Department of Environmental Geosciences

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Sustainable Nanotechnologies Project

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Single particle ICPMS based methods for tracking environmental leaching of nanoparticles from consumer products

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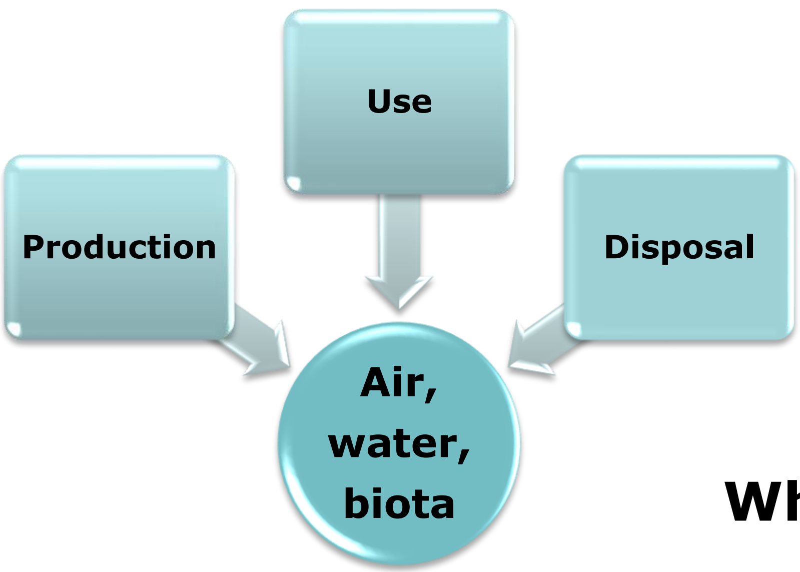
Introduction

- Need to screen for nanomaterials that raise environmental and toxicological concerns

- Nanomaterials produced in high volumes: TiO_2, ZnO, CuO, CeO_2, SiO_2, NiO_2, Al_2O_3, Fe_2O_3

- Nanoproduct lifecycle



Risk of environmental release and subsequent human exposure

What, how much, at which rate?

Release testing of ENM

- High demands on the analytical methods

- Not all fit for release testing (DLS, NTA, TEM)

- Challenges for analysis at relevant exposure and release concentration levels (ng/L)

Single particle ICPMS:

✧ **Quantification tool for release (ng/L)**
✧ **Element specific particle counter (p#/L)**

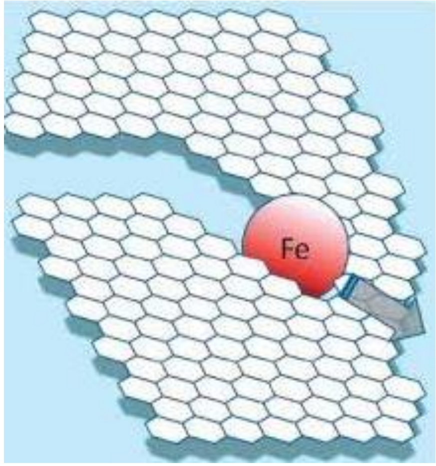
- spICPMS analysis difficult for metal oxide nanoparticles

- Several naturally abundant isotopes, interfered masses

Limitations of spICPMS

- **Size detection limit:**
Instrumental background
Presence of the dissolved ions

- **Particle number detection limit:**
Deviations in nebulisations efficiency
Counting statistics (false positive spikes)



spICPMS method optimisation for Fe, Cu and Ti based nanoparticles

application of these methods to investigate release from consumer products into environment

CHALLENGE 1: Iron oxides nanoparticles

α, β, γ, ε - Fe_2O_3, Fe_3O_4, FeO

Industrial, environmental, medicine application

Isotope	Abundance (%)
^{54}Fe	5.845
^{56}Fe	**91.754**
^{57}Fe	2.119
^{58}Fe	0.282

^{56}Fe: Highest instrumental sensitivity

1st IP: 7.90eV
Easily ionised in argon plasma

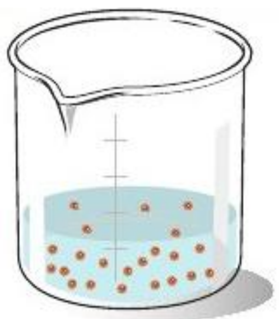
Plasma based interference: ^{56}Fe ($^{40}Ar^{16}O^+$), ^{57}Fe ($^{40}Ar^{16}OH^+$)

