Intercomparison of Aerosol Spectrometers for Ambient Air Monitoring

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Three aerosol spectrometers measuring the number concentration distribution of particles in the diameter range 0.01 to 2.5 μm were compared by running them side-by-side for 385 h under ambient air conditions in Erfurt, Germany in October 1997. From the spectral data the measured hourly number concentrations in 3 size fractions, the ultrafine fraction (0.01–0.1 μm), the accumulation fraction (0.1–0.5 μm), and the coarse fraction (0.5–2.5 μm), were analyzed. The systematic component of the difference between the instruments was assessed as the geometric mean of the ratio of the measured concentrations (GMR) and the random component as the geometric standard deviation of this ratio (GSR). Previous statistical methods to compare instruments were developed further. A nonlinear multivariate regression method was used to compare the aerosol distribution consisting of several size fractions. Also, the imprecision of the individual instruments (GSI) was estimated. Comparing the instruments within the ultrafine and accumulation fractions, both the GMRs and GSRs ranged between 1.06 and 1.23 and correlations were above 0.98. In the coarse fraction, the GMR of the number concentrations ranged between 0.25 and 4.19, the GSRs between 1.81 and 2.61, and the correlations between 0.72 and 0.85. The GSIs of the instruments were below 1.2 for all fractions but the coarse fraction. To explore possible differences in the classification of particles into the accumulation and coarse fractions, coarse fractions were regressed with the coarse and the accumulation fractions of the other instruments. Using a conversion based on

this regression, the GSRs between instruments were minimized to 1.35 and the GSI to below 1.3. In conclusion, the aerosol spectrometers were in good agreement in the ultrafine and accumulation size fractions. The differences in the measured number concentrations in the coarse fraction were effectively corrected by using a regression method taking into account also the concentration in accumulation fraction, which suggests possible differences in particle sizing at 0.5 μm .

INTRODUCTION

Urban air particulate pollution has been shown to be associated with cardiorespiratory mortality and morbidity. However, it is not known which characteristics of ambient particles are responsible for these health effects and it has been hypothesized that aerosol particles of different sizes have different effects on human health (Oberdörster et al. 1995; Seaton et al. 1995; Peters et al. 1997; Pekkanen et al. 1997). Therefore integral characteristics of ambient aerosol, e.g., mass concentration like PM_{10} , $\text{PM}_{2.5}$, or black smoke, may not give adequate information to characterize the health effects of ambient particles (Eldering et al. 1994).

Instruments that can provide detailed data on variations of aerosol size distribution, e.g., aerosol spectrometers (Whitby et al. 1972; Hämeri et al. 1991; Hillamo 1994; Horvath et al. 1989; Eldering et al. 1994; Kikas et al. 1996), are rather complex and critical in their operation. These instruments have mostly been developed to measure aerosol characteristics under laboratory conditions and their performance is usually tested with known laboratory-generated aerosols (Ankilov et al. 1994; Fissan et al. 1996). The results obtained in the laboratory can, however, only be partly transferred to ambient air measurements.

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In ambient aerosol monitoring, particle concentrations need to be measured simultaneously in a wide size range from a few nanometers up to 10 μm in diameter. That usually requires several instruments of different operation principles running in parallel. The matching of their results is not always possible since the instruments of different operation principles are differently affected by the properties of ambient particles. Although it is often sufficient to divide the ambient aerosol into a few modes only (like nucleation, accumulation, coarse ones; Whitby et al. (1972)), the ambient aerosol varies rapidly in both concentration and the shape of the size distribution that challenge the dynamic performance of the instruments. Additionally, in ambient monitoring the instruments need to maintain their performance characteristics for months under field conditions.

Performance of the instruments cannot be verified against standard instruments since no commonly acceptable verification method or reference spectrometer is available so far. Thus data on the reliability and comparability of different instruments to measure ambient particle size distributions can directly be gained by running the instruments side-by-side under ambient conditions and the instruments can only be compared with each other statistically (Kinney and Thurston 1993).

In this study the comparability of 3 wide range aerosol spectrometers is analyzed based on a 2 week side-by-side comparison under ambient conditions. The aim was to compare the practicality, reliability, and comparability of the instruments in ambient air monitoring with special reference to future use in epidemiological studies. A statistical method for simultaneous comparison of several size fractions is also elaborated on.

METHODS

The Intercomparison of Spectrometers

An intercomparison of 3 aerosol spectrometers was performed under ambient air conditions in Erfurt, Germany in October 1997 following the protocol used in an earlier intercomparison between 2 of the spectrometers in Erfurt, 1996 (Tuch et al. 2000), and another intercomparison with all 3 spectrometers in Petten, The Netherlands, using both ambient and laboratory-generated test aerosols (Kreyling et al. 1999; Khlystov et al. 2001). All instruments were run according to their standard measurement protocols and were serviced in the way regularly used in ambient air monitoring (Tuch et al. 1997, 2000). Side-by-side with the aerosol spectrometers, particle total number concentration was monitored by 2 condensation particle counters (CPC and CPCB; TSI, model CPC3022A).

The mobile aerosol spectrometer (MAS), developed at the GSF, combines the differential electrical mobility analyzer DMPS (TSI 3071 and CPC TSI 3010) for particles in the size range smaller than 0.5 μm with an optical particle counter Laser Aerosol Spectrometer (LAS-X) for particles $>0.1 \mu\text{m}$ (Brand and Ruoss 1992). To combine the spectral data of the DMPS and LAS-X, weekly calibrations were performed by which the optical LAS-X spectrum—based on the calibration

of the manufacturer—was calibrated in terms of electrical mobility of monodisperse fractions of the ambient aerosol particles selected by the DMPS in the overlapping size range between 0.1 and 0.5 μm (Tuch et al. 1997, 2000). A tailored software package has been developed for processing and data inversion (Brand et al. 1991, 1992).

