

The Molecular Identification of Organic Compounds in the Atmosphere: State of the Art and Challenges

Barbara Nozière,^{*,†} Markus Kalberer,^{*,‡} Magda Claeys,^{*,§} James Allan,^{||} Barbara D'Anna,[†] Stefano Decesari,[⊥] Emanuela Finessi,[#] Marianne Glasius,[▽] Irena Grgić,[○] Jacqueline F. Hamilton,[#] Thorsten Hoffmann,[◆] Yoshiteru Iinuma,[¶] Mohammed Jaoui,[△] Ariane Kahnt,[§] Christopher J. Kampf,[▲] Ivan Kourtchev,[‡] Willy Maenhaut,^{§,□} Nicholas Marsden,^{||} Sanna Saarikoski,[■] Jürgen Schnelle-Kreis,[◇] Jason D. Surratt,[▼] Sönke Szmigelski,[★] Rafal Szmigelski,[★] and Armin Wisthaler[○]

[†]Ircelyon/CNRS and Université Lyon 1, 69626 Villeurbanne Cedex, France

[‡]University of Cambridge, Cambridge CB2 1EW, United Kingdom

[§]University of Antwerp, 2000 Antwerp, Belgium

^{||}The University of Manchester & National Centre for Atmospheric Science, Manchester M13 9PL, United Kingdom

[⊥]Istituto ISAC - C.N.R., I-40129 Bologna, Italy

[#]University of York, York YO10 5DD, United Kingdom

[▽]University of Aarhus, 8000 Aarhus C, Denmark

[○]National Institute of Chemistry, 1000 Ljubljana, Slovenia

[◆]Johannes Gutenberg-Universität, 55122 Mainz, Germany

[¶]Leibniz-Institut für Troposphärenforschung, 04318 Leipzig, Germany

[△]Alion Science & Technology, McLean, Virginia 22102, United States

[▲]Max Planck Institute for Chemistry, 55128 Mainz, Germany

[□]Ghent University, 9000 Gent, Belgium

[■]Finnish Meteorological Institute, FI-00101 Helsinki, Finland

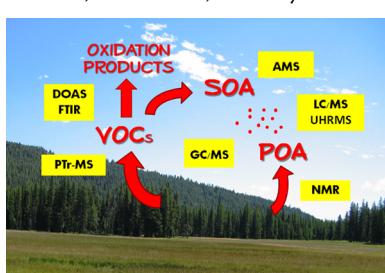
[◇]Helmholtz Zentrum München, D-85764 Neuherberg, Germany

[▼]University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States

[★]University of Bern, 3012 Bern, Switzerland

[☆]Institute of Physical Chemistry PAS, Warsaw 01-224, Poland

[○]University of Oslo, 0316 Oslo, Norway



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1. INTRODUCTION

The Earth's atmosphere offers a striking contrast with other known planets by its rich organic composition, which results almost exclusively from the presence of life on the planet.

About 2000 Tg/yr of organic compounds are estimated to be emitted into the atmosphere as gases, another 300 Tg/yr as particulate matter (aerosols), and a smaller, yet nonestimated, fraction is dissolved in cloud or fog droplets. While these quantities represent only a few percent of the total carbon budget, dominated by CO₂, they represent a diversity of 10⁴–10⁵ distinct compounds,¹ which play essential roles in many atmospheric processes. The importance of organic gases (or volatile organic compounds, VOCs) in air quality and tropospheric ozone formation was recognized as early as the 1950s,² while their role in the atmospheric radical cycles was evidenced in the 1970s.³ Their role as precursors for secondary organic aerosols (SOAs) then started to be unveiled in the 1980s and 1990s, and, for the last two decades, their contribution to the Earth's radiative budget, through their optical and cloud-forming properties, has been discussed and is progressively taken into account in the model calculations of the Intergovernmental Panel for Climate Change (IPCC). This growing realization of the importance of these compounds in the atmosphere has been accompanied by an exponential increase of the research activities and scientific articles on this subject, making organic compounds a main research area in atmospheric science today.

To a large extent, understanding the processes involving organic compounds in the atmosphere depends on how well these compounds are identified. Yet obtaining this information for atmospheric samples involves a number of challenges, such as their collection, separation, the decoupling of meteorological and chemical processes, small masses, complex mixtures, and the low concentrations of individual compounds. New instruments have thus been developed and analytical techniques from other disciplines modified to overcome these problems. These efforts started slowly in the 1970s and 1980s but have undergone a tremendous evolution over the last decades. This Review presents a state-of-the-art account of this rapidly expanding field of atmospheric organic compound identification. In particular, it presents an overview of the core concepts in analytical chemistry and provides guidelines and recommendations on the performances and limits of different techniques that are aimed at the wide range of scientists with diverse backgrounds studying these questions today (physicists, meteorologists, chemists, biologists, engineers, etc.).

Section 2 of this Review introduces the main definitions related to molecular identification, and discusses the different degrees of identification required by atmospheric problems or offered by techniques. Section 3 presents the strategies to ensure the quality of the analyses in atmospheric sciences. Section 4 summarizes the different techniques available today or under development to characterize atmospheric organic compounds and their various levels of identification. Section 5 presents current key questions involving organic compounds in atmospheric science and approaches to solve them. Finally, section 6 summarizes the main trends, current challenges, and potential future directions of this field of research.

2. DEFINITIONS AND APPLICATION TO THE ATMOSPHERE

2.1. Molecular Identification: Definitions

Before discussing organic identification in atmospheric chemistry and how to achieve it, it is important to give some definitions. An organic compound is fully identified only if its molecular structure is entirely known, including its isomeric

and spatial (stereo) configuration. While this information can be obvious for small molecules (C_1 , C_2), it becomes increasingly challenging to obtain as their size and molecular weight (MW) increase. Furthermore, full structural identification usually requires different types of analyses, such as some focusing on the molecular composition and others on the structure.

Scientific societies such as the International Union for Pure and Applied Chemistry (IUPAC), the American Chemical Society (ACS), the American Society for Mass Spectrometry (ASMS), and journals thus require the identity of isolated organic compounds to be supported by a minimum of two types of information, such as the molecular weight and the structure. An additional challenge in environmental sciences is to identify organic compounds present in complex mixtures. The most common method used to solve this problem is chromatographic separation, which, combined with comparison of their chromatographic and mass spectrometric behaviors with those of reference compounds (or standards), can lead to unambiguous identification (section 4.2.1).

As discussed in section 4.2.3, the MW of a compound is the basis to determine its molecular formula, by comparison with the exact weights of various theoretical formulas. The number of matching theoretical formulas depends on the accuracy with which the measured MW is determined and increases exponentially with MW. Knowing the elements present in the molecule, for instance, that they are limited to C, H, O, S, and N, reduces the number of matching formulas. Scientific societies, in particular the ASMS, have thus established that a molecular formula is elucidated if the accuracy on the measured MW corresponds to a single matching formula. Thus, in the absence of other complementary information, current high-resolution MS techniques can only identify a formula for compounds up to $300\text{--}350 \text{ g mol}^{-1}$.¹ Beyond this, and in some cases for lower MW,⁴ the identification requires additional information such as isotopic composition or fragmentation (tandem MS). As explained above, chromatographic separation and comparison of their chromatographic and mass spectrometric behaviors with those of authentic standards also solve these problems. In this case, the comparison between the compounds in the sample and authentic standards must be made with sufficient accuracy.

Besides the elemental composition given by the molecular formula, the full spatial structure of organic compounds, that is, their different isomers or spatial configurations, can be obtained from NMR techniques (section 4.1) or tandem MS (section 4.2.3) (successive fragmentation of the precursor ion). Chromatographic methods and comparison with an authentic standard can also provide full structural information if suitable standards are available (i.e., in the form of specific isomers). The full structural identification of an unknown molecule is therefore a considerable analytical challenge, especially in complex environmental samples.

2.2. Describing the Level of Identification: Factor " I "

Not all atmospheric problems require the full identification of organic compounds. Intermediate levels of identification exist, focusing on specific classes of compounds or functional groups, which can be sufficient to answer many atmospheric problems. In this Review, the level of identification required by a problem or offered by a technique will be described by a "factor I " defined as $I = \text{number of possible molecules matching the}$

information requested or measured by a specific analytical technique.

Thus, by definition, full identification is equivalent to $I = 1$. However, if a compound has two or more isomers that are not separated, then $I = 2$ or higher. For instance, the 2-methyltetrosols, which have been found in many aerosols and were proposed as secondary products of isoprene, have isomers (diastereoisomers), 2-methylerythritol and 2-methylthreitol, each of them having two enantiomers (mirror-image isomers). Thus, the exact MW of these compounds identifies them with only $I = 4$. Using nonchiral gas chromatography (GC) columns can separate the two isomers, thus identifying them with $I = 2$.⁵ Finally, separation on chiral columns can distinguish each enantiomer and identify them with $I = 1$.⁶ Typically, for a compound with a MW determined by MS, $I = \text{number of molecules matching MW} \times \text{number of possible isomers and spatial configurations}$. By contrast, optical spectroscopies generally result in the identification of organic compounds with large I factors. For example, the analysis of mixtures from secondary organic aerosol products by infrared (IR) spectroscopy only gives the relative distribution and temporal evolution of functional groups ($I \geq 100$).⁷ While this provides some overall information on the bulk composition, no structural information on specific compounds can be derived. Similarly, with MS using hard ionization techniques such as electron ionization with 70 eV electrons, the very large number of fragments introduce large uncertainties in the determination of the MW of specific compounds and for the identification of their structure.

Factor I will be used throughout this Review to describe the levels of identification offered by different techniques (section 4) or required by specific atmospheric problems (section 5).

2.3. How Well Do Atmospheric Organic Compounds Need To Be Known?

Trying to identify all the organic compounds present in the atmosphere or in atmospheric samples would not only be a staggering task but also largely redundant as many problems can be solved with only a partial knowledge of these compounds. Different types of problems, corresponding to different levels of information, can be distinguished.

2.3.1. Inventorying Compounds According to Their Properties ($I \geq 100$). The first type of problem is when organic compounds need to be inventoried for the purpose of establishing a budget. Generally, such budgets are required to gain insights into specific properties of the compounds, such as their optical properties for the global energy budget or their volatility for SOA precursors. In such cases, the organic compounds do not need to be individually identified, but only quantified on the basis of this common property. These questions can thus be solved by performing functional group analyses (section 4.1), which would provide identification with $I \geq 100$ (probably even ≥ 1000).

2.3.2. Capturing Chemistry in a Turbulent Atmosphere: Real-Time Monitoring ($10 \geq I \geq 100$). A common problem in atmospheric chemistry is the investigation of chemical processes or sources in a rapidly changing environment (boundary layer height changes or influence of different air masses). This type of problem does not necessarily require the full identification of the organic compounds either but demands that the analytical techniques characterize organic compounds on time scales of seconds to minutes. For this purpose, "on-line" instruments have been developed to monitor

gaseous or particulate organic compounds in real-time (section 4.2.1). Despite the fast measurement frequencies, the identification of gases with such techniques can be adequate when combined with high-resolution MS techniques ($I \leq 10$ with proton transfer (PTR)-time-of-flight (TOF) MS, section 4.1). Some real-time aerosol measurements however use hard ionization techniques (section 4.1), resulting in extensive fragmentation and precluding in-depth identification of the organic compounds ($I \geq 100$).

2.3.3. Monitoring Known Processes or Sources: Relative Identification ($I \leq 10$). A category of problems requiring a higher level of knowledge of the organic compounds is when known processes (for instance, chemical reactions) or sources need to be monitored or quantified in a given region of the atmosphere. An example is the quantification of the SOA mass resulting from one specific precursor, such as isoprene or α -pinene, at a given site. The approach usually employed consists of monitoring a few compounds that are unique to these processes or sources, called "markers" (section 3). The compounds present in the atmospheric samples do not need to be fully identified but only to match the properties of the reference compound characterized in laboratory. Such comparisons are often carried out by chromatographic methods (section 4.2.2) whereby the chromatographic and mass spectrometric behaviors of the targeted and reference compounds are compared. For small compounds, an identification based solely on direct MS can be considered, provided that sufficient resolution can be achieved. However, such an approach does not warrant the full identification of a compound, as the technique used does not necessarily distinguish between different stereo- and positional isomers.

2.3.4. Identifying Unknown Processes or Sources: Full Identification ($I \leq 2-3$). Atmospheric problems for which organic compounds need to be fully identified include those in which an unknown process or source is investigated. For instance, identifying specific organic products in aerosols gives some clues on the reactions taking place in these aerosols. Similarly, the identification of the organic compounds conucleating with sulfuric acid in the atmosphere is essential to understand the mechanisms of new particle formation (section 5.5). In these cases, it is necessary to aim at the maximum level of identification of the organic compound, which is only possible by combining different approaches or techniques (section 4.2). By definition, this level of identification corresponds to very small I values, ideally 1. The upper limit of 2–3 indicated above only accounts for potential stereoisomers of the same molecule.

3. COPING WITH ATMOSPHERIC COMPLEXITY

3.1. Sampling Gaseous and Particulate Material

Sampling is the first step of the characterization of compounds, both in the gas and in the particle phase, and the choice of sample collection, preparation methods and appropriate analytical techniques can be crucial for their identification. This section aims to provide information on the sampling techniques for gaseous compounds and particulate material, and on the challenges and difficulties associated with the molecular identification of selected analytes.

3.1.1. Sampling of Gaseous Compounds. VOCs are commonly monitored in indoor and outdoor air. Methods for air sampling should leave the composition of the samples unaltered until analysis, be suitable for the type and

concentrations of the compounds of interest, and allows the analysis with sufficient sensitivity, accuracy, selectivity, precision, and cost efficiency. Various such techniques are available, including "whole air sampling", where air samples are collected in containers, sampling on solid adsorbents, continuous air sampling and on-line techniques. An overview of these sampling methods has been presented in previous review articles,⁸ and only a short summary will be made here.

With "whole air sampling", stainless steel canisters and Tedlar bags are the main containers used, and they give rise to different potential artifacts. Canisters can keep air samples unaffected for up to 30 days until analysis, whereas Tedlar bags generally require the analysis to be performed within 24–48 h. While samples collected in Tedlar bags can be subject to permeation through the walls and degradation due to sunlight, those collected in stainless steel canisters are mostly affected by sorption and reaction on walls, which hamper the sampling of reactive compounds or those prone to isomerization. However, canisters⁹ are widely used, especially for very volatile and nonpolar compounds.¹⁰ Their wide use in air monitoring has resulted in the development of a number of protocols for the analysis of a broad range of VOCs (e.g., the U.S. Environmental Protection Agency methods TO-14, TO-14A, TO-15, and ASTM D-5466).

Sampling by adsorptive enrichment can be used both for sampling itself and for preconcentrating the VOCs prior to GC/MS analysis, as summarized in review articles.¹¹ Depending on the type of compounds studied, they are followed either by thermal desorption or by solvent extraction. No single sorbent or extraction technique is suitable for the entire range of ambient VOC volatilities and polarities. The use of a combination of different sorbents, in increasing order of adsorbent strength, partly addresses this challenge. In addition, cotrapped atmospheric oxidants (e.g., ozone) can lead to interferences by reacting with the sorbent material or with the trapped VOCs. Samples with high water content are also a problem, not only for the adsorbing materials but also for the subsequent analysis, for example, by accumulating in the cryogenic traps, which are used for preconcentration prior to GC analysis. The addition of derivatization reagents on solid sorbents, cartridges, denuders, or into a trapping solvent in impingers, can increase the selectivity of the sampling toward targeted compounds. Such methods are used, for instance, for the determination of semivolatiles, such as carbonyl compounds, by using 2,4-dinitrophenylhydrazine as the derivatization agent.

Continuous and on-line sampling methods for VOCs avoid most of the sampling artifacts described above. New developments for these methods include miniaturization and techniques enabling higher time resolution or sensitivity, which have a potential for laboratory automation or on-site analysis. Examples include in-needle trap devices that allow for potential solvent-free sampling/sample preparation and introduction devices,¹² or are used in direct coupling to mass spectrometry, that is, fiber introduction mass spectrometry.¹³ Also, membrane-based methods, such as membrane inlet mass spectrometry^{12,14} or membrane extraction with a sorbent interface,^{13,15} have been described.

In conclusion, a wide range of parameters have to be taken into account when selecting an appropriate sampling method, including the chemical properties of the target analytes, the complexity of the sample matrix, and the compatibility of the

Table 1. Overview of Synthesized Reference Standards for Some Atmospheric VOC Reaction Products^a

precursor (class)	marker compound	characterization method ^a	synthesis ref	lab/field evidence ref
hemiterpenes (isoprene)	2-methylthreitol	GC/MS	30	30,31
	2-methylerythritol	GC/MS	30	30
	(2S,3R)-, (2R,3S)-, (2S,3S)-, (2R,3R)-2-methyl-tetros	NMR, GC/MS	32	6,32b
	2-methylglyceric acid	GC/MS	30	30
	2-methylglyceric acid oligoesters, sulfates, nitrates	NMR	33	31,34
	methyl vinyl ketone, methacrolein sulfonates	HPLC/MS, 3Q-ESI–MS (on-line, off-line)	33	33
	cis- and trans-3-methyl-3,4-dihydroxytetrahydrofuran	NMR, GC/MS	35	35b
	isoprene epoxydiols (IEPOX)	NMR, GC/MS	36	36
	methacrylic acid epoxide (MAE)	UPLC/ESI-QTOFMS, NMR	37	37
	isoprene nitrate	NMR	38	38
monoterpenes (α , β -pinene)	3-hydroxyglutaric acid, 3-methyl-1,2,3-butanetricarboxylic acid	GC/MS GC/MS, HPLC/ESI–MS	34,39	34,39
	cis-pinic acid	NMR	40	40
	hydroxy-pinonic acid	NMR	41	42
	hydroxy-pinonaldehyde	NMR	41	42
	terpenyllic/terebic acid	HPLC/ESI–MS	42	30,43
sesquiterpenes (β -caryophyllene)	diatepenyllic acid acetate	NMR, HPLC/ESI–MS	44	44
	diatepenyllic acid	HPLC/ESI–MS	44	43,44
	β -caryophyllene aldehyde, β -nocaryophyllene aldehyde	NMR, GC/MS, ESI–MS	45	45
	β -caryophyllonic acid, β -nocaryophyllonic acid, β -caryophyllinic acid, 3,3-dimethyl-2-(3-oxobutyl)-cyclobutanecarboxylic acid, 2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid	NMR, GC/MS, APCI–MS, HPLC/ESI–MS	46	46

^aAcronyms: See list of abbreviations.

sampling method with various extraction and analytical techniques.

3.1.2. Sampling of Particulate Material. Sampling of particulate organic material (organic aerosols) is generally accomplished by collection on filter samplers or, to a lesser extent, with cascade impactors (e.g., MOUDI;¹⁴ DLPI, www.dekati.com). The topic has been the subject of review articles¹⁶ and addressed in textbooks;¹⁷ thus only a brief overview will be presented here, with emphasis on sampling artifacts and gas-/particle-phase distribution.

The choice of the filter material on which the samples are collected is critical. When the samples have to be analyzed by thermal-optical analysis¹⁸ for total organic, elemental, and total carbon (OC, EC, and TC), quartz fiber filters are mandatory because they are the only type able to sustain high-temperature treatments. Otherwise, other materials can also be used, for example, polytetrafluoroethylene (Teflon), or aluminum foil in cascade impactors. However, they all give rise to artifacts. In particular, all filter types can result in negative artifacts as the particulate-phase organics collected on the filter may volatilize during sampling. It was suggested that about 40% of aerosol carbon is volatilized during sampling,¹⁹ but losses up to 80% have also been reported.¹⁵ Quartz fiber filters are also prone to positive artifacts due to their large adsorption capacity for volatile and semivolatile organic compounds.¹⁶ Several approaches have been proposed to avoid or to assess these artifacts. They vary from the simple use of double quartz filters (so-called Q1Q2 or QBQ setups), to tandem filter setups^{16a} or the use of denuders to remove organic and inorganic gases from the air sampled,²⁰ to more sophisticated systems such as the Brigham Young University organic sampling system and its variants,²¹ where a denuder is used before the quartz fiber filter

and an adsorbent bed (for collecting volatilized organics) is used after it.

Several studies have investigated the artifacts linked with the use of quartz fiber filters in the analysis of total OC²² and water-soluble OC (WSOC).^{22b} Yet such studies have rarely been performed on individual organic species, with the exception of dicarboxylic acids (DCAs)²³ and polycyclic aromatic hydrocarbons (PAHs) and related compounds such as polychlorinated biphenyls.²⁴ In addition, the gas-phase/particle-phase distribution of the species of interest has to be considered especially for long sampling durations. In recent studies,²³ this distribution was found to be close to or higher than unity in summer for 2-methyltetros and levoglucosan.

An alternative to collecting the particulate and gas phases separately is collecting the two phases together, as in a study reporting the measurement of a total of 180 compounds, including mostly *n*-alkanes, PAHs, and polar organic compounds, in field samples by GC/MS.²⁵ This approach has however the disadvantage that the information on the concentrations in each of the two phases is lost.

In summary, sampling artifacts and semivolatile behavior exist for a number of particulate-phase organic species. Their extent depends on many parameters such as temperature, relative humidity, sampling site, sampler type, collection substrate, sampling duration and sampling face velocity, and vapor pressure of the species. Some species are also prone to specific artifacts such as organic acids, for which the sampling efficiency depends on the degree of neutralization. Artifacts may be avoided by using denuders upstream of the sampler or an absorbent pad (e.g., polyurethane foam) to collect the species that are desorbing during sampling. More studies of

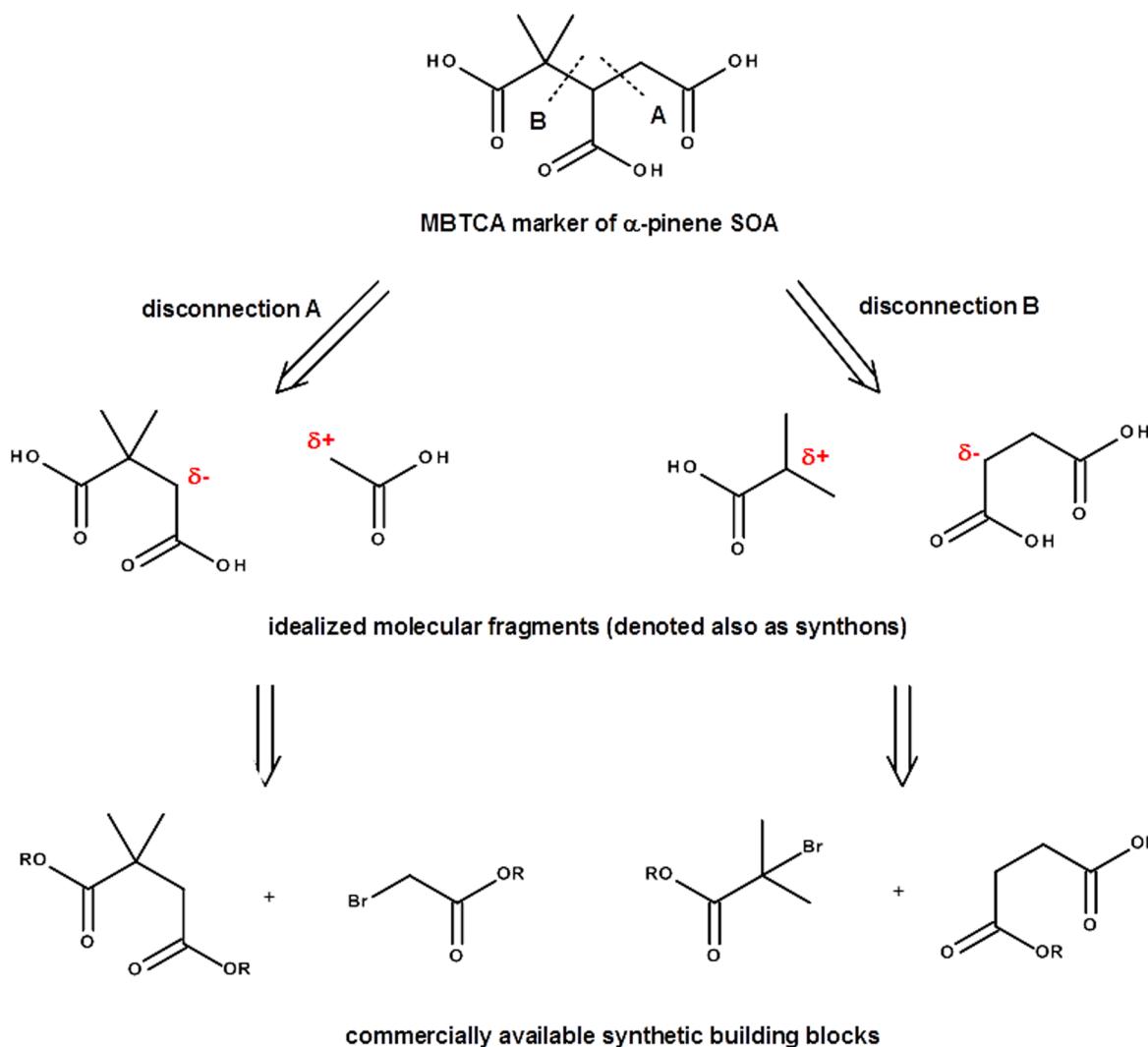


Figure 1. Application of the retrosynthetic analysis for the design of the synthetic pathways leading to 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), a relevant marker for α -pinene SOA aging.³⁹

sampling artifacts are necessary, especially for the compounds used in source apportionment.

3.2. Standards and References

In atmospheric chemistry, the identification of specific processes or sources requires full molecular identification and is often achieved by comparing specific tracers, or, more exactly, marker compounds (see definition and discussion below in this section), to well-characterized reference compounds. When no authentic standards are available proxy compounds can be used, but only for quantification. For example, because authentic organosulfate standards are not commercially available, camphorsulfonic acid²⁶ sulfate is often used as surrogate standard for the quantification of α -pinene-related nitrooxy organosulfates. In this section, we provide information on commercially available reference standards and standards that have been synthesized and characterized by different research groups and used as marker compounds for specific scientific questions.

3.2.1. Availability of Authentic Standards. A number of molecules representing anthropogenic organic compounds such as linear and branched alkanes and alkenes,²⁷ alkynes,²⁸ aromatics, polycyclic aromatic hydrocarbons, and their oxygenated and nitro-substituted products²⁹ (e.g., nitro and

hydroxy xylenes, nitro methylnaphthalene)²⁹ are available commercially. Some oxidation products of more complex molecules representing important atmospheric biogenic VOCs such as isoprene, monoterpenes (i.e., α -pinene, β -pinene, limonene, myrcene, terpinylene), and sesquiterpenes (i.e., β -caryophyllene, α -humulene, α -cedrene, β -farnesene, etc.) are also available commercially. This is however not the case for the many other oxidation products. Table 1 gives an overview of reference standards for compounds, which are not commercially available, but have been synthesized and characterized in noncommercial laboratories using a variety of analytical techniques.

3.2.2. Synthetic Approaches toward Authentic Standards for Analysis. The lack of authentic standards for atmospheric compounds seriously hampers unambiguous structural elucidation. There are a number of manufacturers and/or fine chemicals suppliers that offer custom synthesis of authentic standards. Year by year this list expands, including small or medium-sized enterprises that have expertise with the synthesis of a narrow class of organics; for example, Extrasynthèse offers a wide range of terpenes. Information about fine chemicals suppliers can be retrieved using on-line comprehensive databases, such as SciFinder (a product of the

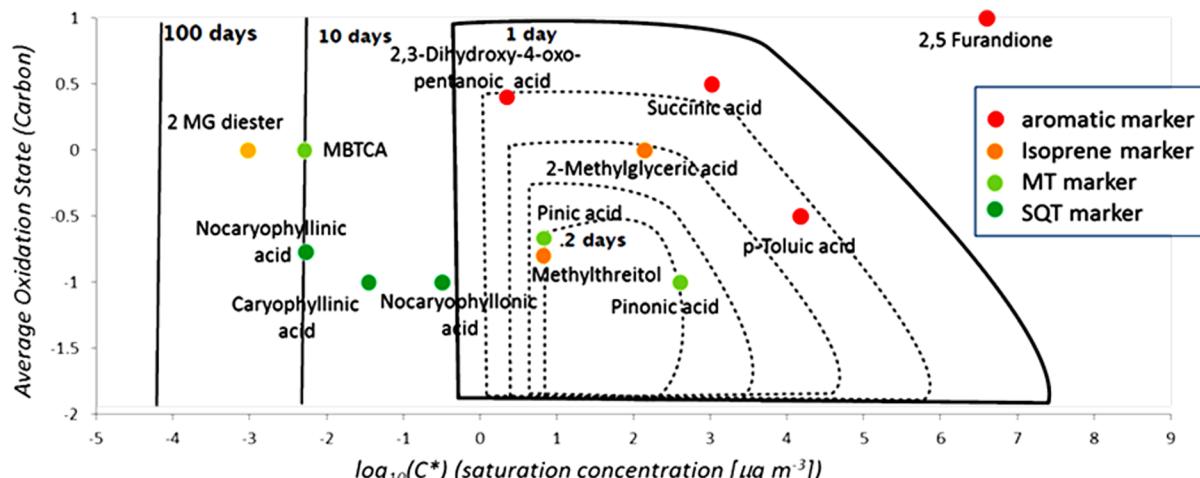


Figure 2. Estimated atmospheric lifetimes of selected SOA marker compounds according to their volatility.⁵⁹⁰

ACS) and Beilstein (a product of Elsevier B.V.), or, alternatively, using free-of-charge Internet resources, such as Chem Blink (<http://www.chemblink.com>) and Chemical Book (www.chemicalbook.com). Because of the lack of commercially available standards, research groups focusing on the molecular characterization of unknown organic compounds in the atmosphere have resorted to organic synthesis. Some studies have already demonstrated the value of organic synthesis to obtain reference compounds for hemi-,³⁹ mono-,³⁴ and sesquiterpene⁴⁶ oxidation products or potentially relevant light-absorbing species formed through simple reactions in aerosol proxies.⁴⁷

A useful approach for the synthesis of an unknown compound in atmospheric research is based on the retrosynthetic analysis of the target structure, a concept of molecular decomposition according to simple rules.⁴⁸ This approach involves the fragmentation of a target structure through a number of idealized molecular fragments denoted as synthons and continues until simple or commercially available structures are generated. Figure 1 shows an example of retrosynthetic approach applied to the synthesis of 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), a marker for aged α -pinene SOA.^{34,39} It was not until 2007 that the structure of this unknown marker was proposed and confirmed using this approach (disconnection B in Figure 1).³⁹ In the synthesis of MBTCA, α -bromoisobutyrate served as the synthetic equivalent for the electrophilic synthon, while alkyl succinate was selected as the synthetic equivalent for the nucleophilic synthon. Following the same strategy, MBTCA has recently been synthesized with high yield (78%) using methyl 2-methylpropanoate and dimethyl maleate as synthons.⁴⁹ The retrosynthetic synthesis approach could be applied to support the structural elucidation of other unknown compounds obtained from laboratory experiments or field studies.

In conclusion, targeted organic synthesis is a useful approach to support the unambiguous structural identification of unknown compounds in ambient aerosols and could be carried out either by commercial vendors or by research laboratories using a variety of strategies. However, targeted synthesis of the proposed compounds remains an expensive and/or a time-consuming task. Methods based on separation science can be employed as an alternative to organic synthesis. For instance, semipreparative LC has been recently used to obtain SOA

markers in laboratory experiments for identification and quantification purposes.⁵⁰

3.2.3. Assessing the Atmospheric Lifetime of Marker Compounds. By definition, an atmospheric tracer is “an entity which preserves its identity as it moves with the air from a known source, where the tracer is created or otherwise introduced into the atmosphere, to a known sink where it is destroyed or removed from the atmosphere”.⁵¹ In this Review, preference has been given to the term “marker” instead of “tracer” as organic compounds in the atmosphere generally do not fulfill the requirement of preservation (e.g., due to reactions decreasing their concentrations in the atmosphere).

The identification of appropriate marker compounds for specific atmospheric processes is a difficult task due to the wide range of complexity and concentrations encountered in smog chamber and atmospheric samples. Important quality criteria for suitable marker compounds are reactivity, stability, and, for condensed-phase compounds, volatility.

For the markers of condensed-phase organic compounds, volatility is one of the major parameters determining the atmospheric lifetime. Aqueous-phase reactions in clouds or condensed-phase reactions in aerosol particles can also be important for compound degradation, especially in the case of reactive species such as aldehydes. However, data on condensed-phase degradation or transformation processes are still very limited and the subject of ongoing research and discussion. The atmospheric lifetimes for the markers of SOA from most precursors, including isoprene, monoterpenes, and aromatics, are rather short (<1 day) (Figure 2) and are determined from their volatility, the latter being estimated from the number of carbon atoms and functional groups. A few exceptions to these short lifetimes include acidic sesquiterpene markers (estimated lifetime 2–10 days), the marker for aged α -pinene SOA MBTCA (estimated lifetime ~10 days), and oligomeric esters of acidic isoprene oxidation products (2-methylglyceric acid diester, estimated lifetime >10 days).

