
Helium Diffusion Sampling for Personal Monitoring by EPA Method T015



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Abstract

A new, simplified approach for filling air sampling canisters during personal monitoring of work place airborne chemicals is described. Helium Diffusion Sampling Personal Monitors (HDS-PM) are filled with helium and a surrogate after cleaning. Proper time integrated sampling is performed simply by removing the valve and allowing helium to leak out through a calibrated orifice, which simultaneously draws in the same volume of air. Orifice sizes are available for performing a range of integration times from 15 minutes to 8 hours, without the need for an external flow controller. A description of the technique is provided, including data showing that this is just another means of performing active T015 sampling and analysis, as no diffusion based variances between light to heavy compounds were detected.

Discussion

Helium Diffusion Sampling (HDS) represents the latest approach for collecting organic vapors in the workplace or indoor air environments. These devices collect air samples at a constant rate from 15 minutes to 8 hours without the use of pumps or any electrical energy whatsoever. Each sampler is charged with helium and a recovery surrogate (Bromofluorotoluene - BFT) to verify proper sampling and container inertness. During sampling, helium is allowed to escape through a diffusion zone, creating a vacuum in the container that slowly draws in the sampled air. Sampling continues



through 25-40% of the helium exchange, during which time the exchange rate is virtually constant. Since air is drawn into the vial as fast as helium is escaping, the diffusion zone always has a 1:1 ratio of helium and air both at the start and end of sampling, which helps to maintain the constant sampling rate. Above 40%, the sampling rate starts to drop off, so the diffusion zone is tailored to exchange about 30-35% of the helium with air. HDS Personal Monitors are weighed after sampling to determine how much air was actually collected, since air is about 7.2x heavier than helium. The amount of weight gain relative to the evacuated sampler accurately determines the volume of sample collected, in contrast to other passive samplers that offer no proof that any sample was ever collected at all.

HDS Personal Monitors inherently bring with them a lot of Quality Assurance. Not only is the HDS-PM weighed to determine how much air was actually sampled, the samplers are typically charged with helium that is spiked with Bromofluorotoluene, a recovery surrogate compound that validates both the inertness of the container, and the absence of leaks. Prior to analysis, the sampler is also pressurized with Fluorobenzene in nitrogen (both samples and calibration standards). This validates the actual injection volume into the GCMS. The response of Fluorobenzene is used as an Internal Standard to normalize any corrections needed to create the most accurate analysis possible.

The sampling professional will need the appropriate HDS Personal Monitor for the sampling time desired and a simple pressure gauge to verify that there is still positive pressure in the sampler. Each sampler is charged with

helium above atmospheric pressure, allowing a simple gauge to be used at the time of sampling to prove that the sampler did not leak or start sampling prior to the intended collection event. With helium being a smaller molecule than air or the chemicals to be collected, helium will diffuse through any marginal seals faster than air, so a positive pressure of helium at the time of sampling is proof that the sampler is still contamination free.

Sample Pressure Normalization – The total pressure in the sampler after returned to the laboratory will be affected by the elevation at the sampling site, and by any new diffusion loss of remaining helium after the HDS Personal Monitor is sealed back up after sampling. In order to normalize this pressure, each monitor is first pressurized back to 15 psia with helium, as this is just over atmospheric pressure at sea level, and no sampler should already be above this. After this the HDS samplers are weighed to allow determination of the % air vs helium in the sampler in order to provide an extremely accurate dilution factor. The sampler only has a small Mylar serial number label which is shown to minimize any weight change of the canister as humidity levels change. No other label should be attached to the container. Instead, the plastic transparent transfer case can be used to attach any label or markings necessary.

