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

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Humidity is a key environment parameter for VOCs detection technology. A study of effects of humidity on 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 humidity degrees. A total 3 types of VOCs (ketones, alcohols and aromatics) were chosen as detection samples, and a self-developed UV-FAIMS as measurement instrument. The results show that the sensitivity is inversely proportional to humidity for all VOCs. Also, the resolution-humidity relation exhibits a 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%~30.9%, 40.3%~64.3% and 75.1%~91.6% respectively. However, increasing humidity significantly enhanced the resolution of ketones, alcohols in the range of 1.82~11.82, 1.23~6.69 times and hardly affect that of aromatics. Consequently, appropriate humidity of carrier gas is of great importance to the use of UV-FAIMS.

Introduction

High-field asymmetric ion mobility spectrometry (FAIMS) is a kind of separation and identification method based on the difference in ion mobility under high and low electric 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, 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 electric field. However, at high electric field it becomes field strength dependent (eq 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} is specific coefficients of even powers of the electric field, E is the electric 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 volta-

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ge mixed with negative long duration low voltage) to the ion filter in order to generate a variable electric field. The system takes advantage of the variation in the ion mobility for high and low electric fields to separate the desired ions and discard the others. Finally, the filtered ions are deflected towards the detection electrodes and registered by a weak current detection system.

The Ultraviolet lamp (UV) ionizes the molecules by collisions between ultraviolet photons and gaseous substances. It is a soft ion source that leads to low ion fragmentation.¹⁰ For this reason, UV is usually used to ionize VOCs. The main kind of product ions from UV ionized ketones and aromatics are polar protonated ions and nonpolar or weakly polar molecular ions, while alcohols will produce both kinds of ions.¹¹

The addition of polar neutrals such as water molecules changes the α function by enhancing formation of clusters in a field-dependent way, increasing the high and low field mobility difference.¹²⁻¹⁵ Furthermore, polar water molecules are easier to cluster with polar ions. The humidity's effects on chemical detection have been widely studied. However, studies 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.

Experiment

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Samples and sample introduction

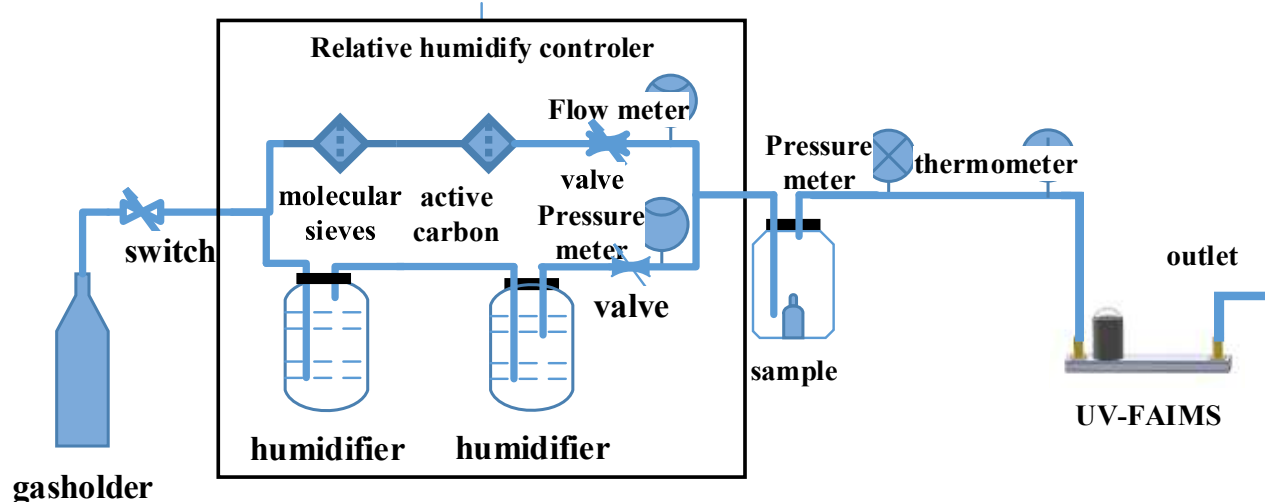


Fig.1 A schematic diagram of the relative humidity controller which was calibrated by a standard sensor and the standard deviation was in the range of 0.5-3% RH.

