http://dx.doi.org/10.5012/bkcs.2012.33.5.1693

Determination of MTBE, TBA and BTEX in Soil by Headspace Gas Chromatography-Mass Spectrometry

Ho-Sang Shin

Department of Environmental Education, Kongju National University, Kongju 314-701, Korea. E-mail: hshin@kongju.ac.kr
Received January 5, 2012, Accepted February 17, 2012

A headspace gas chromatographic mass spectrometric (GC-MS) assay method was developed for the simultaneous determination of methyl tertiary butyl ether (MTBE), *tert*-butyl alcohol (TBA) and benzene, toluene, ethyl benzene and xylene (BTEX) in soil contaminated with gasoline. 2 g of soil sample were placed in a 10 mL headspace vial filled with 5 mL of phosphoric acid solution (pH 3) saturated with NaCl, and the solution was spiked with fluorobenzene as an internal standard and sealed with a cap. The vial was heated in a heating block for 40 min at 80 °C. The detection limits of the assay were 0.08-0.12 μg/kg for the analytes. For five independent determinations at 10 and 50 μg/kg, the relative standard deviations were less than 10%. The method was used to analyze fifty six soil samples collected from various regions contaminated with gasoline in Korea. The developed method may be valuable for the monitoring of the analytes in soil.

Key Words : MTBE, TBA, BTEX, Soil, HS GC-MS

Introduction

Methyl *tert*-butyl ether (MTBE) is used throughout the world as an antiknock additive that increase the octane number and it has gained much attention over the past decade because of its widespread contamination in the environment as a result of leaking underground fuel storage tanks. *Tert*-butyl alcohol (TBA) is a degradation intermediate of MTBE and is also applied as a fuel additive.[1] MTBE is considered to be a possible human carcinogen and TBA is considered to be a probable human carcinogen by the US Environmental Protection Agency (EPA).[2,3] Benzene, toluene, ethyl benzene and xylene (BTEX) are also major constituents of gasoline, and MTBE, TBA and BTEX are contaminated in soil at the same time.

MTBE, TBA and BTEX in soil are frequently measured using standard U.S.EPA methods 8015 and 8021.[4,5] Method 8015 is a determinative method by gas chromatography-flame ionization detector (GC-FID). FID is non-selective detector and creates a potential for many non-target compounds present in samples to interfere with this analysis. Method 8021 is a determinative method of aromatic and halogenated volatiles by GC using photoionization (PID) and/or electroconductivity (ElCD) detectors. PID or EICD is most sensitive to compounds that contain double bonds but MTBE and TBA do not contain double bonds. Therefore, the detection of MTBE and TBA by PID or EICD may be subject to interference and false positives when real soil samples contain significant amounts of other contaminants such as petroleum hydrocarbons. And this method is not recommended as a determinative method for MTBE and TBA. Mass spectrometry (MS) has the potential to become a standard analytical tool for simultaneous detecting these compounds and sensitive analysis is usually accomplished by GC-MS. Therefore, method 8260 offers the advantages of unambiguous identification and sensitive detection of target compounds from soil,[6] but this method has not been validated for use with MTBE and TBA.

Another important point taking into consideration for the analysis of MTBE, TBA and BTEX in soil is the sample preparation method. Although many procedures utilize generally GC to quantify the analytes, they differ substantially with respect to sample extraction and concentration. Purge and trap (P&T) is by far the most frequently applied technique for the extraction and concentration of MTBE, TBA and BTEX in soil[7-9] and in water.[10,11] However, it can produce false quantification of MTBE and TBA in hydrocarbon mixtures due to contamination in the P&T system with the target or non-target compounds having similar retention times in the presence of high concentrations of hydrocarbons. To date many specific and highly sensitive methods for MTBE, TBA and BTEX analysis in water,[12-21] soil[22] or gasoline[23] have been developed by headspace solid phase microextraction (SPME). The methods have many advantages in it being convenient and having rapid and automatic extraction, but other limitations such as its elevated cost due to use the SPME fibre and the short life time of the fibre. Among other conventional methods, solvent extraction method,[24] a vacuum distillation (VD)[25,26] and headspace (HS) procedure[27-29] can be used for MTBE, TBA and BTEX in soil samples. HS is recommended for the determination of MTBE, TBA and BTEX in soil samples in a viewpoint of reproducibility and analysis time, but no sufficient validation data of HS in conjunction with GC-MS has been published. We published a head space (HS) procedure of the trace MTBE, TBA and BTEX in water combined with analysis of gas chromatography-mass spectrometry-selected ion monitoring (GC-MS-SIM).[30]

This paper describes a HS procedure of the trace MTBE, TBA and BTEX in soil combined with analysis of GC-MS-

SIM). This paper focuses on the validation of sample conservation, preparation and detection methodologies. The developed method was applied to the determination of MTBE, TBA and BTEX in soil contaminated with petroleum hydrocarbons in Korea.

