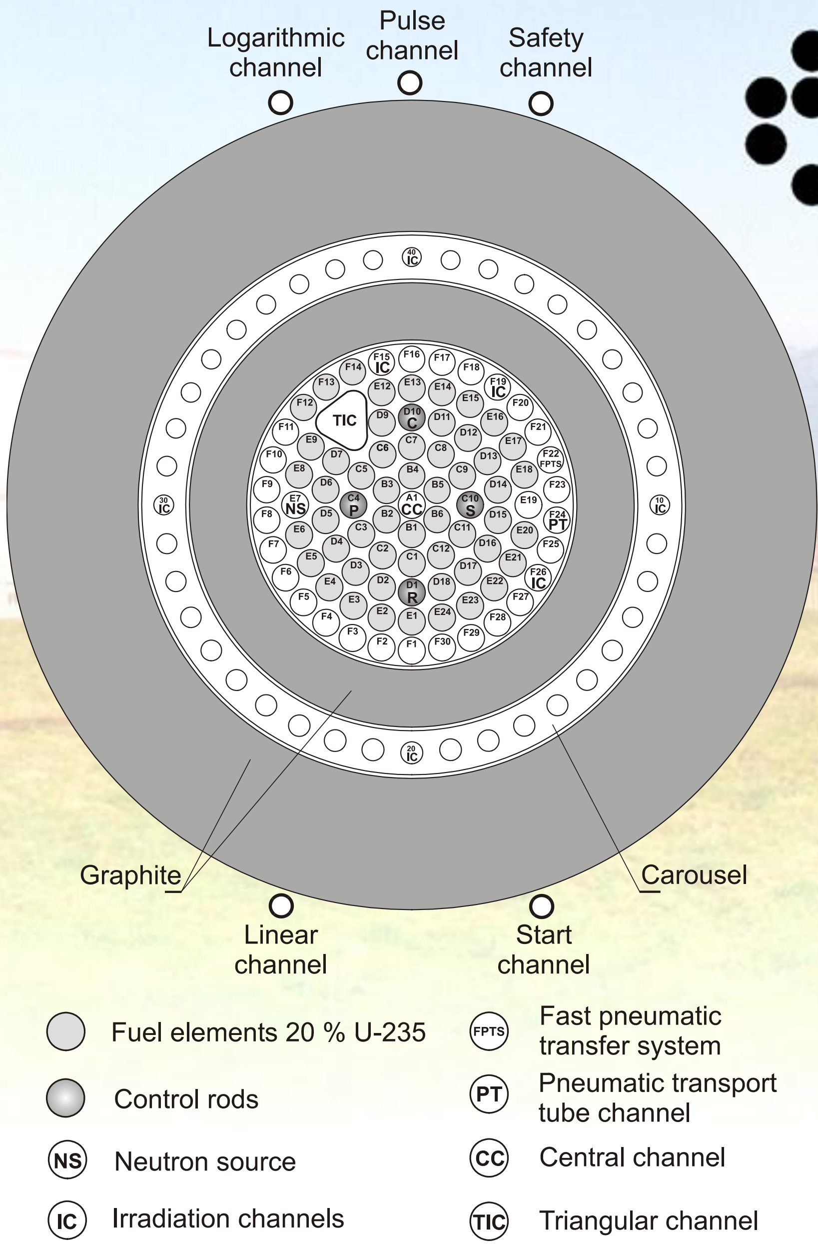
  $\varphi_{th} \sim 10 \cdot 10^{12}\ cm^{-2}\ s^{-1}$

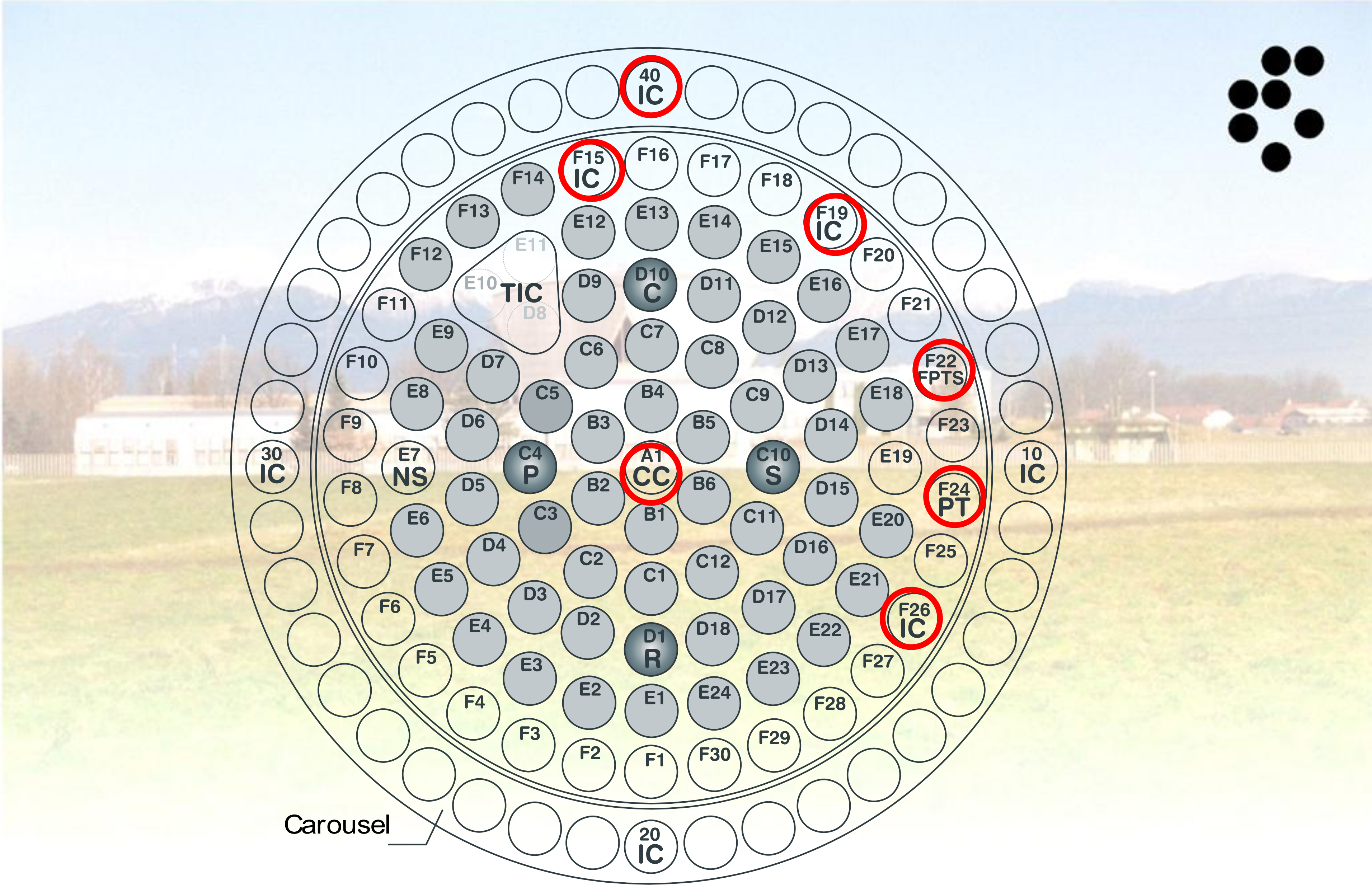
- Short irradiation in the PT and in the FPTS (up-to 30 min.)

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

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

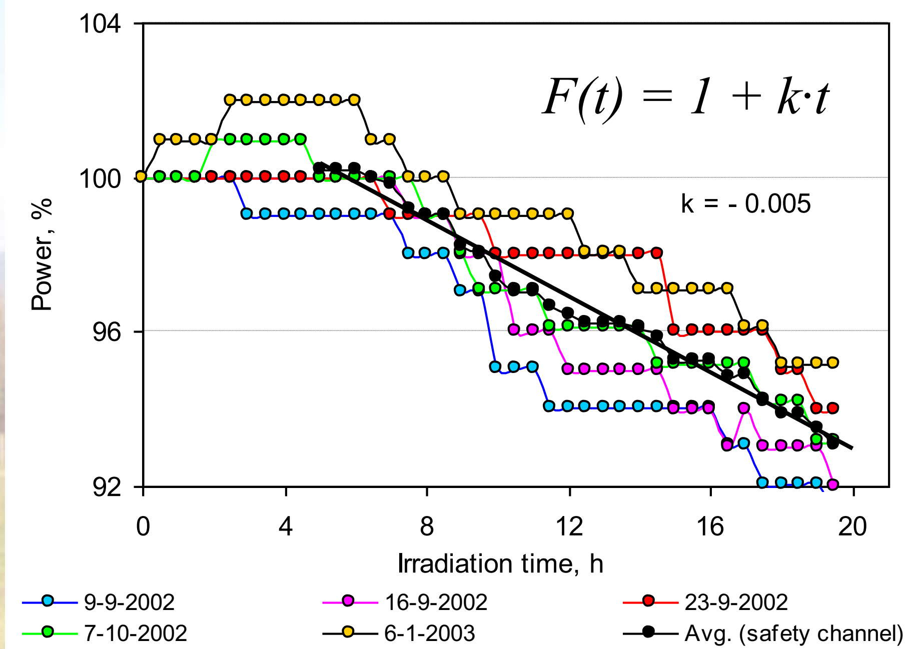
  $\varphi_{th} \sim 1.1 \cdot 10^{12}\ cm^{-2}\ s^{-1}$





