Chemical and Morphological Characterisation of Aerosol Particles in the Tropopause Region

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Chemical and Morphological Characterisation of Aerosol Particles in the Tropopause Region

Doctoral thesis

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Department of Physics
Lund University, Sweden
2007

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To my parents and my family

Abstract

The aim of this work was to study atmospheric aerosols, focusing on the chemical composition, the morphology and the origin of the aerosol in the upper troposphere and lowermost stratosphere. An aerosol sampler was developed for this purpose. A new method for quantitative analysis of the major components of the aerosol, i.e. C, N and O was developed, and methodologies for single-particle analysis to gain information on particle morphology and chemical composition were adapted and used for the aerosol samples.

Samples collected during 60 intercontinental flights from 1999 to 2002 were analysed with regard to elemental composition with particle-induced X-ray emission. The results were used to study the properties and the origin of the aerosol in the lowermost stratosphere at northern mid-latitudes, focusing on the sulphur concentration. The results of this study show that particulate potassium and iron in the lowermost stratosphere originate in the troposphere and are transported across the tropopause, whereas particulate sulphur has a strong stratospheric origin in addition to transport across the tropopause. Approximately half of the mass of particulate sulphur transported from the stratospheric overworld to the lowermost stratosphere was formed from carbonyl sulphide the remainder being dominated by particulate sulphur and sulphur dioxide that was transported across the tropical tropopause. The production of particulate sulphur in the stratosphere was estimated to be 0.066 Tg S/y.

A new multi-channel aerosol sampler was developed and calibrated for the second phase of the CARIBIC project, which improved the time resolution and produced samples for quantitative and individual particle analyses. It was found that the collection efficiency of the sampler was as high as 97% for particles larger than approximately 0.2 µm in diameter, and the cut-off was 0.08 µm at the calibration conditions. The time resolution of each sample was 1.5 hours. This sampler is a powerful tool for aerosol characterization from an aircraft.

A new method for the analysis of carbon, nitrogen and oxygen based on the use of PESA has been developed for use on CARIBIC samples, which are collected on an organic backing film. For example, the detection limits of C, N O, S and Fe are 3, 1, 2, 2 and 0.1 ng/m^3, normalized to STP. This analytical protocol is truly unique because it offers low detection limits and high analytical capability over a wide range of elements. Moreover, it yields quantitative information. This is the first quantitative measurement of the concentration of the carbonaceous aerosol component and other components such as N and O in the upper troposphere and the lowermost stratosphere. It was found that they, together with sulphur, are the major constituents of the aerosol in this region.

Individual particles’ characteristics have also been studied based on classification of individual particles with respect to morphology and composition along a transect from 50º N to 30º at 10 km altitude. The classification comprised of more than 30 particle types. Their morphology is complex and varied. A dependence of morphology on the location where they were collected was found. For further investigation of these aerosol particles, chemical analysis was undertaken. Two techniques, PIXE and PESA, were used to quantitatively determine the concentration of carbon and sulphur. Then the particulate carbon to sulphur ratio was used to express the composition of the samples. This ratio varied over the aerosol samples in a range 0.5 to 3.5. The largest value of this ratio appears at around the equator, south of ITCZ, whereas the lowest one was found in the lowermost stratosphere. Further chemical investigation using EFTEM was made to reveal the distributions of carbonaceous and sulphurous matter of individual particles. The results were used to explain the complex structures and the large variation in morphology of the aerosol from different regions. Particles with satellite patterns usually are interpreted as being composed of sulfuric acid. Analyses by EFTEM presented here show that these particles have a central particle composed of both carbonaceous and sulfurous matter and the satellites are composed of carbonaceous matter. Hence a morphological analysis alone could erroneously classify these mixed particles as being pure sulfuric acid.

Populärvetenskaplig sammanfattning

Små partiklar i form av vätska eller fast material mellan 0.001 till 100 µm i diameter, kan sväva i luften och kallas då aerosolpartiklar. De påverkar direkt på klimatet genom att reflektera solstrålar ut till rymden. Detta gör att vi får ett kallare klimat. Indirekt kan de påverka klimatet genom att verka som kondensationskärnor vid molnbildning. Med detta påverkar de molnens strålningsegenskaper och livstid. Trots deras viktiga roll för klimat är kunskap om dem mycket mager. Min forskning gick ut på att utvidga den befintliga kunskapen om aerosolernas kemiska sammansättning, deras morfologi och ursprung. För detta syfte utvecklades en aerosolprovtagare, en ny metod för att kunna göra kvantitativ analys på huvudämnen (C, N och O) som finns i aerosolpartiklar och en ny metodik för att studera enskilda aerosolpartiklars morfologi och kemiska sammansättning.

I det första arbetet analyserades prover som samlades under 60 flygningar mellan 1999 till 2002 för selektiva grundämnen med hjälp av den känsliga PIXE-metoden. Analysresultat användes sedan för att studera egenskaper av och källa till aerosoler i den lägsta delen av stratosfären vid norra jordklotets mittlatitud. Det visade sig att kalium och järn som finns på aerosol partiklar i den lägsta delen av stratosfären kommer från troposfären over tropopausen. Resultatet visade också att svavel transporterades till den lägsta delen av stratosfären från högre nivå i stratosfären samt från troposfären över tropopausen.

En mångkanalprovtagare utvecklades och kalibrerades för användning inom ett internationellt projekt, CARIBIC (Civil Aircraft for Regular Investigations of the atmosphere Based on an Instrument Container). Med den här provtagaren förbättrades tidsupplösningen för provtagning av aerosol. Dessutom kan prov samlas för både kvantitativ analys och individuell partikelanalys. Vidare är insamlingseffektivitet 97 % för partiklar med diameter större än eller lika med 0.2 µm. Den är ett effektivt instrument for karakterisering av aerosolpartikel från ett flygplan.

Utveckling av en ny metod för analys av kol, kväve och syre baserad på PESA-metod (particle elastic scattering analysis) genomfördes. Med den här metoden kan man analysera t.ex. ett kolrikt ämne som finns på ett underlag som just innehåller ämnet. Med hjälp av metoden kan man för första gången kvantitativt studera kol, kväve och syre i partiklar från övre troposfären och lägsta stratosfären. Mätningarna visar bl.a. att de här ämnena tillsammans med svavel är huvudämnen på aerosoler i tropopausområdet.

Slutlighen har jag utvecklat en ny metodik för att studera individuella partiklar från tropopausen och mellan södra och norra jordklotet. Den går ut på att klassificera enskilda partiklars utseende och kemiska sammansättning längs flygrutten. Partiklarnas morfologi och kemiska sammansättning varierade med position där de samlades. Bland annat kan man hitta stora partiklar med komplicerad struktur på norra jordklotet och södra jordklotets midlatituder. Partiklar i över troposfären kan ha bildats där uppe genom koagulation och olika gas-till- partikelprocesser. Partiklar i den lägsta delen av stratosfären visade sig vara mer grenad struktur än de som fanns på övre troposfären. Detta beror troligen på att stratosfäriska partiklar befanns sig en längre tid i atmosfären än troposfäriska partiklar.

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- Finally, my wife, my son Thien Tran and my new born daughter, thank you for your loves, supports and encouragements!

List of publications

This thesis is based on the following papers, which will be referred to by their Roman numerals in the text. The papers are appended at the end of the thesis.

I Bengt G. Martinsson, Hung N. Nguyen, Carl A.M. Brenninkmeijer, Andreas Zahn, Jost Heintzenberg, Markus Hermann , Peter F.J. van Velthoven (2005)
*Characteristics and Origin of Lowermost Stratospheric Aerosol at Northern Midlatitudes under Volcanically Quiescent Conditions Based on CARIBIC Observations***.** J. Geophy. Res., 110, D12201

II Hung N. Nguyen, Anders Gudmundsson, and Bengt G. Martinsson (2006)
Design and Calibration of a Multi-Channel Aerosol Sampler for Tropopause Region Studies from the CARIBIC Platform. Aerosol Sci. Technol. 40:649-655

III Hung N. Nguyen, Bengt G Martinsson (2007)
Analysis of C, N and O in Aerosol Collected on an Organic Backing using Internal Blank Measurements and Variable Beam Siz. Nucl. Instr. and Meth. B. in press, corrected proof.

IV Hung N. Nguyen, Bengt G. Martinsson, Jakob B. Wagner, Eric Carlemalm, Martin Ebert, Carl A. M. Brenninkmeijer, Jost Heintzenberg, Markus Hermann, Peter F. J. van Velthoven, and Andreas Zahn
Chemical Composition and Morphology Variation of Individual Aerosol Particles from a 10 km Altitude Flight between 50^0 N *to* 30^0 S *(CARIBIC).*

My contribution to the papers

Paper I	I contributed to the analysis and data evaluation.
Paper II	I was responsible for the calibration of the sampler, data analysis and wrote the paper.
Paper III	I was responsible for the analysis, made part of the data evaluation and wrote part of the paper.
Paper IV	I planned the study and evaluated the results. I also performed some of the experimental work and wrote the paper.

Contents

1. Introduction

The climate affects our daily lives in many ways. Thus, it is important that we understand the earth’s climate system, both in the past and the present, to be able to predict the changes that may take place in the future. Airborne particles and cloud droplets in the atmosphere play important roles in the earth’s climate, which is why it is necessary to perform measurements on aerosols, so we can understand them and control them.

This work deals with the aerosol in the upper troposphere and lowermost stratosphere, which is also known as the tropopause region. In this work, an aerosol sampler was developed for aerosol sampling from the Civil Aircraft for Regular Investigations of the atmosphere Based on an Instrument Container (CARIBIC) platform. The project was described by Brenninkmeijer et al. (2007). A new method was also developed for the quantitative analysis of major aerosol components such as C, N and O. Additionally, a methodology was developed for single-particle analysis focusing on the morphology and chemical composition.

1.1 Aerosols

An aerosol is defined in its simplest form as a collection of solid or liquid particles suspended in a gas (Hinds, 1998). Aerosols are usually stable for at least a few seconds, and in some cases may last a year or more. There are two main types of aerosols, which occur in different environments. One is called the atmospheric aerosol, and the other the indoor aerosol. Important research is being carried out on indoor aerosols as they are directly related to the working environment, and thus human health. However, this is outside of the scope of this study. The subject of this work is the atmospheric aerosol, and it will be described in more detail below.

The atmospheric aerosol affects the climate directly and indirectly (IPCC, 2007). The effects of aerosol particles on the scattering and absorption of solar radiation and the absorption and emission of thermal radiation are the direct effects. The indirect effect is the result of an aerosol changing the radiative properties of the clouds by acting as cloud condensation nuclei and ice nuclei. However, it is difficult to quantify these effects. Many studies are still required to broaden our knowledge of the fundamental physical and chemical processes taking place in an aerosol in the atmosphere. To be able to study aerosols, a large number of measurements have to be carried out to obtain information on the number concentration (number of particles per unit volume of air) and the mass concentration (mass of particles per unit volume of air). More complete characterization of an aerosol can be obtained by measuring its size distribution, chemical composition and morphology.

