

Trace Analysis of Ethanol and MTBE
in Water Using Solid Phase Micro-extraction
and
Gas Chromatography/Mass Spectrometry

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Table of Contents

1.0 Introduction	1
2.0 Experimental	3
2.1 Method Calibration	3
2.2 SPME Conditions	3
2.3 Gas Chromatographic Conditions	4
2.4 Mass Spectrometric Conditions	4
3.0 Results	7
3.1 Detection Limit Determination and Sample Analysis	8
4.0 Conclusions	9
5.0 References	11

Lists of Tables and Figures

Tables

Table 1	Quantitation and Confirming Ions Used for all Analysis	6
Table 2	Method Detection Limits and Recovery for Each Analyte in Fortified Blanks and Matrix Samples	6

Figures

Figure 1	Total ion chromatogram (TIC) and selected ion monitoring (SIM) chromatograms for a 100 ppb standard extracted for 25 minutes with 25 percent NaCl.	5
Figure 2	Effect of extraction time on the response of ethanol, <i>iso</i> -propyl alcohol, TBA, MTBE, ETBE, and TAME.	7
Figure 3	Effect of sodium chloride (NaCl) concentration on the response of ethanol, <i>iso</i> -propyl alcohol, TBA, MTBE, ETBE, and TAME.	8

Lists of Acronyms

DAI	direct aqueous injection
DIPE	diisopropyl ether
EPA	United States Environmental Protection Agency
ETBE	ethyl tertiary-butyl ether
FID	flame ionization
GC	gas chromatography
IDL	detection limit
MS	mass spectrometry
MSD	mass selective detection
MTBE	methyl tertiary butyl ether
SIM	selected ion monitoring
SPE	solid phase extraction
SPME	solid phase micro-extraction
TAME	tertiary-amyl ethyl ether
TBA	tertiary-butyl alcohol
TIC	total ion chromatogram

1.0 Introduction

The Clean Air Act of 1990 requires the use of emissions-reducing oxygenated fuels in areas failing to meet national air-quality standards. Methyl tertiary butyl ether (MTBE) and ethanol are most commonly selected by refiners for producing cleaner-burning gasolines, although ethyl tertiary-butyl ether (ETBE), tertiary-amyl ethyl ether (TAME), diisopropyl ether (DIPE), tertiary-butyl alcohol (TBA), and methanol are also used. Due to its widespread use since the 1980s and its environmental mobility and persistence, reports of MTBE detections in ground and surface water have been increasing. Recently, the United States Environmental Protection Agency (EPA) Office of Ground Water and Drinking Water established an advisory panel to examine the behavior of oxygenates in the environment and causes of groundwater contamination by oxygenated fuels (Federal Register, 1998). Unfortunately, most of the information currently available on gasoline oxygenates in ground and surface water is limited to the occurrence of ethers, primarily MTBE. To date, very little information is available regarding the occurrence of ethanol in water. This is, in part, due to ethanol's low toxicity and persistence, but primarily due to the lack of a sensitive and reliable method for determining this compound in water at trace concentrations (ppb levels).

Parts per million (ppm) levels of ethanol in water are relatively easy to measure using gas chromatography (GC) with direct aqueous injection (DAI) techniques using flame ionization (GC/FID) or mass selective detection (GC/MSD). Potter (1996) describes a method for analysis of petroleum-contaminated groundwater using DAI GC/FID with a detection limit for ethanol near 0.10 mg/L. Beihoffer and Ferguson (1994) utilized DAI-GC/MSD for determination of alcohols and carboxylic acids in groundwater with detection limits in the low ppm range. Some EPA Solid Waste methods (SW-846) indicate that ethanol may be determined by direct aqueous injection using either FID or MSD but, again, sensitivity is limited to ppm concentrations. The primary limitations with respect to the sensitivity of direct aqueous injection methods are related to: 1) the amount of sample injected is limited to no more than 5 to 10 μL ; 2) the response and selectivity of the detector; 3) the selectivity of the column in the presence of water and other polar organics; and 4) degradation of the stationary phase by water.

Trace levels of ethers have been reported to be more successfully analyzed by direct aqueous injection methods. Church et al. (1997) describe a method for determination of MTBE and related compounds by DAI-GC/MSD with a detection limit reported to be near 0.1 $\mu\text{g/L}$ for MTBE by maximizing the amount of sample injected (10 μL) and venting the water after injection. However, a detection limit for ethanol by this method was not reported. In addition, instrument detection limits of DIA-GC/MS for acetone and *iso*-propyl alcohol is 10 to 100 times higher than that of the ethers. This reduced sensitivity for these compounds is most likely limited due to greatly increased noise levels for ions with masses less than ~ 100 amu, as well as the difficulty of chromatographically separating the more polar and highly miscible alcohols from the water matrix. In general, both the flame ionization and mass selective detectors require nanogram quantities of low molecular weight organics (< 100 amu) to produce a measurable signal. In comparison, a DAI injection of 10 μL of water containing 1.0 $\mu\text{g/L}$ of MTBE is equivalent to ~ 0.010 nanograms (10 pg) of the target compound injected.

Purge and trap methods, including closed loop stripping (Grob, 1974), have been employed in an attempt to increase the amount of material that is injected into the gas chromatograph. Closed loop stripping methods — coupled with GC/MSD — produce a highly sensitive technique capable of detecting parts per trillion concentrations of many trace polar organics, such as terpenes and phenols (APHA, 1996). However, very polar and miscible low molecular weight compounds, such as ethanol, have low and variable recoveries, resulting in poor sensitivity (Kopfler et al. 1976; Ramstad and Nestruck, 1981; Church, 1995).

For over 10 years, solid phase extraction (SPE) has been widely used for concentrating a wide variety of compounds in water. In SPE, a water sample is passed through a packed column of suitable stationary phase, such as resin, polymer, or carbon, which selectively sorbs analytes of interest. Target compounds are then flushed from the stationary phase with organic solvents. However, the high polarity and miscibility of ethanol in water severely constrain the analytical chemist's choice of available stationary phases. Nonpolar bonded silica phases are unlikely to partition ethanol from water. Although activated carbon may extract ethanol from water before breakthrough, it may be difficult to find a suitable solvent that would efficiently elute ethanol from the carbon phase. SPE experiments with more novel stationary phases, such as zeolites (Ogawa, 1981), indicate minimal retention of low molecular weight alcohols from water.

A relatively new form of SPE, known as solid phase micro-extraction (SPME), has been successfully utilized to rapidly concentrate and analyze a wide variety of polar and nonpolar organic compounds in aqueous matrices (Pawlisyn, 1997). SPME is a solventless extraction technique that relies on direct partitioning of analytes from either sample headspace or matrix to a small amount of stationary phase bonded to a fused silica fiber. Extraction is then followed by analysis using direct thermal desorption of the analytes from the fiber in a narrow-bore GC injection port. The selectivity of SPME for different classes of compounds is highly dependent on the composition of the stationary phase.

In the past 5 years, SPME-GC/FID has been successfully utilized to determine ppm levels of ethanol in water (Shirley et al. 1995), beverages (Yang and Peppard, 1995), and blood and urine (Lee et al. 1998). Lee et al. (1998) used a relatively new SPME fiber consisting of a mixture of divinylbenzene, Carboxen™ (a porous carbon molecular sieve), and polydimethylsiloxane. Lee et al. (1998) indicated that the detection limits for ethanol in blood and urine using the SPME-GC/FID method are significantly lower than other reported methods. This SPME sorbent is over 20 times more efficient at sorbing ethanol than the polyacrylate used by Shirley et al. (1995) and Yang and Peppard (1995). It also has been successfully used for SPME headspace extraction and GC/MS analysis of part per trillion concentrations of very polar odor-causing compounds in drinking water (Lloyd et al., 1998).

In this paper, we describe a sensitive SPME-GC/MS method for the analysis of ethanol, MTBE, ETBE, TAME, and TBA in water at trace concentrations.

2.0 Experimental

Reagents and Materials

Ethanol (dehydrated, 200 proof) was obtained from Pharmco Products, Inc. (Brookfield, CT). *iso*-Propyl alcohol (Optima grade) and MTBE (HPLC grade) were obtained from Fisher Scientific (Pittsburgh, PA). ETBE (99 percent), TAME (97 percent), and TBA (HPLC grade) were obtained from Aldrich Chemicals (Milwaukee, WI). Purified water was obtained by passing distilled water through a Fisher Barnstead 4-Module Nanopure cartridge system. Sodium chloride (NaCl, certified A.C.S. grade) was obtained from Fisher Scientific and purified by heating overnight at 110°C. Fused silica capillary GC columns were obtained from J&W Scientific, Inc. (Folsom, CA). Helium (Ultra Pure Carrier Grade) was obtained from Air Products and Chemicals, Inc (Allentown, PA). SPME fibers and sample vials (4 ml, clear, screw top, hole cap, PTFE/Silicone septa) used in this study were obtained from Supelco, Inc. (Bellefonte, PA).

