

Centro de Energia Nuclear na Agricultura Campus "Luiz de Queiroz"

XRF Microscopy and Micro-Spectroscopy

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DVTEC – Laboratório de Instrumentação Nuclear

Campinas 22/08/2016



Overview



- □ Micro-speciation, what for?
- Sample preparation strategies
- PCA and LC
- □ Hands on: Quantitative analysis of Zn accumulation spot the
- body of Daphnia magna
 - **USB Stick**
- Lecture
- Data for hands on tutorial
- Literature







Micro-speciation, what for?



Speciation using hard X-ray

- Which spectroscopic tools?
- **XANES**
- Pre-edge
- EXAFS
- XRF weak lines



The SCR of NOx with NH₃ Examined by Novel X-ray Emission and X-ray Absorption Methods

of nanomaterials

T. Günter 1 · D. E. Doronkin 1,2 · A. Boubnov 1 · H. W. P. Carvalho 1,3 · M. Casapu 1 · J.-D. Grunwaldt 1,2



Why Micro-Speciation ?



A simple example from materials science

\Box A catalytic reactor: A tube filled with SiO₂+ few wt% of a transition metal



□ Is the metal chemical species the same along the tube?

Cu and Zn species depend on the position



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What about plants?

- □ Plants are far more complex than a glass tube with SiO₂ inside!
- Two approaches:
 Where is it?
 What is it?



Phaseolus vulgaris, stem cross section Tatiane Nishida, Masters Thesis CENA-USP







What about plants?

Plants are far more complex than a glass tube with SiO₂ inside!

- Two approaches:
 Where is it?
 What is it?
- Would you expect Fe and Ca to be homogenously distributed?

Phaseolus vulgaris, stem cross section Tatiane Nishida, Masters Thesis CENA-USP





Elemental distribution





Distribution is discrete!And the speciation?

Phaseolus vulgaris, stem cross section **Tatiane Nishida, Masters Thesis CENA-USP** Data record at LIN-CENA with an Orbis PC EDAX

Fe







Phytopatology

□ leaf of *Syzygium spp. c*arrying rust disease. At the disease spot one can see higher P and S concentration, whereas Ca is lower and K completely absent. Fe is distributed along the leaf presenting hotspots

















Sample preparation strategies

XRF Microscopy and Micro-Spectroscopy



cena

Is this procedure correct?



□ For micro distribution: maybe yes...

For speciation: probably not

w.agencia.cnptia.embrapa.br/Repositorio/muda 000fkmu488h02wyiv80sq98yq5k5aq1s.jp

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Some examples from our group @CENA-USP

□ In vivo spectroscopy



XAFS2-LNLS





PCA and LC

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Procedure/mechanics



How many components in total?

The same as the number of spectra

How many principal components?

PCA tells us you

How do I know whether a reference is part of the mixture? *Target transformation*Once you know how many PC and the references....

Perform linear combination fitting

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Example: Transformation of Mo under reaction conditions

How is Mo converted from one state to another?

Are there any intermediates?

How many principal components?



Journal of Catalysis 328 (2015) 208-215

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Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Activity and stability of Mo_2C/ZrO_2 as catalyst for hydrodeoxygenation of mixtures of phenol and 1-octanol

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Example: Transformation of Mo under reaction conditions

□ How many principal components?



Three PC seems to be suitable

Activity and stability of Mo_2C/ZrO_2 as catalyst for hydrodeoxygenation of mixtures of phenol and 1-octanol

Journal of Catalysis

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Example: Transformation of Mo under reaction conditions



Linear combination analysis

Activity and stability of Mo₂C/ZrO₂ as catalyst for hydrodeoxygenation of mixtures of phenol and 1-octanol

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Hands on:

Quantitative analysis of Zn accumulation spot in the body of *Daphnia magna*



Daphnia magna is a bio indicator

Chemical image recorded in our lab at CENA-USP







Daphnia magna is a bio indicator

Our equipment, Orbis PC, already plots the intensities





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Use a standard reference material to determine the sensitivity

Standard: ZnTe 47.70 μg cm⁻² Zn 16.16 μg cm⁻²





1st open the 'Padrão Zn micromatter' excel file
 2nd Since the reference is not homogenous, take the average signal

3rd Determine the equipment's sensitivity for Zn

http://www.micromatter.com/xrf.php



Plot the D. magnas' data

4th open the 'D_magna_nano_ZnO_treated' excel file
 5th Convert the intensities to concentration using the formula C =If / S
 6th Plot the data



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Plot the D. magnas' data



D. magna Joyce Paula, Doctoral Thesis CENA-USP Data recorded at our lab



Summary



Micro analysis:

Useful when samples are not homogenous in micro scale level

Allows you to locate and explore the chemical environment

□ Sample preparation:

□ Main rule: don't change your sample into something else

PCA and LC:

Helps you to solve mixtures

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Recommended Literature



Regular courses @CENA-USP / 2nd Semester

CEN5792- Principles of Nuclear and Electronic Spectroscopy (Aug-Sep)

CEN5785- Introduction to XRF and XAFS Spectroscopy (Oct-Dec)



Thank You

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http://hudson731.wix.com/xraysatcena Group of Applied X-ray Spectroscopy



Laboratório Nacional de Luz Síncrotron







□ Young Researcher FAPESP 2015-2019/05942-0

- Multi-User Equipment FAPESP 2015-2017/19121-8
- SPRINT FAPESP 2016-2018/50014-6
- FINEP 01.12.0535.00

USP-Santander Mobilidade Novos Docentes 2016/2017

Photons for Agriculture and Environment

X-rays Enlightening the Fate of Nanomaterials in Agriculture and Environment





Nota 7 Capes Título: Ciências





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