The second instrument was an electrical aerosol spectrometer (EAS) developed at the University of Tartu, Estonia. It measures particle size distribution in the size range 10 nm to 10 μm using only the electrical mobility method (Mirme 1994; Ankilov et al. 1994; Kikas et al. 1996; Tuch et al. 2000). Particles of the ultrafine and submicrometer size range were measured using diffusion charging, and the coarse particles were measured using field charging. The interference of particles of different sizes is corrected mathematically by using the difference in the particle charging methods (Mirme 1994).

EAS measurement performance depends on a number of operation parameters including about 7 aerosol and clean airflows and about 10 electric voltages and charging currents. The measurement quality is ensured by continuous automatic verification of most critical parameters. They are also recorded in parallel with the measurement data for later inspection.

The third spectrometer developed at ECN (denoted as DAS) is similar to MAS. DAS consists of a scanning electrical mobility analyzer SMPS (TSI 3934) and LAS-X with the difference that the optical counter was manufacturer calibrated with latex aerosol and aerosol sampling was performed at a high aerosol flow rate (300 $\text{cm}^3 \text{min}^{-1}$) in contrast to the low flow rate (60 $\text{cm}^3 \text{min}^{-1}$) of LAS-X of MAS. The standard software developed by the manufacturer of SMPS and LAS-X were used.

The measurement site was in the downtown area of Erfurt, Germany. Measurements lasted from October 20 to November 5, 1997. The instruments were located side-by-side in 2 cabins. MAS and first condensation particle counters (CPC; CPCA) were at their routine position in the first cabin (Tuch et al. 2000). The aerosol was sampled through a chimney 4 m aboveground with the air velocity of 1 m s^{-1} . The second cabin with the other CPC (CPCB), EAS, and DAS was 2 m from the first one. The aerosol sampling system was similar to that of the first cabin.

Aerosol Size Distribution Data Format

The data were first processed according to the original routine of each instrument and then converted to an intercomparison format as follows:

- hourly average number concentration (particles/ cm^3) in size ranges 0.01 to 0.1 μm (ultrafine fraction, Nu), 0.1 to 0.5 μm (accumulation fraction, Na), and 0.5 to 2.5 μm (coarse fraction, Nc), and
- hourly average total number concentrations of particles below 2.5 μm (TN, particles/ cm^3).

An hourly average value was considered valid if 66% of the data of the respective hour was available. Otherwise, all the data were used as delivered by the instruments. The protocol followed the one used earlier (Tuch et al. 1997, 2000).

Statistical Methods

The performance of instruments can be compared visually using time series plots (Watts et al. 1992; Ruoss et al. 1993). This is possible when the measured data set is rather small. However, in ambient air monitoring the data sets are large, so statistical analysis is needed.

The correlation coefficient is used to measure the correlated part of the variations of concentrations measured by different instruments (Suh et al. 1994; Holländer et al. 1990). This correlated part of the variation in concentrations is one estimate of the variation of the real aerosol. However, correlation coefficients do not indicate the characteristics of actual difference between the instruments.

Assessment of Spectrometer Intercomparison Parameters in Ambient Aerosol Monitoring

The conventional comparison of the spectrometers has been thoroughly discussed by Tuch et al. (2000) and by Kreyling et al. (1999) for ambient aerosol and by Khlystov et al. (2001) for the laboratory-generated test aerosols. Typical daily mean volume density distribution of ambient aerosol in Erfurt is presented in Tuch et al. (2000). Therefore the present study focuses on new methods of quantitative characterization of comparability between spectrometers.

Quantitative estimates of the comparability between the instruments can be gained via statistical decomposition of the differences in the reading by the instruments into regular ("bias") and random ("imprecision") parts (Kinney and Thurston 1993). However, some modifications of previous approaches are needed when comparing aerosol spectrometers measuring aerosol in multiple size fractions in parallel. Aerosol spectrometers first classify particles according to the particle size and then the concentrations of the selected size fractions are evaluated. Different instruments may measure not only the concentrations differently, but instruments may also size the particles differently into the fractions. This is especially true when the instruments use different detection principles. When doing a comparison, it is necessary to take into account both the difference in the concentration estimates and the possible difference in particle sizing. That is partly accounted for by using a minimum number of the size fractions following roughly the size modes of the ambient aerosol. However, that may not be good enough for adjacent size fractions.

A comparison of 2 spectrometers, A and B, measuring in n size fractions can be made by regressing the aerosol concentration Ci_A in fraction (i) given by instrument A on the aerosol concentration Cj_B in size fractions $j = 1$ to n given by instrument B. The concentration C can be a number (N) or any other concentration measure of the aerosol. The regular part of the difference (bias) is given by regression coefficients Hij_{AB} and the random part by the residual random variation of the difference, ζi_{AB}^k . The estimates can be made for each size fraction of instrument A and then the comparability of the spectrometers can be characterized via a set of regression coefficients Hij_{AB} , which

can be expressed as a comparison matrix, and a set of deviation estimates of ζi_{AB} , ($i, j = 1$ to n), which can be expressed as a comparison uncertainty vector. In essence, a comparison can be interpreted as a measurement of one instrument by another one.

Instrumental noise is traditionally considered additive (Lloyd et al. 1997). However, in ambient conditions the concentration may vary by a factor of more than 100, which amplifies the variations produced by fluctuations of instrumental parameters like air flows, charging, and counting efficiencies. These fluctuations change the concentration estimates proportionally to the concentrations. Therefore in ambient conditions the instrumental error is best represented by a multiplicative error model.