Another important parameter that determines an aerosol's characteristics is the source. The aerosol may be of natural and/or anthropogenic origin. Examples of the natural sources of aerosols are sea spray, volcanic eruptions, forest fires and the mechanical action of the wind on the earth's surface. The natural sources include also the aerosols that are of biogenic origin, for example, plants, animals (including humans), soil and water. Anthropogenic aerosols arise from human activities such as combustion and cultivation.

The size of an aerosol particle is an important parameter. Atmospheric aerosol particles have diameters between 0.001 µm and 100 µm (Hinds, 1998). Depending on their size, they can remain in the air for hours, weeks or even more. Aerosol particles have been divided into various size intervals, or modes: *ultrafine*, *accumulation* and *coarse* by Whitby (1978), and the *Aitken* mode, which was defined by Hoppel and Frick (1990) as being between the accumulation mode and ultrafine mode. Ultrafine particles, with diameters from 0.001 to 0.02 µm, originate almost entirely from the condensation of precursor gases by the nucleation of the clustering of gas molecules. These particles will grow rapidly to form fine aerosol particles, or the Aitken mode (0.02 to 0.1 µm), by condensation of gases and coagulation of particles. Thus, ultrafine particles are removed very quickly from the atmosphere by contributing to the aerosol particles in the Aitken mode. The largest Aitken mode particles serve as cloud condensation nuclei. Liquid phase reactions cause further gas-to-particle conversion, forming the accumulation mode (0.1 to 0.7 µm). Growth beyond 1 µm is very slow because the mass transport is too slow to appreciably affect the size of these large particles. Coarse particles (above 1 µm) are often generated by the mechanical action of the wind on the earth's surface. The removal mechanism of sedimentation only has a significant effect on these coarse particles. The finer particles, with diameters less than 1 µm, have such a small sedimentation velocity that they can remain in the atmosphere for a long time, if they are not removed by other mechanisms such as rain-out and wash-out. A particle is said to be rained out when it grows and becomes a raindrop, falling to the earth's surface by its own weight. Wash-out is the process in which a particle is "scavenged" from the atmosphere by raindrops.

Particles of different sizes may have different chemical compositions. Particles in the coarse mode often contain sea salt, soil dust, and vegetation debris, whereas fine aerosol particles (less than 1 µm) are often composed of sulphates, nitrates, soot and organic matter. Therefore, it is important to study the chemical composition of an aerosol if we are to understand its properties.

The composition of an atmospheric particle is very dependent on the geographic location. A particle originating from the condensation of a gas, for instance sulphuric acid, can be modified by the condensation of other gases such as NH_3 and HNO_3, as well as other organic and inorganic compounds. Thus, the properties of aerosol particles change during transport. This demonstrates the importance of studying the transport processes of aerosols in both the vertical and horizontal directions.

The chemical composition and the physical properties of aerosol particles may be inferred by examining their morphology. Morphology may thus be used as a means of classifying particles. Each class can then be analysed with regard to chemical composition by techniques such as electron energy loss spectroscopy and energy-filtering transmission electron microscopy. In addition, the study of particle morphology will help us to determine the physical properties of the aerosol as the drag force and settling velocity of an aerosol particle are influenced by its shape.

A large number of studies have been carried out on tropospheric aerosols, and the results have elucidated many questions related to the fundamental behaviour of aerosols in this region. However, many questions of great scientific interest concerning the aerosol in the tropopause region remain unanswered. I hope that this work makes a contribution to answering some of these questions.

1.2 Aerosol sampling

Many techniques have been used to study the atmospheric aerosol in the tropopause region. Remote sensing techniques such as LIDAR (light detection and ranging), and satellite measuring techniques have been used (Zuev et al., 2001; Baumann et al., 2003), as well as direct techniques using balloon-borne and aircraft-borne equipment (Hofmann, 1993; Hermann et al., 2003). Aerosol sampling from a civil aircraft has been used to collect samples for subsequent analysis at a ground-based laboratory (Papaspiropoulos et al., 1999). The most suitable technique should be chosen depending on the purpose of the study. In this work, aerosol sampling from an aircraft for subsequent analysis was used. The sampling technique is described in Chapter 2.

1.3 Ion beam analysis

Ion beam analysis has been applied to many types of samples including aerosol samples (Cahill et al., 1984; Martinsson, 1986; Johansson et al., 1995). In this work, two ion beam techniques were investigated and applied to analyse aerosol samples collected from the upper troposphere and the lowermost stratosphere. The basic principles of these two techniques are described in Section 3.1.

Section 4.2.1 describes the specific problems that must be solved and their solutions for the analysis of the present samples.

1.4 Electron beam analysis

Electron microscopy is a well known technique in single-particle analysis (Buseck, 1992; Pósfai et al., 1994), but it is not necessarily the best technique for analysing the present aerosol samples. Many techniques were investigated, and three were chosen to obtain information in this study. Their basic principles are given in Section 3.2. Single-particle analysis using these techniques is described in Section 4.2.2. Further details on other techniques that have been tested, but the results could not be used in this work, may be found elsewhere. For instance, scanning transmission electron microscopy, energy-dispersive X-ray microanalysis, and selected-area electron diffraction are described by Williams and Carter (1996), atomic force microscopy is described in the review by Ricardo and Ruben Perez (2002), and environmental scanning electron microscopy is presented by Danilatos (1980).

1.5 The aim of this work

The aim of this work, which was part of the international project, CARIBIC, was to systematically characterize the aerosol in the tropopause region on a global scale by studying its chemical composition and its morphology. To this end, an aerosol sampler was developed and used to collect aerosols from the CARIBIC platform for both quantitative analysis and single-particle analysis. Moreover, a new method was developed for the analysis of CARIBIC samples to obtain quantitative information on major components of the aerosol in the above mentioned region. Additionally, the methodology for single-particle analysis using electron microscopy was developed in order to analyse CARIBIC samples. The methodology was then applied to a series of samples collected during a flight between the northern hemisphere (Frankfurt, Germany) and the southern hemisphere (Santiago de Chile via Sao Paulo, Brazil). Many samples have been analysed using particle-induced X-ray emission, PIXE, resulting in new information on the aerosol in the upper troposphere and lowermost stratosphere.

2. Aerosol sampling

2.1 Aerosol sampling with the impaction technique

Many scientists have used and developed the impaction technique for aerosol collection and analysis (e.g. Biswas and Flagan, 1984; Marple and Klaus, 1976; Flagan, 1982). The impactor was used in the first half of the previous century to collect dust for the evaluation of occupational environments, and it has been used since the 1960s for the measurement of particle size distribution by mass (Hinds, 1998). It has been also used to collect aerosols for subsequent chemical composition analysis (Martinsson et al., 2001).

The impaction technique is based on the inertial impaction of the aerosol particles onto a collection surface. When aerosol particles are travelling in a gas flow, an obstacle forces the gas to bend and move around it. Some of the aerosol particles with a high inertia will not be able to follow the gas stream, but continue travelling in their original direction, i.e. straight forward, and impinge on the obstacle's surface. The inertial impactor is an application of this principle.

Figure 2.1 shows a simple diagram which describes the working principle of all inertial impactors. An aerosol flow is accelerated through a nozzle. Downstream of the nozzle, the flow is impeded by an obstacle, an impaction plate, which deflects the flow in a new direction, usually by 90° to the original one. All particles with an inertia higher than a certain value will impact on the impaction plate in the ideal case. Smaller particles will follow the flow without hitting the impaction plate. This value of inertia may be translated into an aerodynamic diameter by calibration. This diameter is called the cut-off diameter, and is one of the characteristics of an inertial impactor.

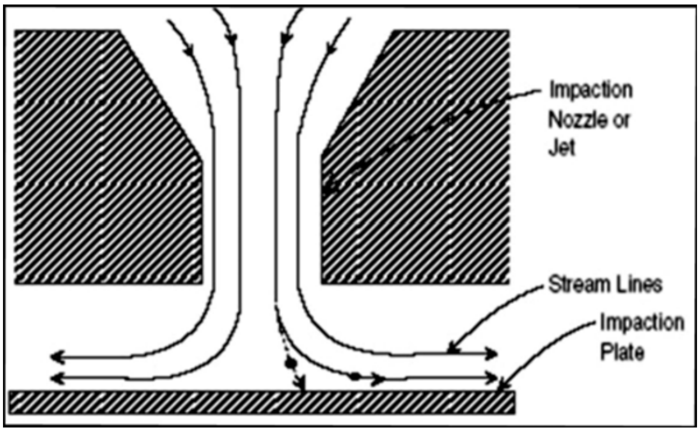


Figure 2.1: *Cross-sectional view of an inertial impactor [Hinds, 1998].*

For a conventional, circular impactor, the cut-off diameter can be calculated from the equation:

$$d_{50} = \sqrt{\frac{9\eta W}{\rho_p C_c U}}\sqrt{Stk_{50}} \qquad (2.1)$$

where:
Stk_{50} = 0.24
ρ_p = particle density
C_c = Cunningham slip correction factor
D_p = particle diameter
U = average air velocity at the nozzle exit (= $Q/\pi(W/2)^2$) for a round nozzle and
(= Q / LW) for a rectangular nozzle impactor, where
Q = volumetric flow rate through the nozzle and
L = nozzle length for a rectangular impactor
W = nozzle diameter for a circular impactor or the nozzle width for rectangular impactor
η = air or gas viscosity

When using the impaction technique, two non-dimensional numbers are important. The first is the Reynolds number (Re). This number characterizes the state of gas flow inside of the nozzle and is given by:

$$\mathrm{Re} = \frac{\rho V W}{\eta} \qquad (2.2)$$

where V is the relative velocity between the fluid and the nozzle.

The second one, the Stokes number (Stk), characterizes the curvilinear motion of a particle in the flow field. This number is given by:

$$Stk = \frac{\rho_p C_c d_p^2 U}{9\eta W} \qquad (2.3)$$

where d_p is the particle diameter. Note that Stk_{50}, which corresponds to the cut-off particle size is often used in the calculation of d_{50}. Stk_{50} is dependent on the Reynolds number. When $500 < \mathrm{Re} < 3000$, Stk_{50} is approximately constant.

There are different types of impactors; cascade impactors and virtual impactors being two of them. The cascade impactor comprises several impactor stages in series; each stage has the same design as shown in Figure 2.1. They are arranged so that the nozzle sizes are in decreasing order. With this arrangement, each stage will collect aerosol particles in a certain size interval. Thus, the cascade impactor can be use to study the size distribution of aerosol particles by mass. The virtual impactor is based on the same principle as other inertial impactors, but a collection probe is used instead of an impaction plate. This is often used to overcome the problems of bounce and overloading, which may occur in an inertial impactor. The collection probe samples aerosol particles within a certain size range. Particles with sizes below or above this range will be collected on separate downstream filters. However, this kind of impactor has the drawbacks that it is difficult to obtain sub-micron cut-off sizes, and there is some mixing of small particles with the large particles due to the carrier air stream.

In this work, the inertial transfer mechanism was used as the working principle of the aerosol sampler, which is presented in Paper II and is briefly discussed in the next section.

