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International Journal of Mass Spectrometry 263 (2007) 1–11

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Development of a PTR-TOFMS instrument for real-time measurements of volatile organic compounds in air

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Received 14 December 2006; received in revised form 10 January 2007; accepted 10 January 2007
Available online 20 January 2007

Abstract

A proton transfer reaction-time-of-flight mass spectrometer (PTR-TOFMS) has been developed for real-time measurements of volatile organic compounds in air. The instrument is designed to be operated with a hollow cathode discharge ion source and an ion drift tube at relatively high pressures. Each component of the system, an ion source, a drift tube, an ion transfer region, and a time-of-flight mass spectrometer, are in detail characterized by a number of laboratory experiments. The optimized instrumental configuration enables us to gain high intensities of hydronium (H_3O^+) ions, typically $\sim 7 \times 10^5$ counts for 1-min integration at a drift tube pressure of $\sim$5 Torr. It also suppresses background signals, and interferences from sample air (NO^+ and $O_2{}^+$), which undergo fast reactions with volatile organic compounds, to $\sim$0.5% of those of H_3O^+ ions. We find that the use of the custom-built discharge source show higher overall sensitivities than of a commercially available radioactive source. Potentials to detect oxygenated VOCs (aldehydes, ketones, and alcohols), halocarbons, and amines are also suggested. The detection limits for acetaldehyde, acetone, isoprene, benzene, toluene, and *p*-xylene were determined to be at the sub-ppbv levels for a 1-min integration time. A good linear response at trace levels is certified, but slight sensitivity dependency on water vapor contents is revealed. We finally demonstrate that the instrument can be used for on-line monitoring to detect large variations from emission sources in real-time.

Keywords: Proton transfer reaction; Time-of-flight mass spectrometry; Volatile organic compound; Chemical ionization; PTR-MS

1. Introduction

Volatile organic compounds (VOCs) are a generic name of the compounds that are readily vaporized into the atmosphere at normal temperature and pressure. It is well known that VOCs are emitted from a variety of sources into the atmosphere, and play important roles in controlling air quality by acting as a fuel for gas-phase photochemistry, leading to the formation of ozone and secondary aerosols [1,2]. However, there exist hundreds of VOCs, in particular, around urban area where VOC emissions from human and industrial activities are diverse and strong [3], prohibiting accurate and precise evaluations of the roles of VOCs in air quality issues. It is also widely known that overwhelming amounts of VOCs are emitted from the biosphere including land ecosystems and the ocean into the atmosphere [4,5]. Majorities of biogenically emitted VOCs are short-lived due to their high reactivity, and play a part in not only photochemistry but also in the carbon cycle of the earth [6]. For both anthropogenic and biogenic VOCs, unsaturated (alkene, diene), oxygenated (aldehyde, ketone, alcohol), and aromatic hydrocarbons are recently highlighted in several field studies [7–11]. Owing to a variety of speciation and high reactivity (hence short lifetime and low abundance in air), understanding of the behavior and the roles

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doi:10.1016/j.ijms.2007.01.009

of these VOCs in the atmosphere is still limited by quantity and quality of the measurements, and requires advancement in measurement technologies.

A gas chromatographic (GC) method has been widely used for identification and quantification of VOCs, often being coupled with a mass spectrometer (MS) and/or a flame ionization detector (FID). Although a so-called GC/MS technique has an advantage of separating a number of VOC species and of detecting trace amounts, it commonly suffers from time-resolution. The GC/MS method needs pre-treatment including pre-concentration with cryogenic traps followed by thermal desorption of target species. Also, when air is sampled with canisters or adsorbents, the analysis is off-line and requires further time. Thus analysis with GC/MS is time consuming, and typically takes at least tens of minutes per sample [12]. Also, during sample storage and pre-treatment, species with high reactivity are subject to possible loss and/or transformation by uptake onto metal-surface and by reactions with oxidants (e.g., ozone), respectively [12].

Proton transfer reaction-mass spectrometry (PTR-MS) is a newly developed on-line method that might compliment the conventional GC technique. The proton transfer reaction (PTR) ionization is one of chemical ionization (CI), which enables soft ionization of chemical species that have a proton affinity higher than that of the reagent species (i.e., water in many cases). The PTR from hydronium ions (H_3O^+) occur with many VOCs except low-molecular weight non-methane hydrocarbons (NMHCs), and it produces predominantly protonated ions with less fragmentation than electron-impact ionization (El) does. The PTR-MS instrument was first reported by the group at Innsbruck University [13,14] who coupled a hollow cathode discharge ion source and a drift tube with a quadrupole mass spectrometer (QMS). This development allows on-line measurements of VOCs at parts per trillion by volume (pptv) levels without any pre-concentrations, and is now used to identify the speciation of VOCs and quantify their mixing ratios in environmental, medical, and food applications [15]. However, simultaneous detection of several VOCs is not achieved due to the use of a quadrupole mass spectrometer for the detection of ions.

