



## Comparison of two particle-size spectrometers for ambient aerosol measurements

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### Abstract

There is an ongoing debate on the question which size fraction of particles in ambient air may be responsible for human health effects observed in epidemiological studies. Since there is no single instrument available for the measurement of the particle-size distribution over the full range of the fine fraction (diameter  $< 2.5 \mu\text{m}$ ) of the atmospheric aerosol, two instruments, the mobile aerosol spectrometer (MAS) and the electrical aerosol spectrometer (EAS), have been tested in a side-by-side comparison measuring ambient aerosol for a time period of six weeks in spring 1996 in the city of Erfurt, Germany. Furthermore, total particle number concentration measured by a condensation particle counter (CPC) and mass concentrations  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  were determined. Both spectrometers, MAS and EAS, are based on electrical mobility measurements for particles  $< 0.1 \mu\text{m}$  and  $< 0.5 \mu\text{m}$ , respectively, while MAS applies optical particle spectrometry and EAS applies again electrical mobility analysis for particles up to 2.5 and  $10 \mu\text{m}$ , respectively. Both instruments proved to be reliable during this comparison providing data availability of  $> 94\%$ . To compare the spectral data, particle numbers were integrated within three size ranges:  $0.01 - 0.1$ ,  $0.1 - 0.5$ ,  $0.5 - 2.5 \mu\text{m}$ . Hourly mean number concentrations of each size range observed during the six week comparison was:  $2.6 \times 10^4 \pm 19500$  ( $2.48 \times 10^4 \pm 1.79 \times 10^4$ ),  $3.1 \times 10^3 \pm 1.5 \times 10^3$  ( $4.1 \times 10^3 \pm 2.0 \times 10^3$ ),  $50 \pm 45$  ( $1.9 \times 10^2 \pm 1.2 \times 10^2$ )  $\text{cm}^{-3}$  for MAS (EAS), respectively. Both aerosol spectrometers followed the variations of the ambient aerosol in a similar manner and yielded almost identical results for particle number concentrations of particles with diameters smaller than  $0.5 \mu\text{m}$ . Furthermore, the total particle number concentration derived from MAS and EAS measurements ( $29000 \pm 20000$ ;  $29000 \pm 19000 \text{ cm}^{-3}$ ) is well comparable with the number concentration derived from an integral counting CPC ( $31100 \pm 22000 \text{ cm}^{-3}$ ). The results of this side-by-side comparison suggest that MAS and EAS together with  $\text{PM}_{2.5}$  measurements are suitable to reliably characterize size-distribution parameters of number and mass concentration of ambient aerosols. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Aerosol spectrometers; Ambient aerosol; Particle number distribution

### 1. Introduction

Ambient aerosol particles cover a size range from a few nanometers up to several tens of micrometers in dia-

meter. Ultrafine particles with diameters less than  $0.1 \mu\text{m}$  originate mainly from gas-to-particle conversion or combustion processes. These ultrafine particles coagulate rapidly depending on their concentration and thermodynamic conditions forming larger particles attributed to the accumulation mode which ranges from  $0.1$  up to  $1.0 \mu\text{m}$ . However, particles in the accumulation mode are not exclusively formed by coagulation of ultrafine

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particles but may originate also from diverse anthropogenic and natural sources. Particles larger than  $1\ \mu\text{m}$ , defined as the coarse mode of the ambient aerosol, originate mostly from mechanical dispersion processes. Due to different processes of particle formation the chemical composition of particles in different size ranges may be substantially different.

Acute health effects associated with ambient particulate matter have been reported from several epidemiological studies (Dockery and Pope, 1995; Brunnekreef et al., 1995). The health-related findings of these studies were associated with either the total mass concentration of suspended particles (TSP) or the mass concentration of particles with aerodynamic diameters smaller than  $10\ \mu\text{m}$  ( $\text{PM}_{10}$ ) or smaller than  $2.5\ \mu\text{m}$  ( $\text{PM}_{2.5}$ ). Recent inhalation studies using laboratory animals (Oberdörster et al., 1995a, b) and first results from epidemiological studies (Peters et al., 1997a, b; Pekkanen et al., 1997) suggest that the inhalation of ultrafine particles may cause adverse health effects. Since the mass concentration of these particles is negligible compared to the mass concentration of larger particles, the ultrafine particle mass concentration seems to be an inadequate parameter. Therefore, it may be more appropriate to correlate the number concentration or the surface area concentration of particles in different size ranges with the observed health effects.

The total mass concentration of ambient particulate matter and the particle number concentration are only weakly correlated as determined earlier for the ambient aerosol of Erfurt, Germany (Tuch et al., 1997). Therefore, the number concentration of ultrafine particles, cannot be estimated based on gravimetric methods. Only particle-size spectrometers are capable to yield this information.

There are no commercially available instruments, which can measure the particle-size distribution of ambient aerosols with a sufficient size and time resolution over the whole size range of fine particles ( $d_{ae} < 2.5\ \mu\text{m}$ ). Instruments used are modifications of laboratory-type versions which do not cover the entire size range. In addition, these instruments are based on different measurement principles. It needs to be noted, that there is no standard instrument available for measurement of the particle-size distribution of the fine fraction of the atmospheric aerosol. Therefore, in the present study, an approach was undertaken, to compare size-distribution data obtained from different spectrometric instruments as well as integral counting and sampling instruments during continuous side-by-side measurements of ambient aerosols. This instrument intercomparison will provide the basic information for further comparisons of measurements of the size distribution of ambient aerosols performed at different places in Europe.

