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Humidity effects on resolution and sensitivity of UV-FAIMS in VOCs detection

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Humidity is a key environmental parameter for VOCs detection technology. A study of the effects of humidity on both resolution and sensitivity of UV-FAIMS was performed at ambient temperature and pressure. This study was based on the detection and analysis of the differences in spectra (height, position and shape) and the α function of VOCs under different degrees of humidity. A total of three types of VOCs (ketones, alcohols and aromatics) were chosen as detection samples and a self-developed UV-FAIMS as a measurement instrument. The results show that sensitivity is inversely proportional to humidity for all VOCs. In addition, the resolution–humidity relationship exhibits strong dependence on the polarity of the sample ions. As relative humidity increased from 0% to 100%, the sensitivity of ketones, alcohols and aromatics was reduced by 30.9–73.0%, 40.3–64.3% and 75.1–91.6%, respectively. However, increasing humidity significantly enhanced the resolution of ketones and alcohols in the ranges of 1.82–11.82 times and 1.23–6.69 times, respectively, and hardly affected that of aromatics. Consequently, the appropriate humidity of carrier gas is of great importance in the use of UV-FAIMS.

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Introduction

High-field asymmetric ion mobility spectrometry (FAIMS) is a type of separation and identification method based on the difference in ion mobility under high and low electrical fields at atmospheric pressure.¹ The main advantages of FAIMS are quick detection, high sensitivity and portability.² While its main application is the detection of explosives, chemical warfare agents, pharmaceuticals, and volatile organic compounds (VOCs), it is also being gradually applied in the study of protein conformer identification and other biological fields.^{1,3–8}

Ion mobility in the gas is constant under low electrical fields. However, at high electrical fields, it becomes field strength-dependent (eqn (1)):⁹

$$K = K_0(1 + \alpha_{(E/N)}) = K_0(1 + \sum \alpha_{2n}(E/N)^{2n}), \quad (1)$$

where K_0 is the mobility coefficient under low field and $\alpha_{(E/N)}$ is the α function, α_{2n} are specific coefficients of even powers of the electrical field, E is the electrical field and N is a parameter related to pressure and temperature. The FAIMS filters the ions

by applying a train of pulses (positive short-duration high voltage mixed with negative long-duration low voltage) to the ion filter in order to generate a variable electrical field. The system takes advantage of the variation in the ion mobility for high and low electric fields for separating the desired ions and discarding the others. Finally, the filtered ions are deflected towards the detection electrodes and registered by a weak current detection system.

An ultraviolet lamp (UV) ionizes the molecules by collisions between ultraviolet photons and gaseous substances. A soft ion source leads to low ion fragmentation.¹⁰ For this reason, UV is generally used to ionize VOCs. The main type of product ions from UV-ionized ketones and aromatics are polar-protonated ions and nonpolar or weakly polar molecular ions, whereas alcohols will produce both types of ions.¹¹

The addition of polar neutrals such as water molecules changes the α function by enhancing the formation of clusters in a field-dependent way, increasing the high- and low-field mobility differences.^{12–15} Furthermore, polar water molecules are easier to cluster with polar ions. The effects of humidity on chemical detection have been widely studied. However, studies have focused on radioactive ion resources or ion mobility spectrometry (IMS).^{16–18}

In this paper, the UV-FAIMS spectra characteristics, *i.e.* the height, position and shape, were investigated and determined by measuring three types VOCs at various levels of humidity.

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Experiment

Samples and sample introduction

As a carrier gas, 99% nitrogen was purchased from a commercial supplier (Shangyuan). Common ketones, alcohols and aromatics obtained from Sinopharm were selected as the samples: acetone, 2-butanone, 3-pentanone, 2-hexanone, 3-heptanone; ethanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, 1-hexanol; and *o*-xylene, aniline, benzylamine, *o*-toluidine.

Water vapor was introduced using humidifiers placed in the gas flow path. Well-defined relative humidity (RH) values of the carrier gas were generated by keeping two mixed gas flows at 5 L min⁻¹ and adjusting the ratio of dry gas to saturated humid gas. A schematic diagram is shown in Fig. 1.

