

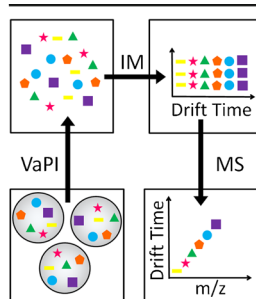
Aerosol Vacuum-Assisted Plasma Ionization (Aero-VaPI) Coupled to Ion Mobility-Mass Spectrometry

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Abstract. In this communication, we report on the real-time analysis of organic aerosol particles by Vacuum-assisted Plasma Ionization-Mass Spectrometry (Aero-VaPI-MS) using a home-built VaPI ion source coupled to a Synapt G2-S HDMS ion mobility-mass spectrometry (IM-MS) system. Standards of organic molecules of interest in prebiotic chemistry were used to generate aerosols. Monocaprin and decanoic acid aerosol particles were successfully detected in both the positive and negative ion modes, respectively. A complex aerosol mixture of different sizes of polymers of L-malic acid was also examined through ion mobility (IM) separations, resulting in the detection of polymers of up to eight monomeric units. This noncommercial plasma ion source is proposed as a low cost alternative to other plasma

ionization platforms used for aerosol analysis, and a higher-performance alternative to more traditional aerosol mass spectrometers. VaPI provides robust online ionization of organics in aerosols without extensive ion activation, with the coupling to IM-MS providing higher peak capacity and excellent mass accuracy.

Keywords: Plasma ionization, Aerosol analysis, Prebiotic chemistry

Received: 15 August 2017/Revised: 8 December 2017/Accepted: 19 December 2017/Published Online: 5 February 2018

Introduction

Few mass spectrometry (MS) platforms are available for aerosol particle analysis that have both high temporal and high mass resolution [1]. Current online analysis methods suffer from limitations such as insufficient peak capacity, limited mass accuracy, unpredictable adduct formation, extensive ion activation, and slow response [2–8]. Developing soft aerosol ion sources that can be coupled to most high resolution mass spectrometers would thus enable more robust molecular identification of organics from aerosol particles, yielding more easily interpretable insights into aerosol chemistry mechanisms and composition.

One of the most commonly used mass spectrometers in the aerosol field is the high-resolution time-of-flight aerosol mass spectrometer (aerosol HR-ToF-AMS) [3]. It utilizes electron ionization, yielding complex fragment mass spectra absent of

molecular ions, hindering the ability to easily track intact species [1]. Later, a Filter Inlet for Gases and AEROSols (FIGAERO) was developed and coupled to a high-resolution time-of-flight chemical ionization-mass spectrometer (aerosol HRTof-CIMS) [6], which relies on filter collection of particles followed by thermodesorption prior to ionization. Because of the finite filter collection time, aerosol particle measurements with the FIGAERO-HRTof-CIMS lack high temporal resolution, and are susceptible to on-filter reactions causing artifacts during sampling and measurement [9]. Ambient ionization techniques such as extractive electrospray ionization [8], direct analysis in real time (DART) [4], flowing atmospheric-pressure afterglow (FAPA) [2], and droplet assisted inlet ionization [5] have also been used for improving aerosol analysis. However, these MS techniques can still suffer from extraction efficiency limitations, ion suppression, incomplete aerosol sampling, high background, or oxidation reactions. More recently, an aerosol flowing atmospheric-pressure afterglow (AeroFAPA) ion source was developed to detect organic compounds in aerosols [10]. Also, Zenobi et al. developed a dielectric barrier discharge plasma technique [11] used for studying offline-vaporized liquid or solid samples [12], and for real-time breath analysis [13]. Further enhancements to aerosol MS

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s13361-017-1872-z>) contains supplementary material, which is available to authorized users.

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analysis have been achieved through the coupling of MS to ion mobility (IM), enabling the separation of isobaric species in aerosol mixtures [14].

