Creating Accurate Low Level TO15 Standards with the Entech 4700 Precision Diluter

Application Note:

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Background

The analysis of Air Toxics TO-15 compounds in air by GCMS requires the accurate preparation of low level standards to fulfill 3 distinct requirements:

1. Create GCMS response factors for each target compound across the full range of expected concentrations
2. Validate the canister preconcentration system for consistent preconcentration and matrix management without loss of target compounds during analysis by GCMS
3. Provide inexpensive preparation of low level standard to allow recovery testing of all sampling canisters in a laboratory's inventory for inertness validation

The ability to meet item #1 could simply be achieved by performing a loop injection of high concentration standards, but this would not meet the requirements of #2 and #3, which require the standards to be diluted down to ambient levels, often times below 1 PPBv. As described in more detail later, it is best to use at least 2 standards when creating a GCMS calibration curve, as this typically allows method calibrations over a wider concentration range, often times up to 1000x or more. Large concentration ranges can reduce the number of dilutions and reruns that are necessary by a laboratory, thereby increasing productivity. For example, generating a calibration curve from 0.04PPBv to 40 PPBv would allow all samples within this range to be quantified without further dilution, whereas reducing the range to just 0.04PPBv to 4 PPBv would require any samples with target compounds in the range of 4 to 40 PPB to be rerun using smaller sample volumes, or after diluting a representative aliquot into a second canister.

Items #2 and #3 in the previous list are extremely important when performing accurate TO15 analyses, yet are often not given the consideration they deserve. Creating standards that are as similar to the concentration and matrix of real samples is critical to prove that target compounds will be recovered properly during the preconcentration and matrix elimination process. Although calibration standards are stable in Silonite coated canisters without the presence of water, it is recommended that canisters be made up with between 50-70% relative humidity just so the sample preparation system can be challenged just as it will be with real samples. A discussion follows that describes how moisture levels in this range can be used to challenge the analytical system with extremely large or small amounts of total water just by varying the preconcentration volume.

Properly challenging the analytical system also means avoiding the temptation of using a different canister for every point on the curve. This can make it easier to get a curve to pass because using the same volume out of every canister will make the total amount of water introduced into the preconcentrator a constant. However, a passing curve does not mean that real air samples will be analyzed properly with this system. It is understood that water in field samples can easily vary by 10x or more, whcn comparing dry, cold weather samples to those collected during a humid Summer day. Water is the biggest interferent when analyzing air samples, and proving the management of both high and low concentrations is critical to proving that all air samples will be analyzed correctly. It is the recommendation of Entech to challenge the analytical system by using at least a 10 fold difference in the

amount of water processed while generating a calibration curve, while making sure that at least one point introduces more water than can ever be introduced during a sample analysis. The easiest way to do this is by using just 2 or at most 3 canister standards at 50-70 %RH, varying the volume by at least 10x from the lowest to highest volume used, and making at least 1 point on the curve using a volume that is twice that of the nominal sample volume. For example, making two canisters that are at 20PPB and 0.4PPB at 60% Relative Humidity, and selecting 250cc as the nominal volume that will be analyzed when running canister samples, a 0.04PPB to 40PPB calibration curve can be generated as follows:
0.4PPB canister;
25cc(0.04PPB), 100cc(0.160PPB), 250cc (0.40 PPB), 625cc (1 PPB)
20 PPB canister;
50cc (4 PPB), 100cc (8 PPB), 250cc (20PPB), 500cc(40PPB)

We can see that both the 1PPB and the 40PPB points are challenging the system with more than 200% of the normal sample volume (625cc and 500cc). Since the humidity level is at 60%, the amount of water transferred into the preconcentrator will be equivalent to 120% RH at 250cc, which would actually be 100% RH as the excess water would fall out in the canister. That is, even on the most humid day of the Summer, those moist canisters would fail to introduced as much water into the preconcentrator at 250cc as the 60% RH standard at 500 and 625cc. Therefore, the water management will have been tested to work under the most difficult of conditions. The approach of using the same volume from 7 different canisters at some intermediate humidity will fail to properly challenge the method to validate it for very wet, or for that matter very dry samples which may affect preconcentration systems in totally unexpected ways. The two canister, multi-volume approach validates the linearity of the system under the wettest and dryest of conditions.

