

Analytical Methods

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ARTICLE TYPE

Non-polar modifier assisted analysis of aromatic compounds by means of planar differential ion mobility spectrometry with ^{63}Ni ionization source†

Andriy Kuklya,^{*a} Florian Uteschil,^a Klaus Kerpen,^a Robert Marks^a and Ursula Telgheder^{a,b}⁵ Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

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In this paper we demonstrate that the choice of an appropriate non-polar modifier which can provide sufficient chemical interaction with target analytes may lead to the improvement of the selectivity and the sensitivity of differential ion mobility spectrometric (DMS) methods. The influence of the aromatic modifier (benzene) on the DMS sensitivity and separation ability was proven on examples of five aromatic compounds (toluene, ethylbenzene, *p*-xylene, 1,2,4-trimethylbenzene (TMB), and naphthalene). These compounds can provide the π - π interaction with the chosen modifier. The influence of the modifier concentration on the compensation voltage, peak area, and peak width was investigated and discussed. The peak capacity for the mixture of toluene, ethylbenzene, *p*-xylene, TMB, and naphthalene was increased by about four times when the concentration of the benzene in the carrier gas was 0.09 %. The strong influence of the proton affinity of analytes on the peak area in the measurements with a modifier was demonstrated. The peak area of the compounds of low proton affinity (toluene, ethylbenzene) significantly decrease with the increase of the aromatic modifier concentration. However, the peak area of the compounds of high proton affinity was significantly increased when benzene was added into the carrier gas. When the concentration of benzene in the carrier gas was 0.4 % the peak area of naphthalene was more than tripled and the peak area of TMB was almost doubled. The increase of the peak area in the DMS equipped with ^{63}Ni -ionization source was explained by the improved ion transport within the DMS filter region. This differs from the DMS equipped with the APPI-source, which demonstrates increased signal intensities in the presence of aromatic dopants due to the increased ionization efficiency of analytes. Despite the higher response of the DMS in the presence of an aromatic modifier, the limits of detection for calibrations without a modifier and with 0.015 % of benzene are within the same range (14.2 - 99.9 and 10.6 - 89.5 ng L⁻¹, for the calibration without and with modifier, respectively). This originates mainly from a higher background signal caused by benzene and benzene dimer.

1. Introduction

The development of new analytical methods for the analysis of aromatic compounds is an important issue. The continuously increasing production and use of fossil fuels results in considerably increased contamination of water resources, particularly groundwater and aquifers. The contamination of aquifers and groundwater by fuels is an environmental issue of major concern worldwide and may lead to risk of drinking water supply.^{1,2}

Due to the leaking of oil tanks and pipelines the groundwater is contaminated by petroleum products such as gasoline, diesel fuel and heating oil. This is the one of the most common sources for contamination of groundwater with BTEX (benzene, toluene, ethylbenzene, xylenes) and PAHs (polycyclic aromatic hydrocarbons). BTEX accounts for as much as 90% of the gasoline components that are found in the water-soluble fraction when a gasoline contacts with the water.³ The fraction of all C3-

benzene isomers was found to be about 1% of the total aromatics. The same study demonstrates that naphthalene and its methylated derivatives are the dominating compounds in the water fraction among the other PAHs which were found in trace amounts. Therefore, toluene, ethylbenzene, *p*-xylene, 1,2,4-trimethylbenzene (TMB), and naphthalene were selected as representative aromatic model compounds for this study.

Due to the potentially rapid spread of water contaminants the continuous improvement of early warning systems and the development of new online water monitoring methods is a challenge for modern analytical chemistry. Most of the existing methods for analysis of gasoline contaminated samples are laboratory-based and therefore require time-consuming sampling and transport procedures. The most commonly used extraction methods for analysis of gasoline contaminated water samples are "headspace", "purge and trap", "liquid-liquid extraction", "solid phase extraction" (SPE), and "solid phase micro-extraction"

(SPME). Headspace analysis is recommended as a screening method by the US Environmental Protection Agency (EPA), thought it also performs well in particular situations, especially field analysis.⁴ In many cases derivatisation or extraction steps are required. Moreover, these methods frequently include the GC or LC pre-separation steps.⁵ Despite the fact that chromatography is an effective and well-established method, in the case of the complex samples it can be very time consuming. Therefore, the interest in miniaturized systems for on-site rapid monitoring has grown in recent years. Driving forces for the development of miniaturized systems are the reduced cost and analysis time, as well as the possibility to integrate all steps (e.g. sampling, sample preparation, separation techniques, and detection of the analytes) in a single and portable device.

The differential ion mobility spectrometry (DMS), also known as planar high field asymmetric waveform ion mobility spectrometry (FAIMS), is a rapidly advancing technology that is both sensitive and fast, operates at atmospheric pressure, and provides a unique type of selectivity, which is orthogonal to most of other separation techniques.^{6,7} In contrast to the conventional Time of Flight Ion Mobility Spectrometry (ToF-IMS), in which the separation of ions is based on specific coefficients of ion mobility in a uniform electric field, DMS separates ions based on a nonlinear dependence of the mobility coefficient on the electric field strength. The dependence of the ion mobility coefficient on the electric field can be explained by the reversible cluster formation model, which describes field dependent cluster formations that lead to variation of the average ion cluster cross section.⁸ The functional principles of the DMS are described elsewhere.^{9,10}

In the last decades the DMS has found many applications as a stand-alone analyser (with and without GC pre-separation) as well as a fast and an effective pre-separation technique for atmospheric pressure ionization mass spectrometry.^{7,11} Separation based on ion mobility is fast in comparison with chromatographic methods and provides separation on the MS time scale. It was demonstrated that the methods based on ion mobility can significantly enhance the chromatographic separation or even be considered as an alternative to the chromatography.^{12,13} The employment of DMS prior to mass spectrometer improves both selectivity and signal to noise ratio of MS measurement. Moreover, the ability of DMS to separate the isobaric and isomeric compounds enhances the differentiation ability of the mass spectrometer.

The spectrometers with curved electrodes geometry are usually named FAIMS (high field asymmetric waveform ion mobility spectrometry) and the spectrometers with planar electrodes geometry are named DMS. Comparison of the performances of DMS with planar and cylindrical electrodes design has been previously published.^{14,15} Planar geometries usually offer higher resolving power at a cost of lower ion transmission, whereas curved geometries provide greater ion transmission due to an electrostatic focusing effect at a cost of resolving power.

Over the last decade it was demonstrated that addition of the appropriate amount of volatile organic compounds (modifiers) to the transport gas can significantly enhance the resolving power of planar DMS.^{16,17,18,19} For curved geometries the introduction of a solvent vapor of high concentration is problematic, since the

focusing effect causes a dramatic decrease in ion signal or even a complete signal loss.^{20,21} The intensity of the ion signal in the spectrometers with planar electrodes geometry is not as affected by solvent vapors due to the lack of ion focusing effect. Typically polar modifiers (2-propanol, acetone, ethylacetate, etc.) are utilized for improvement of the spectrometer resolving power.^{12,16,22} The addition of non-polar modifiers to the transport gas for improvement of the DMS separation is rarely presented. As reported in the literature, the addition of non-polar modifiers (e.g. cyclohexane) to the carrier gas results only in a negligible effect on observed separation.¹² It is assumed that polar modifiers may induce the cluster/cluster mechanism, which provides an increase of the ion separation in comparison with the measurements with pure nitrogen. The separation efficiency is dependent on the strength of the interaction between the analyte and the modifier. Similar to nitrogen, non-polar modifiers have demonstrated no improvement in separation of the polar compounds due to the weak analyte-modifier interaction.¹² In our previous publication we have demonstrated that the utilization of polar modifiers, which are usually applied for the improvement of separation ability of DMS based systems (water vapors and 2-propanol), do not improve the separation of non-polar aromatic compounds.²³ The most likely reason for the independence of the compensation voltage (CV) to the polar modifier concentration is a weak interaction of for non-polar aromatic analyte-ions with the polar modifiers. Due to the weak analyte-ion to polar modifier interaction, the analyte-ion size is almost independent of the modifier concentration and no significant dependence of the analyte peak CV on the polar modifier concentration can be observed. Moreover, the peak area of the non-polar aromatic compounds decreases with the increase of the polar modifier concentration. Due to this limitation no advantages from the addition of the polar modifier to the transport gas of the DMS can be expected for a variety of the non-polar compounds, including a number of environmentally important non-polar aromatic compounds.

In this paper, we demonstrate on the example of benzene that the choice of the appropriate non-polar modifier which can provide sufficient chemical interaction with the target analytes leads not only to the improvement in the selectivity but also in increased sensitivity of the analysis of aromatic compounds with planar DMS. Five aromatic compounds of low polarity (toluene, ethylbenzene, *p*-xylene, 1,2,4-trimethylbenzene, and naphthalene), which can provide a π - π interaction with the aromatic modifier, were selected to prove the influence of the concentration of benzene on the compensation voltage and signal area.

2. Experimental

2.1 Experimental Setup

The principle scheme of the experimental setup used in this study is shown in Fig. 1. The overall nitrogen flow entering the DMS was prepared by mixing the main flow of pure nitrogen (99.999 %, Air Liquide, Germany), controlled by a mass flow controller (MFC, Pneutronics, VSO-GC), with an additional nitrogen flow containing the modifier. The main and additional flows of pure nitrogen were dried over molecular sieves (MSR, 4Å, Typ 514, Roth). The homemade vapor generator (VG) included a

temperature controlled saturated vapor source and a flow of nitrogen. The nitrogen flow containing the modifier was controlled by a mass flow controller (GFC17, 0-50 mL min⁻¹ N₂, Aalborg, USA). The overall nitrogen flow, controlled by a solid state flow meter (MFM, Restek 6000, Restek, UK) located on the exhaust of DMS, was kept constant at 300 mL min⁻¹. The pressure was monitored using the pressure sensor from the DMS, which is built on the input to the analyser. The samples for the measurements were introduced via the syringe pump (SP).

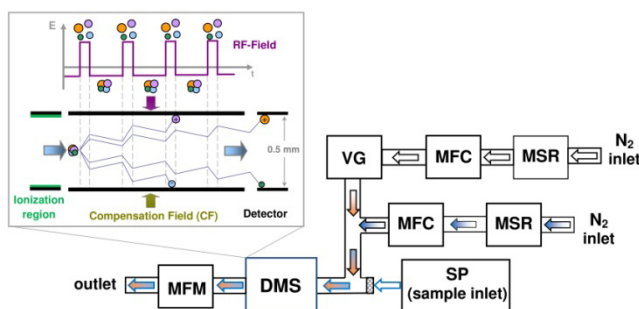


Fig. 1. The principle scheme of the experimental setup: differential ion mobility spectrometer (DMS), syringe pump (SP), mass flow controller (MFC), mass flow meter (MFM), molecular sieves reservoir (MSR), vapor generator (VG).

2.2 Chemicals

To prove the influence of an aromatic modifier of low polarity (benzene, AppliChem, 99+ %) on the signal compensation voltage, FWHM, and area, five aromatic compounds of low polarity (toluene [J.T. Baker, 99.9 %], ethylbenzene [Fluka, 99+ %], *p*-xylene [Fluka, 99+ %], 1,2,4-trimethylbenzene [Aldrich, 98 %], and naphthalene [Sigma-Aldrich, 99 %]) were selected. The molecular weights, the proton affinities, and the vapor pressures of modifier and model compounds are summarized in Table 1.

Table 1. List of compounds used in the current study with the corresponding molecular weights (MW), proton affinities (PA), and vapor pressures (VP).

Compound	MW [g mol ⁻¹]	PA [kJ mol ⁻¹]	VP at 20 °C [hPa]
Benzene	78.11	744.8 - 750.4 ^{24,25,26}	99.5 ²⁷
Toluene	92.14	782.4 - 784.0 ^{24,25,26}	29.1 ²⁸
Ethylbenzene	106.17	788.0 - 789.9 ^{25,26}	9.5 ²⁹
<i>p</i> -Xylene	106.17	785.4 - 794.4 ^{24,25,26}	8.7 ³⁰
TMB	120.19	~837 ³¹	2.3 ³²
Naphthalene	128.17	800.0 - 802.9 ²⁶	0.08 ³³

The samples for the measurements were prepared as follows: an analyte sample volume of 1 mL was transferred into a 20 mL vial under nitrogen atmosphere. The vial was closed with the screw cap equipped with Butyl/PTFE septa (S/N 100032, BGB, Germany) and equilibrated for 1 hour at 20 °C. The samples were taken from the headspace of the vial using a Hamilton gas-tight syringe (10, 50, and 500 µL size). The concentration of the analyte in the carrier gas of DMS was controlled by the injection rate of syringe pump (kdScientific, KDS Legato 210) equipped with a Hamilton gas-tight syringe.

The concentrations of model compounds in the carrier gas for the

measurements performed in chapter 3.2 (Effect of the benzene concentration on the compensation voltage and peak area of model compounds) were as follows: 3564 ng L⁻¹ for toluene, 1366 ng L⁻¹ for ethylbenzene, 626 ng L⁻¹ for *p*-xylene, 113 ng L⁻¹ for TMB, and 105 ng L⁻¹ for naphthalene.

2.3 DMS

The differential ion mobility spectrometer (SVAC-V, ⁶³Ni 185 MBq, Scionex Corp., USA) settings were as follows: sensor temperature = 80 °C, number of steps = 100, step duration = 10 ms, step settle time = 3 ms, steps to blank = 1. The measurements were analysed in the positive (positive ions) mode at RF-Voltage of 1000 V (20 kV cm⁻¹) and nitrogen (99.999 %, Air Liquide, Germany) flow rate of 300 mL min⁻¹, otherwise noted. The compensating voltage range was set from -20 to +5 V.

For each sample three single measurements were recorded using Sionex Expert software (version 2.4.0). For the determination of peak parameters (centre, area, FWHM) the measured data were analysed by the fityk (version 0.9.4) program.³⁴ The peaks were fitted with Gaussian functions using the Levenberg-Marquardt algorithm.

It should be noted that the analyte signal positions on the compensation voltage scale are very sensitive to even minor pressure differences. To enable the comparison of spectra obtained under different experimental conditions the method described by Nazarov et al.³⁵ was used. This method proposes utilization of E/N scaling in Townsend units (Td). In this case the reduced compensation field scale (CF, in [Td]) is utilized instead of the compensation voltage scale (CV, in [V]). In our study utilization of this method has minimized but not completely eliminated the differences between the measurements at different pressures. That is why the data presented in this manuscript were recorded within the narrow pressure gap between 14.45 and 14.57 psi.

3. Results and discussion

The utilization of non-polar aromatic modifiers for the improvement of sensitivity and separation ability of the ⁶³Ni-DMS has hitherto not been systematically investigated. However, it was demonstrated that non-polar aromatic modifiers (e.g. benzene, toluene) can be employed as dopants to improve the sensitivity of the ion mobility devices equipped with atmospheric pressure photo ionization (APPI) sources. Roetering et al. have demonstrated that utilization of traces of benzene (0.260 ppm_v) for the analysis of the pesticides with APPI-DMS results in both an improvement of the sensitivity of the method and a shift of the analyte peaks.³⁶ The increase in the sensitivity was explained by the increased ionization efficiency of analytes over the charge exchange with the photoionized benzene radical cation. Despite the differences in ionization mechanisms proposed for APPI (depends on ionization potential) and ⁶³Ni-ionization-based (depends on proton affinity) sources, these findings demonstrate the prospects for the utilization of aromatic modifiers for the improvement of the peak separation in the differential ion mobility based methods.

Not much information is found in the literature about the utilization of non-polar modifiers for the improvement of the separation ability of the differential mobility based devices for

ionization sources, other than APPI [12]. Hill et al. have demonstrated the utilization of the aromatic modifier nitrobenzene for the improvement of the IMS separation power.³⁷ This compound can provide π - π interaction with the aromatic compounds but has a proton affinity of 800.3 kJ mol⁻¹.²⁵ Due to the rather high proton affinity the utilization of nitrobenzene for all selected model compounds except TMB is problematic (see Table 1).

Due to the relatively low proton affinities of toluene, ethylbenzene, and *p*-xylene (see Table 1) the choice of the modifier is very limited. The modifier should have a proton affinity lower than, or comparable to, those of the analytes. Furthermore, the modifier should be able to cluster with the analyte in a reversible manner. In the current work the effect of the aromatic modifier (benzene) on sensitivity and separation power of DMS for aromatic compounds was examined. This modifier provides separation based on the π - π modifier-to-analyte interaction. Therefore, this type of modifier can be utilized for a large number of substances containing π -electrons. This includes all compounds which have aromatic structural components. The effect on the compounds with double and triple bonds can also be expected. Because of the low proton affinity benzene can be used as modifier for a large number of the compounds.

3.1 Effect of the benzene concentration on the reactive ion peak (RIP)

The dependences of compensation field (CF) and area of benzene peaks on benzene concentration are presented in Fig. 2 (top). The addition of benzene into the carrier gas caused complete replacement of the RIP peak by a new peak (Fig. 2, top, Peak 1). When the concentration of the benzene was less than 0.01 %, this peak demonstrated the identical CF-values as was observed in the standard measurements of the pure benzene samples. Therefore, this peak was assigned to the product ions of benzene. The following increase in the benzene concentration results in appearance of the second peak (Fig. 2, top, Peak 2). The appearance of this peak is supposed to be induced by the dimerization of the protonated benzene cation with a neutral benzene molecule. The further increase in the benzene concentration (within the range of 0.015 to 0.06 %) leads to the complete replacement of these two peaks by a new peak (Fig. 2, top, Peak 3). The further increase of benzene concentration leads to significant increase of Peak 3 area. The maximum of Peak 3 area is observed at benzene concentration of ~ 0.4%. Within the benzene concentration range of 0.4 to 1.5 % the area of Peak 3 slightly decreases. Additionally, the Peak 4 was detected at benzene concentrations as high as 0.15 %. The area of this peak is continuously increasing within the benzene concentration range of 0.15 to 1.5%. The possible reason for the formations of Peak 3 and Peak 4 is a further complexation of the cation of benzene dimer with neutral benzene molecules. To prove this hypothesis further investigations are required. With the increase in benzene concentration all peaks undergo a shift on the CF scale toward more negative CF values. Peaks 1 and 2 undergo the higher shift in comparison to the Peaks 3 and 4. This shift toward the negative CF values can be explained by the reversible cluster formation model, which describes field dependent cluster formations that lead to variation of the average ion cluster cross section.⁸ This

model demonstrates that ion-cluster size and the ion-cluster mobility are dependent on the concentration of the clustering particles (in this case the benzene concentration), cluster temperature, and complex formation energy. With an increase of electric field strength the effective ion-cluster temperature rises, resulting in a rapid declustering due to a high collision rate at atmospheric pressure. Hence, the average ion-cluster size is reduced. A reduction in the average ion-cluster size may increase ion mobility significantly. Under a low electric field a higher benzene concentration in the gas phase leads to an increase in the average ion-cluster size. An increase in the ion-cluster cross-section, which correlates with the benzene concentration, results in reduced ion-cluster mobility and a corresponding increase in frequency of cluster to carrier gas collisions. As a result the difference between mobility of the ions in the low and in the high electric fields at higher benzene concentrations increases, leading to an increase of the signal shift on the CF scale.

