Continuous on-line determination of methyl *tert*-butyl ether in water samples using ion mobility spectrometry

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Abstract

A rapid analytical procedure for the on-line determination of methyl *tert*-butyl ether (MTBE) in water samples was developed. A new membrane extraction unit was used to extract the MTBE from water samples. The concentration of MTBE was determined using ion mobility spectrometry with [63]Ni ionization and corona discharge ionization without chromatographic separation. Both ionization methods permit the sensitive determination of MTBE. A detection limit of 100 µg/L was established for the on-line procedure. Neither the inorganic compounds, humic substances nor gasoline were found to exert a significant influence on the peak intensity of the MTBE. The screening procedure can be used for concentrations of monoaromatic compounds (benzene, toluene, xylene) up to 600 µg/L. No sample preparation is required and the analysis results are available within 5 min. In order to determine concentrations between 10 µg/L and 100 µg/L, a discontinuous procedure was developed on the basis of the same experimental set-up.
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1. Introduction

Methyl *tert*-butyl ether (MTBE) is used as fuel oxygenate and is added to gasoline in order to increase the octane number. More than 2 million tons of MTBE are used in gasoline production in Europe every year [1].

However, the widespread use of MTBE has resulted in groundwater resources at numerous industrial sites becoming contaminated through a variety of causes, such as leaking storage tanks and spillage during production or transportation [2]. The rapid transfer of MTBE from gasoline leaks or spills to the surrounding water phase is due to MTBE's high solubility in water (approximately 50 µg/L) and the low sorption of MTBE in soils [3]. Although the toxicity of MTBE is not clearly understood, the low odor and taste thresholds (20 µg/L) can provide a hazard for groundwater [4].

The procedures commonly used to detect MTBE in water samples are based on gas chromatographic (GC) methods combined with mass spectrometry (methods of Environmental Protection Agency (EPA) 8240B and 8260B), flame-ionization detection (American Society for Testing and Materials (ASTM) method D4815) or photoionization detection (EPA method 8020A) [5]. Purge and trap techniques [6,7], headspace analysis [8,9], solid-phase microextraction [10,11], headspace solid-phase microextraction [12,13] and membrane inlets [14,15] have been developed as sample preparation techniques for these analytical procedures.

In contrast to these laboratory methods, the on-site monitoring of waters enables the concentrations and spatial distribution of chemical compounds to be quickly assessed without the need to take and transport samples to a laboratory (hence ruling out these sources of error). The results are available within a few minutes using field screening techniques. Furthermore, these techniques make analysis cheaper.

Ion mobility spectrometry (IMS) is a suitable field monitoring method due to the devices' technical parameters (power supply, size, weight), the measuring conditions in which they operate (ambient pressure, air as drift gas), and their fast, accurate measuring performance (high sensitiv-

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ity, recording of ion mobility spectra). Therefore, IMS can be used for the on-site determination of a broad range of chemical compounds in environmental and industrial analysis. In particular, the high sensitivity of spectrometers and the additional information from the ion mobility spectra harbor some advantages over commonly used field screening methods [16,17].

IMS is based on determining the drift velocities attained by ionized sample molecules in the weak electric field of a drift tube at atmospheric pressure. Therefore, determining ion mobilities initially requires the formation of ions from neutral sample molecules. Subsequently, the ions formed are separated within the drift tube and the drift velocities are determined [18].

The most commonly used ion mobility spectrometers are equipped with beta ionization sources. Unfortunately, these ionization sources contain radioactive nickel ([63]Ni ionization). Photoionization (PI) and corona discharge (CD) ionization were developed as alternative non-radioactive ionization sources in IMS [19,20].

The IMS technique using [63]Ni ionization has been successfully used for the analysis of MTBE. Stach et al. [21] developed a procedure based on using water-adsorbing polymers. The gas phase above this adsorbent is transferred into the IMS and concentrations of MTBE >30 µg/L can be determined. A more sensitive dynamic headspace/IMS method was developed by Pozzi et al. [22]. MTBE is purged from the water sample and reconcentrated on Tenax tubes, allowing detection limits of 20 µg/L. A GC–IMS method was introduced by Baumbach and co-workers [23,24] for the investigation of complex samples.

However, these methods require either sample preparation or an extensive experimental set-up.

Therefore, we developed a new procedure for the fast, simple on-line determination of MTBE without the need for any sample preparation. This analytical method is based on the extraction of MTBE from water using a new membrane extraction unit equipped with mechanically stabilized flat membranes. The concentration of MTBE was determined in the gas phase using IMS without chromatographic separation. We compared different ionization sources including the non-radioactive ionization techniques (CD ionization and PI). The influence of the sample matrix and accompanying substances on the ion mobility spectra of MTBE was studied. The results of ion mobility measurements were compared with those obtained by a standard procedure used in the laboratory (GC–PID).

2. Experimental

2.1. Preparation of inlet membranes

To minimize the initial outlay, we developed procedures for the in-house production of membrane materials. Another aim was to improve mechanical stability by using suitable grids within the membrane. Preliminary investigations included the study of different preparation techniques. We then developed the procedure described and used these flat membranes for the following studies.

One gram of commercially available colorless silicon rubber was dissolved in 7 mL *n*-hexane. This mixture was stirred for 20 min using a magnetic stirrer. A special Teflon casting mould was used, which can be disassembled in order to remove the membrane after drying. A stainless steel net (32 µm mesh) was fixed in the mould and 5 mL of the silicon rubber solution was poured into the casting mould. After being left to dry for 48 h at room temperature, the membranes were removed and cut. The inlet membranes obtained had a thickness varying between 250 µm and 300 µm, including the steel net.