UV-FAIMS instrument

A portable, self-developed UV-FAIMS instrument was used for the experiments. The instrument was equipped with a 10.6 eV UV lamp, a FAIMS ceramic chip with a drift region dimension of 15 mm × 10 mm × 0.5 mm, a high-voltage power source with a frequency of 1 MHz and a duty cycle of 30%, a weak current detection module, and a compensation voltage source from -30 to 30 V at a 0.1 V step. The WinCE-based program ARM (S3C2440) was used for measurements and data processing.

Results and discussion

Effect of humidity on peak height and sensitivity

Peak height with DV = 0 V is equivalent to the abundance of a given sample ion and can be used to evaluate the sensitivity of UV-FAIMS. Each experiment in this study was made in 20% relative humidity steps ranging from 0% to 100% and back to 0%. The peak height is normalized to an equal initial value as shown in Fig. 2. The increase in humidity leads to a decrease in

peak height in the range of 30.98–73.04%, 40.32–64.3% and 75.12–91.6% for ketones, alcohols and aromatics, respectively.

The reduction of sensitivity of the UV-FAIMS at ambient temperature and pressure is most likely caused by the absorption of ultraviolet light by vaporized water. The wavelength of ultraviolet light produced by the 10.6 eV UV lamp in the experiment is near 100 nm, which is likely absorbed by vaporized water. Cluster reactions between ions and water neutrals and small amounts of oxygen contained in water might also lead to sensitivity reduction.

Effect of humidity on peak position and alpha coefficient

The samples at different humidity levels were measured with increased DV to locate the corresponding major peak position in the spectra and to calculate the alpha coefficient. The spectra of acetone, ethanol, and *o*-xylene as the model analytes of their homologous series are depicted in Fig. 3. It can be seen that with increased humidity, the major peak of acetone and ethanol clearly shifts rightwards (towards the higher CV), whereas that of the *o*-xylene major peak remains almost unchanged. The increase of relative humidity from 0% to 100% leads to an increase of 2.09 times in the compensation voltage for acetone, *i.e.* from 6.52 V to 19.34 V, and 0.41 times for ethanol, *i.e.* from 16.03 V to 22.59 V. Generally, it has been found that the magnitude of the compensation voltage variation was caused by moisture reduced from ketones to alcohols and aromatics.

The impact of humidity on the CV is strongly dependent on the formation of hydrated ions, which are formed by collisions between ions and water neutrals. The cluster reaction of ketones and alcohol ions occurs at a higher rate likely due to the generated polar-protonated ions, which are susceptible to collision with more polar water molecules. The stability of the position of the aromatics spectra means that the degree of salvation of molecular ions ionized by UV is constant and independent of water. It is probable that they are not solvated.

