DETERMINATION OF THIODIGLYCOL IN GROUNDWATER USING SOLID PHASE EXTRACTION FOLLOWED BY GAS CHROMATOGRAPHY WITH MASS SPECTROMETRIC DETECTION IN THE SELECTED ION MODE

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DETERMINATION OF THIODIGLYCOL IN GROUNDWATER USING SOLID PHASE EXTRACTION FOLLOWED BY GAS CHROMATOGRAPHY WITH MASS SPECTROMETRIC DETECTION IN THE SELECTED ION MODE

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A highly-sensitive analytical procedure is described for determining thiodiglycol in groundwater. Samples are initially fortified with 3,3'-thiodipropanol (surrogate), then both species are extracted using sequential solid phase extraction with C_{18} and Ambersorb 572 columns in tandem. The C_{18} column, which removes extraneous groundwater components, is discarded; the Ambersorb 572 column is dried thoroughly before eluting polar components with a small volume of dichloromethane. The extract is taken to dryness using dry flowing nitrogen, and the resulting residue is derivatized using MTBSTFA and pyridine. The derivatized products are diluted to a final volume with toluene, chromatographed using a fused-silica capillary column, and detected with a quadrupole mass spectrometric detector in its selected-ion mode. Two independent statistically unbiased procedures were used to evaluate the detection limits for thiodiglycol; the values ranged between 4 and 16 $\mu g\ L^{-1}$ groundwater.

INTRODUCTION

Sulfur mustard (HD, *syn.* bis-(2-chloroethyl)sulfide, CAS Registry No. [505-60-2]) is an organosulfur blister agent that was first deployed in World War I and has been used occasionally worldwide ever since. It was manufactured by several agencies during World War II, including the US Army Rocky Mountain Arsenal between December 1942 and May 1943[1]. Sites such as the Rocky Mountain Arsenal are currently being remediated and converted to non-military uses. In order to ensure that the final site contains soil and groundwater with contaminant levels below those maximum levels allowed by the regulatory agencies, rigorously-tested analytical methods must be available that will (a) demonstrate the presence or absence of HD at regulatory levels in soil or groundwater samples, (b) be readily implemented by most commercial analytical laboratories, (c) be rapid and convenient to use, and (d) generate minimal final quantities of chemically-hazardous waste. The determination of traces of HD and its decomposition products is crucial to support efforts in the remediation of contaminated sites at many military installations and the verification of arms control agreements in compliance with the Chemical Weapons Convention.

The primary environmental fate mechanism of stored or buried HD is hydrolysis[2]. Although HD is rapidly hydrolyzed (half-life of 8.5 min at 25°C)[3], its rate is limited by the slow rate of dissolution. The hydrolysis mechanism is complex and, depending upon the availability of water, occurs by two routes, both of which lead to the initial formation of thiodiglycol (TDG, *syn.* 2,2'-thiodiethanol, CAS Registry No. [111-48-8]) and hydrochloric acid. Hence, the presence of TDG in a groundwater sample is an

excellent indicator of legacy HD manufacture or storage. The current Target Reporting Limit (TRL) set by the US Army Rocky Mountain Arsenal for TDG in groundwater[4] is 5 μg $L^{-1.}$

The open literature describes a variety of analytical procedures for TDG in aqueous matrices, but few exhibit both the required sensitivity and selectivity required and ready availability within most commercial analytical laboratories. Some of the high-pressure liquid chromatography-based methods reported for this purpose employ sulfur flame photometric detectors[5,6], capillary electrophoresis with UV detection[7], and mass spectrometric detectors employing either electrospray[8,9] or atmospheric pressure chemical ionization[10,11]**.** Methods based on gas chromatography are particularly attractive when combined with a derivatization step both to reduce tailing of thiodiglycol and to improve sensitivity and selectivity. For example, Black and Read[12] converted the urinary metabolites of sulfur mustard, including TDG, to their corresponding bis(pentafluorobenzoate) derivatives prior to gas chromatography-tandem mass spectrometry (GC-MS-MS) or electron-capture negative ion chemical ionization mass spectrometry in the selected ion monitoring mode[13]. TDG present in the urine of exposed rats or guinea pigs has been derivatized with heptafluorobutyric anhydride prior to gas chromatography with mass spectrometric detection, with excellent results[14,15].

The present method expands the work of Leong et al.[16] to provide a viable method for quantitating TDG and 3,3'-thiodipropanol (TDP, CAS Registry No. [10595-09-02]), a proposed surrogate, in groundwater at low μg/L (ppb) concentrations. The detection limits and recoveries for both derivatized species were rigorously determined using protocols mandated by both the US Army Rocky Mountain Arsenal and the US Environmental Protection Agency. The final chemical waste produced requiring disposal did not exceed 1 mL per sample.

REAGENTS, APPARATUS, AND INSTRUMENTATION

Thiodiglycol (*syn.* 2,2'-thiodiethanol, CAS Registry No. [111-48-8]), 3,3'-thiodipropanol (CAS Registry No. [10595-09-02]), and *N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide (MTBSTFA, CAS Registry No. [77377-52-7]) with 1% *t*-butyldimethylchlorosilane (TBDMS-Cl, CAS Registry No. [18162-48-6]) were purchased from the Aldrich Chemical Co. at 99+% purity. Silylation grade pyridine (CAS Registry No. [110-86-1]) was obtained from Sigma. Toluene (CAS Registry No. [108-88-3]), HPLC-grade water, acetonitrile (CAS Registry No. [75-05-8]), and dichloromethane (CAS Registry No. [75-09-2]) were purchased in HPLC grade or better purity from J. T. Baker or Allied Signal, Inc., Burdick & Jackson. Reagent-grade sodium chloride and anhydrous sodium sulfate were procured from Fisher Scientific, Inc., and EM Scientific. All chemicals were used without further purification.

Ambersorb 563 and Ambersorb 572 (20-50 mesh) were purchased from Supelco, Inc. These sorbents were packed as required into empty 6-mL capacity surgical polypropylene columns (J. T. Baker) with customary 20 μm porosity Teflon® frits. Columns (6-mL) containing 500 mg Envi-Carb were obtained from Supelco. Disposable 6-mL columns packed with 500 mg Bakerbond spe™ octadecyl C_{18} and 75-mL empty surgical polypropylene sample reservoirs were purchased from J. T. Baker.

All groundwater samples were extracted using a 12-position solid phase extraction manifold with Teflon® valves and needles and vacuum applied from the stainless steel top, rather than the side, of the glass chamber (Burdick & Jackson, part no. 9400). Dichloromethane extracts were collected and derivatized (as described below) in 8-mL shell vials and sealed using 15-425 plastic black caps with open tops and PTFE-faced silicone rubber septa. Derivatized and diluted residue was ultimately transferred to 2-mL amber silanized automatic sampler vials bearing hole caps with Teflon®-silicone rubber-Teflon® septa.

Two Multi-Block Heaters were used during sample preparation. One, which was used strictly for extract concentration, was positioned underneath a nine-port Reacti-Vap™ Evaporator attached to a nitrogen cylinder (99.999% purity). The usual cast aluminum heating block was turned over, enabling shell vials to stand under the vanes of the evaporator in full view of the analyst. The block temperature was maintained at 45°C. The second, which was used strictly for derivatization, was maintained at 105°C and employed a heating block drilled for 12/13 mm diameter vessels (i.e., 8 mL shell vials) and a thermometer.

A Hewlett-Packard Model 5890 Series II gas chromatograph interfaced to a Hewlett-Packard Model 7673 automatic sampler and Hewlett-Packard Model 5989A quadrupole mass spectrometer was used for all measurements. The injector was equipped with a double-gooseneck injector sleeve. The fused-silica gas chromatographic column was an HP-5MS Ultra Low Bleed (5% diphenyl-95% dimethylsiloxane), 30 m x 0.25 mm i.d., 0.25 μm film thickness. The head pressure of the carrier gas (helium, 99.99% purity) was 54 kPa (7.8 psi). The automatic sampler syringe was flushed twice each with methanol and toluene before injecting 1 μL sample into the gas chromatograph.

The injector, detector, and mass transfer line temperatures for the gas chromatograph were 250, 280, and 280°C, respectively. The column oven temperature was increased linearly from 100°C (hold for 3 min) to 270°C (hold for 1 min) at 10°C/min. The mass spectrometer operated at source and quadrupole temperatures of 200° and 100°C, respectively, and a source manifold pressure less than 8×10^{-6} torr. The ionization mode was electron impact (70 eV), with an electron multiplier voltage of 50 V above the "tune" voltage. The "solvent delay", or the time after the start of a given analysis until the mass spectrometer was turned on, was 14 min. The GC/MS system was operated in its "selected ion monitoring" (SIM) mode, in which the mass-to-charge ratio (m/z) monitored for TDG was 293, while those monitored for TDP were 321 and 363. The selected ions for TDG were scanned between 14 and 16.5 min, while those for TDP were scanned between 16.5 and 19 min. The "dwell time", or time spent monitoring a given m/z value, for 293, 321, or 363 was 400, 400, or 100 msec, respectively. The "low mass resolution" feature was "on", allowing a mass peak width of 0.9 amu. The increased peak width (normally 0.5 amu) increased sensitivity with little loss in specificity.

EXPERIMENTAL PROCEDURES

An aliquot of calibrating solution (normally 10 to 100 μL) was combined with 100 μL each pyridine and MTBSTFA with catalyst in a 2-mL silanized automatic sampler vial. The vial was capped and heated to 105°C for 1 hr, then cooled to room temperature. The contents of the vial were diluted to 1 mL with toluene, then analyzed for TDG and TDP by GC-MS-SIM according to the parameters noted above. If reanalysis of the extracts is either expected or desired, the vials may be recapped and stored at 4°C for at least seven days. Daily calibration of the mass spectrometer with derivatized standards is recommended.

100 mL portions of model groundwater (100 mg/L each in chloride and sulfate as their sodium salts in ASTM Type II water)[17] were fortified to a desired concentration of TDG (2-100 ng TDG/mL). In addition, each groundwater sample was fortified with TDP (surrogate, 25 μg TDP/L).

The solid phase extraction column train was prepared as follows: The C_{18} "guard" column was conditioned with two column volumes each of methanol and HPLC-grade water, while the "extraction column" (100 mg Ambersorb 572) was conditioned with a single column volume of methanol and two column volumes of HPLC-grade water. *Once the column conditioning process has begun, neither the C_{18} nor the Ambersorb 572 column should be allowed to go dry.* The solid phase extraction column train consists of (a) 75 mL reservoir, (b) C_{18} "guard" column filled with water, and (c) Ambersorb 572

extraction column filled with water, all connected using the hardware supplied with the reservoirs. The completed train is then mounted on the solid phase extraction manifold. The fortified groundwater sample is added to the reservoir, and liquid flow is adjusted to a flow of 2-3 mL/min, with vacuum applied as required. (Note that some groundwater samples may contain an excessive quantity of particle fines that will clog the "guard column" rapidly. In that case, "off-line" filtration of the fortified sample may be required prior to solid phase extraction.) After the entire 100 mL sample has passed through the Ambersorb 572 column, the train is disassembled and the Ambersorb 572 column is dried under full vacuum for at least one hour.

Materials collected on the Ambersorb 572 column are eluted, slowly if possible, into an 8-mL shell vial using three 3-mL portions of dichloromethane (typically, 8 mL dichloromethane extract are recovered). A 100 μL aliquot of pyridine is added to the extract as a "keeper", and the resulting solution is taken to dryness both by warming the bottom of the shell vial (to 45°C) and by using dry flowing nitrogen. The resulting residue is derivatized in the 8-mL shell vial at 105°C for 1 hr with 100 μL each additional pyridine and MTBSTFA with catalyst. After the derivatized mixture has cooled, it is diluted to a final volume of 1 mL with 800 μL toluene, transferred to a 2-mL automatic sampler vial, and analyzed for TDG and TDP by GC-MS-SIM using the parameters described above. If reanalysis is either expected or desired, the vials may be recapped and stored at 4°C for at least seven days.

The measured integrated peak area for either TDG or TDP is calculated using the "integrate" function of HP 5989A mass spectrometer data system. The peak areas from the derivatized standards were fit to a quadratic calibration curve of the form $C = aA^2 + bA + c$, where C is the concentration of analyte in the extract in μg/mL, A is the measured peak area, and a, b, and c are regression constants, all of which should be considered statistically significant. The extract concentration was later corrected in the usual manner for the groundwater sample volume, 100 mL.

RESULTS AND DISCUSSION

In principle, TDG could be removed and concentrated from aqueous samples using either liquid-liquid or solid-phase extraction. Both approaches exhibited deficiencies and challenges. TDG is so soluble in water that partitioning with a variety of organic solvents, e.g., ethyl acetate and dichloromethane, produced overall recoveries not greater than approximately 20% at a test concentration range of 20-120 μg/mL. This situation persisted even when the pH of the aqueous sample was adjusted to <1 and salt (~25% w/v) was added. To compound the problem, liquid-liquid extraction generated a considerable quantity of organic solvent waste. For all of these reasons, this approach was set aside.