Experimental

Reagents and Chemicals. MTBE, TBA, benzene, toluene, ethyl benzene, xylene and fluorobenzene were purchased from Aldrich (St. Louis, MO, USA). Analytical grade sodium hydrogensulfate monohydrate, sodium chloride, phosphoric acid, acetone and methanol were from J. T. Baker (Phillipsburg, NJ, USA). Water was purified by milli-Q equipment (Millipore Corp., Milford, MA, USA).

Performance Sample Preparation. Soil was collected from non-polluted sites for the performance sample preparation. Loss on ignition was 15.8% and particle size analysis by dry sieving gave the following results; gravel 14.4%, sand 68.7% and silt (including clay) 16.9%. The primary soil sample was air dried for 24 hours and sieved. Particle size fraction of < 2 mm was used for all experiments. For the preparation of performance samples, sub samples of soil fraction were selected randomly and were spiked with a methanol based standard, and immediately capped with Teflon-faced silicon septa.

Soil Sample Collection. Soil samples were collected from contaminated sites to evaluate the performance of the sampling procedure. Samples were collected with a Terra Core sampler (En Novative Technologies, Industrial Drive Green Bay, WI, USA) at a depth > 0.5 m near the underground fuel storage tank. The soil was drilled with an electric push-hammer (diameter 50 mm) and a hydraulic push machine that was used to survey the soil profile and to gather the sample.

For composite sampling for soil analysis, core samples were collected and cut into sections at 20, 40, 60 and 80 cm below the ground surface. After each cut, approximately 2.0 g of soil was removed from the newly exposed surface (top end of the cut) using a truncated syringe and placed in a preweighed 10-mL headspace vial filled with 5 mL of phosphoric acid solution (pH 3) saturated with NaCl. A second 2.0 g sample was removed from each core at the 20, 40, 60, and 80 cm intervals and combined in a preweighed 40-mL vial containing 5 mL of phosphoric acid solution. All soil samples were stored at 4 °C before further analysis. Moisture contents in soil were calculated by the weight difference before and after heating in an oven for 4 hours at 110 °C.

Extraction Procedure. 2.0 g of soil sample were placed in a 10 mL headspace vial filled with 5 mL of phosphoric acid solution (pH 3) saturated with NaCl, and the solution was spiked with 50 ng of fluorobenzene (F-benzene) as an internal standard and sealed with a cap. The vial was placed in a heating block for 40 min at 80 °C (± 0.1 °C).

Soil Preservation Method. Soil samples should be properly preserved to avoid losses of VOCs. Four different additives for VOCs conservation (water, methanol, $NaHSO_4$ solution and phosphoric acid solution (pH 2) saturated with NaCl) were tested. Soil samples controlled to the concentration of 20-30 μg/kg with MTBE, TBA and BTEX standards in soil contaminated with gasoline were used for the experiments. 2 g of soil sample were placed in a 10 mL headspace vial filled with 5 mL of three different conservation solutions, sealed tightly with a cap, and cooled to 4 °C until analysis. Recoveries of spiked soil samples after 1, 2, 3 and 4 weeks were calculated. Three replicates of each treatment were analyzed.

