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Applications of liquid chromatographic techniques in the chemical characterization of atmospheric aerosols

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Abstract

This paper presents a comprehensive literature review on liquid chromatography (LC) techniques, singular and/or in tandem with mass spectrometry (MS), applied to identify and quantify inorganic and organic chemical constituents in atmospheric aerosols. Significant contributions in the field of aerosol chemical composition, obtained either by field measurements or laboratory investigations, are also highlighted. The two major LC techniques that have been used to date to identify aerosol chemical constituents are ionic chromatography (IC) and high performance liquid chromatography (HPLC). They have been used more often in off-line than in on-line mode and both of them can be coupled with several types of mass spectrometry (MS). The two techniques seem to be suitable to obtain information on water-soluble inorganic and organic ions with low molecular weight (IC) or on organic compounds with higher molecular mass (HPLC). LC-MS with electrospray ionization is among the most powerful LC techniques to elucidate possible major contributors to the so-called “unidentified substances” fraction, and it is often reported in studies aimed to investigate the chemical composition of the aerosols. The information generated by liquid chromatography, especially related to different organic compounds into the aerosol particles, helped to elucidate some reaction pathways or improve some postulated mechanisms that may be responsible for the formation of secondary organic aerosols (SOA). However, despite the efforts made to elucidate the aerosols chemical composition, a significant part still remains highly unclear. It is expected that new studies carried out by using complementary analytical techniques will help answering such questions, but further development is needed to make such techniques applicable to large-scale analysis all over the world.

Keywords: aerosols, particulate matter, atmosphere, liquid chromatography, ion chromatography, high performance liquid chromatography tandem mass spectrometry

1 Introduction

Atmospheric aerosols, usually defined as colloidal systems of liquid and/or solid particles suspended in a gas, have great importance for a wide range of environmental and health problems at both local and global scales. The primary parameters that determine the environmental and health effects of aerosol particles are their concentration, size, structure and chemical composition.[1] Within the atmospheric aerosol species, particulate matter (PM) has received special attention in recent years. It is mainly divided in coarse (PM_{10}, particles with aerodynamic equivalent diameter, AED, less than 10 μm, i.e., 10000 nm) and fine modes ($PM_{2.5}$, particles with AED < 2.5 μm, i.e., 2500 nm). Ultrafine particles have also been increasingly studied and they are usually considered as having AED < 0.01 μm, i.e., 10 nm. Particles with diameters in the range of 2000 - 100000 nm (2 - 100 μm) are heavy enough to be quickly removed from the atmosphere by gravitational settling. In contrast the smaller particles, especially those with diameters ranging from ~2 to ~1000 nm, are less susceptible to gravitational settling and stay airborne for long periods. They can be transported across continents and oceans. The most important particles with respect to atmospheric chemistry and physics are those in the 0.002 - 10 μm range.[2-3] It is reported that continental atmospheres often contain between 1000 and 100000 particles cm^{-3} with diameters between 10 and 1000 nm and mass concentration from a few up to ~100 $\mu g\ m^{-3}$.[4] In each of its forms, particulate matter represents an ubiquitous component of the atmosphere and plays an important role in many areas of atmospheric sciences. They include the effects of air pollution on human health, atmospheric visibility reduction, acid deposition, and the earth's radiation budget.

Aerosols in ambient air derive from a variety of anthropogenic (such has transport, industrial activities, fuel combustion, biomass burning) and natural sources (including volcanic eruptions, sea salt, soil dust suspension, natural forest fires.). They are the result of direct emission of PM (primary PM) and of gaseous aerosols precursors (mainly sulfur dioxide, SO_2, nitrogen oxides, NO_x, ammonia, NH_3, as well as anthropogenic and biogenic volatile organic compounds, VOC_S, all producing secondary PM).[3] Within the natural sources, soil dust resuspension may occur especially during severe dust storm events when large amounts of soil are moved across land and ocean.[5] However, considerable uncertainty still exists regarding the contribution of resuspended soil and road dust to the organic carbon fraction of fine atmospheric particles in various areas.[6] New particles are formed by nucleation of the least volatile gas-phase compounds, emitted from either biogenic or anthropogenic sources.[7] Some particles are likely to undergo phase changes with varying relative humidity (e.g., sea salts and partially neutralized nitrates and sulfates), may show a hygroscopic response without deliquescence (e.g., sulfates and oxygenated organics), or may exhibit only surfaces changes (such as reversible water adsorption) with altered relative humidity (e.g., freshly entrained soot and mineral dust particles).[8] Condensation of volatile chemicals oxidized by photochemical processes and/or condensation of semivolatile species that are first thermally vaporized and then exposed to colder air represent another important route for particles formation.[9]

In 1996 the Intergovernmental Panel on Climate Change (IPCC) reported an yearly emission of about 3400 million tons of PM on a global scale, of which anthropogenic sources accounted for about 15% and natural primary particles for about 85%.[10] In the year 2000, anthropogenic emissions of PM_{10} and $PM_{2.5}$ reached about 5600 and 3800 million tons, respectively, and the PM profiles over the period 1997-2002 did not follow the trends of the reported emissions of precursors gases.[11]

Aerosols have direct and indirect effects on climate,[12] and climate in turn might have a significant impact on air quality and aerosol concentration.[13-14] Moreover, atmospheric chemical reactions might influence the ion composition of aerosol particles.[15] In 2007, the IPCC report suggested that the anthropogenic contributions to the aerosols budget could induce a total radiative forcing of -0.5 [-0.9 to -0.1] W m^{-2} and an indirect albedo cloud forcing of -0.7 [-1.8 to -0.3] W m^{-2}. Such effects would counterbalance to a certain extent a part of the global warming induced by the green house gases (GHG_S), of which CO_2 concentration as risen dramatically over the last decades. According to the 2007 IPCC Report, the global radiative forcing induced by human activities is +1.6 W m^{-2}.[12] Because aerosols have a non-negligible effect on radiative forcing, a perturbation in their tropospheric distribution can significantly affect climate.[16] Such effects can also be linked to changes in the amounts of sulfate, nitrate and carbonaceous aerosols induced by natural and anthropogenic activities. Sulfate and nitrate aerosols induce a direct effect on climate, primarily through the scattering of solar radiation which produces a negative radiative forcing that tends to cool the Earth's surface. In contrast, carbonaceous aerosols have a warming effect. The investigation of the PM impact on climate is mostly directed to estimating the changes in the cooling effect due to a change in the atmospheric aerosol burden, although the impacts of anthropogenic and natural aerosols still represent major uncertainties in the global radiative forcing of the earth-atmosphere system.[16-17] Aerosols might also act as cloud condensation nuclei (CCN) and their contribution is thought to produce an indirect cooling effect that is believed to be twice higher than the direct effect.[16]

Based on health considerations, PM_{10} and $PM_{2.5}$ rather than total suspended particulate (TSP) matter are selected as indicators of air pollution on which to focus regulatory concerns, because PM_{10} and $PM_{2.5}$ particles are small enough to enter the thoracic region.[18] It has also been suggested that PM, and especially its fine fraction ($PM_{2.5}$), leads to a wide range of acute and chronic health problems in many countries. There is evidence that aerosol (particularly in the form of PM_{10} and $PM_{2.5}$) poses potentially important risks to human health at concentrations values that are currently experienced by urban populations in both developed and developing countries. On local to regional scales, epidemiological studies have shown that persistent mass loadings of atmospheric particles above ~10 – 20 $\mu g\ m^{-3}$ are strongly associated with adverse human health effects, including increased mortality from cardiopulmonary diseases and lung cancer.[19-21] It is well documented that $PM_{2.5}$ is an aerosol fraction characterized by strong acidity,[22] and the impacts of $PM_{2.5}$ on human health might have a greater influence than the impacts of larger particles. This happens because $PM_{2.5}$ particles can be inhaled deep into the alveolar sections of the lungs.[21]

Presently, air pollution with PM is assumed to be responsible of a reduction in life expectancy of about 8.6 months on average in the 25 countries joining the EU in 2006[11]. An increase of 10 $\mu g\ m^{-3}$ in PM_{10} concentrations, as compared with the limit value set by the EU directive (20 $\mu g\ m^{-3}$ annual mean), is expected to result in an increase of premature deaths by 1% up to 5% for short- and long-term exposure, respectively.[20,23] Overall, the health impact of the aerosols may vary according to their physical (size, shape) and chemical (composition) characteristics.[24-25] Nevertheless, despite the present state of knowledge concerning the differences among PM constituents, it is currently not possible to precisely quantify the contributions of different PM components to the health effects caused by human exposure to the atmospheric PM load. It is assumed that the presence of metals in aerosols increases lung or cardiopulmonary injuries,[26] while nitrates, sulfates and chlorides are PM components that show lower toxic potency.[11] However, it is also suggested that no single chemical species dominates the health effects that may be due to a combination of different compounds.[27]

2 Characterization of atmospheric aerosol species by advanced monitoring techniques

Tropospheric aerosols have great importance because of their potential impact on human health, Earth's climate and visibility. They require dedicated monitoring of their concentration and chemical and physical properties at the global scale.[28] Current information, which is often limited to regulated parameters such as PM_{10} or $PM_{2.5}$, is not sufficient to provide the entire range of details that are of interest to air quality and climate studies. Therefore, it is now important to have insight into the trends of advanced aerosol variables, such as size-segregated aerosol chemical composition.

Atmospheric aerosols have a wide range of sizes (Figure 1). The smallest nucleation mode consists of new particles formed in the atmosphere, with diameters ranging from 1-3 nm up to ~10 nm. These particles last only a few hours before condensation. Particles with diameters between 10 to 100 nm are termed Aitken nuclei, while those with diameters between ~100 to 1000 nm are named accumulation mode particles. Typical atmospheric lifetimes of such particles, produced by agglomeration of the 0.03 μm particles with larger ones, are between few days and few weeks. The nucleation and accumulation mode particles are collectively called fine particles. Particles larger than a few μm are termed coarse-mode particles and they generally have relatively short atmospheric lifetimes before being removed by precipitation or gravity. The smallest ultrafine particles are produced by homogeneous nucleation and tend to contain secondary species such as sulfate and organics. Combustion processes, coagulation of smaller particles and condensation of low-vapor-pressure products of gas-phase reactions, are mainly responsible for the production of Aitken nuclei.[3]

The composition of the internally mixed aerosols (individual particles with uniform chemical composition) or the externally mixed aerosols (particles with chemical composition different from the ensemble composition) depends on the particle sources and on the atmospheric aging processes (coagulation, gas-particle partitioning, chemical reactions). A wide range of instrumental analytical methods have been used for the physical and chemical analysis of aerosol particles and components.[1] However, in practice, the selection and combination of analytical methods depend both on sample type and target parameters and also on equipment and labor expenses.

Most aerosol measurement techniques fall into the off-line and the *in situ* measurement categories. While the first category relies on the collection of aerosol particles on a substrate (i.e., filter) for subsequent laboratory analysis, the second category allows much faster and near real-time measurements.[29] Traditional techniques to chemically characterize PM rely on collecting many particles and on measuring their average chemical composition. The ideal atmospheric PM measurement would produce data on the chemical composition as a function of particle diameter, in the range from a few nm to tens of µm. In addition to PM size, composition and mass loading, many other physical and chemical properties are of interest and they should be preferably measured at the same time. For instance, climate scientists need to correlate size and chemical composition with the particle's ability to scatter and absorb radiation from the infrared to the near ultraviolet, and with the ability to nucleate water droplets at low water supersaturation levels.[17]

Health scientists suspect that surface area and surface composition may be a key to understanding how particles interact with lung tissues to affect pulmonary functions and transfer chemicals into the blood stream.[30] Therefore, measurements of particle morphology and of surface-adsorbed species are of growing interest. Finally, atmospheric chemists are interested in the physical phase (liquid or solid), surface area, and surface composition because these properties can strongly affect the interaction of atmospheric trace gases with airborne particles. This interaction affects the chemical composition of both the gaseous and condensed-phase components of the atmosphere.[4]

A full understanding of the effects of atmospheric particulate matter on health, climate and visibility requires a detailed characterization of the chemical composition of particles. However, given the large number and variability of the chemical constituents and sources of the aerosols and their possible transformation, such characterization is still very challenging. The largest uncertainty is associated to the secondary organic aerosol (SOA) fraction, which consists of particulate matter formed by chemical transformation of atmospheric volatile organic compounds (VOCs). SOA is important in a wide range of geophysical and environmental problems, ranging from local issues (e.g., pollution) to the global scale (e.g., climate change).[31] Unfortunately, the abundance of organic compounds, the variability of the physical properties and the existence of both natural and anthropogenic sources cause great difficulties to sample and chemically characterize the atmospheric particulate matter.[32] Nevertheless, a complete chemical characterization of, most notably, poorly volatile organic species in the particle phase is extremely useful for both laboratory and *in situ* studies. For instance, while it has been suggested that biogenic precursors dominate regional SOA formation, measurements with new advanced technology in the field of atmospheric science revealed that SOA is strongly coupled with tracers of anthropogenic emissions.[33-34]

During the last decades, the performance of the analysis methods used in the investigation of the aerosol chemical composition has extensively increased.[35-36] Such methods can be divided into three major classes: *(i)* methods which can provide chemical data off-line, *(ii)* methods giving chemical data on-line, and *(iii)* methods that are actually a combination of the first two classes. In the case of off-line techniques, it should be mentioned that besides the problem of sampling artifacts, they hardly allow the resolution of the high spatial and temporal variability that characterize atmospheric aerosols. The off-line analysis methods can be divided into several classes. One is based on mass spectrometry with laser desorption ionization, LDI-MS,[37] matrix-assisted laser desorption ionization (MALDI-MS)[38] and Fourier Transformed (FT) ion cyclotron resonance.[39-40] A second class is based on chromatographic methods such as gas chromatography (GC),[41-44] high performance liquid chromatography (HPLC),[45-48] and ionic chromatography (IC).[49-50] The third class combines the chromatographic systems with mass spectrometry: examples include GC-MS, typically after a first step of derivatization to enhance the compounds volatility, [51-53] and HPLC coupled with several alternative MS techniques such as ion trap, quadrupole and time-of-flight.[54-60] A fourth class is based on nuclear magnetic resonance (NMR) spectroscopy. Proton (^{1}H) NMR is used for functional group analysis of the water-soluble fraction[61-62] and for the analysis of ketones or carboxylic groups, usually after appropriate derivatization.[63] Carbon (^{13}C) NMR can be used for the analysis of heavily loaded aerosol samples.[64]

