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Method Detection Limit Determination and Application of a Convenient Headspace Analysis Method for Methyl *tert*-Butyl Ether in Water

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Methyl *tert*-butyl ether (MTBE) is a common groundwater contaminant, introduced to the environment by leaking petroleum storage tanks, urban runoff, and motorized watercraft. In this study. a simplified (static) headspace analysis method was adapted for determination of MTBE in water samples and soil water extracts. The MDL of the headspace method was calculated to be 2.0 μg L^{-1} by the EPA single-concentration design method[1] and 1.2 μg L^{-1} by a calibration method developed by Hubaux and Vos (Hubaux, A.; Vos, G. *Anal. Chem.* 1970, *42*, 849−855). The MDL calculated with the Hubaux and Vos method was favored because it considers both a true positive and a false positive. The static headspace method was applied to analysis of a tap water sample and a monitoring well sample from a gasoline service station, a river sample, and aqueous extracts from soil excavated during removal of a leaking underground storage tank (LUST). The water samples examined in this study had MTBE concentrations ranging from 6 to 19 μg L^{-1}. Aqueous extracts of a soil sample taken from the LUST site had 8 μg L^{-1} MTBE.

Methyl *tert*-butyl ether (MTBE) is a volatile organic compound (VOC) produced from natural gas. It is primarily used for the oxygenation of fuel to reduce carbon monoxide emissions and has been widely used in this role since the late 1970s. Used throughout the United States, MTBE was by far the most common oxygenate added to reformulated fuels.[3] MTBE is highly water soluble at 40−50 000 mg L^{-1}. It has been estimated that only 8% of the total MTBE present in an aquifer would be sorbed to aquifer materials.[4] Therefore, MTBE can move at virtually the same velocity as groundwater.[5] The U.S. Geological Survey National Water-Quality Assessment Program (NAWQA) (1985−1995) revealed MTBE to be the second most detected volatile organic compound in groundwater.[6] MTBE has been tentatively classified as a possible carcinogen,[7] and the USEPA recommends MTBE concentrations in drinking water be limited to 20−40 μg L^{-1}.[8] Sources of MTBE are leaky or abandoned aboveground or underground storage tanks, urban runoff from fuel tank overfills, or motorized watercraft leaks, all of which are problematic in the northeastern United States The state of New Hampshire's drinking water standard was lowered from 70 to 13 μg L^{-1} in May 2000,[8] and the action level for the state of Vermont is 1 μg L^{-1}, which is one of the lowest nationally.[9]

Many of the current methods for determining the concentrations of MTBE in drinking water require specific equipment or space not available in all laboratories. Cost-benefit comparisons of published analytical methods for MTBE and a summary of detection limits by method are given by Schmidt et al.[10] The U.S. Environmental Protection Agency (EPA) method 8260B[11] is a purge-and-trap method for the analysis of volatile organic compounds including MTBE. Three additional methods of MTBE analysis include direct aqueous injection, solid-phase microextraction, and headspace analysis. The purge-and-trap method is very sensitive but requires appreciable laboratory space to accommodate a purge-and-trap system and liquid nitrogen used for cryotrapping. Another disadvantage of this method is the

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possibility of contamination of the analytical column from highly polluted samples.[10] Direct aqueous injection (DIA) is inexpensive and sensitive,[12] though instrument failure is possible due to the large amount of water vapor produced,[10] and modification of typical gas chromatographic configuration is often necessary.[13] Solid-phase microextraction requires the use of specialized fibers inserted into a specialized injection liner, and high-level samples may require dilution.[17]

