Analytical Measurements of Atmospheric Urban Aerosol

Understanding the complex nature of atmospheric urban aerosol mandates the utilization of analytical technology. In this feature article, we provide a glimpse of several analytical techniques that are most commonly used for urban atmospheric aerosol measurements, with an emphasis on particle mass spectrometry methods.

Shan-Hu Lee*† and Heather C. Allen*‡

†Kent State University, College of Public Health, 850 Hilltop Drive, Kent, Ohio 44240, United States
‡The Ohio State University, Department of Chemistry, 100 West 18th Avenue, Columbus, Ohio 43210, United States

Aerosols are small solid or liquid particles that suspend in air. While large size particles can rapidly settle out, smaller particles ($\leq$ 1 micron) have longer atmospheric lifetimes, on the order of up to weeks to months. Thus, these small particles affect climate, air quality, and human health. In urban environments, aerosols vary in composition and size, and are commonly in higher atmospheric concentrations compared to rural environments. The composition depends on the proximity to the source location, meteorological conditions, and types of emissions.

There are roughly two types of urban aerosols. As illustrated in Figure 1, primary aerosols are directly emitted from natural or anthropogenic sources. In urban environments, primary aerosols are produced from incomplete burning of fossil fuels and wind-driven, industrial or traffic-related suspension of road materials where road dust and black carbon soot are the most common. Secondary organic aerosols (SOA) are formed from gas to particle conversion (nucleation), condensation of low volatility species on preexisting aerosols, and heterogeneous reactions of aerosols. The most distinctive feature of urban aerosols, primary and secondary, is the complexity in their chemical composition.

Another important feature is that these aerosols contain a high mass fraction (10–90%) of organic compounds. In addition to chemical composition, aerosol size also controls the rate of diffusion, coagulation, settling, and other key properties such as how aerosols interact with radiation, form clouds, and penetrate into biological tissue such as in the lung lining. Primary aerosols are usually in the accumulation mode (>100 nm). Nucleation produces new aerosols in the size ranges smaller than 10 nm (nuclei mode), but these newly formed aerosols can grow larger by condensation and coagulation processes. Aitken mode aerosols include particles in the size range between $\sim$10 and 100 nm. Therefore, whereas primary aerosols can directly contribute to atmospheric aerosol mass concentrations, secondary aerosols can control both mass and number concentrations. Coagulation takes place between different sizes of aerosols. For large aerosols, wet and dry deposition (settling) is the sink process, whereas for small aerosols, coagulation is the major sink. An important climate effect is that aerosols can act as cloud condensation nuclei (CCN; larger than 50–60 nm) and can then contribute to cloud formation.

In addition to outdoor urban sources of aerosol, indoor sources are also of concern where indoor air quality is an important contributor to human health. Both indoor and outdoor aerosols have been strongly correlated to pulmonary and cardiovascular diseases. Although indoor particle concentrations can be similar to those in the outdoor environment, building filtration differences can result in significant variation in the relative compositional concentrations indoors. Indoor combustion processes such as smoking, cooking activities, and burning food are significant sources of indoor particles as are particles generated from cleaning activities and climate control systems. In addition to the home, the contribution of ultrafine particles from the workplace, especially from within offices, is also significant.

Research in atmospheric chemistry has come a long way since the 1948 Donora, Pennsylvania and the 1952 London Smog events. During the cold war of the 1950s, aerosol size distributions were measured by the Soviet Union as an intelligence strategy. Plumes provided signatures for the type of aircraft from characterizing aircraft emissions. However, understanding the composition of the emitted aerosols was more elusive, and there

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was a limited understanding of its importance.9 It was not until years later that sampling of aerosols became standard protocol. In the mid 1950s, the U.S. Congress recognized and addressed air pollution with legislation, and about a decade later, the Clean Air Act of 1963 was enacted with many subsequent revisions. Yet it was not until the late 1990s that the U.S. EPA recognized the potential health risk of fine aerosols, that is PM$_{2.5}$ (particulate matter <2.5 μm).10 Thus, the U.S. EPA’s records only show PM$_{2.5}$ measurement data since ~2000, although PM$_{10}$ (particulate matter <10 μm) measurements go back further in time. Aerosol mass measurements of PM$_{2.5}$ have not been sufficient to provide information to understand the complex urban aerosol source, chemical and physical processes, and their impact on climate, air quality, and human health. Recently, there has been great interest in developing technologies that allow one to measure aerosol chemical composition, sizes, aerosol mixing status, aging, and multiphase reactions as a function of location and time.

