IBA in SIAM

NFFA And Nanosafety Workshop

Jorge Mejia & Julien Colaux

January the 9th, 2020

SIAM

Synthesis Irradiation & Analysis of Materials

UNIVERSITÉ DE NAMUR

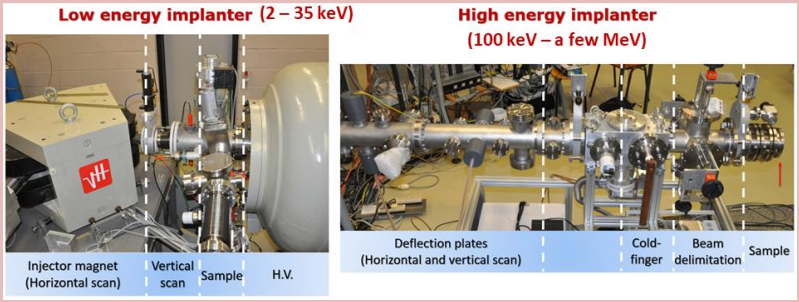
SIAM Platform - unique facilities

Plasma treatment

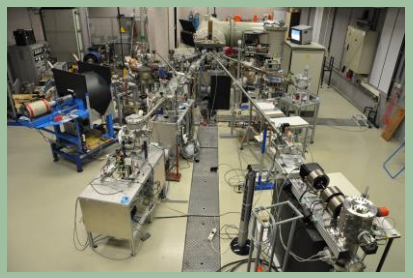
Thin films

Powders

Ion implantation (2MV Tandetron)



Ion Beam Analysis



ToF-SIMS

XPS

Others

- Nanomaterials characterisation
- Tribology characterisation

Cells irradiation (2MV Tandetron)

Cells & small animals irradiation (X-ray irradiator; 225 kV)

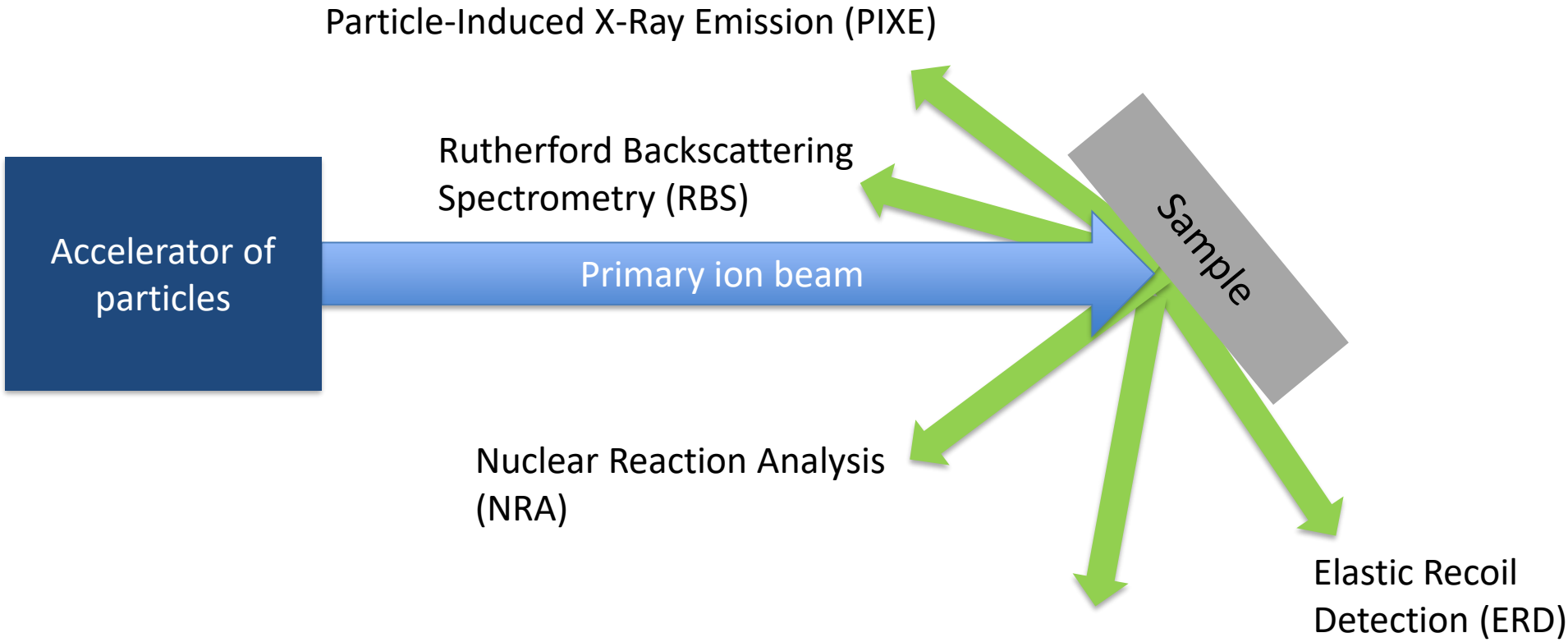
Equipment:

- 6 Plasma treatment installations
- 2MV Tandetron
- 2 XPS
- ToF-SIMS
- Tribology characterisation
- NPs characterisation
- X-ray irradiator
- …

SIAM

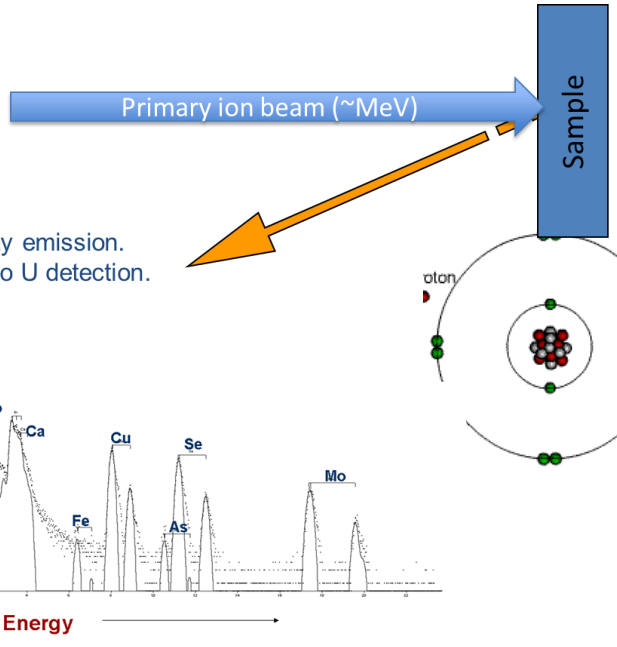
Synthesis Irradiation & Analysis of Materials

What is Ion Beam Analysis?



