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Bulk organic aerosol analysis by PTR-MS: an improved methodology for the determination of total organic mass, O:C and H:C elemental ratios and the average molecular formula

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ABSTRACT: We have recently shown in this journal (Müller et al., *Anal. Chem.* 2017, 89, 10889-10897) how a proton-transfer-reaction mass spectrometry (PTR-MS) analyzer measured particulate organic matter in urban atmospheres using the “*Chemical Analysis of Aerosol Online*” (CHARON) inlet. Our initial CHARON studies did not take into account fragmentation of protonated analyte molecules, which introduced a small but significant negative bias in the determination of bulk organic aerosol parameters. Herein, we studied the ionic fragmentation of 26 oxidized organic compounds typically found in atmospheric particles. This allowed us to derive a correction algorithm for the determination of the bulk organic mass concentration, m_{OA} , the bulk-average hydrogen-to-carbon ratio, $(\text{H:C})_{\text{bulk}}$, the bulk-average oxygen-to-carbon, $(\text{O:C})_{\text{bulk}}$, and the bulk-average molecular formula, MF_{bulk} . The correction algorithm was validated against AMS data using two sets of published data. Finally, we determined MF_{bulk} of particles generated from the reaction of α -pinene and ozone and compared and discussed the results in relation to the literature.

Submicrometer-sized particles that are suspended in the atmosphere over cities and forests are predominantly composed of organic matter. The organic particle fraction consists of thousands of individual compounds with widely varying chemical and physical properties (*e.g.*, volatility, polarity, water solubility). This makes the sampling, separation and detection of particulate organic matter (POM) one of the major remaining challenges in atmospheric analytical chemistry¹.

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is a well-established and widely used online monitoring technique for organic trace gases in the atmosphere^{2,3}. The recently developed “*Chemical Analysis of Aerosol Online*” (CHARON) particle inlet⁴ enables PTR-MS instruments to measure POM online (*i.e.*, without preconcentration on a filter or an impaction plate) and in real time⁵⁻¹⁰. The CHARON inlet consists of an activated charcoal denuder which strips off gaseous organic compounds from the sample flow, an aerodynamic lens system which enriches the particle concentration in the instrument subsampling flow, and a vaporizer which evaporates POM prior to its introduction into the PTR-MS instrument. The PTR-MS analyzer in its standard configuration uses hydronium (H_3O^+) ions to ionize organic analytes via proton transfer reactions¹¹. H_3O^+ ions react with all larger organic molecules at unit efficiency, which means that the PTR-MS signal response to typical atmospheric POM constituents varies by less than a factor of 2.5. This makes PTR-MS stand out from other emerging POM analyzers^{12,13} and well suited for a quantitative bulk organic aerosol analysis.

An accurate measurement of the bulk organic mass concentration, m_{OA} , is essential for obtaining mass closure of submicrometer-sized atmospheric particulate matter. Bulk elemental ratios are widely used reduced parameters for describing the chemical state of POM. The bulk-average hydrogen-to-carbon ratio, $(\text{H:C})_{\text{bulk}}$, and the bulk-average oxygen-to-carbon, $(\text{O:C})_{\text{bulk}}$, have been linked to important POM properties such as density, volatility, hygroscopicity, oxidation state, and refractive index¹⁴⁻¹⁸. m_{OA} , $(\text{H:C})_{\text{bulk}}$ and $(\text{O:C})_{\text{bulk}}$ are nowadays routinely measured by the Aerodyne aerosol mass spectrometer (AMS)¹⁹. The AMS is, however, not capable of determining the bulk-average molecular formula, MF_{bulk} , because most organic analytes decompose in this instrument before detection. MF_{bulk} is also difficult to determine with soft ionization methods which usually do not universally and quantitatively ionize all constituents of POM. The accurate determination of MF_{bulk} of atmospheric POM thus remains a major analytical challenge.

