Gerda meeting

LNGS 26-28/06/2006

Report on ICP-MS measurement carried out at LNGS on different GERDA samples

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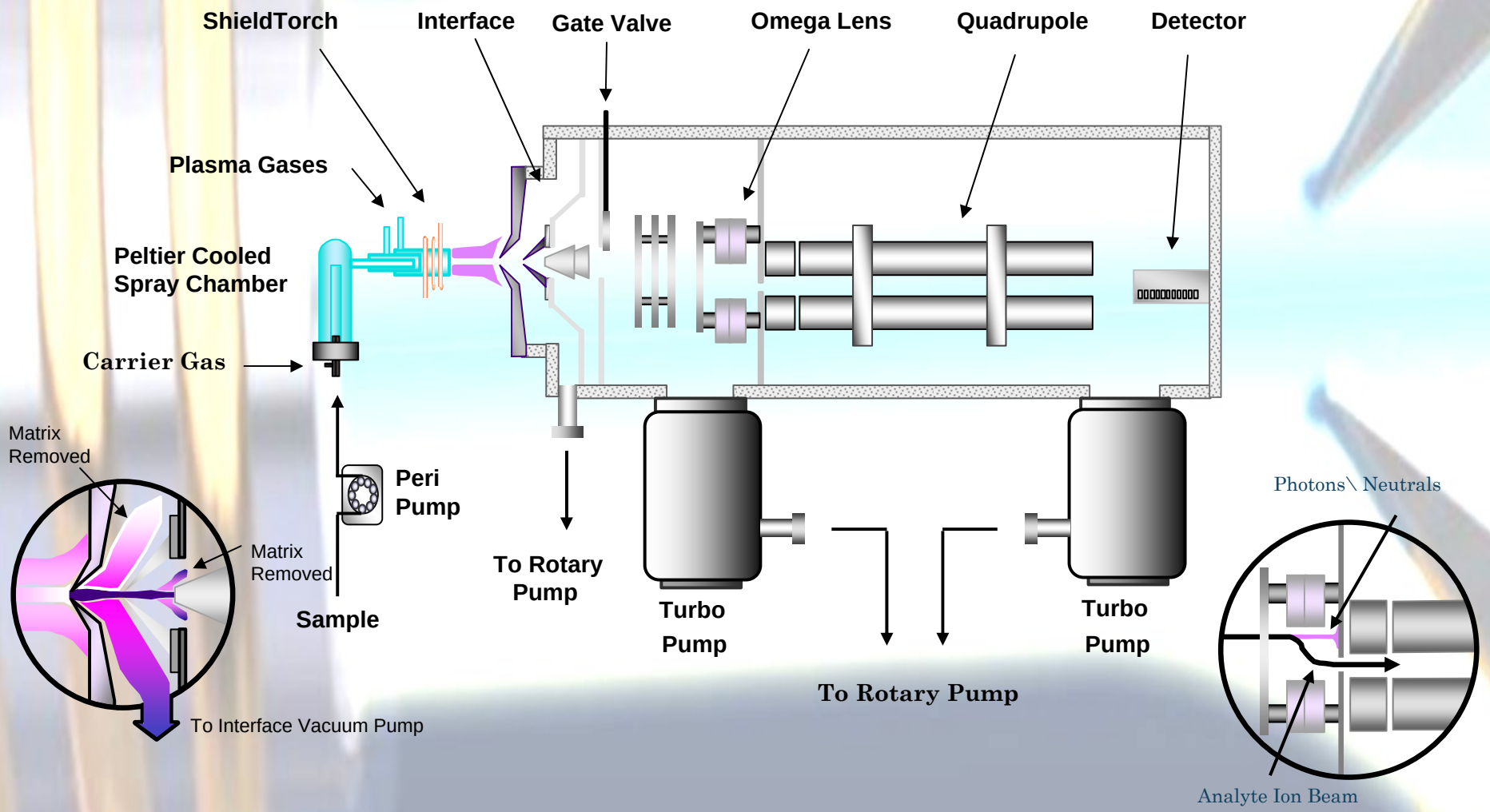
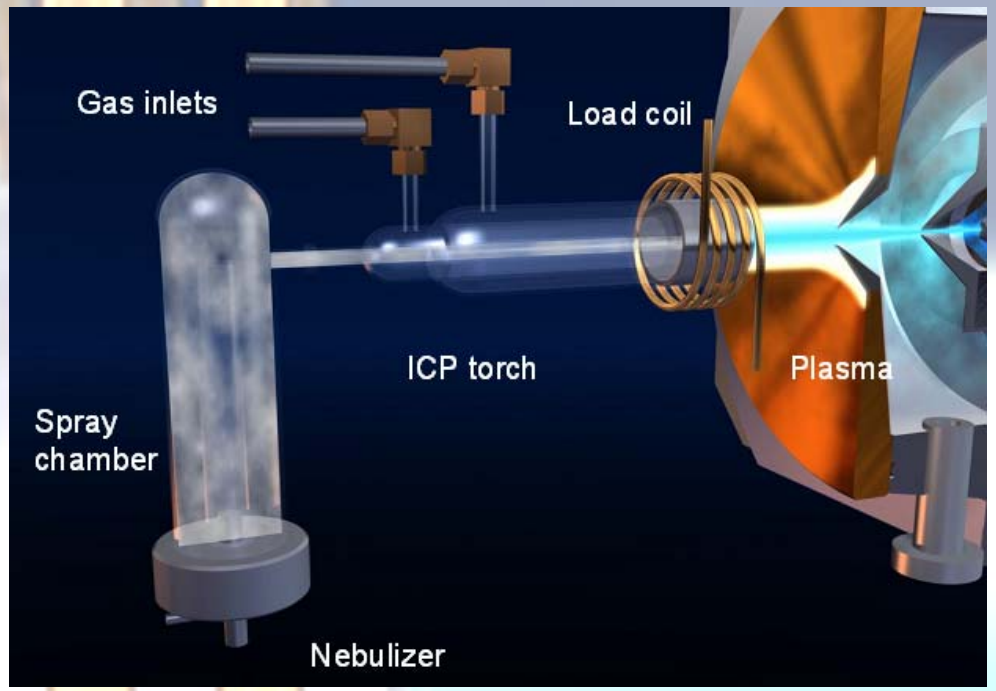
What is ICP-MS ?

