



Determination of alcohol compounds using corona discharge ion mobility spectrometry

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Abstract

Ion mobility spectrometry (IMS) is a very fast, highly sensitive, and inexpensive technique, it permits efficient monitoring of volatile organic compounds like alcohols. In this article, positive ion mobility spectra for six alcohol organic compounds have been systematically studied for the first time using a high-resolution IMS apparatus equipped with a discharge ionization source. Utilizing protonated water cluster ions $(\text{H}_2\text{O})_n\text{H}^+$ as the reactant ions and clean air as the drift gas, alcohol organic compounds, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol and 2-octanol, all exhibit product ion characteristic peaks in their respective ion mobility spectrometry, that is a result of proton transfer reactions between the alcohols and reaction ions $(\text{H}_2\text{O})_n\text{H}^+$. The mixture of these alcohols, including two isomers, has been detected, and the results showed that they could be distinguished effectively in the ion mobility spectrum. The reduced mobility values have been determined, which are in very well agreement with the traditional ^{63}Ni -IMS experimental values. The exponential dilution method was used to calibrate the alcohol concentrations, and a detection limit available for the alcohols is in order of magnitude of a few ng/L.

Key words: alcohols; VOCs; ion mobility spectrometry; proton transfer reaction

Introduction

Alcohols have long been used in large quantities as industrial solvents. They have also been used as motor vehicle fuels and additives to gasoline. Natural emission source of alcohols include volcanic gases, vegetation, human breath, microbes and insects. It is known that the oxygenated organic compounds, alcohols, are harmful to organism (Stutte *et al.*, 2006), and in the troposphere it may influence some important atmospheric processes, producing free radicals and influencing the oxidization capacity and the ozone-forming potential of the atmosphere. It also may contribute significantly to the organic component of aerosols (Grosjean *et al.*, 1993; Grosjean, 1997; Singh *et al.*, 1995). The monitoring and analysis of volatile organic compounds (VOCs), such as alcohols, in ambient air are typically performed using canister gas collection and sample enrichment, and analyte identification and quantification is normally achieved using thermal desorption GC/MS (Allen *et al.*, 2001). The conventional GC/MS method is valid in the determination of alcohol com-

pounds. However, this technique requires time-consuming gas collection, preconcentration, extraction and separation steps prior to MS analysis, thus it is difficult for GC/MS technique to carry on real-time monitoring on-site. Besides, MS instrument must work in a high vacuum environment and the whole GC/MS system is bulky and expensive.

Ion mobility spectrometry (IMS) is small and inexpensive equipment running under atmospheric pressure, thus it is excellently suited for on-line selective monitoring of VOCs. IMS distinguishes ions on the basis of their differences in ionic drift velocities through a gas under applied electrostatic field. Ions with different masses or structures possess different movement velocities in a uniform field, thus they can be separated.

IMS has been demonstrated to be a sensitive technique for the detection of trace organic compounds. Its ppbv or pg detection limit, a few second response time, and compact instrumental volume have made it become increasingly popular in determining organic gaseous compounds in air (Buryakov, 2003). For instance, in early 1990s IMS was used to detect the halothane, enflurane, and isoflurane anesthetics in atmosphere (Eiceman *et al.*, 1989), the concentrations detected for the three compounds were about 10, 10 and 100 ppbv respectively. In recent years, important pollutants benzene, toluene, xylene, phos-

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gene, and acrolein in air have been determined by using a high resolution IMS (Leonhardt *et al.*, 2000).

The capability of IMS to detect alcohols was demonstrated by several research groups (Karasek and Kane, 1972; Eiceman and Karpas, 2005; Kotiaho *et al.*, 1995). In these measurements, the ionization sources they employed in the IMS were ^{63}Ni . The potential problem in the ^{63}Ni -IMS application is a limited range of measurable concentration and a lot of regulatory requirements as to the usage of radioactive material. In 2001, Sieleman *et al.* (2001) reported the detection of alcohol compounds using UV photo-ionization ion mobility spectrometry (UV-IMS) equipped with a 10.6-eV UV lamp. The available detection sensitivity is a few ppm. As well known, the UV lamp normally is somewhat expensive and has a usage lifetime of about 1–2 years owing to contamination and deliquescence on the optical windows.