Because this is a perspective as opposed to a review article, our intention is to briefly summarize only some aspects of analytical instruments currently used for aerosol composition and size analysis for the nonspecialist. Emphasis is placed on particle/aerosol mass spectrometers, as these instruments in recent years have had the largest impact on the understanding of size-resolved chemical composition of atmospheric aerosols. For a more comprehensive description of the instruments mentioned here and other aerosol measurement techniques, authors are directed to several excellent comprehensive reviews.3,11–14 In addition, the Chow15 review provides a wealth of information on regulatory compliance measurements and filter measurements of aerosol particles. In this article, instruments used to characterize aerosol optical properties (e.g., total and back scattering, absorption, and refractive index) are not included; however, the reader is directed to other reviews11,12,16 for descriptions of various optical instruments such as the nephelometer, aethalometer, and cavity ring down spectroscopy.

### REAL-TIME ONLINE CHEMICAL ANALYSIS

In the 1990s, analytical instruments were specifically designed to investigate aerosol composition in real time. Several research groups worked on instrumental variations of mass spectrometry to analyze atmospheric aerosol, and within these groups, a new era of in situ atmospheric aerosol analysis began. Several review articles describe the detailed history of aerosol mass spectrometry.14,17–21 The first real time single particle mass spectrometer was developed by Davis in 1973, but significant progress was made starting in the 1990s and there are now more than 20 different aerosol mass spectrometers. Since 2000, more than 700 papers have been published using in situ methods for compositional characterization of atmospheric aerosols in addition to simultaneous information on particle size distributions. Compared to traditional filter sample methods which employ the gas- or liquid-chromatography technique, aerosol mass spectrometers have tremendous advantages in providing vast information of aerosol chemical composition in real time with minimal change of aerosol chemical properties during sampling analysis processes. A unique feature of aerosol mass spectrometers is that they can be used in field observations to provide characteristic chemical and physical properties of atmospheric aerosols in real time. The high time resolution allows one to correlate wind direction and speed with particle composition and thereby identify primary emission sources.22

An aerosol/particle mass spectrometer typically is comprised of a sampling inlet, the desorption/ionization region (e.g., laser desorption/ionization and thermal desorption followed by electron impact or chemical ionization), and a mass analyzer (e.g., time-of-flight (TOF) and quadrupole). Sizing is done during or after, the particles are introduced into the vacuum chamber for desorption/ionization processes. Simultaneous measurement of size thus allows size-resolved chemical composition analysis. Aerosol/particle mass spectrometers can be classified into two major classifications: (i) single aerosol mass spectrometers using laser vaporization/ionization method combined with a TOF mass analyzer and (ii) aerosol mass spectrometers using thermal desorption and electron impact or chemical ionization combined with a quadrupole, TOF, or ion trap mass analyzer. As described individually in the cited reviews,14,17–21 the first major classification includes rapid single-particle mass spectrometry (RSMS) by Johnston, particle analysis by laser mass spectrometry (PALMS) by Murphy, aerosol time-of-flight mass spectrometry (ATOFMS) by Prather, real time mass spectrometry (RTMS) by Riley and co-workers, single particle mass spectrometry by Miller and Baer, single particle laser ablation time-of-flight mass spectrometry (SPLAT) by Imre and Zelenyuk, and single particle analysis and sizing system (SPASS) spectrometry by Erdmann and co-workers.25

The second major classification includes Aerodyne aerosol mass spectrometry (AMS) by Aerodyne Inc., thermal desorption mass spectrometry (TDMS) by Ziemann, atmospheric pressure chemical ionization mass spectrometry (AP-CIMS) by Hoffmann, aerosol chemical ionization mass spectrometry (Aerosol-CIMS) by Smith, and thermal desorption chemical ionization mass spectrometry (TD-CIMS) by Smith and Eisele. At present, the ATOFMS and the Aerodyne AMS have been commercialized by TSI and Aerodyne Inc., respectively, and both possess a large group of users worldwide.

In PALMS,19 aerosols enter the ionization region and pass through a continuous YAG laser beam. The scattering signal triggers an excimer laser and the triggered excimer laser desorbs and ionizes the particles. The produced ions are transferred to the TOF mass analyzer. ATOFMS24,25 also uses a very similar ionization method but simultaneously measures positive and negative ions with two TOF mass analyzers. PALMS and ATOFMS both measure particle sizes with two visible lasers by measuring the time required for a certain size aerosol to move a known distance (aerosol size-time-of-flight). Different from most other single
aerosol laser mass spectrometers which size aerosols down to submicrometer sizes, RSMS detects particles down to ∼10 nm with aerodynamic focusing or an electrodynamic field lens.\textsuperscript{18,20} A major advantage of the laser ablation ionization method is that it can detect a wide range of chemical compositions including both refractory (sea salt, soot crustal residues, and metal elements) and nonrefractory material (sulfate, nitrate, ammonium, and organics) in real time. However, laser mass spectrometers usually do not provide quantitative information about chemical species due to strong fragmentation (especially for organic compounds), matrix effects (for sea salt, dust and metal containing particles), and rapid ion recombination reactions. Simultaneous measurements of PALMS, ATOFMS, and RSMS in Atlanta showed that each individual urban aerosol particle often contains a complex mixture of sulfate, nitrate, ammonium, crustal aluminum and silicon oxides, sea salt, black carbon soot, and various organic components.\textsuperscript{26} Single particles measurements made in other urban cities in the U.S., such as Houston and Pittsburgh, also showed the complex chemical composition of urban aerosol, including sulfate, ammonium, nitrate, ammonium, and other unidentified oxygen- and nitrogen-containing organic components\textsuperscript{27,28} demonstrating serious potential health effects of urban aerosols.

The Aerodyne AMS\textsuperscript{29} is currently the most widely used thermal vaporization aerosol mass spectrometer. It uses an aerodynamic lens inlet together with thermal vaporization and electron-impact mass spectrometry to measure the nonrefractory chemical composition of particles between ∼50 and 1000 nm. It utilizes electron impact ionization with a TOF mass analyzer and produces averaged data of ensemble aerosol particles.\textsuperscript{29} A large number of AMS observations made at various locations in both hemispheres have elucidated how organic aerosol (OA) transformed and transported globally (Figure 2); very often even freshly formed OA also rapidly undergo further aging and oxidation reactions with hydroxyl (OH) radical, ozone, and nitrate radical (NO$_3$) to become low volatility oxygenated OA (LV-OOA). In particular, OOA is found ubiquitous in urban environments\textsuperscript{7} (Figure 2). For example, a recent AMS measurement further showed that about 40–55% of urban aerosol in Los Angeles is OOA, with an O/C ratio of around 0.5.\textsuperscript{30} AMS measurements made in Mexico City also showed primary organic aerosol (POA) is semivolatile, while secondary organic aerosol (SOA) is less volatile than POA and aged SOA is essentially nonvolatile, indicating aging effects on the OA volatility.\textsuperscript{31}

TD-CIMS is designed to measure chemical composition of nanometer size aerosols (∼10 nm) using an aerodynamic lens.\textsuperscript{32} Combined with electron impact or chemical ionization, the thermal desorption method can provide quantitative or semiquantitative information of chemical species, which is an advantage over laser ionization mass spectrometers, but refractory material cannot be thermally vaporized and so are not detected with this method. TD-CIMS measurements by Smith et al.\textsuperscript{32} revealed that even nanometer size particles contain sulfate, ammonium, and organics including aminium in various atmospheric conditions including urban environments such as Atlanta and Mexico City.

\section*{OTHER CONTINUOUS OR SEMICONTINUOUS ONLINE CHEMICAL ANALYSIS}

Beyond mass spectrometry, various online chemical methods have been developed for urban aerosol analysis. These methods are often coupled with aerosol mass spectrometers to complement each other in determining chemical information and allow inter-comparison. Particle-into-liquid-sampler with ion chromatography (PILS-IC) measures aerosol bulk composition continuously online.\textsuperscript{33} In PILS, ambient aerosols are mixed with saturated water vapor to produce liquid droplets that can be analyzed by IC. PILS-IC measures the soluble ion fraction of aerosols and quantitatively measures a wide variety of ions, including NH$_4$\textsuperscript{+}, K$^+$, Na$^+$, Mg$^{2+}$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, and some short-chain organic acids are quantitatively detected with a time resolution of several minutes.\textsuperscript{33} PILS can also measure water-soluble organic compounds such as formate, acetate, and oxalate.\textsuperscript{34} These organic acids are a unique group of oxygenated organic compounds, formed either from primary aerosols or by aqueous oxidation reactions in aerosols, similarly to that in clouds and fogs.

Turpin et al.\textsuperscript{35} have developed the total (elemental/organic carbon) EC/OC instrument for in situ, quantitative measurements of fine aerosol EC and OC total mass concentrations. This technique converts both gas phase and aerosol phase organic compounds into carbon dioxide first with MnO$_2$ catalyst at 1000 °C and then to methane in a nickel-firebrick methanator at 500 °C. The resulting methane is measured by a flame ionization detector to calculate carbon content. By subtracting carbon content measured only from gas phase samples from those from both gas and aerosol phase together, total aerosol carbon concentrations are measured.

The use of natural isotope carbon-14 ($^{14}$C) from the total EC and OC further enables one to distinguish organic aerosols (especially OOA) between those formed from fossil fuel combustion and biogenic emission.\textsuperscript{36} In fossil material, $^{14}$C has already decayed significantly and thus the ratio of $^{14}$C/$^{12}$C can be used as an unambiguous marker for source apportionment of carbonaceous aerosols. This $^{14}$C method, also known as modern carbon measurement, can provide important information on how urban aerosols transported to rural areas and affect regional and global air chemistry.

The single particle soot photometer (SP2), developed by Droplet Measurement Technologies, Inc., measures light absorbing black carbon (BC) containing particles based on laser-induced incandescence.\textsuperscript{37} Unlike other instruments that measure optically absorbing aerosol masses, such as the multiangle absorption photometer (MAAP) and the photoacoustic spectrometer (PAS),\textsuperscript{1,16} this single particle instrument also identifies the mixing status of BC.

\begin{figure}
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\caption{Location of the AMS data sets analyzed. Colors for the study labels indicate the type of sampling location: urban areas (blue), <100 miles downwind of major cites (black), and rural/remote areas >100 miles downwind (pink). Pie charts show the average mass concentration and chemical composition: organics (green), sulfate (red), nitrate (blue), ammonium (orange), and chloride (purple) of nonrefractory particulate matter less than 1 micron in diameter. Reprinted with permission from ref 29. Copyright 2009 AAAS.}
\end{figure}
containing aerosols. Aerosol mixing status is crucial for addressing radiative forcing caused by soot.

Laser induced fluorescence (LIF), a technique well-known for detection of low concentrations of OH radicals in the atmosphere, has been also used to detect single particles containing organic carbon. A virtual impactor concentrator is used along with an aerodynamic-focusing-nozzle which forms a focused aerosol jet where single aerosols can be interrogated on-the-fly with a pulsed UV laser. Crossed diode laser beams indicate when an aerosol is traversing the sample region and are used to trigger the UV laser to fire, and fluorescence spectra are obtained. Measurements made with this new aerosol LIF technique in Maryland showed a unique capability to identify humic-like substances, dicyclic aromatics, and heterocyclics including the amino acid tryptophan in biological aerosols such as bacteria and spores.

