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Determination of methyl *tert.*-butyl ether and *tert.*-butyl alcohol in seawater samples using purge-and-trap enrichment coupled to gas chromatography with atomic emission and mass spectrometric detection

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Abstract

A rapid and simple analytical method has been established for the determination of methyl *tert.*-butyl ether (MTBE) and *tert.*-butyl alcohol (TBA), in seawater. The method involves purge-and-trap enrichment followed by gas chromatographic (GC) determination. Two different detection systems have been compared: atomic emission detection (AED) and MS (selected ion monitoring mode). Validation parameters and possible matrix effects have been evaluated. The linearity and analytical precision was good with both methods, but limits of detection reached by AED (10 μg l^{-1}) were not low enough to evaluate current environmental concentrations. GC–MS detection presented much better sensitivity [limits of detection (LODs) of 0.04 μg l^{-1} for MTBE and 0.09 μg l^{-1} for TBA] and selectivity, providing a more reliable determination. The analysis of samples collected from various marinas in the south of Spain (Almería and Málaga) showed, in all cases, detectable concentrations of MTBE that ranged from below LOD to 1842 μg l^{-1}, depending on the sampling point and time. TBA was also detected in some cases, with concentration levels that ranged from 400 to 600 μg l^{-1}. These preliminary results should be followed by monitoring programs in coastal waters, in order to establish real levels of presence of MTBE in our coasts and its possible effect on the marine environment.
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1. Introduction

Fuel oxygenates have been used in the USA as additives in gasoline since the 1970s, in order to produce cleaner burning gasolines [1]. Subsequently, their use was extended to Europe as octane enhancers [2]. From these compounds, mainly dialkyl ethers and alcohols, methyl *tert.*-butyl ether (MTBE) is by far the most widely used and its production increased dramatically in the mid-1990s [3–5]. As a consequence of its large production and physico-chemical properties, such as high volatility and water solubility, MTBE has been frequently detected, in the last few years, in the aquatic [6–8] and atmos-

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pheric [9,10] environment of different countries in the USA and Europe. This fact, together with its resistance to biodegradation in water and the potential and scarcely studied effect on human health and aquatic organisms [11–13], explain the increasing interest of environmental scientists and public officials in this compound [14,15].

Many studies relating to concentrations, sources and fate of MTBE, in environmental water have been carried out in groundwater [16–18], lakes and reservoirs for drinking water [6,19,20]. These studies have revealed leaking underground fuel tanks and motorized boating emissions as the main sources of groundwater and surface water contamination, respectively. Spillage of other fuels and motor oil may also contribute to widespread MTBE contamination [21,22]. However, the presence of MTBE in the marine environment has been scarcely investigated. There is only reference to studies carried out on the coast of California [23,24] where the highest average MTBE concentration of 8.8 mg l^{-1} was measured at marinas and areas used intensively for recreational boating. These results have increased concerns over the potential effects of MTBE contamination in marine ecosystems and the concentration levels that marine life are exposed to [13]. *tert*.-Butyl alcohol (TBA) is also of importance because it is the major degradation product of MTBE in aqueous systems but its presence has not been extensively evaluated because it is difficult to measure at low concentrations in water [25,26].

Studies published concerning the presence of MTBE in environmental water report concentration levels that can change considerably from environmental background levels (in the low μg l^{-1} range) to sites affected by point sources (high mg l^{-1} levels), thus requiring different analytical strategies. A comparative study of the analytical methods more extensively applied to the determination of MTBE in environmental matrices has been included in a recent review that dealt with the analysis of fuel oxygenates in the environment [27]. These methods include purge-and-trap (P&T) [26,28,29], headspace (HS) analysis [29], direct aqueous injection (DAI) [25,30,31] and solid-phase microextraction (SPME) [32–36], generally combined with gas chromatography (GC) connected to different detection systems (flame ionisation detection, photoionisation detec-

tion, MS). The choice of a particular method mainly depends on the concentration range to be analysed. In this sense, P&T–GC–MS, and more recently, SPME–GC–MS methodologies have provided the best results for measurements of background concentrations, due to their high sensitivity. Other possibilities, such as the use of atomic emission detection (AED) have not yet been described for environmental analysis of fuel oxygenates [27], although the use of AED coupled with P&T has been previously described for the analysis of volatile organic compounds in water [37,38] with good results.

