A short introduction to the FFFF principles and uses

M. BOUBY, BelBar Training course, 14 October 2015

1. FFFF: History, principle, coupling
2. First application example: standard particles/polymers
3. General context
4. Examples of applications
5. Conclusions

FFFF ?

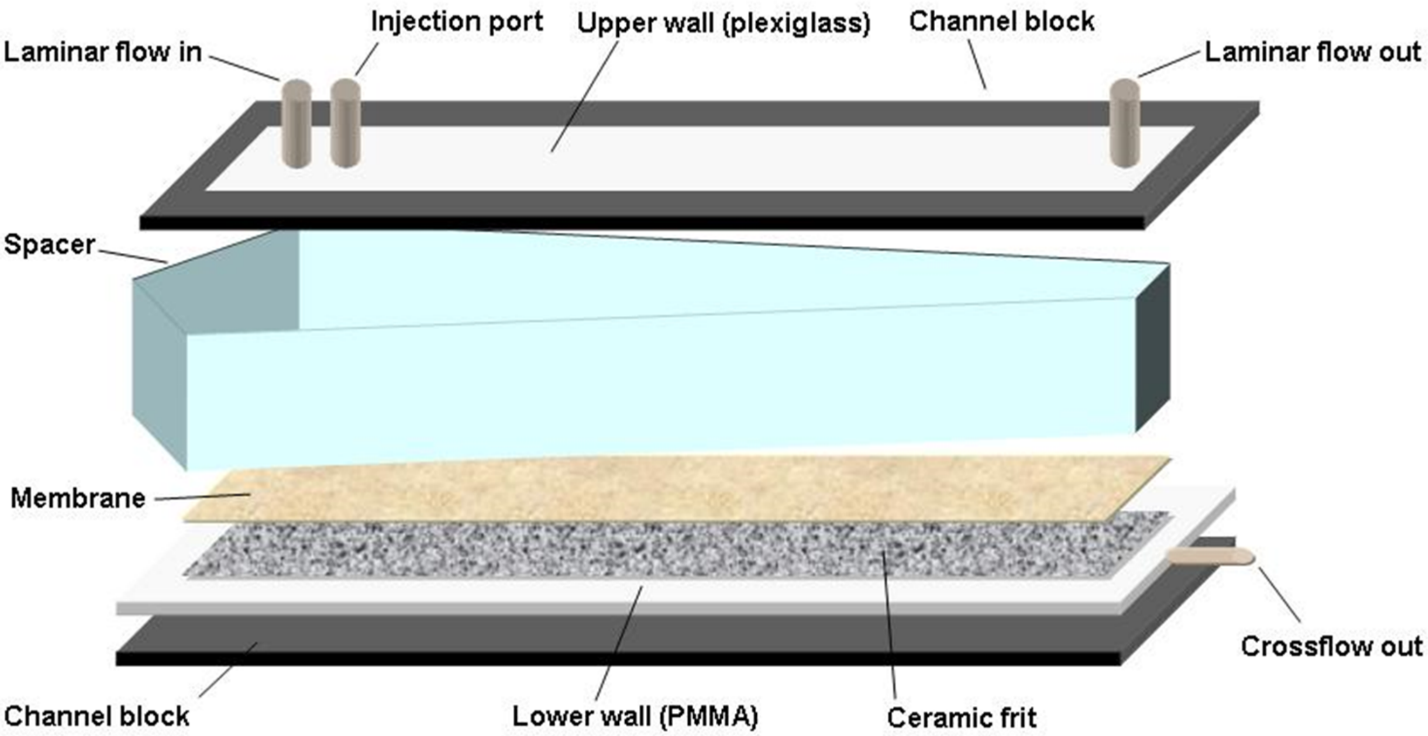
Favorite French Female Firearm ?

Favorite French Female Fishing rod ?

Flow Field-Flow Fractionation

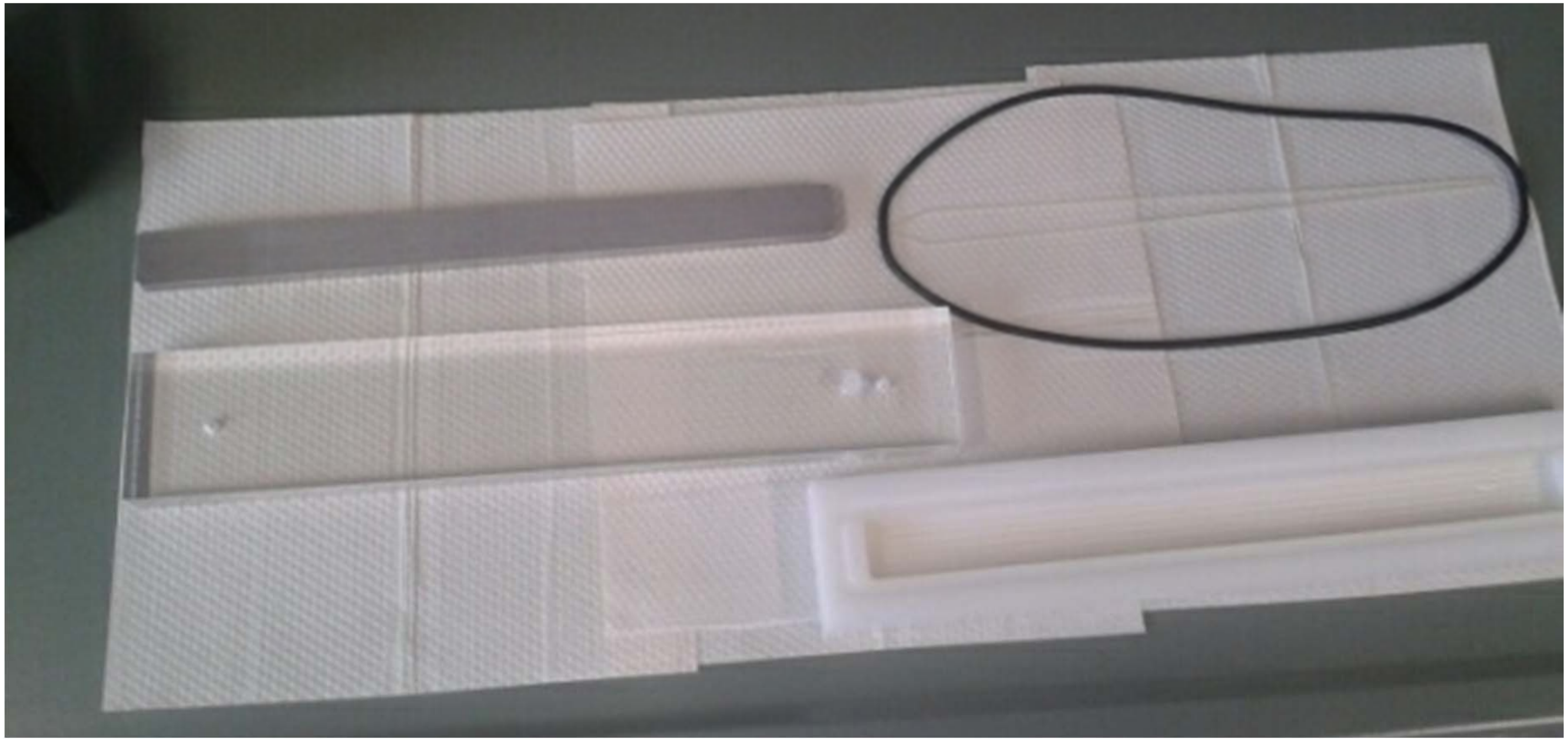
FFFF principle (0): Inside the „Black Box“

Postnova Analytics (HRFFF 10.000 AF4)



FFFF principle (0): Inside the „Black Box“

Postnova Analytics (HRFFF 10.000 AF4)



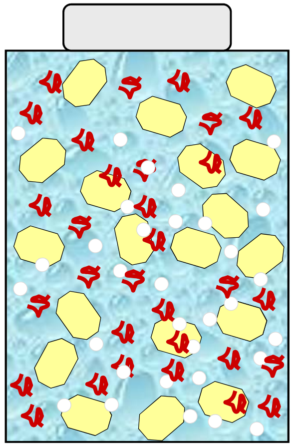
FFFF principle (0): Inside the „Black Box“

Postnova Analytics (HRFFF 10.000 AF4)

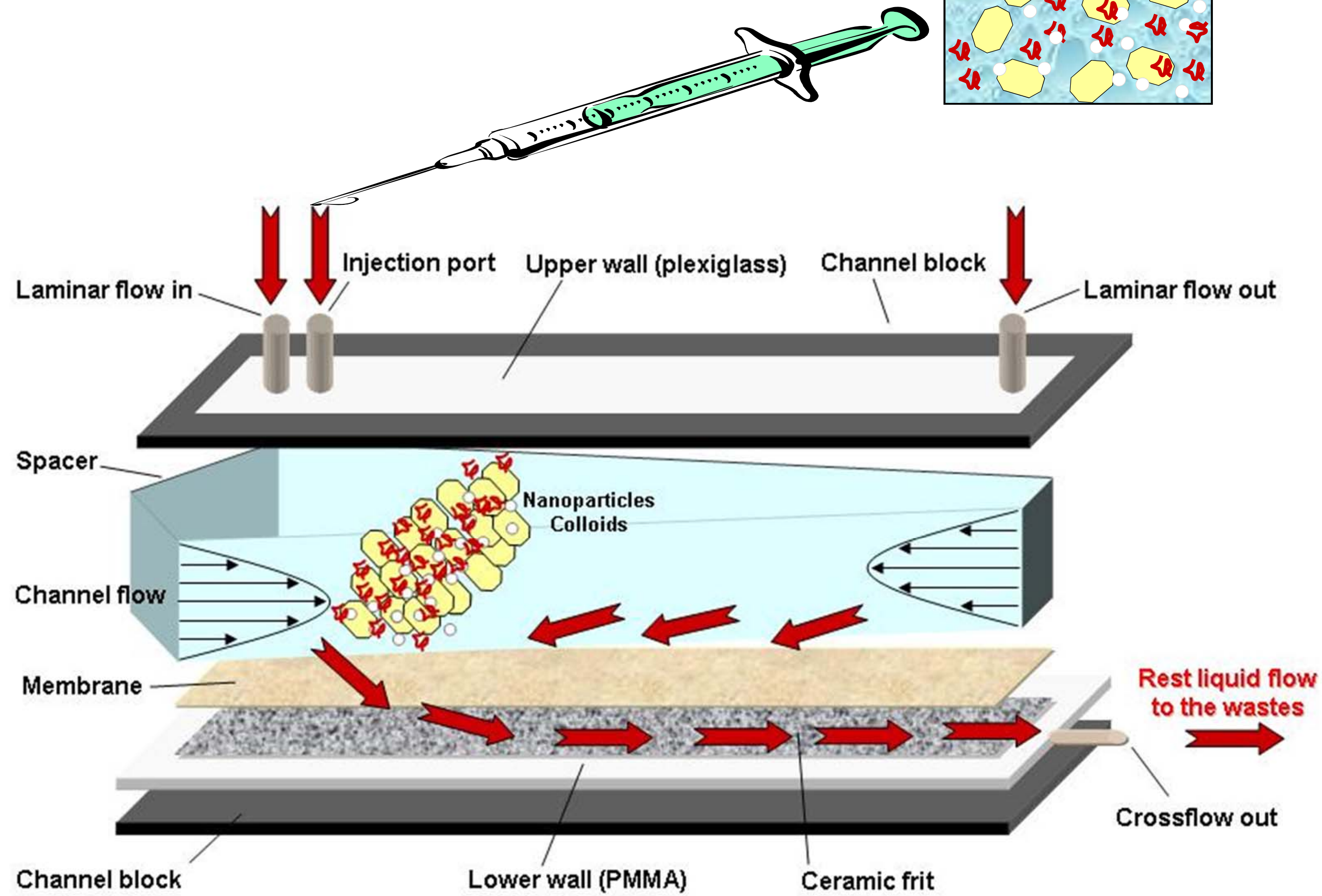
FFFF principle (1): Injection - Focusing

