Comparative parallel characterization of particle populations with two mass spectrometric systems LAMPAS 2 and SPASS

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Abstract

Two transportable laser mass spectrometers, Single Particle Analysis and Sizing System (SPASS) and Laser Mass Analyzer for Particles in the Airborne State (LAMPAS 2), have been applied to investigate the dependence of spectra patterns on instrumental parameters and data evaluation procedures in an inter-comparison experiment. Laboratory experiments showed the spectral response of both instruments for mineral particles before and after heterogeneous reactions. During a period of 47 h, both instruments determined size and chemical composition of several thousand single particles of an ambient particle population. Time-resolved evaluation (1-h resolution) of specific ion signals, which showed a characteristic temporal evolution, in combination with meteorological information, was used to select four periods for separate evaluation of particle spectra. Application of the two particle classification algorithms, fuzzy c-means clustering and k-means clustering, on the same data set (SPASS) showed only minor differences in spectral patterns and class abundances caused by the clustering method ("soft" or "hard" clustering). Spectral patterns determined for the data sets of two instruments (SPASS and LAMPAS 2) were similar for some particle types and could be compared directly (e.g., mineral or carbonaceous particles). For other types of particles, spectral patterns differed from each other and had to be interpreted using additional information on instrumental parameters (e.g., laser wavelengths or irradiance) and experimental conditions. The different response of SPASS and LAMPAS 2, as reflected in the different abundances of particle classes, indicates the necessity to determine adjustment factors for each instrument, for different particle classes, to enable a direct comparison of quantitative information from such online aerosol mass spectrometers and from bulk analysis. The reported results are an important basis for a general database of single particle spectra, spectral patterns of common and specific particle classes and abundances of these classes for atmospheric aerosols, showing their dependence on particle size, geographic location, meteorological conditions and time of analysis.
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1. Introduction

During the last 15 years, aerosol science has been strongly influenced by analytical data from improved measurement techniques for particle characterization. The development of online techniques for particle analysis [1–7] provides a reduction of artefacts and chemical modifications by particle sampling and transportation. The use of specific inlet systems that transfer particles from their natural environment into the analytical system,

and the development of transportable and reliable instruments with long-term stability of all operating parameters were the basis for an enhanced application of the technique. Online mass spectrometric instrumentation with single particle detection is ideal for an instantaneous and detailed high throughput chemical characterization of single particles. These instruments provide the required high temporal resolution combined with a highly specific characterization of aerosol particle populations, especially when using bipolar ion detection [3]. Transportable mass spectrometers have been applied during several field campaigns, e.g., for the determination of basic data for source apportionment of traffic and industry emissions [8–12], for bioaerosol detection [13–15], for investigations of atmospheric chemistry for climate

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modelling [16–22] or for the characterization of micro-meteorological states of the atmospheric boundary layer [23].

Statistical, computer-based analysis of mass spectrometric data from single aerosol particles is the second major task for a successful analysis, apart from the reliable operation of the instrument. Classification algorithms are used to sort the measured mass spectra into groups according to similarities and to determine basic particle classes out of large populations, thus yielding detailed information on the aerosol composition [24–27]. A particle class displayed as a spectral pattern is representative for a certain type of aerosol particles and can be interpreted chemically.

A major advantage of this online technique is the determination of size and chemical composition of particles with high temporal resolution. Applications of the method in atmospheric science showed evolutions of specific chemical components, single particle mass spectra or particle classes as a function of time, size and/or geographic location with a direct correlation to meteorological conditions or atmospheric processes [20,28].

At present, the variety of analytical methods for online particle characterization differs in instrumental parameters (e.g., particle inlet system, laser wavelength, laser pulse energy, irradiance, mass spectrometric analyzer) and data evaluation techniques (e.g., fuzzy or k-means clustering, artificial neural networks) [21,24,26,28]. The statistical methods for data handling used so far in single particle analysis are not well compared, resulting in sometimes deviating particle classes, class abundances and different interpretations of aerosol populations. The enhanced application of data from online mass spectrometric particle analysis for source identification, in climate modelling or other fields depends essentially on the comparability, reproducibility (precision) and correctness (accuracy) of measurement results. Comparative investigations using different online mass spectrometric instruments, and other analytical methods (e.g., bulk analysis), including the evaluation of different data analysis procedures, are urgently needed for data validation.

In December 2002, an inter-comparison experiment was performed at the Institute for Environment and Sustainability of the European Commission in Ispra, Italy, to investigate the dependence of spectra patterns on instrumental parameters and data evaluation procedures. The two transportable laser mass spectrometer instruments Single Particle Analysis and Sizing System (SPASS [28]) and Laser Mass Analyzer for Particles in the Airborne State (LAMPAS 2 [29]) were applied in laboratory and ambient measurements for a direct comparison of mass spectral information from single aerosol particles. Combination of the data should provide the means for an improved data interpretation by establishing common rules for the assignment of spectra patterns to specific particle classes. A basic goal of the experiments was to establish the first combined database of mass spectrometric data (single particle spectra, spectral patterns of common and specific particle classes, etc.) of ambient particles determined with different instruments as a basis for future common use.

This paper presents the mass spectra of single particles, in various size ranges, acquired simultaneously with SPASS and LAMPAS 2 to study the response of both instruments and to find similarities and differences of the detected spectra.

A second major task of the reported investigations was a first comprehensive comparison of two independent evaluation methods for single particle mass spectrometric data. The two basic clustering methods, k-means clustering and fuzzy c-means clustering, were applied to the same ambient data set (SPASS) to characterize the influence of evaluation procedures on the results.

The combined time-correlated and size-resolved evaluation of ambient data sets from both instruments, SPASS and LAMPAS 2, with the same clustering method (fuzzy c-means clustering) was used to obtain patterns of particle classes and their abundances that reflected the different response of both instruments to the investigated ambient particle population. A comparative evaluation of similarities and differences of results from both instruments are discussed with respect to instrumental parameters and data evaluation techniques, in order to define rules for spectra interpretation and for the evaluation of determined class abundances (e.g., by using instrumental adjustment factors for the abundance of specific particle classes).

2. Experimental

2.1. Instrumentation

The two mobile online systems for mass spectrometric analysis of single aerosol particles, SPASS and LAMPAS 2, were built for a fast, size-resolved determination of particle compositions in continuous long-term measurements. A short description is given here showing the main similarities and differences between both instruments that influence spectral patterns and abundances. More detailed descriptions of the instruments are published elsewhere [28,29,36].

Impact-free particle inlet into the mass spectrometers is realized by employing either an aerodynamic lens (SPASS) or a differentially pumped nozzle/skimmer system (LAMPAS 2). The aerodynamic lens of SPASS is optimized for a particle size range between 400 nm and 4 μm, whereas the inlet system of the LAMPAS 2 instrument transfers particles with diameters between 200 nm and 5 μm. For particle detection, both instruments use a laser velocimeter, consisting of two cw laser beams (laser wavelengths: $\lambda = 488$ and 514 nm for SPASS and $\lambda = 532$ nm for LAMPAS 2). These are separated by a fixed distance of 4 cm (SPASS) and 2.5 mm (LAMPAS 2), respectively. When a particle crosses both laser beams, the transit time between the two detected scattered-light signals is used as a measure of the size-dependent particle velocity. After particle detection, a pulsed UV–laser (Nd:YAG laser with $\lambda = 266$ nm in SPASS and nitrogen laser with $\lambda = 337$ nm in LAMPAS 2) is actively triggered to ionize the detected particles downstream of the detection region. Although the laser pulse energies ($E = 40$ mJ and 260 μJ) for the SPASS and LAMPAS 2 instruments are very different, the laser power density is approximately 5×10^9 W/cm^2 in both systems due to the different focus diameters ($d = 300$ and 30 μm) and different laser pulse lengths ($t = 8$ and 3 ns) in the SPASS and LAMPAS 2 systems. The distances between the second

detection laser beam and the particle ionization region are 28 cm (SPASS) and 1.5 mm (LAMPAS 2). In both instruments, positive and negative ions are simultaneously analyzed by two time-of-flight (TOF) mass analyzers. The SPASS system uses one linear TOF analyzer and one reflectron TOF analyzer with mass resolving powers of $M/\Delta M = 150$ and 1000, respectively. Under normal operation conditions, positive ions are detected by the reflectron and negative ions by the linear TOF system, although the polarities can be inverted if necessary. The LAMPAS 2 instrument is equipped with two linear mass analyzers reaching a mass resolving power of $M/\Delta M = 300$ for both ion polarities.

During laboratory measurements, the number size distribution of particles was measured by an optical particle counter (OPC, model 1.108, Grimm GmbH, Ainring). Ambient particle detection was accompanied by determination of physical (size, number size distribution), and chemical aerosol parameters (using bulk samples from the EMEP site in Ispra [30]). Meteorological data (e.g., temperature, relative humidity from [31]) were also incorporated into the evaluation. Ambient particle sampling was realized using a PM 10 inlet system (Derenda, Germany) with Tygon tubes for aerosol transport (i.d. = 4 mm) of 2 m and 8 m for SPASS and LAMPAS 2, respectively.

2.2. Measurement site

During the inter-comparison experiments performed from December 10 to 17, 2002, aerosol particles from various populations were measured simultaneously with the SPASS and the LAMPAS 2 instruments. Several laboratory experiments using a glass chamber (230 L) or a Teflon bag (2.4 m^3) as reaction chambers as well as ambient measurements were performed. The measurement site (Institute for Environment and Sustainability (IES) of the European Commission's Joint Research Centre in Ispra, Italy) is located about 5 km east of the lake Lago Maggiore and approximately 60 km north-west of Milan at an altitude of 220 m (45°48′43.4″North–8°37′37.4″East). The ambient aerosol can be influenced by local emissions and long distance transportation from the industrial area of Milan or the Po Valley.

