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Development of negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) for the measurement of gas-phase organic acids in the atmosphere

Patrick Veres[a,b,*], James M. Roberts[b], Carsten Warneke[b,c], Daniel Welsh-Bon[a,b], Mark Zahniser[d], Scott Herndon[d], Ray Fall[a,c], Joost de Gouw[b,c]

[a] *Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, USA*
[b] *Chemical Sciences Division, Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80305, USA*
[c] *Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309, USA*
[d] *Aerodyne Research Inc., Billerica, MA, USA*

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ABSTRACT

We have developed a negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) technique for on-line analysis of gaseous organic and inorganic acids. In this detection scheme, acetate ions ($CH_3C(O)O^-$) react very selectively with atmospheric trace acids, by proton transfer, to produce unique product ion species. We tested this ion chemistry for 11 species of which only four showed measurable fragmentation. We investigated both the time response of the inlet and humidity dependence for both formic acid and pyruvic acid measurements. A formic acid calibration was performed and found a sensitivity of 21 ± 4.3 counts per second per pptv. Formic acid measurements made during two separate informal ambient air intercomparisons: (1) with a quantum cascade IR laser absorption system (QCL) and (2) a proton-transfer reaction mass spectrometer (PTR-MS) show good agreement validating this measurement technique. The measurements of the NI-PT-CIMS and PTR-MS agree to within 5% with a high degree of correlation ($r^2 > 0.93$). We have found the NI-PT-CIMS detection limit for formic acid is approximately 80–90 pptv for a 1 s integration period, and is currently limited by the formate background in the instrument. The fast time response and high sensitivity of the NI-PT-CIMS method make it a promising technique for the measurement of organic acids in ambient conditions.

1. Introduction

Organic acids are important atmospheric trace gases contributing to the acidity of atmospheric condensed water and precipitation. As end products of oxidation, organic acids reflect the photochemical history of an air mass. Organic acids have been measured in both the gas [1] and aerosol phase [2–4]. They may have a significant impact on climate as a result of the contribution of organic aerosols to total aerosol loading and to cloud condensation nuclei [5].

Research suggests that carboxylic acids are one of the most abundant classes of organic compounds present in the atmosphere [6–9]. Carboxylic acids are directly emitted by both biogenic and anthropogenic sources [10]. Secondary production via photo-oxidation of hydrocarbons occurs by the following chemistry: O_3–alkene chemistry, $RC(O)OO + HO_2$ chemistry, $RC(O)OO$ + aqueous droplets, and particle phase oxidation of organic compounds involving OH and O_3 [11,12].

Small carboxylic acids are of particular interest as products of particle phase formation and oxidation of secondary organic aerosol (SOA). Recent research has shown a link between the photochemical production of SOA and gas-phase organic acids [13,14], which presents the possibility of using gas-phase measurements of organic acids as a marker of SOA chemistry. The contribution of organic acids in SOA chemistry is currently underestimated by an order of magnitude [6,15].

Despite their importance in atmospheric chemistry, the adsorptive nature of carboxylic acids has made on-line measurements a challenge. Carboxylic acids have been measured in the field by a variety of analytical methods including filter [16], mist chamber [17], and cryogenic sampling [18] with ion chromatography or high-performance liquid chromatography (HPLC). Filter sampling is the most widely used method; however, it cannot provide high time resolution data and often has positive and negative artifacts associated with it [19]. Recent research has been focused on the

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* Corresponding author at: Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, USA. Tel.: +1 303 497 5797.
E-mail address: patrick.veres@noaa.gov (P. Veres).

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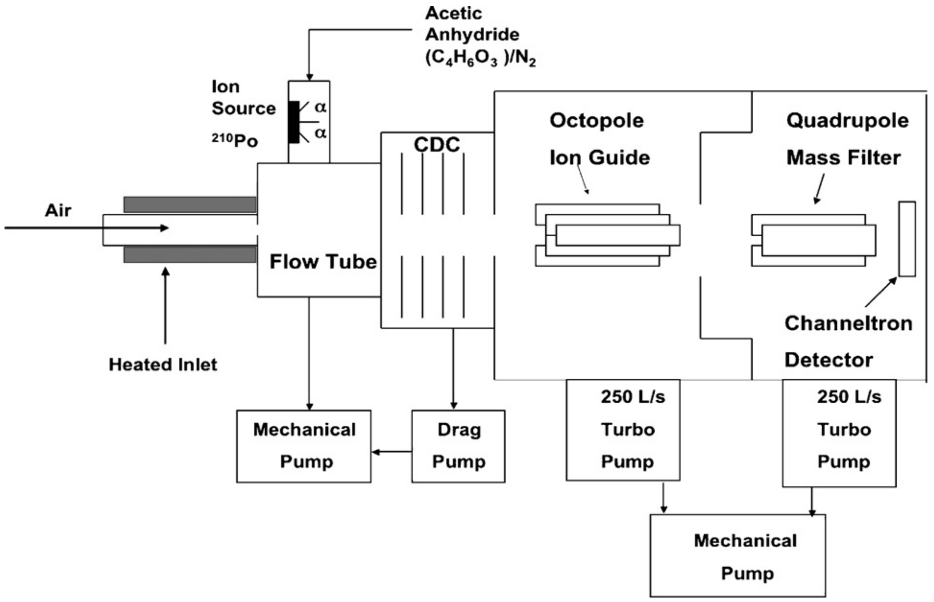

Fig. 1. NI-PT-CIMS instrument schematic.

development of on-line measurement techniques for carboxylic acids that provide higher time resolution data [4].

