Ground Water Monitoring&Remediation

Rapid Analysis of 1,4-Dioxane in Groundwater by Frozen Micro-Extraction with Gas Chromatography/Mass Spectrometry

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Abstract

An innovative micro-extraction of aqueous samples coupled with gas chromatography/mass spectrometry in selected ion-monitoring mode (GC/MS-SIM) was developed to selectively analyze for 1,4-dioxane with low part-per-billion detection sensitivity. Recoveries of 1,4-dioxane ranged from 93% to 117% for both spiked laboratory reagent water and natural groundwater matrices, the later having elevated organic carbon content (8.34 ± 0.31 mg/L as total organic carbon). We observed that freezing the aqueous sample along with the extraction solvent enhanced the extraction efficiency, minimized physical interferences, and improved sensitivity resulting in a limit of detection for 1,4-dioxane to approximately 1.6 μg/L. This method substantially reduces the labor, time, reagents and cost, and uses instruments that are commonly found in analytical laboratories. This method requires a relatively small sample volume (200 μL), and can be considered a green analytical method as it minimizes the use of toxic solvents and the associated laboratory wastes.

Introduction

1,4-Dioxane (dioxane) is a cyclic ether that has been commonly used as a stabilizer and corrosion inhibitor for chlorinated organic solvents, mainly 1,1,1-trichloroethane (1,1,1-TCA) (Mohr 2001). In recent years, dioxane has attracted increasing attention as it is likely to be present at thousands of sites impacted by chlorinated solvent spills (Mohr et al. 2010). As an emerging contaminant, dioxane has also been detected in drinking water, surface waters, groundwater, and waste water (Zenker et al. 2003). The International Agency for Research on Cancer has classified it as a possible human carcinogen (B2) and U.S. EPA issued a health drinking water advisory concentration of 3 μg/L at a 10^{-6} lifetime cancer risk level (IARC 1999; U.S. EPA 2000). Therefore, dioxane was included in the Final Third Drinking Water Contaminant Candidate List (CCL3) by U.S. EPA in September 2009 (U.S. EPA 2009).

Although a maximum contaminant level (MCL) for dioxane in drinking water has not yet been established, several states have set water quality guidelines and standard levels ranging from 3 to 85 μg/L (Mohr 2001). However, the analysis of dioxane in aqueous matrices at such low parts-per-billion concentration is a very challenging undertaking due to dioxane's high miscibility in water (and associated low volatility), commonly encountered matrix interferences, and the high cost associated with more sophisticated and novel analytical approaches, as discussed in the following text (Table 1).

As with other highly soluble, volatile compounds such as alcohols and ketones, direct aqueous injection (DAI) followed by analysis using gas chromatography (GC) equipped with a flame ionization detector (FID) has been traditionally applied to analyze dioxane, but this technique typically yields a limit of detection (>0.1 mg/L) with relatively low sensitivity due to limitations in sample loading (Parales et al. 1994; Draper et al. 2000; Mahendra and Alvarez-Cohen 2006; Li et al. 2010). Increasing sample injection volumes is not a viable solution as this often results in extinguishing the hydrogen flame of the detector. Purge and trap (P&T) technology is used as a means to concentrate volatile compounds onto a GC/MS, as in U.S. EPA Methods 524.2, 1624, and 8260. However, because dioxane is fully miscible with water, its purging efficiencies are typically low (<1%) and are not easily concentrated (Munch and Eichelberger 1992). Hence, the typically encountered limits of detection for such P&T methods are normally 10 to 100 times greater than the more efficiently purged organic volatiles (Draper et al. 2000). Although salting and heating techniques have been shown to improve the purging efficiencies, analytical

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Table 1
Comparison of Different Dioxane Analytical Methods

