Trends in Analytical Chemistry 175 (2024) 117698

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Characterisation of atmospheric organic aerosols with one- and multidimensional liquid chromatography and mass spectrometry: State of the art and future perspectives

Stefanie Hildmann, Thorsten Hoffmann *

Chemistry Department, Johannes Gutenberg - University, Mainz, 55128, Germany

ARTICLE INFO

Keywords:
Atmospheric aerosol
(Multidimensional) liquid chromatography
(High-resolution) mass spectrometry
Chemical characterisation/identification
(Non/semi)-targeted approach

ABSTRACT

Aerosol particles are important components of the Earth's atmosphere and affect air quality and climate. They are small enough to penetrate deep into human lungs and are associated with serious short- and long-term health effects. However, aerosols also affect Earth's climate directly through scattering and absorption of solar radiation and indirectly through their role as cloud condensation nuclei. A large fraction (~50 %) of the submicron aerosol mass in the troposphere consists of organic material. In recent years in particular, some progress has been made, especially in the molecular characterisation of individual target analytes and in the determination of the physicochemical properties of organic aerosol constituents. However, knowledge gaps remain, especially information on low- and semi-volatile, often highly oxidized organic compounds or highly reactive compounds. For these classes of compounds, different liquid chromatography-mass spectrometry (LC-MS) systems have become preferred analytical methods in recent years. Although these methods offer a wide range of applications, they can be limited to specific analytes. Therefore, multidimensional LC and MS methods have also been introduced in atmospheric sciences to increase either the fraction of organic mass analysed or the degree of identification of individual components. In this review article, we present the main applications of advanced one- and multidimensional LC and MS methods in the analysis of atmospheric particles in non-targeted and targeted approaches, highlight their opportunities and limitations, and outline the main challenges for future applications in atmospheric sciences.

Abbreviations

2,4-DNPH	2,4-Dinitrophenylhydrazine
HULIS	Humic like substances
ACN	Acetonitrile
AMS	Aerosol mass spectrometer
APCI	Atmospheric pressure ionisation
APPI	Atmospheric pressure photo ionisation
ASM	Active solvent modulation
BVOC	Biogenic volatile organic compound
CIMS	Chemical ionisation mass spectrometer
CPLC	Chiral phase LC
DBE	Double bond equivalents
DOAS	Differential optical absorption spectroscopy
EI	Electron ionisation
ESI	Electrospray ionisation
FLD	Fluorescence detector
FT-ICR-MS	Fourier transform ion cyclotron resonance MS
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
HILIC	Hydrophilic lipophilic interactions chromatography
HOM	Highly oxidized molecules
HPLC	(High performance) liquid chromatography
IR-MS	Isotope ratio MS
IT-MS	Ion trap MS
LC-LC	Heart cut LC
LCxLC	Comprehensive LC
LOQ	Limit of quantification
MCR	Maximum carbonyl ratio
mLC-LC	Multiple heart cut LC
MRM	Multiple reaction monitoring
MS	Mass spectrometry
MS^n	Tandem mass spectrometry
MW	Molecular weight
NPLC	Normal phase LC

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* Corresponding author.
E-mail address: t.hoffmann@uni-mainz.de (T. Hoffmann).

https://doi.org/10.1016/j.trac.2024.117698
Received 8 November 2023; Received in revised form 21 February 2024; Accepted 5 April 2024
Available online 16 April 2024

(*continued*)

NTA	Non-targeted analysis
O/N-PAHs	Oxygenated and nitro-substituted PAHs
OA	Organic aerosols
OS	Organosulfates
PAH	Polycyclic aromatic hydrocarbon
PERCI	Photoelectron resonance capture ionisation
PFBHA	Pentafluorobenzyl hydroxylamine
PI	Photo ionisation
PTR	Proton transfer reaction
Qq-ToF-MS	Quadrupole time of flight MS
ROS	Reactive oxygen species
RPLC	Reversed phase LC
SCX	Strong cation exclusion chromatography
SEC	Size exclusion chromatography
SOA	Secondary organic aerosols
SPAM	Stationary phase assisted modulation
SPE	Solid phase extraction
SRM	Selected reaction monitoring
STA	Semi-targeted analysis
TA	Targeted analysis
ToF-MS	Time of flight mass spectrometry
tQ-MS	Triple quadrupole MS
UHR-MS	(Ultra) high resolution mass spectrometry
VEM	Vacuum evaporation modulation

1. Introduction

One of the current analytical challenges in atmospheric sciences is the chemical characterisation of atmospheric organic aerosol (OA) particles. Due to their impact on human health [1–4], climate and geochemical cycles [5–8], there is great interest in elucidating their chemical composition. Based on the latest chemical and physicochemical understanding of the processes leading to the formation of atmospheric aerosols [9,10], quantitative information on low- and semi-volatile, often highly oxidized organic compounds in the ultra-trace region is particularly needed. However, the chemical and physicochemical properties of aerosol-bound organics such as volatility, polarity, reactive oxygen content, reactivity, and complexity, which classify these compounds as interesting target analytes, at the same time make it difficult to reliably measure their concentration. Despite some progress in this field, the search for techniques to identify and quantify suitable tracers for understanding atmospheric processes as well as source attribution continues, with liquid chromatography-mass spectrometry (LC-MS) emerging in recent years as popular analytical techniques for the determination of organic compounds in aerosols [11,12]. LC-MS methods, while offering a wide range of applications, are limited in a basic design to specific analyte classes only. Therefore, multidimensional LC and MS methods have been introduced in atmospheric sciences to increase either the fraction of organic mass analysed or the degree of identification of individual components. This review article therefore aims to present the main applications of advanced one- and multidimensional LC and MS methods for the analysis of organic aerosol components in the atmosphere, but also to highlight their limitations and outline the main challenges for future applications in atmospheric sciences.

1.1. Identification factor I

One of the ways to describe the degree of identification of an organic compound is to specify the identification factor *I*. *I* is defined by the number of possible compounds that correspond to the information requested or measured by a specific analytical technique. Thus, a complete and unambiguous molecular identification corresponds to $I = 1$. For a compound determined by mass spectrometry, *I* is defined by equation (1.1) [13]:

$$I = \text{number of molecules matching } MW \times \text{number of possible isomers and spatial configurations} \quad (1.1)$$

Depending on the overall analytical method used (use or non-use of one- or multidimensional chromatography, ionisation method, resolution of the selected mass spectrometer), the identification factor can range from $1 \leq I \leq 100$ also when using mass spectrometers. In particular, the use of real-time methods (e.g. aerosol mass spectrometers (AMS)) and comparatively unspecific ionisation techniques such as electron ionisation (EI) leads to higher *I* factors. The factor *I* decreases drastically with upstream chromatography, as a second information dimension, e.g. the retention time, is added. Mass analysers with low mass resolution, e.g. MS with unit mass resolution, result in several possible compounds that can be assigned to a measured *m/z*, which increases *I*. *I* is now the number of isobaric compounds that are simultaneously ionised and eluted, e.g. the number of possible (non-separated) structural or stereoisomers. The use of a high-resolution mass spectrometer (HR-MS) leads to a lower number of compounds, as the molecular formula can be clearly assigned to a specific *m/z* value. If a suitable, authentic standard of the compound to be characterised is available, a complete characterisation can be achieved by an appropriate matching ($I = 1$) [13].

1.2. From functional group to molecular analysis of OA

Different atmospheric research questions require different levels of identification of the organic components, which can be provided by different analytical techniques. For example, to investigate the optical properties for the global energy budget of secondary organic aerosols (SOA), it is not necessary to identify the compounds individually, but to quantify them on the basis of common properties. Typically, functional group analyses (e.g. based on Fourier transform infrared spectroscopy (FTIR)) [14–17] can be used, which would allow identification with $I \geq 100$. For real-time monitoring to detect chemical processes in a turbulent atmosphere, excellent temporal resolution with time scales from seconds to minutes is also more important than the complete identification of individual compounds. Online analytical techniques such as aerosol mass spectrometers (AMS) are often used for these purposes. AMS systems are operated at high vaporisation temperatures (~600 °C) and use electron ionisation (~70 eV). This allows the characterisation of chemical features due to similar structures and functionalities leading to similar fragmentation patterns on excellent time scales [18–21]. On the other hand, mass spectra from different molecules evaporating simultaneously from the probe cannot be deconvoluted due to highly fragmented ions, resulting in a loss of molecular information (higher *I*-factor). In combination with high-resolution mass analysis to separate isobaric ions (decreasing *I*), quantitative information on the elemental composition of organic matter in atmospheric particles and their changes over time can be obtained [22,23]. To circumvents the disadvantages of hard ionisation techniques, soft ionisation methods have been developed for online MS devices. Examples include chemical ionisation (CI) [24–26], e.g. proton-transfer-reaction (PTR) [27–29], photo-ionisation (PI) [30] and photoelectron resonance capture ionisation (PERCI) [31], where high-resolution mass analysers [32–34] can provide additional molecular specifity. In addition, tandem-MS can be performed in an ion trap (IT) mass analyser [27]. Using the mentioned online techniques for OA characterisation can provide excellent time resolution and an *I* value of $10 \leq I \leq 100$, depending on the ionisation method and the mass resolution of the analyser. In summary, there are several online MS techniques and instruments that have been used in the past and are constantly being developed to enable real-time chemical characterisation of OA in a turbulent atmosphere. Interested readers wishing to deepen their knowledge of these techniques are referred to the excellent reviews [12,13,26].

