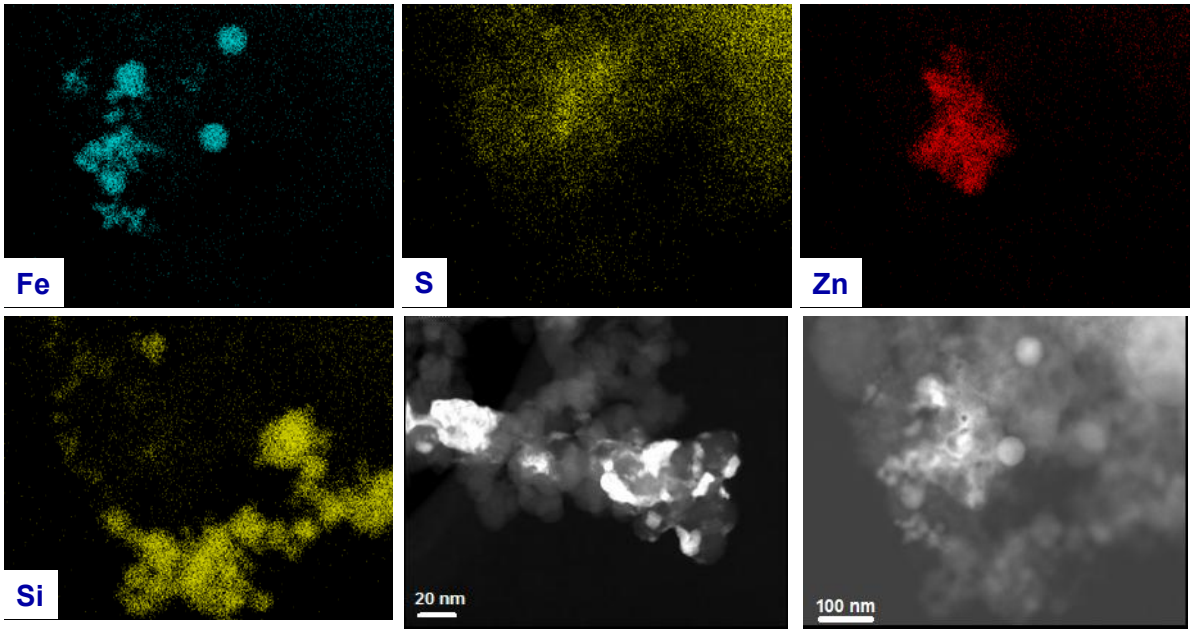
Final Report

Individual Particle Analysis of Ambient $PM_{2.5}$ Using Advanced Electron Microscopy Techniques



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DISCLAIMER

ABSTRACT

The overall goal of this project was to demonstrate a combination of advanced electron microscopy techniques that can be effectively used to identify and characterize individual particles and their sources. Specific techniques to be used include high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), STEM energy dispersive X-ray spectrometry (EDX), and energy-filtered TEM (EFTEM).

A series of ambient $PM_{2.5}$ samples were collected in communities in southwestern Detroit, MI (close to multiple combustion sources) and Steubenville, OH (close to several coal-fired utility boilers). High-resolution TEM (HRTEM) -imaging showed a series of nano-metal particles including transition metals and elemental composition of individual particles in detail. Submicron and nano-particles with Al, Fe, Ti, Ca, U, V, Cr, Si, Ba, Mn, Ni, K and S were observed and characterized from the samples. Among the identified nano-particles, combinations of Al, Fe, Si, Ca and Ti nano-particles embedded in carbonaceous particles were observed most frequently. These particles showed very similar characteristics of ultrafine coal fly ash particles that were previously reported. By utilizing HAADF-STEM, STEM-EDX, and EF-TEM, this investigation was able to gain information on the size, morphology, structure, and elemental composition of individual nano-particles collected in Detroit and Steubenville.

The results showed that the contributions of local combustion sources – including coal-fired utilities – to ultrafine particle levels were significant. Although this combination of advanced electron microscopy techniques by itself can not identify source categories, these techniques can be utilized as complementary analytical tools that are capable of providing detailed information on individual particles.

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EXECUTIVE SUMMARY

The project titled as "Individual Particle Analysis of Ambient $PM_{2.5}$ Using Advanced Electron Microscopy Techniques" was designed to characterize individual nano-scale particles and their source categories, with an emphasis on coal-fired power plant-derived particles. In the past, scanning electron microscopy has been widely used to characterize micro-meter scale individual particles. However, freshly generated particles from fossil fuel combustion sources are mostly nano-scale (ultrafine); analytical techniques that are capable of providing information on the size, morphology, crystalline structure, and elemental composition of nano-scale individual particles are limited, hindering determination of specific combustion sources and their contributions. Specific techniques to investigate nano-scale particles included high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), STEM energy dispersive X-ray spectrometry (EDX), and energy-filtered TEM (EFTEM). These techniques were able to provide information on the size, morphology, and elemental composition of individual nano-scale particles.

First, the project collected a series of ambient $PM_{2.5}$ samples in urban communities in southwestern Detroit, MI (close to multiple combustion sources) and Steubenville, OH (close to several coal-fired utility boilers). Measurements of gaseous pollutants and meteorological parameters including wind speed, wind direction, temperature, relative humidity, and solar radiation were conducted. Next, nano-scale elemental mapping was conducted using the advanced electron microscopy techniques. High-resolution TEM (HRTEM)- imaging revealed a series of nano-heavy metal particles and elemental composition of individual particles in detail. Submicron and nano-particles with Al, Fe, Ti, Ca, U, V, Cr, Si, Ba, Mn, Ni, K and S were observed and characterized from the samples. Among the identified nano-particles, combinations of Al, Fe, Si, Ca and Ti nano-particles embedded in carbonaceous particles were observed most frequently. These particles showed very similar characteristics of ultrafine coal fly ash particles that were previously documented. The results showed that the contributions of local combustion sources – including coal-fired utilities – to ultrafine particle levels were significant in the urban communities in southwestern Detroit and Steubenville.

PROJECT DETAILS

Introduction

Epidemiological studies have shown associations between elevated mass concentrations of ambient fine particulate matter (mean aerodynamic diameter <2.5 μm; $PM_{2.5}$) and adverse health effects including respiratory and cardiovascular diseases. In particular, fossil fuel combustion has been hypothesized as the primary source of atmospheric $PM_{2.5}$ believed to be responsible for the observed health effects. As a result, recent studies have been focusing on the use of multiple analytical techniques to characterize particulate matter to better understand the relationship between anthropogenic emission sources and ambient $PM_{2.5}$. Information on individual aerosol particles is essential to the understanding of particle sources, formation, transport, and deposition mechanisms as well as the impact of particles deposited in the respiratory system.

In the past, scanning electron microscopy has been widely used to characterize micro-meter scale individual particles (Nelson et al., 2000; Mamane et al., 2001). However, freshly generated particles from fossil fuel combustion sources are mostly nano-scale (ultrafine); analytical techniques that are capable of providing information on the size, morphology, crystalline structure, and elemental composition of nano-scale individual particles are limited.

By using high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), the image is formed by an incoherent scattering process, and the contrast is correlated to the atomic mass and specimen thickness; heavier elements as well as thick areas have a brighter contrast. Thus, HAADF-STEM can be a useful tool for detecting ultrafine heavy metal particles. The proposed project utilized a combination of advanced electron microscopy techniques to identify and characterize samples of environmental interest that contain nano-particles.

Research Goals:

The overall goal of this project was to demonstrate a combination of advanced electron microscopy techniques that can be effectively used to identify and characterize individual particles and their sources. Specific techniques included high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), STEM energy dispersive X-ray spectrometry (EDX), and energy-filtered TEM (EF-TEM). Although these individual techniques have not been used widely in the environmental field, these techniques could provide information on the size, morphology, and elemental composition of individual nano-scale particles, especially from those samples of relatively low concentration. The proposed work consisted of two specific aims to achieve the overall objective:

AIM 1: To collect a series of ambient $PM_{2.5}$ samples in communities in southwestern Detroit, MI (close to multiple combustion sources including motor vehicle/diesel, incinerators, and oil and coal combustion sources) and Steubenville, OH (close to several coal-fired utility boilers) utilizing a recently built, state-of-the-art mobile laboratory.

