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VALIDATION OF AN IMPROVED METHOD FOR THE SEPARATION AND MEASUREMENT OF Pb-210 AND Po-210

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Outline

- Why measurement of Pb-210 and Po-210 required?
- Procedure
  - Former method
  - optimized method
- Results of validation
- Comparison Ag and Ni discs for ^{210}Po autodeposition
- Conclusion

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Why measuring Pb-210 and Po-210?

- European drinking water directive 98/83/EC
  - WHO recommendations
  - Calculation of Total Indicative Dose (TID)
    - ^{210}Pb-^{210}Po activities needed
- Analysis of radioactivity in natural and drinking waters
  - Pb-210 and Po-210 part of the natural radionuclides
  - No normative method
  - Sensitive methods needed with low DL

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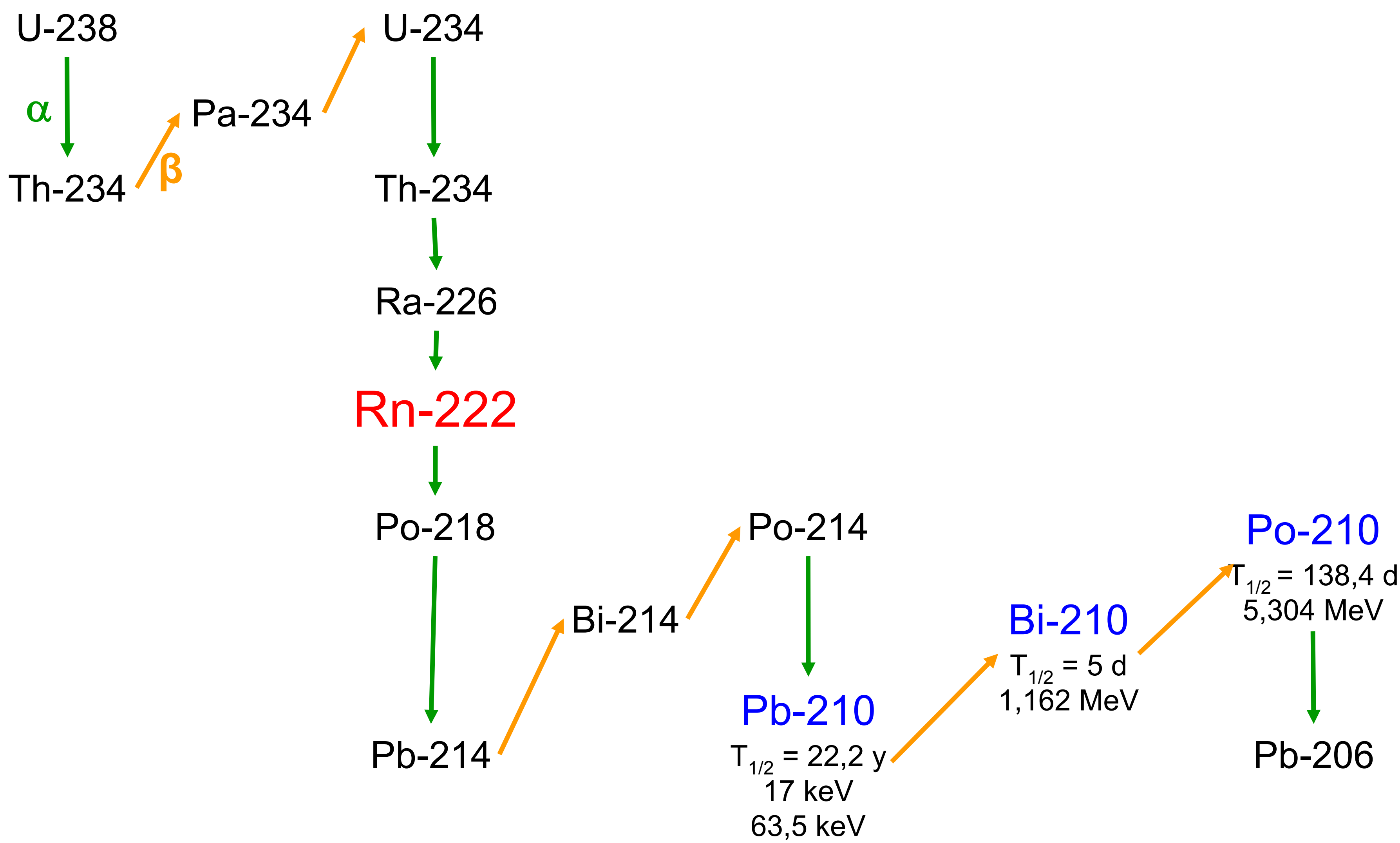
Reminder



