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USING X-RAY ABSORPTION SPECTROSCOPY

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ABSTRACT

A variety of air particulate samples were measured for their Zn, Fe and Cu chemical composition using X-ray absorption spectroscopy. The K x-ray absorption edges of the samples were scanned using synchrotron radiation from the Stanford Synchrotron Radiation Laboratory (SSRL). The spectra were obtained using both ion chamber transmission detectors and three Si(Li) fluorescence detectors. Analysis of the spectra shows that the chemical composition of the particular elements studied can be determined to $\pm 7\%$ by comparing the spectra to reference spectra. This technique shows promise for the non-destructive determination of the primary chemical form of dilute elements in complex samples.

INTRODUCTION

The objective of any air particulate monitoring program is the characterization of the atmospheric aerosol in as complete detail as possible. Ideally, this would include the concentrations of the pollutants, their spatial and temporal variations, and some information regarding the chemical composition and possible transformations which the various species undergo. Much of this information can be obtained from a careful analysis of air particulates filtered from the air.

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Modern aerosol monitoring procedures employ samples which collect particles from discrete size ranges onto separate filters. The acquisition of size separated samples is essential since the origin, composition, and interaction with other aerosol species depends on the aerodynamic size of the particles. Inherent in the methods used for separating the particle sizes is the fact that only very small (<1 mg) quantities of particulates can be acquired easily.

Total mass and elemental compositions can be measured for such samples using several sensitive, non-destructive techniques (1,2). In order to obtain the chemical form of a specific element, it is necessary to employ less sensitive and normally destructive methods to analyze for specific constituents.

We describe preliminary results in which high resolution x-ray absorption spectroscopy is used to determine the chemical form of elements normally encountered in air pollution samples. The method is sensitive, non-destructive, and specific enough to distinguish between various chemical compounds of interest in air pollution research and monitoring. The application of the method to ambient air samples is discussed.

DESCRIPTION OF METHOD

This technique relies on the measurement of the energy dependence of the photoelectric cross section of the element of interest in the region of a major absorption edge. The data are obtained by scanning the energy region near the edge with a nearly monochromatic variable-energy photon beam.

The absorption edge structure occurs in the energy region where the photoelectric cross section for the creation of an inner-shell vacancy goes from zero to its maximum value as the incident photon energy is increased above a threshold value necessary to eject the bound electron. This normally "abrupt" transition exhibits considerable structure when measured using an x-ray beam with a narrow energy spread (3). Figure 1 shows the K shell absorption spectrum for a particular Mo compound which illustrates several features of fine structure in the region of the edge. For incident photon energies below the K binding energy, it is possible to create vacancies in the K shell by promoting the 1s electron to bound but vacant levels in the atom. This gives rise to a series of discrete but overlapping lines in the

photoelectric absorption spectrum. Insofar as these lines reflect the energy difference and occupation probability of the atomic or molecular levels, they can be used as indicators of the chemical state of that particular atomic species.

At an energy equal to the binding energy of the K shell, continuum excitation can occur and the rapid increase in cross section is observed. As the energy is increased further, there are observed fluctuations in the photoelectric cross section which continue for several hundred eV above the edge. These fluctuations are termed Extended X-ray Absorption Fine Structure (EXAFS). This structure is the result of a scattering of the very low energy photoelectrons which have been ejected by the photons and have energies only slightly above the absorption edge. As the outgoing photoelectron amplitude encounters nearby atoms, a portion of the amplitude can be backscattered toward the ionized atom where it can then reinforce or decrease the total photoelectric cross section. These fluctuations are dependent on the location and scattering characteristics of nearby atoms and can therefore be used as a probe of molecular structure.

The phenomena associated with x-ray absorption fine structure have been studied extensively and theoretical models describing the process have been developed (4,5). Previous experimental limitations due to x-ray source intensity have largely been eliminated with the development of intense synchrotron radiation sources associated with high-energy electron storage rings. The unique characteristics of these x-ray sources have stimulated further experimental and theoretical research in the field of x-ray absorption fine structure, particularly EXAFS. In the present work, we have explored the sensitivity of the method for identifying specific compounds of interest in air pollution studies and other environmental problems. Several examples of analyses of ambient air particulate samples are shown and the results discussed.

EXPERIMENTAL PROCEDURE

Figure 2 shows a schematic of the system used for studying x-ray absorption fine structure. A very high resolution ($dE/E = 10^{-4}$) variable energy x-ray beam at the Stanford Synchrotron Radiation Laboratory (SSRL) is incident on the sample. Ionization chambers measure the total incident intensity

(I_0) and the beam transmitted by the sample (I). Simultaneously, a semiconductor detector x-ray spectrometer measures the fluorescence intensity of the characteristic x-rays (N). As the energy of the incident beam is scanned, the absorption and fluorescence signals measure the energy dependence of the photoelectric cross section.

