Interlaboratory comparison study on AuNPs

WG 2 – Analytical Toolbox
COST Action ES1205 – ENTER

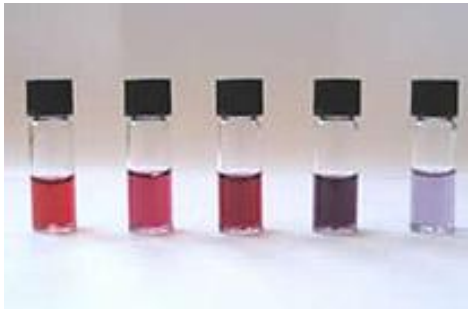
in cooperation with

NORMAN WG4 Engineered Nanomaterials

WG4 - Engineered Nanomaterials

Tasks

- 5 AuNPs samples were distributed
    * three monodmodal samples
    * two mixtures
    * one blank



- tasks:
    * determination of particle sizes / concentration
    * determination of total Au concentration
    * based on of EU definition: nano – yes/no?!

Thanks to NORMAN for funding

Attendees

 # 1 - Tommaso Serchi & Sebastien Cambier
CRP Gabriel Lippmann – Luxembourg

 # 2 - Geert Cornelis
Gothenburg University – Sweden

 # 3 - Irena Ciglenečki – Jušić & Marija Marguš
Institute Ruđer Bošković – Croatia

 # 4 - Allan Philippe
Institute for environmental sciences, University of Koblenz/Landau – Germany

 # 5 - Thomas Bucheli & Alexander Gogos
Institut Agroscope – Switzerland

 # 6 - Frank v.d. Kammer & Stephan Wagner
University of Vienna – Austria

 # 7 - Martin Tröster
DVGW-Technologiezentrum Wasser (TZW) – Germany

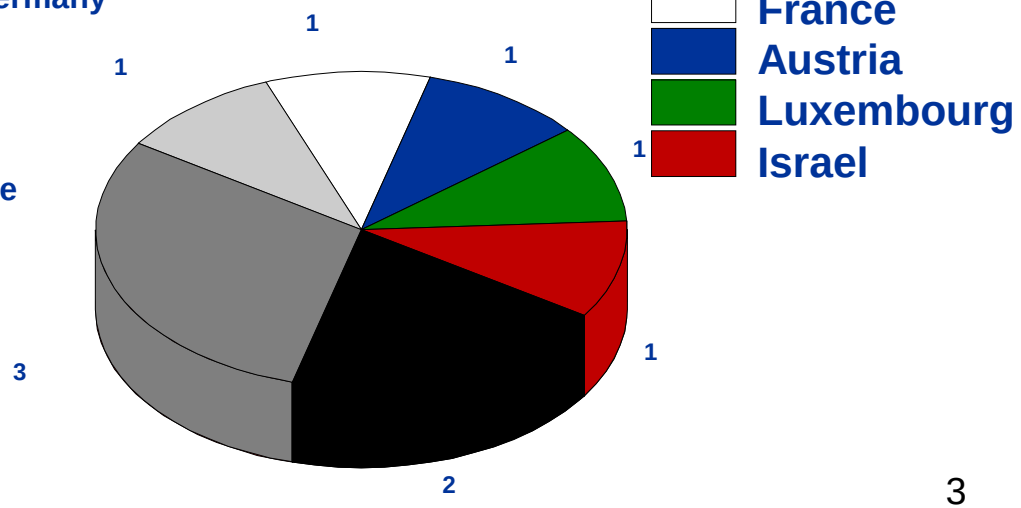
 # 8 - Ralf Kaegi
Eawag – Switzerland

 # 9 - Mickaël Tharaud & Yann Sivry
Institut de Physique du Globe de Paris – France

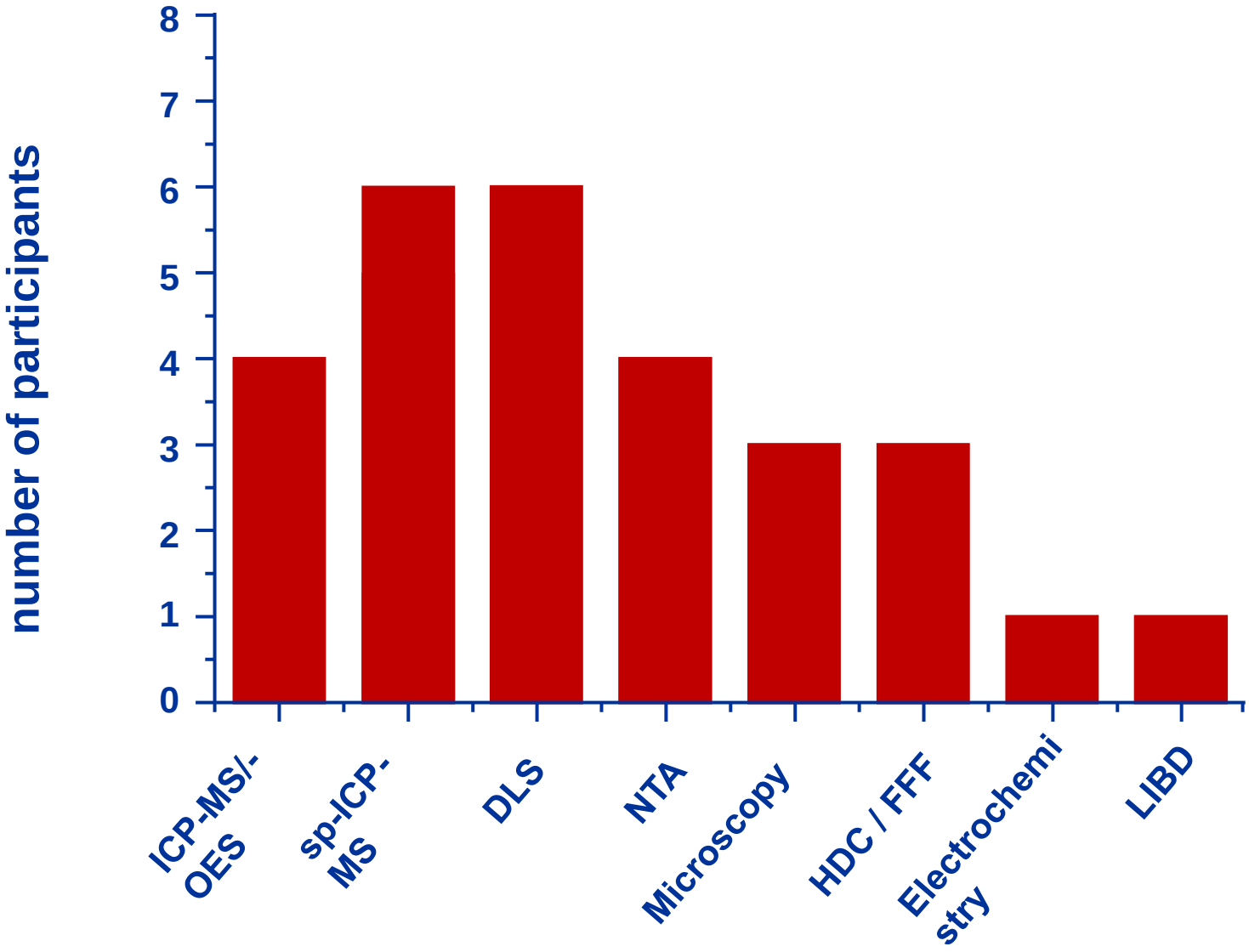
 # 10 - Ilit Cohen-Ofri
Institute of Science – Israel

 # 11 - Rute Isabel Ferreira Domingos
Instituto Superior Tecnico – Portugal

 # 12 - Björn Meermann
Federal Institute of Hydrology – Germany#



Overview – techniques deployed



Standards and Samples

