Personal Exposure to Ultrafine Particles in the Workplace: Exploring Sampling Techniques and Strategies

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Recently, toxicological and epidemiological studies on health effects related to particle exposure suggest that ‘ultrafine particles’ (particles with an aerodynamic diameter of <100 nm) may cause severe health effects after inhalation. Although the toxicological mechanisms for these effects have not yet been explained, it is apparent that measuring exposures against mass alone is not sufficient. It is also necessary to consider exposures against surface area and number concentration. From earlier research it was hypothesized that results on number concentration and particle distributions may vary with distance to the source, limiting the reliability of estimates of personal exposure from results which were obtained using static measurement equipment. Therefore, a workplace study was conducted to explore the performance of measurement methods in a multi-source emission scenario as part of a sampling strategy to estimate personal exposure. In addition, a laboratory study was conducted to determine possible influences of both distance to source and time course on particle number concentration and particle size distribution. In both studies different measurement equipment and techniques were used to characterize (total) particle number concentration. These included a condensation particle counter (CPC), a scanning mobility particle sizer (SMPS) and an electrical low pressure impactor (ELPI). For the present studies CPC devices seemed to perform well for the identification of particle emission sources. The range of ultrafine particle number concentration can be detected by both SMPS and ELPI. An important advantage of the ELPI is that aerosols with ultrafine sizes can be collected for further analysis. Specific surface area of the aerosols can be estimated using gas adsorption analysis; however, with this technique ultrafine particles cannot be distinguished from particles with non-ultrafine sizes. Consequently, estimates based on samples collected from the breathing zone and scanning electron microscopic analysis may give a more reliable estimate of the specific surface area of the ultrafine particles responsible for personal exposure. The results of both the experimental and the workplace study suggest both spatial and temporal variation in total number concentration and aerosol size distribution. Therefore, the results obtained from static measurements and grab sampling should be interpreted with care as estimates of personal exposure. For evaluation of workplace exposure to ultrafine particles it is recommended that all relevant characteristics of such exposure are measured as part of a well-designed sampling strategy.

Keywords: exposure; measurement methods; sampling strategy; ultrafine particles; workplace

INTRODUCTION

Ultrafine particles or nanoparticles, generally defined as particles of low solubility with aerodynamic diameters <100 nm, tend to be formed through nucleation, gas to particle reactions or evaporation. The majority of workplace ultrafine particles are likely to arise by the nucleation route, either as combustion products, e.g. vehicle exhaust emission, or within saturated vapours arising from processes such as smelting, welding, soldering, laser ablation, etc. (Gijsbers et al., 2000; Riediger and Möhlmann, 2001; HSL, 2002; Wake et al., 2002). In addition, ultrafine particles may be generated during mechanical processes like grinding, cutting or polishing (Zimmer...
and Maynard, 2002). Currently, there is an increase in the use of nanophase technology to produce new and improved products. Consequently, the numbers of workers exposed to ultrafine particles may increase dramatically in the near future compared with the number of workers exposed to ultrafine particles originating from more conventional sources.

Health effects

Ultrafine particles differ from larger (respirable) particles with respect to deposition and alveolar clearance. Epidemiological studies suggest that exposure to ultrafine particles may cause pulmonary diseases, cardiovascular health effects and impairment of the immune system (Dockery and Pope, 1994; Hagdnagy et al., 1998). The toxicological mechanisms behind these effects are not entirely clear. There is evidence to suggest that the relationship between adverse health effects and particulate ambient air concentrations should be accounted for by the ultrafine particle fraction, which is negligible in terms of mass concentration. The possibility of a correlation between the number concentration of ultrafine particles and toxicity was first demonstrated by Oberdörster et al. (1996), who showed a strong dose–response curve between pulmonary inflammatory responses and particle number in rats exposed to 20 nm PTFE particles. More recent research has begun to indicate a possible material-independent link between particle surface area and the initiation of pulmonary inflammation (e.g. Donaldson et al., 2000).

Instrumentation

For risk evaluation purposes, exposure assessment should be aimed at determining biologically relevant exposure for individual workers. However, it is not clear which different metrics associated with ultrafine exposure in addition to the chemical composition, i.e. number concentration, mass concentration, surface area and particle morphology, are relevant. Technologies to measure some of these metrics for nanoparticles in situ have been identified, e.g. to determine number concentration. However, these are not readily available, particularly in a form which may be used to measure personal exposure on a routine basis. Most instruments capable of detecting one or various characteristics are large and cumbersome devices that are not very suitable even as static monitors.

