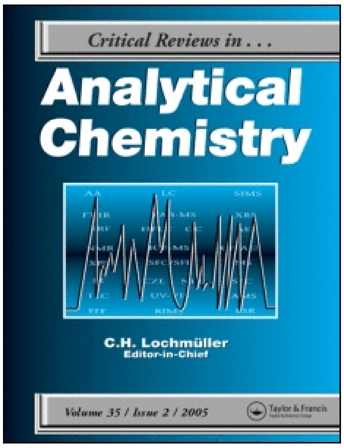

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State of the Art in the Determination of MTBE in Natural Waters and Soils

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State of the Art in the Determination of MTBE in Natural Waters and Soils

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Methyl tert-buthyl ether (MTBE) is used as an oxygenate additive in gasoline, and in the last years contamination of natural water, soils or air has taken place as result of MTBE use. Furthermore, MTBE is the second most common volatile compound (VOC) detected in a survey of shallow urban aquifers. This review focuses on the most critical steps, for sample preparation methodologies from an analytical point of view. Several enrichment and injection techniques are discussed, including direct injection, headspace analysis, purge and trap and solid-phase microextraction. The methods for the determination of methyl tert-butyl ether (MTBE) in environmental samples have been rapidly developed during last decade. Also, the current status of the analytical methods used in the determination of MTBE in water and soil is reviewed including the compound-specific stable isotope analysis (CSIA), which is an important tool in environmental sciences and allows the allocation of contaminant sources.

Keywords MTBE, environmental, water, soil, enrichment, GC

INTRODUCTION

Methyl tert-butyl ether (MTBE) is the most common oxygenate added to gasoline formulations due its low cost, easy production, favourable transfer, and blending features. It is also used in reformulated gasolines in order to lower tail-pipe emission of volatile organic compounds and carbon monoxide. Lower amounts of other ethers are used for gasoline oxygenation, including ethyl tert-butyl ether (ETBE), and tert-amyl methyl ether (TAME). Alternative fuel oxygenates included alcohols such as ethanol obtained from renewable sources (e.g., corn fermentation).

The use of MTBE in gasoline is very questioned in the United States and Europe because it is carcinogen (1), and its use has been forbidden in the United States since 2003. European directive 98/70/EC allows concentration of ethers up to 15% (v/v), concentration similar to that used in reformulated gasoline in USA; most European fuel blends contain concentrations lower than 5% (2).

MTBE is released to the environment during the manipulation or storage of petrol fuel and it has become a groundwater pollutant due to its chemical and physical properties such as high water solubility (25–50 g/l), low octanol-water partition coefficient (log K_{ow} 0.94–1.43), and a low organic carbon-based partition coefficient (log K_{oc} 0.55–0.91), which results in minimal sorption and retardation in natural aquifers. Also, due to their low Henry's constant (5.5×10^{-4} atm. m^3/mol), MTBE is hard to remove from water by aeration. Furthermore MTBE has high mobility (moves at about the same rate as groundwater) and limited degradation, especially under anaerobic conditions, and it has therefore high potential to bioaccumulate (3). Ultraviolet oxidation in atmosphere can degrade MTBE at tertiarybutyl formate (TBF) and formaldehyde, but the main degradation product of MTBE is tert-buthyl alcohol (TBA) (4). Several studies have shown that microorganism can degrade MTBE under different conditions (4–6). Consequently, MTBE has been found to be a groundwater contaminant in recent years, raising serious concerns regarding environmental toxicity hazards (7). MTBE concentrations of 8.8 μg/l have been found in lakes (8) and concentration in coastal waters can range from 5 to 800 μg/l (9). Furthermore, the presence of MTBE can substantially enhance the toxicity of other pollutants such as pesticides which are often present in the same environment (10), has a very strong taste and odor at aqueous concentrations around 20–40 μg/l and is responsible of the quick deterioration of the quality of drinking water. For these reasons, the knowing of MTBE levels and distribution in natural water (groundwater and surface) and soil is a challenging task.

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Methodologies for determination of MTBE have been modified over the years for the purpose of providing quantifiable data in environmental samples. Regulatory laws and limits for oxygenates are as complex as the sample matrices analyzed.

The determination of MTBE and its degradation products is not easy in aqueous samples using conventional methods, such as liquid-liquid (L-L) extraction coupled to gas chromatography (CG) (11). The improved functionality and reproducibility of the GC has allowed generating specific pressure, flow and temperature programs in order to separate and isolate many oxygenates from other fuel hydrocarbons. On the other hand, levels of MTBE reported in environmental water can change considerably from μg/l in aquifers to mg/l in sites affected by point sources, thus requiring different analytical strategies (12–15). This state/site specificity of the clean-up levels for fuel oxygenate requires methodologies that can detect a wide range of oxygenate concentration in matrices from drinking water to non-aqueous phase liquid. GC is by far the most widely used technique in the analysis of MTBE in water and soil using several detectors such as flame ionization (FID), photoionization (PID) or mass spectrometry (MS), as can be seen in several reviews (16, 17). In 1999, the U.S. Environmental Protection Agency (USEPA) adopted a new maximum MTBE contaminant level of 13 μg/l in water, replacing the existing range 20–40 μg/l set in 1997. These developments have led to a growing interest in the problem of how to provide increasingly simple and sensitive methods for MTBE detection (18–20). In particular, a rapid and cheaper screening test for water could provide the basis for knowing and reducing, where necessary, the contaminant effects of this pollutant.

The first problem for MTBE determination is sample preparation. Diluted or complex samples often need specific treatments to ensure effective separation and detection. Many enrichment techniques have been described, which vary according to the analytical method used, such as direct aqueous injection (DAI) (11), purge and trap (PT) (21), headspace (HS) (22), and solid-phase microextraction (SPME) by direct immersion and headspace. Due to environmental reasons, the trend of implementing green analytical chemistry favours the use of "solvent free" sample preparation methods. PT and SPME comply with this requirement. Normal PT conditions generally provide responses that permet to quantifiy MTBE down to 1–2 μg/l. For alcohols (TBA and ethanol) under the same conditions, responses may yield detection limits in the 200–250 μg/l range. However, placing the sparge tube on the PT in a water bath at 40–80°C will increase the purge efficiency of these compounds 2–5-fold. MTBE detection limits will approach the 0.1–0.2 μg/l range and alcohol detection limits should range from 25–100 μg/l. Sample size may also be increased from 5 ml to 10–25 ml, which will decrease the detection limits another 2–5-fold. Although SPME is not a standarized method for MTBE analysis, it has received recent attention as an easy and sensitive sample preparation technique.

For each above mentioned methodologies there is a table which summarizes the most important parameters. However the DL values reported are not comparable because the methods used for their determination or calculation are different.

Related to sample preservation no special treatment is needed in aqueous samples due to the MTBE slow biodegradation. Hermetically closed, cool storage and analysis sample within a week is generally pursuited aimed. For groundwater samples, the adjusting of the pH (< 2) after collected is traditionally done with HCl when the analysis of gasoline constituents is required. This acidic media causes chemical hydrolysis of MTBE, TAME and ETBE (23, 24). Currently, trisodium phosphate is at least as effective as HCl as preservative for water samples, because ethers are not prone to alkaline catalyzed hydrolysis (24).

Fluorbenzene (25, 26), methyl propylketone or methyl ketone, diisopropyl ether, terbutane, butylethyleter and d_3MTBE (20) have been used as internal standards for the quantitation of MTBE. In samples contaminated with carbon bisulphide d_{12}MTBE is to be employed as internal standard (27), while for the analysis of TBA and other alcohols, d_{10}TBA is the most employed.

Recently, in the Barcelona conference on MTBE, scientists reflected the interest and the efforts carried out by European Union to identify and to solve the problems caused by MTBE contamination. Barceló and Petrovic (28) summarized the main conclusions and recomendations, such as the need of a monitoring program on the real situation of MTBE levels in acuifers; the establishment of a common guide value for MTBE in Europe, and if feasible, also in the United States; and the convenience of a pollution prevention policy on MTBE at the European level. Finally, full-scale demonstration projects are needed to show the utility of the new technologies.

The aim of this paper is to provide an overview of the state of the art of the different analytical methods used for MTBE determination, their advantages and drawbacks. Also, the main trends for the determination of this contaminant are exposed. Finally, the application of compound-specific isotope analysis (CSIA) to determination of the isotopic composition of MTBE is given.