Horizontal section of the TRIGA Mark II reactor (core No. 176)

Temporal variation of the neutron fluence rate in the IC-40 channel



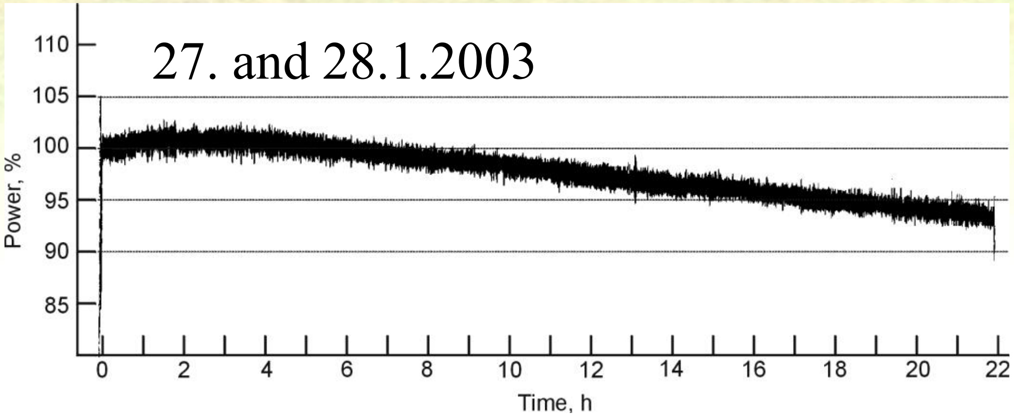
$$S' = \int_0^{t_{irr}} F(t)\,\lambda\,e^{\lambda(t-t_{irr})}\,dt$$

$$S' = S\left(1 + k\cdot t_{irr}\left(\frac{1}{S} - \frac{1}{\lambda\cdot t_{irr}}\right)\right)$$

$$F(t) \equiv 1 \Rightarrow S = 1 - e^{-\lambda\, t_{irr}}$$

Correction factor for saturation in the carousel, especially in the IC-40 position for continuous irradiation for 20 h (F_{sat})

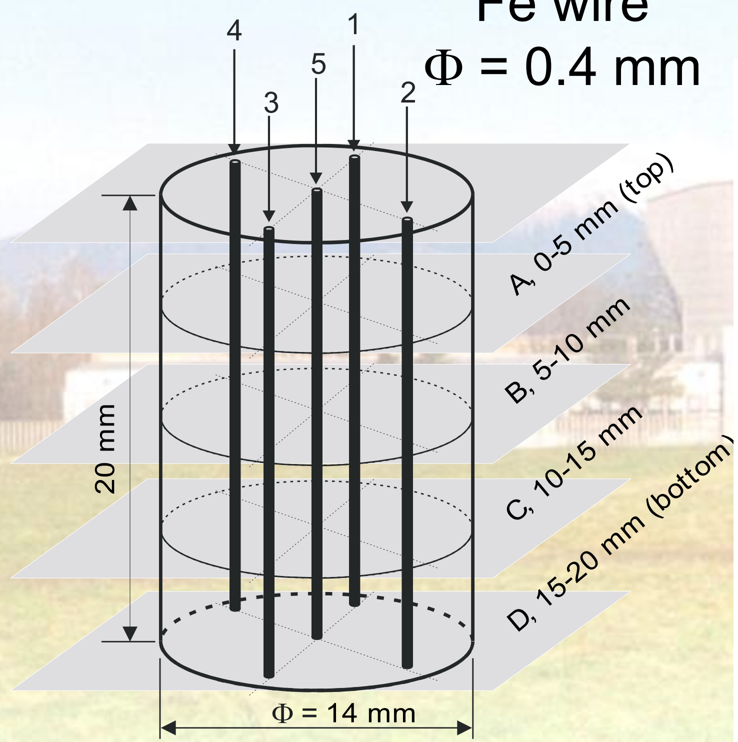
$$F_{sat} = \left(\frac{S'_c\, S_a}{S'_a\, S_c} - 1\right)\cdot 100$$

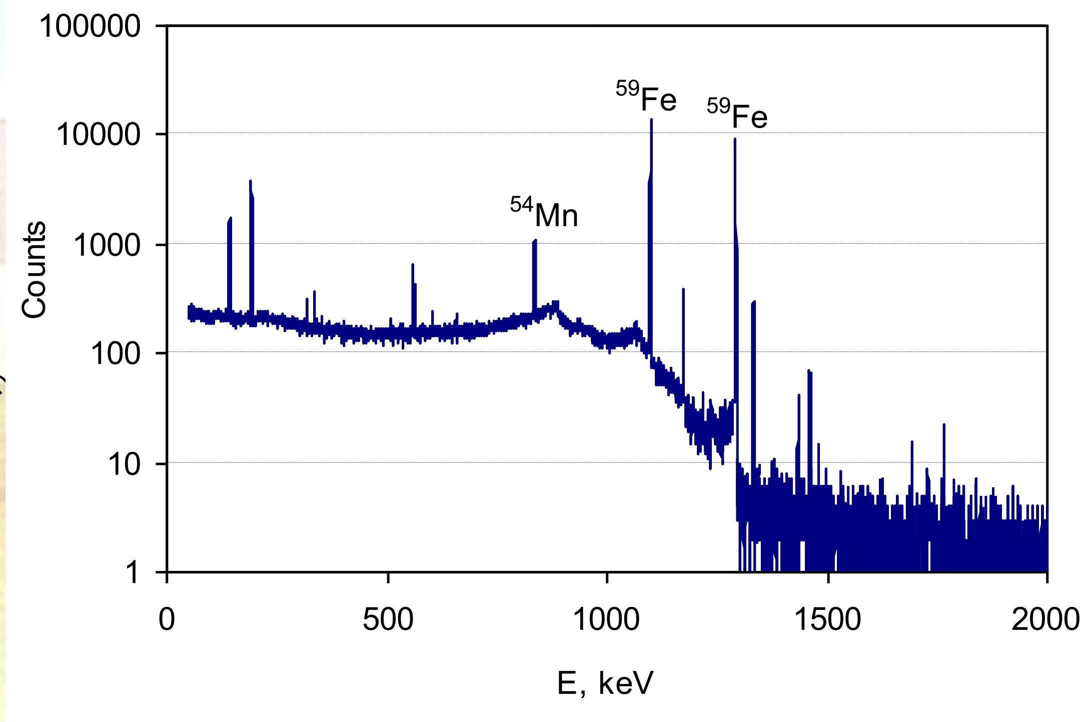


Correction factor for saturation (F_{sat}) in the IC-40 channel

El.:	Nuclide	$T_{1/2}$ (min)	Activ. type	F_{sat} (%)			
				5 h	10 h	15 h	20 h
Au	^{198}Au	3880.8	I	0.00	0.00	0.00	0.00
Na	^{24}Na	0.000337; 897.6	IVb	0.04	0.14	0.32	0.56
K	^{42}K	741.6	I	0.05	0.18	0.40	0.70
Ca	^{47}Ca	6531.84	I	0.00	-0.02	-0.04	-0.07
	^{47}Sc	6531.84; 4822.56	IIa	-0.42	-0.84	-1.26	-1.68
	^{49}Ca	8.718	I	1.12	2.29	3.42	4.50
Fe	^{59}Fe	64080	I	-0.01	-0.04	-0.09	-0.16
Co	^{60m}Co	10.467	I	1.10	2.27	3.40	4.48
	^{60}Co	10.467; 2772383	IVb	-0.01	-0.04	-0.10	-0.17
Zn	^{65}Zn	351792	I	-0.01	-0.04	-0.10	-0.17
	^{69m}Zn	825.6	I	0.04	0.16	0.35	0.62
	^{71}Zn	2.45	I	1.19	2.37	3.49	4.57
Zr	^{95}Zr	92188.8	I	-0.01	-0.04	-0.09	-0.16
	^{95}Nb	92188.8; 5196;50356.8	IIIa	-0.42	-0.86	-1.30	-1.75
	^{97}Zr	1004.4	I	0.03	0.12	0.28	0.48
	^{97}Nb	1004.4; 0.878; 72.1	IIIa	-0.25	-0.27	-0.17	-0.01
	^{97m}Nb	1004.4;0.878	IIa	0.03	0.12	0.27	0.47
Eu	^{152m}Eu	558.72	I	0.07	0.26	0.56	0.97
	^{152}Eu	7121622.405	I	-0.01	-0.04	-0.10	-0.17
	^{154}Eu	46; 4519653	IVb	-0.01	-0.04	-0.10	-0.17
U	^{239}U	23.45	I	0.95	2.12	3.25	4.33
	^{239}Np	23.45; 3394.08	IIb	0.00	0.01	0.01	0.02

