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INTER NANO

Analysis of engineered inorganic nanoparticles in environmental systems

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Nanoparticle analysis in real-world situations

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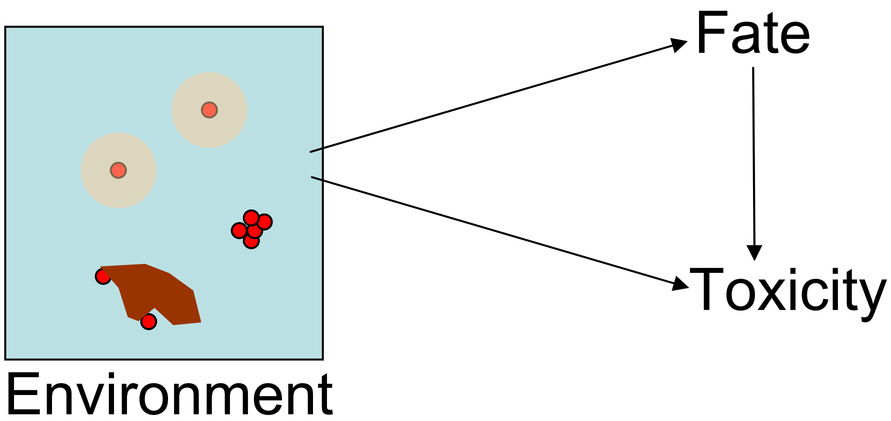


Elemental composition

Size & shape

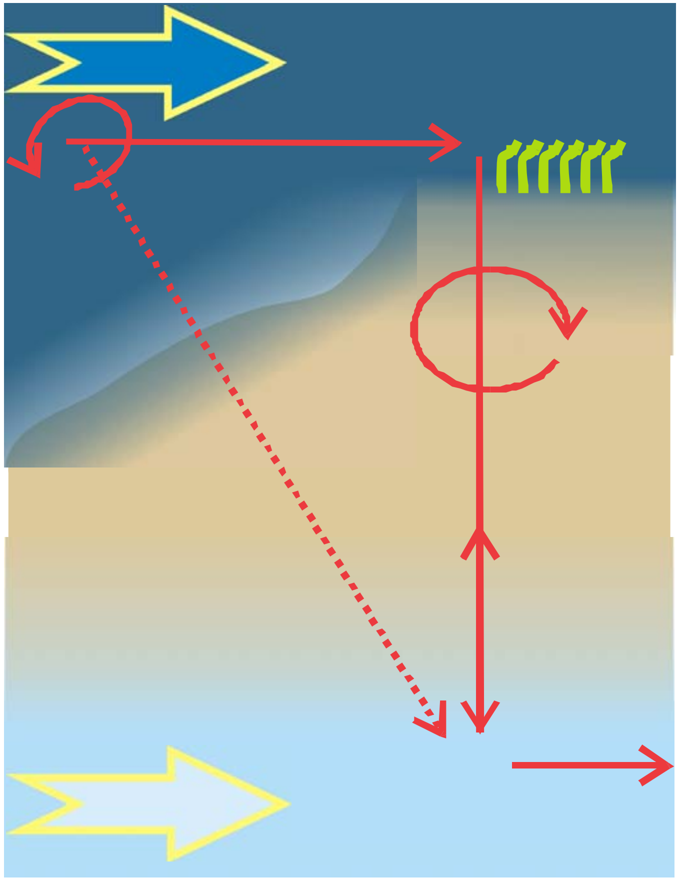
Coating

Aging status

Aggregation status

Matrix & natural colloids

Nanoparticle analysis in real-world situations



- Elemental composition
- Size & shape
- Coating
- Aging status
- Aggregation status
- Dispersibility
- Mobility
- Matrix & natural colloids

Nanoparticle analysis in real-world situations

	Elemental composition
	Size & shape
	Coating
	Aging status
	Aggregation status
	Dispersibility
	Mobility
(Ultra)filtration, (Ultra)centrifugation	Matrix & natural colloids
High performance analytics, enrichment	Low concentration (ppb)

