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Recent Advances and Some Remaining Challenges in Analytical Chemistry of the Atmosphere

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The atmosphere is a complex mixture of natural and anthropogenic compounds with diverse properties, producing adverse effects on human health, ecology, ozone depletion, visibility, and climate. Increasing our understanding of the chemical properties of these compounds and their physical processes is vital for properly assessing their roles in pollution and climate and ultimately establishing effective control strategies. However, the identities and concentrations of many atmospheric species, particularly organic components, are still unknown. To characterize the chemical composition of the complex atmosphere, a complementary collection of different analytical methodologies is typically used. This review discusses recent instrumental developments and advances made between the years 2000 and 2002, for measuring gas-phase components—oxides of nitrogen, SO₂, volatile organic compounds (VOCs)—and particulate matter. Gas-phase species and their reaction processes are far better characterized and understood than their particle-phase counterparts, since detailed measurements of gas-phase components have been carried out for decades. In the field of particle-phase measurements, new instruments are being developed at a rapid rate in an effort to produce methods with lower detection limits, shorter temporal resolution, and increased selectivity with the goal of increasing our understanding of atmospheric processes. The disparity in numbers of new techniques for the gas versus particle phases is reflected in this review, which briefly discusses the current state of gas-phase measurements for major pollutants and highlights the many recent advances in particle-phase measurements. The need for new analytical methodologies and the areas where key challenges remain in atmospheric chemistry are highlighted.

Last year marked the 50th anniversary of the infamous London fog event. Stagnant weather and increased levels of pollutants such as SO₂ and soot particles led to a sharp rise in mortality levels. Today, the most visible form of air pollution is smog. Vehicular

and industrial emissions are major contributors to poor air quality in urban areas. During hot sunny days, high-density metropolitan areas, such as Los Angeles and Mexico City, are affected by “brown smog” due to photochemical reaction processes among organic compounds, oxides of nitrogen, and ozone. National Ambient Air Quality Standards (NAAQS) have been established for certain gas-phase species as well as particulate matter (O₃, NO₂, SO₂, CO, PM₁₀, PM_{2.5}, and Pb).

The focus of air quality research over the years has been on gas-phase species, with less efforts placed on particle-phase characterization. Measurements of gas-phase pollutants such as ozone and NO_x (= NO + NO₂) are relatively routine, but more sensitive and selective techniques are still being developed. In this review, recent instrumental advances for several important gaseous pollutants including oxides of nitrogen, SO₂, and VOCs are discussed. Key processes between oxides of nitrogen and VOCs leading to ozone formation are well documented (1, 2). Anthropogenic emissions of oxides of nitrogen and VOCs are produced by a wide range of combustion processes. Oxides of nitrogen are key players in pollution on the west coast, whereas sulfur species, in particular SO₂, play a dominant role on the east coast. Sulfur dioxide is emitted anthropogenically by combustion processes of materials including fossil fuels and coal, can dissolve in aqueous droplets, and react to form sulfates and other compounds that affect climate, contribute to the acidity of rain and fogs, and harm humans.

Aerosols are stable solid or liquid suspensions in air. Throughout this review, the terms “aerosol” and “particle” are used interchangeably. The environmental impact of particles is wide ranging. Particles directly affect climate by enhancing the scattering and absorption of solar radiation, therefore altering the amount of solar radiation reaching the Earth’s surface (3). Also, light scattering from aerosols leads to visibility degradation (4, 5). Aerosols have an indirect effect on climate by acting as cloud condensation nuclei (CCN) hence affecting cloud properties and the hydrological cycle (3, 6). They can also act as sinks for reactive species since their exposed surfaces can catalyze heterogeneous reactions (2, 7–14). Despite their importance, key obstacles remain in creating robust, reproducible techniques for quantitatively characterizing particles with high time resolution. Limited information exists on the spatial and temporal variability of particles in the atmosphere.

Suspended particles have diameters ranging from several nanometers up to 100 μ m. Coarse particles, such as wind-blown dust, pollen, plant fragments, and sea salt, are mechanically generated and usually larger than 1 μ m. In contrast, particles in the fine mode, generated from combustion and photochemical

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processes, are generally smaller than 1 μm . The ultrafine mode includes particles with diameters below 100 nm. Particles are not as long-lived as gases and generally only remain in the atmosphere for time periods of days to weeks, depending on their size (15). Particle toxicity is strongly dependent on chemical composition and physical properties (i.e., size and surface area) (16–19). Epidemiological studies correlating mortality to particle concentrations have concluded that airborne particles, in particular those with diameters below 1 μm , produce a range of adverse effects on human health, including respiratory and cardiovascular disease (16, 20, 21). Recent health effects studies have led the United States Environmental Protection Agency (EPA) to add a $\text{PM}_{2.5}$ (particles with aerodynamic diameters smaller than 2.5 μm) standard (<http://www.epa.gov/airs/criteria.html>).

Since the NAAQS modification, field-intensive campaigns have been conducted in various regions throughout the United States with recent focus placed on EPA Supersites (<http://www.epa.gov/ttn/amtic/supersites.html>) to characterize particulate matter, support health effects and exposure research, and test new emerging technologies. Also, EPA PM health effects centers have been established (<http://www.epa.gov/ttn/amtic/pmcenter.html>) to examine the health effects of particulate matter, specifically investigating exposure, dosimetry and extrapolation modeling, toxicology, and epidemiology. Several international campaigns have been carried out at different locations throughout the world. These multidisciplinary campaigns have involved multiple satellites, aircraft, ship-based, and ground-based measurements aimed at determining the climate forcing by aerosols, their outflow and evolution, and feedbacks on regional and global climate. Some recent campaigns include the Indian Ocean Experiment (INDOEX, <http://www.indoex.ucsd.edu>), the Pacific Exploratory Missions (PEM, http://www-gte.larc.nasa.gov/pem/pem_hmpg.htm), the Transport and Chemical Evolution over the Pacific (TRACE-P, <http://www-gte.larc.nasa.gov/trace/tracep.html>), the Tropospheric Aerosol Radiative Forcing Observational Experiment (TARFOX), and the International Global Atmospheric Chemistry (IGAC) Aerosol Characterization Experiments (e.g., ACE-1, ACE-2, ACE-Asia, <http://www.igac.unh.edu>, <http://saga.pmel.noaa.gov/>).

Numerous methods have been developed and employed to characterize the complex mixture of gases and particles that make up the atmosphere. Several factors must be taken into consideration when instruments are being developed for these measurements. Ideally, the technique should be fast enough to track changes in concentration, composition, or both as they occur, sensitive enough to detect the species of interest, and free of interferences from other species present in the same air mass. Further considerations may include weight and portability of the developed instrumentation.

Substantial advancements and discoveries have been achieved in the past decade with the use of a wide variety of techniques. However, due to the restriction on the total number of references (200), this review focuses on the recent instrumental developments between 2000 and 2002 in atmospheric chemistry, specifically describing those methods used for tropospheric measurements. Trends, advancements, and developments for the different techniques employed for measuring several inorganic gases (oxides of nitrogen, SO_2), organic species (VOCs), and particulate matter are presented in this paper. Some of the remaining key

Table 1. List of Acronyms

ACE	Aerosol Characterization Experiment
AMS	aerosol mass spectrometer
CCN	cloud condensation nuclei
CIMS	chemical ionization mass spectrometry
CRDS	cavity ring down spectroscopy
CCSEM/EDX	computer-controlled scanning electron microscopy with energy-dispersive X-rays
DOAS	differential optical absorption spectroscopy
DMA	differential mobility analyzer
EC	elemental carbon
EI	electron impact
EDX	energy-dispersive X-ray
EPA	Environmental Protection Agency
EPMA	electron probe X-ray microanalysis
FAGE	fluorescence assay gas expansion
FA-SIFT-MS	flowing afterglow selective ion flow drift tube mass spectrometer
FT-ICR-MS	Fourier transform-ion cyclotron resonance-mass spectrometry
FT-IR	Fourier transform infrared spectroscopy
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
HPLC	high-performance liquid chromatography
IC	ion chromatography
IEC	ion exchange chromatography
ICPMS	inductively coupled plasma mass spectrometry
IGAC	International Global Atmospheric Chemistry
INDOEX	Indian Ocean Experiment
IR	infrared spectroscopy
ITMS	ion trap mass spectrometry
LCW	liquid core waveguide
LDI	laser desorption ionization
LIF	laser-induced fluorescence
MIESR	matrix isolation electron spin resonance
MIMS	membrane introduction mass spectrometry
NAAQS	National Ambient Air Quality Standards
Nd:YAG	neodymium–yttrium aluminum garnet
NMR	nuclear magnetic resonance
OC	organic carbon
PAH	polycyclic aromatic hydrocarbon
PAN	peroxyacetyl nitrate
PEM	Pacific Exploratory Mission
$\text{PM}_{2.5}$	particulate matter with aerodynamic diameter $\leq 2.5 \mu\text{m}$
PM_{10}	particulate matter with aerodynamic diameter $\leq 10 \mu\text{m}$
PTR-MS	proton-transfer reaction mass spectrometer
REMPI	resonance enhanced multiphoton ionization
SEC	size exclusion chromatography
SIMS	secondary ion mass spectrometry
SOA	secondary organic aerosol
SPI	single-photon ionization
SPE	solid-phase extraction
SPME	solid-phase microextraction
SPMS	single-particle mass spectrometry
TDLS	tunable diode laser spectroscopy
TDPBMS	thermal desorption particle beam mass spectrometer
TOF	time-of-flight mass spectrometer
TARFOX	Tropospheric Aerosol Radiative Forcing Observational Experiment
TRACE-P	Transport and Chemical Evolution over the Pacific
UV	ultraviolet absorption spectroscopy
VOCs	volatile organic compounds
VUV	vacuum ultraviolet
WSOC	water-soluble organic carbon

challenges are highlighted, showing the opportunities for new and exciting research in the area of air pollution.

GAS-PHASE MEASUREMENTS

Table 1 summarizes many of the acronyms used throughout this paper. The field of gas-phase measurements spans decades

of instrumental development with a wide range of techniques used for these measurements. Gas-phase measurements have been recently reviewed by Parrish (22) and Finlayson-Pitts (15). Measurements of organic compounds in air are discussed in detail by Aragon (23). In this review, only recent instrumental developments for measuring several major gas-phase inorganic species (i.e., oxides of nitrogen, SO_2) and VOCs are discussed.