Axial and radial gradients of the neutron fluence rate



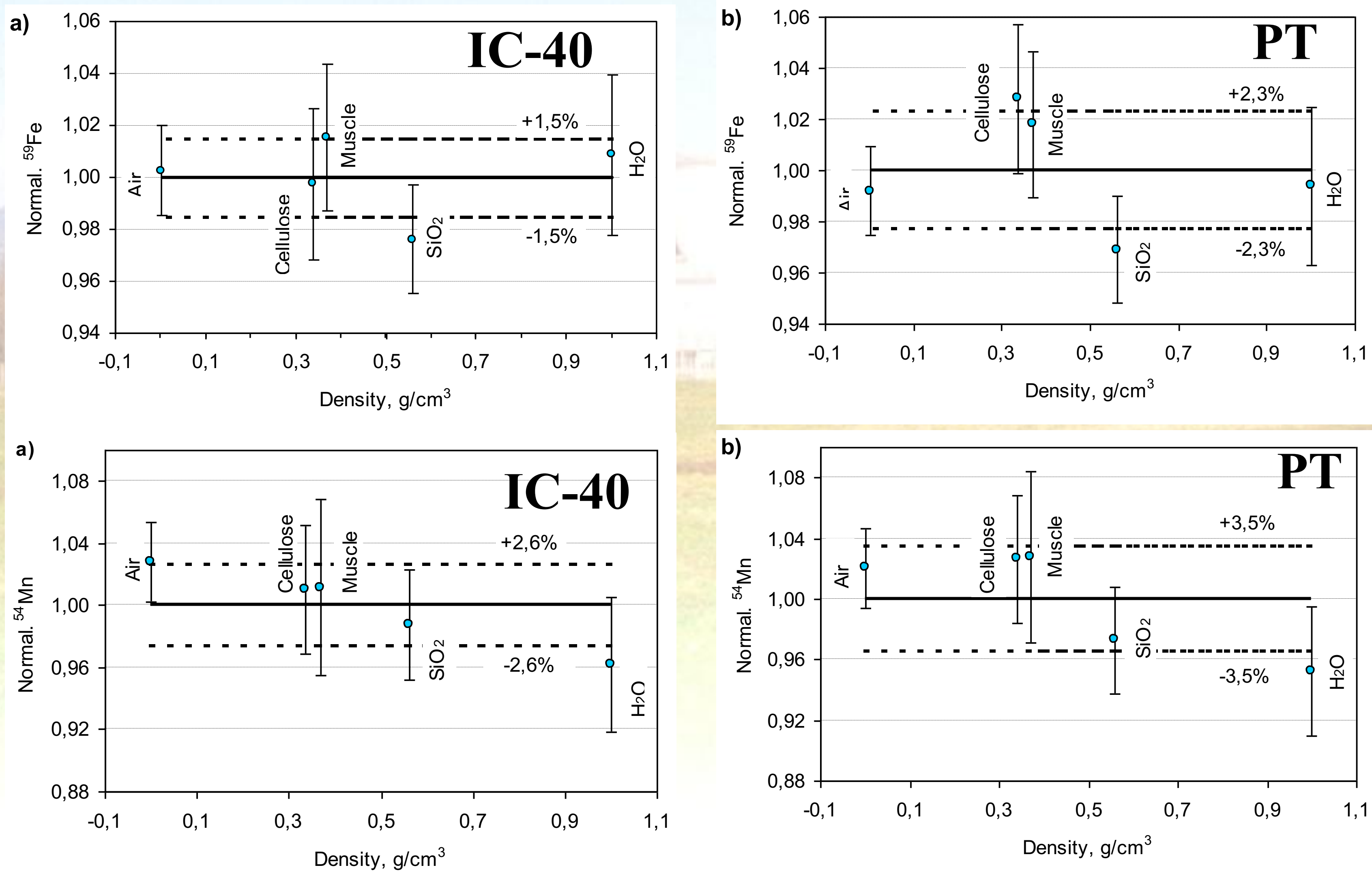


Thermal neutron fluence rate: $^{58}Fe(n,\gamma)^{59}Fe$

Fast neutron fluence rate: $^{54}Fe(n,p)^{54}Mn$

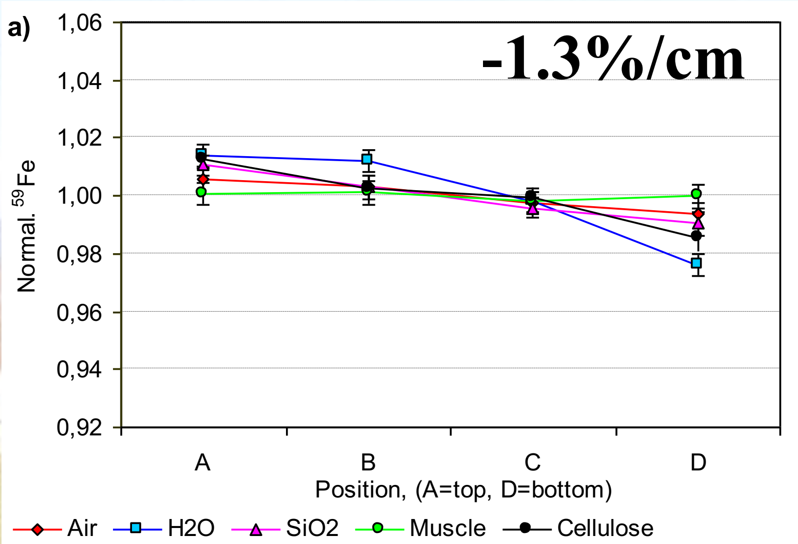
From the same γ spectrum !!!

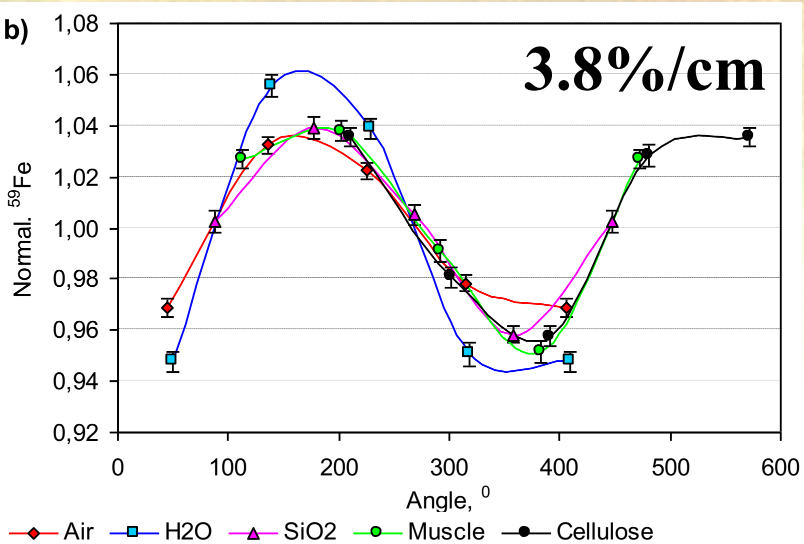
Normalized specific activities of ^{59}Fe vs. density for five matrices in the IC-40 and in the PT channels



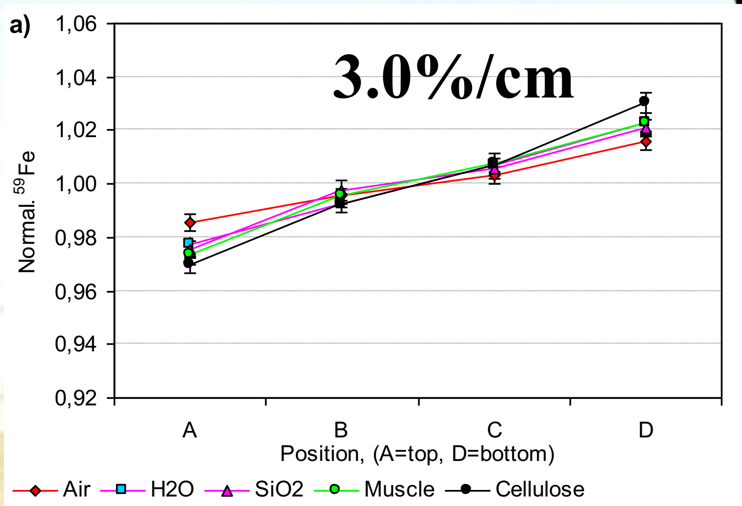
Axial and radial gradients of the **thermal** neutron fluence rate in **different samples**

