

Analysis of C, N and O in aerosol collected on an organic backing using internal blank measurements and variable beam size

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Abstract

A method with low MDL (minimum detection limit) was developed for analysis of carbon (C), nitrogen (N) and oxygen (O) in aerosol samples collected on an organic backing. An accelerator-produced beam of protons interacting with the sample and the detection of elastically scattered protons (PESA; particle elastic scattering analysis) and emitted X-rays (PIXE; particle-induced X-ray emission) were the basic components of the setup. The method is based on measurement of internal blank concentrations, i.e. measurement of the blank concentration outside the aerosol deposit in each sample, and the use of two sizes of the beam in order to improve the MDL of the analysis. Large beam size covering the entire aerosol deposit was used to obtain quantitative analysis with PIXE. Small beam was used to obtain relative elemental concentrations with PESA and PIXE, which were transformed to absolute values by the aid of large-beam analysis. The small-size-beam served two purposes: to make internal blank measurements feasible and to improve the signal ratio of aerosol-deposit to backing. Compared with the traditional way of analysis, using a beam that is larger than the deposit and specially prepared blank samples, the new method reduced the MDL of C, N and O by a factor of 130, 70 and 90, respectively. The new method was applied to aerosol samples collected in the upper troposphere and the lowermost stratosphere from the CARIBIC platform. As far as the authors know, these measurements are the first quantitative determinations of C, N and O in the aerosol of this part of the atmosphere. The results show that these elements together with sulfur are major components of the aerosol.

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1. Introduction

The interaction of aerosols with climate has been the subject of much discussion lately. Not only the aerosol in the boundary layer but also aerosol along the whole vertical profile of the atmosphere influences the climate. It may have direct effect on climate by scattering light or indirect effect by changing the cloud properties [1–4]. However, there is a great need to broaden the scope of our knowledge of chemical composition of the aerosol in the upper tropo-

sphere (UT) and the lowermost stratosphere (LS) in order to identify the sources and processes forming the aerosol.

A large number of measurements of the atmospheric aerosol chemical composition have been undertaken close to the ground. Data on chemical characteristics of the UT/LS aerosol are scarce. The CARIBIC project (Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrument Container) [5], is the first one doing regular chemical characterization of aerosol in the UT and the LS. Sampling and in situ measurements are undertaken from an Airbus 340-600 in regular, intercontinental traffic. In that project, we have used PIXE (particle-induced X-ray emission) to obtain elemental concentrations [6–8]. PIXE normally is limited to analysis of elements that have

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atomic numbers larger than about 12. Campaign-wise measurements of UT/LS aerosol for inorganic ions using IC (ion chromatography) have been reported [9]. Murphy et al. [10] using single particle analysis based on laser mass spectrometry found that aerosol in the upper troposphere (UT) and the lowermost stratosphere (LT) contains carbonaceous material. However, laser mass spectrometry is not a quantitative method. There is a need of an analytical method that provides quantitative analytical results on the concentration of the light elements, and in particular on the carbonaceous component.

Various ion beam analysis (IBA) methods have been used in combination with PIXE to detect light elements in aerosol on different kind of substrates. Cahill et al. [11] combined forward alpha scattering techniques with PIXE to analyze aerosol deposit on Teflon-filter. The carbon-to-fluorine ratio of the filter was used to estimate the needed subtraction of blank carbon in the collected aerosol samples. With this method, the minimum detection limit (MDL) for carbon was determined to be $2.0 \mu\text{g}/\text{cm}^2$. In another study, PESA (particle elastic scattering analysis) as the complementary technique to PIXE was used to analyze light elements in aerosol deposited on aluminum substrate [12]. The detection limit of carbon was $10 \text{ ng}/\text{cm}^2$ when using a 3.58 MeV proton beam. Nuclear reaction analysis (NRA) and PESA were used to investigate the potential of analyzing light elements on particulate matter deposited on silver filter [13]. With the NRA method, the estimated MDL of carbon was $2 \mu\text{g}/\text{cm}^2$.

