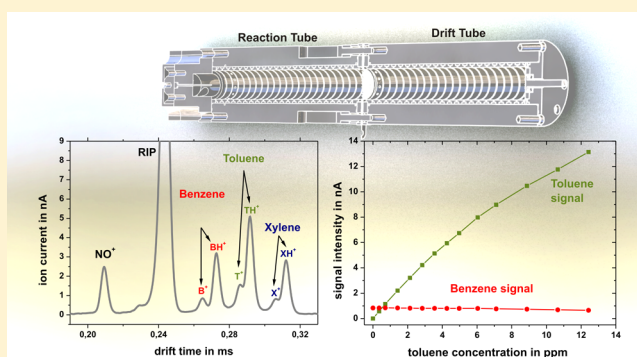


Quantitative Detection of Benzene in Toluene- and Xylene-Rich Atmospheres Using High-Kinetic-Energy Ion Mobility Spectrometry (IMS)

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ABSTRACT: One major drawback of ion mobility spectrometry (IMS) is the dependence of the response to a certain analyte on the concentration of water or the presence of other compounds in the sample gas. Especially for low proton affine analytes, e.g., benzene, which often exists in mixtures with other volatile organic compounds, such as toluene and xylene (BTX), a time-consuming preseparation is necessary. In this work, we investigate BTX mixtures using a compact IMS operated at decreased pressure (20 mbar) and high kinetic ion energies (HiKE-IMS). The reduced electric field in both the reaction tube and the drift tube can be independently increased up to 120 Td. Under these conditions, the water cluster distribution of reactant ions is shifted toward smaller clusters independent of the water content in the sample gas. Thus, benzene can be ionized via proton transfer from H_3O^+ reactant ions. Also, a formation of benzene ions via charge transfer from NO^+ is possible. Furthermore, the time for interaction between ions and neutrals of different analytes is limited to such an extent that a simultaneous quantification of benzene, toluene, and xylene is possible from low ppb_v up to several ppm_v concentrations. The mobility resolution of the presented HiKE-IMS varies from $R = 65$ at high field (90 Td) to $R = 73$ at lower field (40 Td) in the drift tube, which is sufficient to separate the analyzed compounds. The detection limit for benzene is 29 ppb_v (2 s of averaging) with 3700 ppm_v water, 12.4 ppm_v toluene, and 9 ppm_v xylene present in the sample gas. Furthermore, a less-moisture-dependent benzene measurement with a detection limit of 32 ppb_v with ca. 21 000 ppm_v (90% relative humidity (RH) at 20 °C) water present in the sample gas is possible evaluating the signal from benzene ions formed via charge transfer.



Benzene is a widely used aromatic chemical compound that is classified by the International Agency for Research on Cancer (IARC) as carcinogenic to humans (Group 1).¹ It is a natural constituent of crude oil and currently is mainly used as a precursor to benzene derivatives such as styrene and phenol. The current European legal exposure limit for benzene (2004/37/EG) is 1 ppm_v . The threshold limit value (TLV) provided by the U.S. National Institute for Occupational Safety and Health (NIOSH) for a time-weighted average is 500 ppb_v . However, the recommended airborne exposure limit is usually lower than the threshold exposure limit. Thus, a benzene concentration of <100 ppb_v should be accurately and regularly quantified. Benzene is often found in mixtures together with toluene and xylene in comparable or even higher concentrations; these three are collectively referred to as BTX. Therefore, a sensor system suitable for monitoring benzene in ambient air must be able to quantitatively measure benzene down to low- ppb_v levels in the presence of varying amounts of toluene, xylene, and water, as well as other volatile organic compounds (VOCs) and compounds such as N_2 , O_2 , and CO_2 . Multiple methods for a measurement of BTX are described in the literature, varying from preconcentration via thermal

desorption systems and analysis with a gas chromatography (GC) system coupled with a flame ionization detection (FID) device² or a mass spectrometer (MS), to a direct detection with proton transfer reaction mass spectrometry (PTR-MS).³ Furthermore, ion mobility spectrometry (IMS) devices with GC preseparation and a continuous atmospheric pressure chemical ionization (APCI) or direct optical ultraviolet ionization (UV)⁴ are used, as well as IMS-MS⁵ and IMS with pulsed ionization sources.⁶ Also, the absorption of mid-infrared radiation emitted by quantum cascade lasers (QCLs) in hollow wave guides⁷ and Bragg grating sensors⁸ were investigated. However, in order to simultaneously analyze gas mixtures containing BTX with sufficient limits of detection for benzene, all described methods either necessitate preconcentration (QCL, GC-MS), preseparation (IMS), or a comparably high instrumental effort (PTR-MS). Measurement systems based on the spectral absorption do not provide sufficient sensitivity, while more-sensitive systems based on the ionization at

