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Measurements of Size-Segregated Emission Particles by a Sampling System Based on the Cascade Impactor

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A special sampling system for measurements of size-segregated particles directly at the source of emission was designed and constructed. The central part of this system is a low-pressure cascade impactor with 10 collection stages for the size ranges between 15 nm and 16 μm. Its capability and suitability was proven by sampling particles at the stack (100 °C) of a coal-fired power station in Slovenia. These measurements showed very reasonable results in comparison with a commercial cascade impactor for PM_{10} and $PM_{2.5}$ and with a plane device for total suspended particulate matter (TSP). The best agreement with the measurements made by a commercial impactor was found for concentrations of TSP above 10 mg m^{-3}, i.e., the average $PM_{2.5}/PM_{10}$ ratios obtained by a commercial impactor and by our impactor were 0.78 and 0.80, respectively. Analysis of selected elements in size-segregated emission particles additionally confirmed the suitability of our system. The measurements showed that the mass size distributions were generally bimodal, with the most pronounced mass peak in the 1–2 μm size range. The first results of elemental mass size distributions showed some distinctive differences in comparison to the most common ambient anthropogenic sources (i.e., traffic emissions). For example, trace elements, like Pb, Cd, As, and V, typically related to traffic emissions, are usually more abundant in particles less than 1 μm in size, whereas in our specific case they were found at about 2 μm. Thus, these mass size distributions can be used as a signature of this source. Simultaneous measurements of size-segregated particles at the source and in the surrounding environment can therefore significantly increase the sensitivity of the contribution of a specific source to the actual ambient concentrations.

Introduction

One of the more pernicious problems in air quality is the persistence of fine suspended particulate matter. Until recently, the total mass concentration of airborne particulate matter (TSP) was the only standard for particulates used for air quality assessment. New developments in aerosol measurement techniques enabled size-dependent analyses of aerosol particles, thus better classifications and more comprehensive studies of the effect of ambient aerosols are feasible. Exposure to elevated concentrations of respirable ambient aerosol particles has been associated with various health problems (*1*, *2*). Particle size and shape are key factors controlling the extent of particle penetration into the human respiratory tract. In addition, the potential health effects depend on many other factors, such as chemical and physical characteristics of aerosols, the amount of toxic substances, and their solubility in biological fluids, etc. (*3*, *4*). As a result of numerous studies on the health effects and epidemiological investigations, the regulations have focused on controlling PM_{10}, which refers to the mass concentration of inhalable particles with an aerodynamic diameter less than 10 μm and $PM_{2.5}$, which refers to the alveolar size fraction with a diameter less than 2.5 μm (*5*, *6*).

Among the combustion sources that have the most significant relative contribution to air pollution are power and industrial plants, with coal the most commonly used fuel for commercial power generation due to its relatively abundant reserves (*7*). The emission of particles is a complex function of fuel type and quality, combustion technology, type and size of facility, and control technology, etc. (*8*, *9*). Despite the progress in emission reduction technology, which has greatly decreased the emission of TSP (e.g., particulate controls in power stations have high efficiency rates), considerable amounts of particles are released into the environment. This fact is true particularly for the big power stations with high coal consumption (*10*).

Therefore, information on the particulate matter emission from combustion sources is important for a number of reasons, such as examination of source status according to regulations, generation of emissions inventories, prediction of ambient air quality in the areas affected by the source as well as source apportionment and exposure assessment for the affected human population and ecological systems. Formerly, emissions at the source have been monitored by measuring TSP, e.g. using plane filter devices according to the methods by the Environmental Protection Agency (EPA) or VDI (*11*, *12*). Whereas for the determination of mass size distribution of particles at the source, measurements were performed by cascade impactors or cascade cyclones (*13*, *14*). Measurements of emissions typically involve much more complicated sampling approaches, such as source dilution and isokinetic conditions (*9*, *15*, *16*). Recently, for more precise measurements of PM_x, a new $PM_{10}/PM_{2.5}$ cascade impactor (GMU-impactor Johnas) for in-stack measurements was developed (*17*, *18*).

