Contrôle de la qualité de synthèse d'un polymère par EDS

Quality control of polymer synthesis by EDS

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Institut de Chimie de Nice
Université Côte d'Azur

CCMA : the Electron microscopy facility of Université Côte d'Azur

Centre Commun de Microscopie Appliquée

Common Facility for Applied Microscopy

Location :
Campus Valrose
(under the University Library)

The team :

- Director : Sandra Lacas-Gervais (MCF)
- François Orange (IR)
- Sophie Pagnotta (IE)
- Christelle Boscagli (Tech)

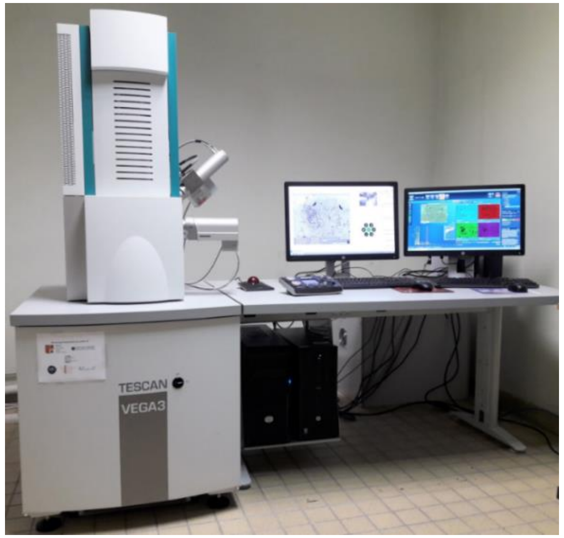
- 35 years of expertise in electron microscopy
- Open to all laboratories or private companies
- Multidisciplinary : mostly life sciences, but also provides local solutions for material sciences

CCMA : the Electron microscopy facility of Université Côte d'Azur

2 Scanning Electron Microscopes

- **JEOL JSM-6700F** (2004)
- Field emission gun
- Resolution 1 nm
- Cryo-SEM module

- **Tescan Vega 3 XMU** (2016)
- Tungsten filament
- Resolution 3 nm
- Large specimen chamber
- EDX detector for elemental analyses
- Low vacuum mode

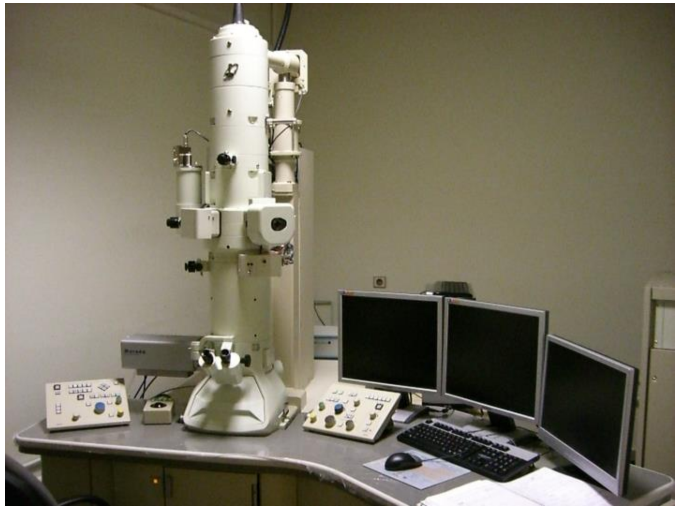


1 Transmission Electron Microscope

- **JEOL JEM-1400** (2009)

-120 kV

- Resolution 0.4 nm
- Optimized for biological samples (ultra-thin sections)



Institut de Chimie de Nice

« Arômes - Parfums - Synthèses – Modélisation » Team

(current director : Véronique Michelet)

- Daphné Hector, Sandra Olivero, Elisabet Duñach, Jean-François Gal

- Research topics : synthesis of small perfumed molecules
- Study of catalysis within this context
- Development of polymer-based solid catalysts
- Polymers : easier to collect and to recycle, harder to characterize

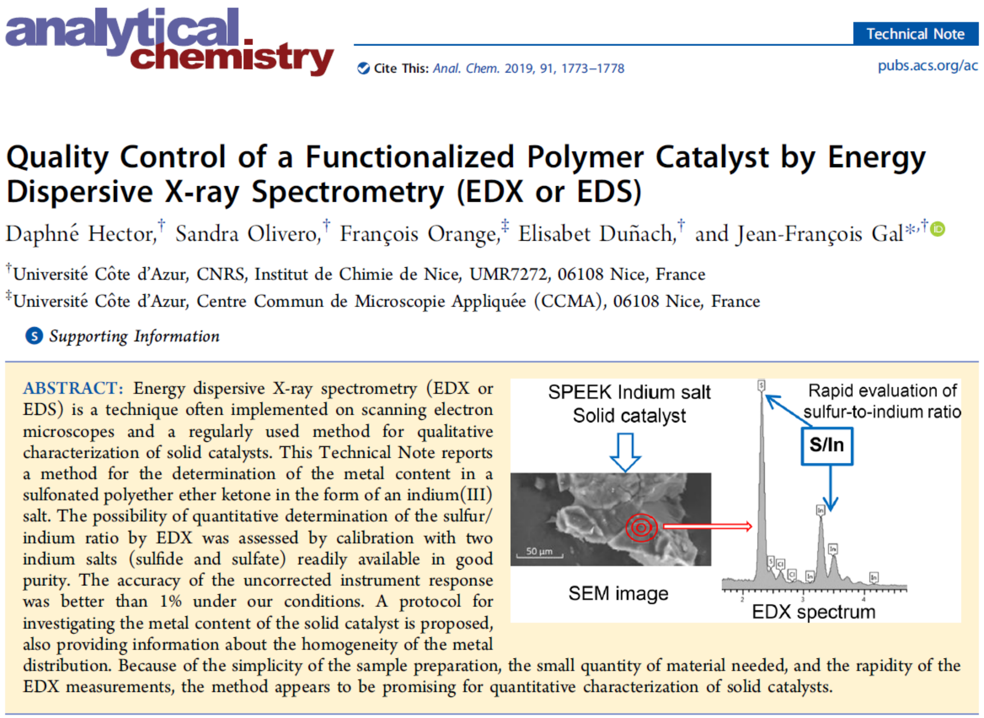
This presentation

Hector *et al.* (2019) Quality Control of a Functionalized Polymer Catalyst by Energy Dispersive X-ray Spectrometry (EDX or EDS). *Analytical Chemistry*, 91, 1773-1778

- Timeline of this article
- EDX on polymers : methodology, multiple verifications
- Comparison with other analytical results
- Reviewers comments ➔ additional verifications

- Extreme care taken to ensure the validity of the methodology
- We thought the reviewers would not be pleased

- I would be glad to have your opinion on it



analytical chemistry

Technical Note

Cite This: *Anal. Chem.* 2019, 91, 1773−1778

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Quality Control of a Functionalized Polymer Catalyst by Energy Dispersive X-ray Spectrometry (EDX or EDS)

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Supporting Information

ABSTRACT: Energy dispersive X-ray spectrometry (EDX or EDS) is a technique often implemented on scanning electron microscopes and a regularly used method for qualitative characterization of solid catalysts. This Technical Note reports a method for the determination of the metal content in a sulfonated polyether ether ketone in the form of an indium(III) salt. The possibility of quantitative determination of the sulfur/indium ratio by EDX was assessed by calibration with two indium salts (sulfide and sulfate) readily available in good purity. The accuracy of the uncorrected instrument response was better than 1% under our conditions. A protocol for investigating the metal content of the solid catalyst is proposed, also providing information about the homogeneity of the metal distribution. Because of the simplicity of the sample preparation, the small quantity of material needed, and the rapidity of the EDX measurements, the method appears to be promising for quantitative characterization of solid catalysts.

SPEEK polymers

- Metal triflates $M(CF_3SO_3)_n$: efficient catalysts for a wide range of reactions.
    - Example: Indium(III) triflate $In(CF_3SO_3)_3$

➔ Search for solid and recyclable equivalent: In(III) sulfonate derived from a polymer ?

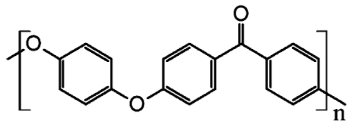
- PolyEtherEtherKetone or PEEK : chemically and thermally resistant.