Instruments to determine number concentration are usually based on the principle of growing the particles in a saturated vapour atmosphere so that they become large enough to be detected by optical counters (Dahmann, 2001). Condensation nuclei or particle counters (CNC or CPC) can detect particles in situ in the size range 3–3000 nm. They can be either mains-powered static monitors or battery-powered monitors. The latter option does not meet the criteria for a personal device, but it enables its use as a screening instrument to determine particle emitting sources. The lack of size discrimination is a major limitation.

Number-weighted size distributions of ultrafine particles can be measured in situ using a scanning mobility particle sizer (SMPS) or an electrical low pressure impactor (ELPI). The SMPS combines an automatically scanned electrical aerosol analyser with a CPC. The SMPS relies on bringing an aerosol to charge equilibrium ensuring that the aerosol has a known charge distribution. A differential mobility analyser (DMA) selects airborne particles of uniform sizes by selective stripping according to electrical mobility. This type of device covers a mobility size range of ~5–800 nm. Subsequently, particles are counted by a CPC to determine particle number concentration for each size range.

The ELPI is a real-time measurement device for particle size selective number concentrations. Particles are drawn into a corona charger by a vacuum pump and are given a certain charge. A 13 stage low pressure impactor (LPI) classifies the particles in different aerodynamic diameter sizes (D50 cut-off range 6.8 nm to 10 μm) and each charged particle that impacts a stage is detected. In addition to its aerodynamic size classification characteristics, a major advantage of the ELPI is that it collects the particle fractions, thus allowing gravimetric or other analysis.

Low pressure cascade impactors, e.g. Berner LPI, or micro-orifice cascade impactors, e.g. MOUDI, enable the capture of aerosols on the impactor stages. The Berner impactor consists of a pre-selector, eight stages (from 8000–16 000 nm to 60–125 nm) and a back-up filter, whereas the MOUDI consists of eight stages (D50 cut-off 15 000–71 nm) and a back-up filter (Hewitt, 1995; Gijsbers et al., 2002a). For both devices the ultrafine fraction will be located on the last stage and the back-up filter. Both devices are equipped with heavy duty pumps and are unsuitable for personal sampling.

For the measurement of ultrafine particle concentration in terms of the surface area metric, only two instrument types have been identified (Maynard, 2003). Briefly, the instruments, i.e. the epiphanimeter and the aerosol diffusion charger/electrometer, measure the attachment rate of unipolar ions to particles, to derive active surface area of the aerosols (Maynard, 2003). The epiphanimeter is not well suited to use in workplaces due to the inclusion of a radioactive source, whereas the diffusion charger/electrometer type of instrument has been reported to have a response closer to a larger, non-ultrafine range of particles.

Off-line measurement of a specific surface area of collected samples is possible using the Brunauer Emmett Teller (BET) nitrogen (or CO2) absorption method. BET analysis also allows detection of micro-
pores and gives a better estimate of total surface area compared with methods that estimate microscopic surface area, e.g. electron microscopy. BET analysis requires large particle samples (Maynard, 2003).

Alternatively, aerosol surface area can be measured indirectly by measuring the aerosol size distribution and estimating the surface area-weighted distribution by assuming a specific particle geometry. Size distributions are obtained through SMPS measurements, whereas CPC results are used to obtain number concentrations. This method has recently been explored by Maynard (2003). The author has successfully demonstrated that the use of results obtained by readily available parallel direct reading instruments provide a good estimate of the magnitude of surface area with minimal additional effort.

Another method to estimate the surface area of airborne particles from the results of direct reading instruments is based on the fractal dimensions of the particles. The fractal dimension is related to the space filling properties of particles (Rogak et al., 1993). By putting ELPI (aerodynamic diameter) and SMPS (mobility diameter) in series the fractal dimensions can be calculated and verified by electron analysis. Together with a proxy for the size of the primary particles (from microscope analysis), the number concentration (from SMPS) is used to estimate the surface area.

As stated, particle identification, e.g. morphology and geometry, identification of single particles and agglomerates and determination of optical diameters can be derived from electron microscope analysis.

For SEM the surface of a sample is scanned using a finely focused electron beam in a low pressure environment. Imaging takes place by using interaction effects such as secondary electrons to control the intensity of the electron beam of a cathode ray tube with synchronized scanning. Transmission electron microscopy (TEM), using interference patterns between the forward scattered and diffracted electron waves from the specimen, visualized on a fluorescent screen, produces a higher resolution than can be achieved with SEM.

The low pressure of electron microscopy has also been associated with loss of the liquid fraction of particulate matter (Shi Ping et al., 2002)

In addition, samples can be used for further elemental identification, e.g. energy dispersive X-ray analysis (EDX), often coupled with SEM or TEM devices.

Table 1 lists the readily available instruments and techniques for the characterization of ultrafine aerosols.

