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A high sensitivity elemental analysis methodology for upper tropospheric aerosol

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Abstract

In this study, a sampling and analysis tool for aerosol particles has been developed. Its purpose is to characterize upper tropospheric aerosols, where concentrations are low. Since measurements will be made from an airplane, a time resolution of one hour is desirable. These conditions require efficient sampling and analysis with low detection limits. To accomplish this, our sampler uses impaction, concentrating the aerosol deposit on a small area. The impactor has 14 parallel sampling lines which are used sequentially to achieve the time resolution. The elemental analysis is done with Particle-Induced X-ray Emission (PIXE), profiting from its high absolute sensitivity. The aerosol is expected to contain primarily sulphur (S) and emphasis is placed on this element, however the multi-elemental nature of PIXE is of course used. Several substrates have been investigated regarding minimum detection limits. Scanning Transmission Ion Microscopy (STIM) analysis has been conducted on two outdoor aerosol samples, rendering three-dimensional images and mass distribution profiles. The setup was tested at ground level with high time resolution (5 min). Results show that the detection capabilities are excellent. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

A sampling and analysis methodology for studies of the aerosol in the upper troposphere has been developed. In this part of the atmosphere, the aerosol concentration is low [1] and dominated by sulfates [2]. Thus, it is of major importance that the analysis can be done with high absolute sensitivity, primarily regarding sulphur. Given these

conditions, Particle-Induced X-ray Emission (PIXE) is an analytical technique which provides all these qualities [3,4].

Another essential is to concentrate the aerosol particles and create a spot sample. The impaction technique is well suited for this purpose [5]. Optimizing further, the PIXE beam area can be minimized so as to cover only the impactor sample and a minimum of the backing. To accomplish this it is needed to create a visual representation of the sample. Scanning Transmission Ion Microscopy (STIM) is a well-suited technique [6] for this purpose.

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This paper describes a sampling and analysis tool for upper tropospheric aerosol, combining impaction technique with PIXE. It was developed for time-resolved flight measurements (14 parallel impactors in sequence) and results of various tests of the setup are presented. Studies were made regarding (i) sample shape and mass distribution, where the impactor deposit was characterized with STIM, and (ii) MDL dependence on backing substrates, analyzed with PIXE. Also, feasibility test was carried out, where the impactor collected outdoor aerosol for 5 min in each step and the samples were analyzed with PIXE. The results show excellent detection capabilities, not least regarding sulphur.

2. Experimental setup

2.1. The aerosol sampler

A sampler was developed for airborne, time-resolved sampling in the upper troposphere. A key feature in this environment is to collect the aerosol particles on a small surface. This way the mass concentration will be high and a well collimated proton beam will give good detection capabilities. To achieve this high mass concentration, the impaction technique was chosen. The impactor, shown in Fig. 1, has been specially designed for

aircraft operation. It consists of 14+1 parallel sampling lines, where the idea is to have two lines open at any given time during the flight. One of these two lines will be open and collecting particles during the entire flight and the others will be open 1 h each (in sequence) to achieve the time resolution.

The impactor nozzles were examined in a microscope. The holes were found to be 0.62 ± 0.01 mm in diameter, and the critical volume flow-rate was measured to 3.21 ± 0.06 l/min for all the nozzles (error values = standard deviation). These results show that the individual measurements in the time series obtained from the sampler are comparable.

In Fig. 1, the impactor is seen with its lid in an open position. The circular, white impaction plates in the lower impactor houses are visible. The nozzles are inserted and fixed in the lid so that they will come into position exactly above the plate when the impactor is closed.

The aerosol flow through the impactor is achieved by a pump connected to the outlet of the impactor houses. Below each house is a magnetic valve. In operation, the aerosol will be drawn from the inlet up into the lid, through the nozzle belonging to the house whose valve is open, and down onto the impaction plate, where particles with diameter larger than 65 nm will be collected at upper tropospheric conditions. The valves are controlled by a computer program which follows the sampling protocol described above.

