# The Extraction and Analysis of 1,4-Dioxane from Water Using Solid-Phase Microextraction Coupled with Gas Chromatography and Gas Chromatography–Mass Spectrometry

**Robert E. Shirey** and **Christopher M. Linton**
Supelco, Inc., Bellefonte, PA 16823

## Abstract

**In this study, two methods are developed for the extraction of 1,4-dioxane (dioxane) from water using 80-µm carboxen–polydimethylsiloxane solid-phase microextraction fibers followed by either gas chromatography (GC)–flame ionization detection (FID) or GC–mass spectrometry (MS). With GC–FID, the lower limit of detection (LOD) for 1,4-dioxane is 2.5 µg/L (ppb) with a linear range of 5 to 10,000 µg/L, obtained by immersing the fiber in the sample for 20 min with agitation. Using GC–MS, the lower limit of quantitation is 0.5 µg/L, and the LOD is 0.25 µg/L. The upper linear range limit is 100 µg/L. Samples are extracted in 20 min using either heated headspace with agitation or direct immersion with agitation.**

## Introduction

Dioxane is a cyclic ether that is commonly used as a stabilizer in chlorinated organic solvents, primarily 1,1,1-trichloroethane (TCA). It is also used as and industrial solvent in the cosmetic, paint, and pharmaceutical industries and as a wetting and dispersing agent in the textile and dye industries (1). It is a highly water-soluble organic with a low Henry's Constant (2) that is not easily extracted out of water. Dioxane is not hydrolyzed or easily biodegraded and is included on the United States Environmental Protection Agency (U.S. EPA) list of potential carcinogens (2). As a result, some states are regulating the presence of dioxane in drinking water down to concentrations of 1 µg/L. Most of the states have higher limits, ranging from 5–100 µg/L (3).

In 1985, the U.S. EPA reported that approximately 90% of all dioxane manufactured in the U.S. was used as a stabilizer in chlorinated solvents (4). Dioxane is more water soluble than the chlorinated solvents and does not bind to clay and sediment. In cases of spills, it will flow ahead of the chlorinated solvent plume (5). A simple, sensitive testing method for dioxane could help authorities to locate the chlorinated solvent plume prior to it entering an aquifer.

The U.S. EPA requires testing for dioxane by commercial laboratories primarily in three different testing methods, EPA 524.2, EPA 8260, and EPA 8270 for drinking water, hazardous waste, and ground water, respectively. Methods 524.2 and 8260 are for volatile compounds and require the use of purge and trap for extraction and concentration. Because of poor efficiency using purge and trap, the EPA is allowing labs to use the semi-volatile method 8270 that utilizes liquid–liquid extraction of the analytes. Method 8260B allows for modifications to 8260, including the use of single ion monitoring (SIM), so that lower detection limits can be met (6).

Purge-and-trap methods require the use of 25 mL of water, which is difficult to purge efficiently. To improve the sparging efficiency, heating is often required. This delivers a large amount of water into the trap, reducing trap capacity for the analytes (6). Desorption of the trap subsequently introduces water into the column, which can hinder chromatography.

Other extraction methods have been developed for the extraction of dioxane. Song and Zhang (7) developed a method utilizing liquid–liquid extraction followed by solid-phase extraction to concentrate the sample. The authors report a lower limit of detection (LOD) of 50 µg/L. Draper et al. (8) reported detection of dioxane down to 0.2 µg/L using continuous liquid–liquid extraction with dichloromethane followed by isotope dilution GC–MS. Black et al. (9) used azeotropic atmospheric distillation followed by GC to detect dioxane in cosmetics. Poss et al. (10) and Walla-Jerzykeiwicz and Szymanowski (11) reported the use of standard headspace extraction from surfactants. In both cases, the minimum detection levels were in the µg/mL or µg/g (ppm) range. In some of these techniques, the detection limits are not low enough for environmental sampling or are labor intensive.

Nakamura and Daishima (12) demonstrated that solid-phase microextraction (SPME) was suitable for the extraction of dioxane with a LOD of 1.2 µg/L and a linear range of 5–100 µg/L

with the 100-µm polydimethylsiloxane (PDMS) fiber. With the carboxen (CAR)–PDMS fiber, they report a linear range of 0.1–1 µg/L using headspace extraction at 60°C. This extraction was carried out with 25 other analytes, which may have limited the capacity of the fiber.

A simple, automated method is needed to detect dioxane at trace levels and for screening purposes. For trace level, detection by GC–MS is desirable. For screening of samples in the field, an analyst may have some restrictions. In the field, analysts may not have the capability to heat samples; therefore, an ambient extraction method coupled with a flame ionization detector (FID) was developed in this study. The screening and trace analysis methods for analyzing dioxane will be discussed.

## Experimental

### Preparation of standards and samples

All of the chemicals used in this study were American Chemical Society grade and purchased from Aldrich Chemical Co. (Milwaukee, WI). A stock standard of dioxane was prepared in water at a concentration of 100 µg/mL. From this solution, a second dioxane standard was prepared at 10 µg/mL. Two internal standard solutions, 1,4-dioxane-$d_8$ and isopropanol (IPA), were prepared separately in water, each at 100 µg/mL. For extraction time studies, one stock solution was prepared containing dioxane at 100 µg/mL and IPA at 300 µg/mL.

For preparation of the GC–FID samples, 1.2 mL of water containing 25% NaCl and 0.1M sodium phosphate buffer pH 7 was put into a 2-mL large-opening vial (Supelco, Bellefonte, PA). Using syringes, each vial was spiked with the appropriate standards to the desired concentration. The vials were spiked, then immediately sealed with unpunctured PTFE-lined silicone septa. IPA at 300 µg/L was used as the internal standard.

For the GC–MS analysis, 5 mL of the previously listed buffered saltwater solution was placed in a 10-mL screw capped vial. The vials were spiked with the appropriate standard solutions and capped with 1.5-mm thick PTFE-lined silicone septa. Dioxane-$d_8$ at 25 µg/L was used as the internal standard. In an additional study, TCA was spiked into the vial along with dioxane and dioxane-$d_8$.

### Ambient extraction of samples for GC–FID screening analysis

The samples were extracted with an 80-µm CAR–PDMS metal fiber assembly (Supelco) controlled by a Varian 8200Cx autosampler (Varian, Palo Alto, CA). The autosampler was controlled by software (8200/SPME PC software, Varian) that enabled the analyst to set multiple methods to vary the extraction times and control agitation. The fiber was set to a depth that immersed it in the sample. In a part of this study, a 0.8-mL sample in a 2-mL vial was used for headspace extraction of dioxane. The extraction time was 20 min, and agitation was used unless otherwise noted.

After the extraction was complete, the fiber was desorbed for 4 min at 310°C in the injection port of a Varian 3400 GC (Varian Inc.), containing a 0.75-mm i.d. straight glass liner and sealed with a Merlin Microseal (Supelco). The injection port split vent was closed for the initial 0.75 min and then opened at 50 mL/min.

The analytes were separated on 30-m × 0.32-mm, 4.0-µm bonded PDMS column (Supelco) connected to an FID. The column was programmed from 45°C with a 1.5 min hold to 80°C then to 230°C at 20°C/min. Chromatographic-grade helium was used as a carrier gas set at 40 cm/s at 45°C and run with a constant pressure of 13 psi.

### Extraction of samples for trace analysis by GC–MS

The samples were extracted with a CAR–PDMS metal fiber assembly controlled with the CombiPal sampling system (CTC Analytics, AG, Zwingen, Switzerland). The sampling system was designed to control heat, extraction time, fiber and needle depth, and agitating parameters. In all cases throughout this study, the vial was preincubated for 1 min at the desired temperature followed by extraction. For most of this study, the extraction was 20 min at 55°C. The agitator during extraction was set at the default value of 250 rpm.

In one part of the study, heated headspace extraction by SPME was compared with ambient direct immersion of the fiber in the water sample. The samples used for direct fiber immersion contained 8 mL of buffered saltwater instead of the 5 mL used in headspace sampling. The sampling time and agitation rate remained the same.

After the extraction was complete, the fiber was desorbed for 4 min at 310°C in the injection port of a Varian 3800 GC (Varian Inc.), containing a 0.75-mm i.d., straight glass liner and sealed with a Merlin Microseal. The injection port split vent was closed for the initial 0.75 min and then opened at 50 mL/min.

The analytes were separated on 60-m × 0.25-mm, 3.0-µm bonded PDMS column (Supelco) connected to a Saturn 2200 ion trap MS (Varian, Inc.). The column was programmed from 50°C with a 1.5 min hold to 230°C at 16°C/min. Chromatographic-grade helium was used as a carrier gas, set at 1.3 mL/min constant flow with an initial pressure of 21 psi. MS detection was accomplished using 2 mass ranges set at *m/z* 86 to 98 and *m/z* 57 to 67. The quantitating (target) ions used were 88 for dioxane and 96 for dioxane-$d_8$, with qualifying ions of 58 and 66, respectively.