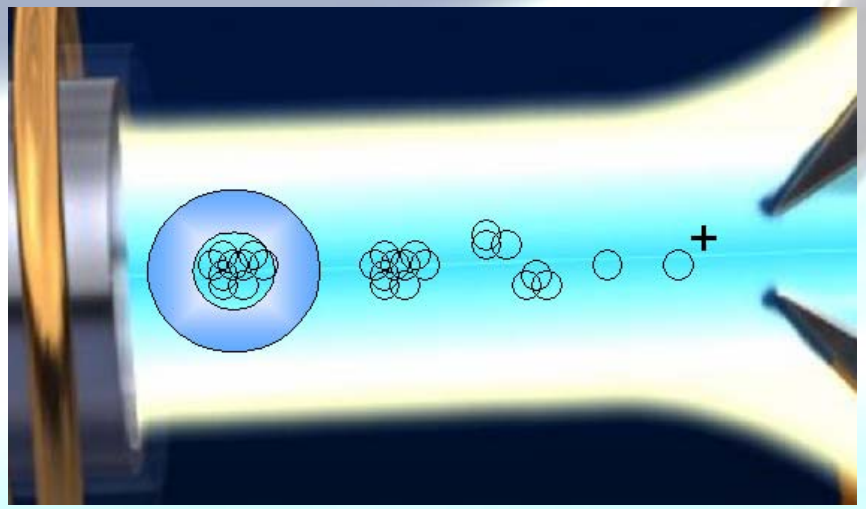
- An inorganic (multi-elemental) analytical technique
- ICP - Inductively Coupled Plasma
  - high temperature ion source decompose and ionize all elements present in the sample
- MS - Mass Spectrometer
  - quadrupole scanning spectrometer
  - mass range from 3to 260 amu (Li to U...)
  - separates all ions in rapid sequential scan
  - ions measured using dual mode detector
    - ppt to ppm levels
    - isotopic information available