An alternative to these approaches is headspace analysis. Ambient headspace analysis requires little sample preparation, is nondestructive, can be used with even highly polluted samples, and can be used with standard GC columns with little possibility of column damage. Headspace analysis approaches range from manually controlled[14−16] to robotically controlled[17] heating or injection systems. Intermediate to these approaches, while still automated, is a simple, inexpensive, and rapid static headspace analysis method introduced by Szelewski and Quimby.[18] The approach involves the use of automatic sample injection instrumentation such as a sample turret and an injection tower, which are typical components of many gas chromatographs. In general, the disadvantage of headspace methods has been higher method detection limits (MDLs) for MTBE. However, headspace methods can have detection limits lower than safe drinking water limits for MTBE. Because headspace methods can be used with high- and low-level samples, they can be ideal research tools for environmental studies, for screening samples for the presence of MTBE, and for verifying the effectiveness of MTBE cleanup at contaminated sites. The objectives of this study were to (1) adapt the simplified static headspace analysis method for determination of MTBE in water samples and soil water extracts and (2) compare two approaches for determining the MDLs of the static headspace method.

EXPERIMENTAL SECTION

Water and Soil Samples. Water samples were collected from a tap and a monitoring well at a gasoline service station in Stratham, NH. An additional sample was collected from the Squamscott River, NH, ∼1 mi above the river entry point into the Atlantic Ocean via Great Bay, NH. All well, river, and tap water samples were collected on March 8, 2002, with the exception of a tap water sample collected previously, from the same service station, on November 18, 2001. Tap and river water samples were collected directly in methanol-rinsed 40-mL amber VOA vials (one VOA vial per matrix was collected). VOA vials (40 mL, amber, screw top, PTFE/silicone septa) were obtained from VWR Scientific (Bridgeport, NJ). Well samples were obtained with a PVC bailer and were poured into clean VOA vials. The bailer provided two VOA vials full of sample from the well. All VOA vials were completely filled to eliminate headspace.

Soil was sampled from a site that had been contaminated by a leaking underground storage tank (LUST) in Concord, NH. The soil had been excavated by order of the New Hampshire Department of Environmental Services (DES), during retrieval of a leaking underground tank. The soil had been placed in mounds on the surface at the site. Samples were obtained from the mounds within 3 days of the excavation using a clean shovel and were placed in acetone-rinsed metal barrels. The barrels were capped and refrigerated at 4 °C until subsamples were withdrawn for analysis.

Chemicals. MTBE (CAS 1634-04-4) (HPLC grade) was obtained from EM Science (Gibbstown, NJ). Methanol (CAS 67-56-1) (nanograde) was obtained from Mallinckrodt Baker, Inc. (Paris, KY). Sodium sulfate (CAS 7757-82-6) (certified ACS. grade) was obtained from EM Science. Purified water was obtained by passing distilled water through a Millipore Milli-QUV plus 4-Module cartridge reverse-osmosis system. Helium (ultrahigh purity grade) was obtained from Airgas Northeast, Inc. (Salem, NH). Safety considerations: MTBE is highly flammable and must be stored and handled appropriately, with proper ventilation.

Gas Chromatographic and Mass-Selective Detection Conditions and Configuration. Samples were analyzed with an Agilent Technologies model 6890 gas chromatograph (GC) equipped with a 5973N mass-selective detector (MSD) (Agilent, Palo Alto, CA). Chromatographic separation was accomplished with a fused-silica capillary column (Agilent, HP-5MS 5% phenyl methyl siloxane, 30 m by 250 μm i.d., 0.25-μm film thickness). The GC conditions and configurations used in this study were modified from the headspace method of Szelewski and Quimby.[18] The injection port liner used with the static headspace method was a deactivated 1-mm i.d. (Restek, Bellefonte, PA). The injection port was equipped with a Merlin Microseal septum (Agilent). Headspace samples were withdrawn by an Agilent 7683 autosampler tower using a gastight 100-μL syringe (Agilent), designed for use with the Merlin microseal septum. The sampling depth was 20 mm below the septum of the vial, which was well above the liquid level.

