A New Cryogenless TO15 Canister Preconcentrator with Reduced System Carry-Over When Exposed to Higher Concentration Samples

Application Note:

A-3741-04

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Overview

A new preconcentrator design is presented which eliminates the need for liquid nitrogen or complicated electronic cooling while performing US EPA Method TO15 analysis[1]. A new technology called Multi-Capillary Column Trapping System (patent pending), or MCCTS, is used to concentrate all TO15 compounds at 35°C, which is achieved simply by using cooling fans. Two stages are used: the first to trap the sample, calibration standards, and internal standard; and the second to further focus the concentrate prior to GCMS injection.

The new solution uses multiple capillary columns in series with increasing strength to trap compounds boiling from -50°C to >230°C, using volumes from 10-500cc. The trap design shows considerably less susceptibility to contamination when exposed to high concentration soil gas samples, reducing the downtime laboratories experience when accidentally analyzing these samples prior to dilution. Full TO15 validation is demonstrated, including blank levels immediately after running higher concentration samples containing BTEX, PCE, and TCE, which are compounds often found in soil gas at elevated concentrations.

Introduction

The need for accurate monitoring of chemicals in ambient and indoor air continues to grow in importance as our understanding of their impact on human health continues to evolve. Many of these compounds have been shown to interfere with the hormonal system (endocrine disruptors), which is particularly concerning during prenatal and early development. Improvements in analytical technology for accurate determination of chemicals at PPB and sub-PPB levels are critical to obtaining more accurate and sensitive measurements on a wider range of compounds to allow the most comprehensive monitoring possible.

Analysis of hazardous Volatile Organic Compounds, or VOCs, from sub-PPB to PPM levels can be performed in a few different ways, but the gold

Figure 1 - The only capillary column based TO15 Preconcentrator.

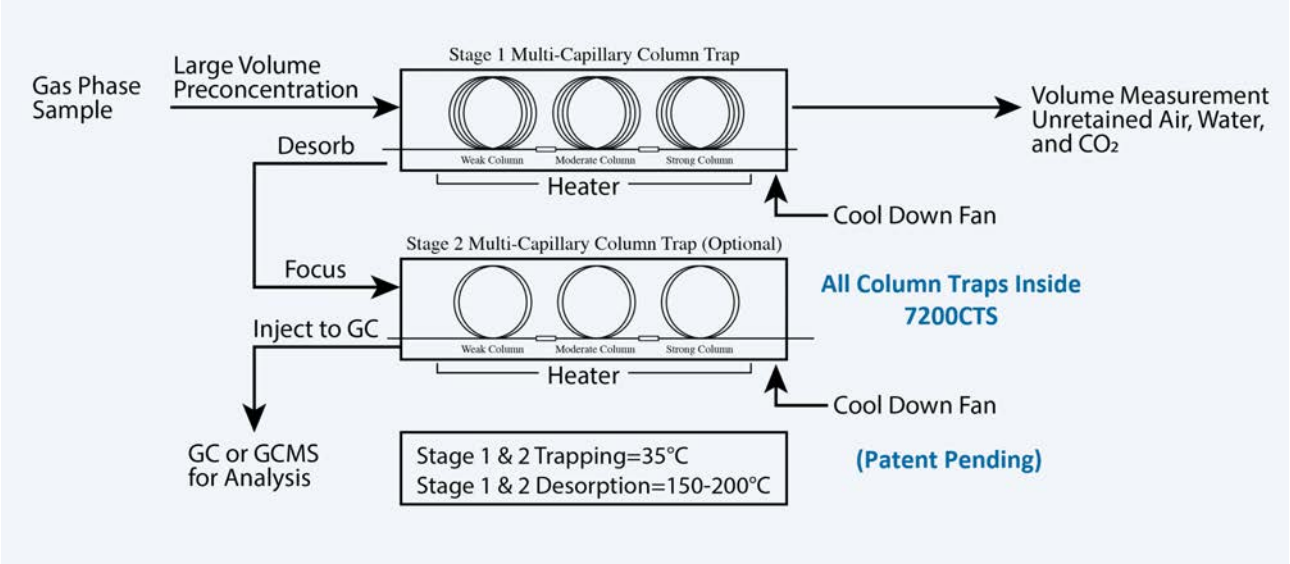


Figure 2 Schematic of TO15 sample flow path. Both stages contain multiple columns which allow the trap and release of all compounds. Each stage is back-flushed to minimize residence time in heated columns.

standard continues to be the use of stainless steel canisters as described in US EPA Method TO15.

Unlike thermal desorption tubes which extract the sample from air at the time of collection, thereby altering the preconcentration system with every sample collected, canisters follow the Scientific Method more closely by simply collecting the entire, unmodified sample in the field for transport to a laboratory for analysis. In the lab, canister sample preconcentration prior to GCMS analysis is performed on a fully validated system. By running quality assurance (QA) checks on these systems, such as calibration curves, continuing calibration verifications (CCVs), and blanks, the number of uncontrolled variables are reduced using canisters. In general, more sophisticated preconcentration techniques can be employed in the laboratory, rather than using a simple tube with 1 to 3 adsorbent beds, a technology which first appeared approximately 40 years ago.

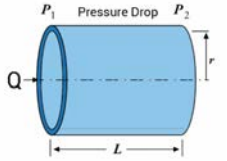
Figure 3 - Traps operate well below their maximum temperature and should last for years, however, plug-in Multi-Capillary Column Traps are easy to replace, making maintenance easy for the user.

Elimination of the Channeling Effect

Cryogenic preconcentration systems for canister analysis which utilize three trapping stages to perform sample preconcentration, water management, and on-column focusing for rapid injection, have been the leading solution for performing US EPA Methods TO14A and TO15 for the past 25 years. The design of these systems allowed them to remain very stable, easily meeting TO15 calibration and blank level requirements. By eliminating the strong, multi-stage adsorbents found in non-cryogenic systems, these LN2 based solutions clean up faster when exposed to higher concentration samples. However, all TO15 preconcentrators until now utilize packed traps and are susceptible to "channeling," a phenomenon which negatively affects system precision, while also adding to the potential for system carryover.

Channeling is caused by the normal expansion and contraction of the adsorbent when it is heated and cooled. Like most materials, when adsorbents are cooled they shrink, and this causes micro channels to form in the adsorbent and along the walls of the traps. Considering the flow through a tube or channel for any Newtonian fluid can be defined by Poiseuille's Law[2], which states that the flow (Q) of fluid is related to a number of factors: the viscosity (n) of the fluid, the pressure gradient across the tubing (P), and the length (L) and the radius (r) of the tubing and is expressed as;

$$Q = \frac{\pi \Pr^4}{8\eta l}$$



Simply put, doubling the diameter of the channel increases the flow rate by 16 fold. Therefore, any small increase in the separation between the adsorbent particles or along the inner wall causes a huge decrease in the resistance to flow relative to tightly packed regions within the adsorbent, resulting in the flow of a relatively large amount of the sample through these channels thereby increasing the depth of penetration of chemicals into the adsorbent.

During desorption, heating the trap causes the channels to collapse as the adsorbent expands, eliminating these low impedance paths, and resulting in lower recoveries. This increase may not cause a large enough issue to prevent systems using these traps from meeting EPA Method calibration criteria when concentrations are low, but channeling is the primary reason why high concentration samples create a real problem for preconcentrators using packed traps, especially when these micro-channels allow heavier compounds to reach a second, stronger adsorbent used in multi-bed packed traps.

A revolutionary technology has been developed which uses open tubular capillary columns with increasing strength to trap complex air samples containing compounds over a wide range of volatilities. The lightest compounds are trapped by the strongest stage placed in the back of the trap, while weaker columns are placed closer to the front of the trap to retain the heavier compounds. Only the walls of the capillary columns are coated, so there is no chance for channeling to occur, as most of the internal diameter of the tubing contains no adsorbent. During heating and cooling, the difference in the size of the opening through the traps is negligible, preventing the possibility of inconsistent penetration of compounds during trapping, and subsequent sealing of these compounds within an adsorbent bed. This just isn't possible using open tubular capillary traps.