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Direct detection and identification

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- UV/VIS spectroscopy, Fluorescence (Ag, Au, CdTe, TiO2)
- Elemental composition (ICP-MS)
- Oxidation state and structure (XAS: EXAFS, XANES, XRD)
- Composition, properties (Thermal analysis)
- Coating/Interaction with organic materials (SERS, TERS)

Size and shape

Direct methods

- Dynamic light scattering
- Static light scattering techniques
    - Multi angle light scattering, e.g.,
    - Small angle X Ray scattering SAXS

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Small Angle X Ray Scattering (SAXS)

- Static light scattering
- Intensity as function of the scattering vector q

$$q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

$$I(q) \sim P\,S$$

Structural factor
→ Intraparticular interactions
→ Determines I at higher concentrations

Shape factor α
→ Determines I in dilute samples
→ $|\alpha| = 0 \rightarrow$ sphere
$|\alpha| = 1 \rightarrow$ cylinder

Small Angle X Ray Scattering (SAXS)

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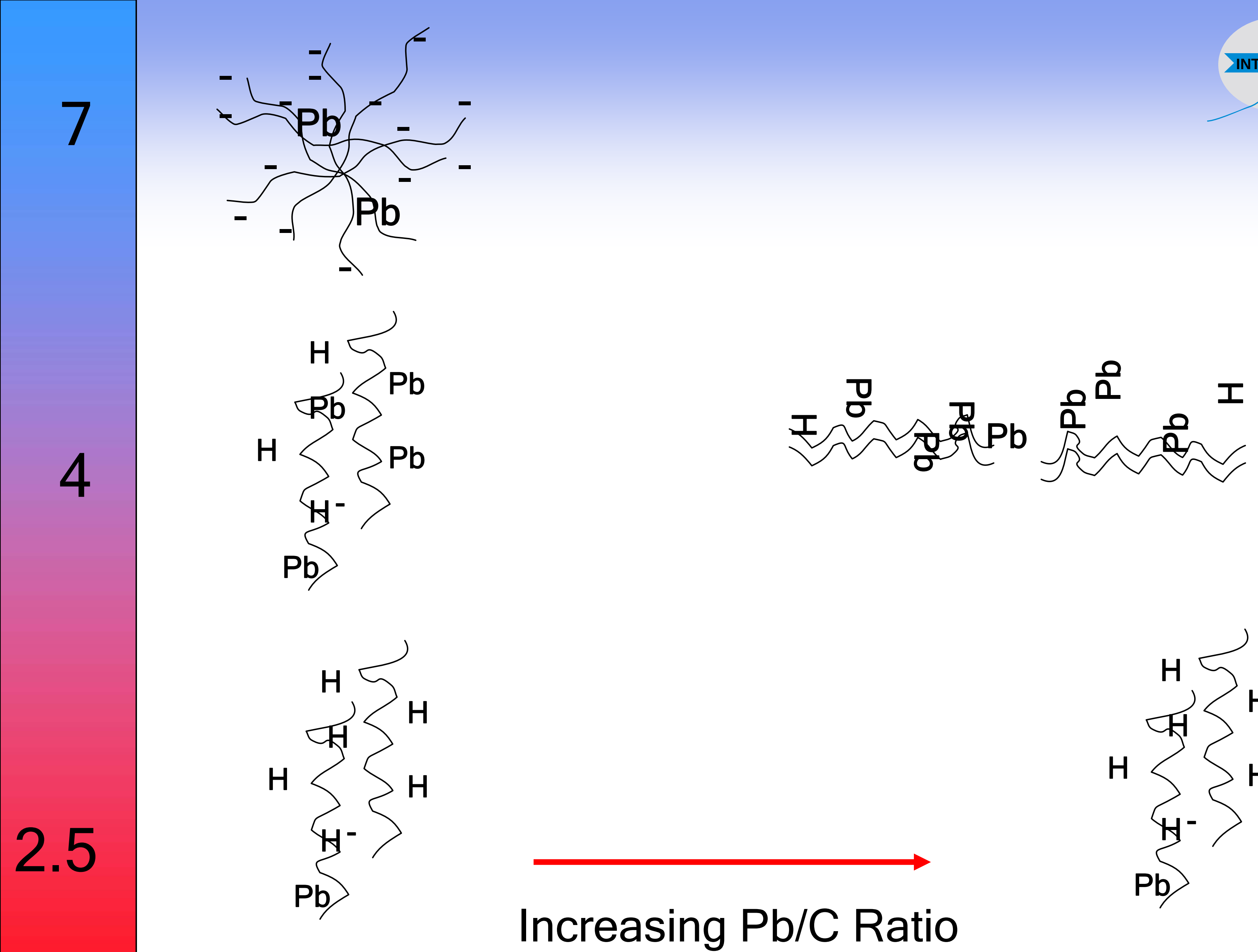
See Figure 1 in:
Lang, F., Egger, H. & Kaupenjohann, M. 2005. Size and shape of lead-organic associations. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **265**, 95-103.
For comparison between the following three types of scattering curves:

Type 1:
α=0.5
High pH, low Pb

Type 2:
α=1
Low pH, high Pb

Type 3:
α=1
pH 4, 0.1 mM Pb
Structural influences



Lang et al. 2005, Colloids & Surfaces A

Small Angle X Ray Scattering (SAXS)

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- Static light scattering
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Structural factor
→ Intraparticular interactions
→ Determines I at higher concentrations

Shape factor
→ Determines I in dilute samples

- Shape analysis if size is known and if background is suitable
- Applied for organic soil colloids (forest floor samples)
- Limited to well-medium defined systems
- Unsuitable for ill-defined systems with high polydispersivity
- High colloid concentration required

Size and shape

Direct methods

- Dynamic light scattering
- Static light scattering techniques
  - Multi angle light scattering, e.g.,
  - Small angle X Ray scattering SAXS
- Nanotracking Analysis
- Laser induced breakdown detection
- PFG-NMR techniques: Diffusion NMR spectroscopy

Diffusion Ordered NMR Spectroscopy

See Figure 5 in:
Simpson, A.J., Kingery, W.L., Spraul, M., Humpfer, E., Dvortsak, P. & Kerssebaum, R. 2001. Separation of Structural Components in Soil Organic Matter by Diffusion Ordered Spectroscopy. *Environmental Science and Technology*, **35**, 4421-4425.

