Trace element analysis of fine aerosol particles with high time resolution using SR-TXRF

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Air quality monitoring and assurance is a transboundary issue involving co-ordinated environmental action and policies among neighboring countries. This is especially valid for aerosols that can be strongly related to the health of the citizens. Water-soluble components of aerosols can be measured by means of combined ion chromatography technique with very high temporal resolution (< 10 min) [1]. Our aim is to develop a multielemental analytical technique that has similar capabilities for the total aerosol. SR-TXRF applications provide several great advantages for aerosol characterization. Because of its natural collimation, high intensity and low background SR-TXRF allows detection of trace and ultra trace amounts (ng/g, fg/g) of most elements.

Aerosol samples have been collected on silicon wafers using a seven-stage May cascade impactor [2], at different background and urban locations. In order to investigate the fine aerosol fraction exclusively, aerosol collection was performed only at stages 5, 6 and 7. The May impactor has an impacting slit at each stage and thus the aerosols collected on the silicon substrate show a pattern of a thin strip.

Measurements were performed at HASYLAB Beamline L using the total-reflection X-ray fluorescence vacuum chamber (TXRF V.C.) [3]. A special sample holder was used to mount the 20×20 mm² Si wafer pieces with the aerosol samples collected in strip form with approximate dimensions 20 mm × 0.3 mm. The synchrotron radiation was tuned to 17.5 keV by means of the NiC multilayer monochromator. The TXRF alignment was done in checking the visibility of the reflection condition by a CCD camera and after scanning the left right position of the sample to the beam. The height scan was not affecting the total reflection conditions.

In a first attempt the Vortex Radiant SDD detector in use was equipped with a circular diaphragm of 6-mm inner diameter. The Si wafer was mounted with the strip in the vertical position. The SR beam had a vertical dimension of 1 mm. So the sample was scanned over a length of 6 mm in 6 steps. It turned out that the results given as counts for each element detected was fluctuating strongly. This was explained as influence of the round collimator and realistic inhomogeneities and some dust grains aside the real strip of aerosols. (No cleanroom is available at HASYLAB, even careful handling can contaminate samples.) In order to overcome the inhomogeneity problems, the collimator was modified with a 1.5-mm wide slit made of Mo. Measurements with the new collimator resulted in excellent reproducibility of the individual scan steps and are shown in Fig. 1 from two independent standard strips. The interpretation is clearly a shielding of the off-lier contaminants as the slit prevented their detection and the geometry of the detector collimator fits to that of the sample.

