

# Chromium and Zinc Speciation in Airborne Particulate Matter Collected in Ulaanbaatar, Mongolia, by X-Ray Absorption Near-edge Structure Spectroscopy

Gerelmaa Gunchin<sup>1\*</sup>, Janos Osan<sup>2</sup>, Alessandro Migliori<sup>3</sup>, Dagva Shagjjamba<sup>4</sup>, Christina Streli<sup>1</sup>

<sup>1</sup> Vienna University of Technology, Atominstitut, Vienna, Austria

<sup>2</sup> Environmental Physics Department, Centre for Energy Research, Budapest, Hungary

<sup>3</sup> Nuclear Science and Instrumentation Laboratory, Physics section, IAEA, Seibersdorf, Austria

<sup>4</sup> Nuclear Research Center, National University of Mongolia, Ulaanbaatar, Mongolia

## ABSTRACT

This study examined the chemical speciation of atmospheric particulate matter (PM) samples collected in Ulaanbaatar, Mongolia. The health effects of atmospheric aerosol depend on the particles' size distribution, elemental composition and chemical species as well as other factors, which vary according to the pollution sources and meteorological conditions. Employing the International Atomic Energy Agency (IAEA) supported X-ray fluorescence (XRF) beamline at Elettra Sincrotrone Trieste, Italy, we used a small incidence angle for the synchrotron emission radiation in this ultra-high-vacuum environment to analyze the fine and the coarse mode (PM<sub>2.5</sub> and PM<sub>2.5-10</sub>, respectively) through X-ray absorption near-edge structure (XANES) spectroscopy, which was applied to the K-edges of the chromium (Cr) and zinc (Zn) in PM samples selected via energy-dispersive XRF (EDXRF) analysis for their high concentrations of these transition metals. The spectroscopic results identified trivalent chromium sulfate [Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>] and chromium oxide (Cr<sub>2</sub>O<sub>3</sub>) compounds as the major chemical forms of Cr in both the coarse and the fine PM fraction. Furthermore, both fractions contained abundances of sulfate (ZnSO<sub>4</sub>) and silicate (Zn<sub>2</sub>SiO<sub>4</sub>) compounds, but only the fine mode contained Zn oxalate (ZnC<sub>2</sub>O<sub>4</sub>), whereas only the coarse mode contained Zn chloride (ZnCl<sub>2</sub>). These Cr and Zn species seemed to originate from local anthropogenic sources, e.g., combustion products or traffic-related resuspended road dust.

Our findings, which are based on the first chemical speciation analysis from Ulaanbaatar, provide insight into the physiochemical characteristics of atmospheric aerosols as well as information on the potential sources of Cr and Zn species bound to fine and coarse PM.

**Keywords:** XANES, Cr and Zn speciation, Atmospheric PM, Ulaanbaatar

## OPEN ACCESS

**Received:** January 29, 2021

**Revised:** April 29, 2021

**Accepted:** May 6, 2021

\* **Corresponding Author:**

[g.gerelmaa@gmail.com](mailto:g.gerelmaa@gmail.com)

**Publisher:**

Taiwan Association for Aerosol  
Research

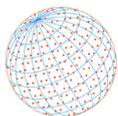
ISSN: 1680-8584 print

ISSN: 2071-1409 online

 **Copyright:** The Author(s).  
This is an open access article distributed under the terms of the [Creative Commons Attribution License \(CC BY 4.0\)](https://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are cited.

## 1 INTRODUCTION

Atmospheric particulate matter (PM) originating from anthropogenic and natural sources represents a common concern worldwide due to their associations with climate change, atmospheric visibility and more importantly with human health (Fittschen, 2014). The size of PM is considered significant since an epidemiological study revealed a correlation between PM mass of coarse particles with diameter of less than 10 μm, (PM<sub>10-2.5</sub>) and especially fine particles with diameter of less than 2.5 μm (PM<sub>2.5</sub>) and a variety of adverse effects on health (Cruz *et al.*, 2015). Causes and consequences of PM depend on the size distribution, concentration level, elemental composition and especially on the type of chemical species. These features characterize the toxicity of PM, including physical and chemical properties and this might vary from one place to another,



characteristics of an area and contributing sources. Therefore, chemical speciation studies are important for the assessment of the toxicity of certain elements, particularly of heavy metals (Osan *et al.*, 2010), as well as for the identification of PM sources.

X-ray absorption near-edge structure (XANES) spectrometry is one of the most suitable techniques to characterize different oxidation and chemical states of elements in atmospheric PM samples. Other techniques, such as ultraviolet-visible (UV-Vis) spectroscopy, inductively coupled plasma mass spectrometry and X-ray emission techniques, can measure only the total concentration of the element and require either a wet extraction or separation step for the speciation analysis (Ashley *et al.*, 2003; Unceta *et al.*, 2010). However, the experimental conditions adopted for the extraction may significantly influence the reliability of the measurement results (Pettine and Capri, 2005). Great advantages of XANES rely on the fact that it does not require any chemical pretreatment of the sample and can distinguish between different compounds of the same metal, including different oxidation states (e.g., Cr(VI), Cr(III), and Cr(0)) as well as different compounds with the same oxidation state (e.g., Cr<sub>2</sub>O<sub>3</sub> vs. Cr(OH)<sub>3</sub>) (Werner *et al.*, 2007). Moreover, XANES allows non-destructive speciation of metals in solid samples, even for minor or trace concentrations (< 1%) (Osan *et al.*, 2010).

The X-ray absorption measurements require an excitation source with high monochromaticity and energy tunability to scan with fine energy steps the selected absorption edge of the probed element and reveal the fine structure. When the probed element is available only in minor/trace amounts, the high intensity is an additional strict requirement for the X-ray source to allow short measuring times. Synchrotron radiation is optimally suitable for such studies, when using a double-crystal monochromator providing a resolving power  $\Delta E/E$  better than  $10^{-4}$ .

A number of studies have been published on chromium and zinc speciation of airborne PM samples by XANES. Ohta *et al.* (2006) examined the variation of chemical compositions and speciation of Zn and other elements in different particle size aerosols in aeolian dust during their transportation from China to Japan. The results suggested that Zn originated primarily from crustal aerosols during the dust event, except for that in fine grains, and that the fraction of anthropogenic materials increased from 40% to 80%, concomitant with decreasing particle size. Wang *et al.* (2007) also applied XANES to Zn, Cr and other metals on two fractions of aerosol samples from different sites of Shanghai, China. Close to iron and steel industrial area, the main chemical components of Cr in PM were chromite and oxides of trivalent chromium. Werner *et al.* (2007) studied Cr speciation in three different areas of north California, USA. For every sampling station, trivalent chromium oxides, Cr-Fe and chromite-like phase were found to be the dominant species, while some reduced Cr species (i.e., Cr(0) or Cr<sub>3</sub>C<sub>2</sub>) were also identified as minor chemical components. Cr(VI) containing particles were only found at the site of the most urban character. Similarly, in Saudi Arabia, the dominant state of chromium in two-fractioned aerosol samples was the trivalent chromium oxide, while Cr(VI) was a minor contribution with range of 7–9% (Shaltout *et al.*, 2018). Many other studies were successfully conducted using XANES analysis for elemental speciation (Huggins *et al.*, 2000; Boman *et al.*, 2004; Galbreath and Zygarlicke, 2004; Goodzari *et al.*, 2008).

