ELSEVIER

Journal of Chromatography A, 857 (1999) 205–216

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Analysis of methyl *tert*.-butyl ether and its degradation products by direct aqueous injection onto gas chromatography with mass spectrometry or flame ionization detection systems

Song Hong, Christian M. Duttweiler, Ann T. Lemley*

Field of Environmental Toxicology, Cornell University, Ithaca, NY 14853-4401, USA

Received 16 March 1999; received in revised form 29 June 1999; accepted 29 June 1999

Abstract

A method was developed to analyze methyl *tert*.-butyl ether (MTBE) and its degradation products by gas chromatography with mass spectrometry (GC–MS) or flame ionization detection (FID) with direct aqueous injection. The column had dimensions of 30 m×0.25 mm with film thickness 0.25 μm and a stationary phase of FFAP (nitroterephthalic acid-modified polyethylene glycol). The optimized GC conditions for non-acid components were as follows: carrier gas flow-rate,1 mL/min; oven temperature, 35°C for 5.5 min, ramped to 90°C at 25°C/min, then ramped to 200°C at 40°C/min and held at 200°C for 8 min. The conditions for the acid components were: carrier gas flow-rate, 1 mL/min; oven temperature, 110°C for 2 min, ramped to 150°C at 10°C/min, then ramped to 200°C at 40°C/min. The injection port contained a silanized-glass reverse-cup liner filled with Carbofrit. The minimum concentrations for the linear range for the selective ion monitoring mode were 30 to 100 μg/L, depending on the analytes. The minimum detection limit was 1 mg/L for MTBE and *tert*.-butanol when using FID. More components could be analyzed with the FFAP-type column than with the cyanopropylphenyl–dimethyl polysiloxane-type column.

Keywords: Direct aqueous injection; Injection methods; Gasoline; Water analysis; Environmental analysis; Methyl *tert*.-butyl ether

1. Introduction

Methyl *tert*.-butyl ether (MTBE) has been widely used as an oxygenate and octane enhancer in gasoline. However, it has become a known contaminant of surface water and groundwater due to its high solubility in water. Its release to the environment has generated great public and governmental concern because of the toxicity of MTBE and its degradation products [1,2]. The degradation pathway of MTBE most reported is free radical oxidation by the hydroxyl radical and molecular oxygen [2–6]. Microbiologically mediated hydrolysis and oxidation have also been reported [7,8]. The degradation products reported are carbon dioxide, *tert*.-butanol, *tert*.-butylformate, acetone, formic acid, methyl acetate, and formaldehyde.

A good remediation technique for MTBE should degrade it to products of lower toxicity than the parent compound and ones that are more susceptible to further detoxification in the environment. It is critical to analyze MTBE and its degradation products when remediating MTBE-contaminated water. Direct aqueous injection (DAI) on GC is more

*Corresponding author.

0021-9673/99/$ – see front matter
PII: S0021-9673(99)00781-5

economically accessible and easier to operate than purge-and-trap or headspace techniques. Church et al. developed a DAI–GC–MS method to analyze MTBE, TAME (*tert*.-amyl methyl ether), and some of their degradation products using a 10 μL injection volume, a microbore column with a stationary phase of polyethylene glycol (PEG), and a MS system with relatively larger capacity on the vacuum than a bench-top MS system [8]. Potter developed a DAI–GC–FID (flame ionization detection) method to analyze MTBE in water using on-column injection and a megabore column with a stationary phase of 6% cyanopropylphenyl- and 94% dimethylpolysiloxane [9].

In the work reported, a direct aqueous injection method was developed to analyze samples that had been treated in various types of Fenton [10,11] systems containing dissolved NaCl and iron ions. The injection, column, and oven parameters of DAI–GC–MS were optimized so that aqueous samples of MTBE and its degradation products could be identified and quantified.

2. Experimental

2.1. Chemicals

MTBE, its possible degradation products (*tert*.-butanol, *tert*.-butyl formate, acetone, methanol, ethanol, formic acid, acetic acid, methyl acetate, ethyl acetate, formaldehyde, and acetaldehyde), hexanoic acid and ammonium sulfide were purchased from Aldrich (St. Louis, MO, USA). Ferrous chloride and ferric chloride were obtained from Fisher Scientific (Springfield, NJ, USA). The helium and nitrogen used were 99.9995% pure.

2.2. Accessories

The fillings for the GC injection-port liner were silanized glasswool (Supelco, Bellefonte, PA, USA) and Carbofrit (Restek, Bellefonte, PA, USA). Nylon membrane (0.20 μm) filters encased in polypropylene cartridges were obtained from Alltech Associates (Deerfield, IL, USA). The pH meter was an Accumet Model 25 (Fisher Scientific).

2.3. Sample preparation

The MTBE waste water was prepared by dissolving MTBE into tap water supplied from one of the creeks that feed Cayuga Lake in Ithaca, NY, USA. It was then subjected to advanced oxidation in an electrochemical Fenton system; ferrous iron, hydrogen peroxide and sodium chloride were added in the course of the treatment. The tap water was also treated by the same process. The hydroxyl radical and excess hydrogen peroxide were destroyed and ferrous and ferric ions were precipitated when 2 *M* ammonium sulfide aqueous solution was added (20 μL for each milliliter of above solutions). Aqueous ammonia solution (10%, less than 5 μL for each milliliter of above solutions) or hexanoic acid aqueous solution (1 *M*, less than 5 μL for each milliliter of above solutions) was added to adjust the pH to near 7 for more complete precipitation of ferrous and ferric ions. All standard solutions were prepared by spiking chemical standards to the tap water treated as above to match the matrix of the real samples. Aqueous ammonia solution (10%) or hexanoic acid aqueous solution (1 *M*) were added again if the pH changed after the addition of standards. The solution was kept at 4°C for 3 h, then centrifuged for 5 min. The supernatant was filtered through nylon filters with a pore size of 0.2 μm. The effluent was injected into the GC for analysis. Ammonium sulfide, ammonia and hexanoic acid were selected because of their volatilities.

2.4. GC–MS operating conditions

MTBE and its degradation products were analyzed on a Hewlett-Packard (Sunnyvale, CA, USA) GC 5890 Series II coupled to a HP 5971A MS system. Operating conditions were as follows: ionization voltage, 70 eV; interface temperature, 320°C; MS temperature, 180°C; electronic multiplier, 200 V above manual tune for selective ion monitoring (SIM). The MS was tuned daily with perfluorotetrabutylamine (PFTBA). The manual tune was used for both scan and SIM mode to increase the sensitivity on MS ion fragments with mass-to-charge ratio (m/z) from 29 to 100. The three ions used in the manual tune were 69, 93, and 100 (m/z). The threshold for the scan mode was 500.