3.3. Quality Control and Intercomparison

Intercomparisons between different techniques or between instrument operators have for objective to evaluate the analytical repeatability and reproducibility of the measurements and to highlight any bias or factor influencing the results. They are thus important for the quality control of the sampling and analysis method. For instance, an interlaboratory comparison

(ILC) allows laboratories to assess and demonstrate their performance in a particular test, calibration, or measuring sector. While several ILCs have been organized for the measurement of VOCs, very few have been organized for the measurement of aerosol organic compounds. However, an interlaboratory comparison has recently been organized for the measurement of levoglucosan, mannosan, and galactosan within the European ACTRIS project.⁵² The results evidenced small standard deviations between the measurements of levoglucosan, mannosan, and galactosan made by the 13 participants. This ILC also revealed the lower detection limits of most GC/MS methods compared to those based on high-performance anion-exchange chromatography (HPAEC) with mass spectrometric or photodiode-array detection. Despite the great benefits of ILCs for the quality of the measurements, it is not realistic to propose such intercomparison activities for a large number of compounds. However, this would be desirable for major markers in ambient aerosol such as fungal spore markers (arabitol and mannitol) and biogenic SOA markers (2-methyltetrosols, 2-methylglyceric acid for isoprene SOA; MBTCA, pinonic, pinic, terpenyllic, and terebic acid for α -pinene SOA).

4. THE ANALYTICAL TOOLS

In this section, analytical techniques used and developed for the analysis of atmospheric trace gases and particles are described. First, in section 4.1, one-dimensional techniques are presented, which consist of using only one physical-chemical property as parameter for the separation and identification of compounds, such as their optical or nuclear magnetic properties or molecular weight. In section 4.2, multidimensional techniques are described, which combine more than one one-dimensional technique and property for the identification, such as retention time in a chromatographic system and molecular weight measurement. In general, multidimensional techniques offer a higher degree of identification (i.e., a lower I factor) than one-dimensional ones but are more challenging instrumentally. They also rely mostly on laboratory instruments, whereas many of the one-dimensional techniques have been developed into on-line and field-deployable instruments. The main classes of techniques discussed in this Review are compared in terms of their I factor in Figure 3.

4.1. One-Dimensional Techniques

4.1.1. Optical and Magnetic Spectroscopies. Optical and magnetic spectroscopies were classical identification techniques for atmospheric compounds before multidimensional techniques were developed. As they are based on the interactions of molecular functional groups with light or magnetic fields, they provide generally functional information, that is, specific to chemical groups or bonds, rather than full structural information. However, absorption spectroscopies (UV-vis and FTIR) are suitable for the speciation of very small atmospheric organic compounds (C_1 , C_2), and a greater variety of atmospheric compounds have been successfully identified by FTIR spectroscopy.⁵³ Optical spectroscopies are also the only analytical techniques applicable to remote sensing. Their latest development over the past decade has been in the form of cavity ring down spectroscopy and related techniques, the sensitivity of which is considerably enhanced, which allows for the detection and quantitation of atmospheric compounds in the low parts per trillion (ppt) or subppt ranges. The techniques listed in Table 2 will only be briefly described in

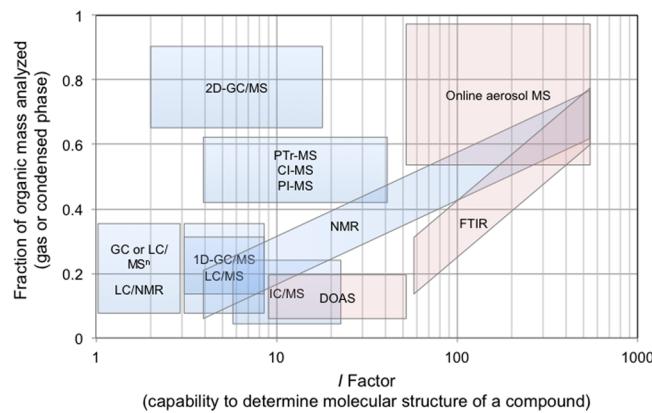


Figure 3. Summary of the most abundant analytical techniques used to characterize atmospheric organic compounds as function of their I factor. A decreasing I factor describes the increasing ability of a technique to identify the molecular structure of a compound. The y -axis describes the fraction of the total organic mass of atmospheric samples characterized by a technique. The coupling of two techniques (often involving chromatography) significantly decreases the I factor. Techniques frequently coupled to chromatography or suitable to coupling with chromatography are shown in blue, the other in red.

Table 2. Non-Mass Spectrometric Detection Methods for Atmospheric Gas-Phase Organic Compounds^a

chemical species	detection method	refs
hydrocarbons	FTIR, GC-FID, CRDS, LP-DOAS (aromatics), chemiluminescence (alkenes)	53,55
HCHO	FTIR, DOAS, derivatization-fluorescence, LC/derivatization-UV	53,56
other OVOCs	DOAS, GC-FID, and HPLC/UV techniques	57
PAN	FTIR, GC-ECD	58
halocarbons	FTIR, GC-ECD	59

^aAcronyms: See list of abbreviations.

this Review, and the reader can refer to recent reviews and books⁵⁴ for a more comprehensive summary. The optical spectroscopies [FTIR, ultraviolet (UV)-visible (vis), etc.] are described below, followed by nuclear magnetic resonance. Only one-dimensional NMR methods are discussed in this section, while the combination of NMR detection with chromatographic separation will be presented in section 4.2.

4.1.1.1. FTIR and UV-Visible Absorption Spectroscopy. All organic molecules absorb light both in the IR (wavelength = 0.7–25 μm) and in the UV-vis (0.1–0.7 μm) regions, which can be used for the characterization of their molecular structure. However, as the information obtained is mostly functional rather than structural absorption spectroscopies are more widely used for the quantification of known trace gases than for the identification of unknown compounds in the atmosphere.

In IR spectroscopy, the spectral lines originate from the vibrational–rotational transitions of chemical bonds or functional groups in the molecules. The first important characteristic of these spectral lines, or bands, is their position in wavelength (or frequencies), which depends on the energy of the corresponding transition. Most of the absorption bands of interest for organics are between 500 and 4000 cm^{-1} (near and mid-infrared region). While the high frequency portion ($\geq 1300 \text{ cm}^{-1}$) displays the characteristic stretching bands of important functional groups such as OH, NH, and C=O, the ring bending absorption bands of aromatics appear below 900 cm^{-1} .

Absorption patterns in the intermediate region (1300–900 cm⁻¹) are more complex and specific to some molecules, and can therefore be used for identification (fingerprint region). In addition to frequencies, the width and shapes of the absorption lines are also important for both qualitative and quantitative measurements. In the condensed phase, intermolecular interactions make the IR absorption bands of organic compounds much broader than in the gas (spectral resolutions of the order of tenths cm⁻¹), thus limiting their molecular specificity. The typical *I* factor for solid-state FTIR spectroscopy is therefore very high (>10²), and this technique has been used mainly for laboratory studies,⁶⁰ functional group characterization, and spectral fingerprints (similarly to NMR as discussed below).^{7b,61} Organic gases, however, exhibit fine spectral features with typical line widths of 0.1 cm⁻¹ in the troposphere and of 0.01 cm⁻¹ in the stratosphere, providing a suitable tool for molecular identification and quantification.^{54b} The measurements are either performed with a tunable solid-state laser or a broadband IR source and a FTIR spectrometer. The former allows for sensitive measurements in a narrow wavelength range, while the latter is used for molecular speciation but at the expense of sensitivity (roughly 3 orders of magnitude lower than lasers). Tunable solid-state lasers are therefore used to identify and quantify simple organic molecules, such as CH₄, CH₂O, HCN, OCS, and inorganic trace gases,⁶² while FTIR spectrometry has been successfully applied to the speciation of a range of VOCs including CH₄, C₂H₄, CH₃COOH, CH₂O, CH₃OH, HCN, HCOOH, C₂H₂, furan, and glycolaldehyde.⁵³ However, the poor detection limits (e.g., ca. 10–20 ppb for HCHO) make the FTIR method more suitable for laboratory applications or field measurements close to strong emission sources, such as fires.⁶³ An important advantage of FTIR spectroscopy over alternative methods for VOC analysis such as PTR-MS is the simultaneous detection of organic and inorganic trace gases (including H₂O, CO₂, CO, NH₃, and HONO).

In UV-vis spectroscopy, the absorption bands result from electronic transitions in the molecules and are fairly broad. Various types of electronic transitions can occur, but those resulting in the highest molar absorptivity ($\epsilon \geq 1000$) above 200 nm (i.e., the cutoff of most common solvents) are $\pi \rightarrow \pi^*$ transitions and, in case of polyconjugations, $n \rightarrow \pi^*$ transitions. The structural information obtained from UV-visible spectra in the condensed phase is very limited as the corresponding bands are not specific. This technique has thus been mainly used in combination with other techniques (e.g., LC–UV–vis). Yet in the gas phase the combination of vibrational and electronic transitions greatly enhances the specificity of the bands. If the resulting spectrum contains sufficient fine structures with characteristic narrow bands (≤ 10 nm), the technique can be very selective. Most applications of UV-vis spectroscopy to organic identification are limited to a few very simple molecules (HCHO, CS₂), although larger molecules with strong chromophores (benzene, toluene, naphthalene, phenol, *p*-cresol) can be also observed. Thus, overall UV-vis spectroscopy has a low capacity to identify unknown compounds, corresponding to *I* factors in the range of >10², and is mostly used to monitor known compounds. In addition, its lower sensitivity compared to modern PTR-MS instruments limits its in-situ atmospheric applications.^{55c}

4.1.1.2. Differential Optical Absorption Spectroscopy (DOAS) and Cavity Ring-Down Spectroscopy (CRDS). DOAS and CRDS are the latest developments of IR and

UV-vis spectroscopies, and have been designed to improve one of their weakest points: their low detection sensitivities. This is mostly done by extending the optical pathlengths. In its simplest configuration, long-path DOAS consists of a continuous light source, that is, a Xe-arc lamp, placed at the focal point of a parabolic mirror generating a well collimated light beam and, at some hundreds of meters away, a telescope coupled to a detector. Absorption spectra of air molecules in the UV-vis region are typically dominated by a broad-band signal caused by the Rayleigh scattering. Such signal must be subtracted to provide the characteristic narrow-band (≤ 10 nm) absorption of the gases of interest (their “differential” spectrum).⁶⁴ These fine bands allow, in principle, DOAS to identify and quantify a wide range of gases. However, while this technique is routinely used to quantify inorganic trace gases (O₃, NO₂, SO₂) and some VOCs, the identification of organic compounds is limited to a few small molecules, such as formaldehyde, glyoxal, methylglyoxal, and aromatic hydrocarbons.⁶⁵ The “open path” configurations normally employed for long-path (LP)-DOAS were used to extend the path length also in IR spectroscopy.^{63b} Besides the systems employing artificial light sources, passive measurements can be carried out with DOAS and IR spectroscopy by using extraterrestrial light sources (the sun, the moon),⁶⁶ typically over very long paths (thousands of kilometers). Passive measurements are the principle of remote sensing. Combined with the identification and characterization of VOCs in laboratory and in the field, DOAS is the only identification technique applicable to remote sensing and is widely used for the retrieval of the total column and vertical concentration profiles of many trace gases. Satellite DOAS sensors such as GOME and SCIAMACHY, measuring individual atmospheric trace constituents in the UV-vis and near-IR region and using recent characterizations of formaldehyde and glyoxal by these techniques,⁶⁶ have thus provided global concentration maps for these compounds.

A further way to expand the optical path length and increase the sensitivity of atmospheric measurements is to flow the air samples through a closed cell where a laser beam is reflected between two highly reflective mirrors. These multipass cells allow achieving pathlengths of 200 m with a cell, which is only 1 m long. Pathlengths of a few kilometers can be reached in cavity absorption spectroscopy and pulsed CRDS, using a laser and a high-finesse optical cavity. In CRDS, the measurement is carried out after the light source is switched off, and the extinction produced by the substance of interest is determined from the decay of the intensity of the laser leaving the cell (the “ring-down”).⁶⁷ CRDS is mostly used in the atmosphere to monitor small inorganic molecules and their isotopic composition, but is, in principle, applicable to the analysis of (a few) C₁–C₂ VOCs, as demonstrated in laboratory and some field conditions.⁶⁸ A further development of CRDS is cavity-enhanced DOAS, with which 10–40 km pathlengths are now routinely achieved. This has important benefits for the sensitivity of the technique, as it enables on-line measurements close to atmospheric conditions in laboratory settings.⁶⁸

4.1.1.3. NMR Spectroscopy. Nuclear magnetic resonance spectroscopy is a *quasi-universal* technique for the analysis of organic compounds, and the main technique of reference to support the structural elucidation of organic compounds. It is however less used in environmental chemistry where sample loading can be too small to apply ¹³C and heteronuclear NMR techniques. The general principles of NMR spectroscopy have been described in many text books.⁶⁹ The principle is that

nuclei with a nuclear spin different from zero, such as ^1H , ^{13}C , and ^{15}N , change orientation when subjected to an external magnetic field and absorbing a radiofrequency. Yet in addition to the “magnetic resonance” at the fundamental nuclei frequency, small deviations, of the order of a few part per millions (ppm), are induced by the chemical environment of the nucleus, thus providing local information on the structure of the molecule. Typical NMR spectra record these chemical shifts and allow to correlate one nucleus to another and to reconstruct the entire chemical structure. When only a limited number of compounds are present in a sample, stereoisomers can be differentiated, and I factors approaching 1 can be reached. Molecular identification in complex mixtures containing hundreds of resonances can also be performed with NMR but require procedures to reduce peak overlap. This can be achieved by increasing the magnetic field, hence reducing peak width and narrowing multiplets. Alternatively, series of samples from the same experiment can be analyzed by chemometric techniques (e.g., factor analysis) to attempt spectral deconvolution.⁷⁰ Finally, if a sufficient amount of sample is provided (typically 1 mg of carbon), two-dimensional (2D) NMR techniques can also be applied, such as correlation spectroscopy or heteronuclear single quantum coherence or even heteronuclear multiple bond correlation,⁷¹ which establish the connectivity between chemically distinct H or C atoms in a molecule, and allow the reconstruction of the chemical structure. Thus, 2D NMR has the potential to achieve low I factors even in complex mixtures.

However, while NMR spectroscopy is optimal for liquid samples, it is unsuitable to the analysis of gases and allows the analysis of amorphous solids only with a much lower resolution, that is, with chemical shifts of around 100 kHz for ^1H NMR.⁷² Another advantage of NMR spectroscopy over other techniques is that quantitative spectra can be obtained relatively easily, especially with ^1H spectroscopy, as the line intensity is, in first approximation, directly proportional to the molar concentration of the nucleus of interest.

Unfortunately, the most interesting nucleus in organic chemistry, ^{12}C , has a nuclear spin of zero and is therefore NMR-silent. By contrast, the isotope ^{13}C is magnetically active, but because its natural abundance is only 1.1%, the sensitivity of ^{13}C NMR spectroscopy is almost 4 orders of magnitude lower than that of ^1H NMR. Thus, the vast majority of NMR studies of atmospheric organic compounds is made with proton NMR techniques, and deals with aerosol extracts, cloud, fog, or rainwater, or aqueous solutions of polar VOCs. It is worth noting that strong magnetic fields (≥ 600 MHz) allow the resolution of hundreds of resonances in atmospheric samples⁷³ with opportunities to discover new aerosol constituents.

A common assumption in atmospheric science is that the sensitivity of NMR spectroscopy is too low for a widespread application. While this is true for ^{13}C and heteronuclear NMR methods, and for the ^1H NMR analysis of small aerosol volumes (e.g., in reaction chambers), it is not the case for ^1H NMR analysis of ambient aerosols. ^1H NMR spectra of aerosol water-extracts containing less than 100 μg of carbon (sample loadings reached even in remote areas) can be easily recorded at 600 MHz. Typical detection limits for individual compound ^1H NMR analysis are in the subng m^{-3} levels (for time-integrated samplings of 12–24 h), thus not inferior to that of standard gas chromatography (GC)/MS or liquid chromatography (LC)/MS methods.^{91a} The real limitations of NMR with respect to alternative off-line chemical methods consist of (i)

the complexity of the spectra for compounds with extensive J -couplings, (ii) the difficulty to acquire a second dimension, (iii) the difficulty of hyphenation with other spectroscopic and chromatographic techniques, and (iv) limited automaticity preventing the analysis of large number of samples. A further caveat specific to atmospheric applications is the lack of NMR spectra libraries for atmospheric markers. This is a major limitation because the critical step when investigating atmospheric organic compounds by ^1H NMR spectroscopy is the spectral analysis and compound identification. Table 3

Table 3. Published Chemical Shift Data for Compounds of Atmospheric Importance

chemical compounds or chemical classes	refs
pinonaldehyde	82
ketoaldehydes from monoterpenes	50,83
organic acids from α -pinene oxidation	50,84
cis-pinonic photo-oxidation products	79
α -pinene epoxide, isoprene epoxide reaction products	78a–c
sesquiterpene oxidation products	46
tetrols and 2-methyltetrols	32b,78d
2-methylglyceric acid	33
organic acids from toluene oxidation	85
chemical condensation products between glyoxal and NH_3	75a
hydroxyl-carboxylic sulfate esters	77a
hydroxyl-alkyl nitrates	86
guaiacol oxidation products	87
oleic acid oxidation products	88
PAH oxidation products	89

provides a compilation of research papers reporting chemical shift data for compounds of atmospheric importance. The vast majority of these studies were published in the last five years, indicating that the use of NMR tools for atmospheric organic speciation is rapidly expanding.

An area of atmospheric chemistry where NMR tools have gained the widest application is the kinetic and mechanistic studies in aqueous media. The systems studied include the oligomerization of carbonyls and carboxylic acids,^{33,74} condensation between carbonyls and ammonia or amines,⁷⁵ oxidation of phenolic compounds,⁷⁶ hydrolysis of organo-sulfates and organo-nitrates,⁷⁷ hydrolysis of epoxides,⁷⁸ and photochemistry of carbonyls and carboxylic acids.⁷⁹ NMR spectroscopy has however been less applied to the investigation of the composition of SOA produced in reaction chambers.⁵⁰ This is due to the complexity of these samples,^{75b,80} the lack of chemical shift libraries, and the relative small amounts of sample produced in such experiments under atmospherically relevant concentrations. Yet the development of continuous SOA production methods in chambers will certainly allow the application of highly informative off-line techniques such as multidimensional NMR methods in the near future.^{50,81}

Some examples of successful molecular identification in ambient aerosols using NMR methods can be found in the recent literature. They include the identification of low-MW compounds such as dimethylamine, diethylamine, methanesulfonate, and hydroxyl-methane-sulfonate, as well as some major C_6 – C_{10} compounds, formate, pinonic and pinic acid, and levoglucosan.⁹¹ Other studies focus mainly on functional group analysis.⁹² Interestingly, the resolution of mono- and bidimensional ^1H NMR spectroscopy allows to identify spectral

fingerprints characteristic of specific chemical classes, such as aliphatic compounds carrying linear methylenic chains.⁹³

4.1.2. Mass Spectrometric Techniques. *4.1.2.1. Key Characteristics of Mass Spectrometry.* The principle of mass spectrometric techniques is to analyze compounds of interest (or analytes) based on the ions they produce. These techniques thus involve three main components: an ionization unit, a mass analyzer, and a detector. While the detectors are fairly common to all mass spectrometers, wide ranges of ionization and mass filtering techniques are now available, each of them being affected by a number of parameters. These different techniques and parameters determine the performance of a mass spectrometer and the classes of compounds that can be analyzed.

4.1.2.1.1. Ionization Methods. This first section presents the different ionization techniques available for analytes. Over the last decades, a large number of ionization techniques have been developed for organic compounds, each of them having specific advantages and drawbacks. Only the most frequently used in atmospheric sciences are discussed in this section.

One of the most widely used ionization techniques is electron ionization (EI), which consists of colliding the analytes with 70 eV electrons. Such energetic collisions ensure the ionization of nearly all organics. It also mostly leads to fragmentation,^{94,95} which provides structural information on single analytes, for instance, after separation from a mixture with a chromatographic system (sections 4.1 and 4.2). In this case, the identification power can be very high (*I* factor close to 1), because the mass spectra obtained are specific, reproducible, and comparable with library database spectra, and thus can serve as fingerprints for the identification of unknown compounds. However, the interpretation of fragmentation patterns obtained with EI becomes challenging or even impossible for complex mixtures that are not subjected to prior separation. Another energetic ionization (or “hard ionization”) method is laser desorption/ionization (LDI),^{94,95} which suffers from the same limitations for the analysis of complex samples. Thus, the identification power of MS techniques using hard ionization such as EI or LDI, when used alone, is generally low and the *I* factor correspondingly large.

By contrast, soft ionization techniques result in much less fragmentation of the analyte, thus decreasing the *I* factor in complex mixtures. However, soft ionization techniques, while having relatively high ionization efficiencies, often suffer from poor sensitivity due to signal loss resulting from the transfer of the ions from ambient pressure into the vacuum system. Chemical ionization (CI) is a relatively soft ionization technique where the analytes are ionized by reaction with specific reagent ions to produce diagnostic ions.^{94,95} Both reagent and diagnostic ions are then detected by the mass spectrometer. Vacuum and atmospheric pressure CI (atmospheric pressure chemical ionization, APCI) are today frequently used in atmospheric mass spectrometry, and on-line sampling techniques have been developed for both.^{96,97} Another type of soft ionization technique uses a light source (photoionization, PI), for instance, in the UV or vacuum UV (VUV) range, the wavelength of which can be optimized to improve detection limits of specific compounds.⁹⁸ Such ionization technique can also be applied in the vacuum region of the spectrometer or at ambient pressure (APPI).^{99,100} Electrospray ionization (ESI) is another frequently used ionization technique for atmospheric samples.^{94,95} It has the advantage of being very soft but is only

efficient for fairly polar compounds. Another drawback is that the ionization efficiencies, and thus peak intensities, of various compounds in complex mixtures vary strongly with sample composition and ionization conditions, so that ESI mass spectra are generally not representative of the overall sample composition. Besides conventional ESI analysis, a number of ESI techniques have successfully combined the sample workup and ionization of atmospheric samples in recent years, such as desorption electrospray ionization (DESI),¹⁰¹ nano-DESI,¹⁰² and liquid extraction surface analysis.¹⁰³ They allow organic aerosol samples to be extracted and analyzed directly from filters or impactor plates without time-consuming sample extraction.^{102,104} Extractive electrospray ionization,¹⁰⁵ where a continuous aerosol flow is combined with an extraction solvent electrospray within the ionization source, has recently been shown to be quantitative for on-line organic aerosol analysis.¹⁰⁶

In general, neither soft nor hard ionization techniques can reach *I* factors better than 10 when employed alone. Achieving a low *I* factor with these techniques requires one to combine them with chromatographic separation (section 4.2).

4.1.2.1.2. Resolution, Accuracy, and Dynamic Range. This section discusses the factors affecting the mass filtration and detection in mass spectrometry. Three parameters characterize the performance of mass filtration and the ability of an instrument to analyze highly complex mixtures: mass resolution, mass accuracy, and dynamic range. The resolution of an instrument is defined as the ability to resolve neighboring mass spectral peaks (eq 1):

$$R = (m/z)/\text{peak width at half maximum} \quad (1)$$

where *m/z* is the mass-to-charge ratio of an ion.

A high mass resolution can separate two compounds with mass differences of a few milli-dalton or less, and ultrahigh-resolution mass spectrometers achieve a resolution of several 100 000s (section 4.2.3.6). This is especially relevant for the analysis of atmospheric aerosols where several hundred or thousands of mass spectral peaks are often measured over a mass range of a few 100 *m/z*.

Mass accuracy is defined as the difference between the measured and theoretical mass, relative to the theoretical mass (eq 2), and is generally expressed in parts per million (ppm).

$$\Delta m/z = \left(\frac{\frac{m}{z}_{\text{experimental}} - \frac{m}{z}_{\text{theoretical}}}{\frac{m}{z}_{\text{theoretical}}} \right) \times 10^6 \quad (2)$$

High-resolution mass spectrometers (section 4.2.3.6) achieve an accuracy in the low or subppm range. High resolution and high accuracy instruments allow not only the characterization of the entire complexity of atmospheric samples (which is especially important for one-dimensional techniques), but also the assignment of the elemental composition of all (or most) peaks observed in the mass spectrum.

Both mass resolution and mass accuracy directly affect the *I* factor that can be achieved with an instrument. Combined with other features such as chromatographic separation and/or tandem mass spectrometry, very low *I* factors approaching 1 can be reached with high resolution and high accuracy instruments.

Finally, the dynamic range is defined as the range of analyte concentration over which the signal from the detector is directly proportional to this concentration. Although the dynamic range is not directly related to the identification

Table 4. Overview of the Main Direct CI-MS Techniques Currently Used for Organic Trace Measurements in the Atmosphere^a

acronym	CI reagent ion	analytes	diagnostic ion	MS
PTR-MS	H ₃ O ⁺	alkenes, alcohols, carbonyls, aromatics, acetonitrile	[A + H] ⁺	Q, HR-TOF, QIT, LIT
CIT-CIMS	CF ₃ O ⁻	organic hydroperoxides, carboxylic acids, multifunctional organic compounds	[CF ₃ O + A] ⁻ [A + F] ⁻	Q, TQ, LR-TOF
NI-PT-CIMS	CH ₃ C(O)O ⁻	carboxylic acids	[A - H] ⁻	Q
TD-CIMS	I ⁻	peroxyacetyl nitrates	[A - NO ₃] ⁻	Q
CIMS	C ₂ H ₅ OHH ⁺	ammonia, amines	[A - C ₂ H ₅ OHH] ⁺	Q

^aAcronyms (except those in the list of abbreviations): QIT, quadrupole ion trap; LIT, linear ion trap; CIT, California Institute of Technology; TQ, triple quadrupole; LR, low resolution; NI, negative ion; PT, proton transfer; TD, thermal desorption.

power of an instrument, it can affect the detection of low-concentration compounds in mixtures that are dominated by highly abundant ones. For instance, if the full scan mass spectra of mixtures are dominated by very abundant species, the detection and subsequent identification of less abundant compounds is compromised. This can be overcome by increasing the resolution of the chromatographic separation, and avoiding the coelution the highly abundant and trace compounds. However, resolving such problems and avoiding to reach the maximum of the dynamic range generally requires specific strategies such as specific instrument settings and/or sample pretreatment (e.g., the application of sample fractionation).

4.1.2.2. Direct MS Techniques for Organic Trace Gases: PI-MS, CI-MS, and PTR-MS. Direct mass spectrometric techniques for the analysis of atmospheric gases, that is, those applied to atmospheric samples without prior separation, are generally based on photo- or chemical ionization because, as explained in the previous section, these ionization techniques can achieve small *I* factors under such conditions. In the absence of preparation or separation of the samples, the level of identification obtained depends mostly on the selectivity of the ion chemistry, that is, the uniqueness of the diagnostic ion produced from a given analyte, and on the mass accuracy or MS/MS analysis of the diagnostic ions. In complex matrixes such as atmospheric samples, only a few organic trace gases can be reasonably identified ($1 \leq I \leq 5$). However, direct CI-MS was primarily designed to carry out fast measurements (0.1–1.0 s time resolution), to study, for example, transport processes or detect highly reactive species (e.g., hydroxyhydroperoxides).

Atmospheric applications of direct CI-MS were pioneered in the mid-1980s.¹⁰⁷ The main direct CI-MS techniques currently used for the measurement of organic trace gases in the atmosphere are summarized in Table 4. The most widely used is proton-transfer-reaction mass spectrometry,¹⁰⁸ where many of the organic gases present in air samples are ionized by accepting a proton from hydronium ions (H₃O⁺). While the protonated diagnostic ions are fairly specific to their parent analytes, all PTR-MS instruments are somewhat prone to interferences from dissociative proton or electron transfer reactions, and thus to some degree of fragmentation. Early PTR-MS instruments used quadrupole filters for mass analysis, resulting in poor identification capabilities. Numerous intercomparisons with other analytical methods have shown that 10–15 organic gases could be detected by quadrupole CI-MS in the atmosphere without major interferences,¹⁰⁹ although their identification is not made by the quadrupole PTR-MS instrument alone but based on previous studies and plausibility arguments (the presence of only C, H, O, and N atoms in the molecules).

These compounds include oxygenated VOCs (methanol, acetaldehyde, acetone/propanal), biogenic VOCs (isoprene, methyl vinyl ketone/methacrolein, sum of monoterpene isomers), aromatics (benzene, toluene, sum of xylene isomers) and acetonitrile, an important atmospheric biomass burning marker. The analytical deficit of the quadrupole PTR-MS instrument has been partly overcome with the proton-transfer-reaction time-of-flight mass spectrometer, allowing for high mass resolution.¹¹⁰ This instrument can determine the elemental composition of ions, but still under the assumption that they contain only C, H, O, and N atoms. Under this assumption, organic analytes can be identified down to the isomer level, thus with *I* factors between about 2 and 5.¹¹¹ Prototype PTR-MS instruments with isomer-resolving MS/MS capability (ion traps) have also been developed but have been limited to a few field studies.^{112,113}

Direct CI-MS methods using other reagent ions have been developed to target selected classes of analytes. Yet because none of them involves accurate mass measurements (time-of-flight), the identification achieved relies on the (validated or nonvalidated) assumption that no interferences are present in the atmospheric matrixes.

An example of direct CI-MS is the California Institute of Technology – CI-MS technique, which uses trifluoromethoxy anions, CF₃O⁻, to detect organic hydroperoxides, carboxylic acids, and multifunctional organic compounds.¹¹⁴ These analytes are detected as CF₃O⁻ adducts by low-resolution MS. Selected isobars/isomers are distinguishable via MS/MS analysis in the triple quadrupole version of the instrument. Isomeric carboxylic acids and hydroxycarbonyls can be differentiated via isomer-specific side reactions (F⁻ transfer to carboxylic acids). Applications of this instrument to the atmosphere have led to the measurement of peroxyacetic acid,¹¹⁴ formic acid, acetic acid, propionic, and peroxyacetic acid,¹¹⁵ isoprene hydroxyhydroperoxides,¹¹⁶ and epoxydiols,¹¹⁷ methyl hydroperoxide,¹¹⁸ acetic acid, glycolaldehyde, and hydroxyacetone,¹¹⁹ and multifunctional organic nitrates¹²⁰ including isoprene hydroxynitrates. In addition, hydroperoxyaldehydes were detected in recent field studies (J. Crounse, personal communication).

A negative-ion PTR CI mass spectrometer¹²¹ using acetate ions, CH₃C(O)O⁻, has been developed to detect carboxylic acids via selective proton abstraction reactions. The resulting conjugate carboxylate anions, RC(O)O⁻, are detected by quadrupole mass spectrometry. This instrument was used to measure formic, acrylic, methacrylic, propionic, and pyruvic/butyric acid in the atmosphere, the latter being isomers that cannot be resolved.¹²²

A CIMS technique to detect ammonia using protonated ethanol or acetone ions as CI reagent ions was also developed.¹²³ The same ion chemistry was further incorporated

to measure amines and ammonia simultaneously, at the pptv or subpptv level with a time resolution less than 1 min.¹²⁴ A PTR CI mass spectrometer was also used to measure amines and ammonia at atmospheric concentrations.¹²⁵

Thermal dissociation CI-MS¹²⁶ is used to measure peroxyacetyl nitrates (PANs), which are formed in the atmosphere from association reactions between peroxyacetyl radicals, RC(O)O_2 , and nitrogen dioxide, NO_2 . In the thermal dissociation CI-MS instrument, this reaction is reversed in a heated inlet, and peroxyacetyl radicals react with iodide anions, I^- , in an O^- abstraction reaction. The resulting carboxylate anions are detected by quadrupole MS or ion trap MS.¹²⁷ Thermal dissociation-Cl-MS was originally assumed to be highly selective, but recent studies suggest that carboxylate anions may also be formed via secondary proton abstraction reactions from organic acids¹²⁸ and via OH^- abstraction reactions from peroxyacetic acids.¹²⁹

In conclusion, direct CI-MS techniques are efficient for the detection of many organic gases in the atmosphere, and even their identification if coupled with high-resolution MS. Their strong advantage is the fast measurements, and they are very complementary to other techniques for the identification of organic gases such as GC/MS.