2.3. Data evaluation

Single particle spectra evaluation was performed in different ways for laboratory and ambient measurements.

The investigation of the response of both instruments on an identical particle composition was performed in laboratory measurements. Single particle spectra detected before and after reaction in a smog chamber were qualitatively compared and evaluated.

The main goal of the study was the comparison of large data sets from two instruments and the comparison of clustering methods. Datasets of both instruments from a long-term ambient aerosol measuring period were evaluated to find the characteristics of the instruments and the statistical evaluation methods. Time-resolved evaluation of single particle spectra was possible

on the basis of several criteria such as particle size, detection time, specific ion signals or chemical classes, etc.

A data pre-processing tool was necessary to extract the information contained in each original spectrum: peak masses, peak intensities, peak areas. Common information on detection time, particle size, etc. was also stored in the resulting data table of each particle.

Because of the instrumental differences, the pre-processing of spectra from SPASS and LAMPAS 2 for further statistical evaluation was also different. In the SPASS instrument, the detection efficiencies vary for negative and positive ions as a consequence of the very different flight tube lengths (454 and 1428 mm) and the use of two different mass analyzers (linear and reflectron). For data pre-processing, the spectra were peak-analyzed first (positive-ion and negative-ion mass spectra of each particle were normalized separately to their respective maximum value) and then combined into one vector. The resulting data matrix contained masses and relative peak intensities.

The LAMPAS 2 instrument has an almost identical setup for positive and negative ion detection and similar detection sensitivities for both ion polarities. Therefore, the two mass spectra of an individual particle were combined into one vector directly and then automatically peak-analyzed, resulting in a list of masses and peak areas normalized to the highest value of both spectra.

In addition, both pre-processing algorithms were employed to convert the mass values into nominal masses (i.e., integer values).

Data matrices can be sorted with respect to several criteria or can be used for correlations to other available data, to display time lines of specific ion signals or to establish a data matrix of spectra of interest for further classifications. Statistical classification algorithms (hierarchical cluster analysis, principal components analysis, k-means clustering, fuzzy clustering, artificial neural networks) are typically used to sort the particle spectra and to reduce the number of single particle spectra to a few particle classes for extraction of the most important information available in the data set [24,26–28].

Classification of the detected bipolar ion spectra from SPASS and LAMPAS 2 was realized in this study by two independent algorithms. The fuzzy c-means algorithm (fuzzy clustering) allows a "soft" attribution of individual particles to classes (groups of chemical similar particles) using membership degrees of similarity [24]. Alternatively, a "hard" clustering was used (k-means algorithm) assigning the particles to classes by a yes/no decision [28]. Classification of spectra populations was repeated at least five times and specific cluster criteria were used to select the best clustering result.

3. Results and discussion

3.1. Laboratory experiments

During the joint experiment in Ispra, several laboratory experiments were performed simultaneously with the SPASS and the LAMPAS 2 instruments for basic investigations of particle interactions with inorganic and organic particles or gases. As an example of these investigations, single particle spectra detected
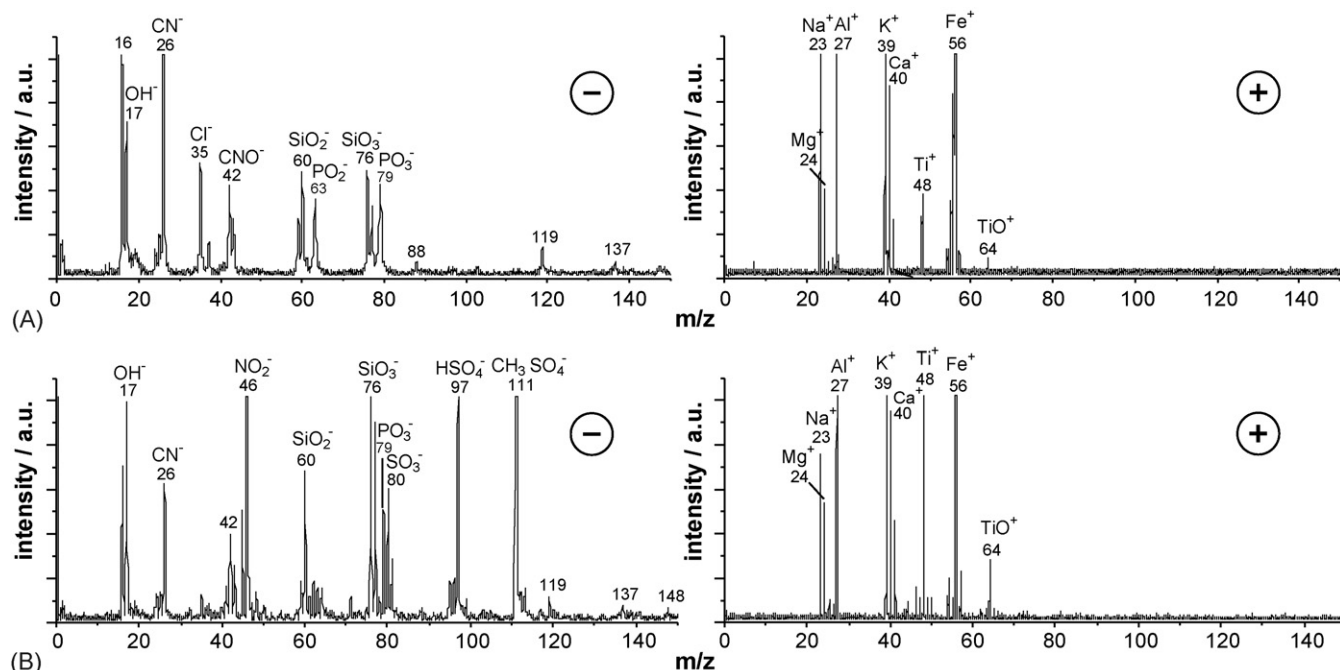
Fig. 1. Mass spectra of two single mineral particles (Cap Verde) measured with SPASS before (A) and after (B) the reaction with sulphur dioxide gas and OH-radicals, produced via photolysis of CH_3ONO. Aerodynamic particle diameters are 0.95 and 1.1 µm, respectively.

with the two instruments before and after the reaction of mineral particles with sulphur dioxide gas and OH-radicals, produced via photolysis of CH_3ONO, are shown in Fig. 1 (SPASS) and Fig. 2 (LAMPAS 2).

The spectra of un-reacted particles were detected immediately after dispersion of mineral particles (Saharan dust from Cap Verde) into the teflon bag smog chamber (2.4 m³). The introduction of CH_3ONO (3 ppm) and sulphur dioxide gas (3 ppm)

combined with light from UV-lamps lead to additional signals in the particle spectra of both instruments. Comparison of the spectra of pure mineral particles (Figs. 1A and 2A) shows that the main peaks for the identification of minerals obviously appear in the patterns of both instruments, including aluminium (Al^+, $m/z = 27$), calcium (Ca^+, $m/z = 40$), iron (Fe^+, $m/z = 56$), titanium (Ti^+, $m/z = 48$), silicon (as SiO_3^-, $m/z = 76$) and phosphate (PO_2^-, $m/z = 63$; PO_3^-, $m/z = 79$). The sensitivity for some of
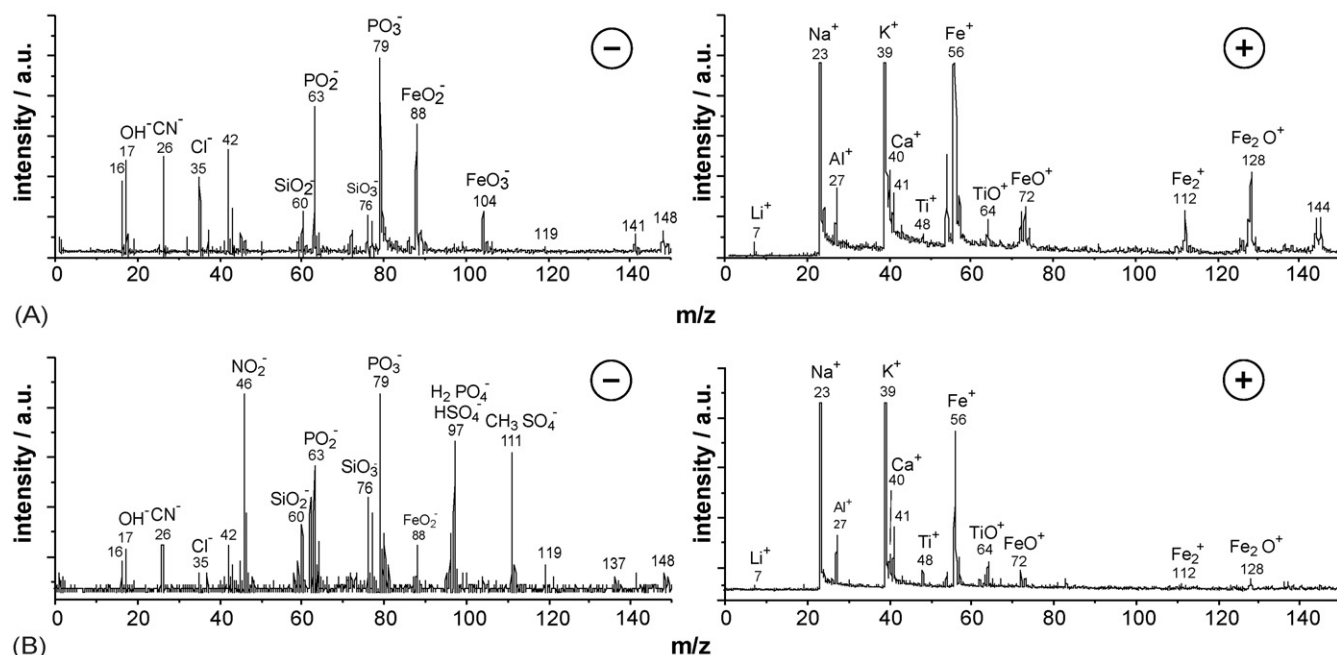

Fig. 2. Mass spectra of two single mineral particles (Cap Verde) measured with LAMPAS 2 before (A) and after (B) the reaction with sulphur dioxide gas and OH-radicals produced via photolysis of CH_3ONO. Aerodynamic particle diameters are 1.3 and 1.0 µm, respectively.

these components is better in SPASS spectra (e.g., titanium, silicon and aluminium), whereas in LAMPAS 2 spectra phosphate and iron oxides can be identified more easily.

