Improved Performance And Dynamic Range For EPA Method TO-15 using the Entech 7200 and Agilent 7890B/5977 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 Agilent 7890B/5977 GCMS system is demonstrated here which improves productivity and analytical accuracy. Every aspect of the sample preparation 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 State driven Low Level TO-15 Method requirements. Improvements in recovery and linearity also reduce the downtime previously caused by systems that were only marginally meeting required method linearity criteria. The following application note will describe the new advancements in the 7200/7890B/5977 TO15 Analyzer 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 preconcentrated 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°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. During this process, the gas phase concentration of water is reduced from as high as 30,000 PPM (100% RH at 25°C) to just 2-100 PPM via this first stage at -40°C, which lowers it to 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°C. The extremely inert Silonite-D coating process keeps the target compounds from sticking to the walls of the tubing at -40°C, making this approach work much better than when using non- Silonite-D coated traps. The VOCs then collect on a second stage Tenax trap at -40°C. Tenax is approximately 100 times stronger at -40°C than at +30°C, allowing it to trap even the lightest VOCs. After trapping the internal standard and the calibration standard or sample, the empty M1 Silonite-D coated trap is heated to +10°C to transfer an additional 50cc of UHP nitrogen or helium through to the M2 Tenax trap at -40°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. This Extended Cold Trap Dehydration technique was first introduced by Entech in 1995, and has been perfected over the years by improved system designs, advancements in software control, and better surface coatings.

Accu-Sample™ Technology

Optimizing canister analysis requires sample preparation systems that perform accurate measurement of the sample volumes, properly transfer each compound through the preconcentration system, and substantially isolate each sample from the next to prevent cross-contamination. The Entech 7200 accomplishes this using 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 are unreliable at the beginning of trapping, and the inability to measure volumes accurately when the sample matrix changes from air to other matrices, such as CO2, Methane, or Helium. The7200'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 prior dilution. Direct Volume measurement directly translates to improved linearity and increased laboratory productivity. The EVC's response is also not affected by the matrix, allowing mixtures of Methane, CO2, 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

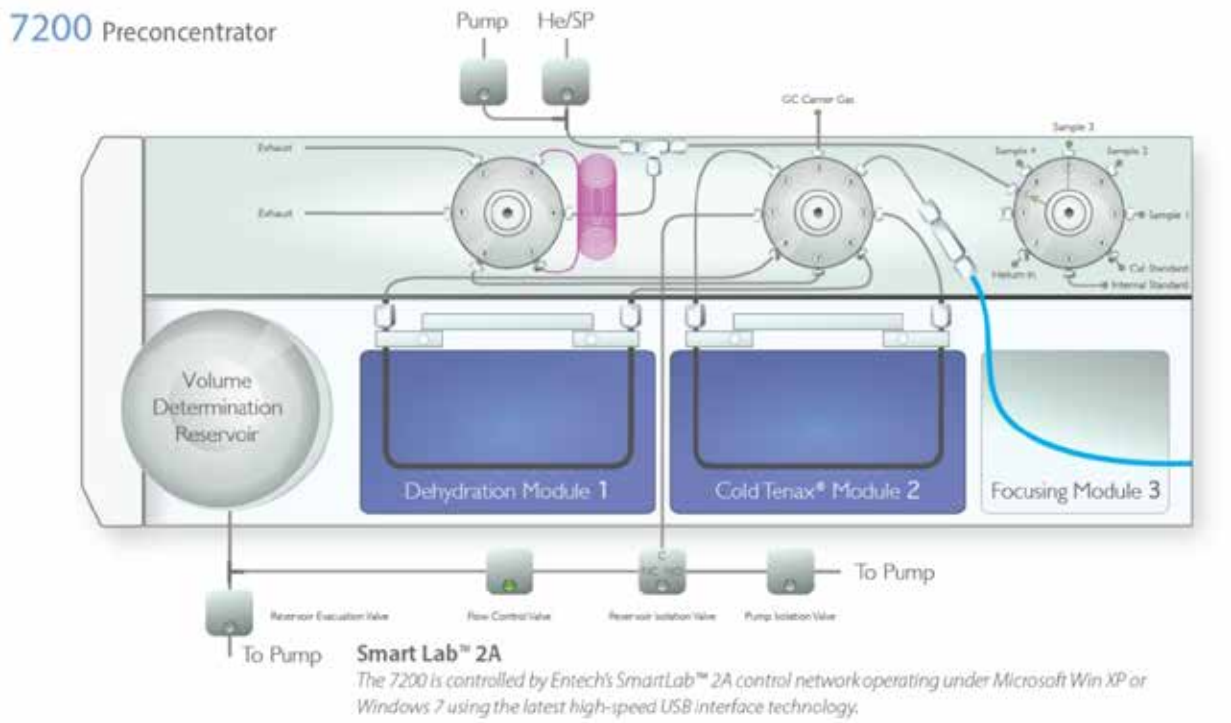
inlet system. The 7650 Robotic Autosampler as a front end to the 7200 further isolates each sample by having them completely disconnected from the analytical system until the moment of sample extraction.