## Results and Discussion

### Optimizing extraction conditions

There are several factors to investigate when optimizing an extraction using SPME. Most importantly, it is critical to select the appropriate fiber coating. In a paper by Shirey (12), it was determined that the CAR–PDMS-coated fiber was the best coating for extracting dioxane. There were over two orders of magnitude greater response with the CAR–PDMS coating compared with other fiber coatings. Nakamura and Daishima also showed that the minimum linear limit was 50 times lower with the CAR–PDMS fiber compared with the 100-µm PDMS fiber (13). Because sensitivity was important, this coating on a metal fiber core was selected for this study. The elastic metal assembly containing the coated elastic metal fiber was more durable than stainless steel assemblies (14). This is particularly important when the fibers are used with an autosampler and multiple

extractions are required.

Modifying the sample with salt and pH buffer may be important. Shirey (13) noted that the addition of NaCl at 25% to the water greatly enhanced the recovery of dioxane compared with extraction of dioxane from deionized water. The effect of pH was minimal (13). This study did not attempt to further optimize the salt concentration or type of salt. All of the samples contained 25% NaCl and were modified to pH 7 with 0.1M phosphate buffer.

Other factors for optimizing extraction of analytes were the extraction time, type of extraction (headspace or immersion), and use of agitation. Figure 1 shows dioxane response versus time when extracted by immersion and ambient headspace with and without agitation. The concentration of the dioxane was 100 µg/L, and the concentration of IPA was 300 µg/L.

The goal in the screening study was to develop an ambient extraction method detected with a GC–FID. Only ambient headspace was compared with immersion in this study. Heated headspace was investigated in further detail and is described in the GC–MS section. Results indicate that heated headspace was more efficient than immersion for the extraction of dioxane. This option should be used if the analyst has the capability to heat the samples. Fiber life will increase when using headspace because there is less chance of contaminating the fiber with nonvolatile compounds.

Generally, with smaller molecules such as dioxane, there is an initial rapid rise in response versus time. As the time increases, the response eventually levels off. This is typically seen with absorption-type fiber coatings such as PDMS. However, when adsorbents are present in the coatings, the response curves versus extraction time may take longer to reach equilibrium. It appears that this is the case for dioxane when extracted with the CAR–PDMS fiber coating.

Because the pores of CAR 1006 used in the fiber coating can physically trap the analytes, they do not readily diffuse out of the coating at ambient temperature and pressure. Thus, the response continues to increase with time. In all four types of extractions, the response was nearly directly proportional with time. There did not appear to be any flattening of the analyte response curve. Direct immersion with agitation was the preferred method for extraction of dioxane compared with the other three ambient extraction options.

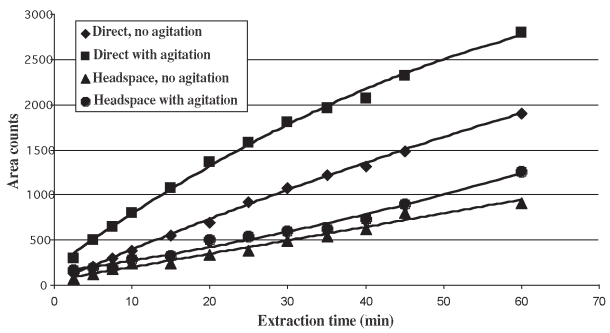


**Figure 1.** Dioxane response at 100 µg/L versus extraction time with CAR–PDMS-coated fiber using four different extraction conditions: ambient direct immersion with agitation; ambient direct immersion without agitation; headspace with agitation; and headspace without agitation.

Certainly beyond 60 min the extraction time becomes impractical. The cycle time for the GC to run through its program and cool down is 20 min. Most of the data in this study were obtained using a 20 min extraction. For cases when extremely low detection limits are desired, longer extraction times could be used. Longer extraction times may result in displacement of the desired analyte if other analytes of similar size are present in higher concentrations or have a greater affinity for the fiber coating (15).

To further determine the affinity of the analytes, log–log plots of the dioxane response versus concentration at three extraction times were generated (see Figure 2). It was expected that the dioxane response would level off when the fiber capacity was reached or exceeded. There is no strong evidence that the dioxane responses are leveling off even at 10,000 µg/L. The extraction times did not appear to make much difference on upper limit or coating capacity, but the longer times did allow lower detection limits. The limits will be discussed in greater detail in later sections.

### Extraction and analysis by GC–FID

Based upon the information previously described, directly immersing the fiber in the sample with agitation for 20 min was selected. IPA was selected as the internal standard because its extraction response was similar to dioxane and does not readily appear in the environment. Also, relative responses were similar when the extraction conditions were changed. Because the relative responses did not change, this indicates that the internal standard and analyte were extracted similarly.

The first test was to determine the lower detection limit and the linear range of the study using the chosen conditions. A calibration curve was generated from 1 to 10,000 µg/L. Both absolute and relative responses along with response factors are shown in Table I. A second desorption was made immediately after the analysis of the 10,000 µg/L sample. No carryover of dioxane was observed from the fiber.