Two particle-size spectrometers, the MAS (Brand et al., 1991; Tuch et al., 1997) and the EAS (Mirme et al.,

1984; Kikas et al., 1996), have been tested in a side-by-side comparison for a time period of six weeks in spring 1996 in the city of Erfurt, Germany, a city of current epidemiological investigations (Spix et al., 1993; Cyrus et al., 1995; Brauer et al., 1995; Peters et al., 1996; Peters et al., 1997a, b). While the MAS is similar to the instruments used during the Los Angeles air monitoring survey (Eldering et al., 1994), the EAS represents a new development of an aerosol spectrometer based entirely on the measurement of the electrical mobility of particles in the whole size range. To compare the spectral data of the two instruments, three size ranges were chosen for the time series analysis to distinguish the number concentration of ultrafine particle fraction ( $0.01\ \mu\text{m} < d < 0.1\ \mu\text{m}$ )  $\text{NC}_{0.01-0.1}$  from the number concentration of the lower part of the accumulation fraction ( $0.1\ \mu\text{m} < d < 0.5\ \mu\text{m}$ )  $\text{NC}_{0.1-0.5}$  and from the number concentration of the lower part of the coarse fraction ( $0.5\ \mu\text{m} < d < 2.5\ \mu\text{m}$ )  $\text{NC}_{0.5-2.5}$ . The total particle number concentration measured by a condensation particle counter (TSI, CPC 3022A) was determined during this study. In addition, measurements of mass concentrations  $\text{PM}_{10}$  (Harvard Impactor) and  $\text{PM}_{2.5}$  (Harvard Impactor) were incorporated to provide compatibility to previous studies of ambient aerosols based only on those measurements (USEPA, 1996). While the mass concentration measuring instruments yielded only daily averages the particle counting instruments provided time resolutions of 5 min (MAS) and 10 s (EAS and CPC).

This intercomparison was undertaken to prove that the two aerosol spectrometers, MAS and EAS, reliably provide comparable spectral data and number concentrations of the ambient aerosol over long time periods. Furthermore, the derived total number concentrations are verified by integral counted number concentrations determined by a CPC. Based on these results, spectral aerosol data obtained from different locations can be compared in the future. The ultimate aim of these intercomparisons will be the inquiry of time series of comparable ambient aerosol parameters measured with MAS and EAS at different locations. These data will then be used to correlate with health effects observed by epidemiological studies in an attempt to specifically associate adverse health effects to distinct fractions and constituents of the ambient air.

## 2. Methods

For the determination of particle size, properties of electrical and mechanical mobility, impaction, sedimentation, diffusion and light scattering are commonly used depending on the size of the particles. Since the fine particles range from a few nanometers to  $2.5\ \mu\text{m}$ , different physical measuring principles need to be applied. To elucidate the similarities and the differences of

the two aerosol spectrometers MAS and EAS, principles of measurement, calibration and analysis are briefly described.

### 2.1. The mobile aerosol spectrometer (MAS)

The MAS was described earlier (Brand, 1989; Brand et al., 1991, 1992; Tuch et al., 1997). It consists of two different, commercially available, instruments covering different size ranges. Particles in the size range from 0.01 to 0.5  $\mu\text{m}$  are measured using a differential mobility analyzer (DMA, TSI model 3071) combined with a condensation particle counter (CPC, TSI model 3760). This set will be termed differential mobility particle sizer (DMPS) in the following. Particles in the size range from 0.1 up to 2.5  $\mu\text{m}$  are classified by an optical laser aerosol spectrometer (LAS-X, PMS model LAS-X).

The DMA allows the separation of particle fractions of uniform electrical mobility from a polydisperse aerosol. The number of particles selected by the DMA is counted by the CPC. The raw count rate of the CPC is used to calculate the particle number concentration in the selected size range taking into account the charging probability of the particles (Knutson, 1976), diffusional losses in the DMA (Reineking and Porstendorfer, 1984, 1986) and the counting efficiency of the CPC 3760 (Zhang and Liu, 1991). The number concentrations of the separate particle fractions are measured as a function of the diameter in 13 discrete size ranges between 0.01 and 0.5  $\mu\text{m}$  using an adapted inversion algorithm for multiple charge correction. The four upper channels between 0.1 and 0.5  $\mu\text{m}$  are used for the mobility calibration and for quality checks of the overlapping spectra obtained from the DMA and the LAS-X, see below.

The optical laser aerosol spectrometer (LAS-X) classifies particles according to their light scattered into 45 size-dependent channels. The intensity of light scattered by a particle depends on the particle diameter, shape and optical properties such as the refractive index of the particle material (Hinds and Kraske, 1986; Szymanski and Lui, 1986; Kim, 1995; Reisert et al., 1991). The counting efficiency of the LAS-X is 1 for particles in a size range of 0.1–1  $\mu\text{m}$  and decreases only slightly to 0.95 for 2.5  $\mu\text{m}$  particles (Hinds and Kraske, 1986; Brand, 1989; Gebhart et al., 1989).

*Aerosol sampling:* Both, DMPS and LAS-X, are located in a van. With an air flow velocity of 1 m/s, a sample flow is drawn through a chimney of a diameter of 22 cm and a height of 4 m above the ground into the van. Each instrument samples isokinetically from this main sample stream (Tuch et al., 1997). The aerosol flow rates of the DMA and LAS-X are 610 and 60  $\text{cm}^{-3} \text{min}^{-1}$ , respectively.

*Electrical mobility calibration of the LAS-X data:* To classify ambient aerosol particles of unknown refractive indices by the LAS-X, a calibration procedure is applied in the MAS, which uses the DMA to provide mono-

disperse fractions of the ambient aerosol in the size range from 0.1 to 0.5  $\mu\text{m}$  (Liu et al., 1974; Brand et al., 1991, 1992). These particle fractions are then used to calibrate the LAS-X in terms of mobility equivalent diameters (electrical mobility calibration).

*Data acquisition and performance:* Control of the measurements, data acquisition and evaluation are performed by a personal computer. A complete particle-size distribution is obtained every 5–6 min.

*Analysis of aerosol concentration parameters:* MAS yields a differential particle number distribution. From this the integral number concentrations of particles of the total distribution and integral particle number concentrations of selected size ranges are calculated. In this study hourly averages of total particle number concentrations ( $\text{NC}_{0.01-2.5}$ ) and of particle number concentrations in size ranges 0.01–0.1  $\mu\text{m}$  ( $\text{NC}_{0.01-0.1}$ ), 0.1–0.5  $\mu\text{m}$  ( $\text{NC}_{0.1-0.5}$ ), and 0.5–2.5  $\mu\text{m}$  ( $\text{NC}_{0.5-2.5}$ ) were used to characterize the ambient aerosol. An hourly average was considered valid if 66% of the data were available. Additionally, the differential volume distribution of particles was calculated from the particle number distribution presuming spherical particles. To estimate the mass distribution the particle density is required. Therefore, the  $\text{PM}_{2.5}$  data from the time period of the intercomparison and the corresponding daily average of volume distributions measured by the MAS, were used to calculate the apparent mean density of ambient particles. In addition, approximately 700 gravimetric  $\text{PM}_{2.5}$  measurements and according MAS determinations, obtained during a long-term study in Erfurt, were also used to calculate the mean particle density of the ambient aerosol (Tuch et al., 1998). Using the obtained apparent mean density, integral mass concentrations of all counted particles ( $\text{MC}_{0.01-2.5}$ ) and of the subclasses  $\text{MC}_{0.01-0.1}$ ,  $\text{MC}_{0.1-0.5}$  and  $\text{MC}_{0.5-2.5}$  were calculated from the differential mass distributions.

