Spectroscopy

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X-RAY SPECTRO-MICROSCOPY AND MICRO-SPECTROSCOPY IN THE 2100 eV TO 12000 eV REGION (INVITED)

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ABSTRACT

An x-ray microprobe beamline was recently developed and commissioned at the Center for Advanced Microstructures and Devices (CAMD), Louisiana State University. It achieves a moderate horizontal and vertical focal spot size of 18.8 μm x 7.0 μm (σ), respectively. The beamline and end-station are designed and optimized to perform (*i*) spatially-resolved x-ray fluorescence spectroscopy (spectro-microscopy) using the broad intense spectrum of the white synchrotron radiation, and (*ii*) spatially-resolved x-ray absorption spectroscopy (micro-spectroscopy) in the energy region of 2100 eV to 12000 eV. These dual capabilities enable K-edge measurements and mapping, in non-vacuum conditions, of low-Z elements down to Cl, S, and P that are of both environmental interest and technological importance. In this paper, an application of this novel synchrotron tool to elucidate the elemental distribution (microstructure) and chemical state (speciation) of Mn, Cl, S, and P-containing particulates emitted from automobile engines burning methylcyclopentadienyl manganese tricarbonyl- (MMT-) added fuel will be discussed in detail. Future opportunities of this microbeam technique in materials science and materials characterization will also be outlined.

INTRODUCTION

The storage ring of the Center for Advanced Microstructures and Devices (CAMD) at the Louisiana State University was designed and optimized for soft x-ray lithography [1]. The ring usually operates at 1.3 GeV with an average injection current of 200 mA, having a critical photon energy of ~ 1660 eV. In order to take full advantage of the high photon flux in the low-energy region of the CAMD storage ring, we designed, installed and commissioned a x-ray microprobe beamline and end-station using an achromatic mirror focusing system in Kirkpatrick-Baez configuration [2-4]. The large emittance of the CAMD storage ring combined with the desire to accept as much incident radiation as possible in the energy range between 2000 eV to 6000 eV, triggered the choice of a Kirkpatrick-Baez (KB) mirror focusing system [5]. Due to this set-up we are able to perform (*i*) spatially-resolved elemental determination via x-ray fluorescence spectroscopy (micro-XRF) using high intensity polychromatic (white) radiation and (*ii*) spatially-resolved x-ray absorption near-edge structure spectroscopy (micro-XANES) using monochromatic radiation of a double crystal monochromator. Resolution

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measurements show that we obtain a horizontal and vertical focal spot size of 18.8 μm x 7.0 μm (σ), respectively, and a monochromatic photon flux of ~ 10^8 photons per second per 100 mA in the low-energy energy region.

In this paper we show part of a study investigating the elemental distribution and the chemical state of particulate matter with a spatial resolution of ~ 26 μm (σ). The particulate matter was produced by an automobile engine burning regular gasoline fuel with the additive methylcyclopentadienyl manganese tricarbonyl- (MMT-). Micro-XRF results were used to locate concentrations of constituent elements. Micro-XANES measurements at the appropriate elemental K-edges were then performed at selected points-of-interest (POI's) corresponding to areas of high concentration. The K-edges scanned include sulfur and phosphorus. This thus serves as an excellent example of the capabilities of the system, including elemental mapping using polychromatic light, micro-XANES using monochromatic light, and covering the K-edges of lighter elements (S and P).

EXPERIMENTAL SET-UP OF THE MICROPROBE END-STATION

A detailed view of the microprobe end-station is presented in Figure 1. A double crystal monochromator (DCM) in Golovchenko configuration (not indicated in Figure 1) is located upstream of the end-station and connected through a vacuum pipe, a thin Kapton window and a bellows to the end-station. The set-up allows us to either use monochromatic or direct white radiation by simply translating the DCM crystals in/out of the white beam and translating the kinematic table vertically. The entire end-station is housed in a Plexiglas enclosure (HE), which is purged with helium during operation. A motorized 4-jaw entrance slit (HS) defines the horizontal and vertical acceptance of the KB-system. The sample (SH) with a maximal size of 45 mm x 15 mm is mounted under 45° to the incident focused beam. To collect data in transmission a photo-diode (PD) is positioned behind the sample in the direct beam. Fluorescence data, on the other hand, is acquired with an energy-dispersive germanium detector (GE), which is also coupled in to the helium atmosphere. To obtain an optical microscope image of the sample, a long-working distance microscope (MI) is pointed through a view port under 90° to the sample. To collect the primary intensity of the focused x-ray beam, an ion-chamber (IC) is located between the KB-system and the sample [5].