As carrier gas, 99% nitrogen was purchased from a commercial supplier (Shangyuan). Common ketones, alcohols and aromatics of 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; O-xylene, aniline, benzylamine, O-toluidine.

The water vapor was introduced from humidifiers placed in the gas flow path. Well-defined relative humidity (RH) values of the carrier gas were generated by keeping two mixed gas flow at 5L/min 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 drift region dimension 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 steps. The WinCE-based program ARM (S3C2440) was used for measurements and data processing.

Results and discussion

Effect of humidity on the peak height and the 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 up to 100% and back to 0%. The peak height is normalized to an equal initial value as shown in Fig. 2. The increase of humidity leads to a decrease of 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 probably caused by the

absorption of ultraviolet light by the vaporized water. The wavelength of ultraviolet light produced by the 10.6 eV UV la-

mp 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 the 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, O-xylene as the model analyte 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 higher CV), while 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 6.52V to 19.34V, and 0.41 times for ethanol, i.e. from 16.03 V to 22.59V. Generally, it has been found that the magnitude of the compensation voltage variation 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. Hydrated ions are formed by the collisions between ions and water neutrals. Cluster reaction of ketones and alcohols ions occurs in a higher rate probably due to the generated polar protonated ions, which are susceptible to collide with more polar water molecules. The stability of the position of the aromatics spectra means that the degree of salvation of molecule ions ionized by UV is constant and independent of water. It is probable that they are not solvated.

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, O-xylene is presented in Figure 4. Increasing the DV results in an increase of the CV to restore the transport of sample ions through the ion filter electrodes. This is consistent

with the increase in the ion mobility at higher field strengths (as eq 1). As mentioned above, increased humidity levels result in increasing CV in case of acetone and ethanol, and constant CV in case of O-xylene when DV is well-defined. The trend obser-

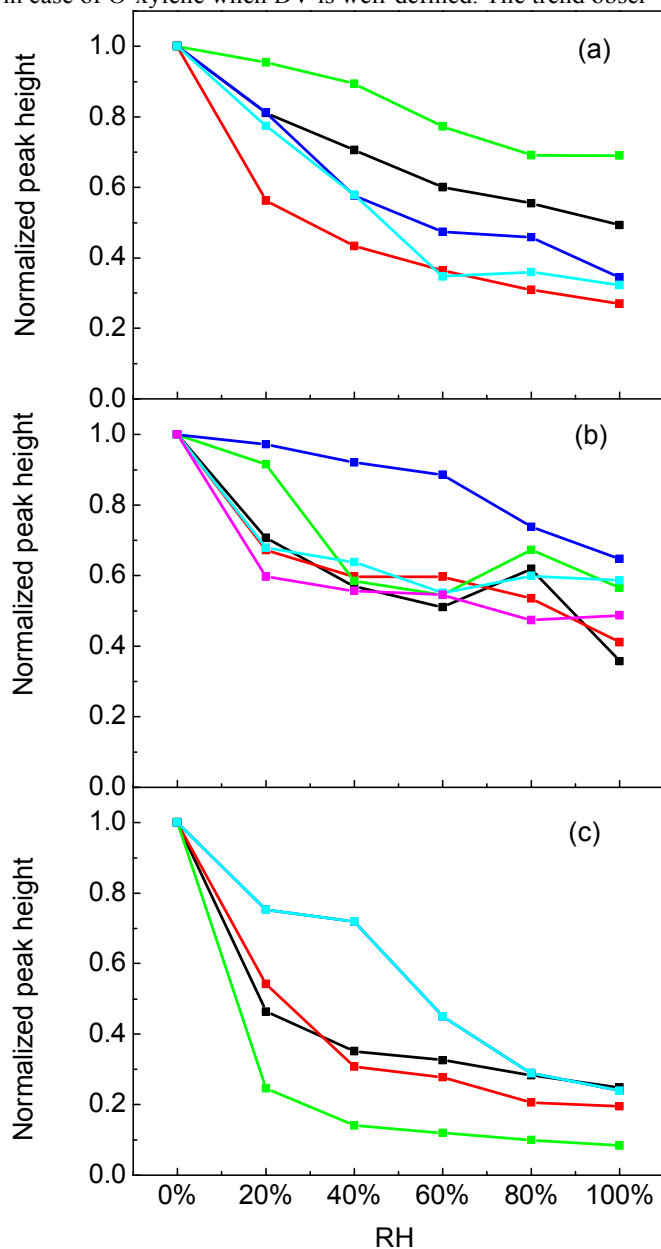


Fig.2 Normalized peak height at different humidity levels of (a)ketones;(b)alcohols;(c)aromatics

ved above 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 increasing molecular mass and the plots of the aromatics resemble plateaus. The positive α function from ions with major peak are associated with the collision cross sections for ion-molecule interactions.¹⁵ Declustering of ions at high E/N is

partly responsible for the α function, polar neutrals such as water should influence. 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 th-