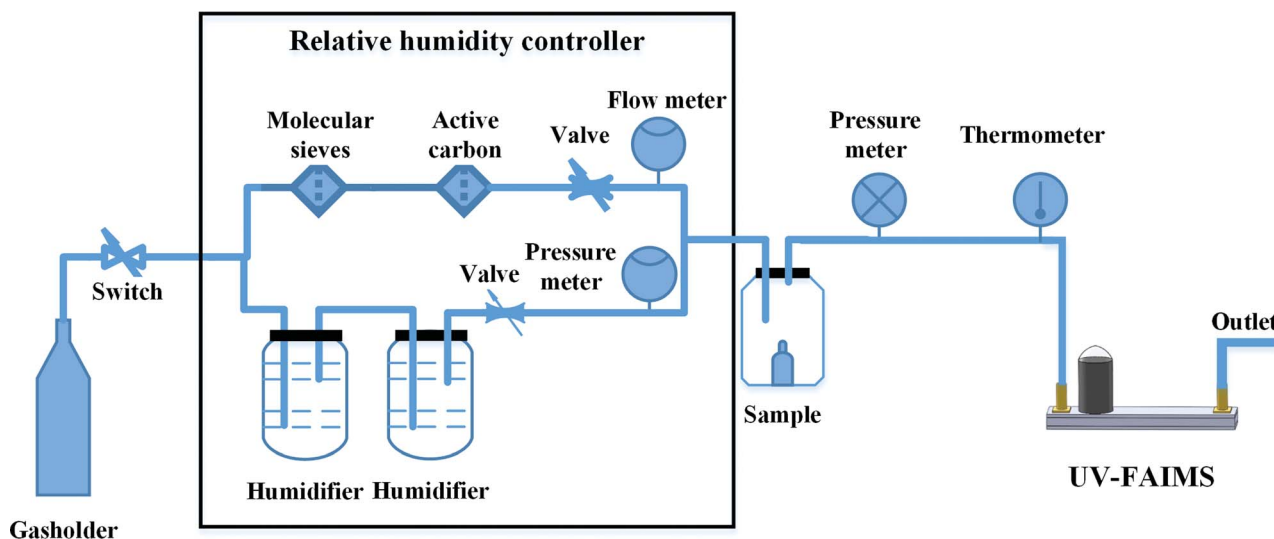


Fig. 1 A schematic diagram of the relative humidity controller, which was calibrated by a standard sensor, and the standard deviation was in the range of 0.5–3% RH.

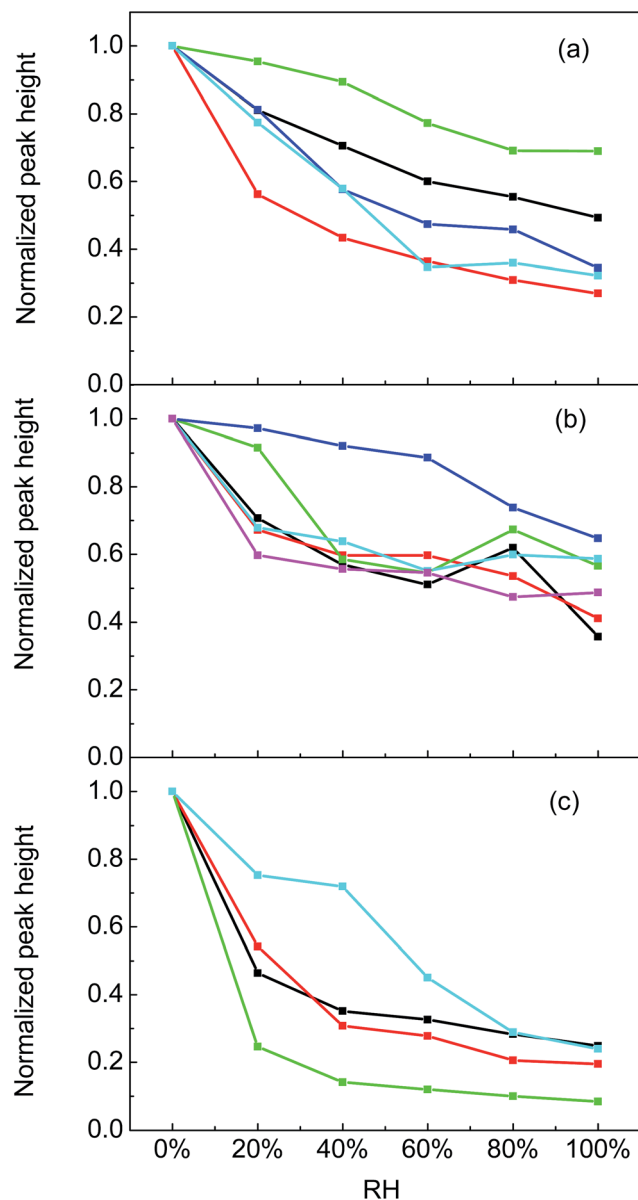


Fig. 2 Normalized peak height at different humidity levels of (a) ketones; (b) alcohols; (c) aromatics.

