

Atmospheric Chemistry Analysis: A Review

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The monitoring of our atmosphere is a vital component of analytical chemistry, on the basis of the fact that air quality has a direct impact on the environment and human health. Air pollution has been shown to be involved in numerous pathologies, typically cardiovascular and respiratory based, but also links to reproductive function have been made. (1) Many impacts of air pollution are complex and result from the chemical and physical interactions of a number of atmospheric species from a plethora of sources. (2) A recent review, for example, explored the interplay of air pollution, food production, and food security, where food production incurs air pollution which in turn negatively impacts food security. (3) It is clear that it is insufficient to merely determine the levels of air pollutants, such as particulate matter of diameter 2.5 μm or less ($\text{PM}_{2.5}$), to estimate human health impacts, (4) as the chemical composition thereof has a great bearing on toxicity, which varies considerably spatiotemporally. The atmosphere is a shared resource; therefore, the scale of air pollution impacts may range from local to transboundary. Many air pollutants are known to incur deleterious effects at trace concentrations, while potential effects of chronic exposure to low concentrations of some species in the atmosphere have not yet been determined. This necessitates the ongoing development of sensitive and selective analytical methods for an ever increasing range of analytes to drive the science forward and allow for a better understanding of this complex field.

Studies to monitor the atmosphere differ substantially in terms of geographical and temporal coverage, which have concomitant differing requirements in terms of sampling and analytical approaches. Additional drivers that inform the choice of the analytical approach include target analytes, legislative requirements, and available resources. In this Review, developments over approximately the last two years (methodologies and applications published since 2017, with a few exceptions that deserve mentioning due to their fundamental relevance) in the field of atmospheric chemistry monitoring are explored (Figure 1), covering sampling and analytical approaches, where the latter focuses on laboratory based analyses, although pertinent applications of sensor and remote sensing technologies are described. The Review focuses on recent developments in the monitoring of gas and particle phase atmospheric species and does not include occupational or indoor air quality monitoring (refer to Farmer (5) regarding the latter topic). It should be noted that a significant number of atmospheric chemistry analyses that are published are based on “traditional” or standardized analytical approaches and are therefore outside the ambit of this Review on developments in the field, except where there are new aspects to the methodology or in the application thereof.

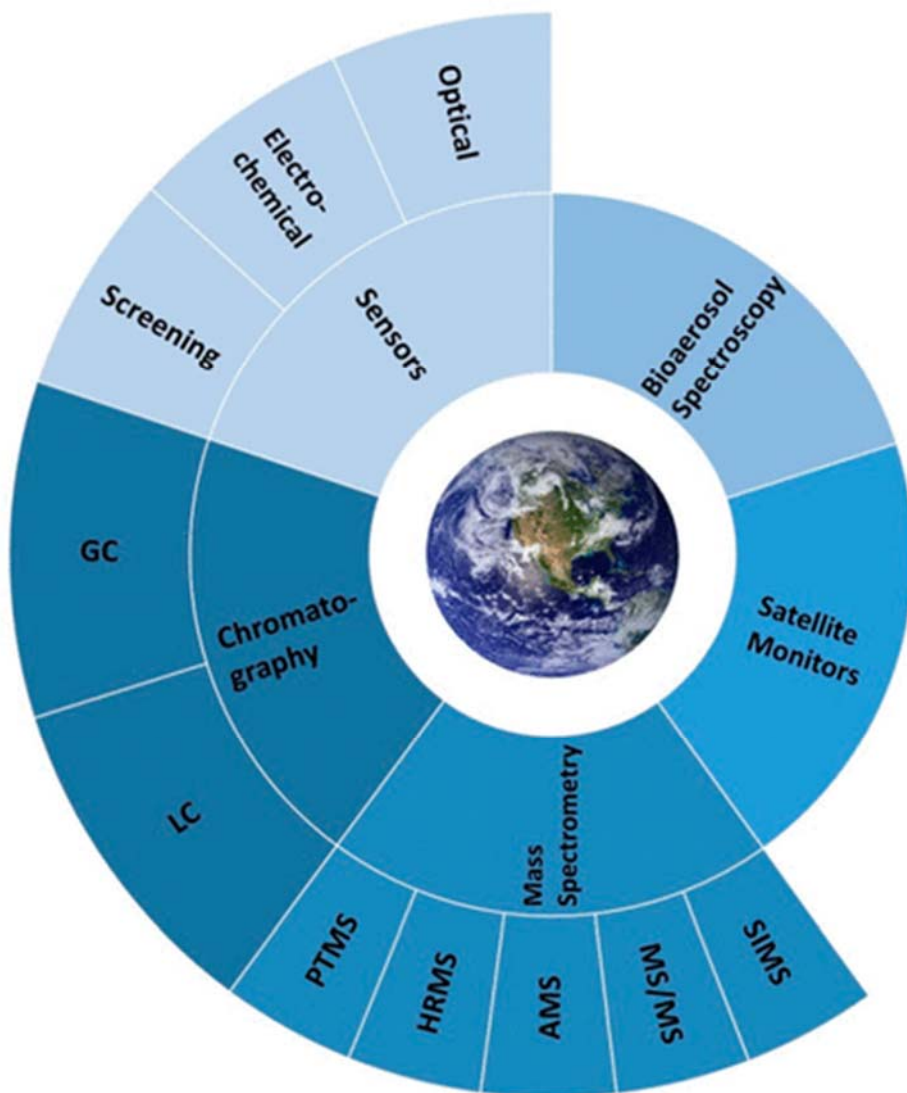


Figure 1. Schematic of the atmospheric chemistry analytical methods covered in this Review, based on recent developments in this regard (image courtesy of NASA).

Recent publications dealing with the monitoring of the atmosphere have covered analytes ranging from those that are commonly regulated, such as inorganic gases (SO_2 and NO_x), to those that can be considered emerging chemical pollutants (ECPs). These are typically defined as compounds that may have an impact on human health or the environment but do not currently have regulatory status. (6) The compounds thus falling within this definition vary across countries with differing legislative frameworks. On the basis of recent publications, the development of new techniques to monitor atmospheric levels of ammonia, flame retardants, polycyclic aromatic hydrocarbons, bioaerosols, and secondary organic aerosols (SOAs) have received much attention. SOAs are formed through the oxidation of volatile organic compounds and are comprised of thousands of compounds, posing extreme challenges to their characterization. Similarly, methods are being developed for the determination of radical species in the atmosphere, such as the use of fluorescence assay by gas expansion (FAGE) for methyl peroxy (CH_3O_2) radicals, (7) where the reactivity of

these species presents significant challenges in sample handling and analysis. Developments in the field of atmospheric chemistry monitoring have been facilitated by improvements in the selectivity and sensitivity of analytical methods, while time, labor, and cost savings as well as a reduction in environmental impacts (green chemistry approaches) have also stimulated progress.

Air Sampling Approaches

Sampling is a critical step in the analytical process. Monitoring may be online, providing real-time information regarding the chemistry of the atmosphere. Such approaches may avoid sampling artifacts arising from volatilization, degradation, or reaction of analytes during sample collection and storage. An approach to online atmospheric sampling in metropolitan areas that provides cost saving synergies is the deployment of monitoring equipment (such as particulate matter (PM) and O₃ monitors) on news helicopters (8) or electrified light-rail public trains. (9) The spatial and time-resolved air quality data is retrieved in real-time and may be combined with ground based observations to provide useful information for both research and public awareness.

With respect to environmental samples, concentrations of target analytes may be at trace levels. In order to enhance method detection and quantification limits, off-line sampling methods that allow for preconcentration of analytes may thus be advantageous. Additional considerations in the choice of the sampling method include cost, portability, reuse potential, and ease of use. In this section, various sampling approaches that have recently been applied in atmospheric chemistry monitoring are reviewed, with a focus on new developments and applications.

Passive Air Sampling

Passive samplers (PASs) may be widely deployed due to their low cost, and as they do not require an energy source, (10) the spatial resolution this affords comes at the cost of temporal resolution, as passive samplers provide time integrated concentrations. It has been suggested that air concentrations determined by passive samplers may be dominated by high night time concentrations of air pollutants due to boundary layer dynamics. (11) Analysis of some passive samplers is also lengthy, requiring extraction, cleanup, and preconcentration steps prior to instrumental analysis using analyte appropriate methods. Passive samplers are, however, particularly useful in monitoring air in remote areas; thus, they have been employed to determine levels of airborne pesticides and flame retardants in tropical forest areas, which are protected for their biodiversity. (12)

Polyurethane foam (PUF) disks have been extensively utilized as passive samplers in atmospheric monitoring for some time; however, the means to derive sampling rates and to calculate air concentrations of target analytes vary. Polyurethane foam/air partition coefficients were determined experimentally for a number of semivolatile organic compounds (SVOCs), including polycyclic aromatic hydrocarbons (PAHs), alkylated-PAHs, and organochlorine pesticides (OCPs) over the temperature range of 5–35 °C, in order to calculate effective air sampling volumes and thereby concentrations of air pollutants. (13) The results corroborated those determined using the octanol–air partition coefficients

based on polychlorinated biphenyl (PCB) uptake kinetics, although it is recommended that experiments are also conducted for additional chemical classes for which PUF based PASs are employed. This is especially relevant to compounds such as perfluoroalkyl substances (PFASs), which do not partition in the same manner as nonpolar hydrophobic analytes. (13)

The uncertainties in determining SVOC air pollutant concentrations (specifically PAHs, polychlorinated biphenyls (PCBs), and OCPs) using PUF passive samplers were investigated on the basis of long-term air monitoring data in comparison to active air sampling. (14) Although individual monthly results varied significantly between the two sets of data, annual average concentrations were of the same order of magnitude with the exception of particle phase PAHs. This is because passive sampling theory applies to gas phase sampling, but particles may also infiltrate into the PUF of the PAS. This infiltration varies with sampler design and PUF density as well as with site specific parameters such as wind speed and direction. (14) Uncertainties in air monitoring data of SVOCs that may be particle bound (such as the heavier PAHs) are therefore larger, and this needs to be borne in mind when reporting results.

A recent study showed that polyurethane foam was a suitable passive sampler for both gas and particle phase halogenated flame retardants, as there was no significant difference between results obtained for the passive sampler and that of the colocated traditional high volume active sampler when the total (gas plus particle phase) concentrations of polybrominated diphenyl ethers and dechloranes were considered. (15) Studies have also reported the use of sorbent impregnated PUF (SIP) passive samplers to assist with the collection of more volatile analytes, for example, PUF impregnated with finely ground XAD-4 resin for atmospheric organophosphate flame retardant monitoring. (16) A miniature passive sampler based on PUF and a glass fiber filter was designed for monitoring atmospheric halogenated flame retardants, where the elliptical shaped, lightweight (2.72 g) samplers were bird-borne, in an attempt to better understand sources of the elevated levels of these pollutants found in the tissues of ring-billed gulls. (17)

Aside from PUF sampling, XAD-2 resin based passive samplers have been used to assess trends in atmospheric PAH, PCB, and pesticide levels, (10) while an activated charcoal sorbent has recently been used in an in-house radial passive sampler design for the cost-effective monitoring of atmospheric volatile organic compounds (VOCs). (18) A disadvantage is that extraction with toxic CS₂ is required in this case prior to analysis. The application of PUF and XAD-2 based passive samplers was tested for monitoring per- and polyfluoroalkyl substances (PFASs) in suburban ambient air. (19) It was found that the variability between the passive and active sampling approaches was significant and more research is therefore needed before passive samplers can be used for these compounds.

Polydimethylsiloxane (PDMS) coated stir bars have been employed as passive air samplers for monitoring phosphorus flame retardants in air at pg m⁻³ levels. (20) The stir bars have the advantage of allowing for thermal desorption as a means of sample introduction into a gas chromatograph-mass spectrometer (GC/MS), avoiding the need for solvents and being time efficient (10 min desorption at 300 °C). It should be noted, however, that thermal desorption is not suitable for heat-labile compounds and less volatile analytes may not be completely desorbed, leading to inaccuracies and carryover effects. In addition, adequate

calibration and compound specific sampling rates are required for the use of stir bars as passive samplers in atmospheric monitoring applications. (20)

Biomonitors of Air Pollution

Biomonitors are a subset of passive samplers, where a cell membrane may serve as the diffusive barrier, and the sampler is a lichen, moss, or conifer needle, for example. Accumulation of air pollutants in the biomonitor may provide an efficient, specific, and cost-effective monitoring option. (21) A range of air pollutants have been monitored using biomonitors for many years. Originally, these were primarily inorganic; however, the scope of application of biomonitors in atmospheric chemistry monitoring has since been expanded to include organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), pesticides, polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). (22) An application of biomonitors in the elucidation of atmospheric chemistry is that of analyzing pine tree rings (dendrochemistry) to determine high temporal resolution information regarding atmospheric levels of mercury. (23) This is particularly useful in regions where freshwater lakes are limited or absent, preventing the use of sediment cores for this purpose.

