

Technical Bulletin

Analytical Methods and Recommendations for the Analysis of 1,4-Dioxane



FLORIDA DEPARTMENT OF ENVIRONMENTAL
PROTECTION

BUREAU OF LABORATORIES

2600 BLAIR STONE ROAD

TALLAHASSEE, FLORIDA 32399

October 12, 2010

Technical Bulletin: Analytical Methods and Recommendations For the Analysis of 1,4-Dioxane

Introduction:

Analysis of the compound 1,4-dioxane in water historically presented a challenge for environmental laboratories, particularly when reporting to concentration levels in the sub-parts-per-billion (ppb or $\mu\text{g/L}$) range. In fact, until recently the sub-ppb range was typically not achievable by most routine analytical methods. However, achieving this level of performance has become increasingly important as action levels are currently set in the low ppb range (3.2 $\mu\text{g/L}$ in groundwater). Tracking contamination plumes, due to the high mobility of 1,4-dioxane in ground water, makes the need for low-ppb and even sub-ppb method detection limits (MDLs) all the more critical.

Previously, the Florida Department of Environmental Protection investigated the analysis of 1,4-dioxane using EPA Methods 8260C, 8261, and 8270D.¹ This past year FDEP evaluated EPA Method 522, recently published for the analysis of 1,4-dioxane in water.² Method 522, which is a drinking water method, uses solid phase extraction to extract and concentrate 1,4-dioxane for analysis. In our application, the method was applied more broadly to include a variety of ground and surface waters. This work is still on-going, but the FDEP laboratory has sufficient information to now strongly recommend the SPE technique for the analysis of 1,4-dioxane in ground and surface water samples. Sub-ppb detection limits for 1,4-dioxane in environmental water analysis are routinely achievable using EPA Method 522. The advantages, disadvantages, and applications of available methods for the determination of 1,4-dioxane will be discussed.

Background:

A historical review of the compound 1,4-dioxane, its properties, and significance to the environmental community has been described in detail in several publications,³⁻⁶. The main point to be made, from an analytical perspective, is that 1,4-dioxane has historically been an “invisible” environmental contaminant because laboratories have had limited methodological options to detect and monitor the compound at trace levels. Consequently, there are concerns that 1,4-dioxane in the environment has mostly gone undetected or at least under-reported.

In our previous study of 1,4-dioxane,¹ the FDEP laboratory recommended using EPA methods 1624, 8261A, or 8260C with heated purge and the surrogate compound 1,4-dioxane- d_8 . All of these methods yielded acceptable results and provided detection limits below 3 ppb, but were not without significant shortcomings. The findings from the FDEP laboratory were also supported by earlier work⁷⁻⁸ performed by the consulting groups BBL Environmental Services and Environmental Conservation Laboratories, Inc., utilizing isotope dilution. Both our study and the reports from the consulting groups came

to similar conclusions, putting forward that the most advantageous analytical approaches involved volatile analytical methods utilizing selected-ion monitoring (SIM) and isotope dilution techniques. Another proposed method for preparing and analyzing samples for 1,4-dioxane was the extraction technique for semi-volatile compounds described in EPA Method 8270D. As an extractable compound, 1,4-dioxane was found to exhibit limitations due to its high solubility in water and potential loss during the concentration step in sample preparation. Due to these limitations FDEP does not recommend EPA method 8270D for reporting 1,4-dioxane.

Since those initial studies, there has been continued interest concerning how best to address the analytical challenges involving the analysis of 1,4-dioxane. The objective of this document is to provide a brief update of ongoing work with 1,4-dioxane and to provide guidance on the use of analytical data collected by various analytical techniques.

Analytical Methods: Performance Compared

The MDL for 1,4-dioxane was determined by several different analytical techniques as shown in Figure 1 below. It is clear that EPA Method 8260¹⁰ using full scan techniques, cannot achieve the groundwater cleanup target level of 3.2 ug/L. However, by employing selected ion monitoring (SIM) and isotope dilution (ID) with heated purge (HP) it is possible to achieve MDLs below the risk or cleanup target levels. Figure 2 provides the data used for the MDL determination for the 8260C/ SIM/ID technique. In this method modification, deuterated 1,4-dioxane (1,4-dioxane-d8) is added to each sample as an internal standard. The isotope behaves as 1,4-dioxane in every aspect of the analysis except it is not found in nature and has distinct mass spectral ions, allowing for quantification of both 1,4-dioxane and 1,4-dioxane-d8. The recovery efficiency of 1,4-dioxane-d8 can then be used to correct the results for 1,4-dioxane. Even so, the 8260C/SIM/ID method attains the 3.2 ug/L threshold marginally, assuming a Practical Quantitation Limit (PQL) of 4 times the MDL, and does not afford the level of confidence needed to consistently provide data below the target level.

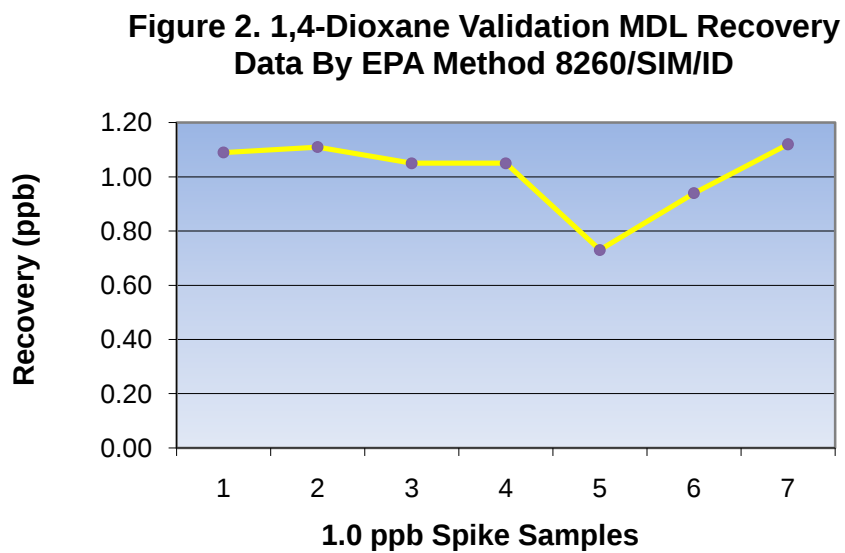
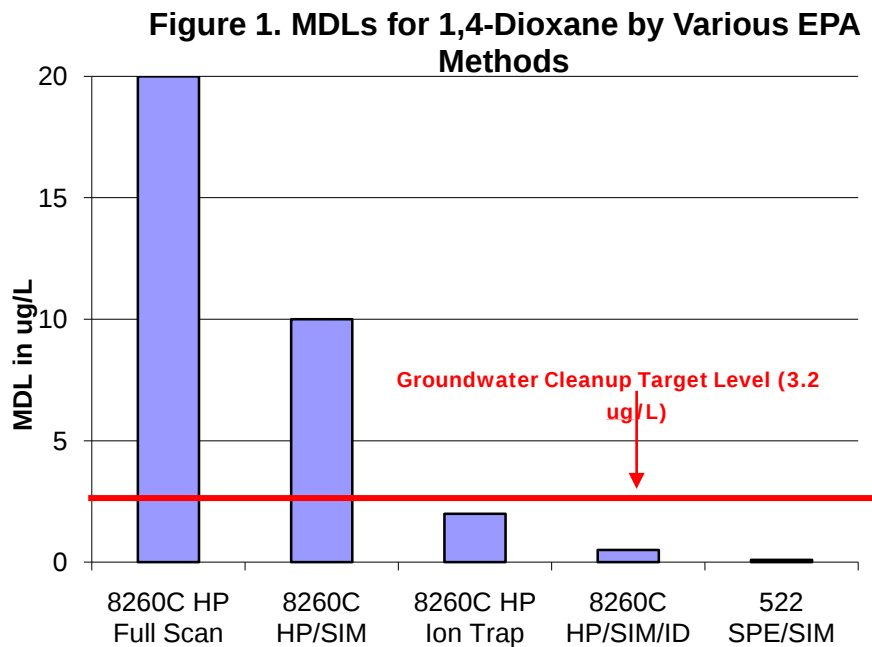
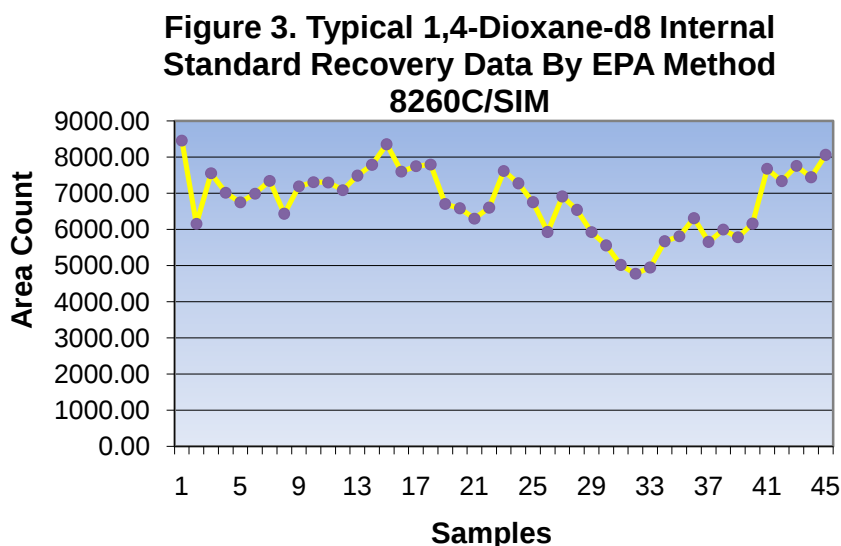
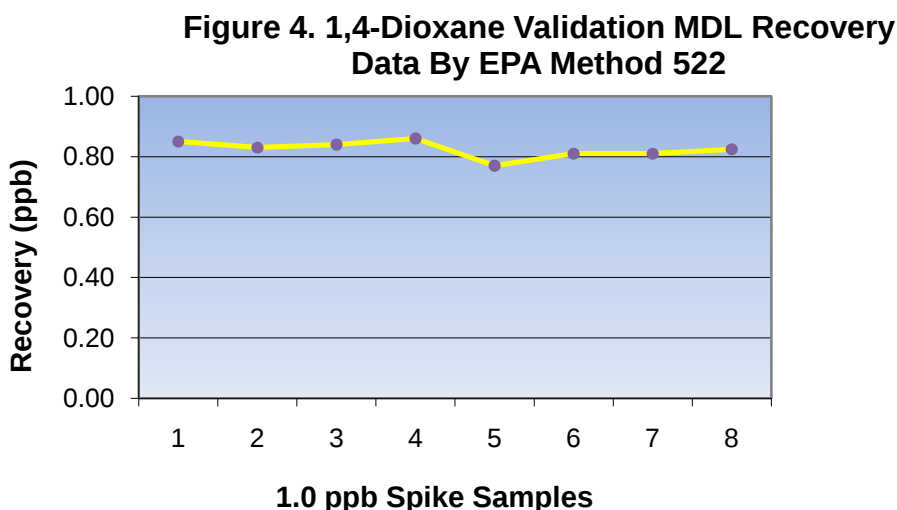


