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Sulphur speciation of PM10 samples by XANES spectroscopy

Research Article

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Abstract: Sulphur K-edge X-ray absorption near edge structure (XANES) spectroscopy was used to identify sulphur compounds in PM10 samples collected simultaneously at two sites with different environmental situations in the province of Trieste (NE of Italy), during summer and winter seasons respectively. The first site is an industrial site located near a steel mill plant and the second is a coastal site. The sulphur speciation at the industrial site has shown the presence of the following sulphur compounds in both seasons: organic compounds (thiophenes or Polycyclic Aromatic Sulphur Heterocycles - PAHs) and sulphates while in the winter season sulphites were also present. In the coastal site organic compounds (thiophenes or PASHs) and sulphate were found during winter season, moreover bisulphates were found during summer season. Relative percentages of the different sulphur compounds have shown that sulphate is the most abundant form of sulphur in the industrial site samples during both seasons and in the coastal site sample collected during the winter season (> 98%); in the coastal site sample collected during the summer season the relative percentages of bisulphate and sulphate were around 40% and 60% respectively.

Keywords: *Synchrotron radiation • Industrial pollution • Steel mill • Thiophenes • PASHs • sulphites*

1. Introduction

Among the most diffused air pollutants such as SO_2, O_3 and NO_x, a peculiar role is played by the particulate matter of aerodynamic size less than 10 μm in diameter (PM_{10}). PM_{10} has a variable and complex composition that includes a wide range of both organic and inorganic compounds.

Among the major elements that constitute PM_{10}, such as C (both organic and inorganic), O, N, Fe, K and Ca, sulphur is usually present in a percentage around 4% [1] and mainly in the sulphate form [2,3].

Aerosols containing sulphate ions are one of the causes of many environmental effects like Earth's temperature and climate change by sunlight backscattering [4,5], acidification of soil and water through wet and dry depositions [6], weathering of monuments and deterioration of museum objects [7]. Moreover they have adverse respiratory effects on human beings [8].

The predominant sources of sulphate (around 82%) are combustion of sulphur-containing fossil fuels (mainly coal and heavy oil) and industrial processes; the remaining percentage is due to natural sources like biogenic sources, volcanoes and sea spray [9,10].

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In addition to sulphate, other sulphur compounds, even if in smaller quantities, are present in PM_{10}. Among these, the more significant are:

- sulphides originated from natural sources (crude oil, natural gas, volcanic gases, hot springs and bacterial breakdown of organic matter) and industrial sources (food processing, coke ovens, paper mills, tanneries and oil refineries)
- organic sulphur compounds such as Methane Sulphonic Acid (MSA) originated from the photochemical oxidation of dimethylsulfide of biogenic origin [11]
- Polycyclic Aromatic Sulfur Heterocycles (PASHs) whose major sources are diesel engine exhaust gases and thermal processing activities of coal [12].

No direct methods for speciation of different sulphur forms are available in the case of amounts like those collected with PM_{10} samples (usually no more than a few milligrams).

Moreover usual wet chemical methods already used for soils [13] are not applicable, while chromatographic techniques such as GC-MS have several drawbacks, which are discussed in [12], due to other compounds largely present in PM10 such as PAHs (Polycyclic Aromatic Hydrocarbons).

An alternative approach can be provided by X-ray absorption near edge spectroscopy (XANES), that has already been used to distinguish and measure species of S in several matrices such as coal [14], petroleum and asphaltenes [15], minerals [16], biological samples [17-19], soils [13,20,21], as well as in matrices similar to PM_{10} like residual oil fly ash particulate matter [22,23].

Very few previous works focused on sulphur XANES speciation. Huggins and colleagues [24] worked on some standard reference materials and on just one real PM_{10} sample; in this case, the only S species that have been detected were sulphates. Takahashi *et al*. [25] report speciative S analyses from size-fractionated aerosols from a single site, collected in Japan during an episode of heavy dust transport from China and in absence of such transport. Matsumoto and colleagues [26] report some S speciative analyses on diesel vehicular emissions.

In the present study our analyses is on four PM_{10} samples collected in two seasons and in two sites with different environmental situations (one close to an industrial plant and the other three kilometers apart). Questions on the stability of reduced sulphur species in PM_{10} daily samples can also arise, due to the sampling procedure that implies continuous pumping of atmospheric oxygen on the sample during the sampling period (usually 24 h). Recent papers have shown how oxidants can have influence on organic pollutants sampled on PM [27-29].

In the present paper our aim is to confirm XANES adequacy for PM_{10} microanalyses of different sulphur compounds from real samples by recording spectra of the unknown samples and then comparing it with spectra of standard samples of the different sulphur compounds [30].

2. Experimental Procedures

2.1 Sampling sites

PM_{10} samples were collected, during winter and summer seasons respectively, at two sites in the province of Trieste (NE of Italy): one site is located in the city of Trieste in a mixed industrial-residential area within 1 Km east from an integrated steel mill plant (from here on termed industrial site) and the other located in the municipality of Muggia on the sea coast 3 km south of the steel mill (from now termed coastal site)(See Fig. 1).

The plant is a source of major environmental complaints for the inhabitants of the residential area since the coke plant, even if a small one (coke production: 450.000 tons year^{-1}), has relevant pollutant emissions in the atmosphere.

The coke is produced using the so-called “byproduct” process. In this process the coal is pyrolyzed in coke oven batteries for 12 - 20 hours and then it is pushed out of the ovens, quenched and sent to the steel production part of the plant.

Owing to fugitive emissions during coke production, several pollutants are emitted, such as Particulate Matter (0.7 to 7.4 kilograms per ton of produced coke), Volatile Organic Compounds (VOCs), Polynuclear Aromatic Hydrocarbons (PAHs), methane, ammonia, carbon monoxide, hydrogen cyanide, sulphur oxides and hydrogen sulphide (especially from pushing operations) [31,32].

2.2 Sample collection and handling

The PM_{10} samples were collected simultaneously on 46 mm quartz fibre filters by a TCR Tecora® Skypost PM sampling system with an EN 12341 European PM_{10} sampling head.

The flow rate and the sampling time following the European Union (EU) regulations (1999/30/CE) were set at 2.3 $m^3\,h^{-1}$ and 24 h respectively, resulting in a nominal sampling volume of 55.2 m^3.

The net mass of the PM_{10} was measured by weighing the filters before and after sampling by an electronic microbalance with a precision of 0.01 mg.

To obtain a reliable mass measurement, the filters were conditioned for 48 h in an Aquaria® Activa Climatic

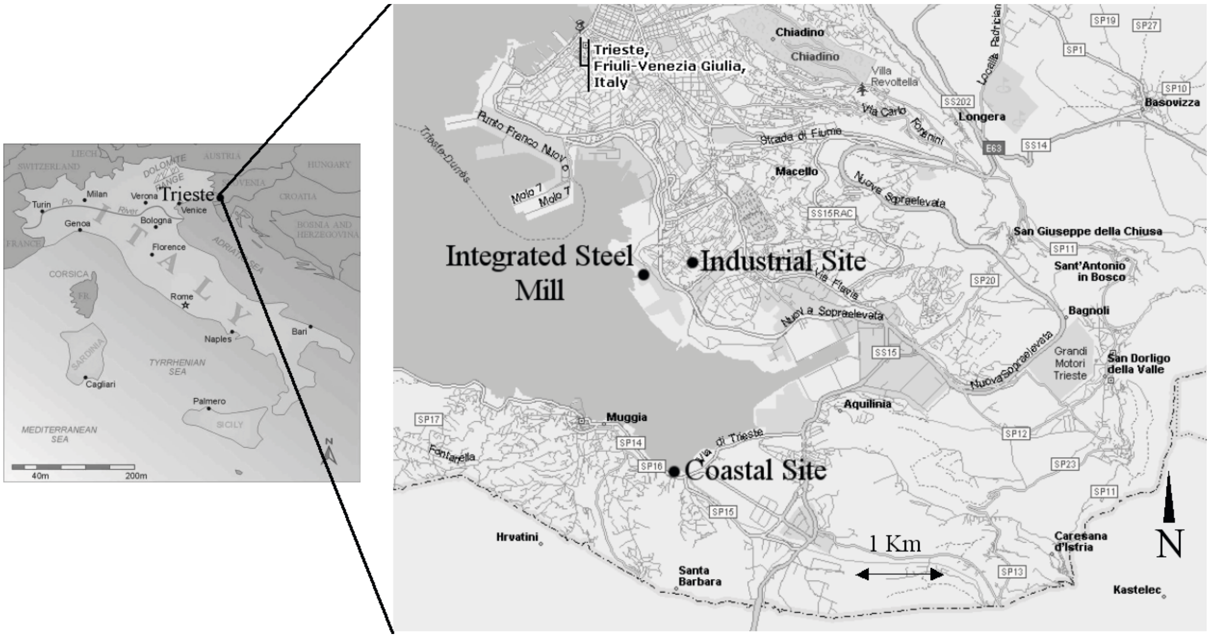

Figure 1. Map of Trieste and the surroundings, showing the locations of two sampling sites and the integrated steel mill.

conditioning chamber at a temperature of 20 ± 1°C and humidity of 50 ± 5%, before and after the sampling.

After the sampling, the filters were frozen until the measurements were carried out.

2.3 Facility and beamline

The XANES measurements were made at the beamline ID-21 at European Synchrotron Radiation Facility of Grenoble (F). The beamline is described in [33].

In synthesis, the scanning X-ray microscope uses a Fresnel zone plate as focusing optics, which demagnifies the synchrotron X-ray source, produced by an electron beam (energy: 6 GeV; average current: 190 mA), to generate a sub-micron probe with high flux. The monochromaticity of the beam and the energy scan were ensured by a fixed exit double crystal Si <1 1 1> monochromator located upstream from the microscope.

The sulphur K-line X-ray fluorescence was recorded with a Röntgen detector. The scanning transmission X-ray microscope at beamline ID-21 allows for NEXAFS studies at the K-absorption edge of sulphur at E = 2472 eV combined with fine spatial (300 nm) and spectral resolution (0.35 eV) .

We collected XANES spectra by irradiating disks of 10 mm diameter obtained subsampling the 47 mm quartz filters with X-rays in the energy range between 2440 and 2580 eV with stepwise increasing energies in 0.2 eV increments and a dwell time (duration of irradiation with X-rays of a distinct energy) of 0.1 s. The intensity of transmission and fluorescence at the various energies was recorded and the spectra were acquired in fluorescence mode. Repeated comparisons between the transmission and the fluorescence spectra of selected samples assured that self-absorption was not a problem during the XANES measurements. For each spectrum, the signals of 15 scans were compiled. The energy calibration was done with pure $CaSO_4$ (white line peak maximum: 2482.5 eV) and CaS.

The speciation of S was assessed in the standard substance and samples by recording XANES spectra in a nonfocussed mode (with the zone plate removed), the size of the beam being determined by a 200 μm pinhole. In this mode an area of 0.13 mm^2 of the sample was analysed integrating the signal from all material in that area. The incident beam intensity was monitored using a photodiode with a central hole, inserted in the beam and measuring the fluorescence signal from a thin 0.8 mm Al foil covering it.

2.4 Data Reduction

All data were baseline-corrected and normalized to the edge jump. The original spectra were smoothed by means of the Golay–Savitzky algorithm.

Data reduction and analyses were performed by using commercial software packages (Microcalc Origin) and free software packages (XOP by ESRF and APS).

3. Results and Discussion

At first glance, the spectra obtained from industrial and coastal site samples in both seasons (Figs. 2 and 3) consisted of a very strong peak at 2482.5 eV.

However a detailed analysis of the spectra (zoomed areas a and c in Figs. 2 and 3) revealed, for both sites and seasons, the presence of another weaker peak near 2474.1 eV. In the winter samples at both sites and in the summer industrial sample another weak peak around 2475.8 eV was found. The zoomed area b on Fig. 2 revealed for the winter industrial sample an even further weaker peak at 2479.0 eV, partially covered by the strong peak at 2482.5 eV.

To confirm the observation obtained from the direct examination of the above mentioned spectra about the number of sulphur species present in the samples, the second derivative of the data was calculated since this is a good way to determine the number of components that constitute a sample of unknown composition [34].

Fig. 4 shows the second derivative of the data for samples collected during winter season in both sites, while the zoom boxes a, b, c and d display the areas at 2474.1 eV and 2479.0 eV in more detail; the vertical lines show the different sulphur species.

The second derivative analysis confirmed the presence of four sulphur species in the PM$_{10}$ sampled at the industrial site, while three species were present at the coastal site.

The second derivative of the data for samples collected during the summer season in both sites is shown in Fig. 5, while the zoom boxes a, b, c and d display the areas at 2474.1 eV and 2479.0 eV in more detail; the vertical lines show the different sulphur species again.

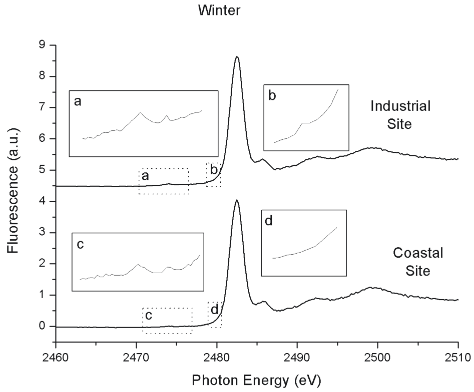

Figure 2. Sulphur K-edge XANES spectra for the PM10 samples of the two sites collected during the winter season (zoomed areas a and c: detail between 2470 eV and 2478 eV; zoomed areas b and d: detail between 2478 eV and 2480 eV).

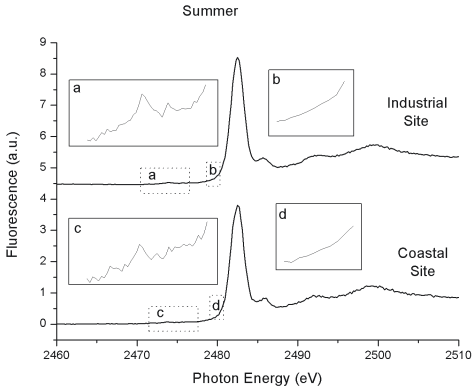

Figure 3. Sulphur K-edge XANES spectra for the PM10 samples of the two sites collected during the summer season (zoomed areas a and c: detail between 2470 eV and 2478 eV; zoomed areas b and d: detail between 2478 eV and 2480 eV).

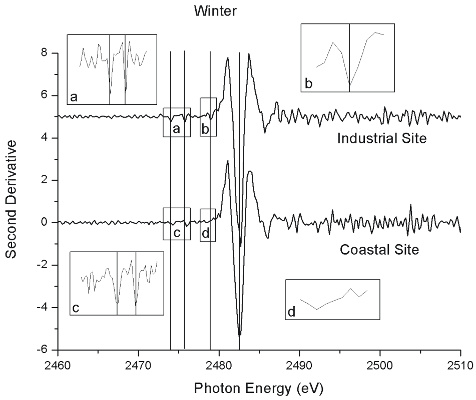

Figure 4. Second derivative of the sulphur K-edge XANES spectra for the PM10 samples in the two sites of the two sites collected during the winter season (zoomed areas a and c: detail between 2470 and 2478 eV; zoomed areas b and d: detail between 2478 and 2480 eV).

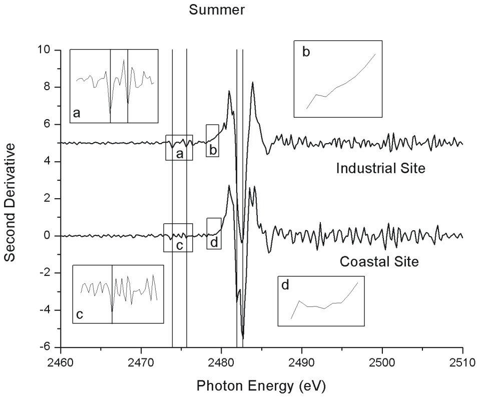

Figure 5. Second derivative of the sulphur K-edge XANES spectra for the PM10 samples in the two sites of the two sites collected during the summer season (zoomed areas a and c: detail between 2470 and 2478 eV; zoomed areas b and d: detail between 2478 and 2480 eV).

The second derivative analysis confirmed the presence of three sulphur species in the PM$_{10}$ sampled at the industrial site. The second derivative marked a significant difference between the summer coastal sample and the other three samples: the strong peak at 2485.2 eV has shown an asymmetry that was almost unnoticeable in Fig. 3. This finding provides indications about the presence of three sulphur species in this sample.

The sulphur compounds in the two samples were identified by comparing the energies of peak maxima of a spectrum (first derivative = 0 second derivative < 0) with the white line energies of different sulphur standard compounds shown in Table 1.

The energy position of the white line for the sulphur s → p transition peak varies between 2469 and 2483 eV, depending on the type of oxidation states of sulphur. It can also be noted that the absolute values obtained for the same S species from different studies at different beamlines differed slightly from each other and also between a solid sample and dissolved sample of a given compound [17]. However, a strong correlation between the electronic oxidation state of the S atom in an S-containing compound and the peak energy of the white line can be observed [20].

The strong peak at 2482.5 eV in both seasons for the industrial site samples and winter coastal sample was associated with sulphur in sulphate form; however the asymmetry of this peak in the summer coastal sample suggests [35] the presence of bisulphate sulphur forms together with the sulphate forms.

Comparing the shape of the peak and also its second derivative with literature data for different sulphate salts [25], as well as the standard CaSO$_4$ spectrum, it may be deduced that the sulphate is present predominately in the CaSO$_4$ form. These sulphate particles are likely formed by the reaction between CaCO$_3$ and sulphate ions in the atmosphere [36].

The small peaks near 2474.1 and 2475.8 eV are associated with sulphunated organics such as thiophenic compounds or PASHs (Polycyclic Aromatic Sulphur Heterocycles) [23,24,35,37]. These compounds are released mainly by diesel engines and during coal thermal processes like coke production [12,38,39] and are associated with organic carbon in atmospheric aerosols.

