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## Improved Performance And Dynamic Range For EPA Method TO-15 using the Entech 7200 and Thermo Scientific ISQ QD GCMS

### Application Note:

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### Abstract

Canister sampling and analysis for measurement of volatile chemicals is finding use in a growing number of diversified applications. This has required air laboratories to accommodate an even wider dynamic range of sample concentrations, and a growing list of compounds to include those once thought to be incompatible with canister sampling techniques. New materials for the internal lining of canisters and field sampling systems, as well as laboratory analyzers optimized using 3D Computer Assisted Design software have provided the improved performance needed to meet these challenges.

A new Air Toxics TO-15 Analyzer based on the Entech 7200 Preconcentrator and Thermo Scientific ISQ QD GCMS system is demonstrated here, creating performance levels well beyond what was previously possible. Every aspect of the sample preparation and analysis process has been optimized to improve linearity, recovery, sensitivity, and dynamic range. Linear calibrations that meet TO-15 criteria are now possible over a dynamic range of 100-2000 fold, reducing the number of dilutions necessary, while lowering detection limits to meet today's Low Level TO-15 standards. The improved recovery and linearity also reduces the downtime previously caused by systems that were only marginally meeting the method linearity requirements. The following application note will describe the new

advancements in the 7200/ISQ GCMS system that have resulted in a dramatic improvement over prior technology.

### Preconcentration and GC/MS Analysis

In order to reach low ppb or ppt detection limits, an aliquot of the canister collected air sample must be concentrated before injection into a GCMS. Although Oxygen, Nitrogen, and Argon in air are easily eliminated during the preconcentration process, Carbon Dioxide and Water are a little more difficult to remove without affecting recoveries of target VOCs. To minimize interference from water and carbon dioxide in air, a 3 stage trapping procedure called "Extended Cold Trap Dehydration" is utilized. An empty Silonite-D treated trap cooled to  $-40^{\circ}\text{C}$  is used to eliminate water by a direct gas to solid phase transition. As the sample passes through this trap, the air and most of the VOCs pass right through to the second trap. However, almost all of the water freezes out in the first stage trap, simply because it has been cooled far below its saturation point. Another way to think of this is, the gas phase concentration of water is reduced from as high as 30,000 PPM (100% RH at  $25^{\circ}\text{C}$ ) to just 2-100 PPM via this first stage at  $-40^{\circ}\text{C}$ , which is now at a concentration that will not affect the operation of the GCMS. The VOCs of interest are already well below this concentration, and therefore have little or no retention because they are still below their saturation point at  $-40^{\circ}\text{C}$ . This approach only works by using the extremely inert Silonite-D coating process that keeps the target compounds from sticking to the walls of the tubing at  $-40^{\circ}\text{C}$ . The VOCs then collect on a second stage Tenax trap at  $-40^{\circ}\text{C}$ . Tenax is approximately 100 times stronger at  $-40^{\circ}\text{C}$  than at  $+30^{\circ}\text{C}$ , allowing it to trap even the lightest VOCs. Silonite-D coated trap is heated to  $+10^{\circ}\text{C}$  to transfer an additional 50cc of UHP nitrogen



or helium through to the M2 Tenax trap at  $-40^{\circ}\text{C}$ , just in case a small percentage of the heavy or polar VOCs had dropped out. Afterwards, the second stage Tenax trap is back desorbed to a third ultra low volume trap for final focusing before rapid injection into a GCMS system for analyte detection and measurement.

### **Accu-Sample™ Technology**

Optimizing canister analysis requires sample preparation systems that perform accurate measurement of the sample volumes, proper transfer of each compound through the preconcentration system, and substantial isolation of each sample from the next to prevent cross-contamination. The Entech 7200 accomplishes this using its new Accu-Sample™ Technology. This 3-part technology includes (a) Electronic Volume Control, (b) Digital Rotary Valve Control, and c) Silonite D transfer tubing throughout the flow path. Each will be described briefly.

### **Electronic Volume Control (EVC) -**

In the past, canister preconcentrators used Mass Flow Controllers (MFCs) to measure the flow rate, and would time integrate the flow to indirectly measure the volume of sample that had passed through the traps. This has several drawbacks, including observed MFC flow rates and output signals that were unreliable at the beginning of trapping, and the inability to measure volumes accurately when the sample matrix change from air to other matrices, such as  $\text{CO}_2$ , Methane, or Helium. The 7200's new Electronic Volume Control eliminates these inaccuracies by directly measuring the volume that has passed through the preconcentration traps rather than

estimating the volume by the output of the mass flow controller. This yields much more consistent volume measurements, especially at lower sample volumes which are often needed both to calibrate the instrument and to allow the analysis of higher concentration samples without having to first dilute the sample. This directly translates to improved linearity and increased laboratory productivity. The EVC's response is also not affected by the matrix, allowing mixtures of Methane,  $\text{CO}_2$ , or other bulk gases to be analyzed as accurately as ambient air.

### **Digital Rotary Valve Control -**

The 7200 uses digitally controlled actuators that can stop "between" ports to provide system isolation at key times during the sampling process. For example, rather than selecting the next stream by rotating past other ports, with potential contamination into the trapping system as high concentration samples or standards are momentarily exposed to the system, the 7200 can "close" the down-stream 2 position valve so that zero cross-contamination is observed during sample selection. This was simply not possible with the 7100A, which required the air chemist to be mindful of mixing high and low level samples on the 4-sample inlet. The accuracy of the analysis is greatly affected by the degree of sample isolation that can be achieved, and only so much isolation is possible using a rotary valve inlet system. The 7650 Robotic Autosampler as a front end to the 7200 further isolates each sample by having them completely disconnected from the analytical system until the moment of sample extraction.

## Silonite-D Transfer Lines -

The next generation in inert tubing has been achieved through years of research by measuring the interaction of TO-15 compounds on treated tubing. Silonite-D takes coated tubing to the next level by truly making the surface as inert as a GC column, maximizing the recovery of compounds even more challenging than those found in routine TO-15 standard mixtures. Maximizing transfer line inertness results in nearly 100% of the sample being transferred to the GCMS, while leaving very little to be baked out, and even less to carry over into the next analysis.