The spectra measured at benzene concentrations of 0.02, 0.03, 0.15, and 1.50 % are demonstrated in Fig. 2 (bottom).

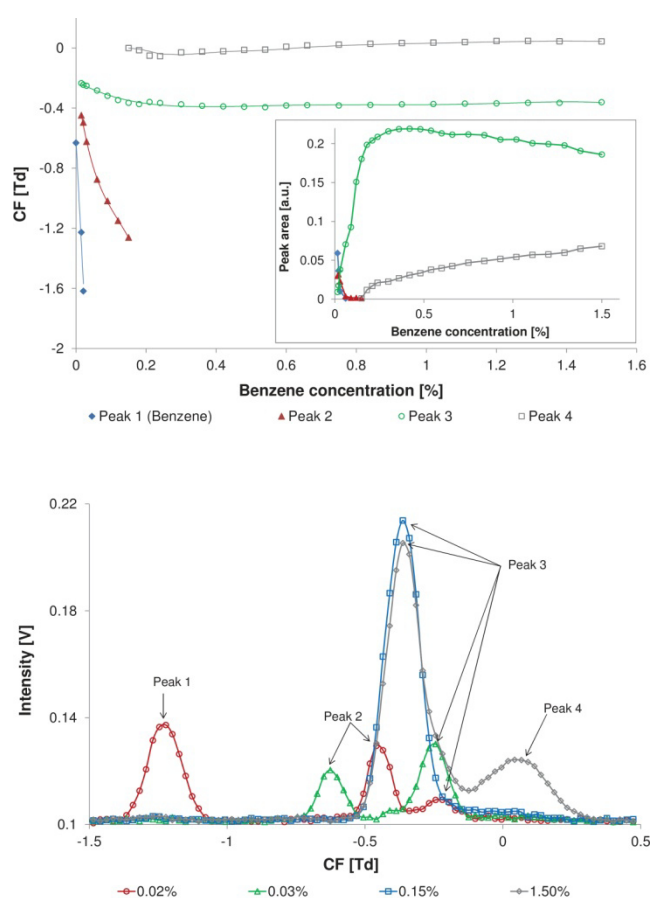


Fig. 2. Top: the relationship between the compensation field (CF) of benzene peaks and the concentration of benzene in the carrier gas. The relationship between the area of benzene peaks and benzene concentration is shown in the insert. Bottom: the spectra recorded at benzene concentrations of 0.02, 0.03, 0.15, and 1.50 %

3.2 Effect of the benzene concentration on the compensation voltage and peak area of model compounds

Benzene is the smallest representative of non-polar aromatic compounds. The rather low proton affinity of benzene (~ 750 kJ

mol⁻¹, see Table 1) allows the efficient ionization of most of the aromatic compounds.

When the concentration of the benzene was less than 0.01 %, the peaks of all model compounds were observed at usual positions on the CF scale. With the increase in benzene concentration all peaks undergo a shift on the CF scale toward the more negative CF values (Fig. 3, top). The compounds with lower molecular weight undergo the higher shift in comparison to the compounds with a higher molecular weight. The highest effect was observed for the peak of toluene. This shift toward the negative CF values can be explained by the reversible cluster formation model, in correspondence to that discussed in the Chapter 3.1 for the benzene clusters.