The organic carbon (OC) content of the atmospheric aerosols can be determined by using a thermo-optical transmission carbon analyzer. These measurements are performed through temperature and gas control and by a laser transmission that corrects for the elemental carbon that is pyrolytically generated during the OC analysis.[65] A number of studies have been conducted by combining on-line collection of aerosols with fast off-line analysis. Reduction of the potential for sample contamination represents the first advantage of such a tandem approach. An example of such a technique is the on-line Sunset Labs OC/EC two-step analyzer. In the field model the sample is collected on-line on quartz filter that, after the end of the sampling, is heated in an inert atmosphere to vaporize the organic species. The amount of the evolved carbon is measured after catalytic conversion. In a second step of measurement, oxygen is injected in order to burn off the remaining refractory carbon while the sample undergoes further heating. The technique allows the discrimination of the mass concentration of organic and elemental carbon.[66]

Information regarding the organic fraction can be obtained as well using a gas chromatographic system coupled with a thermal desorption aerosol unit. The sample is collected on-line on an impactor for a period of about 30 min before subjecting it to thermal desorption and GC-MS/FID analysis. This tandem is used to identify and quantify various organic species.[67]

The advantages of the recently developed on-line analytical techniques are overshadowing those of the off-line analysis methods. However, the two approaches often provide complementary information needed for environmental studies in terms of both air quality and climate change.[28,68-69]

Over the past few years, substantial progress has been made in the development of aerosol mass spectrometers for real-time measurements of size-selected (single) particles. As the methods of vaporization, ionization, calibration, and data analysis are improved, the aerosol time-of-flight mass spectrometer (AMS) instruments promise reliable quantitative analyses, especially for chemical elements and inorganic species.[1] Actually, the AMS instrument is among the most revolutionary analytical techniques in the field of the chemical characterization of atmospheric aerosols. It allows for a clear discrimination between anthropogenic and biogenic fractions of aerosols on the local, regional and global scales.[70-72] AMS based on thermal desorption,[4] as well as aerosol time-of flight mass spectrometer (ATOFMS) with laser desorption and ionization (LDI), represent key achievements for the application of mass spectrometric techniques to the real-time measurement and characterization of atmospheric aerosols. However, their major advantages are shielded to some extent by important limitations. For example, within LDI instruments, the chemical components may interact during desorption; the energy and charge are not evenly distributed among the molecular species; the interaction between the focal point of the desorption laser and the particle beam controls particle detection, and the data analysis is very challenging. The AMS system gives simultaneous information on size distribution and chemical composition of an observable particle ensemble with a high time resolution, but its main limitation is the relatively small number of components that can be detected. While ammonium, sulfate, nitrate and organic matter are very well detected, species such as elemental carbon, sea salt and dust are not entirely seen by the instrument.[28] Schneider et al. (2004) report about on-line mass spectrometric aerosol measurements in Crete, Greece, where results from the AMS system were compared with filter sampling methods and particle sizing techniques. The authors report that the different techniques agreed with the finding that the fine particle mode ($D < 1.2$ μm) consisted mostly of ammonium sulfate and of organic material.[73]

3 Instrumental liquid chromatographic techniques used for the analysis of small and water-soluble inorganic and organic ionic constituents of atmospheric particulate matter

Ambient PM contains many inorganic elements in the form of ions (sulfate, SO_4^{2-}, nitrate, NO_3^-, chloride, Cl^-) and trace metals, as well as elemental carbon (EC) and a wide variety of organic compounds (organic carbon, OC) and water. The $PM_{2.5}$ fraction is mainly composed of SO_4^{2-}, NO_3^-, OC and EC. While SO_4^{2-} and NO_3^- are produced within the atmosphere *via* oxidation of SO_2 and NO_x, OC is mainly produced by oxidation of non-methane volatile organic compounds (NMVOCs). Particles larger than 2.5 μm typically contain elements from soil and sea salt.[3, 74-75] Actually, from the inorganic point of view, atmospheric aerosols can be seen as mixtures of many components including especially inorganic acids (e.g. H_2SO_4 and HNO_3), their salts (e.g. $(NH_4)_2SO_4$, $(NH_4)HSO_4$, Na_2SO_4, NH_4NO_3, $NaNO_3$, NaCl, KCl) and water.[3,76] Inorganic ions such as NH_4^+, SO_4^{2-} and NO_3^- are major components of ambient particulate matter and ion chromatography (IC) has become one of the most widely used analytical methods for the determination of ionic concentrations in ambient particles. Heintzenberg (1989) claimed that by the 90s it was still very difficult to extract globally representative data on atmospheric particle composition from the literature.[77] However, during the past decades, much effort has been devoted to an almost complete characterization of the water-soluble ionic chemical composition of atmospheric aerosols in the fine,[78-85] coarse,[86-91] fine and coarse,[92-100] size-segregated[101-104] or bulky aerosol modes.[105-107]

Many theoretical and modeling approaches have been used to investigate the chemical composition of atmospheric aerosols and its sensitivity to various parameters.[108-110] Moreover, several inorganic aerosol thermodynamic equilibrium models have been developed over the years to investigate the sensitivity to changes in the concentration of ammonia (NH_3) and sulfur dioxide (SO_2), the molar ratios of ammonium to sulfate (NH_4^+/SO_4^{2-}), nitrate to sulfate (NO_3^-/SO_4^{2-}) and sodium chloride to sulfate ($NaCl/SO_4^{2-}$), the relative humidity (RH), and temperature (T).[9,111-113]

However, the use of reliable techniques to completely characterize the water-soluble ionic constituents of atmospheric aerosols is of great importance and ionic assignment and analytes quantification are both required. Ion chromatography (IC) is the most valuable technique used in the off-line mode in order to determine concentrations of water-soluble ions in stabilized aqueous extracts of sampled atmospheric aerosols (chloroform is usually added as a biocide to inhibit bio-decomposition processes). The coupling of ion-exchange columns with the suppression of eluent conductivity allows the development of analysis methods for a variety of analytes,[114] including Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, Br^-, I^-, NO_3^-, NO_2^-, SO_4^{2-}, SO_3^{2-}, PO_4^{3-}, and many amines, quaternary ammonium compounds and organic acids.

Especially for certain critical species such as SO_4^{2-}, NO_3^- and Cl^-, sampling artifacts during particulate matter collection can be quite severe. In such cases it is quite difficult to show conclusively the existence of an inorganic species in a specific form,[3] and the analysis by ion chromatography of the water-soluble ionic constituents of atmospheric aerosols becomes very challenging. Mulika et al. (1976) were among the first to undertake a successful application of ion chromatography to the off-line analysis of total water-soluble SO_4^{2-} and NO_3^- in ambient aerosols.[115] More recently, a system facilitating direct on-line analysis of collected atmospheric aerosol samples has been developed and improved.[116] The technique is known as PILS-IC and consists of an ion chromatograph (IC) coupled to a particle-into-liquid sampler (PILS). Proper selection of columns and elution phases allows the separation of 9 major inorganic species (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, $Cl^−$, $NO_3^−$, $NO_2^−$, $SO_4^{2−}$) in 3.5-4 min, while acetate, formate, and oxalate can also be analyzed in 15 min. The collection efficiency of the PILS unit, for particle diameters between 0.03 and 10 μm, is higher than 97%.

In most recent papers dealing with the ion chromatographic analysis of water-soluble ionic constituents of atmospheric aerosols, the main reported cations are Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}. The most often identified and quantified anionic species consist of inorganic anions such as F^-, Cl^-, Br^-, NO_2^-, NO_3^-, SO_4^{2-} and PO_4^{3-}, and of organic anions present as mono- (formate, Fo^-, acetate, Ac^-, propionate, Pr^-), di- (oxalate, Ox^{2-}, malonate, Ma^{2-}, succinate, Sc^{2-}, glutarate, Gt^{2-}) and keto- (pyruvate, Py^-) carboxylate forms. Malonate (Ma^{2-}) and methane sulfonate ($CH_3S(O_2)O^-$, MS^-) are also reported. The analysis of mono-, di- and ketocarboxylic anions deserves special attention because these compounds are ubiquitous chemical constituents of the troposphere and contribute to both the acidity of precipitation and to the particulate organic carbon budget. They may also act as condensation nuclei (CN) and cloud condensation nuclei (CCN).[117-118] The analysis of low molecular weight mono- and dicarboxylic acids is often reported.[119-121]

The ion chromatography methods used by Bardouki et al.[101] and Kouvarakis et al.[122] are often cited in many research papers dealing with the analysis of water-soluble ions in atmospheric aerosols. Bardouki et al.[101] used a Dionex AS4A-SC column with ASRS-I suppressor in auto-suppression mode for the analysis of Cl^-, Br^-, NO_2^-, NO_3^-, SO_4^{2-} and Ox^{2-}. All these anions were determined and quantified under isocratic elution at 2.0 L min^{-1} of $Na_2CO_3/NaHCO_3$. A Dionex AS11 analytical column and NaOH (0.1-3.5 mM) as eluent in a gradient mode was used for the analysis of MS^- and of the light mono-, di- and keto-carboxylic organic anions. Under experimental conditions that were similar to those used by Jaffrezo et al.[119] and Kerminen et al.[123], a very good separation is reported for the organic acids with the exception of malonate. For the analysis of Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}, Bardouki et al.[101] have used a CS12-SC column with CSRS-I suppressor, eluting under isocratic conditions with 20 mM methane sulfonic acid (MSA) as mobile phase at a flow rate of 1.0 mL min^{-1}. The reproducibility of the measurements was better than 2% and the detection limit ranged from around 1 ppbv for the main anions and cations, to below 0.1 ppbv for the main organic ions including MS^- (1 ppbv was assigned to correspond to 0.37 ng m^{-3} for a mean air volume of 40 m^3). The reported mean blank values were 5-10 ppbv for Na^+ and Ca^{2+}, <3 pbbv for the other main anions and cations, 5-10 ppbv for Ac^- and Fo^-, 1 ppbv for MS^-, 0.5 ppbv for Py^- and Ox^{2-}, and below the detection limits for the other organic ions. Pathak et al.[22] also report detection limits of 2, 1, 1, 1 and 1 nmol m^{-3} for NH_4^+, Na^+, SO_4^{2-}, NO_3^-, and Cl^-, respectively, by ion chromatography, although the details of the instrumental setup are not reported. The ion chromatographic analysis with conductivity detection of water-soluble, short-chain organic anions in ambient particulate matter has been carried out by Raman and Hopke on samples collected in south-western and northern New York, USA.[124] An Ionpac AS17 analytical column (4 mm) and an Ionpac AG17 guard column (4 mm) were used for anion separation, eluting in gradient mode with KOH flow rate maintained at 0.8 mL min^{-1}. A decrease in KOH concentration and a consequent increase in the run time resulted in a better resolution for glutaric, succinic, malic, maleic and malonic acids. Duplicate analyses were randomly performed and the relative standard deviation for duplicate samples was within 10%. The calibration curves were linear, with R^2 values of 0.995 or higher.

Sciare et al.[102] analyzed by IC one-half section of the filters collected by using stacked filter unit (SFU) and MOUDI impaction. They followed the analytical procedure mentioned in Kouvarakis et al.[122] and the major analyzed inorganic ions included Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, Br^-, SO_4^{2-} and PO_4^{3-}. Among the light organics, the authors mentioned Ac^-, Fo^-, MS^-, Py^- and Ox^{2-}. The maximum estimated uncertainty was 0.03 µg m^{-3} for each ion, on the basis of a maximum uncertainty of 10 ppb in the analysis of the major inorganic ions. An intercomparison exercise was performed for the MOUDI samples, which were analyzed by both IC and particle induced X-ray emission (PIXE) with short irradiation instrumental neutron activation analysis (PIXE/INAA). The intercomparison for some major anions and cations (Cl^-, SO_4^{2-} as sulfur, K^+, Mg^{2+}, Ca^{2+}) showed a very good correlation coefficient (i.e. 0.97) and a slope of about 1.04. The authors suggest that a quantitative solubilization was operational for the ions analyzed by IC, which has important implications for some species (e.g., calcium used as a tracer element for crustal particles). The ionic balance from IC analysis was also used for quality assurance, but it could not be employed as a quality control of the IC measurements because H^+ and carbonates were not determined in the analyzed samples. For the fine fraction, which was assumed to be more acidic, the ionic balance of the investigated samples was not achieved without taking H^+ into account. In the coarse size fraction, which is assumed to contain mainly sea salt and dust aerosols (in particular calcium carbonate) and that is potentially more basic than the fine fraction, the ionic balance was almost achieved without taking into account H^+ or carbonates.

In 2011, Arsene et al.[42] reported about the analysis of water-soluble anions (Cl^-, NO_3^-, SO_4^{2-}, Fo^-, Ac^-, Ox^{2-}, MS^-, Pr^-, Py^-) and water-soluble cations (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}) from fine and coarse particulate matter collected in north-eastern Romania. They employed similar analytical conditions as those given by Bardouki et al.[101]. The reproducibility of the measurements was better than 2% and the recovery of each ion was in the range of 92 – 105%.[42] The limits of detection (defined as 3 times the standard deviation of blank measurements, relative to the sensitivity of the method) were in the range of 1 - 5 μg L^{-1}. Furthermore, by using the ionic balance as a quality assurance test for both the coarse and fine fractions and by means of specific meteorological factors (especially temperature and relative humidity) for the investigated period, it was possible to get insight into the role of inter-particle and gas-particle interactions in establishing the particle chemical composition.

Wang et al.[125] report about the ion chromatographic analysis of ten anions (SO_4^{2-}, NO_3^-, Cl^-, F^-, PO_4^{3-}, NO_2^-, Ac^-, Fo^-, MS^-, Ox^{2-}) and five cations (NH_4^+, Ca^{2+}, K^+, Mg^{2+}, Na^+) present in the $PM_{2.5}$ aerosol fraction collected in Beijing. They used a Dionex Ionpac AS11 column for the anions analysis and a CS12A column for the cations. Gradient elution for the anions used 76.2 mM NaOH + H_2O, while 20 mM MSA was used for cation separation. The recovery of each ion was in the range of 80–120%, and the reproducibility test yielded a relative standard deviation (SD) <5% for each ion. The reported limits of detection are <0.04 mg L^{-1} the for anions and <0.006 mg L^{-1} for the cations. The quality assurance was routinely carried out by using Standard Reference Materials (GBW 08606) produced by the National Research Center for Certified Reference Materials, China.

Kocak et al.[96] and Metzger et al.[107] also report about the ion chromatographic analysis of the water-soluble ionic chemical composition of aerosols, with similar equipment as previously described and similar operation modes.[101,126-127] Metzger et al.[107] also report detection limits that range from around 5 ppb for the main anions and cations to below 0.2 ppb for the organic anions. Reproducibility was better than 2%.

