# Accurate Collection of Low Level TO-15 Compounds using Low Flow, 1 Week Time Integrated Sampling into Silonite Coated Canisters

## Application Note:

## A-3736-05

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## Abstract

An improved technique is demonstrated for the accurate collection of TO-15 compounds over 1-7 days. Constant sampling rates and good recoveries of all TO15 compounds are demonstrated, using very low sampling rates that could potentially result in target compound losses and carryover if exposed filters and surfaces are not properly passivated. Consistent sampling rates and analyte recoveries are demonstrated using 3 Silonite coated and 2 uncoated CS1200E5 samplers as collected into 5 different Silonite coated canisters. Sampling rates were below 1cc/min to simulate the sampling rates used for collecting one week samples into 6L canisters. Five CS1200E5 samplers were also connected to 6L canisters and allowed to sample for 1 week to demonstrate consistent target compound recovery, and consistent final fill pressures using an updated flow control design which improves consistency for 1 week sampling.

## Background

EPA Method TO15 requires that sampling trains be tested to show 80% or better recovery of target compounds using a challenge mixture. This is not always practical to demonstrate on a "per sample train" basis, but should at least be validated for a few of the sample trains being used by a laboratory to collect TO15 compounds. The method does not specify where the validation is to be conducted, and this may in fact be demonstrated by the manufacturer of the sampling trains.

Entech has been offering solutions for the collection and analysis of air samples for 25 years. Fifteen years ago, Entech published Application note #902 which detailed how to collect TO14 compounds properly when performing 24 hour sampling. In particular, it was found that losses of TO14 compounds WILL occur when using non-electropolished stainless steel inlet lines, and when using standard, non-silica treated Nupro filters. It also showed how temperature and humidity levels affected fill rates and recoveries during time integrated sampling.

The current application note 2014-05 expands upon App Note #902 by showing an extended range of compounds to include the typical TO15 polar compounds monitored by today's air laboratories. The concentration of the challenge mixture was also decreased by 20x down to 0.5PPB per component to better assess recoveries at trace levels. Slowing down sampling rates to below 1cc/min to perform 1 week sampling into a 6L canister results in even a longer residence time of the sample in the sample train, and therefore more potential for adsorption onto any active surfaces. Certainly, it should never be assumed that proper sampling is occurring simply because the vacuum is being reduced at a constant rate, as this does not prove that compounds are being transferred successfully to the canister. Collecting the right amount of Oxygen, Nitrogen, and Argon is not the goal, but rather the contaminants in

air down into the part-per-trillion range.

This application note demonstrates that when performed properly, 1 day to 1 week sampling into canisters still provides the only comprehensive approach for collecting all airborne VOCs, rather than being limited to benzene and heavier when using thermal desorption tubes for 1 week sampling under passive sampling conditions (no pump).  Five 1.4L Silonite canisters were used in this study with sampling rates of 0.8cc/min to simulate the filling of 6L canisters over a 1 week period of time.  The smaller canisters are used to demonstrate recoveries through the CS1200E sample train at these slow flow rates without having to maintain the external challenge standard at a 0.5PPB for an entire week.  Theoretically, the use of a smaller canister is even more challenging, as any losses that occur in the CS1200E are expected to be a fixed amount, so sampling 5 times less through the CS1200E should result in a larger percentage loss in a smaller canister.  Demonstrating good recovery in these smaller canisters should then indicate a minimum recovery expected when using a larger 6L canister.

The other important requirement for sampling over an entire week into 6L canisters is the ability for the flow controller to accurately sample at rates as low as 0.5cc/min.  Previous attempts to do this by Entech and others have not achieved the fill rate consistency needed to make this routine and easily accomplished.  A new modification to the Entech CS1200E5 flow controller has greatly improved flow stability and consistency, making 1 week sampling into 6L canisters as reliable as 24 hour sampling.  This will be demonstrated using 5 CS1200E5 samplers connected to 5 different 6L canisters to show consistency  of the final canister pressures and consistency in target analyte recovery.

## Experimental

Calibration standards were obtained from both Linde Gas and Air Liquide.  Three cylinders at 1 PPMv were blended together using an Entech Instruments
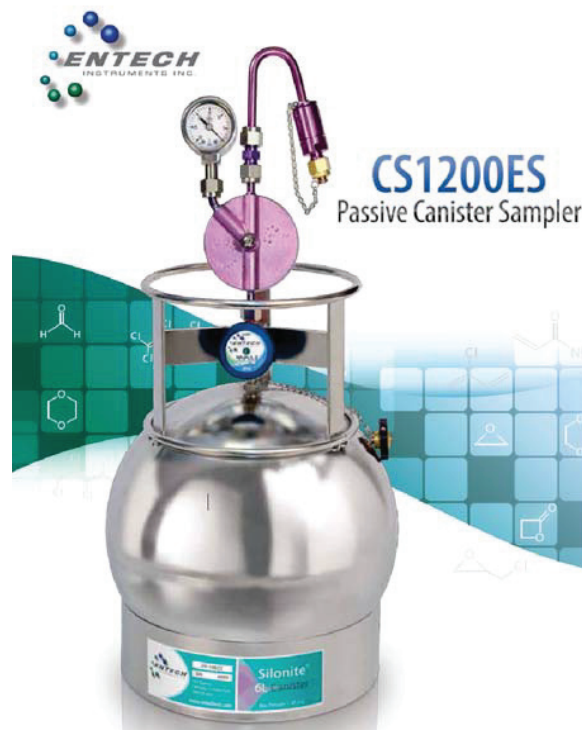


*Figure 1*    *CS1200ES5 shown on a 6L Silonite coated canister with a Toxic Organics Valve (TOV-1).  Tool free connection is possible in the field using Entech's Micro QT quick connect valves on both the canister and flow controller*

Model 4700 Precision Dilution system to 20 PPBv, and then this was again blended down with the 4700's unique reblend feature down to 1PPBv to 40 psia into a 15L Silonite canister.  The pressure was doubled using UHP Nitrogen to yield a final 0.5 PPBv TO15 standard.

A challenge manifold shown in Figure 3 was constructed to allow constant exposure of the 15L challenge canister to 5 CS1200E5 flow controllers.  The flow controllers and manifold were vacuum cleaned on an Entech 3100D Canister Cleaning System to ensure a completely clean, non-equilibrated flow path to maximize the potential for losses should any active surfaces be present.   A 0-50 sccm MFC was used to slowly transfer the challenge mixture at  10cc/min through a manifold containing five CS1200E flow controllers and five MC1400QT MiniCans which were sampling at 0.8cc/min.  The excess was allowed to flow out the end of the

**Figure 2**  *All inlets and inline filters are Silonite coated, as a standard feature, as non-coated filters and inlet lines were shown in the previous 902 application note to cause loss of heavier TO14 compounds.  The need for extreme inertness has increased further with the inclusion of polar compounds in TO15, along with the requirements to drop detection limits well into the part-per-trillion range.*
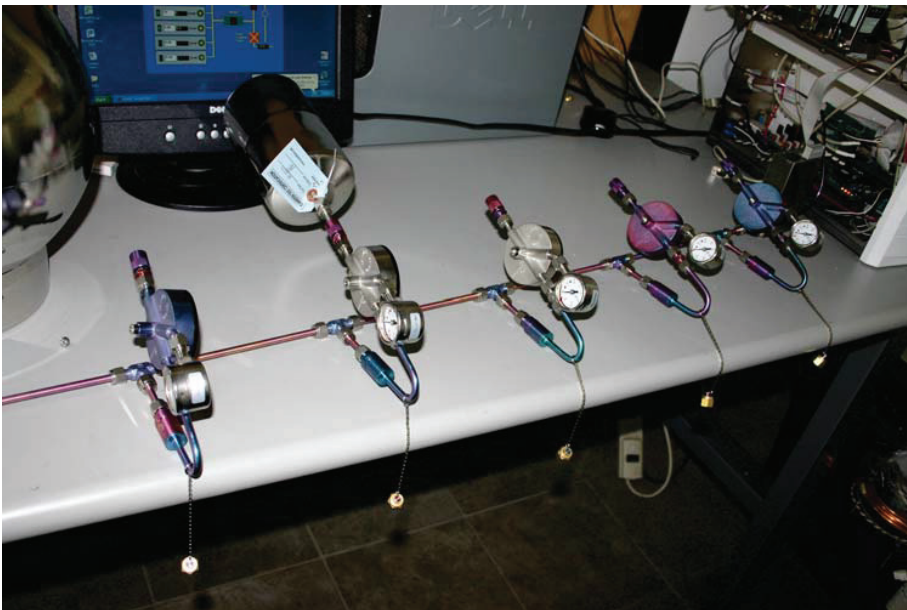