PRELIMINARY STUDIES: STANDARD METHODS

Different methods which are commonly used for the analysis of contaminants in soil and water samples have been developed by the USEPA. The two most widely available are SW-846 methods 8021 and 8260B, and do not contain a validated protocol for MTBE determination (29). The only difference between the two methods is the detection system, method 8021 uses a photoionization detector (PID) sometimes coupled with FID while 8260B method uses a mass spectrometer detector.

Little data have been published on the accuracy and precision of standard methods for the measurement of MTBE. Until 1996, groundwater samples contaminated by gasoline were routinely analysed (30) using the non-selective, but inexpensive, EPA methods 8015 (GC-FID), 8020 (31) and 8021B, both using GC-PID (29).

TABLE 1
Features of standard methods and sample preparation for MTBE

Method	Primary equipment	Analytes	Other comparable EPA methods	Quality parameters		Sample preparation
				DL(μg/l)	Selectivity	
EPA 8015	GC/FID	Aromatic and aliphatic hydrocarbons; Non halogenated VOCs; MTBE			Poor	L-L, PT and HS for VOCs Azeotropic distillation for non halogenated VOCs
EPA8021	GC/PID	Aromatic VOCs; MTBE	8020,602,502.3	0.2	Good	PT
EPA8260B	GC/MS	VOCs	8240,624,524.2	0.2–1	Excellent	PT; Azeotropic distillation
ASTM D4815	GC/FID	MTBE, ETBE, TAME, DIPE, TBA and C_1 to C_6 alcohols		1.1	Excellent	

The GC-FID technique is considered fraught with analytical problems in the measurement of the MTBE in environmental samples. Maybe the main problem of this methodology is the presence of interferences due to the co-elution of non-target compounds that generate false positive results. Also, the relatively poor detection limit (DL) of the GC-FID technique could limit the utility of data generated using EPA method 8015, in MTBE investigations.

Capillary GC-PID seems to be emerging as a screening technique for MTBE (EPA 8021B method). This technique shows less interference in highly contaminated samples, lower detection limit and also benzene, toluene, ethyl benzene and xylene (BTEX) can be simultaneously determined. The sensitivity using GC-PID is typically better than in GC-FID techniques, and it is also the cheapest ($30–$50 per sample). However, other compounds including some alkanes could interfere and a confirmatory 8260B method is required.

The leading method for the measurement of MTBE in environmental samples is nowadays capillary GC-MS (EPA method 8260B) (29). This method is highly selective, providing an unique identification pattern for virtually any compound. It also provides the best detection limit (0.05 μg/l for MTBE) and minimizes the presence of false positive results. However, it is more expensive ($100–$150 per sample) than those previously described.

The performances of the EPA methods used for MTBE measuring are summarized in Table 1, including the sample preparation procedures.

The American Society for Testing and Materials (ASTM) has proposed a multidimensional GC-FID method (ASTM D4815) for the determination of MTBE, ETBE, TAME, DIPE (Diisopropyl ether), TBA and C1 to C6 alcohols in gasoline. In 1998, a non-specific two-dimensional purge and trap GC-FID method based on ASTM D4815 (32, 33) was approved. In the original protocol, samples are directly injected into a gas chromatograph equipped with two columns. The primary column has polar characteristics and retains oxygenated compounds, whereas hydrophobic gasoline components are vented off. Upon reversal of the flow direction, analytes go into a non polar column for compound separation. In the modified version, PT sample treatment is used, expanding the applicability to the trace analysis of oxygenates and alcohols in aqueous samples (34). This method is moderately expensive (>$100).

Halden et al. (21) have evaluated several standard methods for the analysis of MTBE and related oxygenated compounds in gasoline contaminated groundwater. They showed that, when EPA methods 8020/21 were used in samples containing high levels of TPH, inaccurate or false positive results were obtained.

Standard methods are also successfully applied to purified water samples achieving a detection limit for MTBE of 0.2, 0.2–1 and 1.1 μg/l for methods 8021B, 8260B and ASTM D4815, respectively. On the other hand, the EPA 8260B and ASTM D4815 methods are accurate, precise and widely applicable as monitoring tools for ether and TBA analysis. The limitations and advantages of the standard EPA methods to measure MTBE in environmental media are summarized by Uhler et al. (35).

As can be seen, the extraction-based EPA methods also have some disadvantage of co-elution of other gasoline compounds being labour and equipment intensive. This is traduced in a high cost per analysis and limits the field applications. Other drawbacks are related to the interferences introduced by contaminated extraction media and analyst exposure to toxic solvents.

DETERMINATION MTBE IN WATER

Direct Aqueous Injection (DAI)

A potential alternative for rapid MTBE determination is the employment of capillary-GC using direct aqueous injection. In this method, aqueous samples are injected into the GC system without any pre-treatment, which minimises the possibility

TABLE 2
Features of direct aqueous injection

	Chromatographic conditions								
	Injection			Quality parameters					
Detector	Mode	Vsample (μ l)	Column	DL (μg/l)	RSD (μg/l)	Linear range (μg/l)	Other characteristics	Application	Ref.
FID	Hot on-column (165°C)	1–5	6% cyanopropylphenyl 94% dimethylpolysiloxane	[a]50 MTBE and TBA	—	50–10.000	Rapid (30 min), suitable for automatization, benzene and 1-butanol coeluted	Aqueous gasoline extracts	40
MS-SIM	Splitless	1	Nitroterephathalic acid modified polyethylenglycol	[a]30 MTBE and TBA	—	30–250.000	Reverse cup liner filled with carbofrit	Process studies	19
FID			FFAP	1000					
MS-SIM	Hot Splitless (130°C)	10	Polyethylenglycol	[b]0.1 ethers and TBA	—	0.1–10.000	Protrusion of the glass wool packed liner	Contaminated groundwater and soil column studies	11
MS-SIM	Cold on-column	10	Stabilwax fused–silica carbowax-polyethylenglycol	[c]0.05-0.14 MTBE 0.96-1.2 TBA 0.05-0.45 BTEX	7.7%	1.6–160	Good separation of MTBE and ETBE. Column retains the water. MTBE-d3 and TBA-d10 as ISs	Contaminated groundwater. Aqueous gasoline extracts	36
MS-SIM	Hot Splitless (130°C)	10	Polyethylenglycol	0.1 (MTBE) 0.1 (TBA) 0.5 (TBF)				Degradation Process studies	39

[a] Minimum conc. of linear range.

[b] S/N 10/1.

[c] 3.SD of 10 spike samples, 0.59 μg/l.

ISs Internal standard.

of analyte losses. GC-DAI shows several advantages over extractionbased techniques including low analysis time and cost, few equipment requirements and sample manipulations, reduced sample volumes, and the possibility of the simultaneous analysis of ethers and alcohols. Furthermore, the accuracy could be enhanced because duplicate or triplicate analyses of the same sample can be carried out easily. However, instrument failure is possible due to the large amount of water vapour produced in the column, and modification of typical configuration is often necessary (11). Also, more frequent column maintenance is required in the direct analysis of water samples, due to accumulation of salts. On the other hand, the sensitivity reached for MTBE analysis (about 0.1 μg/l) is not enough for all applications. The limitation in sensitivity is related to the amount of sample injected (between 5 and 10 μl), the behaviour of the column in the presence of water and other polar organics, the degradation of the stationary phase by water and the response and selectivity of the detector.

Table 2 summarizes the experimental conditions of different DAI methods for MTBE reported in the literature. Frequently, DAI is used for investigation of contaminated sites by MTBE and alcohols, such as TBA (11, 36–39). This technique is nowadays a common approach in water analysis with GC-FID. A prerequisite in all DAI applications is the use of a wide bore precolumn that has to be shortened and exchanged regularly. The combination of DAI with GC-MS is more difficult due to the large amount of water vapour generated and very efficient pumps are required to maintain a stable vacuum in the ion source.

Most analyses for MTBE in water are currently performed using conventional PT methods. However, most of the expected degradation products of MTBE, have lower Henry's gas constant than the parent compound, making conventional PT methods unsuitable for simultaneous analyses of both parent and products at low concentrations.

In order to perform simultaneous analyses, a DAI technique using GC with a highly polar column and MS detection was developed by Church et al. (11) to determine MTBE, TAME and some of their degradation products, using a 10 μl injection volume with splitless injection. The polar polyethylene glycol column used in this work retains water more strongly than the analytes, which opens up a retention window of several minutes between the injection and the water vapour flush. The MS system (SIM mode) has a relatively larger capacity on the vacuum than a bench-top MS system. The DLs for the tested analytes are 0.1 μg/l for MTBE, ETBE, TAME and TBA. The method gives excellent agreement with conventional PT methods for MTBE over a wide range of environmental concentrations.

