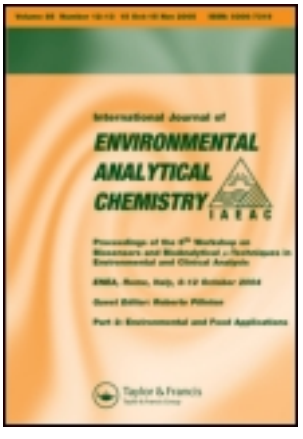

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Proton-transfer-reaction mass spectrometry (PTR-MS) is a powerful technique for the real time trace gas analysis of volatile organic compounds (VOCs). However, quadrupole mass spectrometer (MS) used in PTR-MS has a relatively low mass resolution and is therefore not suitable for differentiating isobars. Furthermore, because of the lack of chemical separation before analysis, isomers can not be identified, either. In the present study, by varying the reduced-field E/N in the reaction chamber with a range of 50–180 Td in PTR-MS, we studied the product ion distribution (PID) of three sets of isobars/isomers, i.e. n-propanol/iso-propanol/acetic acid, propanal/acetone and four structural isomers of butyl alcohol. The profiles of the reduced-field dependence (PFD) of the PID under the chosen *E/N-values* show obvious differences which can be used to discriminate between these isobars/isomers thus enabling the titled method. Noticeably, we have observed that even the isomers, in the case of four structural isomers of butyl alcohol, which show little difference with each other at high reduced-field, can be discriminated easily at low reduced-field. Finally, two examples for the application of this method are discussed: (1) cyclohexanone was identified to be a major compound in the headspace of medical infusion sets; and (2) the differentiation and quantification of propanal and acetone in three synthetic mixtures with different ratios. This study presents a potential method to distinguish and quantify isobars/isomers conveniently in practical applications of PTR-MS analysis without additional instrumental configurations.

Keywords: proton-transfer-reaction mass spectrometry (PTR-MS); cluster ion; collision-induced dissociation (CID); isobar; isomer; trace gas analysis

1. Introduction

Proton-transfer-reaction mass spectrometry (PTR-MS) is a powerful technique for the real time trace gas analysis of volatile organic compounds (VOCs). Due to its advantages, such as fast response time (to 200 ms), absolute concentration measurements, and low detection limit (low ppt range), PTR-MS has been used in many fields, such as environmental research, science and technology for food and flavour, physiology and medicine, detection of explosives and screening drug precursor chemicals in recent years [1–8].

PTR-MS is a technique that combines the soft ionisation method of chemical ionisation with the advantages of well-defined ion-molecule reaction conditions using drift

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tube technique. By using H_3O^+ ion as the precursor ions, which does not react with most of the major components within the air, such as N_2, O_2, CO_2, and Ar, etc. [1] $VOCH^+$ product ion species are formed for most VOCs with little other fragmental ions and cluster ions in the drift tube when the *E/N-values* for the reduced-field is set in the range of 100–140 Td (where E is electric field across the drift tube and N is the gas number density in the drift tube. 1 Td = 10^{-17} V cm^2). However, quadrupole MS used in PTR-MS has a relatively low mass resolution and is therefore not suitable for differentiating isobars. Furthermore, because of the lack of chemical separation before analysis, isomers can not be differentiated, either. With additional configurations for PTR-MS, the discrimination of isomers and isobars is the subject of several studies: GC-PTRMS [9,10], PTR-ITMS [11,12] and the technology of two-stage PTR ion source [13]. Without additional configurations for PTR-MS, Hansel *et al*. [14] have attempted several methods based on isotopic abundances and the fragmentation patterns, etc. to discriminate the isomers/isobars. Isotope analysis is the simple identification of the isobars. However, it is helpless to isomers. Lindinger *et al*. [1] brought forward a method based on the break-up of protonated component as dependent on the break-up voltage between the last two drift rings and the end plate at the downstream end of the drift tube. Glosik *et al*. [15] had applied this method [1] to identify the isomers of $HC(OH)_2^+$ and H_2COOH^+. Warneke *et al*. [16] reported on the identification of propanol in the breath by increasing E which leads to an increase in the relative kinetic energy, KE_{cm}, between the reactants; however, they were not able to differentiate between n-propanol and iso-propanol in that particular study, due to the similarities between the PFD of PID of the two isomers at high KE_{cm}. Buhr *et al*. [17] studied the fragmentation patterns of 53 flavour compounds measured by PTR-MS at an applied drift voltage of 600 V to discriminate isomeric/isobaric compounds. Fortner and Knighton [18] quantitatively resolved mixture of acrolein and 1-butene by measuring the change in response at two different reduced-fields *E/N-value* = 106 Td and 127 Td.