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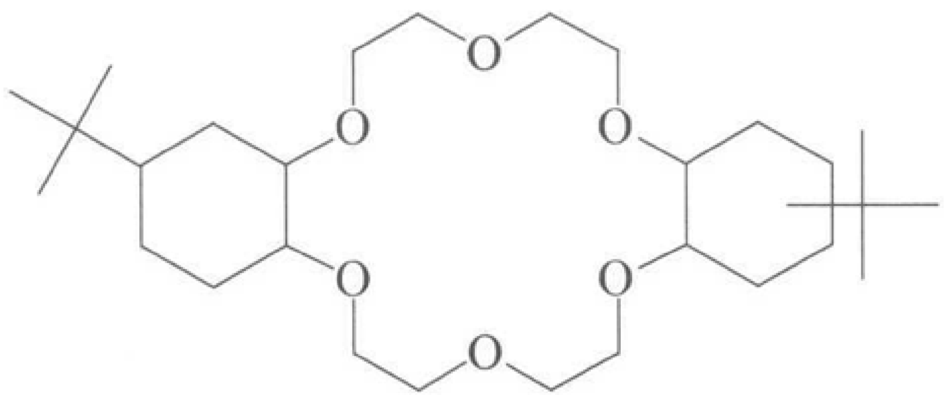
Existing data on Pb Resin (1/2)

- Extractant : crown ether (same as Sr Resin)



Existing data on Pb Resin (2/2)

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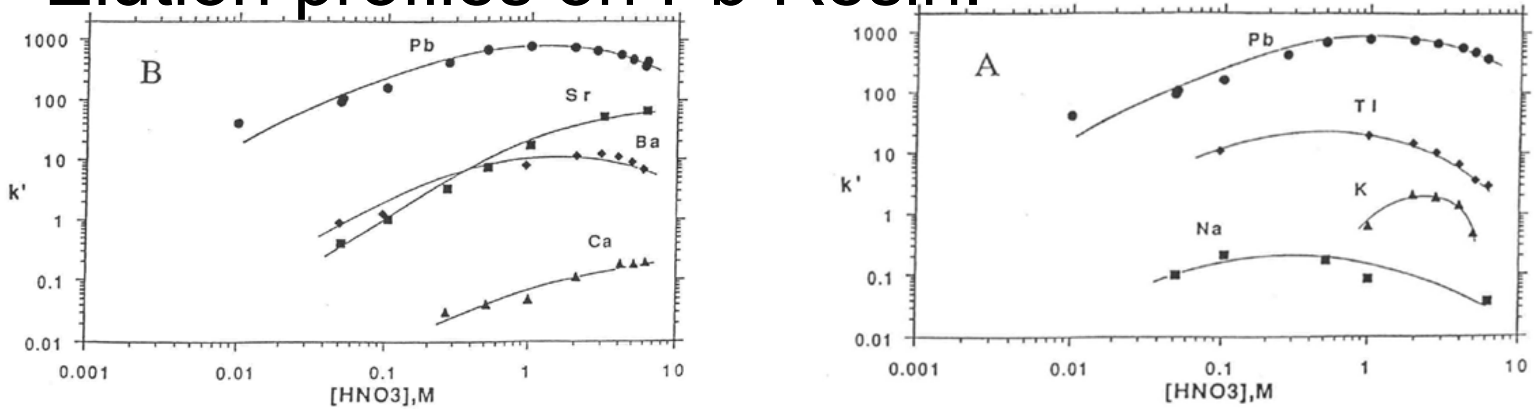
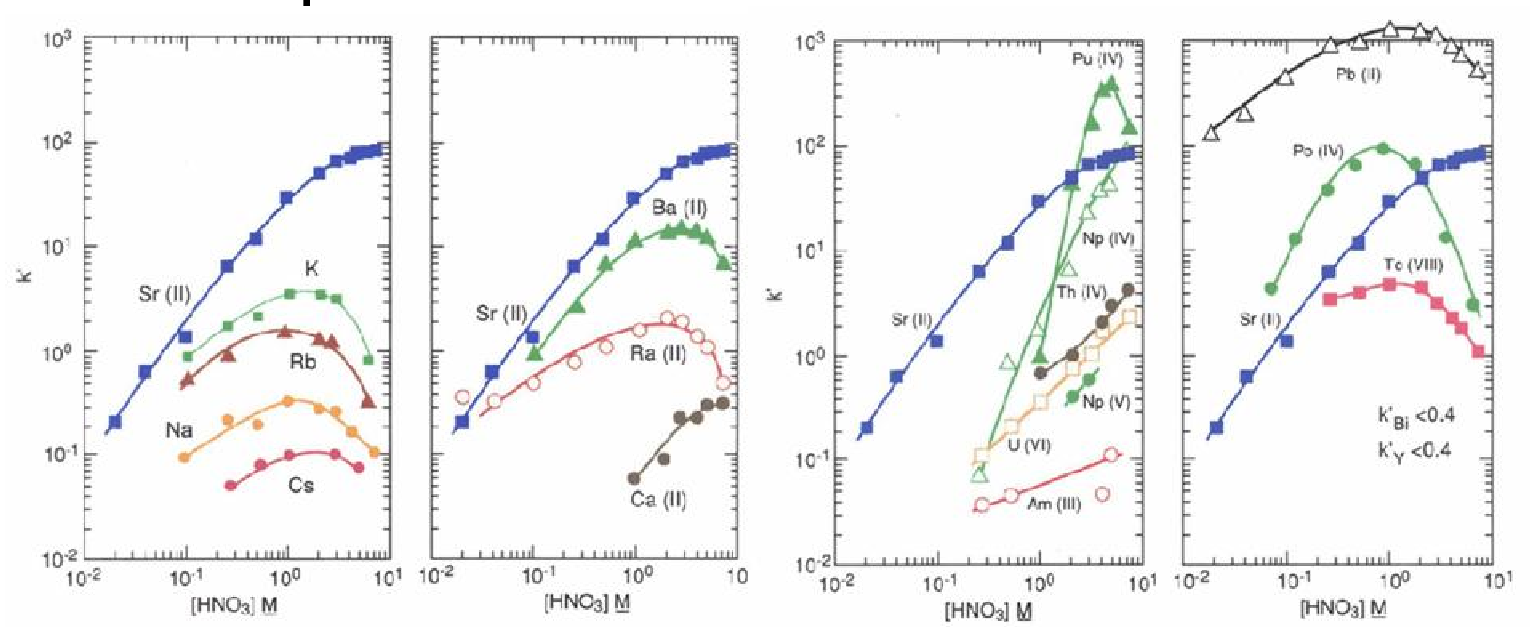
- Elution profiles on Pb Resin:



- Elution profiles on Sr Resin:



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Experiments

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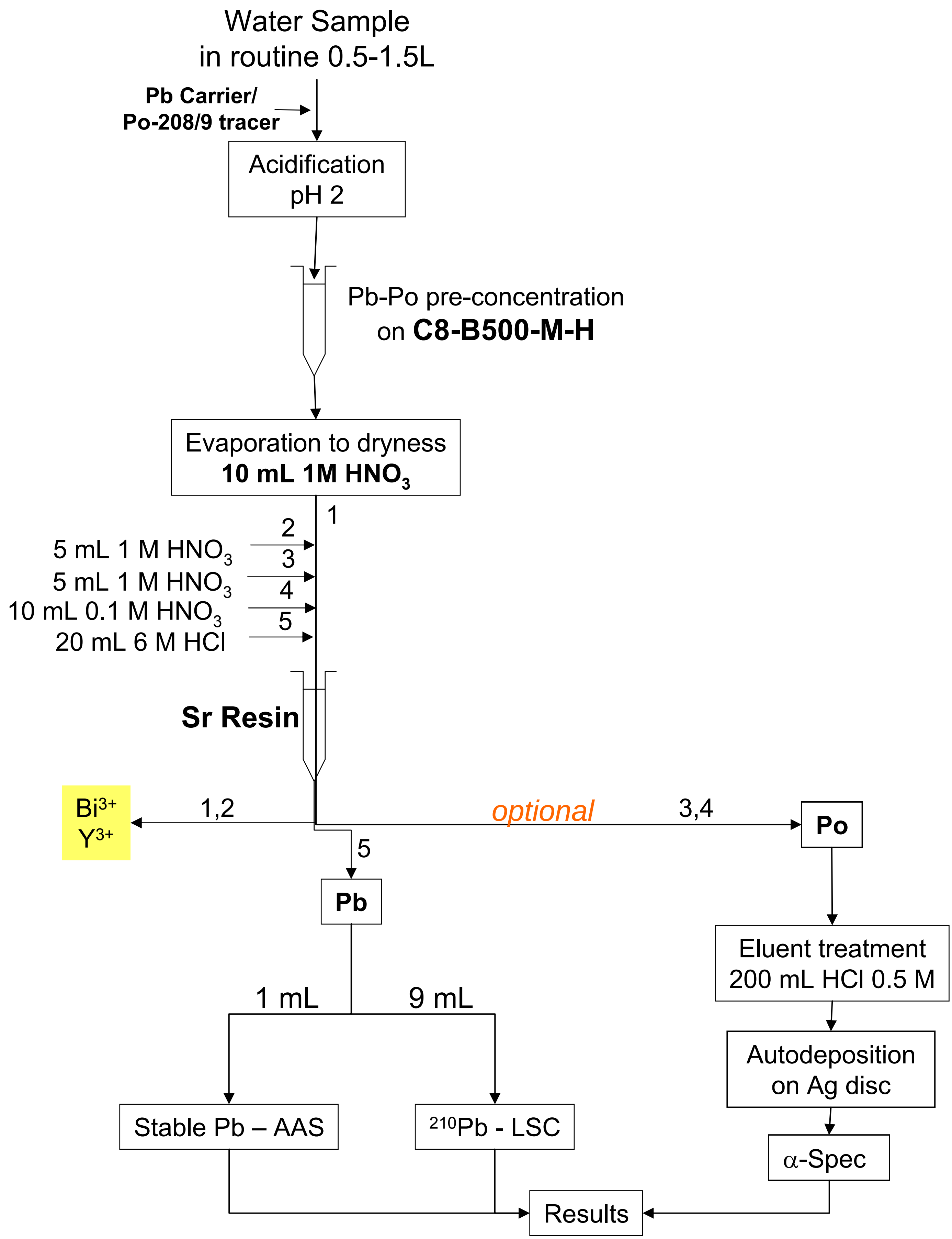
^{210}Pb-^{210}Po separation procedure: former method

- Pb-Po pre-concentration on cationic resin (C8-B500-M-H)
- Sequential separation on Sr Resin of Po and Pb
- Po auto-deposited on Ag disc for α-spec
- Pb:
  - 1mL for AAS measurement→determination of chemical yield
  - 9mL for LSC measurement