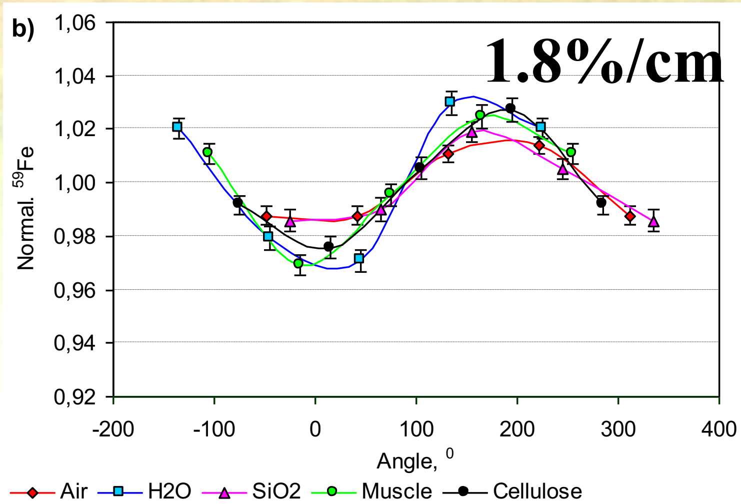
PT





IC-40





Specific activities and G_{th} factors

Sample	PT			IC-40		
	Normal. ^{59}Fe	rsd, %	Total rsd, %	Normal. ^{59}Fe	rsd, %	Total rsd, %
Air	0.992	2.57	**2.31**	1.002	1.69	**1.50**
Cellulose	1.028	3.17		0.998	2.86	
Muscle	1.018	3.30		1.015	2.73	
SiO_2	0.969	2.77		0.976	2.08	
H_2O	0.994	4.85		1.009	2.99	

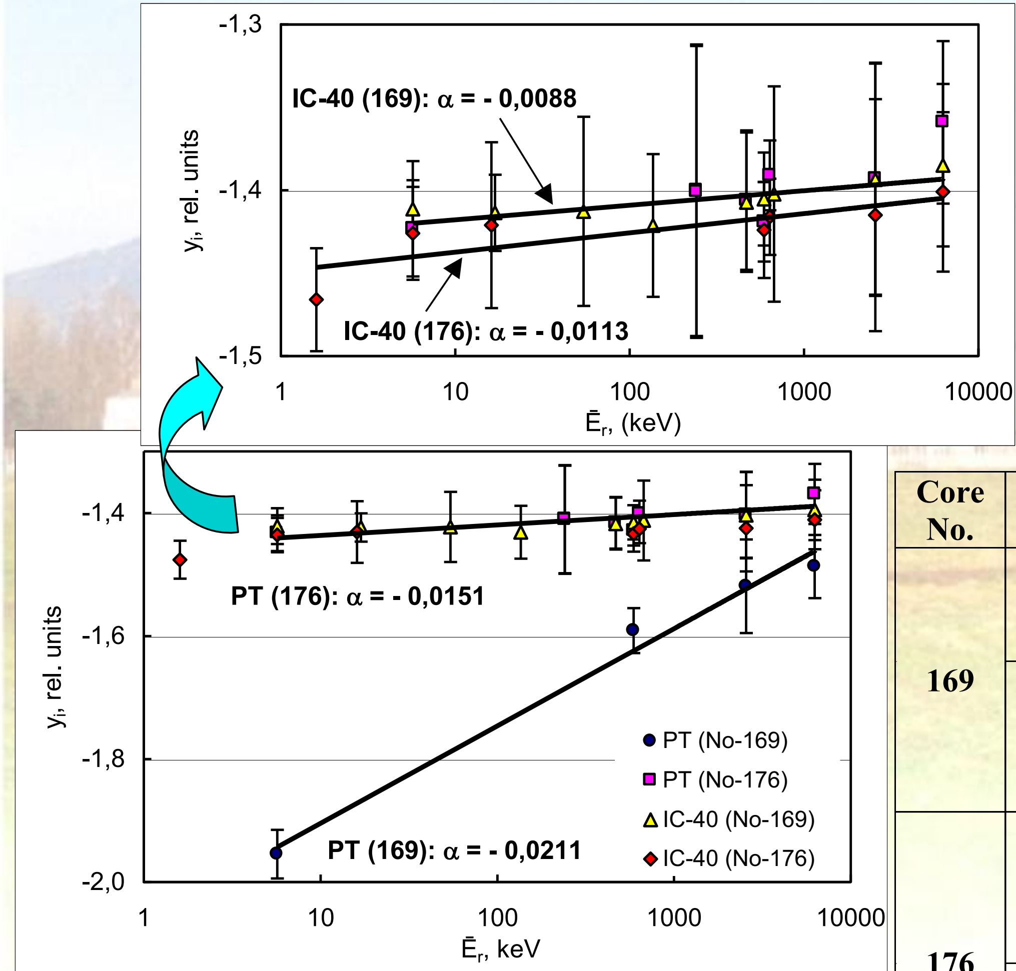
G_{th} - not characteristic of nuclei, but dependent on dimensions and composition of the sample

Cellulose
Muscle →
H_2O

$G_{th,org}$ = 1.01

$G_{th,inorg}$ = 0.97 ← SiO_2

Spectral parameters of the neutron fluence rate: *f* and α



$$y_i = -\alpha \log \bar{E}_{r,i} - \log\left[\left(F_{Cd,i}\ R_{Cd,i} - 1\right) Q_{0,i}(\alpha)\ G_{e,i} / G_{th,i}\right]$$

$$y_i = -\alpha\, x_i - b_i$$

$$\alpha = -\frac{\sum_{i=1}^{N} x_i\, y_i - \frac{\sum_{i=1}^{N} x_i \sum_{i=1}^{N} y_i}{N}}{\sum_{i=1}^{N} (x_i)^2 - \frac{\left(\sum_{i=1}^{N} x_i\right)^2}{N}}$$

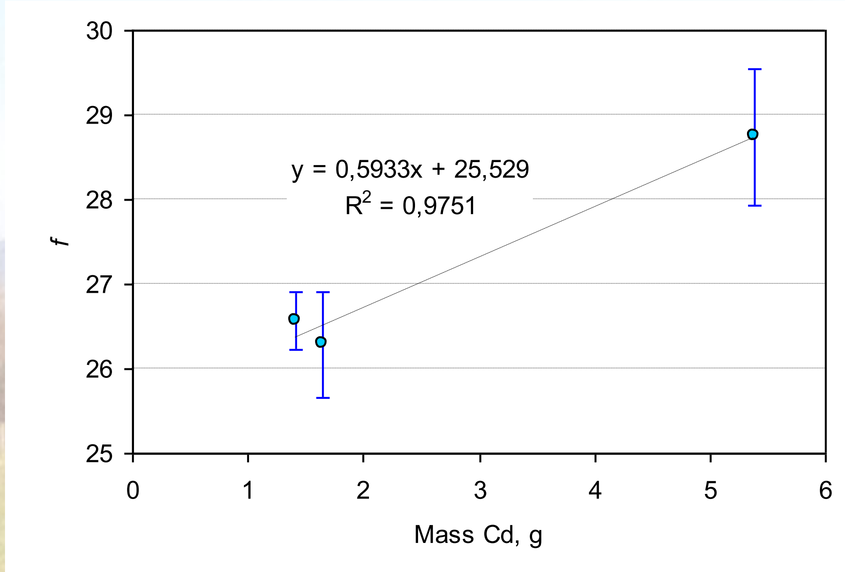
$$b = -\frac{1}{N}\left[\sum_{i=1}^{N} y_i + \alpha \sum_{i=1}^{N} x_i\right]$$

$$f = Q_{0,r}(\alpha)\left(F_{Cd,r} R_{Cd,r} - 1\right)\frac{G_{e,r}}{G_{th,r}}$$

Core No.	Irr. channel	Monitors Cd-ratio method	f	α
169	PT 13.6.2000	^{198}Au-^{69m}Zn-^{65}Zn-^{95}Zr	31.78±0.71	-0.0211±0.0059
	IC-40 8.3.2001	^{198}Au-^{60}Co-^{56}Mn-^{101}Tc-^{233}Pa-^{239}Np-^{69m}Zn-^{65}Zn-^{95}Zr	27.34±0.43	-0.0088±0.0062
176	PT 3.4.2002	^{198}Au-^{59}Fe-^{56}Mn-^{99}Mo-^{99m}Tc-^{69m}Zn-^{65}Zn-^{95}Zr	28.03±0.81	-0.0151±0.0068
	IC-40 16.4.2002	^{198}Au-^{59}Fe-^{116m}In-^{176m}Lu-^{69m}Zn-^{65}Zn-^{95}Zr	28.74±0.81	-0.0113±0.0046

Zr, Au, Zn, Co, U, Mn, Mo, Th, In, Fe, Lu (foils, wires, alloys)

Correction factor for inaccuracy in the determination of parameter *f* by "Cd-ratio for multi-monitor" method



$$q = \frac{G_{th,c} f + G_{e,c} Q_{0,c}(\alpha)}{G_{th,a} f + G_{e,a} Q_{0,a}(\alpha)}$$

$$\frac{\partial q}{\partial f} = \frac{Q_{0,a}(\alpha) - Q_{0,c}(\alpha)}{(f + Q_{0,a}(\alpha))^2}$$