Weighing must be done before analysis, and again after analysis upon evacuation of the sampler to ultimately determine the weight of the gas itself. The HDS Personal Monitor should be measured to the nearest 0.1mg. Fingerprints will only add about 0.01mg to the weight of monitor, so handling errors should not be significant. However, clean hands should be used to handle HDS Personal Monitors as a precautionary measure. After running the sample, the sampler should be evacuated down to less than 0.15 psi absolute to create a 1% or less error in the measurement. For those laboratories with a canister cleaning system, vacuums of 0.0001 atm (less than 76 mtorr) can easily be achieved. Entech provides a simple spreadsheet for taking the original weight and empty weight to arrive at the %air collected, and therefore the dilution factor. The dilution factor needs to be calculated into the analytical results to obtain the actual concentrations at the time of sampling. Contact Entech for a free copy of the HDS %Air Sampled Excel Worksheet.

Sample Dilutions - Due to the limited dynamic range of today's GCMS systems, dilution of the sample prior to analysis may be needed for high PPM level samples. Dilutions can be easily done using a glass, gas-tight syringe fitted with a 16 gauge blunt-end needle. After bringing the sample to 15 psia with helium, a 1/2 cc aliquot can be withdrawn from the container and injected into a second container under vacuum followed by filling with either nitrogen or helium to 15 psia. The dilution factor would be calculated based on the ratio of the injected volume to the total volume of the container at 15 psia. Using 14.7 psia at standard atmospheric pressure, the dilution of 1/2cc of sample into a second evacuated 50cc HDS Personal Monitor would be $(50 \times 15/14.7)/0.5 = 102x$

Automated Analysis - HDS Personal Monitors are analyzed in the laboratory by either using a 0.25cc injection via a sample loop without using cryogenic trapping, or by extracting 10-20cc using the Entech 7650-M/7200 sample preparation system. Prior to analysis, the HDS Personal Monitor is pressurized with Fluorobenzene at 1-10 PPM. The pressure is raised from 15 psia to 20 psia. This is done for both standards and samples, eliminating the need to account for this dilution. The resulting positive pressure allows a sample loop to be flushed under the pressure of the sample container. The Fluorobenzene acts as an Internal Standard to validate the amount actually delivered to the GCMS, and corrects for any fluctuation in GCMS sensitivity. Fluorobenzene is typically added to each monitor before placing the sample in the autosampler tray, using the Entech Digital Dilution System, or DDS. Due to the small volume of the HDS Personal Monitor, connection to a rotary valve inlet is not recommended. Instead, the 7650 is a robotic based autosampler that extracts the sample from the HDS-PM by inserting a 1/16" Silonite-D treated transfer line directly into the Micro QT Valve, completely eliminating any dead volume or need for sample preflushing. This is critical in getting an accurate measurement of sample during the analysis.

The results of the GCMS analysis must be multiplied by the HDS Personal Monitor's dilution factor, since the monitor did not contain 100% air. Again, this is calculated by entering the weights of the initial pressure

equilibrated sampler and fully evacuated sampler into the Entech provided spreadsheet. If the air% collected was 33.3%, the dilution factor would be 3x, and a value of 1.5PPM determined during the GCMS analysis would then become $1.5\text{PPM} \times 3 = 4.5\text{PPM}$ at the sampling location. Due to the extreme accuracy of both the gravimetric and chemical measurements, HDS Personal Monitors are extremely reliable, as proven by collecting multiple samplers simultaneously.

Preparing HDS Personal Monitors for Workplace Monitoring

The HDS Sampler Prep Station is used for both the



Figure 1 HDS Sampler Prep Station for both cleaning and preparing HDS Personal Monitors for resampling

cleaning of previously used samplers, and for the preparation of samplers prior to sending back out to the field for new sample collection. Either use the 10 PPM Bromofluorotoluene (p/n 01-40-HDS-BFT-H) for the entire procedure below (cleaning and sample prep), or use nitrogen for steps 1-2, and the BFT mix for step 4.

1) Attach Personal Monitors to the Entech Sampler Prep Station (**Figure 1**, PN: HDS-PS1). A 4 position expander is available for preparing 4 samplers at a time (PN: HDS-PM-4XM) in which case all times below should be multiplied by 2x.

2) Using the 3-way valve, select the evacuation position and wait 15 seconds, then select the fill position and wait 5 seconds, then again evacuate for 15 seconds.

3) Remove the sampler and place into an oven at 70- 80 deg C overnight.