The objectives of this study were to design and construct a special sampling system for measurements of size-segregated particles in the size range from 15 nm to 16 μm directly at the source of emission. To prove the feasibility and capability of this system, it was used for size-segregated sampling of particles at the stack of a coal-fired power station in Slovenia, and the first results of mass and chemical size distribution of emission particles are presented. In addition, for checking the accuracy of our sampling system the measurements were performed simultaneously with the commercial impactor (GMU-impactor Johnas). Since size segregation of some typical elements depends on the source, an insight into their size distributions at the source and comparison with the surrounding ambient concentrations

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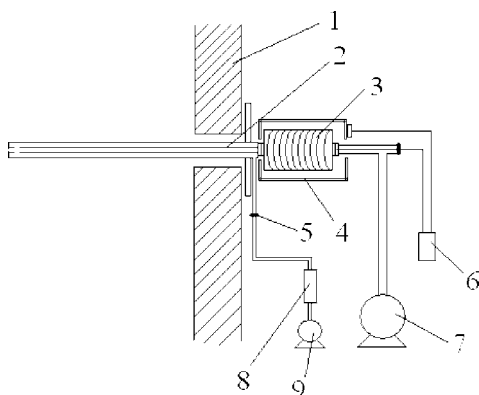§ Electroinstitute Milan Vidmar.

FIGURE 1. Simplified scheme of the sampling system: 1, stack wall; 2, sampling probe; 3, 10-stage low-pressure Berner impactor; 4, oven; 5, filter holder with filter for removing particles in ambient air; 6, system for controlling and measuring the temperature inside impactor; 7, vacuum pump; 8, device for delivering constant volumetric air flow; 9, compressor unit.

and size distributions can significantly improve our knowledge on the contribution of the individual source to the actual ambient air pollution by particulate matter.

Experimental Section

Sampling Device. The measurements were carried out by a specially constructed sampling system illustrated in Figure 1. The central part of our system is a Berner low-pressure cascade impactor (HAUKE, LPI 25/0,015/2) with 10 collection stages for the nominal size ranges expressed in D_{ae} (aerodynamic equivalent diameter): 0.015–0.03 μm; 0.03–0.06 μm; 0.06–0.125 μm; 0.125–0.25 μm; 0.25–0.5 μm; 0.5–1.0 μm; 1.0–2.0 μm; 2.0–4.0 μm; 4.0–8.0 μm; 8.0–16.0 μm. The sampling probe consists of two tubes of different diameters. The central one is connected to the impactor inlet on one side, and on the other side it is opened to the flue gas inside the stack. The system for controlling and measuring the temperature inside the impactor enables the impactor to be heated to the temperature of the flue gas and also enables the desired temperature to be maintained during the sampling. In the case of undiluted sampling, the filter holder with a filter for removing particles from ambient air, the device for delivering constant volumetric air flow, and the compressor unit were not used, and the inlet to the outer tube was blocked. The nominal flow rate through this impactor is 25.8 L min^{-1}. Because of technical problems (i.e., small sampling port and mechanical instability of the sampling probe because of the rather bulky impactor), the impactor was positioned outside the chimney stack, while a sampling probe was placed into the chimney. Before the flue gas enters the stack it is washed in a gas scrubber in order to remove a considerable part of the SO$_2$ formed during the combustion of the coal. Therefore, the flue gas contains a lot of water vapor at around 100 °C. Thus, to prevent water condensation on the particles the inside of the impactor was heated to the temperature of the flue gas before sampling and kept constant during sampling. As shown in Figure 1 the sampling probe was designed to also allow dilution of the flue gas by compressed and filtered ambient air. The flow rate of dilution air was controlled by the device for delivering constant volumetric air flow. According to selected conditions several dilution rates are possible.

Emission Measurements. The measuring campaign was performed in June 2005 and May 2006 at the stack of the coal-fired power station in Slovenia. Sampling was conducted from the 50 m platform on the stack using existing sample ports, i.e., holes with an opening of 12 cm on the outer side and 30 cm on the inner side of the stack and with a depth

of 50 cm. The sampling times were from 10 min to 1 h (without dilution) and 5 h when dilution was introduced. The impaction plates were covered with annular Tedlar foils, and on top of these folded aluminum foils were placed. This arrangement enabled the simultaneous determination of the mass and chemical composition with one sampling only.