Analytical Method	Sample Size (mL)	Recovery (%)	Extraction Efficiency (%)	Typical LOD (µg/L)	Specialized Instrumentation	References
DAI	0.05	~100	100	2000	No	Draper et al. (2000)
P&T	5–25	60–90	<1	10	Yes	Draper et al. (2000), Park et al. (2005); Epstein et al. (1987); Munch and Eichelberger (1992).
SPME	1–10	90–110	NA	1	Yes	Nakamura and Daishima (2005); Shirey (2000); Shirey and Linton (2006)
SPE	50–1000	90–110	18–94	<1	Yes	Epstein et al. (1987); Grimmett and Munch (2009); Isaacson et al. (2006); Kawata et al. (2001, 2003); Park et al. (2005); Song and Zhang (1997)
HS-SPDE	0.5–1	NA	NA	0.8	Yes	Jochmann et al. (2006)
LLE	100–1000	80–110	40–55[1]	1	No	Draper et al. (2000); Park et al. (2005)
FME	0.2	93–117	60–75	1.6	No	This work

NA = not available.
[1]When solvent (methylene chloride) to water ratio equals to 1:1 (v/v).

reproducibility of the purging can be compromised by addition of a large amount of salts (i.e., 1.6 M Na_2SO_4) and potential instrument problems due to the exposure of excess water vapor (Epstein et al. 1987; Zenker et al. 2003).

Solid-phase micro-extraction (SPME) coupled with GC-FID or GC/MS is a suitable approach to detect low concentrations of dioxane in small water samples (normally 1 to 10 mL). A limit of detection of 1.2 µg/L was obtained using 100 µm polydimethylsiloxane (PDMS) fiber with 30 min headspace (HS) exposure at 60°C, and with a limited linear range of 5 to 100 µg/L; GC/MS was used as the analytical finish (Nakamura and Daishima 2005). In other work, carboxen-polydimethylsiloxane (CAR-PDMS) fiber was shown to exhibit higher extraction efficiency than other fiber coatings (Shirey 2000). By immersing the CAR-PDMS fiber in water samples for 20 min with agitation, a 2.5 µg/L limit of detection was obtained, with a linear range of 5 to 10,000 µg/L and GC-FID as the analytical finish. With an MS detector, a lower limit of quantification of 0.5 µg/L was achieved with background subtraction, although with this technique, the upper linear range was limited to 100 µg/L (Shirey and Linton 2006). Besides the relatively high costs of specialized instrumentation and automation systems associated with this SPME technique, interferences can be encountered as common co-contaminants (e.g., 1,1,1-TCA) in samples exhibit much higher affinity for the fiber, and their sorption competitively displaces dioxane. Moreover, the extraction temperature, duration, salt concentration, and pH may need to be modified and optimized for different sample sources and water chemistry.

Solid-phase extraction (SPE) is another alternative to concentrate dioxane prior to analysis. A coconut-shell charcoal tube enrichment method represents another alternative as a carbon-based sorbent which can be used to extract dioxane from water samples (Epstein et al. 1987). The desorbate of charcoal tubes using carbon disulfide/methanol solvents was analyzed by GC-FID, which yielded an instrumental limit of detection of less than 1 µg/L (with an average recovery of 77.5%) when a 4 L sample was extracted. Thereafter, different SPE methods consisting of different formations of activated carbons (e.g., fiber felt, disks, and Sep-Pak cartridges) were developed. Usually, acetone and methylene chloride were used as the solvent eluent and the extract was analyzed by GC/MS, which yielded notably enhanced recoveries (>90%) and low limits of detection (<1 µg/L), but still required a relatively large water sample volume (80 to 500 mL) (Kawata et al. 2001; Kawata et al. 2003; Park et al. 2005; Isaacson et al. 2006; Tanabe et al. 2006; Grimmett and Munch 2009; Kawata and Tanabe 2009). In these cases the high water content in the eluates must be managed, either by pretreatment using air drying or centrifugation of the SPE materials (Kawata et al. 2001; Park et al. 2005; Isaacson et al. 2006; Grimmett and Munch 2009), or by post-treatment using freezing separation of the water layer from organic extracts (Kawata et al. 2003; Tanabe et al. 2006; Tanabe and Kawata 2008; Kawata and Tanabe 2009). Moreover, matrix interferences and total suspended solids in water samples have been shown to hinder the successful application of this technique (Park et al. 2005).