4) Allow the sampler to cool, place it back onto the prep station, fill for 5 seconds, evacuate 30 seconds, then fill one last time for 5 seconds to around 7 psig.

The sampler is ready to send to the field. Note that for those laboratories with an Entech canister cleaning system capable of high vacuum, steps 1-2 can be



Figure 2 Testing sampler pressure in the field prior to sampling to ensure helium is still above 3 psig. Even Though helium may have dropped down from the initial 7 psig, the presence of any positive helium pressure is an indication that no air or contaminants have entered the sampler.



Figure 3

replaced by pumping each monitor down to a high vacuum prior to allowing for equilibration in an oven overnight. The overnight bakeout simply allows time for complete outgassing of internal surfaces to eliminate any memory effects.

Field sampling with HDS Personal Monitors

1) Just before sampling, the sampling professional should verify that the pressure in the container is still above about 3 psig using a small test gauge. This will ensure that sampler did not get contaminated in transit. (**See Figure 2**)

2) Place the HDS PM protective holder in the breathing zone and properly secure it. Magnetic clips and lanyards are available for this purpose, but other straps, special vests, velcro strips, etc, can be utilized as well to keep the holder firmly in position. Place the sampler in the protective holder. To start the sampling process, remove and store the HDS sampling valve in the side pocket of the nylon sampler holder. (**See Figure 3**).

3) After the desired sampling time has elapsed, re-attach the isolation valve to stop the sampling process. Note the sampling times, re-pack the samplers in their shipping containers, and return to the laboratory for analysis.

Laboratory Analysis of HDS Samplers

Prior to weighing in the laboratory to determine the amount sampled, use the Entech DDS to carefully pressurize the sampler with helium to 15 psi absolute as explained earlier. An absolute pressure of 15 psia has been set because no sampling location is at a higher pressure than this. If during adjustment with helium to 15 psia it is determined that the pressure is already higher than 15 psia, then it must be concluded that the sampler was not properly opened in the field.

Note that pressures used here for dilution calculations are given in psi absolute (psia), and that atmospheric pressure at most labs is roughly 14-14.7 psia, so very little helium will need to be added. It is critical that you use an absolute pressure gauge, like the Entech Digital Dilution System gauges to maintain good analytical accuracy.

2) Weigh the vessel using a scale that can measure to ± 0.1 mg and record the weight in the Entech spreadsheet provided.

3) Pressurize the sample to 20 psia with Fluorobenzene (FB) in Nitrogen again using the DDS. (Figure 4). It is recommended that a second DDS system be used so that it isn't necessary to keep moving the same one back and forth between the 15 psia helium equilibration and the 20 psia Fluorobenzene pressurization. The Fluorobenzene standard can be made by the laboratory by using accepted gas standard preparation techniques, or by purchasing pre-made cylinder standards from Entech or local specialty gas suppliers.



4) Analyze the sample using either the Entech 7410D or 7650-L10 for PPM level analysis, or by using the Entech Million Air system (7650-M/7200) for measuring from low PPB to high PPM levels

5) After checking the results, if re-analysis becomes necessary, use the DDS/Helium pressurization station from step 1 to increase the pressure by 1.5x, then re-analyze the sample. Note that pressurizing with helium

rather than the ISTD will maintain the original ratio of sample to Internal Standard so that both will be diluted equally and no adjustment for this dilution will be needed when using an internal standard calibration method.

6) After analysis, evacuate the HDS PM and re-weigh and record this weight for each vessel.

7) The % Air and Sampling Dilution Factor are determined by the following formula or by using the Excel spreadsheet provided by Entech Instruments. Apply the sample Dilution Factor to all GCMS results.

Wa = Weight of air in the test HDS Personal Monitor filled to 15 psia with air. This measurement only has to be done once. Since this is slightly above atmospheric pressure, the sampler should be evacuated and filled with room air, then pressurize to the final 15 psi absolute with zero air or nitrogen

We - Weight of the test HDS Personal Monitor empty

Wao - Weight of Air only where $Wao = Wa - We$.

