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Determination of fuel ethers in water by membrane extraction ion mobility spectrometry

Sanna Holopainen*, Marjaana Nousiainen, Mika Sillanpää

Lappeenranta University of Technology, Faculty of Technology, Department of Energy and Environmental Technology, Laboratory of Green Chemistry, Sammonkatu 12, 50130 Mikkeli, Finland

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ABSTRACT

Fuel oxygenates are environmentally detrimental compounds due to their rapid migration to groundwater. Fuel oxygenates have been reported to cause taste and odour problems in drinking water, and they also have long-term health effects. Feasible analytical methods are required to observe the presence of fuel oxygenates in drinking and natural water. The authors studied ion mobility spectrometry (IMS) to determinate isomeric fuel ether oxygenates; ethyl *tert*-butyl ether (ETBE), diisopropyl ether (DIPE), and *tert*-amyl methyl ether (TAME), separated from aqueous matrices with a pervaporation membrane module. Methyl *tert*-butyl ether (MTBE) was also membrane extracted and detected with IMS. The authors demonstrated that fuel ethers (MTBE, ETBE, DIPE, and TAME) can be quantified at μg/L level with membrane extraction IMS. A membrane extraction module coupled to IMS is a time and cost effective analysis method because sampling can be performed in a single procedure and from different natural water matrices within a few minutes. Consequently, IMS combined with membrane extraction is suitable not only for waterworks and other online applications but also in the field monitoring the quality of drinking and natural water.

1. Introduction

Gaseous emissions from motor fuels can be reduced by improving fuel burning through adding 2–15% fuel oxygenates to petrol. However, fuel oxygenates can enter natural water and soil from accidental spills during transport and from leaking petrol containers. Methyl *tert*-butyl ether (MTBE) is the most used fuel oxygenate and has been detected in concentrations of up to 830 mg/L in groundwater near refinery sites in Germany and the USA. In surface and wastewater worldwide, fuel oxygenates are found in the higher level of μg/L [1,2].

Fuel oxygenates are oxygen containing compounds viz. ethers and alcohols, including MTBE, ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), diisopropylether (DIPE), *tert*-amyl ethyl ether (TAEE), dimethyl ether (DME), methanol (MeOH), ethanol (EtOH), and *tert*-butanol (TBA) [2–4]. The production of fuel oxygenates in Europe was approximately 6 million tons in 2009 [5]. The United States produced 12 billion litres of MTBE alone in 1998, though production has declined since 2000 [2,3]. The use of MTBE was banned in the USA in 2006 [3]. Alternative fuel ether oxygenates are replacing MTBE because it has been found to be mutagenic to animals [6]. Nevertheless, the International Agency for Research on Cancer (IARC) has categorized MTBE in Group 3 (“not classifiable as to its carcinogenicity to humans”) [7]. ETBE has received increased interest as an alternative due to its potential as a biofuel component, although the preliminary results of its environmental impact are similar to those of MTBE [1].

Fuel ethers have adversely affected the quality of the environment, mainly because of their physico-chemical properties (Table 1). For example, they have higher water solubilities and lower octanol–water partition coefficients in comparison to the other major organic compounds in petrol [2]. Fuel ethers have low Henry’s law constants, and thus a relatively low tendency to volatilize from water. Fuel ethers migrate readily to groundwater because of their low sorption to soil, and in water, they are relatively resistant to biodegradation [1].

Abbreviations: ASTM, American Society for Testing and Materials; BTEX, Benzene, toluene, ethyl benzene, xylene; CD, Corona discharge; CSIA, Compound-specific isotope analysis; DIPE, Diisopropyl ether; DME, Dimethyl ether; 2,6-D*t*BP, 2, 6-Di-*tert*-butyl pyridine; ETBE, Ethyl *tert*-butyl ether; EU, European Union; FID, Flame ionisation detector; FT-IR, Fourier-transform infrared spectroscopy; GC, Gas chromatography; IARC, International Agency for Research on Cancer; IMS, Ion mobility spectrometer; LOD, Limit of detection; LOQ, Limit of quantification; MCC, Multicapillary column; MS, Mass spectrometry; MTBE, Methyl *tert*-butyl ether; PCE, Tetrachloroethylene; PDMS, Polydimethylsiloxane; PID, Photoionisation detector; SBSE, Stir-bar sorptive extraction; SPME, Solid phase microextraction; TAEE, *tert*-amyl ethyl ether; TAME, *tert*-amyl methyl ether; TBA, *tert*-butanol; TCE, Trichloroethylene; (US) EPA, (United States) Environmental Protection Agency; WHO, World Health Organization

* Corresponding author. Tel.: +35 8406 8297 70.
E-mail address: sanna.holopainen@lut.fi (S. Holopainen).

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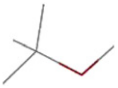
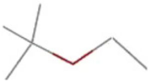
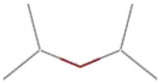
Table 1
Physico-chemical properties of studied compounds [6].

