MnO_2 Resin

09/05/2008 - Madrid

Outline

- pH dependency of D_W
- Kinetics
- Capacity / Amount of resin
- Interferences
- Flow-rate
- Applications

Information on MnO2

Bill Burnett et al:

Use of de-ionised , ground and sea waters

- Study with variation of
  - pH
  - Kinetics
  - Ratio resin mass vs volume of solution
  - Salinity
  - Flow rates
- Use of ^{133}Ba as Ra homologue

Josue Moreno (TU Munich):

- D_W values of natural radionuclides
- Capacities
- Interferences

pH dependency

Experimental

- Batch experiments
- 5 mL aqueous phase and 100 mg MnO_2 Resin OR
  10 mL aqueous phase and 25 mg MnO_2 Resin
- pH adjustment with HCl or NaOH
- Magnetic stirring, 60 minutes, room temperature
- Phase separation by filtration (0,1 µm pores)

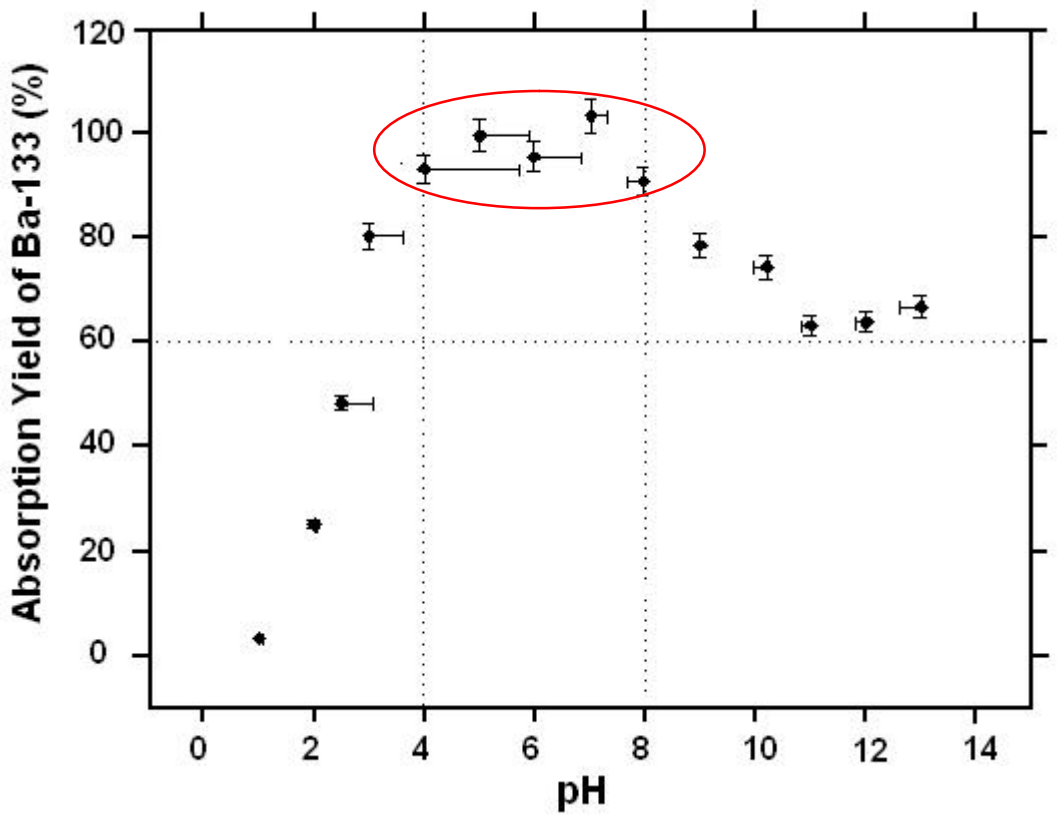
Observation

- Strong shift of the pH in aqueous phase

Measurement

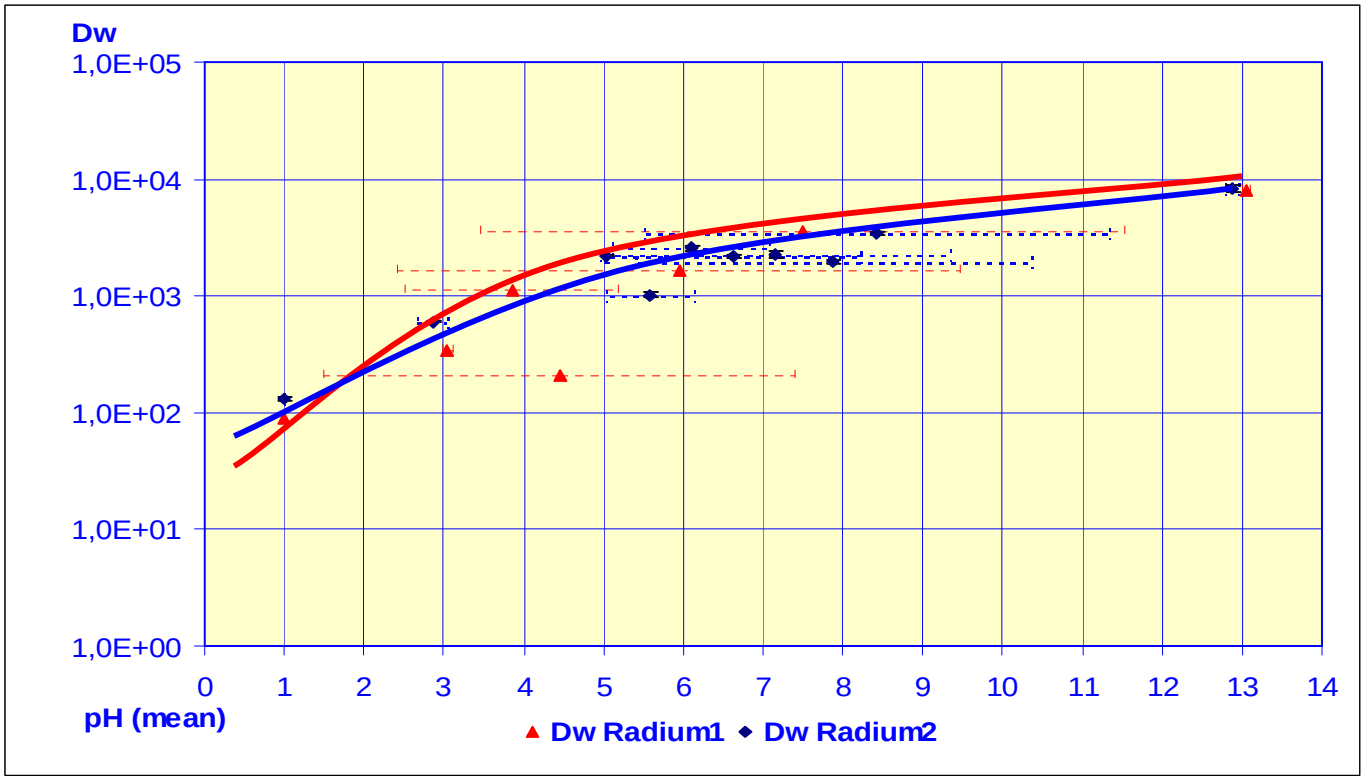
- filtered MnO_2 via γ-spec or LSC (after resin elution)
- aqueous phase via γ-spec or LSC

pH dependency Ba-133



Burnett et al.

