

# Atmospheric Analytical Chemistry

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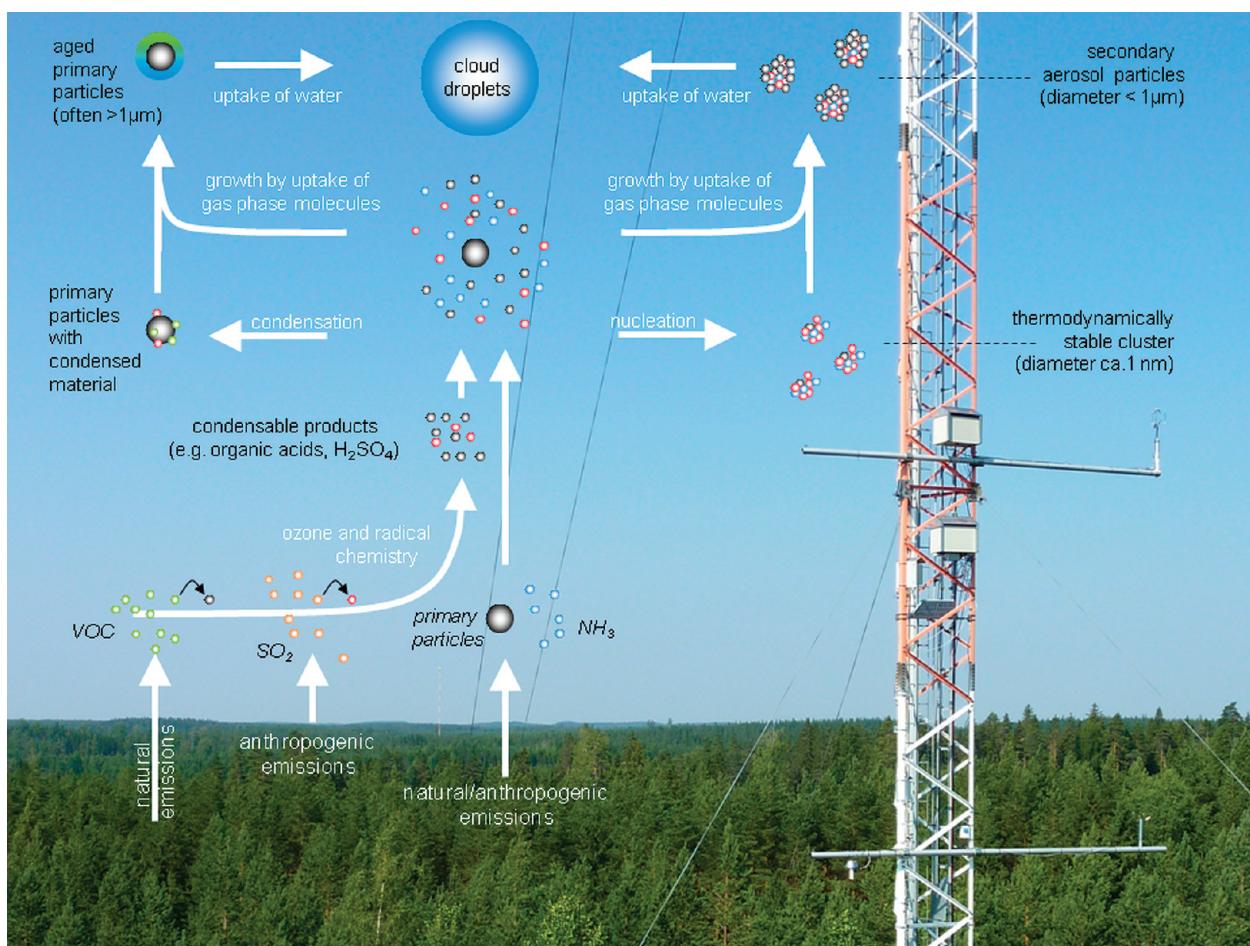
## CONTENTS

General Interest and Reviews		Particle Phase	J
Introduction	A	Laser Desorption/Ionization Aerosol MS	J
Review Article	C	Quadrupole and TOF-Aerosol Mass	J
Halogens	D	Spectrometers (Q-AMS or TOF AMS)	J
Reactive Halogen Species	D	Soft Ionization Methods for Aerosol Mass	
Online Optical Spectroscopy	D	Spectrometry	J
Differential Optical Absorption	D	High-Resolution Mass Spectrometric	K
Spectroscopy	D	(HR-MS) Techniques	K
Cavity Based Spectroscopy	E	Chromatography/Mass Spectrometry-	
Fluorescence Spectroscopy	E	Marker Compound Measurements	K
Online Mass Spectrometry	E	Spectroscopic Techniques	L
Off-Line Techniques	F	Biographies	L
Mist Chamber Technique	F	References	L
Photoactive Halogen Detector	F		
Denuder Technique	F		
Indirect Methods	F		
Particle Phase	G		
Radicals	G		
Online Techniques for Gas Phase Species	G		
Differential Optical Absorption Spectroscopy	G		
(DOAS)	G		
Laser Induced Fluorescence (LIF, or Fluorescence Assay by Gas Expansion, FAGE)	G		
PErOxy RadiCal Amplification (PERCA)	G		
Chemical Ionization Mass Spectrometry	H		
(CIMS)	H		
Cavity Ringdown Spectroscopy (CRDS)	H		
Off-Line Technique for Gas Phase Species	H		
Matrix Isolation Electron Spin Resonance	H		
(MI-ESR)	I		
Particle Phase	H		
Electron Paramagnetic Resonance (EPR)	I		
Organic Compounds	I		
Gas Phase	I		
Proton Transfer Reaction Mass Spectrometry	I		
(PTR-MS)	I		
Gas Chromatography (GC)	I		
Peroxy Nitrates (PN)	I		

## GENERAL INTEREST AND REVIEWS

**Introduction.** In this Review, we focus on the most significant and essential progress in atmospheric analytical chemistry published during the past few years. The preceding review in *Analytical Chemistry* with a related topic is from the year 2005<sup>1</sup> (Recent Advances in Our Understanding of Atmospheric Chemistry and Climate Made Possible by Online Aerosol Analysis Instrumentation). A comprehensive coverage of the entire research field over the whole period since 2005 would be beyond the scope of this Review. Consequently, we focus our Review on selected topics of atmospheric analytical chemistry, such as the measurement of halogens, radicals, and organic compounds in the troposphere, a selection that is based on both analytical challenges and importance for atmospheric chemistry. In general, the challenge to chemically characterize relevant components of the Earth's atmosphere is probably greater than many analytical chemists might expect, which is mainly due to the large number of organic and inorganic compounds present in the atmosphere and the large chemical space these compounds cover, e.g., with respect to volatility, polarity, or molecular weight. One obvious reason for the complexity is the fact that the atmosphere is a multiphase system. Not only gas phase compounds have to be

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**Figure 1.** Mechanisms of atmospheric particle formation (background: Measurement station SMEAR II in Finland, Research station to study Atmosphere – Biosphere Interactions).

considered but also, at the same time, solid or liquid particulate matter; additionally, the atmospheric aqueous phase plays a major role in atmospheric chemistry. Moreover, often the most interesting and relevant compounds are present in ultratrace amounts, such as organic or inorganic radicals (ppt to ppq levels) or the material forming nanometer particles during a typical atmospheric nucleation event (here, the concentrations are often given in molecules per unit volume). Despite their very low concentrations, these components are among the major drivers which shape atmospheric chemistry; i.e., hydroxyl radicals control the oxidizing power of the atmosphere, and nanometer particles act as cores to finally form climatically relevant cloud condensation nuclei. As in many scientific fields, also in the atmospheric sciences, major progress is often driven by the introduction of new or improved analytical techniques. For example, the recent introduction and frequent use of aerosol mass spectrometers in field measurements greatly improved the understanding of organic aerosol components.<sup>2</sup> Besides the gain in knowledge, the application of sophisticated analytical instrumentation sometimes manifests a major gap of understanding of certain fundamental processes, which were thought to be generally understood, such as the role of organic peroxy radical chemistry over pristine forests following VOC and radical measurements in the Amazon.<sup>3</sup>

What are the current analytical challenges in the atmospheric sciences? The chemical characterization of atmospheric aerosol particles is certainly among these challenges, in particular for

organic components. One reason is the impact of atmospheric aerosols on both climate and health and the fact that knowledge of the variation of their chemical composition with particle size is key to understanding both effects. On the basis of the current physicochemical understanding of atmospheric aerosol formation processes, especially quantitative information about low and semivolatiles, often highly oxidized organic compounds are needed. Figure 1 illustrates the principle mechanisms for atmospheric particle formation and growth; both processes in which such compounds are speculated to play key roles. However, exactly the chemical and physicochemical properties that classify them as interesting target analytes (i.e., volatility, polarity, gas/particle partitioning, reactivity) complicate a reliable measurement of their concentration (analyte losses during sampling, poor recoveries). Nevertheless, the search for techniques to detect suitable tracers for process understanding or source attribution using both traditional off-line as well as online techniques for aerosol characterization will continue. For organic compounds to be considered as suitable molecular tracers, their potential degradation due to chemical processing in the gas and particle phase (multiphase chemistry) has to be characterized; a topic recently discussed intensively but not a well understood process. With respect to inorganic aerosol components, it is today recognized that the determination of the total burden of a specific element, i.e., the total amount of a trace metal in aerosols, provides insufficient information. To understand source and



Figure 2. PM2.5 Aerosol inlet for atmospheric aerosol sampling.

transformation of aerosol constituents, the analysis of the distribution of an element among defined chemical species is necessary. Even more important is elemental speciation to predict the relevance and fate of individual aerosol constituents; e.g., the hygroscopicity of particle phase compounds will affect the particle's ability to act as cloud condensation nuclei, its vapor pressure will affect the gas-particle partitioning, and its solubility will affect the bioavailability and potential toxicity of the individual species. Therefore, analytical strategies for the separation and quantification of the different elemental species are needed.