Matrix based interference: ^{56}Fe ($^{40}Ca^{16}O^+$), ^{57}Fe ($^{40}Ca^{16}OH^+$)

Isobaric interference: ^{54}Fe (Cr), ^{58}Fe (Ni)

source: www.webelements.com

CHALLENGE 2: Copper oxides nanoparticles



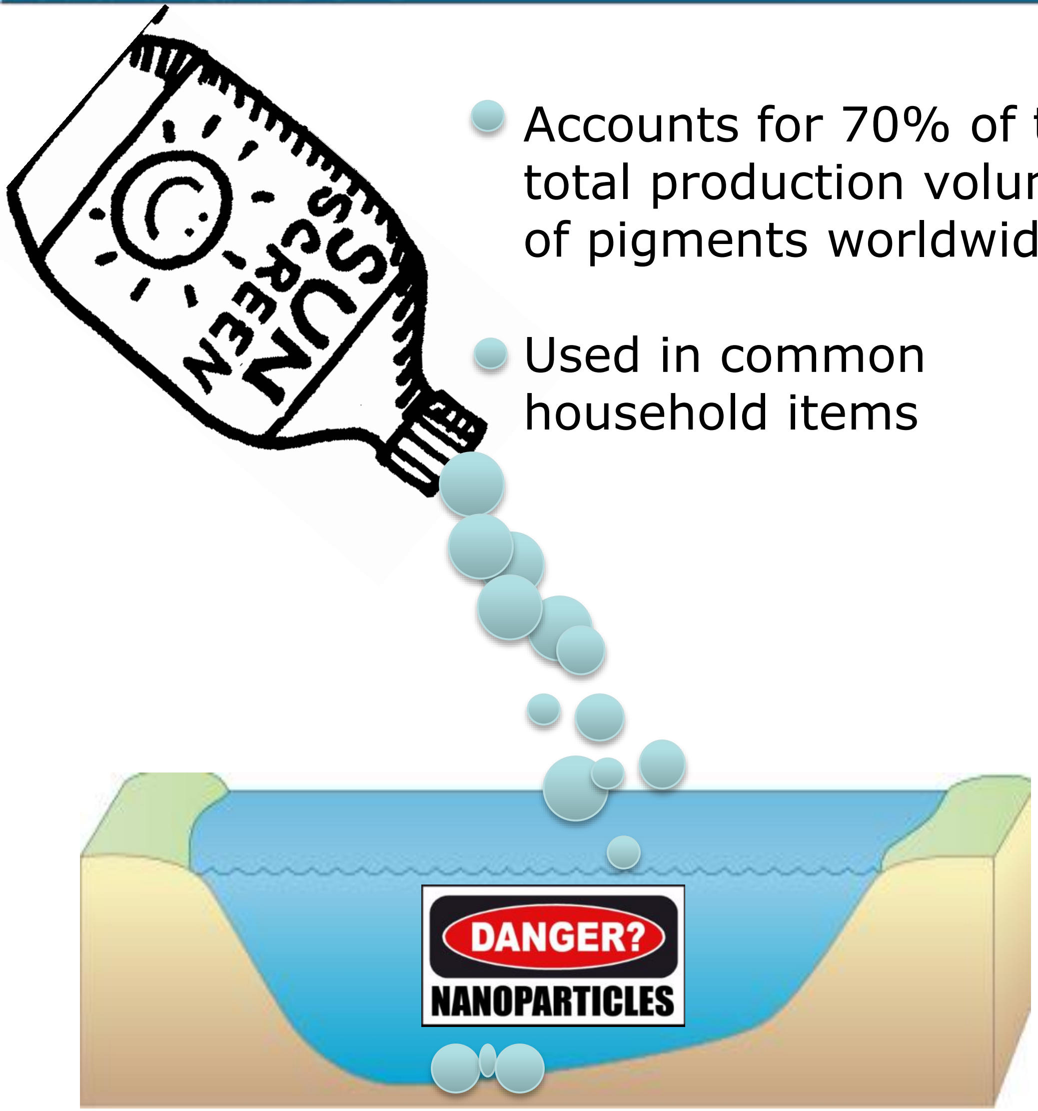
Antifouling paints for boats

Contamination of aquatic ecosystem

Isotope	Abundance (%)
^{63}Cu	69.17
^{65}Cu	30.83

Matrix based interference $^{40}Ar^{23}Na$ (m/z=62.95)

CHALLENGE 3: Titanium dioxides nanoparticles



- Accounts for 70% of the total production volume of pigments worldwide
- Used in common household items

$[Ti] < 1$ ppb

^{46}Ti	8.0%
^{47}Ti	7.3%
^{48}Ti	73.8%
^{49}Ti	5.5%
^{50}Ti	5.4%

$[Ca] \approx 40{,}000$ ppb

^{40}Ca	96.941%
^{42}Ca	0.647%
^{43}Ca	0.135%
^{44}Ca	2.086%
^{46}Ca	0.004%
^{48}Ca	0.187%

Several polyatomic interferences: $^{32}S^{16}O^{+}$

Pure isobaric interference

Problem in natural water samples

Agilent 8800 ICP MS/MS

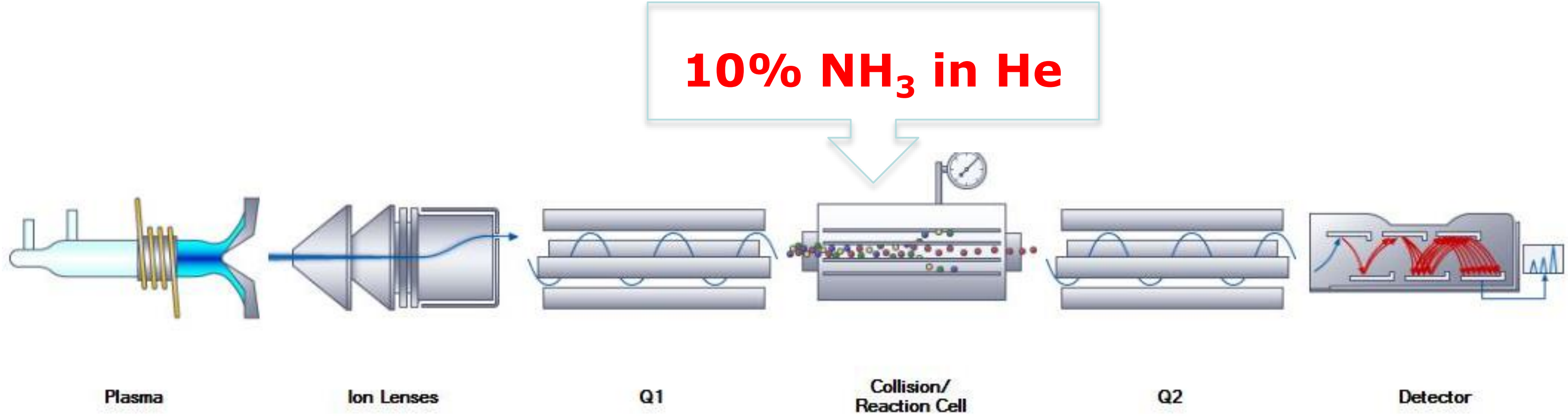
ft mode:
n has a higher
the precursor
shift)