The aerosol substrate used in the CARIBIC project is a $15 \mu\text{g}/\text{cm}^2$ polyimide film (API™). This thin film has excellent mechanical properties, thus allowing aerosol collection in small spots on the substrate by impaction technique. These properties and low impurity levels make API an excellent substrate for PIXE analysis. When combining PIXE with methods for analysis of light elements on API, difficulties arise from the fact that the film contains large amounts of the light elements of interest (C, N and O).

In this study, we investigated the potential of analyzing atmospheric aerosol deposited on a substrate that contains the elements of interest as major components, using PESA combined with PIXE. In order to circumvent the problem of the high blank levels of the substrate, internal blanks, i.e. irradiation outside the aerosol deposits, and a small-size beam to improve the aerosol-to-backing signal ratio were used. An investigation was carried out based on 22 API aerosol samples collected from the CARIBIC platform on flights between Frankfurt, Germany and Santiago de Chile. The method proved to have excellent MDL, and to be superior in comparison with the traditional method of analysing and to retrieve blank estimates.

2. Materials and methods

Aerosol samples were collected from the CARIBIC platform using an aerosol sampler [14] based on impaction technique. The aerosol particles were sampled with a

four-jet arrangement and formed four spots of aerosol deposit on the API film, which was mounted on a $40 \times 28 \text{ mm}$ Plexiglass frame over a 16 mm diameter hole. The spots of approximately 0.5 mm diameter formed a square pattern, and the minimum distance between two spots was 1.3 mm.

The investigation was carried out in a high vacuum chamber that is equipped with facilities for simultaneous PIXE and PESA analysis. The single ended 3 MV accelerator (NEC 3 UH) in Lund was used in the experiment. Two kinds of experiments were carried out, one where PIXE was applied with the beam diameter 5.5 mm and the other where PIXE and PESA were used simultaneously with the beam collimated to 1 mm diameter. In the former analysis, the entire aerosol deposit on the film was irradiated with the beam current 150 nA and the collected charge was $120 \mu\text{C}$, thus yielding quantitative determination of the elemental masses of the aerosol deposit. The second method of analysis was carried out with the beam current 15 nA and the collected charge was $3.2 \mu\text{C}$. This analysis was carried out with the beam positioned on one aerosol spot of the sample, and, in addition, in two positions on the API film 3 mm away from the closest aerosol spot. The latter two irradiations form the basis for estimating individual blank masses of the films. In order to keep conditions in the backing film constant during the analysis of all three spots, the thin film was facing the beam. That way, effects of energy loss in the aerosol deposit did not affect the signal from the backing film at the aerosol spot. The analyses carried out with 1 mm beam produce relative compositions. Quantification is obtained by relating to the quantitative analysis carried out with 5.5 mm beam by the use of an element (sulfur) that has been detected in both kinds of analyses.

Only one out of the four aerosol spots are analyzed with the 1 mm beam, because the aerosol sampler is protected by a cyclone placed upstream of the sampler that removes particles larger than $2 \mu\text{m}$ equivalent aerodynamic diameter [14]. To reach the detection limit (to be presented below), several tens of particles of the $2 \mu\text{m}$ cut-off size in each deposit spot are needed, and, at a size typical of the maximum of the particle mass size distribution, $0.4 \mu\text{m}$ equivalent aerodynamic diameter, several thousands of particles are needed. Each of the four spots consists of large number of particles collected from the same air mass. A single aerosol deposit spot can thus be expected to be representative of the relative composition of the entire deposit.

PESA measurements were done using an annular, partially depleted surface-barrier detector manufactured by Ortec, with a thickness of $300 \mu\text{m}$, the nominal area of 300 mm^2 and with a 14 mm diameter hole. It was positioned at a scattering angle of 156° and the target to detector distance was 20 mm. This positioning of the surface barrier detector close to the target is of premium importance, because this method requires a large solid angle in order to obtain the needed pulse statistics in a reasonable time. PIXE measurements were done using a 100 mm^2

HPGe X-ray detector model GUL0105 manufactured by Canberra. It was placed at a distance of 32 mm from the target and X-rays were detected at an angle of 45° to the sample normal. No absorber was used during the PIXE measurements in the low-current measurements undertaken with a small beam, whereas a Hostaphan™ film of 25 μm thickness was used in the large-beam-area measurements. The angle of the beam to the sample normal was 23° in both experiments. A current digitizer (Ortec 439) was used to measure the beam charge.