### 2.2. The electrical aerosol spectrometer

The Electrical Aerosol Spectrometer (EAS), based on a theoretical model by Tammet (Tammet, 1975, 1992), was developed at the University of Tartu (Estonia). As described earlier (Kikas et al., 1996) the EAS was particularly designed to measure particle-size distributions of ambient aerosol in urban and rural environments. The EAS measures the particle sizes in the range from 10 nm to 10  $\mu\text{m}$  using two analyzers in parallel both being based on the measurement of electrical particle mobility. EAS utilizes unipolar diffusion charging in the size range of 0.01–0.5  $\mu\text{m}$  in one analyzer and strong electrical field charging in the size range from 0.3 to 10  $\mu\text{m}$  in the other analyzer, each made up of a series of eight electrometers per size decade determining the charge of particles of equal electrical mobility. In this study the EAS provides four size intervals per size decade based on weighted

means of neighboring electrometers (Mirme, 1994). Because of the spatial separation of the aerosol particles by the serial electrometers, all charges of all particles provide the entire distribution at the same time. That enables short measuring times avoiding possible errors due to fast variations in the particle distribution. Furthermore, particles of high electric mobility travel a short distance to one of the first of the series of electrometers which results in a smaller diffusion path length as compared to that of the DMPS of the MAS in which each particle trajects to the same sampling slit.

*Aerosol sampling:* During the side-by-side comparison the EAS was attached to a sample inlet similar to the inlet of the MAS. The sampling air velocity in the chimney was determined by the EAS sample flow of  $800 \text{ cm}^3 \text{ s}^{-1}$ . EAS was operated at ambient temperature in a small hut outside the measurement van.

*Calibration:* A sufficient mathematical modeling of the EAS is rather difficult because of the complex nature of charging and the parallel use of both diffusion and field charging. The calibration used in this study was achieved combining theoretical modeling with the experimental approach using sodium chloride and silver iodide aerosols (Kikas et al., 1985). The charge distribution of the particles has been estimated using four statistical moments with a detailed modeling of the ion density in the chargers (Mirme, 1994).

*Analysis of aerosol concentration parameters:* From the particle-size distribution, integral particle number and volume concentration are calculated similar to MAS. The mean particle density was calculated from the  $\text{PM}_{2.5}$  data and from the corresponding daily average of volume distributions measured by the EAS during intercomparison.

### 2.3. Statistical analysis

When comparing the characteristics of ambient aerosol, medians and interquartile ranges provide statistically

more reliable estimates than mean values because the distribution of concentration profiles of the ambient aerosol over time tends to be not normally distributed. Therefore, non-parametric Spearman rank order correlation for statistical estimates was used which is less sensitive to the shape of the distribution.

### 2.4. Additional instrumentation

Hourly averages of the total particle number concentration were measured using a condensation particle counter (CPC, TSI model 3022A). Twenty-four-hour samples of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  were taken with Harvard Impactors (MS & T Air Sampler). Concentrations of NO and  $\text{NO}_2$  were determined using a two channel chemiluminescence monitor (Environnement S.A, model NH30M), the concentration of  $\text{SO}_2$  was determined using a UV-absorption type monitor (Environnement S.A., model AF21M). Temperature and relative sensors humidity (RCI, model FT3205-M) were mounted in the chimney outside the vehicle. Wind speed and wind direction (Albin Sprenger, model E 14051.61 H) were determined 4.5 m above the ground. Note that gas pollutants and meteorological data are not used in this study but provide additional information on the environmental situation in Erfurt during this intercomparison used in other studies.

### 2.5. Site of measurement

The measurements were performed in the city of Erfurt, Germany. The city is surrounded by mountains from three sides. In addition, the air exchange is hindered by buildings located at the fourth side. Therefore, temperature inversions during winter time can cause elevated levels of ambient pollutants in this city. During the measuring period domestic heating was still based to a small extent on the use of surface coal with high sulfur

Table 1  
Meteorological and pollutant parameters during study period

Parameter	Unit	N	Mean	S.D.	Minimum	Maximum
$\text{PM}_{10}$	$\mu\text{g m}^{-3}$	40	72.1	32.2	17.8	153.5
$\text{PM}_{2.5}$	$\mu\text{g m}^{-3}$	37	55.1	26.1	10.4	111.1
Number concentration CPC	$\text{cm}^{-3}$	837	31149	21993	4425	170401
NO concentration	$\mu\text{g m}^{-3}$	912	117.5	59.7	27.8	682.5
$\text{NO}_2$ concentration	$\mu\text{g m}^{-3}$	912	163.4	59.6	34.7	651.2
$\text{SO}_2$ concentration	$\mu\text{g m}^{-3}$	746	28.3	32.4	2.9	222.9
Temperature	$^{\circ}\text{C}$	912	2.85	4.62	- 6.3	19.5
Relative humidity	% rH	888	80.2	15.7	26.4	100
Windspeed	m/s	912	0.8	0.5	0	2.9

Note: Basic statistics of daily averages of  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$  and CPC aerosol parameters and hourly averages of gaseous pollutants and meteorological parameters. *N* is the number of available data.

contents. However, both local power stations and most domestic heating systems have been rebuilt using gas and oil fuels after the re-unification of Germany. As a result the present pollutant mixture (Table 1) is close to that of western European cities without major industrial sources of air pollution. The measuring site is located in a dwelling area at a distance of 2 km from the center of the city. It is located approximately 50 m east of a major road. The air pollutant mixture at this location is primarily influenced by traffic emissions and domestic heating, thus, representing a typical air pollution situation in this city.