The injection port temperature was 200 °C with a helium head pressure maintained at 6.54 psi. The injection port was operated at a 2:1 split to allow for greater sensitivity. The initial GC oven temperature was 35 °C and held for 2 min prior to being ramped at 18 °C/min to 70 °C. A second ramp followed during which the oven temperature was raised at 45 °C/min to 250 °C. The oven was programmed to cool immediately upon reaching 250 °C. MTBE eluted in 1.93 min, and the total time of analysis was 7.94 min. The MSD was operated in selected ion monitoring (SIM) mode. The ions selected for detection were the quantification and confirmation ions making up MTBE and one of its breakdown products, *tert*-butyl alcohol (TBA): **73**, 57, 41, 43 and **59**, 41, 43, respectively.

Sample Preparation for MTBE Analysis. Calibration stock solutions were prepared by adding 40 μL of pure MTBE to 40 mL of MeOH in a 40-mL VOA vial. The mixture was manually agitated for ∼3 min. Sets of standards containing MTBE at milligram per liter levels (0−735 mg L^{-1}) were prepared by adding the proper amount of stock solution to 2-mL screw top vials containing 1.5 mL of methanol. Standards at microgram per liter levels (0−735 μg L^{-1}) were prepared in salted deionized water as

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follows: 0.25 g of sodium sulfate was weighed into 2-mL crimp-top vials (Agilent Technologies). One milliliter of deionized water was added, and the salt and water were then allowed 12 h to equilibrate at 25 °C. Following equilibration, 1 μL of each milligram per liter standard was added to the vials containing water and salt to achieve corresponding microgram per liter concentrations. The vials were then refrigerated for 12 h at 4 °C and allowed to warm to 25 °C before analysis. Tap and river water samples were prepared in a similar manner: 1 mL of the water was added to a 2-mL crimp-top vial containing 0.25 g of sodium sulfate. The samples were allowed to equilibrate at 25 °C for 12 h before being refrigerated at 4 °C for another 12 h. Two deionized water blanks were prepared and analyzed with each set of standards. To verify that our MTBE concentrations were comparable to those obtained by a commercial laboratory, a well water sample was submitted to a commercial laboratory (Eastern Analytical, Concord, NH), for purge-and-trap analysis.

Soil samples were removed from refrigerated storage barrels using a methanol-rinsed trowel and were placed in methanol-rinsed 1-L glass amber jars with Teflon-lined lids. The soil in the jars was thoroughly homogenized prior to subsampling 8 g for analysis. The 8 g of soil was placed in a 40-mL amber VOA vial and mixed with 20 mL of deionized water. The mixture was then agitated for ~5 min by hand. The vial was then inverted for 12 h at 25 °C. The water was then subsampled through the septum of the VOA vial using a 2.5-mL syringe and placed in the 2-mL crimp-top vial with 0.25 g of sodium sulfate. The salt and soil extracts were allowed to equilibrate for another 12 h before analysis.

RESULTS AND DISCUSSION

Method Detection Limit Calculations. Two MDL calculation approaches were used in this study: the EPA approach as defined in the U.S. EPA Electronic Code of Federal Regulations[1] and the Hubaux and Vos approach.[2,19,20] The EPA MDL approach utilizes a single-concentration design estimator. The first step is to determine an initial concentration to begin MDL calculations for the EPA approach. The EPA recommends calculating an estimated detection limit (EDL). An EDL is defined as a concentration of a compound in a clean water matrix, which maintains a signal-to-noise ratio of approximately 5 to 1. The EDL approach has long been used as a rule of thumb for approximating MDLs. The EDL is then used to choose the concentration at which standards should be prepared. The EPA recommends using a concentration that is between 1 and 5 times the EDL. Initially we deemed the EDL calculated for our method to be too low and chose a starting concentration close to the New Hampshire standard for drinking water. Seven aliquots of the sample concentration (12 μg L^{-1}) were prepared using the method, and the standard deviation for the peak areas calculated. The experimental data used to calculate MDLs (data set 1) are given in Table 1.