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 by 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°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. Water removal in the first trap occurs via a direct transition from the gas phase to the solid phase, preventing the loss of polar compounds which are soluble in liquid water but do not "stick" to ice crystals at these temperatures. Both of these approaches for water management place no restrictions on how low the second stage is cooled, 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. Tenax in the second trap is effectively 100 times stronger at -40°C at retaining VOCs than Tenax at ambient temperatures, allowing the use of this relatively weak adsorbent to trap the entire range of TO15 compounds with volumes up to 1000cc without breakthrough. Unlike stronger adsorbents designed to trap at ambient temperatures, Tenax cleans up easily without having to raise the temperature high enough to cause thermal decomposition and artifact formation, ultimately changing the trapping and analyte recovery characteristics of the adsorbent. Over 25 years of experience with over a thousand systems using these techniques has shown that maintaining lower temperatures during the trapping process helps to maintain consistent recoveries longer without trap or flow path replacement.



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.

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 sensitivity and reproducibility, while greatly reducing the potential for carry-over when a high concentration sample is accidently 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 accidently 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 temperatures cannot be achieved using electronic cooling. Until a technology presents itself that allows for the same level of analytical performance, liquid nitrogen based cooling will continue to be the best choice for the TO- 15 production laboratory.

Experimental

Analytical data was generated with the Entech 7200 Preconcentrator interfaced to an Agilent 7890B/5977 GCMS. The GC oven initial temperature was 35°C(5 min), was ramped at 6°C/min to 120OC, and 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 detection of Formaldehyde and to monitor the m/z 31 peak found in many light oxygenated compounds. After 7 minutes, the scan was changed to 33-280 to avoid any residual air. 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, then this was used to create a 0.4PPBv standard into 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 250cc, with varying calibration points created by altering the volume between 25 to 500cc. Eight replicate injections at 0.08PPB (50cc from the 0.4 PPB std) 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.

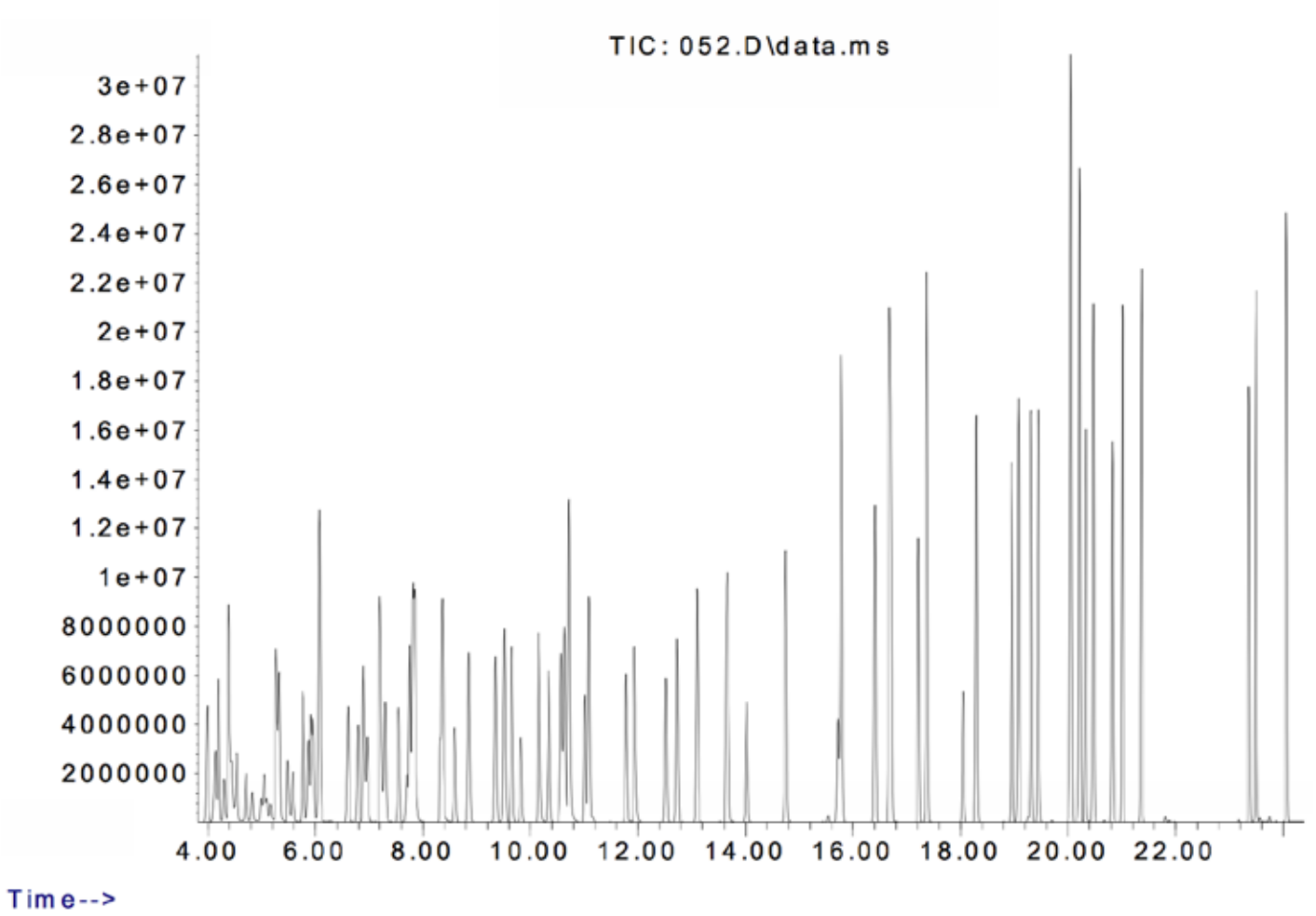


Figure 2 - 250cc 10 ppbv 82 Component TO15 Standard, ECTD Method, 7200/7890B/5977, Full Scan EI Mode.