An alternative approach involved the adsorption of TDG onto a carbonaceous sorbent(s), with subsequent elution and analysis. Several sorbents were evaluated, i.e., Ambersorb 563, Ambersorb 572, and Envi-Carb. Ambersorb 572 was an attractive choice because it has been used successfully for the determination of other small water-miscible analytes, such N-nitrosodimethylamine, in groundwater[18]. Envi-Carb is available commercially in small prepacked columns and would be convenient for routine analyses. Small columns packed with 500 mg of each sorbent were challenged with 100 mL model groundwater samples fortified to 2-50 μg TDG/mL. The analyte was eluted with a variety of solvents, including dichloromethane, ethyl acetate, methanol, and acetone. The nominal eluting condition was three 3-mL portions of each solvent, which were pooled. The resulting extract was taken to dryness and derivatized with MTBSTFA, as described below.

It became clear that passing the sample through Ambersorb 572 and eluting TDG with dichloromethane was the preferred choice of sorbent and eluting solvent. Ambersorb 563 was less successful than Ambersorb 572, while the Envi-Carb sorbent never retained TDG at all. Even with an

optimized sorbent and desorbing solvent, the recoveries of TDG were both low and inconsistent. Subsequent experiments demonstrated that the lengthy concentration periods using dry flowing nitrogen, often more than 1 hour, were slowly and irreproducibly volatilizing trace quantities of TDG, a compound normally considered "nonvolatile". By adding a small quantity (100 μL) of pyridine as a "keeper" and warming the bottom of the shell vial slightly (to 45°C), the sample concentration time was reduced to approximately 30-45 min, while the analyte recovery was increased to approximately 40% at test concentrations ranging between 0.25-2 μg TDG/mL. We believe, but cannot prove, that the effectiveness of Ambersorb 572 in this method is related to its specific surface area that, at 1100 m^2/g, is the highest of the three sorbents evaluated.

The use of a carbonaceous adsorbent presented several additional challenges and considerations. First, such a sorbent is nonselective and will retain any non-ionic neutral analyte present in an authentic contaminated groundwater sample. Having all of these materials present in the final extract would provide an excessive and unwanted level of interferences, even for the most selective detectors. For that reason, a guard column was placed in tandem and ahead of the Ambersorb 572 column. The initial choice for the guard column was a 500 mg C_{18} octadecyl SPE column, which would be capable of retaining modest quantities of nonpolar interferences. Other guard columns might be more appropriate, depending upon further characterization of the interferences. Second, it is very difficult to elute the desired analytes quantitatively from an adsorption column with a small volume of organic solvent, although that is commonly done with a reversed-phase column. For example, when we attempted to elute TDG from a 500 mg Ambersorb 572 cartridge (test conditions, 0.25-2 μg TDG/mL, 100 mL sample) using three 3-mL aliquots of dichloromethane, significant quantities (up to 25% of the expected mass) of TDG were observed in the combined second and third aliquots.

Two approaches to improve the overall recovery and convenience were investigated. First, an alternative and more powerful eluting solvent was considered. This approach was immediately set aside because we had found no common organic solvent that was more effective for stripping TDG from Ambersorb 572 than dichloromethane. Second, reducing the bed mass would prevent TDG from migrating further into the bulk sorbent upon elution and possibly becoming re-adsorbed. For that reason, adsorption columns containing 500, 200, and 100 mg Ambersorb 572 were evaluated. When each of these was challenged with a 100 mL model groundwater sample containing 0.25-2 μg TDG and TDP/mL, the recoveries observed in the initial 3-mL dichloromethane extract were similar, and ranged between 25-40%, regardless of the bed mass. Based on these data, we hypothesize that the adsorption of TDG and TDP on Ambersorb 572 is basically a surface phenomenon, occurring on the very top of the adsorption column. As long as the expected concentration of TDG is trace-level and the capacity of the surface sorbent is not exceeded, the rest of the bed mass is extraneous and, in fact, inhibits quantitative recovery of analyte. For that reason, further work focused on Ambersorb 572 columns employing a 100 mg bed mass. Three 3-mL column washes with dichloromethane were employed to ensure that the sorbent was thoroughly exposed to solvent while simultaneously allowing a high ratio of eluting solvent to sorbent bed volumes. At the same time, further significant improvements in overall recovery are not expected unless advanced instrumentation featuring extraction under elevated temperature and pressure conditions (Accelerated Solvent Extraction™) is employed.

Because most commercial service analytical laboratories would possess GC-MS capabilities, the current method emphasizes derivatization of TDG with a reagent that would convert the analyte into a stable and volatile species amenable to highly-selective and sensitive selective ion monitoring. Of the reagents available, MTBSTFA was particularly attractive, for the following reasons: (a) neutral volatile by-products are produced; (b) the butyldimethylsilyl ether products are stable to hydrolysis; and (c) simple readily-predicted mass spectra feature an $(M-57)^+$ ion, which represents loss of a tertiary butyl group, and is both diagnostic and of medium to high intensity.