However, for certain atmospheric questions, relative ($I \leq$ 2–3) or

complete ($I = 1$) identification of individual organic components is required. Molecular analysis is needed to identify molecular markers that can be attributed to a specific source or process that generates OA. In addition, molecular analytical methods are inherently suited for quantitative analysis, which is crucial for determining the relative contributions of different sources or processes to OA. Analysing molecular markers can elucidate mechanisms and rates of aerosol formation and decay or reconstruct physico-chemical properties (e.g. the proportion of light absorbing molecules in the particles correlates with the ability to absorb solar radiation [35,36]). Nevertheless, molecular analysis of OA is analytically challenging due to chemical diversity, low concentrations, matrix effects, chemical transformations and sampling artefacts [37]. Atmospheric concentrations of organic particulate matter (PM) are in the order of 1–10 $\mu g/m^3$ with individual compounds ranging pg/m^3 to ng/m^3 [13,38]. Consequently, the sensitivity limits of analytical instruments can hinder accurate measurement of low-concentration species. Organic particulate matter consists of a diverse mixture of compounds originating from various sources such as biogenic emissions, combustion processes, and anthropogenic activities, and may contain thousands of different organic compounds with a wide range of chemical structures and properties, e.g. volatility or polarity [39–42]. Analysis of this chemical diversity requires techniques that can detect and characterise a wide range of molecules. Furthermore, the presence of other aerosol components, such as inorganic salts and water, can interfere with the analysis of organic compounds. Matrix effects can affect the performance of analytical techniques and lead to biased results if not adequately accounted for [11]. Furthermore, organic aerosols undergo chemical transformations such as oxidation reactions during atmospheric ageing [42,43] These transformations can change the composition and properties of organic compounds, complicating their identification and quantification. Finally, the collection and storage of aerosol samples can lead to artefacts or losses of volatile or semi-volatile compounds, which affects the representativeness of the analytical results [44]. To address these challenges, mass spectrometers with upstream gas or liquid chromatography are typically used for the molecular analysis of OA.

1.3. GC- and LC-MS for molecular analysis

GC-MS and LC-MS techniques are well suited for comprehensive analysis of OA and overcoming the challenges associated with its molecular characterisation. These techniques combine separation performance, sensitivity, selectivity, identification and quantification. Mass spectrometric detectors are the closest approach to a universal detector for organic compounds, offering high sensitivity combined with high temporal resolution. It is suited to ultra-trace analysis like no other technique, and has undoubtedly already contributed significantly to our understanding of the role of organic compounds in the atmosphere. In particular, off-line MS techniques that allow the use of tandem MS experiments (MS^n) or high-resolution mass analysers enable near-complete characterisation of atmospherically relevant compounds at trace concentrations [45]. This selectivity is crucial for distinguishing between different organic species in complex aerosol samples and reducing interference from matrix components [46]. In addition, MS systems can be easily coupled to chromatography systems such as GC or LC, allowing for even higher sensitivity, selectivity and $1 \leq I \leq 2$–3 due to excellent separation performance, as the separation of a complex OA mixture into individual compounds results in higher signal-to-noise ratios and smaller matrix effects [11,47]. While compounds are separated based on their affinity for the stationary phase in the LC column, separation in GC is essentially based on differences in volatility [48]. Depending on the choice of stationary phase for the separation columns, LC-MS and GC-MS can be used to analyse a wide range of organic compounds, including polar and non-polar species [49,50]. This versatility makes them suitable for studying the different chemical composition of organic aerosols originating from different sources and subject to different atmospheric processes. Finally, LC-MS and GC-MS allow the accurate quantification of organic compounds in aerosol samples by comparing the signal intensity of target analytes with that of internal or external standards [48]. This quantitative capability enables to determine concentration values and the assessment of the contributions of different sources to OA composition.

Application of GC-MS for the molecular characterisation of atmospheric OA dates back to the late 1970s [51–53] when a limited number of compound classes could be investigated. In recent decades, GC-MS has contributed significantly to our understanding of the contribution of OA and its specific sources to the atmospheric aerosol. Experiments in which particles from specific sources were analysed by GC-MS allowed accurate identification of molecular source signatures and at the same time expanded the number of compounds analysed. Examples include fossil fuel combustion in motor vehicles [54], biomass burning [55], cooking [56] or cigarette smoke [57,58]. Molecular markers identifying each source could consist of a single compound, e.g. Levoglucosan as the most prominent marker for wood combustion [59]. While GC-MS is a mature, robust method for molecular identification and quantification, there are significant limitations. Firstly, only a certain range of compounds can be eluted from the GC columns as many organic compounds are highly polar or thermally labile. Secondly, a certain amount of eluted organic compounds cannot be chromatographically resolved and identified, as quantitative GC-MS usually uses EI, which significantly increases I [60]. To partially overcome the limitation that many compounds are difficult to evaporate and to elute by GC, derivatisation methods have been developed, of which silylation [61] is the most prominent one [62,63]. To address the problem that atmospheric aerosol is complex on a molecular level and one-dimensional separations are sometimes not able to resolve the large number of compounds present, two-dimensional (2D)-GC methods have been implemented in atmospheric research [50]. These approaches focused on coupling 2D-GC with time-of-flight (ToF) mass analysers [64–69]. These techniques enabled an increase in the peak capacity, where the effluent from a non-polar primary column was collected at regular intervals and eluted through a polar secondary column [70,71]. Using this method, up to 10,000 different chemical species have been found in atmospheric samples [70]. GC-MS is usually favoured over LC-MS when analysing atmospheric aerosols because of its superior separation efficiency, high sensitivity, and relative resistance to ion quenching effects. Furthermore, 2D-GC couplings are more easily adaptable as modulation techniques are nowadays well implemented compared to 2D-LC setups [72]. Nevertheless, LC-MS plays a crucial role in the identification of polar, non-volatile and thermally labile molecules that cannot be eluted by GC, even if they have been derivatised.

An early study utilizing LC-MS with a reverse-phase column and electrospray ionisation (ESI) to investigate atmospheric aerosols revealed a complex array of species within the 100–800 m/z range [73]. Many nominal m/z values exhibited multiple chromatographic peaks, indicating the presence of isomeric and/or isobaric compounds. These findings emphasise the need for high-resolution mass measurements to distinguish isobaric elemental formulae and the need for authentic standards to confirm molecular assignments and enable quantitative analyses [12]. Another advantage of using LC-MS in aerosol science is the ability to analyse high molecular weight (MW) compounds, such as dimers and oligomers of secondary organic aerosols (SOA) [74,75]. Our understanding of SOA dimers and high MW compounds in atmospheric chemistry is still incomplete, but great efforts have been made in recent years. These compounds can make up a significant fraction of the organic aerosol mass and serve as precursors for nucleation and early particle growth [75–78]. Finally, great emphasis must be placed on the ability to operate LC-MS systems using soft ionisation techniques such as ESI, atmospheric pressure chemical ionisation (APCI) and atmospheric pressure photo ionisation (APPI). Electrospray ionisation is most commonly used for OA analysis with LC-MS but there are also several applications of APCI [79] and APPI [80–83], especially when aromatic

compounds are investigated. The use of soft ionisation techniques can decrease *I*, allowing the identification of new molecular markers. Moreover, it enables detailed, non-targeted analysis by identifying several thousands organic compounds at the molecular levels [77,84]. In combination with high-resolution MS techniques, $I \leq 2$–3 can be reached, which is not always possible with GC-EI-MS techniques. Nevertheless, LC faces the same challenge compared to GC-MS as it can only analyse and resolve a certain range of compounds. While GC-MS is limited to compounds that are volatile and stable enough, LC-MS is restricted to certain polarity ranges that depend on the stationary phase used in the separation column. To overcome this disadvantage, multidimensional LC techniques can be used. While 2D-GC-MS approaches are increasingly used in atmospheric chemistry, the number of applications for multidimensional LC techniques is comparatively low, although they are already well utilised in polymer analysis, biopharmaceutics or proteomics [72,85,86].

