International Journal of Mass Spectrometry 274 (2008) 48–55

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

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

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ARTICLE INFO

Article history:
Received 15 January 2008
Accepted 30 April 2008
Available online 16 May 2008

Keywords:
Organic acid
Chemical ionization
Acetate ion
Atmospheric measurement
Proton transfer

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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doi:10.1016/j.ijms.2008.04.032

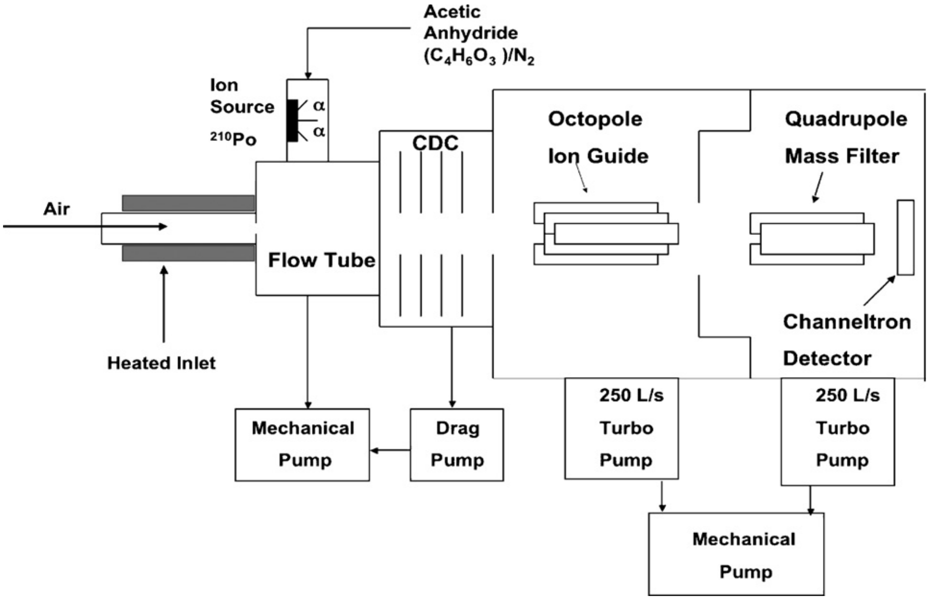

Fig. 1. NI-PT-CIMS instrument schematic.

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:

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

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.

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

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-

Table 1
Gas-phase acidities, anion masses and anion abundances of common acids

Compound	Formula	ΔG (Kcal/mol) [20]	Anion observed (m/z)	Detectable species
Hydrochloric acid	HCl	328.15	35 (76%), 37 (24%)	–
Formic acid	CH_2O_2	338.2	45	Yes
Nitrous acid	HNO_2	333.7	46	–
Acetic acid	$C_2H_4O_2$	341.5	59	N/A
Nitric acid	HNO_3	317.8	62	–
Acrylic acid	$C_3H_4O_2$	337.2	27 (8%), 71 (92%)	Yes
Propionic acid	$C_3H_6O_2$	340.1	73	Yes
Glycolic acid	$C_2H_4O_3$	327.8	75	Yes
Hydrobromic acid	HBr	317.9	79 (51%), 81(49%)	–
Methacrylic acid	$C_4H_6O_2$	337.1	85	Yes
Butyric acid	$C_4H_8O_2$	339.1	87	Yes
Pyruvic acid	$C_3H_4O_3$	326.5	43 (1%), 87 (99%)	Yes
Oxalic acid	$C_2H_2O_4$	N/A[a]	89	No
Lactic acid	$C_3H_6O_3$	330.3	89	Yes
Methanesulfonic acid	CH_4SO_3	315.5	95	–
Sulfuric acid	H_2SO_4	300	97	–
Malonic acid	$C_3H_4O_4$	N/A[a]	103	No
Trifluoroacetic acid	$C_2HF_3O_2$	316.3	113	–
Benzoic acid	$C_7H_6O_2$	333	121	Yes
Hydroiodic acid	HI	308.98	127	–
Nitrophenols	$C_6H_5NO_3$	320.9-329.5	138	Yes
Trichloroacetic acid	$C_2HCl_3O_2$	N/A[b]	161	–
Pentafluoropropionic acid	$C_3HF_5O_2$	N/A[b]	19 (3%), 119 (67%), 163 (30%)	Yes

Species that are measurable on the NI-PT-CIMS are denoted with 'Yes', unmeasurable species are denoted as such with a 'No', and species which have not yet been studied are marked with '–'.

[a] Data not readily available. However, the first proton of these diacids is much more acidic in solution than the mono carboxylic acids.

