Improved Performance And Dynamic Range For EPA Method TO-15 using the Entech 7200 and Shimadzu QP2010 Ultra GCMS

Application Note:

A-3736-01

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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 Shimadzu 2010 Ultra GCMS system is demonstrated here, creating performance levels well beyond what was previously possible. Every aspect of sample preparation and analysis process has been optimized to improve linearity, recovery, sensitivity, and dynamic range. Linear calibrations that meet TO-15 criteria are now possible over a dynamic range of 100-2000 fold, reducing the number of dilutions necessary, while lowering detection limits to meet today's Vapor Intrusion standards. The improved recovery and linearity also reduces the downtime previously caused by working with systems that were only marginally meeting the method linearity requirements. The following application note will describe the new advancements

available in the 7200/2010 system that have resulted in the dramatic improvement over prior technology.

Preconcentration and GC/MS Analysis

In order to reach low ppb or ppt detection limits, an aliquot of the canister collected air sample must be concentrated before injection into a GCMS. Although Oxygen, Nitrogen, and Argon in air are easily eliminated during the preconcentration process, Carbon Dioxide and Water are a little more difficult to remove without affecting recoveries of target VOCs. To minimize interference from water and carbon dioxide in air, a 3 stage trapping procedure called "Extended Cold Trap Dehydration" is utilized. An empty Silonite-D treated trap cooled to -40°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 is has been super-saturated due to its initial high concentration in the sample. The way to think of this is, the gas phase concentration of water is reduced from 10,000 - 30,000 PPM to just 2-100 PPM via this first stage at -40°C, which is too low a concentration to 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. This approach only works by using the extremely inert Silonite-D coating process that keeps the target compounds from sticking to the walls of the tubing at -40°C. 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 M1 empty 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.

Accu-Sample™ Technology

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

Electronic Volume Control (EVC) -

In the past, canister preconcentrators used mass flow controllers to measure the flow rate, and from that would infer the volume of sample that had passed through the traps. This has several drawbacks, including flow rates and output signals that were unreliable at the beginning of trapping, and the inability to measure volumes accurately when the sample matrix change from air to other matrices, such as CO_2, Methane, or Helium. The 7200's new Electronic Volume Control instead directly measures 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 recoveries, especially at lower sample volumes, which are often needed both to calibrate the instrument and to allow the analysis of higher concentration samples without having to first undergo dilutions. This directly translates to improved linearity and increased laboratory productivity. The EVC's response is also not affected by the matrix, allowing mixtures of Methane, CO_2, or other bulk gases to be analyzed as accurately as ambient air.

Digital Rotary Valve Control -

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

Silonite-D Transfer Lines -

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

Advanced Water Management

The 7200 performs water management differently than most other preconcentrators. Rather than trying to dry purge a multi-bed adsorbent trap, relying solely on a chemical difference between the water and all other compounds to be monitored, the 7200 performs water management by taking advantage of it being the only component in air that is anywhere close to its saturation point. Because of this, 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 simply 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 through the first trap on the way to a cold Tenax trap. This approach places no restrictions on how cold or aggressively the trapping is performed in the second stage, allowing the 7200 to trap polar VOCs and C2 hydrocarbons in the same analysis; a capability that remains unique to the 7200 and its predecessor, the 7100A. Sub-ambient temperature trapping allows the use of much weaker adsorbents, such as Tenax, as these can be made 100 times stronger just by cooling them down to -40°C, yet remain very easy to clean up without having to heat the adsorbent to high enough temperatures to cause thermal decomposition, artifacts, and non-volatile decomposition products which change the characteristics of the adsorbent. As dehydration occurs in the first trap, water is removed via transition directly from the gas phase to the solid phase, eliminating the loss of polar compounds which are soluble in liquid water. All 3 traps in the 7200 are Silonite-D coated as are the internal 1/16" transfer lines, creating the most inert flow path possible to ensure maximum sample recovery.