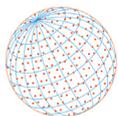
The aim of the present paper is to gain information about chemical speciation of two elements of interest (Cr and Zn) in atmospheric PM<sub>2.5</sub> and PM<sub>10-2.5</sub> samples, which were collected from Ulaanbaatar, the capital city of Mongolia. These two transition metals were selected because of their importance and abundance in the collected atmospheric samples. Acquiring knowledge on Cr and Zn speciation in local atmospheric PM is important for the assessment of toxicity as well as for better characterization of their corresponding sources.

The present study provided enhanced insights in Ulaanbaatar's size-fractioned atmospheric aerosols' physiochemical nature. It delivers further information on the potential origin and contributing pollution sources of the selected elements through their speciation for the first time.

## 2 MATERIALS AND METHODS

### 2.1 Sample Collection

Atmospheric particles were collected on polycarbonate filters at the air quality monitoring site, 4 km east of the center of Ulaanbaatar (latitude 47°55', longitude 106°55', 1300 m above sea level). More information about the sampling site is described in Gunchin *et al.* (2019). In total, 52 samples



were collected, twice a week (every Monday and Thursday) throughout the period June 2016–January 2017. A GENT sampler (Maenhaut *et al.*, 1993) was used, comprising a PM<sub>10</sub> impactor-type size-selective inlet and a stacked filter unit (SFU) assembly connected to a pump and an air flow meter. The SFU is made up of two filters arranged sequentially, allowing the fractionation of particles on two different stages. The top filter (pore size 8 µm) collected the coarse (PM<sub>10-2.5</sub>) particle fraction and the bottom filter (pore size 0.4 µm) collected the fine (PM<sub>2.5</sub>) particle fraction.

The sampler was operated with the average flow rate of 16.0 L min<sup>-1</sup> in alternating 30 min on- and 30 min off-periods over the course of the 24 hours as to provide a representative sample for the whole day. However, due to atmospheric conditions and the level of the pollution of that sampling day, it was not possible to collect over the entire 24 hours as high pollution resulted in clogging of the filters. Due to this fact, the flow rate of the sampler was varying between 18.0–14.0 L min<sup>-1</sup> and averaging and calculations of the total air volume for each sample measurement were done accordingly. Gravimetric masses of PM samples were subsequently normalized by the estimated volume.

The filter cassette was mounted approximately 2.5 m above the ground. The sampling point is surrounded by buildings, traditional dwelling areas (*ger khoroolol*), and the combinations of asphalt and unpaved roads.

## 2.2 Selection of Samples for XANES Measurements

For the XANES measurements, six PM<sub>2.5</sub> samples and three PM<sub>10-2.5</sub> samples were selected for the speciation of two elements of interest—Cr and Zn. Selections were based on the highest relevance when these elements were found at elevated concentrations. The elemental analysis of the fine and coarse PM samples was performed by means of the PANalytical Epsilon 5 energy-dispersive X-ray fluorescence (EDXRF) spectrometer at the premises of the Nuclear Science and Instrumentation Laboratory of the International Atomic Energy Agency (IAEA), Seibersdorf, Austria (Gunchin *et al.*, 2019). The spectrometer features various secondary targets, such as Al, CaF<sub>2</sub>, Fe, Ge, Zr, Mo, Ag and Al<sub>2</sub>O<sub>3</sub> (Barkla polarization target) which are irradiated by a 600 W Sc-W anode X-ray tube. The characteristic X-ray radiation emitted by the sample is detected by an LN<sub>2</sub>-cooled LGe detector with energy resolution of about 150 eV at Mn-Kα (5.89 keV).

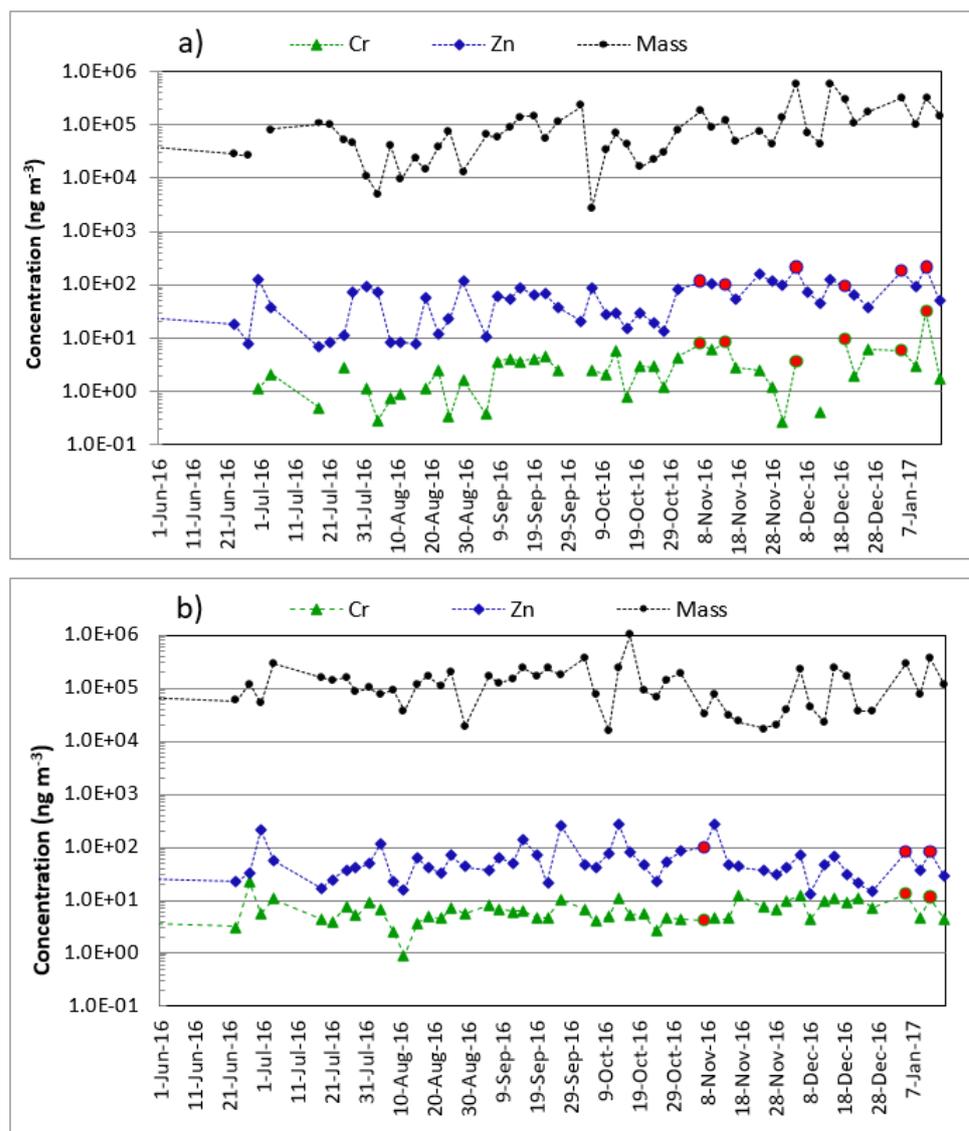
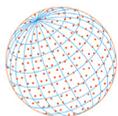
Fe and Ge secondary targets were used for Cr and Zn determination, respectively. Operational conditions for both secondary targets were 75 kV and 8 mA. The live time for each secondary target was set to 300 s. The analysis was performed under vacuum conditions.

