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Fe and Mn speciation in road dust particles by XAS

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Abstract. The speciation of Fe and Mn in road dust particles, collected on the walls and floor of the ventilation shaft of Traforo del San Bernardo highway tunnel, was studied by means of XAS spectroscopy. Absorption spectra were recorded on BM8 at the ESRF (Grenoble, France) at the Fe and Mn K-edges. Several reference compounds were measured along with the samples, and a standard reference material of road dust (BCR723) was also analyzed. Principal Component Analysis (PCA), Least Square Fitting (LSF), analysis of the edge features, and structural refinements (EXAFS), were applied to give complementary information on the speciation, average oxidation state and local structure of Fe and Mn in the collected samples.

1. Introduction

The study of elemental speciation in atmospheric Particulate Matter (PMx, where x indicates particle size, in microns) and in road dust is important under several aspects. In particular, it helps to understand the formation and origin of air pollution, as well as to evaluate the toxicity of fine particles in road dust, which actually contribute to airborne particulate via resuspension [1]. Aim of this work is the study of the speciation of iron and manganese in road dust samples collected on the walls and floor of the ventilation air shaft of Traforo del San Bernardo highway tunnel. Also due to the high dilution of Mn and Fe in the samples (35 and 2 mg/g, respectively), this is accomplished by means of X-ray Absorption Spectroscopy, which has been shown to be a useful tool in a wide range of environmental issues [2,3,4]. The ventilation air shaft of Traforo del San Bernardo tunnel is an ideal sampling area, because inside it the road dust: i) represents the average emission from different vehicles that utilize different fuels; ii) comes from only vehicular emission (no other source of particulate is relevant); iii) is not affected by important temperature fluctuations throughout the year; iv) photo-induced effects, such as photochemical reactions, are prevented.

2. Experimental

Samples were collected at different heights from the road level and sieved, after drying, using four decreasing meshes. Only particles with size in the ranges 63–250 μm and <63 μm were analyzed. The
set of reference compounds included metallic Fe foil, FeO, Fe$_2$O$_3$, Fe$_3$O$_4$, FeCl$_3$, Fe(NO$_3$)$_3$, FeSO$_4$, as well as Mn metal foil, MnO$_2$, MnO, Mn$_2$O$_3$, Mn$_3$O$_4$, MnCl$_2$, MnSO$_4$. A standard reference material of road dust, BCR-723 [5], was also analyzed. XAS measurements were performed at low temperatures (77K) at the Mn and Fe K-edges (6539 eV and 7112 eV, respectively) on the BM8 beamline at the European Synchrotron Radiation Facility (Grenoble, France). The energy resolution at the Fe and Mn K-edges energies was about 0.4 eV and the beam spot size on the sample about 250(H) x 200(V) µm$^2$.

Figure 1. Absorption spectra of all the samples and reference compounds studied in this work. Spectra are normalized to unity and shifted for clarity.

3. Data analysis and results

3.1. PCA and LSF

Semi-quantitative information on samples’ speciation was obtained by means of Principle Component Analysis (PCA) and consequent Least Square Fitting (LSF) using reference compounds, which are well established procedures for environmental samples [6]. PCA allows determining minimum number of components necessary to reconstruct an experimental spectrum, and identifying the best candidates among a set of reference spectra. LSF can give an estimation of the relative concentration of the candidates selected by PCA. It is worth noting that these procedures only give consistent results if the reference set chosen is fully representative of the samples’ composition. PCA and LSF procedures were applied on the XANES region of the absorption spectra. Structural parameters were also refined applying EXAFS analysis up to the fourth coordination shell (when present). Complementary information on the average oxidation state of the samples were carried out following distinct routes for Mn and Fe edges, both based on the analysis of the edge features of the absorption spectra [6,7].

| Sample    | Group | %Fe$_2$O$_3$ | %FeCl$_3$ | %FeSO$_4$ | Group | %Mn$_2$O$_3$ | %MnCl$_2$ |
|-----------|-------|--------------|-----------|-----------|-------|--------------|-----------|
| 1II63     | 1     | 73           | 19        | 9         | 1     | 50           | 53        |
| 1II63-250 | 1     | 67           | 30        | 3         | 1     | 56           | 46        |
| 4II63     | 1     | 69           | 25        | 5         | 1     | 53           | 47        |
| 4II63-250 | 1     | 62           | 38        | -         | 1     | 64           | 40        |
| BII63     | 1     | 52           | 48        | -         | 1     | 51           | 49        |
| PAI63     | 1     | 74           | 18        | 8         | 3     | 26           | 76        |
| EXTM63    | 1     | 79           | 9         | 12        | 3     | 28           | 73        |
| BCR723    | 1     | 71           | 20        | 9         | 1     | 62           | 40        |
| PAI63-250 | 2     | 46           | 54        | -         | 1     | 62           | 40        |
| EXTPD63   | 2     | 32           | 65        | -         | 3     | 74           | 33        |
| EXTTP63   | 2     | 45           | 55        | -         | 1     | 53           | 49        |
| EXTP63-250| 2     | 39           | 53        | -         | 2     | 70           | 32        |

Table 1. Relative compositions for each sample as determined from LSF procedure. The group assignment for each sample is also reported. Errors on percentage are about 5%. No data is available for sample BCR723 at the Mn K-edge.

