Cross-Validation of Methods Used for Analysis of MTBE and other Gasoline Components in Groundwater

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Key Words

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Summary

Head space gas chromatography with flame-ionization detection (HS-GC-FID), and purge and trap gas chromatography-mass spectrometry (P&T-GC-MS) have been used to determine methyl-*tert*-butyl ether (MTBE) and benzene, toluene, and the xylenes (BTEX) in groundwater. In the work discussed in this paper measures of quality, e.g. recovery (94 – 111%), precision (4.6 – 12.2%), limits of detection (0.3 – 5.7 µg L^{-1} for HS and 0.001 µg L^{-1} for PT), and robustness, for both methods were compared. In addition, for purposes of comparison, groundwater samples from areas suffering from odor problems because of fuel spillage and tank leakage were analyzed by use of both techniques. For high concentration levels there was good correlation between results from both methods.

Results from P&T analysis showed that 20 of the 21 samples from the vulnerable areas contained MTBE at concentrations up to 666 µg L^{-1}. Levels in seven samples exceeded maximum permissible levels for odor and taste set by the USEPA (20 – 40 µg L^{-1}); for thirteen of the samples levels were between 0.28 and 17.9 µg L^{-1}. The sensitivity of HS-GC-FID was, however, two to three orders of magnitude lower and concentrations of 6 – 10 µg L^{-1} could not always be detected, leading to false negatives. The same behavior was observed for analysis of BTEX – the lower sensitivity of HS-GC-FID and coelution of peaks led to results of poor reliability, and confirmation by GC-MS was always necessary. The applicability of two analytical methods widely used for routine monitoring of VOC thus depends on the organoleptic thresholds of MTBE and BTEX in groundwater (20 µg L^{-1}) and the need to survey trace concentrations of persistent MTBE in vulnerable aquifers.

Introduction

In order to replace antiknock leaded derivatives in gasoline which caused toxic emissions towards the atmosphere, oxygenates derivatives such as alcohols and aliphatic ethers are utilized as octane boosters [1]. Methyl *tert*-butyl ether (MTBE) is currently the most widely used ether oxygenate and is added to gasoline at concentrations up to 30% by volume, depending on national policies [2]. MTBE enters the environment during all phases of the petroleum fuel cycle (e.g. auto emissions, evaporative losses from gasoline stations and vehicles, storage tank release, pipeline leaks, accidental spills, and refinery stock release) [3]. An extensive monitoring study conducted in the US revealed that as a result of the high usage of the compound more than 10% of groundwater samples in urban areas contained MTBE at levels of 0.2–23 000 µg L^{-1} [4]. MTBE has also been detected in lakes [5], in stormwater [6], in run-off water [7], and in the atmosphere [8]. A comprehensive review of the environmental behavior and fate of MTBE indicates that partition of the compound between different compartments depends on their physicochemical properties [9]. In short, because of the high solubility of MTBE (25–50 g L^{-1}), low octanol-water partition coefficient (*K*ow; 0.94–1.43), and low Henry's Law constant (55.3 Pa m^3 mol^{-1}), it remains dissolved in surface water from where it can be volatilized to the atmosphere. A small fraction can partition into soil and eventually reach ground water where it is slow to biodegrade and can persist for a long time [10]. Even at very low concentrations it is responsible for taste and odor problems in groundwater [11].

A threshold of 20–40 µg L^{-1} MTBE has recently [12] been imposed in the US. As a result of its persistence and increasing presence in the environment, a major aspect of the monitoring of MTBE is its detection at low levels in different environmental compartments, from water to

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the atmosphere. A recent review indicates that different sampling and analytical techniques are used for its analysis in a wide range of environmental matrices [13]. The analytical approach needed for its unequivocal determination – sampling and preservation of samples, preparation of standard solutions, extraction and analysis, and final quantification procedure – is, however, somewhat complex. These aspects of the analysis are, in general, the main sources of error in all laboratories involved in the monitoring of MTBE, especially in groundwater, because of the combination of high volatility and low concentration levels.