Many analytical techniques applied in atmospheric sciences are still based on a time integrating sampling step (using cartridges, filters, etc.) with the inherent risk of positive and negative artifacts during the multistep analytical procedure. As an example, Figure 2 shows a PM2.5 aerosol inlet often used upstream of a filter unit for atmospheric aerosol analysis. This type of sampling severely limits both spatial and temporal sampling densities. Therefore, analytical techniques to monitor trace amounts of analytes with a high time resolution are required, especially for the understanding and control of highly dynamic systems as the atmosphere. For certain atmospheric research platforms, such as aircrafts, rapid online systems are even mandatory. Therefore, the major future developments in atmospheric analytical chemistry will include the further improvement of fast online operating techniques. Mass spectrometric systems, such as Proton-Transfer-Reaction MS for VOC analysis or the different developments in aerosol mass

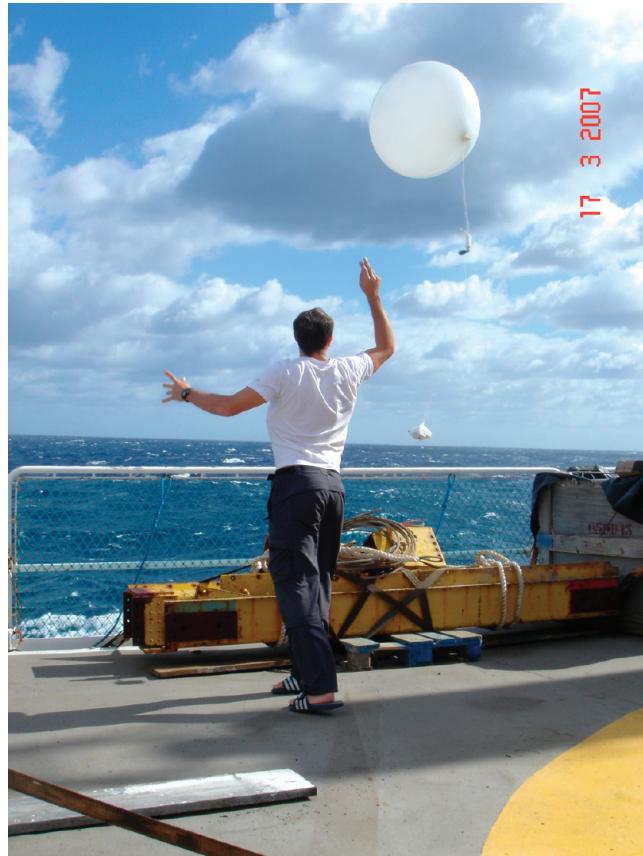


Figure 3. Launch of an ozonesonde from the French research vessel "Marion Dufresne".

spectrometry (thermal methods and laser based techniques) are already widely established. Nevertheless, a rapid development in ionization and analyzer techniques will keep this an active field of analytical chemistry in the coming years. Beyond mass spectrometry, also, other instrumental fields are developing rapidly, such as the use of differential optical absorption spectroscopy (DOAS) for spatially resolved measurements of trace gas distributions. Especially height profile measurements of certain trace gases are required, such as ozonesonde balloon measurements (see Figure 3). Consequently, the development of miniaturized, lightweight analytical instrumentation will continue.

**Review Article.** To the best of our knowledge, no general overview over the whole field has been published in the past few years. As already mentioned above, Sullivan and Prather published the last review article in *Analytical Chemistry* in 2005, in which they focused on real-time analysis techniques for aerosol particle analysis.<sup>1</sup> Bernath summarized a Canadian-led satellite mission that is measuring the concentrations of more than 30 atmospheric constituents by absorption spectroscopy using the Sun as a light source.<sup>4</sup> Lai and co-workers published an overview of recent advances in instrumentation and methodologies for measuring atmospheric composition changes from space, aircraft, and the surface as well as recent improvements in laboratory techniques that permitted scientific advance in the field of atmospheric chemistry.<sup>5</sup> In a comprehensive review about formation, properties, and impact of secondary organic aerosol (SOA), Hallquist et al. also discuss the various techniques to measure SOA chemical composition.<sup>6</sup> A feature article in *Analytical Chemistry* by Finlayson-Pitts describes some of the current

techniques and future needs for inorganic halogens in air. Heard and Pilling performed a comprehensive review of HO<sub>x</sub> measurement techniques and field experiments.<sup>7</sup> Hamilton recently reviewed two-dimensional gas chromatography with a focus on atmospheric applications,<sup>8</sup> and Blake et al. reviewed comprehensively proton transfer reaction mass spectrometry.<sup>9</sup> Several articles appeared recently, in which the analysis of organic particulate matter are reviewed. Baltensperger and co-workers<sup>10</sup> present a short overview about mass spectrometric techniques for the analysis of atmospheric particles. The authors briefly discuss the specific advantages and disadvantages of the individual techniques and present examples of applications of the various mass spectrometric techniques for laboratory and field studies. Farmer and Jimenez published a feature article, in which they provide a summary of recent advances in field instrumentation, including particle analysis instrumentation.<sup>11</sup> Again, the authors discuss specific advantages and disadvantages of the individual techniques, focusing on the unique instrumental requirements for atmospheric analytical chemistry (i.e., time resolution, portability, ease of calibration, stability with respect to ambient temperature and pressure fluctuations, need for inlet design). In addition, the authors identify new frontiers of analytical aerosol instrumentation needed in future studies. Prather et al.<sup>12</sup> provide a brief review of the current state of the science in the analysis of atmospheric aerosols, with a focus on real time single-particle mass spectrometry, e.g., to investigate the mixing state of atmospheric particles. Aubriet and Carre discuss the potential of laser mass spectrometry for the analysis of environmental dust particles.<sup>13</sup> Their review provides the fundamental aspects of online and off-line laser based mass spectrometry, presents a selected number of applications, and considers both the capabilities and the drawbacks of laser mass spectrometry to analyze dust particles. Zelenyuk and Imre focus in their review also on laser based aerosol mass spectrometry.<sup>14</sup> They elaborate on the differences between individual particle analysis and bulk analysis and review the recently developed methods to simultaneously measure in situ and in real time individual particles using single particle mass spectrometers. In this paper, the critical aspects of approaches developed for classification, visualization, and mining of large data sets produced by single particle mass spectrometry are discussed. Russell presents a review about single-particle mass spectrometry focusing on the characterization of microorganisms.<sup>15</sup> Developments in online and off-line single particle matrix-assisted laser desorption/ionization (MALDI) are highlighted as well as limitations of current approaches and necessary future achievements. Finally, Lin et al. provide an overview of the latest developments in chemical characterization approaches for identification and quantification of individual compounds in fine atmospheric particles (organic marker approach).<sup>16</sup> Specific organic particle phase compounds can be used to differentiate specific inputs from various emissions and, thus, are helpful in identifying the major sources.

## ■ HALOGENS

**Reactive Halogen Species.** Reactive halogen species (RHSs: X, XY, XO, OXO, HOX, XNO<sub>2</sub>, and XONO<sub>2</sub>, where X and Y denote different halogen atoms) play an important role in a wide variety of atmospheric processes, which can lead to (i) catalytic destruction of ozone, (ii) altering the partitioning of NO<sub>x</sub> (NO<sub>2</sub>/NO) and HO<sub>x</sub> (HO<sub>2</sub>/OH), (iii) oxidation of organic compounds (e.g., dimethyl sulfide, DMS), (iv) removal of elemental mercury, and (v) new particle formation in the marine boundary

layer. Therefore, specific identification and quantification of RHSs are essential for a quantitative understanding of halogen chemistry and their impact on the atmospheric oxidation capacity and climate change on a local, regional, and global scale. However, the measurement of RHSs is still a challenging task due to their low atmospheric concentrations (typically ranging from low parts per trillion (ppt) to a few parts per billion (ppb)), very short atmospheric lifetimes, and high reactivities and thus high temporal and spacial variability. The currently available approaches for RHSs generally fall into three categories: online techniques (optical spectroscopy and mass spectrometry), offline techniques, and indirect methods.

**Online Optical Spectroscopy.** Spectroscopic techniques typically take advantage of the absorption of molecules in the UV-vis absorption band or resulting energy emission and can be divided into direct absorption, cavity, and fluorescence approaches.

**Differential Optical Absorption Spectroscopy.** Differential optical absorption spectroscopy (DOAS) is a well established technique to identify and quantify trace gases in the atmosphere. The instrumentation and applications to atmospheric measurements have been described in detail in a recent book by Platt and Stutz.<sup>17</sup> The identification of trace gases of interest is based on their specific narrow band absorption, and this unique spectral signature is separated from broadband absorption cross sections of light extinction derived from scattering and absorption in the atmosphere or variation of the light source or detector. Stimulated by the roles Cl and Br might play in the stratospheric ozone depletion, DOAS measurements of RHSs (i.e., BrO and OCIO) were initially made in the stratosphere over the polar regions by ground based and airborne spectrometers using scattered sunlight or direct moon light as light source (referred to as passive DOAS).<sup>18–20</sup> These measurements were later extended to the midlatitudes (e.g., refs 21 and 22). These studies have greatly improved our understanding of the impact of ClO–BrO cycles on ozone depletion in the stratosphere, leading to the phase-out of their source gases (e.g., anthropogenic halocarbons).