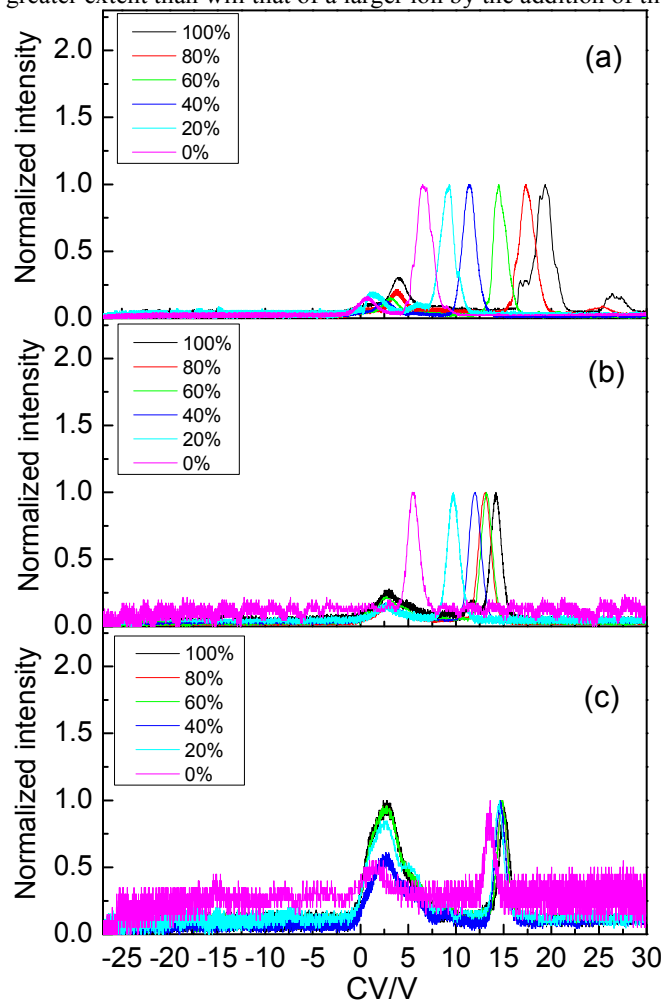


Fig.3 UV-FAIMS spectra at different relative humidity levels with DV=1500V of (a)acetone;(b)ethanol;(c)O-xylene

e same number of water molecules. Two kinds 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 structure dependence in the α function). In the case of aromatics, the increased CV is independent of the molecular mass probably due to the very small solvation degree 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 the 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 made from these results owing to the not yet determined calculation method. However, certain general features concerning the alpha coefficient for the samples at normal pressure can be clearly observed in Figure. 6.

These include: (A) the α_2 values of ketones and alcohols increase with humidity while that of aromatics are almost constant; (B) the α_4 values of the samples are very small ($\sim 10^{-10}$ Td $^{-4}$) and 4 orders of magnitude smaller than of their corresponding α_2 values ($\sim 10^{-6}$ Td $^{-2}$). Therefore, α_2 is the m-