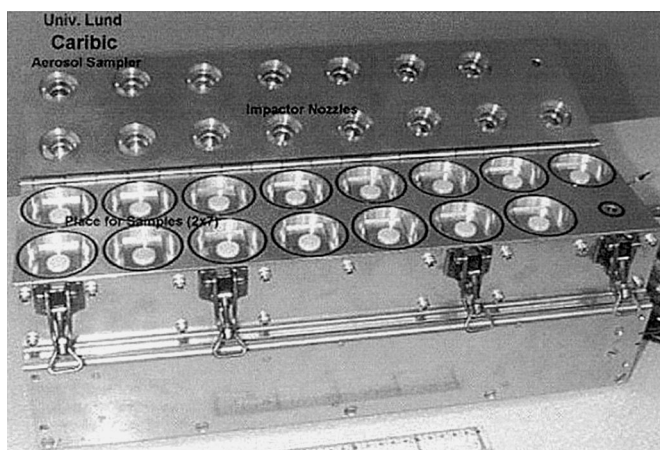


Fig. 1. The Aerosol Sampler with its lid in open position, consisting of 14+1 parallel impactors.

2.2. Elemental analysis setup

The elemental analysis was done at the 3 MV tandem accelerator (NEC 3 UDH) in Lund, in the PIXE-chamber normally used for trace-element analysis [7]. The X-rays were generated by a 2.55 MeV proton beam and detected at an angle of 135° relative to the incident beam, by an 80 mm^2 lithium-drifted silicon detector (KevexTM). The beam can be collimated in different ways allowing spot sample analysis and the setup is optimized for PIXE measurements with large solid angle (80 msr).

2.3. STIM setup

The STIM analysis was done at the Lund Nuclear Microprobe, a single-ended 3 MV accelerator (NEC 3 UH) in Lund. The analysis was performed on-axis with a 2.55 MeV proton beam, focused to about $1 \mu\text{m}^2$, hitting the sample. Since the magnitude of this energy loss in the transmitted particles depends on the sample areal density, a three-dimensional image of the sample can be achieved by scanning the proton beam in the X and Y directions.

2.4. Sample preparation

For the elemental analysis with PIXE the whole impactor sequence was used, with a time resolution of 5 min. Totally 14 samples deposited on Kimfol backing substrate were prepared.

Additionally, two samples were prepared for STIM. In order to get a heavy enough loading and thereby create a well-defined image, the sampling times were 70 and 180 min respectively.

3. Results and discussion

3.1. Minimum detection limits of spot samples

Given a spot sample it is of interest to know the relationship between the beam radius and the minimum detection limit (MDL) for some element of interest. Two scenarios can be distinguished.

(I) The wanted element is not present in the backing substrate. The number of pulses N_p in the

characteristic peak from the aerosol deposit can be expressed as

$$N_p = J \cdot A_s \cdot t \cdot \xi_s \cdot i_s, \quad (1)$$

where J is the beam current density, A_s is the sample spot area, t is the irradiation time, ξ_s is the areal density of element of interest in the sample spot and i_s is the intensity per unit charge and unit areal density of the wanted element. Furthermore it is assumed that the background generated in the sample spot is small compared to that of the backing. The number of pulses N_{MDL} is then given by

$$N_{MDL} = \lambda_\alpha \sqrt{N_{bg}}, \quad (2)$$

where λ_α is the factor of the percentile α prescribed for detection (commonly set to 0.001, corresponding to $\lambda_\alpha = 3.09$ for the normal distribution). The number of background pulses under the peak (N_{bg}) is given by

$$N_{bg} = J \cdot A_b \cdot t \cdot I_f, \quad (3)$$

where A_b is the beam area and I_f is the background intensity under the characteristic peak per unit charge of the backing used. The minimum detection limit in this case is proportional to the beam diameter since the number of X-rays (N_p) does not change when the beam diameter is larger than the sample spot for a given current density and irradiation time.