The other optimized GC–MS conditions were as follows unless stated otherwise elsewhere: injection liner, reverse-cup silanized-glass liner (Supelco) filled with 0.5 cm Carbofrit (Restek) right above the cup; injection temperature, 250°C; injection mode, splitless for 1 min before purging the injection port; injection volume, 1 μL by hand or by HP7673A autosampler (Hewlett-Packard); guard column, intermediate polarity (phenyl/methylpolysiloxane coating, 5 m×0.25 mm, Supelco).

The injection port liners (Supelco) investigated were silanized-glass reverse-cup liner, cylindric silanized-glass liner (I.D. 4 mm), and single-taper silanized-glass liner (I.D. 4 mm). The fillings inside the liners tested were silanized glasswool and Carbofrit (Resteck), both at a height of 0.5 cm. The types of fused-silica guard columns (5 m×0.25 mm for each) tested were: non-polar (polymethylsiloxane coating, Supelco), intermediate polarity (phenyl/methylpolysiloxane coating, Supelco), high polarity (PEG coating, Supelco), and high-temperature silylation (Alltech). Columns were connected with a fused-silica capillary column connector (Supelco), and the junctions were sealed with polyimide resin (Supelco).

Two DB-FFAP columns, with a stationary phase of nitroterephthalic acid modified PEG (J&W Scientific, Folsom, CA, USA) and dimensions of 30 m×0.25 mm I.D., film thickness 0.25 μm and 30 m×0.25 mm I.D., film thickness 0.5 μm, were evaluated individually as the analytical column. One SPB-624 column (30 m×0.53 mm I.D., film thickness 3 μm, stationary phase: 6% cyanopropylphenyl- and 94% dimethylpolysiloxane) was also tested. The optimized conditions for SPB-624 were as follows: oven temperature maintained at 110°C, solvent vented from 7.5 to 9.2 min, 0.5 μL of sample injected by on-column injection mode, the column-head pressure was 15.8 kPa, the MS vacuum was $5\cdot10^{-3}$ Pa, and the guard column was 5 m×0.53 mm I.D. polar fused-silica tubing (Supelco).

2.5. DAI–GC–FID operating conditions

An HP 5890A GC system (Hewlett-Packard) with FID was used. The optimized conditions for the DB-FFAP (30 m×0.25 mm I.D., film thickness 0.25 μm) column were: column-head pressure, 86 kPa; flow-rate of N_2 carrier gas, 1 mL/min; flow-rate of hydrogen gas, 30 mL/min; flow-rate of compressed air, 400 mL/min; flow-rate of make-up gas (N_2), 20 mL/min; detector temperature, 250°C; and oven temperature, maintained at 35°C for 5.5 min, ramped to 90°C at 25°C/min, then ramped to 200°C at 40°C/min and held at 200°C for 8 min. The guard column and the injection parameters were the same as those listed for GC–MS. When the SPB624 column (30 m×0.53 mm I.D., film thickness 3 μm) was used, the optimized conditions were as follows: guard column, 5 m×0.53 mm polar fused-silica tubing (Supelco); carrier gas, 2.5 mL/min; oven temperature, 108°C; column-head pressure, 48 kPa; injection, 1 μL and split at a ratio of 1:10. The remaining parameters for the injector and the FID system were the same as those for the DB-FFAP column.

3. Results and discussion

After Fenton or electrochemical Fenton treatment the aqueous MTBE samples had pH values around 2.5 and iron concentrations ranging from several μg/mL to 1 mg/mL. A blank test confirmed that the presence of dissolved iron catalyzed the degradation of MTBE on the DAI–GC–MS (data not included). Thus, iron salts were precipitated before the analysis of MTBE and its degradation products. This same approach was used by the authors in previous work with alachlor [12], where the pH was adjusted to the 6 to 7 range. Since most of the iron was in the ferric form due to the Fenton reaction in the treatment system, increasing the pH effectively removed the several mg/mL dissolved iron from the aqueous samples. The relevant equilibria for the precipitation of iron hydroxides are as follows [10]:

$$Fe^{2+} + 2OH^- = Fe(OH)_2\downarrow,$$
$$K_{sp} = [Fe^{2+}][OH^-]^2 = 10^{-14}\,M^{-3} \quad (1)$$

$$Fe^{3+} + 3OH^- = Fe(OH)_3\downarrow,$$
$$K_{sp} = [Fe^{2+}][OH^-]^3 = 10^{-36}\,M^{-4} \quad (2)$$

In the current work, because of the Fenton treatment conditions, in some of the experiments most of the

iron is in the ferrous form and would not be precipitated completely at pH 7. In order to precipitate all the iron, a pH of 11 would be required. To avoid pH values that high, which might degrade some analytes, ammonium sulfide was chosen to precipitate ferrous and ferric ions. The solubility product for ferrous sulfide is $6 \cdot 10^{-18}$ M^{-2}, low enough to allow precipitation at lower pH values. Ammonium sulfide and hexanoic acid were used to adjust the pH to 7. These were selected because they are highly volatile and cause no interference with GC–MS of the analytes. Following filtration of the iron sulfide and iron hydroxide precipitates, the aqueous solutions were injected directly into the GC–MS system for analysis. If ammonium hexanoate were to form in the GC inlet it would be pyrolyzed to ammonia and hexanoic acid.

Due to the treatment method used, sodium chloride was present at concentrations of several tens of milligrams per milliliter in the aqueous samples to be analyzed. Salt particles had to be trapped on the fillings of the injector liner in order to protect the capillary analytical column. The split/splitless injection mode was used because it traps non-volatile components in the injection port better as compared with on-column injection [14]. Splitless injection was chosen instead of split injection to increase the sensitivity of the analysis [15]. The GC–MS response with silanized-glass reverse-cup liner was lower than that with cylindrical silanized-glass liner or single-taper silanized-glass liner. The responses with the latter two liners were close. The peaks produced using the first liner were slightly broader than those produced by the latter two. However, silanized-glass reverse-cup liner trapped non-volatile components more efficiently.

The silanized glasswool became active for degradation of *tert*.-butyl formate after a few DAIs, then became active for degradation of MTBE after several more DAIs. There was no difference in GC–MS between using factory-packed glasswool and using our own packed glasswool for the fillings inside the injection liner. Carbofrit, on the other hand, remained inert toward the analytes even after 30 DAIs. It is critical to completely clean out the Carbofrit debris before installing the injection liner because the fragile Carbofrit may have debris that can fall down to the column and deteriorate the chromatogram. The response without fillings was higher than that with it. For the sake of better protection of the analytical column and analytical reliability, silanized-glass reverse-cup liner filled with Carbofrit was chosen for this method. The Carbofrit needed to be replaced for every 30 DAIs.