Here, we describe a technique based on a combination of proton-transfer reactions and negative-ion chemical-ionization mass spectrometry (NI-CIMS) as a method for the on-line measurement of carboxylic acids. Negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) utilizes reactions of the acetate ion ($CH_3C(O)O^-$) to detect organic acids in ambient air. Acetic acid has the lowest gas-phase acidity of the common atmospheric acids. The gas-phase acidity of a molecule is defined by the Gibbs free energy change of the following reaction:

$$HA \rightarrow H^+ + A^- \quad (1)$$

A summary of a number of gas-phase acids is presented in Table 1 [20] along with their gas-phase acidities. The low gas-phase acidity of the acetate ion makes it an ideal reagent ion for the detection of organic acids via proton transfer.

$$RCOOH + CH_3C(O)O^- \rightarrow RCOO^- + CH_3C(O)OH \quad (2)$$

Other analogs such as inorganic acids and dicarboxylic acids are detected in a similar manner.

In addition, other VOCs such as alcohols, ketones, and aldehydes will not undergo proton exchange with the acetate ion making it a very selective reagent ion.

In this study, we have developed and characterized an instrument for measurements of various atmospheric acids. We use a modified version of a thermal decomposition PAN CIMS (TD-PAN-CIMS) instrument [21] to perform laboratory experiments to characterize this technique. These experiments demonstrate the viability of this ion chemistry and this measurement technique. Comparison of formic acid measurements made with a quantum cascade IR laser absorption system (QCL) and proton-transfer reaction mass spectrometer (PTR-MS) serve to validate the measurement technique presented here.

2. Instrument setup

2.1. Instrumentation

The instrument used in this work has been modified from the TD-PAN-CIMS described in Slusher et al. [21] as shown in Fig. 1. Ambient air is sampled into the NI-PT-CIMS instrument by a heated 0.25 in. o.d. PFA (perfluoroalkoxy) Teflon tubing. The Teflon tubing in front of the flow tube is heated to an external temperature of 75 °C to minimize inlet effects that will be discussed later. The total inlet flow rate was 2 slpm.

The $CH_3C(O)O^-$ ion is synthesized by dissociative electron attachment to acetic anhydride, $CH_3–C(O)–O–C(O)–CH_3$. For this experiment we flowed 1 sccm of saturated $C_4H_6O_3/N_2$ mixture into a ^{210}Po ion source mixed with an additional 2 slpm of nitrogen. Ambient air is drawn into the flow tube (32 Torr) and mixes with $CH_3C(O)O^-$ reagent ions. Ion molecule reactions occur over the entire 12 cm length of the flow tube. The resulting analyte ions are then accelerated through the collisional dissociation chamber (CDC) via an electric field of approximately 25 V cm^{-1}. The CDC is maintained at 0.15 Torr with a molecular drag pump. The molecular collisions in the CDC serve to dissociate weakly bound cluster ions such as $CH_3C(O)O^-(H_2O)_n$ into their core ions, simplifying the resulting mass spectra. An octopole ion guide at 10^{-3} Torr collimates the beam of ions and transfers them into a quadrupole mass filter. An electron multiplier at a pressure less than 7×10^{-5} Torr is used to detect the ions.

An inlet system was designed to provide a calibration source and background measurement that was used to zero the instrument. A schematic diagram of the inlet used in laboratory studies is shown in Fig. 2. The inlet consisted of three Teflon PFA fittings connected to the front of the heated inlet. The fittings were 1/4 in. tees to which the standard source could be added and excess flow vented.

A capillary diffusion cell was used to provide steady state concentrations of organic acids in all laboratory studies, except for formic acid where a permeation source was used. A 5 sccm flow of nitrogen was passed through the headspace of the diffusion cell, and then diluted with humidity-controlled zero air. Concentrations were calculated as described by Altshuller and Cohen [22] using the relevant Henry's law constants [23].

A Quantum Cascade Laser (QCL) system and a PTR-MS system were utilized to perform both instrumental intercomparisons and validation of the NI-PT-CIMS technique. The Quantum Cascade Laser (QCL) system used in the qualitative comparison monitored formic acid, formaldehyde, and ethene during TexAQS 2006 field campaign. This technique utilizes the absorption of a 1765 cm^{-1} laser by formic acid as a detection method followed by a spec-