It was always thought that PTR-MS instrument has difficulties in identifying isomers/isobars unless coupled with other techniques; however, results from the previous studies above [1,13–18] have indicated that such problem could be solved with the potential of exploiting the difference between the profiles of reduced-field dependencies (PFDs) of product ion distribution (PID) between isobars/isomers, which we present in this paper. Also, we are interested in comparing the PID of ion-molecule reactions in our newly built PTR-MS system [19] with the published data in the literature, although this is not the major focus of the paper. In this experiment, we vary *E/N-value* across the whole drift tube by changing the drift voltage with a range of 50–180 Td to obtain the PFDs of PID for three sets of isomers/isobars, i.e. n-propanol/iso-propanol/acetic acid, propanal/acetone, and four structural isomers of butyl alcohol. Finally, two examples were used to illustrate this method: (1) the direct identification of cyclohexanone as the major component in the headspace of medical infusion sets, and (2) the differentiation and quantification of propanal and acetone in three synthetic mixtures with different ratios of 15.2%/84.8%, 45.8%/54.2% and 64.6%/35.4%.

2. Experimental

2.1 *The elements of PTR-MS*

The PTR-MS used in this experiment, Hefei PTR-MS-01, was built in our laboratory at Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, in Hefei.

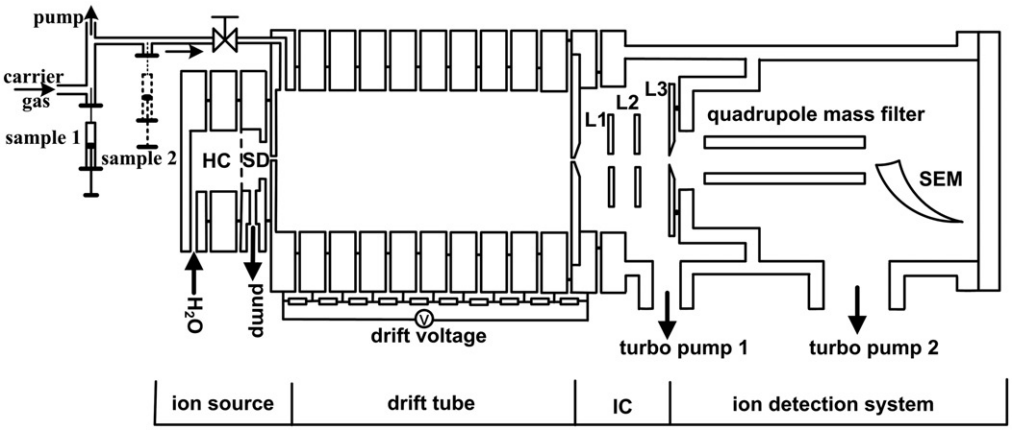

Figure 1. The schematic of Hefei PTR-MS-01. HC, hollow cathode; SD, source drift region; IC, intermediate chamber; EM, electron multiplier; L1-3, Lens 1-3.

The demonstration of its construction and performance has been reported elsewhere [5,7,19]. The schematic of Hefei PTR-MS-01 is shown in Figure 1. It chiefly comprises an ion source, drift tube, intermediate chamber and the ion detection system. A homogeneous electric field within the drift tube is obtained by applying the drift voltage to 11 equidistant drift rings by using a cascade of equal resistors. Generally, the pressure in the drift tube is around 200 Pa, and the pressure in mass spectrometry chamber is about 2.0×10^{-4} Pa; and the sample flow rate is 6–8 ml min^{-1}.

The reagent ions H_3O^+ generated from ion source are introduced into the drift tube. If the trace VOC (denoted with R in following text) has a proton affinity (PA) larger than that of H_2O (PA = 691 kJ/mol), proton transfer reaction can occur between R and the reagent ion, H_3O^+, in the drift tube as Equation 1. The concentration of R in the gaseous sample, [R], is determined by Equation 2 [20].

$$H_3O^+ + R \xrightarrow{k} RH^+ + H_2O \tag{1}$$

$$[R] \approx \frac{i(RH^+)\tau}{i(H_3O^+)_0 k \Delta t} \tag{2}$$

In Equation 2, $i(H_3O^+)_0$ is the intensity of reagent ion, H_3O^+; $i(RH^+)$ is the intensity of product ion, RH^+; τ is a parameter dependent on individual instrument; k is the rate coefficient for the proton-transfer reaction (1); Δt is the reaction time.

However, without a well-defined *E/N-value* in drift tube, the product ions will undergo dissociation reactions to form fragmental ions, and undergo association reactions with water to form cluster ions and with the sample itself at high concentration to produce dimer ions. These ions were usually regarded as affecting the quality of the analysis [1]. However, as discussed above, these cluster ions and fragmental ions at different *E/N-value* could be exploited in the discrimination of the isobars/isomers [1,13–18]. So the PID for isobars/isomers can be studied at every chosen *E/N-value* by continuously varying the voltage across the drift tube, then the PFD of PID can be used to discriminate the isomers/isobars.

2.2 *Methods and reagents*

In this experiment, the single pure gas samples and mixture gas samples were introduced to the gas inlet of PTR-MS at a fixed concentration as shown in Figure 1. First, to obtain the single pure gas sample, a syringe with a small volume liquid sample (about 0.2 ml) was placed upwards at sample 1 position. For the acetic acid and tert-butyl alcohol sampled from a reagent storeroom with a lower temperature, solid sample was placed directly at sample 1 position to obtain the pure gas sample. The saturated stream upon the liquid/solid sample was admixed into laboratory air, and then introduced into PTR-MS. Second, to synthesize the mixture gas sample, the sample 1 and 2 positions were adopted together. And a syringe pump was used to adjust the concentration of propanal at sample 2 position, and the laboratory air was used as carrier gas to adjust the concentration of acetone at sample 1 position. So three sets of mixtures with different concentration ratios of propanal to acetone were prepared.