Tests showed that the GC–MS responses decreased with injection temperature, decreasing from 250, to 230, then to 130°C. Injection temperatures higher than 250°C were not tested due to the volatile nature of the analytes. Thus, the injection temperature was set at 250°C for this method. The boiling points for MTBE and most of its degradation products are between 50 and 80°C. To obtain the solvent effect for sharper peaks [12,13] and enough resolution for quantification of peaks, the initial temperature for the oven temperature program was optimized at 35°C. This is close to 40°C, the minimum that is recommended by the manufacturer (J&W Scientific) for DB-FFAP-type open-tube columns with a stationary phase of nitroterephthalic acid modified polyethylene glycol.

A guard column with high polarity shifted the retention time axis of the chromatogram to 0.4 min longer and resulted in fair chromatographic peaks and baselines, even with an injection volume of 5 μL, except for *tert*.-butanol whose peak was too broad. Although tests showed that the GC–MS responses doubled with 2 μL injection and increased 3 to 4 times with 5 μL injections when using the high-polar guard column, to avoid quick build-up of salts inside the injection liner and to move the sample vapor upstream along the carrier gas line due to the limited volume of the injection liner, the injection volume was set to 1 μL. The chromatograms did not change significantly when using other types of guard columns. The guard column with intermediate polarity was used for the results listed in this paper.

Two or three fragment ions were chosen for the SIM mode (Table 1). The GC–MS sensitivity in the SIM mode was 10 to 50 times higher than in the scan mode. However, it was still 2.5 to 300 times less than obtained by Church et al. [8] and about the same as Potter achieved [9]. Fig. 1 shows the chromatogram obtained with the DB-FFAP column (30 m×0.25 mm, 0.25 μm) analyzing MTBE and the acids simultaneously. The conditions were as

Table 1
Characteristic fragments on GC–MS with electron impact ionization of MTBE and its degradation products

Compound	Molecular ion, *m/z*	Base peak, *m/z*	Ions for SIM
MTBE	88	73	57, 73
Formaldehyde	30	29	29, 30
Acetaldehyde	44	29	29, 44
Acetone	58	58	43, 58
Methyl acetate	74	43	43, 74
Ethyl acetate	88	43	43, 45, 61
tert.-Butyl formate	102	59	57, 59, 87
Methanol	32	32	29, 31
tert.-Butanol	74	59	59
Ethanol	46	31	31, 45, 46
Formic acid	46	29	45, 46
Acetic acid	64	60	45, 60
Propionic acid	74	57	74, 57

follows: column-head pressure, 48 kPa; MS vacuum, $4.6 \cdot 10^{-3}$ Pa; carrier gas flow-rate, 0.7 mL/min; water vent, 7 to 11 min; oven temperature, 35°C for 5.5 min, then ramped to 150°C at 25°C/min and held at 150°C for 4 min.

The linearities for MTBE, acetone, and *tert.*-butanol were acceptable ($R^2 > 0.99$), but were poor for the acids ($R^2 = 0.3–0.94$) (Table 2). The retention times for the acids shifted randomly from injection to injection by nearly 4% (data not shown). When non-acid components were chromatographed from one injection (Fig. 2) and the acids were chromatographed from another injection under different GC conditions (Fig. 3), the response linearities of all the components were acceptable (Table 2) and retention times were stable. The conditions for the former were: column-head pressure, 62 kPa; MS vacuum, $5.4 \cdot 10^{-3}$ Pa; carrier gas flow-rate,1 mL/min; water vent, 7.7 min to the end of the run; oven temperature at 35°C for 5.5 min, then ramped to 90°C at 25°C/min, then ramped to 200°C at 40°C/min and held at 200°C for 8 min. The conditions for the latter were: column-head pressure, 103 kPa; MS vacuum, $5.9 \cdot 10^{-3}$ Pa; carrier gas flow-rate, 1 mL/min; water delay, 4 min; oven temperature at 110°C for 2 min, then ramped to 150°C at 10°C/min, then ramped to 200°C at 40°C/min.

The methanol peak was only slightly separated from the *tert.*-butanol peak (Fig. 1). However, methanol was determined not to be a degradation

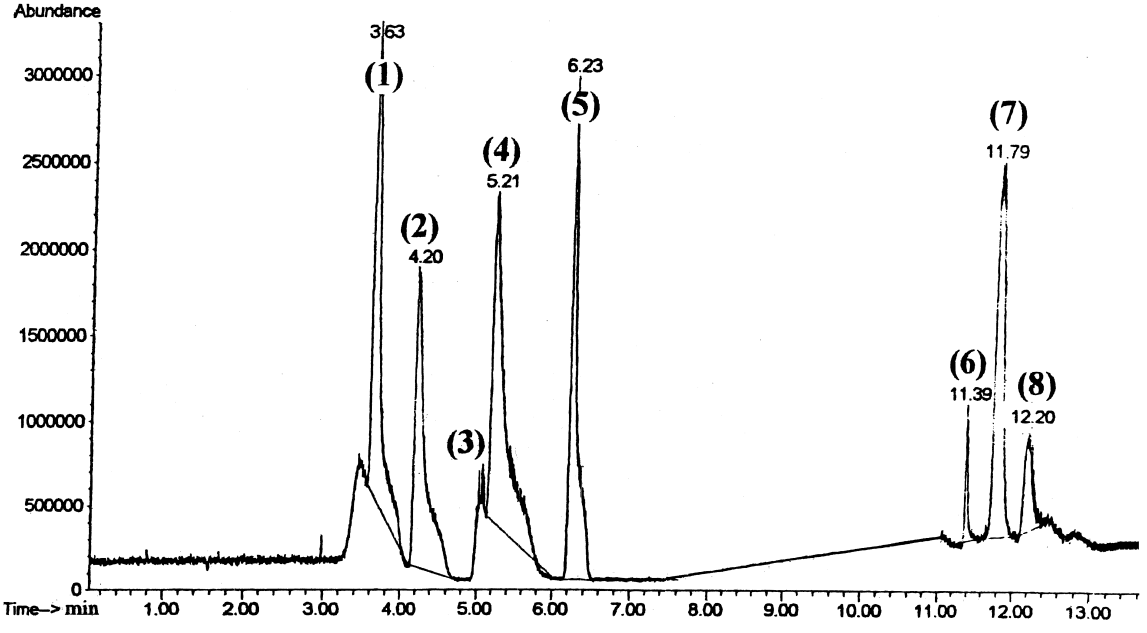

Fig. 1. GC–MS-Scan total ion chromatogram of MTBE and its degradation products in aqueous solution: (200 mg/L) on DB-FFAP column (30 m×0.25 mm I.D., film thickness 0.25 μm): (1) MTBE, (2) acetone, (3) methanol, (4) *tert.*-butanol, (5) isobutyl formate (for internal standard purposes), (6) acetic acid, (7) formic acid, and (8) propionic acid.

