

Strategies for ambient aerosols characterisation using synchrotron X-ray fluorescence: a review

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Introduction

Ambient aerosols are of interest in many different regards, e.g., human health,¹ cloud formation and their effect on global temperatures, as well as transport of nutrients to the oceans. The elemental load and the particle size are important information required to determine the impact of the aerosols in terms of their penetration into the lungs, and their toxic effects on human health, their activities as condensation nuclei and their transport efficiencies.^{2,3} To be able to resolve atmospheric events like a storm front which lasts from 2 h to 6 h, monitoring intervals of 1 h are desirable. Accordingly, trace elemental detection limits for micro amounts of sample materials are required. Until now characterisation of aerosols representative for short time scales (1 h and less) remained a challenging analytical task. Size-resolved determination of major particulate matter components using conventional bulk analytical techniques typically fall short of being capable of providing time resolutions of between 6 h and 24 h. Fast bulk on-line methods are available for non-metal compounds. Calibration with model aerosols allows, to some extent, for quantification on a mass per sampled air volume.⁴ Quantification of specific single-particles or particle ensemble components is still a challenge.⁵ A major drawback of these on-line methods is their destructive nature, which in general does not allow for further analyses of the sample. In this sense X-ray

fluorescence related techniques have been established in many fields of aerosol research. In this review aerosol characterisation using synchrotron excitation X-ray fluorescence related techniques are highlighted with respect to studies of environmental relevance and atmospheric elemental transport. The review does not claim to give a full overview of all the work that has been done in these fields, but highlights procedures and results by selected examples.

Size fractionation

The general approach for size fractionated sampling of atmospheric aerosols in most off-line procedures is the separation of particles of different inertia by impaction. This is translated into their aerodynamic diameter, by assuming a standard density (1 kg L^{-1}) and shape (spherical). Impactors are often designed to separate particulate matter in air as dictated by regulation, monitoring PM₁₀ (particulate matter $\text{Ø} < 10 \text{ }\mu\text{m}$), PM_{2.5} (particulate matter $\text{Ø} < 2.5 \text{ }\mu\text{m}$) and ultrafine dust (particulate matter $\text{Ø} < 1 \text{ }\mu\text{m}$).

The general setup of an impactor is depicted in Figure 1.

The air is sucked through the impactor by a vacuum pump. The air flow is controlled by nozzles and directed to the impaction plates. The air has to go round the plates. Particles of high inertia cannot follow the airflow and impact on the plates. Usually the plates are covered

with a filter material to collect the particles and allow for determination of mass of, e.g. PM₁₀ or PM_{2.5}. The amounts of airborne matter collected during 1 h is limited by the airflow through the impactor, which is in the range of $1 \text{ m}^3 \text{ h}^{-1}$ for the devices used in the work cited here.

To achieve the sensitivity allowing short sampling times with synchrotron radiation X-ray fluorescence (SR-XRF) analysis background noise stemming from the sample carrier has to be minimised. Two to three nm penetration of

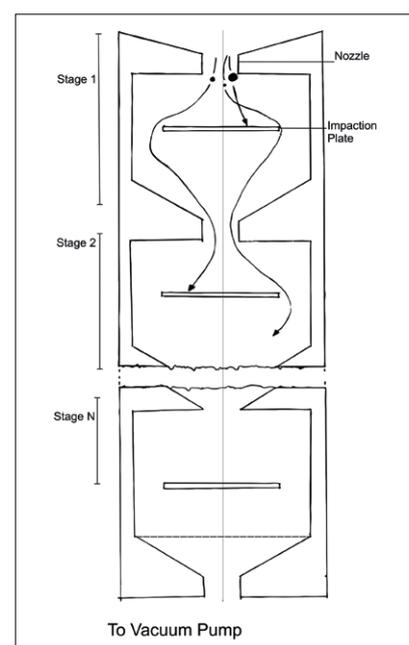


Figure 1. Schematic drawing of a cascade impactor.