2.2 The aerosol sampler

Several criteria were applied in the design of the new aerosol sampler. As this work was part of the CARIBIC project, the aerosol sampler was intended to be used in a scientific container, which is installed on a civil aircraft. Thus, it had to be so small that it could be installed together with other instruments inside the CARIBIC container. In addition, it had to fulfil the safety regulations for equipment operating inside an aircraft. (The latter will not be discussed in detail here.) Another criterion was that the sampler must collect sequential aerosol particles for subsequent analysis at the ground-based laboratory. The analysis was to provide quantitative and morphological information about the aerosol in the upper troposphere and the lowermost stratosphere.

Impaction was found to be suitable as the working principle of an aerosol sampler to meet the above mentioned criteria. The aerosol particles were focused into small spots on a thin organic backing film (AP1^{TM}) (CARIBIC quantitative analysis). The smaller the aerosol spots, the better the minimum detection limit of the quantitative analysis (Papaspiropoulos et al., 1999). The impaction technique was also used to collect aerosols on carbon-coated Cu TEM-grids (transmission electron microscopy) for the study of individual particles using electron microscopy (CARIBIC EM samples). Furthermore, to be able to study the geographical distribution of the aerosol particles, series of aerosol samples had to be collected sequentially. The sampler therefore had to consist of many impactors that are able to operate one after the other in sequence.

In general, aerosol sampling takes place as follows. After passing through an inlet system (Hermann et al., 2005) placed outside the boundary layer of the aircraft itself, the aerosol passes through an arrangement consisting of a cyclone and connectors. This defines the aerosol sample's upper size limit before entering and being collected by the aerosol sampler. Aerosol sampling is not started until the aircraft reaches an atmospheric pressure of 350 hPa and is stopped when the pressure exceeds 450 hPa. This is to avoid contamination by aerosols from the ground.

In more detail, the sampler consists of 16 parallel channels. Fourteen of them are used to collect samples sequentially (sequential samples) (see Figure 2.3). Each channel of these 14 channels is open for about 100 minutes. The remaining two channels are open during the entire outbound or return flight to provide integral samples. The operating time of one of these two channels is approximately 700 minutes. These two channels are used to check for contamination. The control will be carried out when performing the quantitative analysis, by requiring that the detection of an element in a sequential sample is reflected in the integral sample.

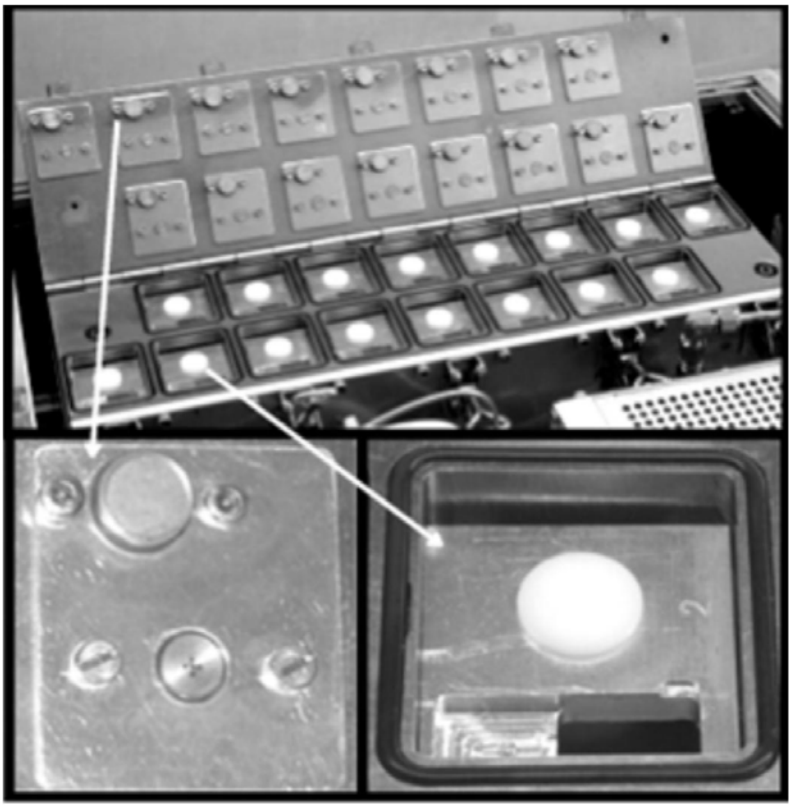


Figure 2.2: *The aerosol sampler with the lid open, showing the impactors. The inserts show one channel with its nozzles (left) and the position where the film and the TEM-grids are placed (right).*

Each of the two channels that collect integral samples contains one type of nozzle (nozzle type 1). Nozzle type 1 has only one opening, with a diameter of 0.5 mm. Moreover, the distance between the orifice and the impaction plate is 6 times the nozzle opening diameter. The critical volume flow rate is 2.0 ± 0.03 l/min.

Each of the fourteen channels that collect sequential samples contains two nozzles (nozzle types 2 and 3) (see Figure 2.2). Nozzle type 2 has four openings, each with a diameter of 0.5 mm. The critical flow rate of this nozzle type is 8.0 ± 0.08 l/min. Nozzle type 3 has two openings, each with a diameter of 0.15 mm. This nozzle has a critical flow rate of 0.37 ± 0.01 l/min. The distance between these openings is 4.2 µm. With this distance, it is possible to collect two samples in each channel.

Nozzle type 2 is used for collecting samples for quantitative measurements of elemental concentrations. In order to obtain quantitative information the nozzle and the cyclone arrangement have to be calibrated (Nguyen et al., 2006). The results of the calibrations are shown in Figs. 2.3 and 2.4. As can be seen in Figure 2.3, the cut-off size of the cyclone arrangement is 2 µm. The upstream pressure of the arrangement was kept at 360 hPa during this calibration.

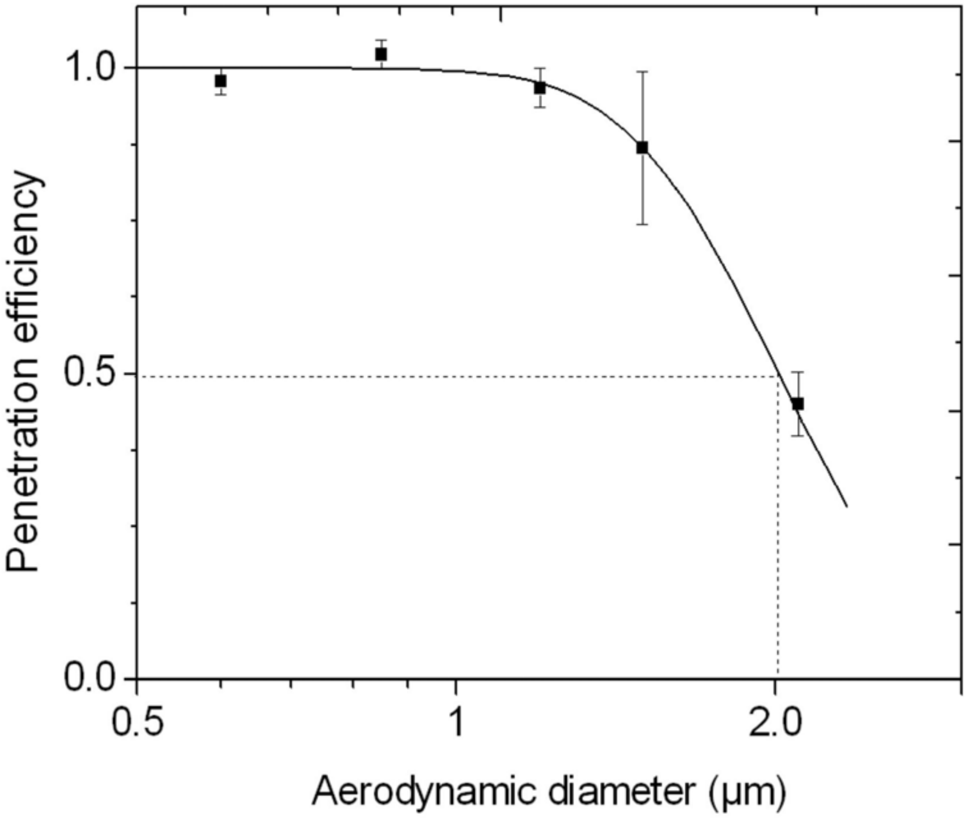


Figure 2.3: *The penetration as a function of the particle size of the arrangement that defined the upper size limit of the aerosol particles before being collected.*

In Figure 2.4, the filled squares show the results obtained when the maximum pump capacity was used to reduce the ratio (r) of the downstream to upstream static pressure to 0.2. Under this condition, the collection efficiency was as high as 96.5%, on average, for large particles. The cut-off size was found to be 0.08 µm for the nozzle type 2. These results were obtained from the calibration performed at sea level. In our case, the pressure upstream of the nozzle will be between 300 and 400 hPa and the downstream pressure less than 100 hPa. Consequently, the actual 50% cut-off size will be lower than the 50% cut-off size according to the calibration. Details of the sampler are discussed in Paper II.

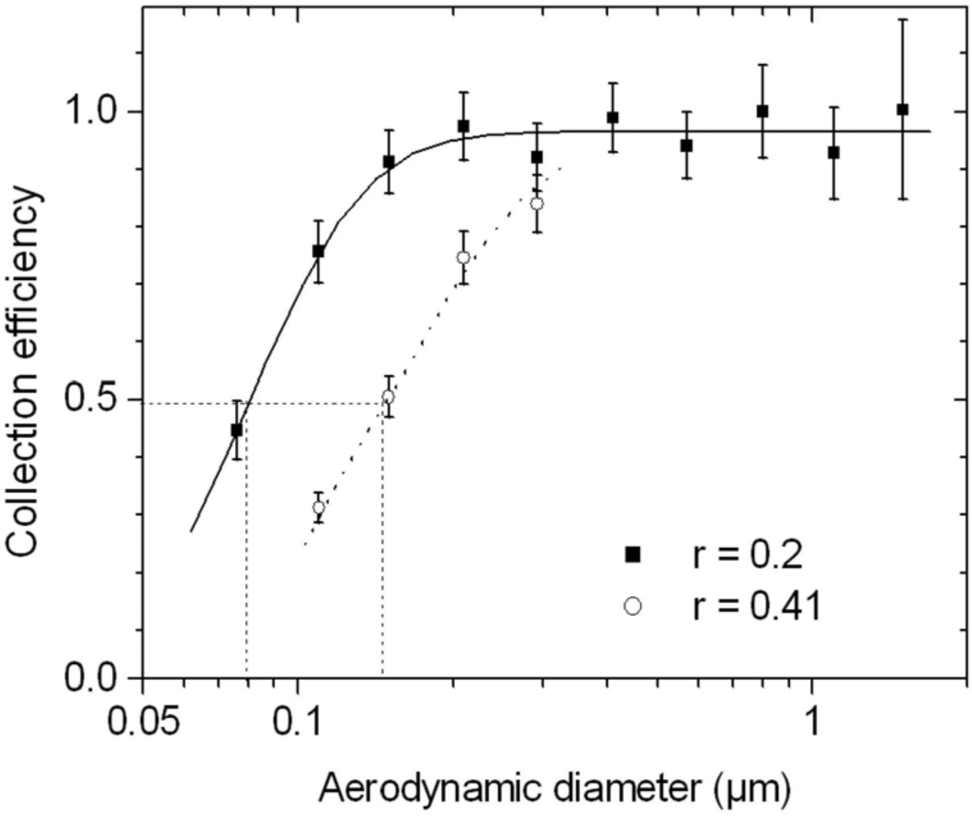


Figure 2.4: *The collection efficiency of the aerosol sampler as a function of particle size.*

3. Analysis methods

3.1 Quantitative analysis

3.1.1 Particle-induced X-ray emission

PIXE, which is an acronym for particle-induced X-ray emission, is a technique with high absolute sensitivity used for multi-elemental analysis. This technique was first introduced at the Lund Institute of Technology in 1970 by Johansson and Campbell (1988). Since then, it has been frequently used by the analytical community, and its high absolute sensitivity has solved many analytical problems in the aerosol science community (Martinsson et al., 2005; Denker et al., 2004). With this technique, the elemental composition of a specimen can be identified and quantified without destroying the specimen.