Agilent Technologies 7500 Series ICP-MS Schematic

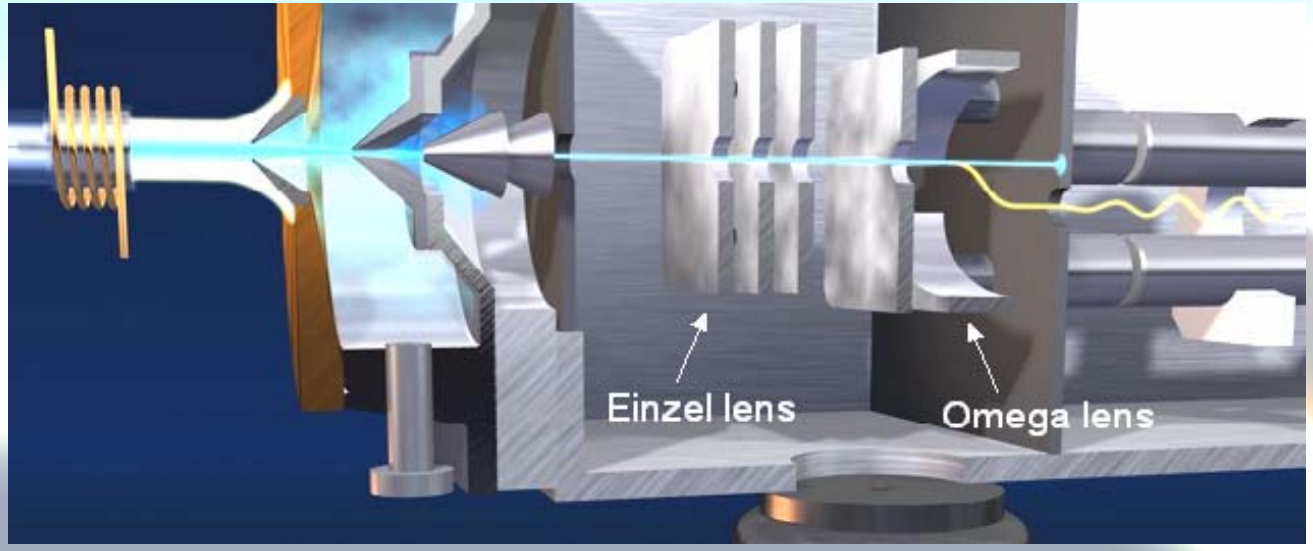


ICP MS Agilent 7500a:





- Sample introduction;
- Aereosol drying, Atomization, Ionization;
- Analysis;
- Detection.