Water Sample
in routine 0.5-1.5L
Pb Carrier/
Po-208/9 tracer
Acidification
pH 2
Pb-Po pre-concentration
on C8-B500-M-H
Evaporation to dryness
10 mL 1M HNO3
1
2
5 mL 1 M HNO3
3
5 mL 1 M HNO3
4
10 mL 0.1 M HNO3
5
20 mL 6 M HCl
Sr Resin
Bi3+
Y3+
1,2
optional
3,4
Po
5
Pb
1 mL
9 mL
Eluent treatment
200 mL HCl 0.5 M
Autodeposition
on Ag disc
Stable Pb – AAS
210Pb - LSC
α-Spec
Results

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^{210}Pb-^{210}Po separation procedure: optimized method

- Pb-Po co-precipitation with $Fe(OH)_3$
- Sequential separation on Pb Resin of Po and Pb
- Po auto-deposited on Ag disc for α-spec
- Pb:
  - 1mL for AAS measurement→determination of chemical yield
  - 9mL for LSC measurement

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Optimisation of ^{210}Po-^{210}Pb separation (A)

- Conditions
  - Resin conditioning with 10 mL 2M HCl
  - Load of sample
  - Rinsing with 10 mL 2M HCl
  - Elution of Po with 10 mL 0.1M HNO_3
  - Elution Pb with 20 mL H_2O

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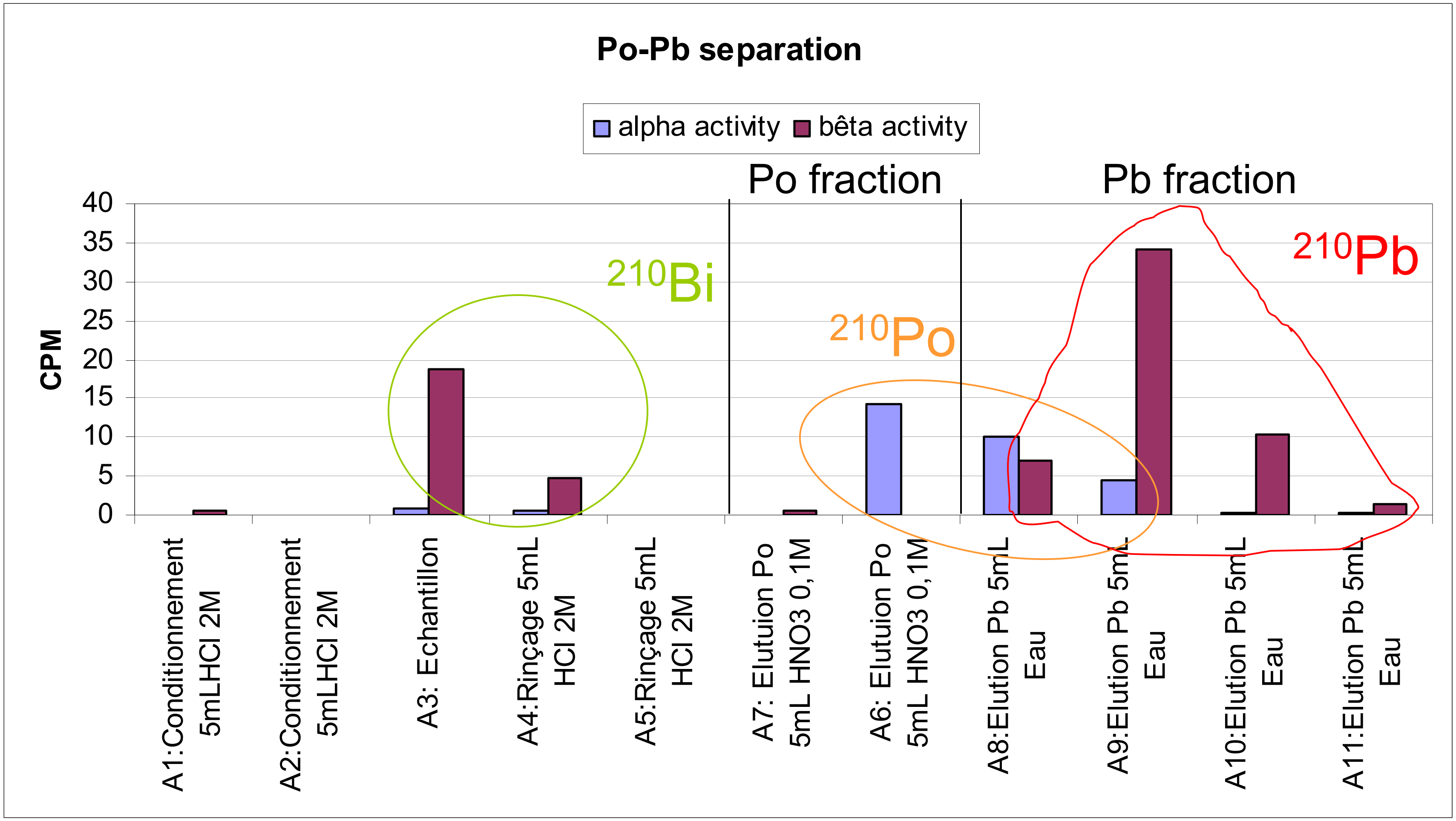