➔ Chlorosulfonation of PEEK

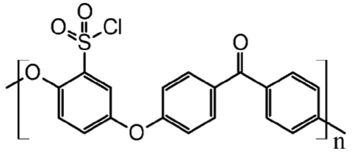
➔ Hydrolysis : various degrees of HSO_3^- functionalized PEEK ➔ **SPEEK**

- Reaction with indium metal (or indium salt) gives **the polymeric In(III) catalyst**

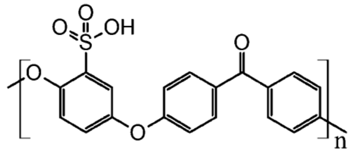
PEEK



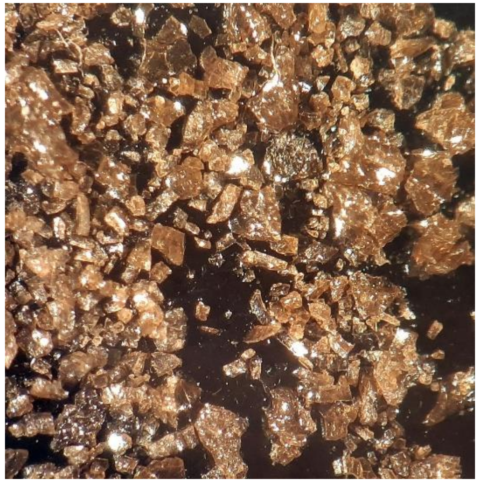
Chlorosulfonated **PEEK**



Sulfonated **PEEK = SPEEK**



$(RSO_3)_3In$?



Aims of this study and analytical challenges

<u>Quality control of polymeric In(III) catalyst</u>

- Verification of the Indium (III) content
- Number of sulfonate groups coordinated to In^{3+}

➔ **S/In ratio = 3**

- Homogeneity of the material ? Impurities ?

<u>How to do this ?</u>

- To obtain the full elemental composition
    - C , H, S : Service Central d'Analyses (ISA, Villeurbanne, France)
    - In : Inductively coupled plasma atomic emission spectroscopy (ICP-AES) : Genay, France
- Not fast nor convenient enough

- **Solution with EDX ?**
    - Fast but many analytical challenges

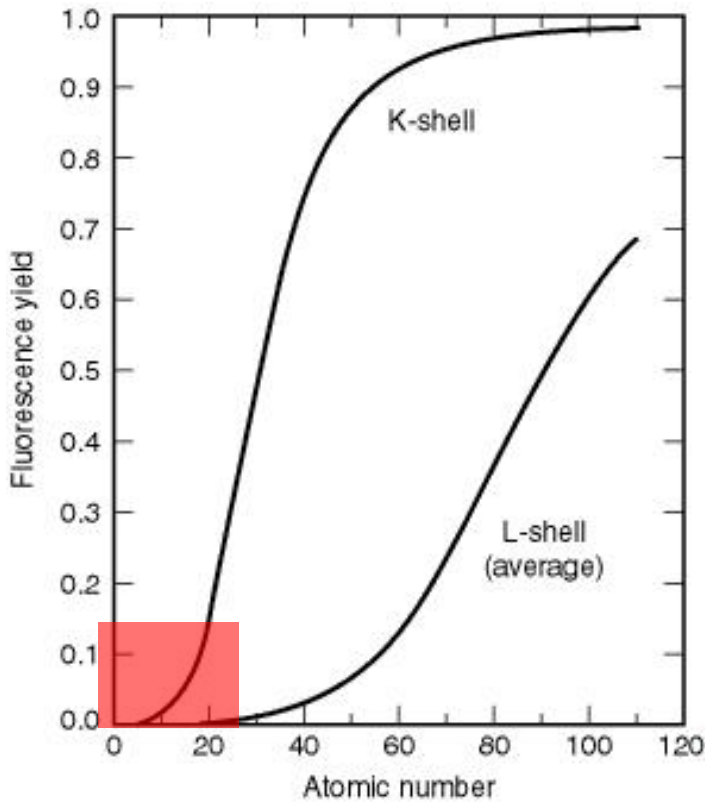
Analytical challenges

A lot of challenges

- EDX not efficient on light elements
  - Light elements generate less X-rays
  - These X-rays are more easily absorbed by the sample
  - ➔ Weak signal

- EDX on carbon : not an easy thing
  - Accumulation of carbon as a contaminant
  - Carbon coating

➔ Difficulties to obtain quantitative EDX data on polymers



Possible solution : measure only the S/In Ratio

Methodology

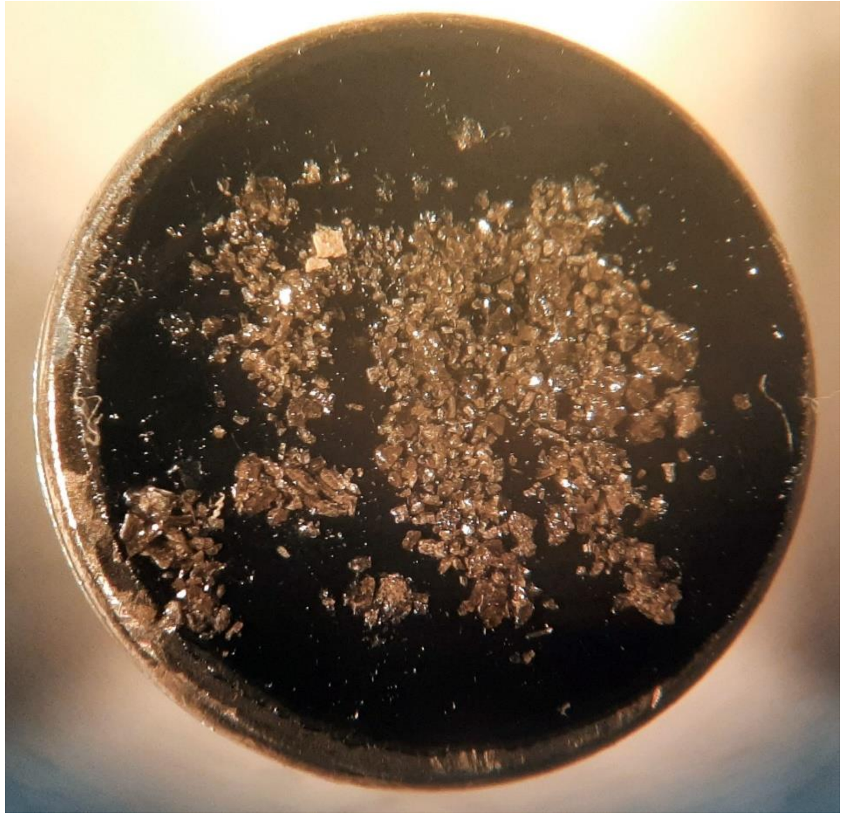
Standards chosen :

- $In_2(SO_4)_3$
- In_2S_3

> 99,99 % purity

Samples chosen :

- SPEEK-In prepared from In(0)
- SPEEK-In prepared from indium acetate $In(OAc)_3$
- SPEEK-In prepared from indium acetate $In(OAc)_3$ recycled
    - Used 3x as catalyst
- SPEEK-In/Na prepared from indium acetate $In(OAc)_3$ + NaOH