The flat membranes produced (7 cm^2) were fixed in a special membrane holder (acrylic glass). The sample solution to be analyzed was passed through the water-bearing side of the membrane (diameter: 30 mm, height: 11 mm) using a peristaltic pump. A magnetic stirrer (15 mm × 1.5 mm, 500 rpm) was located in this part of the extraction cell in order to improved mass transfer. The vapor space on the other side of the membrane had a volume of 3.5 cm^3 (diameter: 30 mm, height: 5 mm). Cleaned air primed by the ion mobility spectrometer's internal sample gas pump was passed through it.

The flat membranes produced in combination with the extraction unit described enable the MTBE concentration in water samples to be rapidly assessed. As can be seen from all the measurements performed, the equilibrium of permeation was achieved within 3 min for all detectable concentrations.

Long-term stability was investigated over 2 months. No significant changes in peak intensities were found. Therefore, monthly recalibration is sufficient depending on the sample matrices investigated. In our practical work, we used the flat membranes with mechanical stabilization to determine MTBE in groundwater over a period of 1 year.

2.2. Extraction unit for the determination of MTBE in water samples

The extraction unit used for the determination of MTBE in water samples is shown in Fig. 1. The sample solution is transported using a peristaltic pump to the extraction cell at a flow rate of 40 mL/min. A second peristaltic pump enables the continuous dilution of the water sample, allowing the detectable concentration range to be extended. The calibration curves determined can be used for higher concentrations if the resulting flow rate of the sample solution and diluting water is also 40 mL/min.

The extraction unit is positioned on a magnetic stirrer using the conditions described above. The gas stream through the vapor space is primed by the ion mobility spectrometer's internal sample gas pump, which has a capacity of 416 mL/min. The analytes are transported to the ion mobility spectrometer in this way. All tube connections comprise Teflon tubes, which have an internal diameter of 3 mm (gas flow) and 5 mm (water flow).
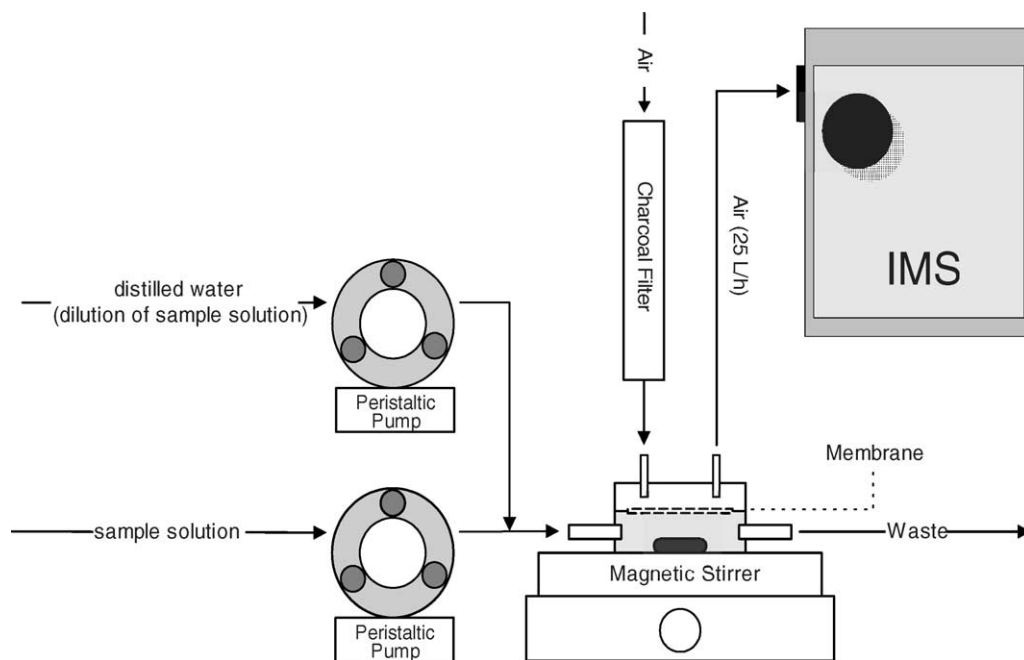
Fig. 1. Membrane extraction system for the determination of MTBE in water samples.

As is known from the literature, the humidity of the sample gas stream may considerably affect the ion mobility spectra. Therefore, our initial investigations using this extraction unit included determining the permeability of water. These studies were performed using the experimental conditions described at room temperature. The investigations showed that the relative humidity of the sample gas stream does not exceed 3% at room temperature, a level which does not affect the ion mobility measurements.

2.3. Ion mobility measurements

The measurements were performed with Bruker Raid 1 ion mobility spectrometers [25] using different ionization techniques. With the exception of ionization, all the measuring parameters were kept constant to ensure identical operating parameters (membrane inlet, gas flow, temperatures in the inlet system, ionization region and drift tube). The standard operating characteristics used for the ion mobility spectrometers are listed in Table 1.

IMS works by measuring the drift velocities of the ionized sample molecules. The drift velocity is proportional to the strength of electric field (E) and the mobility (K) of ions. The reduced mobility values (K_0 values) were calculated according to the conventional equation [26]:

$$K_0 = \frac{d}{tE}\frac{p}{760}\frac{273}{T}\,(\mathrm{cm^2\ V^{-1}\ s^{-1}}) \qquad (1)$$

where d = drift length (cm); t = drift time (s); E = field strength (V/cm); p = pressure (torr) and T = temperature (K).

