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A method is presented in which ions are generated and manipulated in the ambient environment using polymeric electrodes produced with a consumer-grade 3D printer. The ability to focus, separate, react, and detect ions in the ambient environment is demonstrated and the data agree well with simulated ion behaviour.

Mass spectrometry (MS) is arguably one of the most widely used scientific tools with applications ranging from complex mixture analysis to molecular biology and even large-scale purification and materials preparation. One challenge faced in all of these applications is the low pressure environment inherent to MS analysis. The development of atmospheric pressure interfaces (APIs) alleviated the vacuum incompatibility of many samples and paved the way for ambient ionization methods in which a sample is directly interrogated with little-to-no sample preparation. While ambient ionization provides a means of sampling, the transfer, the focusing and analysis of these ions must still be done under vacuum. As vacuum pumps are cumbersome both physically and electrically, this presents a challenge in the miniaturization of MS systems and their practical use in potential application areas due to the size and power requirements of commercially available MS platforms.

Ion mobility spectrometry (IMS) is another method commonly used to analyze gas-phase ions and is often coupled to MS platforms to provide another dimension of separation. In IMS ions are separated based on their interaction with a background gas in combination with electric fields. IMS instruments are typically operated at pressures much higher than that of an MS system, including atmospheric pressure, yet all rely on the establishment of a laminar gas flow along the ion path.

In their current forms, both MS and IMS share commonalities in regards to the creation of ions in the ambient environment and their subsequent transfer into an analysis region in which pressure, temperature, and humidity are well regulated. The spatial control of ions under vacuum is a mature subject and is employed in a wide range of instruments which includes MS and IMS systems as well as electron microscopes, particle accelerators, as well as a variety of surface analysis and modification methodologies. However, the control of ions at or near atmospheric pressure is much less developed, despite the rich chemistry accessible at these more manageable conditions. In recent years there has been a number of publications highlighting the unique reactivity of gaseous ions under ambient conditions and their use in the preparation of surfaces. The manipulation and control of these ions is crucial if they are to be utilized to full potential.

This work aims to perform operations of MS/IMS systems through a demonstration of ion generation, ion transfer/focusing, gas-phase ion/molecule reactions, ion separation, and subsequent ion detection all in the ambient environment using plastic electrodes produced via rapid prototyping. In some experiments the device is used to prepare ions for mass analysis in a mass spectrometer while in other cases it is used in a stand-alone fashion as a reactor/analysis system.

**Production and Focusing of Ions in Air**

One common method of producing gas phase ions for MS and IMS is electrospray ionization (ESI). ESI is based on the principle that upon desolvation, electrosprayed droplets produce ions of organic molecules with little-to-no fragmentation. Today, spray ionization is one of the most widely used techniques in MS and IMS workflows and is the basis for many ambient ionization sources including: desorption electrospray ionization (DESI), laser ablation electrospray ionization (LAESI), extractive electrospray ionization (ESEI), paper spray ionization (PS), etc. Low ionization efficiency, combined with the dispersive nature of ESI result in only a small fraction of ions created being subsequently sampled for analysis in MS experiments. This decreases analytical sensitivity and complicates product collection in preparative experiments such as ion soft landing.
While it is only ions that produce the signals measured in MS and IMS, the presence of adventitious neutrals can produce undesirable effects in both instances. Neutral species place a larger load on the vacuum system (notably evaporating solvent droplets) and may undergo reactions with the ions of interest to produce unexpected species that complicate analysis. Additionally, in the case of ion soft-landing, neutral impingement on the deposition surface negates the highly discriminatory nature of the ion selection prior to the surface collision.