In summary, it can be stated that current toxicological and epidemiological research has not revealed agreement on the most relevant dose-metric(s) to express human exposure to ultrafine (nano)particles. Moreover, methods and equipment that are available to measure identified characteristics of health-relevant exposure, e.g. mass and particle concentration and surface area, are relatively large and cumbersome and so are primarily applicable for static sampling. In addition, some instruments do not afford full-shift measurements, for example when ‘over-sampling’ may occur, e.g. with impactors.

Research into the relationship between the results of static sampling compared with personal sampling for particles and fibres in workplaces suggests that in

<table>
<thead>
<tr>
<th>Metric</th>
<th>Device</th>
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<tr>
<td>Mass</td>
<td>Size-selective personal sampler</td>
<td>No specific separation in UF size range</td>
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<td></td>
<td></td>
<td>Off-line gravimetric detection</td>
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<td></td>
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<td>Results of other (static) size-selective devices (impactors) could be used to establish the relation between different size ranges</td>
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<tr>
<td>Number</td>
<td>CPC</td>
<td>Real-time number concentration not specified for UF size range</td>
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<td></td>
<td>SMPS</td>
<td>Real-time size distribution (mobility diameter) detection of number concentration</td>
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<td></td>
<td>ELPI</td>
<td>Real-time size distribution (aerodynamic diameter) detection of number concentration</td>
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<td></td>
<td>Size-selective sampling for other (off-line) analysis</td>
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<tr>
<td>Surface area</td>
<td>Series of SMPS and CPC</td>
<td>Estimates based on projected area equivalent diameter</td>
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<td></td>
<td>Series of SMPS and ELPI</td>
<td>Estimates based on fractal dimensions (differences mobility and aerodynamic diameters)</td>
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<td>Identification</td>
<td>SEM off-line analysis</td>
<td>Off-line microscopic analysis of morphology.</td>
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<td></td>
<td>TEM off-line analysis</td>
<td>Samples may be collected by personal sampling or size-selective static samplers (e.g. ELPI, impactors)</td>
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<td>X-ray microanalysis</td>
<td>Off-line analysis following SEM/TEM element identification</td>
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<td>XRF/XRD</td>
<td>Off-line analysis</td>
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<td>Samples may be collected by personal sampling or size-selective static samplers (e.g. ELPI, impactors)</td>
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general personal exposure is higher compared with environmental concentrations, especially for scenarios where dust generation is operator-dependent (Niven et al., 1992; Ogden et al., 1993; de Pater et al., 2002). Koch et al. (1999) showed that for exposure to flour in a bakery the concentrations of the respirable fraction as determined by personal sampling and static sampling were close, whereas the fractions of the larger particles, i.e. the thoracic and the extrathoracic fractions, showed large differences in measured concentration. Since in all cases static sampling was performed at a greater distance from the source compared with personal samplers, these results indicate spatial variations in particle size distribution and concentration. For workplaces the likelihood of both spatial and temporal variations in particle size distribution and concentration is even higher compared with ambient air due to additional factors, e.g. multi-source and intermittent sources of dust generation.

Due to the lack of suitable personal samplers for ultrafine particles for workplace exposure risk evaluation, results of measurements on fixed locations over relatively short time intervals have to be interpreted in terms of full-shift personal exposure for ambulatory persons. Thus, occupational health risk researchers have been challenged to use available instruments in the optimum way. This paper reports on the results of both a workplace study (Brouwer et al., 2002) and a laboratory study (Gijsbers et al., 2002b) to evaluate method performance and explore a proposed sampling strategy that incorporates a variety of methods to determine characteristics of worker exposure to ultrafine particles.

MATERIALS AND METHODS

Sampling strategy

To estimate personal exposure to ultrafine particles in the workplace from the results of static samplers that determine various health-related characteristics, a preliminary sampling strategy was proposed. The first step is identification of sources of ultrafine emissions in the workplace atmosphere. Non-size-selective portable instruments to trace real-time particle number concentration would generate appropriate information (i) to trace major sources and (ii) to estimate sampling duration for gravimetrical analysis-based methods, i.e. impactors. The next step is to identify air movements and currents, e.g. using smoke tubes or generators and/or (direction-selective) air velocity detectors. Especially relevant in selecting the sampling location and to evaluate outdoor aerosol penetration are air movements from the source(s) and from outdoors towards the workplace. Air exchange rates, as a parameter for general ventilation, are important in the case of time-limited aerosol-generating sources. In addition to air movements, various factors will affect the selection of sampling locations. A preliminary observation of the workers‘ tasks including their fixed or moving position will also determine the sampling location(s), but even more practical consideration, e.g. suitability for the placement of large instruments, should be taken into account during selection. When the sampling location(s) has been selected, in situ size-selective sampling for number concentration is conducted. Sampling is also conducted for determination of mass concentration and specific surface area and particle identification. During the sampling period observations are made of workers tasks, as well as (possible other) aerosol emission activities. Finally, temperature and relative humidity are recorded.