The model for comparison of aerosol spectrometers with ambient aerosol used in this study (Equation (1)) is mathematically the same as the traditional spectrometer response equation (Lloyd et al. 1997) with the exception that the random error is multiplicative, not additive.

$$Ci_A^k = \left(\sum_j Hij_{AB} Cj_B^k \right) \cdot \zeta i_{AB}^k, \quad [1]$$

where Ci_A^k is the concentration C in the size fraction i , $i = 1$ to n , at time k measured by instrument A, Cj_B^k is the concentration C in the size fraction j , $j = 1$ to n , at the same time k measured by instrument B, Hij_{AB} is the regression coefficient, and ζi_{AB}^k is the error term for the k th observation (k takes the values from 1 to $k_{\max}$). In the present study, size fractions i and j get values u for ultrafine fraction, a for accumulation fraction, and c for coarse fraction and k refers to a hour of observations of the intercomparison. The error term, ζi_{AB}^k , is assumed to be lognormally distributed with unity mean value. The lognormal distribution of ζi_{AB}^k can be converted into normal distribution by taking logarithm of Equation (1):

$$\text{Log } Ci_A^k = \text{Log} \left(\sum_j Hij_{AB} Cj_B^k \right) + \text{Log } \zeta i_{AB}^k. \quad [2]$$

The normality of $\text{Log } \zeta i_{AB}^k$ and the lognormality of ζi_{AB}^k , respectively, in the present material was confirmed by inspection of the distribution of the error terms. It can also be confirmed by studying the differences between the instruments in the estimated aerosol concentrations (Figures 1–3), which are quite uniform on the logarithmic scale.

The task of the comparison is to assess the regression coefficients Hij_{AB} and the variance of ζi_{AB}^k .

Equations (1) and (2) enable us to compare the spectrometers with different classifications of aerosol size fractions. However, when comparing single fractions only or total concentrations, Equation (2) can be simplified as

$$\text{Log } C_A^k = \text{Log} (H_{AB} C_B^k) + \text{Log } \zeta_{AB}^k. \quad [3]$$

Figure 1. Time variations of ultrafine aerosol fraction (0.01–0.1 μm) by the spectrometers. Data are presented as hourly mean number concentrations.

This can be further written as

$$\text{Log } \frac{C_A^k}{C_B^k} = \text{Log } H_{AB} + \text{Log } \zeta_{AB}^k. \quad [4]$$

The formulae is similar to the approach by Kinney and Thurston (1993), so the regular component of the difference (the “bias”) is $\text{Log } H_{AB}$ and the random component of the difference (the “imprecision”) is the standard deviation of $\text{Log } \zeta_{AB}^k$, denoted as $S(\text{Log } \zeta_{AB}^k) = \sqrt{D(\text{Log } \zeta_{AB}^k)}$. Therefore the discussion above can be treated as an extension of the comparison method by Kinney and Thurston (1993) to the comparison of the spectrometers, taking into account the features of ambient aerosol.

Both $\text{Log } H_{AB}$ and $S(\text{Log } \zeta_{AB}^k) = \sqrt{D(\text{Log } \zeta_{AB}^k)}$, where D denotes variance, can be directly assessed from the measured data. Thus $\text{Log } H_{AB} \pm S(\text{Log } \zeta_{AB}^k)$ characterizes the 68% confidence band of instrumental difference. Converting back to the linear

Figure 2. Time variations of accumulation aerosol fraction (0.1–0.5 μm) by the spectrometers. Data are presented as hourly mean number concentrations.

Figure 3. Time variations of coarse aerosol fraction (0.5–2.5 μm) by the spectrometers. Data are presented as hourly mean number concentrations.

scale, $\text{Exp}(\text{Log } H_{AB}) = H_{AB}$ can be called the geometric mean of the ratio (GMR_{AB}) and $\text{Exp}(S(\text{Log } \zeta_{AB}^k))$ the geometric standard deviation of the ratio (GSR_{AB}) between the concentrations measured by 2 instruments. Using the comparison parameters above, it is possible to model k reading by instrument A from a respective reading by instrument B. Also, the uncertainty of the model can be assessed using GSR_{AB} :

$$\begin{aligned} C_{B>A}^k &= H_{AB} \cdot C_B^k \cdot \text{Exp}(\pm S(\text{Log } \zeta_{AB}^k)) \\ &= \text{GMR}_{AB} \cdot C_B^k \left\{ \begin{array}{l} \cdot \text{GSR}_{AB} \\ \div \text{GSR}_{AB} \end{array} \right. \end{aligned} \quad [5a]$$

The subscript $B > A$ denotes the conversion from B to A. Thus Equation (5a) enables us to model the readings that would have been gained if instrument A had been used when the actual instrument used was instrument B. This way it is possible to compare the aerosol concentrations at different sites measured with different instruments.

For multiple size fractions (Equation (1)), Equation (5a) can be generalized as

$$C_{B>A}^k = \left(\sum_j H_{ijAB} \cdot C_{jB}^k \right) \left\{ \begin{array}{l} \cdot \text{GSR}_{iAB} \\ \div \text{GSR}_{iAB} \end{array} \right., \quad i = (1, \dots, n) \quad [5b]$$

In the case of comparison to the multiple fractions, the systematic difference is expressed via a set of coefficients H_{ijAB} . However, the comparison uncertainty is a single parameter derived for fraction (i) and can be calculated from Equation (2) as

$$\text{GSR}_{iAB} = \exp \sqrt{D(\text{Log } \zeta_{iAB}^k)}. \quad [6]$$

In this study the comparison parameters (GMR, GSR) were estimated using Equation (4) when comparing single fractions or total concentrations. When multiple fractions were compared the comparison parameters for Equation (5b) were calculated from

Equation (2) using an iteration method. At each iteration step Equation (2) was linearized by using the approximation of the logarithms in the form $\text{Log}(1+x) \cong x$. The correction function x of the coefficients Hij_{AB} was calculated using a linear multiple regression. The iteration process converged with 5–6 steps.