When determining m_{OA} , $(\text{H:C})_{\text{bulk}}$ and $(\text{O:C})_{\text{bulk}}$ by CHARON PTR-MS, we have hitherto not taken into account the fragmentation of protonated analyte molecules and thus accepted a small but significant negative bias in the measurement of these parameters. The work presented herein quantifies this bias using the conceptual approach that Aiken et al.²⁰ and Canagaratna et al.²¹ have developed for characterizing the AMS analyzer. This approach consists in studying the instrument’s response to a large number of analytes thought to be representative of atmospheric POM and in relating the biased measured data to the known molecular composition. In most

urban and rural atmospheres, POM mainly consists of oxidized species²² wherein oxygen is predominantly bound in hydroxy, carboxylic and keto groups²³. We have studied the fragmentation of 26 compounds with these functionalities to derive an algorithm for correcting m_{OA} , $(H:C)_{bulk}$ and $(O:C)_{bulk}$. We have further validated this correction algorithm against AMS data using two sets of published data. Finally, we have determined MF_{bulk} of particles generated from the reaction of α -pinene and ozone and compared it with literature values.

MATERIALS AND METHODS

Fragmentation study. The 26 oxidized organic compounds studied in this work are listed in Table S1 in the Supplement. The compounds were individually dissolved in distilled water (isopropanol in the case of levoglucosan) and nebulized in a home-built nebulizer that was pressurized with ultra-pure air. The nebulizer outflow was diverted through a heated (80°C) tube and a diffusion dryer for removing water and two activated charcoal denuders (NovaCarb F, Mast Carbon International Ltd., Guilford, UK) for removing any volatile organics present. The resulting flow of polydisperse particles was then injected into a differential mobility analyzer (DMA, TSI model 3070), with only 300 nm particles being transmitted to the CHARON PTR-MS analyzer.

α -pinene ozonolysis study. 400 ppb of α -pinene (98%, Sigma-Aldrich), 525 ppb of ozone and 300 nm ammonium sulfate seed aerosols ($\sim 1500 \text{ cm}^{-3}$) were injected into a borosilicate flow tube (length: 3 m, volume: 30.6 l) that was continuously flushed at a rate of 1 liter per minute with humidified ultra-pure air (RH $\sim 30\%$). The residence time in the flow tube was approximately 30 minutes, enough to generate abundant secondary organic aerosol (SOA) from the reaction of α -pinene and ozone. The tube outflow was sampled by the CHARON PTR-MS analyzer via a home-built thermodenuder⁶, *i.e.*, a heated tube combined with an activated charcoal denuder. The residence time in the thermodenuder was approximately 40 seconds, enough for equilibration. The thermodenuder temperature was increased in 10°C steps from room temperature to 105°C.

PTR-MS operation and data analysis. The CHARON inlet has been described in the introduction and in greater detail by Eichler et al.⁴ The inlet we used had a particle enrichment factor of ~ 44 . The vaporizer was operated at 140°C and ~ 8 mbar absolute pressure. The CHARON inlet was connected to a commercial PTR-TOF 8000 analyzer (Ionicon Analytik GmbH, Innsbruck, Austria). The drift tube was kept at 120°C and operated at different reduced electric field strengths (see Results section). The raw data were processed using the *PTR-ToF Data Analyzer*²⁴. We assigned a molecular sum formula to each ion signal based on the measured accurate m/z and quantified it according to its elemental composition. The Langevin-Gioumoussis-Stevenson theory²⁵ was used for quantifying signals assigned to pure hydrocarbon ions. The Su and Chesnavich parameterized capture rate theory²⁶ was used for quantifying signals associated with heteroatom-containing ions. Isotropic molecular polarizabilities were determined from the ions' elemental composition using the parametrization proposed by Bosque and Sales²⁷. An average dipole moment of 2.75 D was used for quantifying ion signals associated with heteroatom-containing ions. This quantification procedure is described in more detail in Müller et al.⁵ The Supplement of Müller et al.⁵ describes how to derive m_{OA} ,

$(H:C)_{bulk}$ and $(O:C)_{bulk}$ from the elementally-resolved and quantified signals.

