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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:** Red-ox speciation and mixing state of iron in Saharan dust	**Experiment number**: 08-01-999
Beamline: BM08	**Date of experiment**: from: 29/10/2015 to: 03/11/2015	**Date of report**: 15/12/2015
Shifts: 12	**Local contact(s)**: Alessandro Puri	*Received at ESRF:*

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Report:

Scientific Background

Saharan dust is a peculiar aerosol type originated by wind erosion on the Saharan desert surface[1]. This aerosol, rich in Fe-bearing minerals such as alluminosilicates and iron oxides and hydroxides, is transported for long distances across the Atlantic Ocean, where it represents the major source of iron for marine ecosystems[2], and over Europe[3]. The Mediterranean basin is often affected by this kind of events of transport and the identification and characterization of mineral dust has become a key issue in European atmospherical research. Mass and number concentration, size distribution, chemical composition and mineralogy of dust influences its impact on visibility, climate and human health. Moreover, chemical composition of aerosol can change during its permanence in atmosphere by means of many mixing and ageing processes, such as cloud interactions and photochemical reactions[4]. XAS techniques have been recently applied to aerosol samples in order to determine local order and valence state of iron in suspended particulate matter[5,6], however, a study of long range transported Saharan dust has not been carried out yet. The aim of this experimental session was the investigation of iron speciation in desert dust collected during a very intense event of transport and to compare the results obtained for desert dust to other kind of particulate matter of different origin (anthropogenic, regional) which has undergone a different fate in atmosphere.

Experimental details, measurement strategy

XAS (XANES and EXAFS) spectra at the Fe K-edge (7112 eV) have been collected at the CRG-LISA beamline (BM08). For each sample the XAS spectrum has been recorded in fluorescence mode with the sample positioned 45° with respect to the beam, and it has been also recorded the spectrum of a reference sample (metallic Fe foil) for all the experiments in order to provide internal energy calibration of the monochromator for each spectra. Most of the samples had a Fe concentration far above the beamline lower limit for fluorescence measurements (10^{13} atoms/cm^2), however, several spectra per sample have been averaged in order to improve the signal-to-noise ratio. For the only really diluted sample, two pieces of the polycarbonate sampled filter have been impilated in order to increase sensitivity.

Samples details

Aerosol samples were collected at two sampling sites: the rural regional background station of Monte Martano[7] and the urban station of Borgo Rivo, Terni, by means of three different kinds of samplers. High volume sampler and low volume samplers deposited aerosol on quartz fiber filters of different thickness, while polycarbonate filters have been sampled with an additional low volume sampler at Monte Martano. Between November 30th and December 1st 2014, an outstanding Saharan dust event has been observed in Central Italy. In this experiment we analysed several samples of the same Saharan dust event collected in different conditions: clean background conditions at Monte Martano and heavily polluted urban conditions in Terni. Comparison between Saharan and non Saharan aerosol samples of different origin, and between different sampling substrates has also been carried out.

Figure 1 – Sampling sites location: Monte Martano (MM) 1100m a.s.l. and Terni (TR) 130m a.s.l.

Results obtained

During the experimental session at the CRG-LISA beamline we were able to measure all the 16 selected samples: eleven samples belonging to the Saharan dust event occurred in December 2014, one mixed saharan dust sample and four samples of aerosol of different provenience. Up to three XAS spectra (between 6900 and 7700 eV) have been acquired for each sample and the obtained spectra have been then averaged to improve the signal-to-noise ratio. As shown in figure 2, the spectra quality is not the same for all the samples and results lower for the ones which were less concentrated, however, it allowed to perform a quantitative analysis on both the XANES and the EXAFS part of the spectrum for each one of the samples measured. Quantitative fitting of the pre-edge features (figure 3) and of the EXAFS part of the spectrum with specific programmes such as Athena and Artemis[8] is actually in progress.

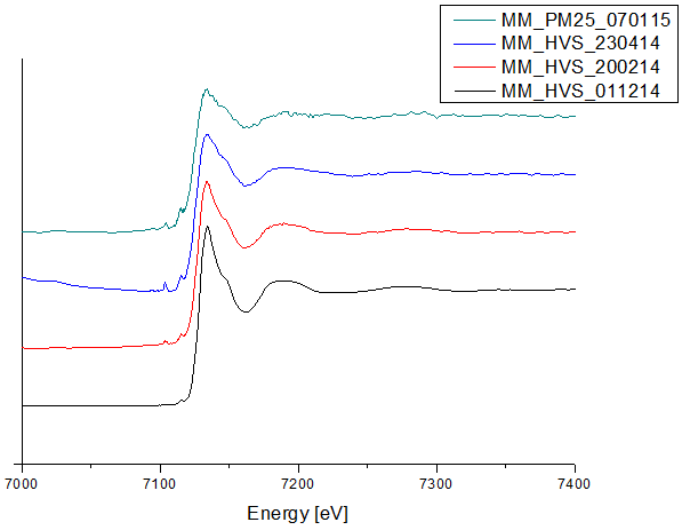

Figure 2 – XAS spectra of different filter samples

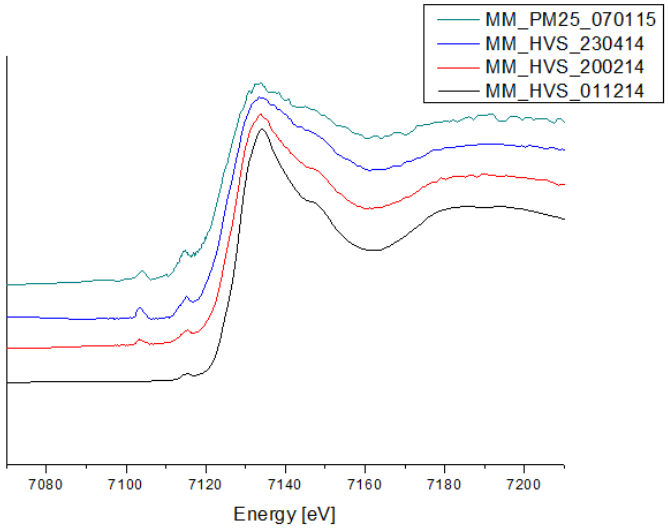

Figure 3 – XANES spectra: differences in the pre-edge features

References

[1] Goudie A. S. and Middleton N. J. "Saharan dust storms: nature and consequences" Earth Science Reviews 56, 179-204 (2001)
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[3] Mattsson J. and Nihlèn T. "The transport of Saharan dust to southern Europe: a scenario" Journal of Arid Environments 32, 111-119 (1996)
[4] Nickovic S. et al. "Atmospheric processing of iron carried by mineral dust" Atmospheric Chemistry and Physics 13, 9169-9181 (2013)
[5] D'acapito F. et al. "Local order and valence state of Fe in urban suspended particulate matter" Atmospheric Environment 99, 582-586 (2014)
[6] 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)
[7] 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)
[8] Ravel B. and Newville M. "ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT" Journal of Synchrotron Radiation ISSN 0909-0495