Another DAI method using a cold on-column injection into a long deactivated pre-column is reported by Zwank et al. (36). The separation of fuel oxygenates and BTEX was achieved in a single chromatographic run. The column provides a better separation of MTBE and ETBE than the reported by Church et al. (11) and retains water enough to prevent a breakdown of the vacuum in the ion source. DLs in the range 0.05–0.45 μg/l for MTBE, dialkylethers, benzene and toluene were reported when 10 μl samples are injected. However, the DL for TBA was one order of magnitude higher than the reported for the other compounds (11).

Hong et al. (19) developed a simple, fast and reproducible DAI method for the analysis of MTBE and its degradation products by GC-MS and GC-FID. Under the optimized conditions, limits of quantification for the SIM mode were between 30 and 100 μg/l, depending on the analyte. In order to avoid contamination of the column by the high salt content of samples, a reverse-cup liner filled with Carbofrit was used in a split/spitless injector. However, the limit of quantification was only 1 mg/l for MTBE and TBA when FID was used.

Potter (40) developed a procedure for the analysis of MTBE in water by GC-DAI-FID using on-column injection of 1–5 μl at 165°C, and found much better performances than employing split or splitless injection modes. Using a megabore column with a stationary phase of cianopropylphenyl-dimethylpolysiloxane, water is eluted before the analytes, and the confirmation of alcohols and other polar compounds in water is also possible. The method is rapid and suitable for automation. However, it shows several limitations, such as the co-elution of benzene and 1-butanol, higher retention time when analytes are injected into a non polar organic column, and finally the limited sensitivity and selectivity of FID often not enough for environmental analysis requeriments.

DAI is also used in assays of toxicity. A study of the possible volatilization losses of MTBE was carried out by Hernando et al. (10) using GC with Atomic emission detector (AED) in intervals of time ranging between 0 to 100 h.

Membrane-Introduction Mass Spectrometry (MIMS)

Another technique described for the determination of MTBE uses a flow injection module and a silicone membrane, which allows the analytes and MTBE to directly diffuse from water into ion source of a MS. The technique is named membrane-introduction mass spectrometry (MIMS). The membrane inlet system acts as an analyte enrichment and as sample introduction device for the MS.

Membrane extraction enables rapid (few minutes), simple and solvent–free sample preparation, and it is suitable for continuous on-site and on-line monitoring of VOCs in natural waters. Hence, unlike PT, MIMS allows a high sample throughput (5 min/sample), and enables real-time sampling and monitoring of organic compounds in the environment. Also, relatively simple analysis can be performed with DLs in the sub-μg/l range. As only organic compounds pass through the membrane, salts and any suspended particles are excluded and matrix effects are eliminated. Direct analysis of MTBE in water using automated MIMS is reported by Lopez-Avila et al. (41) with a DL of 0.1 μg/l and a linear range higher than two orders of magnitude. However, in spite of increasing the analyte concentration approximately 1000 fold in the ion source of MS, the sensitivity is not enough in trace and ultra-trace analysis. Other drawback is the poor selectivity showed since MIMS does not involve chromatographic separation. For these reasons, mass spectrum corresponds to all components in the pervaporate and the quantification of isomers or compounds with overlapping mass fragments is not possible. Furthermore, other disadvantages are the slow instrument response time relative to capillary inlets (42), the temperature dependence of the transmission efficiency of the analytes through the membrane, and the potential membrane breakdown during the use.

Headspace Analysis (HS)

Headspace employs the partitioning of compound from water to air in a closed system. Direct headspace (HS) determination of VOCs in aqueous or organic matrices has been extensively employed because it overcomes the sample matrix interferences. Typically the HS is directly sampled with a microsyringe, usually for analysis by GC; however, it requires a large Henry's constant, and it is only applicable to extremely volatile compounds. In spite of this, MTBE evaporates sufficiently into the atmosphere of a sample vial, and analytical methods based on HS sampling have been developed successfully for its determination.

Headspace is a non-destructive methodology that requires little sample preparation and can be used with standard GC columns. HS is a static technique and detection limits lower than safe drinking water levels for MTBE are achieved. As HS methods can be used for high and low contaminated samples, they could be used as ideal research tools for environmental studies, such as the screening for the presence of MTBE and the investigation of contaminated sites, to verify the effectiveness of MTBE cleanup. As can be seen in Table 3, the DL decreases when the HS sampling methods are combined with GC-MS detection (43–45). The addition of salts to the samples, and working at high temperature, enhances the volatilization of MTBE increasing the efficiency of extraction process, and consequently the sensivity. This procedure has also been applied to a more complex matrix such as sea water by Flieger et al. (46), but unfortunately it is not sensitive enough.

Several authors have compared static headspace and PT methods for the determination of MTBE (43, 44). The most interesting aspect of this study lies in the complementary performance of these methods, each in its specific range, for the determination of MTBE in water samples. HS-GC-FID was used as a screening technique in routine analysis, while PT-GC-MS was used as a confirmatory method for the negative results.

A simplified static HS analysis method with MS detection using the selective ion monitoring (SIM) mode was developed

TABLE 3
Features of HS methods

	Extraction conditions		Chromatographic conditions		Quality parameters					
Detector	Salt (g/l)	T (°C)	Column	Inj. Vol. (ml)	DL (μg/l)	RSD % (at μg/l)	Linear range (μg/l)	Other characteristics	Application	Ref.
FID	0	60	Capillary fused silica CP-Sil 8 CB	—	50	7 (60)	50–1000		Contaminated groundwater	43
FID	0	70	Fused-silica DB-624	1	^{b}5.7	7.9	1–100	α,α,α-trifluorotoluene as lSs	Contaminated groundwater	44
MS-SIM	250	25	5% phenyl methyl siloxane	0.1	^{b}1.2–2, ^{a}1.2	^{b}4.5 (12), ^{a}3.3	—	Autosampler Split injection	Contaminated groundwater and riverwater	45
FID	232	35	5% biphenyl 95% PDMS	2.10^{-3}	^{c}0.06	4.8	0.1–500	HSME Toluene as ISs	Tap, well, spring water, groundwater	51[d]

[a] Calculated by Hubaux and Vos (47).

[b] t (N-1, 1-$\alpha = 0, 99$)* SD.

[c] Based on the signal that differed three times from the blank average signal.

[d] HSME .

ISs Internal standard.

for determination of MTBE in water and soil samples by O'Neill et al. (45). The DL reached, 2 μg/l (USEPA) or 1.2 μg/l (47), depends on the calibration method. Also, Mealy et al. (48) determine volatile compounds, including MTBE, in water samples using HS-GC-MS in scan mode at μg/l levels.

The headspace solvent microextraction (HSME) is a novel proposal of sample preparation for chromatographic analysis (49, 50). This system involves a microdrop of a high boiling point organic solvent allocated on the needle tip of a gas chromatographic syringe, which is exposed to the headspace above the sample. After VOCs are extracted and concentrated in the microdrop, they are swept in the microsyringe and injected directly into the chromatograph. The high volatility and low polarity of MTBE implies a fast diffusion to headspace and an enhanced distribution into the microdrop, respectively.

Bahramifar et al. (51) have developed a simple and efficient method for extraction and determination of MTBE in water samples by HSME and GC at μg/l level. Different variables, such as type of solvent, extraction time, salt concentration, microdrop volumes and stirring rate were optimised. This method was applied to the determination of MTBE in tap, well and spring waters, as well as a groundwater sample contaminated by gasoline in a calibration range of 0.1–500 μg/l, with a DL of 0.06 μg/l. This DL is better than that achieved by DAI-GC-FID (40) and similar to that reported for PT-GC-FID (21) and HS-SPME-GC-MS (52, 53).

