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Fast detection of methyl *tert*-butyl ether from water using solid phase microextraction and ion mobility spectrometry

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ABSTRACT

Methyl *tert*-butyl ether (MTBE) is commonly used as chemical additive to increase oxygen content and octane rating of reformulated gasoline. Despite its impact on enhancing cleaner combustion of gasoline, MTBE poses a threat to surface and ground water when gasoline is released into the environment. Methods for onsite analysis of MTBE in water samples are also needed. A less common technique for MTBE detection from water is ion mobility spectrometry (IMS). We describe a method for fast sampling and screening of MTBE from water by solid phase microextraction (SPME) and IMS. MTBE is adsorbed from the head space of a sample to the coating of SPME fiber. The interface containing a heated sample chamber, which couples SPME and IMS, was constructed and the SPME fiber was introduced into the sample chamber for thermal desorption and IMS detection of MTBE vapors. The demonstrated SPME–IMS method proved to be a straightforward method for the detection of trace quantities of MTBE from waters including surface and ground water. We determined the relative standard deviation of 8.3% and detection limit of 5 mg L^{-1} for MTBE. Because of short sampling, desorption, and detection times, the described configuration of combined SPME and IMS is a feasible method for the detection of hazardous substances from environmental matrices.

1. Introduction

MTBE is a common automotive fuel oxygenate used for improving the octane rating and burning of gasoline and reducing airborn toxic hydrocarbon pollutants. Its content in gasoline is typically 1–5% by volume although some countries use concentrations up to 15% by volume. In Europe, about 2 million tons of MTBE is annually added to gasoline [1]. In spite its technical advantages and effects on better air quality, MTBE as a highly water soluble and slowly degradable chemical can cause considerable contamination problems in surface and groundwater, e.g., when gasoline is leaked from storage tanks or flowed over during transport or refueling [2]. Due to lack of attention to gasoline spills, leaking storage tanks are threatened to pollute water resources in many regions worldwide. Consequently contaminated ground water supply stations have been closed and various regions are under control. For instance, in contaminated sites near refueling stations in Finland, MTBE concentrations up to 300 mg L^{-1} have been measured [3].

Various estimations of harmfulness of MTBE are available. The hazardous nature of MTBE is emphasized by findings showing that high concentrations of MTBE causes cancer in rats and mice [4,5]. Carcinogenic effects of MTBE on human health, however, are still not clear. US EPA has listed MTBE as a possible human carcinogen at high concentrations [6,7] and by late 2006 in the United States the usage of MTBE has largely been banned in gasoline. Other problems caused by MTBE are its unpleasant odor and taste even at very low concentrations. Although MTBE degrades relatively fast during its vaporization into air, its degradation in soil or water is very slow. For this reason the damages in odor and taste can provide a severe hazard, especially for drinking water supplies. Consequently, MTBE is categorized as a minor toxin in Europe and only concentrations exceeding the taste and odor thresholds (40 and 15 $\mu g\,L^{-1}$) are typically regarded as unacceptable [2]. Additionally, MTBE significantly strengthens the toxic effects and expedites the expression of the toxic response of pesticides often in the same waters than MTBE [8]. Therefore, MTBE contamination in surface water can cause irretrievable toxic effects on an aquatic ecosystem.

Abbreviations: 2,6-DtBP, 2,6-di-*tert* butyl pyridine; GC, gas chromatography; GC–MS, gas chromatography mass spectrometry; IMS, ion mobility spectrometry; LOD, limit of detection; MTBE, methyl *tert*-butyl ether; PDMS/CAR, polydimethylsiloxane/carboxen; PTFE, polytetrafluoroethylene; RIP, reactant ion peak; SPME, solid phase microextraction.

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Various efficient physico-chemical treatments for the toxic organic contaminants have been developed in recent years [9–16]. Although MTBE is a hazardous chemical and treatment technologies for removal of MTBE have been widely explored and reported [17–20], most of the public water systems do not include equipment that could completely remove it. Therefore, a growing demand for methods to monitor MTBE and related compounds exists. Especially techniques that can be used in field for fast monitoring of water contamination are needed.