Table 1. GC-MS conditions used for the analysis of MTBE, TBA and BTEX

Conditions	Value		
Column	30 m × 0.25 mm i.d. × 0.25 μm film Innowax		
Carrier gas	He at 0.9 mL/min		
Oven temperature	35 °C (1 min) to 70 °C (3 min) at 5 °C/min		
Split Ratio	1 : 10		
Injector temperature	250 °C		
Transfer temperature	280 °C		
Selected ion group	Group	Start time (min)	Selected ions, *m/z*
	1	1.0	73, 57, 41
	2	2.2	59, 57
	3	3.0	78,
	4	3.5	96
	5	4.2	91, 92
	6	5.5	91, 106

Gas Chromatography-Mass Spectrometry. An Agilent 6890/5973 N instrument and a Combipal Autosampler (Agilent Technologies, Santa Clara, CA, USA), which allows automated HS injections, were used. The ion source was operated in the electron ionization mode (EI; 70 eV, 230 °C). Full-scan mass spectra (*m/z* 40-800) were recorded for the identification of analytes at a high concentration. Confirmation of trace chemicals was completed by two MS characteristic ions, the ratio of the two MS characteristic ions and GC-retention times matches to the known standard compounds. The ions selected in this study and the operating parameters of the GC-MS are shown in Table 1.

Calibration and Quantification. Calibration curves for MTBE, TBA and BTEX were established by extraction after adding 1.0, 10, 50, 200, 1000 and 2000 ng of standards and 50 ng of internal standard (F-benzene) to 2.0 g of soil. The ratios of the peak area of standard to that of internal standard were used in the quantification of the compounds. The final concentrations of the analytes were compensated with water contents in soil.

Results and Discussion

Optimization of Headspace Conditions. Method optimization was principally performed on the selection of the best headspace temperature and heating time for the simultaneous analysis of MTBE, TBA and BTEX in the soil samples.

The influence of temperature of headspace generation was

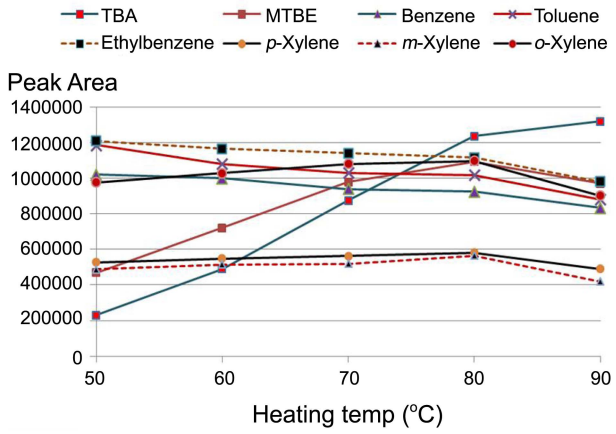


Figure 1. Changes in peak area of target compounds according to the change of heating temperature (Each point means average value of analyzing three spiked soil samples and errors were less than 9.0%).

studied as following: Preliminary tests at 50, 60, 70, 80 and 90 °C were performed by analyzing three spiked soil samples and the peak area of each compound was used for the comparison. BTE showed the highest intensity at a low temperature (50 °C), and the intensity slightly decreased at the temperature higher than 50 °C as shown in Figure 1. Thus BTE may be lost or partly at heating temperatures above 50 °C. But MTBE showed the highest intensity at 80 °C and the intensity rapidly decreased at the temperature lower or higher than 80 °C due to its high solubility in water. Otherwise, the intensity of TBA peak increased still to 90 °C. The decrease of MTBE peak and the increase of TBA peak above 80 °C show the possibility of TBA production by acid hydrolysis of MTBE during heated headspace analysis as suggested by other authors.[31,32] We selected 80 °C as optimal heating temperature, because of having relatively good efficiencies for all analytes at the temperature.

The optimum heating time of the target compounds was performed by analyzing three spiked soil samples. The target compounds were analyzed at heating times of 10, 20, 30, 40, 50 and 60 min at 80 °C. The maximum peak areas of all analytes except for TBA were obtained in 40 min of heating time (Fig. 2). These analytes may partly be leaked in 40 min due to cap losses. The intensity of TBA peak increased still after 50 min. The decrease of MTBE peak and the increase of TBA peak in 50 min show also the possibility of TBA production by acid hydrolysis of MTBE. Therefore, we selected 40 min as optimal heating time having relatively good efficiencies for all analytes.