To test the iteration method, Hij_{AB} and $S(\text{Log } \zeta_{AB}^k)$ were also estimated by directly solving the model (Equation (1)) using a nonlinear multiple regression with a penalty function $Li_{AB} = (\text{Log}(Obs) - \text{Log}(Pred))^2$ (STATISTICA 1996 user-specified regression in nonlinear estimation section), where $Obs = Ci_A$ and $Pred = \sum_j Hij_{AB} \cdot Cj_B$. This estimation gave identical results to the iteration method result but required much more time (30–50 steps).

Imprecision of the Individual Instruments

According to Kinney and Thurston (1993), imprecision of individual instruments can be estimated for 2 instruments using the difference in the measured aerosol concentrations obtained in a side-by-side comparison. This approach assumes that the imprecisions of the individual instruments are not correlated, i.e., covariance is zero. With only 2 instruments, they also had to assume equal imprecision of the 2 instruments. With 3 or more instruments available, as in the present study, this assumption is not needed and the imprecision of individual instruments can be estimated as follows.

The variance of $\text{Log } \zeta_{AB}^k$ (Equation (4)) consists of 3 parts:

$$D(\text{Log } \zeta_{AB}^k) = D(\text{Log } \zeta_A^k) + D(\text{Log } \zeta_B^k) - 2 \cdot \text{Cov}(\text{Log } \zeta_A^k, \text{Log } \zeta_B^k). \quad [7]$$

Assuming zero covariance between the instruments ($\text{Cov}(\text{Log } \zeta_A^k, \text{Log } \zeta_B^k) = 0$), as was also assumed by Kinney and Thurston (1993), Equation (7) can be written for each pair of 3 instruments as

$$\begin{aligned} D(\text{Log } \zeta_{AB}^k) &= D(\text{Log } \zeta_A^k) + D(\text{Log } \zeta_B^k), \\ D(\text{Log } \zeta_{AC}^k) &= D(\text{Log } \zeta_A^k) + D(\text{Log } \zeta_C^k), \\ D(\text{Log } \zeta_{BC}^k) &= D(\text{Log } \zeta_B^k) + D(\text{Log } \zeta_C^k). \end{aligned} \quad [8]$$

This set of equations can be solved using the least square method. Converting back to linear scale, the imprecision of each instrument (GSI) can be estimated as

$$\text{GSI}_A = \text{Exp} \sqrt{D(\text{Log } \zeta_A^k)}. \quad [9]$$

Equation (8) provides a way to separate the random variations of the instruments, which may relate to the random measurement error of the instrument. However, the method is based on comparison between instruments, so the estimate for a particular instrument depends on the other instruments used. Equation (8) also assumes that all covariances between the imprecisions of instruments are zero. Therefore the method may underestimate

the imprecision, if the random component of the variation is correlated between the instruments, e.g., because of the similar measurement principle, and, respectively, may overestimate the imprecision for the other, uncorrelated instruments

RESULTS

General Description

The measurement period lasted from noon on October 20 until noon on November 5, 1997, a total of 385 h. MAS produced valid 382 hourly average values (99.2%) and EAS 373 hourly average values (96.9%) (Table 1). For the accumulation and coarse fraction of DAS and for the 2 CPCs, the number of valid hours was somewhat less, but for the ultrafine fraction DAS measured only 240 hourly average values. This was caused by a defective butanol-draining valve of the CPC 3010 of the SMPS, which caused butanol flooding of the condenser chamber leading to erroneous CPC counts. This malfunction was detected only after a delay of 2 days, because the readings were not completely nonsense, but were still not comparable to the other spectrometers. Subsequent cleaning and drying of the condenser chamber took longer than the rest of the period of the intercomparison, so no data could be recorded anymore. EAS was not serviced during the whole measurement period, whereas MAS and DAS had a regular daily service, which was, however, usually short enough that no missing hourly means occurred.

Table 1

Statistical characteristics of aerosol particle total and fraction number ($1/\text{cm}^3$) concentrations and total mass ($\mu\text{g}/\text{m}^3$) concentration. N is the number of valid measurement hours; total number of the hours was 385

	N	Geom. mean	Geom. std. dev.
Total number concentration			
CPCA	362	23600	2.17
CPCB	343	24900	2.01
MAS	382	21800	2.19
EAS	373	19800	2.20
DAS	237	19400	2.22
Number concentration in ultrafine fraction (0.01–0.1 μm)			
MAS	382	18500	2.33
EAS	373	16900	2.31
DAS	240	17200	2.25
Number concentration in accumulation fraction (0.1–0.5 μm)			
MAS	382	2590	2.19
EAS	373	2390	2.07
DAS	358	2130	2.11
Number concentration in coarse fraction (0.5–2.5 μm)			
MAS	382	10.7	4.10
EAS	373	44.0	2.14
DAS	360	10.2	2.66

Figure 4. Scatter of coarse fraction (0.5–2.5 μm) concentrations by DAS and EAS versus MAS. Data are presented as hourly mean number concentrations.