MTBE has been generally detected by gas chromatography (GC) or gas chromatography mass spectrometry (GC–MS) by direct injection or with the combination of some enrichment and advanced injection technique suitable for volatile organic compounds [21–24]. One of the most widely used methods for the extraction of MTBE prior to the analysis has recently been headspace SPME [25–28]. SPME is a fast and relatively sensitive technique to concentrate various organic compounds from liquid samples at low cost [29,30]. Selective extraction of analytes by immersing the SPME fiber of high affinity into the sample matrix or sampling from the headspace above the sample followed by thermal desorption of analytes in the heated inlet of chromatographic system make SPME straightforward method that usually requires no sample purification before analysis.

The combination of SPME and IMS has only been reported a few times, e.g., in studies of drugs, herbicides, and warfare agents [31–36]. SPME enables chemical detection in a water matrix by IMS that is otherwise limited to detection of gas phase samples. The IMS technique separates and characterizes ionized organic compounds based on drift velocities of ions in an electric field under atmospheric conditions [37]. Ionization of analyte vapor takes place via ion-molecule reactions in the reaction region from where the ions in small portions are introduced into the drift region for separation under the influence of a uniform weak electric field. In IMS, ions of different mass, shape, and electrical property are characterized by drift time and mobility coefficient.

IMS is an ideal technique for real time screening of vapors of chemical substances, because of its fast response, portability, and low cost and power requirements, offering an advantage of early detection of potential contaminants directly in the environment. IMS alone or in combination with some other separation method has been used for the detection of chemical warfare agents [38–42] and explosives [43–46]. In recent years, IMS has also found its place in monitoring of environmentally relevant compounds such as toxic industrial materials [47–53].

For MTBE determination in water, some approaches combining extraction and IMS have been introduced. In 2002, water adsorbing material in an evacuated vial was successfully used for MTBE extraction from distilled or drinking water prior to injection of the gaseous MTBE into an ion mobility spectrometer [54]. In the following year, MTBE from distilled water was measured on a laboratory scale by the combination of membrane extraction unit with flow of nitrogen and ion mobility spectrometer with ^{63}Ni ionization source showing a detection limit of about 20 mg L^{-1} [47]. Later, the combination of membrane extraction by peristaltic pumps and IMS was used to extract MTBE from environmental ground water at lower concentration levels [49]. An ion mobility spectrometer was also combined with the dynamic headspace system consisting of a set of Drechsel bottles and Tenax trap for the measurement of MTBE in spiked tap water and regenerated ground water [55].

We describe for the first time the combination of SPME and IMS in sampling and screening of MTBE from water. The aim is to show that commercially available SPME fiber and ion mobility spectrometer could be an alternative method for straightforward measurement of MTBE. The suitability of the method was tested by changing variables such as extraction time, concentration, temperature, and water matrix. The approach was applied to environmental surface and ground water samples. The detection limit and repeatability were investigated. The results were compared with data obtained using a gas generator from which the MTBE vapors were directly introduced to IMS detector.

2. Materials and methods

2.1. Chemicals

MTBE (>99.5%) was obtained from Merck (Darmstadt, Germany) and its aqueous solutions for the SPME–IMS experiments were prepared in water at known concentrations ranging from 2.5 up to 500 mg L^{-1}. Ultrapure laboratory water as well as local surface and ground water were used for the investigations. 2,6-Di-*tert* butyl pyridine (2,6-D*t*BP) (>97%) was purchased from Sigma–Aldrich (Steinheim, Germany). 2,6-D*t*BP was used as a calibration reference in ion mobility calculations since it produces well defined monomer ions of known reduced mobility [56]. Filtered air was used as a carrier gas and nitrogen (99.9990%) as a drift gas in ion mobility measurements.

2.2. SPME

SPME fiber assembly containing a partially crosslinked 75 μm stationary phase of polydimethylsiloxane/carboxen (PDMS/CAR) and SPME fiber holder were obtained from Supelco (Bellefonte, PA, USA). The PDMS/CAR fiber coating has been previously evaluated to have efficient extraction characteristics in the detection of MTBE and other related ethers [57]. Prior to the first use, the fiber was conditioned at 300 °C for 1 h in a GC injector port and cooled to room temperature. All sampling was performed in 15 mL glass vials with polytetrafluoroethylene/silicone (PTFE/silicone) septa screw top caps (Supelco, Bellefonte, PA, USA). Before extraction, the samples of 10 mL in volume were heated for at least 30 min at 30 °C in a water bath using a heated magnetic stirrer to reach the equilibrium between aqueous solution and gas phase of the headspace. For the microextraction process, the fiber in the needle of the holder was passed through the septum and exposed to the headspace above the sample (Fig. 1a). Times ranging from 30 s to 10 min were used for the extraction. Thereafter the SPME fiber was retracted into the needle and withdrawn from the sample vial. The SPME fiber was cleaned at 250 °C for 1 min between each analysis and blank runs were performed to test the purity of the fiber.