Preparation for SEM

- Polymer or powder on a SEM stub
- Carbon coating

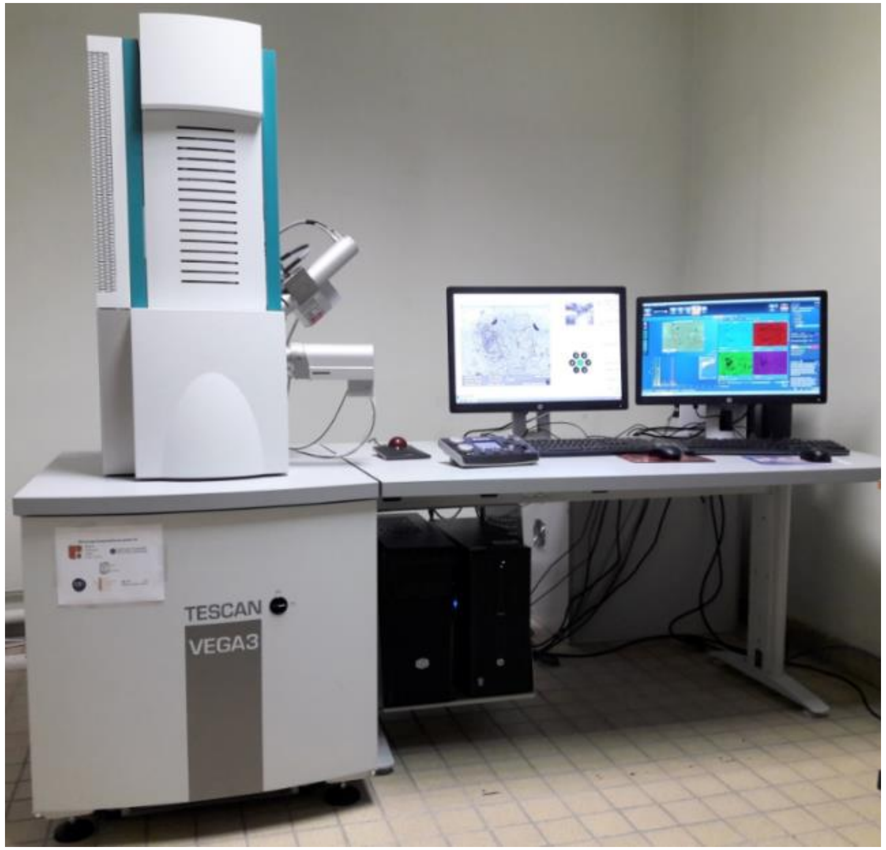
Methodology

Equipment

- Tescan VEGA 3 XMU scannning electron microscope
- X-Max^N 50 EDX detector (Oxford Instruments)
    - 50 mm^2 silicon drift detector (SDD), take-off angle 30 °, resolution 129 eV at the Mn K-L_3 line
    - Aztec v3.2 software

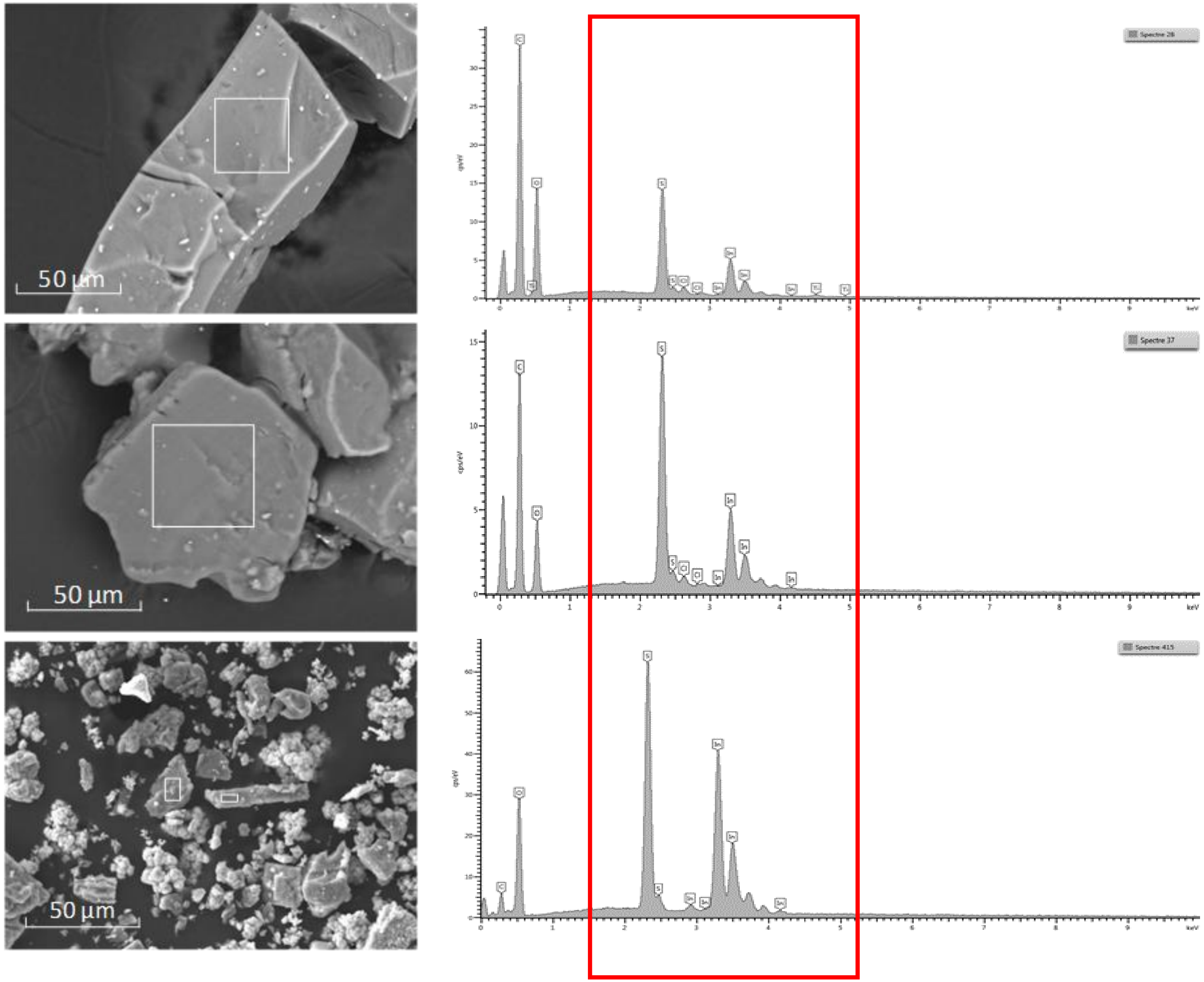
EDX parameters

- Precisely and progressively defined and chosen
- 20 kV
- Working distance 10 mm (precisely)
- 1500x magnification
- 170 nm beam size
    - ➔ Probe currrent 1.1 – 1.5 nA
    - ➔ 10000 – 15000 cps, dead time ~10%
- Beam optimization on Mn standard
- Automatic acquisition time : ~30 seconds (310000-320000 total counts)



Samples SEM images and typical EDX spectra

- SPEEK-In prepared from In(0)
- SPEEK-In prepared from In(OAc)$_3$
- $In_2(SO_4)_3$



Fragmented, glassy solid particle (20-200 µm)

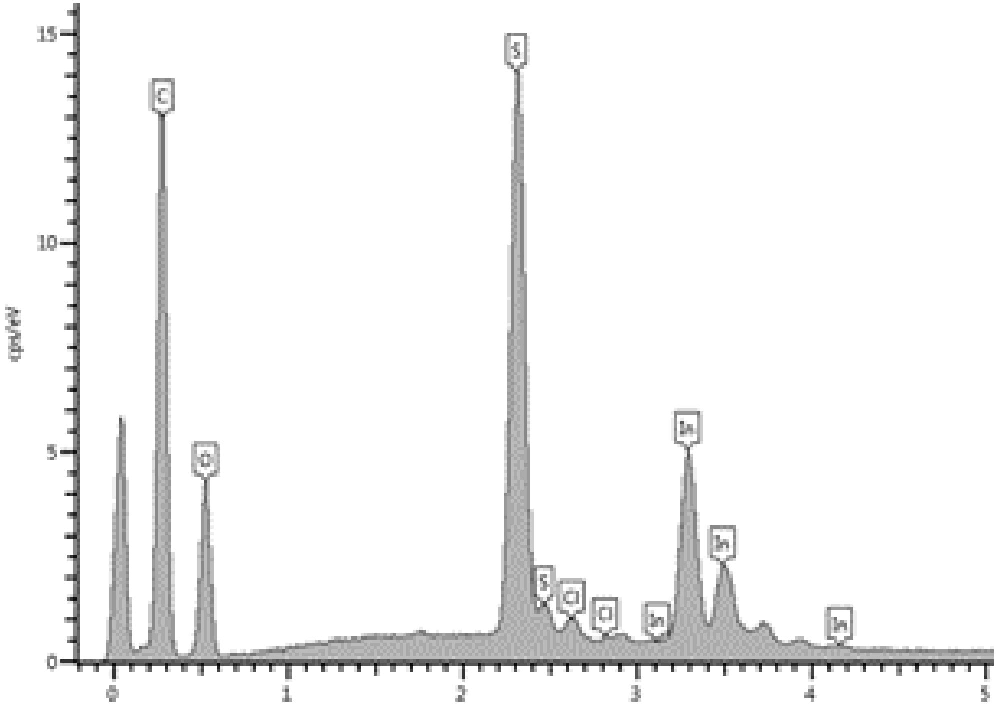
Quantitative data from EDX

Aztec Software

- Quantitative data are obtained from the spectra after matrix correction using the XPP exponential model procedure (Pouchou & Pichoir)

