



TO-14 Application Note

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Abstract

The Entech Model 7100 automated air concentrator and HP 5973 GCMS have been evaluated to show they meet the requirements of EPA Method TO14. Calibration and internal standards were prepared in stainless steel canisters and used to determine system reproducibility and method detection limits. The correlation coefficients showed excellent linearity between the five points for all compounds.

A method detection limit (MDL) study was performed using seven replicate injections and the MDLs were calculated. The values were in the range of 15 to 70 parts per trillion (ppbtv) for most compounds indicating that the VOC's listed in EPA Method TO14 could be analyzed at concentrations present in ambient air.

Introduction

Air pollution is an important global problem, especially in developing countries. A major part of air pollution is due to the presence of volatile organic compounds which are themselves toxic and may contribute to ozone formation.

In order to determine the concentration of volatile organic compounds (VOC's) in ambient air, samples can be collected in passivated stainless steel canisters and analyzed by Gas Chromatography/Mass spectrometry (GC/MS). Due to the low concentrations of VOC's in ambient air (generally sub-PPB), samples must be concentrated prior to analysis in order to detect the VOC's present.

The procedure for sampling and analyzing VOCs in ambient air is described in EPA Method TO14. The air is collected in passivated stainless steel canisters and analyzed by GC/MS. The toxicity of some VOC's has resulted in legislation mandating very low detection limits, in parts per trillion, for these compounds. Until recently, however, these very low detection limits could not be achieved. The presence of moisture and CO₂ in the sample, difficulties in managing large sample volumes, and limitations in GC/MS sensitivity are among the problems associated with reaching sub-PPB detection limits.

The application presented here describes an Entech Model 7100 air concentrator attached to a HP 6890/5973 GC/MS system. The Entech 7100 performs the concentration of VOC's with excellent water and CO₂ management and is capable of accurate measurement of small or large sample volumes with very good precision. It can be equipped with one or two 16 position autosampler(s) for unattended operation.

The SmartLab software controlling the preconcentrator generates an extensive QA/QC report for each sample concentration performed, recording all actual runtime parameters. This QA/QC report can easily be accessed and can be used as a very useful diagnostic tool.

Experimental Parameters

The instrumental parameters are summarized in *Table 1*.

Table 1. Instrumental Parameters

Entech 7100 Concentrator

Module	Trap	Trap Temp (C)	Preheat Temp (C)	Desorb Temp (C)	Bake Temp (C)	Bake Time (Min)
1	Glass Bead	-150	20	20	130	5
2	Tenax	-50	----	180	190	5
3	Cryofocusing	-150	----	50 – 70	50 – 70	2

Additional Parameters:

Module 2 Desorb Time (min): 3.5
 Module 3 Inject Time (min): 2

HP 6890 GC

Oven

Initial Temp: 35 C
 Initial Time: 5 min
 Ramp 1: 5 deg. C per min to 150 C
 Ramp 1 Final Time: 0 min

Ramp 2: 15 deg C per Min to 220 C
Ramp 2 Final Time: 2 min

Column

HP-1 Methyl Siloxane
Length: 50 m, Diameter: 0.32 mm, Film Thickness: 1.0 um
Column Flow rate: 1.5 ml per min (constant flow)

HP 5973 MSD

Tune: BFB autotune
Scan Parameters: 30 to 180 a.m.u., A/D = 2⁴ for the first 6 minutes
33 to 260 a.m.u., A/D = 2³ for the rest of the run

Threshold: 150 counts
Solvent Delay: none
EMV: +200 over tune setting
Quad Temp: 150 deg C
Source Temp: 230 deg C

Tuning and Calibration

The tuning of the mass spectrometer was performed using the automated tune routine of the HP ChemStation software and was tuned to BFB (bromofluorobenzene) specifications.