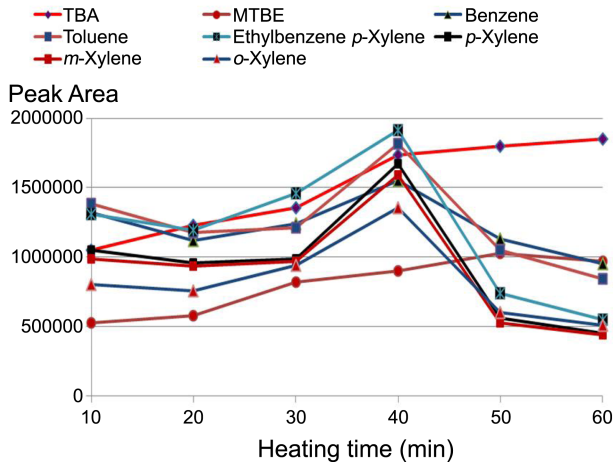


Figure 2. Changes in peak area of target compounds according to the change of heating times (Each point mean average value and errors were less than 9.0%).

Soil Preservation Method. EPA methods[2,5,6] recommend four different additives for VOCs conservation: water, methanol, $NaHSO_4$ solution and phosphoric acid solution (pH 2) saturated with NaCl. EPA methods were originally developed for the analysis of BTEX and other volatile compounds, therefore an experiment to assess the effects of storage conditions for the analysis of MTBE and TBA is needed. The goal of the study is to evaluate the stability of all target compounds on the four different conservation methods: filled with pure water, filled with methanol, filled with $NaHSO_4$ solution and acidified with phosphoric acid solution (pH 3) saturated with NaCl. The pH of the phosphoric acid solution in the EPA method is originally pH 2.[27] But several authors[31,32] reported the possibility of TBA production by acid hydrolysis of MTBE during heated headspace analysis of acidified samples giving pH of between 1 and 2, and pH of sample is changed to 3 in this study.

The stability of each target compound along time was studied by calculating the percentage of recoveries of spiked soil samples after 1, 2, 3 and 4 weeks.

Considerable BTEX losses were detected during conservation with water or 1 M $NaHSO_4$ solution, and slight BTEX losses happened during conservation with methanol. In the cases of MTBE and TBA, the conservation solutions seem to be not so critical, and there is rather an increasing tendency in the case of TBA. The biodegradation of MTBE to TBA is suggested to be occurred during conservation with water and 1 M $NaHSO_4$ solution. When the phosphoric acid solution (pH 3) saturated with NaCl was used as a conservation additive, all target compounds showed the best stability (Table 2). Moreover, MTBE recoveries were not found appreciably lower to prove the hydrolysis.

Verification of Method Performance. For the GC separation of BTEX, MTBE and TBA, the use of the semi polar stationary phase was found to be efficient. A chromatograms is shown in Figure 3. As can be seen from the figure, the peaks of BTEX, MTBE and TBA and internal standard are symmetrical and separation of the analytes from the background compounds in the soil samples was good. The retention times of MTBE, TBA, benzene, F-benzene (ISTD), toluene, ethylbenzene, *p*-xylene, *m*-xylene and *o*-xylene were 1.55, 2.75, 3.13, 3.81, 4.63, 6.34, 6.52, 6.57 and 7.75 min, respectively. The main contamination sources of BTEX, MTBE and TBA in soils include the spill of petroleum and the interference of considerable kinds of hydrocarbons such as gasoline and kerosene constituents was predictable in the analysis of the soil. In order to verify the performance of the developed procedure, it was evaluated the interference of

Table 2. Concentration change (mean ± SD, μg/kg) of BTEX, MTBE and TBA in soil by several conservation methods

Compound	Conservation solution	Elapsed time after sample preparation (week)				
		0	1	2	3	4
BTEX	Water	23.1 ± 1.5	20.7 ± 2.2	13.4 ± 1.2	12.2 ± 1.8	11.1 ± 1.9
	1 M $NaHSO_4$	23.1 ± 1.5	21.3 ± 1.8	16.5 ± 1.8	15.2 ± 1.9	14.7 ± 2.3
	Methanol	23.1 ± 1.5	22.9 ± 1.5	18.1 ± 1.1	17.9 ± 1.7	17.5 ± 1.5
	Phosphoric acid solution (pH 3)	23.1 ± 1.5	23.0 ± 2.5	22.9 ± 2.5	22.9 ± 2.1	22.0 ± 2.0
MTBE	Water	26.4 ± 1.2	23.2 ± 3.1	22.3 ± 2.6	22.0 ± 2.9	21.0 ± 3.0
	1 M $NaHSO_4$	26.4 ± 1.2	23.9 ± 2.5	23.2 ± 2.8	22.7 ± 2.8	21.9 ± 2.2
	Methanol	26.4 ± 1.2	24.6 ± 2.4	24.3 ± 2.3	23.8 ± 2.3	22.9 ± 1.9
	Phosphoric acid solution (pH 3)	26.4 ± 1.2	25.9 ± 2.9	25.3 ± 2.5	25.2 ± 2.2	25.1 ± 2.6
TBA	Water	25.2 ± 1.8	25.7 ± 2.3	25.9 ± 2.4	26.2 ± 2.7	26.6 ± 3.4
	1 M $NaHSO_4$	25.2 ± 1.8	25.4 ± 2.5	25.8 ± 2.7	26.1 ± 2.3	26.4 ± 3.5
	Methanol	25.2 ± 1.8	25.1 ± 2.1	25.6 ± 2.3	25.8 ± 2.5	25.9 ± 2.7
	Phosphoric acid solution (pH 3)	25.2 ± 1.8	25.0 ± 1.9	25.5 ± 1.7	25.1 ± 2.0	25.5 ± 1.7