Figure 3 provides data for typical internal standard area counts for the internal standard 1,4-dioxane-d8 used in the Method 8260C/SIM/ID technique. The area counts for 1,4-dioxane-d8 varied significantly more than our other volatile internal standards due to the compounds poor purging efficiency. The poor purging efficiency also explains why 1,4-dioxane has significantly more problems with sample carryover and occasional matrix enhancement. The 1,4-dioxane carryover may also manifest itself as a low-level background ion signal that is difficult to eliminate.



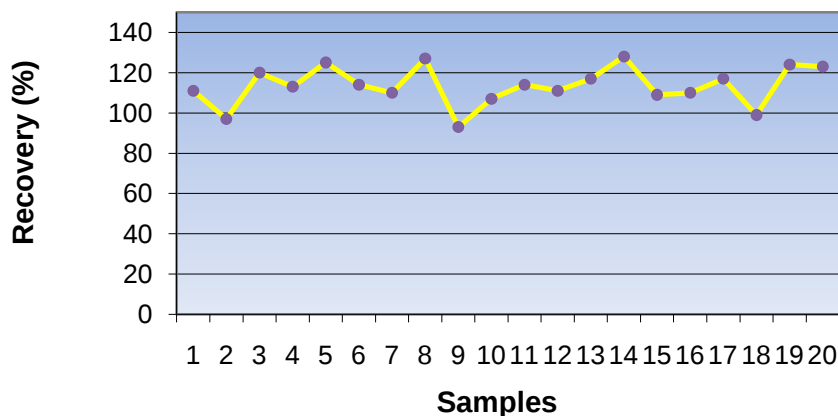
Fortunately, there is another analytical option available that can provide PQL values consistently below the 3.2 ug/L target for 1,4-dioxane. The solid phase extraction technique found in EPA Method 522 yielded an MDL of 0.10 ug/L and PQL of 0.40 ug/L in our initial method validation exercise. A plot of the validation spike recovery data is provided in Figure 4. The EPA Method 522 states that an MDL of < 0.05 ug/L is achievable, but we did not attempt to push the method performance to this low of a detection level. In our validation, we opted to use a 100 mL extraction volume and the correspondingly smaller SPE cartridges as described in the method. The larger SPE cartridges described in the method were also evaluated and provided a slightly lower detection limit. However, the small SPE cartridge was selected for routine use due to the small sample size required, shorter preparation time, and reduced reagent consumption. Additional technical information is available upon request.



Over this past year, a variety of ground and surface water matrix types were evaluated by EPA Method 522 without any significant problems. Figure 5 shows our typical recoveries for the surrogate 1,4-dioxane-d8 acquired recently for both ground and surface water matrix types. The surrogate recoveries consistently yielded values in the 70-130% range. Based on these findings, the EPA Method 522 has been deemed sufficiently robust to analyze routine ground and surface waters, in addition to potable water samples.