The experimental setup was calibrated for a beam of 2.55 MeV protons. PIXE was calibrated using a large number of Micro-Matter™ standards and modeling of analytical parameters [15]. The inaccuracy is estimated to be within 10%. The PESA setup was calibrated by irradiating five Micro-Matter™ standards of heavy elements (molybdenum, silver, tin, barium and gold). The results were related to the Rutherford cross-section [16] and the solid angle was computed for each of the five elements. This quantity agreed within 6% among the elements, in line with the inaccuracy of the standards of $\pm 5\%$. The average of the five irradiations was taken as the solid angle (0.33 sr) of the PESA setup. The analytical sensitivities of carbon, nitrogen and oxygen were then obtained from the cross-section models of Gurbich [17–19].

3. Results and discussion

The common way to determine minimum detection limits is to prepare special blank samples that are analyzed for the components to be analyzed in the actual samples. Since the backing in this study (API) is composed of the elements of interest, carbon, nitrogen and oxygen, difficulties to separate the signal from the aerosol deposit from that of the backing can be expected. Nevertheless, 22 blank spots on API films were analyzed with 1 mm collimator for carbon (C), nitrogen (N) and oxygen (O). The relative standard deviation in areal density varied between 0.02 and 0.026 for the three elements. Based on this variability, the detection limits at the 99% probability level were estimated to 500, 70 and 150 ng/cm^2 for C, N and O. These detection

limits are too high for detection of these elements in aerosol deposits on the backing. Improved methodology is needed to reach the goal of C, N and O detection in the samples.

3.1. Results of the three-spot analyses

To improve the probability of detection, a method was attempted based on improved aerosol-to-backing signal ratio and blank measurements on each sample. The latter part of the method improves the estimate of the backing thickness. The present samples were taken by impaction technique, which results in small spots of aerosol deposit on the backings. That way it is simple to find unexposed parts of the backing that are available for blank measurements. Just measuring the blank in a single spot on each sample will not reveal the variability in backing thickness over a sample. At least two blank spots need to be irradiated on each sample to obtain a measure of the internal variability in backing thickness.

Each of the samples was irradiated in three spots. Two of these spots are placed outside the aerosol deposit, whereas the third analysis spot is centered over an aerosol deposit spot. Fig. 1 shows the results of sulfur measurements on the aerosol samples by PIXE using the three-spot technique. The samples were taken at 10 km altitude in the CARIBIC project. Each column coinciding with a gridline corresponds to a measurement of an aerosol spot, whereas the two following columns show the result of the blank spots of that sample. The blank spot measurements were taken 3 mm away from the aerosol spots, at either side of the deposit. The horizontal line in Fig. 1 shows the blank concentration of sulfur from previous PIXE analyses of a large number of unexposed API films. It can be seen that the measurements in the blank spots shows similar concentrations as unexposed films, and that the concentrations in the aerosol spots mostly is much higher than the blank concentration. From these measurements, it can be concluded that the blank spot measurements were taken with no, or very little influence from the aerosol deposited 3 mm away.

The pair of blank spot measurements of C, N and O was internally compared with one another by plotting the result

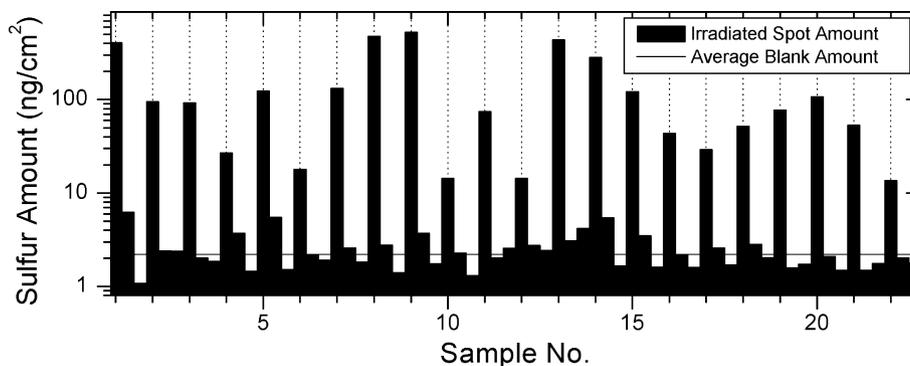


Fig. 1. Sulfur amounts in 22 aerosol samples deposited onto API films. Columns at a grid line show the results from aerosol deposit spots, and the two columns closest to the right are blank spot analyses from the same sample. The horizontal line shows the average sulfur amount from analyses of a large number of blank API films.