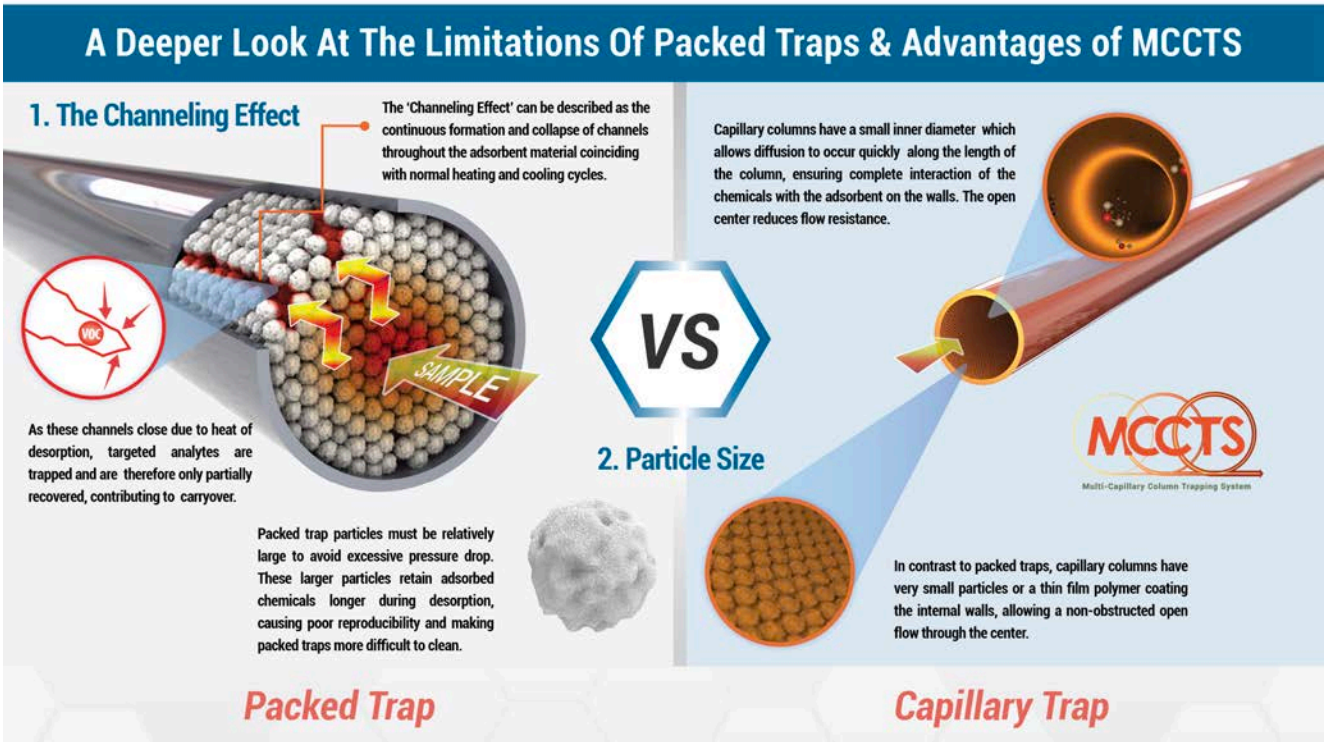


Figure 4 - Many of the limitations of today's preconcentration systems come from the use of packed traps themselves. Using capillary columns side steps many of the issues of packed traps including inconsistent recoveries due to the Channeling Effect described above.

In addition, particles used on the walls of the traps have diameters that are at least 10x smaller with internal volumes that are 1000x smaller than the particles in packed traps, allowing them to completely release the adsorbed sample much faster during desorption. Even when exposed to high concentrations, the particles take very little time to release everything back into the gas phase, virtually eliminating memory effects in the trap.

Superior Water Management

Water management is also improved with the Multi-Capillary Column trap design. Water is almost unretained by the traps, resulting from both the hydrophobic nature of the adsorbent, and the much smaller adsorbent particle sizes than those used in packed traps. Even though they are hydrophobic, any particles with pores will have water molecules diffusing through them, and the larger the particle, the longer it will take for the diffusion to release enough water during dry purge water removal so the GCMS is not affected. The extremely small particles in the new capillary traps require almost no dry purging to remove the water because water can more quickly diffuse in and out of these particles. In contrast, packed traps can require 50-200cc of dry purging to remove about 97% of the water, with the negative affect of pushing the sample even further into the trap, affecting recoveries.

Packed traps cannot use extremely small particles (mesh 1000) because there would be so little gap between the particles that the pressure drop across the trap would be too high and the resulting flows too low to be practical. This is not a problem when the particles are only coating the walls of the capillary traps. Typical water peaks when scanning m/z 18 are up to 10,000 times smaller than when using packed traps or cold trap dehydration, meaning that the GCMS spectrometer will have almost no water to bake out, resulting in vastly improved sensitivity stability even when running an increased number of samples in any given day with shorter intervals between injections.

Finally, systems which eliminate water via cold trapping at -10 to -40°C show losses of more highly polar compounds such as 1,4-Dioxane, many alcohols, light fatty acids, and mono-glycol esters. These compounds are recovered perfectly using the new Multi-Capillary Column Trapping System, offering a more complete solution for measuring a wider range of compounds.

Elimination of Cryogen

After trapping TO15 compounds on a primary, multi-stage trap, the sample is back-flushed during heating to a second trap with smaller column lengths to allow even faster injection into the GCMS to yield optimal peak shape of the lightest through the heaviest compounds. Both the first and second stages operate at 35°C during trapping, so only fan cooling is needed. This avoids complicated and maintenance intensive Peltier cooled traps.

The new Multi-Column Capillary Traps should last a very long time, as do GC columns which are not overheated or forced to forward elute heavy chemicals which may decompose or otherwise permanently adsorb to the column walls. This creates a TO15 preconcentration solution with improved longevity and lower operational costs through elimination of cryogenic fluids.

Significantly Minimizing Carryover

Carryover has been substantially reduced not only using capillary traps, but by eliminating sources of dead volume and absorptive surfaces throughout the flow path. Unlike other systems, flow control devices are not placed prior to the traps, so there are no seals and sensors to outgas into later runs. All Teflon, such as PTFE, has been removed from the flow path, as perfluorocarbons are known to absorb and outgas freons, as found in EPA Method TO15. Digitally controlled rotary valves eliminate the potential for cross-contamination during stream selection, while robotic autosamplers are available which eliminate cross contamination by offering 100% isolation of samples from each other.

For added quality assurance, the internal standard is not delivered into the traps via loop injection, but rather via direct preconcentration, identical to the calibration standards and samples. Systems which use loop injection to deliver internal standards do not continually test the accuracy of their volume measurement systems, leading to uncertainty in the analytical results. Verifying consistent internal standard recovery when performing the same preconcentration and volume measurement as used when running samples validates that the technology is working correctly during every analysis.

Experimental

A 7200CTS non-cryogenic preconcentrator (Entech Instruments) incorporating the Multi-Capillary Column Trapping System (MCCTS) was used in the study. Calibration Standards were prepared into two 6L Silonite Canisters (Entech Instruments) using a 4700 Precision Diluter (Entech Instruments) to create canister concentrations at 20PPBv and 2PPBv from a 1PPM stock standard (Linde) so a wide calibration range could be achieved[3]. A 1PPM cylinder of a 4 component Internal standard was also used to create a 50PPBv working internal standard in a 6L Silonite canister so that 50cc could be added to every analysis. The 7200CTS preconcentrator was attached to a 6890/5973 GCMS (Agilent Technologies, Inc., Palo Alto, CA) using a 60m, 2µm, 0.32mm ID GC column, and the system was used to create a calibration from 0.1PPBv to 30PPBv by varying the volume from the 2PPBv and 20PPBv calibration canisters. Blanks were run after the high concentration standard to show no carryover in the system. Seven replicates were run at 0.1PPBv using 12.5cc out of the 2PPB standard canister to determine method detection limits. A CCV standard was run on consecutive days to show very little change in system performance.

Results and Discussion

EPA method TO15 requires calibrating the analytical system with a minimum of five concentrations and showing linearity of 30% RSD (Relative Standard Deviation) or less. As shown in **Table 1**, the presented solution surpassed this requirement with many compounds resulting in single digit %RSDs.

Calibrating is easily performed by changing the volumes for varying concentrations. For example, when using a nominal volume of 250cc of a 20ppbv calibration standard, 375cc is equal to 30ppbv, 250cc is equal to 20ppbv, 125cc is equal to 10ppbv, 50cc is equal to 4ppbv. A 2ppbv calibration standard was also prepared from the original 20ppbv. The 250cc is equal to 2ppbv, 125cc is equal to 1ppbv, 50cc is equal to 0.4ppbv, 25cc is equal to 0.2ppbv, and 12.5cc is equal to 0.1ppbv. Using this approach helps to validate the system is linear relative to various volumes and varying levels of water loaded into the preconcentrator, which is necessary to allow smaller sample volumes to be analyzed when concentrations exceed the calibration range.

Table 2 shows the method detection limit and sensitivity is adequate to calibrate to an even lower concentration if needed. **Figure 1** shows the chromatography obtained with this cryogen free preconcentrator. **Figure 2** is a blank analyzed after the high point in the calibration curve and has no reportable target compounds. The peaks observed are internal standards and low-level siloxane compounds.

Figure 5 - The 7650 Million Air Autosampler quickly screens six 6L or 3.2L canisters (shown above) for high concentration samples in just over half an hour, therefore 60-80 samples can be screened in an 8 hour shift. One 7200CTS/7650-M can screen enough samples to keep 4-5 other systems safe and productive.

Figure 6 - The two Multi-Capillary Column Trapping Stages are shown above: Stage 1: Trap; Stage 2: Focus. Simple fans are used to cool traps down to 35°C. No complicated electronic cooling makes it easier to operate and maintain by the laboratory chemist.

Table 1 Response Factor Report 0.1-30PPBv

Response Factor report (ppbV)									
Compound	0.1	0.3	0.6	2	6	12	30	Avg	%RSD
Propene	4.601	3.726	3.619	3.745	3.649	3.299	3.617	3.751	10.7
Dichlorodifluoromethane	1.988	1.567	1.5	1.644	1.604	1.494	1.541	1.620	10.6
Chloromethane	6.673	5.496	5.057	5.087	5.004	4.609	4.941	5.267	12.8
Dichlorotetrafluoroethane	1.413	1.189	1.141	1.226	1.22	1.13	1.136	1.208	8.2
Vinyl chloride	6.997	6.23	5.81	5.975	6.003	5.618	5.832	6.066	7.5
1,3-Butadiene	5.148	4.385	3.983	4.168	4.219	3.944	4.217	4.295	9.4
Bromomethane	6.002	5.052	4.695	5.211	5.205	4.923	4.922	5.144	8.1
Chloroethane	3.904	3.208	2.919	3.12	3.102	2.887	3.009	3.164	10.9
Bromoethene	6.226	5.692	5.34	5.457	5.596	5.373	5.297	5.569	5.8
Ethanol	2.15	1.56	1.483	1.513	1.552	1.549	1.697	1.643	14.2
Acetonitrile		2.73	3.208	3.326	3.551	3.329	3.68	3.304	10.0
Trichlorofluoromethane	1.769	1.538	1.515	1.582	1.573	1.468	1.493	1.563	6.4
Acetone	1.395	1.134	1.027	0.842	0.879	0.828	0.918	1.004	20.4
Isopropyl alcohol		1.508	1.184	0.853	0.875	0.83	0.884	1.022	26.4
Acrolein	1.373	1.249	1.058	0.949	1.049	0.989	1.11	1.111	13.5
1,1-Dichloroethene	6.368	5.354	4.983	5.263	5.419	5.212	5.132	5.390	8.4
Acrylonitrile	4.378	3.632	3.611	3.833	4.24	4.105	4.329	4.018	8.1
Trichlorotrifluoroethane	1.404	1.173	1.117	1.197	1.191	1.109	1.129	1.188	8.5
Allyl chloride	8.509	6.84	6.652	7.296	7.37	6.827	7.422	7.274	8.6
Methylene chloride	7.002	5.388	5.167	5.009	5.306	4.844	4.882	5.371	13.9
tert-Butanol	1.55	1.435	1.422	1.521	1.597	1.518	1.567	1.516	4.3
Carbon disulfide	1.895	1.77	1.688	1.755	1.765	1.679	1.711	1.752	4.2
trans-1,2-Dichloroethene	1.176	1.011	0.963	0.975	0.975	0.912	0.945	0.994	8.6
Methyl-tert-Butylether	2.345	2.096	2.026	2.181	2.211	2.077	2.144	2.154	4.9
Vinyl acetate	1.305	1.282	1.366	1.384	1.45	1.355	1.467	1.373	5.0
1,1-Dichloroethane	1.403	1.147	1.128	1.194	1.185	1.087	1.135	1.183	8.8
2-Butanone	3.299	3.178	3.193	3.259	3.452	3.288	3.34	3.287	2.8
Hexane	2.179	1.956	1.679	1.84	1.769	1.678	1.671	1.825	10.3
cis-1,2-Dichloroethene	1.063	0.926	0.874	0.925	0.916	0.852	0.894	0.921	7.4
2-Chloroprene	6.313	5.376	5.277	5.594	5.78	5.531	5.468	5.620	6.1
Ethyl acetate	2.625	2.158	2.203	2.273	2.295	2.03	2.127	2.244	8.5
Chloroform	1.822	1.537	1.459	1.562	1.544	1.438	1.487	1.550	8.3
Di-isopropylether	7.465	6.172	5.966	6.169	6.308	5.966	5.759	6.258	9.0
Tetrahydrofuran	3.918	3.44	3.33	3.423	3.463	3.186	3.194	3.422	7.2
Ethyl-tert-Butylether	2.663	2.324	2.252	2.463	2.446	2.261	2.265	2.382	6.4
1,1,1-Trichloroethane	1.875	1.601	1.525	1.642	1.662	1.567	1.669	1.649	6.8
1,2-Dichloroethane	1.29	1.104	1.045	1.121	1.124	1.059	1.134	1.125	7.1
Benzene	2.417	2.076	1.996	2.117	2.109	2.005	2.053	2.110	6.8
Carbontetrachloride	1.669	1.462	1.412	1.519	1.562	1.495	1.609	1.533	5.7
Cyclohexane	1.341	1.032	0.979	0.955	0.956	0.895	0.895	1.008	15.3
tert-Amylmethylether	6.515	5.647	5.48	5.971	6.122	5.731	5.676	5.877	6.0