The MDL was calculated as the product of the Student's t value (at ν degrees of freedom and α confidence level, 1% in this study) and the standard deviation, s_d.

$$\mathrm{MDL} = t_{\nu,\alpha} s_d$$

Using this approach, the MDL is defined as the minimum concentration of an analyte that can be identified, measured, and reported to be above zero at the 99% confidence level.[1] To ensure uniform variance across concentrations, the variance was calculated on a separate data set (data set 2, Table 1). The EPA suggests that data be obtained over a period of several days or more. The EPA stipulates that an F-test be performed to ensure that the difference in variance values for the two data sets (data set 1 and data set 2) is statistically insignificant. This indicates whether the variances are statistically similar enough to conclude that the method was uniform across the curve. For this study, a Levene test was used to compare the variances instead of the F-test, because when variances across groups are not equal, the usual analysis of variance assumptions are not satisfied and the F-test is not valid. A Levene test showed the results of an F-test from an analysis of variance (ANOVA) in which the Levene F was the absolute value of the difference of each area and the group mean area. This was useful for testing for unequal variances across concentrations, as well as for calculating the differences about the variances. Our Levene test failed to find significant differences about the variances. This allowed us to pool the two sample variances as follows:

$$s_{\mathrm{d\ pooled}}^2 = (\nu_1 s_{\mathrm{d1}}^2 + \nu_2 s_{\mathrm{d2}}^2)/(\nu_{1+}\nu_2)$$

where $s_{\mathrm{d\ pooled}}^2$ is the pooled variance, ν_1 and ν_2 are the degrees of freedom for data set 1 and data set 2, respectively, and s_{d1}^2 and s_{d2}^2 are the variances for data set 1 and data set 2, respectively. It was then possible to calculate the pooled standard deviation, $s_{\mathrm{d\ pooled}}$. A new Student's t-test value was obtained based on the

Table 1. Data Obtained with Replicate Solutions of MTBE-Spiked Deionized Water

EPA Approach

data set 1		data set 2	
concn	area	concn	area
12	11 656	6.3	8300
12	11 667	6.3	8184
12	10 691	6.3	7483
12	10 541	6.3	8144
12	10 763	6.3	8122
12	10 523	6.3	7867
12	10 984	6.3	8165
mean	10 975.00		8037.86
std dev	493.45		277.38

Hubaux and Vos Approach

areas				
1.0 μg L^{-1}	2.9 μg L^{-1}	6.3 μg L^{-1}	12 μg L^{-1}	24 μg L^{-1}
1005	2551	5567	10 541	20 024
1003	2548	5436	10 763	19 878
998	2458	5214	10 525	19 957
993	2413	nd[a]	10 984	nd[a]

[a] Data not available.

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(20) Ramsey, P. J.; Coleman, D. E. Assessing the Detection Capability of Diagnostic Systems. The 1992 Fall Technical Conference of the American Society for Quality, Philadelphia, PA. 1992.

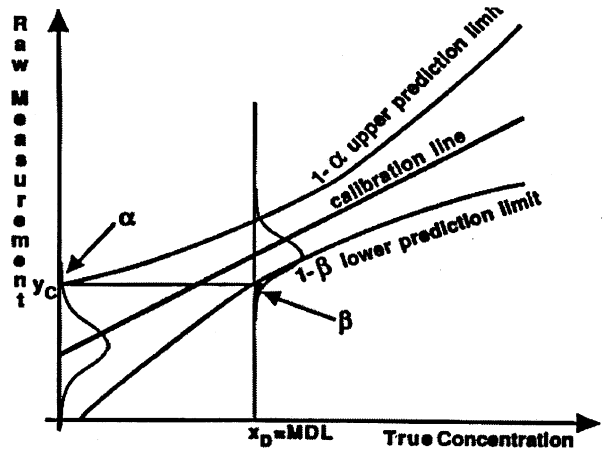

Figure 1. Graphical representation of Hubaux-Vos MDL determination based on a calibration curve.

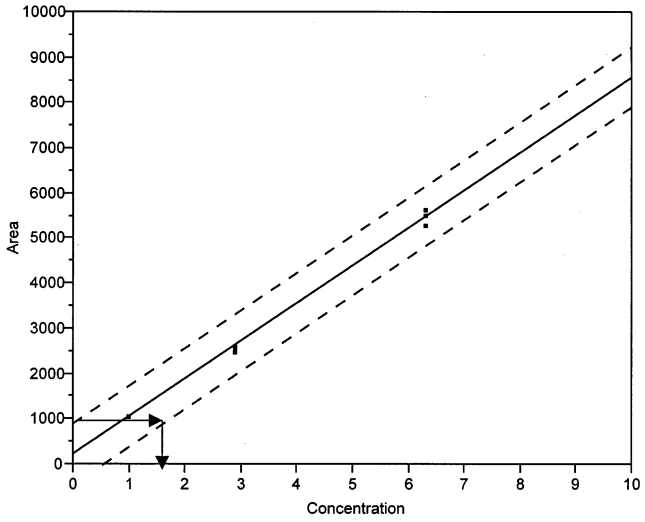

Figure 2. Bivariate of fit of area by concentration and graphical determination of MDL using the Hubaux−Vos approach. The linear regression equation for 18 observations was Area = 231.19568 + 832.97397 (Conc), r^2 = 0.998 122, adjusted r^2 = 0.998004, root-mean-square error 304.2855, and mean response 7380.889.

total degrees of freedom, $t_{\nu 1+\nu 2,\alpha}$. The MDL for the method was then computed as follows:

$$\mathrm{MDL} = t_{\nu 1+\nu 2,\alpha} s_{\mathrm{d\ pooled}}$$

One of the disadvantages of this method is that variability in analytic measurements is usually proportional to concentration. If the variability of the response is proportional to concentration, then at higher concentrations the standard deviation of the response increases. Therefore, lower MDLs can be achieved simply by performing analyses at low concentrations, close to the EDL. Our MDLs for the EPA method could have been lower if we had simply chosen lower concentrations for our MDL determination.

An alternative approach to MDL determination is that of Hubaux and Vos,[2,19,20] which can be adapted to the situation where the response is proportional to the concentration (heteroscedasticity). Hubaux and Vos defined MDL as the minimum concentration that can be measured and reported with 100(1 − α)% confidence that it is greater than zero; furthermore, when the true concentration is the MDL, it will be detected with probability (1 − β)[2]. Hubaux and Vos suggested that the MDL be obtained graphically by locating where the upper confidence limit intersects the *y* axis and plotting a line horizontally from that point to the lower confidence limit. The *x* value at the intersection point is the MDL (Figure 1).

Ramsey[20] provided a formula for calculating Hubaux−Vos MDLs:

$$\mathrm{MDL}_{\mathrm{H-V}} = \frac{s}{b}\left\{t_{\nu,1-\alpha}\left[1+\frac{1}{n}+\frac{\bar{X}^2}{\mathrm{SS}_X}\right]^{0.5} + t_{\nu,1-\beta}\left[1+\frac{1}{n}+\frac{(X_{\mathrm{MDL}}-\bar{X})^2}{\mathrm{SS}_X}\right]^{0.5}\right\}$$

where *s* is the standard error (RMSE), *b* is the slope, *n* is the number of observations, and $t_{\nu,1-\alpha}$ is the Student *t* percentile with ν degrees of freedom (n − 2) and α of 0.01. SS_x is the sum of squares of the *x* values (concentrations) centered by the mean of *X*, $t_{\nu,1-\beta}$ is the student percentile with ν degrees of freedom (n − 2) and β of 0.05, and $\bar{X}$ is the mean of *X*. X_{MDL} is an arbitrary starting value for the MDL, and $\mathrm{MDL}_{\mathrm{H-V}}$ is the Hubaux−Vos MDL. The equation is solved through iteration, replacing X_{MDL} with calculated $\mathrm{MDL}_{\mathrm{H-V}}$ values and performing the calculation until convergence is achieved. To determine the MDL using this method, a series of standards having various concentrations within the anticipated range of the MDL were prepared. The MDL calculated using the Hubaux and Vos formula provided by Ramsey[20] has more power than the EPA approach because the EPA approach considers only the probability of committing a false positive in determining whether a signal is detected indicating the presence of the analyte. A false positive occurs when no analyte is actually present; however, a false signal is detected. For the EPA method, the probability of a false positive occurring is controlled by the significance level α = 0.01.

