Determination of Ra in environmental samples

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Scope

- Aqueous samples
  - Ra-226/8 Method
  - Ra-226 via Ra NucFilm Discs
- Rapid method for the determination of Ra-226 in environmental samples
- Rapid method for the determination of Ra-228 in environmental samples

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Determination of Ra-226/8 in water samples

- Eichrom methods RAW03 (cation exchange and LN Resin) and RAW04 (MnO_2 Resin and DGA)
- MnO_2 Resin allows for analysis of Ca rich water samples
- Variation of the RAW04 method (optimized by Sherrod Maxwell)
  - 1,25g MnO2 per 1L water (routine: 1 – 1,5L), pH 6 – 7
  - Addition of 25 mg Ca – minimum amount of Ca necessary for high yields
  - Addition of Ba-133
  - Sample load onto MnO_2 at 15 $mL.min^{-1}$
  - Ra elution with 4M HCl/1.5% H_2O_2 (destruction of MnO_2 resin)
  - 36h wait in case Ra-228 to be determined (Ac-228 ingrowth)
  - Loading of the eluate onto stacked LN/DGA cartridges
    - LN: U and Th retention
  - Ba and Ra in eluate, Ac on DGA cartridge
    - Source preparation via microcoprecipitation, yield via Ba-133
  - Ac separation and elution on DGA
    - Direct measurement via LSC or Cerenkov, yield via Ce
    - Sourceprep for GPC: via CeF_3 coprecipitation, yield via Ce

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Determination of Ra-226/8 in water samples

- Recent improvements:
  - Ce yield via ICP-MS instead of gravimetry
  - Microprecipitation from isopropanol solution
    - 23 mL 1.5 mL HCl
    - Addition of 3g ammonium sulphate, 50µg Ba carrier and 5 mL isopropanol
    - Ice bath / Vortex
    - No ‘Seeding suspension’ needed
  - MnO_2-PAN Resin
    - MnO_2 fixed more strongly in resin matrix
    - Elution with 5M HCl, no complete destruction of the resin

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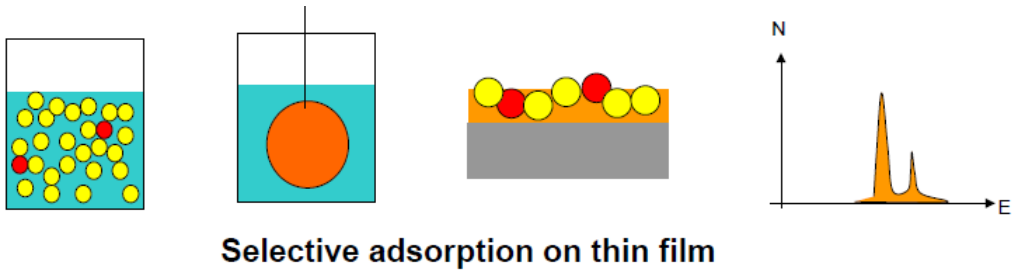
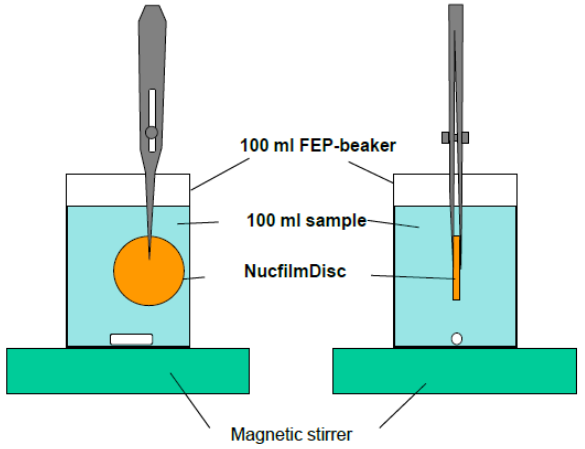
Ra-226 via Ra NucFilm Discs

- Thin MnO_2 layer on nylon disc
  - Very smooth surface
- Direct Ra extraction from water samples
  - 100 mL
  - Min. 4 – 6h, pH 4 – 8
  - EDTA to lower matrix effects
- Yield via Ba-133
- After rinsing sample ready for α-spectrometry
- Yield typically 75 – 90% (depending on matrix)
  - Ca, Ba



Selective adsorption on thin film



Ra-226 determination via MnO_2 discs accredited method (Subatech, France)

- Sample volume 50 - 100 mL (filtered water, acidified to pH = 0,5 – 2)
- Addition of Ba-133 (10 - 100 Bq) as internal standard
  - **Ba content of the sample < 10µg**
- Addition of EDTA to complex interferents

⇩

- pH adjustment to 7 - 8,5 with NaOH and addition of $NaHCO_3$ (buffer)
- Measurement of original Ba-133 activity in the solution (γ-spectrometry)

⇩

- Place MnO_2 disc in sample holder
- Sir for 10 h

⇩

- Withdraw MnO_2 disc, rinse and dry
- Measurement of Ba-133 activity in the solution after extraction (γ-spectrometry)