Wsf = Weight of the sampler after being equilibrated to 15 psia with Helium upon receipt to the laboratory.

Wse = Weight of the sampler after analysis, and after being fully evacuated (sampler empty weight)

The following equation is simply the ratio of the weight of the sample at some mixture of air and helium, minus the weight of helium in the same size container, over the weight of air in that same size container:

$$\%Air = (Wt\ Sample - Wt\ He) / (Weight\ Air - Wt\ He)$$

If we determine the molecular weight of air at 50% RH, this will be very close to the weight at all humidities:

$$MW = (28 \times 0.77) + (32 \times 0.205) + (40 \times 0.01) + (18 \times 0.015) = 28.79\ g/mole$$

Then, by taking the ratio of the molecular weight of air vs helium ($28.79/4 = 7.20$), we can substitute the helium weight out of the above formula, and upon rearrangement, obtain the following equation:

$$(Wsf - Wse) - Wao / 7.20$$

$$\%Air = \frac{(Wsf - Wse) - Wao}{7.20 \times Wao} \times 100\%$$

The Entech spreadsheet uses the above formula when making its calculations. Contact Entech for a copy of this spreadsheet.

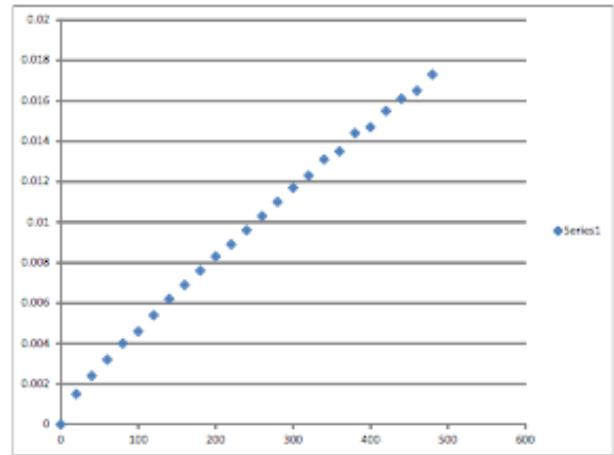
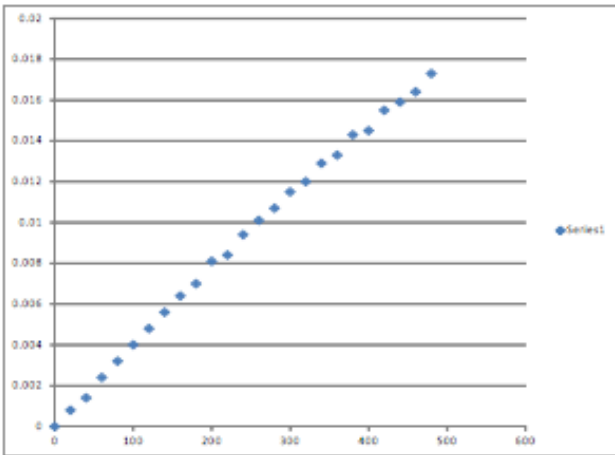
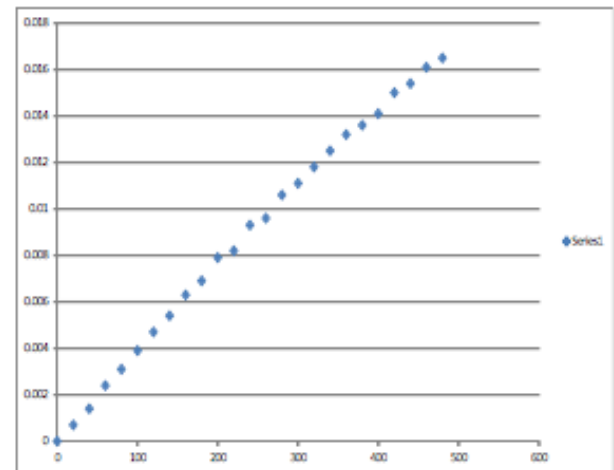
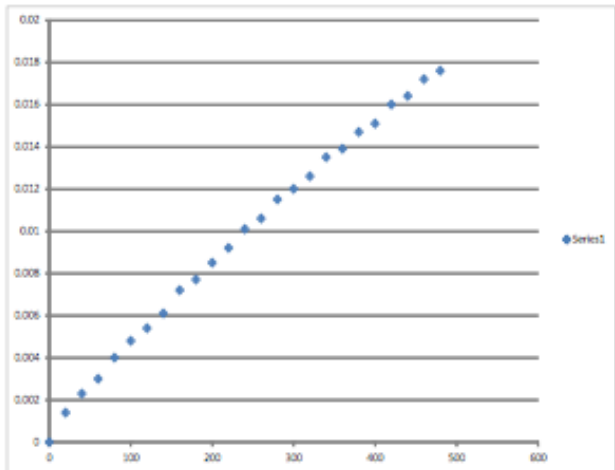