Accordingly, this review article discusses to what extent and for which atmospheric issues and samples one- and multidimensional LC techniques are applicable today or when one-dimensional techniques are even superior. Besides the addition of a second LC dimension, the incorporation of further detector dimension, such as the coupling of UV/Vis with MS detection or tandem MS experiments, is also discussed as an alternative way of obtaining extended information.

2. Analytical approaches and resulting analytical conditions

In the chemical characterisation of organic aerosols, there are essentially three analytical approaches, which must satisfy different instrumental criteria: targeted analysis (TA), non-targeted analysis (NTA) and semi-targeted analysis (STA). Fig. 1 shows the schematic representation of exemplary data generated with TA, NTA and STA approaches in the field of atmospheric organic aerosol research.

2.1. The targeted approach

In the context of TA, a selected number of previously determined target compounds are analysed. The selection of the analytes is subject to their atmospheric chemical significance or uniqueness as so-called marker substances for sources or source processes. Targeted methods have very high selectivity and often better sensitivity than non-targeted methods and are therefore especially suitable for the quantification of ultra-trace concentrations. However, TA can only be performed if an authentic standard of the analyte is available. A number of target analytes representing oxidation products of important biogenic volatile organic compounds (BVOCs) in the atmosphere, such as isoprene, monoterpenes, and sesquiterpenes, are commercially available [13]. For many other oxidation products of both, anthropogenic and biogenic origin, the same is not true and those products have to be synthesised in the laboratory. A good overview of synthesised reference standards for corresponding oxidation products that are not commercially available can be found in Refs. [13,87]. The quantification of the analytes is comparatively straightforward due to the use of internal and external standards for the selected analytes. In addition, the desired performance criteria of the method, i.e. thresholds for selectivity, sensitivity, accuracy, and precision, are well defined, generally accepted, and adaptable to any application [88].

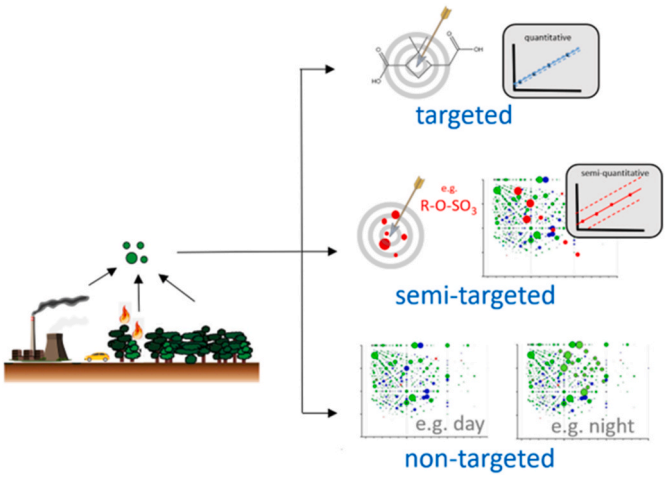

Fig. 1. Schematic representation of TA, NTA and STA approaches in the field of atmospheric organic aerosol research. While pinic acid, as a biogenic SOA marker, can be precisely quantitatively determined in the TA, the determination of organosulfates in the STA is only semi-quantitative. For the NTA, for example, a qualitative comparison of two van Krevelen plots is made to visualise diurnal influences on the chemical composition of OA.

The determination of molecular markers in submicrometer aerosol is important because it can provide information about aerosol sources or ageing processes such as oxidation or formation of light-absorbing compounds. Interested readers will find a good review article on markers for biomass combustion in Ref. [55] and on markers for SOA formation from isoprene in Ref. [89]. Furthermore, there are numerous individual articles on suitable marker substances for SOA formation from monoterpenes and sesquiterpenes [90–94] as well as aged organic aerosol [95,96]. In addition, interest in the dedicated determination of stereoisomers in aerosol chemistry, particularly from biogenic hydrocarbons, has increased in recent years [97–100]. For example, Leppla et al., 2023 quantified the optical isomers of α-pinene oxidation products in OA using a chiral stationary phase (CP) by LC-MS measurements and showed, using vertical profiles in the Amazon rainforest, that the chiral ratio of α-pinene oxidation products varied at different heights above the forest canopy. The authors concluded that characteristic emissions of chiral aerosol precursors from different forest ecosystems could provide large-scale information on differential contributions to biogenic SOAs through analysis of chiral particle-bound degradation products [101]. In addition to the increasingly specialised markers for terrestrial biogenic SOA sources, there is further work on biomarkers for marine aerosol [102,103], fungal spores [104,105], and anthropogenic sources [106,107].

Clearly, the TA is a very popular approach in organic aerosol research which is constantly expanding and requires excellent LC-MS methods to enable identification and quantification at trace concentrations. The most commonly operated LC technique is reversed-phase chromatography (RPLC), as it allows separation of a wide range of medium-polar to non-polar compounds. For highly polar species, variations of normal phase chromatography (NPLC), such as hydrophilic interaction liquid chromatography (HILIC), are applied. For more specialised applications, ion exchange (IEC) or size exclusion chromatography (SEC) are also used. In terms of detectors, mass spectrometers with MS/MS capabilities such as ToF-MS or triple quadrupole mass spectrometers (tQ-MS) are commonly applied for TA. An overview of current and known LC-MS methods is given in Table 1.

2.2. The non-targeted approach

An NTA ideally searches for all organic components present in the sample, both known and unknown, maximising the number of compounds detected. By recording and storing all detectable signals, an inventory of the chemical composition of each sample is permanently available for further analysis. Non-targeted approaches are most appropriate for detecting unexpected changes in chemical composition. The goal is to maximise the number of substances detected providing the opportunity to observe unexpected changes. NTA also makes it possible to find new molecular markers for atmospheric processes or sources, which is essential for the advancement of atmospheric chemistry research. In particular, important atmospheric processes where more knowledge is still needed, such as the role of organic compounds in

Table 1
List of examples for applying different one- and multidimensional LC and MS methods and analytical approaches to characterise atmospheric organic aerosols in different samples in recent years. Multidimensional LC methods are written bold.

Targeted approaches

Analytes	Sample, Analytical approach	Extraction	Analysis Technique	References
Aliphatic & aromatic carboxylic acids	Filter	Water	RPLC-ESI-ToF-MS	[108]
Aliphatic & aromatic aldehydes and ketones	Speleothems	MeOH	RPLC-ESI-HR-Orbitrap-MS	[109]
	Filter	ACN/Water 1/1 + 2,4-DNPH	RPLC-UV/Vis	[110]
	Filter	MeOH/Water 1/1 + 2,4-DNPH	RPLC-UV/Vis-ESI-IT-MS/MS	[111,112]
	SPE	ACN/Water + 2,4-DNPH	**RPLCxRPLC-UV**	[113]
Phenols	Filter	ACN/Water	RPLC-ESI-IT-MS	[114]
Nitroaromatics	Filter	MeOH	RPLC-ESI-MS/MS	[115]
Heterocyclic & aliphatic amines	Filter	Water	RPLC-ESI-QqToF-MS/MS	[116]
	Filter	MeOH	RPLC-ESI-IT-MS/RPLC-APCI-IT-MS/RPLC-APPI-IT-MS	[80]
	Filter	MeOH	RPLC-UV	[117]
Terpene-oxidation products	Filter	Water	RPLC-ESI-IT-MS	[118]
Pinic acid, Pinonic acid	Ice cores	Evaporation	**mRPLC-CP-ESI-HR-Orbitrap-MS**	[119]
	Filter	MeOH/Water 9/1	CP-ESI-HR-Orbitrap-MS	[101]
	Filter	Water	RPLC-ESI-tQ-MS/MS	[120]
Anhydrosugars	Speleothems	MeOH	RPLC-ESI-HR-Orbitrap-MS	[121]
Sugar alcohols	Filter	MeOH	NPLC-ESI-MS	[122]
Polycyclic aromatic hydrocarbons	Filter	Ethylacetate	RPLC-MS/MS	[123]
	Filter, PUF	ACN	RPLC-UV/Vis	[124]