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- α-spectrometry

➢ LD: 5 - 10 mBq.L^{-1} for 50 – 100 mL samples and 24 – 48h counting

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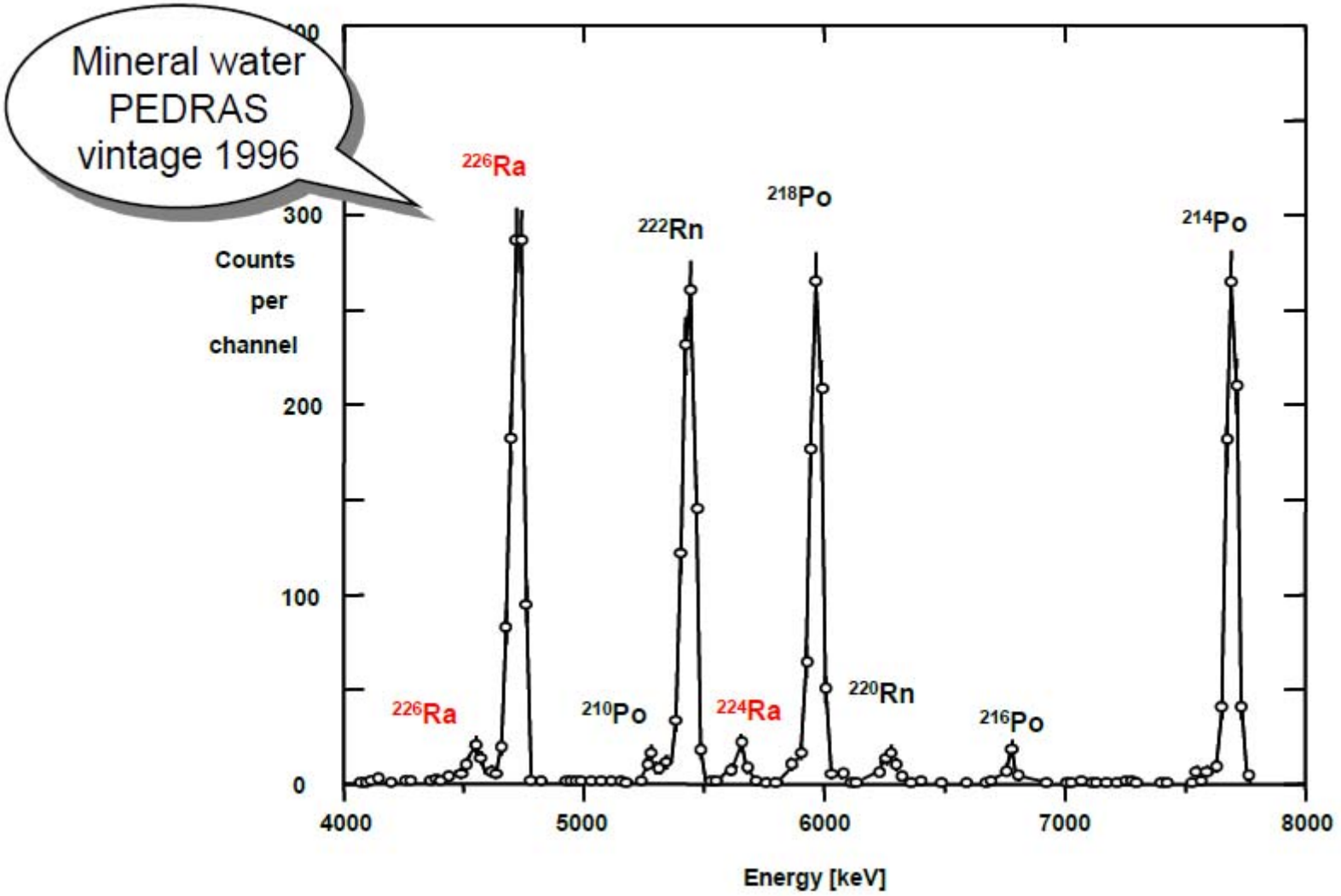

Surbeck 2010

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Rapid determination of Ra-226 in environmental samples

- For solid samples use of MnO_2 resin not possible
  - High matrix load after sample dissolution, precipitation at pH 7
- Solid samples frequently contain elevated amounts of Ba
  - Problematic for preparation of source for α-spectrometry
  - Polyatomic Interferences at ICP-MS measurements
- Ba removal necessary
  - Ba/Ra separation (e.g.SR Resin)
  - Ba-133 can not be used as internal standard
  - Alternative: Ra-225/At-217 (from Th-229), advantage: α-Spectrometry

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Rapid determination of Ra-226 in environmental samples

- Rapid method Sherrod Maxwell (SRS)
  - Filter, 5g vegetation, 1g soil, brick or concrete, 150 mL water samples
  - Ashing (2h 700°C, wet ashing, 5 – 10 min 600°C)
  - NaOH fusion in Zr crucible
  - Carbonate precipitation
  - Cation exchange (Ca removal)
  - Optional: SR Resin (for Ba-rich samples)
  - LN Resin (Ac, Ca,… removal)
  - Microprecipitation and α-Spectrometry

