# Ground-based Aerosol Measurements

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This article summarizes the collection methods and analytical approaches used for the analysis of time-integrated samples (i.e. samples collected over a period of time and returned to the laboratory for analysis) and continuous methods (i.e. in-field measurements) for the measurement of airborne particles. The collection method needs to be considered an integral part of the quantification process since how samples are collected can impact whether the results represent what is in the air or have been modified. Thus, the primary focus of this article is on measurement process, collection and analysis, with only a short description of the motivation for these measurements.

## **1 INTRODUCTION**

Atmospheric particulate matter (PM) is a complex chemical mixture of liquid and solid particles suspended in air.<sup>(1)</sup> Measurements of this complex mixture form the basis of our knowledge regarding particle formation, source-receptor relationships, data to test and verify complex air quality models, and how PM impacts human health, visibility, global warming, and ecological systems.<sup>(2)</sup>

Historically, PM samples have been collected on filters or other substrates with subsequent chemical analysis in the laboratory and this is still the major approach for routine networks<sup>(3,4)</sup> as well as in research studies. In this approach, air, at a specified flow rate and time period, is typically drawn through an inlet, usually a size selective inlet, and then drawn through filters, also at a specified flow rate.<sup>(5)</sup> Measurements of PM composition in routine networks in the United States typically include sulfate, nitrate, ammonium, organic carbon (OC), elemental carbon (EC), and trace elements. These components are routinely determined in the laboratory by ion chromatograph (IC; ions), thermal-optical analysis (TOA; OC and EC). X-ray fluorescence (XRF: trace elements), and inductively coupled plasma-mass spectrometry (ICP-MS; trace elements).<sup>(4)</sup> After applying correction factors for other species associated with trace elements, converting OC to organic material (OM), and applying stoichiometry for compounds such as ammonium nitrate and ammonium sulfate, the measured mass is typically accounted for within  $\pm 10-20\%$  as illustrated in Figure 1. Major uncertainties in this comparison include negative artifacts associated with loss of semivolatile species with the Federal Reference Method (FRM) mass measurement, not accounting for particle associated water either with the FRM or measured components, and conversion of OC to OM as well as trace elements to compounds. These routinely measured compounds have been the bases for source apportionment modeling.<sup>(7,8)</sup> Research studies also have determined the concentration of numerous individual organic species and trace elements,<sup>(9)</sup> the latter not determined by XRF.<sup>(8,10)</sup> Many of these individual species are considered to be molecular markers for specific sources or source categories, e.g. levoglucosan for biomass burning; cholesterol for meat cooking; vanadium and nickel for oil combustion.<sup>(7,8)</sup>

Over the last two decades, a range of semicontinuous and continuous methods (herein referred to as continuous with a time resolution often at or less than 1 h) have been developed that measure bulk chemical composition

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**Figure 1** Monthly average  $PM_{2.5}$  mass and composition in Pittsburgh, PA. The 'missing' component is the difference between the FRM (Federal Reference Method) measurement and the sum of the chemical components. The FRM mass is greater than the sum of the chemical components for July–January, and less than the sum of the chemical components in February and March. The error bars represent uncertainty in the mass balance on a monthly average basis. OM is defined as  $1.8 \times OC$ . (Reproduced with permission from Ref. 6 © Elsevier, 2004.)

in various size ranges.<sup>(11,12)</sup> In these methods, the collection and analysis steps both occur in the field with the ability to provide data in real time as opposed to filterbased methods where the sample is brought back to the laboratory for analysis and may require significant time (30 days) for results. Clear advantages of having high time resolution, continuous data collection, and much lower cost for sampling media, shipping, and laboratory processing is weighted by the higher capital costs of realtime measurement instruments and increased requirement of field maintenance and calibration. Single particle mass spectrometers also have been implemented in the field to obtain the chemistry of single particles across a large particle size range (nanoparticles to  $10\,\mu$ m). This approach provides data at high time resolution.

Examples of continuous methods are provided within but their use in routine monitoring networks has not materialized. Several continuous methods stand out and are used in research studies. These include, for example, the particle-into-liquid sampler (PILS<sup>(13,14)</sup>) and the ambient ion monitor (AIM<sup>(15)</sup>) for ions, select elements and water soluble OC; in situ XRF<sup>(16)</sup> and semicontinuous elements in aerosol sampler-III (SEAS-III<sup>(17)</sup>) for trace elements; TOA for OC and EC;<sup>(4)</sup> absorption methods for black carbon (BC<sup>(11)</sup>); thermal aerosol desorption (TAD) gas chromatography/mass spectrometry (MS)<sup>(18)</sup> for organic compounds; and aerosol and particle mass spectrometers,<sup>(12,19)</sup> the former providing bulk mass concentrations of non-refractory species simultaneously between about 0.05 and  $1 \mu m$ , the latter the chemical composition of single particles across a large size range.

In the last 5 years, there has been a significant paradigm shift in the approach to air pollution monitoring, moving away from large, stationary, expensive monitors to miniature monitors referred to as air pollution sensors.<sup>(20,21)</sup> These monitors are not only small, but they are portable, of relatively low cost and low power, and are becoming ubiquitous in the environment partially driven by the emergence of Citizen Science.<sup>(22)</sup> In the United States, sensors are being evaluated by the EPA (United States Environmental Protection Agency) and the South Coast Air Quality Management District and readers are referred to their publications for more information on this topic.<sup>(23,24)</sup>

This article summarizes collection methods and analytical approaches used for the analysis of time-integrated samples (i.e. samples collected over a period of time and returned to the laboratory for analysis) and continuous methods (i.e. in-field measurements) for the measurement of airborne particles rather than the atmospheric science behind the measurements. The collection method needs to be considered as an integral part of the quantification process since how samples are collected, handled, transported, and extracted can impact whether the results accurately represent what is in the air or have been modified. Thus, the primary focus of this article is on measurement process, collection, and analysis, with only a short description of the motivation for these measurements.

## 2 COLLECTION AND ANALYSIS METHODS

#### 2.1 Particle Mass

While the focus of this article is the chemical analysis methods used to determine the chemical composition of particle mass in air, mass is a fundamental measurement and is currently the parameter regulated by the EPA because of the relationship of PM mass to adverse health effects, visibility impairment, and global warming.<sup>(2,25)</sup> The chemical components of PM mass are likely to have a causal role in these important issues and this is why it is essential to obtain measurements that represent what is in the air, for which, the analytical chemical analysis methods described later in this article are critical. However, PM mass is a challenging parameter to measure since it is composed of thousands of species, a significant fraction of which are semivolatile. Depending on the environmental conditions and sampling method, the measured particle mass may not represent PM mass concentrations as present in the atmosphere. In this section, methods to measure PM mass in relevant size ranges are described.

#### 2.1.1 Federal Reference Methods

In 2012, the EPA established new National Ambient Air Quality Standards for PM in the size range below 2.5 µm aerodynamic diameter (AD) and below 10 µm AD.<sup>(26)</sup> FRM and Federal Equivalent Methods (FEM) are detailed as part of this standard.<sup>(27)</sup> In general, PM mass is obtained in the field employing FRM samplers operating at a flow rate of 16.7 L min<sup>-1</sup> over a sampling period of 24 h.<sup>(28)</sup> FRM samplers use Teflon (47 mm polytetrafluoroethylene, PTFE) filters that are equilibrated and weighed before and after sampling at a specified temperature  $(20-23\pm2^{\circ}C)$  and relative humidity  $(30-40\pm5\%)$  for not less than 24 h. Filters are shipped to and from the field under reduced temperature (e.g. <4°C for Chemical Speciation Network or CSN). PM mass is obtained gravimetrically, using a balance by subtracting the initial mass (clean filter) from the final mass (sampled filter). Concentrations of PM in air, typically in microgram per cubic meter, are obtained by dividing the determined mass by the volume of air sampled. A number of samplers have been approved by the EPA as either FRM or FEM.<sup>(28)</sup> FRM methods are all manual methods where the filter needs to be changed in the field whereas FEM methods are mostly continuous (Section 2.1.2). For PM<sub>2.5</sub> (particulate matter with an aerodynamic diameter greater than  $2.5 \,\mu\text{m}$ ), 18 FRM samplers and 16 continuous or FEM samplers have been identified.<sup>(28)</sup> While National Ambient Air Ouality Standards have not been developed for coarse particles  $(PM_{10} - PM_{2.5})$  or particles in the size range between 2.5 and 10 µm AD, 11 FRM and FEM samplers have been designated.<sup>(28)</sup> These FRM and FEM samplers determine coarse mass either by difference  $(PM_{10} - PM_{2.5})$  or by the use of a dichotomous sampler that employs a virtual impactor<sup>(29)</sup> that separates particles less than 2.5 µm AD from particles above 2.5 µm AD. A  $PM_{10}$  (particulate matter with an aerodynamic diameter less than 10 µm) inlet removes particles greater than 10 µm AD.<sup>(28)</sup> There are also 31 FRM and FEM PM10 samplers.<sup>(28)</sup>

#### 2.1.2 Continuous and Semi-continuous Methods

Rather than transport filters between the laboratory and field performing chemical analysis in the laboratory, continuous methods bring the analytical method to the field. Continuous methods require little operator intervention and can provide near continuous data in real time. FEM methods when used for regulatory purposes report 24-h average data as required by the  $EPA^{(27)}$ ; however, when used for other purposes they can report data down to 1 min time resolution depending on the method.<sup>(11)</sup> FEM methods estimate PM mass using beta attenuation, the tapered oscillating micro balance (TEOM) with or without the filter dynamic measurement system (FDMS), light scatting, or a combination of beta attenuation and light scattering. The beta attenuation monitors (BAM) and TEOM/TEOM-FDMS directly measure the mass of particles collected on the filter, whereas light scattering is considered an indirect method. Continuous methods are often employed to measure PM mass in research studies. The FDMS accounts for the potential loss of semivolatile components of PM mass (i.e. water associated with particles, ammonium nitrate, and semivolatile organic compounds).<sup>(6)</sup> In addition to light scattering, particle size distribution data also has been used to estimate PM mass. However, this method and light scattering require additional information about the measured particles, such as shape, density, and/or composition to obtain accurate estimates of PM mass. Variations in temperature and relative humidity can impact the accuracy of these methods as well. Additional details of these methods can be found elsewhere.<sup>(11)</sup>

Ultrafine particles (UFPs), defined as particles with diameters less than 100 nm, are of significant concern with regard to their impact on human health.<sup>(25)</sup> A brief summary of the characteristics, health effects, and measurement methods are described.<sup>(11,25,30)</sup> UFPs have little mass, so inertial methods are typically not applicable. Typically, UFP mass is derived from size distributions data, such as that obtained from a scanning mobility particle sizer (SMPS), which measures mobility diameter based on the application of an electrical field to size the particles. Mobility diameter can be related to AD

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if the effective density, which can be estimated from the aerosol mass spectrometer measurements<sup>(12)</sup> is known. An SMPS, in conjunction with aerodynamic particle sizer (APS), can obtain a particle size distribution from a few nanometers up to  $10 \,\mu m.^{(11,30)}$ 

#### 2.2 Ionic Species

#### 2.2.1 Extraction Methods

Extraction of ionic species from collected PM is relatively straightforward as the species targeted are highly soluble in aqueous solutions and extraction only requires relatively mild agitation over short periods of time.<sup>(4)</sup> In applications where a hydrophobic PTFE filter is used to collect PM for subsequent laboratory analysis, a wetting agent (e.g.  $50 \,\mu$ L of ethanol<sup>(31)</sup>) can be used to ensure adequate contact between the aqueous solution and the filter media/collected sample.

