Fast US EPA TO15 Analysis Providing Higher Productivity using the new Entech 7200A and Agilent 7890B/5977 GCMS

Application Note:
A-3742-01

Authors
Daniel B. Cardin
Tom Robinson
Victoria L. Noad
Entech Instruments
Simi Valley, CA 93065

Introduction

Canister sampling and analysis for measurement of volatile chemicals is finding use in a growing number of diversified applications. This includes analysis of VOCs in Ambient Air, Indoor Air, Vapor Intrusion, Soil Gas, Landfill Gas, Stack Gas, Fixed Gas Cylinder Purity, and others. As the EPA Method TO15 market continues to grow, there is an increasing need to improve laboratory throughput. Reducing cycle times between injections requires having shorter GCMS run times as well as more efficient sample preparation techniques that reduce the time needed to concentrate the sample, perform water elimination, focus, inject, and cleanup the preconcentration system prior to the next analysis. Both cryogenic and cryogen-less systems are available for this purpose, but until now most of these have required GCMS run times of 28-35 minutes, with cool down times and subsequent preparation for the next injection bringing the total cycle time from injection to injection to around 45- 60 minutes.

A new US EPA Method TO-15 compatible analyzer is presented that dramatically increases sample throughput when compared to prior technology. The Entech 7200A Cryogenic Preconcentrator combined with the Agilent 7890B/5977 GCMS system is shown to reduce cycle times from injection to injection while maintaining high analytical accuracy and sensitivity. The 7200A (A for Accelerated) utilizes a new, high speed injection technique which nearly triples the rate of delivery of the sample to the GC column, allowing short, narrow bore columns with thinner films to be used rather than the traditional 60m x 0.32mm ID x 1um volatiles columns which have been the standard for air analysis in the past. Fast injection rates and short, narrow bore columns allow all TO15 compounds to elute in under 9 minutes with peak widths of 1.5-2.3 seconds, while also reducing the time needed to bake out the column due to the thinner film thicknesses and shorter column lengths. Total cycle time from injection to injection is roughly 24 minutes, which is approximately half the time required in the past. Therefore, the new 7200A does not just represent technology that is a little faster than its predecessors, but rather twice as fast, allowing a single preconcentrator to have the throughput of two, and likewise one GCMS system to have the throughput of two, without the added benchspace, system cost, and maintenance expense.

Figure 1 - Entech 7200A Preconcentrator with the Agilent 7890B/5977 GCMS

This application note provides a description of the system, and explains how the 7200A improves water management and reduces chemical interferences relative to Entech's prior line of cryogenic preconcentrators which are currently used by 85-90% of all labs performing EPA Method TO15.

Preconcentration and GC/MS Analysis

In order to reach low to sub-PPB 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 H2O and CO2 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 water freezes. As the sample passes through this trap, the air and most of the VOCs pass immediately 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 initial concentrations as high as 30,000 PPM (100% RH at 25°C) to just 2-100 PPM via this first stage at -40°C, which is low enough to substantially reduce the effects on the operation of the GCMS. The VOCs of interest are already well below this concentration, and therefore have little or no retention because at -40°C, they are still below their saturation point. At this low temperature, the extremely inert Silonite-D coating keeps the target compounds from sticking to the walls of the tubing, making this approach more effective than those which utilize uncoated traps. The VOCs then collect on a second stage Tenax trap at -50°C. Tenax is approximately 100 times stronger at -50°C than at +30°C, allowing it to trap even the lightest VOCs. To address the possibility that a small percentage of heavy or polar VOCs have dropped out, 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 30-50cc of UHP Helium and any remaining VOCs to the M2 Tenax trap. This short purge transfers only a small amount of water vapor, and very little of this extra water will reach the mass spectrometer, as will be explained in greater detail in the following pages. Then, 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.

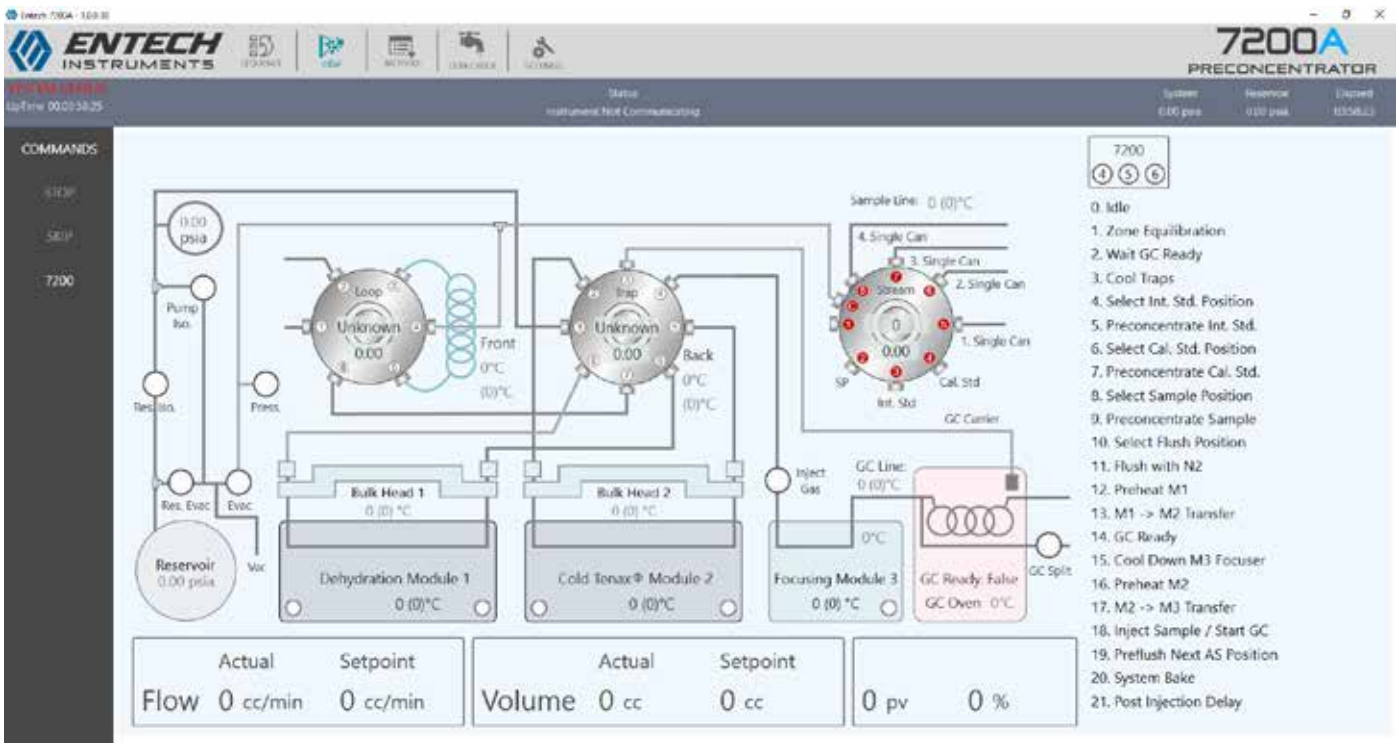
The basic sequence of events that occur during each preconcentration are given below:

- Warm up zones and cool down traps
- Dehydrate through M1 and trap on M2
- Trap Internal Standard (50cc typical)
- Trap Cal STD (0-1000cc)
- Trap Sample (0-1000cc)
- Helium Flush
- Warm M1, then 30-50cc M1-M2 Transfer
- Cool M3, transfer M2 to M3 Focuser
- Inject M3, Start GCMS
- Bake Out Traps

Speeding up the Preconcentration Process

One of the major advantages of cryogenic preconcentrators has been faster cool down times to get ready for the next sample preconcentration. The 7200A cools down to trapping temperatures in under 2 minutes, as opposed to Peltier Cooled traps which can take 20 minutes or more to cool down. This alone constitutes a 10x speed improvement when using LN2. Considering that $2-3 worth of LN2 per analysis enables a system with 2x the productivity overall, then it is clearly demonstrated that this acceptable laboratory consumable provides a superior economic advantage over the alternative electrically cooled trapping systems. It should also be noted that the cost in electricity per sample is not negligible. At approximately $1 per analysis, depending on ambient conditions, this further marginalizes the implied cost of LN2.

The four biggest improvements over the 7200 is the ability to synchronize the bakeout of the Module 3 Focusing trap with the initial cool down of the GCMS, the increase in injection rates allowing the use of shorter, more narrow columns to speed up the analysis, reduced liquid nitrogen consumption, and approximately a 3x improvement in water management that allows for reduced cycle times with minimal reduction in Internal Standard response from run to run. These four new improvements will be described separately.



7200A and SmartLab™ 2
The 7200A is controlled by Entech's SmartLab™ 2 control network operating under Microsoft Win 7 or Win10 using the latest high-speed USB interface technology.

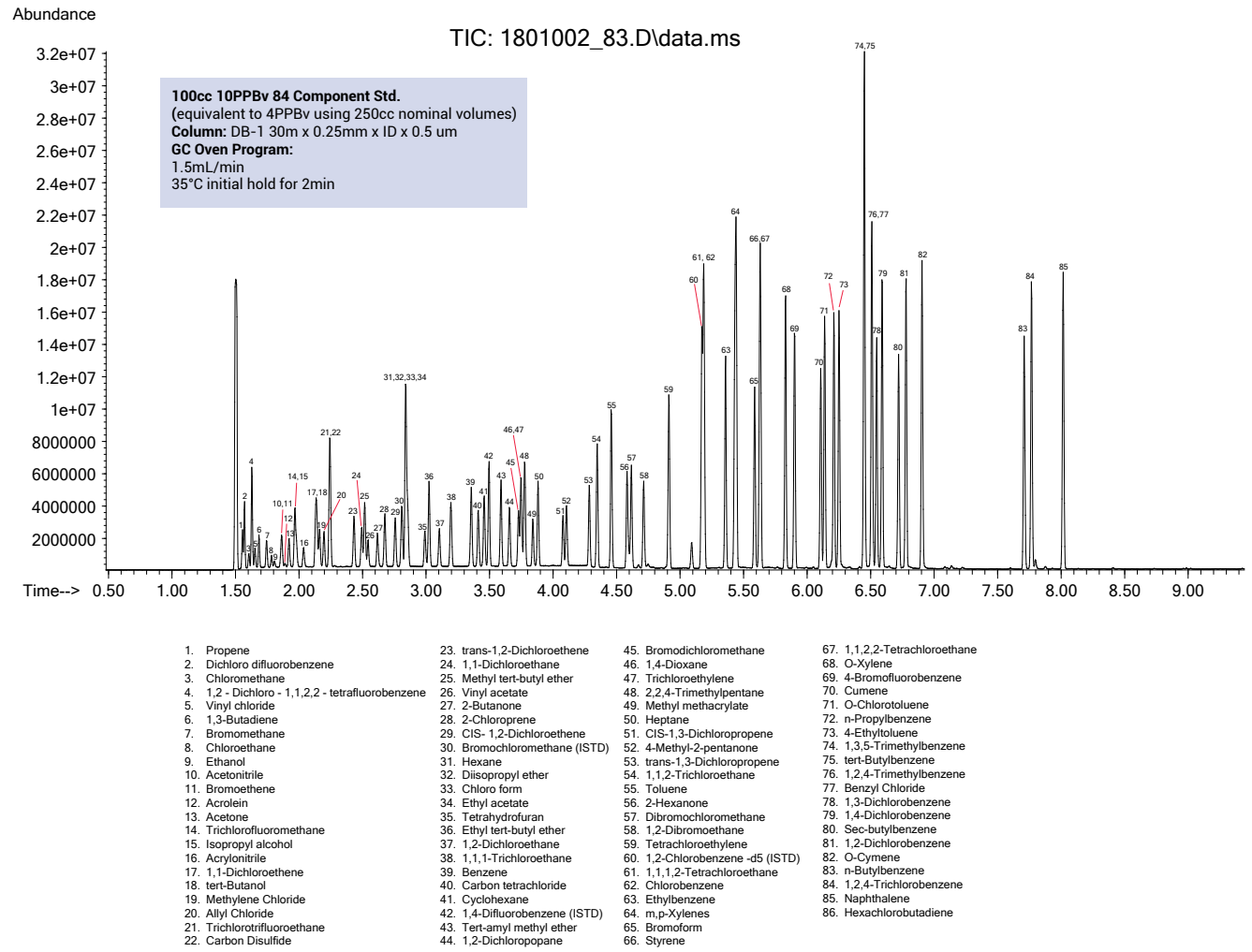
Synchronizing M3 Bakeout with GCMS Cool Down

Entech has been using an approach for sample focusing which is unique to Entech preconcentrators. An open tubular column containing no adsorbent or coating whatsoever focuses the sample at -150°C from the M2 Tenax trap, and then the focuser is heated almost instantly by injecting a hot gas around the outside of the 1/32" Silonite coated pre-column. This rapidly brings the column up to 45-60°C, which releases all TO15 compounds almost instantly. However, the injection process only occurs for about 0.6 minutes, which leaves some condensed water behind and perhaps heavier contaminants on the M3 focuser. Since the heated gas only goes through a narrow sleeve which surrounds the pre-column, the module/chamber itself remains very cold, which allows any remaining water to re-freeze after the hot "inject gas" is removed. This reduces the amount of water injected with the sample, but requires the elimination of the remaining water prior to the next sample analysis.