**Figure 3**  *Test manifold shown with 3 Silonite coated and 2 uncoated CS1200E5 flow controllers, with one of the MC1400 Minicans attached.  Using the Micro QT quick connects allowed tool free connection and removal of the sampling canisters, with the added benefit of eliminating room air contamination when not sampling.*

manifold unrestricted, ensuring that the inlet of each CS1200E was at atmospheric pressure.   Under these conditions, there was plenty of standard to last for a few days, although sampling into the MC1400 canisters was completed in 24 hours.    After collection was complete, the 5 canisters were analyzed using a 7200 Preconcentrator (Entech) and a 6890/5973 GCMS (Agilent) in full scan mode. Percent recovery was determined by comparing the response of a 250cc aliquot relative to the direct analysis of the 15L challenge canister.

To validate the CS1200E for stability in performing 1 week sampling, the same 5 flow controllers were first calibrated to 0.5cc/min using the simple procedure shown in Figure 4,   and were then attached to 5 separate evacuated 6L canisters.   These were allowed to sample for exactly 168 hours, or 1 week, to verify that the new improved CS1200E's provided better consistency and fill rate stability.     Each canister was then analyzed to verify consistent TO15 analyte recovery.

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| Compound | | | CS-S #1 | CS-S #2 | CS #1 | CS #2 | CS-S #3 |
|---|---|---|---|---|---|---|---|
| Propene | | | 0.49 | 0.47 | 0.48 | 0.53 | 0.46 |
| Dichlorodifluoromethane(F-12) | | | 0.50 | 0.50 | 0.48 | 0.51 | 0.49 |
| Chloromethane | | | 0.47 | 0.49 | 0.51 | 0.53 | 0.54 |
| Dichlorotetrafluoroethane (F-114) | | | 0.50 | 0.50 | 0.50 | 0.52 | 0.50 |
| Vinyl Chloride | | | 0.48 | 0.52 | 0.47 | 0.53 | 0.54 |
| 1,3-Butadiene | | | 0.44 | 0.47 | 0.45 | 0.52 | 0.56 |
| Bromomethane | | | 0.52 | 0.51 | 0.55 | 0.51 | 0.51 |
| Chloroethane | | | 0.47 | 0.56 | 0.50 | 0.57 | 0.60 |
| Bromoethene | | | 0.51 | 0.50 | 0.52 | 0.51 | 0.52 |
| Trichlorofluoromethane | | | 0.47 | 0.47 | 0.48 | 0.49 | 0.47 |
| Acetone | | | 0.48 | 0.46 | 1.04 | 0.97 | 0.60 |
| 1,1-Dichloroethene | | | 0.51 | 0.50 | 0.50 | 0.50 | 0.51 |
| Trichlorotrifluoroethane (F- 113) | | | 0.50 | 0.49 | 0.50 | 0.50 | 0.48 |
| Allyl Chloride | | | 0.42 | 0.46 | 0.46 | 0.47 | 0.43 |
| Methylene Chloride | | | 0.46 | 0.49 | 0.49 | 0.50 | 0.47 |
| Carbon Disulfide | | | 0.48 | 0.48 | 0.47 | 0.49 | 0.48 |
| trans-1,2-Dichloroethene | | | 0.50 | 0.49 | 0.47 | 0.48 | 0.49 |
| Methyl tert-Butyl Ether (MTBE) | | | 0.48 | 0.47 | 0.49 | 0.52 | 0.51 |
| Vinyl Acetate | | | 0.49 | 0.48 | 0.44 | 0.51 | 0.46 |
| 1,1-Dichloroethane | | | 0.50 | 0.53 | 0.58 | 0.55 | 0.53 |
| 2-Butanone (MEK) | | | 0.51 | 0.48 | 0.46 | 0.48 | 0.46 |
| Hexane | | | 0.53 | 0.45 | 0.51 | 0.54 | 0.55 |
| cis-1,2-Dichloroethene | | | 0.50 | 0.49 | 0.47 | 0.48 | 0.49 |
| Ethyl Acetate | | | 0.49 | 0.46 | 0.50 | 0.52 | 0.48 |
| Chloroform | | | 0.49 | 0.45 | 0.45 | 0.50 | 0.48 |
| Tetrahydrofuran | | | 0.56 | 0.69 | 0.65 | 0.57 | 0.53 |
| 1,1,1-Trichloroethane | | | 0.50 | 0.51 | 0.49 | 0.49 | 0.50 |
| 1,2-Dichloroethane | | | 0.49 | 0.49 | 0.49 | 0.52 | 0.48 |
| Benzene | | | 0.52 | 0.51 | 0.51 | 0.52 | 0.51 |
| Carbon Tetrachloride | | | 0.48 | 0.50 | 0.50 | 0.51 | 0.50 |