(II) The element of interest is present in the backing material. The assumption now is that the blank is dominant over the continuous background. N_{bl} , the number of pulses for the wanted element in the blank is given by

$$N_{bl} = J \cdot A_b \cdot t \cdot \xi_{bl} \cdot i_s, \quad (4)$$

where ξ_{bl} is the areal density of the element in the blank. The expression for the MDL will be

$$N_{MDL} = N_{bl}(1 + \lambda_\alpha \cdot \sigma_{rel}), \quad (5)$$

where σ_{rel} is the relative standard deviation of the blank for the element of interest. In this case the detection limit depends quadratically on the beam diameter as long as it is larger than the sample spot.

In summary, depending on the nature of the backing disturbance, the MDL decreases linearly

to quadratically with decreased beam diameter. Thus, known the area of the sample, the beam size can be adjusted to lower the MDL.

3.2. The size of the aerosol deposit

In order to optimize the beam area it was important to image the sample deposits. This was realized with STIM and two images were made. Fig. 2 shows a three-dimensional representation of the most heavily loaded sample regarding areal density (ξ_σ), with arrows giving the scale in length and width.

The mass distributions of the samples were examined. Fig. 3 shows the relative cumulative masses, going outward from the mass center. The contribution from the backing has been subtracted. The two samples show very similar behaviour, reaching 100% of the mass after about 0.9 mm.

It was concluded that for this setup, the sample diameter is about 1.8 mm (2.6 nozzle diameters). As the combined uncertainty in positioning the sample and the beam was estimated to be 0.5 mm, the whole sample spot will be analyzed using a beam diameter larger than 2.8 mm.

3.3. MDL related to backing

Five substrates were analyzed with PIXE. The analysis was of course multi-elemental but attention was primarily concentrated on the detection of sulphur (S) and MDLs were primarily calculated for this element.

The MDL depends upon backing thickness. In Table 1 an overview of the five substrates is given, along with the areal density (ξ), the number of analyzed samples for each substrate and a calculation of “intrinsic” MDL for sulphur, referring to a non-contaminated case, where there would be no sulphur involved in the blank. The PIXE spectra of the substrates have been plotted in Fig. 4, where it can be seen that the AP1 [8] is definitely the substrate with lowest background signal, while Nuclepore and Millipore would give poor MDL values in comparison.

Two of the AP1 samples were contaminated with respect to silicon and one of these also with respect to chlorine and potassium. However, sulphur was present in all investigated filters and foils, implying that the MDL of sulphur depends quadratically on the beam diameter.

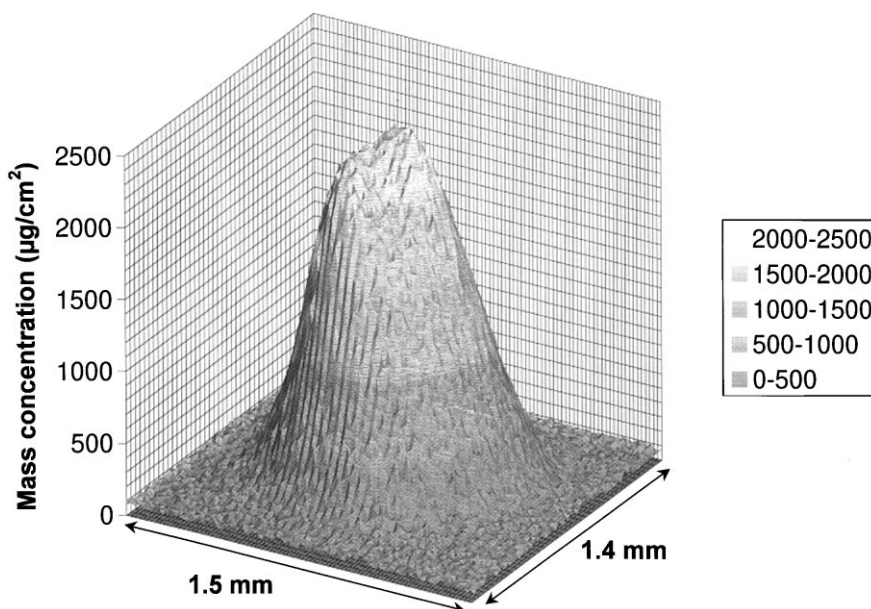


Fig. 2. Areal density image of the aerosol deposit obtained with STIM. The sampling time was 180 min.

