
A New Approach to Whole Air Sampling using Deactivated Glass Bottles



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Abstract

Current EPA Methods TO-14 and TO-15 call for the use of metal canisters to collect whole air samples for transport and subsequent analysis at the laboratory. Tedlar bags are a lower cost alternative for collecting volatiles in air, but are more limited due to shorter holding times and poor stability of heavier VOCs. It is this lower recovery and much shorter holding time that prevents the use of Tedlar bags for the ambient whole air methods TO-14A and TO-15. A more cost-effective approach to air sampling and analysis that yields similar performance to stainless steel canisters has now been obtained from deactivated glass containers called Bottle-Vac™ samplers. Data is presented that demonstrates the inertness and ease of use of this new type of air sampler.

Introduction

The advantages of collecting whole air samples rather than concentrating samples onto adsorbent traps out in the field are well understood. They include:

- No need to calibrate collection equipment, analytical sample volume is determined in the laboratory



32 oz and 16 oz Bottle-Vac Samplers with ultra-leak-tight Micro-QT Valves.

- The ability to re-analyze a sample should something go wrong with the analysis, such as inappropriate sample injection amount for the GCMS.
- A reduction in surface activity, minimizing artifact formation

Elimination of site history requirements to determine proper sampling volumes and media choices
- The ability to analyze any fraction of the collected sample, rather than performing a one-time thermal desorption

While whole air sampling provides many advantages, the higher cost of canisters and the inconsistent performance obtained from Tedlar bags has limited their acceptance.

Bottle-Vac samplers are deactivated glass containers which have canister-like performance at a cost that is just a few times that of Tedlar bags. Each Bottle-Vac sampler is fitted with a low volume valve called a Micro-QT Valve that allows the container to be cleaned and evacuated prior to field sampling. Like canisters,

Bottle-Vac samplers are cleaned by alternating between evacuating and filling with humidified nitrogen or zero air, usually while heating the container. A final evacuation into the mtorr range is then performed before deployment to the field. Two to three cycles of filling and evacuation are generally enough to clean the container to sub-PPB levels.

Higher-level source samples may require only a single evacuation to prepare the bottle for sampling if detection limits are in the high PPB or PPM range. The normal particulate filters required for canister sampling become less necessary since the glass bottle itself is inexpensive enough to replace after 5-10 sampling events. The Micro-QT valve on the Bottle-Vac sampler is small enough to be vacuum baked in quantities using large vials (500mL) fitted with the same type of sampling valve. Although vacuum baking the fittings will rapidly out-gas contaminants, it is generally only necessary if the valves are exposed to high sample concentrations.

Bottle-Vac sampling is performed either by connecting a restricted inlet device for time-weighted sampling, or simply by unscrewing the cap and tilting the valve to break the vacuum seal to obtain a grab sample. Instant grab sampling is the preferred sampling procedure for indoor air quality and mold investigations (MVOC monitoring) because VOC concentrations tend to be more constant than in outside air, eliminating the need for time-weighted averaging. This results in a very fast and low cost solution for indoor air quality monitoring.

Experimental Section-Sampling

A source level study was performed by introducing an EPA Method TO-14 standard (Spectra Gas, NJ) containing 39 different aromatic and halogenated compounds at 1 PPM into two 16 oz Entech Bottle-Vac samplers, two 1 Liter SKC Tedlar Bags, and two Entech 0.6 Liter Silonite Mini-Cans. The containers were analyzed for recovery via loop injection using an Entech 7032A-L and an Agilent 6890/5973 GCMS. This system generally provides very good reproducibility (+-3%RSDs) which was important both to obtain high confidence in the reported results, and to show any small differences between the sampling devices. The holding time was only 3 days for the Tedlar bags, since most methods describe this as the maximum allowable time before

recoveries are no longer acceptable. The Bottle-Vac Samplers and Silonite MiniCans were analyzed after 5 days to demonstrate their longer holding times relative to Tedlar bags.

