UNIVERSITAT DE BARCELONA

Radionuclide determinations with:

- **PSresin** (separation and detection)
- **MASS** (automated separation)
- **WaterRadd** (on-line detector)

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- **PSresin** (separation and detection)
- **MASS** (automated separation)
- **WaterRadd** (on-line detector)

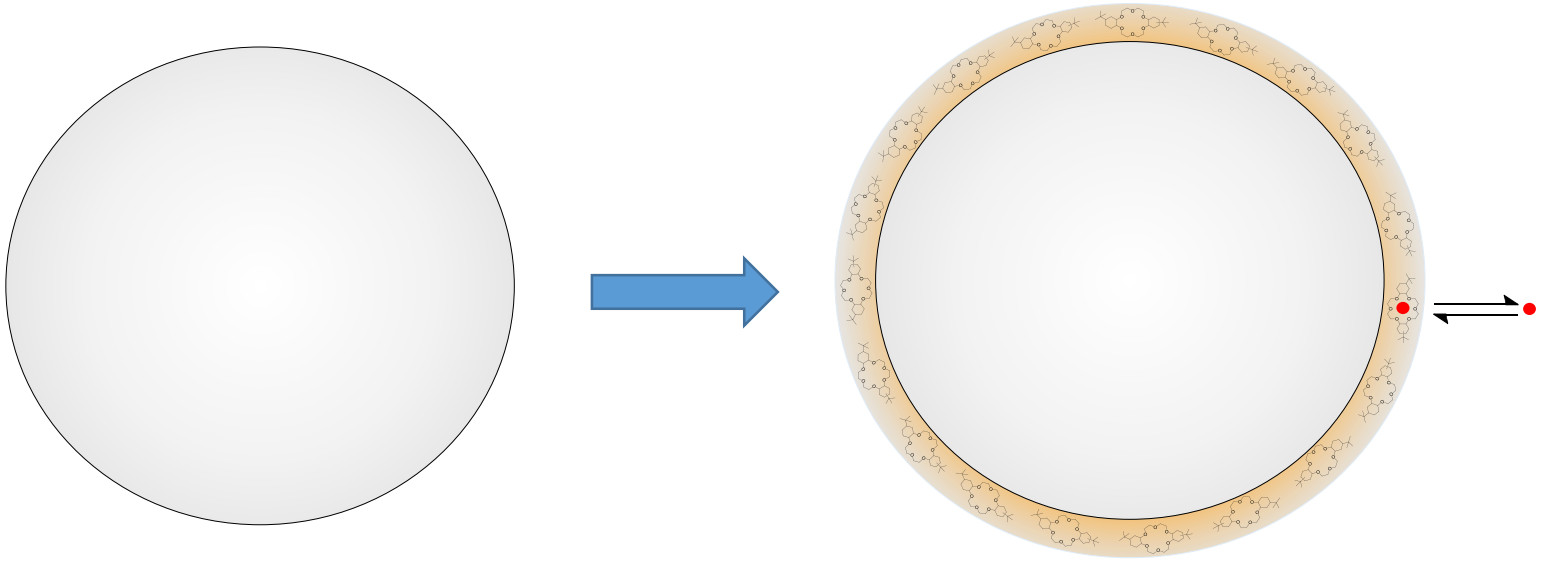
Common purpose: - increase **laboratory capability** by reducing
. Reagents
. Waste
. man-power
. time

- **easier** and **friendly** radionuclide determinations

PSresin (Separation and detection)

Plastic Scintillating resins (PSresin) – Extractive Scintillating resins

PSresin is a Plastic Scintillating microsphere (PSm) with a selective extractant



PSm

PSresin

Detection provided by the PSm

Selectivity based on the extractant interaction

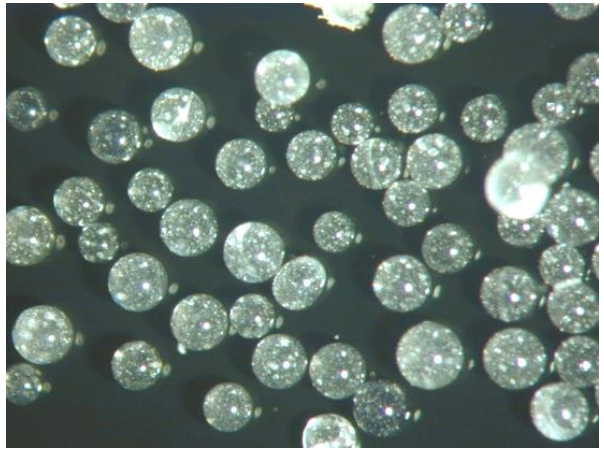
Psresin UNIFIES CHEMICAL SEPARATION + PREPARATION FOR MEASUREMENT STEPS

PSresin (Separation and detection)

Plastic Scintillating microspheres (PSm)

PSm is a solid "scintillation cocktail"

PSm solid platform to implement separation strategies



Composition: . Solvent: . Polystyrene, Polyvinyiltoluene.

. Scintillators: PPO, POPOP, , p-T, bis-MSB ....

Format: . Plastic scintillator microspheres (PSm) (10 – 300 µm)

. Plastic scintillator foils (PSf) (50 – 100 µm)

Detection capabilities.

. Sample solution

Beta

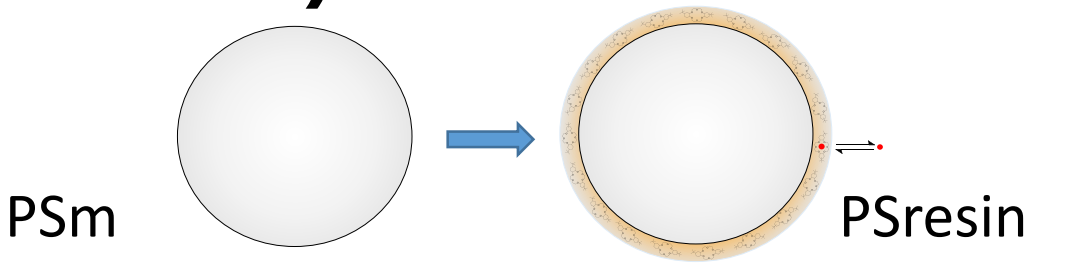
Particle size (µm)	^{3}H (%)	^{14}C (%)	^{90}Sr/^{90}Y (%)
57	1,8	63	190

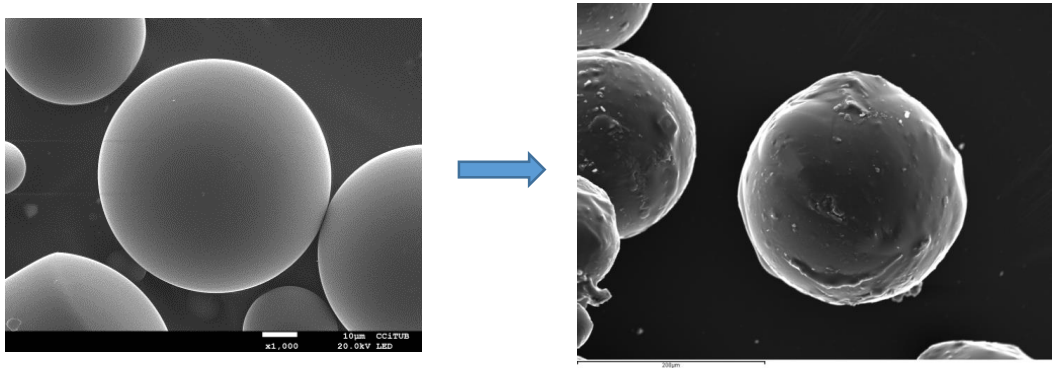
Alpha

Particle size(µm)	^{241}Am(%)	^{236}U (%)
70 µm	96	75

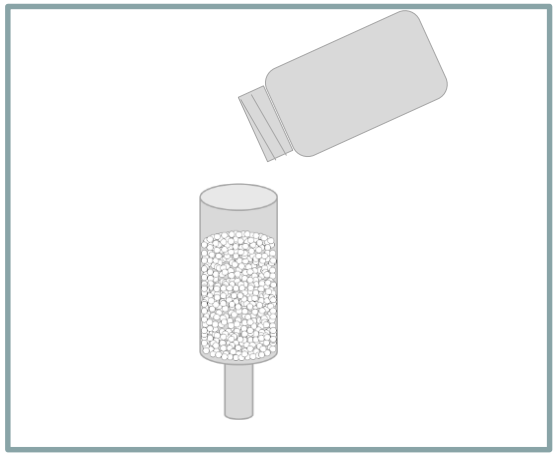
PSresin (Separation and detection)

PSresin in practice

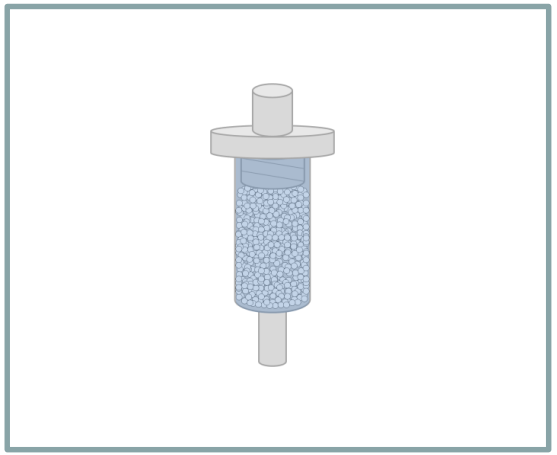




Cartridge preparation



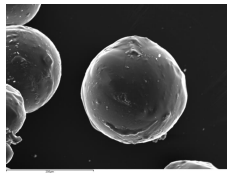
Add 1-1.5 g PSresin



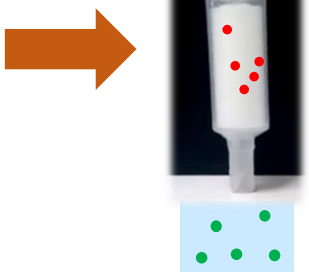
Package the column

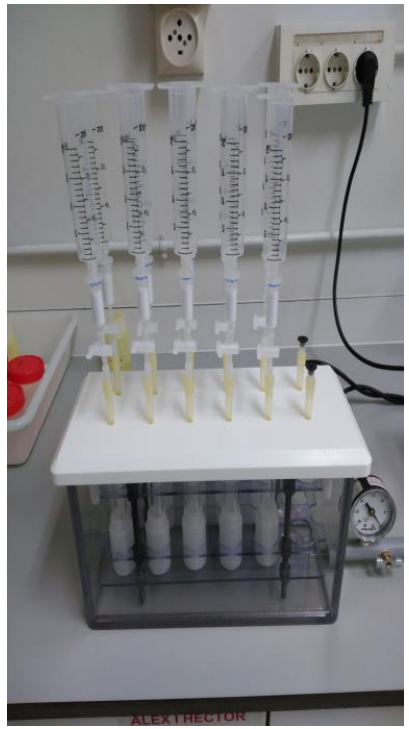
PSresin (Separation and detection)