Prior versions of Entech preconcentrators had to use a "Post Injection Delay" to allow the M3 module to bake out at the end of the run, but in so doing wasted time that could have been used to start preconcentrating the next sample. The delay was to ensure that the M3 trap did not bake out during compound analysis or while the GC column was hot, otherwise interferences and column damage could occur, respectively. The 7200A takes an approach that vastly improves productivity. Right after bake out, the 7200A starts preconcentrating the next sample rather than waiting to bake out the M3 Focuser at the end of the GCMS run. During preconcentration, the GCMS oven temperature is monitored, and when it begins to rapidly fall, the M3 bake out is initiated completely independent of the preconcentration of the next sample. This saves anywhere from 10-15 minutes, depending on the GC run time, which is significant when multiplied by the number of samples run every day. Synchronization with GC cool down has two added benefits. First, the water is released when the oven is cooling down, which prevents damage to the GC column phase. At the same time, a split valve turns on which allows most of the remaining water and contaminants to go out through a split, rather than onto the GC column and ultimately to the MS, thereby reducing the amount of water the MS needs to pump out. Also released from the M3 trap are any heavy compounds that remained after the previous injection. Delivering those contaminants onto the GC column while it is still hot (100-150°C) allows them to move far enough that they will not be additive with the next injection. That in turn reduces carryover potential of the heavier compounds when using the 7200A as compared to its 7100 and 7200 predecessors.

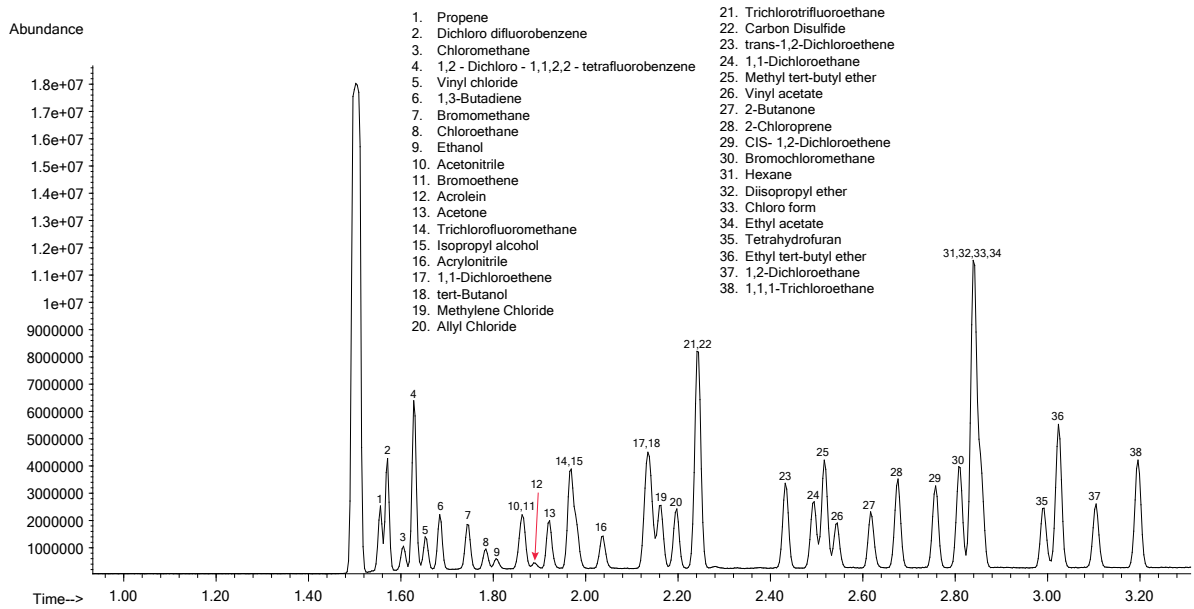
Faster Injection Rates Allowing Fast GCMS

The second major improvement provides support to perform pulsed-splitless injections to increase the rate of sample delivery to the GC column. Combining a pressure ramp (flow rate increase) just after the start of injection compresses the sample to yield much narrower peaks. The true advantage of open tubular cryofocusing is thereby taken full advantage of, resulting in peak widths of just 1.5 to 2 seconds. This will not work with systems using microbore packed traps to focus the sample, as the release time from the particles in the trap is typically on the order of 7-14 seconds rather than 0.5-1 second. Faster injection rates allows the 7200A to use shorter and narrower columns (30m x 0.25mm ID x 0.5um, DB1). With peak widths under 2 seconds, the centroid of each peak need only separate by 2 seconds to provide baseline resolution, but 6 second separations are needed with 6 second wide peaks which are more typical on prior TO15 analyzers. This is why the shorter and faster columns can be used, as far less separation is needed when peak widths are much narrower. Therefore, elution of all target compounds can occur in under 9 minutes rather than the 27 minutes needed for the 7200 and 7100A, with virtually no loss in target compound resolution.



1. Propene
2. Dichloro difluorobenzene
3. Chloromethane
4. 1,2 - Dichloro - 1,1,2,2 - tetrafluorobenzene
5. Vinyl chloride
6. 1,3-Butadiene
7. Bromomethane
8. Chloroethane
9. Ethanol
10. Acetonitrile
11. Bromoethene
12. Acrolein
13. Acetone
14. Trichlorofluoromethane
15. Isopropyl alcohol
16. Acrylonitrile
17. 1,1-Dichloroethene
18. tert-Butanol
19. Methylene Chloride
20. Allyl Chloride
21. Trichlorotrifluoroethane
22. Carbon Disulfide
23. trans-1,2-Dichloroethene
24. 1,1-Dichloroethane
25. Methyl tert-butyl ether
26. Vinyl acetate
27. 2-Butanone
28. 2-Chloroprene
29. CIS- 1,2-Dichloroethene
30. Bromochloromethane (ISTD)
31. Hexane
32. Diisopropyl ether
33. Chloro form
34. Ethyl acetate
35. Tetrahydrofuran
36. Ethyl tert-butyl ether
37. 1,2-Dichloroethane
38. 1,1,1-Trichloroethane
39. Benzene
40. Carbon tetrachloride
41. Cyclohexane
42. 1,4-Difluorobenzene (ISTD)
43. Tert-amyl methyl ether
44. 1,2-Dichloropopane
45. Bromodichloromethane
46. 1,4-Dioxane
47. Trichloroethylene
48. 2,2,4-Trimethylpentane
49. Methyl methacrylate
50. Heptane
51. CIS-1,3-Dichloropropene
52. 4-Methyl-2-pentanone
53. trans-1,3-Dichloropropene
54. 1,1,2-Trichloroethane
55. Toluene
56. 2-Hexanone
57. Dibromochloromethane
58. 1,2-Dibromoethane
59. Tetrachloroethylene
60. 1,2-Chlorobenzene -d5 (ISTD)
61. 1,1,1,2-Tetrachloroethane
62. Chlorobenzene
63. Ethylbenzene
64. m,p-Xylenes
65. Bromoform
66. Styrene
67. 1,1,2,2-Tetrachloroethane
68. O-Xylene
69. 4-Bromofluorobenzene
70. Cumene
71. O-Chlorotoluene
72. n-Propylbenzene
73. 4-Ethyltoluene
74. 1,3,5-Trimethylbenzene
75. tert-Butylbenzene
76. 1,2,4-Trimethylbenzene
77. Benzyl Chloride
78. 1,3-Dichlorobenzene
79. 1,4-Dichlorobenzene
80. Sec-butylbenzene
81. 1,2-Dichlorobenzene
82. O-Cymene
83. n-Butylbenzene
84. 1,2,4-Trichlorobenzene
85. Naphthalene
86. Hexachlorobutadiene

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



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28. 2-Chloroprene
29. CIS- 1,2-Dichloroethene
30. Bromochloromethane
31. Hexane
32. Diisopropyl ether
33. Chloro form
34. Ethyl acetate
35. Tetrahydrofuran
36. Ethyl tert-butyl ether
37. 1,2-Dichloroethane
38. 1,1,1-Trichloroethane

Figure 3 - Close up of front end of TO15 standard showing very narrow peak shapes with no tailing, and good separation of the light volatile compounds.