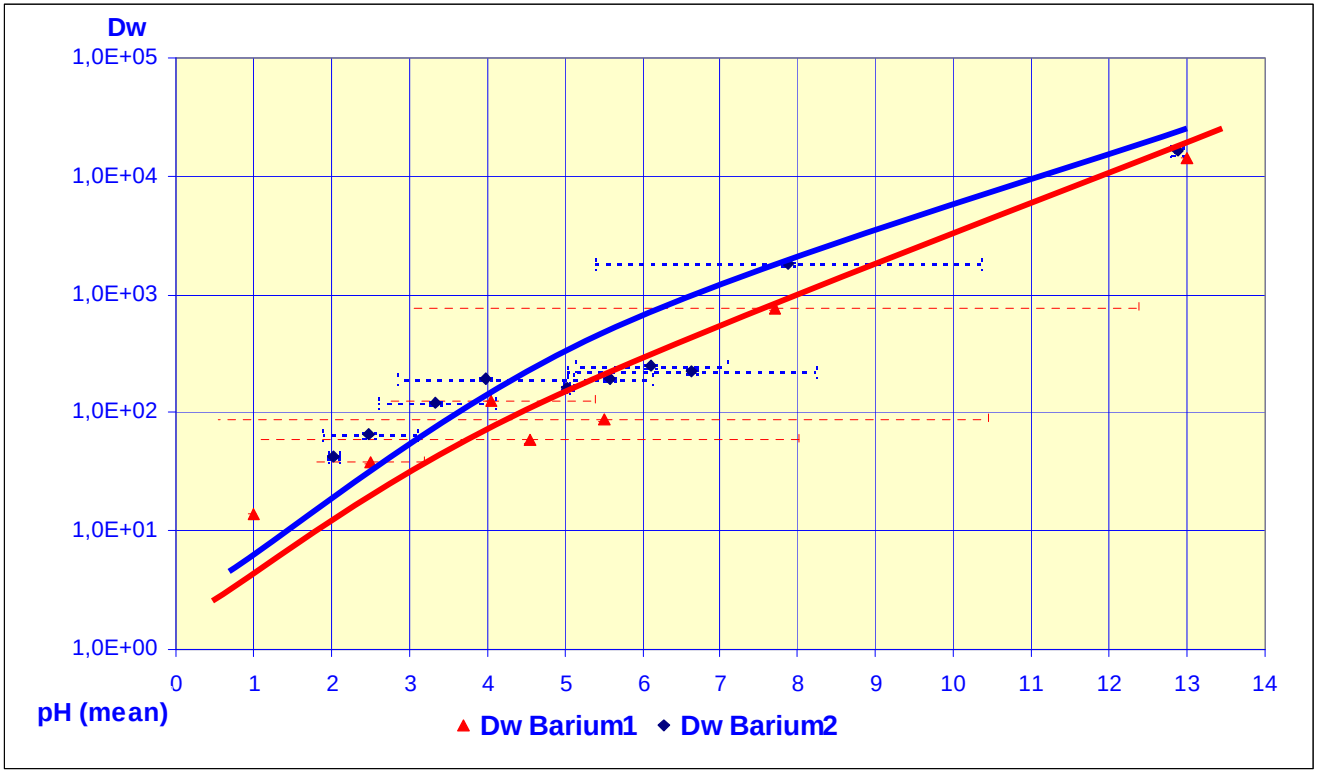
D_w - Ra-226



Moreno

- High retention over the whole pH range
- Radium adsorption greater than 99% for pH>3

D_w - Ba-133



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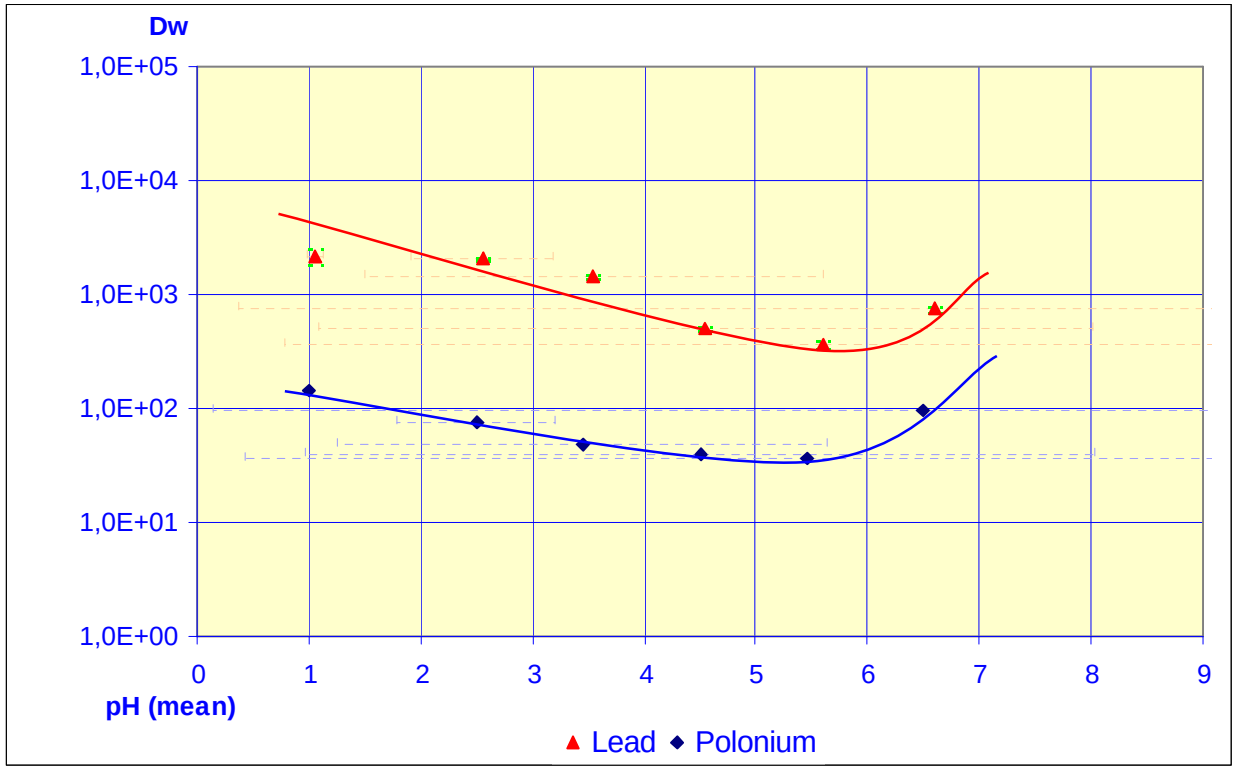
- Overall high retention above pH 4
- Barium adsorption greater than 99% for pH>5

D_w - Pb-210/ Po-210



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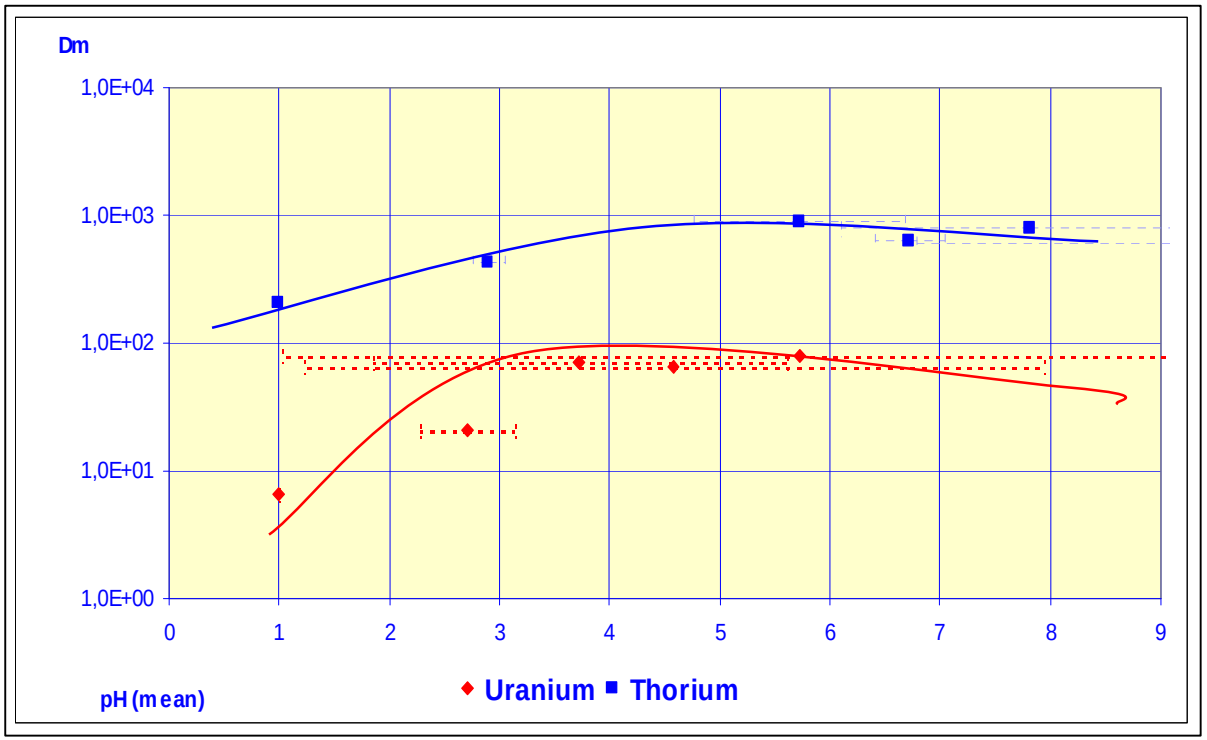
- Pb: High D_w values (500 > D_w > 1000)
- Po: Similar to the behaviour of Pb
- D_w(Po) overall lower (factor 10)

