Determination of Methyl *tert*-Butyl Ether and *tert*-Butyl Alcohol in Water by Solid-Phase Microextraction/Head Space Analysis in Comparison to EPA Method 5030/8260B

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Abstract

Methyl *tert*-butyl ether (MTBE) is now one of the most common groundwater contaminants in the United States. Groundwater contaminated with MTBE is also likely to be contaminated with *tert*-butyl alcohol (TBA), because TBA is a component of commercial grade MTBE, TBA can also be used as a fuel oxygenate, and TBA is a biodegradation product of MTBE. In California, MTBE is subject to reporting at concentrations greater than 3 μg/L. TBA is classified as a "contaminant of current interest" and has a drinking water action level of 12 μg/L. In this paper, we describe the development and optimization of a simple, automated solid phase microextraction (SPME) method for the analysis of MTBE and TBA in water and demonstrate the applicability of this method for monitoring MTBE and TBA contamination in groundwater, drinking water, and surface water. In this method, the headspace (HS) of a water sample is extracted with a carboxen/polydimethylsiloxane SPME fiber, the MTBE and TBA are desorbed into a gas chromatograph (GC), and detected using mass spectrometry (MS). The method is optimized for the routine analysis of MTBE and TBA with a level of quantitation of 0.3 μg/L and 4 μg/L, respectively, in water. MTBE quantitation was linear for over two orders of concentration (0.3 μg/L -80 μg/L). TBA was found to be linear within the range of 4 μg/L-7,900 μg/L. The lower level of detection for MTBE is 0.03 μg/L using this method.

This SPME method using headspace extraction was found to be advantageous over SPME methods requiring immersion of the fiber into the water samples, because it prolonged the life of the fiber by up to 400 sample analyses. This is the first time headspace extraction SPME has been shown to be applicable to the

measurement of both MTBE and TBA at concentrations below regulatory action levels. This method was compared with the certified EPA Method 5030/8260B (purge-and-trap/GC/MS) using split samples from laboratory bioreactors treating MTBE contaminated water and applied to environmental samples collected throughout the East Bay area of California. Results from the SPME-HS/GC/MS method were directly comparable to the EPA Method 5030/8260B. This method provides an simple, inexpensive, accurate, and sensitive alternative to EPA Method 5030/8260B for the analysis of MTBE and TBA in water samples.

Introduction

Concerns over deteriorating air quality in urban and metropolitan areas have lead to increasingly strict vehicular emission controls. The Clean Air Act Amendments of 1990 requires the use of reformulated gasoline, which contains fuel oxygenates, such as methyl *tert*-butyl ether (MTBE) and *tert*-butyl alcohol (TBA), in regions that exceed ozone standards. MTBE has been the most widely used oxygenate and the choice of industry because it blends completely with gasoline and it is inexpensive to produce. The extensive use of MTBE in gasoline and the high solubility of MTBE in water has resulted in widespread contamination of groundwater and surface water throughout the United States. There are numerous sources of MTBE contamination including leaking underground storage tanks, surface runoff, and precipitation (*1-4*). In California, MTBE contamination of groundwater and drinking water is widespread (*5,5a*). The extent of TBA contamination in the environment has not been thoroughly investigated, but TBA contamination may be widespread as well because TBA is frequently found at MTBE contaminated sites when appropriate analyses are applied. TBA can be present in the environment from its use as a fuel oxygenate or as an intermediate product of MTBE biodegradation.

The high aqueous solubility of MTBE contributes to rapid plume migration in aquifers, threatening potential receptors, such as community water systems (CWSs). CWSs are subject to contamination by both point and non-point source pollution and may be subject to chronic low-level contamination. The United States Environmental Protection Agency (EPA) has issued a drinking water advisory that recommends keeping the maximum level of MTBE in drinking water between 20 and 40 μg/L to protect

drinking water aesthetics. MTBE is included as a regulated compound under California drinking water standards and has a public health goal and a maximum contaminant level of 13 μg/L. In California, MTBE is subject to reporting at concentrations greater than 3 μg/L. TBA is classified as a "contaminant of current interest" and has a drinking water action level of 12 μg/L, based on a non-cancer endpoint assessment (*5a*).

Drinking water suppliers and others need a rapid and reliable analytical method for detecting trace quantities of MTBE and TBA in water to protect public health. This method needs to be acceptable to scientists, state and federal agencies. However, a recent study (*6*) has concluded that lack of an approved or required method for MTBE analysis poses serious difficulties to the management of the nation's MTBE contaminated sites, which may number in the hundreds of thousands.

There are a few analytical protocols for MTBE using purge-and-trap (P&T) techniques in combination with gas chromatography (*6,7,8*). The U.S. Environmental Protection Agency (EPA) Method 5030 in combination with Method 8260B is commonly used for MTBE analysis in groundwater and drinking water and can be used for the analysis of TBA as well (*7*). The EPA Method 5030/8260B, though expensive, is the most generally accepted P&T method for the analysis of MTBE and TBA in water. This method generates legally defensible and quantifiable data using gas chromatography (GC) followed by mass spectrometry (MS). This method can achieve MTBE lower detection limits of 0.05 μg/L and levels of quantitation between 0.2 and 1.1 μg/L, with a linear range of up to 20 μg/L without requiring sample dilution (*1, 7, 8*). The cost associated with P&T/GC/MS methods comes largely from the maintenance of the MS. The P&T system introduces a broad range of compounds into the GC/MS, not just the

analyte of interest, and the MS often needs to be disassembled for cleanup after analysis of environmental samples that have a high organic concentration. P&T sampling also introduces small but significant quantities of air and moisture into MS. P&T/GC/MS instruments typically experience downtime for maintenance after analysis of 30-50 samples. Thus there are limited numbers of samples that can be analyzed for a given time and capital investment.

Direct aqueous injection (DAI) (*9, 10*) with detection by MS is a proposed analytical method for MTBE. It has comparable reproducibility to P&T/GC/MS and comparable sensitivity for detecting MTBE degradation products such as TBA. A DAI/GC/MS method (*10*) can achieve a level of quantitation of 0.1 μg/L for MTBE. DAI/GC/MS requires a sector instrument to trap moisture, as smaller mass spectrometers can not tolerate water injection. Manufacturers do not recommend injecting water into either mass spectrometers or GC columns. Given the extent of MTBE contamination and sampling requirements for drinking water monitoring (*11*), P&T/GC/MS or DAI/GC/MS methods may not be economically feasible and development of an alternative analytical method at lower cost would be useful.

Solid-phase microextraction (SPME) is a relatively simple, inexpensive, fast and solvent-free extraction method (*12*). Previously described SPME methods for MTBE extract the sample by immersing the SPME fiber into water samples to which approximately 25 % sodium chloride (w/w) has been added (*13-16*). These immersion methods have sub-μg/L levels of quantitation, however the life of the SPME fiber is limited to 20-30 samples, because the fibers become fragile when exposed to salt (*16*). This is undesirable due to the high cost of the fiber.

Headspace sampling, where the fiber is exposed in the headspace of a partially filled vial, offers an alternative method to immersion for the extraction and analysis of MTBE with SPME fibers. Hunkeler *et al*. (*16a*) developed a SPME based method for measuring the carbon isotope ratios of MTBE under different conditions of degradation. They compared an immersion protocol to a headspace extraction protocol and determined that significant isotope fractionation did not occur during the mass phase partitioning integral to the headspace method. The headspace extraction method consisted of a twenty minute extraction of a rapidly mixed sample and was not automated. The method was applied by Gray *et al*. (*16b*) for the measurement of carbon and hydrogen isotope fractionation during biodegradation. It was determined that the method detection limits for this headspace SPME method were not adequate for the analysis of water contaminated with MTBE at concentration less than 350 μg/L (*16b*).

This study describes an automated method using headspace SPME combined with GC and MS (SPME-HS/GC/MS) for the quantitative analysis of MTBE and TBA at low μg/L concentrations. The method uses a small sample volume and does not require the sample to be mixed or agitated during extraction. This method was optimized for MTBE analysis and then applied for the analysis of TBA. This method was compared to the EPA Method 5030/8260B using split samples collected from laboratory bioreactors treating MTBE contaminated water. The method was used to measure MTBE and TBA in environmental and drinking water samples collected in Northern California. This SPME-HS/GC/MS method gave comparable results to EPA Method 5030/8260B with very low maintenance, suggesting that SPME-HS/GC/MS would be particularly useful for routine monitoring and drinking water surveys at municipal treatment facilities. This

method offers a simple, less expensive alternative for MTBE detection, allowing more frequent monitoring economically.

Materials and Methods

Chemicals and Materials.

MTBE stock solution (2000 μg/mL) and 1-fluorobenzene (FB) for internal standard (2000 μg/mL) were obtained from Supelco (Bellefonte, PA) and used for preparation of standards at lower concentrations. Standards were prepared in HPLC-grade water by serial dilution and preserved at 4^{o} C for up to 4 weeks. MTBE and TBA were obtained from EM Science (Gibbstown, NJ) and Sigma (St. Louis, MO), respectively, in the highest purity (>98%) available. Sodium chloride (99%) was purchased from EM Science. Screw cap sample vials with PTFE/Silicone/PTFE septa were purchased from Kimble (Vineland, NJ) and I-CHEM EPA certified 40 mL sampling vials with Teflon/silicone septa screw cap (VOA vials) were purchased from Nalgene (Rochester, NY).

Sampling.

Samples were collected in 40 mL VOA vials using standard water sampling techniques for VOCs (*17*) except in the case of stormwater runoff. Storm runoff water was collected using 50 mL glass pipettes to draw water from puddles formed by rain and transferred to VOA vials. Drinking water samples were collected at the kitchen tap in homes and apartments in the East Bay. Effluent water samples were collected from a 1.5 L fluidized bed bioreactor (19). The bioreactor contained granular activated carbon (GAC) as a bed material and was used to treat tap water spiked with 10 mg/L MTBE (final concentration). Samples were preserved by adding 0.1 mL of water diluted HCl

(1:1 v/v) to each vial (final pH less than 2). Samples were placed on ice immediately after collection and refrigerated at 4^{o} C until analysis. The laboratory reactor and field samples were collected in duplicate for both EPA Method 5030/8260B and SPME-HS/GC/MS analysis. SPME-HS/GC/MS analysis was performed in triplicate for each sample and the mean value was reported. For autosampler vial preparation, 2 mL of water sample was withdrawn from the VOA vial using a gas-tight syringe and 0.5 mL was dispensed into autosampler vials in triplicate. Internal standard was dispensed into the vial using a 10 μl syringe. Sample holding time for the 5030/8260B and SPME-HS/GC/MS analysis was less than 2 and 4 weeks, respectively.

SPME-HS/GC/MS.

Chromatographic analysis was performed using a Varian 3400 gas chromatograph (Walnut Creek, CA) equipped with Varian Saturn 2000 mass spectrometer. Samples were introduced into the GC with Varian 8200 autosampler with SPME modification. Separation of the analytes was performed using a 60 m x 0.25 mm I.D. J&W DB-WAX (J&W Scientific, Folsom, CA) column with a film thickness of 0.25 μm. The column oven temperature was initially held at 40^{o} C for 4 min, then increased at a rate of 10^{o} C/min to a maximum 230^{o} C, and held for 10 min. Helium served as carrier gas at a flow rate of 1.0 mL/min. Data was collected and integrated using Saturn GC/MS Workstation software (Varian). Mass spectra were scanned in the range 20-400 *m/z*. MTBE was quantified using the *m/z* 73 peak with *m/z* 43 and 41 as the reference spectra. For TBA and FB quantification, mass spectrum of *m/z* 59 and 96 were used with reference spectra m/z 41, 39 and 97, 70, respectively. Quantification and reference spectra are summarized in Table 1. The level of quantitation was determined as the concentration of analyte

yielding a 10:1 signal to noise ratio. The lower level of detection was the concentration of analyte yielding a 2:1 signal to noise ratio in distilled water.

SPME extraction was performed using a Supelco SPME 75 μm carboxen/polydimethylsiloxane (carboxen/PDMS) SPME fiber. This fiber was chosen based on the manufacturers recommendation and has been used previously for analysis of MTBE (15). Before each analysis, the SPME fiber was thermally conditioned, to remove any organic residues that may accumulate during storage. For conditioning, the SPME fiber was inserted into the injection port (inlet) for 5 min, which is maintained at 280^{o} C with a column temperature of 240^{o} C. A blank sample analysis was performed to confirm no carry-over after the conditioning and also in between triplicate sample analyses.

EPA Method 5030/8260B.

P&T/GC/MS analysis was performed according to EPA Methods 5030 and 8260B (*7*) in the Environmental Measurement Laboratory (EML) at LBNL. The EML is a State of California certified analytical laboratory. Analysis was performed using an Agilent 6890 GC with an Agilent 5973 network mass selective detector. A Tekmar 300 (Mason, OH) was used for purge and trap and an RTX-WAX capillary column (Restek, 60 m by 0.25-mm i. d., 1.40 μm coating, Bellefonte, PA) was used for chromatographic separation. The MTBE reportable limit was 5 μg/L.

HS/GC/FID.

A static headspace analysis (HS) was used for pre-screening of samples to identify samples containing high concentrations of MTBE (> 100 μg/L). For the analysis, a Varian 3400 GC equipped with a flame ionization detector (FID) and an 8200 autosampler was used. Chromatographic separation was performed using a 30 m by 0.25

mm i. d., 0.25 μm film thickness DB-WAX capillary column (J & W Scientific). Sub-samples were collected from the VOA vials using a gas-tight syringe and 0.5 mL of sub-sample was dispensed into 2-mL autosampler vials in triplicate. The autosampler collected 50 μL of headspace sample from the sample vial and injected the sample into the GC. A blank water sample was run between triplicate samples to prevent sample carry over. The temperature was maintained at 40^{o} C and the inlet and detector temperature were 150^{o} C and 225^{o} C, respectively. Helium as a carrier gas flowed at 1.0 mL/min with a 1:6 split ratio. MTBE had a retention time of 1.96 min and a quantitation limit of 100 μg/L by this method.

Result and Discussion

Method Development.

For the development of this method, adsorption and desorption time and inlet temperatures were examined for optimum MTBE recovery from distilled water at a concentration of 14.8 μg/L. MTBE recovery increased with the exposure time of the fiber in the headspace (Figure 1). Maximum response was obtained at 45 min of adsorption. There was only 10 % significant difference in adsorption capacity between 30 min and 45 min adsorption. Thirty min of adsorption time was chosen as optimal for this method, because longer adsorption time did not improve recovery sufficiently to warrant additional time costs. The adsorption time coincides with the GC temperature program for one sample run, which takes approximately 30 min, maximizing the utilization of analysis time on the instrument.

The effect of SPME fiber residence time in the injector after adsorption (desorption time) on MTBE recovery was investigated. The difference between 1 to 10

min of desorption was within 10 % and increasing desorption time did not increase sensitivity (Figure 2). The highest recovery of MTBE was achieved between 1 and 2 min, so 1.5 min of desorption time was chosen for the final method. MTBE recovery increased with increasing inlet temperature with a 1.5 minute desorption time (Figure 3). It is the manufacture's recommendation to use a desorption temperature not to exceed the analytical column temperature, which is at 240^{o} C. Thus desorption temperature was set at 240^{o} C.

Under the final method conditions (30 min extraction, 1.5 min desorption, and 240^{o} C inlet temperature) the level of quantitation was 0.30 μg/L (n=10) with 10% relative standard deviation (RSD). The lower detection limit was determined to be 0.03 μg/L for MTBE. The presence of MTBE in a water sample was confirmed by measuring *m/z* 73 and 43 of the sample with a signal to noise ratio of 2:1 or better from triplicate samples. Standard curves for MTBE with this method were linear over more than two orders of magnitude (0.3 μg/L -80 μg/L) with regression coefficients (r^2) greater than 0.99. The SPME-HS extraction was not linear with concentration over 80 μg/L. This result is similar to results the SPME extraction of other volatile organics using immersion techniques (*20*). The linear range in this method is particularly applicable to drinking water samples, which are usually found to be below 5 μg/L. The analysis of higher concentration samples can be streamlined by pre-screening samples with HS/GC/FID analysis to determine dilution rates. The level of quantitation for TBA was 4.0 μg/mL with 10% relative standard deviation (RSD). The linearity of TBA standard curves was extended to nearly 4 orders of magnitude (4 μg/L-7,900 μg/L) with coefficients (r^2)

greater than 0.99. The comparison of this method to other MTBE analytical methods is summarized in Table 2.

We also examined the effect of salt on MTBE recovery (Figure 4). For SPME immersion methods, changing the ionic strength of the sample by the addition of salt increased the recovery of MTBE (*15*). Our result show that adding salt also increased the extraction efficiency of headspace sampling as well. A doubling of extraction efficiency was observed at a sodium chloride concentration of 30% (w/w) compared to no salt addition. The optimal salt concentration for this method was a bit higher than that (25%, w/w) of studies where the SPME fiber was immersed in the aqueous sample (*15, 16*). Although the addition of salt can increase sensitivity for this method, for the simplicity of sample preparation, salt addition is not recommended for this SPME-HS/GC/MS method, because the method already achieved a low quantitation limit of 0.3 μg/L, which is more than adequate to meet regulatory requirements for the monitoring of drinking water, groundwater and surface water.

Comparison of SPME-HS/GC/MS and EPA Method 5030/8260B.

This new SPME-HS/GC/MS method was compared with EPA Method 5030/8260B using samples from laboratory bioreactors treating MTBE spiked tap water (19). For comparison of SPME-HS/GC/MS with EPA Method 5030/8260B, four replicate laboratory reactor effluent samples were collected on the same day for each sampling event. Two VOA vials were sent to the certified laboratory for EPA Method 5030/8260B analysis and two were analyzed by SPME-HS/GC/MS in our laboratory. Samples were prescreened by HS/GC/FID analysis and if the MTBE concentrations were detectable by this method the sample was diluted appropriately for SPME-HS/GC/MS.

Figure 5 shows that the SPME-HS/GC/MS and the EPA Method 5030/8260B are in good agreement over nearly 3 orders of magnitude. There was some scatter between the two analysis, but the variation is within accepted variation for the quality control limits of EPA methods (85-115% limits of internal standard recovery). These results can be compared favorably to other studies that examined MTBE and MTBE metabolite analysis by different detection methods (MS, FID and photoionization detector) with the same sampling method (P&T) (*6*) or for different sampling methods (P&T and DAI) with the same detection method (MS) (*10*).

Environmental Sample Analysis.

