The Abdus Salam
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Workshop on Understanding and Evaluating Radioanalytical Measurement Uncertainty

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Rapid methods for ALMERA Network in an Emergency situation analysis methods for radionuclides

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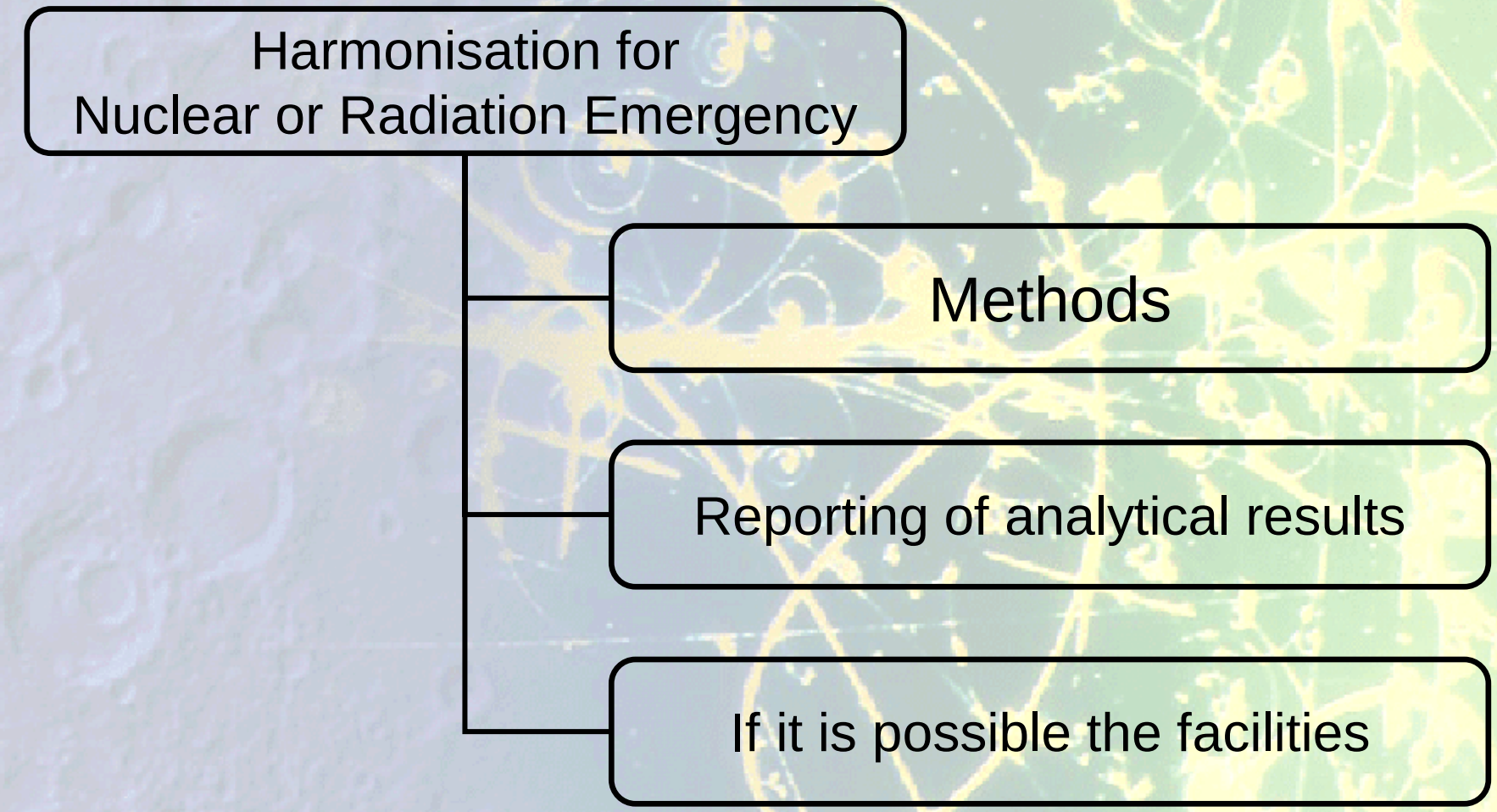
Rapid Methods for ALMERA Network in Emergency Situation

(The first report of the „rapid method” group)

S. Tarjan, C. K. Kim, B. Varga, …

4th ALMERA Co-ordination meeting,
Trieste 5-7 November 2007

ALMERA => environmental monitoring



WHO recommendation for public dose:

1 mSv / year

from man made radionuclides

Current Guideline Levels by WHO for Food (in Bq/kg or litre)

CAC/GL 5-2006

- ***Conditions***
  - fraction of contaminated food is not higher than 0.1
  - total food consumption is 550 kg/year for adult
  - total food consumption is 200 kg/year for children
  - the activity concentrations of each radionuclide should be added together (within the same group)

Radionuclides in Food	Guideline Level (Bq/kg)	
	Infant Foods	Other Foods
^{238}Pu, **^{239}Pu**, **^{240}Pu**, **^{241}Am**	1	10
^{90}Sr, ^{106}Ru, **^{129}I**, **^{131}I**, **^{235}U**	100	100
^{35}S, **^{60}Co**, ^{89}Sr, ^{103}Ru, **^{134}Cs**, **^{137}Cs**, **^{144}Ce**, ^{192}Ir	1000	1000
^{3}H, ^{14}C, ^{99}Tc	1000	10000

ASSESSMENT OF EFFECTIVE DOSE FOR INFANTS AND ADULTS FROM INGESTION OF IMPORTED FOODS IN A YEAR

Radionuclide	Guideline Level (Bq/kg)		Effective dose (mSv)	
	Infant foods	Other foods	1st year after major contamination	
			Infants	Adults
^{238}Pu	1	10	0.08	0.1
^{239}Pu			0.08	0.1
^{240}Pu			0.08	0.1
^{241}Am			0.07	0.1
^{90}Sr	100	100	0.5	0.2
^{106}Ru			0.2	0.04
^{129}I			0.4	0.6
^{131}I			0.4	0.1
^{235}U			0.7	0.3
^{35}S*	1000	1000	0.2	0.04
^{60}Co			1	0.2
^{89}Sr			0.7	0.1
^{103}Ru			0.1	0.04
^{134}Cs			0.5	1
^{137}Cs			0.4	0.7
^{144}Ce			1	0.3
^{192}Ir			0.3	0.08
^{3}H**	1000	10000	0.002	0.02
^{14}C			0.03	0.3
^{99}Tc			0.2	0.4

* This represents the value for organically bound sulphur.
** This represents the value for organically bound tritium.

CAC/GL 5-2006, WHO

Food consumption by age groups, kg/year

(World wide averages)

Food	1 year	10 years	adult
Milk and milk products	120	110	105
Meat	15	35	50
Cereals	45	90	140
Leafy vegetables	20	40	60
Other vegetables and fruits	60	110	170
Fish	5	10	15
Total food	**265**	**395**	**540**
Drinking water and beverages	150	350	500

UNSCEAR 2000

Proposed detection limits and methods for milk

Type of radiation	Nuclide	Half life	Sample weight, g	Sample preparation	MDA, Bq/kg	Method	Duration
Gamma-emitters	Co-60	5.27 y	500.0	n.a.	0.20	HPGe-gsp, 450ccm Marinelli-beaker, 30% rel. eff. detector, 10 cm lead shielding, 10000s	4 hours
	Ru-103	39.26 d			0.20		
	Ru-106	373.6 d			0.80		
	Cs-134	2.065 y			0.15		
	Cs-137	30.04 y			0.15		
	I-125	59.4 d			3.00		
	I-131	8.02 d			0.50		
	I-132	2.34 h			0.40		
	Ce-144	284.9 d			0.50		
Beta-emitters	H-3	12.33 y					
	C-14	5730 y					
	Sr-89	50.5 d	50 ml	IAEA TECDOC 1092	0.10	IAEA TECDOC 1092	10 hours
	Sr-90	28.74 y					
	Pu-241	14.35 y					
Alpha-emitters	Pu-238	87.7 y	50 ml	IAEA TECDOC 1092	0.10	IAEA TECDOC 1092 (183)	12 hours ???
	Pu-239	24110 y			0.10		
	Pu-240	6564 y			0.10		
	Am-241	432.2 y					

