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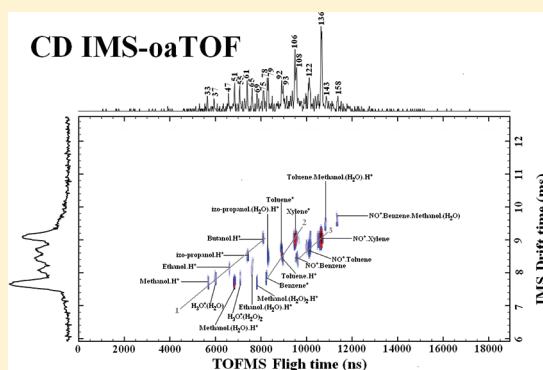
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# Corona Discharge Ion Mobility Spectrometry with Orthogonal Acceleration Time of Flight Mass Spectrometry for Monitoring of Volatile Organic Compounds

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**ABSTRACT:** We demonstrate the application of corona discharge ion mobility spectrometry with orthogonal acceleration time of flight mass spectrometry (CD IMS-*oa*TOF) for volatile organic compounds (VOCs) monitoring. Two-dimensional (2D) IMS-*oa*TOF spectra of VOCs were recorded in nearly real time. The corona discharge atmospheric pressure chemical ionization (APCI) source was operated in positive mode in nitrogen and air. The CD ion source generates in air  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  and  $\text{NO}^+$ . The  $\text{NO}^+$  offers additional possibility for selective ionization and for an increase of the sensitivity of monoaromatic compounds. In addition to  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  and  $\text{NO}^+$ , we have carried out ionization of VOCs using acetone as dopant gas ( $(\text{CH}_3)_2\text{COH}^+$ ). Sixteen model VOCs (tetrahydrofuran, butanol, *n*-propanol, iso-propanol, acetone, methanol, ethanol, toluene, benzene, amonnia, dioxan, triethylamine, acetonitrile, formaldehyde, *m*-xylene, 2,2,2-trifluoroethylamine) were tested using these ionization techniques.



There exists increasing demand for volatile organic compounds (VOCs) monitoring and analysis in various fields of science and applications. Industrial and environmental applications require air and wastewater quality monitoring. The monitoring of pollutants is important in indoor and outdoor environments because of their impact on human health. On the other hand, the analysis of VOCs exhaled from human breath, especially those of endogenous origin, seems to be a promising method for the noninvasive diagnosis of diseases and prevention.

The gas chromatography (GC) techniques like GC-flame ionization detection (GC-FI),<sup>1</sup> GC-infrared detection (GC-IR),<sup>2</sup> and GC/mass spectrometric detection (GC/MS)<sup>3</sup> are considered as a standard for VOCs analysis due to their high sensitivity and high selectivity. However, the higher time consumption is the main drawback of the GC techniques. The supercontinuum cavity ring down spectroscopy (SCRDS)<sup>4</sup> is characterized by high sensitivity (sub ppb level) and relatively quick response. The requirement of tunable lasers and high reflectance mirrors, suitable for a given wavelength, complicates wider deployment of such instruments. The mass spectrometric techniques like atmospheric pressure chemical ionization mass spectrometry (APCI-MS),<sup>5,6</sup> proton transfer reaction mass spectrometry (PTR-MS),<sup>7</sup> and selected ion flow tube mass spectrometry (SIFT-MS)<sup>8</sup> are due to their high sensitivity and fast response preferred techniques in many applications. The fragmentation in the case of PTR-MS and APCI-MS could complicate the data analysis of more complex spectra. In order to reach high sensitivity, these devices require longer data acquisition or preconcentration techniques, which can adversely affect the time