Experimental

Workplace study. For the workplace study, measurements were conducted on 3 consecutive days in a workplace (40 × 50 × 8 m) in which were located six different welding stations. The workplace was provided with a local exhaust ventilation system consisting of four local units, of which a maximum of two were in use. The system (Multidust, PlymoVent, Banbury, UK) uses a 100% recirculation and the air is cleaned by PE filters. On day 1 a location was selected near a welding station where workers assembled cheese racks by welding the crossing points of the steel bars. On days 2 and 3 the sampling units were placed near (at ∼1 m) a welding robot, where small parts were welded to steel bars. The robot arm could turn 180° and was placed in between two frames with a supply of bars. While welding took place on one side, the worker loaded and unloaded the frames on the other side. There was no physical barrier between the two welding sides and no local exhaust ventilation (LEV) unit was located near the welding robot. Nearby, the workstations central air system blower inlets were located in the ceiling.

During all welding operations (gas metal arc welding) a stainless steel core with a copper shield consumable was used with an argon/CO₂ mixture gas shield.

Other activities that took in the workplace during the measuring period were grinding and internal transport.

Laboratory study. The test room dimensions for the experimental study were 7 × 4 × 2.5 m. The floor consisted of rough concrete that was cleaned before the start of the experiments. An open ventilation shaft in the wall was sealed to prevent outdoor air from coming in. An arc welding machine was used to generate ultrafine particles. Welding was performed on a water-cooled, turning pipe of 8 mm non-treated iron at 24 V and 220 A. The welding consumable was a SG2 wire (1 mm diameter) at a rate of 640 cm/min.
An argon/CO₂ welding gas (Protegon; argon + 15% CO₂) at 15 l/min was used for protection against corrosion. During welding the turning pipe was set to 0.4 r.p.m. and the welding took place at a speed of 40 cm/min. The stick-out length of the welding wire was 12 mm.

A mannequin was placed where a welder would perform his work. The mannequin was always positioned at a distance of 80 cm from the welding source.

A mobile LEV unit (Multi Fume Caddy, type MFC 1000/3; Plymovent, UK) was located opposite the mannequin at different distances (35 and 55 cm) from the welding machine, with a hood angle of 45° upward. The unit was equipped with an aluminium pre-filter, an enlarged active filter and an active charcoal filter. The performance of the LEV was checked with a thermo-anemometer.

Five experiments were conducted at different sampling locations. During one experiment the horizontal distance to the welding arch was 0 cm, i.e. in the welding plume, during two experiments the distance was 60 cm and during two other experiments the distance was 360 cm. For experiments at the same distance from the welding machine, the distances of the LEV from the source were 35 and 55 cm, respectively.

Instrumental

Workplace study. During the workplace study a mains powered CPC (model 3025A; TSI, St Paul, MN) was used to identify sources of (ultrafine) particles. The instrument has a size detection lower limit of 50% of 7 nm particles and an upper limit of >3 µm. The maximum number concentration was 9.99 × 10⁴ particles. Every 2 s the output signal is recorded using an Eltek Datalogger (1000 Series Squirrel; Grant, Cambridge, UK). To avoid exceeding the maximum number concentration, on day 3 a three-way valve was used to dilute the air feeding into the CPC (‘peak mode’). The maximum number concentration could be increased by a factor of ~7. Air flow was checked with a Drycal DC1 air flow calibrator.

For aerosol size distribution measurements a TSI model 3071 SMPS was used. The device consisted of a differential mobility analyser (DMA) (model 3071; TSI) and a CPC (model 3022; TSI), in combination with TSI software. A mobility size range of 15 to ~650 nm was selected. A full scan of all mobility sizes requires ~2 min.

A Berner LPI (Dr Berner, model 30/0.06) consisting of a pre-selector and eight stages (from 8000–16 000 nm to 60–125 nm) was used to trap particles on aluminium foils. A back-up filter (5 µm Nuclepore, type LS; Millipore) was placed after the last stage, filtering about a quarter of the air flow at the entrance to the impactor (7.5 l/min). The impactor foils and final filter were pre- and post-weighted to within ±0.001 mg using a balance (MC 5; Satorius, Germany), located in a climate controlled chamber.

Samples cut from the (Berner) aluminium impactor stages were analysed using a Philips XL-30 FEG scanning electron microscope with a Noran Vantage X-ray microanalysis system. An electron beam with an acceleration voltage of up to 10 kV was used for imaging. For EDX analysis (to identify the chemical composition of the sample) a voltage of 3 kV was used. The lower voltage was used to keep penetration of the primary electrons as low as possible in order to prevent the aluminium substrate from disturbing the analysis. Metals of interest in the particles, such as iron and chromium, could still be analysed in the L lines at 3 kV.