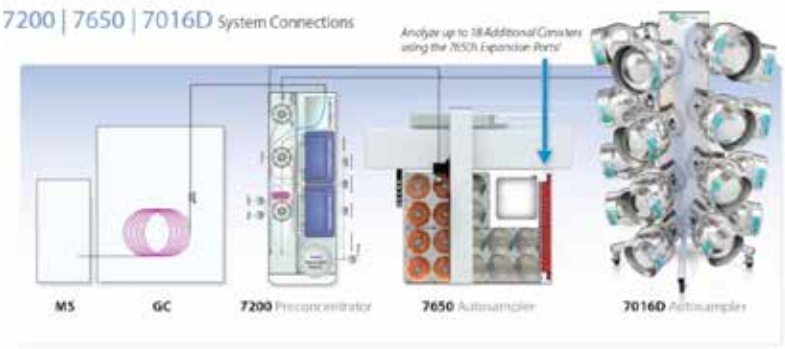


Figure 3 - 7200 with 7650 and 7016D Autosamplers for maximum flexibility and productivity

Figure 4 - 7200 with 7650 Robotic Autosampler virtually eliminates cross sample contamination

Compound Concentration (PPB)	0.04	0.08	0.2	0.4	0.8	2	4	10	20	40	Avg	%RSD
2) Formaldehyde	*	*	0.573	0.531	0.533	0.502	0.513	0.487	0.471	0.427	0.51	8.8
3) Propene	5.492	4.624	4.039	4.171	4.126	4.708	4.561	4.17	3.874	3.465	4.32	12.8
4) Dichlorodifluoromethane	1.44	1.398	1.323	1.395	1.385	1.587	1.538	1.416	1.323	1.041	1.39	10.6
5) Chloromethane	5.965	5.735	5.333	5.316	5.29	6.092	5.901	5.409	5.115	4.764	5.49	7.7
6) Dichlorotetrafluoroethane	1.215	1.18	1.067	1.121	1.091	1.234	1.198	1.088	1.009	0.917	1.11	9.0
7) Vinyl Chloride	5.918	5.588	4.976	5.189	4.945	5.768	5.597	5.036	4.7	4.575	5.23	8.8
8) Acetaldehyde	*	*	2.273	2.054	1.92	1.9	1.8	1.622	1.453	1.336	1.80	17.4
9) 1,3--Butadiene	4.256	3.914	3.612	3.802	3.693	4.287	4.18	3.777	3.54	3.299	3.84	8.5
10) Methanol	*	*	*	1.508	1.303	1.416	1.311	1.18	1.08	0.979	1.25	14.9
11) Bromomethane	4.37	3.934	3.583	3.634	3.608	3.986	3.867	3.582	3.466	3.245	3.73	8.5
12) Chloroethane	2.736	2.744	2.412	2.375	2.328	2.581	2.519	2.325	2.244	2.161	2.44	8.1
13) Bromoethene	4.547	4.19	3.673	3.885	3.739	4.163	4.064	3.767	3.663	3.523	3.92	8.0
14) Ethanol	*	*	1.804	1.753	1.635	1.751	1.685	1.492	1.413	1.309	1.61	11.2
15) Acetonitrile	3.548	3.08	2.789	2.714	2.765	3.145	3.092	2.798	2.6	2.459	2.90	11.0
16) Trichlorofluormethane	1.359	1.293	1.221	1.262	1.263	1.452	1.402	1.273	1.199	1.063	1.28	8.6
17) Propanal	*	1.859	1.511	1.584	1.44	1.562	1.493	1.32	1.224	1.074	1.45	15.6
18) Acetone	*	2.678	2.138	2.056	2.011	2.171	2.083	1.833	1.626	1.3	1.99	19.3
19) Isopropyl Alcohol	*	*	*	1.523	1.31	1.092	1.02	0.904	0.858	0.791	1.07	24.6
20) Acrolein	*	*	1.587	1.578	1.523	1.68	1.619	1.502	1.441	1.387	1.54	6.2
21) 1,1-Dichloroethane	1.073	1.053	0.964	1.027	1.01	1.158	1.128	1.035	0.989	0.908	1.04	7.2
22) Acrylonitrile	5.064	4.818	4.62	4.596	4.603	5.24	5.06	4.715	4.55	4.304	4.76	6.0