AIM 2: To utilize HAADF-STEM, STEM-EDX, and EF-TEM to provide information on the size, morphology, structure, and elemental composition of individual particles collected in Detroit and Steubenville.

Experimental Methods

Measurement Sites:

Southwest Detroit, Michigan: The mobile air research laboratory, AirCARE1, was located next to Maybury Elementary School in an urban residential community in southwest Detroit, MI. The site is located one-half mile from the Ambassador Bridge. The Michigan Department of transportation estimates daily traffic volume near this site to be as high as100,000 vehicles/day. Furthermore, the densest industrial activity in the city is located on southwest area of Detroit

including iron-steel manufacturing, coke ovens, chemical plants, refineries, sewage sludge incineration, and coal-fired utilities (Keeler et al., 2002). According to the USEPA, multiple coal combustion utilities located in southwest Detroit are large emission sources of atmospheric $PM_{2.5}$ in the region (USEPA, 1999). In our previous investigations of ambient air monitoring and animal inhalation exposure studies at this site, we have reported possible associations between the adverse pulmonary health effects and ambient $PM_{2.5}$ emitted from the local combustion sources (Harkema et al., 2004; Morishita et al., 2004 & 2006).

Steubenville, Ohio: The Steubenville site was located on the campus of the Franciscan University overlooking the Ohio River. This monitoring site was selected because of its proximity to numerous anthropogenic air pollution sources in the Ohio River Valley. There are five large coal-fired utility boilers within a 50 km radius of the site and seventeen within 100 km (Keeler et al., 2006).

Urban Ambient Aerosol and Gaseous Pollutant Measurements:

All sample processing and analysis were carried out in the Class 100 clean laboratory at the University of Michigan Air Quality Laboratory. A set of seven $PM_{2.5}$ samples was collected from both Detroit and Steubenville sites to gauge impacts from different sources. $PM_{2.5}$ cyclone samplers were used to collect 24-hour integrated filter samples. Fine particle mass was sampled onto 47-mm Teflon (PTFE) membrane filters (Gelman Sciences, Ann Arbor MI). Vacuum pumps were used to draw air through a Teflon-coated cyclone inlet (URG Inc.) at a flow rate of 16.7 LPM. The volume of air drawn through each particulate sampling train was determined using a calibrated dry test meter (DTM) (Schlumberger, Owenton, KY). The DTMs were calibrated against a spirometer, a primary calibration standard, before and after being deployed in the field. In addition, a calibrated rotameter was used to check the flow rate at the beginning and end of the sampling period.

Furthermore, measurements of gaseous pollutants including SO_2, NO_x, and CO were performed. Continuous ambient CO measurements were made using a non-dispersive infrared analyzer (TECO 48S). The instrument specifications list the LOD and precision of the instrument as 0.04 ppm and ±0.1 ppm, respectively. Ambient NOx concentrations were measured using a commercial chemiluminescence detector (TECO 42S). The instrument has a single photomultiplier tube that automatically cycles between the NO and NOx modes. Signals from the photomultiplier tube are conditioned and then send to the microprocessor where a mathematical algorithm is utilized to calculate three independent outputs - NO, NO_2 and NOx. The LOD of instrument and precision were listed as 0.4 ppb and ±0.4 ppb, respectively. Ambient SO_2 concentrations were measured using a pulsed fluorescence technique (TECO 43S). The instrument specifications list the instrument LOD as 0.6 ppm and precision as ±1 ppb. Continuous measurements of wind speed, wind direction, temperature, relative humidity, and solar radiation were performed to understand how meteorological parameters affected the sites.

High-resolution transmission electron microscopy and analytical electron microscopy:

Samples were characterized in detail by field emission gun scanning electron microscopy (FE-SEM; Philips XL-30), high-resolution transmission electron microscopy (HRTEM) and analytical electron microscopy (AEM) using JOEL 2010F at the University of Michigan Electron Microbeam Analysis Laboratory. TEM specimens were prepared by dispersing the samples from the filters onto holey carbon grids. Before STEM analysis, the TEM specimen holder was cleaned with a plasma (Fischione Model C1020) to minimize contamination. Nano-scale elemental mapping with heavy elements were also conducted using high-angle annular dark-field scanning TEM (HAADF-STEM) and STEM-EDX mapping (Emispec: EsVision version 4.0).

Results and Discussions

In southeastern Michigan (i.e., Detroit), a great portion of the air pollution is generated by emissions from the local industries as well as motor vehicles within the city. In addition, during summer months, contribution of transported aerosol becomes the strongest. Polissar et al. (2001) reported that coal combustion emission sources extends from the lower Great Lakes to the south of the Ohio River Valley, encompassing the locations of many large electricity-generating plants and industrial sources in the Midwest. Thus, very large contribution of relatively remote coal combustion/transported aerosol sources was expected during the summer measurement campaign. The average ambient $PM_{2.5}$ mass concentrations measured during the measurement campaigns in July and August 2005 was 23.2±13.6 $\mu g/m^3$ (Figure 1).

In order to maximize the probability of finding particles that have been emitted from coal combustion sources, the ambient filter samples that had the highest Se concentration were selected for the microscopic analysis. High concentrations of S and Se are known tracers for coal combustion emission sources and transported aerosol (USEPA 2004; Chiaradia and Cupelin, 2000; Huang et al., 1994). As shown in Figure 2, the highest Se concentration was observed on the 2nd and 3rd of August in Detroit. Furthermore, elevated levels of SO_2 concentration were observed on the 3rd, especially in the afternoon when the predominant wind direction was south to southwest (Figure 3). As described before, the densest industrial activity in the city is located on southwest area of Detroit, and thus combined data on gaseous pollutants, meteorological parameters and chemical composition suggested that the probability of finding particles emitted from coke ovens and coal-fired utilities was relatively high on those days.

Next, a combination of advanced electron microscopy techniques including HAADF-STEM, STEM-EDX, and EFTEM were utilized to obtain detailed information on the size,

morphology, structure, and elemental composition of individual particles collected in Detroit and in Steubenville. As expected, numerous nano-metal particles that were most likely emitted from fossil fuel combustion sources were detected. Figures 4-8 show the particle size and morphology of individual particles in Detroit from HAADF-STEM and the elemental composition determined by the EDS spectra. Figure 9 shows the elemental distributions of nano-particles in the Detroit sample. As shown, numerous Fe and Si nano-particles are observed on the surface of submicron carbonaceous and sulfur particles.

More specifically, submicron and nano-particles with Al, Fe, Ti, Ca, U, V, Cr, Si, Ba, Mn, Ni, K, Pb, Sb and S were observed and characterized from the Detroit samples. Among the identified nano-particles, combinations of Al, Fe, S, Si, Ca and Ti nano-particles embedded in carbonaceous particles were observed most frequently. Although these inorganic elements including Al, Fe, Si, and Ca are generally regarded as crustal/soil elements, especially in the larger size modes, the observed particles in the ultrafine size fraction came from combustion processes and were formed by the vaporization-condensation mechanism. The observation of these elements were associated with numerous spherical particles in the ultrafine size fraction confirms that these particles were formed through combustion processes.

The results for the Steubenville samples are shown in Figures 10-15 for the particle size and morphology from HAADF-STEM and the elemental composition determined by the EDS spectra. In addition, Figure 16 shows the elemental map distribution. These nano-particles in Steubenville showed very similar morphology and elemental composition of individual particles that were collected in Detroit.

Chen et al. (2005) previously characterized and documented ultrafine coal fly ash particles by using high-resolution transmission electron microscopy. Their study reported that a

combination of Ti-Al-Fe ultrafine particles has been found in Western Kentucky coal fly ash most frequently, and oxides of Fe, Ti, and Ca constitute the major single-element categories, and Ti-Al-Fe, Fe-Si-Al, Ti-Si-Al, and Al-Mg-Fe are the major three-element categories (Chen et al., 2005). Our investigation also found the very similar combination of ultrafine coal fly ash particles. Table I shows the similarity between what we have observed in ambient $PM_{2.5}$ samples and what have been found in coal fly ash ultrafine particles in previously published studies.