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atmospheric pressure suffer from competing ion–molecule reactions. Solely PTR-MS and SIFT-MS (selected ion flow tube) enable a sensitive real-time measurement, but a sophisticated high-vacuum system is always necessary, making the design of compact systems difficult. Anyhow, we recently introduced a high-kinetic-energy ion mobility spectrometer (HiKE-IMS), which is operated at a pressure of 20 mbar and reduced electric fields up to 120 Td. (The unit Td represents a townsend; $1 \text{ Td} = 10^{-17} \text{ V cm}^2$.) As described in the following section, this enables simultaneous ionization and detection, even of low proton affine compounds, in a humid environment.⁹ In this context, the reduced field is a measure of the ions' average kinetic energy, which can be gained by acceleration through the electric field between two ion-neutral collisions. The reduced field in HiKE-IMS is more than 1 order of magnitude higher than the reduced field in conventional drift tube IMS, which is <10 Td. For a 2-s-averaged signal, a limit of detection (LOD) of 7 ppb_v toluene, independent from the moisture of the sample (up to 5400 ppm_v of water) gas, was presented. Furthermore, HiKE-IMS enables an observation of additional orthogonal parameters related to an increase in kinetic ion energy such as fragmentation and field-dependent ion mobility, which may help to separate compounds that have similar ion mobility under low field conditions. In this work, we show that it is possible to quantify traces of benzene in air with different concentrations of toluene, xylene, and water without preconcentration or preseparation using HiKE-IMS.

THEORETICAL BACKGROUND

In IMS, ions are separated and identified based on their compound specific ion mobility (K). In a drift-tube IMS process, the reduced ion mobility (K_0) can be calculated using the length of the drift tube (L), the time needed for ions to traverse the drift tube (τ), and the applied voltage (U), as well as the pressure (p) and temperature (T) of the drift gas:

$$K_0 = \frac{L^2}{U\tau} \left(\frac{p \times 273 \text{ K}}{T \times 1013 \text{ mbar}} \right)$$

Even though the mobility is constant under defined conditions, it may vary with the changing water content of the drift gas or kinetic energy of the ions. Thus, values of the mobility must be compared with care. A comprehensive introduction into ion mobility is given by Eiceman et al.¹⁰ and Revercomb and Mason.¹¹

In APCI, reactant ions are initially generated by ionization of the main constituents of the sample gas, which is usually air. Because of the residual water that is present, even in dry and clean air, the positive reactant ions are mainly H_3O^+ , NO^+ , and O_2^+ , which can form water clusters with several neutral water molecules. It is known that comparably large amounts of NO^+ reactant ions are typically generated in a corona discharge ionization.¹² However, with increasing water concentration, larger water clusters are formed and $\text{NO}^+(\text{H}_2\text{O})_n$ and $\text{O}_2^+(\text{H}_2\text{O})_n$ lose their charge in a ligand-switching reaction with water. The resulting reactant ion water cluster distribution is dependent on the kinetic ion energy and the water concentration.¹³ Positive analyte ions are generated either by charge transfer, association, proton transfer, or ligand switching reactions with these positive reactant ions. The reaction constant (k) for such a gas-phase reaction is typically in the order of the collision rate, resulting in a very efficient and fast ionization.¹⁴

Benzene (B) can be ionized via proton transfer from H_3O^+ and charge transfer with NO^+ and O_2^+ , as well as by association of NO^+ , resulting in BH^+ , B^+ , and BNO^+ product ions. Especially, the generation of BH^+ is extremely moisture-dependent. Toluene (T) and xylene (X) can also be ionized by $\text{H}^+(\text{H}_2\text{O})_2$ clusters; therefore, the moisture dependence is less pronounced here. However, when BTX are present in an atmospheric-pressure chemical ionization (APCI) source, the amount of benzene ions will drastically decrease, because of competing ionization processes. Toluene and xylene have higher proton affinity and lower ionization energy, compared to benzene (values are given in Table 1). This is also true for

Table 1. List of Proton Affinities and Ionization Energies

name	formula	proton affinity ^a (kJ/mol)	ionization energy ^b (eV)
water	H ₂ O	691	12.621
nitric oxide	NO	531.8	9.2642
oxygen	O ₂	421	12.0697
benzene	C ₆ H ₆	750.4	9.2437
toluene	C ₇ H ₈	784.0	8.828
<i>p</i> -xylene	C ₈ H ₁₀	794.4	8.44
<i>m</i> -xylene	C ₈ H ₁₀	812.1	8.55
<i>o</i> -xylene	C ₈ H ₁₀	796.0	8.56

^aData taken from ref 16. ^bData taken from ref 17.

ultraviolet (UV) ionization at atmospheric pressure, because of the high frequency of ion–molecule collisions. Thus, a quantitative measurement of benzene in ambient air with IMS is not possible without preseparation, because of moisture dependence and competing ion–molecule reactions.

However, the equilibrium water cluster distribution can be shifted toward a greater abundance of H_3O^+ with increasing kinetic energy of the reactant ions.¹⁵ This is possible by increasing the quantity E/N , the so-called “reduced electric field”, which is defined as the electric field (E) divided by the concentration of neutral molecules (N). At E/N values of >100 Td, a significant amount of H_3O^+ can be present, even in moist gases. The presented HiKE-IMS is operated at 20 mbar and using electric fields up to 60 V/mm, resulting in E/N values of up to 120 Td. In order to provide a water cluster distribution that is relatively independent of the water content of the analyzed sample gas, an additional and constant amount of water is introduced into the reaction tube. Thus, the comparably much lower amount of water introduced with the sample gas can be neglected.

The reaction time in HiKE-IMS is dependent on the E/N value in the IMS reaction tube, where both reactant ions and neutral analyte molecules are present. At the maximum E/N value, the reaction time is on the order of 100 μs . Therefore, the relative abundances of different ion species do not reflect the thermal distribution. Even at reaction rates k on the order of the collision rate (k_c), the effect of competing ionization processes of analytes present in the ppm_v range is significantly suppressed.

EXPERIMENTAL SETUP

The basic setup of the HiKE-IMS has recently been published.⁹ The main components are a reaction tube and a drift tube, which are separated by an ion gate consisting of three metallic grids. The experimental setup is shown in Figure 1, and the default operating parameters are given in Table 2. The length and diameter of the drift tube have been slightly modified from

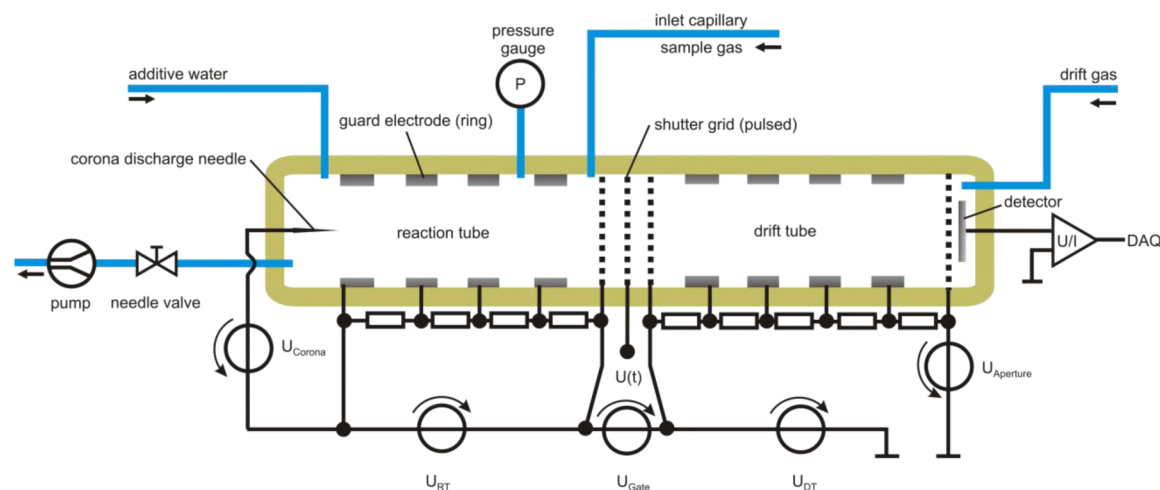


Figure 1. Experimental setup of the high-kinetic-energy ion mobility spectrometry (HiKE-IMS) system.

