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Measurement of fine, coarse and ultrafine particles

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Summary. - Over the last decade a large number of measurement methods for fine, coarse and ultrafine particles have been developed to characterize ambient $PM_{2.5}$ as well as personal $PM_{2.5}$ exposures. These new devices will enable us to improve our understanding of factors affecting human exposure to particulate and gaseous air pollutants. A brief description and commentary on these methods is presented. Broadly, these techniques can be divided into two categories: integrated methods that are mostly filter-based, and continuous methods which are based on the measurement of physical properties of particles. In addition, we also review how our personal multipollutant sampler has been used in field studies in various locations in the United States of America.

Key words: particulate matter, sampling methods, impactor, Harvard Impactor, multipollutant sampler.

Riassunto *(Misura delle particelle fini,* coarse *e ultrafini)*. - Nel corso dell'ultimo decennio sono stati sviluppati numerosi metodi di misura per le particelle fini, grossolane ed ultrafini con lo scopo di caratterizzare il $PM_{2.5}$ nell'ambiente e l'esposizione personale al $PM_{2.5}$. Questi nuovi strumenti consentiranno di migliorare le conoscenze dei fattori che determinano l'esposizione umana alle particelle e agli inquinanti gassosi aerodispersi. Viene presentata una breve descrizione di questi metodi ed una sintesi delle loro prestazioni. Da un punto di vista generale, questi strumenti possono essere divisi in due categorie: metodi integrati basati per lo più sull'uso di filtri, e metodi continui, che si fondano sulla misura delle proprietà fisiche delle particelle. Oltre a ciò viene presentata una rassegna delle applicazioni sul campo in varie località statunitensi di un campionatore personale multinquinanti sviluppato dagli autori.

Parole chiave: materiale particellare, metodi di campionamento, impattore, *Harvard Impactor,* campionatore multinquinanti.

Introduction

Numerous studies have shown associations between outdoor concentrations of $PM_{2.5}$ and a variety of adverse health outcomes, including increased hospital admissions, increased emergency room visits, exacerbation of asthma, decreased lung function and increased mortality [1-7]. The consistency of these findings is remarkable given the fact that these studies were conducted in a variety of locations with diverse study populations, designs and meteorologic and air quality conditions.

Despite this consistency, areas of uncertainty remain. Investigators have yet to determine whether the observed health effects are related to specific size fractions of ambient fine particulate matter or whether the effects are caused by various toxic components. Recent toxicologic results have indicated that ultrafine particles (particles with a D_a da less than 0.1-0.2 μm) are associated with increased inflammatory response in animal and human models [8]. Other studies have suggested that specific toxic components are responsible for irregular heart function in animal models [9]. Additionally, weak correlations between outdoor particulate matter (PM) concentrations and total personal PM exposures reported in various cross-sectional exposure studies have also been offered by others as proof that ambient $PM_{2.5}$ concentrations used by epidemiologic findings are poor indicators of exposure [10].

As a result of these remaining uncertainties, in 1998 the National Research Council recommended that further research be conducted to characterize ambient $PM_{2.5}$ personal exposures to $PM_{2.5}$, including its relationship to ambient $PM_{2.5}$ and other multi-pollutant exposures [11].

Over the last decade a large number of measurement methods for fine, coarse and ultrafine particles have been developed to characterize ambient $PM_{2.5}$ as well as personal $PM_{2.5}$ exposures. These new devices will enable us to improve our understanding of factors affecting human exposure to particulate and gaseous air pollutants. A brief description and commentary on these

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methods will be presented. Broadly, these techniques can be divided into two categories: integrated methods that are mostly filter-based, and continuous methods which are based on the measurement of physical properties of particles. In addition, we will also review how our personal multipollutant sampler has been used in field studies in various locations in the USA.

Integrated sampling techniques for PM_{10}, $PM_{2.5}$ and coarse particles

Devices such as the United States Environmental Protection Agency (USEPA) Federal Reference Method (FRM), the dichotomous sampler, the Harvard Impactor (HI), and the Low Volume Impactor, are some of the most commonly used particle samplers for the collection of PM_{10} and $PM_{2.5}$ integrated samples. All these devices use either conventional or virtual impactors to separate particles according to their aerodynamic size. Coarse particles can be measured either indirectly as the difference of PM_{10} minus $PM_{2.5}$ or directly using virtual impactors such as the dichotomous sampler (Fig. 1) [12, 13].