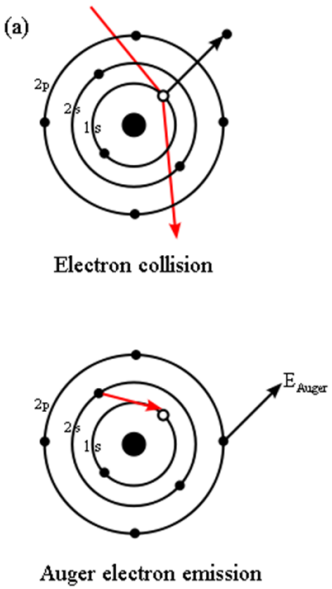
Quantitative (sensitivity ~10 wt.ppm)
Non-destructive
Model-free
Depth profiling (depth resolution ~1-10 nm)
2D elemental maps (lateral resolution ~1 µm)
H depth profiling capability

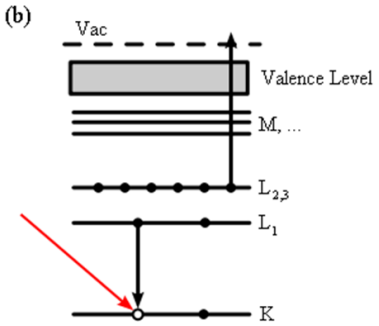
Ion Beam Analysis - Particle-Induced X-Ray Emission (PIXE)



PIXE

Characteristic X-ray emission.
Simultaneous Na to U detection.
Sensitivity: ppm





electron in, electron out = Auger

electron in, photon out = SEM-EDX

photon in, electron out = XPS

ion in, photon out = PIXE

Taken from the Wikipedia article on Auger Electron Spectroscopy 18Feb09
Auger_Process.svg from Wikipedia Commons.

Application fields for PIXE

Materials science

Quantitation of CNTs catalysts
Photovoltaics
Airborne particulate matter (APM)

Forensics


INNOVATION

Authentification de bouteilles de vin anciennes par faisceaux

X-RAY SPECTROMETRY

Explore this journal >

Research Article

Trace element profiling of gunshot residues by PIXE and SEM-EDS: a feasibility study

M. J. Bailey, K. J. Kirkby, C. Jeynes

First published: 20 February 2009 Full publication history

DOI: 10.1002/xrs.1142 View/save citation

Cited by (CrossRef): 15 articles Check for updates Citation tools

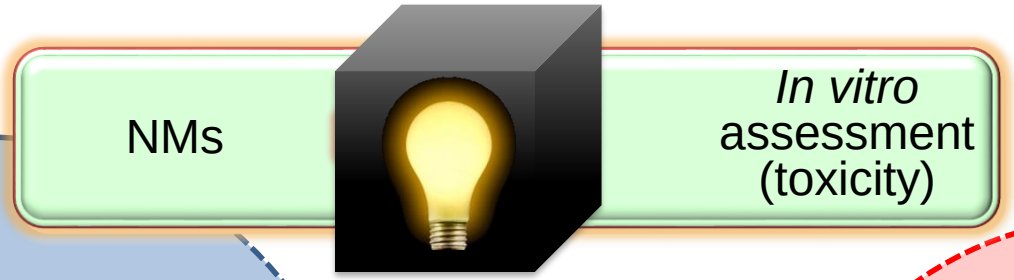
Abstract

A feasibility study was carried out into the use of particle-induced x-ray emission (PIXE) on the ion microprobe for the characterisation of gunshot residues (GSR). We compare these results with the conventional technique, scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS). Samples of gunshot residue from four different sources were collected. Individual particles of GSR were analysed by SEM-EDS using a 30-keV electron beam focussed to ~10 nm, and PIXE using a 2.5-MeV proton beam focussed to ~4 μm. PIXE revealed trace or minor elements undetectable by SEM-EDS, thereby strengthening the discrimination between different types of GSR. Copyright © 2009 John Wiley & Sons, Ltd.

Life science

Bio-distribution and bio-persistence of ENMs
Protein structure

Assessing the possible hazard associated to NPs



NMs

In vitro assessment (toxicity)

Powder

Pre-dispersion in biocompatible medium

?

Dispersant

Protocol of dispersion

?

Method of dispersion, time of application, concentration

Characterization (key parameters)

?

Powder and/or pre-dispersion, evolution of the physicochemical parameters (size, surface composition)

Methods for assessment (cell viability, oxidative stress, inflammation, genotoxicity)

?

Dosimetry issues, adsorption of molecules, Interactions (size, surface composition)

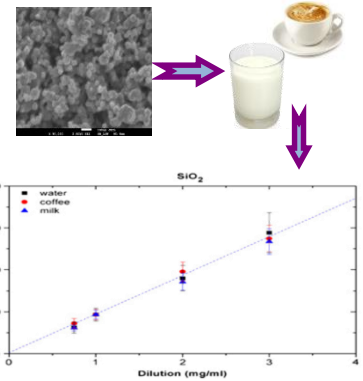
Nanosafety related characterization

Quantitative analysis of NPs in complex systems

Characterisation of NMs

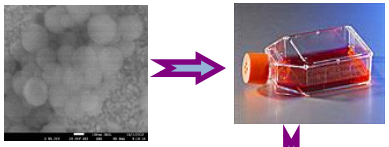
CLS, XPS, SEM, TEM, Turbiscan, PIXE, BET, XRD

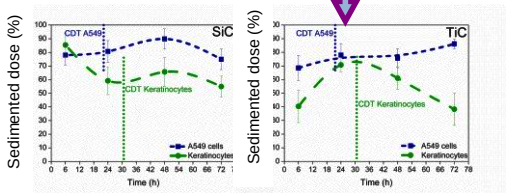
Quantification of NMs in complex media
(i.e. Quantification of SiO_2 NPs in water, coffee and milk)



Lozano, Mejia et al, Analytical and Bioanalytical Chemistry. 403, 10, 2835-41.