Based on these previous considerations, the aims of this study were: (i) to establish a rapid and sensitive analytical method to detect and quantify the presence of MTBE and TBA in seawater, (ii) to evaluate the utility of the atomic emission detector for this application and (iii) to perform a preliminary study to assess the presence and concentration levels of these compounds in different marinas from southern Spain.

2. Experimental

2.1. Chemicals and reagents

MTBE (purity>99.8%) and TBA (purity>99%) were obtained from Riedel-de Haën (Seelze, Germany) and from Aldrich (Milwaukee, WI, USA), respectively. Working standard solutions were prepared separately in both seawater and Ultrapure water (obtained from a Milli-Q water purification system, Millipore, Bedford, MA, USA). Ultrapure water standard solutions were used for optimising P&T operating conditions and seawater standard solutions for validation of the method. Special care had to be paid during the preparation of these solutions in order to avoid volatilisation losses. To this end, a volumetric glass flask was 90% filled with water and a known volume of pure liquid compound was then slowly added with a micropipette below the surface of the solvent. After that, the flask was filled up to the mark and immediately stoppered. These aqueous solutions were prepared daily and discarded after the analysis.

2.2. Seawater samples

Seawater samples were taken from six marinas located in Almería and Málaga, two provinces sited in the south of Spain. Fig. 1 shows the location of the marinas along the coast. The size of the marinas was between 20 000 and 40 000 m^2, with an average number of boats between 100 and 200. Samples were collected from the coast. Two or three sampling points, depending on the cases, were selected in the marinas. Samples were also taken at a reference site, out of the marinas, where the presence of the analytes studied was not detected. Samples were collected at a depth of 30–40 cm in 2.5-l glass bottles, which were filled to overflowing to prevent volatilisation losses during sampling and storage. Analyses were carried out, whenever possible, on arrival at the laboratory or stored at 4 °C for no more than 1 or 2 days.

2.3. Purge-and-trap system

A Tekmar 3100 P&T concentrator (Cincinnati, OH, USA) was used for the enrichment of the samples. The system was equipped with a 5-ml sample container and a 30 cm×0.312 cm I.D. absorbent trap packed with Tenax/Silica Gel. The P&T was interfaced to different gas chromatographic systems by means of a heated transfer line in order to avoid analyte condensation during the analyses.

Teklink (2.02 Version) software was used for system control.

A typical P&T operating process was applied, including three main steps: sample purge, analyte desorption and bake. A sample volume of 4 ml was loaded into the sample vessel. Helium was used as purge gas at room temperature. The concentrator trap was set at an initial temperature of 30 °C during analyte adsorption and then rapidly heated at 220 °C during the desorption step. The analytes are swept with the GC carrier gas, through a transfer line (line temperature, 150 °C; valve temperature, 150 °C), onto the chromatographic column. After desorption, the P&T system turns the moisture control system (MCS) and the concentrator trap heaters up to bake temperatures (MCS temperature, 300 °C; trap temperature, 225 °C).

In addition to the operation parameters already described, those that more significantly affect the process efficiency, purge time and desorption time, were optimised in order to obtain the highest recoveries for the studied compounds. The optimisation process was carried out using a MTBE solution at 100 µg/l in Milli-Q water (as discussed in Section 4). Final values adopted were: purge time, 11 min, and desorption time, 4 min.

2.4. GC–AED analyses

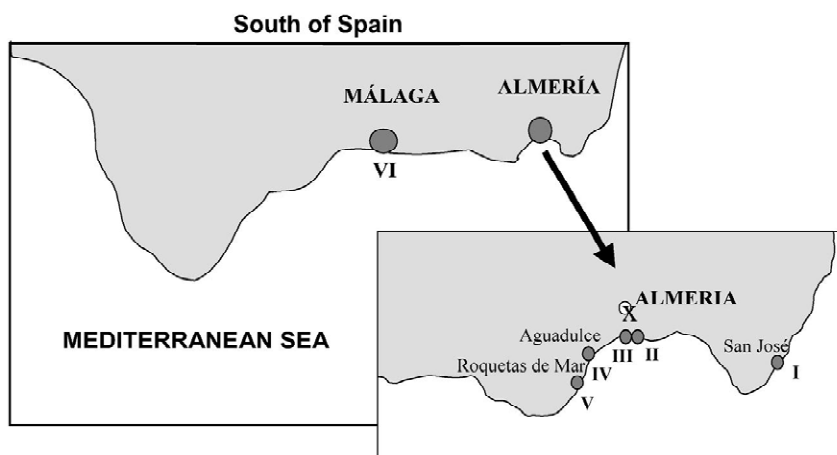A GC–AED system coupled with P&T was used

Fig. 1. Map of the southern Spanish coast showing sampling locations.

for determination of MTBE and TBA. In AED, the analytes coming from the GC column are atomized in a microwave-induced plasma. The resulting atoms and ions, in the excited state, emit light of a characteristic wavelength as they return to the ground state. The polychromatic light is dispersed in a spectrometer and emission intensity of the characteristic wavelengths is measured using a photodiode array [39].

GC–AED analyses were carried out on a Hewlett-Packard 6890 series gas chromatograph (Palo Alto, CA, USA) equipped with a Hewlett-Packard G2350 AED system. HP ChemStation software (B.02.05 version) was used to control the instrument, data acquisition and treatment. The analytical column connected to the system was a CP-Select 624 CB (6% cyanopropylphenyl, 94% dimethylsiloxane) capillary column (Chrompack) 30 m×0.32 mm, 1.80-μm film thickness. Helium was used as the carrier gas at a flow-rate of 1.0 ml min^{-1} in the constant flow mode. The initial oven temperature was 40 °C. After 8 min, the temperature was programmed to 120 °C (2 min) at 18 °C min^{-1} and then to 180 °C at 20 °C min^{-1}. Injection was in split mode (split ratio 20:1). One run with two selected wavelengths, hydrogen at 486 nm and carbon at 496 nm, was used for each analysis.

The make up and reagent gases used were: oxygen at 36.0 p.s.i. and hydrogen at 11.2 p.s.i (1 p.s.i.= 6894.76 Pa). Make up gas flow was set at 35 ml min^{-1}. The heated zones temperatures were: transfer line and cavity 250 °C.

2.5. GC–MS analyses

GC–MS analyses were run on a HP 6890 series gas chromatograph (Hewlett-Packard) interfaced to a HP 5973 mass-selective detector. Data acquisition and processing, and instrument control were carried out by the HP MSD ChemStation software. The analytical column and oven temperature program were the same as described for the GC–AED analyses. Helium was used as the carrier gas at 1.3 ml min^{-1} in the constant flow mode. A split/ splitless injector, maintained at 250 °C, was used in split mode, with a split ratio of 20:1.

The autotuning software optimised typical MS operating conditions. Electron impact (EI) mass spectra were obtained at 70 eV electron energy. The ion-source and quadrupole analyser temperatures were fixed at 230 and 106 °C, respectively.

2.6. Validation studies

All validation studies were carried out by fortifying analyte-free seawater samples previously analysed. The linearity in the response was studied by analysing standard solutions prepared in both blank matrix (seawater) and Milli-Q water to investigate possible matrix effects. Seven-point calibration curves were constructed. For GC–AED analyses, the concentration range studied was from 10 to 1000 μg l^{-1} and peak area data for the peaks corresponding to the carbon signal were used to construct the curves. In the case of GC–MS analyses, the linearity range was from 0.05 to 50 μg l^{-1} and integrated peak area data for the selected quantification masses were used, in this case, to construct the curves. The repeatability of the method was estimated following 10 analyses of seawater containing each compound at the concentration levels of 50 μg l^{-1} (level 1) and 0.2 μg l^{-1} (level 2). The limit of detection (LOD) was determined as the analyte concentration that gave a S/N of 3, as calculated by the instrument software and empirically verified by analysing standard mixtures of these compounds at these concentration levels in matrix extracts. Evidence for the presence of TBA traces during GC analysis of MTBE standards suggested the possibility of MTBE degradation during the analytical procedure. For that reason, all validation studies were done separately (separate injections) for both compounds.

