

This discussion paper is/has been under review for the journal Atmospheric Measurement Techniques (AMT). Please refer to the corresponding final paper in AMT if available.

A novel inlet system for on-line chemical analysis of semi-volatile submicron particulate matter

P. Eichler¹, M. Müller¹, B. D'Anna², and A. Wisthaler^{1,3}

¹Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Innsbruck, Austria

²CNRS, UMR5256, IRCELYON, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, Villeurbanne, Université de Lyon, Lyon, 69626, France

³Department of Chemistry, University of Oslo, Oslo, Norway

Received: 28 July 2014 – Accepted: 19 September 2014 – Published: 30 September 2014

Correspondence to: A. Wisthaler (armin.wisthaler@uibk.ac.at)

Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

We herein present the concept of a novel modular inlet system that allows using gas-phase analyzers for on-line chemical characterization of semi-volatile submicron particles. The “chemical analysis of aerosol on-line” (CHARON) inlet consists of a gas-phase denuder for stripping off gas-phase analytes, an aerodynamic lens for particle enrichment in the sampling flow and a thermo-desorption unit for particle volatilization prior to chemical analysis. We coupled the CHARON inlet to a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) which quantitatively detects most organic analytes and ammonia. The combined set-up measures submicron organic and 5 ammonium nitrate/sulfate particles online. Two proof-of-principle studies were carried out for demonstrating the analytical power of the new set-up in analyzing primarily emitted and secondarily generated particles. Oxygenated organics and their partitioning between the gas and the particulate phase were observed from the reaction of limonene 10 with ozone. Abundant quasi-molecular ions of organic particulate constituents were observed when submicron particles were sampled from diluted mainstream cigarette smoke. 15

1 Introduction

The characterization of the organic fraction of atmospheric aerosol, which in the following refers to both particles and gases dispersed in air, is still a major analytical 20 challenge. Collection, storage and preparation of atmospheric samples followed by off-line analysis are time and labor intensive and often prone to analytical artifacts. This has driven the demand for direct sample introduction or on-line analytical techniques.

While optical methods are well-suited for the on-line detection of small gas-phase organic molecules (e.g. formaldehyde), chemical ionization mass spectrometry (CI-MS) 25 is the method of choice for detecting more complex organic analytes in an on-line manner. On-line CI-MS techniques for gas-phase organics currently used in atmospheric

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research include PTR-MS (Hansel et al., 1995), TD-CIMS (Slusher et al., 2004), CIT-CIMS (Crounse et al., 2006) and NI-PT-CIMS (Veres et al., 2008).

Particulate organic matter is more difficult to measure on-line. Currently used on-line mass spectrometers for particulate organic matter rely on 70 eV electron impact (EI) ionization or photoionization (PI) which both lead to intense fragmentation of most organic analytes (Hoffmann et al., 2011, and references therein). CI methods face the challenge of separating the gas phase from the particulate phase prior to analysis. This is currently achieved by collecting particles on metal or PTFE surfaces followed by thermal desorption in an inert gas atmosphere and subsequent CI-MS analysis (Voisin et al., 2003; Thornberry et al., 2009; Holzinger et al., 2010; Yatavelli and Thornton, 2010; Müller et al., 2012; Aljawhary et al., 2013; Lopez-Hilfiker et al., 2014). Such methods are, however, not truly on-line and may not avoid surface collection artefacts. Hellén et al. (2008) developed a true on-line method suitable for chamber studies with high particle concentrations. A true on-line CI-MS method for atmospheric particulate organic matter was recently reported by Vogel et al. (2013).

Herein, we present a novel true on-line inlet system that

1. efficiently strips off gas-phase analytes,
2. enriches the particle concentration in the sample, and
3. vaporizes the particles for subsequent chemical analysis.

We show results from two proof-of-principle studies to demonstrate how the novel inlet can be used for on-line analysis of sub-micron particles, both primarily emitted and secondarily generated, by PTR-MS.

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2 Experimental

2.1 Chemical analysis of aerosol on-line (CHARON)

We herein present a novel modular inlet system for on-line chemical characterization of aerosol, i.e. both gas-phase and particulate-phase organics in air. The “chemical analysis of aerosol on-line” (CHARON) inlet consists of:

1. a gas-phase denuder (GPD) for stripping off gas-phase analytes,
2. an aerodynamic lens (ADL) for on-line particle enrichment,
3. a thermo-desorption unit (TDU) for particle volatilization.