Besides CI-MS techniques, PI-MS techniques were applied to the detection of organic compounds in the gas phase. Because PI is largely fragmentation-free, isobaric compounds with different elemental compositions are separable if the mass resolution is sufficiently high. Isomeric compounds can even be separated by MS by tuning the PI wavelength. A relatively large number of PI-MS applications deal with on-line monitoring of pyrolysis and combustion gases. From the beginning of this century, the sensitivity of jet-resonance-enhanced multiphoton ionization, initially applied to the investigation of emission sources,^{98a} has increasingly allowed ambient atmosphere applications.¹³⁰ Aromatic compounds have been investigated in the subppb range applying jet-resonance-enhanced multiphoton ionization using a time-of-flight mass spectrometer downwind of a road.¹³¹

4.1.2.3. Direct MS Techniques for Aerosols: The Aerosol Mass Spectrometer (AMS). The Aerodyne aerosol mass spectrometer (AMS) was developed for the on-line measurement of organic and inorganic components of aerosols.¹³² The principle of the instrument is to draw particles into a vacuum chamber¹³³ and impact them on a tungsten surface (molybdenum in early versions) heated to 600 °C prior to being analyzed by 70 eV EI-MS. Most of the gas material is removed by differential pumping. As explained above, while the 70 eV EI energy implies extensive molecular fragmentation, it ensures the ionization of nearly all molecules, organic and inorganic, and the compatibility of the data with existing mass spectral databases. The mass spectrum for the aerosol sample is derived by subtracting an internal background obtained from periodically blocking the particle beam. Yet as it contains contributions from both the nonrefractory particles (those evaporating on the impaction plate) and the air that was not skimmed off, these contributions are removed by using a “fragmentation table” approach, where marker peaks in the mass spectra are used to quantify these components.¹³⁴ For other aspects of quantification, the reader is directed to ref 132b.

4.1.2.3.1. Marker Ion Analysis. Because of the two-stage desorption and ionization process, the AMS mass spectral data are a quantitative, linear combination of the contributions of

the various particle components. It is thus possible to gain quantitative information on the overall organic composition and contributions from various sources. One of the simplest forms of analysis is the determination of the fractional contribution of key peaks to the total organic mass concentration. Because m/z 44 mainly corresponds to CO_2^+ from the thermal decomposition of dicarboxylic acids and multifunctional compounds,¹³⁵ the fractional contribution of m/z 44 can be taken as a proxy for the oxygen content of the organic fraction.¹³⁶ When this is compared to the fractional contribution from m/z 43 (C_3H_7^+ from aliphatic chains and C_2OH_3^+ from alcohols, monocarboxylic acids, and carbonyls), correlations with the general level of atmospheric processing of the organic material can be seen.^{137,138} Similarly, the fractional contribution of m/z 60 (associated with anhydrosugars such as levoglucosan, mannosan, and galactosan) can be used in conjunction with m/z 44 to monitor the evolution of biomass burning aerosols.¹³⁹

4.1.2.3.2. Multicomponent Analysis (MCA) and Positive Matrix Factorization (PMF). Beyond bulk properties, it is also desirable to quantify the contributions of different sources to the organic aerosol mass. One of the first methods for this application used the fragment ion at m/z 57 (C_4H_9^+ from alkanes) and at m/z 44 as the basis for deriving estimates for “hydrocarbon-like” and “oxygenated” organic aerosol, respectively (HOA and OOA).¹⁴⁰ These data were found to correlate well with traffic emissions and secondary sources.¹⁴¹ A modification of this technique known as multicomponent analysis allows the identification of a second component of OOA through the analysis of residuals.¹⁴² These two types of OOA have been linked to SOA in various stages of atmospheric processing and with different volatilities.¹⁴³

A more general approach was developed with the use of PMF,¹²¹ a technique imported from source apportionment methods. Its principle is to identify a number of model contributions, or “factors”, to the overall mass spectrum and to decompose the latter in (weighted) linear combinations of these factors by inverting the corresponding matrix.¹²² The model factors derived are comparable to separate characterizations of known sources such as biomass burning and cooking.¹²³

While this approach is a powerful tool in the analysis of the spectra,¹²⁴ some cases may be difficult to resolve when a significant number of mass spectral features are in common between factors, such as cooking and exhaust particles or when using a low-resolution mass spectrometer.

4.1.2.3.3. Comparison with Other Techniques and Instrument Variations. A major advantage of the AMS and other on-line MS techniques over off-line techniques is their time resolution. While the AMS is normally operated at a resolution of minutes for ambient sampling, subsecond data can be obtained if necessary, for instance, for aircraft measurements.¹⁴⁸ An additional strength lies in the quantification of the overall organic fraction rather than in the identification of specific chemical species. While some species such as methyl sulfonate,^{90,149} PAHs,¹⁵⁰ methyl furan,¹⁵¹ and caffeine¹⁵² are unambiguously identified on the basis of unique ions, they are exceptions rather than the rule. Trends in specific ions can be taken as indicative of functional groups or source types, and as these signals are quantitative they can be used for a mass budget analysis. Such source quantification efforts are especially effective when combined with more compound-specific techniques. For instance, off-line two-dimensional GC

(GC \times GC)/MS of filter samples¹⁰⁵ has been used to identify methyl furan at m/z 82 while gas-phase PTR-MS provided evidence for isoprene oxidation, supporting its identification as a marker for SOA from isoprene.

While the initial versions of the AMS used quadrupole mass filters, a major improvement of the technique occurred by using TOF mass filters^{153,154} and later high-resolution (HR) TOF systems.¹⁵⁵ This improved the $\Delta m/m$ resolution to around 2000–4000 and allowed for the elemental analysis of the ions and the resolution of peaks with multiple contributions such as $C_2OH_3^+$ and $C_3H_7^+$ at m/z 43. The instrument can thus generally resolve pure hydrocarbon peaks from oxygenated peaks up to around m/z 100, and some nitrogen- and sulfur-containing peaks.¹⁵⁶

High-resolution data can also be used to quantify the elemental abundance by comparing signal intensities¹¹³ of ions of different elemental compositions. The apparent abundances of elements can be biased by losses of neutral and negative fragments, and positive fragments such as H_2O^+ and CO^+ can be confounded by interferences from other particle- and gas-phase signals, so their contributions to the overall elemental composition must be estimated on the basis of laboratory data.¹⁵⁷ While the accuracy of this method is limited in the case of individual organic species, these inaccuracies tend to average out in aerosol samples composed of a large number of different species.¹¹³ Therefore, the derived elemental ratios (O/C, H/C, and N/C) and associated organic matter fractions should be seen as estimates of the ensemble, not as direct measurements of individual molecules.

In conclusion, the identification of unknown compounds with the AMS is generally achieved with very large I factors, in the range of $>10^2$, and is not the main strength of this technique.

Milder ionization methods than 70 eV EI have been evaluated to gain additional chemical information, such as vacuum UV (VUV) photoionization,¹⁵⁸ using photons of around 10 eV energy (124 nm wavelength), and thus limiting fragmentation. However, to date, this has only been achieved with a synchrotron source and has not been applied to atmospheric sampling.

4.1.2.4. Direct MS Techniques for Aerosols: Single Particle Mass Spectrometry. Single particle mass spectrometry is similar to other on-line aerosol mass spectrometric techniques in that particles are drawn into a vacuum chamber to form a particle beam before being desorbed and analyzed on-line by MS. However, the use of a pulsed laser vaporizing individual particles allows the obtention of mass spectra for these individual particles.¹⁵⁹ Numerous instruments using these principles exist, many having been custom-made at research institutes.¹⁶⁰ The most common commercial version of this instrument is the aerosol TOF mass spectrometer¹⁶¹ (ATOFMS) from TSI Inc., but others exist such as the Livermore Instruments Inc. single particle aerosol mass spectrometer and the Aeromegt laser ablation of aerosol particles time-of-flight mass spectrometer. Examples of bespoke instruments include the particle analysis by laser mass spectrometry¹⁶² instrument, the single particle laser ablation time-of-flight mass spectrometer,¹⁶³ and the nanoaerosol mass spectrometer,¹⁶⁴ among many others.

4.1.2.4.1. Single-Step Techniques. The simplest form of operation of the instrument is combined laser desorption and ionization (LDI).¹⁶⁵ The light from a laser is used to detect the presence of a particle, which triggers the LDI laser (typically an

ultraviolet excimer, e.g., ArF at 193 nm, or a frequency-quadrupled Nd:YAG at 266 nm). The particle components both desorb and ionize, and the data collection by the time-of-flight mass spectrometer, either in positive and negative ion mode, is initiated by the laser pulse. The real-time, single-particle nature of the measurement means that it can bring unique insights into key atmospheric processes such as nucleation¹⁶⁶ or aerosol-cloud interactions.¹⁶⁷ Also, unlike thermal vaporization, LDI allows for the study of refractory species such as oligomeric material that is difficult to analyze with other techniques.¹⁶⁸

However, the main disadvantage of the technique is that the particle components can interact during the vaporization/ionization process, known as “matrix effects”, and result in variable ionization efficiencies and signal intensities.¹⁶⁹ Thus, the mass spectral response of different atmospheric aerosol constituents can be highly variable. In addition, the relative lack of control in the desorption and ionization processes makes the identification of organic species by single-step LDI non-reproducible. Some information on functionality is retained in the mass spectral fragments¹⁷⁰ and can be used for source apportionment^{170b,171} or the identification of organic molecules such as amines,¹⁷² organosulfates,¹⁷³ and aromatics.¹⁷⁴ However, a more sophisticated characterization of organic compounds with LDI-MS techniques is generally not possible, and their I factor is thus as high as for AMS, in the range of $>10^2$.

4.1.2.4.2. Two-Step Techniques. To avoid the matrix effects of single-step LDI, the desorption and ionization processes can be separated by using two laser pulses. The first one, which can be produced by an infrared laser (e.g., CO_2), evaporates the particle and generates a neutral vapor, and is rapidly followed by a second pulse from a UV laser to photoionize the vapors.¹⁷⁵ The obtained mass spectra are more reproducible and quantitative.¹⁷⁶ The drawbacks for atmospheric applications¹⁷⁷ are that sensitivity can be significantly reduced and that the technique is not as sensitive to refractory species as single-step LDI. This makes it generally less applicable to atmospheric aerosols and more suited for laboratory studies, the latter being, in turn, less accessible to single-step LDI. Particles can thus be partially vaporized and their internal structure probed.¹⁷⁸ Less energetic lasers can also be used to limit the extent of fragmentation during ionization.¹⁷⁹

The first laser can also be replaced with a heated surface, as in the Aerodyne AMS, but still using a laser or VUV lamp for photoionization.^{99,175b,180} Although the instruments can no longer be classed as “single particle”, this has the benefit of reducing thermal fragmentation without impacting the ability to detect and quantify organic molecules, as in the photoionization aerosol mass spectrometer.¹⁸¹

Two-step single particle mass spectrometry thus provides limited data on MW and basic functionality compared to other mass spectrometric techniques due to the lack of chemical separation. However, its ability to study individual particles and their internal structure means that key aerosol processes¹⁸² and molecular diffusion within particles¹⁸³ can be studied in ways not otherwise possible.

4.1.2.5. Isotopic Separation in Aerosols. An alternative approach to the methods discussed above to characterize the wide complexity of organic material in aerosols is isotope analysis, which can be applied to the bulk or to individual compounds. The principle is to measure the isotopic fractionation between isotopic pairs such as $^{2}H/^{1}H$, $^{13}C/^{12}C$,

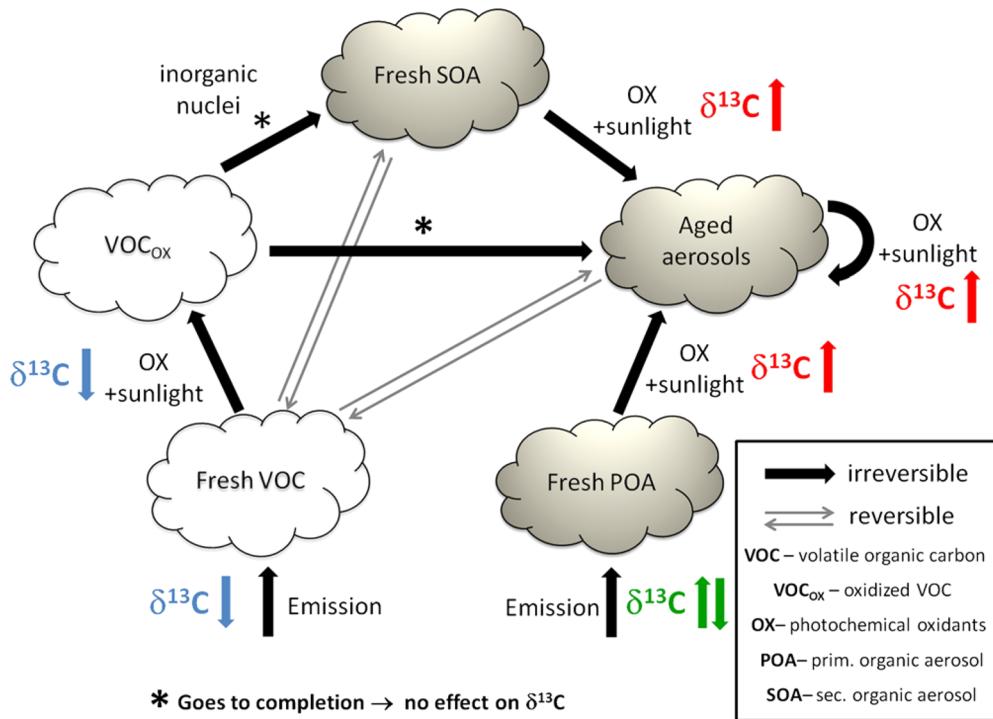


Figure 4. Illustration of the effect of various atmospheric processes on the $\delta^{13}\text{C}$ of carbonaceous aerosols. Blue arrows denote depletion in the heavy isotope (lowering of the $\delta^{13}\text{C}$), red arrows denote enrichment (increasing $\delta^{13}\text{C}$), and green arrows indicate processes that may change in both directions. Reprinted with permission from ref 185. Copyright 2013 American Geophysical Union and John Wiley & Sons, Inc.

$^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$, or $^{34}\text{S}/^{32}\text{S}$ with isotopic-ratio mass spectrometry and with high precision rather than high mass resolution.¹⁸⁴ The results are expressed as an isotopic shift relative to a reference, such as

$$\delta^{13}\text{C} = [({^{13}\text{C}}/{^{12}\text{C}}(\text{sample}) - {^{13}\text{C}}/{^{12}\text{C}}(\text{standard})) / ({^{13}\text{C}}/{^{12}\text{C}}(\text{standard}))] \times 1000 (\text{\textperthousand}) \quad (3)$$

For instance, for $\delta^{13}\text{C}$, the standard reference is Pee Dee Belemnite. These isotopic shifts, or fractionation, reflect kinetic isotope effects (KIE), that is, differences between the rates of the reactions with the heavier and lighter isotope, which are involved in a number of processes such as volatilization, chemical reactions, and condensation (Figure 4). Thus, they can reflect the degree of atmospheric processing of the organic compounds in gas or aerosol bulk or as individual compounds.^{184,185} The identification of sources is also possible if some precursors have different isotopic compositions (see section “Characterization of the Bulk: Source Apportionment”).

4.1.2.5.1. Identification at the Molecular Level: Characterization Processes. The identification of isotopic signals at the molecular level is often limited because isotopic-ratio MS systems are optimized toward high precision and accuracy of the isotopic signal (e.g., better than $\pm 0.1\text{\textperthousand}$ on $\delta^{13}\text{C}$) but not compound identification. The separation of individual compounds for isotopic-ratio mass spectrometry is based on chromatography techniques, that is, GC and LC (section 4.2). Because of the low natural abundance of the isotopes of interest (^{13}C , ^2H , etc.), the achievable factor I is limited by the quality of the chromatographic separation and the amount of sample available for the measurement. Hence, only major organic aerosol components have been investigated by compound-specific isotope analysis in laboratory and ambient air.

In chamber experiments, stable isotope measurements are used either to determine the signature KIE's for specific processes, to be applied later to atmospheric aerosols, or for the investigation of mechanisms and rate constants of complex reactions by adding an isotopically depleted or enriched precursor.¹⁸⁶ Thus, it was shown that progressively enriching β -pinene with the heavy carbon isotope increased the partitioning of its ozonolysis product, nopinone, into the aerosol phase and resulted in the enrichment of its $\delta^{13}\text{C}$ by $2.3\text{\textperthousand}$ compared to the gas.^{186f} The KIE of β -pinene enrichment during this reaction was also found to have a significant temperature dependence, larger enrichment taking place at lower temperature.¹⁸⁷ An enrichment of $\delta^{13}\text{C}$ for the unreacted oxalic acid was shown in the aqueous-phase photolysis of oxalic acid in the presence of H_2O_2 and UV,¹⁸⁸ but only in the presence of Fe species catalyzing Fenton reactions. These studies indicate that, even in laboratory, the understanding of the KIE resulting from various reactions and processes requires further investigation. In addition, the enrichment factors and KIE determined in laboratory are usually limited to specific compounds and experimental conditions, and difficult to apply to other systems.¹⁸⁹ Nevertheless, some mechanisms have been successfully elucidated using these approaches, such as the uptake of the heavy oxygen isotope into dicarboxylic acids, oxocarboxylic acids, and hydroxyketocarboxylic acids in the ozonolysis of monoterpenes in the presence of ^{18}O -enriched water vapor¹⁹⁰, which clearly indicate a direct implication of H_2O in the ozonolysis mechanism.

The measurement of stable isotope fractionation in the atmosphere has mostly been applied to small carboxylic acids, and in combination with ion chromatography (IC) or high-performance LC (HPLC), to the separation and collection of the fractions of interest. A correlation between the $\delta^{13}\text{C}$ of

gaseous formic acid and ozone concentrations was observed in the atmosphere.¹⁹¹ However, similar correlations for particulate-phase oxalic acid were small or insignificant, probably because of opposite isotopic shifts resulting from the gas reaction (ozonolysis producing the acids) and the aerosol formation processes. These results confirm the challenges in using quantitative compound-specific isotope analysis to investigate atmospheric aerosols, and the need for further studies to assess the feasibility of this approach.

Isotope analysis has been used more frequently for source apportionment than for mechanism investigation, for instance, to distinguish between continental and marine oxalate by their $\delta^{13}\text{C}$ in size-segregated aerosols in Bermuda.¹⁹² The use of both ^{13}C and ^{14}C isotope measurements provides more information. For instance, when applied to formic and acetic acid, this analysis revealed a mainly biogenic (as opposed to anthropogenic) origin of air masses at several European sites.¹⁹³ Yet because both chemical processing and source characteristics influence the isotopic fractionation, the differentiation between these factors is often difficult.¹⁹⁴

4.1.2.5.2. Characterization of the Bulk: Source Apportionment. Isotope measurements of bulk aerosol fractions are mainly dedicated to source apportionment and sometimes to the monitoring of the extent of secondary aerosol formation.^{185,194,195} For the source apportionment of organic aerosols, ^{13}C is the most employed stable isotope, and has been shown to display differences between plants with C3 and C4 biochemical carbon fixation mechanisms in photosynthesis, marine, and continental organic and liquid, solid, and gaseous fuels.^{185,196} However, these differences are often small compared to the natural variability of individual sources. Thus, for the investigation of organic aerosol precursors, isotope measurements have been performed on aerosol fractions enriched with secondary material, such as WSOC or humic-like substances (HULIS).^{185,196b,197} If a single isotope is considered, the apportionment is oftensemiqualitative only but can improve with a multi-isotope approach.^{185,196b,198} Another example of apportionment is the distinction between fossil, biogenic, or biomass burning sources using the long-lived radioisotope radiocarbon (^{14}C).¹⁹⁹ In particular, ^{14}C provides a robust attribution between fossil and nonfossil sources.^{185,193,197,200} For example, radiocarbon measurements of OC were compared to model results^{199c} and showed that nonfossil OC mainly stemmed from regional biogenic SOA, primary and secondary biomass burning aerosols, and primary and secondary nonfossil urban aerosols. In combination with aerosol mass spectrometry, ^{14}C analysis enables source apportionment of fossil versus nonfossil precursors for SOA-related factors such as low-volatile and semivolatile oxygenated organic aerosol.²⁰¹

Thus, the combination of ^{13}C and ^{14}C isotopes may provide deeper insights on sources and processes, such as the simultaneous distinction between marine, continental biogenic, and fossil sources or the estimation of primary and secondary sources of marine aerosols.^{196b}

4.2. Multidimensional Techniques

As pointed out in the previous sections, only a very limited number of one-dimensional techniques can achieve a satisfactory structural identification ($I < 10$), and for limited classes of atmospheric organic compounds. To identify a wider range compounds or complex ones, it is often necessary to combine several techniques, including some presented above.

This combination dramatically lowers the overall I factor of the analysis, generally to a few units ($I \leq 5$).

A powerful and widely used tool to characterize complex samples is to combine chromatographic separation techniques with sensitive and specific detectors. These approaches allow to identify compounds in complex matrixes and distinguish isobaric compounds (i.e., compounds with the same nominal but a different exact MW)²⁰² and, in some cases, isomers that cannot be distinguished with the direct MS techniques described above. Two-dimensional chromatography, for example, in GC or LC, can further increase the resolving power for components with similar physical chemical properties, by combining different separation mechanisms.

In this section, techniques combining chromatographic separation and a detector (e.g., mass spectrometry) or involving two or more stages of gas chromatography (i.e., GC \times GC) or mass spectrometry (i.e., tandem mass spectrometry) are defined as two- or multidimensional. The analysis of organic aerosols by GC- and LC-based methods presents several challenges because of their complexity and the occurrence of compounds spanning from nonpolar to very polar compounds. Complex organic aerosols containing semivolatile compounds have been successfully determined with GC \times GC-based methods. Polar compounds containing hydroxyl, oxo, and carboxylic acid functions can be measured either with GC with prior derivatization or with LC-based methods, whereas polar compounds containing sulfate groups require LC-based approaches. Details and examples of such analytical tools are given below with their achievable I -factors.

4.2.1. Separation. The characterization of individual aerosol constituents at the molecular level in highly complex mixtures generally requires chromatographic separation. The two most employed techniques are GC, often with prior derivatization, and HPLC. The selection of a chromatographic column is crucial in the development of a suitable analytical method and must consider the chemical and physical properties of the analytes (volatility, polarity, molecular weight, solubility, etc.). In particular, if the polarities of the stationary phase and of the analyte are similar, their attractive forces are strong and result in a better retention (compound appearing late in the chromatograms). The selectivity and resolution of a column are determined by the intermolecular forces between the stationary phase and the target molecules, including van der Waals, hydrogen bonding, and dipole–dipole interactions. Its physical parameters, such as the thickness of the stationary phase, inner diameter, and length, also need to be considered. Commercially available GC columns are based on stationary phases ranging from nonpolar (100% dimethyl-polysiloxanes)²⁰³ to increasingly polar ones, where diphenyl groups are incorporated (e.g., 5% diphenyl/95% dimethyl-polysiloxane)²⁰⁴ or which are functionalized (e.g., 14% cyanopropylphenyl/86% dimethyl-polysiloxanes).²⁰⁵ Columns with highly polar phases (e.g., polyethylene glycol-based)²⁰⁶ or specific materials, for example, for the separation of chiral components (e.g., cyclodextrin-modified phases),⁴² are also available.

Similar principles apply to LC analysis. However, its optimization is more flexible than for GC as both the stationary phase and the mobile phase of the column are participating in the separation process and can be modified (while in GC only the mobile phase ensures the transport of the medium through the column). LC analysis can be used for any compound soluble in a liquid phase. Many different types of separation can be achieved depending on the combination of the stationary

Table 5. Overview of Derivatization Reagents Commonly Used in GC and LC Analysis^a

principle	targeted compound class	derivatization reagent	analytical technique	ref
alkylation	carboxylic acid and other compounds with active hydrogen	diazomethane	GC/MS	39,216,219
		BF ₃ in methanol	GC/MS	34,220,221
		BF ₃ in butanol	GC/MS	222–224
		pentafluorobenzyl bromide	GC/MS	225,226
		tetrabutylammonium hydroxide	SPE-LC-GC/MS	227
		tetramethylammonium hydroxide/tetrabutylammonium hydroxide	GC/MS	228
		bis-trimethylsilyltrifluoroacetamide/1% trimethylchlorosilane/pyridine	GC/MS	216,230
		N-methyl-N-trimethylsilyltrifluoroacetamide containing 1% trimethylchlorosilane	GC/MS	231,232
		trimethylsilylimidazole	GC/MS	233,234
		acetic anhydride/4-dimethylaminopyridine in pyridine	GC/MS	235
oxime formation	carbonyl compounds	O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride	GC/MS	236
		2,4-dinitrophenylhydrazine	HPLC/MS	237,238
hydrazone formation	carbonyl compounds	hydroxylamine		239
		6-aminoquinolyl-N-hydroxysuccinimidyl carbamate/NaOH	HPLC/MS	240
oxime formation	amines			

^aAcronyms: See list of abbreviations. Additional acronym: SPE, solid-phase extraction.

and mobile phase: polarity, hydrophobicity, electrical charge, and molecular size. The physical parameters of the column, such as its retention capacity (influenced by surface area, carbon load, pore size, volume of the packing material), size and shape of the stationary phase material, and dimensions (internal diameter, length), are also critical and need to be selected carefully.

The most commonly applied LC technique is undoubtedly reversed-phase chromatography because it enables the separation of a wide range of polar and nonpolar solutes (e.g., refs 207–210). Other techniques include variations of normal phase chromatography for highly polar species such as hydrophilic interaction liquid chromatography (HILIC),²¹¹ or for specific applications such as ion exchange or size exclusion chromatography used for the characterization of HULIS.²¹²

Choosing the appropriate chromatographic separation for the chemical properties of the targeted compound usually leads to a high selectivity and high level of identification. The obtained *I*-factors vary, but separation techniques generally achieve at least *I* ≤ 3.

4.2.2. Multidimensional Techniques for Gas Analysis (GC and GC_xGC). GC separation is suited to any volatile organic compounds and, in combination with various detectors, has been the technique of reference to measure organic gases in the atmosphere. It remains unsurpassed by other techniques such as PTR-MS, as it allows the detection of a much wider range of compounds than those undergoing chemical ionization. In combination with preconcentration techniques, it can also reach much lower detection limits. Finally, it can even be used in semi-on-line mode with measurements frequencies up to 1/5 min.

Commonly used detectors in combination with GC include the flame ionization detector (FID), often for quantification, the electron capture detector (ECD), sensitive to halogenated species,²¹³ the nitrogen phosphorus detector for nitrated

compounds,²¹⁴ and a range of mass spectrometric techniques enabling more detailed structural characterization.^{30,34,215,216}

The organic gas samples collected by the methods described in section 3.1 are transferred to the GC instrument via a thermal desorption or solvent extraction step. Because of the low concentration of organic gases in the atmosphere, this transfer often includes an additional preconcentration or enrichment step, for example, cryofocusing, following a protocol specific to the compound classes or their chemical and physical properties.

4.2.2.1. Derivatization. For compounds that are not volatile enough or thermally too labile to pass through the injector and/or the column, derivatization procedures can be applied to the samples prior to their GC analysis. They consist in reacting the analyte with a derivatization reagent to produce specific compounds that can be observed by the detector, such as characteristic ions when using mass spectrometric detection.^{217,218} Derivatization can also increase the specificity of the analysis and the level of identification of certain compounds, such as mid- and larger-chain (>C₁₀) or multifunctionalized ones. The derivatization step often takes place prior to the transfer of the sample to the GC instrument, although postcolumn derivatization protocols exist. The most common derivatization reagents are summarized in Table 5. Usually, they target specific classes of compounds such as carboxylic acids, carbonyl compounds, or hydroxylated compounds. For instance, the derivatization of gaseous carbonyl compounds has been of considerable interest in atmospheric science. One of the most commonly used derivatization reagents is O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride. This reagent enables the identification of multifunctional carbonyl compounds, such as those produced by the oxidation of isoprene, which can be then identified by MS techniques such as ion trap MS.²⁴¹ Other derivatization procedures used in combination with GC analysis

include those for amines,²⁴² amino acids,²⁴³ or more specific compounds.²⁴⁴

This reagent enables the identification of multifunctional carbonyl compounds, such as those produced by the oxidation of isoprene, which can be then identified by MS techniques such as ion trap MS.²⁴¹ Other derivatization procedures used in combination with GC analysis include those for amines,²⁴² amino acids,²⁴³ or more specific compounds.²⁴⁴

Because derivatization implies a chemical reaction, it can also trigger side reactions, which can interfere with the structural assignment of the analyte. This is especially critical when investigating unknown and/or multifunctionalized compounds. In these cases, alternative approaches can be necessary such as the use of different derivatization procedures^{225,245} on different samples of the same series, or the derivatization of different fractions of a sample obtained by flash chromatography.^{246,247} More common approaches include multistep derivatizations, which target the different hydroxyl, carboxylic acid, and/or keto- or aldehyde groups of multifunctional compounds. Generally, the carboxylic acid group(s) are esterified first to methyl esters, followed by trimethylsilylation of the nonacidic hydroxyl groups and/or an additional conversion of keto- or aldehyde-groups into oxime derivatives.²⁴⁸ In particular, this approach has led to a better characterization of monoterpenederived²⁴⁹ and toluene photooxidation products.²⁵⁰ Another approach is to combine different types of ionization techniques in the GC/MS analysis, such as electron and chemical ionization. Comparing the different types of mass spectra usually leads to a higher level of identification, the chemical ionization spectra providing mainly the molecular mass of the derivative(s).²⁴⁸ The combination of derivatization and comprehensive mass spectral characterization is a powerful tool leading to *I* factors as low as 2.

4.2.2.2. On-Line Applications. In the past decades, methods have been developed to reduce the long times usually required for GC analysis, leading to semi-on-line field instruments and enabling comparisons with important atmospheric species such as ozone, carbon monoxide, or NO_x. Those include coupling of GC with real-time detection techniques, such as PTR-MS,²⁵¹ or the direct coupling of fast extraction techniques to the analytical instrument, leading to high time resolution.²⁵² Such fast extraction techniques include the use of supercritical CO₂, which is chemically inert, has a low toxicity, and is available in high purity. Another advantage is that the critical point of CO₂ is easily accessible at 31.1 °C and 72.9 bar, where it behaves as a gas in surface tension and as a liquid in density. The first applications of this technique to atmospheric aerosols were reported in the 1990s.²⁵³ In combination with in situ derivatization, this technique has been shown to allow the identification of polyfunctionalized species such as dicarboxylic acids, oxo-acids, and hydroxyl-acids in the ozonolysis of sabinene.²⁵⁴ Other fast extraction techniques that have been directly coupled to GC and applied to bulk aerosol analysis include Curie-point pyrolysis²⁵⁵ and other thermodesorption techniques.²⁵⁶ In Curie-point pyrolysis, the sample is applied onto a foil of ferromagnetic metal and rapidly heated by induction. When reaching its Curie-point temperature, the metal becomes paramagnetic and enables a fast and controlled evaporation of the analytes into the GC instrument. This technique has been applied, for example, to PAHs,²⁵⁵ alkanes,²⁵⁷ and, with an additional derivatization step, organic acids.²⁵⁸ Other thermally assisted extraction methods^{259,260} combined with derivatization have been described^{229,261} and

offer powerful tools for the identification of unknown compounds. In particular, a field deployable thermal desorption aerosol gas chromatograph (TAG) using both FID and MS and enabling high time-resolution for aerosol analysis has been developed.²⁶² This instrument incorporates a custom-designed inlet where the aerosols are collected and thermally desorbed into the GC column. The system is automated and allows for continuous speciated measurements of organic compounds in aerosols every hour. The inlet has recently been modified to allow less volatile gases and particles to be measured simultaneously,²⁶³ thereby allowing to study their gas-particle partitioning.

Thus, the semi-on-line GC techniques described in this section are valuable tools for real-time monitoring of organic compounds both in the gas and the particle phases, and nicely complement on-line techniques such as PTR-MS and AMS.

4.2.2.3. GC×GC. Two-dimensional gas chromatography is a powerful tool to improve the identification of organic compounds in complex mixtures, both in the gas and in the condensed phase.²⁶⁴ It consists of coupling two GC columns in series,²⁶⁵ generally functioning on different separation mechanisms.²⁶⁶ The chromatograms are usually represented with the retention times for each column in *x*- and *y*-axes, respectively, and the peak height as colored contour. GC×GC is often coupled with either a flame ionization detector (for quantification) or a mass spectrometer, usually a TOFMS instrument (for identification).²⁶⁷ Better selectivity has been sought by using more element-specific detectors such as a nitrogen chemiluminescence detector²⁶⁸ and a nitrogen phosphorus detector, which have been applied to 15 organic nitrogen species.²⁶⁹ Yet, while targeting specific compounds (here nitrogen-containing ones), element-specific detector do not provide the structural information typically provided by mass spectrometry.