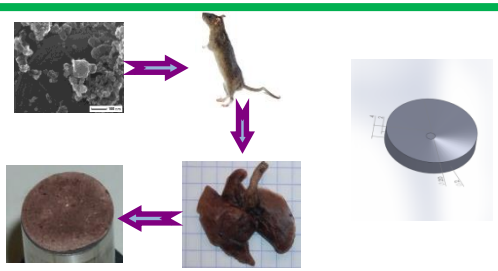
***in vitro* safety assessment**

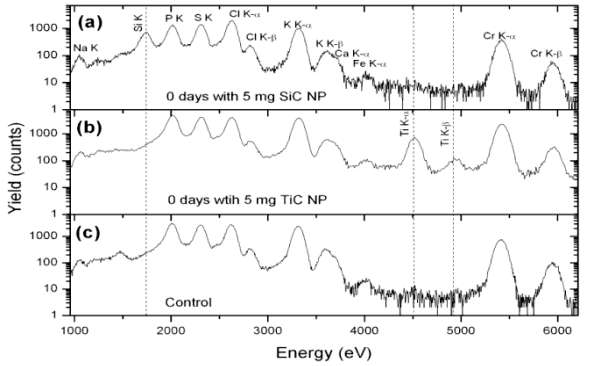


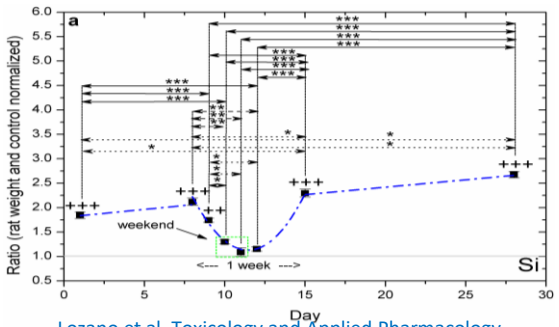


Mejia et al, Journal of Nanoparticle Research (2013) 15, 8, 1875

Biodistribution and biopersistence (*in vivo*) of NMs
(Biopersistance of NPs in rat organs)





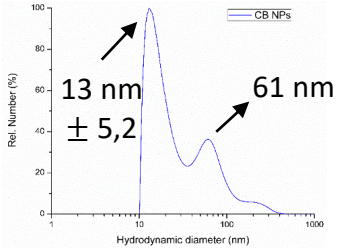


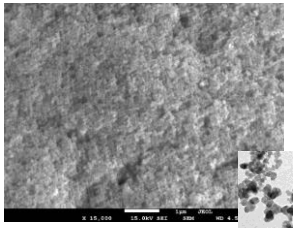
Lozano et al, Toxicology and Applied Pharmacology 264 (2012) 232–245

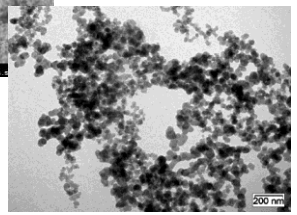
NPs fate in paints

NanoGeCo
Nanoparticle generation by atomization process in spray coating

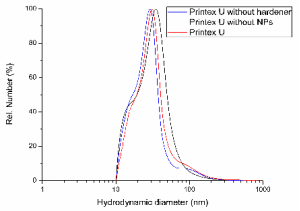
CB NPs in H_2O

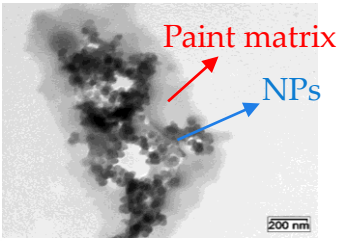


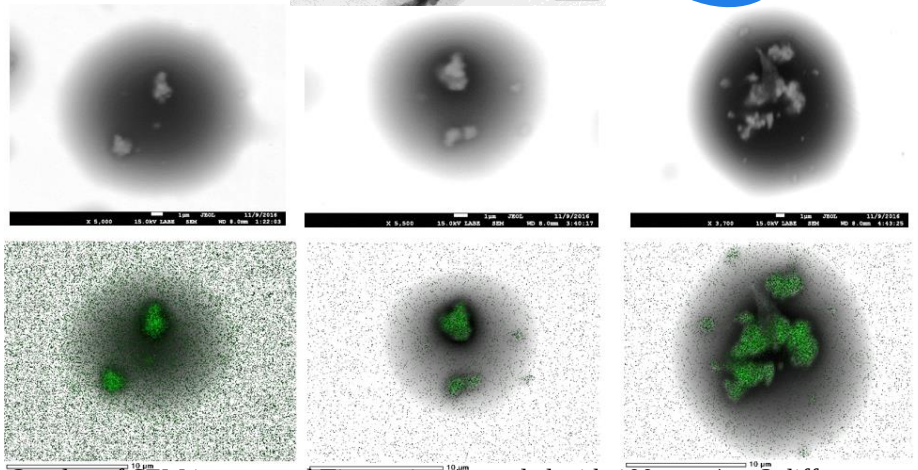




CB NPs in paint
(Dilution 20×)







Overlay of SEM images and Ti mapping (recorded with 100 scans) at 3 different locations in the paint overspray sample. Sample was analyzed with a JEOL 7500 F operating at 50 keV, 20 µA and with LABE detector (backscattered electrons are detected)

Whole-body exposure chamber

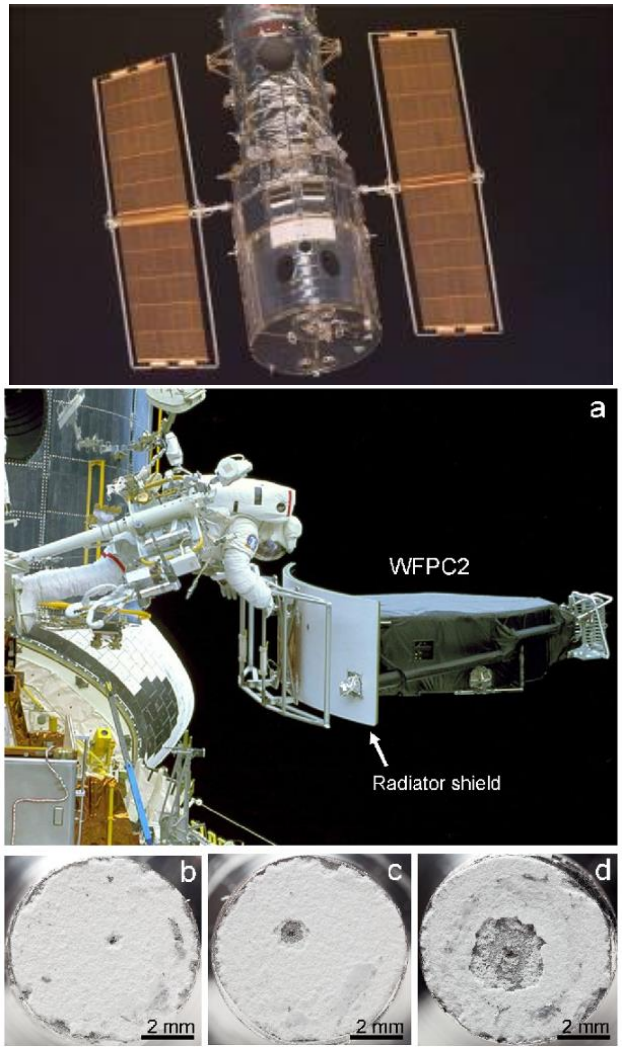
Inhalation model designed for in-vivo experiments on mice. The system is composed of a mixing chamber, an animal cage and ELPI instrument.