Size and shape

Direct methods

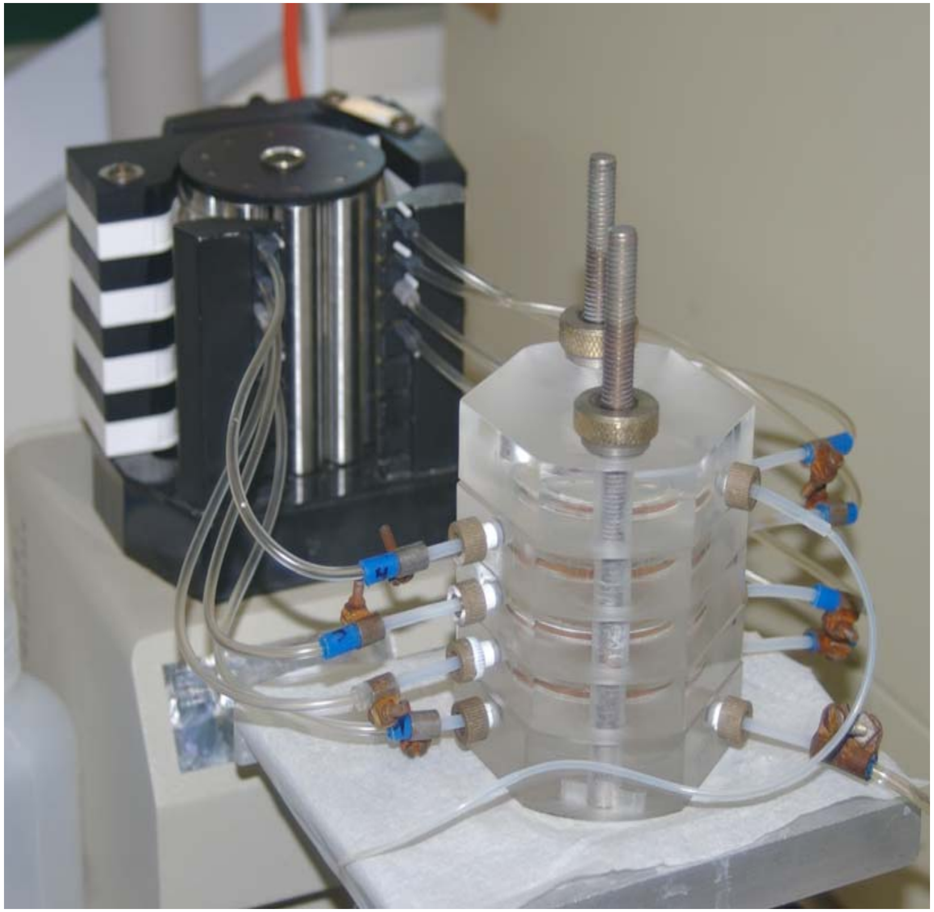
- Dynamic light scattering
- Static light scattering techniques
  - Multi angle light scattering, e.g.,
  - Small angle X Ray scattering SAXS
- Nanotracking Analysis
- Laser induced breakdown detection
- PFG-NMR techniques: Diffusion NMR spectroscopy
  - Organic NPs or inorganic NPs with organic coating
  - Size and structural information
  - High NP concentration required

Separation techniques

- Ultracentrifugation, Ultrafiltration
- Cross flow and tangential flow filtration techniques