Recent analytical chemistry research in the field of biomonitoring has focused on the development of more efficient and reproducible extraction methods for target analytes and on the use of a new means to provide sensitive and selective analyses. Techniques to extract PAHs from lichens were compared, which included both traditional approaches (Soxhlet, ultrasound-assisted solvent extraction and microwave-assisted extraction) and a new means to extract these analytes by means of the quick, easy, cheap, effective, rugged, and safe (QuEChERS) technique. (24) This novel approach using *n*-hexane/acetone (1:1, v/v) was comparatively fast, used less solvent and energy, and provided good recoveries (96%). The presence of chlorophyll in biomonitor extracts may lead to strong matrix effects; thus, the use of matrix-matched standards in analyzing PAHs in lichen extracts, for example, is important. (24)

Studies have shown the importance of rigorous sample collection (specifically regarding chemical cleanliness) and handling protocols (removal of adhering substratum and other nontarget material from the lichen sample) for the determination of the elemental composition of lichen biomonitors, (25) as deviations from best practice lead to significantly different results. The sample preparation procedures were also shown to have a significant impact on the extraction efficiencies of metal(loid)s from lichens, (26) where cryogenic freezing provided the best reproducibility upon storage for total metal extractions, but poor metal extractions were observed when a sequential extraction technique was employed. Due to the known difference in toxicity of metal(loid) species present in the environment, research is being conducted into the development of analytical methods to provide speciated concentration information. A method to determine the inorganic arsenic species in lichens was developed, for example, which was based on high performance liquid chromatography–inductively coupled plasma mass spectrometry (HPLC-ICPMS). (27) Differences in the abundance of individual arsenic species present in lichens from urban and rural areas were noted.

In contrast, a nonspecified analytical approach combining three spectroscopic techniques (near-infrared spectroscopy (NIRS), front-face fluorescence spectroscopy (FFFS), and a plant efficiency analyzer, which determines chlorophyll α fluorescence) with chemometrics allowed for the differentiation between lichens, which were from either polluted or nonpolluted areas. (28) The FFFS data also provided some differences between lichens exposed to industrial or traffic related air pollution. This combined approach was seen as being fast, simple, and environmentally friendly as it does not require solvent use as the NIRS and FFFS analyses were conducted on pulverized lichen samples. The proposed method does not provide information on the individual compounds present in the biomonitor samples, which is a limitation thereof as metabolically derived organic acids also produce NIR and FFFS responses in addition to PAHs and organic acids from the atmosphere. (28)

Sampling Approaches To Address Gas-Particle Partitioning

The coexistence of particle and gas phases of semivolatile organic compounds, such as PAHs, in the atmosphere presents sampling challenges, due to the dynamic nature thereof and the ease with which the equilibrium can be disturbed. Effective and efficient sampling of each phase simultaneously is critical, however, in order to understand atmospheric chemistry processes and potential impacts of the target analytes. (29,30) Some samplers are prone to sampling artifacts, have unpredictable sampling efficiencies, or are not able to adequately differentiate between phases. Verification of particle transmission through gas phase denuder samplers is important in this regard. (31) In the case of high volume samplers, which collect gas phase analytes downstream of a filter, it is necessary to verify that gas phase analytes are not sorbed onto the filter medium. This artifact was noted in the sampling of perfluorooctanoic acid, where sorption occurred onto glass fiber filters even when they were deactivated, (32) indicating that high volume sampling could only provide total atmospheric concentrations (if operated below breakthrough conditions) and not partitioning results. Similarly, gas phase organophosphate esters have been shown to extensively sorb onto glass and quartz fiber filters, resulting in erroneous partitioning estimates, particularly for the more volatile species. (33)

The gas-particle partitioning of traditional and novel halogenated flame retardants was investigated in Spain to determine the effects of seasonality and environmental conditions in this regard, where dechlorane levels were found to be higher in the particle phase than in the gas phase. (15) Here, the traditional high volume sampling approach (operating at $30 \text{ m}^3 \text{ h}^{-1}$) utilizing polyurethane foam (PUF) for gas phase collection with downstream particle collection onto a glass fiber filter was employed, followed by Soxhlet extraction prior to analysis (refer to High Resolution Mass Spectrometry). Such an approach, which was similarly employed for determining gas-particle partitioning of nitro-polycyclic aromatic hydrocarbons, (34) has the potential for artifact formation leading to inaccurate results (29) and is also environmentally unfriendly. In some cases where high volume sampling is employed, two PUF cartridges are used in series to prevent loss due to breakthrough. Alternatively, sandwich gas phase collectors consisting of two PUF plugs separated by an XAD-2 resin cartridge are used, such as in the sampling of gas and particle associated polybrominated diphenyl ethers (PBDEs). (35)

A two stage wet denuder was employed to better elucidate the gas-particle partitioning of atmospheric glyoxal and methylglyoxal, which are produced from VOCs such as isoprene. (36) Here, a parallel wet plate denuder was used to sample the gas phase, followed by particle capture in a spray-type particle collector, which demonstrated good collection efficiencies. This multicomponent system is, however, relatively large and not very portable.

Novel Sorbents for Atmospheric Monitoring

New sorbent materials for atmospheric pollutants are constantly being sought, which offer advantages in terms of capacity, selectivity, and cost. The use or conversion of agricultural waste material into a sorbent for pollutants has been applied to both sampling and purification of air. A recent example is the pyrolysis of spent coffee grounds into biochar for use as a sorbent for ambient PAH sampling. (37) Although such approaches may utilize a waste material, the overall environmental impact regarding the use thereof must be considered, as the pyrolysis step may utilize a significant amount of energy, and moreover, the product requires a long cleanup procedure at elevated temperatures using relatively large solvent volumes (dichloromethane) prior to use. This is because the pyrolysis step actually generates PAHs, which would otherwise contaminate the sorbent. (37) After 6 h of cleanup, PAHs were still present in the sorbent at detectable concentrations. In this example, the ultrasonic extraction of the sampled PAHs required 25 mL of dichloromethane and 2-propanol (4:1) for 30 min at low temperatures (<10 °C) to prevent volatilization losses, which also required energy for cooling.

Sandwich sorbent beds are useful when a range of analytes need to be sampled with different physicochemical properties such as volatilities and polarities. Recently, a range of adsorbents were tested in sandwich traps for airborne pesticides in a rural area of Spain, using PUF, XAD-2, and XAD-4 in different configurations with low volume sampling. (38) It was found that a PUF-XAD-2-PUF sampler gave the best retention capacity and microwave extraction efficiencies with ethyl acetate were in the range of 75–120%. Ten polar pesticides were found in the air samples (160 m³ sample volume collected at 1 m³ h⁻¹) upon ultra high performance liquid chromatography-high resolution mass spectrometric (UHPLC-HRMS) analysis. (38)

A concentrically packed air sampler was manufactured in which the sorbent layers (consisting of >1 g Tenax TA and Carboxen sorbents) were packed around an empty permeable tube to reduce back pressure and thereby facilitate higher sampling flow rates (>10 L min⁻¹) and shorter sampling time periods. (39) Benzene, toluene, ethylbenzenes, and xylenes (BTEX) were collected by drawing air through the central channel using a vacuum pump. Analytes were then thermally desorbed from the sorbents onto a needle trap device to allow for their introduction into a gas chromatograph-mass spectrometer (GC/MS) for analysis, as the sampler was too large (~2.3 cm diameter) for commercial thermal desorber systems and gas volumes of >50 mL were needed for desorption of analytes. The needle was compatible with standard GC inlets, but this transfer resulted in analyte loss; therefore, a system that avoids multisample transfer steps is preferable. Typically, needle based extraction techniques are used directly for other environmental matrices and for occupational indoor air monitoring rather than for ambient air, due to sensitivity issues arising from the small sorbent volume, as reviewed by Kędziora-Koch and Wasiak. (40)

Research into the development of nanomaterials as solid phase extraction sorbents for environmental applications has been reviewed by Azzouz et al., (41) as the unique structural and surface properties of these materials offer promising enhanced sorption capabilities. In terms of atmospheric analytes, sorbents for a range of VOCs have been investigated, such as those based on metal–organic frameworks (MOFs). (42) Here, a binary sorbent mixture of the commercial Tenax-TA sorbent with a MOF (specifically, Zn based MOF-5) was used to sample C1 to C5 aldehydes, followed by thermal desorption-GC/MS (TD-GC/MS). Better sensitivity and reproducibility was found as compared to commercial sorbents, and no solvent extraction or derivatization was required. There are still challenges with this technology regarding potential coadsorption of nontarget analytes; therefore, further material development and structural modifications are required.

Sample Preparation Approaches

Research is ongoing to improve sample extraction efficiencies in a manner which is cost-effective, time efficient, and “green” in terms of minimizing solvent and energy use. Thermal desorption of atmospheric analytes sampled onto sorbents may provide a number of these advantages; however, it is costly and may not offer the possibility of reanalysis of samples. A cost-effective alternative for PAHs sampled onto multichannel silicone rubber traps, for example, is the use of a plunger assisted solvent extraction (PASE) method, which is fast (2 min extraction) and simple and uses a small solvent volume (2 mL per sample). (43)

As mentioned in *Biomonitoring of Air Pollution*, the speciation of inorganic atmospheric species is of relevance in terms of atmospheric chemistry as well as environmental fate. Sample collection and extraction processes can greatly impact the integrity of the chemical species, as has been found with soluble iodine in atmospheric aerosols, for example. (44) Here, the optimal method involved high volume sample collection onto glass fiber filters with 30 min of mechanical agitation for extraction prior to analysis by ion chromatography-inductively coupled plasma-mass spectrometry (IC-ICPMS), while ultrasonic extraction from cellulose fiber filters was found to lead to variations in both iodine species and recoveries.

A recent novel extraction approach was applied to particle bound airborne pesticides sampled onto filters, where a hard cap espresso machine was employed followed by UHPLC-HRMS (Orbitrap) analysis with limits of quantitation (LOQs) in the range of 6.5 pg m^{-3} . (45) Each filter (sampling volume of $\sim 760 \text{ m}^3$ collected at $30 \text{ m}^3 \text{ h}^{-1}$) was folded and placed into a refillable stainless steel capsule with a dispersing agent and was covered with a borosilicate filter to avoid sample loss (Figure 2). This extraction technique has the advantages of being fast (20 s), having a low cost, and using small amounts of solvents and reagents (50 mL of 20% (v/v) acetonitrile in water and 8 g of NaCl for salting out which improved recoveries from 70% to 129%) compared to alternative pressurized liquid or microwave assisted extractions (PLE and MAE, respectively). The system operates at $72 \text{ }^\circ\text{C}$ and 19 bar; thus, these milder conditions compared to PLE and MAE may assist in reducing the degradation of thermally labile compounds. (45) A drawback of this technology is safety concerns, as the machines are designed for coffee extraction using water, although they have been modified to be more compatible to organic solvent use. The extraction conditions are also fixed, which limits the potential to optimize the extraction method.



Figure 2. Filters with collected particulate matter, hard cap espresso machine, and reusable stainless steel caps used for sample extraction. The inset shows the NaCl salting-out effect using a coloring agent for ease of visualization. (Reprinted from *J. Chromatogr. A*, Vol. 1506, López, A.; Coscollà, C.; Yusà, V.; Armenta, S.; de la Guardia, M.; Esteve-Turrillas, F. A., *Comprehensive analysis of airborne pesticides using hard cap espresso extraction-liquid chromatography-high-resolution mass spectrometry*, pp. 27–36 (ref (45)). Copyright 2017, with permission from Elsevier.)