The higher identification level of GC×GC compared to classical one-dimensional GC²⁷⁰ results from the fact that fewer compounds coelute, providing cleaner mass spectra and a unique set of three independent variables (retention time 1, retention time 2, and mass spectrum). This technique has thus the potential for full identification (*I* = 1) but can also provide useful partial structural information using the structured nature of the chromatograms, where isomers, such as linear and branched alkanes, are grouped together. The first GC×GC analysis of VOCs in air was performed with a flame ionization detector and showed that much of the hydrocarbon loading in an urban atmosphere was unaccounted for using conventional one-dimensional GC-FID techniques as many species at low concentrations coelute to form a raised baseline. Later studies using GC×GC-FID with a simple cooled loop injection reported the monoaromatic composition of gasoline, gasoline vapors, and urban air samples and that many of the larger aromatic species present in gasoline vapor were also present in urban air. A total of 147 monoaromatic isomers were isolated from a polluted urban air sample and calculated to be a potentially significant source of tropospheric ozone. GC×GC has subsequently been used in a range of studies of the atmospheric composition at different locations corresponding to different sources and degrees of aging.

Despite these examples, the use of GC×GC as a routine instrument by the atmospheric community has been slow, in part due to difficulties with quantification and because the large number of species that can be separated creates data handling problems.

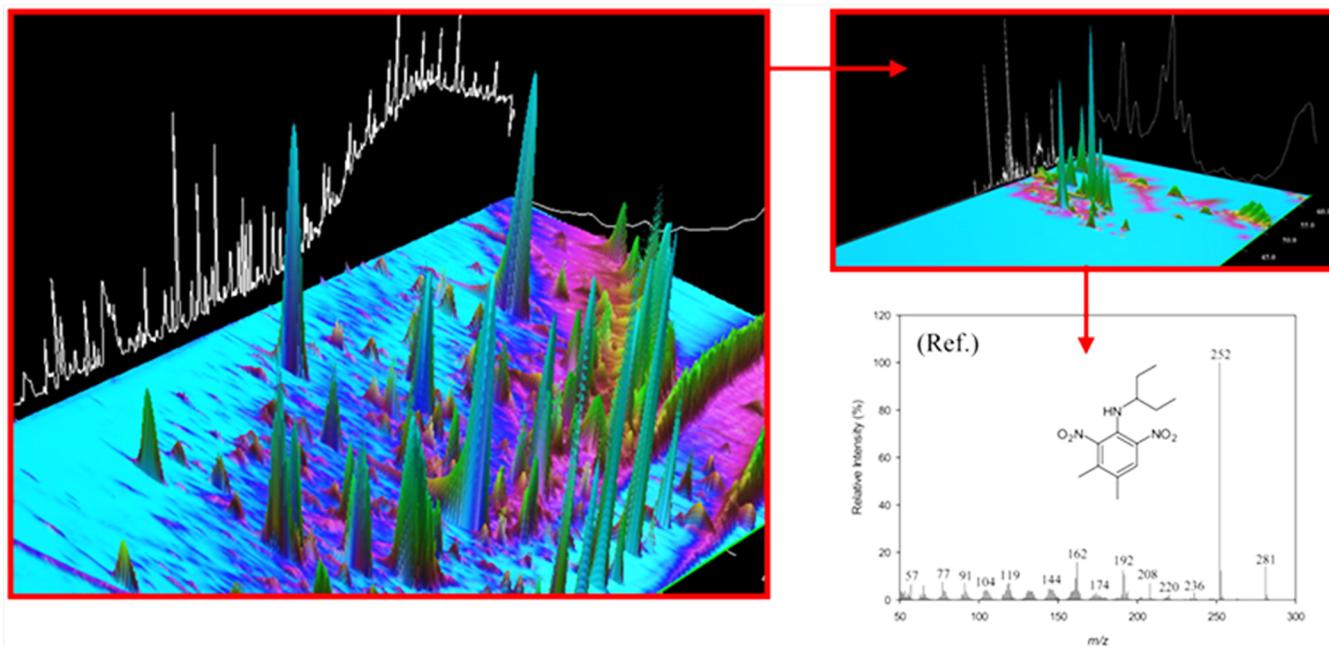


Figure 5. Contour plot of the total ion current chromatogram of an urban aerosol sample examined by GC \times GC-TOFMS (left) and the mass spectrum of a compound to identify aerosol constituents (right). Reprinted with permission from ref 277. Copyright 2013 Elsevier.

4.2.3. Multidimensional Techniques for Aerosol Analysis.

4.2.3.1. GC-ECD and GC/MS. A large part of the GC techniques discussed in the previous section also apply to the analysis of aerosols, in particular GC \times GC. Initial studies of organic aerosols by GC \times GC resulted in the separation of over 10 000 organic compounds including alkanes, alkenes, cycloalkanes, *n*-alkane acids, alkyl- and alkenyl-substituted aromatics, polar benzenes, PAHs, and oxy-PAHs.^{271,272} The complex of information gained from such techniques is associated with difficult and time-consuming data analysis. Recently, the profiling of complex aerosol samples was achieved by advanced scripting methods based on mass spectral properties.²⁷³ Important areas of application of GC \times GC are the identification of chemical markers and oxidized products, as the oxidized material can be separated from the rest of the sample by using a polar second column, such as 50% phenyl polysilphenylene siloxane or polyethylene glycol columns. New oxidation products and pathways have been identified by this technique in chamber experiments. This technique has also proven very efficient for the analysis of atmospheric samples, with over 100 oxidized species observed, many linked to aromatic precursors, in filter samples from a roadside in London.²⁷⁴ Similarly, over 50 organic compounds including oxygenated monoterpenes and previously unknown oxidation products of α -pinene were identified in organic aerosols from a coniferous forest in Finland.²⁷⁵ Oxidation products of naphthalene and phenanthrene were also identified in PM_{2.5} samples from Seoul, South Korea.²⁷⁶ GC \times GC has also been used to identify markers for primary sources such as manufacturing processes²⁷⁷ (Figure 5) and wood combustion,²⁷⁸ and for the size-resolved analysis of particles collected by a differential mobility analyzer in a boreal forest in Finland, evidencing the presence of less compounds but higher proportion of hydrocarbons, aldehydes, halogenated, and nitrogenated compounds in smaller particles (30 nm) than in larger ones (50 nm).²⁷⁹

In addition to the laboratory instruments described above, a two-dimensional version of the field TAG instrument described

above (2D-TAG),²⁸⁰ for instance coupled with a TOFMS detector,²⁸¹ can provide mass spectral data with high time-resolution based on the same principle. If authentic standards or mass spectral libraries are available, this instrument can achieve the full identification ($I = 1$) of organic aerosol components while enabling the investigation of time-dependent processes such as sources, aerosol aging, and correlations with important atmospheric species such as VOCs, ozone, carbon monoxide, and NO_x.²⁸² Other advantages of this instrument have been demonstrated in laboratory, such as information on the volatility and extent of aerosol oxidation during sesquiterpene ozonolysis, without identifying individual species.²⁸³

4.2.3.2. IC and IC/MS. Ion chromatography was developed as early as in the 1970s but is still the leading technique for the trace analysis of inorganic and organic ionic compounds in all types of environmental samples. As it offers a simple, reliable, and inexpensive separation and determination for organic ions in complex mixtures, it is also usually the first choice for the determination of low-MW organic acids in atmospheric aerosols and aqueous (cloud, fog, rain) samples.

The prerequisite that the analyte produces water-soluble ions makes IC a rather selective analytical technique. Ion chromatography is based on two possible separation mechanisms, ion exchange and ion exclusion. The former is typically used for polar organic compounds such as low-MW dicarboxylic acids,²⁸⁴ while the latter is generally applied to less polar organics such as weak acids.^{285,286} Early versions of IC instruments were coupled with UV detectors,²⁸⁷ while conductivity detectors are mostly employed nowadays.²⁸⁸ For special applications, such as atmospherically relevant carbohydrates (sugar alcohols, monosaccharides, and monosaccharide anhydrides), high-performance anion exchange chromatography coupled to pulsed amperometric detection can be used.²⁸⁹

Ion chromatography can be used off-line or semi-on-line. In off-line configurations, the particulate samples, collected on filters or cascade impactor foils, are extracted in water, filtered,

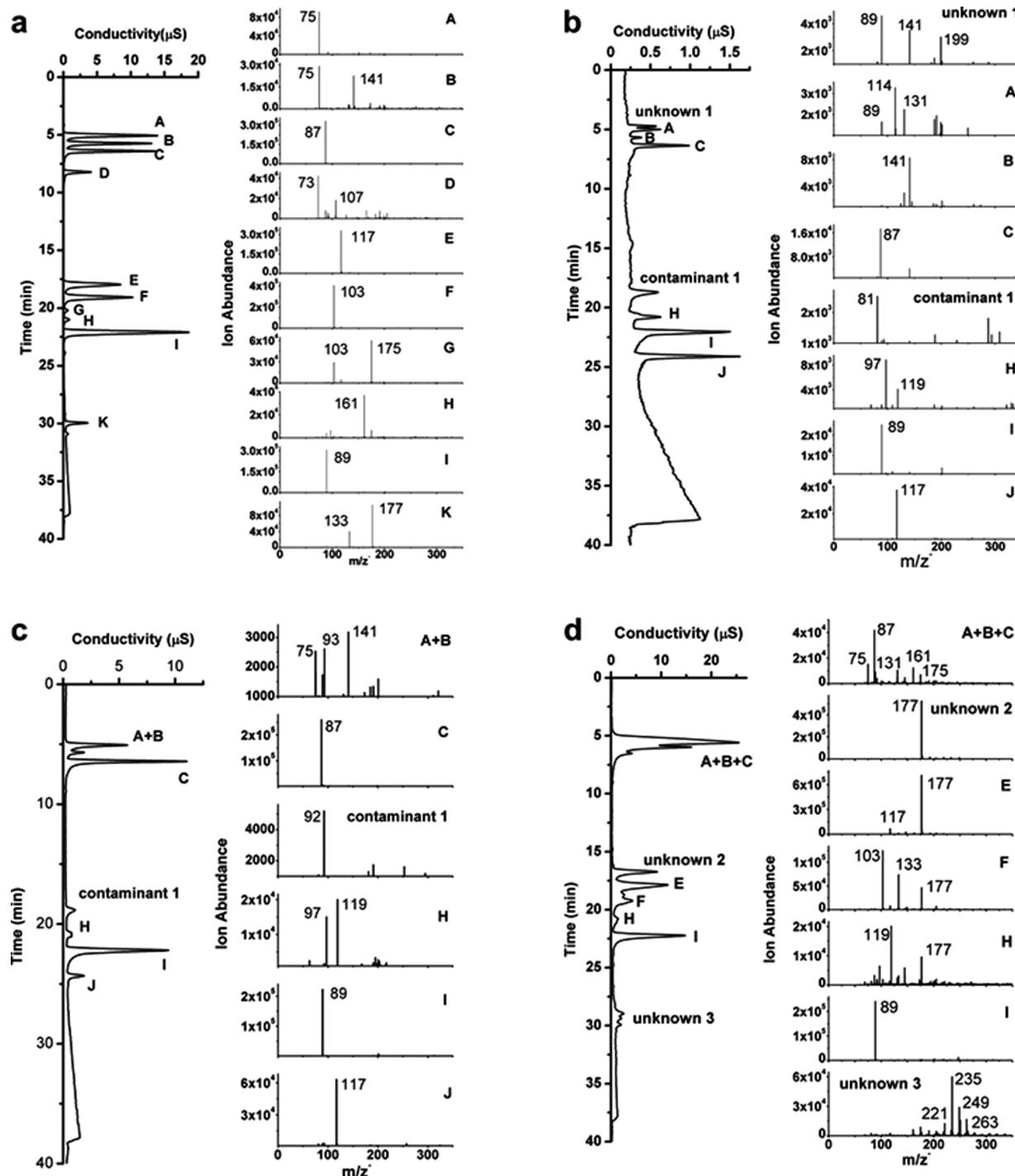


Figure 6. Examples of organic acids formed in the oxidation of methylglyoxal and analyzed using IC/ESI-MS. (a) IC-ESI mass spectra of a mixed standard of acids: (A) acetic (not detected in ESI-MS) and glycolic (m/z 75), (B) formic (not detected in ESI-MS), (C) pyruvic (m/z 87), (D) glyoxylic (m/z 73), (E) succinic (m/z 117), (F) malonic (m/z 103), (I) oxalic (m/z 89). (b)–(d) IC/ESI-MS spectra of acids at increasing concentrations of methylglyoxal. (b) 30 μ M: (A) the retention time (t_r) of acetic/glycolic acids, (B) t_r of formic acid, (C) pyruvic acid, (I) oxalic acid, (J) mesoxalic acid (m/z 117). (c) 300 μ M: (A + B) t_r of acetic/glycolic acids + formic acid, (C) pyruvic acid, (I) oxalic acid, (J) mesoxalic acid. (d) 3000 μ M: (A + B + C) t_r of acetic/glycolic acids + formic acid + pyruvic acid, (E) t_r of succinic acid, (F) t_r of malonic acid, (I) oxalic acid. Reprinted with permission from ref 308a. Copyright 2010 Elsevier.

and then injected onto the IC column.²⁵⁶ In semi-on-line configurations, the sampling system is directly connected to the IC instrument and allows for the real-time detection of organic compounds. Examples of such semi-on-line sampling systems include particle-into-liquid sampler (PILS),^{290–294} wet effluent

diffusion denuder/aerosol collector,^{295,296} and ambient ion monitor-ion chromatography system.²⁹⁷

The atmospheric organic compounds identified by IC include water-soluble low-MW organic acids in aerosols, the most common being monocarboxylic (i.e., formic, acetic, pyruvic, and glyoxylic acids), dicarboxylic (i.e., oxalic, succinic,

fumaric, malic, tartaric, glutaric, maleic, malonic, α -ketoglutaric, and oxaloacetic acids), and tricarboxylic acids (i.e., citric and *cis*-aconitic acids).^{284,288,296,298} Some aromatic acids (i.e., phthalic, syringic, 3-hydroxybenzoic, 4-hydroxybenzoic, vanillic, and isovanillic acid) have also been identified in aerosol particles from smoke samples,²⁵⁶ and methanesulfonic and methane-sulfinic acids both in ambient aerosols and in chamber studies.^{299,300} More recently, IC has been applied to the detection of saccharide markers, such as levoglucosan, mannosan, and galactosan, in biomass burning aerosols, inositol, glucose, galactose, and fructose, in pollen, and erythritol, arabitol, and mannitol, in fungal spores.^{289,301} IC has also been used for the detection of aliphatic amines such as methyl-, dimethyl-, trimethyl-, ethyl-, diethyl-, and triethylamine,^{297,299,302–304} although the column used (Dionex CS-17) did not allow the separation of trimethyl- and dimethylamines.²⁹⁷

Examples of ongoing and promising further applications of IC include its coupling with electrospray ionization high-resolution mass spectrometry allowing the identification of polar ionizable organic compounds that are otherwise difficult to determine by LC/MS.^{305,306} This type of coupling, combining the high selectivity of IC with the structural identification potential of MS, is very promising for the full identification of low-MW carboxylic acids,³⁰⁷ as the IC separation would reduce the number of eluting compounds, thus facilitating the interpretation of the mass spectra, and enabling the MS differentiation of coeluting compounds.

However, there were only a few attempts to couple IC with MS, especially in atmospheric science.^{295,308} Examples include the determination of the total anionic composition of urban ambient aerosols.³⁰⁹ Although this approach led to the identification of more than 10 organic acids (e.g., glycolic, acetic, lactic, formic, methanesulfonic, pyruvic, malic, malonic, oxalic, *o*-phthalic) with an AS-15 column and two coeluting acids (malic and succinic) with an ICE-AS6 column, several peaks remained unknown and many more compounds, mostly organic acids, unresolved. IC/MS coupling was also used for the identification of organic acids in the gas and in aerosols during the photooxidation of trimethylbenzene and propene in smog chamber experiments. The sampling was made with a wet effluent diffusion denuder/aerosol collector connected to the IC.²⁹⁵ The fractions collected after IC separation (on a AS11-HC column) were analyzed by APCI-MS using a quadrupole mass analyzer with atmospheric pressure ionization for the identification of unresolved organic acids. Series of mono- and dicarboxylic acids, that is, from formic to citric acid ($I = 1$), were thus unambiguously identified, and the MWs of a number of unknown compounds up to 234 determined.

Recently, another coupling approach of IC and ESI-MS was successfully applied to the analysis of reaction products (pyruvic, succinic, malonic, oxalic, mesoxalic acid) in the oxidation of methylglyoxal (Figure 6) and acetic acid,^{308a,310} and in the photochemical aging of isoprene SOA in aqueous phase.^{308b} Equipping the IC instrument with a membrane ion suppressor (e.g., ASRS-ultra suppressor avoiding the formation of uncharged species at the interface operated in external water mode) eliminated the sodium ions from the mobile phase and increased the sensitivity of the MS detection.³¹¹ Other setups are based on the combination of IC, ESI-MS,^{308b,311} and UV detection.^{305,306}

4.2.3.3. CE/MS. Capillary electrophoresis is an efficient alternative to GC or LC as its separation is based on different

principles. In this technique, separation is achieved by a strong electrical field. The resulting retention times of the ionizable analytes depend on their electrophoretic mobilities. With this technique, both inorganic and organic ions, such as carboxylic acids,^{255,312,313} can be separated in a single run. Other advantages, especially for atmospheric applications, include the requirement of only small sample amounts, such as a single drop of rain or fog,³¹⁴ the broad linear detection range, and the absence of extensive sample preparation, even for complex compounds such as HULIS.^{315,316} CE is usually coupled with UV-vis^{313,314} or conductivity detectors,³¹⁷ but coupling with MS has also been performed.^{318–324} However, the buffers used in CE separation can interfere with the MS ionization process, and the use of sheath liquid can lead to a loss of MS sensitivity. The second problem could be avoided by coupling CE to nanospray interfaces. Examples of coupling of CE with high-resolution MS³¹⁸ or MS² have been reported³²³ and should lead to the identification of unknown compounds with low I -factors (<5).

Taking advantage of the small amounts of sample required, several miniaturizations of this technique have been developed for field applications and semi-on-line analysis. Those include the use of microchip CE analysis^{325,326} and coupling to PILS samplers,³²⁷ which are promising approaches for routine analysis in the field. However, no structural characterization of organic aerosol components has been reported from these applications so far.

4.2.3.4. LC-UV and LC/NMR. While, as discussed in section 4.1, UV-vis spectroscopy is not specific and provides mostly bond/functional group identification ($I \geq 100$), its coupling to liquid chromatography greatly improves the level of identification by adding information on retention times and the possibility to compare with reference standards. One of the early important applications of HPLC-UV-vis to organic aerosols has been the determination of toxic compounds such as PAHs, which are naturally strong UV chromophores due to their aromatic structure. But this application has progressively fallen out of favor because of its poorer sensitivity compared to GC/MS methods.

In addition to separation, derivatization can enable the detection of compounds that are not natural chromophores, and be very selective, resulting in $I \leq 10$, by targeting specific functional groups. Numerous methodologies for HPLC/UV-vis analysis with pre- or postcolumn derivatization have thus been developed, and a number of derivatizing agents specific to carbonyl, hydroxyl, carboxyl, or ester groups can be used. The most common derivatizing agent for carbonyl compounds (aldehydes and ketones) is 2,4-dinitrophenylhydrazine, which has been extensively used for their off-line determination in gas- and particulate-phase atmospheric samples.^{328–331} The studies of ambient samples have shown that the detection limits of this technique are comparable to those of derivatization-GC/MS methods.³³² The organic compounds identified in atmospheric aerosols by this method span from low-MW carbonyl compounds, such as formaldehyde and acetone, to heavier ones such as pinonaldehyde and substituted benzaldehydes.³³³ Further improvements of this method include clean-up procedures and coupling with tandem MS detection. The latter enhanced the selectivity (via multiple reaction monitoring) of the detection of the α -dicarbonyls glyoxal and methylglyoxal in ambient aerosol samples.^{237,334}

Other atmospherically relevant classes of compounds that can be selectively detected by UV-vis spectroscopy include

organic peroxides and nitrates. For instance, a thermal desorption particle beam mass spectrometer coupled with HPLC/UV-vis detection at 210 nm was used for the identification and quantification of organic nitrates in particulate samples.^{86,335} This method is interesting because of the lack of detection techniques and standards for organic nitrates, in spite of their importance in the atmosphere. The method is very selective and sensitive for alkyl nitrates because their molar absorptivity at this wavelength is much higher than that of alcohols, ketones, carboxylic acids, or alkenes.

Finally, HPLC/UV-vis coupled with MS detection is particularly attractive for the characterization of light-absorbing organic compounds in aerosols (brown carbon) as it allows one to target a subset of compounds absorbing at specific wavelengths. This approach has been recently used in the study of nitrogen-containing compounds with chromophoric properties such as nitroaromatics and imidazoles.^{47,336} Yet the level of identification in complex mixtures remains low, and coupling high resolution MS with HPLC/UV-vis detection is necessary to increase it.⁸³

4.2.3.4.1. LC/NMR. On-line coupling between LC and NMR was introduced for the first time in the early 1980s, but, although it is a powerful technique for the structural characterization of organics, its applications remain scarce as compared to other LC-couplings because of the low NMR sensitivity and its high costs. However, the recent development of superconducting magnets, new probe technology (especially cryogenic probes), and efficient methods for solvent suppression has remarkably improved NMR sensitivity and encouraged its application in many fields. Besides numerous publications in pharmaceutical and food science, it has been recently applied to the investigation of the chemical composition of organic compounds in aerosols, where it can be used for the structural characterization of unknown compounds. Semipreparative LC was used to isolate a series of nitro-aroamatic compounds, 4-nitroguaiaicol, 6-nitroguaiaicol, and 4,6-dinitroguaiaicol, produced by the aqueous-phase photonitration of 2-methoxyphenol, which were structurally identified by ¹H, ¹³C, and 2D-NMR, and ESI-MS².³³⁷ These compounds were then collected and used as references for comparison with ambient aerosol samples. Reference compounds for biogenic secondary products were also recently produced by a similar approach: semipreparative HPLC/UV-vis was used to obtain milligrams of pure pinonaldehyde and ketolimononaldehyde in the low-temperature ozonolysis of α -pinene and limonene in dichloromethane.⁸³ The isolated products were then characterized by ¹H NMR spectroscopy and high-resolution MS. Recently, the use of NMR for the quantification of SOA markers produced in laboratory was further exploited by isolating them by semipreparative LC at submilligram levels.⁵⁰

Thus, the use of preparative LC coupled to NMR analysis can offer a high identification level, with *I*-factors = 1, but as a relatively high amount of a pure sample (ca. 10 μ g) is required this approach is limited to the most abundant species in aerosol.

4.2.3.5. LC/MS and 2D-LC/MS. LC/MS is one of the most robust analytical methods for the chemical characterization and quantification of highly and moderately polar organic analytes. In contrast to GC/MS methods where the critical factor for separation is the vapor pressure or boiling point of the analyte, LC separation is typically driven by the polarity strength of the individual component of the mixture. Because oxygenated

organic compounds are abundant in atmospheric aerosols,¹⁴³ LC/MS provides an interesting method to investigate the chemical composition and changes of these polar organic aerosol components.

The reliability of the data obtained from LC/MS analysis depends strongly upon sample preparation and operating conditions. An important factor is to select the least destructive solvent for the analyte extraction. The use of polar solvents such as acetonitrile, water, and a mixture of tetrahydrofuran/water, which are compatible with ESI, is highly recommended. However, for certain organic mixtures, such as isoprene-derived SOA constituents, methanol was found to be the most efficient for filter extraction.³³⁸ It has thus been widely used for the extraction of these and other polar organic constituents from filters.^{31,39,207,338,339} Yet potentially detrimental features of this solvent have been recently evidenced by the loss of some carboxylic acids, such as terpenoic acids, probably by reaction between the solvent and the analytes.³⁴⁰

In laboratory, LC/MS techniques have been used to investigate SOA formation and aging from a range of precursors,^{190,338,339,341} including glyoxal,³⁴² methylglyoxal,^{308a,310} methyl vinyl ketone,^{74a} glycolaldehyde,³⁴³ and acetic acid.³¹⁰ LC/MS techniques have also been critical to identify organosulfates and their nitrated derivatives (nitrooxy organosulfates) in atmospheric samples, and reveal their large aerosol concentration.^{207,339d,344} Prior to 2005, organosulfates were largely missed because GC/MS techniques are not able to measure them due to their low volatilities and chemical instability to derivatization.²⁰⁷ Using LC/ESI-MS techniques in the negative ion mode provided the first molecular identification of organosulfates in aerosol samples (i.e., particulate matter with an aerodynamic diameter $\leq 10 \mu\text{m}$ (PM_{10})).³⁴⁵ This work was followed by other studies performing similar analyses in $\text{PM}_{2.5}$ samples^{339c} and by analyses of ambient $\text{PM}_{2.5}$ and laboratory-generated aerosols^{31,207,339d} investigating the formation pathway for organosulfates in aerosols.^{31,339d,341c,344b,346} More recently, LC/ESI-MS analyses have identified organosulfates produced in laboratory experiments^{35b,344a,346b,347} and in Arctic aerosols.³⁴⁹ However, many challenges limit the application of LC/ESI-MS techniques, such as the lack of authentic standards for aromatic-derived organosulfates.³⁴⁸ Future work should focus on synthesizing these compounds.³⁴⁹

4.2.3.6. Ultra-High-Resolution MS (UHRMS). Ultra-high-resolution MS (UHRMS) is a relatively new tool for the analysis of organic aerosols, which has two important features: (i) high mass resolving power and (ii) high mass accuracy, as defined in section 4.1.2. High accuracy coupled with high resolution allows one to determine unambiguous elemental formulas for each ion peak, which can, in turn, be used to characterize and categorize a large number of compounds present in complex organic mixtures. The organic fraction of atmospheric aerosols often contains hundreds to thousands of species in a *m/z* range of 100–500, and, frequently, more than 10 compounds are observed within 0.1 Dalton (Da), clearly illustrating the necessity of high mass resolution techniques to investigate its chemical composition.

There are three major types of high-resolution mass analyzers: the Fourier transform ion cyclotron (FTICR), the Orbitrap, and the high-resolution quadrupole (Q) TOF (HR-Q-TOF). FTICR offers the best resolving power with a record resolution of 40 000 000 that was reached for reserpine at *m/z* 609 at a magnetic field of only 7 T.³⁵⁰ Orbitrap instruments

have shown to provide resolving power in excess of 1 000 000 at $m/z < 300\text{--}400$ within a 3 s detection time making it compatible with several types of chromatographic separations.³⁵¹ Finally, HR-Q-TOF instruments have a fairly uniform resolving power of up to 40 000 across a m/z 100–500 mass range.

Mass accuracy, on the other hand, strongly depends on various parameters including scan rate, signal-to-noise ratio, and resolving power of the instrument.⁹⁵ Using appropriate internal mass calibration, the highest mass accuracy is generally achieved by FTICR-MS (<0.5 ppm), followed by Orbitrap MS (1–5 ppm), and by Q-TOF MS (1–10 ppm).

The high resolving power of UHR mass spectrometers allows the characterization of thousands of organic species in a single mass spectrum by introducing the sample directly into the source without prior chromatographic separation.³⁵² This technique is generally referred to as direct infusion. A range of soft ionization techniques such as ESI,^{353–356} atmospheric pressure photoionization,³⁵⁷ and a variety of atmospheric pressure surface ionization methods, for example, nano-DESI³⁵⁸ and liquid extraction surface analysis,¹⁰⁴ can be coupled with UHR mass analyzers. Soft ionization techniques allow the formation of ions with very little or no fragmentation and thus simplify the interpretation of mass spectra of highly complex mixtures.

Despite high analytical throughput of direct infusion, this method is known to be prone to matrix artifacts such as changes in the ionization efficiency of an analyte due to the presence of “matrix” compounds in the mixtures. For example, sulfates, nitrates, and ammonium salts are important constituents of atmospheric aerosols³⁵⁹ and can cause ion suppression, adduct formation, and a rapid deterioration of instrument performance if injected into the ESI source.³⁶⁰ Thus, changes in peak intensities have to be interpreted with care when comparing mass spectra of samples with different salt content or widely varying organic composition. Another limitation of direct infusion is its inability to discriminate between isomeric compounds solely on the basis of accurate mass. In addition, noncovalent adducts (including noncovalent dimers) formed in the ESI source can lead to peaks with high m/z values, which do not reflect compounds present in the actual sample. Such potential artifacts can be minimized by varying the ionization method, the ionization voltage, or the concentration of the sample.

4.2.3.6.1. UHRMS Data Analysis. Molecular formula assignment is the most critical and laborious step in UHRMS analysis. Even with a mass accuracy of <1 ppm, several molecular formulas can often match a single measured mass. The number of theoretically possible assignments increases exponentially with the mass. For example, for masses of >600 Da, more than 15 different molecular formulas can be assigned to each detected mass within a mass tolerance of 1 ppm.³⁶¹ Therefore, to reduce the number of matching formulas, those not likely to occur in nature are eliminated by applying a number of constraints when determining elemental formulas from the accurate mass measurements. Although various data filtering approaches are applied, there are several essential steps, which include (i) instrument error and mass drift check, (ii) restriction for the number of possible elements assumed to be present in the molecule (e.g., C, H, O, N, and S), (iii) incorporation of isotopic pattern into analysis, (iv) consideration of only chemically meaningful elemental ratios, for example, reasonable oxygen to carbon (O/C) and hydrogen to

carbon (H/C) ratios, and (v) nitrogen rule and double bond equivalent checks and additional sample specific constraints.^{4,361}

4.2.3.6.2. Visualization Methods. Because UHRMS generates very large amounts of data, their discussion and interpretation is often facilitated by visualization methods, which aim to group or categorize data sets and help to identify patterns, such as differences between sampling locations or atmospheric processes in atmospheric chemistry. These visualization methods include the double bond equivalent, van Krevelen diagrams, Kendrick mass analysis, and carbon oxidation state, and are described below.

4.2.3.6.3. Double Bond Equivalent (DBE). The DBE, often referred as the index of hydrogen deficiency, is the number of double bonds and rings in a molecule. For formulas of the general type $C_cH_hN_nO_o$, the DBE can be calculated using eq 4:

$$\text{DBE} = 1 + c - 0.5h + 0.5n \quad (4)$$

where c , h , and n correspond to the number of C, H, and N atoms in the molecule. Other monovalent elements besides hydrogen (e.g., F, Cl, Br, I) can be counted as “hydrogens”, trivalent elements (e.g., P) are counted as “nitrogen”, and tetravalent elements (e.g., Si, Ge) can be calculated as “carbon”.⁹⁵ However, when using eq 4, the DBE of molecules containing elements with multiple valences (e.g., S) should be considered with caution. The DBE is useful not only for molecular assignments by eliminating molecules with unreasonable high numbers of rings and double bonds but also for comparison of the molecular composition of different environmental samples. The data can be visualized, for example, by plotting the DBE either against the number of carbon atoms in the individual formula or the m/z ratio.^{362–364} For example, aromatic hydrocarbons and their oxidized derivatives that are generally characteristic for anthropogenic emissions have relatively large DBE values (>5) and thus can be easily identified in the large data set. Therefore, DBE plots provide additional insights into the sources and precursors of aerosols.^{363,364}

4.2.3.6.4. van Krevelen (VK) Diagrams. The VK diagram, in which the H/C ratio is plotted as a function of the O/C ratio for each mass and corresponding formula identified in a sample, is often used to describe the evolution of organic mixtures. The method was initially developed to study the coalification process³⁶⁵ and is applied to categorize aerosol samples. VK diagrams can also be used to differentiate potential sources of the organic aerosols by identifying major known classes of natural and anthropogenic organic compounds as illustrated in Figure 7 (see ref 353 and references therein). In general, the most oxidized species populate the lower right part of the VK plot and the most reduced/saturated species lie in the upper left part of the diagram. Moreover, aliphatic compounds typically have high H/C ratios (≥ 1.5) and low O/C ratios (≤ 0.5), while aromatic hydrocarbons have low H/C ratios (≤ 1.0) and O/C ratios (≤ 0.5).³⁵⁴ VK diagrams are frequently plotted as three-dimensional figures with ion signal intensities included as an additional dimension.³⁵⁵ Ion signal intensities have been used to identify concentration ratios, but because in direct infusion ion intensities do not directly reflect the concentration of the analyte but rather its ability to ionize in the media, the interpretation of this information should be done with caution. A drawback of VK diagrams is that formulas with different atom numbers but identical atomic ratios (H/C, O/C, etc.) cannot be distinguished. Thus, the complexity of samples is sometimes not well represented by VK diagrams.