Particles of the desired particle size range are collected on a filter medium, usually a Teflon membrane. Filter samples are weighed using electronic microbalances to determine the mass of collected particles. The time interval for the filter-based methods is usually 24 h, although samples can be collected for shorter periods (a few hours) or for longer periods (up to a week). Integrated particle samplers, such as the HI, are relatively inexpensive and easy to use and maintain, however, they are labor intensive (Fig. 2). Although their design and costs differ extensively, results from field studies suggest that these methods are equivalent. Therefore, low volume samplers could be easily and cost effectively implemented for large monitoring networks. It is recommended to use sensitive gravimetric analysis methods, with sample flows not higher than 10-16 liters per minute.

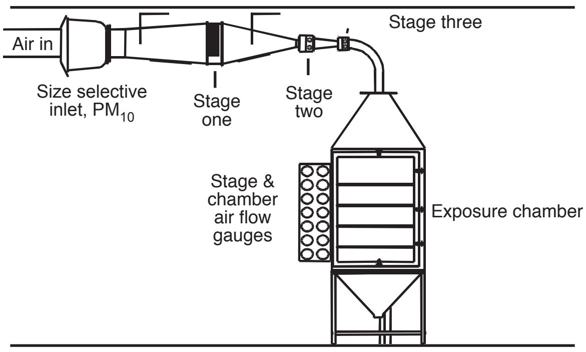

Fig. 1. - Diagram of coarse particle virtual impaction.

Filter based methods are prone to positive and negative artifacts. For instance, a large fraction of semivolatile organic or inorganic compounds can be adsorbed of desorbed from the filter sample during particle collection [14]. In general, desorption artifacts increase with the air face velocity of the sample air through the filter media. Also temperature gradients between the filter media and the sample air can enhance either volatilization or adsorption of semivolatile particle phase compounds. Finally, gas/particle and or particle/particle chemical reactions can take place during sampling, resulting in positive or negative artifacts [15].

The development of a personal multi-pollutant sampler is also part of our ongoing efforts to improve personal and microenvironmental aerosol sampling technologies. This sampler can be used for measuring exposures to particulate matter and criteria gases. The system uses a single personal sampling pump which operates at a flow rate of 5.2 l/min (a picture of the Harvard multi-pollutant sampler is available online within the full text of this article, at www.iss.it/annali). The basic unit consists of two impaction-based samplers for $PM_{2.5}$ and PM_{10} attached to a single elutriator. Two mini $PM_{2.5}$ samplers are also attached to the elutriator for organic carbon (OC), elemental carbon (EC), sulfate and nitrate measurements. For the collection of nitrate and sulfate, the mini-sampler includes a miniaturized honeycomb glass denuder which is placed upstream of the filter to remove nitric acid and sulfur dioxide and to minimize artifacts. Two passive samplers can also be attached to the elutriator for measurements of gaseous co-pollutants such as ozone (O_3), sulfur dioxide (SO_2) and nitrogen dioxide (NO_2).

Using integrated particle sampling technologies in exposure assessment field studies

During the past five years, we have been able to conduct a series of exposure assessment studies measuring ambient concentrations and personal exposure to multiple pollutants in Baltimore, MD, Boston, MA, Steubenville, OH, Atlanta, GA, and Los Angeles, CA. For each of these studies, we used Harvard Impactors to characterize 24 h integrated ambient PM concentrations and the personal multi-pollutant sampler to characterize 24 h integrated personal PM concentrations. These studies have enabled us to examine both associations between ambient concentrations and corresponding personal exposures as well as associations among personal exposures to PM and its gaseous co-pollutants. In Baltimore, for example, personal multi-pollutant exposures and corresponding ambient concentrations were measured for 56 subjects living within the metropolitan Baltimore area. Simultaneous 24 h integrated personal exposures were measured for a combination of the following pollutants: $PM_{2.5}$, PM_{10}, O_3, NO_2, SO_2, EC/OC and VOCs. Sample results from the Baltimore exposure assessment can demonstrate the types of analyses facilitated using the novel particle sampling technologies.