A new analytical method for determination of MTBE in air and water, named ion mobility spectrometry (IMS) was introduced recently, allowing efficient analysis and characterization of gaseous analytes. IMS can be used for the on-site determination of a broad range of chemical compounds in environmental analysis. This technique combines low detection limits and short analysis times. The HS coupled to ion mobility spectrometry (IMS) has shown to be a portable and relatively inexpensive technique that uses a hand-held device for monitoring VOCs. Using high-speed GC with temperature program allows achieving separation times of some seconds. IMS can operate at room temperature with separation times up to 1 minute and no vacuum is required. The number of applications of this technique in industrial and environmental fields has increased due to the simplicity of the instrumentation and the excellent detection limits (in the range of a few μg/l). In IMS, vapour samples are first ionised by nonradiactive ionisation sources lamps (UV-IMS) with a rated photoionization energy of 10.6 eV being the most common. Radiactive ionization ^{63}Ni is also applied. For the determination of MTBE in the presence of monoaromatic compounds (BTEX), both IMS methods (^{63}Ni and UV ionization sources) need to be coupled to a multicapillary column (MCC) in order to obtain fast preparation of samples.

A well-designed method for the rapid analysis of water-borne MTBE using IMS has been developed by Stach et al. (54). This produced a good reproducibility and DL in the 30 μg/l range. For the separation of MTBE from water and other VOCs, a water binding material in headspace vials was used and the gas phase was injected into the IMS via an inlet port. Finally, the results were verified by GC-MS.

A combination of an ion mobility spectrometer with radioactive ionization source and equipped with a MCC was used as a new analytical method for the detection of MTBE by Xie et al. (55). A simple, effective, and easy to automate membrane extraction unit was set up and used for MTBE extraction. The analyte could be either directly extracted from water, when the membrane was completely steeped in the sample, or by head space if the membrane was held in the gas phase. For both methodologies a DL of approximately 50 μg/l of MTBE in water could be achieved. The reproducibility was good, with a standard deviation ranging from 8.9% (head space) to 11.5% (aqueous phase).

Finally, by coupling a ^{63}Ni-IMS and UV-IMS to a MCC, an easy and sensitive method for the determination of MTBE and BTEX in water was developed by Baumbach et al. (56). The DLs achieved for MCC-UV-IMS and MCC-^{63}Ni-IMS systems were 20 mg/l and 1 μg/l, respectively. As expected, IMS equipped with a radioactive source is more sensitive than IMS with UV ionization source, due to a higher ionization yield. The total analysis time at room temperature takes only a few seconds and the membrane extraction provides a system able of on-line and on-site monitoring.

An ion mobility spectrometry combined with the membrane extraction unit developed by Borsdorf et al. (57), allowed the sensitive detection of MTBE at concentration >10 μg/l with ^{63}Ni ionization and corona discharge without chromatographic separation. Neither inorganic compounds, humic substances nor gasoline were found to significantly affect the peak intensity of the MTBE. The procedure is applicable for concentrations of BTEX up to 600 μg/l. More complex samples require the use of GC-IMS (56) or standard procedures used in laboratory. The method developed does not require any sample preparation and the analytical results are available within 5 minutes.

Purge and Trap (PT)

In dynamic headspace method, commonly known as purge and trap (PT), compounds are stripped from water samples by a continuous flow of an inert gas through or above the liquid phase. Following the extraction, the volatiles are focused on a sorbent cartridge or a cryotrap. The analytes are released by thermal desorption and often subjected to a cryogenic refocusing prior to injection to the GC-column. Despite the fact that a high Henry's constant is desirable, the efficient enrichment carried out by PT allows the analysis of compounds with low Henry constant such as MTBE.

PT provides reliable data, and sensitivities (DL) about ng/l could be achieved. However, it is time-consuming and labour intensive, particularly when many samples are involved. In spite of this, the major drawback of the PT method is the high amount of water vapour generated at the purge stage, which causes peak distortion and plugging of the cryotrap, with the chromatographic problems associated with it. Typically, a cryogen liquid such as nitrogen or carbon dioxide is used to remove water. However, large amounts of the cryogen are consumed, resulting in an increase of expenses. In addition, it requires complex instrumentation and appreciable laboratory space to accommodate a PT system and liquid nitrogen used for cryotrapping. For this reason, a previous checking by HS is necessary for the analysis of unknown samples. Moreover, this method shows contamination of the analytical column from highly polluted samples. Thus, PT enrichment is recommended for clean water samples, such as drinking water, uncontaminated surface water and groundwater, where MTBE concentrations are very low. When concentration is high, samples should be diluted prior to analysis. Table 4 summarizes the parameters of reviewed PT methods.

Several authors incorporated PT in analytical protocols adopted by the USEPA (21, 58, 59) and the US Geological Survey (USGS) (25, 26). These methods have been used for determination of MTBE in surface and groundwater samples with good DLs (0.09 μg/l).

In 1996 an improved method was developed by Nouri et al. (43) for the quantitative determination of MTBE over a large range of concentrations in water samples, based on two complementary techniques: HS and PT chromatography. The precision was good and DLs of 50 μg/l for HS-GC and 2 μg/l for PT-GC, were reached. Very low DLs (1–3 ng/l) were obtained by other authors (27, 44, 60) using PT-GC-MS. On the other hand, in 2002 Lacorte et al. (44) compared HS-GC-FID and PT-GC-MS for determination of MTBE and BTEX in groundwater discussing different parameters such as precision (4.6–12.2%), DL (0.3–5.7 μg/l for HS and 0,001 μg/l for PT) and robustness. These authors analyzed well and groundwater samples from areas suffering from odour problems because of fuel spillage and tank leakage, by both techniques. The sensitivity of HS-GC-FID was 2 or 3 orders of magnitude lower than PT-GC-MS method and concentrations under of 10 μg/l could not always be detected, leading to false negative. Confirmation by GC-MS was always necessary.

Rosell et al. (61) developed a simultaneous determination of MTBE and its degradation products, BTEX, and other oxygenate additives, in groundwater samples by PT-GC-MS. The method enabled to detect concentrations at ng/l or sub-μg/l levels. Samples with high levels of MTBE contained 0.1–60 μg/l of TBA, indicating in situ degradation of parent compounds. In all cases, BTEX was at low concentrations or not detected, showing less solubility and persistence than MTBE. This fact confirmed the suitability of MTBE as an indicator for gasoline contamination in natural and drinking waters.

A survey has been carried out in the Netherlands by Morgenstern et al. (62), investigating the presence of MTBE in drinking water and the corresponding sources by a PT sampling and GC-MS equipped with an automated thermal desorption sampler (TDS-GC-MS). The developed procedure enabled the analysis of at least 40 samples per day and provided a quantification limit of 2 ng/l. The mean concentration of MTBE in the selected drinking water samples was 20 ng/l.

The effectiveness of Fenton's reagent (a combination of hydrogen peroxide and ferrous sulphate) as oxidant of MTBE in water and slurry matrices was quantified by a PT-GC-FID (63) and atomic emission detection (PT-GC-AED) (64). The byproducts were identified using GC-MS. Baker et al. (65) used a PT-GC-FID technique to determine MTBE, BTEX and TAME at mg/l level in motor oil-contaminated water.

Mezcua et al. (9) established a rapid and simple analytical method for determination of MTBE and TBA in seawater involving PT enrichment followed by GC determination, comparing

TABLE 4
Features of purge and trap methods

							Quality parameters					
Detector	V_{Sample} (ml)	Purge: time/flow /T min/ (ml/min)/°C	Trap	t_{Desor}/T (min)/(°C)	T_{Cryof} (°C)	Chromatographic support column	DL (μg/l)	RSD % (at μg/l)	Linear range (μg/l)	Other characteristics	Application	Ref.
FID	5	11/40/RT	Tenax	2,5/200	−60	Fused silica capillary CP-Sil 8 CB	2	2 (5/60)	1–80		Contaminated groundwater	43
MS full Scan	5	11/40/RT	Tenax-silicagel-charcoal	4/180	−10	Fused-silica DB-624	^{a}0.09	5.6 (0.4) 2.5–3.6 (20)		Fluoro-benzeneas ISs Moisture control module	—	58 59
MS full Scan	25	11/40/RT	Carbopack B/CAR 1000	4/250	−20		^{a}0.083	7 (1.1)		Fluoro-benzene as ISs		25
MS	44	10/−/40	Tenax TA	10/220	−180	Fused-silica capillary DB-VRX	^{c}0.0029	3.4 (0.06) river water Ground-water 2.1(0.06) sea water		MTBE-d12 as ISs	river water groundwater sea water	27
MS SIM	^{b}15	^{b}13/35/RT	Tenax-silicagel-charcoal	^{b}4/225	—	Fused-silica capillary DB-624	^{a}0.001	11 (1/50/500)	0.02–10	MTBE-d3 as ISs	Contaminated groundwater	44
MS SIM	5	30/30/60	Tenax-silicagel-charcoal	4/180	—	HP-1	0.0033 (TBA 0.0025)	1.9 (0.006)	0.006–0.600	—	Contaminated groundwater	60
MS SIM	15	13/35/RT	Tenax-silicagel-charcoal	4/225	—	Fused silica capillary	^{c}0.001	10.27 (0.001)	0.002–10	Fluoro-benzene, MTBE-d3 as ISs	groundwater	61
AED	4	11/−/30	Tenax-silicagel	4/220		6% cyanopropyl phenyl 94% dimethyl siloxane	^{c}10 (TBA 0.09)	17(50)	0.05–50	—	Seawater	9
MS SIM							0.04	3(50)				
IMS	100	— 417(ml/min)	— Tenax	— 70°C		No chromato-graphic method	20 0.5 with Tenax trap	4.7–8.4 (50)	20–200	Dynamic HS automatic Tenax-cryotrapping with liquid N_2	Tap water groundwater	68