Care must be taken during sampling to ensure that gaseous species do not interfere with the measurement of particulate ionic species. For most approaches, this is accomplished by using a tubular, annular, or honeycomb denuder upstream of the collection substrate to remove basic or acidic gaseous species before the sampled air passes through the filter. In a denuder, the high diffusivity of gases leads to migration and collection on the walls, while the high inertial momentum and low diffusivity of particles in air allows them to pass through.<sup>(4,5)</sup> To remove acidic gases the denuder is coated with a thin film of a basic compound, such as  $Na_3CO_3$  or MgO. To remove basic gases the denuder is coated with a thin layer of an acidic compound, such as phosphorus or citric acid. When sampling over extended periods, the sampling approach must also be designed to minimize or account for volatilization of ionic species from the vapor phase (e.g. ammonium nitrate), such as using a sorbent material downstream from the primary filter media.<sup>(32)</sup>

#### 2.2.2 Continuous Methods

Continuous methods to measure a range of cations and anions are available commercially and have been used in a number of research studies. These approaches typically include solubilization of the ionic species into solution for analysis in the aqueous phase followed by a variety of analysis methods that have been designed for use in the field.<sup>(11)</sup> Ion chromatography is the most widely used analytical method for continuously measuring ions in situ in PM. Using commercially available IC systems, a wide range of inorganic cations and organic and inorganic anions can be measured. The IC systems are similar to those widely employed in the laboratory and will not be discussed further here. However, several different approaches have been developed to incorporate the particles and ions into solution.

After removing gaseous interferences with gas denuders, the particle-into-liquid  $IC^{(13)}$  (PILS-IC) combines the particle-laden air stream with steam to grow particles through condensation as shown in Figure 2. With



Figure 2 Schematic of the particle-into-liquid sampler (PILS) taken from Orsini et al. Preceding denuder not shown. (Reproduced with permission from Ref. 13 © Elsevier, 2003.)

greater inertia through condensational growth, particles are impacted on a surface that is continuously washed and the wash is collected in a sample loop for analysis by IC. Time scales of less than 5 min have been achieved, quantifying, for example, four inorganic anions and four inorganic cations as well, acetate, formate, and oxalate with a time resolution of 15 min.<sup>(13)</sup>

The AIM system provides time-resolved direct measurement of anionic compounds contained in ambient fine PM using a size-selective inlet, a diffusion denuder to remove interfering acidic and basic gases, a supersaturated growth chamber to grow particles, and an inertial impaction collector.<sup>(33,34)</sup> Selective detection of nitrate and sulfate is performed by an automated IC system.

A wet rotating denuder is used to initially collect gas phase components in the Monitor for AeRosols and Gases in Air<sup>(35,36)</sup> (MARGA) system. Particles remaining in the airstream are grown via a steam jet and collected using a cyclone separator based on their increased inertia. The solution from the cyclone separator and the solution from the wet rotating denuder are separately analyzed by IC for particulate and gaseous species, respectively.

Finally, an alternative approach for the continuous measurement of ions uses thermal reduction with detection by gas analyzers (e.g. sulfate,<sup>(37)</sup> nitrate, and/or ammonium<sup>(38,39)</sup>). In this category, the sampled air is drawn through a denuder to remove interfering gases and then either heated in the presence of a catalyst while in the air stream or particles are grown by condensation, impacted on a surface in the presence of a catalyst and heated to generate gases. In all cases, the gases are detected using a gas analyzer (e.g. NO-ozone chemiluminescence monitor that detects NO/NO<sub>2</sub> for nitrate and ammonium; high-sensitivity pulsed fluorescence SO<sub>2</sub> analyzer for sulfate).

#### 2.3 Carbonaceous Components

Carbonaceous particles in the atmosphere contain a complex mixture of organic compounds as well as inorganic constituents that contain carbon. This mixture is often simply classified into three major components as OC, EC, and carbonate carbon (CC), although in reality the OC is composed of a very large number of individual species. The sum of these major components represents total carbon (TC), where the separation of particulate carbon into OC, EC, and CC is operationally defined based on the method of analysis.<sup>(11,40)</sup> In parallel to this compositional categorization, watersoluble organic carbon (WSOC) is a measure of the water soluble components of TC.<sup>(41)</sup> Measurement of these components is commonly done from samples collected on glass- or quartz-fiber filters with subsequent

analysis in the laboratory or with a continuous sampler in the field described later. BC is similar to EC but is measured by optical methods. BC is measured in the laboratory from samples collected on PTFE filters by absorption using a transmissometer. There are multiple in situ continuous analysis approaches.<sup>(10,40)</sup> Measurements of BC are more relevant to understanding visibility and the earth's radiation balance or global warming.

#### 2.3.1 Bulk Characterization

Direct measurement of the TC, as well as separation into OC and EC fractions, is done through instruments designed to heat collected particles in varying atmospheres and measure the evolved carbon. As temperature steps and gases used can vary and impact the results of this approach, the operational definition of OC and EC depends on method specifics.<sup>(11,42)</sup> As a result, TC is generally consistent  $(\pm 20\%)$  between measurement approaches, while different methods provide different quantification of OC versus EC ( $\pm 20-50\%$  for OC, up to 200% for EC). First, samples are initially heated in an inert atmosphere, usually He, with different temperature steps allowing OM to volatilize and be quantified as  $CO_2$  using a nondispersive infrared detector<sup>(43)</sup> or the  $CO_2$  is reduced to methane and detected using a flame ionization detector.<sup>(44)</sup> During this initial heating, some of the collected OC may pyrolyze or char to EC, which darkens the filter. This artifact of the analysis method is corrected on the basis of changes in the optical properties of the sample during analysis employing a measurement of either reflectance or transmittance of light from or through the sample.<sup>(45)</sup> After heating in an inert atmosphere, a small percentage of oxygen is added allowing graphitic material to be oxidized and measured as EC. The pyrolized OC, actually measured as EC, is added to the measured OC quantified during heating in the inert atmosphere.<sup>(45)</sup> The combination of thermal and optical approaches has resulted in methods following this principle being labeled TOA. As these methods only quantify the carbon contained in a PM sample, the OC fraction is multiplied by an inferred factor to account for the H, O, S, N, and other elements contained in the organic matter (OM). As the mass of other elements in the organic matter varies based on the characteristics of the OM, values from 1.2 to 2.2 have been used as the multiplication factor to convert OC into OM.<sup>(46)</sup> While measurement of TC, OC, and EC is fundamental to complete the bulk characterization of the constituents contributing to the particle mass,<sup>(10)</sup> the relative contribution between OC and EC has also been used to monitor secondary organic aerosol formation.<sup>(47)</sup> More recently, OC and EC have been estimated by analyzing functional groups

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Separately, CC can be quantified through acidification of the sample and comparison to an untreated sample with the difference in measured TC between untreated and acidified sample representing CC.<sup>(43)</sup> If CC is present in high enough concentration, a carbonate peak can be resolved in TOA during the highest temperature step in the inert atmosphere, allowing a single measurement to resolve TC into OC, EC, and CC.<sup>(50)</sup> Entrainment of crustal material is the primary source of CC to the atmosphere.<sup>(51)</sup>

While EC is operationally defined by the TOA method used, a related measurement, BC, is also widely reported. Reviews of the range of methods to measure BC and EC as well as their limitations and uncertainties are available.<sup>(11)</sup> Concentrations of BC (associated with diesel exhaust and also referred to as soot) and brown carbon (associated with wild fires and residential wood burning) are obtained through measurement of light absorption, as opposed to chemical structure, and subsequently converted to an atmospheric concentration by applying Beer's law and an empirically defined absorption coefficient.<sup>(52)</sup> The absorption coefficient ranges from about 7.5 to  $15 \text{ m}^2 \text{ g}^{-1}$  due to the age of the aerosol, particle size, and composition among other parameters.<sup>(52)</sup> Measurement of BC, as opposed to EC, is typically motivated to quantify visibility and climate impacts of particles<sup>(52,53)</sup> as BC is a direct measure of atmospheric absorption from which the absorption coefficient can be determined. Measurement of BC or EC is also motivated by the impact of these components on the health effects of exposure to particles.<sup>(54)</sup> Beyond the visible spectrum, measurements of light absorbing carbon in the ultraviolet spectrum have been used to track ultraviolet absorbing particulate matter (UVPM), which can track emissions from sources such as wildfires.<sup>(55)</sup> Information about approaches that measure BC and related compounds are discussed under Section 2.3.4.

WSOC, often an important component of OC,<sup>(56)</sup> is commonly measured by extracting collected particles in deionized water and then through direct analysis of carbon using a total organic carbon (TOC) instrument or by spiking the extract onto a blank filter for analysis by TOA.<sup>(57)</sup> Continuous methods also have been developed for WSOC and are briefly described later.

#### 2.3.2 Bulk Chemical Properties

To investigate the structural properties of carbonaceous particles suspended in the atmosphere, a variety of spectroscopic approaches such as ultraviolet/visible<sup>(58)</sup> (UV/VIS),  $FTIR^{(59)}$ , and nuclear magnetic resonance<sup>(60)</sup> (NMR) have been applied to aerosol samples. These

approaches have been developed to characterize functional groups (e.g. aromatic, alkane, or alkene; carboxylic acids; esters; organonitrates; amines) present in particles. These techniques have been used for various atmospheric applications such as aerosol characterization,<sup>(61)</sup> tracking the atmospheric oxidation of OM by monitoring the generation and loss of specific functional groups,<sup>(62,63)</sup> determining the contribution of macromolecules to particle burdens,<sup>(64)</sup> or estimating the correlation between OC and OM.<sup>(48,65)</sup> While these approaches have easy sample preparation, there is lack of quantification, although recent work has used FTIR quantitatively for several functional groups.<sup>(66)</sup>

#### 2.3.3 Organic Speciation

Measurement of individual organic compounds present in the condensed phase is motivated by understanding the original source of the particles emitted through source attribution,<sup>(7,8)</sup> elucidating the chemical transformation mechanisms in the atmosphere,<sup>(63,67)</sup> evaluating the toxicity or mutagenicity of the organic fraction of ambient particles,<sup>(68,69)</sup> or tracking the long-range transport of pollution to distant receptors.<sup>(70)</sup> While OC often represents a significant fraction (10-70%) of the of the total dry particle mass in the atmosphere, the presence of hundreds or even thousands of individual species with different chemical structures, the bulk ( $\geq 80\%$ ) of which have not been identified, poses significant analytical challenges.<sup>(71)</sup> To this end, a range of methods have been developed to quantify compounds in the organic fraction of PM to provide better information for improving our understanding of health effects, global warming, atmospheric chemistry, and source impacts of PM.<sup>(72)</sup> Figure 3 details the overall analytical separation of organic matter emitted from motor vehicles while Table 1 lists some of the important organic marker or tracer species used in source apportionment models to link source impacts at receptor locations.

For detailed quantification of organic species using filter-based methods, sufficient sample must be collected on the filter media. Thus collection often entails extended sampling periods, aggregation of multiple samples collected independently, or use of high-volume aerosol samplers. Laboratory quantification of the collected organic species may include multiple approaches, each targeting different categories of compounds such as polar species, nonpolar species, or macromolecules.<sup>(74–76)</sup> Most approaches initially spike the PM sample with a suite of isotopically labeled standards to monitor recovery of material during extraction and concentration. A suite of suitable organic solvents or water is used for dissolution of the target species with multiple extraction steps, where the extract from the multiple steps is typically

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Figure 3 The analytical separation of organic compounds emitted from motor vehicles as total organic compounds, extractable and elutable compounds, resolved species, and identified species. (Reproduced with permission from Ref. 73 © Elsevier, 1999.)

 Table 1
 Organic compounds used for source attribution

Organic aerosol sources	Specific organic markers	Important organic markers/source indicators
Gasoline-powered engine exhaust		Hopanes, steranes, PAHs, EC
Diesel engine exhaust		Hopanes, steranes, EC
Natural gas combustion		PAHs
Fuel oil combustion		Hopanes, steranes, EC
Coal combustion – uncontrolled	Picene	Hopanes, steranes, PAHs, EC
Biomass burning (cellulose) (associated sources: wildfires, forest fires, residential wood combustion)	Levoglucosan	Resin acids, methoxyphenols, phytosterol, β-sitosterol, stigmasterol, campesterol, saccharides
Soft wood burning (associated sources: wildfires, forest fires, residential wood combustion)	Resin acids	
Hard wood burning (associated sources: wildfires, forest fires, residential wood combustion)	Syringyl derivatives	
Fugitive dust from cultivated land	Saccharides: mycose, sucrose,	
(associated sources: wildfires, forest fires)	$\alpha$ -, $\beta$ -glucose	
Meat cooking	Cholesterol	Tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, palmitin stearin
Plastic waste burning		Even carbon alkanes
Vegetative detritus		<i>n</i> -Nonacosane, <i>n</i> -triacontane, <i>n</i> -hentriacontane, <i>n</i> -dotriacontane, <i>n</i> -tritriacontane
Leaf surface waxes (associated sources: burning vegetative detritus, soil dust, vegetarian cooking)		Odd-carbon <i>n</i> -alkanes (> $C_{25}$ ); Even carbon <i>n</i> -alkanoic acids (> $C_{23}$ )
Cigarette smoke	iso-Nonacosane, anteiso-triacontane, iso-hentriacontane, anteiso-dotriacontane,	
SOA	1,2-Benzenedicarboxylic acid, methyl-1,2- benzenedicarboxylic acid	Not well defined

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This article is © 2017 John Wiley & Sons, Ltd. This article was published in the *Encyclopedia of Analytical Chemistry* in 2017 by John Wiley & Sons, Ltd. DOI: 10.1002/9780470027318.a9582 combined. Ultrasonic agitation,<sup>(77)</sup> Soxhlet extraction,<sup>(78)</sup> or pressurized fluid extraction<sup>(79)</sup> have been used to increase recovery of OM from PM filter samples. For solvent extraction, the combined extract is concentrated to improve method detection limits. This concentration necessitates strict control of contamination in the solvents as well as in the filter material or other substrate used for sample collection, handling, and analysis.<sup>(77,80-82)</sup> Once concentrated, a portion of the extract undergoes analytical separation using a method such as gas chromatography (GC) or liquid chromatography (LC). After separation, individual compounds are detected, identified, and quantified using a variety of approaches such as flame-ionization detection<sup>(83)</sup> (FID); MS using electron impact,<sup>(7)</sup> negative chemical ionization,<sup>(84)</sup> or positive chemical ionization;<sup>(85)</sup> UV/VIS spectrometry,<sup>(86)</sup> fluorescence,<sup>(87)</sup> or electron-capture detection<sup>(88)</sup> (ECD). Alternatively, a thermal denuder can be used to volatilize organic compounds from the sample. The evolved gas is then cryofocused and analyzed using GC-MS without the use of solvent extraction.<sup>(89,90)</sup> This method also is often referred to in the literature as TAG GC/MS-FID.<sup>(89)</sup>

Using any of these approaches to identify and quantify organic species in air leaves a large unresolved fraction that is slowly being identified. Many of these unidentified compounds are oxygenated macromolecules, and oligomers.<sup>(71,75)</sup> An alternative approach to analysis of polar compounds is chemical conversion of polar functional groups to nonpolar derivatives and subsequent analysis including conversion of fatty acids to their methyl-ester derivatives via addition of diazomethane<sup>(91)</sup> or conversion of hydroxyl and carboxylic acid groups to their trimethylsilyl esters through reaction with bis(trimethylsilyl)trifluoroacetamide.<sup>(92)</sup>

#### 2.3.4 Continuous Methods

Commercial approaches that provide near real-time measurements of TC, OC, and EC are available based on the TOA approach.<sup>(93)</sup> This approach continuously collects particles on a quartz-fiber filter over a user-defined period (e.g. 1h), after which the sample is analyzed by TOA. A wider range of continuous approaches target BC, as optical sensing is more suitable for continuous measurements.<sup>(11,94)</sup> Aethalometers continuously measure the light absorption properties of particles collected on a PTFE-coated borosilicate glassfiber filter tape, either at one wavelength (e.g. 880 nm) or more recently up to seven wavelengths (370–990 nm) where BC is measured at 880 nm.<sup>(95)</sup> Absorption in the near-UV (e.g. 370 nm) provides an estimate of what is referred to as brown carbon, which is correlated with wood smoke.<sup>(96)</sup> Photoacoustic spectrometers (PAS) measure the expansion of gases caused by heating when

the particle-containing air stream is illuminated at a specific wavelength.<sup>(97)</sup> The change in pressure by rapid cycle illumination generates a sound wave measured by a microphone, which is converted into a corresponding BC concentration. The PAS has the advantages that it does not use a filter and can be calibrated with NO<sub>2</sub> <sup>(98)</sup> Continuous multiangle absorption photometers (MAAP) measure light absorbed and scattered from a filter as particles are deposited to allow for a continuous determination of the light-absorbing BC. As the name implies, it measures at multiple angles and in contrast to the other methods, the MAAP usually does not use empirical corrections.<sup>(94)</sup> The continuous light-absorption photometer (CLAP) provides measurement of the light absorption of particles deposited at multiple points on a single filter with internal reference filter spots.<sup>(99)</sup> The particle soot absorbing photometer (PSAP) measures the change in transmittance through a filter at up to three wavelengths.<sup>(100)</sup> Comparisons among methods, using TOA EC as a basis for converting absorption  $(m^{-1})$  to concentration  $(\mu m m^{-3})$ , indicate that the absorptivity coefficient or mass absorption coefficient varies with the method.<sup>(52,101)</sup>

WSOC is measured by using a PILS linked to a continuous TOC analyzer.<sup>(41)</sup> Secondary organic aerosol species have been measured using a PILS followed by a mass atmospheric ionization time-of-flight mass spectrometer (ToFMS).<sup>(102)</sup> Organic species recently have been measured continuously using TAG<sup>(18)</sup> with hourly or better time resolution. A combined TAGaerosol mass spectrometry (AMS) system provides both typical AMS components (Section 2.5) collected through one inlet and organic species that are separated by the TAG system through a second inlet and measured by the AMS.<sup>(89)</sup> AMS has also provided an estimate of hydrocarbon-like organic aerosols (HOA) and oxygenated organic aerosols (OOA) where OOA correlates with secondary organic aerosols and HOA with relatively fresh emissions.<sup>(103)</sup>

#### 2.4 Trace Elements

While trace elements may change oxidation state during their lifetime in air, the bulk element is conserved. This is important since specific sources or source categories have unique trace element signatures and this provides an additional tool for identifying sources of PM at receptor sites. Table 2 lists some of the important trace element marker species used in source apportionment models to link sources to receptor locations.

Analysis of elements in atmospheric PM is typically performed after collection of particles on filters as the range of concentration for trace elements spans several orders of magnitude, as shown in Figure 4.

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 Table 2
 Important trace element marker species for major PM sources<sup>(10,72)</sup>

Source	Marker species	Descriptions
Wild forest fires, residential fuel combustion	K, Cl	Forest fires, wood combustion, cooking, and space heating
Waste burning and disposal	K, As, Pb, Zn	Agriculture burning, incineration, prescribed burning
Oil combustion	Ni, V	Oil refining; diesel-powered vehicles including locomotives and heavy-duty trucks and ships
Coal combustion	S, Se	Electric utility
Industrial processing	Zn, Pb, Cu, Mn, As, Hg	Chemical, food and agriculture, mineral processes, non-ferrous metal processes, wood and paper, glass and related products, electronics
Iron and steel production	Fe, Cr, Ca, Cu, Rb	1
Municipal waste incineration	Cd, Pb, Hg, Sb	
Soil-related components, road dust, windblown dust, construction and demolition	Al, Si, K, Ča, Fe	Soil; paved and unpaved roads, farm lands; buildings, road construction dust
Sea salt	Na, Cl	Marine aerosol



**Figure 4** Concentration (in  $ng m^{-3}$ ) of bulk components (TC, OC, EC, nitrate and sulfate) and trace elements. Plotted data from Phoenix, AZ. (Reproduced from data in Ref. 104 © Air & Waste Management Association, 2011.)

The filter substrates commonly used are PTFE or cellulose, which in many instances were precleaned by washing with acids. Other types of collection substrates including polyurethane foam, polyethylene as well as glass or quartz fiber have also been evaluated<sup>(105)</sup> but are rarely used owing to contamination within the media itself and/or challenges in effectively

extracting or digesting elements from the collection media.

Different approaches are used to measure the mass of elements collected on the filter. These include the direct analysis on the filter without sample pretreatment, solubilization of the metals off the substrate, and complete digestion of the sample and filter material.

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## 2.4.1 Direct Filter Analysis

XRF spectroscopy has been used for many years for the direct analysis of PM collected on filters, primarily PTFE filters.<sup>(32)</sup> Directly analyzing the sample on the filter has multiple advantages. First, by avoiding sample pretreatment, this approach allows for rapid, high throughput sample analysis making the method suitable for application in large air monitoring networks, such as the Interagency Monitoring of Protected Visual Environments (IMPROVE) network or the EPA CSN.<sup>(4)</sup> In fact, improvements in XRF technology have resulted in lower detection limits, reducing the number of methods needed to obtain a full range of elements [e.g. in 2001 IMPROVE changed from dual analyses (proton induced X-ray emission or PIXE: Na-Mn; energy dispersive Xray fluorescence or EDXRF: Na-Pb) to only EDXRF (Na-Pb)].<sup>(4)</sup> Secondly, the methods are commonly considered nondestructive, and although sample damage has been reported,<sup>(106)</sup> filters can be analyzed by alternate methods for other nonvolatile components. Semivolatile components (e.g. ammonium nitrate and semivolatile organics) can be volatilized due to the XRF beam heating the sample or loss when samples are analyzed using a vacuum-based XRF method,<sup>(107)</sup> so secondary analyses may provide inaccurate results for those species.

The most serious limitation in XRF and similar direct methods, even given recent advances, are relatively high method detection limits compared to the spectrometric methods detailed in Table 3. For example, IMPROVE and CSN EDXRF methods can analyze for up to 48 elements in a typical 24-h sample, but for CSN, only 10–15 elements are above their detection limit and for IMPROVE, only 15–20 elements<sup>(4)</sup> and most of the detected elements are sulfur and crustal species (e.g. Fe, Ca, Mn, Ti). This limits their usefulness in source apportionment and health studies.

Besides XRF, PIXE<sup>(108,109)</sup> and instrumental neutron activation analysis<sup>(110)</sup> (INAA) also have been used for direct analysis but their application is limited due to the lack of availability of these instruments.

Recent developments in the area of direct trace metal analysis include the use of synchrotron-based techniques, such as X-ray absorption near-edge structure (XANES) spectroscopy<sup>(111)</sup> to determine directly, without sample preparation, the chemical speciation of a specific element on the substrate such as the oxidation state of iron [Fe (II) vs Fe (III)]<sup>(112)</sup> or arsenic.<sup>(113)</sup>

#### 2.4.2 Analysis after Sample Preparation

Many analytical approaches for total elemental concentrations as well as soluble metal concentrations or chemical speciation measurements require sample preparation, typically extraction or digestion.<sup>(104)</sup> Extraction uses a solvent, often an aqueous buffer solution, to maintain a specific pH (e.g. to simulate lung fluids or cloud droplets) to extract or leach out the soluble metals.<sup>(114)</sup> Alternatively, total metal concentrations are obtained after digestion of the collected particles or in some cases the whole sample (substrate plus particles). The digestion process typically involves mixtures of strong acids (e.g. HNO<sub>3</sub>–HCl) and heating, and can include the addition of oxidative agents (HClO<sub>4</sub> or H<sub>2</sub>O<sub>2</sub>) or hydrofluoric acid (HF), the latter in cases where silicon containing soil material is expected.<sup>(115)</sup> Typically, digestion is performed in pressure vessels using microwave digestion systems.<sup>(115)</sup>

The resulting liquid samples (extracts or digests) are then analyzed using spectrometric techniques including atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and ICP-MS.<sup>(115–117)</sup> INAA,<sup>(110)</sup> noted earlier, has proved to be a powerful analytical method used to determine the elemental composition of PM, even in samples collected at the South Pole.<sup>(118)</sup>

AAS overall has relatively higher detection limits than the other methods so the number of elements observed is limited. Today, major, minor, and trace multielement analysis of particles is typically performed using ICP-OES or ICP-MS, the latter becoming increasingly common. Both ICP methods provide low detection limits and high reproducibility.<sup>(119)</sup> ICP-MS has a linear response over several orders of magnitude and overall has less analytical interferences than ICP-OES. However, while Fe determination using ICP-MS is problematic, improvements are observed when collision or reactor cell technology is employed.<sup>(32)</sup> Analysis of silicon using ICP-MS remains challenging and is typically less sensitive than ICP-OES. Neither methodology allows for analysis of light elements, such as C, O, and N. While frequently over 50 elements can be measured in urban PM samples, a major drawback is the requirement of sample pretreatment to extract or digest samples, which is more costly than direct elemental analysis methods. ICP-MS and ICP-OES also have been coupled to chromatographic separation techniques to determine the speciation of metals in atmospheric particles.<sup>(113)</sup>

Advances have been made recently using laser ablationinductively coupled plasma-mass spectrometry<sup>(120)</sup> (LA-ICP-MS). LA-ICP-MS eliminates the need for sample pretreatment while taking advantage of the low detection limits and multielement capabilities of ICP-MS. However, quantitation remains a major challenge.<sup>(121)</sup>

A unique advantage of MS in elemental analysis is the ability to determine specific isotopes.<sup>(111)</sup> This allows for the use of isotope ratios as a tool to apportion the sources of specific metals in atmospheric PM.

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	Table 3	Detection	limits for	select	trace	metals	in ai	r (ng	$(m^{-3})$	for	various	analy	tical	approaches
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		EDXRF (CSN 2012) <sup>a</sup>	EDXRF (IMPROVE 2012) <sup>a</sup>	ICP/MS <sup>b</sup>	ICP-OES <sup>c</sup>	INAA <sup>c</sup>
Sodium	Na	57	3.7	57.97	_	0.18
Magnesium	Mg	19	2.7	5.75	5.3	231
Aluminum	Al	27	1.9	24.73	13.5	5
Silicon	Si	19	2.8	-	37.8	-
Phosphorus	Р	18	0.23	7.03	22.9	-
Sulfur	Si	11	0.26	-	-	-
Chlorine	Cl	11	0.26	-	-	9.2
Potassium	Κ	11	1.1	39.52	45.1	0.92
Calcium	Ca	8.3	2.0	51.44	22.7	231
Titanium	Ti	5.8	0.3	0.63	0.7	4.6
Vanadium	V	4.2	0.1	0.11	1.5	0.04
Chromium	Cr	2.8	0.12	0.83	2.6	92.5
Manganese	Mn	2.9	0.25	0.48	0.9	0.02
Iron	Fe	3.4	1.4	16.84	7.5	4629
Cobalt	Со	2.0	NA	0.09	3.3	0.4
Nickel	Ni	1.9	0.1	1.26	3.1	1.8
Copper	Cu	2.6	0.21	0.41	3.3	0.9
Zinc	Zn	8.8	0.25	2.35	26.4	9.2
Gallium	Ga	NA	NA	0.10	-	-
Arsenic	As	2.8	0.19	0.20	5.5	0.09
Selenium	Se	2.7	0.21	0.51	34.3	9.2
Bromine	Br	2.5	0.2	0.00	-	0.04
Strontium	Sr	3.8	0.24	0.45	0.2	0.4
Zirconium	Zr	25	1.2	1.11	1.8	92.6
Molybdenum	Мо	-	_	1.43	1.9	5
Silver	Ag	40	_	0.20	-	0.04
Cadmium	Cď	24	_	0.03	1.1	4.2
Tin	Sn	39	_	0.30	9.2	9.2
Antimony	Sb	56	_	0.25	5.5	0.4
Barium	Ba	60	_	0.35	0.7	2.3
Cerium	Ce	-	_	0.02	10.6	9.2
Tungsten	W	-	_	1.18	12.5	0.09
Gold	Au	-	_	23.17	1.9	0.09
Mercury	Hg	-	_	0.00	12.1	0.9
Lead	Pb	6.4	0.62	0.36	7	_

<sup>a</sup>Solomon et al.<sup>(4)</sup>

<sup>b</sup>Upadhyay et al. (2015); nanogram per cubic meter obtained by assuming 24 h sampling at 16.9 L min<sup>-1</sup>.

<sup>c</sup>US EPA 1999 Compendium of Methods for the determination of Inorganic Compounds in Ambient Air, EPA/625/R-960/010a, Office of Research and Development, Washington, DC, 1999.

## 2.4.3 Continuous Methods

Methods for high time resolution data of trace elements fall into two categories: collection in the field with subsequent laboratory analysis and in situ collection and analysis of trace elements in the field. They both provide a semi-continuous high temporal resolution record of elemental concentrations in the air but the former approach is not capable of providing real-time data. For the former, two more common approaches are the Davis rotating-drum universal-size-cut monitoring (DRUM) impactor<sup>(122)</sup> and the SEAS-II<sup>(123)</sup> and SEAS III.<sup>(17)</sup> The DRUM impactor collects particles in up to eight size ranges using a separate Mylar filter tape with each size fraction. Tapes are brought back to the laboratory for analysis by, for example, PIXE, proton elastic scattering analysis (PESA), synchrotron XRF, or other similar methods.<sup>(122,124,125)</sup> PESA allows for the measurement of hydrogen, which has been used as a surrogate for organic content.<sup>(126)</sup> The rotation speed of the DRUM and size of the analysis spot dictate the time resolution of the results. SEAS collects particles as small as 80 nm by condensational growth from direct steam injection into vials for periods as short as 30 min. The slurry is analyzed in the laboratory using, for example, graphite furnace AAS or ICP-MS.<sup>(17,123)</sup>

Several continuous in situ measurement methods for elements in atmospheric PM have been developed over the last decade or so. These include methods that employ XRF for bulk elemental measurements and PILS-XRF or

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PILS-liquid waveguide capillary cell (LWCC) for water soluble elements.

Two commercial in situ XRF instruments are available: the Xact<sup>TM</sup> (Cooper Environmental Services, Beaverton, OR, USA) and the atmospheric heavy metals monitoring systems (AMMS-100, Focused Photonics (Hangzhou), Inc., China). Comparison of 24-h averages of the hourly Xact measurements (K, Ca, Fe, Mn, Ti, Cu, V, Ni, Zn, As, Ba, and Pb) to laboratory EDXRF on 24-h integrated filter samples show good agreement<sup>(127)</sup> with a coefficient of determination  $(r^2)$ ranging from 0.73 to 0.97 with regression slopes of 0.84-2.37 for 12 elements. Water-soluble elements have been continuously determined using PILS coupled to either the Xact or an LWCC coupled to an absorbance spectrophotometry. Soluble Fe was determined by the latter method<sup>(128,129)</sup> whereas the concentration of 14 water-soluble elements (S, K, Ca, Ti, Mn, Fe, Cu, Zn, As, Se, Br, Sr, Ba, and Pb) were determined by the former.(130)

#### 2.5 Particle Mass Spectrometry

There are generally two types of particle MS instruments: ones that volatilize and ionize particles in one step utilizing laser desorption/ionization and the aerodyne aerosol mass spectrometer (AMS), where particles are impacted onto a surface, the surface heated followed by electron impact to ionize the components as shown in Figure 5. In the latter, results represent the bulk mass concentrations of non-refractory species (e.g. sulfate, nitrate, ammonium, and organics) typically in submicron particles as a function of particle diameter. The former provides the chemical composition of individual particles. Another difference is that the AMS, until recently, could not analyze refractory components, such as BC. That changed with the development of the soot particle aerosol mass spectrometer<sup>(132)</sup> (SP-AMS) and the SP2-AMS, the latter briefly described below. The AMS also has utilized a range of mass spectrometers to detect the ions generated, including a quadrupole (Q), time-offlight (ToF), or high-resolution (HR)-ToF mass analyzer.



**Figure 5** Schematic diagrams of the four particle mass spectrometers that operated during the Atlanta Supersite Project. (a) Particle analysis by laser mass spectrometer (PALMS), (b) aerosol time-of-flight mass spectrometer (ATOFMS), (c) rapid single-particle mass spectrometer II (RSMS-II), and (d) aerosol mass spectrometer (AMS). (Reproduced with permission from Ref. 131 © John Wiley and Sons, 2003.)

Four particle MS were first compared during the 1999 Atlanta Supersites Experiment<sup>(131)</sup> (Figure 5) and included the Aerosol Time-of-Flight Mass Spectrometer (ATOFMS), Rapid Single-Particle Mass Spectrometer II (RSMS-II), and Particle Analysis by Laser Mass Spectrometer (PALMS), all of which utilize laser desorption/ionization, and the AMS. This was the first field experiment for three of the particle MS (PALMS, RSMS-II, and AMS). Since then particle mass spectrometers have provided a wealth of information on the chemistry of PM in air as a function of particle size and at high time resolution. Reviews of particle mass spectrometers have been published including a review of online aerosol instrumentation available in 2005,(133) the AMS and variations of the AMS,<sup>(12)</sup> and a review of a range of particle MS methods.<sup>(19)</sup> These reviews do not discuss the SP-AMS,<sup>(132)</sup> which is unique in that it measures refractory BC.

The SP-AMS combines the HR-ToF-AMS<sup>(134)</sup> with the Single Particle Soot Photometer (SP2). The SP-AMS incorporates an intracavity Nd:YAG laser (1064 nm) that vaporizes particles similar to those used in the SP2 instrument, which are then detected by the HR-ToF-AMS. As with the standard AMS, the SP-AMS provides bulk BC results as a function of particle size whereas the SP2, as its name implies, reports single particle BC results. The SP-AMS design, mass spectral interpretation, calibration, and sensitivity have been well described.<sup>(132)</sup> The method has a  $3\sigma$  detection limit of less than 0.1 µg m<sup>-3</sup> for a 60 s averaging time and a sensitivity of greater than 140 carbon ions detected per picogram of refractory BC mass.

## **3 SUMMARY**

The goal of an atmospheric scientist investigating the chemical composition of PM is to determine that composition as it is present in air. This is difficult since PM is a complex mixture of solid and liquid particles consisting of a wide range of species, including ionic components (e.g. ammonium nitrate), carbonaceous components (e.g. OC, EC, and potentially 1000s of organic species), and trace elements that cover the full spectrum of the periodic table. Thus, no single method is capable of measuring all of them. Also because of this complexity, multiple methods are needed to collect samples while attempting to avoid changes in the collected sample during sampling, transport, and storage. The analysis methods themselves can result in sampling artifacts. Many analytical and sampling methods have been developed and employed and this article has attempted to highlight both and to identify some of the challenges. The approaches include filterbased methods where the sample is collected in the field with subsequent chemical analysis in the laboratory, and continuous methods where the sampling and analysis both occur in the field. The latter provides potential for near-real time data. In many cases, the sampling and analytical measurements are well established, while new ones are continuously being developed and evaluated. This is important since data collected by these methods have and will continue to play a critical role in our understanding of atmospheric chemistry, identifying source impacts at receptor locations, data to test and verify complex air quality models, and most importantly how atmospheric particles impact human health, ecosystems, visibility, and global warming.

## **4 DISCLAIMER**

The United States Environmental Protection Agency through its Office of Research and Development collaborated in the development of this article. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement, certification, or recommendation for use.

## **ABBREVIATIONS AND ACRONYMS**

AAS	Atomic Absorption Spectrometry
AD	Aerodynamic Diameter
AIM	Ambient Ion Monitor
APS	Aerodynamic Particle Sizer
ATOFMS	Aerosol Time-of-Flight Mass
	Spectrometer
BAM	Beta Attenuation Monitor
BC	Black Carbon
CC	Carbonate Carbon
CLAP	Continuous Light-absorption
	Photometer
CSN	Chemical Speciation Network
DRUM	Davis Rotating-drum
	Universal-size-cut Monitoring
EC	Elemental Carbon
ECD	Electron-capture Detection
EDXRF	Energy Dispersive X-ray Fluorescence
EPA	United States Environmental
	Protection Agency
FDMS	Filter Dynamic Measurement System
FEM	Federal Equivalent Method
FID	Flame-ionization Detection
FRM	Federal Reference Method
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
HF	Hydrofluoric Acid

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HOA	Hydrocarbon-like Organic Aerosol
HR	High-resolution
IC	Ion Chromatograph
ICP-MS	Inductively Coupled Plasma-mass
	Spectrometry
ICP-OES	Inductively Coupled Plasma Optical
	Emission Spectrometry
IMPROVE	Interagency Monitoring of Protected
IIII Ito i L	Visual Environment
ΙΝΑΑ	Instrumental Neutron Activation
11 17 17 1	A palveis
I A ICP MS	Analysis Loser Ablation inductively Coupled
LA-ICI -MIS	Plasma mass Spectrometry
IC	Liquid Chromotography
LWCC	Liquid waveguide Capillary Cell
MAAP	Multiangle Absorption Photometer
MARGA	Monitor for AeRosols and Gases in Air
MS	Mass Spectrometry
NMR	Nuclear Magnetic Resonance
OC	Organic Carbon
OM	Organic Material
OOA	Oxygenated Organic Aerosol
PALMS	Particle Analysis by Laser Mass
	Spectrometer
PAS	Photoacoustic Spectrometer
PESA	Proton Elastic Scattering Analysis
PILS	Particle-into-liquid Sampler
PIXE	Proton Induced X-ray Emission
PM	Particulate Matter
PSAP	Particle Soot Absorbing Photometer
PTFE	Polytetrafluoroethylene
0	Quadrupole
RSW2-II	Ranid Single-Particle Mass
1051015-11	Spectrometer II
SEAS III	Somicontinuous Elements in Aerosol
3EA3-111	Semilar III
CMDC	Samplet-III
SIVIES	Scaling Woolinty Particle Sizer
SP-AMS	Soot Particle Aerosol Mass
	Spectrometer
TAD	Thermal Aerosol Desorption
TC	Total Carbon
TEOM	Tapered Oscillating Micro Balance
TOA	Thermal-optical Analysis
TOC	Total Organic Carbon
ToF	Time-of-flight
ToFMS	Time-of-flight Mass Spectrometer
UFP	Ultrafine Particle
UV/VIS	Ultraviolet/Visible
UVPM	Ultraviolet Absorbing Particulate
	Matter
WSOC	Water-soluble Organic Carbon
XANES	X-ray Absorption Near-edge Structure
XRF	X-ray Fluorescence

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## REFERENCES

- 1. J.H. Seinfeld, S.N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 3rd edition, John Wiley & Sons, Inc, Hoboken, NJ, 2016.
- US Environmental Protection Agency, 'Final Report: Integrated Science Assessment for Particulate Matter EPA/600/R-08/139F', Washington, DC, 2009.
- J.C. Chow, 'Measurement Methods to Determine Compliance with Ambient Air-quality Standards for Suspended Particles', J. Air Waste Manage. Assoc., 45, 320–382 (1995).
- P.A. Solomon, J.J. Lantz, D. Crumpler, J.B. Flanagan, R. Jayanty, E.E. Rickman, C. McDade, L. Ashbaugh, 'United States National PM2.5 Chemical Speciation Monitoring Networks – CSN and IMPROVE: Description of Networks', J. Air Waste Manage. Assoc., 64, 1410–1438 (2014).
- J.G. Watson, J.C. Chow, 'Ambient Aerosol Sampling', in Aerosol Measurement: Principles, Techniques and Applications, 3rd edition, eds P. Kulkarni, P.A. Baron, K. Willeke, John Wiley and Sons, Inc, Hoboken, NJ, 2011.
- S.L. Rees, A.L. Robinson, A. Khlystov, C.O. Stanier, S.N. Pandis, 'Mass Balance Closure and the Federal Reference Method for PM2.5 in Pittsburgh, Pennsylvania', *Atmos. Environ.*, 38, 3305–3318 (2004).
- J.J. Schauer, W.F. Rogge, L.M. Hildemann, M.A. Mazurek, G.R. Cass, B.R.T. Simoneit, 'Source Apportionment of Airborne Particulate Matter using Organic Compounds as Tracers', *Atmos. Environ.*, **30**, 3837–3855 (1996).
- P.K. Hopke, 'Review of Receptor Modeling Methods for Source Apportionment', J. Air Waste Manage. Assoc., 66, 237–259 (2016).

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- B. Nozière, M. Kalberer, M. Claeys, J. Allan, B. D'Anna, S. Decesari, E. Finessi, M. Glasius, I. Grgić, J.F. Hamilton, T. Hoffmann, Y. Iinuma, M. Jaoui, A. Kahnt, C.J. Kampf, I. Kourtchev, W. Maenhaut, N. Marsden, S. Saarikoski, J. Schnelle-Kreis, J.D. Surratt, S. Szidat, R. Szmigielski, A. Wisthaler, 'The Molecular Identification of Organic Compounds in the Atmosphere: State of the Art and Challenges', *Chem. Rev.*, **115**, 3919–3983 (2015).
- P.A. Solomon, P.K. Hopke, J. Froines, R. Scheffe, 'Key Scientific and Policy- and Health-Relevant Findings from EPA's Particulate Matter Supersites Program and Related Studies: An Integration and Synthesis of Results', J. Air Waste Manage. Assoc., 58, S1–S92 (2008).
- P.A. Solomon, C. Sioutas, 'Continuous and Semicontinuous Monitoring Techniques for Particulate Matter Mass and Chemical Components: A Synthesis of Findings from EPA's Particulate Matter Supersites Program and Related Studies', *J. Air Waste Manage. Assoc.*, 58, 164–195 (2008).
- 12. M.R. Canagaratna, J.T. Jayne, J.L. Jimenez, J.D. Allan, M.R. Alfarra, Q. Zhang, T.B. Onasch, F. Drewnick, H. Coe, A. Middlebrook, A. Delia, L.R. Williams, A.M. Trimborn, M.J. Northway, P.F. DeCarlo, C.E. Kolb, P. Davidovits, D.R. Worsnop, 'Chemical and Chemical and Microphysical Characterization of Ambient Aerosols with the Aerodyne Aerosol Mass Spectrometer', *Mass Spectrom. Rev.*, **26**, 185–222 (2007).
- D.A. Orsini, Y. Ma, A. Sullivan, B. Sierau, K. Baumann, R.J. Weber, 'Refinements to the Particle-into-liquid Sampler (PILS) for Ground and Airborne Measurements of Water Soluble Aerosol Composition', *Atmos. Environ.*, 37, 1243–1259 (2003).
- R.A. Washenfelder, A. R. Attwood, C.A. Brock, H. Guo, L. Xu, R.J. Weber, N.L. Ng, H.M. Allen, B.R. Ayres, K. Baumann, R.C. Cohen, D.C. Draper, K.C. Duffey, E. Edgerton, J.L. Fry, W.W. Hu, J.L. Jimenez, B.B. Palm, P. Romer, E.A. Stone, P.J. Wooldridge, S.S. Brown, 'Biomass Burning Dominates Brown Carbon Absorption in the Rural Southeastern United States', *Geophys. Res. Lett.*, 42, 653–664 (2015). DOI:10.1002/2014GL062444.
- M. Manigrasso, F. Abballe, R.F. Jack, P. Avino, 'Timeresolved Measurement of the Ionic Fraction of Atmospheric Fine Particulate Matter', *J. Chromatogr. Sci.*, 48, 549 (2010).
- US Environmental Protection Agency, 'Environmental Technology Verification Report. Cooper Environmental Services LLC Xact 625 Particulate Metals Monitor EPA/600/R-12/680', Washington, DC, 2012.
- J.P. Pancras, M.S. Landis, 'Performance Evaluation of Modified Semi-continuous Elements in Aerosol Sampler-III', *Atmos. Environ.*, 45, 6751–6759 (2011).
- B. Williams, A. Goldstein, N. Kreisberg, S. Hering, 'An In-Situ Instrument for Speciated Organic Composition of Atmospheric Aerosols: Thermal Desorption Aerosol

GC/MS-FID (TAG)', Aerosol Sci. Technol., 40, 627–638 (2006).

- K.A. Pratt, K.A. Prathner, 'Mass Spectrometry of Atmospheric Aerosols-recent Developments and Applications. Part I: Off-line Mass Spectrometry Techniques', *Mass Spectrom. Rev.*, **31**, 1–16 (2012).
- E. Snyder, T. Watkins, P.A. Solomon, E. Thoma, R. Williams, G. Hagler, D. Shelow, D. Hindin, V. Kilaru, 'The Changing Paradigm of Air Pollution Monitoring', *Environ. Sci. Tech.*, 47, 11369–11377 (2013).
- P. Kumar, L. Morawska, C. Martani, G. Biskos, M. Neophytou, S. Di Sabatino, M. Bell, L. Norford, R. Britter, 'The Rise of Low Cost Sensing for Managing Air Pollution in Cities', *Environ. Int.*, **75**, 199–205 (2015).
- 22. R. French, 'Public Participation in Air Quality Monitoring: A New Frontier in Citizen Science', *Environmental Manager*, August, 16–21, (2015).
- 23. US Environmental Protection Agency, 'Air Sensor Toolbox for Citizen Scientists', accessed from https://www.epa.gov/air-sensor-toolbox, June 2016.
- 24. South Coast Air Quality Management District, 'Air Quality Sensor Performance Evaluation Center (AQ-SPEC)', accessed from http://www.aqmd.gov/aq-spec/home, June 2016.
- P.A. Solomon, M. Costantini, T.J. Grahame, M.E. Gerlofs-Nijland, F. Cassee, A.G. Russell, J.R. Brook, P.K. Hopke, G. Hidy, R.F. Phalen, P. Saldiva, S. Ebelt-Sarnat, J.R. Balmes, I.B. Tager, H. Özkaynak, S. Vedal, S. Wierman, D.L. Costa, 'Air Pollution and Health: Bridging the Gap from Sources to Health Outcomes: Conference Summary', *Air Qual. Atmos. Health*, 5, 9–62 (2012).
- 26. US Environmental Protection Agency, *National Ambient Air Quality Standards for Particulate Matter; Final Rule* 40 CFR Part 50, US Environmental Protection Agency, Washington, DC, 2013.
- 27. US Environmental Protection Agency, Ambient Air Monitoring Reference and Equivalent Methods 40 CFR Part 53, US Environmental Protection Agency, Washington, DC, 2016.
- 28. US Environmental Protection Agency, *List of Designated Reference and Equivalent Methods*, US Environmental Protection Agency, Office of Research and Development, Research Triangle Park, NC, January 2017. https://www3.epa.gov/ttnamti1/files/ambient/criteria/reference-equivalent-methods-list.pdf.
- 29. B.W. Loo, C.P. Cork, 'Development of High Efficiency Virtual Impactors', *Aerosol Sci. Technol.*, **9**, 167–176 (1988).
- P.H. McMurry, 'A Review of Atmospheric Aerosol Measurements', *Atmos. Environ.*, 34, 1959–1999 (2000).
- 31. M.R. Derrick, J.L. Moyers, 'Precise and Sensitive Water Soluble Ion Extraction Method for Aerosol Samplers

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This article was published in the *Encyclopedia of Analytical Chemistry* in 2017 by John Wiley & Sons, Ltd. DOI: 10.1002/9780470027318.a9582

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Collected on Polytetrafluoroethylene Filters', *Anal. Lett.*, **14**, 1637–1652 (1981).

- P.A. Solomon, M.P. Fraser, P. Herckes, 'Methods for Chemical Analysis of Atmospheric Aerosols', in *Aerosol Measurement: Principles, Techniques and Applications*, 3rd edition, eds P. Kulkarni, P.A. Baron, K. Willeke, John Wiley and Sons, Inc, Hoboken, NJ, 2011.
- R. Al-Horr, G. Samantha, P.K. Dasgupta, 'A Continuous Analyzer for Soluble Anionic Constituents and Ammonium in Atmospheric Particulate Matter', *Environ. Sci. Technol.*, 37, 5711–5720 (2003).
- W. Nie, T. Wang, X. Gao, R. Pathak, X. Wang, R. Gao, Q. Zhang, L. Yang, W. Wang, 'Comparison Among Filterbased, Impactor-based and Continuous Techniques for Measuring Atmospheric Fine Sulfate and Nitrate', *Atmos. Environ.*, 44, 4396–4403 (2010).
- M. Markovic, T. VanderBoer, J.G. Murphy, 'Characterization and Optimization of an Online System for the Simultaneous Measurement of Atmospheric Watersoluble Constituents in the Gas and Particle Phase', J. Environ. Monit., 14, 1872 (2012).
- H. TenBrink, R. Otjes, P. Jongejan, J. Slanina, 'An Instrument for Semi-continuous Monitoring of the Sizedistribution of Ammonium Nitrate Aerosol', *Atmos. Environ.*, 41, 2768–2779 (2007).
- S.V. Hering, M.R. Stolzenberg, J.L. Hand, S.M. Kreidenweis, T. Lee, J.L. Collett, D. Dietrich, M. Tigges, 'Hourly Concentrations and Light Scattering Cross Sections for Fine Particle Sulfate at Big Bend National Park', *Atmos. Environ.*, 37, 1175–1183 (2003).
- M.R. Stolzenburg, S.V. Hering, 'Method for the Automated Measurement of Fine Particle Nitrate in the Atmosphere', *Environ. Sci. Technol.*, 34, 907–914 (2000).
- E.S. Edgerton, B.E. Hartsell, R.D. Saylor, J.J. Jansen, D.A. Hansen, G.M. Hidy, 'The Southeastern Aerosol Research and Characterization Study: Three Continuous Measurements of PM2.5 Mass and Composition', *J. Air Waste Manage. Assoc.*, 56, 1325–1341 (2006).
- H.P. Schmid, L. Laskus, H. Abraham, U. Baltensperger, V. Lavanchy, M. Bizjak, P. Burba, H. Cachier, D.J. Crow, J.C. Chow, T. Gnauk, A. Even, H. TenBrink, K. Giesen, R. Hitzenberger, C. Hueglin, W. Maenhaut, C.A. Pio, J. Puttock, J. Putaud, D. Toom-Sauntry, H. Puxbaum, 'Results of the Carbon Conference International Aerosol Carbon Round Robin Test: Stage 1', *Atmos. Environ.*, 35, 2111–2121 (2001).
- A.P. Sullivan, R.E. Peltier, C.A. Brock, J. de Gouw, J. Holloway, C. Warneke, A. Wollny, R.J. Weber, 'Airborne Measurements of Carbonaceous Aerosol Soluble in Water Over Northeastern United States: Method Development and an Investigation into Water-Soluble Organic Carbon Sources', J. Geophys. Res. Atmos., 111, D05314 (2006).

- J.G. Watson, J.C. Chow, L. Chen, 'Summary of Organic and Elemental Carbon/Black Carbon Analysis Methods and Intercomparisons', *Aerosol Air Qual. Res.*, 5, 65–102 (2005).
- J.C. Chow, J.G. Watson, L.C. Pritchett, W.R. Pierson, C.A. Frazier, R.C. Purcell, 'The DRI Thermal/optical Reflectance Carbon Analysis System: Description, Evaluation and Application Species in U.S. Air Quality Studies', *Atmos. Environ.*, 8, 1185–1201 (1993).
- M.E. Birch, R.A. Cary, 'Elemental Carbon-based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust', *Aerosol Sci. Technol.*, 25, 221–241 (1996).
- J.C. Chow, J.G. Watson, L. Chen, W.P. Arnott, H. Moosmüller, K.K. Fung, 'Equivalence of Elemental Carbon by Thermal/Optical Reflectance and Transmittance with Different Temperature Protocols', *Environ. Sci. Technol.*, 38, 4414–4422 (2004).
- B.J. Turpin, H.J. Lim, 'Species Contributions to PM2.5 Concentrations: Revisiting Common Assumptions for Estimating Organic Mass', *Aerosol Sci. Technol.*, 35, 602–610 (2001).
- B.J. Turpin, J.J. Huntzicker, 'Identification of Secondary Organic Aerosol Episodes and Quantification of Primary and Secondary Organic Aerosol during SCAQS', *Atmos. Environ.*, 29, 3527–3544 (1995).
- A. Polidori, B.J. Turpin, C.I. Davidson, L.A. Rodenburg, F. Maimone, 'Organic PM<sub>2.5</sub>: Fractionation by Polarity, FTIR Spectroscopy, and OM/OC Ratio for the Pittsburgh Aerosol', *Aerosol Sci. Tech.*, 42, 23–246 (2008).
- M. Reggente, A.M. Dillner, S. Takahama, 'Predicting Ambient Aerosol Thermal-optical Reflectance (TOR) Measurements from Infrared Spectra: Extending the Predictions to Different Years and Different Sites', *Atmos. Meas. Tech.*, 9, 441–454 (2016).
- M. Sillanpää, A. Frey, R. Hillamo, A.S. Pennanen, R.O. Salonen, 'Organic, Elemental and Inorganic Carbon in Particulate Matter of Six Urban Environments in Europe', *Atmos. Chem. Phys.*, 5, 2869–2879 (2005).
- Y.Q. Wang, X.Y. Zhang, R. Arimoto, J.J. Cao, Z.X. Shen, 'Characteristics of Carbonate Content and Carbon and Oxygen Isotopic Composition of Northern China Soil and Dust Aerosol and its Application to Tracing Dust Sources', *Atmos. Environ.*, 36, 2631–2642 (2005).
- T. Bond, R. Bergstrom, 'Light Absorption by Carbonaceous Particles: an Investigative Review', *Aerosol Sci. Technol.*, 40, 27–67 (2006).
- M.Z. Jacobson, 'Strong Radiative Heating due to the Mixing State of Black Carbon in Atmospheric Aerosols', *Nature*, 409, 695–697 (2001).
- N.A. Janssen, G. Hoek, M. Simic-Lawson, P. Fischer, L. van Bree, H. TenBrink, M. Keuken, R.W. Atkinson, H.R. Anderson, B. Brunekreef, F.R. Cassee, 'Black Carbon as

*Encyclopedia of Analytical Chemistry*, Online © 2006–2017 John Wiley & Sons, Ltd. This article is © 2017 John Wiley & Sons, Ltd. This article was published in the *Encyclopedia of Analytical Chemistry* in 2017 by John Wiley & Sons, Ltd. DOI: 10.1002/9780470027318.a9582

an Additional Indicator of the Adverse Health Effects of Airborne Particles Compared with PM10 and PM2.5', *Environ. Health Perspect.*, **119**, 1691–1699 (2011).

- S. Kimbrough, M. Hays, B. Preston, D. Vallero, G. Hagler, 'Episodic Impacts from California Wildfires Identified in Las Vegas Near-Road Air Quality Monitoring', *Environ. Sci. Tech.*, 50, 18–24 (2016).
- P. Saxena, L.M. Hildemann, 'Water-soluble Organics in Atmospheric Particles: A Critical Review of the Literature and Application of Thermodynamics to Identify Candidate Compounds', J. Atmos. Chem., 24, 57–109 (1996).
- H. Yang, Q. Li, J.Z. Yu, 'Comparison of Two Methods for the Determination of Water-soluble Organic Carbon in Atmospheric Particles', *Atmos. Environ.*, 37, 865–870 (2003).
- M. Schnaiter, H. Horvath, O. Mohler, K. Naumann, H. Saathoff, O.W. Schock, 'UV–VIS-NIR Spectral Optical Properties of Soot and Soot-containing Aerosols', *Aerosol Sci.*, 34, 1421–1444 (2003).
- C. Coury, A.M. Dillner, 'A Method to Quantify Organic Functional Groups and Inorganic Compounds in Ambient Aerosols using Attenuated Total Reflectance FTIR Spectroscopy and Multivariate Chemometric Techniques', *Atmos. Environ.*, 42, 5923–5932 (2008).
- S. Decesari, M.C. Facchini, S. Fuzzi, C.B. McFiggans, H. Coe, K.N. Bower, 'The Water-soluble Organic Component of Size-segregated Aerosol, Cloud Water and Wet Depositions from Jeju Island during ACE-Asia', *Atmos. Environ.*, 39, 211–222 (2004).
- B. Graham, O.L. Mayol-Bracero, P. Guyon, G.C. Roberts, S. Decesari, M.C. Facchini, P. Artaxo, W. Maenhaut, P. Koll, M.O. Andreae, 'Water-soluble Organic Compounds in Biomass Burning Aerosols over Amazonia – 1. Characterization by NMR and GC-MS', *J. Geophys. Res.*, 107, D8047 (2002).
- D.T. Allen, E. Palen, J. Haimov, I.H. Mitchell, S.V. Hering, J.R. Young, 'Fourier Transform Infrared Spectroscopy of Aerosol Collected in a Low Pressure Impactor (LPI/FTIR): Method Development and Field Calibration', *Aerosol Sci. Technol.*, 21, 325–342 (1994).
- M. Jang, R.M. Kamens, 'Newly Characterized Products and Composition of Secondary Aerosols from the Reaction of alpha-pinene with Ozone', *Atmos. Environ.*, 33, 459–474 (1999).
- 64. N.P. Havers, P. Burba, J. Lambert, D. Klockow, 'Spectroscopic Characterization of Humic-like Substances in Airborne Particulate Matter', *J. Atmos. Chem.*, **29**, 45–54 (1998).
- 65. T.C. Ruthenburg, P.C. Perlin, V. Liu, C.E. McDade, A.M. Dillner, 'Determination of Organic Matter and Organic Matter to Organic Carbon Ratios by Infrared

Spectroscopy with Application to Selected Sites in the IMPROVE Network', *Atmos. Environ.*, **86**, 47–57 (2014).

- S. Takahama, G. Ruggeri, A.M. Dillner, 'Analysis of Functional Groups in Atmospheric Aerosols by Infrared Spectroscopy: Sparse Methods for Statistical Selection of Relevant Absorption Bands', *Atmos. Meas. Tech. Discuss.*, 9, 3429–3454 (2016). DOI: 10.5194/amt-9-3429-2016
- T.R. Hoffmann, R. Bandur, U. Marggraf, M. Linscheid, 'Molecular Composition of Organic Aerosols Formed in the alpha-pinene/O<sub>3</sub> reaction: Implications for New Particle Formation Processes', J. Geophys. Res., 103, 25569–25578 (1998).
- 68. J. Lewtas, 'Air Pollution Combustion Emissions: Characterization of Causative Agents and Mechanisms Associated with Cancer, Reproductive, and Cardiovascular Effects', *Mutat. Res. Rev.*, **636**, 95–133 (2007).
- J.L. Durant, W.F. Busby, A. Lafleur, B. Penman, C. Crespi, 'Human Cell Mutagenicity of Oxygenated, Nitrated and Unsubstituted Polycyclic Aromatic Hydrocarbons Associated with Urban Aerosols', *Mutat. Res.*, **371**, 123–157 (1996).
- M.P. Fraser, K. Lakshmanan, 'Using Levoglucosan as a Molecular Marker for the Long-range Transport of Biomass Combustion Aerosols', *Environ. Sci. Tech.*, 34, 4560–4564 (2000).
- B.J. Turpin, P. Saxena, E. Andrews, 'Measuring and Simulating Particulate Organics in the Atmosphere: Problems and Prospects', *Atmos. Environ.*, 34, 2983–3013 (2000).
- M. Viana, T. Kuhlbusch, X. Querol, A. Alastuey, R. Harrison, P. Hopke, W. Winiwarter, A. Vallius, S. Szidat, A. Prevot, C. Hueglin, H. Bloemen, P. Wahlin, R. Vecchi, A. Miranda, A. Kasper-Giebl, W. Maenhaut, R. Hitzenberger, 'Source Apportionment of Particulate Matter in Europe: A Review of Methods and Results', J. Aerosol Sci., 39, 827–849 (2008).
- M.P. Fraser, G.R. Cass, B.R.T. Simoneit, 'Particulate Organic Compounds Emitted from Motor Vehicle Exhaust and in the Urban Atmosphere', *Atmos. Environ.*, 33, 2715–2724 (1999).
- 74. B.R.T. Simoneit, 'Chemical Characterization of Submicron Organic Aerosols in the Tropical Trade Winds of the Caribbean using Gas Chromatography-mass Spectrometry', *Atmos. Environ.*, **36**, 5259–5263 (2002).
- 75. E.R. Graber, Y. Rudich, 'Atmospheric HULIS: How Humic-like are they? A Comprehensive and Critical Review', *Atmos. Chem. Phys.*, **6**, 729–753 (2006).
- M. Maricq, 'Chemical Characterization of Particulate Emissions from Diesel Engines: A Review', *Aerosol Sci.*, 38, 1079–1118 (2007).
- 77. M.A. Mazurek, B.R.T. Simoneit, G.R. Cass, H.A. Gray, 'Quantitative High-Resolution Gas Chromatography and High-resolution Gas Chromatography/Mass

*Encyclopedia of Analytical Chemistry*, Online © 2006–2017 John Wiley & Sons, Ltd. This article is © 2017 John Wiley & Sons, Ltd.

This article was published in the *Encyclopedia of Analytical Chemistry* in 2017 by John Wiley & Sons, Ltd. DOI: 10.1002/9780470027318.a9582

Spectroscopy Analysis of Carbonaceous Fine Aerosol Particles', Int. J. Environ. Anal. Chem., 29, 119–139 (1989).

- L.C. Marr, K. Dzepina, J.L. Jimenez, F. Reisen, H.L. Bethel, J. Arey, J.S. Gaffney, N.A. Marley, L.T. Molina, M.J. Molina, 'Sources and Transformations of Particlebound Polycyclic Aromatic Hydrocarbons in Mexico City', *Atmos. Chem. Phys.*, 6, 1733–1745 (2006).
- H.A. Bamford, D.Z. Bezabeh, M.M. Schantz, S.A. Wise, J.E. Baker, 'Determination and Comparison of Nitratedpolycyclic Aromatic Hydrocarbons Measured in Air and Diesel Particulate Reference Materials', *Chemosphere*, 50, 575–587 (2003).
- B.T. Mader, J.F. Pankow, 'Gas/Solid Partitioning of Semivolatile Organic Compounds (SOCs) to Air Filters.
   An Analysis of Gas Adsorption Artifacts in Measurements of Atmospheric SOCs and Organic Carbon (OC) When Using Teflon Membrane Filters and Quartz-fiber Filters', *Environ. Sci. Tech.*, **35**, 3422–3432 (2001).
- B.R.T. Simoneit, 'Biomass Burning A Review of Organic Tracers for Smoke from Incomplete Combustion', *Appl. Geochem.*, 17, 129–162 (2002).
- S.R. McDow, M.A. Mazurek, M. Li, L. Alter, J. Graham, H.D. Felton, T. McKenna, C. Pietarinen, A. Leston, S. Bailey, S.W.T. Argao, 'Speciation and Atmospheric Abundance of Organic Compounds in PM2.5 from the New York City area. I. Sampling Network, Sampler Evaluation, Molecular Level Blank Evaluation', *Aerosol Sci. Tech.*, 42, 50–63 (2008).
- I.G. Kavouras, N. Stratigakis, E.G. Stephanou, 'Isoand Anteiso-alkanes: Specific Tracers of Environmental Tobacco Smoke in Indoor and Outdoor Particle-size Distributed Urban Aerosols', *Environ. Sci. Tech.*, 32, 1369–1377 (1998).
- 84. A. Albinet, E. Leoz-Garziandia, H. Budzinski, E. Villenave, 'Simultaneous Analysis of Oxygenated and Nitrated Polycyclic Aromatic Hydrocarbons on Standard Reference Material 1649a (Urban Dust) and on Natural Ambient Air Samples by Gas Chromatography–Mass Spectrometry with Negative Ion Chemical Ionization', J. Chromatogr. A, 1121, 106113 (2006).
- M.L. Walser, Y. Desyaterik, J. Laskin, A. Laskin, S.A. Nizkorodov, 'High-resolution Mass Spectrometric Analysis of Secondary Organic Aerosol Produced by Ozonation of Limonene', *Phys. Chem. Chem. Phys.*, 10, 1009–1022 (2008).
- Z. Kitanovski, I. Grgic, F. Yasmeen, M. Claeys, A. Cusak, 'Development of a Liquid Chromatographic Method Based on Ultraviolet–visible and Electrospray Ionization Mass Spectrometric Detection for the Identification of Nitrocatechols and Related Tracers in Biomass Burning Atmospheric Organic Aerosol', *Rapid Commun. Mass* Spectrom., 26, 793–804 (2012).

- A.H. Miguel, A. Eiguren-Fernandez, P.A. Jacques, J.R. Froines, B.L. Grant, P.R. Mayo, C. Sioutas, 'Seasonal Variation of the Particle Size Distribution of Polycyclic Aromatic Hydrocarbons and of Major Aerosol Species in Claremont, California', *Atmos. Environ.*, 38, 3241–3251 (2004).
- J.H. Xu, F.S. Lee, 'Quantification of Nitrated Polynuclear Aromatic Hydrocarbons in Atmospheric Particulate Matter', *Anal. Chim. Acta*, 416, 111–115 (2000).
- B.J. Williams, J.T. Jayne, A.T. Lambe, T. Hohaus, J.R. Kimmel, D. Sueper, W. Brooks, L.R. Williams, A.M. Trimborn, P.L. Hayes, J.L. Jimenez, N.M. Kreisberg, S.V. Hering, D.R. Worton, A.H. Goldstein, D.R. Worsnop, 'The First Combined Thermal Desorption Aerosol Gas Chromatograph – Aerosol Mass Spectrometer (TAG-AMS)', *Aerosol Sci. Tech.*, 48, 358–370 (2014).
- J.C. Chow, J.Y. Yu, J.G. Watson, S.S.H. Ho, T.L. Bohannan, M.D. Hays, K.K. Fung, 'The Application of Thermal Methods for Determining Chemical Composition of Carbonaceous Aerosols: A Review', *J. Environ. Sci. Heath A*, 42, 1521–1541 (2007).
- W.F. Rogge, M.A. Mazurek, L.M. Hildemann, G.R. Cass, 'Quantification of Urban Organics at a Molecular Level: Identification, Abundance and Seasonal Variation', *Atmos. Environ.*, 27, 1309–1330 (1993).
- C.G. Nolte, J.J. Schauer, G.R. Cass, B. Simoneit, 'Highly Polar Organic Compounds Present in Wood Smoke and the Ambient Atmosphere', *Environ. Sci. Tech.*, 35, 1912–1919 (2001).
- B.J. Turpin, R.A. Cary, J.J. Huntzicker, 'An In Situ, Timeresolved Analyzer for Aerosol Organic and Elemental Carbon', *Aerosol Sci. Tech.*, **12**, 161–171 (1990).
- H. Moosmuller, R.K. Chakrabarty, W.P. Arnott, 'Aerosol Light Absorption and its Measurement: A Review', J. Quant. Spectrosc. Radiat. Transfer, 11, 844–878 (2009).
- W.P. Arnott, K. Hamasha, H. Moosmuller, P.J. Sheridan, J.A. Ogren, 'Towards Aerosol Light-absorption Measurements with a 7-wavelength Aethalometer: Evaluation with a Photoacoustic Instrument and 3-wavelength Nephelometer', *Aerosol Sci. Tech.*, **39**, 17–29 (2005).
- Y. Chen, T.C. Bond, 'Light Absorption by Organic Carbon from Wood Combustion', *Atmos. Chem. Phys.*, 10, 1773–1787 (2010).
- D.A. Lack, E.R. Lovejoy, T. Baynard, A. Pettersson, A.R. Ravishankara, 'Aerosol Absorption Measurement using Photoacoustic Spectroscopy: Sensitivity, Calibration, and Uncertainty Developments', *Aerosol Sci. Tech.*, 40, 697–708 (2006).
- T.C. Bond, T.L. Anderson, D. Campbell, 'Calibration and Intercomparison of Filter-based Measurements of Visible Light Absorption by Aerosols', *Aerosol Sci. Tech.*, 30, 582–600 (1999).

