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# Enhanced Performance And Dynamic Range For EPA Method TO-15

## Application Note: 103

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### Abstract

As the negative effects of low-level exposure to toxic organics in air become more evident, the push for lower detection limits continues. The result is more sensitive and selective detectors that must be calibrated to continually lower levels. The tradeoff is the loss of the upper dynamic range where most source level and remediation site testing samples are found. For these samples it becomes necessary to dilute the sample prior to analysis. Traditionally, dilution of air samples has been performed in several ways. However, each has limitations in applicability and each has the potential to bias results, positively or negatively.

A technique utilizing the increased sensitivity of detectors without sacrificing the ability to get accurate quantitative results for the more concentrated samples is needed. Since mass spectrometers used in the analysis of TO-15 samples have a rather limited workable dynamic range, expansion of the dynamic range must be performed on the inlet side of the instrumentation. This is accomplished by combining calibration

standards for ambient methods with calibration standards for source level methods on the same instrument, using the same acquisition parameters. Ambient methods require concentration of up to several hundred milliliters (or cc's) of sample. Source level samples require 0.01 cc to 2 cc of sample, often times involving loop injection and quantitative splitting prior to sample introduction to the analytical system. A new way of performing both types of sample introduction using the same analytical equipment is discussed. This approach simplifies the analytical process and increases productivity through automation of the techniques utilized. Data will be presented showing precision and the compatibility of high and low concentration samples on the same inlet system.

### Introduction

Although improvements in instrument design and manufacturing processes have resulted in better overall sensitivity, there remain significant limitations to current TO-15 analyses. The limited "practical" range and number of compound classes that can be analyzed is of foremost concern. Lower detection limits are needed as evidence mounts that low-level exposure may result in significant health problems. Low-level exposure, however, is a result of diffusion from higher-level sources. Due to the limited dynamic range of the analytical equipment, higher-level samples have required dilution in order to run them on the same analytical system. Dilutions can be performed in a number of ways, but each has drawbacks. Dilutions introduce sources of error and they require additional time and resources. Accuracy, precision, and efficiency are essential characteristics for laboratory success. By reducing the number of dilutions these characteristics can be fostered. Accuracy and precision can further be demonstrated through the addition of certain Quality Assurance/Quality Control (QA/QC) measures. Analytical methods for water and soil incorporate QA/QC guidelines such as surrogate spiking to assure data quality. The current TO-15 method lacks similar guidelines. Surrogate spiking allows the analyst to determine the effectiveness of sample preparation. In the case of air testing, surrogate spiking is the only way to verify accurate and precise sample delivery to the analytical system. Due to the wide range of sample concentrations, the ability to verify sample delivery becomes even more important.

Different means of sample introduction are necessary to utilize the increased sensitivity of detectors without sacrificing the ability to get accurate quantitative results for the more concentrated samples. Since many detectors (such as Mass Spectrometers) have a limited workable dynamic range, expansion of the dynamic range must be performed on the inlet side of the instrumentation. This is done by combining ambient level standards, requiring concentration of several hundred milliliters, with source level standards requiring sample loops and quantitative splitting prior to sample injection. Surrogate recoveries can be used to verify the volume sampled and delivered to the GC. Listed below are typical volumes used for sample concentrations and the methods used to deliver these volumes.

Sample Concentration Measurement Method	Sample Volume
0.05 - 100 ppb (ambient) Mass Flow	50 - 1000cc
1 - 5000 ppb Mass Flow	10 - 100 cc
0.1 - 50 ppm (source) Sample Loop	0.1 - 2cc
0.1 ppm - % (source) Sample Loops	0.001-2cc with splitting

In order to handle high and low concentration samples, the inlet system must be capable of acting as two different types of inlets.

The Entech 7032A-L, a 21-position autosampler configured in the hybrid mode, and connected to the Entech 7100A concentrator is designed to handle both high and low level samples. In the hybrid mode, the front 12 positions utilize the internal sample loop, and the back 9 positions are for direct delivery of the sample to a 7100A Preconcentrator for large volume concentration. Although housed in the same analytical instrument, these inlets have separate flow paths to prevent contamination of low level samples.

## Experimental Section

A 10 ppb TO-15 standard was prepared using the Entech 4600A Dynamic Diluter connected to two 1-ppm gas cylinders (Spectra Gas), and nitrogen from a Dewar of liquid nitrogen. The 4600A has a built-in humidifier that automatically humidifies the standard. The first two points of a 6 point calibration were run on the first (front) position of the 7032A-L equipped with a 5.0 ml sample loop. The remaining 4 points were run by attaching the can to the first position of the back 9 positions for large volume concentrations. A 6-point calibration was run as follows: 0.10 ppb = 1:5 dilution of 5 cc loop; 0.50 ppb = No dilution of 5 cc loop; 4 ppb = 40 ml of 10 ppb STD; 15 ppb = 150 ml of 10 ppb STD; 40 ppb = 400 ml of 10 ppb STD; and 100 ppb = 1000 ml of 105 ppb STD. The loop standards were introduced to module 1, after the internal standard, in the same manner as the larger volumes from the 10 ppb canister.