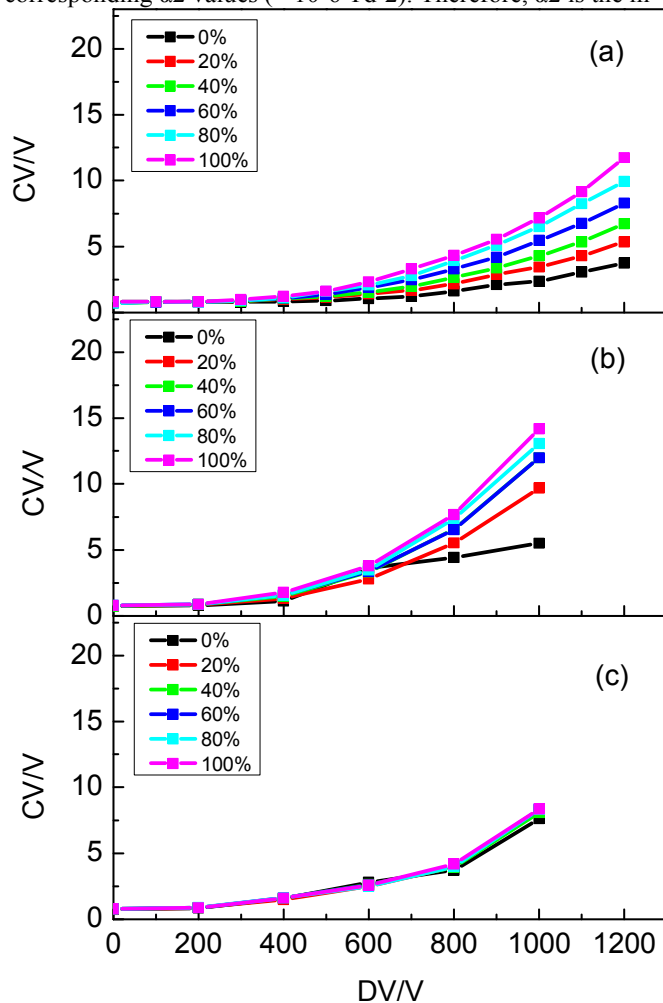


Fig.4 Plots of CV versus DV at different humidity levels: (a) acetone; (b) ethanol; (c) O-xylene

and determinant, in comparison with α_4 , when this research on the effect 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 to determine the compensation voltage at high electric fields. Consequently, these analytes are absent from the plots. From the features above, 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 the 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 (FWHM). The FWHM is defined as the width of FAIMS spectrum at half maximum peak. Figure 7 depicts the plots for

normalized FWHM of the ketones, alcohols, aromatics 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 FW

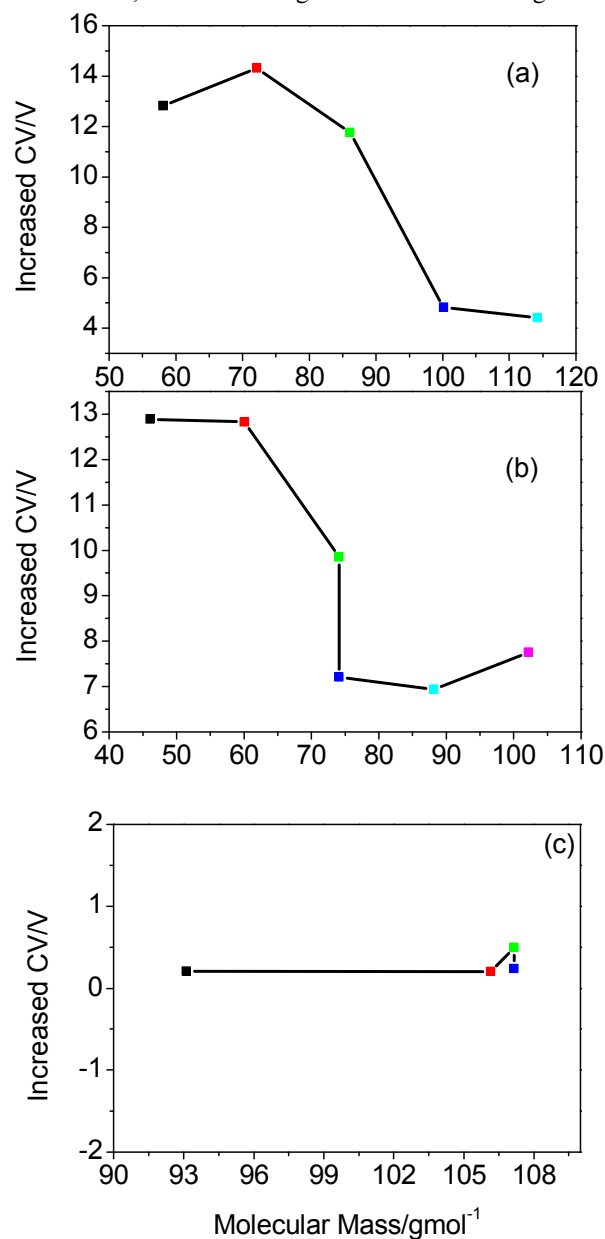


Fig.5 Increased CV with molecular mass when RH=100% and RH=0% (a) ketones with DV 1200V; (b) alcohols with DV 1200V; (c) aromatics with DV 1000V

-HM values is between 1V to 4V. 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 calculation when the peak shape becomes abnormal with high DV. The variation on FWHM with different humidity may be associated with the ion-molecular reactions.