After photo-reaction, additional signals of nitrate and sulphate (NO_2^-, $m/z = 46$ and NO_3^-, $m/z = 62$; HSO_4^-, $m/z = 97$) and methane sulphate (the photo-reaction product $CH_3SO_4^-$, $m/z = 111$) could be detected with both instruments. The appearance of reaction signals especially in the negative ion spectra underlines the importance of bipolar ion detection [3].

As a result of these investigations it can be concluded that both instruments, SPASS and LAMPAS 2, clearly have the capability to identify typical signatures for mineral particles, independent of chemical modifications on the surface of these particles. Further combined investigations of other particle types (e.g., organic or carbon particles) and of mixtures of these types have to be carried out with different online particle mass spectrometers to determine mass spectral signatures and detection efficiencies of the instruments for the various particle types. The final goal would be the determination of adjustment factors for certain particle types (also called "particle classes") to adjust the abundances of corresponding classes to each other. The determination of such adjustment factors in the laboratory by comparing instruments response for artificial particle types and especially for complex mixtures of particle types (as can be found in ambient particle populations) is feasible only with high uncertainties due to the large variability in such populations. Therefore, in the reported study an ambient particle population was investigated to compare directly the mass spectral signatures and abundances of particle classes determined with the two mass spectrometric systems LAMPAS 2 and SPASS. The performed experiments were only a first attempt in this direction. Further comparisons would have to be conducted for a much larger set of different ambient populations, to come to a conclusive and relevant list of adjustment factors that would eventually lead to more quantitative information from single particle mass spectrometers.

3.2. Ambient measurements

During a long-term measurement period of 47 h, SPASS and LAMPAS 2 were operated in parallel to analyze ambient particles. During this time, both instruments detected a similar total number of 6026 and 10,491 mass spectra for SPASS and LAMPAS 2, respectively. The size distributions of detected particle spectra (Fig. 3) are quite similar for both instruments with a maximum of detected spectra around a particle diameter of 1.0 μm. The differences of the size distributions are probably a result of the two different inlet systems (nozzle/skimmer system in the LAMPAS 2 instrument and an aerodynamic lens in the SPASS instrument).

Although the focus of this paper is not the investigation of correlations between particle composition and atmospheric processes, the evolution of meteorological conditions and common particle parameters is still an important issue here because it directly influences the choice of periods suitable for statistical spectra evaluation.

The mean temperature during the ambient measurements was 4.8 °C (ranging from 1.6 to 9.4 °C) with precipitation only on
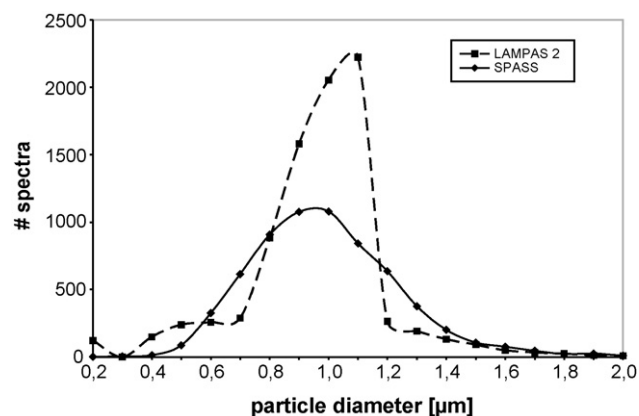

Fig. 3. Size distribution of single particle mass spectra detected and analyzed by SPASS and LAMPAS 2 instrument during the ambient measurement period in Ispra, December 2002.

December 15, 2002, of 1 mm (between 10 and 11 a.m.) and westerly wind with speeds always below 10 km/h. The temporal variation of several meteorological parameters (Fig. 4) showed significant changes during the measurement period. Changes in the chemical composition of the particle populations and/or abundances of chemical classes were thus expected during this period.

Particle number concentrations were measured with an optical particle counter (OPC, model 1.108, Grimm GmbH, Ainring) in a diameter range from 0.3 to 10 μm and a system consisting of a differential mobility analyzer (DMA) and a condensation particle counter (CPC, model 3010, TSI GmbH, Aachen, Germany) for particles between 10 and 600 nm. The time course of the data from DMA and OPC in comparison to the number of detected particle spectra per hour of SPASS and LAMPAS 2 is shown in Fig. 5.

The evolution of temperature, atmospheric pressure, OPC data and detected spectra in Figs. 4 and 5 shows interesting similarities, e.g., the time course of detected spectra (LAMPAS 2) reflects in a good agreement the measured number concentration of sub-micron and micron particles (OPC data). A reason for the reduced detection efficiency of the SPASS instrument especially in the last third of the ambient measurements might be due to changes in instrumental parameters (e.g., the flow characteristics of the aerodynamic lens caused by partial obstruction of the inlet aperture or a reduction of ionization laser irradiance—see also Section 3.4).

Taking into account the time courses in Figs. 4 and 5, a time-resolved evaluation of specific ion signals of all spectra from SPASS and LAMPAS 2 with 1-h resolution was performed. This evaluation gave a time resolved chemical histogram of the data sets [8,32,33]. Temporal variation of the relative abundances of secondary components (NH_4^+, $m/z = 18$; NO_2^-, $m/z = 46$ and NO_3^-, $m/z = 62$; HSO_4^-, $m/z = 97$), carbonaceous material (C_2^-, $m/z = 24$; $C_3^{+/-}$, $m/z = 36$; C_4^-, $m/z = 48$) and organic substances ($C_7H_7^+$, $m/z = 91$; $m/z = +284$ (org2); $m/z = +299$ (org3)) were determined by counting mass spectra showing these ions. The result of this evaluation is shown for LAMPAS 2 data in Fig. 6.
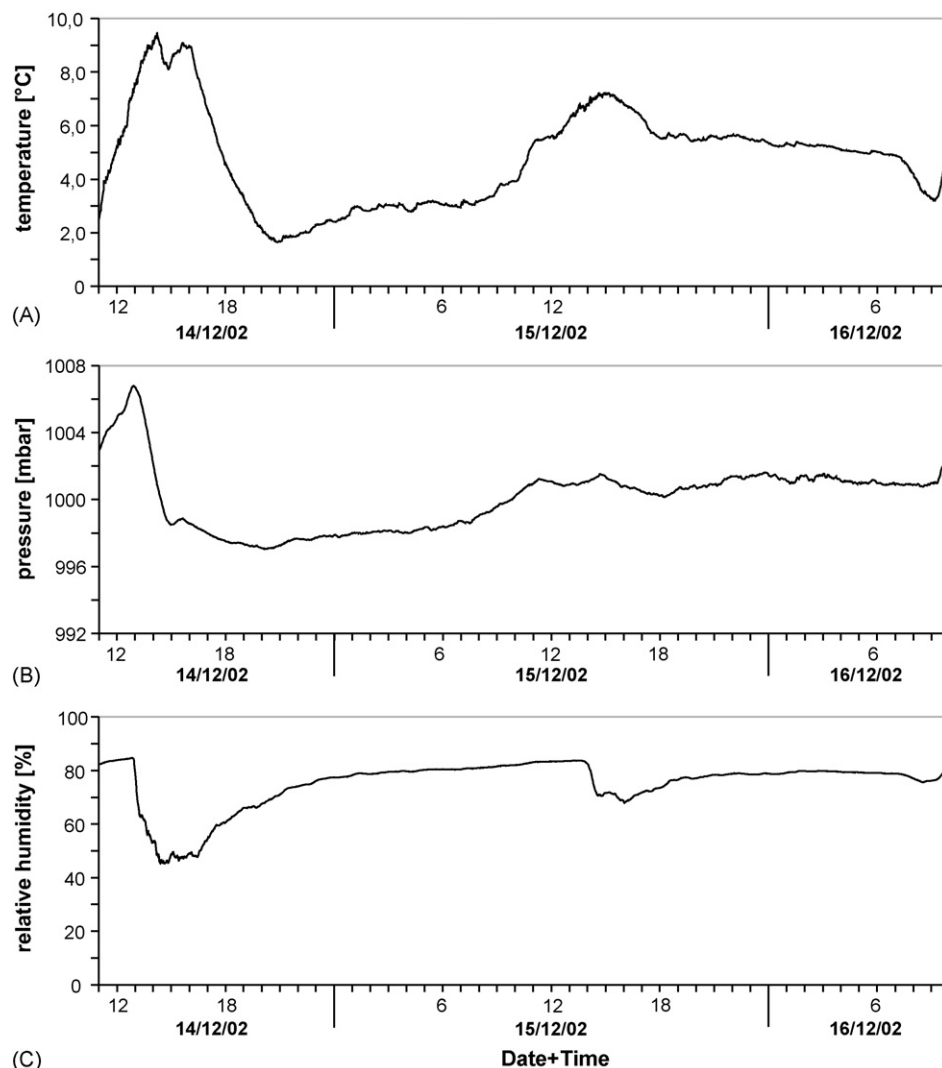
Fig. 4. Time courses of temperature (A), barometric pressure (B) and relative humidity (C) during the ambient measurement period in Ispra, starting on 14 December 2002, 11:00 o'clock.

