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Chemical speciation of chlorine in atmospheric aerosol samples by high-resolution proton induced X-ray emission spectroscopy

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ABSTRACT

Chlorine is a main elemental component of atmospheric particulate matter (APM). The knowledge of the chemical form of chlorine is of primary importance for source apportionment and for estimation of health effects of APM. In this work the applicability of high-resolution wavelength dispersive proton induced X-ray emission (PIXE) spectroscopy for chemical speciation of chlorine in fine fraction atmospheric aerosols is studied. A Johansson-type crystal spectrometer with energy resolution below the natural linewidth of Cl K lines was used to record the high-resolution Kα and Kβ proton induced spectra of several reference Cl compounds and two atmospheric aerosol samples, which were collected for conventional PIXE analysis. The Kα spectra which refers to the oxidation state, showed very minor differences due to the high electronegativity of Cl. However, the Kβ spectra exhibited pronounced chemical effects which were significant enough to perform chemical speciation. The major chlorine component in two fine fraction aerosol samples collected during a 2010 winter campaign in Budapest was clearly identified as NaCl by comparing the high-resolution Cl Kβ spectra from the aerosol samples with the corresponding reference spectra. This work demonstrates the feasibility of high-resolution PIXE method for chemical speciation of Cl in aerosols.

1. Introduction

Urban atmospheric aerosol pollution is one of the leading environmental problems. In order to work out effective mitigation strategies the knowledge of atmospheric particulate matter (APM) sources is essential. Atmospheric aerosols are a complex mixture of particles suspended in the air. Different emission sources can be described by characteristic chemical composition or characteristic elemental ratios [1]. Commonly applied analytical methods for the determination of the composition of APM are ion and gas chromatography, ICP-MS, ICP-OES, instrumental neutron activation analysis (INAA), and Fourier transform infrared spectroscopy (FTIR) [1]. For the determination of major, minor and trace element content of aerosol samples collected on filters nondestructive nuclear techniques like PIXE and X-ray fluorescence (XRF) are widely used [1,2]. The advantages of the PIXE method are that it requires very little sample preparation and provides absolute, quantitative concentrations for elements between Mg and U without using any internal or external standards. However, this method yields elemental composition only but it is not sensitive to the chemical environment of the X-ray emitting atom and consequently it cannot provide the chemical speciation of APM components which is of primary importance in source characterization [3]. In order to determine chemical composition, statistical analysis performed on large database of measured samples is usually employed to look for correlations between particular components [4]. However, this approach provides only average chemical composition characteristic of the majority of the samples, and does not give information about individual events. Single particle analysis employing proton or electron microprobes [5–7] is another method used to determine chemical composition. In this case the statistical analysis is performed on a database of individual aerosol particles measured on a particular sample [8]. This method is expensive, time consuming, and there is limitation in the size of the particles. Generally 0.4–0.5 μm is the smallest particle size which can be studied this way [5], whereas the majority of accumulation mode particles have an aerodynamic diameter between 0.1 and 0.5 μm [9]. In addition, light elements (H, C, N, O) and their compounds are often not included in the analysis due to the limitation of the analytical techniques or the background originating from the support material.

Alternatively, chemical characterization of a (single) bulk sample can be performed by high-resolution PIXE method employing wavelength dispersive X-ray (WDX) spectroscopy. The influence of the chemical environment is reflected in energy shifts of the characteristic lines, formation of satellite lines and changes in the emission linewidths and relative intensities. If we can push the experimental resolution towards the natural linewidths of the measured lines, it is feasible to make a chemical state analysis of bulk aerosol samples. In this case, the limiting factor is the sensitivity of the method,

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which is reduced due to the relatively low efficiency of WDX crystal spectrometers. It was demonstrated earlier that chemical speciation of S and P in environmental samples including aerosols is possible by the wavelength dispersive PIXE method [10–13] by measuring the shifts of the Kα X-ray lines.

Chlorine is a significant component of atmospheric PM. One of the biggest natural sources of APM is the oceans and seas: according to the IPCC 3340 Tg primary sea salt aerosol was emitted globally in the year 2000 [14]. Sea salt aerosols play an important role in the energy balance of the Earth both in direct (absorption and reflection of solar radiation) and indirect (serves as cloud condensation nuclei) ways [14]. In addition, the volatilization of sea salt is one of the sources of reactive chlorine, which is responsible for ozone depletion [15]. The size distribution of Cl collected in industrial and urban areas usually shows a bi-modal shape [16,17]. Typically, the main source of Cl in the coarse size fraction (10 μm ≥ aerodynamic diameter ≥ 2.5 μm) is sea spray, whereas fine Cl-containing aerosols (aerodynamic diameter < 2.5 μm) have anthropogenic origins (industry, biomass burning, agriculture, detergents, waste incinerators, water works). Reis et al. [18] showed that the extreme concentration of Cl in the PM2.5 fraction in Portugal originated from organic pesticides and these can lead to serious health problems.

At the Institute of Nuclear Research in Debrecen we have studied urban aerosol pollution for more than 20 years. Despite the fact that Hungary lies well inside the European continent, and thus the effect of sea is negligible [19], chlorine was found to be a major constituent of particulate matter in Hungarian cities; in some cases up to 20–30% concentrations were measured in both size fractions. Sources of coarse fraction chlorine were determined by single particle analysis using ion and electron microscopy [20]. Unfortunately, in the case of the fine fraction the above mentioned methods did not provide any useful information about the chemical composition of chlorine. When observing the hourly evolution of elemental components we have noted that Cl very often appeared in episodic peaks together with metals (eg. Cu, Zn, Pb) or with K [20,21]. The origin of these emission episodes remained unclear, and it was also not clear whether these elemental components were chemically bound together.