Full scan data was collected to allow mass fragmentation patterns to be compared to an NIST spectral library for verification of compound identity. The mass spectrometer is initially set to start scanning at 30 amu to allow detecting of light compounds in the sample, such as methanol and hydrogen sulfide. After 6 minutes, the scan range is changed to 33-260 amu to avoid over exposure of the mass spectrometer electron multiplier to residual oxygen (32 amu) in the source.

For the calibration of the mass spectrometer, a certified TO14 gas standard from Matheson Gas Products containing 39 compounds in the mixture was used. The nominal concentration of each component of this mix was 1 ppm. This standard was diluted to 10 ppbv using an Entech Model 4600 Dynamic Diluter. A gas mixture of 4 internal standards (IS) and 3 surrogate compounds with a concentration of 20 ppbv for each compound was prepared and analyzed with all blanks, calibration standards, and samples. A five-point calibration was performed by analyzing 10, 40, 100, 400, and 1000 ml volumes of the 10 ppbv working standard. Small volume pressure compensation was used to correct any offset in volumes introduced due to sample pre-pressurization into the "non-zero" trap volumes, particularly when loading the 10 and 40 ml standard volumes. Using a nominal volume of 400 ml for sample analysis, the above volumes used for calibration correspond to a range of 0.25 to 25 ppbv. *Figure 1* shows the total ion chromatogram obtained when preconcentrating a 400 ml volume of 10 ppbv TO14 standard. *Figure 2* is a chromatogram of a blank run including 100 ml of internal standard and surrogate compounds at 20 ppbv.