These determined time lines were the basis for the selection of four periods for a separate evaluation of particle spectra from SPASS and LAMPAS 2 as indicated by the arrows in Fig. 6B. The characteristic temporal evolution of the species in comparison to ambient temperature, pressure and particle number concentration reflects the necessity of a time-correlated spectra evaluation. During each of the four time periods, almost uniform particle populations were expected due to stable atmospheric conditions. The application of statistical classification procedures should show differences in spectra patterns and abundances of particle classes between the four periods.

In period 1, the number of mass spectra acquired by SPASS and LAMPAS 2 was relatively low, 330 and 177, respectively. During the other periods the detected number of spectra varied between 879 and 1791 for SPASS and between 1622 and 3563 for LAMPAS 2. The spectra of periods 2–4 could therefore be further sub-divided into two size ranges of sub-micron and super-micron particles to find additional differences in the chemical composition dependent on particle size. As a result of this subdivision, seven populations for each data set (SPASS and

LAMPAS 2) were generated and for the classifications between 382 and 1068 spectra of SPASS and 670–1859 spectra of LAMPAS 2 were used (periods 2–4).

3.3. Comparison of classification procedures

For the SPASS data set, the two classification algorithms fuzzy and k-means clustering were applied to sort the spectra of the seven sub-populations into classes. The classification of each of the seven (sub-) populations was repeated at least five times, to improve the precision of the clustering result. Optimization of clustering criteria in both algorithms resulted in the determination of an optimum number of classes for the description of each sub-population. The representative particle classes (seven to eight for each sub-population) were then compared to each other using a hierarchical cluster analysis (HCA) to find similarities of the patterns and to further reduce the overall number of classes. HCA was applied first to the 56 k-means classes and 70 fuzzy classes (from all sub-populations) separately and in a second step to all 126 classes together. Seven major particle
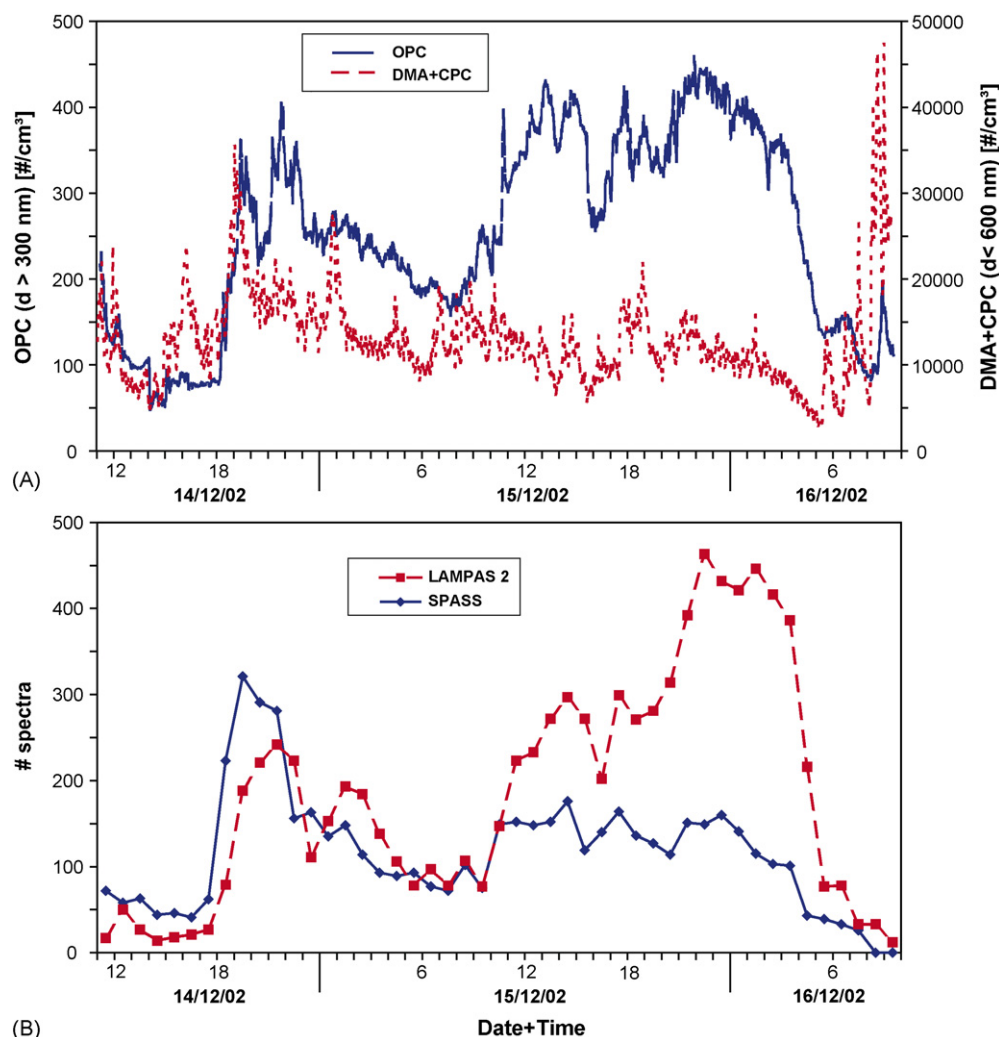
Fig. 5. Number concentration of particles measured with a condensation particle counter (DMA + CPC) and optical particle counter (OPC) (A) and number of particles detected and analyzed per hour by SPASS and LAMPAS 2 instrument (B) during the ambient measurement period in Ispra, December 2002.

classes were identified by this procedure for the SPASS spectra, both after k-means clustering and after fuzzy clustering. As an example, spectra patterns representing the class centres of fuzzy clustering are shown in Fig. 7.

The patterns in Fig. 7a and b are very similar and represent mineral particles, with differences in peak intensity ratios. The patterns include characteristic signals for mineral components such as sodium (Na^+, $m/z = 23$), magnesium (Mg^+, $m/z = 24$), aluminium (Al^+, $m/z = 27$), calcium (Ca^+, $m/z = 40$), iron (Fe^+, $m/z = 56$), and titanium (Ti^+/TiO^+, $m/z = 48/64$). In addition, secondary components (NH_4^+, $m/z = 18$) and a variety of anions can be identified (e.g., O^-, OH^-, $m/z = 16$ and $m/z = 17$, nitrate fragments NO_2^-, $m/z = 46$, and NO_3^-, $m/z = 62$, phosphate fragments, PO_2^-, $m/z = 63$, and chloride, Cl^-, $m/z = 35/37$).

The patterns of Fig. 7c and d show carbon ion signals for both ion polarities (C_n, $n = 1$–4) and secondary components like ammonium (NH_4^+, $m/z = 18$), nitrate and sulphate (NO_2^-, $m/z = 46$; NO_3^-, $m/z = 62$; HSO_4^-, $m/z = 97$). Additional signals of organic fragments and hydrocarbon ions can be identified ($COOH^-$, $m/z = 45$; CH_3COOH^-, $m/z = 59$; $C_2H_5COOH^-$,

$m/z = 73$; $C_3H_7^+$, $m/z = 43$; $C_4H_3^+$, $m/z = 51$; $C_5H_3^+$ $m/z = 63$; $C_6H_5^+$, $m/z = 77$). The pattern in Fig. 7e is dominated by salt and secondary components and the pattern of Fig. 7f shows very high intensities of secondary components with an additional indication of organic substances at $m/z = 111$ for $CH_3SO_4^-$ in the negative ion pattern (see also Fig. 1).

The pattern in Fig. 7g can be unambiguously attributed to carbonaceous particles, mixed with small amounts of secondary components.

The spectra patterns shown in Fig. 7 are similar to those found in earlier campaigns in this area of northern Italy, indicating a regional aerosol influenced by the urban area of Milan under winter conditions [28].

The patterns determined for the SPASS populations by k-means clustering were similar to the fuzzy clustering patterns in Fig. 7, with variations of peak intensities below 20%. This was verified by HCA, where similar patterns of both algorithms (k-means clustering and fuzzy clustering) resulted in identical chemical groups. Differences between k-means clustering and fuzzy clustering patterns result from different strategies of
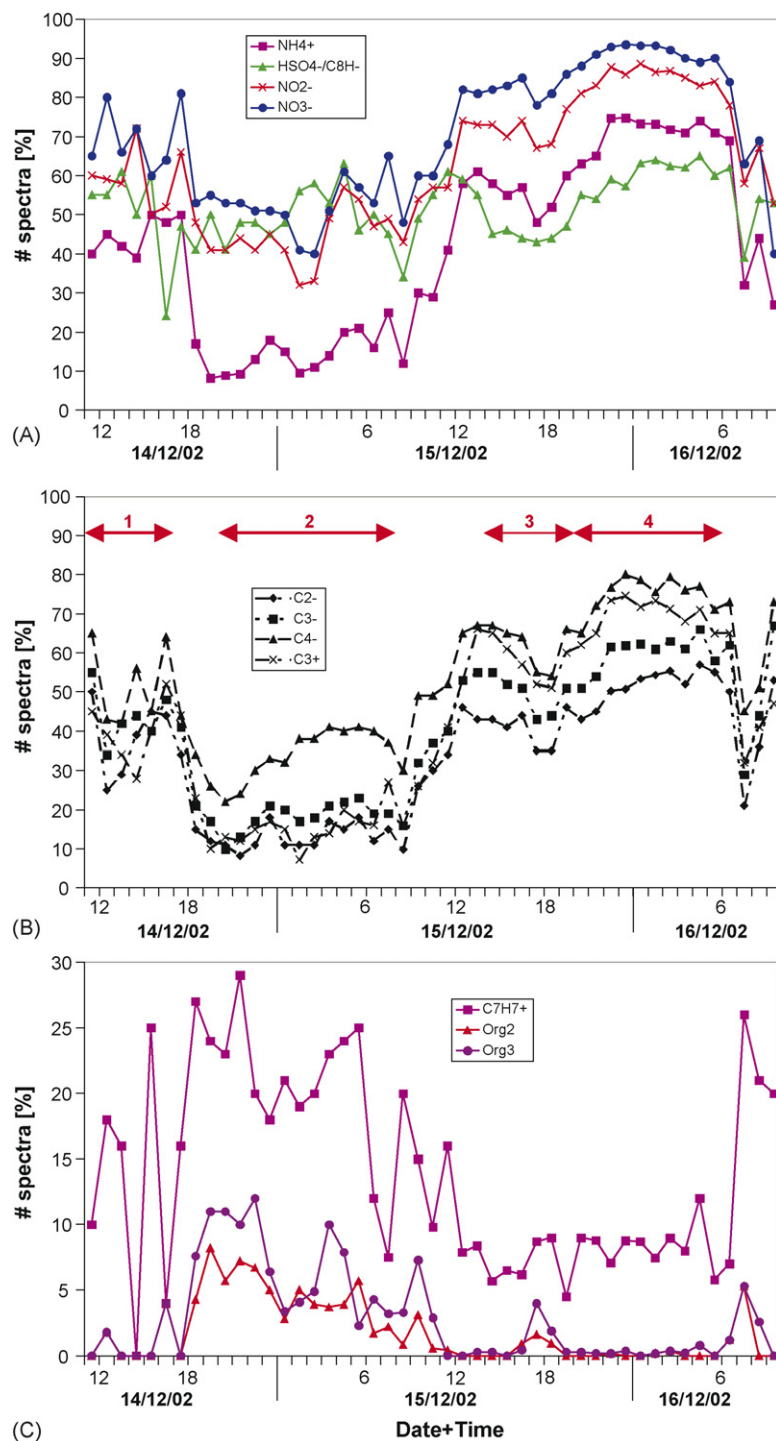
Fig. 6. Time lines of specific ion signals of LAMPAS 2 spectra for secondary components (A), carbonaceous material (B) and organic substances (C) during the ambient measurement period in Ispra, December 2002.

