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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Iron speciation and local order in industrial and urban aerosol and in Saharan dust: characterization of specific aerosol sources	**Experiment number**: EV-201
Beamline: BM08	**Date of experiment**: from: 22/09/2016 to: 27/09/2016	**Date of report**: 01/02/2017
Shifts: 12	**Local contact(s)**: Giovanni Orazio Lepore	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

PETROSELLI Chiara *(PhD student), Università degli Studi di Perugia Dipartimento di Chimica, Biologia e Biotecnologie

MORONI Beatrice, Università degli Studi di Perugia Dipartimento di Chimica, Biologia e Biotecnologie

CAPPELLETTI David, Università degli Studi di Perugia Dipartimento di Chimica, Biologia e Biotecnologie

Report:

Scientific Background

Atmospheric aerosol is a suspension of solid or liquid particles in the atmosphere. Its chemical composition is very variable and depends on sources (natural or anthropogenic) and on atmospheric processing (ageing and mixing). Aerosol physico-chemical properties such as mass and number concentration, size distribution, chemical composition and mineralogy influence its impact on visibility, climate and human health. XAS techniques have been recently applied to aerosol samples in order to determine local order and valence state of iron in suspended particulate matter[1,2], but a characterization of Fe-bearing aerosol sources is auspicable to better understand the pure aerosols' characteristics and put down the basis for a detailed understanding of mixed aerosol types. The aim of this experimental session was the investigation of iron speciation in steel production emission fumes, sampled in the chimney stacks of the ThyssenKrupp – Acciai Speciali Terni (TK-AST) plant located in the Terni city (Central Italy). Steel production emissions consists mainly in iron spinels where the Fe atoms can be substituted by other metals (such as Cr, Ni or Mn) present in the welding matrices. These compounds are poorly soluble so iron is less bioavailable with respect to that included in the alluminosilicatic matrix of Saharan dust.

Experimental details, measurement strategy

XAS (XANES and EXAFS) spectra at the Fe (7112 eV), Cr (5989 eV), and Mn (6539 eV) k-edge have been collected at the CRG-LISA beamline (BM08). Spectra have been recorded at room temperature in moderate vacuum conditions. Three scans per sample have been recorded in fluorescence mode, in order to improve the signal-to-noise ratio. However, no evidence of beam damage was found by comparing the first and the last spectrum. For each sample, it has also been recorded the transmission spectrum of a reference (metallic Fe or Mn foil) in order to provide internal energy calibration.

Samples details

Aerosol samples were collected inside the chimney stacks of the TK-AST steel production plant in Terni. The four investigated samples correspond to two smelters and two converters of the plant. The sample collected at the rural regional background station of Monte Martano[3] on December 1st 2014 during an extremely intense Saharan dust outbreak and analysed in the 08-01-999 experiment at the Fe k-edge, was analysed at the Mn k-edge. The mixed urban Saharan sample collected at the urban station of Borgo Rivo in Terni on the same day was investigated at the Fe k-edge. All the samples were collected on quartz fiber filters (Whatman QM 47mm) and the filter spectrum was recorded for every metal in order to evaluate its contribution to the samples, which resulted always negligible.

Results obtained

During the experimental session at the CRG-LISA beamline we measured the four samples of steel production fumes at Fe, Mn and Cr k-edges. The four spectra are very similar to each other suggesting the same local order for the three metals in every part of the plant. The differences we observed in the chemical characterization of the four samples are not evident in the XAS analysis.

As shown in figure 2 and 3, the spectra quality is better for the more loaded filters (E45 and E52) and it decreases for the less loaded ones. These differences are far less evident in the Fe spectra (figure 1).

As regards Fe, the AST spectra are very similar to that of magnetite and preliminary fitting tests show that it can be reproduced using both the tetrahedral and the octahedral magnetite paths. Marked differences are evident between the AST and the urban sample, which is very similar to that of Saharan dust recorded during the 08-01-999 experiment.

