The Combination of 3 New Sampling Techniques Paired with GCMS for Determination of Uptake Rates and Accurate Monitoring of SVOC Endocrine Disruptors in Indoor Air

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OVERVIEW

A novel approach for the quantitative passive sampling of SVOCs in ambient and indoor air down to low part per trillion levels is presented. The new approach solves issues which have prevented quantitative passive monitoring in the past, including:

1. Obtaining accurate uptake rates for all target compounds.
2. Performing quantitative spiking of diffusive monitors or tubes to achieve equivalent recoveries compared to passive field sampling.
3. Creating effective procedures for GCMS calibration and method validation.

Simple diffusive samplers are placed at the sampling location for between 1-30 days to allow passive collection of SVOCs. Uptake rates for each SVOC were determine by co-locating active samplers that were collecting air at just 0.5cc/min, and responses were compared to determine diffusive sampling rates for the SVOCs detected. Conversion of area counts to actual ng on tube can then be done by diffusively loading calibration standards onto the tubes, followed by splitless thermal desorption into the GCMS. Similarly, calibration curves can also be created by diffusive loading onto tubes prior to splitless GCMS injection.

INTRODUCTION

Many compounds in indoor and outdoor air in the C10-C20 range are known to create health hazards, including PCBs, Phthalates, PFOA/PFOS, PAHs, Pesticides, Fire Retardants, and others. Not only are a large number of these compounds carcinogens, but many are considered to be Endocrine Disruptors.

Endocrine Disruptors:

- Cause of many health conditions plaguing modern society.
- Affect the proper functioning of the human Endocrine system disrupting metabolism, the immune system, the nervous system, and other functions.
- Many materials and products found in indoor environments have been shown to give off Endocrine Disruptors, and poor ventilation in many cases cause these compounds to build up to unacceptably high levels.

Current techniques for measuring SVOCs in air use solvent compatible sorbents that require very large volumes of air to be sampled using high volume samplers, and therefore a substantial source of power. There has been a large push to eliminate solvent extraction due to health risks, affects on the environment, and the extensive labor and lab space required. Elimination of solvents using thermal desorption techniques have been largely unsuccessful, which has been partially attributed to the affects of channeling that allows compounds to migrate further into the adsorbent than expected. In addition, active sampling again requires a source of power which in some locations is not available when long, time integrated sampling is needed.

A new passive sorbent sampling device operating without the need for power has been successful in monitoring SVOCs including carcinogens and Endocrine Disruptors in indoor and outdoor air. The sorbent is simply placed in the location to be sampled for 1 to 30 days, and then is returned to the laboratory for analysis. A special thermal desorber (5800, Entech Instruments) desorbs the sample directly into a dual column GC where the first column preconcentrates the SVOCs while fixed gases and lighter compounds are mostly split out prior to the second, analytical GC column. After desorption, the split between the first 2 columns is turned off, and 100% of the SVOCs are directed onto column 2 and ultimately to the mass spectrometer. If sampling is allowed to occur for 2 weeks, approximately 5-10L is effectively sampled, with rates varying from about 0.2 to 0.4 cc/min for each compound. This volume allows the potential for measurement down to 1-5 part per trillion for each compound using full scan, single quad GCMS, or well into the sub part per trillion range if unneeded using targeted GC/TSQ or GC/TOF analyzers.

This paper describes the process for determining uptake rates and response factors for a wide range of SVOCs, with qualitative sampling rates determined without the need to obtain analytical standards.

EXPERIMENTAL PROCEDURE

For diffusive sampling of SVOCs, Uptake rates were determined by comparing the recovery from multiple diffusive samples placed immediately next to active samplers that were collecting at 0.5cc/min, and ratios in recoveries between the active and passive samplers were used to determine effective sampling rates for each compound recovered. **Figures 1** and **2** (below) shows the positioning of 3 Diffusive Sorbent Pens (DSPs) around 1 Active Sorbent Pen (ASP) whose sampling rate was controlled using a CS1200E6 Flow controller and an evacuated 6L canister (Entech Instruments). The ASPs have a very narrow inlet to inhibit reverse desorption even at active flow rates down to 0.1cc/min.

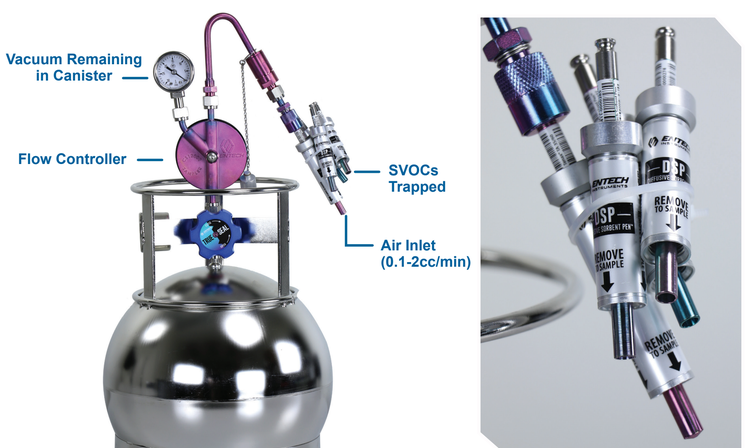


Fig 2 - 3 DSP samplers placed in close proximity to ASP sampler to compare sampling rates.

Figure 1 - 6L can and flow controller set to sample at 0.5cc/min to accurately draw 1-4L of air through an Active Sorbent Pen. Three DSP passive samplers are placed in close proximity to the inlet of the active sampler to allow exposure to exactly the same air to compare uptake rates relative to 0.5cc/min active sampling.

The DSP, ASP, and Headspace Sorbent Pens (HSP) are shown in **Figure 3**. On the inside of the ASPs, the tube ID expands to 5mm, at which point most compounds have a fast enough diffusion rate at this cross-sectional area to almost eliminate the occurrence of channeling into the adsorbent, even though channels can form with heating and cooling of the adsorbent.

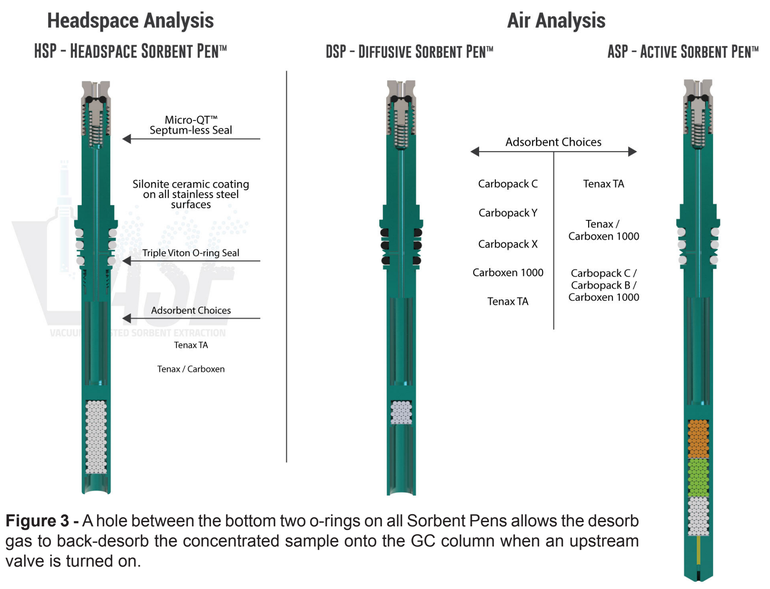


Figure 3 - A hole between the bottom two o-rings on all Sorbent Pens allows the desorb gas to back-desorb the concentrated sample onto the GC column when an upstream valve is turned on.

Areas were compared between the ASPs and triplicate DSPs to determine update rates per compound, represented as effective cc/min collection rates. For example, if the DSP diffusive samplers had half the response for Butyl Phthalate as the ASPs had at 0.5 cc/min, the Butyl Phthalate sample rate would be 0.5/2 = 0.25cc/min.

Active and Diffusive sampling were performed co-located for 72 hours, and the change in the pressure within the 6L canister confirmed that just over 2L were sampled through the active ASP samplers. The DSPs and ASPs were isolated, and then individually desorbed into a 5800 thermal desorber system (**Figure 4**.) for focusing onto a pre-column, followed by splitless transfer to a second column for separation and measurement. A large number of compounds were identified in the indoor environment where the sampling took place, so a large number of effective sampling rates could be determined.

Splitless Trace Analysis Procedure for SVOCs

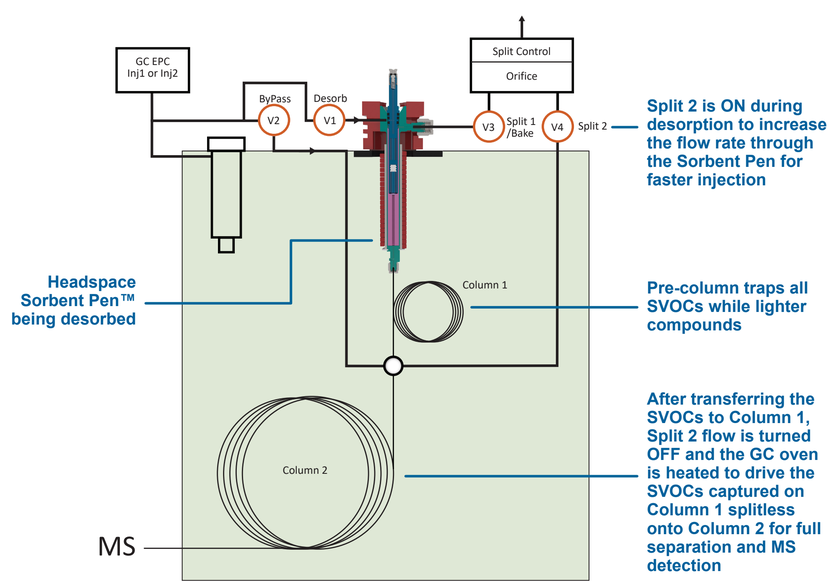
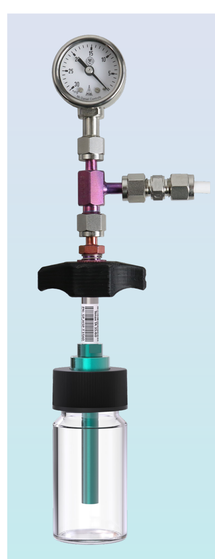


Figure 4 - 5800 Sorbent Pen Desorption Unit (SPDU) diagram. Using a series of two columns in the flow path after thermal desorption, with forward and backward flushing capabilities for the first column, a wide range of applications can be performed to analyze compounds ranging in boiling points from -100°C to 500°C. Water management can be performed through condensation, splitting, and back flushing. A series of 4 valves controls each method process and the location of each valve is shown: Desorb, Valve 1 (V1); Bypass, Valve 2 (V2), Split 1/Bake, Valve 3 (V3), and Split 2, Valve 4 (V4).



Sorbent Pen Spiking Procedure

1. Inject a known amount of each standard compound by weight into a vial through a special liner which allows the DSP to seal at the top of the vial.
2. Insert the DSP sampler and immediately evacuate the vial by attaching a vacuum to the top of the DSP.
3. Remove the vacuum source after about 20 seconds when full vacuum has been achieved and allow the extraction and transfer to the adsorbent to occur for a determined amount of time.
4. Use a separate vial and DSP for each point on a multi-point calibration curve.
5. Remove the DSPs and place them in their protective sleeves until they can be desorbed using the 5800 SPDU mounted onto a GCMS.
6. Analyze each DSP sampler to test the acceptability of the adsorbent for each chemical and create response factors and calibration curves.
7. Place the DSP sampler back into its protective sleeve.
8. Automation of this process and for the analysis of collected samples are possible using 7850 Autosampler.

Figure 5

RESULTS

GCMS responses of compounds identified from desorbing the 3 ASP active samplers and 9 DSP passive samplers were recorded and compared using the following equation to solve for the unknown DSP semi-volatile organic compound uptake rate:

$$\frac{\text{ASP Response}}{\text{ASP Uptake Rate}} = \frac{\text{DSP Response}}{\text{DSP Uptake rate (unknown)}}$$

Compound: **Diethyl Phthalate** (known endocrine disruptor)

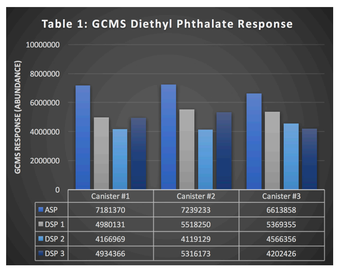
ASP Response for Diethyl Phthalate = **7181370** (Quantitation ion 149)

ASP Flow Rate = **0.5cc/min** (determined by using the initial and final 6L canister pressures to calculate a volume of 2.1L sampled over 72 hours)

DSP 1 Response for Diethyl Phthalate = **4980131** (Quantitation ion 149)

DSP Uptake Rate: **Unknown**

After using the ASP and DSP responses for Diethyl Phthalate and the confirmed ASP active flow rate, the equation was solved to equal a 0.347cc/min uptake rate for Diethyl Phthalate for DSP 1 attached to Canister #1. This equation was applied to the other 2 DSPs attached to Canister #1 and the samplers on Canisters #2 and #3. **Table 1** shows agreement not only between the 3 ASP active samplers, but also for all 9 of the DSP passive samplers respectively. **Table 2** illustrates the similarity between the 9 total Diethyl Phthalate uptake rates calculated using the equation above for each set of 3 DSPs attached to each canister.