Emission measurements were also carried out with the filter sampler for TSP (SICK, Gravimat SHC 502) and with the cascade impactor for PM$_{10}$ and PM$_{2.5}$ (Paul Gothe Bochum, GMU cascade impactor Johnas). Samples were taken in parallel either by both the LPI and Johnas impactor or one impactor and TSP sampler. Simultaneously, continuous measurements of TSP were performed with a dust concentration monitor (OMD41).

Mass and Chemical Analysis. Mass size distribution of particles was determined gravimetrically using aluminum foils, while for chemical analysis Tedlar foils were used (*19*). On the basis of preliminary experiments done with certified material (Reference Material 1648, Urban Particulate Matter) and samples of TSP collected on quartz fiber filters at the stack of the thermo-power plant, the extraction with concentrated HNO$_3$ was selected because of the lower detection limits for some of the elements in comparison with other extraction methods (i.e., HNO$_3$/H$_2$O$_2$ and HNO$_3$/HF digestion) and its simplicity. The applied extraction procedure leads to the total recovery of Zn, As, Se, Cd, and Pb. For Mg, V, Mn, and Ni, recoveries were in the range of 60 to 80%, while for K and Co lower recoveries were obtained (approximately 50%). After extraction of aerosol deposits on Tedlar foils as well as PM$_{2.5}$, PM$_{10}$, and TSP samples in HNO$_3$, measurements of Mg, K, V, Mn, Co, Ni, Zn, Ga, As, Se, Sr, Mo, Cd, and Pb were performed by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500ce system with collision reaction cell). After extraction of deposits on aluminum foils in Milli-Q water, SO$_4^{2-}$ was determined by ion exchange chromatography, with a Dionex IonPac AS4A separation column and a mixture of Na$_2$CO$_3$/NaHCO$_3$ as the eluent (*19*).

Results and Discussion

Mass Concentration and Chemical Composition of Emission Particles. The results of particle mass concentrations measured at the stack of the thermo-power plant in Slovenia by different techniques are shown in Table 1. All the results are expressed at normal conditions (273 K, 1013 mbar). During the first sampling in 2005, measurements were performed in parallel using one plane filter device (for TSP) and our upgraded system with a 10-stage Berner impactor, while measurements with the GMU-impactor Johnas were only feasible immediately after sampling with our system. For sampling during 2006, this technical problem was solved allowing measurements with the GMU-impactor Johnas and our impactor to be carried out simultaneously. Although the energy production was practically the same during these two sampling periods, there were differences regarding the particle mass concentrations. Due to some improvements in the operating technology and emission reduction technology, the concentrations were reduced by more than twice in the second period. TSP concentrations in 2005 were about 25 mg m^{-3} over the whole sampling period, while in 2006 the concentrations were much lower. For particles collected by the Berner impactor, the concentrations of PM$_{10}$ and PM$_{2.5}$ were determined graphically from the dependence of particle cumulative mass on the aerodynamic diameter of particles. From Table 1 it is evident that for concentrations of TSP above 10 mg m^{-3} our measurements are in good agreement with those made by a commercial impactor, even though they were performed in series. However, from Table 1 it is obvious that particle concentrations vary for about 20% during one working day. Measurements with the Johnas

TABLE 1. Comparison of Particle Mass Concentrations (in mg m^{-3}) Measured at the Stack of the Coal-Fired Power Station in Slovenia by Different Techniques: Dust Concentration Monitor (OMD41), TSP Sampler (SICK, Gravimat SHC 502), Emission Cascade Impactor (GMU-Cascade Impactor Johnas), and Upgraded 10-Stage Cascade Impactor (Berner Type)

sample	OMD41 TSP	Gravimat TSP	Johnas impactor PM$_{2.5}$	Johnas impactor PM$_{10}$	Berner impactor PM$_{2.5}$	Berner impactor PM$_{10}$
29.6.05 13.10–13.40	25.7	25.7			19.7	26.2
29.6.05 15.05–15.20	27.7	21.3			16.8	21.5
29.6.05 16.15–16.25	28.0	20.5			11.7	13.5
30.6.05 13.40–14.20	21.7		9.5	12.2		
30.6.05 14.30–15.10	20.1		8.5	10.9		
16.5.06 12.25–12.55	7.2		5.3	6.6	4.0	4.6
16.5.06 14.35–15.05	7.3		6.3	7.8	5.2	5.4
16.5.06 16.25–16.55	6.8		5.7	7.3	5.1	5.3