4600A  
Dynamic Diluter

## Analytical System

GCMS Inlet System: 7100A Preconcentrator and 7032A-L 21 Position Autosampler (Entech Instruments, Inc.)

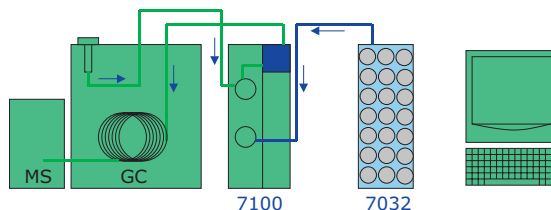
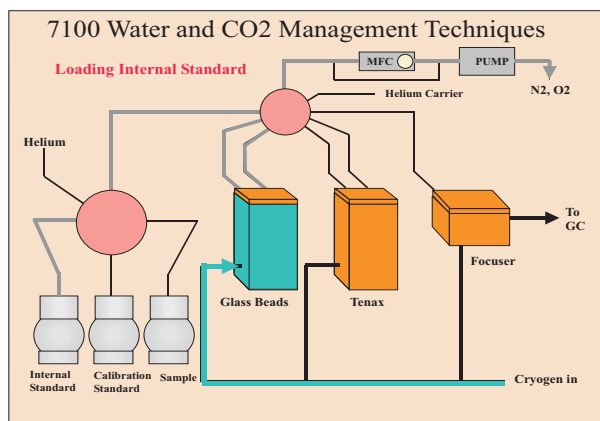
7100A Mode of Operation: Microscale Purge and Trap

GCMS: Agilent 6890/5973N (Palo Alto, CA)  
Column: DB-5MS, 0.32mm ID, 60 m, 1µm  
Temperature Program: 35C (5 min), 6C/min to 140C, 15C/min to 220C. Hold @ 220C for 3 min.

## Preconcentration and GC/MS Analysis

In order to reach low ppb or ppt detection limits, an aliquot of the air sample must be concentrated before injection into the GCMS. Water and Carbon Dioxide are two common compounds that can interfere with GCMS analyses. To minimize interference from water and carbon dioxide in air, a 3 stage trapping procedure called "Micro-scale Purge and Trap" was employed. The first stage involves a glass bead filled trap cooled down to -150°C. As the sample is passed through this trap, the major constituent gases (nitrogen, oxygen, and argon) pass through the trap while water, carbon dioxide, and all the compounds of interest are condensed onto the glass beads. The glass bead trap is then warmed to 10°C before passing a small volume (40 cc) of helium to transfer the carbon dioxide and compounds of interest to a tenax trap which has been cooled to -30°C. Most of the water remains condensed on the glass beads in module 1 and is baked off later. The carbon dioxide passes through the Tenax at -30°C and is pumped away. However, the 40 cc transfer volume is not enough to cause even the lightest TO-15 compounds to break through the tenax trap at this reduced temperature. After the 40 cc transfer from M1 to M2, a third trap is cooled to -170°C. M2 is then heated to +180°C and back-flushed with Helium to transfer the sample from M2 to the pre-column focusing trap (M3). At -170°C the VOCs and any remaining water are condensed onto a 1/32" OD Silonite coated stainless steel transfer line to refocus the sample before introduction to the GC. M3 is then rapidly heated to >50°C. At this temperature the

VOCs volatilize and are swept onto the GC column. Some of the water remains condensed on the walls of the pre-column and are baked off near the end of the GC run so as not to interfere with the sample. Following the injection, the first two traps (M1 and M2) are baked out to prepare them for the next sample. The diagrams below illustrate the 3-trap design and the sample flow paths between instruments.



7100A  
Preconcentrator



7032A  
Autosampler

## Results and Discussion

One of the best ways to improve the efficiency of TO-15 analyses is by increasing the dynamic range of the analytical equipment. Typical inlet systems for ambient air utilize MFCs that can accurately measure 20 cc to 1000 cc. If the capability of doing loop injections is added along with the ability to quantitatively split the loop, the dynamic range of the analytical system can be dramatically increased. This will only work if ambient and source level samples have separate autosampler inlets and flow paths. The quantitative nature of this method was demonstrated by running a 6-point calibration curve using a 10 ppb standard. The first two points were generated by using the loop, and the last four points were generated using large volume concentrations. The effective levels (relative to a standard 100 cc sample injection volume) ranged from 0.10 ppb to 100 ppb, covering a dynamic range of 1000x.

The calibration results are given in Table 1. All Relative Response Factors (RRFs) are within  $\pm 30\%$  as required by EPA TO-15. The agreement between the loop and large volume analyses is very good. There were a couple of compounds that had higher than expected RRFs for the lowest level and were therefore not included in the table. Slight contamination of the internal standard, as seen later in the blank, led to these elevated responses. The largest deviation came from the 100 ppb standard. The drop in relative response factors (RRFs) for this standard is likely due to near saturation of the MS signal at this concentration. This would explain why those compounds with the least amount of fragmentation exhibit the greatest drop in RRFs at this level. Reducing the sensitivity of the MS for the higher-level standards or using secondary/tertiary ion quantitation could mitigate this effect. However, even without these kinds of corrections, the system was able to calibrate over 20 times the typical calibration range for MS work and still stay within acceptable QA/QC parameters.

Following the calibration table is a chromatogram (Figure 1) of the low standard, 0.10 ppb. The signal to noise ratio for these compounds suggests

that the detection limits for most of these compounds is well below the low level standard. The detection limit study shown in Table 2 supports this observation.

Based on this study, most of the detection limits are less than half of the low-level standard. That is, using full scan, detection limits are below 50 ppt. Four of the compounds have detection limits above 100 ppt, which is probably due to slight contamination of the internal standard in the blank.

Next, a high level standard (1 ppm) was run. Even though this standard is above the calibration range generated, it can be run at a low enough volume to fall within the calibrated range and then multiplied by the correct dilution factor to get the actual level.

The expected concentration is arrived at by comparing the volume of the 1 ppm standard run to the nominal value of the calibration standard that defines the calibration curve. The calibration curve was generated with a 10 ppb standard. 100 ml was chosen as the nominal value to define 10 ppb. There are 3 dilutions to consider. Since a 5 ml loop was used to take the standard:

$$100/5 = 20 \text{ fold dilution } -(\text{dilution \#1})$$

Also the standard was diluted 2 fold when it was pressurized with a surrogate standard- (dilution #2). The 5 ml loop was also split 20:1 by the 7032A-L- (dilution #3). Therefore the final dilution is:

$$20 \times 2 \times 20 = 800$$

The expected concentration is:

$$1 \text{ ppm}/800 = 0.00125 \text{ ppm} = 1.25 \text{ ppb}$$

The actual values recorded in Table 3, with few exceptions, are in very good agreement with the expected values. Dichloromethane is 36% greater than expected, but the other data explain this variation. As seen earlier in the calibration curve and detection limit determinations, and will be seen later in the blank, there was some contamination in the internal standard. MIBK and 2-Hexanone also have high recoveries, but not

outside acceptable QA/QC criteria. Background from co-eluting hydrocarbons or other species could have contributed to the elevated response for these compounds. All the other VOCs show excellent agreement.

Immediately after the high level standard was run, a blank was run on the same position of the autosampler. The chromatogram for this blank is shown in Figure 2. There are 5 major peaks in this chromatogram. The first is CO<sub>2</sub> and the remaining 4 are internal standards and/or surrogates. There are also a few small peaks in the blank. All compounds are less than 0.05 ppb except IPA 0.075 ppb, CS<sub>2</sub> 0.08 ppb, and Dichloromethane 0.11 ppb. Subsequent blank analyses lead to the conclusion that these and a few other non-target compounds were contaminants in the Internal Standard.

Although not specifically examined, surrogate spiking was used in these studies and is an important QA/QC issue absent in the current TO-15 method. Field samples contain unknown levels of contaminants. There is nothing of known concentration to reference and thus determine that a known volume was successfully delivered from the canister to the detector. Mass flow controller (MFC) feedback is meaningless if there is a leak between the sample and the MFC. Canister pressure drops might corroborate a measured volume, but not if there is a leak between the MFC and the analyzer. MFC's are not used in loop injections and pressure drops of the canister are insignificant due to the small volumes used. Surrogate spiking is the only sure way to prove that the sample was transferred properly from the canister to the GC. This is why surrogates are an important part of most other EPA methods.

In order to demonstrate sample delivery, we recommend using a Fluorobenzene standard at 20 ppm for source level loop injection samples and 20 ppb for ambient level samples. Using these spike standards, samples can simply be doubled in pressure resulting in a dilution factor of 2x for every sample. For example,

- 14 psia can -> 28 psia
- 12.2 psia can -> 24.4 psia
- 8.5 psia can -> 17.0 psia

If standards are likewise doubled in pressure with a surrogate, there is no need to calculate dilution factors for samples. Such surrogate spikes can be generated easily and economically (a few cents per sample) in the lab. Spiking of the cans is automated by the 7032A-L. The analyst attaches a canister of any size, tells the system what dilution is desired, and the system completes the dilution.