The influence of the dispersion voltage (DV) on the compensation voltage (CV) depends on the ion alpha parameter. A plot showing the influence of the DV on the CV for acetone, ethanol, and *o*-xylene is presented in Fig. 4. An increase in the DV results in an increase in the CV to restore the transport of sample ions through the ion filter electrodes, which is consistent with the increase in the ion mobility at higher field strengths (as eqn (1)). As previously mentioned, increased humidity levels result in increasing CV in the case of acetone and ethanol and constant CV in the case of *o*-xylene when DV is well-defined. The trend previously observed with the analytes seems to continue with their homologous series.

The absolute magnitude of the CV variation increases inversely with molecular mass as depicted in Fig. 5. The plots of the selected ketones and alcohols are inclined to decrease with

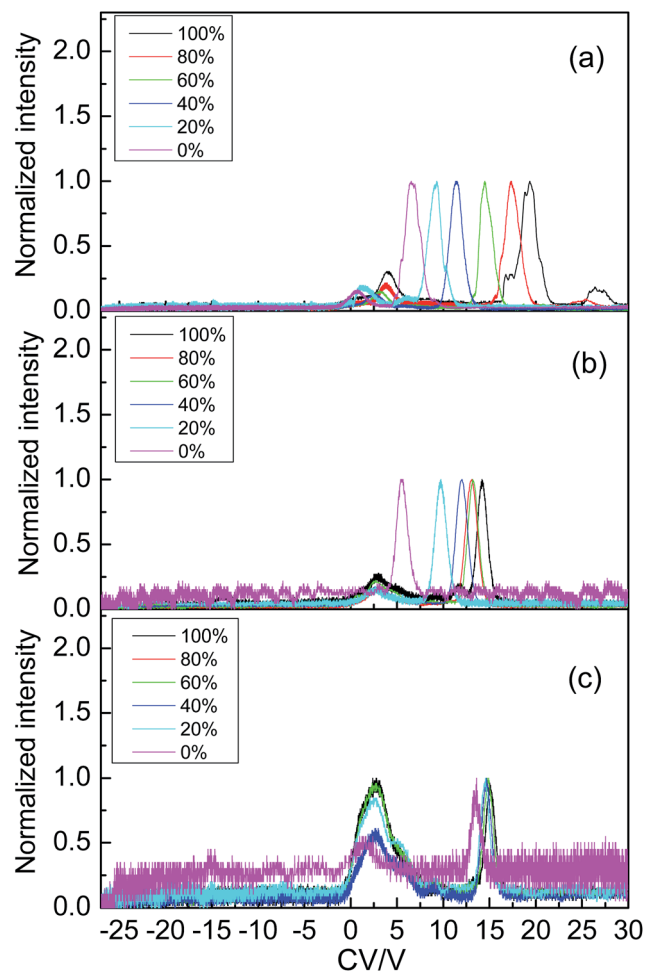


Fig. 3 UV-FAIMS spectra at different relative humidity levels with DV = 1500 V of (a) acetone; (b) ethanol; (c) *o*-xylene.

increasing molecular mass, and the plots of the aromatics resemble plateaus. The positive α function from ions with major peaks are associated with the collision cross sections for ion-molecule interactions.¹⁵ The declustering of ions at high E/N is partly responsible for the α function, and should be influenced by polar neutrals such as water. For the ions in this study, lower mass implies a smaller ion cross section, which will change to a greater extent than will that of a larger ion by the addition of the same number of water molecules. Two types of ions are exceptions to this trend: higher increased CV is exhibited by 2-butanone and 1-hexanol despite having a larger molecular mass (suggesting a structural dependence in the α function). In the case of aromatics, the increased CV is independent of the molecular mass, likely attributed to the very small degree of solvation by neutral molecules.