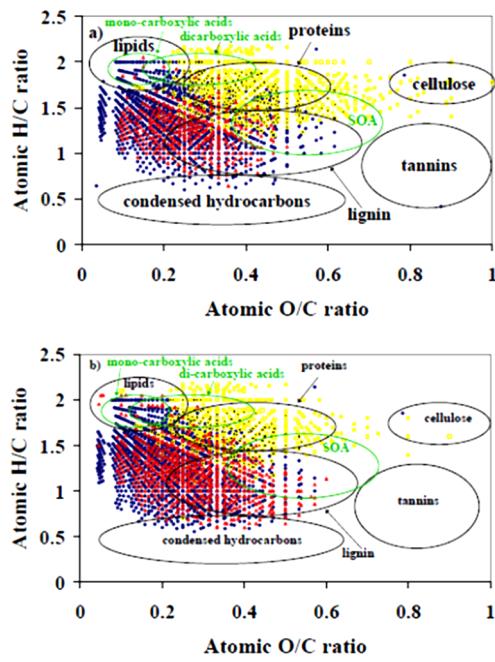


Figure 7. van Krevelen plots for molecular formulas assigned to FTICR mass spectra peaks in aerosol samples from (a) New York and (b) Virginia. Blue diamonds represent compounds containing only C, H, and O, yellow squares represent S-containing compounds, and red triangles are N-containing compounds. Black ovals represent traditional potential source molecular classes. The green SOA oval represents data from laboratory investigations of SOA. Adapted from ref 353.

4.2.3.6.5. Kendrick Mass (KM) Analysis. KM analysis is typically used for both formula assignment and data visualization.³⁵¹ It is another useful tool to observe the composition and evolution of complex organic mixtures and is frequently used to identify compound classes.³⁶⁶ In addition, it can be applied to identify homologous series of compounds differing

only by the number of a specific base unit (e.g., a CH₂ group). The Kendrick mass of the CH₂ unit is calculated by renormalizing the exact IUPAC mass (14.01565) of CH₂ to 14.00000. The KM defect is calculated from the difference between the nominal mass of the molecule and the exact KM.³⁶⁷ A consequence of this renormalization of the atomic mass scale is that compounds that differ only by the number of base units (e.g., CH₂) have exactly the same KM defect and can thus easily be identified and grouped into a homologous series. Therefore, the molecular formula elucidation of one compound in a homologous series allows identification of the remaining peaks in the series. KM analyses have been used to illustrate composition differences in biomass burning particles from various wood sources and to identify potential specific marker compounds.³⁶⁸ However, if compounds are identified only via KM defect analysis as members of a homologous series, their structural similarity cannot be inferred. The elucidation of chemical structures needs to be supported by additional analytical techniques, for example LC/MS or NMR, discussed in the previous sections, and tandem mass spectrometry, discussed in section 4.2.3.7.

4.2.3.6.6. Carbon Oxidation State (OS_C). O/C ratios may not accurately describe the degree of oxidation of organics because other nonoxidative processes (e.g., hydration and dehydration) can affect atomic ratios in a molecule as well.³⁶⁹ The OS_C is suggested as an alternative metric to describe the chemical composition of atmospheric aerosols. OS_C is shown to be strongly linked to aerosol volatility and thus is a useful parameter to classify SOA.³⁷⁰ The carbon oxidation state can be calculated from the following equation:

$$\text{OS}_C = - \sum_i \text{OS}_i \frac{n_i}{n_C} \quad (5)$$

where OS_i is the oxidation state associated with element *i*, and n_i/n_C is the molar ratio of element *i* to carbon.³⁶⁹ Generally OS_C is used for molecules that do not have a multiple valence, for example, containing C, H, and O atoms only. OS_C were

Table 6. Characteristic Product Ions and Neutral Losses Observed upon Fragmentation of Protonated or Deprotonated Molecules Useful for Molecular Characterization of SOA Products^a

precursor ion	neutral loss (Da)	product ion (<i>m/z</i>)	structural feature	refs
[M + H] ⁺	H ₂ O (18)		carboxyl, epoxy, keto, aldehyde, hydroxyl, and lactone groups	42,341b
	H ₂ O + CO (46)		carboxyl group	42
[M - H] ⁻	CH ₃ [•] (15)		aromatic methoxy group	381
	H ₂ O (18)		hydroxyl, epoxy, keto, aldehyde, and carboxyl groups	208,341b,382
	H ₂ CO (30)		hydroxymethyl group	341d,382
	NO (30)		aromatic nitro group	381
	CH ₃ [•] + OH [•] (32)		1,2-methyl and hydroxyl groups	42,382
	C ₂ H ₂ O (42)		acetyl group	382
	CO ₂ (44)		carboxyl and lactone groups	42,208,341b
	C ₂ H ₄ O (44)		1-hydroxyethyl group	383
	HNO ₂ (47)		aliphatic nitrate group	339d
		NO ₂ ⁻ (46)	aromatic nitrate group	384
			carboxymethyl group	382
	C ₂ H ₂ O ₂ (58)		acetate group	42
	CH ₃ COOH (60)		two carboxyl groups	42,341b
	CO ₂ + H ₂ O (62)		aliphatic nitrate group	338,339d,341d
	HNO ₃ (63)		1,2-methyl and nitrate groups	338,341d
	CH ₃ [•] + ONO ₂ [•] (77)		sulfate group	339d,341d,345,383
	SO ₃ (80)	HSO ₄ ⁻ (97) HSO ₃ ⁻ (81)	1,2-sulfate and nitrate groups	339d,341d
		O ₂ N-OSO ₃ ⁻ (142)		

^aAcronyms: See list of abbreviations.

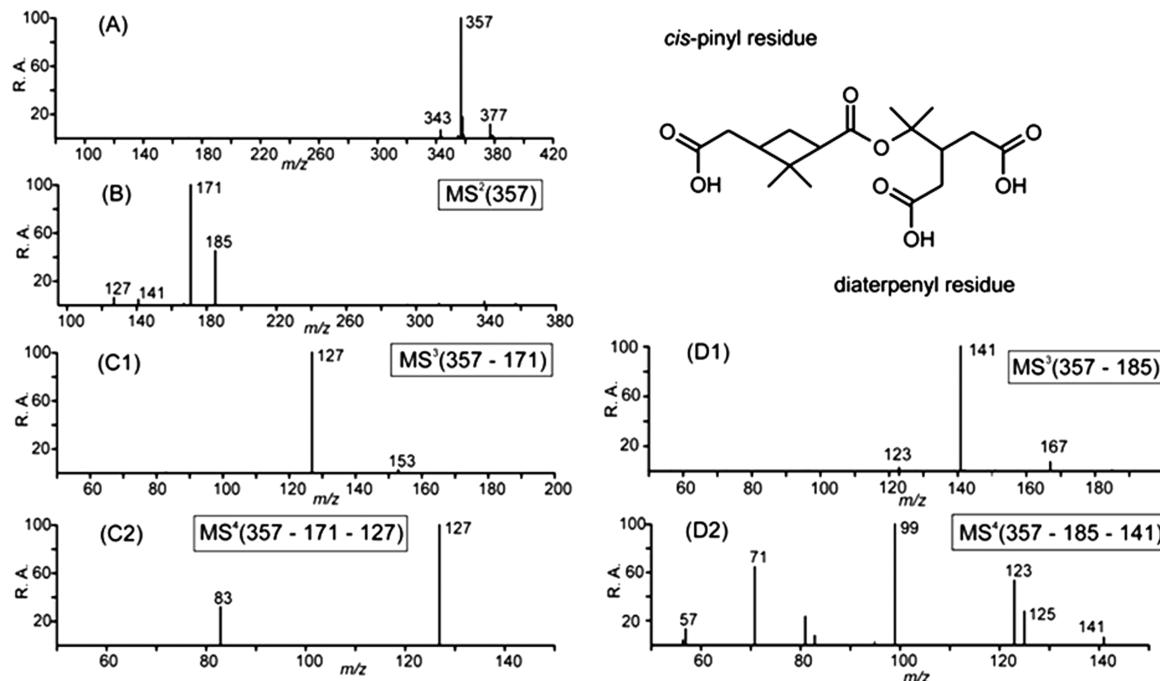


Figure 8. (–)ESI-ion trap MS data for a prominent high-MW 358 dimer present in α -pinene ozonolysis SOA, assigned to a pinyl diaterpenyl ester: (A) first-order mass spectrum; (B) m/z 357 MS^2 spectrum; (C1 and C2) m/z 357 \rightarrow m/z 171 MS^n ($n = 3, 4$) spectra; and (D1 and D2) m/z 357 \rightarrow m/z 185 MS^n ($n = 3, 4$) spectra. The MS^n data obtained by fragmentation of m/z 171 establish that diaterpenylic acid is a monomeric unit, whereas those obtained by fragmentation of m/z 185 identify *cis*-pinic acid as a second monomeric unit, because exactly the same MS patterns are found by fragmenting deprotonated terpenylic and *cis*-pinic acids. Adapted from ref 43.

combined for a large number of ESI–HRMS and AMS ambient data from various sampling locations,³⁶⁹ leading to a relationship between different aerosol classes and OS_C . For instance, semivolatile (SV) and low-volatility (LV) OOA produced by multistep oxidation reactions have OS_C values between –1 and +1 with 13 or less carbon atoms (n_C). OOA and HULIS lie between the large, reduced species ($n_C \geq 5$, OS_C , –1) and the oxidative end point CO_2 . Biomass burning organic aerosol (BBOA) corresponding to primary particulate matter have OS_C between –1.5 and 0 with 7–21 carbon atoms. HOA has lower $OS_C < -1.5$ and higher $n_C > 19$ atoms as compared to BBOA.

Thus, UHRMS offers new possibilities to characterize the complexity of atmospheric organic samples due to its ability to assign molecular formulas to the majority of the peaks measured in the sample. However, to achieve levels of unambiguous identification (i.e., I -factor of 1–2), a coupling to a chromatographic technique, such LC, is needed.

4.2.3.7. Tandem Mass Spectrometry. Tandem mass spectrometry (MS/MS or MS^n) is widely applied to obtain structural and sequence information about organic molecules. A tutorial review of these techniques is given by ref 371. The technique is used to produce structural information about a compound by fragmenting its molecular ion inside the mass spectrometer and identifying the resulting product ions. This information can then be assembled to reconstruct the structure of the initial molecule. Tandem mass spectrometry also enables the detection of specific compounds in complex mixtures on account of their specific and characteristic fragmentation patterns. Four different types of tandem MS experiments are possible depending on the instrumentation available, that is, product ion scanning, precursor ion scanning, constant neutral loss scanning, and selected/multiple reaction monitoring. Of these, product ion scanning offers the highest level of molecular

identification, especially if used in combination with a chromatographic technique such as LC and if an authentic standard is available. In the latter case, unambiguous identification of an organic compound can be achieved ($I = 1$).

Product ion scanning is particularly useful for providing structural information on small organic molecules ($MW < 300$) such as terpenoic acids formed upon photooxidation or ozonolysis of terpenes. The structural information includes characteristic product ions as well as neutral losses, providing not only information about functional groups but also on other structural features such as locations of functional groups. An overview of specific product ions and neutral losses that are useful for characterization of SOA products, and selected references, is provided in Table 6. As most SOA products are acidic (i.e., containing one or more carboxyl groups, a nitrate, a sulfate, a phenol, or a catechol group), Table 6 mainly contains data for product ions formed by fragmentation of deprotonated molecules. Product ion spectra have also proven to be useful to derive structural information on the monomeric units of high-MW covalent dimers and oligomers.^{43,338,372–377} Figure 8 illustrates how ion trap MS^n ($n = 2, 3$, and 4) data have been used to elucidate the structure of a prominent high-MW 358 dimer as a pinyl diaterpenyl ester, which is formed upon ozonolysis of α - and β -pinene and is also detected in ambient fine aerosol from forested environments.^{43,364,378–380}

Furthermore, accurate mass data can be obtained not only for precursor ions but also for their product ions with high-resolution FTICR, Orbitrap, and Q-TOF instrumentation.^{238,341d,356,375,376,385} Precursor ion and neutral loss scanning have also been used occasionally for screening complex atmospheric aerosol samples. Precursor ion scanning has been applied to monitoring groups of compounds, which fragment to common product ions, for example, nitro-aromatic

compounds resulting in m/z 46 (NO_2^-).^{384,386} Constant neutral loss scanning has been used to monitor carboxylic acids in positive ion APCI after conversion to methyl esters, which result in loss of methanol (32 Da),³⁸⁷ and nitro-aromatic compounds in negative ion APCI, which result in loss of NO (30 Da).³⁸⁴

Selected/multiple reaction monitoring is particularly useful to confirm unambiguously both the presence and the identity of compounds in atmospheric samples, for example, the detection of carboxylic acids²¹¹ and of nitro-aromatic marker compounds that are specific to biomass burning.³⁸⁸ This scanning mode is not only highly specific but also highly sensitive. Unlike for the other tandem MS experiments, the targeted analyte must be known and have been well characterized previously before this type of experiment is performed.

Thus, tandem MS techniques used in combination with LC are very advanced analytical tools for both the detection and the detailed mass spectrometric characterization of organic compounds in complex atmospheric samples.

5. CURRENT CHALLENGES INVOLVING ATMOSPHERIC ORGANIC COMPOUNDS

This last section presents specific topics in atmospheric chemistry where organic compounds are essential and important questions remain to be elucidated. The objective is both to provide examples of applications of the techniques presented above to the identification of organic compounds in different contexts and to identify some possible future applications or developments.

5.1. Secondary Organic Aerosols

This section focuses on secondary organic aerosols (SOAs), which are expected to have a large contribution to ambient aerosols, air quality and pollution, climate, and the biogeochemical cycles. Section 5.1.1 presents the main definitions and challenges linked to this subject. Section 5.1.2 presents the main approach to determine atmospheric SOA mass from condensable precursors (source apportionment) and summarizes the other processes expected to contribute to SOA formation and aging (condensed-phase reactions). Section 5.1.3 focuses on the molecular markers for biogenic SOA. Finally, section 5.1.4 provides some future directions on the molecular characterization of SOA.

5.1.1. Terminology and Background. The terminology associated with atmospheric organic aerosol is not coherent and often leads to confusion, inconsistency, and misunderstanding.³⁸⁹ SOA is defined as liquid or solid particles created in the atmosphere by the transformations of organic gases.³⁹⁰ These transformations can include gas-phase oxidation followed by condensation on pre-existing atmospheric particles and/or condensed-phase reactions in or at the surface of pre-existing particles (aerosols or cloud droplets).^{390b} By contrast, primary organic material or primary organic aerosol (POA) is condensed-phase organic material emitted directly from non-atmospheric sources. Because these definitions are based on processes rather than on properties of the organic compounds, they make it challenging to differentiate primary from secondary organic compounds directly in atmospheric aerosols. For this reason, most of the current knowledge on SOA, including their formation mechanisms, markers, or contributing multiphase reactions, is based on laboratory or smog chamber experiments and introduce many unknowns and uncertainties when extrapolated to the atmosphere. In addition, because the

above definition of SOA potentially includes various formation processes, it can lead to many different practical descriptions of atmospheric SOA and of their corresponding mass, markers, and properties. Therefore, the main challenges concerning atmospheric SOA today relate to its identification and quantification, and are illustrated by the large discrepancies between modeled and measured atmospheric SOA mass debated for nearly a decade. More recent studies have also started to tackle other challenges, such as the characterization of other SOA properties: overall composition (O/C and H/C ratios...), optical properties, and cloud-forming properties.

The first practical description of SOA was entirely based on the smog chamber investigations of the gas-phase oxidation of various precursors in the presence of inorganic seeds, and led in the mid-1990s³⁹¹ to the first SOA formation model: the gas-to-particle partitioning theory.³⁹² This theory, which is still today the most widely used in atmospheric models, is based on the thermodynamic equilibrium of condensable organic compounds between the gas and the particulate phase. Initially, only limited classes of gas precursors were identified by the experiments, terpenes and aromatic compounds. Their oxidation products, to which those of isoprene were later added, thus provided the first markers for SOA and the first method to quantify them in the atmosphere by source apportionment studies (see next section).

The development and applications of the Aerodyne AMS (section 4.1.2.3) in the 2000s led to other practical descriptions of SOA and different markers, which were also validated by smog chamber experiments. SOA were assimilated to the low- and semivolatile oxygenated organic fractions LV-OOA and SV-OOA, respectively, corresponding to different stages of aging.¹⁴³ Their markers are the fragmentation patterns obtained with the same instrument for smog chamber SOA. Statistical tools such as PMF, CMB, or their combination thus allowed the quantification of atmospheric SOA with this instrument with high time resolution.¹⁴⁷

However, while atmospheric models estimated SOA to represent a large, sometimes dominant, fraction of the atmospheric organic particles mass,^{385,393,394} it became evident in the 2000s that they still underestimated this mass by several orders of magnitude.³⁹⁴ A new SOA formation model was proposed to account for this missing mass: the volatility basis set (VBS).³⁹⁵ It consists of widening the range of precursors taken into account in the gas-to-particle partitioning to all semivolatile compounds. This introduced a somewhat different practical description of SOA, represented by semivolatile markers. The adequacy of this model was demonstrated with the SOA produced by the Deepwater Horizon spill, which was mostly accounted for by the contribution of semivolatile compounds.³⁹⁶

Implementing the VBS in atmospheric models succeeded in reducing some of the discrepancies between predicted SOA masses and observations, but was not sufficient in some cases, for instance, for above Europe with the EMEP model.³⁹⁷ A number of directions are currently being explored to account for these remaining differences. Recent works, using the gas-phase oxidation of α -pinene as an example, indicated the important contribution of extremely low-volatility oxidation products (ELVOCs) to SOA mass, currently not taken into account in models.³⁹⁸ In addition, over the past decade, several classes of condensed-phase reactions were identified as likely to contribute to SOA mass and properties (see next section). But

they are still under investigation and their applications to atmospheric models so far limited.

Organic identification has been key in all these developments and in most of the progress accomplished in the understanding of SOA over the past three decades. It will continue to be key in elucidating the remaining unknowns in this topic.

5.1.2. Source Apportionment and Condensed-Phase Processes.

As explained above, the main criterion used so far to evaluate our understanding of atmospheric SOA has been the comparison between their modeled and measured masses. Only recently have other criteria started to be considered, such as their average elemental composition (ratios O/C, H/C,...),^{143,399} now accessible with HRMS instruments such as the AMS or LC/HRMS. This section presents the main approach to estimate the atmospheric SOA mass resulting from condensable precursors, source apportionment, and summarizes the other processes currently expected to contribute to SOA mass and properties.

5.1.2.1. Source Apportionment for Condensable Precursors.

SOA precursors include VOCs emitted by biogenic (terrestrial and marine ecosystems) and anthropogenic sources (biomass burning, fossil fuel combustion). Globally, the biogenic precursors dominate, isoprene corresponding to the main one.⁴⁰⁰ Other biogenic and anthropogenic hydrocarbons such as oxygenated biogenic compounds (1,3-butadiene, and 2-methyl-3-butene-2-ol),^{3,401} terpenes, sesquiterpenes, and aromatics also contribute, but to a smaller extent. At local or regional scale, however, these precursors can have a significant contribution to SOA mass. Another potential source of SOA is the oxidation of evaporated POA vapors.^{395b} The nonvolatile POA from diesel exhaust and biomass burning is known to include low-volatility compounds that partition between the gas and aerosol phase. These compounds can then undergo gas-phase oxidation to form species of different volatilities that form SOA.^{395b,402}

The identification of SOA markers in smog chamber experiments made possible the investigation of the contribution of specific precursors to atmospheric SOA.^{401a,b,403} However, while unique chemical markers are available for primary sources such as motor vehicle exhaust, wood combustion, coal combustion, meat cooking, and tobacco smoke,^{390b} the construction of unique chemical profiles for SOA requires complex source apportionment models. Recently, several such SOA source apportionment studies have been conducted to assess the impact of SOA in global, regional, and local air quality, including a SOA molecular marker method⁴⁰⁴ and the use of SOA molecular markers in CMB and other receptor models,⁴⁰⁵ and for studying SOA gas-to-particle partitioning compounds,⁴⁰⁶ OA aging/gas-to-particle partitioning of semi-volatile VOCs in source apportionment models (CMB and PMF),⁴⁰⁷ and reactions contributing to ambient OA.³⁷⁹

Source apportionment in time-resolution of minutes can be achieved with the AMS technique, while classical filter collection techniques provide the same information with a frequency of about a day. Using the AMS, SOA is quantified with statistical tools such as PMF, CMB, or their combination.^{143,147} These approaches require a prior classification of SOA precursor types from individual sources, as illustrated with 17 compounds for the determination of atmospheric SOA from isoprene, monoterpenes, β -caryophyllene, and aromatics.⁴⁰⁸ However, because the quantification of these individual sources relies on laboratory studies and may vary considerably with the experimental conditions, this approach is to be applied to

ambient SOA with caution. The combination of AMS and ^{14}C analysis enables a more reliable source apportionment for fossil versus nonfossil precursors for OOA, as the ^{14}C analysis is quantitative and independent of emission factors or potential chemical transformations in the SOA. This approach was illustrated by the apportionment of a major fraction of nonfossil sources to total OOA in Zurich, and to LV-OOA, and a smaller fraction to SV-OOA, respectively, in Los Angeles.^{201c,409}

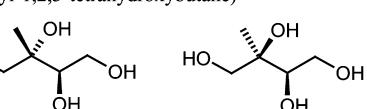
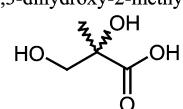
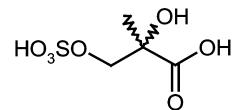
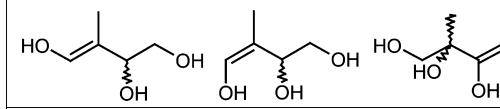
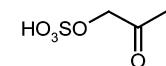
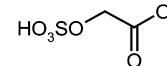
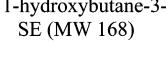
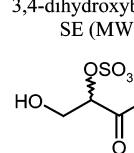
5.1.2.2. Condensed-Phase Reactions Contributing to SOA.

Since the beginning of the 2000s, evidence has accumulated that condensed-phase reactions contribute to SOA formation and aging. Some evidence was obtained from atmospheric observations and other from laboratory studies. The first type of evidence is the identification of compounds clearly resulting from condensed-phase reactions in ambient aerosols. Some of the first and most important examples were the 2-methyltetrosols,⁵ which were found in a wide range of atmospheric aerosols and identified as products of isoprene. However, their hydroxyl functional groups clearly indicated another origin than gas-phase oxidation alone, as the latter produces essentially carbonyl or acid groups. These compounds were proposed to result from the liquid-phase hydrolysis^{346b,410} of the gas-phase epoxydiols¹¹⁷ produced in the low-NO_x ($\text{NO}_x = \text{NO} + \text{NO}_2$) atmospheric oxidation of isoprene. The reactive uptake of these epoxydiols on acidic sulfate aerosols was also demonstrated to contribute to SOA mass.^{346b,410a,411} Another important class of compounds found in ambient aerosols and clearly resulting from condensed-phase reactions are organosulfates. As explained in section 4.2.3, their ubiquity and abundance in atmospheric aerosols⁴¹² was mostly revealed by LC/MS techniques.^{339c,345} Their organic structures indicated that they resulted from biogenic precursors, which had undergone secondary reactions in sulfate-containing aerosols. Laboratory and smog chamber investigations have shown that these compounds were produced by the gas-phase oxidation of isoprene and terpenes followed by the reaction of the epoxy-containing products with sulfuric acid in acidic sulfate aerosols,^{31,207,339d,341c,344b,346} thus providing a plausible formation pathway in the atmosphere. Radical mechanisms, in particular involving the sulfate radical, were also shown to produce the same compounds but at neutral pH.⁴¹³ The exact mechanism accounting for the large concentrations of organosulfates in ambient aerosols still remains to be determined.⁴¹²

Other types of atmospheric observations indicating the contribution of condensed-phase reactions to SOA consist of mass or chemical budgets. An example was the unexpectedly low gas-phase concentration of glyoxal in the MCMA-2003 campaign in Mexico City, matching an unaccounted SOA mass, and indicating the formation of SOA by condensed-phase reactions of this precursor.⁴¹⁴ The role of glyoxal as SOA precursor has been, since then, largely confirmed by laboratory and smog chamber^{28,415} and is still under investigation (see below).

Substantial evidence that condensed-phase reactions contribute to SOA has also been obtained from laboratory and smog chamber investigations. Toward the end of the 1990s, the ionic reactions of organic compounds in atmospheric aerosols, thus in the dark but in the presence of catalysts, started to be explored.⁴¹⁶ The importance of acid catalysis for C–C bond-forming reactions such as aldol condensation,^{416,417} and C–O–C bond-forming reactions such as acetal and oligomer formation,⁴¹⁸ was studied first. These reactions received ample attention as they were shown for the first time to have

Table 7. Overview of Isoprene SOA Markers Reported in the Period 2004–2009 and Since 2009, and Selected References on Their Structural Characterization^a

Chemical structure and name (MW)	Selected references
<i>Markers reported in the period 2004–2009 [for a more complete compilation, see Hallquist et al.^{39b}]</i>	
2-methyltetrols (MW 136) (2-methyl-1,2,3-tetrahydroxybutane)	⁵ Claeys et al. (2004) ⁴³¹ Wang et al. (2004) ³³⁸ Surratt et al. (2006)
	
2-methylthreitol (2R,3R) + 2S,3R isomer	2-methylerythritol (2S,3R) + 2R,3S isomer
2-methyltetrol derivatives 2-methyltetrol organosulfates (MW 216) 2-methyltetrol nitrooxy organosulfates (MW 261) 2-methyltetrol dinitrooxy organosulfates (MW 306)	²⁰⁷ Surratt et al. (2007) ^{341d} Gomez-Gonzalez et al. (2008) ^{339d} Surratt et al. (2008)
	³⁰ Claeys et al. (2004) ³³⁸ Surratt et al. (2006) ⁴³² Szmigelski et al. (2007)
2-methylglyceric acid SE (MW 200)	^{341d} Gomez-Gonzalez et al. (2008)
	
C ₅ -alkene triols (MW 118)	²³² Wang et al. (2005) ³³⁸ Surratt et al. (2006)
	
<i>Novel markers reported since 2009</i>	
polar organosulfates related to methacrolein or methyl vinyl ketone	
hydroxyacetone SE (MW 154)	^{77a} Olson et al. (2011) ^{413d} Schindelka et al. (2013) ³⁸³ Shalamzari et al. (2013)
	
glycolic acid SE (MW 156)	
	
1-hydroxybutane-3-one SE (MW 168)	3,4-dihydroxybutan-2-one SE (MW 184)
	
<i>cis</i> - and <i>trans</i> -3-methyltetrahydrofuran-3,4-diols (MW 118)	³⁶ Zhang et al. (2012)
	

^aAbbreviation: sulfate ester, SE.

large contributions to SOA mass.⁴¹⁹ This contribution was due to the very large apparent Henry's law constant of the precursors in acidic media, itself resulting from their equilibrium with their many dissolved forms (protonated, enols, etc.).^{417b,d} However, such large Henry's law constants and significant reaction rates were only achieved for very large acid concentrations (>50% wt H₂SO₄ ~7 M of H⁺). Thus,

while efficient to produce SOA in smog chamber, these acid-catalyzed processes were concluded to be negligible in tropospheric aerosols. This prompted the investigation of other catalysts enabling the same reactions at neutral pH and other typical tropospheric conditions. Iminium catalysis met these criteria, and was first illustrated with amino acids,⁴²⁰ then shown for the first time with inorganic ammonium ions,

NH_4^+ ^{420a,421} one of the most abundant components of tropospheric aerosols. However, unlike with acid catalysis, the uptake of many precursors on neutral ammonium-containing seeds does not contribute significantly to SOA mass.^{415a} Notable exceptions are, however, glyoxal, and to a lesser extent methylglyoxal, for which the formation of SOA on neutral ammonium seeds in the dark^{28,415,422} and the uptake on amino-acid-containing solutions⁴²³ have been demonstrated. In addition to the catalytic channels, the reactions of carbonyl compounds with $\text{NH}_4^+/\text{NH}_3$ involve noncatalytic condensation channels producing C–N compounds strongly absorbing light in the UV–vis region. Thus, the formation of imidazoles absorbing up to 300 nm in the SOA produced by glyoxal and ammonium sulfate seeds^{47,75a,415b} or in amino-acid or amine-containing media⁴²⁴ was reported. More recently, the condensation of a keto-aldehyde from limonene in ammonium salt solutions was shown to produce compounds absorbing near 500 nm.^{75b,83,424d,425} Such condensation reactions in ammonium salts are important for the formation of brown carbon and the optical properties of SOA, and are also discussed in section 5.3.

Condensed-phase reactions other than ionic ones have also been reported from SOA smog chamber experiments, such as those producing oligomers, which were identified using matrix-assisted laser desorption ionization and ESI mass spectrometry.⁴²⁶ These reactions seem to have radical mechanisms, similar to those taking place in more diluted, aqueous media. Note that it is important to distinguish between “aqueous-phase” conditions,⁴²⁷ which are typical of cloudwater and in which the solute is in small concentrations (<0.1 M), from condensed-phase conditions, typical of aerosols, where inorganic salts and other compounds are at much larger concentrations ($\gg 1$ M) and water molecules are minor.

Finally, the role of light-induced condensed-phase reactions to SOA has also been evidenced. For instance, glyoxal was shown to produce much more SOA mass in the light than in the dark.²⁸ These light-induced processes have been recently proposed to result from photosensitized reactions, where some imidazoles produced by glyoxal act as efficient photosensitizers.⁴²⁸

All of these condensed-phase reactions are still under investigation, but the contribution of some of them to SOA in the atmosphere has started to be evaluated by atmospheric models. This is, in particular, the case for the reactions of glyoxal,³⁹⁹ which were found to have a significant impact on the average O/C ratio of the SOA.³⁹⁹ The evaluation of the role of these reactions in atmospheric SOA would now require to identify some of their markers in atmospheric aerosols, such as the imidazoles from glyoxal or more complex condensation products with ammonium salts.

5.1.3. Molecular Markers for Biogenic SOA. This section focuses especially on molecular markers for biogenic SOA because biogenic VOCs are the dominant precursors for SOA⁴²⁹ and the molecular markers for anthropogenic SOA are rather well known,^{390b} except for biomass burning SOA markers, which have been more recently characterized (section 5.2).

The identification and quantification of specific molecular markers for SOA from different precursors are essential for the accurate assessment of their impacts in source apportionment studies. In addition, molecular speciation provides fundamental insights into SOA source processes, that is, the chemical reactions leading to their formation. Furthermore, molecular

markers can serve as a “clock” for measuring the OA aging state. Molecular speciation activities started in the late 1990s for monoterpene SOA,^{190,221,249,341a,372,430} but started much later for isoprene SOA, that is, after 2004 following the discovery of the 2-methyltetros.⁵ During the past two decades, substantial progress has been made with the structural elucidation (high identification level $I \leq 2$) of biogenic SOA markers. In this section, an update will be given for markers related to isoprene and α -pinene, and information for markers related to other selected BVOCs (i.e., β -pinene, *d*-limonene, Δ^3 -carene, β -caryophyllene, and 2-methyl-3-butene-2-ol) will be briefly presented.

5.1.3.1. Isoprene SOA Markers. A compilation of isoprene SOA markers and selected references about their structural characterization is given in Table 7.