Proposed detection limits and methods for vegetation samples

Type of radiation	Nuclide	Half life	Sample weight, g	Sample preparation	MDA, Bq/kg fresh	Method	Duration
Gamma-emitters	Co-60	5.27 y	250.0	n.a.	1.00	HPGe-gsp, 450ccm Marinelli-beaker, 30% rel. eff. detector, 10 cm lead shielding, 10000s	4 hours
	Ru-103	39.26 d			0.80		
	Ru-106	373.6 d			5.80		
	Cs-134	2.065 y			0.74		
	Cs-137	30.04 y			0.86		
	I-125	59.4 d			10.00		
	I-131	8.02 d			0.78		
	I-132	2.34 h			0.96		
	Ce-144	284.9 d			5.00		
Beta-emitters	H-3	12.33 y	40.0	combustion	0.50	LSC counting	32 hours
	C-14	5730 y	40.0	combustion		LSC counting	32 hours
	Sr-89	50.5 d	50.0	radiochemical separation	10.00	IAEA TECDOC 1092 (183)	13 hours ???
	Sr-90	28.74 y					
	Pu-241	14.35 y					
Alpha-emitters	Pu-238	87.7 y	50.0	radiochemical separation		IAEA TECDOC 1092 (183)	19 hours ???
	Pu-239	24110 y			0.10		
	Pu-240	6564 y					
	Am-241	432.2 y					

* It was calculated from the real spectrum of fresh grass by WINNER GAMMA software

Drinking water

Type of radiation	Nuclide	Half life	Sample weight, ml	Sample preparation	MDA, Bq/l	Method	Duration	Guideline levels*, Bq/kg adult*
Gamma-emitters	Co-60	5.27 y	500.0	n.a.	0.20	HPGe-gsp, 450ccm Marinelli-beaker, 30% rel. eff. detector, 10 cm lead shielding, 10000s	4 hours	49
	Ru-103	39.26 d			0.20			228
	Ru-106	373.6 d			0.80			24
	Cs-134	2.065 y			0.15			9
	Cs-137	30.04 y			0.15			13
	I-125	59.4 d			3.00			11
	I-131	8.02 d			0.50			8
	I-132	2.34 h			0.40			575
	Ce-144	284.9 d			0.50			32
Beta-emitters	H-3	12.33 y	100.0	destillation	4-10	IAEA TECDOC 1092	2-3 hours	9259
	C-14	5730 y						287
	Sr-89	50.5 d	1000.0	radiochemical separation	0.10	IAEA TECDOC 1092	8 hours	64
	Sr-90	28.74 y						6
	Pu-241	14.35 y						35
Alpha-emitters	Pu-238	87.7 y	1000.0	radiochemical separation		IAEA TECDOC 1092 (183)	10 hours ???	0.72
	Pu-239	24110 y			0.10			0.67
	Pu-240	6564 y						0.67
	Am-241	432.2 y						0.83

* Calculated for 0.1 mSv/year without gut transfer factor using 1.6 l/day drinking water intake rate(IBSS 115)