- We have not tried to obtain full quantitative data for all elements
- **Focus on the S/In ratio**
- Carbon coating layer and other elements were taken into account for the calculation
- Ratio calculated with
    - S : K-series peaks (main peak at 2.46 keV)
    - In : L-series peaks (main peak at 3.29 keV)
- Validity of EDX measurements :
    - Background noise up to 20 keV
    - Total un-normalized mass ratios between 96 and 104 %

(100 % measured on the Mn standard for optimization)



Main results

Standards

Calibrant	Expected S/In ratio	Number of analyses	Measured S/In		
			S%	In%	Ratio
$In_2(SO4)_3$	3/2	14	60.32	39.68	**1.521 ± 0.011**
In_2S_3	3/2	10	60.52	39.48	**1.533 ± 0.011**

SPEEK samples

SPEEK-In(III) sample and origin	Expected S/In ratio	Number of analyses	S%	In%	S/In ratio by EDX	S/In ratio elemental & ICP-AES analyses
SPEEK-In(III) from In(0)	3/1	10	71.04	28.96	**2.464 ± 0.142**	**2.41**
SPEEK-In(III) from $In(OAc)_3$	3/1	10	71.89	28.11	**2.566 ± 0.132**	**2.39**
SPEEK-In(III) from $In(OAc)_3$ Recycled catalyst	3/1	10	71.86	28.14	**2.565 ± 0.144**	**2.90**
SPEEK-In/Na [$In(OAc)_3$ + NaOH]	4/1	11	81.83	18.17	**4.520 ± 0.209**	**5.34**

Main results

S/In ratio calibration on $In_2(SO_4)_3$ and In_2S_3

- Repeatability 0.7 % (95% confidence level)
- Expected S/In ratio = 1.50, found 1.51-1.52
- No correction necessary to instrument response

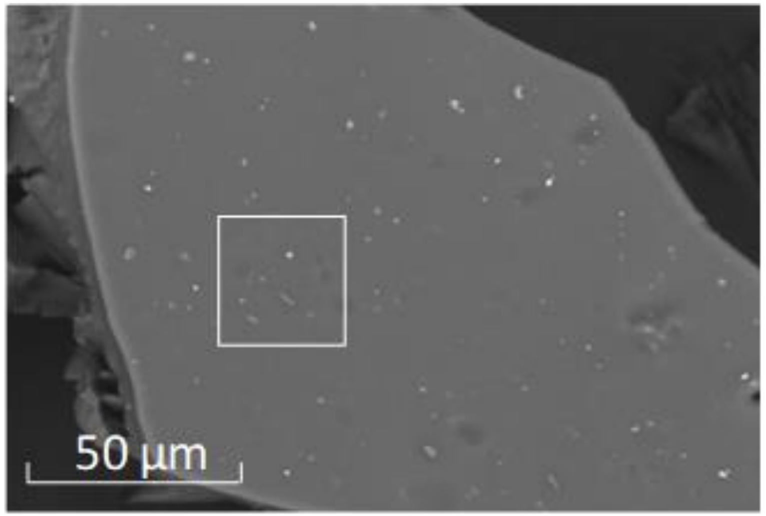
S/In ratio on SPEEK-In(III)

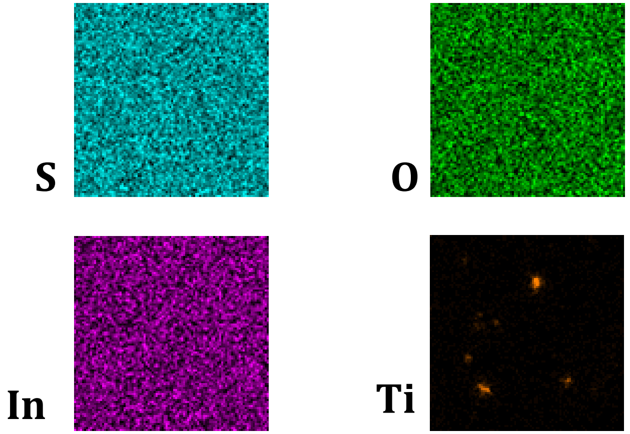
- Typical repeatability 3-7 % depending on sample homogeneity
- Expected S/In ratio = 3 from the stoichiometry of an In(III) sulfonate
- Measured S/In ratio ~ 2.5: lower than expected stoichiometry, in agreement with elemental analysis

Images of SPEEK-In(III)

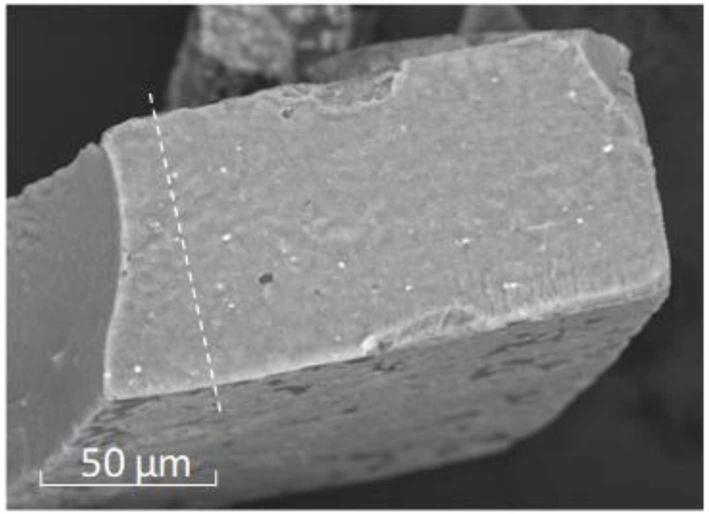
- Size and shape of material particles
- Location & identification of extraneous materials

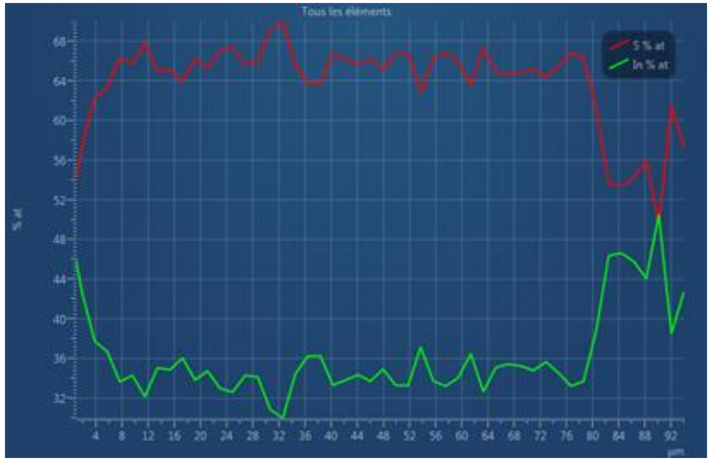
Composition homogeneity, impurities





Only small Ti impurities : titanium-containing material coming for the ultrasound probe





Composition homogeneity

Reproducibility and repeatability tests

- **Reproducibility** : same measurements with an other instrument and other operator
    - ~ repeat the experiment in the long time range, with a new calibration

- **Repeatability** : same measurements within a short amount of time

Reproducibility

	Sample	Expected S/In ratio	Number of analyses	S%	In%	S/In ratio
First set of measurement	$In_2(SO4)_2$	3/2	10	60.11	39.89	**1.507 ± 0.012**
Second set of measurement		3/2	10	60.52	39.48	**1.533 ± 0.011**
First set of measurement	SPEEK-In(III) from In(0)	3/1	10	71.04	28.96	**2.464 ± 0.142**
Second set of measurement		3/1	11	71.23	28.77	**2.488 ± 0.146**