Semi-targeted approaches

Analytes	Sample, Analytical approach	Extraction	Analysis Technique	References
Aliphatic & aromatic carboxylic acids	Filter	MeOH	**SCXxRPLC-ESI-ToF-MS**	[125]
	Filter	Water	NPLC-ESI-MS/MS	[126]
	Filter	MeOH/Water 9/1	RPLC-ESI-QqToF-MS	[127]
Organosulphates	Filter	MeOH	**mRPLC-RPLC-ESI-IT-MS**	[128]
	Filter	Water	NPLC-ESI-MS/MS	[126]
	Filter	Water	HILIC-ESI-MS/MS	[107]
	Filter	MeOH	HILIC-ESI-QToF-MS	[129]
	Rain, snow, hail	Evaporation	RPLC-ESI-HR-MS	[90]
Carbohydrate-like substances	Filter	Water	NPLC-ESI-MS/MS	[126]
Nitroaromatics	Filter	MeOH	RPLC-UV/Vis	[130]
	Filter	MeOH/Water 9/1	RPLC-ESI-QqToF-MS	[127]
Heterocyclic amines	Filter	MeOH/ACN 1/1	RPLC-ESI-QqToF-MS	[131]
Terpene-oxidation products	Filter	MeOH	**SCXxRPLC-ToF-MS**	[125]
Pinic acid, Pinonic acid	Filter	MeOH	RPLC-ESI-HR-Orbitrap-MS/MS	[95]
	Filter	MeOH/Water 9/1	RPLC-ESI-QqToF-MS	[127]
	Filter	MeOH	**SCXxRPLC-ESI-ToF-MS**	[125]

Non-targeted approaches

Identified species	Sample	Extraction	Analysis Technique	References
Organic acids, anhydrosugars, sugar alcohols, terpen-oxidation products	Ice cores	Evaporation	**HILIC-RPLC-ESI-HR-Orbitrap-MS**	[132]
Organic acids, nitophenols	Rainwater, filter	Evaporation, ACN/Water 1/1	RPLC-ESI-HR-Orbitrap-MS	[133]
Organic acids, aldehydes & ketones, phenols, nitroaromatics. benzenes	Filter	MeOH	RPLC-ESI-ToF	[134]
Terpen-oxidation products	Filter	MeOH	RPLC-ESI-HR-Orbitrap-MS	[77]
Terpene-oxidation products, nitroaromatics, organosulpates	Ice cores, filter	SPE, MeOH/Water 14/1	RPLC-ESI-HR-Orbitrap-MS	[84]
Organosulphates, reduced N-containing compounds, PAHs	Filter	Water, SPE	**mSEC-RPLC-ESI-FT-ICR-MS**	[135,136]
Organosulphates	Filter	ACN/Water 1/1	RPLC-ESI-HR-Orbitrap-MS	[137]
Plasticisers, flame retardants, pesticides, drug metabolites	Dust, filter	MeOH, SPE	**RPLCxRPLC-ToF-MS**	[138]
Sum of water soluble organic matter	Filter	Water	**HILICxSEC-UV-FLD**[a]	[139]
	Filter	Water	**HILICxSEC-UV/Vis**[a]	[140]

[a] No molecular analysis.

nucleation, cloud formation processes or in the ageing and processing of aerosol components, would benefit from the identification and characterisation of new molecular markers. The challenges here are generally similar to those in environmental science, engineering, and regulation, where a variety of known but also unknown organic contaminants exist, and the use and advancement of non-target methods based on high-resolution mass spectrometry have greatly expanded the analytical window in recent years [141]. However, while the performance evaluation of analytical methods in TA is already widely known and accepted, the performance criteria for analytical NTA methods are not yet universally defined. Interested readers will find a discussion on the definition of NTA performance criteria in Ref. [88].

HR-MS instruments suitable for routine analysis are now affordable and capable of detecting thousands of substances almost simultaneously and sensitively, if necessary, within the short time required for chromatographic separation. The essential criteria for high-resolution mass spectrometry are a high mass resolving power, but also a high mass accuracy. Initially, Qq-ToF-MS were used, but in recent years, Fourier transform mass spectrometers (FT-ICR-MS) and Orbitraps, have been increasingly operated (see Table 1). This allows the determination of unique molecular formulas for each ion peak. This development has given NTA a tremendous momentum, also in the analysis of organic aerosol constituents. The organic fraction of atmospheric aerosols contains hundreds to thousands of species in an m/z range of 100–500, and often more than 10 compounds are observed within 0.1 Da (Da), emphasising the need for high mass resolution [13,142]. Therefore,

compared to a TA, an NTA can be used to analyse a larger fraction of the organic mass. The number of matching theoretical formulas, and thus the *I* - value, depends on the accuracy with which the measured MW is determined and increases exponentially with MW. For MW > 300, identification also requires additional information, such as isotopic composition or fragmentation (tandem MS).

Nevertheless, the high mass resolution of HR-MS allows direct input of the collected aerosol samples into an ion source, usually in the form of filter extracts (aqueous or organic solvents) by direct infusion. The idea is obvious since the omission of chromatographic preseparation increases the number of compounds detected (limited by the choice of solvent for extraction and detectability) and allows higher measurement frequencies. For these reasons, methods using direct infusion have also been successfully applied several times in atmospheric aerosol analysis [143–145]. However, this method always includes the risk of producing artefacts due to adduct formation in the ion source, thereby also increasing complexity and, last but not least, raising questions about quantification by ion suppression. Particularly with the goal of building the non-target approach on the detection of real individual substances (avoiding ion source artefacts), the coupling with LC is advised, accepting that the fraction of the analysed organic mass may decrease. Currently, reversed-phase (RP)LC-HR-MS methods are most commonly used for the characterisation of OC in NTA in aerosol chemistry because they can cover a comparatively wide polarity range of analytes [77,84,133].

The increasing complexity and size of the datasets in terms of individual compounds imposes new requirements and challenges regarding the interpretation and visualisation of NTA results. Discussion and interpretation of data generated by NTA is usually facilitated by visualisation methods that categorise and group data sets to identify patterns (see Fig. 1.). For example, these patterns allow discrimination between different sampling locations or different atmospheric processes. Popular visualisation methods include plotting double bond equivalents (DBE) [146,147], element ratios (e.g. van Krevelen diagrams) [77,84,142], degree of oxidation [77,84,142], or are based on Kendrick mass analysis [147]. Recently, Zhang et al. also introduced the maximum carbonyl ratio (MCR) as a new index and visualisation method for structural classification of SOA components in NTA [148]. More detailed explanations of the various methods can be found in Ref. [13].

2.3. The semi-targeted approach

Semi-targeted methods are a hybrid between untargeted and targeted approaches. This approach aims to quantify a large number of substances whose identity is often known only in terms of their substance class. This method usually uses a calibration curve generated for one or a few reference compounds for a whole class of substances (i.e. compounds with a similar chemical structure) instead of generating a separate calibration curve for each target analyte. The approach therefore allows the quantification (or semi-quantification) of analytes for which there is no authentic standard for the generation of external calibrations. For STA, as for NTA, high-resolution mass spectrometers are required, which is why Orbitrap-MS or Quadrupole-ToF-MS are often used.

In the field of SOA analysis, STA is currently widely used for the analysis of monoterpene and isoprene SOA markers and organosulphates (OS) [149,150]. In recent years, numerous studies have been conducted on the molecular characterisation, formation mechanisms, and source attribution of SOAs from isoprene. For molecular characterisation, mass spectrometric methods combined with separation techniques play a crucial role. Chamber experiments and tandem MS measurements have allowed the identification of many organic markers, and the preparation of some reference compounds has enabled unambiguous structural characterisation [95,129,151–153]. Interested readers will find an excellent review article on the current state of research on SOA formation of isoprene in Ref. [89]. Chemically structurally similar standards are often used for the quantification of isoprene SOA markers, in this case erythritol and threitol for the quantification of 2-methyltetroles and C_5 -alkentrioles [5,154,155]. Furthermore, response factors of camphorsulfonic acid, methanesulfonic acid, and octylsulfate have been used for the quantification of organosulfates [156,137]. In addition to isoprene SOA and OS markers, imidazoles also represent a class of compounds in atmospheric aerosol particles that require the use of STA due to an insufficient number of authentic standards. Recently, STA was combined with data driven acquisition and auto-MS/MS scans measurements using UHPLC-HR-MS/MS to quantify ten imidazoles using reference standards, identify five imidazoles without standards, and discover three imidazoles that had never been measured before [157,131]. In this example, using STA is superior to TA in terms of effectiveness and information gain. Nevertheless, using response factors for accurate quantification of marker substances can lead to significant over- or underestimation of the specific concentrations. For example, camphorsulfonic acid, methanesulfonic acid and octylsulfate show a large difference in ESI response compared to authentic terpene-derived organosulfates, which has led to an underestimation of OS concentrations in PM of several orders of magnitude [133]. It should be remembered that STA can only indicate trends of concentration, while reliable quantitative results can only be achieved with TA.

Generally applicable performance criteria exist for the STA in hybrid form. First, performance can be judged by the generally applicable thresholds for selectivity, sensitivity, trueness, and precision of the method, relative to the standards used. For the identification of new compounds, the current state of performance evaluation is the same as for NTA methods, whose evaluation the interested reader will find in Ref. [88]. Analytically, the same requirements are necessary for an STA as for a TA.