classification of the two methods. k-means clustering assigns mixed particles "hard" to the class with the highest correlation and calculates class centers as averages of all spectra assigned to a certain class [28]. The abundance of a class is the sum of all particles assigned to the class relative to all particles of the population. In contrast to this procedure, fuzzy clustering determines membership degrees of similarity between class center and single particle spectrum ("soft" clustering). The position of

the class centers is determined by an iteration process [24] and the class abundance is the sum of all membership coefficients of the particle population to the relevant class.

The seven or eight particle classes determined by k-means and fuzzy clustering for each sub-population of the SPASS data set were combined to five chemical groups using a HCA procedure and manual confirmation. This procedure of post-combination of classes to chemical groups was preferred to the
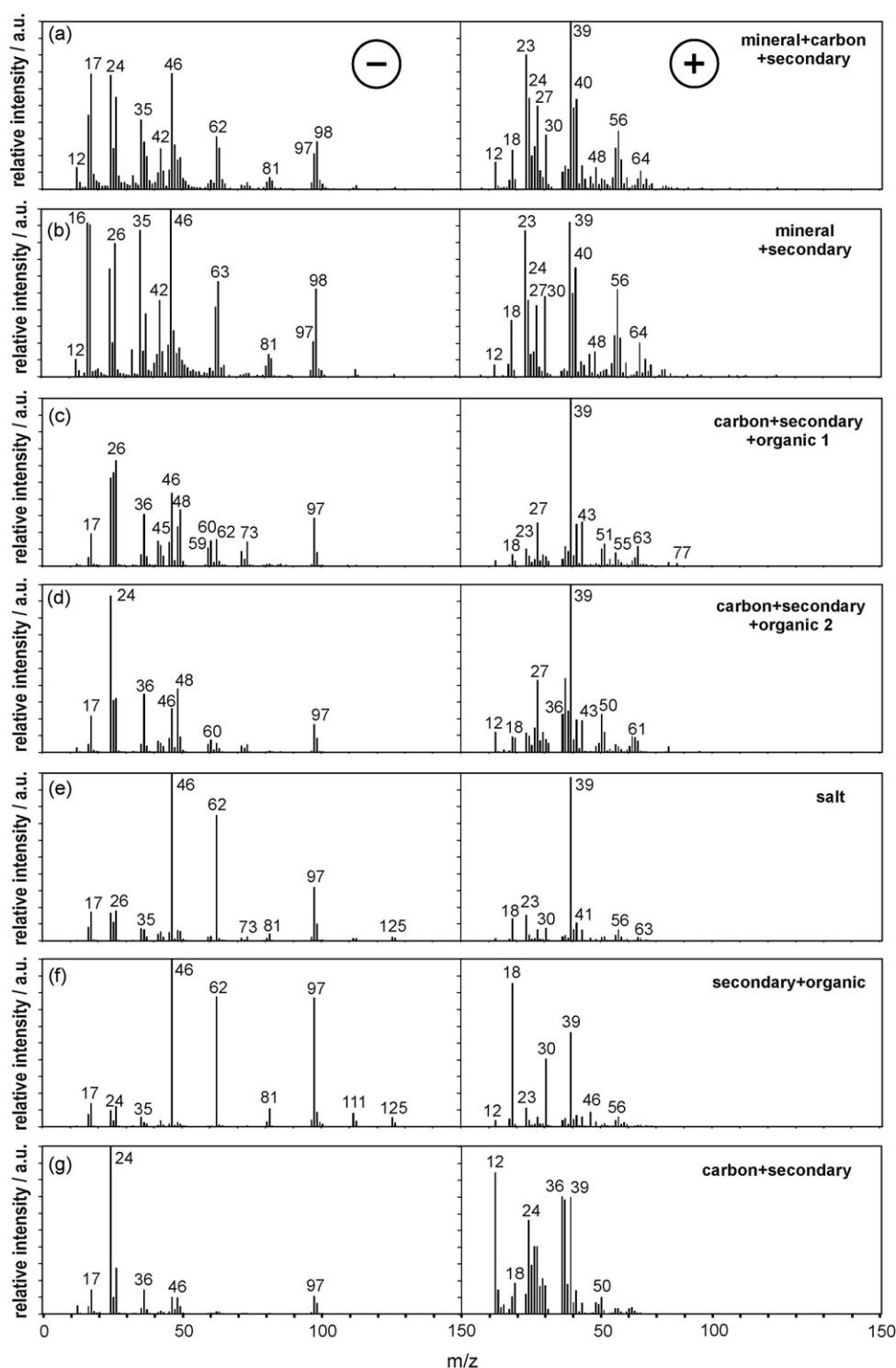
Fig. 7. Spectra patterns of seven main chemical classes (a–g) representing part of the complete measuring period and the full size range determined with fuzzy clustering algorithm and HCA for SPASS spectra.

use of a smaller number of classes in the clustering step. The latter would lead to a stronger averaging of spectra. Classes with low abundance, especially if they show only small deviations in their patterns from dominant classes, would then be lost completely. Comparison of the abundances of the five chemical groups divided into two size ranges is shown in Fig. 8 for the four periods.

The abundances of the five chemical groups show a significant variation depending on period and also on particle size. For example, a higher abundance of mineral particles is observed in the super-micron size range. Periods 3 and 4 show similar abundances of mineral/salt (~40–50%) and carbon/organic particles (~50–65%). In contrast to this, in period 2 very high abundances of ~70–90% carbon/organic particles are observed. This
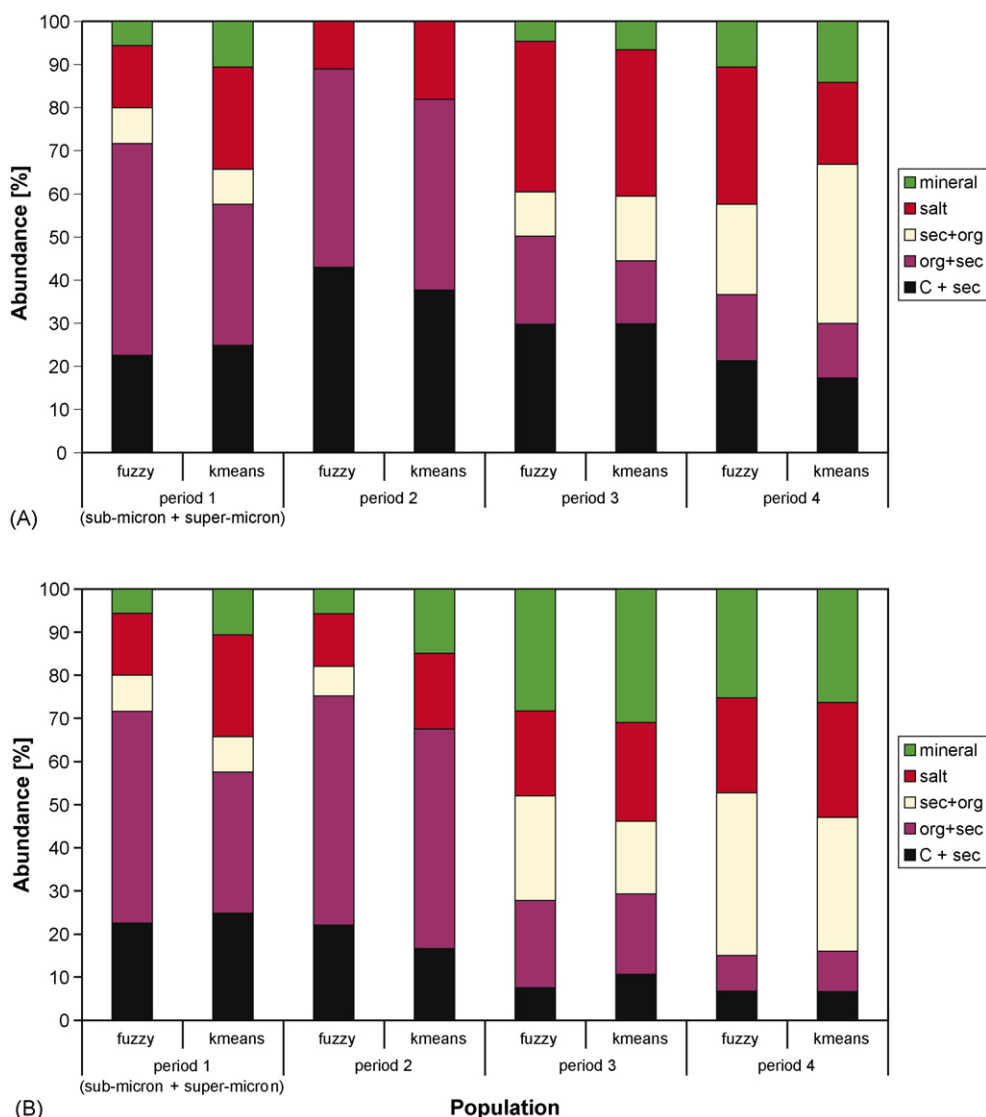
Fig. 8. Abundances of 5 chemical groups in two size ranges for sub-micron (A) and for super-micron particles (B) for four time periods during the ambient measurement in Ispra, December 2002, as determined with k-means clustering and fuzzy clustering for SPASS spectra.