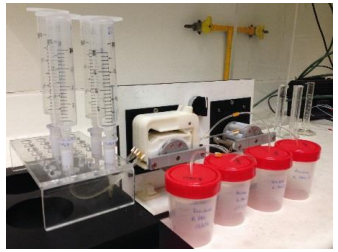
PSresin in practice



PSresin

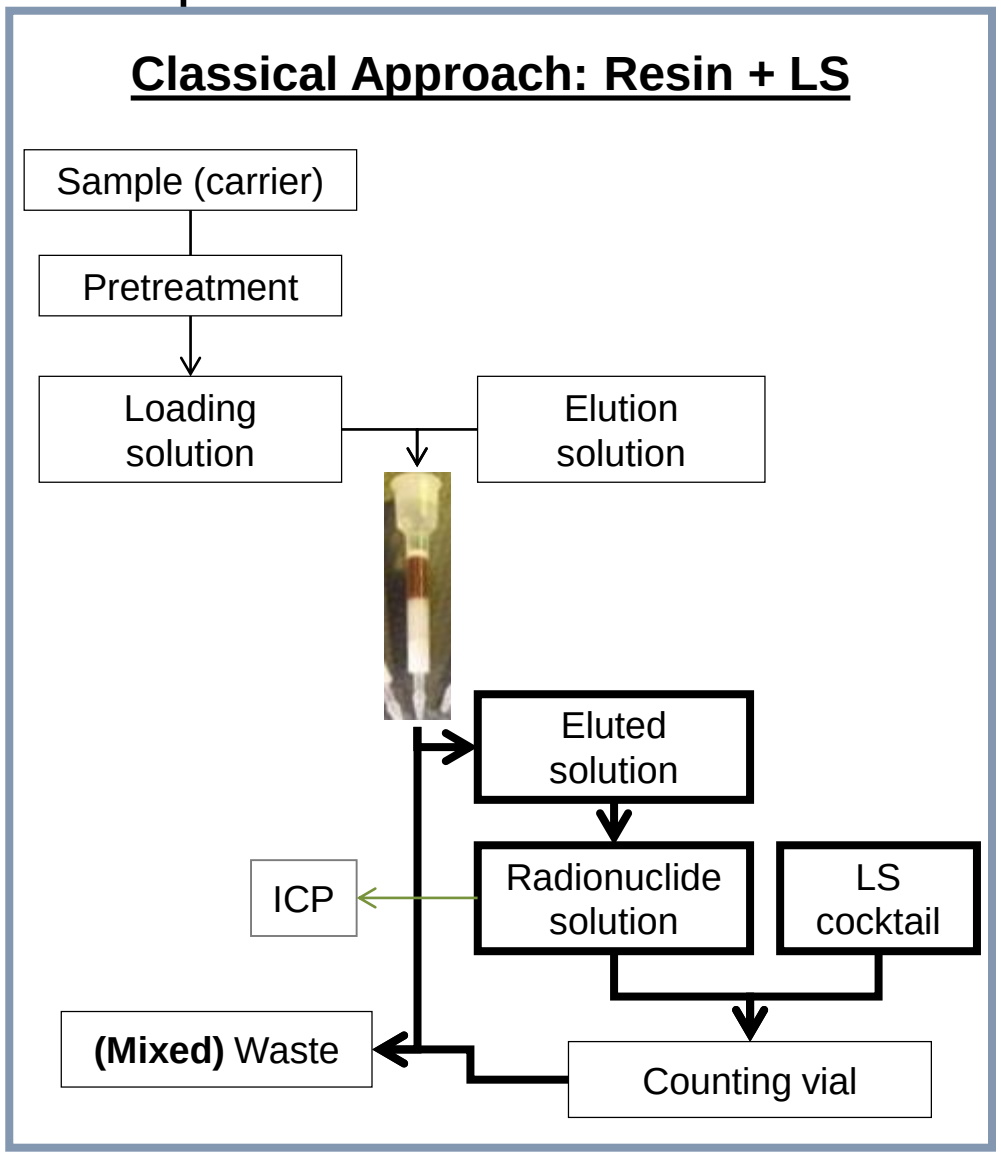


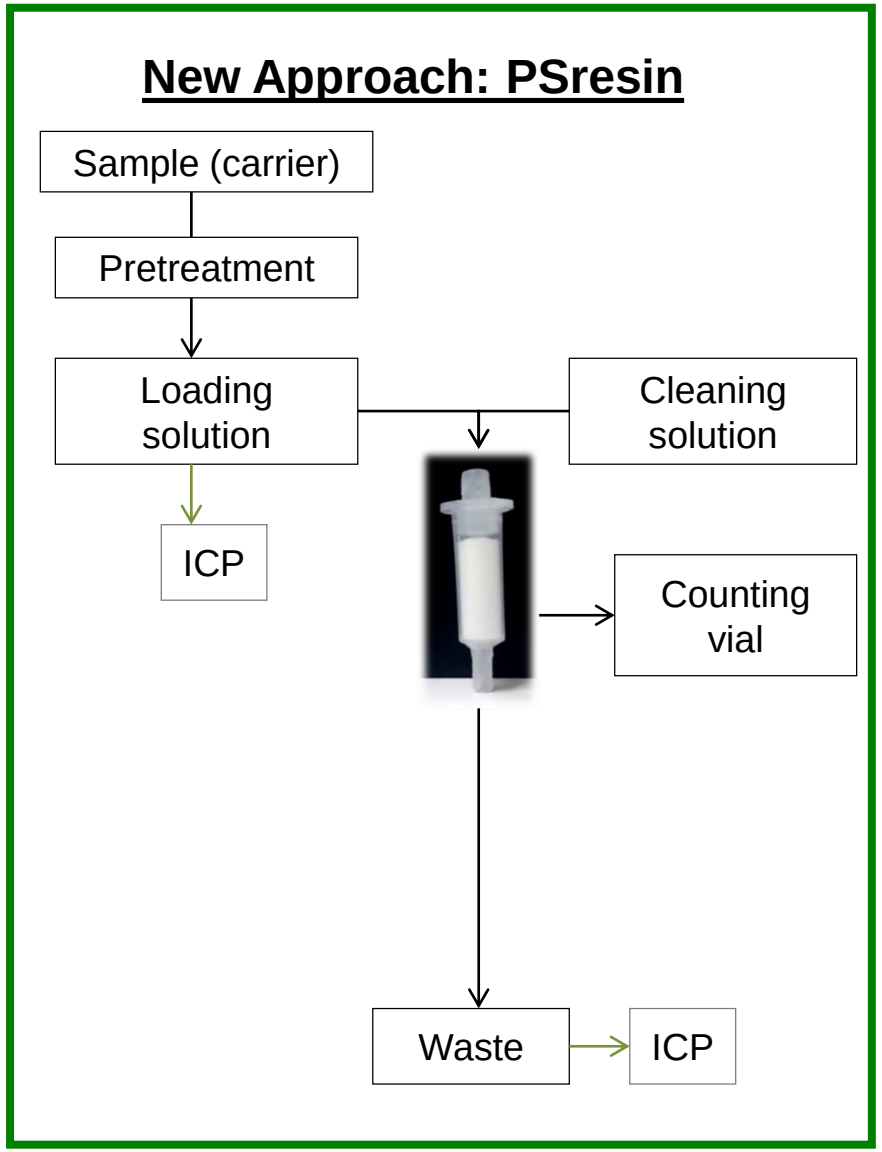




PSresin (Separation and detection)

PSresin in practice





Save….

PSresin (Separation and detection)

PSresin applications

- **Determination of ^{99}Tc in aqueous/urine samples**
- Determination of ^{14}C in radiotracer samples
- **Determination of ^{89}Sr/^{90}Sr in milk samples in emergency situations**
- Determination of ^{210}Pb in water
- Determination of ^{210}Pb in Bronze sculptures

PSresin (Separation and detection)

PSresin applications: Determination of ^{99}**Tc** in **aqueous/urine** samples

PSresin: **UB - PSm of 60 µm**

Vial-column format: **2 mL SPE cartridge**

Separation device: **vacuum box**

Carrier**: 1 mg of Re**

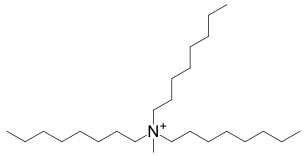
Recovery of Rhenium (by ICP-OES)	> 98.8 %
Recovery of ^{99}Tc (by LS):	> 98.8 %
^{99}Tc Detection Efficiency (%):	89.5(0.6)
Background (cpm):	1.09
Quenching Parameter (SQP(E)):	787(7)

Extractant: Aliquat 336

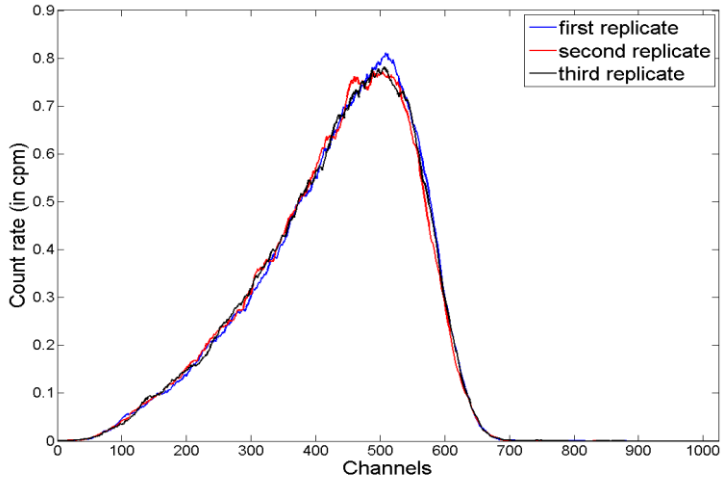
Conditioning: 2 mL HCl 0.1M

Sample: 10 mL in HCl 0.1M

Cleaning: 2 mL water 4 times



Breakthrough volume > 200 mL



PSresin (Separation and detection)

PSresin applications: Determination of ^{99}**Tc** in **WATER** samples

Extractant: Aliquat 336

Spike sample to achieve HCl 0.1M

Cleaning: Water

Sample	Activity (dpm mL^{-1})	Activity Calc (dpm mL^{-1})	Error (%)
Sea Water	24,3	23,0	**-5,3**
Sea Water	24,3	25,1	**3,3**
Sea Water	24,2	22,8	**-6,2**

PSresin (Separation and detection)

PSresin applications: Determination of ^{99}**Tc** in **URINE** samples

Extractant: Aliquat 336

Sample: 100 mL of urine

Pretreatment:

- Add 10 mL of 65% HNO3 and evaporate to dryness
- Dissolved in 5 mL of 65% HNO3
- Evaporated to dryness
- Heat at 550 C in a muffle oven for 30 min.
- Dissolved in 3mL of HNO3
- Treated with 100 mL of D.D. water
- Add 5 mL of H2O2 and heated to 90 C for 1 h

Cleaning: Water

Sample	Activity (dpm mL^{-1})	Activity Calc (dpm mL^{-1})	Error (%)
Urine	0,43	0.44	**2,4**
Urine	0,46	0,42	**-6.5**

- **MDA (100 mL, 24h):** 0.036 Bq L^{-1}

MASS (Modular Automated Separation System)

PSresin + MASS. Determination of **^{99}Tc in WATER** samples - **Automatic vs. Manual**:

MASS:
Similar to manual process.

. Modular
. Vacuum chamber
. No valves (easy maintenance)

Procedure

1. Conditioning: 2 mL HCl 0.1M
2. Sample loading: 10 mL
3. 1st, 2nd and 3rd cleaning: 2 mL HF 0.1M/HNO_3 0.1M
4. 4th cleaning : 2 mL H_2O

Calibration

10mL containing 240 dpm of ^{99}Tc, 1 mg of Re in HCl 0.1M

	Manual [%]	Automatic [%]
Background (cpm)	1.28	1.06
Yield	Quantitative (>98.8%)	Quantitative (>99.8%)
SQP(E)	802(8)	795(5)
Detection efficiency [%]	85.3(1.3)	88.2(1.3)

MASS (Modular Automated Separation System)

PSresin + MASS. Determination of **^{99}Tc in WATER** samples - **Automatic vs. Manual**:

River water sample	Activity [Bq/Kg]	Activity measured [Bq/Kg]		Deviation [%]	
		Manual	Automated	**Manual**	**Automated**
1st replicate	18.2	16.9	18.6	**-7.3**	**2.1**
2nd replicate	16.8	17.0	16.8	**1.2**	**0.1**
3rd replicate	18.0	18.3	17.7	**1.7**	**-1.5**
Mean				**-1.5(5.1)**	**0.2(1.8)**

Sea water sample	Activity [Bq/Kg]	Activity measured [Bq/Kg]		Deviation [%]	
		Manual	Automated	**Manual**	**Automated**
1st replicate	17.5	17.4	17.6	**-0.8**	**0.6**
2nd replicate	17.4	17.2	18.1	**-1.2**	**4.0**
3rd replicate	18.9	18.0	17.7	**-5.0**	**-6.4**
Mean				**-2.4 (2.3)**	**-0.6 (5.3)**

PSresin (Separation and detection)

PSresin applications: Determination of ^{14}C in **OIL RESERVOIR** radiotracer

Oil reservoir radiotracer: **$S^{14}CN^-$**
Secondary recovery
Study of oil reservoir dynamics

Pre-treatment:

Filter
Concentration & purification with ionic exchange column
Elute with $NaClO_4$ 6 M

Extractant: Aliquat 336

Separation conditions: water

- **Recovery:** 100 %
- **Detection efficiency:** 54(1)%
- **MDA (100 mL, 5h):** 0.084 Bq L^{-1}

Sample	Conductivity (mS cm^{-1})	TOC (mg L^{-1})	Activity (Bq L^{-1})	
			PS resin	IFE
1	52.1 ± 0.1	13.6 ± 0.3	2.89 ± 0.14	2.98 ± 0.09
2	51.5 ± 0.2	18.4 ± 0.3	2.01 ± 0.04	2.21 ± 0.06
3	50.8 ± 0.2	22.4 ± 0.7	1.00 ± 0.09	1.02 ± 0.07
4	51.3 ± 0.1	39.2 ± 0.6	1.42 ± 0.02	1.36 ± 0.05
5	51.5 ± 0.2	18.4 ± 0.7	2.66 ± 0.08	2.76 ± 0.08

Analytica Chimica Acta 736 (2012) 30– 35

PSresin (Separation and detection)

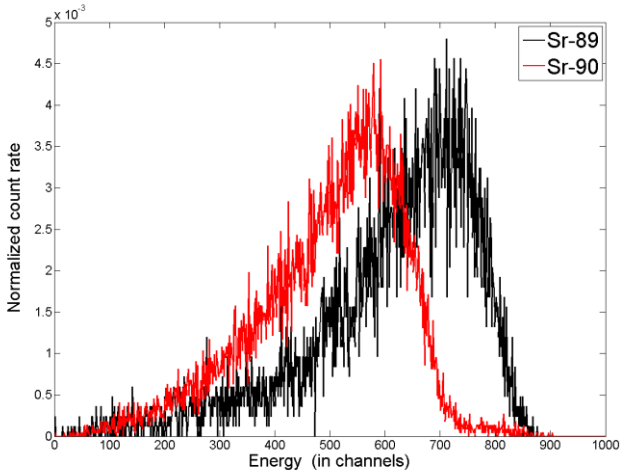
PSresin applications: Determination of **^{89}Sr/^{90}Sr** in **milk** in **emergency** situations

Objective: reduction of total **analysis time**.

Extractant: 4,4'(5')-di-t butylcyclohexane 18-crown-6 1M Octanol

Sample: 100 mL milk

Detection efficiency



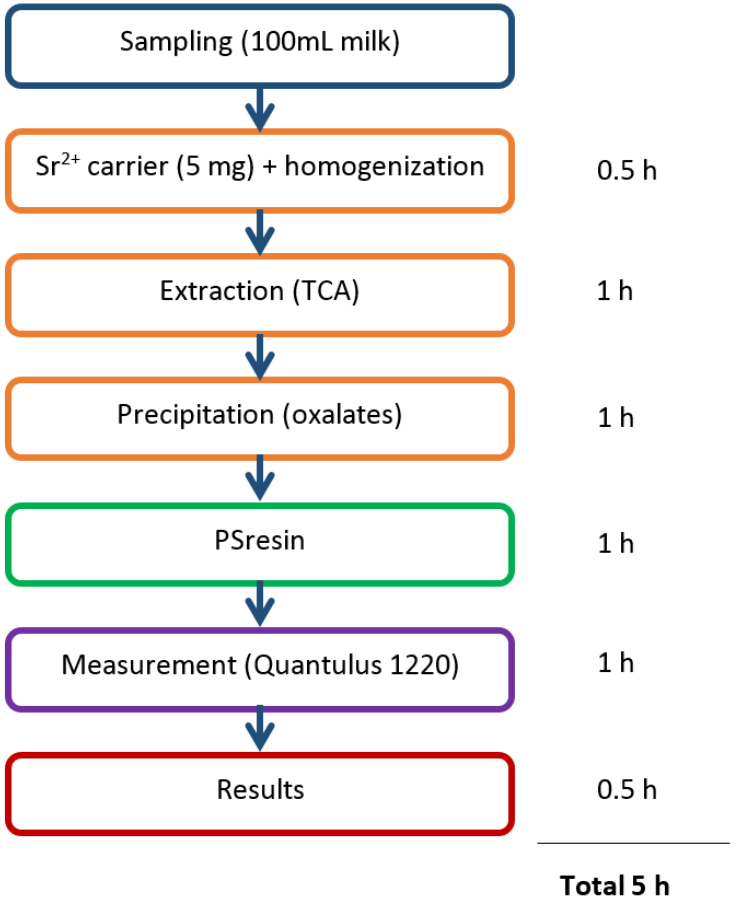
	^{90}Sr	^{89}Sr
Stable Sr) (mg)	3, 4, 5, 6, 7	3, 4, 5, 6, 7
Average SQP(E)	789(8)	791(4)
Average Efficiency) (%)	82(7)	89(4)

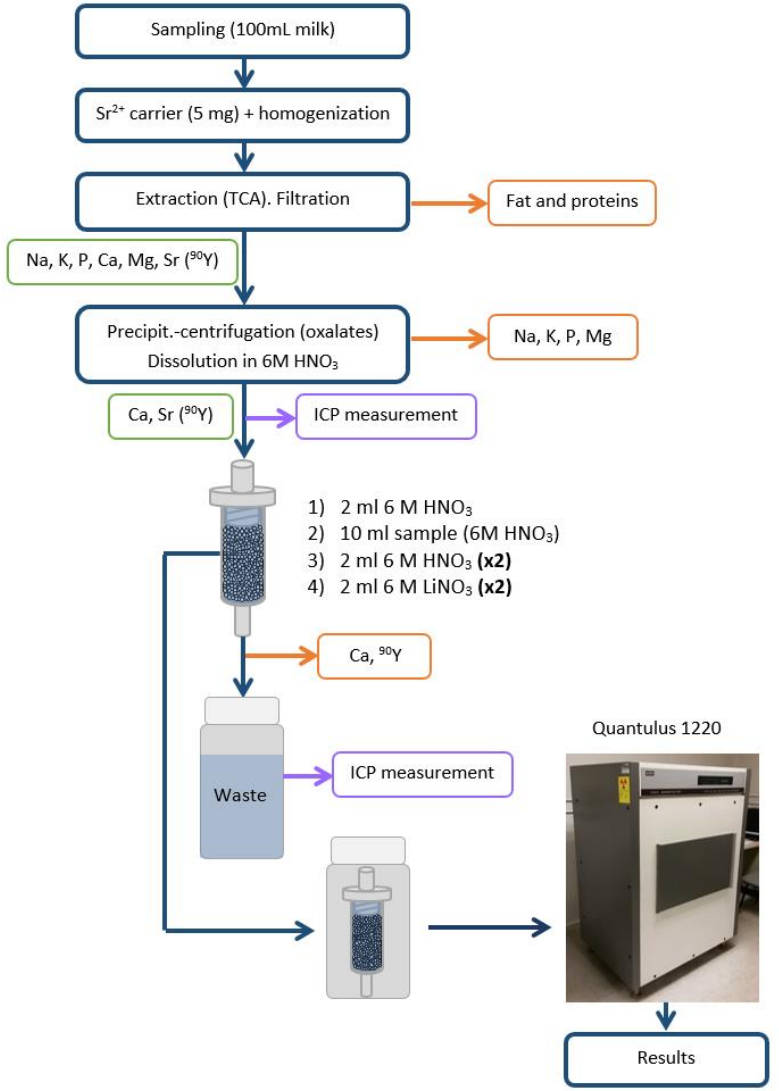
^{90}Sr+^{89}Sr Average Efficiency (%): 86(6)

PSresin (Separation and detection)

PSresin applications: Determination of $^{89}Sr/^{90}Sr$ in **milk** in **emergency** situations

Objective: reduction of total **analysis time**.