Kouyoumdjian and Saliba[128] also analyzed fine and coarse particles for anions (SO_4^{2-}, $NO_3^-$and Cl^-) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+) by ion chromatography with conductivity suppression. The anionic column was a Novosep A-1 anion, 150×4.6, mm×mm, the cationic one was a Universal cation, 100×4.6 mm×mm. A carbonate buffer (1.7 mM $NaHCO_3$ + 1.8 mM Na_2CO_3) was used as mobile phase for the anions, and 3 mM methane sulfonic acid for the cations. The calibration curves had a regression range (R^2) between 0.993 and 0.999.

According to Hu et al.[83], who report on the analysis of water-soluble inorganic aerosol constituents, the uncertainty of measurements was below 15% depending on ambient concentrations. The method detection limit (MDL) was determined by repeatedly analyzing a quality control solution. The reported detection limits for Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}, in ng m^{-3} (calculated from MDL × volume of analyte solution (10 mL)/average sampling volume (40 m^3)) were 3.5, 6.0, 13.5, 6.5, 5.25, 23.3, 14.3, and 30.8 ng m^{-3}, respectively.

Terzi et al.[89] measured concentrations of Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-} by ion chromatography. A quarter of each loaded quartz filter was extracted with 10 mL of a ultra-pure water-isopropanol mixture (9:1 v/v) in a ultrasonic bath for 20 min. Cations were separated on an Alltech Universal Cation column using 3 mM methane sulfonic acid. Anions were separated on an Alltech Allsep Anion column using as mobile phase a mixture of phthalic acid and lithium hydroxide 4 mM. Column temperature was held constant at 35 °C. The reported method detection limits were 0.06, 0.03, 0.09, 0.02, and 0.03 mg L^{-1} for Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+} and 0.03, 0.07, 0.26 mg L^{-1} for NO_3^-, SO_4^{2-} and Cl^-, respectively.

Analysis of some water-soluble anions (SO_4^{2-}, NO_3^-, Cl^- and Ox^{2-}) was recently carried out with a new generation ion chromatographic system (Dionex ICS-2000), equipped with an IonPac AS11HC with 2×250 mm analytical column and an IonPac AG11HC with 2×50 mm guard column.[129] Potassium hydroxide was used as mobile phase at a flow rate of 0.38 mL min^{-1}.

In the current scientific literature, much information can be found concerning the ion chromatographic analysis of the water-soluble ionic chemical composition of atmospheric aerosols. However, inconsistencies in the implemented analytical approaches and quality assurance may overshadow the importance of the scientific findings. Only few research papers report checks on the quality assurance, and in many articles insufficient information is given on the adopted instrumental techniques. Moreover, a set of consistent and universally applicable experimental conditions should be implemented in each research laboratory where aerosols ionic constituents are determined by ion chromatography, so that the requirements of the EMEP monitoring strategy can be entirely fulfilled.[130]

4 Instrumental liquid chromatographic techniques used for the analysis of organic molecular constituents of atmospheric aerosols

Organic aerosol (OA) components are considered to account for a large (sometimes even the dominant) fraction of air particulate matter.[131-132] The composition of the organics is very complex[133], with hundreds of compounds being detected in air particulate matter[1], even in remote areas with very little contributions from combustion processes.[1,3] Many organic constituents may influence the physical and chemical properties of the aerosol particles and thus affect the atmosphere and climate through interaction with reactive trace gases, water vapor, clouds, precipitation, and radiation. Actually, organic substances have been recognized as active cloud condensation and ice formation nuclei for several decades.[134] In a critical assessment study, some topical areas related to the role of organic aerosols in the atmosphere, climate and global change have been addressed.[135]

Organic compounds typically represent 10-50% of the fine particulate mass[136] and organic carbon (OC) is one of the most important components of atmospheric aerosols.[68] Organic carbon can be directly emitted to the atmosphere in the particulate form, or it can be formed by gas-to-particle conversion in the atmosphere. Primary organic compounds include long-chain hydrocarbons, plant waxes and resin residues, while secondary organic compounds mainly include multifunctional oxygenated molecules (i.e., carboxylic acids, alcohols, carbonyls, nitrates). Some dicarboxylic acids might have both primary and secondary sources.[2]

Even in the most comprehensive investigations, only 10–40% of the organic particulate matter (OPM) content estimated from OC measurements has been unambiguously identified at the molecular level.[1] Organics usually identified in nonurban aerosols include organic acids (e.g., pelargonic acid, capric acid, lauric acid, tridecanoic acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid), aliphatic hydrocarbons (e.g., n-alkanes in the C_{10}-C_{35} range, n-decane, n-undecane, n-pentadecane, n-octadecane, n-eicosane, n-tricosane), polycyclic aromatic hydrocarbons, PAHs, (e.g., naphthalene, acenaphtalene, acenaphtene, fluorine, phenantrene, anthracene, chrysene, benzopyrene, perylene), polar compounds (coumarine, xanthone, anthrone, flavone, carbazole), organic bases (quinoline, isoquinoline, aniline, indole, methylindoles, dimethylindoles, dimethylquinolines, α-naphtylamines, benzoquinoline, acridine, phenanthridine) and non-identified substances. Organics produced by biogenic emissions include mainly n-alkanoic acids, n-alkanols and some monounsaturated fatty acids. The presence in the condensed phase of long-chain organics with one or more polar functional groups (e.g., carboxylic acids and nitrates) suggests that these chemicals may act as surfactants, forming an organic coating layer over the surface of the aerosol. It is believed that biogenic processes produce complicated mixtures of organics that are structurally large and have sufficiently small vapor pressure. Moreover, particles collected in regions affected by anthropogenic emissions or found in aged air masses are even more complex than those occurring in remote regions.[3] However, given the paucity of quantitative molecular data about organic aerosols, it is important to address the problem of which data are needed.[137]

Particulate matter is also rich in photosensitisers (e.g. quinones and aromatic carbonyls), which are partially derived from the photodegradation of polycyclic aromatic hydrocarbons (PAHs) and that can induce degradation of other molecules upon radiation absorption.[138] Furthermore, PAHs are considered to be among the key compounds in PM toxicity and details concerning sample preparation (including both extraction and clean-up), PAHs separation and detection have already been addressed.[139] However, the source apportionment for the indoor-emitted PAHs and phthalates is less straightforward.[140] Nitrophenols (i.e., 2- and 4-nitrophenols) are assigned as the prevailing nitrated compounds in whole atmospheric samples, including also particles.[141-142]

In 2001, Krivacsy et al. performed investigation on the chemical nature of water-soluble organic compounds in fine atmospheric aerosols.[143] The water-soluble organic matter was found to be composed of two main fractions: *(i)* highly polyconjugated, acidic compounds with a varying degree of hydrophobicity and *(ii)* slightly polyconjugated, neutral and very hydrophilic compounds. The authors observed that separation into individual components was impossible, by either HPLC or capillary electrophoresis (CE). It was considered as an indication of the presence of a high number of chemically similar but not identical species. Using ultrafiltration and HPLC-MS, it was possible to suggest that the molecular weights were in the order of several hundreds Daltons (Da). Acidic compounds deriving from the oxidation of different terpenes (pinic and pinonic acid, acidic products from the oxidation of sabinene, 3-carene and limonene) were detected in atmospheric aerosol samples using a capillary-HPLC-ESI-MS-MS technique.[144] Using a newly developed LC/tandem MS method, it was suggested that esters, peroxides and organosulfates were also important carboxylic SOA compounds.[145]

A class of organic molecules that are also extracted from atmospheric aerosol particles has been termed HUmic-LIke Substances (HULIS), due to a certain resemblance to terrestrial and aquatic humic and fulvic acids.[146] During the last decades, HULIS have received increasing attention due to their ubiquitous occurrence, active participation in atmospheric chemistry and important environmental and health effects.[147] Macromolecules such as cellulose and proteins (molecular mass >>1 kDa) and other compounds with relatively high molecular mass (>>100 Da) such as HULIS account for a large proportion of organic particulate matter (OPM) and of water-soluble organic carbon (WSOC).[1] Biopolymers and humic substances are emitted as primary organic aerosol (POA) components (soil and road dust, sea spray, biological particles), which may be modified by chemical aging and transformation in the atmosphere (e.g. formation of HULIS by oxidative degradation of biopolymers).

Knowledge of the organic content in aerosols is very important because organics may significantly affect the formation, growth and removal of ambient aerosols.[17] They also play a key role in the hygroscopicity,[148] toxicity,[149] and in the direct radiative properties of atmospheric aerosols.[150] During the last fifteen years, many review articles have clearly underlined the state-of-the-art regarding the occurrence and behavior of organic aerosols in the atmosphere.[68,151-152] Recent attention has also been devoted to organic constituents in fogs and clouds, because particulate organic matter can enter fog and cloud droplets through nucleation scavenging as particles act as cloud condensation nuclei (CCN).[153]

4.1 Studies of organics from ambient atmospheric aerosols

Humic-like substances (HULIS)

A significant part (in the 10-70% range) of organic matter in atmospheric aerosols is water-soluble, and the water-soluble fraction usually contains oxygenated multifunctional compounds such as diacids, polyols and amino acids.[121] HULIS represent an important part of the water-soluble organic carbon (WSOC), as they account for about 15-60% of the fine-particle WSOC.[146] HULIS are actually regarded as material with strong polar, acidic and chromophoric properties. Graber and Rudich suggest that atmospheric HULIS differ substantially from terrestrial and aquatic humic substances. The major differences between HULIS and humic substances include the facts that HULIS have smaller average molecular weight, lower aromatic moiety content, higher surface activity and better droplet activation ability.[146] Moreover, when taking into account the extraction procedures of HULIS from aerosols, it should be noted that the vast majority of studies are related to the water-soluble fraction. In surface-water samples, the corresponding (water-soluble) fraction of humic substances would only include fulvic acids and exclude humic acids (base-soluble) and humin (insoluble in water). The analysis of HULIS in atmospheric aerosols is very challenging, especially because extraction and isolation methodologies affect substantially the chemical and physical nature of the studied material. Therefore, preparative aspects should be given comparable importance as the analytical methods. For complex matrices, such as those occurring in the atmosphere (i.e. aerosols), a combination of different extraction techniques is often required.[154]

Our understanding of organic aerosols composition, physical and chemical properties, sources, transformation and removal characteristics are very limited, and the estimates of their actual environmental effects are highly uncertain.[69] Unfortunately, the chemical complexity of organic aerosols and the technical limitations of the present analytical tools have reduced the importance of most of the attempts that have been undertaken to characterize organic aerosols. Usually, for the identification and quantification of individual organic compounds, filter and impactor samples are extracted with appropriate solvents, and the extracts are analyzed by advanced methods of separation and detection: gas and liquid chromatography, capillary electrophoresis, absorption and fluorescence spectroscopy.[1] Size exclusion chromatography (SEC) and high performance liquid chromatography (HPLC), combined with various detectors such as absorption, fluorescence and mass spectrometry, are used for the analysis of larger, little volatile organics found in atmospheric particles. HPLC has been used for the separation, detection and measurement of polycyclic aromatic hydrocarbons.[3] Liquid chromatography is extensively used for the molecular speciation of organic compounds in aerosols, especially in tandem with mass spectrometry (LC-MS).[69]

Preparative approaches

Many contributions are reported in the literature about the extraction approaches for HULIS characterization but, unfortunately, inter-comparison between the different methods has not been carried out. Moreover, the methods have not been validated with mixtures of low molecular weight (LMW) organic acids and humic substances.[146] The work of Zappoli and coworkers, which was initially aimed at the determination of the total amount of WSOC in atmospheric aerosols, is often cited in the literature. During their work, the authors developed some extraction techniques for atmospheric aerosol samples that allowed three new classes of carbon-containing components to be obtained: the solvent-extractable, non-polar organic compounds (n-hexane, SENOC), the solvent-extractable, polar organic compounds (CH_2Cl_2/acetone, SEPOC), and the non-extractable (insoluble) component (NEC).[155] Decesari et al. exploited the acidic nature of HULIS to separate aerosol WSOC into fractions by preparative ion exchange chromatography.[61] A drawback of the developed method is that salts are not removed. However, the complex mixture of aerosol/fog WSOC was separated into three main classes of compounds: (1) neutral/basic compounds; (2) compounds containing one or two charges per molecule, usually mono- and di-carboxylic acids; (3) polyacidic compounds, with at least three negative charges per molecule. The deprotonated carboxylic acids were separated under alkaline pH using a weak anion exchanger (DEAE) stationary phase. By gradually increasing the ionic strength of the eluent buffer, inorganic and organic anionic species with increasing charges per molecule were eluted sequentially and were detected at 254 nm.

A solid phase extraction (SPE) method that is capable of isolating approx. 60% of WSOC from aerosol samples has been developed and proposed.[156] The authors tested the isolation of water-soluble organic matter from atmospheric aerosol on four silica-based and two polymeric reversed-phase columns. C_{18} SPE packing and a polymer-based Oasis HLB SPE packing were used during investigations. The optimized method involved acidification of the water extract to pH 2 and extract application to an Oasis HLB SPE cartridge, followed by elution in methanol (MeOH). The isolated organic matter was nearly free from inorganic ions, which are major constituents of atmospheric aerosol. The organic matter that was eluted from the SPE cartridge in MeOH contained more than 90% of the fluorescence and about 70% of the UV activity of the total WSOC fraction. A two-step separation method was also tested by the authors, and it involved sorption of aerosol-extracted WSOC onto C_{18} stationary phases in tandem at different pH values. In this method, about 25% of the WSOC passed directly into the column effluent, while another 15% was absorbed irreversibly on the cartridges.

The average molecular weight (AMW) of HULIS in rural fine aerosols collected in Hungary was investigated after applying ultrafiltration as a preparative step.[157] Ultrafiltration was applied to the total WSOC fraction and the authors made the assumption that virtually all the water-soluble organic matter passed through the ultrafiltration membrane having a 500 Da nominal molecular weight (MW) cut-off. A significant portion (more than half) of the water-soluble organic matter was isolated by the authors in pure form and was further analyzed by LC coupled to MS. The performed analyses confirmed that the isolated organic matter was mostly composed of HULIS and the mass spectrometry indicated that the AMW of these substances was in the 200–300 Da range. The authors admitted that their estimate could be negatively biased to some extent by unwanted processes in the mass spectrometer. To reduce uncertainties in the MW estimates, they applied another independent technique (vapor pressure osmometry) that gave AMW estimates in the range of 215–345 Da.