Methods have been developed to integrate sample preparation steps in order to simplify the process and reduce the amount of time and labor involved as well as the cost. Such an approach is the integrated ultrasonic probe extraction of PAHs and nitro-PAHs (NPAHs) from ambient air particles sampled onto glass fiber filters using a medium volume sampler with sample cleanup. (46) The extract was directly passed through a purification tube containing Mg–Al layered double oxide and silica gel adsorbents avoiding sample transfer steps and was eluted with hexane/dichloromethane (3:7, v/v), before being blown down under nitrogen prior to GC/MS analysis. (46)

A fully automated system involving online dynamic in-tube extraction (ITEX) with GC/MS analysis has been developed for continuous quantitative monitoring of atmospheric VOCs. (47) The ITEX was packed with 50 mg of electrospun polyacrylonitrile nanofibers, which

proved to be robust and provided extraction efficiency toward VOC trapping, and quantitation limits 2 to 3 times lower than headspace dynamic ITEX and other needle trap methods were achieved.

Chromatography

Gas Chromatography

Gas chromatography (GC) is generally limited to volatile analytes (unless derivatization of less volatile analytes is performed prior to analysis); therefore, many compounds participating in the chemistry of the atmosphere are amenable to GC based monitoring methods. For the analysis of atmospheric particulate matter, direct thermal desorption (TD) of analytes prior to GC analysis provides an alternative to solvent extraction thereof, which is a more traditional approach in this regard. TD is typically more time efficient, reduces analyte losses, and avoids the use of solvents and thereby associated potential contamination. (48)

Traditionally, GC coupled to a mass spectrometer (MS) or selective detector has been employed for a plethora of atmospheric monitoring applications. Typically, electron impact ionization (EI) is employed, as this means of ionization and fragmentation is reproducible and robust, allowing for the compilation of libraries of mass spectra, which are extremely useful in the identification and quantification of the analytes. The combination of the separating power of GC with the improved identification, which is provided by high resolution mass spectrometry (refer to High Resolution Mass Spectrometry), is a powerful analytical tool in the identification and structural elucidation of volatile and semivolatile organic compounds (VOCs and SVOCs, respectively), as reviewed by Špànik and Machyňáková, (49) in which a useful comparison of the characteristics of commercially available GC-HRMS instruments is provided. Most GC-HRMS research previously focused on the analysis of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), as required by many international standards, while current research explores novel applications particularly around multitarget screening. On the other hand, the use of GC with tandem mass spectrometry (GC/MS/MS) allows for new insights into legacy air pollutants, such as polychlorinated biphenyls. (50)

GC/MS continues to be used in a range of atmospheric monitoring applications. Recent examples include the determination of polybrominated diphenyl ether (PBDE) flame retardants in ambient particulate matter (PM) in the vicinity of electronic waste (e-waste) reclamation sites in Bangkok, Thailand. (51) Here, samples were collected onto filters for 6 h at 2 L min⁻¹ and were subsequently extracted with dichloromethane for 40 min using a speed extractor prior to GC/MS analysis. The results showed that thermal treatment methods may result in congener transformation and emissions of more toxic lower brominated PBDEs.

In another study, the occurrence of plastic additives in ambient particulate matter (specifically PM₁₀) was investigated in Spain by means of GC/MS. (52) These compounds include UV-stabilizers and aromatic and phenolic antioxidants, which are added to polymers to improve quality and chemical stability. Some of these analytes and their degradation products are poorly ionized by electrospray ionization utilized in related LC-MS methods,

but here EI was employed in the GC/MS analysis of extracts derived by pressurized liquid extraction of quartz fiber filters with ethyl acetate. The optimized method provided pg m^{-3} detection limits and >85% recoveries. (52) For similar reasons this research group also determined the high production chemicals, benzothiazole, benzotriazole, and benzenesulfonamide derivatives, in particulate matter (PM_{10}) collected from ambient air for the first time using similar collection and analytical methods employing GC/MS. (53)

Atmospheric pressure chemical ionization (APCI) is a soft ionization technique utilizing a corona discharge between a needle and the transfer capillary of the MS. APCI is used in the negative ion mode for the detection of organic acids and organic analytes containing carboxylic acid functional groups, while in the positive mode, electron rich moieties, such as amines, alcohols, and carbonyls are detected. (54) APCI has been employed with GC-tandem mass spectrometry in the simultaneous determination of 18 nitro-PAHs present in fine PM (specifically, $\text{PM}_{2.5}$ sampled onto quartz fiber filters) in China. (55) This softer ionization source enhances the abundance of the molecular ion and thereby sensitivity. The sample extraction process was rather tedious, as a 24 h Soxhlet extraction with *n*-hexane/acetone (1:1 v/v) was employed. The analysis utilized a triple quadrupole MS operating in positive APCI mode, where multiple reaction monitoring (MRM) provided chromatographic peaks with high intensity by filtering out background signals. (55)

Enhanced resolution and peak capacity can be achieved by means of comprehensive GC \times GC systems, which rely on the efficient modulation of peaks eluting from the first GC column prior to separation on the secondary column. Cryogenic cooling is typically employed in the modulator, which is costly; therefore, alternatives have been explored such as thermal solid-state modulators using Peltier cooling capable of trapping very volatile hydrocarbons down to C₂. (56) In this application, a hybrid primary dimension column was also used to enhance the separation of C₂ to C₄ compounds, where the first part of the column was housed in a separate oven, which was cooled to 10 °C. This, however, required the use of liquid nitrogen, as did the sample preconcentration system, indicating that additional modifications are necessary to develop a cryogenic-free system.

For a number of atmospheric chemistry applications, on-site monitoring is advantageous. A miniaturized micromachined GC based system has thus been developed, which employs universal and selective detectors (thermal conductivity detector, diode array detector, and a radio frequency modulated ion mobility spectrometer). (57) The instrument is compact and transportable and has been applied in the analysis of targeted volatile organic compounds.

Liquid Chromatography

Liquid chromatography (LC) allows for the separation of isomers, providing an additional dimension to MS analyses. Another advantage of LC-MS is that ion suppression due to matrix components is reduced during ionization, thereby allowing for improved detection limits and quantification.

High performance liquid chromatography (HPLC) has been used in the characterization of atmospheric aerosols arising from biomass burning (58) (also refer to High Resolution Mass Spectrometry for more information). Upon the use of two ionization modes, it was found

that nonpolar chromophores, such as polycyclic aromatic hydrocarbons (PAHs), were only detected using positive mode atmospheric pressure photo ionization (APPI), while negative electrospray ionization (ESI) allowed for the detection of polar components, such as nitroaromatics, aromatic acids, and phenols. (58) These ionization modes thus provide selectivity for the analytical method. It was noted that the number of compounds detected by HPLC-APPI/HRMS was substantially smaller than those detected by direct infusion APPI/HRMS analysis, which was ascribed mainly to the acidic mobile phase employed, which suppresses negative APPI processes and possible incomplete elution of larger molecules from the column. (58)

Ultra high pressure liquid chromatography (UHPLC) coupled to HRMS (Orbitrap) has been employed in the quantification of 28 atmospheric gas phase polar pesticides sampled onto an adsorbent sampler (38) (also refer to Novel Sorbents for Atmospheric Monitoring and High Resolution Mass Spectrometry). Here, a binary gradient was used for separation, which was achieved in 16 min (mobile phase was (A) water with 0.1% formic acid and 4 mM ammonium formate and (B) methanol with the same formic acid and ammonium formate concentrations). Electrospray ionization in positive ionization mode was employed, and LOQs ranged from 32 to 129 pg m^{-3} , indicating the potential of this method for pesticide surveillance programs. A similar method was applied by these researchers in the determination of particle bound pesticides collected onto filters. (45)

In another study, UHPLC-tandem mass spectrometry (MS/MS) utilizing electrospray ionization (ESI) was employed in the monitoring of isoprene-derived organosulfates in collected PM, which are potential markers of SOA formation. (59) Analyses were hampered by a lack of reference standards and mass spectral libraries as well as close similarity of isomeric forms. Different extraction solvents were tested and were found to greatly influence the resulting separation efficiency in terms of peak width and the presence of ghost peaks. Reverse phase C_{18} and HILIC columns were compared with each having advantages depending on the required outcomes of the analyses, as the HILIC method showed poor retention of less polar analytes but provided better separation for the isoprene-derived organosulfates. (59)

An investigation by Zhao et al. (60) into the organic peroxide content of SOA collected onto filters using iodometry assisted LC-ESI-MS showed that there is a potential degradation of multifunctional peroxides sampled onto filters into small peroxides, which can be determined using iodometry with spectroscopic analysis (UV-vis, which provides total peroxide content but not molecular level identification) but not by the proposed LC-MS method. A C_{18} column was employed with 0.1% formic acid in water and acetonitrile as mobile phases, and both positive and negative ionization modes were used. Iodometry treatment of samples, which would have removed organic peroxides, was applied before LC-ESI-MS analysis; therefore, it was hypothesized that the identification of organic peroxides could be achieved by comparison of treated and nontreated sample results. Organic peroxides are challenging to analyze due to the lack of standards and reactivity of the target analytes. The study was based on laboratory synthesized SOA and target analytes; thus, the application thereof to real atmospheric samples would require additional developments and optimization, as it was found that the assignment of organic peroxides only based on MS signatures can be misleading as detection is highly sensitive to the specific instrumental

conditions employed. (60) In addition, the iodometry treatment method involved a 5–7 h long reaction, which makes the analytical procedure very time-consuming. The stability and possible decomposition of organic peroxides on filters and in sample extracts also requires further investigation. (60)

Mass Spectrometry

Mass spectrometry has the capability to provide a wealth of information regarding atmospheric chemistry, and this has been an area of major recent developments regarding a range of target analytes. Alternative approaches in terms of ionization techniques, particularly those which are softer and provide molecular ion information, as well as mass analyzers with high resolution have opened the door to new atmospheric chemistry monitoring methodologies, facilitating a better understanding of reaction pathways and formation mechanisms. Multidimensional gas chromatography has also enhanced the resolution of complex atmospheric samples, as discussed in Gas Chromatography, while tandem MS allows for enhanced selectivity. Both off-line and real-time MS analysis of atmospheric samples is possible, providing a wide ambit of potential applications of this powerful analytical technique to atmospheric monitoring. (48)

Proton Transfer Mass Spectrometry

Proton transfer mass spectrometry (PTR-MS) relies on the chemical ionization of compounds present in trace levels in gaseous samples, followed by their MS analysis. It has been widely used to better understand the emissions, distributions, and atmospheric chemistry of VOCs. (61) Typically, an electrical discharge from a hollow cathode or a radioactive emission source is used to generate hydronium ions from water vapor. These reagent ions are injected into a drift tube where they ionize organic analytes in the sample gas by proton transfer at around 2 mbar. (62) PTR-MS offers direct, real time analyses without the need for preconcentration, where analytes are identified on the basis of their protonated molecular masses with limited fragmentation. The degree of fragmentation is highly dependent on the type of VOC, as can be seen in Figure 3. (61) The limited fragmentation may hinder the elucidation of the chemical structure of the analytes; thus, GC/MS may provide complementary and confirmatory information to allow for correct identification thereof. (63) An approach to facilitate this is “fast-GC” injection, where the sample is periodically trapped and injected into a GC equipped with a short column interfaced with PTR-MS. (62)

PTR-MS allows for rapid quantification (analyses are completed within 100 ms to a few s depending on the target analytes and MS employed) (62) and low detection limits and does not require a carrier gas, which has made it a viable option for the analysis of complex mixtures of, for example, volatile organic compounds (VOCs). (63) PTR-MS has also allowed for the monitoring of oxidation intermediates, such as RO₂ radicals, in the atmosphere for the first time. (62)

In real-time PTR-MS analyses, the lack of sample preconcentration necessitates the use of sensitive MS detectors such as the time-of-flight MS (ToF-MS). The nature of the proton transfer reaction means that only compounds with a proton affinity (PA) greater than that

of water (691 kJ mol^{-1}) may be analyzed, (61) which excludes the analysis of common atmospheric analytes such as short chain hydrocarbons, methane, carbon monoxide, and carbon dioxide. This may be seen as a key advantage of this technique, as the major constituents of air samples are unreactive to proton transfer. (62) Where deprotonation may occur in the drift tube, such as with formaldehyde (which has a low PA), an alternative reaction agent to the hydronium ions may be needed. (63) Alternatives include NH_4^+ , NO^+ , and O_2^+ , which have different ionization potentials, thereby providing additional information. Elevated E/N , which is the electric field strength to buffer gas density, is required in the drift tube to prevent clustering of reagent and product ions with water molecules present in the sample. (62)

