Determination of Thiodiglycol in Groundwater Using Solid-Phase Extraction Followed by Gas Chromatography with Mass Spectrometric Detection in the Selected-Ion Mode

Bruce A. Tomkins and Gary A. Sega
Organic Chemistry and Separations Section
Chemical and Analytical Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6120

In its heyday, the South Plants Area, Rocky Mountain Arsenal

What were the objectives of this work?

- **Demonstrate the presence of HD (sulfur mustard) at regulatory levels in groundwater (thiodiglycol, TDG, is a marker compound)**
- **Provide unambiguous identification of the target compound**
- **Exhibit desired sensitivity (RMA TRL is 5 μg TDG/L) even in the presence of expected salt concentrations and organic contaminants of groundwater**
- **Demonstrate method performance via use of a surrogate**
- **Be readily implemented by most commercial analytical laboratories**
- **Be rapid and convenient to use**
- **Generate minimal final quantities of chemically hazardous waste**

What was the approach taken; how was it justified?

- **Liquid-liquid extraction produced too much chemical waste, unacceptable recoveries, insufficient sensitivity**
- **Groundwater samples contained organic contaminants, including neutral species left over from non-military uses at the Arsenal (e.g., organochlorine pesticides)**
- **Use a solid-phase extraction-based procedure to use more sample, reduce waste, and improve sensitivity**
- **Use a "guard" cartridge ahead of the extraction cartridge to remove contaminants. A C_{18} cartridge was evaluated initially; other cartridge chemistries may also be effective.**

What was the approach taken; how was it justified? (continued)

- **TDG was not retained on reversed-phase or polar extraction phases**
- **Not all carbonaceous sorbents were equally effective for retaining TDG.**
- **Recoveries of TDG were modest (~ 30%).**

- **Use carbon to retain polar TDG, and elute it with dichloromethane.**
- **Columns containing 500 mg of either Ambersorb® 563 or Envi-Carb were ineffective. Amber-sorb® 572 (same mass) appeared optimal.**
- **As long as the TDG levels are low, the extraction efficiency appears to be independent of bed mass.**

Small extraction columns containing ca. 100 mg of Ambersorb® 572 in tandem with a “guard” column were capable of extracting TDG from groundwater

The finished apparatus employs a sample reservoir, C_{18} "guard" column, and Ambersorb® 572 extraction column

- **Pass the groundwater sample (nominally 100 mL) through the extraction "train".**
- **Dismantle the "train", set the guard column aside.**
- **Dry the Ambersorb® 572 column at full vacuum for at least 1 hr.**
- **Elute TDG with a small volume of dichloromethane (3 x 3 mL into a shell vial; 8 mL recovered).**

What was the approach taken; how was it justified? (continued)

- **TDG normally exhibits poor chromatographic behavior (tailing on column)**
- **What should be used as the surrogate compound?**
- **Final determination and quantitation requires either simple detector with two different columns or GC/MS with appropriate selected ions for each analyte**
- **Take dichloromethane extracts to dryness, derivatize with MTBSTFA in the presence of pyridine**
- **Use 3,3'-thiodipropanol (TDP) as a surrogate**
- **Use GC/MS in the selected-ion mode. The ions monitored are characteristic of derivatized TDP and TDG. The method becomes self-confirming.**

Method performance was verified using a standardized unbiased procedure specified by the U. S. Rocky Mountain Arsenal

- **On two independent certification days, synthetic groundwater samples fortified between 0.5-20 times TRL (2.5-100 μg TDG) were subjected to the proposed method.**
- **"Found" concentrations were plotted against "true" values to obtain the Method Reporting Limit (MRL) for TDG.**
- **Nine independently-prepared groundwater samples (seven required) fortified to 5 times TRL (25 μg each TDG and TDP) were analyzed using the proposed method.**
- **The standard deviation of the measurements was multiplied by the appropriate Student's-t value (2.896) to obtain the Method Detection Limit (MDL) for TDG and TDP.**

Comparison of "Found" vs "True" Concentrations for TDG Using the GC-MS-SIM Method in MRL Certification Samples

"True" TDG Concentration, μg/L	"Found" TDG Concentrations, μg/L	
	Day 1	Day 2
0.0	0.78	0.72
2.5	1.0	1.1
5.0	1.7	1.8
10	3.5	2.6
25	12.5	7.0
50	22.6	16.8
100	40.9	34.1
Method Reporting Limit, μg/L		16.2
Estimated recovery, %		38

Determination of the MDL for TDG and TDP Using the GC-MS-SIM Method ("true" concentration = 25 μg/analyte)

Sample number	Measured TDG (μg/L)	Measured TDP (μg/L)
1	4.40	3.62
2	4.78	3.76
3	4.98	4.00
4	5.48	4.01
5	5.54	4.05
6	5.94	4.18
7	5.96	4.33
8	7.15	4.75
9	8.31	4.91
Average ± std dev	5.84 ± 1.22	4.17 ± 0.43
MDL μg/L	3.5	1.2
Analyte recovery, %	23	17

Summary and Conclusions

- **Unambiguous detection was provided using GC-MS-SIM with m/z values 293 for TDG, 321 and 363 for TDP (surrogate)**
- **The calculated MRL (16.2 μg/L) and MDL (3.5 μg/L) for TDG approximated the desired TRL of 5 μg/L and would be satisfactory for Rocky Mountain Arsenal purposes.**
- **The recovery and detection limits of TDP mirrored those of TDG, making it a reasonable surrogate compound.**
- **The typical analysis rate was12-16 groundwater samples per 8-hr working day.**
- **Method readily implemented by most commercial analytical service laboratories.**
- **Approximately 1 mL chemically-hazardous waste was generated per groundwater sample.**

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