The effect of humidity on the α function is explored by plots for the alpha coefficients (mainly α_2 , α_4) versus humidity. The alpha coefficients are extracted from CV versus DV plots using the method described in the literature.¹⁵ These plots are fundamental features of the ions because the alpha coefficient is independent of the FAIMS drift-tube dimensions. Few quantitative conclusions can be drawn from these results owing

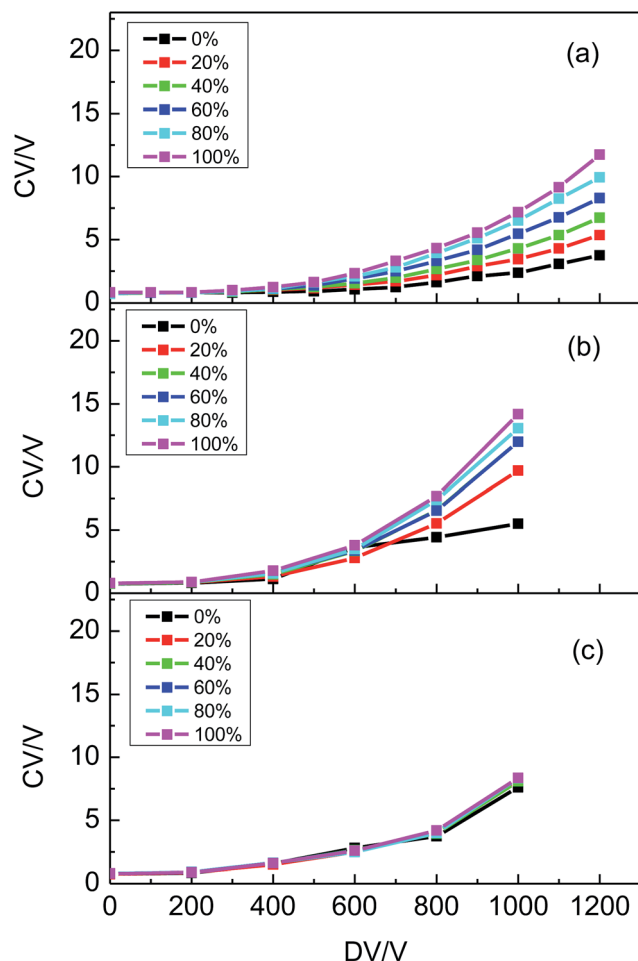


Fig. 4 Plots of CV versus DV at different humidity levels: (a) acetone; (b) ethanol; (c) *o*-xylene.

to the as-yet undetermined calculation method. However, certain general features concerning the alpha coefficient for the samples at normal pressure can be clearly observed in Fig. 6.

These include (A) the α_2 values of ketones and alcohols increase with humidity, whereas that of aromatics are almost constant; (B) the α_4 values of the samples are very small ($\sim 10^{-10} \text{ Td}^{-4}$) and 4 orders of magnitude smaller than those of their corresponding α_2 values ($\sim 10^{-6} \text{ Td}^{-2}$); therefore, α_2 is the main determinant in comparison with α_4 , when this research on the effects of humidity is oriented toward qualitative analysis on α function or mobility; (C) the ion intensity for samples of very low saturated vapor pressure, such as 2-hexanone, 3-heptanone and aniline, is insufficient for the determination of compensation voltage at high electrical fields. Consequently, these analytes are absent from the plots. From the aforementioned features, it can be concluded that the effects of humidity on the α function are consistent with the effects of humidity on the peak position of the UV-FAIMS spectra.

Effect of humidity on peak shape and resolution

Resolution is the key performance parameter of FAIMS. It is an expression of CV versus the full width at half-maximum peak