KIT Karlsruhe Institute of Technology

Scheme: Bouby et al., ABC, 392(2008), p1447

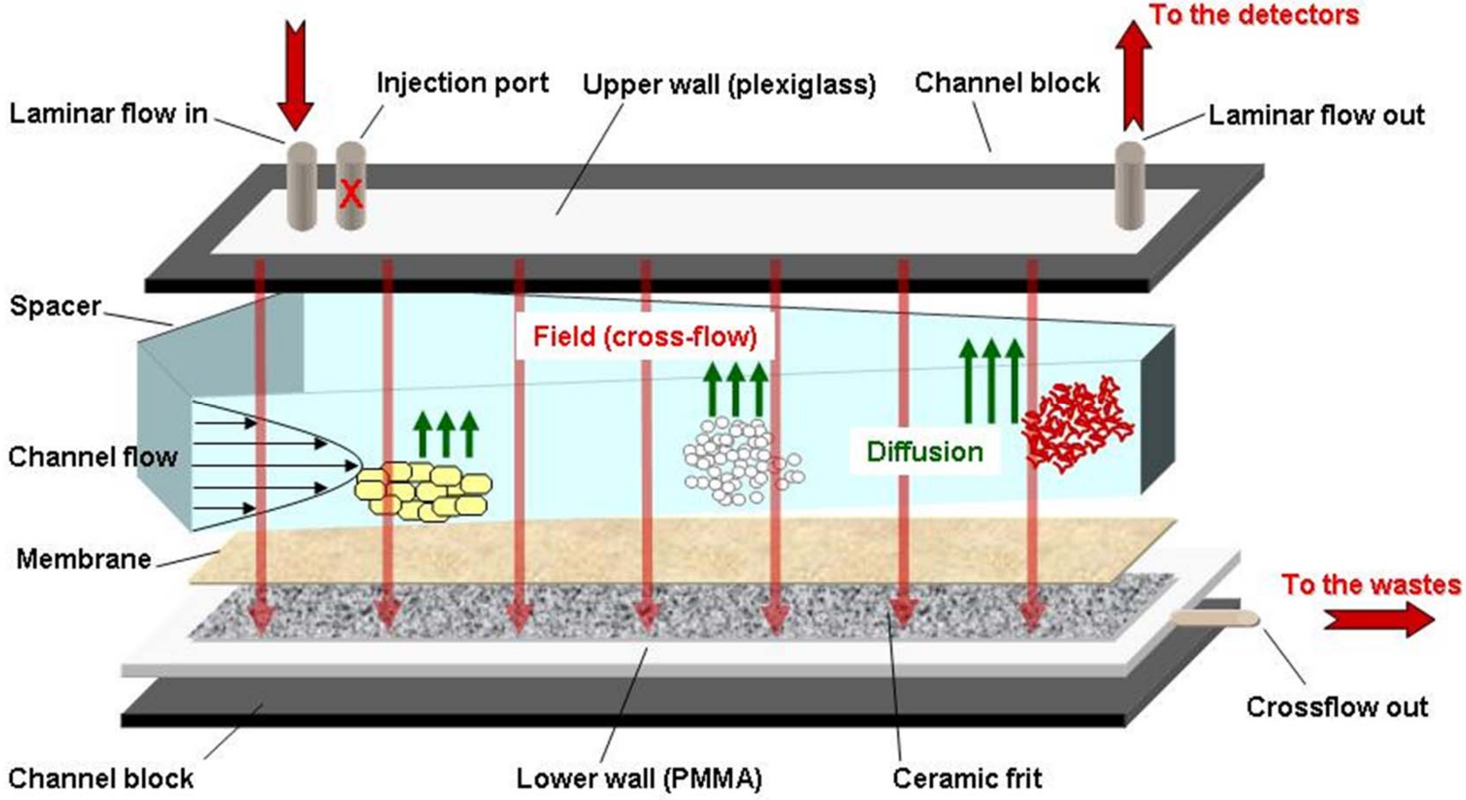


Characterization of colloidal / nanoparticles suspensions



FFFF principle (2): Elution

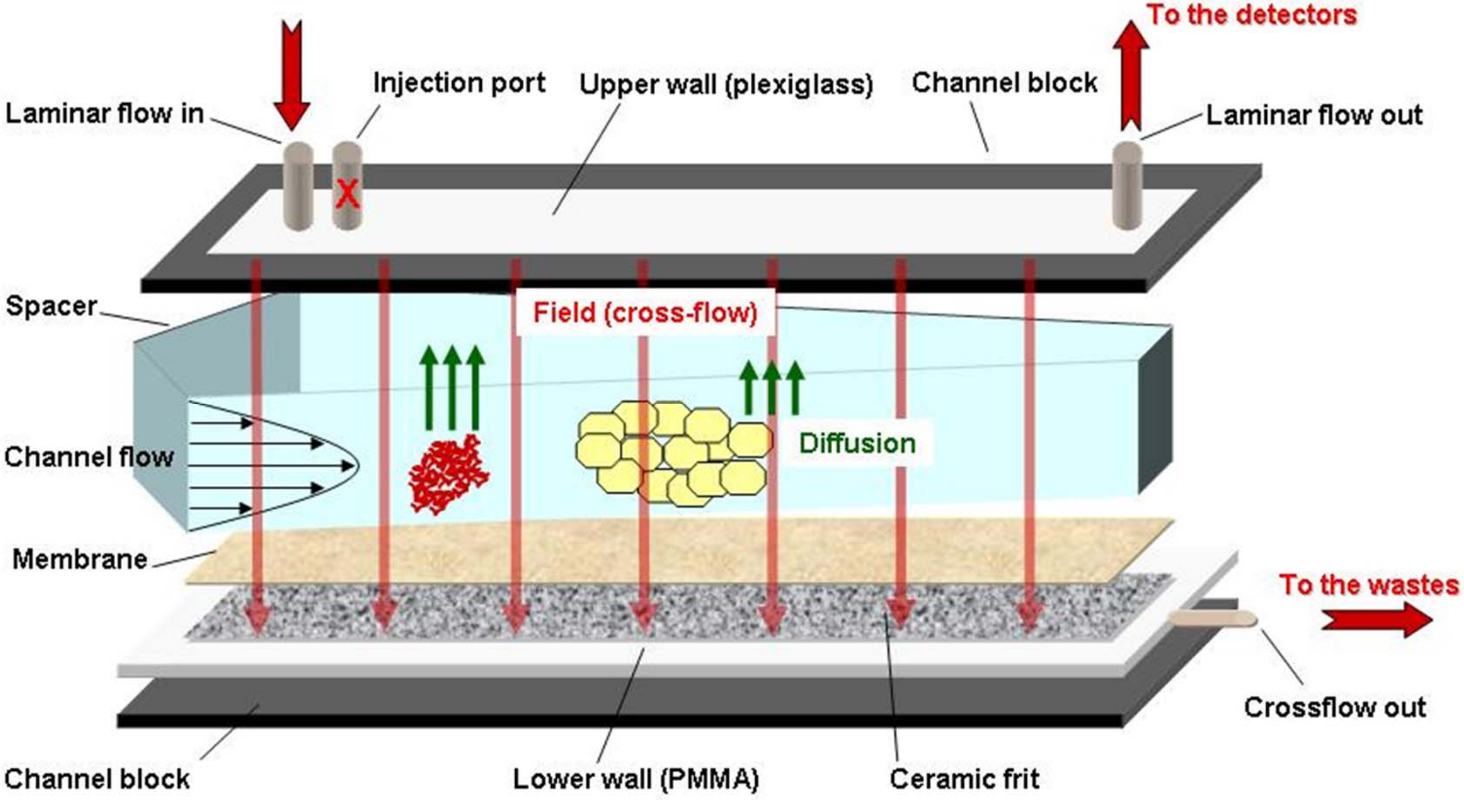
Scheme: Bouby et al., ABC, 392(2008), p1447



Elution in „Normal mode“

FFFF principle (3): Elution

Scheme: Bouby et al., ABC, 392(2008), p1447



Elution in „Steric mode“

Luo et al. (2006), JCA, 1120, 158-164, reported an inversion point in the range 800-1000 nm particle diameter

- Various on-line detection methods....

ICP-MS
Inorganic element content

UV-VIS
light absorbing colloids
Rel. size and [C]

LIBD
Very high sensitivity
Rel. size and [C]

LLS
absolute molar mass and size

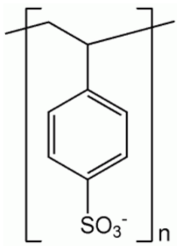
- Various off-line detection methods after fraction collections:
TRLFS, STXM, TEM, NMR …

... For an experimental metal ion speciation: differentiation of colloids/NPs - bound fractions and dissolved species at trace concentrations

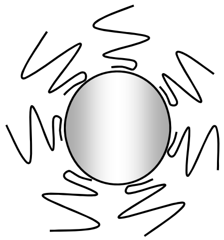
2. First application example: polymer and nanoparticle standards

AsFlFFF calibration with polymer and NP standards

Poly(styrene sulfonate) standard Na-salts (PSS)



Carboxylated polystyrene NP (LC)



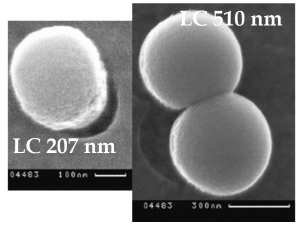
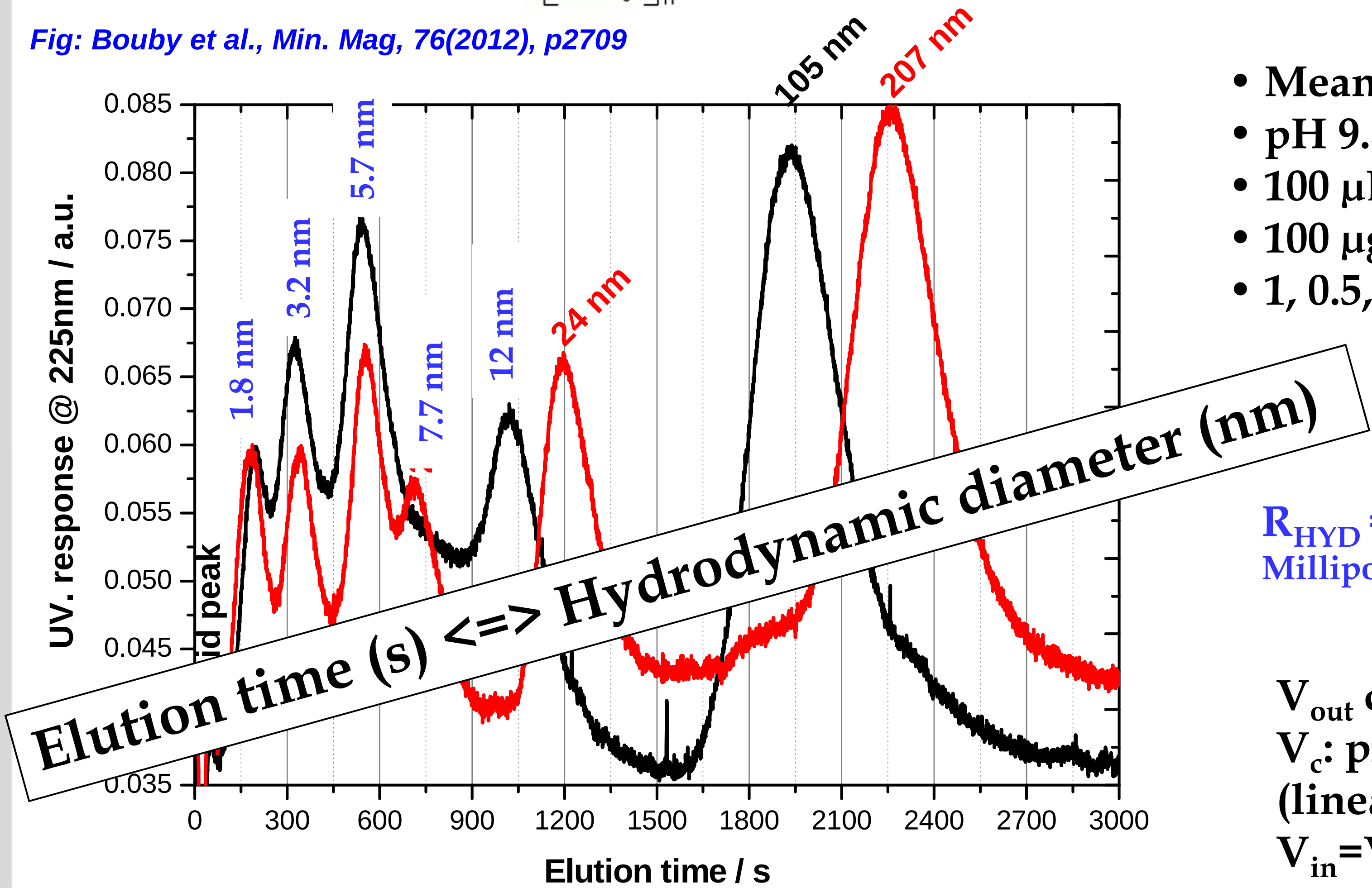


Fig: Bouby et al., Min. Mag, 76(2012), p2709



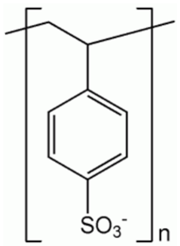
- Mean of 3 meas.
- pH 9.3 (MQ+NaOH)
- 100 µL injected
- 100 $\mu g.L^{-1}$ PSS
- 1, 0.5, 0.5 $mg.L^{-1}$ LC

$R_{HYD} = f\ (M_w)$
Millipore data, 2000

V_{out} constant
V_c: programmed (linear decrease)
$V_{in} = V_c + V_{out}$

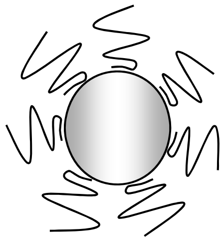
AsFlFFF calibration with polymer and NP standards: Reproducibility tests

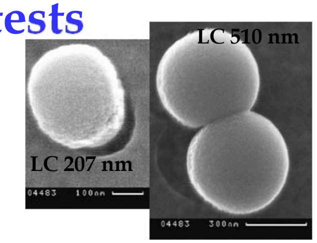
Poly(styrene sulfonate) standard Na-salts (PSS)