- Standards

  * Au NP standards from BBI (UK)

    Thanks to NORMAN for funding

  * three different sizes

  * supplier information:

Material	D [nm]	V_{Std} [L]	d[nm]1)	c [#/mL]1)	c [mg Au/L] 1)
Au in citrate	10	1.0	9.5	5.7×10^{12}	57.6
Au in citrate	50	1.0	49.8	4.5×10^{10}	56.8
Au in citrate	250	1.0	253.5	3.6×10^{8}	56.8

1) No information on measurement method applied by supplier

Standards and Samples

- pre-treatment
  - * Shaking
- flasks and vials
  - * New, unused and cleaned 0.5 L and 1 L borosilicate glass flasks
  - * New, unused and cleaned 20 mL borosilicate glass vials
- **monodisperse** samples (samples 1 - 3)
  - * Standards “as obtained”

Sample Nr.	Nominal Size [nm]	Concentration [particles/mL]	Concentration [mg Au/L]
1	250	3.6×10^{8}	56.8
2	50	4.50×10^{10}	56.8
3	10	5.70×10^{12}	57.6

Standards and Samples

- Polymodal samples (samples 4 + 5)

  * Mixtures of different size standards

Sample 4					
	Nom. Size [nm]	**Vol. Fraction**	**Conc. in mix. [particles/mL]**	**Part-fract. in mix. [nr-%]**	**Conc. in mix. [mg Au/L]**
Standard 10 nm	10	0.3	1.71×10^{12}	98.7	17.28
Standard 50 nm	50	0.5	2.25×10^{10}	1.3	28.4
Standard 250 nm	250	0.2	7.20×10^{07}	0.004	11.36
Total			1.73×10^{12}		57.04

➔ Nanomaterial

Sample 5					
	Nom. Size [nm]	**Vol. Fraction**	**Conc. in mix. [particles/mL]**	**Part-fract. in mix. [nr-%]**	**Conc. in mix. [mg Au/L]**
Standard 10 nm	10	0.0	0	0	0
Standard 50 nm	50	0.05	2.25×10^{9}	86.8	2.84
Standard 250 nm	250	0.95	3.42×10^{8}	13.2	53.96
Total			2.59×10^{9}		56.8