An extraction method by which the obtained isolate can contain neutral hydrophobic compounds in addition to HULIS has been proposed.[158] The authors applied an acidified WSOC aerosol particle extract to tandem XAD-8 and XAD-4 resin columns, and eluted with a 2:3 solution of MeOH:water. Recoveries from XAD-8 and XAD-4 in the MeOH:water eluate represented 60% and 9%, respectively, of the total WSOC.

Contributions within the preparative steps for the carbon-specific determination of humic-like substances in atmospheric aerosols, based on a two-step isolation procedure, are also reported.[159] The first step involved separation on a C_{18} SPE phase, to separate HULIS from inorganic and hydrophilic organic compounds in aqueous solution. The second isolation step was performed on a strong anion exchanger to separate HULIS from the remaining carbonaceous compounds. This ion chromatographic separation step, including the subsequent on-line detection of HULIS carbon, was performed in a fully automated way to avoid the risk of sample contamination and to enhance the reproducibility of the method. The isolation step was followed by on-line detection of carbon with a TOC analyzer. Similarly to Varga et al.,[156] the authors reported about 25% irreversible sorption on the SPE cartridge.

A procedure to extract HULIS of the fulvic acid type (FA-HULIS) from the filters and to separate them from other aerosol components by an isolation procedure has been reported.[160] The procedure was developed on the basis of the scheme used by the International Humic Substances Society (IHSS) for separating aquatic humic acid and FA. The method was adapted to airborne particulate matter collected on quartz fiber filters, and it involved consecutive extractions with water and with a basic aqueous solution. HULIS were separated from other water-soluble and base-soluble organic and inorganic species by adsorption onto an intensively pre-cleaned XAD-8 resin (Supelco Inc.), followed by elution with a basic solution. The eluant was cation-exchanged on an H^+-saturated cation-exchange resin (AG MP-50, Bio-Rad Laboratories) to produce protonated acids.

HULIS investigation by size exclusion chromatography (SEC) and capillary electrophoresis (CE)

Size exclusion chromatography (SEC) has been often employed to characterize WSOC extracts of atmospheric aerosol.[155,161-162] In SEC, the larger-size molecules are eluted first and the elution time increases as molecular size decreases. However, it has been shown over time that it is difficult to extract consistent and significant molecular size information with this technique. Moreover, SEC characterization of complex multicomponent mixtures of polyfunctional polyelectrolytes such as humic substances is difficult and may lead to erroneous results, because of the important presence of separation mechanisms other than size exclusion (e.g., electrostatic and molecular interactions with the stationary phase).[146] Despite its shortcomings, SEC is a widely used analytical technique for the measurement of HMW compounds (macromolecules) in atmospheric aerosols, because small amounts of sample can be analyzed, and because it is a relatively fast technique.[162] SEC is also considered to be well suited for the separation and measurement of compounds with molecular weights below 5000 Da (the range expected for atmospheric HULIS), while other known techniques are more appropriate to measure wider molecular weight ranges. However, after years of application of SEC to humic materials, there is still controversy about optimal elution and detection systems, as well as molecular size interpretations of SEC chromatograms.[146]

Zappoli et al. estimated the concentration of HULIS by SEC with UV-VIS detection. They found 0.6-2.5 $\mu g/m^3$ HULIS in aerosol, with an upper limit of 3000 Da for the molecular weight using humic acid (HA) as standard.[155] SEC experiments were performed using a Toso Haas TSK-GEL G4000PWXL column and UV-Vis/spectrofluorimetric detection. In the chromatogram of an aqueous extract of an aerosol filter, the authors observed three overlapping peaks. The retention time of the first peak was very close to that of the HA model. Furthermore, the authors separately collected the three eluted fractions of the aerosol sample at the end of the SEC column and recorded the UV-Vis spectrum of each fraction, to be compared with the spectrum of HA. Higher relative absorbance in the visible range was specific for the first eluted fraction as compared with the HA standard, leading to the conclusion that this fraction was mainly composed of macromolecules (MMC), derived most probably from biomass burning.

Krivacsy et al. developed a research strategy by considering the fact that the bulk of the organic carbon in the atmospheric aerosol and fog could be contained in an "air polymer", associated with HULIS, whose chemical nature was poorly understood.[161] The authors used SEC and CE in order to obtain new information about some properties of the HULIS found in fog water, and in aqueous extracts of interstitial aerosol samples collected in the Po Valley and of standard humic acid (Nordic River Humic Acid (NRHA) from the IHSS). CE was used to determine the range of HULIS protonation constants. The obtained electrophorograms for both the NRHA standard and the aerosol samples had the typical broad humps that represent a multitude of compounds of differing charge-to-size ratios. For the NRHA standard, the resolution was better in borate compared to phosphate buffer, probably due to complex formation between borate and the 1,2- and 1,3-diol groups of humic acid. In the case of the aerosol samples, the broad hump in the electrophorograms occurred over a shorter migration time range. This indicates an overall lower mobility of ionic compounds, with many small peaks superimposed to the hump. In aerosol samples there was little difference in electrophoretic behavior between the two buffers, suggesting that a negligible amount of 1,2- and 1,3-diol groups was present. The electrophoretic mobility of the aerosol sample increased continuously with increasing pH of the electrolyte, with a sharp increase between 4.28 and 5.90, and a slower increase in the pH range of 5.90–9.10. At pH 4.28 the interstitial aerosol electrophoretic hump disappeared entirely, suggesting that most of the acidic functional groups were protonated.

Capillary electrophoresis was also used for the analysis of organic acids (i.e. dicarboxylic acids, hydroxylated dicarboxylic acids) in size-segregated atmospheric aerosol particles collected in Sagres (Portugal) and at the Institut für Troposphärenforschung research station in Melpitz (Germany).[163]

A novel approach for the fractionation of WSOC in atmospheric aerosols and cloud drops has been described.[164] The method is based on the preliminary adsorption of the sample, acidified at pH 2, on a polymeric styrene-divinylbenzene resin (XAD-2) and on the subsequent elution with a series of solvents. The elution leads to the fractionation of the sample into three classes of compounds that are specific for the HULIS fraction (*vide infra*). The method was set-up by using synthetic mixtures of organic compounds and was then applied to selected samples of atmospheric aerosols and cloud drops. Moreover, SEC analysis was useful both to provide information on the organic content of the samples and to characterize the macromolecular compounds (MMCs) in the investigated samples. Synthetic samples, prepared by using humic, fulvic and tannic acid to simulate the naturally occurring MMCs, were also subjected to fractionation. In the first fraction, eluted with HCl, only the most soluble organic compounds were collected (oxalic acid, formic acid and acetic acid). In the second fraction, eluted with methanol, the major part of the organic material was collected together with the most hydrophilic constituents of humic substances. In the third fraction, it was possible to separately recover the most hydrophobic components of humic substances. The fractionation method on XAD-2 was also applied to selected atmospheric samples, yielding three classes of organic compounds. In each sample, a non-negligible amount of compounds with dimensional and chemical properties similar to humic substances were collected in the third fraction. A noteworthy chromatogram at 254 nm was also evidenced, the chromatographic area of which presented a clear linear correlation with the total organic carbon (TOC) values.

Samburova and coworkers used high pressure size exclusion chromatographic measurements for the analysis of HMW compounds in urban atmospheric particles.[162] The instrumental set up consisted of a Waters Ultrahydrogel 120 column (300 mm×7.8 mm, hydroxylated polymetacrylate stationary phase), a System Controller (SCL-10Avp), a Solvent Delivery Module (LC-10Atvp) and a Diode Array Detector (SPD-M10Avp). The DAD spectra were recorded between 190 and 800 nm. Prior to SEC analysis, Milli-Q water and NaOH extracts from the filter samples and from Suwannee River Fulvic Acid (SRFA) standards were filtered with a PVDF filter (0.45 μm pore size). The authors used a mobile phase consisting of an aqueous buffer solution (0.3 M NaCl, 0.03 M NH_4Cl, pH 10-11 adjusted with NH_4OH) at a flow rate of 1 mL min^{-1}.[161] The chosen eluent composition is expected to help minimizing secondary effects during SEC analysis. First of all, the high alkalinity is expected to reduce hydrophobic interactions between the stationary phase and the analytes. Moreover, the high salt concentration in the eluent is expected to suppress electrostatic interactions. A comparison was carried out of the size exclusion chromatograms of the two extracts of filter samples, in Milli-Q water and in 0.1 M aqueous NaOH. It was concluded that the solubility of the HULIS fraction can increase significantly in an alkaline extraction environment, most likely due to the HULIS acidic character. Furthermore, by monitoring the signal at 240 nm, multiple retention times specific for HMW compounds were observed. An attempt was made to perform size calibration of the used SEC column toward a sufficient number of standards in the molecular size range below 4000 Da, which should be suitable for HULIS. Large discrepancies were observed, especially between ionogenic and non-ionogenic standards having different polarities but the same nominal mass (i.e. ionogenic polymethacrylic acids (PMA) and non-ionogenic polyethylene glycols (PEG)). The observed discrepancies were mainly assigned to the chemical properties of the calibration compounds, and to their interaction with the stationary phase. Changes in the expected retention times were partly explained by the basic eluent (pH=11), but also by the stationary phase of the SEC column (hydroxylated polymethacrylic acid). Moreover, the chromatograms showed compounds of significantly lower polarity than the used standards. Overall, it was obtained additional evidence that the SEC characterization of complex multicomponent mixtures extracted from atmospheric aerosols is a quite controversial research subject. To get further insight into the size distribution of the samples, the authors also used the laser desorption/ionization mass spectrometry (LDI-MS) technique, with the main purpose of comparing its results with SEC. LDI mass spectra were recorded for the water extracts of the filter samples, and a broad range of peaks between m/z 100–550 was detected. Signals with lower intensities were present up to m/z 700, but no peaks were observed at higher mass. The use of matrix to aid desorption/ionization did not change the size distribution.

High-performance SEC coupled with inline dissolved organic carbon detection (SEC-DOC) was used to characterize organic matter in fogs, clouds and aerosols collected in Fresno (CA), Whistler (BC), Davis (CA) and Selinsgrove (PA).[165] The molecular weight (MW) distributions obtained by SEC showed a fractional overlap of atmospheric samples with terrestrial fulvic acids, although smaller MW material was dominant for clouds and aerosols. In cloud and fog samples, a larger fraction of LMW organic species was observed compared to the water-soluble fraction of aerosols. This is consistent with the partitioning of LMW volatile species into the atmospheric aqueous phase. The results obtained with the inline SEC-DOC system were confirmed by using a second SEC set-up with different column and detection system.

HULIS investigation by liquid chromatography tandem mass spectrometry (HPLC-MS)

Liquid chromatography-mass spectrometry has evolved to become one of the most powerful analytical tools in the investigation of many complex matrices, since the introduction of electrospray ionization (ESI) by Fenn and coworkers, who were awarded the Nobel Prize in Chemistry in 2002 for this finding.[166-167]

The average molecular weight (AMW) distribution of HULIS in fine aerosol collected in Hungary was estimated with liquid chromatography-electrospray ionization mass spectrometry (HPLC-ESI-MS).[157] Ultrafiltration was first applied to the total water-soluble organic fraction. It was supposed that virtually all the water-soluble organic matter passed through the ultrafiltration membrane having a nominal molecular weight (MW) cut-off of 500 Da. A significant portion (more than half) of the water-soluble organic matter was isolated in pure form in order to undertake final analysis by liquid chromatography coupled to mass spectrometry. It was confirmed that the isolated organic matter mainly consisted of HULIS, which had been previously suggested on the basis of elemental analysis and different spectroscopic studies. The mass spectrometric characterization indicated that the AMW of these substances would be in the 200–300 Da range, and it was concluded that water-soluble macromolecular compounds should have MW < 500 Da. In 2005, Karst published the first paper on liquid chromatography-electron capture-atmospheric pressure chemical ionization-mass spectrometry (LC-EC-APCI-MS), a technique with high potential for the analysis of compounds with functional groups having high electron affinity.[168]

In 2005, Romero and Oehme proposed organosulfates as a new component of HULIS in atmospheric aerosols.[169] The authors used ion trap mass spectrometry (ITMS) in order to obtain qualitative information about the chemical composition of HULIS in PM_{10}. In their investigations, HULIS were separated from inorganic salts by SEC and were detected by electrospray ionization in the negative ion mode (ESI(−)). Based on the observed fragment spectra, the authors suggested the existence of sulfate covalently bound to HULIS.

Later, liquid chromatography - tandem mass spectrometry (LC-MS/MS) was used by Stone et al. to characterize the functional groups present in HMW WSOC of atmospheric aerosols.[170] The performed chemical analysis targeted identification and quantification of functional groups such as aliphatic, aromatic and bulk carboxylic acids, organosulfates, and carbohydrate-like substances that comprise species with MW of 200–600 Da. The authors also applied hydrophilic interaction chromatography (HILIC), as a novel approach to better understand the chemical structure and origin of HULIS. In a review article, HILIC is described as a type of normal-phase liquid chromatography technique that uses common reversed-phase solvents in the mobile phase and that is mainly used for the separation of polar and ionized compounds.[171]

Stone et al. analyzed PM_{10} and $PM_{2.5}$ samples by using a liquid chromatograph interfaced to a triple quadrupole mass spectrometer (API 4000, Applied Biosystems/MDS Sciex) with negative TurboIon Spray (TIS) ionization, a variant of electrospray ionization (ESI).[170] LC separation was achieved using an Atlantis HILIC Silica column (4.6 mm i.d., 150 mm length) and a mobile phase consisting of acetonitrile and water with 10 mM ammonium formate buffer. The mobile-phase flow rate was 800 μL min^{-1} and the injection volume was 10 μL. To eliminate the possibility of organosulfate formation as analysis artifacts, isotope experiments were conducted. They consisted of adding isotopically labeled ^{34}S-sulfate to the ambient samples at various points in the extraction and in the LC-MS/MS analysis procedures, followed by parallel analysis of labeled and unlabeled samples. The final outcome was that organosulfates were not artifacts of either sonication, extraction in water or LC-MS/MS analyses.