Recently, applications of the PTR ionization method to other mass spectrometric detections including ion trap and time-of-flight mass spectrometers (TOFMS) have been reported. The use of ion trap mass spectrometry (ITMS) has the advantage of a high duty cycle. It also has applications of collision-induced dissociation to help diagnose molecular structure of the target species analyzed. For example, a proton transfer reaction-ion trap mass spectrometer (PTR-ITMS) has a potential to distinguish isobaric species (e.g., methacrolein and methylvinyl ketone) [16,17]. The use of TOFMS has an advantage of high mass resolution, leading to explicit identification of the compounds of interest. Proton transfer reaction-time-of-flight mass spectrometer (PTR-TOFMS) instruments with a high mass resolution ($m/\Delta m > 1000$) have been reported, being coupled with radioactive and hollow cathode ion sources [18–20]. Practically, separation of isobaric compounds would be easier with PTR-TOFMS than with PTR-QMS. For example, formic acid (46.0055 amu) and ethanol (46.0419 amu) can be distinguished by PTR-TOFMS [20]. However, the sensitivity of this discharge-based instrument was far less than that of current PTR-QMS instruments. Also, a large amount of NO^+ and $O_2{}^+$ ions were produced, likely due to the back-diffusion of air from the drift tube to the hollow cathode ion source [20]. Since the existence of NO^+ and $O_2{}^+$ ions makes interpretation of PTR mass spectra more complicated by producing unfavorable ions in the reaction with VOCs, the formation of NO^+ and $O_2{}^+$ ions should be suppressed both in the ion source and the drift tube.

We have developed a PTR-TOFMS instrument for simultaneous and real-time detection of VOCs that play important roles in the formation of ozone and secondary organic aerosols (SOA) in air. These species include unsaturated (alkene, diene), oxygenated (aldehyde, ketone, alcohol), and aromatic hydrocarbons. Our PTR-TOFMS instrument is a combination of a custom-built ion source/drift tube and an orthogonal time-of-flight mass spectrometer. The hollow cathode discharge ion source was designed to be coupled with an ion drift tube operated at a pressure of ∼5 Torr, which is higher than that of the current PTR-QMS and PTR-TOFMS instruments using a hollow cathode discharge ion source. This has a potential advantage to enhance sensitivity, because a larger amount of sample gases can be introduced into the drift tube. We report here the design and characteristics of our PTR-TOFMS system, and demonstrate its overall performance.

2. Instrumental description

The National Institute for Environmental Studies (NIES) PTR-TOFMS is a custom designed and built instrument, and has been characterized by a number of laboratory experiments. A schematic diagram of the instrument is shown in Fig. 1. It consists of four components: (1) an ion source, (2) a drift tube, (3) an ion transfer chamber, and (4) a time-of-flight mass spectrometer. Air samples are delivered to the instrument by means of 1/8-in. PFA-Teflon tubing with a residence time of less than 10 s. The sample inlet is pressure-controlled by means of a back-pressure controller, but is not temperature-controlled. No particle filter is placed at the inlet to avoid artifact from organics deposited on the filter. The instrument is relatively compact in size, and the overall dimension excluding electronics is 800 mm (*W*) × 500 mm (*D*) × 800 mm (*H*).

In the ion source reagent ions are generated from water vapor introduced as a reagent gas by either radioactive or discharge ion sources. The drift tube is a region where proton transfer reaction occurs from reagent ions to sampled VOCs. In the drift tube, gas phase samples are introduced at the top of it, and ion–molecule reactions between hydronium ions and VOCs take place. Each VOC sampled is then ionized to be VOC·H$^+$, as expressed in the following Eq. (1):

$$\mathrm{VOC} + \mathrm{H_3O^+} \rightarrow \mathrm{VOC{\cdot}H^+} + \mathrm{H_2O} \tag{1}$$

The ion transfer chamber is an interface of the drift tube to a TOFMS. The protonated ions outgoing from the drift cell are extracted, and then directed to a pulse extraction region through