SAMPLE PREPARATION AND DATA ACQUISITION

The particulate samples were collected on Teflon-coated fiberglass filters in such a way that an approximately 36 mm diameter area was exposed to the exhaust particulates. The filters were attached to the exhaust of a 1997 Ford Taurus with a 3.0 L V6 engine operating on gasoline containing MMT at 0.3125 g-Mn/gal. Further details of the sample preparation appear in the bulk XANES investigation of these samples by Ressler et al. [6]. The particulate sample investigated here corresponds to Sample #12 in that study.

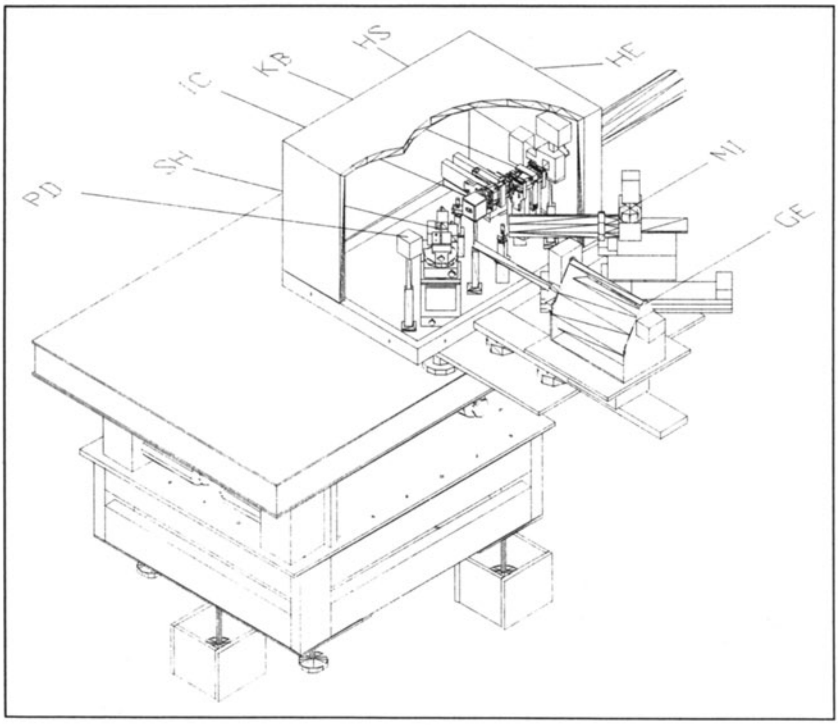

Figure 1. The experimental setup of the microprobe end-station.

The sample was mounted on the x-z sample stage, positioned under 45° to the incident focused beam and the energy-dispersive germanium detector (Ge-detector). The distance between the sample and the Ge-detector varied depending upon data collection (micro-spectroscopy or spectro-microscopy) between 5 mm and 50 mm. The experimental chamber was purged with helium to suppress air absorption.

The elemental maps depicting the elemental distributions in the particulate samples were collected with focused, white/polychromatic x-ray beam with a horizontal and vertical focal spot size of 26 µm x 17 µm (σ). The grazing angles of the focusing mirrors in the Kirkpatrick-Baez focusing system were set to 8 mrad, resulting in a high-energy cut off at ~ 8000 eV. To elucidate the elemental distribution of P, S, and Mn in the particulate samples, regions-of-interest (ROI's) were set around the characteristic x-ray fluorescence lines in the multi-channel analyzer software and the integrated counts of the 3 ROI's were simultaneously acquired while scanning the sample through the incident focused beam in the x and z directions.

For the micro-XANES experiments at the K-edges of Mn, S, and P, the Si(111) crystals of the LNLS double crystal monochromator were translated into the white beam

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and the experimental chamber was lowered to adjust for the resulting vertical offset of ~ 20.4 mm [6]. Prior to the data acquisition at the S and P K-edges, harmonic rejection was performed by detuning the Si(111) crystals approximately 50% of the peak intensities of the rocking curves. For the energy calibration of the DCM, at the Mn K-edge the first inflection point of elemental Mn was set to 6539 eV. Similarly for the calibration at the S and P K-edges the sharp white lines of the zinc sulfate ($ZnSO_4$) at 2481.4 eV and $ZnPO_4$ at 2150 eV were used. Micro x-ray absorption near-edge structure (micro-XANES) spectra were collected in fluorescence mode at selected points-of-interest (POI's), utilizing the integrated ROI count rate of the appropriate K_α elemental fluorescence line collected with the energy-dispersive Ge-detector.