RESULTS AND DISCUSSION

Reduced fragmentation at 60 Td. The fragmentation of analyte ions in PTR-MS instruments is, to a large extent, caused by the energetic action of the electric field in the ionization region (*i.e.*, in the drift tube). The electric field prevents the hydration of ions and thus ensures that bare H_3O^+ ions are the main ionizing agents. This is typically achieved by applying a reduced electric field strength, E/N (E being the electric field strength and N the gas number density), in the range between 100 and 160 Td ($1 \text{ Td} = 10^{-17} \text{ V cm}^2$) to the ionization region²⁸.

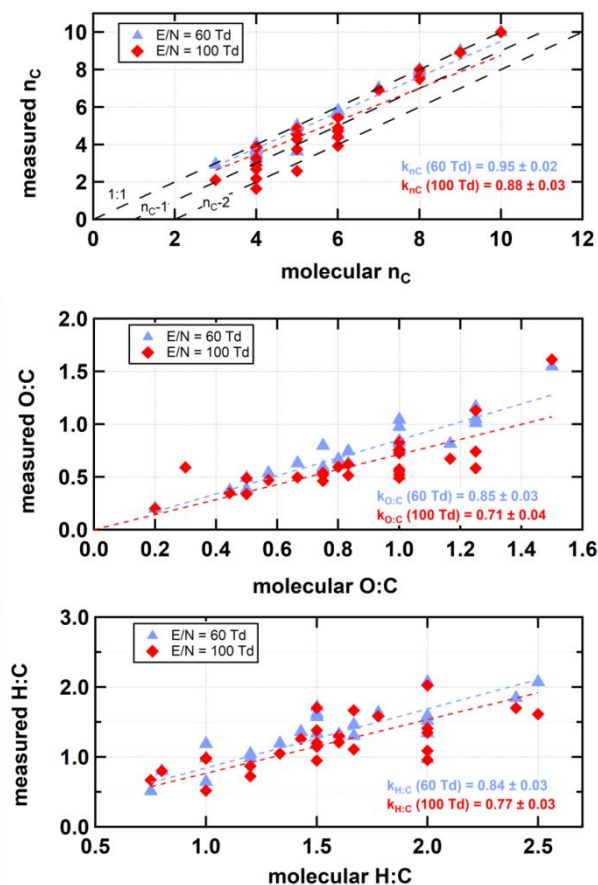


Figure 1. Scatter plots of measured n_c vs. molecular n_c (upper panel), measured O:C vs. molecular O:C (middle panel), and measured H:C vs. molecular H:C (lower panel), as obtained when pure-compound particles generated from 26 oxidized organic compounds, were sampled at 100 Td (red points) and 60 Td (blue points), respectively.

CHARON PTR-MS analyzers do, however, operate in the H_3O^+ mode down to an E/N of 60 Td due to the dehumidifying action of the charcoal denuder and the increased drift tube temperature. We have recently shown on the example of *cis*-pinonic acid particles that considerably less fragmentation occurs at 60 Td.⁷ This was investigated further in the present study by obtaining the mass spectra of 26 compounds at 100 and 60 Td, respectively. The relative product ion abundances are reported in the Supplement. At 100 Td, 19 of the investigated compounds fragmented to more than 90%. At 60 Td,

fragmentation was considerably reduced, especially for the carboxylic acids (see Supplement). Importantly, at 60 Td 11 of the compounds studied did not exhibit any fragmentation of carbon-carbon bonds. It is also important to note that none of investigated compounds thermally decomposed (*e.g.*, via decarboxylation) in the vaporizer or in the heated drift tube.