LC-ESI-MS/MS was used in 2008 for the characterization of organosulfates generated during the photooxidation of isoprene and unsaturated fatty acids in ambient aerosols.[172] Separation has been performed under gradient mode, using as mobile phase 0.1% (v/v) acetic acid (A) and methanol (B) at a flow rate of 0.2 mL min^{-1}. The chosen column (Atlantis dC$_{18}$) had several advantages, including the fact that the difunctionally bonded C$_{18}$ alkyl residues prevented the collapse of the stationary phase when using an aqueous mobile phase. Therefore, it could provide increased retention of the polar organosulfates compared to a classical C$_{18}$ column. On the selected column, separation between inorganic sulfate (detected at m/z 195 as the adduct $H_2SO_4{:}HSO_4^-$) and the organosulfates of 2-methyltetrols was successfully performed, while it was not achieved in a previous study.[173] Moreover, this result is supposed to provide additional evidence that the initial identifications related to organosulfates were not artifacts formed in the mass spectrometer due to coelution. The characterized polar organosulfates were considered to be of climatic relevance, because they may contribute to the hydrophilic properties of fine ambient aerosol. However, Claeys et al. consider that further work will be needed to characterize organosulfates, nitrooxy organosulfates and higher molecular weight oligomers in HULIS.[174]

In 2012 the group of Claeys reported on the chemical characterization of HULIS from fine atmospheric aerosols samples (PM$_{2.5}$), using liquid chromatography and detection by DAD and ESI-MS.[174] Unprocessed aqueous aerosol extracts and dissolved HULIS samples were subjected to detailed organic analyses. The separation of the HULIS components was achieved using a T3 Atlantis C$_{18}$ column, containing trifunctionally bonded C$_{18}$ alkyl chains to improve the retention of polar analytes. Acetic acid 0.1% (v/v) (A) and methanol (B) was used as mobile phase under gradient mode. The LC-DAD/MS instrumental set-up consisted of a Surveyor Plus LC system equipped with a photodiode array detector, ESI(−) interface and a LXQ linear ion trap mass spectrometer. A comparison was performed by the authors between their (-)ESI-MS data recorded for unknown acidic and nitroaromatic compounds with data available from previous studies obtained under the same LC/MS conditions.[175-176] In the investigated HULIS samples, the most abundant tracers were attributed to the class of nitro-aromatic catecholic compounds (4-nitrocatechol being the most prevalent), suggesting that aromatic hydrocarbons emitted during biomass burning are potentially important gas-phase precursors for HULIS.

Further articles report about organosulfates in ambient aerosols with modified liquid chromatography - tandem mass spectrometry assemblies. Ultra performance liquid chromatography (UPLC) coupled to negative electrospray ionization triple quadrupole

(TQ)MS was used for the identification and quantification of organosulfates in ambient aerosols collected in various areas.[177-178] Organosulfates and nitrooxy-organosulfates were often observed as the most intense peaks in the ESI(-) spectra of the HULIS fraction isolated from aerosol samples collected at a rural location of the Pearl River Delta Region (PRD), China. Samples were analyzed using both ESI(+) and ESI(-), coupled with an ultrahigh resolution mass spectrometer (UHRMS).[179]

Measurements of high molecular weight carboxylic acids in atmospheric aerosol particulate

Different separation techniques such as ion chromatography, tandem liquid chromatography-mass spectrometry, two dimensional liquid chromatography-time-of-flight mass spectrometry, hydrophilic interaction liquid chromatography tandem mass spectrometry, capillary electrophoresis and tandem gas-chromatography-mass spectrometry are often used for the determination of carboxylic acids in atmospheric aerosols. While ion chromatography offers information for a limited number of LMW carboxylic acids, all the other techniques can be used to investigate HMW carboxylic acids. Capillary electrophoresis was used for the analysis of organic acids (i.e. dicarboxylic acids, hydroxylated dicarboxylic acids) in size-segregated atmospheric aerosol particles collected in Sagres (Portugal) and in Melpitz (Germany).[180]

Analysis of the WSOC fraction of atmospheric aerosols was performed by HPLC separation with UV detection.[181] For extraction, aerosol filter samples were soaked in 3 mL of Milli-Q water for 24 hours. The extracts were then filtered on PTFE membranes to remove suspended particles, and analyzed at a constant flow rate of 0.7 mL min^{-1} on an HPLC equipped with a 100-µL loop, an ion exchange column (DEAE-TSK gel column, 7.5 mm i.d. × 7.5 cm length), and a UV detector. The separation was achieved by using a ionic strength gradient of the mobile phase, while pH was held constant at 8.0. Absorbance was monitored at 254 nm, where organic and inorganic anionic species with increasing number of charges per molecule may absorb. However, most of the detected peaks were attributed to absorbing organic species. HPLC/UV achieved separation of three classes of compounds, i.e.: *(i)* neutral compounds (N), which are not retained by the column; *(ii)* monocarboxylic and dicarboxylic acids (MDA), and *(iii)* polycarboxylic acids (PA), polycharged compounds with at least three carboxylic groups per molecule. The sum of these three groups accounted for about 70% of the WSOC, with MDA and PA being most abundant (about 50%).

Oxodicarboxylic acids, described by the general formula $C_nH_{2n-5}O_5$, are linear dicarboxylic acids with an additional carbonyl group that have been detected in atmospheric aerosol particles. Measurements of oxodicarboxylic acids with 9-11 carbon atoms were for the first time reported in 2006, by using the LC/MS-TOF technique.[54] Ultrasonication (ice bath, 30 min) in 10% aqueous methanol was applied twice to the aerosol filter samples, to enhance the extraction process (the extraction efficiency was about 98% for all the analyzed dicarboxylic acids). About 100 μL of the extract were directly injected into the HPLC. For the separation, a ReproSil-Pur C_{18}-AQ (250 mm×2 mm ID, 5 μm particle size) with a PEEK (poly(ether-ether-ketone)) cartridge was used as analytical column. The mobile phase was a mixture of 0.1% formic acid in water (eluent A) and acetonitrile (eluent B), in gradient mode. The HPLC system was coupled to a hybrid mass spectrometer (quadrupole and time-of-flight (TOF)) QSTAR by an ESI interface. By combining tandem mass spectrometry (MS/MS) with the high mass resolution of a TOF detector, it was possible to reduce the mass measurement error below 10 ppm.

Analysis of C_8-C_{22} mono- or dicarboxylic acids in atmospheric aerosols collected from various stations in Finland was performed on a comprehensive two-dimensional liquid chromatograph, connected via ESI to a micro-TOF mass spectrometer. It was used a strong cation-exclusion (SCX) column of 1 mm i.d. in the first dimension, and a C_{18} packed column of 3 mm i.d. in the second dimension.[182] The LC×LC coupling of the two instruments was ensured by a 10-port high-pressure two-position valve. A binary mobile phase consisting of acetonitrile (A) and water with 17.5 mM acetic acid (B) was used for gradient separation. The microTOF-LC mass spectrometer was operated in negative mode, with the detected mass range set to 80–800 m/z. The flow from the LC×LC was split with a laboratory-made T-splitter before entering the ESI. With the above-mentioned configuration and instrumental operating conditions, a very effective tool was obtained for the screening of unknown acidic compounds because of the combined information given by the elution pattern and by the sensitive and accurate mass spectral data.

Zhang and coworkers report on the analysis of carboxylic acids (aliphatic C_5-C_{16} dicarboxylic acids, phthalic, pinic and pinonic acid, 3-MBTCA) in a large set of fine and coarse aerosol particle samples collected over a period of one year in central Europe (Mainz, Germany).[183] The instrumental set-up for the HPLC/MS system included hybrid Qq-TOF mass spectrometers QSTAR with ESI interface.

In 2011, a sensitive HILIC/ESI-MS/MS method was developed for the quantitative determination of aliphatic mono- and dicarboxylic acids (C_2-C_9), alicyclic mono- and dicarboxylic acids and aromatic di- and tricarboxylic acids in coarse atmospheric aerosols.[184] The analyzed compounds included selected aliphatic (i.e. malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, maleic, fumaric, glycolic and pyruvic acid), alicyclic (i.e. cispinonic and pinic acid) and aromatic carboxylic acids (i.e. trimesic, phthalic acid and its isomers). It was used an HPLC system with DAD detector, coupled to a triple quadrupole-linear ion trap hybrid mass spectrometer (LC/MS/MS) with a TurboIonSpray (TIS) source (a variant of ESI). The above instrumental set-up was actually used to optimize the ESI-MS/MS conditions. The interest analytes were separated on an amide column (XBridge Amide column, 100 mm×3.0 mm i.d., 3.5 μm particle size), using a gradient elution with a mobile phase having a final 10 mM constant ionic strength and containing acetonitrile and aqueous ammonium acetate buffer (pH 5.0). The authors have studied the influence of the buffer type, pH, polar modifier and temperature on analyte retention under HILIC. The ion suppression effects during HILIC-ESI/MS/MS were also examined, which is quite important especially during method development for trace analysis in complex samples. Direct experimental evidences are reported of strong (possibly affecting cis-pinonic, maleic and trimesic acid) and moderate ion suppression (observed in the region were phthalic acid eluted). Phthalic-d_4 and succinic-d_4 were used as internal standards to ensure proper precision and accuracy, when phthalic and other studied acids were investigated. The limits of detection ranged from 0.03 to 16.0 μg L^{-1} in selected reaction monitoring mode (SRM). In addition to the applicability to carboxylic acids in ambient aerosol particles, a big advantage of the newly proposed method is its ability to detect and separate the isobaric compounds of the investigated carboxylic acids.

An LC-MS (Q-TOF) and microwave-assisted gas-phase hydrolysis methodology has been developed for the detection of native (underivatized) amino acids (AA) in both free (FAA) and combined (CAA) forms in atmospheric aerosols.[185] Within the HPLC system, the separation of the target AA analytes was facilitated by the use of ion pairing chromatography with a Zorbax Eclipse XDB-C_{18} column (4.6×50 mm, 1.8 μm particle size). During the experimental run the column temperature was maintained at 40 °C, by ramping the mobile phase consisting of H_2O (0.8 mM PFHA/0.05% TFA/0.05% formic acid) and MeOH (0.03% formic acid) at a flow rate of 0.40 mL min^{-1}. The multimode ion source was operated in ESI(+) mode. Under these experimental conditions the authors could separate asparagine, serine, aspartic acid, glycine, hydroxyproline, glutamine, threonine, glutamic acid, cysteine, alanine, proline, cystine, methionine, valine, tyrosine, isoleucine, leucine, phenylalanine, tryptophan, histidine, arginine and lysine. The big advantage of the developed methodology derives from its ability to quantify AA in aerosol samples without derivatization, which reduces time-consuming preparation procedures while providing selective mass determination for important organic nitrogen (ON) species. Furthermore, the preparation procedure eliminates the freeze-drying approach that is typically practiced for water removal with biological samples and exploits the advantages of the vapor-phase microwave hydrolysis. In 2013, Samy and Hays reported about quantitative LC-MS analysis of water-soluble heterocyclic amines in $PM_{2.5}$ aerosols collected at Duke Forest, USA.[186]

Other chemical classes present in atmospheric aerosols

Pesticides contaminate the atmosphere through various pathways, and air pollution due to pesticides is still a persistent problem in modern agriculture.[187] Various pesticides, in the form of herbicides, insecticides or fungicides, and polychlorinated biphenyls (PCBs) are chemical compounds still widely applied in the world. Pesticides are semi-volatile organic compounds, which can be simultaneously present in both the gas and particulate phases in the atmosphere. Pesticides hydrolysis (e.g. parathion) is suggested as a possible source of atmospheric 4-nitrophenol.[188] Pesticide extraction from airborne particulate matter is usually performed using Soxhlet.[189] Gas chromatography (GC) in combination with electron-capture detection (ECD) or mass spectrometric detection are the conventional analytical approaches used for the determination of pesticides in various samples. However, owing to the evolution of LC-MS instruments that have dramatically improved the quality of their performance and the scope of their applications, and also because of the greater polarity of the currently used pesticides, there is a recently increased interest in the use of liquid chromatography for pesticide analysis. The benefits of LC-MS/MS in terms of wider scope, increased sensitivity and better selectivity are obvious and these characteristics, together with the ability to perform most determinations without derivatization, make LC-MS/MS the preferred technique that is currently available for the determination of pesticide residues in various samples.[190]

A rapid procedure for the trace-level determination of four fungicides (carbendazim, thiabendazol, imazalil and bitertanol), three insecticides (imidacloprid, methidathion and pyriproxyfen), one helicide (methiocarb) and one acaricide (hexythiazox) in fine airborne particulate matter ($PM_{2.5}$) has been developed.[191] Extraction of $PM_{2.5}$-bound pesticides was performed by pressurized liquid extraction (PLE). The optimized extraction conditions are reported as follows: extraction solvent, acetone; oven temperature, 50 ^{o}C; pressure, 1750 psi; heatup time, 2 min; static cycles, 2; static time, 1 min. The preparative step was followed by a direct injection into LC-MS/MS. Separation was performed on a Luna C_{18}(2) column (150 mm×2.0 mm i.d., particle size 5 μm). The mobile phase consisted of H_2O with 0.01% acetic acid (A) and methanol (B), used at a flow rate of 200 μL min^{-1} under gradient conditions. All pesticides were detected with the MS using ESI in the positive mode. The same group also reported about a rapid procedure for the determination of 30 currently used pesticides (CUP) in fine airborne particulate matter ($PM_{2.5}$) at trace level. The method used extraction of $PM_{2.5}$-bound pesticides by microwave-assisted extraction (MAE), followed by a direct injection into LC–MS/MS.[192] The instrumental conditions were almost similar to those of the previous paper,[191] apart from the composition of the mobile phase A (H_2O, 0.1% acetic acid and 5 mM ammonium formate). Microwave extraction (MAE) of pesticides from $PM_{2.5}$ filters was carried out using a Mars system equipped with 100 mL Teflon® TFM extraction vessels. The filters were extracted at 50 ^{o}C for 20 min, using a power of 1200 W and 30 mL of ethyl acetate. After extract filtration, 100 μL of diethylene glycol were added to the extracts that underwent evaporative concentration. The extracts were finally re-dissolved with 1 mL of water:methanol (70:30) and filtered through a 0.22 μm GHP Acrodisc filter prior to the LC-MS/MS determination. The developed method allowed analysis of pesticides such as omethoate, imidachloprid, carbendazim, acetamiprid, dimethoate, thiabendazole, imazlil, malathion, flusilazole, metalaxyl, methidathion, azoxystriobin, methiocarb, fenhexamid, buprofezin, pyriproxyfen, chlorpyrifos, pyridaben and fenazaquin. The same authors also presented the first data on the particle-size distributions in the atmosphere of currently used pesticides, by using LC-MS/MS characterization.[193-194]

Another interesting work reports about trenbolone acetate (TbA) analysis in airborne particulate matter, by liquid chromatography tandem mass spectrometry.[195] TbA is a potent synthetic anabolic steroid that was approved by the FDA as growth promoter in beef cattle in 1987. Given the endocrine-modulating activity of TbA and its metabolites in all vertebrates, the authors developed a method that incorporates solid phase extraction and LC-MS/MS for the simultaneous and sensitive determination of the three major TbA metabolites (trendione, 17α-trenbolone, 17β-trenbolone) in total suspended particulate matter (TSP) samples. Furthermore, in areas located in semi-arid to arid climates, with limited surface water and infrequent runoff events, the environmental conditions limit the entry of trenbolone (TbOH) into the aquatic ecosystems but facilitate its long-range transport via PM. Sample preparation involved PLE followed by laborious cleanup on SPE cartridges. The analytes were separated with a Phenomenex Gemini-NX C_{18} analytical column (150 mm × 2.0 mm, 3 μm particle size), using an aqueous methanol gradient at a flow rate of 0.2 mL min^{-1}. MS analyses were conducted on a LCQ Advantage ion trap mass spectrometer with ESI(+) interface.