Although the Henry's Law constant of dioxane is as low as 5×10^{-6} atm m^3 mol^{-1} at 20°C (Schwarzenbach et al. 2003), enhanced HS sample concentration techniques were examined by progressively increasing the equilibration

temperatures. However, even with temperatures up to 80°C, a relatively high limit of detection of 0.82 mg/L was achieved when GC-FID was used as the analytical finish (Urakami et al. 2004). Trace (ppb-level) analysis for dioxane can be improved by using similar mechanisms to SPME (i.e., head space solid-phase dynamic extraction (HS-SPDE) sample concentration) followed by a GC/MS analytical finish. In previous work, the optimum concentration/extraction was observed under equilibrium temperature at 70°C, with 50 aspiration cycles and the addition of a 25% NaCl (w/w) salt solution (Jochmann et al. 2006). Comparing four commercial coating materials, the polar WAX coated needle achieved the lowest limit of detection (0.8 µg/L) for dioxane (Jochmann et al. 2006).

Traditional continuous liquid-liquid extraction (LLE) techniques coupled with GC/MS analysis have also been reported to achieve low limits of detection (e.g., 0.2 µg/L) (Draper et al. 2000; Park et al. 2005). However, large sample and solvent volumes are required, and concentrating the extracts in a nitrogen evaporator for analysis is time-consuming and typically generates considerable amounts of hazardous waste. A rapid GC/MS determination method combining LLE (hexane/methylene chloride, 80:20, v/v) and SPE (C_{18} cartridge) has also previously been developed (Song and Zhang 1997). Although the required sample volume is substantially lower (viz., 1 mL); the reported analytical sensitivity of 50 µg/L is not sufficiently low enough relative to current toxicological benchmarks.

Recognizing the need for sufficiently low limits of detection in situations when very limited sample volume is available for analysis, we aimed to develop an analytical technique that is reliable, sensitive enough to detect dioxane at the low concentrations required by environmental regulations, easy to implement using commonly available equipment, and minimizes hazardous waste generation. In this article, we report a novel method of sample preparation using a frozen micro-extraction (FME) technique followed with GC/MS-SIM detection for dioxane using very small volumes of water samples (200 µL). An important aspect of this rapid pretreatment with minimal sample handling is that it minimizes dioxane degradation activities during sample extraction, such as attack by monooxygenase-expressing bacteria or chemical oxidation by reactive oxygen species used in some site remediation schemes (Zenker et al. 2003; Mahendra and Alvarez-Cohen 2006; Mahendra et al. 2007; Li et al. 2010). As part of method validation activities, the precision, accuracy, and suitability of this analytical method were examined in both synthetic and natural groundwater samples.

Methodology

Chemicals and Reagents

1,4-Dioxane (99.9%, stabilized with 10 mg/L sodium diethyldithiocarbamate) was purchased from EM Science, Cherry Hill, NJ. Both 1-butanol (99.9%) and methylene chloride (99.9%) were obtained from Fisher Scientific, Fair Lawn, New Jersey. 1,4-Dioxane-d_8 (99%) and 1,1,1-TCA (≥99.8%, for GC) were purchased from Sigma Aldrich, St. Louis, Missouri. 1,4-Dichlorobenzene-d_4 (2000 µg/mL in methanol) was purchased from Supelco Analytical, Bellefonte, Pennsylvania. Methanol (99.9%, for GC, HPLC, Spectrophotometry, and Gradient Analysis) was purchased from EMD Chemical, Darmstadt, Germany. Anhydrous sodium sulfate was purchased from Thermo Fisher Scientific, Waltham, Massachusetts. The laboratory reagent water was prepared from tap water using reverse osmosis followed by a Millipore Milli-Q Academic polishing unit (Billerica, Massachusetts).

Sample Preparation and FME Procedure

About 0.3 mL water samples were collected with a sterile 1 mL syringe, and filtered through a 0.2 µm, 13 mm Nylon syringe filter to remove suspended matter in the water. A 200 µL aliquot of the filtered sample was transferred to a clean Agilent screw cap 1.5 mL glass vial by pipette, and subsequently spiked with 1 µL of a methanol mixture containing 40 mg/L 1,4-dioxane-d_8 as the internal standard (IS) and 20 mg/L 1,4-dichlorobenzene-d_4 as the surrogate standard (SUR). Therefore, concentrations of 1,4-dioxane-d_8 and 1,4-dichlorobenzene-d_4 in the sample were 200 and 100 µg/L, respectively. An equal volume of methylene chloride (200 µL) was added into the glass vials. The capped vials were then gently shaken for 30 s and placed on glass plates inclined at an angle of 45° from the horizon to reduce the potential of cracking of the vials once the water freezes. After freezing in a refrigerator set at −80°C for 20 min, only the water phase is frozen, but not the methylene chloride solvent with the extracted dioxane. The liquid phase (~200 µL) of the methylene chloride solvent was removed with a gas-tight glass syringe and quickly transferred to a fresh instrument vial to avoid re-melting of the ice. The extract was then ready and stored at −20°C until analysis.

GC/MS Apparatus

An Agilent mass spectrometer Model 5973 and Agilent gas chromatograph Model 6890 equipped with an electronic pressure control system and an HP-5 column (30 m × 0.25 mm i.d., 0.25 µm film thickness) were used for analysis. The inlet temperature was 200°C. The inlet pressure was 10.0 psi, with inlet "pulse" pressure set to 40 psi for 0.2 min. The septum purge to split vent was set at 40.3 mL/min for 1.0 min. Pulsed splitless injection of 1 µL was applied to minimize residence time in the liner and improve peak shape. The gas flow in the column was constant at 1.3 mL/min with helium of ultra high purity. The oven temperature was initially held at 35°C for 5.0 min, and then run with a 20°C/min ramp to 100°C, followed by a 50°C/min ramp to 275°C and held isothermal at 275°C for 1.0 min. The duration of the total run was 12.75 min. For MSD acquisition, a solvent delay of 5.0 min and EM offset of 200 were set. The monitored ions for quantification are listed in Table 2. The SIM parameters were divided into two groups and each ion was assigned a dwell time of 100 µs. The ratios of peak areas of the monitor ions to those of the IS were used for concentration calculations.

Table 2
Retention Times and Selection Ions for GC/MS-SIM Determination

Compound	SIM Ions (m/z)	Retention Time (min)	Segment[1]
1,4-Dioxane	58, 88	5.78	1
1,4-Dioxane-d_8	64, 96	5.69	1
1,4-Dichlorobenzene-d_4	115	9.78	2

[1]Segment 1 monitored ions for dioxane and the IS from 5.0 to 9.0 min; segment 2 monitored ions for the SUR from 9.0 to 12.75 min.

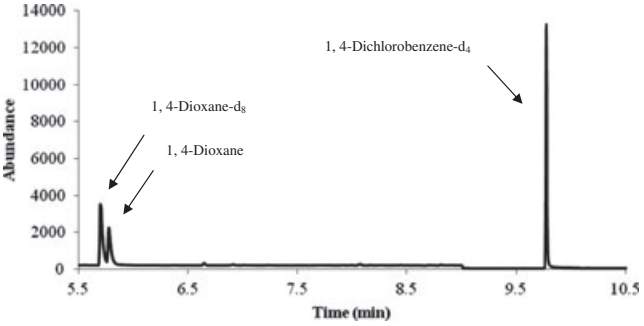

Figure 1. Total ion chromatogram of a 100 µg/L dioxane standard processed by FME.

Results and Discussion

Frozen Micro-Extraction

The low-pressure ultra filtration membrane has been shown to effectively remove bacteria and suspended particulates, but not dioxane, which is a neutral organic compound with a low molecular weight of 88 g/mol (Baker 2004). However, some chemical species that generate hydroxyl radicals (e.g., O_3 or H_2O_2) that are typically used in advanced oxidation treatment processes, as well as enzymes capable of degrading dioxane (e.g., monooxygenases produced in bioremediation schemes; Mahendra and Alvarez-Cohen 2006; Vainberg et al. 2006), have the potential to break through in the permeate. Consequently, freezing the extract was tested as a means of drying and separating such elements that could interfere with quantitative dioxane analysis, without the need to add scavengers or quenchers. This feature also makes the subject method suitable for monitoring the performance of different dioxane treatment processes as samples could be frozen quickly (<15 min) at −80°C, and allows a thorough separation of solvent and ice for solvent aliquot removal.

To understand possible limitations with regard to the temperature at which extractions are performed, frozen extractions were also conducted at −20°C for 45 min with other procedures unchanged. The dioxane spike recoveries (data not shown) were within the same range as those obtained when frozen at −80°C. These results suggest that extreme frozen temperatures are not an essential prerequisite of the subject method.

GC/MS Analytical Performance

Using the above instrument settings resulted in the IS dioxane-d_8 eluting within 6 min, and dioxane eluting shortly afterward. The system monitoring compound 1,4-dichlorobenzene-d_4 eluted well after these two compounds, at just after 9.5 min (Figure 1). The extended run ensures that other compounds that may be present in the samples are eluted before the next run. The dioxane and dioxane-d_8 peaks separated well at a low dioxane concentration (<200 µg/L) (Figure 1), but overlapped when the concentration of either compound exceeded 200 µg/L. The extracted ion current profiles for both the IS and dioxane were also well-formed and free of chromatographic interferences.

Based on the wide range of dioxane concentrations found in impacted aquifers, a linear calibration curve with seven points including 25, 50, 100, 200, 400, 800, and 1600 µg/L was developed (Figure 2). The continuing calibration verification (CCV) standards were prepared at 100 µg/L from a neat standard made independently from the initial calibration curve (ICAL) and run at the start of every 12 h work shift. The CCVs were routinely less than 20% different from the ICAL, indicating a stable instrumentation condition for our experiments.

An assessment of dioxane recovery and analytical precision (i.e., the relative standard deviation, expressed as a percentage of the mean) is summarized in Table 3. These data show that over the concentration range tested (10 to 1600 µg/L), the precision was high (i.e., within 8%) and easily meets the 30% guideline for Method 8270D SW-846 suggested by U.S. EPA (2007).

Extraction Efficiency

The IS dioxane-d_8 was spiked into the samples prior to extraction in a technique referred to as stable isotope dilution. Both dioxane and its labeled analog dioxane-d_8 are equally extracted and separated by GC. Thus, adding a known amount of this labeled analog to a sample prior to extraction enables correction for dioxane recovery. The

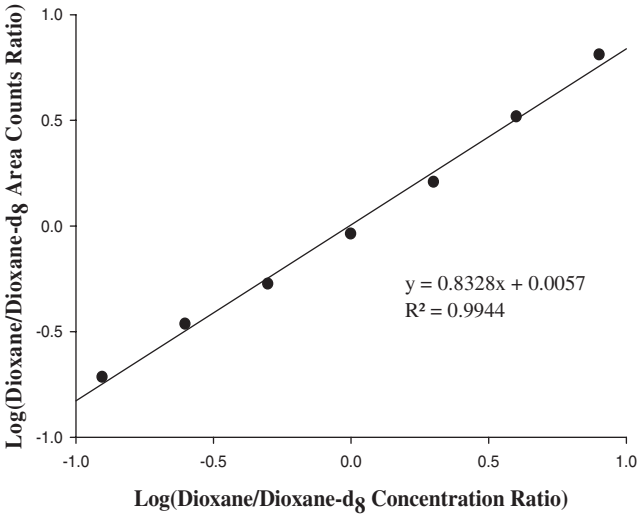

Figure 2. Log-log calibration curve of relative area response vs. dioxane concentration (25 to 1600 µg/L range), relative to the IS (200 µg/L dioxane-d_8).

Table 3
Assessment of Dioxane Recovery and Precision Using FME Method

Spiked Concentration (µg/L)	Successive Detection Data Results Four Trials (µg/L)				Average Recovery (%)	Relative Standard Deviation (% of Mean)
1600	1696.6	1489.7	1634.0	1575.1	99.9	5.5
500	470.5	501.4	529.8	476.1	98.9	5.4
100	112.8	108.7	117.4	112.8	112.9	3.1
25	25.0	28.3	25.2	28.5	107.1	7.2
10	10.7	11.3	10.7	10.4	107.6	3.7

extraction efficiency was determined by comparing the response of the IS with and without extraction (i.e., spiked into the sample to be extracted vs. spiked into the methylene chloride extractant that was directly injected into the GC). The average extraction recovery of dioxane-d_8 was 67.9% with an estimated relative standard deviation of ±7.5%. This is a nearly 20% higher recovery than that by LLE reported by Park et al. (2005). Overall, frozen extraction significantly improved the LLE for both dioxane-d_8 and dioxane ($p < 0.05$) (Table 4). Specifically, the partitioning of dioxane from the water phase to the solvent phase is dramatically enhanced at the freezing temperature compared to that of LLE at room temperature.