Fig. 3 shows the relationship over a twelve-day sampling period between ambient $PM_{2.5}$ concentrations measured at a central monitoring site and corresponding personal $PM_{2.5}$ exposures for a subset of 5 subjects who were measured simultaneously. Fig. 4 shows the relationship among several particle and gas measurements over a twelve-day for a given subject. Similar to findings from recent studies [16, 17], longitudinal personal-ambient associations for $PM_{2.5}$ for the Baltimore subjects were strong. These strong associations did not exist for any of the gaseous co-pollutants, however, suggesting that ambient concentrations of O_3, NO_2 and SO_2 were poor surrogates of their respective personal exposures [18].

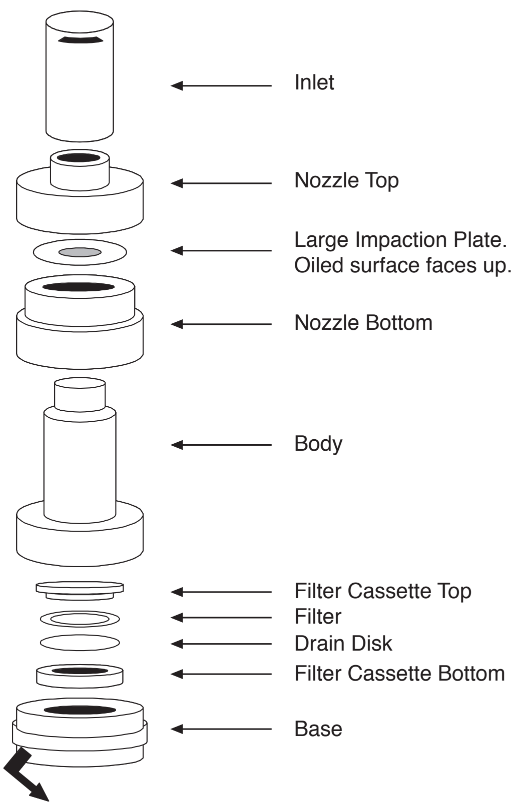

Fig. 2. - Diagram of the Harvard Impactor.

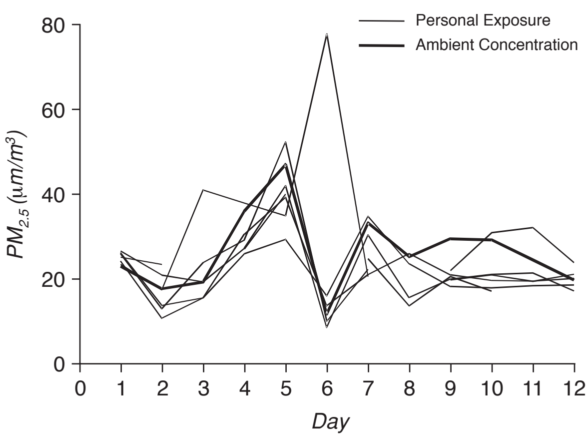

Fig. 3. - Associations between ambient $PM_{2.5}$ concentations and corresponding personal $PM_{2.5}$ exposure.

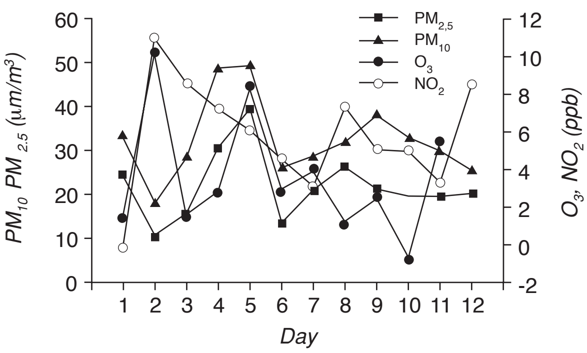

Fig. 4. - Associations among personal particulate and gaseous pollutant exposure.

