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GAS CHROMATOGRAPHY

Determination of Aromatic Arsines in Environmental Solids by Direct Thermal Desorption Gas Chromatography

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ABSTRACT

To quantify aromatic arsines in the environment, such as World War I era chemical warfare agents and degradation products of arsenicals used in agriculture, a sensitive, selective, and direct method is needed. We describe the development and optimization of a method for the measurement of trace levels of triphenylarsine used as a model aromatic arsenic compound. Triphenylarsine was determined at low µg/g levels in sand, soil, and lake sediment by thermal desorption before gas–liquid chromatography (GC) with mass spectrometric and pulsed flame photometric detection. The dithiol derivative of phenylarsonic acid was used as an internal standard, thereby significantly improving the precision of the method. The desorption conditions were studied and found to be optimal at 350°C for 15 min. Significant improvement in precision was realized by preparing the solid samples as slurries in acetone and by inserting a small (~100 mg) quartz wool plug into the sample vial. The method was applied to determine triphenylarsine in authentic soil and sediment samples that had been fortified with triphenylarsine and aged for at least 15 days. Recoveries for soil samples ranged from 84.3 ± 2.3 to $87.7 \pm 1.3\%$, while lower recoveries were obtained for sediment samples ($75.1 \pm 3.0\%$). The detection limit for triphenylarsine in soil was 3.14 ng with a precision of 7.10% ($n = 4$). Using these optimized conditions, the performance of the direct thermal desorption GC method for sample introduction was greatly improved compared to methods that have been reported in the literature.

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KEYWORDS
Direct sample introduction; gas chromatography; thermal desorption; triphenylarsine

Introduction

Arsenic is ubiquitous in nature and is used in a variety of industries that include agriculture, semiconductor technology, and pharmaceuticals. Arsenic has several oxidation states (+III, +V, 0, −III) and occurs naturally in a multitude of inorganic and organic forms. The chemical speciation of arsenic in the environment encompasses five general classes: inorganic mineral forms, inorganic oxyacids, alkylated derivatives of the oxyacids, arsenosugars, and arsines (Cullen and Reimer 1989; Frankenberger 2001; Leermakers et al. 2006; Deschamps and Matschullat 2011). With the advent of chemical warfare during the First World War (WWI), arsines were prime candidates for weaponization. A variety of arsines for use as lachrymators (tear gases and vomiting agents) and vesicants (blister

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agents) were stockpiled (Prentiss and Fisher 1937; Ellison 2000). The aromatic arsines were developed as lachrymators for battlefield usage, and they are still of considerable interest, particularly in Germany and Japan where the remediation of contaminated production and storage sites is a high priority (Sanderson, Fauser, and Thomsen 2010; Yao et al. 2012; Bundschuh, Holländer, and Ma 2014). In addition, the WWI era chemical warfare agents are considered a potential terrorist threat given that they require relatively unsophisticated chemical engineering technology to prepare (Shea 2003).

In environmental analysis, the ability to minimize steps in a procedure has definite advantages in terms of maintaining sample integrity. The ChromatoProbe, a novel device for direct sample introduction (DSI) of solid samples in gas chromatography (GC), was first described in 1997 (Amirav and Dagan 1997). The thermal desorption probe was designed as a simpler and more flexible alternative to conventional "direct probe" techniques in GC. The method for using the probe is based upon placing a solid sample into a glass microvial, placing the vial within a customized probe, and then inserting the probe into a conventional GC injection port. Direct thermal desorption is then performed to introduce the sample into the chromatograph. The thermal desorption GC method is designed to simplify sample preparation, increase sample throughput, and improve detection sensitivity. The primary drawback of the device has been the typically semiquantitative nature of the measurement, arising from the imprecision of the direct introduction of the sample into the GC.

The literature for the thermal desorption probe over the two decades since its introduction is comprised of method development studies, numbering approximately 20 articles, and applications, numbering well over 100 studies (Hays and Lavrich 2007; de Koning, Janssen, and Brinkman 2009; Poronsky and Cutrone 2017). For the development of novel methods using the thermal desorption probe, the most common applications that have appeared in the literature have been for the determination of narcotics in bodily fluids and the determination of pesticides in food residues (Jing and Amirav 1997). More recently, applications have been extended to other analytes in complex matrices, giving rise to many interesting reports, including volatile organic compounds found in diesel engine piston deposits (Diaby et al. 2009); 5-aminosalicylic acid in an intestinal obstruction (calcified foreign bodies or "stones") (Orioli et al. 2004); fatty acids in archaeological samples (cave painting, cooking residue, soil) (Brown-Sinha 2007); compounds used in the preparation of molecularly imprinted polymers as chromatographic resins (Cummins, Duggan, and McLoughlin 2011); volatile organic compounds in human skin as a means to study mosquito vectors implicated in the transmission of diseases (Dormont et al. 2013); polybrominated diphenyl ethers in indoor dust (Espino and Leon 2014); and the analysis of crystalline acenes used in organic semiconductors (Voloshenko et al. 2013). In the last reference, it is worth noting that the authors examined anthracene, tetracene, and pentacene for impurities, finding that the probe was superior to other DSI techniques because it minimized their thermal degradation.