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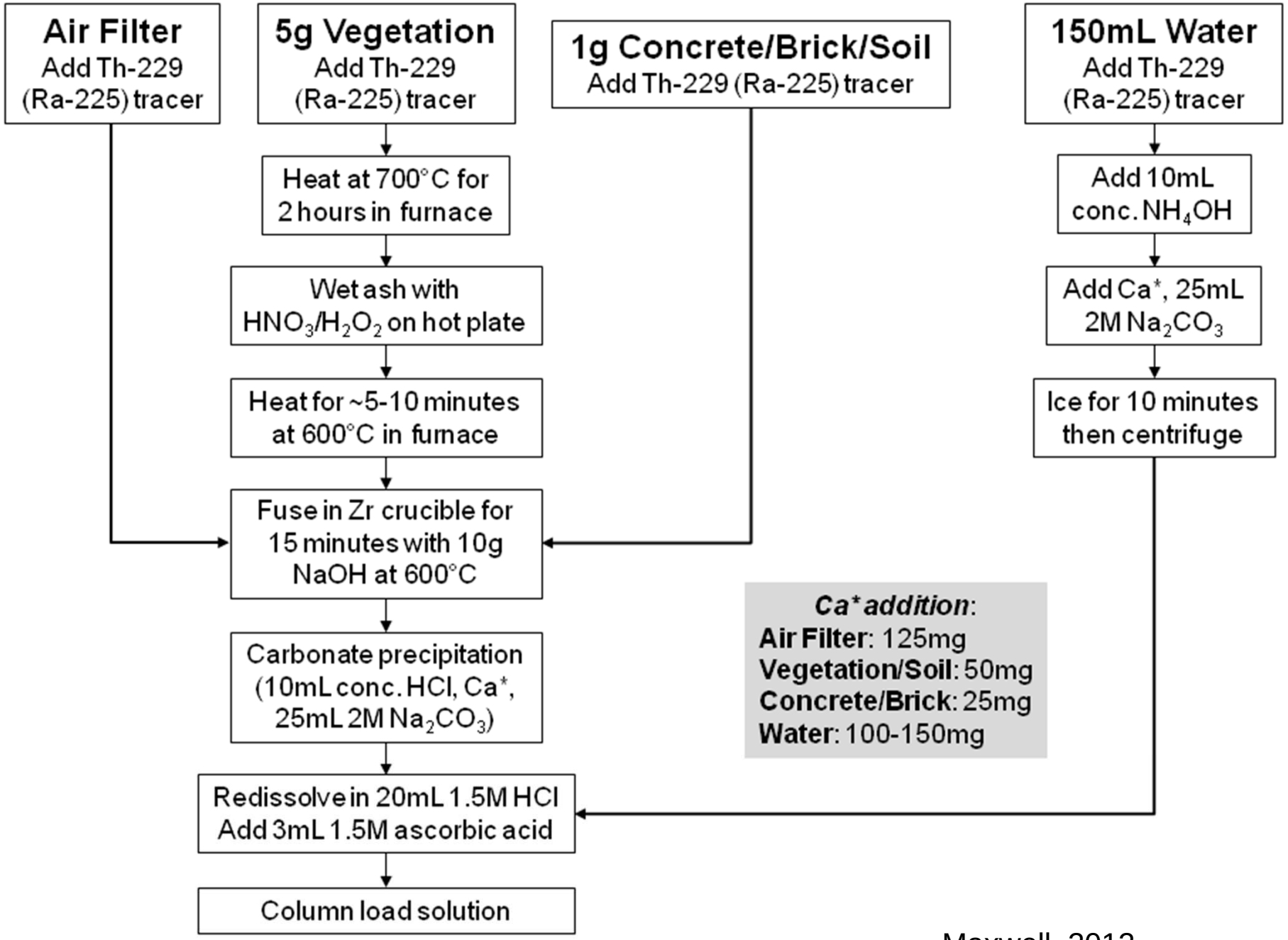
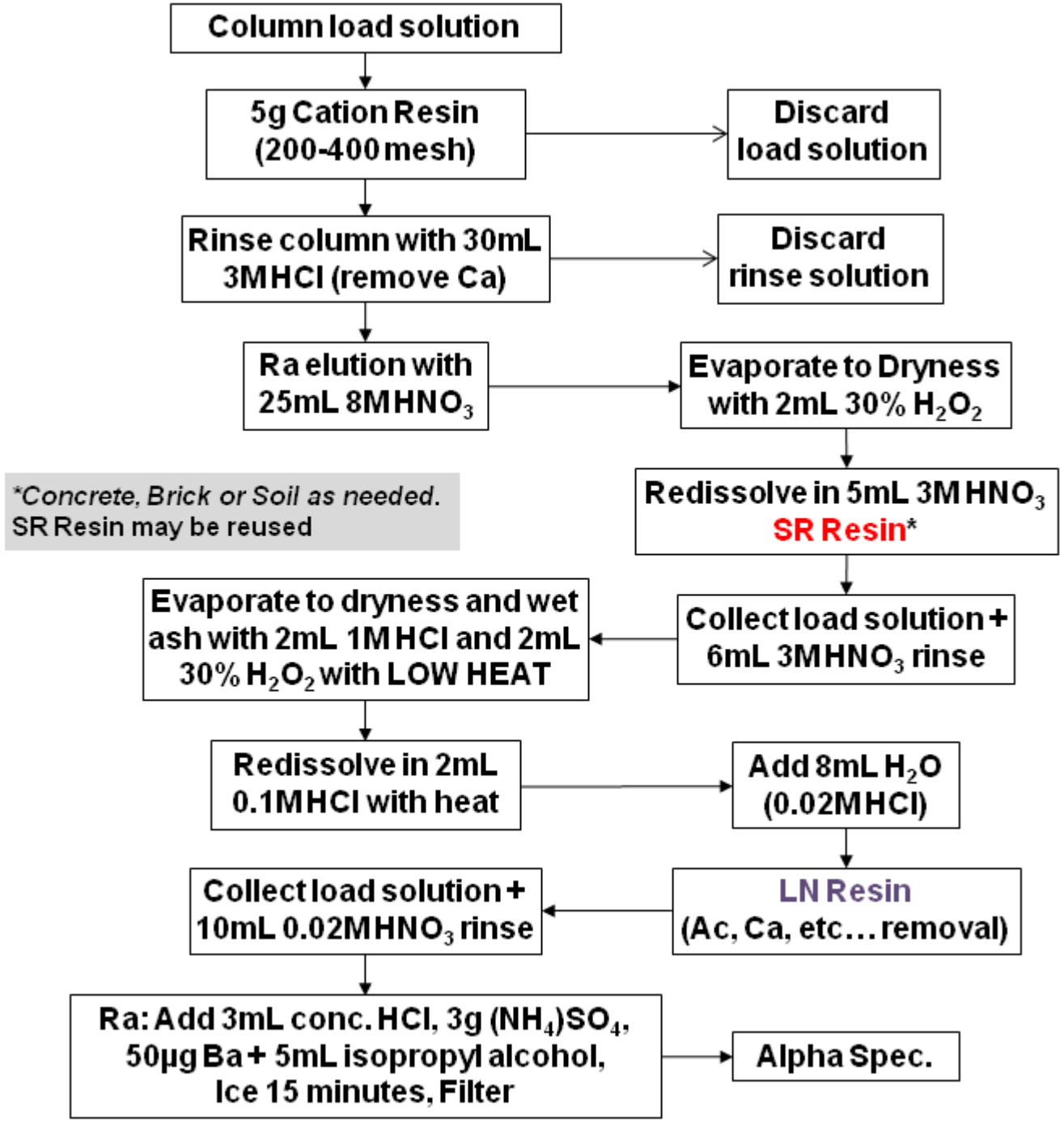