The objective of the work discussed in this paper was to determine quality data for analysis of the gasoline additive MTBE and the volatile aromatic compounds benzene, toluene, ethylbenzene, and the xylenes (BTEX), constituents of petrol commonly used as indicators of contamination, by use of the two methods most commonly used for analysis of VOC – static headspace sampling then analysis by gas chromatography with flame-ionization detection, and purge-and-trap extraction coupled with gas chromatography with mass spectrometric detection, according to EPA method 624 [14]. This paper reports the detection limits, recoveries, and reproducibility obtained by use of both methods. In addition, cross validation was performed by analysis of real groundwater samples; this report indicates the main advantages and disadvantages of each method, and its applicability to real water samples.

Levels of MTBE and BTEX in two aquifers contaminated by tank leakage (Tarragona) and a gasoline spill (La Batlloria) are also reported.

Experimental

Chemicals and Reagents

A standard mixture of benzene, toluene, ethylbenzene, *m* + *p*-xylenes, *o*-xylene, and methyl *tert*-butyl ether (MTBE) was obtained from Supelco (Barcelona, Spain). The mixture was dissolved in methanol and this solution was added to organic-free water. All preparation of standards (dilution, spiking, etc.) was performed over solid carbon dioxide to avoid losses of any of the compounds of interest.

For static headspace GC-FID analysis, α,α,α-trifluorotoluene was used as internal standard. For P&T-GC-MS, deuterated MTBE was used, and fluorobenzene for BTEX analysis. Acetone used for cleaning glassware was from Merck (Darmstadt, Germany).

Sampling Procedure

For the comparison exercise, 21 groundwater samples were taken from two "hot spot" areas in Catalonia in which:

(i) an accidental gasoline spill at a petrol service station (La Batlloria) had occurred in 1997; and
(ii) oil refinery storage tanks had leaked (Tarragona).

These areas had been monitored since these problems occurred and residue levels between 10 and 600 μg L^{-1} were still being encountered [15]. Groundwater samples were collected by use of a Niskins bottle. Samples were transferred to 500-mL amber glass bottles, avoiding passage of air bubbles through the sample and leaving no headspace volume, which could cause losses of the target analytes. For P&T analysis samples were transferred directly to similar 40-mL Tekmar amber glass vials (EPA Method 524.2), which were thereafter used for analysis. Each sample was placed in three such vials which were then immediately placed in a portable freezer and transported to the main laboratory where they were stored at 4 °C. Samples were not acidified but care was taken to ensure samples were analyzed within seven days of collection.

Headspace Analysis with GC-FID

Water samples (10 mL) were sealed in 22-mL headspace vials with an open-center aluminum cap and PTFE-faced butyl rubber septum and, after spiking with 10 μL of 100 μg mL^{-1} solution of the internal standard α,α,α-trifluorotoluene, analyzed by static headspace analysis and gas chromatography with flame ionization detection [16].

Headspace analysis was performed with a Varian Genesis headspace autosampler connected to a Varian Star 3600 gas chromatograph. Samples were equilibrated at 70 °C for 4 min, mixed at 80% of full power for 7 min, and, after mixing, stabilized for 1 min. The sample loop volume was 1 mL, line and valve were maintained at 150 °C, and vials were pressurized at 7 psig. These conditions resulted in the highest sensitivity and reproducibility. Compounds were separated on a 75 m × 0.53 mm × 3 μm film DB-624 fused-silica column from J&W. The GC operating temperatures were: injector 160 °C, detector 300 °C, oven 40 °C (5 min) programmed at 5° min^{-1} to 250 °C. Helium, at 9 psig, was the carrier gas.

Purge and Trap and GC-MS

Tenax-silica gel-charcoal cartridges of the Tekmar 3100 purge and trap concentrator were used. An Aquatek 70 liquid autosampler (Tekmar-Dohrmann) was used to dispense 13-mL samples automatically into a 25-mL purging device. The sample was purged with helium gas at 35 mL min^{-1} for 11 min at ambient temperature. After sample loading the trapped sample components were desorbed by heating the Tenax cartridges at 225 °C and passing helium gas at 3 mL min^{-1} for 3 min, with the injector in splitless mode. These conditions were chosen because they resulted in the maximum response to a large number of volatile organic compounds [17]. GC-MS was performed by means of a Trace GC coupled to a Voyager (ThermoQuest, UK) MS in electron-impact (EI) mode at an electron energy of 70 eV. Compounds were again separated on a 75 m × 0.53 mm × 3 μm film DB-624 fused-silica column from J&W. Helium, at 3.5 mL min^{-1}, was used as carrier gas and the column was programmed from 35 °C (5 min) to 70 °C at 3° min^{-1} (5 min) and then to 210 °C at 6° min^{-1}. The final temperature was maintained for 5 min and the total run time was 50 min. The source and GC interface temperatures were 200 and 250 °C, respectively. The emission current was 100 μV and the detector potential 380 V. Acquisition was performed in time scheduled selected-ion monitoring mode using three ions per compound: MTBE (*m*/*z* 73, 57, and 43), benzene (*m*/*z* 78, 77, and 52), toluene (*m*/*z* 91, 92, and 65), ethylbenzene (*m*/*z* 91, 106, and 77), and the xylenes (*m*/*z* 91, 106, and 77). The internal standard (IS) ions monitored were *m*/*z* 76, 57, and 43 for deuterated MTBE and *m*/*z* 96, 70, and 50 for fluorobenzene.

During GC-MS acquisition the trap was cleaned by baking at 230 °C for 10 min; system blanks were obtained by use of these conditions.

Table I. Quality data obtained from analysis by static HS-GC-FID and P&T-GC-MS.

Compound	Range*		R^2		%*RSD*		Std devn (%)		*LOD* (μg L^{-1})	
	HS	P&T	HS	P&T	HS	P&T	HS	P&T	HS	P&T
MTBE	15000	10.0	0.999	0.9954	102.4	101.0	7.9	11.0	5.7	0.001
Benzene	1000	10.0	0.999	0.9991	95.1	97.7	12.2	10.6	0.6	0.002
Toluene	1000	10.0	0.999	0.9901	100.6	111.8	11.7	4.6	0.6	0.001
Ethylbenzene	1000	10.0	0.999	0.9992	100.4	94.1	8.2	8.1	0.4	0.001
m- + *p*-Xylenes	1000	10.0	0.999	0.9992	99.9	96.0	4.8	10.6	0.3	0.001
o-Xylene	1000	10.0	0.999	0.9967	101.2	96.6	6.3	7.8	0.4	0.002

* Upper limit of the linear range (μg L^{-1}).

Calibration and Quantification

For both types of analysis internal standard calibration was used. For headspace-FID analysis a calibration plot was constructed in the range 1 to 1000 μg L^{-1}; α,α,α-trifluorotoluene was used for quantification. For P&T GC-MS calibration plots were constructed by spiking HPLC water with the test compounds at concentrations from 0.02 to 10 μg L^{-1}. Deuterated MTBE and fluorobenzene (each 1 μg L^{-1}) were added to the sample before extraction.

Recovery studies were performed by spiking HPLC water at a concentration of 10 μg L^{-1} for GC-FID analysis and at 1 μg L^{-1} for GC-MS. These samples were processed automatically as described above. Precautions that must be taken in the analysis of VOC are detailed elsewhere [17].