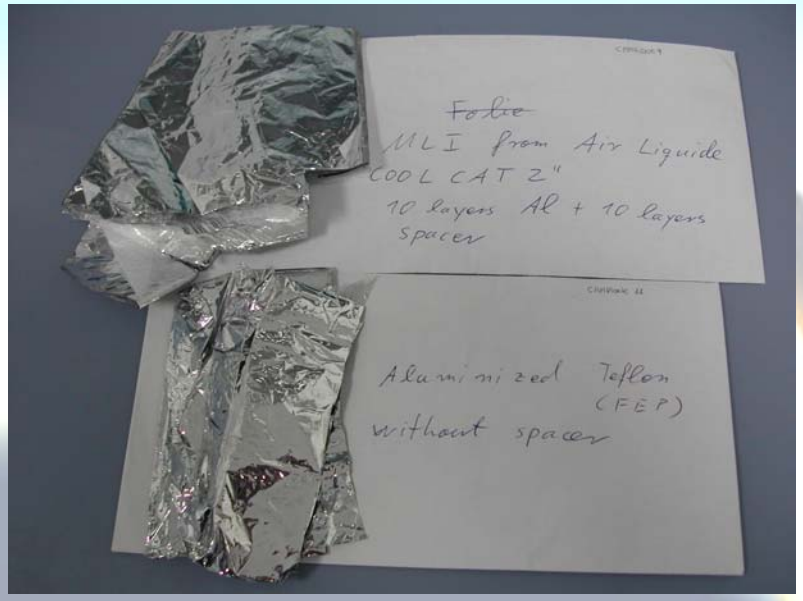


ICP-MS potentiality&sensitivity depending on matrix type

	"cleaned" Solution	Metallic sample	Plastic sample
Ideal sample amount	10ml	0,1-0,5g	0,5-5g
Element	ppb	ppb	ppb
^{39}K	25	2500	250
^{208}Pb	0,005	0,5	0,1
^{232}Th	0,001	0,1	0,01
^{238}U	0,001	0,1	0,01

ICP-MS measurements for GERDA

Purpose: evaluate the K, Pb, Th and U contamination in polymeric substrates with and without metallic cladding by means of ICP-MS



sample #	Sample description
	PLASTIC FOILS
1	Pure PEN (PolyEthylen-Naphthalate)
2	Pure PET (PolyEthylen-Terephtalate)
	MULTI-LAYER SAMPLES
3	PEN + (Cr+Cu sputtered) + (Cu galvanic deposit) + (PCB processing)
4	PET + (Cr+Cu sputtered) + (Cu galvanic deposit) + (PCB processing)
5	PEN + (Cr+Cu sputtered) + (Cu galvanic deposit)
6	PET + (Cr+Cu sputtered) + (Cu galvanic deposit)
7	PEN + (Cr+Cu sputtered)
8	PET + (Cr+Cu sputtered)
	SUPER-INSULATION MATERIALS
9	"COOL CAT 2" from Air Liquid, 10 layers Al+10 layer spacer
10	NAC-2 foil Polyester spacer "bonded" with Al
11	Aluminized Teflon (FEP) without spacer

Before starting trace analysis: choose of reagents…

	K [ppb]	Pb [ppt]	Th [ppt]	U [ppt]
HNO_3 UP 20%	<25	<10	<1	<1
HNO_3 SP 20%	<25	15	<1	<1
HCl UP 20%	<25	20	<1	<1
Detergent ELMA65 1%	<25	120	1	13
DETERGENT8 ALCONOX 1%	250	5	<0.2	<0.2

✓ Ultra-pure acids selected for all steps of the sample preparation;

✓ Detergent8 fine for the purpose even if K level is quite high;

… and containers: polyethylene bags for washing

	K [ppb]	Pb [ppt]	Th [ppt]	U [ppt]
PE bag H_2O demi rinse HNO_3 UP 2%	<25	8	<1	<1

and crucibles for ashing

	K [ppb]	Pb [ppt]	Th [ppt]	U [ppt]
Pt crucible *	<25	1300	30	28
Quartz crucibles 1 *	<25	310	~1	<1
Quartz crucibles 2 *	<25	59	<1	<1
Porcelain crucible 1 *	<25	130	6	2
Porcelain crucible 2 *	<25	27	3	1
Quartz crucible HNO_3 UP 1% 5 days	<25	<5	<1	<1

contamination level is the lowest also after high T thermal cycle

* 2h muffle furnace 600°C + HNO_3 20% 80°C 30 min
→ procedure simulation

SAMPLE PREPARATION (1)