of blank spot 1 of a sample against that of blank spot 2 in Fig. 2. The error bars show the standard deviation originating in pulse statistics. It is clear that the two blank spot measurements taken on the same backing correlate, implying that the internal thickness variability of an API film is much smaller than the variation between different films. Hence, making blank measurements on the film containing the deposited aerosol can be expected to reduce substantially the detection limits compared with the “traditional” detection limits that were described above.

Due to the strong signal from the backing, the differences between the aerosol and the blank spots for C, N

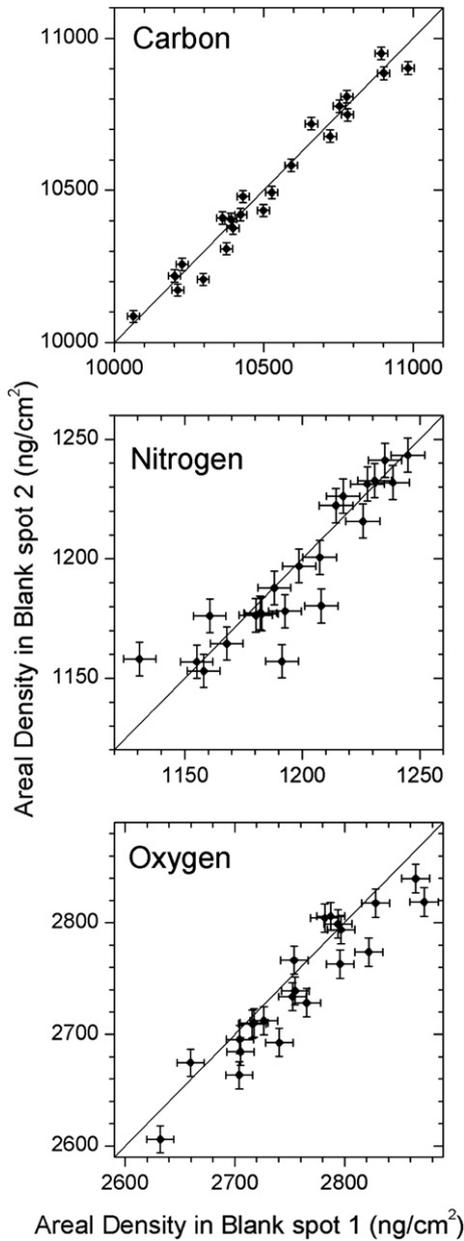


Fig. 2. Carbon, nitrogen and oxygen analysis in one blank spot plotted against that of the second blank spot from the same sample. The error bars show the standard deviation of the measurements due to pulse statistics.

and O from the PESA analyses are not as distinct as that of sulfur obtained with PIXE. Fig. 3 shows the spectra from two CARIBIC aerosol samples, one lightly-loaded and one with a dense aerosol deposit. The original spectra (left Y-axis) from the aerosol spot and the blank spots can hardly be distinguished in the scale used in the chart. Also displayed is the difference between the spectrum of the aerosol spot and the average of the two blank spots (right Y-axis). The sample with a dense aerosol deposit (Fig. 3(a)) shows a clear detection of all three elements, C, N and O in the difference spectrum, and, at higher energy, the peak from S can be seen. The lightly-loaded sample in Fig. 3(b) shows the scatter in the individual spectrum channels of the difference spectrum due to poor pulse statistics resulting from the difference of two large, almost equal numbers. A method to determine the minimum detection limit is needed to handle the special situation of this method, where deposits are analyzed for elements that are major components of the backing.