The variable energy beam is obtained by rotating the double crystal spectrometer which selects a narrow range of wavelengths from the incident radiation. The synchrotron radiation spectrum is a continuous distribution which results from the acceleration of electrons in the circular orbit of a storage ring (6). The photon distribution extends from very low energies in the optical region out to a maximum x-ray energy determined by the energy and radius of the electron storage ring. The present study was performed at SSRL where the storage ring energy varies typically between 1.5 GeV and 3.5 GeV ($1\text{GeV} = 10^9 \text{ eV}$) corresponding to synchrotron radiation spectra which range up to 20 keV in usable x-ray intensity (7). This restricts the range of elements available for study to those with absorption edges between 3 keV and 20 keV. This corresponds to the K edges and elements from Ca to Mo in the periodic table together with the L edges for many heavier elements.

Figure 3 shows a series of spectra measured for selected Zn compounds which illustrate the differences in the relative cross section for the various chemical forms. These cross sections were obtained from the measured spectra by taking the logarithm of the data (if measured by sample transmission), subtracting a continuous background, and normalizing the results to an equivalent average cross section. The normalization procedure is necessary in order to allow the comparison between standards and unknowns and comparison of results obtained from either fluorescence or absorption measurements.

A detailed theoretical analysis of the absorption edge spectra shown in the figure would potentially yield information regarding the degree of ionization of the Zn atoms and the distance and scattering properties of its nearest neighbor atoms. However, in the case of unknown samples where mixtures of compounds are likely to occur, such analysis would be extremely difficult and largely unnecessary. Most analytical problems of interest involve the determination of the concentration of one or more specific compounds from among a set of possible constituents. By comparing the absorption spectrum of the unknown sample directly to the spectra obtained in pure samples of potential constituents, one should be able to interpret the unknown spectrum as a linear combination of spectra associated with the constituents.

The potential advantages for the method are several. Since it is non-destructive, the samples can be re-analyzed by other techniques and the results compared. Since the absorption edge scan is specific to a particular element, individual elements in the sample can be studied with negligible interference from other elements. Edges corresponding to several elements can be measured in the same sample if required. Finally, since the average absorption length of the x-rays is large compared to the particle sizes in the sample, the experiment measures the bulk properties of the air particulates. This is an important feature since many other physical methods, such as photoelectric and Auger spectroscopy, measure surface properties only.

RESULTS

We have selected samples from among 30,000 air particulate samples obtained as a part of the St. Louis RAPS Study (8). These were collected using automatic dichotomous samplers operating with a cut-point between fine and coarse particles at $2.4\text{ }\mu\text{m}$. The elements studied in the present work were Zn, Fe, and Cu. Samples were normally chosen on the basis of anomalously high concentration of the respective element. This was done both to enhance the sensitivity of the measurement and because of the intrinsic interest in the causes of elevated concentrations of certain elements during episodes.

Typical samples consisted of particle deposits of 50 to $200\text{ }\mu\text{g}/\text{cm}^2$ on a $5\text{ mg}/\text{cm}^2$ cellulose membrane substrate. The concentrations of the particular elements studied were typically 1 to $5\text{ }\mu\text{g}/\text{cm}^2$. Due to the low concentrations of the elements relative to the substrate mass, the spectra for the unknown samples were acquired in the fluorescence mode using a system with three large area silicon semiconductor detector spectrometers to measure the fluorescence signal (9).

Figure 4 shows plots of absorption edge spectra for the element Zn taken on two samples representing the coarse and fine particle fractions for a six-hour interval at an urban sampling site. Spectrum (a) is the fine particle fraction, and (b) is the coarse. A qualitative comparison of these spectra with the standards shown earlier indicates that the fine particles are predominantly composed of ZnSO_4 or $\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2$ whereas the coarse composition is apparently ZnO .

The difference in chemical composition between the two Zn samples illustrates the independent behavior of the fine and coarse particle fractions. The difference could be a reflection of two or more distinct Zn sources in the vicinity of the sampling site. Unlike many other elements present in the urban aerosol, Zn is not readily associated with a major source of particulates: a more definitive interpretation in these terms would require a more detailed study of the sampling environment. A second explanation for the difference in Zn chemical form results from the reaction of Zn containing particles with the SO_2 present in the air mass. The sub-micron particles could be converted to a SO_4 form more readily due to their much higher surface to volume ratio. The difference is further enhanced by the volume sensitivity of the x-ray absorption method.