There was almost no difference in the time walks between the aerosol spectrometers in the ultrafine fraction (Figure 1), except for a few scattered hours when EAS tends to measure lower concentrations than the other aerosol spectrometers. As the ultrafine fraction contributes most of the total number concentration, there was also almost no difference between the total number and ultrafine concentrations (Table 1). The time walks of total number concentrations measured by the 3 spectrometers and 2 CPCs matched very well with each other and were practically indistinguishable in a time variation graph (not presented). There were small differences in the time variations of the accumulation fraction when MAS tends to measure higher concentrations than the other aerosol spectrometers (Figure 2).

In the coarse fraction, EAS measured higher particle number concentrations than the other aerosol spectrometers and the ratio was not always constant (Figures 3 and 4). During the second half of the measurement period, MAS even measured higher levels than EAS during a few high pollution days.

The instruments produced similar mean levels and geometric standard deviations of particle number concentrations in the ultrafine and accumulation fractions and in the total concentrations (Table 1). Major differences were observed only in the coarse fraction, where EAS measured the highest levels, but had the lowest geometric standard deviation. DAS had a slightly higher variation, while that by MAS was clearly the highest. The degree of agreement between the instruments was characterized by the values of Spearman rank order correlation coefficients. The total number concentrations correlate highly between all the instruments, including both CPCs, and the correlation in the ultrafine and accumulation fractions was almost similar to that of the total number concentration (Table 2). The worst correlations were observed in the coarse fraction.

Table 2
Spearman rank correlation of aerosol number concentrations in different fractions by 3 spectrometers, pairwise deletion of the data

	MAS	EAS	DAS
Ultrafine fraction	With ultrafine fraction		
MAS	1	0.98	0.98
EAS		1	0.98
DAS			1
Accumulation fraction	With ultrafine fraction		
MAS	0.61	0.67	0.79
EAS	0.67	0.73	0.85
DAS	0.64	0.69	0.82
Coarse fraction	With ultrafine fraction		
MAS	0.01	0.03	0.48
EAS	0.22	0.25	0.70
DAS	0.06	0.10	0.62
Accumulation fraction	With accumulation fraction		
MAS	1	0.98	0.98
EAS		1	0.99
DAS			1
Coarse fraction	With accumulation fraction		
MAS	0.59	0.55	0.55
EAS	0.76	0.74	0.75
DAS	0.55	0.52	0.53
Coarse fraction	With coarse fraction		
MAS	1	0.85	0.72
EAS		1	0.81
DAS			1

Characteristics of the measured aerosol and possible differences between the aerosol spectrometers in the sizing of particles can also introduce covariance between the different size fractions. There was a fairly high correlation (0.5–0.8) between the adjacent size fractions, i.e., between the ultrafine and accumulation fraction and between the accumulation and coarse fractions (Table 2). The ultrafine fraction of DAS had the highest correlation with the accumulation fractions measured by the 3 instruments, whereas the coarse fraction of EAS had the highest correlation with the accumulation fractions.

The correlation of the coarse fractions measured by MAS and DAS with the ultrafine fractions were generally low (<0.1). The coarse fraction of EAS correlated more (0.25) with the ultrafine fractions. The ultrafine fraction of DAS showed high correlation, 0.48, 0.47, and 0.62, with the coarse fraction measured by MAS, EAS, and DAS, respectively.

Comparison of Aerosol Particle Concentrations Measured by the Spectrometers

Estimation of the instrument comparability was then made using Equations (4) and (5a). The results are presented in a form of comparison parameters, split into the systematic component of the instrumental differences, the GMR, and the random component, the GSR (Equations (4) and (5a)).

The average levels of the total number concentration between the 2 CPCs differed by only 1% (Table 3). The highest agreement in average level between the aerosol spectrometers and CPCs were observed for MAS (10–11%) and the lowest for used for DAS (30–33%). Also, the smallest random component (GSR) of the ratio between the instruments was observed for MAS and the largest for DAS. This good agreement agrees with the high correlation between the total number concentrations (Table 2).

The agreement in the ultrafine and accumulation fractions was similar to that for the total number concentration (Table 4). The largest systematic and random components of the difference between the instruments were observed between MAS and

Table 4
Comparison parameters of aerosol spectrometers in different aerosol size fractions, 225 h

	GMR	GSR
Ultrafine fraction		
MAS to EAS	1.10	1.15
MAS to DAS	1.16	1.23
EAS to DAS	1.06	1.19
Accumulation fraction		
MAS to EAS	1.08	1.16
MAS to DAS	1.21	1.19
EAS to DAS	1.12	1.15
Coarse fraction		
MAS to EAS	0.25	2.39
MAS to DAS	1.05	2.61
EAS to DAS	4.19	1.81

DAS, but the differences are not large. This suggests that these fractions are measured correctly enough and the exact equations (Equations (1), (2), and (5b)) are not needed.

