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Carboxylic acid characterization in nanoparticles by thermal desorption chemical ionization mass spectrometry

James N. Smith*, G. Jeffery Rathbone

Atmospheric Chemistry Division, National Center for Atmospheric Research, 1850 Table Mesa Dr., Boulder, CO 80305, United States

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ABSTRACT

Recent improvements in the operation of the thermal desorption chemical ionization mass spectrometer allow for the characterization of organic species in 8–40 nm diameter particles. Here we describe the application of this technique to monocarboxylic and dicarboxylic acids, focusing on the response of the instrument to picogram amounts of pure and multicomponent mixtures. Monocarboxylic acids underwent minimal decomposition during analysis, and were identified by the deprotonated parent ion with a sensitivity of 3–8 Hz of integrated ion signal per picogram of sample. Measurements of a binary mixture of monocarboxylic acids showed that desorption and subsequent ionization of these compounds occur independently and have mass-normalized responses identical to pure samples. Dicarboxylic acids appear as the deprotonated parent ion as well as an important decomposition product corresponding to the loss of formic acid from the deprotonated parent. Sensitivities towards these compounds were up to 100 times higher than for the monocarboxylic acids. Experiments using 10–30 nm diameter butanedioic acid particles showed a linear response to collected particulate mass with sufficient sensitivity to support the application of this technique to the characterization of carboxylic acids in ambient atmospheric nanoparticles.

1. Introduction

The current understanding of the formation and growth of sub-50 nm diameter atmospheric aerosols, referred to here as nanoparticles, is limited by a lack of information on the chemical compounds that are responsible for these processes. While sulfuric acid is widely recognized to play an important role in nucleation and subsequent new particle formation [1], current models of the growth of newly formed particles that depend solely on sulfuric acid condensation underpredict growth rates, especially in the afternoon when photochemical activity is at its peak [2,3]. Several investigators have shown that organic compounds are in large part responsible for these observed growth rates [4–6]. However, the specific organic compounds responsible for the growth of nanometer sized particles have thus far not been identified.

The measurement of nanoparticle composition is difficult for the following reasons: (1) low mass loadings for such small particles, typically in the order of a million times lower than the accumulation mode particles, require high sampling rates and long integration times; (2) since nanoparticles exist in such low concentrations in the atmosphere, a clean separation is required between these and both ambient air and larger particles; (3) the chemical compounds that are able to partition into nanoparticles have very low vapor pressures and, once they are volatilized, often stick to surfaces of the instrument and sample lines and then are slowly released thereby increasing background levels; and (4) these chemical compounds are often quite complex and are susceptible to fragmentation if high ionization energies are used in analysis. Instruments that have addressed the need to measure nanoparticle composition accomplish this either indirectly or directly. Particle composition may be inferred indirectly by measuring some other behavior of the aerosol, such as the hygroscopicity or volatility of size-classified particles [7,8]. Direct measurements can be divided into offline and online techniques. Offline approaches are exemplified by experiments performed by Mäkelä et al. on newly formed particles at a coastal setting [9] and in a boreal forest [10]. Online approaches have thus far provided information on the elemental composition (e.g., refs. [11–13]) and lumped speciation into classifications of “primary” and “oxidized” organic compounds for particles with aerodynamic diameters larger than 20 nm [14].

Thermal desorption chemical ionization mass spectrometry (TDCIMS) is a direct, online technique that has been previously used to characterize inorganic compounds [15,16]. Recently the technique was applied to the study of organic aerosols in Mexico

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* Corresponding author. Tel.: +1 303 497 1468; fax: +1 303 497 1400.
E-mail address: jimsmith@ucar.edu (J.N. Smith).

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City, where it was able to identify some classes of organic compounds such as organic acids and nitrogen containing organics [4]. TDCIMS is, however, potentially well-suited for identifying specific organic aerosol constituents. Since it relies on chemical ionization mass spectrometry to ionize and detect compounds in the aerosol, it is both sensitive and imparts less fragmentation to the parent ion compared to techniques that rely on electron impact ionization or laser ablation and ionization [17]. In addition, its use of a triple quadrupole mass spectrometer, which allows for the identification of complex ions and structural isomers by collision-induced dissociation of selected ions, is of great utility in identifying multifunctional compounds expected in ambient nanoparticles.