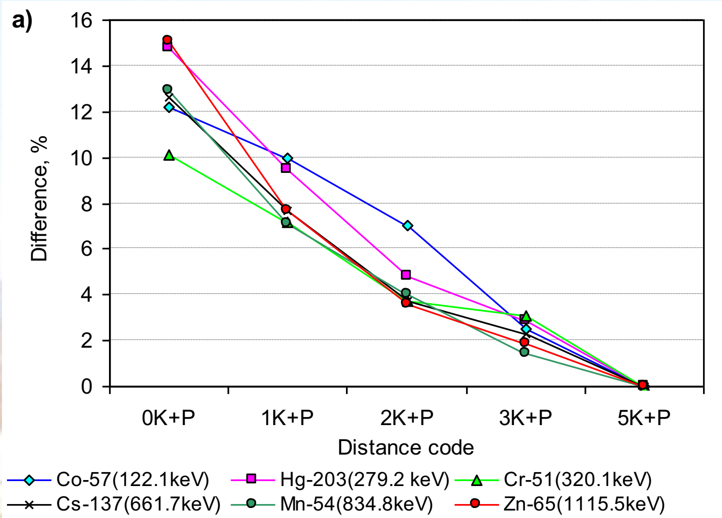
$$F_{masaCd} = \left(\frac{q_{corr}}{q} - 1 \right) \cdot 100$$

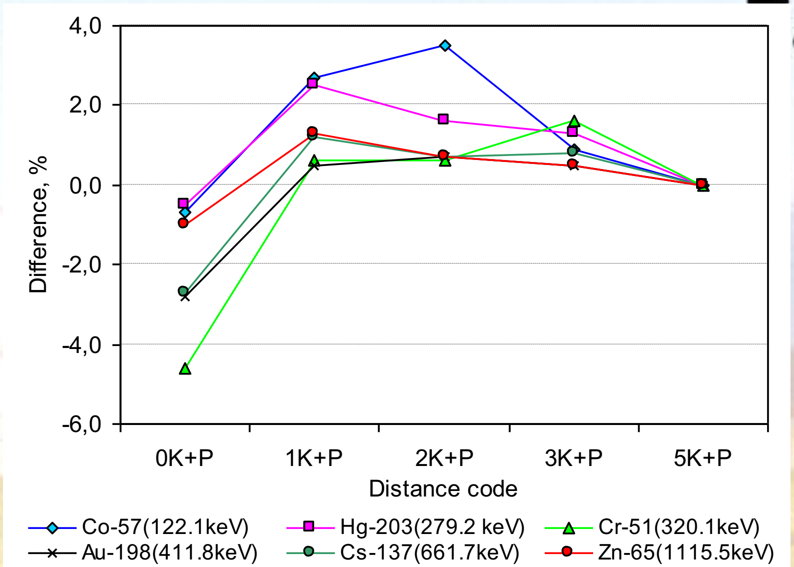
IC-40 channel: α = - 0.0113;

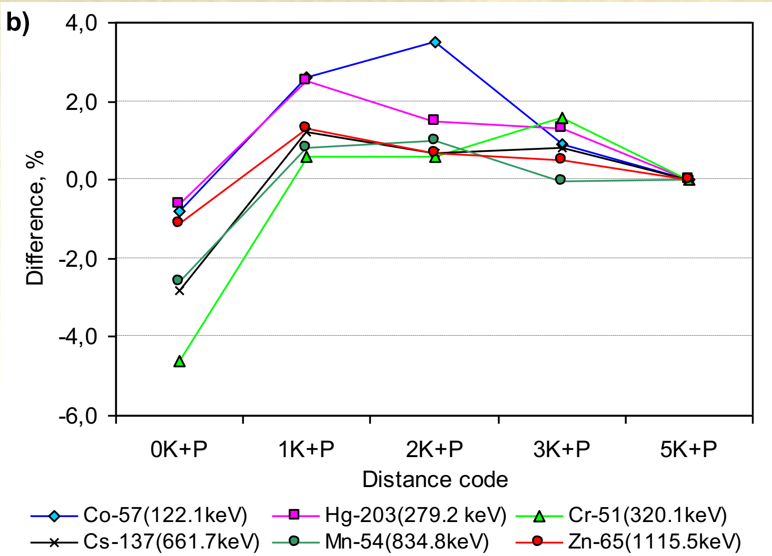
f **= 28.74 (5.39 g Cd);** f_{corr} **= 26.57 (1.41 g Cd)**

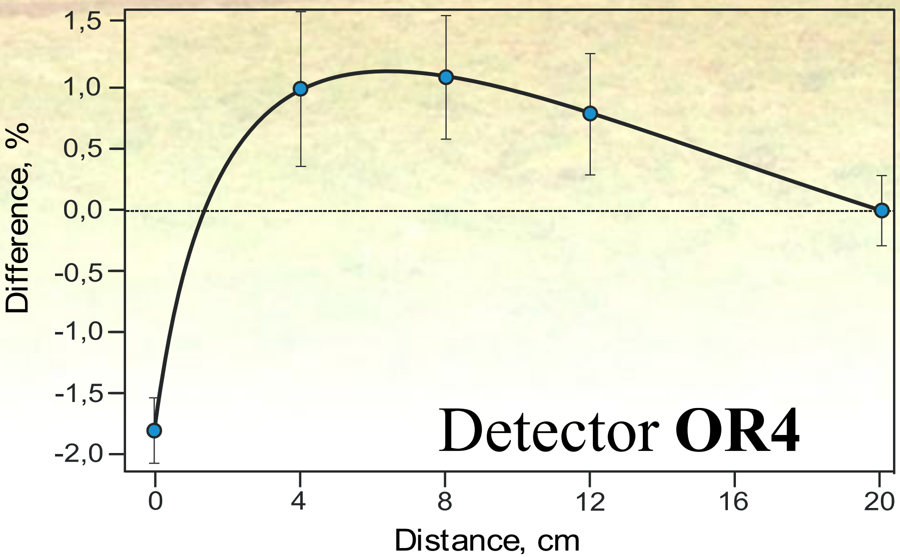
El.:	Nuclide	Q_0	$\bar{E}_r$, eV	$Q_0(\alpha)$	F_{masaCd} (%)
Au	**^{198}Au**	**15.71**	**5.7**	**16.020**	**≡ 0.00**
Dy	**^{165}Dy**	**0.19**	**224**	**0.182**	**2.87**
Cr	**^{51}Cr**	**0.53**	**7530**	**0.548**	**2.77**
Zn	**^{65}Zn**	**1.908**	**2560**	**2.052**	**2.37**
Zn	**^{69m}Zn**	**3.19**	**590**	**3.403**	**2.04**
Zr	**^{95}Zr**	**5.306**	**6260**	**5.819**	**1.53**
Rb	**^{86}Rb**	**14.8**	**839**	**15.943**	**0.01**
Rb	**^{88}Rb**	**23.3**	**364**	**24.883**	**-0.84**
U	**^{239}Np**	**103.4**	**16.9**	**106.75**	**-3.30**
Zr	**^{97m}Nb**	**251.6**	**338**	**268.69**	**-4.15**

Geometrical correction factor for absolute calibration of OR4









Correction factor for measuring geometry (F_{geom})

Distance	Detector			
	OR1	OR2	CA1	OR4
0K+P	-7.7 ± 0.9	-4.1 ± 0.2	-6.5 ± 0.8	-1.8 ± 0.3
0.5K+P	-0.8 ± 0.9	+1.7 ± 0.9	+1.3 ± 0.7	+1.3 ± 0.7
1K+P	0.0 ± 0.6	+1.6 ± 0.6	+1.0 ± 0.6	+1.0 ± 0.6
2K+P	+1.1 ± 0.8	+0.8 ± 0.9	+1.1 ± 0.5	+1.1 ± 0.5
3K+P	-	-	-	+0.8 ± 0.8
4K+P	≡ 0.0 ± 0.4	≡ 0.0 ± 0.4	-	-
5K+P	-	-	≡ 0.0 ± 0.4	≡ 0.0 ± 0.3