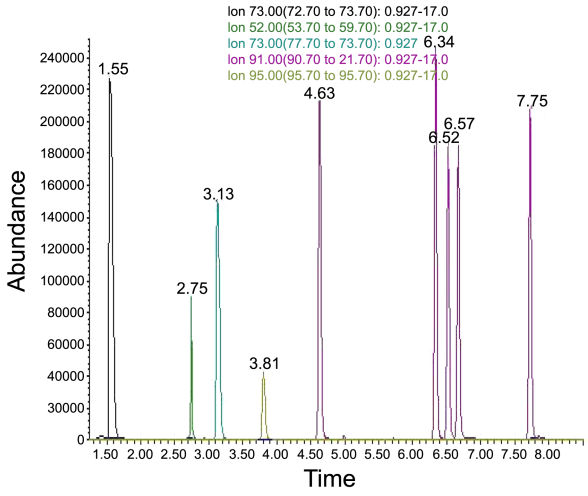


Figure 3. Chromatogram of standards of MTBE, TBA and BTEX extracted from soil spiked in the concentration of 25 μg/kg. 1.55: MTBE, 2.75: TBA, 3.13: Benzene, 3.81: ISTD (F-Benzene), 4.63: Toluene, 6.34: Ethylbenzene, 6.52: *p*-Xylene, 6.57: *m*-Xylene, and 7.75: *o*-Xylene in the chromatogram above.

increasing amounts of the commercial kerosene or diesel in the concentration from 1000 mg/kg to 10,000 mg/kg. We can notice that the presence of hydrocarbons does not interfere on BTEX, MTBE and TBA determination in contaminated soils. There were no extraneous peaks observed in a chromatogram of spiked soil in the time range of between 1.0 and 8.0 min.

Calibration curves of MTBE, TBA and BTEX were constructed by extraction of spiked soil samples. Examination of the typical standard curve by computing a regression line of peak area ratios for BTEX, MTBE and TBA to the internal standard on concentration using a least-squares fit demonstrated a linear relationship with correlation coefficients being greater than 0.995 (Table 3).

The method detection limit (MDL) was defined by 3.14 times of standard deviation for replicate determinations (n = 7) from samples spiked at the concentration of 0.05 μg/kg in soil,[33] in which MDL was calculated to 0.08-0.12 μg/kg for BTEX, MTBE and TBA, respectively (Table 4). The high sensitivity of the target compounds by HS GC-MS permits the determination of target compounds well below those reported previously (Table 4).

The range and standard deviation values for the precision and accuracy are given in Table 5. For five independent determinations at 10.0 and 50.0 μg/kg, precision (the coefficient of variation) was less than 10% and accuracy was in the range of 70-110%.