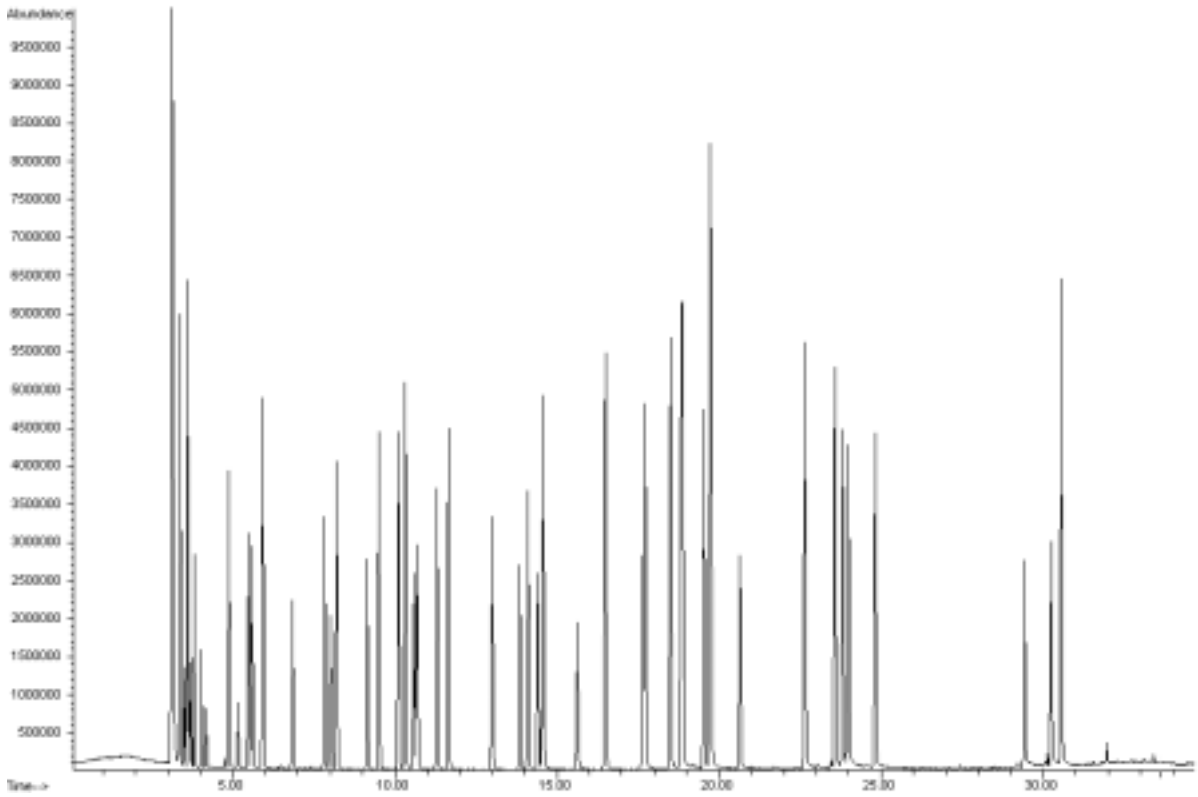


Figure 1
400cc of 10ppbv TO14 Standard

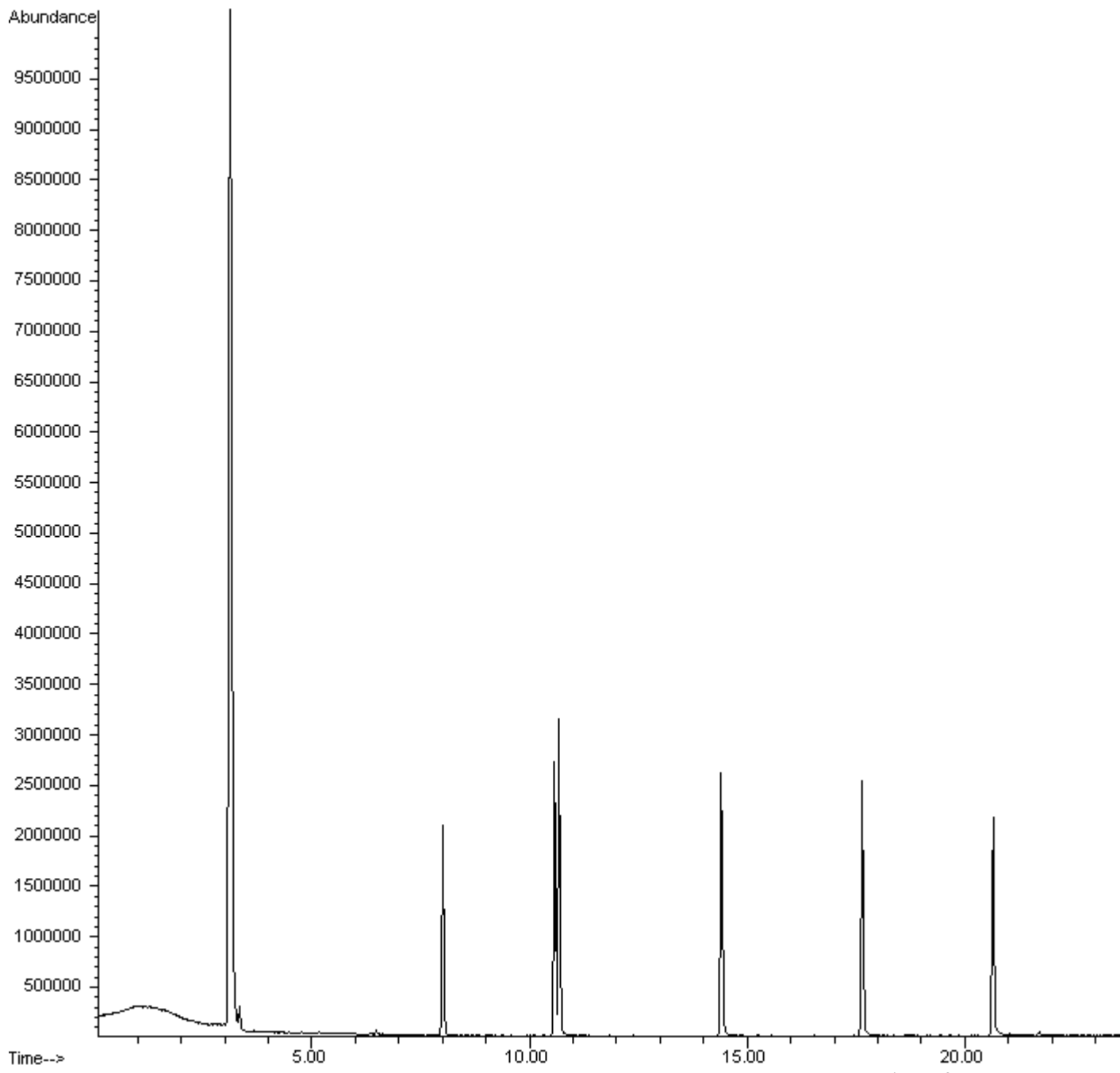


Figure 2
Blank Run

The calibration data for each compound were fitted to a line using the linear least square option in the HP ChemStation software. The correlation coefficients for the equations of all compounds were in the range of 0.999 to 1.000, except for one which was 0.995. These are very good results bearing in mind the wide range of concentration covered. The excellent correlation coefficients obtained demonstrate the ability of the 7100 preconcentrator to trap variable volumes reproducibly and deliver the VOCs quantitatively to the GCMS. Correlation coefficients are listed in *Table 2*. The calibration curves of a few compounds are shown in *Figure 3*.

Table 2. Correlation Coefficients

Compound	Retention Time	Correlation Coefficient
Dichlorodifluoromethane (Freon 12)	3.38	0.995
Chloromethane	3.51	1.000
1,2-Dichloro-1,1,2,2-tetrafluoethane (Freon 114)	3.61	0.999
Vinyl Chloride	3.70	1.000