Ambient level recovery testing was also performed with a lower level EPA Method TO-15 standard containing 64 different aromatic, halogenated, and oxygenated compounds. The 10 ppb standards were prepared from 1.0 ppm Spectra Gas stock cylinders using an Entech 4600A Dynamic Diluter. The standards were prepared in duplicate into 0.6 Liter Silonite Canisters, and 16 oz Bottle-Vac Samplers. Recovery testing was performed at room temperature after 7 days, and then again at 60 deg. C after 11 days to investigate any advantages of heating during the analysis.

Sample Introduction Systems

High Level:

7032AQ-L 21 position loop autosampler 7100A Preconcentrator (Entech Instruments, Inc.)

Low Level:

7500 Autosampler with sample heating oven 7100A : Extended Cold Trap Dehydration

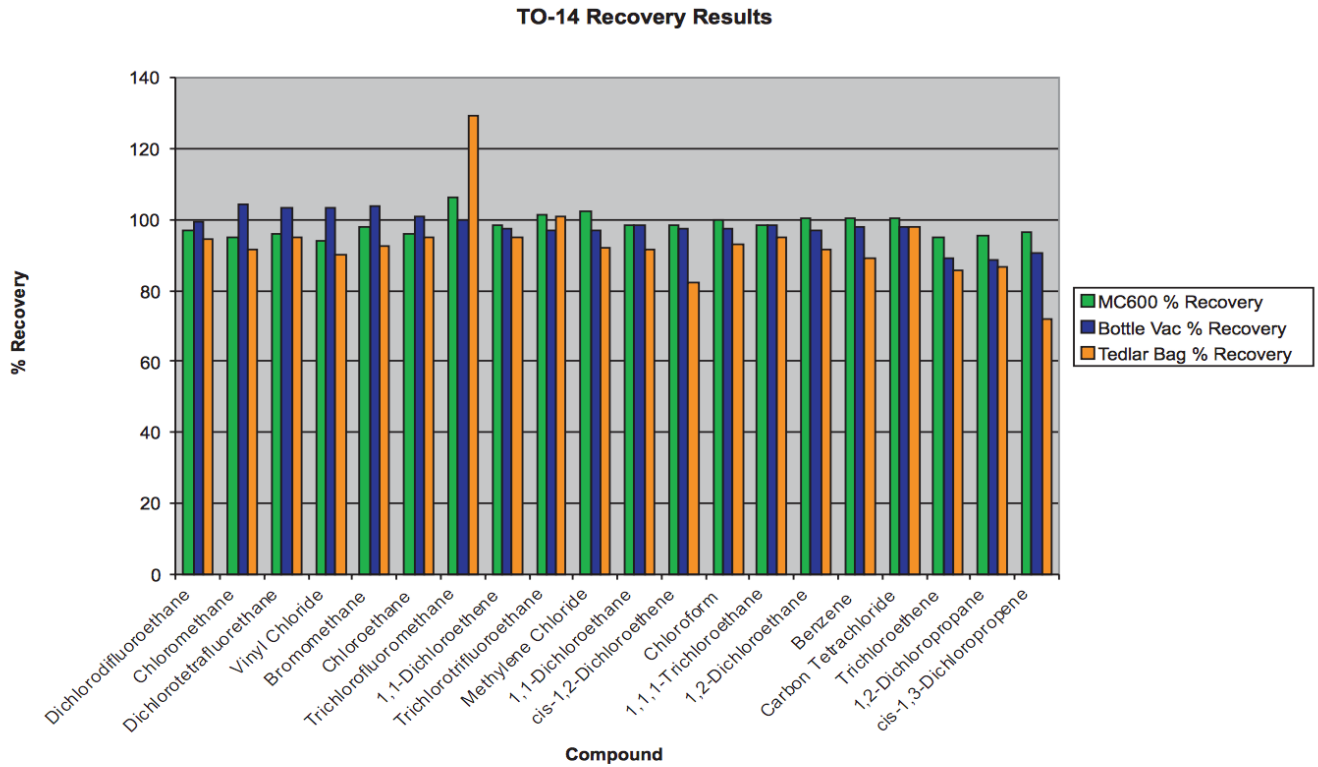
A 7032AQ-L/7100A was used to analyze 1cc of the standard from each container by first concentrating the 1cc down to a few microliters in the 7100A in order to make a splitless injection into the GCMS. Although the 7032AQ-L can also be used to direct large volumes of up to 1L to the 7100A, for this study the 7500 Robotic Autosampler was used for the trace level analysis due to its ability to individually heat all samples prior to analysis.