Results and Discussion

Quality Data

The two methods most commonly used for extraction of MTBE from water are headspace (HS) and purge and trap (P&T) enrichment, although new methods such as solid-phase microextraction are becoming more popular [13]. Basically HS is rather suitable for highly polluted samples which can cause matrix and carry-over problems. P&T enrichment, in accordance with EPA method 624 [14], is the most widely used method for analysis of MTBE and volatile organic compounds in general, because of the large number of compounds that can be analyzed simultaneously and the easy automation. Table I reports quality data obtained for both methods. For HS-GC-FID, calibration equations obtained for each analyte were determined by using of α,α,α-trifluorotoluene at 100 ppb as internal standard. *LOD* were calculated from the standard deviations (S_c) obtained from seven replicate analyses of BTEX at 1 μg L^{-1} and MTBE at 14 μg L^{-1}, by use of the equation [18]:

$$\mathrm{LOD} = t_{(N\text{-}1,1\text{-}\alpha\,=\,0.99)} \times S_c$$

SD% was obtained from the means of 13 replicate analyses at three different concentrations (1, 50, and 500 μg L^{-1}) over the entire linear range. The linear range of HS-GC-FID enables detection of MTBE and BTEX from the limit of detection to 15 mg L^{-1} and 1 mg L^{-1}, respectively. The linear range of P&T-GC-MS is from the limit of detection to 10 μg L^{-1}. When this concentration is exceeded the system suffers from memory effects and poor linearity; highly polluted samples should, therefore, be diluted before analysis. Recoveries and intra-day variation were, on the other hand, excellent for both methods, as indicated by a maximum standard deviation of 12.2%. Recoveries were satisfactory for both methods. The main difference between the methods was, however, their sensitivity. Whereas for P&T the limit of detection was 0.002 μg L^{-1} for all the analytes studied, that for HS was much lower – up to 5.7 μg L^{-1} for MTBE and 0.3–0.6 μg L^{-1} for BTEX. From the results reported it is clear that either HS or P&T is sufficiently sensitive for determination of MTBE at levels higher than 10 μg L^{-1} and will obviously be adequate as an alarm technique for detection of samples containing 20–40 μg L^{-1}, the threshold for odor and taste problems [16]. HS might not, however, be sufficiently sensitive for trace-level determination of MTBE in groundwater, in which residues might be encountered at the low μg L^{-1} level. An additional problem of HS-GC-FID is the need for confirmatory analysis of all positive samples. As a result, P&T-GC-MS is highly recommended for low-level determination of MTBE and BTEX, because of the high sensitivity and reproducibility obtained, the possibility of automation which enables high sample throughput, and quantitative and confirmatory analysis in a single run, with no need for further confirmation. HS-GC-FID is, however, an appropriate option for the direct analysis of highly polluted samples. Both techniques are highly precise and easy to use.

Cross-Validation Studies with Real Environmental Water Samples

For purposes of comparison twenty-one groundwater samples were analyzed in parallel by use of HS-GC-FID and P&T-GC-MS. Figure 1 shows an HS-GC-FID chromatogram obtained from a groundwater sample; a typical degraded gasoline profile is seen with dicyclopentadienes, cyclopentadienes and derivatives, and branched aliphatic hydrocarbons [19]. If standards are available GC-FID is a good means of determination of such compounds, although GC-MS confirmation is always necessary because of coelution problems. Figure 2 shows a typical P&T-GC-MS chromatogram obtained by SIM. The advantage of the latter technique is that with SIM acquisition a neater chromatogram is obtained; this makes identification and quantification easier at even very low concentration levels. The MTBE and BTEX levels found are reported in Table II. For each experiment quality control and blank analyses were included, with the intention of monitoring time variations. All the samples analyzed came from areas in which a fuel spill or tank leakage had occurred during 1997. These areas had been surveyed since the accidents and levels of MTBE and other fuel additives had been encountered at levels up to 300 μg L^{-1} [15]. In this work, a larger number of wells was monitored and of the compounds studied, MTBE was found in 20 of 21 wells sampled, at higher concentrations than discovered in previous work. This is attributed to the long half life of the compound in groundwater compared with BTEX, which can undergo degradation [20].