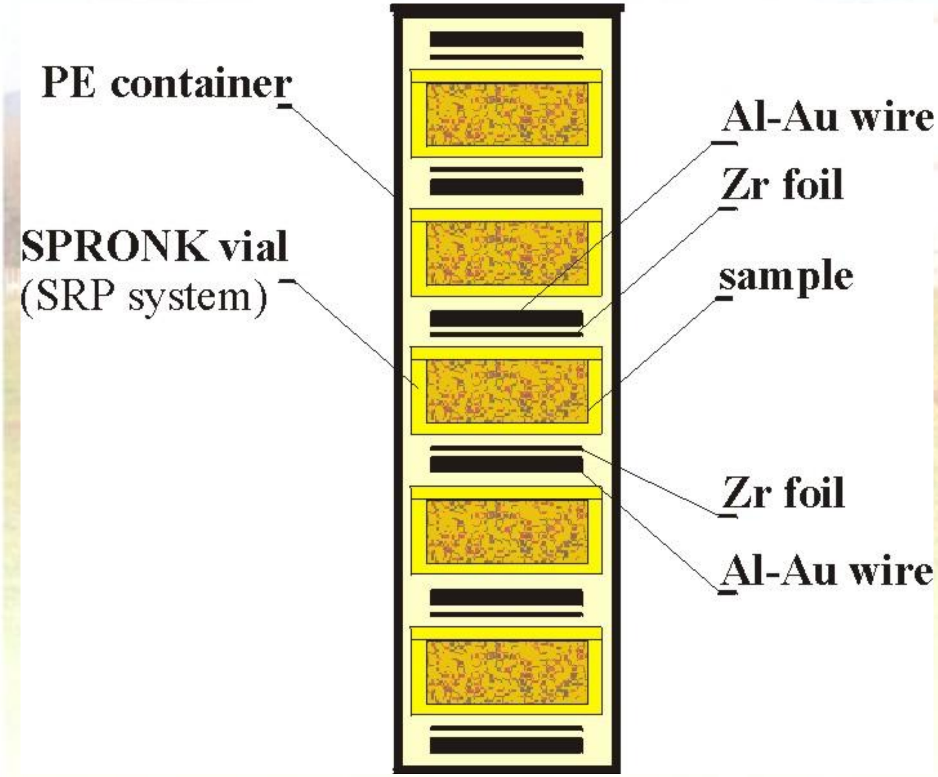
Code: 1K = 4 cm; Data for F_{geom} are given in %

Total correction factor (F_c) for inorganic matrix

$$F_c = \left(1 + \frac{F_{sat}}{100}\right) \cdot \left(1 + \frac{F_{inorg}}{100}\right) \cdot \left(1 + \frac{F_{masaCd}}{100}\right) \cdot \left(1 + \frac{F_{geom}}{100}\right)$$

El.	Nuclide	Distance	Total correction factor F_c			
			OR1	OR2	CA1	OR4
As	**^{76}As**	**Reference**	**1.024**	**1.024**	**1.024**	**1.024**
Co	^{60}Co	0K+P	0.970	1.008	0.983	1.032
Cr	^{51}Cr	0K+P	0.976	1.014	0.988	1.038
Cs	^{134}Cs	0K+P	0.944	0.981	0.956	1.004
Rb	^{86}Rb	1K+P	1.018	1.034	0.994	1.028
Sb	^{124}Sb	0K+P	0.924	0.960	0.936	0.983
Sc	^{46}Sc	0K+P	0.976	1.014	0.989	1.038
Sr	^{85}Sr	0K+P	0.942	0.979	0.954	1.002
Ta	^{182}Ta	**0K+P**	**0.920**	0.956	0.932	0.979
Yb	^{175}Yb	**1K+P**	1.058	**1.075**	1.034	1.069
Zn	^{65}Zn	0K+P	0.970	1.008	0.983	1.032

k_0-INAA analytical procedure



- Sample and standard are prepared in sandwich form and irradiated in the carousel facility of the TRIGA Mark II reactor (250 kW)
- Measurement on an HPGe absolutely calibrated detector
- Evaluation of the spectrum by HyperLab program
- Calculation of the effective solid angle between sample and HPGe detector
- Calculation of element concentration by KAYZERO program

Verification of the corrected k_0-NAA procedure

- inorganic matrices:
  - BCR-320 River Sediment (n = 14)
  - IAEA SL-3 Lake Sediment (n = 3)
  - IAEA Soil-7 (n = 15)
  - IAEA-405 Estuarine Sediment (n = 3)
- organic matrices:
  - IAEA Sea plant (n = 4-11)
  - IAEA 336 Lichen (n = 5-7)
  - NIST 2871 Domestic Sludge (n = 3)
  - IJS PT-SL1 Sewage Sludge (n = 5-6)

IAEA Soil-7
Detector **OR4**

El.	Nuclide	Experimental data					Literature data		
		δ_{nocorr}, %	δ_{corr}, %	s_d, %	$s_{a,tot}$, %	(n)	Recomm. mg/kg (dry weight)	s_{RM}, %	(n)
As	^{76}As	6.5	9.9	1.72	4.35	15	13.4	6.34	25
Ce	^{141}Ce	-13.6	-8.3	4.48	5.45	15	61	10.7	15
Co	^{60}Co	-7.4	-2.2	3.26	4.39	15	8.9	9.55	32
Cr	^{51}Cr	8.3	15.2	3.21	4.39	15	60	20.8	41
Cs	^{134}Cs	-0.3	2.5	1.81	4.58	15	5.4	13.9	16
Eu	^{154}Eu	2.9	7.5	3.39	4.72	15	1.0	20.0	10
Hf	^{181}Hf	-10.9	-6.0	3.61	4.73	15	5.1	6.86	11
La	^{140}La	-7.0	-0.9	4.29	5.32	15	28	3.57	12
Nd	^{147}Nd	-19.3	-14.2	6.22	6.96	15	30	20.0	7
Rb	^{86}Rb	0.6	3.6	3.31	4.60	15	51	8.82	24
Sb	^{124}Sb	4.4	5.1	3.56	4.97	15	1.7	11.8	18
Sc	^{46}Sc	-4.2	1.9	3.35	4.49	15	8.3	12.6	22
Sm	^{153}Sm	-8.7	-5.9	1.84	3.44	15	5.1	6.86	12
Sr	^{85}Sr	1.3	4.7	5.49	11.2	15	108	5.09	19
Ta	^{182}Ta	-4.5	-4.2	3.67	5.23	15	0.8	25.0	12
Tb	^{160}Tb	8.7	10.9	2.26	4.00	15	0.6	33.3	12
Th	^{233}Pa	-3.5	-0.5	1.26	3.30	15	8.2	13.4	18
U	^{239}Np	-2.6	-4.1	5.99	6.85	15	2.6	21.1	14
Yb	^{175}Yb	-14.3	-8.1	4.04	5.05	15	2.4	14.6	12
Zn	^{65}Zn	-8.9	-3.7	3.30	4.44	15	104	5.77	44
Zr	^{95}Zr	-0.4	4.0	7.16	7.76	15	185	5.68	15

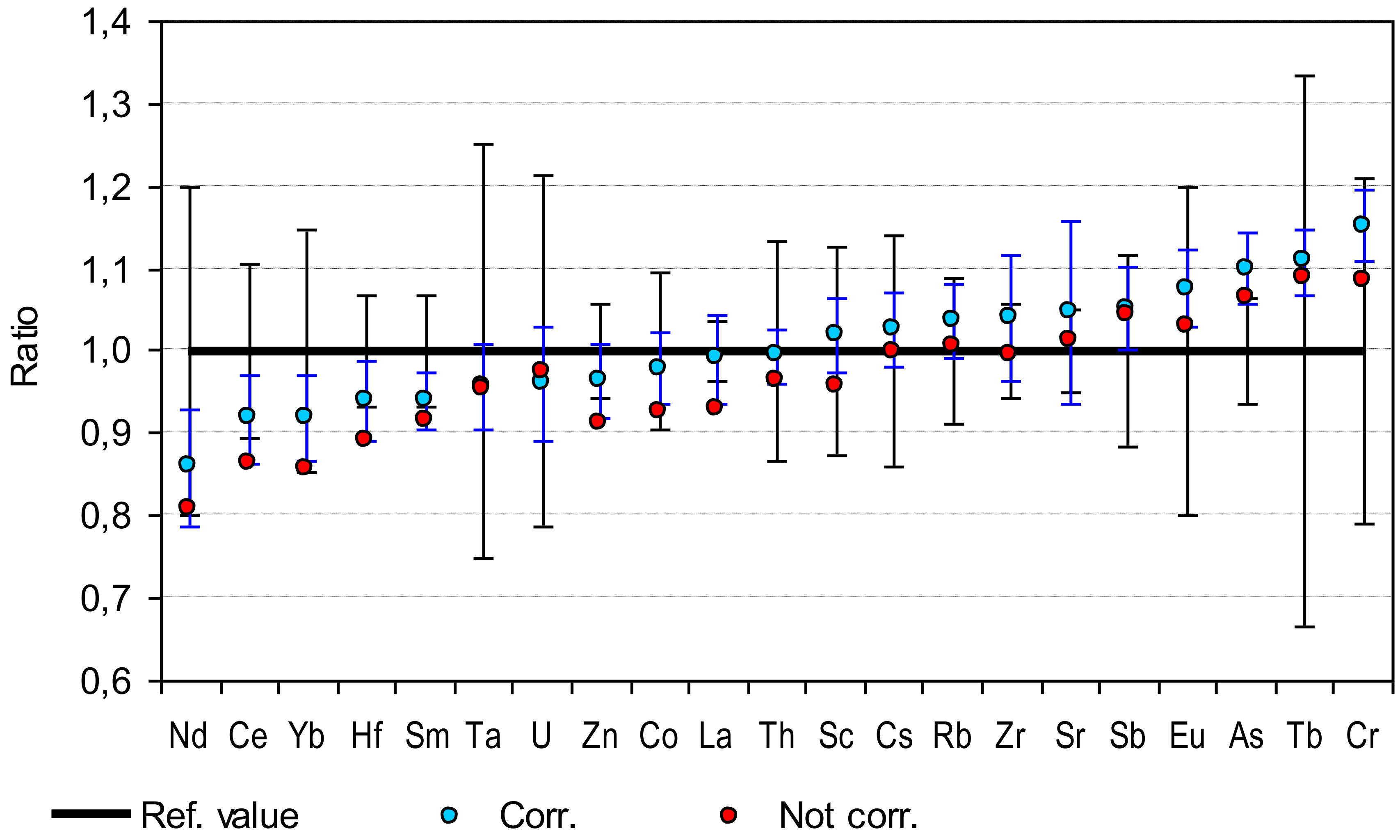
s_{RM} – 95% confidence interval of the reference material (RM)