S allows the
of these
reaction products

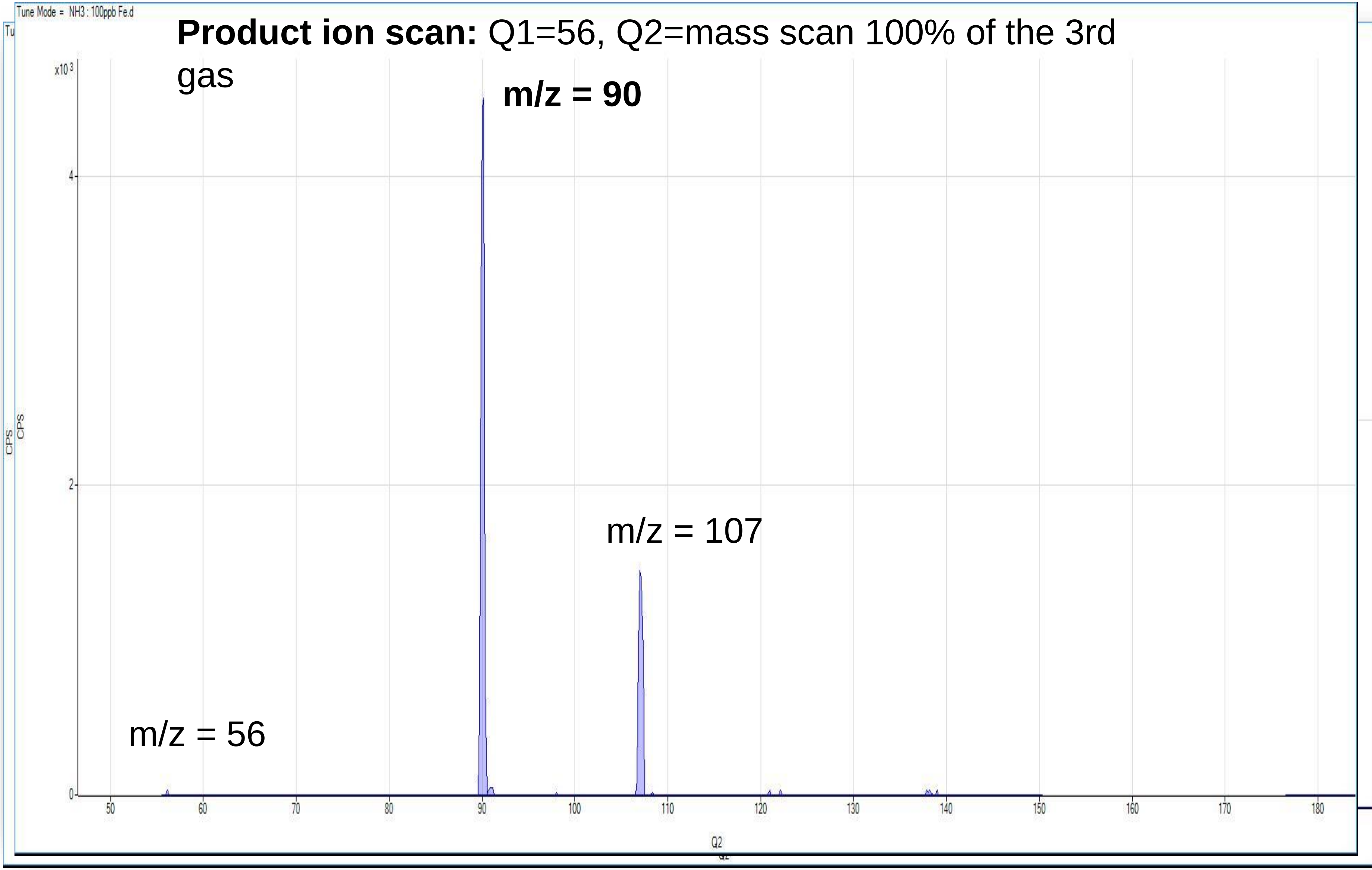
Removal of the interferences on ^{56}Fe

NH_3 as a reaction gas and clustering ligand:
$[Fe(NH_3)_x]^+$ $x = 1 – 4$

<u>Scan for the reaction products</u>
Q1 prefilter, set to m/z 56 (precursor ion)
Q2 scan for product ion which is interference free



Reaction profile of the clustering reaction



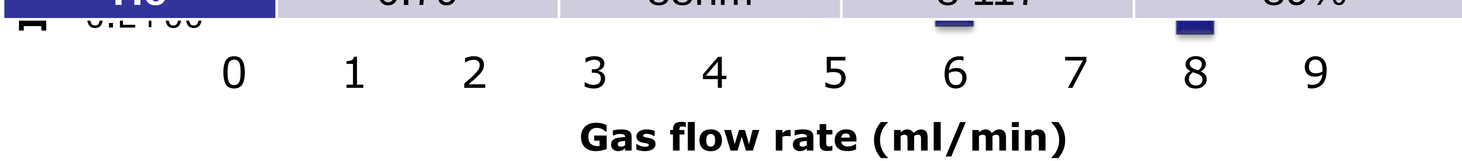
Removal of the interferences using He and H_2