With different pressure of saturated stream for different liquid/solid sample and the different flow rate (6–200 ml min^{-1}) of laboratory air, the gas samples with concentrations at ppm/ppb level can be obtained. This ensures that the product ion count rate I_{mi} is much smaller than the reagent ion count rate I_{H_3O+} (I_{mi}/I_{H_3O+} is less than 10%). For eliminating the potential interferences from the relative humidity and temperature, we kept them at around 63% and 298 K respectively during the experiment. All samples used in experiment are analytical reagent. The medical infusion sets were obtained from a pharmacy in Hefei. Multiple ion detection in the operating software was used to detect the concerned product ions.

The background signals of the laboratory air were scanned at every chosen *E/N-value* for background subtraction. The data were averaged over N_c scanning cycles. The background corrected data were presented by normalising the counts per second of the total concerned product ions to a value of 100%. The relative abundance (A) for concerned product ion ($m_1 \ldots m_i \ldots m_n$) was calculated by the background corrected intensity of concerned product ion and the total concerned product ions at selected *E/N-value* as Equation 3:

$$A_{m_i} = \frac{I_{m_i}}{\sum_{j=1}^{n} I_{m_j}} \tag{3}$$

where I_{mi} is the background corrected intensity at m_i.

The errors of the relative abundances (δA) for concerned product ions are presented by Y-error bars, which are calculated as Equation 4:

$$\delta A_{m_i} = \frac{\sum_{j=1}^{n} I_{m_j} - I_{m_i}}{\left(\sum_{j=1}^{n} I_{m_j}\right)^2} \times \delta I_{m_i} \tag{4}$$

In this equation, δI_{mi} is the error of the background corrected intensity. They are given as Equation 5:

$$\delta I_{m_i} = \delta I_{m_i}(sig) - \delta I_{m_i}(bk) = \frac{3 \times NS(sig)}{\sqrt{N_c}} - \frac{3 \times NS(bk)}{\sqrt{N_c}} \tag{5}$$

$$NS(sig) = \frac{I_{m_i}(sig)}{\sqrt{I_{m_i}(sig) \times dwell_{mi}}} \tag{6a}$$

$$NS(bk) = \frac{I_{m_i}(bk)}{\sqrt{I_{m_i}(bk) \times dwell_{mi}}} \tag{6b}$$

The Equation 6 about noise statistic (NS) is given by Hayward *et al*. [21] and the 3NS is considered in calculation of δI_{mi} in Equation 5. With some further mathematical steps from Equations 4, 5 and 6 we get δA_{mi} finally which is considered as error bar of each point:

$$\delta A_{m_i} = \frac{\sum_{j=1}^{n} I_{m_j} - I_{m_i}}{(\sum_{j=1}^{n} I_{m_j})^2} \times \frac{3}{\sqrt{dwell_{m_i} \times N_c}} \times (\sqrt{I_{m_i}(sig)} - \sqrt{I_{m_i}(bk)}) \tag{7}$$

where the $dwell_{mi}$ is the dwell time for scanning m_i.

3. Results and discussion

3.1 *N-propanol (C_3H_8O), iso-propanol (C_3H_8O) and acetic acid ($C_2H_4O_2$), molecular weight (MW) = 60*

The PFDs of PID for n-propanol, iso-propanol and acetic acid are significantly different as shown in Figure 2. In Figure 2(a) and (b), the main product ion is not the protonated propanol ($m/z = 61$) but the fragmental ion at $m/z = 43$ at the general *E/N-value*. Buhr *et al*. [17] observed the similar result when the drift voltage was 600 V, and attributed it to $(RH\text{-}H_2O)^+$ which was common for many alcohols [22,23]. Even though the PFDs of the ions are similar for n-propanol and iso-propanol between 100 Td and 180 Td, the difference in PFDs of the PID of the ions become more obvious at lower *E/N-value* towards 40 Td. From the results of Warneke *et al*. [16], which have obtained PID of n-propanol and isopropanol over an increasing *E* which leads to an increase in the relative kinetic energy, KE_{cm}, however, the similarities between the PID of the two isomers under the chosen conditions were not enough for their differentiation; in the present study two more product ions at $m/z = 39$ and $m/z = 41$ were observed compared with the results of Warneke *et al*. [16], further investigations are required to determine whether this is due to different instrumental settings or experimental conditions. However, these results did illustrate the potential of obtaining the PFD of PID in an extending *E/N* range in the differentiation between isomers. Comparing with that in Figure 2(c), the PFD of ions at $m/z = 39$ and 41 in Figure 2(a) and (b) are distinct at high *E/N-value* and their relative abundance are primary at high *E/N-value*. However, in Figure 2(b), the protonated acetic acid ($m/z = 61$) is the primary product ion at $E/N = 100$ Td, and the peaks at $m/z = 39$ and 41 are minor. These important characteristics can be used to discriminate them.