The Hubaux and Vos approach considers the probability of both a true positive and a false positive. A true positive occurs when the analyte is actually present in the sample and a signal associated with the analyte is detected. In the Hubaux and Vos method, the probability of a false positive is controlled by the significance level α, and the probability of a true positive is controlled by the power of the test 1 − β, where β represents the probability of a false negative (analyte is present, but a signal is not detected). A graphic representation of the MDL determined in this study using the Hubaux and Vos method is shown in Figure 2, and associated data are given in Table 1.

A comparison of the MDLs demonstrates that the method chosen for MDL calculations noticeably influences the resulting detection level. The MDL obtained with the EPA-EDL method was 0.4 μg L^{-1}, that from the EPA single concentration design approach was 2.0 μg L^{-1}, and that from the Hubaux and Vos method calculated with the equation from Ramsey[20] was 1.2 μg L^{-1}. Despite disagreement among the methods, all the methods indicated that the headspace analysis method used in this study provides detection levels below all state safe drinking water limits for MTBE.

Water and Soil Samples. The water samples examined in this study had MTBE concentrations ranging from 6 to 19 μg L^{-1}.

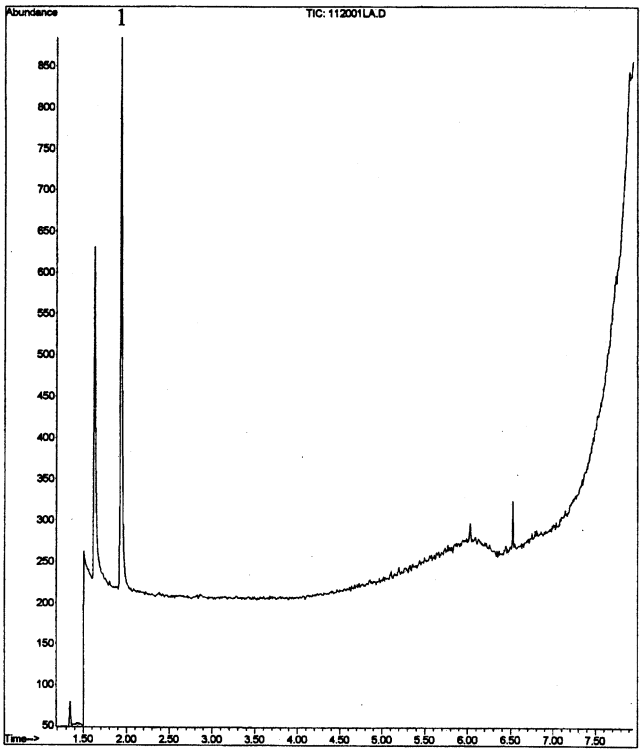

Figure 3. Chromatogram from a tap water sample collected at a gasoline service station in Stratham, NH. Peak 1 is MTBE.