## Summary

A 3-stage canister preconcentrator has been shown that maximizes recovery of most of the 97 compounds in the TO-15 method. Improved recovery was demonstrated by the low % RSDs that were achieved for both polar and non-polar VOCs as well as the low carryover experienced after running high level standards. The dynamic range was extended to a factor of 1000, resulting in increased productivity by substantially reducing the need for dilutions by the lab chemist.

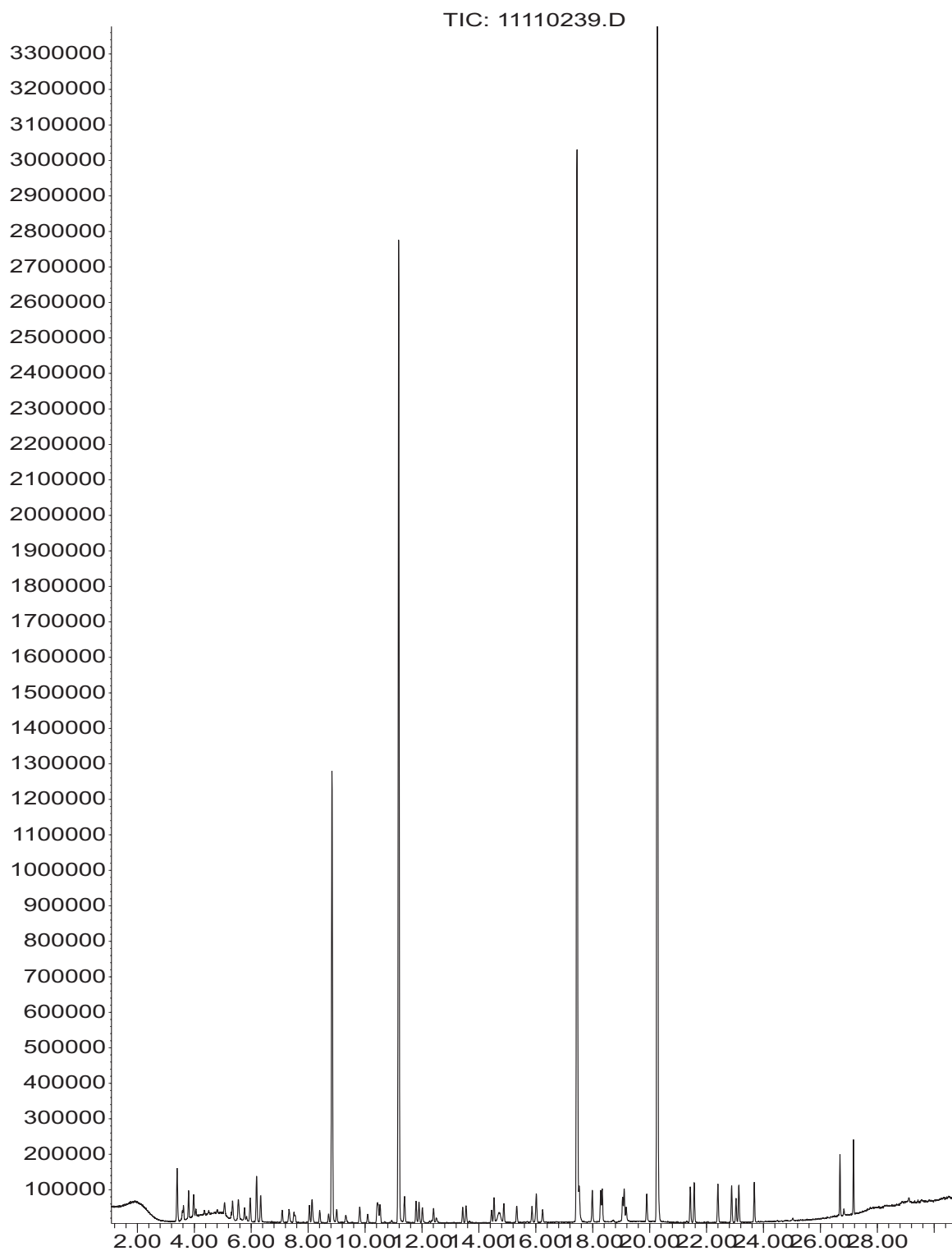
Key Words: TO-15; VOCs; Calibration; Sensitivity; GC/MS; Surrogates