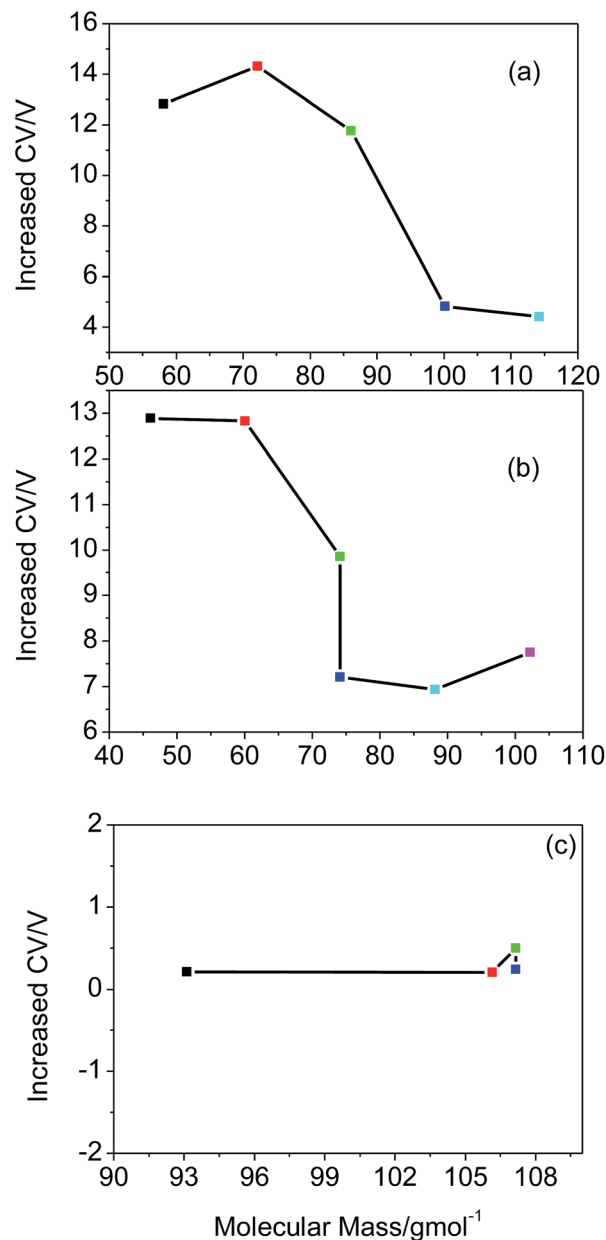


Fig. 5 Increased CV with molecular mass when RH = 100% and RH = 0%: (a) ketones with a DV of 1200 V; (b) alcohols with a DV of 1200 V; and (c) aromatics with a DV of 1000 V.

(FWHM). The FWHM is defined as the width of the FAIMS spectrum at half-maximum peak. Fig. 7 depicts the plots for normalized FWHM of the ketones, alcohols, and aromatics that are obtained at maximum DV, beyond which the FAIMS signal cannot be detected. It is found that the effect of humidity on FWHM (an important parameter of the peak shape) is lower than on the CV, as shown in Fig. 7. The observable range of FWHM values is between 1 V to 4 V. As the humidity of the carrier gas increases, almost all values of FWHM change in the range of ± 0.2 times. As an exception, benzylamine has a value 0.77 times larger, possibly as a result of the calculation when the peak shape becomes abnormal with high DV. The variation on