3.2 *Propanal and acetone, C_3H_6O, MW = 58*

Figure 3 shows the PFDs of PID for the isomer: (a) propanal and (b) acetone. As can be seen in Figure 3(a) when *E/N-value* is higher than 130 Td, the relative abundance of the protonated propanal is decreasing greatly and that of fragmental ions, such as $m/z = 39$ and 31, are increasing. However, as can be seen in Figure 3(b) the PFD of PID for acetone is very different from that for propanal in Figure 3(a). The relative abundance of protonated acetone is nearly constant over a wider range of *E/N-value*. And, the intensities of fragmental ions at $m/z = 31$ and 39 are negligible for acetone when the *E/N-value* is less

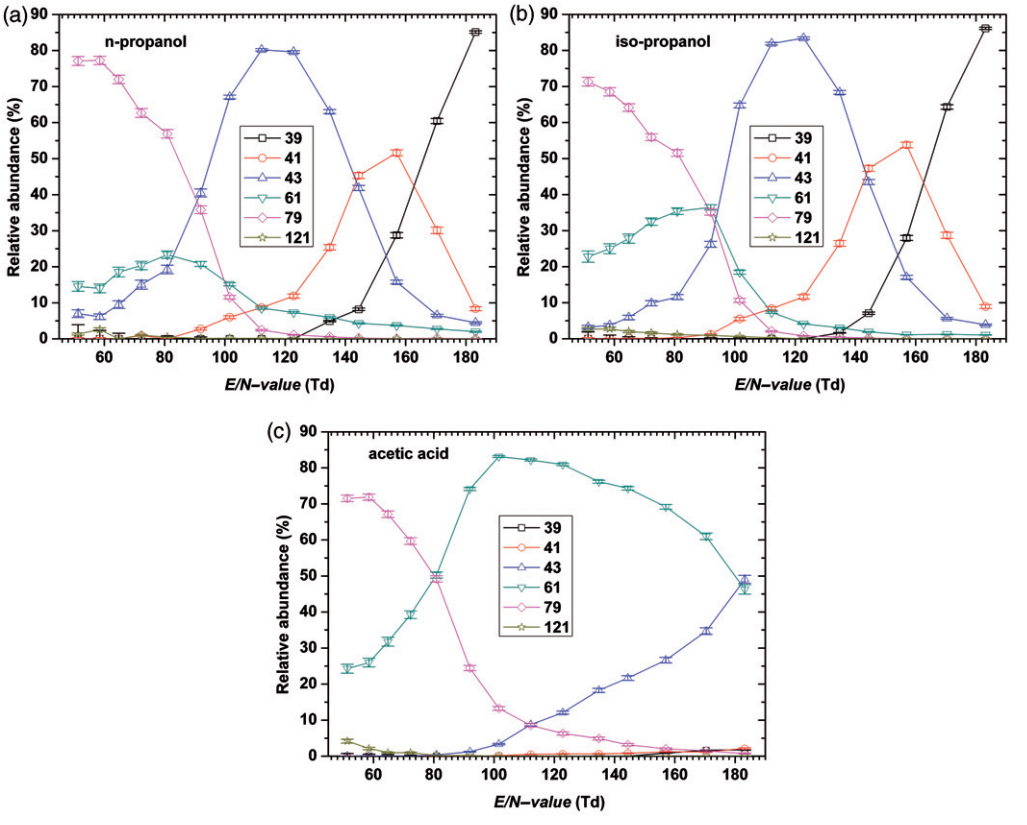

Figure 2. The PFD of PID for (a) n-propanol, (b) iso-propanol and (c) acetic acid. E/N-*value* = 51.3, 58.5, 64.8, 72.3, 80.9, 92.0, 101.6, 112.2, 122.8, 134.8, 144.4, 157.0, 170.4, 183.2 Td; $dwell_{mi} = 0.5$ s; $N_c = 20$. The errors of the relative abundances (δA) for concerned product ions are presented by Y-error bars, which are calculated based on Equation 7.

than about 170 Td. In general, these break-up characteristics (including that of the propanols and acetic acid), are consistent with the observations of Lindinger *et al*. which are discussed in an earlier study [1], in which the E/N-*value* was set at about 120–140 Td along the drift section and the voltage was varied between the last two drift rings and the end plate at the downstream end of the drift tube from 10 V to 50 V.

Furthermore, the PFD of the cluster ions RH_3O^+ ($m/z = 77$) in Figure 3 also indicates the differences between propanal and acetone at low E/N-*value*. Compared with that of acetone, the cluster ions of propanal are becoming more abundant at lower E/N-*value*, which is a significant difference in the PFDs of two isomers, and further investigations of the reaction mechanisms for such various PFDs of PID could be carried out and be pursued from here.