is in agreement with earlier measurements where carbonaceous material dominated during periods of low particle concentration [28]. For period 1, all particle sizes are classified together due to the small number of detected spectra. Therefore the abundances are an average over all particle sizes and are identically presented in both diagrams for the two size ranges.

For the given SPASS data, the abundances are similar for the two classification methods with deviations below 10% in all periods and size ranges. A necessary requirement to reach such a good agreement is time-correlated and size-resolved data evaluation to reduce effects of strong averaging or overestimation of specific chemical classes due to suppression of minor classes and class mixtures.

3.4. Comparison of instruments, SPASS and LAMPAS 2

In addition to the evaluation of SPASS populations, the fuzzy clustering algorithm was used to classify the spectra in the seven populations of the LAMPAS 2 data set. The 70 patterns resulting for the seven sub-populations were then compared using hierarchical cluster analysis (HCA) to find similarities within the patterns and to reduce the number of classes. As a result of this procedure, seven major classes of particles were identified for LAMPAS 2 spectra (Fig. 9).

In Fig. 9, only the mass range up to $m/z = 150$ is displayed to facilitate a comparison between LAMPAS 2 and SPASS patterns (Fig. 7). The SPASS spectra typically showed no ion signals in the mass range above $m/z = 150$ u.

The LAMPAS 2 pattern for mineral particles in Fig. 9a is characterized by a high sodium ion signal combined with lithium ($m/z = 7$ u), calcium ($m/z = 40$ u), iron ($m/z = 56$ u), and phosphate (PO_3^-, $m/z = 79$ u) signals. Additionally, carbon ion signals (C_n^-/C_n^+ with $n = 2$–11) and secondary components (ammonium with $m/z = 18$ for NH_4^+; nitrate with $m/z = 46$, 62 for NO_2^-, NO_3^-; sulphate with $m/z = 97$ for HSO_4^-) are identified.
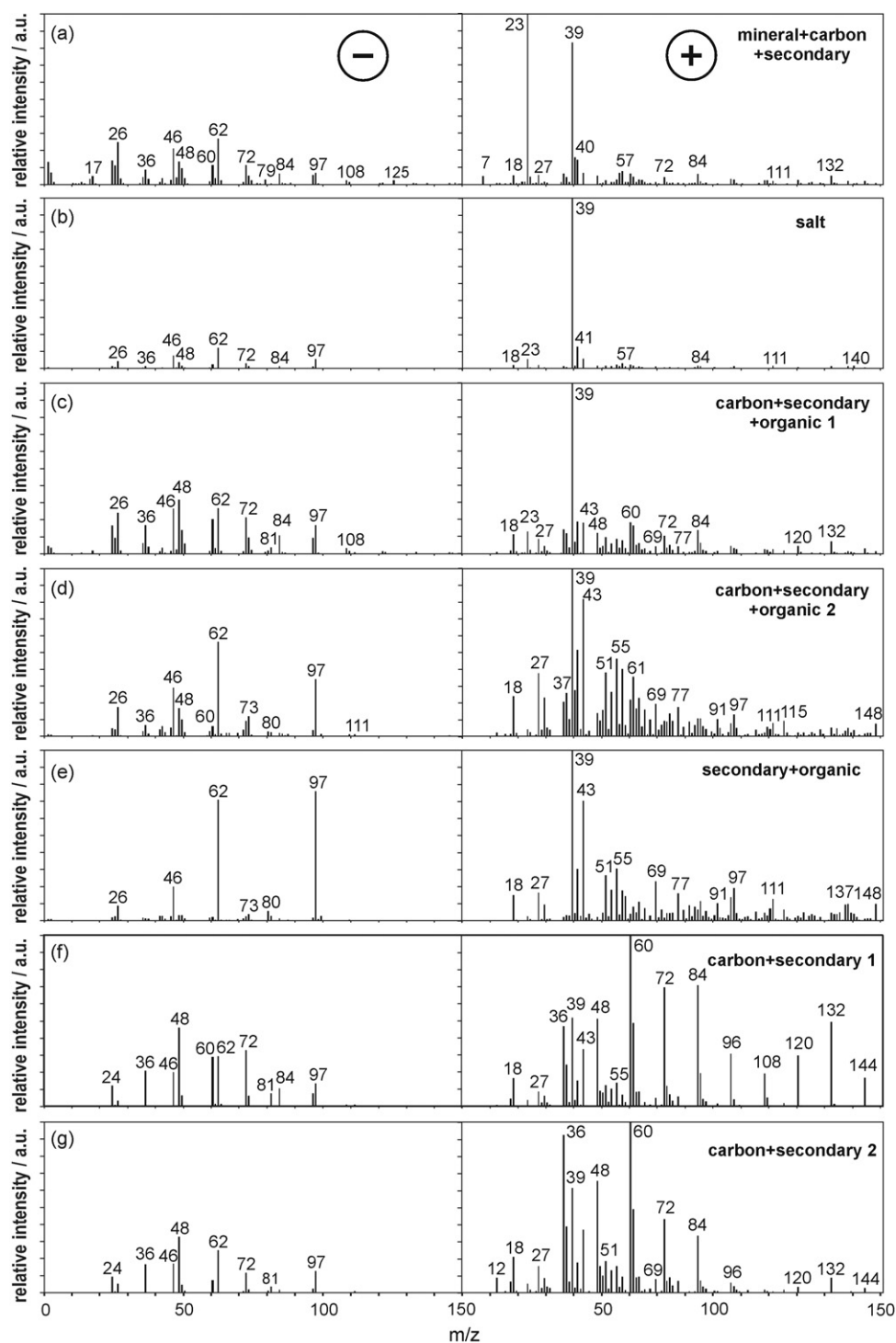
Fig. 9. Spectra patterns of seven main chemical classes (a–g) representing part of the complete measuring period and the full size range determined with fuzzy clustering algorithm and HCA for LAMPAS 2 spectra.

Potassium ions dominate the pattern in Fig. 9b. This pattern also shows carbon ion signals with lower intensity (e.g., C_2^-, C_3^-, C_3^+, C_4^-, C_6^-, $m/z = 24, 36, 48, 72$).

The pattern in Fig. 9c shows a mixture of carbon particles with secondary and organic components. The latter are assigned as $C_3H_7^+$, $m/z = 43$; $C_4H_3^+$, $m/z = 51$; $C_5H_3^+$ $m/z = 63$; $C_6H_5^+$, $m/z = 77$.

The two classes that are dominated by carbon ion and secondary ion signals (Fig. 9f and g) mainly differ in the intensity of carbon ions at higher m/z values. A possible reason for this could be variations in the effective laser irradiance for ionization of the same particle type. Therefore the abundances of these two classes are added into one chemical group of particles.

Patterns similar to those in Fig. 9 (except d and e) were also observed at other rural and urban locations [17,29,34–36] and reflect "common" particle classes. In contrast to this, the patterns in Fig. 9d and e, which show very high intensities in the organic ion signals were observed in a field study with LAMPAS 2 for the first time, indicating "typical" patterns for the Ispra location under the specific conditions. The original single particle spectra and the spectral patterns of both classes also showed ions with masses of up to $m/z = 300$ u and more.

A qualitative comparison of the patterns determined form SPASS spectra (Fig. 7) and LAMPAS 2 spectra (Fig. 9) is possible using the appearance of certain ion signals or groups of signals in the patterns. Five main groups of patterns can be identified:

1. patterns with mineral signals (Fig. 7a and b for SPASS and Fig. 9a for LAMPAS 2);
2. patterns of salt particles (Fig. 7e for SPASS and Fig. 9b for LAMPAS 2);
3. patterns with significant organic signals (Fig. 7c and d for SPASS and Fig. 9c and d for LAMPAS 2);
4. patterns dominated by secondary components (Fig. 7f for SPASS and Fig. 9e for LAMPAS 2);
5. patterns dominated by carbon signals (Fig. 7g for SPASS and Fig. 9f and g for LAMPAS 2).

The intensity ratios and structure of the patterns of these five groups vary, of course, for the two instruments due to the instrumental differences and due to the different pre-processing algorithms. Different detection sensitivities for identical ions, for example, are caused by the different ionization laser wavelengths of the two instruments. In addition, different pre-processing algorithms are used for the spectra of the two instruments. Normalization to the highest value of peak areas for both ion polarities of a particle is used in the LAMPAS 2 instrument. This procedure conserves the quantitative information contained in the spectra for both ion polarities. As a result, the signal intensities can vary significantly between positive and negative ion patterns (see Fig. 9). In contrast to this, the SPASS spectra were normalized separately and peak intensities instead of peak areas were used. Therefore, the SPASS patterns for both ion polarities appear with similar signal intensities.