the primary X-rays into the reflector and therefore minimal background scattering is observed in total reflection XRF (TXRF) geometry.⁶ Total reflection of X-rays is realised by using polished reflectors and very small angles of the excitation beam, less than the critical angle of total reflection of X-rays. In TXRF, Si-wafer impaction plates have been used with the dual purpose of being, first, the impaction plate for aerosol collection and, subsequently, the sample carrier reflector for total reflection X-ray fluorescence.^{7–9} It has been shown that SR-TXRF is a very potent method for elemental determination of size fractionated aerosols.^{10,11} In addition to SR-TXRF, other synchrotron-assisted XRF techniques have been applied successfully for size-resolved elemental determination in aerosols. Bukowiecki *et al.*¹² used a conventional 45° geometry micro-XRF setup and a thin 1.8 µm thickness polymer film (Mylar[®]) as impaction plates and sample carrier, which produce negligible background scatter comparable to TXRF.

Low limits of detection

For both; TXRF geometry and micro-XRF geometry low limits of detection (DL) are usually in the single digit pg m⁻³ regime for, e.g., transition metals from Ti to Zn and Pb. Bukowiecki *et al.*¹² report DLs of 17 pg m⁻³ Fe and 19 pg m⁻³ Pb (hourly monitoring and 15 s XRF spectra collection time) studying ambient air in areas in Zürich, Switzerland. Fittschen *et al.*¹³ found DLs of 0.8 pg m⁻³ Fe and 2 pg m⁻³ Pb (hourly monitoring and 100 s XRF spectra collection time) monitoring air in Hamburg, Germany. For both studies the bending magnet beam line L at DORISIII at the DESY, Hamburg, was used as the SR source. SR-XRF analysis not only benefits from higher flux of the excitation beam and polarisation but often the SR-beam line allows for optimising excitation and detection parameters. This has been demonstrated for the analysis of P in atmospheric aerosols. XRF analysis of low Z elements like P usually is unfavourable because of low fluorescence yield and absorption effects. At the ANKA Fluo beam-line at Karlsruhe the excitation energy was set to 3.5 keV to have optimal excitation of the P K-edge and to prevent from Ca K_α escape peak inter-

ferences exciting below the Ca K-edge energy of 4.04 keV by Fittschen *et al.*¹⁴ In addition, the evacuated sample environment reduced absorption of the relatively low energy P K lines, which are otherwise easily absorbed in air atmosphere. These optimisations resulted in DLs for P of 200 pg m⁻³ (hourly monitoring and 100 s XRF spectra collection time; nine size fractions from 15 nm to 16 µm). P in aerosols is of interest with regard to nutrient transport to the far oceans. The relevance of intercontinental transport of P from Saharan dust to the South-American rain forests has been controversially discussed.^{15,16} Because of the low absolute amounts of P (< 10 ng m⁻³) in atmospheric aerosols the impact of atmospheric P transport on marine plankton and plant growth in nutrient depleted areas remains unclear.

With the high sensitivity for P established using SR-TXRF it was possible to show the high variability of P in aerosols with respect to their particle size fraction and location. Figure 2 shows TXRF spectra of aerosols of different particle sizes. It can be seen that the 250–500 nm fraction (blue) shows the highest P content, which corresponded to 180 ng m⁻³, and the coarse fraction (1–2 µm; red) the lowest content of 7 ng m⁻³.

Automated sampling, fractionation and small particle collection

The impaction devices used in the studies cited here provide different advantages. Best suited for continuous monitoring of atmospheric aerosols is the rotating drum impactor first designed by Lundgren in 1967.¹⁷ A modified design was developed at the "Eidgenössische Materialprüfungs- und Forschungsanstalt" (Empa)¹². The aerosols are collected on a polymer film through a line shape orifice. The film is installed on a wheel, which is rotated after a certain time, e.g. 1 h, to collect a new charge of aerosol. Figure 3 shows the rotating drum impactor.