Reproducibility and repeatability tests

Repeatability

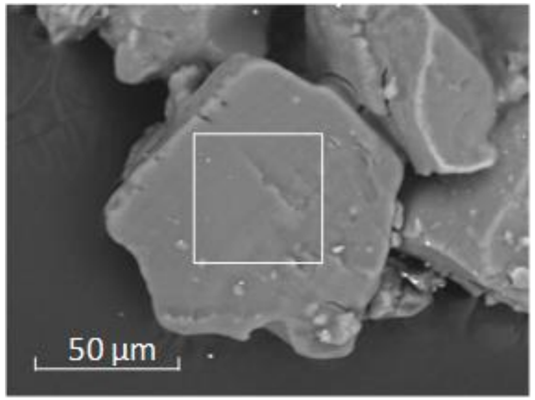
Sample	Expected S/In ratio	Number of analyses	S%	In%	Standard deviation on S(%) and In(%)	Confidence interval CI_{95}	% uncertainty (as) on S/In value
$In_2(SO4)_2$	3/2	10 x means of 3 analyses	60.27	60.27	**0.40**	**0.29**	**1.2**
	3/2	30 analyses altogether			**0.42**	**0.16**	**0.66**
SPEEK-In(III) from In(0)	3/1	10 x means of 3 analyses	71.17	28.83	**1.97**	**1.41**	**3.7**
	3/1	30 analyses altogether			**1.90**	**0.71**	**3.2**

The mean value for n = 10 and n = 30 is the same, but standard deviations and confidence intervals are different

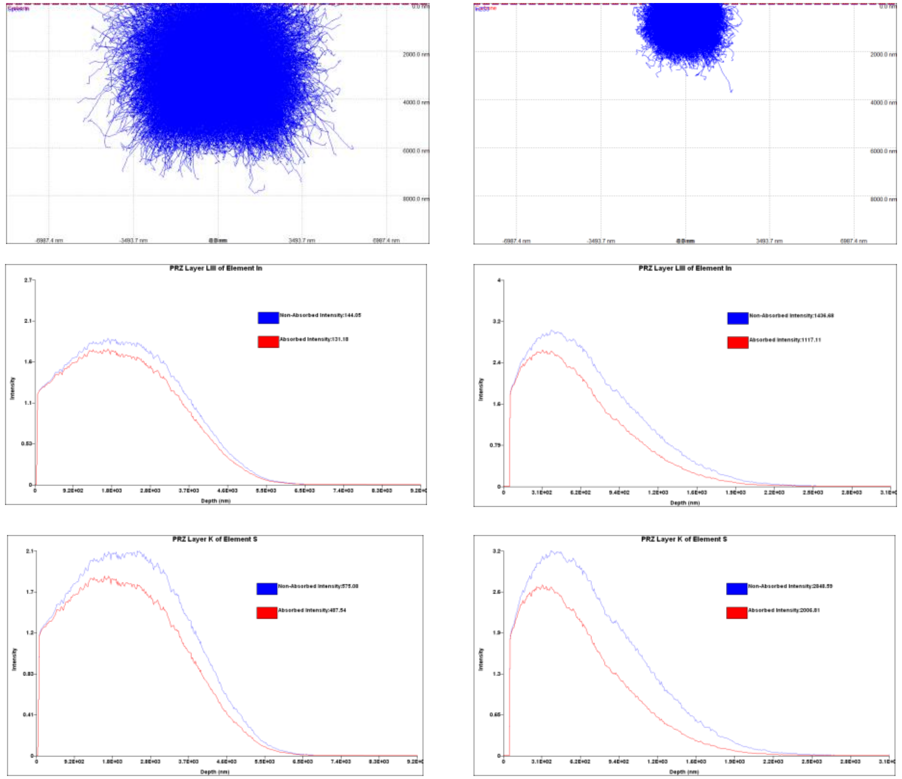
➔ The reviewers will ask us to be more precise on this point

Monte Carlo simulations

- Modelisation of the size and depth of the electron interaction volume
- Help to choose the appropriate polymer particles



SPEEK-In $In_2(SO_4)_3$ **In_2S_3**



Sample	Diameter of the electron intraction volume (µm)	Indium L_3 level emission		Sulfur K level emission	
		Maximum around (µm)	Tailing at (µm)	Maximum around (µm)	Tailing at (µm)
In_{23}	3.5	0.36	**2.2**	**0.31**	**2.2**
$In_2(SO4)_2$	5	0.74	**3.7**	**0.74**	**3.7**
SPEEK-In	7	1.7	**6**	**1.6**	**6.5**
SPEEK-In/Na 50/50	7	2.2	**6.5**	**2.3**	**6.5**

Other tests

Effect of coating

	Sample	Expected S/In ratio	Number of analyses	S%	In%	S/In ratio
Carbon coating	**SPEEK-In(III) from In(0)**	3/1	10	71.04	28.96	**2.464 ± 0.142**
Au/Pd coating	**SPEEK-In(III) from In(0)**	3/1	8	70.20	29.80	**2.362 ± 0.129**

Effect of accelerating voltage

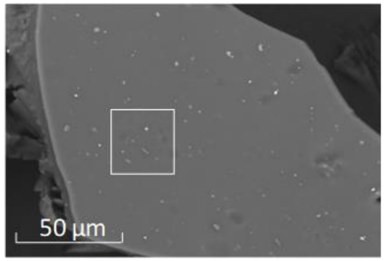
	Sample	Expected S/In ratio	Number of analyses	S%	In%	S/In ratio
10 kV	**$In_2(SO4)_2$**	3/2	10	59.20	40.80	**1.451 ± 0.016**
15 kV	**$In_2(SO4)_2$**	3/2	10	60.25	39.75	**1.516 ± 0.011**
20 kV	**$In_2(SO4)_2$**	**3/2**	**14**	**60.32**	**39.68**	**1.521 ± 0.011**
30 kV	**$In_2(SO4)_2$**	3/2	11	60.36	39.64	**1.522 ± 0.015**

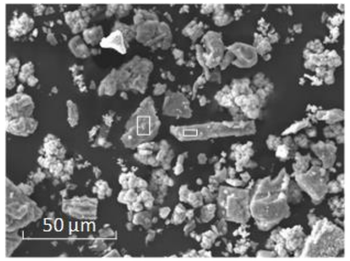
Reviewers

Reviewers actually gave interesting comments :

Geometric effects

- Polymer particles = flat
- Standards powders = rough





Beam damage and composition change

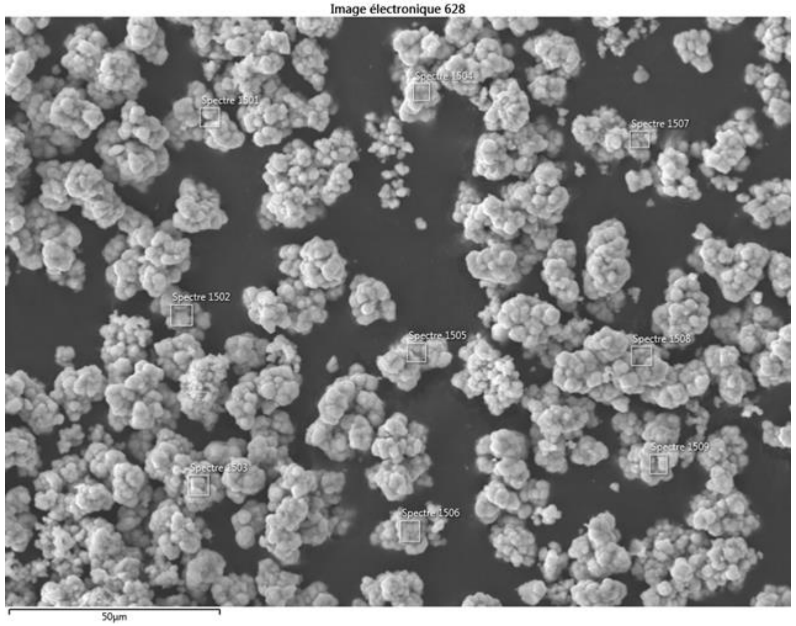
-"The SPEEK matrix is likely to be vulnerable to beam damage "

Sodium migration

- In the SPEEK-In/Na 50/50
- "Migration of Na under electron beam bombardment is a well known phenomenon"