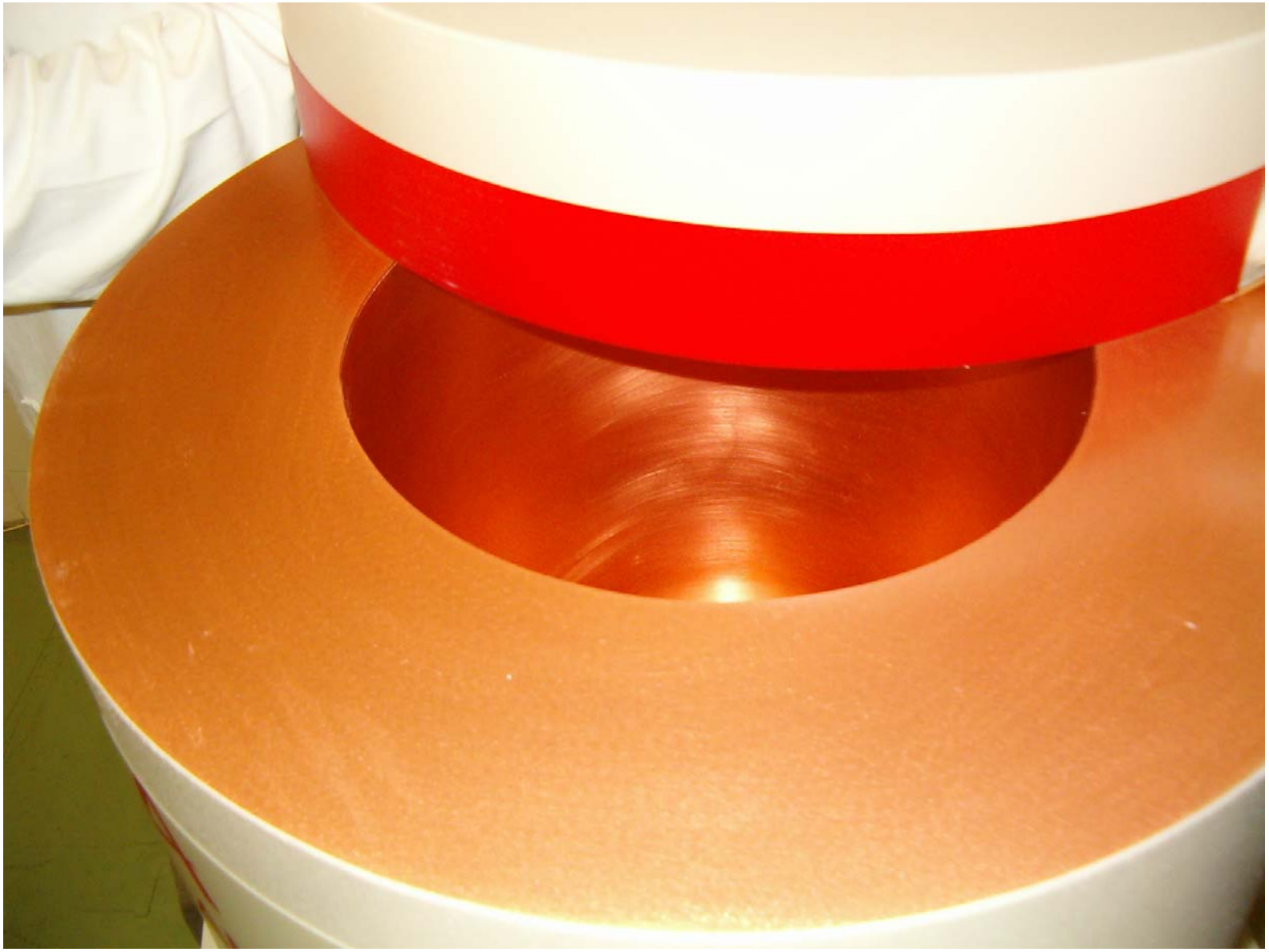
Aerosol

- WHO recommendation for internal dose by inhalation pathway is 0.1 mSv
- the breath rate (IBSS 115)
  - for children is 1400 m^3/year
  - for adult is 8400 m^3/year
- there are no any guideline levels expressed in Bq/m^3

Derived "guideline levels" from 0.1 mSv internal dose through inhalation pathway and radioanalytical methods for aerosol samples (IBSS 115)

Type of radiation	Nuclide	Half life	Sample weight, m^3	Sample preparation	MDA, Bq/m^3	Method	Duration	Guideline levels, Bq/m^3	
								adult	children
Gamma-emitters	Co-60	5.27 y	10.0	n.a.	0.03	HPGe-gsp, 30% rel. eff. detector, 10 cm lead shielding, 10000s	4 hours	0.38	0.83
	Ru-103	39.26 d			0.02			3.97	7.14
	Ru-106	373.6 d			0.15			0.18	0.31
	Cs-134	2.065 y			0.02			1.80	9.78
	Cs-137	30.04 y			0.02			2.59	13.23
	I-125	59.4 d			0.06			0.52	1.40
	I-131	8.02 d			0.02			1.61	0.99
	I-132	2.34 h			0.03			108.23	74.40
	Ce-144	284.9 d			0.11			0.22	0.40
Beta-emitters	H-3	12.33 y	It is required a special sampling and desorber tools (molecular sieve system)						
	C-14	5730 y							
	Sr-89	50.5 d	100.0	radiochemical separation	0.005	IAEA TECDOC 1092	32 hours	1.51	2.38
	Sr-90	28.74 y						0.07	0.18
	Pu-241	14.35 y	100.0					0.01	0.07
Alpha-emitters	Pu-238	87.7 y	100.0	radiochemical separation	0.00003	IAEA TECDOC 1092	36 hours	0.00026	0.00097
	Pu-239	24110 y						0.00024	0.00093
	Pu-240	6564 y						0.00024	0.00093
	Am-241	432.2 y						0.00028	0.00104