23) Trichlorotrifluoroethane	9.84	9.526	8.768	9.132	8.801	9.802	9.441	8.463	8.02	7.261	8.91	9.3
24) Allyl Chloride	2.641	2.28	2.094	2.187	2.141	2.464	2.374	2.202	2.148	2.062	2.26	8.1
25) Methylene Chloride	5.507	5.103	4.553	4.653	4.56	5.042	4.881	4.515	4.381	4.214	4.74	8.2
26) tert-Butanol	1.563	1.376	1.216	1.255	1.248	1.482	1.426	1.309	1.254	1.114	1.32	10.3
27) Carbon Disulfide	1.671	1.579	1.451	1.495	1.459	1.642	1.592	1.446	1.372	1.207	1.49	9.3
28) trans-1,2-Dichloroethene	0.963	0.922	0.861	0.897	0.893	1.013	0.984	0.911	0.882	0.823	0.92	6.3
29) Methyl tert-Butylether	1.622	1.467	1.453	1.504	1.493	1.699	1.664	1.557	1.502	1.262	1.52	8.2
30) Vinyl Acetate	1.901	1.782	1.642	1.732	1.75	2.013	1.659	1.494	1.423	1.209	1.66	14.2
31) 1,1-Dichloroethane	1.202	1.179	1.094	1.11	1.096	1.243	1.209	1.114	1.075	0.997	1.13	6.6
32) 2-Butanone	9.228	8.301	7.468	7.818	7.789	8.726	8.488	7.764	7.382	6.805	7.98	9.0
33) Hexane	1.103	1.082	0.981	1.027	1.02	1.156	1.127	1.048	0.996	0.936	1.05	6.6
34) cis-1,2-Dichloroethene	9.173	8.676	8.307	8.486	8.59	9.808	9.53	8.823	8.5	7.893	8.78	6.6
35) 2-Chloroprene	4.276	3.908	3.751	4.031	3.956	4.471	4.388	4.097	3.96	3.788	4.06	6.0
36) Ethyl Acetate	2.483	2.244	2.029	1.946	1.965	2.332	2.253	2.109	1.887	1.677	2.09	11.4
37) Chloroform	1.288	1.242	1.157	1.202	1.181	1.361	1.345	1.211	1.149	1.01	1.22	8.5
38) Di-isopropylether	5.299	4.949	5.541	5.692	5.679	6.296	6.386	5.717	5.532	5.19	5.63	8.0
39) Tetrahydrofuran	3.203	2.543	2.358	2.355	2.446	2.785	2.703	2.548	2.507	2.403	2.59	10.0
40) Ethyl tert-Butylether	7.17	7.004	6.585	6.909	6.905	7.905	7.786	7.3	7.034	6.574	7.12	6.3
41) 1,1,1-Trichloroethane	1.31	1.22	1.173	1.257	1.243	1.422	1.382	1.287	1.234	1.119	1.27	7.2
42) 1,2-Dichloroethane	0.973	0.963	0.904	0.951	0.925	1.067	1.04	0.959	0.915	0.843	0.95	6.8
43) Benzene	5.343	4.863	4.374	4.376	4.228	4.259	4.101	3.827	3.668	3.489	4.25	12.9
44) Carbon Tetrachloride	1.366	1.361	1.284	1.349	1.347	1.544	1.505	1.396	1.331	1.177	1.37	7.6
45) Cyclohexane	8.142	7.263	6.854	7.139	7.107	8.054	7.763	7.254	7.075	6.665	7.33	6.7