Water samples were collected around the east side of the San Francisco Bay (East Bay) in Northern California and were analyzed by SPME-HS/GC/MS. Results from water samples collected in March, April and September from the Easy Bay and the analysis data are summarized in Table 3.

Only one out of nine storm runoff water samples collected had any detectable MTBE (approximately 0.03 μg/L, equal to our level of detection). This result is consistent with the report from USGS that concluded MTBE in California urban storm runoff is generally less than 2 μg/L (*21*). Achten and Püttmann (*15*) showed that MTBE concentrations in rainwater precipitation collected in Germany were between 0.07 μg/L in December 1998 and at 0.009 μg/L in April 1999. These results indicate that stormwater runoff in California and elsewhere contain concentrations of MTBE that are significantly lower than drinking water action levels. This method was optimized for the analysis of MTBE and TBA at concentrations applicable to drinking water action levels, application to stormwater sampling will require further modification of the method,

perhaps by extending extraction time, increasing sample volumes, adding salt, and narrowing the scanning range on the MS.

MTBE concentrations in drinking water around the cities in East Bay were substantially higher than in stormwater runoff. MTBE was detected in 9 out of 20 drinking water samples analyzed. Only one sample (14.6 μg/L) out of 20 was higher than California's primary MTBE drinking water action level (13 μg/L). Drinking water in East Bay cities are supplied from protected watersheds of the Mokelumne River Basin (*22*) that collects melted snow from the west slope of the Sierra Nevada range. Padree Reservoir, which collects the water from the river, distributes the water to five terminal reservoirs: Briones, San Pablo, Upper San Leandro, Lafayette, and Chabot reservoirs. The household drinking water sampled in this study originated in the San Pablo reservoir. The reservoir system is largely protected from any human activity, however, a survey of water entering the San Pablo reservoir in 1996-1997 showed MTBE concentrations ranging from 1.6 to 5.5 μg/L (*23*). Results of the current study indicate that there might be additional sources of MTBE contamination in the distribution system. Possible sources include shallow groundwater infiltration into older potable water distribution pipes. This result suggests that frequent monitoring of drinking water is required in area where the use of MTBE is high and that monitoring should include distribution systems as well as source waters.

Aqueous samples were collected along beaches and marinas in the East Bay. Beaches had higher MTBE concentrations than marina parks (Table 3). This result is surprising, as marinas included docks for watercraft and, in some cases, evidence of recently spilled oil or gasoline (a metallic sheen on the water surface) was apparent in

the marinas during sampling. It may be possible that the presence of a hydrocarbon phase partitioned MTBE out of the aqueous phase resulting in the apparently lower concentrations in the marina. Considering the urban setting and the amount of marine traffic in the bay, however, it is not surprising to find measurable MTBE contamination at the beaches. The salinity of the estuary water is thought to have minimal effect on analysis, because of low average salinity of 0.35 % in seawater. The range of MTBE concentrations in the near shore estuary found in this study is similar to that of other surface waters in California (*21*).

Use of MTBE in reformulated gasoline will be prohibited in California by 2003. Ethanol is being adopted as an alternative fuel oxygenates to meet federal air quality guideline. However, MTBE contamination will still be of concern even after it is prohibited in gasoline, because of its recalcitrance and persistence in environments. The method described in this study provides a cost-effective and reliable analytical method for MTBE detection. This method is particularly useful for monitoring drinking water and provides a practical alternative for small or large distribution systems, allowing EPA mandated MTBE monitoring to be achieved with less cost.

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References

1. Landmeyer, J.E.; Chapelle, F.H.; Bradley, P.L.; Pankow, J.F.; Church, C.D.; Tratnyek, P.G. *Ground Water Monit. Remediation*. 1998, 18, 93-102.

2. Grosjean, E.; Grosjean, D.; Gunawardena, R.; Rasmussen, R.A. *Environ. Sci. Technol*. 1998, 32, 736-732.

3. Pankow, J.F.; Thomson N.R.; Jhonson R.L.; Baehr, A.L.; and Zogorski, J.S. *Environ. Sci. Technol*. 1997, 31, 2821-2828.

4. Squillace, P.J.; Zogorski, J.S.; Wilber, W.G.; Price, C.V. *Environ. Sci. Technol*. 1996, 30, 1721-1730.

5. *An Evaluation of MTBE Impacts to California Groundwater Resources*. Report NO. UCRL-AR-122207. Lawrence Livermore National Laboratory: Livermore, CA, 1998.

5a. *Drinking Water Action Levels: Contaminants of Current Interest*. Online electronic publication file. http://www.dhs.ca.gov/ps/ddwem/chemicals/AL/actionlevels.htm. California Department of Health Services, Berkeley, CA 2001.

6. Halden, R.U.; Happel, A.M.; Schoen, S.R. *Environ. Sci. Technol*. 2001, 35, 1469-1474.

7. *SW-846 Method 8260B*, *Testing Methods for Evaluating Solid Waste, Physical/Chemical Methods,* SW-846, 3rd ed., update II. U.S. Environmental Protection Agency: Washington, D.C., 1997.

8. Askari, M.D.F.; Maskarinec, M.P.; Smith, S.M.; Beam, P.M.; Travis, C.C. *Anal. Chem*. 1996, 68, 3431-3433.

9. Potter, T.L. *Ground Water Monit. Remediation*. 1996, 16, 157-162.

10. Church, C.D.; Isabelle, L.M.; Pankow, J.F.; Rose, D.L.; Tratnyek, P.G. *Environ. Sci. Technol*. 1997, 31, 3723-3726.

11. *Drinking Water: Overview of Monitoring Results 1994-2002, and an Indication of Dominant Contaminants.* Online electronic publication file. http://www.dhs.ca.gov/ps/ddwem/chemicals/monitoring/results94-02.htm. California Department of Health Services, Berkeley, CA 2001.

12. Zhang, Z.; Yang, M.J.; Pawliszyn, J. *Anal. Chem*. 1994, 66, 844A-853A.

13. Gaines, R.B.; Ledford, Jr., E.B.; Stuart, J.D. *J. Microcolumn Seperat*. 1998, 10, 597-604.

14. *Trace Analysis of Ethanol and MTBE in Water Using Solid Phase Micro-Extraction and Gas Chromatography/Mass Spectrophotometry*. Report No. NWRI-99-07. National Water Research Institute: Fountain Valley, CA, 1999.