Table 1 (continued) Response Factor Report 0.1-30PPBv

Response Factor report (ppbV)									
Compound	0.1	0.3	0.6	2	6	12	30	Avg	%RSD
2,2,4-Trimethypentane	9.178	7.967	7.856	8.305	8.164	7.479	7.323	8.039	7.6
Heptane	1.967	1.681	1.557	1.636	1.659	1.634	1.657	1.684	7.8
Trichloroethene	2.689	2.297	2.222	2.364	2.342	2.176	2.196	2.327	7.5
1,2-Dichloropropane	2.165	1.799	1.737	1.823	1.836	1.697	1.722	1.826	8.7
1,4-Dioxane	1.628	1.356	1.293	1.275	1.323	1.228	1.189	1.328	10.8
Bromodichloromethane	4.881	4.142	4.003	4.274	4.35	4.049	4.176	4.268	6.9
Methylmethacrylate	0.751	0.675	0.62	0.644	0.678	0.641	0.611	0.660	7.2
cis-1,3-Dichloropropene	3.343	2.916	2.816	2.96	3.031	2.79	2.772	2.947	6.8
4-Methyl-2-pentanone	3.593	3.185	3.147	3.409	3.495	3.227	3.216	3.324	5.2
trans-1,3-Dichloropropene	2.795	2.676	2.482	2.59	2.667	2.556	2.664	2.633	3.8
Toluene	6.882	6.259	5.784	6.069	6.133	5.706	5.917	6.107	6.4
1,1,2-Trichloroethane	2.452	2.085	1.97	2.089	2.14	2.03	2.03	2.114	7.5
2-Hexanone	1.985	1.883	1.773	1.904	1.97	1.825	1.863	1.886	4.0
Dibromochloromethane	3.811	3.583	3.413	3.555	3.796	3.677	3.899	3.676	4.6
Tetrachloroethene	2.838	2.609	2.417	2.551	2.627	2.576	2.726	2.621	5.1
1,2-Dibromoethane	3.425	3.211	2.972	3.083	3.174	2.971	3.009	3.121	5.3
Chlorobenzene	2.703	2.518	2.268	2.159	2.23	2.152	2.045	2.296	10.1
1,1,1,2-Tetrachloroethane	1.561	1.418	1.332	1.353	1.418	1.407	1.355	1.406	5.4
Ethylbenzene	4.232	3.868	3.541	3.508	3.668	3.578	3.629	3.718	6.9
m,p-Xylenes	3.313	3.014	2.769	2.787	2.859	2.756	2.658	2.880	7.7
Styrene	2.181	2.14	1.871	1.881	1.963	1.934	1.825	1.970	7.0
o-Xylene	3.257	2.993	2.729	2.766	2.832	2.711	2.73	2.860	7.0
Bromoform	1.44	1.54	1.444	1.438	1.611	1.652	1.71	1.548	7.3
1,1,2,2-Tetrachloroethane	2.526	2.333	2.169	2.166	2.211	2.129	1.98	2.216	7.8
Cumene	4.722	4.312	3.759	3.967	4.122	4.155	4.186	4.175	7.2
o-Chlorotoluene	1.177	1.043	0.95	0.991	1.017	0.988	0.949	1.016	7.7
n-Propylbenzene	1.138	1.058	0.929	1.011	1.038	1.009	0.979	1.023	6.4
4-Ethyltoluene	4.062	3.861	3.482	3.703	3.847	3.725	3.798	3.783	4.7
1,3,5-Trimethylbenzene	3.623	3.451	3.156	3.385	3.475	3.335	3.417	3.406	4.2
tert-Butylbenzene	4.493	4.178	3.854	4.078	4.338	4.267	4.014	4.175	5.1
1,2,4-Trimethylbenzene	3.598	3.188	2.906	3.208	3.424	3.21	3.224	3.251	6.6
1,3-Dichlorobenzene	2.443	2.35	2.017	2.016	2.151	2.119	2.206	2.186	7.4
Benzyl chloride	3.731	3.731	3.4	3.487	3.845	3.74	3.748	3.669	4.4
1,4-Dichlorobenzene	2.487	2.299	2.033	2.006	2.117	2.126	2.174	2.177	7.7
sec-Butylbenzene	5.494	5.152	4.642	5.571	5.691	5.262	5.052	5.266	6.8
1,2-Dichlorobenzene	2.316	2.051	1.798	1.869	2.018	1.998	2.146	2.028	8.5
o-Cymene	4.141	3.988	3.699	4.175	4.453	4.388	4.261	4.158	6.1
n-Butylbenzene	4.331	3.783	3.324	3.828	4.166	4.061	4.028	3.932	8.3
1,2,4-Trichlorobenzene	1.701	1.651	1.357	1.458	1.68	1.769	1.873	1.641	10.8
Naphthalene	3.598	3.673	3.26	3.472	4.124	4.234	4.187	3.792	10.2
Hexachlorobutadiene	1.574	1.486	1.337	1.365	1.542	1.61	1.535	1.493	7.0

Table 2 Method Detetion Limit Concentration 0.1PPBv

Method Detection Limit Concentration 0.1 ppbv										
Compound	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7	AVG	STDEV	MDL
Propene	0.133	0.123	0.139	0.129	0.12	0.115	0.124	0.126	0.008	0.026
Dichlorodifluoromethane	0.0978	0.098	0.1	0.0945	0.0928	0.0922	0.0977	0.096	0.003	0.009
Chloromethane	0.165	0.161	0.18	0.158	0.158	0.168	0.144	0.162	0.011	0.035
Dichlorotetrafluoroethane	0.0923	0.0962	0.09	0.095	0.0999	0.0888	0.102	0.095	0.005	0.015
VinylChloride	0.095	0.098	0.106	0.101	0.103	0.0972	0.1	0.100	0.004	0.012
1,3-Butadiene	0.115	0.0848	0.121	0.114	0.0875	0.0893	0.0972	0.101	0.015	0.047
Bromomethane	0.107	0.107	0.111	0.106	0.0997	0.105	0.111	0.107	0.004	0.012
Chloroethane	0.107	0.101	0.121	0.109	0.111	0.0995	0.0989	0.107	0.008	0.025
Bromoethene	0.0963	0.092	0.104	0.093	0.0874	0.0938	0.102	0.096	0.006	0.018
Ethanol	0.15	0.146	0.127	0.132	0.134	0.139	0.128	0.137	0.009	0.028
Acetonitrile	0.143	0.12	0.118	0.115	0.088	0.172	0.187	0.135	0.035	0.109
Trichlorofluoromethane	0.09	0.0961	0.0989	0.0992	0.0911	0.0926	0.0941	0.095	0.004	0.011
Acetone	0.13	0.128	0.131	0.118	0.118	0.133	0.123	0.126	0.006	0.019
IsopropylAlcohol	0.159	0.162	0.183	0.161	0.16	0.164	0.188	0.168	0.012	0.038
Acrolein	0.125	0.111	0.121	0.138	0.113	0.137	0.134	0.126	0.011	0.035
1,1-Dichloroethene	0.0984	0.104	0.0916	0.0934	0.0932	0.0988	0.0965	0.097	0.004	0.013
Acrylonitrile	0.0841	0.097	0.0885	0.0931	0.0745	0.0914	0.117	0.092	0.013	0.041
Trichlorotrifluoroethane	0.0953	0.0947	0.101	0.0936	0.0934	0.094	0.0993	0.096	0.003	0.009
Allyl chloride	0.103	0.107	0.112	0.101	0.099	0.0952	0.0943	0.102	0.006	0.020
Methylene chloride	0.113	0.108	0.0926	0.108	0.106	0.107	0.111	0.107	0.007	0.021
tert-Butanol	0.0957	0.09	0.0993	0.0973	0.0956	0.0898	0.103	0.096	0.005	0.015
Carbon disulfide	0.0999	0.0997	0.103	0.0988	0.0977	0.0921	0.0954	0.098	0.004	0.011
trans-1,2-Dichloroethene	0.102	0.104	0.0985	0.0981	0.0932	0.0961	0.107	0.100	0.005	0.015
Methyl-tert-butylether	0.0951	0.0939	0.0959	0.0972	0.0925	0.0937	0.1	0.095	0.003	0.008
VinylAcetate	0.094	0.09	0.0906	0.087	0.088	0.0889	0.104	0.092	0.006	0.018
1,1-Dichloroethane	0.097	0.0985	0.105	0.0967	0.0997	0.0944	0.0969	0.098	0.003	0.011
2-Butanone	0.101	0.0951	0.107	0.0955	0.0925	0.098	0.117	0.101	0.009	0.027
Hexane	0.091	0.106	0.108	0.0993	0.1	0.105	0.102	0.102	0.006	0.018
cis-1,2-Dichloroethene	0.0948	0.101	0.105	0.102	0.0971	0.0979	0.096	0.099	0.004	0.011
2-Chloroprene	0.0911	0.0929	0.095	0.089	0.0844	0.0845	0.101	0.091	0.006	0.019
Ethyl acetate	0.101	0.11	0.11	0.0944	0.0992	0.0983	0.103	0.102	0.006	0.019
Chloroform	0.0965	0.0976	0.104	0.0994	0.0986	0.0972	0.0983	0.099	0.002	0.008
Di-isopropyl	0.0976	0.0986	0.103	0.1	0.1	0.1	0.0996	0.100	0.002	0.005
Tetrahydrofuran	0.106	0.109	0.101	0.106	0.104	0.113	0.114	0.108	0.005	0.015
Ethyl-tert-butylether	0.0951	0.0968	0.1	0.0986	0.0947	0.0957	0.096	0.097	0.002	0.006
1,1,1-Trichloroethane	0.0969	0.0937	0.098	0.095	0.0994	0.0923	0.0973	0.096	0.003	0.008
1,2-Dichloroethane	0.0945	0.0992	0.1	0.097	0.0998	0.0971	0.0994	0.098	0.002	0.006
Benzene	0.0963	0.0988	0.101	0.0991	0.0959	0.0949	0.102	0.098	0.003	0.008
Carbontetrachloride	0.0952	0.0926	0.0963	0.0963	0.0905	0.0922	0.0986	0.095	0.003	0.009
Cyclohexane	0.111	0.112	0.113	0.113	0.11	0.108	0.112	0.111	0.002	0.006
tert-Amylmethylether	0.0936	0.093	0.0972	0.0965	0.0909	0.0912	0.0948	0.094	0.002	0.008