Table 2. Default HiKE-IMS Operating Parameters

parameter	value
temperature	35–35.5 °C
pressure	19–20 mbar
drift tube length	145 mm
reaction tube length	108 mm
inner electrode diameter	21 mm
drift tube voltage, U_{DT}	650–7400 V
reaction tube voltage, U_{RT}	1500–6050 V
reduced drift field, E_{DT}/N	10–110 Td
reduced reaction field, E_{RT}/N	30–120 Td
injection time	6 μ s
gate voltage, U_{Gate}	12 V
corona voltage, U_{Corona}	1000 V
$U(t)$ voltage shutter grid (open)	$U_{DT} + \frac{1}{2}U_{Gate}$
$U(t)$ voltage shutter grid (closed)	$U_{DT} + \frac{1}{2}U_{Gate} + 12$ V
aperture voltage, $U_{Aperture}$	20 V
drift gas flow	5 sccm dry clean air (<1 ppm water)
sample gas flow	6.5 sccm via capillary flow restriction
reaction chamber additive water	1 sccm

the previously published setup in order to increase the mobility resolution and the sensitivity. The body of the IMS is composed of polyether ether ketone (PEEK), the electrodes from stainless steel. Polytetrafluoroethylene (PTFE) foil is used for electrical insulation of the gate electrodes and sealing. The reaction tube and drift tube are installed in a temperature-controlled housing. The HiKE-IMS is evacuated via a small membrane pump (Pfeiffer Vacuum, Model MVP 003-2). The resulting pressure is monitored via a capacitive pressure gauge (Pfeiffer Vacuum, Model CMR 362). If pressure fluctuations occur, the drift-tube voltage (U_{DT}) and the reaction-tube voltage (U_{RT}) are automatically adjusted in order to achieve a constant reduced reaction field (E_{RT}/N) and drift field (E_{DT}/N) during data acquisition. Reduced fields E_{RT}/N and E_{DT}/N can be independently increased up to 120 Td. Corona discharge (corona needle APCI, Agilent) is used for primary ionization. A constant amount of water vapor is added close to the corona needle in order to promote the generation of H_3O^+ -based reactant ions. Furthermore, the water content in the reaction tube is mainly governed by this intentionally introduced amount of water and the influence of sample gas moisture is decreased. The sample gas is directly introduced

through a PEEK capillary into the reaction tube. In order to keep the drift tube free of any contaminants, a constant flow of dry and clean air is used as drift gas. This drift gas flows through the drift tube and the reaction tube and mixes within the reaction tube with the sample gas. To inject ions into the drift tube, the center gate electrode is set to the mean potential between the first and last gate electrode. To close this ion gate, the potential of the center electrode is increased to 12 V above the potential of the first electrode. The gate opening time is 6 μ s. A longer injection leads to an increase in signal intensity, but also to a decrease in mobility resolution. A fast current amplifier (developed in-house, 150 kHz, gain = 3×10^8 V/A) is connected to the detector. Spectra are recorded and averaged using in-house developed data acquisition hardware and software. All voltages can be inverted in order to analyze positive and negative ions. The experimental setup including the reaction tube, drift tube, heating, water reservoir, amplifier, data acquisition, pressure gauge, gate switch, and membrane pump fits into conventional 19 in. housing with six RU (rack units) and a height of 26.7 cm. The repetition rate can be set to 500 Hz; thus, 1000 spectra can be acquired and averaged within 2 s. All shown spectra and all given detection limits refer to a spectrum that has averaged 1000 times.

For sample gas preparation, two permeation ovens (VICI, Model 150) are used. The carrier and dilution gas is provided by a zero-gas generator (JAG, Model ZA350S). The moisture of the sample gas can be increased by adding a defined amount of clean air through a gas-washing bottle filled with water (Fluka, GC headspace tested). Benzene (Fluka, analytical standard), toluene (Sigma–Aldrich, Chromasolv, HPLC, 99.9%) and different isomers of xylene (Fluka, analytical standard) are used as analytes. The analyte concentration of the sample gas is calculated from the weight loss of a permeation tube.

EXPERIMENTAL RESULTS

In this section, the ion mobility spectrum of benzene at high kinetic energy is shown and the relative abundances of different benzene peaks, as a function of E_{RT}/N , are given. Furthermore, the benzene detection limits in dry (<1 ppm_v) and moist sample gas (3700 ppm_v) are calculated. Spectra of toluene and xylene are shown, and the influence of these analytes on the benzene signal is analyzed. Furthermore, the spectra of different xylene isomers are shown.

A separation of the benzene peaks from the reactant ion peak (RIP) is possible at $E_{DT}/N \geq 90$ Td. As described in previous work,⁹ because of the decrease in average water cluster size in the drift tube with increasing E_{DT}/N , the RIP mobility increases to such an extent that it can be separated from the benzene peaks. The mobility resolution (drift time divided by the full width at half-maximum) of the analyte peaks under these conditions is $R \approx 65$. The shape of the RIP under these conditions is asymmetric, rather than Gaussian, possibly due to the presence of smaller, faster water clusters. The mobility resolution can be further increased up to $R = 73$ if a value of $E_{DT}/N = 40$ Td is used. This is in accordance with theoretical work¹⁸ that describes the optimal IMS resolution as a function of the drift field. However, under these conditions, the first benzene peak and the RIP merge. Thus, a value of $E_{DT}/N = 90$ Td is chosen in this work as the best tradeoff.

In Figure 2, the positive ion mobility spectrum of 4.3 ppm_v benzene in dry sample gas is shown at different E_{RT}/N values.

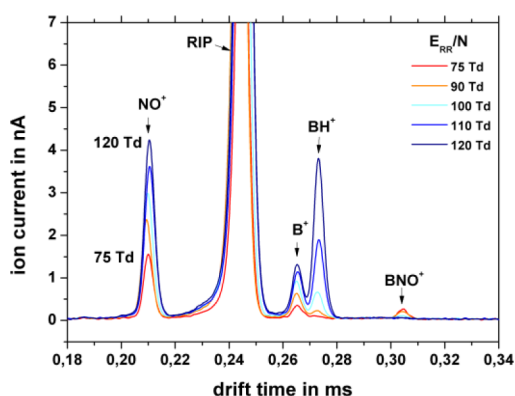


Figure 2. Positive ion mobility spectrum of 4.3 ppm_v benzene in clean and dry air at different E_{RT}/N values (75–120 Td) and at $E_{DT}/N = 90$ Td.

Besides the RIP, there are up to four different peaks visible in the spectrum. As described in earlier work,⁹ the signal intensity (peak height) of these peaks depends on E_{RT}/N , because of fragmentation, declustering, different possible ionization pathways, and an increase in the amount of charge injected into the drift tube with increasing E_{RT}/N . At a drift time of 209 μ s, a peak left of the RIP is visible, which is also present in the spectrum of dry and clean air. Thus, we expect it to be NO^+ . The maximum intensity of the RIP is 26 nA at $E_{RT}/N = 120$ Td.

As described in the Theoretical Background section, there are three different ionization mechanisms possible for benzene, which lead to three different analyte ions. In the given spectrum, three peaks with different ion mobilities (see Table 3, presented later in this work) are visible, which correlate to the presence of benzene in the sample gas. We expect these peaks to be B^+ , BH^+ , and BNO^+ . This assumption seems sound if the relative signal intensity of these peaks (signal intensity divided by the RIP intensity) is evaluated for different E_{RT}/N values, as shown in Figure 3. At $E_{RT}/N < 50$ Td, no significant benzene peaks are observed. With increasing E_{RT}/N , the amount of NO^+ within the reaction tube increases and BNO^+ and B^+ are generated. The maximum relative intensity for BNO^+ is observed at $E_{RT}/N = 70$ Td. With further increases in E_{RT}/N , BNO^+ dissociates and the relative intensity decreases until no BNO^+ is observed above 110 Td. Above $E_{RT}/N = 100$ Td, the