Table 2
Linear regression on the GC–MS-SIM and GC–FID response (height $\times 10^{-4}$) versus concentration for MTBE and its degradation products

GC condition	Analyte	Intercept	Slope	Range (mg/L)	R^2
Fig. 1	MTBE	−3.529	0.03353	0.03 to 250	0.999
Fig. 1	Acetone	1.386	0.21877	0.03 to 250	0.999
Fig. 1	*tert*.-Butanol	−4.129	0.04698	0.03 to 250	0.989
Fig. 1	Isobutyl formate	8.534	0.13960	0.1 to 250	0.988
Fig. 1	Acetic acid	−6.033	0.06326	0.1 to 250	0.942
Fig. 1	Formic acid	−2.24	0.49714	0.1 to 250	0.303
Fig. 2	MTBE	0.3754	0.011274	0.03 to 200	0.996
Fig. 2	Acetaldehyde	1.543	0.015734	0.1 to 200	0.997
Fig. 2	Acetone	0.3713	0.040142	0.03 to 200	0.996
Fig. 2	Methyl acetate	0.4836	0.032061	0.1 to 200	0.991
Fig. 2	Ethyl acetate	0.6902	0.074646	0.03 to 200	0.998
Fig. 2	*tert*.-Butyl formate	0.3868	0.15060	0.1 to 200	0.996
Fig. 2	*tert*.-Butanol	0.1088	0.019891	0.03 to 200	0.999
Fig. 2	Ethanol	0.9012	0.032879	0.1 to 200	0.989
Fig. 3	Acetic acid	−2.468	0.100384	0.1 to 200	0.999
Fig. 3	Formic acid	−5.062	0.084309	0.1 to 200	0.997
Fig. 3	Propionic acid	1.633	0.10038	0.1 to 200	0.9999
Fig. 4	MTBE	0.2787	0.57910	0.1 to 200	0.992
Fig. 4	*tert*.-Butanol	0.0983	0.81414	0.1 to 200	0.997
Fig. 4	Acetic acid	Not linear		5 to 200	
Fig. 5	MTBE	−20.2	5.7267	2.5 to 500	0.949
Fig. 5	Acetone	−6.7	12.177	2.5 to 500	0.9999

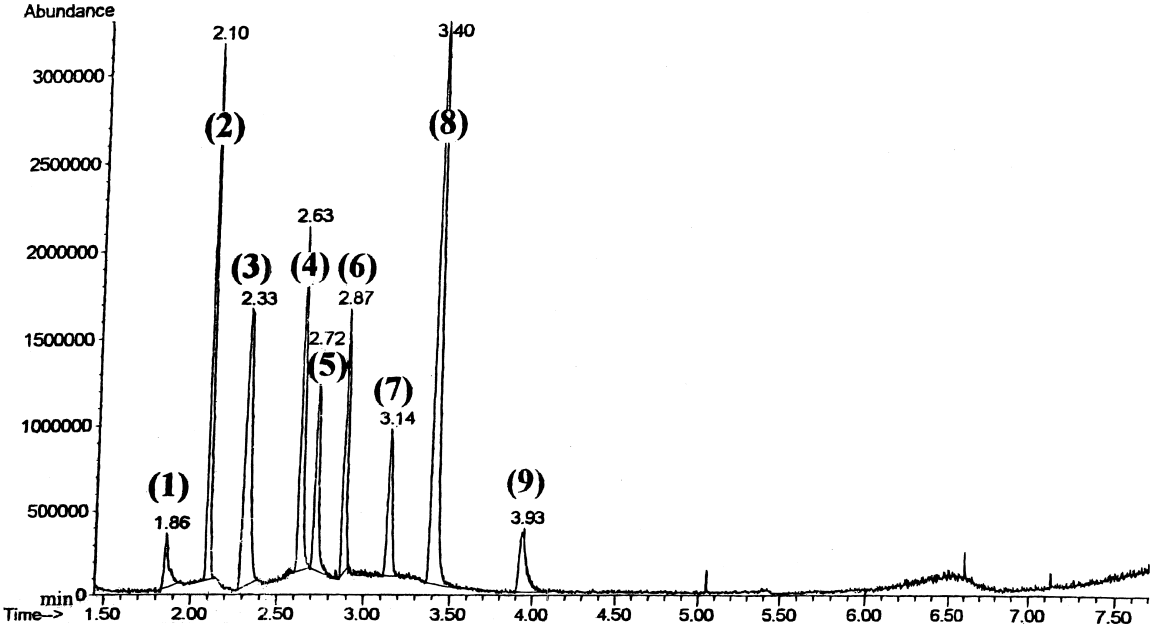

Fig. 2. GC–MS-Scan total ion chromatogram of MTBE and its non-acid degradation products (25 mg/L; carbon dioxide, concentration unknown) in aqueous solution on DB-FFAP column (30 m×0.25 mm I.D., film thickness 0.25 μm): (1) carbon dioxide dissolved from the air, (2) MTBE, (3) acetaldehyde, (4) acetone, (5) methyl acetate, (6) ethyl acetate, (7) *tert*.-butyl formate, (8) *tert*.-butanol, and (9) ethanol.