In this report, we describe our work in improving the precision of the thermal desorption probe and extending its application to the determination of an aromatic organoarsine at low μg/g levels in environmental solids. Previous reports have been regarded as "semiquantitative" because of the relatively low recoveries and poor precision that has been observed. In contrast, we describe several simple improvements to the thermal desorption method that allow for more quantitative figures of merit to be realized.

Experimental

Reagents

All reagents used were analytical reagent grade or better. Organic solvents were HPLC grade (Acros Organics, Morris Plains, NJ, USA). Reagent water (18 MΩ-cm) was prepared by passing house deionized water through a NanoPure filtration system (Barnstead, Dubuque, IA, USA) equipped with an ultraviolet lamp (D_2, 14 W). All glassware and plasticware were washed with Citranox (Alcanox, New York, NY, USA) and then soaked for at least 48 h in 5% (v/v) nitric acid (analytical reagent grade, Fisher), followed by copious rinsing with reagent water. The model analyte used for method development was triphenylarsine (98%, Alfa Aesar, Ward Hill, MA, USA). Stock solutions of 200 mg/L of triphenylarsine were prepared in HPLC-grade *n*-hexane or acetone and stored at 0°C in opaque glass bottles with aluminum-lined caps. Standards less than 40 mg/L were made on the day of use. The internal standard for normalization of the triphenylarsine signal was the propanedithiol derivative of phenylarsonic acid (99% Aldrich), prepared as described previously (Killelea and Aldstadt 2001).

Instrumentation

Triphenylarsine was determined using a Varian Saturn system (Walnut Creek, CA, USA) which consisted of the following components: Model 3800 capillary gas–liquid chromatograph (DB5-MS column, 30 m × 0.25 mm with 0.25-μm film, J&W Scientific, Folsom, CA, USA) with Model 1079 split/splitless injector; electron impact (EI) ionization source (70 eV); pulsed flame photometric detector (PFPD); and Model 2000 quadrupole ion trap (10-650 *m/z* range, unit resolution). The optimized MS and PFPD methods (Table 1) were based on our previous work (Killelea and Aldstadt 2001) in which a high-pass (>695 nm) optical filter (Schott RG695, BES Optics, Warwick, RI, USA) and Model R5070 photomultiplier tube (Hamamatsu, Bridgewater, NJ, USA) were used. GC instrument control and data acquisition were performed on a Pentium personal computer (Dell, Optiplex GX1, Dallas, TX, USA) using Saturn System software version 5.21 and PFPD analysis software version 1.0 (Varian).

Sample preparation

For method development, sand, soil, and sediment samples were used. Sand was purchased from Sigma-Aldrich (Milwaukee, WI, USA), soil was collected locally, and surficial sediment was collected in Green Bay using a Ponar (grab) sampler. Soil and sediment samples were dried at 60°C for 1 week, filtered over a 2-mm sieve, homogenized using a shaker for at least 24 h, and then finely ground using a (ceramic) mortar and pestle. Samples were stored at room temperature in opaque high-density polyethylene bottles.

Thermal extraction experiments were performed using a thermal desorption probe (Model ChromatoProbe, Varian, Walnut Creek, CA, USA). Small quantities of dried solid samples (~100 mg for sand or ~2–10 mg for soil and sediment) were fortified with a triphenylarsine standard (varied between 5–80 mg/L) and placed in a glass vial (15 mm length, 2.5 mm o.d., 1.8 mm i.d.). Sample delivery was controlled by variation of the injector temperature and the split vent flow ratio to efficiently vaporize the analytes for

Table 1. Conditions for the optimized gas chromatography method.

Mobile phase (He)	1.2 mL/min (29.2 cm/s)
Injector	
Initial	120°C (1 min)
Gradient	200°C/min
Final	450°C (15 min)
Injector split ratio	
Initial	Off
0.01 min	1:100
1.01 min	Off
10.01 min	1:100
15.01 min	Off
Oven	
Initial	50°C (5 min)
Gradient	100°C/min
Final	290°C (15 min)
Column	DB5MS, 20 m × 0.25 mm with 0.25 µm film thickness
Pulsed FPD	
PMT voltage	610 V
Gate delay	16.3 ms
Gate width	9.1 ms
Trigger level	200 mV
Air-1 flow	17.0 mL/min
H2 flow	16.6 mL/min
Air-2 flow	10.0 mL/min
Mass spectrometer	
Mass range	10–350
Filament delay	2.0 min
Filament emission	10 µA
Ion trap temperature	220°C
Axial modulation	4.5 µA
Peak threshold	0
Target ion count	20,000
Ionization mode	EI Auto
Max ionization time	25,000 µs
Prescan ionization time	100 µs

transfer to the GC column. Samples were analyzed before fortification and found to be free of contamination by arsenicals.

Sand was placed in a glass microvial and fortified with triphenylarsine (varied between 5–200 mg/L) and internal standard (propanedithiol-phenylarsonic acid). The initial injector temperature was set at 120°C, then ramped to 350°C at 200°C/min, and held isothermally for X min (where X is the desorption time, ranging from 0.5 to 5.0 min). The split vent valve was closed during the desorption period, and then opened at 0.5 min at a ratio of 1:100 until the end of the GC run. The GC oven temperature was initially constant at 75°C for 2 min, and then ramped to 275°C at 100°C/min.

The GC conditions used for soil and sediment samples differed from those used for sand samples. The injector temperature was ramped from 120 to 450°C at 200°C/min and held isothermally for 10 min. The injector split vent valve was closed during the first 10 min, and then opened at a ratio of 1:100 until the end of the run. The GC oven temperature was constant at 30°C for 10 min, ramped to 275°C at 100°C/min, and finally, held isothermally for 5 min.

For "aging" studies of soil and sediment samples, aqueous slurries (1 g in 25 mL) were fortified with triphenylarsine and the ionic strength was adjusted to 0.15 M with $CaCl_2$. The samples were mechanically rotated for 48 h and then stored in the dark at room

temperature (~22°C) for a minimum of 15 days. The samples were air-dried at room temperature and then homogenized using a ceramic mortar and pestle before being subjected to the optimized thermal desorption method.

Results and discussion

A drawback of using DSI techniques is an often high degree of variability as a result of inconsistent recovery. Precision, expressed as percent relative standard deviation can vary widely, with reports greater than 50% not uncommon. Variation in the efficiency by which the analytes are desorbed is probably the primary source of imprecision. For example, a method to determine narcotics in human hair found that the thermal extraction efficiency varied over a wide range and the precision was therefore poor, with relative standard deviation values ranging from ~20 to 60% (Wainhaus et al. 1998). A method for the determination of 19 organophosphorus pesticides in blood observed recovery values from 48 to 162% and relative standard deviation values that ranged up to 109% (Kakimoto, Kitagawa, and Hori 2001). Therefore in developing a thermal desorption method for the direct determination of organoarsenicals in soil, we focused on optimizing the conditions such that the method would be repeatable with good precision as well as minimize "carry-over" into subsequent samples. We also wanted to demonstrate the utility of the method by applying it to environmental solids.

Gas chromatography–mass spectrometry

We chose to work with triphenylarsine as a model compound because of its low toxicity yet structural similarity to organoarsenicals of interest in environmental research. The electron impact (EI) mass spectrum for triphenylarsine is shown in Figure 1. Triphenylarsine (306.24 g/mol) produced seven significant ions (defined as >10% abundant); the molecular

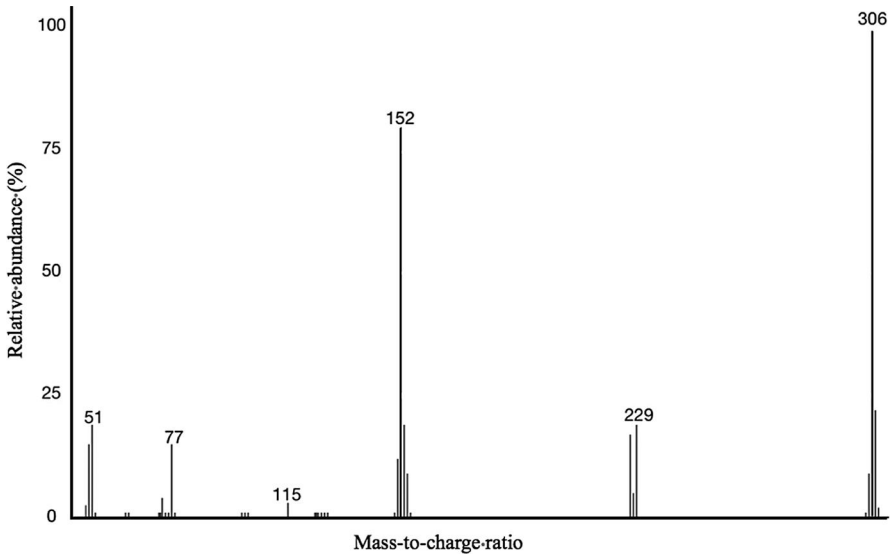

Figure 1. Electron impact mass spectrum for triphenylarsine (25 ng injection). Method conditions are described in the text and putative structures are listed in Table 2.

Table 2. Suggested identities of the major species that were observed in the electron impact mass spectrum of triphenylarsine.

Ion (*m/z*)	Intensity (% base peak)	Possible structure
307	22	MH^+minus$(HAs(C_6H_5)_3^+$
306	100	MH^+minus$(As(C_6H_5)_3^+$
229	19	M minus one phenyl group $(As\ (C_6H_5)_2^+)$
227	17	M minus one phenyl group and 2H, $H(As(C_6H_4)_2^+)$
153	20	MH minus two phenyl groups, $(HAs(C_6H_5)^+)$, possibly M^{++} also
152	80	M minus two phenyl groups, $(As(C_6H_5)^+)$
77	15	Phenyl group $(C_6H_5)^+$, possibly $H2As^+$ also

ion was the base peak (suggested structures are listed in Table 2). Interestingly, the ion corresponding to the loss of two phenyl groups (M-154) at *m/z* 152 was fourfold more abundant than the M-77 ion at *m/z* 229. We observed that the baseline signal was more stable whenever triphenylarsine was introduced by syringe rather than through the thermal desorption probe (results not shown). This is undoubtedly a function of the sensitivity of the MS to ambient air entering the injection port, i.e., when the thermal desorption probe is used, the injection zone is more susceptible to the introduction of ambient air. Hence, more oxygen and/or water may reach the MS to potentially interfere with the ionization process. Consequently, the total ion count for atmospheric species would increase and thereby adversely affect the baseline noise. This does not preclude the use of the thermal desorption probe with MS detection, but one must be vigilant in minimizing the amount of ambient air that enters the system to enable productive searching of mass spectral databases to identify unknown compounds.

We compared conventional syringe injection to the thermal desorption probe over a range of injector (desorption) temperatures (200, 250, 300, and 350°C). A mass of 20 ng of triphenylarsine (1.0 µL in acetone) was introduced directly by syringe into the injector or into the glass microvial, the latter either empty or containing sand (~75–100 mg), as shown in Figure 2. The retention factor (k') for triphenylarsine was 2.81 ($t_m = 1.14$ min), and the effective number of theoretical plates (N_{eff}) was $\sim 4.7 \times 10^4$ (peak width at half-height = 2.1 s). We noted that the chromatographic peak shapes for triphenylarsine were quite similar and the variation in peak width was relatively low (<10%) ($n = 3$) (results not shown). This was somewhat surprising because we expected to observe significantly wider peaks for the thermal desorption probe because of the broader injection bandwidth. We also observed slightly (~10%) higher k' values when sand was used as the sample matrix in the thermal desorption probe ($k' = 2.70$ for the sample vial with sand vs. $k' = 2.45$ for syringe injection or an empty sample vial). As expected, triphenylarsine appears to be briefly retained (i.e., delayed) by the sand during the desorption period.

Thermal desorption conditions

The variation of injector temperature for the three injection methods, expressed as percent relative standard deviation in peak area, peak width, and retention factor (k'), is shown in Figure 3. Several points are worth noting. First, variation among the peak descriptors was relatively low (<10%). Second, lower relative standard deviation values were generally observed, particularly at higher temperatures, for both peak area and peak width. For example, the percent relative standard deviation in peak area ranged from 2.91 to 3.58 at an injector temperature of 350°C, compared to a range from 1.05 to 8.36 at injector

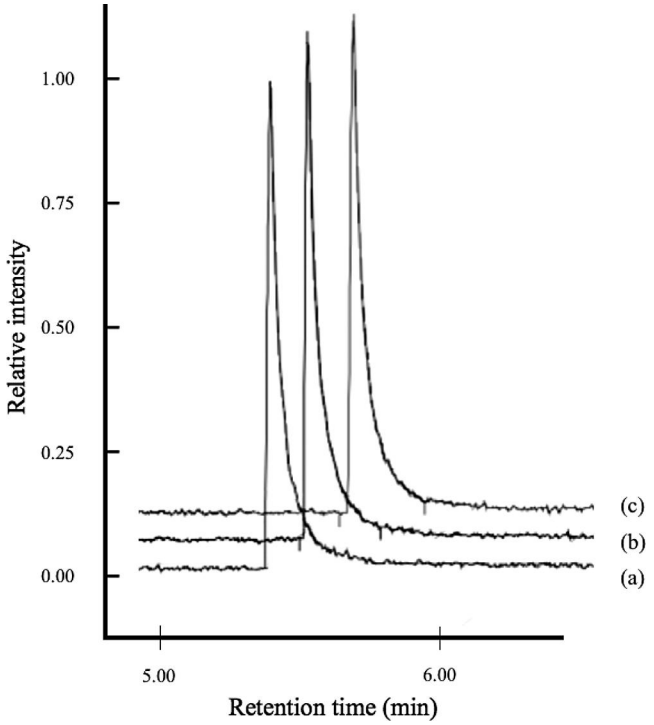

Figure 2. Chromatograms obtained using gas chromatography-pulsed flame photometric detection by injecting 1.0 µL of a 20 mg/ L triphenylarsine standard by use of (a) syringe, (b) empty direct sampling probe vial, and (c) direct sampling probe vial containing sand. Method conditions are described in the text.

temperatures of 200 or 250°C. The percent relative standard deviation in peak width ranged between 3.25–10.28 at 200°C compared to 2.68–5.67 at 350°C. Finally, the mean percent relative standard deviation in peak area and peak width at the four injector temperatures was calculated for the three methods. Better repeatability was obtained with syringe injection compared to that obtained for the thermal desorption probe (i.e., with or without sand). The percent relative standard deviation for syringe injection was 1.98 ± 0.78 for peak area, compared to a percent relative standard deviation of 5.50 ± 2.2 for peak area when using the probe.

We also examined "carryover" between samples (defined as the analyte response for a blank sample that is run immediately following a sample run, expressed as relative percent peak area of the first measurement) as a function of desorption temperature. As shown in Figure 4, carryover was below 5%. Not surprisingly, however, approximately a 10-fold higher degree of carryover was observed at the lower temperatures that were studied (~6% at 200°C vs. ~0.7% at 350°C). Thus, an injector temperature of 350°C was chosen as optimal for subsequent work.

The desorption time was defined as the period until the moment when the split ratio changed to 1:100. A mass of 40 ng (1.0 µL of 40 µg/g standard of triphenylarsine) was fortified on dry sand (~100 mg) inside of a quartz microvial. As shown in Figure 4a, desorption time of 2.0 min permitted the quantitative transfer of triphenylarsine onto the column with minimal carryover (i.e., <0.7%). However, poor repeatability for replicate