The basic principle of this method can be inferred from its name, PIXE. The specimen to be analysed is bombarded by a beam of charged particles with high energy, often protons or alpha particles. When these particles enter the specimen, electrons of the target atoms will be excited. The de-excitation of these excited atoms results in the emission of characteristic X-rays. These X-rays are detected producing a spectrum from which the elemental concentrations in the specimen can be determined.

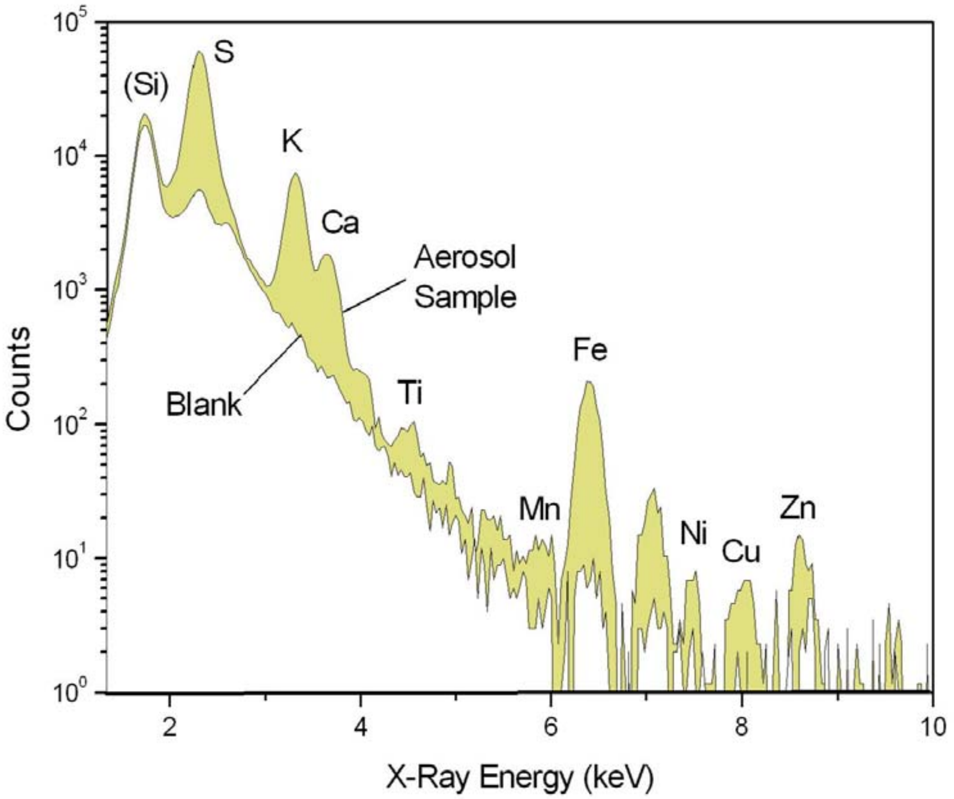


Figure 3.1: *A typical spectrum obtained by PIXE analysis of a sample from the CARIBIC platform together with a spectrum from a blank AP1 film.*

A typical PIXE-spectrum with the characteristic X-ray peaks identified is shown in Figure 3.1. In the figure, the continuum background up to 6 keV can be seen. This background is the result of different processes that occur during the interaction between the projectile and the target. The contributions to the continuous background in this case are from bremsstrahlung that results from the deceleration process of the primary protons, and from bremsstrahlung emitted by electrons inside the specimen itself. Another contribution that can sometimes be seen in PIXE spectra at higher energies is from gamma rays emitted by nuclear reactions inside the specimen if it contains elements such as sodium or fluorine. This contribution is not clearly visible in Figure 3.1, due to its low intensity. However, the contributions from proton bremsstrahlung and from gamma rays are much less than that from electron bremsstrahlung. This major contribution is secondary electron bremsstrahlung (SEB), which arises from the scattering of ejected electrons by the Coulomb field of the nucleus inside the specimen. Quasi-free-electron bremsstrahlung arises from the scattering between an electron and the projectile’s Coulomb field, while atomic bremsstrahlung arises when the electron excited to a continuum state falls back to its initial bound state in the atom. All these background signals may be reduced greatly depending on where the detector is placed. The background signals are maximal at 90° relative to the beam direction and are decreased by factors of 1.6 at 135° and 2.6 at 160° (Folkmann et al., 1984).

Figure 3.1 also shows the elements that are often present in the CARIBIC aerosol samples on thin AP1backing film. As can be seen in the spectrum, many elements in the sample were revealed by PIXE analysis. For a thin, homogeneous specimen, the PIXE yield is given by:

$$Y = \sigma \omega b t \varepsilon \frac{\Omega}{4\pi} \frac{\xi}{M} \frac{Q}{e} \frac{1}{\cos\alpha} \qquad (3.1)$$

where σ is the ionization cross-section for the incident proton energy, ω the K or L fluorescence yield, b the fraction of K or L X-rays that appears in the K_α or L_α line, t the X-ray transmission between the sample and the detector, ε the detector efficiency, Ω the solid angle, ξ the areal density, Q the beam charge hitting the target, M the mass of the target nucleus, e the elementary charge, and α the angle between the specimen surface and the ion beam.

To be able to perform quantitative analysis, the set-up must be calibrated. This is usually done with known standards, for instance, standards from Micro-Matter^{TM}. The calibration, in principle, consists of the determination of analytical sensitivity factors (S), which are expressed:

$$S = \frac{Y}{\xi Q} = \frac{\sigma \omega b t \varepsilon}{M e \cos\alpha} \frac{\Omega}{4\pi} \qquad (3.2)$$

The elemental mass information can then be obtained by using a spectrum evaluation program. The program first fits the peaks using the least-squares method to obtain the area of each peak, i.e. the PIXE yield, Y_0. Then the areal density of each element is calculated based on the relation:

$$\xi = \frac{Y}{QS} \qquad (3.3)$$

When the mass of an element has been calculated based on the values of Y_0, a decision has to be made as to whether the element is present in the sample or not by comparing its mass with the minimum detection limit (MDL) of that element. The MDL depends on the analytical situation. When no blank concentrations need to be considered, the MDL is obtained from the product of the square root of the spectrum background counts and the factor describing the desired level of detection confidence (λ_α). In the other extreme, when blank concentrations determine the detection limit, the MDL is given by the product of the standard deviation of the blank concentration and λ_α.

3.1.2 Particle elastic scattering analysis

To identify and quantify light elements, such as carbon, nitrogen and oxygen in a sample, particle elastic scattering analysis (PESA), a complementary technique to PIXE, is often used (Cahill et al., 1987; Nejedly et al., 1997). This technique is based on the use of the Coulomb electrostatic force between the positively charged nucleus and the positively charged projectile particles (a proton beam in this work). This technique makes use of the same principle as Rutherford backscattering spectrometry, in which a high-energy beam (2.55 MeV in this work) is directed towards a sample. Particle scattering will occur when the beam hits the sample. The backward-scattered particles can be detected by placing a surface barrier detector at a certain angle (156° in this work). A kinematic factor can then be defined by E_1/E_0, where E_0 and E_1 are the energies of the projectile atom before and after the collision. The energy E_0 is determined by calibration of the accelerator, while E_1 is measured by the detector. E_1 depends not only on the incident beam energy but also on the ratio of the masses of the incident particle and the sample atom, as well as the scattering angle. The scattering angle and the masses of the target atom and the projectile are known. Thus, the kinematic factor can be calculated. The mass of the atom inside the sample with which the particle collided can then be determined using equation below:

$$K = \left[\frac{\sqrt{(1-(M_1/M_2)^2 \sin^2\theta)} + (M_2/M_2)}{1+(M_1/M_2)} \right]^2 \qquad (3.4)$$

where M_1 and M_2 are the mass of the projectile and target atom, respectively. The angle θ is that between the detected, backscattered particle and the incident beam direction. The amount of a certain atom in the sample can be derived from:

$$Y = \int \frac{\xi}{M}\frac{Q}{e}\frac{d\sigma}{d\Omega}d\Omega \cong \frac{\xi}{M}\frac{Q}{e}\left\langle \frac{d\sigma}{d\Omega} \right\rangle \Delta\Omega \qquad (3.5)$$

where Y is the PESA yield and $d\sigma/d\Omega$ the differential cross-section; the other symbols are defined in Section 3.1.1.

A sensitivity factor can then be calculated using following equation:

$$S = \frac{Y}{\xi Q} \qquad (3.6)$$

where ξ is obtained experimentally by the analysis of standard samples.

Thereafter, the surface density of the element of interest in the analysed sample can be calculated by using the following equation:

$$\xi = \frac{Y}{QS} \qquad (3.7)$$

A typical PESA spectrum of a CARIBIC sample is shown in Fig 3.2. This spectrum was obtained by bombarding the CARIBIC sample with protons at an energy of 2.55 MeV at the Lund Nuclear Microprobe. It shows elastic C, N, O, and S peaks. They were then evaluated to obtain the yield.