Isotope dilution enables accurate calculation of recovery without hindering the linearity of the analyte response as it compensates for a reduction in precision that may occur with low-volume injections (Draper et al. 2000). This is evident by comparing the dioxane/dioxane-d_8 ratio calibration curve (Figure 2) to the absolute ion response for dioxane (concentration range from 25 to 1600 µg/L, Figure 3), both of which depict high R^2 values (>0.99).

Method Detection Limit

Analysis of seven successive spikes at the lowest concentration tested (10 µg/L) was used to estimate the method detection limit (MDL) of dioxane by FME. The MDL was calculated using the following equation (Kawata et al. 2001):

$$\text{MDL} = S \times T\,(n - 1,\ 1 - \alpha = 0.99)$$

where S is the standard deviation of the replicate analysis in µg/L; α is the level of significance; $T\,(n - 1, 0.99)$ is the T value at the 99% confidence level with $n - 1$ degrees of freedom; and n is the number of replicate analyses.

The MDL was calculated to be 1.6 µg/L, which adequately meets the 3 µg/L drinking water advisory proposed by the U.S. EPA for a 10^{-6} lifetime cancer risk level (IARC 1999; U.S. EPA 2000), and compares well with the MDLs for other analytical methods (Table 1). Based on the assessment of the method performance, even lower detection limits and higher sensitivities might be possible to achieve by reducing the concentration of the IS (to reduce peak broadening), increasing injection volume, calibrating with a lower level curve (e.g., 5 to 50 µg/L), excluding the secondary ions for SIM detection (i.e., m/z 58 for dioxane and m/z 64 for dioxane-d_8), and increasing the GC column film thickness (e.g., 1.4 µm) (Grimmett and Munch 2009). Several pretreatment parameters are also adjustable to meet different experimental needs. For example, as shown earlier, freezing the extracts at −20°C yielded similar results, but required longer freezing time. The water-to-solvent ratio can be also increased to 1:2 (v/v) to reach higher extraction recoveries (94.9%), but the dioxane concentration would be diluted (Park et al. 2005).

Table 4
Extraction Efficiencies (n = 4) for Dioxane and Dioxane-d_8 with or Without Freezing Procedure of the Micro-Extraction for 100 µg/L Dioxane Spiked Samples

Extraction Recoveries (%)	Dioxane-d_8	Dioxane
With frozen procedure	60.7 ± 7.6	55.0 ± 13.3
Without frozen procedure	49.0 ± 10.7	35.6 ± 7.6

Potential Impact of 1,1,1-TCA

Since dioxane is predominantly used as a stabilizer (and metal inhibitor) of 1,1,1-TCA, whose K_{ow} is about 575 times higher than dioxane (Schwarzenbach et al. 2003), it is valuable to estimate the potential impact of TCA on the process of frozen extraction. Three TCA concentrations

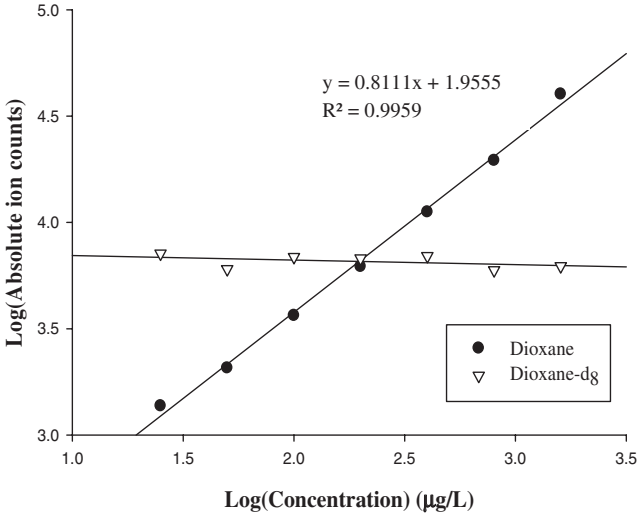

Figure 3. Absolute ion response for dioxane and IS (200 µg/L dioxane-d_8) in log-log plot.