δ_{nocorr} – difference between arithmetic mean value of standard k_0-procedure and recommended value

δ_{corr} – difference between arithmetic mean value of corrected k_0-procedure and recommended value

$\delta_{a,tot}$ – total uncertainty

Inorganic matrix: IAEA Soil-7 (n = 15) - **OR4**



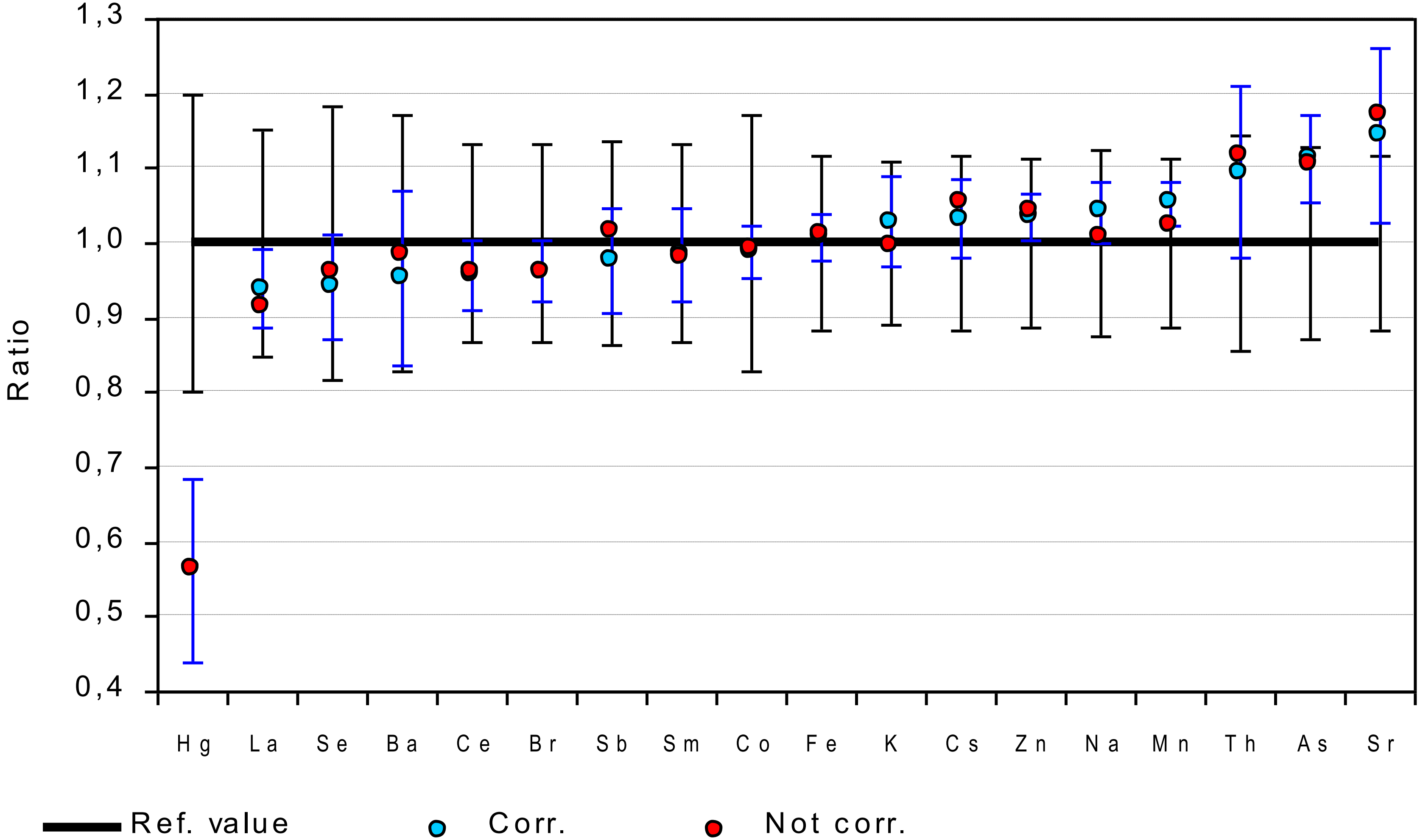
IAEA 336 Lichen
Detector **OR4**

El.	Nuclide	Experimental data					Literature data		
		δ_{nocorr}, %	δ_{corr}, %	s_d, %	$s_{a,tot}$, %	(n)	Recomm. mg/kg (dry weight)	s_{RM}, %	(n)
As	^{76}As	10.6	11.4	4.16	5.77	5	0.63	12.7	17
Ba	^{131}Ba	-1.5	-4.7	8.31	11.6	5	6.4	17.2	11
Br	^{82}Br	-3.8	-3.8	2.33	3.99	6	12.9	13.2	18
Ce	^{141}Ce	-4.1	-4.3	3.39	4.59	5	1.28	13.3	13
Co	^{60}Co	-0.6	-1.2	1.57	3.33	5	0.29	17.2	19
Cs	^{134}Cs	5.6	3.2	3.14	5.25	5	0.110	11.8	13
Fe	^{59}Fe	1.1	0.8	0.70	3.05	5	430	11.6	35
Hg	^{203}Hg	-43.6*	-44.8*	11.8	12.3	5	0.2	20.0	15
K	^{42}K	-0.4	2.9	5.12	5.94	7	1840	10.9	24
La	^{140}La	-8.5	-6.1	4.35	5.37	5	0.66	15.1	12
Mn	^{56}Mn	2.5	5.3	#	3.02	2	63	11.1	29
Na	^{24}Na	0.9	4.2	2.82	4.12	7	320	12.5	20
Sb	^{124}Sb	1.5	-2.2	6.06	6.98	5	0.073	13.7	12
Se	^{75}Se	-3.9	-5.8	4.47 $	6.91	5	0.22	18.2	12
Sm	^{153}Sm	-2.0	-1.5	5.62	6.33	5	0.106	13.2	15
Sr	^{85}Sr	17.2	14.5	6.39	11.6	5	9.3	11.8	19
Th	^{233}Pa	11.8	9.5	11.1	11.5	5	0.14	14.3	16
Zn	^{65}Zn	4.2	3.6	0.69	3.04	5	30.4	11.2	38

* - "outlier";
$ – standard deviation (s_d) of independent measurements < standard deviation of N_p (net peak area in the spectrum 6.0%);
# – for s_d was taken into account standard deviation of the N_p (0.3%)
s_{RM} – 95% confidence interval of the reference material (RM)
δ_{nocorr} – difference between arithmetic mean value of standard k_0-procedure and recommended value
δ_{corr} – difference between arithmetic mean value of corrected k_0-procedure and recommended value
$\delta_{a,tot}$ – total uncertainty

Organic matrix: IAEA 336 Lichen (n = 5-7)

OR4



Statistical uncertainties

$$\bar{\bar{\delta}} = \frac{\sum_{i=1}^{N} \bar{\delta}_i \cdot w_i}{\sum_{i=1}^{N} w_i}$$