Comparison of the mineral patterns indicates a higher sensitivity of SPASS for several mineral components (e.g., calcium, iron, titanium) as described in Section 3.1 for Figs. 1 and 2. The molecular fragmentation of organic and carbon-rich molecules is much more pronounced in the SPASS patterns compared to LAMPAS 2 patterns, probably caused by the different laser irradiation conditions. As a consequence, organic components can be identified easier in LAMPAS 2 spectra.

The appearance of ammonium ions ($m/z = 18$ for NH_4^+) in all patterns and of organic signals in many of the patterns with both instruments is specific for the particle populations measured during the ambient field campaign in Ispra as compared to other campaigns [17,29,34–36]. This is in agreement with the observation of relatively high concentrations of ammonium and

nitrate observed in ambient particles in the Ispra and Milan area during winter [30].

A quantitative comparison of the evaluations of the seven sub-populations of both instruments is shown in Fig. 10.

For both instruments, the abundances of the five main chemical groups of particles show characteristic variations depending on particle size and measurement period. A preferred detection of specific particle groups for selected size ranges was found with both instruments (e.g., mineral particles in the super-micron range). The appearance of mineral particles in the sub-micron size range and their higher abundances determined with SPASS is an indication for a higher detection efficiency of these particles in comparison to the LAMPAS 2 instrument. The SPASS instrument also determined higher abundances for particles with secondary components probably as a result of the shorter ionization laser wavelength. This was observed by other research groups as well. The detection response for ammonium ions in comparison to sodium measured for nebulized salt solutions, for example, was observed to be about three times higher for an ionization laser wavelength of 266 nm (as in the case of SPASS) than for 337 nm (LAMPAS 2) [36,37]. The higher abundances of organic particles in periods 3 and 4 determined with LAMPAS 2 reflect their easier detection by the LAMPAS 2 instrument.

In periods 3 and 4 a similar trend for the group of mineral/salt and for the group of carbon/organic particles is observed for SPASS and LAMPAS 2. In periods 3 and 4 the abundances of mineral/salt determined for SPASS (39–48%) and LAMPAS 2 (20–40%) and for carbon/organic particles accordingly show a quite good agreement considering the discussed differences of the instruments and of the data pre-processing. In periods 1 and 2, the combined abundances of the two chemical groups, mineral/salt and carbon/organic, for SPASS and LAMPAS 2 show similar trends in both size ranges, but in the SPASS populations the carbon/organic group is dominating whereas in LAMPAS 2 the mineral/salt groups have higher abundances. A reason for this result might be a difference of atmospheric conditions compared to periods 3 and 4 as reflected in a lower number concentration of particles in period 1 (Fig. 5A) and in a drop of temperature during period 2 (Fig. 4A). These different conditions could lead to a change of the particle population. In combination with the different sensitivity of the instruments to specific particle classes this might lead to an overestimation of specific chemical classes if one assumes a dominance of specific particle classes during periods of high and low number concentrations [28].

The total number of particles detected with SPASS and LAMPAS 2 in periods 3 and 4 were significantly different (Fig. 5B). A change in instrumental conditions of the SPASS instrument during the course of the measurement campaign (e.g., a clogging of the particle inlet orifice, leading to losses in the particle beam formed by the aerodynamic lens or a misalignment of the detection laser beams) is a possible reason for this discrepancy. However, the number of mass spectra determined with SPASS during these periods was high enough to enable high quality statistical evaluation. Furthermore, the determined particle classes were comparable to those of the other periods suggesting no significant influence of the reduced number of spectra.
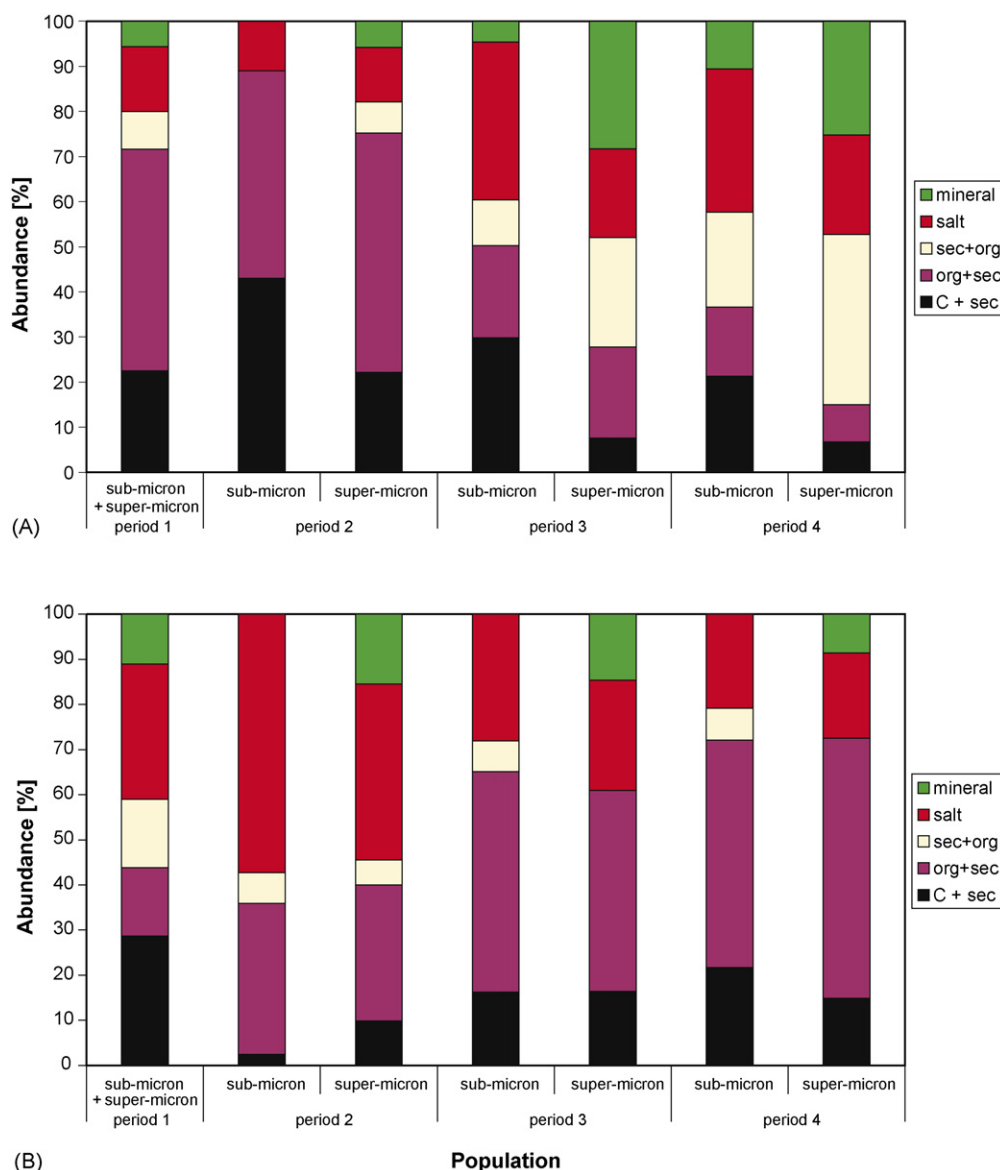
Fig. 10. Abundances of five chemical groups in SPASS (A) and LAMPAS 2 (B) populations for four periods during the ambient measurement in Ispra, December 2002, determined with a fuzzy clustering algorithm.

In period 1 only a small number of particles were detected and particles of all sizes were classified together for SPASS and LAMPAS 2. Therefore, the determined patterns and abundances are an average of all particle sizes, but they also reflect the variations in the response of the two instruments on the measured particle population. It is important to note that the SPASS particle inlet system biases the detection of particles towards the upper sub-micron and super-micron size range due to the chosen parameters of apertures and pressures compared to the LAMPAS 2 instrument with a lower size cut of 200 nm (see also the size distributions of particles measured with both instruments, shown in Fig. 3). This leads to an overestimation by the SPASS instrument of particles which are more abundant in the upper sub-micron range. This can also explain the similarity of class abundances of sub-micron and super-micron particles for SPASS classes.

3.5. Comparison of single particle and bulk abundances

It is not the goal of this paper to discuss in detail the results of single particle analysis in the context of atmospheric processes. Fig. 11 summarizes the results of available bulk analysis for the two relevant days during the ambient measurements.