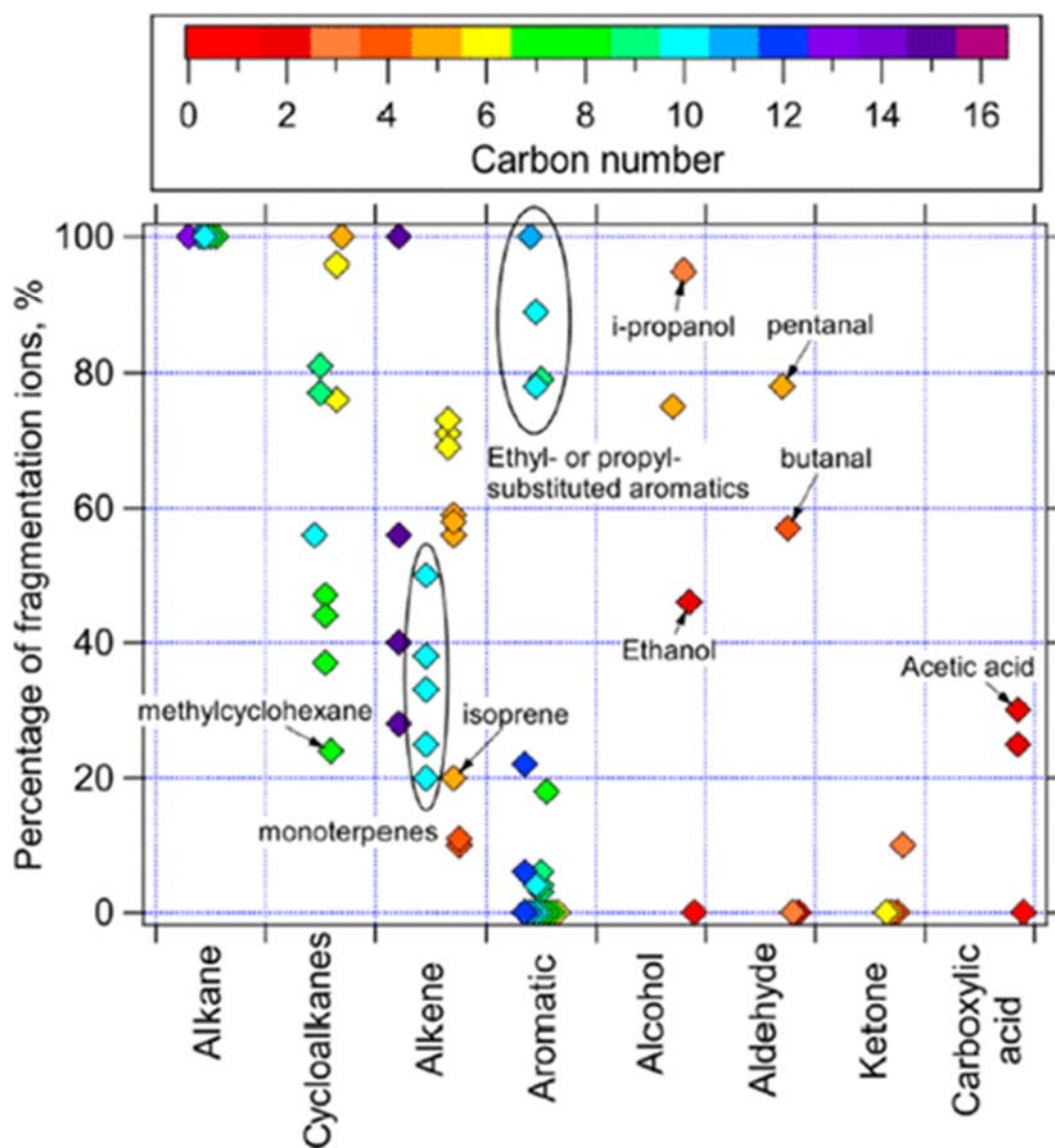
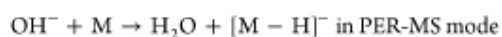
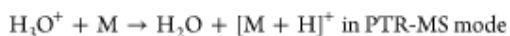


Figure 3. Degree of fragmentation of different VOCs by PTR-MS, expressed as the percentage fragmentation to total product ions at $E/N \sim 120 \text{ Td}$. (Reproduced from Yuan, B.; Koss, A.; Warneke, C.; Coggon, M.; Sekimoto, K.; de Gouw, J. *Chem. Rev.* **2017**, *117*, 13187–13229 (ref (61)). Copyright 2017 American Chemical Society.)

Dipolar proton transfer (DP-PTR-MS) was introduced in 2017, and its potential application in VOC analyses was demonstrated by the detection of volatile ketones. (64) Although PTR is a soft ionization technique, a few cluster ions and fragment ions are invariably produced, which hinders the positive identification of analytes. With DP-PTR-MS, PTR with hydronium ions is alternated with proton extraction reactions (PER) utilizing hydroxyl ions by merely switching the polarity with only water vapor in the hollow cathode ion source. The relevant general reaction equations (where the analyte, in this case a ketone, is denoted by M) are



The molecular weight of the ketone (in the gas phase diluted with high purity nitrogen) can be identified by comparing the m/z value of the product ions in each mode, which is an advantage of this adaptable system along with sensitive and fast analyses. In addition, the use of water vapor as a reagent gas is preferable to oxygen, dry air, or ammonia, which are alternatives used in some applications.

PTR-MS employing a quadrupole MS (QMS) and hydronium ion reagent ions was used in a study to better quantify and characterize chemically reactive compounds present in the ambient air as a result of biomass combustion, which have an impact on ozone and SOA chemistry in the atmosphere. (65) The increased hydroxyl reactivity found was associated with compounds including acetaldehyde, acetonitrile, and acetone. Although PTR-QMS only has unity mass resolution, potential isobaric interferences were carefully considered to assist with data interpretation and the detection limit was typically less than 100 ppt. (65) A quadrupole PTR-MS system was also employed in the simultaneous monitoring of organic peroxy radicals in order to better understand the kinetics and reaction mechanisms of these highly reactive atmospheric species. (66)

Time-of-flight PTR-MS provided useful insight into the characterization of VOCs present in the atmosphere in Beijing, China, during a winter haze period. (67) This was important as VOCs are key contributors to the formation of SOAs, and useful information that could contribute to understanding the atmospheric chemistry could be obtained with respect to diurnal variations, emission ratios, and variations in reactivity. The use of a ToF-MS instead of a quadrupole based system, as had been used previously, allowed for enhanced mass resolution (although in this case, a low time resolution was employed to enhance the signal-to-noise ratio), and PTR-MS circumvented the need for pretreatment of air samples (aside from filtration through a Teflon membrane) required with GC/MS analyses. Potential limitations regarding poor signal-to-noise ratios as a consequence of a lack of analyte preconcentration should not be forgotten with this technique, especially when target analytes are present at trace concentrations in the atmosphere. In this study, hydronium ions were used as the reaction ions. Possible interferences of alcohols (specifically methanol and ethanol) on formaldehyde detection as well as protonated isoprene on cycloalkanes and 1,4-pentadiene were noted. (67) Uncertainties due to changes in humidity are also a concern with PTR systems employed in atmospheric chemistry analyses, as it can result in a change in the ratio of primary hydronium reagent ions and cluster ions, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, within the drift tube. (67) The humidity dependence of sensitivity to VOCs is more prominent at lower E/N , while at higher E/N , the sensitivity to VOCs may be hindered due to

fragmentation and shorter reaction times, resulting in the need to calibrate the instrument under different humidity conditions. (61) Sensitivity to alcohols is higher under more humidified conditions, as under dry conditions, they may be present as dehydrated ions. (61)

Response times of PTR-MS instruments can be enhanced by operating the drift tube at elevated temperatures, which assists in the analysis of less volatile compounds and even particle bound analytes. (61) However, the potential for degradation and reaction of target molecules under such conditions needs to be considered and tested to ensure correct interpretation of the resulting mass spectra.

A new gas inlet and reaction chamber design were developed for a PTR-ToFMS system to allow for longer reaction times, providing better sensitivities for VOCs, SVOCs, and highly oxidized organic molecules (HOMs). (68) The system was tested using laboratory based ozonolysis experiments of α -pinene but may find an application in atmospheric studies.

Different aerosol sample introduction systems (including a denuder system to strip gas phase analytes from particles) for PTR-ToF-MS were compared with respect to the characterization of biogenic SOA formed from ozonolysis of monoterpenes and tree emissions during a chamber study. (69) It was noted that the sampling and desorption methods employed could provide additional comparable information on the volatility of individual compounds and thereby atmospheric fate information, although thermal breakdown of analytes cannot be excluded. Total aerosol recoveries were found to vary. This was ascribed primarily to the differences in the field strength (E/N) in the drift tube reaction ionization chamber, which resulted in differing extents of fragmentation (relatively lower E/N leads to longer ion residence times and higher sensitivities), and also due to differences in collection and desorption conditions. (69)

High Resolution Mass Spectrometry

High resolution mass spectrometry (HRMS) opens the door to the determination of a wide array of analytes in complex samples, without the need for authentic standards (70) and in some cases without upfront separation of mixtures, due to the fact that the HRMS provides an additional dimension in the analysis in terms of selectivity by resolving peaks of small mass difference. Many developments in the use of HRMS for atmospheric analyses have recently been reported, due to ongoing improvements in instrumental performance and reduction in the cost thereof, although HRMS has been a cornerstone of some analyses such as that of airborne polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) for a long while. (71)

In this context, HRMS is a potentially powerful screening tool in environmental analyses, allowing for nontargeted analyses. (72) This may be facilitated by coupling the HRMS to LC or GC systems to enhance resolution as well as by high performance computing to handle the processing of the large data sets, which are generated in nontargeted approaches.

HRMS has been employed in the development of quasi-targeted analytical methods for the identification of emerging and new pollutants, such as that proposed by Tang and Tan (73) for halogenated organic pollutants (HOPs), including polychlorinated dibenzo-*p*-dioxins

(PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) as well as their brominated homologues in a range of matrices including ambient air. Here, GC-HRMS (specifically double focus magnetic sector HRMS) was employed in multiple ion detection mode. Theoretically simulated isotopologue distributions of potential novel HOPs were compared to detected mass spectra, and predicted retention times based on empirical calculations were aligned to detected retention times in order to exclude interferences. The method was validated using reference standards and was subsequently applied to environmental samples, which allowed for a number of previously unreported HOPs (such as mix- and polyhalogenated compounds) to be identified. (73) The authors noted the potential of this approach to provide higher sensitivity and mass accuracy with fewer interferences and lower sample consumption than typical nontargeted methods, although it must be mentioned that some idea of the structures of interest is required for this quasi-targeted approach, which may be time-consuming to set up, and it remains a screening approach.

Another application of HRMS in atmospheric chemistry analysis relates to the comprehensive molecular characterization of atmospheric brown carbon (BrC), which are light absorbing components of organic aerosols. (58) BrC is ubiquitous in the atmosphere and has potential impacts related to climate change and human toxicity, thereby making the chemical characterization thereof important. Such analyses are very challenging, however, due to the complexity of the aerosols. Lin et al. (58) therefore used a combination of analytical approaches in the study of BrC generated by biomass burning. Two complementary ionization techniques, namely, atmospheric pressure photo ionization (APPI) and electrospray ionization (ESI) were employed with high performance liquid chromatography (HPLC) (refer to Liquid Chromatography for more information) and HRMS to allow for the separation and identification of both polar and nonpolar components in the BrC. Very different mass spectra were obtained for the two ionization modes and also for the positive and negative charge modes in each case, as seen in Figure 4. Overall, 2209 unique elemental formulas were determined by these HRMS approaches, with a larger fraction being detected by APPI- and APPI+ modes and with little overlap between the detection of the same species by different modes. No compounds at all were detected by all four modes. A photodiode array detector (PDA) was also used to characterize the light absorption properties of the components. By employing these complementary methods, it could be determined that more than 40% of light absorption of the solvent-extractable BrC was due to relatively nonpolar compounds, such as PAHs, which require APPI for their determination, while less than 30% of the light absorption by the BrC was due to water-soluble, polar compounds that are detected by ESI. (58) This study highlighted the importance of employing a range of complementary analytical approaches in the analyses of atmospheric samples that contain diverse molecular structures with a broad range of polarities and molecular weights.