### 3. Results

Side-by-side measurements were performed for a time period of 40 days during spring 1996 (March 7th through April 16th). Fig. 1 shows the daily mean number density distribution of the ambient air at day 19 during the intercomparison. This distribution was calculated from approximately 250 individual particle-size distributions from each instrument.

*Performance of instrumentation:* The electrical mobility calibration of MAS was performed weekly. The ability of the instruments to continuously measure ambient aerosol can be estimated from the amount of valid measurement data. From total time of 975 h only 38 h are missing for MAS and 50 for EAS. Most of the breaks were due to standard calibration procedures and computer failures. CPC data are missing during 187 h. Daily average  $PM_{10}$  measurements are available for the whole time periods whereas 3 days of  $PM_{2.5}$  are missing.

*Total particle number concentration:* Both Spearman rank correlation coefficients between MAS and CPC and

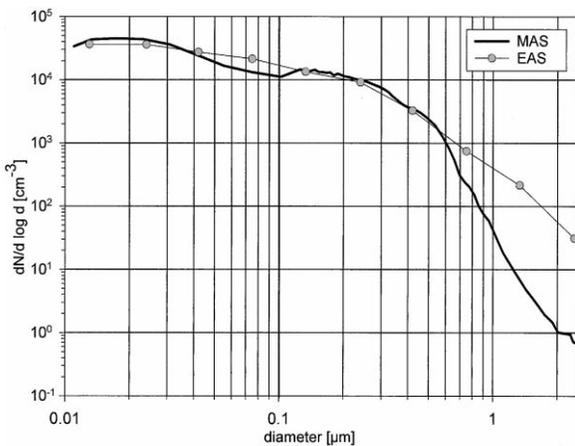


Fig. 1. Daily mean number density distribution of the ambient air at day 19 during the intercomparison calculated from MAS and EAS 5 minute size distributions.

Table 2

Correlation of particle number concentrations measured by MAS, EAS and CPC

Size range:	Instrument	MAS	EAS	CPC
0.01–2.5 μm	MAS	1	0.96	0.97
	EAS		1	0.98
	CPC			1
0.01–0.1 μm	MAS	1	0.95	0.96
	EAS		1	0.98
	CPC <sup>a</sup>			1
0.1–0.5 μm	MAS	1	0.94	0.56
	EAS		1	0.62
	CPC <sup>a</sup>			1
0.5–2.5 μm	MAS	1	0.86	0.27
	EAS		1	0.35
	CPC <sup>a</sup>			1

Note: Spearman rank correlation coefficients of total particle number concentrations and number concentrations in the size ranges 0.01–0.1, 0.1–0.5 and 0.5–2.5 μm.

<sup>a</sup>total number concentration as determined by CPC.

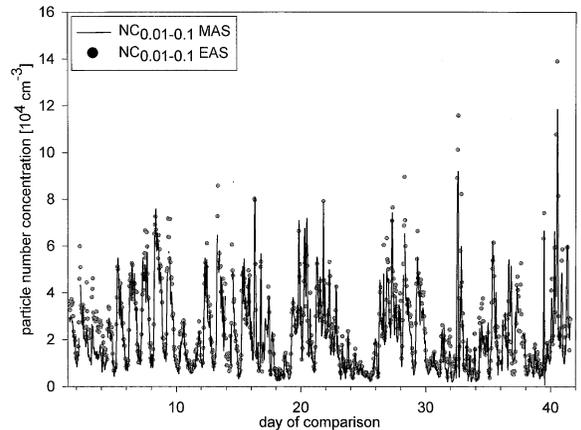


Fig. 2. Time series of hourly average particle number concentrations in the size range 0.01–0.1 μm derived from MAS and EAS measurements.

between EAS and CPC are as high as 0.95 (Table 2) indicating that both aerosol spectrometers reliably measure the total particle number concentration of an ambient aerosol.

*Particle number concentrations in different size ranges:* The time series plot of hourly average particle number concentrations  $NC_{0.01-0.1}$  of ultrafine particles in the size range from 0.01 to 0.1 μm (Fig. 2) shows that both instruments followed the concentration variations quite well. EAS and MAS yielded almost identical particle number concentrations in this size range. The Spearman rank correlation coefficient between measurements of both

Table 3  
Particle number concentration in different size ranges

		NC <sub>0.01-0.1</sub> [cm <sup>-3</sup> ]	NC <sub>0.1-0.5</sub> [cm <sup>-3</sup> ]	NC <sub>0.5-2.5</sub> [cm <sup>-3</sup> ]	NC <sub>0.01-2.5</sub> [cm <sup>-3</sup> ]
MAS (N = 938)	Mean	26000	3100	50	29000
	Median	24000	2900	30	24000
	S.D.	19000	1500	50	20000
	25% Perc.	11000	1900	10	14000
	75% Perc.	36000	4000	80	39000
EAS (N = 926)	Mean	25000	4100	190	29000
	Median	21000	3900	180	25000
	S.D.	18000	2000	120	19000
	25% Perc.	10000	2600	80	14000
	75% Perc.	34000	5400	280	39000
CPC (N = 798)	Mean	—	—	—	31000
	Median	—	—	—	26000
	S.D.	—	—	—	22000
	25% Perc.	—	—	—	14000
	75% Perc.	—	—	—	43000

Note: Statistical parameters of the particle number concentration measured by MAS, EAS in different size ranges and integral particle number concentration measured by CPC.

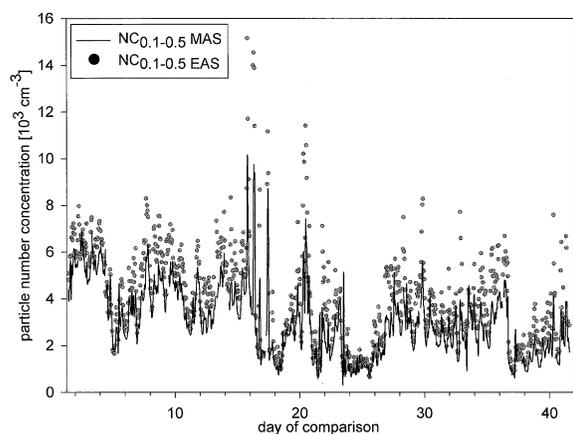


Fig. 3. Time series of hourly average particle number concentrations in the size range 0.1 – 0.5 μm derived from spectrometer measurements.

instruments is 0.95 (Table 2) suggesting that the results of both measurements are well comparable. Eighty to ninety percent of the total particle counts were observed in this size range (Table 3).