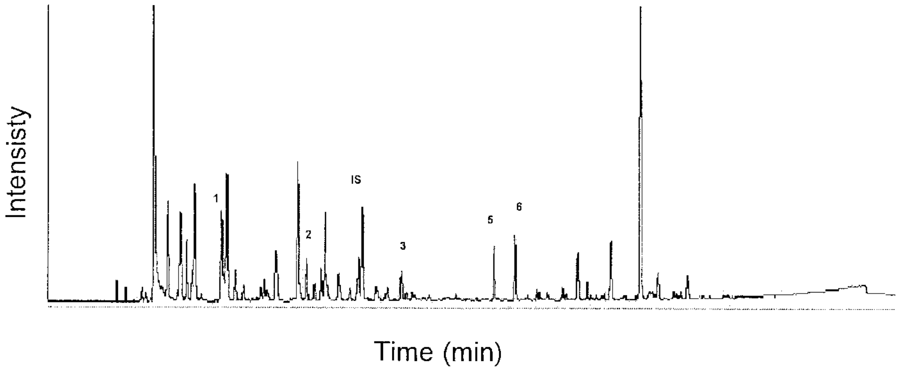

Figure 1. HS-GC-FID chromatogram obtained from a groundwater sample; the target compounds are identified amid the degraded gasoline profile. Peak identification: **1** = MTBE, **2** = benzene, **3** = toluene, **5** = *m* + *p*-xylenes, **6** = *o*-xylene.

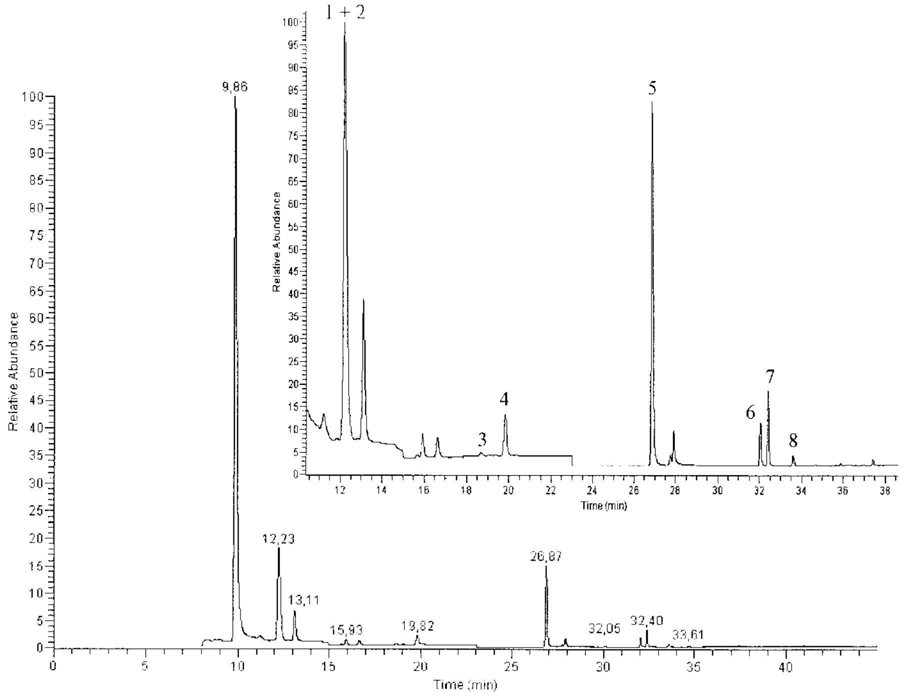

Figure 2. Chromatograms obtained by use of automated P&T-GC-MS, with time-scheduled selected-ion monitoring, from groundwater samples from the Tarragona area. Peak identification: **1** = MTBE, **2** = MTBEd$_3$, **3** = benzene, **4** = fluorobenzene, **5** = toluene, **6** = ethylbenzene, **7** = *m* + *p*-xylenes, **8** = *o*-xylene.