## Advanced Water Management

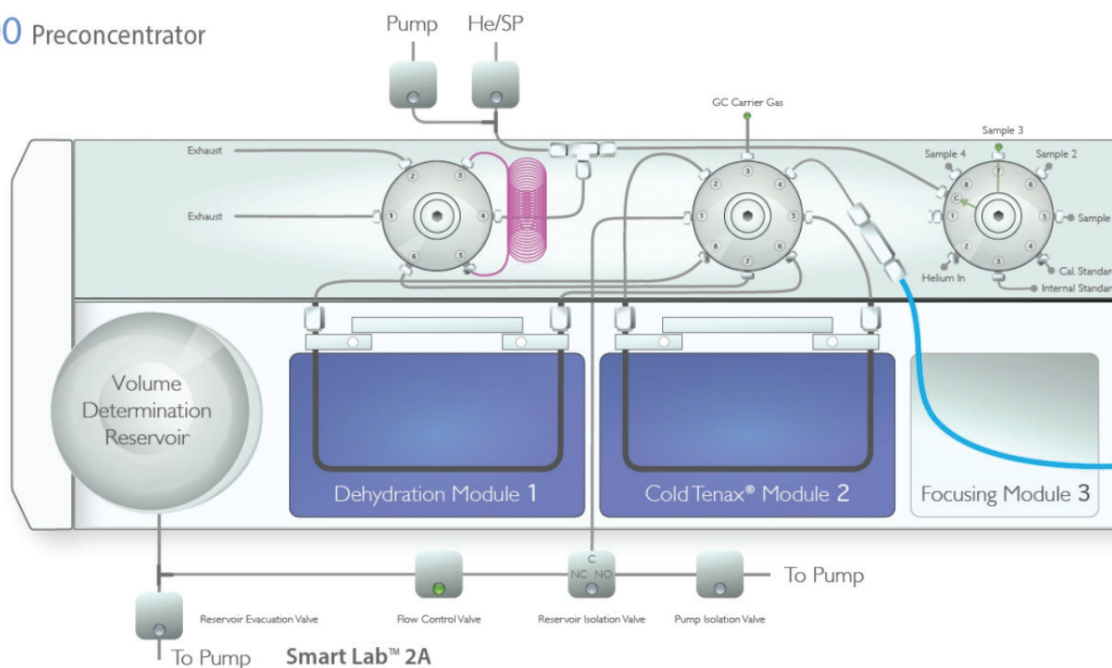
The 7200 performs water management differently than most other preconcentrators. Rather than trying to dry purge a multi-bed adsorbent trap, relying solely on a chemical difference between the water and all other compounds to be monitored, the 7200 performs water management by taking advantage of water being the only component in air that is anywhere close to its saturation point. The 7200 can either condense the water and VOCs in the first trap followed by a limited purge transfer to a second trap (Microscale Purge & Trap), or the first stage trap can be cooled down to  $-40^{\circ}\text{C}$  to dehydrate the sample as it travels through this stage to a second trap. All other compounds are at too low a concentration to condense in the first trap, and continue on to the cold Tenax trap. Both of these approaches for water

management place no restrictions on how low a temperature the second stage is cooled to, allowing the 7200 to trap polar VOCs and C2 hydrocarbons in the same analysis; a capability that remains unique to the 7200 and its predecessor, the 7100A. Sub-ambient temperature trapping allows the use of much weaker adsorbents, such as Tenax, as these can be made 100 times stronger just by cooling them down to  $-40^{\circ}\text{C}$ , yet they remain very easy to clean up without having to heat the adsorbent to high enough temperatures to cause thermal decomposition, artifacts, and non-volatile decomposition products which will change the characteristics of the adsorbent. As dehydration occurs in the first trap, water is removed via transition directly from the gas phase to the solid phase, preventing the loss of polar compounds which are soluble in liquid water. All 3 traps in the 7200 are Silonite-D coated as are the internal 1/16" transfer lines, creating the most inert flow path available to ensure maximum sample recovery.

## Reducing Carryover/Improving Recovery

Providing a preliminary moisture elimination trap and using sub-ambient temperature trapping on an adsorbent offers other advantages. Cold adsorbent trapping keeps the sample much closer to the very front of the adsorbent bed, making its recovery more complete and faster upon back desorption. This improves

### 7200 Preconcentrator



#### Smart Lab™ 2A

The 7200 is controlled by Entech's SmartLab™ 2A control network operating under Microsoft Win XP or Windows 7 using the latest high-speed USB interface technology.

sensitivity and reproducibility, while greatly reducing the potential for carry-over when a high concentration sample is accidentally analyzed prior to dilution. Some multi-bed traps operated at +30°C during trapping have been known to require up to a week of purging to clean up when accidentally exposed to high concentration soil gas samples. When contamination occurs, any samples run afterwards in an automated sequence will have to be rerun, assuming there is enough sample left. This can severely impact laboratory throughput while causing some samples to be lost altogether. It is the use of liquid nitrogen that allows the 7200 traps to be operated at -40°C, creating the lowest carryover possible by eliminating the need for stronger adsorbents. These low temperature cannot be achieved using electronic cooling. Until a technology presents itself that allows for the same level of analytical performance, liquid nitrogen will continue to be the best choice for the TO-15 production laboratory.

## Experimental

Analytical data was generated with the 7200 Preconcentrator interfaced to a Thermo Scientific ISQ QD GCMS. The GC oven started at 35°C (5 min) ramped at

6°C/min to 120°C, then at 10°C/min to a final temperature of 220°C (5 min). The MS acquisition was from 28 to 280 amu to include Formaldehyde in the analysis, otherwise a starting mass of 30 amu would be recommended for the first 8 minutes to maximize the response of some of the lighter polar compounds. Calibration standards were obtained from both Linde Gas and Scott Gases. Three cylinders at 1 PPMv were blended together using an Entech Instruments Model 4700 Dynamic Dilution system to 20 PPBv, and then this was used to create a 0.4PPBv standard a second 6L Silonite canister using the 4700's unique reblend feature. The combination of using varied calibration volumes from the two standard canisters allowed an extended calibration range from 0.04 to 40 PPBv, for a total of a 1000x dynamic range. The nominal sample volume was chosen to be 250 PPBv, with varying calibration points created by altering the volume between 25 to 500cc. Seven replicate injections at 0.2 PPB (125cc from the 0.4PPBstd) were used to create the MDL values. The 10 point calibration is shown in Table 2, and the MDLs in Table 3.