The relation between resolution and humidity has also been studied, Figure 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 si-

gnificantly improve the resolution at the condition of this study.

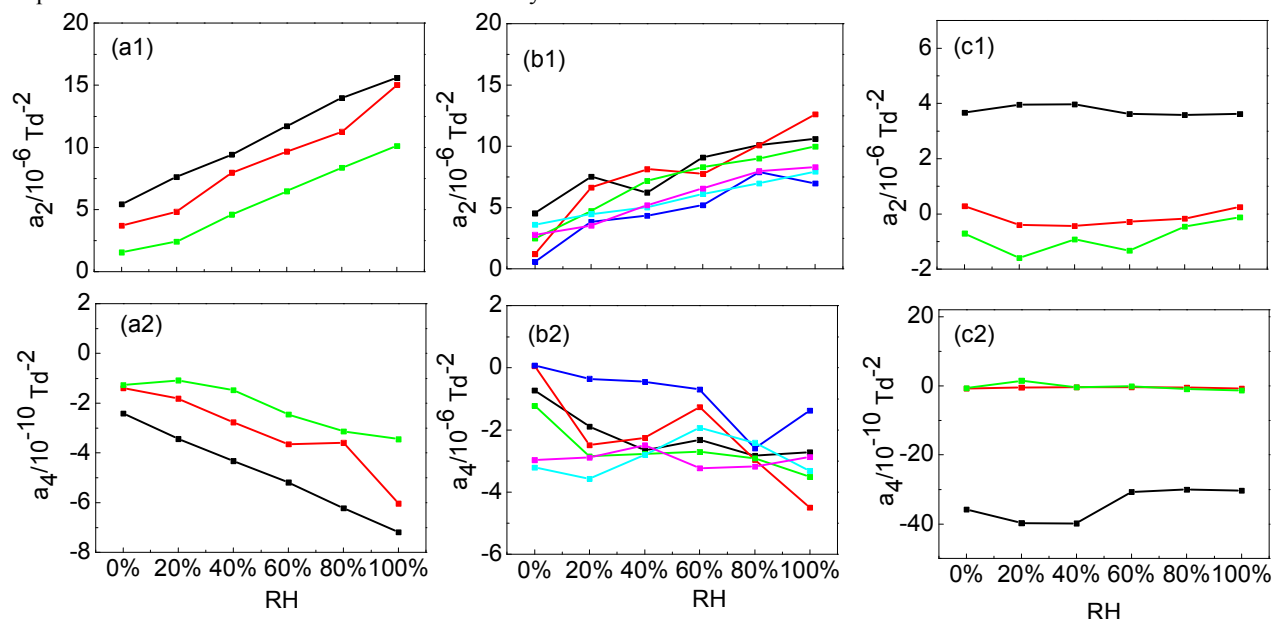


Fig. 6 α_2 and α_4 of VOCs with different humidity at 20 \square and 101 Kpa (a1) and (a2) ketones; (b1) and (b2) alcohols; (c1) and (c2) aromatics

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

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 of height of UV-FAIMS spectra with DV=0V, which means reduction of 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), while those of aromatics stay unmoved. A possible explanation is that the ions of aromatics ionized by UV are scarcely hydrated (cluster with water molecular). It has been shown that humidity does not drastically affect the FWHM. Despite of the decrease of sensitivity, humidity can significantly improve the resolution in case of ketones and alcohols.