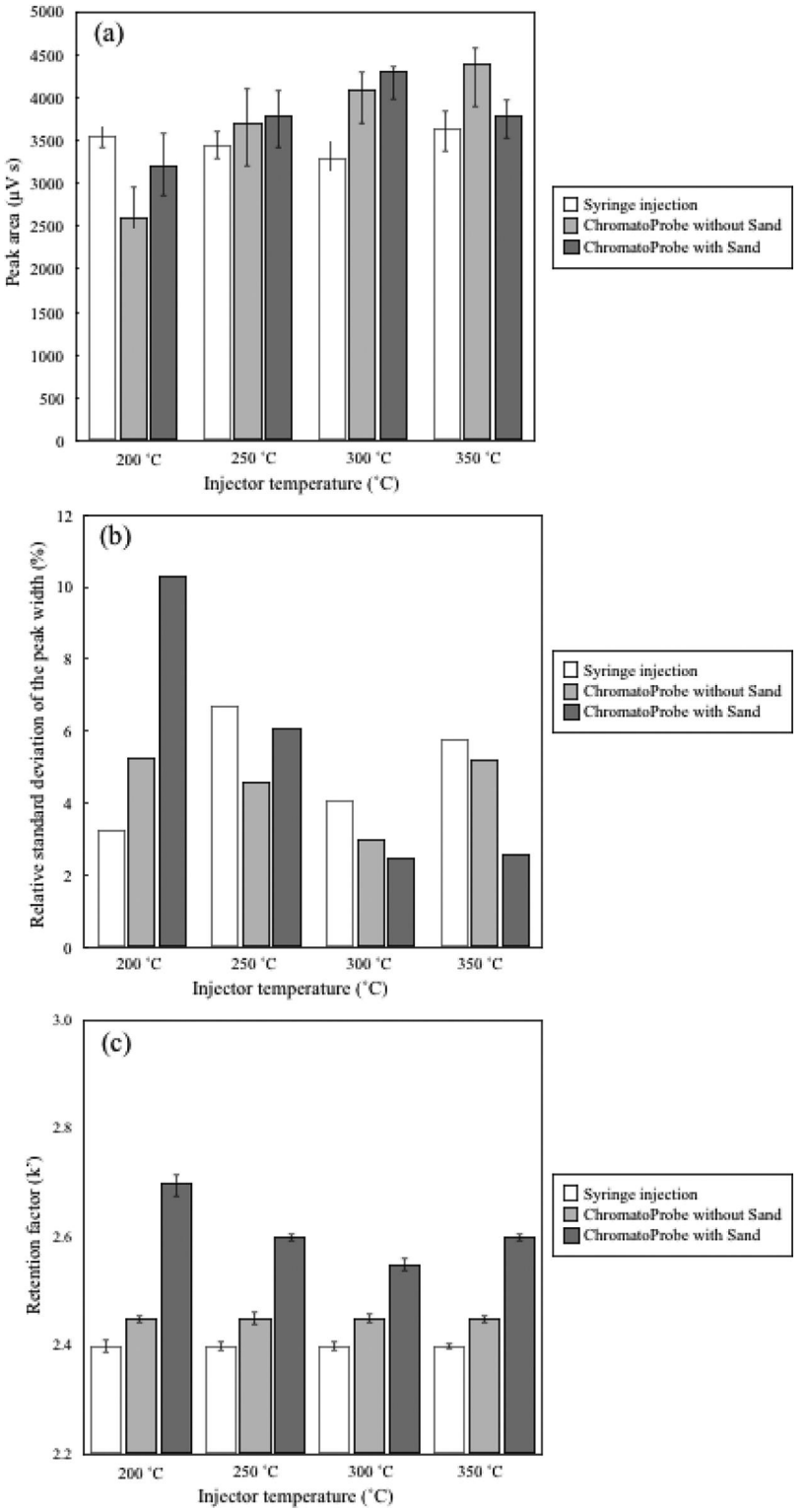

Figure 3. Effect of injector temperature on the triphenylarsine response for the three injection methods (syringe injection, empty sampling probe, and sampling probe with ~75 mg of sand) using 1.0 µL of a 20 mg/L triphenylarsine standard. Error bars are based on Student's *t*-value (two-tailed) at the 95% confidence interval ($n = 3$).

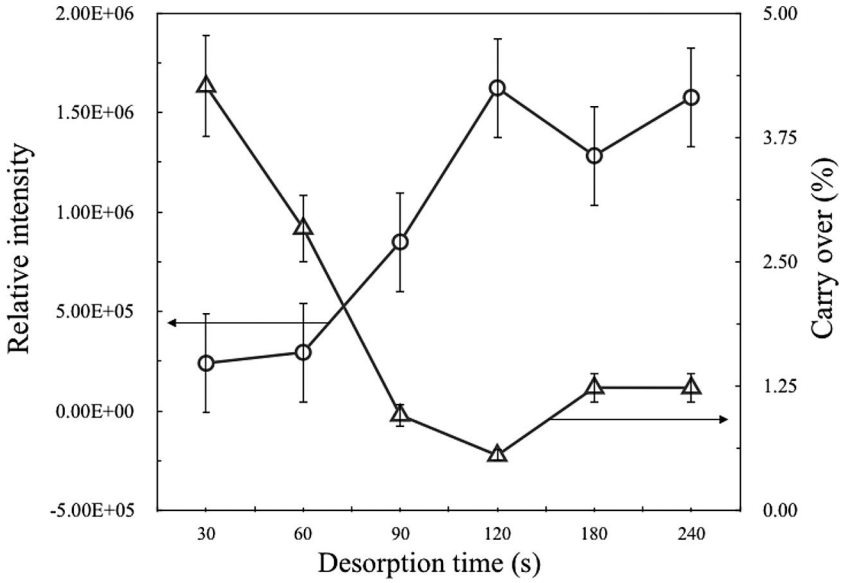

Figure 4. Effect of desorption time on the peak area of triphenylarsine and carryover (expressed as the percentage of peak area) using gas chromatography–mass spectrometric detection. 1.0 µL of 40 ppm triphenylarsine was spiked on dry sand (~100 mg) inside of a quartz microvial. Error bars are based on Student's *t*-value (two-tailed) at the 95% confidence interval ($n = 3$).

measurements of triphenylarsine was observed, with the percent relative standard deviation in peak area ranging from 24.2 to 49.3% ($< x > = 34.3 \pm 10.6\%$).

These results led us to examine the utility of an internal standard as a means to improve the precision of the measurement. The ideal internal standard for an organoarsenical such as triphenylarsine should be chemically similar (e.g., an aromatic arsenical), absent in the environment (or present at a negligible level), simple to prepare (or commercially available), nontoxic, and be well separated from triphenylarsine in the chromatogram. We chose to use the thiol derivative of phenylarsonic acid, a compound that is prepared simply by reacting phenylarsonic acid with propanedithiol to form the cyclic dithiaarsenoline (Killelea and Aldstadt 2001). A 1:1 mixture of triphenylarsine (80 µg/g w/v in hexane) and propanedithiol-phenylarsonic acid (i.e., an extract of internal standard in 1 mL hexane) was analyzed by GC with pulsed flame photometric detection, with propanedithiol-phenylarsonic acid eluting at 3.96 min and triphenylarsine eluting at 4.32 min (results not shown). For a void time (t_m) of 1.14 min, k' values for propanedithiol-phenylarsonic acid and triphenylarsine are 2.47 and 2.79, respectively (the selectivity factor (α) was 1.13 and the resolution (R_s) was 4.57).