RESULTS AND DISCUSSION

Before beginning data acquisition, knife-edge scans were performed to determine the beam size on the sample. For this study, a moderately focused beam was used, with a measured horizontal x vertical spot size of 26 μm x 17 μm (σ).

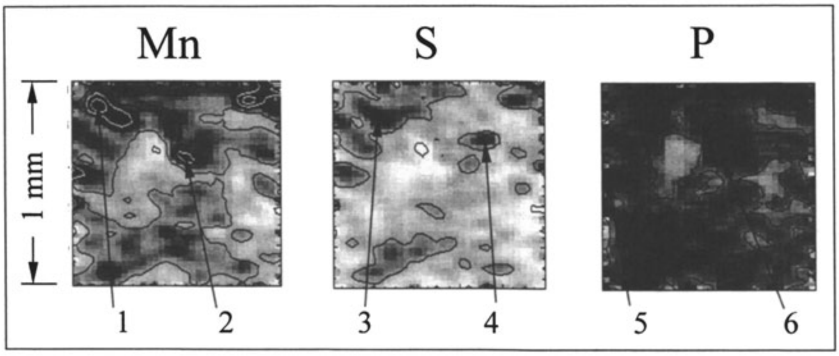

Figure 2. Fluorescence maps from Sample #12, indicating the distributions of Mn, and S. Points-of-interest (POI's) from which micro-XANES spectra were collected are labeled.

Fluorescence maps were collected from 3 areas located along the radius of the filter, with each area having dimensions of 1 mm vert. x 1 mm hor. (at 45° to the beam direction). Each area was scanned using steps of 20 μm vertical and 30 μm horizontal (at 45° to beam direction). Fluorescence data were simultaneously collected using regions-of-interest (ROI's) corresponding to the K_α lines of P, S, and Mn, (and others). These maps reflected a trend with a higher concentration of Mn-particulate matter near the center of the filter than at the edge. Therefore, the points-of-interest (POI's) for this sample were all taken from this central region. The Mn, S, and P fluorescence maps for the 1 mm x 1 mm area near the center of Sample #12 appear in Figure 2. Distinct particles or agglomerations of manganese, sulfur, and phosphorus can be observed in the appropriate maps. From visual comparison of these elemental distributions, specific

POI's were selected for micro-XANES measurements. These spots are labeled in Figure 2.

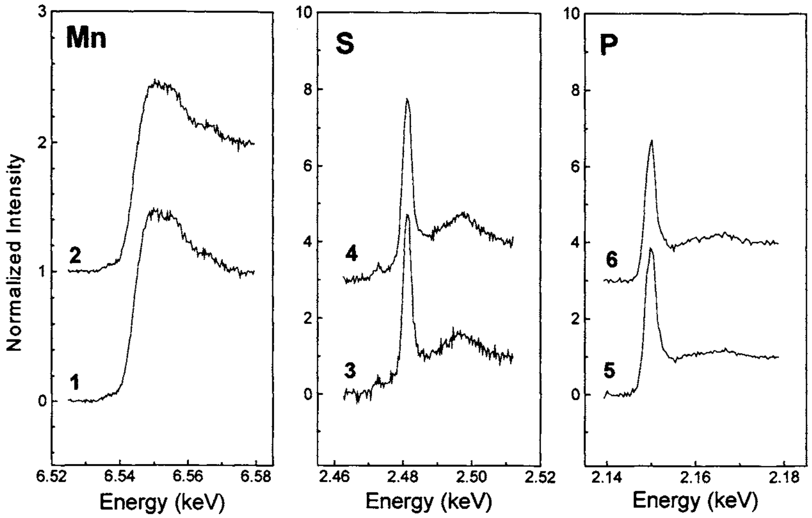

Figure 3. Micro-XANES spectra collected at the K-edges of Mn, S, and P from Sample #12 (Group II). The labels correspond to POI's indicated in Figure 2.

Micro-XANES measurements were performed at the Mn, S, and P K-edges at the appropriate POI's labeled in Figure 2. The resulting spectra are shown in Figure 3. The Mn spectra look similar to the bulk spectrum for this sample reported by Ressler et al. [6]. In that study, this spectrum was described in terms of a mixture of three phases: Mn_3O_4, $MnSO_4 \cdot H_2O$, and $Mn_5(PO_4)[PO_3(OH)]_2 \cdot 4H_2O$. The similarity between the micro-XANES and the bulk XANES spectra suggests a relatively homogeneous distribution of the constituent phases down to a scale of ~ 26 µm, the σ-value of the focused x-ray beam at the sample. The S spectra both exhibit a prominent sulfate peak at about 2481 eV, and an indication of a feature at a lower energy that could indicate the presence of a more reduced species (most likely a sulfide). In the P XANES, the sample spectra reveal the presence of phosphate, represented by a strong white line at about 2150 eV.