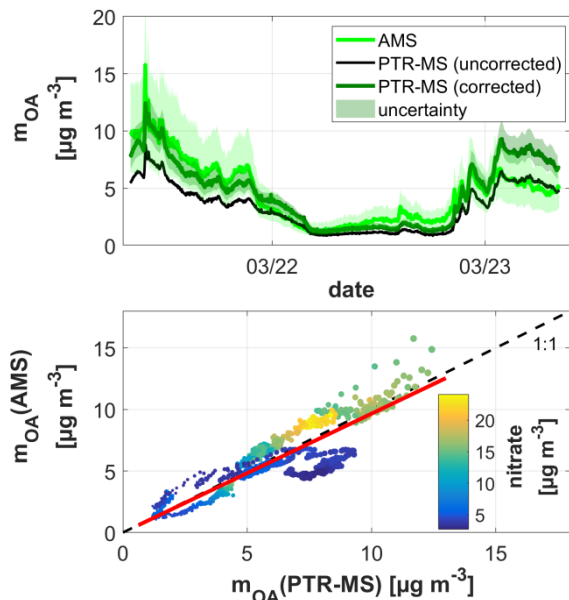


Figure 2. Time series of m_{OA} as measured by the AMS and the PTR-MS instrument (uncorrected, fragmentation-corrected) during a 3 day side-by-side intercomparison⁵ in Lyon (upper panel). Scatter plot of m_{OA} (AMS) vs. m_{OA} (PTR-MS, fragmentation-corrected) (lower panel)

Fragmentation correction algorithm. The bulk-average parameters that can be extracted from the PTR-MS mass spectra are biased low due to analyte ion fragmentation. The upper panel of Figure 1 shows that measured number of carbon atoms, n_{C} , is, on a bulk average, by 12 % (100 Td) and 5% (60 Td) lower than the molecular n_{C} . The measured O:C is, on a bulk average, by 29% (100 Td) and 15% (60 Td) lower than the molecular O:C (Figure 1, middle panel). The measured H:C is, on a bulk average, by 23% (100 Td) and 16% (60 Td) lower than the molecular H:C (Figure 1, lower panel). Based on these data, a simple correction algorithm can be derived for the number of carbon atoms, the number of oxygen atoms, n_{O} , and the number of hydrogen atoms, n_{H} , respectively.

$$n_{\text{C}}^{\text{corrected}} = \frac{n_{\text{C}}^{\text{measured}}}{k_{\text{C}}} \quad (1)$$

k_{C} is 0.88 and 0.95 for 100 Td and 60 Td, respectively. Here and in the equations below, k generally denotes a correction factor.

$$n_{\text{O}}^{\text{corrected}} = \frac{(\text{O:C})^{\text{measured}}}{k_{(\text{O:C})}} \cdot n_{\text{C}}^{\text{corrected}} \quad (2)$$

$k_{(\text{O:C})}$ is 0.71 and 0.85 for 100 Td and 60 Td, respectively.

$$n_{\text{H}}^{\text{corrected}} = \frac{(\text{H:C})^{\text{measured}}}{k_{(\text{H:C})} \cdot \text{CF}_{\text{H}}} \cdot n_{\text{C}}^{\text{corrected}} \quad (3)$$

$k_{(\text{H:C})}$ is 0.77 and 0.84 for 100 Td and 60 Td, respectively. The correction factor CF_{H} comes from an iterative correction process and is 0.96 and 1.05 for 100 Td and 60 Td, respectively.

The corrected m_{OA} is obtained from:

$$m_{\text{OA}}^{\text{corrected}} = f \times m_{\text{OA}}^{\text{measured}} \quad (4)$$

The correction factor f for correcting m_{OA} is given by:

$$f = \frac{n_{\text{C}}^{\text{corrected}} m_{\text{C}} + n_{\text{O}}^{\text{corrected}} m_{\text{O}} + n_{\text{H}}^{\text{corrected}} m_{\text{H}}}{n_{\text{C}}^{\text{measured}} m_{\text{C}} + n_{\text{O}}^{\text{measured}} m_{\text{O}} + n_{\text{H}}^{\text{measured}} m_{\text{H}}} \quad (5)$$

m_{C} , m_{O} and m_{H} are the masses of carbon, oxygen and hydrogen atoms, respectively. The lower boundary of uncertainty for $m_{\text{OA}}^{\text{corrected}}$ is given by $1 - \frac{n_{\text{C}}^{\text{corrected}}}{n_{\text{C}}^{\text{measured}}}$. The upper boundary of uncertainty for $m_{\text{OA}}^{\text{corrected}}$ is given by $1 - \frac{n_{\text{C}}^{\text{corrected}}}{n_{\text{C}}^{\text{measured}} + 2}$.