D_w - Th and U



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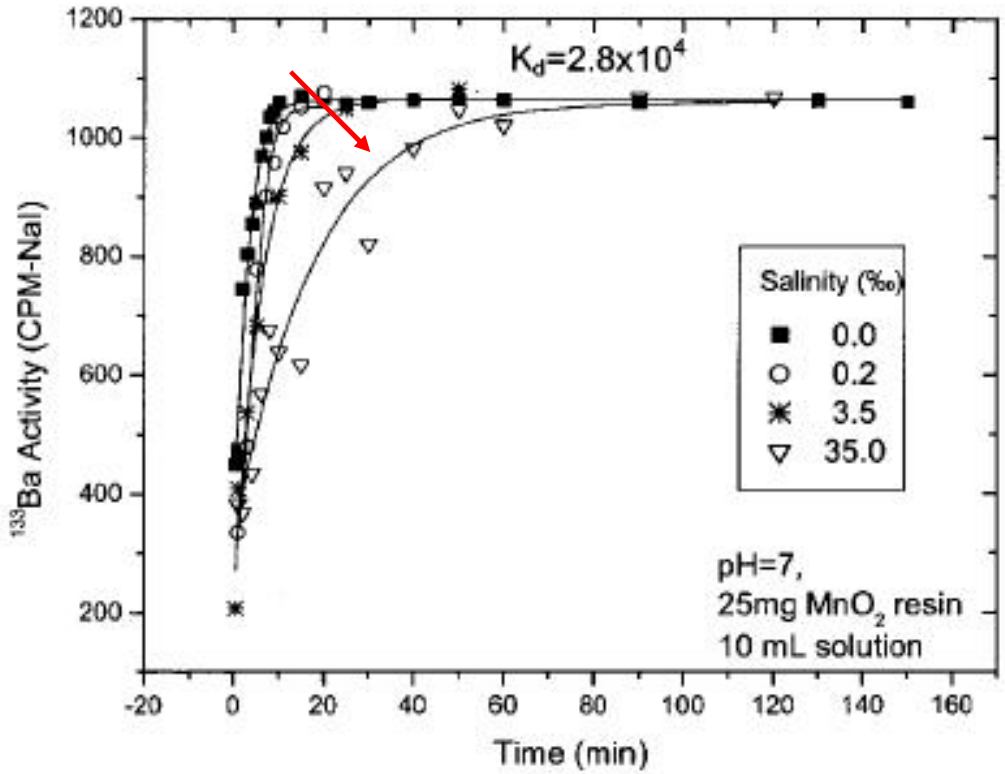
- U: rather good retention in near neutral pH range (D_w • 100)
- Th: overall very good retention 300 < D_w < 1000

Kinetics

- 10 mL water samples spiked with Ba-133 (0, 0.2, 3.5 and 35‰ salinities)
- 25 mg MnO_2 resin
- Magnetic stirrer
- pH = 7.0
- 1.0 to 90 minutes contact
- Measurement of filtered MnO_2 in NaI well-type gamma counter

Kinetics



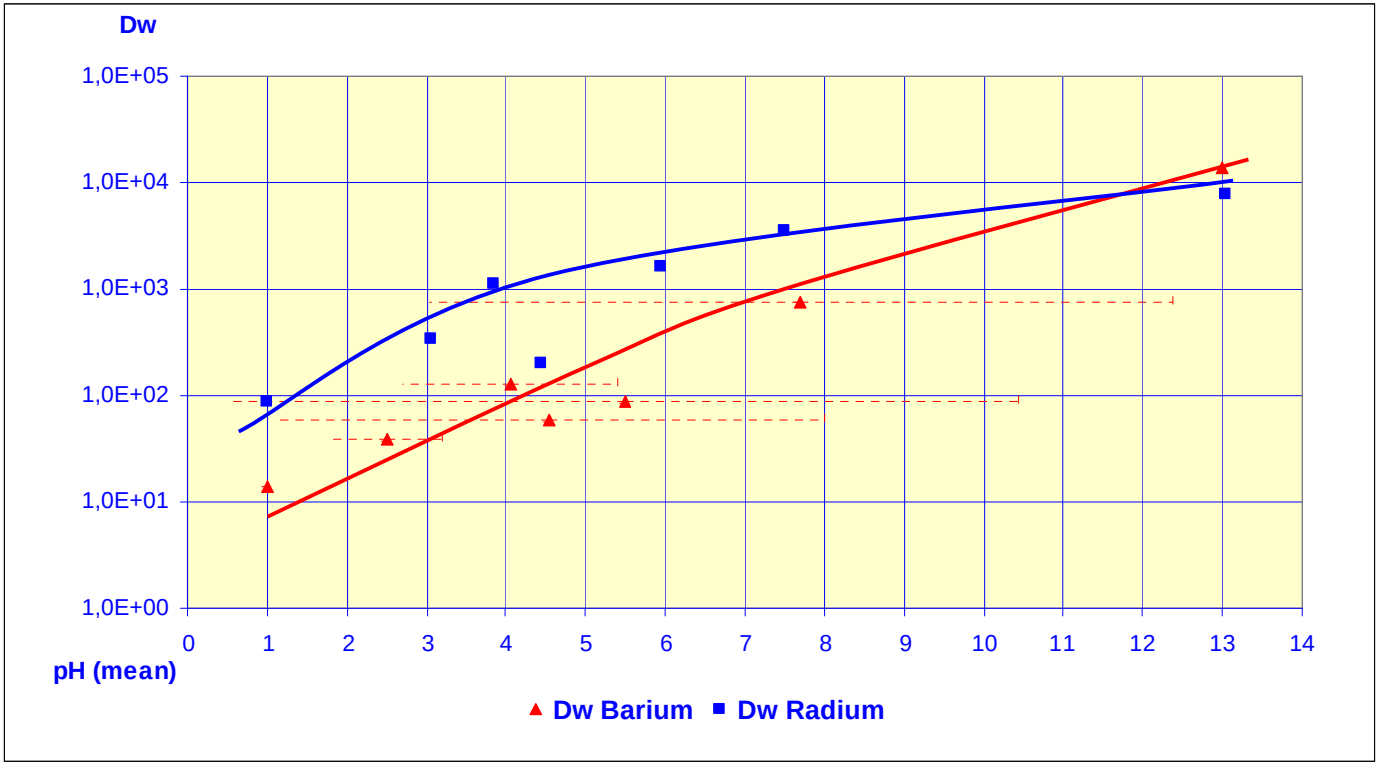
Burnett et al.

§ Uptake kinetics depend on salinity

Ba/Ra homology

- Batch experiments
  - 100 mg MnO_2 / 5 mL solution
- Column
  - 1 g MnO_2 resin
  - Geometry: ∅i = 0.9 cm, H = 6,5 cm
  - Water samples: de-ionised and synthetic sea water

Ba/Ra homology - batch



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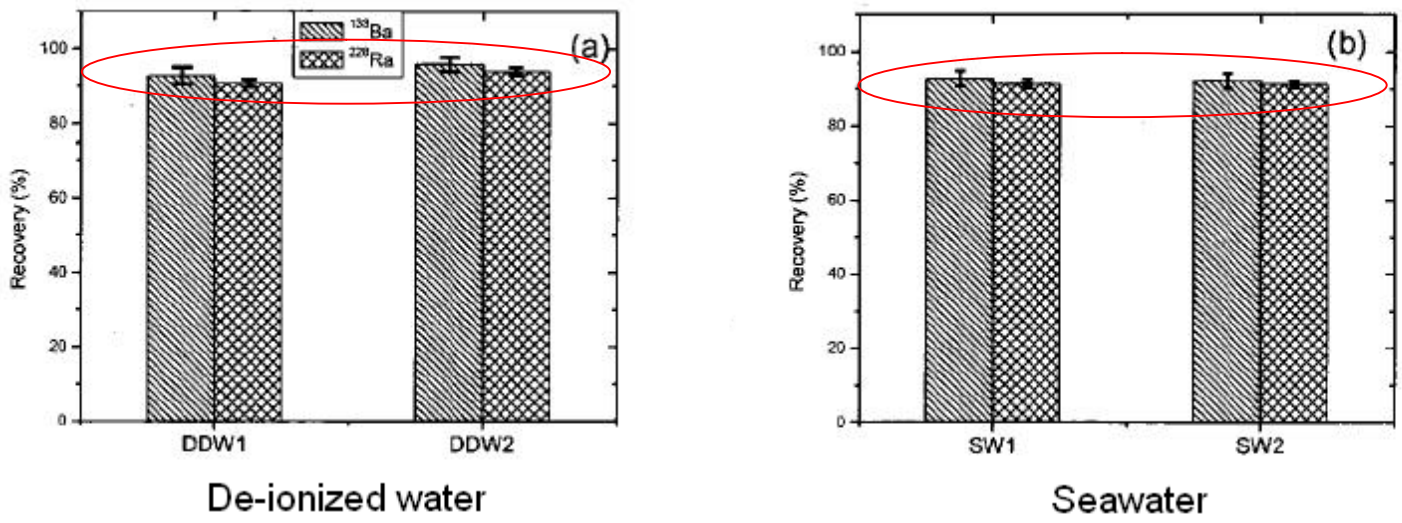
- High retention (>99%) above pH 5 for both
- Good correspondence between Ra and Ba for pH values > 6-7
- Significant deviation for low pH