3.3 *Butyl alcohols, $C_4H_{10}O$, MW = 74*

The PFDs of PID for (a) n-butyl alcohol, (b) iso-butyl alcohol, (c) sec-butyl alcohol and (d) tert-butyl alcohol are shown in Figure 4. For all four compounds, the most abundant

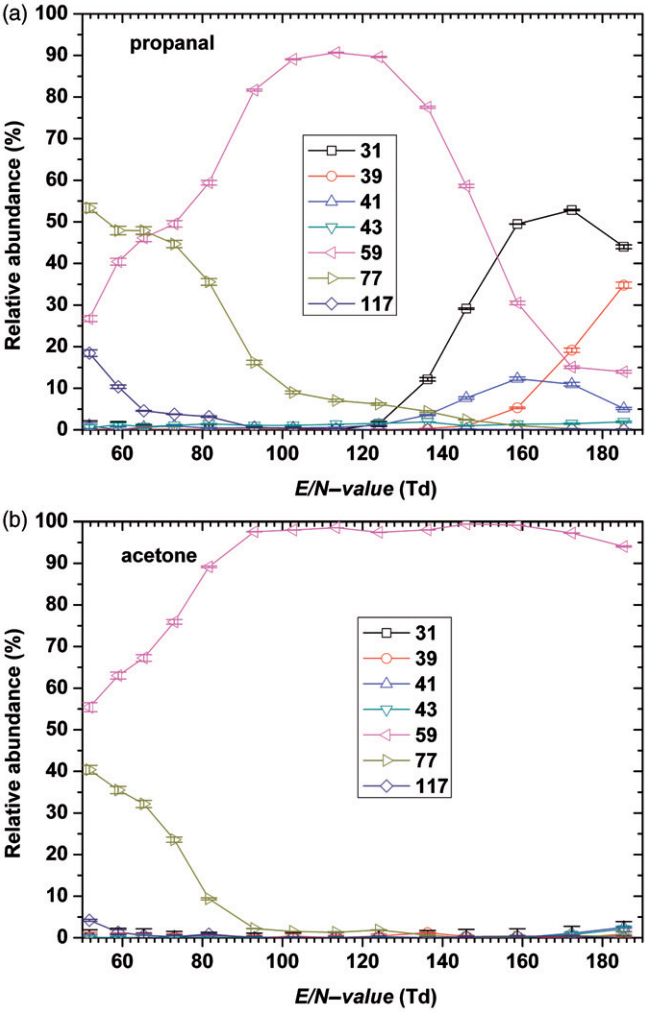

Figure 3. The PFD of PID for (a) propanal and (b) acetone. E/N-*value* = 51.7, 59.0, 65.4, 73.0, 81.6, 93.0, 102.7, 113.4, 124.1, 136.3, 146.0, 158.7, 172.3, 185.3 Td; $dwell_{mi} = 0.5$ s; $N_c = 20$. The δA for concerned product ions are presented by Y-error bars, which are calculated based on Equation 7.

product ion is not the protonated butyl alcohol ($m/z = 75$) but the fragmental ion at $m/z = 57$ at typical E/N-*value* between 100 Td and 140 Td. This attributes to $(RH\text{-}H_2O)^+$ which holds the same formation mechanism to the ion at $m/z = 43$ from the protonated n-propanol and iso-propanol in Figure 2. There is no obvious difference in the break-up patterns of protonated butyl alcohols at high reduced-field. However, by extending to the lower reduced-field, difference between the PID of each isomer can be clearly seen. Moreover, amongst the four, the relative abundance of ion $m/z = 57$ from tert-butyl alcohol is nearly constant over a wider range of E/N-*value* (80–140 Td). And that from n-butyl alcohol is nearly constant over a narrower range of E/N-*value* (110 Td–140 Td). These differences indicate the usefulness of varying the E/N-*value* with wide range across the whole drift tube.