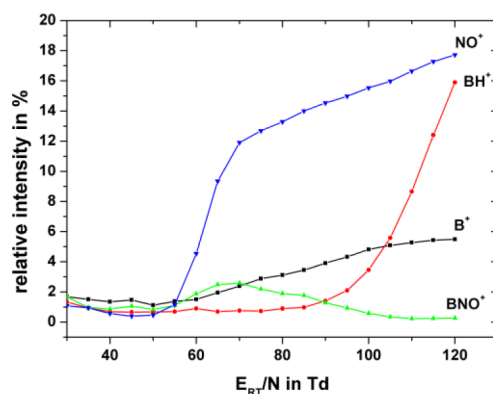


Figure 3. Relative signal intensities for the different peaks observed in the spectrum of 4.3 ppm_v benzene in clean and dry air (<1 ppm_v water) at different E_{RT}/N values from 30 Td to 120 Td. Peak intensities are normalized to the RIP intensity.

average size of water clusters within the reaction tube is decreased to such an extent that a significant amount of H_3O^+ is present and benzene can be ionized via proton transfer, leading to BH^+ ions. With increasing fraction of H_3O^+ , the BH^+ peak also increases and becomes the most prominent peak in the spectrum above 105 Td. A similar behavior has been described⁹ for toluene. However, toluene can be also ionized by $\text{H}^+(\text{H}_2\text{O})_2$. Thus, an increase in abundance of the protonated toluene ion is observed at lower E_{RT}/N . The ion mobility of BH^+ is significantly lower than the mobility of B^+ . We expect this not to be caused by the mass shift of 1 u but rather by the increase in dipole moment by protonation, possibly resulting in an increase in effective collision cross section. However, the exact nature of this observation is not clear.

The limit of detection (LOD), which is the concentration at which the signal intensity is three times higher than the standard deviation of the noise, can be calculated from the response curve displayed in Figure 4. The most sensitive

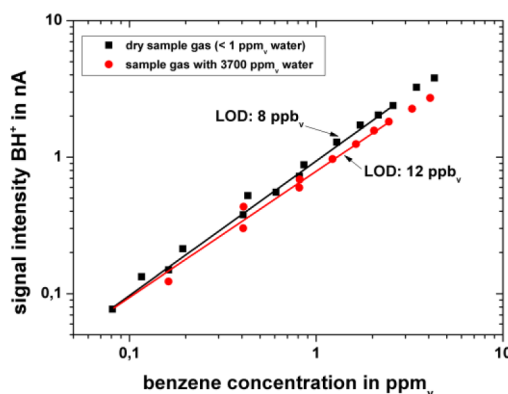


Figure 4. Response curve of the BH^+ peak with increasing benzene concentration in dry and moist sample gas ($E_{RT}/N = 120$ Td, $E_{DT}/N = 90$ Td).

detection of benzene with a LOD of 8 ppb_v (2 s of averaging, 2.5 pA standard deviation of the noise, 0.925 pA/ppb_v slope) in dry air (<1 ppm_v water) is possible when evaluating the intensity of the BH^+ peak. However, even when increasing the water content of the sample gas to 3700 ppm_v, the sensitivity only changes by ca. 30% resulting in a LOD of 12 ppb_v. Evaluating the B^+ peak, which is less water-dependent, because

of the different ionization mechanism, the detection is less sensitive and the LOD in dry sample gas is 25 ppb_v. However, an increase of the water content of the sample gas up to >21 000 ppm_v (90% relative humidity at 20 °C) only leads to a decrease in B⁺ intensity by 27%, which enables a fast and direct and almost moisture-independent quantification of benzene with a LOD of 32 ppb_v, even in very moist environments.

Besides the influence of the water content of the sample gas, masking effects that occur when mixtures of different compounds are analyzed are a major problem when using IMS without preseparation. In Figure 5, the spectra of benzene

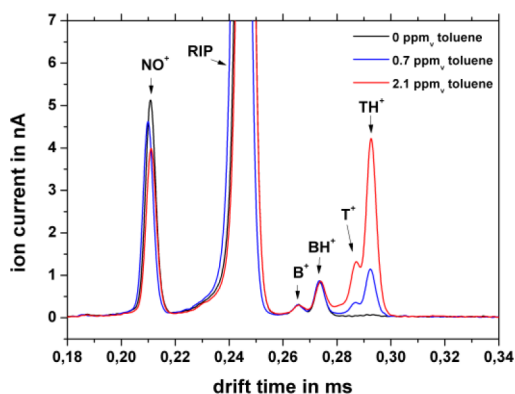


Figure 5. Positive ion mobility spectrum of benzene (850 ppb_v) and different toluene concentration from 0 ppm_v to 2.1 ppm_v in dry (<1 ppm_v water) sample gas ($E_{RT}/N = 120$ Td, $E_{DT}/N = 90$ Td).