**Table 1**   *Results showing a 24 hour sampling into 1.4L MiniCans at a flow rate of 0.8 cc/min through 5 CS1200Ex flow controllers using a 0.5 PPBv TO-15 standard.  The deviation from the expected 0.5 PPBv is a combination of the error in sampling, sample preconcentration, and GCMS analysis.  In general, almost all compounds were at the target concentration +-10%, meeting the requirements of EPA Method TO15*

| Compound | CS-S #1 | CS-S #2 | CS #1 | CS #2 | CS-S #3 |
|---|---|---|---|---|---|
| Cyclohexane | 0.53 | 0.54 | 0.55 | 0.54 | 0.56 |
| 2,2,4-Trimethylpentane | 0.49 | 0.48 | 0.47 | 0.51 | 0.49 |
| Heptane | 0.50 | 0.48 | 0.50 | 0.50 | 0.47 |
| Trichloroethylene | 0.48 | 0.49 | 0.48 | 0.50 | 0.48 |
| 1,2-Dichloropropane | 0.51 | 0.51 | 0.47 | 0.50 | 0.48 |
| 1,4-Dioxane | 0.49 | 0.57 | 0.54 | 0.39 | 0.52 |
| Bromodichloromethane | 0.48 | 0.48 | 0.47 | 0.49 | 0.46 |
| cis-1,3-Dichloropropene | 0.47 | 0.45 | 0.46 | 0.48 | 0.46 |
| 4-Methyl-2-Pentanone (MIBK) | 0.52 | 0.51 | 0.51 | 0.45 | 0.50 |
| trans-1,3-Dichloropropene | 0.48 | 0.49 | 0.48 | 0.50 | 0.48 |
| Toluene | 0.57 | 0.55 | 0.58 | 0.59 | 0.57 |
| Ethane, 1,1,2-trichloro- | 0.50 | 0.50 | 0.51 | 0.54 | 0.51 |
| 1,2-Dibromoethane (EDB) | 0.48 | 0.49 | 0.48 | 0.48 | 0.49 |
| Chlorobenzene | 0.52 | 0.51 | 0.52 | 0.53 | 0.52 |
| Ethylbenzene | 0.52 | 0.51 | 0.51 | 0.55 | 0.53 |
| m&p -Xylene | 0.50 | 0.57 | 0.61 | 0.58 | 0.51 |
| Styrene | 0.49 | 0.51 | 0.50 | 0.52 | 0.52 |
| o-Xylene | 0.50 | 0.52 | 0.53 | 0.56 | 0.52 |
| Bromoform | 0.53 | 0.58 | 0.52 | 0.51 | 0.53 |
| 1,1,2,2-Tetrachloroethane | 0.49 | 0.49 | 0.50 | 0.50 | 0.49 |
| 4-Ethyltoluene | 0.56 | 0.56 | 0.58 | 0.60 | 0.56 |
| 1,3,5-Trimethylbenzene | 0.51 | 0.50 | 0.52 | 0.55 | 0.51 |
| 1,2,4-Trimethylbenzene | 0.53 | 0.50 | 0.52 | 0.54 | 0.53 |
| 1,3-Dichlorobenzene | 0.52 | 0.49 | 0.53 | 0.54 | 0.51 |
| Benzyl Chloride | 0.65 | 0.65 | 0.69 | 0.68 | 0.65 |
| 1,4-Dichlorobenzene | 0.51 | 0.48 | 0.53 | 0.53 | 0.48 |
| 1,2-Dichlorobenzene | 0.50 | 0.48 | 0.49 | 0.52 | 0.48 |
| 1,2,4-Trichlorobenzene | 0.46 | 0.44 | 0.46 | 0.46 | 0.45 |
| Naphthalene | 0.45 | 0.44 | 0.46 | 0.45 | 0.43 |
| Hexachlorobutdiene | 0.50 | 0.50 | 0.52 | 0.54 | 0.49 |