15. Achten, C.; Püttmann, W. *Environ. Sci. Technol*. 2000, 34, 1359-1364.

16. Cassada, D.A.; Zhang, Y.; Snow, D.D.; Spalding, R.F. *Anal. Chem*. 2000, 72, 4654-4658.

16*a*. Hunkeler, D.; Butler, B. J.; Aravena, R.; Barker, J. F. *Environ. Sci. Technol*. 2001, 35, 676 - 681.

16*b*. Gray, J. R.: Lacrampe-Couloume, G.: Gandi, D.; Scow, K. M.; Wilson R. D.; Macay, D. M.; Sherwood Lollar, B. *Environ. Sci. Technol*. 2002, 36, 1931-1938.

17. *Ground-water Data Collection Protocols and Procedures for the National Water-Quality Assessment Program: Collection and Documentation of Water-Quality*

Samples and Related Data. Open File Report 95-33. U.S. Geological Survey: Denver, CO, 1995.

18. *U.S. Geological Survey Laboratory Method for Methyl Tert-Butyl Ether and Other Fuel Oxygenates*. Fact Sheet 219-95. U.S. Geological Survey: Denver, CO, 1995.
19. Stringfellow, W. T. and K. -C. Oh. *J. Environ. Eng.* 2002, 128, 852 – 861.
20. Thomas, S.P.; Ranjan, R.S.; Webster, G.R.B.; Sarna, L.P. *Environ. Sci. Technol*. 1996, 30, 1521-1526.
21. *U.S. Geological Survey Water Resources of California MTBE*. Online electronic publication file. http://water.wr.usgs.gov/mtbe. U.S. Geological Survey: Denver, CO, 2001.
22. *Urban Water Management Plan 2000*. Online electronic publication file. http://www.ebmud.com/pubs/wtrsupply/uwmp.html. East Bay Municipal Utility District: Oakland, CA, 2000.
23. *MTBE in Drinking Water: Surface Water Sources*. Online electronic publication file. http://www.dhs.ca.gov/ps/ddwem/chemicals/MTBE/surfacewater.htm. California Department of Health Services, Berkeley, CA 2001.

TABLE 1. Quantitation and Reference Ions and Retention Times of Analytes and Internal Standard

	quantitation ion (*m/z*)	reference ion (*m/z*)	retention time (min)
Analytes			
MTBE	73	43, 41	3.38
TBA	59	41, 39	5.36
Internal standard			
FB	96	97, 70	6.50

TABLE 2. Performance Comparison Among Different MTBE Analytical Methods

	SPME-HS /GC/MS (*this study*)	SPME/GC/MS (*15,16*)	P&T/GC/MS (*8,18*)	DAI/GC/MS (*10*)
Sampling method	SPME Headspace	SPME Immersion	Purge and Trap	Direct Aqueous Injection
Level of quantitation (μg/L)				
MTBE[a]	0.3[b]	0.01	0.2 – 1.1	0.1
TBA	4.0[b]	1.8	3.0	0.1
Analytical cost ($ per sample)	50[c]	100[d]	150[c]	NA
GC/MS Maintenance	Low	Medium	High	Very High

[a], California's primary and secondary drinking water action level for MTBE is 13 μg/L and 5 μg/L, respectively.
[b], without added salt.
[c], based on comparison of costs for split sample analysis described in this paper.
d, based on estimated cost for replacement of SPME fiber every 25 samples, not including additional costs for mixing sample during extraction.
NA = cost estimate not available

TABLE 3. Detection of MTBE in Water Collected from Bay Area in Northern California

Sampling sites	Sampling dates	Water type	Sample No.	MTBE(μg/L)	TBA(μg/L)
City drinking water	3/28/01 - 9/12/01	Drinking water	20 (11)[b]	ND - 14.61	ND
Beaches	4/18/01	Estuary	6	0.08 - 13.2	ND
Marina parks	4/18/01	Estuary	7	0.06 - 6.43	ND

[a] ND, not detected, concentration < 0.03 μg/L.
[b] ( ), no. of non detects.

Figure Legends

Figure 1. Influence of headspace extraction time on extraction yield in terms of area response for 73 *m/z* (as % of maximum area measured ± relative standard deviation) for 14.8 μg/L MTBE in distilled water.

Figure 2. Influence of desorption time on extraction yield in terms of area response for 73 *m/z* (as % of maximum area measured ± relative standard deviation) for 14.8 μg/L MTBE in distilled water.

Figure 3. Influence of inlet temperature on extraction yield in terms of area response for 73 *m/z* (as % of maximum area measured ± relative standard deviation) for 14.8 μg/L MTBE in distilled water.

Figure 4. Influence of sodium chloride concentration on extraction yield in terms of area response for 73 *m/z* (as % of maximum area measured ± relative standard deviation) for 14.8 μg/L MTBE in distilled water.

Figure 5. Comparison between SPME-HS/GC/MS and 5030/8260B for measurement of MTBE using split samples from a bioreactor treating MTBE contaminated water.