Fichera, O. et al, Applied Nanoscience. 9, 515-528 (2019).

Focused incident beam (μ-PIXE)

Micrometeoroid impacts on the HUBBLE space telescope **W**ide **F**ield and **P**lanetary **C**amera 2 (WFPC2)

Experiments performed at the University of Surrey (UK)



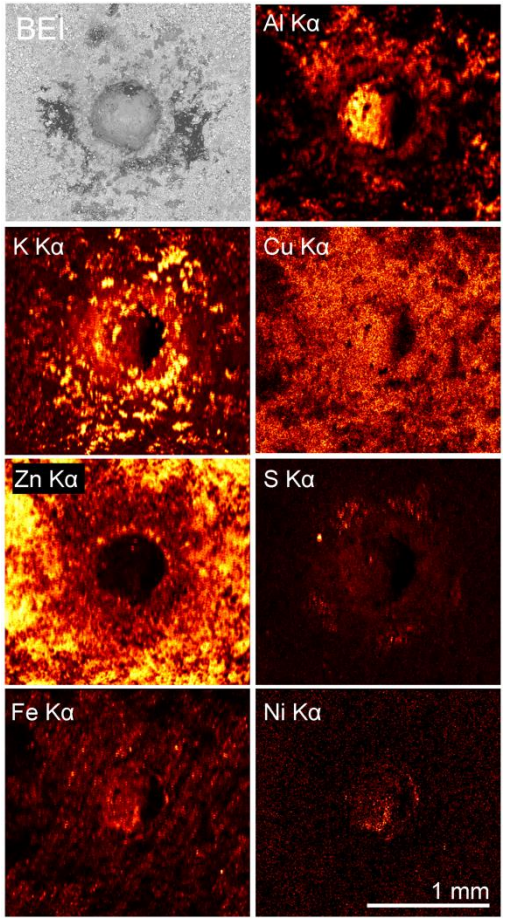
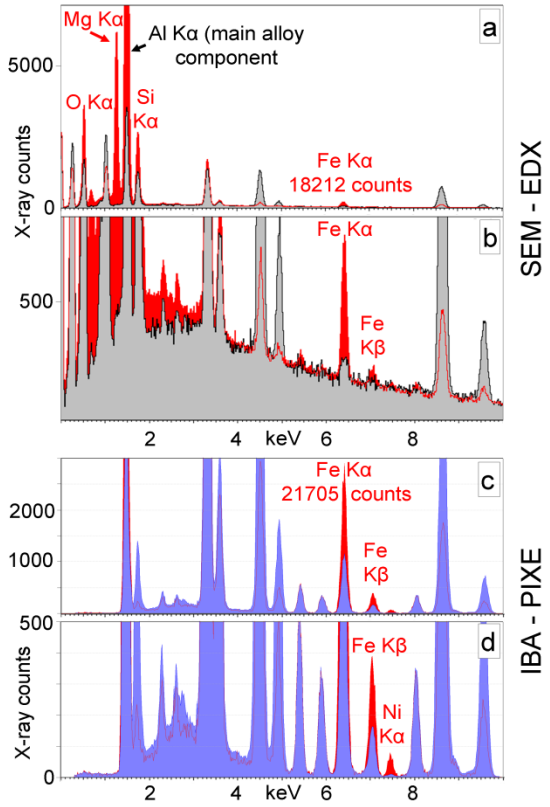


Fig. 2. WFPC2-462: BEI and PIXE maps across centre of feature.

