
5 Analytical Methods

This chapter describes the state-of-the-art analytical methods and instruments typical of those used to measure concentrations in all environmental media that contribute to human and non-human exposure to pollutants. For each topic, research needs are identified, and recommended projects are discussed that would meet these needs. Because the air route of exposure is important for many chemicals, the discussions are devoted to instrumentation and methods for measuring substances in air.

5.1 AIR

5.1.1 PERSONAL EXPOSURE MONITORS

Evaluation of actual exposures occurring at a receptor requires measuring the quantity of contaminant present. Even when relying on fixed location monitors and models, direct verification of actual exposures is necessary. The more mobile the receptor, the more likely it will encounter a variety of microenvironments. These microenvironments can be quite different depending on sources, chemical/physical interactions, and dilution. Under these conditions, fixed location measurements are less likely to represent the total or partial exposure experienced by the receptors; therefore, for mobile receptors, multiple locations, and varied sources, exposure assessment requires the use of portable and personal monitoring equipment.

This section provides a brief review of the current availability and future needs for personal and portable monitors to measure air pollutant exposures. More detailed reviews are available in the accompanying paper by Spengler and Wallace (this volume) and in other published reviews by Wallace and Ott (1982).

Many described devices have been used in human exposure studies. Spengler and Soczek (1984) reviewed most studies completed by 1983. It is noteworthy that laboratory analytical instrumentation has advanced considerably in recent years, and is now commercially available. Instruments and methods such as GC, GC/MS, HPLC, IC, AA, XRF, INNA, plasma induced spectroscopy, proton induced X-ray emissions, UV-visible and IR spectroscopy, constant energy synchronous luminescence, chemical luminescence, electrochemical, and light scattering are available. These techniques have been applied to the analyses of bulk and trace constituents of contaminants in the biosphere. Some ambient monitoring equipment

utilises these principles to routinely measure CO, CO₂, NO₂, O₃, fine particles, hydrocarbons, and the elemental composition of particles.

Recently, thermal activated volatilisation coupled to flame photoionisation devices have been developed to provide continuous speciation of sulfuric acid and other sulfur particle compounds (Huntzicker *et al.*, 1980; Tanner *et al.*, 1980). To some extent, these devices can provide information on air pollutant exposures in a variety of settings. However, since they were developed primarily as ambient monitors, they are not appropriate as portable or personal samplers.

The measurement of personal exposures places new demands on technology because the size, weight, power requirements, and ruggedness of these instruments must be much less than for conventional monitoring instruments. The ideal exposure monitor is quiet, light weight, small, rugged, easily transported, capable of running 24 hours or more without auxiliary power, replenishable, and able to provide continuous readings with the same precision and accuracy as conventional monitors. Unfortunately, personal exposure monitors meeting such requirements are not generally available.

Indeed, personal exposure measurement methods do not exist for many of the most critical environmental pollutants. Thus, human exposure research programs should place emphasis on the evaluation of existing methods and on the development of new measurement methods, including personal exposure models (PEMs), where they are most essential.

Continuous recording portable or personal monitors are not available for most contaminants of interest. However, collecting a sample over time by filtration, diffusion, permeation, absorption in a reagent, adsorption on a matrix (charcoal, molecular sieves), or simply an integrated air sample can provide sufficient quantities of a material for analysis. Utilising this approach, personal exposure studies can be conducted. To meet some of the objectives listed previously, integrated samples are preferable to continuous time records of concentrations. It is usually less expensive to collect and analyse integrated samples, thus enabling a larger sampling size.

As an alternative to direct measurements (either continuous or integrated) exposure assessment studies can still be performed using an indirect approach, that has two components. Knowing the activity/location of the populations of interest and the pollutant concentrations of micro-environments, a model of exposure can be developed. For the indirect approach the instrument requirements are less stringent. They no longer need to be light weight or battery operated. However, the more portable the instruments, the more feasible it is to monitor a greater variety and number of micro-environments. Additional testing is needed to determine if instruments and techniques that have been evaluated for ambient air sampling will be suitable for other environments—primarily indoors.

Besides the usual test parameters of response time, accuracy, and precision, instruments used indoors will encounter a variety of potentially interfering

materials. Development and testing of instruments used for indoor and total exposure assessment must be thoroughly evaluated. The concepts of quality assurance must be rigorously followed, as emphasised throughout this document. Field study protocols should use field blanks and replicates. Good laboratory practices include blanks, spiked samples, split samples, primary and secondary reference materials and interlaboratory comparisons. When possible, external audits of field and laboratory instruments should be incorporated into studies. Obviously, elements of quality assurance are applicable to survey design, sampling, response/non-response rates, and data processing.

5.1.1.1 Gases

A variety of personal exposure monitors now exists for measuring pollutant gases; but the field is at an early stage of development, and additional monitors are needed.

Carbon Monoxide (CO) A 2-lb electrochemical personal exposure monitor (PEM) is available for CO with ± 2 ppm accuracy, 40-hour running time, and continuous read-out. These PEMs employ a liquid or solid electrolyte in which CO is converted to CO₂, generating an electrical signal. Response times are less than 2 minutes. Both pump-driven and diffusion type instruments are available, and the former have been successfully deployed in population exposure field studies (Akland *et al.*, 1985). An inexpensive passive (i.e., non-battery powered) CO monitor is needed for large-scale field surveys of homes, offices, garages, restaurants, arenas, and similar CO micro-environments. A semi-portable, data-logging CO monitor capable of running a month without maintenance also is needed for indoor air quality surveys.

Nitrogen Dioxide (NO₂) Small, light-weight passive personal monitors for NO₂ are available such as Palmes tubes (Palmes and Gunnison, 1973) that weigh less than 10 g, and consist of commercial acrylic tubing. The bottom of the tube is opened to the air, and allows NO₂ to diffuse upward (reducing the probability of dust or moisture falling into the tube). Analysis is dependent on Fick's Law. Following exposure, a reagent is added directly to the sampler, and colour development is read on a spectrophotometer. Other passive NO₂ monitors also are available with similar characteristics.

