



# A Simple, More Reliable Time Integrated Whole Air Sampling Approach To EPA Method TO15 Using Helium Diffusion Sampling

## Application Note: A-3732-01

### Authors

Thomas X. Robinson  
Chris Casteel  
Dan Cardin  
Entech Instruments, Inc.  
Simi Valley, CA 93065

### Abstract

A new, simplified approach for filling air sampling canisters during monitoring of Environmental pollutants in air is described. The new approach uses helium diffusion to drive the sampling process in a way that has several advantages over vacuum sampling. Canisters are filled with helium after cleaning, using a valve and inlet fitting combination that allows the proper time integrated sample to be collected simply by removing the valve and allowing helium to leak out through a calibrated orifice. Orifice sizes are available for performing a range of integration times from 3 hours to 1 month, without the need for an external flow controller. Elimination of the flow controller from the flow path reduces sample loss, prevents contamination from previous sampling events, greatly increases simplicity and reliability of the sampling process, and increases the molecular weight range recoverable to include Semi-Volatile compounds. Utilizing HDS can also reduce the potential for contamination during field and lab leak checking. Data is presented detailing the advantages of HDS, including comparisons with vacuum sampling canisters to show precision and sampling consistency.

### Introduction

EPA Methods TO-14A and TO-15 utilize stainless steel canisters of various sizes to collect ambient air for laboratory analysis of volatile compounds at PPB to sub-PPB levels. Canisters are generally filled



either by taking a grab sample to allow vacuum in the canister to pull the air sample in, or by using a flow controlling device external to the canister to control the flow over time in order to get a time weighted average. To achieve time integrated sampling over several hours or more, flow controllers with a fairly complicated flow path are used to obtain the required constant sampling flow rate. These flow controllers typically have a filter, a small flow limiting orifice, a diaphragm, and a control nozzle, that include 4 o-rings in the flow path. Several problems are associated with time integrated sampling using these external flow controllers, including potential carryover from previous sampling events, reduced recovery due to particulates or deposits in the flow path, and the variability of the flow rate caused by rough handling while transporting to the field.

In addition to potential flow controller issues, using vacuum to collect the sample has its own drawbacks. Vacuum invites the influx of contaminants from the moment the canister is removed from the cleaning system. During shipping to the field, the canister may be exposed to high levels of VOCs in packing materials used to ship the canisters. The EPA methods require

the verification of vacuum in the field prior to sampling, however, the small 1.5" crude vacuum gauges typically used are unable to detect a small leak of 0.1 to 2% of the contents of the canister. If the canister was exposed to high levels during shipping, a 1% leak a 1PPM is equivalent to a 100% leak at 10PPB.

Both in its simplicity and in the elimination of the vacuum checking steps, HDS monitoring solves these problems. With HDS, the control valve is removed, allowing an orifice "built into the top of the canister" to control the sampling. This greatly reduces the potential for losses, because the first surface the sample touches is inside the canister. Carryover from the previous sampling event is also virtually eliminated as the flow controlling device is a part of the canister, and is therefore cleaned right along with the canister. Prior to sampling, HDS canisters are filled to a positive pressure with helium, allowing even the smallest of leaks to be detected, as helium will pass through a leak more quickly than air. While pressure checking in the field prior to removing the control valve, any contamination in the gauge will be pushed further into the gauge rather than back into the canister, as the canister will be higher than atmospheric pressure if there are no leaks. Excess helium in the canister quickly equilibrates to atmospheric pressure upon removing the valve, and the canister then remains at atmospheric pressure during the entire sampling process, eliminating the need to measure the pressure again after sampling and avoiding yet another chance for contamination.

Upon delivery to the lab, the canisters are weighed to determine the amount actually sampled. Due to the weight difference between air and helium, the % air sampled can generally be determined to +/-1% without ever having to open the canister. Pressure measurement in the lab is therefore not necessary, avoiding another potential opportunity for contamination. Since every canister will have a different empty weight, the canister just has to be weighed again after it is evacuated, at which point the % air in the original sample can be determined accurately in order to determine the dilution of the original sample. Approximately 50% of the helium is exchanged with air during sampling. Helium Diffusion

Sampling utilizes both the fact that helium diffuses faster than air, and that it is lighter than air and pollutants in air. Helium exchanges through an orifice of an appropriate size to fill a canister to 50% over the required monitoring period. Since the canister cannot change size, this can be thought of as a helium driven pump that slowly creates a vacuum over time to pull in the sample. One of the reasons that the exchange rate remains virtually constant is that the diffusion zone is a mixture of air and helium from the very start, with a ratio that is very similar at the start vs when nearing 50% air in the canister. Once air and pollutants are sampled into the canister, no losses occur due to their inability to escape through the diffusion tube with the lighter helium present. This has been demonstrated both by using a BFB surrogate which remains at the same concentration during the sampling period, and by exposing the sampler to a high concentration of compounds as light as propane at the beginning of the sampling event, and then placing the sampler in zero air or nitrogen with no subsequent loss of propane over the remaining sampling period.