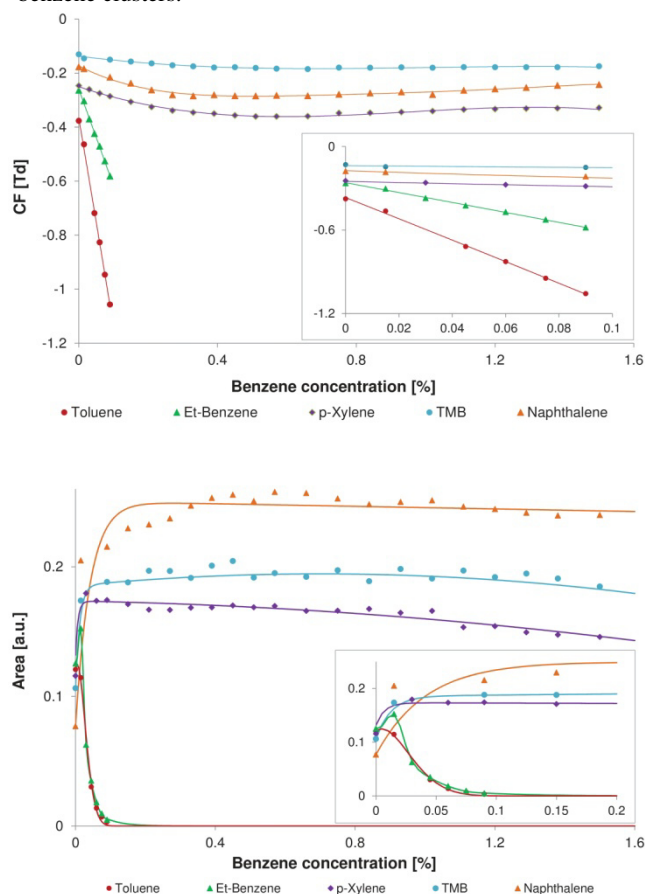


Fig. 3. Top: the relationship between the compensation field (CF) of the model compounds and the concentration of the benzene in the carrier gas. Bottom: the relationship between the peak area of the model compounds and the concentration of the benzene in the carrier gas. The corresponding relationships within narrow CF ranges are presented in the inserts.

The relationship between the peak area of the model compounds and the concentration of the benzene in the carrier gas is shown in the Fig. 3 (bottom). All selected model compounds except

toluene demonstrate an increase of the peak area at benzene concentration of 0.015%. The following increase of the benzene concentration results in extreme decrease of the peak area of toluene and ethylbenzene. The decrease of the peak area for toluene and ethylbenzene can be explained by the low proton affinities of these compounds (see Table 1). The compounds of the high proton affinity, namely naphthalene and TMB, demonstrate no significant decrease of the peak area within a benzene concentration range of 0.15 to 1.5 %. The peak area of naphthalene is slightly increasing within the benzene concentration range of 0.15 to 0.4 % and is almost unchanged within the range of 0.4 to 1.5%. When the concentration of benzene in the carrier gas was 0.4 % the peak area of naphthalene was more than tripled and the peak area of TMB was almost doubled.

The proton affinity of *p*-xylene is only slightly higher than that of ethylbenzene. Despite their comparable proton affinities these two compounds demonstrate a different relationship between the peak area and benzene concentration. In contrast to the ethylbenzene, the peak area of *p*-xylene is only slightly affected within the wide benzene concentration range of 0.15 to 1.5 %.

Sherrill et al. have demonstrated that all complexes of benzene with substituted benzenes (toluene, xylene, etc.) have greater interaction energy than the benzene dimer.^{38,39} It is remarkable that the increase of interaction energy is linear in the series of the benzene complexes with benzene, toluene, *p*-xylene, and 1,3,5-trimethylbenzene. Thus, the interaction of benzene with polysubstituted aromatic compounds should be stronger than the interaction of benzene with mono-substituted compounds. Due to the increase in interaction energy the lifetime of the cluster-ions formed with polysubstituted benzenes (e.g. *p*-xylene) should be increased in comparison with this of monosubstituted benzenes (e.g. toluene and ethylbenzene), which results in an increased peak area. Thus, the increase of the peak area in the DMS equipped with ⁶³Ni-ionization source most likely originates from the better ion transport within the DMS filter region. This differs from the DMS equipped with an APPI-source, which demonstrates the increased signal intensities in the presence of aromatic dopants due to the increased ionization efficiency of analytes.

In Fig. 4 the differential mobility spectra of the aromatic model compounds with no modifier (top) and with 0.06 % of the benzene (bottom) in the carrier gas are demonstrated. At this concentration the analyte peak separation is sufficient and the peak areas of the toluene (Fig. 4, bottom, CF = -0.83 Td) and ethylbenzene (Fig. 4, bottom, CF = -0.48 Td) are high enough for the accurate analysis. It should be noted that at the benzene concentration of 0.06 % the peak of the benzene product at CF = -0.29 Td is not completely replaced by peaks of toluene and ethylbenzene.