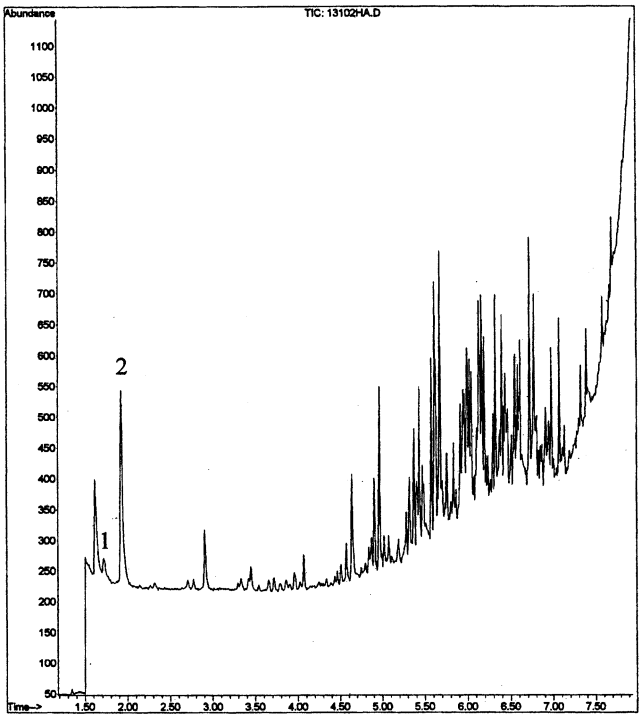

Figure 4. Water extract of soil samples taken from the Concord, NH LUST site, with TBA (peak 1; preliminary determination) and MTBE (peak 2).

The sample taken from the tap at a gasoline service station on March 8, 2002 in Stratham, NH, contained MTBE at 13 μg L^{-1} (Figure 3). The service station did contain a LUST. Samples were also taken from a monitoring well located 100 ft from the LUST. The MTBE concentrations in the well samples were 6 μg L^{-1} in each of the two samples collected from the well. The well sample was sent to a commercial laboratory for comparison. The commercial laboratory, using method 8260B (purge and trap), obtained an MTBE concentration of 7 μg L^{-1}, which was in good agreement with our headspace results. All values for the well were less than the 13 μg L^{-1} New Hampshire drinking water limit. The water taken from the bank of the Squamscott River had 19 μg L^{-1} MTBE. The water samples demonstrate the prevalence of MTBE in disparate bodies of water, 1 mi apart.

The tap water sample obtained from the service station on November 18, 2001 was refrigerated and analyzed four times over a period of 87 days. The concentrations measured were 9 and 11 μg L^{-1} 2 days after collection and 9 and 9 μg L^{-1} when analyzed 7 and 87 days later, respectively. This indicates that the method is reproducible from day to day and that no measurable MTBE was lost to the headspace in the VOA vial even when 3 mL had been removed from the vial.

Aqueous extracts of soil samples taken from the Concord LUST site had 8 μg L^{-1} MTBE in the soil water (peak 2, Figure 4). Assuming 100% extraction efficiency, the soil had 19 μg of MTBE kg^{-1} of soil. There was also a small peak at 1.73 min (peak 1, Figure 4), having the mass spectrum and retention time of TBA. The aqueous extraction approach was only used to obtain water samples having soil matrix components and LUST contaminants; the extraction method was not optimized for MTBE extraction.

The results of the extractions of soil and the well and river sample results indicate that the headspace method can be used with samples having natural matrix components. The use of this method for other compounds such as halogenated ethanes and methanes was demonstrated by Szelewski and Quimby.[18] It was not in this study and apparently has not been extended to other fuel oxygenates. Its effectiveness will be highly dependent on the Henry partition coefficient of the compound. However, this simple approach to headspace analysis could be applied to any compound as or more volatile than MTBE.

CONCLUSIONS

In this study, the modified method of Szelewski and Quimby[18] was demonstrated to have low enough MDLs to detect MTBE at levels below the safe drinking water limits of all states in the United States, though above action levels for certain states. The headspace approach used in this study was convenient, inexpensive, versatile, and sensitive enough to be used for screening low- and high-level samples for MTBE. The MDLs found using this method were not as low as those reported using SPME, DIA, or purge and trap. However, the method used to calculate MDLs clearly influences the final MDL value of an analytical method. The Hubaux and Vos method for determining MDLs is robust and reliable and indicated that the MDL for the convenient headspace method was 1.2 μg L^{-1} for MTBE.

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