3. Instrumental approaches

Fig. 2 gives an overview of the most commonly used multidimensional LC or MS techniques that are used to characterise atmospheric organic aerosol and discussed in this chapter. For multidimensional LC and MS techniques, it is possible to add either a second LC dimension (LCxLC, LC-LC or mLC-LC) or a second detector dimension (UV/Vis or MS). In general, the addition of a second detector or LC dimension leads

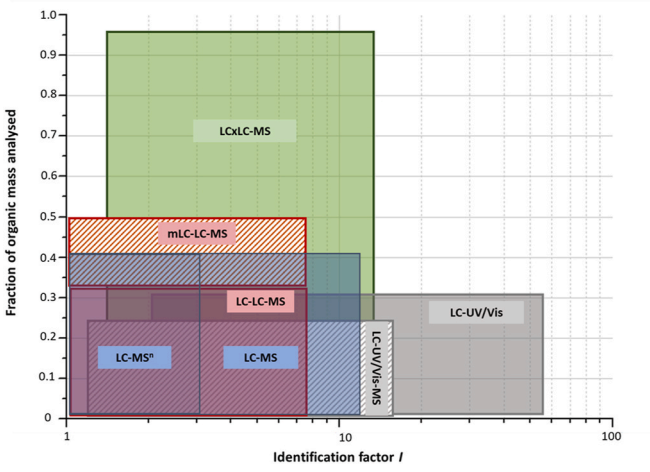

Fig. 2. Summary of the most commonly used multidimensional LC or MS techniques used to characterise atmospheric organic aerosols as function of their *I* factor. A decreasing *I* factor describes the increasing ability of the corresponding technique to identify the molecular structure of a compound and is based on literature values. The *y*-axis represents an estimate of the fraction of the total organic mass of atmospheric aerosols that is characterised by a technique. Modified from Noziere et al., 2015.

to a significantly reduction of *I*. Regarding the fraction of organic mass analysed, visualisation is more difficult, as the addition of a second detector dimension (LC-UV/Vis-MS or LC-MS^n) or a second LC dimension can increase or decrease the fraction of mass analysed.

3.1. LC-UV/Vis and LC-UV/Vis-MS

Based on years of availability and widespread use alone, abundant work exists on LC-UV/Vis or LC-MS analyses for the characterisation of organic aerosol components. UV/Vis spectroscopy is comparatively nonspecific in the characterisation of atmospheric aerosols, allowing mainly the identification of specific compounds or functional groups ($I \geq 100$). Coupling with LC significantly improves the level of identification as it provides information on retention times and allows comparison with reference standards what makes it extremely suitable for TA. LC-UV/Vis analysis has become particularly important for the determinations of harmful compounds such as PAHs, which are strong UV chromophores due to their aromatic structure. Although the introduction of more sensitive GC-MS methods has led to a decrease in work using UV absorption alone, the UV detector continues to be a reliable and easy-to-use detector that responds universally to chromophoric compounds. Interested readers can find an informative review article on the current state of instrumental analysis of PAHs in aerosols in Ref. [158].

For the analysis of non-chromophoric compounds, a derivatisation step must be performed when UV/Vis is used as detection system. On one hand, this increases the time required for method development and sample preparation and limits the proportion of organic matter analysed, but at the same time increases selectivity and allows $I < 10$. In aerosol analysis, carbonyl compounds are usually detected using this method. For these, 2,4-dinitrophenylhydrazine (2,4-DNPH) or pentafluorobenzyl hydroxylamine (PFBHA) are most commonly used for derivatisation, providing comparable detection limits to GC-MS methods [159–161]. In addition, pre-column or post-column derivatisation methods have been developed. Over time, LC-UV/Vis methods have been further improved by performing couplings with tandem MS detections. The coupling of LC-UV/Vis detection with mass spectrometers allows very good degrees of identification, since the information of optical properties and polarities is extended by the information dimensions of MW or even fragmentation patterns. This methodology is particularly attractive in aerosol analysis for the characterisation of light-absorbing organic species (brown carbon) [162–164]. A good overview of the different analytical techniques for humic substances and brown carbon can be found in Refs. [36,165]. For example, by coupling UV/Vis with MS detectors, the selectivity in the detection of glyoxal and methylglyoxal in aerosol samples could be significantly increased [166, 111]. In addition, this approach has been used in the study of chromophoric nitrogen-containing compounds such as nitroaromatics and imidazoles [112,118].

3.2. LC-MS^n

Due to the increasing use of MS/MS capable mass spectrometers (also called tandem MS, MS [2] or MS^n), more and more laboratories are using these instruments for organic aerosol analysis. Here, the selection of selected ions of a particular mass followed by fragmentation of these ions and detection of the fragments provides additional information which is extremely helpful in both, identification and quantification. Fragmentation of the selected *m/z* can occur spontaneously or through an activation process. In addition, it is possible to increase the number of fragmentation steps (MSn with $n > 2$) and further fragment the ions formed in the first fragmentation step. Interested readers will find an excellent review article on the fundamentals and instrumental capabilities of MS/MS techniques in Ref. [167], while here we only discuss the possible applications of corresponding MS^n experiments with respect to atmospheric aerosol analysis.

Depending on instrumental requirements and availability, four types of tandem MS experiments are possible: product ion scanning, precursor ion scanning, neutral loss scanning, and selected/multiple reaction monitoring. Fig. 3 shows a schematic explanation of the different types of MS^n experiments.

3.2.1. Product ion scanning

Product ion scanning in combination with LC is commonly used when analysing organic aerosols with mass analysers such as triple-quadrupole-MS [120] (see Fig. 3), ion traps [168–170], Orbitraps [150,171], FT-ICR-MS [172] and Qq-ToF-MS [173]. In product ion scanning, a precursor ion species is first selected and analysed in the first mass spectrometric dimension (e.g. first quadrupole in case of tQ-MS). This precursor ion species is then fragmented, either by collision with a neutral gas in a collision cell or by other fragmentation mechanisms. The resulting fragments, also called product ions, are then scanned in a second MS dimension (e.g. third quadrupole) and their *m/z* value is determined. This scan mode offers the highest degree of molecular identification and has therefore been frequently used in the past to elucidate the molecular structures of aerosol components. It is particularly useful for obtaining structural information on small organic molecules (MW < 300) and has been successfully used especially in the field of SOA research. Structural information includes both characteristic product ions and neutral losses, which provide information not only about functional groups but also on other structural features such as the location of functional groups. Product ion spectra have also proven useful to derive structural information about the monomeric units of dimers or high MW oligomers [172]. Finally, based on the work with product ion scanning of the target analytes, multiple reaction monitoring (MRM) methods for their quantification are elaborated for the selected components (see below).

3.2.2. Precursor ion scanning

Compared to product ion scanning, precursor ion scanning detects fragment ions of a specific *m/z* in the second mass spectrometric dimension, while all *m/z* that produce the selected fragment ion are scanned in the first dimension. In this way, the precursor ions of the specific fragment can be detected. Precursor ion scanning is commonly utilised with triple quadrupole MS [174] (see Fig. 3), but there are also applications with e.g. ion traps [175] or Orbitraps [176]. It has occasionally been used for screening complex atmospheric aerosol samples. For example, the method has been used to monitor nitroaromatic compounds leading to *m/z* 46 (-NO_2) [174,177].

3.2.3. Neutral loss scan

Neutral loss scans are usually utilised by triple quadrupole MS to analyse OA. In the neutral loss scan, two quadrupole analysers (Q1 un Q3) are scanned with a constant mass offset x. Thus, if an ion of a certain *m/z* ratio fragments into q2 with the defined mass difference x, these ions can successfully pass Q3 and be detected (see Fig. 3). Similar to precursor ion scanning, this scanning mode is useful when the analysis of specific functional groups is desired, i.e., when the focus is not necessarily on individual compounds but on entire compound classes. For example, the neutral loss scan has been used to monitor carboxylic acids after conversion to methyl esters by detecting the loss of methanol (*m/z* 32) [178], to determine carbonyl compounds after conversion to hydrazones and a neutral loss from hydrazone fragmentation [177] or to identify organic hydroperoxides [179]. In addition, nitroaromatic compounds have also been analysed, in this case by the loss of NO (*m/z* 30) [174,178].