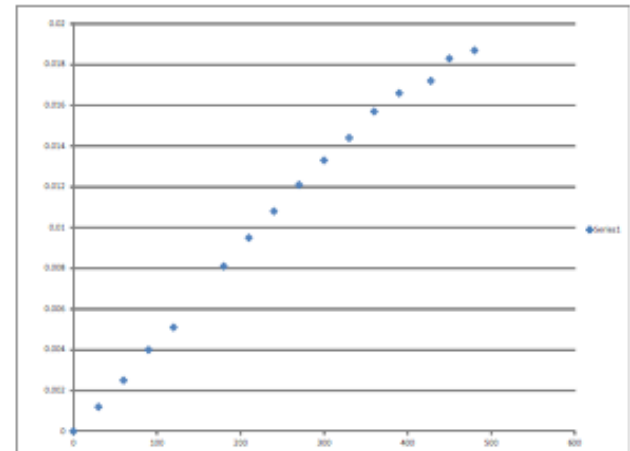
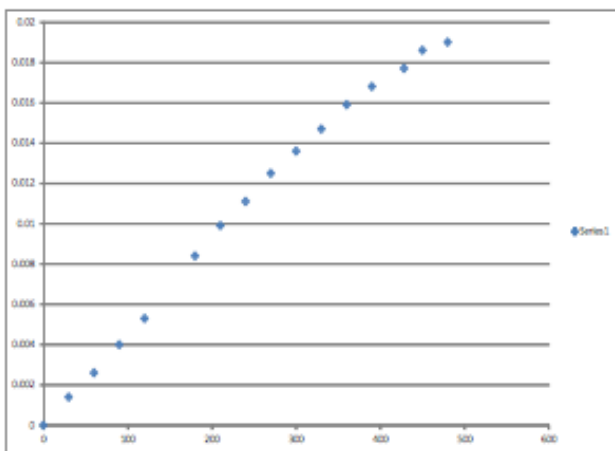


Figure 5 and 6 - Weight gain into 8 hour samplers A and B in the vertical orientation, still air.



Figures 7 and 8 - Weight gain into 8 hour samplers A and B in the horizontal orientation, still air.



Figures 9 and 10 - Weight gain into 8 hour samplers A and B in the vertical orientation, face velocity = 2.0 m/s. Overall weight gain in this relatively strong “breeze” was only about 10% greater than still air.

Sampling Rate Invariance with Position and Face Velocity

Sampler orientation and face velocity at the inlet were evaluated to see what effects they had on sampling rates. Figures 7-8 show the weight gain of two separate 8 hour samplers in virtually still air, while Figures 8-9 show the same two samplers laying down in the horizontal orientation on the scales as they collected air. The samplers in both the vertical and horizontal positions collected air at the same rate. This is not unexpected as the diffusion of helium out through the diffusion tube should not be affected by orientation. Helium isn't rising out of the top of the sampler due to a weight difference, it is simply being slowly replaced with air due to a diffusion difference.