Unlike the stratospheric ozone depletion, which is dominated by the ClO dimer cycle and, to a lesser extent, by ClO–BrO cross reaction, the tropospheric ozone depletion was observed to be mainly regulated by bromine chemistry. The direct detection of BrO (up to 17 ppt) by long-path DOAS (using a strong light source, referred to as active DOAS) at an Arctic site (Alert)<sup>23</sup> gave the first evidence of the “bromine explosion” mechanism. Subsequent measurements by active and passive DOAS techniques further identified an elevated level of BrO (up to 33 ppt) during ozone depletion events in both polar regions.<sup>26–29</sup> Likewise, IO measurements were made in polar regions in recent years using different DOAS techniques. The results reveal that IO is mainly located in the lower troposphere<sup>30</sup> and that the mixing ratios in the Antarctic boundary layer (up to 20 ppt) are much higher than that in the Arctic (<1 ppt).<sup>31</sup> The presence of IO might lead to enhanced ozone destruction via the BrO–IO cross cycle, as suggested by model experiments.

In the marine boundary layer (MBL), most DOAS based observations are carried out using the long-path DOAS (LP-DOAS) techniques with a light path of several kilometers. Measurements of reactive chlorine have not been reported up to now. BrO is the only inorganic gas phase bromine species that can be measured with DOAS, and several groups have tried to measure this species at different sites. The measured maximum mixing ratios are between ~2 and 7.5 ppt in the MBL.<sup>32–34</sup> In contrast, DOAS has provided measurement of IO, OIO, and I<sub>2</sub> in

the MBL. A clear anticorrelation between IO and tidal height and a correlation between IO and solar irradiation are frequently observed.<sup>35,36</sup> The precursors of IO were previously thought to be iodocarbons which are released from seaweed when the plants are exposed to air during low tide. However, the discovery of I<sub>2</sub> by the LP-DOAS technique at Mace Head in 2002, with maximum values of 93 ppt at night and of 25 ppt during the day, revised our knowledge of iodine atmospheric chemistry.<sup>37</sup> The emission of I<sub>2</sub> from low tidal macroalgal exposure is suggested to be the most important process responsible for the observed IO levels in the coastal MBL. More recent observations carried out at Mace Head show further evidence to this seaweed “hot spot” hypothesis.<sup>38,39</sup> IO, OIO, and I<sub>2</sub> were also measured in the semipolluted coastal MBL at Roscoff (France) recently, suggesting that iodine chemistry can play an important role in polluted environments.<sup>40</sup> Other recent observations at Cape Verde (up to 1.4 ppt IO) show that the presence of IO could be rather widespread also in the open-ocean MBL.<sup>33</sup> A common problem that occurs when the LP-DOAS technique is used to measure iodine in the coastal MBL is that the concentrations in the intertidal zone are underestimated since the data derived from LP-DOAS are calculated assuming a constant concentration along the light-path of several kilometers. However, most of the light path extends over the open ocean (representing a lower iodine concentration), and the seaweeds extend only over a short distance of the light path (likely representing higher iodine concentrations). A vertical concentration gradient, as revealed by the passive multiaxis DOAS (MAX-DOAS),<sup>39</sup> might also lead to an underestimation by LP-DOAS given the vertical distance between the DOAS light path and sea level. Besides the regions aforementioned, DOAS techniques have also been used in some specific environments. The mixing ratios of up to 176 ppt BrO over the Dead Sea and of up to 6 ppt BrO and 15 ppt ClO over the Great Salt Lake were observed, indicating that salt lakes are another “bromine explosion” region.<sup>41</sup> The possibility to use DOAS also in extreme environments, e.g., for measurements of ClO, BrO, and OCIO in volcanic plumes, is another advantage of the techniques. Global maps of the total BrO and IO column density can be retrieved with the DOAS technique from satellite measurements by instruments such as SCIAMACHY.<sup>42</sup> Satellite data provide the sum of tropospheric and stratospheric columns with a good coverage on spatial and temporal scales but, suffer from substantial uncertainties derived from cloud effects in the troposphere and the vertical distribution of BrO and IO. In addition to RHESSs, the DOAS techniques can provide simultaneous measurements of other atmospheric constituents such as NO<sub>x</sub>, HO<sub>x</sub>, and O<sub>3</sub>, which facilitates a better understanding of the impacts of RHESSs on the complex atmospheric processes.

**Cavity Based Spectroscopy.** Cavity ring down spectroscopy (CRDS), which is capable of taking *in situ* measurements with a spatial resolution of a few meters, provides an alternative approach for the measurement of inhomogeneously distributed reactive iodine. Broadband cavity ring down spectroscopy (BBCRDS), analogous to a localized version of LP-DOAS, was developed recently for I<sub>2</sub> measurements. This instrument uses light from a pulsed broadband laser to measure the absorption spectrum of the gas phase within a high finesse optical cavity, and I<sub>2</sub> is detected using several absorption bands in the wavelength range of 560–570 nm. The typical detection limits obtained are 10–15 ppt for I<sub>2</sub> with an integration time of 5 min. This approach has been used to measure ambient I<sub>2</sub> at coastal sites<sup>35,43</sup> as well as to measure I<sub>2</sub> release profile from different seaweed

species.<sup>44</sup> Wada et al.<sup>45</sup> developed an open-path CRDS for point measurement of IO. A typical detection limit of about 10 ppt is reported, integrating over 30 s using the absorption at 435 nm. Using this instrument, IO mixing ratios observed during low tide at Roscoff are approximately 5–10 times higher than values reported by LP-DOAS, supporting the assumption that the sources of iodine compounds are mainly located in the intertidal zone. Incoherent broadband cavity enhanced absorption spectroscopy (IBBCEAS) is another approach which can provide point concentration of reactive iodine species.<sup>46</sup> The detection limits for I<sub>2</sub>, OIO, and IO are about 26, 45, and 210 ppt, respectively, which are somewhat higher and not always sufficient for field measurements. However, this approach was used for laboratory studies, such as the investigation of the I<sub>2</sub> release from seaweed.<sup>47</sup>

**Fluorescence Spectroscopy.** In recent years, fluorescence based instruments have also been developed for tropospheric applications to measure I<sub>2</sub> and IO as well as atomic iodine. Whalley et al.<sup>48</sup> measured IO radicals in the atmosphere by excitation at approximately 445 nm and detecting the off-resonance fluorescence at 521 nm. The detection limit is 0.3 ppt with an integration time of 5 min. Bale et al.<sup>49</sup> measured atomic iodine using vacuum UV resonance fluorescence (RF) in the range of 178–184 nm. This RF system can measure either the ambient iodine atoms or the total photolabile iodine loading of ambient air through broadband visible photolysis of the photolabile iodine and subsequent RF detection of the released iodine atoms. Most recently, this system was modified by Gómez Martín et al.<sup>50</sup> to quantify molecular iodine by off-resonance fluorescence. As a result, concurrent measurements of I<sub>2</sub> and atomic iodine could be achieved with a detection limit of 1.2 ppt for iodine atoms and of 13 ppt for molecular iodine.

**Online Mass Spectrometry.** Atmospheric pressure ionization mass spectrometry (API-MS) was first used by Spicer and co-workers to identify and quantify Cl<sub>2</sub>, Br<sub>2</sub>, and BrCl in the troposphere.<sup>51,52</sup> The target molecules in ambient air are sucked into a corona discharge region and are ionized by suitable reactant ions (e.g., O<sub>2</sub><sup>−</sup>) via ion–molecule reactions to produce dihalogen ions. Specificity is provided by use of a tandem quadrupole mass spectrometer to monitor the parent–daughter mass transitions: the dihalogen ions (parent ions) filtered in the first quadrupole undergo collisionally activated dissociation to produce atomic ions (daughter ions, Cl<sup>−</sup> and Br<sup>−</sup>), which are mass filtered in the second quadrupole. The characteristic isotope ratios of halogens provide an additional characteristic to improve specificity. Detection limits achieved are 0.2 ppt for Br<sub>2</sub> and 2 ppt for Cl<sub>2</sub> and BrCl, respectively. This method was used for the first specific measurements of Cl<sub>2</sub> at a coastal site in Long Island (NY, USA) and of BrCl and Br<sub>2</sub> in the Arctic at polar sunrise. In Long Island, unexpectedly high concentrations of Cl<sub>2</sub> (up to 150 ppt) were observed at night. In the Arctic, the concentrations of Cl<sub>2</sub> were below the detection limit of 2 ppt; however, the bromine species were found at levels up to 35 ppt BrCl and 25 ppt Br<sub>2</sub>, and both were anticorrelated with the actual ozone concentration. Finley and Saltzman<sup>53</sup> used a <sup>63</sup>Ni foil, rather than a corona discharge, to generate the primary negative ions, which rapidly form clusters with water and then transfer an electron to the dihalogens leading to the formation of Cl<sub>2</sub><sup>−</sup>, Br<sub>2</sub><sup>−</sup>, and I<sub>2</sub><sup>−</sup>. Again the parent–daughter ion pairs (e.g., 72/35 for Cl<sub>2</sub>, 162/81 for Br<sub>2</sub>, and 254/127 for I<sub>2</sub>) are monitored. The detection limits of this method are 1.0 ppt for Cl<sub>2</sub>, 0.5 ppt for Br<sub>2</sub>, and 0.2 ppt for I<sub>2</sub>, respectively. Maximum ambient

