



Humidity independent mass spectrometry for gas phase chemical analysis via ambient proton transfer reaction



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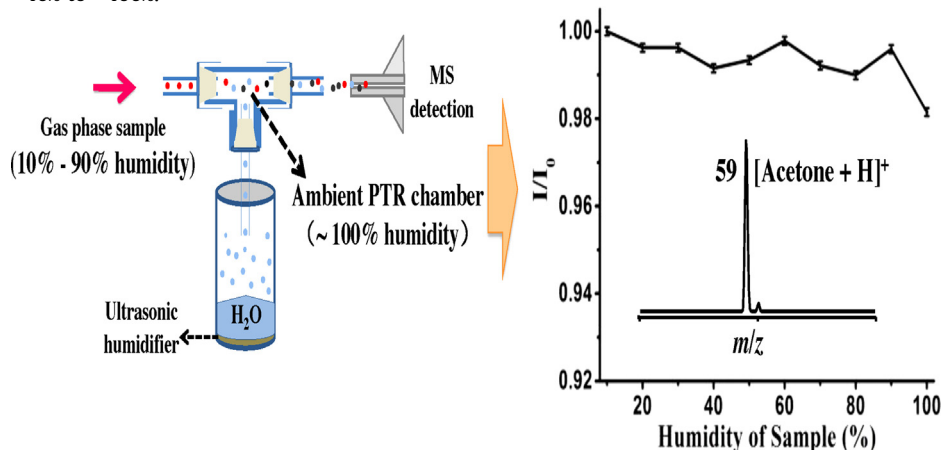
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HIGHLIGHTS

- A humidity independent mass spectrometric method for gas phase samples analysis.
- A universal and good sensitivity method.
- The method can real time identify plant released raw chemicals.

GRAPHICAL ABSTRACT

Direct and humidity independent mass spectrometry analysis of gas phase chemicals could be achieved via ambient proton transfer ionization, ion intensity was found to be stable with humidity ranged from ~10% to ~100%.



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ABSTRACT

In this work, a humidity independent mass spectrometric method was developed for rapid analysis of gas phase chemicals. This method is based upon ambient proton transfer reaction between gas phase chemicals and charged water droplets, in a reaction chamber with nearly saturate humidity under atmospheric pressure. The humidity independent nature enables direct and rapid analysis of raw gas phase samples, avoiding time- and sample-consuming sample pretreatments in conventional mass spectrometry methods to control sample humidity. Acetone, benzene, toluene, ethylbenzene and *meta*-xylene were used to evaluate the analytical performance of present method. The limits of detection for benzene, toluene, ethylbenzene and *meta*-xylene are in the range of ~0.1 to ~0.3 ppbV; that of benzene is well below the present European Union permissible exposure limit for benzene vapor ($5 \mu\text{g m}^{-3}$, ~1.44 ppbV), with linear ranges of approximately two orders of magnitude. The majority of the homemade device contains a stainless steel tube as reaction chamber and an ultrasonic humidifier as the source of charged water droplets, which makes this cheap device easy to assemble and facile to operate. In addition, potential application of this method was illustrated by the real time identification of raw gas phase chemicals released from plants at different physiological stages.

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1. Introduction

Gas phase chemicals analysis plays an important role in a wide range of fields, such as environmental pollution, plant physiology, human health, homeland security and so on [1–11]. For example, European Union has established a strict safety limit for benzene of $5 \mu\text{g m}^{-3}$ (~ 1.44 parts-perbillion) taking effect in 2010 [12]. Gas phase chemicals are routinely monitored by electrochemistry [13], colorimetric [14–17], laser spectroscopy [18], ion mobility spectrometry [2] and mass spectrometry (MS) [1,11,12,19–29]. MS has become one of the most commonly used methods of gas phase analysis, after chromatography separation, GC/MS could provide both structural and quantitative information.

To avoid pre-concentration or chromatography separation, proton transfer reaction mass spectrometry (PTR-MS) [1,11,20,21,24,25,30] and selected ion flow tube mass spectrometry (SIFT-MS) [19,22,23] have been introduced as direct MS analysis methods for gas phase chemicals. However, to maximize proton transfer efficiency, vacuum or sub-vacuum drift tube is necessary for both PTR or SIFT. Moreover, the PTR process is strongly humidity dependent. That is mainly due to the increase in the amount of hydrated hydronium clusters within the drift tube as the humidity of the sample gas increases [1]. In addition, increased humidity will also enhance the rate of the reverse reaction since it increases the concentration of water vapor [1]. Thus, the humidity of the gas phase samples has to be well confined to maintain the domination of H_3O^+ in the reaction chamber [1,12,31]. Direct application of proton transfer in ambient pressure has been tried, known as ambient pressure proton transfer mass spectrometry (AmPMS) [32]. However, its proton transfer efficiency was limited because relative large hydrated hydronium clusters are formed as $(\text{H}_2\text{O})_n\text{H}^+$ ($n = 6-9$), which owns much higher proton affinities than that of traditional PTR-MS (majorly, $n = 1$) [1]. As a result, only chemicals with much higher proton affinities (e.g., amine and ammonia) could be efficiently ionized and analyzed [32]. Therefore, MS method that is free of time- and sample-consuming pretreatment (such as confining humidity) is still in great demand for rapid gas phase chemicals analysis.