Maxwell, 2012



Maxwell, 2012

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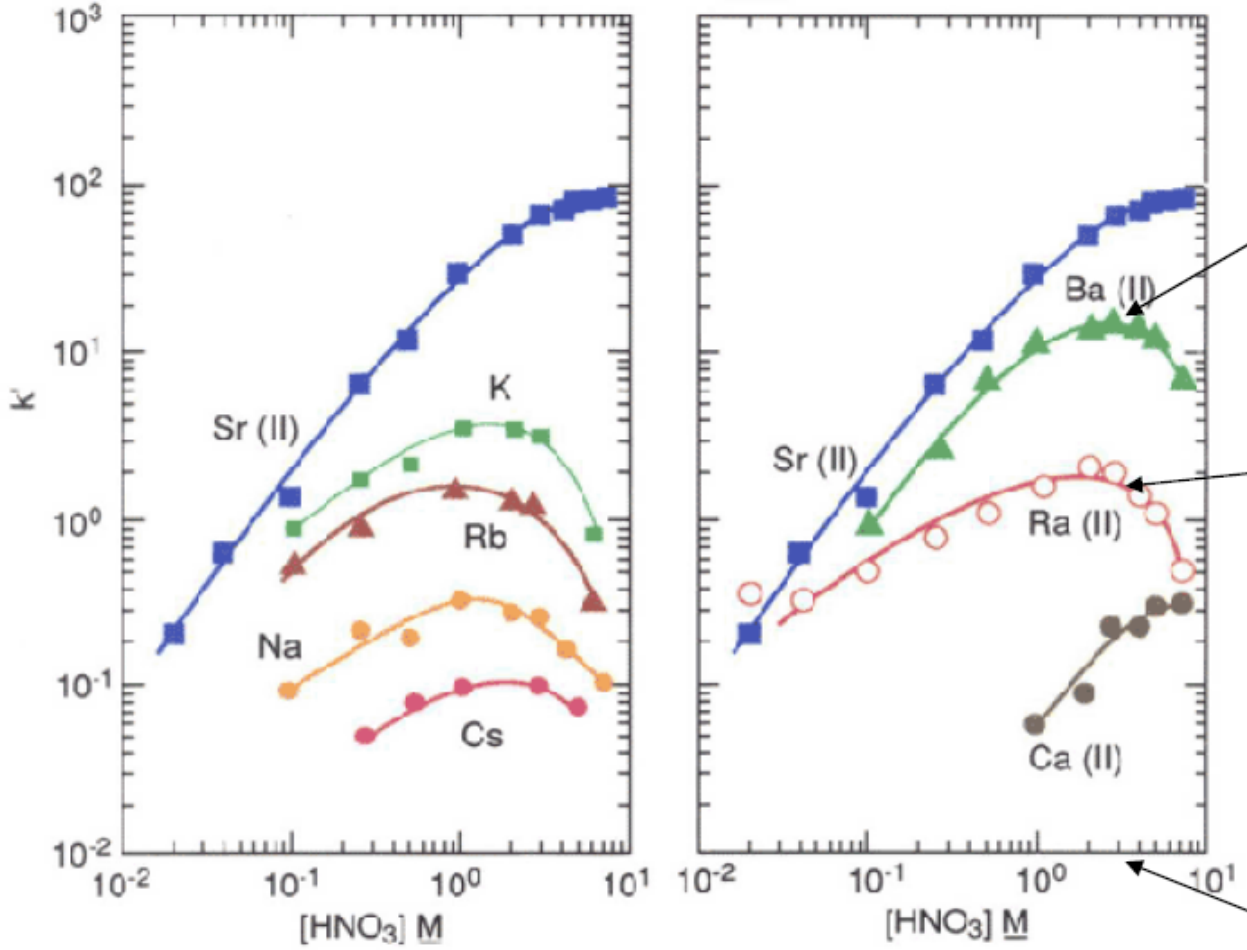
Figures 2 and 3

Acid dependency of k' for various ions at 23-25°C.
Sr Resin



Horwitz, et al., (HP292)