The passive monitors provide only integrated readings over a specified interval consisting usually of days or weeks. To the extent that adverse health effects of NO₂ may be associated with peak exposures of shorter duration, passive monitors are inadequate for exposure monitoring studies. Active monitors for NO₂ are also under development. Electrochemical monitors may be promising if problems with stability and interference can be overcome. Progress has been made in developing a monitor based on

the light-producing reaction between NO_2 and luminol. Air entering the system is pulled through a unit and across the face of a filter wetted with a solution containing luminol. Light is detected on a photodiode, producing a voltage signal proportional to the NO_2 concentration. A prototype luminol monitor has been fabricated for testing that is battery powered, operates for 26 hours, weighs less than 4 kg, and is smaller than a 30 cm cube. Additional testing and development of these monitors is needed. Once a real-time, continuous NO_2 monitor has been successfully developed and field tested in pilot studies, a large-scale study of the NO_2 exposure profiles of a city should be conducted, including such micro-environments as homes, buildings, restaurants, etc.

Polynuclear Aromatic Hydrocarbons (PAH or PNA) A passive diffusion badge has been developed allowing detection of PAH vapours. A filter paper 5 mm in diameter coated with heavy-atom chemicals such as lead acetate and thallium absorbs the vapours. After exposure, the filter is placed in a spectrophotometer and irradiated with ultraviolet light. The adsorbed PAH molecules phosphoresce, with certain PAH's phosphorescing more strongly than normal because of the heavy-metal chemicals. Techniques also are available to measure PAH adsorbed on particles collected on a filter by an active personal sampler (Vo-Dinh *et al.*, 1981). There is a need to deploy these new techniques both in large-scale field studies and in micro-environmental field investigations to characterise population exposure to PAH's.

Formaldehyde Prediction of formaldehyde exposure is extremely difficult because of the influence of temperature and humidity, and because of the nature and age of the matrix upon its emission. A passive monitor is available commercially consisting of a diffusion tube containing sodium bisulfate. This badge is analysed in the laboratory by the chromatographic acid method and is sensitive to 70 ppb of formaldehyde after one day of exposure. Another monitor, still under development, consists of a plastic badge containing a film of monodispersed hydroxybenzoic acid hydrazide. Additional testing of this technique is needed.

Although some of these monitors have been evaluated extensively and used in occupational settings, they have not been applied to large-scale human exposure studies or to field studies of indoor micro-environments. There is a need for pilot testing these methods in indoor and total exposure studies. Should such pilot studies prove effective, there is a need to deploy these monitors in large-scale studies to characterise the exposures of the population to formaldehyde.

Volatile Organic Compounds (VOC) In 1980, a personal monitor was developed that could be worn by the general public and was sufficiently sensitive to quantify normal daily exposure to 20 to 30 toxic or carcinogenic VOCs (Wallace *et al.*, 1987). The monitor consists of a battery-operated pump capable of 12-hour continuous flow at about 30 ml/min. and a cartridge

containing approximately 2 gm of Tenax-GCTM, a synthetic hydrophobic polymer with strong affinity for polar organic compounds. The cartridge is removed, and its contents are analysed by gas chromatography/mass spectrometry (GC/MS). It has been used to measure people's exposures in air, drinking water, and breath and to measure total exposures of 355 residents of Bayonne and Elizabeth, New Jersey, in the total exposure assessment methodology (TEAM) study (Wallace *et al.*, 1987).

Background contamination of Tenax is variable among batches, and particular problems occur with toluene, benzene, and to a lesser extent styrene. Careful preparation and clean-up of Tenax, coupled with extensive precautions during transport, are necessary to ensure good quality data. Mean relative standard deviations range from 25 to 35 percent for nearly all compounds with the exception of benzene (45 percent). Artifacts identified include benzaldehyde and phenol; and high NO₂ and ozone concentrations increase artifact formation.

The VOC personal monitor is sufficiently well-developed to be used in large-scale population exposure studies. Surprisingly high VOC exposures were found indoors in the TEAM study of New Jersey residents. Building on similar exposure field surveys in some cities to determine the prevalence of these high exposures and the circumstances responsible for them, there also is a need to conduct similar total exposure field studies in other countries to determine how cultural differences, lifestyles, and housing characteristics affect exposures.

Pesticides A battery-operated, low volume air sampling system utilising polyurethane foam (PUF) as a trapping medium has been developed and evaluated (Wright *et al.*, 1982; Bristol *et al.*, 1982). The sampler is lightweight, portable, and operates very quietly, making it ideally suited for residential air sampling or as a personal air monitor. Sampling efficiencies have been determined for 17 organochlorine pesticides and industrial compounds, three polychlorinated biphenyl (PCB) mixtures, and 28 organophosphorus, organonitrogen, and pyrethroid pesticides. It can be combined with TenaxTM-GC in a single, reusable sampling cartridge to collect pesticides and VOCs together.

Studies are underway in the U.S. to deploy the PUF technique to determine respiratory exposures of 500 urban-suburban residents to 34 pesticides and PCBs of concern to the pesticide regulatory programs. The same methodology—probability sampling of households and measurement of exposures with personal monitors—could be applied in other countries to determine population exposure distributions, differences in exposures among countries, and relationships between exposures and lifestyles.

5.1.1.2 Particles

Under most circumstances, particles in the environment are a complex mixture of sizes, shapes, and chemical composition. The properties of pesticides that are of interest vary depending on the phenomenon being studied. These characteristics include mass concentration, size distribution, number concentration, morphology, crystalline structure, elemental composition, chemical components, pH, and solubility. To date, personal monitors are available to collect size fractionated particulate samples that are integrated over time. The monitors can separate particles using cyclone or impaction preseparator to provide mass measurements of micron and submicron sized particles. The minimum sampling time depends on concentration, flow rate, and sensitivity of detection device. Mass loadings on filters are usually determined gravimetrically but β -attenuation is also used. In situations such as indoor cooking with biomass fuels and without ventilation, samples of a few minutes at 2 l/min are sufficient. In studies of rural populations not exposed to cigarette smoke, industrial sources, or unvented combustion, sampling times must integrate over several hours. Fractionating particles by size is recommended for exposure studies. The physical and chemical characteristics of aerosols are strongly related to their sources and mechanism of generation. The dynamics of particles emitted into the atmosphere by different sources (primary aerosols) are initially influenced on a microscale by Brownian diffusion and coagulation, and on a large scale by atmospheric processes. During their residence and transport in the atmosphere, a number of chemical processes and physical modifications continually occur, resulting in changes in their properties.