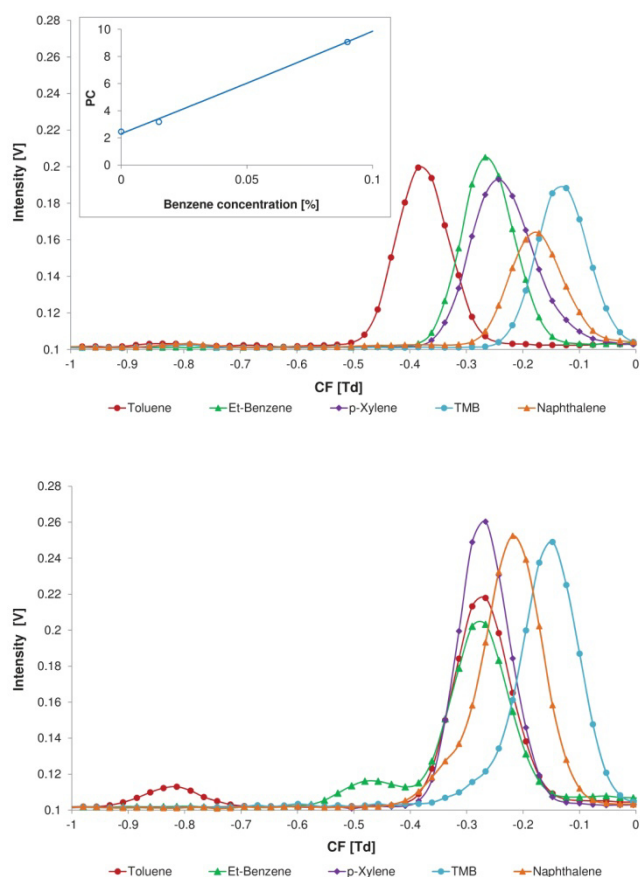


Fig. 4. Differential mobility spectra of toluene, ethylbenzene, *p*-xylene, 1,2,4-trimethylbenzene, and naphthalene with no modifier (top) and with 0.06 % of benzene (bottom) in the carrier gas. The relationship between peak capacity (PC) and the concentration of the benzene in the carrier gas is presented in the insert.

Peak capacity is one way to express the separation capability of an analytical device. For DMS, the peak capacity can be defined as a spread of peaks in the compensation voltage scale divided by the average peak width (see Eq. 1).

$$PC = (C_{\max} - C_{\min}) / FWHM_{av} \quad (1)$$

Where PC is a peak capacity, C_{\min} and C_{\max} are peak centers with minimal and maximal CF values, and $FWHM_{av}$ is an average peak width at half height. According to Eq.1 the peak capacity can be improved by increasing the spread of the peaks in the compensation voltage scale or by decreasing the peak width. In measurements demonstrated in the current paper no significant changes in the peak width were observed with the addition of the modifiers. The FWHM were observed within the range of 0.09 - 0.12 Td with the average value about 0.11Td. According to Eq.1 the peak capacity for the mixture of toluene, ethylbenzene, *p*-xylene, 1,2,4-trimethylbenzene, and naphthalene is increased from 2.4 to 9 at 0.09 % of the benzene in the carrier gas (see Fig. 4, top, insert). It should be noted that the value of the peak capacity is dependent on the choice of compounds in the analysed mixture. Therefore, the peak capacity can only be compared for the measurements of the equivalent mixtures; otherwise the different values of peak capacity are expected.

3.3 Determination of analytical parameters for the model compounds with and without modifier

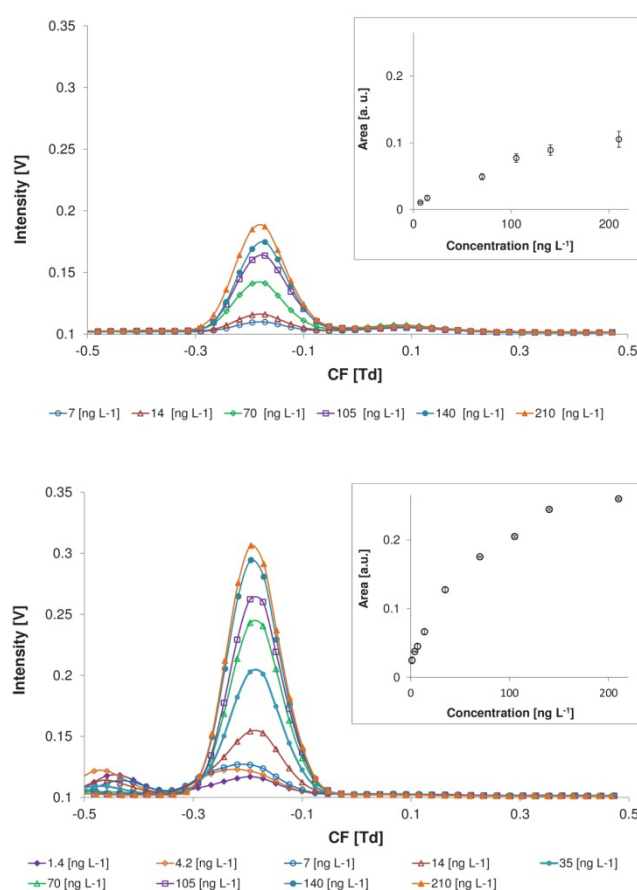


Fig. 5. Differential mobility spectra of naphthalene at different concentrations without modifier (top) and with 0.015 % of benzene (bottom) in the carrier gas.