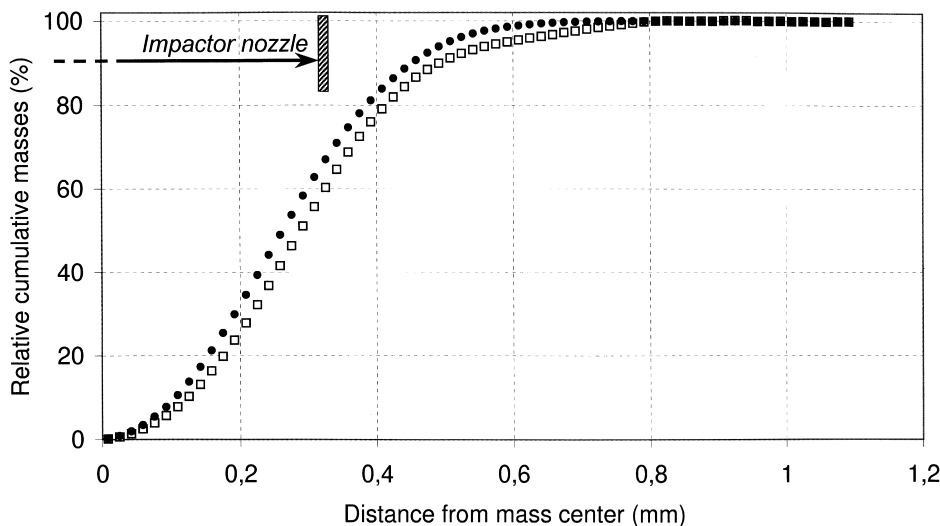


Fig. 3. Relative cumulative masses from the mass center for the two aerosol deposits. The white squares correspond to the 70 min sample and the black dots correspond to the 3 h sample.

Assuming the beam diameter to be 3 mm, the actual MDLs of sulphur for API and Kimfol were found to be 1 and 6 ng/m³ respectively, for upper troposphere measurements with a time resolution of one hour, a current density of 2 nA/mm² and an irradiation time of 10 min. An estimation for several metals gives an MDL of a few pg/m³, under the same conditions as in the sulphur case. The sulphur MDL is low in relation to previously reported aerosol concentrations in the upper troposphere [1].

3.4. Feasibility study

In order to demonstrate the capabilities of the sampling/analysis methodology, atmospheric

aerosol samples were collected at ground level (in Lund) with high time resolution. 14 samples were collected with 5 min time resolution, using Kimfol as the sampling substrate.

The samples were analyzed with PIXE to obtain element concentrations. Results show that the setup has very good detection capabilities. Four elements (S, K, Ni and Zn) were always found above the detection limit, see Fig. 5. It should be noted that the backing used in this study was Kimfol and not API, which means that the MDL can be lowered even more.

This short study of the atmospheric aerosol in Lund demonstrates the unique detection capabilities of this methodology based on sampling with an impaction technique and analysis with PIXE.

Table 1

Overview of the five backing substrates analyzed, sorted by magnitude of MDL for sulphur

Substrate	Composition	ξ ($\mu\text{g}/\text{cm}^2$)	Number of samples	MDL of S (ng/m ³)
Millipore	Polycarbonate	1000	2	0.8
Nuclepore	Polycarbonate	1000	2	0.8
Kimfol	Polycarbonate	200	3	0.4
Polystyrene	Polystyrene	70	2	0.2
API	Polyimide	25	5	0.1