The following presentation describes a system that accomplishes this, providing a truly quantitative representation of headspace concentrations from compounds as light as propane to those as heavy as C24 hydrocarbons.

## Experimental

### 24 Hour Sampling - HDS vs Vacuum

To compare the precision and relative accuracies of classical vacuum sampling compared to HDS, 24 hour sampling of room air was conducted in Simi Valley, CA, at Entech's manufacturing facility. The following canisters were used in the study:

6L Silonite™ evacuated canisters with classical time integrating samplers (x3)

1.4L Silonite™ canisters with HDS Inlets (x3)

0.45L Silonite™ canisters with HDS Inlets (x2)

The 6L canisters used the time tested Entech CS1200E4 which maintains a constant flow rate during a 24 sample collection. These flow controllers were cleaned before sampling, and new filters were installed.

Both the 1.4L and the 0.45L Silonite canisters were fitted with new HDS sampler fittings that give the proper sampling rate for a 24 hour sample collection simply by removing the valve, then replacing it in 24 hours. Samples were collected then analyzed on the following analytical system.

Entech 7500A Robotic Canister Autosampler  
 Entech 7101AR Preconcentrator  
 Agilent 6890/5973 GCMS

Automation of the preconcentration procedure was accomplished using the Entech 7500A robotic autosampler which allows all samples to be analyzed through exactly the same flow path while eliminating rotary valves. Samples were analyzed at room temperature.

Standards were prepared for method calibration using the Entech 4601A Dynamic Diluter, and both the vacuum and HDS canisters were cleaned using the Entech 3120A Canister Cleaner.

The analytical sample volume for the 6L and 1.4L canisters was 400cc, while just 200cc was extracted from each 0.45L canister. The 1.4L and 0.45L MiniCans were weighed to verify that 50% of the helium was properly exchanged with air at the end of 24 hours. Analysis on the 7101AR required that the results be multiplied by 0.83x to account for the difference in mass flow controller response when analyzing a sample of 50% air in helium, rather than a canister filled with 100% air. A new Preconcentrator design, the Entech 7150, uses a novel new approach to volume measurement that eliminates the need to adjust the results, as a true sample volume measurement is made during analysis which is indifferent to the composition of the makeup gas.

$$\%Air = \frac{(\text{Mol. Wt Air}) \times (\text{Wt. Sample} - \text{Empty Wt}) / (\text{Wt. Air} - \text{Empty Wt}) - \text{Mol Wt Helium}}{(\text{Mol. Wt Air} - \text{Mol. Wt Helium})}$$

for 1.4L MC1400H Can and lab elevation of 700 feet, equation simplifies to,

$$\%Air = \frac{30 \times (\text{Wt. Sample} - \text{Empty Wt}) / 1.475 - 4}{26}$$

	10%	20%	30%	40%	50%
Wt. sample	435.346	439.338	435.55	434.709	436.749
Wt. empty	435.004	438.867	434.957	433.99	435.911
Calc %Air	11.4	21.5	31.0	40.9	50.2
Wt. sample	435.354	439.34	435.552	434.707	436.744
Wt. empty	435.014	438.876	434.966	433.998	435.919
Calc %Air	11.2	20.9	30.5	40.1	49.2
Wt. sample	435.357	439.344	435.555	434.71	436.749
Wt. empty	435.013	438.871	434.966	433.996	435.917
Calc %Air	11.5	21.6	30.7	40.5	49.7
STDEV	0.1565	0.3697	0.2747	0.3911	0.5090
MEAN	11.4	21.3	30.7	40.5	49.7
%RSD	1.4	1.7	0.9	1.0	1.0