**Table 1** below shows the sample trapping conditions of the 7200 Preconcentrator.

Event Temp.(°C)	Trap	Sweep	M1-M2	M2-M3
M1 Empty Trap	-40	-40	10	10
M2 Tenax Trap	-40	-40	-40	230
M3 Open Tube	NA	NA	NA	-150
Volume (cc)	250	75	50	20
Flow Rate (cc/min)	100	100	10	6

**Table 1** - 7200 Trapping Conditions Using Extended Cold Trap Dehydration.

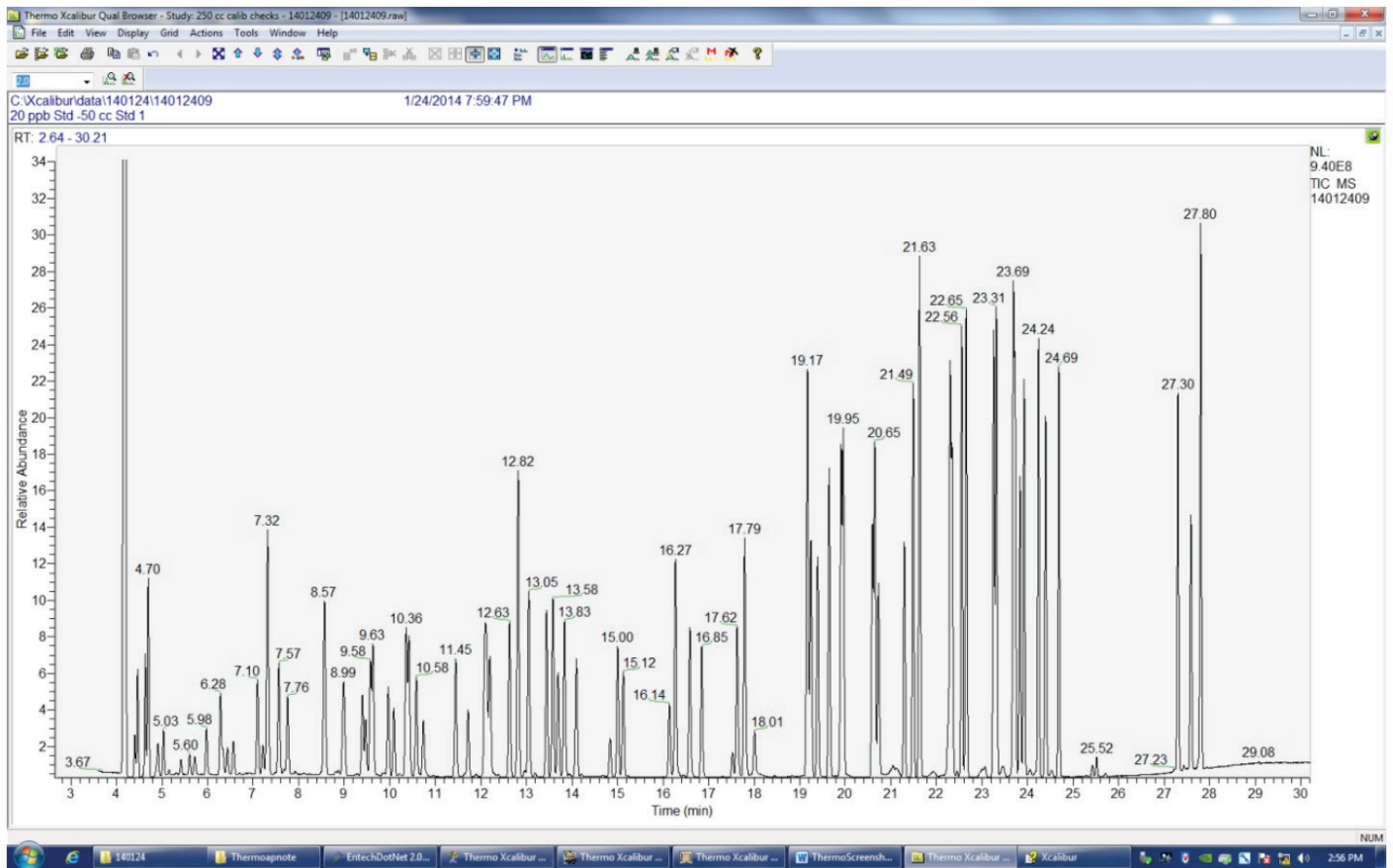
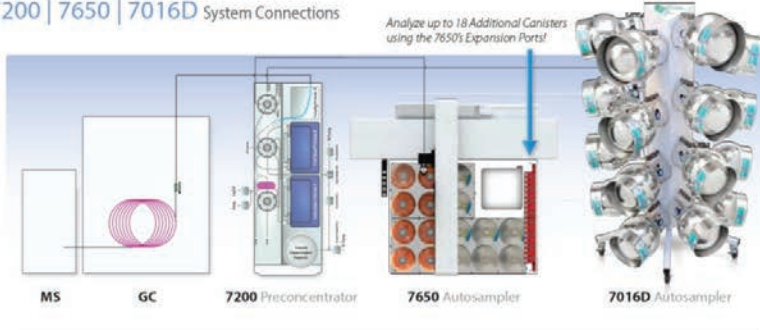


Figure 2 - 250cc 10 ppbv 82 Component TO15 Standard

7200 | 7650 | 7016D System Connections



7200 with 7650 and 7016D Autosamplers for maximum flexibility and productivity



7200 with 7650 Robotic Autosampler virtually eliminates cross sample contamination