Gamma-spectrometry



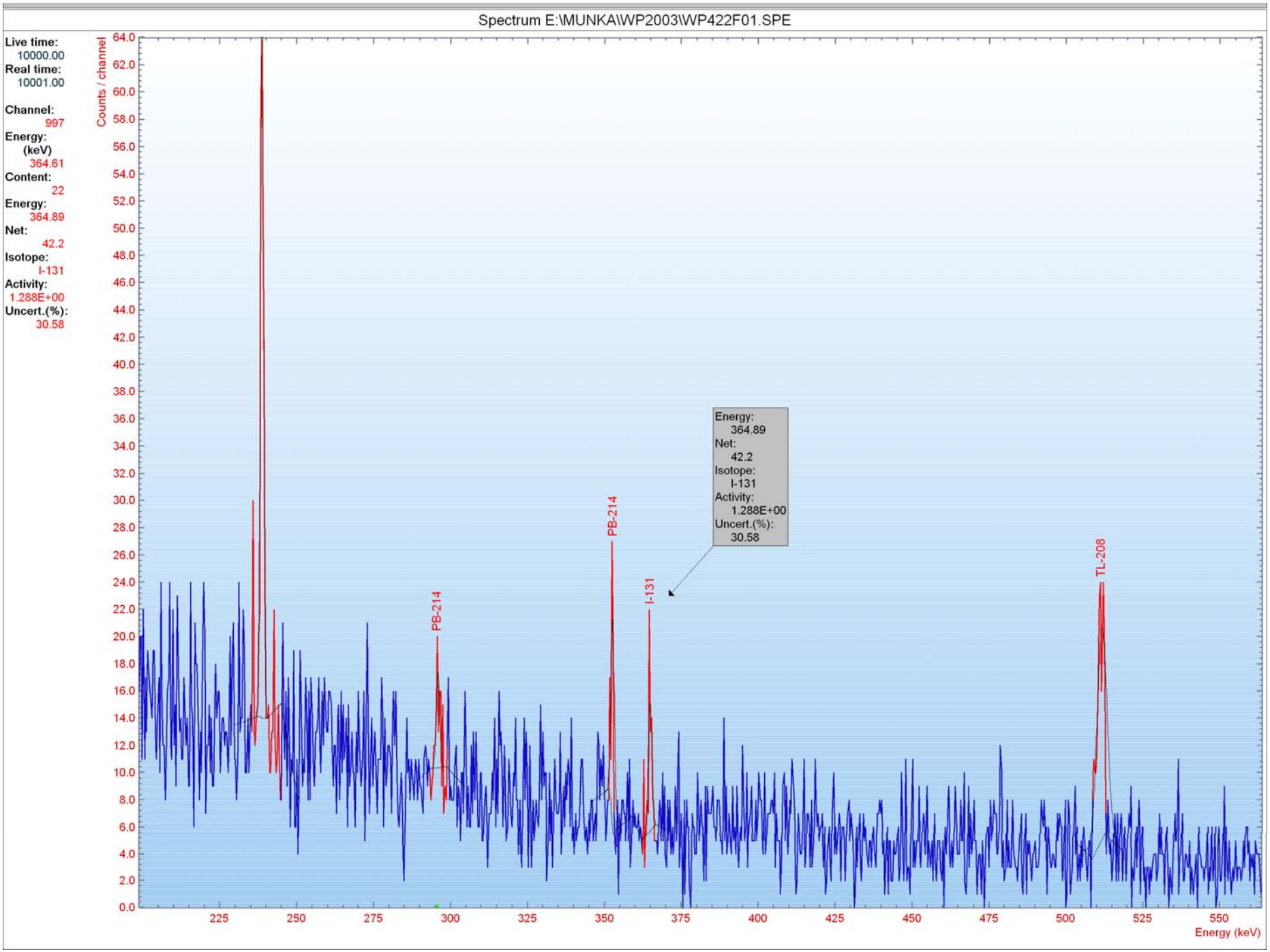
Efficiency (%) of different geometries

Nuclid	E, keV	Geometry			
		Cylindrical, 50 ccm	Cylindrical, 100 ccm	Marinelli 450 ccm	Well-type Det.(8 ccm)
^{241}Am	59.5	8.8	7.0	6.3	90
^{131}I	364	3.2	2.6	3.4	40
^{137}Cs	661.7	1.75	1.56	1.87	21
^{60}Co	1332.5	0.91	0.81	1.01	11