CONCLUSIONS

The design and implementation of the CAMD microprobe beamline have been successfully completed, with the instrument demonstrating the desired capabilities (x-ray micro-fluorescence mapping with polychromatic radiation, and micro-XANES with monochromatic radiation), including the ability to measure in the lower energy region (down to about 2000 eV) to assess the distribution and speciation of lighter elements such as sulfur and phosphorus. These capabilities are demonstrated in the study of the particulate sample collected from the exhaust of an automobile engine burning MMT-containing gasoline. The results show that manganese is present in the emissions in a mixture of several phases, sulfur is identified and is present as a sulfate, and phosphorus is present in the form of a phosphate. While a more detailed study is necessary (and is currently in progress), the current study serves to provide valuable information on the nature of these particulate emissions, and to demonstrate the capabilities of the new end-station.

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REFERENCES

1. R. L. Stockbauer, P. Ajmera, E. D. Poliakoff, B. C. Craft, and V. Saile, Nuclear Instruments and Methods in Physics Research A **291,** p. 505-510 (1990).
2. P. Kirkpatrick and A. Baez, Journal of the Optical Society of America **38,** p. 766-774 (1948).
3. P. Kirkpatrick, A. Baez, and A. Newell, Physical Review **73,** 535-536 (1948).
4. P. J. Eng, M. Newville, M. L. Rivers, and S. R. Sutton, in *X-Ray Microfocusing: Applications and Technique*, edited by I. McNulty (SPIE Proceeding **3449**, Bellingham, WA 1998), p. 145-156.
5. N. Mölders, H. O. Moser, V. Saile, and P. J. Schilling, “Spatially-Resolved X-Ray Spectroscopy at CAMD,” Report No. FZKA **6314** (1999).
6. T. Ressler, J. Wong, and J. Roos, accepted for publication in Environmental Science and Technology (1999).

SURFACE INTERACTIONS OF ACTINIDE IONS WITH GEOLOGIC MATERIALS STUDIED BY XAFS

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ABSTRACT

We have investigated the interaction of the actinyl ion, UO_2^{2+}, with silica, alumina, and montmorillonite surfaces under ambient atmosphere and aqueous conditions using X-ray Absorption Fine Structure (XAFS) Spectroscopy. In acid solution (pH ~ 3.5), the uranyl ion shows a strong interaction with the silica and alumina surfaces, and a relatively weak association with the montmorillonite surface. The extent of direct surface interaction is determined by comparing structural distortions in the equatorial bonding environment of the uranyl ion relative to the structure of a "free" uranyl aquo complex. Based on this formalism, surface complexation on silica and alumina occurs through an inner-sphere mechanism with surface oxygen atoms binding directly to the equatorial region of the uranyl ion. In contrast, sorption on montmorillonite occurs by an outer sphere mechanism in which the uranyl ion retains the simple aquo complex structure and binds to the surface via ion-exchange. In near-neutral solutions (pH ~ 6), sorption on all of the materials is dominated by an inner-sphere mechanism. The formation of surface oligomeric species is also observed on silica and alumina.

INTRODUCTION

Naturally occurring uranium is mined for fuel for nuclear reactors and so is present in the ecosphere as a mineral as well as a waste product of nuclear industry. It has a long half-life and is observed to have coordination chemistry consisting of multiple stable oxidation states and stable solid and aqueous forms within the ecosphere [1-8]. Under standard environmental conditions, uranium typically occurs in the hexavalent form as the mobile, aqueous uranyl ion (UO_2^{2+}). Adsorption of this ion onto geologic materials has been extensively studied since this process can have a significant effect on radionuclide transport properties in the environment [3-4, 6, 8-26].

Traditional investigations of geochemical adsorption concentrate on the macroscopic aspects of the interaction of a particular ionic or molecular species with a mineral surface (i.e, uptake, K_d), but give little direct structural information on the chemical environment around a single atom. X-ray absorption fine structure (XAFS) spectroscopy which includes the extended x-ray absorption fine structure (EXAFS) and the x-ray absorption near-edge structure (XANES), is a technique which can be used to determine local structure and oxidation state of an atom in chemical environments where long range order does not exist, such as liquids, amorphous solids, and surface complexes. Thus it is an ideal tool for the direct determination of the structure of surface-adsorbed complexes and can be used to study the mechanism of adsorption on the molecular scale [1, 4, 6, 8-12, 14, 16-17].