H_2 and He gas flow optimisation

- He: collision gas, reduces instrumental sensitivity
- H_2: effective to eliminate argon interferences
  $ArO^+ + H_2 \rightarrow ArOH^+$

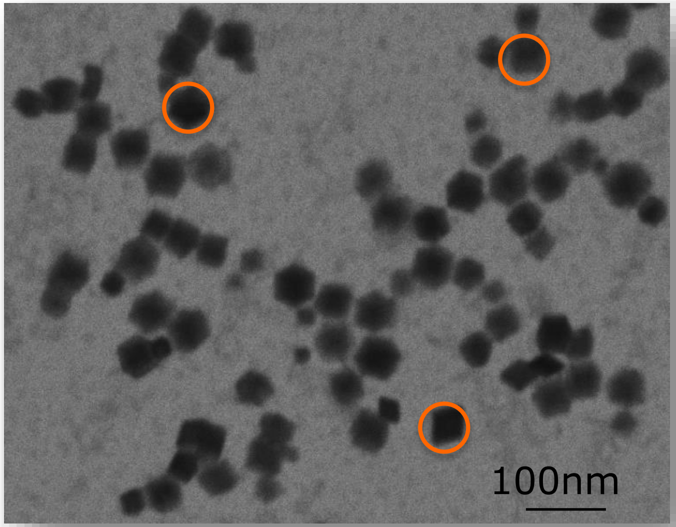
Influence of He and H_2 on intensity of ^{56}Fe (10ppb ionic Fe std.)

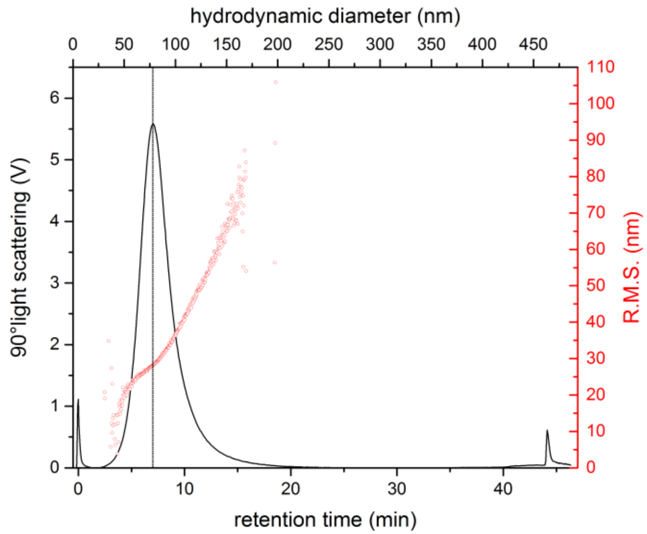
Gas	Detection limit (µg/L)	Size detection limit (nm)	Sensitivity (cps/µgL^{-1})	Accuracy (CRM NIST)
60% NH_3	0.62	114nm	10 884	102%
H_2	0.05-0.08	47-54nm	88 319	99%
He	0.79	88nm	8 117	89%