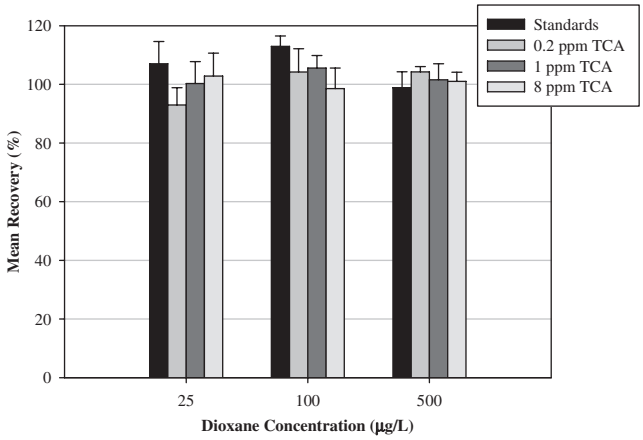

Figure 4. The comparison of the mean recoveries of different concentrations of dioxane spiked with three levels of 1,1,1-TCA (n = 3).

ranging from 0.2 to 8 mg/L were spiked in the samples as background to mimic different TCA contamination levels. Presented on Figure 4 are the extraction recoveries of the TCA-spiked samples with 25, 100, and 500 µg/L dioxane. The dioxane recoveries were in the range from 89% to 112%, which were within 5% of the controls without TCA. Based on student's *t*-test, the TCA co-contamination did not impart significant interference on the dioxane recoveries, at the 95% confidence level. This indicates that this extraction method is not affected by the potential competitive decrease in dioxane recoveries in heavily contaminated samples due to the shortage of sorbent capacity, as reported for SPE carbon disks by Isaacson et al. (2006).

Application to Groundwater Samples of High Total Organic Carbon

The subject method was validated using groundwater samples from a monitoring well tapping a sandy-silt formation at an industrial site in Prudhoe Bay, Alaska. The average concentration of total dissolved organic carbon was relatively high (8.34 ± 0.31 mg/L), which provided an opportunity to evaluate the effect of co-occurring organics on detection accuracy and reproducibility. The samples contained trace levels of dioxane (below the limit of detection), and were spiked with different dioxane concentrations. Samples spiked with 25, 125, or 500 µg/L yielded an average dioxane recovery of 103.8 ± 6.9%, with precisions of 10.5, 2.0 and 3.9%, respectively, indicating low (if any) interference to our extraction method by the high background total organic carbon (Table 5).

Conclusions

The frozen micro-extraction method described herein was developed for dioxane analysis at trace (parts-per-billion) concentrations in which very limited sample volume is available. This approach is relatively simple, quick, labor-saving, and exhibits high accuracy, precision, and sensitivity. Most of the materials and instruments needed are commonly found in commercial analytical laboratories. Whether this approach may also be advantageous for the analysis of other semivolatile organic compounds in water, such as methyl *tert*-butyl ether, *N,N*-dimethylformamide, and tetrahydrofuran, remains to be determined (Kawata et al. 2001; Nakamura and Daishima 2005; Isaacson et al. 2006). The performance of this method in creating an instrument-ready extract in minutes also leads to a variety of potential field applications. Overall, this as an environmentally friendly method that is particularly attractive when sample size, space, cost, time, and waste products all need to be minimized.

Acknowledgments

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Table 5
Analysis of Groundwater Samples Spiked with Different Concentrations of Dioxane

Spiked Concentration (µg/L)	Sample Numbers	Average Detected Concentration (µg/L)	Standard Deviation (µg/L)
500	9	507.4	17.9
125	4	128.3	2.6
25	4	27.5	2.9

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