The results in Table I show that the limit of quantitation (LOQ) was 5 µg/L as indicated by the greatly improved response factor deviation from 46% to 9% after points less than 5 µg/L were excluded from the data. The signal-to-noise ratio (s/n) at 5 µg/L was 3.9 to 1. At 2.5 µg/L, the s/n was down to 2.4 to 1, and at 1

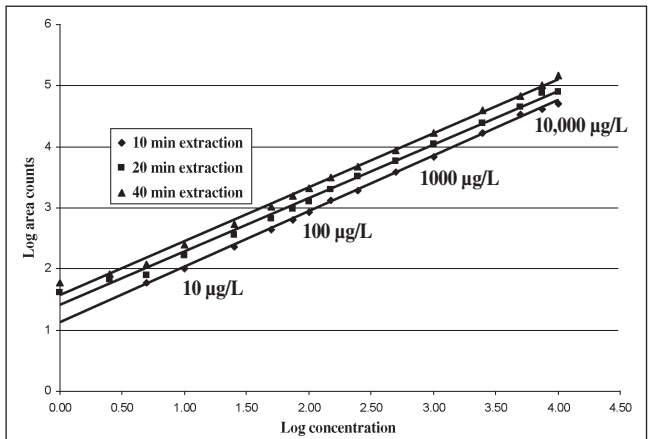


**Figure 2.** Log–log plots of dioxane area response versus dioxane concentration from 1 to 10,000 µg/L extracted with the CAR–PDMS-coated fiber using three different extraction times.

µg/L, the s/n was 1.4 to 1. Several extractions of the buffer with internal standard and no analyte resulted in a peak at the retention time of dioxane between 20–35 area counts. This would explain the increased in response factors below the LOQ of 5 µg/L. The recommended LOQ should have a minimum s/n of 3 and the LOD should have a minimum s/n of 2. Based upon those specifications, the LOQ was 5 µg/L and the LOD was 2.5 µg/L for dioxane.

The results in Figure 3 show that the response is highly linear with a coefficient of determination ($R^2$) of 0.9996. The Y intercept of 29.86 matched closely with the area counts of blank extractions reported in the previous paragraph. A plot of the relative responses from 1 µg/L to 1000 µg/L had a value for $R^2$ of 0.9994. When the curve was extended to 10,000 µg/L, the coefficient of determination decreased slightly to 0.9952. It appears that the fiber has the capacity to extract 10,000 µg/L of dioxane, but with competition, this capacity could decrease. GC–MS could be used for confirmation with lower detection limits.

**Table I. Area Responses, Relative Responses, and Relative Response Factors for Dioxane with Respect to IPA by SPME–GC–FID**

| Dioxane conc. | IPA area counts | Dioxane area counts | Relative response | RRF* | RRF without 2.5 and 1 µg/L |
|---|---|---|---|---|---|
| 1 | 3601 | 42 | 0.012 | 3.499 | |
| 2.5 | 3618 | 66 | 0.018 | 2.189 | |
| 5 | 3602 | 78 | 0.022 | 1.299 | 1.299 |
| 10 | 3538 | 164 | 0.046 | 1.391 | 1.391 |
| 25 | 3567 | 360 | 0.101 | 1.211 | 1.211 |
| 50 | 3582 | 654 | 0.183 | 1.095 | 1.095 |
| 75 | 3485 | 977 | 0.280 | 1.121 | 1.121 |
| 100 | 3523 | 1302 | 0.370 | 1.109 | 1.109 |
| 150 | 3436 | 1963 | 0.571 | 1.143 | 1.143 |
| 250 | 3489 | 3206 | 0.919 | 1.103 | 1.103 |
| 500 | 3359 | 5842 | 1.739 | 1.044 | 1.044 |
| 1000 | 3006 | 10177 | 3.386 | 1.016 | 1.016 |
| 2500 | 2751 | 24261 | 8.819 | 1.058 | 1.058 |
| 5000 | 2477 | 45115 | 18.214 | 1.093 | 1.093 |
| 7500 | 2429 | 76198 | 31.370 | 1.255 | 1.255 |
| 10000 | 2260 | 90788 | 40.172 | 1.205 | 1.205 |
| | | | Average | 1.364 | 1.153 |
| | | | SD† | 0.633 | 0.106 |
| | | | %RSD | 46.4% | 9.2% |

* Relative response factors.
† Standard deviation.