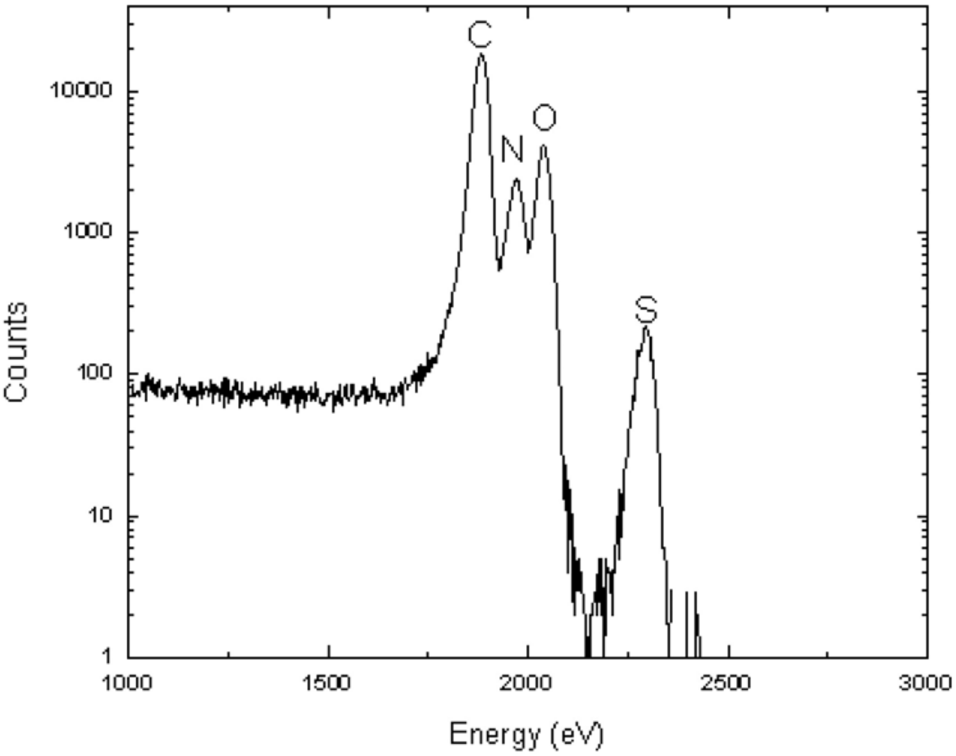


Figure 3.2: *PESA spectrum of a CARIBIC sample o an AP1 film. The elements C, N, O and S are clearly seen in the spectrum.*

3.2 Single-particle analysis

PIXE and PESA were used to quantitatively study the composition of the whole aerosol sampled. As mention in the introduction, the properties of aerosol particles depend not only on their chemical composition but also their morphology. In this work, transmission electron microscopy was used to characterize the morphology and composition of individual particles.

3.2.1 Transmission electron microscopy

The first electron microscope was built by Ruska and Knoll in Berlin in the early 1930s. The idea was described and explained later by Ruska, himself in 1986. After that, in the 1940s, it was further developed in the UK and in Japan. Ruska received the Nobel Prize for the invention of the electron microscope in 1986. With the advent of electron microscopy, the spatial resolution was extended well below that of light microscopy. Theoretical studies related to TEM have been reviewed by Hirsch et al. (1977). .

The working principle of the electron microscope is very similar to that of the light microscope. In the electron microscope, electrons are accelerated and then pass through many magnetic lenses, which focus them in the same way that glass lenses focus light in a light microscope. After having been guided through the electron microscope vacuum column, the electrons pass through the specimen, which must be thin. When passing through the specimen, the electrons interact with the atoms in it. Different amounts of electrons will pass through the specimen depending on its density. Thus, a map of density variation will be formed. This map can be studied directly on a viewing screen or be recorded by a CCD camera for later analysis.

The resolution of optical microscopes is limited by the wavelength of light, and similarly, the resolution of electron microscopes is determined by the energy of the electrons. For example, at an energy of 100 keV the wavelength of electrons is 0.003702 nm, which is 100,000 times shorter than the wavelength of visible light. Thus, electrons have the potential to give a much better spatial resolution than visible light.

A typical TEM image is shown in Figure 3.3. The figure is a TEM BF (bright field) image of atmospheric particles that were sampled by the aerosol sampler on a thin amorphous carbon support film. BF imaging is one of two basic ways to form amplitude contrast images, in which the direct electron beam is selected with an objective aperture placed behind the specimen. The other way to create images is the so-called dark field method, by selecting the scattered electrons with the objective aperture. The dark regions visible in Figure 3.3 represent the aerosol particles (and carbon film) while the bright regions are where the electrons passed through the carbon film.

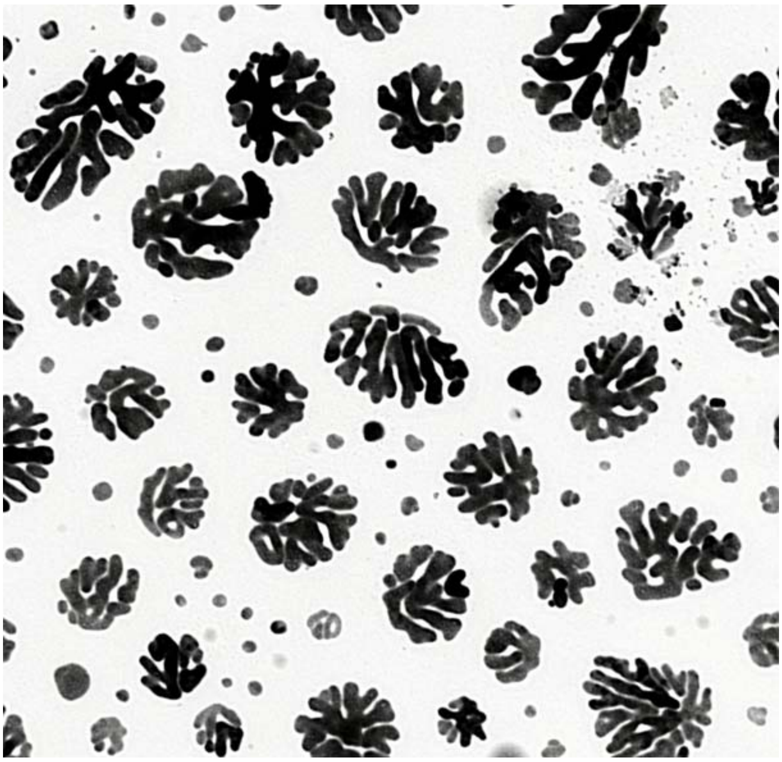


Figure 3.3: *A typical image of an aerosol sample using the TEM BF technique.*

When carrying out TEM studies it is important to be aware of the drawbacks of the technique. Disadvantages of the technique are beam damage to the specimen, the requirement of a thin sample, the small examination area (20 x 20 µm), and the time-consuming analysis of the images. Beam damage is a particular problem during TEM image recording. This problem was partly overcome by using low magnification, low electron intensity and short exposure times. Because of the limitation of the examination area, a strategy must be employed in choosing the analysis area so as to ensure that the most representative area is studied.

The parameters that have the greatest influence on the quality of TEM images are the objective aperture, the acceleration voltage of the electron microscope, the magnification, and the recording device, e.g. a CCD camera. For samples sensitive to the electron beam, such as the CARIBIC samples, it is necessary to systematically optimize these parameters in order to obtain high-quality TEM images.

In this work, TEM was used to study the morphology of individual particles (Paper IV).

3.2.2 Electron energy loss spectroscopy

TEM analysis provides information on the morphology of individual particles. However, it is also desirable to know what they consist of. Energy-dispersive X-ray microanalysis (EDX) is the method normally used for chemical identification. However, the production efficiency of X-rays is low in EDX, particularly for the light elements. In the mid 1940s, James Hillier and R. H. Baker developed a new complementary technique to EDX, so-called electron energy loss spectroscopy, EELS (Hillier and Baker, 1944). This method was not extensively used until the mid 1990s, when electron instrumentation and vacuum technology became sufficiently advanced to facilitate the use of EELS.

When a beam of electrons travels through a thin specimen some of the electrons will interact with the atoms of the specimen. During this interaction, they will lose their energy to the atoms inside the specimen by different processes. One of these processes is the interaction that causes inner shell ionization.

Moreover, the energy loss due to this ionization process is specific. The electrons are dispersed energetically by a magnetic prism, which is mounted in the electron path after the specimen. A spectrometer is placed after the prism to select electrons with specific energy losses to form a spectrum of energy loss versus intensity. Both qualitative and quantitative information about the atoms contained in the specimen be extracted from the spectrum.

As mentioned above, many processes may contribute to the energy loss spectrum. Some of the contributions can be seen in a typical EELS spectrum (Figure 3.5). This spectrum was the result of EELS analysis of a particle from a CARIBIC EM sample. The x-axis shows the energy loss in electron volts (eV) and the y-axis the electron intensity (counts). In the low energy loss region, after the zero loss peak, the plasmon peak can be seen at 30 eV, whose width and height (intensity) depend on the thickness of the sample. At higher energy losses, ionization edges can be seen, for example, at 284, 402, 532 and 165 eV, corresponding to the K-edge of C, N, O and the L-edge of S. The background intensity arises from multiple-scattering events and the tails of the earlier edges, which can be seen as the continuum before every edge in the spectrum.

Ionization edges in the EELS spectra were used for the qualitative microanalysis of aerosol particles. The edge can be identified by comparing its specific energy loss to values in a reference table. In this way, the elemental components of the irradiated part of the particle can be easily determined.

To extract quantitative information from the EELS spectrum, all the contributions to the EELS spectrum except the ionization edges have to be removed. The edges then become a single scattering “hydrogenic“ edge, i.e.

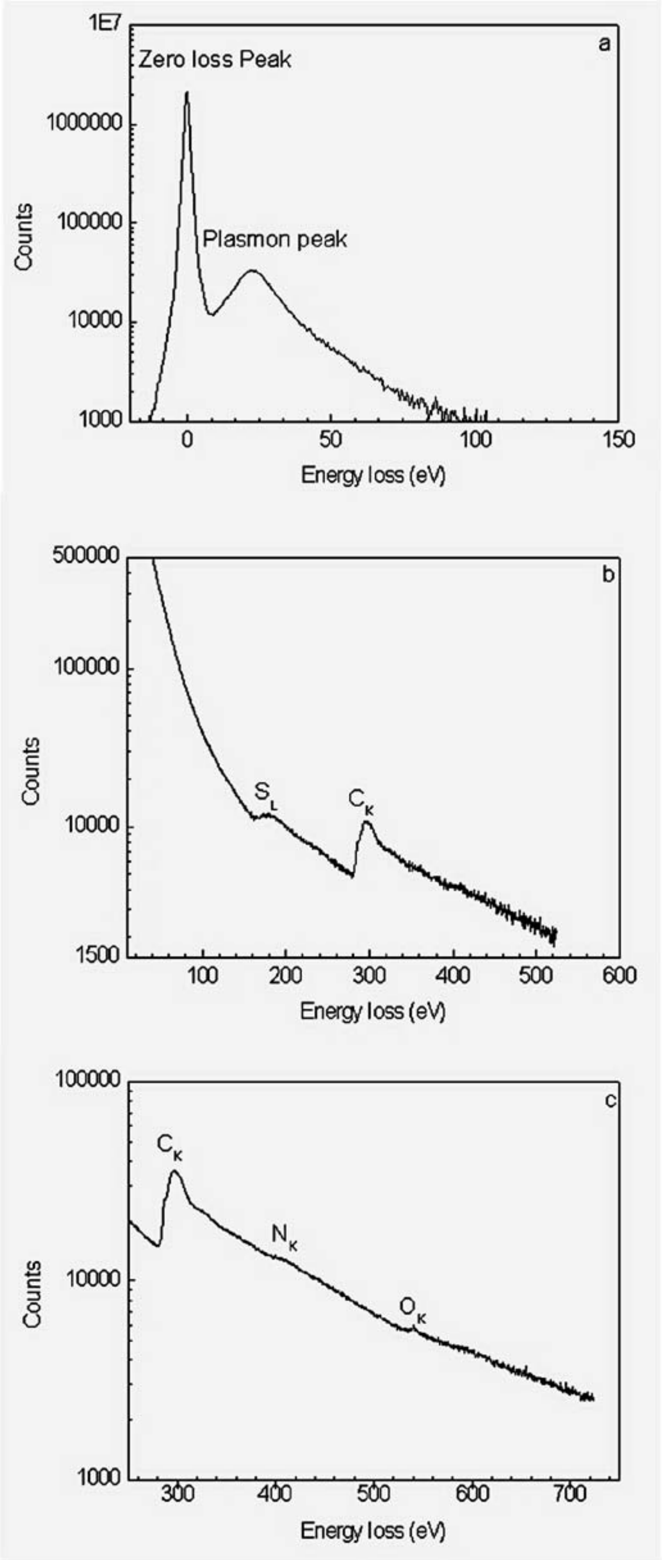


Figure 3.5: *Illustrative EELS spectra obtained from an aerosol particle. (a) shows the effects due to the zero-loss electrons at 0 eV, and the plasmon peak at 30 eV. (b) and (c) show the critical ionization energies required to eject specific L- and K-shell electrons: sulphur (L-edge) at 165 eV, carbon (K-edge) at 284 eV, nitrogen (K-edge) at 402 eV and oxygen (K-edge) at 532 eV.*

