Combination of Methods for Rapid Determination of Mixtures of Alpha and Beta Emitters in Water Samples

Jordi Fons Castells

Laboratory of Environmental Radiology

Dept. Chemical Engineering and Analytical Chemistry

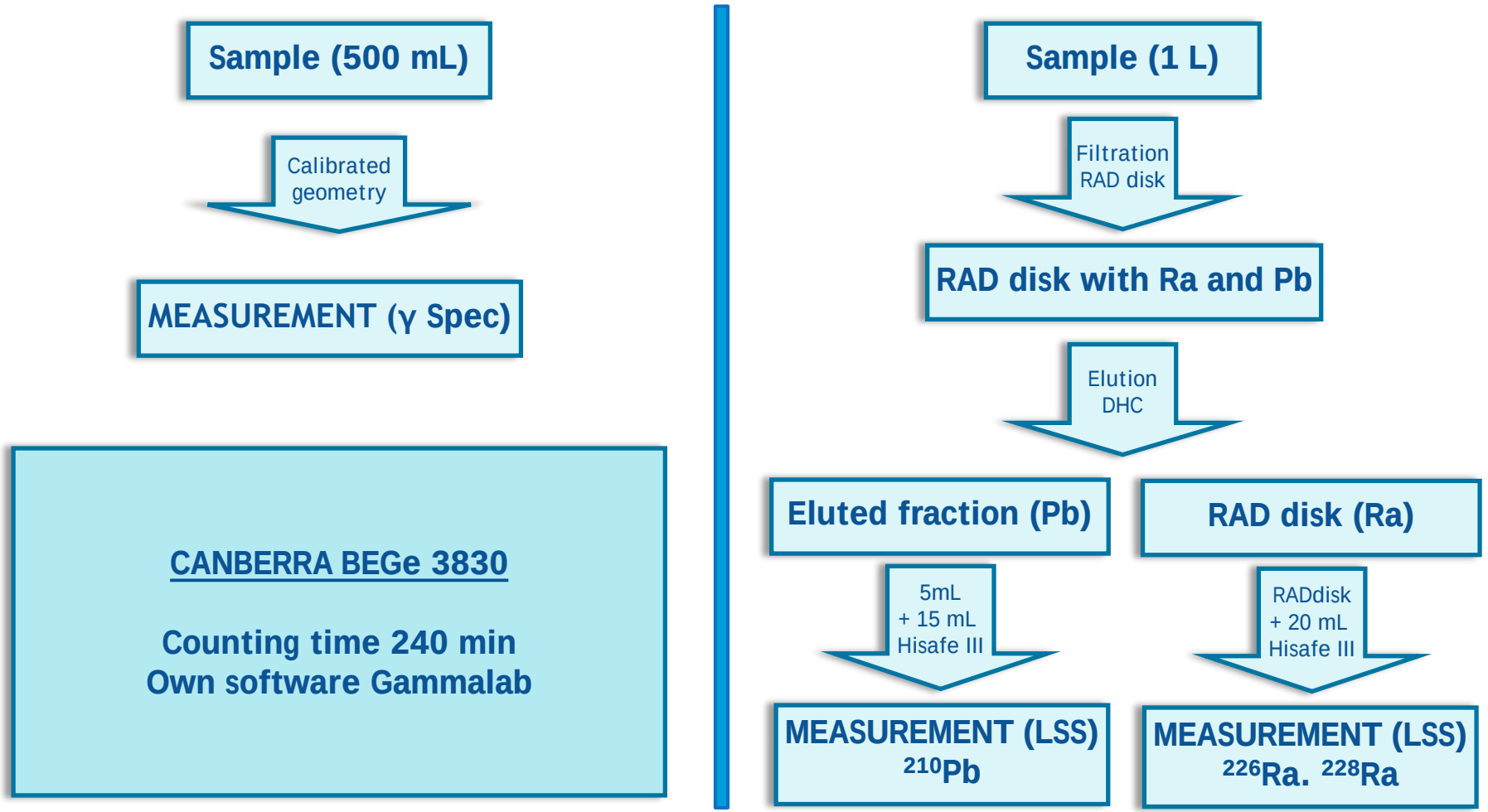
UNIVERSITAT DE BARCELONA

Objetives

- Design a strategy to determine most of the radionuclides included in the Directive 2013/59/EURATOM using rapid methods and multivariate calibration with PLS models.