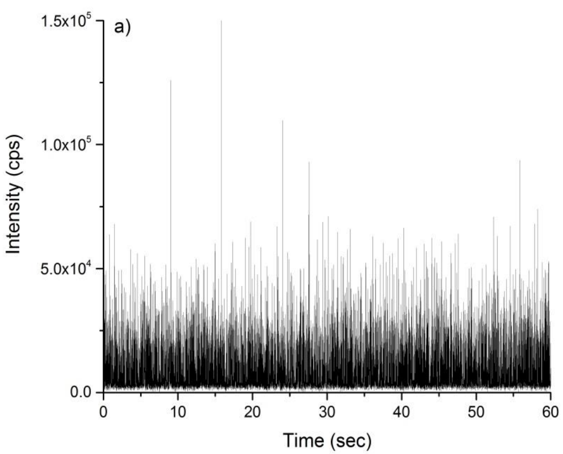


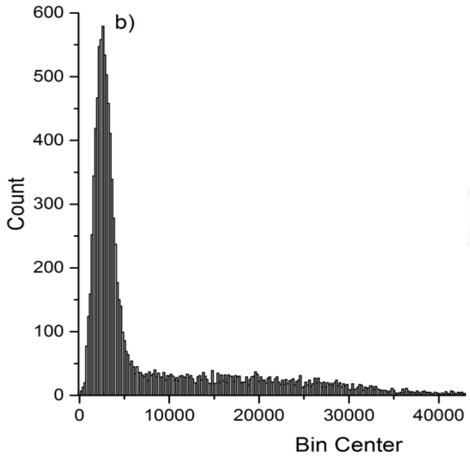
spICPMS of in house synthesised hematite nanoparticles

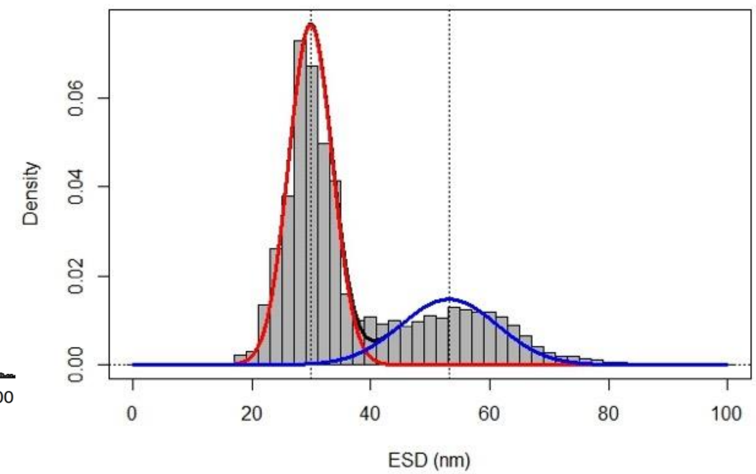
DLS: 66 ±1nm











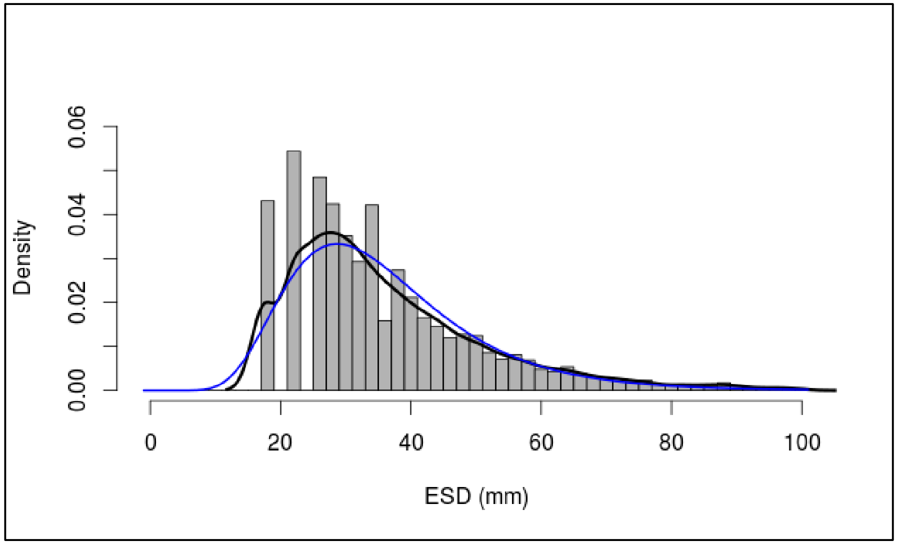
spICPMS on CuO dispersion

Method optimised on the ionic Cu standard
Estimated SDL 15nm (ESD)

Applied on the dispersion of commercial CuO nanopowder in DIW
Problem with sample sedimentation

DLS: 203nm (PDI=0.4)

Experimental conditions	
Instrument	Agilent 8800
Nebulizer	Micromist
Isotope monitored	^{63}Cu
Integration time	5 ms
Sample flow rate	390 µl min^{-1}
Acquisition time	60 sec
Cell gas/ flow rate	He/5 ml min^{-1}