The first sampling area was Tarragona, site of permanent tank leakage from large underground tanks at a petrol service-station. Levels of MTBE up to 600 μg L^{-1} were encountered, with good agreement between both methods. Detritus coarse materials, sands, and conglomerates make up the aquifers involved, which are 8–10 m in depth. These levels are quite relevant, because MTBE is highly water-soluble, moves nearly as rapidly as the groundwater itself, and is considered recalcitrant in the subsurface environment. The possibility of MTBE traveling significant distances and persisting for long periods in subsurface water has important implications for public health officials who have historically relied on BTEX hydrocarbons to alert them to potential gasoline contamination. When concentrations were higher than 10 μg L^{-1}, acceptable correlation was found for MTBE results obtained by use of both techniques, except for sample Pineda 2, for which the concentration obtained by use of HS was 2.6 times higher than that obtained by P&T analysis. In this sample two different phases were clearly observed when sampling. Whereas with HS-GC-FID only a soluble aliquot of the sample was analyzed, with P&T-GC-MS the whole sample was purged. Comparison of results from HS and PT showed that higher levels of MTBE and lower levels of total BTEX were found by use of former technique. Because of the high solubility of MTBE in water, HS-GC-FID was capable of extracting the MTBE from the water but the heavier BTEX led to big differences between both techniques. With P&T all the compounds were detected but the presence of two visible phases in the sample affected the reproducibility of the extraction and in such circumstances it is recommended the analysis be performed in triplicate. Except for Pineda 2, in which BTEX was found by both techniques but at very different concentrations, BTEX were never detected by HS analysis, although high concentrations were found by use of P&T. In sample 'Sorts' concentrations of BTEX up to 3100 μg L^{-1} were observed by use of P&T, because the entire sample was analyzed. When oil droplets are present in the sample, therefore, as happened in this aquifer, there are large discrepancies between the concentrations found by use of the different techniques. This should be taken into consideration when selecting an analytical method. Despite this, the four samples containing the highest concentrations of MTBE also contained the highest BTEX levels, which varied from 387 to 4116 μg L^{-1} total BTEX. For the other samples levels varied from 5 to 74 μg L^{-1}.

In samples from La Batlloria taken five years after the spill it was still possible to detect traces of MTBE from 0.28 to 48 μg L^{-1} and BTEX from 0.02 to 1.43 μg L^{-1}. Good agreement was observed for 'negative' samples, i.e. those in which no contaminants were detected by either P&T or HS. In contrast, however, for some compounds, especially toluene, HS could not detect the target analytes at the 0.1 μg L^{-1} level. The problem of two different phases was never observed for samples taken from this aquifer.

In summary, comparison of concentration levels obtained by use of both techniques showed there was agreement only for samples containing high concentrations of MTBE – for these the difference between the techniques was 14%. For samples containing low μg L^{-1} levels (5–20 μg L^{-1}), however, differences between 12 and 140% were encountered. This was attributed mainly to the low sensitivity of HS-GC-FID, which cannot be used to detect concentrations below 6 μg L^{-1} for MTBE and below 0.6 μg L^{-1} for benzene, toluene, ethylbenzene, and the xylenes. Further discrepancies were attributed to coeluting peaks (e.g. MTBE-acrylonitrile, benzene-isopropyl acetate, and *o*-xylene-

Table II. Cross-validation of results from static HS-GC-FID and P&T-GC-MS analysis of oxygenate additives. Concentrations are given in μg L^{-1}.