The quantification of elements' concentrations was carried out using a calibration performed by measuring thin film single element and compound reference materials. The built-in software of the PANalytical Epsilon 5 was used for spectrum deconvolution, whereas the elemental concentrations were calculated using a sensitivity curve determined from the measured set of reference materials. Thin film approximation was applied. A Standard Reference Material (SRM) of particulate matter on filter media (SRM 2783; NIST, Gaithersburg, MD, USA) was used for validation of the analytical method. The uncertainty of the results were evaluated according to the study of Gutknecht *et al.* (2010), where the following contributing factors were considered: the peak area statistical uncertainty, the fitting error in the calibration (sensitivity) curve, the quoted uncertainties of the elemental areal densities reported for the standards (5%), the estimated error due to the omittance of the self-attenuation effect as well as the relative standard deviation of three replicate measurements (reproducibility in operation). A more detailed description of the evaluation of the combined uncertainty of obtained result can be found in Gunchin *et al.* (2019).

In Fig. 1, the EDXRF results reported as time series of Zn and Cr concentrations in ng m<sup>-3</sup> for all measured fine (a) and coarse (b) particulate samples are shown (Gunchin *et al.*, 2019). The sample selection for XANES analysis was based on higher Zn and Cr concentration: Those samples are marked with red circles in Fig. 1. The selected six fine samples were collected on 7 Nov, 14 Nov, 5 Dec, 19 Dec 2016 and 5 Jan, 12 Jan 2017 and the selected three coarse samples have collection dates of 7 Nov 2016 and 5 Jan and 12 Jan 2017.

## 2.3 XANES Measurement

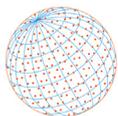
X-ray absorption near-edge structure (XANES) spectra were acquired at the XRF IAEA experimental end station (Lubeck *et al.*, 2016) of Elettra Sincrotrone Trieste (Basovizza, Italy). The experimental



**Fig. 1.** Time series of Zn and Cr concentrations in (a) PM<sub>2.5</sub> samples (fine) and (b) PM<sub>2.5-10</sub> samples (coarse) (red points: selected samples for XANES).

set-up is comprised by a Si(111) double-crystal monochromator, an ultra-thin-window Bruker silicon drift detector (30 mm<sup>2</sup>, energy resolution 135 eV at Mn-K $\alpha$ ), photodiodes and other beam-monitoring devices. The samples were inserted into an ultra-high-vacuum chamber equipped with a multi-axis motorized sample manipulator, which offers the possibility to vary the orientation of the sample surface with respect to the exciting beam direction (Wrobel *et al.*, 2017; Karydas *et al.*, 2018).

The selected PM samples were mounted on Al holders using carbon tape and they were forced to be fixed as flat as possible. For the XANES measurements the samples have been excited under a shallow angle of incidence ( $\sim 1^\circ$ ). The influence of the angle of incidence on detection limits was investigated by Karydas *et al.* (2018) using a thin reference material deposited on polycarbonate filter. The grazing incidence geometry provides a larger beam footprint resulting to an increase of the PM analyzed mass and better counting statistics. The specially designed Al holder allows to measure in this geometry without producing parasitic fluorescence and scattered radiation. The comparison of shallow angle excitation geometry on aerosol sample to a conventional 45°/45° geometry resulted in significantly increased signals ( $\sim 10$ -fold). XANES spectra with satisfactory good statistics could be therefore collected in a shorter time with the beam irradiating the samples with shallow angle. Energy scans were performed around the K-edges of the two elements of interest (5989 eV for Cr and 9659 eV for Zn) using the Si(111) monochromator (energy resolution



of about 1 eV) and recording the corresponding  $K\alpha$  fluorescence intensity in fluorescence mode. The used energy step size varied between 0.5 (edge region) to 2 eV. The measurement time for each energy step varied from 10 to 20 s, depending on the concentration of the element in the PM samples. Two to four repetitions were done for each sample, in order to increase the data quality. Cr and Zn metal foils were used for energy calibration of the Si(111) monochromator.