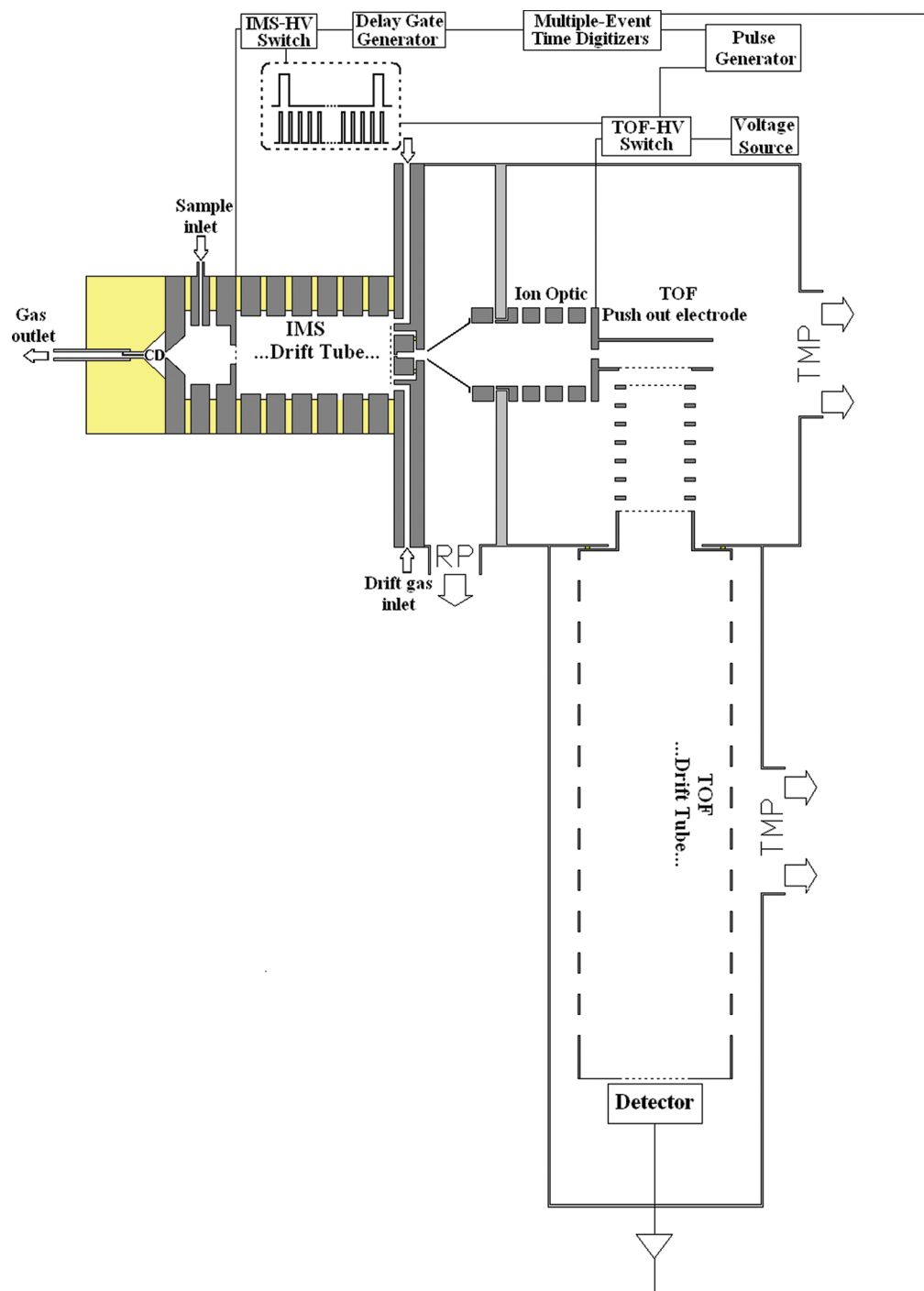
consumption. These problems could be partially solved by replacement of quadrupole MS by more expensive time-of-flight MS (TOFMS). However, even in this case, these MS techniques are not able to resolve the individual isomers.

The ion mobility spectrometry (IMS),<sup>9,10</sup> due to its compact design, high sensitivity, and fast response, is a valuable instrument for VOCs monitoring in various applications.<sup>11–13</sup> However, in the case of analysis of complex mixtures, the IMS as an individual unit does not have sufficient selectivity. This problem could be partially solved by the selectivity in ionization, doping of ionization source of IMS,<sup>14</sup> or by interfacing IMS to other analytical instruments. The combination of IMS with other techniques is found in applications in analytical laboratories all around the world.<sup>15–17</sup> The successful application of GC coupled with IMS is found in air quality monitoring on the international space station,<sup>18</sup> while the multicolumns capillary GC (MCC-GC) IMS combination is used in medical applications for analysis of human breath.<sup>19</sup>

The first instrument combining a drift tube and orthogonal TOF appeared in 1967 by McKnight et al.<sup>20</sup> and has been applied to study ion molecule reactions of nitrogen ions in  $\text{N}_2$ . The operating conditions were different to present IMS devices; the pressure in the drift tube was only  $\sim 133$  Pa. The IMS interfaced orthogonally accelerated TOF spectrometer (IMS-*oa*TOF) was introduced as a high performance analytical instrument.<sup>21</sup> The

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**Figure 1.** Schematic view of CD-IMS-oaTOF instrument.

IMS-oaTOF spectrometry with MALDI and ESI ionization sources was used for lipid, peptide, nucleotide, and human blood analysis.<sup>22–24</sup> Traveling wave IMS-MS (TWIMS-MS) with thermal desorption ESI ionization source was presented in a recent publication by Reynolds et al.<sup>25</sup> for detection of VOCs in human breath.

The corona discharge (CD) ion source offers, in contrast to conventional (radioactive) ion sources used with IMS in air, an additional versatility. In addition to the chemical ionization via proton transfer  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ , the CD ion source generates  $\text{NO}^+$  ions, which offer an additional selective ionization channel. In this paper, we discuss in detail the processes associated with

ionization of selected VOCs with CD ion source and demonstrate the VOCs analysis by linear CD IMS-oaTOF.