**Table 1 - TO-15 Initial Calibration**

Compound	RRF's						Ave RRF	%RSD
	0.10	0.50	4.0	15	40	100		
Propene	4.43	5.11	5.04	5.30	5.02	4.46	4.89	7.38
Dichlorodifluoroethane	1.43	1.96	2.00	1.99	1.80	1.42	1.77	15.53
Chloromethane	6.86	8.63	8.17	7.71	6.20	4.13	6.95	23.56
Dichlorotetrafluorethane	1.44	1.92	1.92	1.80	1.50	1.01	1.60	22.18
Vinyl Chloride	5.11	6.97	6.74	6.69	6.00	4.87	6.06	14.77
1,3-Butadiene	3.88	5.26	5.20	5.30	4.89	4.09	4.77	13.18
Bromoethane	4.57	5.85	5.59	5.59	5.11	4.19	5.15	12.69
Chloroethane	2.55	3.42	3.28	3.29	3.05	2.66	3.04	11.85
Bromoethene	3.96	5.29	5.17	5.08	4.64	3.82	4.66	13.67
Trichlorofluoromethane	1.30	1.86	1.68	1.60	1.39	1.04	1.48	19.90
Acetone	3.44	2.87	2.90	2.51	2.17	1.70	2.60	23.55
1,1-Dichloroethene	0.92	1.27	1.38	1.40	1.30	1.10	3.19	5.80
Trichlorotrifluoroethane	1.18	1.59	1.69	1.59	1.41	1.04	1.42	18.21
Allyl Chloride	2.06	3.01	3.32	3.40	3.11	2.61	2.92	17.27
Methylene Chloride	**	9.20	7.59	7.33	6.55	5.40	7.21	19.39
Carbon Disulfide	**	3.23	2.30	2.22	2.07	1.79	2.32	23.41
trans-1,2-Dichloroethene	0.80	1.09	1.17	1.18	1.09	0.87	1.03	15.47
Methyl tert-Butyl Ether	1.48	2.18	2.22	2.18	2.06	1.73	1.98	15.30
Vinyl Acetate	1.01	1.54	1.85	1.86	1.65	1.23	1.52	22.47
1,1-Dichloroethane	1.12	1.55	1.60	1.59	1.44	1.18	1.41	15.04
2-Butanone	0.89	1.31	1.22	1.18	1.07	0.86	1.09	16.78
Hexane	0.80	1.61	1.76	1.39	1.24	1.04	1.31	27.31
cis-1,2-Dichloroethene	0.80	1.05	1.15	1.17	1.11	0.97	1.04	13.34
Ethyl Acetate	1.10	1.68	1.68	1.70	1.64	1.43	1.54	15.40
Chloroform	1.22	1.73	1.81	1.79	1.67	1.40	1.60	14.93
Tetrahydrofuran	2.37	3.54	3.63	3.74	3.63	3.39	3.38	15.07
1,1,1-Trichloroethane	1.28	1.77	1.90	1.90	1.77	1.44	1.68	15.33
1,2-Dichloroethane	0.84	1.21	1.28	1.28	1.22	1.06	1.15	14.91
Benzene	1.82	2.44	2.58	2.57	2.34	1.85	2.27	15.27
Carbon Tetrachloride	1.20	1.67	1.81	1.82	1.66	1.23	1.57	17.86
Cyclohexane	0.68	0.97	1.10	1.13	1.05	0.93	0.98	16.78
2,2,4-Trimethylpentane	5.71	7.85	8.61	8.60	7.85	6.23	7.48	16.38
Heptane	2.20	1.71	1.73	1.71	1.60	1.37	1.72	15.76
Trichloroethene	1.61	2.24	2.35	2.33	2.19	1.73	2.08	15.49
1,2-Dichloropropane	1.37	1.93	2.03	2.01	1.91	1.62	1.81	14.45
Bromodichloromethane	2.42	3.34	3.75	3.78	3.60	2.88	3.30	16.48
cis-1,3-Dichloropropene	1.86	2.63	3.07	3.16	3.09	2.67	2.75	17.83
4-Methyl-2-pentanone	3.91	4.45	4.06	3.84	3.81	3.04	3.85	11.99
trans-1,3-Dichloropropene	1.56	2.23	2.65	2.78	2.76	2.40	2.40	19.31
Toluene	4.16	5.86	6.49	6.48	6.09	5.03	5.69	16.18
1,1,2-Trichloroethane	1.45	2.02	2.17	2.13	2.01	1.64	1.90	15.27
2-Hexanone	2.12	2.59	2.07	2.14	2.24	2.00	2.19	9.57
Dibromochloromethane	1.87	2.78	3.23	3.37	3.22	2.46	2.82	20.45
Tetrachloroethene	1.91	2.68	2.84	2.73	2.47	1.88	2.42	17.49
1,2-Dibromoethane	2.10	2.96	3.25	3.26	3.08	2.41	2.84	16.86
Chlorobenzene	4.42	5.87	6.07	5.91	5.54	4.54	5.39	13.50
Ethylbenzene	0.68	0.90	1.02	1.00	0.87	0.72	0.87	16.25
m-Xylene	6.34	7.85	8.66	8.07	7.76	6.07	7.46	13.73
p-Xylene	5.69	7.63	8.31	7.87	6.75	6.07	7.05	14.86
Styrene	3.00	4.57	5.97	6.01	5.56	4.65	4.96	23.12
o-Xylene	5.62	8.05	8.70	8.37	7.60	5.81	7.36	18.01
Bromoform	1.92	2.84	3.55	3.56	3.22	2.44	2.92	22.36
1,1,2,2-Tetrachloroethane	4.09	5.87	5.79	5.50	4.93	3.69	4.98	18.36
4-Ethyltoluene	0.55	0.89	1.01	1.00	0.86	0.69	0.83	21.72
1,3,5-Trimethylbenzene	5.85	9.10	9.72	9.35	8.25	6.22	8.08	20.56
1,2,4-Trimethylbenzene	5.75	8.88	9.66	9.44	8.34	6.34	8.07	20.37
1,3-Dichlorobenzene	4.94	6.02	6.00	5.77	5.16	3.91	5.30	15.35
Benzyl Chloride	4.91	7.08	7.64	7.94	7.58	6.19	6.89	16.66
1,4-Dichlorobenzene	5.04	5.94	6.07	5.75	5.13	3.82	5.29	15.79
1,2-Dichlorobenzene	5.02	5.75	5.62	5.37	4.79	3.59	5.02	15.71
1,2,4-Trichlorobenzene	4.05	4.60	4.28	4.13	3.49	2.40	3.83	20.57
Hexachlorobutadiene	3.52	4.19	3.81	3.42	2.70	1.85	3.25	25.98