Compound	Methyl *tert*-butyl ether, MTBE	Ethyl *tert*-butyl ether, ETBE	*tert*-amyl methyl ether, TAME	Diisopropylether, DIPE
Chemical structure				
CAS	1634-04-4	637-92-3	994-05-8	108-20-3
Molecular weight [g/mol]	88.15	102.17	102.17	102.17
Molecular formula	$C_5H_{12}O$	$C_6H_{14}O$	$C_6H_{14}O$	$C_6H_{14}O$
Boiling point [°C]	55	72.6	86.3	68.5
Density [kg/L] (25 °C)	0.7353	0.7360	0.7660	0.7258 (20 °C)
Vapor pressure [mmHg, kPa] (25 °C)	250 mmHg ≈ 33.33 kPa	124 mmHg ≈ 16.53 kPa	75.2 mmHg ≈ 10.03 kPa	149 mmHg ≈ 19.87 kPa
Water solubility (20 °C)	4.8 g/100 g H_2O	1.2×10^4 mg/L	1.07×10^4 mg/L	8800 mg/L
Henry's law constant [atm/m^3/mol, Pa/m^3/mol] (25 °C)	5.87×10^{-4} atm/m^3/mol ≈ 59.5 Pa/m^3/mol	1.64×10^{-3} atm/m^3/mol ≈ 165.2 Pa/m^3/mol	1.32×10^{-3} atm/m^3/mol ≈ 133.7 Pa/m^3/mol	2.30×10^{-3} atm/m^3/mol ≈ 233.0 Pa/m^3/mol
Octanol–water partition constant, log K_{ow}	0.94	1.92	1.55	1.52
Proton affinity [kJ/mol] [8]	841.6	856.0	~ 856	855.5
Molecular volume (the van der Waals volume) [Å^3] [9]	105.60	122.55	122.79	122.42

The US Environmental Protection Agency (US EPA) has established a drinking water advisory for MTBE based on taste and odour criteria at the level of 20–40 μg/L [10]. EU Risk Assessment Reports on MTBE and TAME have been published in the European Union [11,12]. The taste and odour threshold of 15 μg/L MTBE has been included in water quality regulations in several EU member states [5]. Although exact levels have not been set for fuel ethers other than MTBE, since these have similar chemical characteristics, similar levels also apply for them [3]. The WHO has not established a health-based guideline value for MTBE because any guideline value based on adverse effects would be higher than the concentration at which it would be detected by odour [13].

Fuel oxygenates are among the most frequently detected volatile organic compounds in ground water in urban areas. They are typically analysed by gas chromatographic (GC) methods with different detectors such as the flame ionisation detector (FID), photoionisation detector (PID), or mass spectrometric (MS) detector [14–17]. The standard analytical methods EPA 8015, EPA8260B, and ASTM D4815 are based on chromatographical separation [17,18]. Other analytical methods comprise compound-specific isotope analysis (CSIA), Fourier-transform infrared spectroscopy (FT-IR), and ion mobility spectrometry (IMS) [14,15]. Analytical methods such as GC with FI or PI detectors where the identification is based on the expected time spent in the column are traditionally used, but coeluting can cause false positive results [2]. Yet, in mass detectors ions with similar mass to the charge ratio (isobars) are problematic. In this sense IMS is advantageous because it can distinguish isomers due to their different drift properties.

IMS is a sensitive and fast analytical method, has a low power consumption, needs no vacuum, and as a portable device it is feasible for in situ and online analysis. Consequently, IMS has increasing potential in environmental analysis and process applications [19–22], although traditionally it has been used in the field of security, i.e., in detecting explosives, chemical warfare agents, and illicit drugs [23–25]. For aqueous environmental samples, suitable sample preparation methods for IMS analysis include SPME, SBSE, and membrane extraction [26].

Pervaporation membrane extraction is a feasible method in environmental monitoring because analysis can be performed in a single procedure and the method can easily be automated [27–28]. Only a few membrane extraction IMS applications of aqueous environmental samples have been reported recently [29–35]. One of the latest studies focused on the analysis of chlorinated hydrocarbons in water with membrane extraction ion mobility spectrometry (ME-IMS). A hollow polydimethylsiloxane (PDMS) membrane inlet system was developed to extract tetrachloroethylene (PCE) and trichloroethylene (TCE) from water, and IMS was capable of detecting 80 μg/L of PCE and 74 μg/L of TCE in the negative ion mode [29].

MTBE has been determined in water by IMS using various sample introduction methods including gas chromatographic (GC) separation [36], solid phase microextraction (SPME) [37–39] and membrane extraction [32,33], but other fuel ether oxygenates have not previously been studied with IMS. Membrane extraction was utilized in combination with ion mobility spectrometer for continuous online determination of MTBE and other volatile organic compounds in water with ^{63}Ni-ionisation, photoionisation (PI), and corona discharge (CD) ionisation. No sample preparation or extensive experimental setup was required, and the analysis results were available within 5 min. The obtained detection limit for MTBE was 100 μg/L with all studied ionisation methods [32]. MTBE and BTEX compounds have also been determined with a combination of extraction unit and multicapillary column (MCC) separation—IMS. In these studies, a separate membrane extraction unit was used to collect samples from an aqueous matrix. The obtained method detection limits for MTBE in water were 20 mg/L with UV ionization and 1 μg/L with ^{63}Ni ionization [33–35].