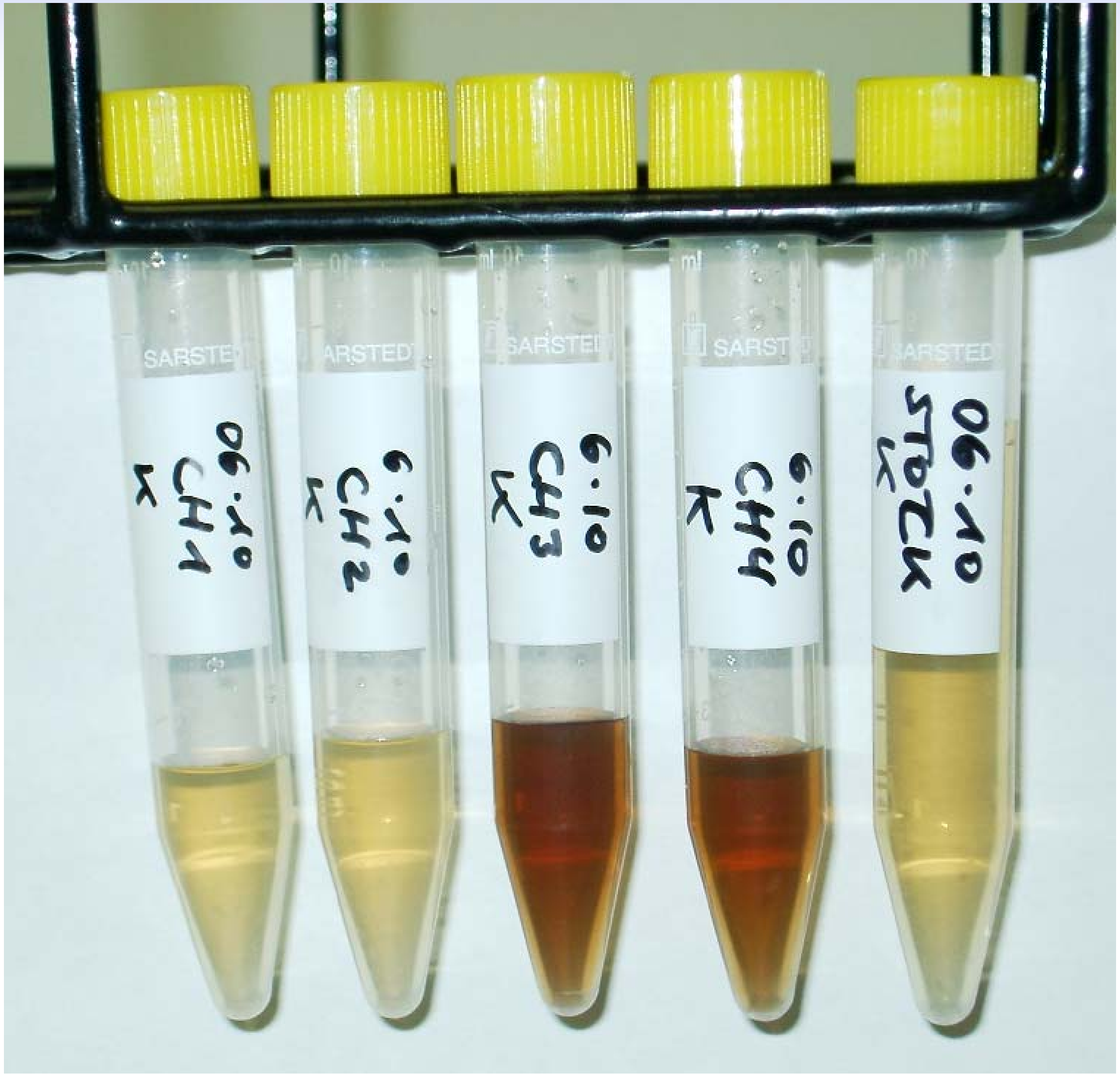
Multistage Tangential Ultrafiltration (MTUF)

- No changes in solution equilibrium
- Reduced adsorption of macromolecules due to selected filter membranes
- Minimal induced coagulation
  - “filter cascade”
  - low pump rates (< 0.1 mL/min)
  - application of tangential flow (range of mL/min)
- Low sample volumes
  - Regulation of duration
  - Requires stable suspensions



Klitzke, PhD thesis, 2007; Klitzke et al, in preparation

Multistage Tangential Ultrafiltration (MTUF)



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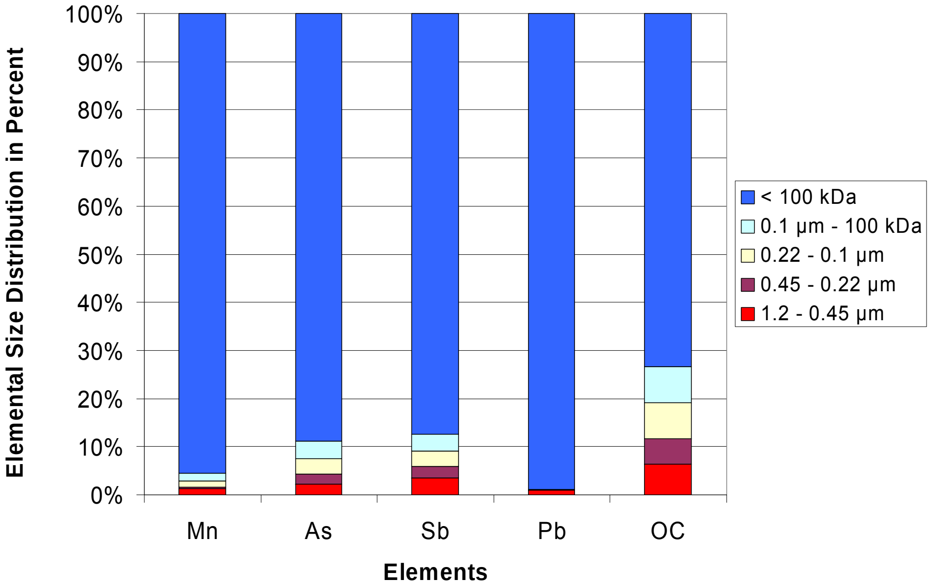