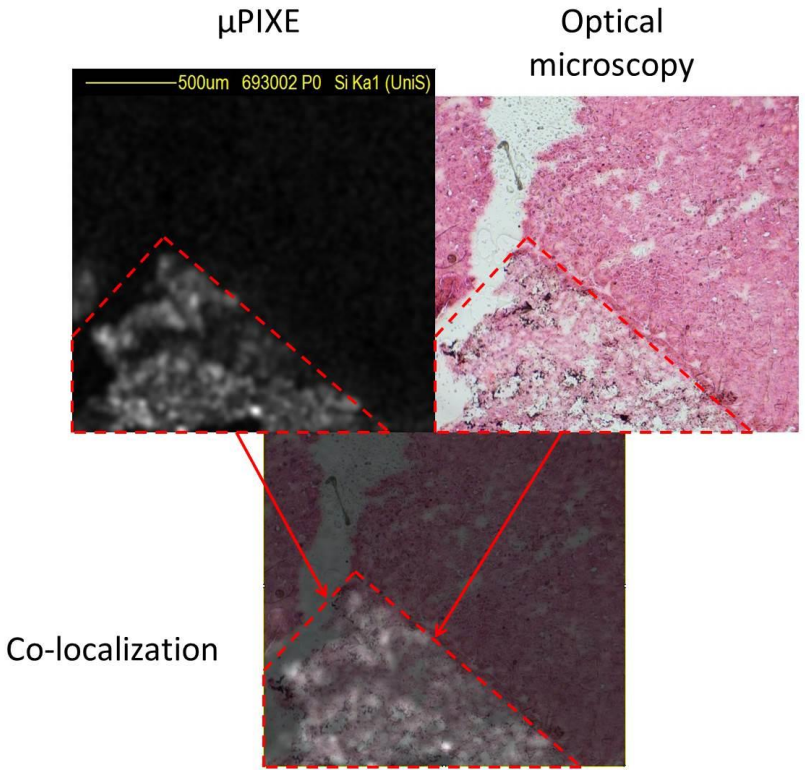


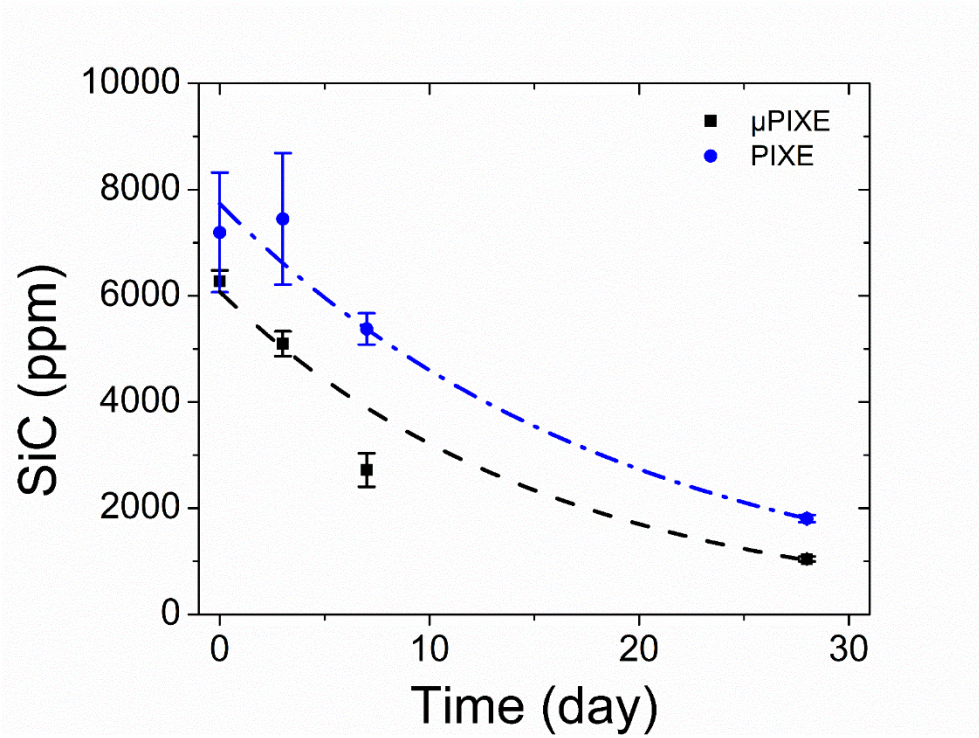
WFPC2-462: a) and b) SEM-EDX of metal in pit (red) and surrounding metal (grey), normalized to background between Cr Kα and Cr Kβ; c) and d) PIXE of metal area inside pit (red) and surrounding metal (blue), normalized to Cr Kα peak area.

μ-Probe now available @ UNamur

Focused incident beam (μ-PIXE)

Analysis of rat lungs





O. Lozano, J.L. Colaux *et* al.,
"Fast, asymmetric and non-homogeneous clearance of SiC nano-aerosol after 5 day exposure using ion beam analysis"
accepted in Nanomedicine (2017)

Know how

- Nanomaterials (NMs) and nanoparticles (NPs) physicochemical characterisation (pristine forms, dispersions, complex matrices, environmental compartments, …)
- Fate and biodistribution studies at cellular and/or organ levels.
- Multielemental determination in complex matrices
- FATE OF NMs: Evolution of NMs (surface) in specific compartments. Released (nano)materials (intentional or unintentional, during manufacturing, after erosion or aging).
- Detection and evaluation of released (nano)materials
- IN SILICO MODELLING (sedimentation of NMs in aqueous media, environmental compartments).

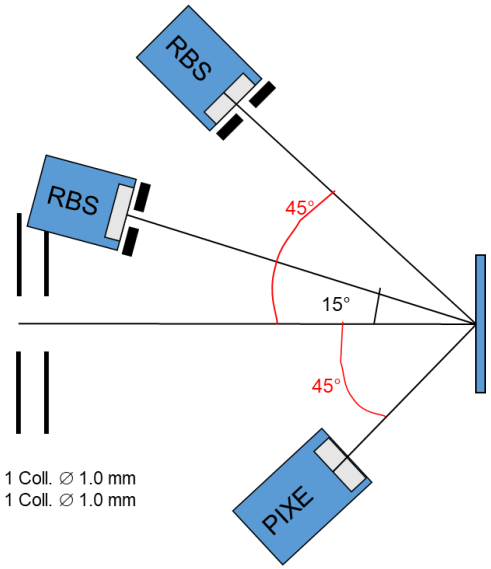
Research Infrastructure QualityNano	NanoValid Developing Reference Methods for Nanomaterials	NANOREG A common European approach to the regulatory testing of nanomaterials	NanoGeCo Nanoparticle generation by atomization process in spray coating	PATROLS Advanced Tools for NanoSafety Testing
(2011-2015) Joint Research Activities, networking activities and provision of Transnational Access functions.	(2011-2015) Development of SOPs for NPs characterization.	(2013-2016) Development and testing of SOPs for characterization and quantification of NMs.	(2015-2018) Characterization of the aerosol (paint with NPs) in real exposure conditions.	(2018-2021) Characterization and dosimetry of NMs in vitro and environmental samples. In silico modelling.

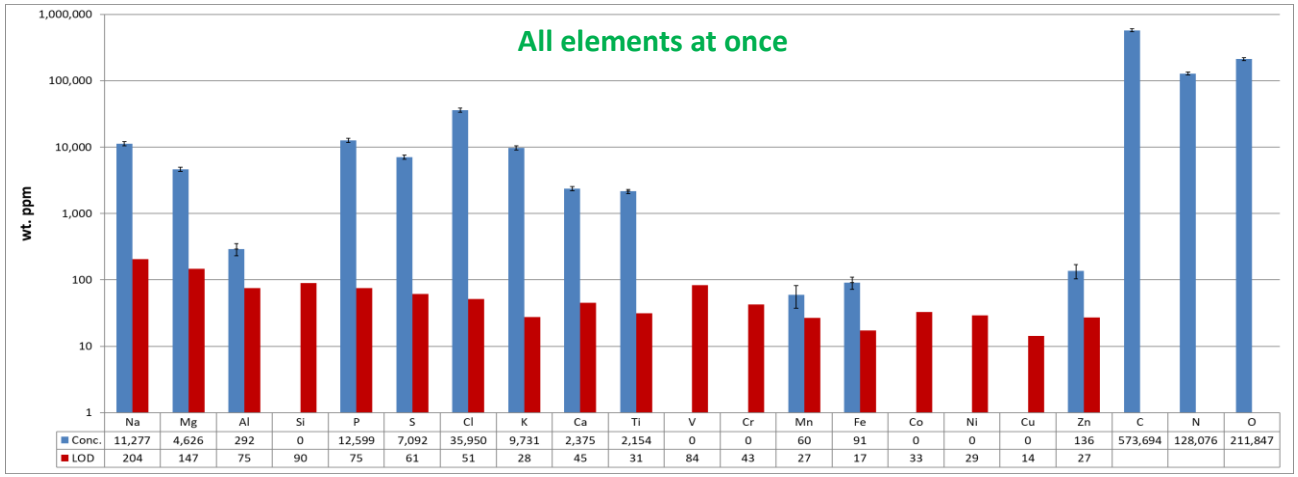
Liquid sample analysis
Zebrafish eggs samples (LU)