TABLE 2. Comparison of Chemical Composition of Particles Collected in 2005 at the Stack of the Coal-Fired Power Station by Berner Impactor, Johnas Impactor, and TSP Sampler

element	Berner impactor (15 nm to 16 μm)	Johnas impactor PM$_{10}$	Gravimat TSP
Mg [mg g^{-1}]	6.5 ± 1.5	8.4 ± 0.2	6.4 ± 0.5
K [mg g^{-1}]	5.7 ± 1.6	7.6 ± 0.9	6.1 ± 0.8
V [mg g^{-1}]	0.16 ± 0.04	0.17 ± 0.01	0.14 ± 0.01
Mn [mg g^{-1}]	0.46 ± 0.13	0.33 ± 0.01	0.34 ± 0.06
Zn [mg g^{-1}]	0.42 ± 0.27	0.46 ± 0.05	0.52 ± 0.13
As [mg g^{-1}]	0.16 ± 0.04	0.16 ± 0.01	015 ± 0.02
Se [mg g^{-1}]	0.24 ± 0.05	0.23 ± 0.01	0.20 ± 0.03
Sr [mg g^{-1}]	0.15 ± 0.03	0.16 ± 0.01	015 ± 0.01
Ni [μg g^{-1}]	44 ± 12	25 ± 4	40 ± 15
Ga [μg g^{-1}]	30 ± 18	27 ± 3	28 ± 5
Mo [μg g^{-1}]	65 ± 14	76 ± 11	74 ± 9
Pb [μg g^{-1}]	46 ± 4	56 ± 45	59 ± 16
Co [μg g^{-1}]	4.1 ± 1.0	6.1 ± 0.8	5.4 ± 0.4
Cd [μg g^{-1}]	1.9 ± 0.8	2.7 ± 0.7	2.9 ± 0.4

impactor showed the average ratio of 0.78 for PM$_{2.5}$/PM$_{10}$, while with the Berner impactor the average ratio was 0.80. Comparison of TSP obtained by Gravimat showed that the third run (29.6.05: 16.15–16.25) deviated from the previous two measurements. The difference of 35% may be attributed to a potential larger emission of particles above 10 μm. For the lower mass concentrations, the comparison is not as good as that for higher ones but it is still adequate. Our system gave about 30% lower values for PM$_{10}$ and about 20% lower values for PM$_{2.5}$ in comparison with the Johnas impactor. This is reasonable because the relative measuring errors increase with lower masses. For the Johnas impactor, the measuring uncertainty of the whole procedure is ±2 mg m^{-3}, which represents nearly 30% of the PM$_{10}$ value in the second period. Similar uncertainty has been determined also for the Berner impactor. In summary, the measurements with our system gave reasonable results. However, to overcome the limitations due to the low concentrations, longer term sampling is necessary.

The suitability of our sampling system was additionally proven on the basis of the chemical composition of the particles emitted from the stack of the power plant. The comparison of total average concentrations of some selected elements in particles collected by Berner impactor, Johnas impactor, and TSP sampler is shown in Table 2. It can be seen that the concentrations of elements determined in particles of the 15 nm to 16 μm size range in PM$_{10}$ and TSP

are generally in good agreement. The best agreement was found for V, As, Se, Sr, and Ga. In addition, concentrations for Mg, K, and Ni determined in particles sampled by the Berner impactor compare well to those determined in TSP. The values for Mg, K, Co, Mo, Cd, and Pb are a bit lower and for Mn and Ni a bit higher in comparison to PM$_{10}$. However, these results can be considered adequate and satisfactory, especially because of measuring uncertainties and some fluctuations in chemical composition of particles during the plant operation. The variations in chemical composition can also be seen in deviations from the average concentrations for most of the elements in particles collected at different times by the 10-stage impactor. Estimated reproducibilities ranged from 7% (for Pb) to 40% (for Cd). Some of these elements (e.g., Mn, V, As, Se, and Ga) can certainly be used as markers of emissions from this particular power plant (7, 8).