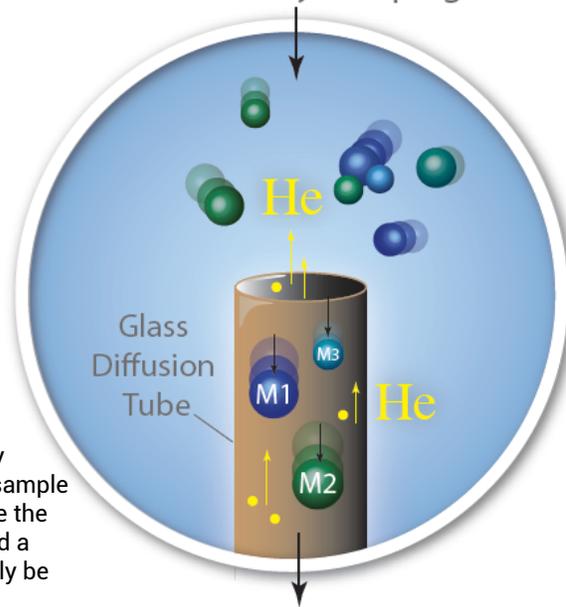
**Table 1** With HDS Monitoring, the amount sampled is not determined by testing the pressure, as the pressure will be 1 atmosphere. Rather, the sample is weighed before it is analyzed and again after evacuation to determine the % air sampled relative to remaining helium. For a given lab elevation and a given canister size, the weight of air at 1 atm is a constant and need only be determined once.

### HDS Sampling Rates vs Face Velocities

	Empty	Sampled	% Air
Closet	461.362	462.100	50.0
Outdoors	469.794	470.530	49.9
Indoors	458.940	459.652	48.3

**Table 2** This table shows the amount of air collected based on weight gain. Under all 3 conditions, the amount of air sampled was virtually identical, indicating that face velocity over the top of the samplers does not affect HDS rates.

Air is actively drawn into the vacuum created by escaping Helium



Compounds "sink" around rising Helium and are captured for analysis

**Figure 1** Graphic display of how HDS works. Helium exchanges through an orifice of an appropriate size to fill a canister to 50%.

## Discussion

### Calculating Amount Sampled

Although the amount of air sampled is very consistent, there is no reason to have to “assume” that the sampling occurred properly. The actual volume of air can be determined without ever having to open the container to measure the pressure. Since HDS samples will be at atmospheric pressure, measuring the pressure would not give any information about the amount of air in the canister. Simply by weighing the canister prior to analysis, and then again after evacuation, the percentage of air can be determined gravimetrically, which is generally more accurate than pressure measurements. Although the general equation used to calculate the % air requires the weight of 100% air in a particular canister, it has been determined that canisters of the same nominal size are so close in their relative internal volumes that this measurement only needs to occur once. In Table 1, 3 different canisters were filled to 10, 20, 30, 40, and 50% air in helium, and the % air was then determined as if each was an unknown. The average weight of air at atmospheric pressure in the 1.4L canisters was determined to be 1.475g, which was then used for each calculation above to fill in the table. Results were all within 1-2% of the target.

### Face Velocity Effects on Sampling Rates

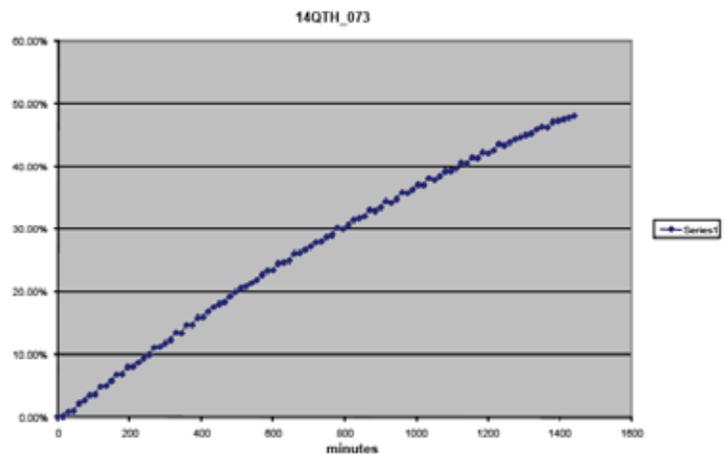
With other diffusive sampling techniques, the rate of air flowing over the sampler can have a dramatic effect on the rate of sample uptake. Badge samplers require a flow rate of at least 0.1 m/sec over the badge to prevent “starving” of the sample, while passive sampling with tubes can easily result in substantial reverse adsorption as well as highly variable sampling rates. Considering both that the diffusion of helium out of the canister results in active transport of air in and that the overall sampling rate is very slow (0.01 to 0.5 cc/min), a change in sampling rate in still vs moving air was not expected to be an issue. To test this, three 24 hour samples were taken as follows:

1. Indoors inside of a closet (still air)
2. Indoors exposed to normal air movement
3. Outdoors in a 1-5 mph wind.

Table 2 shows the amount of air collected based on weight gain. Under all 3 conditions, the amount of air sampled was virtually identical, indicating that face velocity over the top of the samplers does not affect HDS sampling rates.



