

# XANES speciation of mercury in three mining districts – Almadén, Asturias (Spain), Idria (Slovenia)

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The mobility, bioavailability and toxicity of mercury in the environment strongly depend on the chemical species in which it is present in soil, sediments, water or air. In mining districts, differences in mobility and bioavailability of mercury mainly arise from the different type of mineralization and ore processing. In this work, synchrotron-based X-ray absorption near-edge spectroscopy (XANES) has been taken advantage of to study the speciation of mercury in geological samples from three of the largest European mercury mining districts: Almadén (Spain), Idria (Slovenia) and Asturias (Spain). XANES has been complemented with a single extraction protocol for the determination of Hg mobility. Ore, calcines, dump material, soil, sediment and suspended particles from the three sites have been considered in the study. In the three sites, rather insoluble sulfide compounds (cinnabar and metacinnabar) were found to predominate. Minor amounts of more soluble mercury compounds (chlorides and sulfates) were also identified in some samples. Single extraction procedures have put forward a strong dependence of the mobility with the concentration of chlorides and sulfates. Differences in efficiency of roasting furnaces from the three sites have been found.

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**Keywords:** mercury speciation; XANES; Almadén; Idria; Asturias; bioavailability.

## 1. Introduction

Assessing the distribution and mobilization of heavy metals in the environment as a result of natural processes or anthropogenic activities is of special relevance in mining districts. Mercury (Hg) is one of the most toxic heavy metals, as some of its compounds can be absorbed by living tissues in large doses and these compounds or their derivatives can concentrate and be stored over long periods of time. Through the food chain, mercury can eventually affect human beings and cause chronic or acute damage (Förstner, 1998). From a toxicological point of view, the toxicity of heavy metals is primarily controlled by the dose and the corresponding chemical speciation. Accordingly, many recent studies have been devoted to assess heavy metal speciation either through direct or indirect approaches (Horvat, 2005). The most widely used methods are based on sequential selective extractions (Bloom *et al.*, 2003;

Kocman *et al.*, 2004) and X-ray absorption spectroscopy (XAS) techniques (Kim *et al.*, 2000, 2003, 2004; Slowey *et al.*, 2005*a,b*; Bernaus *et al.*, 2005*a,b*, 2006*a,b*). Alternative techniques are based on Hg pyrolysis followed by AAS detection, which allows the differentiation among cinnabar, metallic Hg and matrix-bound Hg (Biester *et al.*, 1999, 2000). XAS techniques have been shown to provide reliable information on the speciation of mercury without requiring sample pretreatment (Kim *et al.*, 2004; Slowey *et al.*, 2005*a,b*; Bernaus *et al.*, 2006*a*). The application of XAS to mercury speciation provides results with good consistency in terms of Hg–S/Hg–non-S and Hg–insoluble/Hg–soluble ratios according to wet-chemistry data (Kim *et al.*, 2003). On the other hand, one of the main limitations of the XAS methods refers to their high detection limits.

Among XAS techniques, both EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption