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K-edge XANES analysis of sulfur compounds: an investigation of the relative intensities using internal calibration

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Sulfur *K*-edge XANES (X-ray absorption near-edge structure) spectroscopy is an excellent tool for determining the speciation of sulfur compounds in complex matrices. This paper presents a method to quantitatively determine the kinds of sulfur species in natural samples using internally calibrated reference spectra of model compounds. Owing to significant self-absorption of formed fluorescence radiation in the sample itself the fluorescence signal displays a non-linear correlation with the sulfur content over a wide concentration range. Self-absorption is also a problem at low total absorption of the sample when the sulfur compounds are present as particles. The post-edge intensity patterns of the sulfur *K*-edge XANES spectra vary with the type of sulfur compound, with reducing sulfur compounds often having a higher post-edge intensity than the oxidized forms. In dilute solutions (less than 0.3–0.5%) it is possible to use sulfur *K*-edge XANES reference data for quantitative analysis of the contribution from different species. The results show that it is essential to use an internal calibration system when performing quantitative XANES analysis. Preparation of unknown samples must take both the total absorption and possible presence of self-absorbing particles into consideration.

Keywords: internal calibration; quantitative analysis; self-absorption; sulfur; XANES.

1. Introduction

Sulfur *K*-edge XANES (X-ray absorption near-edge structure) spectroscopy is very sensitive to the oxidation state with a range of ~15 eV between reduced sulfur compounds in metal complexes and sulfur in the oxidation state +VI as sulfate, sulfonate and sulfate esters (Hedman *et al.*, 1986). Furthermore, several types of sulfur compounds have a unique pattern of transitions on the absorption edge. This makes sulfur *K*-edge XANES very suitable to qualitatively determine the speciation of sulfur compounds in samples with complex composition (Jalilehvand, 2006). A more challenging task is to accurately determine the kinds of sulfur species quantitatively, which will be discussed in this paper.

One common approach is to deconvolute the experimental spectrum into several Gaussian peaks representing the $s \rightarrow p$ transitions and arctangent step functions representing the ejected photoelectrons into the continuum (Vairavamurthy, 1998; Xia *et al.*, 1998). The positioning of the Gaussian peaks is used to determine the electronic oxidation state of the S groups and the arctangent step functions are used to scale the peaks (as the peak area increases with increasing energy position), to allow estimation of the relative abundance of the various groups (Xia *et al.*, 1998). Another approach is to use least-squares linear combination fits of normalized standard spectra of model S compounds, which allows for a more precise separation between S functional groups of similar oxidation state, but with differences in spectral features (Vairavamurthy *et al.*, 1994). Beauchemin *et al.* (2002) used principal component analysis for modelling S XANES spectra to remove the need for *a priori* assumptions and information. While the above methods have all been successfully used to fit spectra of unknown complex samples, there are still a few issues to be considered in order to obtain reliable estimations of the relative abundance of different S groups.

At the energies of the sulfur *K*-edge (2469–2485 eV) the total absorption is very high and only extremely thin samples can be studied in transmission mode. Thus sulfur *K*-edge XANES spectroscopy studies are preferably performed in fluorescence mode using Lytle or solid-state detectors. It is essential to perform the experiments in either a vacuum or in pure helium in order to minimize absorption and scattering from the atmosphere (the latter is preferred on natural samples avoiding evaporation of volatile compounds). The formed fluorescence radiation during relaxation of the core hole for the absorption has a lower energy, 2306 eV

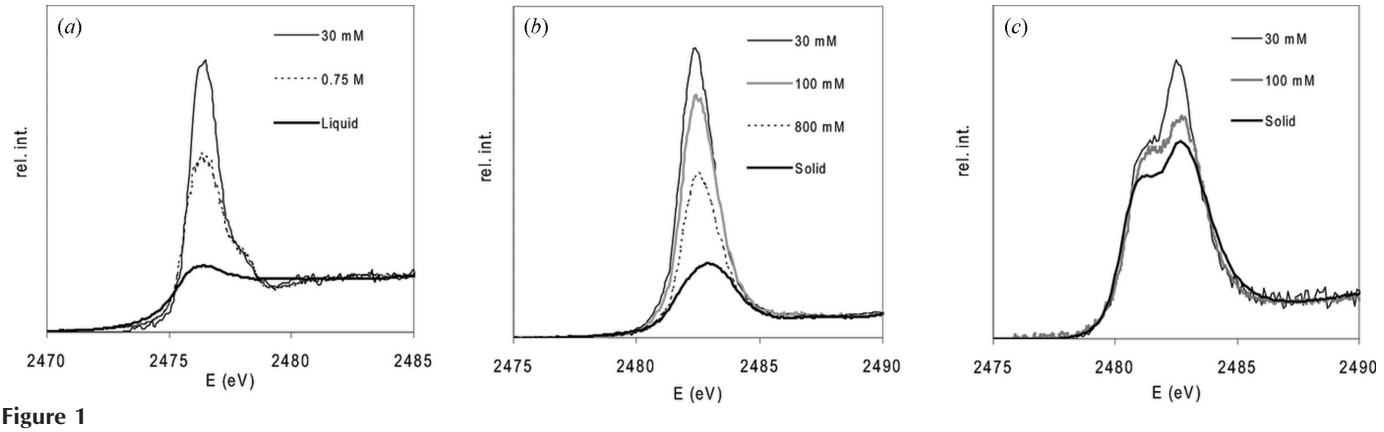

Figure 1
Sulfur *K*-edge XANES spectra of (*a*) liquid DMSO and aqueous solutions of DMSO, (*b*) solid sodium sulfate decahydrate and its aqueous solutions and (*c*) solid chondroitin sulfate ester, sodium salt and its aqueous solutions.

(Thompson *et al.*, 2001), and thus an even higher absorption coefficient. This means that a large portion of the fluorescence radiation formed in the material may be absorbed by the sample itself. The more heavy elements present and the higher density of the sample, the higher the self-absorption and the lower the fraction of the formed fluorescence radiation will reach the detector. This may affect the observed fluorescence spectrum significantly as discussed elsewhere (Pickering *et al.*, 1998). This causes sulfur *K*-edge XANES spectra of pure sulfur compounds to look very different from dilute samples in solvents with no heavier element than sulfur and relatively low density (see Fig. 1). The model compounds used have to be in the same condition as the sample compounds because the absorption peaks can change remarkably depending on factors such as pH (Pickering *et al.*, 1998) and complex formation with metal ions (Jalilehvand, 2006). Furthermore, the varying post-edge absorption intensities for different sulfur-containing compounds need to be considered in a more precise manner.

The aim of the present study was to develop a method for qualitative and quantitative analysis of sulfur compounds which could be applied to natural samples with relatively low sulfur content, such as soil, sediments and archaeological wood, using internally calibrated reference spectra of pure sulfur compounds in dilute (30 m*M* with respect to sulfur) solution.

2. Experimental

2.1. Chemicals

Chondroitin sulfate ester, L-cysteine, L-cystine, dibenzyldisulfide, dimethylsulfite, dimethylsulfoxide (DMSO), diphenyl disulfide, diphenyl sulfide, diphenylsulfoxide, elemental sulfur, L-methionine, L-methionine sulfone, sodium dithiosulfate pentahydrate, sodium hydrogensulfate, sodium methylsulfonate, sodium sulfate decahydrate, sodium sulfite, tetramethylene sulfone and thiosalicylic acid, all from Aldrich, were used as purchased (additional information is given in Table 1). Pyrite (FeS_2) was obtained from Wards Natural Science Marketing Group (Rochester, NY, USA) and ground to a fine powder using an agate mill. MilliPore filtered water was used at the preparation of aqueous solutions.

2.2. Preparation of samples of pure compounds

Sulfur *K*-edge XANES spectra were recorded for all the compounds in the list of chemicals above. The solid compounds were ground into fine powder, put on Sacta XRF sulfur-free tape (Fluxana GmbH & Co. KG), and excess of material was removed to minimize the amount of sample on the tape. Liquid samples were placed in a cell made of a 0.5 mm-thick Teflon frame, covered on each side with a 5 µm-thick sulfur-free polypropylene X-ray film (SpexCertiPrep, Metuchen, NJ, USA).

2.3. Preparation of reference solutions

Aqueous solutions of sodium sulfate of concentrations 0.03, 0.1 and 0.8 *M*, of DMSO of concentrations 0.03, 0.75 and 14 *M*, and of chondroitin sulfate ester, 0.03 and 0.1 *M*, were prepared to study the concentration dependence of the sulfur XANES spectra.

Dilute solutions (30 m*M*) of the different sulfur compounds in combination with DMSO, thiosalicylate or sodium sulfate were prepared in water or ρ-xylene according to Table 1. In the first step the maximum *K*-edge intensities of aqueous sodium sulfate or thiosalicylic acid were calibrated against the intensity of aqueous DMSO (30 m*M*) (see below). All other sulfur solutes were mixed and calibrated against DMSO (30 m*M*), sodium sulfate (30 m*M*) or thiosalicylic acid (30 m*M*) (see Table 1). DMSO was chosen as primary internal reference compound as it is chemically stable, soluble in both polar and non-polar solvents, and the sulfur in DMSO has an absorption edge, 2476.4 eV, which is different from typical reduced and oxidized forms of sulfur.

A multi-species aqueous solution containing L-cysteine, DMSO, methioninsulfonate and sodium sulfate was prepared to evaluate the accuracy of the quantification method.

2.4. XANES data collection

Sulfur *K*-edge XANES spectra were recorded in the energy range 2422–2622 eV at the wiggler beamline I811 of the MAX-

Table 1
Analyzed sulfur compounds in dilute solutions.

Number	Function	Oxidation number	Sulfur compound in solution	Calibration compound and solvent	Maximum peak (eV)	Additional peaks (eV)	Maximum edge intensity relative to DMSO
1	Disulfide	−I	L-Cystine, $[HOOCCH(NH_2)_2CH_2S]_2$	Sulfate, aq, buffer pH 7.0	2472.6	2474.1	0.59
2	Disulfide	−I	Diphenyl disulfide, $(H_5C_6S)_2$	DMSO, *ρ*-xylene	2472.7	2474.4	0.53
3	Disulfide	−I	Dibenzyldisulfide, $(H_7C_7S)_2$	DMSO, *ρ*-xylene	2472.8		0.74
4	Elemental	0	Elemental sulfur, S_8	DMSO, *ρ*-xylene	2472.7		0.78
5	Thio ether	−II	Diphenyl sulfide, $(H_5C_6)_2S$	DMSO, *ρ*-xylene	2473.4	2475.0	0.55
6	Thio ether	−II	L-Methionine, $HO_2CCH(NH_2)CH_2CH_2SCH_3$	Sulfate, aq	2473.6		0.82
7	Thiol	−II	Tiosalicylic acid, 2-$HS(C_6H_4)COOH$	Sulfate, aq, buffer pH 7.0	2473.5		0.50
8	Thiol	−II	L-Cysteine, $NSCH_2CH(NH_2)COOH$	Sulfate, aq, buffer pH 7.0	2473.4		0.59
9	Thiosulfate	−II, +VI	Sodium dithiosulfate pentahydrate, $Na_2SO_3{\cdot}5H_2O$	Sulfate, aq	2479.3	2472.5, 2479.3	1.0
10	Sulfoxide	0	Dimethylsulfoxide, $(CH_3)_2SO$	Aq	2476.4		1.00
11	Sulfoxide	0	Diphenlysulfoxide, $(C_6H_5)_2SO$	Thiosalicyclic acid, *ρ*-xylene	2476.0	2477.6	0.57
12	Sulfite	+IV	Dimethylsulfite, $(CH_3O)_2SO$	Sulfate, aq	2477.7		1.1
13	Sulfite	+IV	Sodium sulfite, Na_2SO_3	Sulfate, aq	2478.3		1.1
14	Sulfone	+II	Tetramethylene sulfone, $C_4H_8O_2S$	Sulfate, aq	2479.6		1.1
15	Sulfone	+II	L-Methionine sulfone, $CH_3SO_2CH_2CH_2CH(NH_2)COOH$	Sulfate, aq, buffer pH 7.0	2480.6		1.0
16	Sulfonate	+IV	Sodium methylsulfonate, $NaCH_3SO_3$	DMSO, aq	2481.1		1.5
17	Sulfate ester	+VI	Chondroitin sulfate ester, $C_{14}H_{19}NO_{14}SNa_2$	DMSO, aq	2482.7	2481.2	0.83
18	Sulfate	+VI	Sodium sulfate decahydrate, $Na_2SO_4{\cdot}10H_2O$	DMSO, aq	2482.4		2.2
19	Sulfate	+VI	Sodium hydrogensulfate, $NaHSO_4$	DMSO, aq, pH 1.0	2482.4		1.4

laboratory, Lund University, Sweden. The workstation was equipped with a Si[111] double-crystal monochromator. The MAX ring operated at 1.5 GeV and a maximum current of 220 mA. The entire experimental set-up was placed in an arrangement where the beam, formed fluorescence radiation, sample compartment and detector were in a helium atmosphere with a slight over-pressure to minimize leakage of air into the experiment; absorption and scattering of air, also at very low concentrations, cause a large increase in the noise level of the fluorescence signal. The data collection was performed in fluorescence mode at ambient room temperature using an energy-dispersive solid-state detector, a single-element Radiant Technology Vortex silicon drift detector (SII Nano Technology USA, Northridge, CA, USA, http://www.siintusa.com/) or a seven-element liquid-nitrogen-cooled Gresham Si(Li) array detector (Gresham Scientific Instruments, Bucks, UK, http://physicsworld.com/cws/company/A100000460). The solid-state detectors were placed perpendicular to the X-ray beam, and the sample at 45° relative to the incoming X-ray beam. Higher-order harmonics were reduced by detuning the second monochromator to 20% of maximum intensity at the end of the scans. Sulfur edge spectra of solid sodium thiosulfate pentahydrate, $Na_2S_2O_3{\cdot}5H_2O$ (Aldrich), were recorded immediately before or after every sample, assigning the maximum of the first peak in the spectrum to 2472.02 eV (Williams *et al.*, 1997).

2.5. XANES data treatment

The raw XANES spectra were background-subtracted using a linear function extrapolated from the pre-edge region, and, if necessary, the same type of correction was performed after the edge region to achieve a slope of zero in the post-edge region ($E > 2500$ eV). The reference data on pure sulfur compounds were normalized by putting the intensity of the spectra at 2490 eV to unity (Fig. 1).

The signal intensities of the different dilute compounds in solution were calculated by normalizing the intensity of the DMSO edge peak at 2476.4 eV to 1.00 (arbitrary units) and relating the maximum *K*-edge intensities of the other compounds to this signal intensity. This is exemplified in Fig. 2 where the spectrum of the mixed solution of DMSO and

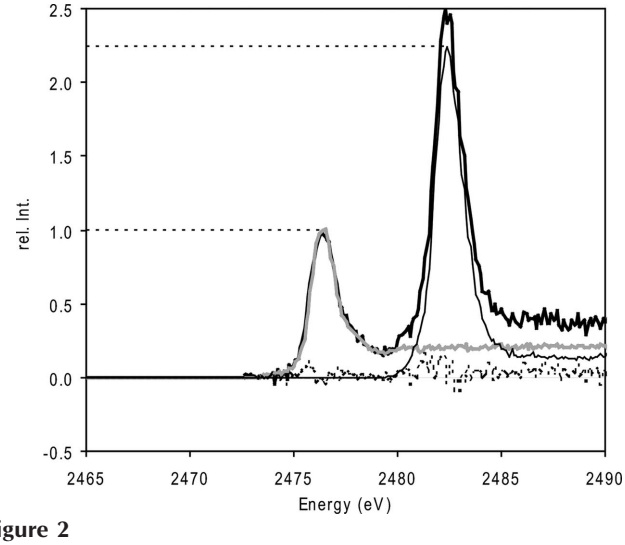

Figure 2
Normalized sulfur *K*-edge XANES spectrum of an aqueous solution containing 30 m*M* DMSO and 30 m*M* sodium sulfate (thick black line), and best fitting by linear regression with spectra of 30 m*M* DMSO (grey line) and 30 m*M* sodium sulfate (thin line). Residuals from linear regression are indicated by the dashed line.

sodium sulfate is fitted by the individual spectra of DMSO and sodium sulfate by linear regression. The sulfate edge peak maximum intensity displayed a factor of 2.2 relative to DMSO on the applied scale. Compounds not analyzed with DMSO were calibrated to the sulfate or thiosalicylate edge peaks (at 2482.4 and 2473.4 eV, respectively) which in turn were related to the DMSO maximum intensity. By this method the maximum *K*-edge signal intensities of all compounds investigated were related to DMSO.

The contributions from different components in prepared samples containing several sulfur species were resolved by linear regression using the LINEST function in Microsoft Excel. The LINEST function uses a least-squares method to calculate a curve that best fits the experimental data and it allows for up to 15 reference spectra to be included at the same time.

3. Results and discussion

The normalized sulfur XANES spectra of DMSO and sodium sulfate as a function of concentration are given in Figs. 1(*a*) and 1(*b*). The absorption maximum of DMSO, 2476.4 eV, is independent of concentration (Fig. 1*a*), while the absorption maximum of solid sodium sulfate decahydrate (2482.9 eV) is observed at 0.5 eV higher energy than the aqueous solutions of this compound (independent of the concentration) (see Fig. 1*b*). The intensity of the main transition is very much dampened in the pure samples, and less dampened in the solutions the more dilute they are, altogether displaying a logarithmic correlation to concentration (Fig. 3). The reason for the damping of the fluorescence signal is most likely due to self-absorption, which increases with increasing concentration. For compounds with lower sulfur content and lower density such as chondroitin sulfate ester, sodium salt, the difference between a pure sample and a 30 m*M* aqueous solution is smaller (Fig. 1*c*). This shows that quantitative determinations are impossible to perform without taking into account the total concentration of different sulfur species present in a sample and that an accurate calibration with diluted solutions is critical. To achieve an acceptable low self-absorption, and still having a good signal-to-noise ratio, the concentration of the samples prepared for internal calibration was chosen to be 0.03 *M* (in total 0.06 *M* sulfur in these mixtures).

The XANES spectra of 19 individual sulfur compounds in dilute solution, all internally calibrated spectra with an intensity related to that of DMSO, are shown in Fig. 4. The relative intensities of the maximum *K*-edge signals, presented in Table 1, display a fourfold difference from the most absorbing compound (sulfate ion) to the least absorbing (diphenyldisulfide). Generally the more oxidized compounds (+II–VI; sulfite, sulfone, sulfonates and sulfates) display higher maximum absorption intensities compared with the reduced and intermediate compounds (−II–0). However, among the sulfate analogous compounds (*i.e.* sulfate, hydrogen sulfate and sulfate ester) the relative intensities differ strongly which may be explained by their different

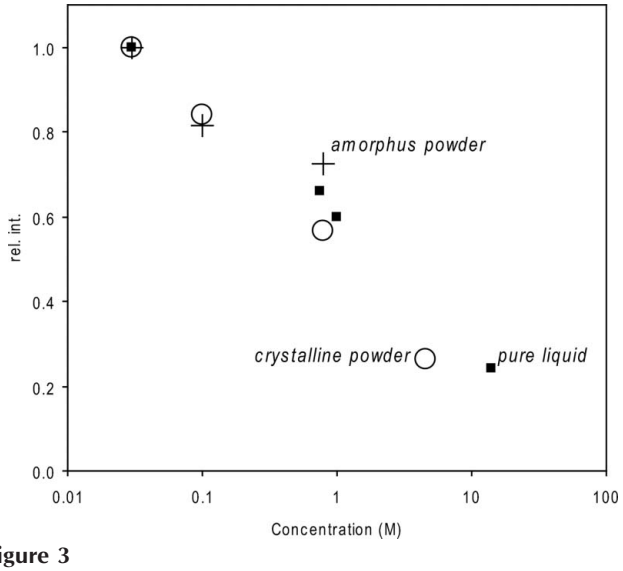

Figure 3
The maximum sulfur *K*-edge XANES intensities of DMSO (squares), sodium sulfate (circles) and chondroitin sulfate ester (crosses) as a function of concentration. The intensities at 30 m*M* are normalized to unity.

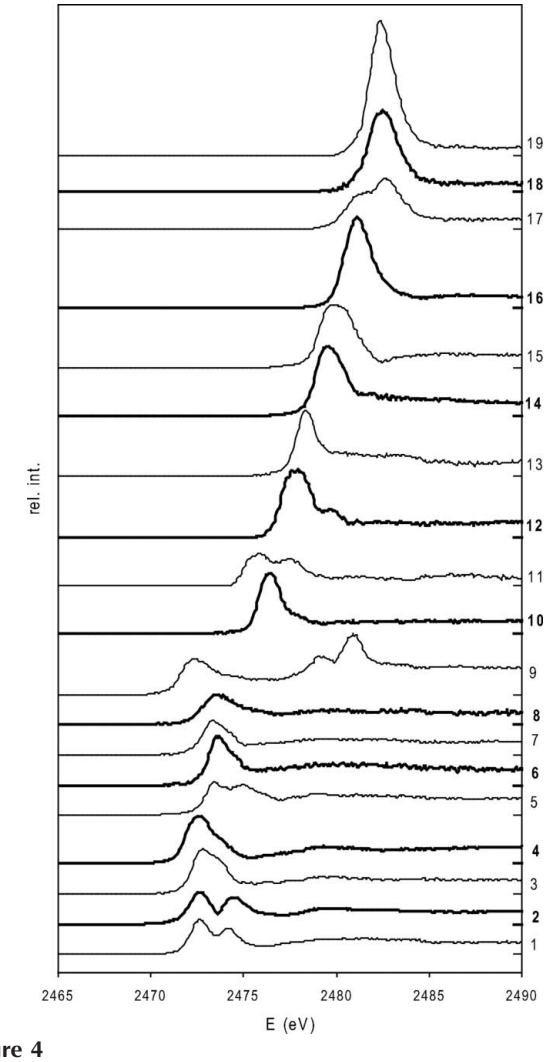

Figure 4
The individual sulfur *K*-edge spectra of the compounds investigated. The numbers to the right refer to the sulfur species presented in Table 1.

symmetry. The intensity of the sulfate ion (Table 1) is exceptional owing to its high symmetry (Jalilehvand, 2006) compared with the intensities of the protonated sulfate (hydrogen sulfate) and the sulfate bound to a carbon (sulfate ester). In the case of hydrogen sulfate the effect of protonation on the intensity reduction must be taken into account when measuring in acidic solutions (pH < 3). Among the reduced and intermediate species the maximum intensities were varying (0.5–1.1 relative to DMSO). In compounds where the sulfur or disulfur group is bound to two phenyl groups (*e.g.* sulfides, disulfides or sulfoxide), a significant reduction of the maximum intensity was observed as compared with compounds without adjacent phenyl groups, indicating influences from the aromatic system on the main transition.

The post-absorption-edge intensity pattern varies a lot between the sulfur compounds (Fig. 4). Previously reported sulfur XANES edge models, prepared without internal calibration, have assumed that the post-edge intensity is the same for all compounds; see for example Fig. 1 in the review article by Jalilehvand (2006). This is certainly not correct, and may introduce errors in the quantitative evaluation. The fact that sulfur compounds have different post-edge intensities can be used to improve the accuracy of fits of samples with unknown composition (see below).

A series of sulfur XANES spectra of fine ground pyrite powder with increasing dilution with boron nitride did not change the spectra (not shown). This indicates that the main part of the self-absorption takes place in the particle where the excitation has taken place. This shows clearly that dilute samples must be modelled with reference data collected under similar conditions, and that quantitative modelling of solid compounds in a sample with unknown composition will be associated with large errors. Morgan *et al.* (2009) reported recently that particles of elemental sulfur need to be smaller than 5 µm to achieve a correlation with the concentration in sediment samples.

Despite the general non-linear dependence of the signal intensity to the concentration, the spectra seemed to be fairly additive in the concentration range of the dilute compounds investigated, *i.e.* 10–60 m*M*. In order to use the normalized spectra in Fig. 4 for a relative quantification of unknown samples, fitting by linear regression was applied. For a satisfying fit both the XANES region and the level of the post-edge intensity in the range 2465–2490 eV should be in agreement with experimental data (see Fig. 5). The method was tested on prepared solutions containing several compounds to determine the relative contributions from the individual components by linear regression and to calculate the concentration of the different species. The estimated errors in the obtained compositions are in the range 5–10%.

4. Conclusions

Owing to significant self-absorption of formed fluorescence radiation in the sample itself the fluorescence signal of sulfur *K*-edge XANES displays a non-linear correlation with the sulfur content over a wide concentration range. Self-absorption is also a problem at low total absorption of the sample when the sulfur compounds are present as particles. The post-edge intensity patterns of the sulfur *K*-edge XANES spectra vary with sulfur compound, with reducing sulfur compounds often having a higher post-edge intensity than the oxidized forms. However, in dilute solutions it is possible to use sulfur *K*-edge XANES reference data for quantitative analysis of the contribution from different species present in an unknown sample. The results show that it is essential to use an internal calibration system when performing a quantitative XANES analysis as presented in this paper. The results have strong implications for analysis of natural samples (*e.g.* sediment, soil and archeological wood) where information regarding the total concentration as well as the possible presence of solid sulfur particles must be taken into account. Data and quantitative determinations for natural samples are reported in separate papers.

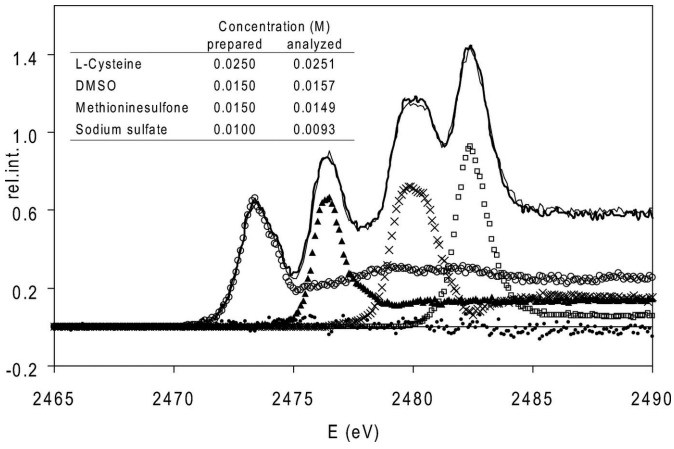

Figure 5
Sulfur *K*-edge spectrum of a solution containing L-cysteine, DMSO, L-methionine sulfone and sodium sulfate (thick line) and fitting by linear regression with the individual normalized spectra of L-cysteine (open circles), DMSO (filled triangles), L-methionine sulfone (crosses), sodium sulfate (open squares), sum of fit (thin line) and residuals (filled circles). The prepared and calculated concentrations of the different species are given in the inset table.

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