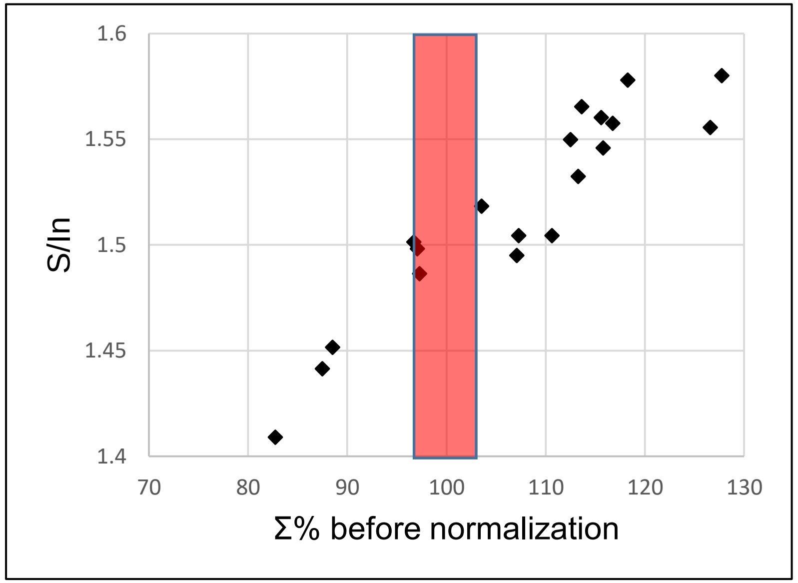
Geometric effects

- Polymer particles = flat
- Standards powders = rough ➔ need to be polished



Answer :

- Analyses at random locations
- Allows to verify the validity of the 96-104 % criterion
- Standards : 3/2 ratio obtained with the 96-104 % criterion
➔ no need for polished samples nor expensive standards
- Polymers : ratios stability above 100%



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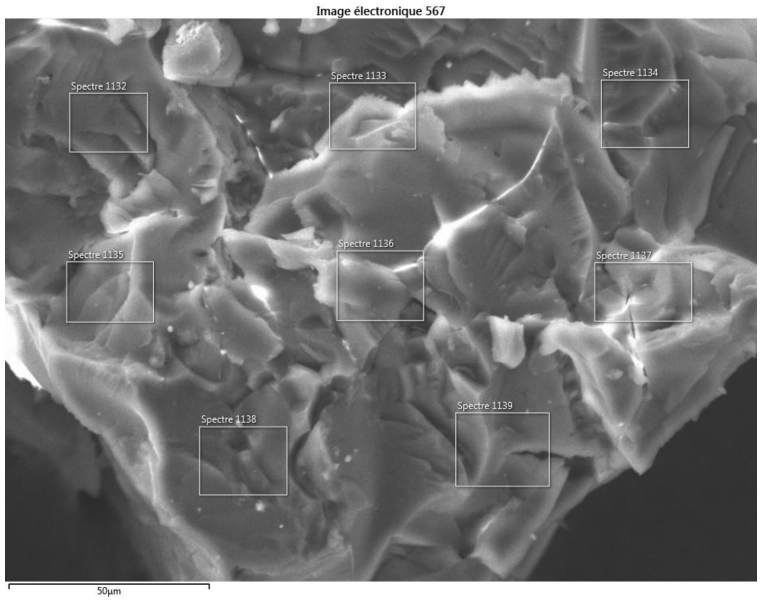

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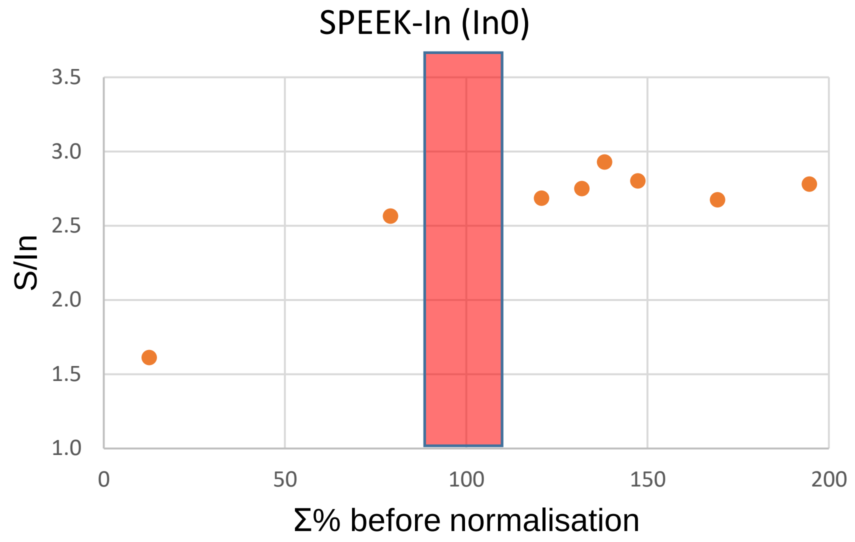