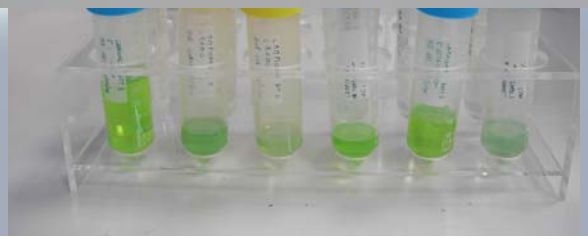
1 solution to
ure for
without
cladding

Cu lay

N or PET) layer

Cu is placed in solutio
with HNO3 (UltraP

g technique:
l decomposition
00°C for 2 h
l ash leached
20% at 85°C



SAMPLE PREPARATION (2)

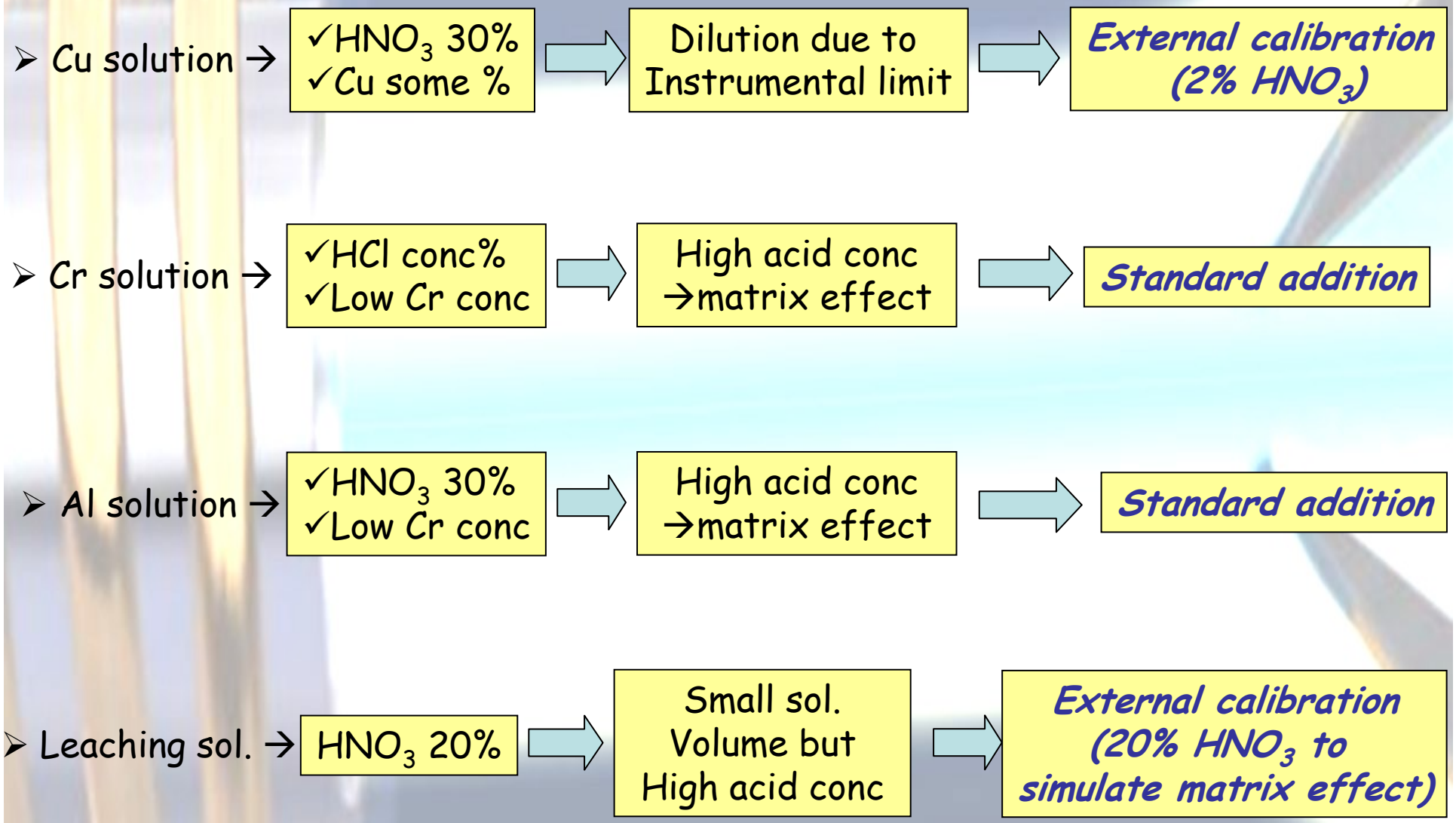
Super-insulation material

1) weighed by analitycal balance;
2) cut;
3) weighed by ultrasound bath (UP water)

Al layer	Plastic layer
Al is placed in solution by acid digestion with HNO_3 (UP)	**Dry ashing technique:** **1) combustible portion destroyed by thermal decomposition up to 600°C for 2 hours** **2) residual ash dissolved in HNO_3 20% at 85°C repeated twice**

2 solutions to measure

Sample treatment



Collected solutions for ICP-MS & AAS

Data analysis

SAMPLE 4				
	K [ppb]	Pb [ppt]	Th [ppt]	U [ppt]
Washing sol. 1%	174 ± 1%	60 ± 2%	<1	<1
BLK for etching	<25	<5	<1	<1
Cu	17 ± 3%	201 ± 2%	<1	<1
Cr	<25	302 ± 22%	2 +/- 25%	2 ± 25%
BLK for ashing	<25	91 ± 4%	<1	<1
PET	<25	1592 ± 6%	19 ± 5%	111 ± 7%

BLK subtraction and dilution factor (Al & Cr weight by AAS)

S 4	**Weight** [%]	**K** [ppb]	**Pb** [ppb]	**Th** [ppt]	**U** [ppt]
Cu	70.58	3014 ± 2.5%	35 ± 1.6%	< 174	< 174
Cr	0.32	<144200	1743 ± 22%	11540 ± 25%	11540 ± 25%
PET	29.1	<560	35.5 ± 6%	433 ± 5%	2470 ± 7%

Taking into account mass fraction of each layer respect whole sample…