Another advantage of using just 2 canisters to generate a calibration curve rather than a separate canister for every point is that it tests whether a system can accurately extract smaller volumes quantitatively when performing preconcentrations. This is very important to allow sample dilutions without actually having to dilute the sample. As an example, if the normal sample volume is 250cc, and instead 25cc is extracted from the canister, there has been effectively a 10:1 dilution of the sample, which is very useful to extend the range of concentrations which can be quantified without actually doing a physical dilution. Note that this should only be done when it has been proven to work by using these smaller volumes when introducing standards, either when the calibration curve is generated, or at least by testing these smaller volumes and verifying that they fall on the established curve. If 25cc is the smallest volume in the curve, then 25cc should be the smallest sample volume attempted without additional small volume accuracy validation.

Finally, item #3 is becoming more important as the average age of the canister inventory in the field continues to increase. The first canisters were produced over 30 years ago, and a lot can happen to a canister's internal surface in a far shorter period than that. Canisters can pull in dust, pollen, spores, SVOCs, aerosols, reactive species, (flies and insects??) and other foreign material during sampling that can affect the recovery of TO15 compounds over time. In addition, many canisters in use today were never checked for inertness by the manufacturer, and may have in fact been producing poor data from the start. Finally, there are a number of "SUMMA-Like" canisters being used that do not have the actual deposition of NiCrOx layer like SUMMA canisters, or a deposited layer of silica like Silonite canisters, and are therefore subject to corrosion from water and oxidation from multiple exposures to PPBv level ozone. The 4700 simplifies the process of making low level challenge standards (1 PPBv or less), using so little of the contents of the standards cylinder that even the smallest cylinders can be used to create a 1PPBv standard in thousands of 6L canisters. With the 4700, the exact target compounds being reported on by air laboratories can be recovery validated in every canister being sent out to the field, perhaps once every 2 years.

This application note describes the operation of the 4700 for producing low level standards from higher level cylinders, or from custom mixes made into low pressure bottles or canisters using a redilution feature through inlet #6. The reproducibility of making

Figure 1 *4700 with four 6R cylinders attached through side Micro QT Quick Connect Ports for rapid exchange of cylinder standards*

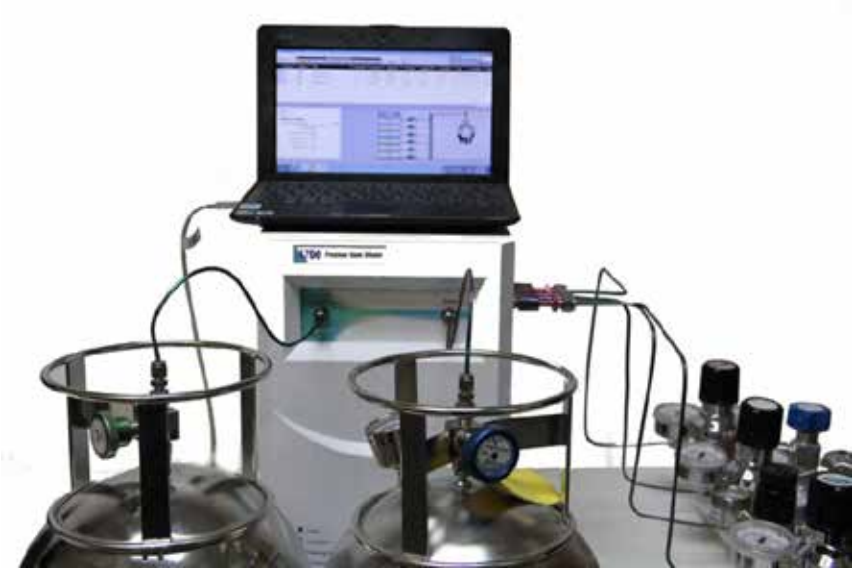

Figure 2 *PPB Level Standard on left attached to input CH6 to create sub-PPB standard mixes into canister on the right. This approach is ideal for making low level calibration standards and for inertness testing field sampling canisters with a 1PPB mix.*