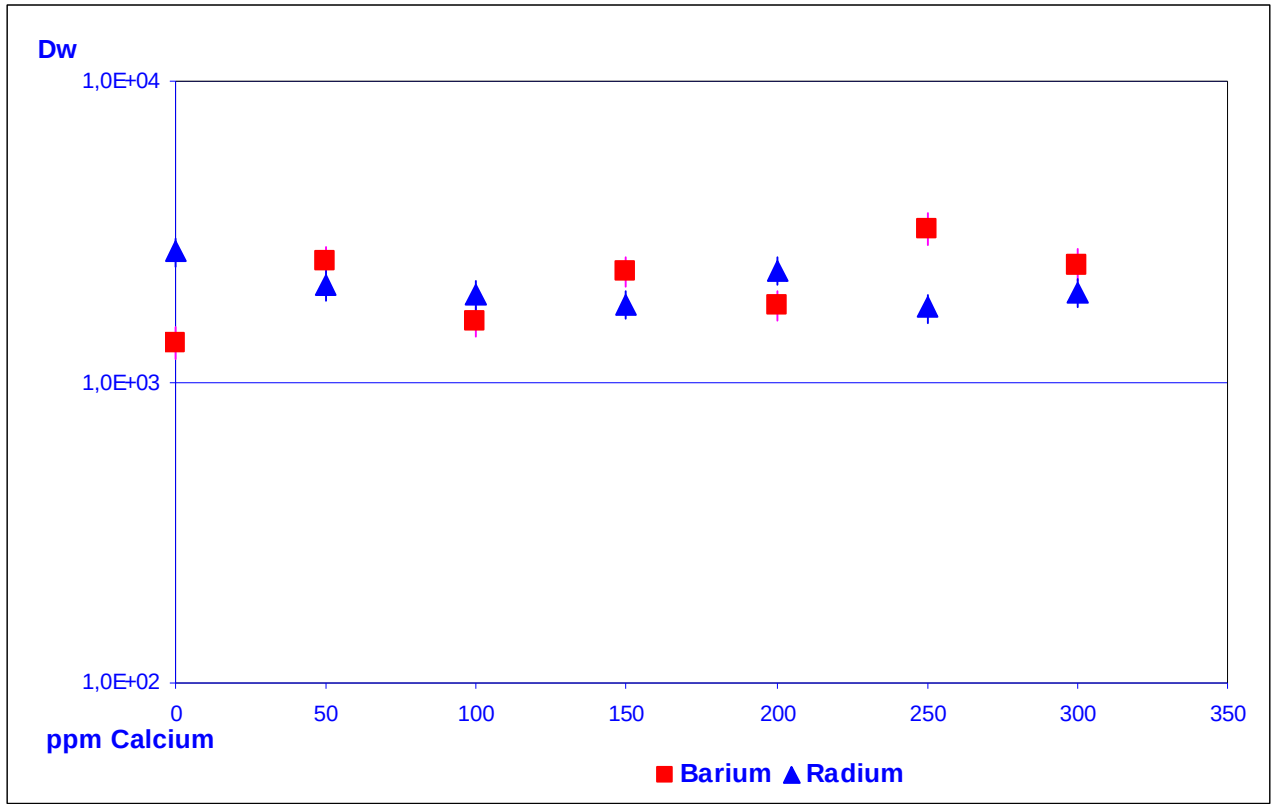
Ba/Ra homology on columns



Burnett et al.

- Good correspondence between Ba and Ra recoveries for de-ionized and Seawater
- Recoveries > 90% for both matrices

Interferences - Ca



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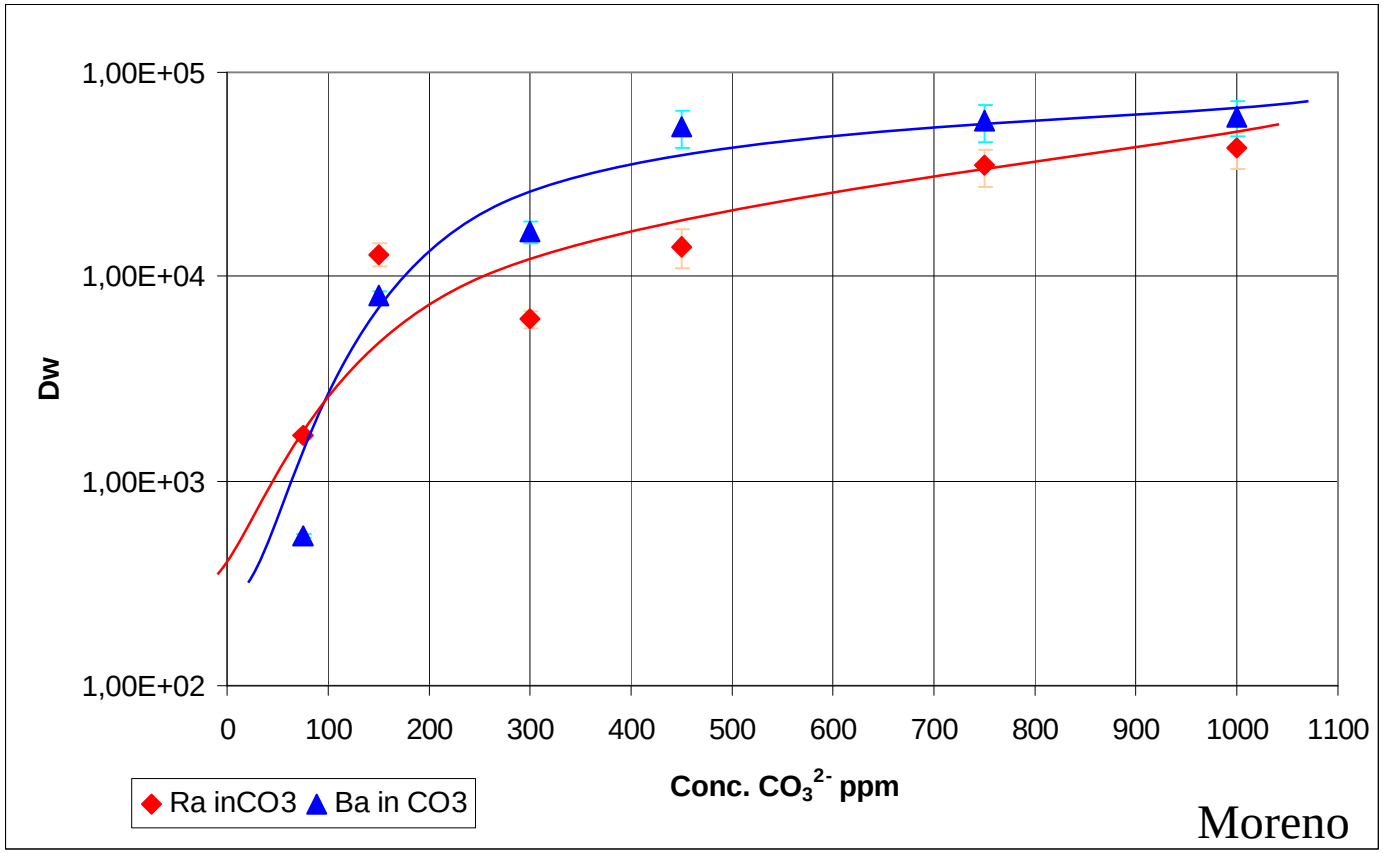
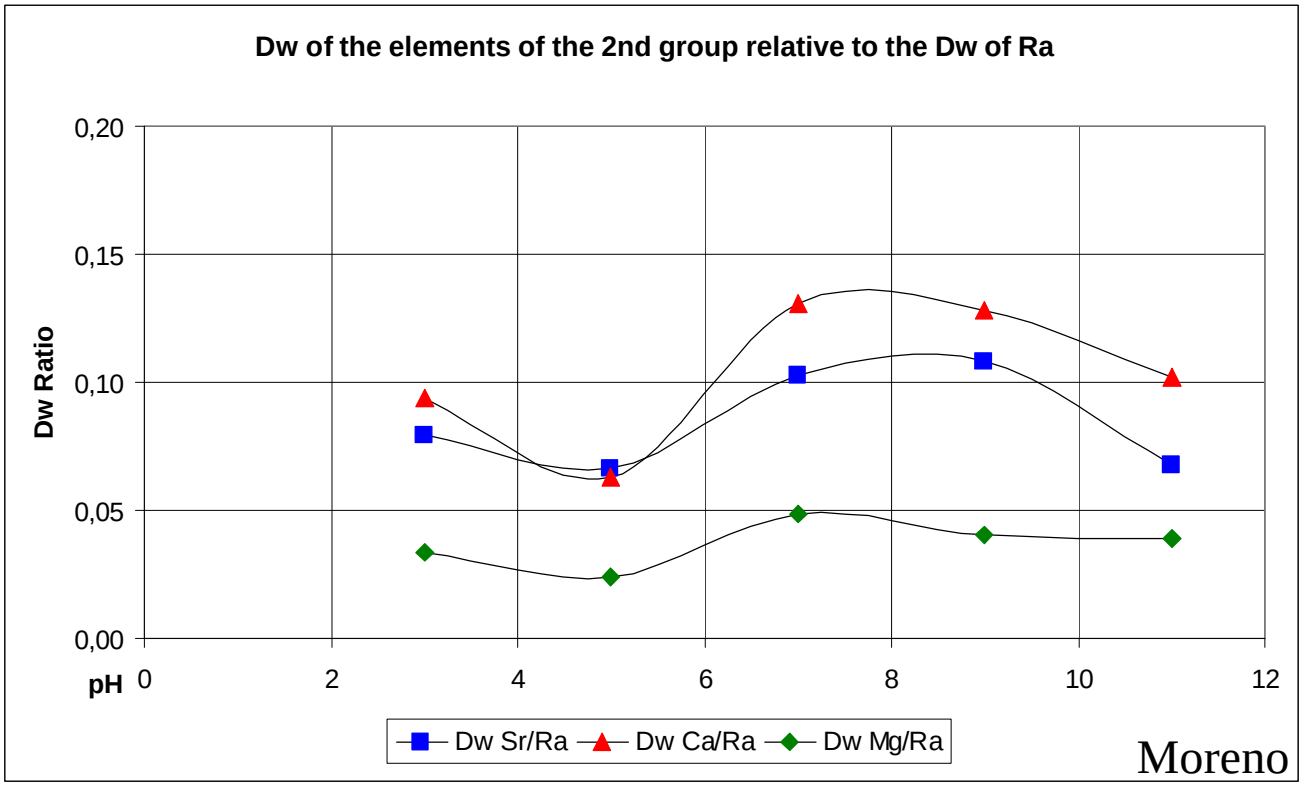
§ For [Ca] ≤ 300 ppm no interference on Ba and Ra retention (D_w) observed