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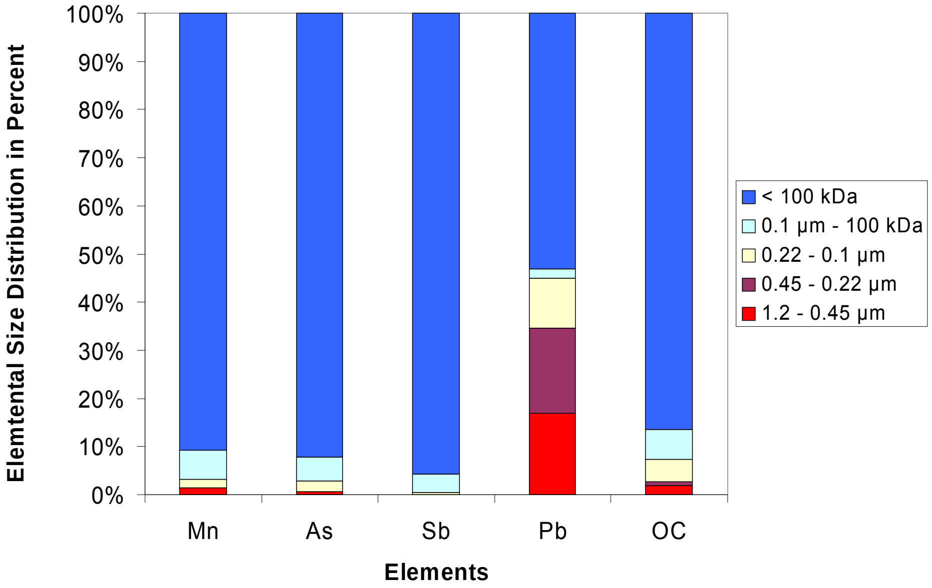

$Ca(OH)_2$

Klitzke, PhD thesis, 2007; Klitzke et al, in preparation

Multistage Tangential Ultrafiltration (MTUF)

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- Low sample volumes
  - Regulation of duration
  - Requires stable suspensions

- Further requirements
  - Minimal sample volume 20-25 mL
  - Fraction size 2-3 mL
  - Suitable for soil suspensions and water samples
  - Sample Preparation: Filtration < 1.2 µm
  - Size range: sub µm … 5 kD
  - Longly particles can interfere

Klitzke, PhD thesis, 2007; Klitzke et al, in preparation

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Separation techniques

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- Ultracentrifugation, Ultrafiltration
- Cross flow and tangential flow filtration techniques
- Size exclusion chromatography (SEC)
- Flow field flow fractionation (FFFF)
- Electrophoresis (CE, GE)
- Hydrodynamic radius chromatography (HDC)

Hydrodynamic radius chromatography

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- Column packed with non-porous beads (15-20 µm)
- Separation via flow velocity and velocity gradient
- Mobile phase: buffer, surfactants etc

Hydrodynamic effect

Electrostatic effect

Figure: see Small, H. & Langhorst, M.A. 1982. Hydrodynamic chromatography. Analytical Chemistry, ***54****, 892A-898A.*

Hydrodynamic radius chromatography

See Figure 3 in
Tiede, K., Boxall, A.B.A., Tiede, D., Tear, S.P., David, H. & Lewis, J. 2009.
A robust size-characterisation methodology for studying nanoparticle behaviour in 'real' environmental samples, using hydrodynamic chromatography coupled to ICP-MS. *Journal of Analytical Atomic Spectrometry*, **24**, 964-972.