## EXPERIMENTAL SECTION

**Instrumental Setup.** The schematic view of a CD-IMS-oaTOF instrument developed at Comenius University is given in Figure 1. The IMS was operated at ambient pressure, in positive mode and in single flow regime with gas outlet located behind the CD. Two positive high voltage power supplies (Heinzinger LNC) were used, one for CD and the second supplied the drift field of the IMS. The shutter grid (SG) of Bradbury-Nielsen type was controlled by high voltage switch (Behlke GmbH). The IMS

typically operated with drift field 430 V/cm; the SG gate was open for 110  $\mu$ s with a period of 15 ms, and the operation temperature was 317 K. The detailed description of CD-IMS was given in our previous work.<sup>26</sup>

The IMS was interfaced to a differential pumping system through a 100  $\mu$ m pinhole in the collector. The differential pumping system consists of three vacuum chambers. The first one was pumped by two rotary pumps (Pfeiffer Vacuum overall pumping speed, 30 m<sup>3</sup>/h) to the pressure of 10<sup>-1</sup> mbar. The second one was pumped by a turbo molecular pump with a pumping speed of 330 L·s<sup>-1</sup> (Pfeiffer Vacuum) to the pressure of 10<sup>-5</sup> mbar. The third chamber was also pumped by a turbo molecular pump with a pumping speed of 250 L·s<sup>-1</sup> (Pfeiffer Vacuum) to the pressure of 5 × 10<sup>-6</sup> mbar. For more details of our differential pumping system, please refer to ref 27.

The ions that passed through the 100  $\mu$ m pinhole of the IMS collector were guided by the ion optic (IO) located in the second vacuum chamber, to the orthogonal acceleration chamber of linear time-of-flight mass spectrometer,<sup>28</sup> located in the third vacuum chamber. The ion optic consists of the skimmer and five electrodes; the operation potential of the skimmer was -3.2 V, and the potential of the remaining electrodes was below -15 V. The orthogonal acceleration chamber of TOF consists of two parallel electrodes. The distance between the electrodes is 5 mm with 2 mm entrance slit (Figure 1). The rear electrode of the orthogonal acceleration chamber of TOF serves as a push out electrode, while the front one was partially shielded by the stainless steel mesh with a transmittance of 60%. The ions shuttered from this region were uniformly accelerated to the drift tube of a oaTOF spectrometer. The acceleration region of oaTOF<sup>29</sup> contains seven electrodes at 7 mm separation between the electrodes, interconnected by the high precision vacuum resistors. The drift tube of the oaTOF was constructed from a stainless steel perforated tube of total length of 547 mm. The multichannel plate (MCP) detector (Tectra) was used. The signal from the detector was processed by a preamplifier (Ortec 9301) and collected by a multiscaler PCI card (FASTComTec GmbH, model P-7888). The TOF was calibrated by FASTComTec software delivered with the multiscaler PCI card.

The push out electrode was pulsed with the 25  $\mu$ s period and 10  $\mu$ s pulse width. The push out electrode was controlled by a high voltage transistor switch (Behlke GmbH) managed by a pulse generator (HAMEG HM8035). The pulse generator was also used for the triggering of a multiscaler PCI card. The multiscaler PCI card was able to generate a synchronic TTL signal additionally modified by a delay gate generator (TENELEC, TC410A) to manage the high voltage switch (Behlke GmbH) of IMS, as it is schematically depicted on Figure 1. Thus, the IMS was synchronically operated with the TOF spectrometer.

**Author:** The present CD IMS-oaTOF instrument was able to operate in three modes: in "Single IMS" mode, in "Single TOF" mode when the SG of IMS was fully open, and in the two-dimensional "2D mode" used when the IMS and TOF spectrometers were operated synchronically. The limits of detection which will be discussed in more detail in the next sections were determined for Single IMS mode with data acquisition time of several seconds. This limit of detection can be achieved as well in Single TOF and 2D mode. The high selectivity in the Single TOF and 2D modes is on the costs of increasing data acquisition time to ~1 or ~5 min, respectively. Operation parameters of the IMS-oaTOF system are summarized in Table 1.

**Table 1. Operation Parameters of IMS-oaTOF Instrument**

IMS	
IMS drift tube length	8.2 cm
drift field intensity	430 V/cm
IMS operating temperature	317 K
drift gas flow rate	0.5 L·min <sup>-1</sup>
IMS pressure	10 <sup>5</sup> Pa
SG pulse width	110 $\mu$ s
SG frequency	78 Hz
average IMS resolving power	60
oaTOF	
TOF pulse width	10 $\mu$ s
TOF pulse frequency	40 kHz
TOF acceleration voltage	3650 V
mass accuracy	0.1 Da
average TOF resolving power	400