Validation. We have used two sets of published data for validating the fragmentation-corrected PTR-MS data against AMS data.

The first set of data is taken from Müller et al.⁵ who compared AMS (cTOF version) and CHARON PTR-MS measurements of urban air in Lyon (France). The main finding was that the data from the two instruments correlate well, with the PTR-MS analyzer systematically underestimating m_{OA} . Figure 2 shows the time series and scatter plot obtained when the fragmentation correction was applied to the PTR-MS data. The AMS and PTR-MS data are now in excellent agreement, except for a period when organics were relatively high and nitrate was low. The linear regression slope decreases from 1.13 (AMS vs. PTR-MS_{uncorrected}, see Müller et al.⁵) to 0.96 (AMS vs. PTR-MS_{corrected}; $R^2=0.75$).

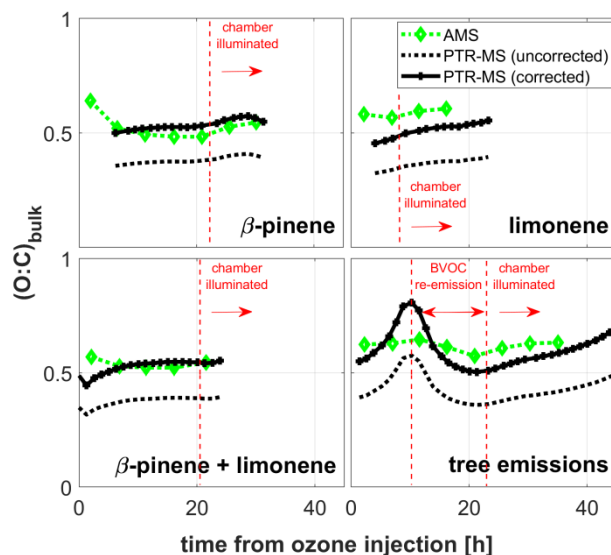


Figure 3. Time series of $(\text{O:C})_{\text{bulk}}$ as measured by the AMS and the PTR-MS (uncorrected, fragmentation-corrected) in the SAPHIR atmosphere simulation chamber⁷ when SOA was generated from the ozonolysis of β -pinene, limonene, a β -pinene–limonene mix and real plant emissions, respectively.

The second set of data is taken from Gkatzelis et al.⁷ who monitored SOA that was generated in the SAPHIR atmosphere simulation chamber from the ozonolysis of β -pinene, limonene, a β -pinene–limonene mix and real plant emissions, respectively. Figure 3 shows that the fragmentation correction brings the $(\text{O:C})_{\text{bulk}}$ values determined by AMS (HTOF version) and PTR-MS in close agreement.

Average molecular formula. For many applications and parameterizations, the chemical description of POM via bulk elemental ratios is an oversimplification. An adequate descrip-

tion of bulk aerosol volatility, for example, needs to include at least the bulk-average molecular weight and the average num-

ber of oxygen atoms. In such a case, MF_{bulk} may be better suited for a simplified chemical description of POM.

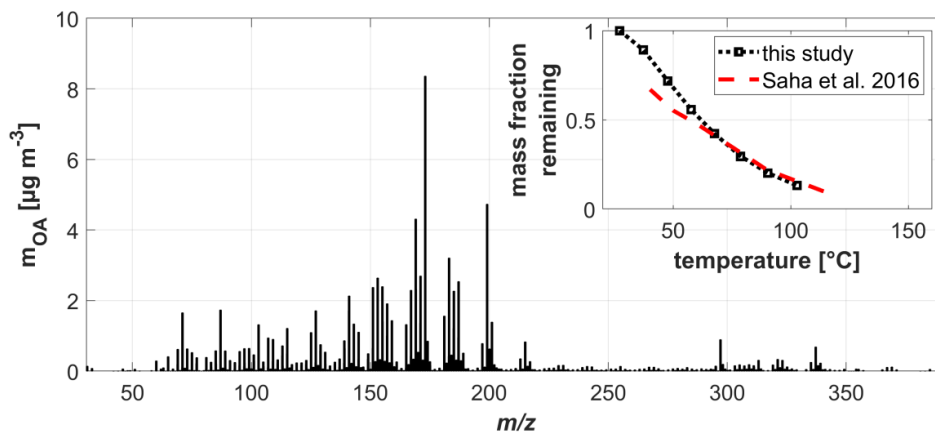


Figure 4. PTR-MS (H_3O^+ mode, 60 Td) mass spectrum of particles generated from the ozonolysis of α -pinene. The insert shows a thermogram of the organic mass fraction remaining when particles were heated before analysis in the CHARON PTR-MS system.