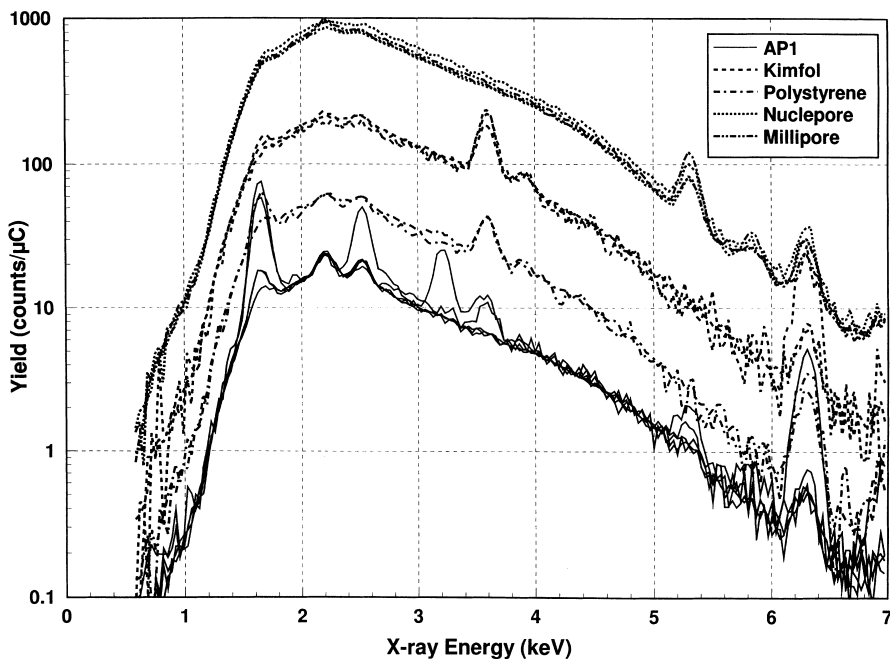


Fig. 4. PIXE spectra for the different backing materials analyzed. Going from the bottom to the top, the substrates are: AP1, Polystyrene, Kimfol and Nuclepore together with Millipore.

4. Conclusions

A methodology for time-resolved characterization of upper tropospheric aerosol based on sampling by impaction technique and elemental

analysis with PIXE has been developed. The aerosol sampler developed consists of 14 parallel impactors for time-resolved measurements. The sampling channels were shown to be able to produce time series of the elemental composition.

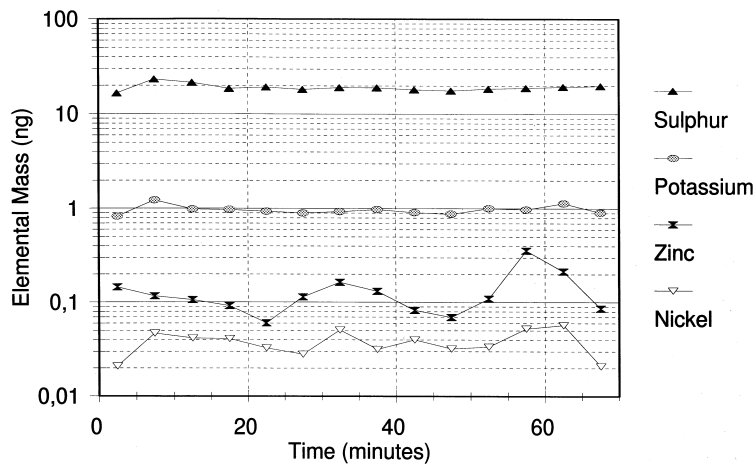


Fig. 5. Elemental mass in the aerosol deposit as a function of time for the four detected elements.

An evaluation of the minimum detection limits of spot samples showed a linear to quadratic dependency on the beam diameter, depending on whether or not the element of interest is absent in the backing. The shape of the aerosol deposit was determined with STIM analysis. It was found that the deposit extended 1.8 mm in diameter for the nozzle diameter used (0.62 mm), supplying the necessary information concerning the beam size to be used.

The analytical setup was optimized for low-loaded samples. Several sampling substrates were investigated with respect to MDL. The MDL of sulphur was found to be 1 ng/m^3 and for several metals the MDL is estimated to a few pg/m^3 for one hour sampling.

A feasibility study on the ground with high time resolution in the sampling (5 min per sample) demonstrated the eminent detection capabilities of the sampling and analysis methodology developed.

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