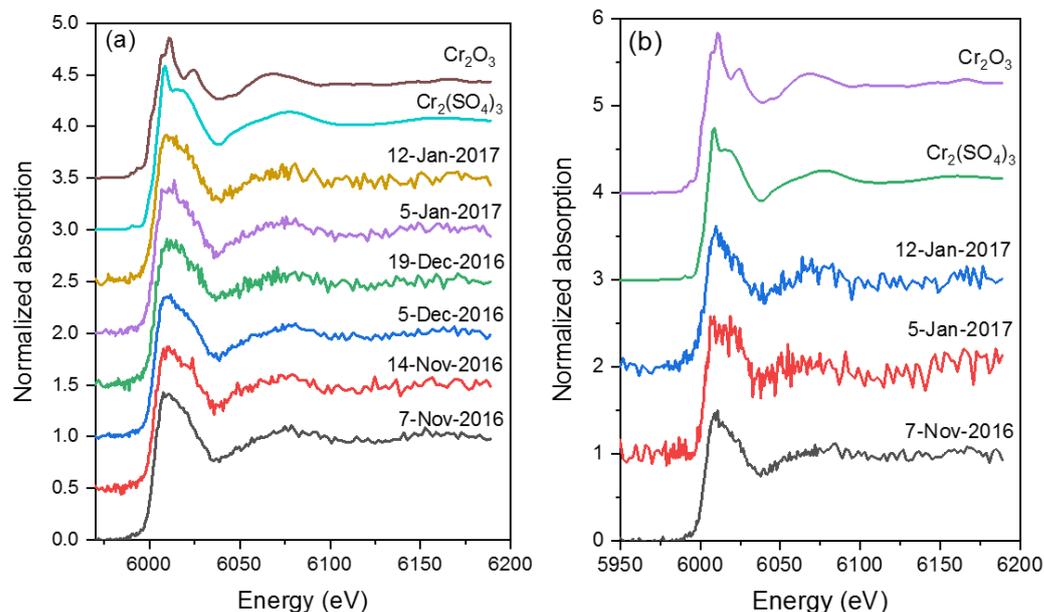
In the case of chromium, XANES spectra of potassium chromate ( $K_2CrO_4$ ), chromium(III) oxide ( $Cr_2O_3$ ), potassium dichromate ( $K_2Cr_2O_7$ ), nickel-based chromite spinel ( $NiCr_2O_4$ ) and trivalent chromium sulfate [ $Cr_2(SO_4)_3$ ] were collected as references; for zinc, zinc carbonate ( $ZnCO_3$ ), zinc nitrate [ $Zn(NO_3)_2$ ], zinc sulfate monohydrate ( $ZnSO_4 \cdot H_2O$ ), zinc silicate/willemite ( $Zn_2SiO_4$ ), zinc oxalate ( $ZnC_2O_4$ ) and zinc chloride ( $ZnCl_2$ ) were used as references. Most of these reference compounds were measured as pressed pellets in transmission mode at the X-ray absorption fine structure (XAFS) beamline of Elettra (Di Cicco *et al.*, 2009).

The obtained spectra were processed with the Athena Demeter software (Ravel and Newville, 2005), which uses a least-squares algorithm to refine the linear combination fit (LFC) of a given number of reference spectra to the measured spectrum. The refining procedure is the following: The sample spectra were initially fit using all of the given reference spectra. After each fitting, any references that accounted for less than 5% of the total amount of species in the sample were removed from the fitting to eliminate both minor components and erroneous fittings. After this, the sample spectrum was fit again with only the references of the remaining species. This process was repeated until the sample spectrum was described by one or more references each accounting for 5% or more of the total species. The quality of the fit can be quantified by an error term (R-factor) which indicates the proper choice of standard compounds. Averaging, background removal and normalization of XANES spectra were done by the Athena software.

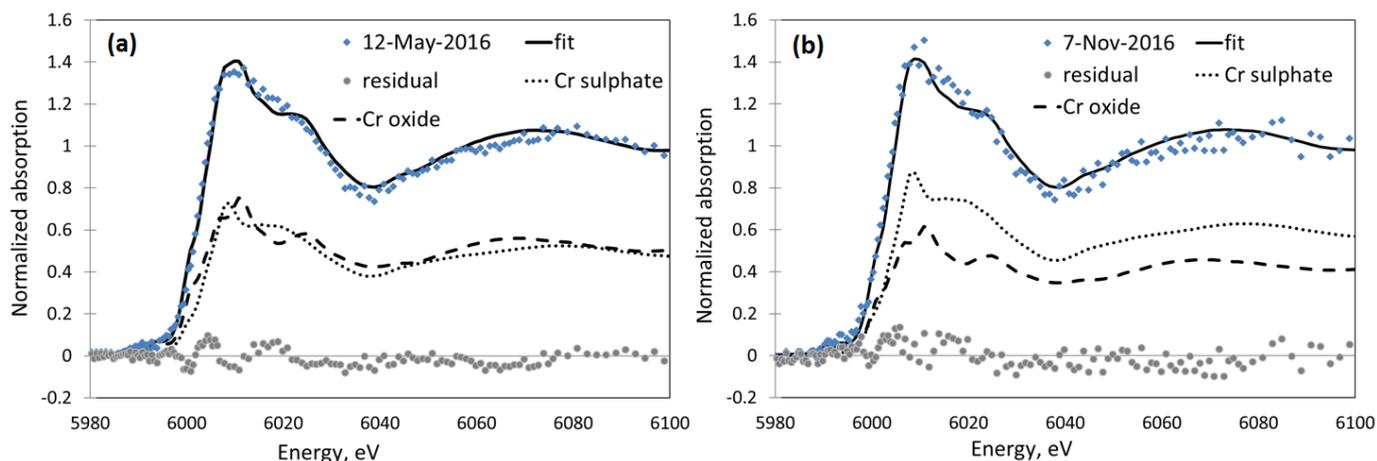
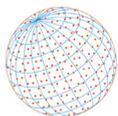
### 3 RESULTS AND DISCUSSION

#### 3.1 Speciation of Chromium

Compositional information derived from LCF suggested that chromium sulfate and chromium oxide are likely present in both the fine and coarse fraction samples. Fig. 2 shows the normalized XANES spectra at the Cr K-edge of the measured fine (a) and coarse (b) sample sets from Ulaanbaatar, together with two reference compounds. Representative XANES spectra of Cr K-edge from the LFC analysis for fine (a) and coarse (b) sample are also illustrated in Fig. 3.



**Fig. 2.** Cr K-edge XANES spectra of (a) fine and (b) coarse samples; standard spectra of Cr sulfate and Cr oxide are plotted for comparison.



**Fig. 3.** Representative LCF spectra of the (a) fine and (b) coarse samples for Cr K-edge. The blue dots are the acquired data, while the black line (smooth) is the linear combination fit to the data; the two pecked lines are reference spectra (fine:  $\text{Cr}_2(\text{SO}_4)_3$  is 49% and  $\text{Cr}_2\text{O}_3$  is 51%; coarse: 58% and 42%, respectively) and the grey dots are the residuals.

The determined relative concentration (or abundance) percentages of chromium sulfate and chromium oxide from XANES measurements, the concentration values of Cr and S in the air from EDXRF analyses and the R-factor, which expresses the quality of the fitting for each fine and coarse sample, are reported in Table 1 and Table 2, respectively.

In both fractions it can be noticed that chromium sulfate is a bit more dominant than chromium oxide, except the sample “5 Dec 2016,” which has almost equal contributions of sulfate and oxide, and the sample “12 Jan 2017,” where the percentage ratio is inverted.  $\text{PM}_{2.5}$  samples are comprised between 49% and 70% of chromium sulfate and 30–51% of chromium oxide. In  $\text{PM}_{10-2.5}$  samples, chromium sulfate is contained in the range of 36–93% and Cr oxide between 7% and 64%. There was no clear correlation observed between speciation abundances and concentration values of Cr and S. The main reason for this might rely on secondary organic aerosol (SOA) and secondary inorganic aerosol (SIA) concentrations in the sample. SOA and SIA are emitted or formed by the oxidation of gas-phase species in the atmosphere (De Gouw and Jimenez, 2009).