The CHARON inlet can, in principle, be used for and adapted to different types of gas-phase analyzers. We coupled it to a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) which quantitatively detects most organic analytes. PTR-ToF-MS also measures ammonia which means that the CHARON inlet can also be used for ammonium nitrate and ammonium sulfate analysis. The modules and working principle of the CHARON inlet are schematically illustrated in Fig. 1.

2.1.1 Gas-phase denuder (GPD)

The gas-phase denuder (GPD) consists of a NovaCarb F activated charcoal monolith (Mast Carbon International Ltd., Guilford, UK) with a channel density of 221 channels per inch (cpi) and an open cross section of 30 %. The 5 cm long denuder is mounted in a stainless steel housing sealed with Viton[®] O-rings. The flow through the GPD is kept at laminar levels (755 sccm, $Re = 309$) to minimize particle loss through surface collisions.

To test the VOC removal efficiency, the GPD was challenged with a test gas atmosphere containing a set of pure and oxygenated hydrocarbons in equimolar concentrations (methanol, acetonitrile, acetaldehyde, acetone, isoprene, methylethylketone,

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benzene, toluene, xylene, 1,3,5-trimethylbenzene, α -pinene). Mixing ratios of individual compounds were varied between 0 and 30 ppbV. The maximum total VOC load onto the GPD was 330 ppbV. The test gas atmosphere was generated by dynamic dilution of a certified gas mixture (Apel Riemer Environmental Inc., Broomfield, USA) with catalytically cleaned (Pt/Pd, 325 °C) laboratory air. A conventional PTR-MS instrument was used for measuring VOC concentrations upstream and downstream the GPD.

The particle transmission efficiency of the GPD was tested by challenging it with monodisperse particles in the 20 to 750 nm mobility diameter range. Sub-micron particles of different chemical composition were generated from solutions of ammonium nitrate (AN, Sigma-Aldrich), ammonium sulphate (AS, Sigma-Aldrich), glutaric acid (GA, Sigma-Aldrich) and methyl glyoxal (MG, Sigma-Aldrich), respectively, using a TSI Aerosol Generator 3079 (TSI Inc., Shoreview, USA). The generated particles were dried using a Nafion® dryer (Perma Pure LLC, Toms River, USA) and neutralized using a TSI Soft X-Ray Aerosol Neutralizer 3087. Subsequently, particles were size-selected in the 20 to 750 nm size range using a differential mobility analyzer (DMA, Leibniz-Institut für Troposphärenforschung e.V., Leipzig, Germany). The resulting monodisperse particles were either passed through the GPD and counted using a TSI 3772 condensation particle counter (TSI Inc., Shoreview, USA) or directly counted by the CPC.

2.1.2 Aerodynamic lens (ADL)

After passing the GPD, the entire sampling flow enters an aerodynamic lens (ADL) through a flow-limiting orifice (300 μ m). ADLs are commonly used to generate focused particle beams and their principle of operation has been described in detail by Liu et al. (1995) and Wang and McMurry (2006). The ADL consists of a relaxation chamber immediately downstream of the critical orifice, four lenses with decreasing diameters, three spacers between the lenses and two outlet lines. A coaxial sampling line collects the particle-enriched flow on the central axis of the ADL while the remaining gas-phase flow is stripped off laterally using a Varian TriScroll 600 pump (Agilent Inc.,

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Santa Clara, USA). The pressure at the outlet of the ADL is approximately 10 mbar. The maximum achievable enrichment factor is defined by the ratio between the ADL inlet flow (~755 sccm) and the flow in the coaxial outlet sampling line (~10 sccm) which is 75.5. The FluentTM software (ANSYS Inc., Canonsburg, USA) was used for ADL design and optimization.

The particle enrichment factor, i.e. the ratio between the particle mass concentration upstream and downstream of the ADL, was experimentally determined as follows. Particles were generated from AN, AS and dimethylaminium nitrate (DMAN), respectively, using a home-built nebulizer. A buffer vessel was installed downstream of the nebulizer for removing excess water droplets and for increasing signal stability. The sample was subsequently heated to 110 °C and passed through a Nafion[®] dryer before being introduced into the GPD. It was then passed through an additional Nafion[®] dryer to minimize any potential humidity bias in particle mass calculations. Subsequently, particles were size-selected in the 100 to 750 nm size range (50 to 100 nm scan steps in 2–3 min intervals) using a differential mobility analyzer (DMA, Leibniz-Institut für Troposphärenforschung e.V., Leipzig, Germany). The resulting monodisperse particle flow was delivered in parallel to the CPC and to the CHARON inlet. The following input parameters were used to derive the CPC mass concentration: AN (shape factor = 0.8, density = 1.72 g cm⁻³), AS (shape factor = 0.8, density = 1.77 g cm⁻³), DMAN (shape factor = 1.0, density = 1.20 g cm⁻³). Thermal decomposition of AN, AS and DMNA particles in the CHARON inlet (see 2.1.3) forms gas-phase ammonia and nitric acid, ammonia and sulfuric acid, and dimethylamine and nitric acid, respectively. The PTR-ToF-MS quantitatively detects ammonia and dimethylamine (see Sect. 2.1.4). The particle enrichment factor was calculated from the ratio between the average PTR-ToF-MS derived mass concentration and the average CPC-derived mass concentration in a given size interval.