As described, Se has been one of signature elements for coal combustion. Although the total Se mass was detected by ICP–MS analysis, we did not locate any Se particle in the ambient samples during our electron microscopy analyses. The most likely explanation is that Se was below the limit of detection of the EDS spectra or that nano-Se particles were embedded in other particles. One possible explanation for the presence of Se within individual particles is that Se is a semi-volatile metal that is vaporized during coal combustion and is then scavenged by a large number of pre-existing particles. The selenium could be spread thinly over the entire particle population and the amount of selenium in any individual particle would be small (Pekney, et al., 2006). In future, use of the particle concentrator may enable us to investigate real-life ambient nano-particles at an increased level and to overcome the limit of detection of trace elements such as Se that can be used to identify source categories. This will further help characterize the temporal chemical variability and potential sources of nano-particles in various locations.

Conclusions

HAADF-STEM, STEM-EDX, and EF-TEM, applied in this investigation provided specific information on the size, morphology, structure, and elemental composition of individual nano-particles collected in Detroit and Steubenville. The results showed that combinations of Al, Fe, S, Si, Ca and Ti nano-particles embedded in carbonaceous and sulfur particles were

observed most frequently, and the contributions of local combustion sources – including coal-fired utilities – to ultrafine particle levels were significant. Although this combination of advanced electron microscopy techniques by itself can not identify specific source categories at this time, these techniques can be utilized as complementary analytical tools that are capable of providing detailed information on individual particles, and provides additional support for source identification when used in concert with other chemical and elemental receptor modeling techniques.

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LIST OF ACRONYMS AND ABBREVIATIONS

HAADF-STEM: High-angle annular dark field scanning transmission electron microscopy

HRTEM: High-resolution TEM

EDX: Energy dispersive X-ray spectrometry

EDS: Energy-dispersive X-ray spectroscopy

EFTEM: Energy-filtered TEM

$PM_{2.5}$: Ambient fine particulate matter (mean aerodynamic diameter <2.5 μm)

ABSTRACTS OF PRESENTATIONS AT NATIONAL SCIENTIFIC MEETINGS

Morishita, M, Keeler, GJ, Wagner, JG, Kamal, AS, Harkema, JR, and Rohr, AC. Associations of Chemical Composition of Ambient $PM_{2.5}$ with Heart Rate Variability in Spontaneous Hypertensive Rats. 7th International Aerosol Conference, St. Paul, MN, September 10-15, (2006).

Table 1. Reported elemental tracers for coal combustion aerosols.

Sampling Location	Elements Identified (this study)	Reference to coal combustion
Detroit	Ca-rich	Chen et al., 2005
	Ti-rich	Chen et al., 2005
	Fe-rich	Chen et al., 2005
	Pb, U	EPA, 1995/Goodarzi, 2006
	Zn, Pb, Mn	Chow, et al., 2004
Steubenville	Si-rich Al-Fe	Chen et al., 2005
	Ti-Si-Al-Fe	Chen et al., 2005
	Ti-Si-Al	Chen et al., 2005
	Fe-rich	Chen et al., 2005
	Pb, Ni, Cr	EPA, 1995/Goodarzi, 2006
	Zn, Pb, Mn	Chow, et al., 2004

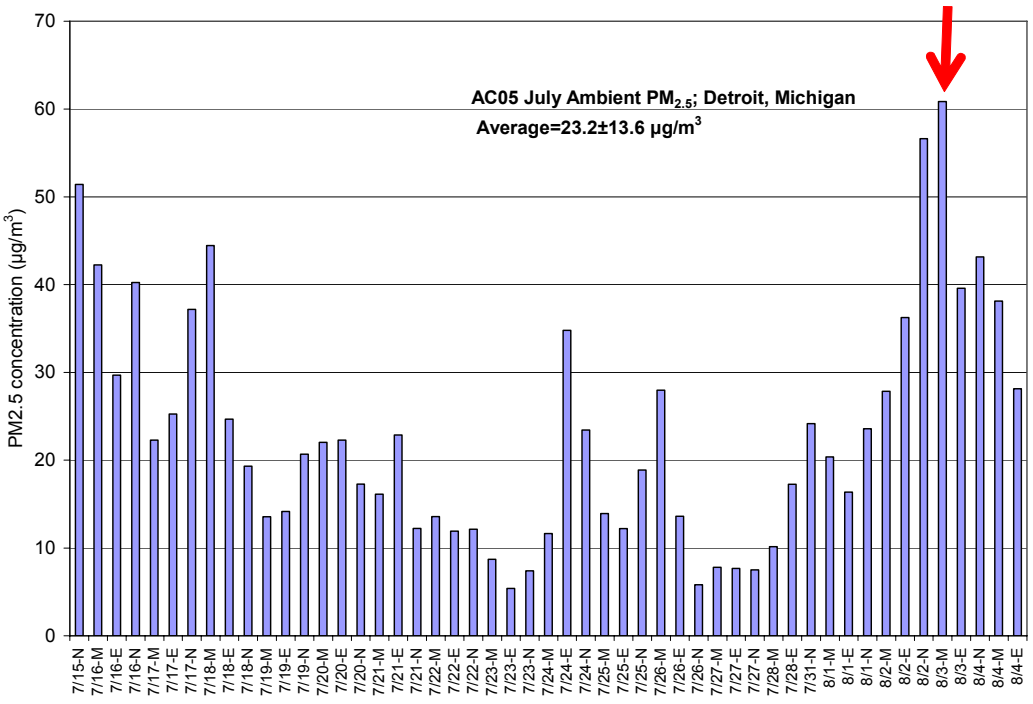


Figure 1. Temporal variations of ambient $PM_{2.5}$ concentrations measured in Detroit in July & August 2005.

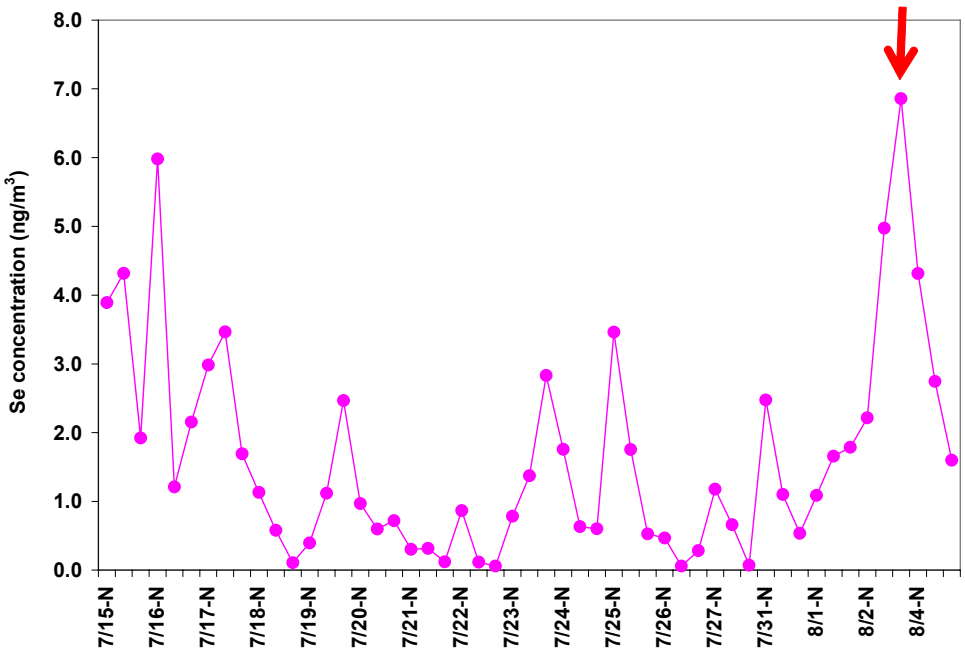


Figure 2. Temporal variations of selenium concentrations in ambient $PM_{2.5}$ samples in Detroit in July & August 2005.