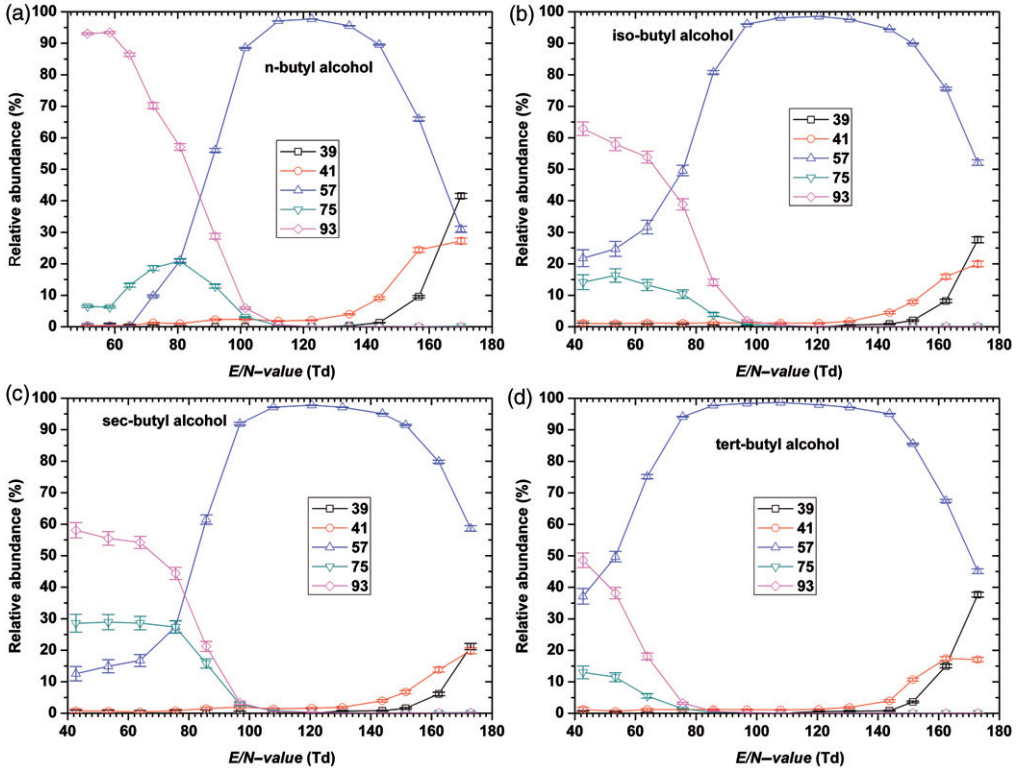

Figure 4. The PFD of PID for (a) n-butyl alcohol, (b) iso-butyl alcohol, (c) sec-butyl alcohol and (d) tert-butyl alcohol. $E/N\text{-}value = 42.7$, 53.4, 63.9, 75.6, 85.7, 96.8, 107.9, 120.5, 130.6, 143.8, 151.5, 162.4, 172.9 Td; $dwell_{mi} = 0.5$ s in (a) and 0.1 s in (b), (c), (d); $N_c = 20$. The δA for concerned product ions are presented by Y-error bars, which are calculated based on Equation 7.

3.4 *An example: Cyclohexanone in medical infusion sets*

The titled method is a convenient method for discriminating pure compounds. In cases of mixtures containing one major compound or binary mixtures, the described method showed to be still applicable to distinguish and quantify isomers/isobars.

Here is an example by using this method for the identification of the residual components in the headspace of a medical infusion sets. An initial analysis of the full scan at $E/N\text{-}value = 143$ Td had shown the intensity of ion at $m/z = 99$ is dominant. This can be tentatively attributed to cyclohexanone ($C_6H_{10}O$) which is usually used as adhesive agent during producing the medical infusion sets [5]. But the other ions at $m/z = 81$ and 117 are unsure. In order to identify these ions including the ion at $m/z = 99$ exactly, the titled method was adopted. The PFDs of PID for compounds in the headspace of the medical infusion sets and the pure cyclohexanone were obtained as can be seen in Figure 5. These results show that the ion at $m/z = 99$ is certainly protonated cyclohexanone. The proposed formation pathways of the product ions m/z 81, 99 and 117 are presented as following Equation 8. At low reduced-field, the primary reagent ion is protonated water cluster. This example indicates that the titled

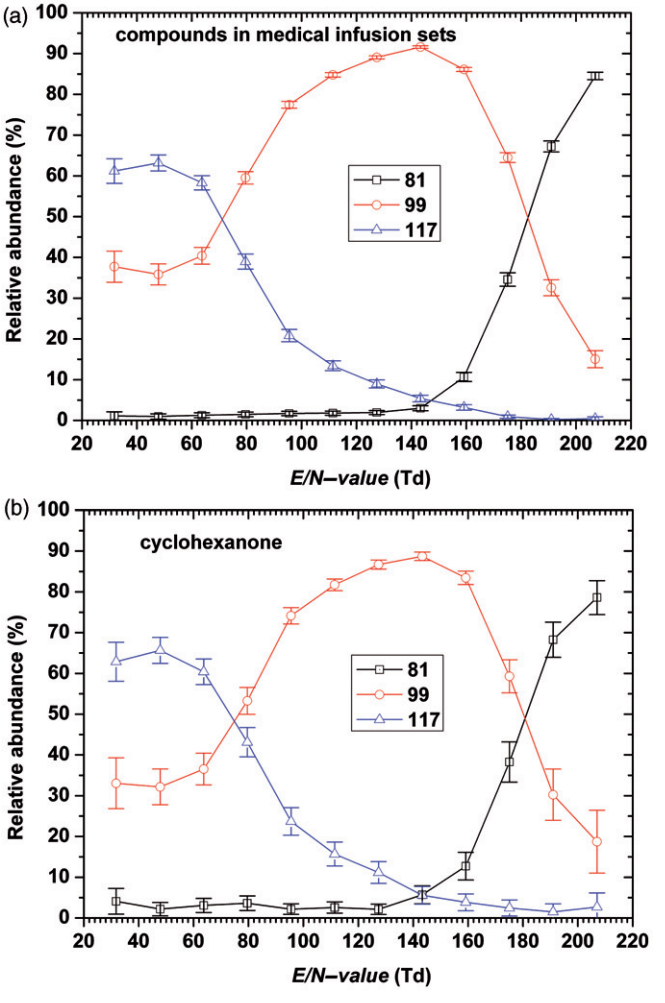

Figure 5. The PFD of PID for (a) compounds in medical infusion sets and (b) cyclohexanone. *E/N-value* = 31.8, 47.8, 63.7, 79.6, 95.5, 111.4, 127.4, 143.3, 159.2, 175.1, 191.0, 207.0 Td; $dwell_{mi} = 0.1$ s; $N_c = 10$. The δA for concerned product ions are presented by Y-error bars, which are calculated based on Equation 7.

method is able to give a positive identification of single compound or a dominant compound in a mixture.