The small peak at 2479.0 eV, present only in the industrial site sample collected during the winter season, can be assigned to sulphite compounds. According to other authors [40], these compounds mostly originate from pollution sources containing SO$_2$ and transition metals, like smelters and coal thermal processes. This is compatible with the integrated steel mill emissions since no other plants using coal are present in the area.

No peaks related with sulphide were found even if coke production releases usually around 50 – 80 g of hydrogen sulphide per ton of coke from pushing operations [31].

This can be explained with the fact that hydrogen sulphide in polluted atmosphere is rapidly oxidized to SO$_2$ [41] and sampling can contribute to flux oxidants over collected PM [27-29].

Table 1. Energy position of the sulphur K-edge white line for different sulphur compounds from literature data: coal [14], petroleum and asphaltenes [15], minerals [16], soils [19-21], residual oil fly ash [22,23].

S Compound	**Oxidation state of the sulphur form**		**Peak energies of the sulphur K-edge white lines (eV)**				
		Reference:	**[14]**	**[15]**	**[16]**	**[20, 21]**	**[22, 23]**
Inorganic sulphide Type 1	S^{2-}	-2			2468.9	2469.4	2470.0
Inorganic sulphide Type 2	S$_2^{2-}$	-1	2471.5		2470.8	2471.9	
Elemental S	S^0	0	2472.0			2472.5	2472.0
Organic polysulphide	R-S-S-S-R’	+0.15				2473.0	
Organic disulphide	R-S-S-R’	+0.2	2472.2	2472.2		2472.6	
Thiol	R-SH	+0.5				2473.4	
Organic monosulphides	R-S-R’	+0.5	2472.7	2473.5		2473.4	
Thiophenes		+1	2473.3	2473.0			2473.3
Sulfoxide	R-S(=O)-R’	+2	2475.4	2476.0		2475.8	
Sulphite	SO$_3^{2-}$	+3.68				2478.7	
Sulphone	R-S(=O)$_2$-R’	+4	2479.5	2480.0		2480.2	
Sulphonate	R-SO$_2$-O-X	+5	24781.1	2481.0		2481.3	
Ester sulphate	R-O-S0$_3$	+6		2482.0		2482.5	
Inorganic sulphate	SO$_4^{2-}$	+6	2482.1	2483.0		2482.5	2482.5

After qualitative analysis, the relative proportions of the sulphur forms were estimated by means of a least-squares fitting procedure using Gaussian curves for the different sulphur forms peaks and an arctangent curve for the edge step at 2481 eV (oxidized S) [20].

However since the area of the S white line peak is also proportional to the number of 3p orbital vacancies in a single one-electron model, and thus increases as the oxidation state of the S atom increases, the contribution of S species with different electronic oxidation states of the S atoms to total S was calculated by correcting the measured peak areas using the weights proposed by [20].

The main sulphur form present in the industrial site samples for both season and in the coastal site sample for the winter season is the sulphate form (more than 98%) while the relative percentages of the other sulphur compounds were not quantified due to the small peak areas; in the summer coastal sample the relative percentages of bisulphate and sulphate were about 40% and 60% respectively.

The spectra of the industrial site sample in both seasons and of the winter coastal sample reported in Figs. 2 and 3 show an high degree of similarity with the one of NIST Diesel PM (SRM 1650) reported in [24] while the spectrum of the summer coastal sample is more similar to the NIST Urban PM (SRM 1648) spectrum from the same paper.

Taking into consideration all the results obtained we can deduce that sulphur XANES is a suitable and sensitive method for direct speciative analysis of sulphur on real PM_{10} samples.

4. Conclusions

This is one of the first studies where real PM_{10} samples were analysed by XANES spectroscopy for sulfur speciation. Two different sites were considered, representing situations from environments close in location; one of these sites is influenced by an industry that is a potential source also for sulphur compounds.

The main benefit of the proposed approach based on XANES appears to be the possibility of achieving information on sulphur compounds belonging to different chemical classes (*i.e.* elemental sulphur, sulphides, sulphates, organic sulphur compounds) with a “one shot” non-destructive analytical approach on atmospheric aerosol samples with a mass of milligrams or less and with minimal sample preparation, avoiding in this way the problem of artefact generation. The evidence of formation of artefacts due to oxidation of different compounds (PAHs), obtained while sampling PM, points at taking into account the opportunity of implementing an oxidant denuder sampler (as suggested in method EN 15549) when aiming at speciation analyses.

The evidence of the presence of several sulphur compounds in the PM_{10} samples calls for further investigations applying also ion and gas chromatographic analyses, with the aim of getting sound basis for source apportionment.

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