A number of additional filters were analyzed for Zn composition with similar results. In most cases, the absorption spectra could be clearly associated with either the ZnO , ZnSO_4 , or $\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2$ standards. In some cases, it was apparent that a mixture of two or more compounds was involved. In order to achieve a more quantitative interpretation, a mathematical method for matching the unknown spectra to the standards was attempted. It employed a least squares minimization procedure to fit normalized spectra for two or more standards to the unknown similar to that of Glen and Hurst (10).

In order to test the accuracy of the mathematical procedure, a series of 1:1 mixtures of various Zn compounds were prepared and their spectra were then measured. Figure 5 shows the results obtained by fitting the absorption spectrum of a 1:1 mixture of ZnSO_4 and ZnO to the sum of their respective absorption spectra. A quantitative measure of the amount of each compound was derived from the fitted coefficients used to weigh the individual spectra. The results are given in Table 1 for both this mixture and a $\text{ZnO} - \text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2$ mixture. The errors are the statistical errors derived from the fitted parameters and do not include additional biases which may be introduced by the background subtraction and normalization procedures ($\approx 5\%$). The deviation of these results from the known 1:1 mixture indicates that the accuracy of the determination is in the region of $\pm 7\%$.

An additional measurement of a 1:1 $\text{ZnSO}_4 - \text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2$ mixture yielded very large errors in the fitted coefficients. This reflected the great similarity in absorption spectra due to their similar crystallographic structures. Figure 3 shows that the spectra are identical except for the

small additional peak below the absorption edge. Since the fits to the absorption spectra are normally performed over a region starting near the edge and extending out several hundred eV above, the effect of such a minor feature on the total fit is negligible. For this reason the fitting procedures are not able to readily distinguish between these two compounds in the analysis.

The data obtained from the analysis of several Zn containing ambient air particulate samples are summarized in Table 2. The station numbers refer to the sampling station in the St Louis Regional Air Monitoring System. The elemental concentrations were obtained from x-ray fluorescence analysis. The samples do not represent typical ambient elemental concentrations in that they were specially chosen samples in which the Zn levels were abnormally high.

Samples 1 and 2 are the coarse and fine particle filters previously discussed. The fitting procedure yields results consistent with the qualitative conclusions that the fine particle fraction is predominantly $\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2$ and the coarse fraction ZnO . In the case of the fine particle filter, the results of a least squares fit to either a $\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2$ - ZnO mixture or a ZnSO_4 - ZnO mixture yields similar results. The choice of the $\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2$ is dictated by the observation of the characteristic peak in the absorption spectra discussed earlier.

The results obtained for the other samples show similar results. One notable exception is filter number 3 where the coarse particles exhibit a predominantly ZnSO_4 spectrum, this can be understood by noting that there exists an anomalously large Ti concentration during that same interval indicating the possibility of local source activity. A detailed interpretation of these data would require more extensive information regarding other variables such as wind speed and direction and concentration of gaseous species such as SO_2 .

Absorption edge scans for the elements Cu and Fe were performed on additional samples. The Fe spectra were found to be consistent with mixtures of FeSO_4 (or $\text{FeNH}_4(\text{SO}_4)_2$) and Fe_2O_3 as the predominant constituents. This is consistent with the fact that most Fe containing particulates (particularly in the coarse fraction) are known to originate from windblown soil. It is reasonable to assume that the Fe_2O_3 absorption properties closely resemble those of soil components particularly when compared with Fe metal, FeSO_4 and $\text{FeNH}_4(\text{SO}_4)_2$. The observation that no particular interval or sampling site exhibits a significantly different composition supports the conclusion that the source is extended rather than specific to a given location.

The Cu analyses indicated a predominance of CuSO_4 in the fine particulate samples studied. Of the five samples which were analyzed by least squares fitting, the fraction of CuSO_4 ranged from 0.80 to 1.00. Since the samples were selected for anomalously high Cu concentrations, the observed particulates should be associated with a particular source. The uniform observation of CuSO_4 in the fine particles may indicate the rapid conversion of the Cu compounds to the sulfate form.

SUMMARY AND CONCLUSIONS

The method of x-ray absorption spectroscopy has been applied to the chemical analysis of thin air particulate samples. This method can determine the chemical form of a specific element by scanning the particular x-ray absorption edge and measuring the characteristics of the absorption pattern. When combined with multiple x-ray fluorescence detectors, a sensitivity adequate for the analysis of $2.5 \mu\text{gm}/\text{cm}^2$ of a particular element in one hour running time is achieved. The characteristics of the absorption patterns are sufficiently distinct to allow the identification of many compounds of interest in air pollution studies. Where binary mixtures of compounds are postulated, the use of a least squares fitting procedure yields relative concentrations accurate to within $\pm 7\%$.

