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Poster Session II. Particle characterisation and monitoring

METHODOLOGY FOR LIGHT ELEMENT ANALYSIS OF INDIVIDUAL AEROSOL PARTICLES USING THIN-WINDOW EPMA

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INTRODUCTION

The determination of the concentration of light elements such as carbon, nitrogen and oxygen in individual atmospheric aerosol particles is of interest in studying environmental pollution. It has recently been recognized that a significant fraction of the enhanced supply of nutrients, which is nowadays causing eutrophication problems in the Southern Bight of the North Sea, may be related to air pollution (e.g. nitrogen oxides, from traffic pollution). These nutrients consist mainly of light elements. Especially nitrogen-containing ions, like ammonium and nitrate, play herein an important role. Due to the absorption of the characteristic X-rays of low-Z elements ($Z < 11$) in conventional EPMA by the Be-window in the EDS detector, these important elements (C, N, O) can not be measured. This problem can be overcome by the use of a modified EPMA-technique, which employs either a windowless or a thin-window EDX detector. As will be demonstrated, using this technique allows to quantitatively determine the concentration of low-Z elements and might give us more information on the molecular composition in individual particles. As already stated, the determination of low-Z elements in individual environmental particles improves the applicability of single particle analysis in environmental problems, like e.g. eutrophication. Furthermore, the diversity and the complicated heterogeneity in atmospheric particles can be investigated in detail using this modified EPMA technique

METHODS

A semi-quantitative analytical method, based on EPMA using an ultra-thin window EDX detector was developed. The X-rays, generated by the electron beam in low-Z elements, are so soft that important matrix effects, mostly due to X-ray absorption, even exist within particles in the micrometer-size range. The characteristic X-rays, especially those of low-Z elements, have experienced different amounts of absorption, depending on the variation in shape and size of the different particles. Monte Carlo calculation, using a modified CASINO program (Hovington *et al.*, 1997) was applied to explain the variation of the observed X-ray intensities. This variation is caused by the variation in geometry and chemical composition of the different aerosol particles at different primary electron beam energies. It was found that the matrix and geometry effects that are important for low-energy X-rays could reliably be evaluated by Monte Carlo calculation (Ro *et al.*, 1999). Therefore, a new data evaluation method and an integrated software have been developed for quantification of individual aerosol particles by thin-window EPMA. This method is based on an iterative Monte Carlo simulation with combination of successive approximation for the elemental composition (Osán *et al.*, 2000) and is capable to determine concentrations of low-Z elements down to C in a microscopic particle. This general analytical procedure was tested rigorously by measurements of standard single particles and a good agreement between the nominal and calculated quantitative composition was found within 3–8 relative % (Szalóki *et al.*, 2000). Beam-sensitive particles such as ammonium sulphate and ammonium nitrate were analysed using a liquid nitrogen cooled sample stage.

In order to improve the analytical capabilities of the method, special attention was paid on the spectral evaluation step. The L- and M-lines of heavier elements can strongly overlap with light-element K-lines. The dependence of the K/L-intensity ratios of K, Ca, and Ti on the size and composition of the particles was studied extensively by Monte Carlo simulations and measurements of standard particles. Taking into account the L-line contributions of K, Ca or Ti in the spectral evaluation, the estimation of the C- and N-concentrations was improved significantly, especially when K, Ca or Ti were present in high concentrations.

CONCLUSIONS

This work demonstrates that the quantitative determination of chemical species in individual particles is possible using ultra-thin window EPMA, coupled with Monte Carlo based quantification. The present semi-automated method was applied to analyse marine and continental aerosol samples collected over the North Sea and at Lake Balaton, Hungary. This is demonstrated by the results, summarized in Table 1. In this table, the results of the single particle analysis of around 500 small individual particles with a submicrometer size down to 0.3 μm are given. Using these results, it is also possible to determine both the light element concentrations and speciation in single particles. By this approach it is possible to quantify the nutrient and organic deposition, important for eutrophication studies. Results obtained by the method can also contribute to studies on particle-gas interactions, e.g. the modification of sea-salt particles in the troposphere.

Type of particles	Organic + S	Organic	Nitrate + sulphate	Sea-salt	NaCl + oxides	Alumino-silicates	Silicates
Abundance (%)	32.0	25.2	23.8	9.0	4.3	1.2	0.6
Diameter (μm)	0.9	0.9	1.1	1.1	0.6	0.7	0.6
Concentration (w%)							
C	39.0	63.1	16.9	4.7	7.0	15.9	27.4
N	8.1	2.3	10.2	---	1.4	---	2.9
O	41.0	25.9	52.9	5.9	27.0	34.1	25.8
Na	0.1	0.2	0.9	39.3	31.1	0.7	---
Mg	2.7	3.4	3.7	0.2	5.1	6.8	3.3
Si	0.6	1.1	1.8	0.6	0.2	15.0	33.8
S	7.8	3.2	10.1	0.2	1.2	1.0	2.1
Cl	0.0	0.1	0.2	47.2	19.4	0.1	0.2
K	0.1	0.0	1.8	0.1	3.4	0.2	---
Ca	0.3	0.2	1.0	0.1	0.9	---	---
Ti	0.0	<0.01	0.0	0.2	0.1	---	0.2
Fe	0.2	0.0	0.3	0.3	--	26.1	3.8
Cu	0.2	0.3	0.2	1.0	3.2	---	---

Table 1. Demonstration of the capability of thin-window EPMA: Classification of North Sea aerosol particles

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