Inorganic Gases (Oxides of Nitrogen, SO_2). As a whole, most of the advances for characterizing gas-phase species in recent years have occurred in than trace gas measurements. To our knowledge, no new developments for ozone analysis have been made during the time period of this review. Many advances have been made with the goal of obtaining higher time resolution and lower detection limits needed for airborne sampling (see reviews 15 and 22). Recent advances in lasers, including diode lasers, have allowed for sensitive and selective on-line trace gas detection in airborne instruments with second to minute temporal resolution (24). For example, Akimoto (25) developed a resonance-enhanced multiphoton ionization time-of-flight mass spectrometer (REMPI-TOF) for monitoring NO with a detection limit of 10 pptv with 1-min integration. Benter (26) reported lower detection limits for both NO and NO_2 by employing REMPI-TOF with photoionization performed near the inlet orifice. Detection limits for this technique are reported to be 0.5 pptv for NO and 5 pptv for NO_2 (20-s integration time). Although sensitive and capable of rapid measurements, mass spectrometry methods have the disadvantages of the cost and size of the required instrumentation. Fluorescence assay gas expansion (FAGE) offers a fast, sensitive, more compact alternative. FAGE was first applied for NO_2 measurements by O'Brien (27). Recently, several NO_2 FAGE methods (28–30) have reached lower detection limits on the order of tens of pptv with less than 1-min temporal resolution. However, as with other fluorescence methods, correction for the effect of humidity is needed. Cavity ring down spectroscopy (CRDS) has also been applied for NO and NO_2 measurements (31–33). However, these instruments have not been field tested and their sensitivity might not be adequate for ambient measurements. Ball (34) and Brown (35) developed CRDS techniques for measuring NO_3 with sensitivities of 2 pptv with 2.5 min and 0.5 pptv with 5-s acquisition times. Brown (35) reported the first field application of CRDS for NO_3 and N_2O_5 in the troposphere. In this determination NO_3 is measured directly in one cavity while N_2O_5 is thermally decomposed to NO_3 , which is measured in a second cavity. The difference between the measured NO_3 concentrations in the two cavities provides a direct measure of the N_2O_5 concentrations with 5-s time resolution. CRDS offers superior time resolution over differential optical absorption spectroscopy (DOAS) and matrix isolation electron spin resonance (MIESR). CRDS instruments are portable with high time resolution, allowing their application in aircraft, ship, balloon, and tower-based measurements.

HONO has been measured by chemiluminescence, DOAS, laser-induced fluorescence (LIF), atmospheric pressure ionization mass spectrometry, and denuder methods. Chemiluminescence cannot distinguish HONO from other oxides of nitrogen such as NO_2 , peroxyacetic nitric anhydride (PAN), or organic nitrates. DOAS is a sensitive technique but is often large and expensive. DOAS provides a compact alternative to LIF with low tens of pptv detection limits after 15-min integration. Denuder methods may

offer a more affordable means of detecting HONO. However, dry denuders suffer from artifacts caused by NO_2 , SO_2 , and PAN and require longer integration times on the order of several hours to obtain several hundreds of pptv detection limits. Wet denuder techniques have been developed for measuring HONO and HNO_3 , which are subject to less artifacts. However, NO_2 can form HONO on the wet surfaces.

Recently, wet chemical colorimetric methods have been automated and incorporated with liquid core waveguides (LCWs). Wiesen (36) and Dasgupta (37) used LCWs to provide a long optical path for the absorption cells. Since the refractive index of the Teflon tubing used was less than the solution contained within it, a LCW is formed where light undergoes multiple total reflections on the inner walls of the tubing resulting in long optical path lengths. A detection limit of 3 pptv after 4 min of integration was reported by Wiesen (36). Dasgupta also applied LCWs to differentiate HONO and NO_2 . NO_2 and HONO differed by their solubility, diffusivity through the polymer, and rate of consumption by the stripping solution. These properties are used to distinguish between HONO and NO_2 using different active lengths of the gas-permeable Teflon AF LCW or wall thickness. Zhou (38) also recently used high-performance liquid chromatography (HPLC) analysis for HONO and HNO_3 detection with a sampling frequency of 10 min with 2-min integration time. Detection limits are less than 1 pptv for HONO and 20 pptv for HNO_3 . Schiller (39) directly measured ambient HONO using tunable diode laser spectroscopy (TDLS) with as low as 300 pptv detection limit with 30-min integration. Although TDLS it is able to measure nocturnal concentrations, some development is needed to measure typical daytime concentrations. Direct measurement of HONO by Fourier transform infrared spectroscopy (FT-IR) is limited by spectral overlap of other absorbing species. Finlayson-Pitts (40) reacted HONO with HCl to produce ClNO and H_2O . The ClNO signal was measured to quantify HONO in laboratory applications. However, heterogeneous reactions on the chamber walls need to be considered. Zhang (41) developed a CRDS for direct measurement of HONO with a tunable dye laser. Absorption of other gases (i.e., NO_2 and SO_2) and background scattering can interfere. It can be used to detect concentrations in the range of 10 ppb–10 ppm by employing three wavelengths with a sensitivity of 5 ppb in 15-s integration. Further developments are needed to extend the instrument to lower detection limits perhaps by using longer integration times and more highly reflective mirrors.

HNO_3 measurements by FT-IR, TDLS, filter pack, denuder, and transition flow reactor methods were compared in a field study and showed a high degree of variability (42). They often lack time resolution, sensitivity, and reliability. Chemical ionization mass spectrometry (CIMS) techniques achieve ~10 pptv detection limits within seconds of integration using SiF_5^- (43) or HSO_4^- (44) as the reagent ion. The sticky characteristics of HNO_3 make quantification difficult since it easily adsorbs to surfaces. In the past two years, the major advances in HNO_3 detection have involved sampling inlet designs used for measuring HNO_3 in the boundary layer (45) and in aircraft measurements (46).

SO_2 has been determined by several techniques including fluorimetry, DOAS, chemiluminescence, gas chromatography (GC), as well as filter, denuder, and wet chemical methods (15, 22). Nicks (47) developed a continuous sulfur dioxide detector

able to measure tens of pptv in less than 1 min. Thornton (48) developed an atmospheric pressure ionization mass spectrometer for SO₂ able to reach lower detection limits with better temporal resolution. Isotopically labeled SO₂ (³⁴S¹⁶O₂) is continuously introduced as an internal standard providing a highly sensitive technique unaffected by sample loss and instrumental fluctuations. The 40-ms temporal resolution allows direct comparison with common tracers such as NO_x, condensation nuclei, and ozone. The temporal resolution of this technique is superior (1 order of magnitude) to that reported for other instrumentation (49).

Trace Organic Gases (VOCs). VOCs are present in the atmosphere at ppb to ppt concentrations. Gas chromatography/mass spectrometry (GC/MS) is one of the most common methods for measuring organic compounds. Generally, VOCs are preconcentrated by solid-phase extraction (SPE), solid-phase microextraction (SPME) (50–56), or sorbent trapping (57) and then thermally desorbed for analysis. SPME is rapidly becoming the method of choice for VOC collection, offering low detection limits and short collection times. SPME involves absorbing the analyte onto fused-silica fibers that are chemical modified and subsequently thermally desorbing the species of interest for analysis. SPME offers a fast, simple, sensitive, solvent-free, reusable technique for VOC collection, making it preferable to other collection methods.

Recently, CIMS has been applied for on-line VOC measurements. CIMS uses ion–molecule reactions that induce soft ionization processes as opposed to electron impact (EI), a technique notorious for generating significant fragmentation. Lindinger (see review by de Gouw (58) and references therein) developed a proton-transfer reaction mass spectrometer (PTR-MS) to monitor VOCs on-line. H₃O⁺ is chosen as the reagent ion for atmospheric trace gases or VOCs since generally they have higher proton affinities than water. Compared to GC/MS, this technique has a fast response time (seconds or less) and detection limits of 10–100 ppt depending on the analyte. For example, the detection limit for PAN can be as low as 70 pptv with 15-s integration (59). The fast response time allows the application of PTR-MS to the study of atmospheric chemistry of VOCs in rapidly changing air masses. PTR-MS has been field deployed for aircraft, ship-based, and ground-based measurements and used to study relevant atmospheric reactions in environmental chambers, for example, OH radical oxidation of α - and β -pinene. To distinguish between isobaric species, PTR-MS can be coupled to GC for preseparation of the compounds of interest. Alexander (60) combined membrane introduction mass spectrometry (MIMS) with PTR-MS using a poly(dimethylsiloxane) (PDMS) membrane for measuring acetone and propanal and demonstrated its ability to resolve isobaric interferences. Alexander suggested MIMS would allow measurements at high humidity that would not be possible otherwise.

Other groups have developed CIMS instruments for detecting VOCs that have yet to be field tested. For example, McEwan (61) developed a flowing afterglow selective ion flow drift tube mass spectrometer (FA-SIFDT-MS) for VOC determination. In this technique, the reagent ion of interest (H₃O⁺, O₂⁺, NO⁺) is mass selected by a quadrupole and subsequently drifts into a reaction flow tube against a pressure gradient through a Venturi orifice undergoing chemical ionization. FA-SIFDT-MS has been applied

for measuring nitrogen compounds in soils, volatile species in smoked and unsmoked cigarettes and marijuana, and the residence time of solvent in the human body with ppb detection limits. Cooks (62) developed a new method using atmospheric pressure chemical ionization mass spectrometry for the analysis of semi-volatile organic compounds. The reagent ions (N₂⁺, O₂⁺, H₃O⁺, O₂⁻) are produced by nebulization in a heated chamber with N₂ sheath gas followed by a corona discharge. With this system, a detection limit of 50 pptv has been reported for methyl salicylate. MIMS was used by Allen (63) with H₃O⁺ as the reagent ion for chemical ionization followed by ion trap mass spectrometry (ITMS). Although water is not excluded from entering the membrane, space charge effects are not observed for air samples when this technique is employed. Reported detection limits for laboratory-generated VOCs and semi-VOCs are on the order of pptv to several ppmv depending on the analyte (after 1-min sampling with a PDMS membrane and O₂⁺ chemical ionization). Further developments for these instruments are needed to extend measurements to the ppt range desirable for ambient measurements. Ion mobility spectrometry has also been used for VOC analysis (64).

Photoionization has also been used for VOC analysis. Zimmerman (65) performed single-photon ionization (SPI) of VOCs with vacuum ultraviolet (VUV) ionization. SPI offers a wider range of applications than REMPI. The use of 118 nm (10.6 eV) allows for the analysis of aliphatic compounds that are not detected by REMPI. Zimmermann also developed a portable time-of-flight mass spectrometer that can be easily switched between REMPI and SPI (65). The method of SPI used in these experiments was introduced several decades ago and involves the generation of VUV radiation by frequency tripling a Nd:YAG by focusing 355-nm pulses into a third harmonic generation rare gas cell. Shot-to-shot variations in the power density make quantification difficult. Zimmerman (66) introduced a less expensive, unique way of producing monochromatic, intense, brilliant VUV radiation using an electron beam (10–20 keV) pumped rare gas excimer lamp. The VUV SPI is coupled with a reflectron TOF for on-line monitoring. Detection limits for some aromatic compounds are reported to be in the low ppmv. Although suitable for measurements of exhaust, further improvements are needed for the application of this instrument to atmospheric measurements.

PARTICLE-PHASE MEASUREMENTS

Methods for measuring particle composition have been recently reviewed by McMurry (67) and Chow (68). Off-line methods rely on the collection of particles onto filters followed by postanalysis with techniques such as scanning electron microscope (SEM), electron probe X-ray microanalysis (EPMA), neutron activation, X-ray fluorescence, atomic absorption, particle-induced X-ray emission, GC, HPLC, ion chromatography (IC), secondary ion mass spectrometry (SIMS), inductively coupled plasma mass spectrometry (ICPMS), and laser microprobe mass spectrometry. Off-line techniques suffer from both positive and negative artifacts. Evaporative losses can occur during sampling, storage, and transport of samples and can cause significant errors. Changes in relative humidity and temperature can affect the partitioning between the gas and condensed phase. Gases can be absorbed onto filters or react with surfaces. Particulate filter loading can lead to some of the sample being blown or bounced

off the filter. Samples may also further react with other compounds within the sample or the collection substrate during storage. These techniques can be costly, results may not be known until months after collection, and long sampling times are required to obtain a detectable signal from the analyte of interest, therefore precluding the observation of short time chemical changes in air masses. Semicontinuous methods automate the sampling and analysis steps, therefore eliminating many of the artifacts associated with off-line methods. Currently, great interest exists for the development of on-line methods for particulate matter analysis (e.g., optical methods, ion chromatography, and mass spectrometry) that can overcome many of the effects mentioned above. Single-particle methods provide real-time information on the chemical composition of individual particles, information that is often coupled with size measurements. In this section, recent developments in off-line, semicontinuous, and single-particle analysis will be reviewed.

Off-Line Methods. Although off-line methods present several disadvantages as mentioned above, they offer the opportunity to gain additional information that cannot be obtained on-line. For example, microscopy methods provide unique information regarding the morphology and chemical inhomogeneity of the particles. Fewer technological advances have been made in the development of new off-line techniques in comparison to those for semicontinuous and single-particle methods. Major developments for the analysis of inorganic and organic components present in aerosols using off-line techniques are discussed below.

Inorganic Species. Isotope measurements previously used to elucidate gas-phase mechanisms show great promise for determining the origin of sulfate and nitrate in particles (69, 70). Van Grieken (71) applied thin-window EPMA for the semiquantitative determination of light elements in single particles. The use of thin-window energy-dispersive X-ray (EDX) detectors instead of Be windows allows for measurement of light elements such as Na, C, N, and O. This technique has been recently applied to the study of samples from sea salt (71), biomass burning, fly ash, and sediments from polluted lakes (72). Laskin (73) recently applied computer-controlled scanning electron microscopy with energy-dispersive analysis of X-rays (CCSEM/EDX) for the analysis of submicrometer particles with diameters as small as 0.1 μm . Grazing exit EPMA has been implemented for the analysis of samples of atmospheric relevance. In this method, an X-ray detector is placed at a very sharp grazing angle relative to the substrate surface, such that the detector is blind to the X-rays from the specimen depth and only particle X-rays are efficiently detected. A single jet of air is used to deposit particles onto moving copper grids supported by carbon films (74), allowing time-resolved single-particle data to be studied. The film has the advantage of having low background in the SEM/EDX and low backscattered electron yield compared to the particles. This allows analysis to be performed on particles down to 0.1–0.2 μm . CCSEM/EDX has been used to monitor nitrate formation on sea salt particles in Houston (75), showing diurnal variations in sea salt conversion to NaNO_3 , consistent with previous observations by single-particle mass spectrometry (SPMS) (76).

Organic Compounds. SIMS is commonly used for depth profiling of aerosols. Peterson (77, 78) applied TOF-SIMS to organic and inorganic species on the surface of single particles

with a gentle, surface-sensitive approach. Most SIMS applications are performed in the dynamic mode that uses high ion doses for elemental analysis as a function of depth. Most of the molecular information is lost when operating under these conditions. Static mode SIMS limits the primary ion doses to 10^{12} – 10^{13} ions/ cm^2 and therefore only allows for molecular information on the ions present in the monolayers of the surface to be obtained. In this technique, the sample is bombarded with a pulsed beam of high-energy Ga^+ ions (5–25 eV). Charged species are ejected off the surface as secondary ions and detected by time-of-flight mass spectrometry. TOF-SIMS has been applied to size-segregated filter samples from forest fires, snowmobile exhaust, lava, sea salt, and dust and has shown that the surface composition of these particles can be very different from the core. For example, forest fire samples were reported to have a characteristic surface layer of amides of *n*-alkanoic acids, traces of nitrates, sulfates, and highly oxygenated organic fragments. Mass spectral analysis of sea salt particles suggested the presence of an organic microlayer over the aqueous layer on these particles.

As described below in further detail, characterization of the organic fraction of aerosols remains a challenge and relatively little is known regarding the detailed chemical species (2, 79, 80). The complex mixture of organic compounds makes molecular identification difficult. Carbonaceous components present in aerosols are typically studied by GC/MS after single or multiple organic extractions and derivatization steps. However, many polar compounds cannot be analyzed using GC/MS. Rogge (81) identified over 80 individual organic compounds, mostly nonpolar and semipolar, although these compounds accounted only for approximately 10% of the total organic fraction. Polar organic compounds can be derivitized to less polar or nonpolar compounds to enable GC separation, therefore allowing identification of a larger fraction of the organic mass. For example, derivatization has been used to identify carbonyl-containing compounds such as mono- and dicarboxylic acids (82). However, derivatization methods require prior knowledge of the aerosol composition since derivatization is compound specific. Recently, Claeys (83) developed a separation method for the analysis of levoglucosan and saccharidic compounds in atmospheric aerosols with characterization by GC/ITMS, which allowed the detection, for the first time, of saccharidic compounds (other than monosaccharidic) such as arabitol, mannitol, glucose, fructose, inositol, and sucrose.

Liquid chromatography can be used for the analysis of low volatility polar compounds. Schrader (84) coupled liquid chromatography with two-dimensional nuclear magnetic resonance (NMR) methods and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) to study the ozonolysis reaction mechanism of α -pinene. The high resolution of FT-ICR-MS allows distinction between isobaric species having different empirical formulas. Two-dimensional NMR not only allows identification of trans and cis isomers but also their connectivity. This technique allows the identification of expected Criegee radicals and low-pressure compounds such as pinonic acid, pinic acid, and hydroxypinonic acid, therefore showing promise for the determination of reaction mechanisms when synthetic standards are not readily available.

Several researchers have taken different, simplified approaches by employing spectroscopic techniques such as fluorescence,

ultraviolet absorption spectroscopy (UV), FT-IR, and proton nuclear magnetic resonance (^1H NMR) (85–88) for functional group identification. Although these techniques have provided valuable information, they rarely account for the majority of the organic carbon present in the aerosols. Also, these methods can only provide information on the functional groups present and no information on the organic species present. However, the combination of chemical separations with other spectroscopic methods offers new possibilities for characterizing the organic fraction of aerosols.

Advances have been made in sampling and characterizing the water-soluble organic carbon (WSOC) in aerosols, fogs, clouds, and rain have also employed functional group analysis (85–90). Although the organic contribution to acid deposition and CCN activity has received increasing interest, less results have been reported for the organic fraction in clouds, fog, and rain compared to their inorganic counterparts (91). Thus, in this review, some attention is placed on the characterization of the water-soluble organic fraction. The presence of inorganic ions in aerosols can interfere with organic characterization by optical methods such as FT-IR and UV. Varga (92) extracted WSOC in aerosol samples by SPE. A large fraction of the WSOC is separated from inorganic components, thus facilitating chemical characterization by optical techniques. For this method, aerosol samples are collected on filters and extracted. The SPE column is then rinsed with water to remove inorganic compounds and dried. The retained organics are then eluted off the SPE columns using methanol. The extracted organic fraction is separated by ion exchange chromatography followed by FT-IR, UV, and fluorescence analysis. The inorganic removal efficiency for this method is confirmed by capillary electrophoresis, with more than 99% efficiency being reported. However, the method designed for this extraction is intended to retain both lipophilic and hydrophilic organic compounds and does not present optimal retention for extremely hydrophilic compounds. About 60% of the WSOC in aerosol samples has been isolated using this procedure, therefore making it possible to apply a number of analytical techniques that were limited by the presence of inorganic compounds in a large fraction of the aerosol.

Fuzzi (93, 94) investigated WSOC in fog, water, and aerosols using ion exchange chromatography (IEC) and ^1H NMR. By coupling these two techniques, they were able to account for 80–90% of the WSOC, identifying several major classes of compounds. IEC can be used to separate carboxylic acids in their ionic form by using an anion exchange stationary phase. Previous findings have reported carboxylic acids as the major class of WSOC in atmospheric aerosols (see ref 95 and references therein), therefore making fractionation by this technique well suited for this application. Results have shown organic acids were the dominant fraction in the studied WSOC (93). The WSOC can be divided into three different groups based on their chromatographic behavior, with the organic matter analyzed by ^1H NMR. The first set of compounds comprises those that are unretained in the chromatographic column, consisting of neutral and basic compounds, mainly polyols and polyethers. The second group of compounds elute at low ionic strength and are identified as mono- and dicarboxylic acids (mostly hydroxylated aliphatic acid compounds). The last set of polyacidic compounds elute at high ionic

strength and are identified as acidic unsaturated compounds (mostly compounds with aliphatic character, some with several hydroxyl groups). Not many aromatic compounds are observed in these fractions.

This fractionation technique has also been applied to laboratory-generated soot particles (96). Soot originates from incomplete combustion and consists of a mixture of elemental and organic carbon. Although believed to be largely hydrophobic, soot can act as CCN and become part of the cloud droplets in the presence of water-soluble inorganic components internally mixed within the soot particle (97–99) or by formation of oxidation products on the particle surface (100–102). Thus, soot particles can act as CCN even in the absence of soluble inorganic compounds. WSOC has been studied for *n*-hexane flame soot as a function of ozone oxidation (96). The oxidation products consisted mainly of aromatic polyacids, which can decrease the surface tension of cloud droplets and therefore influence cloud microphysics and radiative properties (103, 104). The ^1H NMR spectra of these polyacids were analogous to those for humic-like substances (complex class of refractory, high molecular weight, heterogeneous organic compounds often associated with biomass burning and degradation of plant matter).

Size exclusion chromatography (SEC) can be used to separate compounds depending on their molecular weight. Andracchio (105) investigated macromolecular WSOC in aerosols and cloud droplets by SEC. Prior to SEC, the extracts were fractionated using HCl, methanol, and NH_3 solutions. Using this method, separation of organic components by their hydrophilic properties and molecular weight can be accomplished. Krivacsy (106) also studied macromolecular WSOC in fog and aerosol samples by SEC with UV and electrospray ionization mass spectrometry detection. The mass spectra and retention times suggest the presence of humic-like substances in these samples.

Another challenge in the analysis of carbonaceous compounds involves the quantification of the total organic content and the distinction between elemental carbon (EC) (or black carbon depending on the method employed) and organic carbon (OC), species that are commonly quantified by thermographic, optical, and thermal optical analysis (81). In the thermographic methods, the sample is heated in a temperature-programmed chamber in the presence of one or more gases. OC is identified by its evolution under a heating cycle in the presence of either He or N_2 . EC is defined as the fraction that subsequently evolves in a gas mixture containing mainly oxygen. The evolved carbon passes over a catalyst converting the gases to CH_4 or CO_2 and is subsequently quantified by IR or a flame ionization detector. In these methods, the split between EC and OC is based on temperature or the type of purge gas used for analysis. However, some organic carbon compounds pyrolyze or “char” before they evolve under the He/ O_2 segment of the analysis. If not accounted for, this can result in an overestimation of the elemental carbon fraction. Thermal optical methods are often used to correct for this charring. One disadvantage of these methods is the fact that standards for OC/EC analysis suitable for ambient measurements are still lacking. Therefore, the precision of such instrumentation cannot be properly determined. In recent comparative studies on aerosol samples (107–109), the quantification of OC and EC has shown great variability on similar samples because of the different

protocols used. Thus, unless the same protocol is applied for OC/EC determination, measurements from different studies and different sources are not comparable.

Semicontinuous Methods. As mentioned earlier, semicontinuous methods automate the collection and analysis steps. Some of the problems related to off-line techniques can be overcome using semicontinuous methods. For example, an automated thermal optical analysis method has been developed to measure OC and EC concentrations with 2-h averaging and deployed during a recent field campaign (110).

Hering (111) developed an automated particulate nitrate monitor with 10-min averaging time. A 2.5- μm cyclone is placed at the beginning of the inlet to remove larger particles. Particles are drawn through an inlet and collected by humidified impaction through a Nafion dryer. An activated charcoal-impregnated ceramic honeycomb denuder is placed upstream of the humidifier to minimize interferences from vapors such as nitric acid. The particles impact a resistively heated stainless steel strip and flash vaporize into a nitrogen carrier gas stream. Gases pass over a molybdenum catalyst that converts oxides of nitrogen to NO, which is quantified by a chemiluminescent NO_x analyzer (based on chemiluminescence reaction with ozone). Because of the short sampling time and humidifying collection, evaporative losses are reduced. For measurements carried out in the Los Angeles area, the detection limit was 0.4 $\mu\text{g}/\text{m}^3$. Hering also developed a sulfate monitor in a similar fashion employing a SO₂ pulsed fluorescence analyzer.

Automated collection and analysis of soluble particulate matter by ion chromatography has been applied by several research groups. Dasgupta (112) developed a two-channel automated wet denuder system for the analysis of acidic gases and soluble particles using gradient elution. In this instrument, gas is introduced at the bottom of a parallel plate denuder that is continuously wetted. A PM_{2.5} cyclone is placed in the second channel to remove large particles. Aerosols are then processed by a second wet denuder to remove gases and further collected on glass fiber filters. The aerosol samples are preconcentrated prior to IC introduction. The IC alternates between the gas and particle analysis by switching between two anion columns every 15 min. Analysis has been performed for Cl⁻, NO₂⁻, NO₃⁻, SO₄⁻, and oxalate, with detection limits on the order of subnanogram/cubic meter.

Kasper-Giebl (113) also developed an automated wet parallel denuder system for soluble particles and gases. A gradient elution is used instead of an isocratic elution to allow analysis of low molecular weight organic acids and other inorganic components. The denuder consists of a long vertical quartz tube that is flattened in the middle to form parallel plates that are coated with sodium silicate. The denuder is continuously wetted, and air is drawn at the bottom of the denuder. The effluent is collected on a frit and pumped with a peristaltic pump to a concentrator column where it is concentrated prior to chromatographic analysis. Particles are grown by supersaturation in a heated water vapor and the formed droplets impacted onto a cooled Teflon-coated maze impactor. Two chromatographic systems are used for cation and anions, alternating between gas and aerosol measurements every 30 min. The detection limits are on the order of a few to tens of pptv for gas phase and 0.02–0.79 $\mu\text{g}/\text{m}^3$ for particles.

Weber (114) developed a particle into liquid sampler (PILS) based on previous instrumentation by Khlystov (115) and Dasgupta (116) to measure several inorganic ions in particulate matter. Water is pumped through a stainless tube coiled with a heater to produce a flow of steam into the mixing chamber. The temperature in the chamber is held close to ambient to prevent volatility loss. Ambient particles larger than 80 nm are mixed with a saturated water vapor through a stainless steel tube to create droplets that are collected inertially. The walls are cooled to maintain supersaturation and remove water vapor before droplet collection. Implementation of this cooled condenser tube allows separation of the formed droplets from the vapor. Droplets are directed through a single circular nozzle impactor with a 1- μm cut. A single jet inertial impactor is used to collect the droplets onto a vertical glass plate that is continually flushed with water. The liquid sample from the base of the plate is then injected into a dual-channel IC for analysis of anions and cations with isocratic elution. Measurements can be taken every 7 min. Detection limits for Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, Ca²⁺, and K⁺ are 0.1 $\mu\text{g}/\text{m}^3$. Dasgupta (112) has reported lower detection limits for anion measurements. Kasper-Giebl (113) reported detection limits similar to those obtained with PILS but with poorer temporal resolution.

Elemental analysis of aerosols has been performed by inductively coupled plasma-atomic emission spectroscopy and ICPMS using light scattering techniques to measure the particle diameters prior to elemental analysis. However, the light scattering systems have difficulty sizing particles smaller than 0.1 μm . Implementing a differential mobility analyzer (DMA) extends the particle detection to the nanometer range. A DMA selects particles of a certain electrical mobility producing a monodisperse stream of aerosols. The instrumentation described by Myojo (117) utilizes size selection of particles with a DMA prior to ICPMS analysis. An argon sheath flow in the DMA is used instead of particle-free air to reduce the effect of electrical difference between argon and air in the plasma flame. Femtogram sensitivity, comparable to that obtained with previously described techniques, has been reported for lead in 30–140-nm lead nitrate particles. Okada (118) also used a DMA with argon sheath flow to size select 5–40-nm particles. In that case, the spray chamber in the ICPMS is bypassed to directly introduce particles to a plasma torch through a stainless steel pipe. ICPMS was used to measure Sn and Pb concentrations in solder and lead particles. The detection limit for 30-nm particles is 1×10^5 particles/cm³. Although these techniques are targeted toward semiconductor applications, they have potential for real-time size-resolved elemental analysis of ultrafine particles outside the clean room environment.

ICP instruments are quite large, thus limiting their application for field studies. Microwave-induced plasma is an alternative to ICP techniques. Plasma is produced by microwave discharge in a minitorch. This plasma technique can analyze metal and nonmetal compounds. Compared to ICP, it has low power consumption (200 W or less) and better air tolerance, and requires lower gas flows. Duan (119) developed a compact, on-line, portable microwave plasma coupled to atomic emission spectroscopy device using CCD detection for monitoring particulate matter. The reported detection limits are on the order of submicrograms to a

few micrograms per cubic meter. This portable instrument has yet to be field tested for ambient measurements.

Aerosol mass spectrometry methods are becoming more widely used and have been recently reviewed by Prather (120) and Johnston (121). The most recent advances have focused on detecting ultrafine particles and speciating organic compounds (122). In these applications, particles can be size selected by dynamic focusing (123) using an aerodynamic lens system or a DMA prior to introduction. Because of the high transmission efficiency, the implementation of aerodynamic lenses is becoming more widely applied in aerosol mass spectrometers for the analysis of ultrafine particles (124). Tightly focused particle beams are produced by passing the aerosol through a series of contractions and expansions prior to nozzle expansion, using multiple short capillaries or thin-plate orifices with successively smaller or equal diameters on the order of a few millimeters. Close to 100% transmission efficiency of all particles can be obtained over the size range of interest. Worsnop et al. (125) incorporated such an inlet into an aerosol mass spectrometer (AMS) for the analysis of particles between 70 and 500 nm in diameter. In this instrument, particles are tightly focused into a narrow beam using an aerodynamic lens system. After focusing, a skimmer collimates the particles into a sizing region where particles are separated by their terminal velocities (which depend on their aerodynamic diameters). Smaller particles travel faster than larger particles. A rotating chopper with two radial slits modulates the particle beam. Using the known flight distance, time-resolved particle sizing is accomplished. An IR photodiode detector pair defines the start of the time-of-flight cycle used to synchronize the detection. Volatile and semivolatile components are flash vaporized upon impact with a heater tube (typically at 600 °C) and ionized by electron impact. An ensemble of particles is used to quantify the chemical components using quadrupole mass spectrometry. AMS can monitor organic carbon, H₂O, NH₄⁺, nitrate, and sulfate. However, sea salt, dust, and elemental carbon cannot be detected because they are not vaporized by the heater. AMS has two modes of operation—mass scanning without sizing or sizing of particle with a selected m/z .

Ziemann developed a thermal desorption particle beam mass spectrometer (TDPBMS) to investigate secondary organic aerosols (SOAs) formation (126). SOAs are formed from VOC reactions via gas-to-particle partitioning (1). SOA formation is typically studied in chambers by filter sampling followed by GC/MS analysis. Such methods are time-consuming, have relatively low sensitivity, offer poor time resolution for studying reactions, and are subject to sampling artifacts. In addition, the study of polar compounds requires derivatization. TDPBMS overcomes these difficulties. The TDPBMS uses an aerodynamic lens to focus particles with aerodynamic diameters between 20 and 500 nm, which are then collimated by two flat plate skimmers. Particles are vaporized upon impact on a resistively heated V-shaped molybdenum foil. Ionization is carried out by electron impact with ions being mass analyzed by quadrupole mass spectrometry. Particles can be size selected with a DMA prior to analysis. To separate complex mixtures, particles are impacted onto a cryogenically cooled metal foil that is slowly heated to separate components based on their vapor pressures (127). This technique offers a time resolution superior to GC methods. Furthermore,

thermal decomposition is less likely since vaporization occurs quickly and at lower temperatures under vacuum. TDPBMS studies allow reactions to be investigated at relevant atmospheric concentrations. TDPBMS with temperature programming has been used to observe secondary aerosol formation in 1-tetradecene with ozone (128–130) and cyclohexane and other cyclic alkenes with ozone (131). It has also been used to identify products from diesel exhaust (132) where mostly branched alkanes and alkyl-substituted cycloalkanes for unburned fuel and motor oil have been observed along with sulfuric acid particles. The vapor pressures for several organic compounds have also been determined using a TDPBMS (133).

Single-Particle Mass Spectrometry. SPMS allows real-time acquisition of the chemical composition of individual particles. Particle sizing is often performed by light scattering methods using one or two continuous wave lasers. Besides the ability to observe single-particle associations, these techniques can provide information on the presence of organic carbon, elemental carbon, sulfates, nitrates, sea salt, dust, metals, etc. Laser desorption ionization (LDI) is often used for single-particle MS analysis. A single laser is frequently employed to desorb and ionize compounds present in the particles. LDI is often coupled with time-of-flight mass spectrometry. Single-particle analysis provides valuable information on the chemical associations in single particles. The use of dual polarity time-of-flight mass spectrometers allows for complementary chemical information to be obtained, information that is essential for studying heterogeneous processing and determining particle sources.

A number of techniques for SPMS analysis have been developed (120–122) and their application for the characterization of atmospheric particles has increased in recent years (134–158). Variations of basic SPMS techniques have been used for atmospheric analysis (76, 123, 157, 159–168). A bottleneck for SPMS is still present in the development of appropriate data analysis tools (169–173). A major strength of SPMS lies in the ability to track and identify particles from various sources in the atmosphere (174–177). Several approaches have been taken for the quantification of these SPMS methods—correlation with other off-line (177–180) and semicontinuous techniques (136), multivariate methods (144, 181), ensemble averaging (182, 183), and evaluation of relative response factors (184, 185).

Recently developed SMPS have implemented aerodynamic lenses (122). Zachariah (186) developed a single-particle mass spectrometer that has been applied for measuring particle chemical composition and reaction kinetics. Particles are focused through an aerodynamic lens and ablated by a high-power (1.7×10^{10} W/cm) frequency-doubled Nd:YAG (532 nm) laser freely firing at 10 Hz (analogous to a previous design by Reents (182, 183)). Mass analysis is carried out using a reflectron TOF. No molecular information is obtained, but instead the elementary stoichiometry of species in the particle is determined. Implementation of the aerodynamic lens inlet in this system allows higher transmission efficiency over the capillary inlet used by Reents. It has been used for the study of the kinetics of thermal decomposition of metal nitrate aerosols with results compared to those obtained with standardized thermogravimetric analysis.

Single laser methods are adequate for qualitative analysis but quantification can be difficult, especially for organic compounds.

To understand the desorption and ionization processes as they occur in individual particles, a number of molecular dynamic simulations of the involved processes have been performed (187, 188). Depending on the laser fluence, LDI methods that use a single laser can produce extensive fragmentation of organic compounds, thus making speciation and quantification difficult. Furthermore, incomplete vaporization makes ionization more sensitive to species present on the surface than those in the core.

Two-step laser methods perform desorption and ionization using two separate lasers, thus allowing independent optimization of each process. Lower laser fluences are required, thus resulting in less fragmentation. Furthermore, matrix effects that can deleteriously affect quantitation are eliminated by liberating neutral species from the particles with an infrared laser pulse in the first step. Implementing a second laser requires more optimization (e.g., power, alignment, focal volume, and timing of lasers, etc). Prather (189) first investigated two-step LDI with an aerosol time-of-flight mass spectrometer on single particles. Baer further investigated this application and implemented an aerodynamic lens inlet (189, 190). Particles are focused into a narrow beam through and aerodynamically sized by measuring their time of flight between two continuous wave lasers separated by a known distance. The speed of the particle determines the time when a tunable CO₂ (infrared) laser (desorption) and subsequently an excimer (ultraviolet) laser (ionization) fire, and the analysis is followed by time-of-flight mass spectrometry. Baer (191) further improved this system using a VUV radiation for the ionization step in order to carry out single-photon ionization, demonstrating the ability for quantification of polycyclic aromatic hydrocarbons (PAHs) while gaining molecular ion information. This two-step method had also been applied to depth profiling on glycerol samples coated with oleic acid (192). Since dimensions of CO₂ lasers can be quite large for field applications, replacement of the IR or optical parametric oscillator laser with thermal desorption has been introduced as an alternative for portable instruments (193). For this purpose, a cartridge heater is inserted between the ion extraction plates and particles are vaporized at 500–700 K followed by VUV ionization. Oleic acid produced spectra with detection efficiencies comparable to those obtained using a CO₂ laser. No size range has yet been reported for this instrument. However, like AMS, elemental carbon, sea salt, and dust are not vaporized because of the use of thermal desorption, therefore making their determination not possible.

SUMMARY

As highlighted in this review, advances in the past two years have produced more rapid real-time atmospheric analysis techniques, many with higher sensitivity and selectivity. The focus of recent developments for gas-phase characterization involves more compact and sensitive instrumentation with better time resolution. Optical techniques such as FAGE offer lower detection limits with shorter integration times, providing several advantages over previous routine optical techniques. Cavity ring down spectroscopy has been used for ambient measurements of NO₃ and N₂O₅, species not detectable using fluorescence. Several key developments are described using mass spectrometry, which provides a fast and sensitive technique for the study of both the gas- and particle-phase components. Mass spectrometers provide high

temporal resolution but many still have the disadvantage of large instrumental size when compared with optical techniques. However, major advances in reducing the size of mass spectrometers have occurred in recent years motivated by a need for better methods for the detection and rapid identification of biological agents (194,195).

In the area of particle analysis, many novel methods exist for physical measurements (67, 196); however, chemical analysis challenges remain in quantification, organic speciation, lower size analysis limits, increased sampling efficiencies to allow for better time response, miniaturization, and data analysis approaches. The implementation of new inlets including aerodynamic lenses has increased the detection efficiency and thus the analysis speed while extending the lower size limit to include the detection of ultrafine particles. The strength of single-particle MS techniques lies in their ability to use single-particle fingerprints to identify sources and reaction processes occurring on particles in the atmosphere. MS techniques use a variety of different approaches for creating ions including filament desorption coupled with EI, chemical ionization, and LDI. EI sources are well suited for quantification of certain species commonly observed in atmospheric particles, but the use of the thermal desorption process limits their application to the study of compounds that can be vaporized on a heated surface, precluding the observation of many atmospherically relevant components such as elemental carbon, sea salt, and dust particles. These species can be detected using laser desorption methods such as those described herein. MS analysis of individual particles has been extended down to smaller ultrafine particles; however, most of these techniques free fire the LDI lasers, reducing the overall sampling efficiency. In addition, quantification is challenging for LDI methods due to shot-to-shot variations in ion intensities and sample matrix effects that depend on the desorption and ionization processes, but significant progress in this area has been achieved in the past few years. Chemical ionization has been applied successfully for the analysis of organic species in both the gas and particle phases, providing a sensitive and selective tool for organic speciation. CI can be used to selectively detect specific classes of organics, in contrast to EI, which lacks selectivity and produces extensive fragmentation, making interpretation difficult. Two-step LDI methods and shorter wavelengths (191) have also been used for organic analysis, showing reduced fragmentation and promise for the quantification of organic compounds such as PAHs.

One key need for the composition analysis of aerosols is the development of standards for calibrating the rapidly evolving instruments. The most common method for validating an instrument involves comparison with another instrument measuring the same species of interest. However, each instrument has its own set of uncertainties, so a common standard such as NIST standards would allow for direct determination of the accuracy of the measurement. The importance of such validation procedures has been nicely highlighted in a recent article on differentiating between organic and elemental carbon (108).

As methods for aerosol analysis continue to evolve, new challenges arise such as the need for rapid on-line identification tools for bioaerosols (197, 198). It is possible that single-particle MS instruments, whose major strength lies in their ability to differentiate between sources, may allow for on-line differentiation

of spores from other background particles in the environment (199). The ability to distinguish between microorganisms has been demonstrated using off-line MS (200). Extremely exciting times lie ahead in an area where new discoveries are being made on almost a daily basis. There is no doubt that this area of research will certainly benefit from the present and future involvement of analytical chemists who can provide valuable scientific insights and tools to help advance the current state of atmospheric science.

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LITERATURE CITED

- Atkinson, R. *Atmos. Environ.* **2000**, *34*, 2063–2101.
- Jacob, D. J. *Atmos. Environ.* **2000**, *34*, 2131–2159.
- Haywood, J.; Boucher, O. *Rev. Geophys.* **2000**, *38*, 513–543.
- Watson, J. G. *J. Air Waste Manage. Assoc.* **2002**, *52*, 628–713.
- Charlson, R. J.; Schwartz, S. E.; Hales, J. M.; Cess, R. D.; Coakley, J. A.; Hansen, J. E.; Hofmann, D. J. *Science* **1992**, *255*, 423–430.
- Ramanathan, V.; Crutzen, P. J.; Kiehl, J. T.; Rosenfeld, D. *Science* **2001**, *294*, 2119–2124.
- Finlayson-Pitts, B. J.; Hemminger, J. C. *J. Phys. Chem. A* **2000**, *104*, 11463–11477.
- Jang, M. S.; Czoschke, N. M.; Lee, S.; Kamens, R. M. *Science* **2002**, *298*, 814–817.
- Grassian, V. H. *J. Phys. Chem. A* **2002**, *106*, 860–877.
- Gutzwiller, L.; Arens, F.; Baltensperger, U.; Gaggeler, H. W.; Ammann, M. *Environ. Sci. Technol.* **2002**, *36*, 677–682.
- Arens, F.; Gutzwiller, L.; Baltensperger, U.; Gaggeler, H. W.; Ammann, M. *Environ. Sci. Technol.* **2001**, *35*, 2191–2199.
- Usher, C. R.; Al-Hosney, H.; Carlos-Cuellar, S.; Grassian, V. H. *J. Geophys. Res., [Atmos.]* **2002**, *107*, 4713.
- Moise, T.; Rudich, Y. *J. Geophys. Res., [Atmos.]* **2000**, *105*, 14667–14676.
- Betram, A. K.; Ivanov, A. V.; Hunter, M.; Molina, L. T.; Molina, M. J. *J. Phys. Chem. A* **2001**, *105*, 9415–9421.
- Finlayson-Pitts, B. J.; Pitts, J. N. *Chemistry of the Upper and Lower Atmosphere*; Academic Press: San Diego, 2000.
- Pope, C. A.; Dockery, D. W.; Schwartz, J. *Inhalation Toxicol.* **1995**, *7*, 1–18.
- Schwartz, J.; Dockery, D. W.; Neas, L. M. *J. Air Waste Manage. Assoc.* **1996**, *46*, 927–939.
- Laden, F.; Neas, L. M.; Dockery, D. W.; Schwartz, J. *Environ. Health Perspect.* **2000**, *108*, 941–947.
- Morawska, L.; Zhang, J. F. *Chemosphere* **2002**, *49*, 1045–1058.
- Dockery, D. W.; Pope, C. A.; Xu, X. P.; Spengler, J. D.; Ware, J. H.; Fay, M. E.; Ferris, B. G.; Speizer, F. E. *N. Engl. J. Med.* **1993**, *329*, 1753–1759.
- Brunekreef, B.; T., H. S. *Lancet* **2002**, *360*, 1233–1242.
- Parrish, D. D.; Fehsenfeld, F. C. *Atmos. Environ.* **2000**, *34*, 1921–1957.
- Aragon, P.; Atienza, J.; Climent, M. D. *Crit. Rev. Anal. Chem.* **2000**, *30*, 121–151.
- Richter, D.; Fried, A.; Wert, B. P.; Walega, J. G.; Tittel, F. K. *Appl. Phys. B* **2002**, *75*, 281–288.
- Lee, S. H.; Kajii, Y.; Akimoto, H. *Environ. Sci. Technol.* **2000**, *34*, 4434–4438.
- Garnica, R. M.; Appel, M. F.; Eagan, L.; McKeachie, J. R.; Benter, T. *Anal. Chem.* **2000**, *72*, 5639–5646.
- George, L. A.; O'Brien, R. J. *J. Atmos. Chem.* **1991**, *12*, 195–209.
- Thornton, J. A.; Wooldridge, P. J.; Cohen, R. C. *Anal. Chem.* **2000**, *72*, 528–539.
- Matsumi, Y.; Murakami, S.; Kono, M.; Takahashi, K.; Koike, M.; Kondo, Y. *Anal. Chem.* **2001**, *73*, 5485–5493.
- Matsumoto, J.; Hirokawa, J.; Akimoto, H.; Kajii, Y. *Atmos. Environ.* **2001**, *35*, 2803–2814.
- Kosterev, A. A.; Malinovsky, A. L.; Tittel, F. K.; Gmachl, C.; Capasso, F.; Sivco, D. L.; Baillargeon, J. N.; Hutchinson, A. L.; Cho, A. Y. *Appl. Opt.* **2001**, *40*, 5522–5529.
- Everts, R.; Staicu, A.; Dam, N.; Van Vliet, A.; Ter Meulen, J. J. *Appl. Phys. B* **2002**, *74*, 465–468.
- Lauterbach, J.; Kleine, D.; Kleinermanns, K.; Hering, P. *Appl. Phys. B* **2000**, *71*, 873–876.
- Ball, S. M.; Povey, I. M.; Norton, E. G.; Jones, R. L. *Chem. Phys. Lett.* **2001**, *342*, 113–120.
- Brown, S. S.; Stark, H.; Ciciora, S. J.; McLaughlin, R. J.; Ravishankara, A. R. *Rev. Sci. Instrum.* **2002**, *73*, 3291–3301.
- Heland, J.; Kleffmann, J.; Kurtenbach, R.; Wiesen, P. *Environ. Sci. Technol.* **2001**, *35*, 3207–3212.
- Milani, M. R.; Dasgupta, P. K. *Anal. Chim. Acta* **2001**, *431*, 169–180.
- Huang, G.; Zhou, X. L.; Deng, G. H.; Qiao, H. C.; Civerolo, K. *Atmos. Environ.* **2002**, *36*, 2225–2235.
- Schiller, C. L.; Locquiao, S.; Johnson, T. J.; Harris, G. W. *J. Atmos. Chem.* **2001**, *40*, 275–293.
- Wingen, L. M.; Barney, W. S.; Lakin, M. J.; Brauers, T.; Finlayson-Pitts, B. J. *J. Phys. Chem. A* **2000**, *104*, 329–335.
- Wang, L. M.; Zhang, J. S. *Environ. Sci. Technol.* **2000**, *34*, 4221–4227.
- Hering, S. V.; Lawson, D. R.; Allegrini, I.; Febo, A.; Perrino, C.; Possanzini, M.; Sickles, J. E.; Anlauf, K. G.; Wiebe, A.; Appel, B. R.; John, W.; Ondo, J.; Wall, S.; Braman, R. S.; Sutton, R.; Cass, G. R.; Solomon, P. A.; Eatough, D. J.; Eatough, N. L.; Ellis, E. C.; Grosjean, D.; Hicks, B. B.; Womack, J. D.; Horrocks, J.; Knapp, K. T.; Ellestad, T. G.; Paur, R. J.; Mitchell, W. J.; Pleasant, M.; Peake, E.; Maclean, A.; Pierson, W. R.; Brachaczek, W.; Schiff, H. L.; Mackay, G. I.; Spicer, C. W.; Stedman, D. H.; Winer, A. M.; Biermann, H. W.; Tuazon, E. C. *Atmos. Environ.* **1988**, *22*, 1519–1539.
- Huey, L. G.; Dunlea, E. J.; Lovejoy, E. R.; Hanson, D. R.; Norton, R. B.; Fehsenfeld, F. C.; Howard, C. J. *J. Geophys. Res., [Atmos.]* **1998**, *103*, 3355–3360.
- Mauldin, R. L.; Tanner, D. J.; Eisele, F. L. *J. Geophys. Res., [Atmos.]* **1998**, *103*, 3361–3367.
- Furutani, H.; Akimoto, H. *J. Geophys. Res., [Atmos.]* **2002**, *107*, 4016.
- Neuman, J. A.; Huey, L. G.; Dissly, R. W.; Fehsenfeld, F. C.; Flocke, F.; Holecck, J. C.; Holloway, J. S.; Hübler, G.; Jakoubek, R.; Nicks, D. K.; Parrish, D. D.; Ryerson, T. B.; Sueper, D. T.; Weinheimer, A. J. *J. Geophys. Res., [Atmos.]* **2002**, *107*, 4436.
- Nicks, D. K.; Benner, R. L. *J. Geophys. Res., [Atmos.]* **2001**, *106*, 27769–27776.
- Thornton, D. C.; Bandy, A. R.; Tu, F. H.; Blomquist, B. W.; Mitchell, G. M.; Nadler, W.; Lenschow, D. H. *J. Geophys. Res., [Atmos.]* **2002**, *107*, 4632.
- Eisele, F. L.; Berresheim, H. *Anal. Chem.* **1992**, *64*, 283–288.
- Koziel, J. A.; Noah, J.; Pawliszyn, J. *Environ. Sci. Technol.* **2001**, *35*, 1481–1486.
- Koziel, J. A.; Odziemkowski, M.; Pawliszyn, J. *Anal. Chem.* **2001**, *73*, 47–54.
- Koziel, J.; Jia, M. Y.; Khaled, A.; Noah, J.; Pawliszyn, J. *Anal. Chim. Acta* **1999**, *400*, 153–162.
- Wang, L. M.; Lord, H.; Morehead, R.; Dorman, F.; Pawliszyn, J. *J. Agric. Food Chem.* **2002**, *50*, 6281–6286.
- Zini, C. A.; Augusto, F.; Christensen, E.; Smith, B. P.; Caramao, E. B.; Pawliszyn, J. *Anal. Chem.* **2001**, *73*, 4729–4735.
- Augusto, F.; Koziel, J.; Pawliszyn, J. *Anal. Chem.* **2001**, *73*, 481–486.
- Koziel, J.; Jia, M. Y.; Pawliszyn, J. *Anal. Chem.* **2000**, *72*, 5178–5186.
- Wang, J. L.; Chen, W. L.; Lin, Y. H.; Tsai, C. H. *J. Chromatogr., A* **2000**, *896*, 31–39.
- de Gouw, J.; Warneke, C.; Karl, T.; Eerdekens, G.; van der Veen, C.; Fall, R. *Int. J. Mass Spectrom.* **2003**, *223*, 365–382.
- Hansel, A.; Wisthaler, A. *Geophys. Res. Lett.* **2000**, *27*, 895–898.
- Alexander, M.; Boscaini, E.; Lindinger, W.; Mark, T. D. *Int. J. Mass Spectrom.* **2003**, *223*, 763–770.
- Freeman, C. G.; McEwan, M. J. *Aust. J. Chem.* **2002**, *55*, 491–494.
- Charles, L.; Riter, L. S.; Cooks, R. G. *Anal. Chem.* **2001**, *73*, 5061–5065.
- Allen, T. M.; Cisner, M. E.; Hemberger, P. H.; Wilkerson, C. W. *Int. J. Mass Spectrom.* **2001**, *212*, 197–204.
- Li, F.; Xie, Z.; Schmidt, H.; Sielemann, S.; Baumbach, J. I. *Spectrosc. Spectral Anal.* **2002**, *22*, 1025–1029.
- Muhlberger, F.; Zimmermann, R.; Kettrup, A. *Anal. Chem.* **2001**, *73*, 3590–3604.
- Muhlberger, F.; Wieser, J.; Ulrich, A.; Zimmermann, R. *Anal. Chem.* **2002**, *74*, 3790–3801.
- McMurry, P. H. *Atmos. Environ.* **2000**, *34*, 1959–1999.
- Wilson, W. E.; Chow, J. C.; Claiborn, C.; Wei, F. S.; Engelbrecht, J.; Watson, J. G. *Chemosphere* **2002**, *49*, 1009–1043.
- Lee, C. C. W.; Savarino, J.; Cachier, H.; Thiemens, M. H. *Tellus Ser. B* **2002**, *54*, 193–200.
- Savarino, J.; Alexander, B.; Darmohusodo, V.; Thiemens, M. H. *Anal. Chem.* **2001**, *73*, 4457–4462.
- Osán, J.; Szaloki, I.; Ro, C. U.; Van Grieken, R. *Mikrochim. Acta* **2000**, *132*, 349–355.
- Osán, J.; Kurunczi, S.; Torok, S.; Worobiec, A.; Van Grieken, R. *Mikrochim. Acta* **2002**, *139*, 111–117.
- Laskin, A.; Cowin, J. P. *Anal. Chem.* **2001**, *73*, 1023–1029.
- Laskin, A.; Iedema, M. J.; Cowin, J. P. *Aerosol Sci. Technol.* **2003**, *37*, 246–260.
- Laskin, A.; Iedema, M. J.; Cowin, J. P. *Environ. Sci. Technol.* **2002**, *36*, 4948–4955.
- Gard, E. E.; Kleeman, M. J.; Gross, D. S.; Hughes, L. S.; Allen, J. O.; Morrical, B. D.; Fergenson, D. P.; Dienes, T.; Galli, M. E.; Johnson, R. J.; Cass, G. R.; Prather, K. A. *Science* **1998**, *279*, 1184–1187.