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2.1.3 Thermodesorption unit (TDU)

A heating wire is used to heat the coaxial outlet sampling line downstream of the ADL to a defined temperature. For the experiments reported herein, we used a temperature of 150 °C but any temperature between 50 and 250 °C can be set. The effect of 5 different desorption temperatures will be evaluated in future studies. The heated tube (length: 40 cm, outer diameter: 6.35 mm) made of passivated stainless steel (Sulfinert®, Restek, Bellefonte, USA) is terminated by a flow-restricting orifice. Particle evaporation occurs in the gas-phase and on tube and orifice surfaces to which submicron particles rapidly diffuse at 10 mbar operating pressure and 150 °C operating temperature. 10 The TDU was empirically designed to ensure complete vaporization of submicron AS particles.

2.1.4 Proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS)

A heated passivated stainless steel capillary (length: 30 cm, outer diameter: 3.175 mm, material: Sulfinert®) was used to couple the CHARON inlet to a recently developed proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) (Müller et al., 2014). The basics of PTR-MS have been described in great detail elsewhere (de Gouw and Warneke, 2007). Sampling gas is continuously flushed through a low-pressure drift cell (2–4 mbar) where externally generated hydronium ions (H_3O^+) unselectively transfer a proton to most organic analytes (except small alkanes and alkenes) 15 and a few inorganic compounds such as ammonia. Protonated analytes are subsequently detected by a quadrupole or time-of-flight mass spectrometer. The main advantages of the PTR-MS method in the context of aerosol analysis are: 20

1. PTR-MS detects a broad spectrum of organic molecules including ring-structured pure hydrocarbons and functionalized hydrocarbons which are important target analytes in the aerosol,

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2. PTR-MS response factors for different organic analytes typically vary only by $\pm 30\%$ which allows for a quantitative analysis even without external calibration standard.

The main disadvantages of the PTR-MS method in the context of aerosol analysis are:

5 1. one-dimensional mass spectrometric analysis, even at high mass resolving power, does not allow to differentiate between isomeric species,

2. protonation of a functional group (e.g. $-\text{OH}$ or $-\text{ONO}_2$) often results in the ejection of the respective group (via H_2O or HNO_3 loss, respectively) from the analyte ion which complicates mass spectral interpretation.

10 The instrument used for the study presented herein was described in great detail by Müller et al. (2014). It was operated at $E/N = 100 \text{ Td}$, E being the electric field strength and N the buffer gas density ($1 \text{ Td} = 10^{-17} \text{ V cm}^2$). The drift tube was kept at 120°C . The used instrument has a relatively low mass resolving power ($m/\Delta m \sim 1000$). Its acetone response factor is $\sim 125 \text{ cps ppbV}^{-1}$. The 2σ -detection limit of the instrument

15 is in the 50 to 80 pptV range for m/z signals above $m/z 70$ and a 1 s signal integration time.

The instrumental response factor for ammonia was determined experimentally in a previous study (Müller et al., 2014). The instrumental response factor for dimethylamine was derived from ion-molecule collision theory following the procedure described by Cappellin et al. (2012).

2.1.5 Particulate phase, gas-phase and instrument zero measurements

We used different inlet configurations to measure the particulate phase of the aerosol, the instrumental background and the gas-phase component of the aerosol. The PTR-ToF-MS instrument equipped with the CHARON inlet as shown in Fig. 1 (i.e. including GPD, ADL and TDU) measures the concentration and chemical composition of the particulate phase of the aerosol. The instrumental background is measured by placing

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a HEPA filter (HEPA-CAP 75; GE Healthcare UK Limited, Buckinghamshire, UK) in front of the CHARON inlet. The gas-phase component of the aerosol is measured by directly sampling analyte air via a submicron particulate filter.

2.2 Laboratory experiments

5 Two proof-of-principle studies were carried out for demonstrating the analytical potential of our novel instrumental set-up. The CHARON inlet was used to sample volatile and semi-volatile species generated from the reaction of limonene with ozone in an indoor environment and to measure sub-micron particles from mainstream cigarette smoke.