Table 1: Response Factor Report ppbV											
Name	0.05	0.1	0.2	0.05	1	2	4	10	20	Avg	% RSD
Bromochloromethane (ISTD)											
Propene	2.681	2.299	2.212	2.012	1.893	1.826	1.719	1.537	1.602	1.98	18.6
Dichlorodifluoromethane	3.82	3.905	3.691	3.619	3.467	3.221	3.045	2.73	2.828	3.37	12.8
Chloromethane	0.776	0.713	0.587	0.636	0.578	0.556	0.51	0.465	0.474	0.59	17.9
Dichlorotetrafluoroethane	2.633	2.731	2.521	2.305	2.173	2.098	1.953	1.80	1.779	2.22	15.8
Vinyl Chloride	2.067	2.377	2.238	2.281	2.15	2.064	1.943	1.824	1.841	2.09	9.27
1,3--Butadiene	1.846	1.765	1.512	1.573	1.452	1.445	1.376	1.29	1.294	1.51	12.9
Bromomethane	3.206	2.986	2.743	2.444	2.466	2.31	2.177	2.056	2.039	2.492	16.5
Chloroethane	1.472	1.314	1.412	1.159	1.121	1.113	1.055	0.986	0.975	1.19	15.3
Bromoethene	4.28	4.257	3.881	3.842	3.682	3.682	3.601	3.385	3.441	3.78	8.43
Ethanol		0.898	1.107	0.912	0.763	0.716	0.705	0.548	0.568	0.78	24.2
Acetonitile	1.438	2.51	1.857	1.818	1.588	1.433	1.321	1.257	1.231	1.61	25.4
Trichlorofluoromethane	7.273	7.382	6.794	6.679	6.345	6.165	5.93	5.605	5.584	6.42	10.4
Acetone				2.141	2.041	1.894	1.73	1.643	1.644	1.85	11.4
Isopropyl Alcohol		4.755	4.55	4.515	4.425	4.668	4.455	4.448	4.573	4.55	2.53
Acrolein		0.737	0.556	0.521	0.473	0.468	0.440	0.429	0.440	0.51	20.2
1,1-Dichloroethane	4.498	4.345	4.247	4.112	3.953	3.877	3.763	3.628	3.649	4.01	7.77
Acrylonitrile	2.672	3.366	3.022	2.884	2.77	2.717	2.632	2.565	2.596	2.80	9.14
Trichlorotrifluoroethane	5.627	6.259	6.075	5.808	5.575	5.206	5.033	4.806	4.759	5.46	9.91
Allyl Chloride	3.596	3.668	3.393	3.442	3.547	3.759	3.686	3.677	3.747	3.61	3.58
Methylene Chloride	2.967	2.904	2.636	2.544	2.408	2.265	2.218	2.092	2.101	2.46	13.3
tert-Butanol	6.673	6.56	6.625	6.624	6.703	7.325	7.193	7.094	6.814	6.85	4.14
trans-1,2-Dichloroethene	4.56	4.792	4.617	4.402	4.351	4.268	4.057	4.022	4.048	4.35	6.32
Methyl tert-Butyl Ether	2.613	2.424	2.02	2.206	2.193	2.192	2.124	2.137	2.133	2.23	8.12
Vinyl Acetate	0.814	0.728	0.665	0.744	0.763	0.784	0.785	0.806	0.815	0.78	6.38
1,1-Dichloroethane	2.147	2.356	2.134	2.124	2.087	2.049	1.946	1.916	1.915	2.08	6.79
2-Butanone	1.757	2.059	1.932	1.895	1.934	1.99	1.896	1.882	1.903	1.92	4.29
Hexane	1.263	1.226	1.315	1.284	1.312	1.317	1.26	1.209	1.167	1.26	4.14
cis-1,2-Dichloroethene	5.046	4.766	4.627	4.37	4.514	4.423	4.32	4.263	4.218	4.51	5.95
2-Chloroprene	3.072	3.359	3.104	3.203	3.395	3.474	3.444	3.479	3.5	3.34	5.00
Ethyl Acetate	1.353	1.339	1.222	1.239	1.243	1.291	1.259	1.195	1.147	1.25	5.25
Chloroform	5.952	6.019	5.761	5.502	5.591	5.33	5.155	5.108	4.972	5.49	6.85
Di-isopropyl Ether	4.937	4.751	4.666	4.559	4.771	4.857	4.618	4.497	4.365	4.67	3.87
Tetrahydrofuran	2.051	1.848	1.881	1.865	1.895	1.961	1.864	1.898	1.887	1.91	3.32
Ethyl tert-Butyl Ether	5.348	4.751	5.098	5.397	5.552	5.642	5.484	5.466	5.338	5.34	5.05
1,1,1-Trichloroethane	4.971	5.471	5.265	4.995	5.236	5.109	5.022	5.097	5.034	5.13	3.17
1,2-Dichloroethane	1.988	1.856	1.796	1.667	1.695	1.653	1.56	1.535	1.503	1.70	9.46
Benzene	2.917	3.503	3.025	2.957	3.099	2.933	2.874	2.84	2.765	2.99	7.22
Carbon Tetrachloride	2.507	2.529	2.438	2.243	2.407	2.47	2.477	2.55	2.53	2.46	3.82
Cyclohexane	2.131	2.037	1.871	1.903	1.973	2.043	2.007	2.028	1.997	2.00	3.88

Table 1 - TO-15 Calibration over a 1000x calibration range from 50 part-per-trillion to 20 part-per-billion showing good Relative Standard Deviations.