Interferences - carbonate



- Increase of D_w values with increasing carbonate concentration
- Increase of carbonate concentration connected to increase of pH

Selectivity over other earth-alkalines



- Overall good selectivity for Ra over Sr, Ca and Mg
- Sr and Ca show similar behaviour

Capacities

Element	Ba	Ba (300 ppm Ca)	Pb	Th
Capacity [mg/g resin]	~ 10	~ 10	~ 9	~ 1,0
pH value (mean)	5,6	4,5	6,5	5,2

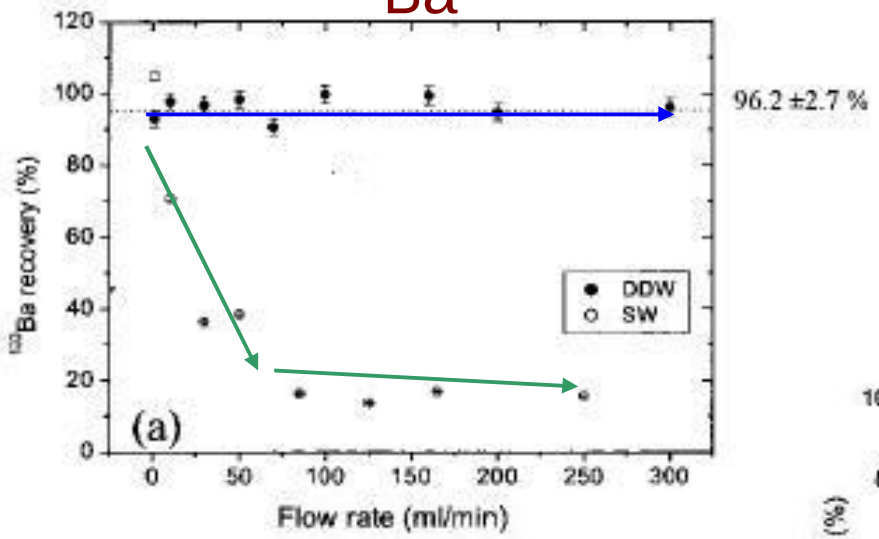
- Capacities in the order of 1 mg/g (Th) to 10 mg/g (Ba)
- At indicated pH values
- Capacities might differ when working at other pH values

Flow rate

- 1.0 L sample water spiked with ^{133}Ba and ^{228}Ra
- 1.0 g MnO_2 resin cartridge
- pH = 7.0
- Peristaltic pump, flow rate 0 -300 mL/min
- Samples: de-ionized and seawater