$$C_6H_{10}O + H_3O^+ \cdot (H_2O)_{n=0,1,2\ldots} \rightarrow [C_6H_{10}O \cdot H_3O]^+ + nH_2O \text{ or } (H_2O)_n \ (n = 0, 1, 2, \ldots) \quad (8a)$$

$$\rightarrow [C_6H_{10}O + H]^+ + nH_2O \text{ or } (H_2O)_n \ (n = 1, 2, 3, \ldots) \quad (8b)$$

$$\rightarrow [C_6H_9]^+ + nH_2O \text{ or } (H_2O)_n \ (n = 2, 3, 4, \ldots) \quad (8c)$$

3.5 *A second example: Mixture analysis, propanal and acetone, MW = 58*

There are three steps for determining individual concentrations of the specific mixture using titled method: (1) The concentration ratio must be determined first by the PFD of PID; (2) The individual ion intensity can be obtained from the total ion intensity at the best E/N condition; (3) Equation 2 can be used to calculate the individual concentration.

As an example, propanal and acetone were quantified in a mixture (Figure 6). The PFDs of PID for these three synthetic mixtures with different ratios were measured and shown as solid line. To obtain the concentration ratios of propanal to acetone in different mixtures, the least square fit (LSF) was adopted, based on the known PFDs of PID for pure propanal and acetone in Figure 3. So the different ratios of propanal to acetone as can be seen in Figure 6 (a) 15.2%/84.8%, (b) 45.8%/54.2%, (c) 64.6%/35.4% could be obtained by making the total error across all E/Ns to be the least in LSF. The dot lines in Figure 6 are the LSF lines, which fit the solid lines perfectly for three samples with different concentration ratios.

For quantifying the concentration of propanal and acetone in mixtures by the concentration ratio respectively, an E/N condition should be chosen, as long as the LSF is good at this E/N-*value*. Take the result in Figure 6(c) for example; the best E/N condition is 113.4 Td which results in the least error. The measured background corrected intensity of ions at $m/z = 59$ is 1430 counts per second (cps) at this E/N condition. Assuming that acetone and propanal both reacts with the same rate coefficients towards the different forms of reagent ion ($H_3O^+(H_2O)_{n=0,1,2\ldots}$) across the E/N-*values*, so we can present following Equations 9 and 10 easily. r denotes the percentage of one compound in the mixture. These equations designate the mass of the ion measured as the subscript while the superscript identifies propanal, acetone and mixture which are abbreviated as 'pro', 'ace' and 'mix' respectively.

$$I^{\text{pro}} = r^{\text{pro}} \frac{I_{59}^{\text{mix}}}{A_{59}^{\text{mix}}} = 64.6\ \% \times \frac{1430}{93\ \%} cps = 993 cps \tag{9}$$

$$I^{\text{ace}} = r^{\text{ace}} \frac{I_{59}^{\text{mix}}}{A_{59}^{\text{mix}}} = 35.4\ \% \times \frac{1430}{93\ \%} cps = 544 cps \tag{10}$$

Based on these ion intensities from Equations 9 and 10, the concentrations of propanal and acetone can be estimated easily to be 3.12 ppm and 1.71 ppm by Equation 2, respectively. Similarly, the estimated concentrations of propanal and acetone are 0.80 ppm and 4.47 ppm respectively at 124.1 Td in Figure 6(a), 2.66 ppm and 3.15 ppm respectively at 102.7 Td in Figure 6(b). The prepared concentrations of propanal and acetone in the mixture are obtained by measuring characteristic ion $m/z = 31$ at E/N-*value* = 146 Td. The result about comparison of prepared concentrations and estimated concentrations using titled method is shown in Figure 7. The slope errors of fit line are less than 10%.

4. Conclusion

In the present study we obtained the profiles of the reduced-field dependence (PFDs) of the product ion distribution (PID) for three sets of isobars/isomers in PTR-MS, i.e. n-propanol/iso-propanol/acetic acid, propanal/acetone and four structural isomers of butyl alcohol using our newly built PTR-MS instrument under a E/N range of 50–180 Td.