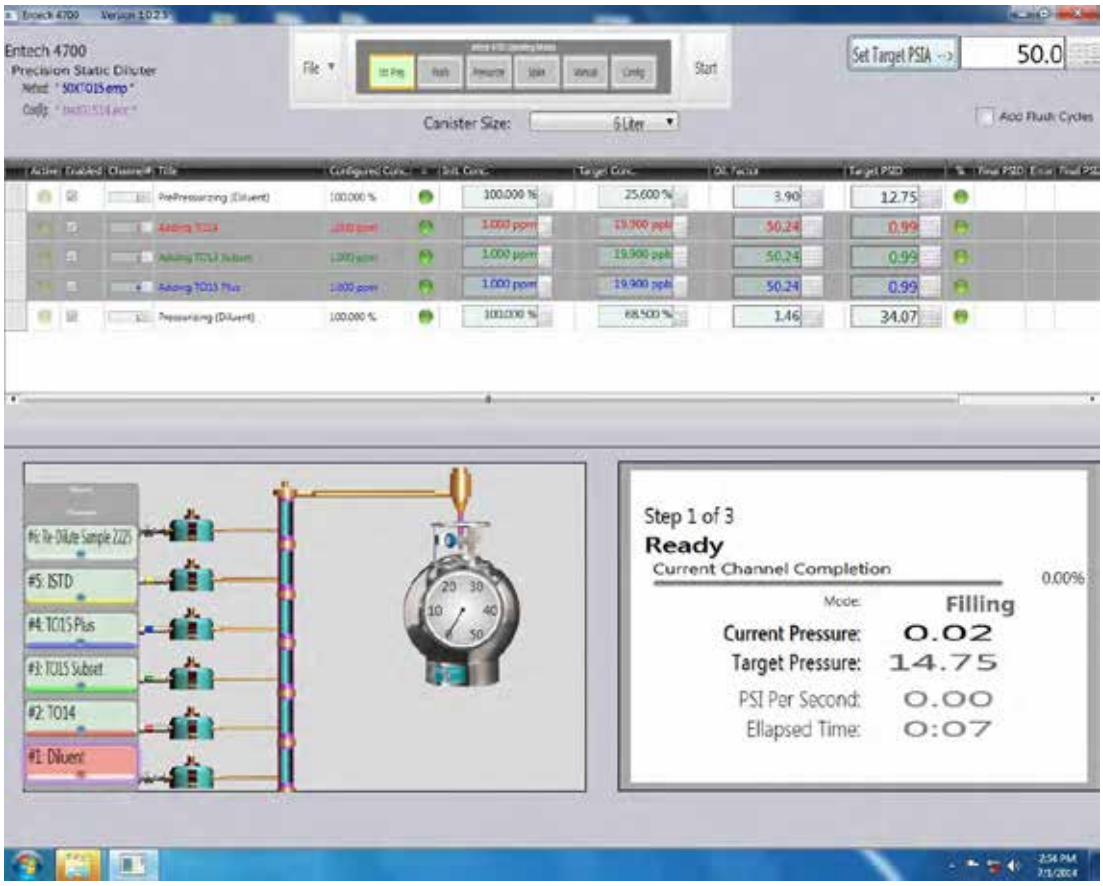

Figure 3 *Preparing to generate a 20 PPBv concentration from 3 6R cylinders and a high purity diluent. Some diluent is first placed into the canister to bring the pressure sensor into a more linear part of its range.*

1PPB challenge standards into 5 different canisters will be demonstrated. In addition, a calibration curve will be shown that was generated by creating a 0.4PPB and a 20PPB standard, and then taking different volumes out of each to create a GCMS calibration over a 1000 fold concentration range. Only by making both the 20PPB and the 0.4PPB standard accurately for all compounds will the curve be able to achieve low % RSDs for each compound, which is ultimately one of the most challenging requirements of the TO15 method.

Experimental

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 this was again blended down with the 4700's unique reblend feature down to 0.4PPB to generate the calibration curve. The combination of using varying calibration volumes from the two standards allowed an extended concentration range from 0.04 to 40 PPBv, for a total of a 1000x calibration range. The nominal sample volume was chosen to be 250 PPBv, which is very common for TO15 laboratories. The 20 PPB standard was also used to create five 1 PPB standards into 5 different canisters, filling them to just atmospheric pressure (15 psia) as a means to test their inertness. These canisters would normally be allowed to sit for at least 1 week followed by analysis to verify recovery of all target compounds, but in this case were analyzed immediately as the purpose here was to show the reproducibility of the 4700 rather than the individual inertness of each canister.

Analytical data was generated with the 7200 Preconcentrator interfaced to a Thermo Scientific ISQ QD GCMS. The GC oven started at 35^{o}C (5 min) ramped at 6^{o}C/min to 120^{o}C, then at 10^{o}C/min to a final temperature of 220^{o}C (5 min). The MS acquisition was from 30 to 280 amu to improve the

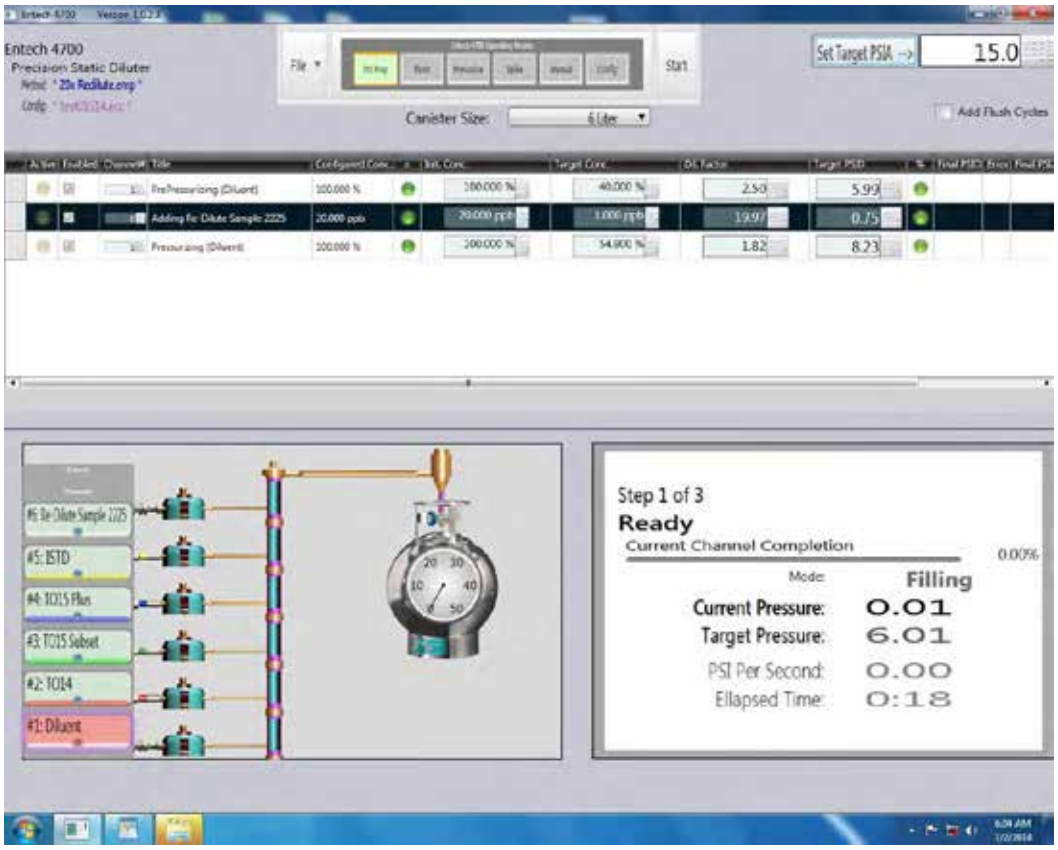

Figure 4 *Process for preparing challenge standards into canisters at 1PPB and atmospheric pressure, for testing a week later by GCMS to determine canister inertness*

detection of oxygenates having m/z 31 ions.

Generating Standards

Figure 3 shows a typical calibration using 3 cylinders to create a 20PPBv final mix at 50 psi absolute into a Silonite canister. Cylinders and their concentrations are defined in a configuration screen, and multiple configurations can also be made and recalled to support more than 5 cylinder standards. During method development, all cylinders are initially shown to allow selection and setting of final target