[b] Data not readily available. The strong electron-withdrawing nature of halogen substituents should shift gas phase acidities to much lower values than corresponding hydrocarbon acids. Our observations are consistent with this assumption.

tral fitting routine to determine the formic acid concentration. The detection limit of this technique is in the sub-ppbv level. More detail on this measurement technique can be found in Herndon et al. [24]. The PTR-MS system utilizes proton-transfer reactions of H_3O^+ to monitor various atmospheric trace gases. PTR-MS allows for the detection of several volatile organic compounds with high sensitivity (10–100 pptv) and response time (1–10 s). This technique has been proven in aircraft, ground based and laboratory studies. A more complete discussion of the PTR-MS system used in this study can be found in de Gouw and Warneke [25].

2.2. Ion chemistry

The selectivity of the ion chemistry in NI-PT-CIMS was tested for a number of acids. Fig. 3a shows a zero air background scan showing the presence of approximately 10^6 primary ions ($CH_3C(O)O^-$, m/z 59). Fig. 3b–d contain the resulting spectra of the reactions of $CH_3C(O)O^-$ reagent ion with formic acid (HC(O)OH), acrylic acid ($CH_2=CHC(O)OH$), and pyruvic acid ($CH_3C(O)C(O)OH$) in zero air, respectively.

For all three species, the dominant product ion observed (m/z 45, 71, 87) is $RC(O)O^-$ corresponding to Reaction (2). In addition to this main product, less abundant ions are also observed, several of which occur in all spectra recorded. These less abundant peaks are the result of impurities in the system, and correspond to the following ions: CH_3^- (15), O_2^- (32), Cl^- (35), NO_2^- (46), and NO_3^- (62). The observation of Cl^- results from previous work with chlorine species in the TD-PAN-CIMS instrument. A high instrument background is observed for m46 and m62, NO_2^- and NO_3^-, however

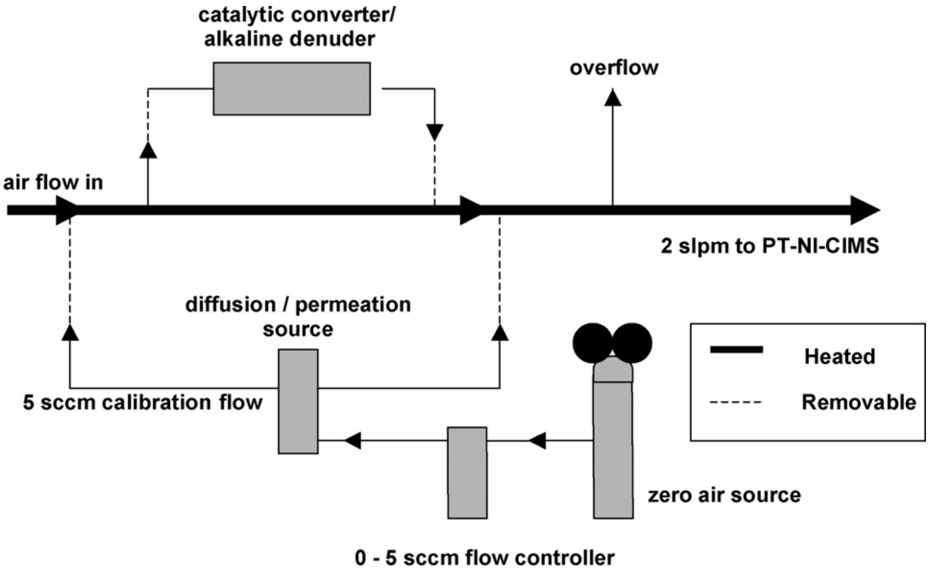

Fig. 2. Schematic diagram of the NI-PT-CIMS inlet.