concentrations of 26 ppt  $\text{Cl}_2$ , 19 ppt  $\text{Br}_2$ , and 8 ppt  $\text{I}_2$  were observed at a coastal site at La Jolla, California. Thornton and co-workers measured  $\text{ClNO}_2$  using  $\text{I}^-$  ion chemistry.<sup>54</sup> Here,  $\text{I}^-$  reagent ions are generated by flowing a  $\text{CH}_3\text{I}$  containing nitrogen stream through a  $^{210}\text{Po}$  radioactive source. The produced  $\text{I}^-$  ions then react with  $\text{ClNO}_2$  to form  $\text{I}^-$  adducts  $\text{IClNO}_2^-$ , followed by detection with a quadrupole MS. The approach has been used for coastal and midcontinental observations.  $\text{ClNO}_2$  at concentration levels up to 1.2 ppb were measured in the Gulf of Mexico, Texas, indicating that  $\text{ClNO}_2$  is likely the major chlorine-containing compound in coastal areas and that the main source is heterogeneous uptake of  $\text{N}_2\text{O}_5$  on sea-salt particles and on chloride-containing particles of continental origin.<sup>55</sup> The strategy to use  $\text{I}^-$  reagent ions for ionization has also been extended to the measurements of other halogen species. Neuman et al.<sup>56</sup> measured  $\text{BrO}$  and  $\text{BrCl}$  in ozone depleted air over the Arctic Ocean. They found that the production of  $\text{I}^-\cdot\text{H}_2\text{O}$  cluster ions can provide better sensitivity to halogen detection than  $\text{I}^-$  alone and that for the measurement of  $\text{Br}_2$  interference from  $\text{HOBr}$  is significant as  $\text{HOBr}$  rapidly converts to  $\text{Br}_2$  in the instrument inlets. Using a similar system, intensive  $\text{BrO}$  measurements were carried out at Barrow, Alaska, and the data derived from online MS were in good agreement with data from concurrent LP-DOAS measurements.<sup>57</sup>

**Off-Line Techniques.** Although online techniques have the advantage of providing near real-time concentration data, the measurements are instrumentally demanding and not directly accessible for most research groups. Alternatively, off-line techniques take advantage of analytical standard instrumentation (e.g., chromatography). Air samples are normally collected by either physical adsorption/absorption or chemical reaction and subsequently analyzed in the laboratory.

**Mist Chamber Technique.** Keene et al. developed a tandem mist chamber to sample chlorine gases in the MBL. In this system, coarse and fine aerosol particles are removed in the inlet. A trace gas concentrator positioned downstream incorporates an acidic mist chamber and an alkaline mist chamber in series. Different gaseous chlorine compounds (including  $\text{HCl}$ ,  $\text{ClNO}$ ,  $\text{ClNO}_2$ ,  $\text{ClONO}_2$ ,  $\text{Cl}_2$ ,  $\text{HOCl}$ ) are collected in the acidic and alkaline mist chambers. Ion chromatography is then used to measure the  $\text{Cl}^-$  in the absorbing solutions. This technique was employed at different locations and showed typical levels of up to 5.7 ppb  $\text{HCl}^*$  (including  $\text{HCl}$ ,  $\text{ClNO}$ ,  $\text{ClNO}_2$ ,  $\text{ClONO}_2$ ) and of up to 421 ppt  $\text{Cl}^*$  ( $\text{Cl}_2$ ,  $\text{HOCl}$ ) in the MBL.<sup>58,59</sup> However, the authors estimate that in the tandem system about 7–10%  $\text{Cl}_2$  is collected in the acidic chamber and that the presence of a significant amount of  $\text{HOCl}$  in the air will lead to an overestimation of the reported  $\text{HCl}^*$ .

**Photoactive Halogen Detector.** A photoactive halogen detector (PHD) was developed by Impey et al.<sup>60</sup> to measure photolabile chlorine ( $\text{Cl}_2$  and  $\text{HOCl}$ ) and bromine ( $\text{Br}_2$  and  $\text{HOBr}$ ). The halogen species are photolyzed in a cylindrical flow cell with a Xe arc lamp. The chlorine and bromine atoms produced then react with propene in the presence of  $\text{O}_2$  and  $\text{NO}$ . The resulting chloroacetone and bromoacetone are collected with PoraPak Q absorbent at cold temperatures followed by laboratory analysis based on gas chromatography.  $\text{X}_2$  and HOX can be differentiated due to their significantly different photolysis rates. This method was used during the Polar Sunrise Experiment 1995 and 1997, and the results showed that photolabile chlorine was typically below the detection limit of 14 ppt with occasional events up to 100 ppt  $\text{Cl}_2$  and that the concentrations of  $\text{Br}_2$  and  $\text{HOBr}$  were

up to ~25 ppt and ~260 ppt, respectively. Although the PHD method provides a potentially useful technique for detecting the presence of photolabile chlorine and bromine, it should be noted that the PHD can also respond to other photoactive halogen species, such as  $\text{XNO}$ ,  $\text{XNO}_2$ ,  $\text{XONO}_2$ ,  $\text{XY}$  and some organic halogens.

**Denuder Technique.** Very recently, Huang and Hoffmann<sup>61</sup> developed a coupled diffusion denuder system which consists of a 1,3,5-trimethoxybenzene (1,3,5-TMB)-coated cylindrical tube as front-denuder coupled upstream of an  $\alpha$ -cyclodextrin/ $^{129}\text{I}^-$ -( $\alpha$ -CD/ $^{129}\text{I}^-$ )-coated tube for the separation and quantitative collection of gaseous activated iodine compounds (AIC:  $\text{ICl}$  and  $\text{HOI}$ ) and  $\text{I}_2$ , respectively. The iodinated derivative of 1,3,5-TMB formed in the denuders is measured by GC/MS. However, the entrapped  $^{127}\text{I}_2$  together with the  $^{129}\text{I}^-$  spike in the  $\alpha$ -CD coating must be converted to organic iodine via a postderivatization procedure prior to GC/MS analysis. It was found that the spike of iodide in  $\alpha$ -CD coating can significantly improve the collection efficiency of  $\text{I}_2$ . It was also demonstrated that when  $^{127}\text{I}^-$  is used as spike the  $\alpha$ -CD-coated denuders is capable of measuring radioactive molecular iodine (e.g.,  $^{129}\text{I}$ ).<sup>62</sup> Denuder methods provide the means for “single-point” in situ measurements of gaseous iodine species at levels down to subppt concentrations. The coupled denuder system has been deployed in field campaigns at several sites, such as Irish West coast, Weddell Sea (Antarctic), and Atlantic Ocean.<sup>36,38</sup>

**Indirect Methods.** There are several indirect methods available to estimate the atmospheric concentration levels of halogen atoms. Estimates of enhanced levels of chlorine and bromine atoms during ozone depletion events (ODEs) can be made by measuring the changes of the ratio of different VOCs, the so-called “hydrocarbon clock”. The basis of this method is the assumption that the difference between the mixing ratios of selected VOCs in ozone-depleted air and “normal” air masses is caused by Cl/Br atoms. This method was used by several groups, and the concentrations of Cl and Br were estimated to be in the range of  $10^3$ – $10^5$  Cl-atoms  $\text{cm}^{-3}$  and  $10^7$ – $10^8$  Br-atoms  $\text{cm}^{-3}$  in the MBL. It should be noted that the “hydrocarbon clock” method can provide only upper limits of the Cl- and Br-atom concentrations.<sup>63–65</sup> The major uncertainty of this method results from inaccuracies in the rate constants for the reaction of the VOCs as well as the initial concentrations of the investigated VOCs. A careful selection of suitable VOCs and a reliable and consistent set of the relevant rate constants will further improve the accuracy of this approach. In contrast to many other VOCs, the typical consumption of methane by Cl-atoms during ODEs is small compared to natural variations in the  $\text{CH}_4$  concentration in ambient air. Also, the change of CO produced via  $\text{CH}_4 + \text{Cl}$ -atoms is much smaller than the natural variation of the CO concentration. However, the reaction of Cl with  $^{13}\text{CH}_4$  is slower than with  $^{12}\text{CH}_4$ . The result is that CO produced via  $\text{CH}_4 + \text{Cl}$ -atoms is about 90% depleted in  $^{13}\text{C}$ . Therefore, the concentration of Cl-atoms encountered by an  $\text{O}_3$ -depleted air mass can be quantified by measuring the extent of the significant depletion in  $\delta^{13}\text{C}$  of ambient CO.<sup>66</sup> Likewise, measurements of  $\delta^{13}\text{C}$  in  $\text{CH}_4$  imply a kinetic isotope fractionation much larger than would be expected if the OH radical is the only  $\text{CH}_4$  sink. A strong candidate for this extra sink is Cl-atoms in the MBL since this halogen atom has a larger kinetic isotope effect compared to OH and produces a larger fractionation of  $^{13}\text{C}$  compared to  $^{12}\text{C}$  in atmospheric  $\text{CH}_4$ . Therefore, the concentration of Cl-atoms can be estimated. Allan et al. inferred summer

maximum and annual mean Cl-atom concentrations in the Southern Hemisphere of  $\sim 7 \times 10^3$  Cl-atoms  $\text{cm}^{-3}$  and  $\sim 3 \times 10^3$  Cl-atoms  $\text{cm}^{-3}$ , respectively.