Measuring MF_{bulk} is, however, a major analytical challenge. As explained above, atmospheric POM mostly consists of oxidized hydrocarbons. While a lot of current research focuses on highly oxidized molecules, compounds including only one oxygen atom (*e.g.*, sterols, aldehydes), two O's (*e.g.*, monocarboxylic acids, ketoaldehydes) or 3 O's (*e.g.*, keto- and hydroxycarboxylic acids, triols) can make up for a significant fraction of the organic matter. Most of the soft ionization methods (*e.g.*, iodide chemical ionization, acetate chemical ionization, electrospray ionization) currently used for POM analysis do, however, either not respond to poorly oxidized analytes or exhibit a highly variable compound-specific response.^{12,13,29,30} It is thus not possible to quantitatively analyze bulk organic aerosol with these ionization techniques. Here is where PTR-MS with its universal (*i.e.*, independent of n_O) and quantitative ionization via H_3O^+ ions fills an important gap.

Figure 4 shows the mass spectrum obtained from $130 \mu\text{g m}^{-3}$ of SOA generated in a flow tube from the reaction of α -pinene with ozone. The uncorrected MF_{bulk} we extract from the mass spectrum is $C_{7.6}H_{10.7}O_{2.6}$; the fragmentation-corrected MF_{bulk} is $C_{8.0}H_{12.7}O_{3.3}$. Being able to detect poorly oxidized species, PTR-MS observes on average 2-3 oxygen atoms less in α -pinene secondary organic aerosol than other ionization techniques.^{31,32} This has, for example, an important implication for bulk volatility calculations. Using the method proposed by Daumit et al.²³, we derive a bulk volatility $\log C_{298K}^* = 4.2$ from the fragmentation-corrected MF_{bulk} . The insert in Figure 4 shows the results from our thermodenuder measurements, which are in good agreement with the data reported by Saha et al.³³ The experimentally derived bulk volatility $\log C_{298K}^*$ is 2.5. This value in good agreement with the number obtained from the PTR-MS derived MF_{bulk} , while an MF_{bulk} with 5 or 6 oxygen atoms would result in a much lower bulk volatility ($\log C_{298K}^*$ on the order of -1 or -2). More details about this topic will be given in a forthcoming publication (Leglise et al., in preparation).

CONCLUSION

We have studied the mass spectral response of the CHARON PTR-MS analyzer to 26 oxidized organic com-

pounds which are thought to be representative of atmospheric POM. Fragmentation was found to be significant both at 100 and 60 Td reduced electric field strength and thus needs to be taken into account for a quantitative bulk aerosol analysis. Linear trends in measured vs. molecular n_C , (O:C) and (H:C) allowed us to derive a correction algorithm for m_{OA} , (O:C)_{bulk}, (H:C)_{bulk} and MF_{bulk} . The work presented herein will help the small but steadily growing user community in establishing the CHARON PTR-MS instrument as a tool for bulk organic aerosol analysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

List of 26 compounds studied with relative product ion abundances as measured by CHARON-PTR-MS at 60 and 100 Td (PDF)

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Author Contributions

JL carried out most of the measurements and part of the analysis and drafted the manuscript. TO and FP supported the measurements. MM supervised the laboratory work and carried out most of the analysis. AW supervised the scientific work and wrote the final manuscript. All authors have given approval to the final version of the manuscript.

Notes

FP and MM both work for Ionicon Analytik, which is commercializing CHARON PTR-MS instruments. AW and MM both profit from a license agreement (CHARON inlet) between the University of Innsbruck and Ionicon Analytik.

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