Flow rates - results

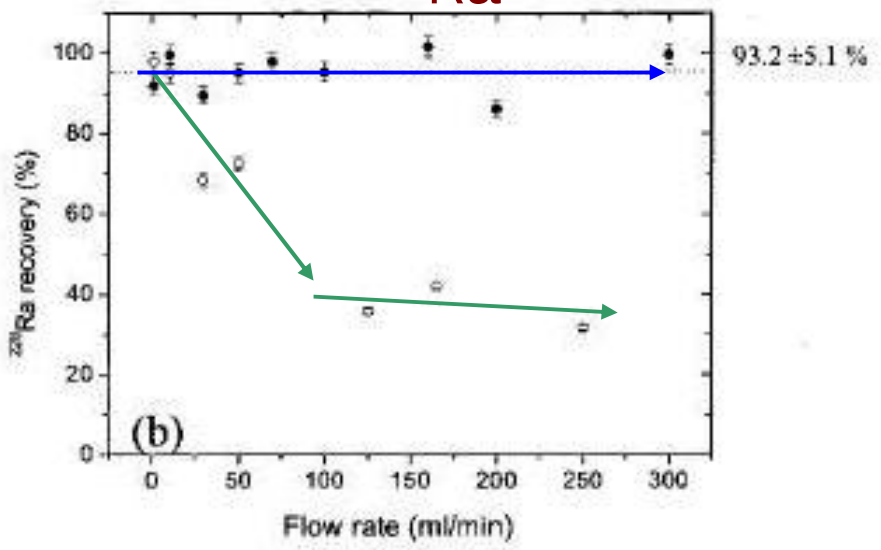
^{133}Ba



- deionized water
- sea water

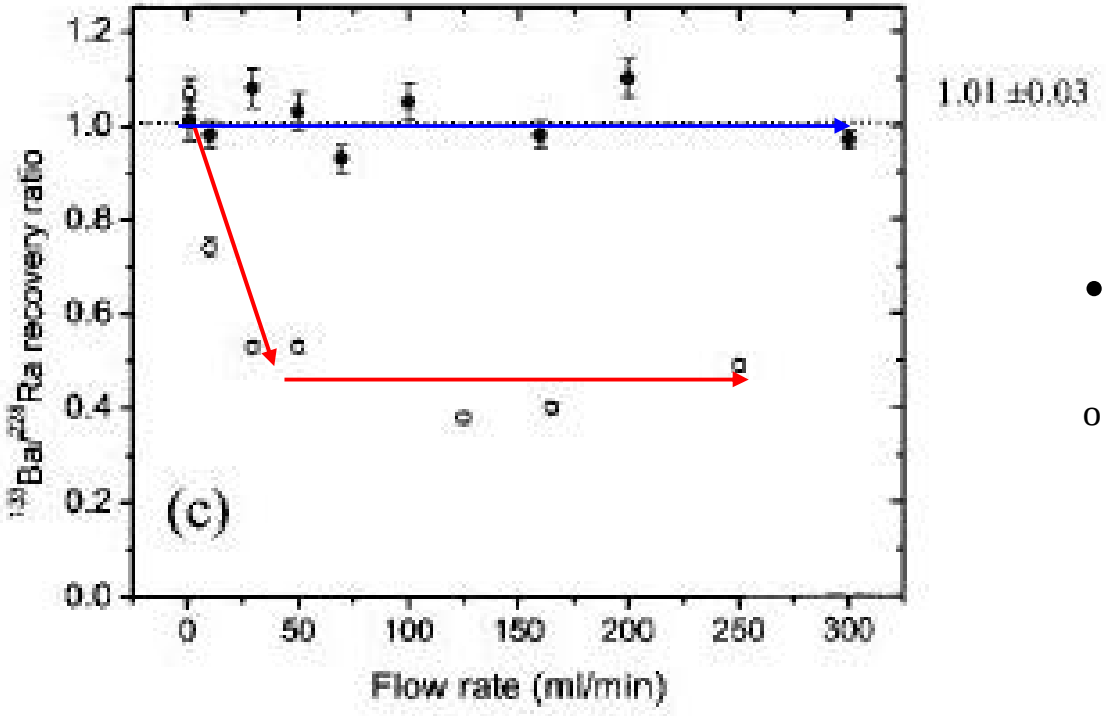
Burnett et al.

^{228}Ra



Ø Problematic: Flow rates for sea water

Flow rates – results: $^{133}Ba/^{228}Ra$



- deionized water
- sea water

Burnett et al.

Summary - Characterisation I -

- Very high D_w (~1000) for Ra, Ba, Th and Pb
- Ba and Ra uptake kinetics depend on salinity
- Good Ba/Ra correspondence for pH >6
- No interference on Ba/Ra uptake from Ca and CO_3^{2-}

Summary - Characterisation II -

- Good selectivity for Ra over Ca, Sr and Mg
- Capacities between 1 mg/g (Th) and 10 mg/g (Ba)
- Flow rates should be kept < 20 $mL.min^{-1}$ especially for high salt samples to assure:
  - High yields
  - Ba/Ra homology

Applications

- Ra-226/8 • updated two column draft procedure
  - MnO_2/DGA
  - Ca rich water samples
  - Ac yield determination via gravimetry (CeF_3)
- Preconcentration of Ba and Ra from 5L water samples for gamma spectrometry

New Ra-226/8 method

- Why new method
  - Increased interest in Ra isotopes (European DW directive)
  - Current methods lengthy and time consuming or need long ingrowth times
- Advantages of the new method
  - High adsorption of Ra, Ra and other natural radionuclides onto MnO_2 resin from neutral pH solutions
  - Rapid preconcentration from large water samples
  - Selective / robust uptake and seperation of Ac and other actinides on DGA Resin

Ra-226/8 Procedure

- Two Resin Method
  - MnO_2 Resin for pre-concentration, Ca removal
  - DGA-Normal Resin for separation of Ac/Ce and Ra/Ba

§ Load sample (0,5 – 1L, pH 7) on 1g MnO_2

§ Strip MnO_2 with 15 mL 5 M HCl-1.5% H_2O_2

§ Add Ce carrier (10 mg Ce)

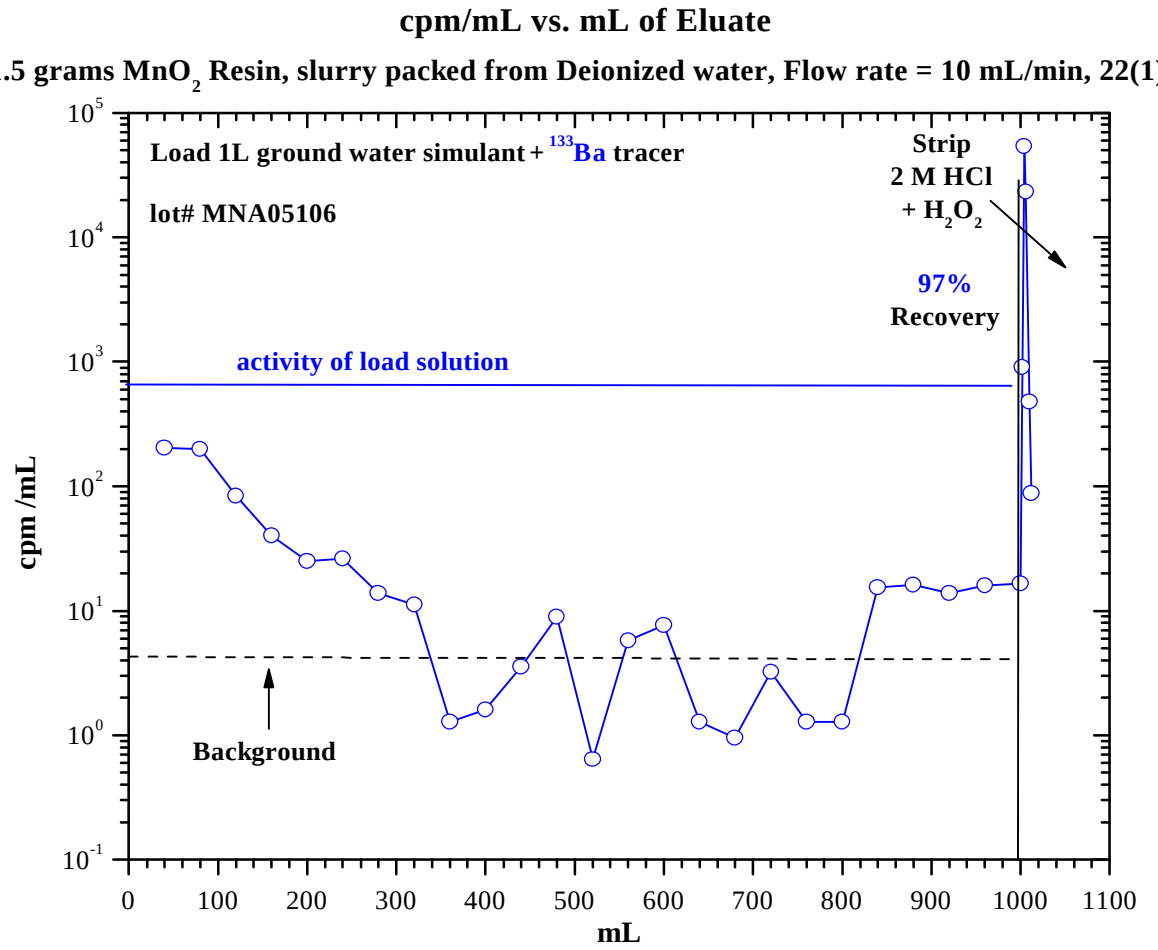
§ Allow > 30 h for Ac-228 ingrowth

§ Load strip solution on DGA, Normal (2 mL)