This manuscript reports the use of TDCIMS for the characterization of picogram level samples of carboxylic acids as well as in pure laboratory-generated carboxylic acid nanoparticles. Key to the success of the technique has been the implementation of a temperature-programmed thermal desorption scheme, which will be described in detail below. We chose carboxylic acids for this study since they are postulated to be important in aerosol formation processes [18,19]. Carboxylic acids have been found in both urban [20,21] and rural aerosol [22,23], and can undergo further oxidation to create highly substituted compounds with very low volatility [24,25]. In Sections 4.1 and 4.2 we present experiments in which picogram amounts of monocarboxylic and dicarboxylic acids are directly applied to the TDCIMS collection filament in order to assess instrument sensitivity and the degree to which these compounds undergo decomposition during analysis. The extension of the method to laboratory generated butanedioic acid aerosol is presented in Section 4.3.

2. Instrument description

The TDCIMS [15,16] is an instrument that is capable of measuring the molecular composition of particles with diameters from 8 to 40 nm at ambient concentrations in the atmosphere. Fig. 1a shows a flow chart that describes TDCIMS operation and Fig. 1b shows a schematic of the actual instrument used in these investigations. In the experimental setup, particles are charged, size resolved, and then collected by electrostatic deposition onto a metal filament. This filament consists of a loop of 0.036 cm diameter platinum (Pt) wire. The loop extends 3.8 cm from its point of attachment in order to minimize temperature gradients along the tip of the loop, where particles are collected. The collection time varies with particle size and concentration, but usually ranges from 5 to 15 min. Following this, the filament is translated into the ionization region of an atmospheric pressure chemical ionization mass spectrometer, where it is resistively heated at atmospheric pressure to evaporate the aerosol. In the present study, ions are created from the neutral species thermally desorbed from particles through either proton or electron transfer with $(H_2O)_nO_2^-$ (with n estimated to be from 1 to 4). Ions are then transferred to a triple quadrupole mass spectrometer for mass analysis.

The most important development for the detection and quantification of organic compounds using TDCIMS has been a temperature programmed thermal desorption scheme similar to that developed by Ziemann and co-workers [26]. In temperature programmed thermal desorption, the current that resistively heats the filament is varied over time by a combination of stepwise changes and linear ramps. Temperature ramping has two advantages. First, it separates the desorbed molecular constituents in time so that reagent ions are not depleted by high concentrations of analyte. This allows one to approximate the reagent ion concentration as invariant, helping to assure quantitative measurements. Secondly, the measured ion abundance can be plotted against the filament temperature in order to characterize the volatility of the compounds being desorbed from the collected particles. This volatility information can be made quantitative, and recent studies have measured the vapor pressures of carboxylic acids in this way [27,28], however this is not the focus of the current investigations nor is the TDCIMS ideally suited for this type of measurement for the following reasons. First, a metal filament is required for the collection surface in the TDCIMS, since charged nanoparticles are collected electrostatically. This metal surface can itself participate in chemical changes in adsorbed species, including deprotonation and additional fragmentation [29]. Secondly, the energy imparted into compounds during thermal desorption may itself cause some degree of fragmentation and chemical change that could influence the temperature at which ion signals appear. Observing the extent to which this occurs with carboxylic acids is an important part of the current study.

Ions are formed from desorbed neutral compounds under conditions of atmospheric pressure and a temperature of 323 K,