Series of positive ion mobility spectra were detected for each sample. After equilibrium, 30 spectra (16 accumula-

Table 1
Standard operating characteristics for BRUKER RAID 1 ion mobility spectrometers

	[63]Ni ionization	Photoionization	Corona discharge
Ionization	555 MBq	10 eV (Kr lamp)	10^6 V/cm
	Identical features for all spectrometers used		
Inlet system	Membrane inlet		
Membrane	Dimethylsilicone		
Inlet temperature	80 °C		
Flow system	Bidirectional flow system		
Carrier flow rate	25 L/h (air)		
Drift flow rate	25 L/h (air)		
Shutter opening time	30 μs		
Temperature of drift tube	50 °C		
Electric field	Approximately 245 V/cm		

tions for each spectrum, 15 s repetition rate) were detected for each sample. The intensities of the product ion peaks formed were determined using the WIN-IMS (V4.1) software by BRUKER. The average value of the sum of the intensities of product ion peaks formed after background subtraction was used to calculate concentrations.

The drift times detected exhibit deviation of 0.06 ms under the experimental conditions described above. This variation leads to differences in the reduced mobility values calculated of about 0.01 cm² V⁻¹ s⁻¹. These differences evidently arise from small differences in air composition and moisture.

2.4. Comparative measurements by gas chromatography

The gas chromatographic measurements of MTBE were performed with a mobile gas chromatograph (ELEKTRO-

CHEMIE HALLE ECH 87.20) coupled with a headspace sampler (DANI HSS 86.50). Ten millilitres of water samples were placed into headspace vials and treated under the following conditions: $80\,°C$ oven temperature, fast agitation of the headspace vials for 30 min. One millilitre of gaseous sample was transported via a transfer line ($120\,°C$) to the split injector ($150\,°C$) of the GC. A $30\,m \times 0.32\,mm$ i.d. SE-54 capillary column with a $1\,\mu m$ film thickness was used for chromatographic separation. The column temperature program was: initial temperature $40\,°C$ for 2 min, increased at $8\,°C/min$ to $150\,°C$. The final temperature was held for 2 min. The substances were detected using a photoionization detector ($10.2\,eV$). The system was calibrated for concentrations up to $7\,\mu g/L$.

3. Results and discussion

3.1. Ion mobility measurements using different ionization techniques

Before investigating water samples, we compared the ion mobility spectra of MTBE obtained using different ionization sources. In order to rule out the influence of membrane extraction and sample matrix on the ion mobility spectra, the initial investigations were performed by measuring the MTBE as gaseous samples. The sample-introduction system used for these investigations is described elsewhere [27].

As is known from the literature, positive product ions using [63]Ni ionization are formed mainly via proton-transfer reactions. Therefore, [63]Ni ionization is suitable for the detection of MTBE because of the higher proton affinity ($841.6\,kJ/mol$) compared to that of water ($691\,kJ/mol$) [28]. PI enables compounds to be determined with an ionization energy below the energy emitted by the radiation source used. The ionization energy of MTBE is $9.2\,eV$ [28] and permits direct ionization using PI with the krypton lamp used ($10\,eV$). The appearance energy of the fragment ions mainly formed ($C_4H_9O^+$) is approximately $9.5\,eV$ [28]. Therefore, the most probable ionization pathway provides $[M]^+$ product ions. Using CD ionization, positive product ions may be formed via different processes due to the varying strength of the electric field around the corona needle. Electron impact, photoionization and proton-transfer reactions can initiate the formation of product ions. However, the formation of product ions can generally be affected by subsequent ion–molecule reactions for all the aforementioned techniques [16].

All ionization methods provide defined spectra for MTBE. The positive ion mobility spectra reveal significant differences depending on the ionization technique used. [63]Ni ionization provides two product ion peaks with reduced mobility values of $1.82\,cm^2\,V^{-1}\,s^{-1}$ and $1.49\,cm^2\,V^{-1}\,s^{-1}$. Only one product ion peak ($1.81\,cm^2\,V^{-1}\,s^{-1}$) was detected with CD ionization at low concentrations. Additional product ions can be detected with increasing concentrations, these peaks appearing at $1.98\,cm^2\,V^{-1}\,s^{-1}$, $1.65\,cm^2\,V^{-1}\,s^{-1}$

and $1.51\,cm^2\,V^{-1}\,s^{-1}$. The reduced mobility values at $1.82/1.81\,cm^2\,V^{-1}\,s^{-1}$ and $1.51/1.49\,cm^2\,V^{-1}\,s^{-1}$ evidently result from the formation of identical product ions for both ionization techniques. Therefore, ion formation through similar ionization mechanisms can be assumed.

The spectra are shown in Fig. 2. Although both methods permit the very sensitive detection of MTBE (detection limit: $0.5\,\mu g/L$ air), CD ionization provides more complex spectra in comparison to [63]Ni ionization. Therefore, the peak evaluation requires additional work.

The spectra obtained using PI consist of one product ion peak at $2.14\,cm^2\,V^{-1}\,s^{-1}$, which can be assigned to $[M]^+$ ions due to the ionization pathway expected. Using CD ionization and [63]Ni ionization, the product ion peaks appear at lower reduced mobility values. This shift in K_0 values indicates the higher ionic masses of the product ions formed. Therefore, the formation of clustered ions can be assumed for the peaks detected at $1.98\,cm^2\,V^{-1}\,s^{-1}$, $1.82\,cm^2\,V^{-1}\,s^{-1}$ and $1.65\,cm^2\,V^{-1}\,s^{-1}$. The product ion peak obtained at $1.49/1.51\,cm^2\,V^{-1}\,s^{-1}$ can attributed to dimeric ions due to the typical monomer-dimer distribution within the detectable concentration range.

The correlation between ionic mass and reduced mobility values can be described by mass-to-mobility correlation curves. Assuming that product ion peaks result from the formation of water–ion clusters and from dimerization ($2.14\,cm^2\,V^{-1}\,s^{-1}$: M^+; $1.98\,cm^2\,V^{-1}\,s^{-1}$: $M(H_2O)H^+$; $1.82\,cm^2\,V^{-1}\,s^{-1}$: $M(H_2O)_2H^+$; $1.51\,cm^2\,V^{-1}\,s^{-1}$: M_2H^+), a linear correlation between ionic mass and reduced mobility values can be derived ($\lg m = -0.476K_0 + 2.965$). The ion detected at $1.65\,cm^2\,V^{-1}\,s^{-1}$ cannot be clearly attributed to certain structures using the mass-to-mobility correlation curve obtained. A detailed structure elucidation requires further investigations.

[63]Ni ionization and CD ionization generally permit the more sensitive detection of MTBE compared to PI (detection limit: $5\,\mu g/L$). This higher sensitivity can evidently be attributed to a higher yield of ions during the ionization reaction. Therefore, the screening method for MTBE was developed on the basis of these two ionization techniques.

The spectra obtained after membrane extraction of MTBE from water samples provide product ion peaks with the same reduced mobilities in comparison to the investigation of gaseous matrix. As can be seen from Fig. 2, the spectra detected are not affected by the small differences in air composition and moisture.

The experimental set-up described above was used for the calibration of MTBE in water samples. Fig. 3 shows the calibration graph used for the further investigations. Both ionization techniques provide similar calibration graphs. The graphs of the second-order fitting were used to calculate MTBE concentrations in water. The polynomial functions (quadratic function) obtained for the ionization techniques used were: [63]Ni ionization: $y = -0.01 + 54.60x - 5.28x^2$ (correlation coefficient $R = 0.99$) and CD ionization: $y = 1.44 + 69.97x - 10.13x^2$
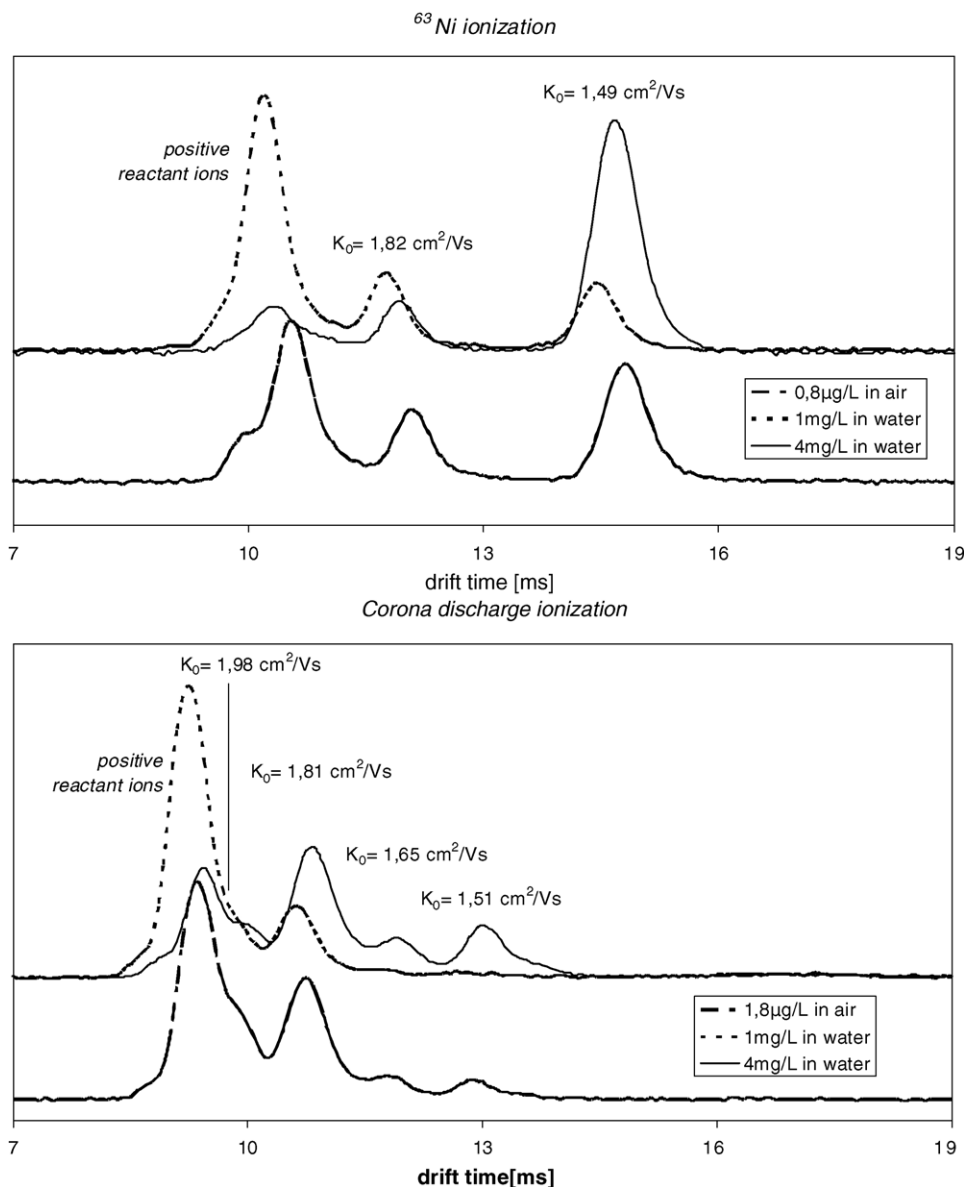
Fig. 2. Ion mobility spectra of MTBE obtained using [63]Ni and corona discharge ionization.

($R = 0.99$). A limit of detection of 0.1 mg/L was calculated for both ionization methods. The calibration graph obtained for CD ionization is applicable up to 5 mg/L while calibration using [63]Ni ionization only permits the determination of MTBE concentrations up to 4 mg/L. These upper concentrations correspond to a decrease in reactant ion intensity of about 90%. However, these concentration ranges can be extended using different dilution ratios of aqueous sample as described above. A standard deviation of approximately 5% was established for the measurements of standard solutions. Calibration was performed at 20 °C.

3.2. Effects of temperature and sample matrix

Before investigating actual groundwater samples, we studied the influence of possible matrix components and oper-

ating parameters on the recovery of MTBE. As is known from the literature, membrane extraction is considerably influenced by the temperature of the water sample [29] due to the different diffusion coefficient depending on the temperatures. The consideration of temperature is especially important for methods developed for field measurements. Therefore, we investigated solutions with a constant concentration of MTBE at different temperatures. The temperature of the sample solutions was adjusted using a thermostat with an integrated cooling system. The measurements were performed at temperatures of 5 °C, 10 °C, 15 °C, 20 °C and 25 °C. The results are summarized in Fig. 4.

As can be seen from Fig. 4, the influence of temperature can cause differences in peak intensities of 50% related to the peak intensities detected at 25 °C. Therefore, the use of membrane extraction as a field monitoring technique re-
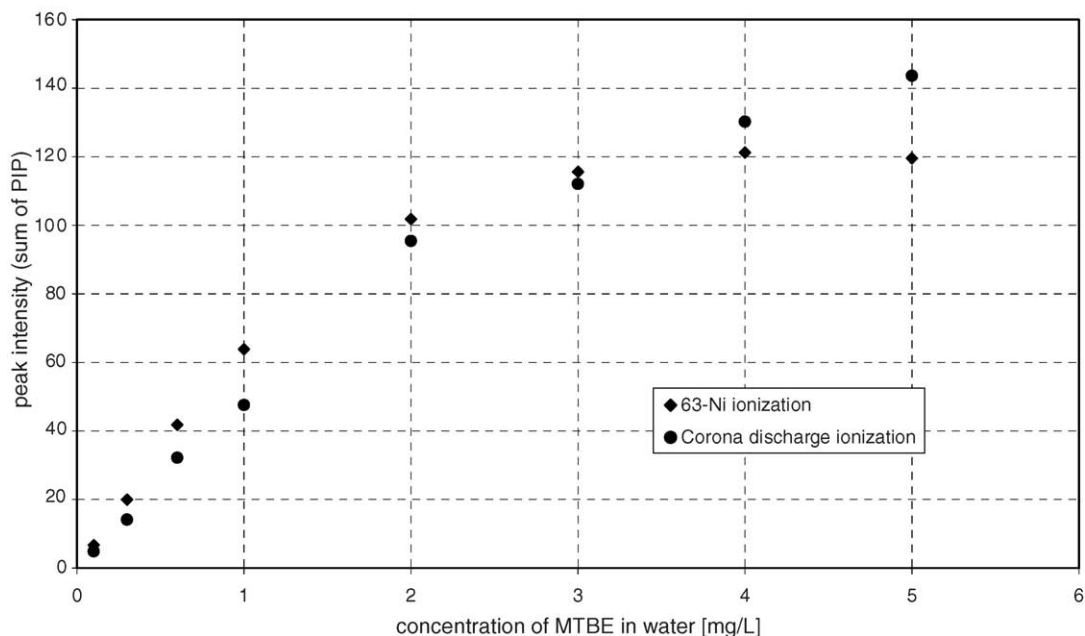
Fig. 3. Calibration curve of MTBE.

quires temperature effects to be taken into account. The simplest way of minimizing these effects is to use correction factors. For the inlet membrane used in this investigation, correction factors of 1.7 (5 °C), 1.35 (10 °C), 1.15 (15 °C) and 0.92 (25 °C) were established for ^{63}Ni ionization, and factors of 1.42 (5 °C), 1.23 (10 °C), 1.04 (15 °C) and 0.95 (25 °C) were found for CD ionization related to a tempera-

ture of 20 °C. However, each membrane produced requires separate calibration regarding the influence of temperature on permeability.

The effect exerted on the MTBE peak areas in ion mobility spectra by inorganic compounds (salinity: NaCl, FeCl$_2$, Na$_2$S), humic acids and organic contaminants (BTEX compounds: benzene, toluene, ethyl benzene and xylene as possi-
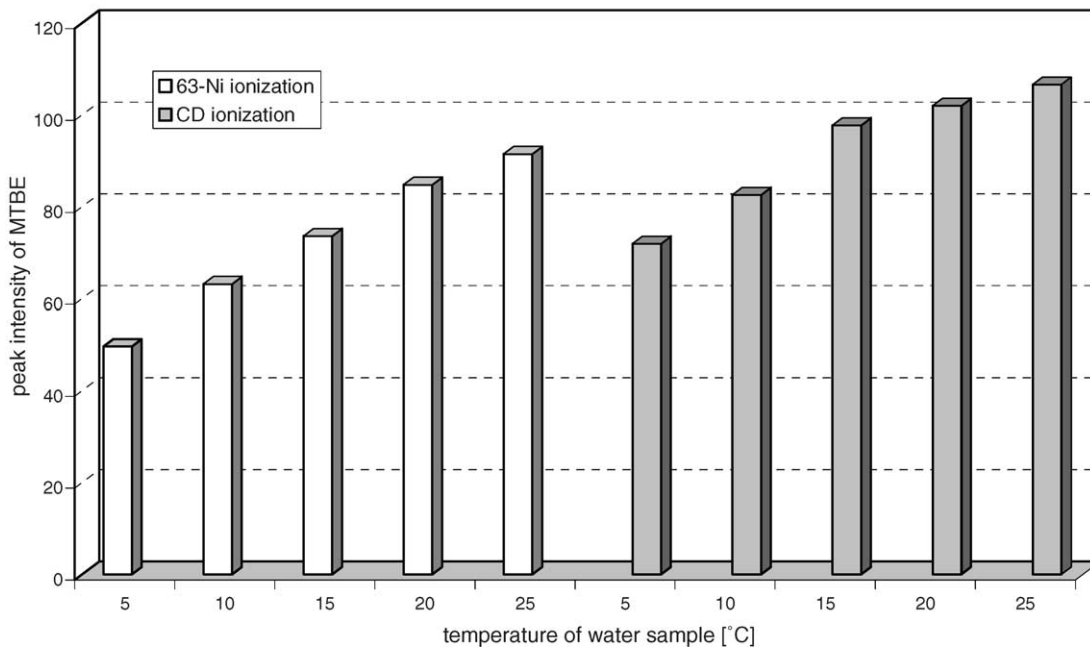

Fig. 4. Influence of sample temperature on extraction yield.

Ion mobility spectra (^{63}Ni ionization) of MTBE depending on the BTEX concentration

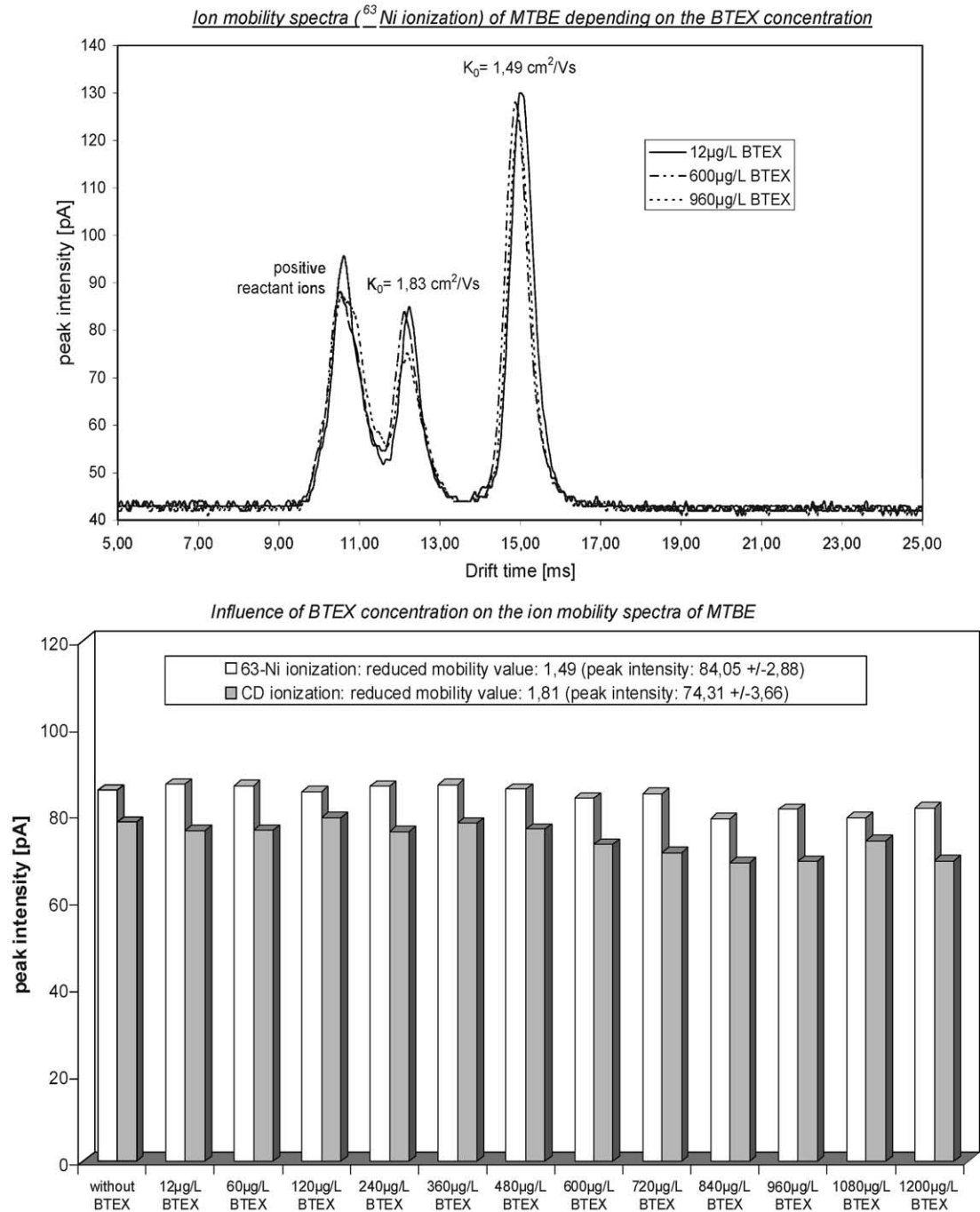Influence of BTEX concentration on the ion mobility spectra of MTBE

Fig. 5. Ion mobility spectra (^{63}Ni ionization) and peak intensities of MTBE depending on the concentration of BTEX compounds.

ble accompanying substances in gasoline, *tert*-butyl alcohol as a possible degradation product and unleaded gasoline) was investigated.