An almost equally good agreement is observed for particle number concentrations NC<sub>0.1-0.5</sub> in the size range from 0.1 to 0.5 μm (Fig. 3). The Spearman rank correlation coefficient of measurements of both instruments in this size range is 0.94 (Table 2). The EAS-derived particle number concentrations tends to be slightly higher than MAS derived number concentra-

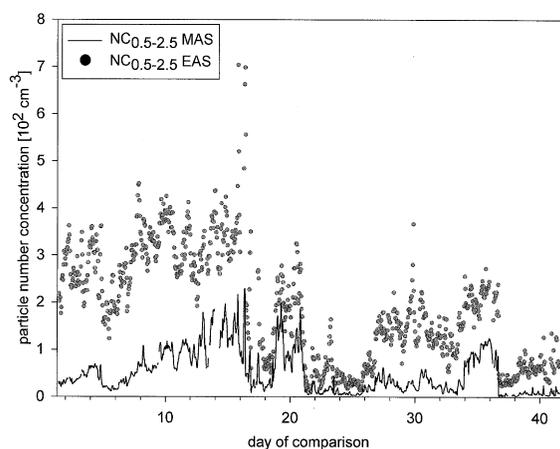


Fig. 4. Time series of particle number concentrations in the size range 0.5 – 2.5 μm measured by MAS and EAS.

tions, but the mean data given in Table 3 are not statistically significant different ( $p > 0.05$ ). In this size range about 10% of the counted particles were found (Table 3).

The largest discrepancy between EAS and MAS was found for larger particles in the size range from 0.5 to 2.5 μm (Fig. 4). However, the total number concentration NC<sub>0.5-2.5</sub> in this size range is small and contributes to less than 1% of the counted particles. The differences in the time series data of both instruments seem however not to be random. The ratio of EAS/MAS derived number concentrations varies between 1.8 and 15 yielding an

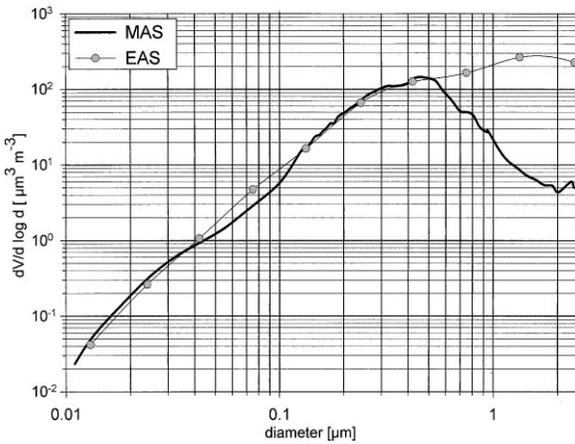


Fig. 5. Daily mean volume density distributions of the ambient aerosol at day 19 during the intercomparison as obtained from MAS and EAS.

Spearman rank correlation coefficient for the side by side comparison of 0.86 (Table 2).

*Apparent mean density of ambient particles:* Mean volume density distributions during day 19 of the intercomparison are shown in Fig. 5. While the ultrafine particle fraction attributes negligibly to the total volume concentration derived by both MAS and EAS, the volume fraction of the 0.1–0.5 µm particles adds 73% to the volume concentration derived from MAS data but only 22% derived from EAS data. Hence, the volume concen-

tration of EAS is mainly determined by the coarse fraction of the particles (76%) but only to a much lesser extent (26%) by MAS data. As a result, the mean particle density derived from corresponding daily averaged particle volume distributions of MAS and PM<sub>2.5</sub> data was  $1690 \pm 240 \text{ kg m}^{-3}$ . This value agrees reasonably well to a calculated mean density of  $1530 \pm 310 \text{ kg m}^{-3}$  based on measurements of PM<sub>2.5</sub> and MAS during 700 days. The mean particle density derived from corresponding EAS and PM<sub>2.5</sub> data was  $550 \pm 150 \text{ kg m}^{-3}$ . The derived particle volume concentrations of each spectrometer are highly correlated with the PM<sub>2.5</sub> measurements (correlation coefficient: 0.97 (MAS), 0.86 (EAS)). Basic statistic parameters of hourly average particle mass concentration parameters and daily average PM<sub>2.5</sub> are summarized in Table 4.

#### 4. Discussion

*Performance of the spectrometers:* The EAS and MAS were successfully deployed in a six week measuring campaign without significant losses of data acquisition time. They reliably recorded spectral number distributions at cycle times of either 1 or 6 min, respectively. It needs to be noted that intensive maintenance is necessary to operate the MAS for long time periods whereas EAS needs almost no maintenance. On the other hand, MAS is measuring continuously since September 1995 with a data availability of 95%.

Table 4  
Particle mass concentration parameters

		MC <sub>0.01-0.1</sub> (µg m <sup>-3</sup> )	MC <sub>0.1-0.5</sub> (µg m <sup>-3</sup> )	MC <sub>0.5-2.5</sub> (µg m <sup>-3</sup> )	MC <sub>0.01-2.5</sub> (µg m <sup>-3</sup> )
MAS (N = 938) Density: 1530 kg m <sup>-3</sup>	Mean	0.9	36	12	49
	Median	0.8	36	7	47
	S.D.	0.6	18	12	27
	25% Perc.	0.5	20	31	25
	75% Perc.	1.2	49	9	69
EAS (N = 926) Density: 1500 kg m <sup>-3</sup>	Mean	1.8	36		
	Median	1.6	36		
	S.D.	1.1	18		
	25% Perc.	1.0	22		
	75% Perc.	2.3	46		
PM <sub>2.5</sub> (N = 40) (daily averages)	Mean	—	—	—	55
	Median				58
	S.D.				26
	25% Perc.				31
	75% Perc.				74

Note: Hourly mean particle mass concentration parameters and daily average PM<sub>2.5</sub>.