Ra-226/8 Procedure

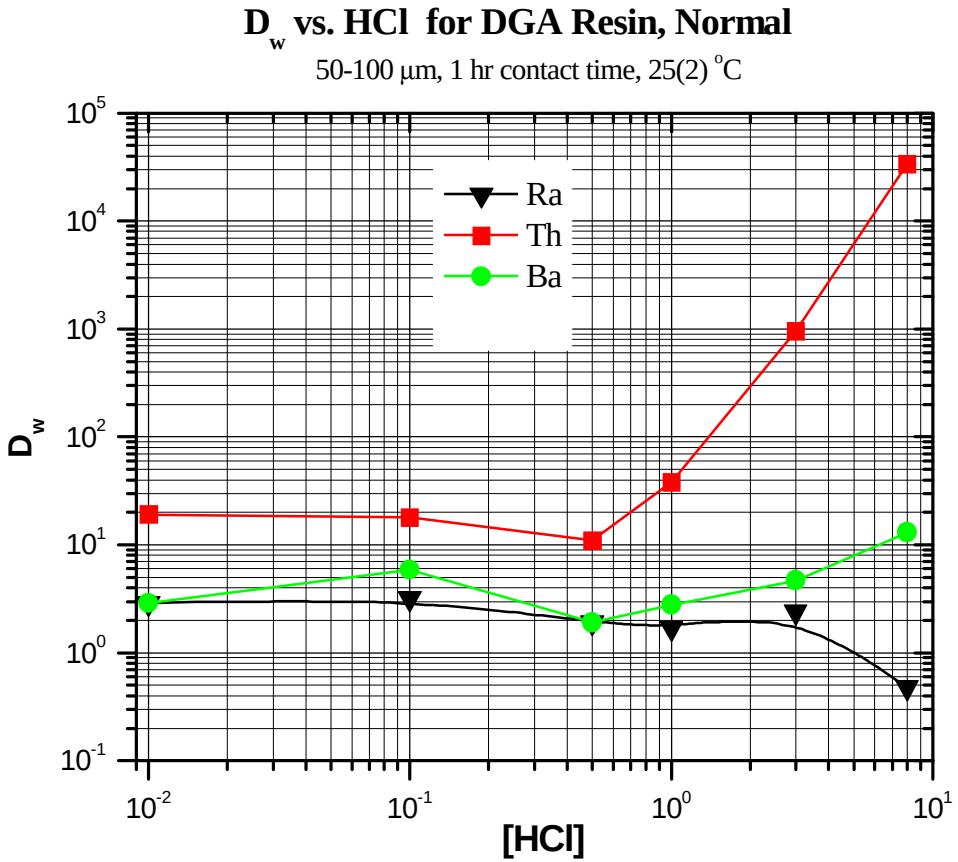
- DGA: U, Th and Ac-228 retention, Ra and Ba pass
- Collect load + 5 mL 5 M HCl rinse for Ra-226 and Ba-133
  - Microprecipitation with $BaSO_4$
  - Yield by γ–spectrometry (Ba-133)
  - Ra-226 (and other α–emitting Ra isotopes) by α-spectrometry
- Strip Ac-228 from DGA with 15 mL 2 M HCl
  - Microprecipitation with CeF_3
  - Gas proportional counting
  - Yield determination Ac on DGA step via gravimetry
  - Yield of preconcentration step via Ba-133

Ra/Ba preconcentration on MnO_2 resin



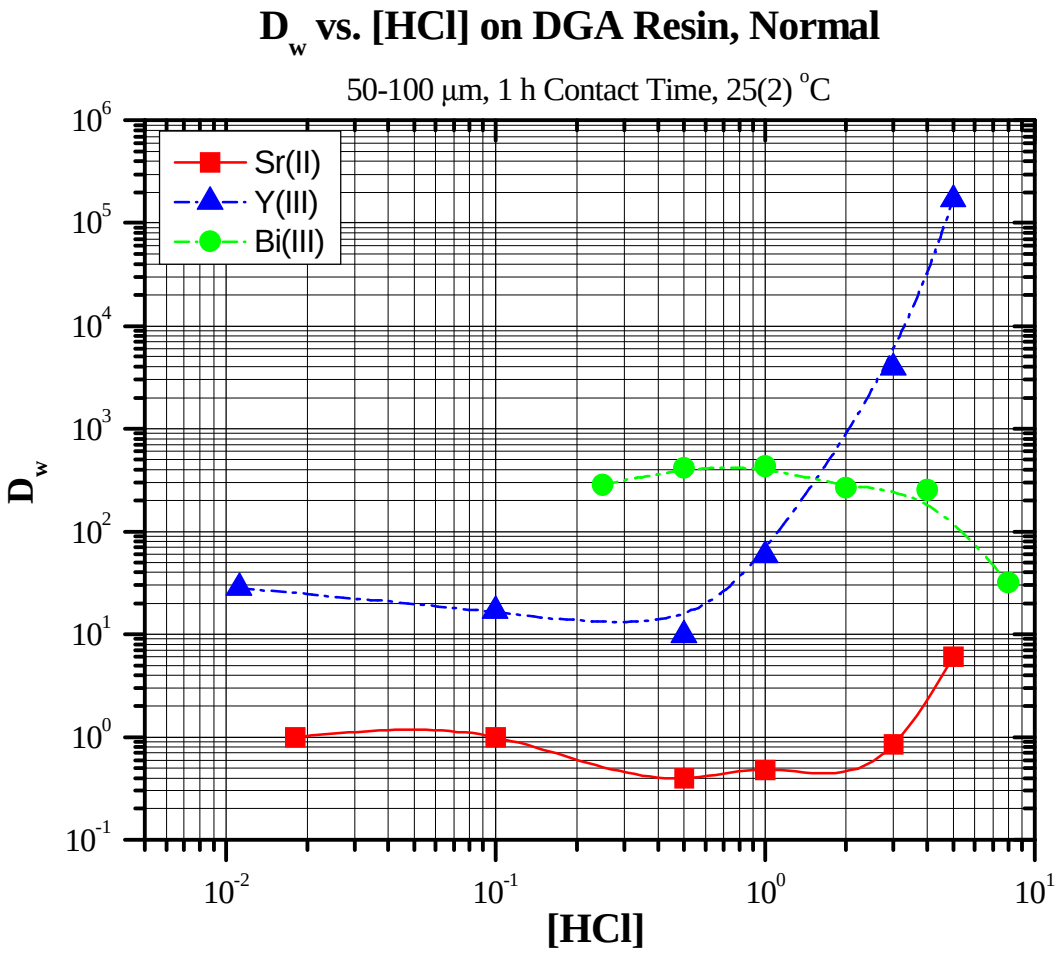
§ Elution profile Ba-133, 1L spiked ground water, 1.5 g MnO_2 resin

Retention profiles - I



- Retention of Ra, Th and Ba on DGA, normal in HCl
- Strong Th uptake at high HCl concentration
- Ba and Ra show low uptake