Table 2 continued Method Detetion Limit Concentration 0.1PPBv

Method Detection Limit Concentration 0.1 ppbv										
Compound	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7	AVG	STDEV	MDL
2,2,4-Trimethylbenzene	0.0998	0.103	0.106	0.102	0.0986	0.0991	0.1	0.101	0.003	0.008
Heptane	0.0962	0.0913	0.107	0.0975	0.1	0.0988	0.0981	0.098	0.005	0.015
Trichloroethene	0.0946	0.0945	0.0999	0.0955	0.0901	0.0953	0.0932	0.095	0.003	0.009
1,2-Dichloropropane	0.0993	0.0973	0.104	0.101	0.1	0.0914	0.101	0.099	0.004	0.012
1,4-Dioxane	0.0971	0.0978	0.102	0.092	0.088	0.0997	0.114	0.099	0.008	0.026
Bromodichloromethane	0.0931	0.0947	0.0989	0.0902	0.0897	0.0895	0.0943	0.093	0.003	0.011
Methylmethacrylate	0.102	0.0885	0.0872	0.0787	0.0777	0.095	0.104	0.090	0.010	0.033
cis-1,3-Dichloropropene	0.0889	0.093	0.0903	0.0934	0.095	0.0886	0.094	0.092	0.003	0.008
4-Methyl-2-pentanone	0.0891	0.0892	0.089	0.0927	0.0874	0.0985	0.108	0.093	0.007	0.023
trans-1,3-Dichloropropene	0.0852	0.0921	0.0934	0.0858	0.0862	0.0861	0.0971	0.089	0.005	0.015
Toluene	0.141	0.14	0.147	0.139	0.139	0.152	0.165	0.146	0.010	0.030
1,1,2-Trichloroethane	0.0855	0.0939	0.0945	0.0901	0.0972	0.0878	0.101	0.093	0.005	0.017
2-Hexanone	0.0872	0.0919	0.0889	0.0837	0.0888	0.0904	0.12	0.093	0.012	0.038
Dibromochloromethane	0.0865	0.0844	0.0875	0.0867	0.0791	0.0887	0.0947	0.087	0.005	0.015
Tetrachloroethene	0.0916	0.0927	0.0944	0.0922	0.0888	0.092	0.0984	0.093	0.003	0.009
1,2-Dibromoethane	0.0879	0.0857	0.0914	0.0874	0.0838	0.0865	0.0952	0.088	0.004	0.012
Chlorobenzene	0.0875	0.0901	0.0928	0.0873	0.0835	0.0911	0.103	0.091	0.006	0.019
1,1,1,2-Tetrachloroethane	0.0874	0.09	0.0878	0.08858	0.0816	0.0863	0.0985	0.089	0.005	0.016
Ethylbenzene	0.0873	0.0904	0.0892	0.0892	0.0839	0.0881	0.0993	0.090	0.005	0.015
m,p-Xylene	0.175	0.176	0.175	0.172	0.162	0.18	0.194	0.176	0.010	0.030
Styrene	0.08	0.0776	0.0792	0.08	0.0731	0.0825	0.0976	0.081	0.008	0.024
o-Xylene	0.0897	0.0868	0.0886	0.0842	0.0818	0.0905	0.0975	0.088	0.005	0.016
Bromoform	0.077	0.0767	0.0794	0.0754	0.0738	0.0789	0.0917	0.079	0.006	0.019
1,1,2,2-Tetrachloroethane	0.0871	0.0875	0.089	0.0813	0.0796	0.0887	0.0974	0.087	0.006	0.018
Cumene	0.0887	0.0887	0.0886	0.0845	0.0819	0.0875	0.101	0.089	0.006	0.019
o-Chlorotoluene	0.0872	0.0867	0.0888	0.0829	0.0832	0.0928	0.098	0.089	0.005	0.017
n-Propylbenzene	0.0872	0.086	0.0853	0.0855	0.0784	0.0872	0.0991	0.087	0.006	0.019
4-Ethyltoluene	0.0864	0.0861	0.0856	0.0848	0.0796	0.0871	0.101	0.087	0.007	0.021
1,3,5-Trimethylbenzene	0.086	0.0857	0.0863	0.0839	0.0781	0.0848	0.0954	0.086	0.005	0.016
tert-Butylbenzene	0.0875	0.0863	0.0872	0.0841	0.0786	0.0867	0.0993	0.087	0.006	0.019
1,2,4-Trimethylbenzene	0.0869	0.0864	0.0839	0.083	0.0797	0.0882	0.0992	0.087	0.006	0.019
1,3-Dichlorobenzene	0.0815	0.0863	0.0884	0.0885	0.0792	0.0896	0.108	0.089	0.009	0.029
Benzyl chloride	0.0816	0.083	0.0819	0.0782	0.0752	0.0838	0.0965	0.083	0.007	0.021
1,4-Dichlorobenzene	0.0885	0.087	0.0873	0.0835	0.0792	0.0886	0.106	0.089	0.008	0.026
sec-ButylBenzene	0.0865	0.0839	0.0864	0.0833	0.078	0.0867	0.098	0.086	0.006	0.019
1,2-Dichlorobenzene	0.0882	0.0917	0.089	0.0838	0.0816	0.0858	0.101	0.089	0.006	0.020
o-Cymene	0.0892	0.0843	0.0862	0.0821	0.0749	0.0861	0.0948	0.085	0.006	0.019
n-ButylBenzene	0.0829	0.0833	0.0837	0.0814	0.0785	0.0875	0.0975	0.085	0.006	0.019
1,2,4-Trichlorobenzene	0.0958	0.0877	0.0922	0.0847	0.0813	0.0999	0.109	0.093	0.010	0.030
Naphthalene	0.0921	0.0866	0.0884	0.0827	0.0804	0.0955	0.119	0.092	0.013	0.041
Hexachlorobutadiene	0.0902	0.0892	0.0918	0.0911	0.0808	0.0874	0.0975	0.090	0.005	0.016