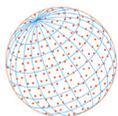
The majority (60–70%) of chromium sources are of anthropogenic origins such as fuel combustions, metallurgical industries, refractory brick production, waste incineration and Cr-containing chemicals (Seigneur and Constantinou, 1995; Werner *et al.*, 2007; Catrambone *et al.*, 2013). The remaining 30% comes from natural sources like crustal matter and volcanic eruptions

**Table 1.** Total mass, Cr speciation, Cr and S concentration of the  $\text{PM}_{2.5}$  samples.

Sample date	Mass ( $\mu\text{g m}^{-3}$ )	Cr chemical form (%)		R-factor	Concentration ( $\text{ng m}^{-3}$ )	
		$\text{Cr}_2(\text{SO}_4)_3$	$\text{Cr}_2\text{O}_3$		Cr	S
07 Nov 2016	189	$59 \pm 5$	$41 \pm 5$	0.0032	11.5	7040
14 Nov 2016	121	$57 \pm 4$	$43 \pm 4$	0.0022	10.0	3340
05 Dec 2016	597	$49 \pm 4$	$51 \pm 4$	0.0017	7.40	12,300
19 Dec 2016	301	$69 \pm 6$	$31 \pm 6$	0.0037	12.0	5560
05 Jan 2017	322	$57 \pm 5$	$43 \pm 5$	0.003	12.0	7100
12 Jan 2017	315	$70 \pm 5$	$30 \pm 5$	0.0025	36.5	11,500

**Table 2.** Total mass, Cr speciation, Cr and S concentration of the  $\text{PM}_{2.5-10}$  samples.

Sample date	Mass ( $\mu\text{g m}^{-3}$ )	Cr chemical form (%)		R-factor	Concentration ( $\text{ng m}^{-3}$ )	
		$\text{Cr}_2(\text{SO}_4)_3$	$\text{Cr}_2\text{O}_3$		Cr	S
07 Nov 2016	63.0	$58 \pm 5$	$42 \pm 5$	0.0033	3.50	2460
05 Jan 2017	64.0	$93 \pm 13$	$7 \pm 12$	0.0177	12.0	1770
12 Jan 2017	116	$36 \pm 9$	$64 \pm 9$	0.0088	11.0	4560



(Catrambone *et al.*, 2013). The fact that smaller grain sizes of atmospheric particles are mainly generated from anthropogenic sources, as well as the coexistence of  $\text{SO}_4^{2-}$ , may indicate that chromium sulfate is the main Cr compound of  $\text{PM}_{2.5}$  samples. Our previous research has shown that the common primary emission sources of Ulaanbaatar's atmospheric PM are traffic, coal combustion and soil (Gunchin *et al.*, 2019). Due to this fact, chromium sulfate may correspond to anthropogenic combustion sources.

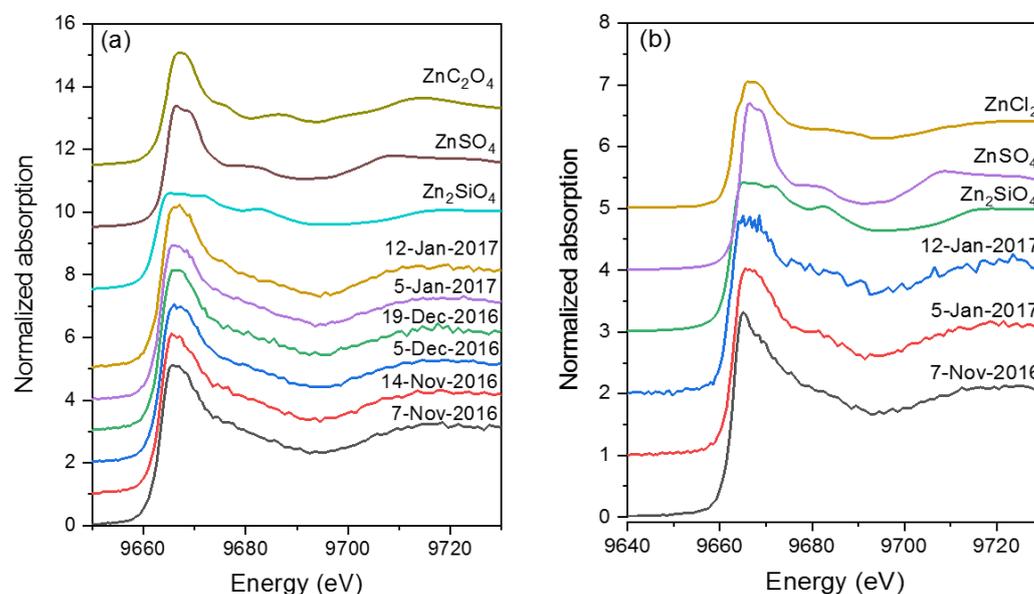
One of the main occurrences of Cr is the trivalent oxidation state in forms of chromium oxides, such as  $\text{Cr}_2\text{O}_3$ . This compound is present in both measured fractioned samples. These results are similar to those reported in the study of Wang *et al.* (2007), which indicated that the main chemical component of Cr in PM was chromite and oxides of trivalent chromium, close to iron and steel industrial area. However, it should be noted that due to geographical and climate differences, the results of these works cannot be compared directly. It is worth to mention that Cr(VI) content, which has high health concern, was not present in the measured samples.

### 3.2 Speciation of Zinc

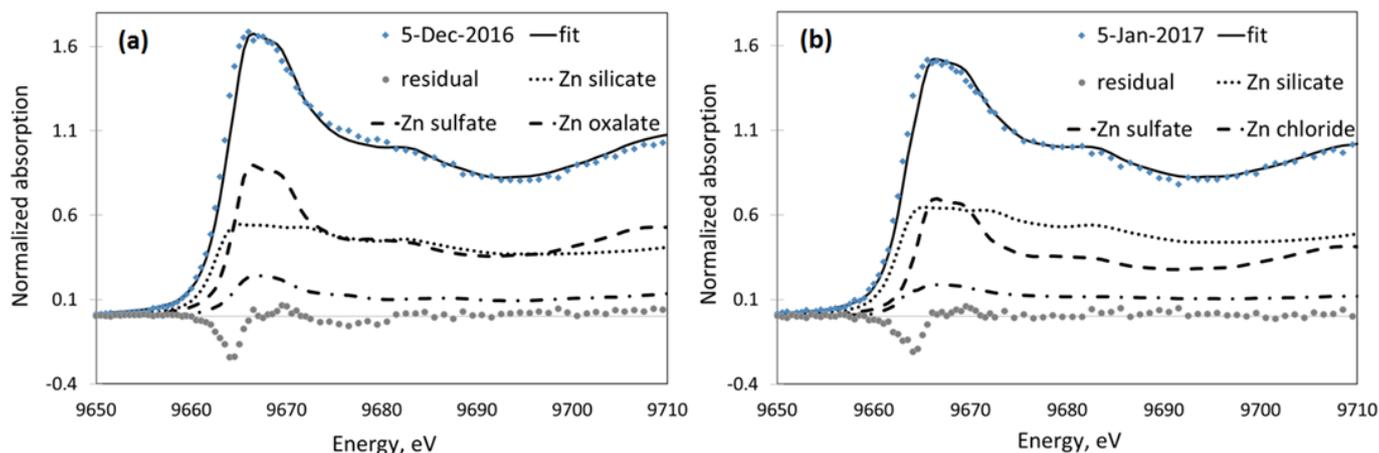
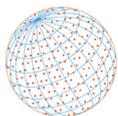
Four Zn compounds were identified in the measured samples: zinc sulfate, zinc silicate, zinc chloride and zinc oxalate. Fig. 4 shows the normalized Zn XANES spectra of the measured fine (a) and coarse (b) samples, together with those of the reference compounds. Representative XANES spectra of Zn K-edge from the LFC analysis for fine (a) and coarse (b) sample are illustrated in Fig. 5.