*Intercomparison of ambient aerosol number concentration:* From the spectral data, hourly means of number concentrations were evaluated for the total size range and for selected sub-ranges. Note that the size ranges chosen in this paper can be changed such that number concentrations of other aerosol classes can be re-analyzed.

Both aerosol spectrometers followed the variations of the ambient aerosol in a similar manner and yielded almost identical results for particle number concentrations of particles with diameters smaller than 0.5  $\mu\text{m}$ . This is reflected in the very high correlation of the total number concentration  $\text{NC}_{0.01-2.5}$  and the number concentrations  $\text{NC}_{0.01-0.1}$  and  $\text{NC}_{0.1-0.5}$  for the size ranges 0.01–0.1 and 0.1–0.5  $\mu\text{m}$  as determined by MAS and EAS (Table 3). In addition, the high correlation (correlation coefficients MAS: 0.97; EAS: 0.98) between  $\text{NC}_{0.01-2.5}$  of the two spectrometers and the integral counting CPC provides evidence that the total number concentration  $\text{NC}_{0.01-2.5}$  is truly recorded by both spectrometers during the entire intercomparison.

The size range 0.01–0.5  $\mu\text{m}$  contains about 99% of the total particles observed in the ambient air of Erfurt. A major difference between both instruments was found for the size range 0.5–2.5  $\mu\text{m}$  in which MAS and EAS apply different measurement principles (optical light scattering versus electrical mobility). The particle number concentration derived from EAS measurements is in average 3.7 times higher than the MAS derived particle number concentration. The time series of these data suggests, that the difference between both instruments is not random. However, particles in this size range contribute to only 0.5% to the total particle number concentration. The true particle number concentration of ambient aerosol particles with diameters between 0.5 and 2.5  $\mu\text{m}$  is not known. A few reasons are known which may play a role for the observed differences in this size range:

1. The observed difference of both instruments may be due to the cutpoint of 0.5  $\mu\text{m}$  between  $\text{NC}_{0.1-0.5}$  and  $\text{NC}_{0.5-2.5}$  which is located on the steep slope of the accumulation mode of the aerosol. A small shift of the cutpoint towards larger particles will therefore yield a significant decrease of the number concentration allocated to the size range  $\text{NC}_{0.5-2.5}$ , whereas a shift towards smaller particles will be obscured by the relatively large number concentration in the size range 0.1–0.5  $\mu\text{m}$ .
2. The counting efficiency of the LAS-X is very close to 1 in the size range between 0.3 and 1  $\mu\text{m}$ . However, the chosen cutpoint of 0.5  $\mu\text{m}$  between the accumulation mode and the coarse mode is located in the flat part of the calibration curve of the LAS-X between 0.4 and 0.8  $\mu\text{m}$  which may lead to mis-classification of particles in this size range by the LAS-X, particularly for

ambient aerosol particles of a refractive index different of that of polystyrene latex particles (Hering and McMurry, 1991).

3. The cutpoint is located in overlap between diffusion charging to field charging of the EAS. This overlap between 0.3 and 0.5  $\mu\text{m}$  is taken into account by data inversion routines. However, these routines judge the noise of the electrometers to decide how the signal of the individual channels are weighted for the calculation of the size distribution. This may result in a different weighing of the channels in the overlap range under different working conditions of the instrument.
4. Furthermore, field charging of particles larger than 0.3  $\mu\text{m}$  depends on dielectric and surface properties of the particles (Willeke and Baron, 1993). Charging pattern of the aerosol particles used for calibration may be different from those of the ambient air.
5. Since MAS measures the particle-size distribution at approximately 30% relative humidity and EAS measures at the humidity of the ambient air, particles in the size range of 0.5  $\mu\text{m}$  may contain a certain amount of water on the surface resulting in particle growth at elevated relative humidities such that the grown particles are classified by EAS in the size range  $\text{NC}_{0.5-2.5}$  while MAS classifies dried particles in the size range  $\text{NC}_{0.1-0.5}$ . However, such a shift towards larger particle number concentrations of  $\text{NC}_{0.5-2.5}$  of EAS was not observed during periods of high relative humidity.

*Intercomparison of particle mass concentration:* Both, the apparent average densities of the aerosol particles of  $1690 \pm 240$  and  $1530 \pm 310 \text{ kg m}^{-3}$  calculated from  $\text{PM}_{2.5}$  data and corresponding MAS volume distributions measured during this intercomparison and during 21 months agree well with  $1500 \text{ kg m}^{-3}$  given in the literature (Joshi, 1988). These results are further supported from extensive measurements of the bulk density of ambient aerosol particles collected at different locations in Germany under different meteorological conditions (Hänel and Thudium, 1977) which vary around  $2000 \text{ kg m}^{-3}$ . Bulk material densities usually are higher than the apparent density of aerosol particles which may be porous and/or aggregated. For instance, the bulk density of NaCl of  $2170 \text{ kg m}^{-3}$  was about 15% higher than the apparent density  $1900 \text{ kg m}^{-3}$  of monodisperse NaCl aerosol particles as determined from geometric and aerodynamic size measurements (Anselm, 1985; Gebhart, private communications). The mean particle density of  $550 \pm 150 \text{ kg m}^{-3}$  derived from the data of EAS and  $\text{PM}_{2.5}$  is very low. As mentioned above the calculated density is mainly determined by the volume fraction of the coarse particles of EAS data. If the number concentration of this particle fraction is too high, the density decreases drastically. From the agreement of the density calculated from MAS and  $\text{PM}_{2.5}$  data and the literature

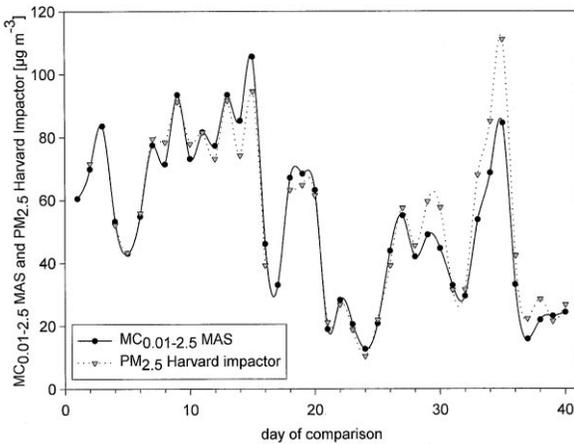


Fig. 6. Time series of daily average MAS derived particle mass concentrations in the size range 0.01–2.5  $\mu\text{m}$  measured by MAS and  $\text{PM}_{2.5}$ .

data it is plausible to conclude that the number concentration of the coarse particle fraction determined by the MAS is reasonably correct. Therefore, MAS measurements can auxiliary be used to estimate mass concentrations of fine particles of the ambient aerosol.