2.3. Thermal desorption and emission

The SPME fiber in the needle of the holder was introduced into the thermally controlled sample chamber through the septum and the fiber was exposed for thermal desorption of MTBE (Fig. 1b). The sample chamber was constructed in the laboratory and consisted of a stainless steel container of i.d. of 50 mm and height of 75 mm. A heating rope (Omega Engineering, Inc., Leichestershire, England) and an insulating belt were coiled around the sample chamber. The chamber was heated using a power supply unit adjusted by a temperature controller (Omron Corporation, Hoofddorp, The Netherland). The temperature was recorded by a sensor placed in the sample chamber. Thermal desorption of MTBE was tested at temperatures from 35 to 55 °C, and the highest desorption was obtained at 50 °C. Relatively low temperature range was chosen because it can be easily applied for onsite measurements. A transfer line to the ion mobility spectrometer was heated to the same temperature as the sample chamber.

Pure MTBE and 2,6-D*t*BP calibration references were emitted using the permeation standards consisting of about 0.5 mL of sample in 1.5 mL vials with rubber/TEF septum caps. The permeation standard was placed in the thermostatic container similar to the

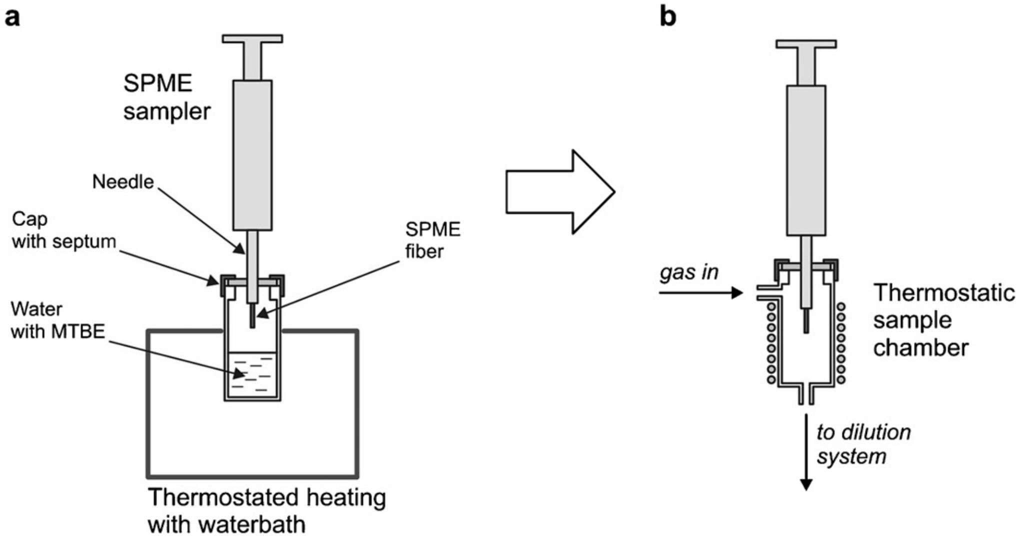

Fig. 1. Schematic model of the measurements with SPME system. Absorption of MTBE vapors in SPME fiber (a) and thermal desorption of vapors (b).

sample chamber except that it contained no septum inlet for the SPME needle. The temperature was set at 35 °C for the emission of MTBE and at 40 °C for 2,6-D*t*BP. The chemical emission rate was determined by the measurement of the mass drop of the sample source by weighing. The emission values were used for the calculation of experimental vapor concentrations.