### OFF-LINE CHEMICAL ANALYSIS

Scanning and transmission electron microscopies (SEM and TEM) have historically played a role and are the well-established off-line analytical techniques that provide the chemical speciation, morphology, and phase of individual aerosols. TEM has been useful for studying the structure of solid particles using electron diffraction and has been used in aerosol measurements. The addition of energy dispersive X-ray spectroscopy (EDX or EDS) provides elemental analysis of the individual aerosols so that chemical composition can be related to morphology and is often found as an attachment to SEM and TEM instruments. One drawback to electron microscopy, and for most imaging and characterization methods, is the time required to properly analyze a complete set of samples. However, the introduction of computer-controlled SEM permits routine analysis of a statistically significant number of aerosols in a sample set. Environmental SEM (ESEM) can operate at higher pressures than traditional SEM; permitting examination of insulating aerosols without the need for a conductive coating. In ESEM, the relative humidity in the sample chamber can be varied, allowing the hygroscopic behavior of an aerosol to be investigated.

Decesari et al. have applied proton nuclear magnetic resonance (1H NMR) spectroscopy to identify organic compound functional groups and to further identify aerosol sources and pollution levels. This unique application also allows relating source fingerprints to integral chemical properties of organic mixtures, which determine their reactivity and physical and chemical properties and fate of organic aerosol particles. Russell and co-workers have used Fourier transform-infrared (FT-IR) spectroscopy for functional group studies of organic and inorganic compounds. By using FT-IR together with Aerodyne AMS, they studied chemical bonds and molecular fragments from organic aerosols in various atmospheric environments.

### SIZE ANALYSIS

As reviewed by McMurray, at present, particle number concentrations are typically measured by condensation particle counters (CPCs) and aerosol sizes are measured by differential mobility analyzers (DMAs) which often are combined with CPCs together. A combination of a DMA and a CPC is also termed as a scanning mobility particle spectrometer (SMPS). These instruments are available commercially and have been used worldwide. Other sizing instruments include optical particle counters (OPC), aerodynamic particle sizers (APS), electrical mobility analyzers, and pulse height analyzers (PHA).

CPCs measure integral aerosol number concentration for aerosols larger than a certain minimum detectable size. In a typical CPC, water or n-butanol alcohol is used as a condensation vapor. Aerosols grow by condensation until they are sufficiently large to be detected optically (micrometer or submicrometer) and their concentrations are subsequently counted, either directly counting the individual droplets formed by condensation or indirectly by measuring light attenuation or scattering by those droplets. The commercially available CPCs can measure sizes larger than 3 nm. For sizes smaller than that, other types of vapor are used. For example, mixing fluids of diethylene glycol can be used to measure sizes as small as 1.5 nm. This new type of CPC allows one to study nucleation processes by observing clusters directly involved in nucleation processes.

SMPS or differential mobility particle sizes (DMPS) are used for size-resolved measurements of aerosols in the size range from ~3 to 1000 nm range. SMPS/DMPS includes a DMA and a particle counter, typically a CPC. The heart of SMPS/DMPS is the DMA. In a DMA, aerosol is first exposed to radiation sources to become multiply charged. The electrical mobility of an aerosol is inversely proportional to the aerosol geometric diameter. Aerosols in a narrow mobility range determined by the classifying voltage and flows are separated from the main flow and delivered to an aerosol counter. To complete the entire size range, it usually takes several minutes and the complete size distribution is obtained by carrying out measurements at a number of classifying voltages. Measurements made with the SMPS/DMPS have provided evidence that nucleation occurs in various atmospheric conditions including a large number of urban cities worldwide. For example, SMPS measurements made in Atlanta and Mexico City showed much higher growth rates of new particles than expected from condensation of sulfuric acid alone, indicating a significant contribution of the low volatility organic compounds on urban aerosol growth processes.

Aerosol hygroscopicity modifies the deposition pattern of inhaled aerosols in the human respiratory tract and therefore plays a role in human health. Hygroscopic properties also play a role in aerosol climate effects. One of the important applications of the DMA technique is in the tandem differential mobility analyzer (TDMA). The TDMA measures aerosol hygroscopic properties, evaporation, chemical reactions, and uptake of organic compounds. The most typical TDMA is the hygroscopic TDMA (HTDMA). In a HTDMA, aerosol particles are first dried. The dry aerosols are size-selected in the first DMA into a narrow quasi-monodisperse size. These size-classified aerosols are subsequently humidified and led into a second DMA where size distributions of these wet aerosols are measured. CPCs are used to determine the aerosol number concentrations in the aerosol outlet flow from the DMAs. Hygroscopic growth factors (the ratios of humidified and dry aerosol diameters) are measured as a function of relative humidity.