10 2.2.1 Indoor SOA from the reaction of ozone with limonene

Limonene (97 %, Sigma-Aldrich) and ozone were released in a 36 m^3 room to generate a particle steady-state mass concentration of $47\text{ }\mu\text{g m}^{-3}$ (single-modal distribution centered at 165 nm). Ozone was generated via a UV-lamp flushed with pure oxygen. Room air was monitored with a differential mobility analyzer (DMA, Leibniz-Institut für 15 Troposphärenforschung e.V., Leipzig, Germany) coupled to a TSI 3772 condensation particle counter (TSI Inc., Shoreview, USA). The following input parameters were used to derive the CPC mass concentration: shape factor = 0.8, density = 0.84 g cm^{-3} . Room air was also monitored by PTR-ToF-MS in the inlet configuration described in Sect. 2.1.5. The PTR-TOF Data Analyzer software was used for data analysis (Müller 20 et al., 2013).

2.2.2 Particles in mainstream cigarette smoke

A cigarette was mounted with its filter onto a stainless steel tube and a 65 sccm flow of air was continuously drawn through the cigarette. The outflow was diluted by a factor of 10 with catalytically cleaned (Pt/Pd, $325\text{ }^\circ\text{C}$) laboratory air and subsequently fed to the CHARON inlet.

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3 Results

3.1 GPD characterization

3.1.1 Gas-phase removal efficiency

The GPD removed 0 to 30 ppbV levels of gas-phase methanol, acetonitrile, acetaldehyde, acetone, isoprene, methylethylketone, benzene, toluene, xylene, 1,3,5-trimethylbenzene and α -pinene with an efficiency $> 99.999\%$. The GPD was regenerated on a monthly basis by baking it at 120 °C for 8 h under a stream of catalytically cleaned (Pt/Pd, 325 °C) laboratory air. No saturation or breakthrough was observed during one month of laboratory operation. We also observed that the GPD efficiently removes gas-phase ammonia at typical indoor levels (single to double digit ppb levels).

3.1.2 Particle transmission efficiency

The transmission efficiency of the GPD for size-selected particles generated from AN, AS, GA and MG, respectively, is displayed in Fig. 2. Particles with a mobility diameter of less than 50 nm are poorly transmitted (< 20 %) as they rapidly diffuse to the GPD surfaces. Particle transmission steeply increases in the 50 to 100 nm size range. The transmission efficiency for 100 nm particles is 75–80 %. About 90 % transmission efficiency is achieved for particles in the 200 to 750 nm mobility diameter range. The data shown in Fig. 2 suggest that the transmission efficiencies for particles of different chemical composition are very similar. The observed data scatter is mostly caused by variations in the particle load onto the GPD when we sequentially measured upstream and downstream of the device.

3.2 ADL characterization

The ADL enrichment factor for AN, AS and DMAN particles in the 200 to 750 nm size range is shown in Fig. 3. The data collected for particles below 200 nm were too

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scattered to report reliable numbers. The average particle enrichment factor calculated from the data shown in Fig. 3 is 25.6 which is a factor of 3 lower than the theoretical optimum. During initial testing we observed an enrichment factor of 73 which, however, degraded over time to reach a stable level of ~ 25 . This was most likely due to particle deposition at and behind the initial critical orifice. We are currently improving the design of the ADL critical orifice and the relaxation region. The lower DMAN values may be explained by the fact that we used a lower particle drying temperature ($80\text{ }^{\circ}\text{C}$) (see Sect. 2.1.2) and thus had a larger contribution of water to the particle mass observed by the CPC.

10 3.3 Indoor SOA from limonene ozonolysis

We used the CHARON inlet to sample indoor SOA ($22.3\text{ }\mu\text{g m}^{-3}$ above 150 nm diameter, i.e. where the CHARON inlet works efficiently) generated from the reaction of ozone with limonene. Figure 4 shows the obtained PTR-ToF-MS mass scan which includes 247 m/z signals in the m/z 33 to m/z 250 mass range. All signals were converted into $\mu\text{g m}^{-3}$ using the observed ionic molecular weight (i.e. loss of neutral fragments was not considered) and using the instrumental response factor for acetone (acetone-equivalents). At the current state of knowledge, this should be considered as a tentative quantification. The highest signals arise from $\text{C}_2\text{H}_3\text{O}^+$ (m/z 43.02) ions, $\text{C}_2\text{H}_5\text{O}_2^+$ (m/z 61.04) ions and $\text{C}_{10}\text{H}_{17}\text{O}^+$ (m/z 153.12) ions, the latter clearly arising from oxidation of limonene. At this stage we refrain from making any chemical assignments or giving any further interpretations which we consider to be out of the scope of this paper. The mass spectrum is shown to demonstrate that the CHARON inlet set-up can indeed be used for generating on-line and real-time PTR-TOF-MS mass spectra of SOA at ambient or near-ambient levels.