Trace gases in the atmosphere, derived from anthropogenic as well as natural sources, also react with each other, other particles, sunlight, and water vapour, cloud droplets, and raindrops. These processes yield a greater number of products, some of which remain in the gaseous form while others undergo a phase transition to form secondary aerosols. Furthermore, the size distributions of the atmospheric aerosols present characteristics which can relate to different mechanisms of formation and transformation (Whitby *et al.*, 1975). Historically, particles were grouped into two size categories: fine particles (diameters $< 2.5 \mu\text{m}$) and coarse particles (diameters $> 2.5 \mu\text{m}$). Coarse particles are formed directly by mechanical processes (i.e. windblown dust, sea salt, fugitive dust from material handling and abrasion); however, the addition of other classes has been performed increasingly. Fine particles are formed through gas-to-particle conversion processes such as condensation of metal or organic vapours and the oxidation of SO_2 , NO_2 , and other gases. This distinction is important. As shown in Figure 5.1, the elemental chemical composition of aerosols will be fractionated by size. Depending on the exposure of interest (e.g., respiratory tract deposition,

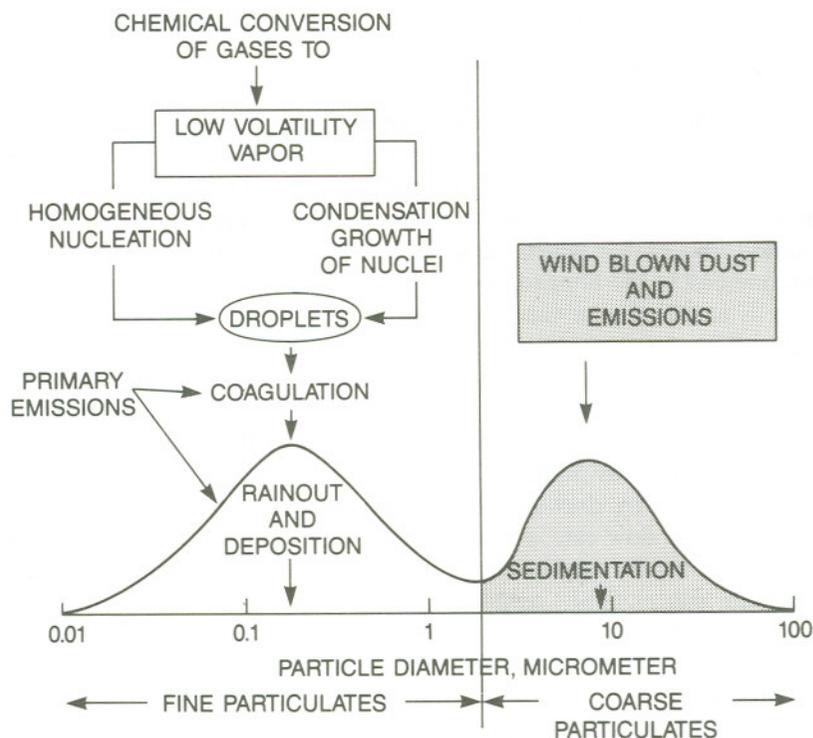


Figure 5.1. Size distributions and origins of particles in ambient air

light extinction, or soiling impacts) the size collection characteristics of the sampling device will be important.

Sampling of the atmospheric aerosol is a complex problem because of the spectrum of particle sizes and shapes. Separating particles by aerodynamic size is somewhat simplistic, because it disregards variations in particle shapes and depends on particle settling velocity. The aerodynamic diameter of a particle is not a direct measurement of its size, but rather corresponds to the diameter of a spherical particle of specific gravity which would have the same settling velocity as the particle in question.

Different samplers have been designed to collect particles within defined ranges of aerodynamic diameters: cascade impactors, dichotomous samplers, and cyclone samplers with selective inlets are the most commonly used samplers with designed collection characteristics. However, most of these particle samplers can underestimate the concentration of particles in the air because of sensitivity to external factors such as wind speed or because of internal particle losses in the measurement system. Samplers of total suspended particles, however, can be used for studies where there is no concern about the size distribution of the particles.

In general, there is no single protocol for aerosol sampling. The sampling

procedure is usually determined by the type of information being sought. The most commonly used samplers in aerosol monitoring studies are described.

Streaker Sampler The time variability of trace elemental concentrations in the air can be obtained easily and automatically by this filter sampler whose exposed surface is changed continuously. This time-sequence filter consists of a single strip of Nucleopore filter stretched on a frame and mounted in a device which causes a sucking orifice to be drawn gradually from one end of the filter to the other (Winchester *et al.*, 1979). The sucking orifice is attached to a vacuum pump; so as the orifice is drawn along the length of the filter, the suction seals the orifice to the smooth back of the Nucleopore while at the same time permitting air to be drawn through the filter. The device is driven by a connected clock motor adjusted so that it takes 7 days for a full transit along the length of the filter.

High-volume Mass Sampler This sampler is designed to collect particles on a glass filter by drawing air through the filter at a flow rate of about 1 m³/min. This flow rate is much higher than the other particle samplers. The hi-vol is widely used to measure the gravimetric mass of total suspended particulate matter (TSP) as does the streaker. Hi-vol can also be used for studies of organic particulate matter, because it collects a sufficient aerosol mass for further analysis by high performance liquid chromatography or by gas chromatography. The hi-vol sampler has cutpoints of 25 μm at a wind speed of 24 km/hr and 45 μm at 2 km/hr. However, wind speed is estimated to produce no more than a 10 percent day-to-day variability for the same ambient concentration for typical conditions. One advantage of the hi-vol sampler is its great reproducibility (3 to 5 percent) in comparison with the other sampling techniques.

There are, however, some disadvantages to the hi-vol samplers. For example, there is a significant problem associated with using glass filters, because acid gases in the air react with the glass causing the formation of an artifact mass. This artifact mass can result in an increase in the total mass collected which is equal to 6 to 7 μg/m³ per 24-hour sample. The hi-vol has been used extensively in the U.S. and Europe for many aerometric as well as epidemiological studies. Hi-vol samplers are not appropriate for indoor monitoring. The high flow rate will sample a volume of air that may approach the air exchange volume. In this case, the hi-vol sample will actually be cleaning the air. Its noise is also a limitation.