Pyrogenic carbon (PyC) results from incomplete biomass combustion and it is found in different environmental matrices. Analysis of PyC in environmental samples is of great interest, especially due to its role in the carbon cycle.[196] An HPLC method that reproducibly allows quantification of benzene polycarboxylic acids (BPCA) as molecular markers for PyC in various kinds of environmental samples is reported in the literature.[197] The separation was performed with an HPLC system equipped with a Poroshell 120 SB-C_{18} column (100 mm × 4.6 mm). The mobile phase consisted of orthophosphoric acid dissolved in water and buffered to pH 1.2 with NaH_2PO_4 (A) and of acetonitrile (B). A purely aqueous gradient to pH 4.7 can be used if there is the need to work without organic solvent.

Bioaerosols (human and animal dander, plant and insect debris, etc.) are considered to be an important portion of the atmospheric particle budget.[198-199] They contain information-rich packets of biochemical data that are specific to the organism of origin, with high potential to be used as a novel finger-printing technique.[200] In 2013, Staton and coworkers reported about the analysis of bioaerosol samples from various indoor environments, with the main aim to create identifiable patterns attributable to a source level of occupation.[201] The aqueous aerosol extracts were thus investigated in order to distinguish signatures of occupation, compared to the environmental background. Protein quantification was performed on an aqueous extract by using a fluorimeter at the excitation/emission wavelength of 470/570 nm, respectively. An HPLC-UV system was used to analyze some methanol extracts, which had been ultrasonicated to lyse any cell in the matrices. Separation was performed on a Zorbax SB-C_3 analytical HPLC column (4.6 × 150 mm) with a Zorbax guard column, using a mobile phase consisting of methanol/water in gradient mode at a flow rate of 1 mL min^{-1}. The results of the study suggest that bioaerosol "fingerprinting" is possible, with the two test environments (occupation vs. background) being distinguishable at a 97% confidence interval.

4.2 Laboratory and environmental chamber experiments on organic aerosols of biogenic origin

During the last years, several atmospheric simulation chamber experiments have been conducted, most of them focused on the estimation of aerosol mass yields from the oxidation of various volatile organic compounds (VOCs). Several groups have focused on the chemical characterization of secondary organic aerosols (SOA) that result after the gas-phase reaction of certain volatile organic compounds. The large number of products (even from a single VOC precursor) and the wide range of their polarities make the molecular-level analysis difficult. However, several classes of products (i.e. alcohols, carbonyls, acids, peroxides, nitrates) have been identified, and numerous laboratory and field studies have shown that various organic acids (monoacids, diacids, hydroxy acids etc.) are major contributors to the particle phase from VOC precursors.[202-205] The oxidation of organics in aerosol particles may affects the aerosol physical properties through the process known as aging, and there is growing evidence that composition effects may play a central role in the atmospheric aging of organic particles.[206] The aging of aerosols would be linked to various oxidation processes induced by radical species.[207-208]

Isoprene

Isoprene, the simplest gas-phase diene, is one of the most important biogenic compounds and it is subjected to numerous studies in terms of its capacity to generate SOA. Isoprene atmospheric oxidation makes a significant contribution to SOA formation at the regional and global scales.[209-211] The daytime sinks of isoprene are reactions with OH radicals and O_3, whereas the nighttime sinks are reactions with NO_3 radicals and O_3. The isoprene lifetimes associated with daytime OH and O_3 reactions, and nighttime NO_3 reaction are 0.95, 17, and 1.3 h, respectively.[212] As a consequence, many laboratory studies are focused on the secondary organic aerosol formation from isoprene oxidation.

In 2008, Sato used an ion exclusion liquid chromatography (IEC-LC) system combined with an ESI-MS method for the analysis of polyols and organic acids, present in an aqueous solution of SOA obtained from diene oxidation (isoprene, 1,3-butadiene, 2,3-dimethyl-1,3-butadiene and 2,4-hexadiene were among the investigated dienes).[213] 2-Methyltetrols (constituting 0.5-2% of the aerosol mass), methylnitrooxybutanetriols (1-7% of aerosol mass), methyldinitrooxybutanediols (0.3-8% of aerosol mass) and nitric acid (4-9% of aerosol mass) were found in the aqueous solution of the SOA samples generated from isoprene. 2-Methyltetrols were also identified in atmospheric aerosols collected in various areas.[214-215] Results obtained within former investigations led to a possible mechanism that could be responsible for 2-methyltetrols formation in aerosols, under low NO_x conditions [56,214,216] (Figure 2a). However, in a later study, a mechanism responsible for the formation of methyldinitroxybutenediols, methylnitrooxybutentriols and 2-methyltetrol from the photooxidation of isoprene under high NO_x was also proposed (Figure 2b).[213] In 2013, Sato and coworkers also reported about the identification of 2-methylglyceric acid (isoprene oxidation product) in aerosols samples, by using LC/TOF-MS in total ion analysis mode.[217] The aerosol sample filters were stored at room temperature until filter pretreatment.[217] For the quality assurance/quality control stage, blank filters were also prepared and analyzed. Each aerosol sample filter for LC/TOF-MS analysis was sonicated in 5 mL methanol for 30 min. The extract was placed in a 5-mL amber vial and concentrated to near dryness under a gentle stream of gaseous N_2. The concentrated extract was then dissolved in 300 μL of formic acid/methanol/water solution. A 10 μL aliquot of the sample solution was loop-injected into the LC/TOF-MS instrument. For sample separation, a C_{18} silica gel column (150 mm length, 3.0 mm i.d., particle size 5 μm) was used. A mixture of aqueous solution with 0.05% formic acid and methanol in gradient mode was used as mobile phase, at a total flow rate 0.4 mL min^{-1}. The analytes were ionized using ESI(−). The generated ions were analyzed using a TOF-MS with a mass accuracy of <3 ppm, which enabled prediction of the chemical formulas of the analytes.

Terpenes

Monoterpenes are major contributors to the biogenic SOA.[219-220] Taking into account structural details, monoterpenes can be divided in two major classes. The first class is related to a number of naturally occurring cyclic terpenes containing an endocyclic C=C double bond (e.g. α-pinene, 3-carene, 2-carene, limonene, α-phellandrene, β-phellandrene, α-terpinene, γ-terpinene, terpinolene, α-humulene, α-cedrene, α-copaene, β-caryophyllene). The second class is related to terpenes containing an exocyclic C=C double bond (e.g. β-pinene, sabinene, camphene, limonene, β-phellandrene, β- caryophyllene, longifolene).[221] Gas-phase oxidation of monoterpenes, initiated by either OH radicals or O_3, has been performed in smog chamber experiments. Among the techniques used for the characterization of the generated aerosols, liquid chromatography was also employed. Most of the available studies are focused on α-pinene and sabinene from first class, β-pinene and 3-carene from the second class, and limonene as a representative compound of cyclic terpenes with two C=C double bonds (one endocyclic and one exocyclic). Low-volatility products in the particle phase have been identified in these studies.[144,221-222] The chemical structures of some cyclic investigated monoterpenes and of the derived carboxylic acids, found in the aerosol phase after gas-phase reaction of the parent terpenes with OH radicals, are presented in Figure 3. Pinic acid, norpinic acid, pinonic acid, norpinonic acid, caric acid, caronic acid, sabinic acid, keto-limonic aicd and keto-limononic acid are important constituents of the aerosol atmospheric samples formed during the ozonolysis process of selected monoterpenes.

A study on the gaseous and particulate products formed in the gas-phase OH oxidation of monoterpenes (i.e., α-pinene, sabinene, β-pinene, 3-carene and limonene) was performed.[221] The smog chamber aerosol extracts were analyzed by LC-MS^n (LC coupled to an LCQ ion-trap mass spectrometer). The aerosols generated by the photooxidative process were collected on PTFE filters, which were extracted by sonication with 10 mL dichloromethane at room temperature. The solvent was evaporated under a gentle stream of nitrogen, and the residues were redissolved in 1 mL acidic methanol-water (75% H_2O, 25% CH_3OH, 17.5 mM acetic acid). Separation was carried out on a 25 cm × 4.6 mm C_{18}-coated silica gel (4 μm) Novasil column, with the mobile phase (mixture of H_2O + 17.5 mM acetic acid and methanol) operated in the gradient mode at a flow rate of 0.8 mL min^{-1}. Polar compounds from the aerosol phase were identified from the LC-MS and MS^n data, by comparison with standards and with previously analyzed SOA extracts from terpene/O_3 reactions.[223-224] Analysis of acidic products was performed under ESI mode, which provides higher sensitivity compared to atmospheric pressure chemical ionization (APCI). However, ACPI was also used in some cases. In most cases the MS was operated with the ion-trap scanned from 70 to 400 m/z in the first run. In additional runs, the ion-trap was operated in the MS^n daughter ion scan mode (15%-30% relative energy), with the primary cycle(s) locked on the m/z value(s) corresponding to the quasi-molecular ion of the suspected target compound or the fragment ion of interest. The daughter ions were scanned from m/z 70 to ca 10 amu above the molecular weight of the ion under investigation. It was also taken into account that oxygenated terpenoids containing keto-groups, hydroxy-groups, and aldehyde-groups have a proton affinity, which can give rise to signals with APCI in the positive ion mode. Therefore, the APCI operation mode was used to screen for polar oxidation products other than carboxylic acids. In this case, the LC was interfaced to the ion-trap through an APCI source run at 450 ^oC at a corona discharge voltage of +5 V. In the study of Larsen et al.[221], the most abundant compounds in SOA from terpenes with an endocyclic C=C double bond were C_{10}-keto-aldehydes, C_{10}-keto-carboxylic acids, C_{10}-hydroxy-keto-carboxylic acids, and C_{10}-hydroxy-keto-aldehydes (pinonaldehyde, pinonic acid, hydroxy-pinonic acid isomers, and hydroxy-pinonaldehyde isomers from α-pinene; 3-caronaldehyde, 3-caronic acid, hydroxy-3-caronic acid isomers, and hydroxy-3-caronaldehyde isomers from 3-carene). The most abundant compounds in SOA from terpenes with an exocyclic C=C double bond were C_9-ketones, C_9-dicarboxylic acids, and C_{10}-hydroxyketo-carboxylic acids (norpinone, pinic acid, and hydroxy-pinonic acid isomers from β-pinene; sabinaketone, sabinic acid and hydroxy-sabinonic acid isomers from sabinene). Decarboxylated analogues of most of the listed compounds were present in SOA in minor concentrations. In SOA from limonene photooxidation, the most abundant compounds were a C_{10}-keto-aldehyde and its oxo-derivative together with hydroxy-derivatives of a C_{10}-keto-carboxylic acid.

Many environmental chamber studies have been devoted to the investigation of the SOA formed during monoterpenes ozonolysis.[144,225-228] The study of Warnke et al. (2006) presents a method for the determination of acidic products from terpene ozonolysis, using a capillary-HPLC-ESI-MS/MS method.[144] The authors investigated similar monoterpenes as Larsen et al.,[221] i.e., α-pinene, sabinene, β-pinene, 3-carene and limonene, but under different reaction conditions (ozonolysis instead of OH). The experiments were conducted in a glass chamber. Particles were collected on quartz fiber filters mounted in stainless steel filter holders. After the experiments, the filters were spiked with a camphoric acid standard to determine the recovery rate. Spiked and unspiked filter samples were extracted in an ultrasonic bath, using methanol as solvent. The extraction solution was evaporated under a gentle nitrogen flow and the residual volume was filtered through 0.45-μm PTFE filters. Finally, the filtered methanol extract was evaporated under nitrogen stream and gentle heating. The residue was re-dissolved in pure water after adding an additional standard of 1,2-cyclohexanediacetic acid for quality control purposes. Analysis was performed by HPLC, using a GromSil "Organic Acids" capillary column (150-mm length × 0.3-mm i.d.), packed with a 5-μm polar endcapped C_{18} RP-material. The mobile phase was a mixture of water with 10 mM formic acid and 2.5% acetonitrile (A) and of acetonitrile with 2.5% water (B). The flow rate was 0.2 mL min^{-1} under a gradient mode. A LCQ DECA ion trap mass spectrometer was used for detection of the separated compounds in the ESI(−) mode. Analysis of the filter extracts with capillary-HPLC-ESI-MS/MS yielded several structural analogues of pinic and pinonic acid. They are both oxidation products, the carbon skeleton of which is derived from the pinene structure. Norpinic, pinic and pinonic acid were quantified using authentic standards. Also based on standards, caric, caronic, sabinic, keto-limononic and norpinonic acid were quantified as well.[144]

Muller and coworkers (2008) performed a study on SOA formation from cyclohexene and cyclohexene/α-pinene ozonolysis. Experiments were carried out in a cylindrical glass reaction chamber, under dark and dry conditions, without seed particles or OH scavengers.[222] To determine the chemical composition of the SOA formed during the ozonolysis process, the authors used both on-line and off-line analysis. In the on-line mode, an ion-trap mass spectrometer with an atmospheric pressure chemical ionization source (APCI-IT/MS^n) was used. In the off-line mode, investigations were performed by using HPLC/ESI-IT/MS^n. Aerosols particles were collected on PTFE-coated quartz fiber filters. For HPLC/ESI-IT/MS investigations, the filter samples were extracted in methanol/water by sonication and the extracts were concentrated under a gentle stream of heated nitrogen. Dimeric products were identified in the aerosol phase, which represent ester compounds such as pentanedioic acid mono(4-carboxypropyl) ester, pentanedioic acid mono(4-carboxybutyl) ester, and hexanedioic acid mono(3-carboxypropyl) ester.[222] However, in other ozonolysis studies of monoterpenes/cycloalkenes, the presence of simpler esters (i.e., methyl- and ethylesters) has been reported.[52,229-230]