The effect of varying the thermal desorption time was re-examined using the internal standard for triphenylarsine. The precision (as percent relative standard deviation) at several desorption times are compared to those that were obtained without internal standard addition (results not shown). Better repeatability was observed in the triphenylarsine results with the internal standard: the percent relative standard deviation in peak area measurements for the internal standard ranged between 13.9 and 26.0% (average of 20.5 ± 5.2) compared to 34.3 ± 10.6 without the internal standard. Similarly, the percent relative standard deviation in peak area measurements ranged between 13.0 and 31.7 (average of

19.9 ± 8.6) with the internal standard compared to an average percent relative standard deviation of 41.5 ± 15.7 without the internal standard. We found that a desorption time of 3.0 min was sufficient to quantitatively transferred triphenylarsine with little carryover (<5%) (results not shown). A desorption time of 5.0 min was adopted for subsequent experiments to more conservatively minimize carryover.

Quantitation and application

To maximize the signal-to-noise ratio, we used pulsed flame photometric detection rather than the mass spectrometer because of the latter's susceptibility to atmospheric contamination through the thermal desorption inlet (as mentioned above). We constructed calibration models for triphenylarsine using propanedithiol-phenylarsonic acid as an internal standard for sand (~100 mg) fortified with 1 μL of the triphenylarsine/internal standard mixture (0–80 ng triphenylarsine on-column). The fortified sand sample was then directly introduced to the GC with pulsed flame photometric detection using the thermal desorption probe. The calibration models were linear between 0–40 ng triphenylarsine, and measurement of 80 ng triphenylarsine showed that saturation of the detector began to occur at ~70 ng triphenylarsine (results not shown). For quantification using peak area, the regression coefficient (i.e., R^2) was 0.983 and the standard error of the estimate in the y-variable (SEE_y) (μV) was 0.034. Thus, internal standard-normalized measurements were very effective for the quantitative determination of triphenylarsine, insuring that repeatability was maximal and carryover was minimal.

The thermal desorption probe with quartz vials was also used to study soil samples. Figure 5 shows superimposed chromatograms for the three sample types (i.e., neat triphenylarsine standard, triphenylarsine fortified on sand, and triphenylarsine fortified on soil). Poor recovery of triphenylarsine from soil was observed, even at high temperature (350°C) and relatively long desorption times (>30 min). There are several possible causes for the observed poor recovery of triphenylarsine from soil. Unlike sand, the presence of "natural organic matter," a poorly understood complex mixture of organic compounds such as humic and fulvic acids, polysaccharides, phenols, and lignin, means that many possible adsorption sites are present in soils and sediments (Martinez and McBride 1999; Kögel-Knabner 2002; Nebbioso and Piccolo 2013). At the higher desorption temperatures that we studied for soil samples, we found that the interior of the thermal desorption probe became severely contaminated by fine particles as well as volatile components and/or pyrolytic fragments of natural organic matter in the sample. We surmised that if triphenylarsine was thermally desorbing, it was likely to partition into the contaminated layer within the body of the probe, thereby markedly reducing the efficiency of the thermal extraction process. Furthermore, the increased surface area and reduced void volume of the fine particles (<10 μm) found in soil no doubt also contributed to the inefficient desorption that we observed. To complicate matters further, a fraction of the fine particles even escaped the sample vial and contaminated the split:splitless injector itself. Apparently, the relatively tortuous flow path of the mobile phase within the thermal desorption probe creates a degree of turbulence around the microvial. To address these problems, we had to resort to replacing the injector liner and cleaning the entire injector housing following each measurement, clearly an impractical situation.

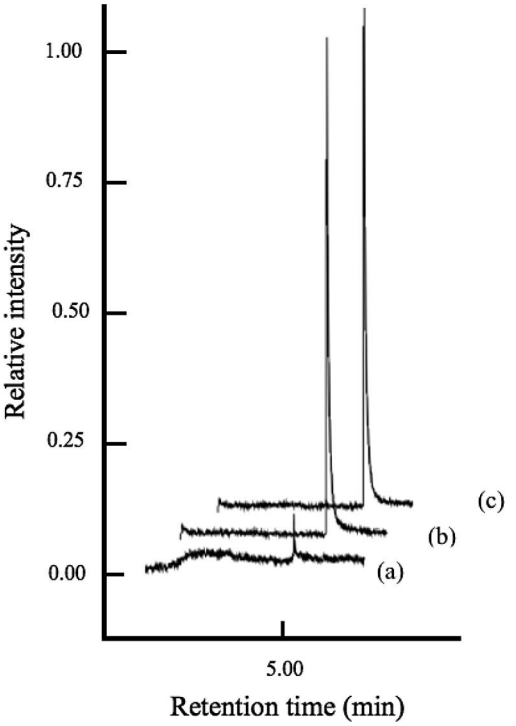

Figure 5. Comparison of triphenylarsine chromatograms obtained by injecting 1 µL of 40 ppm triphenylarsine (w/v in acetone) using the direct sampling probe: (a) empty; (b) spiked on 75 mg sand; and (c) spiked on 10 mg soil.