  - Optimization of rapid analysis procedures
  - Construction of a library of spectra
  - Development PLS models for the deconvolution of LS spectra
  - Design of the strategy
  - Validation and application of the strategy

Procedures

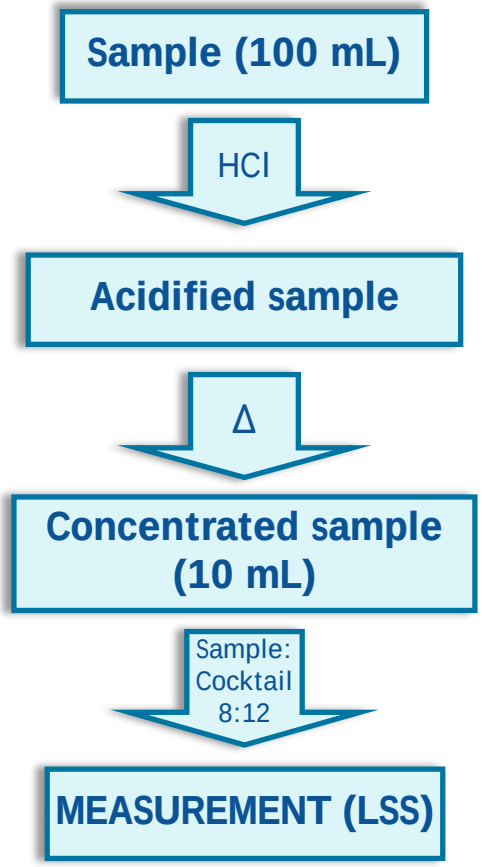


Gamma spectrometry

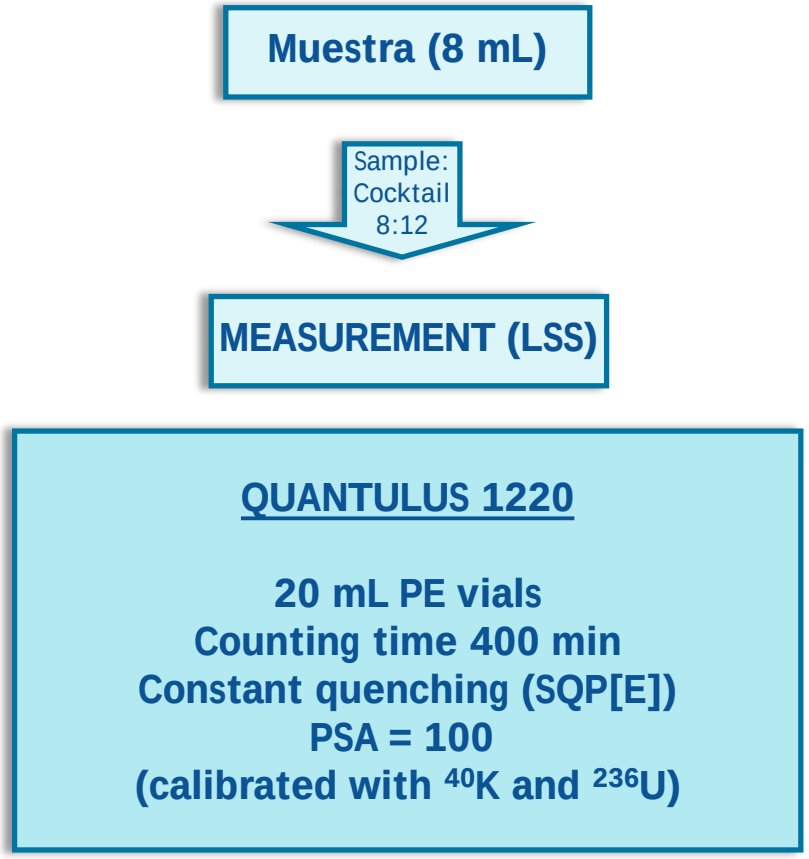
RAD disk (LSS)

J. Fons-Castells et al. 2016 *J. Radioanal. Nucl. Chem.* 309. pp. 1123 -1131.
J. Fons-Castells et al. 2017 *Appl. Radiat. Isot.* 124. pp. 83–89.