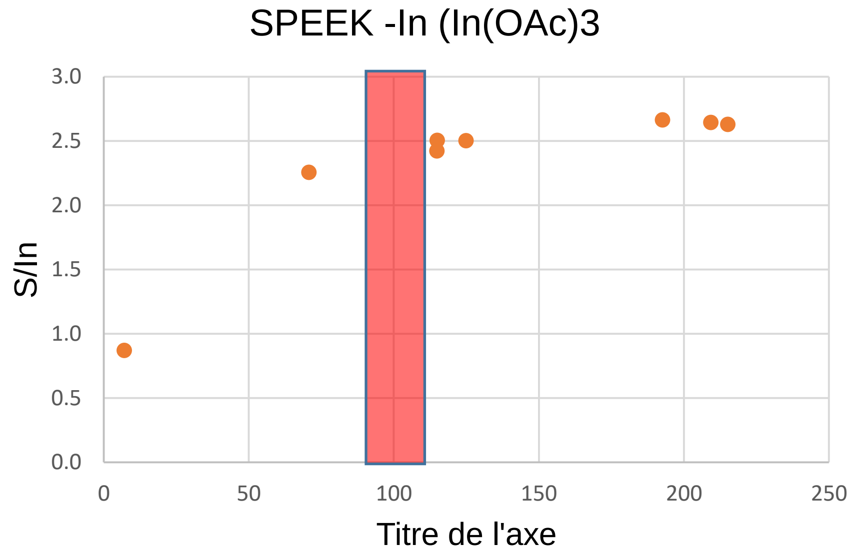

Beam damage

Beam damage and composition change

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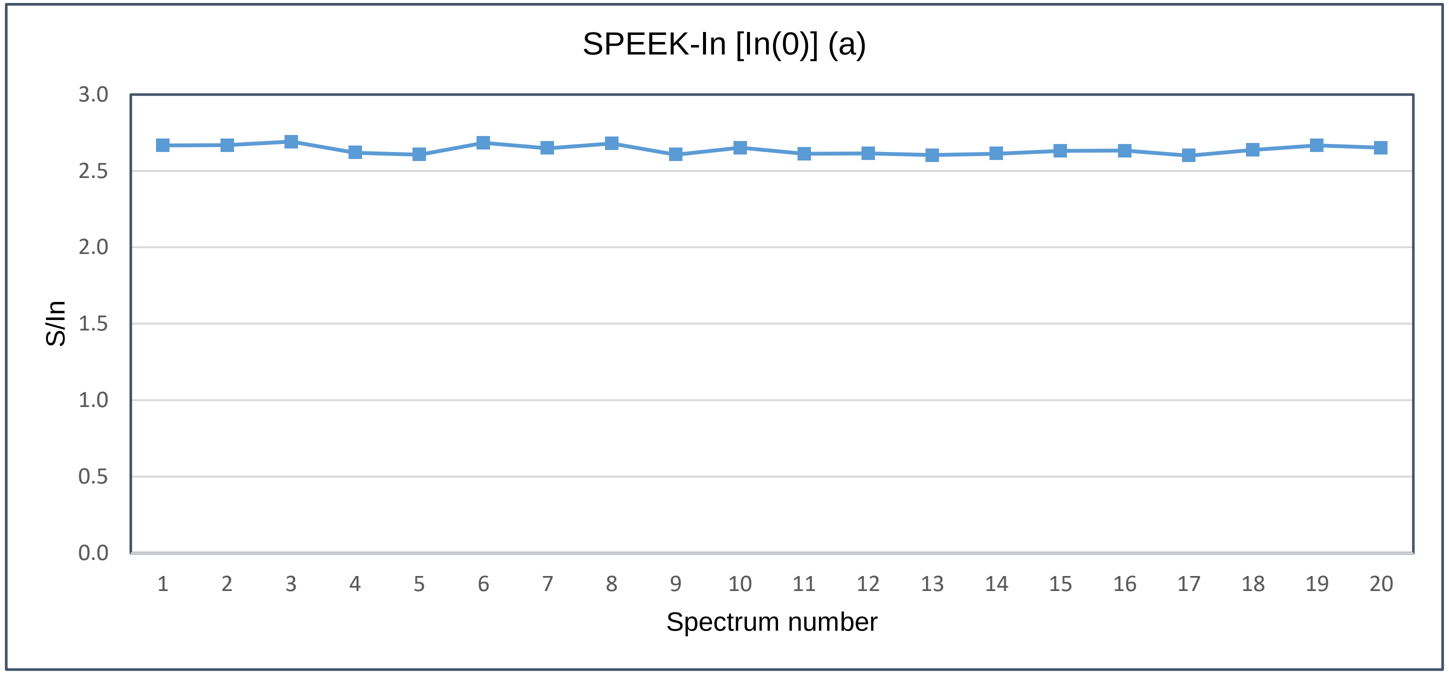
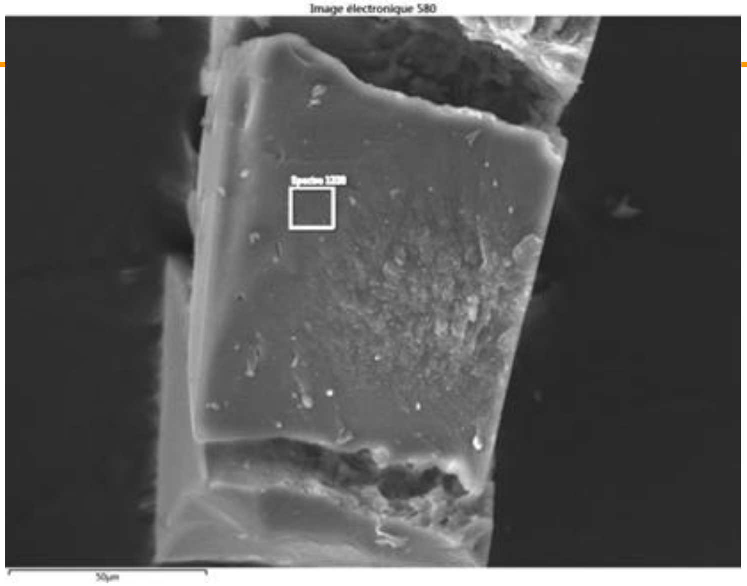
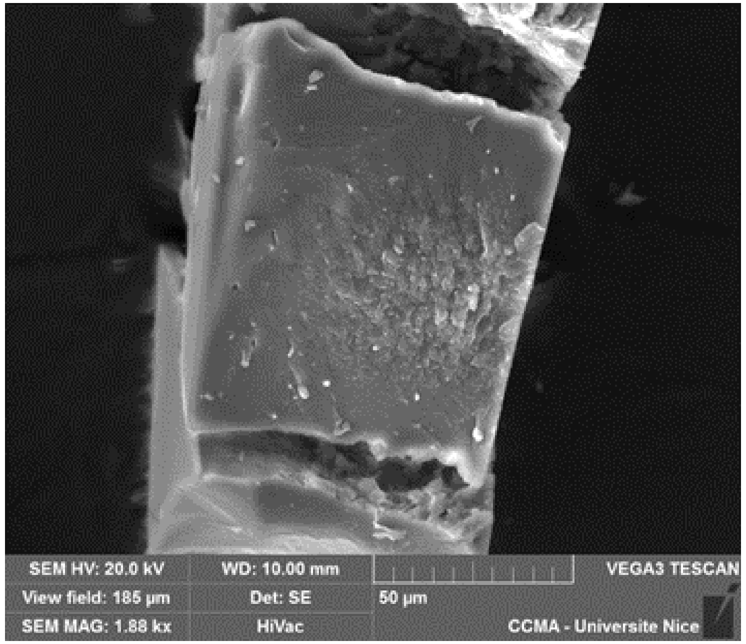






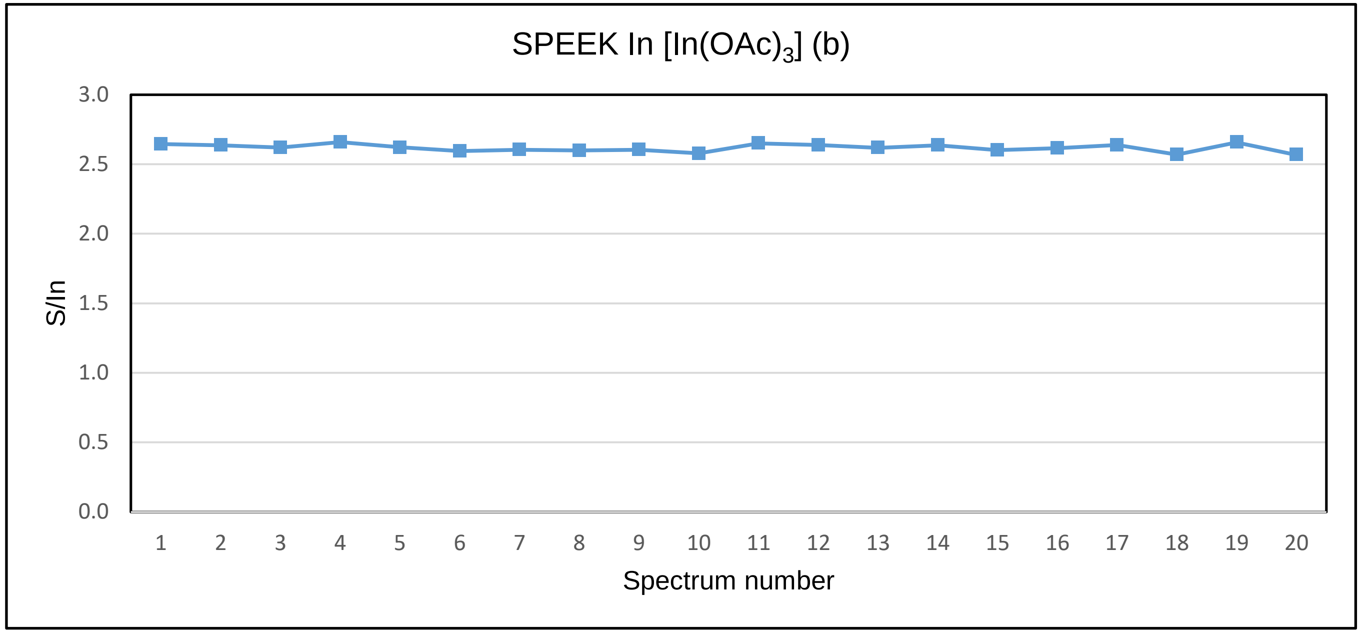
Answer

- 20 successive analyses on the same spot
- Minor visible damage
- No impact on the S/In ratio

Beam damage

Beam damage and composition change

-"The SPEEK matrix is likely to be vulnerable to beam damage "



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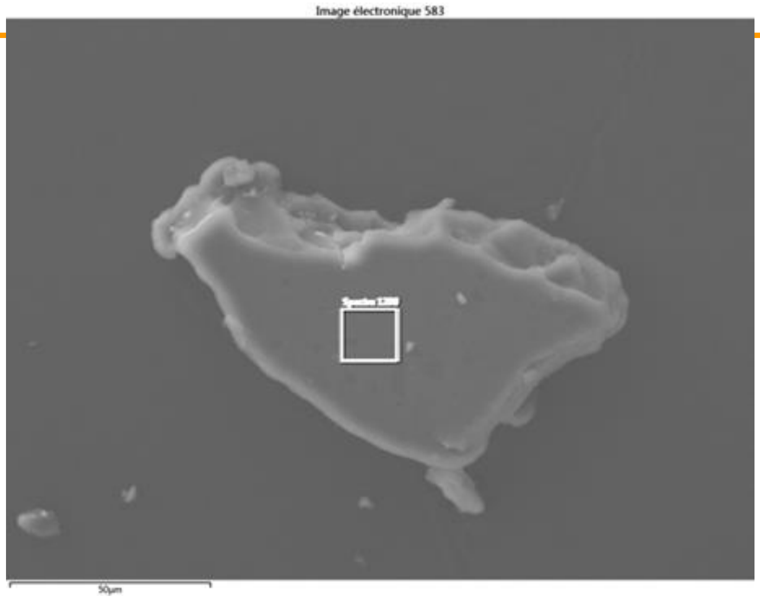