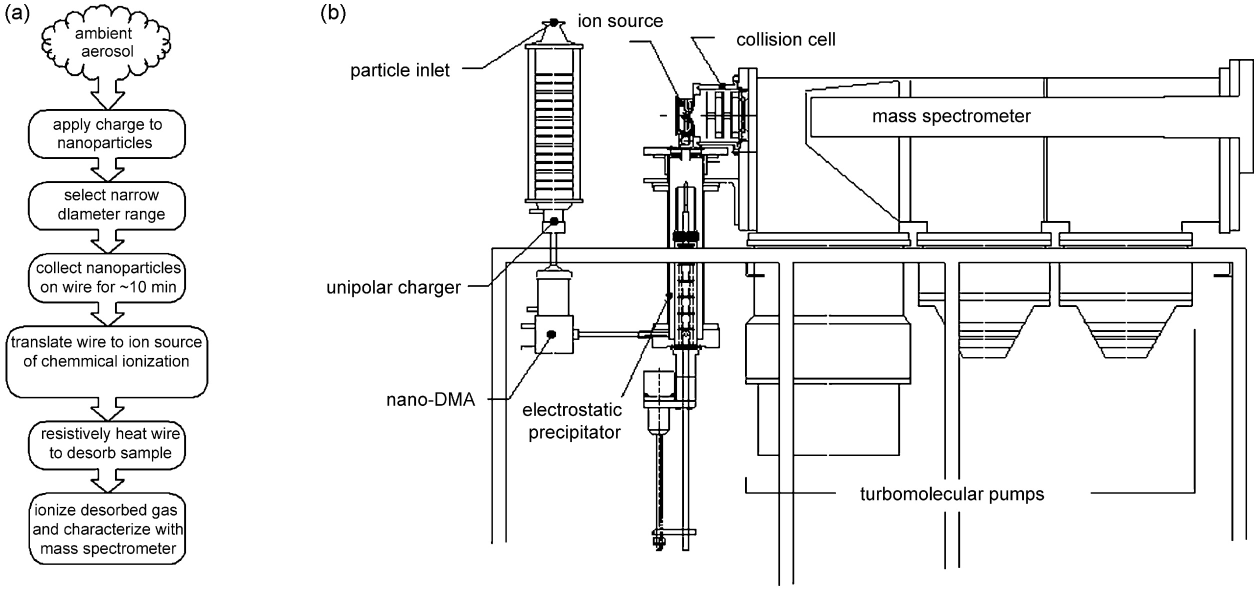

Fig. 1. (a) Flow diagram of TDCIMS particle collection and analysis and (b) TDCIMS schematic.

the latter applied to the ion source to reduce the adsorption of semivolatile vapors. Carboxylic acids are detected as negative ions from the reactions of the neutral acids with O_2^-, similar to the method used by Hoffman and colleagues [30]. O_2^- occurs in high abundance in the chemical ionization source due to the abundance of O_2. Since the ion source operates at atmospheric pressure, water may cluster to the reagent ions, which stabilizes the anion and lowers proton affinity. This limits the application of this ionization technique to those compounds that are able to react with the O_2^-/water clusters. These include many of the expected constituents of secondary aerosol: inorganic and organic acids, oxygenated organics such as alcohols, ketones, and aldehydes, and inorganic and organic bases such as ammonium and amines.

3. Experiment

The carboxylic acids used in this study, listed in Table 1, were chosen to correspond approximately to the range used in a previous study of the vapor pressures of dicarboxylic acid aerosols [31]. Water used for dilutions was taken from a MilliQ Gradient A10 device with Quantum EX and Q-gard 1 filter packs (Millipore Corp.).

Since the focus of the current study is to understand and quantify the response of the instrument to carboxylic acids, we sought to decouple the complex task of generating nanoparticles of pure carboxylic acids (most of which are not amenable to nanoparticle generation) from the actual desorption and analysis of the compounds themselves. We thus adopted the approach of applying picogram levels of carboxylic acids directly to the filament. This is done by preparing dilute aqueous solutions of each acid and then applying the solution to the filament using a microsyringe. By performing multiple dilutions, sample masses as small as 1 fg can be applied to the filament. For the experiments on mixtures of carboxylic acids, described in Section 4.3, mass ratios are created by mixing aqueous solutions of individual carboxylic acid compounds. This mixture is then applied to the collection filament with a microsyringe. Water blanks were used to create background mass spectra that we subtracted from our sample mass spectra. Background spectra were also obtained in which the filament was exposed to ambient air for the same period as that required for sample preparation, but these spectra did not differ from those obtained using water blanks. We typically ran three sample runs and one water blank for each compound or mixture tested.