2.1 Method Calibration

Ethanol, TBA, MTBE, ETBE, and TAME were calibrated with a three-point calibration using *iso*-propyl alcohol as an internal standard. The calibration stock solutions were each prepared separately from the neat materials and diluted in purified water to convenient levels for preparation of calibration samples. Three calibration samples were prepared with respective ethanol and TBA concentrations of 20, 100, and 200 ppb; MTBE, ETBE, and TAME concentrations of 0.04, 2, and 4 ppb; and a constant *iso*-propyl alcohol concentration of 200 ppb. These calibration samples were extracted and analyzed in the same manner as all samples. Calibration curves were linear with coefficients (r^2) greater than 0.98.

2.2 SPME Conditions

The SPME assembly is composed of an 85 μ m Carboxen/Polydimethylsiloxane fiber with a manual injection holder (Supelco, Inc., Bellefonte, PA). A previously unused fiber is preconditioned before use by performing two blank injections at an elevated injection temperature of 260°C. On subsequent days using the same fiber, two blank injections were performed at 220°C to recondition the fiber before analysis. Fibers can be reused for a number of injections, but they are very fragile and care is needed to prevent the breakage of the fiber. The analytes were extracted by submerging the preconditioned fiber into the water sample (3.6 ml), which had been pretreated to contain approximately 25 percent NaCl (w/w). The water sample was magnetically stirred at room temperature during the extraction with an extraction time of 25 minutes.

2.3 Gas Chromatographic Conditions

Chromatographic separation was accomplished with a fused silica capillary column (J&W Scientific, Folsom, CA, DB-1, 30 m by 0.32 mm i.d., 5 μ m film thickness). The initial GC oven temperature was held at 50°C for 4 minutes, increased at 20°C/min to 90°C and held for 3 minutes, and then increased to 200°C at 40°C/min. The GC oven was held at 200°C for 11.25 minutes to allow for elution of higher boiling contaminants. The total time of analysis was 23 minutes.

The injection port was equipped with a Merlin Microseal™ septum (Hewlett Packard, Avondale, PA) and a 0.75 mm internal diameter injection liner (Supelco, Inc. Bellefonte, PA) designed to optimize recovery in SPME analysis. The injection port was operated in the splitless injection mode at injection with the split/splitless purge valve opened at 0.4 minutes. The injection port temperature was 220°C with a head pressure of helium maintained at 34.5 kPa (5.0 psi). The SPME fiber was conditioned for the next analysis in the hot injection liner for 2 minutes after injection, after which it was withdrawn and readied for a new sample extraction.

2.4 Mass Spectrometric Conditions

The analytes were detected by using a HP 5970 Mass Spectrometer Detector (MSD, Hewlett-Packard, Avondale, PA), which used electron impact ionization for fragmentation. For increased sensitivity and specificity, the detector was operated in the selected ion monitoring (SIM) mode with ion dwell times of 100 ms. An example chromatogram is shown in Figure 1. The quantitation ions of interest and ion designations for the oxygenated analytes are given in Table 1.

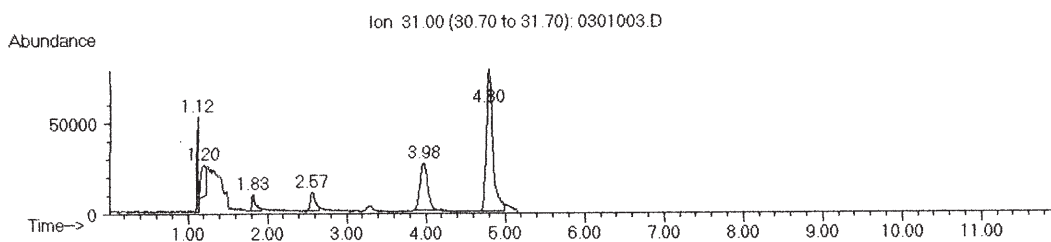
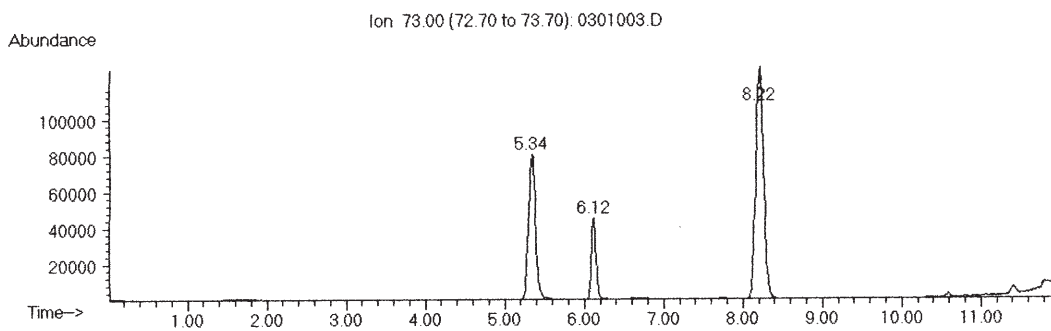
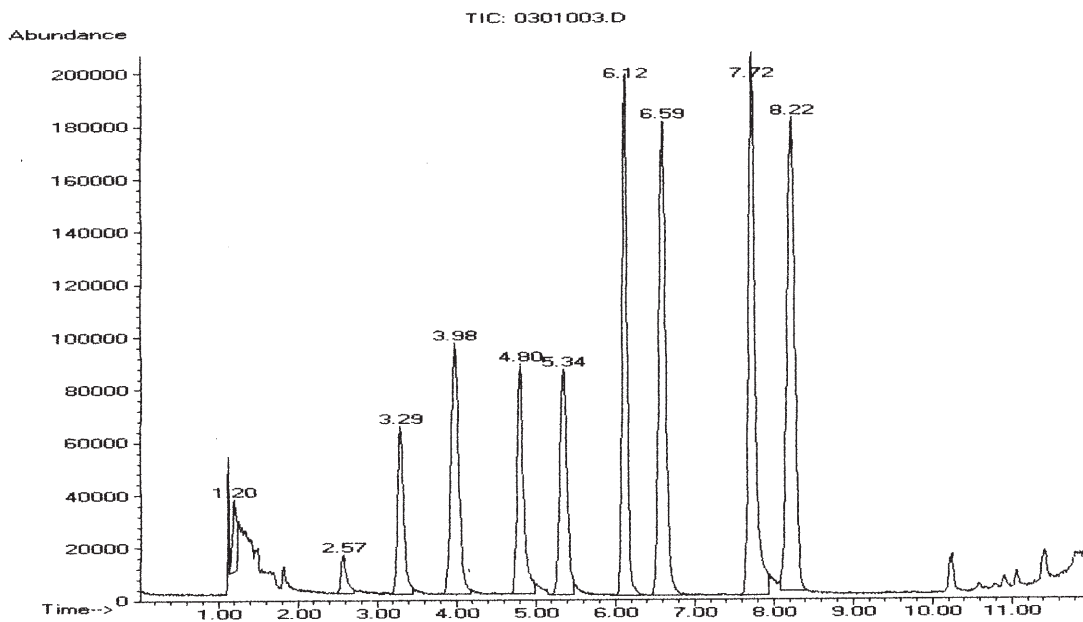


Figure 1. Total ion chromatogram (TIC) and selected ion monitoring (SIM) chromatograms for a 100 ppb standard extracted for 25 minutes with 25 percent NaCl. The retention times for analytes are given in Table 1.

Table 1.
Quantitation and Confirming Ions Used for all Analysis

Analyte	Quantitation ion (m/z)	Confirming ion (m/z)	Retention Times (min)
Ethanol	31.0 (M-CH ₃) ⁺	45.0 (M-H) ⁺	2.57
TBA	59.0 (M-CH ₃) ⁺	31.0 (M-C ₃ H ₇) ⁺	3.98
MTBE	73.0 (M-CH ₃) ⁺	45.0 (M-CH ₃) ⁺	5.34
ETBE	59.0 (M-C ₃ H ₇) ⁺	87.0 (M-CH ₃) ⁺	6.59
TAME	73.0 (M-C ₂ H ₅) ⁺	87.0 (M-CH ₃) ⁺	8.22

Reference ion m/z 45.0 used for the internal standard *iso*-propyl alcohol (Retention Time: 3.25 min).