**Particle Phase.** The most common techniques to chemically characterize airborne particles involve sampling onto filters or impactor plates followed by laboratory analysis of the filter extracts. The measurements of total chlorine, bromine, and iodine can be realized by a variety of approaches such as instrumental neutron activation analysis (INAA), atomic absorption spectroscopy (AAS), and inductively coupled plasma–mass spectroscopy (ICPMS). However, species-specific measurements are frequently required to gain a quantitative understanding of the evolution and reaction cycling of halogens in aerosol particles. Ion chromatography is often used for the separation of halogen ions, and the technique allows for the measurement of chloride and bromide in marine aerosols. However, the speciation of particulate iodine is more difficult due to the presence of various iodine species (i.e., soluble inorganic iodine (SII, iodide and iodate), soluble organic iodine (SOI), and insoluble iodine (ISI)) as well as the fairly low concentration levels of the individual iodine species. In early studies, Baker and co-workers<sup>67,68</sup> used a voltametric approach to measure iodide as well as SII after reduction of iodate with ascorbic acid. A spectrophotometric method, which is sensitive to inorganic iodine in oxidation states from 0 to +5 (predominantly iodate), was also used by the same group. Total aqueous soluble iodine (TSI) was determined either by the spectrophotometric method after extracts were oxidized with UV light or directly by ICPMS. The SOI fraction was then calculated as the difference between TSI and SII.<sup>69</sup> In recent years, ICPMS coupled to various separation systems such as IC<sup>70,71</sup> and gel electrophoresis<sup>72</sup> was used for iodine speciation in aerosol particles. For example, Gilfedder et al. observed up to five anionic iodo-organic compounds in marine aerosols sampled at Mace Head (Ireland) using IC–ICPMS. However, identification of these unknown iodo-organic species is difficult, and further developments are needed to identify and quantify individual iodo-organic species in atmospheric aerosols.

## RADICALS

Inorganic and organic radicals are among the most important compounds in the atmosphere. They are responsible for much of the oxidation and “cleaning” reactions and capacity in the lower atmosphere, mainly initiated by OH<sup>73</sup> during daytime and NO<sub>3</sub> during night time. Even though radicals and especially HO<sub>x</sub> (i.e., the sum of OH and HO<sub>2</sub>) have been measured in a large number of field studies and laboratory studies, there are still significant uncertainties about the concentration of OH and HO<sub>2</sub> when field experiments are compared with model calculations pointing to poorly understood sink processes of these important oxidants.<sup>74</sup> Due to the often very low concentrations, the quantification of radicals in the atmosphere is a very challenging analytical task. The high reactivity of radicals favors the application of fast online techniques, which are able to measure these compounds in situ in the atmosphere. Important radicals discussed here include OH, HO<sub>2</sub>, organic peroxy radicals (RO<sub>2</sub>), and the NO<sub>3</sub> radical. Other nitrogen oxide radicals such as NO and NO<sub>2</sub> are routinely measured with conventional techniques based on chemiluminescence or luminol and are not discussed here. Halogen radicals were discussed in the chapters above.

**Online Techniques for Gas Phase Species.** Differential Optical Absorption Spectroscopy (DOAS). DOAS has been used

to quantify OH in the troposphere for several decades (e.g., refs 75 and 76) and in laboratory experiments<sup>77</sup> with detection limits of about  $1 \times 10^6$  molecules/cm<sup>3</sup>. As mentioned in the section on Halogens, DOAS provides a spatially integrated concentration measurement, which may be a disadvantage if measurements of very short-lived and thus potentially highly inhomogeneous compounds such as OH are performed. Multipass adsorption cell configurations allow one to minimize these shortcomings.<sup>78</sup> In recent years, however, two other techniques have been used more frequently to quantify OH in the atmosphere: laser induced fluorescence and chemical ionization mass spectrometry, which generally achieve lower detection limits. DOAS has also been used to quantify NO<sub>3</sub> radical in field experiments<sup>79–81</sup> with detection limits in the low ppt range. NO<sub>3</sub> vertical profiles up to a 50 km altitude were obtained using a zenith-viewing geometry with highest values in the low to mid troposphere of a few  $10^8$  molecules/cm<sup>3</sup>.<sup>35</sup>

**Laser Induced Fluorescence (LIF, or Fluorescence Assay by Gas Expansion, FAGE).** Laser induced fluorescence is the most widespread technique to quantify HO<sub>x</sub> radicals in the ambient troposphere. Air is continuously pumped into the instrument, which is operated at a pressure of about 1 Torr where the fluorescence measurement is performed. The reduced pressure minimizes artifacts of artificial OH formation in the instrument due to ozone photolysis and increases measurement efficiency due to a longer lifetime of the excited OH and reduced background signal. In all presently operated systems, OH is detected via on-resonance fluorescence at 308 nm. LIF instruments have been used in a large number of field and laboratory studies.<sup>7</sup> Continuous technical developments allow current detection limits for OH of about  $1 \times 10^5$  molecules/cm<sup>3</sup>. Measurements have been performed in various environments on the ground in polluted and remote areas (e.g., refs 82 and 83), onboard of ships,<sup>84</sup> and on aircrafts.<sup>85</sup>

LIF is also used to measure HO<sub>2</sub> after quantitative conversion of HO<sub>2</sub> to OH. HO<sub>2</sub> can be measured in series with OH, if NO is added in excess to the analysis airflow after the OH detection cell. NO reacts quickly with HO<sub>2</sub> to form NO<sub>2</sub> and OH. In a second LIF cell, the sum of newly formed OH (i.e., the converted HO<sub>2</sub>) and the originally present OH is quantified, and consequently, the HO<sub>2</sub> concentration can be calculated as the difference of the two fluorescence measurements. Competing reactions, e.g., of OH with NO (to form HONO), must be accounted for but can be minimized by optimizing reactant concentrations and reaction times.<sup>86</sup> Detection limits of HO<sub>2</sub> of several  $10^5$  molecules/cm<sup>3</sup> have been achieved, which is very low compared to atmospheric concentrations usually in the order of  $10^8$  molecules/cm<sup>3</sup>.<sup>74,84</sup>

Intercomparison studies between different LIF instruments have been performed,<sup>87</sup> demonstrating excellent agreement between systems. Detection methods for NO<sub>3</sub> radicals using LIF have also been developed but are not widespread.<sup>88</sup>

Organic oxygen centered radicals (RO<sub>x</sub> = RO<sub>2</sub> + RO) have been quantified with LIF (ROxLIF) by converting RO<sub>x</sub> to HO<sub>2</sub> in a high excess of NO and CO added to the analysis airflow. HO<sub>2</sub> is then converted in a second reaction cell to OH and measured with LIF as described above.<sup>89</sup> Limits of detection of about 0.1 ppt have been achieved with this set up, which is sufficient to measure RO<sub>x</sub> concentrations in the polluted troposphere typically in the range of several ppt.

**Peroxy Radical Amplification (PERCA).** A technique more widely used to quantify RO<sub>x</sub> (defined as the sum of RO<sub>2</sub> and HO<sub>2</sub>) is PERCA. Here, the addition of NO and CO to a sample

air flow leads to the catalytic formation of CO<sub>2</sub> and NO<sub>2</sub>, which are ultimately quantified. RO<sub>2</sub> and HO<sub>2</sub> react readily with NO to form NO<sub>2</sub>, RO, and OH, respectively. RO and OH are recycled to RO<sub>2</sub> and HO<sub>2</sub> in reactions with CO, which is added in excess to the sample flow. RO<sub>2</sub> and HO<sub>2</sub> then enter a cycle forming NO<sub>2</sub> in reactions with NO resulting in an amplification of the NO<sub>2</sub> formed. The number of HO<sub>2</sub>/OH interconversions (chain length) can reach 150–300<sup>90</sup> and is determined by loss reactions such as wall losses or radical chain termination reactions, e.g., NO + OH → HONO or HO<sub>2</sub> + NO<sub>2</sub> → HNO<sub>4</sub>. The amplified concentration of NO<sub>2</sub> is determined relative to the background NO<sub>2</sub> concentration when no CO is added to the sample air flow and, therefore, OH and RO are not recycled to HO<sub>2</sub> and RO<sub>2</sub>.

Single channel instruments have been developed where CO addition (amplification) and no CO addition (termination, i.e., background) conditions are alternated. Using dual channel instruments allows for a continuous quantification of the radical concentration. The NO<sub>2</sub> concentration is usually measured with conventional techniques based on chemiluminescence or aqueous luminol solution with detection limits of about 0.5 ppt for a 1 min integration time.<sup>91</sup> Figure 4 shows a PERCA instrument installed on a tower of the French research vessel "Marion Dufresne" during a campaign in the South Atlantic Ocean. Cavity ringdown spectroscopy (CRDS) has been used as an alternative detection technique for NO<sub>2</sub> formed in a PERCA instrument.<sup>92</sup> Ground based<sup>90</sup> as well as airborne instruments have been employed.<sup>93</sup>

**Chemical Ionization Mass Spectrometry (CIMS).** Chemical ionization mass spectrometry techniques were developed and continuously improved over the last two decades to quantify OH and HO<sub>2</sub> in laboratory and field studies. Most of these instruments use labeled <sup>34</sup>SO<sub>2</sub> to react OH quantitatively to H<sub>2</sub><sup>34</sup>SO<sub>4</sub><sup>-</sup>, which is detected with high sensitivity and selectivity using NO<sub>3</sub><sup>-</sup> as chemical ionization agent.<sup>94–96</sup> Detection limits of <10<sup>5</sup> molecules/cm<sup>3</sup> have been achieved.<sup>97</sup> Combining this instrument configuration with the peroxy radical amplification technique described above allows also for a quantification of HO<sub>2</sub> and RO<sub>2</sub>.<sup>98–100</sup> NO and SO<sub>2</sub> (labeled or unlabeled) are added to the sample airflow converting RO<sub>2</sub> and HO<sub>2</sub> to OH and ultimately to H<sub>2</sub>SO<sub>4</sub>, which is determined using the NO<sub>3</sub><sup>-</sup>-CIMS technique. Depending on adjustable reaction conditions, the H<sub>2</sub>SO<sub>4</sub> formed is mostly indicative of HO<sub>2</sub> or RO<sub>2</sub>, respectively, with detection limits of about 1 × 10<sup>7</sup> molecules/cm<sup>3</sup>.