3.1.1. Fe K-edge results

PCA suggests that three components are necessary to reconstruct samples’ spectra: Fe$_2$O$_3$, FeCl$_3$, and FeSO$_4$. An indication on the samples’ composition was obtained by fitting the XANES spectra using a weighted linear combination of the reference spectra suggested by PCA. For all samples, the major Fe species present resulted Fe$_2$O$_3$ and FeCl$_3$, while a less important amount of FeSO$_4$ is present in some of the samples (table 1). Plots of this procedure (LSF) at the Fe edge are reported in figure 2a. Samples can be divided in two groups having similar compositions: Group 1, where Fe$_2$O$_3$ is the major component and FeSO$_4$, while present, have amounts of less than 10%; and Group 2, where FeCl$_3$ is predominant and no FeSO$_4$ is revealed. This separation in groups is in agreement with different shape of the absorption spectra for the two groups (figure 1). Also pre-edge peaks and EXAFS analysis,
Figure 2. Selected LSF at Fe (a) and Mn (b) edges representative of each group. Solid lines are the experimental spectra, dotted lines are fits. Estimation of the average oxidation state of the samples at the Fe (c) and Mn (d) edges. Up triangles indicate reference oxides, crosses are the calculated average oxidation state of the samples. Described in the following, confirmed this group assignment. Following the method by Wilke et al. [7] we are able to determine the average samples’ oxidation state. The obtained values (figure 2c) are consistent with PCA and LSF results: samples belonging to Group 1, and having higher relative amount of Fe$_3$O$_4$ (and FeSO$_4$), have lower average oxidation states, contrary to samples in Group 2, which have higher FeCl$_3$ content. EXAFS analysis reported the presence of a highly distorted oxygen first coordination shell at 2.02±0.05 Å, and two Fe-Fe shells at higher distances (3.02±0.05 Å and 3.4±0.1 Å), which are compatible with Fe$_3$O$_4$ structure. Group 2 has an additional contribution from a chlorine shell at 2.15±0.05 Å, which is compatible with the FeCl$_3$ structure and in agreement with the higher content of the latter. Fourier transforms and EXAFS signals of samples representative of each group are reported in figure 3 (panels a and b, respectively).

3.1.2. Mn edge results
At the Mn edge PCA indicates that two components are necessary to reconstruct samples’ spectra: Mn$_3$O$_4$, MnCl$_2$. LSF results individuates three groups, having relative proportion of Mn$_3$O$_4$ and MnCl$_2$ roughly of 50/50, 70/30, and 30/70 (see table 1). This group’s assignment is in agreement with the absorption edge features (figure 1); nevertheless, it can be seen from figure 2 (right up panel) that LSF results are not satisfactory. This could suggest that the reference set of compounds is not fully representative of the samples. Ressler et al. [6] found up to 50% Mn(II)-phosphate in particulate emitted from cars burning zinc-dialkyl-dithiophosphate additives. Nevertheless, our samples may have different origin, as also suggested by the different spectral shape. Estimation of average oxidation state was carried out following the method reported in the work of Ressler et al. [6] (i.e considering the position of the main inflection point, MIP, of the reference oxides and that of the samples. Results, reported in figure 2 (right down panel), show that all samples have an oxidation state close to that of Mn$_3$O$_4$ oxide, and the trend is not in agreement with the relative Mn$_3$O$_4$/MnCl$_2$ content, so that it is not possible to unambiguously assign samples to groups suggested by LSF. The common structure is constituted by a splitted first oxygen coordination shell at distances of 1.90±0.05 and 2.20±0.05 Å, a second chlorine shell at 2.5±0.1 Å, and a third and fourth shell (when present) of Mn ions at 3.0±0.1 and 3.5±0.1 Å. Such structure is consistent with an admixture of Mn$_3$O$_4$ and MnCl$_2$ in different proportions. This can be clearly seen by looking at the Fourier transforms (Figure 3c) of the heights.
of the Mn-O and Mn-Cl peaks (the first and the second) for the three different groups. PCA and LSF procedures gave inconsistent results for sample BCR723. Its average oxidation state is estimated to be close to Mn$^{3+}$O$_4$, while a first oxygen shell is detected at about 2.17±0.05 Å; the lack of a possible reference model prevented reliable fitting of higher coordination shells for this sample.

4. Conclusions

The present study revealed that collected PM samples mainly consist of an admixture of Mn and Fe oxides, sulfates and chlorides, in different relative amounts. Using combined XANES and EXAFS analysis, the speciation of Fe was unambiguously unrevealed. On the other hand, Mn speciation remains uncertain, probably because of a wrong choice of reference compounds. The presence of chlorine in all the samples is interesting from an environmental point of view. We suggest that its origin is related to the salt used to prevent ice formation on the road level. A clear trend as a function of the particle size and the collecting point was not observed. We believe that variations in samples’ composition, which were shown to be linked with variations in the average oxidation state and local structure, are likely due to the high inhomogeneity of the samples. Work is in progress to reveal the speciation of Mn and to compare these results to samples coming from urban and areas.

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