Procedures



LSS evaporation



LSS direct

J. Fons-Castells et al. 2013 *J. Environ. Radioact.* 125. pp. 56-60.

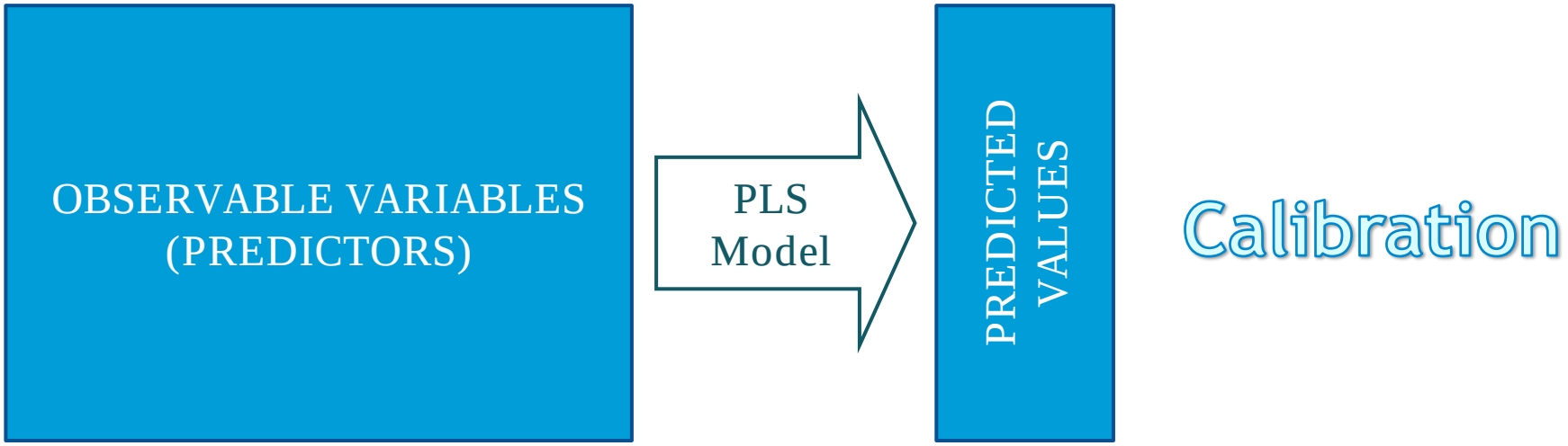
Library of spectra construction

RN	High (Bq kg^{-1})	Intermediate (Bq kg^{-1})	Low (Bq kg^{-1})
^{3}H	100	50	25
^{14}C	100	50	25
^{40}K	10	5	2
^{60}Co	50	25	10
^{90}Sr/^{90}Y	50	25	10
^{134}Cs	50	25	10
^{137}Cs	50	25	10
^{210}Pb	10	5	1
^{226}Ra	10	5	1
^{228}Ra	10	5	1
$^{234+238}$U	10	5	1
$^{239+240}$Pu	10	5	1
^{241}Am	10	5	1

Multivariate calibration in LSS – PLS Model construction

(Matrix of standard spectra)
(LIBRARY)