Myrcene is one of the major monoterpenes in the emissions from coniferous forests, with a 10% contribution to the total monoterpene budget depending on the tree species.[231-232] Myrcene was also subject to SOA investigations by using liquid chromatography,[233] because its acyclic structure provides potential sites of attack for oxidation by O_3 and by OH and NO_3 radicals.[234] The ozonolysis and photooxidation of myrcene (mixtures of myrcene/O_3 or myrcene/CH_3ONO/NO/UV in an environmental chamber) have been recently studied by use of HPLC/ESI-TOFMS for SOA characterization.[233] SOA samples were obtained by an instrumental set-up including a denuder-filter device (5 channel, 400 mm length) and aerosol filter collectors. The denuder was used to avoid positive sampling artifacts on the PTFE filter. To enable the collection and identification of gas-phase oxidation products as suggested by Kahnt et al. (2001),[235] Boge et al.[233] also used a DNPH (2,4-dinitrophenylhydrazine)-coated denuder. After each experiment, the denuder was extracted with acetonitrile and the extract was first derivatized and finally evaporated to dryness. The residue was then reconstituted in methanol, and the resulting methanol solutions were purified by SPE. For the analysis with HPLC/ESI(−)-TOFMS, the purified extract was dried under a gentle stream of nitrogen and reconstituted in acetonitrile/water. As far as filter samples of the aerosol phase are concerned, an orbital shaker was used for the methanol extraction. The extract was filtered through a 0.2 μm PTFE syringe filter. The filter residue was extracted again with methanol and finally reconstituted in a methanol/water mixture. Another portion of the filter was used to determine the carbonyl compounds. Therefore, a filter portion was extracted on an orbital shaker after it was treated with the derivatization reagent (DNPH) and acetonitrile. To remove insoluble material, the extract was filtered through a syringe filter, dried and reconstituted in acetonitrile/water before the HPLC/ESI/TOFMS analysis. Clear evidence was obtained on the presence of terpenylic acid in the SOA samples collected from the ozonolysis of myrcene in the absence of an OH scavenger and from the OH radical-initiated reaction of myrcene. In contrast, no terpenylic acid was detected in samples collected from myrcene ozonolysis in the presence of CO, used as OH radical scavenger.[233] This observation suggests that the formation of terpenylic acid involves the reaction of myrcene with OH radicals. Terpenylic acid has also been reported as one of the most abundant SOA compounds from α-pinene and β-pinene,[236-238] and it is known to be an important constituent of ambient biogenic SOA.[239-240] Considering the information available from the literature, a general potential mechanism responsible for the formation of terpenylic acid in aerosols from myrcene oxidation by OH radicals is presented in Figure 4.

LC techniques were also used to investigate the formation of organic compounds in the particulate phase, produced by photo-oxidation of β-caryophyllene under simulated atmospheric conditions.[241] By LC-MS/MS, a total of 20 organic compounds were identified in SOA formed from photo-oxidation of β-caryophyllene/NO_x mixtures. The most abundant compounds were β-caryophyllonic acid and β-caryophyllinic acid/β-norcaryophyllonic acid. LC-MS/MS analysis was performed on the extracted sample using a HCT Plus ion trap mass spectrometer, after separation with an Eclipse ODS-C_{18} column with 5 µm particle size (4.6mm×150 mm). Elution was achieved with a binary gradient, using (A): 0.1% formic acid in HPLC-MS grade water and (B): HPLC grade methanol, at a flow rate of 0.6 mL min^{-1}. The mass spectrometer was used in both positive and negative ion mode, scanning from m/z 50 to 600.

The potential of the OH radical-initiated oxidation of eucalyptol (1,8-cineole) to generate SOA was recently investigated.[242] Diaterebic acid acetate (2-[1-(acetyloxy)-1-methylethyl]succinic acid, $C_9H_{14}O_6$) and diaterpenylic acid acetate (3-[1-(acetyloxy)1-methylethyl]glutaric acid, $C_{10}H_{16}O_6$) were identified by using LC coupled with ESI-TOF mass spectrometry, in parallel with ion trap MS.

Phenols

Phenols represent another important class of organic compounds that have been investigated with regard to SOA formation, by using liquid chromatography techniques and environmental chamber facility.[243] The focus was on the chemical composition of SOA formed from phenol and methoxyphenols, which are known to be major components of biomass burning.[244-246] Yee et al. (2013) investigated the SOA formation potential of three organic compounds as biomass burning intermediates, i.e. phenol, guaiacol (2-methoxyphenol) and syringol (2,6-dimethoxyphenol).[243] Experiments on mixtures of phenol/H_2O_2/purified air were carried out in a 28 m^3 Teflon environmental chamber. Ammonium sulfate was introduced in the chamber as seed aerosols and to promote the condensation of poorly volatile oxidation products. Photogenerated aerosols were collected on Teflon filters (47 mm diameter, 1.0 µm pore size). Filter sampling of the aerosols was started when the aerosol volume, monitored by a differential mobility analyzer (DMA) system, reached a constant value. Filters were extracted by following the protocol of Surratts et al.[247] To get accurate mass measurements, Yee et al. (2013) analyzed the filter extracts by ultra performance liquid chromatography (UPLC) coupled with a TOF mass spectrometer equipped with an ESI source.[243] Some filter extracts were also analyzed by HPLC coupled to an ion trap mass spectrometer (ITMS) through an ESI source, allowing for tandem MS measurements to be obtained. On the UPLC system, separation was performed on a Waters Atlantis T_3 column (3 µm particle size; 2.1 × 150 mm) with a mixture of 0.1 % acetic acid in water (A) and 0.1 % acetic acid in methanol (B). For MS detection, two scan events were acquired during each chromatographic run. The first scan event was the full scan mode, in which data were collected from m/z 120 to 600 in the negative ionization mode. The second scan event was the mode in which product ions were generated from significant base peak ions observed in first scan event. Under high NO_x conditions, the number of identified organic compounds generated during the oxidation of guaiacol by OH radicals was almost half as those identified under low NO_x conditions. Furthermore, while dihydroxybenzenes, epoxides and some fragments associated with methoxy-hydroxy-butenedial were mainly observed under low NO_x, dihydroxybenzenes with a nitro group prevailed under high NO_x. Based on the results of off-line analysis of the filters by UPLC/ESI-TOFMS, the authors suggested that almost all of the compounds with less than 7 carbon atoms ($<C_7$), identified under low NO_x conditions, were likely ring fragments undergoing further oxidation into the aerosols phase. Conversely, the C_7 compounds generated under the same conditions are likely to be first-generation products. The most important functional groups contained in SOA generated from phenols oxidation include carboxylic acids, carboxylic anhydrides and lactones or esters.[248] The observation of carboxylic anhydrides and lactones suggests that there is potential for additional intra- and inter-molecular reactions, which may occur in the aerosol phase and involve the carbonyl and methoxy groups of SOA products. Based on the available information from the literature, as far as the oxidation of 2-methoxyphenol under low NO_x is concerned, the formation of dihydroxybenzenes, epoxides and fragments associated with methoxy-hydroxy-butenedial can be explained by the general mechanism presented in Figure 5.

5 Conclusions

Research on aerosol chemical composition has gradually intensified over the past couple of decades. Aerosol samples are usually composed of several main components and of hundreds of minor and trace constituents. An accurate determination of the chemical composition of air particulate matter is still a very challenging analytical task. The selection criteria of an analysis method are often governed by instrumental performance and financial issues. Therefore, many laboratories that are interested in atmospheric aerosols research are using off-line characterization techniques to investigate the chemical composition. Accessible analysis techniques such as ion chromatography (IC) and liquid chromatography tandem mass spectrometry (LC-MS) are often employed.

Water-soluble inorganic and organic ionic constituents of atmospheric particulate matter with low molecular weight are usually determined by IC, either in classical configuration or by the newly developed particle-into-liquid sampler-ion chromatograph (PILS-IC) system. By using the IC technique in its various forms, many research groups have been able to identify and quantify several water-soluble ionic constituents of the atmospheric aerosols, such as cations (i.e. Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) and both inorganic (i.e. F^-, Cl^-, Br^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}) and organic anions (i.e. Fo^-, Ac^-, Pr^-, Ox^{2-}, Ma^{2-}, Sc^{2-}, Gt^{2-}, Py^-).

Size exclusion chromatography-liquid chromatography (SEC-LC) and high performance liquid chromatography (HPLC), combined with various detectors such as absorption, fluorescence and MS, have been used for the analysis of larger and poorly volatile organics from atmospheric aerosols.

LC-MS in various forms (e.g., LC/ESI/TOFMS, LC/ESI/TQMS, LC-MS^n, HILIC/ESI/MS/MS and LCxLC/MS) has been extensively used to obtain the molecular speciation of organic compounds in atmospheric aerosols, or in aerosols produced by the oxidation of selected organic compounds under simulated atmospheric conditions in environmental chambers. Aliphatic and aromatic hydrocarbons, PAHs, organic acids, alcohols, carbonyls, esters, epoxides, organo-nitrates, organo-sulfates, etc., have been identified and quantified.

During the last two decades, owing to the considerable developments of MS techniques based especially on ESI-MS and high-resolution MS, coupled with LC separation, various analytical tools have become available that can efficiently address the polyfunctional chemical structures of organics in aerosols samples. However, structural information at the individual-component level is still rather limited nowadays.

Despite the considerable efforts made by many research groups, the molecular-level characterization of the (especially organic) chemical composition of aerosols, sampled from the ambient atmosphere or from environmental chambers, is still a big challenge. To increase the knowledge over these issues, new studies using complementary analytical techniques, such as new on-line ones (i.e. APCI-MS^n) with off-line LC/ESI-MS^n, appears as a straightforward necessity. Further development is needed to make such complementary approach applicable to larger scale.

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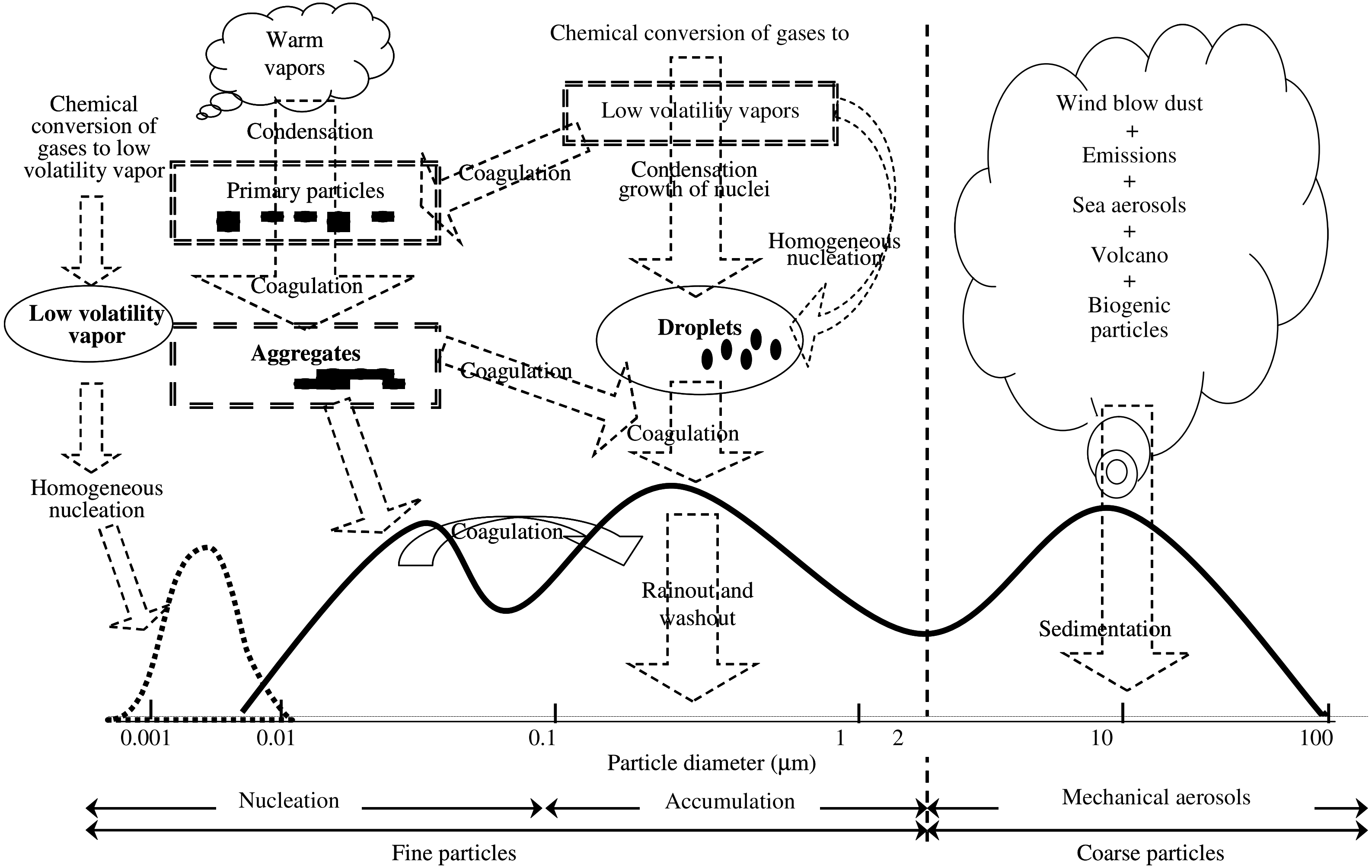

Figure 1: Aerosol size distribution in four modes sustained by the hypothesis under discussion in Finlayson-Pitts and Pitts (2000) and also by the results obtained for size segregated aerosol chemical composition in recent studies.