**Cavity Ringdown Spectroscopy (CRDS).** Cavity ringdown spectroscopy has been used as a sensitive technique to measure a number of atmospheric radicals such as halogen oxides (e.g., BrO, IO<sup>46,101</sup>, HO<sub>2</sub><sup>102</sup> and NO<sub>3</sub><sup>103</sup>). NO<sub>3</sub> radicals have been observed in the ambient atmosphere in concentrations up to 40 ppt for a rural location or 100 ppt for urban locations. High fluctuations of the NO<sub>3</sub> concentration of up to 50% within minutes are often observed in field experiments and explained with the different history of air masses affecting especially short-lived compounds such as NO<sub>3</sub>.<sup>104,105</sup> Broadband cavity enhanced absorption spectroscopy (BBCEAS) has been used in field experiments to detect NO<sub>3</sub> with detection limits of about 0.1 ppt<sup>106,107</sup> and night time concentrations of up to 100 ppt of NO<sub>3</sub> were measured in urban areas.<sup>104,108</sup> Aircraft versions of CRDS instruments with detection limits also in the subppt range have been designed.<sup>109</sup> Off-axis CRDS and incoherent light source broadband cavity-enhanced absorption spectroscopy (IBBCEAS) instruments have been developed with detection limits in the low ppt range, offering simpler technical designs compared to systems described above (e.g., refs 110–112).



Figure 4. Measurement tower for atmospheric trace gas measurements during a campaign in the South Atlantic Ocean (OOMPH-campaign).

**Off-Line Technique for Gas Phase Species. Matrix Isolation Electron Spin Resonance (MI-ESR).** Matrix isolation electron spin resonance is an off-line technique, which is able to quantify a range of radicals, including HO<sub>2</sub>, RO<sub>2</sub>, and NO<sub>3</sub>.<sup>113</sup> An air sample is collected at low pressure and a temperature of 77 K where radicals are trapped in a solid D<sub>2</sub>O ice matrix. A few liters of air are typically collected with a time resolution of about 30 min, and their ESR spectrum is recorded off line. Quantitative results are obtained by comparison with reference spectra. Due to its off-line character and rather low time resolution, MI-ESR has been mostly used as a reference technique in comparison with other techniques in recent years.

Intercomparison studies between MI-ESR and ROxLIF (see above) have been performed in laboratory experiments.<sup>114</sup> Comparisons of MI-ESR and LIF<sup>115</sup> and MI-ESR and DOAS<sup>116</sup> showed good agreement, and intercomparison studies for OH and HO<sub>2</sub> and RO<sub>x</sub> between LIF, DOAS and CIMS, and PERCA and MI-ESR techniques revealed a good agreement between the very different techniques, reassuring that atmospheric trace levels of these short-lived radicals can be determined accurately (e.g., refs 87, 114, and 117–119).

**Particle Phase.** The presence of radicals in aerosol particles is far less studied than gas phase atmospheric radicals, with the exception of radicals in the aqueous phase such as cloud or rain droplets (see ref 120 for a comprehensive review). Aqueous phase radical chemistry will not be discussed here but rather radicals in nonaqueous atmospheric aerosol particles, which have mostly been evaluated in the past from a gas phase point of view. Loss reactions of OH, HO<sub>2</sub>, and NO<sub>3</sub> at the surface or in the bulk

of aerosol particles have been studied in laboratory experiments for a number of particles types such as inorganic salts or organic particles (e.g., refs 121–124). In most of these studies, analytical techniques as discussed for gas phase radicals were used, such as chemical ionization mass spectrometry. A recent review by George and Abbatt<sup>123</sup> summarizes kinetics and reaction mechanisms of gas phase radicals in/on aerosol particles, effects on particle composition and properties, and the release of gaseous compounds as a result of such radical-initiated reactions. Such reaction products include compounds that easily photolyze in the gas phase releasing again radical species such as Br<sub>2</sub>, ClNO<sub>2</sub>, or HONO (e.g., refs 125 and 126). Studies on radical concentrations and speciation in the aerosol phase are still rather sparse and have mostly been motivated in the past by health-related objectives.

**Electron Paramagnetic Resonance (EPR).** Electron paramagnetic resonance spectroscopy has been used for decades to determine the radical concentration in aerosol particles, first in cigarette smoke.<sup>127,128</sup> In complex mixtures, EPR radical identification can be difficult but a reliable quantification is possible without using an authentic standard, which would be needed for most other analytical techniques. Semiquinone radicals have been postulated to be the main radical in cigarette smoke<sup>129</sup> but were also found in ambient particles.<sup>130</sup> Transition metals such as Fe or Cu seem to be responsible for most of the EPR signal intensity in ambient particles (e.g., ref 131). Long-lived, adsorbed NO<sub>2</sub> radical complexes were detected on the surface for salt particles in laboratory studies.<sup>132</sup>

Besides EPR, other techniques have been used to determine concentration levels of radicals in aerosol, such as fluorescence probes. These techniques are often rather unspecific and quantify “reactive oxygen species” (ROS), which is a collection of compounds, including organic and inorganic radicals (e.g., RO<sub>2</sub>, OH, HO<sub>2</sub>, O<sub>2</sub><sup>•-</sup>, CO<sub>3</sub><sup>2-</sup>) but also nonradical compounds such as H<sub>2</sub>O<sub>2</sub>. For health-related studies, such a sum parameter of oxidizing particle components might be a measure that is more easily correlated with biological effects, assuming these oxidizing aerosol components induce cell damage in the lung upon inhalation. DCFH, which is easily oxidized to the highly fluorescent DCF (2'-7'-dichlorofluorescein), has been used as fluorescence probe to quantify ROS in aerosols. Quantitative results are often expressed in equivalent H<sub>2</sub>O<sub>2</sub> concentrations and were reported for ambient particles in a range of 0.01 to 500 nM/m<sup>3</sup> air.<sup>133–135</sup> An online analysis system to quantify ROS with DCFH was developed aiming to capture also very short-lived radicals.<sup>136</sup> Other fluorescence probes have been used, often custom synthesized, and applied to atmospheric particles or particles processed in laboratory experiments.<sup>137</sup>

## ■ ORGANIC COMPOUNDS

**Gas Phase.** Gaseous, volatile organic compounds (VOCs) are routinely measured in field and laboratory experiments. The large number of gaseous organic compounds present in the atmosphere, requires very sensitive and selective analytical techniques capable of being measured with high time resolution. Besides various spectroscopic techniques (e.g., DOAS, FT-IR), gas (GC) and liquid (LC) chromatographic techniques are often applied. In the following chapter, three areas are discussed showing exemplary technical progress in VOC analysis over the last years.

**Proton Transfer Reaction Mass Spectrometry (PTR-MS).** PTR-MS is a technique that allows quantification of a wide range

of organic compounds with high time resolution and with high sensitivity.<sup>138</sup> In a recent comprehensive review, Blake et al.<sup>9</sup> describe in detail instrumental aspects and applications of PTR-MS as a powerful technique to measure VOCs in the ambient atmosphere and for laboratory experiments. Here, only a few important instrumental aspects are described. Due to the soft ionization technique, compound fragmentation is minimized in the ion source of the MS, which simplifies the interpretation of organic compound mixtures. Nonetheless, due to the high complexity of organic compounds in the atmosphere and some fragmentation especially of larger organics,<sup>139</sup> atmospheric studies using PTR-MS often focus on a few selected, small organics. The main strength of this technique is the high time resolution and sensitivity. Detection limits in the ppt range have been reported for many compounds with time resolutions of seconds to minutes.<sup>140</sup> The high time resolution makes this technique highly suitable for flux measurements of VOC, e.g., from vegetation into the atmosphere.<sup>141</sup> PTR-MS has been used in laboratory experiments<sup>142,143</sup> and extensively in field studies using instruments on the ground, on ships, and in aircrafts.<sup>144–146</sup> Several types of mass spectrometers have been combined with a PTR ion source. In recent years, ion traps, which are able to perform MS-MS analyses to obtain structural information<sup>147</sup> and time-of-flight (TOF) MS<sup>140,148</sup> with high mass resolutions, allowing for an improved separation of the highly complex VOC mixtures, have increasingly been used in PTRMS instruments.

**Gas Chromatography (GC).** Often one-dimensional analytical techniques (such as PTRMS) are not sufficient for a comprehensive investigation of the complexity of VOCs present in the ambient atmosphere. Lewis et al.,<sup>149</sup> applied two-dimensional gas chromatography (2D-GC) for the first time to VOC samples and identified over 550 compounds in urban air, many of them previously not considered to be present as gaseous compounds in the atmosphere. Hamilton reviewed recently 2D-GC applications for atmospheric sciences.<sup>8</sup> 2D-GC field instruments capable of analyzing VOCs online, with time resolution of about 1 h, have been employed, and over 650 compounds were identified even at remote sites with little anthropogenic influence.<sup>150</sup> Other recent instrument developments have been aimed at designing micro gas chromatographic systems with subng detection limits<sup>151</sup> or lightweight and low power instruments that can be operated autonomously for several months,<sup>152</sup> which allows one to obtain long-term (e.g., seasonal variability) data sets of VOCs at remote sites and reasonable costs.