n-type 30% HPGe detector

Relative sensitivity of different geometries

Nuclide	E, keV	Geometry, sample density= 1kg/dm^3			
		Cylindrical, 50 ccm	Cylindrical, 100 ccm	Marinelli 450 ccm	Well-type Det.(8 ccm)
^{241}Am	59.5	0.63	1	4.09	1.03
^{131}I	364	0.62	1	5.91	1.23
^{137}Cs	661.7	0.67	1	5.39	1.08
^{60}Co	1332.5	0.57	1	5.55	1.09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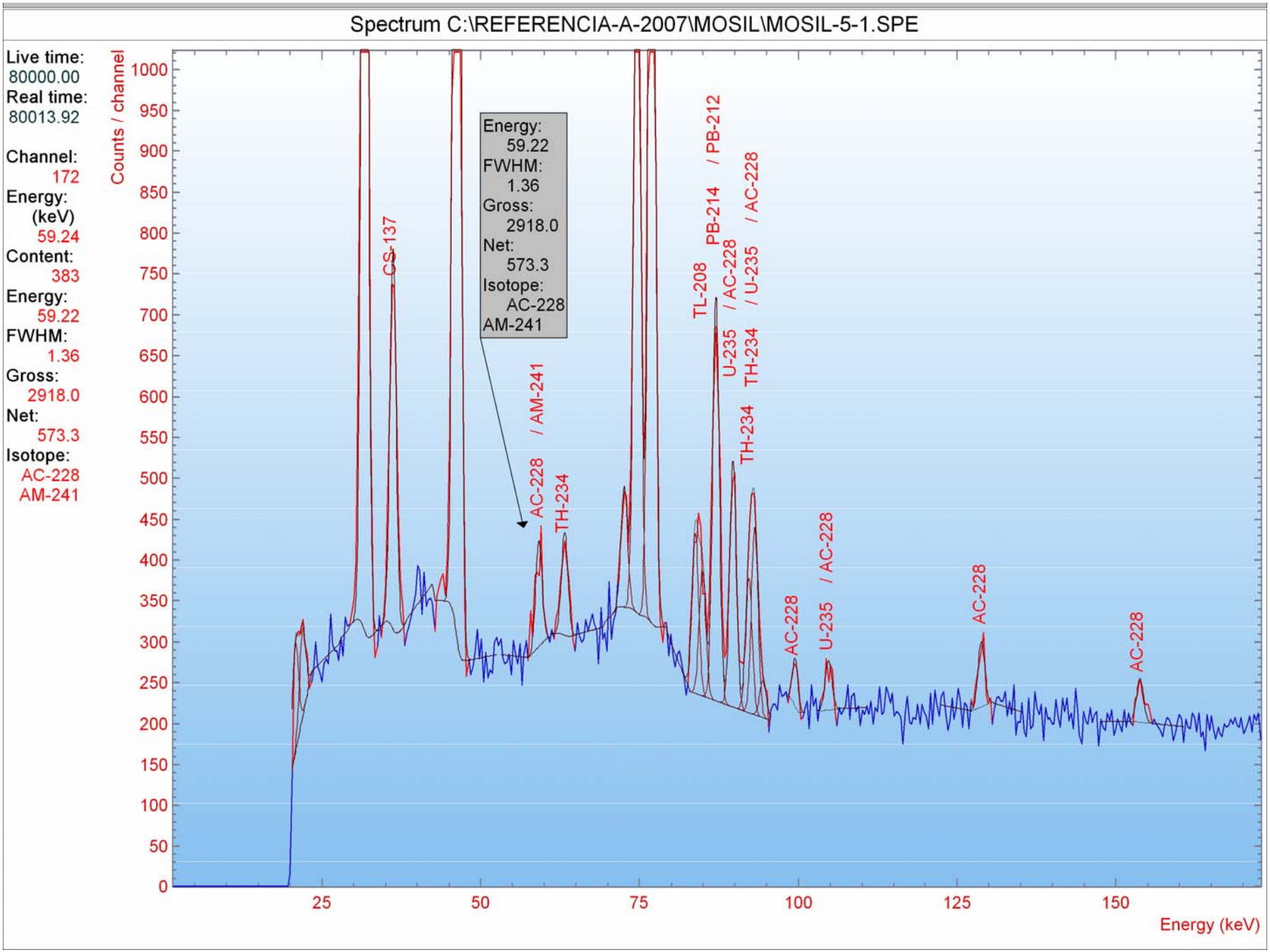
10000.00
Real time:
10001.00
Channel:
997
Energy:
(keV)
364.61
Content:
22
Energy:
364.89
Net:
42.2
Isotope:
I-131
Activity:
1.288E+00
Uncert.(%):
30.58
Counts / channel
Energy:
364.89
Net:
42.2
Isotope:
I-131
Activity:
1.288E+00
Uncert.(%):
30.58
PB-214
PB-214
I-131
TL-208
Energy (keV)