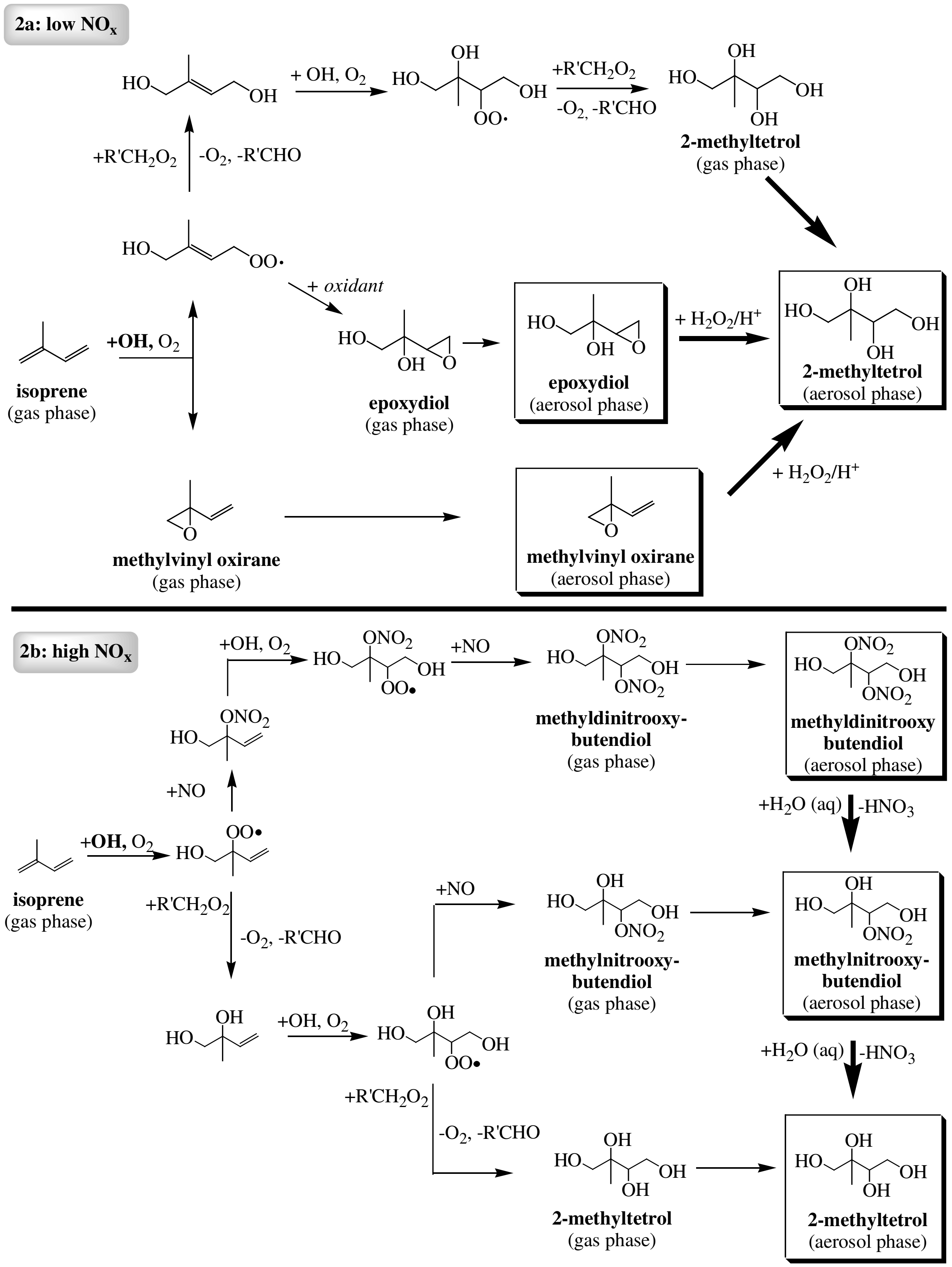

Figure 2: Mechanism explaining eventually methyltetrol, methyldinitrooxybutanediols, methylnitrooxybutanetriol formation in the particle phase by the photo-oxidation of isoprene under low (2a) and high (2b) NO_x conditions.

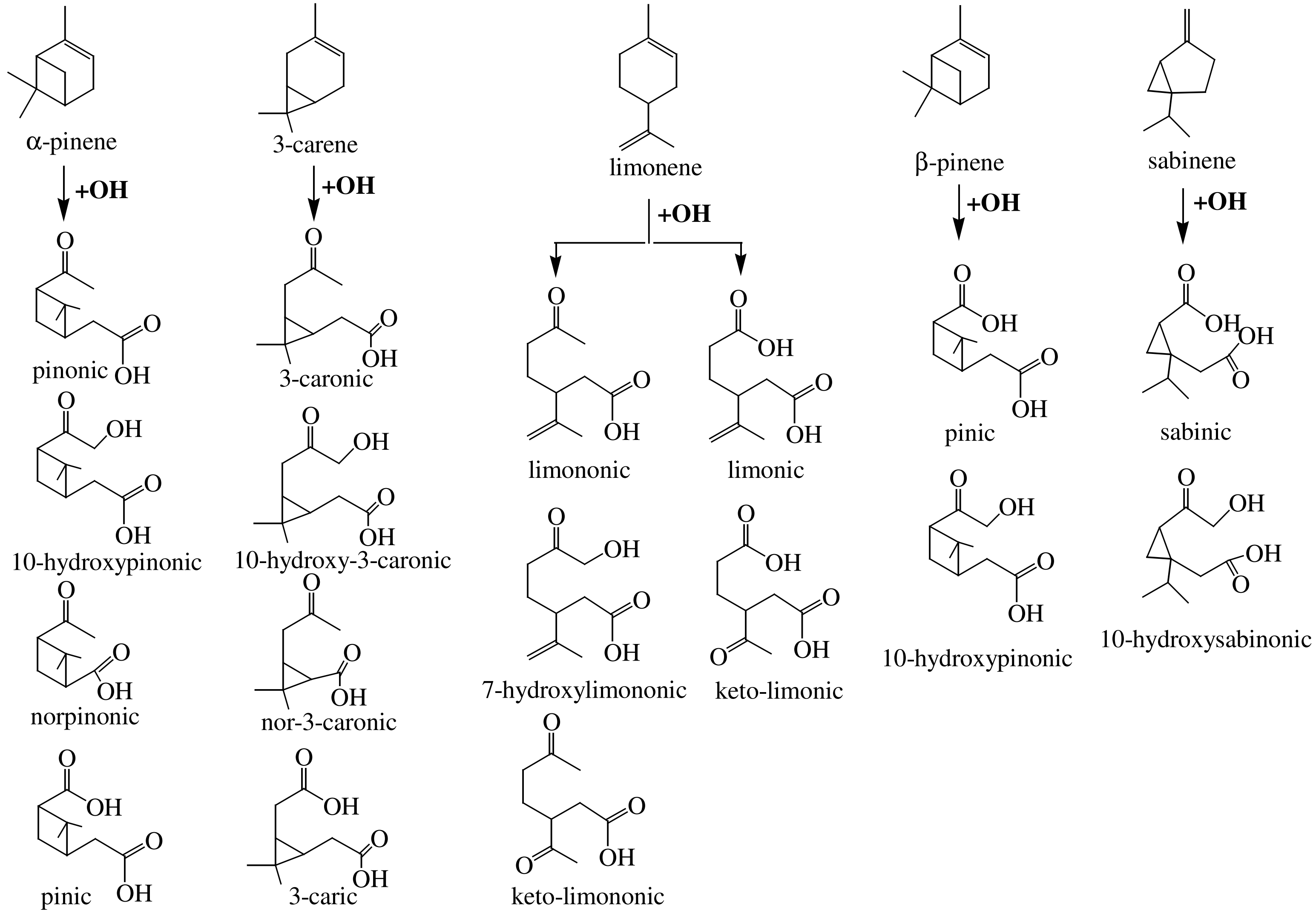

Figure 3: Chemical structures of some cyclic monoterpenes and derived carboxylic acids identified in aerosol phase.

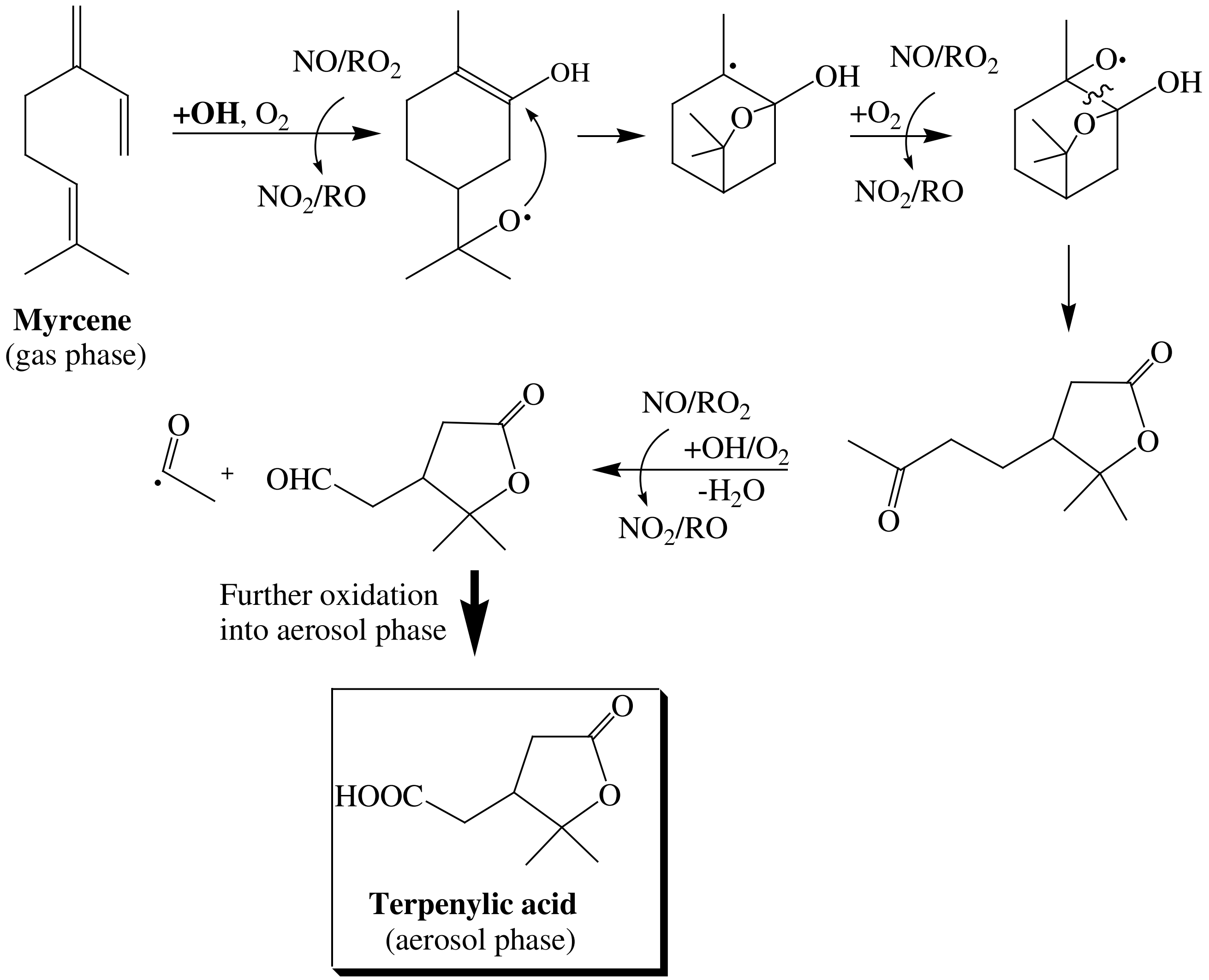

Figure 4: General potential mechanism responsible on the formation of terpenylic acid in aerosols from myrcene oxidation by OH radicals.

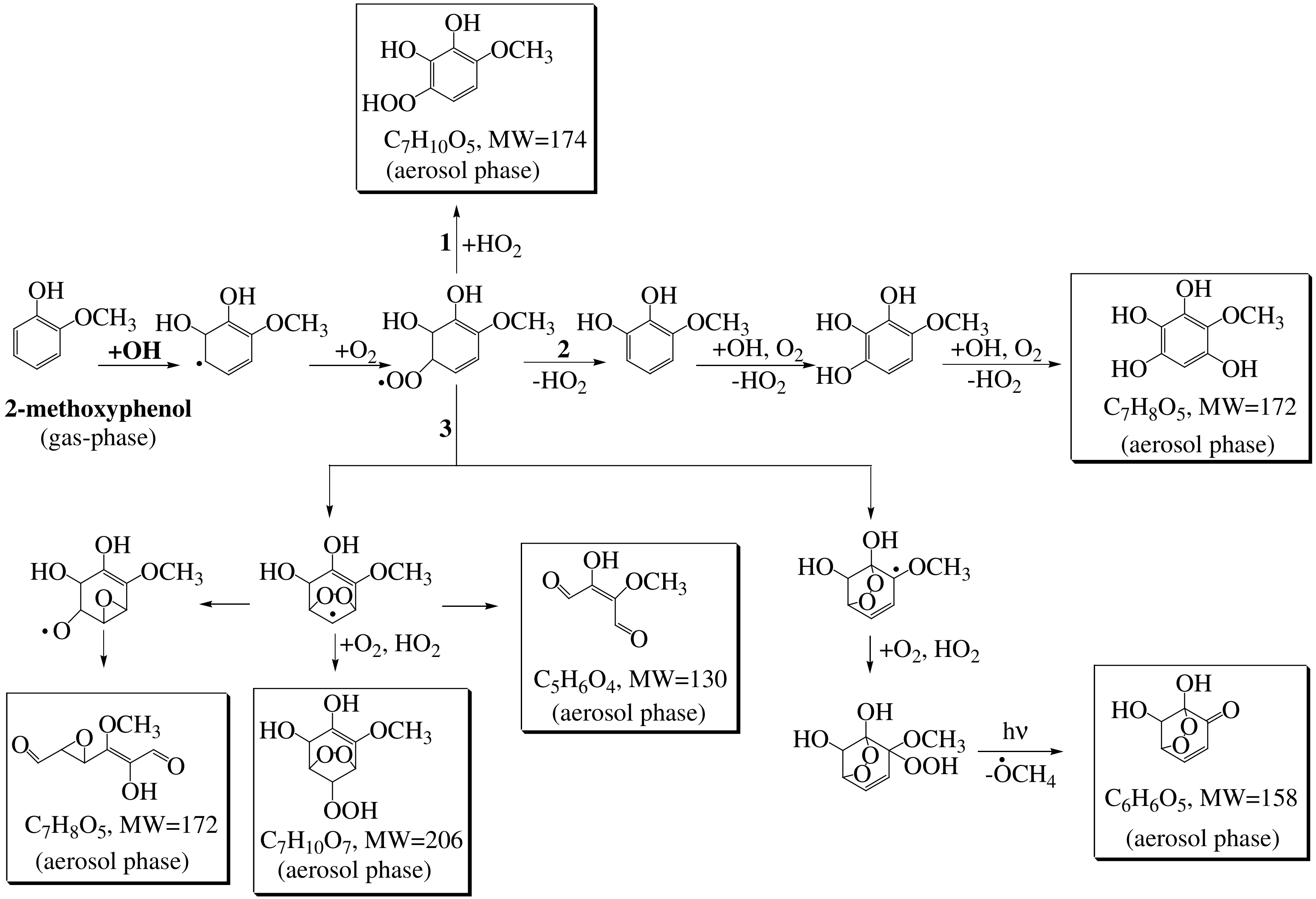

Figure 5: General possible mechanism responsible on the formation in particulate phase of some dihyhydroxibenzenes, epoxides, and some fragments associated with methoxy-hydroxy-butenedial, in the oxidation of 2-methoxyphenol under low NO_x.