PSresin (Separation and detection)

PSresin applications: Determination of $^{89}Sr/^{90}Sr$ in **milk** in **emergency** situations

Objective: reduction of total **analysis time**.

Sample: 100 mL milk (Cow, Sheep, Goat, Semi-skimmed, Skimmed,Powder, Pasteurized)

Pre-treatment:

. TCA, Oxalates, redisolution in HNO_3 6 M.

Cleaning: HNO_3 6 M and $LiNO_3$ 6 M

Carrier: 5 mg Sr^{2+}

Type of milk	Pre-treatment Recovery (%)	Column Recovery (%)	Total Recovery (%)
Total samples	93 (4) (4%)	70(4) (6%)	**65 (5) (7%)**

Type of milk	Pre-treatment recovery (%)	PS resin retention (%)	Total recovery (%)	Activity $^{90}Sr+^{89}Sr$ (Bq/kg dry mass)	Relative bias $^{90}Sr+^{89}Sr$ (%)
IAEA-473 milk powder	88.6	79.6	70.5	207.6 (198.0*)	**-3.5 (0.4*)**
IAEA-473 milk powder	93.1	78.7	73.3	204.6 (195.7*)	**-4.7 (-0.8*)**
IAEA-473 milk powder	92.1	76.7	70.6	203.3 (194.4*)	**-5.2 (-1.4*)**

MDA (100 mL, 1h): 0.36 Bq L^{-1}

PSresin (Separation and detection)

PSresin applications: Determination of **$^{89}Sr/^{90}Sr$** in **milk** in **emergency** situations

Type of milk	Ratio $^{89}Sr/^{90}Sr$	Relative bias (^{89}Sr + ^{90}Sr) (%)
Cow/whole/UHT	0:1	**-2.2 (1.9*)**
Cow/whole/UHT	1:0	**6.6 (3.0*)**
Cow/whole/UHT	1:1	**-1.9**
Cow/semi-skimmed/UHT	1:1	**4.5**
Cow/skimmed/UHT	1:1	**6.1**
Cow/whole/powder	1:1	**1.7**
Cow/whole/pasteurized	1:1	**2.6**
Goat/whole/raw	1:1	**-1.9**
Sheep/semi-skimmed/UHT	1:1	**7.0**
Goat/semi-skimmed/UHT	1:1	**5.2**

Type of milk	Ratio $^{89}Sr/^{90}Sr$	Relative bias (^{89}Sr + ^{90}Sr) (%)
Cow/whole/UHT	2:1	**1.6**
Sheep/semi-skimmed/UHT	2:1	**20.2**
Goat/semi-skimmed/UHT	2:1	**6.5**
Cow/whole/UHT	10:1	**-4.1**
Sheep/semi-skimmed/UHT	10:1	**-3.9**
Goat/semi-skimmed/UHT	10:1	**-4.1**

PSresin (Separation and detection)

PSresin applications: Determination of ^{89}**Sr/**^{90}**Sr** in **milk** in **emergency** situations

Objective: reduction of total **analysis time**.

Procedure	Sample (L)	Sr^{2+} carrier (mg)	Recovery % (SD)	Measurement	Relative Bias ^{90}Sr % (SD)	MDA (Bq L^{-1})	Time (h)
Brun et al., 2002	0.5	10	63 (7)	Gas Flow Proportional Count.	-2 (5)	0.09	**14 - 15**
Maxwell et al., 2009	0.1	4.19	75 (17)	Gas Flow Proportional Count.	1 (6)	0.5	**7 – 8**
Kabai et al., 2011	0.1	10	94 (7)	LSC	-	0.8	**7 – 8**
IAEA, 2013	0.25	10	70 – 75	LSC	<15%	2 - 5	**7 – 8**
Sáez-Muñoz et al, 2018	0.1	5	65 (5)	Plastic Scintillation Counting	4 (1)	0.34	**5**

Sáez-Muñoz, M. et al, JNRC, (2018) 315:543–555

PSresin (Separation and detection)

PSresin applications: Determination of ^{210}**Pb in WATER**

Extractant: 4,4'(5')-di-t butylcyclohexane 18-crown-6 1M Octanol

Separation conditions: HNO_3 2M

- **Recovery:** 91(3) %
- **Detection efficiency:** 44(3)%
- **MDA (10 mL, 1h):** 2.8 Bq L^{-1}

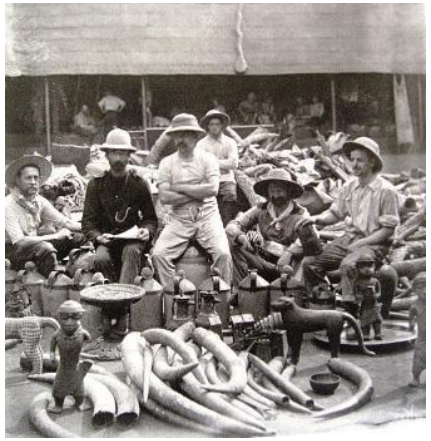
Sample	Activity (dpm/mL)	Activity Calc (dpm/mL)	**Deviation (%)**
Ebro river	10,1	10,8	**-7,0**
	10,1	11,0	**-9,2**
	10,1	9,8	**3,6**
Subterranean water	10,9	11,7	**-7,0**
	11,4	11,4	**0,2**
	11,4	11,8	**-4,1**
Congost river	11,0	11,4	**-4,2**
	10,4	10,7	**-3,3**
	11,4	11,3	**0,7**

Analytica Chimica Acta, 940, 38-45. 2016

PSresin (Separation and detection)

PSresin applications: Discrimination of **BRONZE SCULPTURES based on ^{210}Pb.**

Objective: minimum amount of sample.



Benin Kingdom Nigeria since 1440 –

English Punitive expedition – 1897

4000 artistic objects (sculptures) from Palace in Museums and collections

Problem to contribute to solve:

- restitution of cultural heritage objects
- discriminate fake objects in the market

PSresin (Separation and detection)

PSresin applications: Discrimination of **BRONZE SCULPTURES based on ^{210}Pb.**

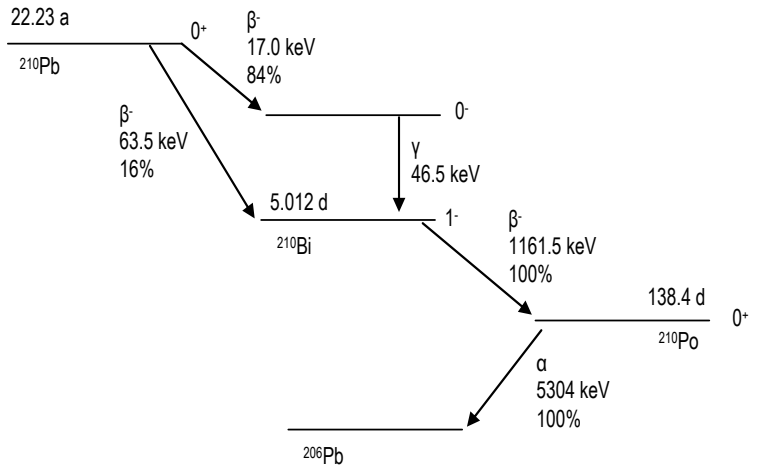
Objective: minimum amount of sample.

Artistic objects - Bronze/Brass sculptures **(Cu, Sn, Zn, Pb major)**

Pb: 1 – 12%

^{210}Pb beta emitter.

Secular equilibrium: ^{210}Bi: 35 d ^{210}Po: 2 y



Hypothesis:

- Initial ^{210}Pb activity of Benin Palace sculptures – material origin
- Maximum ^{210}Pb residual activity of Benin Palace sculptures.
- **Act (sculpture) > Act (maximum residual) → modern or different origin**

PSresin (Separation and detection)

PSresin applications: Discrimination of **BRONZE SCULPTURES based on ^{210}Pb.**

Objective: minimum amount of sample.

Analytical Feasibility.

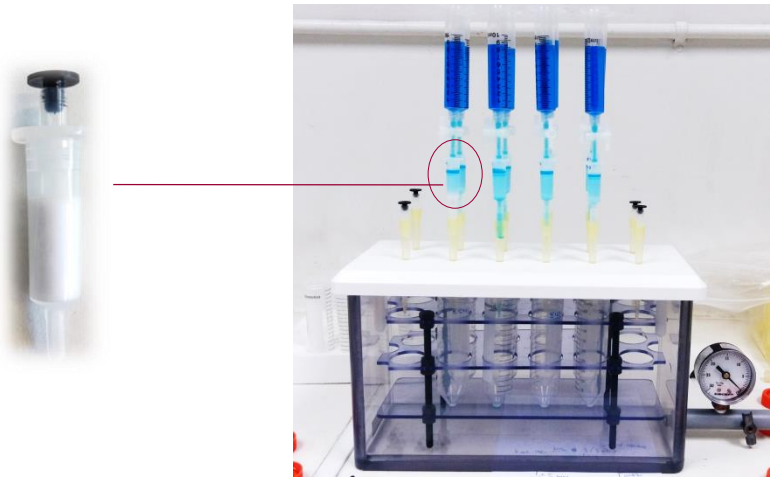
. Bronze dissolution: HF + HNO_3 (heat)

. **Matrix interferences** .

Medium HNO_3 2M

.

Element	Retention (%)
Pb	75 ± 2
Cu	1 ± 2
Sn	1 ± 2
Zn	1 ± 1



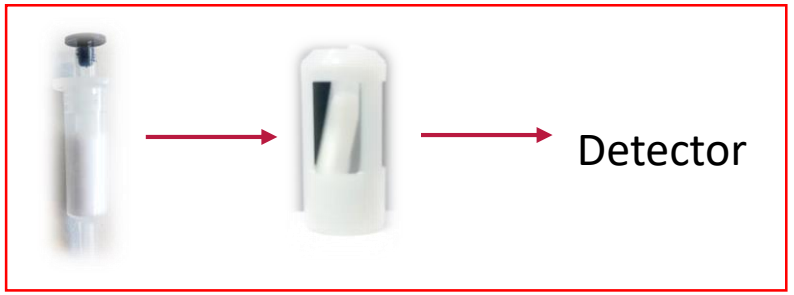
PSresin (Separation and detection)

PSresin applications: Discrimination of **BRONZE SCULPTURES based on ^{210}Pb.**

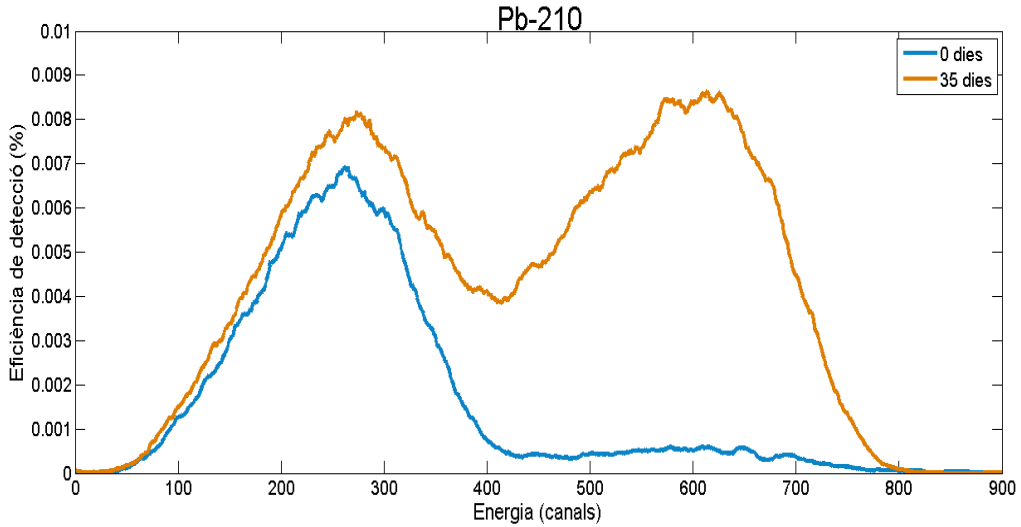
Objective: minimum amount of sample.

Analytical Feasibility.

. **Radiometric detection**



	Detection Eff (%)
t 0 days (^{210}Pb)	47 ± 3
t 35 days (^{210}Pb/^{210}Bi)	134 ± 4



PSresin (Separation and detection)

PSresin applications: Discrimination of **BRONZE SCULPTURES based on ^{210}Pb.**

Objective: minimum amount of sample.

Analytical Feasibility.

Worst scenario

Composition Pb: 1 % (1-12%)
Activity Pb: 10 dpm/g_{Pb} (10 – 110 dpm/g)

	^{210}Pb	^{210}Pb / ^{210}Bi	^{210}Pb / ^{210}Bi / ^{210}Po
Parameters	**time 0 days**	**time 35 days**	**time 2 years**
Detection EFF (%)	46,5 %	136 %	222,35 %
200 min	9,49 g	3,23 g	1,98 g
1 g	11,6 days	1,4 days	12,7 hours
0,5 g	46,5 days	**5,5 days**	2 days

Parameters	**20 dpm/g_{Pb} i 1 %**	**10 dpm/g_{Pb} i 4 %**
200 min	1,62 g	0,81 g
1,4 days	0,5 g	0,25 g
5,5 days	**0,25 g**	**0,12 g**

PSresin (Separation and detection)

PSresin applications: Discrimination of **BRONZE SCULPTURES based on ^{210}Pb.**

Objective: minimum amount of sample.

Determination of maximum ^{210}Pb residual activity (in progress).

.**Collaboration Museum Five Continents (Munich)**

. Two sets: - Original Benin Sculptures
- Non Original Benin Sculptures

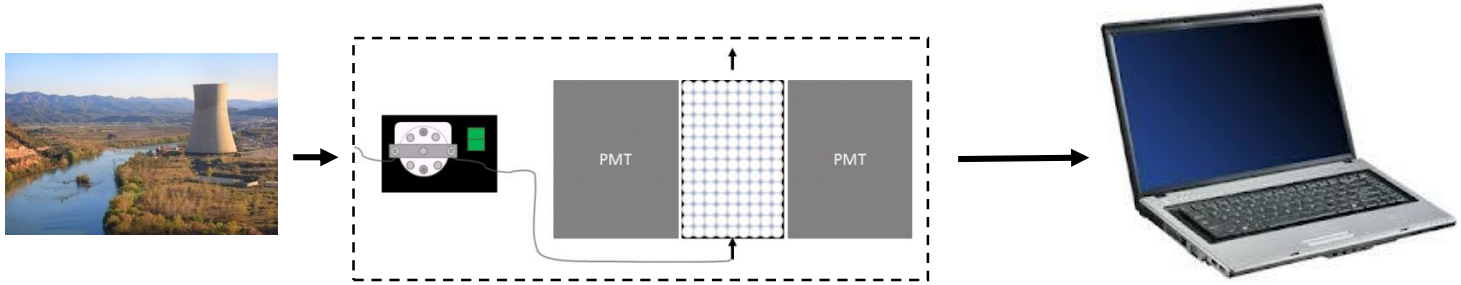
. Data: - Elemental composition (major and minor).
- Stable Pb isotopes composition
- ^{210}Pb activity

WATER-RADD (on-line continuous detector)

Continuous and on-line alpha and beta determination in aqueous samples

No reagents
No waste

How it works?