HRMS has been employed in targeted atmospheric studies, such as in the determination of traditional and novel halogenated flame retardants in the urban ambient air of Madrid, Spain, (15) where seasonality and meteorological effects were investigated using GC-EI-HRMS. Isotopic dilution GC-HRMS using ¹³C-labeled standards has been utilized to determine specific congeners of chlorinated and brominated PAHs in the atmosphere at ultratrace levels. (74) High volume sampling onto PUF cartridges and quartz fiber filters was

employed, with accelerated solvent extraction using hexane and dichloromethane (1:1, v/v). The HRMS (magnetic sector operating in selected ion monitoring (SIM) mode) provided limits of detection that were approximately 3 orders of magnitude lower than GC-quadrupole MS based methods, as losses during sample extraction and preconcentration were corrected for by the isotopic addition.

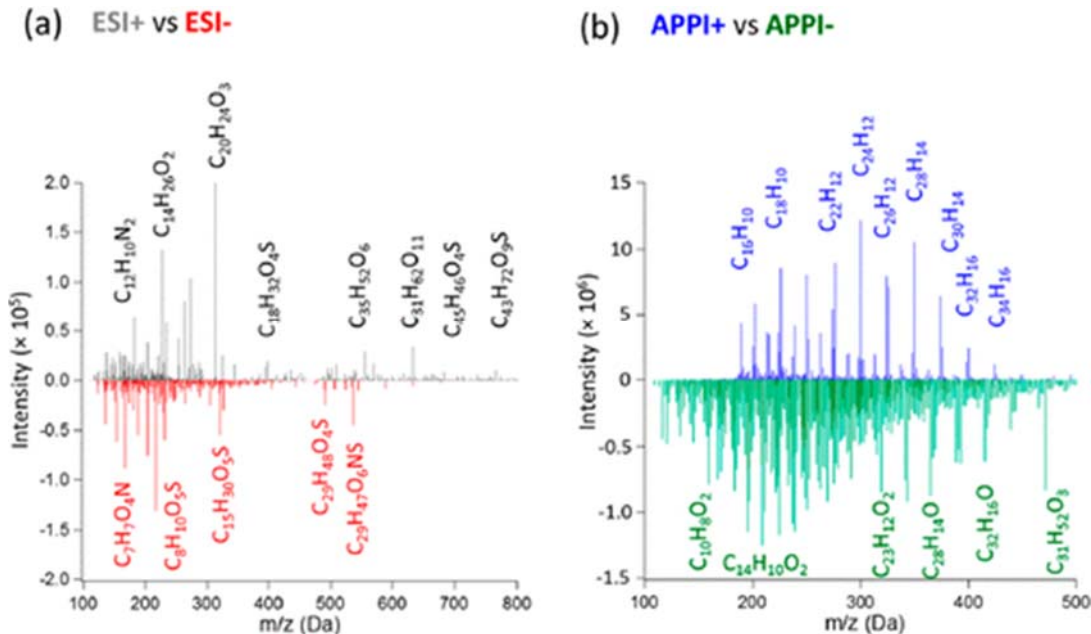


Figure 4. High resolution mass spectra of organic compounds extracted by acetonitrile/dichloromethane/hexane (2:2:1) from biomass burning aerosols analyzed by (a) direct infusion ESI-HRMS and (b) APPI-HRMS in both positive and negative charge modes. (Reproduced from Lin, P.; Fleming, L.; Nizkorodov, S.; Laskin, J.; Laskin, A. *Anal. Chem.* **2018**, *90*, 12493–12502 (ref (58)). Copyright 2018 American Chemical Society.)

Different means to effectively ionize target analytes, particularly the highly oxidized products of ozonolysis of organic molecules in the atmosphere, have received ongoing research attention, due to the complexity involved and the need to have a more complete understanding of the reaction mechanisms of gas phase ozonolysis in the atmosphere. A novel ammonium chemical ionization time-of-flight mass spectrometer ($\text{NH}_4^+\text{-CI-ToFMS}$) was recently developed, which utilizes ammonium ion adduct products to measure oxidized product molecules (such as RO_2 radicals and closed shell products) derived from the gas phase ozonolysis of cyclohexene. (75) This method was compared to acetate-CI-API-ToFMS, as highly oxidized multifunctional organic compounds are able to form stable acetate adduct ions and deprotonation products. Ammonium ions have been used in PTR-MS to provide more selectivity as only a portion of analytes have greater proton affinities than ammonia. In this study, NH_4^+X_n reagent ions were produced in a corona discharge ion source from ammonia and water vapor. (75) The $\text{NH}_4^+\text{-CI-ToFMS}$ was able to detect a range of oxide products from the ozonolysis of cyclohexene including peroxy radicals (RO_2), aldehydes, hydroxyl-carbonyls, peroxy-carboxylics, and hydroperoxides with high sensitivity. The acetate-CI-API-ToFMS, on the other hand, underestimated oxidized products that did not contain an OOH group. The low detection limits obtained with the ammonium based system

suggest the potential future use of this technique for environmental measurements in real-time. (75)

The recently commercialized Orbitrap MS is also a HRMS and is based on ion trap technology, (76) which employs the trapping of pulsed ion beams in an electrostatic field that is created between an axial central electrode and a coaxial outer electrode. (77) Rotations around the central electrode are combined with harmonic oscillations along it to provide stable ion trajectories, where the frequencies of the axial oscillations are based on the mass-to-charge ratio of the ions. (77)

Orbitrap MS instruments are currently more expensive than other high resolution mass spectrometers such as ToFMS and also have limited potential for portability. (61) As commercial instruments have become more readily available, their application to atmospheric chemistry monitoring has grown. Recent examples thereof include the use of APCI-Orbitrap MS analysis of atmospheric organic aerosols online with high mass resolution ($R = 140\,000$) and accuracy (<2 ppm). (54) The aerosol particles were vaporized in a heated ceramic tube inside the ion source prior to ionization. APCI features minimal fragmentation and matrix effects and also allows for fast switching between positive and negative ionization modes, allowing for the identification of a range of analytes in real time (Figure 5). In this study, a nontarget, real-time approach was employed for the first time using this technology under ambient conditions without preconcentration or filter sampling, whereby molecular variability between ambient day and night time aerosol composition could be determined. (54) Analytes found in the aerosol included highly oxidized organic nitrates, organic dinitrates, and nitrooxy-organic sulfates (Figure 5). The authors noted that the development of more instrumentally robust Orbitrap technology that is more routine in operation will facilitate further applications thereof in the study of atmospheric aerosol chemistry. (54)

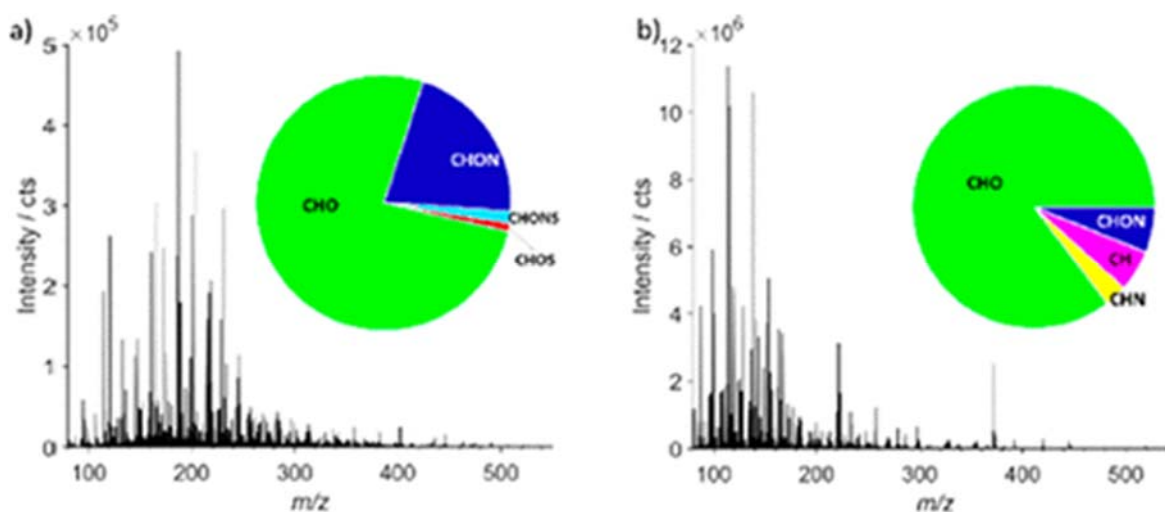


Figure 5. Average background corrected mass spectra of ambient aerosols determined by APCI-Orbitrap MS in (a) negative and (b) positive ionization mode. (Reproduced from Zuth, C.; Vogel, A.; Ockenfeld, S.; Huesmann, R.; Hoffmann, T. *Anal. Chem.* **2018**, *90*, 8816–8823 (ref (54)). Copyright 2018 American Chemical Society.)

Quartz fiber filter samples of PM collected in Shanghai were analyzed by UHPLC-Orbitrap MS using a nontarget screening approach after acetonitrile extraction and pentafluorobenzylhydroxylamine derivatization of carbonyl containing analytes. (70) Gradient elution was employed using 0.1% formic acid in water and 0.1% formic acid in acetonitrile as mobile phases, respectively. Between 810 and 1510 organic compounds were determined in negative electrospray ionization mode (ESI⁻), and 860 to 1790 compounds were found by positive ESI (ESI⁺). Results indicated a potential photochemical source of compounds containing only CHO and detected in ESI⁻ and sulfur containing organics (also detected in ESI⁻) as these were more prevalent in day time samples, while nocturnal nitrate radical chemistry resulted in higher concentrations of nitrogen and sulfur containing organics in night time samples. Product-precursor pair analysis was employed to inform one about possible reaction pathways. (70)

Liquid chromatography with HRMS in the form of an Orbitrap mass analyzer was recently employed in the determination of 28 airborne pesticides that had been sampled onto a PUF-XAD-2-PUF sandwich filter and subsequently microwave extracted with ethyl acetate (38) and similarly for the analysis of airborne pesticides sampled onto filters. (45) An advantage of this method is the potential for future retrospective analysis of samples as additional environmental analytes become of interest.

A combined targeted and nontargeted screening approach to the analysis of hydroxylated PAHs (OH-PAHs) in both ambient urban and car tunnel PM in Stockholm, Sweden, was achieved by LC-Orbitrap MS with heated electrospray ionization in negative ionization mode. This facilitated the investigation of the occurrence of OH-PAHs for which there are no reference standards. (78) Regarding the nontargeted analyses, suspect OH-PAHs were identified by the exact mass of the precursor and product ions (<5 ppm mass accuracy), molecular formulas, isotopic patterns, and fragmentation patterns, as OH-PAHs are known to undergo a loss of neutral CO. A total of 20 OH-PAHs were identified in the samples collected onto glass fiber filters after methanol accelerated solvent extraction (mobile phases were water and acetonitrile), of which 9 were target analytes and the remainder were suspect analytes tentatively identified and semiquantified using an average relative response factor. (78)

Aerosol Mass Spectrometry

Aerosol mass spectrometry (AMS) is evolving into a popular technique to facilitate the direct analysis of atmospheric samples with high time resolution. In AMS, aerosol particles are drawn into a vacuum chamber by means of a set of aerodynamic lenses and are focused into a narrow particle beam. Analytes are then thermally vaporized and ionized by EI with analysis byToFMS. The use of this hard ionization source induces a high degree of fragmentation of analyte molecules, which may hinder identification and quantification of individual organic compounds present in the aerosol sample. (54)

Xu et al. (79) reported on the use of HR-ToF-AMS to chemically characterize nonrefractory submicrometer particles (NR-PM₁) in the atmosphere of Beijing, China. This technology facilitated higher time resolution (in this case 5 min averages) than offline filter based methods, which in turn assists with source apportionment. The impact of biomass burning

on the organic content of the NR-PM₁ could thus be determined, and a positive matrix factorization model was applied to the results to determine the relationships between organic and inorganic components.