From the analytical point of view, humidity has to be taken into account when we are quantifying and identifying the

samples with UV-FAIMS. In order to ensure optimal use of UV-FAIMS, appropriate humidity has to be chosen. Further investigations with analytes from different chemical groups will be carried out to study the effect of humidity. Furthermore, the

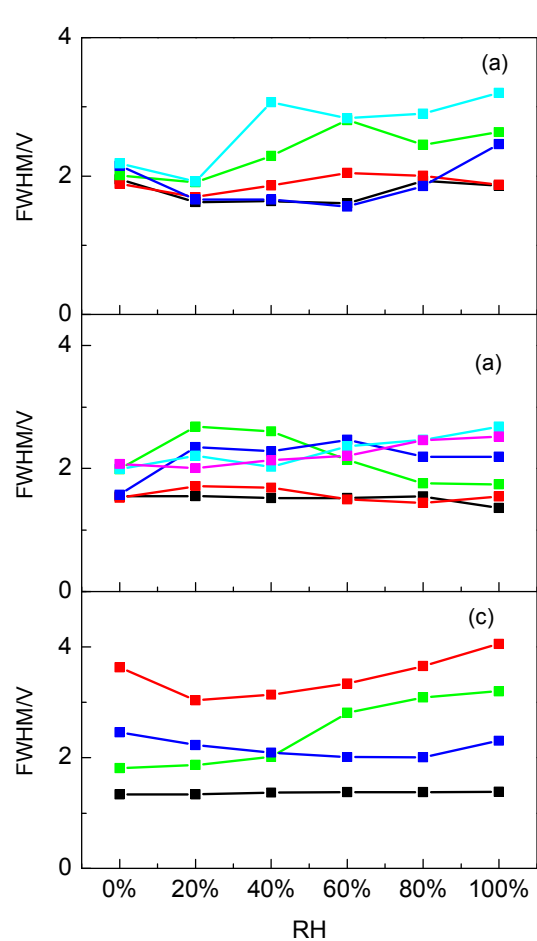


Fig.7 FWHM of VOCs with different relative humidity at 20 □ and 101 Kpa (a)ketones; (b)alcohols; (c)aromatics

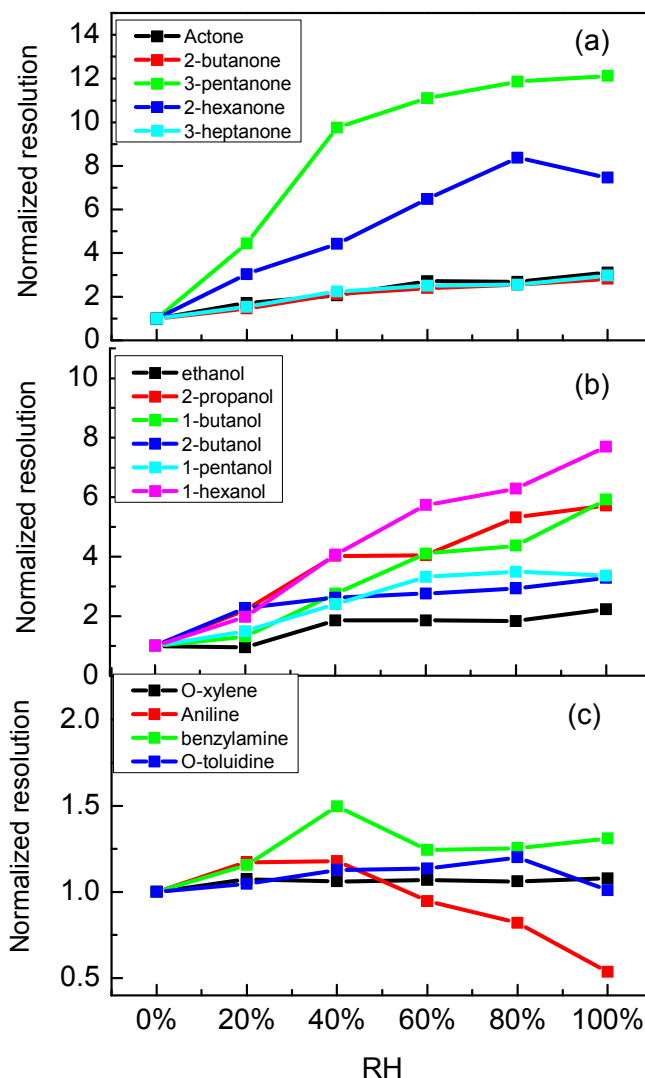


Fig.8 Normalized resolution with different relative humidity at 20 □ and 101 Kpa of (a)ketones; (b)alcohols; (c)aromatics

identification and change of the other ion peaks besides the major peak of UV-FAIMS spectrum is necessary a better understanding in humid carrier gas.

Abbreviations used

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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