The thermal desorption profile that is used for this study is the same as that currently used in our ambient measurements. Fig. 2 shows a representative profile, in which a 450 K constant temperature step is applied for 30 s, followed by a 300 s linear ramp to ~770 K. The 450 K lower limit corresponds to the minimum turn-on voltage of the thyristor circuitry used to control the power applied to filament, whereas the upper temperature was selected to ensure desorption of non-refractory constituents [32]. These temperatures are experimentally determined using a 0.12 mm diameter thermocouple (model CHAL-005; Omega Engineering, Inc.), which allows a direct measurement of the surface temperature while minimally perturbing heat transfer. These measurements show that the temperature of the filament is constant over the region that is in contact with particles, which extends approximately 1 cm from the tip of the filament loop.

Table 1
Chemicals used in the current study

Compound	MW	Density (g ml^{-1})	Melting point (K)	Purity (%)
Butanoic	88	0.96	−5.5	>99
Pentanoic	102	0.93	−34	>99
Hexanoic	116	0.92	−4	>99.5
Heptanoic	130	0.91	−7.5	96
Octanoic	144	0.91	16.3	>98
Butanedioic	118	1.56	185	99
Pentanedioic	132	1.43	98	99
Hexanedioic	146	1.36	151	99
Heptanedioic	160	1.28	105	99
Octanedioic	174	1.27	143	98

TDCIMS mass spectrometer data are acquired as negative ions, first scanning the full range of m/z up to twice the molecular weight of the parent ion in order to identify all major ions and potential clusters. Once these are determined, we monitored only those ions that are generated from the sample during desorption in order to maximize temporal resolution. Ion abundance data will be presented as the instrument response, which we define as the integrated area of the ion signal during sample desorption, corrected for dead time, divided by the mass of analyzed sample. This is to be distinguished from the calibration factor, defined as the instrument response normalized by the integrated area of the reagent ion signal during sample desorption. The difference between these two parameters is important: the instrument response is an indication of the signal that one might expect from a given collected sample under normal operating conditions, whereas the calibration factor takes into account day to day variations in ion transmission caused by temperature, pressure, and minor differences in instrument configuration such as ion lens voltages. In this manuscript we present the ion abundance data in terms of the instrument response since the focus of our study is on the performance of the instrument to carboxylic acids and this is the clearest way of demonstrating performance. Calibration factors for each of the compounds studied have been tabulated for our future studies, but these are not presented below.

In order to confirm the relevance of our approach of directly applying compounds to the collection filament to the analysis of nanoparticles, we performed instrument sensitivity studies with butanedioic acid particles in the 10–30 nm diameter range. These particles were generated using a home-built aerosol atomizer, using the same sample solutions that were prepared for the direct application studies describe above. Both the particle size and collection time were varied to obtain a plot of instrument response versus collected aerosol mass, using techniques described previously [15].

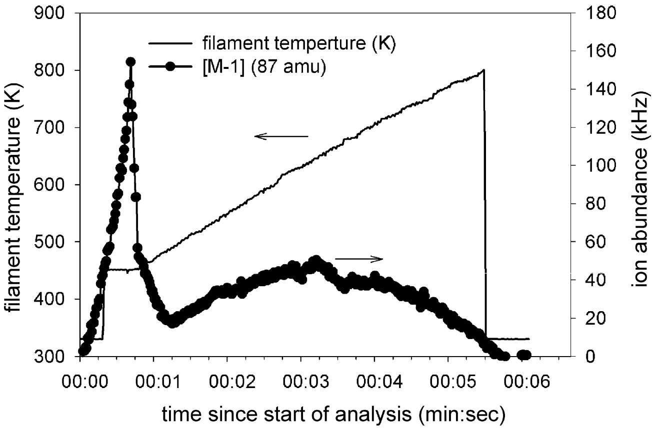

Fig. 2. Abundance of the [M-1]$^-$ ion plotted alongside desorption temperature for butanoic acid that has been directly applied to the filament.