**Peroxy Nitrates (PN).** Besides the attempt to obtain improved information about the overall complexity of VOCs using chromatography systems, many analytical developments aim to identify specific compounds or compound classes. We will discuss here peroxy nitrates (PN) as an example of a compound class where recent technical developments contribute to an improved understanding of these important atmospheric compounds. PNs can influence the NO<sub>x</sub> and O<sub>3</sub> chemistry in remote areas, and thus, quantification of PNs is important to accurately describe the atmospheric chemistry in such areas. PNs in the atmosphere have been measured with GC-electron capture detection for several decades (e.g., ref 153). The inherent low time resolution of chromatographic systems, especially disadvantageous during airborne measurements, has led to the development of alternative techniques. Chemical ionization mass spectrometers (CIMS) using I<sup>-</sup> as chemical ionization agent achieve detection limits of about 0.03 ppt for peroxyacetyl nitrate (PAN) with a time resolution of a few seconds.<sup>154</sup> Employment

of this instrument in an airborne field experiment measured high PAN concentrations up 0.3 ppt in the upper free troposphere with similar values in polluted and remote areas, demonstrating the importance of long-range transport for PNs. Alternative techniques are used to quantify the sum of all PN (rather than individual compounds of the PN family) by thermally decomposing all PNs and quantifying the common reaction product NO<sub>2</sub>, using conventional techniques such as laser induced fluorescence<sup>155</sup> or cavity ringdown spectroscopy.<sup>156</sup>

**Particle Phase.** *Laser Desorption/Ionization Aerosol MS. Online Techniques.* We will not cover in this Review the substantial work on bioaerosol (microorganism) analysis with online mass spectrometers, which often uses matrix assisted laser desorption/ionization (MALDI) techniques and refer to corresponding reviews on that topic (e.g., ref 157). Instruments for online, field experiments to analyze atmospheric aerosols using laser desorption/ionization MS have been developed for about two decades.<sup>158</sup> So-called aerosol time-of-flight (ATOFMS) instruments are most frequently used.<sup>159</sup> The introduction of online aerosol mass spectrometry has revolutionized the chemical analysis of atmospheric aerosols. The general principle is to introduce airborne particles into the instrument, vaporize and ionize the material, and then analyze the ions using mass spectrometry. Recently, several papers on laser desorption/ionization aerosol MS, e.g., for aircraft based studies, describe instrumental developments toward smaller instruments with increased data acquisition capabilities.<sup>160,161</sup> The measurement of vertical and horizontal profiles of atmospheric aerosols using laser/desorption ionization aerosol MS is particularly helpful for understanding the impact of air pollution on regional scales from industrial point sources, especially due to the capability of this technique to detect particle phase metals.<sup>162</sup> Similar instrumental improvements (i.e., data acquisition) also allow the measurement of physical characteristics of atmospheric particles such as particle number concentration, size distribution, asphericity,<sup>163</sup> or particle density.<sup>164</sup> Laser desorption/ionization aerosol MS was also used recently for the identification of the chemical composition of ice residues and cloud droplet residues in field<sup>165</sup> and laboratory studies.<sup>166</sup> Ice residues were observed to be frequently larger than unactivated aerosol due to the formation of aggregates. These studies also showed the important role of mineral dust as ice nuclei. Laser desorption/ionization aerosol MS have also been used to study specific particle phase organics, such as pesticides<sup>167</sup> or organosulfates.<sup>168</sup> Recently, a laser desorption ion trap mass spectrometer was developed.<sup>169</sup> Single particle analysis is realized here by combining pulsed IR laser desorption inside the ion trap with electron impact (EI) ionization. The two-step desorption and ionization process is introduced to minimize matrix effects and to incorporate a universal and well-characterized ionization technique. In this study, also, tandem mass spectrometry has been performed on organic test aerosol particles.

**Off-Line Techniques.** Mainly, samples from laboratory, smog chamber experiments have been analyzed with off-line matrix assisted laser desorption/ionization techniques<sup>170,171</sup> with the emphasis on the characterization of possible oligomeric, high-molecular weight compounds in organic aerosols. Inorganic matrixes such as graphite or TiN were used to enhance ionization of organic particles, which do not absorb efficiently the wavelength of the laser,<sup>172</sup> and to avoid analyte–matrix adducts, frequently observed when conventional organic matrixes are used. Online and off-line (matrix assisted) laser desorption/ionization MS have

been compared and demonstrated good agreement with respect to the oligomer mass region of SOA generated in smog chamber experiments.<sup>173</sup>

**Quadrupole and TOF-Aerosol Mass Spectrometers (Q-AMS or TOF AMS).** In contrast to online laser desorption/ionization aerosol MS, AMS instruments (thermal desorption/electron impact aerosol mass spectrometers) measure the chemical composition of an aerosol ensemble, i.e., averages of thousands of particles. Obviously, the two aerosol MS techniques have complementary analytical characteristics with individual strength and weaknesses.<sup>11,12</sup> The AMS uses thermal vaporization and electron ionization (EI) to quantitatively investigate the nonrefractory composition of aerosols.<sup>174</sup> Data is generally reported as sulfate, nitrate, ammonium, and organic content. The use of 70 eV EI results in strong fragmentation of the organic fraction, and single species cannot be identified. Recently, the quadrupole in the AMS (Q-AMS) has been replaced with a TOF-AMS, increasing the mass resolution of the instrument. One essential reason for the advances in atmospheric analytical chemistry in recent years is the extensive use of Q-AMS and TOF-AMS in field measurements worldwide and quantitative information about the organic fraction of atmospheric particles. Data compilation from dozens of field sites provides improved temporal and spatial data about atmospheric aerosol composition and delivers an integrated picture of tropospheric organic aerosol (OA) and its evolution in the atmosphere.<sup>175,176</sup>

Interestingly, the fact that the EI ionization in regular HR-TOF-AMS instruments essentially breaks down the hundreds or thousands of individual organic aerosol constituents to relatively small fragments can be seen as an advantage of the technique, since it reduces the complexity of OA. Despite this strong fragmentation, important atmospheric processes such as volatilization, oxidation, mixing of air masses, or condensation of higher order oxidation products can still be investigated.<sup>177,178</sup> A similar approach of elemental analysis using HR-TOF-AMS by determination of the distribution of nitrogen in the detected fragments has been studied to evaluate the potential to measure organic nitrates with AMS.<sup>179</sup> Other recent applications of the HR-TOF-AMS report submicrometer organic marine aerosol composition in the N.E. Atlantic and conclude high contributions of primary organic matter to marine aerosol since the peak in concentration was observed to be associated with regions of high biological activity and moderately high wind speeds.<sup>180</sup> The mass spectra revealed a unique marine organic aerosol fingerprint, very likely useful for the differentiation between primary and secondary organic aerosol sources from marine origin. Although most publications describing AMS analyses are concentrating on organic compounds (besides particulate sulfate, nitrate, and ammonia), under certain conditions, also metals can be detected, e.g., particulate lead in and around Mexico City during the Megacity Initiative MILAGRO.<sup>181</sup> Last to mention here is the successful application of TOF-AMS in laboratory experiments, e.g., to understand aqueous phase chemistry and the buildup of organic oligomers.<sup>182,183</sup>

**Soft Ionization Methods for Aerosol Mass Spectrometry.** Due to the high degree of fragmentation of organic compounds induced by EI or LDI, the identification or quantification is usually not possible for individual particle phase organics. Therefore, several approaches have been made recently to introduce softer ionization techniques for aerosol mass spectrometry. One possibility is to use atmospheric pressure chemical ionization (APCI), a well-known technique first introduced in LC/MS.

One of the main advantages is the straightforward coupling of the ion source to the object of investigation, e.g., atmospheric simulation chambers or the ambient atmosphere. Often, these techniques are used to investigate SOA formation, e.g., from aromatic VOCs<sup>184,185</sup> or from biogenic VOCs.<sup>186</sup> The latter paper shows that APCI can even be used for very labile analytes, such as hydroperoxides. Dron and co-workers used this technique to perform functional group composition analysis of organic aerosols.<sup>185</sup> The capabilities of tandem mass spectrometry, which allows obtaining structural information of aerosol components, is often very helpful, since the complexity of OA composition increases the danger of isobaric interferences. The use of a vacuum ultraviolet (VUV) light source for ionization is another possibility to softly ionize organics. Hanna et al. introduced a laser based VUV source for near threshold ionization of organics in atmospheric aerosol particles.<sup>187</sup> The effectiveness of the source for single particle studies with diameters down to 300 nm was demonstrated by the analysis of individual caffeine aerosols vaporized by a pulsed CO<sub>2</sub> laser in an ion trap mass spectrometer. The decoupling of desorption and ionization using two lasers was also realized by Zelenyuk et al. for single particle analysis. The authors demonstrate that the technique delivers sufficient detail to allow molecular identification of organics in the particle phase.<sup>188</sup> Bente and co-workers recently showed that multiphoton ionization, well established for sensitive detection of certain gaseous analytes (e.g., PAHs), can also be applied for the analysis of these compounds in individual aerosol particles.<sup>189</sup>