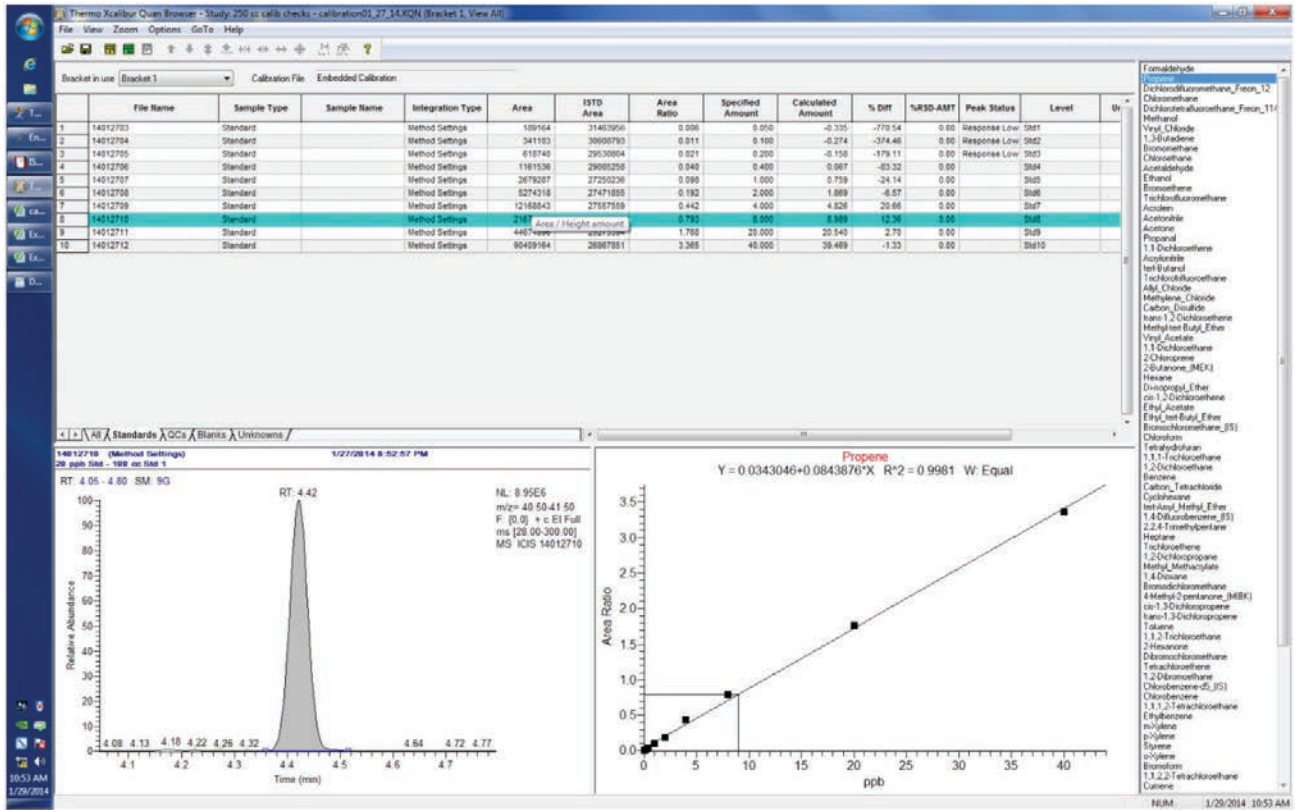


Figure 5 - Propene Chromatography and Calibration Results

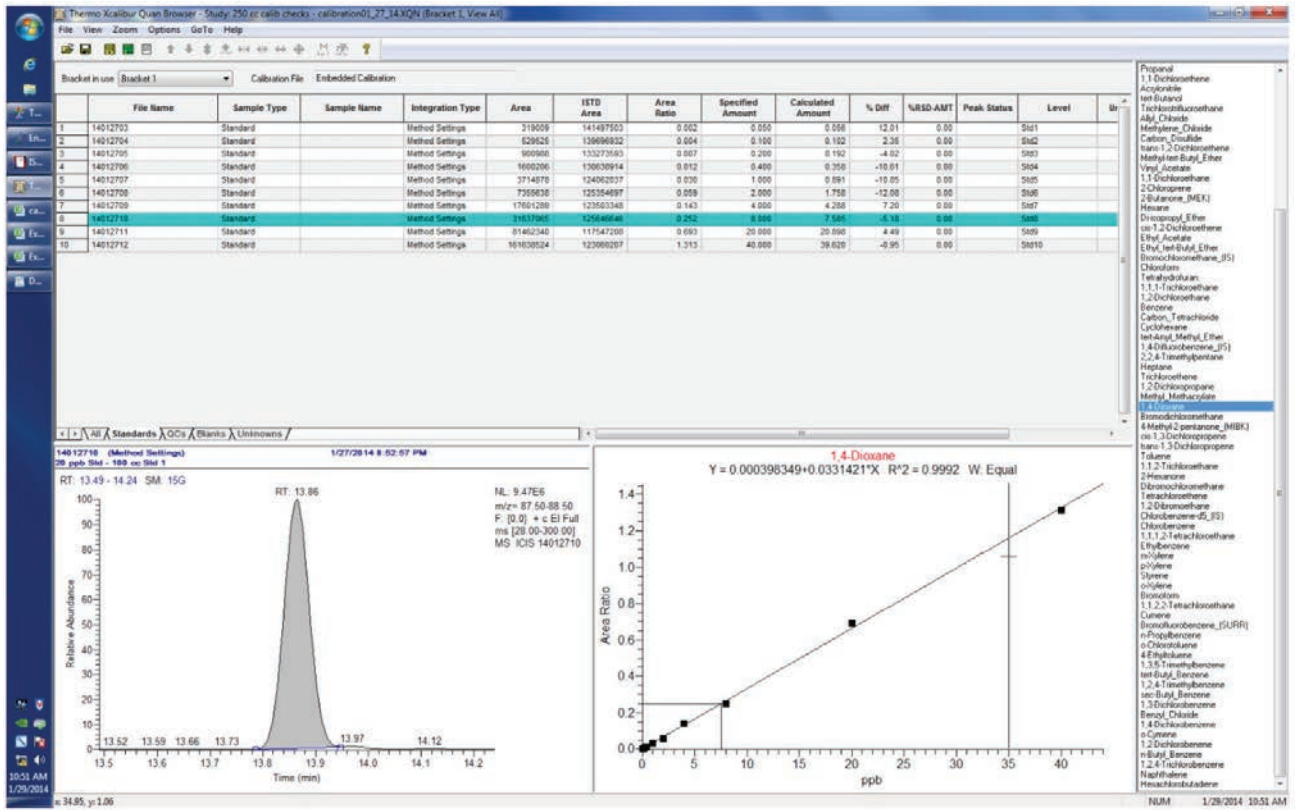


Figure 6 - 1,4-Dioxane Chromatography and Calibration Results

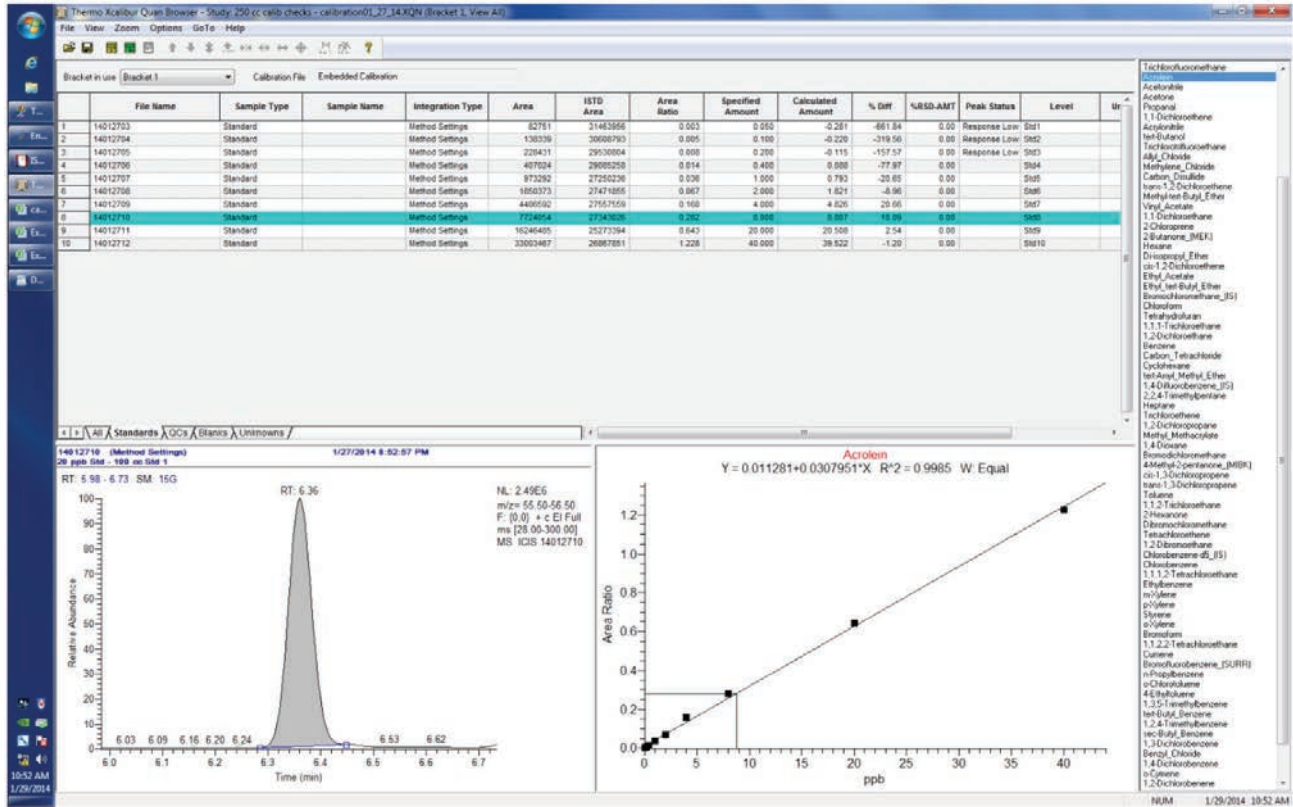


Figure 7 - Acrolein Chromatography and Calibration Results

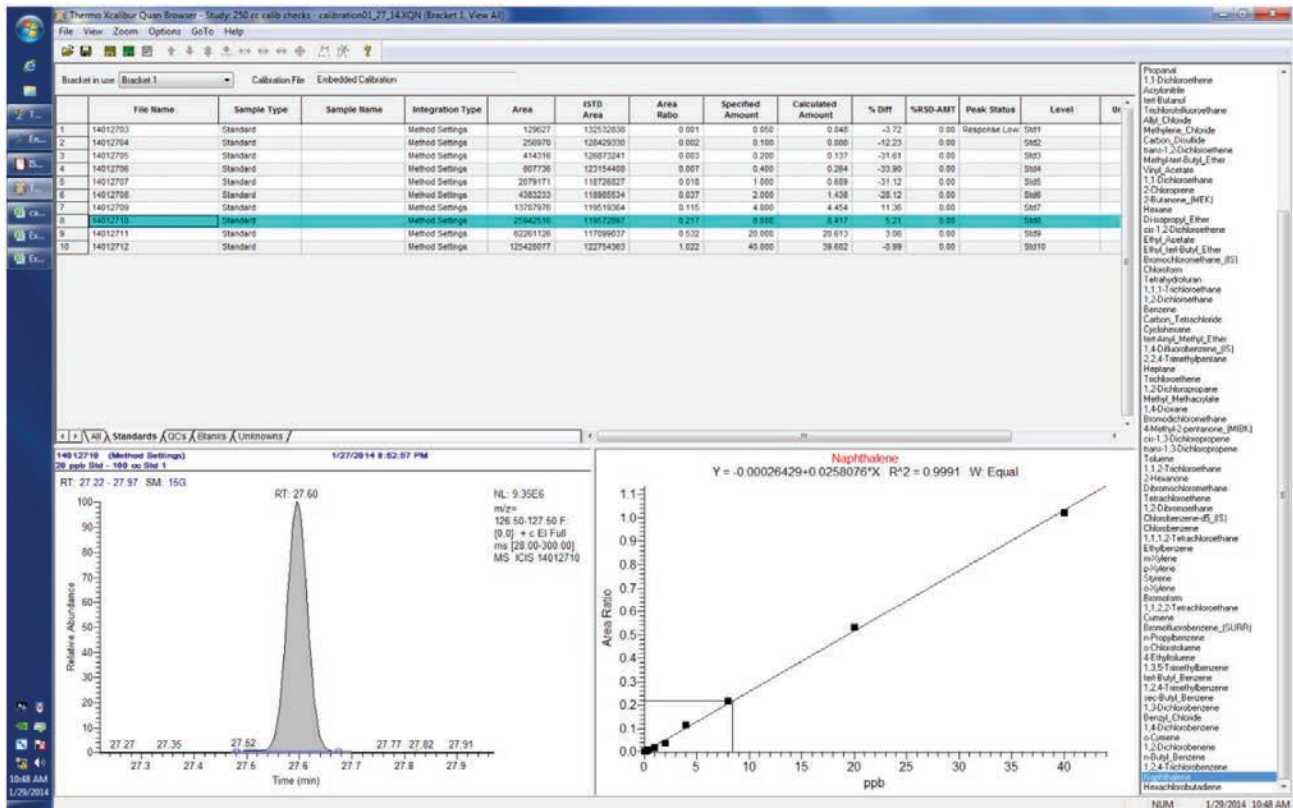


Figure 8 - Naphthalene Chromatography and Calibration Results

Compound	0.04 RRF1	0.10 RRF2	0.20 RRF3	0.40 RRF4	1.00 RRF5	2.00 RRF6	4.00 RRF7	8.00 RRF8	20.00 RRF9	40.00 RRF10	Ave RRF	%RSD
Propene	3.006	2.786	2.619	2.496	2.458	2.400	2.760	2.478	2.210	2.103	2.532	10.7
Dichlorodifluoromethane_Freon_12	3.200	3.414	3.223	3.063	3.017	2.478	3.516	3.176	3.148	2.559	3.079	10.8
Chloromethane	5.374	5.340	4.893	4.470	4.466	4.357	4.941	4.529	4.174	3.621	4.616	11.6
Dichlorotetrafluoroethane_Freon_114	9.154	9.729	8.969	8.415	8.308	8.148	9.464	8.609	8.318	7.062	8.618	8.8
Vinyl_Chloride	3.665	3.850	3.560	3.316	3.355	3.256	3.740	3.458	3.419	3.022	3.464	7.1
1,3-Butadiene	2.571	2.740	2.562	2.444	2.429	2.409	2.804	2.596	2.447	2.180	2.518	7.1
Bromomethane	1.487	1.511	1.371	1.244	1.245	1.203	1.418	1.294	1.277	1.151	1.320	9.2
Chloroethane	1.639	1.739	1.690	1.579	1.586	1.558	1.796	1.667	1.595	1.434	1.628	6.3
Acetaldehyde	0.396	0.229	0.274	0.338	0.287	0.293	0.333	0.308	0.299	0.288	0.304	14.5
Ethanol	2.100	1.769	1.559	1.338	1.278	1.254	1.377	1.278	1.150	1.104	1.421	21.7
Bromoethene	4.280	4.432	4.238	3.953	3.927	3.847	4.499	4.105	3.967	3.567	4.082	7.0