^{a}t (N-1, 1-α = 0.99)* SD of n low level spikes; ^{b} Published in (17); ^{c} Signal/noise = 3; RT Room temperature.

two different detection systems: AED and MS (SIM mode). Both methods showed good linear correlation and precision, but DL reached by AED (10 μg/l) was not low enough for valuating current environmental concentrations. However, it is sensitive to detect alarm points. In addition, GC-AED allows the screening where the presence of other unknown contaminants can be detected. GC-MS detection showed much better selectivity, providing a more reliable determination. This technique was also used by Ekwurzel et al. (66) and a low DL (15 ng/l) was obtained.

PT methods include closed loop stripping analysis (CLSA). This method employs a closed cycle system during the purge interval. Activated carbon filters are used to trap the analytes, which are subsequently desorbed with an appropriate solvent. CLSA (67) has been employed as clean up and preconcentration step to increase the amount of analytes injected into the GC. A close loop stripping method-coupled to GC-MS produces a highly sensitive technique able of detecting ng/l of many trace polar organics. However, very polar and miscible low molecular weight compounds, such as ethanol, have low and variable recoveries, resulting in poor sensitivity (11). Another inconvenient of CLSA comes from the use of the highly toxic carbon disulfide for filter extraction.

Using an original experimental set-up named dynamic HS/IMS, μg/l levels of MTBE were determined in drinking water and groundwater by Pozzi et al. (68). Analysis of reference solutions and real samples showed DL of 20 μg/l and CV of 4.7 and 85% for inter- and intra-day, reproducibility. DL were improved to 0.5 μg/l by means of a Tenax trap cooled with liquid nitrogen, placed between the sample container and the IMS. In conclusion, HS/IMS could well become a simple and cost-effective tool for rapid and on-line analysis of MTBE and other VOCs in water; it improved the DLs achieved so far with off-line HS-IMS (54), and easily attained the lower MTBE concentration recommended by the EPA for drinking water (1).

Solid-Phase Microextraction (SPME)

Solid-phase microextraction is a novel sample preparation technique introduced by Pawliszyn and co-workers (69). The SPME technique integrates sampling extraction and concentration in a single step and it is inexpensive, time efficient and solvent-free.

SPME has been used for MTBE determination (70, 71) with detection limits of 1 μg/l. Sampling can be carried out directly in the field from liquid or air. Also, headspace sampling avoids extraction of high-boiling-point materials, which would affect GC analysis, and enables faster equilibration than sampling from liquid. The HS sampling is more advisable when the matrix could affect the determination of target analyte. On the other hand, HS with respect to immersion extraction often shows an important reduction of extraction time.

SPME coupled with GC-MS has shown to be a viable method for the detection of ng/l levels of MTBE in surface water and groundwater by means of direct inmersion (20, 72, 73) or HS followed by GC-MS (74–77). The DL are better than those obtained by DAI-GC-FID (19), PT-GC-FID (21), direct-SPME-GC-FID (78) and HS-SPME-GC-FID (79, 80). As can be seen in Table 5, the use of a more specific detection method, such as SIM-MS, results in a better DL.

The performances of direct or headspace SPME application in aqueous samples depends on physicochemical properties of the matrix. SPME sampling of MTBE by extraction from the aqueous phase has been reported to lead to a DL of 10 ng/l (20). A disadvantage of the direct immersion method is the fast contamination of the ion source due to the introduction of large amounts of low volatile organic matter or water and the limited lifetime of the fiber. The type of fiber, stirring rate, temperature, extraction time and addition of salt also affected the direct–SPME procedure. These variables also must be taken in account in the HS-SPME procedures. Studies considering one by one the variables to get the best conditions have been showed in several works (18, 52). However, this procedure requires a high number of runs and it is also time consuming.

Consequently, Araujo and Brereton (81, 82) developed an experimental design, for optimizing operational conditions. This design has been used by Dron et al. (79) in order to optimize a HS-SPME-GC-FID method for MTBE determination. Extraction temperature and sodium chloride concentration were significant variables, and 20°C and 300 g/l were chosen for best extraction recovery. Under these conditions, an extraction time of 5 minutes was enough to extract MTBE. Similar conditions were used by Arambarri et al. (80) which developed a HS-SPME-GC-FID method for the simultaneous determination of fuel alkyl ethers and BTEX. The main advantages of the method were the simplicity of the equipment and the rapidity, 10 min was enough for the extraction of the analytes. However, the DL was 1.1 μg/l for MTBE and 0.07 μg/l for BTEX, similar to the DL obtained by other authors using HS-SPME-GC-FID. The main differences with these works are the type of fiber (PDMS or PDM-CAR) and the extraction temperature (room temperature or 40°C) (18). The results were comparable to those given by ASTM method D4815 (FID) (21) and better than those obtained (≤ 2 μg/l for most analytes) working with DAI-GC-MS technique (36). However, the values were higher than when SPME or PT techniques were coupled to a MS detector (61, 72). The comparison with works devoted only to the determination of MTBE showed very close values of DL using HS-GC-MS (45) and PT-GC-PID (83) (1.2–2 μg/l and 1.0 μg/l, respectively), and slightly higher work that PT-GC-FID (0.2 μg/l) results (84). The sensitivity level of 10 ng/l was reached working with SPME-GC-MS and the HS-SPME-GC-MS (20, 52) and 50 ng/l using PT-GC-MS (85). In a previous work (79), a DL of 0.45 μg/l was obtained for MTBE determination using HS-SPME-GC-FID technique.

Lin et al. (86) studied the effect of chlorine on the determination of organic compounds in drinking water. They observed that the presence of chlorine reduces the concentration of MTBE (11–27%) and suggested that dechlorination is necessary when applying SPME to chlorinated waters.

TABLE 5
Features of SPME methods

	Extraction					Chromatographic characteristics	Quality parameters					
Detector	Mode	Fiber	NaCl (g/l)	time (min)	T (°C)	$T_{desorption}$(°C)/ Column	DL (μg/l)	RSD % (at μg/l)	LR (μg/l)	Other characterisitcs	Application	Ref.
FID	HS	75 μm PDMS/CAR	250	10	40	300/ phenylmethylsilicone 5% (1st column)/ Cyanopropyl phenylmethylsilicone 14% (2nd column)	^{a}0.27	7.7 (28.7)	1–75	Two-dimensional GC HS ratio1/2	—	18
FID	HS	65 μm PDMS/DVB	300	5	20	Fused-silica capillary	^{b}0.45	6.3 (250)	5–500	HS ratio 1/2	—	79
FID	HS	65 μm PDMS/DVB	300	10	10	250/100% Dimethylpolysiloxane fused–silica capillary	0.02 (Toluene, Ethylbenzene and xilenes) ^{c}1.1 (MTBE)	$\leq$ 8.5	2–20	HS ratio 1/2 Competition between analytes in samples with level of BTEX below 20 μg/l	River water, Sea water, Fishing harbours	80
FID	HS	65 μm PDMS/DVB	350	30	50	OV-17 steel capillary	^{b}6 MTBE ^{b}199 TBA	3.8 2.6	0.8–160 0.09–9	Micro-cryogenic chromatographic oven HS ratio 1/2	Tap water, River water, Sea water	95
MS Full Scan	Direct	75 μm PDMS/CAR	100	60	5	240/SE-54 capillary (CS)	^{d}0.01	12 (0.01)	—	d_3MTBE as ISs cooled fiber	Surface water Precipitation	20
MS Full Scan	HS	75 μm PDMS/CAR	100	30	35	260/SE-54 capillary (CS)	0.01	10 (0.1) longterm	0.02–5, 0.02–0.1	d_3MTBE as ISs. Split HS ratio 3/5	Surface, groundwater	52
								11 (0.01) shortterm		SPME cooled by cryostat	Precipitation	76
											Precipitation Snow	15
MS Full Scan	Direct	75 μm PDMS/CAR	250	30	Not reported	180/CP Select 624	^{e}0.5 2 (TBA)	1.6 (1707)	1651–1740	d_3MTBE,TBA-d_{10} (for fTBA) as ISs. Splitless	Contaminated groundwater	53
MS	HS	75 μm/ 100 μm PDMS/CAR	300	30	40	300/HP-VOC	^{b}0.05	10.1 (1)	0.1–20	HS ratio $^{1}/_{2}$. Splitless	Bottled mineral water	91
MS SIM	Direct	30 μm DVB/ PDMS/CAR	250	25	Not reported	220/fused silica-capillary DB-1	^{f} 0.008 1. 8 (TBA)	—	0.04–4	Isopropyl or n-propyl alcohol as ISs splitless	Non-contaminated groundwater	72