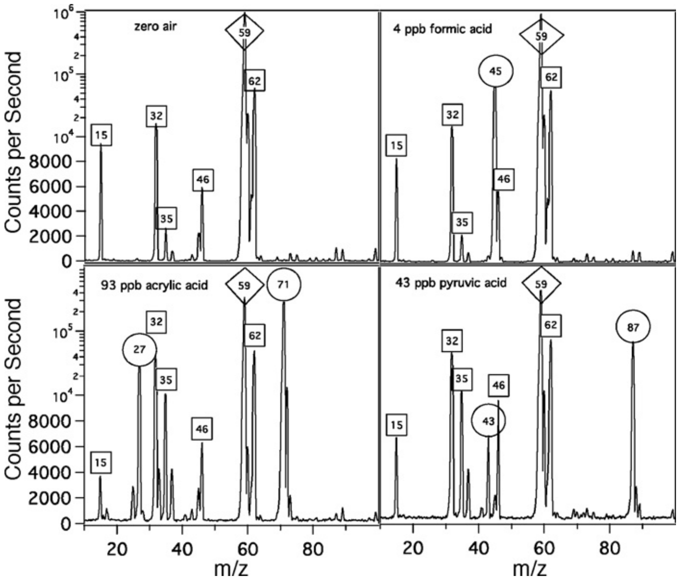

Fig. 3. Primary ion spectrum: m59 $CH_3C(O)O^-$ primary ions, m62 $NO_3{}^-$, m46 $NO_2{}^-$, m35 Cl^-, m32 $O_2{}^-$, and m15 $CH_3{}^-$. (b) Formic acid spectrum: m45 $HC(O)O^-$, m59 $CH_3C(O)O^-$, m62 $NO_3{}^-$, m46 $NO_2{}^-$, m35 Cl^-, m32 $O_2{}^-$, and m15 $CH_3{}^-$. (c) Acrylic acid spectrum: m71 $CH_2CHC(O)O^-$, m27 CH_2CH^-, m59 $CH_3C(O)O^-$, m62 $NO_3{}^-$, m46 $NO_2{}^-$, m35 Cl^-, m32 $O_2{}^-$, and m15 $CH_3{}^-$. (d) Pyruvic acid spectrum: m87 $CH_3C(O)C(O)O^-$, m43 $CH_3C(O)^-$, m59 $CH_3C(O)O^-$, m62 $NO_3{}^-$, m46 $NO_2{}^-$, m35 Cl^-, m32 $O_2{}^-$, and m15 $CH_3{}^-$.

ambient measurements show correlation with formic acid suggesting the presence of nitric and nitrous acid chemistry. The reaction of $CH_3C(O)O^-$ with HX where X is Cl^-, $NO_2{}^-$, and $NO_3{}^-$ is energetically favorable thus we expect these species to be observable using this chemistry.

Several of the spectra collected also show small but unique fragment ions. In Fig. 3c and d ions are present at *m*/*z* 27 and 43, respectively, a result of the loss of CO_2 from the parent ion. The contribution to total ion signal is shown in Table 1 for the species for which this fragmentation occurred.

This type of analysis was also carried out for the following species: propionic acid (C_2H_5–C(O)OH), methacrylic acid ($CH_2 = C(-CH_3)$–C(O)OH), *n*-butyric acid (C_3H_7–C(O)OH), lactic acid ($CH_3CH(-OH)$–C(O)OH), trifluoroacetic acid (CF_3–C(O)OH), benzoic acid (C_6H_5–C(O)OH), 2-nitrophenol ($C_6H_5(-OH)-NO_2$), and pentafluoropropionic acid (C_2F_5–C(O)OH). Of these compounds only trifluoroacetic acid and pentafluoropropionic acid showed significant fragment ions ($CF_3{}^-$ and $C_2F_5{}^-$, respectively) with both spectra showing the presence of the F^- ion.

Table 1 summarizes the ability of NI-PT-CIMS to detect each compound listed. Oxalic acid ($C_2H_2O_4$) and malonic acid ($C_3H_4O_4$) could not be detected because it was not possible to produce large enough gas-phase concentrations with the diffusion cells used. Our observation of Cl^-, $NO_2{}^-$ and $NO_3{}^-$ combined with thermodynamic information suggests the possibility of detecting hydrochloric acid (HCl), nitrous acid (HNO_2), nitric acid (HNO_3), hydrobromic acid (HBr), sulfuric acid (H_2SO_4), and hydroiodic acid (HI). Future experiments will be performed to assess the ability of the NI-PT-CIMS to monitor these and additional compounds.

2.3. Calibration

Calibration of the NI-PT-CIMS was performed using the inlet as shown in Fig. 2. Ambient air is sampled using a 1 m long, heated (75 °C) PFA Teflon inlet. Formic acid calibration gas was added by flowing air over a permeation tube heated to 50 °C followed by subsequent dilution with zero-air at 50% relative humidity. The error in the standard source concentration is assumed to be 20% based on the error associated with the permeation source.

A typical calibration curve for the NI-PT-CIMS is shown in Fig. 4. The slope of each curve gives the sensitivity (calibration factor) for each species in normalized counts per second (ncps) $ppbv^{-1}$ or $pptv^{-1}$ of formic acid. The mixing ratios in ambient air measurements were determined using these calibration factors. The data shown in Fig. 4 have been normalized to a primary ion signal of 10^6 cps. The normalized sensitivity of the NI-PT-CIMS towards formic acid was found to be 21 ± 4.3 ncps $pptv^{-1}$.

Fig. 4 also contains a calibration curve for formic acid in the PTR-MS, which was used in the comparison between NI-PT-CIMS and PTR-MS. The normalized sensitivity of the PTR-MS towards formic acid was found to be 30 ± 1 ncps ppb^{-1}. The lower sensitivity can be accounted for by comparing the reaction time in the two systems. The reaction time in the NI-PT-CIMS is approximately 0.077 s compared to 134 μs in the PTR-MS. Enhancing the PTR-MS sensitivity by this factor yields approximately the same sensitivity observed in the NI-PT-CIMS