Continuous monitoring techniques for $PM_{2.5}$ and PM_{10}

There are several continuous mass measurement methods currently available. These methods include: the Tapered Element Oscillating Microbalance (TEOM) [19], different light scattering and beta-attenuation devices, and the Continuous Ambient Mass Monitor (CAMM) [20]. Continuous methods can be used to measure short-term exposures (from a few minutes to an hour) and are relatively easy to employ for field studies. Although their capital costs are high, their operation and maintenance is relatively inexpensive. However, the accuracy of these methods, determined using gravimetric analysis as the reference method, can be questionable. Therefore, these monitors have to be calibrated often against a reference method. This method is currently being field tested by several investigators in the United States. Therefore there is a great need to further evaluate the accuracy of all of these continuous methods is being addressed by an extensive series of field studies through the USEPA supersite program. In spite of their limitations, the continuous methods can often provide useful information about temporal patterns of particle concentrations.

Measurements of ultrafine particles

Sampling of ultrafine particles is a challenging task for two reasons: first, because of their small mass, separation of fine particles from ultrafine particles by inertial impaction can only be achieved at a relatively high pressure drop, and; second, considering that typical ambient atmosphere ultrafine particle concentrations are less than 1 $\mu g/m^3$, collection of filter samples for gravimetric analysis and chemical characterization is only feasible with novel high volume sampling techniques. For this reason, the most commonly conducted ultrafine particle measurement method is the determination of the particle number concentration. For this, the Condensation Nuclei Counter (CNC) and the P-Trak are the most widely used monitors. The CNC is a very sensitive research grade instrument and has been used mostly in laboratory studies. Because of the recent interest in ultrafine particle research many field studies have started to use this monitor. The P-Trak is portable and less sensitive than the CNC and has been mainly used for occupational environments and only a few exposure studies.

Collection of fine, coarse and ultrafine particles for toxicological and physico-chemical characterization studies

There is a great need to develop samplers for the collection mg to g quantities of ambient particles, for both toxicological and particle characterization studies. To achieve this, the particle sampler must operate at high flow rates, on the order of 1000 LPM. However, existing filtration or impaction methods are not adequate for collecting particles at such high flow rates. For instance, filtration methods such as the high volume (*Hi-vol*) sampler, which operates at a flow rate of 1000 LPM, require relatively large filters (20.3 x 25.4 cm). As a result, these collection media also require relatively large quantities of solvents to recover the collected particles, which severely limits their usefulness for both toxicological and characterization tests. In contrast, conventional inertial impactors have the ability to focus the collected particles on relatively small surfaces, allowing for particle recovery from the impaction surfaces into relatively small extract volumes. Because of the collision of particles with high *momentum* onto the typical solid flat impaction substrate, particles can bounce off of the surface and get re-entrained into the air stream. To overcome this problem, the impaction substrate may be coated with a sticky substance, such as oil or grease. However, the use of oil or grease-coated substrates has significant limitations. The sample may be contaminated by components of such substances, and thus may not be suitable for toxicological or characterization studies. In addition, for relatively large amounts of collected material, the substrate collection efficiency depends on the amount of particles collected, thus only relatively small amounts of particles can be accurately accumulated on greased or oiled solid flat impaction substrates.

Fig. 5. - Schematic diagram and picture of the high volume cascade impactor.

To overcome the bounce-off and low capacity problems we use polyurethane foam (PUF) as an impaction substrate [21]. Although such porous foams were recently suggested as pre-selective inlets, they had problems because of the bounce-off losses of solid particles. However, because of their large pores and relatively low overall density, these materials are suitable as impaction substrates for conventional impactors. These porous materials present negligible particle bounce-off and re-entrainment losses because particles can impinge onto the substrate with a possible gradual decrease of particle velocity. Because of their porosity, these substrates present high collection capacity and can be used to collect mg to g quantities of particles (a picture of impactor plates using polyurethane foam substrates is available online within the full text of this article, at www.iss.it/annali).

A three stage round slit nozzle impactor has been developed at our laboratory that can be used to collect multi-day samples of fine, coarse and ultrafine particles at a flow rate of 1000 liters per minute (Fig. 5) [22]. The ultrafine particles are collected on a relatively small disk of polyurethane foam, downstream of the third stage impactor.

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