Trichlorofluoromethane	8.488	8.719	8.213	7.689	7.875	7.530	8.923	8.026	8.375	7.352	8.119	6.4
Acrolein	1.315	1.130	0.967	0.875	0.893	0.842	0.999	0.883	0.804	0.768	0.947	17.5
Acetonitrile	1.855	2.129	2.017	1.859	1.997	1.915	2.169	1.969	1.850	1.758	1.952	6.7
Acetone	**	3.813	3.309	2.949	2.887	2.715	1.771	1.568	1.442	1.335	2.421	37.5
1,1-Dichloroethene	5.472	5.668	5.133	4.768	4.765	4.723	5.538	4.936	5.011	4.618	5.063	7.4
Acrylonitrile	2.726	2.784	2.646	2.307	2.530	2.326	2.938	2.565	2.667	2.537	2.603	7.5
tert-Butanol	8.919	9.411	8.524	7.983	7.514	7.874	9.338	8.314	8.557	7.623	8.406	8.0
Trichlorotrifluoroethane	10.237	10.566	9.547	9.013	9.001	8.871	10.269	9.124	9.093	8.015	9.374	8.3
Allyl_Chloride	2.102	2.154	2.073	1.941	1.940	1.939	2.255	2.019	2.133	1.944	2.050	5.4
Methylene_Chloride	**	6.964	5.366	4.466	4.118	3.842	4.407	3.935	4.123	3.797	4.558	22.4
Carbon_Disulfide	15.154	14.979	13.646	12.875	12.977	12.734	14.450	12.894	12.978	11.957	13.465	7.9
trans-1,2-Dichloroethene	5.770	5.293	5.052	4.677	4.686	4.673	5.424	4.861	5.129	4.708	5.027	7.5
Methyl-tert-Butyl_Ether	12.918	13.434	12.692	11.902	11.886	11.754	13.461	12.048	12.935	11.704	12.473	5.6
Vinyl_Acetate	7.877	8.560	7.945	7.368	7.495	7.248	8.675	7.884	7.301	6.852	7.720	7.5
1,1-Dichloroethane	7.454	7.875	7.206	6.738	6.812	6.749	8.030	7.068	7.996	7.204	7.313	6.9
2-Chloroprene	4.005	4.340	4.027	3.799	3.917	3.868	4.614	4.171	4.512	4.281	4.153	6.7
2-Butanone_(MEK)	2.583	2.603	2.460	2.375	2.316	2.309	2.629	2.390	2.621	2.517	2.480	5.1