4. Results and discussion

4.1. Studies of directly applied monocarboxylic acids

All monocarboxylic acids tested underwent minimal fragmentation during desorption and analysis, with the main peak corresponding to the loss of the proton $[M-1]^-$. The $[M-1]^-$ ion confirms that the ion source chemistry is dominated by proton exchange with reagent O_2^- ions. Fig. 2 shows plot of the time variability of the ion signal during desorption for the $[M-1]^-$ butanoic acid carboxylate anion. The $[M-1]^-$ signal is characterized by two peaks: one that starts immediately upon inserting the filament into the ion source and peaks during the application of the initial 450 K temperature step function and one at a temperature of 640 K. Previous studies of the vapor pressure of monocarboxylic acids showed that most of these compounds desorb at or below room temperature [28]. Thus, the peak that occurs during the initial temperature step probably corresponds to the evaporation of the butanoic molecules that do not interact with the Pt collection filament surface. We postulate that the high temperature peak corresponds to molecules that adsorb to the metal surface. A similar adsorptive behavior was observed for a gold surface during studies of carboxylic acids using the thermal desorption particle beam mass spectrometer [28], which the authors attribute to van de Waals forces from the alkyl chains of the compounds. This phenomenon is also observed on Pt surfaces for aqueous low molecular weight monocarboxylic acids [33,34] and for dicarboxylic acids [29] at high temperatures in the presence of oxygen, where dissociative adsorption occurs forming a surface acetate species. All other monocarboxylic acids tested showed similar temperature profiles, characterized by an initial peak that occurs during the application of the 450 K temperature step as well as slowly varying peak that appears at increasingly higher temperatures for higher molecular weight species.

Fig. 3 shows a summary of instrument response for the monocarboxylic acids studied. The error bars in the plot show the standard error from the three separate runs performed for each compound, and are more representative of our ability to place a precise volume of aqueous solution on the wire than they are a measure of the inherent variability in instrument response, which typically exhibits a 1% variation in ion abundance. As Fig. 3 shows, the response varies from ~3 Hz pg^{-1} for octanoic acid to ~8 Hz pg^{-1} for butanoic and pentanoic acids. The data show a general trend towards lower sensitivity for the higher MW monocarboxylic acids. Over this *m/z* range, the ion transmission in the mass spectrometer has been determined to be constant.

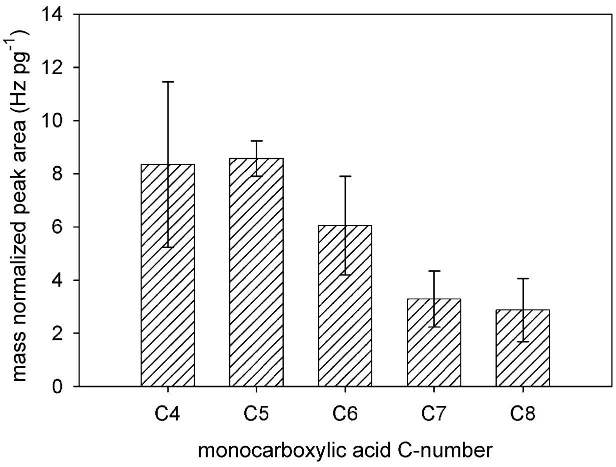

Fig. 3. TDCIMS sensitivity to directly applied monocarboxylic acid samples.

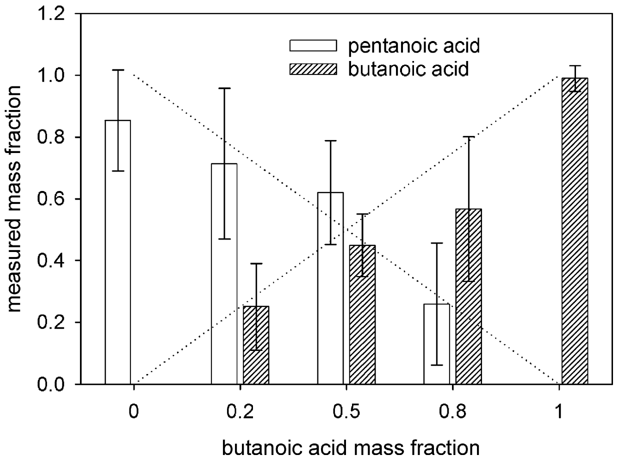

Fig. 4. TDCIMS experimentally derived mass fractions for binary mixtures of butanoic and pentanoic acids. Dashed lines show 1:1 mixture mass fractions.