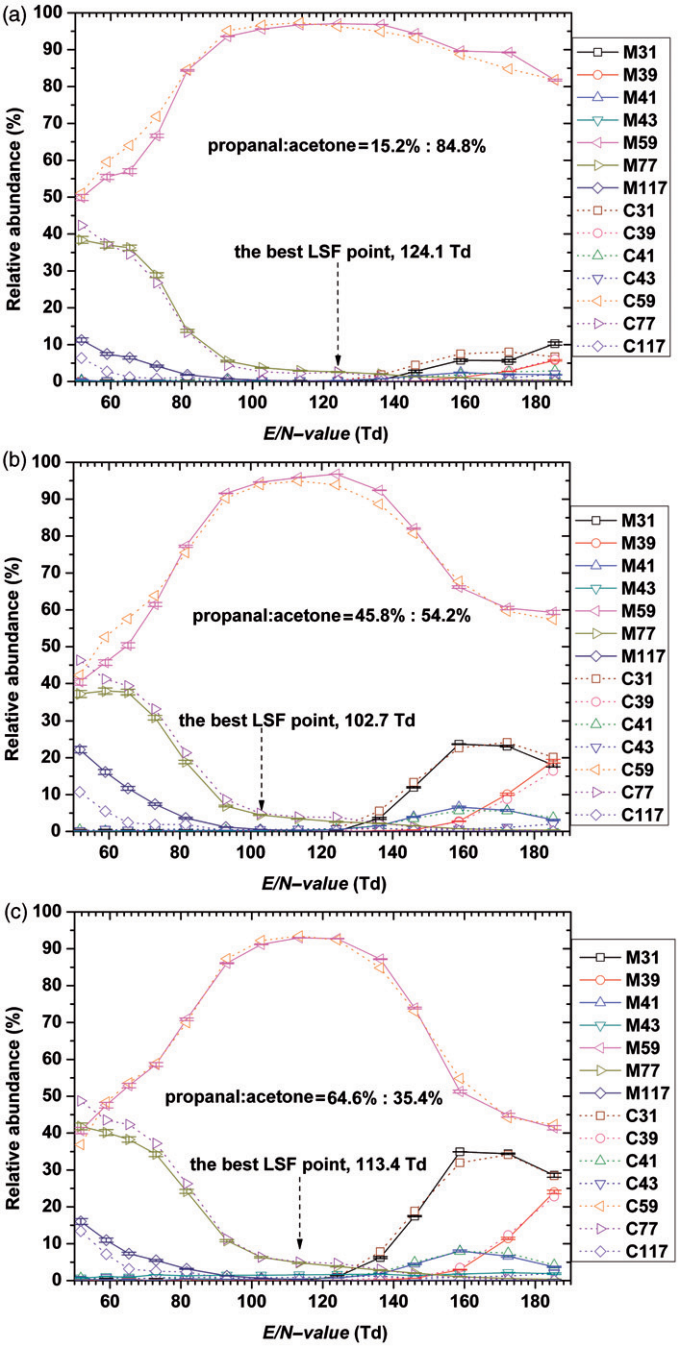

Figure 6. Quantifying propanal and acetone in a mixture of the two together with the PFDs of PID. *E/N-value* = 51.7, 59.0, 65.4, 73.0, 81.6, 93.0, 102.7, 113.4, 124.1, 136.3, 146.0, 158.7, 172.3, 185.3 Td; $dwell_{mi} = 0.5$ s; $N_c = 20$. The δA for concerned product ions are presented by Y-error bars, which are calculated based on Equation 7. The concentration ratio of propanal to acetone is (a) 15.2%: 84.8%, (b) 45.8%: 54.2%, (c) 64.6%: 35.4% respectively, which is obtained from the least square fit (LSF) based on the known PFDs of PID for pure propanal and acetone in Figure 3. The solid lines are the measured PFDs of PID for mixture, and the dot lines are the calculated PFDs of PID for mixture from results in Figure 3.

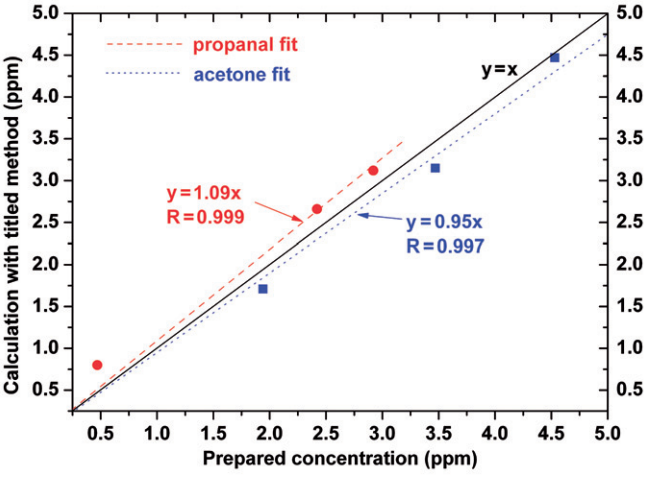

Figure 7. Comparison of the concentrations calculated by titled method with the prepared concentrations in the mixtures of propanal and acetone together. The fit lines are obtained from the linear fit through zero.

And it is demonstrated that with these profiles PTR-MS can be used to identify and differentiate isomers/isobars in the samples without additional instrumental configurations. Two examples have been used to illustrate this convenient method: (1) cyclohexanone was identified to be a major compound in the headspace of medical infusion sets; and (2) the differentiation and quantification of propanal and acetone in three synthetic mixtures with different ratios of 15.2%/84.8%, 45.8%/54.2% and 64.6%/35.4%. This study also illustrate the necessity in extending the range of reduced-field, e.g. more characteristics product ion distribution can be obtained for the butyl alcohols at *E/N-value* below 100 Td which is lower than the normal range (100–140 Td) operated by PTR-MS. However, it must be pointed out that the method in discussion will not be applicable for distinguishing isomers/isobars in the complex mixtures at this stage, however as illustrated in the examples it shows its usefulness in some practical applications in the identification and differentiation of isomers/isobars and as a method for the initial analysis of a sample, without additional instrumental configurations to the PTR-MS instrument. Also, these various PFDs of PID for the compounds presented in this study may lead to further investigations of the reaction mechanisms which are worthy to be carried out and to be pursued from here.

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