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Optimisation of ^{210}Po-^{210}Pb separation (A)

- Results
  - ^{210}Bi in load and rinsing fractions
  - Pb elution with H_2O:
    - 100% Pb
    - 39% Po

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Optimisation of ^{210}Po-^{210}Pb resolution (B)

- Conditions
  - Resin conditioning with 10 mL 2M HCl
  - Load of sample
  - Rinsing with 10 mL 2M HCl
  - Elution of Po with 15 mL 0.1M HNO_3
  - Elution Pb with 20 mL 0.1M citric acid

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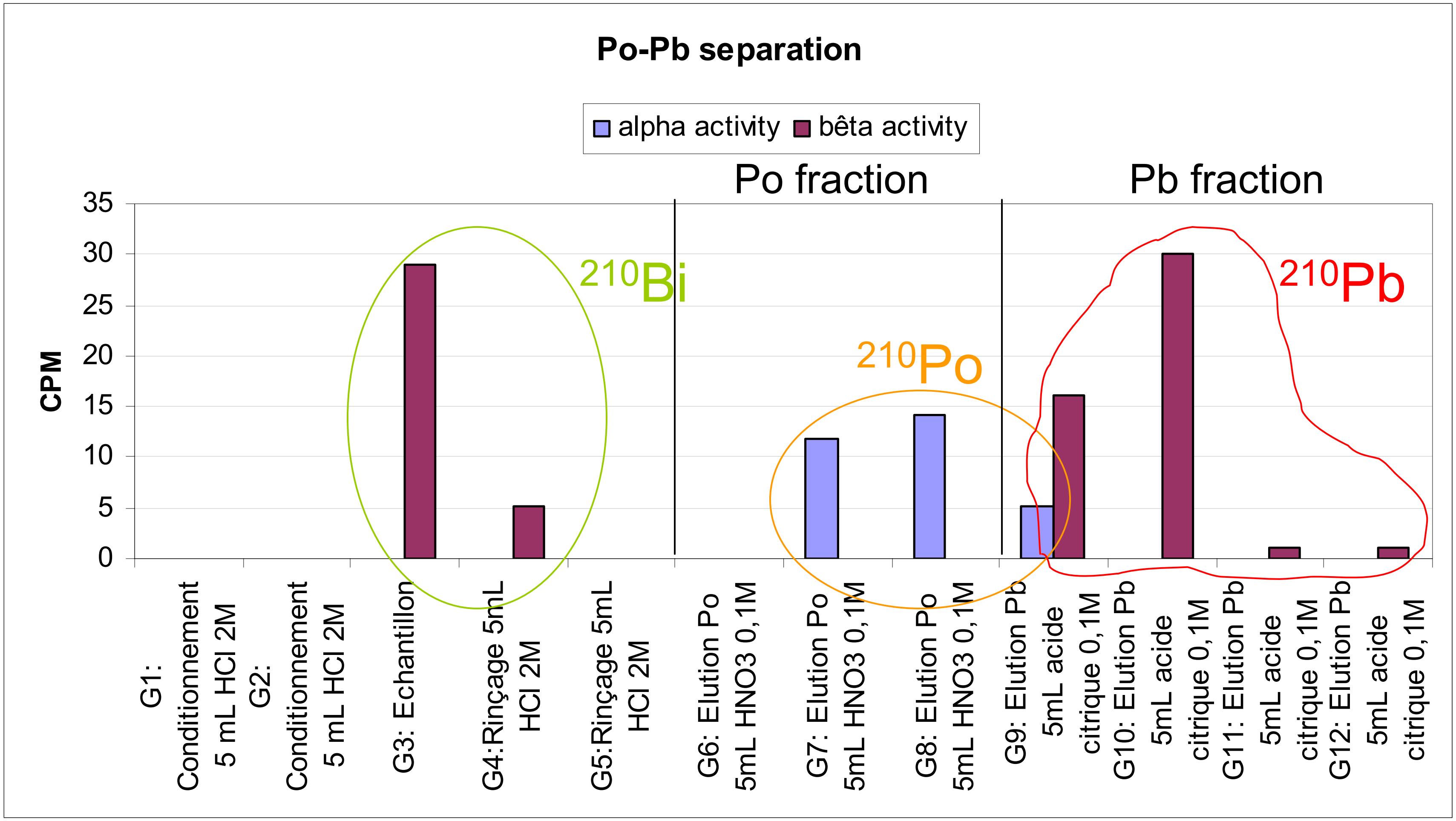

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Optimisation of ^{210}Po-^{210}Pb resolution (B)

- Results
  - Bi in load and rinsing fractions
  - Po elution : less than 0.1% Pb in Po fraction
  - Pb elution :
    - 17% Po in 1st Pb fraction
    - 67% Pb recovery with no Po in fraction

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Optimisation of ^{210}Po-^{210}Pb resolution (C)