Table 3 7200CTS relative humidty test shows little change in recoveries between 40% and 95% relative humidity samples

Date Acquired Sample Name		10/2/17 10 ppb 95% RH trap at 30°C	10/2/17 10 ppb 95% RH trap at 35°C	9/31/2017 10 ppb 40% RH trap at 30°C
Name	Ret Time	Concentration (ppb)	Concentration (ppb)	Concentration (ppb)
Propene	3.25	4.2	8.9	8.4
Dichlorodifluoromethane	3.36	8.0	9.3	8.8
Chloromethane	3.70	10.6	9.5	8.4
Dichlorotetrafluoroethane	3.73	8.5	9.3	8.8
Vinyl Chloride	3.92	9.1	9.5	8.7
1,3-Butadiene	4.11	10.0	9.7	9.1
Bromomethane	4.50	6.1	8.5	9.2
Chloroethane	4.73	9.4	9.3	8.6
Bromoethene	5.20	9.7	10.0	8.9
Ethanol	4.83	9.5	8.8	8.1
Acetonitrile *	5.15	12.1	11.0	10.0
Trichlorofluoromethane	5.72	9.7	9.1	9.1
Acetone	5.45	9.1	8.4	7.6
Isopropyl Alcohol *	5.70	8.7	8.0	8.7
Acrolein	5.32	9.4	8.9	8.7
1,1-Dichloroethene	6.47	9.6	9.5	9.1
Acrylonitrile	6.02	10.7	10.0	9.4
Trichlorotrifluoroethane	6.87	9.5	9.3	8.8
Allyl Chloride	6.70	10.3	9.6	9.0
Methylene Chloride	6.59	9.2	9.3	8.1
tert-Butanol	6.38	10.2	9.9	9.6
Carbon Disulfide	6.99	10.1	9.8	8.9
trans-1,2-Dichloroethene	7.60	9.8	9.5	8.4
Methyl tert-Butyl Ether	7.84	10.2	10.0	9.1
Vinyl Acetate	7.91	10.4	10.0	9.4
1,1-Dichloroethane	7.80	9.7	9.3	8.9
2-Butanone	8.16	10.4	10.4	9.2
Hexane	8.88	9.4	9.6	8.8
cis-1,2-Dichloroethene	8.66	9.7	9.5	8.7
2-Chloroprene	8.40	9.7	9.8	9.4
Ethyl Acetate	8.81	9.9	9.3	8.9
Chloroform	8.95	9.6	9.4	8.9
Di-Isopropyl Ether	8.82	9.6	9.5	9.1
Tetrahydrofuran	9.34	9.8	9.7	8.9
Ethyl tert-Butyl Ether	9.36	9.8	9.6	9.1
1,1,1-Trichloroethane	9.96	9.8	9.6	9.2
1,2-Dichloroethane	9.68	9.7	9.5	9.0
Benzene	10.40	9.7	9.6	9.0
Carbon Tetrachloride	10.56	9.9	9.7	9.5
Cyclohexane	10.69	9.3	9.2	8.3
tert-Amyl Methl Ether	10.92	9.9	9.7	9.3

Table 3 (continued) 7200CTS relative humidty test shows little change in recoveries between 40% and 95% relative humidity samples

Date Acquired Sample Name Name	Ret Time	10/2/17 10 ppb 95% RH trap at 30°C Concentration (ppb)	10/2/17 10 ppb 95% RH trap at 35°C Concentration (ppb)	9/31/2017 10 ppb 40% RH trap at 30°C Concentration (ppb)
2,2,4-Trimethylpentane	11.44	10.0	9.7	8.7
Heptane	11.65	10.0	9.9	9.0
Trichloroethene	11.40	9.6	9.5	8.7
1,2-Dichloropropane	11.18	9.7	9.5	8.9
1,4-Dioxane	11.35	9.7	9.6	8.6
Bromodichloromethane	11.35	10.1	9.8	9.0
Methyl Methacrylate	11.50	9.3	10.0	9.1
cis-1,3-Dichloropropene	12.20	9.7	9.6	8.7
4-Methyl-2-pentanone	12.19	10.5	10.0	9.3
trans-1,3-Dichloropropene	12.69	9.8	9.6	9.0
Toluene	13.17	9.3	9.4	8.6
1,1,2-Trichloroethane	12.88	9.6	9.6	9.1
2-Hexanone	13.33	10.1	10.0	9.0
Dibromochloromethane	13.58	10.2	10.1	9.4
Tetrachloroethene	14.25	9.4	9.5	9.1
1,2-Dibromoethane	13.82	9.5	9.5	8.7
Chlorobenzene	14.87	8.7	9.3	8.1
1,1,1,2-Tetrachloroethane	14.85	8.8	9.3	9.3
Ethylbenzene	15.21	8.9	9.4	8.6
m- and p-Xylene	15.36	18.1	19.0	8.5
Styrene	15.70	9.0	9.8	8.5
o-Xylene	15.81	8.8	9.2	8.4
Bromoform	15.47	9.9	10.6	9.6
1,1,2,2-Tetrachloroethane	15.78	9.1	9.5	8.5
Cumene	16.35	8.4	8.7	8.8
o-Chlorotoluene	16.83	8.3	8.6	8.5
n-Propylbenzene	16.85	8.4	8.7	8.6
4-Ethyltoluene	16.98	9.3	9.6	8.5
1,3,5-Trimethylbenzene	17.05	8.9	9.0	8.9
tert-Butylbenzene	17.47	8.8	9.1	9.3
1,2,4-Trimethylbenzene	17.47	9.1	9.2	8.9
1,3-Dichlorobenzene	17.65	8.5	8.8	8.4
Benzyl Chloride	17.62	9.4	9.6	9.1
1,4-Dichlorobenzene	17.72	8.5	8.9	8.3
sec-Butyl Benzene	17.75	8.6	8.5	9.1
1,2-Dichlorobenzene	18.09	8.6	8.9	8.7
o-Cymene	18.11	8.9	9.0	9.6
n-Butyl Benzene	18.35	8.7	8.5	9.5
1,2,4-Trichlorobenzene	19.99	8.5	8.7	9.6
Naphthalene	20.14	8.7	8.6	9.9
Hexachlorobutadiene	20.51	8.9	9.2	9.3