Figure 1

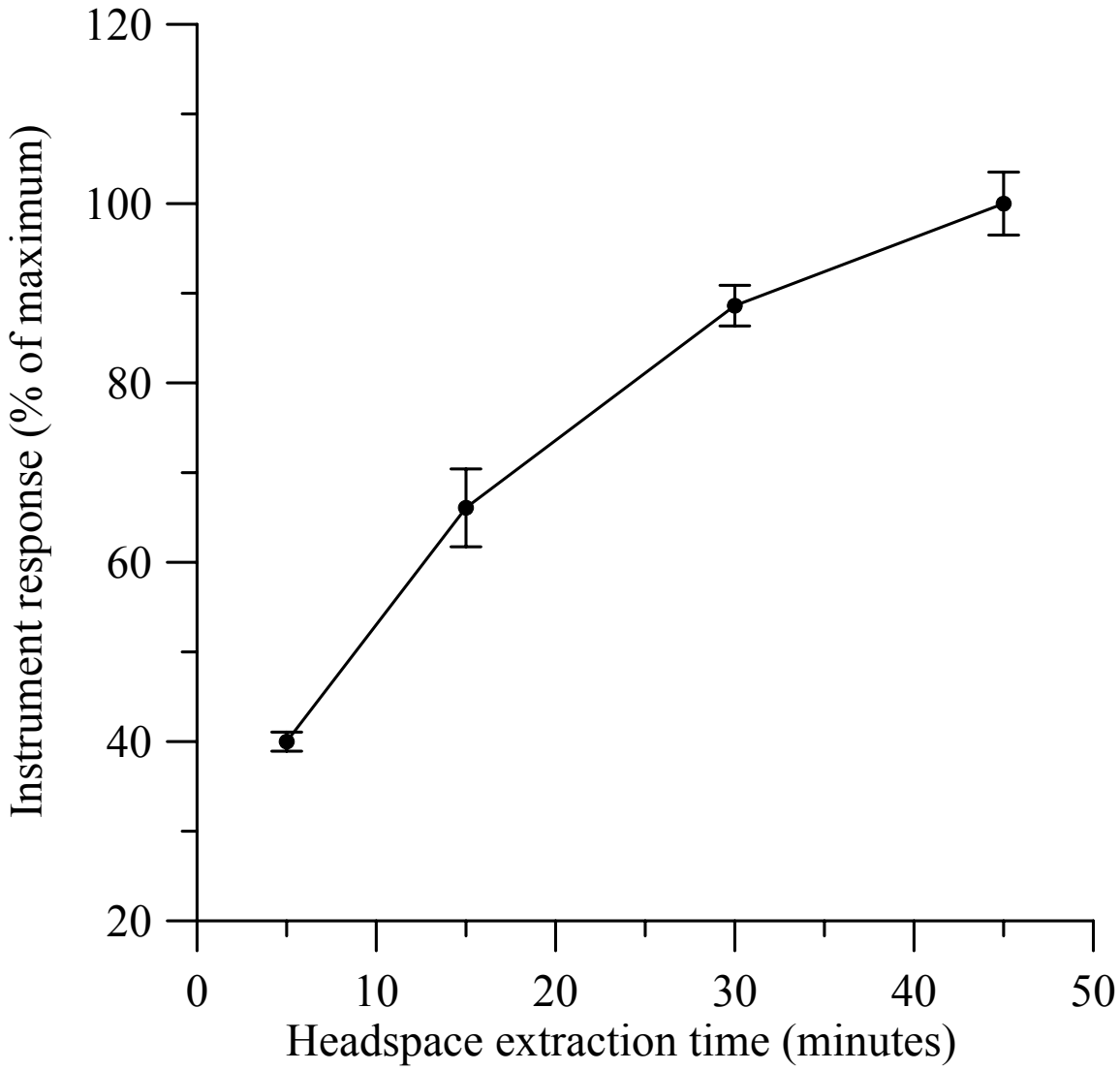

120
100
80
60
40
20
Instrument response (% of maximum)
0
10
20
30
40
50
Headspace extraction time (minutes)

Figure 2

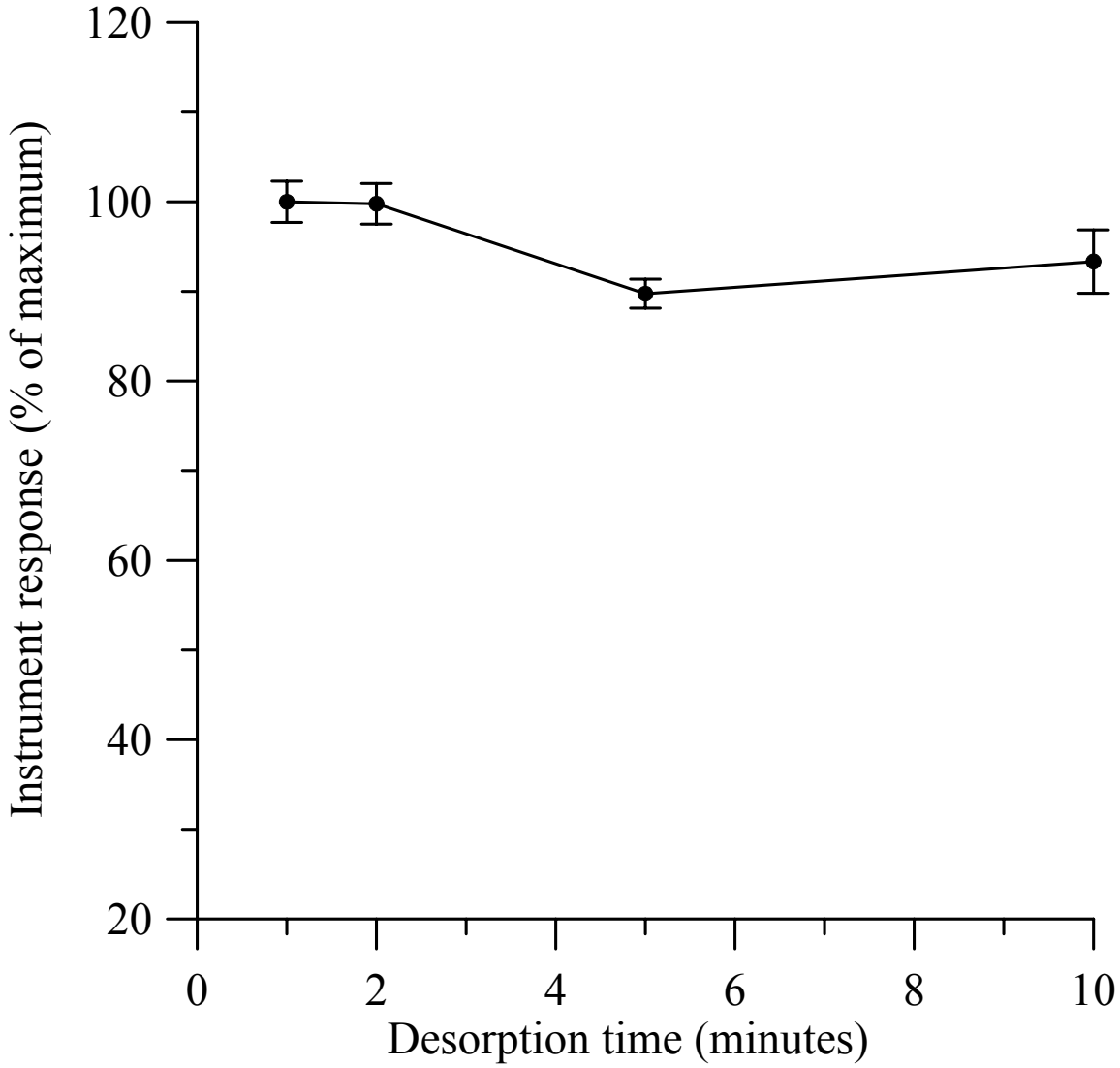

120
100
80
60
40
20
Instrument response (% of maximum)
0
2
4
6
8
10
Desorption time (minutes)