PATROLS
Advanced Tools for NanoSafety Testing

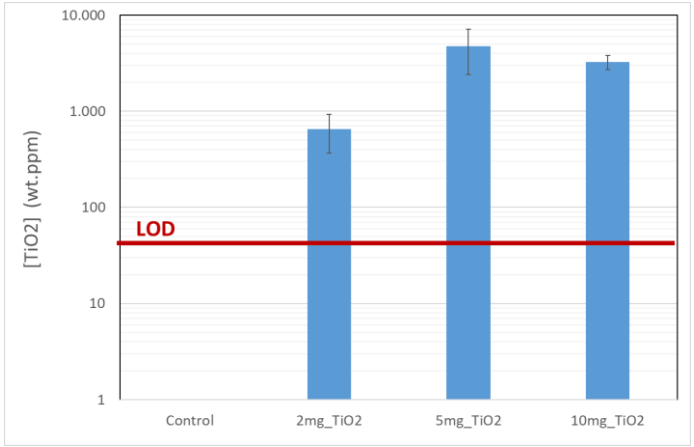
Exposure to TiO2 NPs (NM-105) in ecotox media (M7, egg water)

Experimental setup (2,5 MeV)





	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	C	N	O
Conc.	11,277	4,626	292	0	12,599	7,092	35,950	9,731	2,375	2,154	0	0	60	91	0	0	0	136	573,694	128,076	211,847
LOD	204	147	75	90	75	61	51	28	45	31	84	43	27	17	33	29	14	27			



Solid samples!

=> “pellets”

LOD = 40 wt.ppm

=> Must be improved for ecotox samples

Potential for simulation (data with low uncertainty).

Translocation experiments (apical, basal, membrane, cells).

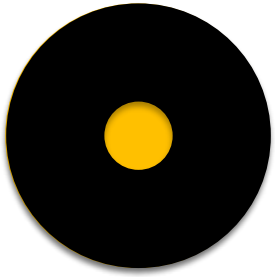
Liquid sample and configuration settings

Sample holder

Side view

Carbon tape
Thin gold layer (~15 nm)
Vitreous carbon

Top view

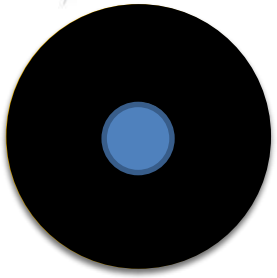


The hole in carbon tape is 3 mm in diameter

(1)

Sampling specific volume (5-10 µL)

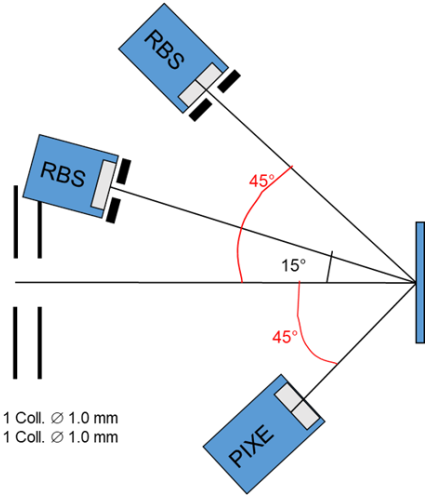
(2)



Deposition on controlled area

(3) Drying (oven 60 °C)

(4) IBA analysis

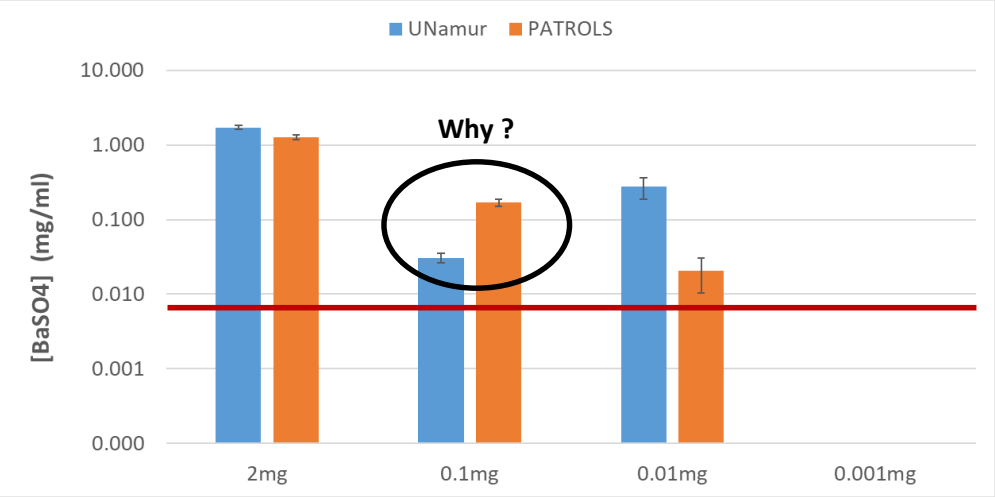


NM-220 ($BaSO_4$), NM-105 (TiO_2), NM-212 (CeO_2), NM-110 (ZnO_2)

Liquid sample results (AMI)

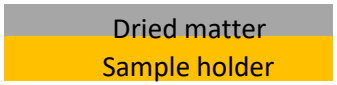
	sample	[Ba] wt.ppm	Unc. Wt.ppm	LOD wt.ppm
UNamur	2mg_BaSO4	612,219	39,251	1,227
UNamur	0.1mg_BaSO4	11,301	1,639	2,861
UNamur	0.01mg_BaSO4	296,200	94,441	2,659
UNamur	0.001mg_BaSO4			1,664
PATROLS	2mg_BaSO4	561,051	36,446	2,042
PATROLS	0.1mg_BaSO4	29,721	3,118	2,541
PATROLS	0.01mg_BaSO4	4,672	2,317	2,733
PATROLS	0.001mg_BaSO4			2,691

	sample	[BaSO4] mg/ml	Unc. mg/ml	LOD mg/ml
UNamur	2mg	1.708	0.1095	0.003
UNamur	0.1mg	0.031	0.0045	0.004
UNamur	0.01mg	0.277	0.0882	0.001
UNamur	0.001mg			0.002
PATROLS	2mg	1.266	0.0822	0.005
PATROLS	0.1mg	0.169	0.0178	0.014
PATROLS	0.01mg	0.021	0.0102	0.012
PATROLS	0.001mg			0.012



Uncertainty values are established from a bottom-up approach (uncertainty budget).