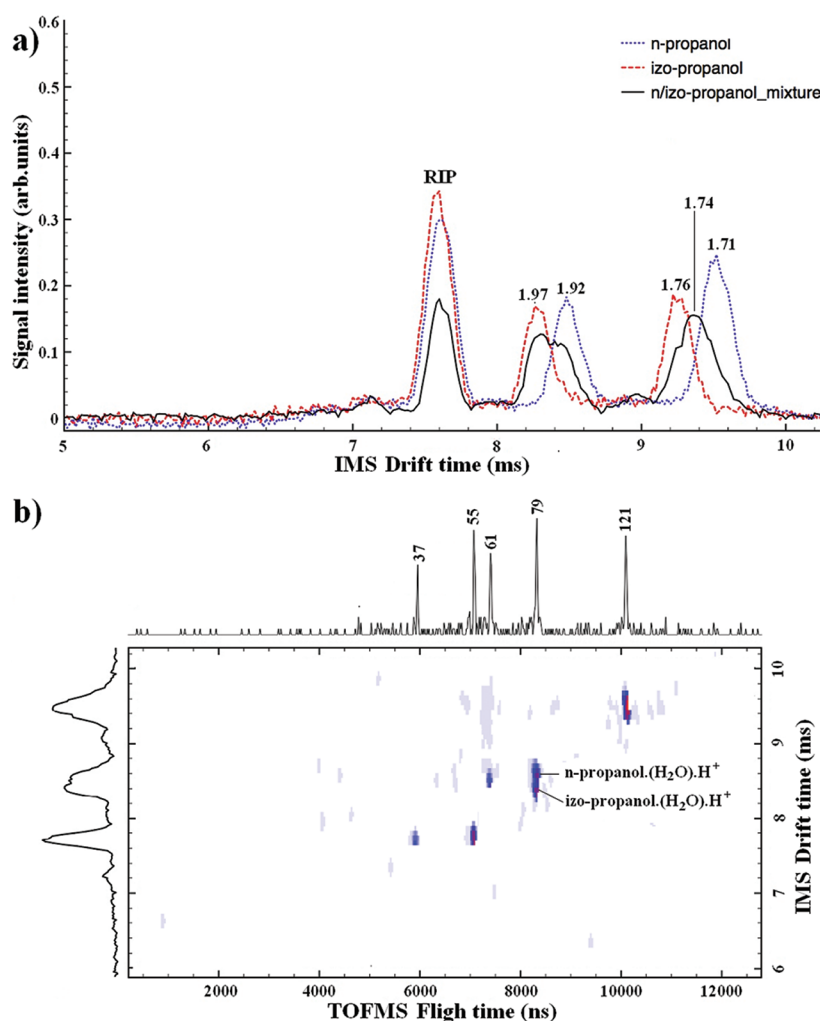
**Gases and Chemicals.** The gases used in this experiment were N<sub>2</sub> and O<sub>2</sub> obtained from Linde Gas with purity up to 5.0 (99.999%). The gases were additionally purified by molecular sieve trap (Aglinet) in order to reduce water concentration down to 14 ppb. The drift gas flow was 500 mL/min, and carrier sample gas stream was 100 mL/min during the experiment.

The chemicals used in this study, tetrahydrofuran, butanol, *n*-propanol, iso-propanol, acetone, methanol, ethanol, toluene, benzene, amomonia, dioxan, triethylamine, acetonitrile, formaldehyde, *m*-xylene, and 2,2,2-trifluoroethylamine, were obtained from different suppliers with stated purity up to 99%. Diluted vapors of the chemicals were dosed to the reaction region of the IMS instrument by the syringe pumps (Kent Scientific, Genie Plus). In order to prevent diffusion, the syringe tip was interfaced to a 15 cm long stainless steel capillary with an inner diameter of 0.2 mm.

## RESULTS AND DISCUSSION

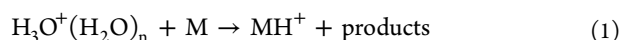
The IMS is a separation technique based on interaction of the ions with molecules of the buffer gas in a weak homogeneous electric field. Among others factors, the separation depends on the mass of the ions and their geometry.<sup>9</sup> This allows separation of isomeric ions.<sup>30,31</sup> This can be considered as an important advantage of the IMS-oaTOF technique. In order to demonstrate this ability, we have prepared a mixture of the *n*-propanol and iso-propanol isomers where the second one is frequently observed in human breath, being partly of endogenous origin.<sup>32</sup> The response of IMS on *n*-propanol and iso-propanol and their mixture in nitrogen drift gas is depicted in Figure 2a. Pure N<sub>2</sub> was used in this experiment in ion source as well as in the drift tube. The formation of the ions in CD in ultrapure N<sub>2</sub> has been studied already by Carol et al.<sup>33</sup> Sabo et al.<sup>34</sup> demonstrated that H<sub>3</sub>O<sup>+</sup>(H<sub>2</sub>O)<sub>*n*</sub> cluster ions (*n* = 0, 1, 2) are dominant in the IMS drift tube even if the H<sub>2</sub>O concentration on N<sub>2</sub> was reduced below 100 ppt.

The ions in the IMS are subjected to collisions with N<sub>2</sub> and H<sub>2</sub>O (at very high collision rate), and this is responsible for establishment of equilibrium between clustering and declustering reactions. Thus, in the IMS spectrum, a single ion peak represents distribution of ion clusters H<sub>3</sub>O<sup>+</sup>(H<sub>2</sub>O)<sub>*n*</sub>; the size of the clusters is governed by equilibrium constants (for clustering and declustering reactions), by the H<sub>2</sub>O concentration, and by the temperature of the drift gas.<sup>35</sup> It has been shown that in the present case the hydronium water cluster ions H<sub>3</sub>O<sup>+</sup>(H<sub>2</sub>O)<sub>*n*</sub> are formed, with *n* > 1.