- (77) Peterson, R. E.; Tyler, B. J. *Atmos. Environ.* **2002**, *36*, 6041–6049.
- (78) Peterson, R. E.; Tyler, B. J. *Appl. Surf. Sci.* **2003**, *203*–*204*, 751–756.
- (79) Jacobson, M. C.; Hansson, H. C.; Noone, K. J.; Charlson, R. J. *Rev. Geophys.* **2000**, *38*, 267–294.
- (80) Turpin, B. J.; Saxena, P.; Andrews, E. *Atmos. Environ.* **2000**, *34*, 2983–3013.
- (81) Rogge, W. F.; Mazurek, M. A.; Hildemann, L. M.; Cass, G. R.; Simoneit, B. R. T. *Atmos. Environ. Part A* **1993**, *27*, 1309–1330.
- (82) Kawamura, K.; Steinberg, S.; Ng, L.; Kaplan, I. R. *Atmos. Environ.* **2001**, *35*, 3917–3926.
- (83) Pashynska, V.; Vermeylen, R.; Vas, G.; Maenhaut, W.; Claeys, M. J. *Mass Spectrom.* **2002**, *37*, 1249–1257.
- (84) Schrader, W.; Geiger, J.; Godejohann, M.; Warscheid, B.; Hoffmann, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 3998–4001.
- (85) Havers, N.; Burba, P.; Lambert, J.; Klockow, D. J. *Atmos. Chem.* **1998**, *29*, 45–54.
- (86) Gundel, L. A.; Daisey, J. M.; Decarvalho, L. R. F.; Kado, N. Y.; Schuetzle, D. *Environ. Sci. Technol.* **1993**, *27*, 2112–2119.
- (87) Blando, J. D.; Porcja, R. J.; Li, T. H.; Bowman, D.; Lioy, P. J.; Turpin, B. J. *Environ. Sci. Technol.* **1998**, *32*, 604–613.
- (88) Suzuki, Y.; Imai, S.; Kawakami, M.; Masuda, Y.; Akasaka, K. *Bull. Environ. Contam. Toxicol.* **1998**, *60*, 355–362.
- (89) Spaulding, R. S.; Talbot, R. W.; Charles, M. J. *Environ. Sci. Technol.* **2002**, *36*, 1798–1808.
- (90) Blando, J. D.; Turpin, B. J. *Atmos. Environ.* **2000**, *34*, 1623–1632.
- (91) Krupa, S. V. *Environ. Pollut.* **2002**, *120*, 565–594.
- (92) Varga, B.; Kiss, G.; Ganszky, I.; Gelencser, A.; Krivacsy, Z. *Talanta* **2001**, *55*, 561–572.
- (93) Decesari, S.; Facchini, M. C.; Fuzzi, S.; Tagliavini, E. *J. Geophys. Res., [Atmos.]* **2000**, *105*, 1481–1489.
- (94) Fuzzi, S.; Facchini, M. C.; Decesari, S.; Matta, E.; Mircea, M. *Atmos. Res.* **2002**, *64*, 89–98.
- (95) Chebbi, A.; Carlier, P. *Atmos. Environ.* **1996**, *30*, 4233–4249.
- (96) Decesari, S.; Facchini, M. C.; Matta, E.; Mircea, M.; Fuzzi, S.; Chughtai, A. R.; Smith, D. M. *Atmos. Environ.* **2002**, *36*, 1827–1832.
- (97) Hallett, J.; Hudson, J. G.; Rogers, C. F. *Aerosol Sci. Technol.* **1989**, *10*, 70–83.
- (98) Lammel, G.; Novakov, T. *Atmos. Environ.* **1995**, *29*, 813–823.
- (99) Weingartner, E.; Bartsch, H.; Baltensperger, U. *Atmos. Environ.* **1997**, *31*, 2311–2327.
- (100) Chughtai, A. R.; Jassim, J. A.; Peterson, J. H.; Stedman, D. H.; Smith, D. M. *Aerosol Sci. Technol.* **1991**, *15*, 112–126.
- (101) Chughtai, A. R.; Brooks, M. E.; Smith, D. M. *J. Geophys. Res., [Atmos.]* **1996**, *101*, 19505–19514.
- (102) Chughtai, A. R.; Miller, N. J.; Smith, D. M.; Pitts, J. R. *J. Atmos. Chem.* **1999**, *34*, 259–279.
- (103) Facchini, M. C.; Mircea, M.; Fuzzi, S.; Charlson, R. J. *Nature* **1999**, *401*, 257–259.
- (104) Facchini, M. C.; Decesari, S.; Mircea, M.; Fuzzi, S.; Loglio, G. *Atmos. Environ.* **2000**, *34*, 4853–4857.
- (105) Andracchio, A.; Cavicchi, C.; Tonelli, D.; Zappoli, S. *Atmos. Environ.* **2002**, *36*, 5097–5107.
- (106) Krivacsy, Z.; Kiss, G.; Varga, B.; Galambos, I.; Sarvari, Z.; Gelencser, A.; Molnar, A.; Fuzzi, S.; Facchini, M. C.; Zappoli, S.; Andracchio, A.; Alsberg, T.; Hansson, H. C.; Persson, L. *Atmos. Environ.* **2000**, *34*, 4273–4281.
- (107) Schmid, H.; Laskus, L.; Abraham, H. J.; Baltensperger, U.; Lavanchy, V.; Bizjak, M.; Burba, P.; Cachier, H.; Crow, D.; Chow, J.; Gnauk, T.; Even, A.; ten Brink, H. M.; Giesen, K. P.; Hittenberger, R.; Hueglin, E.; Maenhaut, W.; Pio, C.; Carvalho, A.; Putaud, J. P.; Toom-Sauntry, D.; Puxbaum, H. *Atmos. Environ.* **2001**, *35*, 2111–2121.
- (108) Schauer, J. J.; Mader, B. T.; Deminter, J. T.; Heidemann, G.; Bae, M. S.; Seinfeld, J. H.; Flagan, R. C.; Cary, R. A.; Smith, D. F.; Huebert, B. J.; Bertram, T.; Howell, S.; Kline, J. T.; Quinn, P.; Bates, T.; Turpin, B. J.; Lim, H. J.; Yu, J. Z.; Yang, H.; Keywood, M. D. *Environ. Sci. Technol.* **2003**, *37*, 993–1001.
- (109) Chow, J. C.; Watson, J. G.; Crow, D.; Lowenthal, D. H.; Merrifield, T. *Aerosol Sci. Technol.* **2001**, *34*, 23–34.
- (110) Lim, H. J.; Turpin, B. J. *Environ. Sci. Technol.* **2002**, *36*, 4489–4496.
- (111) Stolzenburg, M. R.; Hering, S. V. *Environ. Sci. Technol.* **2000**, *34*, 907–914.
- (112) Boring, C. B.; Al-Horr, R.; Genfa, Z.; Dasgupta, P. K.; Martin, M. W.; Smith, W. F. *Anal. Chem.* **2002**, *74*, 1256–1268.
- (113) Loflund, M.; Kasper-Giebl, A.; Tschewenka, W.; Schmid, M.; Giebl, H.; Hittenberger, R.; Reischl, G.; Puxbaum, H. *Atmos. Environ.* **2001**, *35*, 2861–2869.
- (114) Zhang, J.; Chameides, W. L.; Weber, R.; *J. Geophys. Res., [Atmos.]* **2002**, *108*.
- (115) Khlystov, A.; Wyers, G. P.; Slanina, J. *Atmos. Environ.* **1995**, *29*, 2229–2234.
- (116) Simon, P. K.; Dasgupta, P. K. *Anal. Chem.* **1995**, *67*, 71–78.
- (117) Myojo, T.; Takaya, M.; Ono-Ogasawara, M. *Aerosol Sci. Technol.* **2002**, *36*, 76–83.
- (118) Okada, Y.; Yabumoto, J.; Takeuchi, K. *J. Aerosol Sci.* **2002**, *33*, 961–965.
- (119) Duan, Y. X.; Su, Y. X.; Jin, Z.; Abeln, S. P. *Anal. Chem.* **2000**, *72*, 1672–1679.
- (120) Noble, C. A.; Prather, K. A. *Mass Spectrom. Rev.* **2000**, *19*, 248–274.
- (121) Johnston, M. V. *J. Mass Spectrom.* **2000**, *35*, 585–595.
- (122) Hunt, A. L.; Petrucci, G. A. *TrAC, Trends Anal. Chem.* **2002**, *21*, 74–81.
- (123) Mallina, R. V.; Wexler, A. S.; Rhoads, K. P.; Johnston, M. V. *Aerosol Sci. Technol.* **2000**, *33*, 87–104.
- (124) Zhang, X. F.; Smith, K. A.; Worsnop, D. R.; Jimenez, J.; Jayne, J. T.; Kolb, C. E. *Aerosol Sci. Technol.* **2002**, *36*, 617–631.
- (125) Jayne, J. T.; Leard, D. C.; Zhang, X. F.; Davidovits, P.; Smith, K. A.; Kolb, C. E.; Worsnop, D. R. *Aerosol Sci. Technol.* **2000**, *33*, 49–70.
- (126) Tobias, H. J.; Kooiman, P. M.; Docherty, K. S.; Ziemann, P. J. *Aerosol Sci. Technol.* **2000**, *33*, 170–190.
- (127) Tobias, H. J.; Ziemann, P. J. *Anal. Chem.* **1999**, *71*, 3428–3435.
- (128) Tobias, H. J.; Ziemann, P. J. *Environ. Sci. Technol.* **2000**, *34*, 2105–2115.
- (129) Tobias, H. J.; Docherty, K. S.; Beving, D. E.; Ziemann, P. J. *Environ. Sci. Technol.* **2000**, *34*, 2116–2125.
- (130) Tobias, H. J.; Ziemann, P. J. *J. Phys. Chem. A* **2001**, *105*, 6129–6135.
- (131) Ziemann, P. J. *J. Phys. Chem. A* **2002**, *106*, 4390–4402.
- (132) Tobias, H. J.; Beving, D. E.; Ziemann, P. J.; Sakurai, H.; Zuk, M.; McMurry, P. H.; Zarling, D.; Waytulonis, R.; Kittelson, D. B. *Environ. Sci. Technol.* **2001**, *35*, 2233–2243.
- (133) Chattopadhyay, S.; Tobias, H. J.; Ziemann, P. J. *Anal. Chem.* **2001**, *73*, 3797–3803.
- (134) Gross, D. S.; Galli, M. E.; Silva, P. J.; Wood, S. H.; Liu, D. Y.; Prather, K. A. *Aerosol Sci. Technol.* **2000**, *32*, 152–163.
- (135) Hughes, L. S.; Allen, J. O.; Bhawe, P.; Kleeman, M. J.; Cass, G. R.; Liu, D. Y.; Fergenson, D. F.; Morrical, B. D.; Prather, K. A. *Environ. Sci. Technol.* **2000**, *34*, 3058–3068.
- (136) Liu, D. Y.; Prather, K. A.; Hering, S. V. *Aerosol Sci. Technol.* **2000**, *33*, 71–86.
- (137) Guazzotti, S. A.; Coffee, K. R.; Prather, K. A. *J. Geophys. Res., [Atmos.]* **2001**, *106*, 28607–28627.
- (138) Guazzotti, S. A.; Whiteaker, J. R.; Suess, D.; Coffee, K. R.; Prather, K. A. *Atmos. Environ.* **2001**, *35*, 3229–3240.
- (139) Angelino, S.; Suess, D. T.; Prather, K. A. *Environ. Sci. Technol.* **2001**, *35*, 3130–3138.
- (140) Whiteaker, J. R.; Suess, D. T.; Prather, K. A. *Environ. Sci. Technol.* **2002**, *36*, 2345–2353.
- (141) Whiteaker, J. R.; Prather, K. A. *Anal. Chem.* **2003**, *75*, 49–56.
- (142) Lazar, A. C.; Reilly, P. T. A.; Whitten, W. B.; Ramsey, J. M. *Rapid Commun. Mass Spectrom.* **2000**, *14*, 1523–1529.
- (143) Lazar, A. C.; Reilly, P. T. A.; Whitten, W. B.; Ramsey, J. M. *Anal. Chem.* **2000**, *72*, 2142–2147.
- (144) Parker, E. P.; Trahan, M. W.; Wagner, J. S.; Rosenthal, S. E.; Whitten, W. B.; Gieray, R. A.; Reilly, P. T. A.; Lazar, A. C.; Ramsey, J. M. *Field Anal. Chem. Technol.* **2000**, *4*, 31–42.
- (145) Reilly, P. T. A.; Gieray, R. A.; Whitten, W. B.; Ramsey, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 11596–11601.
- (146) Reilly, P. T. A.; Gieray, R. A.; Whitten, W. B.; Ramsey, J. M. *Combust. Flame* **2000**, *122*, 90–104.
- (147) Cziczko, D. J.; Thomson, D. S.; Murphy, D. M. *Meteorit. Planet. Sci.* **2000**, *35*, A46–A46.
- (148) Lee, S. H.; Murphy, D. M.; Thomson, D. S.; Middlebrook, A. M. *J. Geophys. Res., [Atmos.]* **2002**, *107*, 4003.
- (149) Cziczko, D. J.; Thomson, D. S.; Murphy, D. M. *Science* **2001**, *291*, 1772–1775.
- (150) Cziczko, D. J.; Murphy, D. M.; Thomson, D. S.; Ross, M. N. *Geophys. Res. Lett.* **2002**, *29*, 2037.
- (151) Kuckelmann, U.; Warscheid, S.; Hoffmann, T. *Anal. Chem.* **2000**, *72*, 1905–1912.
- (152) Trimborn, A.; Hinz, K. P.; Spengler, B. *J. Geophys. Res., [Atmos.]* **2002**, *107*, 8132.
- (153) Hoffmann, T.; O'Dowd, C. D.; Seinfeld, J. H. *Geophys. Res. Lett.* **2001**, *28*, 1949–1952.
- (154) Warscheid, B.; Hoffmann, T. *Atmos. Environ.* **2001**, *35*, 2927–2940.
- (155) Hoffmann, T.; Bandur, R.; Hoffmann, S.; Warscheid, B. *Spectrochim. Acta, Part B* **2002**, *57*, 1635–1647.
- (156) Warscheid, B.; Hoffmann, T. *Rapid Commun. Mass Spectrom.* **2002**, *16*, 496–504.
- (157) Tan, P. V.; Evans, G. J.; Tsai, J.; Owega, S.; Fila, M. S.; Malpica, O. *Environ. Sci. Technol.* **2002**, *36*, 3512–3518.
- (158) Owega, S.; Evans, G. J.; Jervis, R. E.; Tsai, J.; Fila, M.; Tan, P. V. *Environ. Pollut.* **2002**, *120*, 125–135.
- (159) Galli, M.; Guazzotti, S. A.; Prather, K. A. *Aerosol Sci. Technol.* **2001**, *34*, 381–385.
- (160) Thomson, D. S.; Schein, M. E.; Murphy, D. M. *Aerosol Sci. Technol.* **2000**, *33*, 153–169.
- (161) Trimborn, A.; Hinz, K. P.; Spengler, B. *Aerosol Sci. Technol.* **2000**, *33*, 191–201.
- (162) Phares, D. J.; Rhoads, K. P.; Wexler, A. S. *Aerosol Sci. Technol.* **2002**, *36*, 583–592.
- (163) Kane, D. B.; Johnston, M. V. *Environ. Sci. Technol.* **2000**, *34*, 4887–4893.
- (164) Kane, D. B.; Johnston, M. V. *Anal. Chem.* **2001**, *73*, 5365–5369.
- (165) Kane, D. B.; Oktem, B.; Johnston, M. V. *Aerosol Sci. Technol.* **2001**, *35*, 990–997.

