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Thin-window electron probe X-ray microanalysis of individual atmospheric particles above the North Sea

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Abstract

A recently developed, automated, standardless, quantitative analytical method, based on electron probe X-ray microanalysis using thin-window energy-dispersive X-ray detector technology, has proven to be a valuable tool for single particle analysis with the determination of the concentrations of light and heavier elements. The combined knowledge of low-Z element concentrations and air mass backward trajectories could give us information on the speciation of environmentally important chemical compounds and their reactions in the atmosphere. Individual marine aerosol particles collected over the North Sea with a nine-stage Berner cascade impactor were analysed using this new method, which resulted in a more profound characterization of the analysed aerosol samples. According to air mass backward trajectory analysis, it is inferred that the aerosol compositions of two samples (S1–S2) should be mostly under the marine influence, whereas the other two samples (S4–S5) under the continental influence. This inference is undoubtedly confirmed by the results from the single particle analysis. For the more marine samples (S1–S2), "pure" and "aged" sea salt particles are major chemical species encountered on all stage samples. Various types of particles from continental sources, such as aluminosilicates, ammonium sulfate, organic, iron oxide particles are mostly observed on all impactor stages for the more continental samples (S4–S5). This kind of detailed information on chemical compositions of aerosol samples which is provided by this analytical technique can be very much valuable for the study of atmospheric reactions of marine aerosols, which is linked to many environmental issues like e.g. nutrient deposition and marine eutrophication.

Keywords: Thin-window EPMA; Atmospheric particles; North Sea; Air mass backward trajectories

1. Introduction

The study of atmospheric aerosols has become increasingly important for marine and environmental sciences. During the last decades, many research groups have participated in numerous extensive sampling campaigns all over the world. By sampling on ships, aircrafts, and platforms and at coastal sites, scientists have obtained more and more knowledge on the details of the morphology, structure and chemical composition of atmospheric particles through a variety of analytical techniques (Baeyens et al., 1990; Gard et al., 1998;

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Murphy et al., 1998; Ottley and Harrison, 1992; Pósfai et al., 1994). The combination of the obtained knowledge with meteorological information should provide the necessary insights to understand the complex relations between the natural marine environment and the influence of anthropogenic pollution sources. However, experience has shown that a clear interpretation of the combined data is not always evident with taking into account the limitations of the applied methods for sampling and analysis.

During the last two decades, our research group has participated in numerous extensive aerosol sampling campaigns on the North Sea, either with ships (Bruynseels et al., 1988; De Bock et al., 1994) and aircrafts (Van Malderen et al., 1992; Rojas and Van Grieken, 1993; Otten et al., 1994) or at fixed sampling sites (Injuk and Van Grieken, 1995; Eyckmans et al., 2003). Although many sampling strategies have been developed, it still remains very difficult to avoid interpretation problems due to meteorological interferences. Firstly, it is quite difficult to know during the campaign if the sampled air masses are transported along representative wind directions. For example, the North Sea is surrounded by numerous sources of anthropogenic pollution on the Continent and the United Kingdom. So, if during a sampling campaign, the wind is only coming from one direction, the sampled aerosol might not be representative for the conditions over a longer period. Secondly, samplings on ships and aircrafts can also not be carried out during stormy weather, so often campaigns have to be interrupted, resulting in only a limited amount of data. Thirdly, the sampling location could also be a limitation in view of atmospheric studies. While fixed (coastal) sites are probably cheaper and easier to reach, they only give an idea about the aerosol composition at one location and more sites are required for a thorough investigation of the marine aerosols. Furthermore, the influence of continental sources near the coast could be higher. Although aircrafts can sample at different altitudes and can easier go from one place to another, they are not able or not allowed to sample very close to the sea surface. On the other hand, sampling on research vessels is limited to the marine boundary layers. However, we are convinced that a cautious, but thorough interpretation of the combined meteorological and chemical data should provide valuable knowledge on the transportation and reaction mechanisms of aerosol particles, even if the weather conditions during sampling are not ideal.

Other limitations in marine aerosol research can be found in the applied analytical methods. Several techniques have been applied to analyse and characterize the aerosols, which were collected on different types of filters or substrates with a variety of sampling devices. Besides applying bulk analytical techniques (e.g. ion chromatography or X-ray fluorescence), much effort was also put into the application of microanalytical methods in this field. Among the variety of microanalytical techniques, electron probe X-ray microanalysis (EPMA) is by far the most commonly used, which is capable of simultaneously detecting the chemical composition and the morphology of microscopic volumes. The combination with cluster analysis and/or multivariate techniques makes it a powerful tool for single particle analysis. However, for the adequate chemical characterization and even the speciation of inorganic compounds at the single particle level, the accurate determination of the concentration of light elements like carbon, nitrogen and oxygen is necessary. Thin-Window EPMA (TW-EPMA) is a relatively recent development within EPMA, which allows the detection of elements with low atomic numbers ($Z > 5$). It has been shown that quantitative elemental concentrations can be determined, based on the X-ray intensities, the size and the estimated density of the analysed particle obtained with TW-EPMA (Ro et al., 1999; Osán et al., 2000; Szalóki et al., 2000; Ro et al., 2003). Starting from these calculated elemental concentrations, more detailed information on the possible speciation of inorganic species can be obtained (Ro et al., 2000, 2001a).

Therefore, TW-EPMA could be a useful method to study atmospheric processes, since it could offer additional or new information on the various chemical reactions occurring in and on aerosol particles, which have been studied with a variety of analytical techniques for a long time now. The combined knowledge of low-Z element concentrations and air mass backward trajectories could give us information on the speciation of environmentally important chemical compounds and their reactions in the atmosphere, additional to the information on toxic heavy metal concentrations. Individual marine aerosol particles collected over the North Sea with a nine-stage Berner cascade impactor were analysed using this new method, which resulted in a more profound characterization of the analysed aerosol samples. The enhanced knowledge on light element concentrations appears to be valuable for the study of the sea-salt aging process, which is linked to many environmental issues like e.g. nutrient deposition and marine eutrophication.

2. Experimental section

2.1. Sampling

Five sets of marine aerosol samples (S1−S5) were collected over the North Sea on the research vessel R/V Belgica, between 28 September and 2 October 1998. Fig. 1 shows the exact route that was travelled by the Belgica. The sampling campaign started on 28 September 1998 in the navy harbour of Zeebrugge, a town at