In this article, we describe the experiments with IMS to determinate ETBE, DIPE, and TAME separated from water with a pervaporation membrane module. MTBE is also membrane extracted and detected with IMS. We also consider the feasibility of membrane extraction for determining fuel ethers from natural water.

2. Experimental

2.1. Chemicals

All studied fuel oxygenates (MTBE, ETBE, TAME, DIPE) were obtained from Sigma Aldrich (Steinheim, Germany) with the

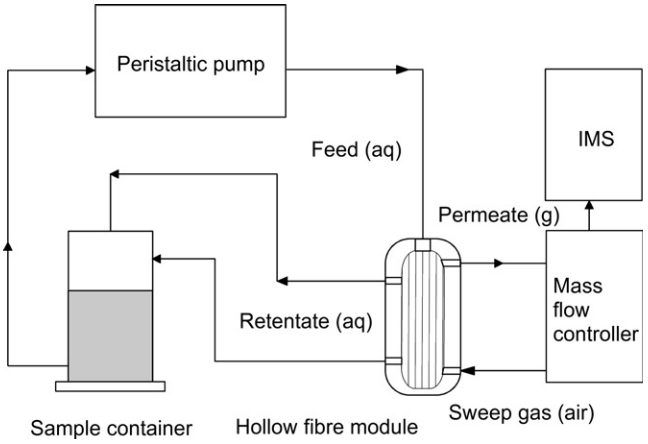


Fig. 1. The experimental setup for pervaporation ion mobility analysis.

highest available purity and used without extra purification. Aqueous solutions were prepared in ultrapure water. Surface and ground water from the Mikkeli area were also used in the determining the matrix effect. Surface water was filtered before use to remove disturbing organic particles. 2,6-Di-*tert*-butyl pyridine (2,6-D*t*BP) (> 97%, purchased from Sigma-Aldrich, Steinheim, Germany) was used as a calibration reference in ion mobility calculations.

2.2. Membrane module

The measurement setup is presented in Fig. 1. The PermSelect 2500 pervaporation membrane module used was purchased from MedArray Inc. (Ann Arbor, MI, USA). The membrane module consisted of a bundle of polydimethylsilicone (PDMS) hollow fibres, and the module contained 3200 fibres with a total membrane area of 2500 cm^2. The inner diameter of PDMS fibre was 190 µm with a fibre wall thickness of 55 µm. Before use, the module was conditioned in an oven (heated at 80 °C for several hours) and flushed with pressured air. The purity of the membrane was checked with IMS before measurements. In this study the PermSelect 2500 module was used in tube side configuration, i.e., liquid flowed inside the hollow fibres. Feed flow was circulated with a Watson Marlow (Wilmington, MA, USA) peristaltic pump Sci-Q 323 and the pump speed was set to 90 1/min. The sample concentrations used were 50–5000 µg/L, and the sample volume was 70 mL. All studies were performed at room temperature (20 °C). Permeated analytes were subjected to an IMS detector with air as a sweep gas at the speed of 190 mL/min. The air was dried with molecular sieves before use, and air flow was controlled by mass flow controllers (Bronkhorst, High-Tech BV, Ruurlo, The Netherlands). Sample spectra were collected after 5 min of sample/membrane stabilization.

2.3. Membrane calculations

Flux through a membrane can be expressed by Fick's first law:

$$J = -D\frac{dc}{dx}, \qquad (1)$$

where J is the rate transfer (or flux) ($g\,cm^{-2}\,s^{-1}$), D is the diffusion coefficient (cm^2/s) and dc/dx is the concentration gradient [28].

According to solution-diffusion theory permeation flux can also be defined experimentally:

$$J = \frac{Q}{A\Delta t}, \qquad (2)$$

where J is the permeation flux of a species through the membrane, Q is the quantity of permeate (in grams or moles) collected in a time interval Δt, and A is the effective membrane area [40].

The separation capability of a pervaporation membrane is measured by the separation factor, α, defined as:

$$\alpha = \frac{x_{p,i}/x_{p,j}}{x_{f,i}/x_{f,j}}, \qquad (3)$$

where $x_{p,i}$ and $x_{p,j}$ are the mole fractions of the permeants i and j in the permeate, and $x_{f,i}$ and $x_{f,j}$ are the corresponding mole fractions in the feed [27].

The separation factor can also be expressed in terms of fluxes:

$$\alpha = \frac{J_i x_{f,j}}{J_j x_{f,i}}, \qquad (4)$$

where J_i and J_j are the fluxes of the preferential and secondary components [27].