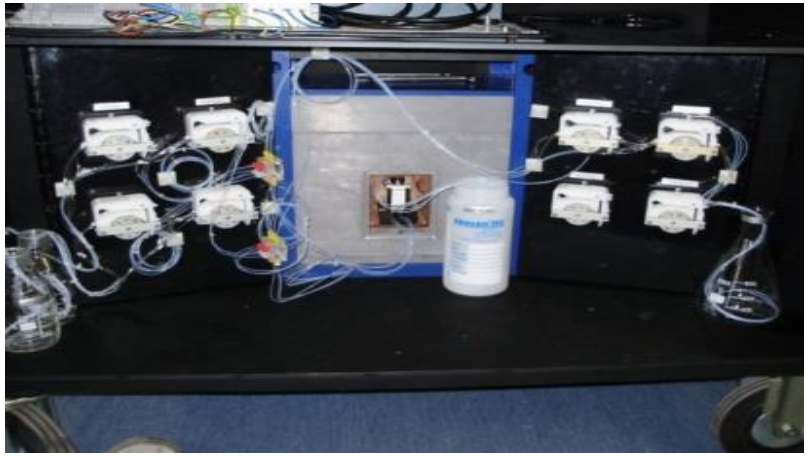
- Sample pass continuously through the counting cell
- Counting cell filled with PSm
- Signals are detected by PMT

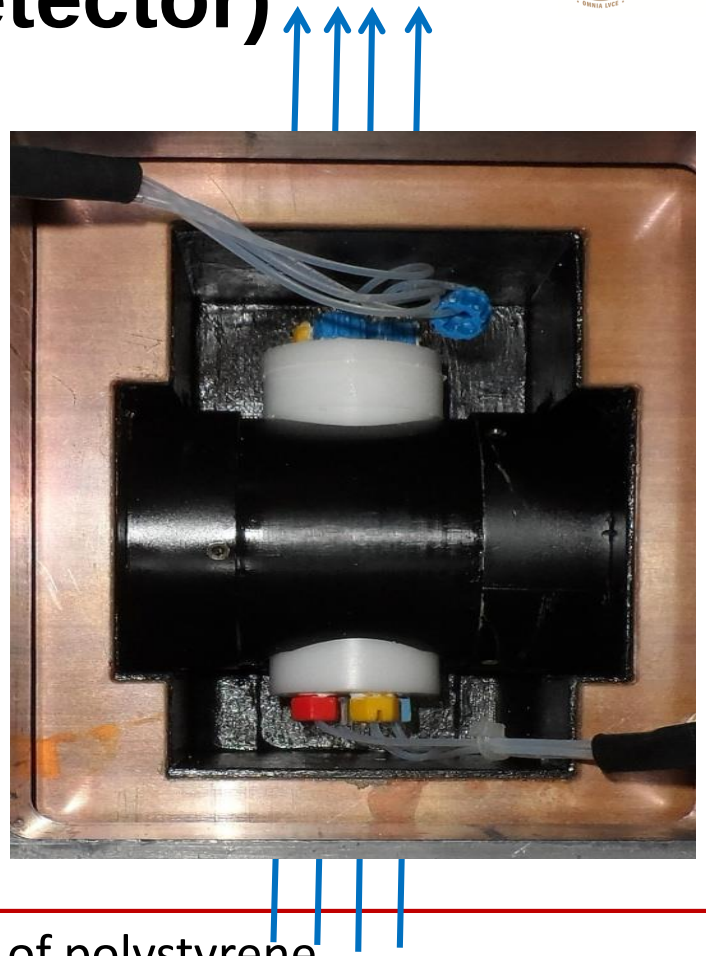
- Hydraulic system for sample and reagents pumping
- Active and passive shielding.
- Remotely controlled by computer (5 ‘ measurements).

WATER-RADD (on-line continuous detector)

Active and passive **shielding**

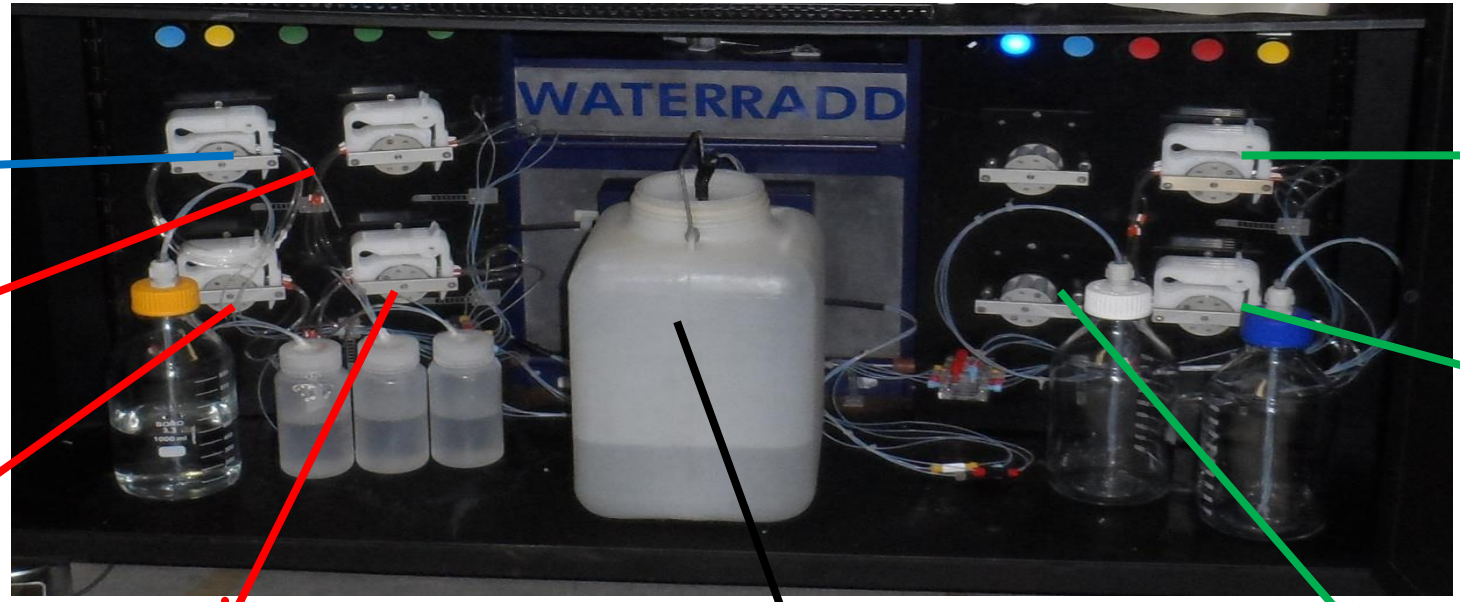
Detection Cell: filled with PSmicrospheres





- Made of polystyrene
- Volume approximately of 10 mL
- Filled with 20 gr. of PSm
- Coupled to a pair of PMT
- Water goes from the bottom to top of the cell
- Flow rate: from 3 to 5 mL/min

WATER-RADD (on-line continuous detector)



SAMPLE

^{3}H (20000 Bq/L)

β (^{90}Sr/ ^{90}Y) 150 Bq/L

α (^{241}Am) 100 Bq/L

WASTE

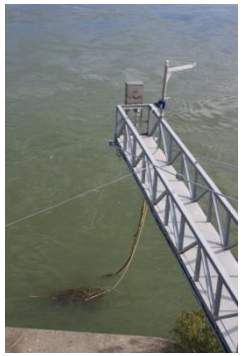
HCl 1M

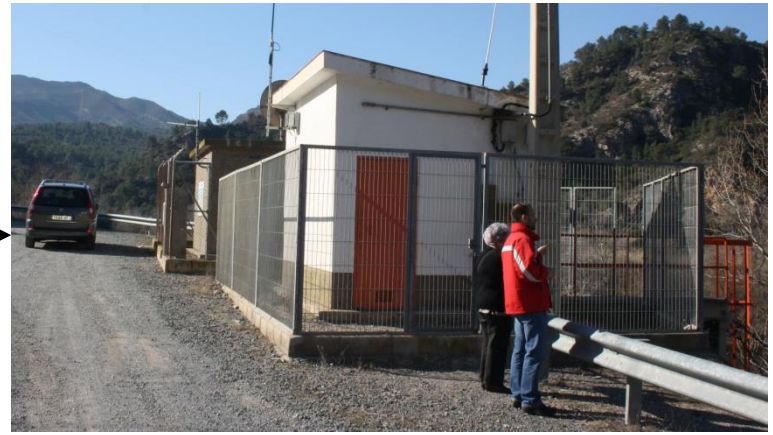
Deionized water

Extra cleaning solution

WATER-RADD (on-line continuous detector)

Continuous monitoring monitoring of Ebro River





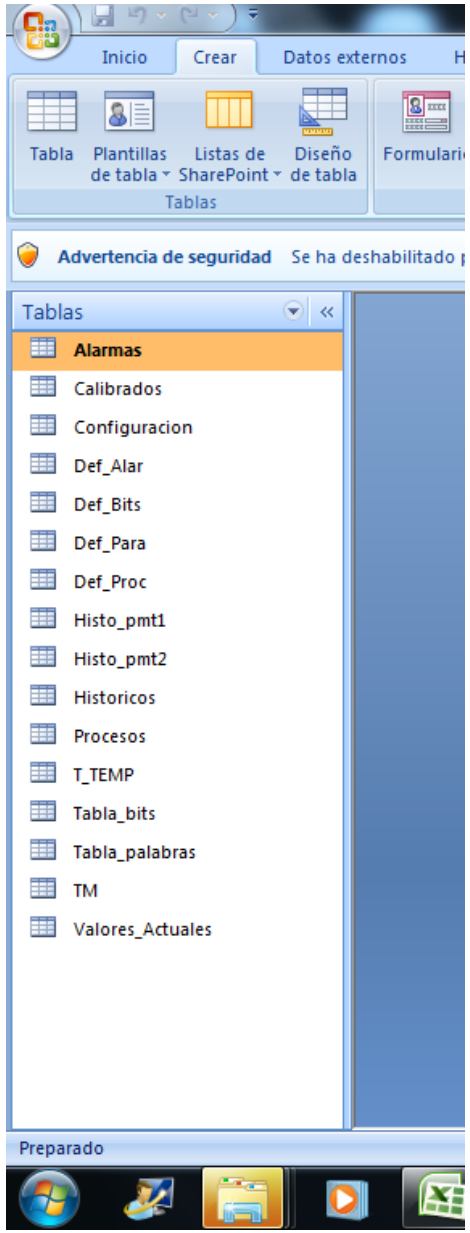
ADASA Sistemas

WATER-RADD (on-line continuous detector)

WATER-RADD: reporting results

- Data is sent to the remote position with a predefined frequency
- Data is stored in an ACCESS database

- Calibration data
- Configuration history
- Spectrum of the PMT1
- Spectrum of the PMT2
- Count and Timing
- Processes
- Temperature
- Count rates (in cps)



WATER-RADD (on-line continuous detector)

WATER-RADD: reporting results

Fecha_y_Hora	C_PMT1	C_PMT2	C_PMT3	C_PMT4	C_C12	C_C34	C_C1234	C_CB	C_CF	C_CA	T_TOTAL_AA	T_MUERTO_BB	T_MUERTO_CC
11-5-12 14:33	166340	74511	92483	101643	252	15739	150	102	71	70	29948	39	344
11-5-12 14:38	167064	75204	92883	104293	251	15696	149	102	73	72	29949	39	344
11-5-12 14:43	166809	75165	95329	101083	216	15678	118	98	64	63	29948	39	344
11-5-12 14:48	167334	75111	93863	102031	229	15863	128	101	72	71	29948	39	346
11-5-12 14:53	167940	75374	92869	101815	209	15671	113	96	72	71	29949	39	346
11-5-12 14:58	169102	75864	96362	101981	237	15507	143	94	63	62	29948	39	349
11-5-12 15:03	168876	75460	93416	105454	248	15727	142	106	72	68	29949	39	348
11-5-12 15:08	169038	75597	95732	107172	236	15806	142	94	56	56	29948	39	349
11-5-12 15:13	169773	75716	93541	102651	222	15847	122	100	66	64	29940	39	349
11-5-12 15:18	170132	76331	95078	104479	231	15994	136	95	69	69	29949	40	352
11-5-12 15:23	170638	76600	93611	102656	216	15676	117	99	69	66	29948	39	350
11-5-12 15:28	171326	76939	97655	106400	258	15667	162	96	72	71	29949	39	353
11-5-12 15:33	171651	76325	94870	103272	232	15806	126	106	72	70	29948	39	353
11-5-12 15:38	172648	76692	93920	102970	244	15477	140	104	70	70	29949	38	351
11-5-12 15:43	173543	76837	96001	105817	238	15810	127	111	78	77	29948	39	353
11-5-12 15:48	173219	78074	93898	102889	257	15619	134	123	85	80	29948	39	352
11-5-12 15:53	173335	77486	94004	103977	205	15590	116	89	69	69	29949	39	354
11-5-12 15:58	174072	77442	94395	103602	234	15751	127	107	75	75	29948	39	355
11-5-12 16:03	173856	77902	94691	103618	251	15703	129	122	76	76	29949	39	353
11-5-12 16:08	174938	77652	94945	104101	222	15703	132	90	57	0	29948	39	357
11-5-12 16:13	176005	78383	95243	104105	255	15736	143	112	77	77	29948	39	357
11-5-12 16:18	175752	78262	96014	104940	227	16084	135	92	63	63	29949	40	358
11-5-12 16:23	176688	78792	95169	104598	253	15776	155	98	60	59	29948	39	357
11-5-12 16:28	176782	78479	95660	104641	211	15820	119	92	70	70	29949	39	358
11-5-12 16:33	177334	78381	95890	104966	226	15490	121	105	77	74	29948	39	358
11-5-12 16:38	177983	78707	95841	106119	251	15733	142	109	82	82	29949	39	358
11-5-12 16:43	177360	79225	95766	104745	255	15705	141	114	89	88	29948	39	360