2.4. Introduction of samples into calibration system

The dilution of sample was performed by a gas generator consisting of thermostatic sample chamber and a two-stage dilution system with four adjustable mass flow controllers (Bronkhorst High-Tech BV, Ruurlo, The Netherlands) (Fig. 2) [58]. The dilution system included a vacuum pump, filters, mixer, and mass-flow controllers. Firstly, the vapors of MTBE were flushed from the sample chamber by filtered air at the constant flow of 0.19 L min^{-1} and thereafter part of the stream was removed by the vacuum pump. The stream bypassing the vacuum pump was diluted with a known flow of filtered air and mixed. In order to keep the flow rate of carrier gas constant in the input of the IMS detector, part of the gas stream was removed before the inlet of the detector. The gas generator enabled obtaining the eventual dilutions of samples from 2.5 to 100-fold.

For the ion mobility measurements of MTBE obtained by thermal desorption from a SPME fiber, the stream of vapor was diluted 8.5-fold by adjusting the filtered air flows. For the investigations of the calibration relationships of gaseous MTBE, the vapors of MTBE were diluted from 2.5 to 100-fold. The concentration of diluted vapor was calculated using the equation:

$$c = \frac{\varepsilon}{R}, \qquad (1)$$

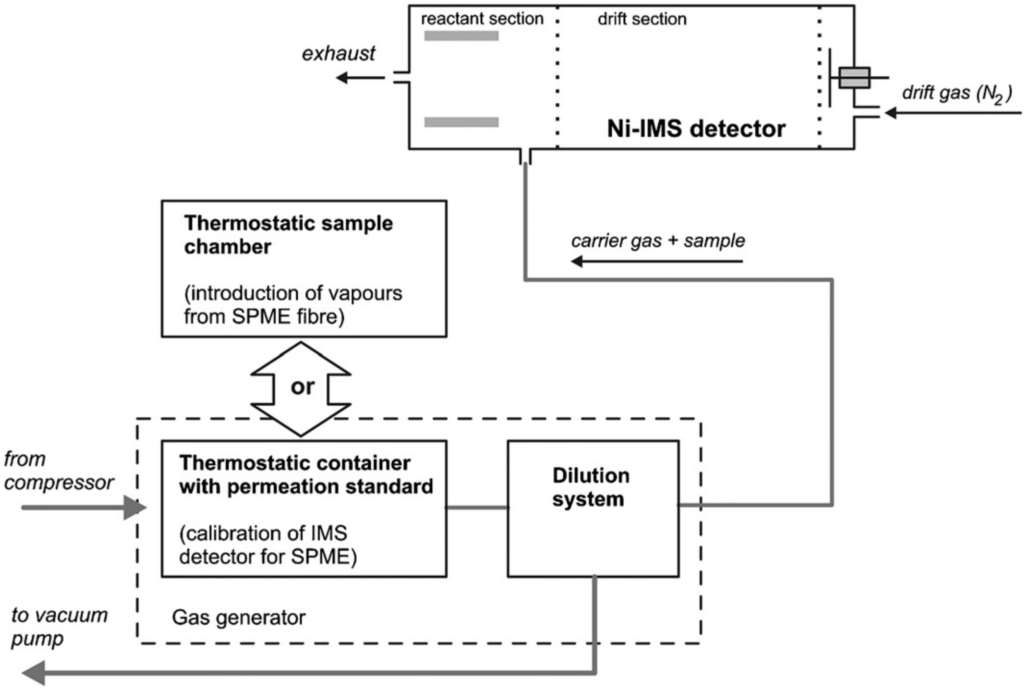

Fig. 2. Introduction of sample into IMS.

where ε corresponds to the emission rate of MTBE vapor from the permeation standard in the measurement conditions, and R corresponds to the dilution of the sample given by the gas generator. The dilutions resulted in gas phase concentrations of MTBE from 0 to 1390 ng L^{-1}.

2.5. Ion mobility spectrometer

Eiceman and Karpas described in detail the principle of IMS and its operation [37]. Carrier gas with gaseous analytes is pushed through an ionization source where the analyte molecules are ionized via ion-molecule reactions at atmospheric pressure. Product ions are passed via shutter grid into the drift region where they are separated according to their size and charge under the electric field. In the detector, the ions induce current which is recorded as a time dependent signal. The IMS detector in this study was the Ni-IMS (G.A.S., Dortmund, Germany) which is a stationary ion mobility spectrometer with a radioactive nickel-63 ionization source, 6 cm long drift region, and a unidirectional flow system. Nitrogen was used as the IMS drift gas. The detector was operated in the positive ionization mode at a temperature of 50 °C and a drift voltage of 3.5 kV. The spectra were collected in a drift time range from 3 to 23 ms with a shutter grid open for 150 μs and the sampling frequency of 50 kHz. Ion signals were processed using digital averaging of 128 scans per spectrum. Each measurement was performed in an identical manner, ensuring comparability of the data. Instrument and data acquisition were controlled by the GASpector software (version 3.99.035 DSP) (G.A.S., Dortmund, Germany).