**Figure 2** 6L Classical sampling canisters collecting 24 hour samples along side smaller 0.45L and 1.4L HDS's.



**Graph 1** Weight gain vs Time for 24 hour 1.4L HDS. Sampling profiles are very consistent due to the ease of controlling the ID of the helium diffusion zone, and the fact that sampling rates are then only dependent on physical constants; primarily, the diffusion rate of helium at atmospheric pressure. Meteorological fluctuations in atmospheric pressure at a given elevation are normally +/- 1%, and can therefore be excluded from the calculations.

Analyte	CS1200E4 + 6L Cans			HDS 1.4L MiniCans			HDS 0.45L MiniCans	
	1	2	3	1	2	3	1	2
Dichlorodifluoromethane	0.47	0.47	0.47	0.42	0.46	0.42	0.49	0.53
Chloromethane	0.30	0.32	0.32	0.38	0.34	0.38	0.38	0.38
Trichlorofluoromethane	0.26	0.28	0.29	0.30	0.30	0.32	0.34	0.34
Acetone	9.9	10.8	10.6	11.9	10.8	12.6	12.1	12.8
Isopropyl Alcohol	3.3	3.9	3.3	3.3	3.2	3.7	5.0	4.0
2-Butanone	0.44	0.48	0.46	0.46	0.44	0.44	0.49	0.57
Hexane	0.13	0.13	0.12	0.14	0.12	0.12	0.11	0.15
Ethyl Acetate	0.40	0.40	0.39	0.36	0.34	0.30	0.38	0.34
Benzene	0.17	0.19	0.18	0.22	0.22	0.22	0.30	0.27
Toluene	0.62	0.69	0.66	0.58	0.56	0.58	0.57	0.53
m,p-Xylenes	0.41	0.45	0.41	0.40	0.40	0.40	0.38	0.38
o-Xylene	0.16	0.17	0.16	0.16	0.16	0.16	0.15	0.15
2,2,4-Trimethylpentane	0.14	0.16	0.13	0.14	0.14	0.14	0.15	0.15

**Table 3** Comparison of 24 hour sample collection using HDS into 0.45L and 1.4L canisters, vs classical vacuum sampling into 6L canisters using CS1200E4 flow controllers. The compact size, ease of implementation, and virtual elimination of the sample train is a major advantage which would be obvious to anyone who has performed TO-14A and TO-15 Environmental Monitoring.



**Figure 3** Close up view of the HDS inlet orifice built right into the 1.4L canister valve.

## Results

The results are shown in Table 3. All compounds detected in the room air were reported, and concentrations determined by the 3 sampling approaches agreed quite well, certainly well within the precision requirements of EPA Methods TO-14A and TO-15. The o-rings in the CS1200 have been shown to contribute 0.1-0.2 PPB toluene to collected samples over 24 hours in the past without an extensive cleanup, which is about the amount that toluene in the 6L vacuum sampled canisters was reported over the HDS samplers. The agreement between the 3 different approaches is particularly impressive considering many of the reported concentrations are near or below the reporting limits for EPA Method TO-15, which usually causes a little more inaccuracy in the results.

## Results

HDS samplers were shown to provide equivalent analytical results to classical vacuum samplers, while allowing even smaller containers to be used. With the elimination of the external flow controller, potential contamination is greatly reduced, improving the reliability of the monitoring event. Elimination of the flow path prior to the canister should also substantially increase the molecular weight range compatibility of HDS samplers relative to vacuum samplers, as the first surface the sample touches is inside of the canister. Although the CS1200E4 samplers connected to the 6L canisters were also shown to give precise results, new flow controllers and filters were utilized. After real world exposure, filters are not always changed out as frequently as needed, which may have a negative impact on target compound recovery and the level of carryover due to particulate build up. Filters are not needed with HDS, since the small orifices required for flow controllers are avoided.

HDS is an important next step in the advancement of canister monitoring technology. Lower costs, expanded molecular weight range, ease of use, and improved precision and reliability are all features of this new technique. HDS works both with Silonite coated MiniCans and glass Bottle-Vac canisters. Particulates can be easily removed from Silonite™ MiniCans, while glass bottles can be discarded after 5-10 samplings.



**[www.entechinst.com](http://www.entechinst.com)**

Entech Instruments, Inc. shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Entech Instruments, Inc.