Measurement date

PMT counts

Coincidences

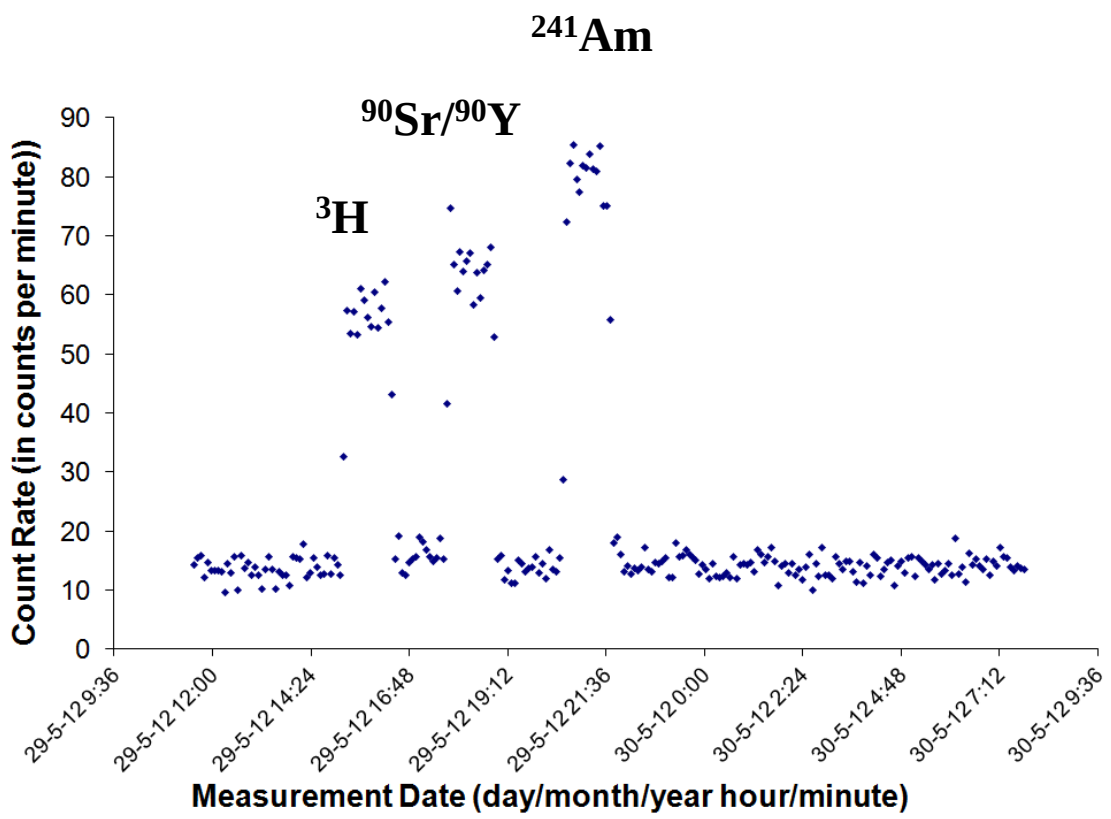
Counting and dead time

WATER-RADD (on-line continuous detector)

Calibration

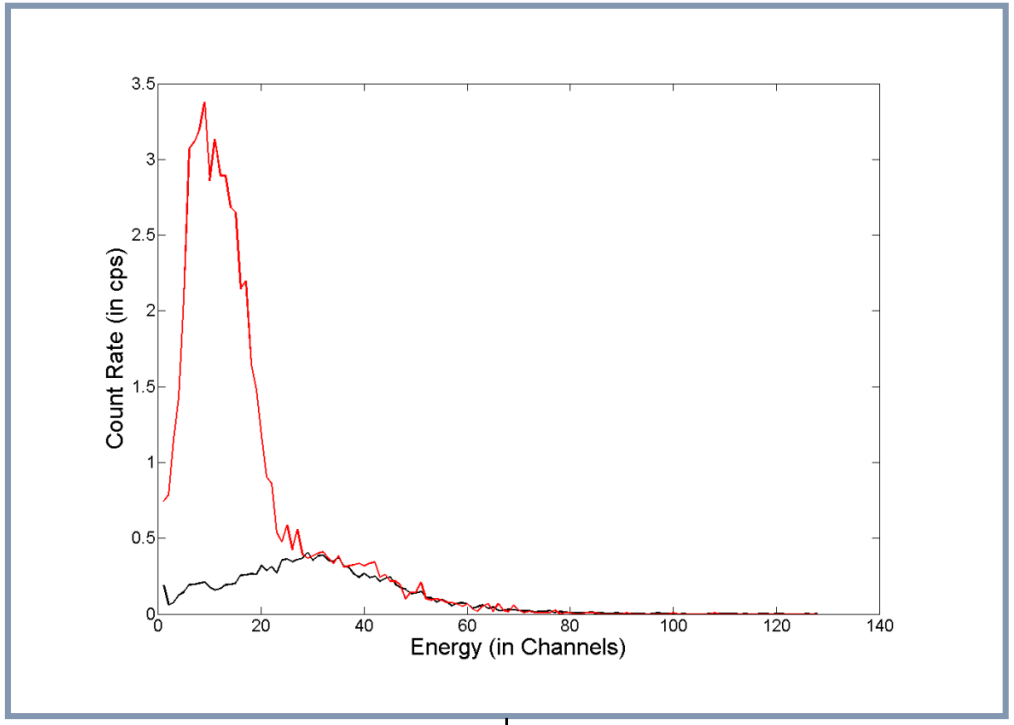
- Background and ^{3}H, $^{90}Sr/^{90}Y$ and ^{241}Am standards was measured in each sequence.
- Three replicate sequences were measured
- Counting time: 60 min

Background count rate (in cpm)
14.1(0.3)



WATER-RADD (on-line continuous detector)

WATER-RADD: ^{3}H

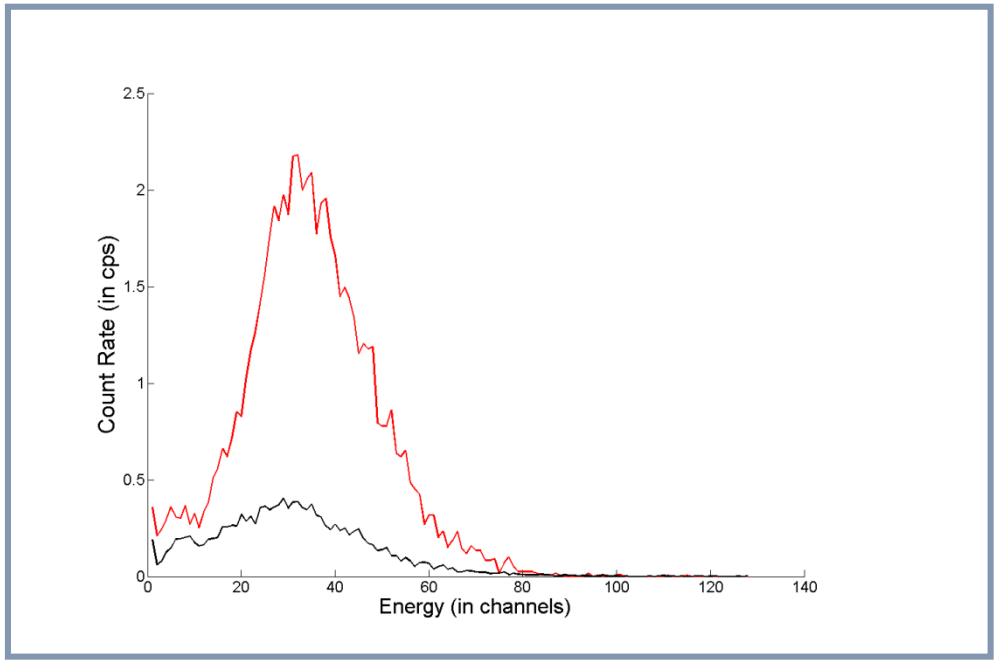


Efficiency (in %) (assuming 10 mL of volume)	0.378 ± 0.08

Optimum window	2-17
Detection Limit (1h)	**486 Bq/L**
Detection Limit (5h)	212 Bq/L
Detection Limit (24h)	96 Bq/L

WATER-RADD (on-line continuous detector)

WATER-RADD: $^{90}Sr/^{90}Y$

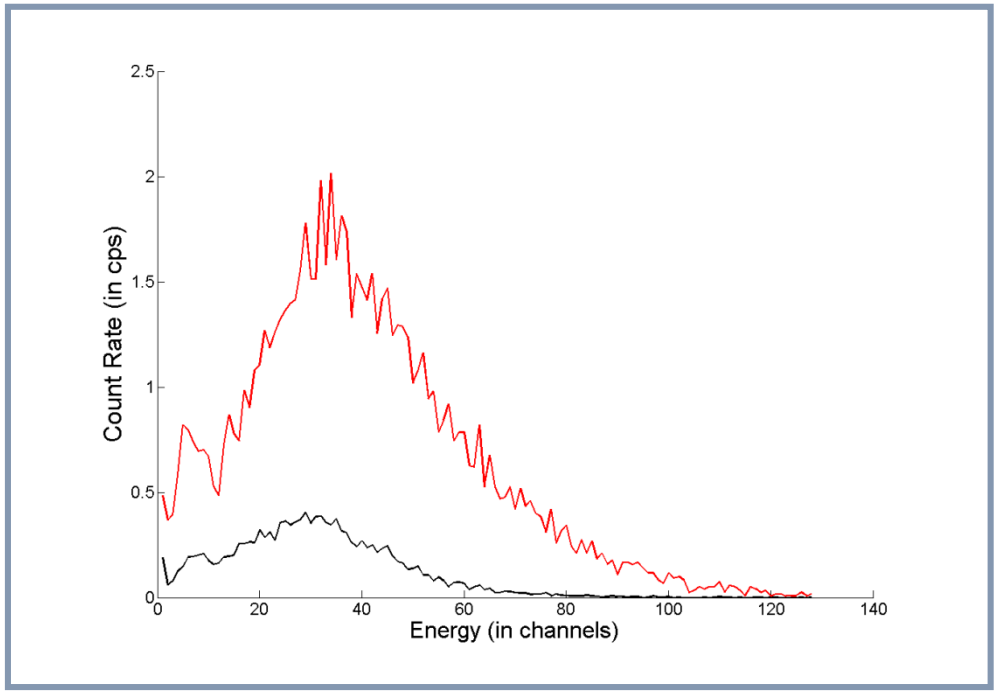


Efficiency (in %) (assuming 10 mL. of volume , up to 200%)	142 ± 6

Optimum window	16-78
Detection Limit (1h)	**3.9 1Bq/L**
Detection Limit (5h)	1.72 Bq/L
Detection Limit (24h)	0.78 Bq/L

WATER-RADD (on-line continuous detector)

WATER-RADD: ^{241}Am



Efficiency (in %) (assuming 10 mL. of volume)	58.1 ± 0.2

Optimum window	2-128
Detection Limit (1h)	**5.20 Bq/L**
Detection Limit (5h)	2.30 Bq/L
Detection Limit (24h)	1.05 Bq/L

Radionuclide determinations with:

- **PSresin** (separation and detection)

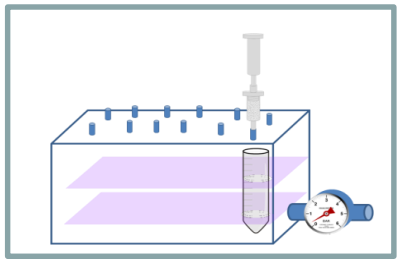
- **MASS** (automated separation)

- **WaterRadd** (on-line detector)

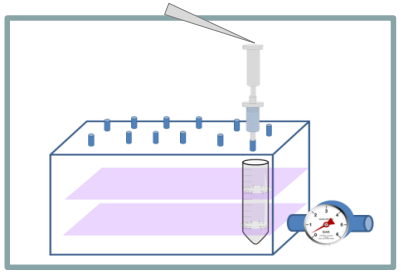
Tarancón, A.; Bagán, H.; García, J .F.

PSresin (Separation and detection)

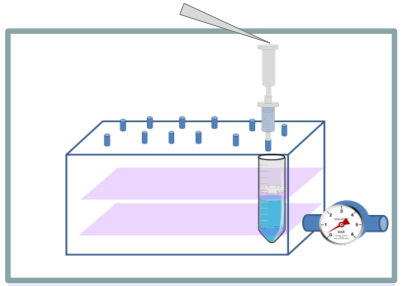
PSresin in practice



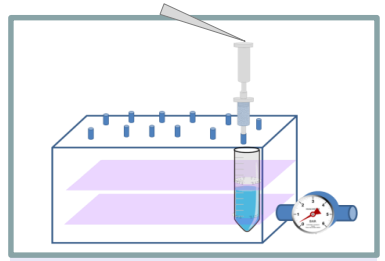
Connect to Chamber



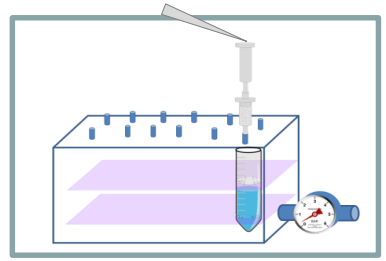
Condition the column 2-5 mL



Add 10 -100 mL of sample (carrier)

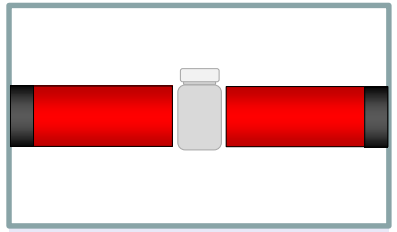


Rinse 4 times with 2-5 mL of H_2O

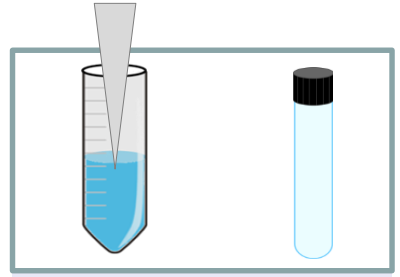


Empty the column

Disconnect the column and place it in a scintillation vial



Measurement of in a scintillation detector

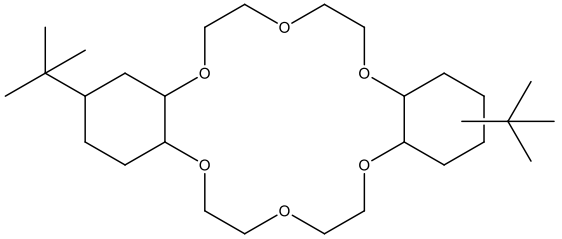


Prepare the ICP tubes for yield calculations

PSresin (Separation and detection)

PSresin applications: Determination of ^{90}**Sr/**^{90}**Y** in **milk** in **emergency** situations

Objective: reduction of total **analysis time**.

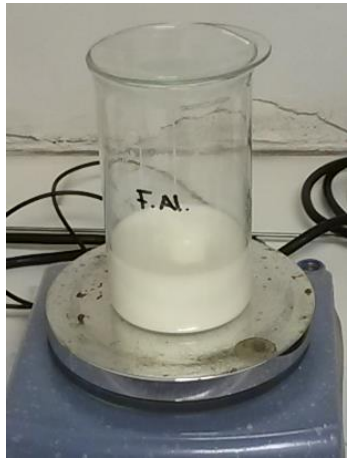


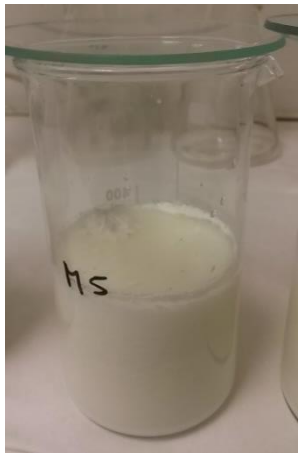
Extractant: 4,4'(5')-di-t butylcyclohexane 18-crown-6 1M Octanol

Sample: 100 mL milk

Pretreatment:

1. Tricloroacetic acid
2. Oxalates precipitation





PSresin (Separation and detection)

PSresin applications: Determination of ^{90}**Sr/**^{90}**Y** in **milk** in **emergency** situations

Objective: reduction of total **analysis time**.