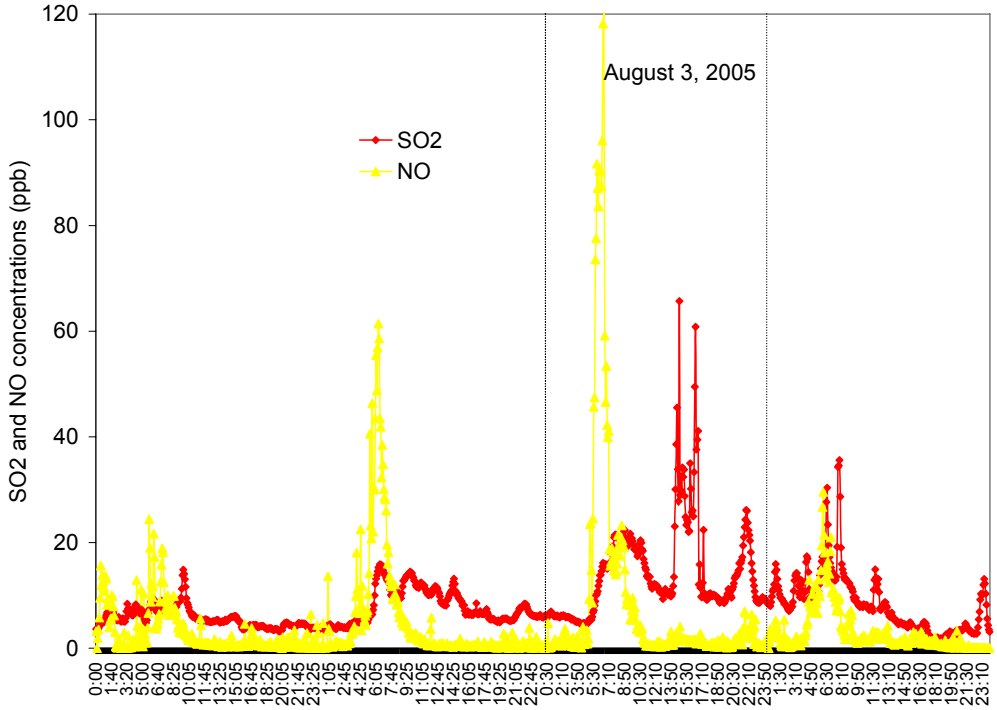


Figure 3. Temporal variations of primary gaseous pollutants in Detroit between August 1st and August 4th.

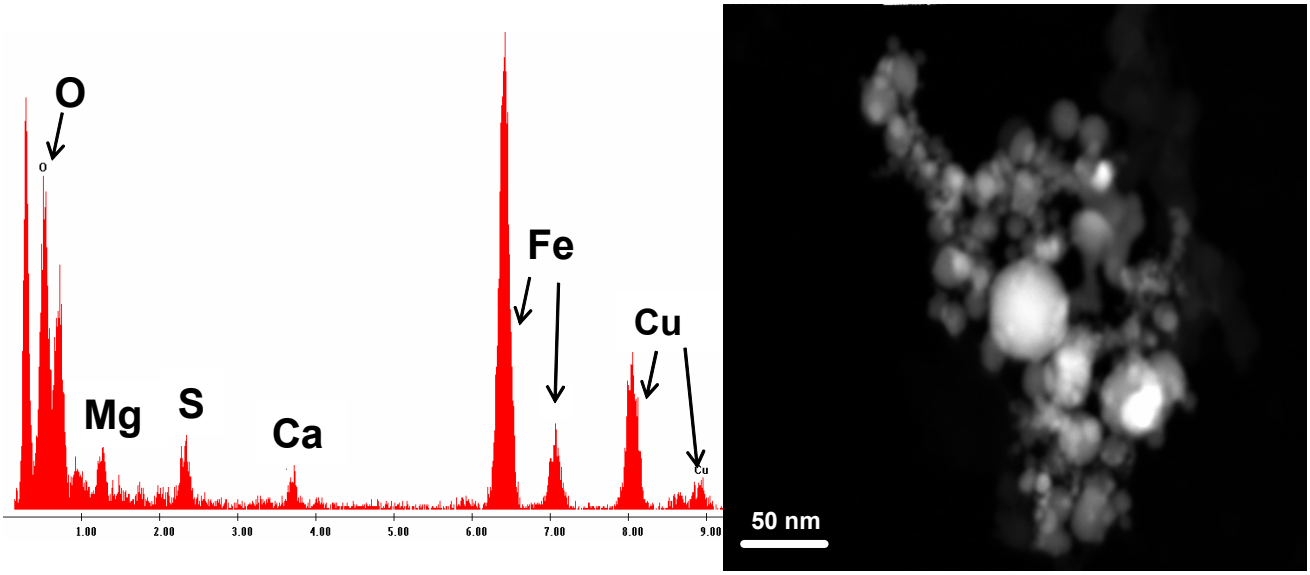


Figure 4. HAADF-STEM image of iron oxide-rich ultrafine particles and soot aggregates collected in Detroit (right) and EDS spectra (left).

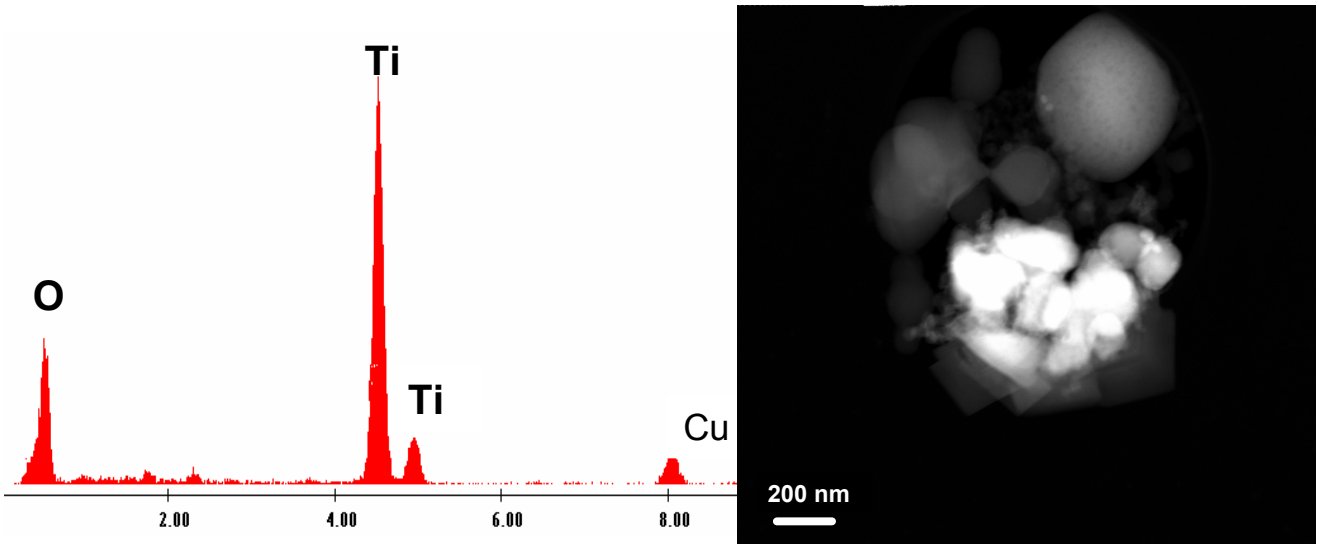


Figure 5. HAADF-STEM image of titanium oxide-rich ultrafine particles collected in Detroit (right) and EDS spectra (left).