polymeric substrates w/o metallic cladding

		Weight	K	Pb	Th	U
		[%]	[ppb]	[ppb]	[ppt]	[ppt]
1	Pure PEN	100	< 393	26 ± 3	< 16	< 16
2	Pure PET	100	480 ± 110	53 ± 5	522 ± 52	3714 ± 37
3	Cu	77.59	3210 ± 160	16.3 ± 0.1	< 124	134 ± 2
	Cr	0.21	< 183	1.4 ± 0.2	<7.3 ± 3.7	<7
	PEN	16.2	< 66	4.2 ± 0.4	< 3	< 3
	Whole samp.		$3210\ ^{+170}_{-160}$	21.9 ± 0.5	$7\ ^{+42}_{-4}$	$134\ ^{+3}_{-2}$
4	Cu	70.58	2127 ± 53	24.7 ± 0.4	< 123	< 123
	Cr	0.32	< 461	5.6 ± 1.2	37 ± 9	37 ± 9
	PET	29.1	< 162	10.3 ± 0.6	126 ± 6	719 ± 50
	Whole samp.		$2130\ ^{+170}_{-50}$	40.6 ± 1.4	$163\ ^{+42}_{-11}$	$756\ ^{+65}_{-51}$
5	Cu	82.03	1646 ± 21	7.0 ± 0.4	< 135	< 135
	Cr	0.25	< 270	3.5 ± 0.2	<10	<10
	PEN	17.72	< 85	4.3 ± 0.3	<3	<3
	Whole samp.		$1646\ ^{+97}_{-21}$	14.8 ± 0.5	<148	< 148
6	Cu	88.26	< 1475	5.9 ± 0.4	< 147	< 147
	Cr	0.17	< 298	3.8 ± 0.4	61 ± 12	19 ± 1
	PET	11.57	84.2 ± 3	7.8 ± 0.4	64.8 ± 8	586 ± 18
	Whole samp.		$84\ ^{+500}_{-3}$	17.5 ± 0.4	$126\ ^{+51}_{-14}$	$605\ ^{+52}_{-18}$
7	Cu	17.29	1290 ± 170	8.6 ± 0.4	< 76	< 76
	Cr	1.68	< 3041	10.4 ± 0.5	< 122	< 122
	PEN	81.03	<365	55 ± 3	< 144	< 90
	Whole samp.		$1290\ ^{+1040}_{-170}$	74 ± 3	< 342	< 288
8	Cu	16.93	1574 ± 79	20.7 ± 0.3	< 85	86 ± 14
	Cr	1.27	< 3430	26 ± 2	< 140	< 140
	PET	81.8	412 ± 29	45 ± 2	452 ± 27	3700 ± 190
	Whole samp.		$1990\ ^{+1150}_{-80}$	92 ± 3	$452\ ^{+61}_{-84}$	3790 ± 190