2.4. Ion mobility spectrometry

Ion mobility spectrometry is based on determining the generated ions' drift mobilities in an electric field at atmospheric pressure. Analyte molecules are transported with carrier gas to the ionization region of the detector where they undergo chemical ionization. In positive mode, IMS reactant ions are hydrated hydronium ions $H^+(H_2O)_n$. Product ions, monomer $(MH^+(H_2O)_x)$ and dimer $(M_2H^+(H_2O)_y)$ ions are formed through ion-molecule reactions with reactant ions. The intensity of formed product ions is concentration dependent, and the generated ions are separated in the electric field according to their size, shape and electrical properties. Ions are identified according to their drift velocities, i.e., average velocities of the ion species. Because ion separation occurs in milliseconds, the total analysis time for one sample can be a few minutes, including sampling, data acquisition, and recognition of the analyte.

The IMS detector used in this study was a Ni-IMS (G.A.S. GmbH, Dortmund, Germany) with an α-ionization source (^{63}Ni). The Ni-IMS detector operates with unidirectional gas flows, using nitrogen (99.999%) as a drift gas and filtered dry air as a carrier gas. Gas flows were controlled with mass flow controllers (Bronkhorst, High-Tech BV, Ruurlo, The Netherlands). The detector was operated at 60 °C with 3.5 kV of drift voltage. The positive mode spectra were collected in a drift time range from 3 to 23 ms with a shutter grid open at 120 µs, and with a 50 Hz sampling frequency. Ion signals were processed with digital averaging (128 scans per spectrum). The instrument's operation and data acquisition were controlled by GASpector software (version 3.99.035 DSP).

2.5. Data processing and calculations

The mobilities, K, of analyte ions can be calculated with formula (5) [23,41,42]:

$$K = \frac{v_d}{E} = \frac{l_d}{E \times t_d(\mathrm{corr.})}, \qquad (5)$$

where v_d is the average velocity of ions in the drift section, l_d is the drift length, E is the electric field intensity, and t_d (corr.) is the corrected drift time. In our experiments, l_d=6 cm, E=313.4 V/cm, and t_d (corr.)=$t_d - 0.5\ \Delta t_{\mathrm{shutter}}$ [43], where t_d is the observed drift time in milliseconds. Mobilities are usually normalized to 273 K and 760 Torr and reported as reduced mobilities, K_0:

$$K_0 = K\frac{273}{T}\frac{p}{760}, \qquad (6)$$

where K_0 is reduced mobility [$cm^2\,V^{-1}\,s^{-1}$], T is operating temperature [K], and p is pressure in Torr [41,42]. The reduced mobility values can also be determined using 2,6-Di-*tert*-butyl pyridine (2,6-D*t*BP) as a standard reference compound:

$$K_0 = \frac{K_0(\text{ref})}{K(\text{ref})} K, \tag{7}$$

where K is the measured mobility, K_0 (ref) is the known reduced mobility value of 2,6-D*t*BP (1.42 cm^2 V^{-1} s^{-1}), and K (ref) is the experimental reduced mobility value for 2,6-D*t*BP [44,45].

Data for quantitative evaluation processed for the reactant ion, monomer, and dimer ions of each compound. Integration was done using a laboratory made Integrator01- programme that allows the calculation of peak integrals from drift time spectrum [46]. The obtained peak information was further processed and analysed with Microsoft Excel. The results are the averages of quadruple experiments in each concentration. Limits of detection were calculated from the linear range of calibration curve by formula:

$$[C_i]_D = \frac{3\sigma}{S}, \tag{8}$$

where $[C_i]_D$ is minimum detectable concentration, σ is the root mean square noise (i.e., the noise above the background spectrum), and S is sensitivity [nA/ppm]. Furthermore, $S=R/C_i$ where R is response [nA], and C_i is the concentration at which detection limit is determined [47,48].

Recoveries of analyte extraction from different water matrices can be calculated by the formula:

$$R_A(\%) = \frac{Q_A(\text{yield})}{Q_A(\text{orig.})} \times 100, \tag{9}$$

where R_A is recovery (%), Q_A (orig.) is the known original and Q_A (yield) is the recovery quantity of the analyte A [48,49].

3. Results and discussion

Membrane module purity was confirmed before the measurements. For qualitative measurements, each of the studied fuel ethers was measured separately, and the results are the averages of quadruple experiments. The reactant ion peak was observed at $K_0=2.01\pm0.02$ cm^{2}V^{-1} s^{-1}, MTBE monomer $K_0=1.78\pm0.02$ cm^{2}V^{-1} s^{-1} and MTBE dimer 1.49 ± 0.02 cm^2 V^{-1} s^{-1}. The reduced mobilities of DIPE, ETBE, and TAME monomer ions were $K_0=1.73\pm0.02$, 1.72 ± 0.02, 1.70 ± 0.02 cm^{2}V^{-1} s^{-1}, and for dimer ions $K_0=1.42\pm0.02$, 1.41 ± 0.02, 1.39 ± 0.02 cm^{2}V^{-1} s^{-1}, respectively. The reduced mobility values of these structural isomers are different due to their different collision cross sections [23], and thus molecular volumes. Because the (reduced) mobilities are inversely proportional to the molecular sizes, DIPE as a symmetric molecule is the fastest isomer, and it also has the smallest van der Waals volume. In contrast, TAME has the largest side chains and the biggest molecular volume of these isomers, and thus the slowest mobility. The mass mobility comparison of the studied fuel ethers is presented in Fig. 2. Although reduced mobilities of structural isomers overlap slightly, the selectivity of mixture analysis could be enhanced by additional chromatographic separation, for example with GC-IMS combination.