- (166) Kane, D. B.; Oktem, B.; Johnston, M. V. *Aerosol Sci. Technol.* **2001**, *34*, 520–527.
- (167) Kane, D. B.; Wang, J. J.; Frost, K.; Johnston, M. V. *Anal. Chem.* **2002**, *74*, 2092–2096.
- (168) Nomizu, T.; Hayashi, H.; Hoshino, N.; Tanaka, T.; Kawaguchi, H.; Kitagawa, K.; Kaneco, S. *J. Anal. At. Spectrom.* **2002**, *17*, 592–595.
- (169) Song, X. H.; Faber, N. M.; Hopke, P. K.; Suess, D. T.; Prather, K. A.; Schauer, J. J.; Cass, G. R. *Anal. Chim. Acta* **2001**, *446*, 329–343.
- (170) Murphy, D. M.; Middlebrook, A. M.; Warshawsky, M. *Aerosol Sci. Technol.* **2003**, *37*, 382–391.
- (171) Phares, D. J.; Rhoads, K. P.; Wexler, A. S.; Kane, D. B.; Johnston, M. V. *Anal. Chem.* **2001**, *73*, 2338–2344.
- (172) Held, A.; Hinz, K. P.; Trimborn, A.; Spengler, B.; Klemm, O. *J. Aerosol Sci.* **2002**, *33*, 581–594.
- (173) Tan, P. V.; Malpica, O.; Evans, G. J.; Owega, S.; Fila, M. S. *J. the Am. Soc. Mass Spectrom.* **2002**, *13*, 826–838.
- (174) Suess, D. T.; Prather, K. A. *Aerosol Sci. Technol.* **2002**, *36*, 1139–1141.
- (175) Silva, P. J.; Prather, K. A. *Anal. Chem.* **2000**, *72*, 3553–3562.
- (176) Silva, P. J.; Carlin, R. A.; Prather, K. A. *Atmos. Environ.* **2000**, *34*, 1811–1820.
- (177) Bhave, P. V.; Kleeman, M. J.; Allen, J. O.; Hughes, L. S.; Prather, K. A.; Cass, G. R. *Environ. Sci. Technol.* **2002**, *36*, 2154–2163.
- (178) Allen, J. O.; Fergenson, D. P.; Gard, E. E.; Morrical, B. D.; Hughes, L. S.; Kleeman, M. J.; Gross, D. S.; Gälli, M. E.; Prather, K. A.; Cass, G. R. *Environ. Sci. Technol.* **2000**, *34*, 211–217.
- (179) Bhave, P. V.; Fergenson, D. P.; Prather, K. A.; Cass, G. R. *Environ. Sci. Technol.* **2001**, *35*, 2060–2072.
- (180) Bhave, P. V.; Allen, J. O.; Morrical, B. D.; Fergenson, D. P.; Cass, G. R.; Prather, K. A. *Environ. Sci. Technol.* **2002**, *36*, 4868–4879.
- (181) Fergenson, D. P.; Song, X. H.; Ramadan, Z.; Allen, J. O.; Hughes, L. S.; Cass, G. R.; Hopke, P. K.; Prather, K. A. *Anal. Chem.* **2001**, *73*, 3535–3541.
- (182) Reents, W. D.; Ge, Z. Z. *Aerosol Sci. Technol.* **2000**, *33*, 122–134.
- (183) Reents, W. D.; Schabel, M. J. *Anal. Chem.* **2001**, *73*, 5403–5414.
- (184) Gross, D. S.; Galli, M. E.; Silva, P. J.; Prather, K. A. *Anal. Chem.* **2000**, *72*, 416–422.
- (185) Reilly, P. T. A.; Lazar, A. C.; Gieray, R. A.; Whitten, W. B.; Ramsey, J. M. *Aerosol Sci. Technol.* **2000**, *33*, 135–152.
- (186) Mahadevan, R.; Lee, D.; Sakurai, H.; Zachariah, M. R. *J. Phys. Chem. A* **2002**, *106*, 11083–11092.
- (187) Schoolcraft, T. A.; Constable, G. S.; Zhigilei, L. V.; Garrison, B. J. *Anal. Chem.* **2000**, *72*, 5143–5150.
- (188) Schoolcraft, T. A.; Constable, G. S.; Jackson, B.; Zhigilei, L. V.; Garrison, B. J. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2001**, *180*, 245–250.
- (189) Morrical, B. D.; Fergenson, D. P.; Prather, K. A. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 1068–1073.
- (190) Cabalo, J.; Zelenyuk, A.; Baer, T.; Miller, R. E. *Aerosol Sci. Technol.* **2000**, *33*, 3–19.
- (191) Woods, E.; Smith, G. D.; Dessiaterik, Y.; Baer, T.; Miller, R. E. *Anal. Chem.* **2001**, *73*, 2317–2322.
- (192) Woods, E.; Smith, G. D.; Miller, R. E.; Baer, T. *Anal. Chem.* **2002**, *74*, 1642–1649.
- (193) Sykes, D. C.; Woods, E.; Smith, G. D.; Baer, T.; Miller, R. E. *Anal. Chem.* **2002**, *74*, 2048–2052.
- (194) Prieto, M. C.; Kovtoun, V. V.; Cotter, R. J. *J. Mass Spectrom.* **2002**, *37*, 1158–1162.
- (195) Ho, J. *Anal. Chim. Acta* **2002**, *457*, 125–148.
- (196) McMurry, P. H.; Wang, X.; Park, K.; Ehara, K. *Aerosol Sci. Technol.* **2002**, *36*, 227–238.
- (197) Snyder, A. P.; Tripathi, A.; Maswadeh, W. M.; Ho, J.; Spence, M. *Field Anal. Chem. Technol.* **2001**, *5*, 190–204.
- (198) Hart, K. J.; Wise, M. B.; Griest, W. H.; Lammert, S. A. *Field Anal. Chem. Technol.* **2000**, *4*, 93–110.
- (199) Ullom, J. N.; Frank, M.; Gard, E. E. *Anal. Chem.* **2001**, *73*, 2331–2337.
- (200) Fenselau, C.; Demirev, P. A. *Mass Spectrom. Rev.* **2001**, *20*, 157–171.

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