25 The total detected mass concentration derived from the observed signals (in acetone-equivalents) is $375\text{ }\mu\text{g m}^{-3}$. This converts into a sampled concentration of $17.5\text{ }\mu\text{g m}^{-3}$ assuming an 86 % particle transmission efficiency and a 25-fold particle enrichment for particles larger than 150 nm . Although this is only a coarse estimate,

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the derived mass concentration is in good agreement (–22 %) with the CPC-derived value confirming that our set-up quantitatively detects SOA. Our PTR-ToF-MS analyzer has a relatively low mass resolving power and sensitivity. A high sensitivity and high mass resolution PTR-ToF-MS instrument (Sulzer et al., 2014) coupled to a CHARON inlet will generate abundant quasi-molecular ion signals combined with highly accurate m/z information. This will significantly improve our capability of detecting specific target compounds on-line. It will also generate valuable data sets for improving elemental (e.g. O:C ratio) and chemometric analyses.

We also used the inlet set-up described in paragraph 2.1.5 to measure both the particulate and the gas-phase component of the aerosol. Figure 5 shows the observed concentrations (in acetone-equivalents, except gas-phase m/z 137.13) of four selected signals: limonene ($C_{10}H_{17}^+$) detected at m/z 137.13, and the three limonene oxidation products $C_{10}H_{17}O_1^+$, $C_{10}H_{17}O_2^+$ and $C_{10}H_{17}O_3^+$ detected at m/z 153.12, m/z 169.15 and m/z 185.16, respectively. The mass axis was not calibrated above m/z 137.13 which explains the relatively poor mass accuracy of the latter two signals. As expected, limonene is exclusively observed in the gas phase. The small signal observed in the particulate phase stems from an interfering compound at m/z 137. During instrument zeroing, the signal slowly decreased to instrumental background levels indicating that it stems from a “sticky” compound and not from limonene. The singly oxygenated product, $C_{10}H_{17}O_1^+$, and the doubly oxygenated product, $C_{10}H_{17}O_2^+$, show an increasing partitioning into the particle phase while the triply oxygenated product, $C_{10}H_{17}O_3^+$, is exclusively found in the particulate phase (gas-phase concentration below detection limit). The particulate phase detection limit for individual compounds is a factor of 10–20 lower than the lowest concentrations shown in Fig. 5, i.e. in the range between 10 and 20 ng m^{-3} . We again refrain from going into further details or analyses. Figure 5 is shown to demonstrate the analytical power of the novel instrumentation to study the partitioning of organic compounds between the gas and the particulate phase.

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3.4 Organic particulate matter from main-stream cigarette smoke

In another proof-of-principle study we used the CHARON inlet to sample 10 fold diluted mainstream cigarette smoke. Figure 6 shows the obtained PTR-ToF-MS mass scan with a prominent peak at m/z 163.12 ($C_{10}H_{14}N_2^+$) corresponding to protonated nicotine.

5 It obviously still remains a challenge to interpret the mass spectrum and assign the plethora of peaks to specific compounds. This study does, however, demonstrate that our novel CHARON inlet can be used to sample particulates at their source and that abundant quasi-molecular ion signals will make source characterization easier.

4 Conclusions and outlook

10 We have shown how our novel CHARON inlet efficiently strips off gas-phase analytes (> 99.999 %), enriches the particle concentration by a factor of 25 and subsequently vaporizes the particles for analysis by PTR-ToF-MS. We have demonstrated in two proof-of-principle studies that the novel inlet can be used for true on-line analysis of particles, both primarily emitted and secondarily generated, in the of 150 to 1000 nm 15 size range. A promising future application is the study of the partitioning of organic compounds between the gas and the particulate phase. We have also shown that PTR-ToF-MS analysis generates abundant quasi-molecular ions from organic analytes. Individual compound identification will still remain a challenge but chemometrics, elemental analysis (e.g. O : C ratio) and tracer detection will strongly benefit from our new 20 experimental approach.

We are currently developing a new CHARON prototype with a 2 to 3-fold improved particle transmission efficiency. Coupling to a high sensitivity high mass resolution PTR-TOF instrument will result in an even more powerful instrument for on-line particle analysis.