This device collects the aerosols in three size fractions corresponding to PM₁₀, PM_{2.5} and PM₁ with a low cut off of 100 nm for the smallest fraction. So, recent measurements indicate a slightly higher cut-off.¹⁹ Much better size fractionation of 11 fractions starting from 16 µm and with a low particle cut off of 15 nm is achieved with the low pressure Berner impactor.¹⁰ The higher number of fractionation steps allows for better diagnostic of air mass origin and chemical species of the elements in the aerosol. The aerosols are collected in multiple

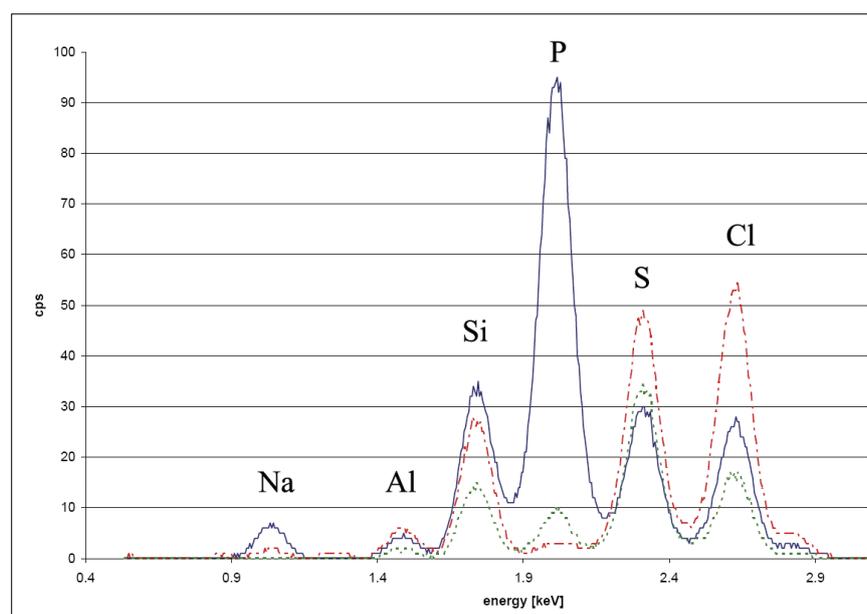


Figure 2. Spectra from three aerosols: 15–30 nm dotted (green) line, 250–500 nm solid (blue) line and 1–2 µm alternating dots-bar (red) line. (Reprinted with permission from Reference 14, Copyright 2014 Wiley.)