➔ Nanomaterial

- Blank (milliQ) (sample 6)

Results - NTA

	Ref		1		4		11		12	
No.	#/mL	d [nm]	#/mL	d [nm]	#/mL	d [nm]	#/mL	d [nm]	#/mL	d [nm]
1	3.6×10^{8}	250	**$4.50E^{8}$**	**243**	$2.81E^{8}$	242	Agg.	Nd	$1.26E^{9}$	274
2	4.50×10^{10}	50	**$3.31E^{11}$**	**47**	$6.16E^{10}$	54	$1.00E^{11}$	49 99	$2.41E^{10}$	63
3	5.70×10^{12}	10	**$2.30E^{8}$**	**48**	$3.22E^{8}$	114	$1.60E^{10}$	104 180	$1.20E^{9}$	96
4	1.71×10^{12} 2.25×10^{10} 7.20×10^{07}	10 50 250	**$1.69E^{11}$**	**46 100 /200**	$6.83E^{10}$	50	$5.60E^{10}$	51 100	$7.14E^{8}$	60
5	2.25×10^{9} 3.42×10^{8}	50 250	**$1.76E^{10}$**	**48 200/300**	$3.77E^{9}$	240	$3.70E^{10}$	102 186	$2.30E^{8}$	259

Monomodal: ok, but size DL > 10 (Au)
Polymodal: poor

Results – sp-ICP-MS I

	Ref		2		4		6		7	
No	**#/mL**	**d [nm]**	**#/mL**	**d [nm]**	**#/mL**	**d [nm]**	**#/mL**	**d [nm]**	**#/mL**	**d [nm]**
1	3.6×10^{8}	250	**$1.25E^{6}$**	**45**	-	271	$1.40E^{8}$	322	**$1.40E^{8}$**	**271**
2	4.50×10^{10}	50	**$1.13E^{12}$**	**47**	-	49	$4.40E^{10}$	58	**$5.20E^{10}$**	**48**
3	5.70×10^{12}	10	**$5.01E^{11}$**	**11**	-	46	$1.60E^{11}$	27	**Nd**	**Nd**
4	1.71×10^{12} 2.25×10^{10} 7.20×10^{07}	10 50 250	**$9.76E^{11}$**	**13** **47**	-	40	$4.85E^{9}$ $1.74E^{10}$	32/60	$9.6E^{10}$/ $2.2E^{10}$/ $3.80E^{7}$	22/48/ 260
5	2.25×10^{9} 3.42×10^{8}	50 250	**$6.13E^{9}$**	**45** **60**	-	60	$4.10E^{9}$ $1.40E^{9}$ $4.9E^{8}$	27 60 315	$4.8E^{8}$/ $1.9E^{9}$/ $1.5E^{8}$	29/47/ 257

… depends on the instrument

Results – overview

Results – general overview

Method	NTA; N=4		sp-ICP-MS; N=6		DLS; N=6		AFM/TEM; N=3	
Sample	average Part/mL Size [nm]	RSD [%]	average Part/mL Size [nm]	RSD [%]	average Size [nm]	RSD [%]	average Size [nm]	RSD [%]
1	$6.63E^{8}$ **253**	79 7	1.68E11 **201**	223 60	**300**	56	**273**	11
2	$1.29E^{11}$ **55**	107 14	7.63E13 **49**	223 9	**45**	19	**48**	8
3	$4.44E^{9}$ **86**	174 39	4E15 **25**	173 63	**12**	25	**9**	13
4	$7.34E^{10}$ 55	95 12	Nd	Nd	52	32	Nd	Nd
5	$1.46E^{10}$ 250	114 5	Nd	Nd	247	23	Nd	Nd
6	Blank	Blank	Blank	Blank	Blank	Blank	Blank	Blank

Conclusions

- NTA, DLS good comparability for monodisperse samples (size);
  polydisperse samples not all fractions detectable (known issue)
- sp-ICP-MS in general good comparability (size; number concentration at least same order of magnitude)
  but: strong dependency on instruments
- AFM, TEM comparable results for monodisperse samples (size)
  but: polydisperse samples strongly influenced by sample preparation; number concentration difficult to achieve
- AF4, HDC good agreement for monodisperse as well as polydisperse samples
  but: determination of number concentration laborious

‘Micro-’ meets ‘Nano-’ particles: ‘Inclusion’ of the Microplastics into the WG4

Microplastic and Nanoparticles are both particulate ‘contaminants’ and thus require tailored sample preparation protocols to preserve the particle size / number (mass is conservative, number not!)

The (quantitative) analytics is very challenging in complex matrices (sewage sludge, sediments) and not routinely established

First joint MP-NP-activities:

SETAC 2016: Session: Detection, identification and quantification of engineered (nano)materials in complex matrices

Patrick Bäuerlein (KWR), Ralf Kaegi (Eawag)

This session aims to integrate contributions focussing on latest developments for **nanoparticle and microplastics** analysis including explicitly sample preparation techniques…