Identification via elemental composition

- Requirements
  - Low detection limit
  - Specific for analyte of interest
  - Robust, specific
- Inductively coupled plasma – Mass spectrometry ICP-MS
  - Solid samples
    - → Spatially resolved elemental distribution via laser ablation
    - → Electrothermal vaporisation (ETV)
  - Liquid samples
    - → Nebulizer
  - Ionization in Argon plasma followed by mass spectrometry
  - Detection limit up to low ng/L range
  - Specific for most elements of periodic table
  - Interferences only for some analytes
    - → Physical, chemical, spectrochemical, isobaric overlaps, ionization effects

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ICP-MS: Mass spectrometers

- Quadrupol MS
  - Stable, robust
  - Low MS resolution (≈ 0.7 amu; R 400-700)
  - Intermediate detection limits (ppb-ppt)
- Sector field MS
  - High resolution MS (R > 10 000)
  - Low detection limits (ppt-ppq)
- Time of flight MS
  - Low resolution (R 500-2000), but fast & simultaneous measurement
  - Optimal for laser ablation
- Collision cell / reaction cell technology
  - Reduction of potential interferences via use of additional gases (H_2, CH_4, NH_3, …)
  - Improved performance for Fe, Ca, As and Se

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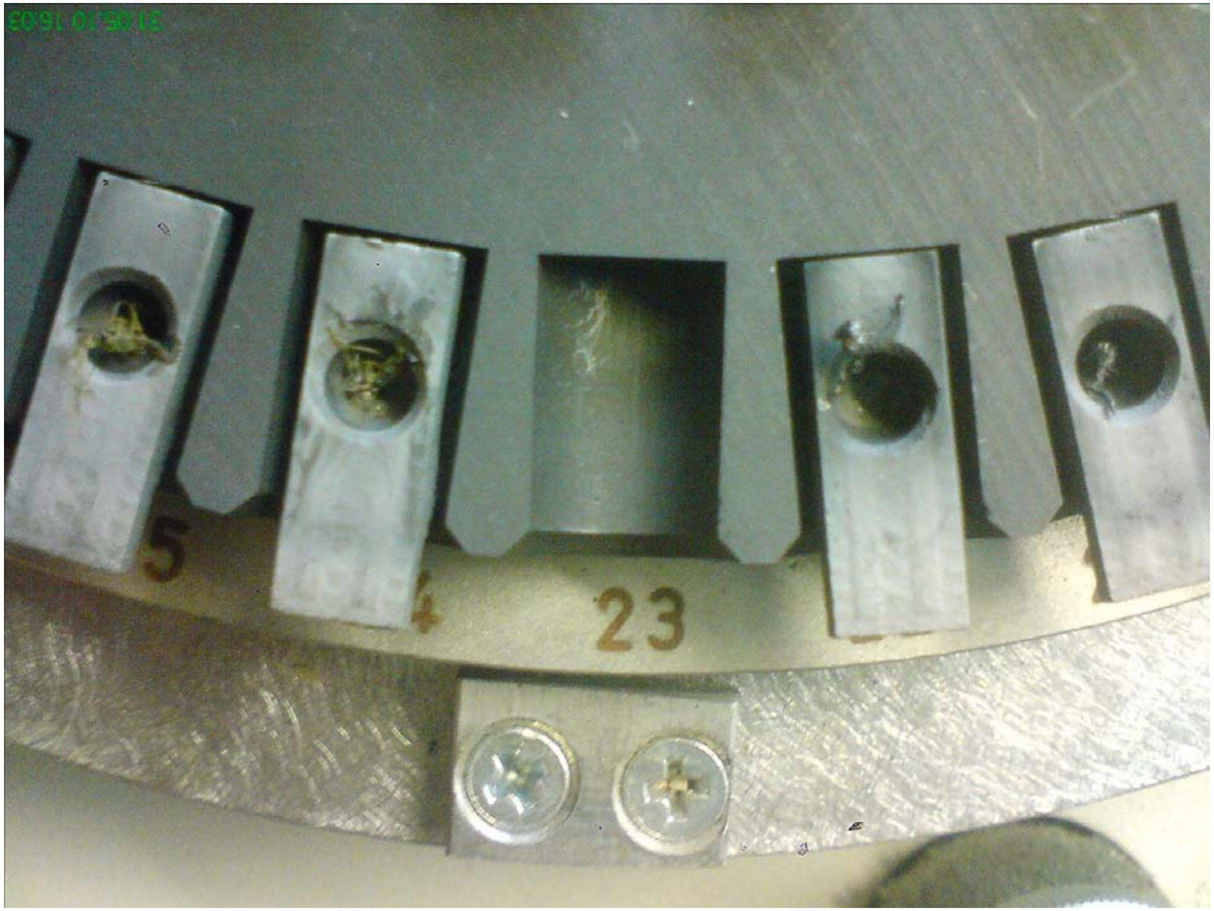
New developments for NP analysis: ETV-ICP-MS

