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EVALUATION OF HAPSITE-ER PERIPHERALS– SPME VS. HEADSPACE

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14. ABSTRACT

The United States Air Force is examining recapitalization of two peripherals employed with the HAPSITE ER. The Air Combat Command/Surgeon General (ACC/SG) has inquired if Solid Phase Micro Extraction (SPME) analysis is comparable to the results obtained by the headspace sampler (HSS). This study examined the relative performance of the two peripherals and provided data on relevant operational parameters, such as limits of detection, linear range and quantification reliability. Results indicate that HSS is more effective for field use than SPME. Many analytes, specifically semi-volatile organic analytes (SVOAs), could not be detected by SPME sampling at any of the tested concentrations. Additionally, SPME testing was inconsistent even under identical sampling conditions. Also, the SPME sampling system uses fibers that are more fragile in comparison to the HSS. These fibers have a finite lifetime that would require regular replacement. Further, SPME required a much higher skill level than HSS. Overall, results suggest that HSS provides several advantages over SPME for field use.

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1.0 ABSTRACT

The Air Force (AF) is examining recapitalization of two peripherals employed with the HAPSITE ER. The Air Combat Command/Surgeon General (ACC/SG) has inquired if Solid Phase Micro Extraction (SPME) analysis is comparable to the results obtained by use of the Headspace Sampling System (HSS). This study examined the relative performance of the two peripherals and provided data on relevant operational parameters. The data will be used to evaluate future purchases and for planning purposes.

2.0 INTRODUCTION

The HSS of the HAPSITE ER samples the gaseous components in a closed space above liquids, vapor emitting solids, or a gaseous sample. Samples are placed into the oven of the HSS unit and are heated. The headspace of the vial is then flushed with carrier gas and transferred to the HAPSITE ER for analysis. The SPME peripheral contains a unit that attaches to the HAPSITE ER, as well as to a fiber and fiber holder. The fiber is a coated fused silica material that extracts and collects analytes from a sample (the material can be specialized for certain compounds). The fiber is exposed to either the headspace above a gas or liquid (SPME Headspace) or submerged into an aqueous sample (SPME Direct Immersion). The fiber is then inserted into the SPME unit where the analytes are thermally desorbed and transferred to the HAPSITE ER via carrier gas for analysis. Both accessories are portable, with the HSS weighing 42 pounds (lbs) including the battery and SPME weighing 4 lbs according to the manufacturer.

This research evaluated the two different HAPSITE ER peripherals by comparing their ability to detect Volatile Organic Analyte (VOAs) and Semi-Volatile Organic Analytes (SVOAs). Inficon methods loaded onto the HAPSITE ER and specifically suited for the analysis of these compounds were used. When possible, the same prepared standards were used on both HSS and SPME analysis. The data will be presented to the ACC/SG for their evaluation.

2.1 Study I— Analysis of Volatiles and Semivolatiles by HSS

Commercially available CWA simulants (diethyl malonate (DEM), methyl salicylate, diisopropylfluorophosphate (DIFP) and dimethyl methylphosphate (DMMP)) and an EPA Method 8260 Volatile Organics Mix were used to prepare standards for analysis. The resulting preparations were analyzed by a HAPSITE ER unit equipped with the HSS. The data was used to create a calibration curve, calculate the coefficient of determination (R^2), and in some cases percent recovery. These results were used to assess the analysis capability of the HAPSITE ER when HSS is used. Several parameters were investigated to determine their possible effect on analysis performance. These parameters included: transfer line temperature, concentrator type, sampling temperature, sampling with water, and sampling with salting.

2.2 Study II— Analysis of Volatiles and Semivolatiles by SPME

The same analytes used with HSS were used to prepare mixtures for analysis by HAPSITE ER with the SPME peripheral. Calibration curves were created from the data and the R^2 and percent recovery was calculated. The resulting data was used to both assess analysis using

SPME as well as compare SPME with HSS. The parameters explored with SPME included: sample stirring, sampling time, sampling temperature, sampling with water, and sampling with salting.

3.0 EQUIPMENT AND SUPPLIES

A HAPSITE ER GC-MS (S/N 70077084) was purchased from Inficon (Syracuse, NY) containing a DB-5 (100%) Polydimethylsiloxane column (15meter X 0.25millimeter X 0.19micrometer film thickness). A Tenax desorber tube (934-448-P1) was used and this system had the CWA Quantitative Methods (930-0395-G1) installed by the manufacturer. *Note: There are several different transfer lines used to fit the various models of the HAPSITEs. It is important not to use transfer lines from the HAPSITE Plus. The correct transfer line part is listed below.*

- The following peripheral and supplies were purchased from Inficon (Syracuse, NY) for the headspace analysis of this experiment: HAPSITE ER Headspace Sampling System (part# 931-205-G2), ER Headspace/SituProbe Transfer Line (931-210-G1), and a Headspace Sample Needle (931-402-P1).

- The following peripherals and supplies were purchased from Inficon (Syracuse, NY) for the SPME analysis of this experiment: SPME Sampling System (part# 934-290-G1), SPME Sampling Kit (934-707-G2), Red Fiber Kit (934-707-G3), and the Blue Fiber Kit (934-707-G4).

- NITROGEN UHP 304CF 99.999% CGA580 (part# SG1959112-300) gas was obtained from Indiana Oxygen Company (Dayton, OH) with a minimum purity of 99.999% when used in a laboratory setting.

- An 8260 Volatile Organics Kit (2,000 µg/mL) was ordered from Restek (110 Benner Circle, Bellefonte, PA 16823), part# 30076. This consists of Mixture#1, part#30042, Lot#A0156895; Mixture#2, part#30043, Lot#A0150030; Mixture#3, part#30044, Lot#A0149684; Mixture#4, part#30045, Lot#A0149456; Mixture#5, part#30046, Lot#A0149447; Mixture#6, part#30047, Lot#A0159491; and Internal Standards Mix, part#30074, Lot#A0159786. See Appendix for a full listing of analytes.

- Headspace Screw-Thread Vials, 18 mm, part# 23086 and Magnetic Screw-Thread Caps, 18 mm, part# 23090 were purchased from Restek (110 Benner Circle, Bellefonte, PA 16823).

- The following were ordered from Fisher Chemical (300 Industry Drive, Pittsburgh, PA 15275) Methanol, Part#A456-4, Lot#193067; Restek™ Hamilton Autosampler Syringes for Thermo Finnigan/CTC/LEAP GCs (10µL), Part#06-712-585; Hamilton™ 1700 Series Gastight™ Syringes: RN Termination (25µL), Part# 14-815-37; Hamilton™ 1700 Series Gastight™ Syringes: RN Termination (50µL), Part# 14-815-61; Water, HPLC Grade, Spectrum™, Part# 18-614-668; big universal nitrogen trap, 1/4", Part# NC1714336; Restek™ Super-Clean™ Gas Filters, Part# 06-711-824;

Thermo Scientific™ Cimarec+™ Stirring Hotplates Series, Part# SP88857100; & Bel-Art™ SP Scienceware™ Flea Micro Spinbar™ Magnetic Stirring Bars, Part# 22-261681.

- Inficon Sample Vials, 40 mL, Part# 070-1204 were purchased from Thomas Scientific (1654 High Hill Road, Swedesboro, NJ 08085).

- The following were ordered from Inficon (2 Technology Place, East Syracuse, NY 13057): Sample Needle, Headspace, Part# 931-402-P1; Canister, Carrier Gas, 24 each, Part# 930-432-P24; Canister, Internal Standard Gas, 12 each, Part# 930-433-P12; and Extended Life Carrier Gas (110 liter), Part# 930-4611-P1; Tenax Kit, Part# 930-251-G1; & SPME Sampling System Blue Fiber Kit, Part# 934-707-G4.

4.0 METHODS

4.1 Instrumental Conditions

4.1.1 Headspace (HSS)

The HAPSITE ER was set up in a laboratory environment that differs from field conditions: 1) The laboratory uses 300 L NITROGEN UHP 304CF 99.999% with a CGA580 regulator was used for continuous operation; whereas, field conditions would have either the 5L nitrogen tank that fits directly into the HAPSITE ER and another into the HSS for the sample purge or the Extended Life Carrier Gas (110 liter). For both field and laboratory setups, the internal standard canister will have to be used in the HAPSITE ER. 2) In the laboratory, line power is used, whereas in the field, batteries are used. Again, one battery is needed for the HAPSITE ER and one for the HSS.