concentration. The final target pressure is entered in at the top right, in this case 50 psia. The 4700 uses an absolute sensor to make the readings completely independent of local atmospheric pressure. This sensor can be calibrated using 11 gravimetric measurements every 5 psi when filling a 1L canister from 0 to 50 psia. Referencing a properly calibrated scale, this allows the 4700 to be calibrated inhouse, as opposed to mass flow controllers used in most other dilution systems which much be sent outside for recalibration, typically at a substantial cost and requiring the in-house dilution system to be down for weeks.

Figure 4 shows the method for making accurate 1PPB standards into 6L field sampling canisters as a part of a quality assurance program to test canisters for proper analyte recovery once every two years. The 4700 uses so little of the standard cylinder mix, that even the smallest 6R cylinders can prepare a 1PPB standard at atmospheric pressure into over 15,000 6L canisters. Here, the canister is cleaned and evacuated as usual, and then filled with a 1PPB mix containing all the target compounds being reported on by the laboratory. The suggested introduction of water is just 12ul to simulate about a 10% RH sample, which is similar to what would be collected on a normal winter day after equilibrating back to laboratory temperatures. Just attach the evacuated canister, start the filling process, then swap out the canister with the next can in about

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 1 *Low % Relative Standard Deviation across TO-15 Standard 1000x calibration range from 40 part-per-trillion to 40 part-per-billion demonstrates that both the 20PPBv and the 0.4PPBv standards were diluted accurately, otherwise a change in response factors would be obvious, causing increased %RSDs*

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
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