Spectrum C:\REFERENCIA-A-2007\MOSIL\MOSIL-5-1.SPE
Live time:
80000.00
Real time:
80013.92
Channel:
172
Energy:
(keV)
59.24
Content:
383
Energy:
59.22
FWHM:
1.36
Gross:
2918.0
Net:
573.3
Isotope:
AC-228
AM-241
Counts / channel
Energy:
59.22
FWHM:
1.36
Gross:
2918.0
Net:
573.3
Isotope:
AC-228
AM-241
CS-137
AC-228 / AM-241
TH-234
TL-208
PB-214 / PB-212
U-235 / AC-228
TH-234 / U-235
TH-234
AC-228
U-235 / AC-228
AC-228
AC-228
Energy (keV)

Spectrum C:\MUNKA\CSERNOBIL\OK24.SPE

Live time: 6431.28
Real time: 6487.54

Channel: 1993
Energy: (keV) 663.41
Content: 1780
Energy: 661.39
Net: 249228.7
Isotope: CS-137
Activity: 5.234E+05
Uncert.(%): 2.81

Counts / channel

1.00E+7
1.00E+6
1.00E+5
1.00E+4
1.00E+3
1.00E+2
1.00E+1
1.00E+0

CS-137 / CS-137 CS-137

CS-137

Energy: 661.39
Net: 249228.7
Isotope: CS-137
Activity: 5.234E+05
Uncert.(%): 2.81

40 50 60 70 80

250 500 750 1000 1250 1500 1750 2000 2250 2500

Energy (keV)

Special applications of gamma-spectrometry as a rapid method

- Well-type detector
  - ^{131}I measurement after enrichment on anion exchange resin from water samples

Journal of Radioanalytical and Nuclear Chemistry, Vol. 256, No. 2 (2003) 225–230
P. Parekh,* A. Bari, P. Harris

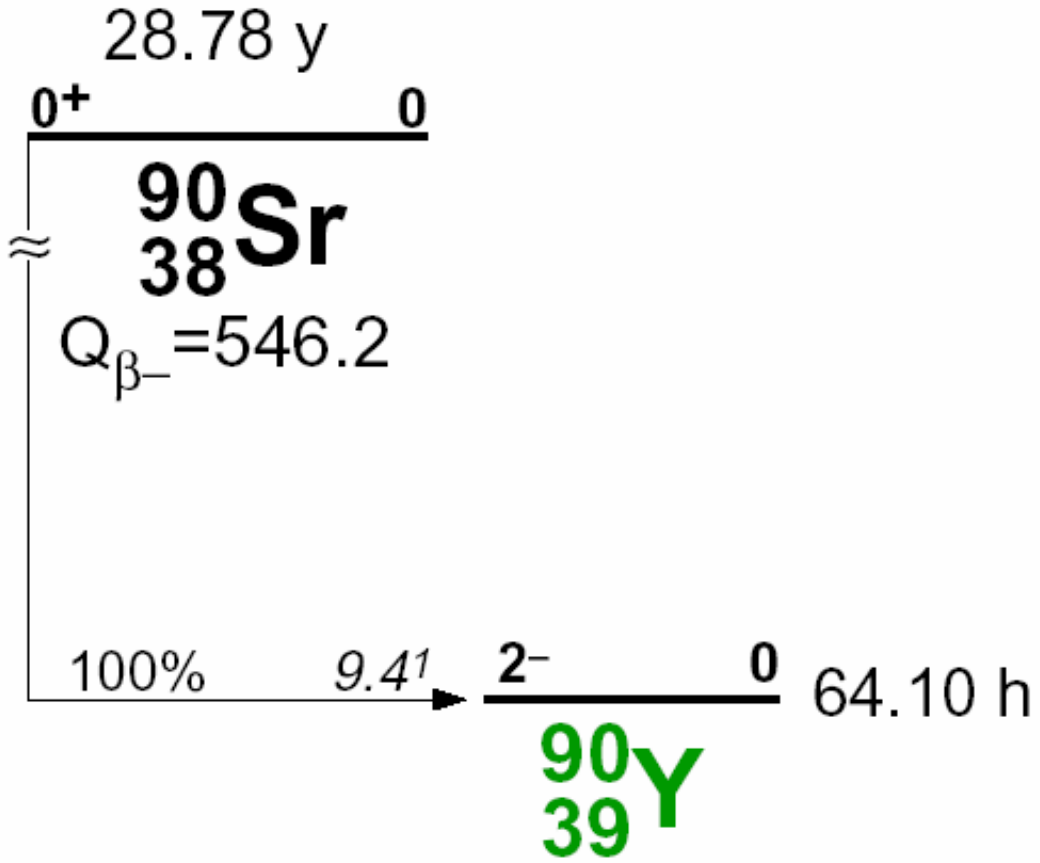
  - ^{241}Am analysis after enrichment and chemical separation