Hexane	5.868	6.201	6.013	5.551	5.665	5.504	6.466	5.810	6.270	5.769	5.912	5.4
Di-isopropyl_Ether	4.598	4.685	4.470	4.180	4.234	4.248	4.947	4.523	4.932	4.662	4.548	6.0
cis-1,2-Dichloroethene	5.622	5.956	5.433	5.173	5.168	5.165	6.096	5.493	5.687	5.333	5.513	6.0
Ethyl_Acetate	7.690	7.695	7.389	6.795	6.876	6.865	8.022	7.248	6.671	6.480	7.173	7.2
Ethyl_tert-Butyl_Ether	13.248	14.036	12.867	12.198	12.293	12.317	14.429	13.070	14.271	13.214	13.194	6.2
Chloroform	9.868	10.153	9.442	8.902	9.123	8.899	10.067	8.986	9.586	8.746	9.377	5.5
Tetrahydrofuran	3.751	3.955	3.590	3.496	3.494	3.436	4.030	3.663	3.275	3.157	3.585	7.7
1,1,1-Trichloroethane	10.128	10.115	9.563	9.059	8.956	8.899	10.591	9.541	10.079	9.123	9.605	6.2
1,2-Dichloroethane	1.322	1.364	1.304	1.235	1.245	1.223	1.462	1.288	1.458	1.324	1.322	6.4
Benzene	5.507	4.672	4.000	3.596	3.456	3.344	3.764	3.273	3.382	3.133	3.813	19.5
Carbon_Tetrachloride	2.126	2.189	2.083	2.002	1.969	1.975	2.282	1.994	2.122	1.922	2.066	5.5
Cyclohexane	1.403	1.440	1.393	1.301	1.289	1.274	1.530	1.347	1.434	1.332	1.374	5.9
tert-Amyl_Methyl_Ether	3.244	3.511	3.224	3.071	3.054	3.004	3.633	3.182	3.437	3.284	3.264	6.3
2,2,4-Trimethylpentane	4.762	4.708	4.409	4.133	4.026	3.973	4.825	4.198	4.479	4.179	4.369	7.2
Heptane	1.185	1.236	1.147	1.104	1.085	1.090	1.312	1.157	1.203	1.164	1.168	6.0

**Table 2** TO-15 Calibration over a 1000x calibration range from 40 part-per-trillion to 40 part-per-billion showing low Relative Standard Deviations