Cascade Impactor In the earlier aerosol studies, a cascade impactor was used as the sampling device to obtain measurements of elemental composition as a function of particle size (Mitchell and Pilcher, 1959). In this type of sampling, air passes successively through a series of circular orifices of decreasing diameter, with the linear air flow rate increasing as it goes through successive stages. Directly downstream of each orifice is a collecting barrier of a sticky Mylar film backed by a solid support surface so that the

largest particles passing through the orifices at each stage impact and stick to the Mylar surface. Smaller particles pass around the impaction surface; but at the next stage, owing to increased air velocity, the larger ones will be collected by impaction. The cascade impactors are typically designed to give 50 percent collection efficiency through the first five stages, so that the range of particle sizes collected at each stage fall in between the chosen cutpoints of 8, 4, 2, 1, 0.5, and 0.25 μm aerodynamic diameter. Particles smaller than those collected at impaction stage 5 are collected by a filter at the end. The pore diameter of the Nucleopore filter used here is sufficiently small to assure at least 70 percent collection of any size particle.

Cascade impactors can separate particles into six or more fractions, but the additional fractionation often does not add more useful information. In contrast, the information concerning the particle size distribution of ultrafine particles can be very important for a better understanding of aerosol formation. Researchers at Harvard University recently developed an aerosol impaction sampler to address this issue (Sexton *et al.*, 1984). Using a two-stage impactor cutting at the same diameter (50 percent at 2.5 μm), bounce or carry over has been eliminated. The device has a mass flow controller to maintain the flow at 4 l/min. It can be built with a 1, 7, or 14 day timer, so that selected periods can be sampled. The impaction stages can be interchanged with ones that provide a 50 percent particle separation at 10 μm . The Harvard Aerosol Impactor was designed specifically for indoor air quality studies, but has been adapted for ambient sampling. The flow is low and it is quiet so it is suitable for indoor use. The pump has been rated up to 50 in H_2O , so typical mass loadings from continuous multi-day sampling have not been a problem. The device is ideal as a particle sampler for developing countries. The purchase price is substantially less than for the more commonly used hi-vol sampler.

Dichotomous Sampler The dichotomous sampler collects two particle size fractions—typically, 0 to 2.5 μm and 2.5 to 15 μm —the latter cut-off point depends on the inlet. This bimodal collection, therefore, approximately separates the fine particles from the coarse.

The particle separation principle used by this sampler was described by Hounam and Sherwood (1965). The separation principle involves acceleration of the particles through a nozzle, after which 30 percent of the flowstream is drawn off at right angles. The small particles follow the right angle flowstream, while the larger particles (because of their inertia) continue toward the collection nozzle.

Inherent in the dichotomous separation technique is a contamination of the coarse particle fraction with a small percentage of the fine particles in the total flowstream. This is not considered a substantial problem for mass measurements, and a simple mathematical correction can be applied.

Researchers at the U.S. National Bureau of Standards have developed a personal particle sampler that can collect in two size fractions—“fine”

(diameters $< 2.5 \mu\text{m}$) and "coarse" (2.5 to $10 \mu\text{m}$) (Fletcher, 1984). Separate sampling heads can be attached to change the upper cut-off size (7, 10, or $15 \mu\text{m}$). The principle of separation is impaction. The first of the tandem filters is a Nucleopore filter. At the flow rate of 6 l/min, depending on the pore size filter selected, only smaller particles will pass through to be captured on a fibre matrix filter. Using 6 D-size batteries, up to 40 hours of continuous sampling is possible.

Cyclone Sampler Cyclone samplers have been used in a great number of studies which are concerned only with the analysis of fine particles. Their small size makes them useful for personal dosimetry sampling. This collection system samples the air, and deposits the fine particles onto a 37 mm diameter filter. The use of cyclone inlets for the collection of particles has the advantage of allowing a variety of sample flow rates and cut-off points to be used by selecting the appropriate cyclone design.

Researchers at Harvard have developed a personal particle sampler using a cyclone pre-separator to obtain respirable size particles (Lindberg *et al.*, 1979). The pump is a Brailsford Brushless type with a flow rate of 0.5 to 3 l/min, regulated by a variable voltage control. The monitor has a nylon cyclone to separate the RSP fraction according to the size criteria suggested by the American Congress of Industrial and Government Hygienists (ACGIH). RSP size particles are collected on a 37 mm Fluoropore filter with a $1 \mu\text{m}$ pore size.

The monitor can be operated for 14 to 20 hours on a 12-V nickel/cadmium battery, or indefinitely off a 120-V line. It is small ($18 \text{ cm} \times 18 \text{ cm} \times 10 \text{ cm}$) and weighs less than 2 kg. Enclosed in an aluminum case, it is quiet enough for use in homes or offices. Using teflon filters, they can be extracted with water and ethanol to determine total soluble sulfates or analysed for metals by atomic absorption or neutron activation analysis.

This sampler has been used in several studies of personal exposure. It has proven to be reliable with an overall precision of about 10 percent. While results from various studies are intercomparable, the cyclone separation has not given consistent results when compared to the fine fraction mass from a dichotomous sampler. The problem is worse in low-mass concentrations, calling into question the accuracy of gravimetric determinations of concentrations when mass loadings are low. Further, nylon cyclones have electrostatic effects which will increase the removal efficiency of smaller particles.

Piezobalance A portable monitor capable of detecting mass, but not chemical composition, of RSP is the Thermosystems Inc. (TSI) Piezobalance, which uses the piezoelectric principle (Sem *et al.*, 1977). The instrument uses a cyclone pre-separator and deposits RSP particles by electrostatic precipitation onto an oscillating quartz target crystal. With increasing mass, the frequency of oscillation decreases. The change in frequency is then used to calculate weight gained over the pre-set intervals of 24 sec or 2 min.

Other sampling times can be used. The piezobalance is portable rather than personal ($40 \times 20 \times 12$ cm). The range of the instrument is from $10 \mu\text{m}/\text{m}^3$ to $10 \text{ mg}/\text{m}^3$. The crystal has to be cleaned periodically, which procedure in polluted atmospheres may be as frequent as every 10 minutes or even less. The device is sensitive to rapid changes in temperature or humidity. Hydrocarbon gas also seems to cause instability. This may be due to adsorption onto particles already collected on the crystal or to interactions with ozone formed in the electrostatic precipitator.

The device has proved useful for surveys of buildings and homes. It is more reliable as a portable monitor that, after stabilising, is capable of fairly reliable measurements above $50 \mu\text{g}/\text{m}^3$. There is no way to calibrate the instrument. Absolute filters can be used to check zero. Intercomparison with filter samples is the only practical way of determining reliability.