(850 ppb_v) in dry air with different toluene (T) concentrations from 0 ppb_v to 2.1 ppm_v are shown. Two additional peaks, T⁺ and TH⁺, related to the toluene concentration are visible which can be separated from the benzene peaks. The LOD for toluene evaluating the TH⁺ peak is 4 ppb_v in dry and 5 ppb_v in moist sample gas (3700 ppm_v water). A detection of TH⁺ with the used parameters is more sensitive than BH⁺, because an ionization via H₃O⁺ and H⁺(H₂O)₂ is possible. At the given benzene concentration, the increase in toluene concentration has no significant effect on the benzene signal. Nevertheless, a minor decrease in NO⁺ and RIP can be observed because charge is transferred from these ions to the toluene ions.

However, for higher toluene concentrations, two effects with opposing influence on the benzene signal are observed that must be considered for a quantitative measurement of benzene in toluene-rich atmospheres. First, in the ion mobility spectrum of toluene, a small but constant percentage (2%) of ions with a similar mobility as the benzene ions is always present, as well as a slight baseline offset between the benzene and the toluene peaks. We expect these ions to be benzene fragments of toluene. The influence of a change in E_{RT}/N on these ions is similar to the influence of such a change on the toluene signal. Thus, we do not expect this effect to be caused by contamination of the toluene analyte or the washing of residual benzene from surfaces by toluene. Especially, when high toluene concentrations are present, this leads to an offset in the benzene signal, which must be corrected. Thus, 2% of the toluene signal are considered as an offset in the benzene signal and are subtracted. On the other hand, the presence of several ppm_v of toluene leads to a decrease in available reactant ions and increases the probability for competing ionization processes. Thus, the response for benzene in the presence of high toluene concentrations is attenuated by several percent.

However, the detection limit for benzene with 12.4 ppm_v toluene and 3700 ppm_v water in the sample gas is 16 ppb_v.

In Figure 6, the influence of increasing the toluene concentration from 0 ppb_v to 12.4 ppm_v on a constant benzene

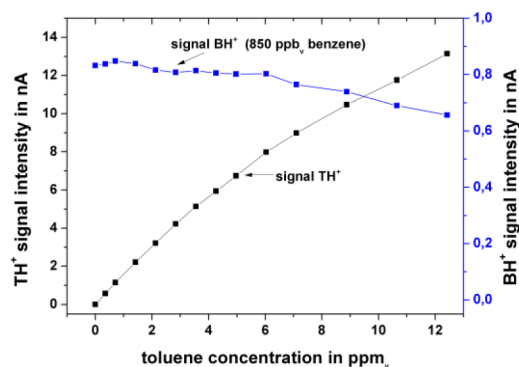


Figure 6. Signal intensity of BH⁺ and TH⁺ at constant benzene concentration (850 ppb_v) and increasing toluene concentration (0 ppb_v to 12.4 ppm_v) in dry (<1 ppm_v water) sample gas ($E_{RT}/N = 120$ Td, $E_{DT}/N = 90$ Td).

concentration (850 ppb_v) is shown. The BH⁺ signal is corrected for a baseline elevation caused by the increasing toluene concentration. A decrease of the BH⁺ peak by only 25% at a toluene concentration of 12.4 ppm_v is observed. The TH⁺ signal is almost linear with a toluene concentration up to ca. 6 ppm_v. Above 6 ppm_v beginning signal saturation can be observed due to the limited number of reactant ions.

In Figure 7, the positive ion mobility spectrum of a mixture of benzene (3.3 ppm_v), toluene (3.2 ppm_v), and *o*-xylene (1.95

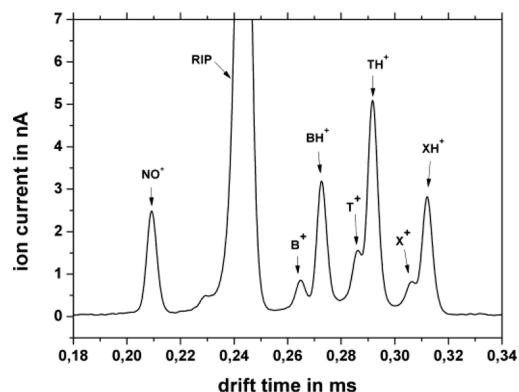


Figure 7. Positive ion mobility spectrum of benzene (3.3 ppm_v), toluene (3.2 ppm_v), and *o*-xylene (1.95 ppm_v) in dry (<1 ppm_v water) sample gas ($E_{RT}/N = 120$ Td, $E_{DT}/N = 90$ Td).