Reducing Carryover/Improving Recovery

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

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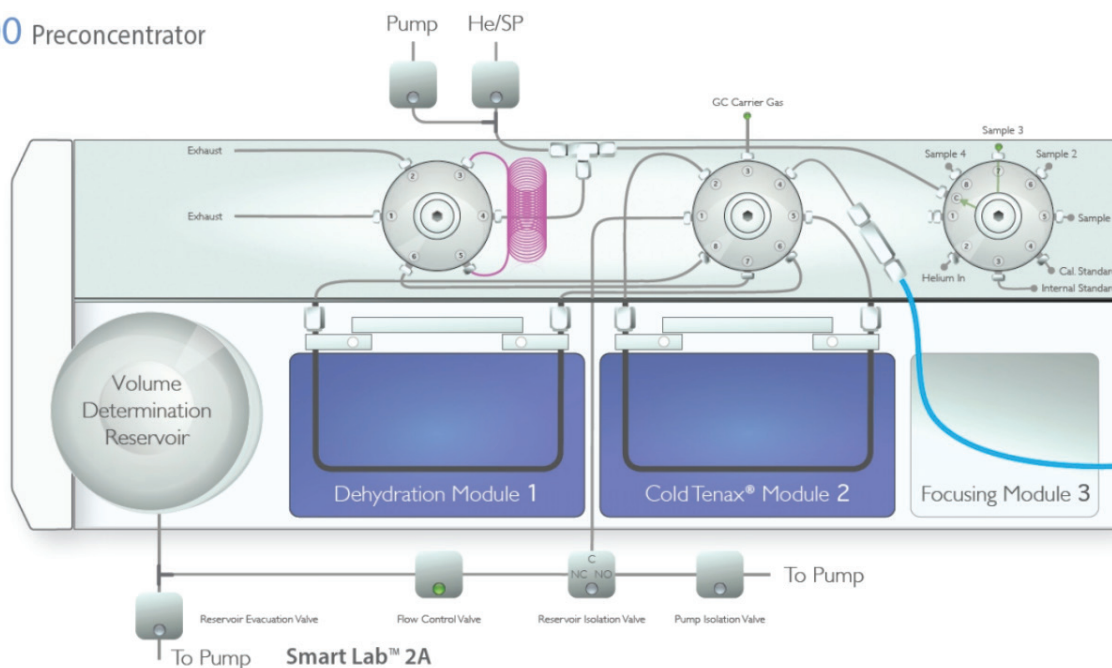
The 7200 is controlled by Entech's SmartLab™ 2A control network operating under Microsoft Win XP or Windows 7 using the latest high-speed USB interface technology.

improves sensitivity, 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. Untilatechnology presents itself that allows for the same level of analytical performance, liquid nitrogen will continue to be the best choice for the production laboratory.

Experimental

Analytical data was generated with the 7200 Preconcentrator interfaced to a Shimadzu QP2010 Ultra GCMS. The GC oven started at 35°C (5 min) ramped at 6°C/min to 120°C, then at 10°C/min to a final temperature of 220°C (5 min). The MS acquisition was from 28 to 280 amu to include Formaldehyde in the analysis, otherwise a starting mass of 30 amu would be recommended for the first 8 minutes to maximize the response of some of the lighter polar compounds. Calibration standards were obtained from both Linde Gas and Scott Gases. Three cylinders at 1 PPMv were blended together using an Entech Instruments Model 4600A Dynamic Dilution system to 10 PPBv for the calibration curve and 2 PPBv for the Method Detection Limit Study. Calibration was performed, referencing 250 mL as the nominal sample volume to be trapped. The curve was obtained by varying the volume of the 10 ppbv standard from 10 to 1000 mL, resulting in a 100 fold calibration from 0.4 to 40 PPBv. Even greater concentrations ranges are being realized using the Model 4700 Precision Diluter that can redilute canister standards to even lower concentrations. Seven 100cc replicates of the 2 PPBv standard (0.8 PPBv equivalent analysis) were used to create the MDL values. The five point calibration and MDLs are shown in Table 2.