The PM 10 total mass for each of the 24 h periods (sampled on quartz filters and determined by weight) is comparable for both days, but the chemical composition of the aerosol varies. The OC/BC values were measured with a carbon analyzer (RA 10M, IHW System Technik, Berlin, Germany) by thermal treatment without optical corrections and the inorganic ions (NH_4, SO_4, NO_3) were determined by ion chromatography (Dionex DX120). On the second day (periods 3 and 4), a decrease of carbonaceous compounds and an increase of secondary and other compounds can be observed. This is also reflected by the SPASS
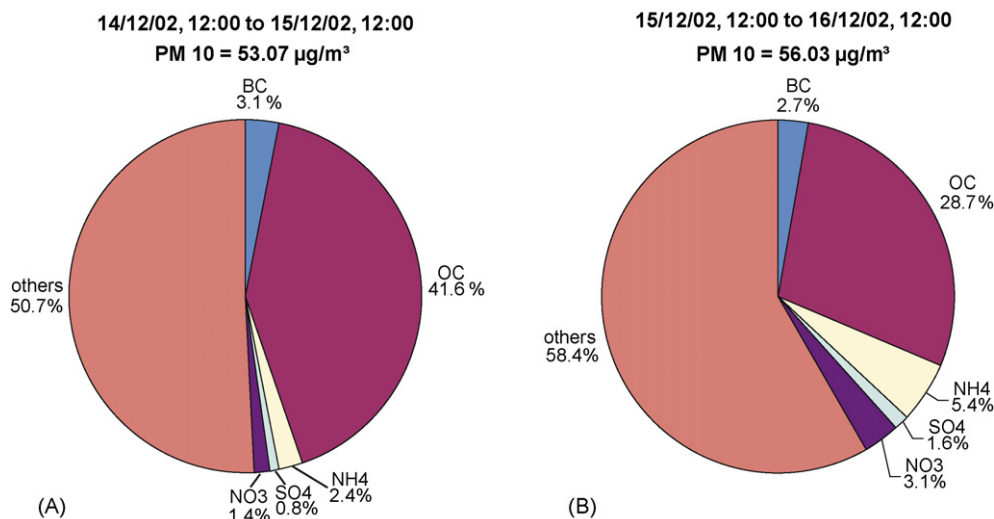
Fig. 11. Bulk (PM10) composition of selected compounds during the ambient measurement period in Ispra, December 2002: (A) 14/12/02–15/12/02 and (B) 15/12/02–16/12/02 (OC, organic carbon; BC, black carbon).

abundances for the relevant classes. Unfortunately, the amount of PM 10 mass that was not assigned to a specific compound is relatively high on both days and makes up more than 50% on the second day (Fig. 11B).

In conclusion it can be said that the different responses of SPASS and LAMPAS 2 reflected in the different abundances of particle groups indicates the necessity to apply adjustment factors for various particle classes for each instrument. Only then can quantitative information from different online mass spectrometers be compared, either to each other or to quantitative bulk analysis of aerosols. Basic investigations are necessary in the future to characterize the influence of instrumental parameters of mass spectrometers on particle spectra and on abundances of particle classes for a better understanding of the reported results.

3.6. Quality of spectra patterns

The advantage of the fuzzy clustering in comparison to k-means clustering is the determination of degrees of membership of single particle spectra to chemical classes. These membership coefficients are listed for all classified spectra and can be used to find particles that belong to a high degree to a certain class (e.g., membership degree μ above 80%) or to find mixed or exceptional particles with low membership degrees to some or all classes (e.g., μ below 40%). The use of membership coefficients is a helpful criterion to characterize the quality of representative class centers displayed as spectra patterns for the given particle groups. For the classification of a chosen number of classes (e.g., 6 classes), the fuzzy algorithm determines the membership degrees of the single particles to each of the classes, which varies between 0 and 100% (the sum of all memberships of a single particle to all classes is 100%). An obvious validity function for the class centers is the number of particles with a high membership degree to a class [24]. The class centers calculated with a fuzzy clustering algorithm for the sub-populations of SPASS and LAMPAS 2 spectra in period 1 were evaluated

using the membership degrees of the respective single particles as a function of the chosen number of classes for two limits of μ (60 and 80%). In Fig. 12, the number of particles that have a membership coefficient above these two limits for numbers of classes between 4 and 10 is displayed.

Fig. 12 shows that for LAMPAS 2 the number of original single particle spectra with high membership coefficients for a certain class is higher than for SPASS spectra, reflecting a better agreement of original single particle spectra with calculated spectra patterns for LAMPAS 2 than for SPASS. For 7 classes, for example, 52.5% of LAMPAS 2 particles and 32.4% of SPASS particles belonged to more than 80% to a single class indicating an external mixing of these particles. The main reason for this result probably lies in the difference of the instrumental setup between SPASS and LAMPAS 2. In the SPASS instrument, the interaction region between the aerosol beam and the particle is rather extended, due to the fact that the laser focus diameter is around 300 μm. In addition, the laser beam is sent in counter propagating to the aerosol beam. Thus particles can be hit across the whole acceptance region of the mass spectrometer (the entrance slit is 4 cm wide in the direction of laser and aerosol beams) and produce ion signals on the detectors. The advantage of this setup is a rather high particle hit rate. The disadvantage is that a substantial number of particles, which finally are registered in the mass spectrometers, are not hit centrally. This means that large differences in the power of the ionizing laser beam are "seen" by the particles and therefore relatively strong variations in ion intensities for different single particles of the same particle class can occur. The situation for the LAMPAS 2 instrument is different. In this case, the focus diameter is a factor of 10 smaller and the ionizing laser beam is sent in perpendicular to the aerosol particle beam. This leads to a small and well defined ionization region and thus a better reproducibility of particle spectra. Another contribution might be due to the differences in pre-processing of the data (use of peak areas for LAMPAS 2 and peak intensities for SPASS, together with a different normalization procedure). Therefore the intensity ratios
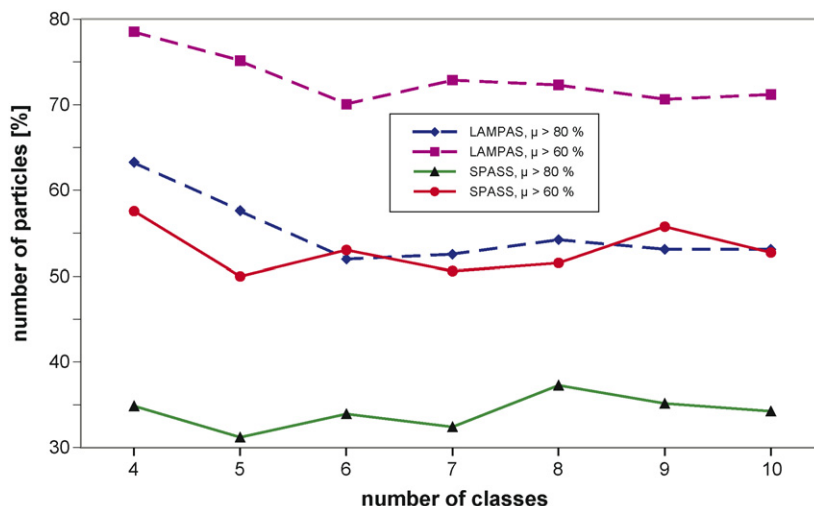
Fig. 12. Portion of particles with a maximum membership coefficient μ above a limit of 60 and 80% vs. numbers of classes for the sub-populations of SPASS and LAMPAS 2 spectra in period 1 of the ambient measurement in Ispra, December 2002, classified with a fuzzy clustering algorithm.

and structure of the single particle spectra used for classification with the fuzzy algorithm can vary significantly between spectra of both instruments and can influence the clustering result. The results in Fig. 12 are an example only. The behaviour has to be confirmed for every new classification and population, but similar results were found for the particle populations of the other sub-populations of SPASS and LAMPAS 2.

4. Conclusion

During the inter-comparison experiment performed in Ispra in December 2002, the two transportable laser mass spectrometers SPASS and LAMPAS 2 were used to investigate the dependence of single particle spectra and spectra patterns on instrumental parameters and data evaluation procedures. Laboratory experiments showed similar responses of both instruments for the major components in mineral particles as well as for additional signals after the reaction of mineral particles with sulphur dioxide gas and OH-radicals (produced via photolysis of CH_3ONO).

Ambient measurements were performed over a period of 47 h. Considering variations of meteorological and sampling conditions during the measurements, a time-correlated spectra evaluation (e.g., during periods of stable meteorological conditions) was necessary. Time courses of specific ion signals with 1-h resolution confirmed the selection of four periods for separate spectra evaluation. The spectra of these four periods were classified separately to identify differences in spectra patterns and abundances of particle classes. The spectra patterns of all sub-populations could be assigned to seven major particle classes. Differences between the periods are mainly reflected in the abundances of the particle classes rather than in differences of patterns. For a given data set (SPASS spectra) two classification procedures (k-means clustering and fuzzy c-means clustering) were applied to determine the main classes in the seven sub-populations. The spectra patterns determined with both algorithms were similar with only slight variations of the signal intensities. The class

abundances calculated by k-means clustering and fuzzy clustering were similar with deviations below 10% in all periods and size ranges. A necessary requirement for this result was the time-correlated and size-resolved data evaluation, used to reduce effects of strong averaging or overestimation of specific chemical classes due to suppression of class mixtures or classes with low abundances.

The comparison of single particle spectra and spectra patterns determined with two mass spectrometers (SPASS and LAMPAS 2) showed both significant similarities and differences. Five main chemical groups of particles could be identified for the ambient particle population: mineral particles, salt particles, particles with mixtures of secondary and organic components, particles dominated by secondary components and carbon particles. The intensity ratios and structure of the patterns of these five groups varied for the two instruments because of instrumental differences and different pre-processing algorithms. For both instruments, the abundances of these five chemical groups were found to depend on particle sizes and measurement period, i.e., on atmospheric conditions. A preferred detection of specific spectral patterns in selected size ranges was found with both instruments (e.g., mineral particles in the super-micron range). Both instruments showed a preferred detection of specific particle groups. The SPASS instrument expressed a higher detection efficiency for mineral and secondary particles whereas the LAMPAS 2 instrument was found to be optimized for detection of carbon and organic particles, probably as a result of the ionization laser wavelengths. Therefore, a future direct comparison of quantitative information from different online aerosol mass spectrometers and from bulk analysis requires the determination of adjustment factors for instruments for different particle classes.

An important requirement for comparability and reproducibility of measurement results from different instruments is a detailed description of measurement conditions, instrumental parameters and pre-processing and data classification procedures. Further combined laboratory and ambient measurements

are necessary to characterize the differences in the spectra of different instruments and to enhance the reliability of mass spectrometric data for aerosol science.

The reported measurements are a necessary step in establishing a universal data treatment system for improved application in single particle mass spectrometry. Further inter-comparisons of data evaluation procedures are necessary to improve the statistical evaluation of single particle spectra. The aim of these future activities should ultimately be to develop a general database of single particle spectra, spectra patterns and abundances for various atmospheric aerosols.

Acknowledgements

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