	10862	13978	13984	10001	10002	Mean	SD	%RSD
Propene	0.98	0.96	0.98	0.88	0.97	0.954	0.0422	4.42
Dichlorodifluoromethane	1.00	1.00	1.00	0.92	0.98	0.980	0.0346	3.53
Chloromethane	1.02	0.98	1.03	0.88	0.98	0.978	0.0593	6.07
Dichlorotetrafluoroethane	1.03	0.96	0.98	0.91	0.98	0.972	0.0432	4.45
Vinyl Chloride	1.01	0.99	0.99	0.93	1.00	0.984	0.0313	3.18
1,3--Butadiene	0.96	0.99	1.02	0.92	0.96	0.970	0.0374	3.86
Bromomethane	1.01	1.01	1.05	0.93	0.97	0.994	0.0456	4.59
Chloroethane	1.02	0.97	1.11	0.92	0.98	1.000	0.0711	7.11
Bromoethene	0.97	0.95	0.99	0.93	0.94	0.956	0.0241	2.52
Acetonitrile	1.10	1.04	0.99	0.98	1.00	1.022	0.0492	4.81
Trichlorofluoromethane	1.09	0.95	1.00	0.97	1.04	1.010	0.0561	5.56
Acetone	1.00	0.96	0.96	0.97	1.00	0.978	0.0205	2.10
Isopropyl Alcohol	0.99	0.94	0.93	0.94	1.00	0.960	0.0324	3.38
Acrolein	0.90	0.96	0.96	0.96	0.90	0.936	0.0329	3.51
1,1-Dichloroethene	0.99	1.00	0.99	0.96	0.97	0.982	0.0164	1.67
Acrylonitrile	0.93	0.95	0.88	0.92	0.95	0.926	0.0288	3.11
Trichlorotrifluoroetha...	1.02	1.02	1.01	0.95	0.98	0.996	0.0305	3.06
Allyl Chloride	0.92	0.96	0.96	0.94	0.96	0.948	0.0179	1.89
Methylene Chloride	1.02	1.01	1.01	0.96	0.99	0.998	0.0239	2.39
tert-Butanol	1.01	1.02	0.97	1.02	0.98	1.000	0.0235	2.35
Carbon Disulfide	1.12	0.98	1.00	0.94	0.98	1.004	0.0684	6.81
trans-1,2-Dichloroethene	0.97	0.95	0.98	0.93	0.96	0.958	0.0192	2.01
Methyl tert-Butyl Ethe...	0.98	0.98	0.98	1.00	1.01	0.990	0.0141	1.43
Vinyl Acetate	0.94	0.93	0.91	0.96	0.99	0.946	0.0305	3.22
1,1-Dichloroethane	0.99	0.98	1.00	0.93	0.99	0.978	0.0277	2.84
2-Butanone	1.02	0.97	0.98	0.98	1.00	0.990	0.0200	2.02
Hexane	1.04	0.96	0.93	0.99	1.00	0.984	0.0416	4.23
cis-1,2-Dichloroethene	0.94	0.93	0.95	0.92	0.95	0.938	0.0130	1.39
2-Chloroprene	1.00	1.00	0.96	0.94	0.97	0.974	0.0261	2.68
Ethyl Acetate	1.09	0.99	0.93	1.00	1.00	1.002	0.0572	5.71
Chloroform	1.02	1.00	1.02	0.96	1.01	1.002	0.0249	2.49
Di-isopropyl Ether	0.97	1.01	0.98	0.95	0.94	0.970	0.0274	2.82
Tetrahydrofuran	0.93	0.95	N.D	0.98	0.95	0.953	0.0206	2.16
Ethyl tert-Butyl Ether	0.97	0.97	0.93	1.03	1.00	0.980	0.0374	3.82
1,1,1-Trichloroethane	1.00	0.98	1.02	0.95	0.98	0.986	0.0261	2.64
1,2-Dichloroethane	1.01	1.00	1.01	0.97	1.00	0.998	0.0164	1.65
Benzene	0.98	0.98	0.99	0.94	0.99	0.976	0.0207	2.12
Carbon Tetrachloride	1.03	1.03	0.99	0.96	0.99	1.000	0.0300	3.00
Cyclohexane	1.00	0.96	0.92	1.03	1.04	0.990	0.0500	5.05
tert-Amyl Methyl Ether	0.97	0.92	0.90	0.99	0.99	0.954	0.0416	4.36
2,2,4-Trimethylpentane	0.99	0.99	1.00	0.97	0.98	0.986	0.0114	1.16

Table 2 *Results of making 5 canisters at 1PPB, at 10% RH and only 15 psia (about atmospheric pressure). Each canister was analyzed on the same day, showing the precision of the 4700 in making these low level standards. Total error is summation of error in dilution, canister recovery, preconcentrator recovery, and GCMS reproducibility.*