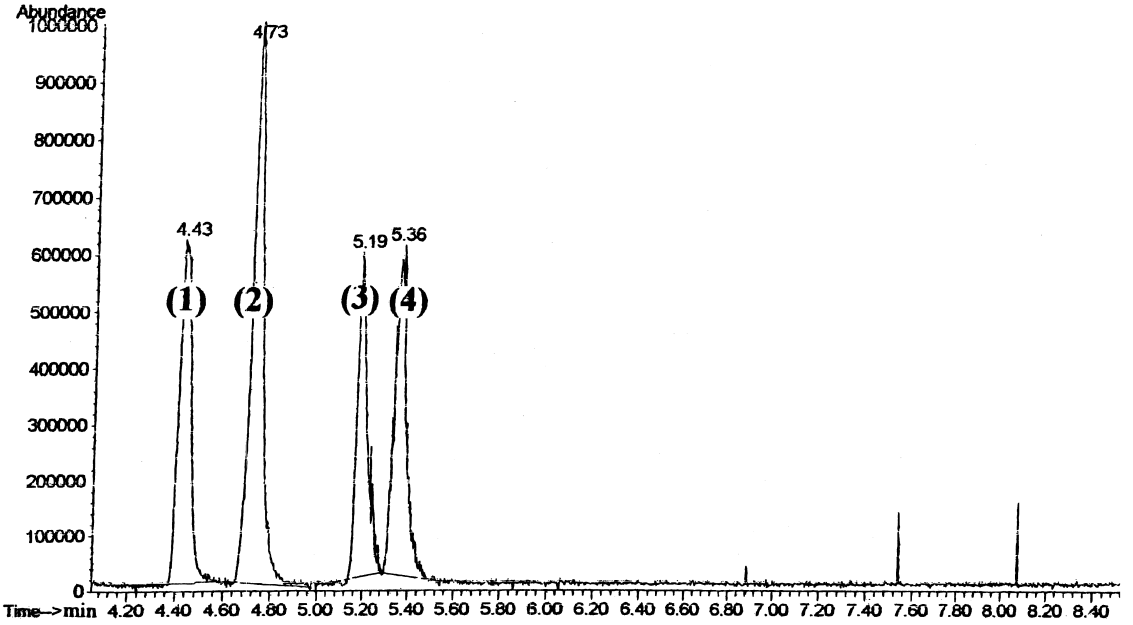

Fig. 3. GC–MS-Scan total ion chromatogram of MTBE acid degradation products (250 mg/L) in aqueous solution on DB-FFAP column (30 m×0.25 mm I.D., film thickness 0.25 μm): (1) octanol-2 (for internal standard purposes), (2) acetic acid, (3) formic acid, and (4) propionic acid.

product in our treatment systems, based on abundance and the abundance ratio of MS fragment ions (at 29, 31, and 32 m/z) and retention times on the GC–MS-Scan chromatograms for the real samples. Thus, it was excluded from our target component list for the analytical method development. It is worth mentioning that the separation of *tert*.-butanol and methanol did not improve even with on-column (cool and hot) direct aqueous injection or static headspace injection under various conditions.

Formic acid generally elutes before acetic acid on an FFAP column. The results in this work show formic acid eluting after acetic acid, confirmed both with retention times of standards and mass spectral identification. The explanation for this apparent anomaly may be based on the injection conditions. The boiling point of formic acid is lower than acetic acid (100.8 vs. 118°C), but formic acid has a lower pK_a than acetic acid (3.77 vs. 4.76), which means that formic acid has stronger hydrogen bonding to the FFAP stationary phase (SP) than acetic acid. The higher the boiling point of the analyte and the stronger the hydrogen bonding of the analyte to SP, the slower the analyte elutes on the column. Formic acid elutes before acetic acid on the FFAP column for non-direct-aqueous injection (NDAI) because the boiling point is more important than hydrogen bonding. However, much more water is in contact with the SP of the column for DAI than for NDAI. Such a large amount of water, relative to the analyte acids, could form cages or clusters around analyte acid molecules along the SP surface and enhance the hydrogen bonding to such an extent that hydrogen bonding is more important than the boiling point in determining the elution order. Thus, the acetic acid elutes before formic acid on the FFAP column for DAI (Figs. 1 and 3). Isobutyl formate can be used as the internal standard for the analysis of the non-acid components for the chromatographic conditions in Figs. 1 and 2. Octanol-2 can be used as the internal standard for the analysis of the acid components (Fig. 3). The minimum concentrations of analytes for the linear range, using SIM, were between 30 and 100 μg/L, depending on the analyte (Table 2). Formaldehyde did not form a peak or interfere with the other analytes under the conditions used. The

carbon dioxide peak was severely tailed and was not good for the quantification of carbonate and hydrogen carbonate in the solution.

Changing the sample pH from 3 to 7 changed the GC–MS responses for MTBE and its degradation products significantly (Table 3) except for MTBE, acetone, methyl acetate, ethyl acetate and *tert*.-butanol. There is no noticeable degradation of MTBE and its degradation products in an aqueous sample at pH 3 or 7 (data not shown). The optimized pH for the final solution was chosen as 7 because the results for pH 7 were satisfactory (Tables 2 and 3) and it is a convenient pH with which to work.

To examine the accuracy of the DAI–GC–MS-SIM method with the GC conditions in Figs. 2 and 3, the analyte concentrations were analyzed in the spiked solutions in treated tap water at different concentrations. The accuracy was better for MTBE, acetone, *tert*.-butanol, acetic acid, and formic acid than for methyl acetate and *tert*.-butyl formate. Ethanol and acetaldehyde had poorest accuracy (Table 4).

The retention time axis shifted to about 0.5 min longer when using the DB-FFAP column (30 m× 0.25 mm I.D.) with a greater film thickness (0.5 μm). The DAI–GC–MS conditions were the same as those for Fig. 2, except the column-head pressure was 55 kPa. The separation between analytes was not improved, and most of the peaks were even broader and more unsymmetrical. Therefore, the column with 0.25 μm film thickness was chosen for the method.

The GC conditions used for the SPB624 column (30 m×0.53 mm I.D., film thickness 3 μm) were a modification of Potter's GC–FID method [9]. Fig. 4 presents the DAI–GC–MS-Scan chromatogram of

Table 4
Analyte concentrations detected by DAI–GC–MS-SIM[a] for solutions spiked with them in different concentrations

	Analyte concentration (mg/L)		
	Spiked 0.200 mg/L	Spiked 20.0 mg/L	Spiked 200 mg/L
MTBE	0.19	21.0	205
Acetaldehyde	0.13	16.5	174
Acetone	0.21	21.2.	188
Methyl acetate	0.18	21.8	184
Ethyl acetate	0.22	21.0	210
tert.-Butyl formate	0.22	18.5	185
tert.-Butanol	0.19	19.4	211
Ethanol	0.17	23.2	219
Acetic acid	0.19	19.4	210
Formic acid	0.22	21.2	191

[a] The GC conditions were the same as in Fig. 2 or Fig. 3, depending on the compound. The pH for spiked solutions was adjusted to 7. Octanol-2 was used as internal standard for acid components. Each detected concentration was the average value from two injections.