3.2.4. Selected reaction monitoring

In selected reaction monitoring (SRM), or multiple reaction monitoring (MRM), only selected *m/z* are recorded in the first and second mass spectrometric dimensions. Accordingly, no scanning takes place. Here, ions selected by the first mass analyser are detected only when

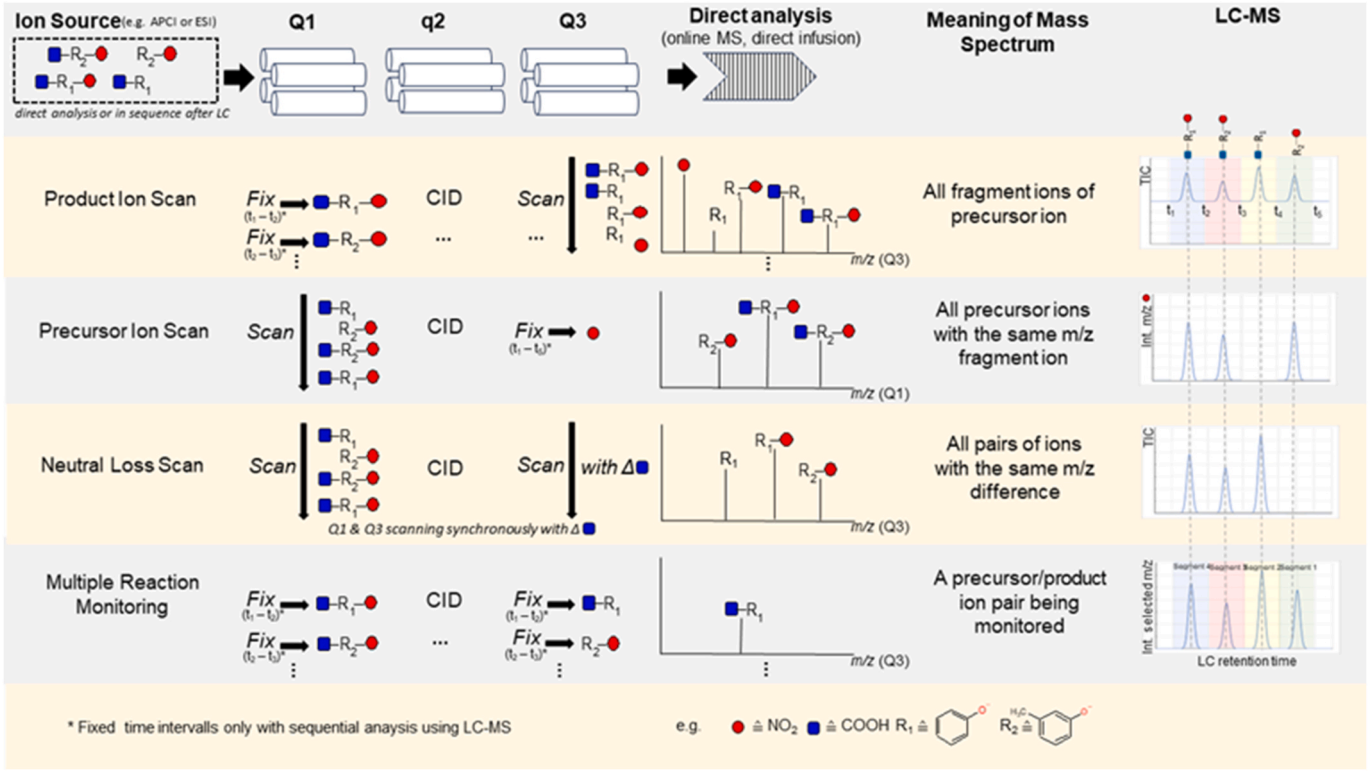

Fig. 3. Tandem mass spectrometry scan modes. (1) Product ion scan: selection of precursor ion with Q1 and scanning with Q3. (2) Precursor ion scan: scan all precursor ions in Q1 that produce a specific fragment ion that is selected in Q3. (3) Neutral loss scan: scanning all ions with a constant mass difference in Q1 and Q3 simultaneously. (4): Multiple reaction monitoring: selection of precursor ion in Q1 and monitoring one or more selected fragment ions in Q3.

they produce a specific fragment by a selected reaction. Since no scanning occurs, the precursor and fragment ions can be in focus for extended periods of time, which increases both, sensitivity and selectivity. High selectivity corresponds to a low probability of detecting an interfering compound, reducing background noise and eliminating most interferences (smaller background in the LC chromatogram in Fig. 3). SRM and MRM are commonly utilised in the analysis of organic aerosols with triple quadrupole MS [115,130,180–182] (see Fig. 3) or ion traps [115,130,183]. The monitoring of selected/multiple reactions is particularly useful to confirm beyond doubt both the presence and quantity as well as the identity of compounds in atmospheric samples. This has been used, for example, to detect carboxylic acids and nitroaromatics [115] as markers for biomass combustion [130]. The MRM scan mode is specific and very sensitive, but can only be performed with STA or TA, as the target analyte must be known in advance and well characterised.

It is clear that tandem MS experiments have significant potential for the analysis of atmospheric organic aerosols. When combined with LC, they represent very advanced analytical tools for both, detection and detailed mass spectrometric characterisation of organic components in complex atmospheric samples. LC-MS^n methods have an increased capacity through efficient structure elucidation and selective detection capability, high sensitivity, and enable rapid analyses of complex mixtures.

3.3. Two-dimensional liquid chromatography

The essential concept of 2D LC is to collect one or more fractions from the 1D column (sampling) and transfer them to a 2D column (modulation). The task of the second column is to separate all analytes that were not resolved in the first dimension based on a different selectivity. If the selectivities, i.e., the retention mechanisms, are independent in two dimensions, the separations are called orthogonal. The latter should be aimed at in order to obtain as much information as possible about the sample under investigation. In liquid chromatographic aerosol analysis, HILIC is usually coupled with RPLC, SEC with RPLC, or CP with RPLC (see Table 1). In the following, we discuss three different instrumental possibilities of how this 2D separation procedure is performed in practice: heart-cut LC (LC-LC), multiple heart-cut LC (mLC-LC), and comprehensive LC (LCxLC). Fig. 4 shows an explanatory illustration of the three modes. Readers interested in learning the detailed instrumental chromatographic setup of each mode are referred to the excellent reviews [85,86,184].

3.3.1. Heart-cut LC (LC-LC)

Heart-cut LC is particularly suitable for TA and represents the two-dimensional method with the smallest fraction of organic mass analysed, but also the smallest *I*-value. In this 2D approach, a single fraction of the first dimension is collected and then injected into a 2D column for further separation. This is usually done via a second valve equipped with a sample loop whose volume is sufficient to hold the entire 1D eluent fraction of interest. LC-LC methods are useful for separating a single target analyte from a complex matrix or for reducing assignment uncertainty. In general, high-purity analyte signals are obtained. Therefore, heart-cut LC methods are ideally suited for aerosol analysis, e.g., to separate stereoisomers. Other advantages of heart-cut LC methods are the very high resolving power, the additional selectivity provided by the second dimension, the wide range of different retention mechanisms, and the ease of combination with MS and tandem MS techniques [85]. However, high-precision quantifications are difficult to achieve with heart-cut methods, e.g., because retention time changes can be caused by matrix effects in real samples or by minor variations in solvent composition. In addition, lower detection sensitivities and problems with incompatibility of phase systems in the two dimensions can be challenging.