In the study by Nakamura and Daishima (12), the linear range with the CAR–PDMS was only 0.1–1 µg/L. Because dioxane was extracted along with 25 other analytes, most likely, displacement of dioxane by less polar analytes, with greater affinity for the fiber coating, occurred. Displacement could be enhanced by the slightly longer extraction time (30 min). The dioxane standards used in our study were prepared in water. Nakumara used methanol as a solvent for all standard mixtures. Even with effort to limit the amount of methanol in the samples, even low concentration levels of methanol could reduce fiber capacity for dioxane and narrow the linear range.

### Analysis by GC–MS

There are a couple of advantages for using GC–MS over GC–FID, besides spectral confirmation. With the use of selected ions, greater sensitivity is achieved. Secondly, isotopic internal standards can be used for the most commonly monitored analytes. In this case, dioxane-$d_8$ was used as the internal standard. Because the isotope has the same structure as the analyte, it should extract similarly.

This method uses narrow scanning ranges to detect both dioxane and dioxane-$d_8$. The narrow mass ranges reduce interferences from other analytes and lowers the background level, which improves the s/n ratio.

The analytical column was selected because it allowed dioxane to be sharply focused on the column. The analytes of interest were well resolved from water interferences. The length of column allowed a good head pressure to be maintained, which enables the Merlin Microseal to properly seal and extend its life.

The first step in optimizing a headspace extraction is to deter-

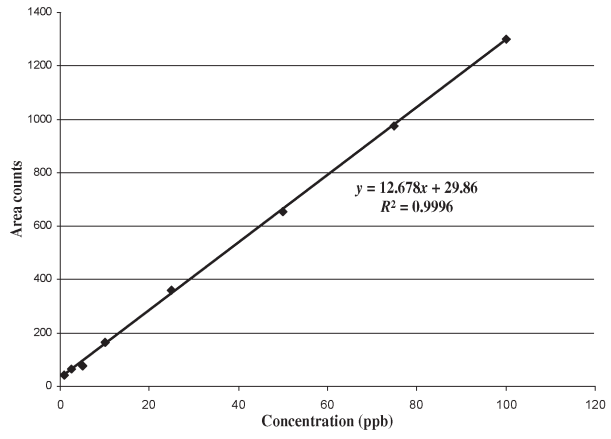


**Figure 3.** Plot of absolute area responses for dioxane versus dioxane concentration from 1–100 µg/L extracted with CAR–PDMS-coated fiber for 20 min.

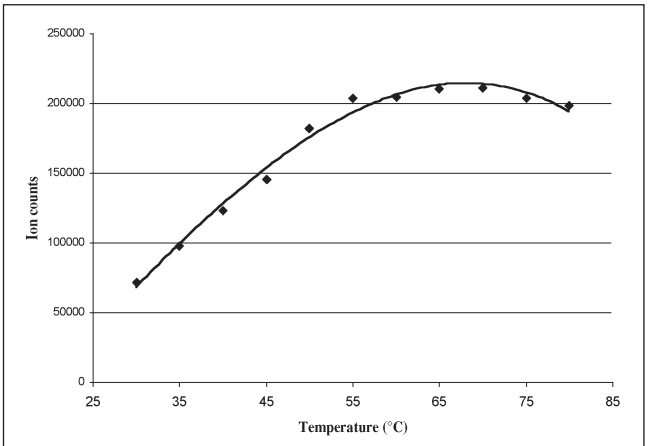


**Figure 4.** Plot of absolute ion response for dioxane at 100 µg/L versus extraction temperature with an extraction time of 20 min using the CAR–PDMS-coated fiber.

mine the best extraction temperature. The time parameter of 20 min set in the GC–FID study was applied to this study. The same salt concentration and pH as used in the GC–FID study were applied, and Figure 4 shows the extraction of 100 µg/L dioxane at various temperatures for 20 min.

The results indicate that the optimum temperature appears to be approximately 65°C. However, more water appears to be extracted at this temperature. Because increased temperature drives more water into the headspace, some may be condensing on the fiber and in the needle opening. The increased water being introduced into the GC–MS system broadens the peaks and increases background noise. The dioxane response at 55°C was only slightly less than at 65°C. Moreover, the amount of water extracted was less, and better precision was obtained with the extraction of multiple samples at 55°C. For these reasons, 55°C was selected as the best temperature for extraction of dioxane with this fiber coating.

The extraction of dioxane at 10 µg/L using the optimized heated headspace temperature of 55°C was compared with direct immersion of the fiber at ambient temperature, both for 20 min with agitation. A total of five extractions were made at each condition. The average dioxane response using heated headspace was 31% higher than the average dioxane response obtained using direct immersion. The precision for headspace was slightly better at 1.7% compared with 2.6% for immersion.