Recently, another non-radioactive ionization source, discharge ionization source has been combined with IMS (Schmidt *et al.*, 2000; Khayamian *et al.*, 2001). And preliminary investigations have shown that corona discharge IMS (CD-IMS) has better sensitivity than the ^{63}Ni -IMS (Borsdorf *et al.*, 2002, 2005). However, these experiments also indicate that some organic compounds display very different ion mobility spectral characteristics from the ^{63}Ni -IMS. This implies that the previously compiled IMS database (Agbonkonkon *et al.*, 2004) in ^{63}Ni -IMS instrument will be no longer applicable if a corona discharge was used as the ionization source in IMS. Thus, it will be necessary to restudy the ion mobility spectrometry once using a more sensitive CD-IMS. In this work, the quantitative determination of six alcohol compounds has been systematically elucidated for the first time on a corona discharge ion mobility spectrometer. The ionic mobility spectra, their reduced mobilities, and the limit of detection have been given.

1 Experimental

The corona discharge ion mobility spectrometer was constructed in our laboratory. Its design is basically analogous to the IMS described by Schmidt *et al.* (2000). The experimental setup is schematically shown in Fig.1. It mainly consists of the ionization source, ion-molecule reaction region, drift region, and detector region.

The ions reacted with alcohol molecules to generate product ions are called reactant ions, which are formed in the ion source of the ion mobility spectrometer. In addition to non-radioactivity, another advantage of corona

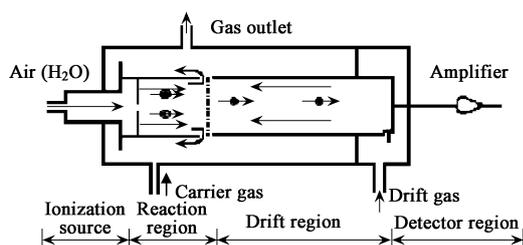


Fig. 1 Schematic diagram of ion mobility spectrometry apparatus.

discharge ionization source is that a higher yield of reactant ions can be gained comparing with ^{63}Ni or UV ionization source (Borsdorf and Rudolph, 2001; Borsdorf *et al.*, 2002; 2005). The enhancement in reactant ionic density may raise IMS response level and discrimination capability. In the reaction region, sample gas molecules were converted to product ions through reactions with the reactant ions. An ion shutter grid between the reaction and drift region was used to emit ion pulses into the drift region. The ions with different masses or structures acquired different drift velocities in the drift region under the influence of electric field, and they arrived successively at the downstream of the drift region, where a Faraday plate was located to transfer the ions signal to an amplifier fixed to the data processing system. The dependence of the ion intensity on the drift time was recorded as the ion mobility spectrum.

The ion drift velocity in an IMS is expressed as Equation (1) (Spangler, 1993).

$$v = KE \quad (1)$$

where, v is the velocity of ions, K is the mobility, and E is the electrostatic field in the drift region. If ionic drift distance is L , transit time in drift region is t , the ionic mobility can be derived according to the equation:

$$K = \frac{v}{E} = \frac{L}{Et} \quad (2)$$

The ion mobility K depends on ionic mass, collision cross-section, and drift gaseous temperature and pressure. Normally, the ion mobility is normalized to the reduced mobility K_0 , which is supposed to be unrelated to gaseous temperature T and pressure P in experiments. (Revercom and Mason, 1975).

$$K_0 = \frac{P}{760} \times \frac{273}{T} K \quad (3)$$

In this work, the temperature and pressure in the drift tube was kept in 287 K and 101 kPa, respectively. The drift and carrier gases used were purified air. The drift gas was brought into the drift region from the end of the tube so as to keep the drift region clean. Flow rates of the carrier and drift gases were 100 and 500 ml/min, respectively. The electric field strength within drift region was adjustable in the range of 300–400 V/cm. Six chemical reagents were ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol and 2-octanol, and they are all analytical reagents with the purities of above 99.7%.

2 Results and discussion

2.1 Reaction ions formation

The reactant ions used in this work were protonated water cluster ions $(\text{H}_2\text{O})_n\text{H}^+$, which were produced through a series of ion-molecule reactions ignited by ionizing the air involved a little amount of water in the ion source of IMS.