Extractant: 4,4'(5')-di-t butylcyclohexane 18-crown-6 1M Octanol

Sample: 100 mL milk

Pre-treatment:

. Tricloroacetic acid

. Oxalates precipitation

. Redisolution in $HNO_3$6 M.

Cleaning: $HNO_3$6 M and $LiNO_3$ 6 M

Carrier: 5 mg Sr^{2+}

Type of milk	Pre-treatment Recovery (%)	Column Recovery (%)	Total Recovery (%)
Cow (x7)	93 (3) (3%)	69 (2) (3%)	64 (3) (3%)
Sheep (x4)	94 (6) (6%)	64 (3) (3%)	60 (6) (10%)
Goat (x4)	96 (3) (3%)	67 (2) (3%)	67 (3) (3%)
Semi-skimmed	87	72	62
Skimmed	90	71	64
Powder (x2)	95 (1) (1%)	68.3(0.5) (1%)	65 (1) (2%)
Pasteurized	95	68	65
Reference material (x3)	91 (2) (3%)	78(2) (2%)	72 (2) (2%)
Total samples	**93 (4) (4%)**	**70(4) (6%)**	**65 (5) (7%)**

PSresin (Separation and detection)

PSresin applications: Determination of **^{90}Sr/^{90}Y** in **milk** in **emergency** situations

	Type of milk	Activity ^{89}Sr (Bq/L)	Activity ^{90}Sr (Bq/L)	Ratio ^{89}Sr/^{90}Sr	Relative bias (^{89}Sr + ^{90}Sr) (%)
M3	Cow/whole/UHT	-	27	0:1	-2.2 (1.9*)
M4	Cow/whole/UHT	15	-	1:0	6.6 (3.0*)
M5	Cow/whole/UHT	27	27	1:1	-1.9
M8	Cow/semi-skimmed/UHT	27	27	1:1	4.5
M9	Cow/skimmed/UHT	27	27	1:1	6.1
M11	Cow/whole/powder	27	27	1:1	1.7
M12	Cow/whole/pasteurized	27	27	1:1	2.6
M13	Goat/whole/raw	27	27	1:1	-1.9
M15	Sheep/semi-skimmed/UHT	27	27	1:1	7.0
M19	Goat/semi-skimmed/UHT	27	27	1:1	5.2

PSresin (Separation and detection)

PSresin applications: Determination of **^{90}Sr/^{90}Y** in **milk** in **emergency** situations

Objective: reduction of total **analysis time**.

	Type of milk	Activity ^{89}Sr (Bq/L)	Activity ^{90}Sr (Bq/L)	Ratio ^{89}Sr/^{90}Sr	Relative bias (^{89}Sr + ^{90}Sr) (%)
M6	Cow/whole/UHT	27	13.5	2:1	1.6
M15	Sheep/semi-skimmed/UHT	27	13.5	2:1	20.2
M19	Goat/semi-skimmed/UHT	27	13.5	2:1	6.5
M7	Cow/whole/UHT	125	13.5	10:1	-4.1
M17	Sheep/semi-skimmed/UHT	125	13.5	10:1	-3.9
M21	Goat/semi-skimmed/UHT	125	13.5	10:1	-4.1

PSresin (Separation and detection)

PSresin applications: Determination of ^{90}**Sr/**^{90}**Y** in **WATER**

Extractant: 4,4'(5')-di-t butylcyclohexane 18-crown-6 1M Octanol

Separation conditions: $LiNO_3$6 M (5 mL)

Sample volume: 10 mL

Cleaning: $LiNO_3$ 6 M (4*5 mL)

Carrier: 100 µg Sr^{2+}

- **Recovery:** 100 %
- **Det. Eff. (1-1024):** 84(2)%
- **Det. Eff. (300-617):** 69.0(0.3)%
- **Bkg) (300-617):** 0.47 cpm
- **MDA) (10 mL, 5H):** 0.46 Bq L^{-1}

	Act (dpm)	Act calc (dpm)	Error) (%)
Drinking water	8.02	8.18	1.94
	7.77	7.66	-1.44
	7.66	7.54	-1.51
Sea Water	7.88	8.06	2.29
	8.00	7.80	-2.56
	7.70	8.01	4.09
River Water	7.86	7.84	-0.28
	7.75	7.60	-1.94
	7.77	7.72	-0.61

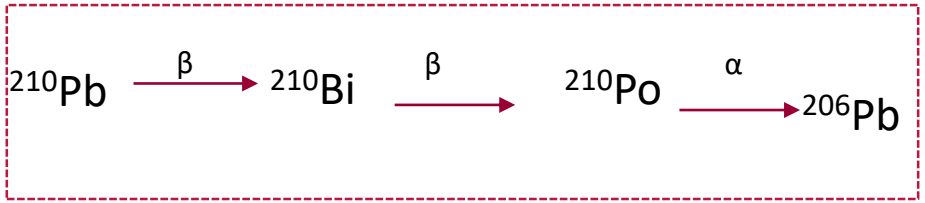
Bagán et al, Analytica Chimica Acta 686) (2011) 50–56

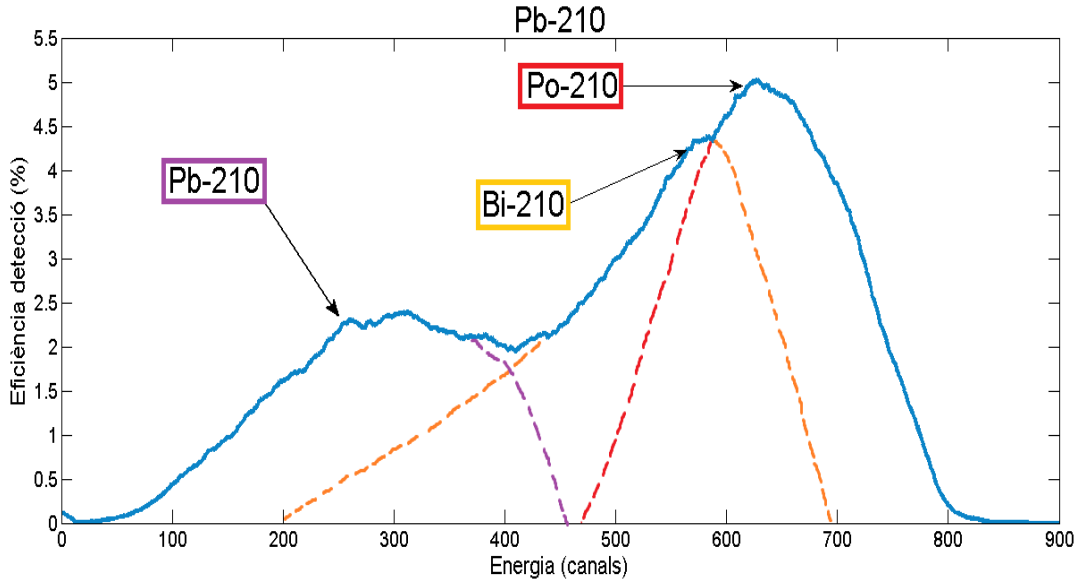
PSresin (Separation and detection)

PSresin applications: Determination of ^{210}**Pb in BRONZE SCULPTURES**

Analytical Feasibility.

. Radiometric detection





Expected Total detection efficiency ^{210}Pb+ ^{210}Bi+^{210}Po: 220 % after 2 years

PSresin (Separation and detection)

PSresin applications: Determination of ^{210}**Pb in BRONZE SCULPTURES**

Analytical Feasibility.

. Minimum amount of sample.

Equations:

$$L_D = 2{,}71 \pm 4{,}65\sqrt{\mu_B} \rightarrow Act_0 = \frac{L_D/t}{Eff} \cdot 100 \rightarrow M_{bronze} = \frac{Act_0 \cdot 100 \cdot 100}{C_{Pb} \cdot Act_{Pb} \cdot Ret_{Pb}}$$

$$\mu_B = CPM \cdot t$$

Parameters:

- Blank: 1,08 CPM
- Composition Pb: 1 – 12 %
- Activity Pb: 10 – 110 dpm/g_{Pb}
- Retention Pb: 80,6 %

Worst Condicions →

- Composition Pb: 1 %
- Activity Pb: 10 dpm/g_{Pb}

PSresin (Separation and detection)

PSresin applications: Determination of ^{210}**Pb in BRONZE SCULPTURES**

Analytical Feasibility.

. Minimum amount of sample.

Composition Pb: 1 %
Activity Pb: 10 dpm/g_{Pb}

	^{210}Pb	^{210}Pb / ^{210}Bi	^{210}Pb / ^{210}Bi / ^{210}Po
Parameters	**time 0 days**	**time 35 days**	**time 2 years**
Detection EFF (%)	46,5 %	136 %	222,35 %
200 min	9,49 g	3,23 g	1,98 g
1 g	11,6 days	1,4 days	12,7 hours
0,5 g	46,5 days	5,5 days	2 days

MASS (Modular Automated Separation System)

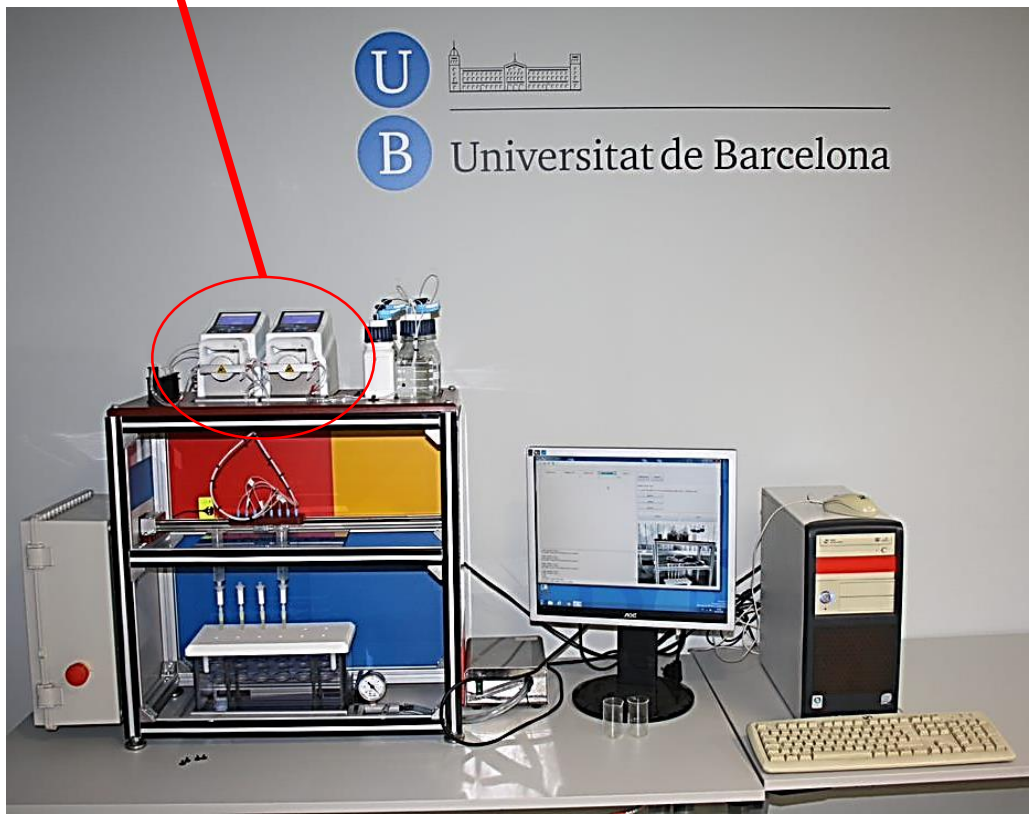
- Automated separation using SPE cartridges (with PSresin)
- Simple design
- Coupled to vacuum box
- Controlled by computer

Easy handling of the samples

Similar set-up compared to manual separation

MASS (Modular Automated Separation System)

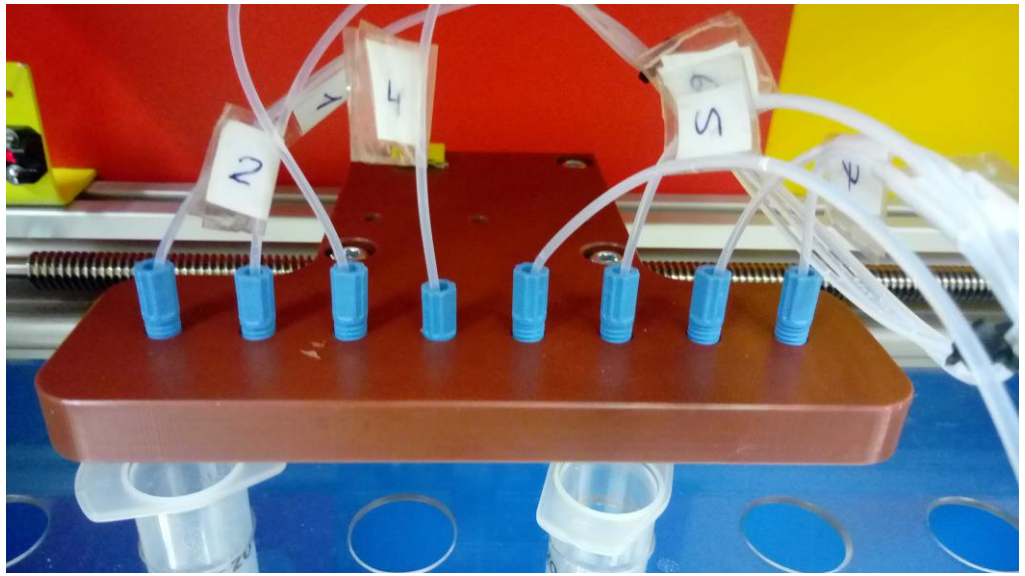
PUMPS



- 2 Peristaltic pumps (samples and reagents)
- Four independent channels in each pump
- Controlled by computer
- Flow: 0.5 to 4 ml min^{-1}

MASS (Modular Automated Separation System)

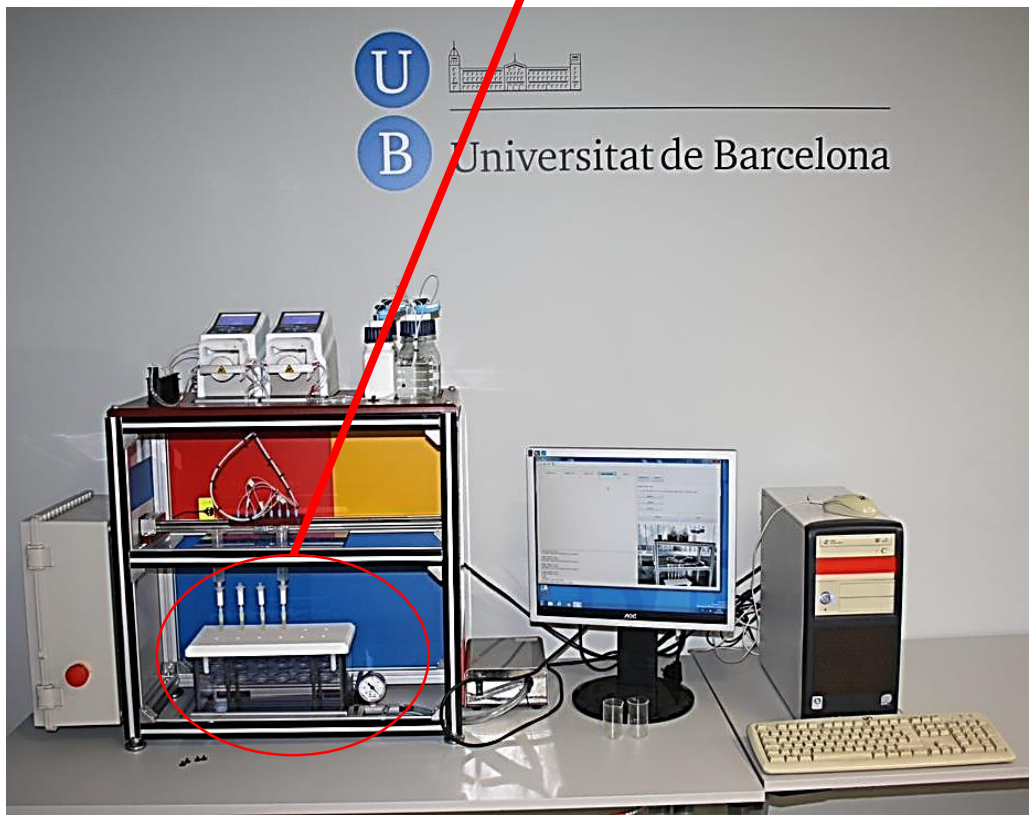
Linear table (Sample/reagents addition)