EXPERIMENT

Sample Preparation

The montmorillonite material used in this study was prepared from a calcium-montmorillonite (SAz-1; source locality: Cheto, Arizona) obtained from the Source Clay Minerals Repository (University of Missouri, Columbia, Missouri). Prior to loading with uranium, the <2 μm fraction was selectively obtained via centrifugation and was converted to the sodium-form by contacting with 2 M NaCl solutions several times. The

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clay was rinsed free of chloride ions and subsequently freeze-dried. The same material was used in previous sorption experiments [21]. Its external surface area, calculated from a multipoint N_2-BET isotherm determined using a Coulter SA3100 surface area analyzer, is 97 m^2/g. The reported cation exchange capacity for SAz-1 montmorillonite is 1.2 meq/g [27].

Γ-Al_2O_3 and amorphous SiO_2, with reported purities of 99.8 % and 99.7 %, respectively, were obtained from Alfa Aesar. The surface areas of the dry, as-received γ-Al_2O_3 and SiO_2 material measured with the Coulter SA3100 surface area analyzer are 87 and 370 m^2/g, respectively. These materials were loaded with uranium without any pretreatment step.

One-liter uranium(VI) solutions in polycarbonate bottles were made from reagent grade $UO_2(NO_3)_2 \cdot 6H_2O$ (Mallinkrodt) and deionized water with a resistivity greater than 17 $M\Omega \cdot cm$. Of the one-liter solutions, 30-mL aliquots were taken and acidified with HCl for later analysis of uranium concentration. Uranium loaded sorbents were prepared by mixing 0.97 gram of the solid with the remaining 970-mL solutions.

The pH values were adjusted by addition of small amounts of 0.5 M NaOH or 0.1 M HNO_3. For each solid, samples were prepared at different pH values so that the effect of pH upon adsorption mechanism(s) could be evaluated. NaCl was added to montmorillonite mixtures G, H, and I to determine if a change in the structure of adsorbed uranium species can be discerned from EXAFS data as the ion-exchange mechanism is suppressed.

The mixtures were kept open to atmospheric $CO_2(g)$ and were agitated at ambient temperature conditions using a gyratory shaker. After about five days of reaction time, the solid phase was separated by filtration and the aqueous phase was sampled for measurement of the pH and final uranium concentration. After filtration, the wet paste samples were kept in sealed plastic vials prior to EXAFS analysis. Chemical data for all prepared samples is summarized in Table 1.

Table 1. Summary of uranium sorption data

Sample	Sorbent	[NaCl] (molal)	Final pH	Initial $[UO_2^{2+}]$ (molal)	Final $[UO_2^{2+}]$ (molal)	Uranium Uptake (%)	Uranium Loading (moles of U per g of solid)
A	silica	0	6.46	4.15E-5	1.02E-6	97.5	4.05E-05
B	silica	0	3.14	0.979E-2	0.970E-2	0.92	9.00E-05
C	alumina	0	6.50	4.18E-5	4.62E-8	99.9	4.18E-05
D	alumina	0	3.48	0.991E-2	0.958E-2	3.33	3.30E-04
E	montmorillonite	0	3.24	0.987E-2	0.949E-2	3.85	3.80E-04
F	montmorillonite	0	4.11	1.00E-4	1.72E-7	99.8	9.98E-05
G	montmorillonite	0.01	4.11	0.979E-4	0.196E-4	80.0	7.83E-05
H	montmorillonite	0.10	4.06	1.00E-4	0.891E-4	10.9	1.09E-05
I	montmorillonite	0.10	6.41	1.02E-4	0.276E-4	72.9	7.44E-05

XAFS Data Acquisition and Analysis

Uranium L_{III}-edge X-ray absorption spectra for samples A and C were collected on beamline X23A2 at the National Synchrotron Light Source (NSLS) using a Si(311) double-crystal monochromator. Spectra for all other samples were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline II-3 using a Si (220) double-crystal monochromator. Beam size was typically cropped to 9 mm (horizontal) by 1 mm (vertical). All spectra were collected in transmission mode at room temperature using argon-filled ionization chambers, and energy calibrated by simultaneous measurement of the transmission spectrum of a solid uranyl nitrate hexahydrate standard