Compound	0.04	0.10	0.20	0.40	1.00	2.00	4.00	8.00	20.00	40.00	Ave RRF	%RSD
	RRF1	RRF2	RRF3	RRF4	RRF5	RRF6	RRF7	RRF8	RRF9	RRF10		
Trichloroethene	2.054	2.031	1.814	1.733	1.704	1.683	2.002	1.779	1.746	1.717	1.826	7.9
1,2-Dichloropropane	1.051	1.112	1.032	0.985	0.977	0.945	1.137	0.998	1.062	1.005	1.030	5.9
Methyl_Methacrylate	1.190	1.164	1.099	1.044	1.065	1.058	1.288	1.147	1.268	1.195	1.152	7.5
1,4-Dioxane	1.127	0.948	0.845	0.766	0.749	0.733	0.891	0.787	0.866	0.821	0.853	13.8
Bromodichloromethane	2.089	2.187	2.059	2.004	2.022	2.007	2.442	2.149	2.361	2.232	2.155	7.0
4-Methyl-2-pentanone_(MIBK)	1.933	1.994	1.971	1.935	1.906	1.884	2.146	1.877	1.759	1.665	1.907	6.8
cis-1,3-Dichloropropene	1.735	1.814	1.737	1.653	1.698	1.682	2.065	1.825	1.991	1.907	1.811	7.6
trans-1,3-Dichloropropene	1.190	1.175	1.137	1.077	1.093	1.079	1.361	1.168	1.332	1.272	1.188	8.6
Toluene	5.375	5.454	4.863	4.658	4.607	4.553	5.334	4.698	4.786	4.537	4.886	7.4
1,1,2-Trichloroethane	1.284	1.309	1.155	1.123	1.113	1.111	1.309	1.161	1.177	1.105	1.185	7.1
2-Hexanone	2.052	2.109	1.920	1.872	1.813	1.846	2.208	1.967	1.754	1.675	1.922	8.6
Dibromochloromethane	2.467	2.696	2.448	2.387	2.414	2.434	2.885	2.597	2.502	2.390	2.522	6.4
Tetrachloroethene	2.659	2.735	2.427	2.270	2.283	2.258	2.617	2.310	2.183	2.096	2.384	9.1
1,2-Dibromoethane	0.957	0.989	0.886	0.838	0.842	0.833	0.986	0.885	0.865	0.859	0.894	6.8
Chlorobenzene	4.510	4.675	4.140	3.937	3.904	3.860	4.507	4.001	3.946	3.805	4.128	7.7
1,1,1,2-Tetrachloroethane	1.989	2.096	1.926	1.854	1.860	1.829	2.140	1.919	1.881	1.783	1.928	6.0
Ethylbenzene	7.017	6.987	6.349	6.057	6.155	6.005	6.904	6.102	6.330	5.657	6.356	7.3
m-Xylene	6.383	6.411	5.407	5.442	5.366	5.077	5.646	5.037	5.133	4.511	5.441	10.8
p-Xylene	6.083	5.591	5.321	5.018	4.979	4.934	5.684	5.115	5.183	4.713	5.262	7.9
Styrene	3.951	4.006	3.649	3.498	3.512	3.532	4.134	3.816	3.840	3.641	3.758	6.0
o-Xylene	5.998	6.136	5.551	5.351	5.360	5.354	5.974	5.410	5.578	4.891	5.560	6.8
Bromoform	2.370	2.557	2.353	2.359	2.395	2.413	2.834	2.572	2.534	2.302	2.469	6.4
1,1,2,2-Tetrachloroethane	3.271	3.398	3.129	3.016	3.012	3.031	3.561	3.185	3.234	2.966	3.180	6.0
Cumene	2.144	2.279	2.068	1.994	2.021	2.007	2.380	2.186	2.137	1.970	2.119	6.3
n-Propylbenzene	2.305	2.402	2.229	2.150	2.171	2.138	2.440	2.285	2.281	2.084	2.248	5.2
o-Chlorotoluene	1.757	1.892	1.750	1.697	1.730	1.802	2.050	1.867	1.861	1.720	1.813	5.9
4-Ethyltoluene	2.298	2.455	2.342	2.275	2.325	2.388	2.802	2.556	2.519	2.238	2.420	7.0
1,3,5-Trimethylbenzene	3.644	3.674	3.428	3.290	3.319	3.389	3.982	3.633	3.581	3.140	3.508	6.9
tert-Butyl_Benzene	1.587	1.660	1.532	1.501	1.508	1.570	1.811	1.629	1.618	1.551	1.597	5.7
1,2,4-Trimethylbenzene	3.765	3.877	3.617	3.496	3.594	3.696	4.290	3.912	3.847	3.446	3.754	6.6
sec-Butyl_Benzene	7.594	8.256	7.671	7.458	7.647	7.837	8.939	8.224	8.016	6.511	7.815	8.1
1,3-Dichlorobenzene	4.575	4.467	4.221	3.998	4.142	4.246	5.184	4.637	4.712	4.270	4.445	7.8
Benzyl_Chloride	1.146	1.229	1.170	1.177	1.237	1.312	1.585	1.455	1.483	1.436	1.323	11.7
1,4-Dichlorobenzene	4.164	4.290	4.006	3.990	4.082	4.208	5.138	4.583	4.664	4.360	4.348	8.2
o-Cymene	5.722	6.187	5.773	5.693	5.775	6.090	7.056	6.456	6.428	5.749	6.093	7.3
1,2-Dichlorobenene	4.268	4.258	3.864	3.769	3.844	3.988	4.802	4.312	4.314	4.107	4.153	7.4
n-Butyl_Benzene	1.835	1.715	1.635	1.579	1.628	1.721	2.060	1.881	1.888	1.733	1.767	8.4
1,2,4-Trichlorobenzene	0.743	0.770	0.677	0.662	0.685	0.747	0.990	0.936	0.940	0.928	0.808	15.7
Naphthalene	0.489	0.500	0.408	0.410	0.438	0.460	0.717	0.678	0.665	0.639	0.540	22.3
Hexachlorobutadiene	1.984	1.911	1.695	1.635	1.600	1.560	1.839	1.613	1.522	1.366	1.672	11.3