As indicated above, cutting out a retention time window of the first

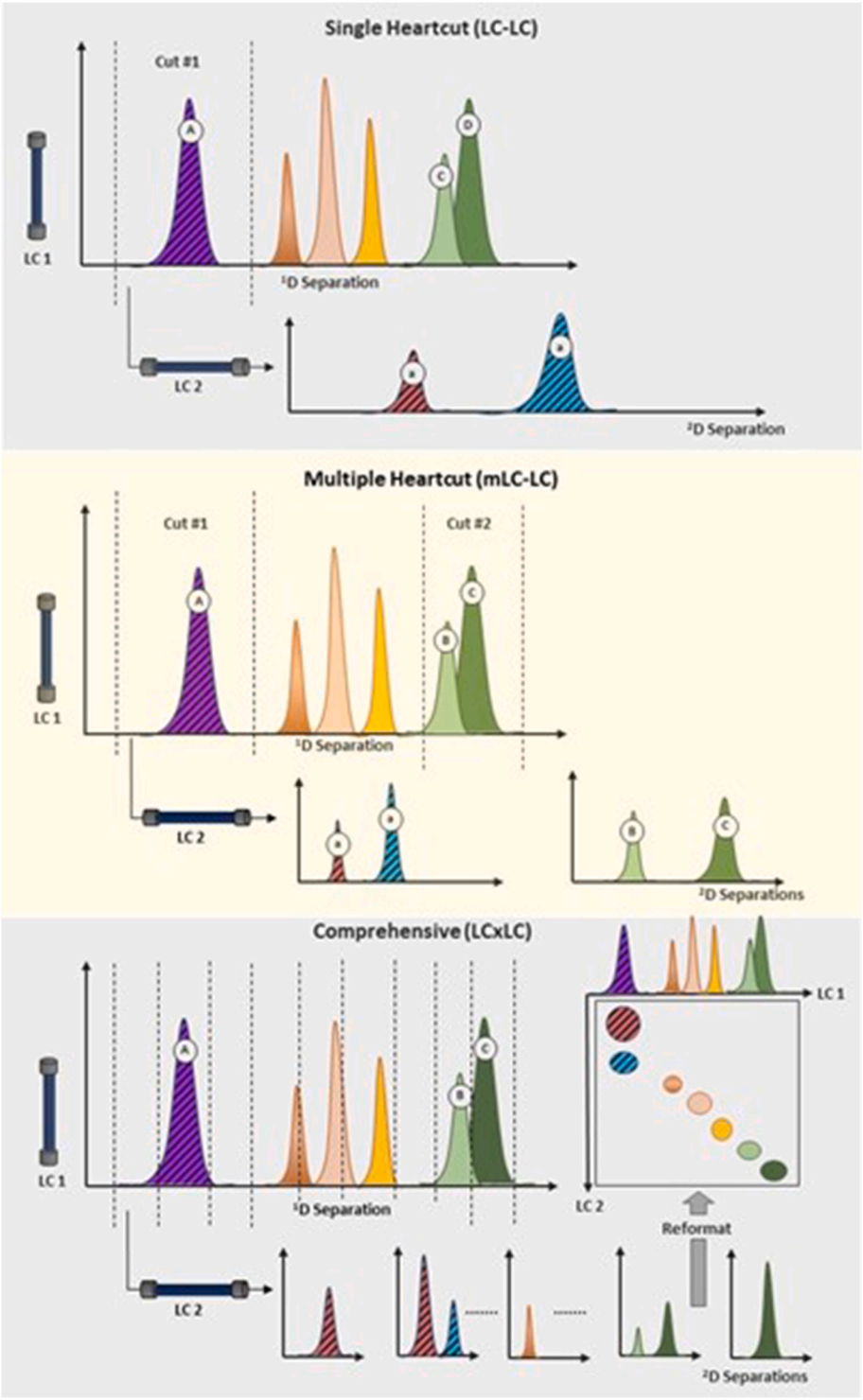

Fig. 4. Illustration of three different modes of 2D LC separation: Heart-cut LC where one (single heart-cut) or more (multiple heart-cut) selected fractions of the 1st dimension are collected and injected into a 2nd column and comprehensive LC where the whole 1D effluent is injected into the 2D column. Modified from Ref. [85].

separation makes the fraction of the analysed organic mass quite small, thus not at all comprehensive in the sense of detecting the largest possible number of components present. This is different if the heart-cut is the void volume region of the first separation, since e.g. in the case of a separation on HILIC phases, the majority of the less polar compounds leave the column at this stage. If this volume is now subsequently separated with an RP phase, one could speak of a quasi-comprehensive analysis. Beschnitt et al. used exactly this type of coupling to study organic atmospheric components in ice cores using an NTA. The researchers collected the void volume of the HILIC column in a sample loop, analysed the separated signals within the first HILIC dimension, and then, while the HILIC column was running in re-equilibration settings, the void volume was analysed in the second RP dimension. In this way, information from the first HILIC dimension was retained while additional information on lower polarity compounds was provided without the need to extend the run time of the method. The method provided good reproducibility and very low detection limits. An example of the obtained results is shown in Fig. 5. While the one-

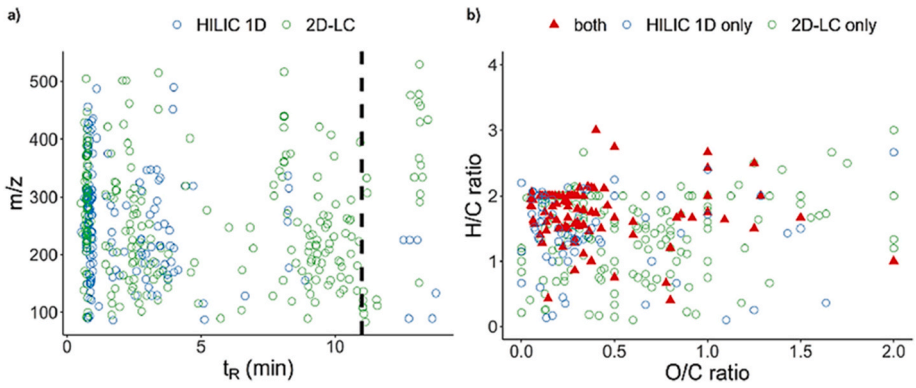

Fig. 5. Example of obtained results by using HILIC-RPLC-HR-Orbitrap-MS as quasi-comprehensive analysis to characterise organic aerosols in ice core samples. The void volume of the 1st HILIC dimension was heart-cut and injected into the 2nd RPLC dimension. (a) plot of *m/z* to retention time (t_R) of signals detected only in the 1D HILIC method (blue) and only in the 2D approach (green). The switch between the two dimensions is marked at $t_R = 11$ min (black). (b) Van-Krevelen plot of H/C to O/C ratios of all signals detected in the 1D HILIC method (blue), 2D HILIC-RPLC method (green), and signals detected by both methods (red). Modified from Ref. [132]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

dimensional HILIC method provided 177 signals, significantly more signals were obtained with the dead-time heart-cut method, beneficial for both, TA and NTA [132].

3.3.2. *Multiple heart-cut LC (mLC-LC)*

The mLC-LC method is a simple extension of heart-cut LC-LC in which individual fractions from several 1D peaks are successively transferred to the second dimension for further separation. This expands the proportion of organic matter analysed, as more analytes can be detected in a single chromatogram [184]. Similar to heart-cut LC-LC methods, mLC-LC systems are particularly suitable for TA, but also open up possibilities for STA.

An interesting application of one type of mLC-LC analysis was a two-dimensional offline chromatographic fractionation for the characterisation of HULIS in atmospheric aerosol particles. PM10 was collected on filters, extracted, followed by a solid phase extraction (SPE) and then separated into five molecular size fractions (SEC) in the first dimension. The five fractions were collected, processed and separated into more eleven fractions with different polarities in the second reversed phase dimension. The RP fractions were collected and processed again and then analysed with direct infusion ESI-FT-ICR-MS by applying a NTA. An interesting result was that the number of assigned molecular formulas increased by a factor of 2.3 for the fractionated sample (18144) compared to bulk sample analysis without fractionation (7819) and allowed the identification of 71240 isomeric compounds [135,136]. Accounting for these isomers with a mLC-LC method could provide both better identification levels (lower *I*-values) and a higher fraction of organic mass analysed compared to direct infusion MS. Other researchers used an mLC-LC method to elucidate the structure of certain organosulfate derivatives and coupled two reversed-phase LC columns simultaneously with an ESI-IT-MS^n and ESI-ToF-MS. The 1D separation was used to obtain the MW distribution of analytes, preliminarily quantify organosulfates and nitroxyorganosulfates, and clean up for 2D separation. Selected 1D fractions were further analysed with the second column to perform tandem MS experiments. This was to ensure that the dimers, oligomers and organosulfates detected in the 1D chromatogram were not caused by artefact formation in the ion source. The researchers found that the molecular weight of nitroxy organosulfates can be as high as that of dimers previously detected in monoterpene oxidation experiments. Furthermore, these compounds were very abundant in the nocturnal samples. The use of a 2D LC approach in this early work enabled the separation of isobaric compounds and improved identification and quantification of organosulfate derivatives, which was of great importance for understanding nocturnal chemistry in aerosol formation [128].

3.3.3. *Comprehensive LC (LCxLC)*

In general, LCxLC methods aim to obtain as much information about the sample as possible from a single 2D run. Therefore, comprehensive 2D LC is particularly suitable for NTA of atmospheric aerosols, as it is able to analyse a large fraction of the organic mass when two orthogonal stationary phases are used. There is a wide range of different retention mechanisms and additional selectivity due to the second dimension. The chromatograms obtained are structured and easy to interpret, and groupwise separation of analyte classes is possible. Compared with 1D LC methods, the uncertainty of peak assignment is much lower, and coupling with MS and tandem MS techniques is possible [85]. In addition, high peak capacities (1.000–10.000) and high peak reproduction rates (typically 1 peak per second) are routinely enabled. It should be noted, however, that very few LCxLC systems have been used in atmospheric aerosol analysis [72]. In 2006, Pol et al. coupled a strong cation exclusion (SCX) column with a RP column in an LCxLC-ESI-ToF-MS setup to study acidic components in rural and urban atmospheric samples following a STA approach. The authors concluded that the comprehensive 2D LC setup was simple and easy to use, and identification from contour plot positions together with mass spectral information was more reliable than in the 1D LC-MS setup. Many compounds and their possible isomers could be determined in one run. Quantification of individual compounds was also reliable and reproducible, providing detection limits of 2–200 ppb [125].