- ETV-ICP-MS to quantify inorganic nanoparticles in complex environmental matrices
  - Graphite furnace electrothermal vaporization – ICP MS
  - Use of Freon 12 or 14 to avoid carbide formation
- Features
  - Direct analysis of nanoparticle suspensions showing broad size distributions
  - Measurement of single invertebrates or tissues of selected organs
  - Leaves or leaf parts of whole plants
  - Elemental analysis of samples investigated by, e.g., AFM
  - Temperature programme 500 °C – 2200 °C
  - Recovery 80%-116% in reference materials

Duester et al. (2010), Journal of Analytical Atomic Spectrometry

New developments for NP analysis

- ETV-ICP-MS to quantify inorganic nanoparticles in complex environmental matrices



Direct analysis of leaf discs and biological materials

See Figure 3 & Title Figure in
Duester, L., Rakcheev D., Bayer, J.V., Abraham P.M., Dabrunz A., Schulz, R. & Schaumann, G.E. 2010. A robust, particle size independent, method for quantifying metal(loid oxide) nanoparticles and their agglomerates in complex environmental matrices by electrothermal vaporisation coupled to ICP-MS. *Journal of Analytical Atomic Spectrometry*, DOI:10.1039/C0JA00149J.

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ETV-ICP-MS

ETV-ICP-MS is useful if:

- only a very small amount of sample is available
- the preparation (e.g. digestion) causes artefacts
- trace amounts of analytes in digestion resistant materials are detected (e.g. contamination of graphite or ceramics)
- wet aerosols cause interferences
- an indirect spatial resolution is needed

Duester et al. (2010), Journal of Analytical Atomic Spectrometry

New developments for NP analysis: HDC-ICP-MS

- HDC coupled to ICP-MS
- Applied to analyse sewage sludge
- Direct application of sample without filtration
- Au nanoparticles suggested as size standards
  - Steric stabilization required
    when used as internal standard
    in high ionic strength samples

Tiede et al. 2009 and 2010, Journal of Analytical Atomic Spectrometry

New developments for NP analysis: HDC-ICP-MS

See Figure 3 in
Tiede, K., Boxall, A.B.A., Tiede, D., Tear, S.P., David, H. & Lewis, J. 2009. A robust size-characterisation methodology for studying nanoparticle behaviour in 'real' environmental samples, using hydrodynamic chromatography coupled to ICP-MS. *Journal of Analytical Atomic Spectrometry*, **24**, 964-972.

See Fig. 2 in
Tiede, K., Boxall, A.B.A., Wang, X.M., Gore, D., Tiede, D., Baxter, M., David, H., Tear, S.P. & Lewis, J. 2010. Application of hydrodynamic chromatography-ICP-MS to investigate the fate of silver nanoparticles in activated sludge. *Journal of Analytical Atomic Spectrometry*, **25**, 1149-1154.

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Thank you

INTER NANO

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