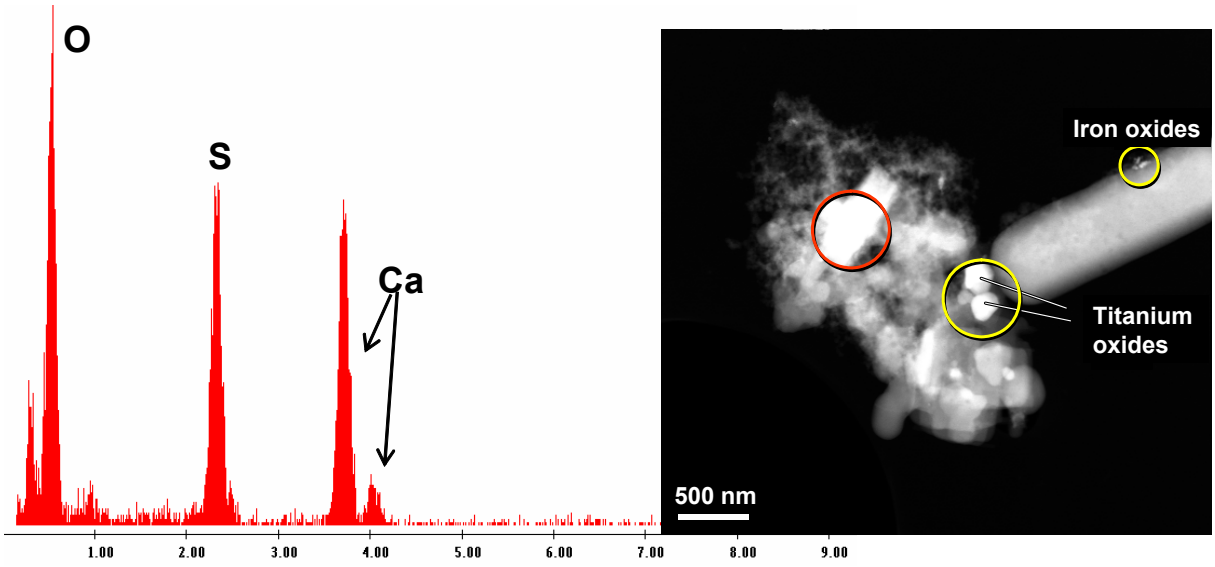
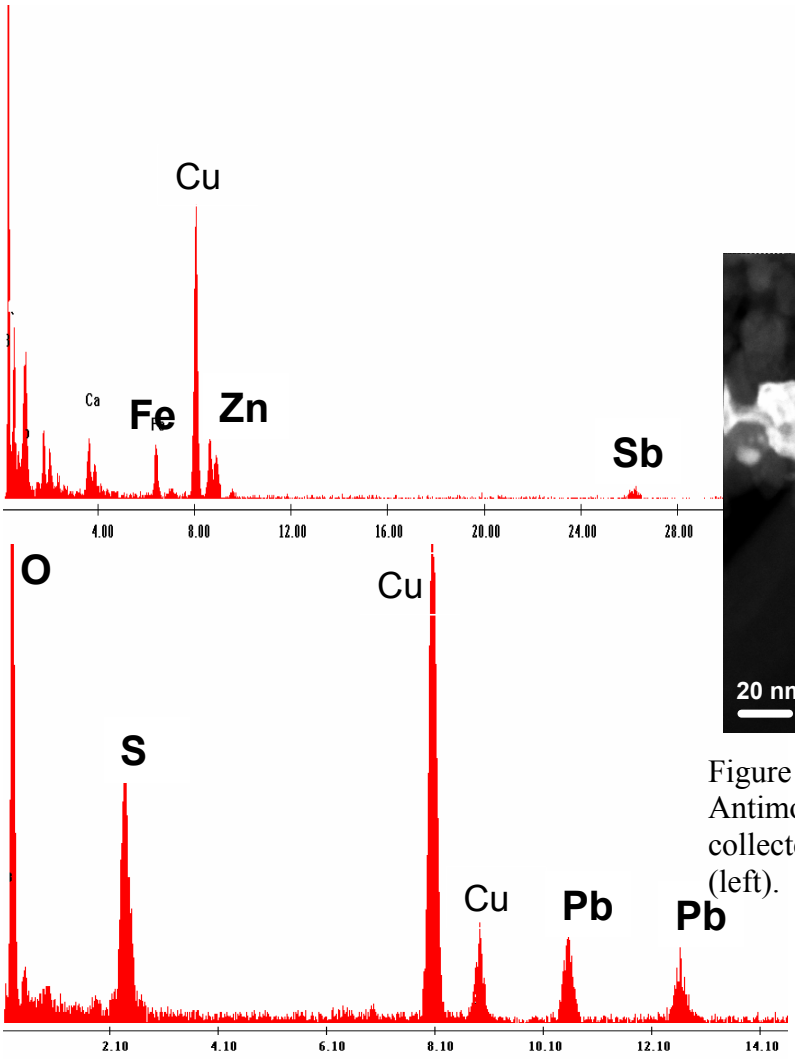


Figure 6. HAADF-STEM image of calcium sulfate and ultrafine particles collected in Detroit (right) and EDS spectra (left).



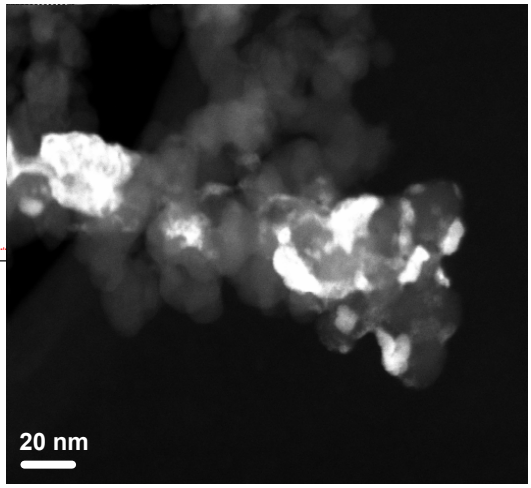
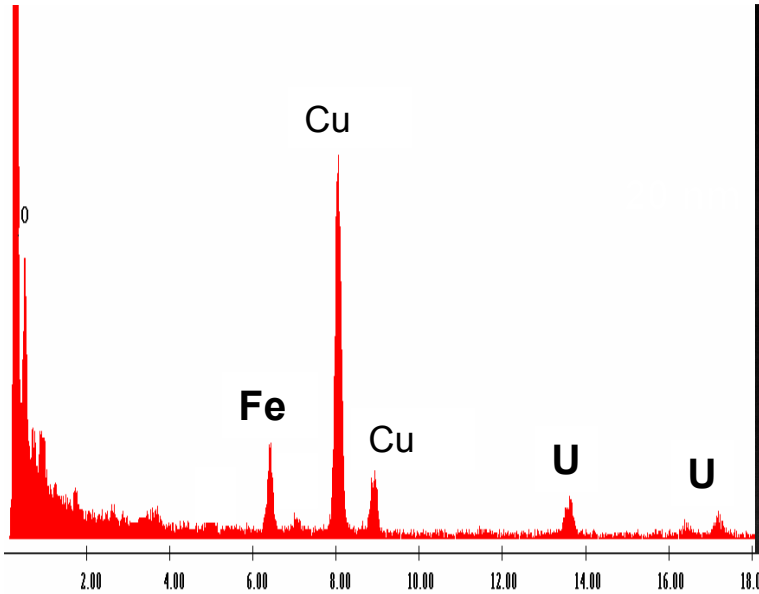


Figure 7. HAADF-STEM image of Zinc, Antimony and Lead and ultrafine particles collected in Detroit (right) and EDS spectra (left).



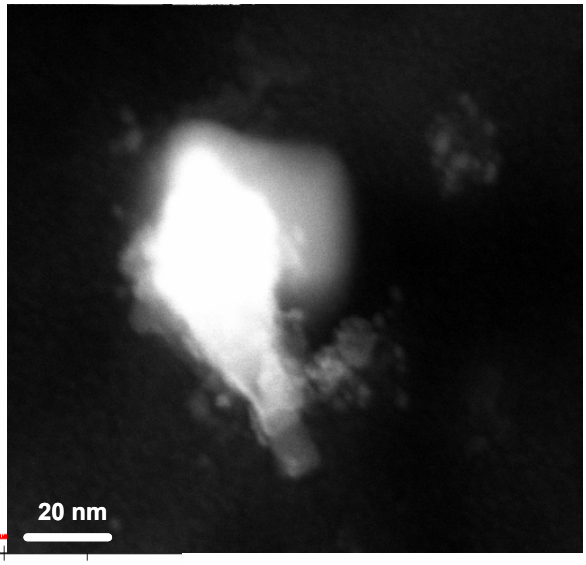


Figure 8. HAADF-STEM image of uranium ultrafine particles collected in Detroit (right) and EDS spectra (left).