edges with a triangular shape. The intensity of each edge is obtained by integrating over a certain energy loss window Δ. Furthermore, the sensitivity factor over this window has to be determined. This sensitivity factor is called the partial ionization cross-section. It can theoretically be determined using Hartree-Slater models (Rez, 1989). The cross-section can also be determined using standards. The absolute number of atoms per unit area of the specimen, and the composition ratio if two elements are present in the specimen, can be determined using equations (3.11) and (3.12), respectively, which were derived by Egerton (1978):

$$N = \frac{I_k(\beta\Delta)}{I_\ell(\beta\Delta)\sigma_k(\beta\Delta)} \qquad (3.11)$$

where N is the number of atoms per unit area of the particle. The term I_k (βΔ) is the integral of the intensity above the background in the K edge over a range of energies Δ and the collection semi-angle β under which the ionization edge was collected, I_k (βΔ) is the corresponding integral for the L edge. The factor $\sigma_k(\beta\Delta)$ is the partial ionization cross-section and $I_l(\beta\Delta)$ the intensity of the zero-loss (non-scattered and elastically scattered beam) electrons with the low-loss electrons over an energy loss window.

$$\frac{N_A}{N_B} = \frac{I_k^A(\beta\Delta)\sigma_k^B(\beta\Delta)}{I_k^B(\beta\Delta)\sigma_k^A(\beta\Delta)} \qquad (3.12)$$

In addition, to obtain the integrated non-background intensity in the K edge ($I_k(\beta\Delta)$) or L edge ($I_L(\beta\Delta)$) the background arising from multiple scattering has to be removed.

Curve fitting and difference spectra are two methods frequently used to remove the background of EELS spectra. In the *curve fitting method*, power-law fits are used to extrapolate the region before and after the edge to obtain the estimated background under the edge. The energy range of the fit should not be less than 10 eV and no more than 30% of $E_{K(L,M)}$, the edge energy. Moreover, the energy range should not be so wide that it includes another edge in the energy range. In the *difference spectra method*, two normal EELS spectra from a particle displaced, for instance, by 1 eV, are collected and one is subtracted from the other giving the background-subtracted edges. This is possible because the background signals vary quite slowly while the signals from the edges vary rapidly.

3.2.3 Energy-filtered transmission electron microscopy

Energy-filtered transmission electron microscopy (EFTEM) using core-loss ionization edges is a very efficient method for measuring the chemical composition and its spatial distribution in a specimen (Grogger et al., 2005). The physical principle of the EFTEM technique is based on the EELS technique, but with the additional used of a post-column or in-column energy filter. The in-column filter is often called the omega filter. The post-column filter is manufactured by Gatan and is therefore called a Gatan imaging filter (GIF). In this work, EFTEM was performed using a GIF. The main components of the GIF system are a magnetic prism, an energy-selecting slit, quadrupole, sextupole and octupole lenses, and a multiscan CCD camera. They can be seen in Figure 3.6.

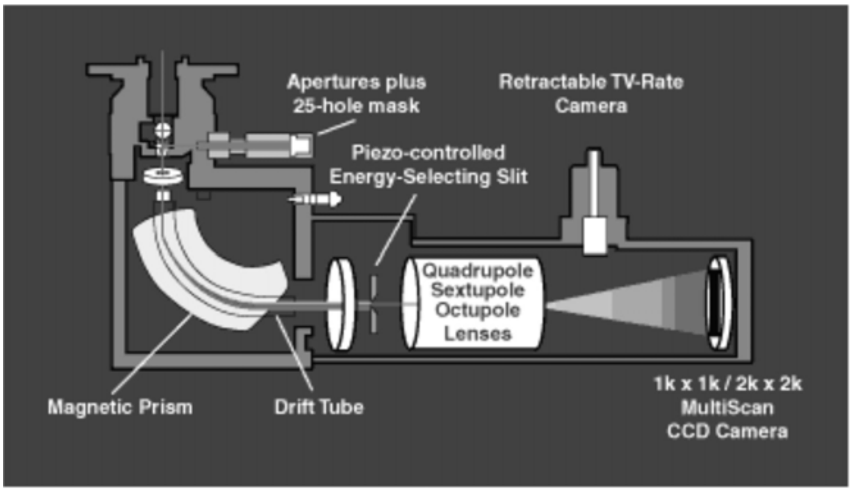


Figure 3.6: *A cross-sectional view of the Gatan image filter system.*

When performing EFTEM, the energy-selecting slit replaces the spectrometer used in the EELS technique. This slit allows only electrons with a narrow range of energies to pass through. After the slit, the electrons carry only spatial information from the specimen, i.e. the x and y values on the two-dimension plane of the specimen. The lenses are mounted after the slit to enhance the spatial information carried by the electrons before they are detected in the CCD camera. Not all the electrons passing through the slit carry information on the core-loss ionization edges. Some of them also carry information on the background. Three different energy ranges are used to subtract the background. Thus, three spectrum images will be obtained: a post-edge image and two pre-edge images. The two pre-edge images are used to estimate the background that is subtracted from the post-edge image. This is done by the software installed in the GIF system.

The EFTEM technique provides elemental information on microstructures with high spatial resolution. The main application of EFTEM is therefore the acquisition of elemental maps of the sample. The quality of the image is influenced by many experimental factors, such us the energy and the shape of the ionization edge of interest, the collection angle, the exposure time, the aberration caused by the TEM objective lens, and the accelerating voltage. In addition, sample drift, radiation damage, the characteristics of the electron detector (point spread function), instrumental instabilities (energy drift) and the electron dose that the electron source can deliver to the sample also influence the quality of the image.

A typical image of an aerosol particle obtained with the EFTEM technique can be seen on the right in Figure 3.7. This image was actually the result of combining two energy-filtered images, both obtained with a JEOL TEM-3000F microscope equipped with a GIF (GIF 2002). The accelerating voltage was 300 keV. The collection angle was 1 mrad, the analysis area was 1.49 x 1.49 µm and the resolution in the nm range. Other parameters are given in Paper IV. The image shows the elemental distribution of the aerosol particle shown on the TEM image (on the left in Figure 3.7).

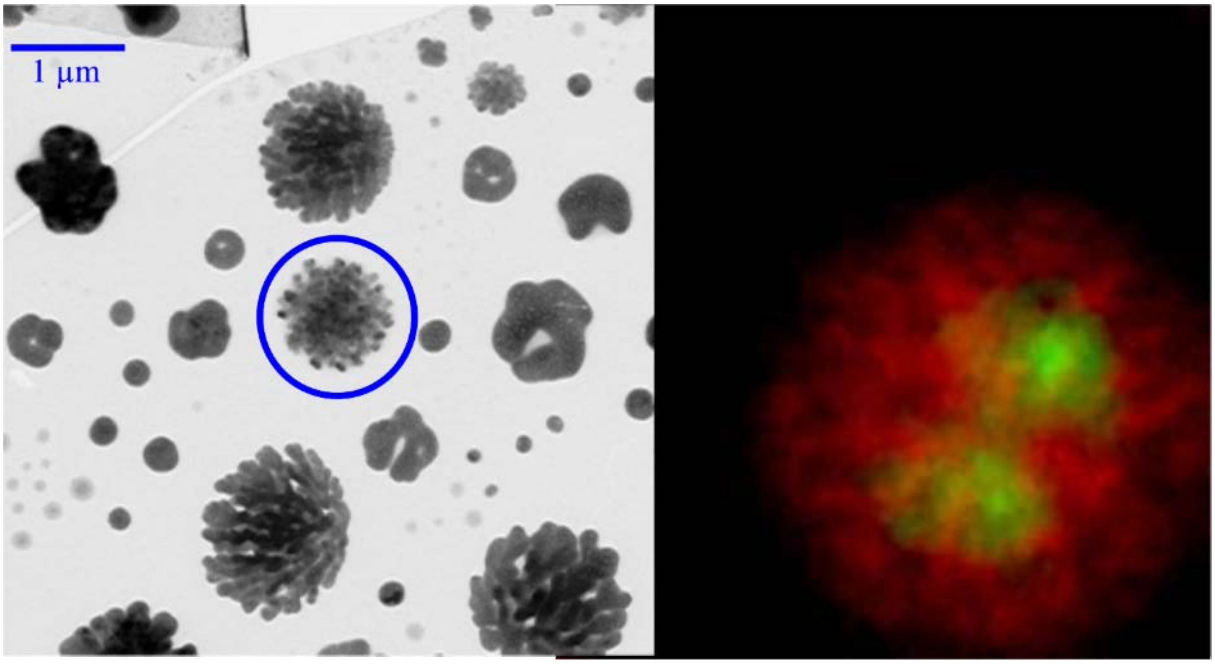


Figure 3.7: *A typical image obtained with EFTEM showing the spatial distribution of sulphur (green) and carbon (red) in an aerosol particle. The same particle is shown on the left in a TEM image* (Enclosed in a circle in the TEM image on the right.)

4. Aerosol particles in the upper troposphere and lowermost stratosphere

4.1 The CARIBIC project

CARIBIC project was undertaken for atmospheric chemistry studies of the upper troposphere and the lowermost stratosphere. It is the result of collaboration between eleven research groups from six countries. The platform comprises many scientific instruments installed in a freight container. When measurements are to be carried out the container is loaded onto a passenger aircraft equipped with an inlet for aerosol and trace gas sampling. Using a passenger aircraft to carry out research measurement reduces the cost compared with traditional aircraft-based measurements. Measurements have been carried out in this way since 1999 and will be continued at a rate of 2-3 flights per month during the next seven years. The aircraft currently used in this project is an Airbus 340-600. It has carried the CARIBIC platform from Germany to South America, to southern Africa, and to the Philippines. A large number of atmospheric trace constituents, including major greenhouse gases, and practically all halogenated compounds, as well as O_3, CO, NO/NO_y, total H_2O, methane, acetone and acetaldehyde have been studied. The aerosol composition and size distribution have also been measured.