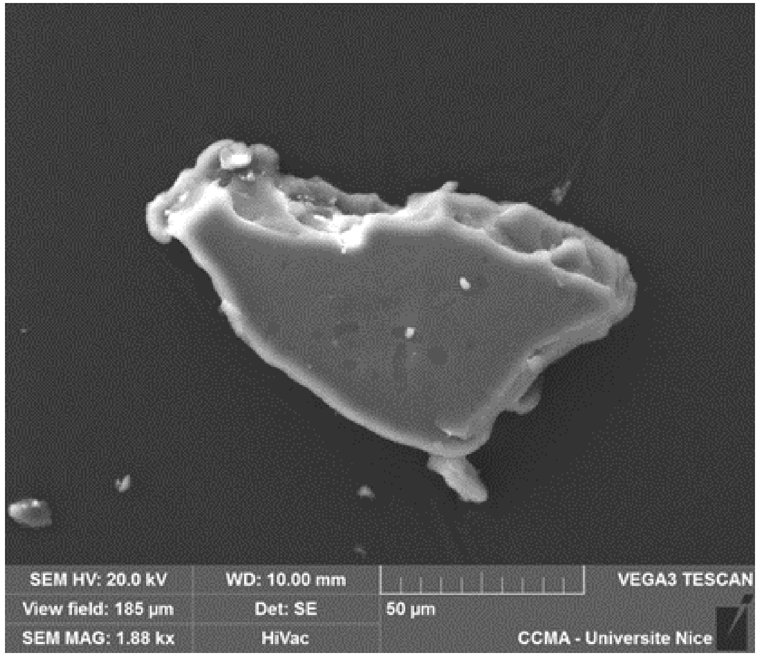

Sodium migration

Sodium migration

- In the SPEEK-In/Na 50/50

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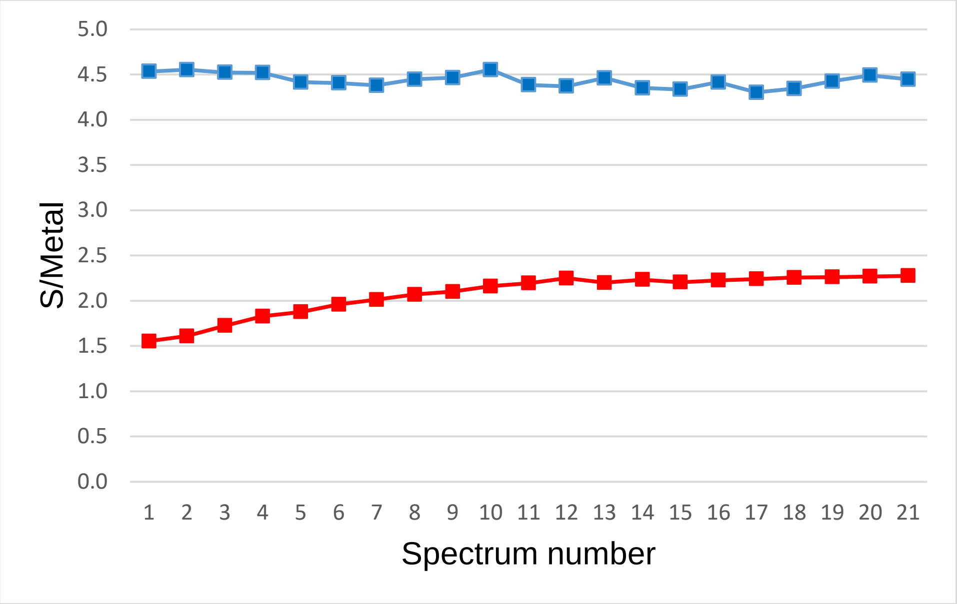

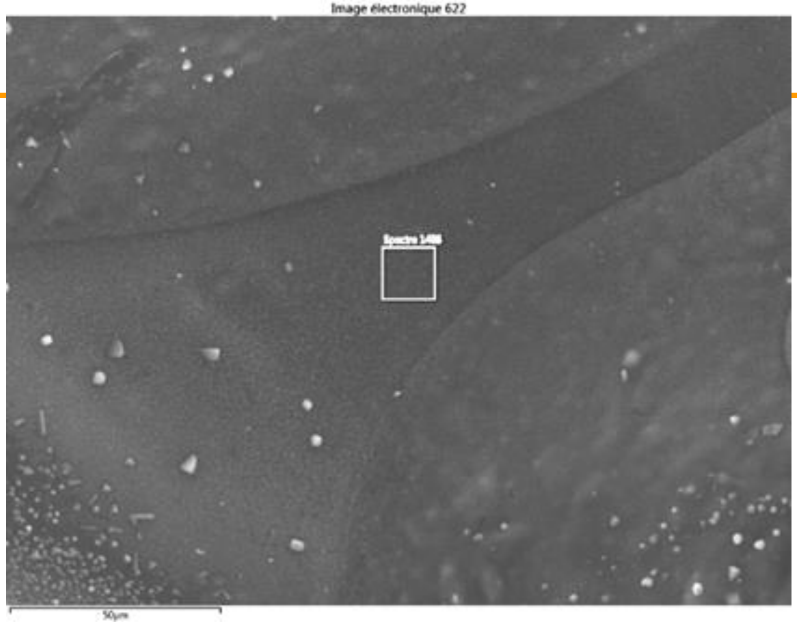

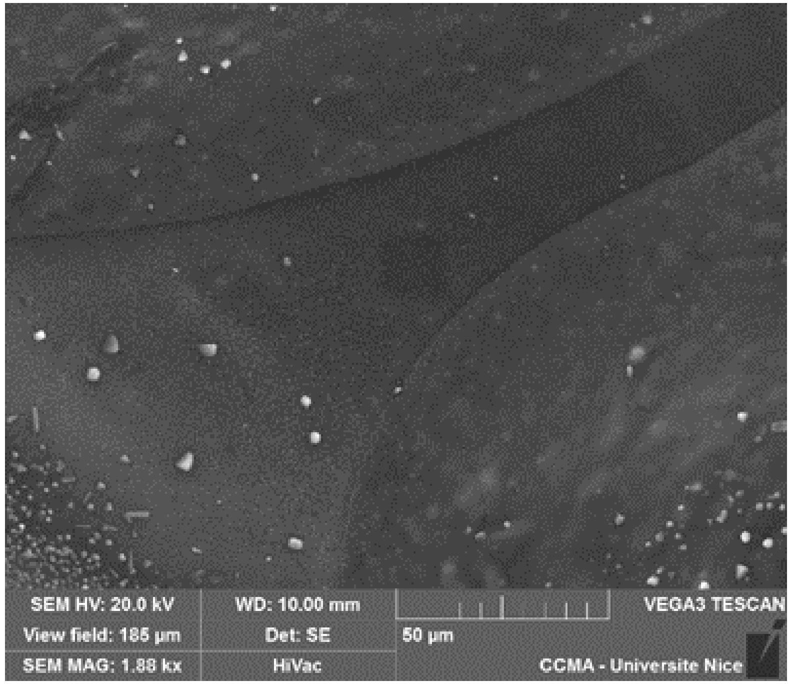

Answer

- Na migration is well evidenced by 20 successive analyses at the same spot

- I would be interested in explanations about the Na migration

Conclusions

- **EDX allows fast measurement of Indium(III) content in SPEEK-In(III)**

- Good precision and accuracy was obtained for the S/In ratio of calibrants.

- Precision on S/In ratio of SPEEK-In(III) by EDX is largely determined by the homogeneity of particles

- Number of sulfonate groups coordinated to In^{3+} are less than 3 in the prepared SPEEK-In(III)

- Simultaneous SEM imaging: complementary information on homogeneity, impurities…