**Figure 1 - 0.10 ppb TO-15 Std**

Abundance



Time-->

## Table 2 - Detection Limit Study

Compound	Responses (ppbv)							Ave Resp	SD	IDL
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7			
Propene	0.12	0.10	0.08	0.11	0.10	0.09	0.09	0.10	0.01	0.04
Dichlorodifluoroethane	0.11	0.09	0.08	0.10	0.09	0.08	0.07	0.09	0.01	0.04
Chloromethane	0.11	0.12	0.10	0.12	0.08	0.10	0.10	0.10	0.01	0.04
Dichlorotetrafluorethane	0.10	0.09	0.08	0.11	0.10	0.08	0.08	0.09	0.01	0.04
Vinyl Chloride	0.11	0.09	0.08	0.11	0.08	0.08	0.08	0.09	0.01	0.04
1,3-Butadiene	0.10	0.09	0.04	0.10	0.08	0.08	0.08	0.08	0.02	0.06
Bromoethane	0.11	0.08	0.07	0.10	0.07	0.08	0.07	0.08	0.02	0.05
Chloroethane	0.10	0.09	0.07	0.10	0.07	0.08	0.08	0.08	0.01	0.04
Bromoethene	0.09	0.08	0.07	0.08	0.05	0.07	0.07	0.07	0.01	0.04
Trichlorofluoromethane	0.14	0.08	0.07	0.09	0.07	0.07	0.06	0.08	0.03	0.08
Acetone	0.10	0.12	0.10	0.13	0.07	0.10	0.10	0.10	0.02	0.06
1,1-Dichloroethene	0.11	0.09	0.08	0.11	0.10	0.08	0.07	0.09	0.02	0.05
Trichlorotrifluoroethane	0.12	0.09	0.08	0.11	0.08	0.09	0.08	0.09	0.02	0.05
Allyl Chloride	0.20	0.10	0.09	0.12	0.08	0.10	0.09	0.11	0.04	0.12
Methylene Chloride	0.29	0.25	0.24	0.20	0.09	0.20	0.13	0.20	0.07	0.21
Carbon Disulfide	0.11	0.15	0.25	0.27	0.20	0.24	0.24	0.21	0.06	0.18
trans-1,2-Dichloroethene	0.11	0.09	0.08	0.12	0.24	0.09	0.08	0.12	0.06	0.17
Methyl tert-Butyl Ether	0.11	0.11	0.08	0.11	0.08	0.09	0.08	0.09	0.02	0.05
Vinyl Acetate	0.11	0.09	0.08	0.07	0.08	0.09	0.08	0.09	0.01	0.04
1,1-Dichloroethane	0.11	0.09	0.08	0.11	0.08	0.09	0.08	0.09	0.01	0.04
2-Butanone	0.15	0.11	0.09	0.11	0.08	0.10	0.08	0.10	0.02	0.07
Hexane	0.10	0.09	0.07	0.10	0.08	0.08	0.08	0.09	0.01	0.03
cis-1,2-Dichloroethene	0.10	0.09	0.08	0.11	0.08	0.08	0.08	0.09	0.01	0.04
Ethyl Acetate	0.11	0.10	0.08	0.10	0.08	0.08	0.08	0.09	0.01	0.04
Chloroform	0.10	0.09	0.08	0.11	0.08	0.08	0.07	0.09	0.01	0.04
Tetrahydrofuran	0.10	0.12	0.08	0.11	0.08	0.10	0.09	0.10	0.01	0.04
1,1,1-Trichloroethane	0.10	0.09	0.07	0.10	0.07	0.08	0.07	0.08	0.01	0.04
1,2-Dichloroethane	0.12	0.09	0.07	0.10	0.07	0.07	0.07	0.08	0.02	0.06
Benzene	0.11	0.10	0.08	0.12	0.09	0.09	0.09	0.10	0.01	0.04
Carbon Tetrachloride	0.11	0.09	0.08	0.10	0.07	0.08	0.07	0.09	0.02	0.05