### FUTURE OUTLOOK

Urban aerosols represent a complex mixture of organic and inorganic compounds due to the diverse nature of their sources. Furthermore, aerosol chemical composition evolves in time through rapid reactions with atmospheric oxidants. The components in aerosols have variable volatility further complicating a full understanding of aerosol formation and aging processes. Yet, development of analytical techniques that can capture and quantify aerosol size, morphology, and complete chemical
composition is challenging. One of the most demanding areas of aerosol analysis is to understand the sources and chemistry of complex organic compounds within the aerosol phases. Because there are thousands of different organic compounds present, it would be useful to further classify (or sort out) chemical information as a function of their functional groups rather than to identify each individual component and to differentiate their sources in terms of primary and secondary organic aerosol. The current approach classifies OA particles roughly into several groups including POA and SOA, and OOA are further classified based on volatility as a function of the integral ratio of carbon to oxygen elements (C/O) and ratio of carbon to hydrogen elements (C/H) using the information obtained from Aerodyne AMS combined with aerosol thermodynamic calculations. Yet a more accurate and detailed understanding of the structure and the functional groups of organic compounds in aerosols is critically needed. Fully understanding their health effects is additionally complex. Because of the lack of such coupled information, the current air quality and climate models fail to accurately simulate the complete evolution and impacts of urban aerosols.

To understand the role of urban aerosol on human health, air quality, and climate, more sophisticated analytical techniques need to be developed and deployed in atmospheric field and health related laboratory studies. Further advances in aerosol mass spectrometry continue to be important to provide size-resolved, quantitative information of chemical species, inclusive of organic functional groups. Tandem mass analysis (MS/MS) (e.g., with ion trap) techniques can be used to identify organic molecular ions and structures. Also, soft ionization methods utilizing chemical ionization and vacuum UV (VUV) ionization and two step laser desorption/ionization can help to produce less fragmentation of organic compounds. Nevertheless, there continues to be an overarching need for improvement in quantitative chemical analysis of organic aerosols. Additionally, statistical analysis is a crucial aspect of handling extremely large aerosol mass spectra data sets. Although there continues to be advances for this application in analytical instrumentation, from mass spectrometry and beyond, there also continues to be a divide in the type of information obtained from the same aerosol sample or sample set. There is a need to identify and quantify organic molecules and their functional groups in addition to inorganic compounds during the same analysis as well as size and morphology of individual aerosols. Additionally, high-throughput analysis combined with advanced data set analysis methods is important to obtain useful statistics from aerosol samples obtained from different locations and sampled continuously to provide more than just a snapshot but to further identify and confirm underlying mechanisms of aerosol aging. Ultimately, to fully understand the health impacts of urban aerosols, complete quantitative atmospheric aerosol data is needed. Only with a proper understanding of these extremely complex systems can appropriate legislation be enacted.

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: slee19@kent.edu (S.-H.L.); allen@chemistry.ohio-state.edu (H.C.A.).

**BIOGRAPHIES**

Shan-Hu Lee is Associate Professor of Atmospheric Chemistry in College of Public Health, Kent State University; her research group is conducting laboratory studies and atmospheric observations of atmospheric aerosol nucleation and growth. She has a B.S. in Analytical Chemistry from Beijing University of Chemical Technology and a Ph.D. in Physical Chemistry from University of Tokyo and was a postdoctoral fellow in Massachusetts Institute of Technology and National Oceanic and Atmospheric Administration.

Heather C. Allen is a Professor of Chemistry in Department of Chemistry, The Ohio State University; her research group conducts laboratory spectroscopy and imaging studies of aequous surfaces to understand molecular organization with relevance to atmospheric aerosol, geochemistry, ocean surface, and biomembranes. She has a B.S., M.S., and Ph.D. in Chemistry from University of California Irvine and was NOAA Postdoctoral Fellow in Climate Change at the University of Oregon.

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