Ba/Sr retained

Ra eluted

3M HNO3 <10 free column volumes

Maxwell, 2012

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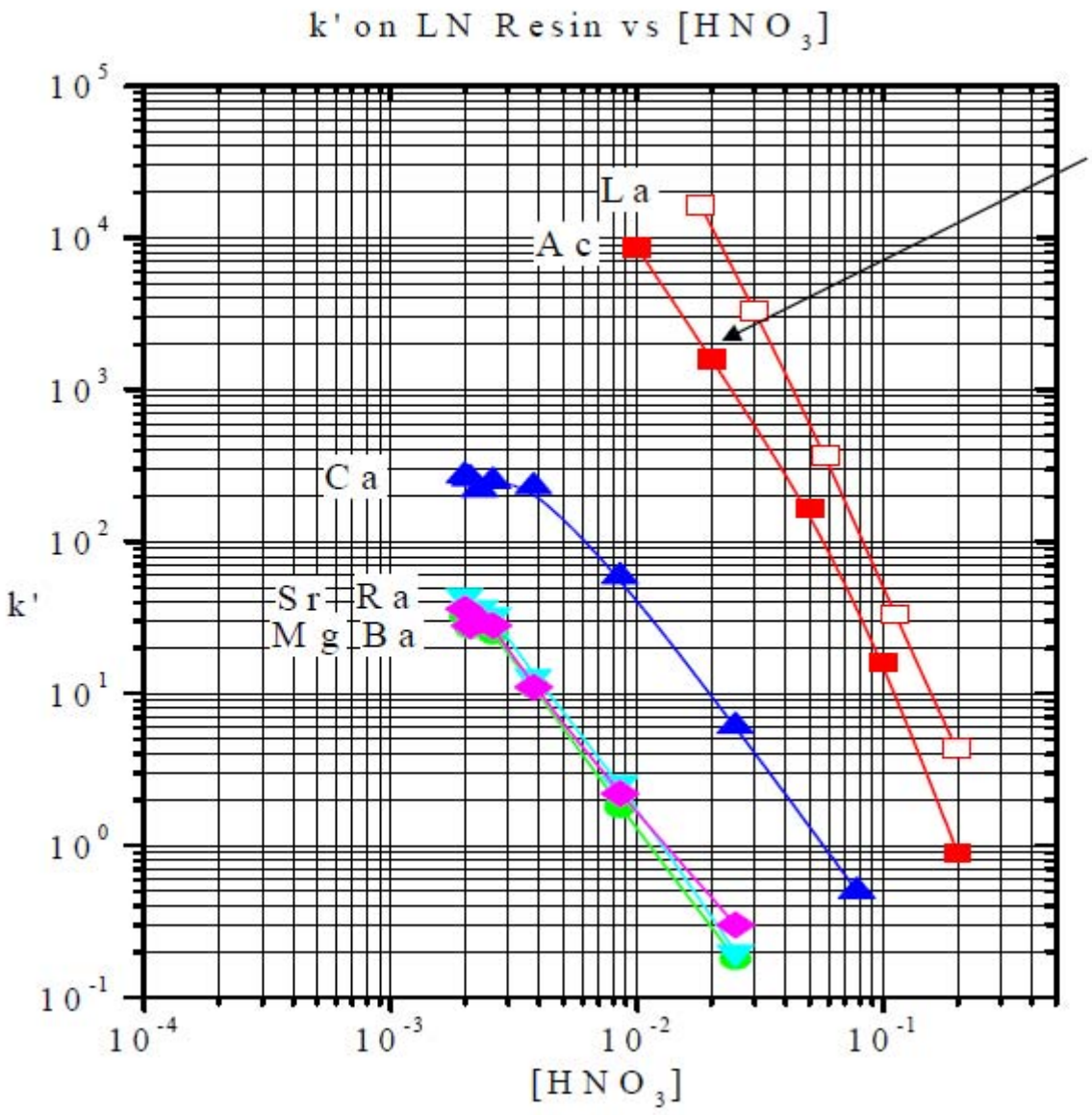


Removal fo Ac-225

Courtesy Dr. Dan McCalister, P&G Research Foundation

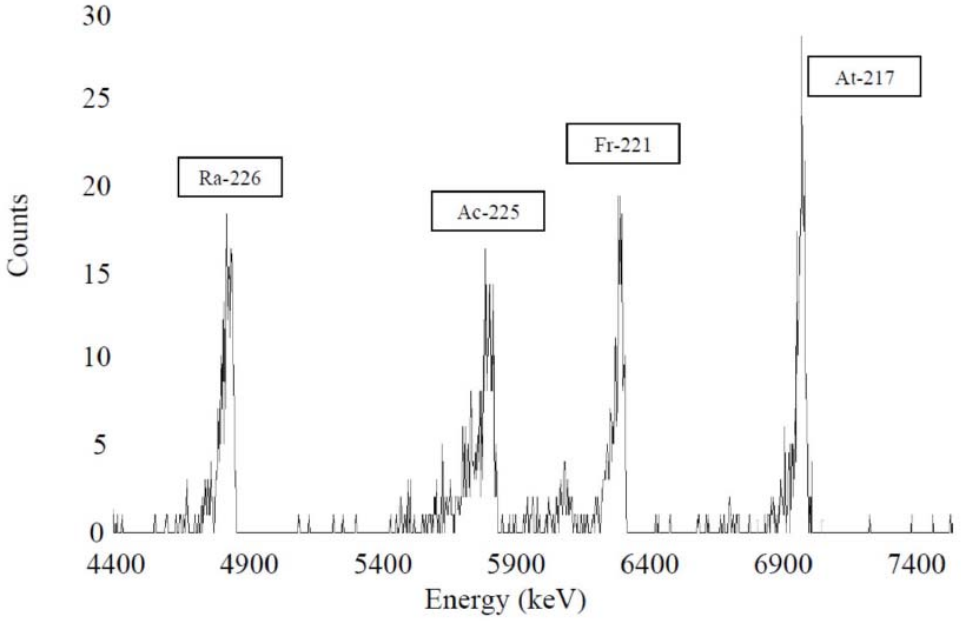
Maxwell, 2012

Results spiked real samples

Matrix	Chemical yield / %	Obtained result / mBq per sample	Reference value / mBq per sample	Bias to ref. value / %
Vegetables	87.1 (5.7)	72.8 (5.1)	73.8	-1.2
Concrete	84.6 (6.8)	180.6 (8.0)	184.5	-2.1
Brick	86.5 (6.6)	77.8 (4.6)	73.8	5.5
Air filter	76.7 (4.2)	77.1 (6.2)	73.8	4.5
Soil	75.3 (1.9)	184.9 (6.2)	184.5	0.2
Water	91.8 (6.7)	70.9 (3.7)	73.8	-3.9