Ambient ionization MS perfectly fits the sample pretreatment feature, which has been developed for chemicals identification in various phases [33–35]. Chemicals on solid surfaces or in liquid solutions could be identified within millisecond scale [36]. However, application of ambient ionization for gas phase samples has not been fully elucidated. An interesting observation was found in our recent investigation of paper assisted ultrasonic spray ionization mass spectrometry (PAUSI-MS) [37], with which huge quantities of fine water droplets were generated from ultrasonic humidifier. In the lower mass range, we found that most spectra were dominated with relative small hydrated hydronium clusters as $(\text{H}_2\text{O})_n\text{H}^+$ ($n = 1-4$), which were believed to be very effective for proton transfer reaction [1,38]. In addition, the amount of hydrated hydronium clusters remained relative stable with increased humidity of sample gas. Thus, we proposed a facile and humidity independent method for rapid MS identification of gas phase chemicals, which is based on the ambient proton transfer reaction between gas phase chemicals and hydrated hydronium clusters provided by PAUSI [37].

Herein, the proposed method, termed as ambient proton transfer ionization mass spectrometry (APTR-MS) was tested and then systematically studied. Proton donor $[(\text{H}_2\text{O})_n\text{H}^+, (n = 1-4)]$ are initially formed by the ultrasonic nebulization/ionization of water, to perform ambient ion/molecule reactions with high efficiency. Due to the large amount of water droplets provided by ultrasonic, humidity of the ambient reaction chamber is nearly over saturated. As a result, the humidity of the sample gas would not affect the proton transfer process, thus the sample humidity

would be no longer concerned in present method. The major advantages of APTR-MS could be concluded as: (1) humidity independent – the ionization efficiency would not be influenced by the humidity of gas phase samples, (2) good sensitivity – no discrimination in identification various chemicals and limit of detection for benzene was ~ 0.1 ppbV and (3) versatility – raw gas phase chemicals released from plant at different physiological stages were directly identified.

2. Materials and methods

2.1. Chemicals and reagents

Methanol, acetonitrile, acetaldehyde (40% water solution), formic acid, acetone, benzene, ethyl acetate and cyclohexanone were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). A Milli-Q-Plus ultra-pure water system from Millipore (Bedford, MA, USA) was used to obtain HPLC-grade water.

2.2. Design of APTR-MS

The schematic of home made APTR device is shown in Fig. 1 a. The setup consists of (1) an ultrasonic humidifier ion source to produce hydrated hydronium clusters, and (2) a stainless steel tube as ambient PTR chamber, for ion/molecule reaction. Gas phase samples containing various concentrations of analyte(s) were introduced into a T piece to mix/react with the hydrated hydronium clusters, which were produced by an ultrasonic humidifier (Yadu Technology Co., China. Model: YC-X100S, frequency: 1.7 MHz, Vp-p: 80V). Then the mixed gas stream entered the stainless steel tube as reaction chamber (10 cm length and ID 1/4 inch).

2.3. Sample introduction and vapor generation

In short, chemicals at various concentrations were prepared via dilution of saturated headspace of pure liquid analytes. The sample vapor generation and introduction method were similar with that of the previous literature [12] (see Supporting information).

The humidity of the sample gas was controlled by the addition of another air stream with saturated humidity, which is generated by continuous bubbling through a water reservoir (Fig. S1). By controlling the flow rate of the two gas streams, the final humidity of the air stream was controlled between relative 10% and 100%, which could be measured with an moisture sensor (Anymeters Instruments Technology Co., Ltd., Germany. Model: TH-2F). Then various gas phase chemicals at different concentrations were injected into that gas stream via a syringe pump with 1:1000 dilution ratios (sample gas flow rate: $30 \mu\text{L min}^{-1}$ and air flow rate: 30 mL min^{-1}).

2.4. Plant subjects

Two hyacinths for each flowering stage were put into a plastic storage box (20 cm \times 20 cm) for 12 h at room temperature. The plastic storage box was equipped with two forty centimeter-long Teflon transfer tube (i.d. 1/8 in.) at the opposite side of the box as gas inlet and outlet, respectively. Fresh room air was pumped into the box with an micro digraph pump (Hongchuangweiyue Electronic Technology Co., China. Model: HCG545DC-24) and the outlet was connected to the reaction chamber with mass flow rate controller.

2.5. Mass spectrometry

All experiments were carried out with a LTQ Velos Pro. mass spectrometer (Thermo Scientific, San Jose, CA, USA). Unless other

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