2.6. Data processing and integration

The mobilities K of analyte ions were calculated using the equation:

$$K = \frac{l}{E \cdot t_{corr}}, \qquad (2)$$

where l corresponds to the length of drift tube (6 cm), E the electric field strength (313.4 V cm^{-1}), and t_{corr} the corrected drift time (s) of the ion. The drift time is corrected by subtracting the half width of the shutter grid pulse from the measured drift time of the ion $t_{corr} = t_d - 0.5\Delta t_{shutter}$ [59].

Furthermore, the reduced mobility values (K_0) can be calculated using the equation:

$$K_0 = K\frac{K_{0ref}}{K_{ref}}, \qquad (3)$$

where K is the measured mobility, K_{0ref} is the known reduced mobility value of 2,6-D*t*BP calibration reference (1.42 cm^2 V^{-1} s^{-1}) [56], and K_{ref} is the experimental reduced mobility value for 2,6-D*t*BP.

For the data processing in quantitative evaluation, the peaks corresponding to the reactant ion, monomer, and dimer were counted. Integration of the ion peaks was done using a laboratory made Integrator01 program that allows calculation of both integrals from peaks in single drift time spectrum and two-dimensional integrals using more than one drift time spectrum [60]. We selected the drift time spectra with the maximum abundance of detected MTBE dimer, because the peak areas change during the acquisition time of the sample from the SPME fiber (Fig. 3) [34]. The peaks corresponding to the ion species were chosen with respect to drift time and spectrum number. The integration included reduction of background signal and resulted in the distribution of peak areas originating from the observed ion species. The data was further processed and analyzed by Microsoft Office Excel. The results are the averages of triplicate experiments in each concentration.

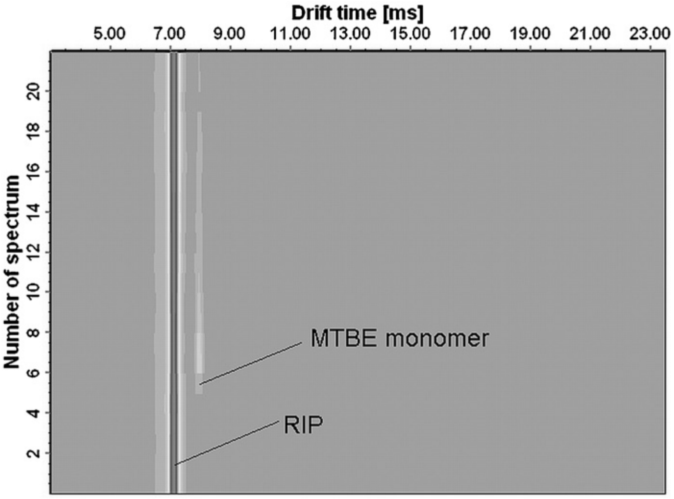

Fig. 3. Detection profile of MTBE (5 mg L^{-1} in water) by SPME–IMS. The sample was acquired after five blank spectra. The maximum abundance of MTBE monomer was detected in the seventh spectrum.

3. Results and discussion

The drift time spectrum reveals a chemical-specific signal from which we calculated the unique mobility constants in the given measurement conditions according to Eq. (3). Fig. 4 shows the drift time spectra obtained from MTBE at concentrations from 34 to 1390 ng L^{-1} using the Ni-IMS ion mobility spectrometer. An increase of the abundance characteristic for MTBE monomer and dimer ions as a function of concentration was apparent. The reactant ion peak (RIP) $H^+(H_2O)_n$ was observed at the drift time of 7.22 ms (experimental K_0 1.99 cm^2 V^{-1} s^{-1}). The peak at the drift time of 8.08 ms (K_0 1.78 cm^2 V^{-1} s^{-1}) originated from MTBE monomer and the peak at the drift time of 9.66 ms (K_0 1.49 cm^2 V^{-1} s^{-1}) from MTBE dimer. The reduced mobility values are similar to those previously obtained assuming that the MTBE monomer is in the form $M(H_2O)_2H^+$, i.e., a protonated cluster of MTBE and water ions containing a single charge, and the dimer is in the form M_2H^+, i.e., a protonated MTBE dimer with a single charge [49].