Table 1. HSS Instrumental Conditions

Parameter	Conditions
Operating Conditions	10–45°C, up to 95% Relative Humidity (non condensing)
Weight (including battery)	12 kg
Power Consumption	30 W @ 24 V
Oven Temperature Range	Ambient to 80°C
Equilibrium Stabilization Time	20 minutes
Practical Quantitation Limit (toluene)	5 µg/L
Physical Orientation for Operation	Gray base side down, ≤15° tilt

Instrumental conditions for the analysis of VOA analytes:

- HAPSITE ER temperatures: column @ 40°C, membrane @ 80°C, valve oven @ 70°C, heated lines @ 70°C. Tenax concentrator used.
- Headspace temperatures: oven @ 40°C, transfer line @ 60°C
- GC temperatures: start @ 40°C, hold for 04:00 minutes; 3°C/minute up to 120°C with no hold; 12°C/minute up to 180°C, no hold, then 26°C/minute up to 200°C, hold for 00:30 minutes. Run time was 36 minutes, 56 seconds.
- MS temperatures and conditions: 15 second filament delay, full scan, start scan at 41 mass-to-charge ratio (*m/z*) and end at 300 *m/z*
- Sample Incubation Time in the HSS: 20 minutes (timed)

Instrumental conditions for the analysis of SVOA analytes:

- HAPSITE ER temperatures: column @ 60°C, membrane @ 120°C, valve oven @ 120°C, heated lines @ 120°C. Tenax concentrator used.
- Headspace temperatures: oven @ 40°C, transfer line @ 80°C
- GC temperatures: start @ 60°C, hold for 01:15 minutes; 8°C/minute up to 90°C with no hold; 25°C/minute up to 200°C, hold for 06:06 minutes, then 1.5°C/minute at 200°C, no hold. Run time was 15 minutes, 30 seconds.
- MS temperatures and conditions: 15 second filament delay, full scan, start scan at 45 m/z and end at 300 m/z
- Sample Incubation Time in the HSS: 20 minutes (timed)

4.1.2 SPME

There are two ways to sample using SPME: 1) headspace where the gases above a liquid is sampled and 2) direct immersion when the fiber is submerged into the aqueous phase during sampling.

Table 2. SPME Instrumental Conditions

Parameter	Conditions
SPME desorption temperature	100–300°C
Methods	Full GC/MS, SPME survey (MS-only), fiber conditioning
Environmental operating conditions	5–45°C, 0–95% RH, non-condensing
Instrument compatibility	HAPSITE ER only
Analytical interface	HAPSITE ER universal interface
Dimensions	4 x 5.5 x 0.75 in.
Weight	1.8 kg (4 lb.)
Power supply	Receives power from HAPSITE ER
Battery power requirement	Receives power from HAPSITE ER
Battery life (HAPSITE ER + SPME)	1–1.5 hrs
Carrier gas	High purity nitrogen, supplied by HAPSITE ER
SPME fiber	23 gauge, various coating options, approx. 50 injections per fiber
SPME liner	Deactivated stainless steel with intrinsic 2µ particle filter, removable/replaceable
SPME fiber seal life (typical)	200 injections
Water sampling detection limits	Trichloroethylene (TCE) low ppb
Air sampling detection limits	Trichloroethylene (TCE) low ppb

Instrumental conditions for the analysis of VOA analytes:

- HAPSITE ER temperatures: column @ 40°C, membrane @ 80°C, valve oven @ 70°C, heated lines @ 70°C. Tri-bed/Carbon concentrator used.
- SPME temperatures: 40°C, desorption @ 250°C for 1 minute
- GC temperatures: start @ 40°C, hold for 04:00 minutes; 3°C/minute up to 120°C with no hold; 12°C/minute up to 180°C, no hold, then 26°C/minute up to 200°C. Run time was 36 minutes, 26 seconds.
- MS temperatures and conditions: 15 second filament delay, full scan, start scan at 41 *m/z* and end at 300 *m/z*
- SPME sampling time: 7.5 minutes
- SPME fiber: Red
- SPME Sampling Conditions: Headspace, room temperature

Instrumental conditions for the analysis of SVOA analytes:

- HAPSITE ER temperatures: column @ 60°C, membrane @ 120°C, valve oven @ 120°C, heated lines @ 120°C. Tri-bed/Carbon concentrator used.
- SPME temperatures: 40°C, desorption @ 250°C for 1 min

- GC temperatures: start @ 60°C, hold for 01:15 minutes; 8°C/minute up to 90°C with no hold; 25°C/minute up to 200°C, hold for 06:06 minutes, then 1.5°C/minute at 200°C, no hold. Run time was 15 minutes, 30 seconds.
- MS temperatures and conditions: 15 second filament delay, full scan, start scan at 45 *m/z* and end at 300 *m/z*
- SPME sampling time: 30 minutes
- SPME fiber: Blue
- SPME sampling conditions: Direct immersion, 40°C with stirring at 300 RPM
- *Note: SVOA analysis required the use of a separate stirring hot plate which would not be available in the field*

4.2 Standard Preparation

4.2.1 Volatiles

4.2.1.1 8260 Volatile Organics Mixture Standards Preparation

The 8260 Volatile Organics Kit has six calibration mixtures each with a concentration of 2,000 µg/mL. An initial working solution (WS) was prepared by taking a 500 microliters (µL) aliquot from each mixture and adding it to a 5 mL volumetric flask and diluting with methanol. This produced a WS with a concentration of 200 ng/µL. From this mixture, a 1,250 µL aliquot was taken and added to a 25 mL volumetric flask and diluted with methanol. This produced a secondary WS with a concentration of 10 ng/µL. Various aliquot volumes of this final working solution were used to produce the required concentrations used for analysis. All vials and working standards were tightly capped, stored at 4°C, and used or discarded after 60 days.

4.2.1.2 NaCl Solution Preparation

A sodium chloride salt (NaCl) solution was prepared to investigate if its presence in the sample vials can improve detection. Based on a literature search[3], 5 g of NaCl was initially added (25% wt/wt) but yielded no observable results. The concentration was then increased to 40% wt/wt, which did not result in complete dissolving of the salt. Finally, a 30% wt/wt solution was prepared by dissolving 149.98 g NaCl into a 500 mL volumetric, sonicated for 15 minutes and then diluted to volume with water. This solution was used for Study I and Study II.

4.2.2 SVOA (CWA Simulants) Preparation

DEM, DEM with a single substituted ^{13}C, DEM with a double substituted ^{13}C, and DEM with a triple substituted ^{13}C were analyzed for this experiment. DEM was employed both as an analyte of interest, but also as a diagnostic tool for troubleshooting. By preparing a single mixture containing DEM_{116} at 25 ng, DEM_{117} at 50 ng, and DEM_{118} at 75 ng, a calibration curve could be set up and the coefficient of determination computed. Using a spike of native DEM_{115}, allowed recovery to be calculated. These techniques have been previously used successfully using thermal desorption tubes and the thermal desorber unit (TDSS) on the HAPSITE ER.[4]

The CWA simulants DIFP and DMMP were also chosen for analysis. A stock solution was prepared by weighing a 10 mg standard, dissolving it in a 1 mL volumetric flask, and diluting to volume with methanol. This produced a standard mixture with a concentration of ~10,000 ng/µL. Five µL of this solution was added to a 5 mL volumetric and diluted to volume with methanol to produce a solution of concentration 10 ng/µL. Various aliquot volumes of this standard was used to produce the needed analytical solution

Additionally, Methyl Salicylate and Methyl Salicylate-d_4 were used as SVOA analytes. These analytes are also useful for diagnostic measures and can be used for spike and recovery to measure the efficiency of the route of sample introduction, much like DEM and its isotopes.

Table 3. DIFP and DMMP Standard Preparation

Analyte	Sigma-Aldrich#	Lot#	Mass (mg)	Volume (µL)	Final Concentration (ng/ µL)	Aliquot (µL) from Working Solution	Volume (µL)	Final Concentration (ng/ µL) in MeOH
DIFP	D0879-1G	MKCK1402	9.8	1,000	9,800	5.1	5,000	10.0
DMMP	D169102-5G	MKCC4295	9.3	1,000	9,300	5.4	5,000	10.0

Table 4. DEM_{115}, DEM_{116}, DEM_{117}, and DEM_{118} Standard Preparation

Preparation of DEM and the three ^{13}C substitutions associated with DEM.

Analyte	Sigma-Aldrich Part #	Sigma-Aldrich Lot #
DEM_{115}	04151-1 mL	BCBW8703
DEM_{116}	281859-1 G	BGBC2417V
DEM_{117}	488798-250 mg	MBBC2236
DEM_{118}	488771-250 mg	MBBB6433V

Table 5. Experimental DEM Concentrations

Analyte	mg	µL	Concentration (ng/µL)	Aliquot (µL)	Total Volume (µL)	Final Concentration (ng/µL) in One Solution of MeOH
DEM_{115}	10.6	1,000	10,600	4.7	5,000	9.96
DEM_{116}	9.6	1,000	9,600	13	5,000	25.0
DEM_{117}	20.5	1,000	20,500	12.2	5,000	50.0
DEM_{118}	30	1,000	30,000	12.5	5,000	75.0

Table 6. Methyl Salicylate and Methyl Salicyclate-d4 Standard Mixture Preparation

Native DEM solution preparation (to be used at various spiking levels)

Analyte	Sigma-Aldrich#	Lot#	Mass (mg)	Volume (µL)	Final Concentration (ng/ µL)	Aliquot (µL)	Volume (µL)	Final Concentration in MeOH (ng/ µL)
Methyl Salicylate	76631-1 mL	BCBP6877V	9.3	1,000	9,300	5.4	5,000	10.0
Methyl Salicylate-d_4	CDN Isotopes	W-575	10.1	1,000	10,100	100	5,000	202

5.0 RESULTS

Analysis using HSS proved more effective than analysis using SPME. This is evident when examining the minimum detection requirements for the analytes of interest (Table 5.1). Many analytes, specifically SVOAs, could not be detected by SPME sampling at any of the tested concentrations while HSS sampling was able to detect these compounds. The only SVOA compound that was detected by SPME was DEM. In addition to inferior analysis capability, the SPME sampling system uses fibers that are more fragile in comparison to the HSS. Care must be taken when exposing and retracting the fiber as it is easy to break or be stripped. Additionally, these fibers have a finite lifetime that would require regular replenishment. *Note: Detection requirements for DEM are not field applicable (Table 7). Heating and continuously stirring the sample would require additional fielded equipment. Furthermore, SPME requires intricate handling and training that may not be practical under field conditions.*

Table 7. Lowest detected analyte level by sampling technique for VOAs, diethyl malonate (DEM), methyl salicylate (MeS), diisopropyl fluorophosphate (DIFP), and dimethyl methylphosphonate (DMMP).

Lowest Detected Analyte Level by Sampling Technique				
Analyte	HSS	SPME		
		SPME Headspace without water	SPME Headspace with water	SPME Direct Immersion
VOAs	10 ng	10 ng	10 ng	10 ng
DEM	10 ng	ND	ND	60 ng[a]
MeS	10 ng	ND	ND	ND
DIFP	10 ng[b]	ND	ND	ND
DMMP	50 ng[b]	ND	ND	ND

[a] Successful detection required sample heating and stirring during sampling

[b] Successful detection required increasing the transfer line temperature of the method from 60ºC to 80ºC

ND = Not Detected

While the minimum detection requirements were illustrated in Table 7, additional parameters are described in the following sections to determine how they impact analysis performance when either HSS or SPME sampling are used. Some of these parameters were HSS specific (transfer line temperature, concentrator type), some SPME specific (stirring, sampling time), and others were applicable to both techniques (sampling temperature, sampling with water, and sampling with salting).

5.1 Headspace Sampler (HSS)

The six VOA mixtures described in Section 4.2.1.1 were used initially for HSS testing with water. Once the GC conditions, MS conditions, transfer line temperature and HSS oven temperature were optimized; these standards were analyzed at five different (10, 25, 50, 75, & 100ng/20 mL H_2O) calibration levels. All of these mixtures are listed in the Appendix A. From this data, the mass fragment used for quantitation (Q_{ion}) from the National Institute of Standards and Technology (NIST) library spectra were extracted and the area counts were plotted in Microsoft® Excel® and the coefficient of determination was computed. Success criteria was established when the R^2 was greater than 0.99. From Table 1 in the Appendix A, 35 analytes were observed and of these, 17 analytes met the success criteria of $R^2 \geq 0.99$[7]. Seventeen of the remaining eighteen analytes did not meet success criteria. *Note: Earlier work with the HAPSITE Plus*[5] *demonstrated success with compounds with BPs<23.7 °C, however, in the development of the HAPSITE ER emphasis was on semivolatile compounds consistent with CWA and the column was shortened from 30M to 15M and it is impractical to lower the initial column temperature of 40 °C to improve column performance.*

The various concentrations were spiked in water to simulate samples collected in the field. It is interesting to note that the highest standard (100 ng) yielded inconsistent results with respect to the linearity of the curve. When this point was removed the linearity met criteria. On a subsequent test run it was determined the 75 ng standard was inconsistent. It should be pointed out that USEPA criteria for successful linearity is an R^2 value ≥ 0.99[5] which was met when the high points were removed. The chromatographic separation is illustrated in Figure 1. Finally, Table 8 illustrates general success with Mixture #4.

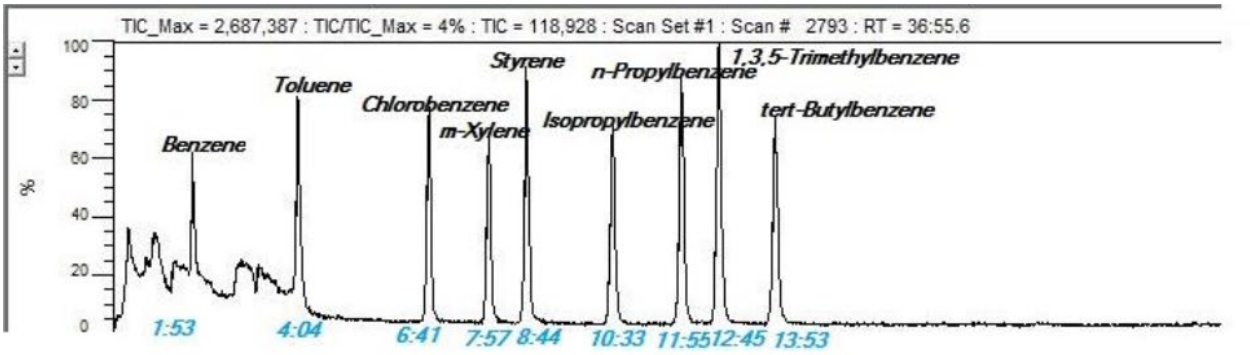

Figure 1. VOA Mixture#4 100 ng Chromatogram Showing Separation and Retention Times for HSS in 20 mL H2O

Table 8. Repeat of VOA Mixture#4 in water with R2 computed with and without 75 & 100 ng data points

	R^2 (all data)	R^2 (75 ng excluded)	R^2 (100 ng excluded)
Benzene	0.9729	0.9950	0.9956
Toluene	0.9727	0.9933	0.9938
Chlorobenzene	0.9647	0.9895	0.9986
m-Xylene	0.9538	0.9907	0.9931
Styrene	0.9763	0.9972	0.9948
Isopropylbenzene	0.9422	0.9960	0.9857
n-Propylbenzene	0.9503	0.9746	0.9990
1,3,5-Trimethylbenzene	0.9579	0.9968	0.9888
tert-Butylbenzene	0.9450	0.9915	0.9899

HSS was completed using a tri-bed concentrator as well as a Tenax concentrator to explore the water management capabilities of each type. Various concentrations of VOA mixture #4 were spiked in water and sampled using HSS. The standards were analyzed using both a tri-bed concentrator and a Tenax concentrator (Table 9). Generally, a concentrator packed with Tenax demonstrated better overall performance.

Table 9. Headspace sampling of VOA mixture #4 standards with water. Both the HSS oven and the transfer line were set at 40 ºC.

Linearity of VOA mixture #4 Standards with H_2O		
Concentrator	Tri-bed	Tenax
	R^2	R^2
Benzene	0.5677	0.9658
Toluene	0.9901	0.9478
Chlorobenzene	0.9703	0.9301
m-Xylene	0.9728	0.9531
Styrene	0.9739	0.9531
Isopropylbenzene	0.7136	0.9412
n-Propylbenzene	0.9587	0.9577
1,3,5-Trimethylbenzene	0.9796	0.9546
tert-Butylbenzene	0.9805	0.9538

For the semi-volatile work, DEM and well-described CWA simulants were used. Successful recovery was observed for samples prepared without water using HSS. The results of the DEM are presented in Figure 2 and the results of the methyl salicylate are presented in Figure 3.

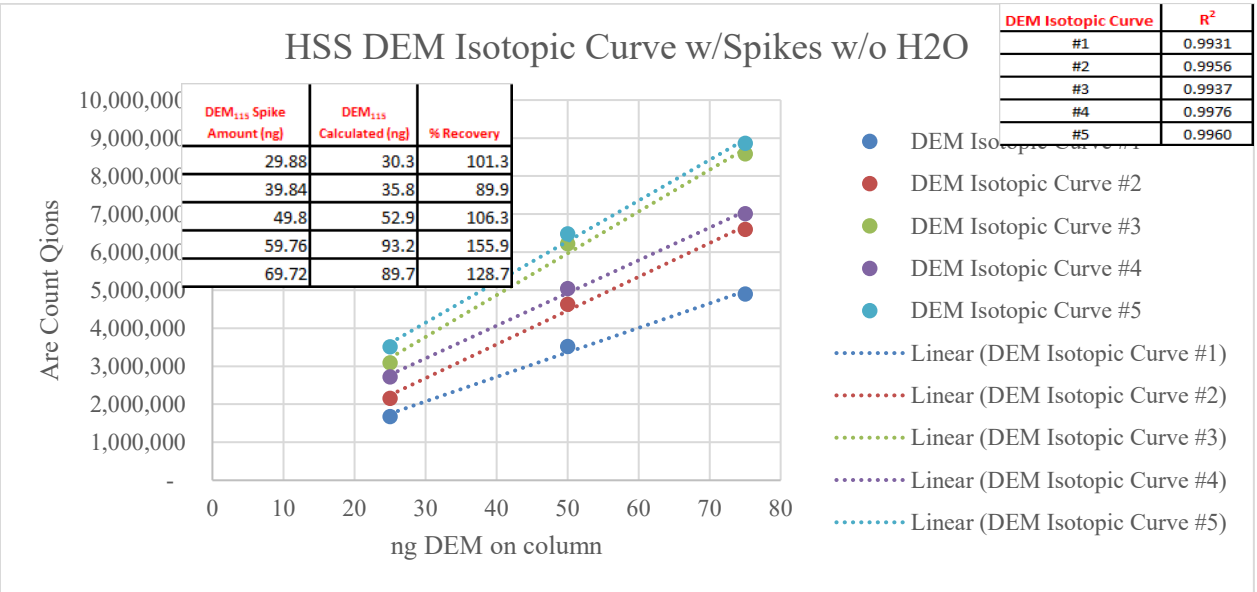

Figure 2. Diethyl Malonate Isotopic Curve with Native Diethyl Malonate Spike at Various Spiking. Analysis was completed using a Tenax concentrator

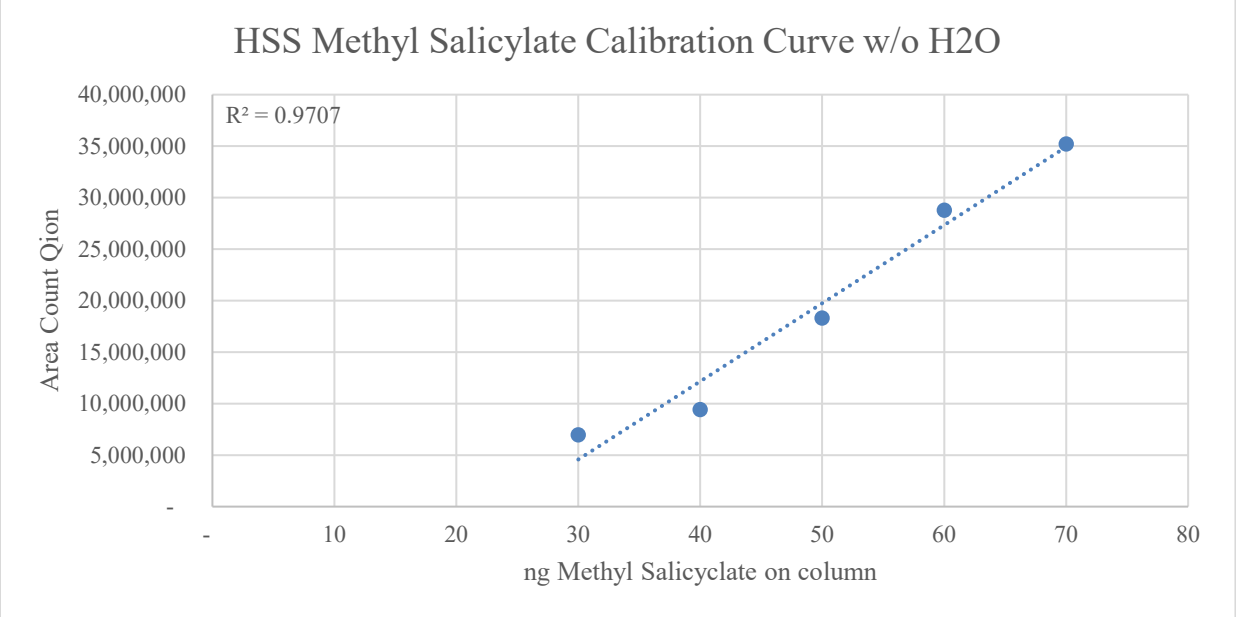

Figure 3. Methyl Salicylate Curve with Coefficient of Determination. Analysis was completed using a Tenax concentrator

SVOA standards without water were analyzed using HSS sampling with both tri-bed and Tenax concentrators (Tables 10, 11). The percent recoveries for DEM_{115} when the Tenax

concentrator was used were better than the tri-bed. Again, it should be noted that better overall performance was achieved with the Tenax concentrator.

Table 10. Headspace sampling of DEM standards without water. The HSS oven was set at 40 ºC, the transfer line was set at 60ºC, and a tri-bed concentrator was used.

DEM Standards without H_2O - Tri-bed		
DEM_{115} spike	Calculated (ng)	Recovery (%)
38.2	50.4	132.0
50.5	25.1	49.8
68.4	(0.2)	(0.3)

Table 11. Headspace sampling of DEM standards without water. The HSS oven was set at 40ºC, the transfer line was set at 60ºC, and a Tenax concentrator was used.

DEM Standards without H_2O - Tenax		
DEM_{115} spike	Calculated (ng)	Recovery (%)
29.88	30.3	101.3
39.84	35.8	89.9
49.8	52.9	106.3
59.76	93.2	155.9
69.72	89.7	128.7

The impact of the transfer line temperature on SVOA analysis using HSS was explored using DEM standards without water (Table 12). The increase in transfer line temperature had a unusual effect on the percent recovery.

Table 12. Headspace sampling of DEM standards without water. The HSS oven was set at 40ºC, the transfer line was set at 80ºC, and a Tenax concentrator was used.

DEM Standards without H_2O				
	Transfer line Temp: 60ºC		Transfer line Temp: 80ºC	
DEM_{115} spike	Calculated (ng)	Recovery (%)	Calculated (ng)	Recovery (%)
29.88	30.3	101.3	63.3	212.0
39.84	35.8	89.9	96.1	241.3
49.8	52.9	106.3	118.7	238.4
59.76	93.2	155.9	59.1	99.0
69.72	89.7	128.7	87.8	126.0

When the sampling temperature (i.e., temperature of the HSS oven) was increased during sampling of DEM standards without water, percent recovery was higher than expected. Table 13 reports the percent recovery for DEM_{115} at two different HSS oven temperatures. The elevated recoveries may be a result of moisture suppression of the isotopic curve.

Table 13. Headspace sampling of DEM standards without water. Transfer line was set at 80°C and a Tenax concentrator was used. HSS oven was set at 40°C or 60°C.

DEM standards without water		
HSS Oven Temperature	40ºC	60ºC
Recovery (%)	83.8	181.7

SVOA testing with DEM standards without water showed improved performance with the Tenax concentrator rather than the tri-bed. Increasing the transfer line temperature does not aid SVOA analysis nor does increasing the sampling temperature of the HSS.

SVOA testing with water was also performed to assess the same parameters but in an environment that reflects field testing. The concentrator types were again assessed for water management. The percent recovery for various spikes were calculated (Tables 14, 15). The tri-bed concentrator resulted in better percent recovery values. This is the opposite of what was observed with DEM standards without water. The data from this experiment yielded data that was contrary to other data and was not used in our overall determinations.

Table 14. Headspace sampling of DEM standards with water. The HSS oven was set at 40ºC, the transfer line was set at 60ºC, and a tri-bed concentrator was used.

DEM standards with H_2O - Tri-bed		
DEM_{115} spike	Calculated (ng)	Recovery (%)
25.2	20.75	82.35
37.9	34.58	91.23
50.5	57.36	113.59

Table 15. Headspace sampling of DEM standards with water. The HSS oven was set at 40ºC, the transfer line was set at 60ºC, and a Tenax concentrator was used.

DEM standards with H_2O - Tenax		
DEM_{115} spike	Calculated (ng)	Recovery (%)
10	39.3	392.5
20	(80.4)	(402.0)
30	(14.1)	(47.0)
40	36.0	90.1
50	91.55	183.1

Transfer line temperature effect was again tested with HSS but with standards that were prepared with water. Though the DEM spike amounts differ, Tables 15 and 16 have the same parameters except for the transfer line temperature. When the percent recoveries were compared, the effect was inconclusive. When water was not present an increase in transfer line temperature negatively affected analysis.

Table 16. Headspace sampling of DEM standards with water. The HSS oven was set at 40ºC, the transfer line was set at 80ºC, and a Tenax concentrator was used.

DEM standards with H_2O		
DEM_{115} spike	Calculated (ng)	Recovery (%)
29.88	(18.3)	(61.2)
39.84	25.1	63.0
49.8	62.8	126.1
59.76	(6.5)	(11.0)
69.72	(10.1)	(14.5)

The effect of the HSS oven temperature or sampling temperature was tested with DEM standards prepared with water (Table 17). Though the difference is arguably negligible, the lower sampling temperature had slightly better percent recovery than the high temperature. This is the same recovery observed when water was not present.

Table 17. Headspace sampling of DEM standards with water. Transfer line was set at 80ºC and a Tenax concentrator was used. HSS oven was set at 40ºC or 60ºC.

DEM standards with water		
HSS Oven Temperature	40 ºC	60 ºC
Recovery (%)	38	34.9

The technique of "salting out", or the addition of salt to the standards, was explored as a way to increase the extraction efficiency of the analytes. Salting out for the SVOAs analytes is a common technique that is used in a laboratory situation. Although initial experiments were inconclusive, when the same standards were compared with no water, water, and 30% NaCl water at two different HSS oven temperatures. The 30% NaCl water improved the quality of the data. *Note: This is not a current field supplied solution. This would need to be addressed if salting out is applied in the field.*

An experiment with the addition of salt/transfer line temperature increase produced noticeably better results than previous attempts as Figure 4 and 5 demonstrate below. The DEM isotopic curve was added into vials with the salt water at a constant amount. Along with this, each of the five vials was spiked with native DEM at levels across the calibration curve range and Methyl Salicylate was added to produce a calibration curve of its own at 30, 40, 50, 60, & 70 ng on column. For the DEM, the calibration curve was successful three out of five runs.

Percentage recoveries are respectable ranging from 90-117% from the curves that met success criteria and in the instance where the curve $R^2 < 0.9500$, the recovery was 169%. The Methyl Salicylate did not provide similar successful recoveries, but experimenting with the salt water and the increasing the transfer line temperature did demonstrate positive vector. The 80°C temperature parameter demonstrated favorable results, so this setting was retained for the remainder of the experiments.

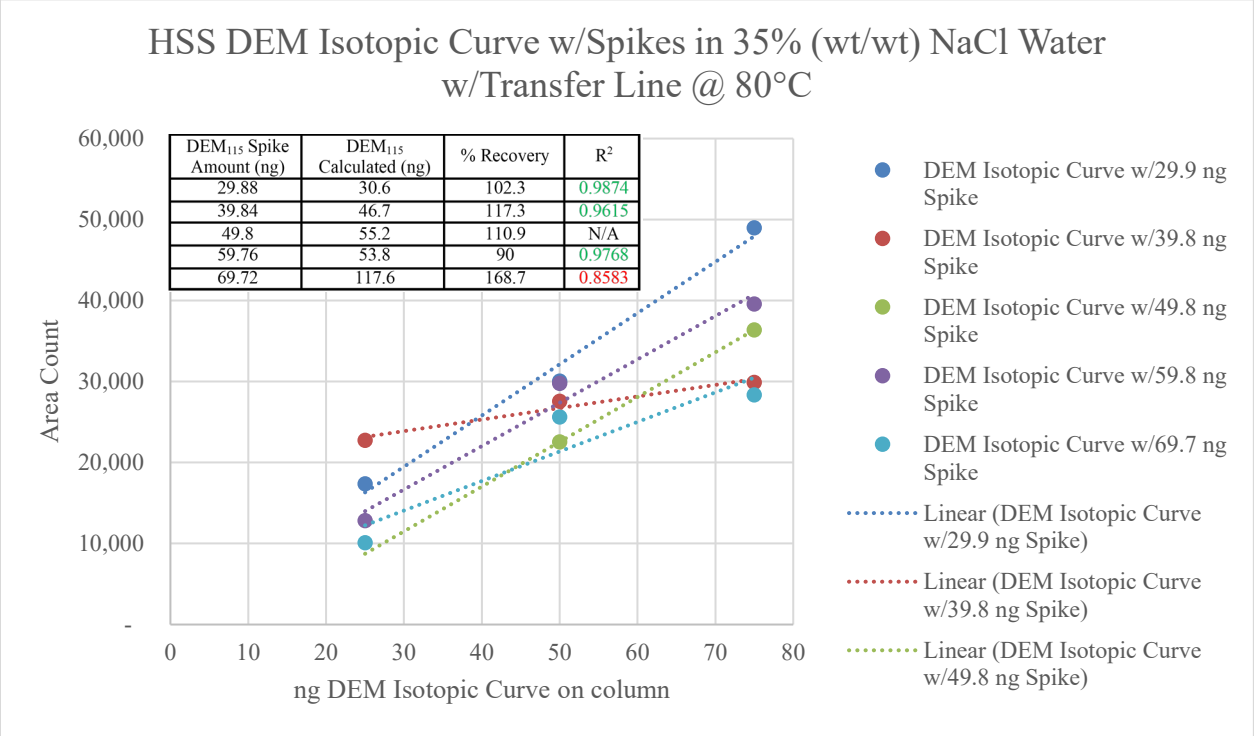

Figure 4. Diethyl Malonate Isotopic Curve with Native Diethyl Malonate Spike at Various Spiking Values Across the Calibration Range with Coefficient of Determination and Spike Recovery. Analysis was completed using a Tenax concentrator.

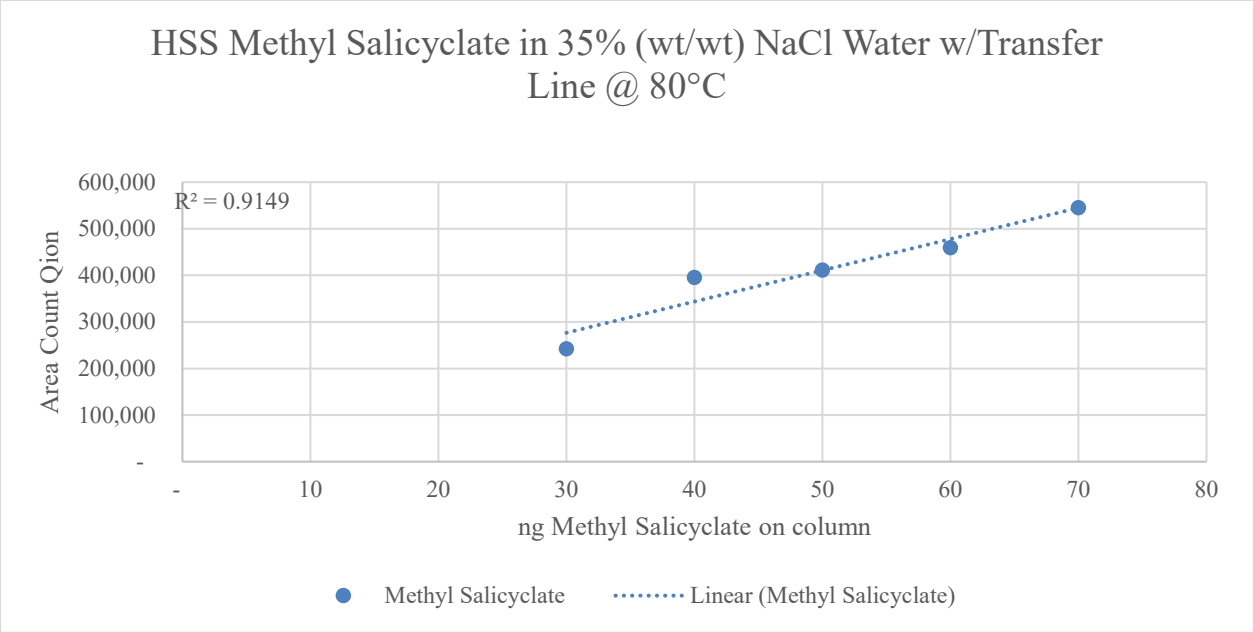

Figure 5. Methyl Salicylate Curve with Coefficient of Determination in 35% (wt/wt) NaCl H2O w/Transfer Line Increased from 60°C to 80°C. Analysis was completed using a Tenax concentrator.

Transfer line increase did not significantly improve the results when salting was employed. Table 18 reports the percent recovery of DEM standards that included a saturated salt solution. The 60°C temperature setting of the oven had better percent recovery than the 40°C oven temperature results. This is the reverse of what was observed when the standards were just in water, but as previously noted, this was a negligible difference.

Table 18. Headspace sampling of DEM standards with salting. Transfer line was set at 80°C and a Tenax concentrator was used. HSS oven was set at 40°C or 60°C.

DEM standards with salting - Tenax		
HSS Oven Temperature	40°C	60°C
Recovery (%)	247.6	214.2

5.2 Solid Phase Micro Extraction (SPME)

VOA mixture #4 was used to optimize the sampling time for SPME headspace analysis. Five standards were prepared with equal concentrations of mixture #4. Standards were sampled by SPME headspace without water at room temperature using the red fiber at varied time points: 30 min, 10 min, 5 min, 1 min, and 0.5 min. The area counts were plotted in Microsoft® Excel® (Figure 6). Area counts increased as the sampling time increased for all analytes until 5 min. After that time point the area count increased for 6 compounds at 10 min sampling and decreased

for 3 compounds at 10 min. After ten minutes, the area counts decreased for all compounds as sampling time increased. Also, 7.5 min was decided as the optimal sampling time for this study.

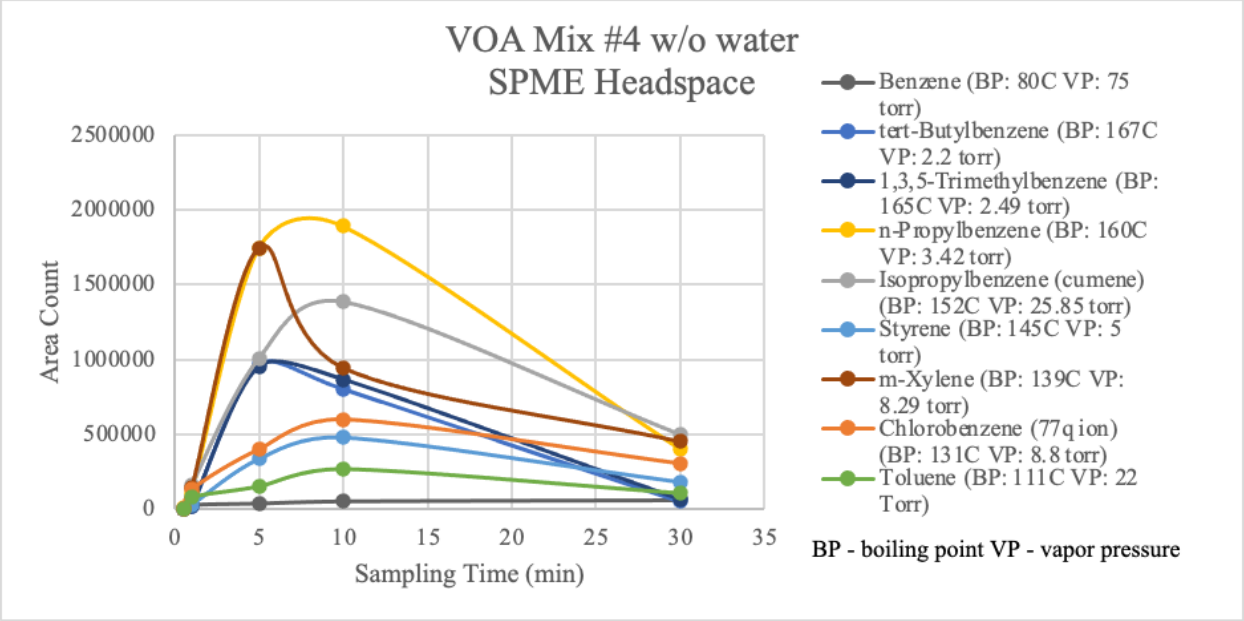

Figure 6. SPME headspace sampling of VOA mixture #4 standards without water at room temperature. The standards were sampled at varying time points using the red fiber. Analysis was completed using a tri-bed concentrator.

In addition, the sampling temperature was also optimized for VOA analysis with SPME headspace sampling without water. Two standards with equal concentration of VOA mixture #4 were prepared and sampled using the red fiber. One standard was sampled at room temperature and the other was sampled at 40ºC. The area counts decreased as the sampling temperature increased (Figure 7).

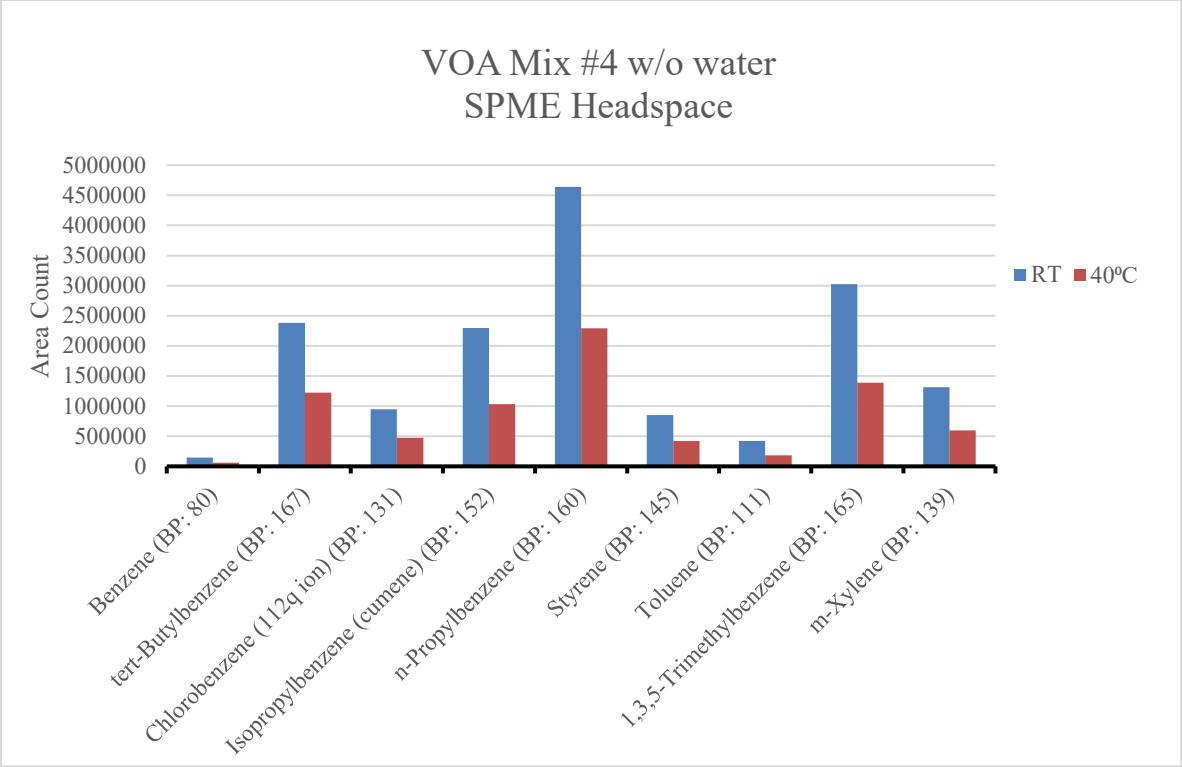

Figure 7. SPME headspace sampling of VOA mixture #4 standards without water for 5 min. The standards were sampled at different temperatures using the red fiber. Analysis was completed using a tri-bed concentrator.

Calibration curves were established for all components of the VOA mixtures (1 – 6) using SPME headspace sampling. The standards were prepared without water and sampled at room temperature for 7.5 min. The results were used to create calibration curves for each component. Only one out of the 35 detected compounds had acceptable linearity (≥0.99).

Additionally, VOA mixture #4 standards with water were analyzed using SPME headspace sampling. The red fiber was again used for sampling. The sampling time was set at 7.5 min and four sampling temperatures were tested: room temperature, 30ºC, 40ºC, 50ºC. Similar to what was observed in Figure 7 with VOA standards without water, the area counts decreased with an increase of sampling temperature (Figure 8). Furthermore, a selection of compounds exhibited an inexplicable drop in analysis performance when standards were prepared with water.

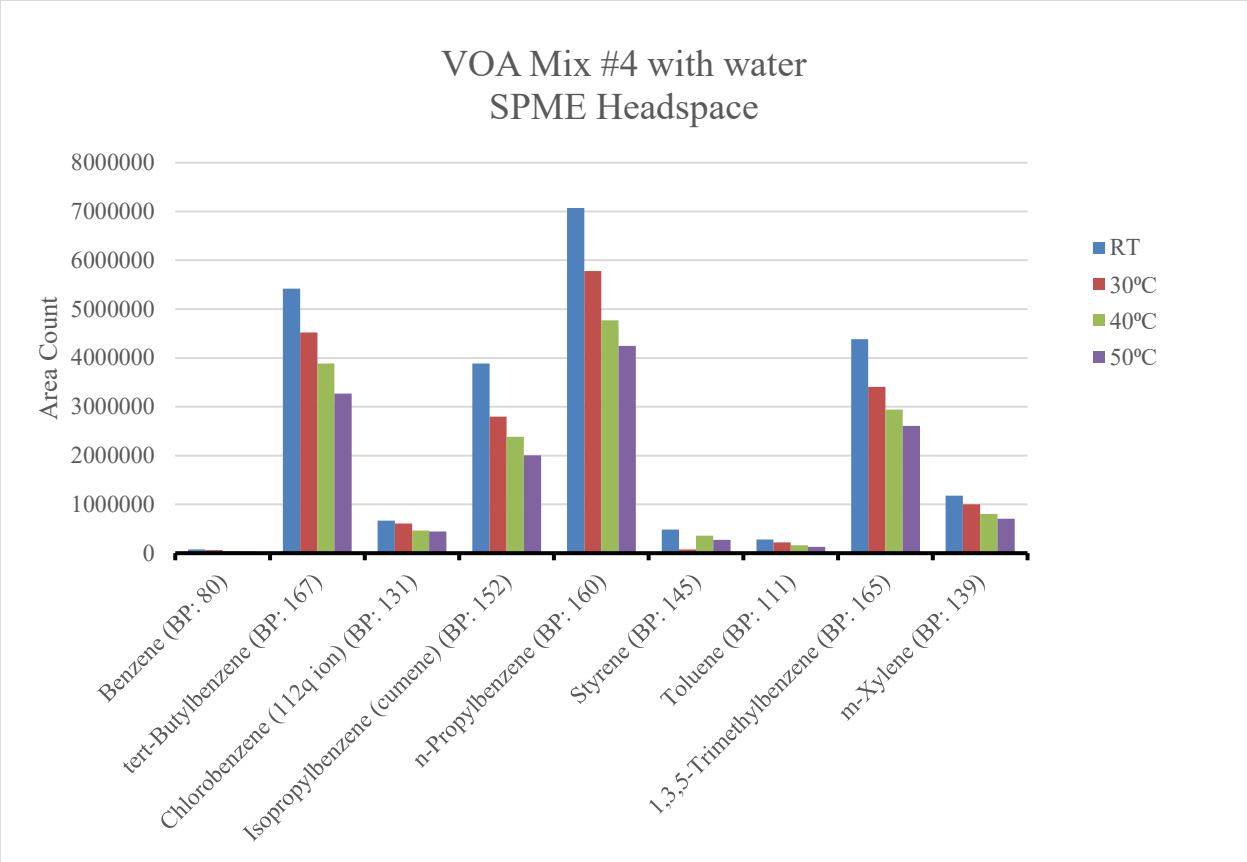

Figure 8. SPME headspace sampling of VOA mixture #4 standards with water for 7.5 min. The standards were sampled at different temperatures using the red fiber. Analysis was completed using a tri-bed concentrator.

In contrast to VOA analysis with SPME, semivolatile organic compounds were not able to be detected with either the red or blue fiber without water. Tested compounds included DMMP, DIFP, MeS, and DEM.

Even with the addition of water, SVOA compounds were again not able to be detected with by SPME headspace. On the other hand, when direct immersion was used instead of headspace, DEM was detected using the blue fiber (Table 19). The sampling temperature had to be increased to 40ºC and stirring was required. DMMP, DIFP, and MeS remained undetected at these sampling conditions.

Table 19. SPME direct immersion sampling of DEM standards for 30 min at 40ºC with stirring. Analysis completed using a tri-bed concentrator. ND = not detected

DEM Standards with H_2O			
	Level (ng)	Area Count	
DEM_{115}	60	22982	7285
DEM_{116}	25	5504	4804
DEM_{117}	50	54732	23761
DEM_{118}	75	ND	4004
% Recovery		39.38%	444.90%
R^2		0.0083	0.0013

DEM_{116}, 50 ng DEM_{117}, 75 ng DEM_{118} and 60 ng DMMP. Standards were sampled by SPME direct immersion at 40 ºC with stirring using the blue SPME fiber (65 um PDMS/DVB). Sampling was done at varied time points: 30 min, 20 min, 10 min, 5 min, and 1 min. The area counts for each component was recorded (Table 20). DMMP was not detected.

Table 20. SPME direct immersion sampling of DEM standards at 40ºC with stirring. For various sampling times. Analysis completed using a tri-bed concentrator. ND=not detected

DEM Standards with H_2O						
Sampling Time		1 min	5 min	10 min	20 min	30 min
DEM_{115}	60 ng	24,783	26,485	ND	44,585	274,859
DEM_{116}	25 ng	ND	ND	ND	8,106	72,368
DEM_{117}	50 ng	53,864	53,947	11,695	ND	637,180
DEM_{118}	75 ng	2,517	4,642	ND	10,025	62,006
	DEM_{115} Calculated	168.9	124.9	N/A	1054	-35.28
	DEM_{115} % Recovery	281.6	208.2	N/A	1757	N/A
	R^2	0.0017	0.006	0	0.0325	0.0002

When salting was added, SVOAs could not be detected by headspace. With direct immersion, DEM could be detected with the blue fiber (Table 21). However, DMMP, DIFP, and MeSal were not able to be detected by SPME direct immersion sampling with salting.

Table 21. SPME direct immersion sampling of DEM standards with salting for 30 min. Sampling temperature was at 40°C and stirring was required. Analysis was completed using a tri-bed concentrator. ND = not detected

DEM Standards with Salting						
DEM_{115} Spike		30 ng	40 ng	50 ng	60 ng	70 ng
DEM_{115} Area Count		ND	42,677	20,859	ND	ND
DEM_{116}	25	ND	ND	ND	ND	ND
DEM_{117}	50	201,170	110,285	35,998	54,140	ND
DEM_{118}	75	ND	12,903	10,295	19,310	ND
	DEM_{115} Calculated	N/A	56.25	76.36	N/A	N/A
	DEM_{115} % Recovery	N/A	N/A	N/A	N/A	N/A
	R^2	0	0.0114	0.0771	0.1238	N/A

6.0 DISCUSSION

Several parameters were studied to determine their effect on analysis performance and provide comparison points between the characteristics of HSS and SPME sampling. Some parameters were specific to a single technique such as concentrator type and transfer line temperature (HSS) and sampling time and stirring (SPME). When HSS was used for sampling, the tri-bed concentrator performed better than the Tenax when the samples were VOAs and SVOAs with water. This is reversed for SVOAs without water where the Tenax performed better. The effect of increasing the transfer line temperature was either inconclusive or negative. Consequently generalizations about concentrator type and transfer line temperature cannot be made for all analytes. Overall, the data was limited and inconsistent and our opinion that Tenax is a better overall choice.

With SPME sampling, as the sampling time increased, detection was improved with VOAs without water but the benefit plateaued. With SVOAs, area counts increased as the sampling time increased until the longest tested sampling time of 30 min. When additional testing was done with longer sampling times, SVOAs were not detected, even though the successful detection conditions were replicated giving another example of the inconsistencies of SPME analysis. Stirring was a parameter used with SPME sampling that would require additional fielded equipment and was shown to be necessary with DEM detection.

Additionally, there were shared variables that were explored for both HSS and SPME including sampling temperature. As the HSS oven temperature increased, there was a negligible effect on analysis performance. In contrast with SPME sampling, it was clear that VOAs analysis performance was negatively affected when sampling temperature was increased. However, the opposite was observed during SVOA analysis. With DEM analysis, an increase of sampling

temperature from ambient temperature was necessary for detection. This additional component for DEM detection would not be field applicable.

Overall, with HSS sampling and SPME sampling, SVOAs were harder to analyze than VOAs. HSS analyses were not reliable with SVOA analytes. Generally, the simulants could be seen when only the compound and no water was added. They became increasingly more difficult to detect and quantify when they were added to 20 mL of water. Similarly, SPME was able to detect VOAs but could not detect any SVOAs in field conditions. When the sample was heated and stirred during sampling, DEM could be detected but DIFP, DMMP, and MeS remained undetected. HSS was a better system for analysis of VOAs and SVOAs. SVOA compounds remained undetected with SPME sampling that were detected by HSS.

The initial operating temperature of the HAPSITE ER is roughly limited to 40°C in a laboratory environment. For this reason, none of the mixture #1 components, the light gasses were seen. There was more variation in the early eluters from the other mixtures since they were coming out along with the solvent front and the resolution in this area was not ideal. There are ways to modify this, e.g., using a cryogenic oven, but this is not a field amenable method and, therefore, is out of the scope of this work. The HAPSITE ER is also limited to a maximum temperature of 200°C for the column. This was not a concern for this study but could be if the analytes of interest have extremely high boiling points. The compounds chosen for a majority of the work in this study fell within the operational limits of the HAPSITE ER.