Table 2.
Method Detection Limits and Recovery for Each Analyte
in Fortified Blanks and Matrix Samples

Analyte	SPME Method Detection Limit (n = 8) (ppb)	Method Detection Limit Concentration (ppb)	Fortified Blank Recover (n = 8) (% ± σ)	Fortified Blank Concentration (ppb)	Fortified Matrix Recovery (n = 8) (% ± σ)	Fortified Matrix Concentration (ppb)
Ethanol	15.0	42.6	98 ± 12	42.6	109 ± 6	106
TBA	1.8	20.7	107 ± 2	41.5	105 ± 7	104
MTBE	0.008	0.042	104 ± 5	0.84	102 ± 7	2.09
ETBE	0.025	0.039	104 ± 8	0.79	105 ± 7	1.97
TAME	0.038	0.040	106 ± 6	0.83	106 ± 5	2.07

3.0 Results

Extraction time and recovery were optimized by extracting a known solution prepared in reagent water for a period of time up to 30 minutes. A graph of extraction time vs. response (Figure 2) for all analytes shows that, for all analytes, there is only a small response increase after the initial 10 minutes and the response is constant or slightly decreasing after 25 minutes. To maximize sample throughput efficiency, an extraction time of 25 minutes was chosen since the GC analysis cycle time (analysis + cool down) of approximately 27 minutes would be equal to the time the fiber spends in both the sample (25 minutes) and injection port (2 minutes).

The addition of sodium chloride (NaCl) to the sample increases the efficiency of the extraction process for all analytes and internal standards (Figure 3). As the amount of salt is increased, the responses increase until it approaches the saturation point for NaCl 26.3 percent (w/w) at 25°C (Merck, 1989). At a salt concentration >25 percent (w/w), the responses of most analytes are nearly constant, but for ETBE and TAME, the responses decreased. This decrease may result from the excess suspended salt crystals in the sample interfering with the extraction process. A sodium chloride concentration of 25 percent (w/w) was chosen to insure that saturation would not be exceeded and high analyte responses would be maintained.

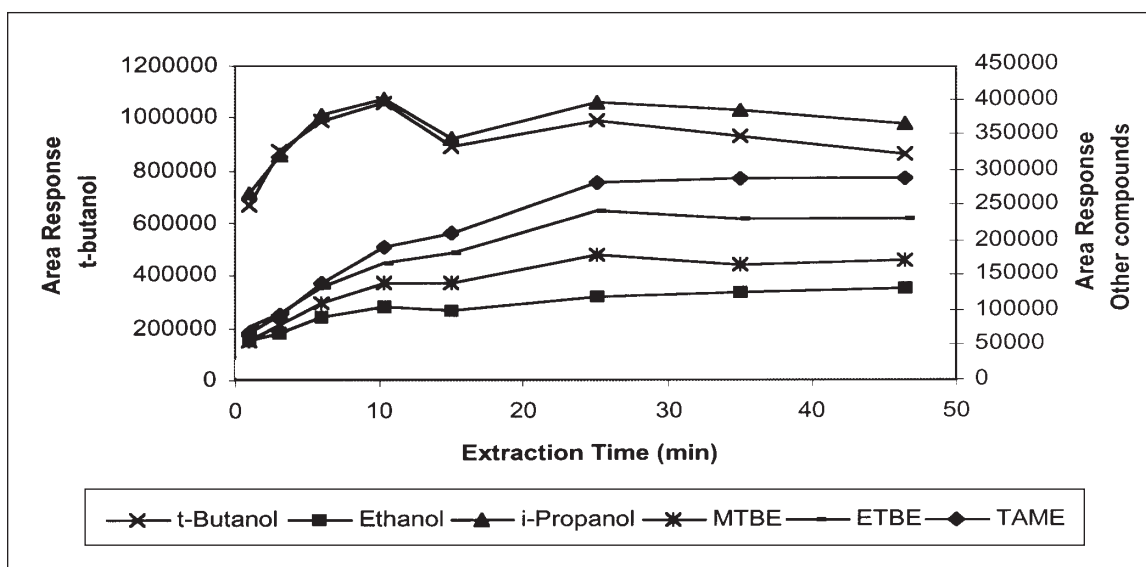


Figure 2. Effect of extraction time on the response of ethanol, *iso*-propyl alcohol, TBA, MTBE, ETBE, and TAME. NaCl concentration: 25 percent (w/w).