In recent years, improved mechanistic insights have been obtained about the formation of isoprene markers under different experimental (smog chamber) conditions. As explained previously, the 2-methyltetros, their corresponding sulfate esters, and the C_5 -alkene triols are generated from the condensed-phase reactions of the C_5 -epoxydiols produced in the gas-phase photooxidation of isoprene under low- NO_x conditions.⁴¹¹ By contrast, 2-methylglyceric acid and its corresponding sulfate ester have been shown to require high- NO_x conditions and methacrylic acid epoxide, formed by decomposition of methacryloylperoxynitrate, as a gas-phase intermediate.³⁷ Insights have also been gained about the formation of the 2-methyltetros and corresponding sulfate esters under high- NO_x conditions, where the oxidation of isoprene with OH radicals partly results in the formation of organonitrates, which subsequently partition to the particle phase and can undergo a nucleophilic substitution with water or sulfate.^{77b,433} Isoprene SOA-related organosulfates that recently have been structurally elucidated and detected in ambient fine aerosol include sulfate esters of 3,4-dihydroxybutan-2-one, glycolic acid, 1-hydroxy-3-oxobutane, and hydroxyacetone.^{77a,383,413d,415b,434} As explained in the previous section, their formation, as well as the sulfate ester of 2-methylglyceric acid, has been explained by multiphase reactions involving either sulfuric acid or the sulfate radical anion.^{77a,413d,415b,434}

The isoprene SOA markers, the 2-methyltetros, the C_5 -alkene triols, and 2-methylglyceric acid have mainly been analyzed with GC/MS with prior trimethylsilylation,^{5,232,431} whereas LC/MS methods based on (−)ESI have been applied to the analysis of isoprene SOA-related organosulfates.^{207,339d,341d,383,413d,434} Because of their high polarity, C_{18} reversed-phase HPLC columns with polar retention have been employed, such as di- and trifunctionally bonded phases, which do not suffer from stationary phase collapse when a mobile phase is used with a high water content (>95%). In addition, ion-pairing reversed-phase LC/MS using dibutylammonium acetate as ion pairing reagent has been applied to polar isoprene-related organosulfates.⁴³⁵ Quantification of isoprene SOA markers (i.e., 2-methyltetros, C_5 -alkene triols, and 2-methylglyceric acid) has mainly been performed using GC/MS with prior trimethylsilylation.⁴³⁶ However, the developed methods have not been fully validated, mainly due to the lack of sufficiently pure authentic standards (>95%) for the 2-methyltetros and 2-methylglyceric acid, and the complete lack of authentic standards for the C_5 -alkene triols. With respect to the quantification of polar isoprene-related organosulfates such as 2-methyltetro and 2-methylglyceric acid sulfate esters, methods based on LC/(−)ESI–MS have been employ-

Table 8. Overview of α -Pinene SOA Markers Reported before and since 2007, and Selected References on Their Structural Characterization^a

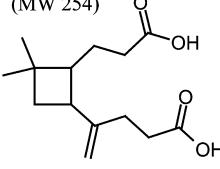
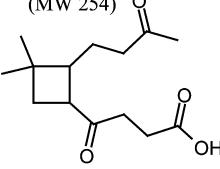
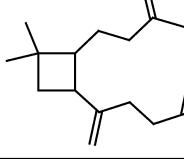
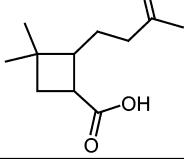
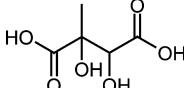
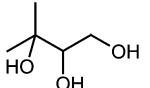
Chemical structure and name (MW)	Selected references
<i>Markers reported before 2007</i>	
<i>cis</i> -pinonic acid (MW 184)	³⁷² Hoffmann et al. (1998) ²²¹ Christoffersen et al. (1998) ²⁴⁹ Yu et al. (1999) ^{341b} Glasius et al. (1999) ^{341a} Larsen et al. (2001)
10-hydroxy- <i>cis</i> -pinonic acid (MW 200)	
<i>Markers reported since 2007</i>	
3-hydroxyglutaric acid (MW 148)	³⁴ Claeys et al. (2007)
3-methyl-1,2,3-butanetricarboxylic acid, MBTCA (MW 204)	³⁹ Szmigielski et al. (2007)
lactone-containing terpenoic acids and related marker	
<i>terpenylic acid</i> (MW 172)	⁴² Claeys et al. (2009)
terebic acid (MW 158)	²⁰⁸ Yasmeen et al. (2011)
diaterpenylic acid acetate (MW 232)	²¹⁹ Kahnt et al. (2014)
2-hydroxyterpenylic acid (MW 188)	
organosulfates and nitrooxy organosulfates	³¹ Surratt et al. (2007)
3-hydroxyglutaric acid SE (MW 228)	^{339d} Surratt et al. (2008)
hydroxypinonic acid SE (MW 280)	
2,3-dihydroxypinano nitrooxy organosulfates (MW 295)	
high-MW dimers	³⁷⁴ Müller et al. (2008)
pinylo-hydroxypinonyl ester (MW 368)	⁴³ Yasmeen et al. (2010)
pinylo-diaterpenyl ester (MW 358)	

^aOnly markers that are detected at substantial concentrations ($>10 \text{ pg m}^{-3}$) in ambient fine aerosol have been included. Abbreviation: sulfate ester, SE.

Table 9. Overview of SOA Markers Related to β -Pinene, Δ^3 -Carene, *d*-Limonene, β -Caryophyllene, and 2-Methyl-3-butene-2-ol, Useful for Molecular Speciation of Ambient Fine Aerosol, and Selected References on Their Structural Characterization^a

Chemical structure and name (MW)	Selected references
<i>Markers for β-pinene</i>	
<i>cis</i> -pinonic acid (MW 184) 	²⁴⁹ Yu et al. (1999) ¹⁹⁰ Glasius et al. (2000) ^{341a} Larsen et al. (2001) ²⁰⁸ Yasmeen et al. (2011) ^{344b} Iinuma et al (2007)
terpenylic acid (MW 172) 	terebic acid (MW 158)
10-hydroxy- <i>cis</i> -pinonic acid (MW 200) 	homoterpenylic acid (MW 186)
1,2-dihydroxypinane SE (MW 250) 	
<i>Markers for Δ^3-carene</i>	
<i>cis</i> -3-caronic acid (MW 184) 	<i>cis</i> -3-caric acid (MW 186)
10-hydroxy- <i>cis</i> -3-caronic acid (MW 200) 	terebic acid (MW 158) (see above)
<i>Markers for <i>d</i>-limonene</i>	
ketolimononic acid (MW 186) 	limonic acid (MW 186)
ketolimonic acid (MW 188) 	¹⁹⁰ Glasius et al. (2000) ^{341a} Larsen et al. (2001) ⁴⁴⁵ Jaoui et al. (2006) ^{339d} Surratt et al. (2008) ²⁰⁸ Yasmeen et al. (2011)
3-carboxyheptanoic acid (MW 204) 	
1,2-dihydroxy-4-acetylcyclohexane nitrooxy organosulfates (MW 298) 	+ positional isomer

Table 9. continued

Chemical structure and name (MW)	Selected references
<i>Markers for β-caryophyllene</i>	
β-caryophyllinic acid (MW 254) 	401 ^b Jaoui et al. (2007) 447 Winterhalter et al. (2009) 46 van Eijck et al. (2013)
β-nocaryophyllonic acid (MW 254) 	
β-caryophyllonic acid (MW 252) 	
	(MW 198) 
<i>Markers for 2-methyl-3-buten-2-ol</i>	
2-methylthreitol and 2-methylerythritol (see Table 7)	403 ^a Jaoui et al. (2012)
2,3-dihydroxyisopentenol (MW 120)	
2,3-dihydroxy-2-methylsuccinic acid (MW 164) 	
	

^aAbbreviation: sulfate ester, SE.

ed.^{436^b,437} Yet these methods have not been validated either and suffer from shortcomings such as the lack of authentic reference standards so that surrogate compounds need to be utilized.

An isoprene SOA marker that occupies a special position is methyl furan, first detected using the AMS technique and GC×GC/MS in a field campaign in the Borneo tropical forest.¹⁵¹ Methyl furan is not in itself present in the particles but is thought to be produced through the decomposition of isoprene epoxydiol-related SOA species such as 3-methyltetrahydrofuran-3,4-diols during the thermal desorption used in both techniques.⁴³⁸ It is a particularly useful marker because it produces a distinctive signal in the AMS mass spectrum at *m/z* 82, allowing source apportionment (section 4.1.2).

5.1.3.2. α-Pinene SOA Markers. A compilation of α-pinene SOA markers with selected references describing their structural characterization is given in Table 8.

Despite the fact that molecular speciation already started in the late 1990s, significant progress has only been made in the past decade with a more complete molecular speciation of α-pinene SOA and insights into their formation processes. A marker that has received particular attention is 3-methyl-1,2,3-butanetricarboxylic acid,³⁹ which is now established as a suitable marker for aged α-pinene SOA.⁴³⁹ For an account on the discovery of MBTCA, see ref 440. Other novel markers that have structurally been characterized include 3-hydroxyglutaric acid,³⁴ the lactone-containing terpenoic acids, terpenylic acid, terebic acid, 2-hydroxyterpenylic acid, 4-hydroxyterpenylic acid, and diaterpenylic acid acetate.^{42,441} Furthermore, high-MW dimers have received ample attention and have been structurally identified and detected in ambient fine aerosol with the two most prominent ones being diesters with MW 368

and 358.^{43,364,372,374,378–380} The MW 368 dimer was shown to consist of a pinyl and a hydroxypinonyl monomeric unit,³⁷⁴ while the MW 358 dimer was found to comprise a pinyl and a diaterpenyl residue.^{43,378} They were demonstrated to be formed through ozonolysis in the gas phase and not, as previously postulated, by acid-catalyzed esterification of monomeric terpenoic acids in the particle phase,⁴³ and were speculated to involve the participation of Criegee intermediates.³⁸⁰ The exact formation mechanism of high-MW dimers warrants further investigation as they are implied in new particle formation.^{372,380}

Organosulfates related to α-pinene detected in ambient fine aerosol include sulfate esters of 2- and 3-hydroxyglutaric acid, hydroxypinonic acid, and isomeric MW 295 nitrooxy organosulfates with a pinane diol skeleton.^{339^d} Monitoring of the latter nitrooxy organosulfates in field studies revealed that they are nighttime products,^{344^b,437} pointing to NO₃ radical chemistry. Furthermore, they have also been detected at substantial concentrations in wintertime ambient fine aerosol that is impacted by biomass burning.⁴⁴²

The α-pinene markers discussed above have been analyzed with LC/MS, mainly with ESI or APCI in the negative ion mode, using regular C₈^{344^b or C₁₈^{341^b,344^b,443} and trifunctionally bonded C₁₈ reversed-phase columns.^{42,43,208,441} Some markers such as terpenylic acid can be readily detected in the positive ion mode,⁴² while pinic acid, pinonic acid, hydroxypinonic acid, and MBTCA can also be analyzed with GC/MS with prior trimethylsilylation.^{39,249} However, valuable markers such as the lactone-containing terpenoic acids escape GC/MS detection and may undergo degradation during the derivatization procedure.⁴⁴¹ Therefore, LC/(-)ESI-MS is the technique of choice as it allows one to determine established markers such as}

pinic acid, pinonic acid, and hydroxypinonic acid, the novel markers, MBTCA, diaterpenylic acid acetate, and the lactone-containing terpenoic acids, as well as α -pinene-related organosulfates. Quantification of terpenoic acids has been achieved using GC/MS with prior derivatization,^{204,444} and more recently with LC/MS based methods.^{50,341d,379,443} As for the quantification of isoprene SOA markers, also most methods have not been validated or only partially, again due to the lack of sufficiently pure reference standards or the complete lack of them. Despite these shortcomings, the methods have been found to be adequate for determining diel variations and time trends of SOA markers in field monitoring studies.

5.1.3.3. Other Biogenic SOA Markers. Table 9 provides a list of markers that are related to biogenic SOA other than isoprene and α -pinene SOA and are due to minor monoterpenes (i.e., β -pinene, *d*-limonene, and Δ^3 -carene), β -caryophyllene, a sesquiterpene,^{46,208,249,341a,401b,445} and 2-methyl-3-butene-2-ol,^{347b,403a,446} and have been detected in ambient fine aerosol at substantial concentrations ($>10 \text{ pg m}^{-3}$).^{46,341d,443} With regard to β -pinene, it is worth noting that several markers for α -pinene SOA are also markers for β -pinene, that is, pinic acid, pinonic acid, terpenylic acid, and terebic acid, whereas homoterpenylic acid, a lactone-containing terpenoic acid, is a unique marker that has recently been reported.²⁰⁸ For the analysis of the markers listed in Table 9, the same methodology as discussed above for α -pinene SOA markers can be applied.

5.1.4. Future Directions in the Investigation of SOA. As emphasized in this section, the identification, quantification, and other characterization of atmospheric SOA involve many challenges. Many of the difficulties and controversies in characterizing atmospheric SOA result from their unspecific and process-based definition. It is thus time for the atmospheric community to propose more specific definitions, better adapted to the current understanding of these aerosols and the current instrumental capacities. For instance, these new definitions could make a distinction between the SOA obtained from condensation and those obtained from surface- or condensed-phase reactions. Important progress has however been achieved over the past three decades, where organic identification has played a key role. The SOA originating from major (isoprene and α -pinene) and other BVOCs (e.g., β -pinene, Δ^3 -carene, *d*-limonene, and β -caryophyllene) is now well characterized at the molecular level, and suitable markers for source apportionment and field monitoring are available. Yet the SOA produced by oxygenated BVOCs, such as the C₆ green leaf volatiles, emitted by wounded or insect-infested plants, is largely unexplored despite the evidence that they are a source for SOA.^{341d,448} Methods for the quantitative determination of SOA markers using GC/MS with prior derivatization or LC/MS are still only partially validated and could benefit from interlaboratory comparisons. In addition, laboratories involved in molecular speciation would welcome the availability of mass spectral libraries so that SOA markers could more readily be identified, without requiring authentic standards.

A new direction of research, which has developed over the past decade, is the investigation of the condensed-phase reactions contributing to SOA mass, composition, and properties. An important future direction of investigation could be the reactions in neutral ammonium seeds because of the prominence of this material in tropospheric aerosols. Other important directions of research in the near future will be the characterization of important SOA properties such as their O/C and H/C ratios, optical properties (section 5.3), and cloud-

forming properties (section 5.4). Organic identification will continue to be key in exploring all these questions.

5.2. Biomass Burning Aerosols

5.2.1. Background. Biomass burning aerosols originate from anthropogenic and natural combustion such as wild fires, agricultural fires, deforestation fires, and residential biomass combustion for cooking and heating. Carbonaceous aerosols from biomass burning are of scientific and public interest because of their occurrence in local, regional, and global environments as well as their impact on human health, air quality, visibility, and climate. Globally, biomass burning is one of the major sources of primary organic aerosols, light-absorbing carbon (brown and black carbon, see section 5.3),⁴⁴⁹ and probably also of SOA.⁴⁵⁰ It has been shown to have adverse health effects such as respiratory diseases.⁴⁵¹ In low- and middle-income countries, the indoor combustion of solid fuels (including biomass) is estimated to cause about 2 million deaths annually.^{451b} Even in high-income countries biomass burning for residential heating has detrimental effects on human health,^{451a,452} although further investigations are warranted to constrain its local and regional impact. Biomass burning aerosols can contribute to the climate budget directly, that is, through its light-absorbing carbon component (section 5.3), but also indirectly by affecting the formation or optical properties of clouds (section 5.6).^{449a}

The main challenges concerning biomass burning are to determine its sources and impacts on regional and local air quality. This is achieved by “source apportionment” approaches, which are based on the identification and quantification of specific molecular markers, such as anhydromonosaccharides (levoglucosan, mannosan, and galactosan) formed by the pyrolysis of cellulose and hemicelluloses.⁴⁵³ Yet large uncertainties remain in these determinations, requiring more studies, in particular the identification of additional markers. The information about the impact of biomass burning on ambient air quality is especially important for a regulatory body to decide if biomass burning should be regulated or controlled. The characterization of markers in such varied and complex mixtures of organic compounds, including nonpolar hydrocarbons to very polar saccharidic compounds, is a showcase for the capability of analytical methods toward molecular identification.

5.2.2. Molecular Organic Markers. The chemical composition of the biomass and type of combustion sustained directly influence the physical and chemical properties of the resulting biomass burning aerosols. Different tree species develop markedly different woody constituents during growth, but all wood consists of various forms of lignin, cellulose, and fillers.⁴⁵⁴ At temperature below 300 °C reduction of MW, evolution of water, CO₂, and CO is observed. While at temperatures between 300–500 °C, the biopolymers rapidly undergo bond cleavage yielding monomeric compounds, at higher temperatures, wood molecules dehydrate, disproportionate, and decarboxylate giving rise to low-MW products.⁴⁵⁵ In the following section, we separate biomass burning marker compounds into nonpolar, polar, and SOA compounds on the basis of suitable analytical techniques for each compound group. As biomass burning aerosols contain a large number of organic compounds with a wide range of properties, it is important to choose a suitable analytical method for the accurate quantification of the marker compounds.

5.2.2.1. Nonpolar Marker Compounds. Nonpolar marker compounds in biomass burning smoke have been almost exclusively analyzed using GC/MS-based methods. These marker compounds are a wide array of low-MW organic compounds, which originate from extractives in biomass and constitute 4–10% dry mass of normal temperate wood species.⁴⁵⁴ The extractives contain fats and waxes, terpenoids, resins, essential oils, mono- and disaccharides, and monomeric phenolic compounds.⁴⁵⁶ They serve as metabolic intermediates, defense chemicals against predators, or energy reserves. During wood combustion, the extractives and their thermal degradation products are released by volatilization and steam-distillation. Some of the organic constituents in the extractives are unique to certain wood types and can be used as marker compounds for source identification of atmospheric aerosols.⁴⁵⁷

A group of nonpolar compounds present at elevated concentrations in wood-smoke emissions (but not specific to wood combustion) are *n*-alkanes, *n*-alkenes, *n*-alkanols, and *n*-alcanoic acids that originate from epicuticular waxes and lipids. *n*-Alkanes emitted from biomass burning show a distinctive odd to even carbon predominance (carbon preference index > 1), especially for higher carbon number homologues with a C_{\max} value between C₂₅ and C₃₁.^{457b,458} On the other hand, *n*-alkenes, *n*-alkanols, and *n*-alcanoic acids show predominantly even carbon preferences (carbon preference index < 1).^{458b–d,459} *n*-Alcanoic acids react with ammonia in biomass combustion processes, forming alkyl amides and alkyl nitriles,⁴⁶⁰ although little is known about the formation mechanisms and concentrations of the latter derivatives in wood smoke. While biomass burning markers originating from plant waxes and their alteration products are not source specific, they are typically found in particles smaller than 1 μm ,^{458b} whereas biologically emitted plant waxes are found mostly in particles larger than 1 μm .⁴⁶¹ Hence, the difference in their size distribution can be used as a fingerprint for the influence of wood smoke in ambient aerosols. *n*-Alkanes, *n*-alkenes, alkyl amides, and alkyl nitriles can be analyzed with GC/MS without prior derivatization steps. *n*-Alkanols and *n*-alcanoic acids are typically analyzed using GC/MS-based methods with a prior derivatization step, either the alkylation of carboxylic OH groups or the trimethylsilylation of all hydroxyl groups.^{457b}

Although polycyclic aromatic hydrocarbons are not unique marker compounds for wood combustion, their occurrence in wood smoke has been known for a long time,⁴⁶² and their identification and quantification in wood smoke has been considered important because of their potential impact on public health. Various analytical techniques have been applied to determine PAHs in ambient aerosol samples in the past, although GC/MS-based methods have been most widely used due to their good chromatographic separation and detector sensitivity. Their application to the analysis of PAHs in atmospheric samples has been reviewed very recently.⁴⁶³ Among PAHs detected in wood smoke, retene is considered to be a unique marker compound for coniferous wood combustion. This compound is suggested to form from thermal degradation of resins, most likely diterpenoids such as abietic acid in the conifer resins.⁴⁶⁴

Sample preparation procedures for the analysis of nonpolar biomass burning makers with GC/MS typically involve organic solvent extraction, clean up, and preconcentration steps prior to analysis. Alternatively, thermally assisted desorption systems such as a Curie-point pyrolyzer^{458b,465} and a variation of

custom-made or commercially available thermal desorbers^{261,262,466} may be used to inject collected aerosol samples directly into GC/MS systems. In comparison to a number of studies reporting their emission factors from combustion sources and concentrations in atmospheric samples, little is reported about artifact formation during sample workup procedures. Because of the extremely complex nature of biomass burning samples, the determination of recovery values for all of the compounds detected may be unrealistic. Nevertheless, reliable quantification of these marker compounds may still be possible when isotope-labeled authentic standard compounds are used as internal standards.

5.2.2.2. Polar Marker Compounds. There are several methods available to analyze polar marker compounds in biomass burning smoke. Traditionally, GC/MS with a prior derivatization step has been used for the characterization of polar marker compounds. Liquid-based separation techniques coupled to mass spectrometry have become more popular tools in recent years due to their simpler sample preparation procedures for the analysis of polar compounds.

Among polar marker compounds, the pyrolysis products of cellulose and hemicelluloses are the most important class of compounds in biomass burning smoke. Cellulose is a macromolecule consisting of several to ten thousand linearly linked D-glucopyranose units, whereas hemicelluloses are smaller macromolecules that contain different monosaccharidic (e.g., mannose and galactose residues) but mainly D-glucopyranose units. Cellulose and hemicelluloses provide a supporting mesh for wood structures and account for 30–40% of woody tissue.⁴⁵⁵ The major pyrolysis products of cellulose and hemicelluloses are anhydromonosaccharides, levoglucosan (1,6-anhydro- β -D-glucopyranose), galactosan (1,6-anhydro- β -D-galactopyranose), and mannosan (1,6-anhydro- β -D-mannopyranose), and they are widely used as biomass burning marker compounds because they are specific and emitted in considerable amounts.⁴⁵³

Another class of polar biomass burning marker compounds is the pyrolysis products of lignin. Lignin is an amorphous biopolymer synthesized by monolignols and accounts for 25–35% of the dry mass of softwood and 18–25% of hardwoods. Its function is to provide strength and rigidity to plant structures.^{455,467} Its pyrolysis produces mostly substituted phenols and substituted methoxyphenols with predominantly *p*-coumaryl alcohol derivatives from grass combustion, *p*-coniferyl alcohol derivatives from softwood combustion, and sinapyl alcohol derivatives from hardwood combustion. This difference may be used as an indicator for the influence of soft- or hardwood combustion in ambient aerosols.⁴⁶⁸

Among the extractives, resins and their thermal degradation products such as abietic acid, dehydroabietic acid, and oxo-dehydroabietic acids are often present in wood smoke influenced ambient aerosols.^{457b,c} These compounds are specific to the combustion of temperate coniferous trees, and can be considered as marker compounds for their combustion.

Because of the presence of polar functional groups in their structures, resin-related markers are best analyzed with GC/MS methods with prior derivatization such as trimethylsilylation.^{233,261,453c,457a,459,469} Alternatively, substituted phenols, substituted methoxyphenols, and abietic acid derivatives can be analyzed underivatized with liquid-based separation techniques coupled to mass spectrometry such as CE/MS^{458b} and LC/MS.^{442,470} In addition, anhydromonosaccharides can be analyzed with HPAEC coupled to a pulsed amperometric

detector (PAD),^{289,471} HPAEC coupled to a mass spectrometric detector,^{294,301} microchip CE coupled to a PAD,⁴⁷² and HPLC/ESI-MS.⁴⁷³ The liquid-based separation techniques have advantages over traditional GC/MS analysis with a prior derivatization step in that their sample preparation procedure is simpler and they enable the direct analysis of aqueous samples such as fog or cloud samples.⁴⁷⁴

Extraction and derivatization steps for GC/MS methods have been extensively characterized and optimized for anhydromonosaccharides^{233,469d,475} and methoxyphenols.⁴⁷⁶ For example, the evaporative loss of methoxyphenols during Teflon filter extraction with a mixture of methylene chloride/acetone under ultrasonication was found to be a significant problem,⁴⁷⁶ and then an extraction with ethyl acetate in a sealed headspace vial was chosen, which yielded a median recovery value of 97% for deuterium-labeled recovery standard compounds. For anhydromonosaccharides, the extraction recovery of levoglucosan was optimized using a dichloromethane/methanol mixture (80:20, v/v), yielding 90.0 ± 2.4 to $97.0 \pm 4.0\%$.⁴⁴⁶ A 99% recovery of anhydromonosaccharides was reported after two consecutive extraction steps from spiked quartz fiber filters with tetrahydrofuran as an extraction solvent for an HPLC/MS method.^{473a} A recovery of $95 \pm 3\%$ was reported for levoglucosan from spiked quartz fiber filters by two consecutive water extraction steps with short vortex agitation and gentle shaking.⁴⁷⁷ A nearly complete extraction of monoanhydrosaccharides from quartz fiber filters was also reported with water by ultrasonic agitation,^{289,471e} and by short vortex agitation and gentle shaking.³⁰¹

5.2.2.3. Biomass Burning SOA Marker Compounds. Until recently, little was known about the formation of SOA in biomass burning and its marker compounds. The formation of SOA in biomass burning smoke was suggested from the aqueous phase-reactions of lignin products such as phenol, guaiacol, and syringol in laboratory experiments.⁴⁷⁸ In these studies, HPLC-UV was used to follow the decay of the precursor compounds, and the product formation was assessed by HR-AMS. Similarly, the photochemical oxidation of wood smoke and changes in its chemical characters were investigated in a smog chamber.^{450,479} In these studies, changes in AMS mass fragments were used to identify the oxidation of primary aerosols and the formation of biomass burning SOA. Another chamber study investigated the formation of SOA from the gas-phase photooxidation of biomass burning marker compounds such as phenols and methoxy-phenols.⁴⁸⁰ In this study, the gas-phase oxidation products were detected using CI-MS with H_3O^+ as a reagent in the positive mode and CF_3O^- as a reagent in the negative mode, whereas UPLC/ESI-MS was used for the analysis of SOA compounds. On the basis of the results from these experiments, the authors cautioned that the use of guaiacol (softwood combustion marker) and syringol (hardwood combustion marker) may not be a suitable marker for atmospheric aerosol as syringol can efficiently form guaiacol and other hydroxylated aromatic compounds during the photooxidation.

Series of smog chamber experiments indicate that the oxidation in the presence of NO_x of *m*-cresol, which is largely emitted from wood combustion,⁴⁸¹ forms methyl-nitrocatechols.⁴⁸² In atmospheric aerosols, nitro-aromatic compounds have been reported to correlate very well with levoglucosan in wintertime and thus are suggested to be suitable molecular markers for biomass burning SOA.^{442,482} They were also found in the HULIS fraction of biomass burning-influenced aerosols

from Hungary and Brazil.³³⁶ In all of these studies, the identification of the nitro-aromatic compounds was achieved by comparing the LC retention times and MS fragmentation patterns of the compounds present in the atmospheric samples, those present in laboratory-generated aerosols, and authentic standards. Recently, the HPLC/ESI-MS/MS analysis of a series of nitro-aromatic compounds in ambient aerosols was improved^{381,388} by separating isobaric isomers, notably of methyl-nitrocatechols and nitro-guaiacol, by substituting acetonitrile with tetrahydrofuran in the LC eluent. The latter method also uses ethylenediaminetetraacetic acid to resolve the peak shape distortions of some nitro-aromatic compounds forming transition metal complexes.

5.2.3. Future Directions in the Investigation of Biomass Burning Aerosols. Over the past two decades, significant progress has been made in the identification and quantification of organic markers of biomass burning aerosols. Yet despite the large body of data obtained, little effort has been done to compare or standardize the different analytical procedures. In particular, as the determination of the concentrations of anhydromonosaccharides in ambient aerosols is becoming a routine analysis, reliable analytical procedures are urgently desirable. To address this need, an interlaboratory comparison for the determination of levoglucosan, mannosan, and galactosan in ambient filter samples has recently been organized (section 3.3).³⁷

Another area of uncertainty is the further oxidation of particle-bound biomass burning markers and their products in the atmosphere, which limits the accuracy in the contribution of biomass burning determined in source apportionment studies. Atmospheric stability has been only investigated for levoglucosan, the most abundant biomass burning marker.^{453b} Yet the results of solar radiation experiments and acid hydrolysis experiments^{469a,483} showing the stability of this compound have been recently contradicted by aqueous-phase⁴⁸⁴ and gas-phase⁴⁸⁵ oxidation experiments with OH radicals concluding a half-life of 3–4 days in wintertime deliquescence particles⁴⁸⁴ and of 0.7–2.2 days in the gas phase in summertime.⁴⁸⁵ Further studies of the oxidation of other biomass burning markers and their products are therefore warranted to improve the source apportionment of biomass burning.

In general, further laboratory, field, and remote-sensing studies are needed to constrain the emission factors, and spatial and temporal distributions of biomass burning marker compounds, SOA formation, and relevant physicochemical properties to obtain better estimates of the global and regional biomass burning emissions and of its contributions to air quality, public health, and climate.

5.3. Optically Active Compounds

This section focuses on another important class of organic compounds in the atmosphere: those displaying specific properties upon interaction with solar light. Solar radiation is the main source of energy in the Earth's atmosphere, and atmospheric components can interact with it in two ways: by absorbing or scattering it. This can give them different roles: a contribution to the Earth's radiative budget (either a warming or a cooling one), or a role as photochemical precursor in atmospheric chemistry. In particular, obtaining an accurate radiative budget depends on the ability to fully inventory all of the absorbing or scattering components present in the atmosphere. Identifying the organic compounds or classes of compounds taking part in these processes is therefore

important. This section summarizes the current knowledge of these compounds, their roles in the atmosphere, and discusses potential future areas of investigations.

5.3.1. Organic Compounds Contributing to the Direct Radiative Forcing. Both organic gases and particulate matter present in the atmosphere can contribute to the climate budget by absorbing or scattering light. Scattering by atmospheric gases (Rayleigh scattering) is generally not taken into account in atmospheric chemistry or the climate budget because it reflects light in all directions and does not affect the radiative balance. Thus, only organic gases absorbing light are discussed below. Atmospheric particles can either absorb solar energy and contribute to warm climate, or scatter it back to space (Mie scattering) and contribute to cool it. Until recently, organic aerosols were assumed to be mostly scattering (see discussion below); therefore, this subsection will focus on the more recent evidence for their light-absorbing properties (brown carbon).

5.3.1.1. Greenhouse Gases. As explained in section 4.1.1, all organic compounds absorb light in the IR region (wavelength, $\lambda > 800$ nm), where the energy is transferred into rotational and vibrational molecular motions and ultimately heat. Most of them also absorb in the near UV and visible region ($\lambda < 800$ nm) and transform some of the energy into heat, either directly or by recycling photochemical energy. Thus, these absorbing properties can have warming contributions to the radiative budget. However, only the gases absorbing at different wavelengths than important atmospheric constituents, in particular water vapor, effectively have a warming contribution and are called greenhouse gases (GHG). Organic GHGs include methane (CH_4), chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), and hydrochlorofluorocarbons (HCFCs).⁴⁸⁶ Their presence and abundance in the atmosphere is mostly inferred from chromatographic analyses (GC-FID or GC/MS) such as described in section 4.2.2. Despite the large number of atmospheric CFCs and HCFCs already known, several new ones have recently been identified by GC/MS.⁴⁸⁷ Thus, it cannot be excluded that more remain to be identified.

The contributions of the organic GHGs other than CH_4 to the global radiative budget are however modest.^{486b} All together, they represent less than 0.5 W m^{-2} , while CH_4 alone contributes for the same amount and CO_2 for about 1.8 W m^{-2} . The individual contributions represent only a few % of the total GHG forcing (in W m^{-2}): CFC-11, 0.06; CFC-12, 0.17; HCFC-22, 0.04; others, < 0.03 . The contribution of yet unknown organic GHGs is thus likely to be small, especially because the probability that their IR spectrum does not overlap with those of previously known GHGs is getting smaller with each new compound. Thus, the identification of new organic GHGs should not significantly modify the global radiative budget. Note, however, that besides GHGs, nearly all organic gases contribute to the global radiative forcing by producing O_3 , another important GHG, as a side-product of their oxidation in the presence of NO_x . Yet because these processes are not directly related to their optical properties, they are not discussed here. Some studies have estimated the radiative contribution of all organic gases at regional or local scale, but mostly in the UV-vis region: nitrated aromatic gases were thus estimated to account for about 1 W m^{-2} in the UV range in the Los Angeles basin, and total organic gases (29 compounds including carbonyls, organonitrates, peroxides, and phenols) to about twice as much.⁴⁸⁸ Identifying and inventorying the light-absorbing organic gases in some regions can thus be important when estimating the visibility and radiative balance.

5.3.1.2. Brown Carbon. For decades, “black carbon”, also termed “elemental carbon” or “light-absorbing carbon”, was the only carbonaceous material thought to absorb in this spectral region. The assumption that organic material does not absorb light is still largely made today, especially in climate models (see discussion below). However, evidence of the contrary has been accumulating for decades, facilitated by the clear contrast between the strong wavelength dependence of the spectrum of organic compounds and the nearly constant spectrum of black carbon.⁴⁸⁹ A strongly wavelength-dependent spectrum, revealing the presence of absorbing organic material in organically extracted fractions of ambient aerosols, was reported as early as the 1980s.⁴⁹⁰ This material was compared to humic substances and given the name of “brown carbon”. Organic fractions with similar wavelength-dependent spectra were subsequently identified from coal burning,⁴⁹¹ biomass burning,⁴⁹² and urban/road-side aerosols.⁴⁹³ This evidence, obtained by chemical analyses, was confirmed by very different approaches such as ground-based measurements of aerosol light-attenuation,⁴⁹⁴ irradiance,⁴⁹⁵ or sun photometer measurements, in particular with the AERONET network.⁴⁹⁶ These measurements evidenced not only similar wavelength dependences in the absorbance of ambient aerosols but clearly demonstrated that brown carbon affects their overall optical properties. Brown carbon seems therefore to be important to take into account when estimating the optical and radiative properties of aerosols. Taking into account brown carbon in the absorbance of ambient aerosols was also underlined as essential to correctly attribute the contributions of black and elemental carbon, the errors made otherwise being estimated to a factor 2–7.⁴⁸⁹ An emerging challenge in the determination of global or regional radiative budgets is therefore the identification of all types and sources of brown carbon. The different types of brown carbon identified so far are described below in sections 5.3.1.2.1 to 5.3.1.2.4.