The most important reactions are (Good *et al.*, 1970):

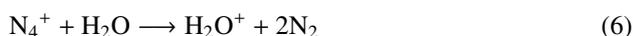


Fig.2 is a spectrum determined without introduction of any sample, in which only one reactant ion peak (RIP) is observable. According to Eqs. (2) and (3), its reduced mobility is $2.21 \text{ cm}^2/(\text{V}\cdot\text{s})$, which is very close to the reported mobility values of $(\text{H}_2\text{O})_3\text{H}^+$ ($2.26 \text{ cm}^2/(\text{V}\cdot\text{s})$), $(\text{H}_2\text{O})_4\text{H}^+$ ($2.19 \text{ cm}^2/(\text{V}\cdot\text{s})$) (Carroll *et al.*, 1975). Therefore, the reactant ions formed in the ion source likely included $(\text{H}_2\text{O})_n\text{H}^+$ ($n=3, 4$). Increase in temperature caused the RIP to change in position, this is due to the declustering of the hydrated cluster ions as reported by Eiceman and co-workers (1998), who studied the ion mobility spectral variation of the protonated water cluster ions $(\text{H}_2\text{O})_n\text{H}^+$ with temperature and moisture of the drifting air.

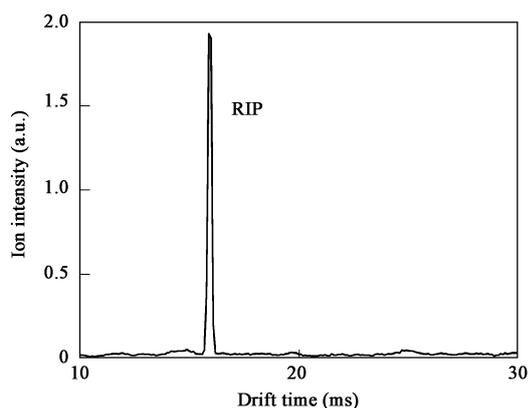


Fig. 2 High resolution ion mobility spectrum of RIP.

2.2 Determination of alcohols

If the cluster ions $(\text{H}_2\text{O})_n\text{H}^+$ are used as reagent ions, the ionic reaction can proceed only when the proton affinity (PA) of the sample molecule is greater than that of water (John, 2002). It is known that the PA of alcohol is always higher than the water. Thus the alcohols studied in this work can be ionized in the reaction region of IMS through the following proton transfer reaction (M =alcohol molecule):



In the experiments, when the alcohol sample was injected to the reaction region of the ion mobility spectrometer with a concentration of approximately $0.1 \mu\text{g/L}$ in the carrier gas of clean air, the intensity of the reactant ions immediately declined and new ion peak appeared in the longer drift time domain. The mobility spectra of ethanol, 1-butanol, 1-pentanol and 2-octanol are illustrated in Fig.3. It can be found that, the ionic drift time increases with the ion mass, thus ionic mobility decreases when ion has a higher mass according to Eq. (1).

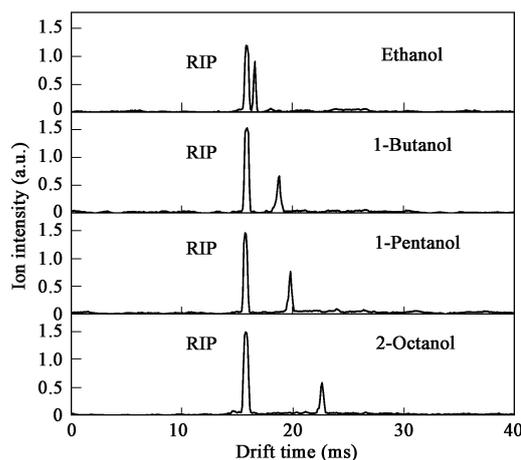


Fig. 3 Mobility spectra of ethanol, 1-butanol, 1-pentanol and 2-octanol.

2.3 Isomer determination

Ion mobility spectrometry distinguishes ionic species based on the differences of ionic masses and structures. This implies that IMS in principle can separate and identify isomeric compounds. But an important prerequisite is the IMS must have enough resolution. The ion separation capabilities of IMS are quantified using the resolving power R ,

$$R = \frac{t_d}{w_h} \quad (10)$$

where, t_d is the ion drift time and w_h is the full-width-at-half-height of the ion peak. As shown in Figs.2 and 3, the resolution of the IMS used in this study is about 60. It is possible to distinguish some isomeric compounds with such a high resolution IMS. Fig.4 displays the ion mobility spectra we measured for approximately $0.1 \mu\text{g/L}$ isomeric alcohols, 1-propanol and 2-propanol.