3. Results and discussion

3.1. P&T and chromatographic conditions optimisation

Most of the P&T operating conditions (trap temperature, helium flow-rate, line and valve temperature, bake step conditions, etc.) were set based on previous publications, manufacturer recommendations or physicochemical properties of the investigated compounds. The only two parameters that have a significant influence on the process efficiency,

purge time and desorption time, were optimised to obtain high recoveries and good reproducibility for the studied compounds. Experiments were carried out varying the purge time between 5 and 13 min at different desorption times, of 1, 2, 4 and 8 min. Results obtained are shown in Fig. 2, where the influence of these parameters on the extraction yield can be seen, expressed as MTBE peak area obtained by GC–AED analysis. It was observed that the extracted amount of MTBE increased with increasing purge time from 5 to 11 min, but above this time, the increase in the signal was not significant. With respect to the desorption time, the signal increased from 1 to 4 min, remaining constant at higher values. In this way, the final values chosen were purge time 11 min and desorption time 4 min. These values are the same as those found in the literature for the P&T analysis of other volatile organic compounds [28,40].

Separation and detection were carried out by GC coupled with two different detection systems: MS and AED. In both cases, a semi-polar DB-624 analytical column, specially recommended for the analysis of volatile priority pollutants [US Environmental Protection Agency (EPA) Method 502.2], was used. Previous analysis using a nonpolar HP-5MS (5% phenyl)methylpolysiloxane-coated capillary did not yield good results for the compounds that eluted very quickly. Fig. 3 shows the GC–MS and GC–AED chromatograms obtained under the conditions described in the Experimental section. In order to achieve the highest sensitivity and selectivity, GC–MS analyses were carried out in selected ion monitoring (SIM) mode by selecting four characteristic ions for each compound (Fig. 3). The ions at m/z 73

$[(CH_3)_2COCH_3^+]$ for MTBE and m/z 59 $[(CH_3)_2COH^+]$ for TBA were used as quantification ions. Both come from the α-cleavage of a methyl group and correspond to the base peak in the spectra. The molecular ion was not present in the spectra. In the GC–AED analyses, atomic carbon and hydrogen emissions at 496 and 486 nm, respectively, were recorded for identification purposes. The sensitivity obtained was similar in both cases and the carbon emission line was selected for quantification. Selection of atomic oxygen emission at 171 nm could provide a better selectivity but the low sensitivity obtained prevents its use at low concentration levels.

3.2. Comparison between GC–AED and GC–MS methods

Validation studies of the developed analytical methods were carried out for both chromatographic systems, GC–AED and GC–MS, in order to compare them in terms of sensitivity, precision, selectivity and identification capability.

Since TBA has been reported as the major degradation product of MTBE in aqueous systems, all validation studies were done separately for both compounds, in order to avoid possible errors in the determination of TBA (over-estimation in the TBA standard concentrations, poor reproducibility, etc.) caused by the degradation of MTBE during the analytical process. In fact, it was observed that the analysis of MTBE standard solutions at high concentrations (>500 μg l^{-1}) showed the presence of significant concentrations of TBA, as a consequence of possible standard degradation.

Table 1 shows the results obtained from the validation studies. Both methods showed good linear correlation, with correlation coefficients R^2 between 0.993 and 0.998. The linearity ranges studied covered three orders of magnitude. Due to the higher response provided by the MS, the calibration curve ranged, in this case, from 0.05 to 50 μg l^{-1}. Determination of higher concentrations of these compounds can be done using a second calibration curve (good linearity was also experimentally observed in a range from 50 to 2500 μg l^{-1}) or by dilution of the samples, in order to avoid significant contamination of the analytical system. In this sense, it is necessary to perform periodic analyses of blanks
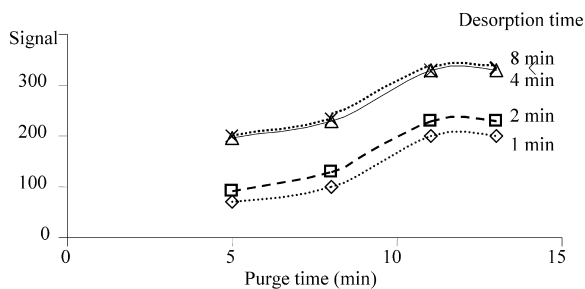