Presuming the mean density also applies for particle densities of the various size fractions, MAS provides also mass concentrations for these size fractions. The good agreement of MAS derived daily mean  $\text{MC}_{0.01-2.5}$  and  $\text{PM}_{2.5}$  is shown in the time series graph (Fig. 6). Based on this assumption and since the number concentrations  $\text{NC}_{0.01-0.1}$  and  $\text{NC}_{0.1-0.5}$  agreed very well between EAS and MAS, EAS data may also be used to estimate mass concentration data up to 0.5  $\mu\text{m}$  using the literature value of the density of 1500  $\text{kg m}^{-3}$ .

Note, however, that both aerosol spectrometers, EAS and MAS, were primarily introduced to determine the number distribution of ambient aerosols as a function of the particle diameter and to calculate number concentrations for selected particle size ranges. It was not anticipated to determine precise particle mass concentrations by these instruments which is principally only possible if the shape and the density of the aerosol particles is known. The latter particle parameters, however, are not known for the entity of ambient aerosol particles and many of its constituent particle classes and fractions. Therefore, it is emphasized that those measurements need to be confirmed by additional measurements using appropriate instruments such as  $\text{PM}_{2.5}$  impactors, etc. Besides the identified discrepancy found for the coarse particle fraction, the overall agreement of both instruments EAS and MAS for more than 99% of the counted particles of the ambient air of Erfurt is appreciably good.

It needs to be mentioned that control of both MAS and EAS needs experienced personal well accustomed

with the instruments. While there is little maintenance required for the EAS, MAS requires more attention by trained staff.

*Motivation for the intercomparison:* This intercomparison proved that data obtained from MAS and EAS are well comparable during side-by-side measurements. Therefore, it is concluded that MAS and EAS data obtained at different locations will also be comparable. These data then may be used in comparative epidemiological studies relating health effects to the number concentrations of fine particles and those of various size fractions. These findings suggest that epidemiological studies correlating health effects with ambient air monitoring may not only use mass concentration parameters as determined by  $\text{PM}_{10}$  or  $\text{PM}_{2.5}$  impactors in the past but, in addition, may use parameters of the particle number concentration determined by aerosol spectrometers like EAS and MAS.

## 5. Conclusions

Both MAS and EAS have proven to be reliable instruments for long-term studies on the particle-size distribution of ambient aerosols. Both instruments require adequate calibration and maintenance for this purpose. The instruments yield comparable results of the number concentration of fine particles. To obtain data on particle mass concentrations, adequate instruments, such as  $\text{PM}_{2.5}$ , should be collocated during epidemiological studies. The results of this side-by-side comparison suggest that MAS and EAS in combination with measurements of  $\text{PM}_{2.5}$  are suitable to reliably characterize the size distribution of ambient aerosols. The availability of two comparable spectrometers allows comparative epidemiological studies in different cities on the effect of ambient aerosols on human health. The detailed characterization of the aerosol in such studies using a new set of parameters – particle number concentrations – may help to increase the understanding which size fraction of the ambient aerosol is relevant for observed health effects associated with the exposure to the ambient aerosol.