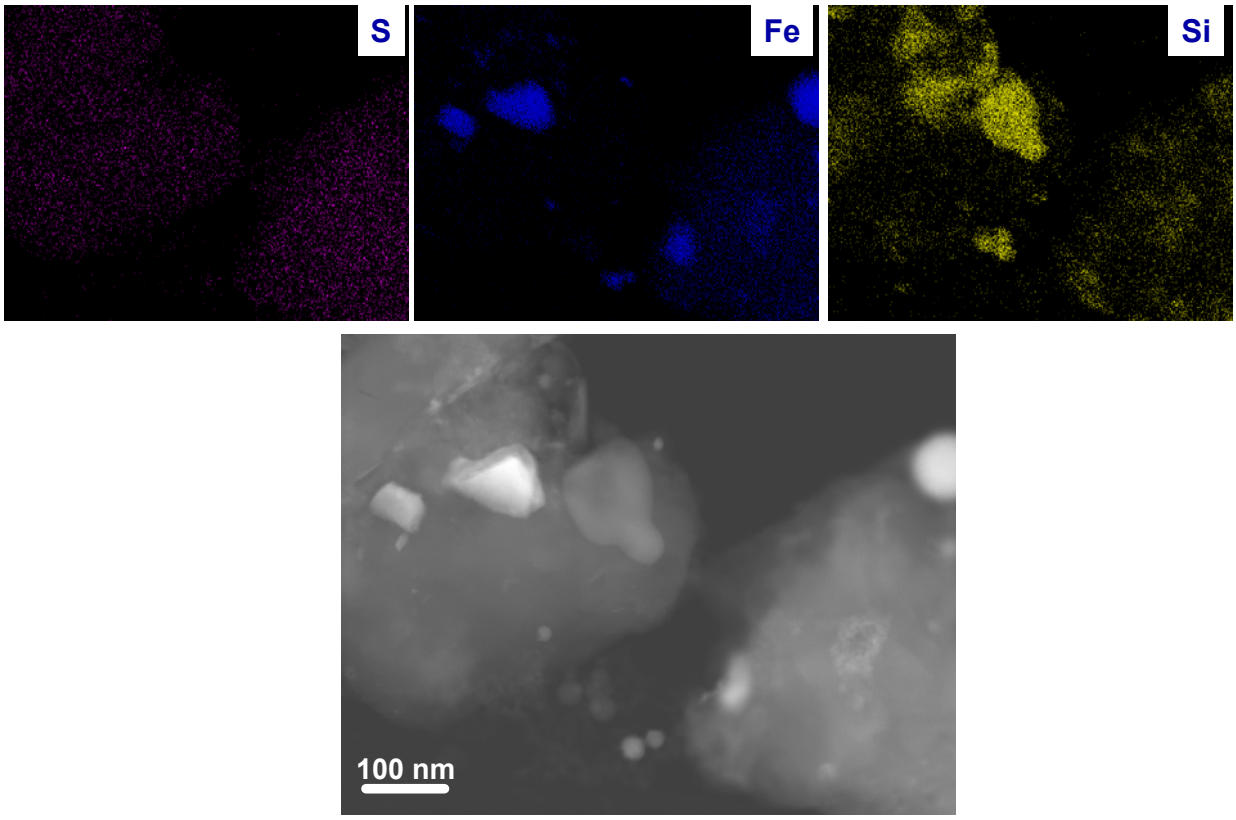


Figure 9. HAADF-STEM image and the elemental map of S-Fe-Si particles.

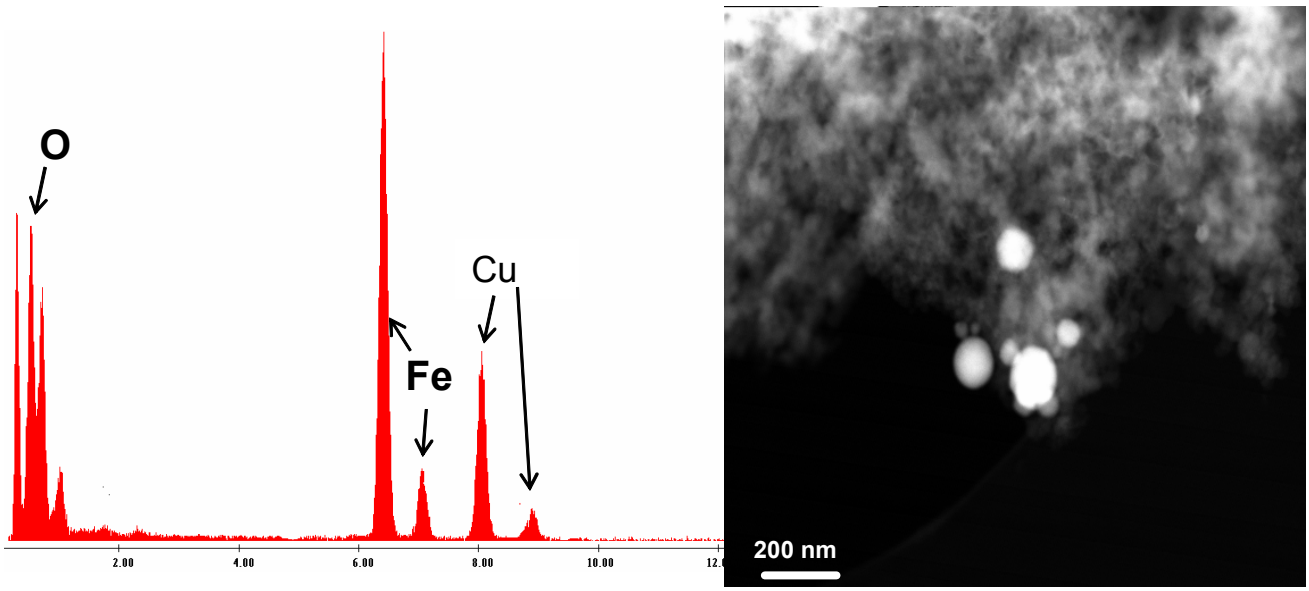


Figure 10. HAADF-STEM image of iron oxide ultrafine particles and soot collected in Steubenville (right) and EDS spectra (left).

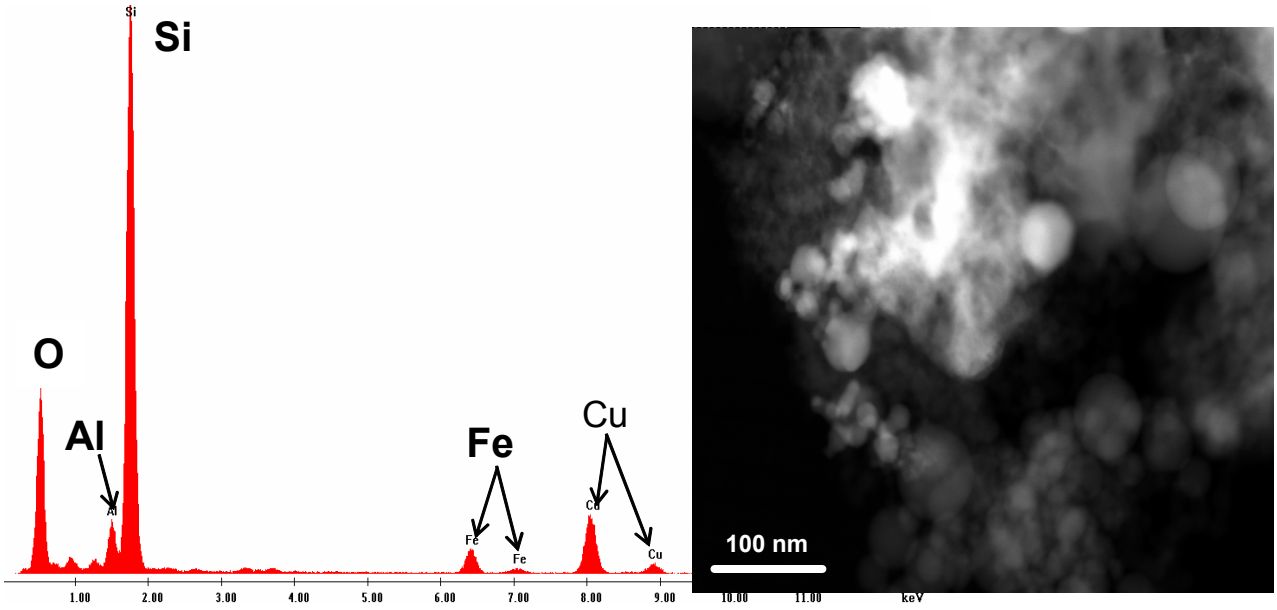


Figure 11. HAADF-STEM image of Si-rich Al-Fe particles collected in Steubenville (right) and EDS spectra (left).