Bromomethane	4.04	1.000
Chloroethane	4.19	1.000
Trichlorofluoromethane (Freon 11)	4.88	0.999
1,1-Dichloroethene	5.49	1.000
Methylene Chloride	5.60	1.000
Trichlorotrifluoroethane (Freon 113)	5.93	1.000
1,1-Dichloroethane	6.85	1.000
cis-1,2-Dichloroethene	7.84	1.000
Chloroform	8.20	1.000
1,2-Dichloroethane	9.15	1.000
1,1,1-Trichloroethane	9.51	1.000
Benzene	10.12	0.999
Carbon Tetrachloride	10.33	1.000
1,2-Dichloropropane	11.30	1.000
Trichloroethene	11.65	0.999
cis-1,3-Dichloropropene	13.00	1.000
Trans-1,3-Dichloropropene	13.86	1.000
1,1,2-Trichloroethane	14.11	1.000
Toluene	14.57	0.999
1,2-Dibromoethane	15.63	1.000
Tetrachloroethylene	16.50	0.999
Chlorobenzene	17.73	1.000
Ethylbenzene	18.50	0.999
m,p-Xylene	18.87	0.999
Styrene	19.54	1.000
1,1,2,2-Tetrachloroethane	19.72	0.999
o-Xylene	19.74	0.999
1,3,5-Trimethylbenzene	22.65	1.000
1,2,4-Trimethylbenzene	23.57	1.000
1,3-Dichlorobenzene	23.82	1.000
1,2-Dichlorobenzene	24.00	1.000
1,4-Dichlorobenzene	24.82	1.000
1,2,4-Trichlorobenzene	29.43	0.999
Hexachloro-1,3-Butadiene	30.56	0.999