Aqueous solutions of MTBE were spiked with the substances mentioned above. The concentrations of MTBE in synthetic solutions were varied between 1 mg/L and 3 mg/L. The following concentrations of inorganic substances and humic substances were added to the standard solutions of MTBE as possible matrix: Na_2S: 10–50 mg/L; $FeCl_2$:

50–1000 mg/L; NaCl: 50–1000 mg/L and soluble humic acid: 5–35 mg/L.

Neither the inorganic compounds nor the humic substances were found to significantly affect the peak intensity of the MTBE in ion mobility spectra obtained by ^{63}Ni ionization and CD ionization.

Fig. 5 shows the ion mobility spectra of 2 mg/L MTBE and increasing concentrations of BTEX compounds obtained using ^{63}Ni ionization. The standard solution used contained

equal concentrations for each compound. Therefore, the BTEX concentrations shown in this figure include the sum of the individual BTEX substances. As can be seen from the ion mobility spectra, the influence of BTEX concentrations on the intensity of product ions detected for MTBE can be neglected up to concentrations of 600 μg/L. Although a reduction in the reactant ion peak can be observed, the product ion peaks of MTBE are not affected by the increasing concentration of BTEX up to 600 μg/L. Higher BTEX concentrations (960 μg/L) provide a reduced intensity for the peak detected at $1.83 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ while comparable intensities were found for the dimeric product ion peak ($1.49 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$) compared to lower BTEX concentrations. The diagram in Fig. 5 shows a detailed evaluation of the intensities of the main peaks detected for MTBE using ^{63}Ni ionization ($1.49 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$) and CD ionization ($1.81 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$). These results indicate that the ionization techniques used enable the determination of MTBE up to BTEX concentrations up to 600 μg/L (CD ionization) and 720 μg/L (^{63}Ni ionization) related to an MTBE concentration of 2 mg/L. These results were confirmed by investigating the individual substances. Generally speaking, the analytical procedure permits MTBE determination in the presence of 30 wt% BTEX compounds without affecting quantitative MTBE determination. Using ^{63}Ni ionization, the presence of higher BTEX concentrations causes only minimal errors if only the dimeric product ion peak is used for the evaluation of intensities.

As described above, the formation of product ions using ^{63}Ni ionization result from proton-transfer reactions depending on the proton affinity of the substances investigated. Evidently, the higher proton affinity of MTBE (841.6 kJ/mol) in comparison with that of benzene (750.4 kJ/mol), toluene (784 kJ/mol), *o*-xylene (796 kJ/mol), *m*-xylene (812 kJ/mol) and *p*-xylene (794.4 kJ/mol) causes the preferred formation of product ion from the substance with the highest proton affinity (MTBE). Therefore, the ion formation of BTEX compounds is clearly suppressed. The small differences between ^{63}Ni ionization and CD ionization result from additional ionization pathways observed for CD ionization, which provide the additional product ions.

Furthermore, different permeabilities of the substances investigated through the membrane inlet may lead to differences in detectable concentrations after membrane extraction.

Similar behavior was observed for *tert*-butyl alcohol (proton affinity: 802.6 kJ/mol). This compound was not found to affect the ion mobility spectra of MTBE up to concentrations of 150 μg/L.

Considerable concentrations of MTBE contaminating sites normally stem from gasoline contamination. Therefore, we used commercially available unleaded gasoline as sample matrix. The gasoline was dissolved in methanol and aqueous solutions were used for the investigations. The results are shown in Fig. 6 for ^{63}Ni ionization by way of example. Increasing concentrations of gasoline were added to a solution containing 1 mg/L MTBE. The peak intensities shown were calculated by using the sum of product ion peak intensities obtained for MTBE ($1.82 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ and $1.49 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$). As can be seen from Fig. 6, the quantitative determination
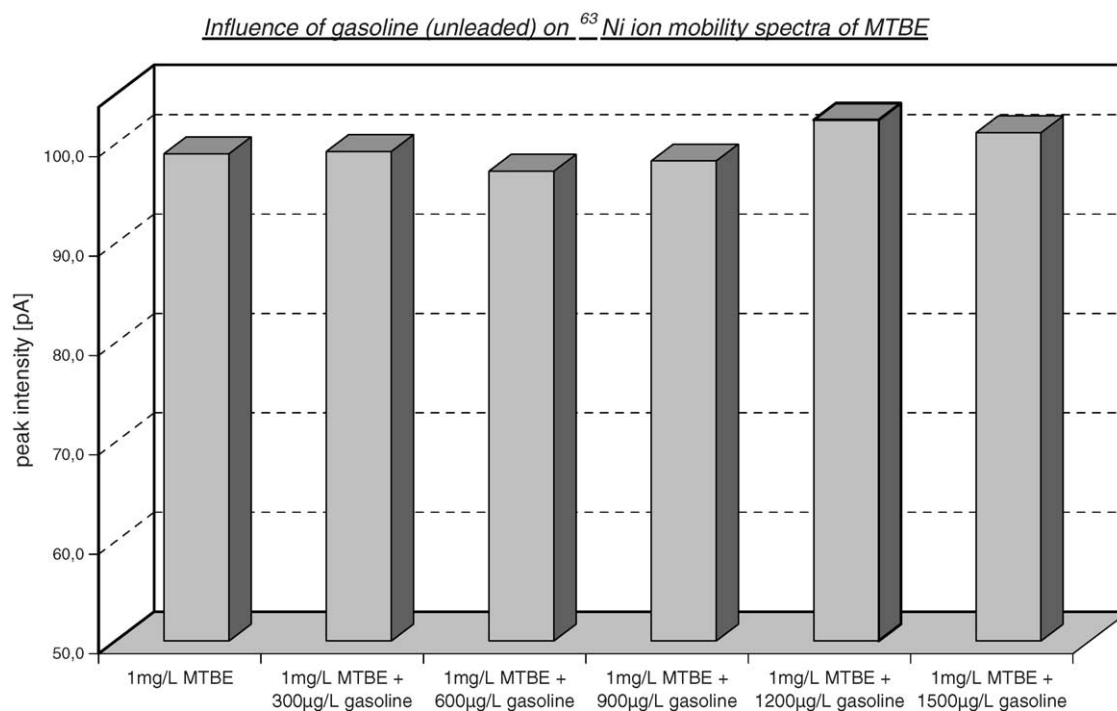