GCMS System

Agilent 6890/5973N (Palo Alto, CA)

Column: DB-1, 0.32mm ID, 60 m, 1um Temperature Program: 35C (5 min), 6C/min to 140C, 15C/min to 220C. Hold @ 220C for 3 min.

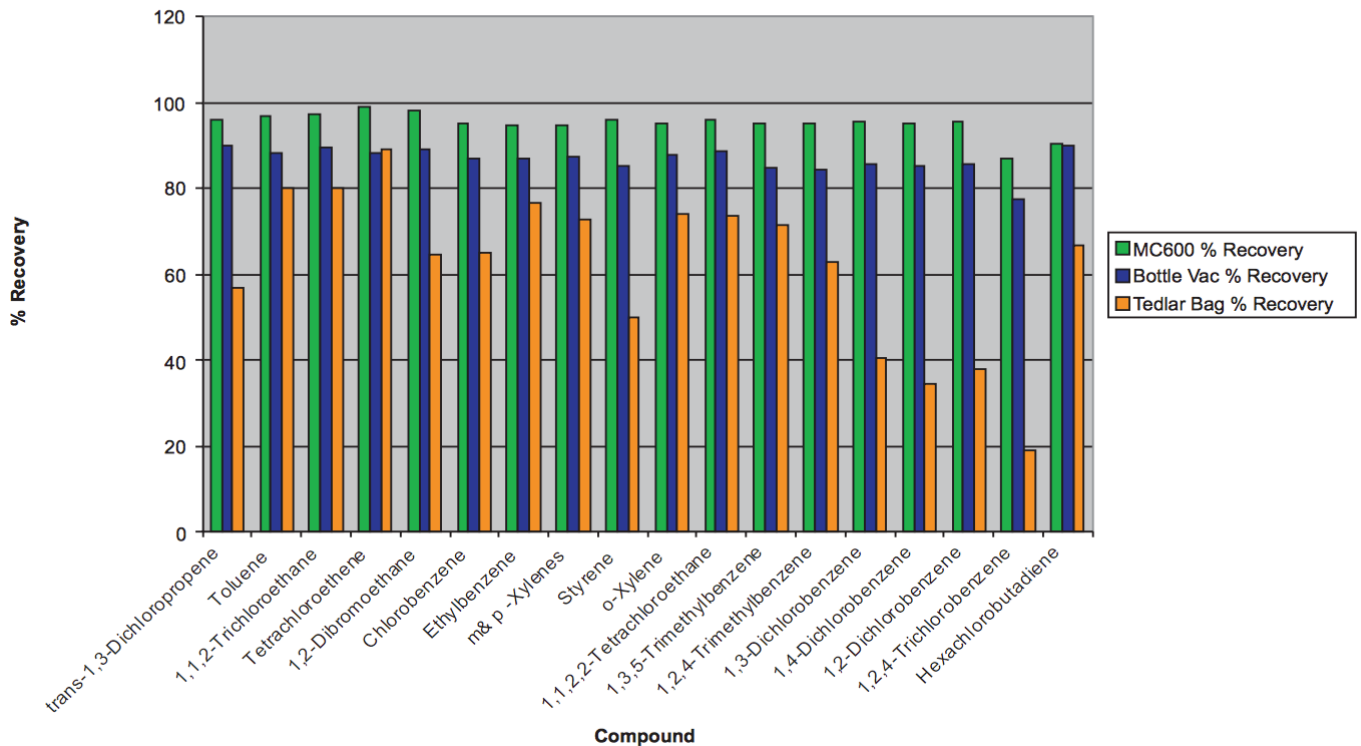
**Figure 1. 3 day Tedlar bag / 5 day Bottle-Vac and Silonite MiniCan Stability Data.
TO-14A Standard @ 1 PPM**



TO-14 Recovery Results

Compound

TO-14 Recovery Results



Results and Discussion

For source level testing the relative recovery of a 1-ppm EPA Method TO-14 standard from two currently accepted and commonly used media, the Silonite coated canister and the Tedlar bag, were compared with the new Bottle-Vac sampler. Two of each media type were run and the averages were calculated for recovery comparisons. Figure 1 represents the 3-day recovery from Tedlar bags (3 days is considered their maximum holding times), and the 5-day recovery results from the MC600L Silonite canister and BV460A Bottle-Vac Sampler.