| CS1200Ex + 6L Canister - Time to drop from 20" to 10" Hg | | | | Time in Seconds |
|---|---|---|---|---|

| Seconds(20-10"Hg) | Code | Target Flow Rate cc/min. | Duration |
|---|---|---|---|
| 9-10 | 4 | 3.5 | 24 Hours |
| 65-68 | 5 | 0.52 | 1 Week |
| 130-138 | 6 | 0.26 | 2 Weeks |

**Figure 4**    *The CS1200E5 can be easily calibrated for a 1 week flow rate using the information above. This uses the combined internal volume of the CS1200Ex and the TO Valve, which are extremely consistent. After attaching the CS1200E to an evacuated canister and quickly evacuating the CS1200E by opening and closing the TO Valve, the time needed for the vacuum to drop from 20" to 10" is proportional to the flow rate. A time of 65 seconds is ideal for 1 week sampling into a 6L Silonite canister using a #5 flow restrictor. Restrictors and times for collecting a 24 hour (#4) and 2 week (#6) sample are also shown.*

| | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |
|---|---|---|---|---|---|
| Final Vacuum Reading (in Hg) | 2" | 2" | 2.5" | 2" | 2.5" |
| | ppbv | ppbv | ppbv | ppbv | ppbv |
| Dichlorodifluoromethane | 0.44 | 0.49 | 0.46 | 0.47 | 0.50 |
| Chloromethane | 0.64 | 0.66 | 0.70 | 0.67 | 0.74 |
| Trichlorofluoromethane | 0.26 | 0.25 | 0.26 | 0.25 | 0.26 |
| Acetone | 9.2 | 9.2 | 9.8 | 9.2 | 9.2 |
| Isopropyl Alcohol | 8.1 | 9.6 | 10 | 8.4 | 8.2 |
| Acrolein | 0.73 | 0.75 | 0.72 | 0.70 | 0.75 |
| Trichlorotrifluoroethane | 0.08 | 0.08 | 0.09 | 0.08 | 0.09 |
| Carbon Disulfide | 0.08 | 0.08 | 0.10 | 0.08 | 0.08 |
| 2-Butanone | 0.73 | 0.73 | 0.72 | 0.71 | 0.73 |
| Hexane | 0.28 | 0.28 | 0.28 | 0.28 | 0.25 |
| Ethyl Acetate | 0.39 | 0.36 | 0.40 | 0.42 | 0.35 |
| Chloroform | 0.07 | 0.08 | 0.08 | 0.08 | 0.08 |
| Carbon tetrachloride | 0.09 | 0.08 | 0.09 | 0.09 | 0.09 |
| Benzene | 0.38 | 0.38 | 0.41 | 0.39 | 0.41 |
| Heptane | 0.18 | 0.22 | 0.18 | 0.17 | 0.18 |
| Toluene | 0.62 | 0.58 | 0.62 | 0.61 | 0.65 |
| Ethylbenzene | 0.11 | 0.11 | 0.12 | 0.12 | 0.12 |
| Total Xylenes | 0.26 | 0.24 | 0.27 | 0.26 | 0.28 |
| Styrene | 0.13 | 0.11 | 0.13 | 0.14 | 0.16 |
| 1,2,4-Trimethylbenzene | 0.10 | 0.07 | 0.11 | 0.07 | 0.10 |