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 Concentration (PPB)	0.04	0.08	0.2	0.4	0.8	2	4	10	20	40	Avg	%RSD
47) tert-Amyl Methylether	4.071	3.709	3.588	3.748	3.762	4.38	4.305	4.06	3.896	3.187	3.87	9.1
48) 2,2,4-Trimethylpentane	3.094	2.854	2.603	2.775	2.752	3.074	2.998	2.737	2.51	2.143	2.75	10.4
49) Heptane	1.846	1.751	1.607	1.672	1.669	1.871	1.807	1.659	1.551	1.392	1.68	8.7
50) Trichloroethene	2.136	2.026	1.85	1.919	1.897	2.138	2.072	1.924	1.826	1.679	1.95	7.5
51) 1,2-Dichloropropane	1.924	1.817	1.675	1.736	1.714	1.944	1.884	1.742	1.665	1.536	1.76	7.3
52) 1,4-Dioxane	1.151	0.936	0.855	0.869	0.9	0.968	0.929	0.845	0.799	0.733	0.90	12.5
53) Bromodichloromethane	3.242	3.195	3.041	3.166	3.136	3.694	3.598	3.354	3.195	2.809	3.24	7.9
54) Methyl Methacrylate	1.644	1.458	1.235	1.286	1.283	1.516	1.49	1.381	1.342	1.27	1.39	9.5
55) cis-1,3-Dichloropropene	2.462	2.404	2.219	2.339	2.325	2.737	2.693	2.565	2.482	2.298	2.45	7.0
56) 4-Methyl-2-pentanone	3.232	3.03	3.028	3.24	3.313	4.046	3.955	3.66	3.383	2.832	3.37	11.9
57) trans-1,3-Dichloropropene	2.373	2.218	2.123	2.252	2.25	2.636	2.645	2.523	2.439	2.26	2.37	7.7
58) Toluene	3.711	3.404	3.033	3.074	3.095	3.453	3.387	3.15	2.998	2.687	3.20	9.1
59) 1,1,2-Trichloroethane	1.947	1.835	1.732	1.798	1.759	1.977	1.932	1.789	1.712	1.574	1.81	6.8
60) 2-Hexanone	1.892	1.862	1.786	1.957	2.02	2.364	2.344	2.215	2.07	1.828	2.03	10.4
61) Dibromochloromethane	3.002	2.879	2.753	2.945	3.027	3.587	3.535	3.272	3.063	2.692	3.08	9.9
62) Tetrachloroethene	2.185	2.05	1.935	1.981	1.97	2.206	2.141	1.958	1.834	1.636	1.99	8.6
63) 1,2-Dibromoethane	2.787	2.58	2.466	2.562	2.578	2.918	2.868	2.705	2.574	2.357	2.64	6.7
65) Chlorobenzene	3.305	2.906	2.756	2.727	2.646	2.82	2.656	2.448	2.29	1.991	2.65	13.4
66) 1,1,1,2-Tetrachloroethane	1.969	1.829	1.693	1.679	1.694	1.874	1.795	1.669	1.558	1.333	1.71	10.4
67) Ethylbenzene	4.274	4.265	3.971	4.138	4.163	4.575	4.396	4.166	4.002	3.62	4.16	6.2
68) m,p-Xylene	5.34	5.076	4.922	5.168	5.166	5.646	5.277	4.863	4.497	3.743	4.97	10.7
69) Styrene	3.054	3.017	3.01	3.255	3.428	3.858	3.78	3.665	3.565	3.247	3.39	9.4
70) o-Xylene	5.156	4.872	4.787	5.127	5.043	5.484	5.172	4.777	4.418	3.783	4.86	9.8
71) Bromoform	5.227	4.868	4.882	5.215	5.399	6.273	6.045	5.616	5.17	4.303	5.30	10.9
72) 1,1,2,2-Tetrachloroethane	5.012	4.639	4.425	4.59	4.672	5.119	4.799	4.416	4.073	3.432	4.52	10.8
73) 4-Bromofluorobenzene	0.524	0.527	0.534	0.538	0.543	0.532	0.523	0.538	0.541	0.537	0.53	1.3
74) Cumene	4.258	3.991	3.757	4.023	3.949	4.451	4.242	3.964	3.754	3.295	3.97	8.2
75) o-Chlorotoluene	3.778	3.593	3.403	3.582	3.624	4.097	3.926	3.67	3.511	3.122	3.63	7.4
76) n-Propylbenzene	3.931	3.957	3.852	4.185	4.284	4.735	4.521	4.253	4.002	3.528	4.13	8.4
77) 4-Ethyltoluene	1.536	1.573	1.554	1.633	1.636	1.914	1.788	1.68	1.607	1.405	1.63	8.6
78) 1,3,5-Trimethylbenzene	1.45	1.325	1.24	1.319	1.372	1.524	1.445	1.36	1.275	1.129	1.34	8.5
79) tert-Butyl Benzene	2.975	2.815	2.845	2.999	3.039	3.324	3.123	2.828	2.562	2.167	2.87	11.2
80) 1,2,4-Trimethylbenzene	6.301	6.289	6.471	6.804	6.98	7.603	7.161	6.519	5.916	4.774	6.48	11.9
81) 1,3-Dichlorobenzene	3.852	3.778	3.57	3.708	3.654	3.849	3.645	3.372	3.104	2.635	3.52	11.0
82) Benzyl Chloride	2.143	2.128	1.879	2.091	2.205	2.554	2.474	2.34	2.178	1.868	2.19	10.3
83) 1,4-Dichlorobenzene	4.501	4.116	3.804	3.743	3.728	3.723	3.596	3.378	3.194	2.793	3.66	12.9
84) sec-Butyl Benzene	3.449	3.476	3.482	3.723	3.933	4.449	4.265	3.993	3.743	3.203	3.77	10.4
85) 1,2-Dichlorobenzene	3.859	3.697	3.443	3.506	3.557	3.83	3.697	3.495	3.306	2.91	3.53	7.9
86) o-Cymene	3.688	3.558	3.528	3.857	3.968	4.499	4.329	4.038	3.743	3.21	3.84	10.0
87) n-Butyl Benzene	3.449	3.476	3.482	3.723	3.933	4.449	4.265	3.993	3.743	3.203	3.77	10.4
88) 1,2,4-Trichlorobenzene	7.505	6.677	6.286	6.52	6.635	6.343	6.31	6.001	5.595	4.344	6.22	13.2
89) Naphthalene	2.821	2.561	2.335	2.485	2.594	2.699	2.697	2.552	2.415	2.1	2.53	8.2
90) Hexachlorobutadiene	3.568	3.429	3.293	3.392	3.329	3.629	3.403	3.052	2.713	2.18	3.20	13.9