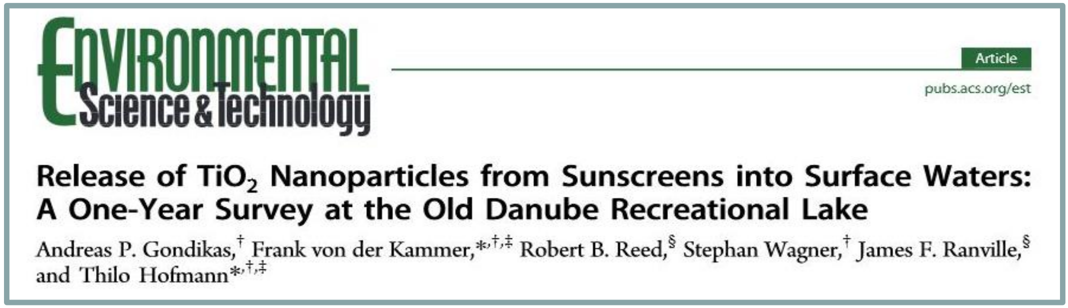
spICPMS analysis of TiO_2 in surface water

spICPMS optimised on Ti ionic standard

m/z = 63 (TiNH)

Calculated SDL 50nm

Application


Environmental Science & Technology

Article

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Release of TiO_2 Nanoparticles from Sunscreens into Surface Waters: A One-Year Survey at the Old Danube Recreational Lake

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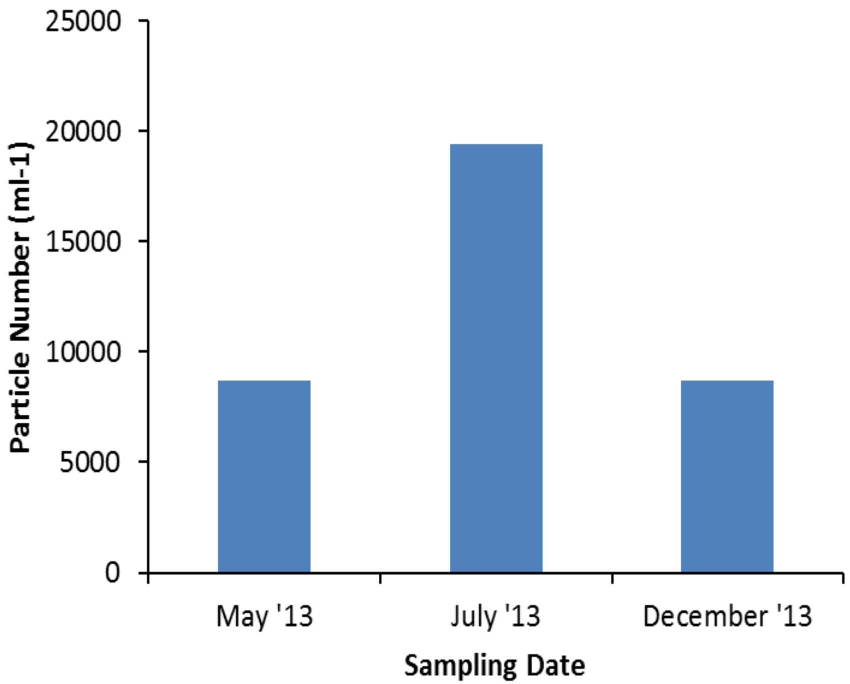

Seasonal increase of TiO_2 particles in Old Danube Lake (Vienna, Austria)

Conclusions and outlook

- spICPMS methods optimised for Fe, Cu, Ti based nanoparticles
- SDL for their oxide form: 40, 15, 50nm (ESD)
- Application of the methods on the release studies
- Robustness of the methods in real environmental media (different water chemistry)

Acknowledgements

Frank

SUN

Sustainable Nanotechnologies Project

Andreas

Stephan

MARINA

MANAGING RISKS OF NANOMATERIALS

SEVENTH FRAMEWORK PROGRAMME

This project is funded by the EU 7th Framework Programme, contract no. 604305

http://www.sun-fp7.eu/

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