2.4. Background determinations

Determination of the instrument background is important because it needs to be subtracted from ambient measurements at low concentrations. Background measurements for these classes of compounds are especially important due to the adhesive nature of these species. In this study, sodium carbonate denuders and a palladium oxidizing catalyst were tested to determine an effective method to zero the instrument. The sodium carbonate denuder cell was prepared as described by Fitz [26] using a one half meter length of 1/2 in. o.d. glass tubing. The catalyst used is a precious metal catalyst on a stainless steel honeycomb substrate (Johnson Matthey

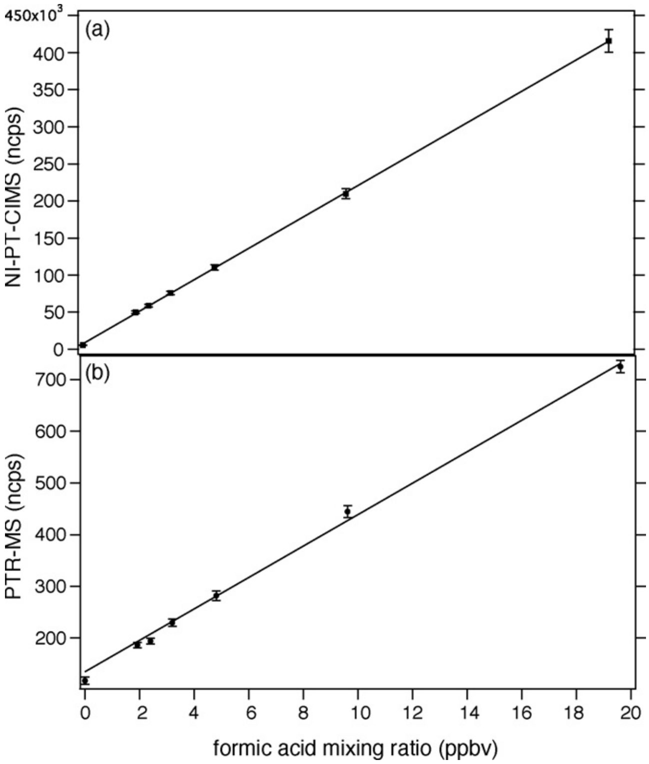

Fig. 4. Results of NI-PT-CIMS and PTR-MS calibration measurement for formic acid. The slope of line (a) was found to be 21 ± 4.3 ncps per pptv with an R^2 of 0.9999. Line (b) gave a slope of 30 ± 1 ncps per ppbv with an R^2 of 0.9985.

Emission Control Technologies). The catalyst was sealed in a glass cell with 1/4 in. ports and heated to 350 °C.

Zero air containing formic and pyruvic acid was passed through each cell to assess the effectiveness of the denuder and the catalyst used. Fig. 5 shows a series of measurements including one ambient background measurement, one calibration addition with the catalyst bypassed, and one calibration addition passed through the catalyst. The efficiency was then calculated as one minus the ratio of the steady state signal during flow through the catalyst to the signal when the catalyst was bypassed.

The denuder successfully removed formic and pyruvic acid with efficiencies of 97.9 ± 5.9% and 94.3 ± 9.2%, respectively. The efficiency of the catalytic converter was found to be 99.5 ± 7.8% for pyruvic acid and 100.1 ± 1.5% for formic acid. The catalytic converter proved more effective than the denuder at removing both acid species.

The 3σ limit of detection was approximated using data from Fig. 5. For a 1 s integration time the limit of detection for formic acid was found to be approximately 80–90 pptv. A high instrument background currently limits the formic acid limit of detection. It is reasonable to expect that further efforts will reduce the instrument background and therefore improve the detection limit.

3. Instrument characterization

3.1. Humidity dependence

Humidity dependence of measurements is a concern whenever ambient measurements are made. In NI-PT-CIMS, changes in the ambient humidity causes variations in the reagent ion signal and water cluster distributions in the flow tube. Measurements of formic acid were performed under varying humidity to better understand this effect. Formic acid was added to zero airflow that has been passed through a glass water bubbler and mixed with varying amounts of dry zero air to control the humidity.

The results of this experiment are shown in Fig. 6. The formic acid signal was not dependent on the humidity of the sampled air within the precision of our measurements (±5%). This is somewhat expected as the CDC effectively breaks up any water clusters that are formed in the flow tube. These results would also suggest that the rates of the following reactions are similar:

$$CH_3C(O)O^- + HC(O)OH \rightarrow HC(O)O^- + CH_3COOH \tag{3}$$

$$CH_3C(O)O^{-}{\bullet}H_2O + HC(O)OH \rightarrow HC(O)O^- + CH_3C(O)OH{\bullet}H_2O \tag{4}$$

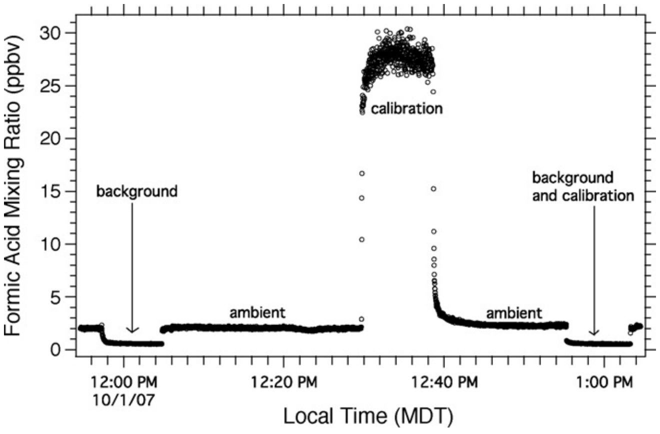

Fig. 5. Time series of normalized 1 s data for one standard addition of formic acid and two background determinations.