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## References

- Anselm, A., 1985. Aufbau und Erprobung einer Messmethode zur Bestimmung der Groessenverteilung hygroscopischer Aerosolteilchen im Atemtrakt des Menschen. Ph.D. Thesis; Johann-Wolfgang-Goethe University, Frankfurt, Germany.
- Brand, P., 1989. Forschungs- und Entwicklungsarbeiten zum Aufbau eines mobilen Messtandes zur Charakterisierung von Umweltaerosolen. Ph.D. Thesis, Johann-Wolfgang Goethe University, Frankfurt, Germany.
- Brand, P., Gebhart, J., Below, M., Georgi, B., Heyder, J., 1991. Characterisation of Environmental Aerosol on Helgoland Island. *Atmospheric Environment* 25A, 581–585.
- Brand, P., Ruoß, K., Gebhart, J., 1992. Technical note: Performance of a Mobile Aerosol Spectrometer for in situ characterisation of an environmental aerosol in Frankfurt city. *Atmospheric Environment* 26A, 2451–2457.
- Brauer, M., Dumyahn, T.S., Spengler, J.D., Gutschmidt, K., Heinrich, J., Wichmann, H.E., 1995. Measurement of acid aerosol species in Eastern Europe : Implications for air pollution epidemiology. *Environmental Health Perspectives* 103, 482–488.
- Brunnekreef, B., Dockery, D.W., Krzyzanowski, M., 1995. Epidemiological studies on short-term effects of low levels of major ambient air pollution components. *Environmental Health Perspectives* 103 (suppl. 2), 3–13.
- Cyrys, J., Gutschmidt, K., Brauer, M., Dumyahn, T., Heinrich, J., Spengler, J.D., Wichmann, H.E., 1995. Determination of acid sulfate aerosols in urban atmospheres in Erfurt (GERMANY) and Sokolov (former CSSR). *Atmospheric Environment* 29, 3545–3557.
- Dockery, D.W., Pope, C.A., 1995. Acute respiratory effect of particulate air pollution. *Annual Review of Public Health* 15, 107–132.
- Eldering, A., Cass, G.R., Moon, K.C., 1994. An air monitoring network using continuous particle size distribution monitors: connecting pollutant properties to visibility via Mie scattering calculations. *Atmospheric Environment* 16, 2733–2749.
- Gebhart J. Brand, P., Roth, C., 1989. High resolution size analysis of submicron particles in liquid suspensions via aerosolization. Proceedings of the IV. European Symposium on Particle Characterization, Nürnberg, 19–21 April 1989, S. 487–499.
- Hänel, G., Thudium, J., 1977. Mean bulk densities of samples of dry atmospheric particles: summary of measured data. *Pure and Applied Geophysics* 115, 799–803.
- Hering, S.V., McMurry, P.H., 1991. Optical counter response to monodisperse atmospheric aerosols. *Atmospheric Environment* 25A, 461–468.
- Hinds, W.C., Kraske, G., 1986. Performance of PMS model LAS-X optical particle counter. *Journal Aerosol Science* 17, 67–72.
- Joshi, P.V., 1988. Density of atmospheric aerosol particles. Twelfth International Conference on Atmospheric Aerosols and Nucleation, Vienna, Austria, 22–27.8.1988. Proceedings of the Conference, Springer, Berlin, p. 134.
- Kim, Y.J., 1995. Response of the active scattering aerosol spectrometer probe (ASASP.100X) to particles of different chemical composition. *Aerosol Science Technology* 22, 33–42.
- Kikas, Ü.E., Mirme, A., Peil, I.A., Tamm, E.I., Tammet, H.F., 1985. Experimental calibration of an electrical aerosol spectrometer by the method of test aerosols. *Acta et Comm. Univ. Tartuensis* 707, 54–71.
- Kikas, Ü.E., Mirme, A., Tamm, E., 1996. Statistical characteristics of aerosol in Baltic Sea region. *Journal of Geophysical Research* 101, 19319–19327.
- Knutson, E.O., 1976. Extended electric mobility method for measuring aerosol particle size. In: Liu, . (Ed.), *Fine particles*. Academic Press, New York, pp. 739.
- Liu, B.Y.H., Marple, V.A., Whitby, K.T., Barsic, N.J., 1974. Size distribution measurements of airborne coal dust by OPC. *American Industrial Hygiene Journal* 443.
- Mirme, A., Noppel, M., Peil, I., Salm, J., Tamm, E., Tammet, H., 1984. Multi-channel electric aerosol spectrometer. In *Eleventh International Conference. On Atmospheric Aerosols, Condensation and Ice Nuclei*. Budapest, Vol. 2, pp. 155–159.
- Mirme, 1994. A electric aerosol spectrometry. Ph.D. Thesis, University of Tartu. Tartu, Estonia.
- Oberdörster, G., Ferin, J., Lehnert, B.E., 1995a. Correlation between particle size, in vivo particle persistence and lung injury. *Environmental Health Perspectives* 102, 173–177.
- Oberdörster, G., Gelein, R., Ferin, J., Weiss, B., 1995b. Association of particulate air pollution and acute mortality: involvement of ultrafine particles? *Inhal. Toxicol.* 7, 111–124.
- Pekkanen, J., Timonen, K.L., Ruuskanen, J., Reponen, A., Mirme, A., 1997. Effects of ultra-fine and fine particles in urban air on peak expiratory flow among children with asthmatic symptoms. *Environmental Research* 74, 24–33.
- Peters, A., Goldstein, I.F., Beyer, U., Franke, K., Heinrich, J., Dockery, D.W., Spengler, I.D., Wichmann, H.E., 1996. Acute health effects of exposure to high levels of air pollutants in Eastern Germany. *American Journal of Epidemiology* 144, 570–581.
- Peters, A., Wichmann, H.E., Tuch, Th., Heinrich, J., Heyder, J., 1997a. Respiratory effects are associated with the number of ultrafine particles. *American Journal of Respiratory and Critical Care Medicine* 155, 1376–1383.
- Peters, A., Dockery, D.W., Heinrich, J., Wichmann, H.E., 1997b. Short-term effects of particulate air pollution on respiratory morbidity in asthmatic children. *European Respiratory Journal* 10, 872–879.
- Reineking, A., Porstendörfer, J., 1984. Measurement of particle losses in a DMA an its influence on the evaluation of size distributions. In: Liu, Piu and Fissan (Ed.), *Aerosols*, Elsevier Publ., New York, p. 75.
- Reineking, A., Porstendorfer, J., 1986. Measurement of particle losses in a DMA (TSI, 3071) for different flow rates. *Aerosol Science and Technology* 5, 483.
- Reisert, W., Roth, C., Gebhart, J., Fischer, P., Schfer, R., 1991. Intercavity laser light scattering: Experimental verification of theoretical response functions. *Journal of Aerosol Science* 22, S355–S358.
- Spix, C., Heinrich, J., Dockery, D.W., Schwartz, J., Vlksch, G., Schwinkowski, K., Collen, C., Wichmann, H.E., 1993. Air pollution and daily mortality in Erfurt. East Germany. *Environmental Health Perspectives* 101, 518–526.
- Szymanski, W.W., Lui, B.Y.H., 1986. On the sizing of laser optical particle counters. *Particle Charact.* 3, 1–7.

- Tammet, H.F., 1975. Introduction to the Finite-Dimensional Linear Theory of Spectrometry. Valgus, Tallinn, 1975, p. 100.
- Tammet, H., 1992. On the techniques of aerosol electrical granulometry. *Acta et Comm. Univ. Tartuensis* 947, 94–115.
- Tuch, Th., Brand, P., Wichmann, H.E., Heyder, J., 1997. Variation of particle number and mass concentration in various size ranges of ambient aerosols in Eastern Germany. *Atmospheric Environment* 31, 4193–4197.
- Tuch, Th., Hietel, B., Kreyling, W.G., Schulz, F., Spix, C., Wichmann, H.E., 1998. Particulate Air Pollution and Daily Mortality in Erfurt (East Germany): Characterization of the Aerosol Size Distribution and Elemental Composition, *Air Pollution: Science and Regulation*, April 5–7, 1998 Boston, Health Effects Institute.
- USEPA United States Environmental Protection Agency Office of Research and Development. *Air Quality Criteria for Particulate Matter*. Washington DC: EPA/600/P-95/001cF, 1996.
- Willeke, K., Baron, P.A., 1993. *Aerosol Measurement, Principles, Techniques and Applications*. Vanoststrand Reinhold, New York.
- Zhang, Z., Liu, B.Y.H., 1991. Performance of TSI 3760 condensation nuclei counter at reduced pressures and flow rates. *Aerosol Science and Technology* 15, 228–238.