To obtain quantitative information, i.e., the calibration curves of fuel ethers, each compound was measured separately four times within a concentration range from 0 to 5000 µg/L. The results were averaged from these quadruple measurements. The calibration curves for TAME, MTBE, ETBE and DIPE are presented in the Figs. 3–6. As an example, the calibration curve for TAME is presented in Fig. 3. Because the linearity range of IMS is known to be relatively short [23], only part of the obtained exponential calibration curves were used to determine LODs. Data collected in the range of 0–250 µg/L for each of the studied ethers in water was fitted. The resulting minimum detectable concentrations (LOD), minimum quantifiable concentrations (limit of quantification, LOQ$=10\times\sigma/S$), and other validation parameters are presented in Table 2. All validation parameters have been calculated

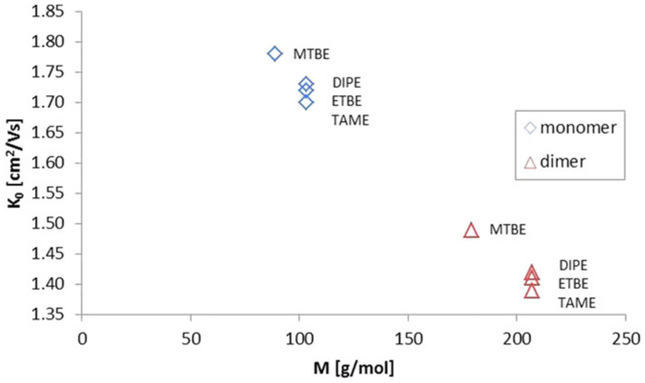


Fig. 2. The mass mobility comparison of studied fuel ethers.

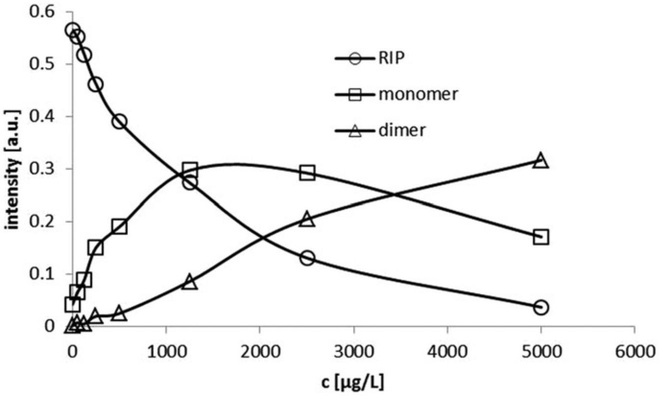


Fig. 3. Concentration dependence of TAME signals extracted with PermSelect membrane.

Table 2
Validation results ($N=4$).

	R^2	Sensitivity [signal/ppb]	Repeatability [%]	LOD [µg/L]	LOQ [µg/L]
MTBE	0.9576	0.0006	10.6	33	109
ETBE	0.9622	0.0009	8.9	24	79
TAME	0.9940	0.0004	16.7	44	145
DIPE	0.9909	0.0004	23.3	44	148

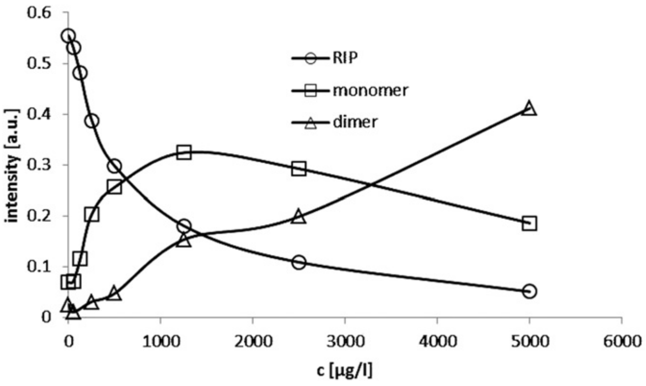


Fig. 4. Concentration dependence of MTBE signals.

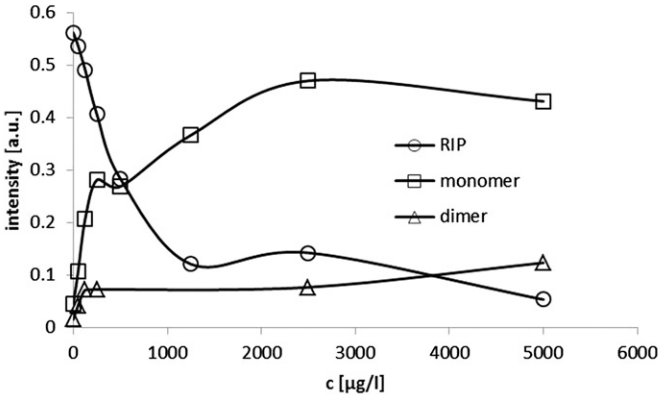


Fig. 5. Concentration dependence of ETBE signals.

