Determination of Phosphorus in atmospheric Aerosols using SR-TXRF

U. E. A. Fittschen[1)], C. Streli[2)], M. Alfeld[1)], F. Meirer[2)]

[1)] University of Hamburg, Institute of Inorganic and Applied Chemistry, Martin-Luther-King Platz 6, D-20146 Hamburg, Germany
[2)] TU-Wien, Atominstitut, Stadionallee 2, A-1020 Vienna, Austria

Introduction

For geo-ecological processes like nutrient transport into the oceans and cloud formation, atmospheric aerosols are of utmost importance[i,ii]. The atmospheric supply of iron (which is an important micro-nutrient to marine plankton) to the oceans has been studied intensively since a couple of years. Beside Fe especially the atmospheric transport of nitrogen and phosphorus containing substances has been a point of interest[iii,iv]. However, the relevance of intercontinental transport of P from Saharan dust as important nutrient source for the oceans and South-American rain forests has been discussed controversially[v,vi]. Because of the low absolute amounts of P (< 10 ng/m3) in atmospheric aerosols the impact of atmospheric P transport on marine-plankton and plant growth in nutrient depleted areas remains unclear.
The aim of this project was to determine P in aerosol particulates with Synchrotron Radiation induced Total-reflection X-Ray Fluorescence analysis (SR-TXRF). Because origin and fade of aerosols strongly depend on the particle size, the aerosols were collected by the aid of a low pressure Berner impactor, which separates the aerosol particulates in eleven size fraction with the smallest fraction from 16 nm to 150 nm.
To determine low Z elements like P measurements have to be performed under vacuum conditions and a Synchrotron source, providing high intensity near the P K-edge is highly recommended. Therefore we used the FLUO beamline at the ANKA Synchrotron for our experiments, which is applicable for a TXRF set up and equipped with a sample changer and a vacuum chamber.

Experimental

The aerosols were collected for one hour in a rural environment in ten size fractions with the aid of a low pressure Berner Impactor, which is very well suited to collect aerosol particulates in the small size fractions (< 2,5 µm, aerodynamic particle size). Plates made from Acrylic glass and silicon reflectors were used as impaction plates. These plates were taken out of the impactor and then mounted directly onto the sample changer of the TXRF set up to determine P in the impacted aerosols (Fig. 1). 130 pL of a standard solution was spotted on a clean Acrylic glass plate as external standard for calibration.

Results and discussions

The comparison of the performance of the Si-reflectors and Acrylic glass as sample carriers for the determination of P in atmospheric aerosols with SR-TXRF showed that Acrylic glass carriers are much more suited for this purpose. The Si K-lines from the Si-carrier showed a strong overlap with the P K-line. Therefore only the Acrylic glass carriers were analysed. Additionally this choice enabled us to determine Si content in the aerosols. Some of the aerosol samples had high concentrations of calcium which lead to an overlap of the Ca escape signal with the P K-line. To prevent this overlap, the energy of the excitation beam was set to 3.5 keV which is below the Ca K absorption edge (4.04 keV).
With the optimized set up the aerosol collected for one hour in ten size fractions from 15 – 30 nm, 30 – 60 nm, 60 – 130 nm, 130 – 250 nm, 250 – 500 nm, 0.5 – 1 µm, 1 – 2 µm, 2 – 4 µm, 4 – 8 µm, 816 µm were analyzed. To optimize the sample position an angle scan and an up-down scan were performed prior to each analysis. Additionally the results from the up-down scan were used to determine blank values. Blank values for P were found to be below the detection limits. The results obtained from the aerosol analysis show that the content of P varies significantly between the different size fractions. The spectra of three different aerosol fractions are shown in Fig. 2.