In this work, we present a home-built Vacuum-assisted Plasma Ionization (VaPI) ion source for aerosols (Aero-VaPI) coupled to a Waters Synapt G2-S HDMS Ion Mobility-Mass Spectrometry (IM-MS) system. The Aero-VaPI ion source is an atmospheric pressure glow discharge plasma that is interconnected with the inlet of an IM-mass spectrometer. The vacuum pull from the mass spectrometer induces a Venturi effect at a sampling tee, enabling the capture and entrainment of the sample aerosol into the metastable atom population of the plasma before going into the mass spectrometer. This arrangement offers advantages such as a cost effective and simple assembly, efficient ionization, aerodynamic Venturi sample entrainment, and more straightforward molecular identification [15, 16]. The applicability of the Aero-VaPI-MS system to particle analysis in a prebiotic chemistry context is presented.

Experimental

Materials

Chemical standards of monocaprin (1-monodecanoylglycerol) and decanoic acid (each $\geq 99\%$) were purchased from Sigma Aldrich, and L-malic acid (99%) from Chem-Impex International. Aerosol samples of monocaprin and decanoic acid were separately generated from aqueous and methanolic ~ 2 mM solutions with a TSI 3076 Constant Output Atomizer at 2 standard liters per minute (SLM) and measured with Aero-VaPI-MS in the positive and negative ion modes, respectively. Poly-L-malic acid was synthesized via heated dry-down reactions previously described by Forsythe et al. (2015) [17], without any purification. An L-malic acid-equivalent 0.50 mM solution of poly-L-malic acid was analyzed with ESI-IM-MS in the negative mode. A nebulizer (SLT8900H, Salter Labs® 8900 Series Small Volume Jet Nebulizer from Medline Inc.) was used to generate aerosols at 6 SLM of the same poly-L-malic acid solution and was measured with Aero-VaPI-IM-MS in the negative ion mode. The nebulizer offered an air jet of lower pressure (10 psi versus 34 psi of N_2), producing a more stable signal for L-malic acid polymers during particle generation. Aerosols were not size-selected prior to mass spectrometry analysis.

Instrumentation

The Aero-VaPI ion source (Figure 1) consists of an enclosed system with an AC-powered point-to-plane glow discharge operating at near atmospheric pressure that intersects an aerosol sample stream suctioned by a Venturi sampling tee. Ions are transferred from the Venturi sampling tee into a Synapt G2-S HDMS (Waters, IMS-TOF) mass spectrometer. The power is supplied by a high voltage plasma generator with a sine wave-form (T&C Power Conversion Inc.; Model AG 0201-HV,

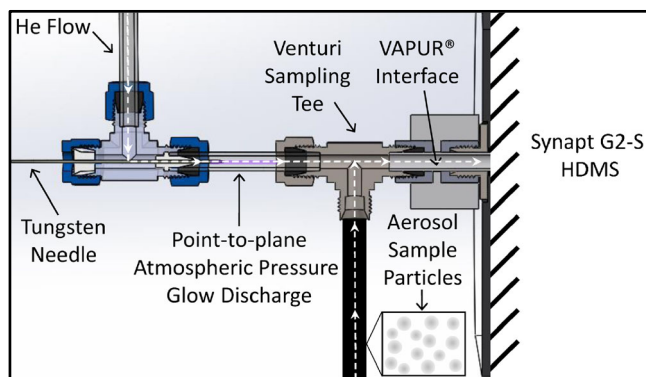


Figure 1. Cross-sectional view of the home-built Aero-VaPI ion source coupled to IM-MS via a VAPUR® interface that had its side vacuum port blocked, serving only as a mechanical adapter

Rochester, NY) with a frequency adjustment of 6.68 and an rf adjustment of 1.34. The discharge frequency and voltage were 370 kHz at 2.9 kV peak to peak, respectively. The VaPI source is mounted on a VAPUR DART interface that had its vacuum port blocked, serving only as a mechanical support for the source, but not providing additional pumping. Analytes within aerosol particles are desorbed by collisions with heated plasma gas within the sampling tee and chemically-ionized through proton transfer reactions with reactive ion species generated by the plasma. The He (UHP300 Airgas) flow, AC power, and temperature of the VaPI sampling tee were optimized to 0.40 SLM in order to maximize the metastable population without putting too much strain on the turbo pumps, 10.0 W forward and 0 W reverse applied to a tungsten needle, and 40 °C, to achieve thermal equilibrium while maintaining the lowest temperature possible to minimize fragmentation and potential z reactions, respectively. The electrode gap from the point of the tungsten tip to the inside of the grounded sampling tee (where the metal is first exposed) is 3 cm. Flows were measured with an Alicat Scientific mass flow meter (M-5SLPM-D, Tucson, AZ). The Venturi sampling tee was heated by heating tape (BriskHeat heating cord Model HTC451006) that was controlled by a temperature controller (BriskHeat; Model SDC120JF-A).