The choice of an appropriate method depends on the individual compounds, the matrix to be investigated and the concentration ranges to be analyzed. SPME methods in the analysis of BTEX, MTBE and TBA in water have many

Table 3. Calibration curves and MDLs of MTBE, TBA and BTEX in soil

Compound	Linear regression	Concentration range (μg/kg)	Correlation coefficient	MDL (μg/kg)
MTBE	Y = 0.0129x + 0.0286	0.5 - 1000	0.9954	0.09
TBA	Y = 0.0120x + 0.0148	0.5 - 1000	0.9964	0.12
Benzene	Y = 0.0323x + 0.0367	0.5 - 1000	0.9962	0.08
Toluene	Y = 0.0512x + 0.1587	0.5 - 1000	0.9958	0.08
Ethylbenzene	Y = 0.0552x + 0.082	0.5 - 1000	0.9985	0.09
p-Xylene	Y = 0.0390x + 0.0964	0.5 - 1000	0.9983	0.08
m-Xylene	Y = 0.0410x + 0.0786	0.5 - 1000	0.9979	0.08
o-Xylene	Y = 0.0465x + 0.0533	0.5 - 1000	0.9983	0.09

Table 4. Comparison of MDL levels in soil samples

Reference	Matrix	Extraction	Measurement	MDL (μg/kg or μg L^{-1})		
				BTEX	MTBE	TBA
[5,8]	Soil	P&T[a]	GC-PID	0.05-0.2	-	-
[6,22]	Soil	VD[b]	GC/MS	0.5-1.7	-	-
[9]	Soil	P&T	GC/MS	0.33-1.63	0.13	1.36
[9]	Water	P&T	GC/MS	0.04-0.34	0.12	1.44
[13]	Water	HS-SPME[c]	GC/MS	-	0.01	-
[18]	Water	SPME	GC/MS	-	0.008	-
[19]	Water	SPME	GC/MS	-	1.0	2.0
[21]	Soil	SPME	GC/MS	10-50-	-	-
[22]	Soil	SE[d]	GC-FID	-	500	-
This	Soil	HS[e]	GC/MS	0.08-0.09	0.09	0.12

a=purge and trap; b=vacuum distillation; c=solid-phase microextraction; d=solvent extraction; e=headspace

Table 5. Intra-laboratory precision and accuracy results for the analysis of MTBE TBA and BTEX in soil

Compound	Spiked Conc. (μg/kg)	Measured Conc. (μg/kg)					Mean ± SD (RSD%)	Accuracy (%)	Precision (%)
MTBE	10	8.7	8.8	9.9	10.8	9.2	9.5 ± 0.9 (9.24)	94.8	9.24
	50	42.6	48.3	52.3	43.8	48.9	47.2 ± 4.0 (8.40)	94.4	8.40
TBA	10	8.8	8.2	8.6	9.2	8.5	8.7 ± 0.4 (4.29)	86.6	4.29
	50	43.7	45.7	52.8	47.4	52.8	48.5 ± 4.2 (8.57)	99.0	8.57
Benzene	10	10.3	10.9	12.2	10.5	10.4	10.9 ± 0.8 (7.2)	109	7.20
	50	43.3	52.1	48.8	53.6	49.6	49.5 ± 3.95 (7.99)	99.0	7.99
Toluene	10	8.4	8.7	9.5	8.9	7.5	8.6 ± 0.7 (8.54)	86.0	8.54
	50	50.7	45.3	53.3	46.4	55.6	50.3 ± 4.4 (8.76)	101	8.76
Ethylbenzene	10	9.0	9.1	9.6	10.1	8.6	9.3 ± 0.6 (6.26)	92.8	6.26
	50	46.6	53.3	49.2	44.1	54.3	49.5 ± 4.33 (8.76)	99.0	8.76
p-Xylene	10	6.9	7.2	7.8	8.1	6.4	7.3 ± 0.7 (9.39)	72.8	9.39
	50	51.3	46.9	42.3	50.3	54.8	49.1 ± 4.74 (9.65)	98.2	9.65
m-Xylene	10	7.2	7.1	7.7	7.9	6.6	7.3 ± 0.5 (7.05)	73.0	7.05
	50	51.1	48.5	46.3	47.9	56.4	50.0 ± 3.95 (7.90)	100	7.90
o-Xylene	10	8.4	8.2	9.5	9.6	8.3	8.8 ± 0.7 (7.83)	88.0	7.83
	50	48.7	44.8	47.1	53.2	54.8	49.7 ± 4.2 (8.42)	99.4	8.42

merits, in which is convenient, rapid, robotic and sensitive.[13,18,19,22] However, the method has the disadvantages in the investigation of contaminated soil because of the sorption competition by frequently found co-contaminants needs to be considered and the limited lifetime of the fiber. Especially, another drawback in the simultaneous investigation method of BTEX, MTBE and TBA in contaminated soil is the limitation of adsorption/partitioning fibers optimal all together to the analytes having various physicochemical properties. Therefore, the HS GC-MS developed from this study is recommended for the simultaneous determination of BTEX, MTBE and TBA in contaminated soil.