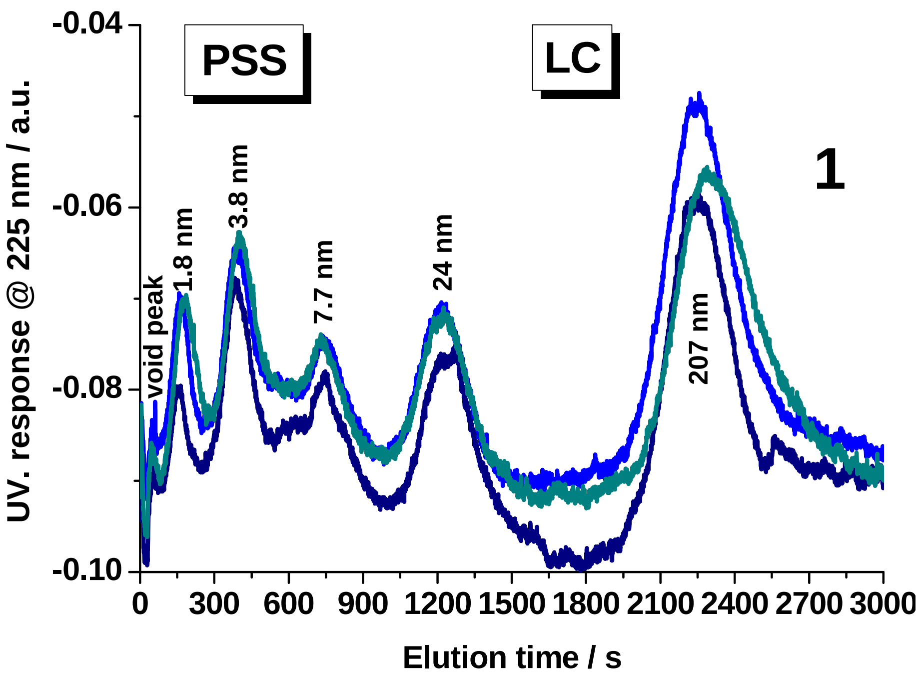


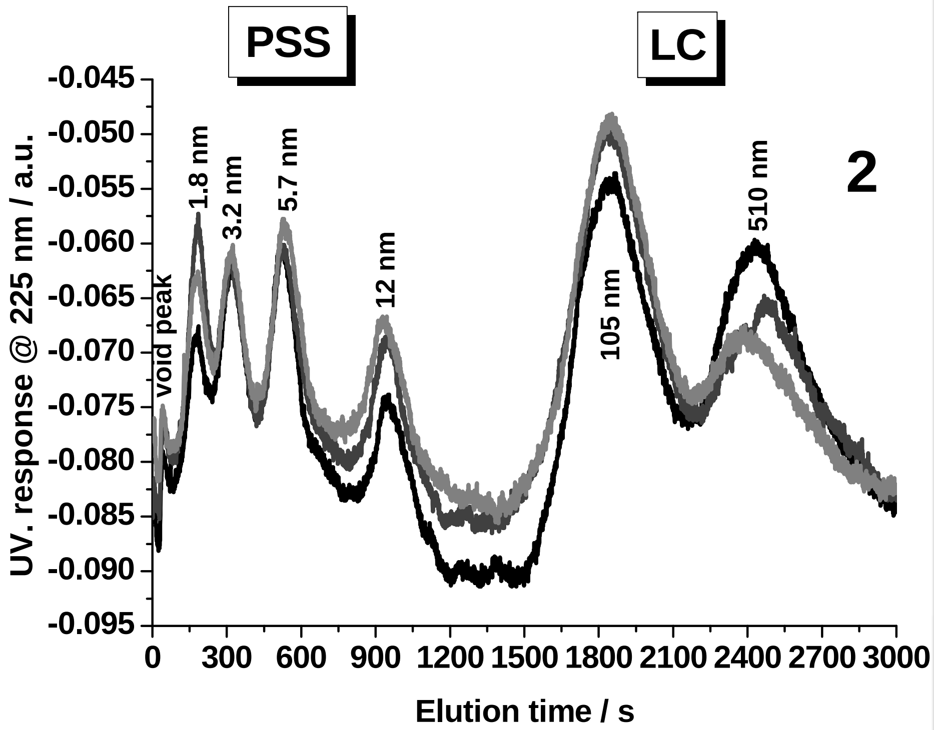
- pH 9.3 (MQ+NaOH)
- 100 µL injected
- 100 µg.L^{-1} PSS
- 1, 0.5, 0.5, 1 mg.L^{-1} LC

Carboxylated polystyrene NP (LC)





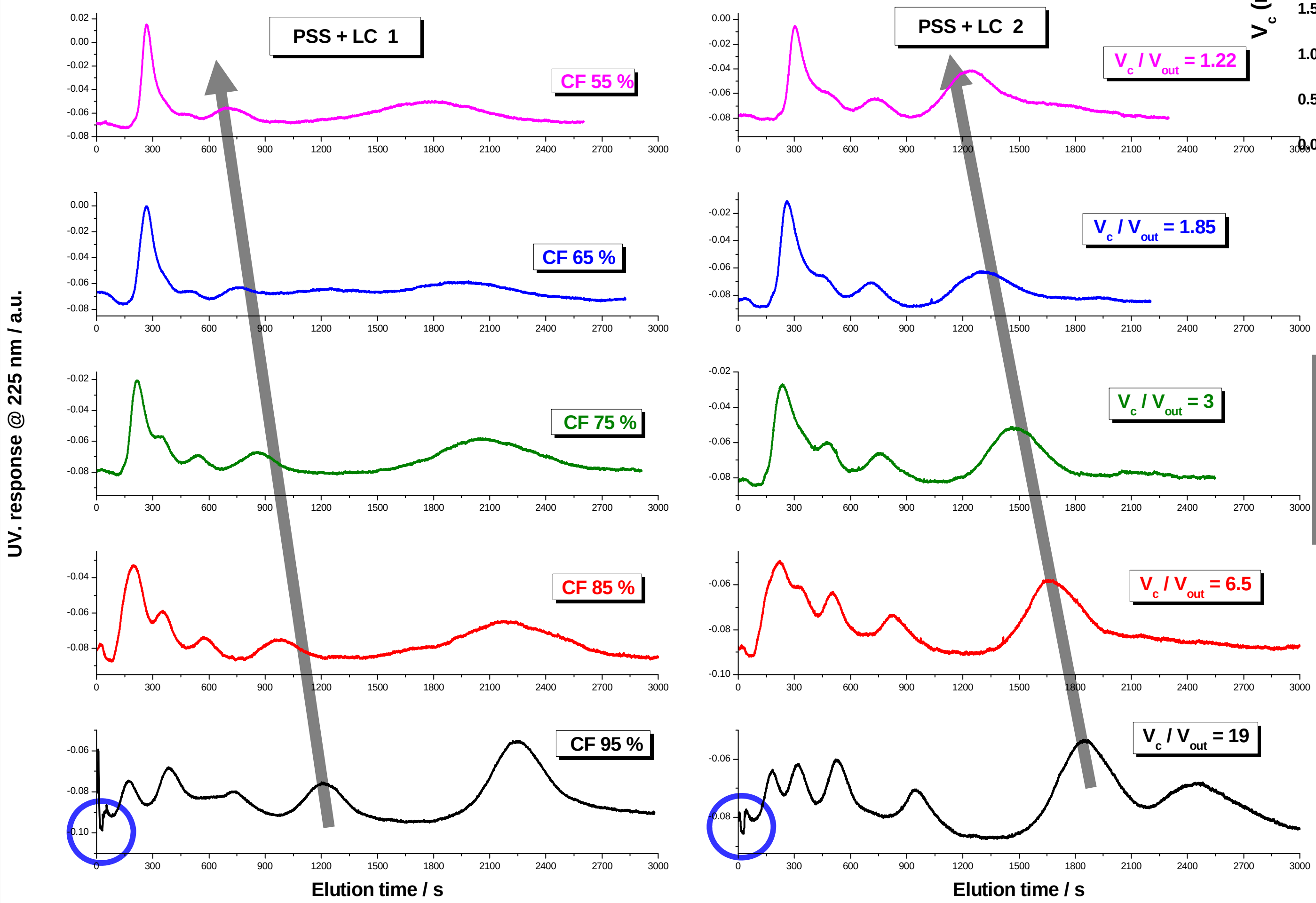


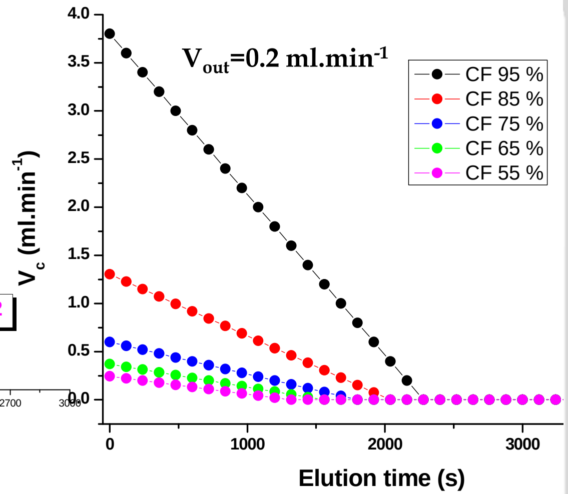


Good reproducibility !

AsFlFFF's flow parameter effects on the fractionation of polymer (PSS) and NP (LC) standards

$$t_R \ \alpha \ V_c / V_{out}$$





Progressive loss of the separation power (resolution)

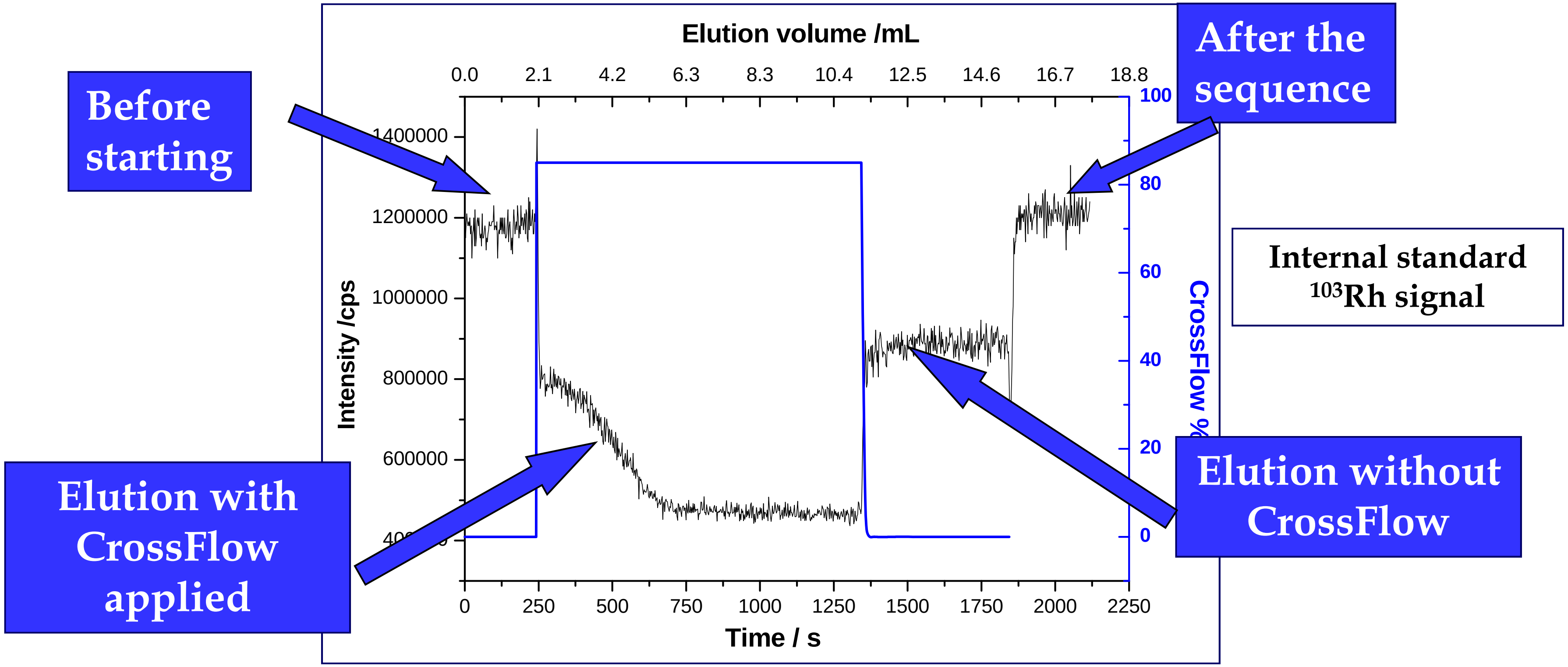
Void peak not resolved

To be optimized: eluent, membrane, injection volumes, separation conditions…

Theoretical formula : $d_{hyd}=f(t_R)$

Constant Flow Rates required!

Obviously not the case with this AsFlFFF…



- No direct size quantification possible ➞ Calibration with standards

- No ICP-MS quantification in concentration but in mass (achieved in 2004/5, validated in 2008)

A growing interest in the world

Source Scopus, 09.10.2015

Key word: Flow Field Flow Fractionation

1960-1999 (40 years): 968 documents

2000-now (last 15 years): 2191

3. Applications in our research activities

General context: INE TOPICS

1. **Long term performance assessment of nuclear waste disposal for HLW (High Level radioactive, heat-producing Wastes)**

- **Geochemical behavior of the actinides and fission products**
- **Efficiency of the multi-barrier concept**

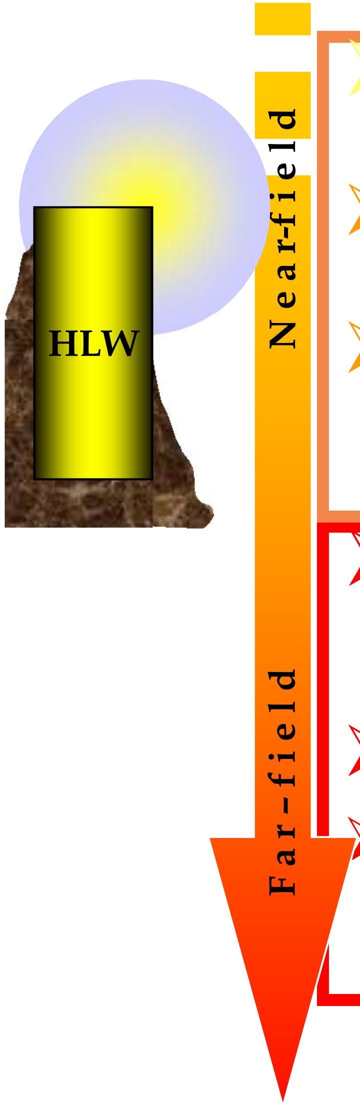
→ **Developing predictive and quantitative modeling codes**

→ **Developing speciation's methods**

Mobility of the RNs ?