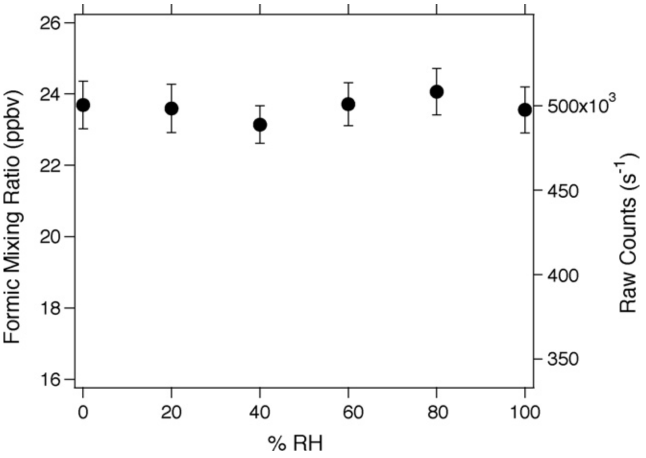

Fig. 6. Dependence of the response of the formic acid signal on relative humidity.

Thermochemistry indicates that that $CH_3C(O)O^{-}{\bullet}H_2O$ is present [20], which may not be the case as the CDC breaks up any clusters present and this ion is not observed. The lack of humidity dependence greatly simplifies data analysis by removing the necessity for a humidity correction factor.

3.2. Inlet tests

The response time of the NI-PT-CIMS instrument is an important characteristic of the measurement, as it determines the time scale upon which measurements can be made. An ideal inlet would provide a signal that resembles a step function going from zero to steady state instantaneously when a concentration change is applied. Fig. 5 shows that a finite amount of time is required to reach steady state when a change in concentration occurs. This effect is observed as the rounded corners in the signal when calibration gas is added or removed. The non-ideal behavior in the response time is a result of the finite amount of time required for organic acids to reach equilibration on inlet surfaces.

To test the time response of the NI-PT-CIMS inlet, a known amount of sample is added to the instrument for a given period of time. The instrument response to the change in concentration was then defined as the time required to reach the steady state response. The steady state response is the system response after the inlet was under the same condition for an extended period (15 min). We define the response time as the time required for a steady state signal to decay to 10% of the initial signal when a background measurement is made.

The result of the tests are shown in Fig. 7 for formic and pyruvic acids. The data were fit to double exponential curves that are shown as the solid and dashed lines in Fig. 7. The increase in pyruvic acid at room temperature showed a slow response and could not be fit to a double exponential. Both the signal rise and decay for each concentration pulse applied is shown for the two trials. The mixing ratios of formic and pyruvic acid used were between 20 and 40 ppb. The data are shown as a ratio of instrument response a given time after change (R_t) to the instrument response at steady state (R_{SS}). Steady state is defined by the average signal level just before or after a concentration change.

It can be seen that response times of 1–2 s can be achieved for formic acid. No significant differences were observed in the response time as a function of water vapor added. The effect of the temperature at which the inlet was maintained is clearly shown in Fig. 7. The response time to formic acid was reduced from 31 s to approximately 1.5 s with inlet heating. Pyruvic acid showed a

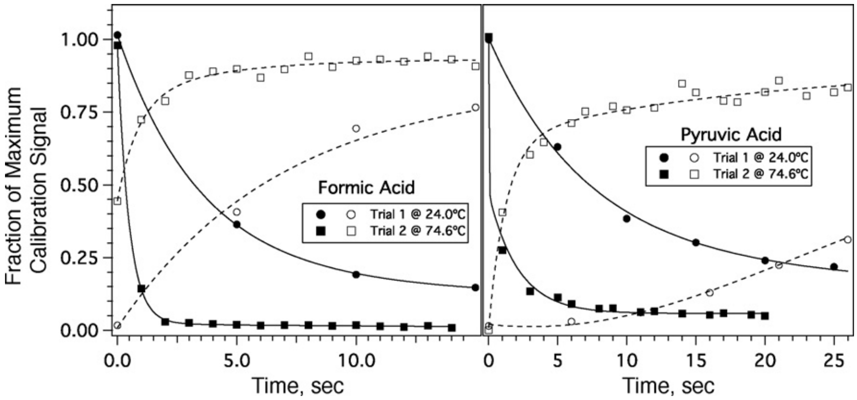

Fig. 7. The response of the NI-PT-CIMS inlet shown as the ratio of the response at time *t* at two different temperatures to that at steady state, versus the time from standard addition or removal. Open symbols show the rise after calibration gas is added. Closed symbols show the decay after calibration gas is removed.

reduction in response time of 85 s to 5.5 s. The signal rise times are significantly longer for pyruvic acid in comparison with the decay time. This difference may be the result of a transient pressure effect that occurs when the sample source is manually added to the inlet flow, and warrants further investigation.