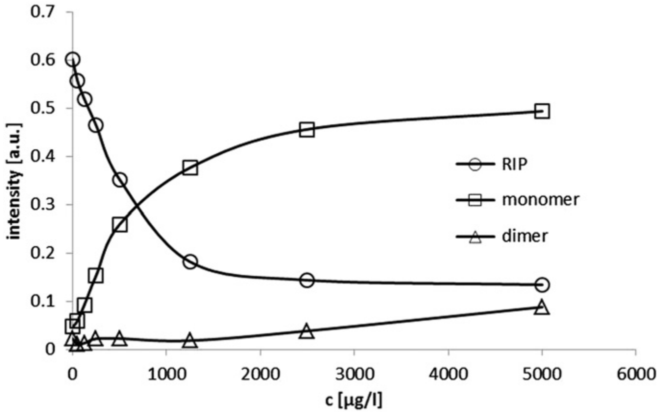


Fig. 6. Concentration dependence of DIPE signals.

for each analyte at a concentration of 250 μg/L. Repeatabilities of each ether measurement were calculated from the average of quadruple measurements and sensitivities were determined at the first derivative of the calibration curve.

For all studied chemicals, reactant ions and monomer ions were the most abundant ions at low concentrations, but for MTBE and TAME, the formation of proton bound dimer ions was favourable at higher concentrations. Yet DIPE and ETBE did not form abundant dimer ions even at the highest studied concentrations. The observed trend of dimer formation, MTBE > TAME > ETBE > DIPE, cannot be explained by the differences in proton affinity values or molecule sizes. Instead it is probable that formation of proton bound dimer is not so favourable for DIPE and ETBE because the location of the oxygen atom, a hydrogen bond acceptor, is more sterically hindered between carbon side chains in DIPE and ETBE molecules than in MTBE and TAME. Thus, the formed DIPE and ETBE dimer ions were less stable and the rate constants for dimer ion formation are lower.

The observed reduced mobilities (K_0=1.78 ± 0.02 cm^2 V^{-1} s^{-1}, 1.49 ± 0.02 cm^2 V^{-1} s^{-1}) for MTBE are comparable to those in earlier studies. For instance, reduced mobilities values for MTBE 1.82 ± 0.01 cm^2 V^{-1} s^{-1} and 1.49 ± 0.01 cm^2 V^{-1} s^{-1} [32], and 1.69 ± 0.03 cm^2 V^{-1} s^{-1} and 1.42 ± 0.03 cm^2 V^{-1} s^{-1} [33] have been obtained with ^{63}Ni ionization IMS. In our current study, the obtained LOD for MTBE (33 μg/L) is within the drinking water guideline values advised by the US EPA (20–40 μg/L), and the obtained LODs for other fuel ethers (24–44 μg/L) are at the same level. Limits of detection are also at the same level as earlier results obtained with membrane extraction IMS. For instance, Borsdorf et al. obtained a LOD for MTBE 100 μg/L in water both with ^{63}Ni and corona discharge ionisation with dimethylsilicone membrane inlet IMS configuration [32]. Baumbach et al. have detected 20 mg/L of MTBE in water with UV ionization and 1 μg/L with ^{63}Ni ionization coupled to multicapillary column IMS. A membrane extraction unit made from silicon tubing was utilized in the study [33].

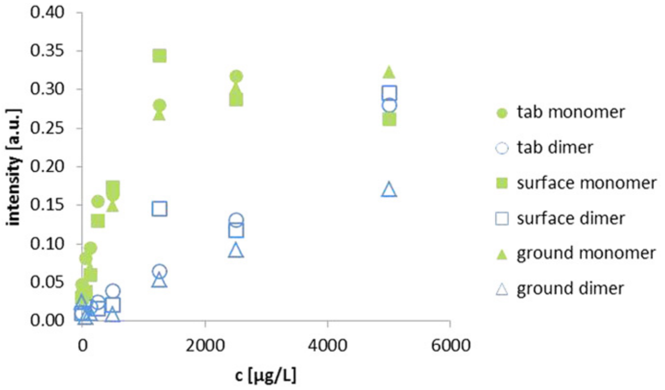


Fig. 7. Matrix effect for membrane module studied with MTBE.

The parameters optimized in our membrane extraction studies were feed concentration and feed pressure. Selectivity of membrane extraction, i.e., separation factors, were calculated at the analyte concentration of 500 μg/L in water with Formula (4), and the results for MTBE, ETBE, TAME and DIPE are 4.0, 6.6, 3.9, 7.2 g cm^{-2}s^{-1}, respectively. The extraction strength order DIPE > ETBE > TAME correlates with vapour pressures and Henry's law constants of isomeric ethers. Analyte structure could also affect solubility to PDMS material: DIPE as the most linear molecule has the greatest solubility to PDMS and TAME as the most bulky molecule passes most slowly through membrane material. To obtain better results and optimize membrane extraction procedure one could also consider the possibility of increasing the flow rate and heating the membrane module to enhance the permeation of analytes [27]. Membrane performance could also be enhanced by adding heated sweep gas to supply the evaporation enthalpy on the permeate side and by adding a condenser on the permeate side [50,51].