5.3.1.2.1. Combustion and Biomass Burning Brown Carbon. The reader is referred to section 5.2 for details on the organic composition of biomass burning aerosols. Generally, their “optically active” components have been identified as polycyclic aromatic material such as PAHs and oxygenated PAHs,⁴⁸⁹ and nitro-aromatic compounds.²⁷⁶

5.3.1.2.2. HULIS. Some atmospheric aerosols have been found to contain light-absorbing fractions having properties similar to those of humic substances, and therefore are termed humic-like substances.^{336,345,490,497} However, since the definition of atmospheric HULIS is based on their extraction procedure,^{490,497a,b} it is difficult to assign them to a single compound class or source. HULIS are often linked to biomass burning aerosols,⁴⁹⁰ but have also been found in a wide range of atmospheric aerosols, including rural and remote ones.^{336,497a,b} Their smaller molecular mass (<400 Da) than terrestrial humic substances questions their similarities with the latter, and their sources have been suggested to be secondary rather than primary.^{497c} The analyses of HULIS report a complex chemical composition, which has remained an identification challenge for years. Increasingly sophisticated techniques, including electrospray ionization in combination with tandem and high-resolution mass spectrometry,^{336,497d,e,498} have been used to investigate their molecular structures and sources. They identified aromatic compounds, polysaccharides, and aliphatic compounds with polar groups such as hydroxyl, carboxy, carbonyl, nitrate, and sulfate among the components. More recent studies³³⁶ confirmed the small MW range of

atmospheric HULIS (<300 Da) and identified nitro-catechols as the main chromophores in urban and tropical biomass burning HULIS, while organic triacids and terpenic acids dominated rural ones. These results confirm the multiplicity of types and sources of atmospheric HULIS, and the challenge involved in determining their contributions to brown carbon.

5.3.1.2.3. Biogenic Primary Organic Matter and POA. Although the presence of biological material (plant debris, cellular debris, spores, pollen, bacteria, etc.) in the atmosphere has been known for a long time,⁴⁹⁹ it has mostly been discussed as an aerosol type (primary biological atmospheric particle, or PBAP) and much less at the molecular level. The biological molecules identified so far in aerosols include amino acids, proteins, sugars, polysaccharides, and fatty acids, which do not absorb in the UV-vis region. However, some PBAPs have been shown to absorb sunlight, and most of them are considered to be fluorescent (see below). The molecules responsible for the absorption have not been identified but could be related to strong biological UV-vis absorbers such as chlorophylls, carotenoids, and tannins. Yet the molecular structure and impact on the aerosol properties of this “biological brown carbon” remain largely to be investigated.

5.3.1.2.4. Secondary Organic Material. As discussed in the previous section, a number of condensed-phase reactions in SOA produce light-absorbing compounds, such as aldol condensation producing C=C conjugated compounds,^{415b,417c,g,420,421b,c,500} and the condensation of dicarbonyl (glyoxal, methylglyoxal) or larger carbonyl compounds with NH₄⁺/NH₃,^{75a,83,415b,424d,425,501b} amino acids and amines,⁴²⁴ all producing conjugated C=N compounds such as imidazoles. While C=C conjugated compounds and imidazoles display a main absorption band below 350 nm, a condensation product of limonene keto-aldehyde with NH₄⁺/NH₃ was recently reported to have a maximum absorbance near 500 nm, thus fully in the visible range.^{83,424d,425,501b} The molecular identification of such highly conjugated compounds is a challenge because, although they have intense absorption coefficients, they are produced in trace concentrations in complex mixtures. Nonetheless, structures were proposed for this and other compounds obtained under similar conditions from other SOA precursors, based on extraction and ESI-HR-MS analyses.⁵⁰² A main challenge in this field of research is now to identify such secondary brown carbon in ambient aerosols using similar types of analyses, identify and quantify their formation mechanisms, and determine their impacts on the optical and radiative properties of aerosols.

The contribution of brown carbon to the global radiative budget is currently not well taken into account in climate models. The 14 climate models taken into account in the latest IPCC report all included primary organic carbon and about half of them modules to simulate SOA formation.⁵⁰³ Although the modeling of SOA was underlined as an important improvement over previous IPCC reports, this effort was exclusively made on SOA microphysics (formation rates, mass loadings, size distribution), while their absorption indices, along with those of POA, were still based on non-peer-reviewed, pre-2000s estimates⁵⁰⁴ or submodule calculations⁵⁰⁵ and assumed to be negligible at all wavelengths. One exception is the HITRAN database,⁵⁰⁶ which includes more realistic optical properties for brown carbon. However, the proxy chosen for SOA are laboratory reactions with amines,^{424c} which are less representative of aerosol brown carbon than the products obtained with NH₄⁺/NH₃, but can be easily updated with the references cited

in this Review. Thus, adding SOA to the climate models in the 2013 IPCC exercise while still neglecting their absorbance merely introduced an additional scattering component in the radiative budget and resulted in a larger cooling contribution of aerosols than in previous reports.

A number of observations, however, support a significant warming contribution of brown carbon to the global aerosol forcing, such as the multiwavelength ground-based measurements of aerosol radiation showing a brown carbon contribution of 28% of the total light absorption at 440 nm in California,^{496a} applying the same method at global scale estimated the global contribution of brown carbon between 0.1 and 0.25 W m⁻² and changed the global contribution of aerosols from the current cooling one to a warming one (+0.025 W m⁻²).^{496b} These results underline the substantial errors made in current climate models by neglecting the absorbance of brown carbon, and the urgency to better identify the molecular structures of the different types of brown carbon and characterize their optical properties.

5.3.2. Light-Absorbing Compounds as Photochemical Precursors.

5.3.2.1. Gases. In addition to contributing to the climate budget, atmospheric organic compounds can act as precursors for chemical reactions. The absorption of sunlight by organic compounds in the UV or vis region triggers electronic transitions, and confers to organic compounds photochemical properties. These transitions often correspond to bond-altering processes such as photolysis or energy exchanges such as photosensitization or fluorescence, and often result in the formation of free radicals. Most of the organic gases absorbing in the UV-vis region (thus at $\lambda \geq 290$ nm) in the atmosphere photolyze and produce radicals. Table 10 summarizes the main

Table 10. UV–Vis Absorbing Organic Gases in the Atmosphere, with the Position of Their Absorption Band, Absorption Cross Sections, σ , and Photolysis Quantum Yield, Φ , at 290 nm

gas	λ_{max} (nm)	$\sigma(290 \text{ nm}) \times 10^{20}$ molecules cm ⁻²	$\Phi(290 \text{ nm})$	ref
HCHO	~ 305	1.2	1.0	507a
CH ₃ CHO	290	4.9	0.5	507a
CHOCHO	298	3.9	0.6	507a
CH ₃ (CO) CH ₃	274	4.9	0.4	507a
CH ₃ OOH	<210	0.7	1.0	507a
CH ₃ (CO) OH	205	<0.1		507b
CH ₃ OH	184	<0.01		507b
CH ₃ ONO ₂	190	0.9	1.0	507a
CH ₃ O ₂ NO ₂	<200	3.9	1.0	507a
CH ₃ (CO) ONO ₂	<200	0.5	1.0	507a
nitro-phenols	320–360			507d
naphthalene				
anthracene	312–365			

types of gases having these properties: aldehydes, dicarbonyls, ketones, peroxides, organo-nitrates, and some aromatic compounds such as nitro-phenols. Their importance as radical precursors depends on the product of their absorption cross section by their quantum yield, which are compared for the ground-level cutoff wavelength of 290 nm in Table 10.⁵⁰⁷

The importance of organic gases as sources for radicals, such as OH and HO₂ (HO_x), or other important compounds for

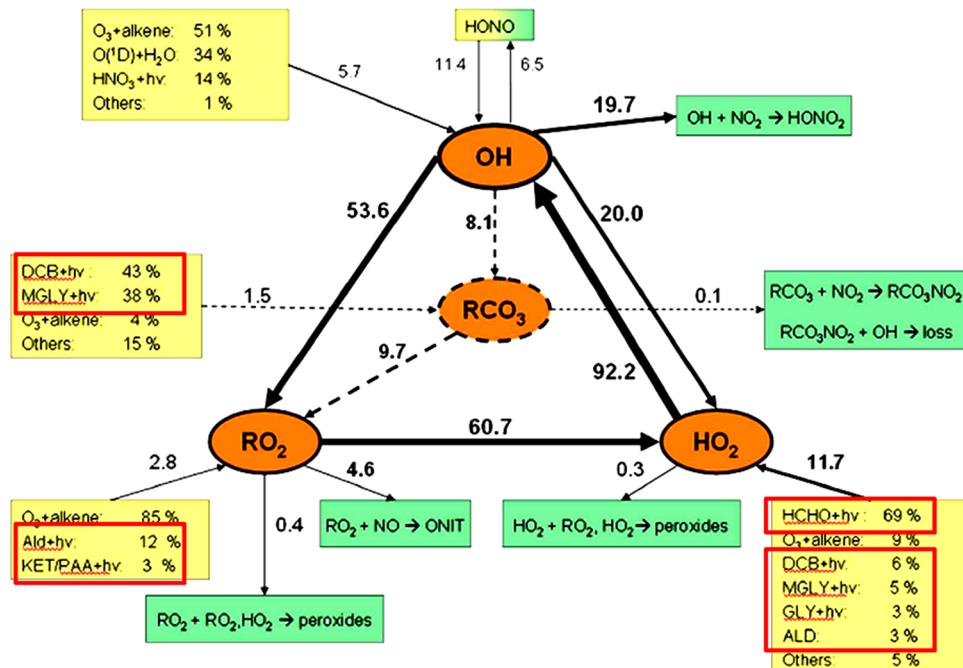


Figure 9. Contributions of different sources, in particular of the photolysis of organic gases (circled in red), to the radical budget in Mexico City during the MCMA-2006 campaign.⁵¹⁰ Acronyms: MGLY, methylglyoxal; GLY, glyoxal; ALD, aldehydes.

atmospheric chemistry, such as NO_x or HONO, depends not only on their spectroscopic properties (Table 10) but also on their atmospheric concentrations. Thus, while the photolysis of organic gases is estimated to be globally a minor source of HO_x radicals in the atmosphere, formaldehyde (HCHO) is estimated to be the main organic contributor to HO_x because of its abundance. In some regions, however, the contribution of photolabile organic gases to the radical budget can be much more important. In a tropical rainforest, the photolysis of organic hydroperoxides (CH₃OOH, ROOH) has a small but non-negligible contribution to the HO_x budget.⁵⁰⁸ At a rural and forested site, the photolysis of HCHO and other organic compounds was estimated to contribute to 23% of the radical sources.⁵⁰⁹ Also, in an urban environment such as Mexico City, the photolysis of HCHO alone was estimated to contribute to 69% of the direct HO_x sources, and dicarbonyl compounds (glyoxal, methylglyoxal) and other aldehydes to an additional 17% (Figure 9). The photolysis of other organic compounds also contributed indirectly to the HO_x sources by producing organic radicals.⁵¹⁰ In a previous campaign at the same location, these contributions were estimated to be even larger, the HO_x sources being almost entirely accounted for by the photolysis of HCHO (over 50%) and other oxygenated compounds (glyoxal, acetaldehyde, ketones, etc., about 45% in total).⁵¹¹ The importance of optically active organic gases in atmospheric chemistry is therefore not questionable. While the organic functions acting as radical sources in the atmosphere are relatively well understood, important unknowns remain in the understanding of the radical cycles today (section 5.6), which could be reduced by systematic investigations of the contributing organic gases and their properties (molecular identification, quantification, absorption coefficients, quantum yields, etc.).

5.3.2.2. Particulate Matter. The organic compounds acting as radical sources in aerosols are much less known than those in the gas. Some organic compounds present in or at the surface

of aerosols or cloud droplets can photolyze when exposed to UV-vis light. The depth at which shortwave radiations can penetrate atmospheric particles is however unclear and can limit direct photolysis in the bulk. Photosensitization can provide alternative radical sources to direct photolysis. A photosensitizer is a compound absorbing light, which, instead of photolyzing, transfers its excitation energy to another compound, thus triggering reaction chains that are propagated by charge or electron exchanges (radical reactions) and terminated by electron acceptors. Photosensitized processes of atmospheric relevance have been evidenced at the surface of aerosol proxies in laboratory, such as the photoinduced formation of HONO,⁵¹² uptake of ozone,⁵¹³ or heterogeneous ozonolysis reactions.⁵¹⁴ More recently, similar processes were also evidenced in the aerosol bulk, and shown to contribute to SOA growth via bulk radical reactions.^{428,515} In these studies, the organic photosensitizers used were humic acids,^{512,515a} benzophenone and benzoic acid-related compounds,^{513–515} and imidazoles.^{428,515b} While humic substances and their proxies, benzophenone and benzoic acid, might not be present in all aerosols, the fact that secondary products of simple precursors, such as imidazoles from glyoxal, can also act as a photosensitizer indicates that such processes could be more common in the atmosphere than previously thought. In order to evaluate the importance of these processes in atmospheric aerosols, the type of organic molecules acting a photosensitizer need now to be further investigated.

5.3.2.3. Fluorescent Organic Compounds. In addition to absorbing and scattering, fluorescence can also confer interesting properties to atmospheric organic compounds and be used to monitor specific classes of compounds. Some highly conjugated gases in the atmosphere, such as 2–4 ring polycyclic aromatics, do not photolyze⁵¹⁶ in spite of their strong absorbance in the near UV and vis regions. This is because their molecular structures allow for more complex transitions, such as fluorescence. When present in or at the surface of

atmospheric particles, such fluorescent properties can be accompanied by photosensitizing abilities,⁵¹⁷ as described above, making these compounds potential radical sources in the particulate phase.

These compounds can be monitored with fluorescent detectors, which were developed about two decades ago to monitor airborne bacteria and biochemical warfare, but later widely used to investigate atmospheric aerosols for scientific purposes.⁵¹⁸ It is well established, however, that not all biological material fluoresces, and that some nonbiological material fluoresces and can interfere with these measurements. Examples of the latter are aromatic compounds and PAHs, which are responsible for the fluorescent properties of cigarette smoke. HULIS are also known to fluoresce,^{497b} although they are not necessarily biogenic. More recently, laboratory studies have evidenced the fluorescent properties of reaction products of organic compounds with NH₃/NH₄⁺.⁵¹⁹ The identification of biological compounds by fluorescence is thus interesting but subject to a number of limitations and artifacts. On the other hand, fluorescence can be used to identify the conjugated compounds, some of them having interesting photochemical properties.

5.3.3. Perspectives on Optically Active Organic Compounds. We saw in this section that the optical properties of many atmospheric organic compounds lead to important roles in the climate budget or as radical sources in atmospheric chemistry. While the role of absorbing gases (GHG or radical sources in the gas) is relatively well understood, most of the current challenges and uncertainties, by far, concern the compounds in the condensed phase (aerosols): the molecular structures and contributions of different types of brown carbon and photosensitizers. The non-negligible contribution of brown carbon to the optical and radiative properties of ambient aerosols is now supported by a large number of direct observations. It is thus urgent to finally include realistic absorption indices for brown carbon in climate models, and determine its effect on the global radiative forcing of aerosols. The potential importance of photosensitized processes in or at the surface of particles in the atmosphere just begins to be revealed by laboratory studies, but already justifies further investigations. These future investigations will have to identify the molecular structures of the compounds involved and determine suitable markers in ambient aerosols. This will require advanced analytical techniques such as LC/MS, in combination with soft ionization and HRMS. This effort is well underway for HULIS and biomass burning material, but remains almost entirely to be done for light-absorbing components of SOA and POA, and for potential photosensitizers present in aerosols. Thus, molecular identification will be key in improving the knowledge of these optically active compounds and of their role in the atmosphere.

5.4. Cloud-Forming Organic Material

Clouds are important components of the atmosphere, not only for their role in the hydrological cycle but also because they are among the main cooling factors in the climate budget.⁵²⁰ This section summarizes the current knowledge of the organic compounds contributing to cloud formation. The formation of liquid and ice clouds in the atmosphere takes place exclusively by condensation of water on aerosol particles called cloud condensation nuclei (CCN) or ice nuclei (IN),⁵²¹ respectively. In both cases, the large uncertainties in the climate budget are due to remaining gaps in the understanding of the physical

chemical processes controlling the condensation of water, in particular those involving organic compounds.⁵²⁰ The formation of liquid cloud droplets is described by the Köhler equation, involving only two terms on which organic compounds can play a role: the Raoult's term, corresponding to water-soluble compounds acting on the vapor pressure around the droplet, and the surface tension. The formation of ice particles is even less understood than the one of liquid cloud droplets, but certain types of organic materials are known to be good IN, in particular biological material such as bacteria, spores, fungi, viruses, algae, and pollen.⁵²² The efficiency of this material as IN is due to proteins present on their membranes and ordering the water molecules along the same patterns as ice crystals. Therefore some biochemical organic material also play a role in ice nucleation.

The formation of liquid cloud droplets from aerosol particles has mostly been studied with two types of instruments: hygroscopicity tandem differential mobility analyzers (HTDMAs) and cloud condensation nuclei counters (CCNCs).⁵²¹ These instruments sample the aerosol particles, expose them to a controlled relative humidity over a certain residence time in a continuous flow chamber, and measure either their growth factor, or "hygroscopicity,"⁵²¹ at the output of the chamber (with HTDMAs) or the number of activated particles (with CCNCs).⁵²¹ Both types of instruments confirm the importance of hygroscopic material, acting on the Raoult's term of the Köhler equation, in the formation of cloud droplets. Beside inorganic salts, some organic compounds such as organic acids, saccharides, HULIS, and even smog chamber SOA have been found to be somewhat hygroscopic. However, to a few exceptions⁵²³ these instruments do not observe any effect of surfactant on the formation of cloud droplets. In general, they observe little effect of the aerosol organic composition on the CCN numbers observed in the atmosphere,⁵²⁴ the latter being generally overestimated by Köhler theory.

For this reason, the presence of organic surfactants in atmospheric particles was investigated directly by sampling, extraction and chemical analysis.⁵²⁵ The presence of organic surface-active compounds in fog water and atmospheric aerosols was evidenced already decades ago^{525,526} but, because of the considerable analytical challenge they involved, these compounds were not identified and the information obtained on them was limited. Recently, the development of a more sophisticated extraction method allowed to isolate the total surfactant fraction of atmospheric aerosols and evidenced the presence of much stronger surfactants than expected in atmospheric aerosols, likely to enhance cloud droplet formation.⁵²⁷ Dynamic investigations of these aerosol surfactants also revealed their slow equilibration, and explained their lack of detection by most HTDMA and CCNC instruments.^{527c} The presence of surfactants in atmospheric aerosols and their role on cloud droplet formation is supported by a growing number of observations, including measurements of atmospheric surfactants concentrations in aerosols by colorimetric methods, experiments with ambient and laboratory-generated aerosols CCNCs in laboratory,⁵²⁸ and HTDMA operating over longer time scales,^{523 528} The understanding of these processes and a definitive confirmation for the role of surfactants will require further studies, including the development of instruments other than HTDMAs and CCNCs, and various, complementary approaches. But only the molecular identification of aerosol surfactants, with advanced techniques

such as LC/ESI–MS, will provide important information on the molecular structure and origin of atmospheric surfactants, including their potential biologic origin suggested by their properties.

5.5. Nucleating Compounds

5.5.1. Introduction. Nucleation is the process in which new solid or liquid particles form directly from gas-phase species. It has been observed in nearly all regions and environments on Earth, from urban to remote locations, to the notable exception of mixed forests with high isoprene emissions such as the Amazonian rain forest.⁵²⁹

Despite these numerous atmospheric observations and a large number of laboratory investigations, many unknowns remain in these processes in particular on the involvement of organic compounds. While sulfuric acid seems to be an essential component,⁵³⁰ its atmospheric boundary layer concentration is generally too low to account for a simple binary nucleation with water vapor alone.⁵³¹ Other gases such as ammonia and organic compounds are thus suspected to be involved and enable nucleation under atmospheric conditions.⁵³²

To discuss the role of organic species in new particle formation in the atmosphere, it is useful to differentiate between the very early steps of new particle formation (cluster or embryo formation, formation of a critical nucleus) and the growth of the critical nucleus to larger sizes (>2–3 nm).⁵³³ Today it is clear that organic species are heavily involved in the second step (the growth process), but their importance in the formation of the critical nucleus is less clear. Although the contributions of physicochemical and chemical processes cannot be clearly distinguished, the growth phase is generally described as being purely driven by the physicochemical properties of the condensing compounds (i.e., their vapor pressure), while chemistry (chemical functionality) is more important for the formation of the cluster or embryo itself. Yet the role of organic compounds in particle nucleation and growth remains to be fully elucidated.

5.5.2. Investigation of Potential Candidate Molecules: Formation of the Critical Nucleus. As mentioned above, chemical interactions are suspected to play an important role in the formation of the critical nucleus. These chemical interactions that draw the molecules from the gas to the condensed phase may span from ionic or covalent bond formation to mere electrostatic interactions.⁵³⁴

In the past few years, the role of acid–base chemistry and salt formation in these processes has been the focus of investigations. In particular, organic amines emitted by soils and oceans have been observed to enhance the nucleation of sulfuric acid by a base-stabilization mechanism involving acid–amine pairs.⁵³⁵ A synergistic effect of amines and ammonia was also shown on the enhancement of sulfuric acid nucleation,⁵³⁶ but the chemical mechanisms responsible for it remain unclear. Theoretical studies have indicated that similar strong interactions exist between dicarboxylic acids and amines in hydrated clusters, suggesting that they can participate in atmospheric aerosol nucleation by forming aminium carboxylate ion pairs.⁵³⁷ This has been confirmed by the observation of aminium salts in nanometer atmospheric particles with thermal desorption-Cl-MS.⁵³⁸

Laboratory studies⁵¹⁴ showed that glyoxal can contribute to the early particle growth of ultrafine sulfuric acid particles by nonoxidative processes such as oligomerization. In line with this, a nucleation process involving one molecule of sulfuric

acid and one molecule of organic compound was suggested,^{532a} which was recently supported by the observations of clusters of sulfuric acid and oxidation products of pinanediol in laboratory.⁵³⁹ Laboratory measurements using atmospheric pressure inlet TOF-MS or CI-API-TOF-MS have also shown that highly oxidized organics play a central role in the early steps of cluster formation,^{398,539,540} but these techniques only provide the MW and empirical chemical formula of the observed compounds, not their chemical functionality or structure.

5.5.3. Investigation of Potential Candidate Molecules: Low-Vapor Pressure Compounds. One of the most important properties of organic compounds for new particle formation, both for the formation of the critical nucleus and for the growth of the particle, is their saturation vapor pressure. Box model calculations⁵⁴¹ showed that, in order to match the observed growth rate of atmospheric particles, the equilibrium vapor pressure of the condensing organics must be as low as 10^{-8} – 10^{-7} Pa in continental forest environments.^{542,543} Because classical chemical oxidation mechanisms do not produce compounds with such low volatilities, their formation pathways are open to speculation. A first possible source for these extremely low volatile VOCs is the second-generation oxidation of semivolatile VOCs by OH in the gas.⁵⁴⁴ Molecular markers for second-generation products from biogenic VOC oxidation (e.g., MBTCA) have been observed in the field^{390b,545} and in laboratory studies.^{439,544b,546} Yet molecular information on second or third generation oxidation products of anthropogenic VOCs is lacking,⁵⁴⁷ partly due to the lack of suitable markers retaining the original anthropogenic VOC skeleton.

Other potential low-vapor pressure candidates are higher-MW dimeric products from biogenic VOC oxidation. This was suggested by the observation of oxidation products of α - and β -pinene displaying dimeric structures in laboratory-generated SOA and ambient fine particles using various HPLC/MS methods.^{43,374,379,548} Their detailed molecular structures and hence their formation pathways are still subject to speculation. However, prominent high-MW dimers from α -pinene ozonolysis (MW 368 and 358) have been structurally elucidated (section 5.1). They were first thought to be noncovalent bonded dimers formed in the gas phase,³⁷² then later suggested to be products from condensed-phase reactions in SOA.^{390b} An alternative explanation is that these high-MW dimers are formed by gas-phase reactions of stabilized Criegee intermediates in the ozonolysis of terpenes, for example, α -pinene.³⁸⁰ This would make them plausible candidates for the early stage of nucleation in monoterpane-rich environments such as boreal forests.

Another potential contribution of organic molecules to particle formation and growth would be heterogeneous or multiphase reactions. Such reactions are known to lead to organic products with low volatility, such as organic acids (e.g., Kroll et al.³⁶⁹). Another example is heterogeneous formation of organosulfates,^{344a,346b,347a,410a,413c} which are expected to have significantly lower vapor pressure than their precursors and would thus accelerate the growth of the ultrafine particles.

5.5.4. Perspectives on Nucleating Organic Compounds. Despite a considerable number of studies and some advances in this topic over the last two decades, crucial gaps remain in the understanding of particle nucleation in the atmosphere, especially concerning the organic molecules involved in the formation of the critical nucleus and particle

growth. Considerable work has focused on these processes in the boreal forest environment, but there is a need for more investigations in other environments such as tropical, marine, Arctic, and urban areas.

Progress in the understanding of these processes will depend directly on the improvement of current instrumentation and methods to achieve the unambiguous identification of the organic molecules involved. Key points of improvement should be the accuracy of the molecular identification, time resolution, and detection sensitivity. Another important point would be to study these highly sensitive systems without changing gas-particle partitioning of the semivolatile compounds or the chemical equilibria of the heterogeneous processes.

5.6. Organic Intermediates

The lifetime of organic compounds in the atmosphere spans over 6 orders of magnitude, from seconds to decades, because of their wide range of reactivity with atmospheric oxidants and various removal processes. While most of this Review addresses the identification of long-lived organic compounds, short-lived ones, acting as intermediates in reaction mechanisms, also play important roles in atmospheric chemistry and are therefore important to identify and monitor. Both for the elucidation of the reaction mechanisms in laboratory and the understanding and prediction of real atmospheric systems, some degree of molecular identification is necessary for these organic intermediates because their reactivity depends widely on their organic structure. Yet their detection and identification involves many more instrumental challenges than for stable compounds. This section presents the most important examples of short-lived organic species in atmospheric chemistry, organic peroxy radicals and Criegee intermediates, and the solutions proposed so far for their monitoring and molecular identification. Some of the techniques presented are still largely under investigation and represent emerging directions of research in this field.

5.6.1. Organic Peroxy Radicals and the Oxidizing Capacity of the Atmosphere. *5.6.1.1. Importance of Organic Radicals in the Oxidative Capacity of the Atmosphere.* Some of the main discoveries on the fundamental radical cycles in the atmosphere were made in the 1970s: the OH radical was first identified as the main atmospheric oxidant,⁵⁴⁹ and found to trigger the oxidation of organic gases and the production of organic peroxy radicals, “RO₂”, where R is an organic group.⁵⁵⁰ The peroxy radicals HO₂ and RO₂’s were then found to play essential roles in the production of O₃ in the troposphere.³ In the following decades, these reactions were implemented in atmospheric models, and, for a long time, the consistencies between modeled and observed O₃ concentrations gave the impression that these radical cycles were well understood. However, more recent measurements of OH and HO₂ showed important discrepancies with models,⁵⁵¹ indicating that important parts of these cycles and of the oxidative (i.e., self-cleaning) capacity of the atmosphere were still not understood. Subsequent investigations suggested that the observed discrepancies were due to yet unknown reactions of the RO₂ radicals.^{508,551d,e,552} However, the lack of techniques able to distinguish between RO₂’s with different organic structures (“speciated” measurements) strongly limits their investigation and definitive understanding of these chemical systems. Yet, because of their fundamental importance in the atmosphere, many techniques have been proposed to monitor RO₂’s^{508,550a} which are presented below.

5.6.1.2. Observation Techniques for RO₂ Radicals. The classical techniques to monitor RO₂’s, still widely employed in laboratory, are optical and magnetic spectroscopies, such as UV^{550a} and IR⁵⁵⁴ absorption spectroscopy, electron spin,⁵⁵⁵ and paramagnetic resonance (ESR and EPR). In particular, despite considerable technical challenges (sampling on ice at 77 K and off-line analyses), ESR was successfully applied to the detection of RO₂’s in the atmosphere.⁵⁵⁵ However, a drawback of this technique, as well as with UV absorption, is that they only detect the radical center (−OO[•]) of RO₂’s, which is hardly affected by their organic structure, making the spectra unspecific.^{555a} These techniques are thus mostly useful in laboratory, for the investigation of known radicals, while, in the atmosphere, ESR provides total peroxy radical concentrations. IR absorption has been shown to be structure-specific⁵⁵⁴ and used in laboratory for the characterization of various RO₂’s. However, the applicability of this technique to complex systems such as the atmosphere remains to be demonstrated.

Other approaches were developed specifically for atmospheric detection, and remain today the main source of information on atmospheric RO₂’s. They are based on “chemical conversion”, which consists of converting all of the RO₂’s into a single compound, easier to detect. A first version was the “peroxy radical chemical amplification” technique (PERCA), where the peroxy radicals were titrated with NO and the NO₂ produced was measured by luminescence.⁵⁵⁶ Because of the interferences of other atmospheric compounds in the NO/NO₂ conversion, alternative conversion systems were proposed, such as ROxMAX and PerCIMS, where the radicals are titrated by ³⁴SO₂ to produce labeled H₂SO₄, in turn measured by MS.⁵⁵⁷ Another variation is ROxLIF, where the RO₂’s are converted into HO₂, then OH, which is measured by laser-induced fluorescence (LIF) or fluorescence assay by gas expansion (FAGE).⁵⁵⁸ Recently, the FAGE approach was shown to be able to differentiate between saturated and unsaturated RO₂’s (alkene- and aromatic-derived ones) based on their conversion kinetics.⁵⁵³ While these techniques are valuable, as the only ones applicable to atmospheric RO₂’s today, the conversion processes suppress most or all information on individual RO₂’s and provide integrated signals (total RO₂ concentrations). In addition, the response of the signals to individual RO₂’s varies widely with their structure, as it depends on their reactivity in the conversion scheme. It is thus difficult to predict for unknown atmospheric RO₂’s. Finally, all of these conversion schemes suffer from interferences in the atmosphere. These instrumental shortcomings are currently the main limitations to the full understanding of the atmospheric radical cycles.

Another group of techniques that shows some promising potential for the speciated detection, and thus the identification, of RO₂’s in the atmosphere is mass spectrometry. As explained in the previous sections, soft ionization techniques, avoiding fragmentation, provide MS signals directly reflecting the molecular weight of the analyte, with a potentially high level of identification for small masses (*m/z* < 300) when using TOF mass filtration. The detection of short-lived species, however, precludes separation prior to sampling, which can limit this identification. Over the last decades, a range of ionization schemes for RO₂’s have been tested in laboratory: negative⁵⁵⁹ and positive⁵⁶⁰ photoionization, electron transfer with SF₆[−], O₂[−], or an excited rare gas,⁵⁶¹ reaction with I[−] or O₃[−],⁵⁶² reaction with O₂⁺,⁵⁶³ and proton transfer with H₃O⁺ and its water clusters. Many of these techniques, while useful in

laboratory, are difficult to apply to atmospheric systems, either because they require low-pressure samples or lead to the fragmentation of the RO₂s. Only proton transfer with H₃O⁺ and its clusters appears to be suitable for atmospheric applications, as it avoids fragmentation and can be applied to atmospheric-pressure samples.⁵⁶⁴ Until now, this approach for monitoring RO₂'s has only been used in laboratory, in most cases with setups where the reaction and ionization regions are integrated.⁵⁶⁴ Adapting this technique to atmospheric sampling could be promising for the speciated detection of atmospheric RO₂'s and the investigation of the RO₂ and HO_x radical cycles.