MS SIM	HS	75 μm PDMS/CAR		15	50	250/Graphite layer open tubular (GLOT)	0.01	4–5 (0.1–10)		HS ratio $^1/_2$	Tap water, Rain water, Sea water Mineral water	77
FID	Direct	85 μm PDMS/CAR	—	25	RT	260/J&W Scientific DB-624	1	—	—	Area response to MTBE concentration Were non-linear in all concentration ranges	Standard solution of known concentration MTBE in water	78
MS SIM	HS	PDMS/CAR	233	15	40	310 / Rtx-502,2	[a]0.0066	4.5 (0.047)	0.05–160	HS ratio 3/10 d_3MTBE as ISs	Rain water Snow	94
MS SIM	HS	50/30 μm DVB/PDMS	250	15	RT	250/VOCOL	[b]0.014	2–8 (0.05–20)	0.05–20	HS ratio $^1/_2$. Splitless	Tap water Surface water Mineral water	74
MS	HS	30/50 DVB/PDMS 65 μm PDMS/DVB 75 μm PDMS/CAR	100	60	5	220/HP-5				HS ratio 3/7. Splitless	Drinking water Effects of chlorine	86
MS	HS	65 μm PDMS/DVB 75 μm PDMS/CAR	360	25	80	200 320/Rtx-Wax-Crossbond-PEG	[g]0.2, 5 (TBA)			HS ratio 6/11 d_3MTBE as ISs desorption with cryotrap		92

[a] Intercept of calibration plot + 3.SD of 7 blanks; ISs Internal standard.
[b] Signal/noise = 3.
[c] Intercept of calibration plot + 3.SD of 5 blanks.
[d] Signal/noise = 10.
[e] Signal/noise = 5.
[f] Calculated by USEPA method (147).
[g] Calculated by Halden (21); RT Room temperature.

The selectivity of SPME for different compounds is highly dependent on the composition of the stationary phase and several materials were developed. The most commonly used for the analysis of pollutants in water include polydimethyl siloxane (PDMS), divinylbenzene (DVB) and carboxen (CAR). PDMS can extract a broad range of non-polar analytes, and offers better performances than other polymers (87). However, the small amount of PDMS typically used (less than 0.5 μl) limits the application of SPME, resulting in low extraction efficiencies for volatiles with low K_{ow} values. Adsorption plays an important role in extraction mechanism of a mixed coating with porous solid-phase such as PDMS-DVB, while absorption occurs in PDMS.

DVB-PDMS-CAR were used for analysis of MTBE (70), geosmin and 2-methyl isoborneol (2-MIB) (88–90). PDMS/CAR used for SPME of low molecular weight analytes showed 10 times higher affinity for MTBE than PDMS (18). Achten and Putmann (20) using direct extraction (60 min at 5°C) and a PDMS/CAR fiber obtain a DL of 10 ng/l for MTBE, lower than those achieved with most PT systems. The same fiber was used by Guidotti et al. (91) with HS extraction for 30 minutes at 40°C, obtaining a DL of 50 ng/l, achieved by USEPA method 8260B.

The HS-SPME with a suitable fiber coating may reduce interferences from other organic compounds, but not from BTEX (18, 92). Recently, the limitations of PDMS/CAR fiber in quantitative analysis have been discussed (92–94). Black and Fine (92) reported that the matrix can significantly affect the amount of analyte extracted by the fiber when compounds with higher affinity for the SPME stationary phase replace compounds with lower affinity. These authors found that the response of deuterated internal standards of MTBE and TBA dropped by more than 65% when aromatic compounds (BTEX and trimethylbenzene of gasoline) above 1 mg/l are present. In this case, internal standards for peak areas correction are necessary. In samples containing high TPH or high aromatic content, static HS-GC-MS are a good alternative to the SPME method. Furthermore, the results reported by Fang et al. (94) suggest that a deuterated isotope is needed for each component analyzed. Dewsbury et al. (53) described a SPME method for the analysis of MTBE, TAME, and TBA in petroleum fuel-contaminated groundwater with DL of 0.5 μg/l for MTBE. They reported that accurate measurement of MTBE could be obtained in a background matrix containing up to 300 mg/l of total BTEX if internal deuterated MTBE standard is used in the analysis.

An improvement in the DL was obtained by Liu et al. (95) for the determination of MTBE and their degradation products using a laboratory-made micro-cryogenic chromatographic oven coupled with HS-SPME. The device had a small size ($6 \times 6 \times 2.5$ cm) and required cryogenic liquid. When this system was applied to water samples DLs ranging from 6 (MTBE) to 206 μg/l (methyl acetate) were achieved. Also the good recoveries (95%–106%) obtained (with RSD $< 4\%$) indicated a negligible matrix effects and a good accuracy and precision for the analytical method.

COMPOUND-SPECIFIC CARBON ISOTOPE ANALYSIS (CSIA)

Organic analysis has benefited greatly by the development of isotope-ratio monitoring gas chromatography mass spectrometry (irmGCMS or GCIRMS) (96). This technique allows continuous-flow acquisition of carbon isotope ratios for individual components in a complex mixture and has become valuable in environmental research.

CSIA using GCIRMS has become a mature analytical technique in many application areas over the last decade. In environmental sciences, successful applications to date include the allocation of contaminated sources on local, regional, and global scale (97), the identification and quantification of biotransformation reactions (98–100) and the characterization of elementary reaction mechanisms that govern product formation. However, in environmental studies it is often difficult to correlate the spilled gasoline with their suspected sources, because the organic compounds are quickly affected by physico chemical processes such as evaporation, photooxidation, water washing and biodegradation.

The assessment of biodegradation processes of specific contaminants at field sites is sometimes impossible. The general resistance of MTBE to biodegradation provides a potential opportunity to identify the origin of gasoline contamination using this technique. GC and GC-MS cannot be used to distinguish sources of a spill, or leakage of gasoline based on the presence of MTBE alone, but it was proposed that unique isotopic signatures might be useful as an information source of MTBE from different suppliers (97). There are few studies related to biodegradation of MTBE at field sites (101–104), possibly due to the lack of adequate tools to monitor biodegradation. Since MTBE frequently migrates over long distances and degradation rates may be low, it is difficult to assess biodegradation based on concentrations or using mass balance approach. Furthermore, occurrence of TBA, the most stable intermediate product, may not be a reliable indicator for biodegradation of MTBE since biodegradation can occur without significant TBA accumulation (105) or TBA may already be present in the gasoline. For that, the incorporation of isotopic data provides a powerful and complementary tool for these purposes.

Compound-specific carbon isotope analysis (CSIA) has become an important tool in environmental in situ remediation, identification of pollutant degradation pathways and kinetic verification of contaminants. In this technique, the sample is injected into a GC and after separation; the organic compounds are transferred to a combustion unit producing CO_2 or H_2O gas. After, the combustion gases are analyzed in an isotope ratio mass spectrometer (IRMS) for isotope detection. By CSIA, it is possible to measure the isotopic composition of individual compounds in the crude oil or refined product to display an isotopic fingerprints for using in correlation studies.