In an attempt to address sensitivity and neutral transmission complications, a curved electrode system was constructed from a conductive polymer using a fused deposition modelling (FDM) 3D printer. The assembly consists of a cylindrical source electrode region (E\text{source}) with an inner diameter (ID) of 20 mm and a length of 30 mm, proceeded by 3 curved electrodes (E\text{a}) with an ID of 15 mm and a swept angle of 45 degrees around a 15 mm radius of curvature. All electrodes are separated by 3 mm with spacers printed in either acrylonitrile butadiene styrene (ABS) or polylactic acid (PLA). Dimensional drawings are provided in the electronic supplementary information (SI) figure S1. The electrode assembly (figure 1) serves to focus ions from a spray source to a well-defined region with the application of an appropriate potential gradient along the ion path. The device is shown in figure 1 interfaced with the inlet of a mass spectrometer along with a cutaway rendering with an overlay of simulated ion trajectories. A strong focusing effect is observed with the application of appropriate DC potentials to individual electrode components. This effect has been previously observed in experiments in which a spray was generated in an ellipsoidal cavity held at kV potentials in close proximity to a grounded surface. At atmospheric pressure, it is not computationally efficient to utilize traditional hard-sphere collision models as the mean free path in air is \(\sim67\) nm. Instead, the SDS algorithm calculates ion motion based on ion mobility and a simulated diffusion in the form of “jumps” in a random direction at each time step, the magnitude of which is determined based on collision statistics. A more detailed discussion of ion trajectory simulation at atmospheric pressure and details of simulation parameters used are included in the SI. The workflow from design to simulation was inherently simplified through the use of the SL toolkit included with SIMION. The SL toolkit allows the user to import geometry in the form of stereolithography (.stl) files to create potential array points which are the basis of the simulation environment in SIMION. Because .stl is the native file format accepted by most software packages to prepare files for 3D printing, the same files may be used for both electrode production and

**Figure 1**: 3D printed electrode assembly interfaced with inlet of MS (a); cutaway rendering of assembly with overlaid ion trajectories shown in red (b); Surface plot of electric field magnitude overlayed with electric field streamlines (green traces) originating in a 10 mm diameter sphere centered in \(E\text{source}\), 11 mm distant from the nanoESI spray tip (c). Electrodes are denoted in blue. Potentials applied to electrodes are identical to figure 2a and 2c.

Simulations of ion trajectories within the device were performed with SIMION 8.0 (Scientific Instrument Services) and the included statistical diffusion simulation (SDS) algorithm. At atmospheric pressure, it is not computationally efficient to utilize traditional hard-sphere collision models as the mean free path in air is \(\sim67\) nm. Instead, the SDS algorithm calculates ion motion based on ion mobility and a simulated diffusion in the form of “jumps” in a random direction at each time step, the magnitude of which is determined based on collision statistics. A more detailed discussion of ion trajectory simulation at atmospheric pressure and details of simulation parameters used are included in the SI. The workflow from design to simulation was inherently simplified through the use of the SL toolkit included with SIMION. The SL toolkit allows the user to import geometry in the form of stereolithography (.stl) files to create potential array points which are the basis of the simulation environment in SIMION. Because .stl is the native file format accepted by most software packages to prepare files for 3D printing, the same files may be used for both electrode production and

**Figure 2**: Experimental (a-b) and simulated (c-d) tetraalkylammonium ion intensity at deposition surface for different electrode potentials. In (a) and (c) potentials on electrodes \(E_1\), \(E_2\), and \(E_3\) were 2.90 kV, 2.60 kV, and 1.80 kV, respectively; In (b) and (d) potentials on electrodes \(E_1\), \(E_2\), and \(E_3\) were 2.95 kV, 2.12 kV, and 1.77 kV, respectively. In each case \(E\text{source}\) was set to 3.00 kV and spray potential was set at 4.65 kV.
Ion/molecule reactions

Ion/molecule reactions (IMR) have been shown to have useful analytical characteristics, especially in the case of structural elucidation. IMRs in the gas phase offer several benefits compared to their solution counterparts. Very little neutral reagent is required for an IMR and often the headspace vapour is sufficient to generate measurable product. Reaction rates and efficiencies are also inherently high for most IMRs, meaning that analytes in trace quantities will still form a detectable product. This is especially true for IMRs performed at atmospheric pressure in IMS instruments, as the number of collisions per second is dramatically increased in comparison to the same reaction performed in an ion trap under vacuum. However, the lack of straightforward identification of products in IMS generally requires the use of tandem IMS-MS instrumentation. Often, significant modification to MS instruments must be made in order to perform ion/molecule reactions, which can be costly and time-consuming. The coupling of IMS to MS instruments suffers from similar drawbacks.

As a proof of concept demonstration of an ion/molecule reaction performed with the plastic electrodes in air, protonated tert-butylamine and cyclohexylamine ions were generated by nanoESI from 10 ppm solutions in methanol and reacted with dimethyl methylphosphonate (DMMP) in the last region (E3) of the electrode system shown in figure 1. DMMP vapor was introduced by replacing the final electrode with an electrode containing a hole on the far side of the swept radius of curvature (figure S2a) and inserting a cotton swap saturated with a solution of 1000 µg/mL DMMP in methanol (figure 1a). The electrodes were positioned with a 3 axis moving stage such that the exiting ions were sampled with the API of an LTQ linear ion trap (Thermo).