We therefore explored several approaches to improve the efficiency of the thermal desorption method for soil samples. First, we placed a fine-gauge spiral wire (0.25 mm diameter, Alfa Aesar, USA) on the top of the soil sample before inserting the probe inside the injection zone, resulting in an improvement of the repeatability of the triphenylarsine recovery more than fourfold (16.0 vs. 69.0% relative standard deviation, ($n = 3$). Second, as shown in Figure 4, an additional four-fold improvement in percent relative standard deviation (4 vs. 16, $n = 3$) was found if the soil sample was prepared as a slurry (using 10 µL of acetone) followed by placing a small plug (~0.1 g) of quartz wool on the top of the soil sample (the plug of quartz wool was found effective in preventing the fine soil particles from escaping the sample vial). The combination of the quartz wool plug and the acetone slurry appeared to make the soil particles adhere to the inner surface of the quartz microvial, thereby preventing soil particles from being blown into the injector. Extraction (partitioning) of the analyte from the soil into the acetone phase undoubtedly contributed to more efficient thermal desorption. Thus, preparing the soil as an acetone slurry and plugging the microvial with quartz wool were effective in improving the overall precision of the thermal desorption GC method for soil samples, an approach that has also been applied recently to the determination of volatile organic matter in diesel exhaust (Diaby et al. 2009).

The optimized method conditions were successfully used to generate calibration models for triphenylarsine-fortified solid samples. For soil, the calibration model (y (µV/s) = 93.01 ± 0.80x (ng triphenylarsine) −87.81 ± 9.20) was linear ($R^2 = 0.999$, $SEE_y = 10.70$) between

Table 3. Recovery values of triphenylarsine from fortified sediment and soil samples. The percent recovery was calculated as (measured/fortified) × 100. The relative standard deviation was calculated for $n = 3$.

Sample type	[Triphenyl arsine] (ng mg^{-1})	Percent recovery	Percent relative standard deviation
Sediment (Green Bay)	5	*not detected*	–
	25	*not detected*	–
	100	75.05	3.04
Soil (UWM campus)	5	86.64	25.6
	25	84.34	11.0
	100	87.65	1.47

0 and 20 ng triphenylarsine. The limit of detection (3σ) for triphenylarsine was 3.14 ng and the average relative standard deviation value was 7.10%. Triphenylarsine was thus more easily desorbed from the solid phase (soil) into the liquid phase (acetone) when the sample was mixed with 10 µL acetone.

The method was applied to determine triphenylarsine in two authentic samples, namely, a surficial sediment sample that was collected from Green Bay (~15 km southeast of Marinette, WI) and a surficial soil sample collected from the university campus (Table 3). To better simulate natural conditions, a set of each sample type ($n = 4$) was fortified with triphenylarsine at four levels (0, 5, 25, and 100 ng triphenylarsine/mg dry sample) and then "aged" for at least 15 days at room temperature in the dark. Triphenylarsine recoveries in soil were based on linear regression models and ranged between 84.34 ± 2.31 and $87.65 \pm 1.29\%$ ($n = 4$). For sediments, adequate recovery ($75.05 \pm 2.28\%$, $n = 4$) for triphenylarsine was observed from the samples that had been fortified at the highest level (100 ng triphenylarsine/mg). However, triphenylarsine was not recovered from samples fortified at lower levels (results not shown). Because surficial sediments contain a high degree of natural organic matter, we conjecture that the recovery of triphenylarsine at the lower levels was made more difficult by the strong retention of triphenylarsine by natural organic matter. Because a standard reference material was unavailable for triphenylarsine, these results were confirmed by inductively coupled plasma-mass spectrometry in which agreement within 10% was observed (results not shown).

Conclusion

In summary, we have shown that by improving the thermal desorption efficiency, the GC method can be successfully applied to the determination of organoarsenic species in environmental solids. The method may be well suited to screening large numbers of soil samples at former military sites that are undergoing remediation. For example, at a former WWII "Clark" factory, the levels of organoarsines have been found to vary from the mg/L range to the low g/L level (N. Stoll, University of Rostock, Germany, personal communication). Aromatic arsines are also of interest in modern agriculture, given that several aromatic arsenicals, most notably roxarsone (4-hydroxy-3-nitrobenzenearsonic), nitarsone (4-amino-3-nitrobenzenearsonic), and *p*-arsanilic acid, are used as feed additives. Proposed mechanisms for their degradation indicate that a variety of intermediate forms, including aromatic arsines, are potentially produced (Garbarino et al. 2003; Rutherford et al. 2003; Conklin et al. 2012). Our current work is focusing on the extension of the thermal desorption probe GC method to the characterization of natural organic matter-complexed arsenic compounds in soil.

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