The matrix effect for membrane extraction was studied for MTBE concentrations of 0–5000 μg/L in tab, surface, and ground waters collected in the Mikkeli area (Fig. 7). Reactant ion peak responses have been excluded from this figure for sake of clarity. The biggest organic particles were filtered from surface water before use. Tab water and ground water were used neat, although the ground water sample was muddy looking and obviously contained some clayish minerals. Some differences were observed due to these impurities which could affect membrane performance and/or IMS response during the measurement. MTBE gave a lower response for dimer ion in ground water matrix than in surface or tab water, which could be caused by the absorption effect of clay minerals. Recoveries from different matrices were calculated also for monomer ions with Formula (9) at a concentration of 2500 μg/L. Results for MTBE were 90% from surface water and 95% from ground water.

4. Conclusions

Ion mobility spectrometry is a fast and sensitive analytical method suitable for evaluating the quality of drinking water when combined with appropriate sample extraction methods. IMS is also feasible to monitor the safety of online processes. For the first time we have shown that fuel ether oxygenates other than MTBE can be quantified at μg/L level from aqueous matrices with the combination of pervaporation membrane module and ion mobility spectrometry. For MTBE, the obtained limits of detection were within the drinking water guideline values advised by the US EPA (20–40 μg/L), and for other studied fuel ethers the LODs were at the same level. Furthermore, a PDMS membrane module was able to extract fuel ethers in the selectivity order DIPE > ETBE > MTBE > TAME, due to ether solubilities in the membrane material. The pervaporation membrane extraction module coupled to IMS was a time and cost effective analysis method because sampling could be performed in a single procedure and from different natural water matrices within a few minutes. Consequently, IMS combined with a membrane extraction is suitable not only for waterworks and other online applications in water but also to monitor the quality of drinking and natural water in the field.