Results and Discussion

Our interest in aerosols stems from our research in the prebiotic de novo synthesis of proto-biopolymers in an origins of life scenario. It has been shown that aerosols can act as chemical reactors in the prebiotic formation of such polymeric species [18–21]. Dobson et al., for example, have proposed that by their ability to concentrate molecules, aerosols could have served as efficient prebiotic chemical reactors for the first protocellular structures [19]. Condensation reactions are important in prebiotic chemistry, and include formation of lipids [18] and far-from-equilibrium polymers [22]. These reactions can be favored in aerosols, where water loss is driven by evaporation. Trainer et al. have hypothesized that organic

species that have functionalities of interest to prebiotic chemistry are more likely to exist in the aerosol phase [23]. Previous studies have focused on amino acid or tholin formation [24, 25], but only few have investigated the molecular composition of products generated via aerosols [26].

As a first experiment, Aero-VaPI-MS was tested for aerosol composition determination in the positive and negative modes with monocaprin and decanoic acid aerosols (Figures S1, S2), respectively. Bulk condensation reactions of glycerol and decanoic acid to form monocaprin have been studied by Apel and Deamer as a route for the production of a more evolved amphiphile leading to proto-cellular membranous structures [18]. In the positive mode monocaprin was detected as the

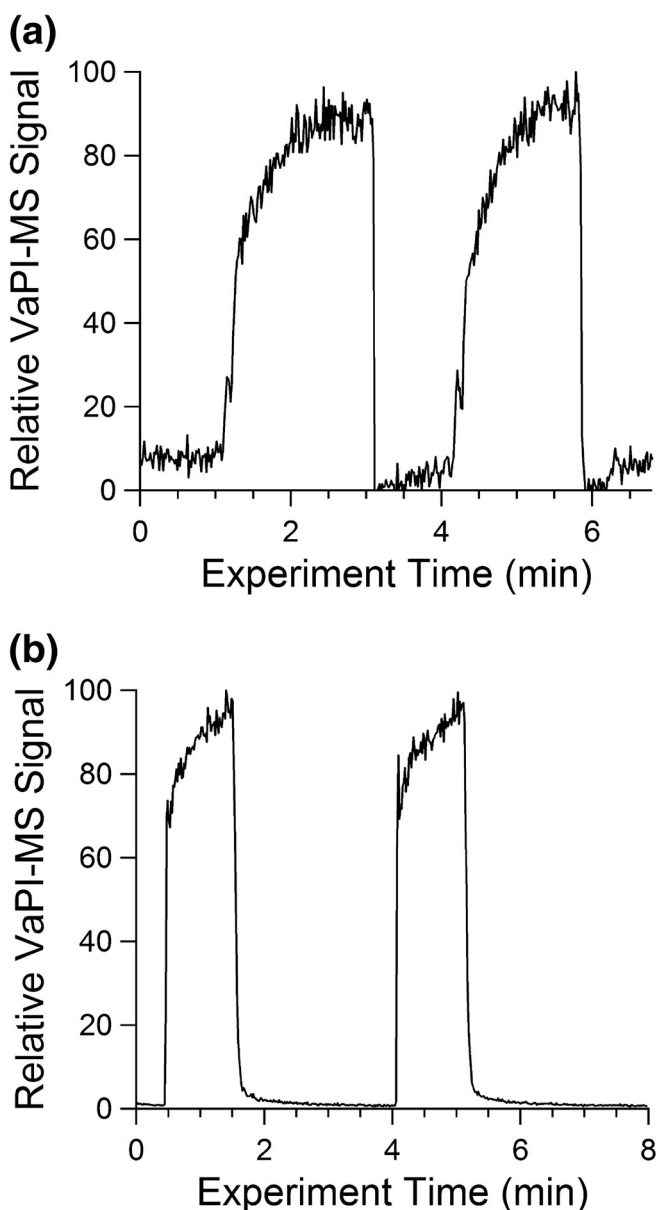


Figure 2. Aero-VaPI-MS signals for aerosol particles consisting of (a) monocaprin in (+)-mode; $[M - H_2O + H]^+$ monitored at m/z 229, from protonation-induced water loss (b) decanoic acid in (-)-mode; $[M - H]^-$ monitored at m/z 171