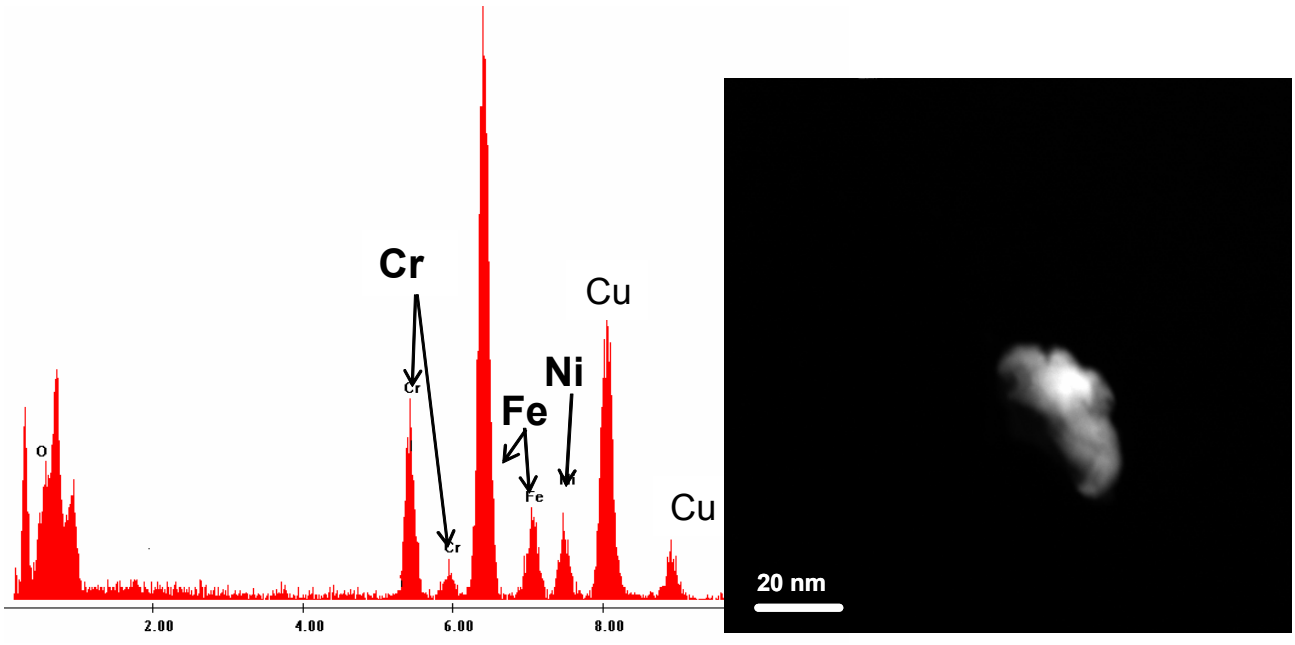


Figure 12. HAADF-STEM image of Fe-rich Cr-Ni particles collected in Steubenville (right) and EDS spectra (left).

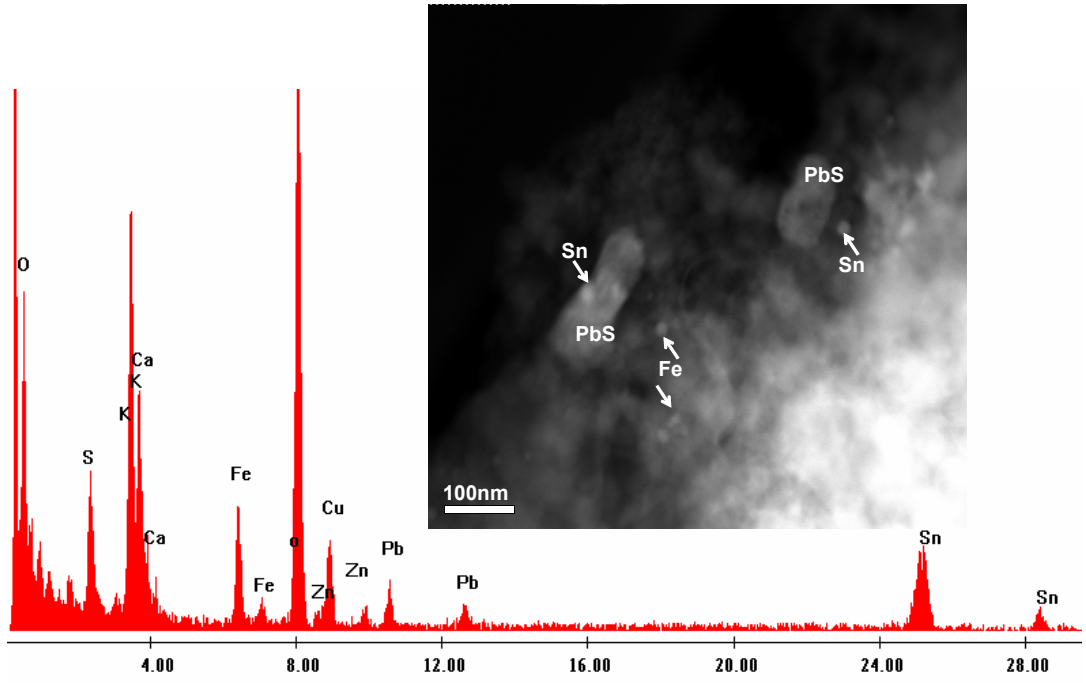


Figure 13. HAADF-STEM image of S-Pb-Sn particles collected in Steubenville (right) and EDS spectra (left).