Cyclohexane	0.11	0.10	0.09	0.12	0.09	0.09	0.09	0.10	0.01	0.04
2,2,4-Trimethylpentane	0.10	0.09	0.08	0.11	0.08	0.08	0.08	0.09	0.01	0.04
Heptane	0.11	0.09	0.08	0.11	0.07	0.08	0.07	0.09	0.02	0.05
Trichloroethene	0.11	0.09	0.08	0.11	0.08	0.08	0.08	0.09	0.01	0.04
1,2-Dichloropropane	0.10	0.09	0.08	0.11	0.08	0.08	0.08	0.09	0.01	0.04
Bromodichloromethane	0.10	0.08	0.07	0.10	0.07	0.07	0.07	0.08	0.01	0.04
cis-1,3-Dichloropropene	0.08	0.09	0.08	0.11	0.08	0.08	0.08	0.09	0.01	0.03
4-Methyl-2-pentanone	0.10	0.11	0.08	0.08	0.09	0.10	0.09	0.09	0.01	0.03
trans-1,3-Dichloropropene	0.11	0.09	0.08	0.11	0.07	0.08	0.07	0.09	0.02	0.05
Toluene	0.11	0.10	0.08	0.12	0.08	0.09	0.08	0.09	0.02	0.05
1,1,2-Trichloroethane	0.10	0.09	0.08	0.11	0.08	0.09	0.08	0.09	0.01	0.03
2-Hexanone	0.10	0.12	0.10	0.10	0.11	0.12	0.10	0.11	0.01	0.03
Dibromochloromethane	0.12	0.08	0.07	0.10	0.07	0.07	0.07	0.08	0.02	0.06
Tetrachloroethene	0.11	0.10	0.08	0.12	0.08	0.08	0.08	0.09	0.02	0.05
1,2-Dibromoethane	0.11	0.09	0.08	0.11	0.08	0.08	0.08	0.09	0.01	0.04
Chlorobenzene	0.11	0.10	0.08	0.12	0.08	0.09	0.08	0.09	0.02	0.05
Ethylbenzene	0.11	0.09	0.08	0.12	0.08	0.09	0.09	0.09	0.02	0.05
m-Xylene	0.10	0.09	0.08	0.10	0.09	0.08	0.07	0.09	0.01	0.03
p-Xylene	0.11	0.10	0.08	0.11	0.08	0.08	0.08	0.09	0.01	0.04
Styrene	0.11	0.10	0.08	0.11	0.08	0.08	0.08	0.09	0.01	0.04
o-Xylene	0.11	0.09	0.08	0.12	0.08	0.09	0.08	0.09	0.02	0.05
Bromoform	0.10	0.10	0.08	0.10	0.07	0.08	0.07	0.09	0.01	0.04
1,1,2,2-Tetrachloroethane	0.11	0.11	0.09	0.12	0.08	0.09	0.08	0.10	0.02	0.05
4-Ethyltoluene	0.12	0.10	0.08	0.12	0.09	0.09	0.08	0.10	0.02	0.05
1,3,5-Trimethylbenzene	0.12	0.11	0.09	0.12	0.08	0.09	0.08	0.10	0.02	0.05
1,2,4-Trimethylbenzene	0.12	0.11	0.09	0.12	0.09	0.09	0.09	0.10	0.01	0.04
1,3-Dichlorobenzene	0.13	0.10	0.09	0.12	0.09	0.09	0.09	0.10	0.02	0.05
Benzyl Chloride	0.11	0.11	0.09	0.11	0.08	0.08	0.07	0.09	0.02	0.05
1,4-Dichlorobenzene	0.12	0.11	0.08	0.12	0.09	0.09	0.09	0.10	0.02	0.05
1,2-Dichlorobenzene	0.13	0.11	0.09	0.12	0.09	0.10	0.09	0.10	0.02	0.05
1,2,4-Trichlorobenzene	0.17	0.16	0.14	0.15	0.13	0.13	0.11	0.14	0.02	0.06
Hexachlorobutadiene	0.13	0.13	0.10	0.12	0.10	0.10	0.09	0.11	0.02	0.05