Mass and Chemical Size Distribution. The results of mass size distribution of particles collected by our sampling system at the stack of the thermo-power plant during sampling in 2005 and 2006 are shown in Figure 2a. An uncertainty of 8% was determined for the size ranges between 60 nm and 4 μm and 21% for the sizes below 60 nm and above 4 μm. The distributions were generally bimodal, with the most pronounced mass peak in the 1–2 μm size range. The second mass peak was observed in the 0.06–0.25 μm size range. Recent literature results suggest that coal fly ash particle
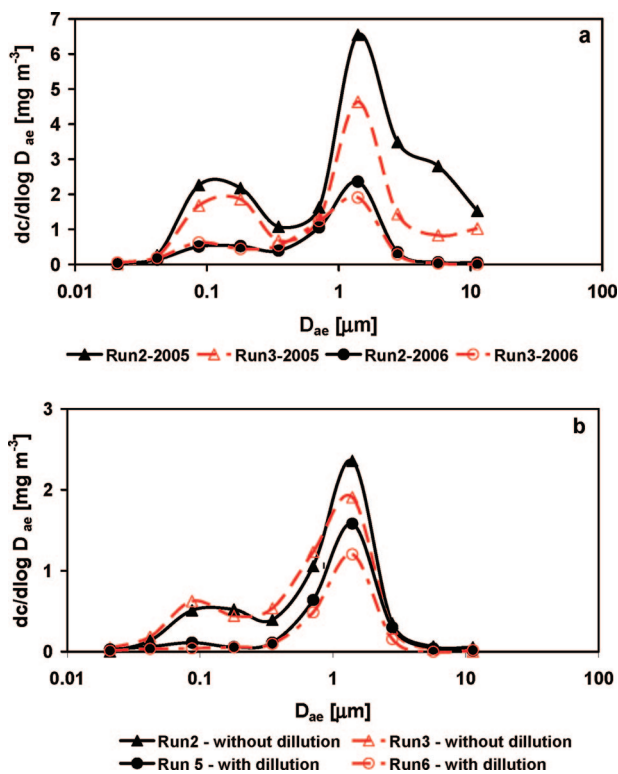
FIGURE 2. Mass size distribution of particles collected at the coal-fired power plant during sampling in 2005 and 2006 (a) and comparison between sampling with and without dilution (b). Concentrations are expressed at normal conditions (273 K, 1013 mbar).

formation is described as a trimodal particle size distribution that includes a submicrometer region at about 0.08 μm, a fine region centered at approximately 2.0 μm, and a bulk or supermicrometer region for particles at about 5 μm and greater (20, 21). Since the stack gases were cleaned prior to emission (gas scrubber and filters) supermicrometer particles were considerably reduced, thus making the third mode less evident. The comparison between the prolonged sampling where dilution with clean air was introduced and sampling with no dilution is presented in Figure 2b. It is evident that in the case of dilution the mass size distribution was rather unimodal. On the basis of the chemical composition of the particles it was established that the reason for this discrepancy lies in the losses of SO_4^{2-} (as H_2SO_4). The largest losses (nearly 30 times) were determined for sizes below 0.125 μm. For the 0.125–0.50 μm size range the concentration of SO_4^{2-} was about 400 μg m^{-3} when no dilution was introduced, while with dilution the concentration was only about 50 μg m^{-3}. For sizes above 0.5 μm the measured concentrations with dilution were 3 times lower. But on the other hand, no losses of elements in emission particles collected with dilution were observed (e.g., the differences for Ga, Se, Pb, and V in all size ranges were in the range of 20%, which can be attributed to measurement uncertainty of the whole procedure). This means that sampling with dilution is suitable for the mass size distribution of important elements. Dilution however reduces the formation of small particles of sulfuric acid. In addition, insight into the molar ratios between SO_4^{2-}, Ca, and Mg (using sampling with and without dilution), showed that the excess of SO_4^{2-} in comparison to the sum of Ca and Mg was most probably evaporated as H_2SO_4. When flue gases are released from the stack it is believed that evaporation and/or recondensation of H_2SO_4 takes place, which changes its distribution over different particle size ranges compared to the situation in the stack.