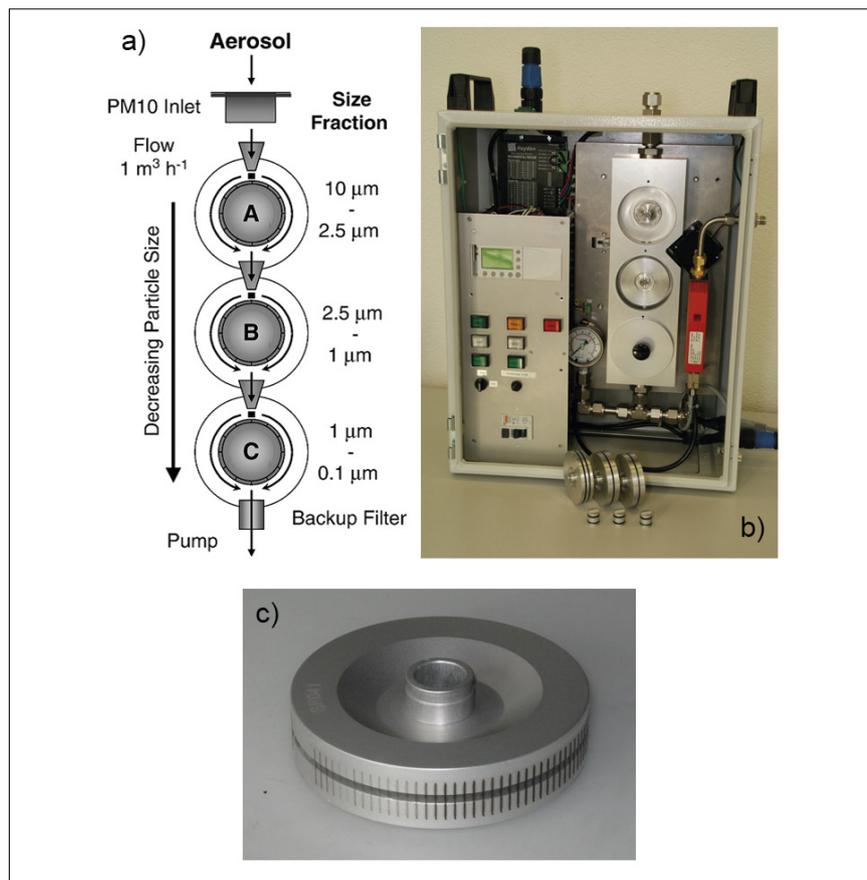


Figure 3. (a) Schematic setup of a Rotating Drum Impactor (RDI). Arrows indicate the aerosol, stream lines. (Reprinted with permission from Bukowiecki *et al.*, Copyright 2008 Elsevier), (b) a photograph of the RDI (by courtesy of Dr Markus Furger, Paul Scherrer Institut, CH-5232 Villigen, Switzerland), (c) RDI aerosol collection wheel (example for the smallest particle size range). Each bar represents the aerosol collected during one sampling interval (ca 1 h) (by courtesy of Dr Markus Furger, Paul Scherrer Institut, CH-5232 Villigen, Switzerland)

spots, which allow for obtaining subsamples but also reduces the effective mass to be analysed. Here a single orifice impactor shows better performance like the May impactor used in a number of SR-TXRF studies by the group of the KFKI Atomic Energy Research Institute in Budapest, Hungary.¹¹ Nonetheless, this device has a low cut off at 250 nm, which means the fine dust fraction cannot be adequately represented.

Calibration

Reliable calibration of the SR-XRF analysis is ambitious. References need to be well defined in both size and shape and generally of a microscopic spatial dimension to represent the sample adequately. Different procedures have been introduced. The most flexible approach is to use "Drop on Demand" (DOD) printing

technology to generate custom made deposits in size, shape and elemental composition introduced by Fittschen *et al.*^{10,20} The deposit may be used as either an internal standard or external reference. The elemental mass is determined by the volume spotted by the printing device. Figure 4 shows Auger electron maps and a scanning electron microscopy (SEM) image of dried Ni deposits on a Si wafer slide.

A modified approach was applied using additives to generate homogeneous films with a DOD-printer.²¹ The procedure allowed for custom made mass per area reference. Another approach is to use reference-free quantification established by Beckhoff at the "Physikalisch-Technische Bundesanstalt" (PTB)^{22,23} at the BESSYII beamline, and lithographic techniques²⁴ or sputtering to generate homogeneous or

structured elemental deposits.²⁵ The latter has not only been used in elemental determination of aerosols, but has become a common diagnostic tool in SR-XRF.

Subsequent analysis with SR-TXRF-XANES

As mentioned previously; the quasi non-destructive XRF analysis of aerosols allows for further/prior characterisation of the sample. The collected aerosols may be digested and analysed using other analytical tools like inductively coupled plasma mass spectrometry ICP-MS or ICP-OES (ICP-optical emission spectrometry), which enable one to obtain additional information.²⁶

With respect to the elucidation of aerosol origin, source apportionment and alteration in the atmosphere chemical, speciation is of utmost importance. X-ray based techniques are excellently suited to study matter in its solid state assuming the sensitivity is sufficient. Micro-X-ray diffraction (XRD) analysis on single particles several micrometres in diameter has been applied by Lind *et al.*²⁷ but falls short for smaller particles. Electron probe micro analysis (EPMA) analysis has served very well in this regard and has been widely applied to identify air borne contaminant with respect to historical site conservation.²⁸

A different approach is to use X-ray absorption near edge fine structure analysis (XANES). Meirer *et al.*²⁹ have shown that speciation in terms of determining valence of arsenic in xylem sap of cucumber plants with concentrations of 30 ppb is feasible using TXRF-XANES.