Compound	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7	Average	SD	MDL
2) Formaldehyde	348	318	294	274	264	262	254	287.71	34.49	108
3) Propene	84.85	91.27	88.67	88.6	91.07	89.18	93.67	89.62	2.772	8.7
4) Dichlorodifluoromethane	84.64	84.47	86.34	85.44	85.24	85.91	87.83	85.70	1.148	3.6
5) Chloromethane	87.9	87.67	88.65	90.23	88.05	92.47	94.27	89.89	2.574	8.1
6) Dichlorotetrafluoroethane	84.04	83.57	83.96	85.74	83.71	88.38	86.38	85.11	1.803	5.7
7) Vinyl Chloride	85.48	88.79	89.59	85.16	87.29	87.02	84.43	86.82	1.918	6.0
8) Acetaldehyde	164.92	171.84	168.61	179.39	166.93	169.11	176.7	171.07	5.266	16.5
9) 1,3--Butadiene	88.54	93.73	91.03	91.56	90.66	87.41	91.44	90.62	2.083	6.5
10) Methanol	75.74	78.39	74.69	76.69	82.6	77.21	72.7	76.86	3.128	9.8
11) Bromomethane	84.25	85.57	85.63	87.01	86.52	87.15	85.17	85.90	1.050	3.3
12) Chloroethane	76.64	83.47	90.00	78.29	81.84	85.91	83.52	82.81	4.503	14.1
13) Bromoethene	90.75	79.96	84.91	77.56	81.91	82.92	84.74	83.25	4.210	13.2
14) Ethanol	92.6	86.26	85.58	85.71	88.65	86.42	89.49	87.82	2.588	8.1
15) Acetonitrile	84.37	100.98	97.79	88.95	109.96	112.09	116.66	101.54	12.100	38.0
16) Trichlorofluormethane	86.09	89.49	89.42	88.12	90.57	89.93	91.24	89.27	1.708	5.4
17) Propanal	133.83	139.73	155.83	132.57	154.48	122.96	143.76	140.45	11.949	37.5
18) Acetone	89.24	89.73	92.77	86.33	94.96	94.55	90.35	91.13	3.115	9.8
19) Isopropyl Alcohol	81.75	78.3	78.25	77.67	77.48	78.9	77.56	78.56	1.495	4.7
20) Acrolein	85.79	74.16	87.69	88.77	84.82	88.35	85.89	85.07	5.026	15.8
21) 1,1-Dichloroethane	83.54	84.18	86.36	84.93	87.03	85.93	86.92	85.56	1.364	4.3
22) Acrylonitrile	90.99	85.8	84.54	85.87	94.81	92.5	89.03	89.08	3.870	12.2
23) Trichlorotrifluoroethane	87.12	87.26	87.42	83.85	85.5	87.4	87.17	86.53	1.359	4.3
24) Allyl Chloride	80.74	86.32	85.52	75.83	80.22	76.44	80.35	80.77	4.021	12.6
25) Methylene Chloride	88.36	83.75	83.45	83.45	83.95	86.43	85	84.91	1.860	5.8
26) tert-Butanol	84.47	84.46	85.5	81.93	82.45	83.61	83.63	83.72	1.233	3.9
27) Carbon Disulfide	84.52	85.94	88.12	83.78	85.36	85.87	84.87	85.49	1.386	4.4
28) trans-1,2-Dichloroethene	84.94	83.99	84.26	81.05	83.49	86.53	85.81	84.30	1.779	5.6
29) Methyl tert-Butylether	83.06	86.1	84.25	77.82	79.62	84.2	77.78	81.83	3.381	10.6
30) Vinyl Acetate	84.58	87.38	87.09	84.17	83.34	84.34	86.82	85.39	1.650	5.2
31) 1,1-Dichloroethane	82.98	86.22	84.16	83.22	84.9	88.56	86.11	85.16	1.965	6.2
32) 2-Butanone	82.54	83.63	83.36	82.78	80.74	83	82.9	82.71	0.940	3.0
33) Hexane	86.33	86.46	84.33	84.18	84.39	84.3	81.68	84.52	1.598	5.0
34) cis-1,2-Dichloroethene	84.63	83.06	84.89	82.25	83.43	84.53	85.59	84.05	1.172	3.7
35) 2-Chloroprene	85.57	86.44	82.11	80.5	80.45	76.11	78.23	81.34	3.720	11.7
36) Ethyl Acetate	80.76	74.13	86.49	74.86	81.59	75.11	85.46	79.77	5.155	16.2
37) Chloroform	83.63	85.99	86.23	82.86	85.68	86.43	87.91	85.53	1.729	5.4
38) Di-isopropylether	80.34	79.71	82.43	66.71	82.39	81.41	78.42	78.77	5.513	17.3
39) Tetrahydrofuran	82.74	74.78	81.63	72.22	83.66	84.16	77.77	79.57	4.696	14.7
40) Ethyl tert-Butylether	82.44	82.84	81.7	77.53	78.1	79.74	78.94	80.18	2.144	6.7
41) 1,1,1-Trichloroethane	83.92	85.8	87.96	81.6	85.47	88.88	87.28	85.84	2.504	7.9
42) 1,2-Dichloroethane	85.69	89.49	89.16	90.19	91.05	93.18	90.63	89.91	2.278	7.2
43) Benzene	82.79	85.52	87.63	83.46	85.52	87.01	82.42	84.91	2.055	6.5
44) Carbon Tetrachloride	84.77	84.07	87.56	83.51	86.09	89.38	88.67	86.29	2.303	7.2
45) Cyclohexane	81.57	79.72	80.59	77.93	76.44	78.66	78.43	79.05	1.721	5.4