When the ion beam exiting the electrode structure was precisely aligned with the inlet of the MS it was found that the signal recorded by the mass spectrometer was largely independent of the position of the nanoESI spray tip within Esource as the mass spectra and recorded intensity remained stable while adjusting the spray tip location. Mass spectra of the products of these two reactions sampled from the last electrode of the polymeric electrode assembly are shown in figure 3. Similar IMRs using analogs of DMMP have previously been demonstrated for the identification of amino functionalities in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. These reactions highlight the potential usefulness of ion manipulation outside the mass spectrometer in exploring ion/molecule reactions for functional group identification. The ability to perform and interrogate these reactions outside the MS may allow for a condition in which an ion separation is performed at atmospheric pressure after a reaction has taken place to identify the presence of a target compound in the analyte mixture.

Separation of ions in air

The separation of gas-phase ions is most commonly done based on their mass-to-charge ratio (m/z), in the case of MS, or on the basis of their interaction with a background gas in combination with electric fields as is done in IMS experiments. A vacuum is necessary in order to accomplish separation based on m/z, while a laminar flowing gas is used in the instance of an ion mobility separation.

In an effort to demonstrate a simplified separation of ions in air without the use of a vacuum or a flowing gas, pulsed voltages were employed with the electrode system as a means to inject ions into the curved ion path and effect a separation of tetraalkylammonium (TAA) cations. A solution of 10 µM each of tetrapropyl-, tetrabutyl-, tetrahexyl-, and tetradodecylammonium bromide in ACN was sprayed with a nanoESI emitter into Esource. The electrode assembly was modified to include an injection region immediately after Esource consisting of 2 stainless steel woven meshes separated by 3 mm (fig. S2b). A floated high voltage pulse (2530 V high, 2480 V low) was applied to the mesh directly after the source region with the second mesh held flush to the opening of the first curved electrode to facilitate electrical contact with E1 (figure S2b). A pulse width of 50 ms with a repetition rate of 1 Hz was used for ion injection. Potentials applied to the nanoESI electrode, Esource, E2, and E3 were 4.50 kV, 3.20 kV, 2.50 kV, 2.33 kV, and 1.45 kV, respectively. A simulation of the separation was performed under identical conditions with all ions originating in the space between the woven meshes. Consecutive scans of the ion trap (figure 4a) at a 10 Hz scan frequency show a modest separation of the TAA cations which agree well with the simulated data (figure 4b).
This proof-of-concept demonstration shows the ability to separate gas-phase ions in air and is meant to highlight a potential use of the 3D printed electrodes as a better resolved separation is surely possible through optimization of applied potentials, ion injection parameters, and electrode geometries.

Materials and Methods
Electrodes were printed at 200 µm layer height with an FDM 3D printer (Prusa i3v, Makerfarm) from 1.75 mm conductive ABS filament (Makergeeks.com). Machine code (g-code) generation for the printed part production was performed in Slic3r v1.1.6 with a 25% hexagonal infill. All nanoESI emitters were pulled from 1.5 mm OD, 1.1 mm ID borosilicate glass capillaries on a Sutter P-97 micropipette puller to a final tip diameter of 5 µm. Dimethyl methylphosphonate, tetrabutylammonium bromide, and tetrahexylammonium bromide were purchased from Fluka Analytical. Cyclohexylamine, and tetrabutylammonium bromide were purchased from Sigma-Aldrich and Macron Fine Chemicals, respectively.

Conclusions
A system composed of small plastic electrodes was fabricated and used to demonstrate several cases of gas-phase ion manipulation in the open air. The only forces acting on the ions are the initial energies associated with sprayed droplets – which are not pneumatically assisted – and the forces due to the static electric fields. It is also noted that the degree of solvation of the ions (if any) remains unknown. These manipulations highlight some of the possible uses of 3D printed plastic electrodes for focusing and transfer of ions to a mass spectrometer, including cases in which an ion/molecule reaction is performed within the electrodes at atmospheric pressure. The modest separation of ions demonstrated in the simple, low-cost system suggests that through optimization a device may be constructed in which ions are purified through soft-landing or directly analysed, all without the constraints of a vacuum system or well defined gas flow. Moreover, the detection and two dimensional profiling of the ion beam under ambient conditions, combined with the low cost of electrode production, may pave the way for distinct surface patterning with unorthodox electrode geometries.

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Notes and references