Fig. 5 shows the calibration relationships of the gaseous MTBE monomer and dimer as a function of MTBE vapor concentration ranging from 0 to 1390 ng L^{-1}. The curve was obtained from pure MTBE placed in the permeation standard made from the vial with

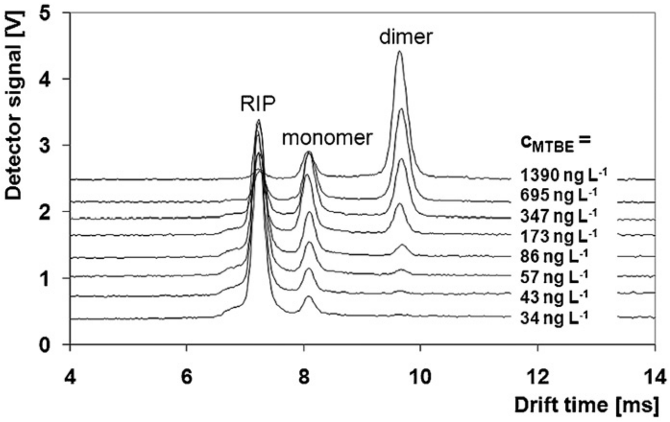

Fig. 4. Ion mobility spectra of MTBE at different gas phase concentrations. Peaks can be assigned to reactant ion (7.22 ms), MTBE monomer (8.08 ms), and MTBE dimer (9.66 ms).

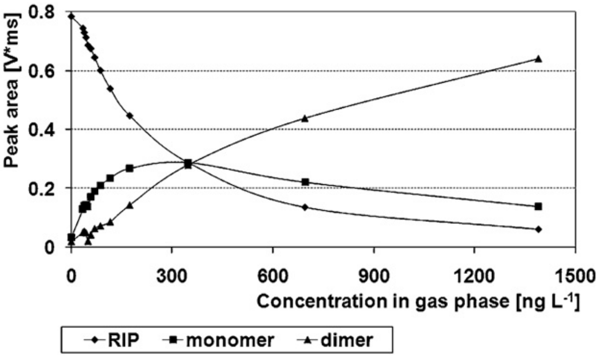

Fig. 5. Signal vs. concentration in the gas phase relationships measured for reactant ion, MTBE monomer and dimer.

rubber/TEF septum. MTBE was emitted through the septum in a heated sample chamber from which the vapor was directed to the IMS detector with the help of known flow of filtered air. The peak area is plotted versus the concentration of MTBE in the gas phase for the reactant ion, MTBE monomer and MTBE dimer. The slopes show that at increasing MTBE concentrations up to 350 ng L^{-1}, the formation of the reactant ion was dominant and the abundance of monomer was higher than the dimer. At MTBE concentrations greater than 350 ng L^{-1}, the abundance of dimer increased significantly whereas the monomer decreased, indicating an equilibrium between monomer and dimer in the gas phase and the formation of dimer by the clusterization of monomer species. The abundance of reactant ion decreased exponentially as a function of MTBE concentration, indicating the phenomenon of product ions generation by collisions between the reactant ions and the sample molecules. Near the detection limit of gaseous MTBE (20 ng L^{-1}), only the monomer species occurred whereas the signal originating from the dimer appeared at concentrations higher than 40 ng L^{-1}.

Solid phase microextraction times from one minute up to more than one hour have been previously reported for organic pollutants [61,62]. We investigated this extraction time influence on the IMS detector response with the test sample containing 30 mg L^{-1} MTBE in water. The SPME fiber was exposed to the headspace above the test sample for 0.5, 1, 2, 3.5, 5, 7.5, and 10 min. Fig. 6 shows the dependence of the detector response on the extraction time. At the concentration used, the curves for the IMS detector response for each detected species (reactant ion, MTBE monomer and MTBE dimer; the curve for the reactant ion is not shown in the figure) reached their relative stabilization in a very short time after which the changes were slow. Within the time frame tested, longer exposure time did not change the signal of MTBE dimer more than 5%. Extraction in few minutes time scale could allow carrying out the SPME–IMS procedure also in the field conditions. Therefore we chose the extraction time of 1.5 min for studying the dependence of IMS detector response on the concentration of MTBE in water during SPME–IMS experiments.