A novel AMS based instrumental development allows for the determination of both inorganic composition and PAH profile of the same, individual atmospheric particle. (80) Positive molecular ions are produced after laser desorption from the particle, where ionization is achieved first by a 248 nm UV-pulse to selectively ionize PAHs by resonance enhanced multiphoton ionization (REMPI) that are then extracted into the first flight tube. A 193 nm pulse then ionizes refractory substances that are analyzed in a second flight tube (laser desorption/ionization, LDI⁺). This approach has allowed for source apportionment of ambient particles (Figure 6) and the assessment of potential health effects. (80)

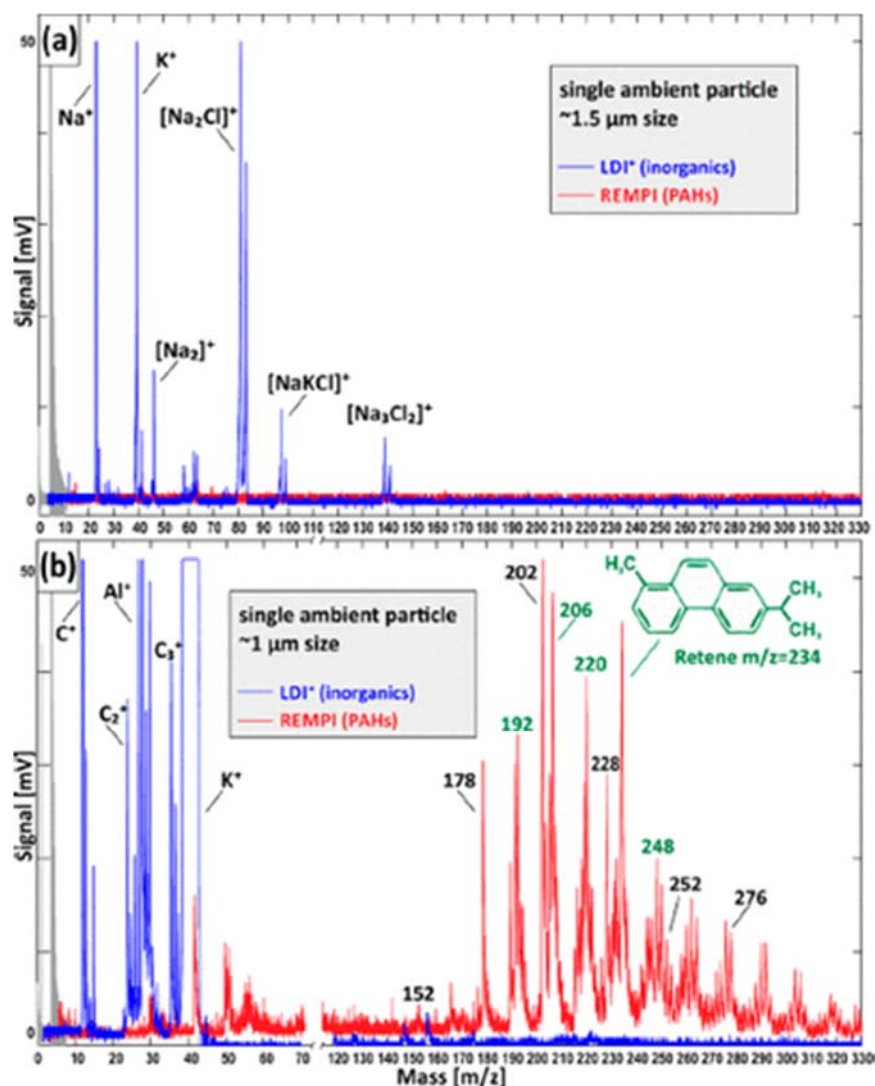


Figure 6. Mass spectra obtained by AMS analysis of individual ambient particles with combined LDI⁺ and REMPI ionization of desorbed components of (a) a sea-salt particle and (b) a PAH-containing particle likely from wood or biomass burning due to the presence of retene. (Reproduced from Passig, J.; Schade, J.; Oster, M.; Fuchs, M.; Ehlert, S.; Jäger, C.; Sklorz, M.; Zimmermann, R. *Anal. Chem.* **2017**, *89*, 6341–6345 (ref (80)). Copyright 2017 American Chemical Society.)

An uncertainty with AMS is collection efficiency (CE) due to potential losses (nondetection) resulting primarily from particle bounce at the vaporizer. (81) Typically, a default CE of 0.5 is employed; however, these effects are dependent on a range of variables, including particle composition, acidity, humidity, and nitrate content. (82) Some of these, such as humidity, can be controlled by the use of in-line desiccants, but usually, default CE correction factors are employed. (79)

Other Mass Spectrometric Methods

Tandem Mass Spectrometry

Tandem mass spectrometry allows for enhanced selectivity of analyses. A recent example of relevance to atmospheric chemistry monitoring is the development of a method to identify individual specific organic hydroperoxides and peroxy acids (ROOH) found in SOA using positive ion atmospheric pressure chemical ionization-tandem MS (APCI-MS/MS). (83) Organic hydroperoxides are formed in the atmosphere via VOC oxidation reactions under low NO_x conditions and are important variables in atmospheric chemistry. Sample introduction was achieved via direct infusion of liquid samples, in this case methanol extracts of SOA generated from ozonolysis of a terpene. Precursor ions of a specific *m/z* were transmitted through the first quadrupole, followed by fragmentation thereof in a collision cell containing argon. The resulting mass fragment product ions were analyzed by the third quadrupole. Ammonium acetate was tested to enhance the signal of the ammonium adducts of the molecular ions in the mass spectra, where unique fragmentation pathways were observed involving the simultaneous loss of ammonia and hydrogen peroxide. (83) A lack of available and stable standards is a big challenge in the monitoring of these highly reactive species, and the proposed method has yet to be tested on real atmospheric samples.

GC/MS/MS employing electron ionization and multiple reaction monitoring (MRM) has recently been employed in the investigation of tetrachlorinated biphenyls (PCB47+48+75, 51, and 68) in the atmosphere of a regional background site in China. (50) Samples were collected by means of high volume sampling (at 300 L min⁻¹) onto PUF (gas phase) and quartz fiber filters (particle phase) and were Soxhlet extracted with dichloromethane for 24 h. Although this sample preparation strategy is very time-consuming and environmentally unfriendly, the results were important in elucidating unintentional production of these PCBs, which have been banned for several decades. It was found that atmospheric levels were strongly correlated to ambient temperature, suggesting volatilization from contaminated surfaces, while a negative correlation with PAHs and a weak correlation to other PCB congeners pointed to a unique unintentional source and not a combustion or industrial thermal process. (50)

Secondary Ion Mass Spectrometry

Secondary ion mass spectrometry (SIMS) is a surface analysis technique in which a focused primary ion beam is used to generate characteristic secondary ions from the sample surface, which are then analyzed by a mass analyzer (such as a ToFMS), as shown in Figure 7. SIMS has been applied to the analysis of atmospheric particulate matter, and recent advances

and applications in this regard have been reviewed by Huang et al. (84) Surface characterization, single particle analysis, and depth profiling may assist in enhancing our understanding of atmospheric processes and particle formation mechanisms. In this context, SIMS may provide high surface sensitivity and high spatial resolution chemical imaging or mapping upon rastering the primary ion beam over the sample surface (the NanoSIMS can provide a lateral resolution of 40 nm). Depth profiling capabilities are possible when a sputter ion gun is employed; thus, both surface and bulk chemical information can be obtained by SIMS regarding inorganic and organic components in PM. (84)

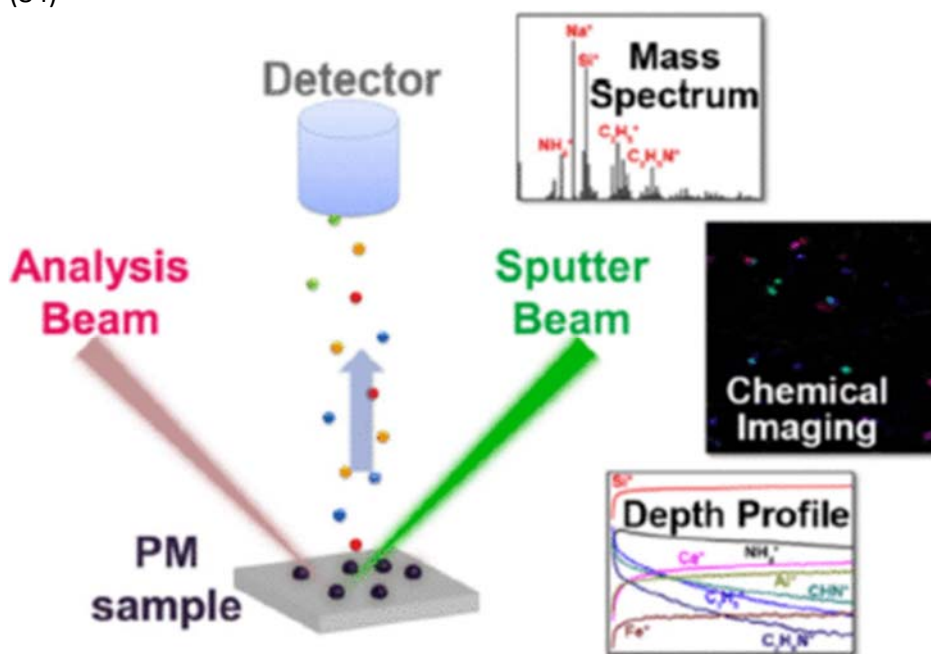


Figure 7. Schematic diagram of the analysis of particulate matter by secondary ion mass spectrometry. (Reprinted from *Anal. Chim. Acta*, Vol. 989, Huang, D.; Hua, X.; Xiu, G.; Zheng, Y.; Yu, X.; Long, Y., Secondary ion mass spectrometry: The application in the analysis of atmospheric particulate matter, pp. 1–14 (ref (84)). Copyright 2017, with permission from Elsevier.)

Challenges in the application of SIMS include the low ionization efficiencies of some compounds of relevance in PM analyses, such as PAHs, which may require the use of cluster ion beams to increase the secondary ion yield. (84) The fragmentation of molecular ions in SIMS analysis, in addition to matrix effects, makes data interpretation and quantification difficult, as secondary ion yields are greatly influenced by the chemical environment of the analytes. (84) For SIMS analysis of PM, the sample is collected on a filter. Desorption losses of volatile and adsorbed gaseous species, including PAHs, from the collected PM under vacuum may lead to inaccuracies regarding their chemical characterization. The use of cryogenic temperatures and alternative filter materials has been found to reduce these effects. (84)

Satellite Based Monitoring

Satellite instruments provide a global view of the state of the Earth's atmosphere (85) as they provide the opportunity to probe the chemistry of the atmosphere, generating spatiotemporal data over extended time periods based on remote spectroscopic methods. These trends are invaluable in assessing changes in air quality and the related potential environmental and human health impacts; therefore, a number of studies to determine and evaluate these trends have recently been published. An example is the evidence of an increase in atmospheric ammonia concentrations over a period of 14 years based on daily measurements over a number of agricultural areas in the world, as determined by the Atmospheric Infrared Sounder (AIRS) aboard the Aqua satellite of NASA. (86) These increases have been related to increased fertilizer use, increasing temperatures arising from climate change, and lower levels of acidic gases in the atmosphere (SO_2 and NO_x), which decrease ammonia concentrations by aerosol formation. The Ozone Monitoring Instrument (OMI), which is a UV–vis solar backscatter grating spectrometer that measures the Earth's radiance spectrum on board NASA's Aura satellite, has also been providing data for an extended time period. (87) Long-term trend data is thus available for several key pollutants including O_3 , NO_2 , SO_2 , HCHO, and aerosols.