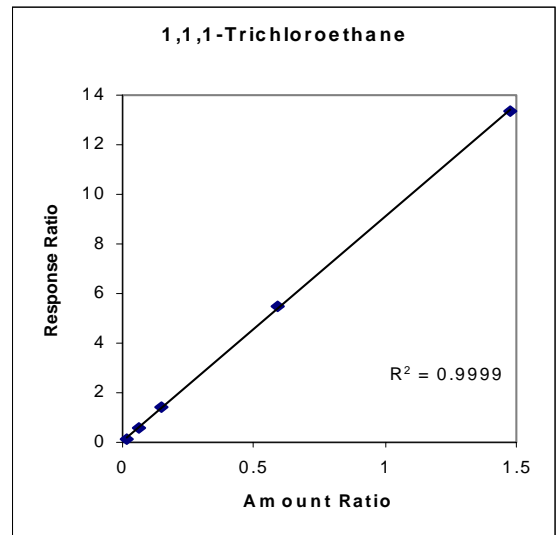
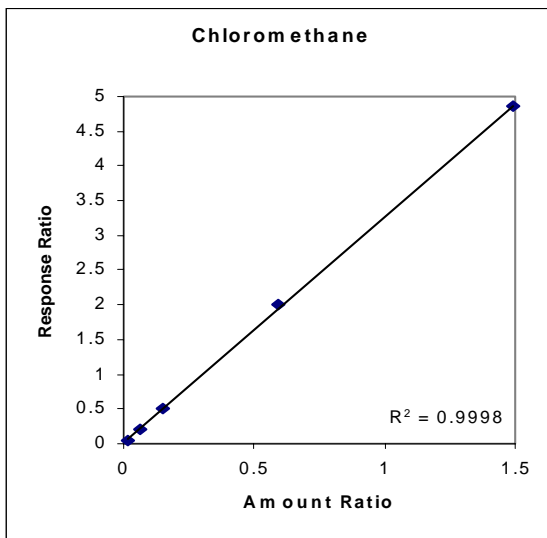
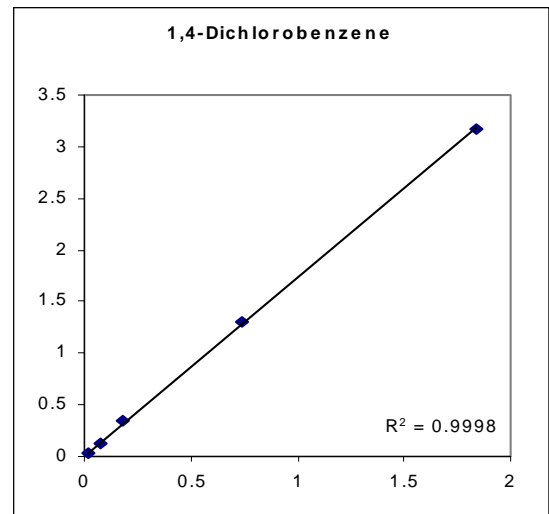
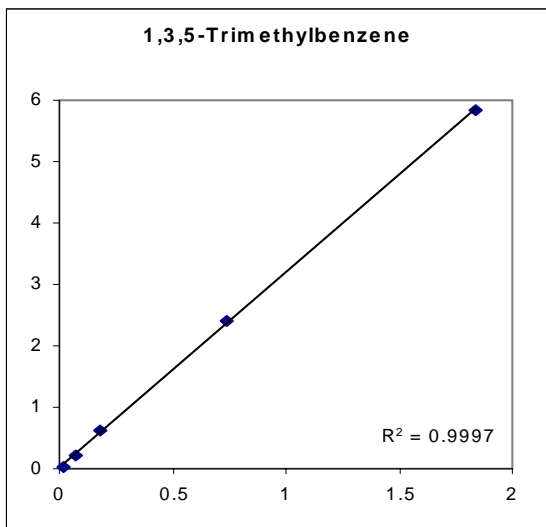


Figure 3



The TO14 working standard in a passivated stainless steel canister showed very good stability and no sign of deterioration during a period of 3 months.

Method Detection Limit Study

The method detection limits (MDL's) were determined by analyzing a low concentration TO14 standard seven times. In general, when doing MDL studies, a concentration of about 5 to 10 times greater than the expected MDL is used.

Seven replicate analyses were made by preconcentrating 100 mls of a 2 ppb standard to provide GCMS injection amounts equivalent to a 0.5 ppbv sample using the standard 400 cc volume. *Table 3* lists the expected concentration values along with the experimental values found for the TO14 compounds. In addition, the standard deviation (SD), MDL, and relative standard deviation (RSD) for each compound are tabulated in *Table 3*.