Table 1: Response Factor Report ppbV											
Name	0.05	0.1	0.2	0.05	1	2	4	10	20	Avg	% RSD
1,4-Difluorobenzene (ISTD)											
tert-Amyl Methyl Ether	0.888	0.910	0.889	0.81	0.810	0.817	0.802	0.796	0.793	0.84	5.58
2,2,4-Trimethylpentane	1.396	1.363	1.353	1.258	1.241	1.181	1.132	1.101	1.066	1.23	9.79
Heptane	1.249	1.232	1.193	1.171	1.195	1.187	1.177	1.146	1.12	1.19	3.33
Trichloroethene	1.551	1.751	1.674	1.564	1.603	1.54	1.498	1.47	1.44	1.57	6.30
1,2-Dichloropropane	0.840	0.932	0.900	0.833	0.833	0.794	0.772	0.754	0.743	0.82	7.78
1,4-Dioxane	1.048	0.824	0.849	0.856	0.824	0.874	0.855	0.836	0.824	0.86	8.16
Bromodichloromethane	1.228	1.314	1.317	1.241	1.311	1.337	1.348	1.377	1.388	1.32	4.14
Methyl Methacrylate	0.426	0.381	0.404	0.391	0.415	0.428	0.438	0.438	0.446	0.42	5.36
cis-1,3-Dichloropropene	1.571	1.46	1.50	1.46	1.572	1.652	1.678	1.738	1.722	1.60	6.77
4-Methyl-2-pentanone	0.886	0.864	0.860	0.891	0.908	0.954	0.950	0.950	0.924	0.91	4.06
trans-1,3-Dichloropropene	1.213	1.139	1.176	1.155	1.289	1.421	1.452	1.528	1.566	1.33	12.6
Toluene	2.593	2.598	2.501	2.404	2.437	2.468	2.474	2.439	2.053	2.44	6.56
1,1,2-Trichloroethane	0.974	1.033	1.04	0.936	0.929	0.913	0.887	0.871	0.858	0.94	7.05
2-Hexanone	0.945	0.912	0.898	1.008	1.121	1.209	1.223	1.251	1.238	1.09	13.6
Dibromochloromethane	1.418	1.432	1.486	1.426	1.567	1.785	1.865	1.994	1.919	1.66	14.2
Tetrachloroethene	1.404	1.447	1.351	1.25	1.242	1.238	1.212	1.176	1.157	1.28	7.97
1,2-Dibromoethane	2.201	2.174	2.293	2.176	2.252	2.273	2.239	2.251	1.962	2.20	4.50
Chlorobenzene-d5 (ISTD)											
Chlorobenzene	1.014	1.063	0.976	0.908	0.894	0.854	0.839	0.818	0.809	0.91	9.98
1,1,1,2-Tetrachloroethane	4.375	4.387	4.185	4.249	4.376	4.499	4.428	4.521	4.51	4.39	2.64
Ethylbenzene	1.325	1.227	1.203	1.221	1.27	1.279	1.28	1.294	1.267	1.26	3.09
m,p-Xylene	3.245	2.968	2.961	3.073	3.173	3.244	3.251	3.195	2.206	3.04	10.9
Styrene	0.981	0.872	0.904	0.953	1.03	1.08	1.126	1.159	1.172	1.03	10.7
o-Xylene	1.545	1.384	1.357	1.491	1.571	1.591	1.59	1.565	1.389	1.50	6.43
Bromoform	0.600	0.611	0.649	0.618	0.715	0.860	0.923	1.008	1.034	0.78	22.8
1,1,2,2-Tetrachloroethane	1.626	1.538	1.496	1.458	1.51	1.458	1.44	1.401	1.311	1.47	6.01
Cumene	6.83	7.316	6.985	6.819	7.054	6.954	6.912	6.721	6.618	6.91	2.93
o-Chlorotoluene	1.34	1.285	1.305	1.261	1.344	1.368	1.371	1.372	0.697	1.26	17.0
n-Propylbenzene	1.336	1.246	1.33	1.38	1.505	1.537	1.546	1.533	1.385	1.42	7.79
4-Ethyltoluene	1.233	1.276	1.295	1.417	1.521	1.56	1.553	1.562	1.403	1.42	9.25
1,3,5-Trimethybenzene	1.879	1.756	1.799	2.00	2.108	2.131	2.137	2.117	1.546	1.94	10.8
tert-Butylbenzene	1.02	0.957	0.972	1.071	1.124	1.167	1.145	1.111	1.075	1.07	6.98
1,2,4-Trimethybenzene	2.044	1.87	2.00	2.259	2.429	2.431	2.415	2.35	1.686	2.17	12.7
1,3-Dichlorobenzene	1.189	1.006	1.159	1.13	1.164	1.103	1.085	1.02	1.026	1.10	6.23
1,4-Dichlorobenzene	1.022	0.901	1.073	1.061	1.092	1.049	1.035	1.02	1.014	1.03	5.34
sec-Butyl Benzene	1.197	1.134	1.235	1.325	1.469	1.449	1.447	1.421	1.316	1.33	9.23
1,2-Dichlorobenzene	1.224	1.194	1.128	1.087	1.144	1.08	1.074	1.064	1.065	1.12	5.26
o-Cymene	1.271	1.221	1.281	1.407	1.556	1.595	1.634	1.598	1.403	1.44	11.1
n-Butyl Benzene	1.048	1.087	1.166	1.311	1.486	1.496	1.545	1.552	1.36	1.34	14.8
1,2,4-Trichlorobenzene	9.991	6.866	7.141	7.454	8.202	7.539	7.966	8.255	8.812	8.03	11.9
Naphthalene	9.342	5.808	6.616	7.234	8.067	8.294	8.845	9.007	9.34	8.06	15.6
Hexachlorobutadiene	1.024	0.830	0.849	0.832	0.837	0.773	0.784	0.774	0.763	0.83	9.64