5.6.2. Criegee Intermediates and Ozonolysis. Ozonolysis is an important reaction for all unsaturated organic compounds in the atmosphere, both in the gas and at the surface of particles. Until very recently, the lack of direct observation of its postulated intermediates, the Criegee intermediates, left many unknowns in atmospheric mechanisms because these intermediates are suspected to react with a number of atmospheric gases, such as H₂O, SO₂, NO, and NO₂. In particular, their reaction with water vapor has been suggested as a source for OH radicals, contributing directly to the atmospheric radical cycles. Recently, the use of synchrotron photoionization allowed one to observe for the first time the simplest Criegee intermediates, CH₂OO,⁵⁶⁵ then CH₃CHOO.⁵⁶⁶ While these intermediates were not created in ozonolysis reactions, they allowed for the first direct measurements of their rate constants with important atmospheric species such as H₂O, SO₂, NO, and NO₂, and evidenced some significant discrepancies with those estimated previously.^{565b,566,567} In addition, photoionization spectra allowed one to distinguish the *anti* and *syn* isomers of CH₃CHOO, and to evidence their very different reactivities with atmospheric gases.⁵⁶⁶ More recently, IR spectroscopy was also used for the detection of Criegee intermediates,⁵⁶⁸ including in gas-phase ozonolysis reactions.⁵⁶⁹ The investigation of Criegee intermediates is now a rapidly expanding field of research, in which the development of techniques for their detection in the atmosphere will be an important direction.

5.6.3. Intermediate Organic Compounds in the Atmospheric Particulate Phase. As mentioned in previous sections, the reactions of organic compounds in atmospheric aerosols and aqueous phases (clouds, fog) have become an important field of investigation in the last decades. Understanding the mechanisms of these reactions is key to determine their importance for atmospheric chemistry at regional and global scale. These mechanisms can be partly investigated by identifying specific reaction products or markers, for instance, with LC/MS techniques, or by following the evolution of the average aerosol composition with real-time techniques, such as aerosol MS (section 4.1.2).^{143,396} However, these approaches do not give access to the most important mechanistic information because stable reaction products or markers can be obtained by different mechanisms. Examples of this are the current debates on whether the organosulfates found in atmospheric aerosols are produced by ionic or radical mechanisms, and whether organic reactions such as condensation, acetalization, or hydrolysis are controlled by acid or iminium (NH₄⁺) catalysis in tropospheric aerosols.^{38,410b,420a,421b,c} The only unambiguous way to elucidate such reaction mechanisms is to directly observe their organic intermediates, which involves considerably more difficulties than investigating gas-phase mechanisms because of the small

sample volumes. The involvement of OH radicals in authentic cloudwater samples has however been inferred by adding aromatics as scavengers.⁵⁷⁰ The involvement of this and other radicals can also be proven by adding unsaturated compounds as scavengers, as was recently illustrated with the organosulfates obtained from the sulfate radical anion.^{413c} To our knowledge, the direct observation of short-lived reaction intermediates in atmospheric condensed-phase samples has not been attempted yet. The direct observation of radicals, including organic ones, in aerosols could potentially be attempted by CRDS techniques in the UV, provided that no other compounds interfere with their observations. NMR and ESI-LC/MS are also able to detect neutral and ionic intermediates, respectively, but would be more applicable to laboratory samples than atmospheric ones. Therefore, the direct observation of reaction intermediates in atmospheric condensed-phase might remain one of the ultimate challenges in atmospheric chemistry. Yet, because of its importance for the understanding of the fate of organic carbon in the atmosphere, it could be an important future direction of research.

5.7. Health-Hazardous Compounds

Besides the importance of atmospheric organic compounds for atmospheric chemistry and climate described in the previous sections, some of them also have toxic properties. The strongest evidence for the negative health effects of air pollution and, in particular, aerosol particles results from epidemiological studies where short- or long-term exposure to increased levels of aerosol particles could be directly linked with pulmonary and cardiovascular diseases, such as chronic obstructive pulmonary disease or asthma.⁵⁷¹ Numerous toxicological studies have linked adverse health outcomes to primary⁵⁷² as well as ambient aerosols.⁵⁷³ Investigations of the chemical properties, molecular interactions, and health effects of hazardous compounds in atmospheric aerosols have been recently summarized in reviews.⁵⁷⁴

Known toxic gases include inorganic compounds such as ozone, nitrogen oxides, or carbon monoxide and a wide range of organic compounds such as small aromatics and aldehydes. Toxic particle-phase compounds represent an equally wide range, including transition metals and a large number of organics from polycyclic aromatic hydrocarbons to highly oxidizing compounds such as peroxides or radicals.⁵⁷⁵

While the toxicity of atmospheric particles has been established for decades, the identity of the compounds contributing to the adverse health effects observed in epidemiological studies and the role of aerosol composition in toxicity are still poorly understood. Some specific toxicity mechanisms have been identified for a limited number of compounds (PAHs) and revealed that reactive metabolites such as diol epoxides of PAHs have the potential to bind to deoxyribonucleic acids and proteins causing genotoxicity and carcinogenicity. Yet such detailed mechanistic understanding is not available for most health-hazardous aerosol components. One obstacle to this understanding is the complexity of the particles directly emitted, combined with the complexity resulting from atmospheric processing,⁵⁷⁶ making the identification of the compounds with adverse health effects a highly challenging task. Other reasons for this poor understanding are the low dose/long-term health effects of atmospheric particles rather than their acute toxicity and the wide range of susceptibility in the population, including potential pre-existing (e.g., respiratory) risks.

This section presents the analysis techniques used to identify and, more importantly for toxicity, quantify two main classes of toxic compounds in aerosol particles: PAHs, requiring structure-specific identification and trace-level quantification, and reactive oxygen species (ROS), representing a wide group of compounds. As discussed below, these two classes of compounds correspond to very different *I*-factors.

PAHs were among the first compounds identified as toxic in air pollution particles, and are produced by fossil fuel combustion and biomass burning. They are present both in the gas and in the condensed phase, but the most toxic PAHs are particle-bound. Both parent PAHs and oxidized and nitro-PAHs have been identified as toxic. A wide range of analytical techniques have been developed to separate and quantify individual PAHs in the gas and particle phase in the atmosphere. GC×GC methods^{271,274} and LC techniques were specifically developed to investigate oxidized and nitro-PAHs,⁵⁷⁷ but the reduced chromatographic resolution of LC methods as compared to GC is often a limiting factor for the analysis of complex samples such as organic aerosols. MS is in many cases the detection technique of choice, and a range of ionization methods were applied to PAHs. Electron ionization is most frequently used with GC, but soft ionization methods such as negative ion chemical ionization have also been applied to PAHs,⁵⁷⁸ allowing for detection limits down to the low picogram levels²⁶¹ and potentially also advanced structure identification via MS/MS. Recently, a thermal desorption GC×GC coupled with tandem mass spectrometry reported detection limits in the subpicogram range for PAHs, oxidized and nitro-PAHs.^{466g} LC offers a wider range of soft ionization methods than GC and APCI, in particular, achieves detection limits down to picogram levels, thus lower than electrospray ionization.⁵⁷⁹ Coupling chromatography and advanced MS techniques allows to identify PAHs with high certainty, even in highly complex atmospheric aerosol samples, often with *I*-factors close to unity.

MS techniques without chromatographic separation have also been applied to PAHs such as two-step laser mass spectrometry (L2MS). In this technique, a first IR laser desorbs the organic material from the collection substrate (filter or impactor plate), and the second wavelength-specific UV laser selectively ionizes the PAHs.⁵⁸⁰ By tuning the ionization laser to selectively ionize the PAHs, this technique avoids artifacts due to other organic compounds present in the sample. L2MS is however generally qualitative, but a few attempts to use it in a quantitative way have been made and resulted in detection limits in the picogram range.⁵⁸¹ Because L2MS is a one-dimensional technique, its *I*-factor is inherently larger than for coupled techniques, and in the range of 10. Resonance-enhanced multiphoton ionization has also been successfully applied to detect PAH in thermally evolved gases from PM samples.⁵⁸²

Taking into account potential sampling artifacts is especially critical in the quantification of reactive compounds such as PAHs. Careful sampling procedures and controls are required to minimize their reaction on the sampling devices, which could lead to a severe underestimation of their concentrations.⁵⁸³ Isotope dilution methods using ¹³C- or ²H-labeled PAHs as references are frequently being used to improve precision and accuracy of the quantification of PAHs by reducing calibration, sample preparation, and matrix problems.

Because the toxicity of PAHs has been recognized for decades, long time series of PAHs atmospheric concentrations

are available, especially at urban locations. In many regions, the concentration of the most toxic ones, such as benzo[*a*]pyrene, has decreased by a factor of 10 over the last 30 years due to improved combustion technology. Yet respiratory diseases have steadily increased,⁵⁸⁴ implying that other aerosol compounds or properties need to be considered for these chronic health effects. Reactive oxygen species have gained significant attention as potential health-hazardous compounds over the last years. ROS is a generic term for all oxidizing compounds in aerosols, including transition metals, inorganic oxidants such as OH and H₂O₂, and organic compounds such as quinones, organic peroxides, and radicals.

The analysis of some organic ROS components is best achieved with the same analytical techniques as used for PAHs and presented above. Quinones, for example, have been quantified with GC/MS and LC/MS after derivatization, and resulted in detection limits in the picogram range.⁵⁸⁵ Other organic ROS such as (hydrogen-)peroxides and radicals are more difficult to analyze. Thus, analytical techniques have been developed to quantify the total concentration of ROS, or compound classes such as peroxides, rather than individual compounds. The total concentration of all (hydrogen-)peroxides in organic aerosols was quantified using an iodometric method, and it was shown that a major fraction of the aerosol organic compounds generated in simulation chambers contains the hydroperoxy group.^{575,586} Other studies have successfully attempted to quantify the total concentration of organic radicals⁵⁸⁷ by pro-fluorescent/fluorescent spin trap pairs, with detection limits in the low nanomole/liter concentration range. On-line methods to quantify ROS have also been developed¹⁰⁴ and showed that some components have very short lifetimes, of only a few minutes. This underlines the need to develop careful protocols to avoid artifacts due to particle collection and sample workup in the quantification of highly reactive compounds such as peroxides or radicals. Other recent efforts to characterize ROS in aerosols proposed a different approach by using surrogate biological systems, such as the natural antioxidants ascorbic acid or glutathione, to quantify the effect of particle-bound ROS on the antioxidant capacity of human lung.⁵⁸⁸ Thus, to the exception of the analysis of specific quinones, which can achieve an *I*-factor of 1, most of the recent techniques to characterize organic ROS focus on its quantification as a group of oxidizing compounds rather than as individual compounds. Thus, the *I*-factor attributed to these techniques is large, of the order of *I* > 100.

In conclusion, the analysis of health-hazardous organic compounds in the atmosphere is highly challenging. The difficulty lies not only in the identification and quantification of specific toxic compounds at trace levels but also in reproducing realistic exposure settings to simulate long time scales/low doses effects. For some compounds such as PAHs, very advanced analytical methods have been established, but other aspects of particle toxicity are still far from a compound-specific identification. The toxicity mechanisms of many organic aerosol components are poorly characterized, and toxic and oxidative stress (triggered by ROS uptake or by the generation of ROS in the body) mechanisms are expected to be multiple.⁵⁸⁹ Future research in this area will thus need to establish quantitative relationships between a wide range of potentially toxic components in atmospheric aerosols and health effects, and to make more efforts to identify the toxicity resulting from specific compounds. Only such a compound-specific knowledge

will ultimately allow to identify the relevant sources and to develop emission reduction strategies.

6. CONCLUSION AND PERSPECTIVES

From an analytical point of view, exploring the chemical composition of the atmosphere and the chemical processes taking place in it involves as many unknowns, and nearly as many challenges, as exploring other unknown environments, such as the deep oceans or other planets. The numerous techniques presented in this Review illustrate the tremendous increase of interest over the last decades for atmospheric constituents that are characteristic for our planet, organic compounds, and the considerable progress accomplished in the analytical tools allowing to study them. To overcome the numerous challenges presented by atmospheric problems, this progress has required not only the use of existing techniques from other disciplines, but also their adaptation to atmospheric applications and the development of entirely new techniques. In about three decades, these techniques have brought a much clearer picture, both qualitatively and quantitatively, of the myriad of organic compounds present in the atmosphere, their sources, and their contribution to important processes such as air quality, the ozone cycle, and SOA formation. Over an even shorter period of time (the last two decades), the tools developed to study organic compounds in the atmospheric condensed-phases (e.g., aerosols and clouds) have revealed the wide complexity of these media and allowed to characterize their sources and compositional changes over their atmospheric lifetime by the identification of markers, in particular for biogenic and biomass burning SOA. Understanding the tight connection between gas- and particle-phase chemistries, the resulting SOA formation, and their contributions to atmospheric chemistry and climate has thus undergone significant advances, and better descriptions can be anticipated in the near future.

However, two main factors hamper this progress. One of them is the analytical expertise needed to identify organic compounds. In particular, nonspecialists tend to overestimate the level of identification of organic compounds provided by a specific analytical technique, leading to reports of unverified or false compounds or processes. We hope that the discussion of the identification capabilities of the different techniques presented in this Review will avoid such shortcomings and stimulate interdisciplinary collaborations between atmospheric scientists of very different backgrounds to explore complex chemical atmospheric processes in the future.

Another main difficulty is the analytical challenge presented by some compounds that are central in some key atmospheric processes. Examples of processes being barely in reach of current analytical capabilities today are given in section 5: the role of organic compounds in nucleation, cloud formation, the aging of aerosol components, the formation of health-hazardous particles, and, via peroxy and Criegee intermediates, the oxidizing cycles of the atmosphere. The investigation of these processes will require further analytical developments, some of which are underway, and which could also benefit other chemical disciplines.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: barbara.noziere@ircelyon.univ-lyon1.fr.

*E-mail: markus.kalberer@atm.ch.cam.ac.uk.

*E-mail: magda.claeys@uantwerpen.be.

Notes

The authors declare no competing financial interest.

Biographies



Barbara Nozière received a Ph.D. in Physical Chemistry from the University of Bordeaux, France, in 1994. After postdoctoral studies at the Technical University of Wuppertal, Germany, and the National Center for Atmospheric Research (NCAR), Boulder, CO, she was an Assistant Professor at the University of Miami, FL, then a Professor at the University of Stockholm, Sweden (Marie Curie Excellence Chair awarded from the European Commission). Since 2011 she is a Senior Researcher at the Centre National de la Recherche Scientifique (CNRS) in Lyon, France. Her expertise and research interests are on the reactivity and physical chemistry of organic compounds in the atmosphere, both in the gas and in aerosols. Current topics include reactions between organic compounds and inorganic salts in aerosols, surface-active compounds and their role in cloud formation, and the detection of organic peroxy radicals in the gas.



Markus Kalberer studied Environmental Sciences at the Eidgenössische Technische Hochschule (ETH), Zurich, and obtained a Ph.D. in Chemistry from the University of Bern (both in Switzerland) in 1998. He subsequently performed postdoctoral studies at the California Institute of Technology in Pasadena, CA. He returned to Switzerland for a Habilitation at ETH, Zurich, and is now Reader in Atmospheric Sciences at the University of Cambridge, UK. His research interests include the formation, reactivity, and composition of organic aerosols, and the investigation of negative health effects of atmospheric particles with chemical and cell culture studies.



Magda Claeys received a Ph.D. in Chemistry from Ghent University, Belgium, in 1974, with research on bio-organic mass spectrometry. Since 1978 she is affiliated with the University of Antwerp, where she held research positions supported by the Research Foundation Flanders (FWO), was promoted to full professor in 2000, and since 2013 continues her research as an emeritus professor. She has a long-standing experience with organic analytical mass spectrometry that was centered on biomolecular mass spectrometry during her early career. For the last 20 years her research focused on the molecular characterization and speciation of atmospheric aerosols. A highlight of her career was the discovery of the isoprene SOA markers, the 2-methyltetrols, in Amazonian aerosols.



James D. Allan graduated in Physics with Computational Physics in 2000 and received a Ph.D. in Atmospheric Physics in 2004, both at the University of Manchester Institute of Science and Technology (UMIST). He has since held a research position in the National Centre for Atmospheric Science (NCAS) at the University of Manchester School of Earth, Atmospheric and Environmental Sciences and currently holds the post of senior research fellow at the latter. Much of his work during his Ph.D. and subsequent has concerned the development of the Aerodyne aerosol mass spectrometer (particularly data analysis techniques) and application to the on-line, in situ measurement of tropospheric aerosols. This has included field work in a wide variety of environments and on ground, ship, and aircraft-based platforms.



Barbara D'Anna graduated in Physical Chemistry at the University of Torino, Italy, in 1996, and received a Ph.D. in Atmospheric Chemistry from the University of Oslo, Norway, in 2001, on the atmospheric degradation of volatile organic compounds. After postdoctoral stays at the University of California at Irvine (UCI) in aerosol photochemistry, and Queensland University of Technology (QUT), Brisbane, Australia, in marine aerosol measurements, she was enrolled at the CNRS, France, in 2006. She is now a Senior Researcher at the CNRS in Lyon, and her main scientific interests involve aerosol reactivity, heterogeneous chemistry, and in situ tropospheric aerosol measurements.



Stefano Decesari is an expert in nuclear magnetic resonance (NMR) spectroscopy applied to atmospheric organic aerosol chemistry. He obtained a Ph.D. in Chemistry from the University of Bologna, Italy, in 2001. He was trained in NMR methods for environmental samples during his Ph.D. and at the Environmental Molecular Sciences Laboratory of the Pacific Northwest National Laboratory (EMSL-PNNL) in Richmond, WA. He was among the first scientists showing the suitability of proton NMR spectroscopy for the characterization of water-soluble organic carbon in aerosol and atmospheric aqueous samples. He developed NMR applications for aerosol source apportionment and discovery of new molecular markers, such as low-molecular weight aliphatic amines for biogenic marine particles. He was involved in 14 international projects, and he has coordinated three intensive field campaigns for sampling and characterizing atmospheric aerosols in polluted environments.



Emanuela Finessi obtained a Ph.D. in Chemistry from the University of Bologna, Italy, in 2010, on the chemical characterization of organic aerosol and source identification. She has over seven years of research experience in atmospheric chemistry, working on a broad range of collaborative projects within both field and simulation chamber experiments. Her research interests include processes related to the formation, transformation, and fate of organic aerosol, brown carbon, and organic nitrogen species in atmospheric particles. Since joining the University of York, UK, in 2011, she has focused on the aqueous processing of reactive carbonyls and interactions with inorganics by using a wide range of mass spectrometric techniques. Recent activities include the development of sensitive and selective methods for the determination of trace organic nitrogen species in complex matrixes.



Irena Grgić obtained a Ph.D. in Chemistry from the University of Ljubljana, Slovenia, in 1990. Currently she is a Senior Scientist at the Analytical Chemistry Laboratory of the National Institute of Chemistry, Slovenia. Since 2003 she is affiliated with the Faculty of Chemistry and Chemical Technology, Ljubljana, and since 2009 she holds an Associate Professorship at the Faculty for Environmental Sciences of the University of Nova Gorica, Slovenia. She has been actively involved in research on atmospheric multiphase processes for more than 20 years. Her research deals with fundamental processes in atmospheric aqueous phase chemistry, chemical composition and reactivity of aerosols, formation of secondary organic aerosols, and analytical methods for environmentally important species, and involves both field measurements and laboratory experiments.



Marianne Glasius obtained a Ph.D. in Chemistry from the University of Southern Denmark, Odense, in 2000, based on investigations of monoterpene oxidation products in aerosols and sources to carboxylic acids in the atmosphere. This research was partly carried out at the European Commission's Joint Research Centre, Ispra, Italy. She has worked with a very broad range of analytical techniques in projects related to environmental chemistry, synthesis, and process understanding. Since 2006 she has been appointed to Associate Professor at the Department of Chemistry, Aarhus University, Denmark. There, she has built up a research group and a laboratory, focusing on the development and application of advanced chemical analyses (using HPLC/q-TOF-MS and GC/MS) for identification and characterization of organic compounds in aerosols and other complex matrixes such as bio-oils.



Jacqueline Hamilton obtained a Ph.D. in Chemistry from the University of Leeds in 2003. She was appointed a Lecturer in Atmospheric Chemistry at the University of York in 2008. She has developed independent research themes in atmospheric aerosol chemistry underpinning a variety of laboratory, simulation chamber, and field observations. She has a strong interest in analytical science, developing methods and instrumentation in comprehensive two-dimensional gas chromatography (GC \times GC), HPLC/MS, and high-resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS). These methods, although designed to study the atmosphere, have been translated to other fields with recent papers in food chemistry, fuels, energy, and health applications. She won the 2009 Desty Memorial Award for Innovation in separation science.



Thorsten Hoffmann obtained a Ph.D. in Chemistry from the University of Dortmund, Germany, in 1992. Since 2003 he is Professor of Analytical Chemistry at the Johannes Gutenberg University of Mainz, Germany. His main research activities are the design and development of tailored methods to chemically characterize biological and environmental matrices. The motivation is a better understanding of biosphere–atmosphere interactions, for example, by the investigation of the sources, formation pathways, and chemical transformation of biogenic aerosol particles, or the development of trace analytical techniques to investigate climate archives (ice cores, speleothems). Most of the analytical research is focused on organic analytes in combination with mass spectrometry (GC/MS, LC/MS) with a certain emphasis on the development of real-time methods for atmospheric aerosol characterization (aerosol mass spectrometry).



Mohammed Jaoui received a Ph.D. in Physical and Analytical Chemistry in 1998 from the University of Metz, France. He carried out postdoctoral research in Atmospheric Chemistry at the University of North Carolina at Chapel Hill, NC. Subsequently, he joined Alion Science and Technology as a Senior scientist, where he is conducting studies in atmospheric chemistry. For the last 15 years his research focused on the molecular characterization and speciation of atmospheric gas and aerosols using mass spectrometric techniques.



Yoshiteru Iinuma received a Ph.D. in Physics with focus on physical and chemical characterization of atmospheric aerosols from the University of New South Wales, Sydney, Australia, in 2002. He joined the Leibniz Institute for Tropospheric Research (TROPOS) in Leipzig, Germany, as a postdoctoral fellow, and in 2008 he became a research scientist at TROPOS. His main research focuses on the physical and chemical characterization of both the gaseous and the particulate organic compounds in field and laboratory-generated samples using various chromatographic and mass spectrometric techniques.

Ariane Kahnt studied Pharmacy at the University of Halle, Germany, and obtained a Ph.D. in Natural Sciences from the University of Leipzig, Germany, in 2012. During her Ph.D. research she studied atmospheric oxidation products and SOA formation from monoterpene ozonolysis under the supervision of Professor Hartmut Herrmann. After postdoctoral studies at the University of Antwerp, Belgium, where she continued to identify organic compounds in atmospheric aerosol samples using mass spectrometric techniques, she recently joined the Faculty of Biology at the University of Auckland, New Zealand. Her current research involves genomic, proteomic, and metabolomic analysis using mass spectrometry.



Christopher J. Kampf studied Chemistry at the Johannes Gutenberg-University Mainz, Germany, where he also did his Ph.D. work in the group of Professor Thorsten Hoffmann and obtained a Ph.D. degree in 2012. His Ph.D. work dealt with the characterization and quantification of reactive dicarbonyl compounds in atmospheric aerosols. Afterward he carried out postdoctoral research at the University of Colorado, Boulder, CO, before starting as a project leader for Analytical Chemistry of Proteins and Organic Aerosols at the Max Planck Institute for Chemistry in Mainz. His current research focuses on the identification of proteins in atmospheric aerosols by means of state-of-the-art mass spectrometry, elucidation of protein modifications and degradation processes introduced by air pollutants, as well as formation processes of light absorbing compounds in secondary organic aerosols.



Ivan Kourtchev studied Chemistry at the Mendeleyev University of Chemical Technology of Russia, Moscow, graduating with an Engineering degree (B.Sc. equivalent) in 1997. After spending two years at the home institution as an engineer, he continued his studies at Oklahoma State University, OK, graduating in 2002 with a M.Sc. in Biosystems Engineering. He subsequently performed Ph.D. studies at the University of Antwerp, Belgium, on the molecular characterization of atmospheric aerosols and obtained a Ph.D. in Chemistry in 2008. His research interests in analytical and physical chemistry strengthened after postdoctoral stays at University College Cork, Ireland, and the Joint Research Centre of European Commission, Belgium. In 2011 he was awarded a Marie Curie Fellowship to perform research in high-resolution mass spectrometry and atmospheric chemistry at the University of Cambridge, UK, where he is currently employed as a research associate.



Willy Maenhaut is an atmospheric and analytical chemist. In 1972 he obtained a Ph.D. degree in Chemistry from Ghent University, Belgium. He has over 45 years of experience in atmospheric chemistry, with emphasis on (experimental) atmospheric aerosol research. He is

(co)author of over 300 refereed publications in international journals and of over 50 book chapters. He is a highly cited researcher in the field of geosciences in the 2014 Thomson Reuters list, and he is a corecipient of the 2014 Haagen-Smit prize of the journal Atmospheric Environment. He is at present editor of the international journals "Atmospheric Chemistry and Physics" (ACP) and "Atmospheric Measurement Techniques" (AMT). Willy Maenhaut is since 1 October 2010 honorary professor at Ghent University, and he is since then also affiliated with the University of Antwerp.



Nick Marsden graduated in Geology from the University of Manchester in 1997 and subsequently worked for a commercial instrument manufacturer (Waters Corp.) in the service, technical support, and development of high-resolution time-of-flight mass spectrometers. He is currently a postgraduate student at the University of Manchester School of Earth, Atmospheric and Environmental Sciences, where he is developing a laser ablation mass spectrometer for single particle analysis.



Sanna Saarikoski obtained a M.Sc. degree in Analytical Chemistry from the University of Helsinki, Finland, in 2002, and obtained a Ph.D. degree from the same university in 2008. Since 2002 she has been employed at the Finnish Meteorological Institute in Helsinki as a Research Scientist. In 2009 she performed postdoctoral research at the Cooperative Institute for Research in Environmental Sciences (CIRES) at Boulder, CO. The focus of her research has been on the chemical composition of aerosols and in recent years especially on aerosol mass spectrometry.



Jürgen Schnelle-Kreis obtained a Ph.D. in Analytical Chemistry from the University of Paderborn, Germany, in 1990. Since 1991 he is active in the analysis of organic composition of airborne particulate matter in different positions at the Institute of Ecological Chemistry of the German National Research Center for Environment and Health, the Institute for Analytical Chemistry of the Technical University of Munich, and the Department of Analytical Chemistry of the Bavarian Institute of Applied Environmental Research and Technology in Augsburg, Germany. Since 2009 he is Deputy Head of the Cooperation Group “Comprehensive Molecular Analysis” of the Helmholtz Zentrum München, German Research Center for Environmental Health. His research is focused on the chemical characterization of organic aerosol and identification of sources as well as health effects of ambient aerosols.



Sönke Szidat received a Ph.D. in Chemistry from the University of Hannover, Germany, in 2000, having carried out research on the long-lived radioisotope ^{129}I in the environment. He performed postdoctoral research at the University of Bern, Switzerland. In 2007, he became group head and lecturer at the University of Bern. He received the Atmospheric Chemistry and Physics (ACP) Award of the ACP Commission of the Swiss Academy of Sciences in 2008, the Fritz-Strassmann-Preis of the Nuclear Chemistry Division of the German Chemical Society in 2009, and the habilitation at the University of Bern in 2009. He is the head of the Laboratory for the Analysis of Radiocarbon with accelerator mass spectrometry at Bern since 2013. His research interests are measurements of the long-lived radioisotope ^{14}C in the environment with focus on source apportionment of carbonaceous aerosols.



Jason D. Surratt received a Ph.D. in Chemistry in 2010 from the California Institute of Technology in Pasadena, CA. The American Association for Aerosol Research awarded him the Sheldon K. Friedlander Award for his “outstanding dissertation work in aerosol science and technology” in 2013. In 2010 he began a tenure-track position as an Assistant Professor at the University of North Carolina at Chapel Hill in the Department of Environmental Sciences and Engineering. He has a wide experience with the detailed chemical characterization of SOA formation using mass spectrometric techniques. A highlight of his career is the discovery of organosulfate formation from the atmospheric oxidations of isoprene and monoterpenes, thus providing a set of molecular markers for secondary organic aerosols of a mixed biogenic/anthropogenic origin.



Rafal Szmigielski received a M.Sc. in Chemistry from Warsaw University of Technology, Poland, in 1999, whereupon he joined the Institute of Organic Chemistry of the Polish Academy of Sciences (PAS) and obtained a Ph.D. in 2004 with research on gas-phase ion chemistry. He performed postdoctoral research at the same institute and between 2006 and 2009 at the University of Antwerp, Belgium. There, he became involved in the molecular characterization of SOA using mass spectrometry and was awarded a Marie Curie Fellowship. A highlight of his career was the discovery of 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), a marker for aged α -pinene SOA. Since 2010 he is affiliated with the Institute of Physical Chemistry of the PAS, where he heads the Laboratory of Environmental Chemistry and continues studying SOA formation and processing using hyphenated techniques and organic synthesis.



Armin Wisthaler received a Ph.D. in Physics in 2001 from the University of Innsbruck, where he subsequently worked as a postdoctoral fellow and assistant professor. He was employed as a Senior Scientist at the Norwegian Institute of Air Research (NILU) between 2011 and 2013 before being appointed Professor of Atmospheric Chemistry at the University of Oslo in 2014. His expertise includes ion chemistry and chemical ionization mass spectrometry (in particular PTR-MS) as well as atmospheric chemistry.

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ABBREVIATIONS

ACS	American Chemical Society
AMS	aerosol mass spectrometer
API	atmospheric pressure ionization
APCI	atmospheric pressure chemical ionization
ASMS	American Society for Mass Spectrometry
ATOFMS	aerosol time-of-flight mass spectrometer
BBOA	biomass burning organic aerosol
BVOC	biogenic volatile organic compound
C _n	organic compound with <i>n</i> carbon atoms
CCN	cloud condensation nuclei
CCNC	cloud condensation nuclei counter
CE	capillary electrophoresis
CFC	chlorofluorocarbon
CI	chemical ionization
CMB	chemical mass balance
CRDS	cavity ring down spectroscopy
2D	two-dimensional
Da	dalton
DBE	double bond equivalent
DCA	dicarboxylic acid
DESI	desorption electrospray ionization
DOAS	differential optical absorption spectroscopy
EC	elemental carbon
ECD	electron capture detector
EI	electron ionization
ESI	electrospray ionization
FAGE	fluorescence assay by gas expansion
FID	flame ionization detector
FTICR	Fourier transform ion cyclotron
FTIR	Fourier transform infrared spectroscopy
GC	gas chromatography
GC×GC	two-dimensional GC
GHG	greenhouse gas
HCFC	hydrochlorofluorocarbon
HFC	hydrofluorocarbon
HILIC	hydrophilic interaction liquid chromatography
HOA	hydrocarbon-like organic material
HO _x	OH + HO ₂
HPAEC	high-performance anion-exchange chromatography
HPLC	high-performance liquid chromatography
HR	high-resolution
HTDMA	hygroscopicity tandem differential mobility analyzer
HULIS	humic-like substances
IC	ion chromatography
ILC	interlaboratory comparison
IN	Ice Nuclei
IPCC	Intergovernmental Panel for Climate Change
IR	infrared
IUPAC	International Union for Pure and Applied Chemistry
KIE	kinetic isotope effect
KM	Kendrick mass
L2MS	two-step laser mass spectrometry
LC	liquid chromatography
LDI	laser desorption/ionization
LP	long-path
LV	low-volatility
MBTCA	3-methyl-1,2,3-butanetricarboxylic acid
MCA	multicomponent analysis
MS	mass spectrometry
MS/MS or MS ⁿ	tandem mass spectrometry
MW	molecular weight
<i>m/z</i>	mass-to-charge ratio
NMR	nuclear magnetic resonance
NO _x	nitrogen oxides (NO + NO ₂)
OC	organic carbon
OOA	oxygenated organic material
OS _C	carbon oxidation state
PAH	polyaromatic hydrocarbon
PBAP	primary biogenic aerosol particle
PAD	pulsed amperometric detection
PAN	peroxyacetyl nitrate
PI	photoionization
PILS	particle-into-liquid sampler
PM _{<i>n</i>}	particulate matter with an aerodynamic diameter $\leq n \mu\text{m}$
PMF	positive matrix factorization
POA	primary organic aerosol

Q	quadrupole
ppm	parts per million
ppb	parts per billion
ppt	parts per trillion
RO ₂	peroxy radical
ROS	reactive oxygen species
SOA	secondary organic aerosol
SV	semivolatile
TAG	thermal desorption aerosol gas chromatography
TC	total carbon
TOF	time-of-flight
UHR	ultrahigh resolution
UPLC	ultraperformance LC
UV	ultraviolet
Vis	visible
VK	van Krevelen
VOC	volatile organic compound
VUV	vacuum ultraviolet
WSOC	water-soluble organic carbon

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