Aquatic colloids-nanoparticles: a KEY in PA of an underground nuclear wastes repository ?...YES!

Karlsruhe Institute of Technology



- Corrosion of the engineered barrier
  - Secondary phase formation (incorporation/sorption of RN)
- „Real“ colloids formation (ex: $PuO(OH)_2$)
  - Solubility limit increased
- Chemistry of the hostrock/backfill material
  - Colloid generation, potential RN-carriers (pseudocolloids)

- Interaction with naturally occuring colloids - nanoparticles
  - organic (humic substances, LMW),
  - inorganic (Al or Fe-oxides/hydroxides, clays, silica...)
- Characterization of natural (ground) water samples
- Migration process understanding
  - in-situ measurements, bore core

Laboratory vs Natural Samples

What should we specify and quantify ?

- Nature, size distribution, stability?
- Colloid-actinide interaction: sorption/incorporation, kinetics?
- Behaviour at the solid-water interface?

Where do the difficulties lie?

- Small size (nm)
- Polydisperse
- Chemically and physically heterogeneous
- Relevant concentration ranges ($\mu g.L^{-1}$ – $mg.L^{-1}$)

Which informations can be obtained from AsFlFFF coupled to analytical devices?

- Colloidal size distribution

HS, iron phases, clays, aluminosilicates, Al_{13}, QDs, …

- Inorganic element content and distribution: complexation, sorption, incorporation

An-HS, An-clays, An-aluminium phases, secondary phases products (iron, sheet silicates), …

- Long term study: stability, kinetics, reversibility

An-HS complexes, colloids, competing ligand

- Colloidal matter heterogeneities

Natural ponds- or ground- waters (Gorleben), Boom Clay pore waters

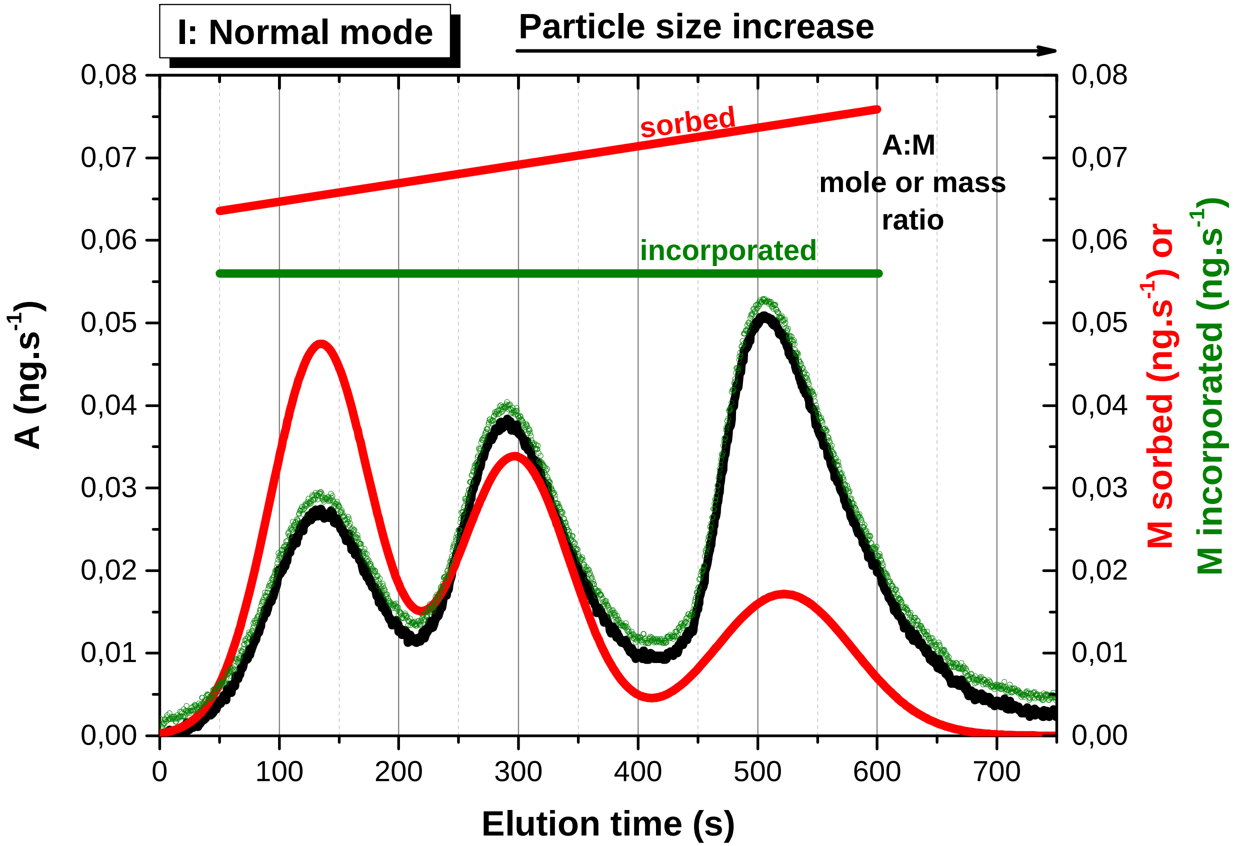
AsFlFFF + analytical devices

Fig: Bouby et al., Chromatography, 2(2015), p545

Adsorption
vs
Incorporation
on
AsFlFFF/ICPMS fractogram

A: main structural element
M: trace component
incorporated
adsorbed

1. A:M mole or mass ratios evolution
2. Recoveries

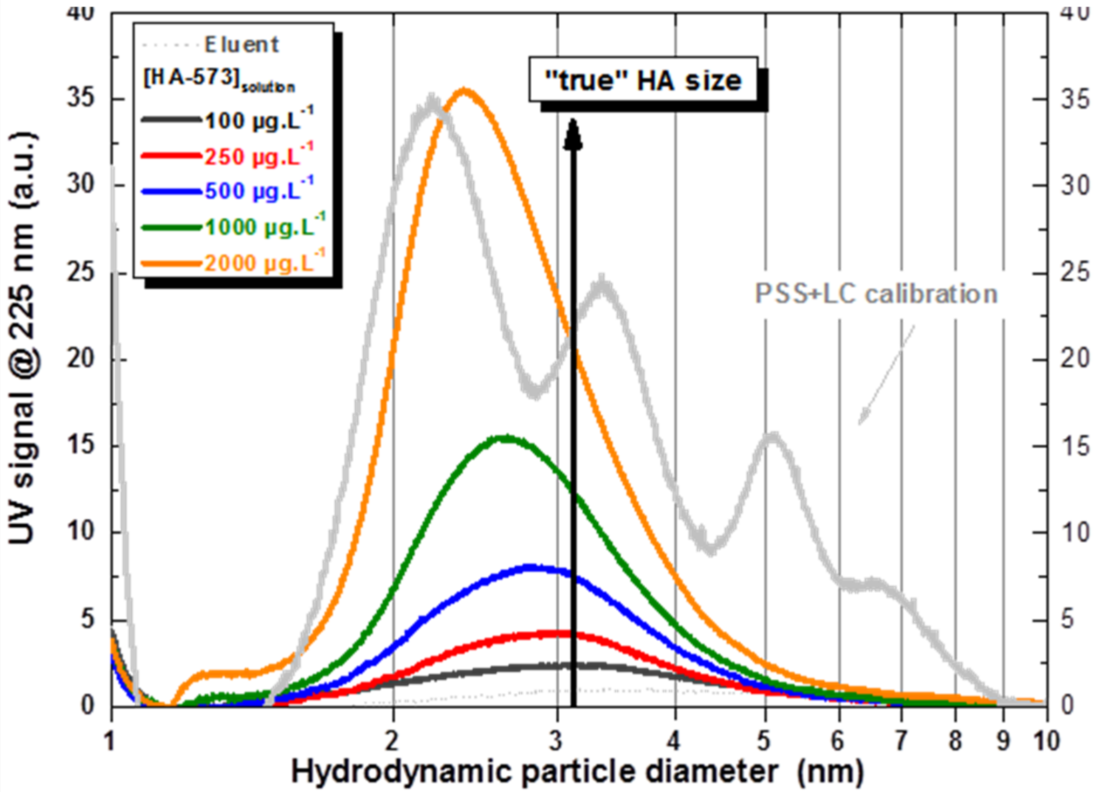


Ideal case…..

4. Examples of applications

AsFlFFF + analytical devices = Colloidal size distribution

- Characterization of purified humic acids: Gohy-HA-573



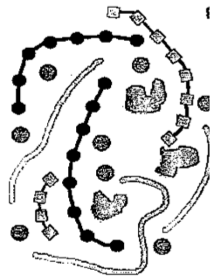
- Confirmed by SEC

- Fraction collections and additional measurements: TRLFS (with Cm^{3+}), STXM,…

pH 9.3 and calibration PSS:
- Size (hyd. ø) = (3.1 ± 0.1) nm

HS: the „new view“
(Simpsons et al., Naturwissenschaften, 2002, 89, p84)

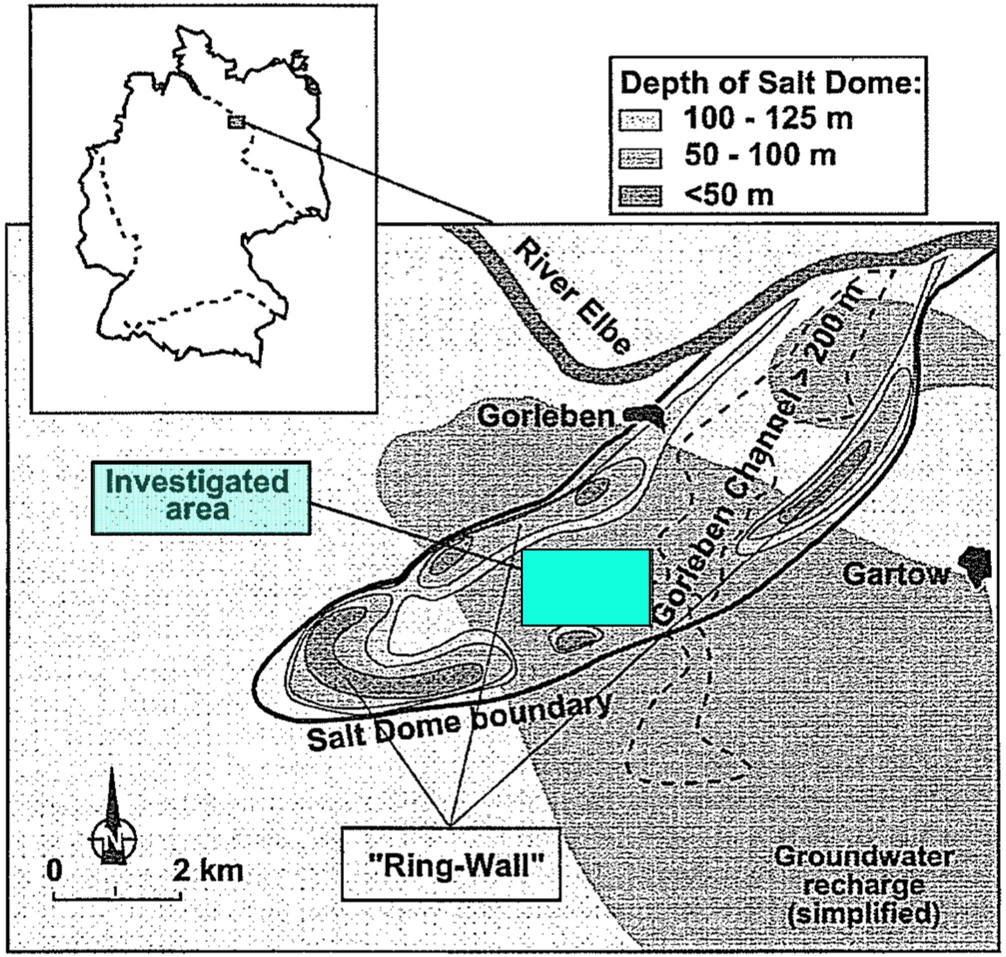
- Assembly of relatively low molecular weight components (polypeptides, polysaccharides, aliphatic chain, lignin fragments…)