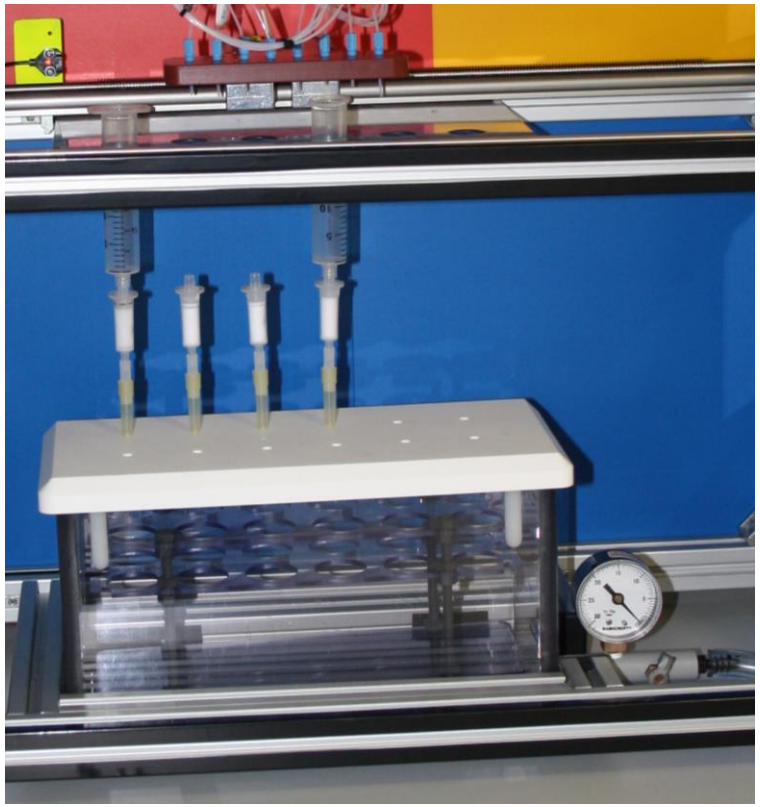


- Movement in one axis
- 8 tubes (4 samples + 4 reagents)
- 4 adding positions (one for each PSresin)

MASS (Modular Automated Separation System)

Vacuum box with PSresin cartridge

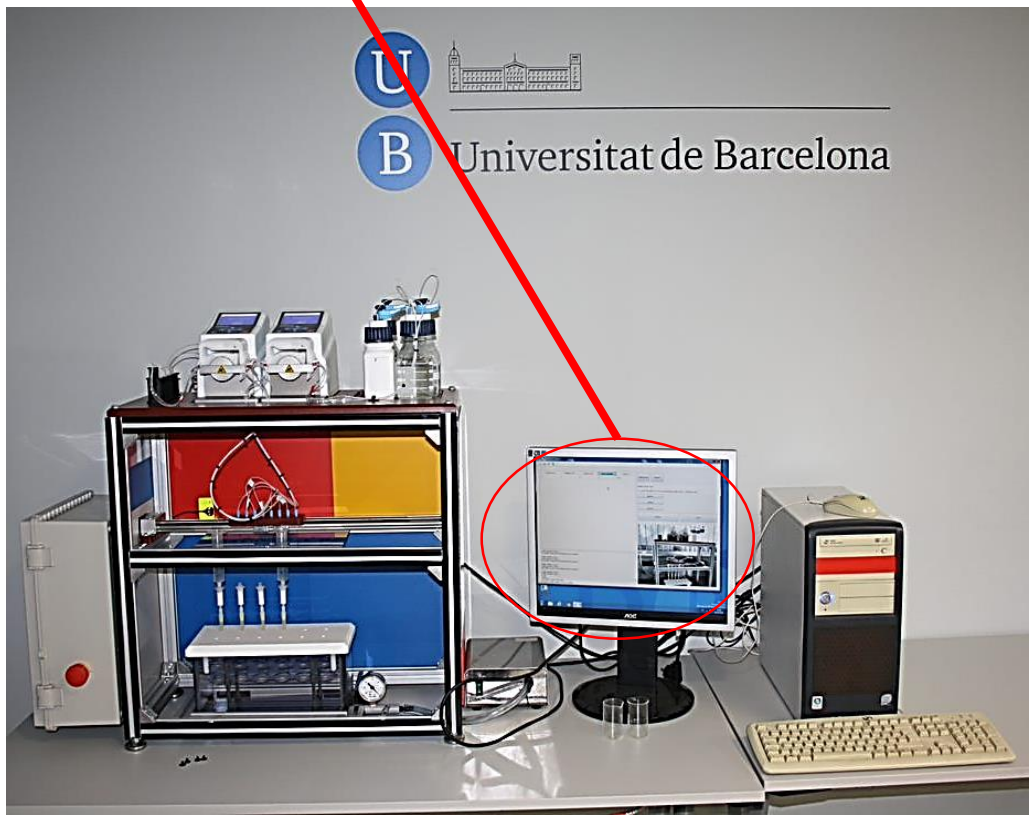


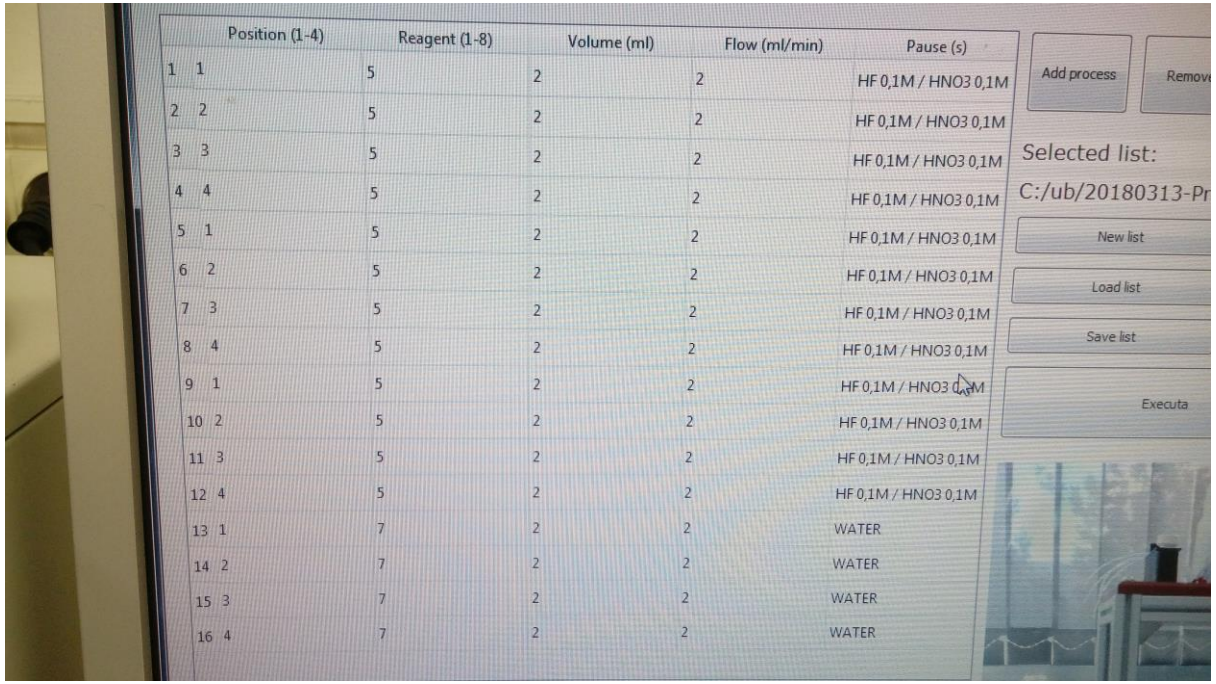


- 12 position vacuum box
- 4 fixed positions

MASS (Modular Automated Separation System)

Control Software





- Define sequential process
- Actions: position (1-4); reagent (1-8); volume; flow
- Possibility to save/load protocols

MASS (Modular Automated Separation System)

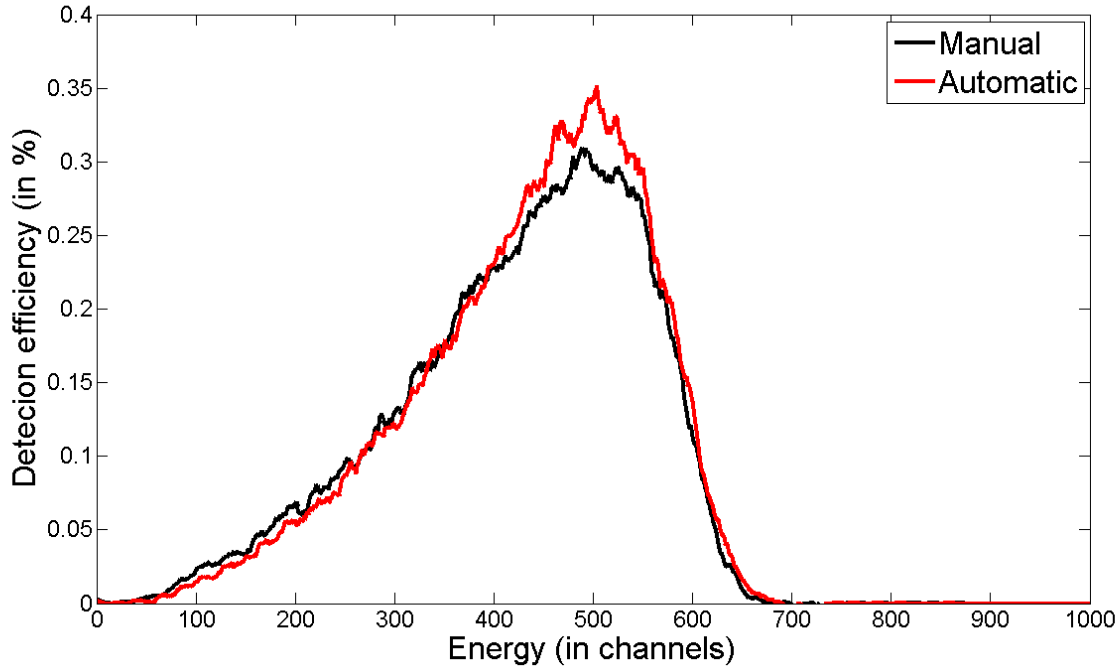
APPLICATION ^{99}Tc DETERMINATION

SEPARATION WITH PSRESIN

1. Conditioning: 2 mL HCl 0.1M
2. Sample loading: 10 mL
3. 1st cleaning: 2 mL HF 0.1M/HNO_3 0.1M
4. 2nd cleaning: 2 mL HF 0.1M/HNO_3 0.1M
5. 3rd cleaning: 2 mL HF 0.1M/HNO_3 0.1M*
6. 4th cleaning : 2 mL H_2O

CALIBRATION

10mL containing 240 dpm of ^{99}Tc, 1 mg or rhenium in HCl 0.1M



	Manual [%]	Automatic [%]
Yield	Quantitative (>98.8%)	Quantitative (>99.8%)
SQP(E)	802(8)	795(5)
Detection efficiency [%]	85.3(1.3)	88.2(1.3)

MASS (Modular Automated Separation System)

SAMPLES

Treatment:

- H_2O_2 at 90ºC for 60 minutes.
- HCl until 0.1M.

Samples:

- River water (50 mL, 16 Bq/L)
- Sea water (50 mL, 16 Bq/L)

MASS (Modular Automated Separation System)

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SAMPLES

River water (50 mL, 16 Bq/L)

River water sample	Activity [Bq/Kg]	Activity measured [Bq/Kg]		Deviation [%]	
		Manual	Automated	**Manual**	**Automated**
1st replicate	18.2	16.9	18.6	**-7.3**	**2.1**
2nd replicate	16.8	17.0	16.8	**1.2**	**0.1**
3rd replicate	18.0	18.3	17.7	**1.7**	**-1.5**
Mean				**-1.5(5.1)**	**0.2(1.8)**

Sea water (50 mL, 16 Bq/L)

Sea water sample	Activity [Bq/Kg]	Activity measured [Bq/Kg]		Deviation [%]	
		Manual	Automated	**Manual**	**Automated**
1st replicate	17.5	17.4	17.6	**-0.8**	**0.6**
2nd replicate	17.4	17.2	18.1	**-1.2**	**4.0**
3rd replicate	18.9	18.0	17.7	**-5.0**	**-6.4**
Mean				**-2.4 (2.3)**	**-0.6 (5.3)**

WATER-RADD (on-line continuous detector)

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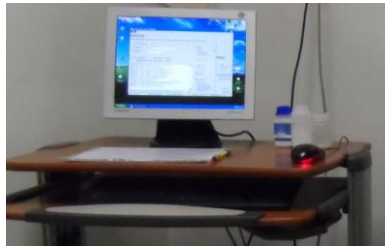
USER LOCATION

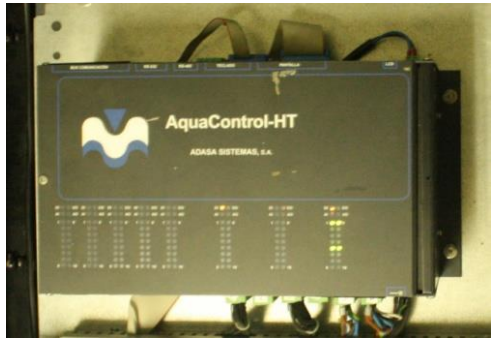


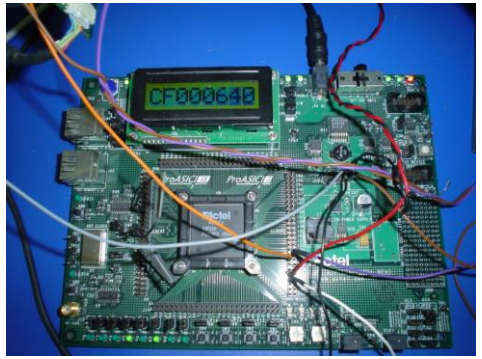
- Number of periods per sample
- Counting time of each period
- Calibration and Cleaning frequency
- Communication frequency

- Serial Port
- 4G

- Counting times
- Number of Counts
- Spectrum

DETECTOR





- In the test performed, data was send each hour and a each subperiod was of 5 minutes