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

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

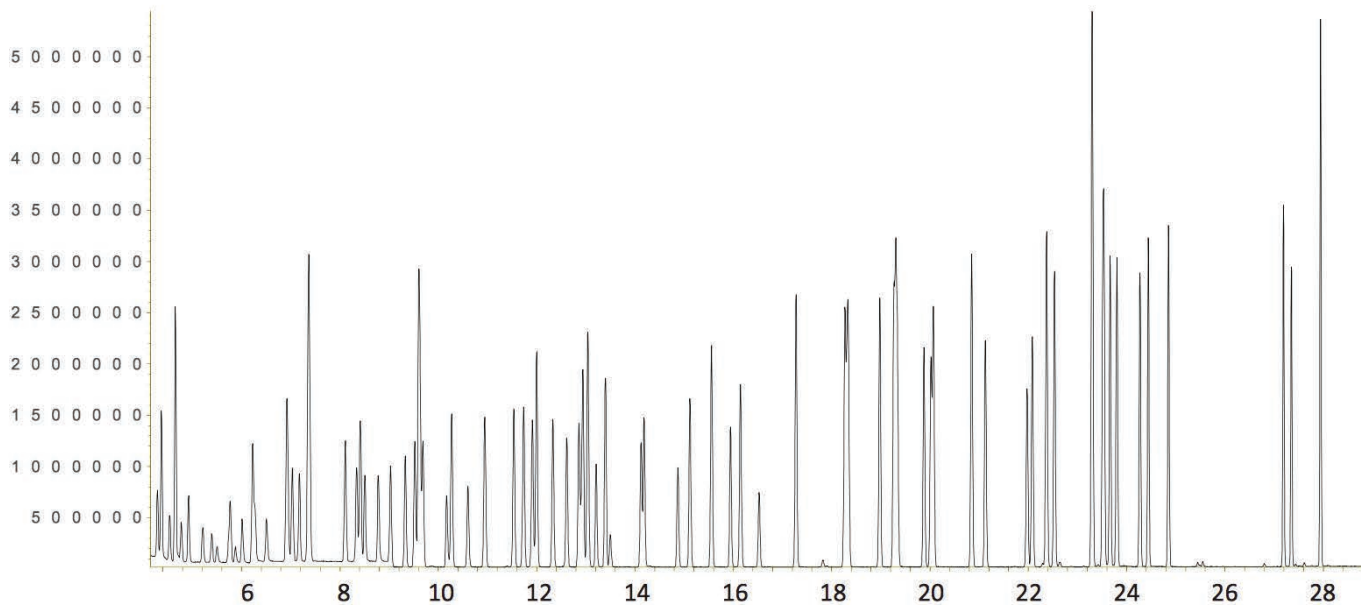**Table 1** - 7200 Trapping Conditions Using Extended Cold Trap Dehydration.
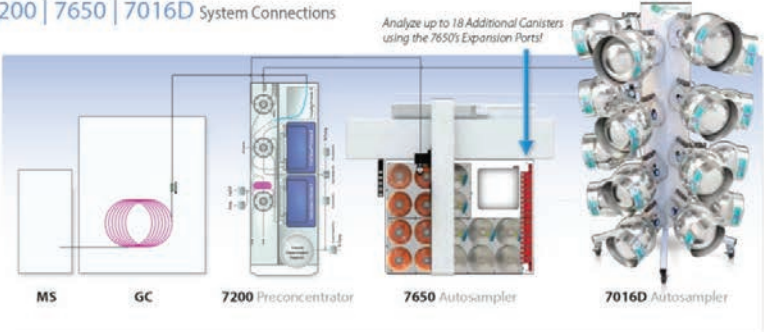
Figure 2 - 250cc 10 ppbv 82 Component TO15 Standard

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

7200 with 7650 Robotic Autosampler virtually eliminates cross sample contamination