4. Intercomparison

4.1. Quantum cascade infrared laser absorption (QCL)

The detection scheme utilized in this work was first observed during work involving a TD-PAN-CIMS fielded during TexAQS 2006. This fortuitous discovery permitted a qualitative comparison of the NI-PT-CIMS method with the QCL instrument also fielded during the TexAQS 2006 mission onboard the Ronald H. Brown research vessel. This qualitative test led to the further work described in this paper.

TD-PAN-CIMS involves the thermal decomposition of PANs into corresponding peroxyradicals. These radicals then react with iodide ions to form the carboxylate ion, RC(O)O$^-$. The system used an internal ^{13}C-labelled PAN standard continuously giving between 6,000 and 8,000 cps of ^{13}C labeled acetate ions, $CH_3C(O)O^-$. The mass spectra generated under ambient sampling showed the presence of the formate ion (*m*/*z* 45). Since there is no formyl PAN compound produced in the atmosphere [27] it was hypothesized that proton-transfer reactions from the acetate ions with formic acid in air present were responsible for the formate ions observed.

The Quantum Cascade IR Laser absorption (QCL) system present during TexAQS 2006 was used to measure formaldehyde, ethene, and formic acid. The system was operated as described by Herndon et al. [24]. During TexAQS 2006, the instrument used a 10 m length of 8 mm i.d. PTFE sampling line heated to 40 C at a reduced pressure of 70 Torr. The inlet was located on the same tower as the TD-PAN-CIMS inlet. This provided a qualitative intercomparison of observed formic acid from 22 to 26 August 2006.

Fig. 8 shows the results of the TD-PAN-CIMS data collected along with QCL measurements of formic acid. The PAN-CIMS *m*/*z* 45 scale was shifted to account for a background, as no instrument zero for formic acid was available. The signal was then scaled to the QCL data as no formic acid calibration was performed using the PAN system. It can be seen that the two techniques correlate very well. It is important to mention that the significantly lower primary ion signal observed during TexAQS 2006, of 6,000 to 8,000 cps, gave a much higher detection limit than that of the QCL and the current NI-PT-CIMS.

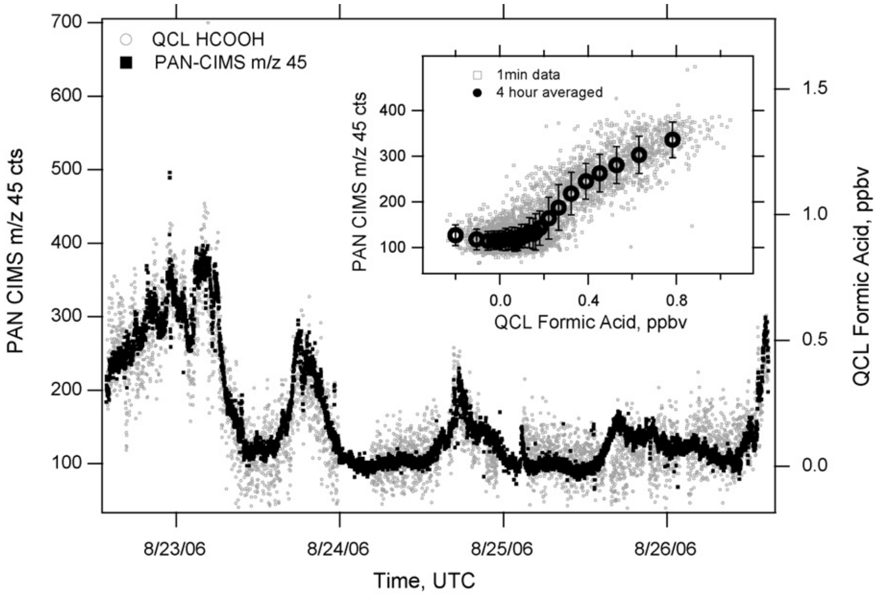

Fig. 8. Time series of formic acid observed simultaneously with PAN-CIMS and QCL in Houston, TX during the TexAQS 2006 experiment.