The determined relative concentration (or abundance) percentages of zinc sulfate, zinc silicate and zinc oxalate from XANES measurements; the concentration values of Zn, S and Si in the air from EDXRF analyses; and the R-factor, which expresses the quality of the fitting for each fine and coarse sample, are reported in Table 3 and Table 4, respectively.

In the fine fraction, zinc sulfate and zinc silicate were identified as the major constituents of all measured samples and zinc oxalate accounted for the rest contribution. Sulfur is often used as a tracer for coal burning in source apportionment studies (Davy *et al.*, 2011) and  $\text{SO}_2$  is produced during combustion processes (Ohta *et al.*, 2006), leading to formation of secondary sulfate particles mainly present in the fine fraction. In Wang *et al.* (2007), the authors report that Zn exists mainly as  $\text{ZnSO}_4$  in  $\text{PM}_{2.5}$  samples from both industrial and agricultural areas of Shanghai city. Therefore, Zn in the form of sulfate can originate either directly from a local anthropogenic emission as  $\text{ZnSO}_4$  or from Zn originally emitted in other forms that condenses to secondary sulfate particles. Mattielli *et al.* (2009) reported that zinc is present as a sulfide ( $\text{ZnS}$ ) or carbonate ( $\text{ZnCO}_3$ ) or as minor constituent of silicate minerals in the natural environment, so that it can be assumed that



**Fig. 4.** Zn K-edge XANES spectra on (a) fine and (b) coarse samples and reference spectra of Zn oxalate, Zn chloride, Zn sulfate and Zn silicate are plotted for comparison.



**Fig. 5.** Representative LCF spectra of the (a) fine and (b) coarse samples for Zn K-edge. The blue dots are the acquired data, while the black line (smooth) is the linear combination fit to the data; the two pecked lines are reference spectra (fine: ZnSO<sub>4</sub> is 46%, Zn<sub>2</sub>SiO<sub>4</sub> is 42% and ZnCl<sub>2</sub> is 12%; coarse: 37%, 51%, and 12%, respectively) and the grey dots are the residuals.

**Table 3.** Total mass, Zn speciation, Cr and S concentration of the PM<sub>2.5</sub> samples.

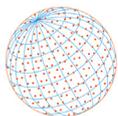
Sample date	Mass ( $\mu\text{g m}^{-3}$ )	Zn chemical form (%)			R-factor	Concentration ( $\text{ng m}^{-3}$ )		
		ZnSO <sub>4</sub>	Zn <sub>2</sub> SiO <sub>4</sub>	ZnC <sub>2</sub> O <sub>4</sub>		Zn	S	Si
07 Nov 2016	189	47 ± 7	36 ± 2	17 ± 6	0.0043	111	7040	1830
14 Nov 2016	121	51 ± 6	42 ± 2	7 ± 5	0.0041	94.0	3340	633
05 Dec 2016	597	46 ± 5	42 ± 2	12 ± 5	0.0026	202	12,300	616
19 Dec 2016	301	40 ± 6	41 ± 2	19 ± 6	0.0035	92.0	5560	636
05 Jan 2017	322	47 ± 6	47 ± 2	6 ± 5	0.0035	173	7100	544
12 Jan 2017	315	41 ± 5	35 ± 2	24 ± 5	0.0029	210	11,500	1400

**Table 4.** Total mass, Zn speciation, Cr and S concentration of the PM<sub>2.5-10</sub> samples.

Sample date	Mass ( $\mu\text{g m}^{-3}$ )	Zn chemical form (%)			R-factor	Concentration ( $\text{ng m}^{-3}$ )			
		ZnSO <sub>4</sub>	Zn <sub>2</sub> SiO <sub>4</sub>	ZnCl <sub>2</sub>		Zn	S	Si	Cl
07 Nov 2016	63.0	35 ± 5	48 ± 8	17 ± 12	0.0071	100	2450	3100	86.0
05 Jan 2017	64.0	37 ± 3	51 ± 4	12 ± 6	0.0021	79.0	1770	2140	2000
12 Jan 2017	116	7 ± 4	54 ± 5	39 ± 8	0.0047	81.0	4560	6340	1130

zinc silicate could be related to crustal sources, or dust resuspension due to traffic. According to the study of Furukawa and Takahashi (2011), zinc oxalate can be the main oxalate species considering its high concentration in aerosols and the presence of this compound particularly in finer particles. Zinc oxalate is an important component of secondary organic aerosol and its formation in the atmosphere can be obtained in several different ways. However, the formation of aqueous phase on the particle surface is dominant; therefore, Zn oxalate is found to be mainly present in the fine fractions.

In the coarse fraction, Zn is contained mostly as silicates which may be a clear indication of crustal source. The second identified constituent in the measured samples was zinc sulfate. Sulfate forms of Zn are usually pronounced and characteristic in winter season. Since all measured samples were taken in mid-winter months, this compound could also be referred to the combustion source. The residual contribution is zinc chloride. In their study, Furukawa and Takahashi (2011) also show that Zn chloride was observed only in the coarser particles, having no relation with the seasons. Nevertheless, Zn chloride (along with Zn silicate) was found as significant component of Zn in fly ash particles sampled directly from the stack of coal and municipal solid waste (Cai *et al.*, 2015; Yu *et al.*, 2009). Origins and formulation of this compound in atmospheric particles can be related to anthropogenic sources. There was finally no clear correlation between speciation abundances and concentration values of Zn, S, Si and Cl.