The contribution of the research group at Lund University to the CARIBIC project is the sampling and characterization of aerosols. Characterization comprises quantitative analysis to obtain the general features, e.g. the mass concentration of the aerosol components, and single-particle analysis to gain specific information on the aerosol, e.g. the morphology. The data are then interpreted using data on other factors related to the collected aerosol such as meteorology and trace gases, which are available within the CARIBIC project. The data are used to study aerosol formation, transport and deposition, and the exchange of the aerosol between the stratosphere and the troposphere, as well as other factors that control the concentration of the aerosol.

The first phase of the CARIBIC project covered the five years from November 1997 to April 2002, and included 75 successful long-distance flights from Germany to the Indian subcontinent (63% of the flights), the Caribbean (29%) and southern Africa (8%). The Lund group developed the CARIBIC aerosol sampler, which was used during all flights from spring 1999 to spring 2002, and optimized the PIXE analysis method for the samples (Papaspiropoulos et al. 1999). Many analyses have been carried out. A large amount of data concerning the concentrations of many trace components, such as sulphur, potassium, iron, calcium titanium, arsenic and bromine, is now available.

The CARIBIC project is now in its second phase. This phase started at the beginning of 2005, after changing the aircraft from a Boeing 767-300 ER (LTU International Airways) to an Airbus 340-600 (Lufthansa), and 2½ years of instrument development. Thus far, 40 successful flights have been carried out from Germany to southern South America (40%) and to Southeast Asia (60%).

4.2 Aerosol characterization

In this section, the analysis of the aerosol samples collected from the CARIBIC platform will be described. As mention above in Section 2.2, two kinds of samples are collected: one for quantitative analysis and the other for single-particle analysis.

4.2.1 Quantitative analysis

Quantitative information about aerosol elemental concentrations is obtained with PIXE (sulphur and other heavier elements), which is routinely performed at the single-ended 3 MV accelerator (NEC 3 UH) in Lund. Elemental concentrations of light elements such as carbon, nitrogen and oxygen, are determined with the newly developed method, in which PESA is combined with PIXE (Nguyen and Martinsson, 2007).

Problems will be encountered when using PESA in connection with PIXE according to the traditional method to analyse CARIBIC samples. Firstly, the aerosol concentration in this part of the atmosphere is low (Clarke, 1993; Martinsson et al., 2001), and the collected aerosol mass in CARIBIC samples is therefore expected to be low, leading to problems with the detection limit. Secondly, the backing of these samples is organic and contains the elements of interest. These problems require the detection limits of the analysis to be very low. As such low detection limits could not be achieved with the traditional method of analysis, which uses a large beam spot that covers the entire aerosol deposit and special prepared blank samples, the method had to be adapted for the analysis of CARIBIC samples.

The newly developed method combines PESA and PIXE in a unique way. The method is based on internal blank measurements and the use of small size of the beam. The internal blanks were measured by measuring two blank spots on each sample beside the analyzing aerosol deposit. This is possible due to the properties of the AP1 film. The film is thin, containing low levels of impurities, while still being strong enough to allow the focusing of collected aerosol particles onto small spots by impaction. The MDLs obtained by measurements of internal blanks were 10 to 18 times lower than that obtained by measurements of prepared blank samples, i.e. the traditional method. These MDLs were further lowered 7.6 times by the use of a small beam area (1 mm), which enhanced the signal from the aerosol deposit relative to that of the backing. In total, the MDLs of C, N and O were lowered by factors of 130, 70 and 90, respectively.

Performing PESA as described above gives the relative elemental concentrations. To be able to convert these relative concentrations into absolute concentrations, a conversion factor is needed. This factor can be obtained by using results from a second irradiation, in which the entire aerosol deposit is analysed with PIXE, in order to obtain a quantitative measurement. The absolute concentration of an element measured with the small beam is then given by:

$$C_i = \frac{C_{ref}}{\xi_{ref}} \xi_i \qquad (4.1)$$

Where C_i and ξ_i are the absolute and the relative concentrations of element i, and the subscript *ref* refers to the concentration of a reference element; C_{ref} is the absolute concentration obtained from the second analysis with PIXE using the large beam size; ξ_{ref} is the absolute concentration obtained from the first analysis with PIXE using the small beam size, which was done simultaneously with PESA. The reference element is sulphur and was chosen because it is the dominant element of those detected with PIXE in the CARIBIC samples. This method is discussed in more detail in Paper III.

4.2.2 Single-particle analysis

In addition to the comprehensive quantitative analysis of the CARIBIC samples, the characterization of individual particles was also carried out. Theoretically, many methods can be used for analysing single particles (Maynard, 2000). A large number of analytical methods were tested to establish which one was most suitable for studying the morphology and chemical composition of the aerosol particles collected. Many of the measurements were done in collaboration with two institutes at Lund University (The National Center of High-Resolution Electron Microscopy at the Faculty of Materials Chemistry and The Department of Electron Microscopy at the Medical Faculty), and one in Darmstadt, Germany (Institut für Angewandte Geowissenschaften, Technische Universität Darmstadt).

Imaging techniques such as transmission electron microscopy (TEM), STEM (scanning TEM), environmental scanning electron microscopy (ESEM) and atomic force microscopy have been applied to CARIBIC samples to obtain morphological information. STEM is normally a suitable method for revealing small-particle morphology with high resolution. However, the particles in our samples were severely damaged when STEM was used to analyse them. This indicates that these particles are sensitive to the high-energetic, intense electron beam used in STEM. Thus a less intense, lower-energy electron beam should be used. ESEM was found to meets these requirements (Martin, 2002). The test results showed that this method was suitable for the imaging of particles in CARIBIC samples. TEM was found to be the best method for studying particle morphology in the CARIBIC project. This method was chosen due to the fact that it provides 2D image of particles without damaging them at low magnification (2200 x), and the productivity of the method is high. About ten TEM images were sufficient to provide an overview of the aerosol deposits in the CARIBIC samples.

For the chemical analysis of individual particles, methods including TEM with X-ray detection, EELS and EFTEM have been investigated. EDX provides qualitative elemental information, but as the X-ray yields are low, it takes a long time to detect a sufficient amount of X-rays from CARIBIC samples. During this time, the electron beam will cause damage to the particle being analysed. The damage was so severe that we can not use this method to perform the individual particle chemical analysis on CARIBIC EM samples. EELS and EFTEM caused less damage to CARIBIC particles. In addition, EELS was used to determine the relative compositions of individual particles, and EFTEM was used to obtain the elemental distribution map of a particle. The elements of greatest interest are carbon and sulphur.

The analysis of individual particles was carried out by first using TEM to obtain a general image of all the particle types collected in a flight. The particle types were then sorted by frequency, and the most common types analysed with EELS and EFTEM. When the relative compositions and the distribution map of the specific particle types have been determined by EELS and EFTEM, they are placed in context in order to be able to localize the source of the particles. Here, the context means the environment from which they were collected. This environment is described by parameters such us the humidity, pressure, wind velocity, altitude and longitude.

4.3 Results from aerosol characterization

Results from this work have revealed the characteristics and origin of the lowermost stratospheric sulphurous aerosol at northern mid-latitudes under volcanically quiescent conditions. It was found that the concentration of elements such us potassium and iron detected in the lowermost stratosphere were not dependent on the potential vorticity (PV) of the air mass (Figure 4.1, left), but on the season of the year (Figure 4.1, right), with peak concentrations in the spring. This finding, together with the results from other study by Papaspiropoulos et al. (2002), which showed that the concentrations of these elements in the upper troposphere reached a maximum at the same time, i.e. in the spring, indicates that they are transported across the tropopause. In the upper left diagram of Figure 4.1 it can be seen that the average content of particulate sulphur in the upper troposphere at northern mid-latitudes is 15.9 ng/m^3 at STP and in the lowermost stratosphere, the average concentration of particulate sulphur can reach a value of 62 ng/cm^3 (at 7 Potential vorticity units). This indicates the production of particulate sulphur in the lowermost stratosphere. It was found that half of the mass of particulate sulphur in the lowermost stratosphere was formed from carbonyl sulphide and the other half was dominated by particulate sulphur and sulphur dioxide which were transported across the tropical tropopause. The production of particulate sulphur in the stratosphere was estimated to be 0.066 Tg S/y. These results are discussed in more detail in Paper I.

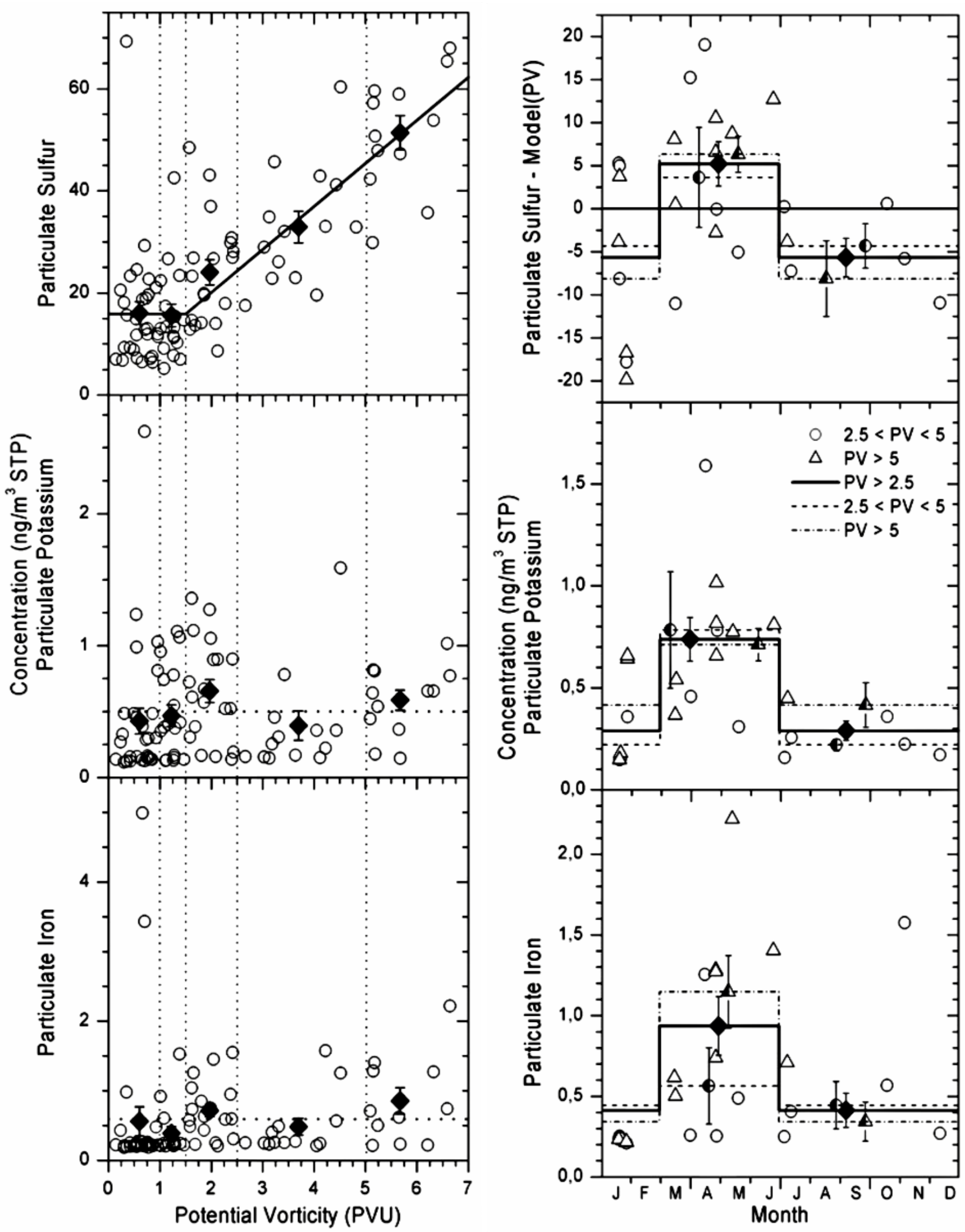


Figure 4.1: *Left: aerosol elemental concentrations at northern mid-latitudes as a function of the average potential vorticity. Open circles represent the measurements. The filled diamonds give averages and their standard deviations over the PV regions indicated by the vertical dotted lines. The dotted horizontal lines show the average concentrations of potassium and iron, while the bold line in the sulphur graph consists of two linear fits to the data. Right: aerosol elemental concentrations at northern mid-latitudes as a function of season for*