Soil Analysis. We analyzed MTBE, TBA and BTEX in 56 soil samples taken at the contaminated sites in near of underground fuel storage tanks in Korea. All samples were collected in duplicate and the reported result is the average of the two samples. After the samples were collected in headspace vials containing 5 mL of phosphoric acid solution, 50 ng of internal standard (fluorobenzene) were added in the solution as soon as possible, and then the vial was sealed with a cap to prevent the further loss. Because the vial is never opened during the sample conservation and analysis, the analytes can be prevented the loss.

The soil concentration of MTBE, TBA and BTEX are studied in two aspects. The first aspect involves applicability test of new developed method through overall procedures. The second involves the correlations between MTBE and TBA, and BTEX in soil at individual sites, respectively.

From the analytical result, the samples revealed MTBE concentrations in the range of 1.7-1,911.4 μg/kg, TBA concentrations in the range of 0.6-2,237.7 μg/kg and total BTEX concentrations in the range of 1.1-689.4 μg/kg. The median and mean concentrations found at the contaminated sites were 102.1 and 201.2 μg/kg for MTBE, 40.8 and 89.6 μg/kg for TBA, and 55.0 and 101.7 μg/kg for total BTEX. In most cases, BTE exhibited the lower concentration, especially at low deep from surface and in dried soil due to its high degradability and volatility. Otherwise MTBE was found at high levels in deep soil close to underground storage tank (UST).

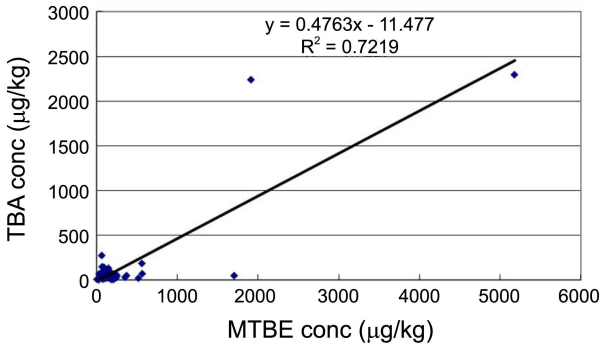


Figure 4. Correlations between MTBE and TBA in the soil at individual sites.

A problem could not be found when the developed method was applied to real samples. The method may be valuable to be used for the national monitoring of MTBE, TBA and BTEX in soil.

The correlations between MTBE and its metabolite, and other gasoline constituents (BTEX) in the soil at individual sites were constructed in Figure 4. MTBE and TBA in soil correlated relatively well with one another (r^2=0.72, P= 0.002) due to their similar physical and chemical properties, while MTBE soil concentration correlated poorly with BTEX (r^2=0.29, P=0.028). MTBE and TBA have high solubility and low affinity for soils and are most often thought to be a fast moving contaminant that forms long plumes which are difficult to remediate.[1] Because of physical and chemical properties of MTBE, MTBE can be effectively remediated by two soil treatment technologies; soil vapor extraction and low-temperature thermal desorption. Therefore, rapid finding and remediation for the contamination of the analytes in soil should be necessary before broad spreading of the contaminant.[34] In the Republic of Korea, soil quality criteria for MTBA and TBA have not established until now. Because the detection BTEX in soil cannot represent the contamination of MTBE or TBA in soil, regulation of MTBE in soil should be considered after sufficient monitoring and risk assessment.

Conclusions

In this paper, we examine the analytical parameters critical to the MTBE, TBA and BTEX headspace extraction method, an additive for conservation and GC-MS characteristics. We have discovered that HS heating temperature of 80 °C, heating time of 40 min and a phosphoric acid solution (pH 3) saturated with NaCl as conservation additive are the most effective.

The peaks of BTEX, MTBE and TBA have good chromatographic properties by using an Innowax column and show sensitive response for the EI-MS (SIM). The method was used to analyze fifty-six soil samples from various regions in Korea. The developed method may be valuable to be used for the national monitoring project of MTBE, TBA and BTEX in soil.