The drift times of the two isomer alcohols are 17.92 and 17.40 ms, respectively, demonstrating that our IMS indeed can distinguish isomeric compounds like 1-propanol and 2-propanol. It can be noted that the 1-propanol product ions have a longer drift time. This is due to 1-propanol product ion has a larger collision cross-section, thus more blocking its movement along electric field direction in the

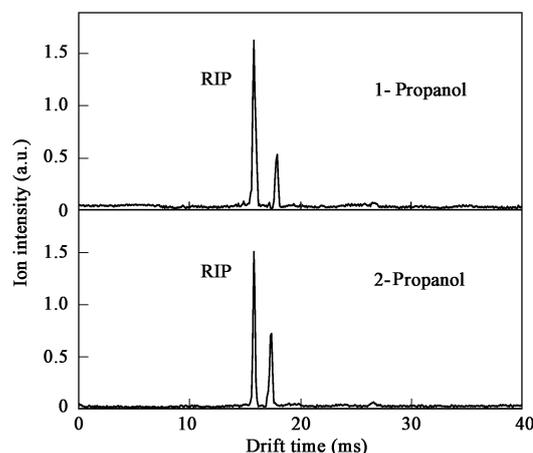


Fig. 4 Mobility spectra of isomer 1-propanol and 2-propanol.

drift gas. The influence of the structure on ion mobility has been reported in literature (Karpa, 1989). The general rules for the dependence of ion mobility on ionic structure are: linear < branched, primary < secondary < tertiary, aliphatic compounds < aromatic compounds, amines < amides.

2.4 Alcohols mixture determination

The simultaneous detection of multiple components of VOCs has been a challenge to the IMS measurement. A high resolution of IMS is essential to implement this task.

Fig.5 illustrates the ion mobility spectrum of a mixture of ethanol, 1-propanol, 2-propanol 1-butanol, 1-pentanol and 2-octanol. The first peak in the spectrum belongs to the reaction ions, and other six peaks are due to product ions arisen from six alcohols respectively. The two isomers, 1-propanol and 2-propanol, can also be separated clearly in this mobility spectrum.

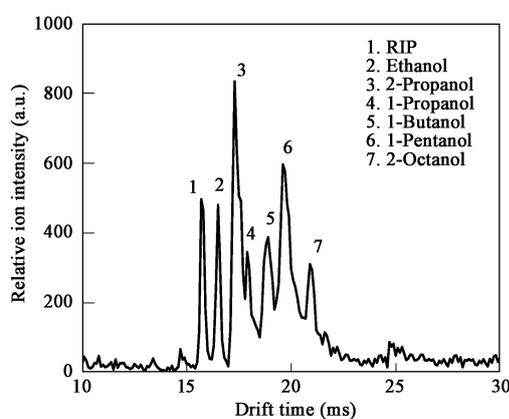


Fig. 5 Ion mobility spectrometry for the mixture of ethanol, 1-propanol, 2-propanol 1-butanol, 1-pentanol and 2-octanol.

2.5 Reduced mobilities

The accuracy of mobilities measured in this work was checked by comparison of the reduced mobility K_0 . The K_0 values for six alcohols, determined based on the Eq. (4), are listed in Table 1 along with the results from ^{63}Ni -IMS measurements and neutral network calculations. Our experimental data are in accord with the experiment and the theory (Matthew *et al.*, 1996).

The reduced mobility values decrease with the increasing in the ions masses of alcohols. As shown in Fig.6, the reduced mobilities are nearly linear correlation with ionic masses, which indicates the drift time of ion in the IMS is

Table 1 Reduced mobility K_0 of ions formed in six alcohol compounds

Compound	Reduced mobility K_0 ($\text{cm}^2/(\text{V}\cdot\text{s})$)		
	This work	^{63}Ni -IMS	Neural network
Ethanol	2.06	2.06	1.97
1-Butanol	1.83	1.82	1.80
1-Pentanol	1.72	1.70	1.71
2-Octanol	1.51	-	-
1-Propanol	1.95	1.93	1.85
2-Propanol	1.99	1.98	1.93

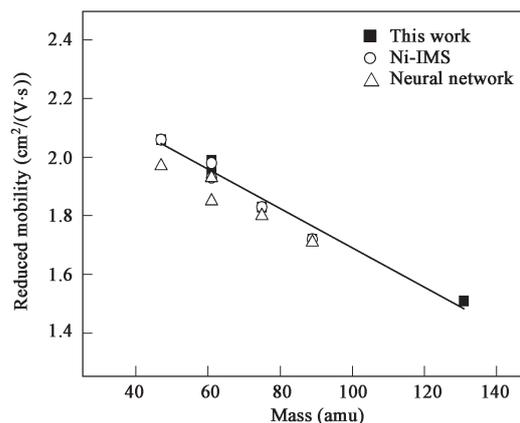


Fig. 6 Dependence of reduced mobility on ionic mass.

primarily proportional to the mass of the product ions.