samples of average potential vorticity of more than 2.5 PVU. The particulate sulphur concentrations are given as the difference between the original value and the value obtained from the linear model shown on the left side of the figure.

This work results in the possibilities to access the quantitative information on C, N and O. It was found that C, N and O together with S constitute the major components of the aerosol in the tropopause region. The average concentrations of these elements are listed in Table 1. Further details of the analysis are presented in Paper III.

Table 1: *Concentrations and minimum detection limits for major elements in the aerosol samples collected from CARIBIC platform.*

	C	**N**	**O**	**S**
No. of 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†), ng/m^3	3.3	1.0	1.6	(0.2*)

†) MDL with the 1 mm beam perfectly centred over the aerosol deposit.

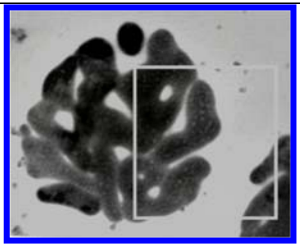
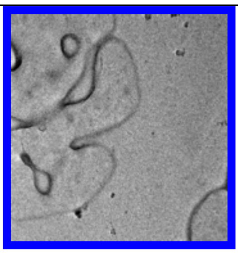
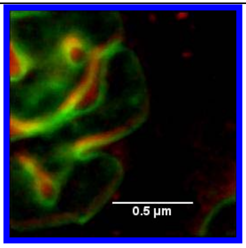
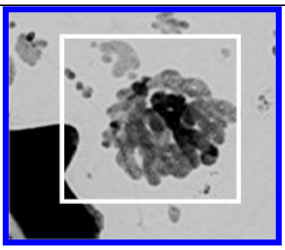
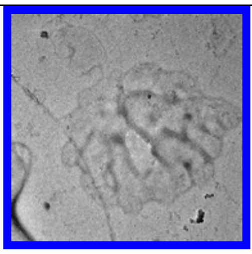
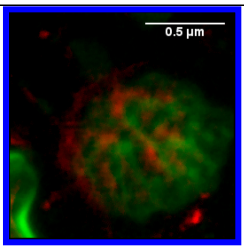
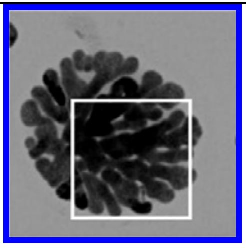
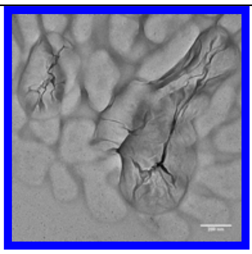
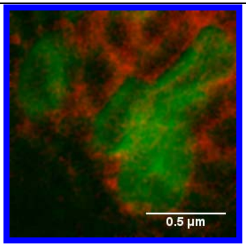
*) Not applicable to the method, because the 1.5 ng/m^3 STP detection limit with 5.5 mm collimator for quantification of atmospheric concentrations need to be exceeded.

Additionally, more than 30 types of aerosol particles appeared in nine samples along a flight track at 10 km altitude between Frankfurt, Germany to Santiago de Chile were identified. A dependence of particle morphology on the location where they were collected was found in this study. Furthermore, sulphur and carbon were quantified by PIXE and PESA. The result shows that the concentration of sulphur varied approximately by a factor of 50 over nine samples. The lowest concentration was found on the sample collected from the inter-tropical convergence zone (ITCZ) and the highest one was found on the sample collected from the stratosphere region. The composition expressed as the particulate carbon-to-sulfur concentration ratio (C/S) varied between 0.5 and 3.5, with the lowest C/S ratio in the lowermost stratosphere and the highest in the tropics of the southern hemisphere.

Figure 4.2 shows images of particles that represent the extratropics of the northern hemisphere (NH), the southern hemisphere (SH), the tropics NH, SH and the ITCZ. In column a, particles were imaged by the TEM technique in low magnification. Column b shows the same particles or the same type (images 6 and 7) of particles taken after EFTEM analysis and with higher magnification. Column c shows EFTEM maps as mixed and colorized images of sulphur (green) and carbon (red). Yellow and orange colors indicate mixture of the two elements. Analyses of individual particles with EFTEM damaged the particles to varying degree. The results can be summarized as follow:

- Almost all particles analyzed contained a mixture of carbonaceous and sulfurous matter.
- Large particles showed complicated, branched structures where the sulfurous and carbonaceous fractions were spatially separated.
- In particular the stratospheric large particles tended to be highly branched indicating carbonaceous interior surrounded by sulfurous matter.
- Central particles of analyzed satellite-containing particles were chemically mixed.
- Satellite particles were found to contain carbonaceous matter.

More results and discussion about these particles can be found in paper IV.

Nr	**a**	**b**	**c**	**Comment**
1				NH extratropics Sample 1 Type S
2				SH extratropics Sample 7 Type S
3				Tropics north of ITCZ Sample 3 Type S

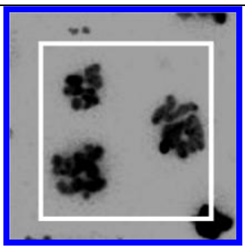
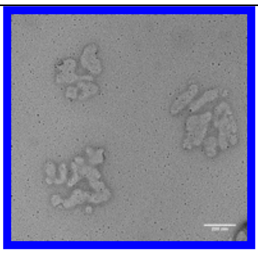
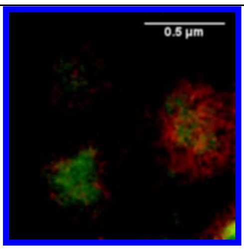
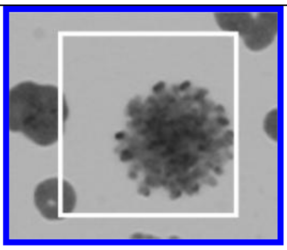
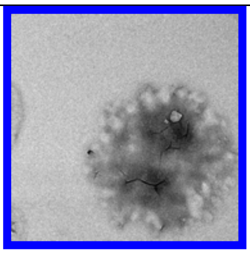
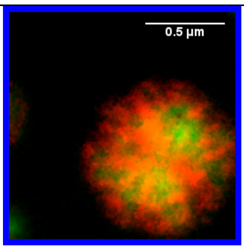
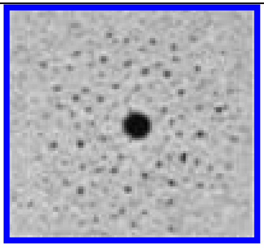
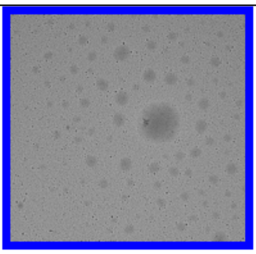
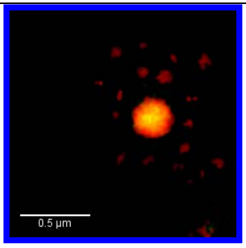
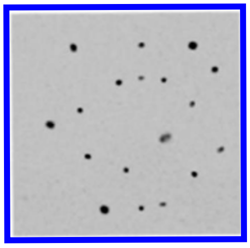
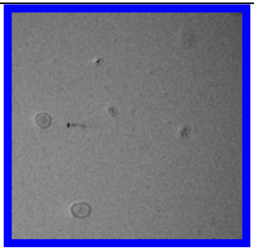
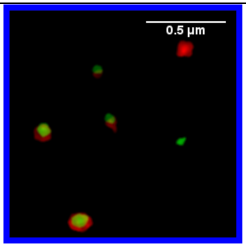
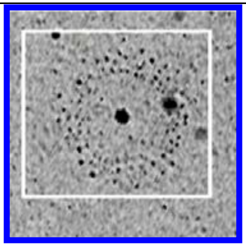
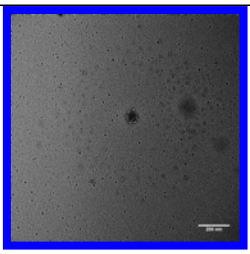
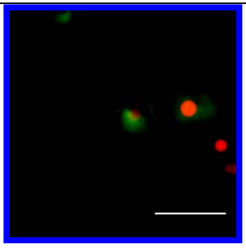
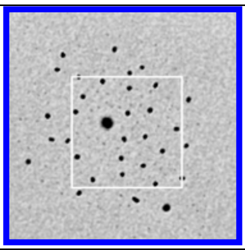
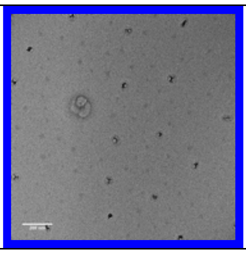
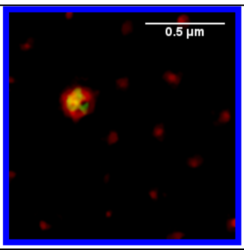
4				Tropics south of ITCZ Sample 5 Type OT
5				Lowermost stratosphere Sample 9 Type SC
6				NH extratropics Sample 1 Type Rs
7				SH extratropics Sample 7 Type OTg
8				ITCZ region Sample 4 Type Rm
9				Lowermost stratosphere Sample 9 Type Rgt2

Figure 4.2: *Typical particles that were chosen to be analyzed for chemical distribution. In column a, particles were imaged by the TEM technique in low magnification. Column b shows the same particles or the same type (images 6 and 7) of particles images but taken after EFTEM analysis and with higher magnification. Column c shows EFTEM maps as mixed and colorized images of sulfur (green) and carbon (read). Yellow and orange colors indicate mixture of the two elements.*

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