The application of a soft ionization technique as described above is often accompanied with a loss in sensitivity. Moreover, the signal intensity on individual *m/z* ratios originating from individual compounds (e.g., the molecular ion) is necessarily much smaller than if hundreds of compounds contribute to the same mass spectrometric signal due to fragmentation. Therefore, several groups focused their developments on the combination of soft ionization techniques with a semicontinuous measurement approach, i.e., including a preconcentration step prior to analysis. For example, Bruns et al. deposited SOA particles onto a ZnSe plate by inertial impaction, followed by thermal desorption and APCI.<sup>190</sup> The impaction plate material enables prior analysis by Fourier transform-infrared spectroscopy (FT-IR) and delivers complementary information from a nondestructive analytical technique. Reddy et al. coupled a micro-orifice volatilization impactor with chemical ionization mass spectrometry (MOVICIMS).<sup>191</sup> The technique allows both gas and condensed phase composition data to be obtained on a semicontinuous basis. Gas phase compounds are analyzed while particles are collected using a single stage, multijet impactor on a brass impaction surface. The thermal desorption of the deposited material in an inert atmosphere is followed by negative ion CIMS with I<sup>-</sup> and SF<sub>6</sub><sup>-</sup> as reagent ions to specifically detect organic acids. A paper published by Geddes and co-workers also describes a particle impaction technique directly combined with aerosol mass spectrometry.<sup>192</sup> The particle components are deposited on an aluminum probe with an aerodynamic lens, followed by near-infrared (1064 nm) laser desorption/ionization aerosol mass spectrometry (NIR-LDI-AMS). Focusing on negative ions and the measurement of organic acids, the authors report minimal fragmentation due to the soft ionization afforded by the NIR photons. Laskin et al. used a MOUDI impactor for size-segregated collection of particles on Teflon substrates, followed by desorption electrospray ionization (DESI) high resolution mass spectrometry.<sup>193</sup> The technique is applied to the investigation of

SOA formation and aging in order to understand the formation of light absorbing organic aerosols in the atmosphere. A similar approach is presented by Li et al., who demonstrate that DESI-MS is particularly promising for the quantitative analysis of organic acids in atmospheric aerosols.<sup>194</sup> Thornberry et al. collect in their instrument particles prior analysis onto a stainless steel collection target (cutoff size of 0.45 μm), followed by thermal desorption; however, here, a PTR-MS instrument is used for identification and quantification of individual organic species.<sup>195</sup> The detection limit is reported to be higher than other recently published aerosol mass spectrometric systems with soft ionization methods. However, for certain analytes with a high proton affinity (e.g., organic amines), such systems might be beneficial. In contrast to the techniques listed above, which all were based on inertial impaction as deposition mechanism, Held et al. use an electrostatic precipitator to collect particles.<sup>196</sup> The aerosol particles are charged in a high efficiency unipolar charger which is located upstream of the precipitator. The purpose of such a collection device is the chemical characterization of ultrafine aerosol particles. After thermal desorption of the collected particles, chemical ionization at atmospheric pressure (<sup>241</sup>Am-foil emitting α particles) is used as ionization technique.

**High-Resolution Mass Spectrometric (HR-MS) Techniques.** HR-MS or ultra-HR-MS (Fourier transform ion cyclotron resonance or Orbitrap mass spectrometers) have successfully been introduced into the field of atmospheric aerosol analysis in the past few years. Due to the very high mass resolution of the instruments, thousands of ions can be separated from each other and often their *m/z* ratio determined with sufficient accuracy to allow molecular formula calculation. The potential of the technique for atmospheric aerosol characterization was recently reviewed by Nizkorodov et al.<sup>197</sup> and Reemtsma.<sup>198</sup> Most of the papers published recently use ESI as ionization technique. Consequently, filter sampling followed by liquid extraction or particle-into-liquid sampling (PILS) precedes the mass spectrometric analysis. Biomass burning aerosols,<sup>199,200</sup> biogenic SOA,<sup>200–203</sup> and fog<sup>204</sup> have been recently investigated by ESI-HR-MS. Often, the work published so far is based on infusion of the complex mixtures into the ion source without prior chromatographic separation. Consequently, relatively high concentrations of analytes are infused into the mass spectrometer, and adduct formation may occur under these circumstances.<sup>198</sup> Especially for the investigation of organic oligomer formation, in which the object of investigation is by itself an adduct of other existing monomers, such artifacts have to be carefully addressed, e.g., by online coupling of separation techniques.<sup>205,206</sup> To avoid artifacts potentially introduced during sample workup and simplify analyses procedures, direct soft desorption electrospray ionization (DESI) techniques have been applied to aerosol samples. Comparison with direct infusion ESI techniques demonstrates good agreement between the two techniques.<sup>193,193,207</sup> A comparison between off-line MALDI and ESI techniques has been presented by Reinhardt et al.<sup>202</sup> for SOA generated in a smog chamber, showing good agreement between these two very different ionization techniques for the oligomeric mass range.

**Chromatography/Mass Spectrometry-Marker Compound Measurements.** When single or multiple individual organic compounds have to be quantitatively measured in the particle phase, for example, to apply chemical tracer methods for source contribution studies, the complexity of the aerosol composition still requires separation techniques, typically followed by mass spectrometric detection. While the determination of POA markers is reasonably well established, secondary OA markers have only

recently been studied.<sup>208</sup> Derivatization-GC/MS is still the method of choice and biomass burning markers<sup>208–210</sup> and SOA tracers from biogenic<sup>208–210</sup> or anthropogenic sources<sup>211</sup> have been measured at various field sites with this technique. In search of biogenic SOA markers, often the analysis is not only focusing on individual biogenic precursors but also aiming to identify products from isoprene, terpene, and sesquiterpene oxidation.<sup>208–210</sup> The highly polar character of many suitable marker compounds, their often extremely low vapor pressure, and the goal to also cover high-MW compounds led to an increased use of liquid chromatography in the past few years. Often, organic acids are determined since they are not only good markers for certain secondary sources but also excellent analytes for ESI-MS analysis.<sup>212,213</sup> Moreover, LC-MS was shown to be useful for monosaccharide anhydrides, which are biomass burning markers<sup>214</sup> and humic-like substances.<sup>215</sup>

**Spectroscopic Techniques.** Mass spectrometry is the dominant technique for the chemical characterization of OA components. Nevertheless, spectroscopic techniques gain in importance due to the unique and often complementary chemical information they deliver. First to mention is Fourier transform infrared spectroscopy (FT-IR) which delivers organic functional group information.<sup>216–218</sup> The quantity of hydroxyl, ketone, alkane, amine, and carboxylic acids groups estimated by FT-IR can then be compared with MS results.<sup>190,219,220</sup> Moreover, X-ray absorption spectroscopy (NEXAFS) has been utilized for functional group analysis.<sup>221,222</sup> Beside absorption measurements, also fluorescence techniques have been introduced for organic aerosol characterization, for example, for selective organic nitrate detection in real-time by thermal dissociation coupled to LIF detection of NO<sub>2</sub>.<sup>223</sup> See also discussion about peroxyinitrates above. Pan and co-workers report an improved version of a real-time single-particle spectrometer based on UV-LIF.<sup>224</sup> Due to the covered size range and the ability to record UV-LIF spectra of individual particles, the instrument is especially suited for biological aerosol measurements. Finally, in the context of spectroscopic techniques and organic aerosol characterization, also proton nuclear magnetic resonance (<sup>1</sup>H-NMR) techniques should be mentioned, by which the functional group compositions of the water-soluble fraction of atmospheric aerosols can be obtained to characterize aerosol sources and pollution levels.<sup>225</sup>

## BIOGRAPHIES

**Thorsten Hoffmann** achieved his Diploma degree in Chemistry from the Technische Universität Dortmund (Germany) in 1988. He continued at the Institute of Spectrochemistry and Applied Spectroscopy (ISAS) in Dortmund with his thesis on analytical method developments for atmospheric VOC measurements and received the PhD degree in 1992 (TU Dortmund). After a postdoc period at the California Institute of Technology (Caltech) in Pasadena (USA) in the group of John H. Seinfeld in 1994/95, he worked as a senior researcher at ISAS leading the research groups “Atmospheric Trace Constituents” and “Analytical Methods in the Life Sciences”. After finishing his Habilitation in 2000, he got a stand-in professorship at the University of Leipzig. Since 2004, he has been a Professor of Analytical Chemistry at the Johannes Gutenberg-University, Mainz, Germany. His domain of expertise covers the analysis of gaseous and particulate organic and inorganic compounds for atmospheric research by means of mass spectrometry and the development of related analytical methods (GC/MS, HPLC/MS, aerosol mass spectrometry).

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**Markus Kalberer** studied Environmental Sciences at ETH Zurich (Switzerland) where he received his Diploma in 1994. He carried out his PhD studies at the University of Bern and the Paul Scherrer Institut, PSI (both Switzerland) followed by a postdoc in John H. Seinfeld’s group at the California Institute of Technology in the US in 1999/2000. He returned to Switzerland for a Habilitation position at the Laboratory of Organic Chemistry at ETH Zurich (group of R. Zenobi). After a short stay at the Laboratory of Atmospheric Chemistry at PSI in 2007–2008, he was appointed to a lectureship in Atmospheric Chemistry in the Department of Chemistry at the University of Cambridge, UK, in 2008. His research interests include the formation, reactivity, and composition of organic aerosols mainly using and developing mass spectrometry techniques. Another topic of his research activities is the investigation of negative health effects of atmospheric particles by developing analytical methods and instruments to accurately mimic particle–lung cell interactions in *in vitro* experiments and to determine health-relevant particle properties.

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