Comparing EPA Method 522 and 8260 SIM/ID reveals that both methods can be used successfully for the analysis of 1,4-dioxane in water. One advantage of Method 8260C/SIM/ID is that it can be used to report additional compounds from the same volatiles analysis, without the need to collect additional sample and dedicate instrumentation for a separate test. However, if improved detection limits (to sub-ppb levels) are an analytical goal, then EPA Method 522 is the clear analytical method of choice. **Note: These recommendations do not constitute approval for any specific regulatory application.**

**Figure 5. Typical 1,4-Dioxane-d8 Surrogate
Recovery Data By EPA Method 522 (2 ppb spikes)**



Conclusions:

The efficacy of EPA's drinking water method 522 for the analysis of ground and surface waters has proven robust and provides detection limits far superior to the other analytical methods evaluated. The primary limitation of this method is its narrow application to only one compound, whereas the other methods are multi-component tests. Despite this limitation, EPA Method 522 fills a needed niche in sampling situations where the need for higher performance and lower detection limits prevails over the additional cost incurred on a per-analyte basis.

For More Detailed Information Contact:

Timothy W. Fitzpatrick
Administrator, Chemistry Section
Florida Department of Environmental Protection
(850) 245-8083

Kerry Tate, PhD
Environmental Manager, Organic Chemistry Section
Florida Department of Environmental Protection
(850) 245-8309

References:

1. Fitzpatrick, Timothy and Tate, Kerry, Florida Department of Environmental Protection, *1,4-Dioxane: An Old But 'Emerging' Contaminant – Analytical Methodology Recommendation Update*, Waste Clean-Up Workshop Presentation, May 2007.
2. U.S Environmental Protection Agency, Method 522, Determination of 1,4-Dioxane in Drinking Water by Solid Phase Extraction (SPE) and Gas Chromatography/ Mass Spectrometry (GC/MS) with Selected Ion Monitoring (SIM), 2008.
3. U.S Environmental Protection Agency, *Emerging Contaminant: 1,4-Dioxane*, Solid Waste and Emergency Response, US-EPA505-F-07-004, April 2008.
4. Mohr, Thomas K.G., Solvent Stabilizers: White Paper, Underground Storage Tank Program- Water Supply Division, Santa Clara Valley Water District, June 2001.
5. Shirey, Robert and Linton, Christopher, *The Extraction and Analysis of 1,4-Dioxane from Water Using Solid-Phase Microextraction Coupled with Gas Chromatography and Gas Chromatography-Mass Spectrometry*, Journal of Chromatography Science, Vol.44, Number 7, August 2006.
6. Grimmett, Paul E. and Munch, Jean W., *Method Development for the Analysis of 1,4-Dioxane in Drinking Water by Solid Phase Extraction (SPE) and Gas Chromatography- Mass Spectrometry*, Journal of Chromatographic Science, Vol. 47, January 2009
7. BBL Environmental Services, Inc, *1,4-Dioxane Comparative Analysis Study – EPA Methods 8260B, 8270C, and 8270 with Isotope Dilution*, Presentation, May 2006.
8. Matthew Foti, Andres Romeu, and Kurt Bentzen, *Isotope Dilution Technique for 1,4-Dioxane Analysis*, Environmental Conservation Laboratories, Inc, Presentation, November 2006.
9. U.S Environmental Protection Agency, CLP Method OLM03.1, *1,4-Dioxane in Water by Selective-Ion Monitoring (SIM) Gas Chromatography/ Mass Spectrometry (GC/MS)*: Revised 12/17/99.

10. U.S Environmental Protection Agency, Method 8260C, *Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)*, Revision 3, August 2006.
 11. U.S Environmental Protection Agency, Method 1624 Revision B, *Volatile Organic Compounds by Isotope Dilution Gas Chromatography/ Mass Spectrometry (GC/MS)*, 1996.
 12. U.S Environmental Protection Agency, Method 8270D, *Semi-Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)*, Revision 4, February 2007.
 13. U.S Environmental Protection Agency, Method 8261A, *Volatile Organic Compounds by Vacuum Distillation in combination with Gas Chromatography/ Mass Spectrometry (VD/GC/MS)*, Revision 1, October 2006.
 14. Florida Department of Environmental Protection, *Standard Operating Procedure SV-015-1.0, Analysis of 1,4-Dioxane in Water by Solid Phase Extraction (SPE) and Gas Chromatography/ Mass Spectrometry (GC/MS) with Selected Ion Monitoring (SIM)*, 2009.
- .