In contrast, the mean number concentration in the coarse fraction measured by EAS was 4 times higher than those measured by the 2 other instruments. Despite that the random variations (GSR) are the largest between MAS and DAS and smallest between EAS and DAS. Therefore the comparison parameters for coarse fraction were recalculated based on Formula 2

$$\text{Log}(N_{cA}) = \text{Log}(Hca_{AB} \cdot Na_B + Hcc_{AB} \cdot Nc_B) + \text{Log} \zeta c_{AB}. \quad [10]$$

Since a difference in sizing may only have an effect on the neighboring fractions, the regular difference between the coarse and ultrafine fractions, Hcu_{AB} , was assumed to be zero. The estimates of the regular difference Hca_{AB} and Hcc_{AB} in the number concentrations in the accumulation (Na_B) and coarse fraction (Nc_B), respectively, for instrument B were calculated using an iteration method. At the i th iteration step the corrections ΔHca_{AB} , ΔHcc_{AB} to the values $Hca_{AB,i-1}$, and $Hcc_{AB,i-1}$ of the previous step were calculated as coefficients of ordinary linear regression (Equation (11)).

$$\text{Log}\left(\frac{Nc_A}{ENc_{A,i-1}}\right) \cdot ENc_{A,i-1} = \Delta Hca_{AB} \cdot Na_B + \Delta Hcc_{AB} \cdot Nc_B, \quad [11]$$

where $ENc_{A,i-1} = (Hca_{AB,i-1} \cdot Na_B + Hcc_{AB,i-1} \cdot Nc_B)$ denotes the estimate of the concentration by instrument A after $i - 1$ iteration steps. The formulae 11 is derived from Equation (10) using the approximation $\text{Log}(1 + x) \cong x$.

According to Equation (10) the comparison of EAS data to the coarse fraction measured by MAS and DAS by taking into account the accumulation fraction of EAS seemed not to be

Table 3

Comparison parameters of instruments in total number concentration, 208 h

	GMR	GSR
CPCA to CPCB	1.01	1.12
CPCA to MAS	1.11	1.13
CPCA to EAS	1.24	1.16
CPCA to DAS	1.33	1.21
CPCB to MAS	1.10	1.20
CPCB to EAS	1.22	1.24
CPCB to DAS	1.30	1.27
MAS to EAS	1.11	1.12
MAS to DAS	1.19	1.18
EAS to DAS	1.07	1.16

Table 5

Comparison parameters between aerosol coarse fraction by first spectrometer (A) with accumulation and coarse fractions of the second spectrometer (B) (Equation (10))

Instrument A		Instrument B		
		Accumulation fraction (H_{ca})	Coarse fraction (H_{cc})	GSR*
Coarse fraction				
MAS	EAS	−0.0026	0.42	2.26
MAS	DAS	0.0011	0.76	2.54
DAS	MAS	0.0022	0.31	1.93
DAS	EAS	−0.00098	0.30	1.80
EAS	MAS	0.0123	0.72	1.39
EAS	DAS	0.0118	1.46	1.35

* $GSR_{cAB} = \exp\sqrt{D(\text{Log } \zeta c_{AB}^k)}$ in Equation (10) according to Equation (6).

effective since the random component (GSR) was still quite large (Table 5). Also, the GSR between MAS and DAS almost did not decrease compared to the GSR for the coarse fraction in Table 4. The only significant decrease of GSR was observed when the accumulation fraction and the coarse fraction of MAS and DAS were compared to the coarse fraction of EAS (last 2 columns of Table 5). Comparing the converted data of MAS and DAS with EAS data resulted in $GSR = 1.39$ and $GSR = 1.35$, respectively, while GMR was forced to be $GMR = 1.0$.

The variations in the coarse fraction using the converted data were very close for the different spectrometers with a correlation of 92–94% between all of the spectrometers.

Imprecision of Individual Instruments

The total number concentration was assessed by the 5 instruments. Although spectrometers are size selective instruments in which the total concentration counts are derived from the distribution data, their individual imprecisions (GSI) were in the same range as direct counting CPCs (Table 6).

The calculated GSIs of the spectrometers in different aerosol fractions were rather close to each other, except that in coarse fraction MAS seemed to have the largest GSI.

The GSIs of the spectrometers in the coarse fraction, when they had been converted to EAS (Equation (10)), were between 1.21 and 1.27, which is reasonably close to that for the other size fractions. Since the coarse fraction measured by EAS was not transformed, the decrease of GSI from 1.36 to 1.25 may indicate some covariance between MAS and DAS (Equation (7)).

DISCUSSION

Three aerosol spectrometers (MAS, DAS, and EAS) and 2 condensation particle counters (CPCs) have been compared to each other by running them side-by-side in ambient air for 385 h in Erfurt, Germany.

MAS and EAS performed reliably during the measurements, obtaining more than 90% of possible hourly data. For DAS only

Table 6

Estimated imprecision of individual instruments in different size fractions (Equations (8) and (9))

Instrument	Imprecision (GSI)
Total number concentration, 208 h	
CPCA	1.08
CPCB	1.17
MAS	1.08
EAS	1.11
DAS	1.17
Ultrafine fraction, 225 h	
MAS	1.13
EAS	1.07
DAS	1.18
Accumulation fraction, 343 h	
MAS	1.14
EAS	1.08
DAS	1.12
Coarse fraction, 345 h	
MAS	2.26
EAS	1.36
DAS	1.66

62% of data were available in the ultrafine fraction due to problems in SMPS arising from the defective butanol-draining valve in the CPC 3010 as described above. MAS and DAS are similar instruments, consisting of an electrical mobility measurement method of bipolar charged particles size-dependently below $0.5 \mu\text{m}$ by CPC counting (DMPS and SMPS principles) and an optical particle counter (LAS-X) in the large particle range. However, MAS and DAS had different calibration and operation procedures to match the readings of the electrical mobility and optical instruments. EAS is composed of 2 electrical mobility analyzers preceded by either unipolar diffusion or electric field charging to operate in the full particle size range. Thus with appropriate servicing the instruments of different operation principles are quite capable of operating continuously in ambient conditions.