For the initial VOA work, all six mixtures, comprising a total of 59 analytes, were used. The entire list resides in Appendix A. Out of these 59 analytes, 35 were able to be detected on the HAPSITE ER. Of these detectable 35 components, 17 of these met the success criteria with the coefficient of determination >0.99. Table A-1, listed in Appendix A, shows the coefficient of determination for a five-point calibration curve in 20 mL Water (No Salt) at 10, 25, 50, 75, & 100 ng (to include Toluene (108-88-3) from separate BTEX standard). HSS of VOA works for about half of the detectable components and is generally considered a success for portable instrumentation.

With VOAs, SPME sampling was able to detect the compounds, but the linearity of the results was worse than for HSS. Furthermore, SPME was shown to be a highly variable sampling technique. For example, benzene was a compound tested with VOAs analysis. Three trials were performed and benzene was detected only two out of the three trials. There were instances where analysis to analysis on the same day, the same analyte at a higher concentration would suddenly be undetected. With SVOAs analysis, only DEM was able to be detected by SPME and the sampling conditions that were necessary were not field applicable. Furthermore, the SPME fibers themselves require considerable more care than the HSS. Fibers can break, be stripped, and have a finite lifetime, requiring regular replacement.

7.0 CONCLUSION

HSS is more effective for field use than SPME. Both techniques were able to detect VOAs better than SVOAs. While DMMP, an SVOA, was not detectable by sampling, DEM, MeSal, and DIFP were detected. In comparison, the only SVOA that SPME could detect was DEM and the detection conditions were not field applicable by current supplied equipment. Even with VOA testing where SPME was able to detect compounds in field applicable conditions, HSS performed better. Additionally, SPME testing was inconsistent even with identical sampling

conditions. HSS works for approximately half of the VOA detectable analytes using EPA defined criteria for success[6]. HSS can observe SVOA CWA analytes though data did not meet EPA criteria[6]. Previous work[7] has shown that the HAPSITE Plus was successful for VOA work than the HAPSITE ER, but the HAPSITE ER uses a 15m column and is no longer suitable for lower boiling components. With the current configuration of the HAPSITE ER, the best performance is seen in analytes with boiling points > 80°C. Although analytes with boiling points below 80°C are still detectable, the reliability of this data should be considered suspect. The use of isotopic focusing agents can improve the reliability of the data in either the detection of VOAs or SVOAs. They are also beneficial in the detection of a malfunctioning HAPSITE.

A final consideration is that SPME required a much higher skill level than HSS. Additionally, SPME required stirring and heating which is not currently available in the field. SPME was not successful for DEM unless direct immersion was used which may be impractical under field conditions for heavily contaminated samples. Overall, results suggest that HSS provides several advantages over SPME for field use.

8.0 REFERENCES

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APPENDIX

Restek Part# 30076 8260 Volatile Organics Kit (2,000 µg/mL) List of Analytes

30042: 502.2 Calibration Mix #1 (gases)
Bromomethane (methyl bromide) (74-83-9)
Chloroethane (ethyl chloride) (75-00-3)
Chloromethane (methyl chloride) (74-87-3)
Dichlorodifluoromethane (CFC-12) (75-71-8)
Trichlorofluoromethane (CFC-11) (75-69-4)

30043: 502.2 Calibration Mix #2
Bromodichloromethane (75-27-4)
Bromoform (75-25-2)
Carbon tetrachloride (56-23-5)
Chloroform (67-66-3)
1,1-Dichloroethane (75-34-3)

30044: 502.2 Calibration Mix #3
Bromochloromethane (74-97-5)
Dibromochloromethane (124-48-1)
1,2-Dibromo-3-chloropropane (96-12-8)
1,2-Dibromoethane (EDB) (106-93-4)
Dibromomethane (74-95-3)

1,2-Dichloroethane (107-06-2)
cis-1,2-Dichloroethene (156-59-2)
1,2-Dichloropropane (78-87-5)
1,1-Dichloropropene (563-58-6)
1,1,1,2-Tetrachloroethane (630-20-6)
1,1,2,2-Tetrachloroethane (79-34-5)
Tetrachloroethene (127-18-4)
1,1,2-Trichloroethane (79-00-5)
1,2,3-Trichloropropane (96-18-4)

30045: 502.2 Calibration Mix #4
Benzene (71-43-2)
tert-Butylbenzene (98-06-6)
Chlorobenzene (108-90-7)
Isopropylbenzene (cumene) (98-82-8)
n-Propylbenzene (103-65-1)
Styrene (100-42-5)
Toluene (108-88-3)
1,3,5-Trimethylbenzene (108-67-8)
m-Xylene (108-38-3)

30046: 502.2 Calibration Mix #5
Bromobenzene (108-86-1)
n-Butylbenzene (104-51-8)
sec-Butylbenzene (135-98-8)
2-Chlorotoluene (95-49-8)
1,3-Dichlorobenzene (541-73-1)
Ethylbenzene (100-41-4)
1,2,4-Trichlorobenzene (120-82-1)
1,2,4-Trimethylbenzene (95-63-6)
o-Xylene (95-47-6)
p-Xylene (106-42-3)

30047: 502.2 Calibration Mix #6
4-Chlorotoluene (106-43-4)
1,2-Dichlorobenzene (95-50-1)
1,4-Dichlorobenzene (106-46-7)
Hexachlorobutadiene (87-68-3)
4-Isopropyltoluene (*p*-Cymene) (99-87-6)
Naphthalene (91-20-3)
1,2,3-Trichlorobenzene (87-61-6)

Table A-1. Headspace Detectable VOA Analytes in 20 mL Water (No Salt) at 10, 25, 50, 75, & 100ng (to include Toluene (108-88-3) from separate BTEX standard)

VOA Mixture #	Analyte (CAS#)	R^2
3	1,1 – Dichloropropene (563-58-6)	0.934
4	Benzene (71-43-2)	0.996
3	Dibromomethane (74-95-3)	0.992
2	Trichloroethene (79-01-6)	0.998
2	cis – 1,3 – Dichloropropene (10061-01-5)	0.931
2	trans – 1,3 – Dichloropropene (10061-02-5)	0.931
3	1,1,2 – Trichloroethane (79-00-5)	0.942
BTEX Standard	Toluene (108-88-3)	0.973
3	Dibromochloromethane (124-48-1)	0.991
3	1,2 – Dibromoethane (EDB) (106-93-4)	0.999
3	Tetrachloroethene (127-18-4)	0.969
4	Chlorobenzene (108-90-7)	0.999
5	Ethylbenzene (100-41-4)	0.99
4	m – Xylene/1,3 – Dimethylbenzene (108-38-3)	0.989
5	o – Xylene (95-47-6)	0.989
4	Styrene (100-42-5)	0.999
5	p – Xylene (106-42-3)	0.989
3	1,1,2,2 – Tetrachloroethane (79-34-5)	0.984
3	1,2,3 – Trichloropropane (96-18-4)	0.998
5	Bromobenzene (108-86-1)	0.967
4	Isopropylbenzene (cumene) (98-82-8)	0.986
6	4 – Chlorotoluene (106-43-4)	0.991
4	n – Propylbenzene (103-65-1)	0.551
4	1,3,5 – Trimethylbenzene (108-76-8)	0.994
4	tert – Butylbenzene (98-06-6)	0.978
5	1,2,4 – Trimethylbenzene (95-63-6)	0.984
6	1,4 – Dichlorobenzene (106-46-7)	0.982
5	1,3 – Dichlorobenzene (541-73-1)	0.982
5	sec – Butylbenzene (135-98-8)	0.974
6	1,2 – Dichlorobenzene (95-50-1)	0.993
6	4 – Isopropyltoluene (p – Cymene) (99-87-6)	0.968
5	n – Butylbenzene (104-51-8)	0.972
6	1,2,3 – Trichlorobenzene (87-61-6)	0.998
6	Naphthalene (91-20-3)	0.969
6	Hexachlorobutadiene (87-68-3)	0.894

Success criteria defined where R^2>0.99.

LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS

ACC/SG	Air Combat Command/Surgeon General
AF	Air Force
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
CWA	Chemical Warfare Agent
DEM	Diethyl Malonate
DIFP	Diisopropylfluorophosphate
DMMP	Dimethyl methylphosphate
GC	Gas Chromatograph
GC-MS	Gas Chromatograph-Mass Spectrometer
HSS	Headspace Sampling System
lbs	Pounds
MeOH	Methanol
MeS	Methyl salicylate
µL	Microliters
MS	Mass Spectrometer
m/z	Mass-to-Charge Ratio
NaCl	Sodium Chloride (salt)
ng	Nanogram
NIST	National Institute of Standards and Technology
R^2	Coefficient of Determination
SPME	Solid Phase Micro Extraction
SVOA	Semi-Volatile Organic Analytes
TDSS	Thermal Desorber Sampling System
UHP	Ultra High Purity
VOA	Volatile Organic Analyte
w/o	Without
WS	Working Solution