Detection of colloidal matter heterogeneities in natural samples

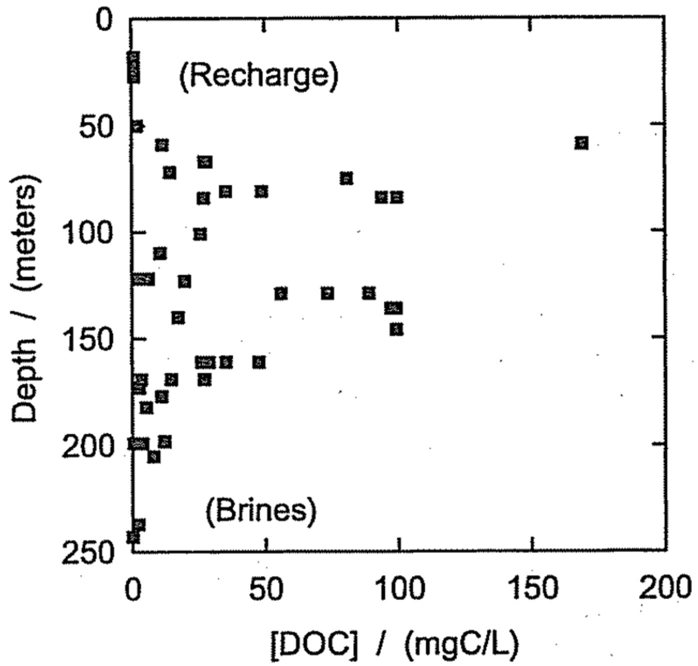
- Ground water sample from Gorleben site, Lower Saxony, North Germany

G. Buckau et al. / Applied Geochemistry 15 (2000) 171–179



Overview of the Gorleben site

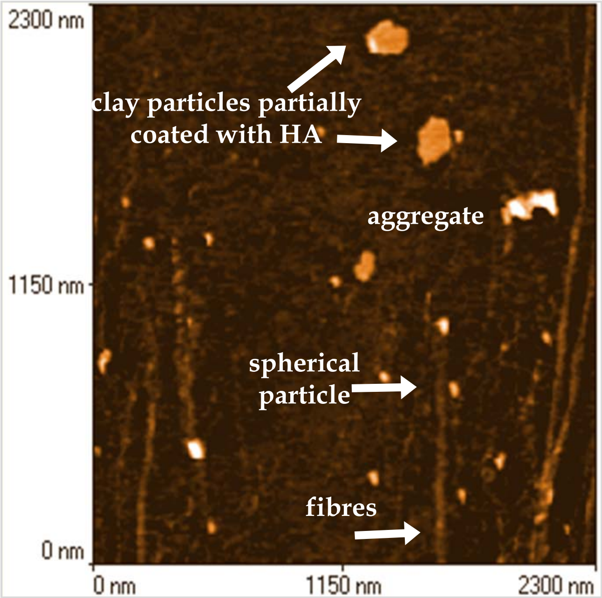
- **Gorleben salt dome is under investigation for radioactive waste disposal**
- **Peculiarity of the surrounding aquifer system: high content of humic colloids**



Detection of colloidal matter heterogeneities in natural samples

- Ground water sample from Gorleben site

- **Gohy-2227, 130 m depth**
- **DOC: 82 mg.L^{-1}, pH 7.7**
- **10 % inorganic components (6% polyvalent metal ions; Ce(III): 4.10^{-8} M, Th(IV): 7.10^{-9} M, U(VI): 3.10^{-9} M)**
- **Stably colloid-bound: no complete desorption even after acid treatment**

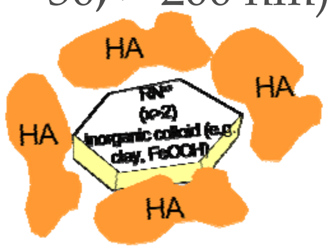


M. Plaschke et al., ES &T 2002, 36, 4483-4488

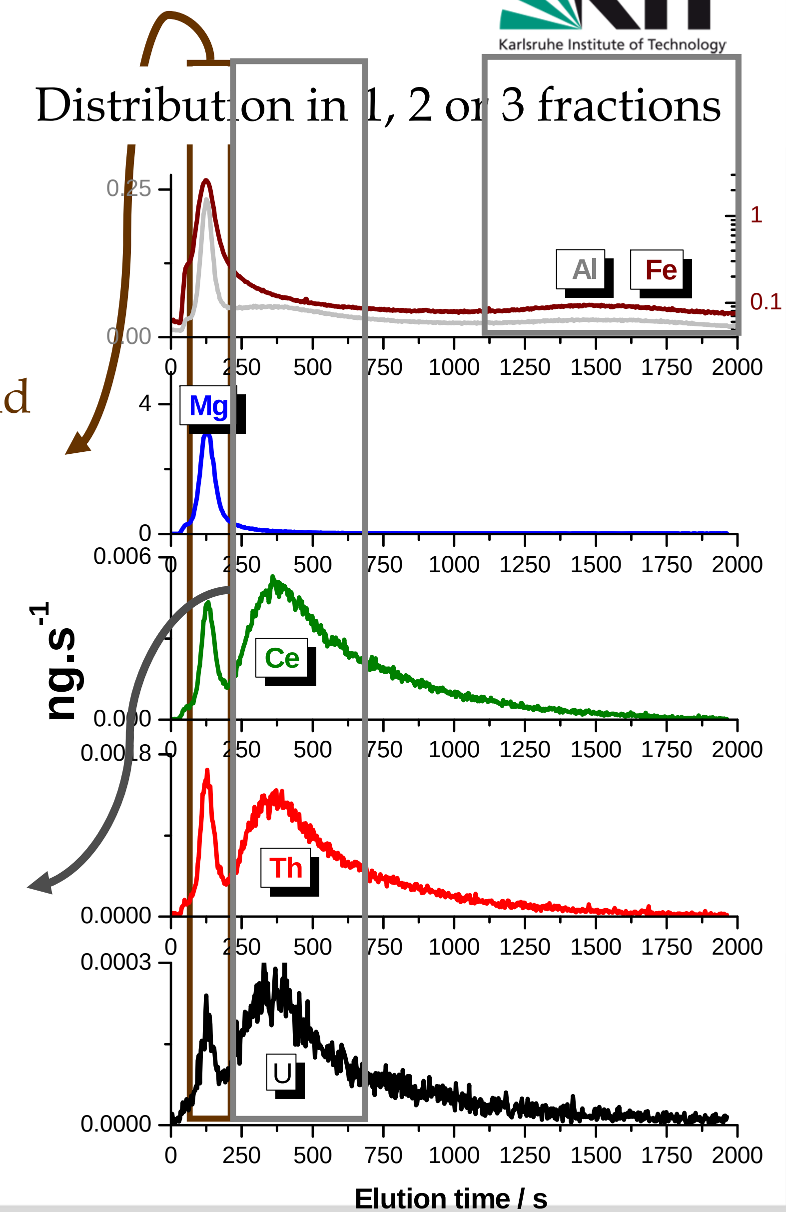
See: Bouby et al., Min. Mag, 76(2012), p2709

Natural OM-bound fraction < 5 nm (UV, C signal)

Inorganic colloids - bound fraction (5-30, > 200 nm)



Distribution in 1, 2 or 3 fractions



AsFlFFF + analytical devices = inorganic element content and distribution: sorption, kinetic, reversibility

- **FEBEX bentonite clay colloids stability and interaction with actinides in GGW ?**

See: Bouby et al., GCA, 75(2011), p3866

Batch experiments under anaerobic conditions using the natural Grimsel granitic ground water

Bentonite | $20\ mg.L^{-1}$

Smaller–sized colloids obtained from the natural product after Li^{+} delamination

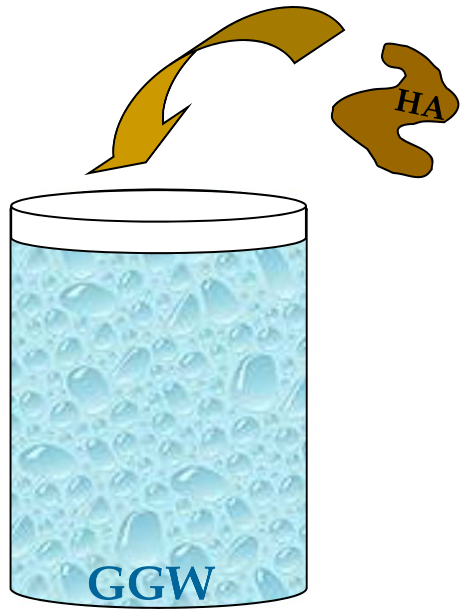
$(\sim 10^{-8}\ M - 10^{-7}\ M)$

Cs(I), Eu(III), Th(IV), U(VI)

HA | $10\ mg.L^{-1}$

Fresh
2 weeks
3 months
5 months
1 year
17 months
3 years

pH 8.6

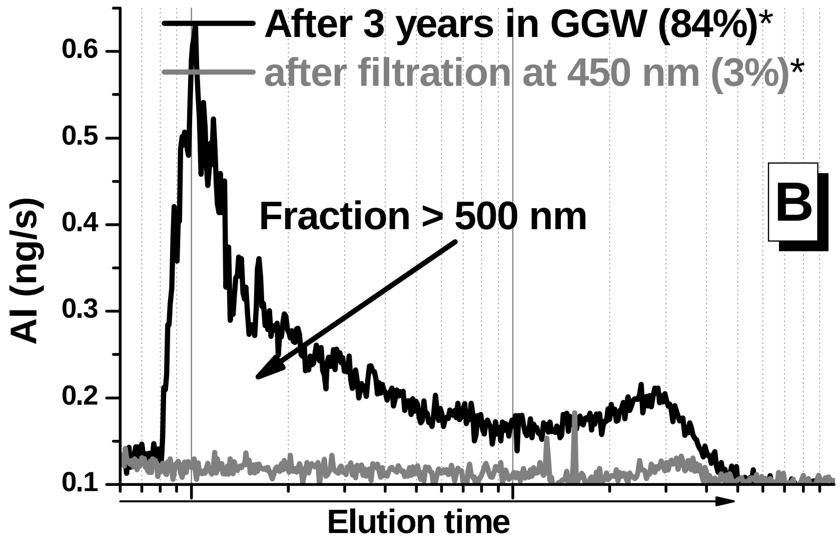


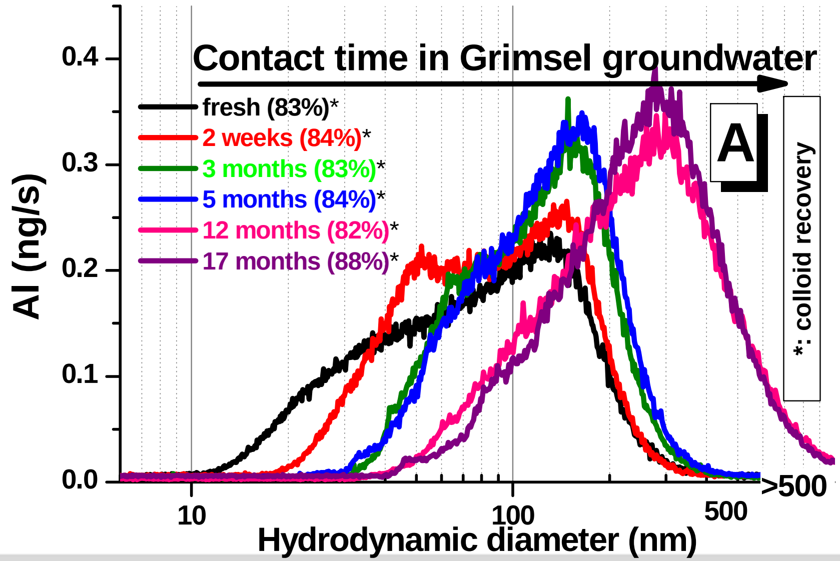
Desorption time effect (DT): From hours up to 1 year

AsFlFFF + analytical devices = inorganic element content and distribution: sorption, kinetic, reversibility

• FEBEX bentonite clay colloids stability and interaction with actinides in GGW ?

Al-fractograms evolution (size, recov.)

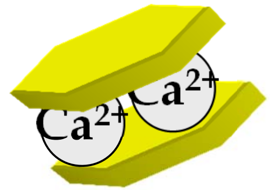




1- Slow agglomeration process over 3 years, reproducible

2- Explanations:

• Ca^{2+} ions induce agglomeration



• CCC = 10^{-3} M in $CaCl_2$ (Seher et al. 2010)

At 3.3 10^{-4} M, pH 9-10, W~ 100; colloid - colloid collision efficiency = 1%

→Slow clay colloid agglomeration not surprising

CCLs:

• The low IS and high pH conditions of the GGW are not sufficient to stabilize clay colloids for long time periods

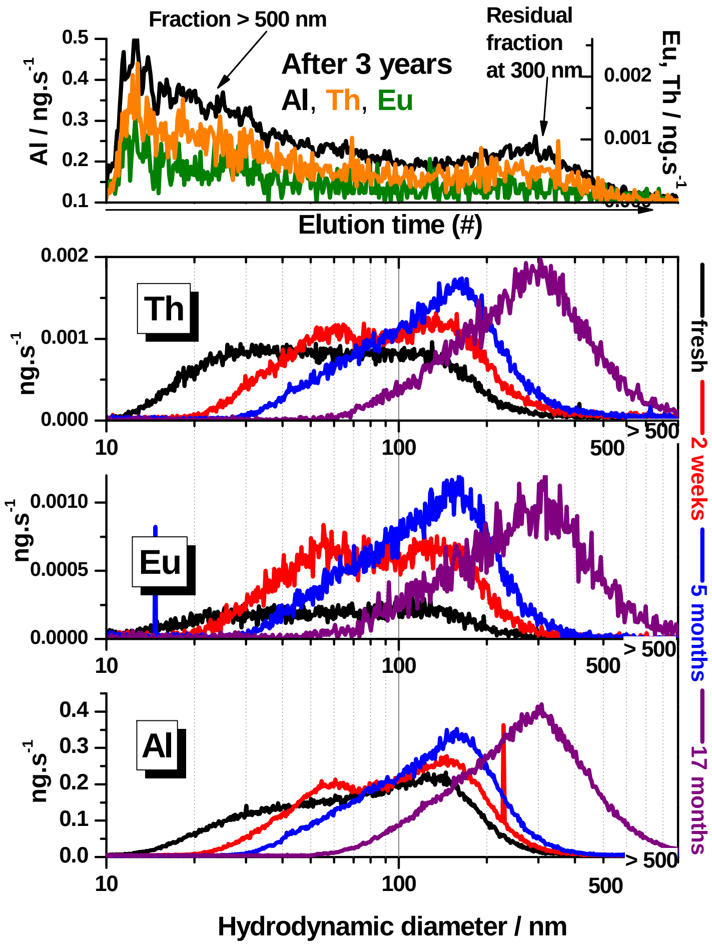
• Agglomeration and sedimentation at the end

See: Bouby et al., GCA, 75(2011), p3866

AsFlFFF + analytical devices = inorganic element content and distribution: sorption, kinetic, reversibility

- FEBEX bentonite clay colloids stability and interaction with actinides in GGW ?