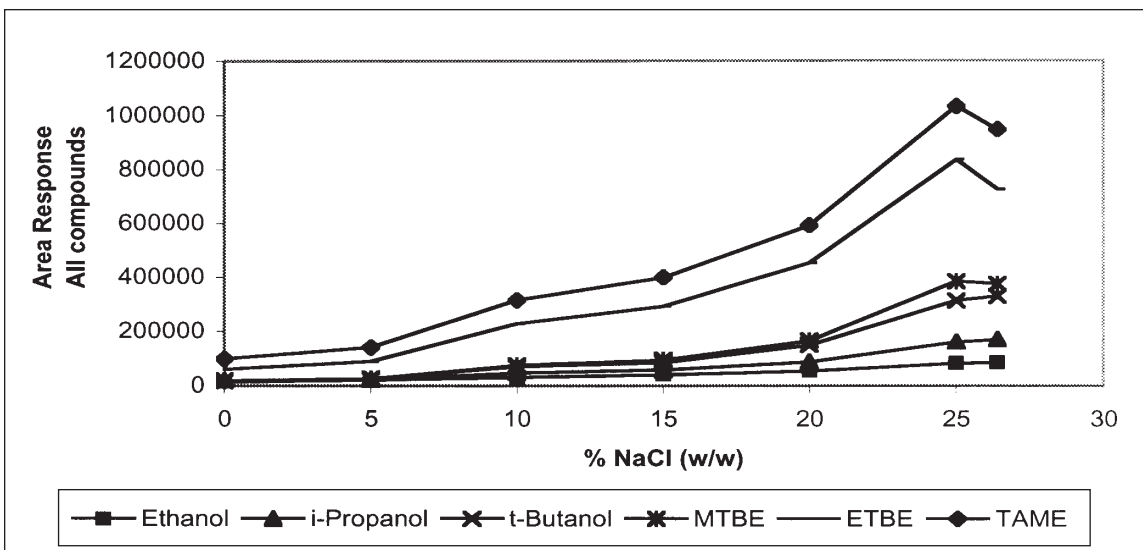


Figure 3. Effect of sodium chloride (NaCl) concentration on the response of ethanol, *iso*-propyl alcohol, TBA, MTBE, ETBE, and TAME. Extraction time: 25 minutes.

3.1 Detection Limit Determination and Sample Analysis

Method detection limits and recoveries for each analyte were determined by the accepted procedure of the EPA (1989). A series of eight replicate samples at 40 ppb ethanol, 20 ppb TBA, and ether concentrations near 0.04 ppb were analyzed and the detection limit determined from the variability of the results (Table 2). Analyte recovery in fortified reagent water at approximately 20 percent of the calibration range (40 ppb and 0.8 ppb for the alcohols and ethers, respectively) indicates that all analytes are quantitatively recovered with recoveries ranging from 98 to 107 percent. Recovery from fortified matrix samples, determined at 50 percent of the calibration range, is also quantitative at 102 to 109 percent (Table 2).

Thirty groundwater samples from multilevel samplers in the Clear Creek watershed in Polk County, Nebraska were analyzed for ethanol, MTBE, and other gasoline oxygenates. None of these compounds were detected in these samples. The lack of detectable levels of gasoline oxygenates in the groundwater from this area may reflect the absence of nearby a source of gasoline or concentrated emissions from oxygenated gasoline.

4.0 Conclusions

The analysis of ethanol and MTBE from water at low ppb levels has been accomplished by SPME extraction and GC/MS detection. The amount of salt (sodium chloride), which is added to the water sample, and the length of extraction time are two factors that influence the extraction efficiency of ethanol. The sensitivity and selectivity of GC/MS detection enables accurate quantification of ethanol and TBA at low ppb levels and MTBE, ETBE, and TAME at mid ppt levels.

Other factors that influence the extraction efficiency still need to be investigated. These factors include sample temperature, sample pH, and fiber composition. The added salt also seems to cause problems with salt crystallizing on the fiber after a hot injection. This occasionally contributes to premature breakage of the fiber when the fiber is retracted back into the fiber holder. However, the increased sensitivity obtained with the salt addition is important. The use of a more volatile salt (e.g., ammonium acetate) to eliminate this problem is a source of future research in this area.

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