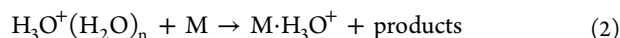


**Figure 2.** (a) IMS spectrum of *n*-propanol, izo-propanol, and the mixture; (b) 2D map of *n*/izo-propanol mixture.

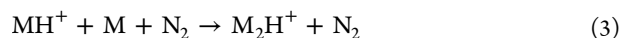
The ionization of the propanol isomers can proceed via proton transfer reaction:



as well as via the switching reaction:



The reaction 1 is followed by further clustering:



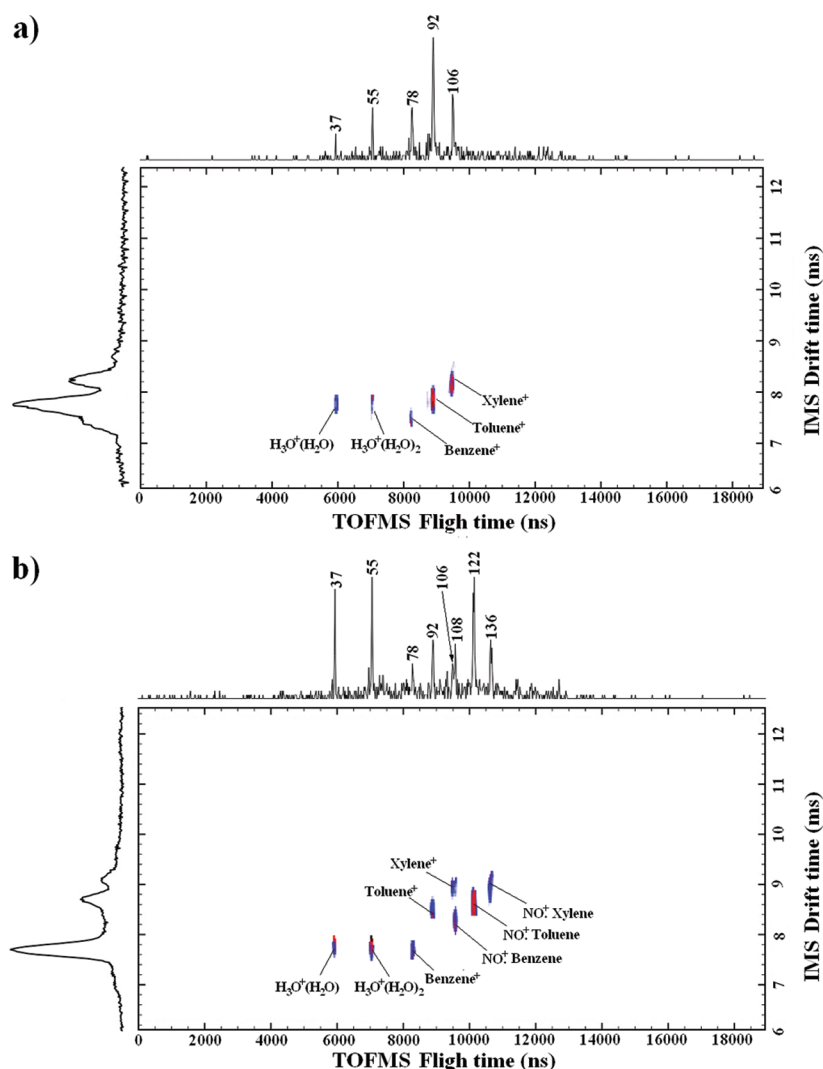
The two peaks of *n*-propanol with reduced mobilities of 1.92 and 1.71  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  correspond to protonated monomers  $[\text{M} \cdot (\text{H}_2\text{O})_n \cdot \text{H}^+]$  ( $n = 0, 1$ ) and its dimer  $[\text{M}_2 \cdot \text{H}^+]$  ions, respectively. On other hand, the protonated izo-propanol monomer and its dimer possess reduced mobilities of 1.97 and 1.76  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  (Figure 2a).

The protonated monomers  $[\text{M} \cdot (\text{H}_2\text{O}) \cdot \text{H}^+]$  are resolved as well, if a mixture of these two isomers is introduced to the reaction chamber of IMS. In contrast to IMS spectra of isolated molecules, in the case of a mixture, a dimer peak with reduced mobility of 1.74  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  is formed, which is located in the center between the dimer peaks of isolated substances (Figure 2a). This suggests formation of an asymmetric dimer complex composed of both propanol isomers. The width of this peak indicates that besides asymmetric dimer still nonasymmetric

dimer ions are present. The monomer peaks are also resolved by IMS-*oa*TOF spectrometry, as we can see from the 2D map in the Figure 2b. This demonstrates the selectivity of IMS-*oa*TOF technique toward the isomers. The high selectivity of IMS-*oa*TOF can be effectively used in applications where analysis of more complex spectra is required, as it has high selectivity not only against isomer but also against isobaric molecules.

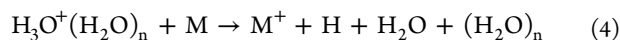
The monitoring of monoaromatic VOCs like benzene, toluene, and *m*-xylene (BTX) has become a case of interest in various fields of environmental<sup>36–38</sup> and medical applications.<sup>32</sup> We have studied the sensitivity as well as the selectivity of APCI associated with IMS-*oa*TOF via different primary ions. The 2D map of BTX compounds measured by CD IMS-*oa*TOF in pure  $\text{N}_2$  is shown in Figure 3a. This figure indicates that the ions formed from these monoaromatic VOCs are molecular ions  $[\text{M}^+]$  with masses  $m/z = 78, 92,$  and  $106$  Da and with corresponding reduced mobilities of 2.19, 2.07, and 1.99  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ . According to Španěl and Smith<sup>39</sup> in the case of benzene, the proton transfer reaction to benzene (1) was possible only for  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$   $n = 0$  and 1; for  $n > 1$ , the reaction was not observed. We assume that a similar situation is also for toluene and *m*-xylene in spite of the fact that they have a little bit of a higher proton affinity (PA) ( $\text{PA}(\text{B}) = 750.4$  kJ/mol,  $\text{PA}(\text{T}) = 784$  kJ/mol, and  $\text{PA}(\text{X}) = 809.1$  kJ/mol). The CD generates reactant ion peak (RIP) containing mainly  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$  and  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ ; the present results indicate that the proton bond