Table 3 Method Detection Limit Determination in Parts Per Trillion for Extended TO15 List created using 7 replicate runs of an 80 part-per-trillion standard. Most compounds are in the low PPTv range.

Compound Concentration (PPB)	0.04	0.08	0.2	0.4	0.8	2	4	10	20	40	Avg	%RSD
47) tert-Amyl Methylether	4.071	3.709	3.588	3.748	3.762	4.38	4.305	4.06	3.896	3.187	3.87	9.1
48) 2,2,4-Trimethylpentane	3.094	2.854	2.603	2.775	2.752	3.074	2.998	2.737	2.51	2.143	2.75	10.4
49) Heptane	1.846	1.751	1.607	1.672	1.669	1.871	1.807	1.659	1.551	1.392	1.68	8.7
50) Trichloroethene	2.136	2.026	1.85	1.919	1.897	2.138	2.072	1.924	1.826	1.679	1.95	7.5
51) 1,2-Dichloropropane	1.924	1.817	1.675	1.736	1.714	1.944	1.884	1.742	1.665	1.536	1.76	7.3
52) 1,4-Dioxane	1.151	0.936	0.855	0.869	0.9	0.968	0.929	0.845	0.799	0.733	0.90	12.5
53) Bromodichloromethane	3.242	3.195	3.041	3.166	3.136	3.694	3.598	3.354	3.195	2.809	3.24	7.9
54) Methyl Methacrylate	1.644	1.458	1.235	1.286	1.283	1.516	1.49	1.381	1.342	1.27	1.39	9.5
55) cis-1,3-Dichloropropene	2.462	2.404	2.219	2.339	2.325	2.737	2.693	2.565	2.482	2.298	2.45	7.0
56) 4-Methyl-2-pentanone	3.232	3.03	3.028	3.24	3.313	4.046	3.955	3.66	3.383	2.832	3.37	11.9
57) trans-1,3-Dichloropropene	2.373	2.218	2.123	2.252	2.25	2.636	2.645	2.523	2.439	2.26	2.37	7.7
58) Toluene	3.711	3.404	3.033	3.074	3.095	3.453	3.387	3.15	2.998	2.687	3.20	9.1
59) 1,1,2-Trichloroethane	1.947	1.835	1.732	1.798	1.759	1.977	1.932	1.789	1.712	1.574	1.81	6.8
60) 2-Hexanone	1.892	1.862	1.786	1.957	2.02	2.364	2.344	2.215	2.07	1.828	2.03	10.4
61) Dibromochloromethane	3.002	2.879	2.753	2.945	3.027	3.587	3.535	3.272	3.063	2.692	3.08	9.9
62) Tetrachloroethene	2.185	2.05	1.935	1.981	1.97	2.206	2.141	1.958	1.834	1.636	1.99	8.6
63) 1,2-Dibromoethane	2.787	2.58	2.466	2.562	2.578	2.918	2.868	2.705	2.574	2.357	2.64	6.7
65) Chlorobenzene	3.305	2.906	2.756	2.727	2.646	2.82	2.656	2.448	2.29	1.991	2.65	13.4
66) 1,1,1,2-Tetrachloroethane	1.969	1.829	1.693	1.679	1.694	1.874	1.795	1.669	1.558	1.333	1.71	10.4
67) Ethylbenzene	4.274	4.265	3.971	4.138	4.163	4.575	4.396	4.166	4.002	3.62	4.16	6.2
68) m,p-Xylene	5.34	5.076	4.922	5.168	5.166	5.646	5.277	4.863	4.497	3.743	4.97	10.7
69) Styrene	3.054	3.017	3.01	3.255	3.428	3.858	3.78	3.665	3.565	3.247	3.39	9.4
70) o-Xylene	5.156	4.872	4.787	5.127	5.043	5.484	5.172	4.777	4.418	3.783	4.86	9.8
71) Bromoform	5.227	4.868	4.882	5.215	5.399	6.273	6.045	5.616	5.17	4.303	5.30	10.9
72) 1,1,2,2-Tetrachloroethane	5.012	4.639	4.425	4.59	4.672	5.119	4.799	4.416	4.073	3.432	4.52	10.8
73) 4-Bromofluorobenzene	0.524	0.527	0.534	0.538	0.543	0.532	0.523	0.538	0.541	0.537	0.53	1.3
74) Cumene	4.258	3.991	3.757	4.023	3.949	4.451	4.242	3.964	3.754	3.295	3.97	8.2
75) o-Chlorotoluene	3.778	3.593	3.403	3.582	3.624	4.097	3.926	3.67	3.511	3.122	3.63	7.4
76) n-Propylbenzene	3.931	3.957	3.852	4.185	4.284	4.735	4.521	4.253	4.002	3.528	4.13	8.4
77) 4-Ethyltoluene	1.536	1.573	1.554	1.633	1.636	1.914	1.788	1.68	1.607	1.405	1.63	8.6
78) 1,3,5-Trimethylbenzene	1.45	1.325	1.24	1.319	1.372	1.524	1.445	1.36	1.275	1.129	1.34	8.5
79) tert-Butyl Benzene	2.975	2.815	2.845	2.999	3.039	3.324	3.123	2.828	2.562	2.167	2.87	11.2
80) 1,2,4-Trimethylbenzene	6.301	6.289	6.471	6.804	6.98	7.603	7.161	6.519	5.916	4.774	6.48	11.9
81) 1,3-Dichlorobenzene	3.852	3.778	3.57	3.708	3.654	3.849	3.645	3.372	3.104	2.635	3.52	11.0
82) Benzyl Chloride	2.143	2.128	1.879	2.091	2.205	2.554	2.474	2.34	2.178	1.868	2.19	10.3
83) 1,4-Dichlorobenzene	4.501	4.116	3.804	3.743	3.728	3.723	3.596	3.378	3.194	2.793	3.66	12.9
84) sec-Butyl Benzene	3.449	3.476	3.482	3.723	3.933	4.449	4.265	3.993	3.743	3.203	3.77	10.4
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88) 1,2,4-Trichlorobenzene	7.505	6.677	6.286	6.52	6.635	6.343	6.31	6.001	5.595	4.344	6.22	13.2
89) Naphthalene	2.821	2.561	2.335	2.485	2.594	2.699	2.697	2.552	2.415	2.1	2.53	8.2
90) Hexachlorobutadiene	3.568	3.429	3.293	3.392	3.329	3.629	3.403	3.052	2.713	2.18	3.20	13.9