Nephelometers The principle of light scattering by particles has been incorporated into several instruments. A nephelometer is used for fixed location monitoring of particle light scattering. The optimal response range is for particles 0.1 to $1 \mu\text{m}$. Because this is the size range for many hygroscopic particles (i.e., sulfates), the instrument can be equipped with a pre-heater to keep relative humidities below 60 percent. In this configuration, particle light scattering has correlations with fine particle sulfate and mass in excess of 0.85. These devices are very useful in providing a continuous record of fine particle concentrations.

The nephelometer has been miniaturised to a size that can be hand-held. The Hand Aerosol Monitor is very useful for industrial surveys and for determining concentrations in homes and offices where the principal source of small particles is tobacco smoke. The device has not been thoroughly evaluated in the concentration ranges of interest, 10 to $1000 \mu\text{g}/\text{m}^3$, or for a heterogeneous mixture of particles. The device can be modified to accommodate a particle filter and pump. Thus, a direct comparison can be made. Otherwise, only the electronic responses to zero and attenuating light filters are available for testing the instrument's performance.

A light scattering device called the MINIRAM has been developed, originally for the U.S. National Institute of Occupational Health and Safety, as a small personal monitor to be worn on the belt of a worker. A light-emitting diode illuminates a small volume of air in a shielded, but open-ended, chamber. Particles passing through this volume scatter the light back to a sensor. The amount of light scattered is proportional to the number of particles. Assumptions about size, density and index of refraction can be inferred. The advantages of this device are its lack of moving parts (no pump or filters). It has a rapid response and has been shown to be reliable in the higher mass loadings of mines and industry. The electronic circuitry provides variable averaging times that can be stored and recalled to an LCD. The disadvantages for personal monitoring are the fact that ambient light at a lower concentration can cause false readings. It has not been

thoroughly evaluated for particles and mass loadings that are more typical of non-industrial settings (10 to 1000 $\mu\text{g}/\text{m}^3$).

5.1.1.3 Filter Media

Most personal sampling equipment uses low flow filtration and measures the mass of particles collected. The advantage of this approach is that a collected mass of particles can then be subsequently analysed for composition. Filter medium is an important consideration if subsequent chemical, elemental, morphological, or acidity analysis is planned for the collected particles. Beyond the issue of filter blank and uniformity of deposition are the concerns for stability and preservation of the sample collected. Reactive particles can interact on the filter with other species, with gases in the atmosphere, or can volatilise during and after collection. The choice of filter media depends on the number and nature of the chemical species to be analysed and on the analytical method and type of sampler to be used. For aerosol sampling, the filter medium selected should meet the following criteria:

- (1) collection efficiencies greater than 90 percent for all particle sizes;
- (2) able to withstand the sampling, transport and analysis processes;
- (3) low resistance to different processes of extraction so that the collected particulate matter is easily obtained; and
- (4) low blank concentrations.

Another important criterion is whether the filter and the collected particulate matter react with acidic gases (SO_2 , NO_2 , CO_2) to form non-volatile species. This reaction can create artifacts which cause uncertainties in the estimates for the sulfate, nitrate, and carbon concentrations. Different filters have different properties in their composition, density, pH, and efficiency which can alter sampling performances. More detailed discussion of this topic and the use of pre-collection to remove reactive gases are presented by Stevens *et al.* (1984).

5.1.2 ANALYSIS OF THE COLLECTED ATMOSPHERIC AEROSOLS

5.1.2.1 Mass Analysis

Before any analysis can be performed, the total collected aerosol mass must be measured. Gravimetric procedures are commonly used because of their low cost and expediency; and by convention, the air filters are weighed under controlled humidity before and after particle collection. Aerosol mass can also be measured by β -gauge, that is, by placing the filter and particle deposit between a radioactive β -emitting source and a detector, and observing the reduction of the count rate (O'Connor and Jaklevic, 1981; Courtney *et*

al., 1982). Results obtained by these two methods have been very similar using Teflon filters (Courtney *et al.*, 1982). However, measurements of aerosol mass collected on quartz filters have been found to be inaccurate, because of the extreme fragility of quartz and of the difficulty in obtaining weight with a micro-balance (Davis *et al.*, 1984).

5.1.2.2 Elemental Analysis

Valuable information concerning sources of trace elements may be obtained by studying the distribution of elemental concentrations over the range of particle size. Furthermore, there is often interest in collecting samples over short periods of time. Since sampling devices for short-term sampling and for particle size selection gather only small amounts of suspended particulate matter, a high degree of sensitivity is required for a suitable elemental analysis. Thus, the choice of the analytical technique(s) is crucial to the study of aerosols. The principal criteria to be taken into account in designing an analytical procedure are:

(1) Expected ranges of concentration of the different elements at the sampling site: since urban, volcanic, industrial, rural, and isolated regions present different levels of aerosol concentrations, the detection limits of the chosen analytical method must correspond to typical ambient levels of the aerosols.

(2) The expected number and nature of the sources that could affect the concentrations of various aerosols at sampling sites: some key or tracer elements should be included in the analysis to confirm the contribution of different sources. Since alternative analytical techniques identify different groups of elements, it is often necessary to combine two or three methods to detect a larger number of tracer elements.

(3) The number of samples to be analysed: if a large number of aerosol samples are to be analysed, a method that does not require considerable sample handling and interpretation is recommended.

(4) The choice of procedures: this is limited to those analytical techniques that are available.

The most commonly used techniques for determining the elemental composition of ambient particles are listed and discussed below.

5.1.2.3 Energy Dispersive X-Ray Fluorescence Analysis (XRF)

This XRF method has been widely used for nondestructive elemental analysis of the ambient aerosol (Dzubay and Stevens, 1975). A secondary-target X-ray tube is used for the excitation of the sample, and the type of tube depends on the element to be analysed (Stevens *et al.*, 1978). Fluorescent X-rays from the sample are detected using a lithium-silicon detector. The spectrum obtained is automatically analysed at the end of the accumulation

period by a microcomputer system which uses a spectrum-stripping program and the stored spectra of the elements to be analysed.