Figures 9 and 10 show the weight gain of the same two samplers while a fan was blowing air over them at 2.0 m/s. The sampling rate overall was about 10% faster, but this additional amount sampled was being accounted for by gravimetric correction, resulting in no net error. Considering that badge sampling rates can drop by 70-80% in still air, the very small difference in sampling between still air and 2.0m/s air for HDS Personal Monitors corresponds to far less error than current badge methods.

Comparison of Collection Rates of Individual Analytes as Compared to Classical Vacuum Canister Sampling

Co-located sampling with comparison to a known and accepted technique may be the best proof of analytical performance. This is probably not done enough to validate current NIOSH and OSHA methods during realworldsampling. Even duplicate sampling, say of two or more badges on a single individual are not done very frequently,

Considering that canisters collect the entire sample allowing careful preparation for GC or GCMS analysis under controlled conditions in the laboratory, canister sampling by TO15 is often considered the "GoldStandard" of air measurements. Onlywiththe canister technique is the original sample preserved up until the point were it is "extracted" by laboratory sample preparation systems that have first been challenged with

blanks and analytical standards across a wide range of concentrations. This reduces the number of uncontrolled variables to a minimum, allowing the Scientific Method to be adhered to more strictly, thereby reducing potential for analytical errors

Four 15 minute and four 8 hour HDS Personal Monitors were used to compare uptake rates of 37 compounds at 1 PPMv relative to TO15 vacuum collected canisters using the chamber shown in Figure 11. The four 15 minute samplers were collected first, followed by the four 8 hour samplers, and finally two evacuated samplers were filled following classical TO15 sampling protocols.

Table1 shows the results of this comparison. The two vacuum samplers were run first, and the GCMS method response factors were adjusted based on the average response of these samplers. All 8 of the HDS samplers were first weighed after sampling to determine the weight gain and therefore the amount of air collected and the corresponding dilution factors. Then, each were analyzed, followed by evacuation and re-weighing so that the dilution factors for each could be determined. The resulting dilution factors shown in Table 1 indicate the consistency in which the samplers collected their respective samples. The results for both the 15 minute and the 8 hour samplers showed no sampling rate dependency on the compound collected, from the lightest to heaviest compounds, indicating that the diffusion component for compounds entering into the sampler is negligible, resulting in sampling rates that were the same for all compounds relative to air. That simplifies things tremendously compared to other diffusive samplers that show a substantial difference on sampling rates for different compounds, and even as the environmental matrix changes. No matrix effects are seen with HDS samplers, as there are no adsorbent boundaries so competitive uptake issues have been eliminated.