We also performed a set of experiments on a mixture of two monocarboxylic acids to investigate whether the instrument sensitivities observed for the individual compounds in a mixture are the same as those of the pure samples. Fig. 4 shows the result for a mixture of pentanoic and butanoic acids. The ordinate of the plot in Fig. 4 is the experimentally determined mass fraction [35], defined as the fraction of collected mass that can be described as the pure compound, which assumes that the calibration factors for the mixture are the same as for pure compounds. The plot shows linear response for each compound in the mixture, which implies that both compounds evaporate completely and are converted to deprotonated forms independently. The latter may be a result of efforts placed on keeping reagent compounds in great excess compared to the analyte, thus minimizing reagent depletion and the resulting competition between desorbed compounds for the reaction with the reagent ions in the ion source, which had been observed in early studies with the TDCIMS prior to the implementation of temperature programming [16].

4.2. Studies of directly applied dicarboxylic acids

Fig. 5 shows a plot of the time variability of the ion signal during the thermal desorption of a representative dicarboxylic acid, butanedioic acid. The data show the prompt formation of low levels of $[M-47]^-$ when the filament is first introduced into the ion

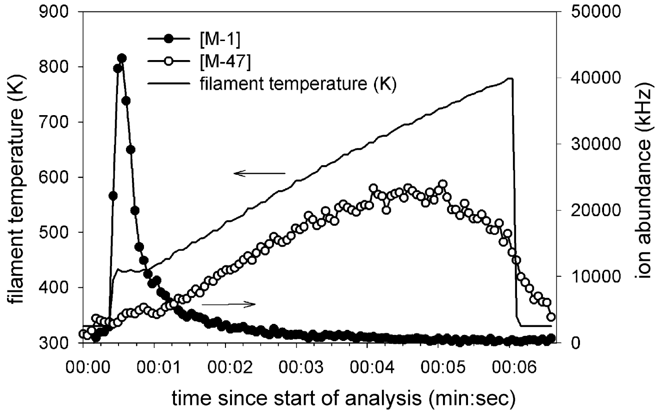

Fig. 5. Abundance of the major ions, plotted with desorption current, for butanedioic acid that has been directly applied to the filament.

source and before resistive heating of the filament. Immediately following the application of the 450 K temperature step, a strong peak is seen in [M-1]⁻, which decays without forming a secondary peak as seen with the monocarboxylic acids (Fig. 2). The increase in [M-47]⁻ occurs at high temperatures (∼700 K) following the decrease in the parent ion concentration. As the temperature of the filament increases, we postulate that the dicarboxylic acids undergo a cyclization reaction [36] resulting in the loss of neutral formic acid. The formic acid will undergo deprotonation in the ion source. We observed a small peak in the 45 *m*/*z* signal that corresponded to the appearance of the M-46 fragment. The overall contribution of the 45 *m*/*z* signal is small, however, and is not reported.

Fig. 6 summarizes the results of sensitivity studies for dicarboxylic acids. As in the case of the monocarboxylic acids, a prominent [M-1]⁻ anion was observed for all of the dicarboxylic acids that we chose to study. No evidence of dianion formation was apparent in any of the spectra. Instrument responses for the [M-1]⁻ ions ranged from 51 ± 5 pg^{-1} for pentanedioic acid to 260 ± 30 Hz pg^{-1} for octanedioic acid. Unlike the monocarboxylic acids, no decrease in instrument response can be associated with increased *m*/*z*. However, a distinct pattern of alternating high and low responses to even and odd carbon number, respectively, can be seen in Fig. 5. The source of this variation is likely the alternation of vapor pressure to carbon number of the dicarboxylic acids, which has been observed in several studies [28,31]. This is attributed to differences in the crystal structures of solid compounds [37]. This alternation in vapor pressure has also been observed with the monocarboxylic acids [28], however this effect is not as pronounced as for the dicarboxylic acids and thus may be masked by other phenomena such as surface interactions. This may be one reason why we did not observe a similar pattern in our studies of monocarboxylic acids. The [M-1]⁻ ion is the prominent ion for all dicarboxylic acids with the exception of butanedioic acid, for which the instrument response for the [M-47]⁻ fragment is 260 ± 36 Hz pg^{-1}, three times that of [M-1]⁻.