Fig. 2. Influence of purge time and desorption time in the MTBE extraction yield, expressed as MTBE peak area obtained by GC–AED analysis.
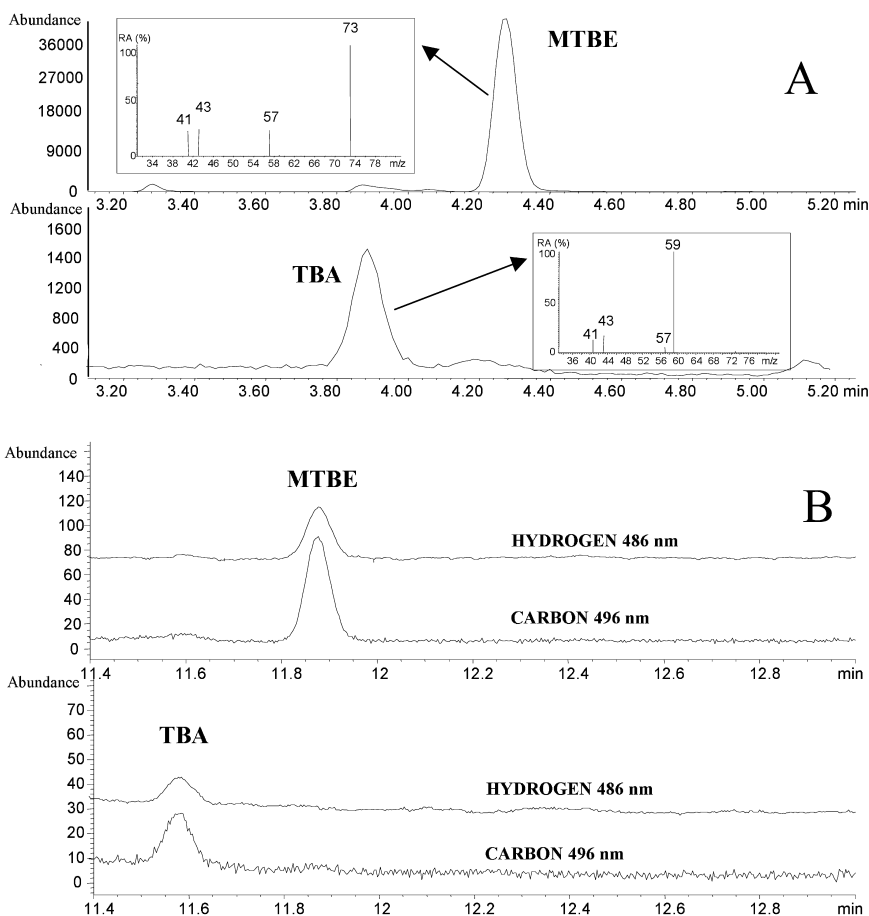
Fig. 3. Chromatograms obtained after the analysis of a seawater sample, fortified with MTBE and TBA (10 mg l^{-1}), by (A) GC–MS-SIM and (B) GC–AED.

to ensure the absence of trace-level contamination [10].

With respect to sensitivity and precision, the MS offers better results than AED (Table 1). The limit of detection obtained in seawater samples with the GC–MS-SIM method for MTBE (0.04 μg l^{-1}) is 250 times lower than that obtained by GC–AED (10 μg l^{-1}). The repeatability in GC–MS-SIM was excellent at the two concentration levels investigated, with coefficients of variation ($n = 10$) of 3–6% in the case

Table 1
Validation data obtained for the target compounds in seawater samples by P&T–GC–AED and P&T–GC–MS

Compound	Linearity (R^2)		LOD (μg l^{-1})		Repeatability (%)			
	AED	MS	AED	MS	Level 1 (50 μg l^{-1})		Level 2 (0.20 μg l^{-1})	
					AED	MS	AED	MS
MTBE	0.993	0.998	10	0.04	17	3	–	6
TBA	0.995	0.996	10	0.09	12	4	–	11

of MTBE and 4–11% for TBA. A worse, but acceptable, precision was observed in AED with coefficients of variation between 12 and 17%.

3.3. Seawater analyses

Numerous studies of the presence of fuel oxygenates in surface water and groundwater have been published. Nevertheless, their presence in seawater has not been evaluated sufficiently and there is no information about the possible influence of this matrix, especially in P&T analysis. It is known, however, that the sample matrix plays an important role in the purge step and an enhancement of the purge efficiency has been reported [10] for other volatile compounds as a consequence of a ''salting out effect'' caused by the high salt content of seawater. For this reason, a study of the possible matrix influence on both identification and quantification of the target compounds has been carried out.