Tab 3
MDL Study Data

<u>Internal Standards</u>	<u>Spike</u>	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>	<u>Run 4</u>	<u>Run 5</u>	<u>Run 6</u>	<u>Run 7</u>	<u>Average</u>	<u>S.D.</u>	<u>R.S.D.</u>	<u>MDL</u>
1) Bromochloromethane		3667162	3756240	3530479	3524668	3559721	3542955	3509181	3584344	92049	3%	
17) 1,4-Difluorobenzene		14942367	15002683	14523439	14039643	14179460	14310568	13861642	14408543	437500	3%	
30) Chlorobenzene-d5		9838654	9941971	10484164	9330425	9012255	10066377	9302327	9710882	515399	5%	
43) 1,2-Dibromobenzene		3109859	3110723	3340881	2838287	3030643	3237331	2805079	3067543	195791	6%	
<u>Surrogates</u>												
20) Fluorobenzene		20.13	20.30	20.03	20.06	20.05	20.18	20.42	20.17	0.146	1%	
26) Toluene-d8		18.21	18.40	19.98	18.56	18.08	19.26	18.63	18.73	0.669	4%	
37) 4-Bromofluorobenzene		16.97	17.64	18.93	17.34	17.44	18.31	18.15	17.83	0.672	4%	
<u>Target Coumpunds</u>												
2) Dichlorodifluoromethane	0.57	0.64	0.67	0.64	0.65	0.66	0.66	0.66	0.65	0.011	2%	0.036
3) Chloromethane	0.60	0.64	0.65	0.62	0.63	0.65	0.61	0.63	0.63	0.015	2%	0.047
4) 1,2 Dichloro 1,1, 2,2 tetra chloroethane	0.59	0.57	0.60	0.59	0.60	0.60	0.60	0.59	0.59	0.011	2%	0.035
5) VinylChloride	0.60	0.56	0.59	0.59	0.58	0.58	0.59	0.58	0.58	0.011	2%	0.034
6) Bromomethane	0.56	0.45	0.45	0.45	0.45	0.46	0.44	0.44	0.45	0.007	2%	0.022
7) Chloroethane	0.62	0.59	0.60	0.59	0.60	0.61	0.59	0.59	0.60	0.008	1%	0.025
8) Trichlorofluoromethane	0.60	0.60	0.61	0.61	0.60	0.62	0.61	0.59	0.61	0.010	2%	0.031
9) 1,1-Dichloroethene	0.57	0.54	0.56	0.56	0.56	0.56	0.55	0.55	0.55	0.008	1%	0.025
10) MethyleneChloride	0.66	0.63	0.67	0.64	0.65	0.63	0.64	0.64	0.64	0.014	2%	0.043
11) Trichlorotrifluoroethane	0.60	0.60	0.59	0.60	0.60	0.59	0.58	0.59	0.59	0.008	1%	0.024
12) 1,1-Dichloroethane	0.58	0.56	0.57	0.57	0.57	0.57	0.57	0.56	0.57	0.005	1%	0.015
13) cis-1,2-Dichloroethene	0.58	0.53	0.56	0.58	0.56	0.55	0.55	0.54	0.55	0.016	3%	0.050
14) Chloroform	0.63	0.62	0.66	0.65	0.64	0.63	0.66	0.65	0.64	0.015	2%	0.047
15) 1,2-Dichloroethane	0.59	0.53	0.55	0.53	0.52	0.54	0.53	0.53	0.53	0.010	2%	0.030
16) 1,1,1-Trichloroethane	0.59	0.56	0.57	0.58	0.56	0.57	0.55	0.56	0.56	0.010	2%	0.031
18) Benzene	0.60	0.57	0.61	0.58	0.58	0.58	0.58	0.60	0.59	0.014	2%	0.044
19) CarbonTetrachloride	0.59	0.55	0.58	0.56	0.57	0.57	0.55	0.56	0.56	0.011	2%	0.035
21) 1,2-Dichloropropane	0.61	0.59	0.59	0.60	0.59	0.60	0.60	0.59	0.59	0.005	1%	0.017
22) Trichloroethene	0.61	0.67	0.70	0.68	0.68	0.67	0.67	0.68	0.68	0.011	2%	0.034