	10862	13978	13984	10001	10002	Mean	SD	%RSD
Heptane	0.89	0.92	0.92	0.97	0.93	0.926	0.0288	3.11
Trichloroethene	0.98	1.00	0.97	0.96	0.97	0.976	0.0152	1.55
1,2-Dichloropropane	0.97	0.99	0.99	0.93	0.97	0.970	0.0245	2.53
1,4-Dioxane	0.94	0.92	0.89	1.03	0.99	0.954	0.0559	5.86
Bromodichloromethane	1.01	1.01	1.00	0.95	0.97	0.988	0.0268	2.72
Methyl Methacrylate	0.96	0.96	0.91	0.94	1.01	0.956	0.0365	3.81
cis-1,3-Dichloropropene	0.98	0.97	0.95	0.97	0.99	0.972	0.0148	1.53
4-Methyl-2-pentanone	0.94	0.95	0.91	1.01	1.00	0.962	0.0421	4.37
trans-1,3-Dichloropropene	1.01	0.99	N.D	0.97	1.03	1.000	0.0258	2.58
Toluene	1.02	1.02	0.99	1.00	1.02	1.010	0.0141	1.40
1,1,2-Trichloroethane	1.01	1.02	0.99	0.94	0.98	0.988	0.0311	3.15
2-Hexanone	1.05	0.93	0.97	1.13	1.05	1.026	0.0780	7.60
Dibromochloromethane	1.07	1.02	1.03	0.94	0.98	1.008	0.0497	4.93
Tetrachloroethene	1.07	1.03	1.01	0.99	0.98	1.016	0.0358	3.52
1,2-Dibromoethane	1.07	1.02	1.04	0.98	1.01	1.024	0.0336	3.28
Chlorobenzene	1.02	1.06	1.05	0.97	1.01	1.022	0.0356	3.49
1,1,1,2-Tetrachloroethane	1.09	1.09	1.09	1.00	1.01	1.056	0.0467	4.42
Ethylbenzene	1.00	0.98	0.96	0.99	1.01	0.988	0.0192	1.95
m,p-Xylene	1.01	1.01	0.99	0.98	1.01	1.000	0.0141	1.41
Styrene	1.05	1.00	0.94	0.94	1.05	0.996	0.0550	5.53
o-Xylene	1.04	1.05	1.01	1.00	1.03	1.026	0.0207	2.02
Bromoform	1.03	1.12	1.03	0.94	0.98	1.020	0.0675	6.61
1,1,2,2-Tetrachloroethane	1.06	1.06	1.04	0.97	1.00	1.026	0.0397	3.87
Cumene	1.16	1.02	0.96	1.04	1.02	1.040	0.0735	7.07
o-Chlorotoluene	1.15	1.10	1.05	1.00	0.99	1.058	0.0676	6.39
n-Propylbenzene	1.20	1.09	1.01	1.03	1.03	1.072	0.0776	7.24
4-Ethyltoluene	0.98	1.03	1.00	0.96	1.00	0.994	0.0261	2.62
1,3,5-Trimethylbenzene	0.99	1.06	1.00	0.99	1.01	1.010	0.0292	2.89
tert-Butyl Benzene	1.14	1.09	1.03	1.01	1.03	1.060	0.0539	5.08
1,2,4-Trimethylbenzene	1.07	1.10	1.03	1.02	1.03	1.050	0.0339	3.23
1,3-Dichlorobenzene	1.07	1.13	1.05	0.99	0.99	1.046	0.0590	5.64
Benzyl Chloride	1.01	1.07	1.03	1.00	1.00	1.022	0.0295	2.89
1,4-Dichlorobenzene	1.09	1.11	1.01	0.99	1.01	1.042	0.0540	5.19
sec-Butyl Benzene	1.17	1.08	1.03	1.00	1.01	1.058	0.0698	6.60
1,2-Dichlorobenzene	1.02	1.08	1.02	0.97	0.98	1.014	0.0434	4.28
o-Cymene	1.18	1.09	1.02	0.99	0.99	1.054	0.0814	7.73
n-Butyl Benzene	1.16	1.11	1.06	0.99	1.01	1.066	0.0702	6.59
1,2,4-Trichlorobenzene	1.00	1.15	1.06	0.95	1.00	1.032	0.0766	7.42
Naphthalene	1.04	1.18	1.03	0.99	1.00	1.048	0.0766	7.31
Hexachlorobutadiene	1.01	1.07	1.02	0.95	0.98	1.006	0.0451	4.48