Journal of Radioanalytical and Nuclear Chemistry, Vol. 274, No.1 (2007) 39–43
R. J. Lagomarsino, N. Latner

- Compton-subtraction spectrometer
  - ^{90}Sr measurement without any sample preparation using bremstrahlung detection

Journal of Radioanalytical and Nuclear Chemistry, Vol. 223, Nos 1-2 (1997) 157-162
C. F. Wang, *+ M. C. Yuan, J. H. Lee****

Radiostrontium



Basic steps of radiochemical analysis

- **sample ashing, digestion**
- enrichment of Sr
  - co-precipitation
  - extraction
  - ion exchange
- separation of Sr and preparatum making
  - classical way (HNO_3 procedure)
  - Sr-spec
- low level counting
  - gas ionising detectors (proportional counter)
  - LSC or LSS
  - ULB plastic (pulse shape discrimination technique)

Special rapid methods

- **Sr-separation from milk 1**
  - extraction of Sr by Dowex 50 WX8 in slightly acidic condition **(pH 5.5)**
  - Sr separation by Sr-spec (chemical yield is 45-60%)
- **Sr-separation from milk 2**
  - extraction of Sr by Dowex 50 prepared with cryptand 222 (cryptand is a bicyclic polyether):

4.7.13.16.21.24-hexaoxa-1.10-dizabicyclo[8.8.8]hexacosan
Merck, product name: Kirptofix 222

C-222 improve the affinity for Sr (Ca, Ba) of the D50WX8

- 85% chemical yield was reached at pH 5.2
- time requirements 15-16h

– *Journal of Radioanalytical and Nuclear Chemistry, Vol. 226, Nos 1-2 (1997) 225-228*
– **D. Tait, G. Haase, A. Wiechen**
– *Journal of Radioanalytical and Nuclear Chemistry, Vol. 253, No. 2 (2002) 191–197*
– **S. Brun,* S. Bessac, D. Uridat, B. Boursier**

Special rapid methods (cont.)

- **Solid Phase Extraction method** with 3M disk (Sr, Cs and Tc available) mainly for water samples
  - *Journal of Radioanalytical and Nuclear Chemistry, Vol. 243, No. 2 (2000) 495–506*
  - *D. M. Beals,1 B. S. Crandall,2 P. D. Fledderman2*
  - *Journal of Radioanalytical and Nuclear Chemistry, Vol. 274, No.1 (2007) 71–78*
  - **Y. Kameo,* A. Katayama, A. Fujiwara, T. Haraga, M. Nakashima**

- **Selective scintillators:** the scintillator contains the crown ether (dicyclohexyl-18-crown-6)
- **In-sulphide**
  - new material, no any analytical application yet

$$[In_{10.5}S_{14.5}].[(H_2NCH_2CH_2–NHCH_2)_2]_{2.5}$$

  - *Journal of Radioanalytical and Nuclear Chemistry, Vol. 273, No.1 (2007) 99–102*
  - **Ying Lan, Zhe Su, Xingliang Li, Zhaoqun Jiang, Jun Jin, Jiali Xie, Shoujian Li***

Pu-isotopes

- HR ICP-MS
  - intensive sampling digestion
  - separation from the isobars
  - questions:
    - sample homogeneity down to 0.1-0.5 g
    - short life radionuclides (^{241}Pu)
    - detection limit


Thank you for
attention!