The $\delta^{13}C$ values of commonly reported groundwater contaminants were in the range of μg/l. In the past, and due to the poor sensitivity of IRMS, GCIRMS was limited to highly

TABLE 6
CSIA methods for the measurement of the carbon isotopic composition of MTBE:

SPME concentration

	Extraction conditions				Quality parameters			
Concentration method	Mode	NaCl (g/l)	$t_{extraction}$ (min)	T (°C)	DL (μg/l)	DL definition	Application	Ref.
SPME 75 μm PDMS/CAR	HS Direct	250 250	20	23	HS:11 (TBA: 860) Direct: 90 (TBA: 370)	Peak height >0.75 V (m/z 44) HS ratio 1/7	Aerobic laboratory microcosms	98
SPME 75 μm PDMS/CAR	HS		20	—	350	Not reported	Aerobic laboratory microcosmos, PM1 cultures	99
SPME 75 μm PDMS/CAR	Direct	0.3	30	30	16	Peak height >0. 5 V (m/z 44)	None	106

PT concentration

	Extraction conditions							Quality parameters			
Concentration method	V_{Sample} (ml)	t_{Purge} (min)	Trap type	T (°C)	$t_{Desorpt.}$ (min)	$T_{Desorpt.}$ (°C)	Cryofocusing	DL (μg/l)	DL definition	Application	Ref.
Purge and trap	—	11	Purge flow	40	4	180	No cryofocusing	15	—	None	97
Purge and trap	5	8	Tenax-silica-gel charcoal		4	180	No cryofocusing	5 (TBA:60)	Not reported	Anaerobic laboratory microcosm, field site with anaerobic	100
Purge and trap	25	30	Carbopack B/CAR 1000 trap Purge flow 40 ml/min	23	1	250	−120	0.63	Peak height >0. 5 V (m/z 44)	None	106

contaminated samples. Table 6 summarizes the experimental conditions of different CSIA methods. Currently, several injection and preconcentration techniques e.g., on-column injection, split-splitless injection, SPME, PT in combination to GCIRMS, enhance the sensitivity of CSIA and allow to characterize MTBE biodegradation in both laboratory and field. Zwank et al. (106) found that the ^{13}C values of the target compounds are determinated by liquid injections of the analytes dissolved in diethyl ether or, in the case of PT and SPME, by extraction from water spiked with the analytes. For these works, PT was the most efficient preconcentration technique, reaching DL from 0.25 to 5 μg/l. This is in agreement with results showed by Smalwood et al. (97). PT was characterised by higher reproducibility and lower isotopic fractionation than SPME. On the other hand, cold on-column injection showed better precision compared to split/splitless injection.

Several authors (98, 107, 108) evaluated the potential of CSIA to assess in situ biodegradation of MTBE in groundwater. The analytical test demonstrates that HS-SPME coupled to GC-IRMS is a very sensitive method for the determination of δ^{13}C of MTBE with a DL of 11 μg/l (the EPA advisory limit was established in 13 μg/l). However, the method is less sensitive for TBA and direct SPME is recommended (lower DL). LDs obtained for MTBE are significantly lower with PT than SPME due to higher sample volumes as well as the higher sorption capacities of the enrichment traps. PT-GC-IRMS only requires a few μg/l of MTBE for reliable δ^{13}C measurements (106) and provides the lowest DL for MTBE (0.63 μg/l) in CSIA. Kuder et al. (104, 109–111) used PT-GC-IRMS for measuring MTBE in environmental samples with sensitivities around μg/l levels. In short, PT-GC-IR-MS is one of the most effective method for determine the carbon isotopic composition of MTBE in groundwater samples. In addition, the low analytical limit reported by Kuder et al. (104) makes the technique useful for environmental applications.

DETERMINATION OF MTBE IN SOILS

Accidental release of fuel to the subsurface results in residuals pools in the unsaturated zone (the unsaturated zone is a porous filter layer in which microbiological degradation naturally attenuates pollutants). Low adsorption ability of MTBE in soils facilitates its easy and fast migration: horizontally, on very large distances, and perpendicularly, to very deep level as far as to water bearing strata (112).

Once MTBE was detected in groundwater, a large scale attempt began to determine its fate and transport characteristics, such as degradation, multiphase partitioning, and dispersion kinetics. On the other hand, MTBE will adsorb to some soil types (113).

The degradation of MTBE was found to be very slow or absent in most aquifers (5, 101). However, biodegradation of MTBE was observed in laboratory experiments under aerobic and anaerobic conditions (5, 98,103).

The sortion capacity of the soil depends on organic matter content that is higher in the soil surface. As consequence, if TPH were contaminating from an underground source, the amount of organic matter under 30–60 cm is minimal, therefore, an increase of contaminants would be expected, because these do not migrate far in the soil profile due to absoption by organic matter (114).

Vapor-phase migration of MTBE and TPH from soil to groundwater has been identified as another important and rapid transport pathway in the unsaturated zone, in other words, it is a potentially contaminant of groundwater (13, 115–117). Vapor transport is also influenced by partitioning between liquid and gas phases, and by sorption onto soil particles. The residual fuel can generate organic vapors in the soil gas phase that can migrate through the unsaturated zone by diffusion (118). Using this model Dakhet el al. (119) showed that MTBE persist for longer than 6 months at concentrations higher than 125 μg/l.

Much literature has been devoted to the subjects of MTBE chemical properties and MTBE soils and groundwater data analyses (37). These previous studies indicate that MTBE concentration in groundwater does not correlate strongly with other gasoline constituents, such as BTEX. A study of MTBE plume length using a modelling approach revelated that MTBE plume length poorly correlates with source concentration or with groundwater hydraulic gradient and speed (119, 120). However few studies have focused on MTBE concentration in soil relative to its groundwater concentration or other gasoline constituents.

Several mathematical models have been proposed to describe the reactive transport of MTBE in the unsaturated zone (13). These models include first-order kinetics to represent biodegradation. They assume constant biomass, but do not reflect biological phenomena such as dependence on substrat concentration, inhibition or preferential substrate utilization (121). Höhener et al. (116) determining kinetic rate laws for the aerobic biodegradation of a volatile mixture of 12 volatile PTH and MTBE in unsaturated alluvial sand. Batch experiment suggested first order disappearance rate laws for all VOCs except for n-octane. MTBE, n-pentane and CFCs were not apparently degraded. The Monte Carlo vadose zone model can serve as a useful tool to assist in determining soil remedial criteria. The model was used by several authors for estimating the risk of exceeding groundwater quality standard given soil remedial concentration (122, 123). Authors conclude that soil remedial concentration for MTBE is established to be 5 μg/kg with a 95% and 10 μg/kg with 50% probability that groundwater concentration will not exceed the water quality objective of 13 μg/l.

Due gasoline spilled to soil arises mainly from the transfer of toxic compounds to groundwater that is used for drinking water, studies of bioremediation are developed for soils using microbial cultures. Many published reports show that the biodegradation of MTBE occurs more difficult as compared with other gasoline components consisting of hydrocarbons only. The isolated culture, named PMI, was used with good results (112). The aerobic degradating capacity of the native microbial community in soils from various gasoline contaminated and non-contaminated sites in Belgium was studied by Moreels et al. (124). In contrast to benzene degradation (all the soils showed a rapid degradation of benzene), aerobic MTBE degradation did not occur in all tested soils. Differences concerning MTBE degradation were observed between samples from non-saturated zone and samples from saturated zone. MTBE-biodegradation in the samples of the non-saturated zone started after 7 days, while long lag-phases (up to 270 days) were obtained with the other samples. Residual MTBE and benzene concentration were monitored by HS-GC-MS, using $d_6$benzene as internal standard. The method provides a DL of μg/l similar that reported by O'Neill (45) in water sampling using the same detector. The presence of ethanol in groundwater may, however, decrease the biodegradation rates of benzene because ethanol is preferentially degraded (125–129).

The specific properties of MTBE make however its reduction in polluted waters and soils difficult and expensive. The problems with MTBE bioremediating is the low rate of the processes. In many environments bioremediation can take years to meet the obligatory regulations.

For all the reasons mentioned, a practical method for quantifying MTBE in soils is needed to fully understand the environmental impact of this contaminant. Groundwater and soil samples from the site should be analyzed to MTBE by USEPA method 8020 or 8260 or ASTM D4815. However, currently there is no standardized method for extracting MTBE from soil solids/soil gas.

The analytical methods are based on extraction of the soil followed by GC analysis of the soil extract using DAI, HS or PT. All of these procedures have different advantages and limitations as can be seen above.