4.3. Studies of pure butanedioic acid nanoparticles

Our experiments with directly applied carboxylic acids show that the TDCIMS has sufficient sensitivity to detect picogram levels of these compounds in condensed phase samples. As a final test of the potential of the instrument for measuring these compounds in aerosols, we generated 10–30 nm diameter particles of butanedioic acid and introduced these particles into the TDCIMS inlet. Measurements were performed on the [M-47]⁻ fragment, since it was shown to have the highest abundance of the ions from butanedioic acid.

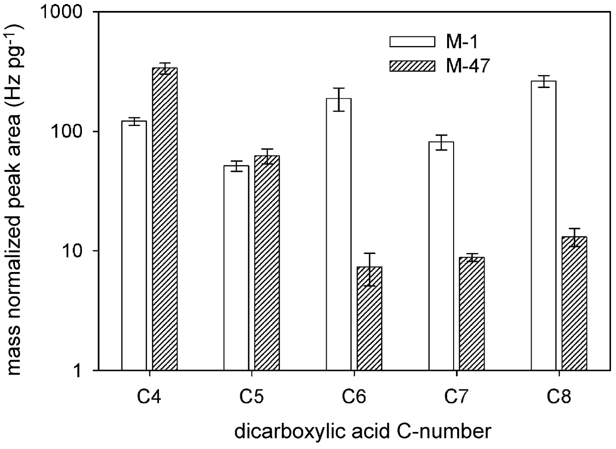

Fig. 6. TDCIMS sensitivity to directly applied dicarboxylic acids. Major fragments are the deprotonated parent ion [M-1]⁻ and loss of formic acid from deprotonated parent [M-47]⁻.

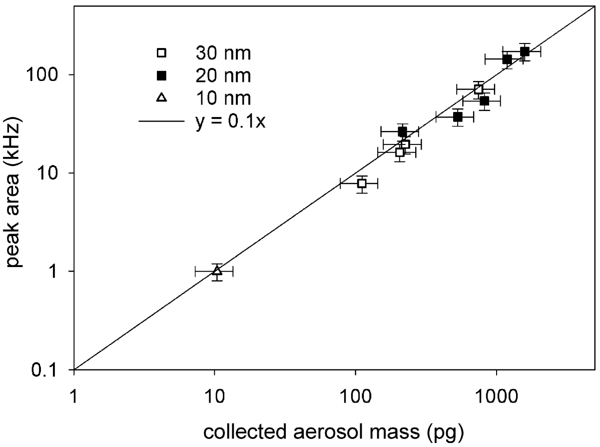

Fig. 7. TDCIMS sensitivity to the [M-47]⁻ ion for laboratory generated butanedioic acid aerosol.

Fig. 7 shows the resulting plot of integrated ion signal, corrected for deadtime, versus collected particulate mass. The collected particulate mass was calculated using the technique described previously [35], in which the exhaust flow from the inlet was monitored before and during collection and the ratio of concentrations used to estimate the amount of aerosol deposited on the collection filament. The plot shows a linear dependence of [M-47]⁻ ion desorption peak area to collected aerosol mass over the 10–30 nm diameter range. This linearity over all particle sizes shows that we have adequately accounted for size-dependent factors in particle sampling. It also confirms our estimates that, even at the highest mass loadings, the coverage of particles on the filament surface is less than one monolayer, since multiple layers of collected particles are likely to exhibit different desorption efficiencies due to different particle-surface interactions and thus result in a non-linear response with collected mass.