The DMS spectra of naphthalene without modifier and with 0.015 % of benzene in the carrier gas, in the positive mode (detection of the positive ions) within a concentration range of 1.4 to 210 ng L⁻¹ (concentration in the carrier gas), are shown in Fig. 5. These measurements were performed at an electric field strength of 20 kV cm⁻¹ (RF=1000V). The DMS spectra of ethylbenzene, *p*-xylene, and 1,2,4-trimethylbenzene recorded under the same experimental conditions, can be found in the supporting information. At a benzene concentration of 0.015 % the peak areas of all of the selected model compounds are significantly increased and the background is not high as compared with those at higher benzene concentrations (see Fig. 2 and Fig. 3).

The reason for the observed minor variations in the analyte peak shapes and compensation voltages, is a deviation of the benzene concentration in the carrier gas during these measurements.

For all of the selected analytes a common for non-direct ionization mechanisms, such as APCI, non-linear signal area to concentration relationship was observed.^{40,41} Due to this reason non-linear second-order calibration functions according to DIN 8466-2 were applied. The relevant equations for the non-linear calibration can be found in the Supporting Information section. Use of the non-linear calibration for the ion mobility spectrometry based methods was found to enlarge the concentrations range in which the analyte can be quantified.^{41, 42} The addition of benzene into the carrier gas results in an increase

of the DMS response for all of the analytes (see Fig. 4 and supporting information). The highest effect was observed for naphthalene. However, the increase of the benzene concentration leads to the reduction of the dynamic range.

Calibration ranges, coefficients of determination, and limits of detection for the ethylbenzene, *p*-xylene, 1,2,4-trimethylbenzene, and naphthalene are summarized in Table 2. Quantification of toluene in the measurements with a modifier was not possible due to an overlap in the toluene signal and the signal of benzene dimer (see chapter 3.1). Limits of detection were calculated according to the concentration of the analyte in the carrier gas. Despite the higher response of the DMS in presence of aromatic modifier, the limits of detection for calibrations without modifier and with 0.015 % of benzene are within the same range (14.2 - 99.9 and 10.6 - 89.5 ng L⁻¹, for the calibration without and with modifier, respectively). This originates mainly from the higher background signal caused by benzene and benzene dimer (see chapter 3.1). These peaks are detected within the CF range that is similar to those observed for the most of the model substances. This results in an interference between the benzene and model compounds signals. The only compound whose LOD was significantly lower in the presence of 0.015 % of benzene than that without a modifier was *p*-xylene. Nevertheless, the analysis of the compounds of high proton affinity, e.g. 1,2,4-trimethylbenzene and naphthalene, was possible even at benzene concentration of 0.6 %.

Table 2. Calibration ranges, coefficients of determination, and limits of detection for the non-linear calibrations of the ethylbenzene, *p*-xylene, 1,2,4-trimethylbenzene, and naphthalene.

	Range [ng L ⁻¹]	R ²	LOD [ng L ⁻¹]
	no modifier		
ethylbenzene	14-1366	0.9916	99.9
<i>p</i> -xylene	38-1880	0.9919	98.7
1,2,4-trimethylbenzene	11-377	0.9967	16.6
naphthalene	7-210	0.9939	14.2
	0.015 % of benzene		
ethylbenzene	14-683	0.9412	89.5
<i>p</i> -xylene	2.5-376	0.9629	30.9
1,2,4-trimethylbenzene	11-302	0.989	18.9
naphthalene	1.4-140	0.9905	10.6
	0.6 % of benzene		
1,2,4-trimethylbenzene	3.8-189	0.9831	16.1
naphthalene	7-140	0.9865	10.4

Conclusions

It was demonstrated that the choice of an appropriate non-polar modifier, which can provide sufficient chemical interaction with the target analytes, can lead to a significant improvement in the sensitivity and the selectivity of the DMS.

The proposed method simultaneously improves two analytical parameters, namely peak capacity and sensitivity (response to the analyte). In our opinion the synergistic effect of these two

improvements will result in increased sensitivity during the analysis of the complex mixtures (e.g. real samples).

The increase of the peak area in the DMS equipped with ⁶³Ni-ionization source was explained by the improved ion transport within the DMS filter region. This differs from the DMS equipped with the APPI-source, which demonstrates the increased signal intensities in the presence of aromatic dopants due to the increased ionization efficiency of the analytes.

The results reported in this paper demonstrate that the use of the proper modifier can potentially improve the sensitivity of ion mobility-based analytical methods. This knowledge is especially interesting for the development of ion mobility-based methods for the analysis of gasoline samples, which contain a high fraction of aromatic compounds.

Notes and references

^a Department of Instrumental Analytical Chemistry, University of Duisburg-Essen (UDE), Universitätsstraße 5, 45141 Essen, Germany.

Fax: +49(0)201 183-6773; Tel: +49(0)201 183-6786; E-mail: andriy.kuklya@uni-due.de

^b IWW Water Centre, Moritzstr. 26, 45476 Mülheim a.d. Ruhr, Germany.

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