The results of these tests are quite revealing. As expected, the overall performance of the Silonite coated canister is superior with nearly 100% recovery for all compounds over the 5-day period. The Bottle-Vac samplers closely follow these results. However, dramatic recovery losses are seen with Tedlar bags, especially with the heavier components, even though the bags were tested only after 3 days rather than 5 days.

Low Concentration Study

The stability of a lower concentration (10 ppb) EPA Method TO-15 standard was also evaluated. The TO-15 standard contains more polar and reactive species and therefore is a more rigorous test of sampling container inertness. This data is included in Table 1.

As seen in the earlier data, a slight reduction was noted for the heavier compounds when analyzed at room temperature. However, when the same containers were heated to 60°C, the recoveries improved to just over 100% relative to the unheated Silonite coated stainless steel canister. Using the 7500 autosampler, the Bottle-Vac containers were heated to the pre-programmed temperature for 15 minutes prior to sample concentration. Pre-heating extends the range of compounds amenable to canister and Bottle-Vac

analysis into the light SVOC range. Pre-heating is typically not an option for bag samples.

Co-collected water can interfere with the analysis of certain reactive compounds such as Formaldehyde, Hydrogen Sulfide, and light mercaptans. These compounds are very soluble in water and can ultimately react in the presence of water. Evidence of this effect is seen in the 7-day versus 11-day recovery results for Formaldehyde. In the 7-day analysis, the Bottle-Vac samplers were analyzed at room temperature. At this temperature, co-collected water forms a layer on the walls of the container causing partial absorption of these highly water soluble compounds. In the 11-day analysis, the samplers were heated to 60°C for 15 minutes prior to analysis. This heating reduces the relative humidity in the sample container and drives the adsorbed water layer off the walls of the container, thus liberating the co-adsorbed, water soluble species. Formaldehyde was shown to increase from 42 to 83% upon heating to 60°C. Sample concentration was performed on the Entech 7100A using Extended Cold Trap Dehydration, which allows recovery of formaldehyde and other polar VOCs while eliminating up to 95% of the water vapor in the sample.

Table 2 shows a holding study conducted with both Bottle-Vac samplers and Silonite canisters. A 30 day holding time exceeds that of Tedlar bags by tenfold, yet all TO-15 compounds tested had acceptable recoveries, including polar VOCs. This confirms that the Viton o-ring used to seal the Micro-QT valve to the bottle does not result in significant absorption of TO-15 analytes. It is recommended that these fittings and their o-rings be vacuum baked separately from the bottle if they are exposed to higher sample concentrations. This is done quite easily on an oven-based canister cleaner using vacuum-compatible headspace vials, available from Entech, which range in size from 125mL to 1000mL.