- ✓ PEN samples cleaner than PET ones.
- ✓ Th & U contribution of Cu and Cr layers under detection limit.
- ✓ In multi-layer samples with a PET core contamination mainly comes from the plastic and there is an indication that during the etching of the Cr layer some contaminants have been extracted from the plastic core.

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Super-insulation materials

#		Weight	K	Pb	Th	U
		[%]	[ppb]	[ppb]	[ppt]	[ppt]
9	Al	0.73	526 ± 32	122 ± 2	44 ± 4	23 ± 4
	MLI	99.27	3860 ± 120	158 ± 6	77 ± 5	92 ± 6
	MLI 2nd		51 ± 4	5.5 ± 0.2	2.8 ± 0.4	< 2.3
	Whole		4435 ± 120	286 ± 6	124 ± 6	115 ± 7
10	Al	0.55	1045 ± 105	545 ± 11	831 ± 50	458 ± 9
	NAC-2	99.45	1775 ± 71	288 ± 12	864 ± 43	1420 ± 71
	NAC-2 2nd		< 270	< 10	84 ± 6	25 ± 5
	Whole		$2820\ ^{+160}_{-130}$	$833\ ^{+17}_{-16}$	1779 ± 66	1903 ± 72
11	Al	1	824 ± 16	138 ± 6	90 ± 7	91 ± 4
	Teflon	99	306 ± 15	13.6 ± 0.8	161 ± 10	23 ± 2
	Teflon 2nd		949 ± 19	4.2 ± 0.1	22 ± 2	4.7 ± 0.3
	Whole		2079 ± 29	156 ± 6	273 ± 12	119 ± 4

Sample 9 ("COOL CAT 2" from Air Liquid) and sample 11 (Aluminized Teflon, FEP) are cleaner than sample 10 (NAC-2).

Specific activities for ^{40}K, ^{232}Th, ^{238}U deriving from the concentrations obtained by ICP-MS

Sample	^{40}K	^{232}Th	^{238}U
	[mBq/kg]	[mBq/kg]	[mBq/kg]
1	< 12	< 0.07	< 0.2
2	14.6 ± 3.3	2.1 ± 0.2	46.1 ± 0.5
3	97 ± 5	$0.03\ ^{+0.17}_{-0.02}$	$1.66\ ^{+0.04}_{-0.02}$
4	$65\ ^{+5}_{-2}$	$0.66\ ^{+0.17}_{-0.04}$	$9.4\ ^{+0.8}_{-0.6}$
5	$49.9\ ^{+2.9}_{-0.6}$	< 0.6	< 1.8
6	$2.6\ ^{+15.2}_{-0.1}$	$0.51\ ^{+0.21}_{-0.06}$	$7.5\ ^{+6.4}_{-0.2}$
7	$39\ ^{+35}_{-5}$	< 1.4	< 3.6
8	$60\ ^{+35}_{-2}$	$1.8\ ^{+0.2}_{-0.3}$	47 ± 2
9	135 ± 4	0.50 ± 0.02	1.43 ± 0.09
10	86 ± 5	7.2 ± 0.3	23.6 ± 0.9
11	63 ± 1	1.11 ± 0.05	1.48 ± 0.05