Elements lighter than Al are relatively difficult to detect, because of their low fluorescence and especially because of the strong absorption of the fluorescent X-rays by the filter matter (and also of the particles themselves) which renders measurement of these light elements highly unreliable. Another potential problem is the interference from heavy element *L* or *M* X-rays; for example, the *K* lines of sulfur suffer interference from one of the *M* lines of lead. In this case, the uncertainty in the result for sulfur is estimated to be about 5 percent of the lead concentration. The complete description of the calibration of the XRF system is provided by Stevens *et al.* (1978). XRF is a fast and inexpensive technique; however, it cannot be used for the analysis of elements lighter than Al, nor routinely to observe some trace elements important for atmospheric pollution such as Se, As, Sb, Cd, and Sn.

5.1.2.4 Proton Induced X-Ray Emission Analysis (PIXE)

X-ray emission induced by charged particles offers an attractive alternative to the tube excited technique (XRF). Proton induced X-ray emission (PIXE) can be used for routine quantitative analysis of 10 to 15 elements simultaneously in atmospheric aerosol samples (Kaufman *et al.*, 1977).

This technique is a non-destructive, multi-elemental procedure in which protons excite the atoms of a sample; the characteristic emitted X-rays are used to identify and quantify the amount of each element. The analysis is carried out by 5 MeV proton irradiation in a Van der Graaf accelerator, and measurement of the characteristic X-rays is by Si-Li detector and X-ray spectrum resolution by small computer.

Although in principle XRF and PIXE are used to analyse the same group of elements, PIXE is capable of measuring smaller quantities of particulate matter. In addition, PIXE allows the analysis of more than 250 samples per 24-hour accelerator day, providing 5000 or more elemental determinations. However, compared with XRF, PIXE is less widely used in aerosol studies because of its cost. Winchester *et al.* (1979) and Lannefors *et al.* (1983) provide examples of studies using PIXE for aerosol analysis.

5.1.2.5 Instrumental Neutron Activation Analysis (INAA)

Although each of the previous methods provide a basis for the elemental analysis of an atmospheric aerosol, at least some samples should be analysed using a different technique to extend the number of elements observed. A particularly useful combination is XRF followed by INAA.

The steps followed in this analysis have been described by Zoller and Gordon (1970). Each filter is folded and heat-sealed in a polyethylene bag,

sealed in polyvials along with monitors containing known amounts of the elements to be measured, and placed in high-density polyethylene irradiation containers. These containers are irradiated with neutrons for up to 4 hours, depending on the species to be measured. The spectra of X-rays emitted by the samples and monitors are taken periodically after irradiations, using lithium-drifted germanium (Ge-Li) detectors. Areas under the peaks of prominent lines of the species of interest are obtained by a computer-fitting procedure that removes general Compton background from beneath the peaks. The expected analytical uncertainties are about ± 5 percent for Na, Zn, K, Cl, Br, I, Sc, Cr, Mn, Fe, Co, As, Se, Sb, La and Ce; errors are ± 5 to 10 percent for Al, V, Pb, Ca, Ba, Ti, Ni, Cd, and Th; about ± 20 percent for Mg; and ± 35 percent for Cu (Kowalczyk *et al.*, 1978). Concentrations of sulfur, Pb (a tracer of automotive pollution), Cd (a toxic element), and Ni (a tracer of oil combustion and other industrial activities) cannot be determined by INAA. In addition, INAA requires considerably more sample handling and interpretation of results than XRF and PIXE, and is considerably more costly per sample.

Complete INAA requires at least two irradiations of the samples for a few minutes to observe species with half-lives < 15 hours, and for several hours to observe species with longer half-lives > 15 hours. To economise, INAA is used as a complementary procedure after XRF analysis to determine elements with short half-lives such as Na, Mg, Mn, and V. However, some important elements that are observed in long irradiations (Cr, Co, As, Se, and Sb) are sacrificed in this approach. The analysis of As and Se can be considered necessary, since these elements are tracers of coal combustion.

5.1.2.6 Atomic Absorption Spectrometry Analysis

Atomic absorption spectrophotometric analysis (AASA) is usually used to complement XRF analysis. The most important advantages of this method are:

- (1) High sensitivity for Na. This element, which is the tracer of marine aerosol, cannot be analysed by XRF or PIXE.
- (2) Analysis of important trace elements such as Cu, Ni, Cr, Pb, Zn, Co, Cd, and Mg, where analysis by XRF, INAA, or PIXE is either not very satisfactory or impossible.

If atomic absorption analysis is used alone for analysis of ambient particles, elements other than those named above can be analysed, such as Ca, Mn, Fe, Al, K, Zn, V, and As. The inability to analyse sulfur with this technique is its major drawback. The length of preparation and careful handling needed before analysis are other disadvantages. The preparation consists of acid mineralisation of the filters (Nucleopore) before analysis.

5.1.2.7 Acidity Measurements

The measurement of acid aerosols requires a particular sampling and filter conservation procedure to eliminate any neutralisation of the particle acidity. Samples are collected on 47-mm Teflon membrane filters mounted on a Teflon filter holder behind a diffusion denuder for ammonia (Ferek *et al.*, 1983). Immediately after sampling, the filters must be removed from the denuder by using Teflon tweezers and quickly placed in clean polyethylene bags/boxes for later analysis.

In the laboratory, the filters are placed into the extraction solution KCl/HClO₄; the vessel is capped, and placed in an ultrasonic bath for 20 minutes to facilitate transfer of soluble species from the filter (Stevens *et al.*, 1984). The above procedure is used for the acidity analysis as well as for the measurement of ionic species such as SO₄²⁻, NO₃⁻, and NH₄⁺. For fine and coarse particle fractions, Stevens *et al.* (1978) found the extraction efficiencies for sulfur to be 98±1 percent and 95±2 percent, respectively.

Titration with 0.04 N NaOH are carried out by using a Radiometer Copenhagen ABU-12 microburet, standard pH electrodes, and a Beckman Model 76 pH meter (Ferek *et al.*, 1983). The titration curve is recorded on a strip chart recorder, and later digitised for a computer program to generate Gran plots from which strong and weak acid components are resolved.

5.1.2.8 Analysis of Soluble Ionic Species

Two-ml aliquots of the above extracted solution can be analysed by ion chromatography (IC) using anion and cation columns. Under favourable conditions, many ionic species can be determined by IC (Mulik and Sawicki, 1979) including NO₂⁻, NO₃⁻, SO₃²⁻, SO₄²⁻, Br⁻, Cl⁻, F⁻, and PO₄³⁻; but the validity of NO₂⁻ and SO₃²⁻ is questionable because of possible instability of the oxidation states. The filters recommended here (Teflon), however, should have negligible artifacts for SO₄²⁻. A SO₄²⁻ artifact test for the different types of filters (Teflon, Nucleopore, Millipore, and Whatman) showed that, for Teflon filters and to a lesser extent for Nucleopore filters, the oxidation of SO₂ to SO₄²⁻ on the filter surface was negligible. In contrast, for the other types of filters, non-negligible quantities of SO₄²⁻ were derived by the SO₂ oxidation onto the filter surface (Appel *et al.*, 1980).