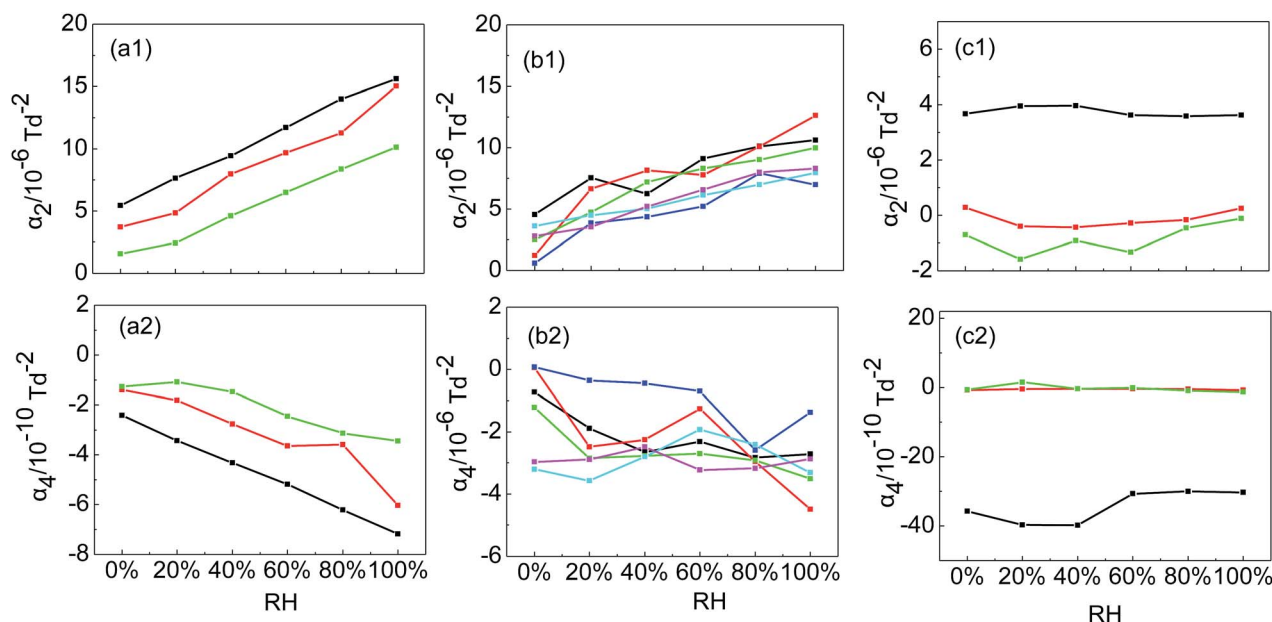


Fig. 6 α_2 and α_4 of VOCs with different humidity at 20 °C and 101 kPa: (a₁) and (a₂) ketones, (b₁) and (b₂) alcohols, and (c₁) and (c₂) aromatics.

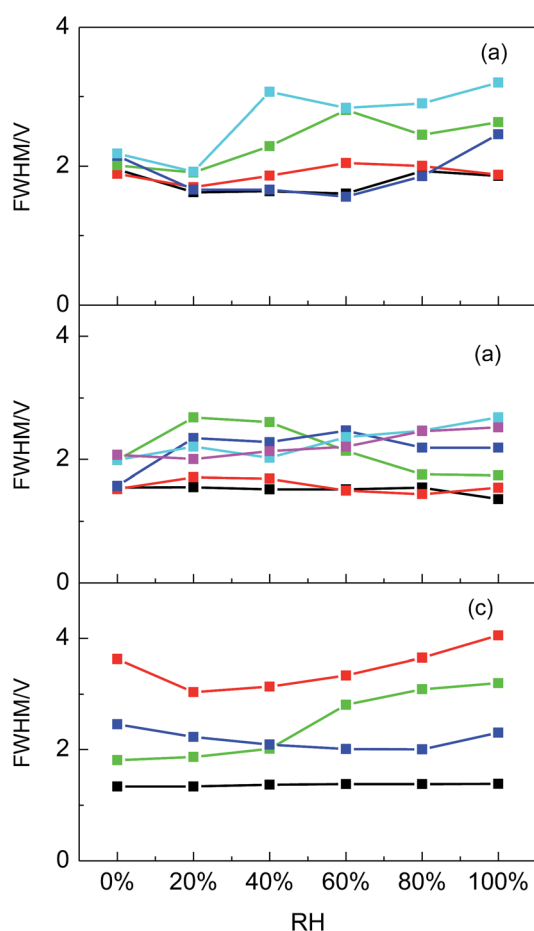


Fig. 7 FWHM of VOCs with different relative humidity at 20 °C and 101 kPa: (a) ketones; (b) alcohols; and (c) aromatics.

FWHM with different humidity may be associated with the ion-molecular reactions.

The relation between resolution and humidity has also been studied. Fig. 8 shows the plots for resolution according to the expression at the maximum DV. The resolution is normalized to an equal initial value. It can be seen that the humidity can significantly improve the resolution at the condition of this study.

This increases the resolution of ketones and alcohols from 0.82 to 10.82 times and 0.23 to 5.69 times, respectively. As expected for aromatics, the change in resolution is slight (0.3 times larger or 0.5 times smaller) at any humidity of carrier gas. As previously mentioned, the enhancement of UV-FAIMS resolution is mainly the result of the integration of a significant increase in compensation voltage and a comparatively minor change in FWHM.