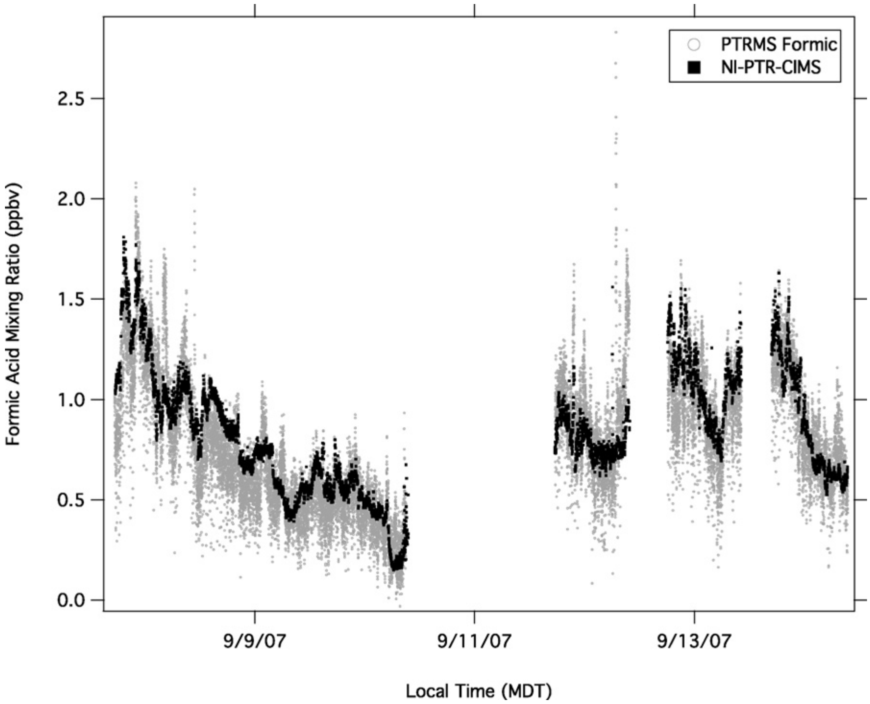

Fig. 9. Time series of 1-min formic acid mixing ratios measured simultaneously with NI-PT-CIMS and PTR-MS in Boulder, CO.

4.2. Proton-transfer reaction mass spectrometer (PTR-MS)

The NI-PT-CIMS and PTR-MS instruments were run side by side in the laboratory 8–14 September 2007. The comparison was run continuously with the exception of weekdays during the hours of 9 am to 6 pm due to instrumental tests. Both instruments sampled from a common 10 m line made of 1/4 in. o.d. PFA Teflon tubing extending 0.5 m out of a first story window at NOAA Boulder, CO. The PTR-MS was run as described by de Gouw and Warneke [2].

A formic acid calibration was performed on both instruments immediately prior to the first day of measurement. A common line was used for the NI-PT-CIMS and the PTR-MS. Results of the calibrations for the NI-PT-CIMS and PTR-MS are those shown in Fig. 4. The PTR-MS data have been normalized according to the method described by de Gouw et al. [28]. The humidity dependence factor used was 0.5, the standard factor for compounds where the humidity dependence is unknown.

The NI-PT-CIMS instrument was run with a total inlet flow of 2 slpm. A 5 s measurement sequence was performed integrating for 0.5 s at masses 10 (noise), 45 (formic acid), 59 (acetate), 61 (acetate isotope), 62 (nitric acid), 73 (propionic acid), 85 (methacrylic acid), 87 (butyric acid, pyruvic acid), 89 (oxalic acid), and 121 (benzoic acid). A sodium carbonate denuder cell was used to obtain background measurements every hour with the NI-PT-CIMS instrument during this measurement period. The mixing ratios were determined by normalizing to the acetate ion signal, subtracting the background measured with the denuder, and dividing by the calibration factor.

Fig. 9 shows the NI-PT-CIMS measurements along with PTR-MS data during the measurement period. The data are presented as 1-min average measurements for both instruments. The NI-PT-CIMS and PTR-MS formic acid measurements were highly correlated ($R^2 > 0.93$) with a slope of 0.97 as shown in Fig. 10. This intercomparison is well within the combined error of the two techniques.

Several possible interferences do exist for the PTR-MS measurement of formic acid at m/z 47. To better understand these effects the QCL formic acid measurement during TexAQS was also compared to the signal recorded at mass 47 using a proton-transfer ion-trap mass spectrometer (PIT-MS) [29] that was run in parallel. The QCL measurement of formic acid compared well with the signal recorded at mass 47 using the PIT-MS instrument onboard the Ronald H. Brown during TexAQS 2006, except in a number of narrow industrial plumes near Houston, TX. In these cases interference at mass 47 was identified as dimethyl ether using GC-PIT-MS measurements. In most urban atmospheres, this interference is not expected to be significant as shown by the NI-PT-CIMS versus PTR-MS comparison in Fig. 10. Interference from ethanol at mass 47 was small in the PIT-MS measurements despite high ethanol mixing ratios of up to 15 ppbv in industrial plumes, as expected from the low sensitivity of PIT-MS towards ethanol [30].