### Table 3 - Source Level Standard Recovery Check

20:1 Split of 5 cc loop of 1000 ppb Std (after surrogate pressurization (2x) final dilution is 40:1)			
Compound	Expected Concentra- tion	Actual Concentra- tion	% Deviation
Propene	1.25	1.21	-3.20
Dichlorodifluoroethane	1.25	1.30	4.00
Chloromethane	1.25	1.35	8.00
Dichlorotetrafluorethane	1.25	1.35	8.00
Vinyl Chloride	1.25	1.29	3.20
1,3-Butadiene	1.25	1.20	-4.00
Bromoethane	1.25	1.19	-4.80
Chloroethane	1.25	1.18	-5.60
Bromoethene	1.25	1.16	-7.20
Trichlorofluoromethane	1.25	1.33	6.40
Acetone	1.25	1.38	10.40
1,1-Dichloroethene	1.25	1.26	0.80
Trichlorotrifluoroethane	1.25	1.34	7.20
Allyl Chloride	1.25	1.30	4.00
Methylene Chloride	1.25	1.70	36.00
Carbon Disulfide	1.25	1.26	0.80
trans-1,2-Dichloroethene	1.25	1.26	0.80
Methyl tert-Butyl Ether	1.25	1.29	3.20
Vinyl Acetate	1.25	1.28	2.40
2-Butanone	1.25	1.38	10.40
Hexane	1.25	1.25	0.00
cis-1,2-Dichloroethene	1.25	1.23	-1.60
Ethyl Acetate	1.25	1.25	0.00
Chloroform	1.25	1.28	2.40
Tetrahydrofuran	1.25	1.30	4.00
1,1,1-Trichloroethane	1.25	1.24	-0.80
1,2-Dichloroethane	1.25	1.24	-0.80
Benzene	1.25	1.33	6.40
Carbon Tetrachloride	1.25	1.26	0.80
Cyclohexane	1.25	1.26	0.80
2,2,4-Trimethylpentane	1.25	1.28	2.40
Heptane	1.25	1.10	-12.00
Trichloroethene	1.25	1.26	0.80
1,2-Dichloropropane	1.25	1.26	0.80
Bromodichloromethane	1.25	1.20	-4.00
cis-1,3-Dichloropropene	1.25	1.19	-4.80
4-Methyl-2-pentanone	1.25	1.50	20.00
trans-1,3-Dichloropropene	1.25	1.14	-8.80
Toluene	1.25	1.25	0.00
1,1,2-Trichloroethane	1.25	1.28	2.40
2-Hexanone	1.25	1.50	20.00
Dibromochloromethane	1.25	1.18	-5.60
Tetrachloroethene	1.25	1.28	2.40
1,2-Dibromoethane	1.25	1.24	-0.80
Chlorobenzene	1.25	1.29	3.20
Ethylbenzene	1.25	1.29	3.20
m-Xylene	1.25	1.20	-4.00
p-Xylene	1.25	1.30	4.00
Styrene	1.25	1.24	-0.80
o-Xylene	1.25	1.33	6.40
Bromoform	1.25	1.14	-8.80
1,1,2,2-Tetrachloroethane	1.25	1.36	8.80
4-Ethyltoluene	1.25	1.29	3.20
1,3,5-Trimethylbenzene	1.25	1.33	6.40
1,2,4-Trimethylbenzene	1.25	1.36	8.80
1,3-Dichlorobenzene	1.25	1.35	8.00
Benzyl Chloride	1.25	1.16	-7.20
1,4-Dichlorobenzene	1.25	1.35	8.00
1,2-Dichlorobenzene	1.25	1.39	11.20
1,2,4-Trichlorobenzene	1.25	1.29	3.20
Hexachlorobutadiene	1.25	1.24	-0.80

**Figure 2 - Blank Run Immediately after 1 ppm Standard**