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References

[1] M. Rosell, S. Lacorte, D. Barceló, in: D. Barceló (Ed.), Fuel Oxygenates, Springer, Berlin, Heidelberg, Germany, 2007, pp. 31–55.
[2] U.S. Environmental Protection Agency (US EPA), Oxygenates in Water: Critical Information and Research Needs, Washington, USA, 1998.
[3] D. Barceló, Fuel Oxygenates, Springer, Berlin, Heidelberg, Germany, 2007.
[4] R.A. Deeb, K. Chu, T. Shih, S. Linder, I. Suffet, M.C. Kavanaugh, L. Alvarez-Cohen, Environ. Eng. Sci. 20 (2003) 433–447.
[5] The European Fuel Oxygenates Association (EFOA), 〈http://www.efoa.eu〉.
[6] United States National Library of Medicine, TOXNET, Toxicology Data Network, Hazardous Substances Data Bank (HSDB), 〈http://toxnet.nlm.nih.gov/〉.
[7] World Health Organization International Agency for Research on Cancer, IARC Monographs. 73 (1999).
[8] E.P.L. Hunter, S.G. Lias, J. Phys. Chem. Ref. Data 27 (1998) 413–656.
[9] MTBE: CSID:14672, 〈http://www.chemspider.com/Chemical-Structure.14672.html〉 (accessed 13:04, Jul 30, 2012), ETBE: CSID:11996, 〈http://www.chemspider.com/Chemical-Structure.11996.html〉 (accessed 13:39, Jul 30, 2012), TAME: CSID:55188, 〈http://www.chemspider.com/Chemical-Structure.55188.html〉 (accessed 13:37, Jul 30, 2012), DIPE: CSID:7626, 〈http://www.chemspider.com/Chemical-Structure.7626.html〉 (accessed 13:40, Jul 30, 2012).
[10] US Environmental Protection Agency (US EPA), 〈http://www.epa.gov〉.
[11] ECETOC European Center for Ecotoxicology and Toxicity of Chemicals, Risk Assessment Report for Existing Substances Methyl tertiary-Butyl Ether, Brussels, Belgium, 2003.
[12] European Commission, European Union Risk Assessment Report 2-methoxy-2-methylbutane (TAME), European Chemicals Bureau, Luxembourg, 2006.
[13] World Health Organization (WHO), Guidelines for Drinking-water Quality, Geneva, Switzerland, 2011.
[14] M.A. Jochmann, T.C. Schmidt, in: D. Barceló (Ed.), Fuel Oxygenates, Springer, Berlin, Heidelberg, 2007, pp. 1–30.
[15] T.C. Schmidt, H. Duong, M. Berg, S.B. Haderlein, Analyst 126 (2001) 405–413.
[16] T.C. Schmidt, Trends Anal. Chem. 22 (2003) 776–784.
[17] JJ. Atienza, P. Aragon, M.A. Herrero, R. Puchades, A. Maquieira, Crit. Rev. Anal. Chem. 35 (2005) 317–337.
[18] R.U. Halden, A.M. Happel, S.R. Schoen, Environ. Sci. Technol. 35 (2001) 1469–1474.
[19] I. Márquez-Sillero, E. Aguilera-Herrador, S. Cárdenas, M. Valcárcel, Trends Anal. Chem. 30 (2011) 677–690.
[20] S. Armenta, M. Alcala, M. Blanco, Anal. Chim. Acta 703 (2011) 114–123.
[21] H. Borsdorf, T. Mayer, M. Zarejousheghani, G.A. Eiceman, Appl. Spectrosc. Rev. 46 (2011) 472–521.
[22] J.I. Baumbach, Anal. Bioanal. Chem. 384 (2006) 1059–1070.
[23] G.A. Eiceman, Z. Karpas, Ion Mobility Spectrometry, second ed., CRC Taylor & Francis Group, 2005.
[24] M.A. Mäkinen, O.A. Anttalainen, M.E.T. Sillanpää, Anal. Chem. 82 (2010) 9594–9600.
[25] M. Mäkinen, M. Nousiainen, M. Sillanpää, Mass Spectrom. Rev. 30 (2011) 940–973.
[26] S. Holopainen, M. Nousiainen, O. Anttalainen, M.E.T. Sillanpää, Trends Anal. Chem. 37 (2012) 124–134.
[27] B. Smitha, D. Suhanya, S. Sridhar, M. Ramakrishna, J. Membr. Sci. 241 (2004) 1–21.
[28] K. Hylton, S. Mitra, J. Chromatogr., A 1152 (2007) 199–214.
[29] Y. Du, W. Zhang, W. Whitten, H. Li, D.B. Watson, J. Xu, Anal. Chem. 82 (2010) 4089–4096.
[30] W. Zhang, Y. Du, Z. Feng, J. Xu, J. Int., Ion Mobility Spectrom. 13 (2010) 65–71.
[31] A.B. Kanu, C.L.P. Thomas, Analyst 131 (2006) 990–999.
[32] H. Borsdorf, A. Rämmler, J. Chromatogr., A. 1072 (2005) 45–54.
[33] J.I. Baumbach, S. Sielemann, Z. Xie, H. Schmidt, Int. J. Ion Mobil. Spectrom. 75 (2003) 1483–1490.
[34] S. Sielemann, Z. Xie, H. Schmidt, J.I. Baumbach, J. Int., Ion Mobility Spectrom. 4 (2001) 69–73.
[35] Z. Xie, S. Sielemann, H. Schmidt, J.I. Baumbach, J. Int., Ion Mobility Spectrom. 4 (2000) 77–83.
[36] F. Liang, K. Kerpen, A. Kuklya, U. Telgheder, J. Int., Ion Mobil. Spectrom. 15 (2012) 169–177.
[37] M. Nousiainen, S. Holopainen, J. Puton, M. Sillanpää, Talanta 84 (2011) 738–744.
[38] N. Alizadeh, M. Jafari, A. Mohammadi, J. Hazard. Mater. 169 (2009) 861–867.
[39] R. Pozzi, F. Pinelli, P. Bocchini, G.C. Galletti, Anal. Chim. Acta 504 (2004) 313–317.
[40] P. Shao, R.Y.M. Huang, J. Membr. Sci. 287 (2007) 162–179.
[41] H. Borsdorf, G.A. Eiceman, Appl. Spectrosc. Rev. 41 (2006) 323–375.
[42] J. Stach, J.I. Baumbach, J. Int., Ion Mobility Spectrom. 5 (2002) 1–21.
[43] G.E. Spangler, Anal. Chem. 65 (1993) 3010–3014.
[44] A.-K. Viitanen, T. Mauriala, T. Mattila, A. Adamov, C.S. Pedersen, J.M. Mäkelä, M. Marjamäki, A. Sysoev, J. Keskinen, T. Kotiaho, Talanta 76 (2008) 1218–1223.
[45] G.A. Eiceman, E.G. Nazarov, J.A. Stone, Anal. Chim. Acta 493 (2003) 185–194.
[46] W. Dziewiecki, S. Holopainen, A. Knap, M. Nousiainen, B. Siodłowski, M. Sillanpää, J. Puton, Anal. Sci. 26 (2010) 983–988.
[47] A.B. Kanu, H.H. Hill Jr, M.M. Gribb, R.N. Walters, J. Environ. Monit. 9 (2007) 51–60.
[48] D. MacDougall, W.B. Crummett, Anal. Chem. 52 (1980) 2242–2249.
[49] D.T. Burns, K. Danzer, A. Townshend, Pure Appl. Chem. 74 (2002) 2201–2205.
[50] X. Feng, R.Y.M. Huang, Ind. Eng. Chem. Res. 36 (1997) 1048–1066.
[51] F. Lipnizki, S. Hausmanns, P. Ten, R.W. Field, G. Laufenberg, Chem. Eng. J. 73 (1999) 113–129.