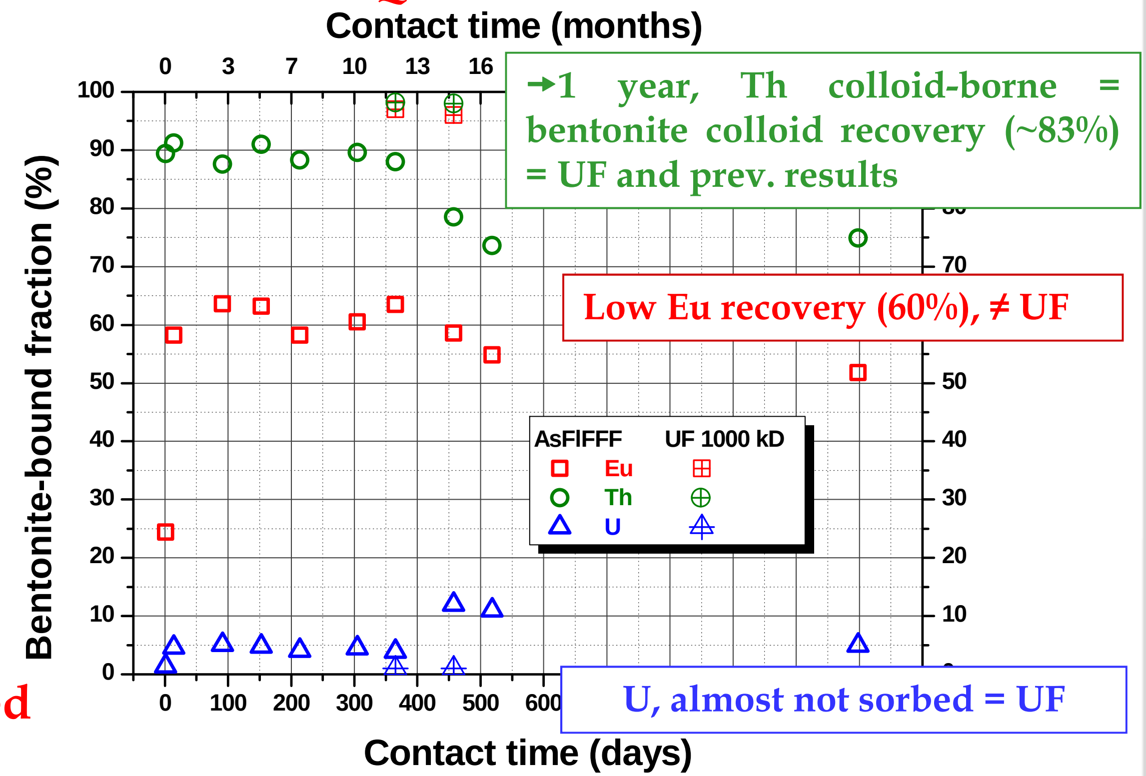
See: Bouby et al., GCA, 75(2011), p3866



Qualitative informations

- Cs, U almost not colloid bound
- Th, Eu follow bentonite colloids
- Smaller-sized colloids favored

Quantitative informations



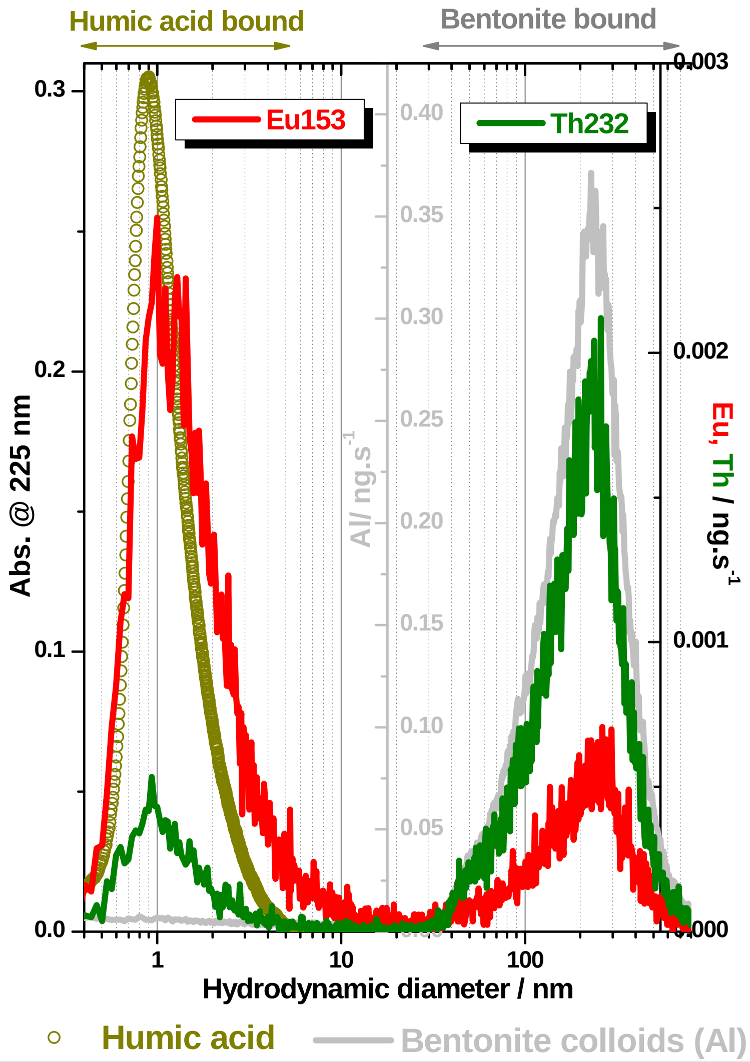
→1 year, Th colloid-borne = bentonite colloid recovery (~83%) = UF and prev. results

Low Eu recovery (60%), ≠ UF

U, almost not sorbed = UF

CCLs: No kinetic effect observed up to one year contact time

- FEBEX bentonite clay colloids stability and interaction with actinides in GGW ?



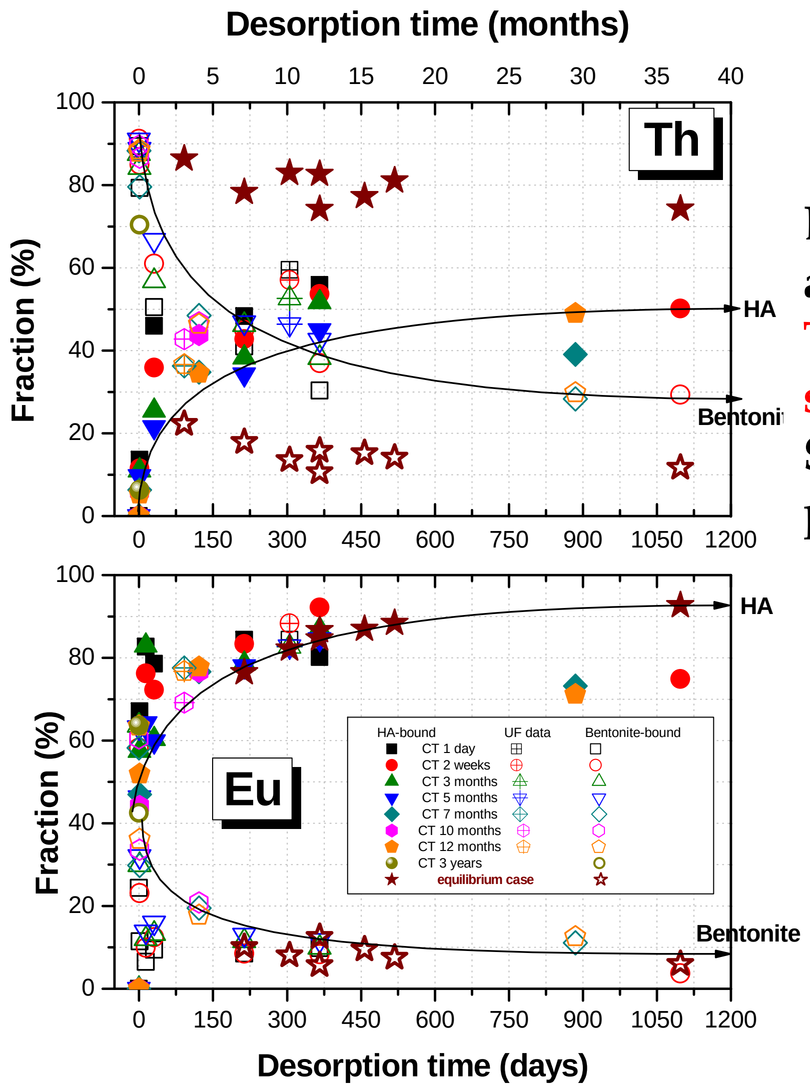
Reversibility?

Eu and Th distribution between humic acids (HA) and FEBEX bentonite colloids in grimsel groundwater (GGW): qualitative and quantitative informations

See: Bouby et al., GCA, 75(2011), p3866

AsFlFFF + analytical devices = inorganic element content and distribution: sorption, kinetic, reversibility

- **FEBEX bentonite clay colloids stability and interaction with actinides in GGW ?**



HA acting as competing ligand

Does not reach „equilibrium“ conditions, even after 3 years!

Th (tetravalent metal) colloid binding is strong; Desorption kinetically hindered: Surface sorbed species or surface (co-) precipitate ?

$\neq$

Eu (trivalent metal) colloid binding to FEBEX bentonite colloids is reversible for contact time up to at least 3 years

See: Bouby et al., GCA, 75(2011), p3866

AsFlFFF + analytical devices = inorganic element content and distribution: incorporation

Hectorite co-precipitated in the presence of La, Eu, Yb & Zr or Th

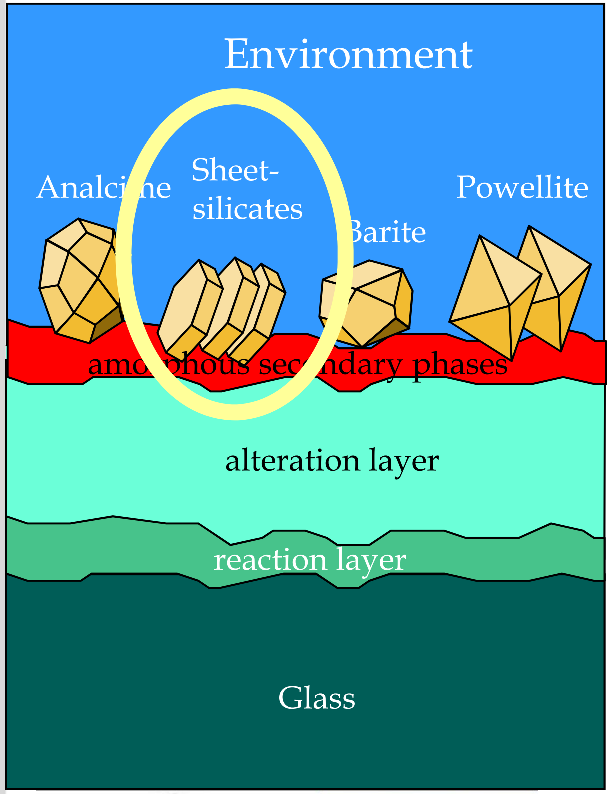
Fig: Bouby et al., Chromatography, 2(2015), p545

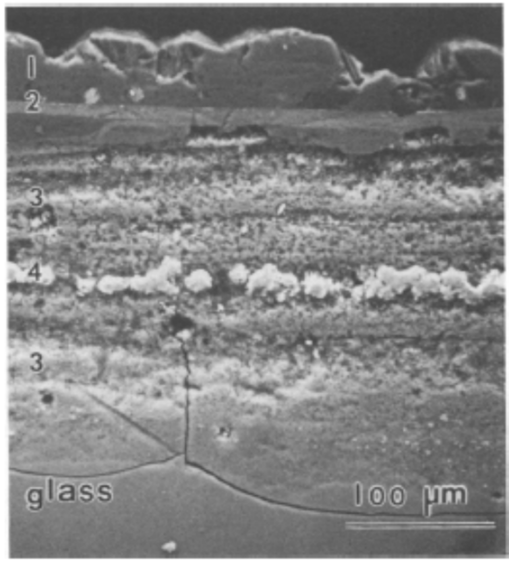
Why hectorite ?