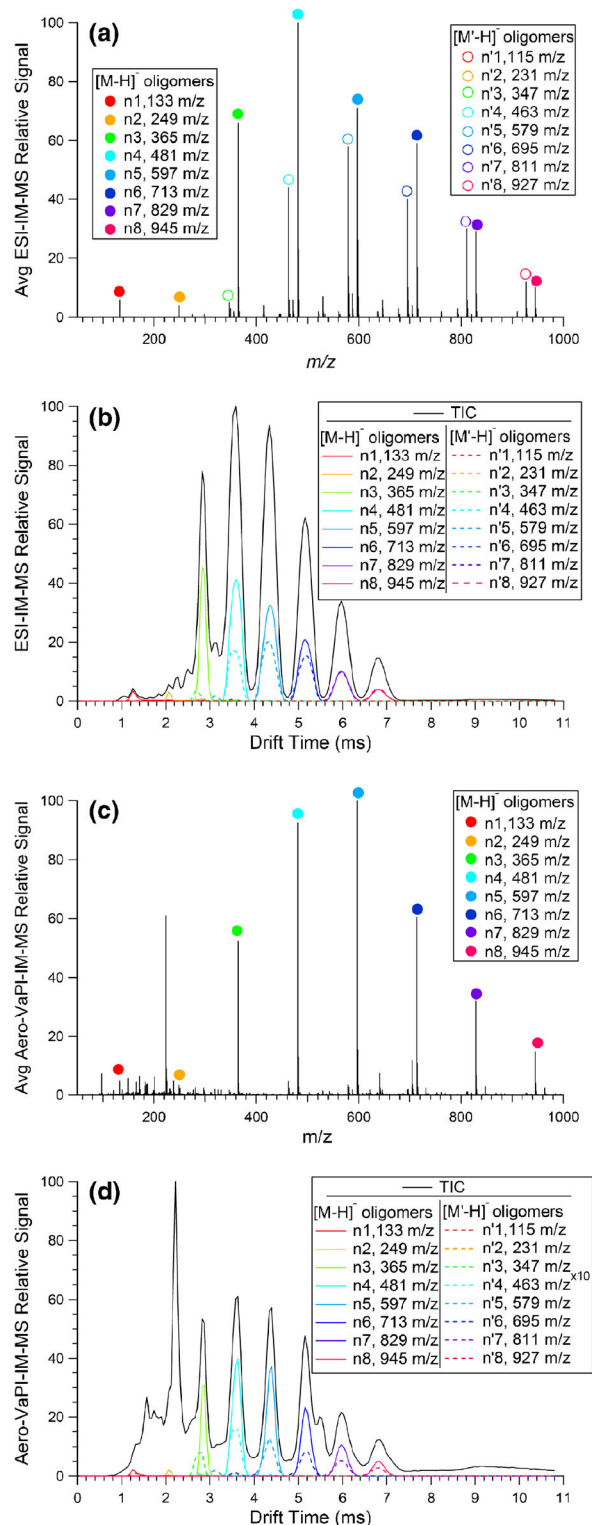


Figure 3. Negative ion mode detection of poly-L-malic acid (a) ESI IM-MS averaged mass spectrum, (b) ESI IM-MS ion mobility arrival time distribution, (c) Aero-VaPI IM-MS averaged mass spectrum, and (d) Aero-VaPI IM-MS ion mobility arrival time distribution. Oligomer $[M - H]^-$ (solid circles) and $[M' - H]^-$ (open circles) signals are denoted by markers colored by the number of monomer units. The ion mobility arrival time distribution signals are colored similarly

$[M + H]^+$, as well as $[M - H_2O + H]^+$ resulting from protonation-induced water loss (Figure 2a). The deprotonated ion of decanoic acid, $[M - H]^-$, was observed in the negative mode, as seen in Figure 2b. In these experiments, the atomizer was sequentially turned on and off to verify that signal returned to baseline following introduction of the analyte. The rise time of the signals for these aerosols was a function of the aerosol equilibration time in the tubing lines. It is expected that during application of this instrumentation to an aerosol reaction system, lines would be equilibrated at the start of the experiment and would continuously sample from the aerosol system, so no subsequent re-equilibration would be needed. It was observed that the signal dipped slightly below the original baseline following each injection event, likely due to a temporary pressure imbalance. Once the baseline was recovered, the next aerosol atomization event was triggered.