In principle, a number of cationic species such as NH₄⁺, K⁺, and Na⁺ are detectable by IC using a different column (Mulik and Sawicki, 1979), but this is not usually done except for NH₄⁺. This cationic species may also be observed by a colorimetric procedure (Harwood and Huyser, 1970).

5.1.2.9 Carbon Analysis

Carbon analysis is based on the oxidation of organic and elemental carbon to CO₂ followed by analysis of the CO₂ evolved. The separation of organic

and elemental carbon is achieved because elemental carbon is non-volatile even at high temperatures, so that organic carbon is oxidised first to CO₂. Quartz is used as the collection medium because it has a low carbon content and is chemically inert.

Presently, the analysis of carbon in aerosol samples is carried out by a modified Dohrman DC-50 organic analyser. This technique measures organic carbon by pyrolysing the carbonaceous portion of the sample to CO₂ at 650°F in a helium atmosphere and reduces the products to methane over a bed of nickel catalyst in an atmosphere of hydrogen.

The methane produced is then measured by a flame ionisation detector. After the analysis of the organic carbon, elemental carbon is determined by combustion of the carbonaceous materials remaining on the quartz filter at 850°F in a 2 percent oxygen, 98 percent helium atmosphere. Total carbon is equal to the sum of the organic and elemental carbon.

Carbon can be converted to CO₂ and then, using a low-background β-proportional counter, the ratio of ¹⁴C to total carbon measured. This ratio indicates the fraction of particulate carbon from fossil fuel versus that from "modern" carbon sources such as the combustion of vegetation or recently living wood. Fossil fuels contain no ¹⁴C, while modern sources present a ¹⁴C-total carbon ratio approximately equal to that of the atmosphere. ¹⁴C can also be measured by using a high sensitivity nuclear particle accelerator method. Samples containing <5 μg carbon (versus milligramme quantities with counters) can be used, thus eliminating the need for high-volume collection.

Organic Compounds The study of organic compounds is necessary for identifying the sources that release mostly carbonaceous particles which provide little or no signal via elemental analysis. Examples include engines burning diesel fuel or unleaded gasoline and home heating. Because of their carcinogenic nature, PAHs are the most studied organics in the atmospheric aerosol. Their determination is a difficult chemical problem, since they are highly reactive in the atmosphere as well as on the filter surface. The analysis is carried out by high performance liquid chromatography with mass spectrometer. The first technique separates the different PAHs, while the second determines their mass. Table 5.1 illustrates 16 PAHs identified in the Paris aerosol by Nikolaou *et al.* (1984), findings confirmed in other locations worldwide.

PAHs may be good tracers of some pollution sources; for example, pyrene, fluoranthene, and phenanthrene are reported to be related to emissions from engines burning diesel fuel, and coronene to gasoline.

Although other classes of organics, especially the long-chain aliphatic compounds, contribute much greater masses of material, few studies refer to these compounds.

Crystals During the past few years, studies have used X-ray diffraction (XRD) patterns for the analysis of various crystalline materials to identify

Table 5.1. 16 PAHs in the Paris aerosol

Anthracene	Benzo(α)anthracene
Chrysene	Benzo(<i>a</i>)pyrene
Coronene	Benzo(<i>e</i>)pyrene
Fluorene	Benzo(<i>b</i>)fluoranthene
Indenopyrene	Benzo(<i>k</i>)fluoranthene
Perylene	Dibenzo(<i>ah</i>)anthracene
Phenanthrene	Benzo(<i>ghi</i>)perylene
Fluoranthene	Pyrene

Source: Nikolaou *et al.* (1984)

particle sources. The greatest bar to applying this method to aerosols is the low mass coverage of the particles on the collecting filters. However, a number of remarkable studies reporting identification of atmospheric aerosol from filters have been completed by Brosset and Ferm (1978). Common to all these XRD studies was that the analyses were carried out separately for each particle size group.

In the Biggins and Harrison study, the particulate matter was collected by an Anderson 2000 cascade impactor modified so that all particulate material below 2.1 μm would be collected on a single stage. The sampling period was one week to collect sufficient material for the analysis. The collection medium which was a glass fibre filter paper was ultrasonically stripped into aromatic-free n-hexane for 30 minutes and then filtered onto a Millipore cellulose ester filter. The samples were analysed by XRD with a Philips XDC700 Guiner camera. The resultant photogrammes were identified by matching of both “*d*” spacings and intensities. The identification of some of the unknown photogrammes was facilitated by the use of standard films obtained from powder samples of ammonium lead halides. A similar study based on the analysis of Teflon filters by XRF for elemental composition and by an XRD procedure with the emphasis on the quartz content was carried out by Davis *et al.* (1984).

Individual Particle Analysis To classify individual particles according to their shapes, sizes, and XRF elemental analyses, Davis *et al.* (1984) used computer-assisted scanning electron microscopy with automated image analysis and X-ray energy spectroscopy (SAX). Each particle was classified according to source type by comparing the measured parameters against those of 25 particle classes in a library. Most of the classes were developed from previous studies.

The analyses of the fine particles were less successful, because of the much higher particle number and density of particles such as secondary sulfates which coated most of the area and made it difficult to observe other particle types. Although the method is still experimental, it holds great

promise because of its high resolution, that is, its ability to sort particles into many classes.

5.1.3 CONCLUSIONS

To date, information on the distributions of personal exposures is limited. The limitations include:

(1) Those few pollutants that have been studied, for the most part, are the ones for which monitors are available: CO, NO₂, particles, Pb, and volatile organics.

(2) Time resolutions of most personal exposure studies are typically of the order of days or perhaps hours. There is little information available on the short-term peak exposures to which individuals are exposed.

(3) Only a small segment of society has actually been studied. Study populations have characteristically been white, urban or suburban, middle-class adults. Those that are employed usually perform non-manual (white-collar) labour. Few children or infants have been studied.