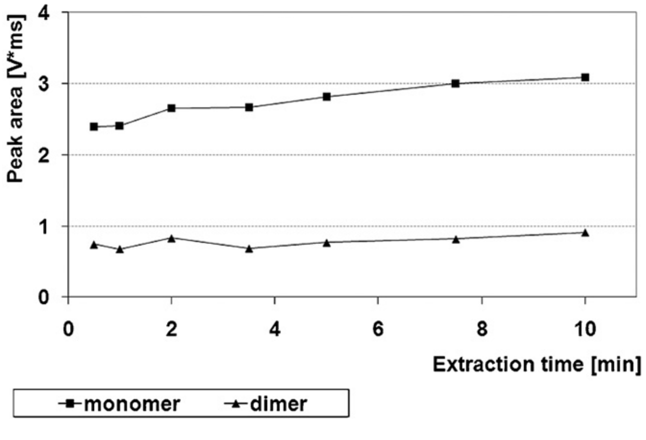

Fig. 6. Dependence between the head space extraction time of MTBE and IMS detector response.

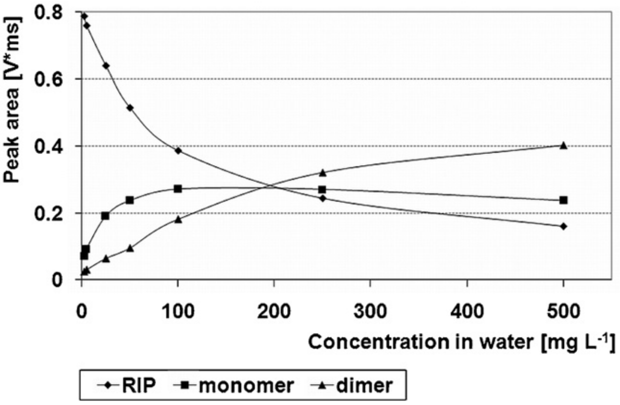

Fig. 7. Dependence between MTBE concentration in water and measured IMS detector response.

We investigated the calibration relationship between signal and concentration of MTBE in water at concentrations ranging from 2.5 to 500 mg L^{-1}. The drift time spectrum of MTBE obtained by SPME–IMS corresponded well with the spectrum obtained by the usual IMS experiment from the gas phase. Fig. 7 shows the results by plotting the IMS detector response as a function of MTBE concentration. The figure shows that the formation of reactant ion remained dominant in the whole concentration range despite the decrease in reactant ion abundance with increasing content of MTBE. The response of the MTBE dimer remained lower than that of the monomer. The results indicate that SPME fiber was not overloaded in the used concentration range. The linearity range of IMS methods is known to be relatively short [37] and limited linearity at high concentrations is also related to SPME fiber [63]. As expected, the slope of the MTBE dimer was nearly linear at concentrations up to 250 mg L^{-1} (R^2 0.9821) but at higher concentrations the slope of MTBE dimer started to curve. The slope of the MTBE monomer was linear at concentrations up to 25 mg L^{-1} (R^2 0.9985) and the slope of reactant ion peaks at concentrations up to 50 mg L^{-1} (R^2 0.9946). Regarding the whole curves of the detected ion species, polynomial equations of third degree (R^2 0.9923 and 0.9996) were fitted to the curves of reactant ion and MTBE dimer, whereas the logarithmic equation (R^2 0.9912) fit the MTBE monomer.

The desorption and IMS conditions were sufficient enough for desorbing all MTBE from the fiber even at high concentrations. As shown by Fig. 3, the detector signal corresponding to analyte ions appeared after few measurement spectra from introduction of sample, reached its maximum, and instantly started to fade as the amount of analyte decreased in the fiber. The fiber was cleaned between each analysis in order to eliminate carryover in the subsequent measurement. Three replicate analyses were performed at each MTBE concentration to test the extraction reproducibility and thermal desorption, and the stability of the ion mobility spectrometer. The drift time spectrum with the highest abundance of detected ions was selected for calculation of concentration and each measured spectra consisted of 128 digitally averaged scans. The relative standard deviation was 8.3% showing good reproducibility.