Sample	MTBE	Benzene	Toluene		Ethylbenzene		*m*- + *p*-Xylenes		*o*-Xylene			
	HS	P&T	HS	P&T	HS	P&T	HS	P&T	HS	P&T	HS	P&T
Tarragona												
Sevil-Caseta	<l.d.*	8.50	<l.d.	1.47	<l.d.	8.89	<l.d.	2.53	<l.d.	1.76	<l.d.	1.30
Sevil-road	n.a.**	28.02	n.a.	1491	n.a.	1351	n.a.	312.0	n.a.	508.5	n.a.	454.9
Sevil-sinia	<l.d.	11.26	<l.d.	1.59	<l.d.	10.18	<l.d.	3.15	<l.d.	2.10	<l.d.	1.58
Gate-well	12.7	20.66	<l.d.	1.71	<l.d.	9.05	<l.d.	2.55	<l.d.	1.79	<l.d.	1.28
Sorts	610	666.3	<l.d.	5.88	<l.d.	3103	<l.d.	25.94	<l.d.	24.05	<l.d.	5.47
Ferrerota	65	74.48	<l.d.	4.60	<l.d.	30.31	<l.d.	7.76	<l.d.	4.43	<l.d.	2.77
Tarragonins	<l.d.	5.62	<l.d.	1.74	<l.d.	8.30	<l.d.	2.18	<l.d.	1.59	<l.d.	1.08
Pineda-2	115	42.66	35.0	8.75	8.0	269.4	<l.d.	36.07	50	31.23	65	43.12
Camping	6.0	10.53	<l.d.	1.96	<l.d.	9.88	<l.d.	2.74	<l.d.	2.02	<l.d.	1.34
Repsol-73	<l.d.	10.13	1.6	1.53	<l.d.	9.52	0.7	3.25	13	2.15	<l.d.	1.58
Repsol-83	<l.d.	8.23	<l.d.	1.84	<l.d.	11.08	<l.d.	3.60	<l.d.	2.24	<l.d.	1.57
La Batlloria												
Formigueta	<l.d.	0.28	<l.d.	<l.d.	<l.d.	0.03	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Comptesa	20.0	48.09	<l.d.	<l.d.	<l.d.	0.13	<l.d.	0.04	<l.d.	<l.d.	<l.d.	<l.d.
Ferreria 1	11.0	13.81	<l.d.	0.02	<l.d.	0.37	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Ferreria 2	57.0	32.85	<l.d.	<l.d.	<l.d.	1.43	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Ferreira 3	<l.d.	2.37	<l.d.	<l.d.	<l.d.	0.05	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Xemani	5.4	8.97	<l.d.	0.09	<l.d.	0.14	<l.d.	0.06	<l.d.	<l.d.	<l.d.	<l.d.
Xemani 2	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	0.07	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Auladell	<l.d.	0.62	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Vias	15	17.97	<l.d.	0.02	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Blancher	<l.d.	1.36	<l.d.	<l.d.	<l.d.	0.09	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.

* below the detection limit for the compound, see Table I; ** not analyzed.

styrene) in HS-GC-FID and to the matrix itself, because no filtration of the sample could be performed.

Conclusions

These data clearly reveal that contamination of groundwater by MTBE is a problem and that regular monitoring is needed to determine the extent of the contamination and then start remediation. Appropriate tools are thus necessary. In the work discussed in this paper the two methods most widely used for the analysis of gasoline oxygenates have been compared by analysis of groundwater samples which reflect real problems of analysis from sampling to the final results. Both HS-GC-FID and P&T-GC-MS are suitable for detection of MTBE and BTEX in groundwater. Whereas the former lacks sufficient sensitivity for detection of trace amounts, it is easier to use, has a wider linear range, and it is especially applicable to the determination of high concentrations of MTBE without the need for sample dilution. For positive samples, however, P&T GC-MS must be used for confirmatory purposes, with previous dilution of the sample when concentration levels are too high. The use of P&T-GC-MS, an EPA standard method, enables more precise and unequivocal measurement.

To avoid poor reproducibility care should be taken during sampling to prevent collection of samples containing two phases. The choice of proper surrogate compounds to enable verification of the entire analytical procedure and for use in quantification might also enhance the quality of the results. In this sense the use of deuterated MTBE is specially suitable for quantification of MTBE when MS detection is used whereas α,α,α-trifluorotoluene is appropriate for the determination of MTBE and BTEX by HS-GC-FID, and results in high-quality data for all the compounds.

In future work other fuel oxygenates, e.g. ethyl *tert*-butyl ether (ETBE), di-isopropyl ether (DIPE), *tert*-amyl methyl ether (TAME), *tert*-butyl formate (TBF), and *tert*-amyl methyl alcohol (TAA), will be included in the analysis. The new method will be used for routine monitoring of MTBE and related fuel oxygenates in our current monitoring programs.