Results and Discussion

Producing calibrations that meet the TO15 linearity requirements is one of the most challenging aspects of this method. Doing this while achieving a concentration dynamic range of 100x or more is even more challenging. Errors in the standards preparation itself, in analyte stability in the canister, recoveries through the preconcentrator, and linearity and reproducibility of the GCMS itself all come into play to create more variability in the results. Attempting to extend the calibration out even further to a concentration range of 1000x requires that each of the previously mentioned sources of error be absolutely minimized to prevent error summations that push several compounds outside of the acceptable linearity requirements.

Using the 4700 Diluter, Silonite or Silonite Ultra Canisters, and the Entech 7200 Preconcentrator combined with today's GCMS technology, meeting EPA Method TO15 linearity requirements over a large concentration range is more readily achievable. Table 1 shows the results of a full scan GCMS calibration from 0.04PPBv to 40 PPB, yielding a 1000x total concentration range by using two separately prepared standards at 20PPBv and 0.4PPBv. The very low, mostly single digit relative standard deviations are only possible if both of these standards are made correctly, and certainly only if the 0.4PPBv standard is actually the intended 50x lower than the 20PPBv standard. Generating these low level standards was previously not possible using other commercially available dilution systems, as most of them use mass flow controllers that show a 1-2% error relative to their total flow rate, or 10-20% when operated at 10% of their total flow rate. These kinds of errors are far too large to allow the creation of these low level standards.

Table 2 shows the results in preparing 5 canisters at 1PPB at atmospheric pressure. Typical errors were less than 5%, which again is the summation of errors in standard preparation, canister recovery, preconcentrator recovery precision, and GCMS precision. Even if the 4700 had created perfect dilutions with 0% error, some scatter in the data would be expected, so the Table 2 data merely shows that the error in the 4700's ability to make these low level standards at atmospheric pressure was not significant enough to create a noticeable variation from canister to canister. This is an important conclusion because for the first time, a fully automated standards preparation system is available that is both accurate and very economical in its use of calibration gas. First creating a 20PPB mix at 50 psi absolute, and then using this to create 1PPBv standards at atmospheric pressure, the calculated number of 6L canisters that can be tested using even the smallest 6R cylinders initially at 1800 psi is over 15,000 canisters. Considering that each cylinder is only certified for one year, a laboratory would be able to test this many canisters AND keep their GCMS systems calibrated. With a program that tested all canisters once every 2 years, only half would be tested yearly. Therefore, even the small 6R gas cylinders would meet the requirements of a lab owning 15,000 x 2, or 30,000 6L canisters. No lab currently has this many canisters in their inventory, so using the 4700, no additional calibration standard should be needed for implementing canister inertness testing beyond what is already needed for method calibration.

Conclusion

The Entech 4700 is a new precision dilution system that uses very little calibration standard while generating very accurate PPB and sub-PPB level standards. The 4700 comes complete with all 6 channels installed, allowing complex standards to be blended from multiple cylinders. The redilution function through inlet #6 allows lower level standards to be prepared than are possible using mass flow controller based dilution systems. Although many labs have produced similar manually operated standards preparation systems, their operation would be too time consuming when performing inertness testing on an inventory consisting of hundreds or possibly thousands of canisters. The fully automated 4700 performs dilutions for testing canisters at 1PPB in about 10 minutes, with walk away automation that allows an air chemist to perform 4-6 dilutions per hour with only the need to manually attach the next canister prior to starting the next dilution.

Key Words: TO-15; VOCs; Calibration Gas; Standards Preparation; Static Dilution, Dynamic Dilution; GC/MS; Canisters; Silonite; SUMMA; Whole Air Monitoring; EPA

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