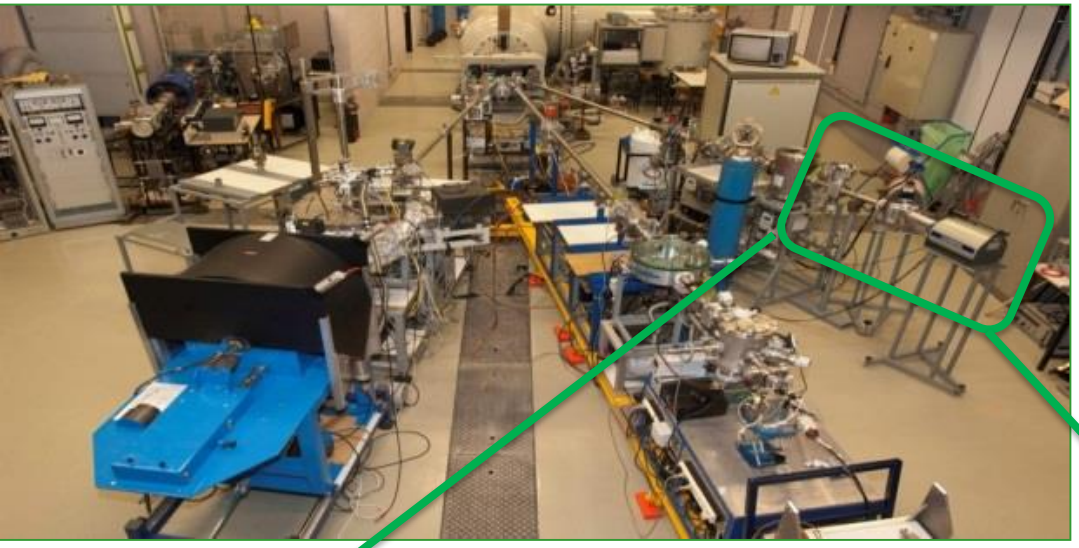
Ideally we should get this:

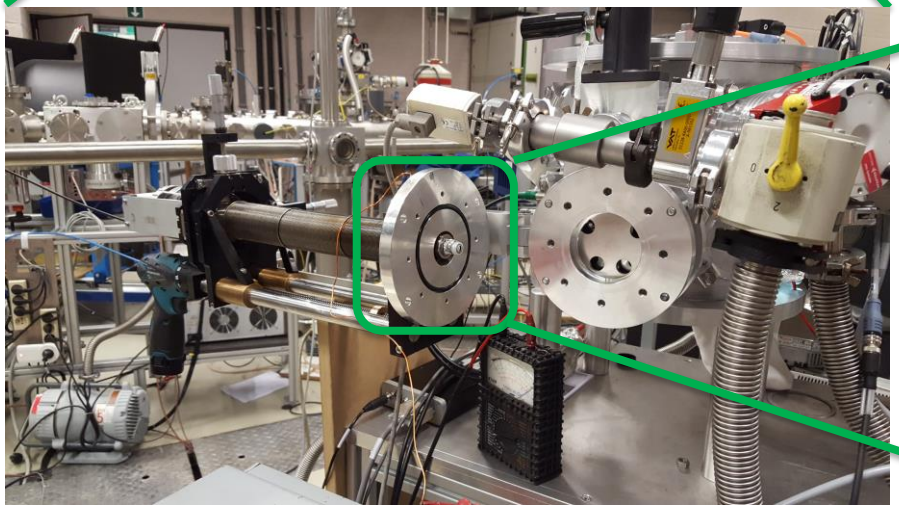


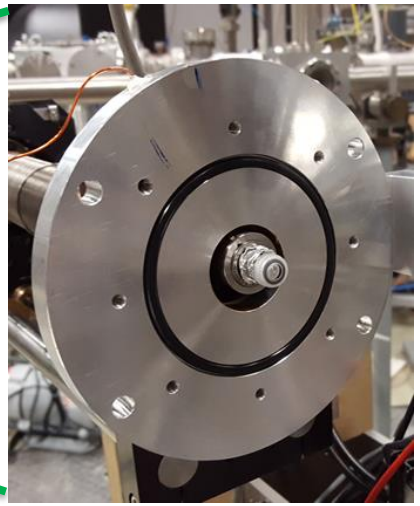
However:

Moreover, LOD still too high!

Measurement of liquid sample by IBA



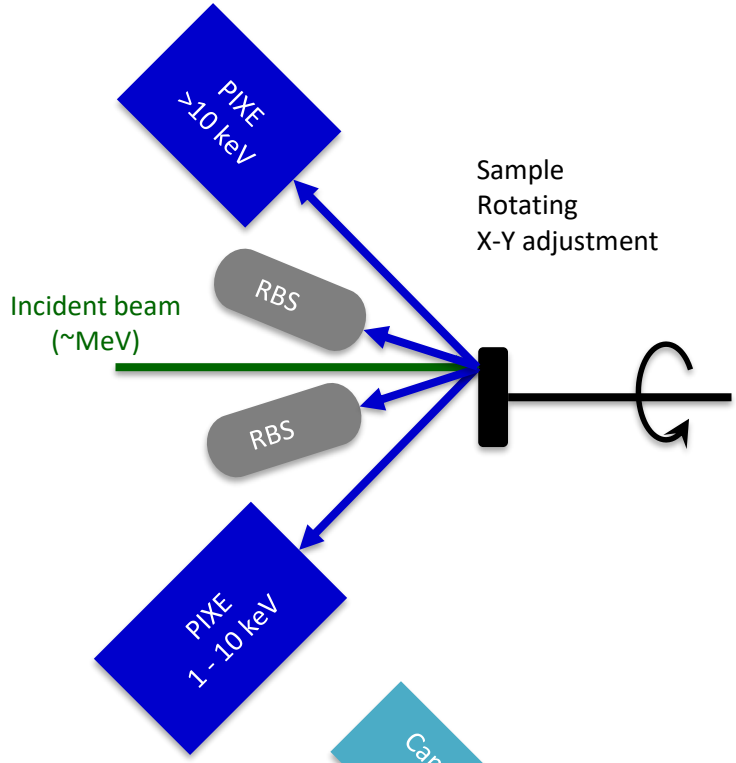




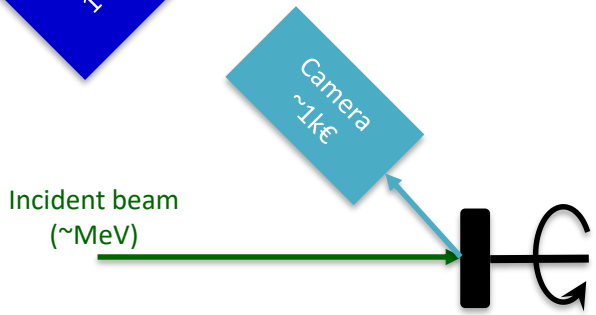
Measurement of liquid sample by IBA

Improving LOD
(set-up under development)