Table 2:7200A Method Detection Limit 50 ppt Concentration										
Compound	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7	STDEV	Avg	MDL
Propene	68.97	57.09	65.51	62.64	67.72	64.34	55.06	5.2	63.0	8.3
Dichlorodifluoromethane	59.13	60.01	61.93	67.46	60.88	62.17	60.69	2.7	61.8	4.4
Chloromethane	56.16	53.01	56.64	73.63	56.96	58.65	58.85	6.7	59.1	11.3
Dichlorotetrafluoroethane	64.37	56.56	65.49	62.7	60.64	59.42	67.5	3.8	62.4	6.1
Vinyl Chloride	58.12	50.45	61.81	58.05	59.78	59.07	57.43	3.6	57.8	6.2
1,3--Butadiene	55.23	56.05	62.66	63.97	58.2	58.27	58.35	3.2	59.0	5.5
Bromomethane	64.34	53.93	65.84	73.96	61.98	55.73	58.63	6.8	62.1	11.0
Chloroethane	68.85	68.88	59.31	60.95	66.84	64.86	61.79	3.9	64.5	6.0
Bromoethene	56.79	57.23	57.53	55.47	61.11	54.83	56.5	2.0	57.1	3.5
Ethanol	149.35	99.13	79.14	130.39	102.04	124.42	97.46	24.0	111.7	21.4
Acetonitile	57.47	67.32	84.63	42.68	66.61	56.05	24.2	19.3	57.0	33.9
Trichlorofluoromethane	61.93	57.83	57.88	58.74	56.6	52.92	57.92	2.7	57.7	4.6
Acetone	114.75	115.21	115.8	113.25	121.76	119.54	110.82	3.7	115.9	3.2
Isopropyl Alcohol	95.28	99.64	101.55	102.66	99.28	100.29	95.63	2.8	99.2	2.8
Acrolein	62.14	69.55	31.49	50.73	33.38	63.84	78.25	17.9	55.6	32.1
1,1-Dichloroethane	56.89	58.96	64.87	55.34	57.24	53.57	55.17	3.7	57.4	6.5
Acrylonitrile	57.05	50.23	56.77	62.46	60.33	60.26	65.7	4.9	59.0	8.4
Trichlorotrifluoroethane	54.98	55.53	55.12	58.38	58.69	58.51	53.18	2.2	56.3	3.9
Allyl Chloride	48.7	47.98	45.1	45.67	45.15	44.85	42.92	2.0	45.8	4.3
Methylene Chloride	67.61	64.55	70.48	61.34	63.86	64.65	57.04	4.3	64.2	6.7
tert-Butanol	48.4	48.83	50.99	42.97	51.82	52.78	52.56	3.5	49.8	6.9
trans-1,2-Dichloroethene	51.85	58.77	56.08	54.79	56.24	51.42	53.97	2.6	54.7	4.7
Methyl tert-Butyl Ether	53.68	50.61	55.64	56.39	52.42	49.88	50.22	2.6	52.7	5.0
Vinyl Acetate	33.94	45.27	42.64	60.91	48.81	41.41	51.3	8.5	46.3	18.4
1,1-Dichloroethane	56.66	51.03	56.47	57.93	60.53	55.16	53.77	3.0	55.9	5.4
2-Butanone	54.97	45.86	53.51	46.61	45.91	48.35	52.93	3.9	49.7	7.9
Hexane	56.1	56.89	50.7	60.37	55.0	55.6	44.45	5.1	54.2	9.5
cis-1,2-Dichloroethene	52.11	52.87	56.35	54.82	55.85	51.93	56.28	2.0	54.3	3.6
2-Chloroprene	46.81	50.28	50.91	50.72	53.55	45.07	50.33	2.8	49.7	5.7
Ethyl Acetate	42.23	59.69	56.81	65.15	60.77	47.38	54.05	8.0	55.2	14.5
Chloroform	55.56	53.24	54.97	56.37	57.39	56.06	52.18	1.8	55.1	3.3
Di-isopropyl Ether	51.9	52.54	57.33	50.46	56.2	51.4	52.58	2.6	53.2	4.8
Tetrahydrofuran	47.26	47.74	56.74	43.08	48.7	41.66	44.56	5.0	47.1	10.5
Ethyl tert-Butyl Ether	52.65	48.79	51.48	44.6	47.63	43.13	51.07	3.6	48.5	7.4
1,1,1-Trichloroethane	53.56	51.4	53.18	50.97	52.17	50.77	50.06	1.3	51.7	2.5
1,2-Dichloroethane	57.28	55.33	63.36	55.42	52.33	55.7	60.11	3.6	57.1	6.4
Benzene	59.16	50.85	55.16	55.25	52.73	55.61	64.1	4.4	56.1	7.8
Carbon Tetrachloride	48.56	46.89	42.7	50.25	45.16	44.4	46.21	2.5	46.3	5.5
Cyclohexane	52.35	47.56	47.25	50.23	45.05	46.96	51.02	2.6	48.6	5.4
tert-Amyl Methyl Ether	54.04	59.38	55.89	59.86	54.41	58.51	55.65	2.4	56.8	4.2

Table 2 - Method Detection Limit Determination in Parts Per Trillion for Extended TO-15 List created using 7 replicate runs of an 80 part-per-trillion standard. Most compounds are in the low PPTv range.

Table 2:7200A Method Detection Limit
50 ppt Concentration

Compound	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7	STDEV	Avg	MDL
2,2,4-Trimethylpentane	54.95	51.33	55.26	52.19	54.96	54.14	56.14	1.7	54.1	3.2
Heptane	51.85	54.36	51.19	50.55	53.92	55.73	50.31	2.1	52.6	4.0
Trichloroethene	54.69	54.39	58.95	56.19	59.3	59.23	56.71	2.1	57.1	3.7
1,2-Dichloropropane	57.87	56.18	60.68	58.81	58.41	52.59	55.93	2.6	57.2	4.5
1,4-Dioxane	36.42	55.93	52.93	50.14	56.28	50.35	52.82	6.7	50.7	13.3
Bromodichloromethane	48.02	49.53	47.83	44.44	48.61	42.73	45.43	2.5	46.7	5.3
Methyl Methacrylate	49.78	58.17	59.32	45.7	47.57	48.86	55.26	5.4	52.1	10.4
cis-1,3-Dichloropropene	43.25	43.72	43.8	44.94	41.99	43.35	46.03	1.3	43.9	2.9
4-Methyl-2-pentanone	47.56	51.02	45.33	51.9	48.79	47.39	52.14	2.6	49.2	5.3
trans-1,3-Dichloropropene	39.24	38.89	41.64	40.78	41.47	38.01	43.34	1.9	40.5	4.6
Toluene	54.28	53.71	55.55	53.14	55.83	56.22	53.75	1.2	54.6	2.2
1,1,2-Trichloroethane	50.6	57.16	53.81	50.91	52.76	56.12	58.55	3.1	54.3	5.7
2-Hexanone	38.76	38.92	42.41	39.27	43.77	43.56	41.38	2.2	41.2	5.3
Dibromochloromethane	34.15	37.15	38.27	36.55	37.79	36.33	38.31	1.5	36.9	3.9
Tetrachloroethene	56.43	56.57	61.6	54.23	52.85	57.88	58.71	2.9	56.9	5.1
1,2-Dibromoethane	47.4	53.06	52.44	50.69	52.63	51.24	53.14	2.0	51.5	3.9
Chlorobenzene	58.11	62.69	65.9	58.54	61.78	59.13	63.25	2.9	61.3	4.7
1,1,1,2-Tetrachloroethane	47.0	49.96	54.3	52.92	53.49	50.56	56.17	3.1	52.1	5.9
Ethylbenzene	52.84	52.35	53.26	49.03	53.79	50.72	50.05	1.8	51.7	3.5
m,p-Xylene	106.28	104.91	105.9	95.32	107.04	95.2	100.79	20.7	95.7	21.7
Styrene	42.86	45.41	47.28	45.03	46.73	45.3	43.43	1.6	45.1	3.5
o-Xylene	51.33	46.99	46.0	48.82	48.39	49.53	49.88	1.8	48.7	3.7
Bromoform	35.84	35.61	34.16	38.58	34.19	30.96	33.0	2.4	34.6	6.9
1,1,2,2-Tetrachloroethane	55.56	54.11	54.4	52.18	54.55	50.25	50.27	2.2	53.0	4.1
Cumene	58.12	52.78	58.59	60.46	57.06	57.81	59.1	2.4	57.7	4.2
o-Chlorotoluene	56.81	55.34	56.65	57.69	56.04	59.26	58.41	1.4	57.2	2.4
n-Propylbenzene	49.49	50.27	51.13	46.07	52.59	47.29	53.64	2.7	50.1	5.4
4-Ethyltoluene	44.13	45.83	48.03	44.45	48.92	41.37	45.27	2.5	45.4	5.6
1,3,5-Trimethybenzene	45.3	48.34	45.14	44.9	44.97	44.26	45.03	1.3	45.4	2.9
tert-Butylbenzene	50.77	49.32	52.5	49.2	47.82	49.52	52.0	1.7	50.2	3.3
1,2,4-Trimethybenzene	43.74	47.66	41.82	46.63	44.5	41.87	47.01	2.4	44.7	5.4
1,3-Dichlorobenzene	44.1	44.59	46.77	42.93	46.43	49.23	44.54	2.1	45.5	4.6
1,4-Dichlorobenzene	52.09	43.96	47.89	45.33	54.84	47.61	44.38	4.1	48.0	8.5
sec-Butyl Benzene	48.26	47.96	48.52	46.79	47.35	44.6	45.69	1.4	47.0	3.1
1,2-Dichlorobenzene	51.03	48.75	51.94	43.31	51.45	50.8	42.4	4.0	48.5	8.3
o-Cymene	46.71	43.27	44.86	42.49	43.41	46.3	42.32	1.8	44.2	4.0
n-Butyl Benzene	40.61	43.4	39.76	40.43	41.46	38.25	40.49	1.6	40.6	3.9
1,2,4-Trichlorobenzene	46.53	44.78	48.37	41.18	44.39	49.33	43.36	2.9	45.4	6.3
Naphthalene	45.3	46.78	49.1	46.73	46.15	48.17	47.07	1.3	47.0	2.7
Hexachlorobutadiene	52.64	56.17	54.37	56.49	49.16	53.54	53.87	2.5	53.7	4.6