Conclusions

In this study, various FAIMS spectra of common ketones, alcohols and aromatics at ambient temperature and pressure were measured in variable but controlled humidity of carrier gas. The detection is based on the major ion peak generated by the analytes.

It has been shown that additional moisture has a noticeable effect on the appearance of the FAIMS spectra: the height, position and shape are dependent on the amount of moisture in various degrees. Humidity leads to significant decrease in the height of UV-FAIMS spectra with DV = 0 V, which means a reduction in sensitivity. Peak positions shift as the results of the change in the α function by the reaction between ions and water molecules. The peaks of ketones and alcohols explicitly shift rightwards (higher CV), whereas those of aromatics remain unmoved. A possible explanation is that the ions of aromatics

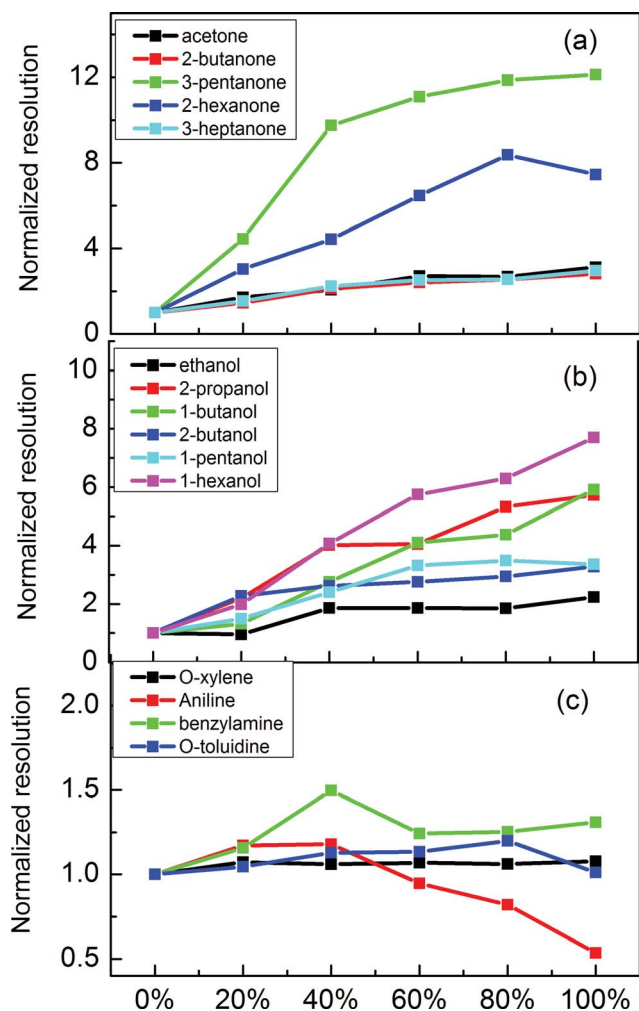


Fig. 8 Normalized resolution with different relative humidity at 20 °C and 101 KPa of (a) ketones; (b) alcohols; and (c) aromatics.

ionized by UV are scarcely hydrated (clustered with water molecules). It has been shown that humidity does not drastically affect the FWHM. Despite the decrease in sensitivity, humidity can significantly improve the resolution in the case of ketones and alcohols.

From an analytical point of view, humidity must be considered when quantifying and identifying samples with UV-FAIMS. To ensure the optimal use of UV-FAIMS, appropriate humidity must be selected. Further investigations with analytes from different chemical groups will be carried out to study the effects of humidity. Furthermore, the identification and change in the other ion peaks in addition to the major peak of the UV-FAIMS spectrum is necessary for a better understanding in a humid carrier gas.

Abbreviations

FAIMS High-field asymmetric waveform ion mobility spectrometry
UV Ultraviolet lamp

VOCs Volatile organic compounds
IMS Ion mobility spectrometry
CV Compensation voltage
DV Dispersion voltage
FWHM Full width at half-maximum

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