Weighted average deviation of RM means from certified value

$\bar{\delta}_i$ Average deviation of independent measurements for a particular RM

$$w_i = \frac{1}{s_{\bar{x}_{i,tot}}^2 + s_{RM}^2}$$

Weight with our and reference standard deviation

$$\bar{s}_{\text{int}} = \frac{1}{\sqrt{\sum_{i=1}^{N} w_i}}$$

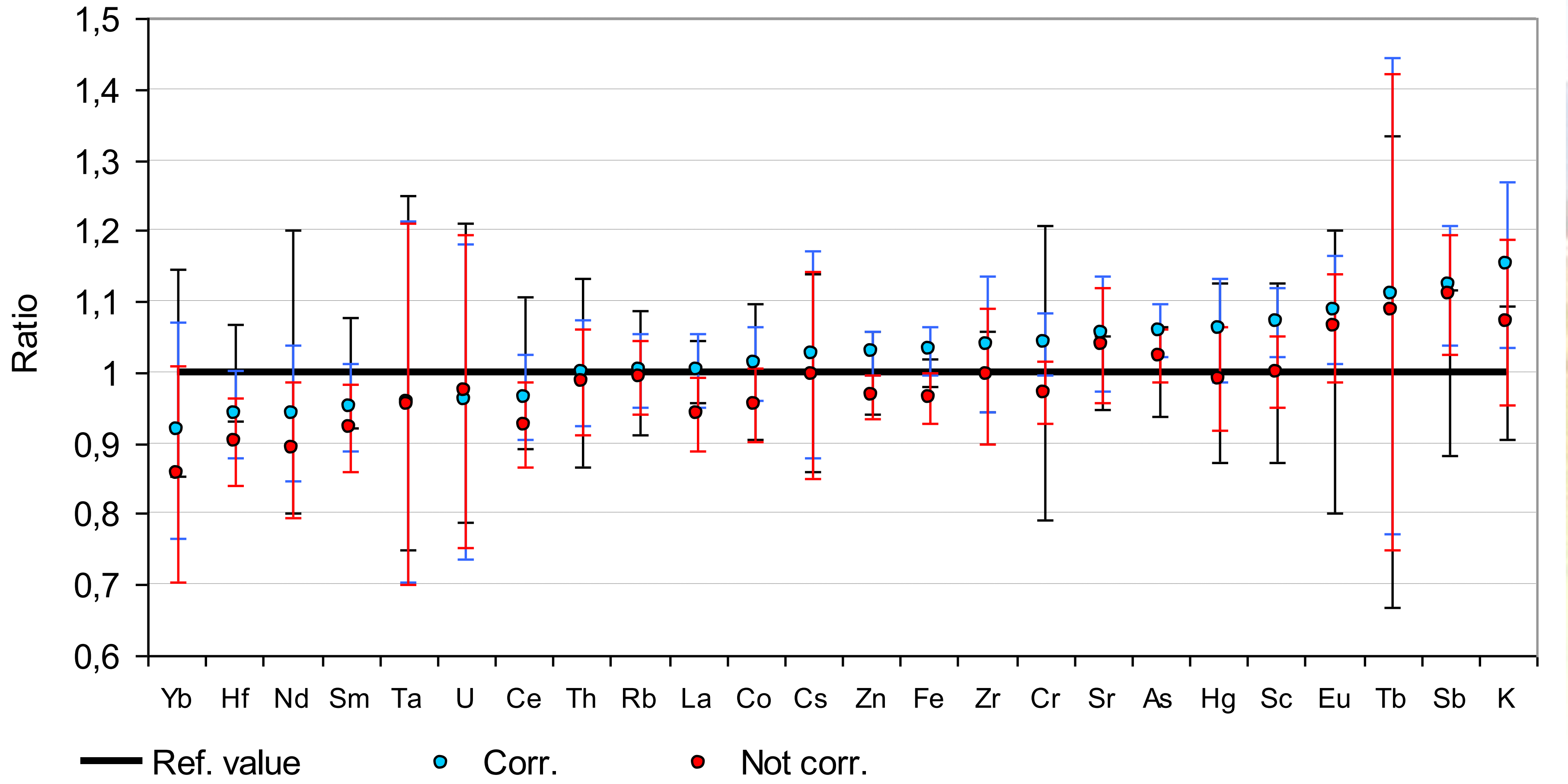
Internal Statistical uncertainty

$$\bar{s}_{ext} = \sqrt{\frac{\sum_{i=1}^{N} w_i \left(\bar{\delta}_i - \bar{\bar{\delta}}\right)^2}{(N-1)\sum_{i=1}^{N} w_i}}$$

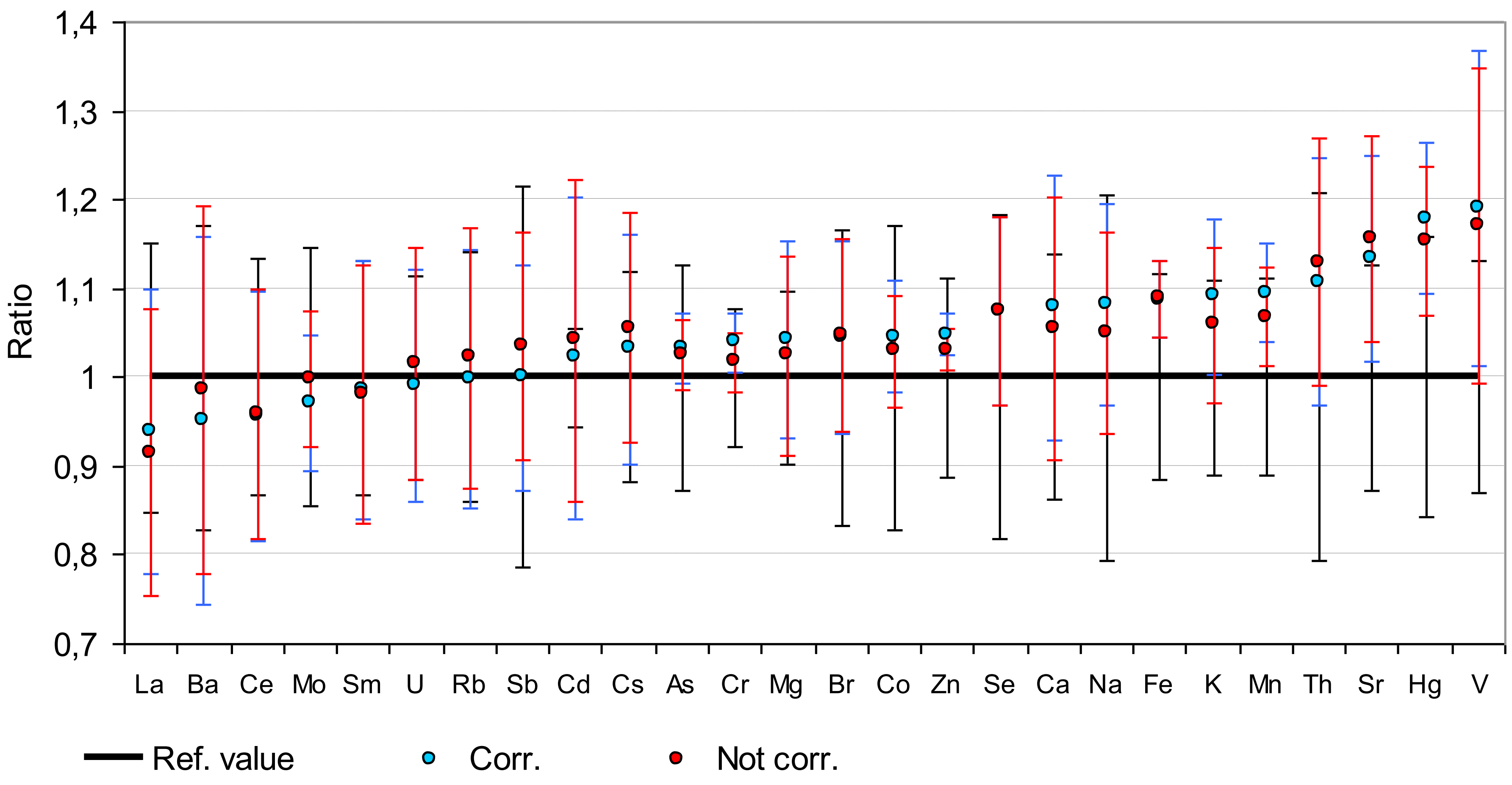
External Statistical uncertainty

- Statistical consistency : $s_{int} \approx s_{ext}$
- $s_{int} >> s_{ext}$: estimation of $s_{xi,tot}$ values contains common systematic uncertainty or average results are biased
- $s_{int} << s_{ext}$: suggested that one or more uncommon uncertainties were not taken into account when estimating the $s_{xi,tot}$ values
- $\bar{\bar{\delta}} << s_{int}$: reliability of the measurement is good

Weighted average for 4 inorganic matrices



Weighted average for 4 organic matrices



Conclusions

- Standard procedure of k_0-NAA (KAYZERO/SOLCOI ver. 5a - February 2003) was applied for determination of major and trace elements in a suite of RMs or CRMs
- Four correction factors were introduced in the standard procedure of k_0 - NAA:
  - F_{sat}
  - F_{org} or F_{inorg}
  - F_{masaCd}
  - F_{geom}
- The results obtained by corrected procedure of k_0-NAA show relatively better agreement with CRMs value than results without correction for mostly recommended or certified elements in organic and inorganic matrices

Conclusions (cont)

- Hg - “outlier” from 95% CI in IAEA 336 Lichen (organic matrix) obtained with both procedures due to losses during irradiation in the semi-open plastic vials
- The biggest difference between standard and corrected procedure of k_0-NAA in organic matrices is for Sb (3.6%)
- The biggest difference between standard and corrected procedure of k_0-NAA in inorganic matrices is for K (8.0%)