2.6 Limit of detection

In order to investigate the sensitivity of the ion mobility spectrometer, the exponential dilution flask (EDF), a traditional calibration technique often employed for gas detectors, was used (Sedlak and Blurton, 1976) to determine the detection limit. The alcohol vapor was injected into the reaction region of IMS by the carrier gas through Teflon tubes connected with the EDF.

When the samples were injected into the reaction region of the ion mobility spectrometer at a high concentration beyond approximately $0.5 \mu\text{g/L}$, the protonated dimer ions $(\text{H}_2\text{O})_m\text{M}_2\text{H}^+$ appeared in the spectrum, which were formed due to the ions reaction between the protonated monomer ions $(\text{H}_2\text{O})_m\text{MH}^+$ and overmuch neutral alcohol molecules. As the concentration of the sample reduced, the intensity of the monomer ions increased and the dimer ions $(\text{H}_2\text{O})_m\text{M}_2\text{H}^+$ decreased till disappearance. If the sample concentration diminished further, the peak height of the monomer ions $(\text{H}_2\text{O})_m\text{MH}^+$ started to gradually decrease, finally approaching to the detection limit level. Such kind of ionic peak height map following the concentration changes of ethanol is illustrated in Fig.7, where the alcohol concentration reduced as the dilution time increased in the EDF. As an example, Fig.8 gives the dependence of

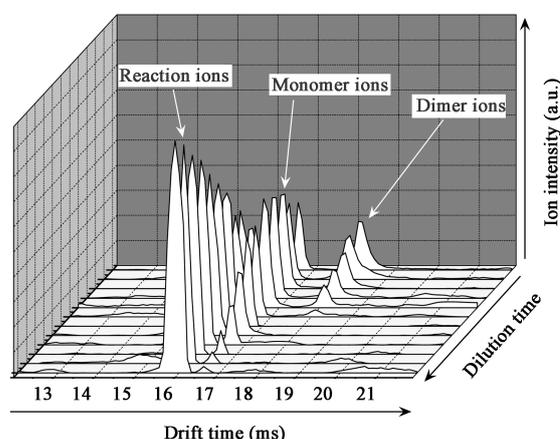


Fig. 7 Dependence map of ion peak height on dilution time in the EDF for ethanol.

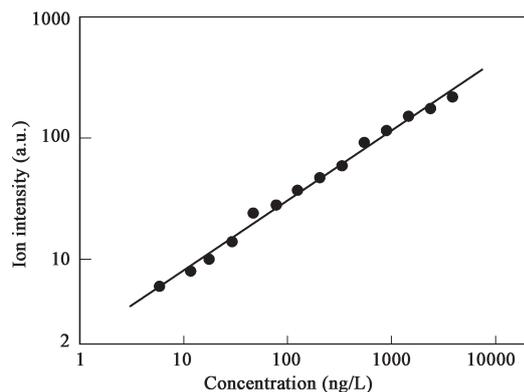


Fig. 8 Dependence of ion intensity on ethanol concentration.

product ion intensities of the protonated monomer and dimer ions on ethanol concentration after the background signal correction, from which a limit of detection around 6 ng/L is obtained.

3 Conclusions

The reactant ions, hydrated cluster ions, are generated in the IMS apparatus using a corona discharge ionization source. The alcohol molecules are ionized through proton transfer reaction with reagent ions, which are comparable to the ion chemical processes happened in the traditional ^{63}Ni -IMS. Due to a high resolution power available in this experiment, the six alcohols mixture containing two isomers can be distinguished in the ion mobility spectrometry. The reduced mobilities of the all alcohols are determined, which are accord with the previously reported values in ^{63}Ni -IMS experiments. The exponential dilution experiment shows that the limit of detection is several ng/L on the corona discharge ion mobility spectrometer.

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