Results and Discussion

A typical TO-15 TIC Chromatogram is shown in Figure 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. As stated earlier, the 7200 avoids the need for dry purging by using a separate cold trap for sample dehydration. 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 or GC injection. Checking for Freon 12 at about 0.4-0.5 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 CO2 peak at the very start of the chromatogram should not be too large, otherwise chromatography and detection of the lighter compounds can be affected. However, some CO2 should still be present as a peak at the beginning of the run, as complete removal is normally not possible unless the final focusing even was not cold enough, in which case of light compounds might also have been lost. 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.

The 10-point calibration results are shown in Table 2. The Relative Standard Deviations are extremely low considering the very wide dynamic range of 1000x, showing values well below the 30% RSDs required by EPATO-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 Agilent 5977 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 cause non-linear results, 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. Some compounds like IPA and Acetone sometimes show elevated background levels preventing ultra low detection limits, especially after new installations. Although these compounds show very little toxicity, they will ultimately drop down to lower levels after systems have been run for a while.

Table 3 shows the consistency of the 7 replicate injections. By using a 0.08 PPBv standard injection (50cc of a 0.4PPBv standard), calculated MDL's down to 0.01PPB are common, and indeed the 0.04PPB SICs in Figures 5 and 6 are typical of most compounds showing substantial S/N ratios at the low level point in the presented curve. The very low calculated MDLs are due to the extremely reproducible and sensitive Agilent 5977 MS, and the implementation of Entech's Accu-Sample Technology which improves the exactness of volumes sampled and ensures that target compounds will be recovered quantitatively. Other issues that affect method MDLs include system blank levels, how quickly the system can re-establish low blank levels once exposed to higher concentration samples, and the inertness level of canisters used to collect samples which in turn affects the reliable recovery from each canister and the reproducibility of the technique as a whole. Entech remains the only TO15 supplier that produces all products needed to perform TO15 sampling, analysis, and canister cleaning, and is the only supplier to test every canister produced to ensure proper inertness for storage and recovery of TO15 compounds.

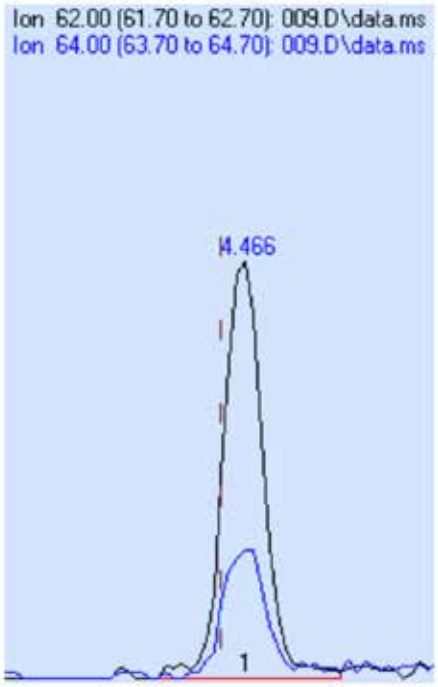

Figure 5 0.040PPB Vinyl Chloride Estimated S/N=30

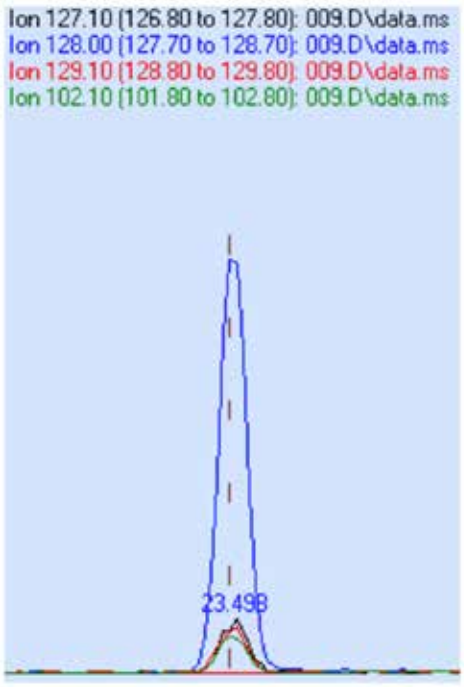

Figure 6 Naphthalene Estimated S/N=100

Conclusion

The Entech 7200 combined with the Agilent 7890B/5977 has been 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 over time. 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 accidently 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 for soil gas and Vapor Intrusion monitoring, as well as other applications requiring advanced TO-15 analysis.

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

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