It is clear that 2D LC methods have great potential for aerosol analytical applications, especially for NTA and STA, but have found comparatively little acceptance in atmospheric science. There are certainly several reasons for why this is the case. In contrast to GC, multidimensional LC presents both, a difficulty in mobile phase compatibility and a greater risk of undersampling the effluent from the first dimension [85]. Also, the low detection limits essential in the analysis of atmospheric aerosols are difficult to achieve with existing 2D LC methods. At the very least, this leads to the need to use the optimal column combinations and chromatographic separation conditions in both dimensions, the latter requiring the optimisation of several parameters (mobile phase composition, isocratic and/or gradient elution, sampling rate and loop volume of the modulator, column dimensions and flow rates). Last but not least, the very small number of instruments and software packages for LC × LC available on the market hinders a widespread use of this technique also in aerosol analysis. A more detailed discussion of this issue in the context of environmental analysis can be found in Ref. [72].

4. Future perspectives

The developed analytical techniques and their application presented in this review highlight the tremendous increase in interest in organic aerosols over the past few decades, as well as the considerable progress that has been made in analytical techniques for their study. Certainly, this has provided a clearer picture of the myriad organic compounds in the atmosphere, their sources, and their contribution to important processes such as air quality, or their role in chemical cycles between biosphere and atmosphere. By identifying markers, not only sources of aerosol components are accessible but also changes in aerosol composition during their atmospheric lifetime, especially for biogenic and anthropogenic secondary organic aerosols but also in the context of aerosol particles formed by biomass combustion. Thus, the understanding of the close relationship between gas and particle chemistry, the resulting SOA formation and its contribution to atmospheric chemistry and climate has made considerable progress, especially the quantitative treatment of organic aerosols e.g. in air quality and climate modelling.

But many challenges remain. In recent years, interest in the chemical characterisation of primary aerosols, especially bioaerosols, has increased significantly. Bioaerosols are natural primary aerosols (primary biological aerosol particles, PBAPs) from living or dead biological organisms, such as fungal spores, bacteria, viruses, and pollen. Estimated total global emissions of PBAPs range widely from 10 to 1000 Tg/yr, depending on size and range and whether cell fragments are included in the estimate [185]. Bioaerosols are known to act as very effective ice nuclei, and are estimated to be particularly important for ice formation in warm clouds (temperature $> -15\ ^{\circ}C$). These biological samples with their complex matrix impose high demands on organic trace analysis, and it is in this area that progress can also be expected in aerosol research, driven in part by the enormous developments in high-resolution mass spectrometry and proteome and metabolome analysis which could benefit from multidimensional LC and MS systems [186–189].

However, many problems in the analysis of organic compounds in aerosols can also be solved with one-dimensional LC-MS setups, as the chromatographic separation and the use of MS already enable excellent quantification and identification of even complex mixtures. For multidimensional LC, optimisation approaches offer the possibility of further developing 2D LC separations. With the aim of improving detection sensitivity, active modulation techniques need to be further implemented. The three most commonly used active modulation techniques are active-solvent modulation (ASM), stationary-phase-assisted modulation (SPAM), and vacuum evaporation modulation (VEM). The principle of ASM is based on the dilution of the 1D eluent stream with an elution-weak solvent in order to focus the area of the analyte at the inlet of the 2D column [190]. SPAM, utilises low volume preconcentration columns, so-called traps. These traps contain stationary phases designed to retain the analytes of the 1D effluent while the 1D solvent mixture leaves the chromatographic system without retention. The valve is then switched and the 2D mobile phase elutes the trapped analytes as sharp, concentrated bands into the 2D column [191,192]. The principle of VEM is based on the evaporation of part of the 1D effluent prior injection into the 2D column. It is mainly used to overcome incompatibility problems when combining NPLC and RPLC separations [193,194]. Although most applications of modulation techniques have been tested with respect to the coupling of HILIC with RPLC [85,195], which is also the most popular coupling in the analysis of organic atmospheric compounds (see Table 1), to our knowledge no modulation techniques have yet been used in the 2D LC analysis of aerosols. This represents a possible branch for the future of multidimensional LC systems in aerosol analysis, as they can significantly improve detection sensitivities.

Work has also already been done on the implementation of predictive tools and optimisation algorithms to determine optimal conditions for the chosen 2D chromatographic separation problem [196]. In the future, efforts should be made in aerosol research to use these implementations to overcome the time-consuming trial-and-error optimisation approach for the development of 2D LC methods. In addition, user-friendly software for data analysis and visualisation should be developed [86,197].

In recent years, one increasingly encounters the term 'aerosolomics', i.e., in reference to the life sciences, the description of the goal of current aerosol research to identify, characterise, and quantify those molecules that are important for the composition, origin, processing, phase state, and especially the effects of aerosol particles in the atmospheric environment [198]. We have certainly come closer to this target, as usual also as a result of immense progress in the field of instrumental analytics. But challenges still exist, such as the role of organic compounds in particle formation, where extremely small amounts of substance in nanometer particles must be analysed, or in cloud formation, where unusually difficult sampling and stark external conditions (e.g., low temperatures) complicate analysis. However, the study of particles that are harmful to human health (e.g. reactive oxygen species (ROS)) also remains a challenge [199]. The study of these processes requires further analytical developments, some of which are already underway and could benefit other chemical disciplines. Moreover, high efforts are also already taken to build up databases for NTA as aerosolomic tools to enable the application to organic aerosol samples by including tandem-MS experiments [198]. This can be expected to become a branch of atmospheric science where more work will be invested in the future.

The increasing widespread use and performance of HR-MS and the consequent impact on atmospheric aerosol analysis have already been mentioned. Related to this, concerning future developments in this research area, would be the analysis of stable isotopes by HR-MS. The analysis of stable isotopes and exploitation of chemically or physically induced fractionation processes of the elements is a widely used method, especially in the geosciences, to trace elemental cycles or to collect paleoclimate data. Typically, stable isotope ratios are measured after the analyte has been converted to a low molecular weight gas by combustion, pyrolysis, microbial fermentation, or other chemical treatments. The gas is then analysed using a magnetic sector isotope ratio mass spectrometer (IR-MS). However, in these methods, much of the intramolecular isotopic information is erased during gas formation and by destructive ionisation in the IR-MS. The very high mass resolution of especially the new generations of Orbitrap mass spectrometers allows the resolution of many near isobaric interferences for compounds containing H, C, N, O and/or S, without question the elements that are also the most important in the field of atmospheric aerosol research [200–202]. The sensitivity of today's instruments allows analysis of subnanomolar samples and quantification of multi-substituted species. The site-specific capabilities arise from the fact that mass spectra of molecular analytes typically contain different fragment ion species, each of which samples a specific subset of molecular sites.

5. Conclusion

In summary, the molecular characterisation of atmospheric aerosol particles is a major analytical challenge due to their diverse chemical composition and the complex physico-chemical properties of some individual components. The importance of understanding these particles lies in their profound impact on human health, climate dynamics and geochemical cycles. Despite advances in analytical techniques, particularly the advent of LC-MS methods, which have undeniable already contributed significantly to our understanding of aerosol formation and growth, e.g. for certain aerosol sources and sinks, the accurate quantification of ultra-trace levels of low- and semi-volatile organic compounds remains a formidable task. While LC-MS is versatile, its inherent limitations in analysing specific analyte classes of analytes necessitate the development of multidimensional LC and MS methods. These advanced techniques aim to improve both the scope of bulk organic

analysis and the identification of individual components. Although progress has been made, there are still challenges. The integration of high-resolution mass spectrometry and multidimensional LC systems promises to overcome these challenges and improve our understanding of aerosol chemistry. Future research efforts should focus on optimising analytical methods (e.g. modulation strategies), developing user-friendly software tools and advancing the field of aerosolomics to better characterise and quantify aerosol components. Additionally, the use of high-resolution mass spectrometry for the analysis of stable isotopes represents a promising avenue for further research, offering greater sensitivity and site-specific capabilities. Overall, advances in atmospheric chemistry are closely linked to advances in analytical chemistry, as they are essential for deciphering the complexity of organic aerosols and their impact on atmospheric chemistry and climate.

Financial support

This research has been supported by the German Federal Ministry of Education and Research (BMBF, grant no. 01LK1602D) and the German Research Foundation (Deutsche Forschungsgemeinschaft DFG: HO 1748/19–1; HO 1748/20–1; TRR 301 – Project-ID 428312742).

CRediT authorship contribution statement

Stefanie Hildmann: Investigation, Methodology, Writing – original draft, Writing – review & editing. **Thorsten Hoffmann:** Conceptualization, Formal analysis, Funding acquisition, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Thorsten Hoffmann reports financial support was provided by Deutsche Forschungsgemeinschaft - DFG. Thorsten Hoffmann reports financial support was provided by Bundesministerium für Bildung und Forschung - BMBF. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

We acknowledge the Max Planck Graduate Center and the Johannes Gutenberg University.

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