



## **Poster Session I. Aerosol chemistry**

### **UNCONVENTIONAL MICROANALYSIS FOR LOW-Z, VOLATILE AND ORGANIC AEROSOL COMPOUNDS**

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#### INTRODUCTION

In studies of atmospheric aerosols, whether of natural or anthropogenic origin, the chemical composition and size distribution of individual species is required. Characterisation of aerosol samples at the level of individual particles, with microanalytical techniques, generally permits to obtain more unambiguous and detailed information, and, hence, it simplifies the recognition of pollutant sources and their processes. Electron probe x-ray microanalysis (EPMA) is capable of providing detailed information about the constitution and the size distribution of aerosol particles. This method has also some limitations. For example, conventional energy-dispersive EPMA is unable to detect elements with low atomic numbers and encounters problems with the analysis of volatile and organic compounds. On the other hand, the information about these compounds in particles is necessary to have a global view in atmospheric chemistry and processes.

#### METHODS

In biogenic aerosols, a large content of organic compounds has been encountered. During conventional automated EPMA, which uses X-ray emission for the determination of the elemental composition, these organic components can not be observed. Therefore, during automated analysis, we can only detect biogenic particles when they are either associated with inorganic components or if they are giving a high enough signal in backscattered electron images (BSE-images). Moreover, even in this case, it remains difficult to assign the right particle type and interpret the particle data, due to the inability of measuring the organic content of biogenic particles (only elements with an atomic number  $Z > 11$  can be measured, i.e. no carbon or oxygen). To solve these problems, the organic particles can be impregnated by heavy metal reagents and increasing as such the average atomic number of the particle. In our experiments RuO<sub>4</sub> was used for staining biogenic particles. Since RuO<sub>4</sub> impregnates a wide variety of organic compounds, biogenic particles exposed to RuO<sub>4</sub> –vapours give a relatively high BSE signal, well in contrast with the uniformly low BSE-image of the unstained filter substrate. Besides a more effective detection during automated analysis, another advantage is that the impregnation causes better conductivity of the particles on the polycarbonate-type filter surfaces.

Determining the concentration of light elements, such as carbon, nitrogen and oxygen, in atmospheric aerosol particles is important for the study of the chemical processes, occurring during atmospheric pollution. The knowledge of low-Z element concentrations gives us information on the speciation of nutrients and toxic heavy metals in the particles. The capability of the conventional EPMA is strongly limited to elements with an atomic number  $Z > 11$ , while the analysis of low-Z elements is hindered by the Be window in the EDX detector, which absorbs the weak characteristic X-rays of these elements. A number of well-developed and rigorously tested quantification procedures is available in EPMA [e.g. the ZAF and  $\phi(\rho z)$  methods]. This is especially useful for the analysis of bulk samples. However, these procedures are limited for light element analysis of individual atmospheric particles (considering the size, shape of the particles and matrix effect for light elements). Therefore, a new quantification method was developed with combination of Monte Carlo simulation and successive approximation.

The method was standardised and tested by measurements on single particles with a known chemical composition. The concentration approach can be performed efficiently for a large numbers of aerosol particles, using integrated software (EP-PROC). Applying this method to a series of samples gave very promising results, although there are still some limitations in case of volatile and sensitive particles. Especially particles containing sulphates, nitrates or ammonium, which are abundantly present in the atmosphere, are susceptible to this problem. A decrease of the sample temperature by cooling with liquid nitrogen can reduce the damage of the beam sensitive particles. However, this decrease in temperature did only postpone the evaporation of these particles and, hence, this cooling method is only of a limited value. Another possibility to analyse beam sensitive particles and to avoid evaporation problems is to make use of spot test methods. These spot test or thin film vapour methods are related to very simple microchemical particle transformations, but have rarely been used for the detection of individual particles. An ionic component in the aerosol particle reacts with a specific reagent. The resulting precipitate forms a reaction spot, which can be visually recorded on the electron microscope.

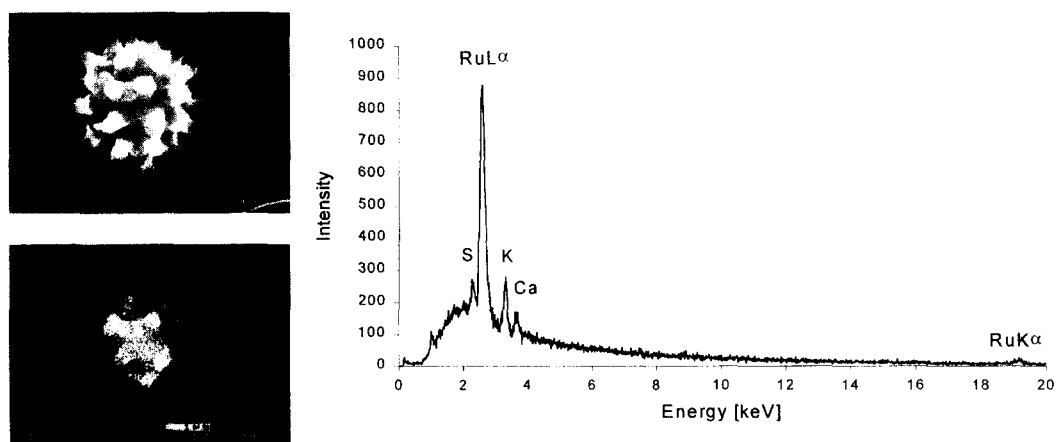


Figure 1. Secondary (A), backscattered (B) electron image and spectrum of a typical biogenic aerosol particle after impregnation with Ru (4 min. exposure time in  $\text{RuO}_4$  vapour) - sample from Amazon basin.

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