Figure 3

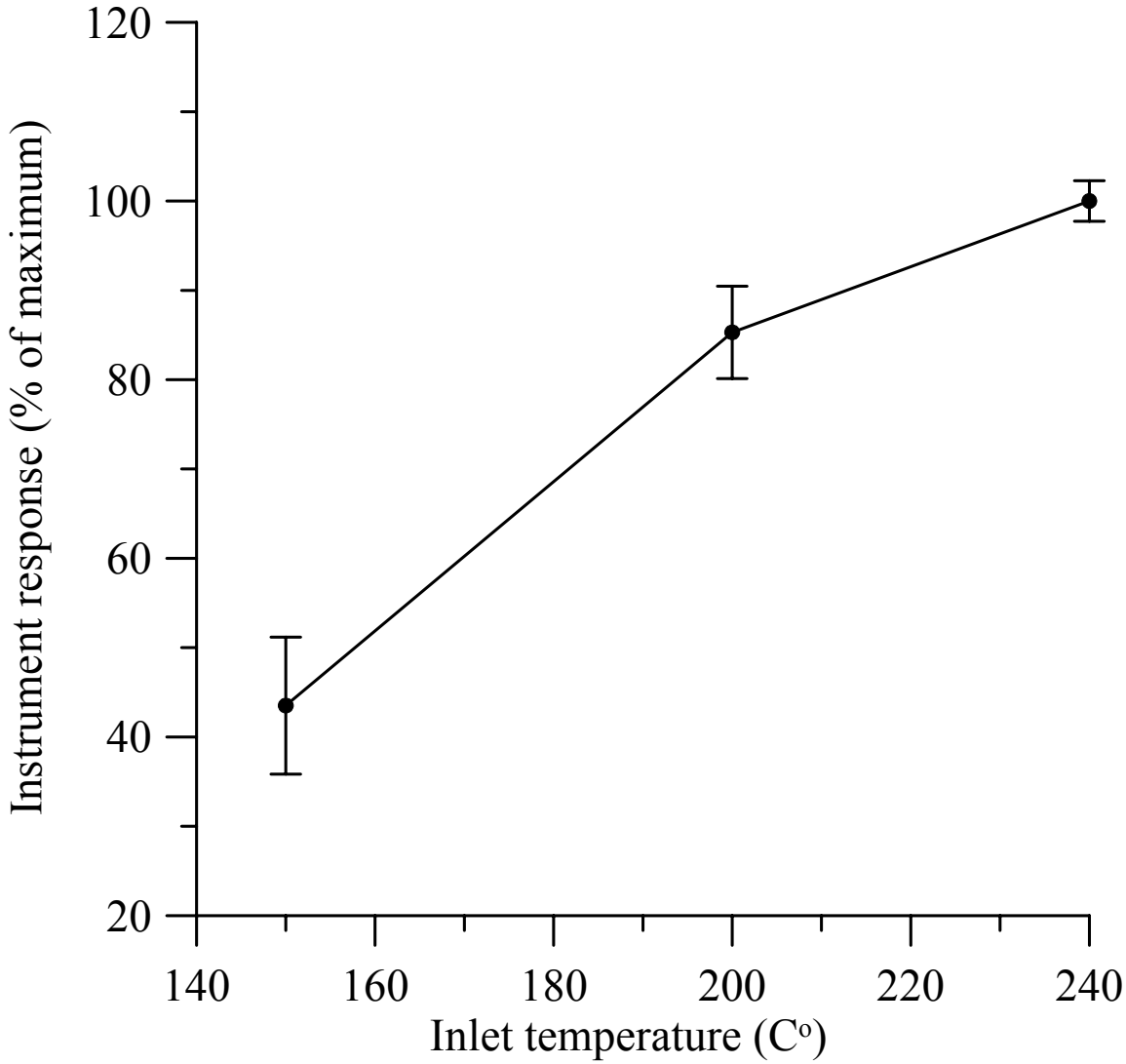

120
100
80
60
40
20
Instrument response (% of maximum)
140
160
180
200
220
240
Inlet temperature (C°)