The number concentrations measured by the different instruments were compared by total number concentration and by dividing the particle size distribution in 3 size fractions, the ultrafine ($0.01\text{--}0.1 \mu\text{m}$), accumulation ($0.1\text{--}0.5 \mu\text{m}$), and coarse ($0.5\text{--}2.5 \mu\text{m}$) fractions, and using in analysis also the total number concentrations measured by CPCs. We assessed the systematic component of the differences in the measured number concentrations between 2 instruments as the geometric mean of the ratio of measured hourly concentrations between two instruments (GMR) and the random component as the standard deviation of this ratio (GSR). The method accounts specifically for highly varying ambient aerosols. The estimates can be considered to be of equal relative reliability in the whole range of the concentration variations. Particularly important is to consider the comparison uncertainty (GSR) since the mean values

alone have little statistical weight. In addition to the comparison between individual size fractions, we also used a nonlinear multivariate regression method to simultaneously compare several size fractions, which enabled us to effectively account for the shift of the spectral scale. We also decomposed the aerosol variation between the instruments to estimate the instrument-specific variances.

Comparisons within Each Size Range. Total particle concentrations measured by all 3 spectrometers and 2 CPCs agreed very well. The largest difference in the GMR between the aerosol spectrometers was observed between MAS and DAS (1.19). The standard deviation of the ratio (GSR) between the 2 CPCs was 1.12, which was similar to the standard deviations of the ratios between the 3 aerosol spectrometers. Slightly larger geometric mean ratios, up to 1.33, were observed when the aerosol spectrometers were compared to the CPCs, which may partly be due to the different counting efficiency patterns of the integral counting CPCs compared to the CPCs used with SMPS and DMPS, i.e., while all spectrometers start to count particles ≥ 10 nm, the CPC 3022A counts all particles > 5 nm with rapidly decreasing counting efficiency which results in a 50% efficiency for 7 nm particles. The correlations between the total particle concentrations measured by the different instruments were all above 0.98.

The results of the ultrafine fraction were closely similar to the results of the total particle concentrations. This is due to the fact that the total particle concentration is dominated by ultrafine particles. The mean ratios and the standard deviations of the ratios in the accumulation fraction were also low (< 1.21) between the 3 aerosol spectrometers. Also, the correlations were always higher than 0.98.

The only large difference was observed in the coarse fraction, i.e., for the particles between 0.5 and $2.5 \mu\text{m}$ in diameter. The average number concentrations measured by EAS were about 4 times higher than those measured by MAS or DAS. However, the variability of the ratio between the aerosol spectrometers was largest between MAS and DAS (GSR was 2.61). This is also reflected in the correlation coefficients, being lowest (0.72) between MAS and DAS and above 0.8 when those 2 instruments were compared to EAS.

Based on the size and number distribution of particles measured, the total volume of the particles smaller than $2.5 \mu\text{m}$ was also estimated (data not shown). Correlation between the total volume concentrations were almost as high (> 0.92) as those of total number concentrations (0.98, see Table 2). Note, however, that MAS and DAS measure 73% and 67% of the total volume in the accumulation fraction, respectively, while EAS measures most of the volume in the coarse fraction (62%).

The 2 instruments, MAS and EAS, have earlier been compared in Erfurt in the spring of 1996 (Tuch et al. 2000). All 3 instruments took part in a short pilot study in Petten in June 1996 (Kreyling et al. 1999). Also, in the previous studies there was good agreement in the ultrafine and accumulation fractions, but in the coarse fraction EAS tended to measure higher particle concentrations and the correlations between all the instruments

were lower in that fraction. In Petten, there was a similar correlation between EAS and DAS in the coarse fraction (0.79) as in this study (0.81). However, the correlation in the coarse fraction between MAS and EAS was lower (0.74) in Petten than in this study (0.85) and the correlation between MAS and DAS was higher in Petten (0.81) than in this study (0.72).

These results suggest that some changes may have happened in MAS between the current and the Petten intercomparison. In fact, after the usual cleaning due to air pollution and the new adjustment of the laser mirrors of the LAS-X—which occurred 4 times during the campaign—the laser intensity increased for several hours to unusually high laser intensities of the factory-new laser. Since this was considered a good performance of the laser (as no problems with high laser intensities had been reported earlier) this led to very high detection sensitivities such that the subsequent signal-analyzing electronics malfunctioned (as we found out after the intercomparison). This malfunction resulted in a shift of particles to larger sizes. Since concentration of particles sized from 0.4 to $1 \mu\text{m}$ dropped drastically, this malfunction caused a considerable shift of particles in the size range of 0.43 to $0.5 \mu\text{m}$ to the range of 0.5 to $0.55 \mu\text{m}$, leading to an artificial but considerable increase of the otherwise low number concentration of the coarse particle fraction and inducing a larger random variability and instrumental imprecision. (The change in the accumulation fraction was negligible.) Note that the artifact of the LAS-X of MAS was only detected by the intercomparison of the 3 aerosol spectrometers side-by-side. It is striking evidence of the importance and value of such an intercomparison. After this experience the standard operation procedure of LAS-X was changed accordingly to prevent malfunction after cleaning and adjustment of the laser mirrors. Although correction would have been possible, we left the original data in this error analysis and found the above-mentioned altered correlation as an indicator of the actual artifact in the coarse fraction of MAS. This, in turn, is valid evidence that the applied error analysis was able to detect such an artifact.

The current and previous results suggest that the total particle number concentrations, and the number concentrations of the ultrafine and accumulation fractions given by the 3 aerosol spectrometers, are comparable without any correction factors and that they reflect absolute levels, overall variance, and hourly variations of atmospheric particles in a comparable fashion. In contrast, this is not necessarily true for the coarse fraction.

