Analytica Chimica Acta 822 (2014) 1–22

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

# Speciation of metal(loid)s in environmental samples by X-ray absorption spectroscopy: A critical review

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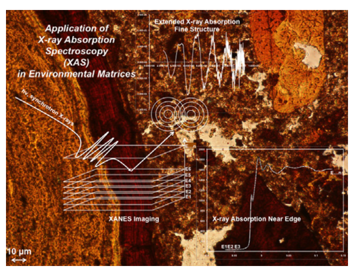
## HIGHLIGHTS

- Strengths and weaknesses of XAS as a speciation technique are reviewed.
- We explain the novel XFM approach referred to as *XANES image stacking*.
- The X-ray absorption process is explained tangibly.
- Linear combination fitting and abstract factor analysis of mixtures is explained.
- Examples of XAS on nanoparticles, redox species, ores and process tailings.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 22 July 2013
Received in revised form 12 February 2014
Accepted 27 February 2014
Available online 5 March 2014

*Keywords:*
Synchrotron
X-ray absorption spectroscopy
Imaging
Chemical state
Abstract factor analysis

## ABSTRACT

Element specificity is one of the key factors underlying the widespread use and acceptance of X-ray absorption spectroscopy (XAS) as a research tool in the environmental and geo-sciences. Independent of physical state (solid, liquid, gas), XAS analyses of metal(loid)s in complex environmental matrices over the past two decades have provided important information about speciation at environmentally relevant interfaces (e.g. solid–liquid) as well as in different media: plant tissues, rhizosphere, soils, sediments, ores, mineral process tailings, etc. Limited sample preparation requirements, the concomitant ability to preserve original physical and chemical states, and independence from crystallinity add to the advantages of using XAS in environmental investigations. Interpretations of XAS data are founded on sound physical and statistical models that can be applied to spectra of reference materials and mixed phases, respectively. For spectra collected directly from environmental matrices, abstract factor analysis and linear combination fitting provide the means to ascertain chemical, bonding, and crystalline states, and to extract quantitative information about their distribution within the data set. Through advances in optics, detectors, and data processing, X-ray fluorescence microprobes capable of focusing X-rays to micro- and nano-meter size have become competitive research venues for resolving the complexity of environmental samples at their inherent scale. The application of μ-XANES imaging, a new combinatorial approach of X-ray fluorescence spectrometry and XANES spectroscopy at the micron scale, is one of the latest technological advances allowing for lateral resolution of chemical states over wide areas due to vastly improved data processing and detector technology.



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http://dx.doi.org/10.1016/j.aca.2014.02.044
0003-2670/

**Contents**



Markus Gräfe is a principal research scientist in the Division of Process Science & Engineering of the Commonwealth Scientific Industrial Research Organisation (CSIRO) in Perth (Western Australia). Markus received his PhD degree in Plant & Soil Sciences from the University of Delaware and has more than 10 years experience with synchrotron X-ray based research. He has conducted experiments at synchrotron facilities in the United States, Japan and Taiwan. His research focus is on interfacial processes of metals and metalloids in environmental and hydrometallurgical scenarios.

Erica Donner is Research Fellow and an ARC Future Fellow at the Centre for Environmental Risk Assessment and Remediation, University of South Australia. She received a PhD in Soil Chemistry from the University of Reading, UK. Erica's research focuses on biogeochemical processes controlling metal(loid) mobility and bioavailability. She has conducted synchrotron research at facilities in Australia, Japan, Italy and the USA.

Richard Collins is a Senior Research Fellow and Australian Research Council Future Fellow at the University of New South Wales (UNSW) and the 2012 recipient of the Australian Fulbright Senior Scholarship in Nuclear Science and Technology. He completed his PhD in soil science at the University of Adelaide in 2002 and worked at the French Atomic Energy Commission for a number of years before commencing at UNSW. His research focuses on the biogeochemically-driven transformations of redox-sensitive elements and has a particular interest in applying non-traditional synchrotron techniques (resonant inelastic X-ray scattering, high resolution and quick-scanning X-ray absorption spectroscopy and X-ray Raman scattering) to this area of research to overcome the technical/experimental limitations imposed by classical X-ray absorption spectroscopy.

Enzo Lombi is Professor and Australian Research Council Future Fellow at the University of South Australia. He received a PhD in agricultural chemistry from the Catholic University of Piacenza, Italy. Enzo has held positions at the University of Agricultural Science in Vienna, at Rothamsted Research (UK), at CSIRO Land and Water in Adelaide and at the University of Copenhagen. His major research focus is on the biogeochemistry of trace elements with a special interest in synchrotron-based techniques for the investigation of biological and environmental processes. He is the current President of the International Society of Trace Element Biogeochemistry.

## 1. Importance of metal(loid) speciation and its challenges

Metals and metalloids play a key role in biological systems and greatly influence ecosystem functioning and resilience. Several metal (loid)s are essential for biological functioning, however, they all have the potential to be toxic when their bioavailability exceeds the homeostatic control of an organism. The bioavailability of metal (loid)s is closely interlinked with their chemical speciation. Various definitions of bioavailability have been proposed, which differ on the basis of the organism considered. For instance, Sposito [1] defined bioavailability for plants in these terms: 'A chemical element is bioavailable if it is present as, or can be transformed readily to, the free-ion species, if it can move to plant roots on a time scale that is relevant to plant growth and development, and if, once absorbed by the root, it affects the life cycle of the plant'. In the case of humans, bioavailability can be defined as 'The fraction of an administered dose that reaches the central (blood) compartment, whether from the gastrointestinal tract, skin, or lungs' [2]. In both cases the link between speciation and bioavailability is apparent.

As is the case for bioavailability, chemical speciation has also been defined in many different ways. Parker et al. [3] gave the definition: 'Speciation of an element is the distribution of elements among their various chemical and physical forms, and possible oxidation states. These include their free ions, complexes, ion pairs, and chelates in solution, and their amorphous and crystalline solid-phases – all of which influence the reactivity, mobility, and