The slope of the line passing through the points in Fig. 7 is a measure of the instrument sensitivity that includes the effects of particle loss within the inlet as well as the non-optimal deposition of particles along the length of the collection filament. This results in an instrument sensitivity for aerosol of 100 Hz pg^{-1}. This is compared with 260 Hz pg^{-1} in the case of [M-47]⁻ anion of directly applied butanedioic acid solution (Fig. 5). The ratio is 0.38, which incorporates both the efficiency by which particles are transported from the filament region to the exhaust port of the TDCIMS as well as the efficiency by which particles deposited onto the filament are ultimately desorbed and analyzed. This is a reasonable value considering the physical effects (e.g., diffusion) that make sampling aerosol different from directly applying samples to the filament.

5. Conclusion

We have reported improvements to the operation of the TDCIMS, most importantly the implementation of a temperature programmed thermal desorption scheme, which has allowed us to characterize organic compounds in picogram levels of condensed phase samples as required for the analysis of ambient atmospheric nanoparticles. Experiments with monocarboxylic acids show that compounds containing four to eight carbon atoms are ionized by the loss of a proton to reagent O_2^- without observable fragmentation and with sensitivities that range from 3 to 8 Hz of integrated ion signal per picogram of sample. We also investigated our ability to quantify the composition of multicomponent samples by analyzing a binary mixture of butanoic and pentanoic acids. Those experiments demonstrated that desorption and ionization for these compounds are independent processes that follow the same calibrated behavior as pure compounds. Similarly, dicarboxylic acids containing four to eight carbon atoms were investigated. The analysis of directly applied, pure dicarboxylic acids showed that the major fragments were the deprotonated parent ion $[M\text{-}1]^-$, and the loss of formic acid from the deprotonated parent $[M\text{-}47]^-$. Sensitivities for dicarboxylic acids are higher than those for the monocarboxylic acids, ranging from 50 to 260 Hz pg^{-1} for $[M\text{-}1]^-$ and 7 to 337 Hz pg^{-1} for $[M\text{-}47]^-$. For comparison, in a similar study performed on ammonium sulfate aerosols we observed an instrument response to the HSO_4^- ion of 100 Hz pg^{-1} (Fig. 6b in ref. [16]), which is consistent with the dicarboxylic acid results. While we have no definitive explanation for why the instrument response is lower for the monocarboxylic acids, it is possible that some of the material may have evaporated after it was applied to the filament and before analysis. As discussed in Section 4.1, this hypothesis is supported by other studies that show that most of these compounds desorb at or below room temperature [28]. However, as Fig. 2 shows, the $[M\text{-}1]^-$ ion abundance is zero when the filament is first inserted into the ion source, which does not support this hypothesis. Further investigations into the causes of this lower instrument response to these compounds are needed.

Finally, we performed experiments with pure butanedioic acid aerosol in the 10–30 nm diameter range. These demonstrated that the extension of these results of directly applied compounds to actual organic nanoparticles is valid.

The Poisson statistical uncertainty for a measurement varies as the square root of the number of counts (e.g., an uncertainty of $\sim$3% occurs when 1000 counts are recorded). During typical sampling conditions of ambient atmospheric aerosols, 10–100 pg of particles are collected. Thus, the sensitivities reported here suggest that statistical uncertainties associated with pure 10 pg samples will be 11–18 and 2–4% for the monocarboxylic and dicarboxylic acid $[M\text{-}1]^-$ ions, respectively. For mixed aerosol, such as that expected in ambient air, sensitivity to about 0.1 pg of particles is desired, corresponding to statistical uncertainties of 20–44% for the dicarboxylic acid $[M\text{-}1]^-$ ions. This is similar to the uncertainties that we observe for sulfate in mixed aerosol samples [35], suggesting that for these compounds the instrument is sufficiently sensitive as to allow for their detection in ambient aerosols.

While the investigations reported in this manuscript focus on carboxylic acids, we expect that many classes of organic compounds can be similarly analyzed with minimal fragmentation and high sensitivity. These include species that are ionized by proton transfer with water to become cations, such as amines, aldehydes, ketones, and alcohols. Additional tests with these and many more compound classes are planned to aid in the interpretation of field measurements.

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