The linear range determined using the optimized extraction of dioxane by GC–MS was 0.5 to 100 µg/L. The primary purpose of this study was to determine the lower LOD. Concentration levels above 100 µg/L could be detected easily with FID. The extraction time was 20 min at 55°C with agitation. Two blank samples containing the internal standard (dioxane-$d_8$) were run prior to the extraction of the dioxane-containing samples. The results from this study are shown in Table II.

The results indicate that the LOQ is 2.5 µg/L without background extraction. By subtracting ion counts for *m/z* 88 at the retention time for dioxane, the LOQ was 0.5 µg/L. This is indicated by the response factors shown in Table II.

With the background subtraction, the error in the average response factors from 0.5 to 100 µg/L improved from 27% to 3.3% relative standard deviation (RSD). Figure 5 shows the linear curve of the absolute responses from 0.5 to 100 µg/L. The $R^2$ value of 0.9983 indicates good linearity. The linearity of relative responses over the same concentration range had a coefficient of determination value of 0.9997. If it is necessary to quantitate below 0.5 µg/L, the extraction time can be increased to 60 min. The additional time doubles the responses of dioxane and dioxane-$d_8$. The increased extraction time lowers the LOQ to 0.3 µg/L and the LOD down to 0.1 µg/L with background subtraction.

### Extraction of dioxane in the presence of TCA

Dioxane is most commonly used as a stabilizer in TCA usually at 0.5% w/v. Because TCA is much less water soluble than dioxane and has a higher affinity for the CAR–PDMS fibers, it is important to determine if low levels of dioxane could be extracted in the presence of higher levels of TCA.

Black and Fine have reported that higher concentrations of less polar analytes can displace polar analytes from CAR–PDMS-coated fibers (15). Because of this concern, an experiment was designed to extract dioxane at 10 µg/L and dioxane-$d_8$ at 25 µg/L from water samples containing TCA from 0.5 to 20 mg/L (ppm). Table III shows the results of this study.

There was a slight decrease in the absolute dioxane response and a larger decrease of dioxane-$d_8$ response. This would indicate that there was some displacement of the analytes in the fiber. However, peak heights were nearly identical for dioxane and dioxane-$d_8$ at all concentrations of TCA. Because the heights remained the same, this would indicate that the same amount of dioxane and dioxane-$d_8$ was being extracted at all of the TCA concentrations.

The reason for the decreased response was a TCA impurity that elutes immediately after dioxane with ions similar to the analytes. As the TCA concentration increased, an impurity peak on the tail end of the analytes interfered with the quantitation of the dioxane

**Table II. Ion Counts and Relative Response Factors for Dioxane Relative to Dioxane-$d_8$ Using GC–MS with and without Background Subtraction**

| Dioxane concentration | Ion counts dioxane-$d_8$ | Ion counts dioxane | Response factors | Ion counts dioxane-$d_8$ | Ion counts dioxane | Response factors |
|---|---|---|---|---|---|---|
| 0.5 | 22292 | 1338 | 3.000 | 22292 | 612 | 1.372 |
| 1 | 20675 | 1961 | 2.371 | 20675 | 1235 | 1.493 |
| 2.5 | 21214 | 4017 | 1.894 | 21214 | 3291 | 1.569 |
| 5 | 18975 | 6391 | 1.684 | 18975 | 5665 | 1.490 |
| 7.5 | 22326 | 10464 | 1.562 | 22326 | 9738 | 1.454 |
| 10 | 20451 | 12899 | 1.577 | 20451 | 12173 | 1.488 |
| 15 | 20138 | 18674 | 1.545 | 20138 | 17948 | 1.485 |
| 25 | 21845 | 32116 | 1.470 | 21845 | 31390 | 1.438 |
| 50 | 21977 | 64421 | 1.466 | 21977 | 63695 | 1.449 |
| 75 | 21981 | 100158 | 1.519 | 21981 | 99432 | 1.508 |
| 100 | 20928 | 124362 | 1.486 | 20928 | 123636 | 1.477 |
| Average | 21164 | | 1.779 | 21164 | | 1.475 |
| SD | 1052 | | 0.485 | 1052 | | 0.049 |
| %RSD | 5.0% | | 27.3% | 5.0% | | 3.3% |