ppm_v) is shown. Two peaks that we expect to be positively charged *o*-xylene (X⁺) and protonated *o*-xylene (XH⁺) can be observed that correlate to the *o*-xylene concentration. The response of these peaks to a shift in E_{RT}/N is comparable to the response of the toluene peaks. Even though the two *o*-xylene peaks are not baseline-separated, all compounds in this mixture can be clearly distinguished. All three xylene isomers have been investigated separately and show only minor influence on the signal intensity of toluene and benzene. At high xylene concentrations, a baseline elevation (3% of the XH⁺ intensity at the BH⁺ mobility to 6% of the XH⁺ intensity at the TH⁺ mobility) between the benzene peaks and the xylene peaks is

observed, which correlates to the xylene concentration. For a quantitative measurement of benzene in a xylene-rich atmosphere, this offset must be considered. Similar to the toluene signal, we expect this elevation to be caused by benzene or toluene fragments of xylene. Furthermore, at high xylene concentrations, the response for benzene is attenuated by several percent. At 9 ppm_v of *o*-xylene, the offset-corrected BH⁺ signal is 55% of the BH⁺ signal without *o*-xylene. However, the resulting sensitivity for benzene in toluene- and xylene-rich atmospheres is significantly higher than that observed when using conventional IMS without GC preseparation. If toluene and xylene are the only VOCs present in comparably high concentrations in the sample gas, the influence of these analytes on the measured benzene signal can be calculated and a quantitative measurement of all compounds in this mixture is possible. The ion mobility of all shown peaks is given in Table 3. It is noteworthy that we observed slightly different mobilities for the three xylene isomers (X⁺ peak).

Table 3. Reduced Ion Mobility in Dry (<1 ppm_v Water) Clean Air at 35 °C and E_{DT}/N = 90 Td

ion	reduced ion mobility, K ₀ ^a (cm ² /(V s))
NO ⁺	2.87
RIP	2.45
B ⁺	2.27
BH ⁺	2.20
BNO ⁺	1.97
T ⁺	2.1
TH ⁺	2.06
<i>p</i> -X ⁺	1.97
<i>m</i> -X ⁺	1.95
<i>o</i> -X ⁺	1.96
<i>p/m/o</i> -XH ⁺	1.92

^aValues listed have a deviation of ±0.005 cm²/(V s).

CONCLUSION

A direct quantitative analysis of benzene, toluene, and xylene (BTX) mixtures even in moist sample gases is possible without any preconcentration and preseparation. The limit of detection (2 s of averaging) for benzene in a sample gas containing 3700 ppm_v water, 12.4 ppm_v toluene, and 9 ppm_v xylene is 29 ppb_v. The mobility resolution in the presented HiKE-IMS varies from R = 60 at E_{DT}/N = 90 Td to R = 74 at E_{DT}/N = 40 Td, which is sufficient to separate all three compounds and identify up to three different peaks for each compound resulting from different ionization pathways. At high E_{RT}/N values (>100 Td), even in moist sample gases, a significant amount of H₃O⁺ is present and protonated ions of all three compounds were observed. Ions generated by charge transfer via NO⁺ are also present in all spectra above E_{RT}/N = 50 Td. The ion mobility of the protonated ions is significantly lower than the mobility of the ions generated via charge transfer. We expect this to be caused by an increase in dipole moment by protonation. One indication for this is that the difference in mobility between B⁺ and BH⁺ is higher than for T⁺ and TH⁺ or X⁺ and XH⁺, because benzene is nonpolar while toluene and xylene are moderately polar. An increase in toluene concentration from 0 ppb_v to 12.4 ppm_v leads to a decrease in BH⁺ signal of only 25%. The influence of 9 ppm_v xylene is more pronounced (45%). Furthermore, a fragmentation of toluene and xylene with a

resulting baseline elevation affecting the benzene signal must be considered for benzene quantification.

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Notes

The authors declare no competing financial interest.

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