A hot wire anemometer (model GGA 65; Alnor) was used to determine air velocity, whereas the direction of air currents was observed visually using smoke generated by smoke tubes (Draeger, Germany).

The type of welding, start time and end time of actual welding activities or other particle emitting activities and materials were recorded for welding activity. In addition, the presence and use of central and local exhaust ventilation were observed, as well as opening and closing of doors and vehicle movements.

Laboratory study. During the experimental study another type of CPC was used (type 3022a; TSI) with a size detection lower limit of 50% of 7 nm particles and an upper limit of >3 µm. The maximum number concentration was 9.99 × 10⁶ particles. The output signal was recorded with the CPC’s own software. In addition, a battery powered CPC (Portacount; TSI) with a detection range of 0.2 to >1 µm particle size and an upper limit for number concentration of 5 × 10⁵ particles was used to determine the emission source strength. The outgoing signal from the Portacount was stored on a personal computer. The Portacount was used to estimate the particle concentration in the welders’ breathing zone. The end of the sample hose was mounted on the mannequin.

For size-selective number concentration measurements a 3936L10 type SMPS (TSI) was used, consisting of a DMA (type 3936) and a CPC type 3010, in combination with TSI software. A mobility size range was selected from ~20 to 800 nm. Maximum particle concentration was 10⁷ particles/cm³. A full scan of all mobility sizes required ~50 s, and 10 s were needed to retrace before a new scan was started.

In addition, an ELPI (Dekati) was used to monitor particle size and number concentration and trap particles at a flow rate of 28 l/min, consisting of a pre-selector and 12 stages (D₉₀ cut-off 6.8–0.030 µm). For the experiments oil-soaked sintered impactor plates, 40 µm average pore size, were used.
Non-oil-soaked plates were used in the case of samples for SEM analysis. Similarly to the workplace study, the same type (model 30/0.06) of Berner LPI was used to trap particles on aluminium foils; however, a different type of back-up filter was used (isopore, type TMTP; Millipore).

Samples cut from the (Berner) aluminium impactor stages and from the ELPI stages were analysed using the same SEM as used during the workplace study.

During one of the experiments in the experimental study the LEV was turned off; thus a large amount of welding fume was emitted. A 37 mm open face sampler was equipped with a 5 µm isopore membrane and a sampling pump at a flow rate of ∼28 l/min. This membrane filter was later used to determine the specific surface of particles (ultrafine and non-ultrafine) emitted during welding by BET analysis (Brunauer–Emmett–Teller) based on the nitrogen adsorbing capacity of the particles (Micromeritics floworb II 2300).

Before the start of the first experiment on each test day, the air exchange rate was assessed from the results of SF6 tracer gas concentrations over time. Gas was released such that the concentration of SF6 in the room reached ∼150 p.p.m. A multiple gas monitor (B&K type 1302) attached to a data logger was used to record the concentration over time.

Temperature and relative humidity was measured using a HMP 45A probe (Vaisala) and recorded on an Eltek data logger (1000 Series Squirrel; Grant).

RESULTS

Identification of sources and variances of concentration

During the workplace study, outdoor CPC particle concentrations (roadside parking with little traffic) averaged over 15 s (‘grab sample’) were about $1.3 \times 10^4$ particles/cm$^3$ (range 0.85–1.6 $\times 10^4$ particles/cm$^3$), whereas indoors (during the day, but with no actual particle emission activities) 15 s averages ranged from 2.5 to $5 \times 10^4$ particles/m$^3$. During actual welding, number concentrations were 3–4 times higher. Activities with a grinder revealed 15 s averages up to $9.9 \times 10^4$ particles/cm$^3$, with peaks up to $9.9 \times 10^4$ particles/cm$^3$, the upper limit of detection. Using the peak mode, number concentrations up to $6.0 \times 10^5$ particles/cm$^3$ were observed. Figure 1A shows CPC output for day 3, whereas Fig. 1B shows total number concentration as determined by SMPS.

Prior to the actual experiments during the experimental study, the outdoor particle number concentration ranged from 1.2 to $2.3 \times 10^4$ particles/cm$^3$, whereas particle number concentration in the test room was always lower (range 0.9–1.4 $\times 10^4$ particles/cm$^3$).

From the observations in the workplace study one could pinpoint the various activities and sources that were responsible for temporal variations in particle number concentrations at a fixed location. Figure 2 shows the SMPS output during a half-day shift. Grinding activities were seen to have a major impact on particle number concentration compared with welding, as did diesel exhaust and resuspension as a result of forklift truck traffic.