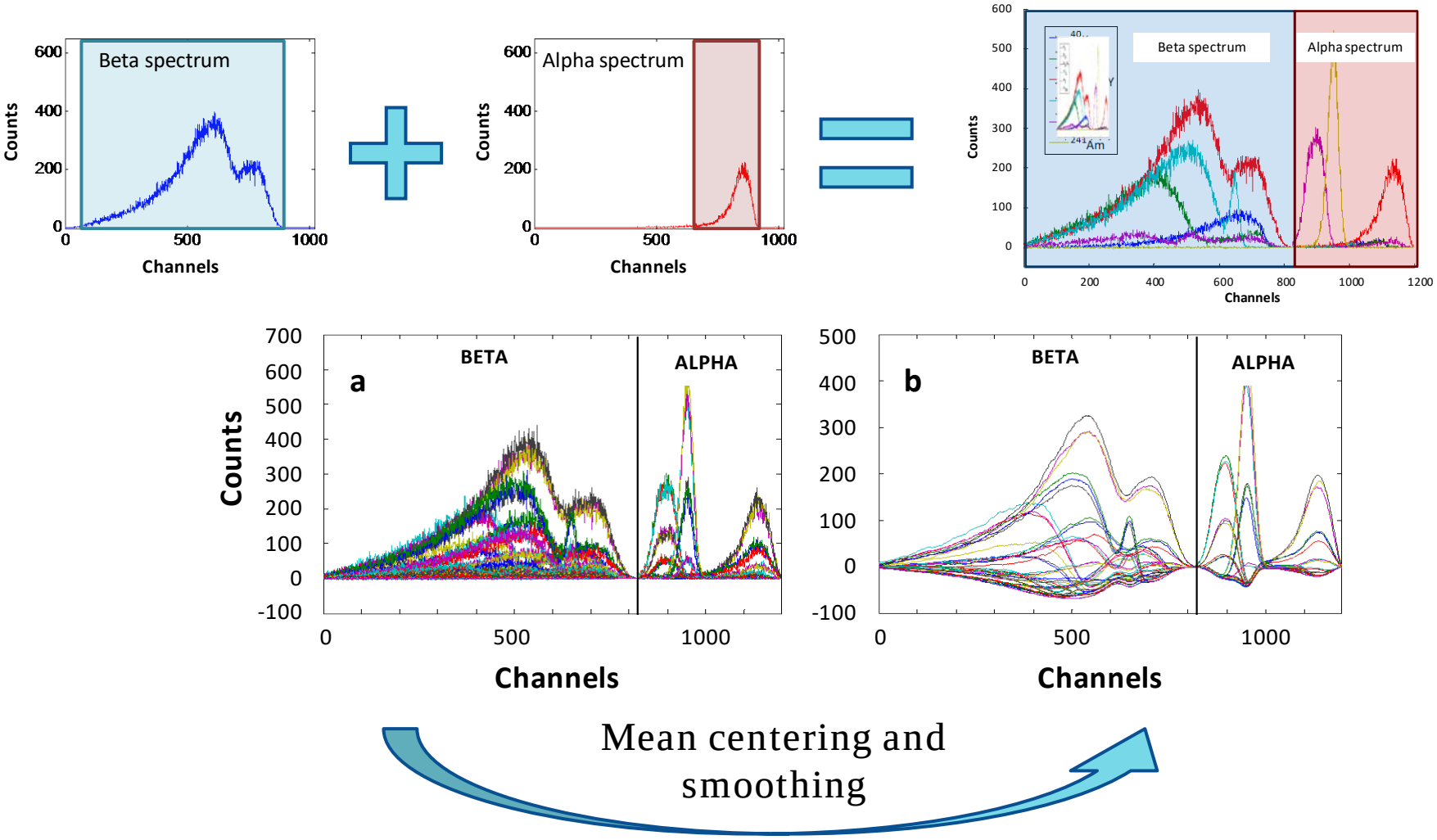
(Standards activity)