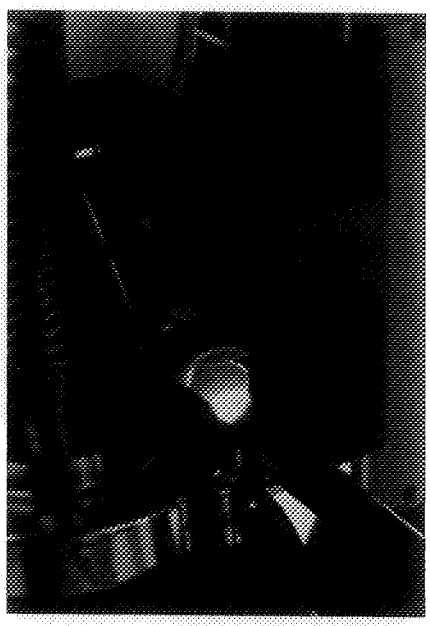

Figure 1: Acrylic glass carriers mounted on the sample changer wheel in the vacuum chamber of the FLUO beamline and the detector mounted in 90° to the plane of the sample carrier.

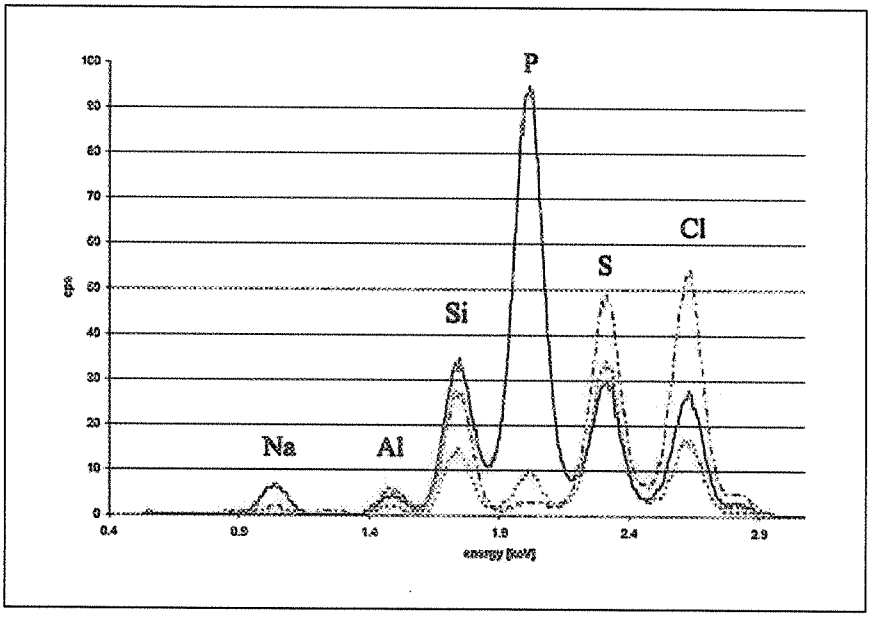

Figure 2: Spectra from three aerosols: 15 – 30nm dotted (green) line, 250 – 500nm solid (blue) line and 1 – 2µm alternating dots-bar (red) line.

Conclusions

The results show that SR-TXRF optimized for the determination of low Z elements at the ANKA FLUO beamline is a powerful tool to determine P in atmospheric aerosols. Due to the low beam intensities during the last hours of an ANKA run it became problematic to detect those low P amounts present in the aerosols. As this can't be optimized further improvements should be done to prevent absorption of the beam coming from the storage ring.

Acknowledgements

The authors would like to thank the Max Plank Institute of Meteorology for the allowance to use its impactor and Rolf Simon from the FLUO beamline for his help adjusting the set up. This work was supported by the ISS Karlsruhe and the Austrian National Science Foundation FWF P18299.

References

[1] M. Andrea and P. Crutzen, Science (1997), 276, 1052-1058
[2] L. Spokes, T Jickells, B. Lim, Geochim. Cosmochim. Acta (1994), 58, 3281 – 3287,
[3] R. Swap, M. Garstang, S. Greco, R. Talbot, P Kllberg,Tellus (1994), 44B, 133-149 iv P. Carbo, M. D. Krom, W. B. Homoky, L. G. Benning, B. Herut, Deep Sea Research II, (2005) 52, 3041 – 1053
[4] W. Werner, Z. Umweltchem. Ökotox. (1999), 11(6), 343 – 351
[5] F. Andrade, C. Orsini, W. Maenhaut, Atmos. Environ. (1994), 28, 2307.2315