In contrast to the multi-source and multi-activity scenario addressed in the workplace study, the experimental study showed a well-defined single source exposure scenario. The size-selective sampling (SMPS and ELPI) results showed a sharp increase in particle number concentration of both ultrafine, i.e. <100 nm, and non-ultrafine, i.e. 100–750 nm fractions during actual welding (for ∼5 min). For comparison with SMPS data (Figs 3A, 4A and 6A), ELPI results for stages 1–7 (mid-point 724 nm) were taken together (Figs 3B, 4B and 6B) to calculate the fraction <750 nm.

Due to mixing, dilution and deposition, a decline to about baseline concentrations could be observed after 90 min (Fig. 3A and B). For similar air exchange rates (∼2.5 p.m), all experiments showed similar concentration curves.

The results of the experimental study show some evidence of temporal variances in aerosol size distribution. During the experiment in which the LEV was positioned at a distance of 55 cm from the source and the sample location at 60 cm, SMPS results showed a sharp decline in the percentage of ultrafine particles immediately after the start of actual welding. This was followed by an increase until the original percentage of ∼55% was reached (Fig. 4A). After actual welding another decline was observed, with a slow increase from ∼30 min after the end of the welding period. The results of ELPI measurements for the same experiment indicate an increase in the fraction of ultrafine particles during actual welding and a slow decrease in the period following actual welding (Fig. 4B).

During the workplace study the results for the Berner LPI also showed differences in particle size specific mass concentrations over different periods that could be related to different activities. This is illustrated in Fig. 5.

In addition to temporal variations, spatial variations in number concentration and particle size distributions can be observed. During the experimental study at a distance of 60 cm from the welding torch the peak number concentration during welding was ∼$3.1 \times 10^5$ and $3.9 \times 10^5$ particles/cm$^3$ for SMPS and ELPI, respectively. At a distance of 360 cm peak number concentrations during another experiment with similar welding conditions were $1.0 \times 10^5$–$1.1 \times 10^5$ particles/cm$^3$, respectively.
Slight differences in particle size distribution can be observed from the SMPS results from different experiments, where the sampling location differed. Figures 4A and 6A show the plots of the percentages of the ultrafine fraction at distances of 60 and 360 cm from the source, respectively. The plots indicate a lower percentage of ultrafine particles over time at 60 cm compared with a distance of 360 cm. This suggestion is supported by the plots of the ELPI results for the same experiments (Figs 4B and 6B). However, for the experiments where the LEV was positioned closer to the source, i.e., at 35 instead of 55 cm, no such differences could be observed.
Surface area and (chemical) identification

During both the experimental study and the workplace study, Berner LPI sample stages were analysed by SEM. Figure 7A and B shows SEM pictures from the ELPI stage with a mid-point aerodynamic diameter of 70 nm. Both pictures show the structure of the (MIG) welding fume and a good view of distinct particles and agglomerates. For the results of SEM analysis of grinding and welding particles in the workplace study, an estimated radius of 5 nm for a single spherical particle was used to calculate a surface area and volume of a particle of $3.14 \times 10^{-16}$ m$^2$ and $5.23 \times 10^{-25}$ m$^3$, respectively. Assuming a density of 5500 kg/m$^3$, the specific surface area of a single particle would be 109 m$^2$/g.

During the experimental study aerosols were sampled in the welding plume when the LEV was switched off. On two filters 23.0 and 38.0 mg mass was collected, resulting in estimates of the specific surface area by BET analysis of $30 \pm 8$ and $31 \pm 5$ m$^2$/g, respectively.

Based on the results of SMPS and ELP measurements, a fractal dimension (or space filling properties) of 2, i.e. a filled surface, was estimated. Together with the approximate size of the primary particles as estimated from SEM analysis, i.e. 10 nm, the estimated specific surface area would be 115 m$^2$/g.

During the workplace study different stages of the Berner LPI were used for analysis of elements by the XRD technique. Iron, oxygen and carbon were detected and from results of quantitative analysis it was speculated that Fe$^{3+}$, as in iron(III) oxide, was the most likely form of iron. The iron(III) oxide was mixed with $\sim 15$ mass % carbon. It is hypothesized that diesel soot was the source of carbon. Shapes and particle sizes of the particles were very similar, so no distinction could be made between carbon and iron oxide particles. Analysis of the larger particles (50–100 nm) showed that iron oxide was the major component.

DISCUSSION

In two small-scale studies, i.e. a workplace and a laboratory study, the performance of a proposed sampling strategy to assess personal exposure to ultrafine particles in the workplace atmosphere was explored. Since a number of parameters are of importance, the sampling strategy aimed at covering all different needs, including in situ determination of (size fractal) number concentration and sampling for laboratory analysis.