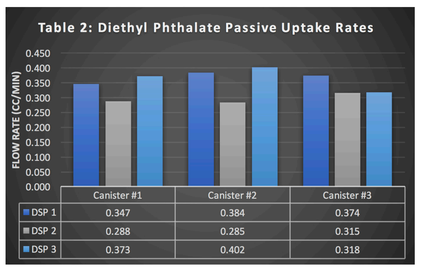


Table 3: Average Diffusive Uptake Rates for SVOC Room Air Compounds

Compound Name	Retention Time (min)	Qion	Average Uptake Rate (cc/min)	STD Dev	%RSD
Decanal	15.05	57	0.10	0.02	19.83
2(3H)-Furanone,5-butyldihydro-	15.84	85	0.50	0.14	27.26
Undecanal	16.72	57	0.18	0.04	19.87
2(3H)-Furanone,dihydro-5-pentyl-	17.53	85	0.32	0.01	4.41
Dodecanal	18.39	57	0.17	0.01	8.00
Undecanoic_acid	19.16	60	0.10	0.02	16.33
Phenylmaleic_anhydride	20.06	102	0.17	0.05	27.57
Dodecanoic_Acid	20.49	73	0.10	0.01	13.40
2(3H)-Furanone 5-heptyldihydro-	20.62	85	0.37	0.04	10.53
Diethyl_Phthalate	20.83	149	0.34	0.04	10.99
Tetradecanal	21.18	57	0.19	0.02	12.11
Benzophenone	21.47	105	0.22	0.02	10.98
Tridecanoic_acid	21.70	60	0.09	0.02	17.40
Tetradecanoic_acid	22.87	129	0.08	0.01	10.75
Pentadecanoic_acid	23.95	129	0.05	0.01	14.02
Dibutyl_Phthalate	24.96	223	0.19	0.06	33.43
Heptadecanal	26.59	43	0.53	0.07	13.45
[1,1':3',1"-Terphenyl]-2'-ol	27.74	247	0.14	0.04	27.76
4-Cyclopentene-1,3-dione,2,4-diphenyl-	27.93	248	0.81	0.09	11.12
Di-n-octyl_Phthalate	30.09	279	0.24	0.09	37.24
4H-Pyran-4-one,2,6-diphenyl-	30.47	248	0.71	0.06	9.04
1,4-Benzenedicarboxylic acid,bis(2-ethylhexyl)ester	31.73	261	0.10	0.01	11.86

Table 3 above shows average passive uptake rates calculated for a variety compounds that were identified and includes the percent Relative Standard Deviation (%RSD) of these uptake rates determined for all passive samplers.

Table 3 shows the DSP passive sampler response agreement for many of the compounds identified (37%RSD was the highest; 4%RSD was the lowest). The calculated passive flow rates were expected to decrease as the size of the compound and retention time increased, however the data shows uptake rates for acids were much slower, therefore uptake rates are also highly affected by chemical properties. The next step is to order standards of the compounds identified and calibrate the GCMS using Vacuum Assisted Sorbent Extraction (VASE) to spike the Sorbent Pens in closed vial with a known amount of standard and then thermally desorb them with the 5800 SPDU as performed using the ASP and DSPs. The responses from calibration curves will be used to determine the concentrations of compounds in the air which were sampled by the DSP passive samplers. Surrogate standards may also be spiked onto Sorbent Pens used to calibrate the GCMS and onto the DSPs before deployment to account for any fluctuation and confirm recovery.

CONCLUSIONS AND FUTURE WORK

1. Diffusive Sorbent Pens (DSPs) greatly improve upon current sample collection devices by eliminating both the need for power during sampling, and the need for solvents during analysis.

2. Active Sorbent Pens (ASPs) can be sampled at flow rates which are slow enough to be comparable to diffusive uptake rates allowing the first-ever accurate comparison of active to diffusive collection, providing for better determination of uptake rates for SVOCs.

3. DSP samplers agreed well enough to meet precision criteria for most Environmental methods.

ASPs and DSPs showed excellent reproducibility respectively, confirming the results of applying these techniques to measure uptake rates for SVOCs in indoor air. The third and final step is to order the standards identified and use the established technique of spiking multiple standards onto Sorbent Pens using Vacuum Assisted Sorbent Extraction (VASE) to create calibration curves which will be used to determine actual concentrations in air. Future work will include a much more extensive list of SVOC compound uptake rates and actual concentrations determined in indoor air.