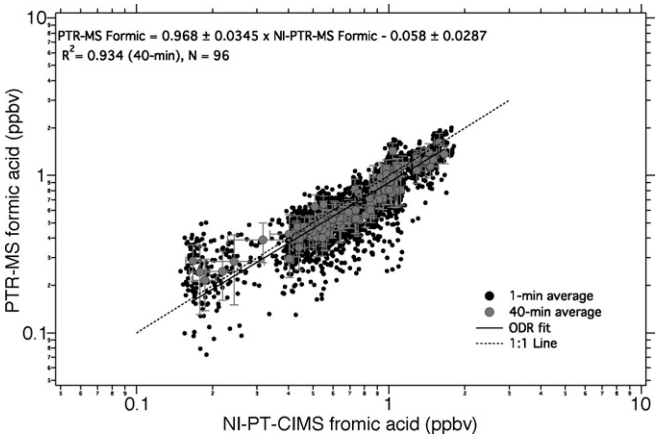

Fig. 10. Scatter plot of NI-PT-CIMS and PTR-MS formic acid (m47) measurements presented as 1 and 40 min averages. The 40 min data has been fit with ODR regression.

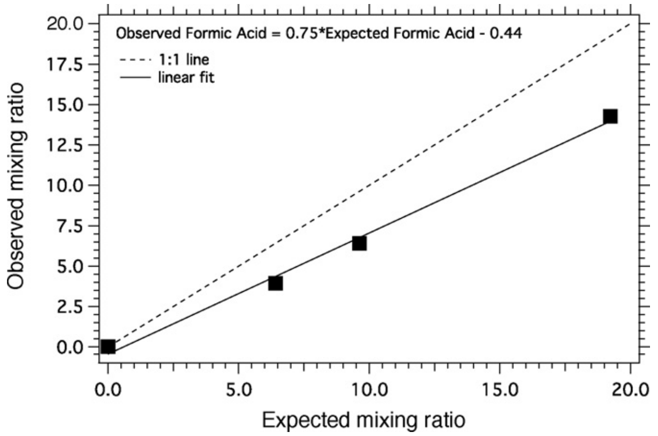

Fig. 11. Formic acid transmission efficiency of the 10 m PFA Teflon inlet used during the intercomparison of NI-PT-CIMS and PTR-MS. The slope of the linear fit was found to be 0.75 ± 0.04 with an r^2 of 0.9972.

A calibration was performed to determine the transmission of formic acid through the 10 m PFA Teflon sampling line used during the comparison. The sampling line was not heated during the intercomparison and this experiment. Formic acid was added in known concentrations to the head of the sampling line and monitored by the NI-PT-CIMS. Fig. 11 presents the results of this experiment for the three different concentrations used. The NI-PT-CIMS measured a total formic acid loss of approximately 25% over the length of the sampling line. The results of this experiment illustrate the importance of selecting proper inlet materials, conditions, and minimizing length of the inlet line.

The additional masses observed in the NI-PT-CIMS measurement sequence were only qualitatively analyzed due to a lack of calibration factors. Signals corresponding to propionic acid, methacrylic acid, butyric acid, pyruvic acid, and benzoic acid were all observed and appeared to zero out during the background measurements. The signal-to-noise ratio's observed were slightly lower than that observed for formic acid. The inlet transmission of these species must be further studied to determine total species loss across the length of the inlet. Additional work must be performed to better assess our ability to quantify these and other species.

5. Conclusions

We have presented a new method for the on-line measurement of gaseous organic acids. The instrument was shown to have the ability to detect a large range of acid species including carboxylic acids, dicarboxylic acids, and potentially inorganic acids. We have reported a limit of detection below 0.1 ppbv for 1-s measurements of formic acid. NI-PT-CIMS ambient formic acid measurements were compared qualitatively to a QCL and quantitatively to a PTR-MS, with excellent agreement. Table 1 provides a summary of species we were able to detect in this study, but thermochemical data indicate that this technique has the potential to measure a number of species not listed in this work.

NI-PT-CIMS can provide organic acid measurement with a time resolution on the order of seconds whereas previous methods, such as filter sampling, are limited to overall temporal resolution of hours. Sub-ppbv detection limits of several organic acids have been observed using the technique described here. The fast time response of this technique combined with the high sensitivity and low limit of detection make this a promising method for airborne measurements. This instrument is also well suited to investigate organic acid emission by various types of vegetation that could be important in global and regional emission models.

Future work will be conducted to further characterize the system and improve the detection limit and sensitivity. Several key problems must be addressed in more detail including the reduction of the inlet response time, development of a calibration system, and further reduction of the instrument background. Additional laboratory and ambient measurements will be made to determine any additional potential interferences and measurable species.

Acknowledgements

The authors gratefully acknowledge the National Science Foundation for funding through grant # ATM-0516610. Thanks also to both Edward R. Lovejoy and Greg Huey for helpful comments and suggestions.

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