Table 1 - TO-15 Stability testing in Bottle-Vac Samplers

| Compound 10ppbv | 7-day Normalized | | |
|---------------------------|--------------------------------------|-------------------------|--|
| | 7-day Normalized MC600 % Recovery | Amber Jar % Recovery | 11-day heated Normalized Amber Jar % Recovery |
| Formaldehyde | 100.0 | 41.7 | 82.8 |
| Propene | 100.0 | 100.9 | 95.2 |
| Dichlorodifluoroethane | 100.0 | 104.3 | 80.0 |
| Chloromethane | 100.0 | 112.8 | 104.0 |
| Dichlorotetrafluoroethane | 100.0 | 104.2 | 84.6 |
| Acetaldehyde | 100.0 | 115.8 | 115.2 |
| Vinyl Chloride | 100.0 | 112.3 | 104.4 |
| 1,3-Butadiene | 100.0 | 111.5 | 105.4 |
| Bromomethane | 100.0 | 109.3 | 102.8 |
| Chloroethane | 100.0 | 110.6 | 105.6 |
| Bromoethene | 100.0 | 106.5 | 102.4 |
| Trichlorofluoromethane | 100.0 | 112.2 | 105.2 |
| Acetone | 100.0 | 115.3 | 120.8 |
| Propanal | 100.0 | 115.2 | 121.4 |
| Isopropyl Alcohol | 100.0 | 106.2 | 106.0 |
| 1,1-Dichloroethene | 100.0 | 98.0 | 98.6 |
| Trichlorotrifluoroethane | 100.0 | 99.7 | 101.0 |
| Allyl Chloride | 100.0 | 96.0 | 98.8 |
| Methylene Chloride | 100.0 | 100.3 | 100.2 |
| Carbon Disulfide | 100.0 | 100.4 | 100.2 |
| trans-1,2-Dichloroethene | 100.0 | 98.2 | 99.0 |
| Methyl tert-Butyl Ether | 100.0 | 95.8 | 98.4 |
| Vinyl Acetate | 100.0 | 97.3 | 96.2 |
| 1,1-Dichloroethane | 100.0 | 100.7 | 100.2 |
| 2-Butanone | 100.0 | 98.4 | 80.6 |
| Hexane | 100.0 | 100.6 | 102.2 |
| cis-1,2-Dichloroethene | 100.0 | 99.1 | 100.6 |
| Ethyl Acetate | 100.0 | 97.6 | 105.0 |
| Chloroform | 100.0 | 100.6 | 102.0 |
| Tetrahydrofuran | 100.0 | 95.2 | 98.6 |
| 1,1,1-Trichloroethane | 100.0 | 98.9 | 101.2 |
| 1,2-Dichloroethane | 100.0 | 100.6 | 101.8 |
| Benzene | 100.0 | 103.3 | 109.6 |
| Carbon Tetrachloride | 100.0 | 99.8 | 102.4 |
| Cyclohexane | 100.0 | 99.3 | 102.8 |
| 2,2,4-Trimethylpentane | 100.0 | 100.4 | 102.0 |
| Heptane | 100.0 | 99.3 | 100.6 |
| Trichloroethene | 100.0 | 99.0 | 102.2 |
| 1,2-Dichloropropane | 100.0 | 99.8 | 102.2 |
| 1,4-Dioxane | 100.0 | 92.8 | 99.8 |
| Bromodichloromethane | 100.0 | 98.5 | 101.2 |
| cis-1,3-Dichloropropene | 100.0 | 97.6 | 100.2 |
| 4-Methyl-2-pentanone | 100.0 | 98.7 | 103.2 |
| trans-1,3-Dichloropropene | 100.0 | 98.4 | 101.8 |
| Toluene | 100.0 | 98.2 | 103.6 |
| 1,1,2-Trichloroethane | 100.0 | 98.3 | 101.8 |
| 2-Hexanone | 100.0 | 93.3 | 99.4 |
| Dibromochloromethane | 100.0 | 96.4 | 101.0 |
| Tetrachloroethene | 100.0 | 97.0 | 102.0 |
| 1,2-Dibromoethane | 100.0 | 99.6 | 104.4 |
| Chlorobenzene | 100.0 | 98.9 | 102.8 |
| Ethylbenzene | 100.0 | 97.1 | 101.2 |
| m& p -Xylenes | 100.0 | 98.0 | 109.2 |
| Styrene | 100.0 | 97.7 | 104.4 |
| o-Xylene | 100.0 | 98.2 | 102.2 |
| Bromoform | 100.0 | 94.4 | 99.4 |
| 1,1,2,2-Tetrachloroethane | 100.0 | 100.4 | 102.8 |
| 4-Ethyltoluene | 100.0 | 95.2 | 103.2 |
| 1,3,5-Trimethylbenzene | 100.0 | 96.2 | 101.6 |
| 1,2,4-Trimethylbenzene | 100.0 | 96.1 | 104.0 |
| 1,3-Dichlorobenzene | 100.0 | 99.1 | 104.4 |
| Benzyl Chloride | 100.0 | 95.6 | 105.4 |
| 1,4-Dichlorobenzene | 100.0 | 100.3 | 107.0 |
| 1,2-Dichlorobenzene | 100.0 | 95.2 | 103.4 |
| 1,2,4-Trichlorobenzene | 100.0 | 87.1 | 106.6 |
| Hexachlorobutadiene | 100.0 | 94.1 | 105.8 |