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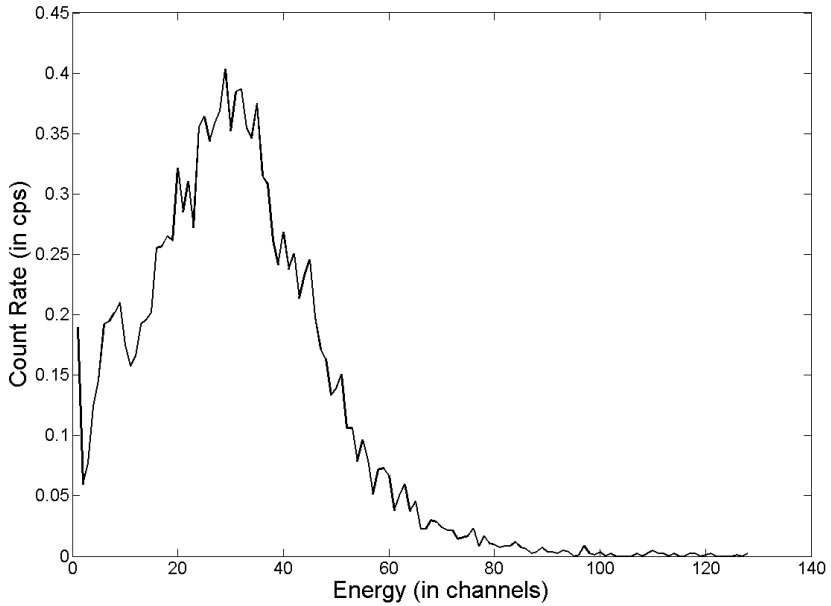
Applications: Continuous monitoring

WATER-RADD: background

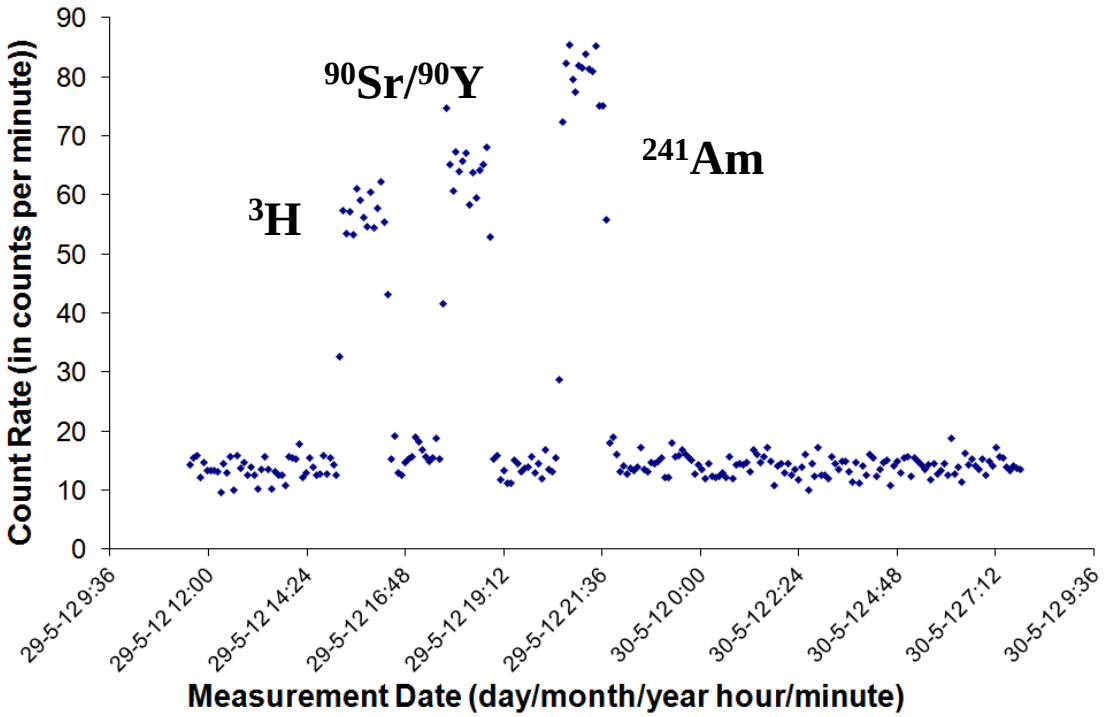


	Count rate (cpm)
1st sequence (n=5)	14.41 ± 0.94
2on sequence (n=6)	13.90 ± 0.54
3th sequence (n=7)	13.98 ± 0.54

WATER-RADD (on-line continuous detector)

Calibration

- Background and ^{3}H, $^{90}Sr/^{90}Y$ and ^{241}Am standards was measured in each sequence.
- Three replicate sequences were measured
- Counting time: 60 min



Background count rate (in cpm)
14.1(0.3)

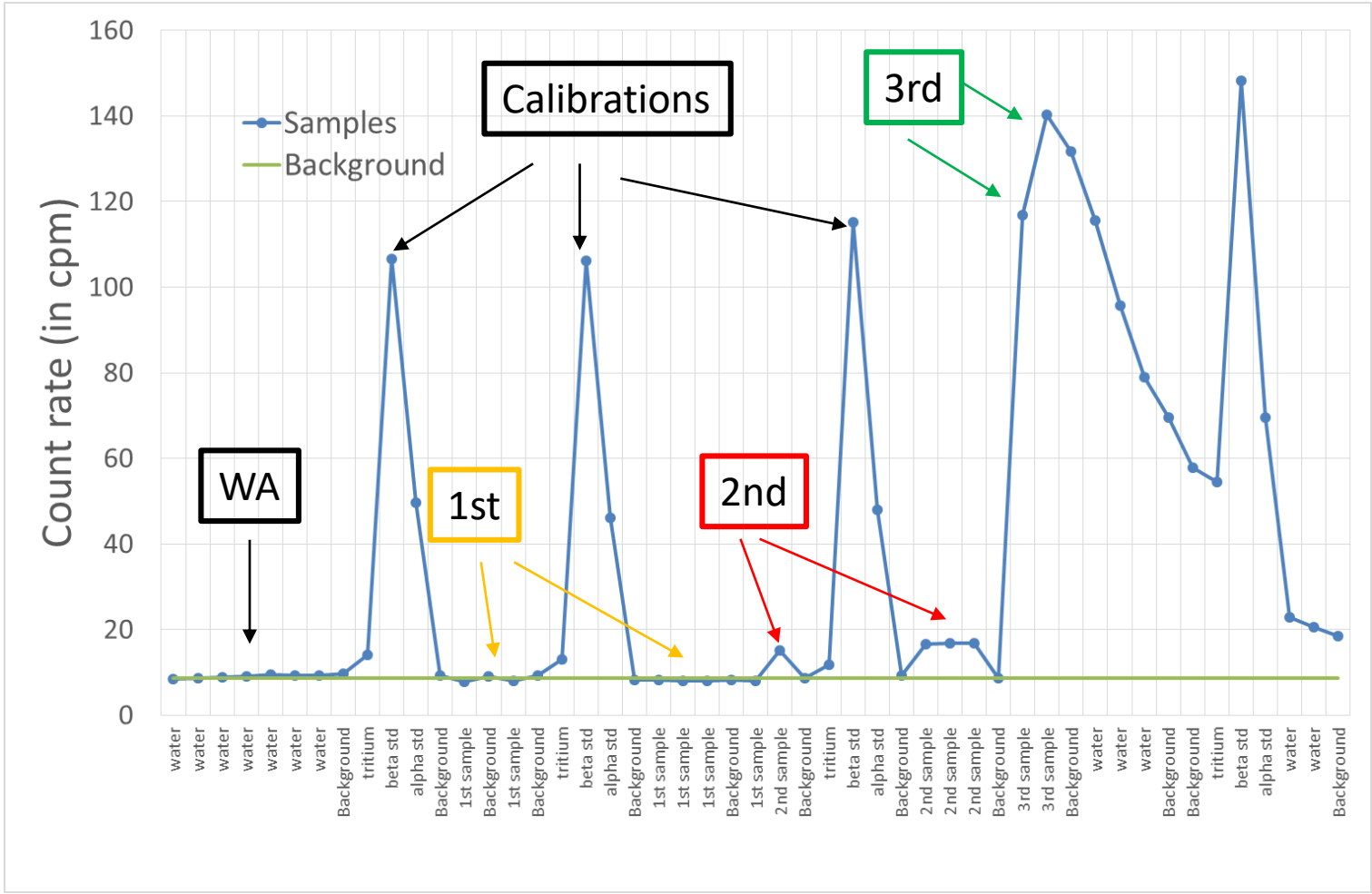
	Efficiency (in %)	Detection Limit (1h)
^{3}H	0.38(0.08)	486 Bq/L
$^{90}Sr/^{90}Y$	142(6)	3.9 Bq/L
^{241}Am	58.1(0.2)	5.2 Bq/L

WATER-RADD (on-line continuous detector)

Analysis of hydraulic fracturing samples

- 3 samples
- Counting time: 60 min
- Beta detection limit: 2.0 Bq/L
- Alfa detection limit: 2.1 Bq/L

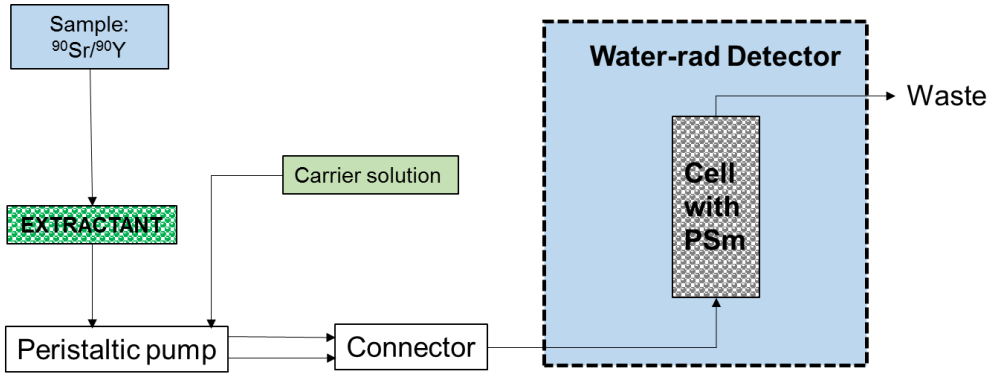
		LS (Bq/Kg)	Water-radd (Bq/Kg)
1st sample	alpha	0.06	< 2.1
	beta	< 0.1	< 2.0
2nd sample	alpha	< 0.8	20
	beta	7.1	19
3rd sample	alpha	310	285
	beta	42	274

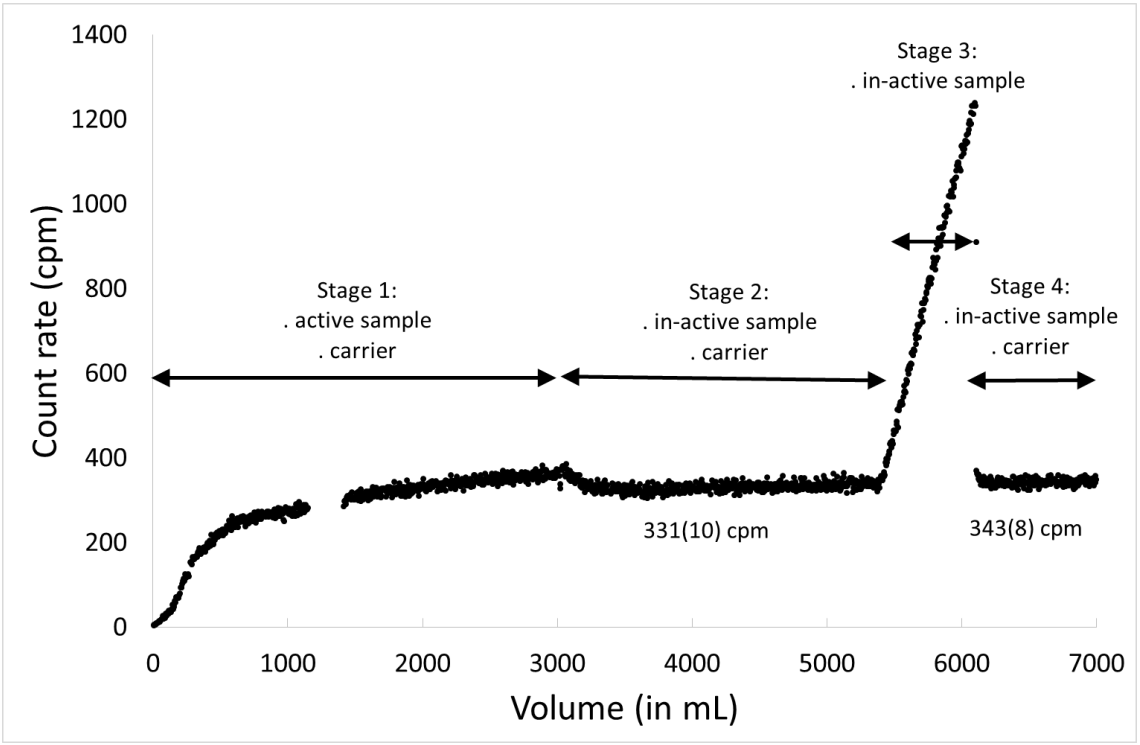


WATER-RADD (on-line continuous detector)

Study of extractant performance

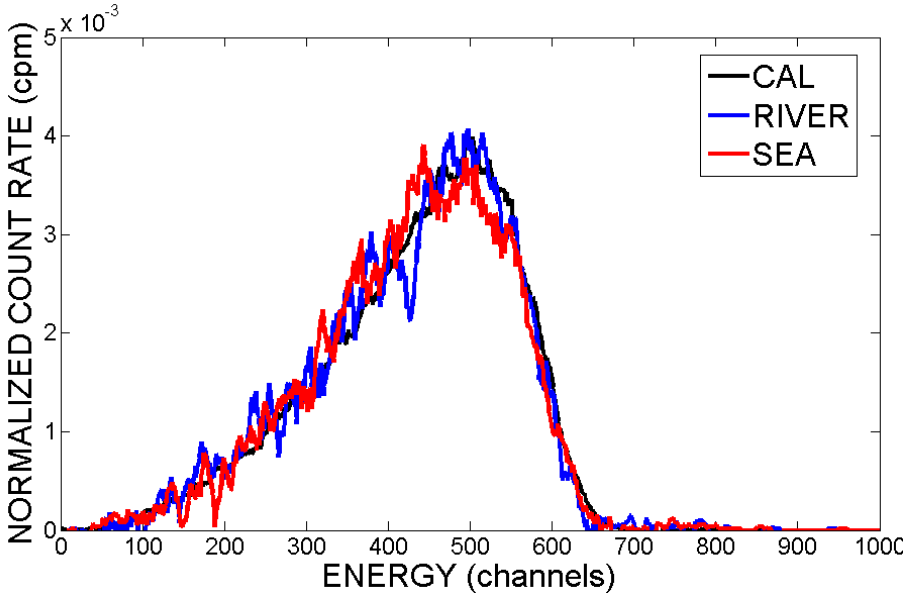
- $^{90}Sr/^{90}Y$ assay
- 150 hours experiment
- 4 different experimental set-up
- Counting time: 5 min





MASS (Modular Automated Separation System)

Automatic vs. Manual: Determination of ^{99}**Tc in WATER** samples



	Limit of detection (Bq/L)
10 mL and 180 min	0.7
500 mL and 180 min	0.014

- Automated and manual separation present equivalent perfomances
- Automated separation with MASS and PSresin can lead to a increase of analysis productivity