Comparisons between Size Ranges. The disagreement between the instruments in the coarse fraction concentrations can partly be due to the differences in the sizing of the particles between the accumulation and coarse fractions. We therefore conducted further analyses, where the coarse fraction concentrations were simultaneously regressed against both the coarse and accumulation concentrations given by the other instrument. This approach enabled us to estimate transformations, which reduced the GSRs between the instruments to 1.35. This suggests that a major reason for the disagreement in the coarse fraction may be due to the differences between the different instruments in

the sizing of the particles between the accumulation and coarse fractions. However, this difference seems to be quite constant over time, since after the transformation the GSR was reduced from 2.6 to a very reasonable level (1.35). A difference in sizing between the optical and electrical mobility instruments has also been observed (Stolzenburg et al. 1998). The difference in sizing yields an even larger difference in the estimated apparent particle volume, as has been observed in comparisons of EAS and MAS (Tuch et al. 2000). In this previous comparison, total volume of the particles smaller than $2.5\text{ }\mu\text{m}$ measured by EAS and MAS was compared with daily $\text{PM}_{2.5}$. Assuming a value reported in the literature on the mean apparent density of 1.5 g/cm^3 of all particles between 10 nm and $2.5\text{ }\mu\text{m}$, MAS gave an average mass concentration similar to $\text{PM}_{2.5}$, whereas EAS gave clearly higher estimates. On the other hand, correlation between the aerosol spectrometers in the total volume concentrations are high. This corresponds to the fact that MAS and DAS measure 73% and 67% of the total volume in the accumulation fraction, respectively, while EAS measures most of the volume in the coarse fraction (62%).

In this study, a major reason for the difference in the average number counts in the coarse fraction may be that MAS and DAS measure coarse particles optically, whereas EAS uses an electrical mobility method also in this size fraction. Furthermore, EAS measures the particles close to the temperature and humidity of ambient air, whereas optical particle counters dry the particles at least partially (Ten Brink et al. 2000). Also, MAS and DAS, despite the similarity in construction, are calibrated in a different way. Another reason may result from the uncertainty caused by the rather flat response curve of LAS-X for particles in the size range 0.4 to $0.8\text{ }\mu\text{m}$. Despite the occasional malfunctioning of the LAS-X of MAS yielding the large variations, the geometric mean number concentrations of DAS and MAS in the coarse fraction are close and a factor of about 4 lower than that of EAS (Table 1).

We generalized a method to estimate imprecision of individual instruments. In this study the imprecision of individual instruments was fairly low, geometric standard deviations of the imprecision (GSI) were generally below 1.2 in the ultrafine and accumulation fractions. In the coarse fraction, geometric standard deviations were clearly larger, up to 2.26. After using the conversion factors for the coarse fraction, the imprecision dropped to around 1.25 also in the coarse fraction.

The present comparison is similar to a laboratory calibration with the difference that none of the instruments used can be considered as an absolute reference instrument. The absolute accuracy in respect to real aerosol cannot be known and may vary a lot, depending on unknown properties of local aerosol particles. Still some statistical uniformity of ambient particles in the cities can be expected, as most of the fine particles originate from traffic. The conversion factors developed in the present paper serve as an extra transform of the data following the primary conversion of the instrument readings to particle size spectrum and thus finalize the calibration at given conditions. However,

the generalization of the present transformations to other situations, where the chemical composition and other characteristics of the ambient particle is not known, should be done only cautiously. The limited data from our pilot study in Petten (Kreyling et al. 1999) give some support for generalizability to at least 2 locations in Europe.

Statistical Method Used. The present paper used a statistical method that divided the differences in the number concentrations measured by the aerosol spectrometers into a systematic and a random component. This is useful, as it not only enables us to derive the mean difference between the instruments, but also to estimate the range of uncertainty of this difference. Using this method, it is also possible to transform the readings of the different spectrometers to each other, which is needed when the aerosol distributions of different cities are being compared. Also, only by knowing the comparison uncertainty range is it possible to evaluate the significance of the observed differences in aerosol concentrations.

For statistical accuracy, the asymmetric variations of ambient aerosol concentrations have been taken into account by using the logarithmic scale. The logarithmic scale also agrees with the requirement of ambient aerosol monitoring to follow aerosol concentration variations in a very wide and asymmetric range. For example, a difference of $10,000$ particles per cm^3 is quite small a difference at concentrations of $100,000$ particles per cm^3 , while the same difference at the measured concentration of $10,000$ particles per cm^3 is rather large. The multiplicative error model used in the present paper (Equation (1)) enables the derivation of the comparison parameters with uniform relative accuracy over the full concentration range. The logarithmic transformation also makes the model linear (Equation (2)), which allows the use of standard linear analysis methods.

CONCLUSIONS

The present results show that all 3 aerosol spectrometers can be used to monitor the size distributions and number concentrations of ambient aerosol. The measured number concentrations were well comparable, especially of the total number of particles and in ultrafine and accumulation fractions, i.e., for particles below $0.5\text{ }\mu\text{m}$ in diameter. Larger differences were observed in coarse fractions (larger than $0.5\text{ }\mu\text{m}$), where EAS measured the highest absolute concentrations, and the largest difference in the variability was observed between MAS and DAS.

However, by applying an appropriate comparison method using data from both the coarse and the accumulation fraction, the instrument differences in the coarse fraction of particle number concentrations were effectively reduced. Using the conversion factors derived from this comparison method, the aerosol distributions in all size ranges were comparable between the instruments with uncertainty of 10–40% and all the correlation between instruments were more than 90%.

The generalization of the conversion factors to other cities in Europe is, however, uncertain. Therefore when attempting a

comparison between different cities in the coarse fraction or in mass concentration, the measurements should be supplemented with direct measurements of the mass ($PM_{2.5}$).

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