Table 2 - Long Term Stability Testing in Bottle-Vacs and Silonite Canisters

| Analyte | Canister % Recovery | | | Bottle-Vac % Recovery | |
|---------------------------------------|---------------------|--------|---------|-----------------------|--------|
| | 2 week | 3 week | 4 Month | 2 week | 30 Day |
| Propene | 99 | 97 | 89 | 100 | 91 |
| Dichlorodifluoromethane | 94 | 95 | 92 | 102 | 95 |
| Chloromethane | 93 | 93 | 90 | 95 | 85 |
| Dichlorotetrafluoromethane | 87 | 91 | 91 | 95 | 96 |
| Acetaldehyde | 99 | 96 | 96 | 96 | 104 |
| Vinyl Chloride | 95 | 93 | 90 | 96 | 95 |
| 1,3-Butadiene | 96 | 94 | 86 | 95 | 100 |
| Bromomethane | 96 | 95 | 94 | 97 | 101 |
| Chloroethane | 95 | 95 | 90 | 96 | 93 |
| Bromoethene | 94 | 95 | 91 | 97 | 93 |
| Trichlorofluoromethane | 95 | 95 | 92 | 97 | 94 |
| Acetone | 91 | 91 | 83 | 103 | 102 |
| Propanal | 93 | 92 | 82 | 100 | 87 |
| Isopropyl Alcohol | 90 | 96 | 92 | 99 | 116 |
| 1,1-Dichloroethene | 96 | 95 | 90 | 95 | 98 |
| 1,1,2-Trichloro-1,2,2-Trifluoroethane | 95 | 95 | 91 | 98 | 98 |
| Methylene Chloride | 96 | 96 | 92 | 99 | 99 |
| Allyl Chloride | 95 | 94 | 86 | 98 | 92 |
| Carbon Disulfide | 98 | 97 | 92 | 97 | 99 |
| trans-1,2-Dichloroethene | 95 | 94 | 88 | 96 | 97 |
| Methyl-tert-Butyl Ether | 89 | 90 | 84 | 93 | 92 |
| 1,1-Dichloroethane | 96 | 95 | 91 | 95 | 96 |
| Vinyl Acetate | 88 | 87 | 76 | 94 | 92 |
| 2-Butanone | 89 | 87 | 77 | 109 | 104 |
| Hexane | 97 | 96 | 89 | 99 | 99 |
| cis-1,2-Dichloroethene | 94 | 93 | 88 | 97 | 89 |
| Ethyl Acetate | 88 | 87 | 76 | 93 | 94 |

Table 2 - Long Term Stability Testing in Bottle-Vacs and Silonite Canisters (Cont'd)