Characteristic mass size distributions (for four different concentration ranges) for some chemical species determined in emission particles collected using the system without dilution are presented in Figure 3. It is evident that SO_4^{2-} exhibits a typical bimodal size distribution, with modes at
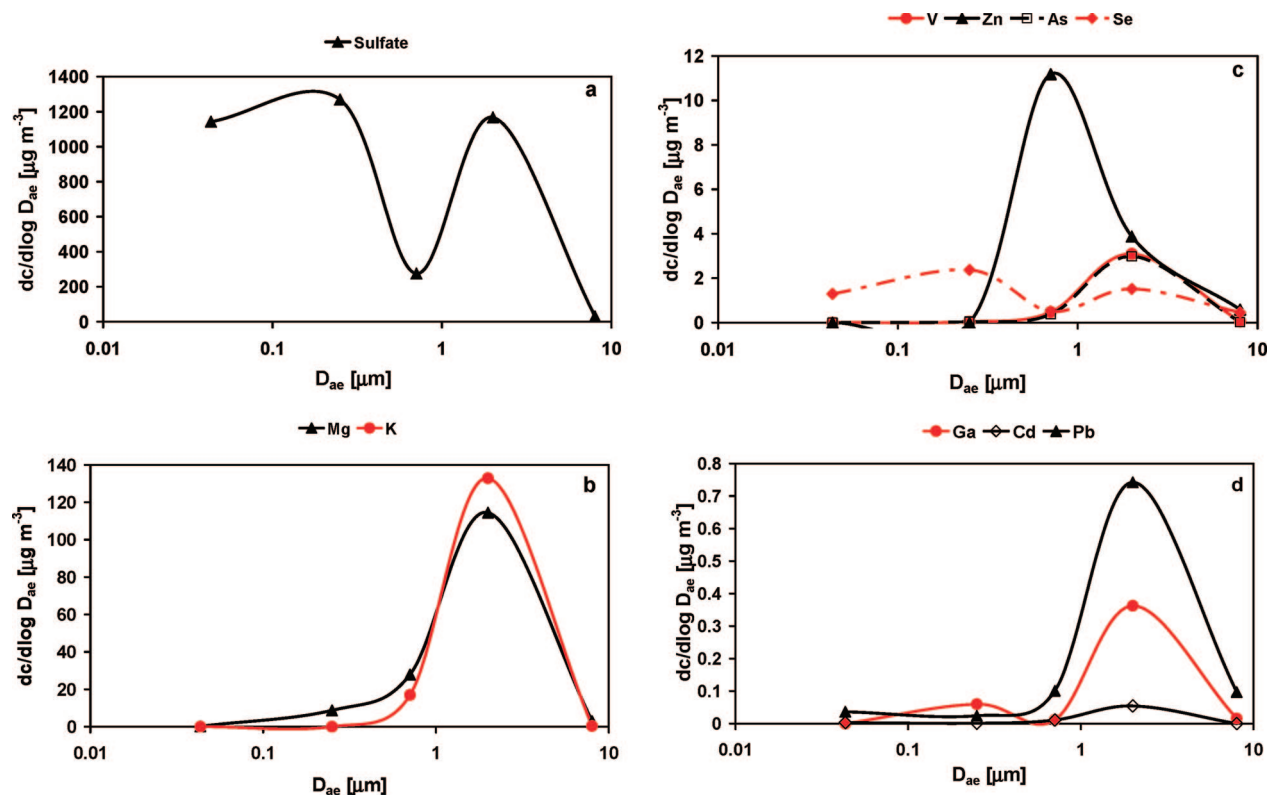

FIGURE 3. Mass size distributions of SO_4^{2-} (a), Mg and K (b), Zn, V, As, and Se (c), and Pb, Cd, and Ga (d) in particles emitted from the thermo-plant.