The Cr spectra of the four samples are very similar. Cr^{3+} should substitute Fe^{3+} in the spinel structure, this will be investigated in detail together with the possible presence of Cr^{6+}.

Regarding Mn, remarkable differences between the AST and the Saharan dust samples are eyecatching; the first show an oscillatory structure that suggests the interaction with other 3d metals, while in the latter we can recognize only a first shell interaction. For the AST samples, the hypothesis of Mn^{2+} substituting Fe^{2+} in octahedral sites will be tested.

Quantitative fitting of the pre-edge features and of the EXAFS part of the spectrum with specific codes (Athena and Artemis[4]) is actually in progress.

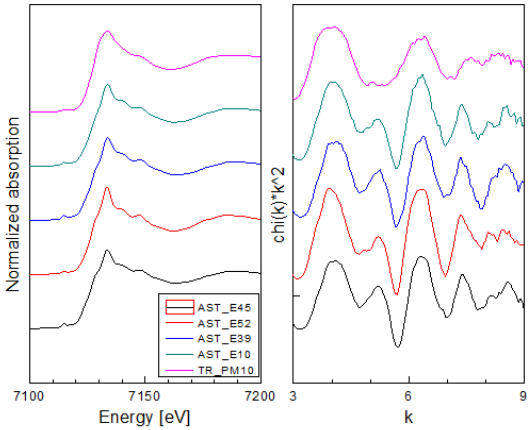

Figure 1 – XAS spectra at the Fe k-edge: AST samples and urban mixed sample (TR_PM10)

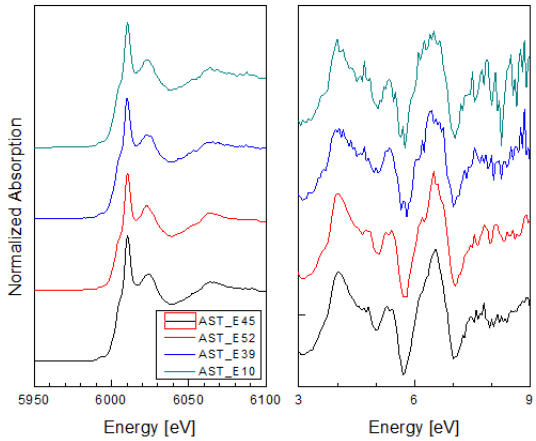

Figure 2 – XAS spectra at the Cr k-edge: AST samples

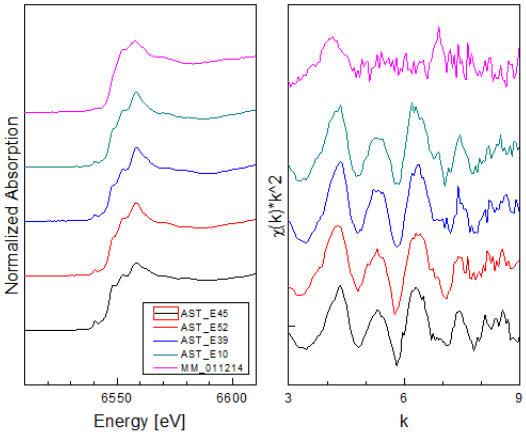

Figure 3 – XAS spectra at the Mn k-edge: AST samples and Saharan dust sample (MM_011214)

References

[1] D'acapito F. et al. "Local order and valence state of Fe in urban suspended particulate matter" Atmospheric Environment 99, 582-586 (2014)

[2] Majestic B. J. et al. "Application of synchrotron radiation for measurement of iron red-ox speciation in atmospherically processed aerosols" Atmospheric Chemistry and Physics 7, 2475-2487 (2007)

[3] Moroni B. et al. "Ground-based measurements of long-range transported aerosol at the rural regional background site of Monte Martano (Central Italy)" Atmospheric Research 155, 26-36 (2015)

[4] Ravel B. and Newville M. "ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT" Journal of Synchrotron Radiation ISSN 0909-0495