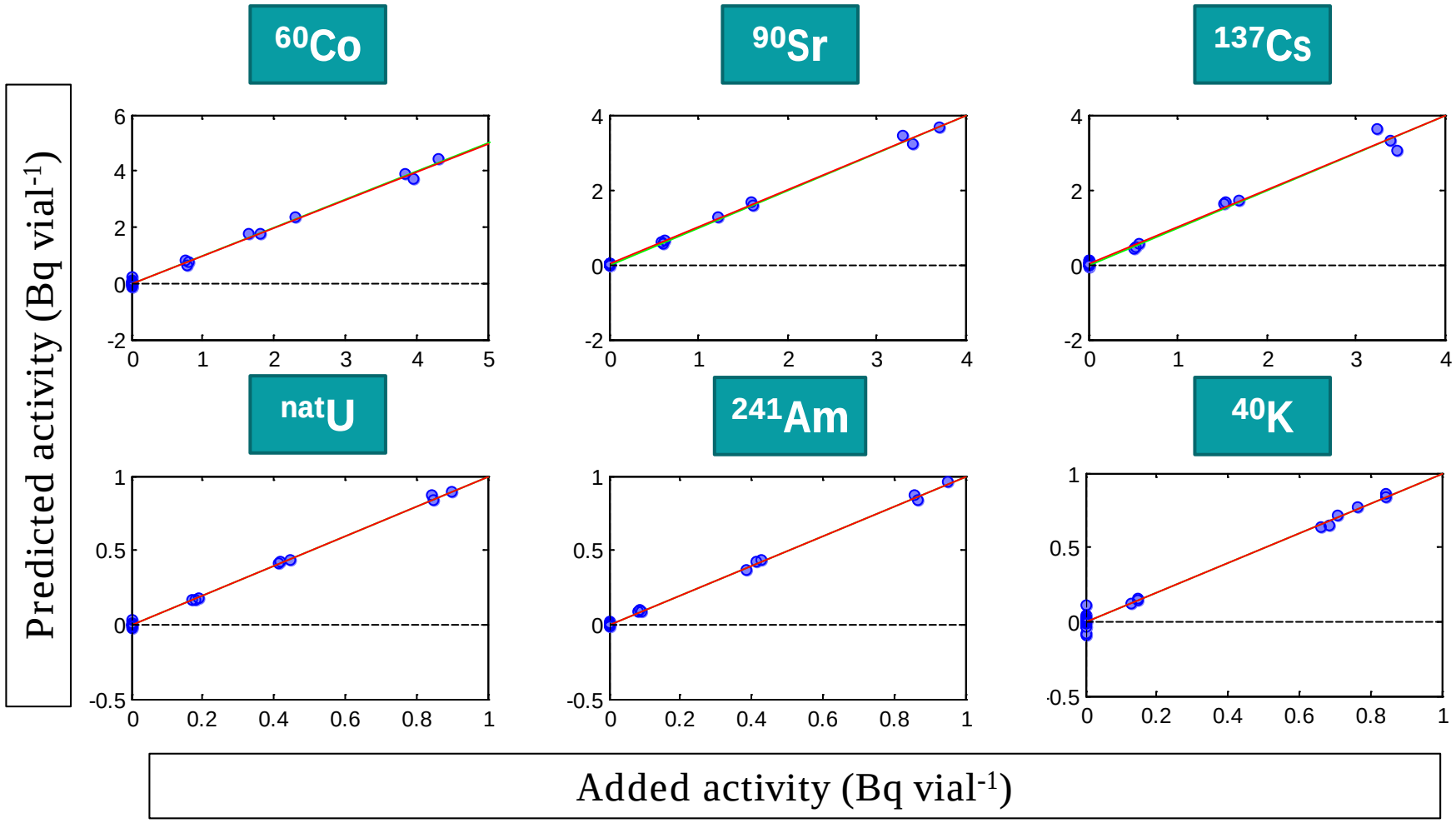
(Matrix of sample spectra)

(Samples activity)

Multivariate calibration in LSS – Spectra pretreatment

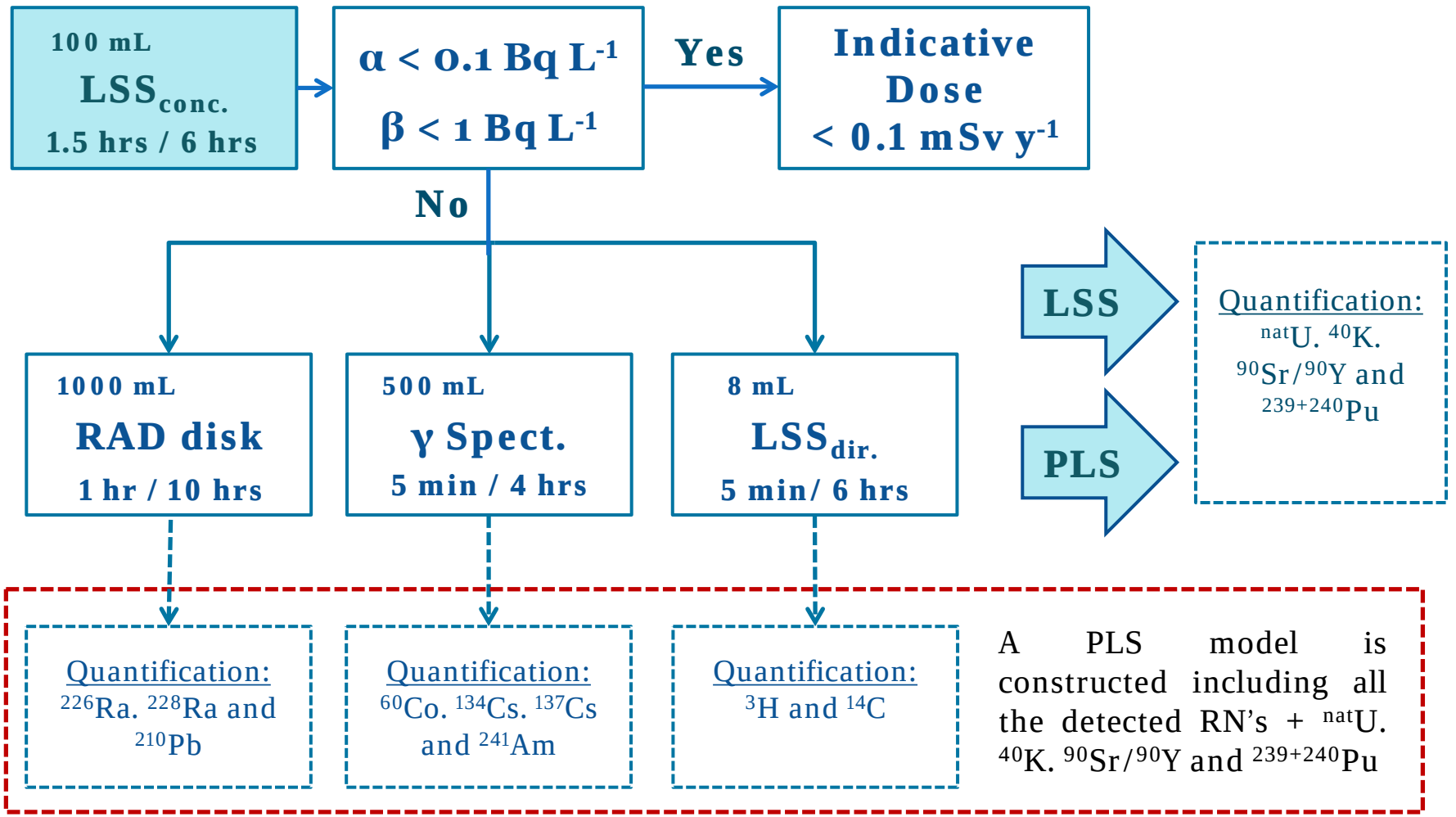


Multivariate calibration in LSS – Cross validation



J. Fons-Castells et al. 2017 *J. Environ. Radioact.* 166. pp. 195-201.

Strategy design and PLS model construction



Validation. Quality control material

IAEA-TEL-2014-03 Sample 3

RN	γ-Spec. (Bq kg^{-1})	RAD disk (Bq kg^{-1})	$LSS_{dir.}$-PLS (Bq kg^{-1})	$LSS_{conc.}$-PLS (Bq kg^{-1})	Organizer (Bq kg^{-1})	Relative Bias (%)
^{3}H	-	-	< 5.2	-	-	-
^{14}C	-	-	< 3.8	-	-	-
^{40}K	< 10.7	-	< 3.6	< 0.4	-	-
^{60}Co	< 0.3	-	-	-	-	-
$^{90}Sr/^{90}Y$	-	-	19.3 ± 2.9	22.6 ± 2.3	24.5 ± 0.2	-8 %
^{134}Cs	23.2 ± 0.4	-	35.2 ± 5.3	31.6 ± 3.2	26.3 ± 0.2	-12 %
^{137}Cs	19.3 ± 0.3	-	12.8 ±1.9	15.2 ± 1.5	19.6 ± 0.1	-2 %
^{210}Pb	12.0 ± 2.7	9.4 ± 0.5	7.6 ± 1.2	9.1 ± 0.9	-	-
^{226}Ra	8.2 ± 0.4[1]	18.6 ± 0.6	15.5 ±2.3	15.2 ± 1.5	17.9 ± 0.1	4 %
^{228}Ra	< 1.6[2]	< 0.03	-	-	-	-
^{nat}U[3]	-	-	7.1 ± 1.1	6.3 ± 0.6	5.48 ± 0.04	14 %
^{241}Am	21.3 ± 0.3	-	21.1 ±3.2	17.0 ± 1.7	20.0 ±0.1	-6 %