Despite the fact that the knowledge of the chemical form of Cl would give direct information about the emitting sources, chemical speciation of Cl in APM has not yet been solved. The common analytical methods used for APM characterization yield information only about the quantity of Cl or chloride ions. High-resolution X-ray emission spectroscopy and synchrotron based X-ray absorption fine structure spectroscopy (XAFS) have the potential for chemical speciation in fine APM [22,23]. However, the chemical speciation of Cl in APM samples by XAFS has met with significant difficulties due to exceedingly weak chlorine spectrum [22]. Very recently, the chemical speciation of Cl in atmospheric aerosols was performed with high-resolution PIXE employing wavelength dispersive X-ray spectrometer [24]. The analysis of thick aerosol deposits showed that Cl speciation was possible on the coarse size fraction, when the concentration of Cl was higher than 1%. However, in the fine size fraction, due to low Cl concentrations resulting in a very weak signal, the speciation of Cl was not possible.

The aim of this study was to show the applicability of high-resolution PIXE spectroscopy for the chemical characterization of Cl on widely used aerosol filters with thin aerosol deposits. High-resolution Cl Kα and Kβ PIXE spectra of two aerosol samples and of several reference chlorine compounds, which could occur in high concentration in fine fraction APM, were recorded at the high resolution PIXE setup of the Jozef Stefan Institute. Chemical speciation of Cl in the aerosol samples was performed by comparing the high-resolution Cl Kβ PIXE spectra of the samples with Kβ spectra of the reference compounds.

2. Experimental

2.1. Reference materials and aerosol samples for chemical state analysis

Aerosol samples were collected in a sampling campaign, which was performed in the winter of 2009–2010 in Budapest and Debrecen, Hungary. Parallel 24 h samples (with separated fine and coarse fractions) were collected with Gent-type stacked filter units on 47 mm diameter nuclepore polycarbonate filters. The concentration of fine and coarse PM was measured by gravimetry and the elemental composition was determined by PIXE in the IBA Lab of Atomki, Debrecen [25]. For the Cl chemical speciation two samples with high Cl concentrations were selected. These samples were collected on 23rd and 26th of January, 2010 in Budapest in an urban background site. The concentration of Cl was 1910 ± 80 ng/m^3 and 1880 ± 80 ng/m^3 respectively, representing 17% and 10% of the total concentration of PM. The load of the filters was 20 and 25 μg/cm^2, respectively. Reference compound targets of NaCl, $CaCl_2$, KCl, $CuCl_2$, and NH_4Cl were prepared in the form of pellets pressed from pure powder materials.

2.2. High-resolution PIXE measurements

The high-resolution PIXE measurements were performed at the Microanalytical Center of the J. Stefan Institute in Ljubljana. Protons were accelerated by a 2 MV tandem accelerator. The incident proton beam with a size of 8×8 mm^2 impinged on a target tilted at 45° with respect to the incoming proton beam. The energy of the proton beam was set to 2 MeV and a relatively low beam current of 150 nA was used in order to avoid radiation damage. In the case of aerosol samples a piece of the nuclepore polycarbonate filter loaded with aerosols was cut and attached to an Al frame, which was used to fix the sample to the target holder of the spectrometer. The target X-ray fluorescence was analyzed with the Johansson type crystal spectrometer described in detail in [26]. The first-order reflection of a Si(111) crystal was used for the Cl measurements. The target was placed well inside the Rowland circle at a distance of 42 cm in front of the crystal. At fixed crystal-detector position set for the energy of the Cl Kβ line, the spectrometer covers the energy range of 70 eV determined by the lateral dimension (770 pixels × 22.5 μm/pixel) of the CCD detector. At the energy of the Cl Kα line the overall energy resolution of the spectrometer is less than 0.5 eV [26], which is significantly below the natural linewidth of the Cl Kα line ($\Gamma_{K\text{-}L2,3} =$ 0.68 eV [27]).

3. Results and discussion

The measured high-resolution Cl Kα spectrum of the NaCl reference sample is presented in Fig. 1. Obviously, the experimental resolution is very high since we can clearly resolve the $K\alpha_{1,2}$ doublet due to LS splitting of the Cl 2p level (1.59 eV [28]). Additional satellite structure on the high energy side (around 2640 eV) is due to KL double ionization. Since only core electrons are involved in the transition it is generally expected that Kα spectral lines should be mostly free from chemical bond effects, except from small energy shifts. These shifts are related to the valence electron population only indirectly due to slight changes in the screening of the effective nuclear potential. As shown in our previous work on S [10,11] and P [12], the energy of the Kα line has a direct correlation with the oxidation state of the element, so the measured chemical shift of the Kα line can be used to determine the oxidation state of the element in the sample. The spectral shape is practically independent on the oxidation state making the analysis simple and robust. However, in case of chlorine the expected oxidation state is practically always the same (−1) due to the high electronegativity of Cl. Consequently, for Cl, we cannot expect any significant chemical effect in the measured Kα lines. This is confirmed by the measurements presented in Fig. 2. The