Compound	MDL(ppb)	Compound	MDL(ppb)
Formaldehyde	0.028	Tert-Amyl Methyl Ether	0.007
Propene	0.014	2,2,4-Trimethylpentane	0.012
Dichlorodifluoromethane (Freon 12)	0.039	Heptane	0.016
Chloromethane	0.017	Trichloroethylene	0.010
Dichlorotetrafluoroethane (Freon 114)	0.017	1,2-Dichloropropane	0.016
Methanol	0.037	1,4-Dioxane	0.020
Acetaldehyde	0.056	Methyl Methacrylate	0.014
Vinyl Chloride	0.012	Bromodichloromethane	0.016
1,3-Butadiene	0.013	cis-1,3-Dichloropropene	0.021
Bromomethane	0.020	4-Methyl-2-Pentanone (MIBK)	0.026
Chloroethane	0.009	trans-1,3-Dichloropropene	0.031
Ethanol	0.016	Toluene	0.020
Bromoethene	0.044	Ethane, 1,1,2-trichloro-	0.035
Trichlorofluoromethane	0.011	2-Hexanone	0.019
Acrolein	0.015	Dibromochloromethane	0.032
Acetonitrile	0.008	Tetrachloroethylene	0.015
Acetone	0.037	1,2-Dibromoethane (EDB)	0.024
Propanal	0.045	Chlorobenzene-d5 (IS 3)	0.000
1,1-Dichloroethene	0.014	1,1,1,2-Tetrachloroethane	0.009
Acrylonitrile	0.008	Ethylbenzene	0.036
Trichlorotrifluoroethane (Freon 113)	0.010	m-Xylene	0.041
Tert-Butanol	0.005	p-Xylene	0.043
Allyl Chloride	0.013	Styrene	0.043
Methylene Chloride	0.007	o-Xylene	0.041
Carbon Disulfide	0.013	Bromoform	0.038
trans-1,2-Dichloroethene	0.018	1,1,2,2-Tetrachloroethane	0.028
Methyl tert-Butyl Ether (MTBE)	0.047	Cumene	0.014
Vinyl Acetate	0.035	n-Propylbenzene	0.010
2-Chloroprene	0.009	o-Chlorotoluene	0.012
2-Butanone (MEK)	0.039	4-Ethyltoluene	0.035
1,1-Dichloroethane	0.015	1,3,5-Trimethylbenzene	0.028
Hexane	0.016	Tert-Butyl Benzene	0.018
Di-isopropyl Ether	0.012	1,2,4-Trimethylbenzene	0.033
cis-1,2-Dichloroethene	0.011	Sec-Butyl Benzene	0.016
Ethyl Acetate	0.044	Benzyl Chloride	0.060
Ethyl Tert-Butyl Ether	0.009	1,4-Dichlorobenzene	0.075
Chloroform	0.011	o-Cymene	0.017
Tetrahydrofuran	0.043	1,2-Dichlorobenzene	0.035
1,1,1-Trichloroethane	0.014	n-Butyl Benzene	0.021
1,2-Dichloroethane	0.013	1,2,4-Trichlorobenzene	0.047
Benzene	0.012	Naphthalene	0.016
Carbon Tetrachloride	0.011	Hexachlorobutdiene	0.017
Cyclohexane	0.013		

**Table 3** Method Detection Limits (PPBv) from 7 Replicate Injections of a 0.2 PPBv Standard

## Results and Discussion

A typical TO-15 TIC Chromatogram is shown in Table 2. Air Chemists should be quite familiar with what to look for in every chromatogram generated from samples and calibration standards to evaluate the effectiveness of the sample preparation and success of the low volume injection. The shape of chromatograms from calibration standards should show an increasing peak height, as most air standards are in PPB by volume, meaning that the actual weight of each compound injected increases with molecular weight. If the peak height (recovery) of the heavier compounds falls off, then there are cold spots, active surfaces, or simply just incomplete recovery from the adsorbent traps, which is often the case when compounds are pushed further onto multi-bed traps during dry purging operations. Again, the 7200 avoids the need for dry purging as explained earlier by using a separate cold trap for water removal. The light end peaks should be as narrow as the mid-range and heavy ends on the column, with no tailing, otherwise a problem occurred during the final focusing. Checking for Freon 12 at about 0.4 PPB in every analysis (Global Background) will confirm that the light ends were trapped properly. The relative peak heights of the internal standards and surrogate(s) should be consistent from injection to injection. Finally, the CO<sub>2</sub> peak at the very start of the chromatogram should not be too large, otherwise chromatography and detection of the lighter compounds can be affected. The 7200 optimizes recoveries, water removal, and injection rates to maximize analytical performance, with SQL database generated reports that detail the setpoints and actual parameters recorded during each analysis.

A range of light, polar, and heavy VOCs are shown in Figures 5-8, revealing little to no difference in chromatographic peak shape or calibration accuracy. The tabulated calibration results are shown in Table 2. The Relative Standard Deviations are extremely low considering the very wide dynamic range, showing values well below the 30% RSDs required by EPA TO-15. This data was achieved by varying the preconcentration volume from two different calibration standard canisters (20PPBv and 0.4PPBv) allowing a wider dynamic range than is possible when just using a single standard canister. The Thermo ISQ QD shows an extremely linear response over 3 orders of magnitude, which is beyond what most air laboratories are able to demonstrate.

The lack of scatter in the data (most %RSD values are very similar) indicates that most of the chemical related interactions or losses have been eliminated. This is the benefit of using cold trapping to avoid reactions that occur on strong multi-bed traps, and the use of ultra inert Silonite-D tubing throughout. The over 20 years of research that has led to the development of the 7200 has addressed most of the problems that lead to non-linear curves, so it's not unusual to achieve 5-15%RSDs for most compounds, even across such a wide range of concentrations. Improving overall system performance makes difficult compounds like Methyl Naphthalene more routine on the 7200 than on other systems.

Table 3 shows the consistency of the 7 replicate injections. By using a 0.2 PPBv standard injection (125cc of a 0.4PPBv standard, with 250cc the normal sample volume), calculated MDL's down to 0.02PPB are common, and indeed the 0.04PPB SICs in Figures 9 and 10 show that compounds like Naphthalene still have a substantial S/N ratio. The very low MDLs are a combined result of the extremely reproducible and sensitive Thermo ISQ HD GCMS, and the implementation of Entech's Accu-Sample Technology which improves the exactness of volumes sampled and ensures that virtually everything will be recovered quantitatively.

## Conclusion

The Entech 7200 combined with the Thermo Scientific ISQ QD GCMS has shown to greatly exceed the requirements of EPA method TO-15. This is important for production laboratories that want to maximize uptime even if system performance varies somewhat overtime. The sensitivity and reproducibility make this a very good choice for today's laboratories that must meet lower and lower detection limits, while being able to recover quickly from high concentration samples that are accidentally run prior to dilution. Achieving high sensitivity using relatively low sample volumes also gives the laboratory the ability to leverage the full throughput capacity of Entech Instruments' robotic autosamplers using smaller canisters to maximize productivity in today's Vapor Intrusion and other markets requiring low level TO-15 analysis.

Key Words: TO-15; VOCs; Calibration; Sensitivity; GC/MS; Surrogates; Canisters; Silonite; SUMMA; Whole Air Monitoring; EPA

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