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

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ABSTRACT

Fuel oxygenates are environmentally detrimental compounds due to their rapid migration to ground-water. 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 $\mu\text{g/L}$ 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.

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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 $\mu\text{g/L}$ [1,2].

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-DtBP, 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


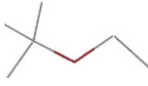

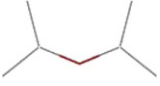
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Fuel oxygenates are oxygen containing compounds viz. ethers and alcohols, including MTBE, ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), diisopropylether (DIPE), *tert*-amyl ethyl ether (TAEE), dimethyl ether (DME), methanol (MeOH), 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].

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

Compound	Methyl <i>tert</i> -butyl ether, MTBE	Ethyl <i>tert</i> -butyl ether, ETBE	<i>tert</i> -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 ₅ H ₁₂ O	C ₆ H ₁₄ O	C ₆ H ₁₄ O	C ₆ H 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 ₂ O	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 <i>K</i> _{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 ⁶³Ni-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 ⁶³Ni ionization [33–35].

In this article, we describe the experiments with IMS to determine 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

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