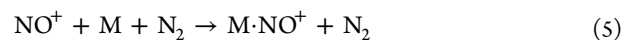
**Figure 3.** (a) 2D map of BTX molecular ions measured in pure  $N_2$ ; (b) 2D map of BTX molecular and  $NO^+$  adducts ions measured in zero air.

energy in RIP ions exceed the PA of BTX compounds. The absence of switching reaction 2 indicates that as well the hydronium ion bond to water in the RIP exceeds those to the BTX. This is the reason why the proton transfer reaction 1 as well as the switching reaction 2 are not operative in CD in pure  $N_2$ . We explain the detection of  $M^+$  ions in MS by dissociative charge transfer reaction:



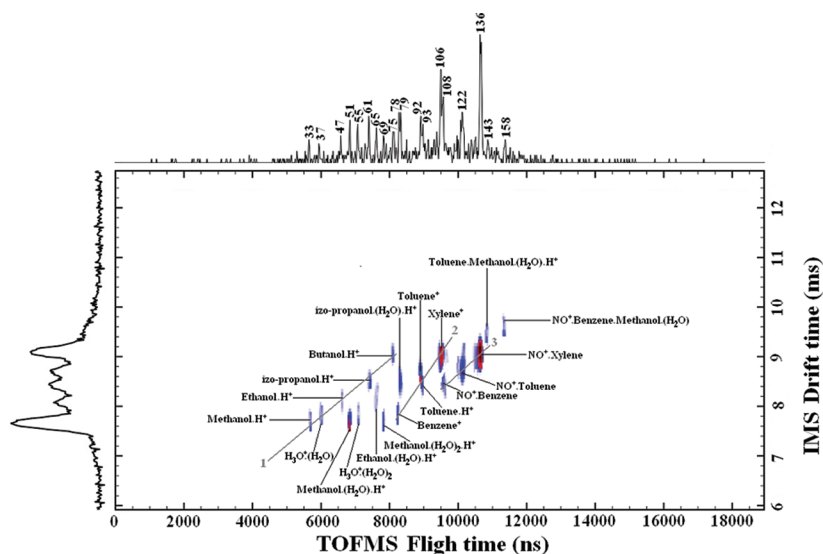
We have evaluated the limit of detection (LOD) for BTX for CD ion source in pure nitrogen for  $H_3O^+(H_2O)_n$  chemical ionization; the values determined were 37 ppb for benzene, 41 ppb for toluene, and 72 ppb for *m*-xylene. The sensitivity of IMS-oaTOF is relatively low for  $H_3O^+(H_2O)_n$  ionization. We may compare it with the PTR-MS technique by Warneke et al.<sup>40</sup> They reported for benzene and toluene a LOD of 9 and 5 ppt, respectively. Huang et al.<sup>6</sup> reported a LOD of 0.2 and 0.5 ppb for benzene and toluene, respectively, using the APCI-MS technique. The high sensitivity of PTR-MS is due to chemical ionization with  $H_3O^+$  and  $H_3O^+(H_2O)$ , which are able to ionize these compounds by proton transfer reaction. The low sensitivity of IMS-oaTOF is due to formation of large cluster ions  $H_3O^+(H_2O)_n$  with  $n \geq 1$  in CD and inability of these clusters to ionize BTX. The ionization via reaction 4 is inefficient.

The situation improves, if we switch to synthetic air as working gas in the CD and IMS. The CD generates in this case two different groups of primary ions  $H_3O^+(H_2O)_n$  and  $NO^+$ . The reactions of  $NO^+$  primary ions with analytes result in appearance of  $[M \cdot NO^+]$  ions in the mass spectra (Figure 3b), which are formed via association reaction in the presence of the working gas  $N_2$  or  $O_2$ :



The association reaction of  $NO^+$  with molecules has been intensively studied by Španěl and Smith using selected ion flow tube (SIFT) for large classes of organic compounds (please see Španěl and Smith<sup>41</sup> and the references therein). Recently, the PTR-MS instrument was modified in order to allow  $O_2^+$  and  $NO^+$  for chemical ionization (Jordan et al.<sup>42</sup>). The application of  $NO^+$  chemical ionization in IMS was reported by Karasek et al.<sup>43</sup> who used radioactive ion sources and the  $NO^+$  reactant ion intensity depended on NO admixture to zero air. Borsdorf et al.<sup>30</sup> reported ionization  $NO^+ \cdot (H_2O)_n$  formed in CD and its reactivity to toluene.

The formation of the  $NO^+$  in the positive CD in air can be considered as an important aspect of the CD ionization source in comparison to the widely used radioactive sources. The  $NO^+$  yield from CD in air depends on many discharge parameters like:



**Figure 4.** Trend lines of alcohols and BTX compounds measured in zero air: 1, trend line of alcohol group; 2, trend line of molecular BTX ions; 3, trend line of BTX  $\text{NO}^+$  adduct ions.