Reduced Liquid Nitrogen Consumption

The Module 3 Trap has been redesigned in the 7200A to provide much better transfer of heat during cooling. Rather than seeing a substantial amount of "liquid" N2 coming from the M3 exaust during cooling, this has been reduced to almost zero during the -150 to -160°C cool down. This extends the number of runs that can be obtained from a single tank of LN2.

Improved Water Reduction for Better MS Stability

Water transfer to the MS has been reduced dramatically using the 7200A as compared to the 7200 and 7100A. Using a 30m x 0.25mmID x 0.5um film column, a low initial flow rate of just 0.6cc/min is used which brings the starting pressure down to about 2 psig. Upon injection, the flow rate is ramped to 1.5cc/min to compress the sample and to create much narrower peaks on-column. Just after injection, the split valve is turned back on, but instead of the 3- 6cc/min that was used to assist in transferring the sample from M2 to M3 during final focusing, the flow out the split increases to about 30-40cc/min due to the ramp in the GC carrier gas pressure, which substantially increases the amount of additional residual water that is split out relative to the 7100A or 7200. A noticeable increase in the amplitude of the lighter volatile compounds is achieved (Figure 2), and the MS has an easier time maintaining a constant response due to the large decrease in water that has to be pumped out. Improved water management is critical in achieving shorter injection to injection times, as the MS has less time to recover. With approximately a 3x reduction in water delivered to the MS, injection of another sample every 24 minutes introduces the same amount of water into the mass spectrometer as injections every 1-1.2 hours when using the 7100A or 7200. Since typical run cycles of 45-60 minutes are common with these older preconcentrators with acceptable MS performance throughout the day and night, the 7200A can achieve the 2x throughput rates with even less MS drop off, as the MS is getting 1/2 the time to pump out 1/3rd the amount of water.

Additional 7200A Features

Several other features that were unique to the 7200 have been retained with the7200A, including 7 years of improvements following the 7200's introduction. These are summarized below:

Accu-Sample Technology

- Electronic Volume Control for vastly improved volume measurements by eliminating Mass Flow Controllers
- Silonite-D Coated Flow Paths
- Digital Rotary Valve Control for improved isolation and small volume accuracy
- Advanced software and report generation

Maximizing Throughput by using Two or Three 16-Position Autosamplers

Faster throughput using cycle times under 25 minutes means that a sequence of 16 samples started at 5PM would be done at 12 midnight when using just a single 16-position autosampler. That is why Entech has made it possible to connect up to three 7016D autosamplers to the 7200 and 7200A preconcentrators. The 7200A can really take advantage of this, with the ability to analyze 32 to 38 canisters unattended overnight, and up to 48 canisters over a weekend. Both speed and high capacity are required when trying to boost productivity, and now the 7200A/7016D (x2 or x3) can provide the high throughput advantage air laboratories need to remain competitive in the growing TO15 market.

Experimental

Analytical data was generated with the Entech 7200A Preconcentrator interfaced to an Agilent 7890/5977 GCMS using a 30m x 0.25mm ID x 0.5um DB1 column. The GC oven initial temperature was 35°C (2 min), was ramped at 25°C/min to a final temperature of 260°C with no hold. This results in a total run time of 11 minutes with all TO15 compounds eluting within 8 minutes. The short bakeout time actually produces better contaminant elimination relative to prior TO15 solutions because of the thinner film, shorter column used. The MS acquisition was from 29 to 180 amu to include detection of Formaldehyde and to monitor the m/z 31 peak found in many light oxygenated compounds. After 4 minutes, the scan was changed to 33-280 to exclude additional residual air from the TIC background. Calibration standards were obtained from both Linde Gas and Air Liquide. Three cylinders at 1 PPMv were blended together using an Entech Instruments Model 4700 Dynamic Dilution system to 20 PPBv, and then after 3 hours of equilibration the 20 PPBv standard was further diluted to create a 0.5PPBv standard in 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 0.05 to 20 PPBv. 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 0.05PPB (50cc from the 0.4 PPB std) were used to create the MDL values. Table 3 below shows the sample trapping conditions of the 7200A Preconcentrator.

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

Table 3 - 7200A Trapping Conditions Using Extended Cold Trap Dehydration

Results and Discussion

The chromatogram obtained from the 7200A "Accelerated" preconcentrator connected to the Agilent 7890/5977 is shown in Figure 2 (page 5). The elution of Trichlorobenzene, Naphthalene, and Hexachlorobutadiene are shown to be under 8.1 minutes, which is less then 1/3rd the elution time on most TO15 systems. This is only possible by combining ultra fast injection rates, narrow bore thin film columns, high ramp rates, and fast scan times. Injection rates this fast are simply not possible when using a packed micro trap as used in other systems, as the diffusion time out of the packed trap particles after pre-heating is measured in seconds rather than milliseconds. Only an open tubular focusing trap with initial heating rates of 1000-10,000 deg per minute can achieve this kind of performance, and that is what is uniquely achieved with the Entech design. Figure 3 (page 5) shows the front end of the TO15 Standard run, with baseline resolution between the Chloromethane and the Freon 114 peak, which can be difficult to resolve with some TO15 systems. Resolution of these and other closely eluting pairs is important as sometimes the primary and secondary ions are shared, causing interferences when full separation is not possible. In addition, improving peak resolution will also prevent interferences as the need for lower detection limits continues to grow in importance, as there is a better chance that non-target interfering compounds will be separated from target compounds.