Specific issues that were addressed during these studies were related to instrument performance and temporal and spatial variations in ultrafine particle concentrations in view of the fact that currently only static instruments are available that are generally not designed to evaluate exposure in occupational settings.

For multi-source scenarios, the use of a CPC for identification of sources was found to be useful. However, the (mains-powered) type of CPC used in the workplace limited optimal (moving) use. For the workplace scenario that was studied it appeared to be rather difficult to identify a single source. Variations
in number concentration over time seemed to be the result of several emission sources and complex processes of transport of particles through the workplace atmosphere. Recordings of ventilation and airflow patterns are necessary supplementary data to interpret CPC data for source identification. A reluctance to use smoke tubes is warranted since small-sized aerosols are emitted and may affect ultrafine

Fig. 3. (A) Particle number concentration as detected by SMPS during experiment 4 (LEV at 55 cm and sample location at 360 cm). (B) Particle number concentration as detected by ELPI during experiment 4 (LEV at 55 cm and sample location at 360 cm).
number concentrations. Alternative methods to determine air movements should be explored. In addition to observation and recording of ventilation, observations of work activities are necessary to interpret CPC data for identification of emissions during activities. For a single particle-emitting source with well-defined periods of active emission as studied in the experimental study, assessment of the air exchange rate may be sufficient to characterize the influence of air movements on particle transport.
Number concentrations, as given by CPC output, will not necessarily reflect particle concentration in the ultrafine range. However, a comparison of CPC and SMPS workplace study data over time indicated an association between number concentration given by CPC and mobility sized number concentration in the ultrafine range as given by the SMPS.

The use of the total number concentration to quantify particles in air should be interpreted carefully, since all particles, including agglomerates, will be detected. SEM analysis showed that single particles were rarely present in the air, thus agglomerates will contribute substantially to the number of particles detected. Moreover, this hampers interpretation of the CPC results for setting the sampling time of the Berner LPI to enable gravimetric analysis. In the preliminary proposed sampling strategy, the results of the CPC measurements would be used to select the sampling time for the mass collection, assuming spherical particles with a density of 1 g/cm³. However, the results of the SEM analysis showed that the particles were not spherical and it was very likely that the density was <1 g/cm³.

In situ size distribution sampling, i.e. SMPS and ELPI, seems to reflect the ultrafine particle concentration more realistically, because of the size separation capabilities and the option of scanning over a period of time. The main difference between the ELPI and SMPS is that they express particle size in a different manner. The ELPI classifies particles according to their Stokes number, which directly relates to the aerodynamic diameter, whereas the SMPS classifies particles according to their electrical mobility diameter. The mobility diameter is a measure of the relative ease with which a particle moves through a gas based on the drag force of the gas on the moving particle. In the SMPS electrical forces on the particle oppose the drag force of the gas.

The results regarding particle size distribution shifts over time, as determined by SMPS and ELPI, illustrate the differences between the two types of size characterization. The SMPS results generally show that there is an initial decrease in the percentage of ultrafine particles. During and directly after welding the percentage of ultrafines increases to about the percentage of ultrafines present before welding. The ELPI results show that the percentage of ultrafine particles increases during welding, while after welding this decreases slowly.

van Gulijk (2002) showed that the mobility and aerodynamic diameter of (fractal-like) agglomerates differ in line with the physical background of size classification. It was also concluded that the mobility
diameter, which is larger than the aerodynamic diameter, gives a better estimate of agglomerate size.

The SEM pictures of the various stages of the ELPI during the experimental study showed that next to some singlet particles of various sizes ranging from $\sim 10$ to $\sim 60$ nm (objective size), mostly agglomerates are present in the welding aerosol, consisting mainly of very open cloudy structures (see Fig. 7A and B). SEM pictures support the assumption that, because of the agglomerated structure of the welding fumes, the

Fig. 6. (A) Ultrafine particle fraction (given as a percentage of total particles) as detected by SMPS during experiment 4 (LEV at 55 cm and sample location at 360 cm). (B) Particle size fractions (given as a percentage of total particles) as detected by ELPI during experiment 4 (LEV at 55 cm and sample location at 360 cm).
mobility diameter of the particles as measured by the SMPS is larger than the aerodynamic diameter, as detected by the ELPI. Since the mobility diameter determines the particle charge, ELPI will overestimate the number of particles. In a UK study it was also concluded that during welding (and also during other activities) there was no evidence that ultrafine particles were aerosolized in an unagglomerated state or remained so for a significant length of time (Wake et al., 2002).