In spite of the obvious advantages, there are additional considerations when using MTBSTFA. Because water, not the analytes, will preferentially react with MTBSTFA, it is important that the Ambersorb 572 bed be completely dry prior to dichloromethane elution. The recommended drying time for the Ambersorb 572 bed is at least one hour. In addition, it is important that *both* hydroxyl groups present on either TDG or TDP be derivatized. Insufficient reaction time or temperature produces both a singly-derivatized species, whose presence reduces the apparent recovery of analyte, as well as the doubly-derivatized entity. For that reason, both a derivatization time (1 hr) and temperature (105°C) higher than normal for such reactions is recommended. Derivatized standards or extracts are reasonably stable to hydrolysis. They may be stored at 4°C and re-analyzed reliably within seven days, as needed. Both the standards and derivatized extracts were ultimately dissolved in toluene, rather than an aprotic polar solvent such as acetonitrile, to minimize peak splitting on the nonpolar HP-MS5 gas chromatographic column.[19]

The performance of the proposed method was evaluated using two statistically-unbiased protocols, viz., those of the US Army Rocky Mountain Arsenal[20] and the US Environmental Protection Agency[21], to determine the Method Reporting Limit (MRL) and the Method Detection Limit (MDL), respectively. The former is equivalent to determining a "found" concentration so that both the false positive and false negative errors are both 5%.[22, 23] By contrast, the latter is the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.

The MRL was evaluated using a procedure established by the US Army and discussed in detail elsewhere[24]. Briefly, 100 mL portions of model groundwater were fortified to 2.5-100 μg TDG/L, or 0.5 to 20 times the Target Reporting Limit (TRL) of 5 μg/L. Each test sample was also fortified with 25 μg/L TDP, which served as a candidate surrogate. Samples were spiked, extracted, derivatized, and analyzed as described above, and the resulting model groundwater concentrations calculated using calibration data obtained on each of two method certification days. The MRL values were calculated using the current version of software recommended by the Program Manager Rocky Mountain Arsenal[25]. Candidate analytical methods employing GC-MS-SIM are considered to be "self-confirming", in that the identity of a given compound is established using both its retention time and mass spectrum or selected ions within. No independent confirmatory method was required. The slope of the calculated linear regression line representing the relationship between the analyzed ("found") and spiked ("true") values may be taken as a measure of analyte recovery. The calculated MRL value for TDG was 16.2 μg/L, with a corresponding recovery of 38%.

MDL values were calculated for both TDG and TDP, the proposed surrogate compound. A single set of nine 100-mL model groundwater samples (seven required) were independently fortified to 25 μg/L in each of TDG (five times the TRL) and TDP, then processed as described above. The resulting concentrations and sample standard deviation for each analyte were calculated. The latter values were multiplied by the appropriate value of the Student's-t distribution, 2.896, representing 99% confidence and (n-1) degrees of freedom (here, 8), where n is the number of data values available. The resulting value is the MDL; it is 3.5 and 1.2 μg/L for TDG and TDP, respectively. The average recoveries for TDG and TDP are 23 and 17%, respectively, and reflect the difficulty in extracting these water-miscible species from a groundwater matrix. However, the recoveries are clearly consistent and reproducible. Similar recoveries were reported for the determination of N-nitrosodimethylamine, which is also a small, highly-polar, water miscible analyte, from aqueous samples using Ambersorb 572 as the extraction sorbent[26,27]. The extraction and derivatization behavior of TDP tracks that of TDG closely, and is therefore an acceptable surrogate compound.

CONCLUSIONS

Thiodiglycol (TDG), a major hydrolysis product of sulfur mustard, may be extracted from groundwater samples using a small column packed with Ambersorb 572, a synthetic carbonaceous sorbent. The analyte is ultimately is derivatized with MTBSTFA, diluted with toluene, and analyzed by GC-MS-SIM. The detection limits for this procedure ranged between 3.5 and 16 μg TDG/L groundwater. Thiodipropanol (TDP) exhibited an extraction behavior and detection limit (1.2 μg TDP/L) similar to that of TDG, and was considered to be an acceptable surrogate compound. The method recovery for both analytes is modest, ranging between 20-40%, and reflects the difficulty in extracting water-miscible analytes from a groundwater sample.

The typical sampling rate for the proposed method is approximately twelve to sixteen groundwater samples per eight-hour working day. Calibration standards may be prepared concurrently with the groundwater extracts, and should also be analyzed daily. It is strongly recommended that all sample preparation be performed during an eight-hour shift, and that all subsequent GC-MS-SIM determinations be performed independently using an instrument equipped with an automated sampler.

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