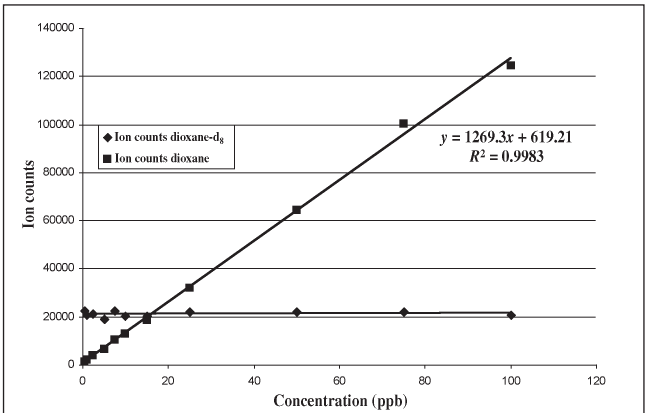


**Figure 5.** Plot of absolute ion response for dioxane and internal standard (dioxane-$d_8$) at 25 µg/L versus the concentration of dioxane from 1 to 100 µg/L.

and dioxane-$d_8$ peaks. These results indicated that TCA is not displacing dioxane out of the fiber. A column with a different polarity could reduce the interferences from TCA.

### Fiber reproducibility

One of the complaints of SPME has been fiber-to-fiber reproducibility. In this study, 10 different 80-µm CAR–PDMS metal fibers were evaluated by extracting 10 µg/L of dioxane and 25 µg/L of dioxane-$d_8$. The results from the testing of the fibers are shown in Table IV.

The results show that the fibers are fairly reproducible, with < 11% error in responses between the fibers. The error drops significantly to 2.5% when relative responses are used. The fiber used to generate the calibration curve was fiber 5, which yielded the lowest response of the 10 fibers. This indicated that all of the fibers would be able to meet the minimum detection limits previously set.

Fiber 5 was used extensively in this study. Over 250 extractions were made with this fiber, resulting in no visible deterioration of the coating bonded to the metal fiber. The area counts were nearly the same for the analytes at a given concentration throughout the study. Also, the needle remained straight because of the elastic properties of the assembly. The extraction temperature of 310°C increased the response over 20% compared with 250°C without damaging the extraction properties as indicated by consistent area counts.

**Table III. The Effect of the Concentration of TCA on the Extraction of 10 µg/L of Dioxane and 25 µg/L of Dioxane-$d_8$**

| TCA concent (mg/L) | Peak area ion counts dioxane-$d_8$ | Peak area ion counts dioxane | Relative response | Peak height ion counts dioxane-$d_8$ | Peak height ion counts dioxane |
|---|---|---|---|---|---|
| 0 | 25943 | 17180 | 0.662 | 4048 | 3324 |
| 0.5 | 25383 | 17452 | 0.688 | 4035 | 3455 |
| 1 | 22427 | 15531 | 0.693 | 4024 | 3235 |
| 2 | 22954 | 15691 | 0.684 | 4060 | 3456 |
| 5 | 21123 | 15244 | 0.722 | 4251 | 3312 |
| 10 | 21761 | 15811 | 0.727 | 3915 | 3167 |
| 20 | 21609 | 15775 | 0.730 | 4095 | 3364 |
| Average | 23029 | 16098 | 0.701 | 4061 | 3330 |
| SD | 1900 | 857 | 0.026 | 101 | 107 |
| %RSD | 8.3% | 5.3% | 3.7% | 2.5% | 3.2% |

**Table IV. Reproducibility of CAR–PDMS Fibers Measured by the Extraction of 10 µg/L of Dioxane and 25 µg/L of Dioxane-$d_8$**

| Fiber | Dioxane-$d_8$ | Dioxane | Relative response |
|---|---|---|---|
| 5 | 20451 | 12899 | 0.631 |
| 4 | 20682 | 13330 | 0.645 |
| 3 | 22591 | 14064 | 0.623 |
| 6 | 26137 | 16631 | 0.636 |
| 10 | 24625 | 16155 | 0.656 |
| 8 | 26524 | 16900 | 0.637 |
| 7 | 28271 | 17336 | 0.613 |
| 2 | 24963 | 15457 | 0.619 |
| 1 | 27048 | 17069 | 0.631 |
| 9 | 25943 | 17180 | 0.662 |
| Average | 24723 | 15702 | 0.635 |
| SD | 2665 | 1682 | 0.016 |
| %RSD | 10.8% | 10.7% | 2.5% |

## Conclusion

SPME methods utilizing the 80-µm CAR–PDMS metal fibers have been developed that will enable the detection of dioxane at trace concentration levels. The fibers can be desorbed on either a 30-m × 0.32-mm, 4.0-µm or 60-m × 0.25-mm, 3.0-µm bonded PDMS capillary columns. Depending upon the type of autosampler being utilized, the extractions can be completed by directly immersing the fiber in water at ambient temperature or by using heated headspace at 55°C. In either case, 20 min is a sufficient extraction time. Either an FID or MS can be used to detect dioxane. With an FID, the minimum LOD was 2.5 µg/L and the linear quantitating range was 5 µg/L to 10,000 µg/L. With an MS, the LOQ was 0.5 µg/L with background subtraction, and the linear range was 0.5 µg to 100 µg/L. By extending the extraction time, the minimum LOD could be reduced to 0.1 µg/L, and the LOQ was lowered to 0.3 µg/L. Good linearity was demonstrated up to 100 µg/L. Higher concentrations were not monitored by GC–MS.