3.2. Minimum detection limits in areal density

In order to estimate the minimum detection limit, it was assumed that the areal density of C, N and O from the

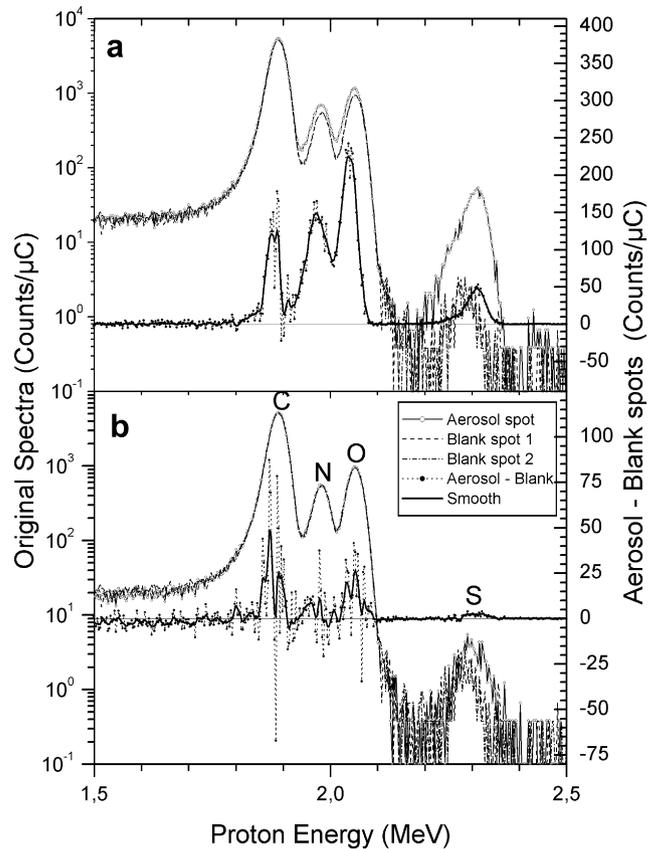


Fig. 3. PESA spectra from a three-spot analysis (aerosol deposit and two blank spots) of an aerosol sample (left Y-axis) and the difference spectrum between the aerosol deposit and the average of the two blank spots (right Y-axis). The bold, full line is the result of seven-point, weighed smoothing of the difference spectrum. (a) Highly loaded aerosol sample and (b) lightly loaded sample.

backing could be described as a Gaussian distribution, N (mean, standard deviation), over its area with the relative standard deviation σ_r . The average of the two blank spots is used to estimate the areal density (ξ) of each element C, N and O originating in the sample backing:

$$\bar{\xi} \in N(\bar{\xi}, \sigma_r \bar{\xi} / \sqrt{2}). \quad (1)$$

The variability in elemental mass of the backing was obtained from the difference between the two blank spots of each sample, i.e.

$$\Delta\xi = \xi_1 - \xi_2 \in N(\Delta\xi, \sqrt{2}\sigma_r \bar{\xi}). \quad (2)$$

For each sample, a measure of the variability was obtained by forming the ratio $\Delta\xi/\bar{\xi}$. A Gaussian approximation was used to estimate its variability:

$$\frac{\Delta\xi}{\bar{\xi}} \in N\left(\frac{\Delta\xi}{\bar{\xi}}, \sqrt{2\sigma_r^2 + \frac{\sigma_r^2}{2}\left(\frac{\Delta\xi}{\bar{\xi}}\right)^2}\right) \approx N\left(\frac{\Delta\xi}{\bar{\xi}}, \sqrt{2}\sigma_r\right). \quad (3)$$

The standard deviation of this ratio was estimated from the collected data. This estimated standard deviation (s) was related to σ_r by Eq. (3), i.e. $s = \sqrt{2}\sigma_r$. Then the standard deviation of the average (Eq. (1)) of the two blank analyses of each sample was obtained as

$$\bar{\xi} \in N(\bar{\xi}, \sigma_r \bar{\xi} / \sqrt{2}) = N(\bar{\xi}, s \bar{\xi} / 2). \quad (4)$$

This expression was then used to estimate the minimum detection limit (MDL) according to

$$\text{MDL} = \lambda_\alpha s \bar{\xi} / 2, \quad (5)$$

where λ_α is the factor of the percentile α prescribed for detection, s the standard deviation based on the entire data set, whereas $\bar{\xi}$ is the average of blank spot analyses of a sample for the elements C, N and O.