- Conditions
  - Resin conditioning with 10 mL 2M HCl
  - Load of sample
  - Rinsing with 10 mL 2M HCl
  - Elution of Po with 5 mL 1M then 10 mL 0.1M HNO_3
  - Elution Pb with 15 mL 0.1M citric acid

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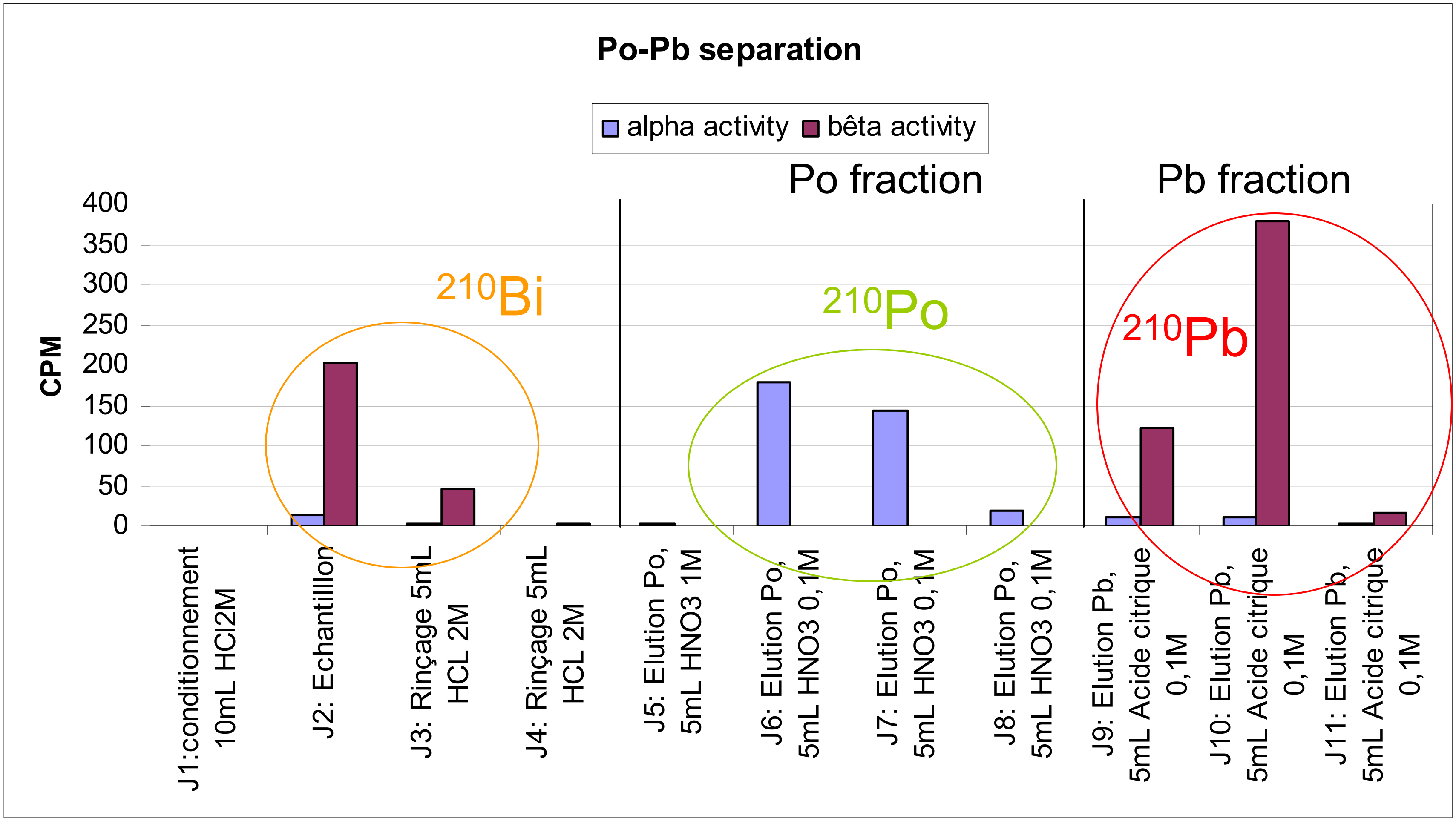

Optimisation of ^{210}Po-^{210}Pb resolution (C)

- Results
  - Bi in load and rinsing fractions
  - Po elution : less than 0.2% Pb in Po fraction, 83% Po recovery
  - Pb elution : quantitative Pb recovery with 6% Po in Pb fraction