25 *Acknowledgements.* We thank Simon Kasseroler for machining parts of the CHARON inlet. This work is funded through the PIMMS ITN, which is supported by the European Commission's

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7th Framework Programme under grant agreement number 287382. The PTR-ToF-MS instrument used for this study was funded through the Austrian Space Applications Programme (ASAP 8, #833451). ASAP is sponsored by the Austrian Ministry for Transport, Innovation and Technology (BMVIT) and administered by the Aeronautics and Space Agency (ALR) of the Austrian Research Promotion Agency (FFG).

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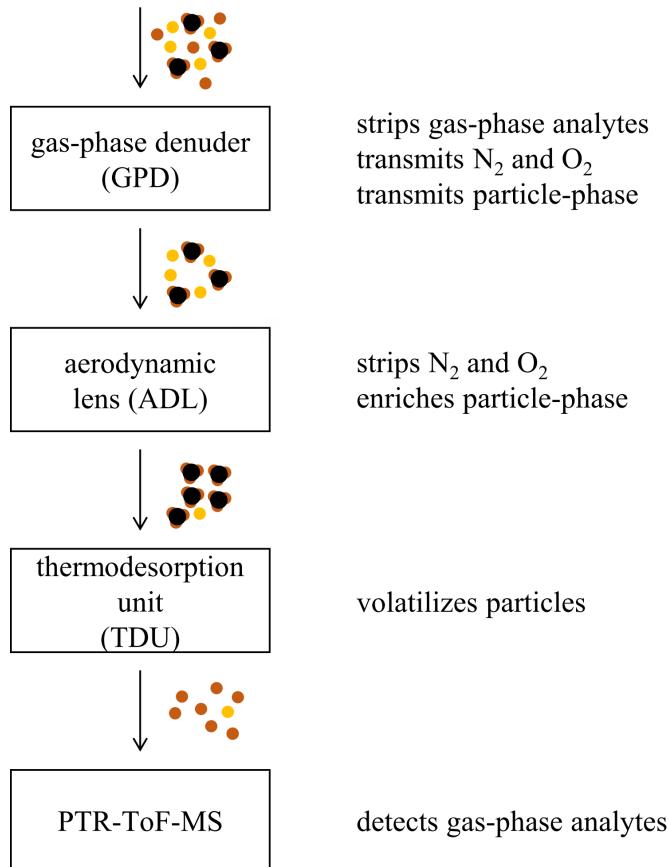
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**Figure 1.** Modules and working principle of the novel CHARON inlet.

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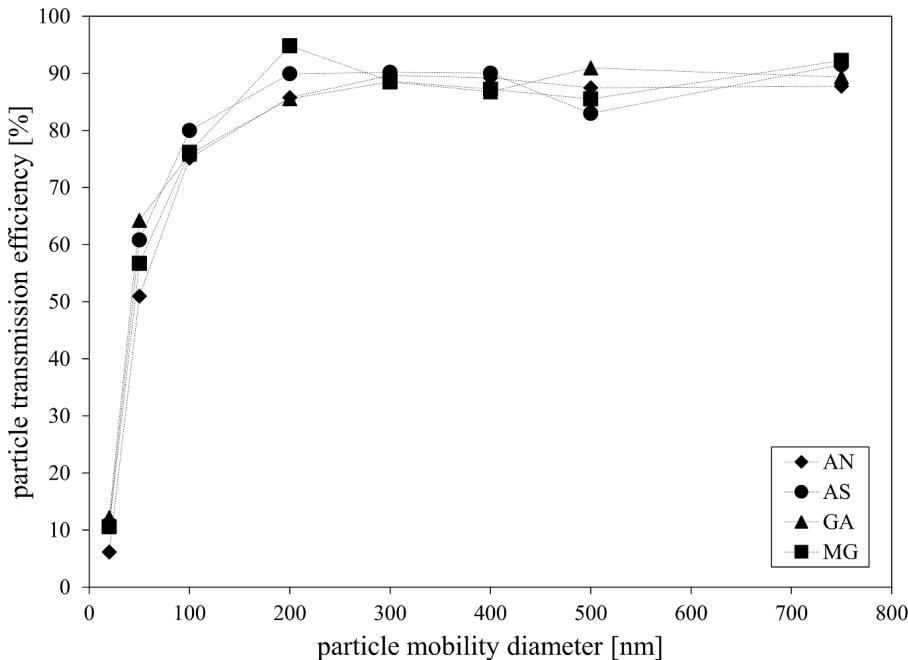


Figure 2. Transmission efficiency of the GPD for size-selected particles generated from ammonium nitrate (AN), ammonium sulfate (AS), glutaric acid (GA) and methyl glyoxal (MG).