## 4 SUMMARY

Using a small incidence angle for the synchrotron radiation, we performed XANES spectroscopy on size-fractionated atmospheric particulate matter (viz., PM<sub>2.5</sub> and PM<sub>2.5-10</sub>) collected on polycarbonate filters in the city of Ulaanbaatar, Mongolia. We characterized the chemical states of the Cr and Zn in the PM<sub>2.5</sub> and PM<sub>2.5-10</sub> and selected suitable PM samples for the XANES spectroscopy through EDXRF analysis. Our results revealed that Cr mainly existed as Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> in both the fine and the coarse fraction. However, the abundances of these constituents varied and showed no direct relation with the concentrations of the airborne Cr or S. Additionally, we only found Zn in its divalent chemical forms. Although both PM fractions contained abundances of sulfate (ZnSO<sub>4</sub>) and silicate (Zn<sub>2</sub>SiO<sub>4</sub>), only the fine mode contained Zn oxalate (ZnC<sub>2</sub>O<sub>4</sub>), whereas only the coarse mode contained Zn chloride (ZnCl<sub>2</sub>). As with Cr, the relative concentrations of these Zn species exhibited no correlations with the levels of the airborne Zn, S or Si. Finally, anthropogenic sources, such as combustion products and traffic-related resuspended road dust, primarily contributed the Cr and Zn species detected in our PM samples.

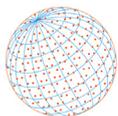
These findings shed light on the physiochemical characteristics and potential sources of metallic constituents in atmospheric fine- and coarse-mode PM, thereby supporting future studies on mixture toxicity and synergistic effects that, in contrast to the current efforts, are not based solely on the total elemental concentrations.

## ACKNOWLEDGEMENT

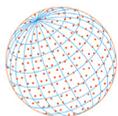
This project was funded by Mongolian Foundation for Science and Technology and supported in part by the International Atomic Energy Agency (IAEA) through the Regional Cooperation Agreement Program RAS/7/023. Moreover, this work has been supported through the joint IAEA and the International Centre for Theoretical Physics (ICTP) Sandwich Training Educational Program (STEP) fellowship C6/MON/15001 granted to Gerelmaa Gunchin. Ms. Gunchin expresses her gratitude to IAEA's former officials Dr. Andreas Karydas and Dr. Iain Darby, XRF end station staffs of Elettra as well as XRF group of Atominstitut, TU Wien, for their support and guidance throughout the beamtime experiment and data evaluations.

## REFERENCES

- Ashley, K., Howe, A.M., Demange, M., Nygren, O. (2003). Sampling and analysis considerations for the determination of hexavalent chromium in workplace air. *J. Environ. Monit.* 5, 707–716. <https://doi.org/10.1039/B306105C>
- Boman, C., Nordin, A., Boström, D., Öhman, M. (2004). Characterization of inorganic particulate matter from residential combustion of pelletized biomass fuels. *Energy Fuels* 18, 338–348. <https://doi.org/10.1021/ef034028i>
- Cai, X., Huang, Q., Alhadj-mallah, M., Chi, Y., Yan, J. (2015). Characterization of zinc vapor condensation in fly ash particles using synchrotron X-ray absorption spectroscopy. *J. Zhejiang Univ. Sci. A* 16, 70–80. <https://doi.org/10.1631/jzus.A1400178>
- Catrambone, M., Canepari, S., Perrino, C. (2013). Determination of Cr(III), Cr(VI) and total chromium in atmospheric aerosol samples. *E3S Web Conf.* 1 07005. <https://doi.org/10.1051/e3sconf/20130107005>
- Cruz, A.M.J., Sarmiento, S., Almeida, S.M., Silva, A.V., Alves, C., Freitas, M.C., Wolterbeek, H. (2015). Association between atmospheric pollutants and hospital admissions in Lisbon. *Environ. Sci. Pollut. Res.* 22, 5500–5510. <https://doi.org/10.1007/s11356-014-3838-z>
- Davy, P.K., Gunchin, G., Markwitz, A., Trompeter, W.J., Barry, B.J., Shagjamba, D., Lodoysamba, S. (2011). Air particulate matter pollution in Ulaanbaatar, Mongolia: Determination of composition, source contributions and source locations. *Atmos. Pollut. Res.* 2, 126–1307. <https://doi.org/10.5094/APR.2011.017>
- Dayan, A.D., Paine, A.J. (2000). Mechanisms of chromium toxicity, carcinogenicity and allergenicity: Review of the literature from 1985 to 2000. *Hum. Exp. Toxicol.* 20, 439–451.