These TXRF measurements were applied to a Cr standard that had a known mass in dimensions identical to the deposited aerosol particles. This leads to a known count rate (cps/mA) for the known mass and can be used in a later measurement and by correcting to the physical fundamental parameters for the excitation to calculate the mass of the other elements present. In reality, the strip produced by the May impactor has a total length of 50 mm for 5 stages. The important issue is to make sure that the measured 6 mm or parts of it are representative for the total length and thus the calculation of the total mass deposited here. Only if this proven, the extrapolation from the mass calculated for 6 mm to the total mass deposition is permitted. The total mass deposited represents the aerosol concentration (ng/m³) in the collected air volume. For this purpose 18 mm of the existing 20 mm strips were measured successively by scanning 3×6 mm along the strip.
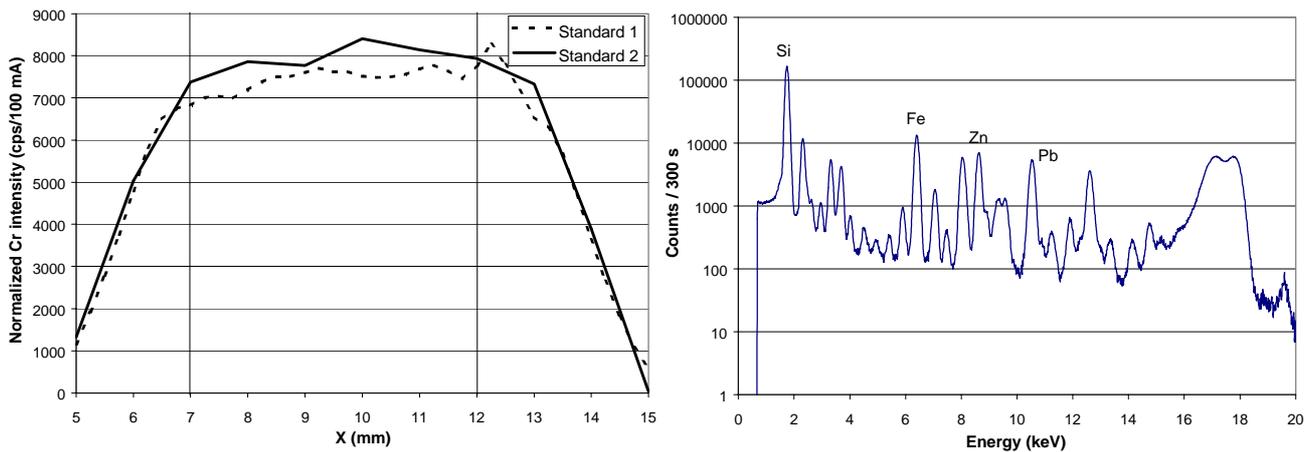
Figure 1. Left: Height scan of two independent standard Si wafers containing 7 ng Cr in a homogeneous strip, right: typical SR-TXRF spectrum of an aerosol sample collected at stage 6 (0.5–1 µm).
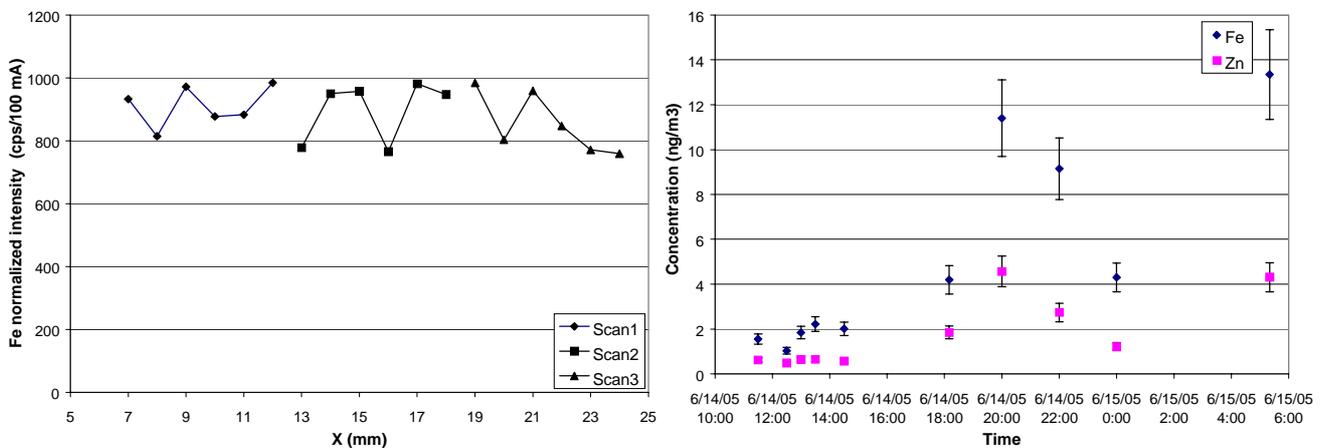
Figure 2. Left: Successive height scans of a stage 6 sample (0.5–1 µm) collected at Mátra, right: temporal variation of Fe and Zn in the 0.5–1 µm aerosol fraction at Mátra (400 l air per sample).

Results shown in Fig. 2 demonstrate that the normalized Fe intensities vary within 10 % relative standard deviation during the three scans, supporting the proposed extrapolation. Using the sum spectra of the 6-mm scans and the results of the Cr standards, the temporal variation of elemental concentrations in the 0.5–1 µm aerosol fraction could be reconstructed. Fe and Zn values presented in Fig. 2 (right) show anticorrelation with the mixing layer height that was expected from aerosol mass measurements at different sites. It could be shown that with SR-TXRF extremely high sensitivities could be achieved from aerosol samples. The masses collected are enough also from short time collection so a time and temporal variation of elemental concentrations in aerosol can be studied. Detection limits in the pg/m^3 range can be reached for a 20-min sampling time in the 0.5–1 µm aerosol fraction. Besides the number of real samples analyzed also fundamental studies to understand and to guarantee an accurate quantification procedure were performed.

References

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