around 0.25 μm and 2 μm. For Mg and K (Figure 3b), V and As (Figure 3b), as well as for Pb and Cd (Figure 3d), a unimodal size distribution with a mode at around 2 μm was determined. For Zn a unimodal size distribution was also found, but with a peak near 1 μm. For Se and Ga two modes were identified, one near 0.25 μm and other at around 2 μm. The mass size distributions of chemical species provide important information, since some elements have a characteristic mode in a limited size range and can be used as markers for the identification of a particular source (i.e., source signature) and further for tracing the source contribution at locations of interest, at various distances from the source. Results from the Johnas impactor only give distributions between the coarse and fine mode with a division at 2.5 μm. So, for the components which have a peak maximum below 2 μm (see Figure 3), the important information is lost. For example, in the case of Zn (Figure 3c), for which measurements with our system gave a maximum mass concentration at about 1 μm, results from the Johnas impactor only gave limited information, as 75% of Zn is present in the range below 2.5 μm. We also want to point out that we are aware of the different techniques applied in flue gas analysis, especially the implication of cascade impactors for the measurement of dust in flowing gases (22). However, the ANDERSEN M III impactor has some limitations, i.e., particles of diameter lower than 0.41 μm are collected on a back-up filter; therefore, information on size-segregated composition below this size is lost. Thus, in our case we would not have seen the ultrafine mode of the combustion aerosols and the behavior of the sulfate aerosol under dilution. In addition, the Berner LPI impactor facilitates a split foil technique allowing the simultaneous collection of aerosols on aluminum foil for gravimetric analysis and on chemically inert Tedlar foil for chemical analysis. This therefore removes any uncertainties introduced by subsequent sampling by different instruments at different conditions of the flue gas.

In the past few years, many studies on the size distribution of elements in ambient aerosol particles from very diverse environments have been done. For example, on the basis of characteristic size distributions of trace metals in atmospheric aerosols at background sites in England three main behavioral types were identified: metals (Cd, Sn, Pb, and Se) whose mass resisted mainly within the accumulation mode, metals (Ni, Zn, Cu, Co, Mn, and Hg) that were distributed between fine, intermediate, and coarse modes, and metals (Fe, Sr and Ba) that were mainly found within coarse particles (23). For four typical urban sites in Budapest, Hungary, it was shown that typical coarse-mode elements (e.g., Na, Mg, Al, Si, Ca, Ti, Fe, Ga, Sr, Mo, and Ba) exhibited unimodal size distributions, while elements typically related to high-temperature or anthropogenic sources (e.g., S, K, V, Cr, Mn, Ni, Cu, Zn, Ge, As, Se, and Pb) either had a unimodal mass size distribution with most of their mass in the fine size fraction or showed a clear bimodal size distribution (24). For the two sites within the Los Angeles Basin, crustal metals (e.g., Al, Si, K, Ca, Fe, and Ti) were predominantly present in the supermicrometer particles (25). Potentially toxic metals, which were mainly partitioned in the submicrometer particles, have been traced to vehicular emissions (Pb, Sn, and Ba) and to emissions from power plants and oil refineries (Ni and Cr). Anyhow, all these results showed that the measured size distributions of elements in ambient aerosol particles are the result of a combination of different processes including local anthropogenic and natural sources as well as long-range transport and resuspension and depend on meteorological conditions, of which wind speed and direction are the most important.

It is evident that our results on elemental mass size distributions showed some distinctive differences with results obtained for atmospheric aerosol particles (23–25). For example, trace elements, like Pb, Cd, As, and V, typically related to other high-temperature sources, especially to traffic emissions, are usually more abundant in the particle size range below 1 μm, whereas in our specific case these elements were found above 1 μm. So, to establish the influence of a specific emission source to the actual ambient aerosol concentrations, elemental mass size distributions can certainly be a very useful tool. This is particularly true in areas relatively close to the source.

In general, for a good understanding of the contribution from different emission sources adequate source fingerprints through direct measurements of size-segregated emission particles are required as well as measurements of size-segregated ambient aerosol concentrations. Ambient air is a complex mixture of pollutants emitted from numerous diverse sources and undergoes continuous changes, but source signatures may show narrower distributions of some key components. By use of this approach, the contribution of a particular source can be more precisely estimated. In this work we showed that size-segregated sampling followed by elemental analysis can be used to define a source signature. Simultaneous measurements of size-segregated particles at the source and in the surrounding environment can therefore significantly improve the insight into the contribution of a specific source to the actual ambient concentrations.

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