Another satellite based atmospheric monitoring system is the Atmospheric Chemistry Experiment (ACE), which provides volume mixing ratios for 37 molecules and 21 related isotopologues derived from a Fourier transform spectrometer and a spectrophotometer (a Measurement of Aerosol Extinction in the Stratosphere and Troposphere Retrieved by Occultation (MAESTRO) system). (85) The TEMPO system (Tropospheric Emissions: Monitoring of Pollution) is currently under development with the aim of measuring atmospheric pollution over North America from space by the employment of ultraviolet and visible spectroscopy. (88) The planned high resolution scale ($\sim 2.1 \text{ km N/S} \times 4.4 \text{ km E/W}$) is expected to facilitate the improvement of emission inventories, estimations of population exposure levels, and enhanced emission control strategies. Although satellite based monitoring of atmospheric chemistry is undoubtedly useful in indicating trends, rigorous validation using long-term ground based measurements is required.

Spectroscopy in the Analysis of Bioaerosols

Bioaerosols are defined as all suspended biological materials in air, including bacteria, fungi, viruses, and pollen as well as their derivatives such as allergens, endotoxins, and mycotoxins. (89) Bioaerosols may incur a diverse range of impacts ranging from human toxicological effects (90,91) (of particular relevance in indoor air) to climate change, although the sources, abundance, composition, and effects of bioaerosols are not yet well characterized. (92,93) Due to the recent increase in research interest regarding the monitoring of bioaerosols, in this section, methods to monitor bioaerosols in the ambient atmosphere will be briefly reviewed.

A significant amount of research has been conducted into establishing the contribution of bioaerosols to haze episodes in China, as recently reviewed by Xie et al. (92) Such haze events are characterized by high levels of $\text{PM}_{2.5}$, where the contribution of bioaerosols has been found to range from 1.5% to 15% and to be 2 to 5 times higher on haze days. (92) The

distribution of bioaerosols is found to be influenced by meteorological (ambient temperature, relative humidity, wind speed, and direction) and environmental conditions (such as anthropogenic emissions of SO₂, PM, and NO_x) in a complex manner. Generally, conditions that promote biological activity, such as moist conditions and elevated levels of airborne nutrients such as nitrates and sulfates (secondary inorganic aerosols), result in higher levels of bioaerosols. (92) The relationship between bioaerosol levels and PM in the atmosphere depends on the composition of the PM and the potential toxicity thereof, although this aspect requires further research.

It has been noted that there is a lack of systematic and consistent results from bioaerosol studies, due to differing sampling and analytical approaches and a lack of standardization. (91,92) Sampling is typically by impaction, impingement, or filtration, while analysis is achieved by culturable or nonculturable methods. It has been noted that only a small portion of microorganisms in bioaerosols can be cultured, thus detecting only these leads to a significant underestimation of bioaerosol loading. (92) Detection techniques can be regarded as either conventional or emerging, as recently reviewed by Sharma Ghimire et al. (94) Analysis includes fluorescence and molecular approaches (the latter has been reviewed by Yoo et al. (90)), bioluminescence, polymerase chain reaction (PCR) and high throughput based sequencing, mass spectrometry, and denaturing gel electrophoresis. Many of these methods require numerous time-consuming steps.

Developments in chemical characterization (as opposed to microbiological characterization) relate particularly to fluorescence spectroscopy and mass spectrometric approaches. For example, a Wideband Integrated Bioaerosol Spectrometer (WIBS) based on ultraviolet light induced fluorescence (UV-LIF) has been employed in detecting fluorescing aerosol particles in the size range of 0.5 to 20 µm in urban Spain, (95) where levels were the highest during the night time and were positively correlated to relative humidity. A WIBS system was used in an industrial zone in China, where bacteria were found to be the dominant bioaerosol species present after cluster analysis of the data was performed. (96) A limitation of the WIBS approach is that it provides integrated fluorescent signals, which limit speciation of bioaerosols. Potential interferences from other fluorophores including PAHs need to be considered, although these are generally weak due to inner quenching effects and can thus be excluded. (96)

An inexpensive single-particle fluorescence spectrometer using laser-induced fluorescence (LIF) has been developed for bioaerosol monitoring. (97) Four excitation wavelengths (280, 350, 405, and 450 nm) provided by diode lasers and light emitting diodes (LEDs) are employed, which correlate to common biological fluorophores and allow for the generation of reproducible spectra. (97) Samples need to contain a low number of particles to prevent spectral overlap, and it is necessary for the detector to be optimized for the fluorescence intensity and size of particles analyzed.

Single particle mass spectrometry has been applied to the analysis of bioaerosol particles using phosphorus as a proxy for bioaerosols. (98) The technique required a machine learning statistical approach based on mass spectra of known particle types due to the complex sources of phosphorus in PM. Aside from the presence of this element in the cell membranes and nucleic acids of bioaerosols, phosphorus can also arise in PM due to its

presence in fly ash from combustion and also from suspended mineral dust, complicating this approach. (98)

The main bioaerosol components have recently been determined by liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) employing MRM. (99) In this case, specific chemical biomarkers were used as unambiguous indicators of particular bioaerosols, for example, ergosterol related to fungal components and dipicolinic acid, to bacterial spores, and required analysis by electrospray ionization with MS analysis or atmospheric pressure chemical ionization with MS/MS analysis for sterols and chlorophylls. Diagnostic ratios between biomarkers were also determined. Size fractionated samples were collected onto Teflon substrates via impactors operating at 30 L min^{-1} . The complex and time-consuming multistep sample preparation and analytical methodology employed are shown in Figure 8. (99)

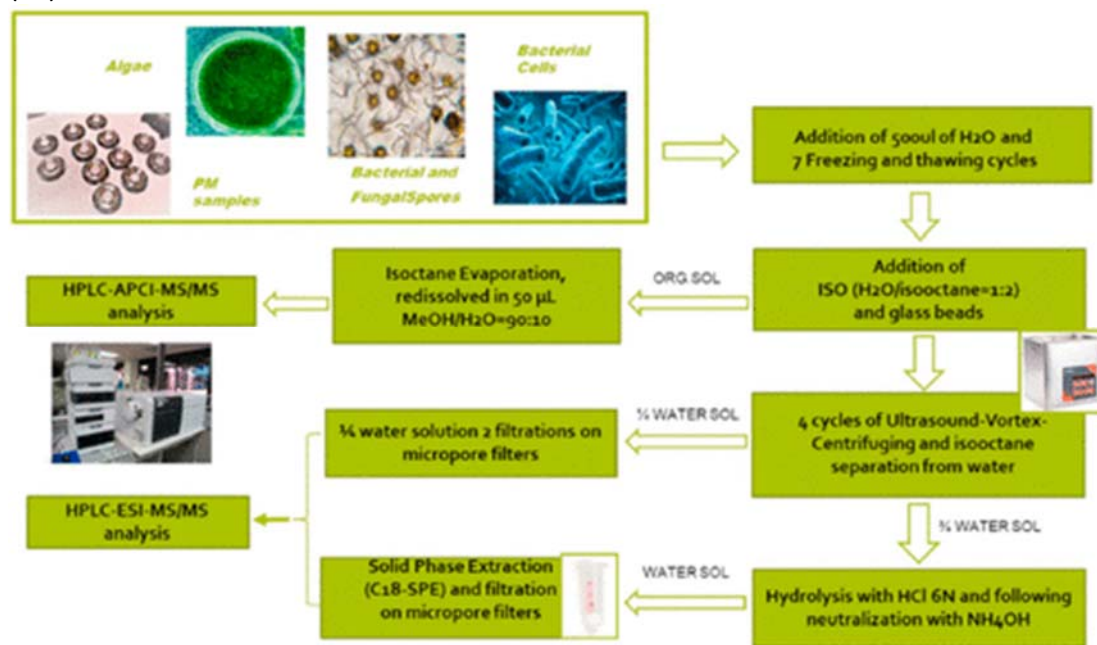


Figure 8. Analytical procedure employed for the extraction and purification of bioaerosols sampled onto filters. (Reprinted from *Microchem. J.*, Vol. 149, Buiarelli, F.; Sonogo, E.; Uccelletti, D.; Bruni, E.; Di Filippo, P.; Pomata, D.; Riccardi, C.; Perrino, C.; Marcovecchio, F.; Simonetti, G., Determination of the main bioaerosol components using chemical markers by liquid chromatography–tandem mass spectrometry, pp. 103974 (ref 99)). Copyright 2019, with permission from Elsevier.)

Sensor Technologies

Sensors provide an alternative option to traditional analytical methods for atmospheric chemistry monitoring, and the relative advantages and limitations of these have been extensively reviewed by Rai et al. (100) They are attractive due to their low cost, which allows for their high density deployment, thereby providing spatiotemporal pollution data. This information may be a useful supplement to data generated using standard methods and can be used to inform exposure estimates and the identification of air pollution hotspots. Sensors offer portability due to their small size and light weight. Moreover, sensor

technologies are typically user-friendly and can enhance community awareness regarding air quality and promote citizen science.

Although it is clear that robust sensors have the potential to revolutionize air quality monitoring, particularly when linked to wireless communication technology, there are challenges with this approach that need to be addressed. The major drawback of sensor technologies is poor data quality, which may arise from a number of sources, including inconsistent product quality and insufficient or inappropriate calibration, particularly when supplier based calibrations are not checked after use and when laboratory based calibrations are not reflective of real conditions. (101) Variation in the sensitivity of sensors as they age, due to high dust levels, or as humidity and temperature varies as well as cross-sensitivity to other ubiquitous gases are also cause for concern. The results generated by sensors thus need to be carefully considered, and data quality should be enhanced by routine calibration checks and by use of statistical data quality assurance techniques. (100,101)

Although they are generally not currently suitable for legislative compliance monitoring or for applications requiring the provision of high accuracy and precise and reliable results, sensors and screening methods may indicate coarse air quality information regarding the extent of pollutant loading (such as low, medium, or high). Multisensor systems have thus been developed and tested for the determination of air quality index values. (102) Another important potential application of sensors is in the monitoring of air quality in postemergency situations, such as after a hurricane was experienced in Puerto Rico. (103) The hurricane resulted in a disruption of the electricity supply and consequently an increase in the use of generators. The existing air monitoring network was damaged; however, air quality impacts of the generator use could be monitored by low cost monitors based on sensor arrays, which were solar powered. (103) Recent developments in sensor technology and screening methods for atmospheric monitoring are reviewed in this section, and opportunities for future improvements are mentioned.

Optical Sensors

Most sensors for monitoring particulate matter are based on light scattering, which provide a low cost option, with low power requirements and quick response times. (100) However, this method is only suitable for PM > 0.3 μm in diameter, and size fractionated collection options, such as an impactor or filter in the air inlet, are not widely available. (100) This should be addressed as the importance of particle size in determining potential human health effects is well-known. The long-term performance of these sensors has not been determined; therefore, Rai et al. (100) noted the necessity of frequent calibration.

Three low cost optical particle counters (OPCs) were deployed in Kenya to evaluate airborne PM (in PM₁, PM_{2.5}, and PM₁₀ size ranges), and good inter instrument precision was found (<10% coefficient of variance). (104) It had been previously noted that these sensors require on-site calibration based on a standard gravimetric approach as well as correction for relative humidity in order to achieve accurate PM mass concentrations. (105) Feenstra et al. (106) found a varying impact of humidity on 12 different low cost PM_{2.5} sensors with some models showing an increased bias error with increasing humidity.

Low cost black carbon (BC) sensors have been deployed in dense networks in urban areas, specifically 100 sensors over 15 km² in California. (107) These sensors are aerosol photometers, which measure the rate of 880 nm radiation attenuation by BC sampled onto a white fibrous filter by means of a pump. Power is provided by a battery and photovoltaic panel; however, widespread pump failures hampered the operation of the network, and a number of the sensors were lost or stolen. The results that were collected did however show complex spatiotemporal dynamics of combustion-related air pollutants. (107)

A volatile organic compound (VOC) sensor based on a hybrid photonic cavity (an optical micro ring resonator) modified with metal-organic framework (MOF) coatings has been developed, which is not sensitive to humidity and can detect trace levels of VOCs. (108) These are not yet readily available commercially, and they have relatively long response times (~30 min, depending on the MOF thickness).