References

1. National Science and Technology Council, Committee on Environment and Natural Resources, *Interagency Assessment of Oxygenated Fuels*, 1997.
2. USEPA EPA/600/R-98/048, *Oxygenates in Water: Critical Information and Research Needs*, 1998.
3. USEPA EPA 420-R-99-021, *Achieving Clean Air and Clean Water. The Report of the Blue Ribbon Panel on Oxygenates in Gasoline*, 1999.
4. USEPA Method 8015C, *Nonhalogenated Organics by Gas Chromatography*, 2007.
5. USEPA Method 8021B, *Aromatic and Halogenated Volatiles by Gas Chromatography using Photoionization and/or Electrolytic Conductivity Detectors*, 1996.
6. USEPA Method 8260B, *Volatile Organic Compounds by Gas Chromatography/Mass spectrometry (GC/MS)*, 1996.
7. USEPA Method 5030, *Purge & Trap*, 1986.
8. USEPA Method 5035, *Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples*, 1996.
9. Rosell, M.; Lacorte, S.; Barcelo, D. *J. Chromatogr. A* **2006**, *1132*, 28.
10. Bianchi, A. P.; Varney, M. S. *J. High Resol. Chromatogr.* **1989**, *12*, 184.
11. Halden, R. U.; Happel, A. M.; Schoen, S. R. *Environ. Sci. Technol.* **2001**, *35*, 1469.
12. Wei, C.; Jiemin, L.; Guibin, J. *Int. J. Environ. Anal. Chem.* **2003**, *83*(4), 285.
13. Achten, C.; Kolb, A. *Fresenius J. Anal. Chem.* **2001**, *371*(4), 519.
14. Stringfellow, W. T.; Oh, K. C. *Ground Water Monit. Rem.* **2005**, *25*(2), 52.
15. Zuccarello, J. L.; Ganske, J. A.; Green, D. B. *Chemosphere* **2003**, *51*(8), 805.
16. Erdem-Senatalar, A.; Bergendahl, J. A.; Thompson, R. W. *Chemosphere* **2004**, *57*(6), 523.
17. Atienza, J.; Aragón, P. *Crit. Rew. Anal. Chem.* **2005**, *35*(4), 317.
18. Cassada, D. A.; Zhang, Y.; Snow, D. D. *Anal. Chem.* **2000**, *72*(19), 4654.
19. Dewsbury, P.; Thornton, S. F.; Lerner, D. N. *Environ. Sci. Technol.* **2003**, *37*(7), 1392.
20. Schmidt, T. C. *Trends in Anal. Chem.* **2003**, *22*(10), 776.
21. Alizadeh, N.; Jafari, M.; Mohammadi, A. *J. Hazard. Mater.* **2009**, *169*, 861.
22. Ezquerrol, O.; Ortiz, G.; Pons, B.; Tena, M. T. *J. Chromatogr. A* **2004**, *1035*, 17.
23. Amini, R.; Rouhollahi, A.; Adibi, M. *Talanta* **2011**, *84*, 1.
24. Lefkowitz, D.; Zambrowski, M.; Uchrin, C. *J. Environ. Sci. Health Part A* **2002**, *37*, 17.
25. USEPA Method 5032, *Volatile Organic Compounds by Vacuum Distillation* 1996.
26. USEPA Method 5031, *Volatile, Nonpurgeable, Water-Soluble Compounds by Azeotropic Distillation*, 1996.
27. USEPA Method 5021, *Volatile Organic Compounds in Soils and Other Solid Matrices using Equilibrium Headspace Analysis*, 1996.
28. Rong, Y. *Environ. Geosci.* **2001**, *8*, 25.
29. Esteve-Turrillas, F. A.; Armenta, S.; Garrigues, S.; Pastor, A.; de la Guardia, M. *Anal. Chim. Acta* **2007**, *587*, 89.
30. Shin, H.-S.; Kim, T.-S. *Bull. Korean Chem. Soc.* **2009**, *30*(12), 3049.
31. O'Reilly, K. T.; Moir, M. E.; Taylor, C. D. *Environ. Sci. Technol.* **2001**, *35*(19), 3954.
32. McLoughlin, P. W.; Pirkle, R. J.; Fine, D. *Ground Water Monit. Rem.* **2004**, *24*(4), 57.
33. USEPA Method SW 846, *Chapter 1 Quality Control* 1992.
34. USEPA EPA/510/F-97/015, *Remediation of MTBE Contaminated Soil and Groundwater*, 1998.