(4) The locations that have been monitored have primarily been homes and some office buildings. Even within these structures, there is no good resolution of concentrations, as they vary temporally and spatially. There is little information on actual in-vehicle exposures during transportation or on occupationally related exposures.

(5) There have been relatively few advances in personal monitoring instruments. Most instruments are passive monitors that integrate exposures over hours to days. Since there is no regulatory requirement to stimulate commercial development, personal monitoring equipment suitable for personal exposure studies of the general public are not readily available. The devices available (with few exceptions) are developed by researchers for specific studies. This, in turn, leads to problems of comparing results from exposures to the same pollutant but using instruments that have not been validated or compared.

5.1.4 RECOMMENDATIONS

(1) Development of Test Protocols. Investigations of indoor air quality and personal exposures have mostly used instrumentation that was originally developed for industrial hygiene applications. For a number of reasons this may not be appropriate. For example, the concentrations of indoor contaminants may have ranges and temporal/spatial variation dissimilar from industrial workplaces. Most often, concentrations in homes and offices are lower than those for which the equipment was originally designed. To accommodate this, the equipment may be required to operate at higher flow rates or for longer durations. At these low concentrations, the effects of interfering gases, fluctuating temperatures, and changes in humidity

encountered in vehicles, residences, and other types of structures have not been investigated adequately. Therefore, test protocols should be developed for evaluating equipment to be used as indoor-personal monitors. These devices should be evaluated over the range of anticipated concentrations addressing the possible effects of temperature, humidity, and interfering compounds. This work is urgently needed for integrating and continuous monitors for NO₂, CO, and formaldehyde. Interfering compounds that should be considered include tobacco smoke, organic and nitrogenated compounds, ammonia and other volatile compounds present in cleaning agents, solvents found in paints and varnishes, and aerosol-spray propellants.

(2) Portable, Continuous NO₂ Monitors. Available integrating samplers for NO₂ (e.g., Palmes tube, filter badge) are inadequate to fully understand personal exposures to NO₂. Sources of NO₂ such as combustion appliances and vehicles are usually intermittent, providing short, intense exposures. The exposures to and subsequent functional or irritant effects of elevated peak concentrations of NO₂ are currently unresolved. To measure the former, lightweight personal or portable NO₂ monitoring equipment is needed. The instruments should be capable of responding to concentrations over a range of 5 ppb to 1 ppm with a 90 percent response time of 5 seconds. The instrument should be insensitive to CO, NO, CO₂, ammonia, and the variety of organic compounds commonly found indoors. The effects of variations in temperatures (0 to 30°C) and humidity (10 to 90 percent) must not compromise accuracy in excess of ±10 percent. The device should be compatible with an electronic data acquisition system.

(3) Portable Continuous CO Monitors. Portable continuous monitoring equipment exists for CO. New personal analysers operating by diffusion (rather than active pumping) and electrochemical sensors/detectors must be evaluated. Concerns for interferences, response characteristics, and low velocities across the sensors need to be evaluated.

(4) Passive CO Survey Sampler. An inexpensive passive CO sampler is needed for large-scale surveys of homes, offices, garages, arenas, and other indoor sites. As a design objective the sampler should have a sensitivity of 25 to 50 ppm-hours and be accurate to within ±10 percent. This is an important challenge for passive diffusion monitors; however, such sensitivity would permit in-vehicle surveys over typical commute times. A sensitivity of 100 ppm-hour would be adequate for surveying buildings for faulty heating/flue systems over a ten-hour nighttime heating cycle, particularly as nighttime is anticipated to have maximum exposures. There is a great need for inexpensive passive monitors for measuring indoor exposures in developing countries. CO is a particular concern for countries where charcoal is used extensively for cooking and heating.

(5) Particulate Sampler. Respirable particulate matter can be measured with several devices currently available. A 10-mm nylon cyclone preseparator operating at 1.7 l/min is commonly used in industrial environments to

provide size-fractionation prior to filtration. Sampling times of 12 to 24 hours or more are needed to obtain sufficient mass to provide reliable measurements of the much lower concentrations found in non-industrial environments. A size selective sampler is needed for collecting inhalable particles ($d < 10 \mu\text{m}$) in a variety of environments over sampling times of 1 to 4 hours. While direct-reading instruments exist that permit 2 to 5 minute integrated data, no physical sample is collected. A particulate sampler should be evaluated (for cut-off size, efficiency, and air velocity effects) with reference to other conventional samplers. Ideally, samplers should be suitable for both fixed locations and personal monitoring. The National Bureau of Standards stack-filter sampler may be appropriate after independent testing. However, the use of tandem stacked filters to achieve size separation requires further evaluation under both laboratory and field conditions.

(6) Tobacco Smoke. Tobacco-specific nitrosamines have been studied by several groups (Hecht *et al.*, 1978; Stehlik *et al.*, 1982). American cigarettes contain 300 to 500 ng of *N*-nitrosodimethylamine and 100 to 300 ng of *N*-nitrosopyrrolidine. Air samples are analysed by extraction and clean-up, followed by gas/liquid chromatography with a thermal energy analyser detector which detects the nitrosamines by pyrolysis, cleaving the N-N bonds and measuring the resulting nitric oxide by chemiluminescence (Jenkins and Guerin, 1984). Tobacco smoke has been demonstrated to be an irritant and is possibly a contributor to respiratory illness. To date, epidemiological studies have not incorporated direct exposure measurements of tobacco smoke. Stable indicators of tobacco-smoke components of indoor suspended particulate matter are needed. *N*-nitrosodimethylamine and *N*-nitrosopyrrolidine appear to be promising indoor tracers. However, since nicotine can exist in both particulate and vapour phases at room temperature, care must be taken to quantify each component.

(7) Organic Compound Determination. Volatile and nonvolatile organic compounds are ubiquitous indoors. Because of the numerous consumer products containing organic chemicals, indoor concentrations are usually higher than outdoors. Within-home and among-home variability of two orders of magnitude have been reported. Several sampling media are currently available, including Tenax, polyurethane foam, molecular sieves, and charcoal. For each of these, sample recovery efficiency, breakthrough volumes, intersample variability, sample stability with temperature and humidity, and artifact formations need to be determined.

(8) Passive Formaldehyde Sampler. An inexpensive passive formaldehyde monitor is needed. This device should be capable of detecting 0.02 ppm over a 1-4 hour exposure period. Such a device would find widespread application in homes and offices.

5.1.5 References

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