A high resolution GC method was developed by Rhodes et al. (130) for the determination of TPH which involve extraction of soil with tetradecane, an efficient solvent for extraction of gasoline TPH from contaminated soils allowing determination of the entire range TPH (including MTBE), using GC-FID. When soil contamination is due to kerosene, diesel, or other heavier hydrocarbons, the chromatograms obtained using this procedure show the peak envelopes due to these other types of hydrocarbons.

GC-FID was the most widely used for determination of residual MTBE in soil in order to evaluate their transport (113–115, 119, 131, 132). Lefkowitz et al. (131) examine the analytical critical parameters to MTBE extraction methods, including solvent and gas chromatograph characteristics. Authors shown that toluene is an effective solvent (exhibiting adequate recovery and excellent separation from MTBE) using a GC-FID with Suppelcowax column. The method is simple, cost-effective, and efficient, and will provide an excellent starting point for more in depth fate and transport modelling. Santamaria-Capetanelis et al. (132) used the same detector for testing MTBE levels in the environment. Adam et al. (114) studied the effect of alcohol addition on the movement of PTH in soil. The determination of diesel fuel and MTBE was carried out by GC-FID and separations were performed on a SGE BPX 5 capillary column. The addition of ethanol to gasoline should enhance the downward migration of MTBE in soil due to increased solubilization of gasoline components in ethanol and the wetting effect of ethanol on the more hydrophobic soil components, and then the risk of contamination of groundwater is higher when ethanol is present.

The analytical methods for determination of fuel oxygenates, particularly MTBE and TBA in soil and groundwater, are discussed by Jaros et al. (133). The authors analyzed the advantages and disadvantages of the USEPA methods 8021(GC-PID) and 8260 (GC-MS). Purge and trap is used to set the volatile compounds free from the matrix by passing an inert gas through the aqueous or soil extract. Kuo et al. (134) found 16 VOCs including MTBE in soil and groundwater according SW-846 method 5035 using PT and methods 8260 B using GC-MS. Kraut and Kraut (135) developed a GC-MS for determination VOCs in water, soil and other matrixes. The advantages of this method over existing USEPA procedure are that it can be fully automated and the need for solvent extraction and confirmation of the results using a different second column are eliminated. The method is suitable for the simultaneous screening of nearly 80 VOCs in different matrixes, in concentrations above 1μg/l or 5 μg/kg. The PT-GC-MS techniques versatility was demonstrated by employing in the field to measure VOCs in soil-gas, groundwater, and soil at a Leaking Underground Storage Tank (136). MTBE was found in water at 17 μg/l and soil at 8.9 μg/kg levels. For most of 60 VOCs tested, the recoveries of the methanolic based verification standard ranged from 80% to 120% and the relative standard deviation values were lower than 20%.

On-site and on-line analytical methods (137) have also been applied for VOCs in water and soil samples. Among these methods MIMS is one of the most suitable technique for VOC in air (138) and water samples (139,140). However, MIMS is not suitable for solid samples. Purge-and-membrane mass spectrometry (PAM-MS), which combines dynamic headspace sampling and membrane inlet mass spectrometry (141–144) has proved to be very promising for the analysis of VOCs in soil samples. Ojala et al. (145) described a detailed evaluation of the suitability of the PAM-MS method for analysis of VOCs from soil samples and compares the method with HS-GC. In this study, the effect of soil type and moisture was evaluated using sand, garden soil and their mixtures, as well as moistures contents of 0,10, and 20%. The moisture of sample had no significant effect on desorption times in sand samples, but in the case of garden soil, the longest desorption time were recorded from dry samples. In the PAM-MS method, the results are rather independent of the soil type if the moisture is higher than 10%. Detection limits varied, depending on soil type. Larger amounts of moisture and organic matter in samples increase the DL. Aging of the spiked soil had only a slight effect on desorption for samples stored at 5°C up two weeks, but differences were observed, after six months of storing.

CONCLUSION

A wide range of analytical methods have been published for the determination of MTBE in water. The choice of an appropriate method depends on the kind of samples to be investigated, the concentration ranges to be determined and the available laboratory equipment. Furthermore, the concentration of MTBE and other fuel oxygenates in water differ by several orders of magnitude between environmental groundwater and sites affected by point sources, thus requiring different analytical strategies. MTBE levels in environmental samples are below 2 μg/l (12–14); when higher concentrations are found, this is a indication of an unknown point source.

The analytical methods for the determination of MTBE in soil are based on previous extraction followed by GC techniques using, DAI, HS or PT. GC-FID are the most used technique, however in the last years GC-MS is widely used.

PT enrichment is adequate for purgeable compounds, requires sample volumes between 5 and 40 ml, about 30 minutes of extraction time and is a very sensitive (ng/l) technique. Nevertheless, this method, although expensive, is adequate for analysis of drinking and uncontaminated surface water and groundwater samples, where MTBE concentrations are very low.

HS and HS-SPME require a sample volume between 5 and 20 ml, and they are applicable to all kinds of samples. The analysis can be carried out in around 60 minutes, and can be automated; however, HS shows a poor sensitivity. Additionally SPME is an effective extraction method, increasing the sensitivity, and making easy and inexpensive the sampling and automation procedures.

In DAI methods, the use of a guard column is essential to preserve the analytical one. Further wises, it requires 0.001 to 0.1 ml of sample and the main criteria is that the analytes eluted before than water.

The overview of the methods employed for analysis of MTBE showed that HS-GC-FID is sufficient for laboratory studies. In spite of HS, SPME or DAI might be used, preferably with GC-MS, for measurement of background concentrations below of 1 μg/l, PT-GC-MS is the only approved method, but it is susceptible to undergo contamination when highly polluted samples are analyzed. Currently, SPME-GC-MS are recommended, however it can show problems of sorption competition. HSME can be applied to determine MTBE at the μg/l level.

MS detector is in all cases the best option due to its selectivity, sensitivity, allowing background and clean water analysis. The main drawbak is it price.

CSIA has emerged as an important complement for the methods above mentioned, and its use has been improved in the last years. CSIA is a powerful tool to characterize the origin of the VOCs in environment, and can be used to determine the isotopic composition of MTBE and related compounds in the low μg/l range. CGIRMS can be used in conjunction with GC and GCMS to make correlations. In some situations, biomarkers can be used to compliment the results from the isotope studies, i.e., where no biomarkers are, the combined carbon and hydrogen isotope fingerprints may be used to discriminate refined products from different sources (146).

The GC-FID is appropriate for background studies, source area studies and transport studies. In uncontaminated soil samples this method is inexpensive and the determination relatively simple.

The studies of transport indicated that MTBE and hydrocarbons released in the soil migrated by vapor-phase diffusion to groundwater, while ethanol vapours were naturally attenuated. After 30 days all soluble compounds including ethanol were transported to groundwater. Ethanol disappeared with TPH (except isooctane) due to biodegradation while MTBE persisted (119). MTBE-free gasoline would be less harmful for groundwater resources, and ethanol is an acceptable substitute.

ABBREVIATIONS

AED	Atomic emission detector
ASTM	American Society for Testing and Materials
BTEX	Benzene, toluene, ethylbenzene and xylene
CAR	Carboxen
CG	Gas chromatography
CSIA	Compound-specific carbon isotope analysis
DAI	Direct aqueous injection
DIPE	Diisopropyl ether
DL	Detection limit
DVB	Divinylbenzene
ETBE	Ethyl tert-butyl ether
FID	Flame ionization detector
GC-ECD	GC-electron capture detector
HS	Headspace
HSME	Headspace solvent microextraction
IMS	Ion mobility spectrometry
irmGCMS or GCIRMS	Isotope-ratio monitoring gas chromatography mass spectrometry
ISs	Internal standard
MCC	Multicapillary column
MS	Mass spectrometry
MTBE	Methyl tert-butyl ether
PAM-MS	Purge-and-membrane mass spectrometry
PDMS	Polydimethyl siloxane
PID	Photoionization detector
PT	Purge and trap
RT	Room temperature
SD	Standard deviation
SIM	Selective ion monitoring
SPME	Solid-phase microextraction
TAME	*tert*-amyl methyl ether.
TBA	*tert*-buthyl alcohol
TBF	*tert*-butyl formate
TDS	Thermal desorption sampler
THMS	Trihalomethanes
TPH	Petroleum hydrocarbon
USEPA	U.S. Environmental Protection Agency
VOCs	Volatile organic compounds

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