Table 3
Effect of solution pH on GC–MS-Scan chromatographic peak heights ($\times 10^{-4}$) and variation[a]

Component	pH 7		pH 3	
	Average peak height	Variation[b]	Average peak height	Variation[b]
MTBE	2012	0.0245	1941	0.0380
Acetaldehyde	820	0.0623	1042	0.0602
Acetone	1503	0.0294	1882	0.0457
Methyl acetate	583	0.0526	460	0.0657
Ethyl acetate	694	0.0467	721	0.0598
tert.-Butyl formate	499	0.0669	553	0.1265
tert.-Butanol	2269	0.0490	2314	0.0278
Ethanol	205	0.0712	332	0.1020
Octanol-2	396	0.0512	496	0.0330
Acetic acid	1197	0.0330	1533	0.0405
Formic acid	588	0.0512	692	0.0625
Propionic acid	821	0.0583	1034	0.1189

[a] The GC conditions were the same as in Fig. 2 or Fig. 3, depending on the compound. The concentration was 20 mg/L for each.
[b] Variation for each component is the standard deviation for the concentrations obtained from three analyses divided by the average of the concentrations. Octanol-2 can be the internal standard for the quantification of the acids in the table.

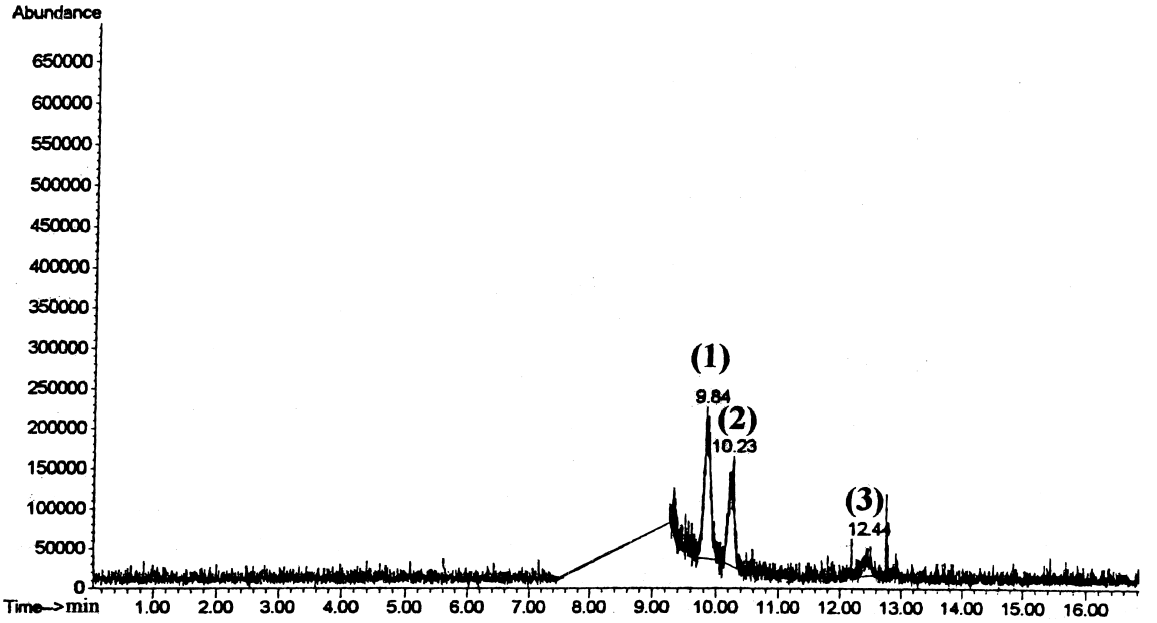

Fig. 4. GC–MS-Scan chromatogram of MTBE and its degradation products (50 mg/L) in aqueous solution on SPB624 column: (1) *tert.*-butanol, (2) MTBE, and (3) acetic acid.

aqueous solutions of MTBE and its possible degradation products using the SPB-624 column. The minimum limit of detection in the scan mode was 50 mg/L for acetic acid and 10 mg/L for *tert.*-butanol and MTBE. Methanol and formaldehyde coeluted with water and became non-detectable. The minimum limit of detection in the SIM mode was 1 mg/L for acetic acid and 0.05 mg/L for *tert.*-butanol and MTBE. The GC–MS-SIM responses were linear with concentration for MTBE and *tert.*-butanol, but not for acetic acid (Table 2). The cyano group on the stationary phase of the SPB-624 column is protonphilic and Lewis basic. Thus the SPB-624 column has the tendency to ionize organic acids and is not suitable for acid analysis. A 0.5 μL volume rather than 1 to 5 μL as used by Potter for his DAI–GC–FID method [9] was used on the DAI–GC–MS because MTBE could not be separated from *tert.*-butanol when the injection volume was 1 μL or more.

Considering the high content of non-volatile substances in the samples, only split and splitless injection modes were tested for GC–FID with the SPB624 column above because they are more tolerant of non-volatile substances [14]. The peaks were broad and MTBE could not be separated from *tert.*-butanol for the test on the splitless injection mode. When the split ratio was equal to or less than 1:5 this problem was resolved. For the split ratio of 1:10, the calibration equation for MTBE was 'mg/L = peak height · 3.3 − 10.89' with $R^2 = 0.989$. The detection limit was 0.5 mg/L, about 20 times higher than Potters [9].

The separation, sensitivity and response linearity for MTBE and acetone on DAI–GC–FID with the DB-FFAP column (30 m × 0.25 mm I.D., film thickness 0.25 μm) (Fig. 5 and Table 2) were similar to those on DAI–GC–MS-Scan shown in Fig. 2. The other analytes seen in Figs. 2 and 3 were not further explored using DAI–GC–FID because DAI–GC–MS was obviously better. However, DAI–GC–FID with the DB-FFAP column should be able to analyze all of the products except acetaldehyde, formic acid and acetic acid. FID is not a proper detection method for analyzing acetic acid, formic acid, or acetaldehyde, due to lack of sensitivity.

The motivation for using the FFAP column to analyze MTBE and its degradation products from the Fenton reaction is as follows. First, the degradation products are more polar than MTBE due to the

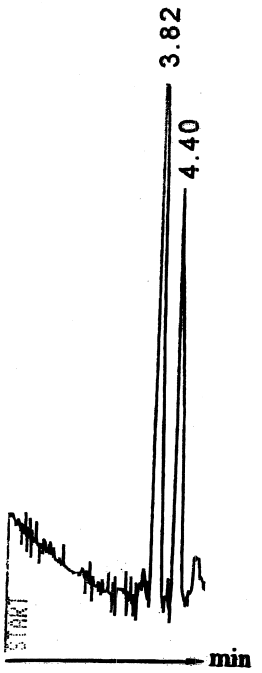

Fig. 5. GC–FID chromatogram of MTBE and its degradation products (20 mg/L) in aqueous solution on a DB-FFAP column (30 m×0.25 mm I.D., film thickness 0.25 μm): (1) MTBE, (2) *tert*.-butanol, and (3) acetic acid.