Maxwell, 2012

- Yields between 75 and 90%
- Good agreement with reference values
- Clean spectra



Maxwell, 2012

Rapid determination of Ra-228 in water samples

Maxwell S.L. et al., Rapid method for determination of ^{228}Ra in water samples, J. Radioanal Nucl Chem, DOI 10.1007/s10967-012-2257-1 (2012)

- Method similar to Ra-226 method
- Calcium carbonate precipitate
  - Addition of phosphate
  - Chemical yield > 90%
- Cation exchange
  - Removes Ca, Pb, Bi, U, Th, Pa
- DGA Resin
  - Ac purification
  - Removes Pb, Bi, Sr, Y,…
- Yield via La (ICP-MS)
  - Ba-133 (γ-Spectrometry) also possible
- Source preparation via Ce/LaF_3 precipitation
- Separation in 4h, results can be obtained in < 6h

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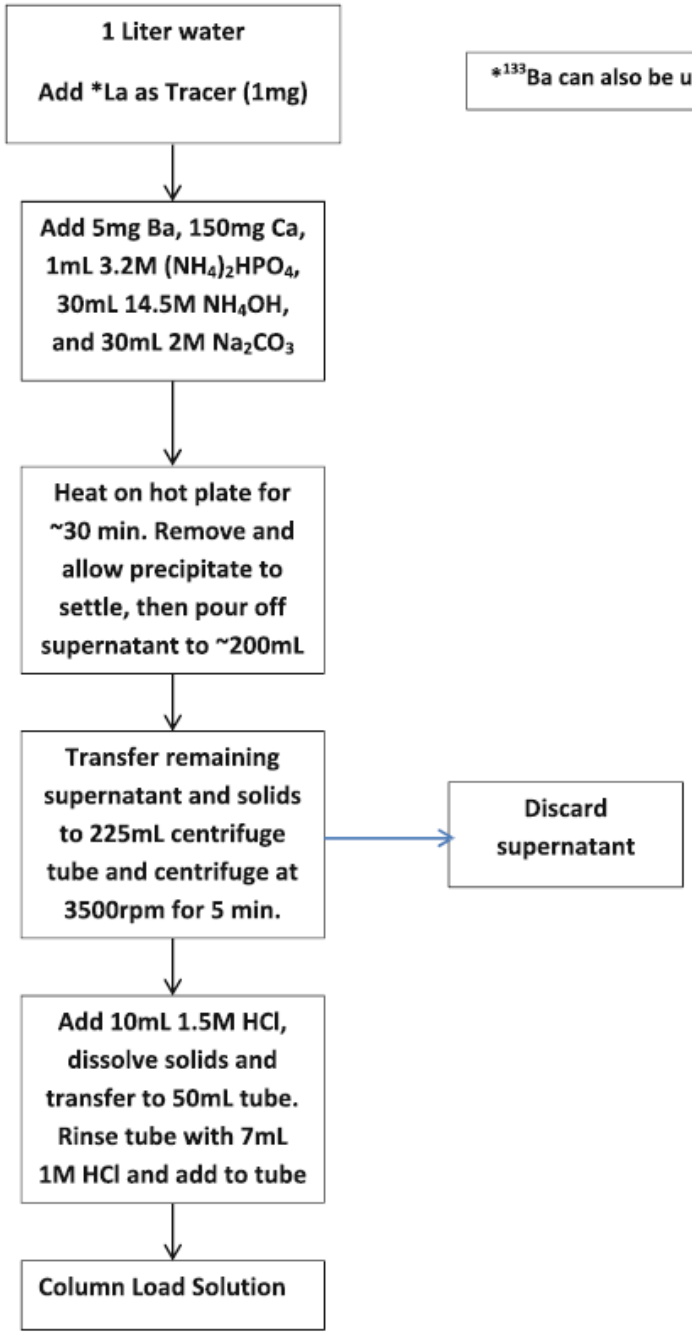