Electrochemical and Semiconductor Based Sensors

Most low cost sensors that have been developed for gaseous air pollutant monitoring are either electrochemical or metal-oxide-semiconductor (MOS) sensors. (100) In MOS sensors, the electrical properties of the metal oxide change upon exposure to the target molecule, such as O₃, NO₂, or CO. Challenges encountered with this technology include sensitivity to environmental conditions (such as humidity and temperature), nonlinear response curves, and poor selectivity with respect to interfering gases; (100) therefore, some commercial gas sensors incorporate filters to remove interferences, such as O₃ removal in NO₂ sensors. (101)

Electrochemical sensors typically measure current changes upon reaction of the target analyte with an electrolyte and may provide better sensitivity and selectivity than MOS sensors, although they are larger and are more costly. In addition, their performance characteristics have not been well-defined (100) and may also be affected by environmental conditions (such as humidity and dust fouling). Studies have found that the rate of change in relative humidity is important, as rapid changes (~20% per min) generated instant large changes in the electrochemical O₃ sensor signal, which took up to 40 min to return to the original values after such an event, while slow changes in relative humidity (~0.1% per min) had little effect on the signal of the sensor. (109)

Standard approaches to the direct calibration of gas sensors are expensive (in terms of both equipment and labor) and thereby negate the choice of this monitoring technology. An alternative approach has been developed with respect to CO₂ sensors, by means of locating higher grade, well-calibrated reference instrumentation within the air quality sensor network. (11)

Nine commercial semiconductor sensors were combined in a gas sensor array to provide low cost online atmospheric gas detection, as shown in Figure 9. (102) Three of these arrays were deployed, and a calibration and normalization procedure was developed to overcome data quality challenges arising from variations between sensors and temporal instability.

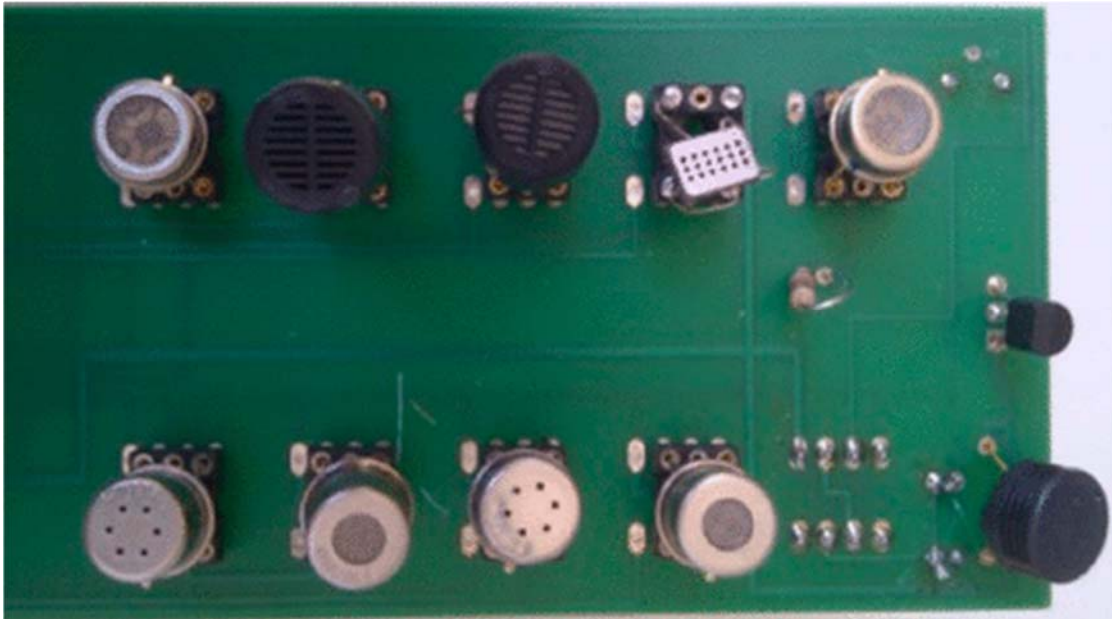


Figure 9. Multisensor array comprised of commercial semiconductor gas sensors. (Reprinted from *Sens. Actuators, B*, Vol. 241, Al Barakeh, Z.; Breuil, P.; Redon, N.; Pijolat, C.; Locoge, N.; Viricelle, J., Development of a normalized multisensors system for low cost online atmospheric pollution detection, pp. 1235–1243 (ref (102)). Copyright 2017, with permission from Elsevier.)

Other Screening Methods

Bioassays have been developed to provide rapid screening detection of atmospheric components, particularly persistent organic pollutants (POPs), and have found use in risk assessments to evaluate potential human toxicity of atmospheric samples. Although bioassays do not provide real-time measurements, in contrast to the sensors described in the rest of this section on sensor technologies, they do provide a screening approach with some similar advantages in terms of the ease of generating spatiotemporal monitoring data.

A novel, sensitive bioassay for compounds activating aryl hydrocarbon receptors (AhR) was developed on the basis of a novel dioxin-responsive domain driven luciferase-reporter plasmid. (110) AhR can have an impact on critical physiological processes including cell proliferation and immune response. The target analytes were dioxins, dioxin-like PCBs, and PAHs in ambient air samples collected by high volume sampling onto a quartz fiber filter followed by a PUF cartridge. These were extracted using toluene and *n*-hexane/dichloromethane (1:1), respectively, by means of ASE. The extracts were cleaned up prior to analysis by GC/MS (in the case of PAHs) or HRGC-HRMS (remaining analytes), in addition to parallel analysis employing the bioassay using a microplate luminometer, which provided a minimal detection limit of 0.1 pM for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. (110) The bioassay derived bioanalytical equivalent (BEQ) values for ambient air sample extracts from Beijing correlated well with the toxicity equivalent (TEQ) values from the chemical analysis for cleaned up extracts (Figure 10). It was found that PAHs contributed significantly to the AhR-related biological impacts in samples taken during haze episodes. (110) As this bioassay approach does not provide selectivity between AhR compounds, other unidentified AhR agonists may have contributed to the high total activations found in crude haze sample

extracts; therefore, a nontargeted chemical analysis should be considered to better elucidate this effect.

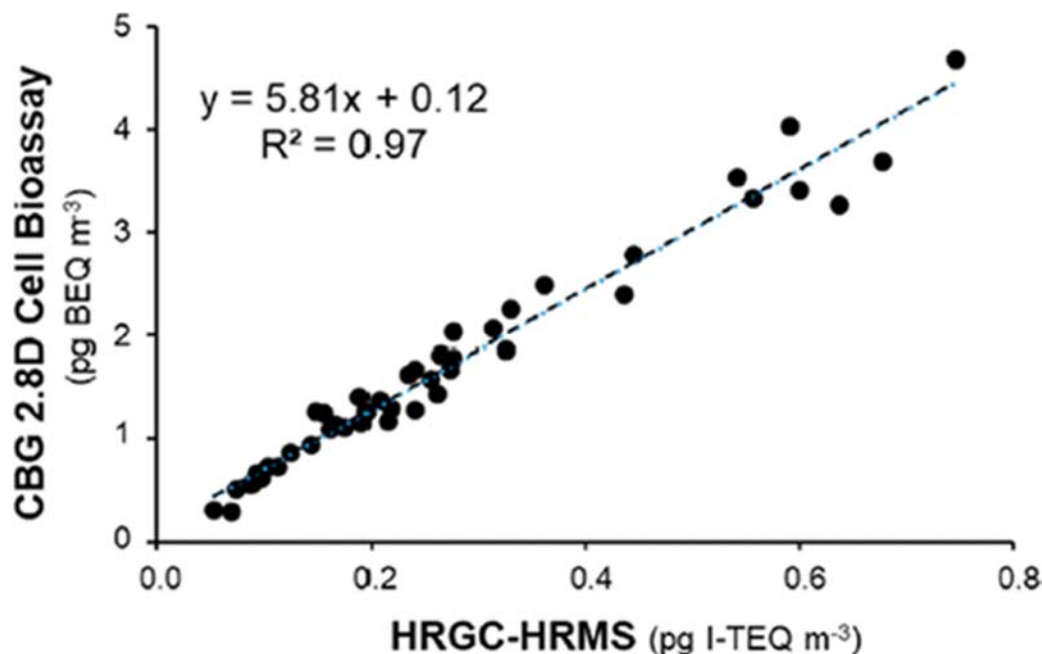


Figure 10. Comparison of toxicity values for 45 ambient air sample cleaned up dioxin-rich extracts collected in Beijing, which were derived from a cell bioassay (expressed as BEQ) and via standard chemical analysis of PCDDs and PCDFs (to provide a TEQ). (Reproduced from Zhang, S.; Li, S.; Zhou, Z.; Fu, H.; Xu, L.; Xie, H.; Zhao, B. *Environ. Sci. Technol.* **2018**, *52*, 2926–2933 (ref (110)). Copyright 2018 American Chemical Society.)

Conclusions and Future Prospects

Atmospheric modeling approaches may assist with a better understanding of the environmental cycling of pollutants on a large scale, such as where an atmospheric transport model was combined with a mass budget analysis and a multiregional input–output model to simulate atmospheric mercury outflow from China. (111) Detailed chemical modeling may also prove useful to better understand monitoring data; global simulations indicate SOA are mostly in a glassy solid phase state in the middle and upper troposphere. (112) This would result in slow diffusion of water, oxidants, and organic molecules and promote long-range transport of reactive and toxic pollutants, including persistent organic pollutants and PAHs, embedded in the SOA, which is corroborated by observations of these species at remote sites. (112) Although air quality models are an effective supplementary tool to atmospheric monitoring, particularly in terms of scenario analysis and forecasting, they require validation by means of suitable measurements, and a clear understanding of the uncertainties in the model predictions is needed.

Multifaceted approaches, combining both monitoring and modeling to determine sources of air pollutants, are valuable, such as in a study of atmospheric ammonia in Shanghai, China (which included passive sampling). (113) A combination of high-frequency atmospheric observations, global monitoring data, and atmospheric chemical transport model simulations has been recently used to trace the main source of increases in atmospheric

trichlorofluoromethane (CFC-11) concentrations, which are likely the result of the new production and use thereof, in contradiction to the phasing out agreement of the Montreal Protocol. (114)

The way in which air sampling is performed is constantly being assessed, and new avenues are being investigated. Recent research has demonstrated the potential for gas sensors to be incorporated into textiles, which could lead to smart clothing. An example is the sensing of gaseous ammonia based on the ohmic resistance of polyester yarn made conductive by dip-coating with polyaniline, which gave a linear response to ammonia gas concentrations over the range of 5 to 25 ppm. (115) A microcontroller facilitates the transfer and updating of results wirelessly to a smartphone. Although such devices are not currently sensitive or selective enough for ambient air monitoring, this is certainly a future prospect with strong linkages to citizen science.

Community based participatory research (CBPR) is typically motivated by concerns regarding air pollution health risks, the proximity of residences to sources of air pollution, and a lack of monitoring data. (116) The development of low cost, user-friendly sensors has facilitated community involvement in atmospheric monitoring; however, communities must understand the limitations and benefits thereof in order to achieve harmony between expected and observed study outcomes. (116) With the rapid developments in sensors, microprocessing, and smartphone technologies, it is expected that citizen science will become increasingly common.

The evolution of analytical instrumentation has allowed for a better understanding of the composition of SOA, particulate matter, and other complex atmospheric samples. The development of multidimensional, comprehensive, and high resolution chromatographic and mass spectrometric methods has significantly reduced the likelihood for misinterpretations of analytical results due to lack of selectivity, leading to better confidence in analytical results and more accurate environmental and human health risk estimations.

Although it is evident from this Review that significant progress continues to be made in the monitoring of the atmosphere, there are a number of challenges that remain such as the resolution of complex mixtures in PTR-MS analyses, (65) the need for reference standards for SOA, and the difficulty in analyzing reactive radical species. Sensitive, high resolution analytical instrumentation generates large data sets, especially where nontargeted approaches are concerned; therefore, improved, user-friendly data processing routines and statistical tools are required to effectively interpret the results obtained. (117) In this manner, ongoing progress can be achieved to better understand the chemistry of the atmosphere and the impacts thereof on both human health and the environment.

Biography

Patricia Forbes is an Associate Professor in Analytical Chemistry at the University of Pretoria, South Africa. She was previously employed as Environmental Manager at Impala Platinum Refineries and then as Head of the Air Quality Research Laboratory of the Council for Scientific and Industrial Research (CSIR), South Africa. Her research focuses on the

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