The result shows that As(V) is converted to As(III) by the plant. In general those oxidation state conversions help detoxification. The element may be converted to a less toxic form or to more volatile compounds, which are emitted from the leaf. Such processes result in a decrease of toxic metal concentration in an organism.

With respect to aerosols the species of a metal may also give important information on elemental transport by air masses and transport conditions. Osán *et al.*³⁰ determined species of Zn and Cu in aerosols collected at different urban locations in Hungary. The species and size of the

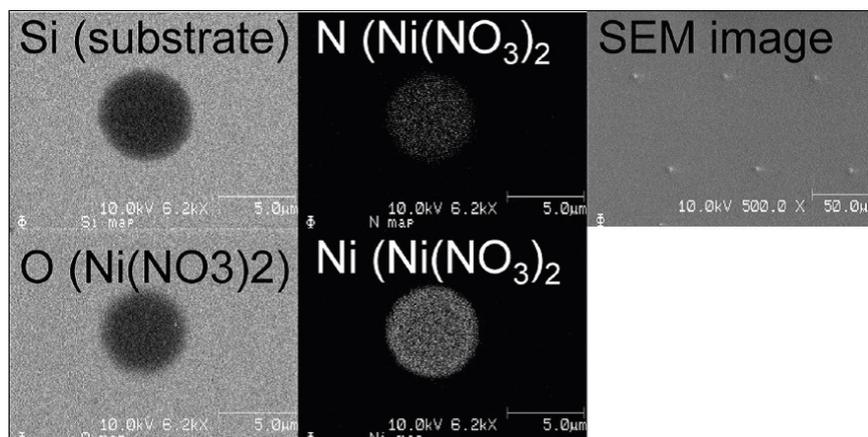


Figure 4. Auger electron maps on a 25fg Ni deposit on a Si-wafer for the element transitions Si (KLL) (substrate), N (KLL) ($\text{Ni}(\text{NO}_3)_2$), O (KLL) ($\text{Ni}(\text{NO}_3)_2$) and Ni (LMM) ($\text{Ni}(\text{NO}_3)_2$), and a scanning electron microscope (SEM) image from a part of the array. (Reprinted with permission from Reference 19, Copyright 2010 American Chemical Society.)

particle was used to draw a conclusion on the origin of the particle. They identified $\text{Zn}(\text{NO}_3)_2$ to be the main compound in the sub-micrometre fraction rather than ZnSO_4 . Both compounds indicate Zn being associated to secondary aerosol particles. They found detection limits for TXRF-XANES to be as low as 50 pg Zn. An amount of 60 pg Zn was found sufficient for a reasonable determination of the species, which for the May impactor corresponds to a concentration of 140 pg m^{-3} .

These analyses were performed at beam line L at DORISIII at the DESY. Speciation on low Z elements is also feasible at beam lines dedicated to soft X-rays, e.g. Osán *et al.*⁵¹ studied nitrate and ammonia content in aerosols from the Antarctic at the Physikalisch-Technische Bundesanstalt (PTB) plane grating monochromator (PGM) beam line at BESSYII.

Besides source apportionment and health aspects, speciation of the oxidation state is important with regard to

nutrient fluxes. Fe(II) as a micro nutrient plays an important role in air borne transport of nutrients to the ocean. Whereas Fe is abundant in freshwater reservoirs, it is a growth limitation factor in the ocean. This is because in the alkaline milieu of the ocean Fe hydroxide/oxides easily sediment. In contrast to Fe(III), Fe(II) is easily consumed by plankton.^{32,33} Fittschen *et al.*¹³ show that using SR-TXRF XANES the oxidation state of Fe from atmospheric aerosols (sampled for 1 h collected in nine size fractions from 15 nm to 16 μm) could be determined for 200 pg Fe absolute, corresponding to 3 ng m^{-3} . Figure 5 shows the XANES spectra of selected Fe references and Figure 6 shows the XANES spectra of the aerosol particles. Fe(III) oxidation state was found for all size fractions.