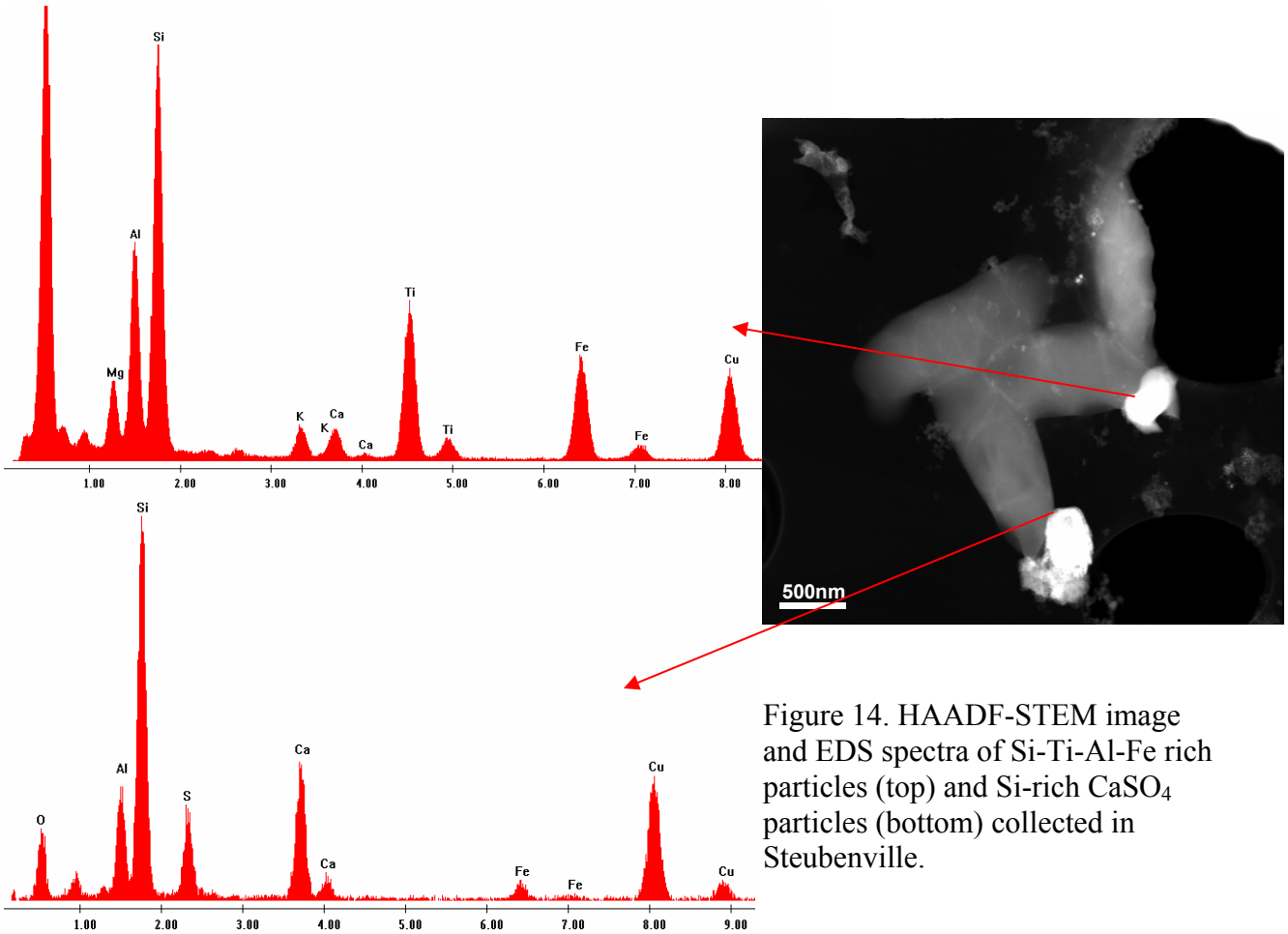


Figure 14. HAADF-STEM image and EDS spectra of Si-Ti-Al-Fe rich particles (top) and Si-rich $CaSO_4$ particles (bottom) collected in Steubenville.

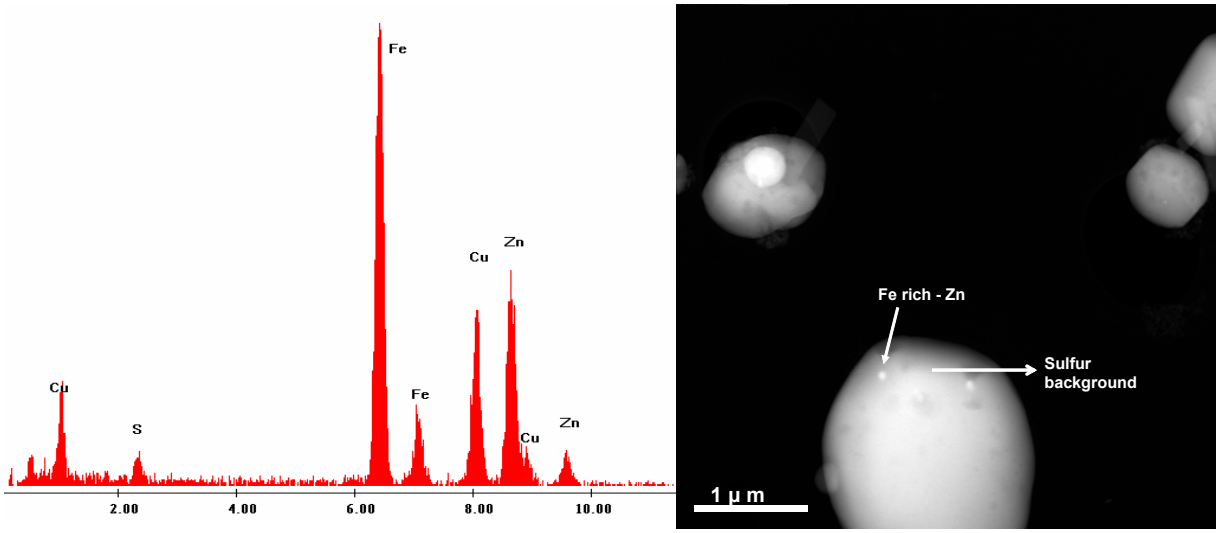


Figure 15. HAADF-STEM image of S-Fe-Zn particles collected in Steubenville (right) and EDS spectra (left).

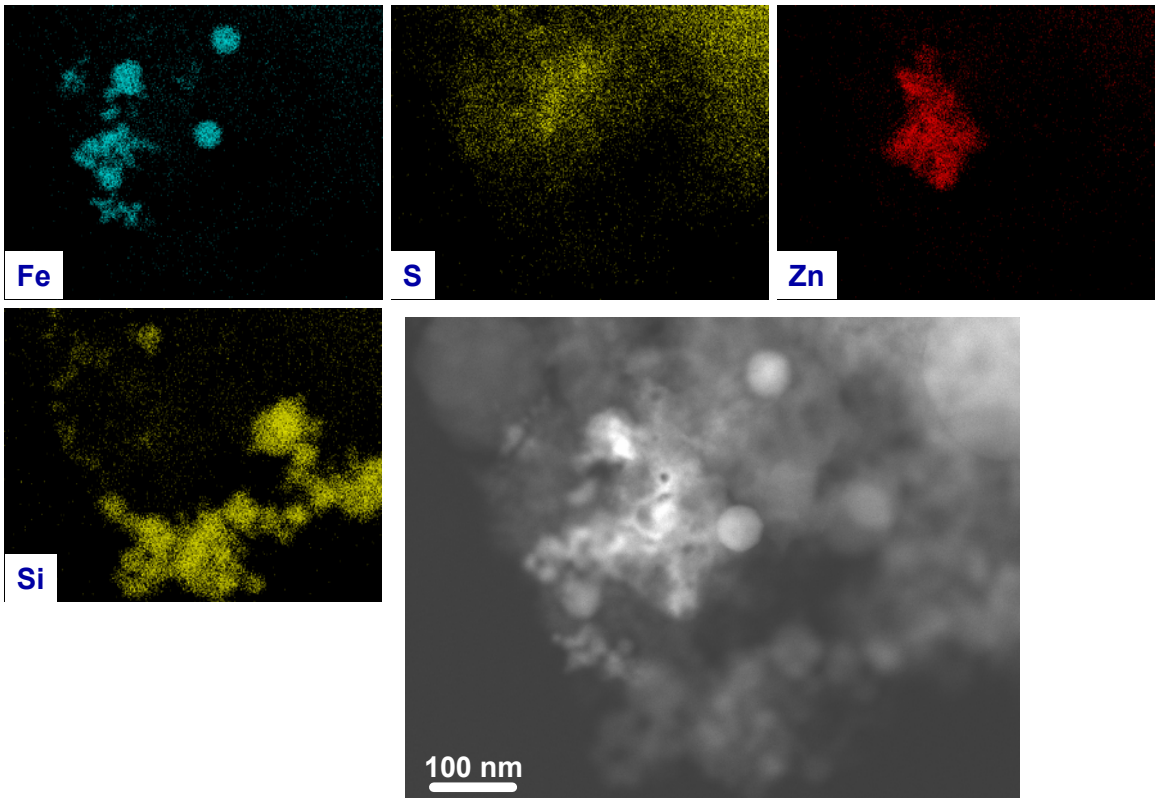


Figure 16. HAADF-STEM image and the elemental map of Fe-S-Zn-Si particles.