Top view



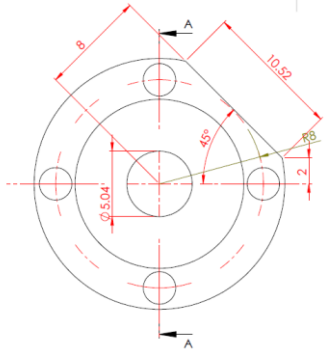
Side view

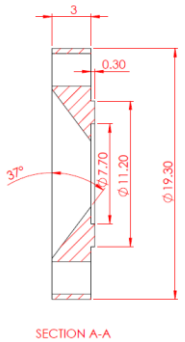


Improving sample uniformity

Cells for liquid sample (50 µL)

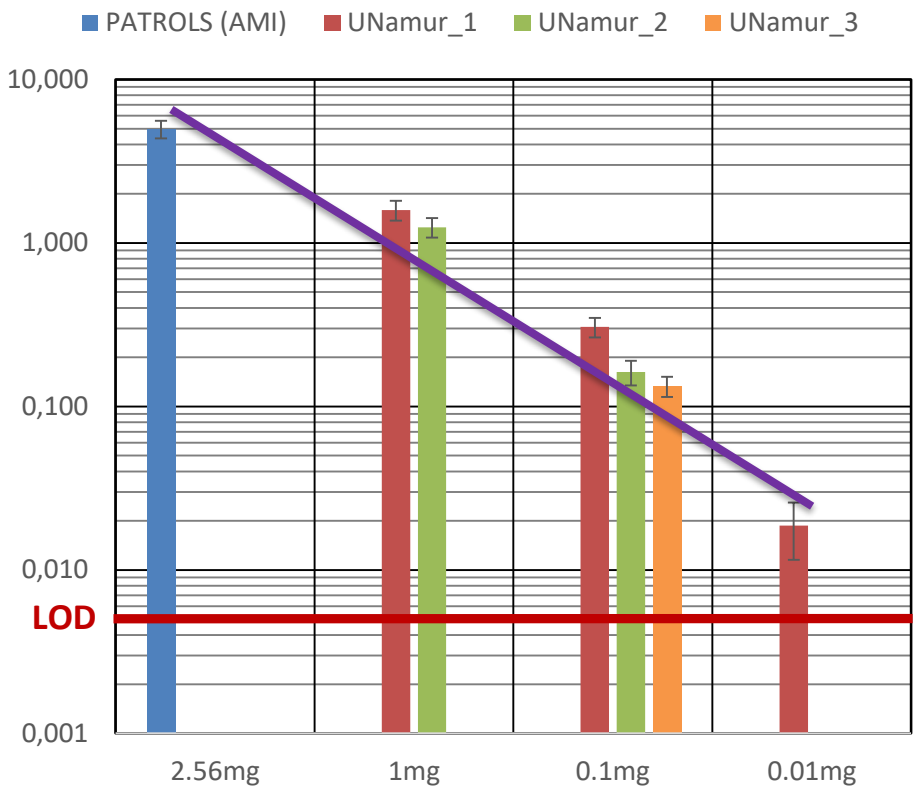
Screws
Stainless steel
Aluminized Mylar
(0,05 µm)





Some last results

NM-105 (TiO_2)



Values given are indicative or typical "best" values.

Different applications may have widely differing performances.

Possible primary beam energies and types are indicated. A wide variety may be used.

	SIMS	XTEM	SAM	GD-OES	XPS	LA - ICP-MS	IBA
Primary beam	keV ions	~100 keV electrons	~100 keV electrons	plasma	X-rays	Pulsed laser	~3 MeV light ions ~30 MeV heavy ions
Detected signal	Sputtered ions	Primary electrons in phase contrast	Auger electrons	visible photons	Photo-electrons	Evapor-ated ions	X-rays; Nuclear reaction products: scattered primaries, target recoils and γ-rays
Destructive	Yes	Yes	Yes	Yes	Yes	Yes	No
Depth resolution	2 nm	0.1 nm	2 nm	20 nm	2 nm	10 nm	2 nm
Information depth	500 nm	100 nm	500 nm	50 µm	500 nm	--	15 µm
Lateral resolution	50 nm	0.1 nm	2 nm	1 mm	3 µm	10 mm	500 nm
Elemental Imaging	Yes	EELS, EDX	Yes	No	Yes	No	Yes
Ambient analysis	No	No	No	No	No	Yes	Yes
Sample preparation	No	Yes	UHV	No	UHV	No	No
Quantitative	?	No	Yes	Yes	Yes	Yes	Yes
Standards needed	Yes	--	Yes	Yes	Yes	Yes	No
Elemental sensitivity	10^{-8}	10^{-1}	10^{-3}	10^{-6}	10^{-3}	10^{-9}	10^{-6}
Accuracy	--	--	10%	10%	5%	5%	1%
Traceability	--	--	--	--	Yes	Yes	primary

C. Jeynes & J.L. Colaux, *"Thin film depth profiling by ion beam analysis"*, **Analyst 141 (2016),** 5944-5985.

Progress so far

- Liquid samples measurements: minimal manipulation and small volumes (~50 µL).
- Geometry OK (improvements are still possible, LOD still to be reduced?)
- Actual LOD is about 0,05 mg/mL, “sample concentration” is required for lower concentrations.
- Sets of data produced per sample (NMs and matrix information in the same run).
- Cross check/validation on the NMs dispersion protocol (exposure concentrations).
- Low uncertainty values and valuable data for simulation purposes.
- High potentiality for analyses of complex samples (in vitro/in vivo/ecotox, …)

On going

- Sample stability study programmed.
- Improving sample preparation for solid samples.

Technological Platform

SIAM Synthesis Irradiation & Analysis of Materials

Thank you for your attention

Expert Ion Beam Analysis
Dr. Julien Colaux
Email: julien.colaux@unamur.be
Phone: +3281725470

Expert Surface Analysis
Dr. Alex Felten
Email: alex.felten@unamur.be
Phone: +3281725236

Business Developer (expert nanomaterials)
Dr. Jorge Mejia
Email: jorge.mejiamendoza@unamur.be
Phone: +3281725468

Director
Prof. Pierre Louette
Email: pierre.louette@unamur.be
Phone: +3281724589

"Your potential partner for surface, materials and nanomaterials characterization"

web: siam.unamur.be