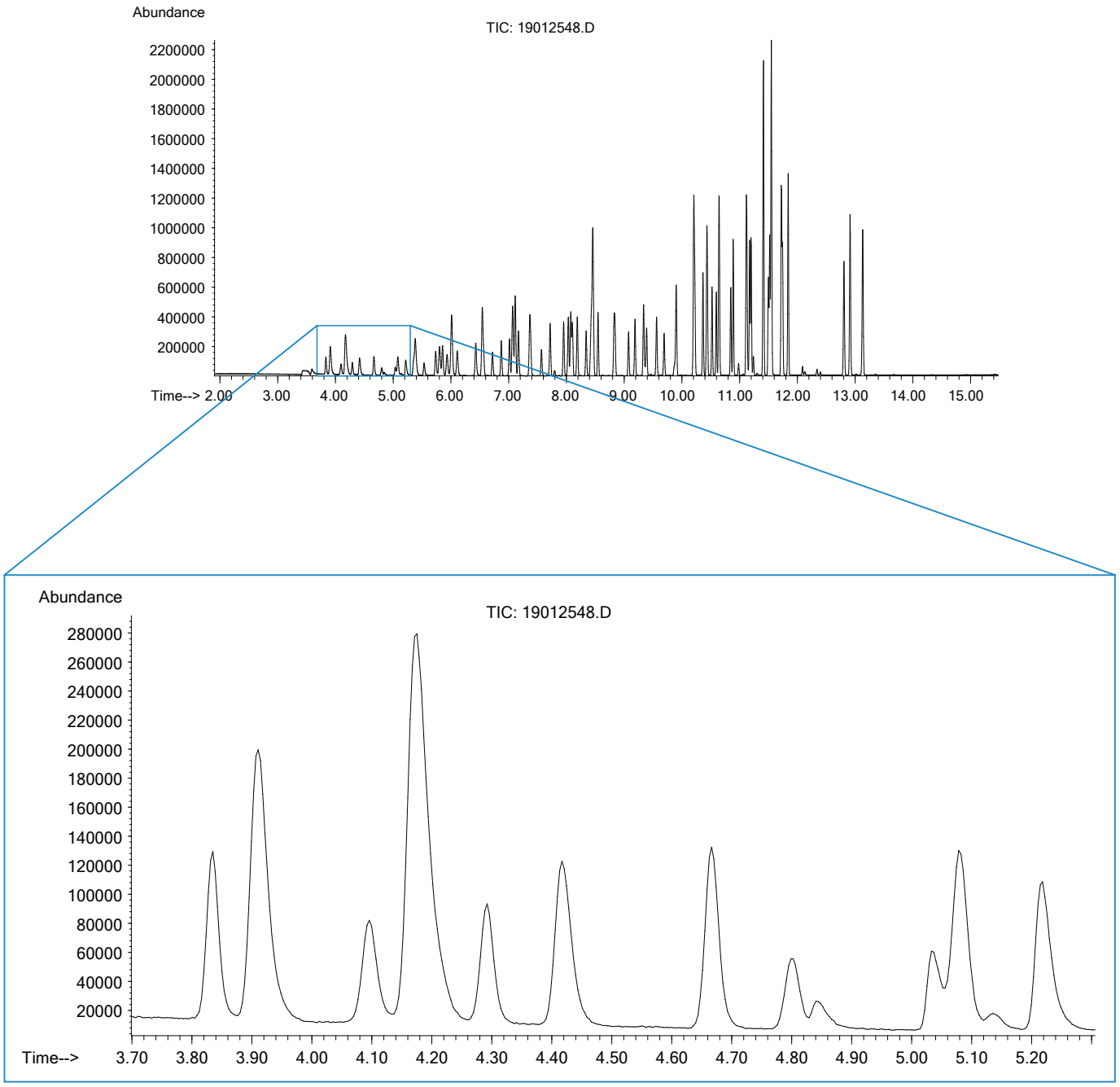


Figure 7 250cc at 10PPBv 84 Component TO15 Standard - Complete recovery through High Boilers.

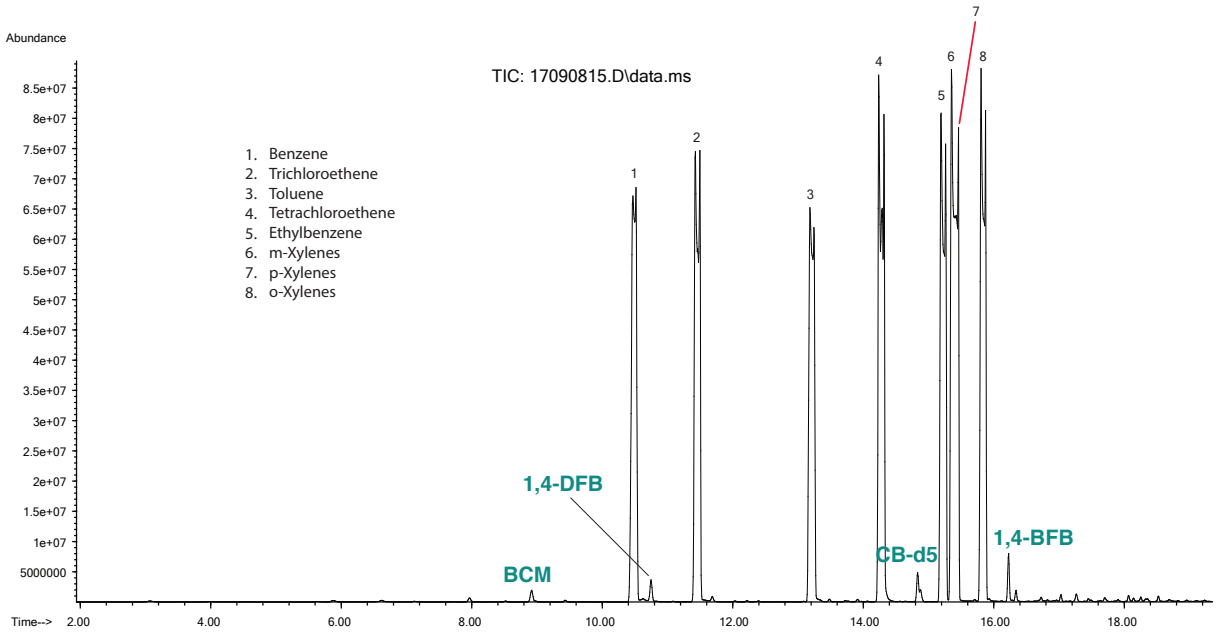


Figure 8 Carry-Over Study – Chromatogram showing 100cc of 10,000 PPBv TCE, PCE, BTEX standard.

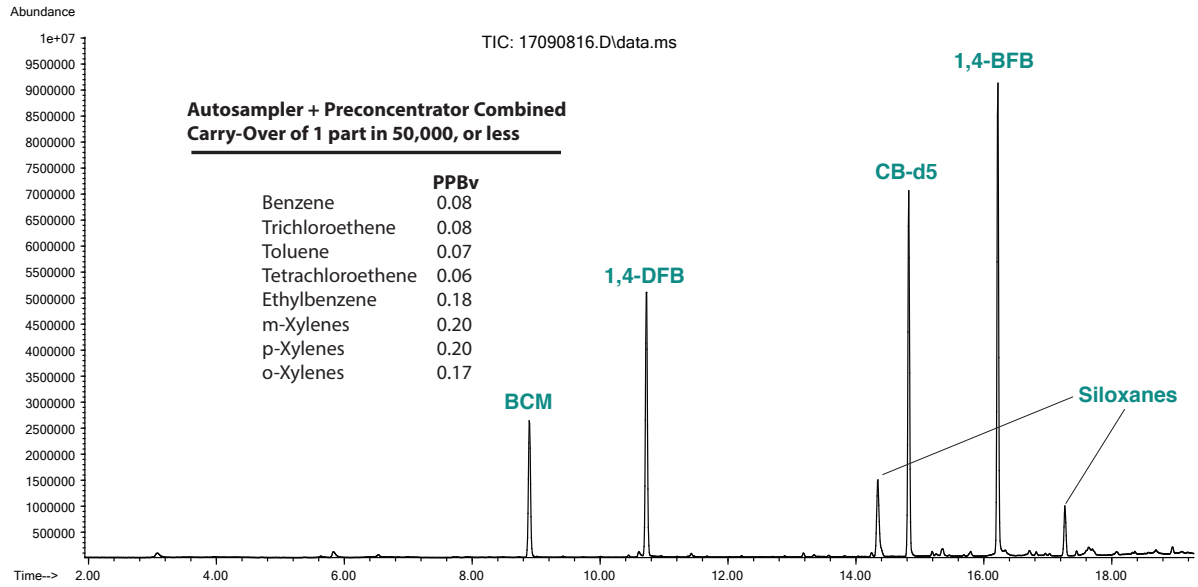


Figure 9 - Carry-Over Study – Chromatogram showing 100cc humidified blank run immediately following 10,000 PPBv Standard (**Figure 8**).