The statistical methodology was applied to the CARIBIC aerosol samples. The standard deviation s of $\Delta\xi/\bar{\xi}$ was found to be 0.0022, 0.0054 and 0.004 for C, N and O and the corresponding minimum detection limits on the 99% significance level were 26, 8 and 13 ng/cm². By the analysis of the areal density of the backing of each aerosol sample in two spots and by the method according to Eqs. (1)–(5), the MDLs of C, N and O in terms of areal density were reduced by a factor of 10–18 compared with the traditional method, with the strongest reduction for C.

3.3. Relative to absolute concentration conversion

The 1 mm beam measurements do not cover the entire aerosol deposit, implying that only relative elemental concentrations can be obtained. For atmospheric aerosol studies, as well as in many other IBA application fields, quantitative determination of concentration is desirable. To that end, the small-diameter-beam measurements were complemented with a second irradiation, where the entire aerosol deposit was analyzed with PIXE, in order to obtain a quantitative measurement. The absolute concentration of

an element measured with the small beam was then obtained by:

$$C_i = \frac{C_{\text{ref}}}{\xi_{\text{ref}}} \xi_i, \quad (6)$$

where C_i and ξ_i are the absolute and relative concentrations of element i , and ref refers to these concentrations of a reference element. The reference element must thus be detected in both kinds of analyses. For the samples studied here, UT/LS aerosol samples taken during CARIBIC flights, sulfur was the dominant element out of the elements detected with PIXE, thus making this element the most suitable for the conversion to absolute concentration. The absolute quantification in this two-step analysis is independent on the degree to which the small beam is centered over the aerosol deposit, because only the relative composition is determined in that step.

3.4. Minimum detection limits in atmospheric concentration

In practice, a good positioning of the small beam over the deposit spot is required, in order to obtain best possible chance of detection. With the 1 mm beam perfectly centered over an aerosol deposit spot, the aerosol-to-backing signal ratio becomes, compared with irradiation of all four spots with the 5.5 mm beam, a factor of $(5.5/1)^2/4 = 7.6$ higher with the small beam. This improved ratio decreases the detectable aerosol elemental mass in the sample by the same factor. Thus, besides the reduction of the MDL expressed in areal density due to internal blank measurements, the MDL in terms of mass, and, hence in terms of atmospheric concentration, becomes further reduced. The resulting reduction in MDL with respect to atmospheric concentration is obtained as the product of the reductions from the two effects. Assuming perfect centering of the 1 mm beam over the deposited spot, the MDL in atmospheric concentration is reduced by a factor of 130, 70 and 90 for C, N and O compared with the use of large beam (5.5 mm diameter) covering the entire aerosol deposit and specially prepared blank samples. The use of a small size beam thus strongly contributes to the technique of internal blank measurements to achieve low detection limits.

3.5. Application to atmospheric aerosol samples

The method was applied to 22 CARIBIC aerosol samples from the upper troposphere and the lowermost stratosphere. Fig. 4 shows the analytical results for C, N and O against that of S. The concentrations are expressed as nmole/m³ STP in order to facilitate interpretation of stoichiometric relations. The O and N concentrations in most cases are present in stoichiometric relations relative to S close to 4:1 and 2:1, respectively, thus indicating ammonium sulfate. The concentration of C does not show any clear co-variation with S. The results show that the composition of the UT/LS aerosol varies substantially, from

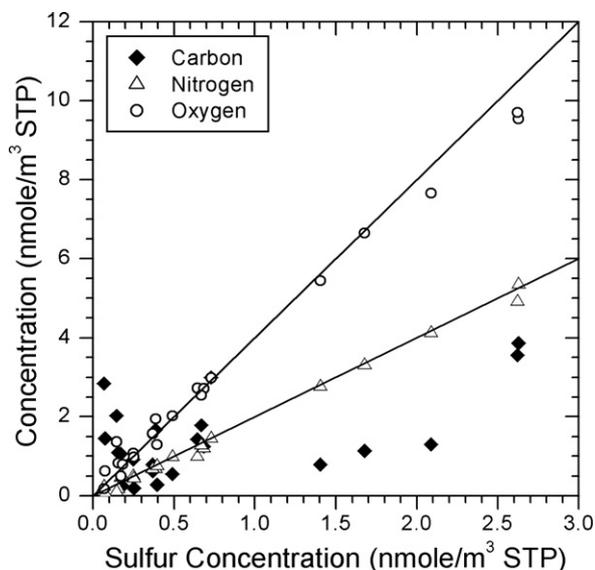


Fig. 4. Atmospheric concentrations of carbon, nitrogen and oxygen as a function the sulfur concentration, expressed as nmole/m³ STP (standard temperature and pressure). Concentrations below the MDL (see Table 1 for frequencies) are represented by MDL/2.