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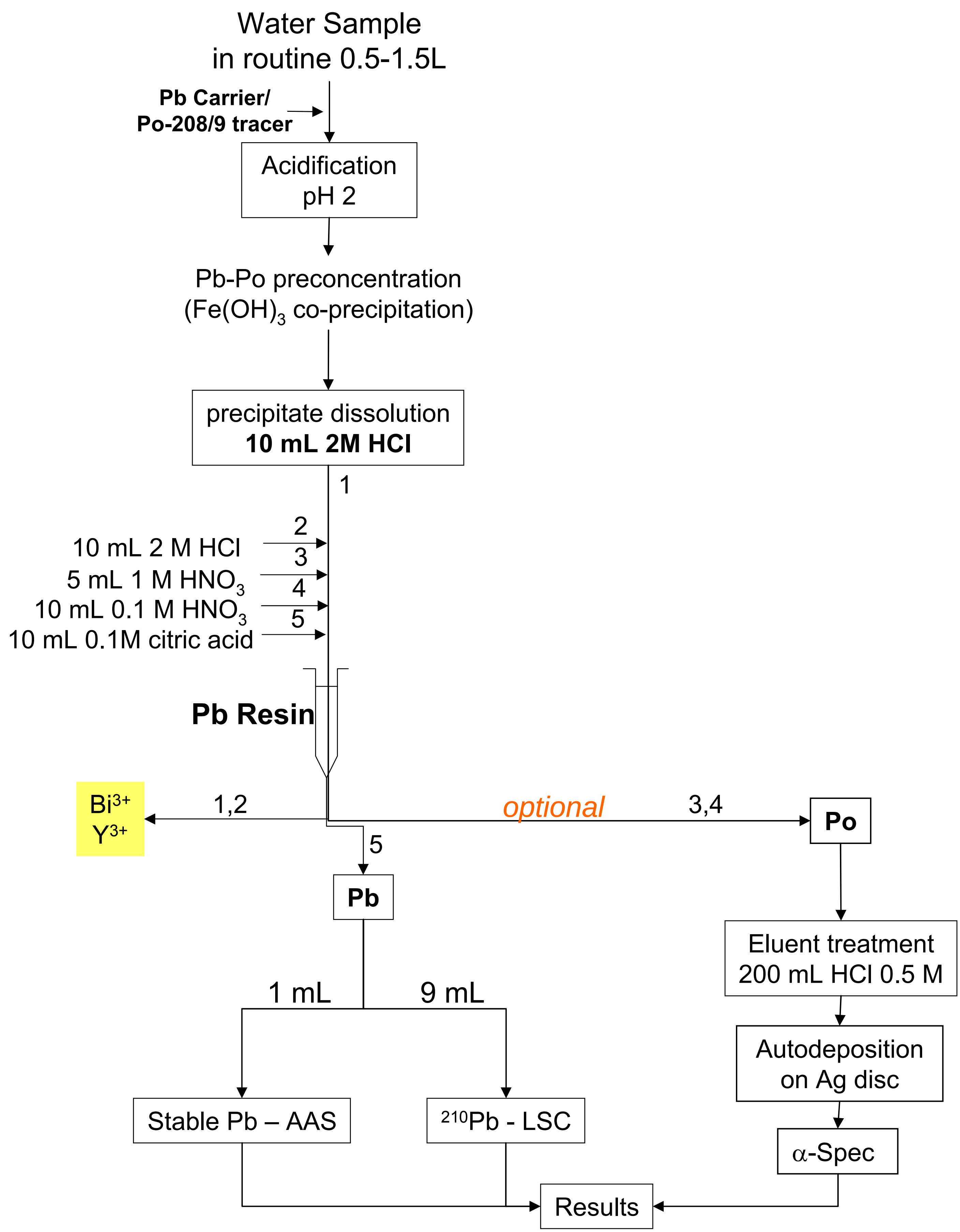
Preliminary conclusions

- Changes:
  - Different pre-concentration method
  - Different resin
  - 2M HCl media instead of 1M HNO_3
  - Better recovery yields for Po: 80% instead of 50%
- Pb elution with H_2O possible
  - ➢ but larger volume needed compared to citric acid
- Pb eluted with 10mL citric acid (97% of total Pb) instead of 20mL 6M HCl



Water Sample
in routine 0.5-1.5L
Pb Carrier/
Po-208/9 tracer
Acidification
pH 2
Pb-Po preconcentration
(Fe(OH)3 co-precipitation)
precipitate dissolution
10 mL 2M HCl
1
2
10 mL 2 M HCl
3
5 mL 1 M HNO3
4
10 mL 0.1 M HNO3
5
10 mL 0.1M citric acid
Pb Resin
Bi3+
Y3+
1,2
optional
3,4
Po
5
Pb
1 mL
9 mL
Stable Pb – AAS
210Pb - LSC
Eluent treatment
200 mL HCl 0.5 M
Autodeposition
on Ag disc
α-Spec
Results

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Results of validation: Selectivity

- Decontamination factors (DCF):
  - overall high for U, Th and Sr,
  - good DCF for Ra in Pb fraction,
  - rather low DCF for Ra in Po fraction - not problematic since Ra is not auto-deposited.

Interfering RN	Pb Fraction		Po Fraction	
	α DCF	β DCF	α DCF	β DCF
Ra-226	182	89	14	45
U-Nat	> 1000	> 1000	> 1000	> 1000
Th-Nat	> 1000	> 1000	> 1000	> 1000
Sr-90	NA	> 1000	NA	> 1000

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Results of validation: Accuracy