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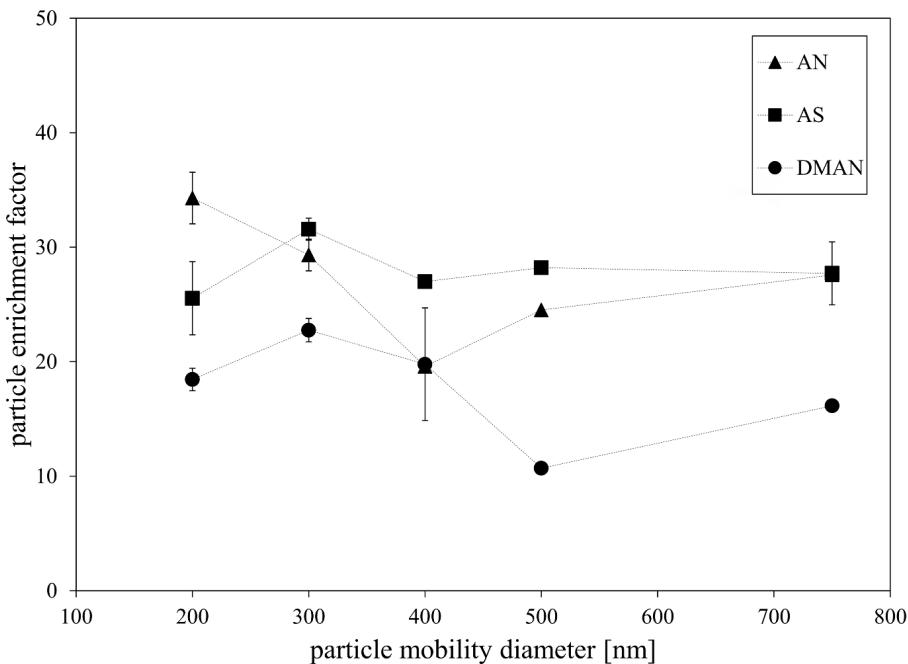


Figure 3. Enrichment factor of the ADL for ammonium nitrate (AN), ammonium sulphate (AS) and dimethylaminium nitrate (DMAN) particles in the 200 to 750 nm size range.

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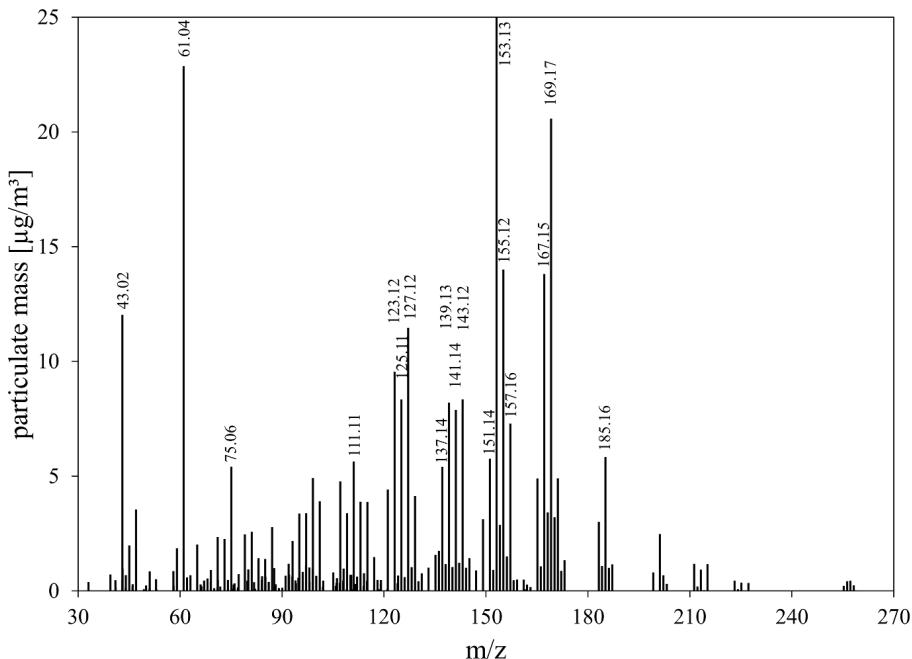


Figure 4. PTR-ToF-MS mass scan obtained from ozone-limonene SOA sampled with the CHARON inlet. Note that the particulate mass is enriched by a factor ~ 25 .