23) cis-1,3-Dichloropropene	0.52	0.30	0.29	0.30	0.28	0.29	0.30	0.28	0.29	0.009	3%	0.028
24) trans-1,3-Dichloropropene	0.55	0.23	0.23	0.25	0.23	0.21	0.22	0.22	0.23	0.013	6%	0.039
25) 1,1,2-Trichloroethane	0.62	0.56	0.57	0.62	0.55	0.57	0.58	0.56	0.57	0.023	4%	0.072
27) Toluene	0.64	0.56	0.56	0.57	0.56	0.56	0.58	0.54	0.56	0.012	2%	0.038
28) 1,2-Dibromoethane	0.58	0.40	0.41	0.44	0.40	0.40	0.42	0.38	0.41	0.019	5%	0.059
29) Tetrachloroethylene	0.64	0.57	0.60	0.61	0.58	0.59	0.61	0.59	0.59	0.015	3%	0.047
31) Chlorobenzene	0.63	0.60	0.58	0.59	0.59	0.61	0.58	0.57	0.59	0.013	2%	0.042
32) Ethylbenzene	0.65	0.55	0.53	0.55	0.55	0.55	0.55	0.52	0.54	0.013	2%	0.039
33) m,p-xylene	1.24	1.03	0.98	1.04	1.06	1.04	1.05	0.99	1.03	0.030	3%	0.095
34) Styrene	0.63	0.33	0.34	0.37	0.37	0.36	0.37	0.35	0.36	0.016	5%	0.051
35) 1,1,2,2-Tetrachloroethane	0.65	0.56	0.54	0.54	0.60	0.59	0.57	0.56	0.57	0.023	4%	0.072
36) o-Xylene	0.65	0.53	0.50	0.51	0.55	0.56	0.53	0.51	0.53	0.022	4%	0.070
38) 1,3,5-Trimethylbenzene	0.74	0.49	0.48	0.47	0.53	0.54	0.49	0.48	0.50	0.027	5%	0.084
39) 1,2,4-Trimethylbenzene	0.70	0.46	0.42	0.44	0.48	0.45	0.44	0.42	0.44	0.021	5%	0.067
40) 1,3-Dichlorobenzene	0.73	0.53	0.51	0.52	0.53	0.53	0.51	0.50	0.52	0.012	2%	0.038
41) 1,2-Dichlorobenzene	0.71	0.45	0.40	0.45	0.44	0.42	0.41	0.44	0.43	0.020	5%	0.063
42) 1,4-Dichlorobenzene	0.74	0.58	0.55	0.56	0.61	0.60	0.56	0.56	0.57	0.023	4%	0.072
44) 1,2,4-Trichlorobenzene	0.65	0.54	0.52	0.51	0.51	0.56	0.50	0.58	0.53	0.030	6%	0.093
45) Hexachloro-1,3-Butadiene	0.55	0.78	0.76	0.69	0.77	0.78	0.72	0.75	0.75	0.034	4%	0.106

The MDL values found are in the range of 15 to 100 pptv. Since MDL's are based on precision, the calculated MDL's show an excellent reproducibility for Entech 7100/HP 5937 analytical system. These MDL's exceed EPA TO14 requirements and Contract Laboratory Program (CLP) contract required quantitation limits (CRQLs).

Conclusion

This study shows the superb performance of Entech Model 7100 preconcentrator in terms of accuracy and precision for EPA Method TO14 Compounds. The volume measurement accuracy was demonstrated by the very good agreement between the chromatographic peak areas and the volume of TO14 standard from 10 to 1000 mls. The consistency in the GCMS response for sample volumes up to 1000 mls indicates the ability of the 7100 Preconcentrator to remove most of the water used to humidify the TO14 standard without loss of analytes.