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References

[1] Begley, R.; Rotman, D. *Chem. Week* **1993**, *152*, 7–14.

[2] US Environmental protection Agency, **1994**, Health Risk Perspectives on Fuel Oxygenates. EPA 600/R-94/217, Washington, DC.

[3] Squillace, P.J.; Zogorski, J.S.; Wilber, W.G.; Price, C.V. *Environ. Sci. Technol.* **1996**, *30*, 1721–1730.

[4] Squillace, P.J.; Moran, M.J.; Lapham, W.W.; Price, C.V.; Clawges, R.M.; Zogorski, J.S. *Environ. Sci. Technol.* **1999**, *33*, 4176–4187.

[5] Reuter, J.E.; Allen, B.C.; Richards, R.C.; Pankow, J.F.; Goldman, C.R.; Scholl, R.L.; Seyfried, J.S. *Environ. Sci. Technol.* **1998**, *32*, 3666–3672.

[6] Delzer, G.C.; Zogorski, J.S.; Lopes, T.J.; Bosshart, R.L. **1996**. Occurrence of the Gasoline Oxygenate MTBE and BTEX Compounds in Urban Stormwater in the United States 1991–95, Report 96-4145, US Geological Survey Water-Resources, Rapid City, SD.

[7] Pankow, J.F.; Thomson, N.R.; Johnson, R.L.; Baehr, A.L.; Zogorski, J.S. *Environ. Sci. Technol.* **1997**, *31(10)*, 2821–2828.

[8] Kirshtetter, T.W.; Singer, B.C.; Harley, R.A.; Kendall, G.R.; Chan, W. *Environ. Sci. Technol.* **1996**, *30*, 661–670.

[9] Squillace, J.P.; Pankow, J.F.; Korte, N.E.; Zogorski, J.S. *Environ. Toxicol. Chem.* **1997**, *16(9)*, 1836–1844.

[10] Borden, R.C.; Daniel, R.A.; LeBrun, I.; Davis, C.W. *Water Resour. Res.* **1997**, *33*, 1105–1115.

[11] Young, W.F.; Horth, H.; Crane, R.; Ogden, T.; Arnott, M. *Water Res.* **1996**, *30(2)*, 331–340.

[12] Drinking Water Advisory: consumer acceptability advise and health effects analysis on methyl tertiary butyl ether (MtBE);

U.S. Environmental Protection Agency, Office Water, **1997**, EPA-822/F-97–008.

[13] Schmidt, T.C.; Duong, H.A.; Berg, M.; Haderlein, S.B. *Analyst* **2001**, *126*, 405–413.

[14] US Environmental Protection Agency. 1984. Method 624 – Purgeables. 40 CFR Part 136, 43373; Federal Register 49, No. 209.

[15] Fraile, J.; Niñerola, J.M.; Olivella, L.; Figueras, M.; Ginebreda, A.; Vilanova, M.; Barceló, D. *The Scientific World Journal* **2002**, *2*, 1235–1242.

[16] Stuart, J.D.; Roe, V.D.; Lacy, M.J.; Robbins, G.A. *Anal. Chem.* **1989**, *61*, 2584–2585.

[17] Martinez, E.; Lacorte, S.; Llobet, I.; Viana P.; Barceló, D. *J. Chromatogr. A* **2002**, *959*, 181–190.

[18] Glaser, J.A.; Foerst, D.L.; Mckee, G.D.; Quave, S.A.; Budde, W.L. *Environ. Sci. Technol.* **1981**, *15(12)*, 1427–1435.

[19] Ventura, F.; Romero, J.; Pares, J. *Environ. Sci. Technol.* **1997**, *31*, 2368–2374.

[20] Johnson, R.; Pankow, J.; Bender, D.; Price, C.; Zogorski, J. *Environ. Sci. Technol.* **2000**, *34*, 210A–217A.

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