Analyte	%RSD	MDLs	Analyte	%RSD	MDLs
Formaldehyde	15.02	1.97	Tert-Amyl Methyl Ether	4.47	0.006
Propene	5.34	0.017	2,2,4-Trimethylpentane	5.02	0.008
Dichlorodifluoromethane	16.44	0.007	Heptane	3.64	0.016
Chloromethane	9.92	0.010	Trichloroethylene	4.54	0.016
Dichlorotetrafluoroethane	10.51	0.011	1,2-Dichloropropane	3.79	0.017
Acetaldehyde	11.17	0.079	1,4-Dioxane	3.91	0.074
Vinyl Chloride	6.97	0.010	Methyl Methacrylate	4.45	0.014
1,3-Butadiene	7.18	0.011	Bromodichloromethane	5.64	0.010
Bromomethane	8.92	0.008	cis-1,3-Dichloropropene	4.71	0.012
Chloroethane	6.75	0.013	4-Methyl-2-Pentanone	6.09	0.013
Ethanol	10.25	0.050	trans-1,3-Dichloropropene	5.10	0.014
Bromoethene	6.84	0.008	Toluene	5.23	0.010
Trichlorofluoromethane	7.70	0.006	1,1,2-Trichloroethane	4.39	0.012
Acrolein	4.79	0.012	2-Hexanone	6.85	0.062
Acetonitrile	4.02	0.012	Dibromochloromethane	6.59	0.007
Acetone	21.73	0.144	Tetrachloroethylene	7.74	0.009
Propanal	5.67	0.068	1,2-Dibromoethane	5.52	0.010
1,1-Dichloroethene	3.91	0.020	Chlorobenzene	4.78	0.008
Acrylonitrile	3.56	0.053	1,1,1,2-Tetrachloroethane	5.41	0.011
Trichlorotrifluoroethane	7.16	0.066	Ethylbenzene	5.84	0.047
tert-Butanol	9.31	0.064	m-Xylene	7.06	0.112
Allyl Chloride	4.24	0.023	p-Xylene	6.66	0.086
Methylene Chloride	5.10	0.012	Styrene	7.53	0.009
Carbon Disulfide	4.40	0.017	o-Xylene	7.75	0.075
trans-1,2-Dichloroethene	3.78	0.012	Bromoform	9.38	0.014
Methyl tert-Butyl Ether	5.63	0.015	1,1,2,2-Tetrachloroethane	6.67	0.013
Vinyl Acetate	4.59	0.008	Cumene	8.50	0.009
2-Chloroprene	3.54	0.012	n-Propylbenzene	9.17	0.011
2-Butanone (MEK)	6.69	0.028	o-Chlorotoluene	9.18	0.006
1,1-Dichloroethane	5.11	0.011	4-Ethyltoluene	10.39	0.011
Hexane	4.35	0.008	1,3,5-Trimethylbenzene	11.41	0.008
Di-isopropyl Ether	3.70	0.013	tert-Butyl Benzene	8.46	0.011
cis-1,2-Dichloroethene	2.83	0.010	1,2,4-Trimethylbenzene	9.75	0.008
Ethyl Acetate	3.94	0.007	1,3-Dichlorobenzene	15.44	0.007
Ethyl tert-Butyl Ether	4.53	0.013	sec-Butyl Benzene	16.05	0.012
Chloroform	4.84	0.012	Benzyl Chloride	10.00	0.007
Tetrahydrofuran	3.86	0.014	1,4-Dichlorobenzene	10.90	0.009
1,1,1-Trichloroethane	5.19	0.009	o-Cymene	10.75	0.010
1,2-Dichloroethane	4.96	0.015	1,2-Dichlorobenzene	10.31	0.010
Benzene	3.16	0.012	n-Butyl Benzene	10.12	0.010
Carbon Tetrachloride	6.26	0.012	1,2,4-Trichlorobenzene	11.40	0.008
Cyclohexane	3.41	0.012	Naphthalene	10.71	0.014
			Hexachlorobutdiene	18.15	0.009

Table 2 % Relative Standard Deviations and Method Detection Limits (PPBv)

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. Again, the 7200 avoids the need for dry purging as explained earlier by using a separate cold trap for water removal. The light end peaks should be as narrow as the mid-range and heavy ends on the column, with no tailing, otherwise a problem occurred during the final focusing. Checking for Freon 12 at about 0.4 PPB in every analysis (Global Background) will confirm that the light ends were trapped properly. The relative peak heights of the internal standards and surrogate(s) should be consistent from injection to injection. Finally, the CO_2 peak at the very start of the chromatogram should not be too large, otherwise chromatography and detection of the lighter compounds can be affected. The 7200 optimizes recoveries, water removal, and injection rates to maximize analytical performance, with reports that detail the setpoints and actual readings recorded during each analysis.

The calibration results and Method Detection Limits (MDLs) are given in Table 2. The Relative Standard Deviations in general are well below the ± 30% RSDs required by EPA TO-15. This data was achieved from a single calibration standard canister, using 10-1000 cc, showing the improvement in low volume measurements over prior technology. Taking a close look at the results reveals that there is very little "scatter" in the data, meaning that the system is probably not being biased by chemical related interactions or losses. All compounds within a given grouping have nearly the same %RSDs. There are several factors that contribute to errors, but the use of cold trapping to avoid reactions that occur on strong multi-bed traps and the use of ultra inert Silonite-D tubing eliminate many of the compound dependent errors, leaving only a few other factors to affect linearity and precision . The over 20 years of research that has led to the development of the 7200 has addressed most of these issues, so that it is not unusual to achieve single digit %RSDs for most compounds. Improving overall system performance makes difficult compounds like Methyl Naphthalene more routine on the 7200 than on other systems.

The MDLs likewise indicate how consistent the 7 replicate injections were. Typically to get very low MDLs, it is better to use lower concentration standards. In this case, replicates at 0.8 PPBv were used (100cc of a 2 PPBv standard), but MDLs were still down in the 10-20 part-per-trillion range, based on the consistency of each injection. This is the combined result of the extremely reproducible Shimadzu 2010 Ultra, and the implementation of Entech's Accu-Sample Technology which improves the exactness of volumes sampled and ensures that virtually everything will be recovered quantitatively. Since reported MDLs of 0.02PPBv would require the standard to be no more than 0.2PPBv, or within a factor of 10, a lower concentration standard would need to be made, which is possible using the Entech 4700 Diluter. Finally, Figures 3 and 4 show the Single Ion Chromatograms at 0.2 PPB for Naphthalene and Acrolein, with an S/N ratio of about 50:1 and 20:1 respectively, indicating that the ultimate detection limits for a 250cc injection is approximately 10 to 20 part per trillion, with another 5-10 times lower detection limits expected when using Single Ion Monitoring.