Fig. 6. Intensity of product ion peaks of MTBE depending on the concentration of gasoline (^{63}Ni ionization).
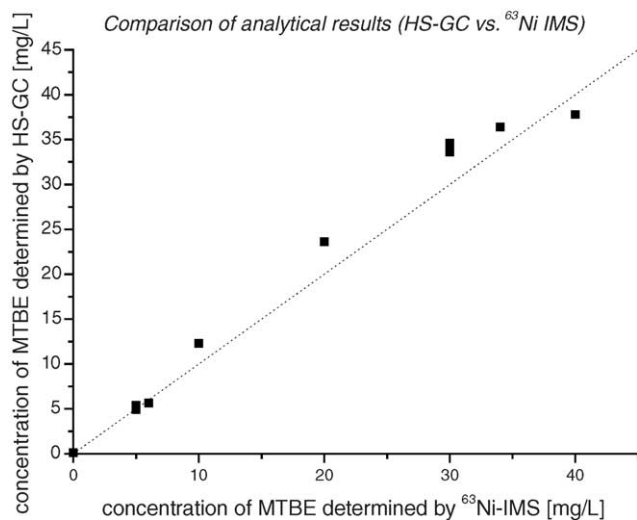
Fig. 7. Comparison of results obtained by IMS and headspace-GC.

of MTBE is not affected by gasoline, although the concentrations of gasoline exceed the concentrations of MTBE. The influence of gasoline constituents such as BTEX compounds, alkanes, cycloalkanes and unsaturated hydrocarbons can evidently be neglected due to their low proton affinities. Comparable results were obtained using CD ionization.

3.3. Investigation of water samples

The analytical procedure was applied to investigate groundwater samples from the LEUNA industrial complex. The sample sites are located in the area of an industrial complex in Saxony-Anhalt, Germany, where groundwater pollution is directly attributable to chemical industry. The results of ion mobility measurements were compared with those obtained by a standard procedure used in the laboratory (GC–PID). Concentrations of MTBE up to 40 mg/L can be detected in this region. The results are presented in Fig. 7. The comparison of 12 samples from different groundwater wells in the contaminated region indicates reasonable agreement between the two analytical methods.

Using the IMS technique, the results are available within 5 min. By contrast, the commonly used procedure based on GC–MS requires considerably more time before the results are known. Moreover, another advantage of IMS is that it does not require any sample preparation.

3.4. Determination of low MTBE concentrations

Although the detection limit of $100 \, \mu g/L$ for the on-line method developed is sufficient for the investigation of contaminated sites, the low odor and taste thresholds ($20 \, \mu g/L$) of MTBE in water require determination in concentrations below $100 \, \mu g/L$. Therefore, we developed an analytical method using the extraction unit described for the detection of lower MTBE concentrations.

Using the inlet membrane as an enriching zone, concentrations between $10 \, \mu g/L$ and $100 \, \mu g/L$ can be determined. For these measurements, the gas flow through the extraction unit is interrupted. About 1 L of the water sample is pumped through the extraction unit at a flow rate of $20 \, mL/min$ and is stirred by the magnetic stirrer while no gas stream passes through the vapor space. Subsequently, the peristaltic pump for the transportation of water and the magnetic stirrer are switched off and the water flow is interrupted. The gas stream through the vapor space is switched on and the analytes are transported to the ion mobility spectrometer. 90 spectra were detected with a repetition time of 1 s. The sum of the intensities of product ions over the 90 spectra was calculated after background subtraction. The linear calibration graph was derived for ^{63}Ni ionization (concentration of MTBE = 0.2081[counts] + 4.3006; $R^2 = 0.9918$). A detection limit of $12 \, \mu g/L$ was established using the operating state described. This equation established was successfully used to determine low concentrations of MTBE.

4. Conclusion

Ion mobility spectrometry combined with the membrane extraction unit developed permit the sensitive detection of MTBE at concentrations $>10 \, \mu g/L$. Neither inorganic compounds, humic substances nor gasoline were found to significantly affect the peak intensity of the MTBE. The screening procedure is applicable for concentrations of BTEX compounds up to $600 \, \mu g/L$. More complex samples require the use of GC–IMS [23] or standard procedures used in laboratories. The method developed does not require any sample preparation and the analytical results are available within 5 min.

Acknowledgement

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