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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,

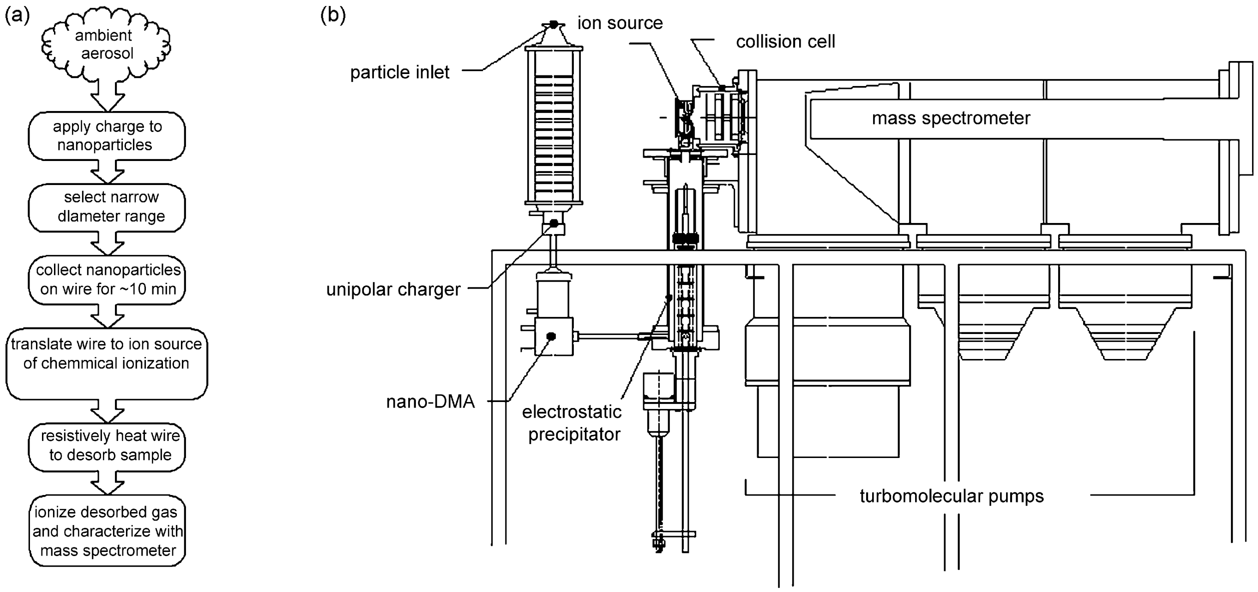

Fig. 1. (a) Flow diagram of TDCIMS particle collection and analysis and (b) TDCIMS schematic.