Fig. 3 Rapid ^{228}Ra sample preparation for water samples

- Addition of phosphate to increase yield

Maxwell, 2012

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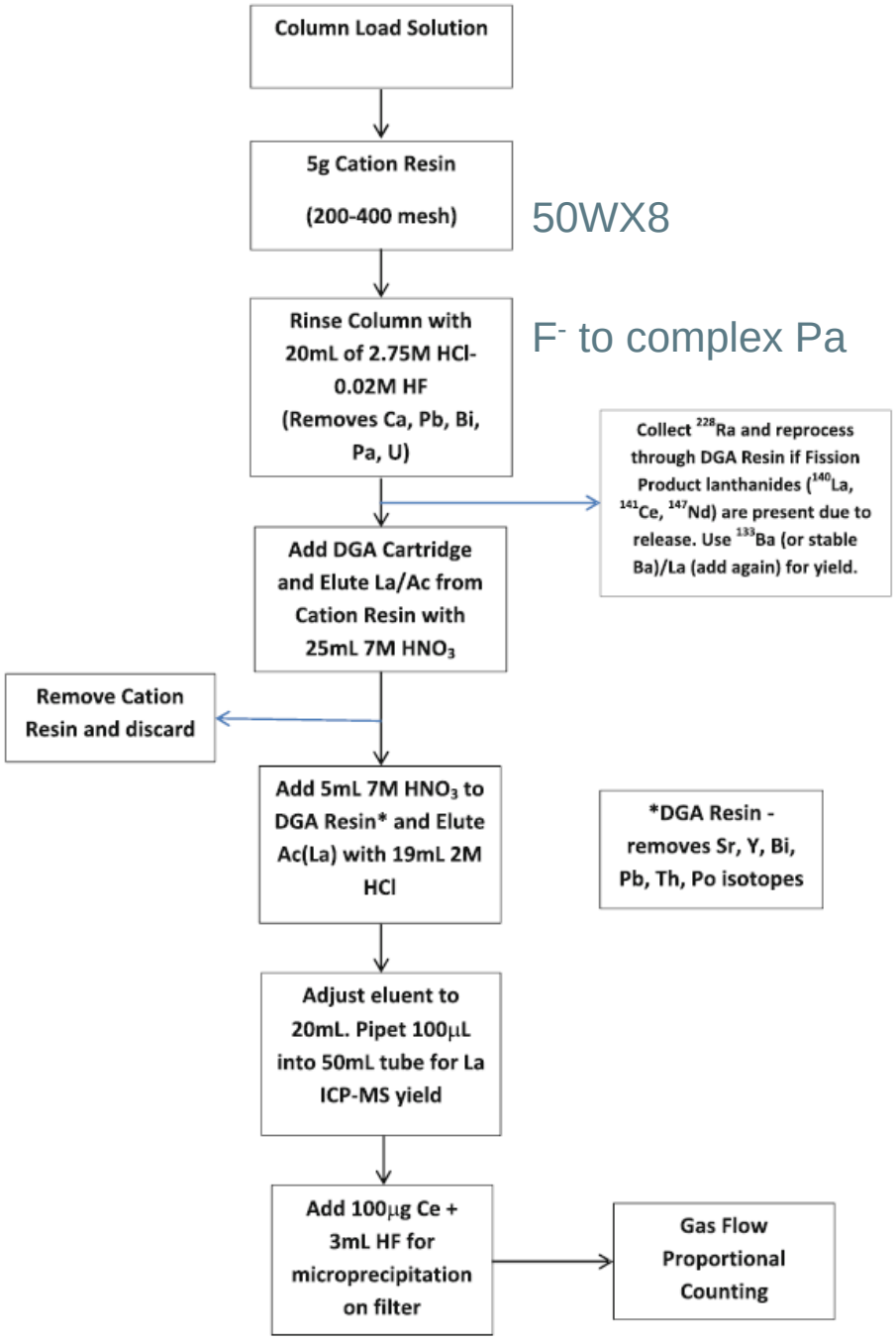

Maxwell, 2012

Fig. 4 Rapid ^{228}Ra column separation for water samples

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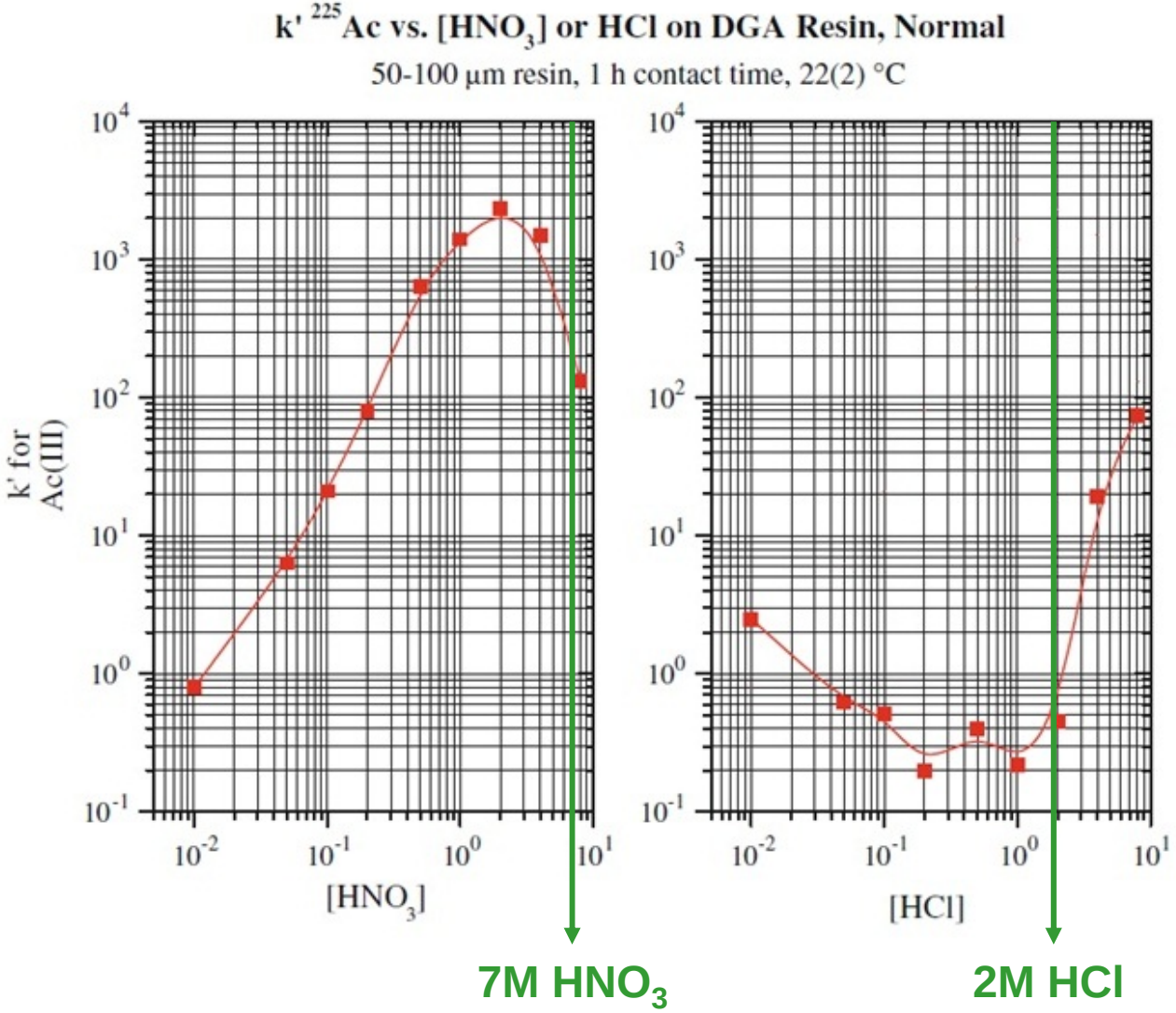
Fig. 1 Retention of Ac(III) on DGA resin courtesy PG Research Foundation, Lisle, IL, USA