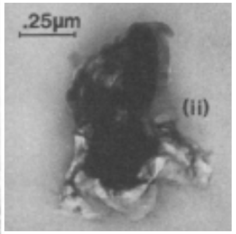
- HLW Storage in deep geological repositories

- Possible water intrusion over geological time scale

- **Canister failure & Glass corrosion**





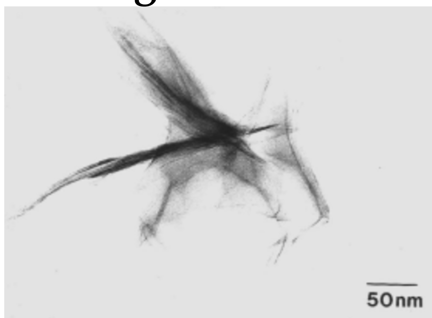


Bates et al., Science 1992, 256, 649-651

1- secondary phases
2- original surface
3- hydrated layer
4- brockite inclusions
(~10 nm) with Th, Am, Pu

- Secondary phases formation, like sheet silicates

Smectite clay colloid in glass leachate



Buck et al., App. Geochem. 1999, 14, 635-653

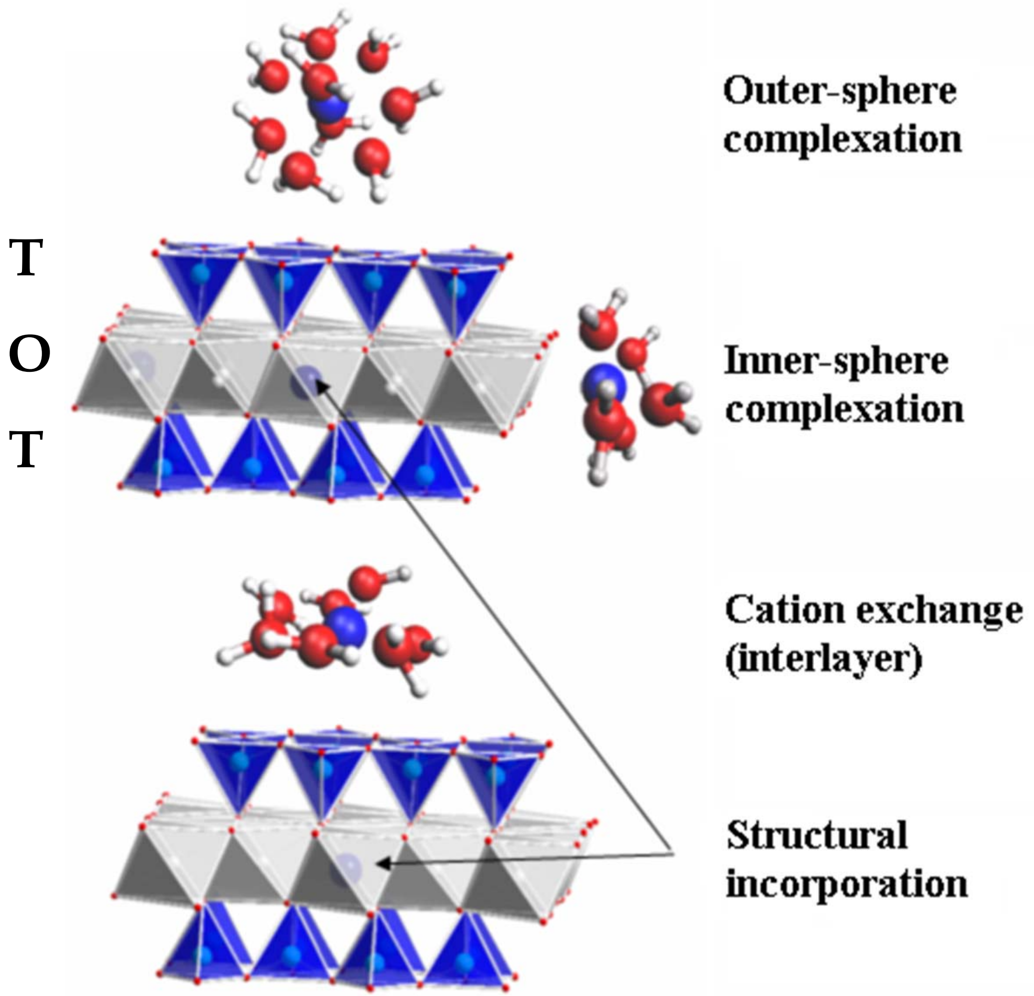
Why hectorite ?

Surface / interface reaction & co-precipitation ?

Studies on the Bulk & Colloidal fraction

Hectorite is naturally rare but it has been identified in glass corrosion layers in previous works:

- **Lederberger et al. 1988, J. Nucl. Mat, 153, 189**
- **Jollivet et al., 2012, Chem. Geol., 330-331, 207**
- **Jollivet et al., J. Nucl. Mat., 2012, 420, 508**



Ln / An retention by hectorite (D. Bosbach, N. Finck)

- **Lu**
  - Co-precipitation **+ polarized XAS: =>** clay-like environment, no adsorption
  - Co-precipitation **+ 2 y aging + AsFlFFF: =>** homogeneous distribution within structure
  - Adsorption **+ polarized XAS: =>** inner-sphere surface complexes
  - *ES&T (2009) 43 8807; Min. Mag. (2012) 76, 2709*

- **Eu**
  - Co-precipitation **+ TRLFS: =>** incorporation within structure
  - Co-precipitation **+ XAS, AsFlFFF: =>** within structure in NPs, ≠ envt. in “bulk”
  - Adsorption **+ XAS, AsFlFFF =>** inner-sphere surface complexes
  - *J. Contam. Hydrol. (2008) 102, 253; Min. Mag. (2012) 76, 2723*

- **Am**
  - Co-precipitation **+ XAS =>** clay-like environment, no adsorption
  - Adsorption **+ XAS =>** inner-sphere surface complexes
  - *Chem. Geol. (2015) 409, 12*

- **Y** *(to be submitted)*, ***Zr*** *(in prep.)*
  - Co-precipitation **+ polarized XAS, AsFlFFF =>** clay-like environment, no adsorption, homogeneous distribution within structure
  - Adsorption **+ polarized XAS =>** inner-sphere surface complexes

Ccls: Feasibility of a single element incorporation demonstrated
> Mg substitution at distorted clay-like octahedral site

Strong affinity for Ln(III)/An(III) and Zr(IV)

Karlsruhe Institute of Technology

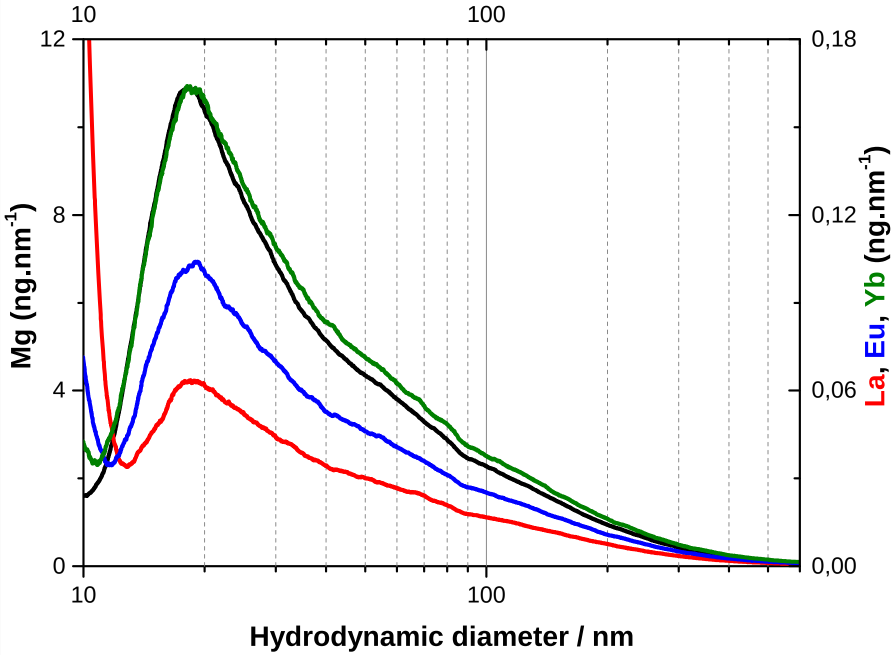
- Smaller and bigger Lns?
- Competition/selectivity?
- In presence of tetravalent elements ?

Effective ionic radii of elements 6-fold coordinated by oxygen (Shannon, 1976)

Structural element	$Si^{(IV)}$	$Mg^{(II)}$	$Li^{(I)}$	$Fe^{(II)}$						
Radius (Å)	0.26	0.720	0.760	0.780						
Element already tested					$Lu^{(III)}$	$Y^{(III)}$	$Eu^{(III)}$	$Cm^{(III)}$		$Am^{(III)}$
Radius (Å)					0.861	0.900	0.947	0.970		1.115
$Element^{(III)}$ in this work					$Yb^{(III)}$		$Eu^{(III)}$		$La^{(III)}$	
Radius (Å)					0.868		0.947		1.032	
$Element^{(IV)}$ in this work		$Zr^{(IV)}$					$Th^{(IV)}$			
Radius (Å)		0.72					0.94			

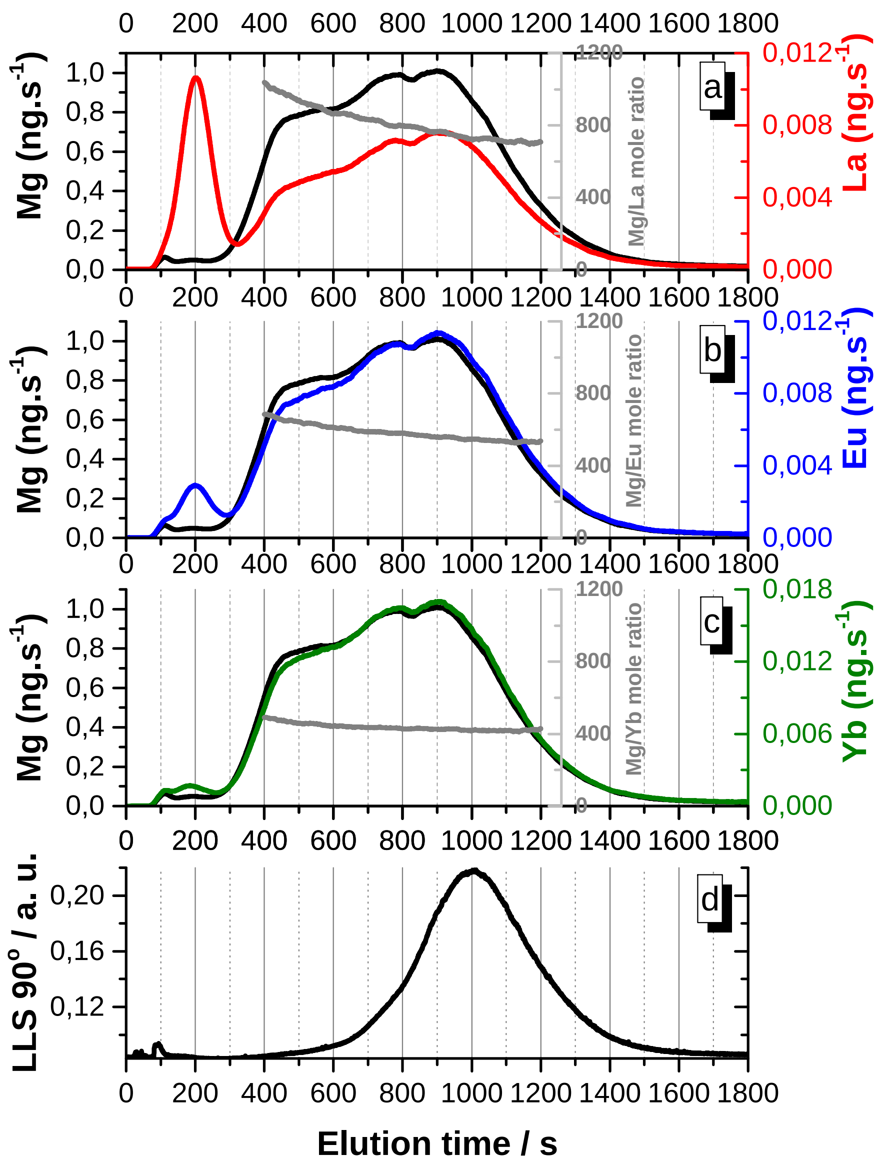
Hectorite co-precipitated in the presence of La, Eu, Yb

- Hectorite NPs can be isolated (Mg)
- Normal mode (LLS)
- Multimodal size distribution (10 -500 nm)