The applicability of the procedure for real samples was investigated with surface and ground water spiked with MTBE at four different concentrations. We also investigated the matrix influence on the response of IMS signal by comparing the results with the data

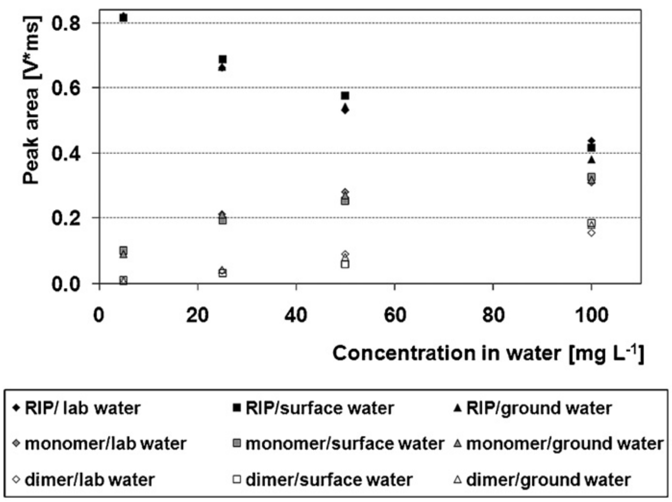

Fig. 8. Dependence between MTBE concentration in ultrapure, surface, and ground water and measured IMS detector response.

obtained from ultrapure (laboratory) water spiked with MTBE. The experimental conditions were identical to those used for obtaining the calibration curve data. Fig. 8 shows a more detailed comparison of the results for MTBE in different water matrixes. The obtained quantitative results are in good agreement. Regardless of water type at each concentration the calculated peak areas are nearly identical, indicating that the matrix did not significantly influence on the response of IMS signal. This is probable due to the extraction procedure taking place in the gaseous phase and thereby minimize interferences from environmental matrix.

Although the measurement of MTBE by the combination of SPME and IMS resulted in an unambiguous signal from MTBE in water, the efficiency of extraction of MTBE was insufficient for the measurements at the concentration levels of taste or odor thresholds. The limit of detection (LOD) of MTBE was derived from the smallest monomer peak with a signal-to noise ratio of 3:1 and it was determined to be in the range of 5 mg L^{-1} in water, indicating the low capacity of the combination of SPME and IMS for the measurements of traces of MTBE. This could be due to lower desorption temperatures and rates than typically used in SPME procedures for GC and GC–MS for determining trace levels of MTBE in water samples [21]. We developed this procedure to be applicable for field conditions, where it is often necessary to use milder experimental parameters than in laboratory scale experiments. This method can be useful when fast detection of the extent of pollution in water systems is necessary, e.g., in case of accidental spills of MTBE or MTBE containing gasoline. Better sensitivity has previously been obtained by dynamic headspace IMS that included the generation of air stream through the MTBE containing water sample in Drechsel bottle and trapping of MTBE vapors in a Tenax trap cooled with liquid nitrogen [55]. Instrument failures, risk of contamination of ion source, limited selectivity and significant matrix interferences, however, are possible due to water vapor generated by direct vaporization. SPME avoids extractions of higher-boiling point interferents. Therefore more selectivity in the analysis can be achieved with the headspace extraction. The sample volumes needed for extraction by SPME method are also relatively low compared to other extraction methods.

4. Conclusions

We have shown that the combination of headspace SPME and ion mobility spectrometer with 63-nickel ion source is a potential detection method for MTBE in aqueous matrix. MTBE was detected from the gas phase at concentration levels of ng L^{-1}, indicating good sensitivity of IMS for MTBE vapors. The efficiency of SPME was relatively low as only mg L^{-1} concentrations of MTBE were detected from water. The special mobile phases or laborious sample preparation prior to the analysis are unnecessary, however, making this method worth further development. SPME–IMS could be a suitable method for onsite analysis in many applications, because IMS detector operates under atmospheric pressure conditions and the screening of pollutants can be performed in few minutes. Therefore, further evaluation using modified extraction conditions and improved efficiency of thermodesorption will provide new information on the possibilities of SPME–IMS in the detection of lower concentrations of MTBE and related contaminants from water, the studies of mixtures of substances, and measurements in field.

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