Retention profiles - II

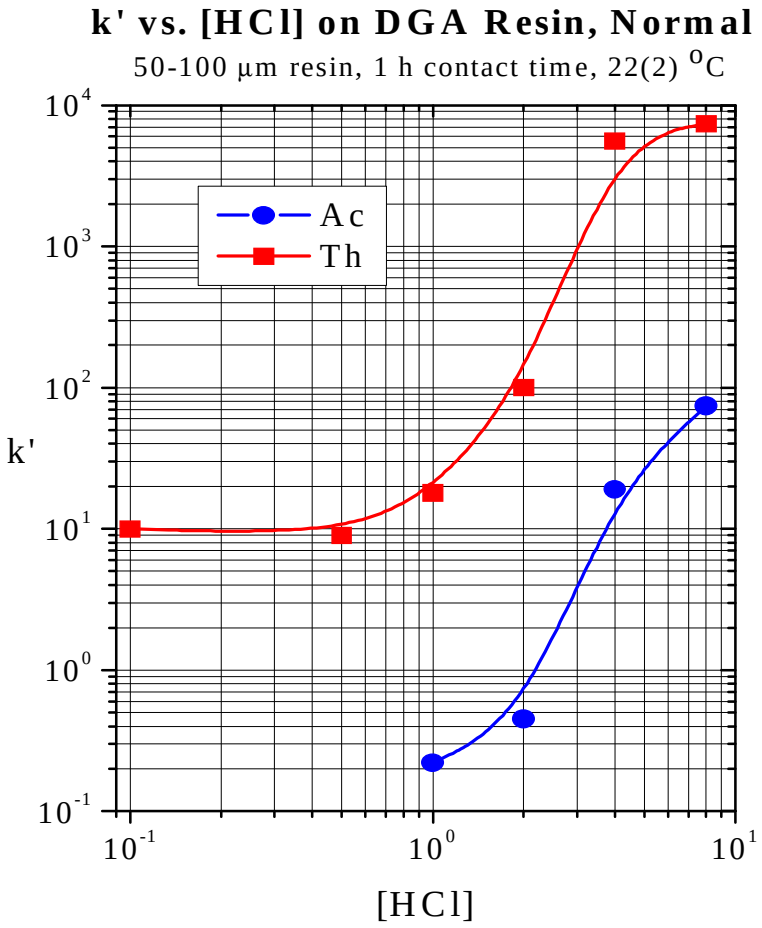


§ Retention of Sr, Y and Bi on DGA, normal in HCl

§ Y and Bi show high uptake at elevated HCl concentration

§ Potential interferents since chemistry similar to Ac

Retention profiles - III

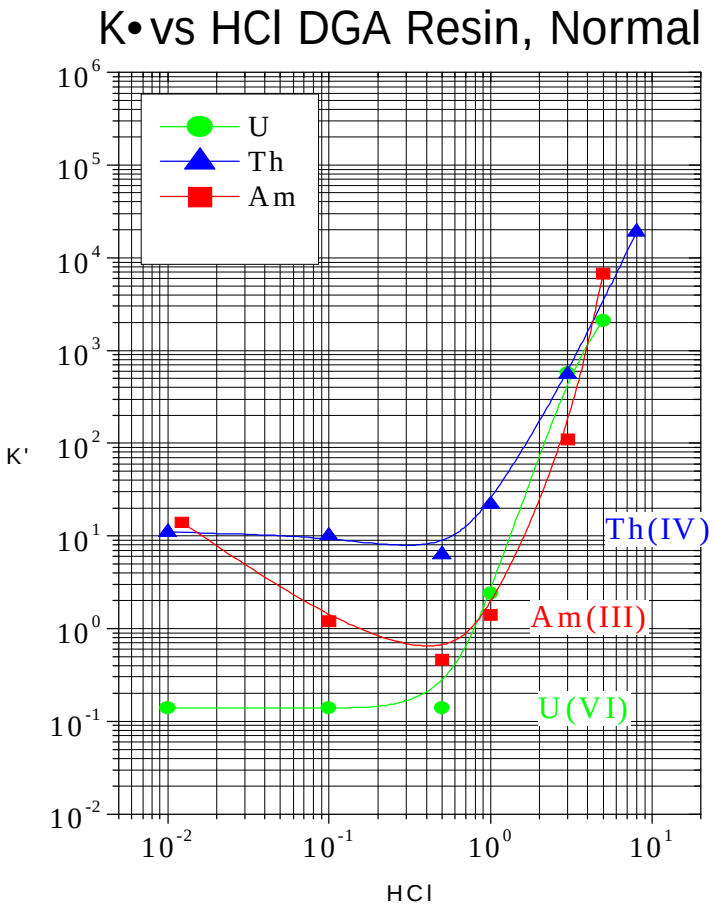


§ Retention of Ac and Th on DGA, normal in HCl

§ Ac: strong retention only for high HCl, significantly lower than Th

§ Th: overall good retention, especially for high HCl

Retention profiles - IV



§ Retention of U, Th and Am on DGA, normal in HCl

§ Very similar for high HCl (> 2M HCl)

Measurement of Ba-133, Ac-228 and Ra

- Ac-228
  - Ac-228 sample preparation via cerium fluoride microprecipitation
  - Counting on GPC
- Ra and Ba-133
  - Sample preparation via barium sulphate micro-precipitation
  - Ba-133 counted by gamma spectrometry
  - Ra isotopes counted by alpha spectrometry

Decontamination Study

- Selectivity of the DGA resin
- Decontamination of commonly occurring alpha and beta emitters such as Pb/Bi, Th, Sr/Y were studied
- 500 mL of tap water spiked with alpha and beta emitters
- Samples processed using the complete method

Interference added	Deconfactor Ac-fraction
Th-228/U-232	>303
Pb-210/Bi-210	>1542
Sr-90/Y-90	>1208

Ø Overall very good decontamination from potentially interfering elements

Ø Even for Y-90 and Bi-210 • MnO_2?

Method Performance Data

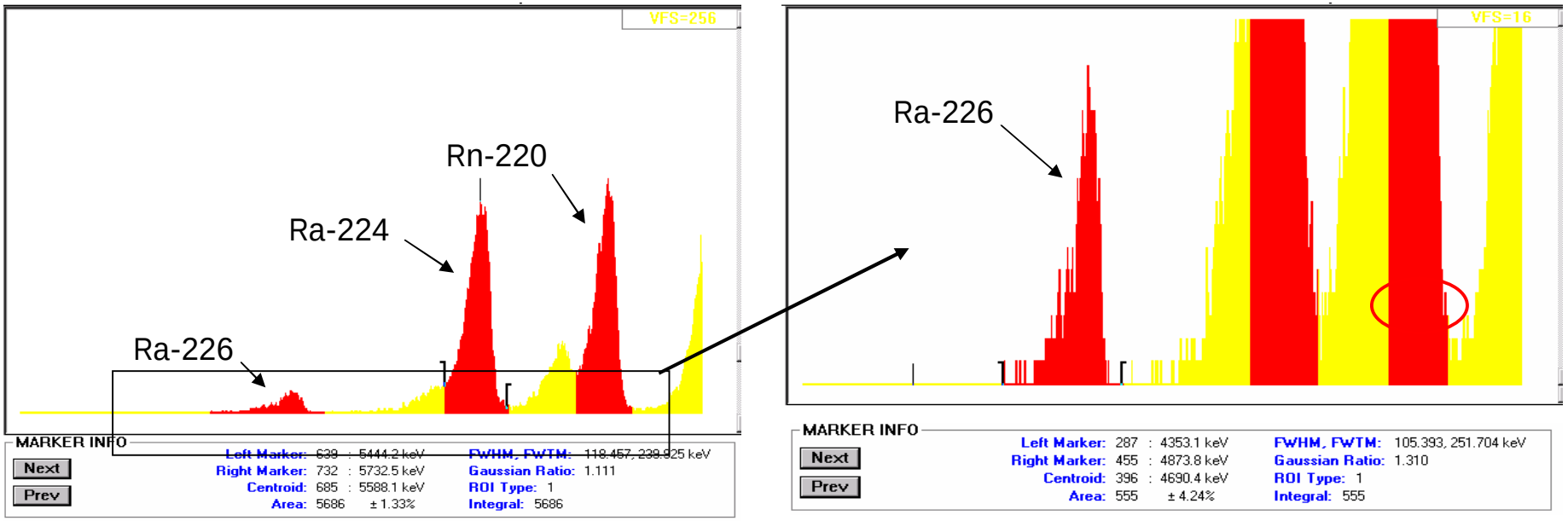
Replicate #	Yield Ba-133	Yield Ra-228	Yield ratio Ba/Ra	Yield bias / %	Yield Ra-226*
1	89	86	1,04	3,4	106
2	76	74	1,03	2,6	93
3	83	77	1,08	7,2	100
Average	83	79	1,05	4,8	99.7
SD	7	6	0,12	0,5	7
RSD / %	8,4	7,6	11,3	11,3	7,0

*Yield corrected

Method Performance Data

- Good correspondence between Ba-133 and Ra-228 yields
  - Overall bias in the order of 5% • Ac-228 separation on DGA?
    - Bias not significant within given uncertainties
    - Correction via Ce yield for improved method
  - Ba-133 also internal standard for Ra-228/Ac-228
- Corrected Ra-226 yield indicates absence of bias
- Relative standard deviation (N=3) in the order of 7 – 8 %

Alpha Spectra: Micro precipitation



1L, Spiked tap water (Ca • 500 ppm)

Ba/Ra preconcentration for γ-spectrometry

- Special interest: Ra-228 determination
- 5L water samples, pH 7
- Ba-133 as internal standard
- 3g MnO_2 Resin
- Stirring over night at room temperature
- Filtration, drying of the filter
- γ–spectrometry after 48 h ingrowth period (Ac-228)

Ba/Ra preconcentration for γ-spectrometry

- Ba-133 yield ~ 80%
- Quicker, less hands-on time than evaporation / precipitation methods
- Better reproducibility of source prep. for very Ca rich samples
- $DL_{Ra\text{-}228}$ (t = 4h, 20% rel. Eff.) = 60 $mBq.L^{-1}$ (*via* Ac-228, 911 keV)
- No significant bias (Reference Material):

Determined activity A(Ra-228) / Bq.L-1	Uncertainty Uc (Ra-228) / Bq.L-1	Reference activity A(Ra-228) / Bq.L-1	Uncertainty Uc (Ra-228) / Bq.L-1	t-value
9,875	0,593	9,264	0,742	0,6

- Extension to Pb-210 determination via γ-spectrometry?

Summary - Applications -

First tests and results for applications:

- Ra-226/8 via two column method
  - Excellent decontamination factors for potential interferents
  - No significant bias
- Ra-228 determination via gamma spectrometry
  - Good yields
  - Application to larger volumes
  - Smaller amounts of MnO_2