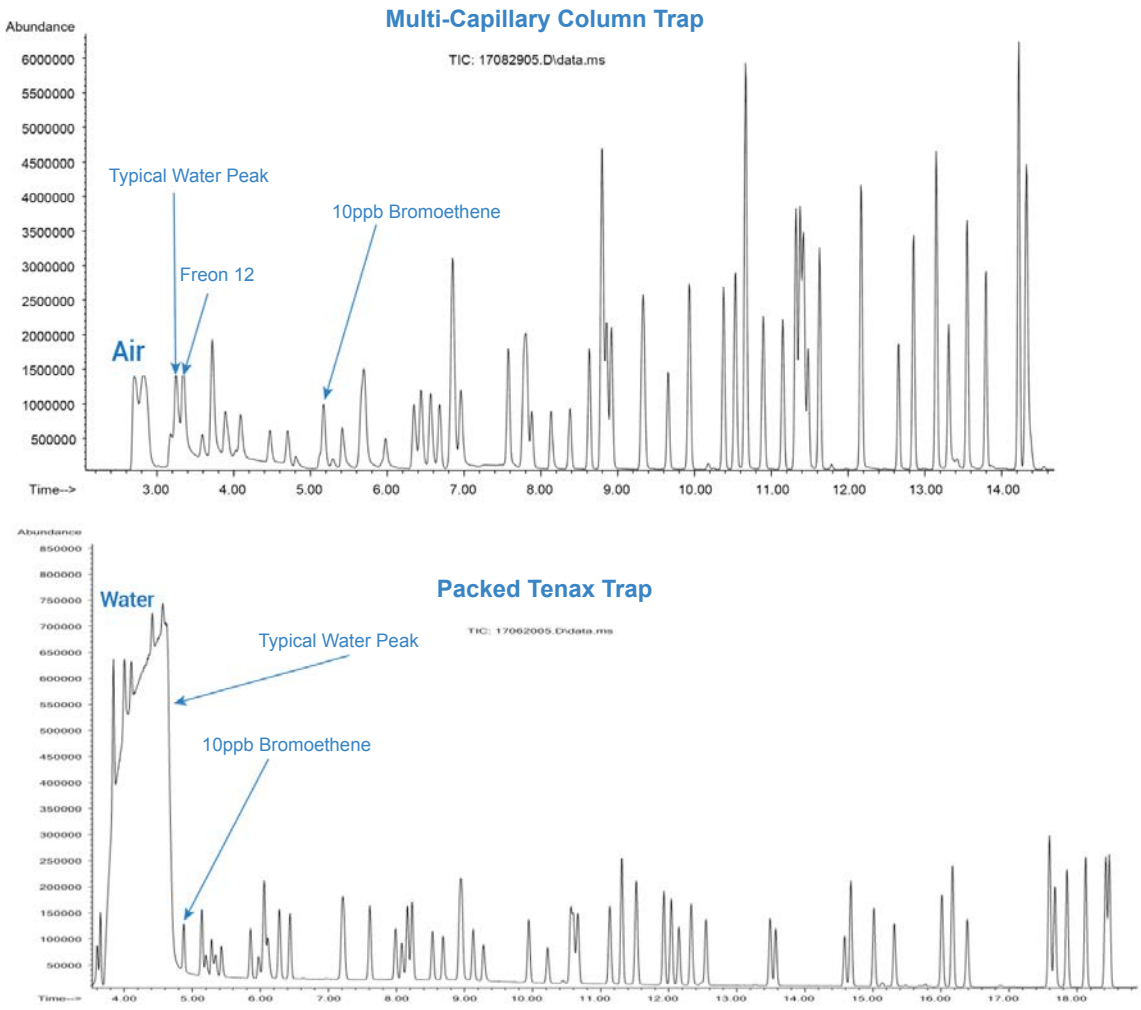


Figure 10 - Although the two chromatograms above are not on the same Y and X axis scale, as they were run using two different instruments, both chromatograms show a 10ppb TO15 standard at 50% RH. TO15 standard compound Bromoethene, shown at 10ppb for both runs, can be used to visually compare the relative amount of water found when scanning down to mass 18 for water using a packed trap vs a capillary column trap. At 25°C, 50% RH is equivalent to 15 million PPBv of water. A typical water peak using packed traps or cold trap water management is 0.5-1 minutes wide, which causes MS suppression of the front-end compounds.

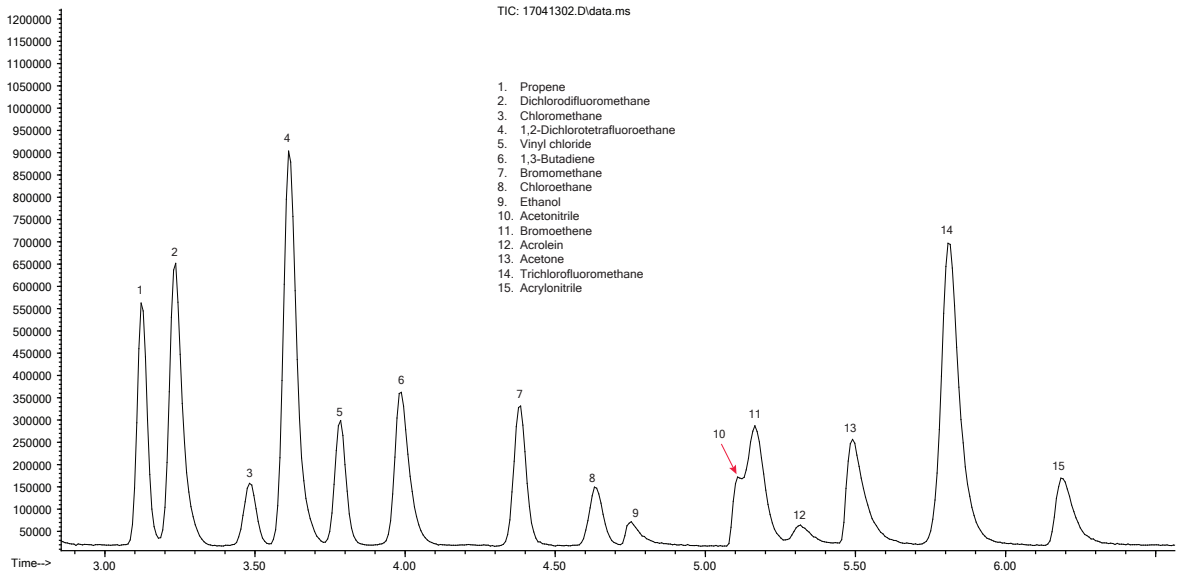


Figure 11 - TO15, 84 Compound Standard, 250cc, 10PPBV - The total ion chromatogram above demonstrates the cryogen-free fast injection of the light end with excellent separation and little or no peak tailing.

Conclusions

- ☑ Full TO15 validation with single-digit %RSDs for most compounds for 0.1-30PPBv standard curve and MDLs 5 times lower than the LOQ
- ☑ Elimnation of cryogen costs
- ☑ Minimizing caryover by using capillary traps and eliminating dead volumne
- ☑ Cleans up quickly after accidentally running high concentration samples, substantially reducing downtime for laboratories
- ☑ Elimination of channeling effect
- ☑ Superior water management

A cryogen free TO15 solution has been demonstrated with superior water management and greater immunity to contamination when accidently running high concentration samples. The ability to clean up a system quickly after exposure to high concentration samples can save laboratories a substantial amount of time, reducing the need for long system bake-outs, trap replacements, and sample re-runs. This means higher productivity and sample throughput for these laboratories to help them to meet customer demands, while achieving their own financial goals.

Even lower carryover can be achieved by eliminating rotary stream select valves found in most commercial canister autosamplers. The 7650-M robotic autosampler makes only momentary contact with the sample using a transfer line completely heated up to 150c, and then immediately flushes the exposed line to eliminate any residual that would otherwise absorb into surfaces and rotors in classical rotary valve based autosamplers.

Elimination of cryogen costs and the dramatic improvement in system hygiene creates a substantial savings for laboratories, while increasing method accuracy and extending system capabilities by recovering a wider range of compounds than ever before. As has been the case of capillary vs packed columns within the GC oven, the new Multi-Capillary Column Trapping System may well lead to the obsolescence of prior packed trap technology.

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