nature of the hydroxyl free radical oxidation; the highly polar PEG column should be better for those polar analytes. Second, the volatile organic acids should also be part of the products, and the FFAP column, with an acid-modified PEG stationary phase, is better than the pure PEG column for such an analysis. Volatile organic acids were not analyzed in the Church et al.'s DAI–GC–MS method with the PEG column [8]. Volatile organic acids are prone to tail and broaden on PEG columns. Third, columns with cross-linked and bonded FFAP stationary phases which can tolerate a few microliter aqueous injections are now commercially available. Compared with the pure PEG column, the FFAP column is more polar and retains water more strongly. Thus, the GC conditions, such as temperature programming and water venting, and the retention time of some analytes were different for the two columns. The higher sensitivity achieved by Church et al. [8] is likely due to the combination of their MS detector (Finnigan 4000) with higher vacuuming capacity and inlet liner instead of the PEG column alone. In other words, if the FFAP column were used with that GC–MS system, it is very likely that similar sensitivity would be obtained. The authors attempted to improve the sensitivity of this method by adapting the inlet settings of Church et al.'s group [8] after their work was published. However, their inlet setting on our GC system coupled to the bench-top HP5971A MS system did not improve the sensitivity. Instead, it broadened the peaks and deteriorated the separation. Such problems may be due to the slower removal of the large volume of water (10 μL) on our bench-top MS system.

The degradation products found with this analytical method for aqueous MTBE solution treated with the Fenton and electrochemical Fenton methods were: carbon dioxide, acetaldehyde, acetone, methyl acetate, *tert*.-butyl formate, and *tert*.-butanol. Acetaldehyde was found in only a few treated samples at concentrations near the minimum detection limit. No ethanol and methanol were found. This method was not able to analyze formaldehyde. Chen et al. reported that *tert*.-butyl formate and 3-methoxy-3-methyl-2-butanone were tentatively identified by purge-and-trap GC–FID when treating MTBE with Fenton reagents [6]. Yeh and Novak reported that acetone and *tert*.-butanol were found by DAI–GC–FID on a packed column after treatment with a combination of the Fenton reaction and biodegradation method [7]. Japar et al. found *tert*.-butyl formate, formaldehyde, and 2-methyl-propanal by Fourier transform infrared spectroscopy (FT-IR) and GC–MS after $^{\cdot}$OH-initiated ($^{\cdot}$OH generated by photolysis of methyl nitrite) and $^{\cdot}$Cl-initiated atmospheric oxidation of MTBE [3]. Tuazon et al. found *tert*.-butyl formate, formaldehyde, methyl acetate, and acetone by FT-IR and GC–FID after oxidation of MTBE in the NO_x–air system, initiated by $^{\cdot}$OH which was generated from photolysis of ethyl nitrite [4]. Kang et al. found *tert*.-butyl formate, methyl acetate, acetone, and *tert*.-butanol by headspace GC–MS for MTBE oxidized by $^{\cdot}$OH generated by sonolysis of ozone [16]. Idriss claimed methanol as a minor product from MTBE by $^{\cdot}$OH involved atmospheric oxidation that was photocatalyzed by fly ash [5]. Obviously, the products from the oxidation of MTBE are very similar when comparing the Fenton reaction with the atmospheric NO_x–air system and

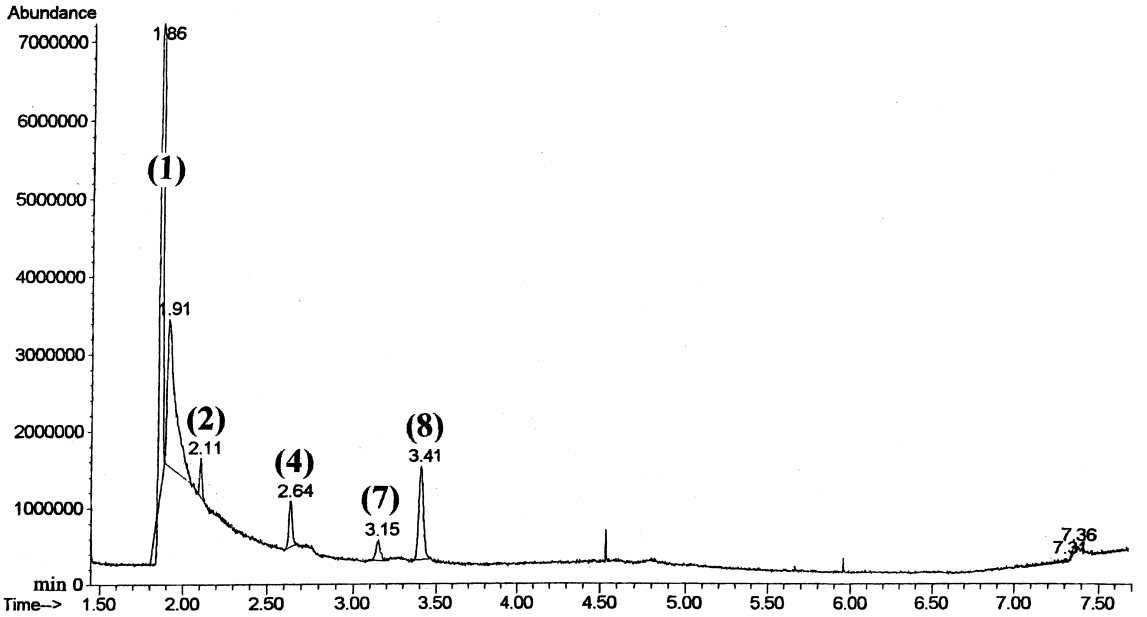

Fig. 6. DAI–GC–MS-Scan chromatogram for MTBE (200 mg/L) aqueous solution, prepared with tap water, treated by the electrochemical Fenton system for 4 min. The conditions and notation were the same as in Fig. 2.

the ozone system. All these reactions involve oxidation by ·OH. However, the quantity of each degradation product may be different due to the different features of the ·OH generation systems. In the Fenton reaction, it can be more complicated because Fe(II) and Fe(III) can participate in the redox reaction and complex with the chemicals in the system.

Fig. 6 is a DAI–GC–MS-Scan chromatogram for MTBE waste water, treated by the electrochemical Fenton system for 4 min. The carbon dioxide built up to such a large amount that the tailing of its peak could affect the quantification of MTBE by the scan mode. However, this problem was overcome by the DAI–GC–MS-SIM. Fig. 7 presents the DAI–GC–MS-SIM chromatogram for the volatile acids in the sample.