	15 Minute Chamber Summary				8 Hour Chamber Summary			
	HDS-1	HDS-2	HDS-3	HDS-4	HDS-1	HDS-2	HDS-3	HDS-4
HDS Dilution Factor	3.42	3.27	3.45	3.31	3.27	3.25	3.23	3.23
Analyte								
Dichlorotetrafluoromethane	1.09	1.05	1.10	1.06	1.11	1.07	1.10	1.10
Vinyl Chloride	0.82	0.82	0.83	0.79	0.82	0.78	0.81	0.84
Bromomethane	0.99	0.95	0.97	0.96	0.98	0.98	0.97	0.97
Chloroethane	0.96	0.92	0.97	0.93	0.98	0.94	0.97	0.94
Trichlorofluoromethane	0.99	0.95	1.00	0.96	1.01	0.98	1.00	1.00
1,1-Dichloroethene	0.96	0.92	0.97	0.93	0.98	0.98	0.97	0.97
1,1,2-Trichloro-1,2,2-Trifluoroethane	1.09	1.05	1.07	1.03	1.11	1.07	1.10	1.07
Methylene Chloride	0.96	0.92	0.97	0.93	0.98	0.98	1.00	0.97
1,1-Dichloroethane	0.96	0.88	0.93	0.89	0.95	0.91	0.94	0.90
cis-1,2-Dichloroethene	0.96	0.92	0.97	0.89	0.98	0.94	0.97	0.94
Chloroform	0.96	0.92	0.93	0.89	0.95	0.94	0.97	0.94
1,1,1-Trichloroethane	0.92	0.88	0.93	0.89	0.95	0.91	0.94	0.90
1,2-Dichloroethane	0.92	0.85	0.90	0.86	0.92	0.88	0.90	0.90
Benzene	1.09	1.01	1.07	1.03	1.08	1.04	1.07	1.07
Carbon Tetrachloride	0.99	0.95	1.00	0.96	1.01	0.98	1.00	1.00
Trichloroethene	0.96	0.92	0.97	0.93	0.98	0.94	0.97	0.97
1,2-Dichloropropane	0.99	0.95	1.00	0.93	0.98	0.98	0.97	0.97
cis-1,3-Dichloropropene	0.92	0.88	0.90	0.86	0.92	0.91	0.90	0.90
trans-1,3-Dichloropropane	0.92	0.88	0.90	0.86	0.95	0.91	0.94	0.94
Toluene	0.96	0.88	0.93	0.89	0.95	0.91	0.94	0.97
1,1,2-Trichloroethane	0.96	0.88	0.93	0.89	0.95	0.91	0.94	0.94
Tetrachloroethene	0.03	0.85	0.90	0.79	0.88	0.81	0.61	1.03
1,2-Dibromoethane	0.82	0.85	0.90	0.86	0.92	0.91	0.90	0.52
Chlorobenzene	0.92	0.85	0.90	0.86	0.95	0.91	0.94	0.90
Ethylbenzene	0.92	0.88	0.93	0.89	0.95	0.94	0.94	0.94
Styrene	0.89	0.85	0.90	0.86	0.95	0.91	0.94	0.90
o-Xylene	0.96	0.92	0.97	0.93	1.01	0.98	1.00	0.97
1,1,2,2-Tetrachloroethane	1.03	0.98	1.04	0.99	1.08	1.04	1.07	1.07
1,3-Dichlorobenzene	0.89	0.85	0.90	0.86	0.95	0.94	0.97	0.94
1,4-Dichlorobenzene	0.92	0.88	0.93	0.86	0.98	0.94	0.97	0.94
1,2-Dichlorobenzene	0.89	0.85	0.90	0.86	0.95	0.94	0.94	0.94
1,2,4-Trichlorobenzene	0.82	0.75	0.83	0.76	0.92	0.91	0.90	0.90
Hexachlorobutadiene	0.96	0.88	0.93	0.89	1.01	1.04	1.00	1.00

Table 1 - GCMS results comparing the collection of a 1 PPMv Standard using HDS Personal Monitors over 15 minutes and 8 hours compared to grab sampling and analysis by vacuum containers following the “Gold Standard” TO15 Method. Results were within the allowable deviation of Method TO15, indicating that Helium Diffusion Sampling collects the air sample “actively”, requiring no determination of individual sampling rates as is needed with badge sampling.

Summary

HDS Personal Monitors have a tremendous advantage over other diffusive samplers used for personal monitoring. To call a Helium Diffusion Sampler a diffusive sampler is incorrect, as it is more of a diffusive "emitter" considering how much faster helium diffuses relative to air or chemicals in air to be measured. Instead, it is better to think of HDS Personal Monitors as having a "helium driven pump" that slowly creates the vacuum that draws the sample in actively. This results in identical sampling rates between light and heavy compounds just as with classical Method TO15. The overall sampling rates are slower than for badges which eliminates the minimum face velocity requirements of 0.1-0.2 m/s. However, a far greater amount of the collected sample is analyzed, so the ultimate sensitivity of the HDS technique is better than with solvent extracted badges, especially for 15 minute STEL measurements. The elimination of solvent in the analysis of HDS samplers makes them ideal for GCMS analysis, creating far more certainty in the results relative to GC/FID instruments that can only identify compounds by retention time rather than additionally by their mass spectral fragmentation pattern. Each HDS Personal Monitor is tested for inertness by introducing a 0.02 PPM level mixture of challenging compounds, followed by analysis 1 week later to confirm recovery. With gravimetric confirmation of amount sampled and TO15 like performance, the HDS Personal Monitor holds great promise as the personal monitor of tomorrow.

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