Conclusion

The Entech 7200 combined with the Shimadzu 2010 Ultra GCMS has shown to greatly exceed the requirements of EPA method TO-15. This is important for production laboratories that want to maximize uptime even if system performance varies somewhat 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.
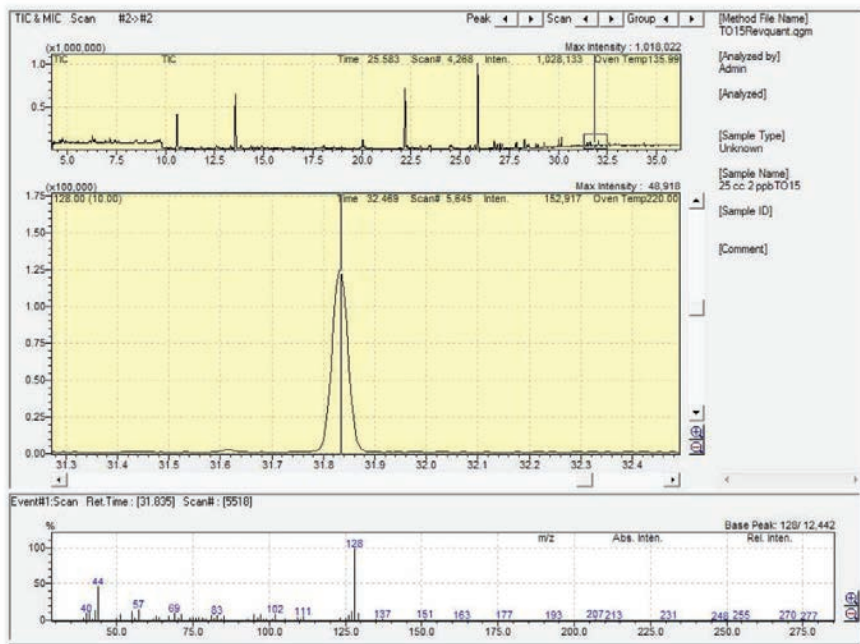
Figure 3 m/z 128 SIC, 0.2 PPB Naphthalene

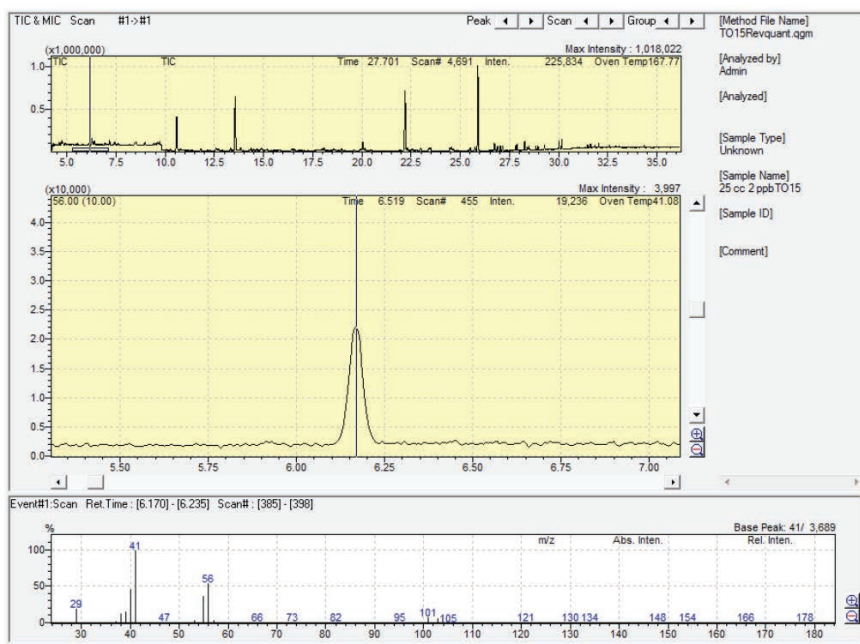**Figure 4** m/z 56 SIC, 0.2 PPB Acrolein

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