Another molecule of interest in prebiotic chemistry is malic acid, being part of both the Calvin and citric acid cycles. Mamajanov et al. have studied the esterification of malic acid under wet/dry batch cycling conditions, proposing a ratcheting mechanism for the formation of far-from-equilibrium polymers [22]. Malic acid has also been proposed as an intermediate in the formation of proto-peptides [27]. Here, we used poly-L-malic acid aerosol as a test for Aero-VaPI-MS detection of products of prebiotic condensation polymerization reactions in aerosols. To this purpose, a solution of poly-L-malic acid was first analyzed by electrospray (ESI) IM-MS (Figure 3a, b). All oligomers were well separated with IM and detected within a drift time of 8 ms. The average ESI IM-MS mass spectrum (Figure 3a) showed $[M - H]^-$ ions for oligomers with chain lengths ranging from 1 to 8, together with their corresponding water loss ($\Delta m/z = 18$) species. Ions with two water losses were also observed, ($\Delta m/z = 36$), though less abundant (Figure S3). The single water loss ion species, denoted as $[M - H]^-$, contributed significantly to the total ion count, as seen in the ion mobility arrival time distribution (Figure 3b). These neutral water losses are common in ESI-MS of acids, occurring by alcohol dehydration or cyclic anhydride formation between adjacent carboxyl groups [28].

Aero-VaPI-IM-MS spectral data for poly-L-malic acid aerosols (Figure 3c,d, and Figure S4.) were very similar to that obtained by ESI IM-MS, with the interesting difference that the water loss signals were much less abundant than with ESI. It was necessary to multiply the $[M - H]^-$ ion signals by a factor of 10 in order to better observe their IM distribution (Figure 3d). As expected, IM enabled the separation of some isobaric species, as discussed in the Supporting Information, Figure S5.

Oligomers did not represent the majority of the total ion signal in some drift time regions, such as the region between 1–2 ms and the shoulder at 5.5 ms. The first arrival time distribution region (1–2 ms) was broad and populated mostly by small ions such as water loss ions $C_4H_1O_3^-$ and $C_4H_3O_4^-$ at m/z 97 and 115, which may be dehydrated forms of malic acid such as maleic anhydride and maleic acid, respectively (Figure S6). Oxidized species possibly arising from these ions, such as

$C_4H_5O_6^-$, $C_4H_6O_6^-$, $C_4H_5O_7^-$, and $C_4H_7O_8^-$, were also observed with corresponding m/z values of 149, 150, 165, and 183. The presence of these smaller ionic species suggests that oligomer ion-molecule reactions do occur within the Aero-VaPI source due to the higher reactivity of plasma sources relative to ESI [29]. VaPI plasma ionization is expected to have an abundance of high energy charge transfer species, as there is no grid electrode to filter them out from the plasma, as in DART [30]. Further experiments are required to investigate these and other phenomena related to ion generation mechanisms in VaPI.

Conclusions

The Aero-VaPI ion source is cost effective, has minimal assembly, provides softer ionization than with standard aerosol mass spectrometers, and, when coupled to IM-MS, can rapidly separate species in aerosol mixtures for the molecular detection of organic analytes in particles. Although organics may undergo a small amount of activation in the VaPI source, no sample handling is required with the Aero-VaPI-MS system, avoiding solvent-dependent extraction efficiency limitations. Initial results suggest that this technique can be applied to monitor aerosol chemistry in real-time, including prebiotic condensation reactions. Future studies of new prebiotic aerosol chemistry with Aero-VaPI-MS are expected to provide insight into the mechanisms of de novo proto-biopolymer formation.

Acknowledgment

This work was jointly supported by NSF and the NASA Astrobiology Program, under the NSF Center for Chemical Evolution, CHE-1004570.

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