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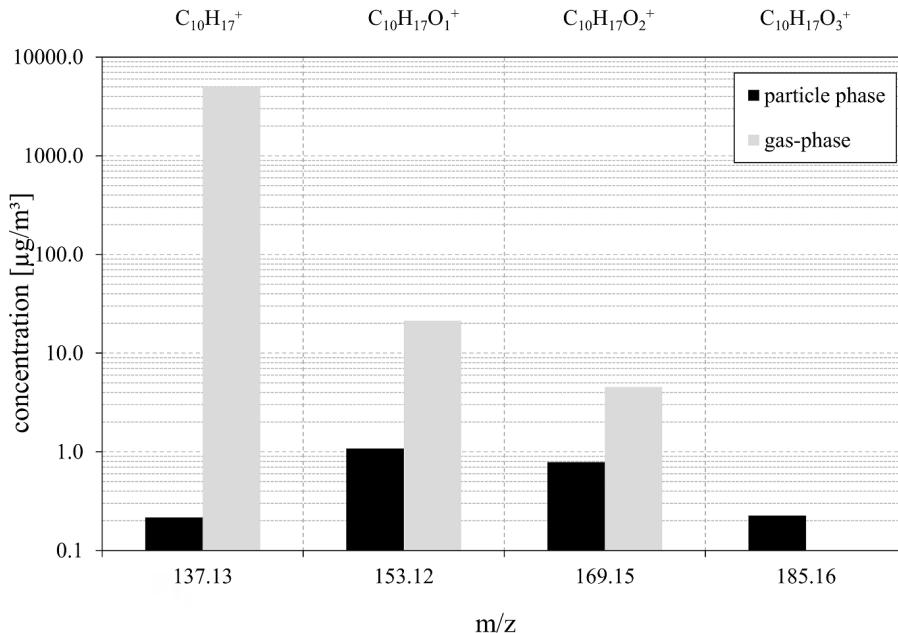


Figure 5. $\text{C}_{10}\text{H}_{17}^+$, $\text{C}_{10}\text{H}_{17}\text{O}_1^+$, $\text{C}_{10}\text{H}_{17}\text{O}_2^+$ and $\text{C}_{10}\text{H}_{17}\text{O}_3^+$ signals (in acetone-equivalents, except gas-phase $\text{C}_{10}\text{H}_{17}^+$) as observed in the gas-phase and particulate phase. Partitioning into the particle phase increases with the degree of oxidation.

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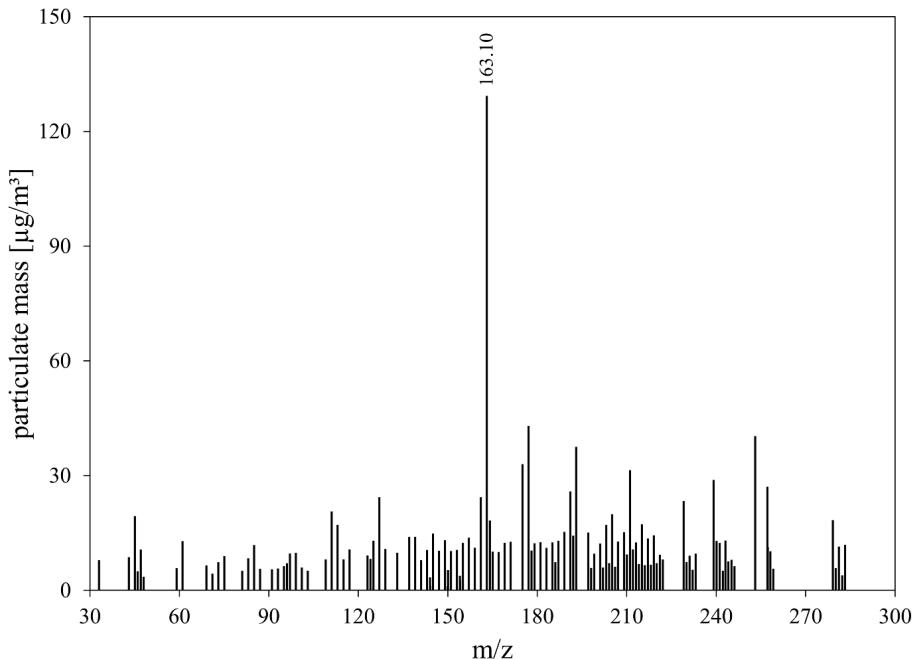


Figure 6. PTR-ToF-MS mass scan obtained when 10 fold diluted mainstream cigarette smoke was sampled through the CHARON inlet. The prominent peak at m/z 163.12 ($C_{10}H_{14}N_2^+$) corresponds to protonated nicotine. Note that the particulate mass is enriched by a factor ~ 25 .