- <https://doi.org/10.1191/096032701682693062>  
De Gouw, J., Jimenez, J.L. (2009). Organic aerosols in the Earth's atmosphere. *Environ. Sci. Technol.* 43, 7614–7618. <https://doi.org/10.1021/es9006004>
- Di Cicco, A., Aquilanti, G., Minicucci, M., Principi, E., Novello, N., Cognigni, A., Olivi, L. (2009). Novel XAFS capabilities at ELETTRA synchrotron light source. *J. Phys. Conf. Ser.* 190, 012043. <https://doi.org/10.1088/1742-6596/190/1/012043>
- Fittschen, U.E.A. (2014). Strategies for ambient aerosols characterization using synchrotron X-ray fluorescence: A review. *Spetosc. Eur.* 26, 10–14.
- Furukawa, T., Takahashi, Y. (2011). Oxalate metal complexes in aerosol particles: Implications for the hygroscopicity of oxalate-containing particles. *Atmos. Chem. Phys.* 11, 4289–4301. <https://doi.org/10.5194/acp-11-4289-2011>
- Galbreath, K.C., Zygarlicke, C.J., Toman, D.L., Huggins, F.E., Huffman, G.P. (1994). Nickel and chromium speciation of residual oil combustion ash. *Combust. Sci. Technol.* 134, 243–262. <https://doi.org/10.1080/00102209808924135>
- Goodzari, F., Huggins, F.E., Sanei, H. (2008). Assessment of elements, speciation of As, Cr, Ni and emitted Hg for a Canadian power plant burning bituminous coal. *Int. J. Coal Geol.* 74, 1–12. <https://doi.org/10.1016/j.coal.2007.09.002>
- Gunchin, G., Manousakas, M., Osan, J., Karydas, A.G., Eleftheriadis, K., Lodoysamba, S., Shagjjamba, D., Migliori, A., Padilla-Alvarez, R., Strelci, C., Darby, I. (2019). Three-year long source apportionment study of airborne particles in Ulaanbaatar using X-ray fluorescence and positive matrix factorization. *Aerosol Air Qual. Res.* 19, 1056–1067. <https://doi.org/10.4209/aaqr.2018.09.0351>
- Huggins, F.E., Huffman, G.P., Linak, W.P., Miller, C.A. (2004). Quantifying hazardous species in particulate matter derived from fossil fuel combustion. *Environ. Sci. Technol.* 38, 1836–1842. <https://doi.org/10.1021/es0348748>
- Huggins, F.E., Huffman, G.P., Robertson, J.D. (2000). Speciation of elements in NIST particulate matter SRMs 1648 and 1650. *J. Hazard. Mater.* 74, 1–23. [https://doi.org/10.1016/S0304-3894\(99\)00195-8](https://doi.org/10.1016/S0304-3894(99)00195-8)
- Karydas A.G., Czyzycki, M., Leani, J.J., Migliori, A., Osan, J., Bogovac, M., Wrobel, P., Vakula, N., Padilla-Alvarez, R., Menk, R.H., Gol, M.G., Antonelli, M., Tiwari, M.K., Caliri, C., Vogel-Mikuš, K., Darby, I., Kaiser, R.B. (2018). An IAEA multi-technique X-ray spectrometry endstation at Elettra Sincrotrone Trieste: Benchmarking results and interdisciplinary applications. *J. Synchrotron Rad.* 25, 189–203. <https://doi.org/10.1107/S1600577517016332>
- Lubeck, J., Bogovac, M., Boyer, B., Detlefs, B., Eichert, D., Fliegau, R., Grötzsch, D., Holfelder, I., Hönicke, P., Jark, W., Kaiser, R.B., Kanngießner, B., Karydas, A.G., Leani, J.J., Lépy, M.C., Lühl, L., Ménesguen, Y., Migliori, A., Müller, M., Pollakowski, B., *et al.* (2016). A new generation of x-ray spectrometry UHV instruments at the SR facilities BESSY II, ELETTRA and SOLEIL. *AIP Conf. Proc.* 1741, 030011. <https://doi.org/10.1063/1.4952834>
- Maenhaut, W., Francois, F., Cafmeyer, J. (1993). The GENT stacked filter unit sampler for collection of atmospheric aerosols in two size fractions. Report No. NAHRES-19, International Atomic Energy Agency, Vienna, pp. 249–263.
- Matsui, Y., Sakai, N., Tsuda, A., Terada, Y., Takaoka, M., Fujimaki, H., Uchiyama, I. (2009). Tracking the pathway of diesel exhaust particles from the nose to the brain by X-ray fluorescence analysis. *Spectrochim. Acta Part B* 64, 796–801. <https://doi.org/10.1016/j.sab.2009.06.017>
- Mattielli, N., Petit, J.J., Deboudt, K., Flament, P., Perdrix, E., Taillez, A., Rimetz-Planchon, J., Weis, D. (2009). Zn isotope study of atmospheric emissions and dry depositions within a 5 km radius of a Pb–Zn refinery. *Atmos. Environ.* 43, 6. <https://doi.org/10.1016/j.atmosenv.2008.11.030>
- Ohta, A., Tsuno, H., Kagi, H., Kanai, Y., Nomura, M., Zhang, R., Terashima, S., Imai, I. (2006). Chemical compositions and XANES speciations of Fe, Mn and Zn from aerosols collected in China and Japan during dust events. *Geochem. J.* 40, 363–376. <https://doi.org/10.2343/geochemj.40.363>
- Osán, J., Meirer, F., Groma, V., Török, S., Ingerle, D., Strelci, C., Pepponi, G. (2010). Speciation of copper and zinc in size-fractionated atmospheric particulate matter using total reflection mode X-ray absorption near-edge structure spectrometry. *Spectrochim. Acta, Part B* 65, 1008–1013, ISSN 0584-8547, <https://doi.org/10.1016/j.sab.2010.11.002>
- Pettine, M., Capri, S. (2005). Digestion treatments and risks of Cr(III)-Cr(VI) interconversions during Cr(VI) determination in soils and sediments - A review. *Anal. Chim. Acta* 540, 231–238. <https://doi.org/10.1016/j.aca.2005.03.040>



- Ravel, B., Newville, M. (2005). ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* 12, 537–54. <https://doi.org/10.1107/S0909049505012719>
- Roberts, D., Nachtegaal, M., Sparks, D.L. (2005). Speciation of Metals in Soils, in Tabatabai, M., Sparks, D. (Eds.), *Chemical Processes in Soils*, John Wiley & Sons, Ltd, pp. 619–654. <https://doi.org/10.2136/sssabookser8.c13>
- Seigneur, C., Constantinou, E. (1995). Chemical kinetic mechanism for atmospheric chromium. *Environ. Sci. Technol.* 29, 222–231. <https://doi.org/10.1021/es00001a029>
- Shaltout, A., Harfouche, M., Ahmed, S., Czyzycki, M., Karydas, A. (2017). Synchrotron radiation total reflection X-ray fluorescence (SR-TXRF) and X-ray absorption near edge structure (XANES) of fractionated air particulates collected from Jeddah, Saudi Arabia. *Microchem. J.* 137, 78–84. <https://doi.org/10.1016/j.microc.2017.10.001>
- Sinclair, A H., Edgerton, E. S., Wyzga, R., Tolsma, D. (2010). A two-time-period comparison of the effects of ambient air pollution on outpatient visits for acute respiratory illnesses. *J. Air Waste Manage. Assoc.* 60, 163–175. <https://doi.org/10.3155/1047-3289.60.2.163>
- Unceta, N., Séby, F., Malherbe, J., Donard, O.F.X. (2010). Chromium speciation in solid matrices and regulation: A review. *Anal. Bioanal. Chem.* 397, 1097–1111. <https://doi.org/10.1007/s00216-009-3417-1>
- Wang, Y., Li, A., Zhan, Y., Wei, L., Li, Y., Zhang, G., Xie, Y., Zhang, J., Zhang, Y., Shan, Z. (2007). Speciation of elements in atmospheric particulate matter by XANES. *J. Radioanal. Nucl. Chem.* 273, 247–251. <https://doi.org/10.1007/s10967-007-0743-7>
- Werner, M.L., Nico, P.S., Marcus, M.A., Anastasio, C. (2007). Use of micro-XANES to speciate chromium in airborne fine particles in the Sacramento Valley. *Environ. Sci. Technol.* 41, 4919–4924. <https://doi.org/10.1021/es070430q>
- Wrobel, P.M., Bogovac, M., Sghaier, H., Leani, J.J., Migliori, A., Padilla-Alvarez, R., Czyzycki, M., Osan, J., Kaiser, R.B., Karydas, A.G. (2016). LabVIEW interface with Tango control system for a multi-technique X-ray spectrometry IAEA beamline end-station at Elettra Sincrotrone Trieste. *Nucl. Instrum. Methods Phys. Res., Sect. A* 833, 105–109. <https://doi.org/10.1016/j.nima.2016.07.030>
- Yu, M., Tian, S., Chu, W., Chen, D., Wang, Q., Wu, Z. (2009). Speciation of zinc in secondary fly ashes of municipal solid waste at high temperatures. *J. Synchrotron Radiat.* 16, 528–532. <https://doi.org/10.1107/S0909049509020032>