Comparison between γ-spectroscopy and ICP-MS measurements

		^{40}K [mBq/kg]	^{232}Th [mBq/kg]	^{238}U [mBq/kg]
NAC-2	γ-spectroscopy	81 ± 19	5.0 ± 2.0	22 ± 2
	ICP-MS	86 ± 5	7.2 ± 0.3	23.6 ± 0.9

ICP-MS technique allows direct determination of Th and U concentration both in the whole sample and in the individual layers. Concerning g-spectroscopy, ^{232}Th and ^{238}U are determined measuring respectively ^{228}Th and ^{226}Ra.

The 2 techniques are therefore complementary and in this case the results are in good agreement

Conclusions

- Developed a reliable methodic for evaluating the K, Pb, Th and U contamination in polymeric substrates with and without metallic cladding by means of ICP-MS;
- Polymeric substrates w/o metallic cladding:
  - ✓ **PEN samples are significantly cleaner in Th and U of about two orders of magnitude than PET ones.**
  - ✓ **The PEN sample that underwent the complete Cu and Cr deposition and PCB processing (sample 3) has an acceptable Th and U concentration. The specific activity of ^{232}Th and ^{238}U is compatible with the specification for cables surrounding crystals to match the rate of 10^{-3} count/(kg·keV·y). [K.Kroninger et al. Techinical Report GSTR-05-019]; ^{232}Th is in the worst case, an order of magnitude below the limit determined by MC (1.7 mBq/kg), while ^{238}U is just at the limit (1.7 mBq/kg).**
- Super-insulation materials:
  - ✓ **Sample 9 ("COOL CAT 2" from Air Liquid) and sample 11 (Aluminized Teflon, FEP) are cleaner than sample 10 (NAC-2). Contamination level in Th and U for samples 9 and 11 are roughly the same and the specific activity of ^{232}Th is well below (about a factor 5) the limit derived from the MC (5 mBq/kg).**

GeO_2 powder isotopic analysis

- Sample 1, Ge 1711, P8. & Sample 2, Ge 1714, P8:
  200 mg of each sample dissolved in solution of nitric acid, hydrofluoric acid, water (1:1:1). The obtained solution has been diluted up to about 1 ppm of Ge before measurement.

	^{70}Ge [%]	^{72}Ge [%]	^{73}Ge [%]	^{74}Ge [%]	^{76}Ge [%]
S 1 Ge 1711	0.0014±0.0001	0.0273±0.0005	0.110±0.001	10.35±0.02	**89.51±0.02**
S 2 Ge 1714	<0.0006	0.028±0.002	0.129±0.004	10.94±0.02	**88.90±0.02**

The uncertainties reported in the table are statistical (1s). The total error of result, evaluated for comparison with previuos measurements, is <1 on ^{76}Ge isotope percentage abundance.

Ge isotopic measurement for GNO

	Ge70 %	Ge72 %	Ge73 %	Ge74 %	Ge76 %
Carrier 70Ge	96,47 96,784	1,14 1,090	0,35 0,320	1,46 1,316	0,57 0,490
Carrier 72Ge	0,36 0,355	98,54 98,609	0,23 0,223	0,73 0,683	0,14 0,129
Carrier 74Ge	0,42 0,444	0,64 0,639	0,23 0,230	98,5 98,486	0,21 0,201

BLUE VALUE=LNGS measure carried out by ICP-MS (quadrupole mass analyzer)
GREEN VALUE=MC-ICP-MS (double focusing-multicollector) carried out from ITU of JRC Karlsrhue