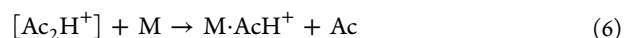
discharge power, gas flow speed, flow direction, and many others.<sup>44,45</sup> The CD source used in this study was designed for efficient removal of the radicals from CD gap<sup>26</sup> and thus not optimized for  $\text{NO}^+$  generation; the total  $\text{NO}^+$  yield from our CD was only 22% for high CD power. However, also, this  $\text{NO}^+$  yield results in a significant increase in the sensitivity for BTX compounds. The LOD for  $[\text{M} \cdot \text{NO}^+]$  product ions was determined to be 1.5 ppb for benzene, 1.4 ppb for toluene, and 2.6 ppb for *m*-xylene. The 2D plot of BTX compounds at 0.1 ppm concentration obtained in zero air is shown in Figure 3b. The ions with reduced mobilities 2.14, 1.95, and  $1.81 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  and masses  $m/z = 78, 92$ , and  $106 \text{ Da}$  were assigned to molecular BTX ions  $[\text{M}^+]$  while the ions with reduced mobilities 2.0, 1.87, and  $1.79 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  and masses  $m/z = 108, 122$ , and  $136 \text{ Da}$  to be assigned to  $[\text{M} \cdot \text{NO}^+]$  ions. The ability of CD in air to produce  $\text{NO}^+$  thus offers an additional way to detect the chemicals via reaction 5. This advantage may be very desirable for more complex analytical tasks.

An important feature of the IMS-*oa*TOF instruments is the ability to record 2D IMS-MS spectra. In the 2D spectra, for particular classes of the chemicals, correlations in mobility-mass spectra exist, also called trend lines.<sup>21</sup> We have prepared a mixture consisting of two different groups of chemicals, (i) alcohols (methanol, ethanol, *iso*-propanol, and butanol) and (ii) monoaromatic compounds (BTX). We have measured 2D IMS-MS spectra of this mixture in zero air (Figure 4). The alcohols were ionized mostly via proton transfer reaction 1 forming  $[\text{MH}^+]$ . For these ions, we are able to find a trend line designed as Nr. 1. The ions formed from monoaromatic VOCs via reaction 4 are situated on the trend line Nr. 2, and those formed via reaction 5 occupy the trend line Nr. 3. The importance of the trend lines for a particular class of molecules is easier identification of the compounds. For the ions of the same class, we can find some variations from the trend line because of differences in the structure<sup>46</sup> and also due to formation of water clusters resulting in a slowdown of the ions swarm in IMS.<sup>47</sup>

To demonstrate the analytical power of the CD IMS-*oa*TOF instrument, we have prepared a complex mixture of VOCs (sixteen VOCs mentioned in the Experimental Section except acetone). The VOCs were put in closed vials into a paper box, and the air from this box was sampled by air flow through the box.

The 2D map of this sample acquired using APCI in air ( $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  RIP ions) at flow of  $0.5 \text{ mL/min}$  through the box is presented in the Figure 5a. As we can see from this figure, the ammonia, methanol, *iso*-propanol, benzene, toluene, tetrahydrofuran, and 2,2,2-trifluoroethylamine were easily detected. The further increase of the gas flow would result in detection of more compounds from the box and disappearance of all reactant ions from the spectrum, which is an unwanted effect.<sup>9</sup>

We have applied a different APCI ionization with acetone as dopant gas. In this case, the reactant ions formed in APCI are acetone dimer ions  $[\text{Ac}_2\text{H}^+]$  (doping of CD ion source<sup>14</sup>). The doping of CD ion source may improve the sensitivity and selectivity of the instruments. The mechanism of the ionization is  $\text{AcH}^+$ , most probably following reaction:

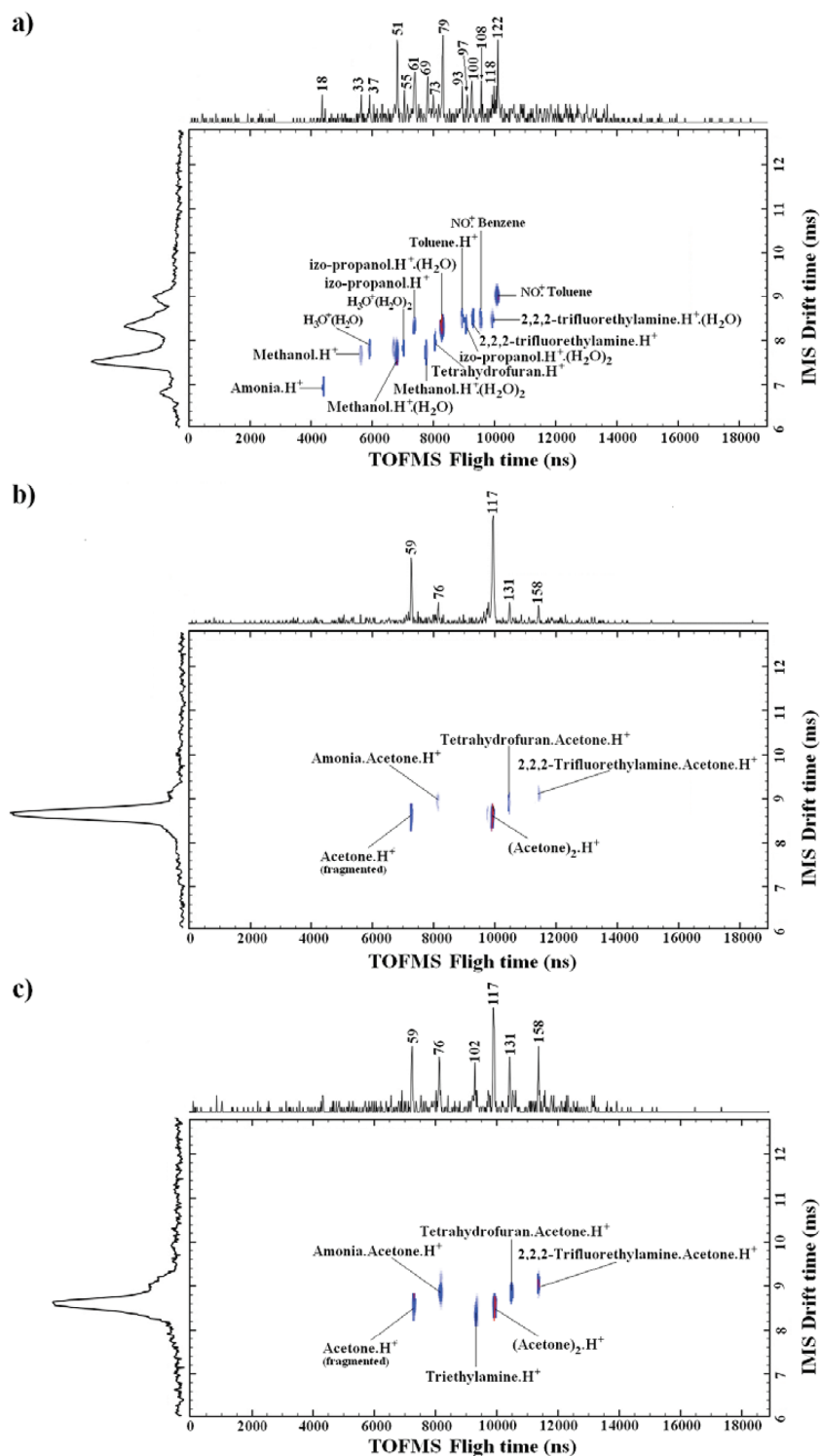


and, thus in this case, only VOCs with  $\text{M} \cdot \text{AcH}^+$  bond higher than  $\text{Ac} \cdot \text{AcH}^+$  are detected (Figure 5b) (ammonia, tetrahydrofuran, and 2,2,2-trifluoroethylamine). The detected ions were asymmetric complex ions<sup>48</sup> consisting of protonated complex acetone and the protonated molecule  $(\text{acetone} \cdot \text{M})\text{H}^+$ . The further increase of gas flow (to  $1 \text{ mL/min}$ ) resulted in detection of triethylamine as we can see from Figure 5c. Unlike the other compounds, triethylamine did not form the asymmetric complex and its protonated ions were observed. The formation of this ion resulted from high PA of triethylamine.

This experiment demonstrated the application of a dopant gas. The dopant can improve the selectivity and sensitivity and also decrease the data acquisition time of the CD IMS-*oa*TOF instrument. In Figure 5b,c, we can also see the fragmentation of acetone dimer to its protonated monomer. Such fragmentation is in general considered as a benefit of IMS-*oa*TOF instruments.<sup>21,33</sup> The parent and fragmented ions had the same mobility drift time in the 2D map. The fragmentation of the dimer ions can be controlled by the skimmer potential in the first vacuum chamber.<sup>21</sup>

## CONCLUSION

We have presented the CD IMS-*oa*TOF instrument as a powerful analytical tool for analysis of isomers and for VOCs



**Figure 5.** (a) VOCs measured from the box with pumping speed of 0.5 mL/min; (b) VOCs measured from the box with pumping speed of 0.5 mL/min after doping of IMS with acetone; (c) VOCs measured from the box with pumping speed of 1 mL/min and [Ac<sub>2</sub>H<sup>+</sup>] reactant ions.

analysis. Due to versatility of the CD based APCI ion source, the instrument offers different chemical ionization methods based on generation of H<sub>3</sub>O<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub>, NO<sup>+</sup> in air, and also with a dopant gas (acetone). These alternative ionization schemes resulted in increase of the sensitivity for detection of monoaromatic compounds and thus are very suitable for VOCs detection. At the present time, the data acquisition time of 5 min for detection of the full 2D map was achieved, which could be sufficient for

various applications where the complex VOCs monitoring is required. In the future, we see the possibility to decrease further the acquisition time. The sensitivity of the instrument, in comparison with other methods like PTR-MS and APCI, was moderate; however, we would like to note that the method and instrument are still under development and further improvements in sensitivity and selectivity are possible. A promising feature of the instrument is the selectivity to isomers and to



isobaric molecules. This could find future applications in the fields of VOCs analysis for environmental, industrial, and medical applications.

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### Notes

The authors declare no competing financial interest.

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