Dioxane, at 10 µg/L, was extracted from water samples containing various concentrations of TCA up to 20,000 µg/L with the CAR–PDMS-coated metal fiber without displacement.

Ten CAR–PDMS metal fibers were evaluated with 10 µg/L dioxane samples for reproducibility. There was an 11% RSD observed between the fibers for absolute response and only 2.5% RSD observed on relative responses.

Over 250 extractions were made at 310°C with one fiber, without any damage to the fiber coating as indicated by consistent area counts throughout the study. The elastic metal fiber assembly remained straight and usable after 250 extractions with the autosampler.

## References


1. N.I. Sax and R.J. Lewis, Sr. *Hawley's Condensed Chemical Dictionary*, 11th ed. Van Nostrand Reinhold Co., New York, NY, 1987, p. 424.
2. U.S. Environmental Protection Agency. 1,4-Dioxane Fact Sheet: Support Document (CAS No. 123-9-1). U.S. EPA, Office of Pollution Prevention and Toxics (OPPT) Chemical Fact Sheet 749-F-95-010a. U.S. EPA, Washington, DC, 1995, p. 13.
3. Lancaster Laboratories. 1,4-Dioxane in environmental samples, Publication no. 9045 0903. Lancaster Laboratories, Lancaster, PA, (2003). http://www.lancasterlabs.com/literature/1-4-Dioxane.pdf (August 2005)
4. D.G. Walsom and B. Tunnicliffe. 1,4-dioxane—a little known compound, changing the investigation and remediation of TCA impacts, *Environ. Sci. Eng.* 10–11 (2002).

5. T.K.G. Mohr. Solvent Stabilizers: White Paper, Santa Clara Water District, San Jose, CA. 2001, p. 55.
6. U.S. Environmental Protection Agency. Analysis of 1,4-dioxane by heated purge and trap GC/MS. EPA Region 9 Laboratory SOP 307, Washington, D.C. (2002).
7. D.M. Song and S. Zhang. Rapid determination of 1,4-dioxane in water by solid-phase extraction and gas chromatography–mass spectrometry. *J. Chromatogr.* **787:** 283–287 (1997).
8. W.M. Draper, J.S. Dhoot, J.W. Remoy, and S. Kusum Perera. Trace-level determination of 1,4-dioxane in water by isotopic dilution GC and GC–MS. *Analyst* **125:** 1403–1408 (2000).
9. R.E. Black, F.J. Hurley, and D.C. Harvey. Occurrence of 1,4-dioxane in cosmetic raw materials and finished cosmetic products. *J. AOAC Internat.* **84:** 666–670 (2001).
10. M. Poss, T. Couch, A. Odufu, J. McCann, J. Mellon, B. Melnick, and D. Jenke. Determination of 1,4-dioxane impurity levels in Triton X-100 raw material by gas chromatography with mass spectrometric detection. *J. Chromatogr. Sci.* **41:** 410–417 (2003).
11. A. Walla-Jerzykeiwicz and J. Szymanowski. Analysis of free oxirane and 1,4 –dioxane contents in the ethoxylated surface-active compounds by means of gas chromatography with headspace sample injection. *Chem. Anal. (Warsaw)* **41:** 253–261 (1996).
12. S. Nakamura and S. Daishima. Simultaneous determination of 22 volatile organic compounds, methyl-*tert*-butyl ether, 1,4-dioxane, 2-methylisoborneol and geosmin in water by headspace solid phase microextraction-gas chromatography–mass–spectrometry. *Anal. Chim. Acta* **548:** 79–85 (2005)
13. R.E. Shirey. Optimization of extraction conditions for low-molecular-weight analytes using solid-phase microextraction. *J. Chromatogr. Sci.* **38:** 109–116 (2000).
14. R. Shirey, C. Linton, L. Sidisky and D. Vitkuske. "The development of a new durable SPME fiber assembly containing coated metal fibers". In *2005 EAS Presentation,* Supelco Publication T405142H. Supelco, Bellefonte, PA, 2005.
16. L. Black and D. Fine. High levels of monoaromatic compounds limit the use of solid-phase microextraction of methyl *tert*-butyl ether and *tert*-butyl alcohol. *Environ. Sci. Technol.* **35:** 3190–3192 (2001).

Manuscript received September 14, 2005;
revision received January 27, 2006.