With respect to identification, no interfering peaks were detected during the analyses of real seawater samples in either GC system. In all cases, MTBE and TBA were correctly identified. If we compared the identification capability of both detection systems it is clear than MS provides more reliability. The reading of mass spectrum, showing characteristic primary and secondary ions at their correct relative abundances, represents a more suitable approach to the confirmation of these compounds than the detection of two ubiquitous elements, such as carbon and hydrogen in AED. The selectivity in the AED analyses could be improved by the detection of the oxygen signal, but this necessitates two different injections for the same sample and increases the limit of detection considerably, at about 50 μg l^{-1} for both MTBE and TBA. On the other hand, although MS (in the SIM mode) is more definitive for target compounds, AED has broader applications, since the information on the presence and ratio of the elements applies to all compounds and can be used for identification and quantification of other unknown volatile compounds also present in the samples, even if the corresponding standards are not available.

The possible influence of matrix components in quantitative analysis of these compounds was also evaluated. For this purpose, calibration curves were plotted from standard solutions prepared in both seawater and Milli-Q water. No differences were observed in either case. The absence of matrix effects can be explained by the physicochemical properties of these compounds, which show high volatility and sufficient Henry's law constants to favour efficient stripping from the aqueous phase, even in the absence of salts.

3.4. Pilot monitoring study

As an application, the presence of MTBE and TBA was investigated in six marinas from Almería and Málaga (two provinces of southern Spain). The study was carried out during the months of July, August, September and October 2001, when intense shipping traffic was expected. As a consequence of the water mobility in the marinas, it would be expected that there would be variations in the MTBE concentration, depending on the sampling point. For this reason, two or three different locations were considered: one or two in the vicinity of point sources (close to the ships or gasoline stations) where the presence of these compounds at high concentration is more probable as a consequence of accidental spills, overflows or leakages, and another one in the marina exit, as an indication of the diffusion of this compound and background levels into the marina. The concentration values found are shown in Table 2. Although the sampling carried out can be only considered as a preliminary study, data obtained revealed the presence of MTBE in all the marinas investigated, so indicating that this compound can be considered as a potential contaminant. Mean concentrations detected generally ranged from 0.033 to 2.20 μg l^{-1}, concentrations that are in concordance with the levels reported in the studies of California coastal waters [23,24]. Nevertheless, higher concentrations, in the range from 101 to 819 μg l^{-1}, were also occasionally detected (Almería II) in the immediate vicinity of gasoline stations or boat-launching facilities. In the last case, the high concentrations detected during August can be related to the more intense boating traffic. Almería III constitutes a special case, since MTBE was always detected at very high concentrations (up to 1842 μg l^{-1}) at the sampling point close to the gasoline station, indicating a continuous dumping of gasoline that can be attributed to different causes (higher

Table 2
Concentrations of MTBE detected in the marinas of southern Spain

	Concentration (μg l^{-1})							
	July		August		September		October	
	AED	MS	AED	MS	AED	MS	AED	MS
Almería I[a]	–	–	–	–	nd	0.075	nd	1.23
Almería I[b]	nd	nd	–	–	nd	0.154	nd	1.34
Almería I[c]	nd	nd	–	–	nd	0.118	nd	2.20
Almería II[a]	–	–	–	–	nd	0.043	nd	1.45
Almería II[b]	816	819	–	–	nd	0.103	nd	0.83
Almería II[c]	131	101	677	768	nd	0.052	nd	1.01
Almería III[a]	nd	0.150	–	–	nd	0.082	nd	1.97
Almería III[b]	33	21	1842	1335	428	513	1157	1238
Almería III[c]	nd	nd	–	–	nd	0.304	nd	1.62
Almería IV[a]	nd	0.181	–	–	nd	0.058	–	–
Almería IV[b]	nd	0.720	–	–	nd	0.120	–	–
Almería V[a]	nd	0.046	–	–	nd	0.033	–	–
Almería V[b]	nd	0.059	–	–	nd	0.061	–	–
Málaga[a]	–	–	–	–	nd	0.166	–	–
Málaga[b]	–	–	–	–	nd	0.126	–	–
Málaga[c]	–	–	–	–	nd	0.093	–	–

nd, not detected.