**Table 2**  *Results of the 5 canisters that were sampled simultaneously using 5 separate CS1200E samplers. All canisters were at 2 - 2.5" Hg vacuum at the end of 1 week, indicating very consistent sample rates. The consistency of the measured compounds likewise shows the inertness of the combined CS1200E5 and 6L Silonite canisters at the slow, 0.5cc/min flow rates*

## Results

Table 1 shows the results for the sampling of the TO15 Challenge mix into 5 different 1.4L Silonite coated MiniCans.   The slow sampling rate of 0.8cc/min allowed for longer exposure to all surfaces in the flow path, including the inlet filter, the inlet tubing, the flow restrictor, the inside of the sampler, and the internal seals.  A longer residence time gives more opportunity for losses, making the inertness of the materials comprising the wetted surface as important as the inertness of the final sampling canisters.  For this reason, the use of materials that cause absorption of Freons, such as Teflon tape, have been removed from the design.  Additionally, 99% of the flow path is either electropolished 304/316 stainless, or Silonite coated stainless steel.  Other metals known to be porous, causing absorption of TO15 compounds have also been eliminated (copper, brass, aluminum, carbon steel).

Table 1 shows that virtually all compounds show a +-10% recovery or better.  Some of the more difficult compounds, such as Benzyl Chloride, actually showed about a +15% bias in all 5 canisters, probably indicating a slight change in the response of this compound since the calibration was performed.  The Silonite coated and non-coated samplers showed equivalent recoveries, except the uncoated flow controllers showed a lot more Acetone background than the Silonite coated samplers, perhaps due to greater adsorption onto the surface and into micro pores in the metal that are covered up by the Silonite coating.  Long term, the Silonite coated samplers may show even a greater improvement in recovery, based on the inability to further oxidize or corrode its surface.  The more challenging heavy compounds, including Trichlorobenzene and Naphthalene showed an 8-12% negative bias, but the extremely good precision between all 5 samplers indicated that the bias may have been partially due to a small change in the response for these compounds.

Table 2 shows the results for the five 6L canisters that were sampled for 1 week.   The improved flow stability of the new CS1200E samplers is shown in the consistency of the final canister pressures.   Each of the 5 canisters was analyzed to monitor whatever was in the room air, showing the consistency in the measurements, including polar compounds such as Acrolein.

## Conclusion

The CS1200E has been shown to meet the requirements of TO15 for 1 week sampling by demonstrating the following:

1.  Recovery of all tested TO15 compounds were within the range of +-20% through the sample train, except for a positive bias for Acetone, which is known to be in human breath at high PPBv levels, making it difficult to achieve sub-PPB level blanks.  However, the Silonite coated CS1200E5 samplers showed a lower blank level for Acetone than the uncoated samplers

2.   Recovery testing was validated using sub-PPBv level standards to more closely represent real world concentrations.   It is no longer acceptable to use 10PPBv challenge mixtures to show performance for TO15 sample trains that have to perform well into the part-per-trillion range

3.  All five 6L sampling canisters had final pressures in the range of 2-3"Hg, showing that true time integrated sampling had occurred throughout the 1 week period, while collecting enough sample to avoid having to pressurize the canister prior to analysis.

The latest model of the CS1200E was used for this study, that included modifications to improve flow stability and consistency.   These improvements in stability have increased the maximum sampling times out to a full 2 weeks using Silonite 6L canisters, allowing continuous monitoring of a given site for long term risk assessment while only generating 2 samples a month per site.   Entech recommends inertness tested canisters when performing 1-2 week sampling, due the longer residence time of compounds in the canister prior to analysis.   A detailed discussion of this can be found in Application Note 2014-04.

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