Figure 4

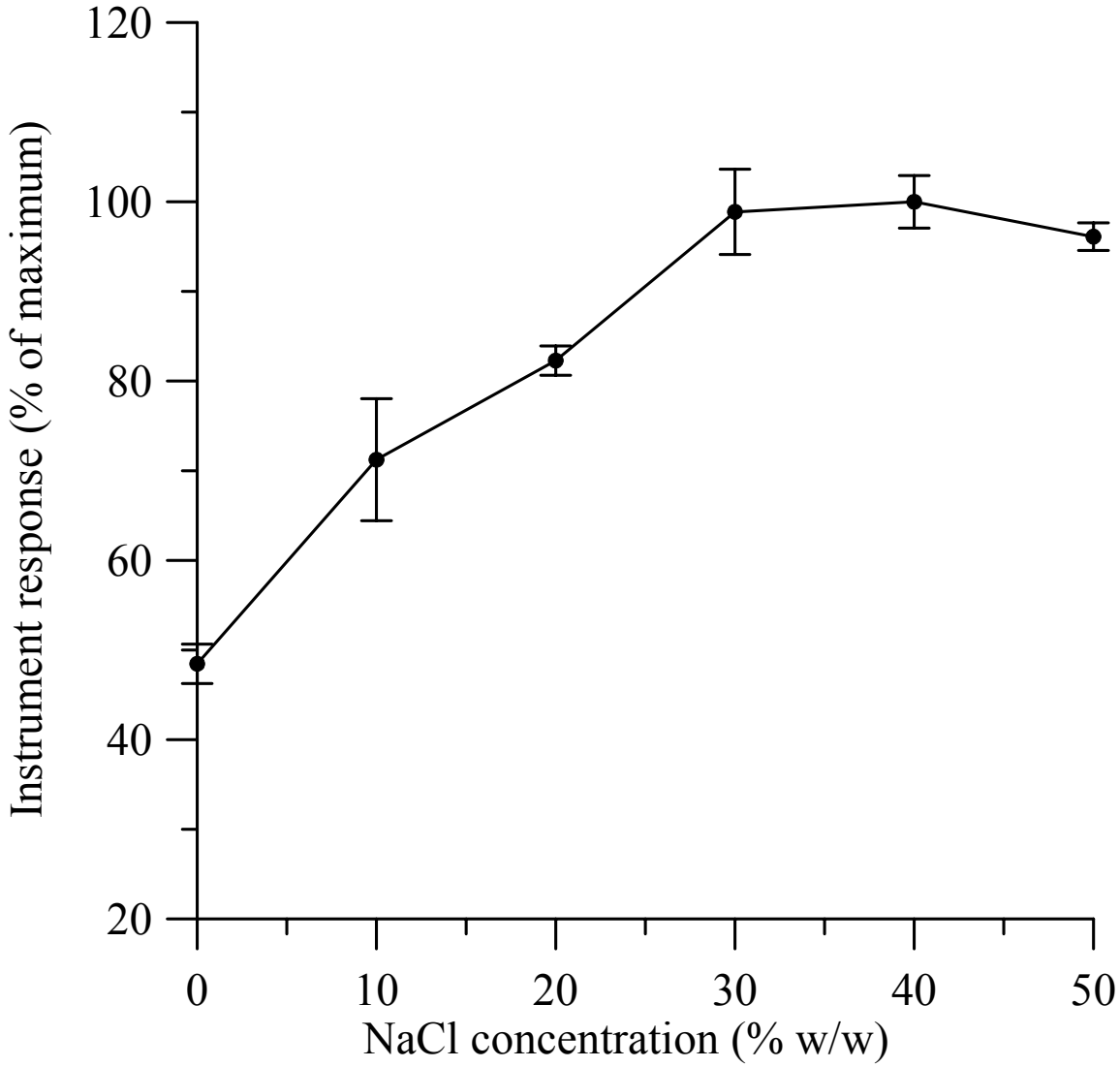
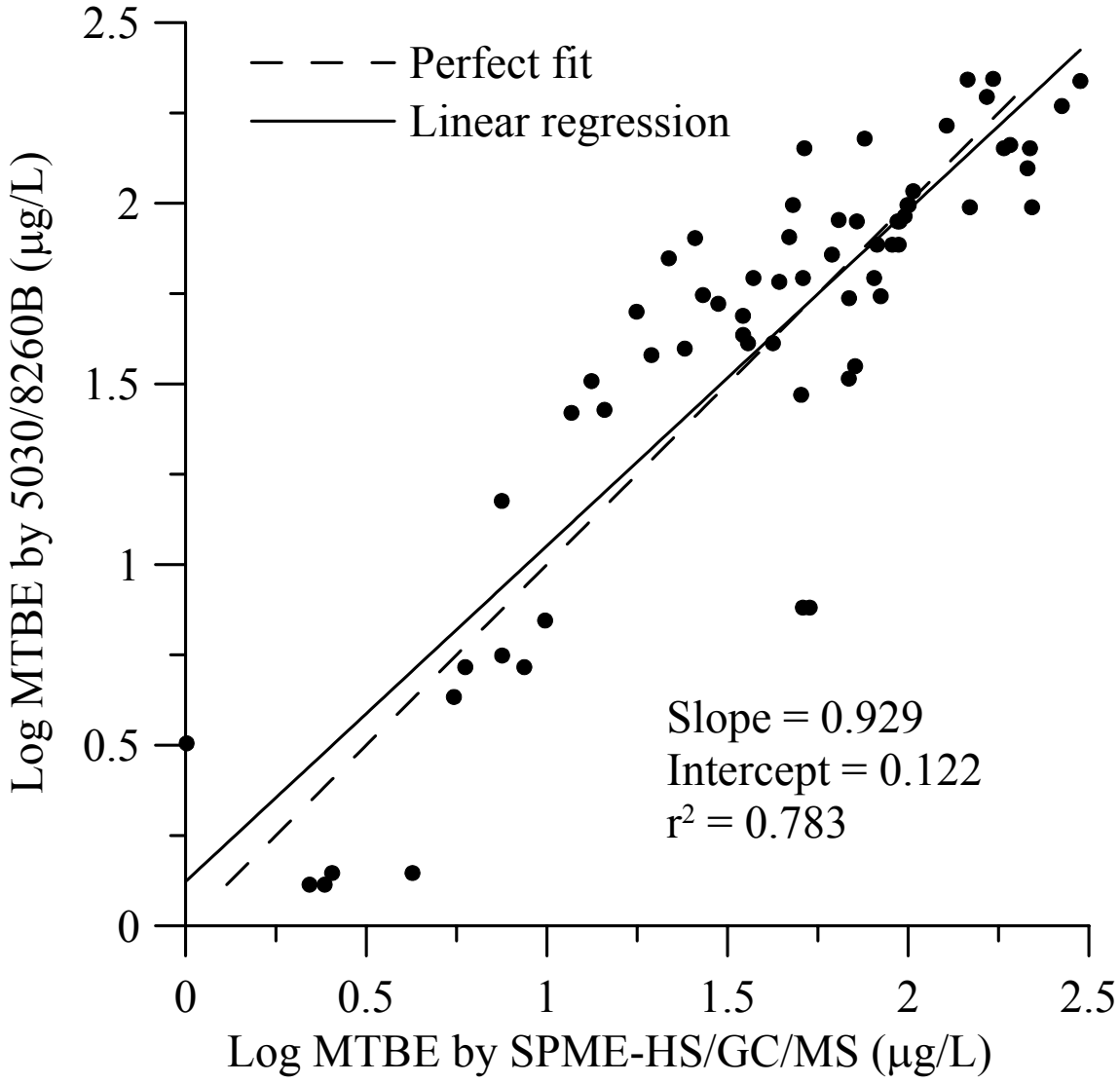

120
100
80
60
40
20
Instrument response (% of maximum)
0
10
20
30
40
50
NaCl concentration (% w/w)

Figure 5


Perfect fit
Linear regression
Slope = 0.929
Intercept = 0.122
r2 = 0.783
Log MTBE by 5030/8260B (µg/L)
Log MTBE by SPME-HS/GC/MS (µg/L)
0
0.5
1
1.5
2
2.5