being mainly sulfurous to being mainly carbonaceous. Overview of the analytical results and detection properties of the analytical setup for C, N, O and S are presented in Table 1, showing the relative composition measurements expressed as areal densities (ng/cm²) as well as the absolute atmospheric concentrations normalized to standard temperature and pressure (ng/m³ STP). It is clear that all three elements (C, N and O) obtained with PESA are major constituents of the UT/LS aerosol. From the known results of previous PIXE analyses, the latter two elements could be expected to constitute a large fraction of the aerosol, because sulfur is usually found in the form of sulfate with various amounts of ammonium in the atmosphere. The results presented here is to our knowledge the first quantitative analysis of the carbonaceous component of UT/LS aerosol. This study shows that besides the sulfate component, the UT/LS aerosol contains a major fraction of carbonaceous aerosol.

Table 1
Concentrations and minimum detection limits

	C	N	O	S
No samples	22	22	22	22
Detection frequency (%)	86	91	100	100
Average amount (ng/cm ²)	95	120	280	145
MDL (ng/cm ²)	26	8	13	1.4
Average concentration (ng/m ³)	17	20	47	24
Median concentration (ng/m ³)	14	10	28	12
Quartiles (ng/m ³)	9–21	6.4–18	16–44	6.3–22
MDL (perfectly centred ^a) (ng/m ³)	3.3	1.0	1.6	(0.2 ^b)

^a MDL with the 1 mm beam perfectly centered over the aerosol deposit.

^b Not applicable to the method, because the 1.5 ng/m³ STP detection limit with 5.5 mm collimator for quantification of atmospheric concentrations needs to be exceeded.

4. Conclusions

A method based on PESA (particle elastic scattering analysis) for detection of elements carbon (C), nitrogen (N) and oxygen (O) was developed for use together with PIXE (particle-induced X-ray emission) on aerosol samples deposited on a thin organic film. The traditional method of blank concentration determination, based on the preparation of special blank samples, was found to yield too high PESA MDL (minimum detection limit). The method involves irradiation with two beam sizes and internal blank measurements, i.e. measurement of the film elemental concentrations outside the aerosol deposit. Quantitative elemental analysis is obtained by using PIXE and a large beam covering the entire aerosol deposit. Relative elemental concentrations are obtained by simultaneous use of PIXE and PESA when irradiating a sample with a small beam in three places, two blank points of the film and one centered over an aerosol deposit spot. The blank spots were used to obtain an internal estimate of the blank concentrations of C, N and O. Absolute amounts were obtained by relating the relative compositions to the absolute measurement with PIXE, using an element that was detected both with the large and the small beam, in this case sulfur (S).

The small beam area provided strongly improved deposit-to-backing signal ratio, and the internal blank measurement strongly improved the estimation of the blank concentration compared with the traditional method. Altogether, the new method improved the detection limits of C, N and O by a factor of 130, 70 and 90, respectively. The resulting detection limits are 3, 1 and 2 ng/m³ normalized to STP (standard temperature and pressure) for C, N and O, which are complemented with PIXE analysis having detection limits in the same samples for e.g. S and Fe (iron) of 2 and 0.1 ng/m³ STP.

This new method was applied to aerosol samples collected in the upper troposphere (UT) and the lowermost stratosphere (LS) in the CARIBIC project. O and N were in most samples found to follow the concentration of S by ratios 4:1 and 2:1, thus indicating the presence of ammonium sulfate in the samples. This was to our knowledge the first quantitative determination of C, N and O concentrations in the UT/LS aerosol. The results presented here show that the UT/LS aerosol besides the sulfurous fraction contains a major carbonaceous component.

Acknowledgements

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