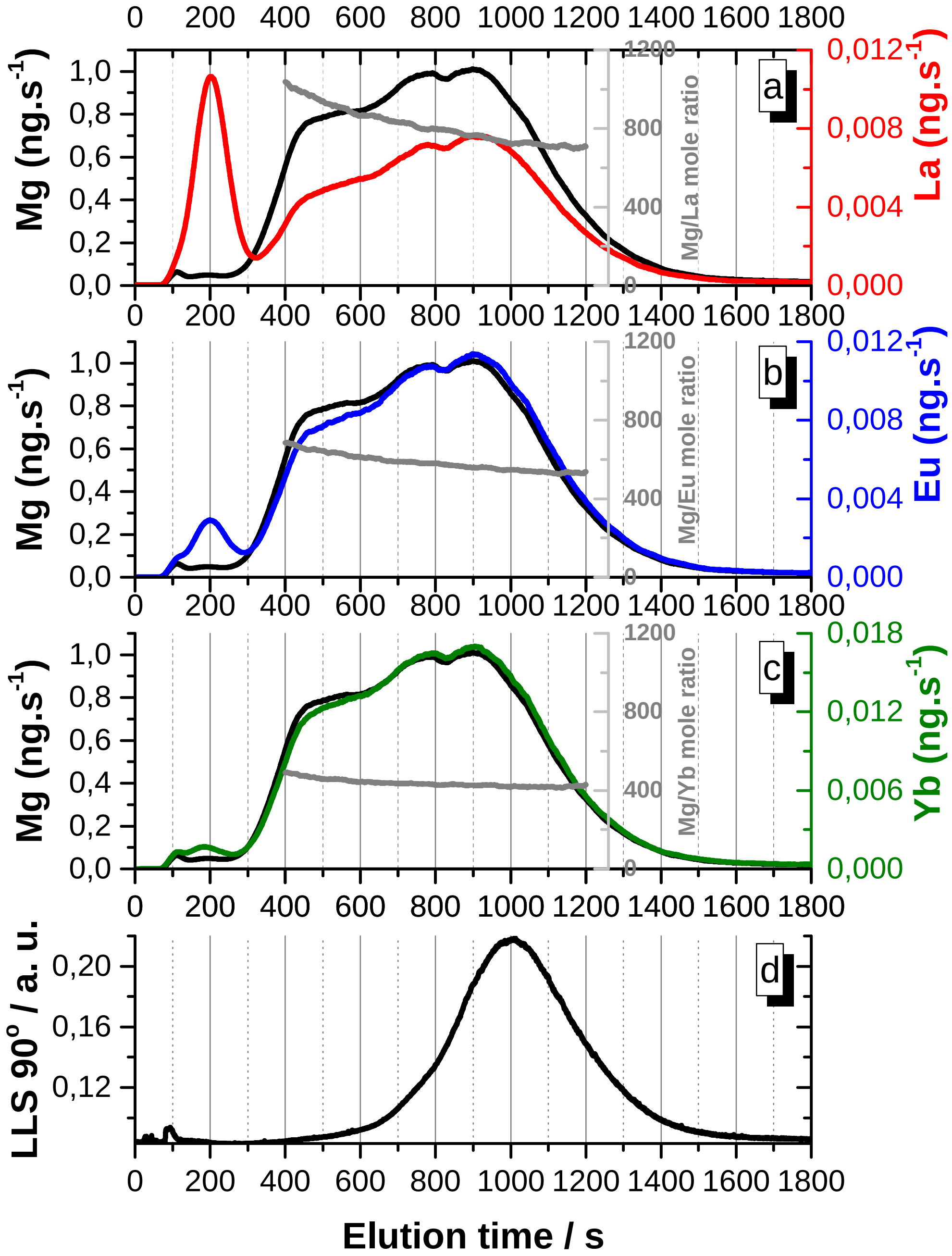
In agreement with literature
(Carrado et al., 1997, Clay Minerals, 32, p29)
and our previous works
(Finck et al. Min.Mag 76(2012), p2723)

Fig: Bouby et al., Chromatography, 2(2015), p545



Hectorite co-precipitated in the presence of La, Eu, Yb

- **Significant increase of the Lns contribution in the NPS sizes < 10 nm (300s) from Yb to La, no Mg**
  - ➢ Exclusion of the larger sized Lns: incompatibility with the hectorite structure
  - ➢ Formation of separate colloidal phases (mixed silica colloids?) during the clay crystallisation
- **In the size range 15 – 500 nm, correlation of the (La, Eu, Yb) fractograms and with the Mg pattern but**
  - ➢ Mg and Yb almost identical, deviation for Eu, much more pronounced for La
  - ➢ Variations apparent in the Mg/M^{n+} molar ratios



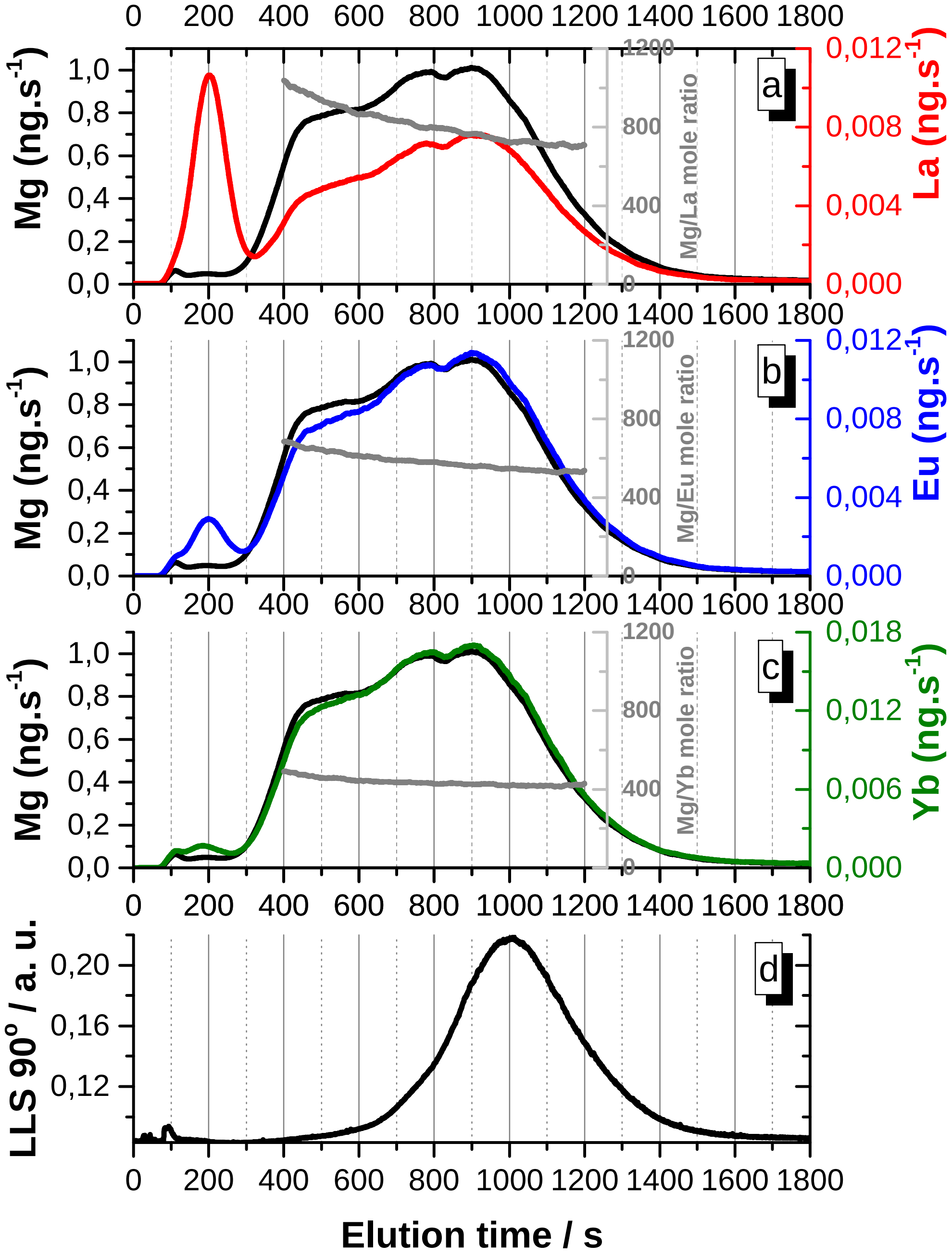
Hectorite co-precipitated in the presence of La, Eu, Yb

3LnCopHec-sup				
	Mg	La	Eu	Yb
Recovery (%) < 300 s	0.40 ± 0.05	7.9 ± 0.1	2.0 ± 0.1	3.8 ± 0.1
Recovery (%) 300 - 1800 s	59 ± 4	45 ± 4	58 ± 4	63 ± 4
Mg/M^{n+} Molar ratio 400-1200 s	-	814 ± 90	584 ± 42	436 ± 19

- Yb : Homogeneous incorporation, in agreement with Lu data
- Eu: Incorporation with a slight preference to larger particles
- La: significant enrichment into hectorite NPs of larger size

=> Preferential incorporation into larger brucite precursor during clay crystallisation: better compensation of the strain and distorsion induced by La substitution for Mg in octahedra

Fig: Bouby et al., Chromatography, 2(2015), p545



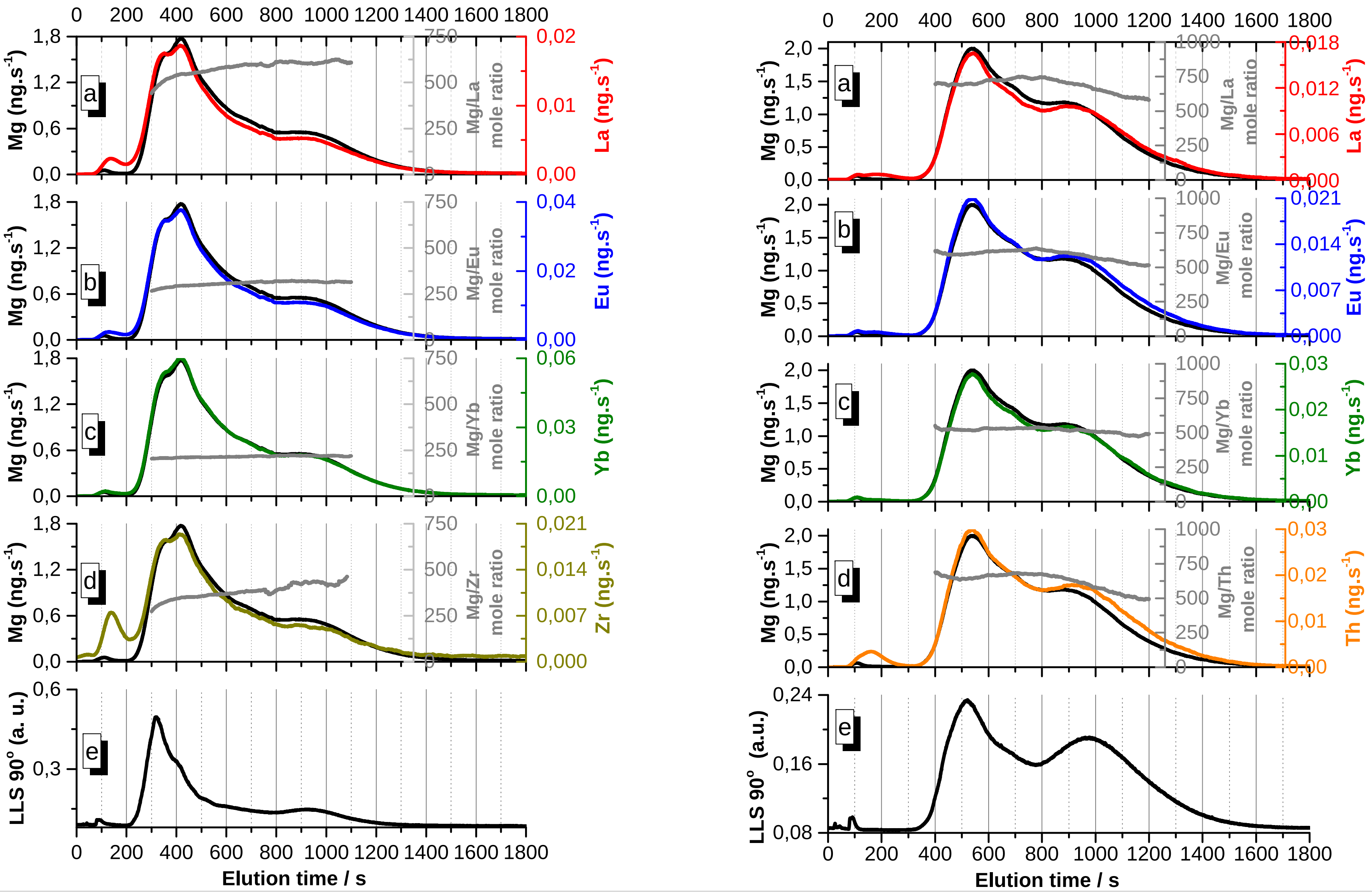
Hectorite co-precipitated in the presence of La, Eu, Yb

- **Adding Ln ions separately or in a mixture apparently does not neither change recovery nor Mg/M^{n+} ratio pattern**
- **Under these experimental conditions, where they are quite diluted, they are incorporated in a highly dispersed way**
- **Clear indication that the Lns incorporation is dependent on their ionic radii**
- **Consistent with the shape of well-known lanthanide pattern found in natural sedimentary clay minerals (Severmann et al., 2004; Uysal et al., 2003; Piper, 1974).**

Bouby et al., Chromatography, 2(2015), p545

Hectorite co-precipitated in the presence of La, Eu, Yb + Zr or Th

Fig: Bouby et al., Chromatography, 2(2015), p545



Conclusions :

- Results identical in the presence of a mixture of several lanthanides ions or in the presence of a single ion
- Apparently the ionic radius of the Ln ion determines the extent of incorporation
- Strain and distorsion appear to be less pronounced for larger particles
- Some tetravalent elements can be incorporated into hectorite NPs

5. Conclusions

- A highly sensitive and powerful analytical technique

- Numerous applications nowadays:
  - food science,
  - pharmaceutical, biomedical, biological and toxicological analysis
  - environmental engineering science, …

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