Figure 4 (page 12) shows the Single Ion Chromatogram (SIC) of Vinyl Chloride with a peak width of under 2 seconds and extremely reproducible retention times that are independent of sample concentrations. Very narrow peak widths require the number of scans per second to be increased, which can reduce overall sensitivity when using older GCMS systems. However, with double the throughput, the concept of obtaining the latest and highest sensitivity GCMS systems makes a lot of sense, as uptime is now even more critical, and profit margins will still be greatly increased even when adding new GCMS technology.

Vinyl Chloride m/z 62 Overlay, <2 Second Wide Peak (1.16-1.19 min)

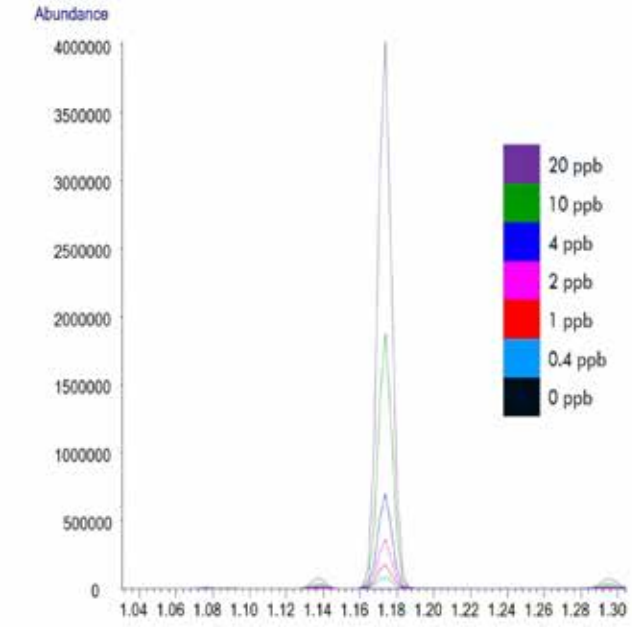

Figure 4 - Vinyl Chloride Calibration showing peak width of 1.7 seconds.

Ethylbenzene, m/p Xylene, and o-Xylene m/z 106 Overlay

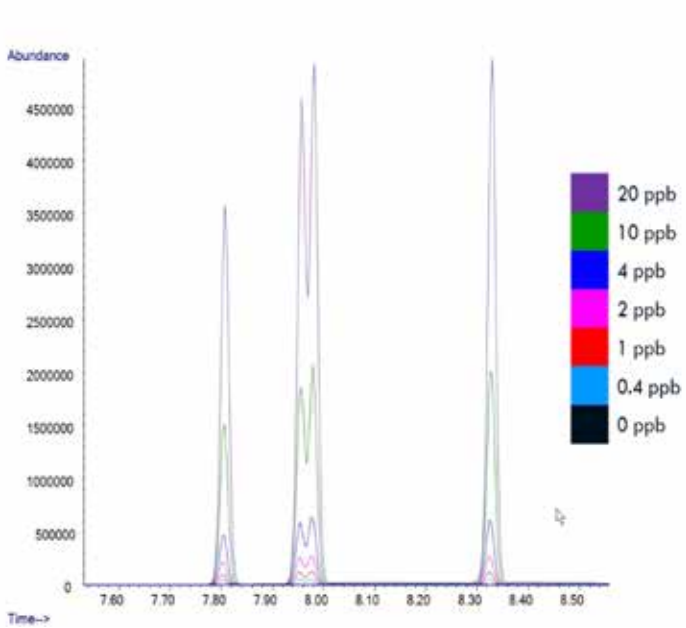

Figure 5 - Ethylbenzene and Xylenes showing 40% Valley Between m,p-Xylenes that usually do not separate on a DB1 column.

Figure 5 shows the Ethyl Benzene and Xylenes overlayed from 0.4 to 20 PPB. The improved resolution is demonstrated by the 40% valley achieved between the meta and para Xylenes, which hardly resolve at all on other TO15 systems. Again, this demonstrates that even though the run times are 3x faster than other systems, the resolution is still superior, allowing better separation from interferring compounds.

The 8-point calibration results are shown in Table 1. The Relative Standard Deviations are very acceptable considering the wide dynamic range, with most 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 0.5PPBv) allowing a wider dynamic range than is possible when just using a single standard canister. Linear calibration curves are one of the many benefits of using cold trapping, which avoids reactions that can occur on strong multi-bed traps. The over 28 years of research that has led to the development of the 7200A 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 7200A 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, and laboratory delivery lines have been purged of these ubiquitous compounds.

Table 2 (page 8) shows the consistency of the 7 replicate injections. By using a 0.05 PPBv standard injection (50cc of a 0.4PPBv standard), calculated MDL's down to 0.01PPB are common. The 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

Data File	Run #	Bromochloromethane	% of Run #2	1,4-Difluorobenzene	% of Run #2	Chlorobenzene -d5	% of Run #2
18102312	2	120140	100.0%	526502	100.0%	95230	100.0%
18102313	3	118839	98.9%	524589	99.6%	95137	99.9%
18102314	4	119679	99.6%	526955	100.1%	95314	100.1%
18102315	5	117612	97.9%	522996	99.3%	94561	99.3%
18102316	6	118968	99.0%	520824	98.9%	94308	99.0%
18102321	10	118614	98.7%	519408	98.7%	94698	99.4%
18102331	20	115263	95.9%	506639	96.2%	93740	98.4%
18102341	30	111103	92.5%	486582	92.4%	90152	94.7%
18102351	40	109523	91.2%	484387	92.0%	92221	96.8%

Table 4 - 40 Consecutive runs of 50cc of Internal Standard and 250cc of Indoor air with injections every 25 minutes showing extremely good reproducibility and less than a 9% drop in Internal Standard Response due to improved water elimination, greatly reducing mass spectrometer recover times.

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.

Finally, Table 4 shows the excellent stability of the Internal Standard response over 40 sequential runs. The ISTD response is shown for runs 2-10, and then run #20, 30, and 40. Even after 40 runs with cycle times of under 25 minutes, the total drop in the Internal standard response was less than 9% for Bromochloromethane, and only about 5% for Chlorobenzene-d5. The improved water management in the 7200A is critical to be able to achieve ISTD stability with such short cycle times.

Conclusion

The Entech 7200A combined with the Agilent 7890/5977 greatly exceeds the requirements of EPA method TO-15, while virtually doubling the sample throughput potential when compared to other TO15 analyzers. This 100% increase in productivity will offer labs a tremendous competitive advantage by lowering the cost of analysis while offering faster turn around times for their customers, allowing more 1-3 day expedited turn around times to be achieved . The ability to add a second or third 16 position autosampler allows labs to run their systems all night, processing roughly 32-38 canisters overnight, or up to 48 canister unattended over the weekend, resulting in productivity improvements of up to 100% over prior TO15 solutions.

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

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Entech Instruments
2207 Agate Court
Simi Valley, CA 93065
Phone: 805-527-5939

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