The method is sensitive, non-destructive, and responds to the bulk properties of the particles in the samples. It can be used to complement surface sensitive measurements such as ESCA and Auger spectroscopy. When combined with total elemental concentrations obtained from x-ray fluorescence analysis, a relatively complete chemical characterization of the particular element can be obtained. In the present study, the results obtained from the analysis of a few selected samples could be tentatively interpreted in terms of very simple models. More detailed interpretation including data from other measurements such as SO_2 concentrations, relative humidity, wind speed and direction is being considered.

Although it is not possible at present to analyze large volumes of samples economically, use of this method in research applications is practical. With the increasing availability of synchrotron radiation facilities, x-ray absorption spectroscopy could become a useful technique for the chemical characterization of air particulate filters and other environmental samples.

Our immediate use of the technique will involve a study of the chemical forms and transformations associated with certain elements in power plant plumes. The complementary results obtained from surface analyses should serve to illuminate the role of these elements in gas-particle interactions in the plume.

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TABLE I. FITTED COEFFICIENTS OBTAINED FROM 1:1
MIXTURES OF COMPOUNDS

COMPOUNDS	COEFFICIENTS
ZnSO_4	0.46 ± 0.03
ZnO	0.54 ± 0.03
$\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2$	0.42 ± 0.04
ZnO	0.58 ± 0.04

TABLE II. SUMMARY OF Zn ABSORPTION EDGE MEASUREMENTS

SAMPLE NO.	STATION DATE/TIME	SIZE RANGE	MAJOR ELEMENTAL CONSTITUENTS ($\mu\text{g}/\text{cm}$)							X-RAY ABSORPTION RESULTS*
			S	Fe	Cu	Zn	Br	Pb	OTHER	
1	#103 (URBAN) 10/4/75 0600-1200	FINE	22.1	0.95	0.23	7.7	1.18	8.66	-	0.91 ± 0.02 $\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2$ 0.09 ± 0.02 ZnO
2		COARSE	3.74	5.14	0.23	11.3	0.15	1.98	-	0.19 ± 0.02 $\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2$ 0.81 ± 0.02 ZnO
3	#103 9/27/75 0000-0600	COARSE	4.86	9.77	0.15	3.08	0.43	0.59	Ti=2.57	0.72 ± 0.04 ZnSO_4 0.27 ± 0.04 ZnO
4	#103 8/29/75 0000-0600	COARSE	3.77	4.11	0.56	18.0	0.09	2.18	Cd=0.53	0.38 ± 0.03 ZnSO_4 0.62 ± 0.03 ZnO
5	#103 11/17/75 0600-1200	FINE	8.12	0.72	3.08	3.08	0.56	4.05	-	0.90 ± 0.02 ZnSO_4 0.10 ± 0.02 ZnO
6	#105 (URBAN) 9/4/75 1800-2400	COARSE	3.76	5.14	0.17	7.46	0.16	1.46	-	0.36 ± 0.03 ZnSO_4 0.64 ± 0.03 ZnO
7	#105 12/22/75 0600-1200	FINE	14.1	3.34	0.41	4.88	0.95	12.1	-	0.55 ± 0.03 ZnSO_4 0.45 ± 0.03 ZnO

*The errors quoted for the fit coefficients were derived from statistical analysis of the fitted parameters. A more realistic error estimate, including systematic effects would be $\pm 7\%$.

FIGURE CAPTIONS

- Fig. 1 X-ray absorption spectrum for Na_2MoO_4 for the energy region near the K shell binding energy. The various structural features are indicated.
- Fig. 2 Experimental system used for x-ray absorption spectroscopy. The primary x-ray beam is derived from the synchrotron radiation with a high energy electron storage ring. In the formula $\tau(E)$ is the photoelectric cross section (cm^2/gm), ρ is the density and x is the thickness.
- Fig. 3 Representative absorption spectra obtained at the Zn K-shell binding energy using a series of standard compounds of potential interest in aerosol studies.
- Fig. 4 Absorption spectra obtained at the Zn K-absorption edge from two samples acquired simultaneously at an urban sampling site. The coarse particles represent the size fraction from $2.4 \mu\text{m}$ to $20 \mu\text{m}$ in diameter, the fine particles are less than $2.4 \mu\text{m}$. The spectra indicate a predominance of ZnO in the coarse particle, $\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2$ in the fine.
- Fig. 5 Spectrum obtained from a 1:1 mixture of ZnO and ZnSO_4 . A least squares fit of single compound standards to this spectrum generated the fitted ratios given in Table 1.

Figure 1

XBL 798-10791

$$N(E) \propto I_0(E) (1 - e^{-\tau(E) \rho x})$$

$$I(E) \propto I_0(E) e^{-\tau(E) \rho x}$$

XBL 797-10597

Figure 2

XBL 797-10599

Figure 3

XBL 797-10598

Figure 4

XBL 797-10596

Figure 5

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