1 Not in secular equilibrium
2 Via ^{228}Ac
3 ^{234}U + ^{238}U

Validation. Proficiency test

IAEA-TEL-2015-03 Sample 1

RN	γ-Spec. (Bq kg^{-1})	LSS$_{conc.}$-PLS (Bq kg^{-1})	Organizer (Bq kg^{-1})	Statistics performance		
				Relative Bias	Robust SD	z-score
^{90}Sr	-	34.1 ± 3.4	29.6 ± 0.8	7.4 %	3	0.7
^{134}Cs	28.5 ± 2.2	31.9 ± 3.2	30.0 ± 0.9	-5.0 %	1.8	0.8
^{137}Cs	30.2 ± 2.4	32.9 ± 3.3	30.1 ± 0.9	0.3 %	1	0.1

Application. Determination of ^{3}H in water samples of surveillance around NPP

	Distillation ^{3}H			*LSS_{dir}-PLS ^{3}H*			
Code	*Activity Bq kg^{-1}*	*Uncert. Bq kg^{-1}*	*AMD Bq kg^{-1}*	*Activity Bq kg^{-1}*	*Uncert. Bq kg^{-1}*	*AMD Bq kg^{-1}*	*Bias*
Mar. 2012	407.5	27.3	1.98	367.3	36.7	3.15	-10%
Mar. 2013	69.1	4.7	1.85	66.6	6.7	3.15	-4%
Sup. 2012	3.07	0.62	1.88	3.55	0.35	3.15	16%
Sup. 2013	< 1.88	-	1.88	< 3.15	-	3.15	-
Sup. 2014	10.10	1.01	2.32	8.90	0.89	3.15	-12%
Sup. 2015	< 1.66	-	1.66	< 3.15	-	3.15	-
Und. 2012	3.75	0.67	1.97	3.25	0.32	3.15	-13%
Und. 2013	2.63	0.60	1.85	< 3.15	-	3.15	-
Und. 2014	4.91	0.80	2.32	3.59	0.36	3.15	-27%
Und. 2015	< 1.65	-	1.65	< 3.15	-	3.15	-
Dri. 2014	7.85	0.81	1.87	7.85	0.79	3.15	0%
Dri. 2015	6.63	1.49	1.85	6.02	0.60	3.15	-9%

Using this model ^{40}K was also determined (around 10 Bq kg^{-1} for marine water) and ^{14}C below the detection limit in all the cases (0.35 Bq kg^{-1}).

Application. Determination natural radionuclides in drinking water

Analyzed with accredited methods using radiochemical separations and alpha spectrometry (uranium and radium) and LSS for ^{210}Pb.

	Strategy (Bq kg^{-1})			Accredited procedures (Bq kg^{-1})			Bias (%)		
Code	^{210}Pb	^{226}Ra	^{nat}U	^{210}Pb	^{226}Ra	^{nat}U	^{210}Pb	^{226}Ra	^{nat}U
S_1	<0.02	0.51	0.80	0.028	0.55	0.78	-	-7	3
S_2	0.13	0.19	6.10	0.11	0.16	5.90	13	15	3
S_3	<0.02	<0.02	0.18	<0.0003	0.005	0.16	-	-	13
S_4	<0.02	<0.02	<0.03	0.001	0.002	0.032	-	-	-
S_5	<0.02	0.08	0.09	0.001	0.070	0.082	-	14	4

^{228}Ra was evaluated below the detection limit (0.04 Bq kg^{-1}) for the entire samples.

Conclusions

- Rapid procedures for the determinations of alpha and beta emitters by LSS were optimized.
- A library of LS spectra for 13 radionuclides at different activity levels was constructed.
- Feasibility of PLS models for LS spectra deconvolution has been proved.
- A strategy which combines the rapid procedures developed and PLS quantification was designed.
- This strategy was validated using a quality control material and a proficiency test.
- It was applied for the determination of ^{3}H and natural radionuclides in water samples with satisfactory results.

Combination of Methods for Rapid Determination of Mixtures of Alpha and Beta Emitters in Water Samples

Thanks for listening

Jordi Fons Castells

Laboratory of Environmental Radiology

Dept. Chemical Engineering and Analytical Chemistry

UNIVERSITAT DE BARCELONA