[a] Marina exit.

[b] Close to the gasoline station.

[c] Close to the ships.

boating activity, problems in the gasoline supply, leaks, etc.). It is important to consider, however, that because MTBE is mobile in seawater, these high concentrations do not affect the whole-marina levels. With respect to TBA, it was only detected in those samples where the highest concentrations of MTBE were found: Almería II[b] (July), Almería II[c] (August) and Almería III[b] (August and October). The concentrations founded ranged from 400 to 600 μg l^{-1}. Previous studies carried out in groundwater have recognized the high persistence of MTBE in aqueous media. Although laboratory studies have shown that microorganisms can degrade MTBE to TBA [41], to date no evidence has been found for the formation of TBA from in situ degradation of MTBE [25]. TBA, however, cannot only be considered as an indicator of biodegradation of MTBE but that it is also a fuel additive, although its use is limited compared with MTBE. Fig. 4 shows the GC–MS and GC–AED

chromatograms of a real seawater sample. In all cases, the criteria established allowed satisfactory identification of the target compounds.

4. Conclusions

The results of this preliminary study show the presence of MTBE in all marinas investigated. In some cases, concentration levels found (in the mg/l range) can be considered significant and would be of concern for aquatic ecosystems. The studies relating to the influence of this individual compound in the marine ecosystems [13] reveal that concentrations of MTBE found pose little risk of toxicity to marine organisms. However, apart from the influence of this single compound, it is necessary to consider the possible synergistic effects due to the presence of other contaminants in the marina seawater, such as
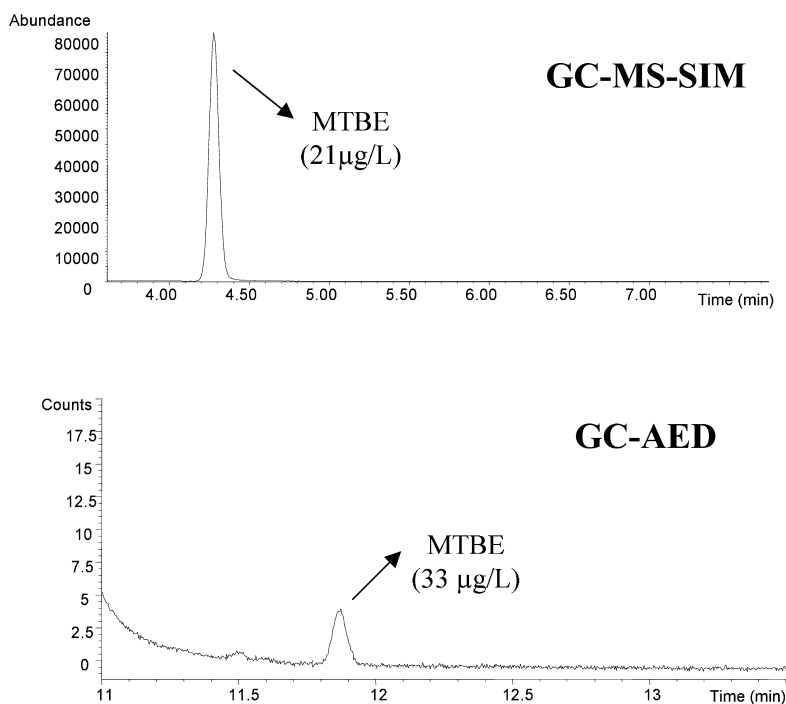
Fig. 4. GC–MS-SIM and GC–AED chromatograms of a real seawater sample where MTBE has been detected at concentrations of 21 and 33 μg l^{-1}, respectively.

biocides [42] that increase the resulting toxicity [43]. This fact makes it necessary to carry out further studies in order to obtain a complete evaluation of the presence, distribution and influence of MTBE in the marine environment.

From an analytical point of view, the methodologies applied for the determination of MTBE and TBA in seawater, i.e. purge-and-trap coupled to GC–AED and GC–MS (SIM mode), have shown good performance with respect to identification and quantification of the target compounds. GC–AED analyses have however shown limits of detection that, in most cases, are not low enough to determine environmental concentrations, but are sufficient to detect alarm points. In addition, GC–AED allows us to perform screening analyses where the presence of other unknown contaminants can be detected.

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