| Analyte | Canister % Recovery | | | Bottle-Vac % Recovery | |
|---------------------------|---------------------|--------|---------|-----------------------|--------|
| | 2 week | 3 week | 4 Month | 2 week | 30 Day |
| Chloroform | 95 | 95 | 92 | 95 | 95 |
| Tetrahydrofuran | 91 | 91 | 81 | 94 | 128 |
| 1,1,1-Trichloroethane | 95 | 95 | 92 | 94 | 94 |
| 1,2-Dichloroethane | 94 | 93 | 89 | 96 | 94 |
| Benzene | 96 | 94 | 90 | 100 | 102 |
| Carbon Tetrachloride | 95 | 94 | 92 | 95 | 93 |
| Cyclohexane | 98 | 97 | 92 | 97 | 98 |
| 2,2,4-Trimethylpentane | 97 | 98 | 97 | 96 | 96 |
| Heptane | 97 | 98 | 97 | 97 | 96 |
| 1,2-Dichloropropane | 96 | 97 | 97 | 98 | 94 |
| Trichloroethene | 95 | 95 | 95 | 97 | 94 |
| Bromodichloromethane | 97 | 97 | 95 | 95 | 96 |
| 1,4-Dioxane | 110 | 105 | 74 | 97 | 94 |
| cis-1,3-Dichloropropene | 91 | 92 | 81 | 97 | 91 |
| 4-Methyl-2-Pentanone | 101 | 103 | 56 | 96 | 94 |
| trans-1,3-Dichloropropane | 82 | 81 | 62 | 97 | 97 |
| Toluene | 96 | 96 | 98 | 100 | 100 |
| 1,1,2-Trichloroethane | 96 | 96 | 97 | 96 | 97 |
| 2-Hexanone | 97 | 98 | 45 | 112 | 100 |
| Dibromochloromethane | 96 | 97 | 93 | 97 | 93 |
| 1,2-Dibromoethane | 92 | 91 | 83 | 99 | 96 |
| Tetrachloroethene | 96 | 96 | 78 | 99 | 94 |
| Chlorobenzene | 96 | 95 | 93 | 102 | 95 |
| Ethylbenzene | 97 | 96 | 96 | 100 | 93 |
| Bromoform | 96 | 100 | 90 | 99 | 97 |
| Styrene | 93 | 92 | 81 | 100 | 99 |
| o-Xylene | 98 | 98 | 99 | 101 | 96 |
| 1,1,2,2-Tetrachloroethane | 100 | 100 | 100 | 99 | 103 |
| 4-Ethyltoluene | 97 | 100 | 93 | 102 | 92 |
| 1,3,5-Trimethylbenzene | 99 | 97 | 100 | 106 | 98 |
| 1,2,4-Trimethylbenzene | 99 | 97 | 100 | 99 | 95 |
| 1,3-Dichlorobenzene | 99 | 96 | 91 | 97 | 93 |
| Benzyl Chloride | 93 | 96 | 65 | 99 | 83 |
| 1,4-Dichlorobenzene | 96 | 91 | 80 | 98 | 95 |
| 1,2-Dichlorobenzene | 104 | 100 | 103 | 96 | 94 |
| 1,2,4-Trichlorobenzene | 102 | 92 | 110 | 82 | 75 |
| Hexachlorobutadiene | 112 | 102 | 120 | 89 | 84 |

Conclusion

The recovery data for Bottle-Vac samplers is very comparable to Silonite Canisters, while demonstrating substantial improvement over Tedlar bags. Although canisters are 20-50 times more expensive than Tedlar bags, the cost of a Bottle-Vac sampler is only roughly 4-5x the cost of Tedlar bags and virtually the same as a multi-bed adsorbent tube. Unlike bags, Bottle-Vac samplers are reusable, resulting in a much more reliable and economical solution overall.

Bottle-Vac samplers share many of the advantages of canisters, including the ability to take quick grab sample or extended time-weighted averages. Unlike bags and tubes, ambient pressure sampling does not require a sampling pump because Bottle-Vacs are typically evacuated prior to field deployment. They offer a tremendous advantage over tube sampling when the concentrations are in the high PPB or PPM

range, allowing 1cc or less of the collected sample to be quantitatively transferred to a GC or GCMS. Finally, the ability to heat the Bottle-Vac using the 7500 Robotic Autosampler dramatically extends the molecular weight range that can be recovered, thereby eliminating one of the few advantages that the tube approach has had over whole air sampling.

Ease of sampling, higher analytical accuracy, and improved reliability make Bottle-Vac samplers an ideal replacement for Tedlar bags. They may be considered as a lower cost alternative to stainless steel canisters for many applications, although more field studies and evaluation have to be done before suggesting the use of Bottle-Vac Samplers in place of Silonite stainless steel canisters for trace level TO-15 applications such as Vapor Intrusion monitoring. Their low cost also make them ideal for performing dilutions in the laboratory when high concentration samples exceed the dynamic range of the inlet and GCMS system.

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