Maxwell, 2012

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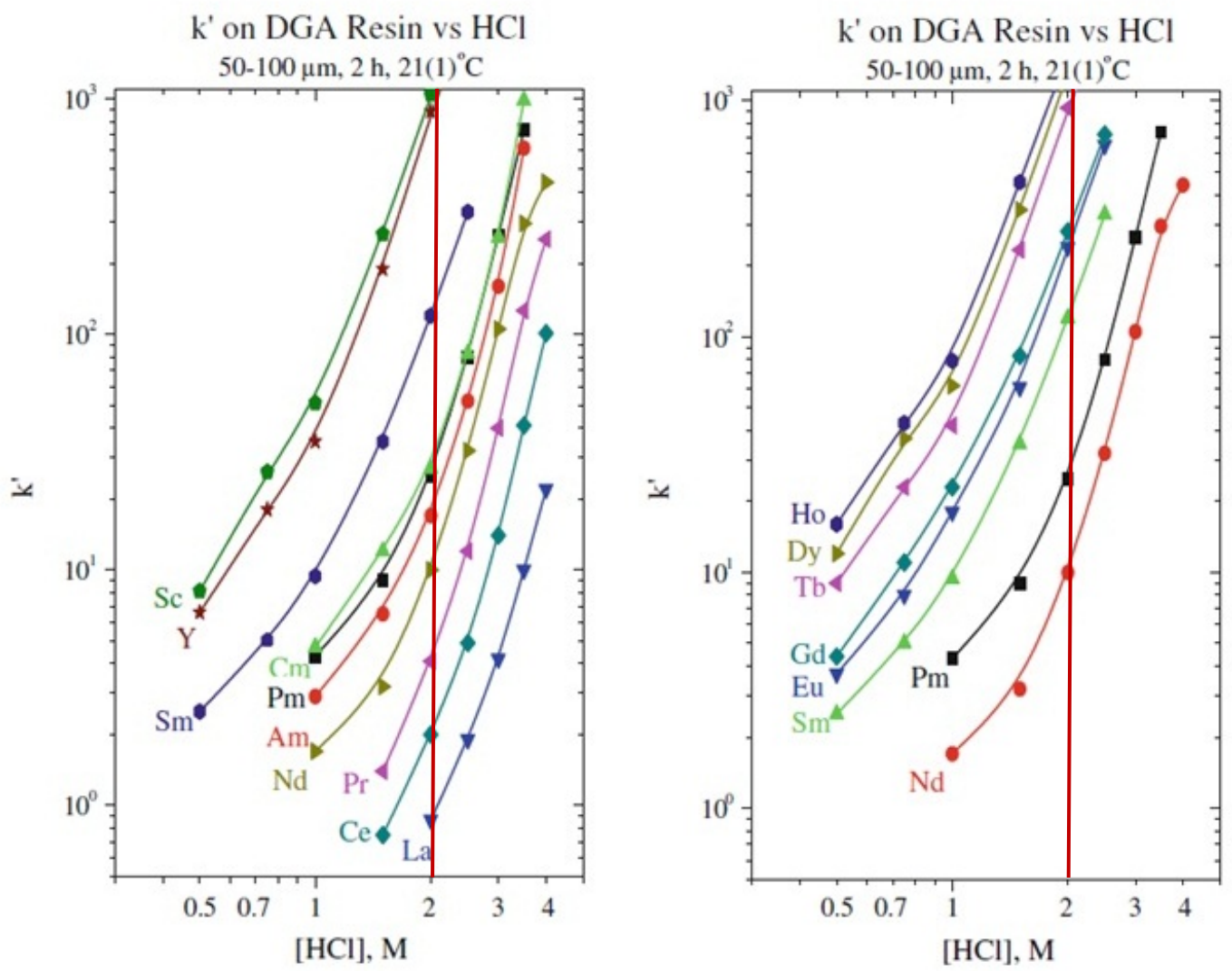
Fig. 2 Retention of lanthanides and yttrium on DGA resin in HCl courtesy PG Research Foundation, Lisle, IL, USA



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Results

- Analysis of three sets of spiked samples
  - Three activity levels (177, 355 and 1046 mBq.L^{-1})
  - 1L samples
  - Counting time: 60 – 90 min
  - Yield via La / ICP-MS
  - Yields > 90%, good agreement with reference activities

N	Yield / %	RSD / %	Activity / mBg.L^{-1}	RSD. / %	Reference activity / mBq.L^{-1}	Difference / %
7	94.3	2.3	177.5	11.6	177.2	0.2
7	92.1	1.5	347.2	7.1	354.5	-2.1
6	95.3	0.9	1008.3	2.8	1046.4	-3.6

Maxwell, 2012

- Decontamination experiments
  - Decontamination factor for Sr-90 > 4000
  - Ra-228 recovery after addition of 29.6 Bq Sr-90, 3.7 Bq U-238 or 4.8 Bq Ra-226 between 93 and 97% :
    - No interference
    - No positive bias

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