- t values ≤ 1 for all analysed samples

	Pb-210					Po-210				
Sample ref.	Ref. A ($Bq.L^{-1}$)	Uc A ($Bq.L^{-1}$)	Exp. A ($Bq.L^{-1}$)	Uc A ($Bq.L^{-1}$)	t value	Ref. A ($Bq.L^{-1}$)	Uc A ($Bq.L^{-1}$)	Exp. A ($Bq.L^{-1}$)	Uc A ($Bq.L^{-1}$)	t value
Water 1^{+}	9.61E-02	2.87E-02	7.00E-02	3.00E-02	0.6	1.30E-02	2.91E-03	1.33E-02	8.54E-03	0.1
Water 2^{+}	< LD		< LD		N/A	2.03E-03	1.15E-03	1.60E-03	6.00E-04	0.3
Spiked Water 1	1.77E-01	1.93E-02	1.60E-01	3.30E-03	0.9	1.60E-01	1.93E-02	1.39E-01	1.84E-02	1.0
Spiked Water 2	1.69E-01	5.15E-03	1.63E-01	8.09E-03	0.7	1.69E-01	5.15E-03	1.55E-01	1.94E-02	0.7
Spiked Water 3	1.66E-01	5.08E-03	1.58E-01	8.09E-03	0.9	1.66E-01	5.08E-03	1.50E-01	2.04E-02	0.7
Spiked Water 4	1.69E-01	5.18E-03	1.63E-01	8.09E-03	0.6	1.69E-01	5.18E-03	1.57E-01	1.80E-02	0.7
Mineralwater*	1.24E-01	1.69E-02	1.02E-01	3.20E-02	0.6	1.06E-01	1.30E-03	1.06E-01	8.76E-02	0.6
CRM (PTB)	8.00E-02	4.00E-03	8.70E-02	2.20E-02	0.3	8.00E-02	4.00E-03	8.50E-02	2.10E-02	0.2

+sample previously measured using accreditated method

*mean of results obtained by other laboratories

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Definition of Accuracy with t value

$$t = \frac{\left| C_{A,det} - C_{A,Ref} \right|}{\sqrt{U^2_{C_{A,det}} + U^2_{C_{A,ref}}}}$$

- t ≤ 1 → No significant difference: accurate
- t > 1 → Results are not accurate

(t corresponds to E_n in ISO/IEC Guide 43-1)

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Results of validation: Accuracy

- t values ≤ 1 for all analysed samples

	Pb-210					Po-210				
Sample ref.	Ref. A ($Bq.L^{-1}$)	Uc A ($Bq.L^{-1}$)	Exp. A ($Bq.L^{-1}$)	Uc A ($Bq.L^{-1}$)	t value	Ref. A ($Bq.L^{-1}$)	Uc A ($Bq.L^{-1}$)	Exp. A ($Bq.L^{-1}$)	Uc A ($Bq.L^{-1}$)	t value
Water 1+	9.61E-02	2.87E-02	7.00E-02	3.00E-02	0.6	1.30E-02	2.91E-03	1.33E-02	8.54E-03	0.1
Water 2+	< LD		< LD		N/A	2.03E-03	1.15E-03	1.60E-03	6.00E-04	0.3
Spiked Water 1	1.77E-01	1.93E-02	1.60E-01	3.30E-03	0.9	1.60E-01	1.93E-02	1.39E-01	1.84E-02	1.0
Spiked Water 2	1.69E-01	5.15E-03	1.63E-01	8.09E-03	0.7	1.69E-01	5.15E-03	1.55E-01	1.94E-02	0.7
Spiked Water 3	1.66E-01	5.08E-03	1.58E-01	8.09E-03	0.9	1.66E-01	5.08E-03	1.50E-01	2.04E-02	0.7
Spiked Water 4	1.69E-01	5.18E-03	1.63E-01	8.09E-03	0.6	1.69E-01	5.18E-03	1.57E-01	1.80E-02	0.7
Mineralwater*	1.24E-01	1.69E-02	1.02E-01	3.20E-02	0.6	1.06E-01	1.30E-03	1.06E-01	8.76E-02	0.6
CRM (PTB)	8.00E-02	4.00E-03	8.70E-02	2.20E-02	0.3	8.00E-02	4.00E-03	8.50E-02	2.10E-02	0.2

+sample previously measured using accreditated method
*mean of results obtained by other laboratories

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Results of validation

- Precision

	Pb-210	Po-210
Repeatability s_r (N=6)	2.2	8.9
Reproducibility s_R (N=12)	4.4	5.2

- s_r and/or $s_R \leq 15\% \rightarrow$ results OK
- s_r and/or $s_R > 15\% \rightarrow$ results not accepted

- Detection limits (DL) for V = 1.5 L
  - Pb-210 in the order of 20 $mBq.L^{-1}$ with counting time of 240 minutes
  - Po-210 in the order of 3 $mBq.L^{-1}$ with counting time of 1000 minutes

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Comparison of ^{210}Po auto-deposition yields on Ni and Ag Discs

	Recovery (%)		FWHM (keV)	
	mean	Std (%)	mean	Std (%)
Ni (N=10)	61	30	18.4	8.2
Ag (N=10)	99	8.6	19.1	15.8

- Ag discs
  - Quantitative auto-deposition
  - Good reproducibility
- Ni discs
  - Reproducibility not stable
- Both discs show very good resolution

Conclusion

- Sequential separation of ^{210}Pb-^{210}Po optimized
- Evaluation of MnO_2 Resin for the pre-concentration of Pb and Po
- Auto-deposition of Po on either Ag or Ni discs