4. Conclusions

The method of choice developed to analyze MTBE and its degradation products by GC–MS and GC–FID with DAI uses the FFAP-type column, with dimensions of 30 m×0.25 mm I.D., film thickness 0.25 μm. The optimized GC conditions for the non-acid components were as follows: column-head pressure, 62 kPa; MS vacuum, $5.4 \cdot 10^{-3}$ Pa; carrier gas flow-rate, 1 mL/min; water vent, 7.7 min to the end of the run; oven temperature at 35°C for 5.5 min, then ramped to 90°C at 25°C/min, then ramped to 200°C at 40°C/min and held at 200°C for 8 min. The conditions for the acid components were: column-head pressure, 103 kPa; MS vacuum, $5.9 \cdot 10^{-3}$ Pa; carrier gas flow-rate, 1 mL/min; water delay, 4 min; oven temperature at 110°C for 2 min, then ramped to 150°C at 10°C/min, then ramped to 200°C at 40°C/min. Direct aqueous injection using optimized sample preparation and GC conditions makes the analytical method developed in this research accurate (for most analytes), simple, fast, and reproducible for the analysis of MTBE and its degradation products. The minimum concentrations for the linear range for the SIM mode under the optimized conditions were 30 to 100 μg/L, depending on the analyte. The minimum detection limit was 1 mg/L for MTBE and *tert*.-butanol when using FID to replace MS. Fewer components were able to be analyzed with the cyanopropylphenyl/dimethylpolysiloxane-type column (SPB624) than the FFAP-type column.

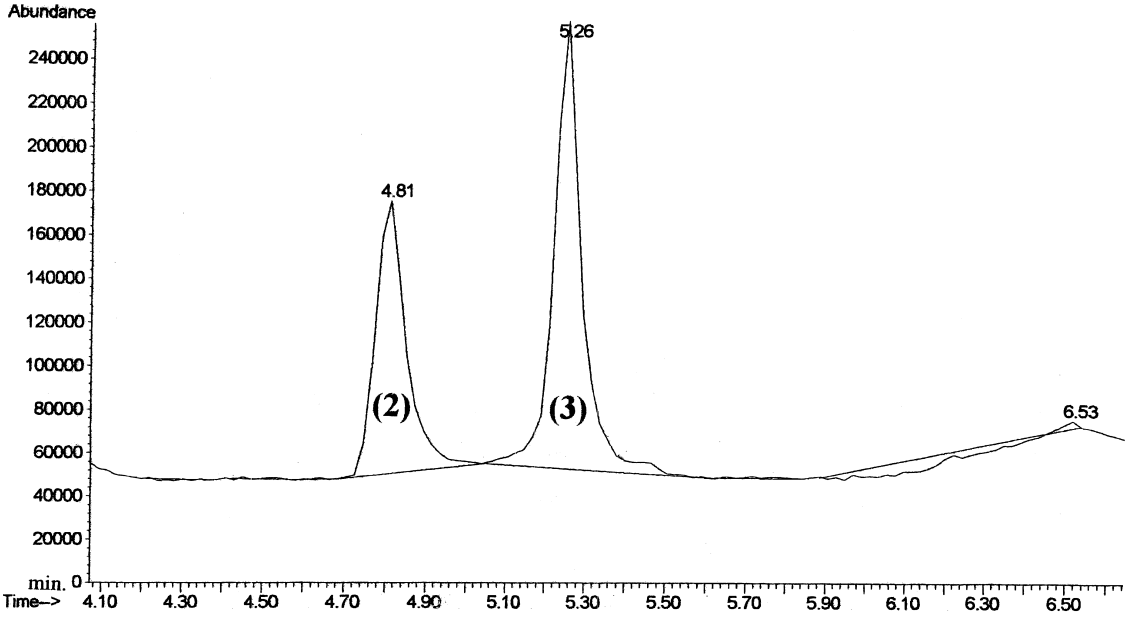

Fig. 7. DAI–GC–MS-SIM chromatogram for MTBE (200 mg/L) aqueous solution, prepared with tap water, treated by the electrochemical Fenton system for 4 min. The GC conditions and notation were the same as in Fig. 3.

Acknowledgements

Our appreciation is extended to Michael Ames and David Saltmiras for helpful technical support and discussion.

References

[1] G.C. Delzer, J.S. Zogorski, T.J. Lopes, R.L. Bosshart, Occurrence of the gasoline oxygenate MTBE and BTEX compounds in urban stormwater in the United States, 1991–1995, Water-Resources Investigations Report 96-4145, US Geographical Survey, Denver, 1996.
[2] P.J. Squillace, J.F. Pankow, N.E. Korte, J.S. Zogoriski, Environ. Toxicol. Chem. 16 (1997) 1836.
[3] S.M. Japar, T.J. Wallington, J.F.O. Richert, J.C. Ball, Int. J. Chem. Kinet. 22 (1990) 1257.
[4] E.C. Tuazon, W.P.L. Carter, S.M. Aschmann, R. Atkinson, Int. J. Chem. Kinet. 23 (1991) 1003.
[5] H. Idriss, A. Miller, E.G. Seebauer, Catal. Today 33 (1997) 215.
[6] C.T. Chen, A.N. Tafuri, M. Rahman, M.B. Foerst, E. Pfetzing, M. Taylor, Oxidation of methyl *tert*.-butyl ether (MTBE) using Fenton's reagent, in: 88th Annual Meeting and Exhibition for Air & Waste Management Association, San Antonio, TX, 18–23 June, 1995.
[7] C.K. Yeh, J.T. Novak, Water Environ. Res. 67 (1995) 828.
[8] C.D. Church, L.M. Isabelle, J.F. Pankow, D.L. Rose, P. Tratnyek, Environ. Sci. Technol. 31 (1997) 3723.
[9] T.L. Potter, Ground Water Monit. Remed. 16 (1996) 157.
[10] C. Walling, Acc. Chem. Res. 8 (1975) 125.
[11] K. Pratap, A.T. Lemley, J. Agric. Food Chem. 46 (1998) 3285.
[12] S. Hong, A.T. Lemley, J. Chromatogr. A 822 (1998) 253.
[13] S. Kotrly, L. Sucha, Handbook of Chemical Equilibria in Analytical Chemistry, Ellis Horwood, Chichester, 1985.
[14] K. Grob, On-column Injection in Capillary Gas Chromatography, 2nd ed., Hüthig, Heidelberg, 1991.
[15] K. Grob, Split and Splitless Injection in Capillary Gas Chromatography, 3rd ed., Hüthig, Heidelberg, 1993.
[16] J. Kang, M.R. Hoffmann, Environ. Sci. Technol. 32 (1998) 3194.