SEM analysis also contributes to a better understanding of the reliability of the assumptions on particle shape that are used for calculations of mass concentration from number concentration results, estimates of size distribution and specific surface area calculations.

The specific surface area of (ultrafine) particles in the present studies has been determined either directly, i.e. by BET analysis, or indirectly, i.e. by calculation using the radius of single particles as determined by SEM analysis assuming the density and a spherical shape. The latter method revealed specific surface areas of 109 m²/g for the workplace study and 115 m²/g for the experimental study, respectively. Results of the BET analysis, however, were a factor 3.5 lower, ∼30 m²/g.

The latter figure is similar to those reported by Hewitt and Gray (1983) and Hewitt (1995) for gas–metal arc welding of mild steel, i.e. 30 and 27.2 m²/g, respectively. In these studies the specific surface area was also determined directly, using a gas absorption method similar to BET analysis. The gas absorption method is very accurate, however, it demands a large mass, i.e. trapped aerosols. In the study by Hewitt this was 70–100 mg, while in the present study this was >20 mg, resulting from an aerosol concentration of ∼0.5 mg/m³. Such a high concentration could only be achieved by switching off the LEV and by non-size-selective sampling. This is a non-representative situation for exposure to ultrafine particles.

The estimates of specific surface areas obtained by SEM analysis in the workplace study are very similar to the estimate obtained by calculations using the fractal dimensions and SMPS and ELPI results for the experimental study, i.e. 109, 115 and 115 m²/g, respectively. The accuracy of these estimates may be limited because of the assumptions that have to be made and its theoretical approach. However, because of its size-selective properties the estimates obtained by these methods will reflect the specific surface area of the ultrafine fraction much better than estimates from BET analysis, since the sampled mass had to be so large that ultrafine and non-ultrafine fractions cannot be distinguished. Since small amounts are necessary for SEM analysis, it enables (ultrafine) size-selective sampling from the breathing zone.

To complete the characterization of the exposure to ultrafine particle aerosols, the chemical composition of the aerosol can be investigated. Additional analysis of the (elementary) composition of the particles is useful for confirmation of other results and in combination with observations. In the workplace study iron(III) and carbon, for example, were expected to be present as a result of the welding and grinding activities and diesel exhaust, respectively. However, the X-ray microanalysis system appeared not to be entirely suitable for chemical analysis, because identification of substances could only be performed at the elemental level and could not be quantified and only solid particles could be analysed due to the high vacuum of the SEM. In further research other techniques should be used for solid particles (mass spectrometry) and for adsorbed substances (high pressure liquid chromatography or gas chromatography) to quantify the chemical composition of the samples.

**CONCLUSIONS**

The present study aimed at testing the performance of available measurement methods and a measuring strategy. The use of in situ detection of particle
number concentration for source identification proved to be useful. For both MIG welding scenarios ultrafine particle concentration seemed to be associated with total number particle concentration. The relative contribution of different sources can be estimated qualitatively.

Particle size-selective measurement of particle concentration seems to be limited in accuracy for both particle size distribution, i.e. SMPS results, and for particle number concentration, i.e. ELPI results. The results of the measurements (in the MIG welding scenarios) confirm the suspected temporal and spatial variation in (number) concentration and aerosol size distribution. From the results it can be determined that both location and time greatly affect both parameters.

Collection of (ultrafine) particles from the workplace air and further analysis generated useful additional information. It is important that the sampling of aerosols should be either (ultrafine) size-selective, e.g. ELPI samples, or from the breathing zone, e.g. personal air samples. A drawback is that only a small mass can be collected, which does not enable BET analysis. However, SEM or additional (microscopic) analysis is possible since overloading of the samples is prevented. Conventional static size-selective sampling methods, where the samples are analysed gravimetrically, are very much hindered by detection limits. Moreover, only a few stages of LPIs cover the nanoparticle range, e.g. in case of the Berner LPI only the last stage and the back-up filter.

Each of the measurement methods has its drawbacks, but when used in combination they may give full insight into the presence of ultrafine particle aerosols in the workplace. Sources of ultrafine particle emission can be identified, estimates of (size-selective) particle number concentrations over time can be obtained and, based on grab samples, identification of some characteristics of ultrafine particles is possible. Field observations are crucial in order to link the results to the various events during the measurements.

Both the workplace study and the experimental study showed that there is spatial variations in both particle number concentration and size distribution. Therefore, the use of static samplers at fixed locations hampers the interpretation of the results for personal exposure of ambulatory workers. Even for workers who are positioned at fixed workstations the interpretation will be very inaccurate. Further research is needed to enable accurate quantification of personal exposure of workers and to identify determinants of exposure. However, the presence of ultrafine particles in the workplace and the potential for exposure can be demonstrated by the approach outlined in the present paper.

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