Conclusions

SR-XRF, in micro-XRF as well as TXRF geometry, is a sensitive analytical tool allowing for elemental determination and speciation of aerosol particulates with limits of detection in the pg m^{-3} range for many elements and collection times as low as 1 h. Hourly monitoring of PM10, 2.5 and ultrafine dust is feasible as well as high size fractionation of particles and

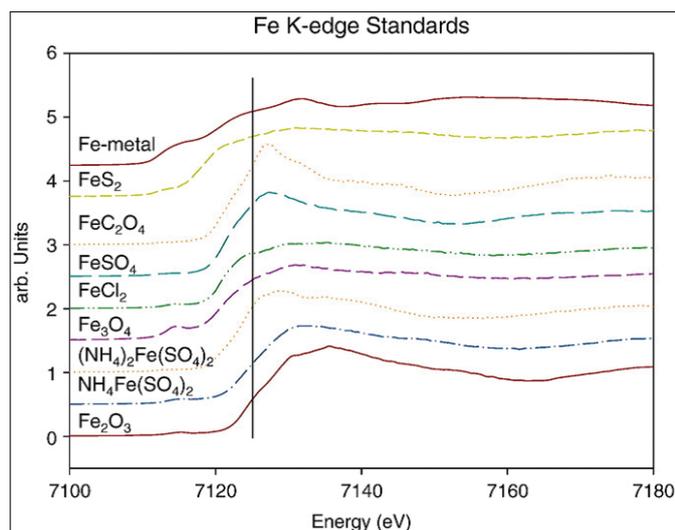


Figure 5. Fe K-edge XANES spectra from different Fe species: Fe-metal, Fe(II)sulfide, Fe(II) oxalate, Fe(II)sulfate, Fe(II)chloride, Fe(II+III)oxide, ammoniumFe(II)sulfate, ammoniumFe(III)sulfate and Fe(III)oxide. (Reprinted with permission from Reference 13, Copyright 2008 Elsevier.)

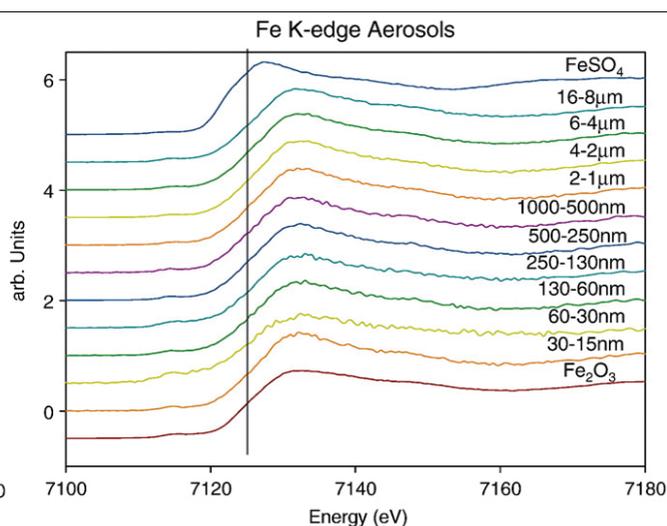


Figure 6. Fe-XANES spectra from different aerosol particle size fractions: particles size from 15 nm to 30 nm, 30 nm to 60 nm, 60 nm to 130 nm, 130 nm to 250 nm, 250 nm to 500 nm, 0.5 μm to 1 μm , 1 μm to 2 μm , 2 μm to 4 μm , 4 μm to 8 μm , 8 μm to 16 μm , in addition to the aerosols one Fe-XANES curve from Fe(II) sulfate and one from Fe(III)oxide are shown. (Reprinted with permission from Reference 13, Copyright 2008 Elsevier.)

particle cut off as low as 15 nm allowing one to solve different scientific questions.

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