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- 99. National Oceanographic and Atmospheric Administration, Earth System Research Laboratory, Global Monitoring Division 'Continuous Light Absorption Photometer', accessed from: http://www.esrl.noaa.gov/ gmd/aero/instrumentation/clap\_desc.html
- A. Virkkula, N.C. Ahlquist, D.S. Covert, W.P. Arnott, P.J. Sheridan, P.K. Quinn, D.J. Coffman, 'Modification, Calibration and a Field Test of an Instrument for Measuring Light Absorption by Particles', *Aerosol Sci. Tech.*, 39, 68–83 (2005).
- 101. K. Park, J.C. Chow, J.G. Watson, D.L. Trimble, P. Doraiswamy, K. Park, W.P. Arnott, K.R. Stroud, K. Bowers, R. Bode, A. Petzold, A. Hansen, 'Comparison of Continuous and Filter-based Carbon Measurements at the Fresno Supersite', *J. Air Waste Manage. Assoc.*, 56, 474–491 (2006).
- 102. C.H. Clark, S. Nakao, A. Asa-Awuku, K. Sato, D.R. Cocker, 'Real-time Study of Particle-Phase Products from alpha-Pinene Ozonolysis and Isoprene Photooxidation Using Particle into Liquid Sampling Directly Coupled to a Time-of-Flight Mass Spectrometer (PILS-ToF)', *Aerosol Sci. Tech.*, **47**, 1374–1382 (2013).
- 103. Q. Zhang, M.R. Alfarra, D.R. Worsnop, J.D. Allan, H. Coe, M.R. Canagaratna, J.L. Jimenez, 'Deconvolution and Quantification of Hydrocarbon-like and Oxygenated Organic Aerosols Based on Aerosol Mass Spectrometry', *Environ. Sci. Tech.*, **39**, 4938–4952 (2005).
- N. Upadhyay, A. Clements, M. Fraser, P. Herckes, 'Chemical Speciation of PM2.5 and PM10 in South Phoenix, AZ', J. Air Waste Manage. Assoc., 61, 302–310 (2011).
- 105. N. Upadhyay, B.J. Majestic, P. Prapaipong, P. Herckes, 'Evaluation of Polyurethane Foam, Polypropylene, Quartz-fiber, and Cellulose Substrates for Multi-element Analysis of Atmospheric Particulate Matter by ICP-MS', *Anal. Bioanal. Chem.*, **394**, 1618–1642 (2009).
- 106. K. Van Meel, A. Worobiec, M. Stranger, R. Van Grieken, 'Sample Damage During X-ray Fluorescence Analysis—Case Study on Ammonium-salts in Atmospheric Aerosols', J. Environ. Monit., 10, 989–992 (2008).
- 107. P.A. Solomon, W. Mitchell, D. Gemmill, M.P. Tolocka, G. Norris, R. Wiener, S. Eberly, J. Rice, J. Homolya, R. Scheffe, R. Vanderpool, R. Murdoch, S. Natarajan, E. Hardison, *Evaluation of PM2.5 Chemical Speciation Samplers for Use in the EPA National PM2.5 Chemical Speciation Network*, US Environmental Protection Agency Office of Air Quality Planning and Standards, Research Triangle Park, NC, 2000. http://www.epa.gov/ttnamti1/files/ambient/pm25/spec/ fourcty.pdf
- S. Johansson, J.L. Campbell, K.G. Malmqvist, *Particle Induced X-ray Emission Spectrometry (PIXE)*, John Wiley & Sons, Inc, New York, 1995.

- 109. K.S. Johnson, A. Laskin, J.L. Jiminez, V. Shutthanandan, L.T. Molina, D. Salcedo, K. Dzepina, M.J. Molina, 'Comparative Analysis of Urban Atmospheric Aerosol by Particle-induced X-ray Emission (PIXE), Proton Elastic Scattering Analysis (PESA), and Aerosol Mass Spectrometry (AMS)', *Environ. Sci. Technol.*, 42, 6619–6624 (2008).
- 110. S. Landsberger, 'Trace Element Determination of Airborne Particles by Neutron Activation Analysis', in *Elemental Analysis of Airborne Particles*, eds S. Landsberger, M. Creatchman, Gordon and Breach Science Publishers, Amsterdam, NL, 1999.
- B.J. Majestic, J.J. Schauer, M.M. Shafer, 'Application of Synchrotron Radiation for Measurement of Iron Redox Speciation in Atmospherically Processed Aerosols', *Atmos. Chem. Phys.*, 7, 2475–2487 (2007).
- B.J. Majestic, A.D. Anbar, P. Herckes, 'Stable Isotopes as a Tool to Apportion Atmospheric Iron', *Environ. Sci. Tech.*, 43, 4327–4333 (2009).
- 113. K. Tirez, C. Vanhoof, J. Peters, L. Geerts, N. Bleux, E. Adriaenssens, E. Roekens, S. Smolek, A. Maderitsch, R. Steininger, J. Gottlicher, F. Meier, C. Streli, P. Berghmans, 'Speciation of Inorganic Arsenic in Particulate Matter by Combining HPLC/ICP-MS and XANES Analyses', J. Anal. At. Spectrom., 30, 2074–2088 (2015).
- N. Upadhyay, B.J. Majestic, P. Herckes, 'Solubility and Speciation of Atmospheric Iron in Buffer Systems Simulating Cloud Conditions', *Atmos. Environ.*, 45, 1858–1866 (2011).
- 115. A.A. Karanasiou, N.S. Thomaidis, K. Eleftheriadis, P.A. Siskos, 'Comparative Study of Pretreatment Methods for the Determination of Metals in Atmospheric Aerosol by Electrothermal Atomic Absorption Spectrometry', *Talanta*, 65, 1196–1202 (2005).
- 116. K. Karar, A.K. Gupta, A. Kumar, A.K. Biswas, 'Characterization and Identification of the Sources of Chromium, Zinc, Lead, Cadmium, Nickel, Manganese and Iron in PM-10 Particulates at the Two Sites of Kolkata, India', *Environ. Monit. Assess.*, **120**, 347–360 (2006).
- N.J. Pekney, C.I. Davidson, 'Determination of Trace Elements in Ambient Aerosol Samples', *Anal. Chim. Acta*, 540, 269–277 (2005).
- G. Tuncel, N.K. Aras, W.H. Zoller, 'Temporal Variations and Sources of Elements in the South Pole Atmosphere.
   Nonenriched and Moderately Enriched Elements', *J. Geophys. Res.*, 94, 13,025–13,038 (1989).
- I. Mori, Z. Sun, M. Ukachi, K. Nagano, C.W. McLeod, A.G. Cox, M. Nishikawa, 'Development and Certification of the New NIES CRM 28: Urban Aerosols for the Determination of Multielements', *Anal. Bioanal. Chem.*, 391, 1997–2003 (2008).
- 120. T. Okuda, J. Kato, J. Mori, M. Tenmoku, Y. Suda, S. Tanaka, K. He, Y. Ma, F. Yang, X. Yu, F. Duan, Y.

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Lei, 'Daily Concentrations of Trace Metals in Aerosols in Beijing, China, Determined by Using Inductively Coupled Plasma Mass Spectrometry Equipped with Laser Ablation Analysis, and Source Identification of Aerosols', *Sci. Total Environ.*, **330**, 145–158 (2004).

- 121. N. Miliszkiewicz, S. Walas, A. Tobiasz, 'Current Approaches to Calibration of LA-ICP-MS Analysis', *Anal. At. Spectrom.*, **30**, 327–338 (2015).
- O.G. Raabe, D.A. Bratten, R.L. Axelbaum, S.V. Teague, T.A. Cahill, 'Calibration Studies of the DRUM Impactor', *J. Aerosol Sci.*, **19**, 183–195 (1988).
- C.B. Kidwell, J.M. Ondov, 'Elemental Analysis of Subhourly Ambient Aerosol Collections', *Aerosol Sci. Tech.*, 38, 205–218 (2004).
- 124. V. Shutthanandan, S. Thevuthasan, R. Disselkamp, A. Stroud, A. Cavanagh, E.M. Adams, D.R. Baer, L.A. Barrie, S.S. Cliff, M. Jimenez-Cruz, T.A. Cahill, 'Development of PIXE, PESA, and Transmission Ion Microscopy Capability to Measure Aerosols by Size and Time', *Nucl. Instrum. Methods Phys. Res.*, **189**, 284–288 (2002).
- 125. N. Li, P.K. Hopke, P. Kumar, S. Cliff, Y. Zhao, C. Navasca, 'Source Apportionment of Time-and Size-resolved Ambient Particulate Matter', *Chemom. Intell. Lab. Syst.*, **129**, 15–20 (2013).
- 126. G. Bench, P.G. Grant, D. Ueda, S. Cliff, K.D. Perry, T.A. Cahill, 'The Use of STIM and PESA to Measure Profiles of Aerosol Mass and Hydrogen Content, Respectively, across Mylar Rotating Drums Impactor Samples', *Aerosol Sci. Tech.*, **36**, 642–651 (2002).
- 127. S. Park, S. Jung, B. Gong, S. Cho, S. Lee, 'Characteristics of PM2.5 Haze Episodes Revealed by Highly Time-resolved Measurements at an Air Pollution Monitoring Supersite in Korea', *Aerosol Air Qual. Res.*, **13**, 957–976 (2013).
- 128. N. Rastogi, M.M. Oakes, J.J. Schauer, M.M. Shafer, B.J. Majestic, R.J. Weber, 'New Technique for Online

Measurement of Water-soluble Fe(II) in Atmospheric Aerosols', *Environ. Sci. Tech.*, **43**, 2425–2430 (2009).

- M. Oakes, N. Rastogi, B.J. Majestic, M. Shafer, J.J. Schauer, E.S. Edgerton, R.J. Weber, 'Characterization of Soluble Iron in Urban Aerosols Using Near-real Time Data', *J. Geophys. Res.*, **115**, D15302 (2010).
- 130. T. Fang, H. Guo, V. Verma, R.E. Peltier, R.J. Weber, 'PM2.5 Water-soluble Elements in the Southeastern United States: Automated Analytical Method Development, Spatiotemporal Distributions, Source Apportionment, and Implications for Heath Studies', *Atmos. Chem. Phys.*, **15**, 11667–11682 (2015).
- 131. A.M. Middlebrook, D.M. Murphy, S.H. Lee, D.S. Thomson, K.A. Prather, R.J. Wenzel, D.Y. Liu, D.J. Phares, K.P. Rhoads, A.S. Wexler, M.V. Johnston, J.L. Jimenez, T.J. Jayne, D.R. Worsnop, I. Yourshaw, J.H. Seinfeld, R.C. Flagan, 'A Comparison of Particle Mass Spectrometers during the 1999 Atlanta Supersites Project', J. Geophys. Res., 108(8424), (2003). DOI: 10.1029/2001JD001213
- T.B. Onasch, A. Trimborn, E.C. Fortner, J.T. Jayne, G.L. Kok, L.R. Williams, P. Davidovits, D.R. Worsnop, 'Soot Particle Aerosol Mass Spectrometer: Development, Validation, and Initial Application', *Aerosol Sci. Tech.*, 46, 804–817 (2012).
- R.C. Sullivan, K.A. Prather, 'Recent Advances in Our Understanding of Atmospheric Chemistry and Climate made Possible by On-line Aerosol Analysis Instrumentation', *Anal. Chem.*, 77, 3861–3885 (2005).
- 134. P.F. DeCarlo, J.R. Kimmel, A. Trimborn, M.J. Northway, J.T. Jayne, A.C. Aiken, M. Gonin, K. Fuhrer, T. Horvath, K.S. Docherty, D.R. Worsnop, J.L. Jimenez, 'Fielddeployable, High-resolution, Time-of-flight Aerosol Mass Spectrometer', *Anal. Chem.*, **78**, 8281–8289 (2006).