Evaluation of Entech Canister System

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Introduction

The development of a process which coats stainless steel with fused silica has led to important advances in chemical sampling and analysis. This material offers the structural strength and impermeability of steel combined with the inertness of fused silica. Evacuated canisters with a capacity of six liters, sometimes called SUMMA canisters, are widely used in EPA applications when sampling for environmental VOC's.[1] Entech Inc., Simi Valley, CA, has combined the fused silica coating with the polished cannister technology in a smaller MiniCan, 390-mL capacity, for use as a personal sampler in industrial hygiene. It is designed to be carried in a holster and fitted with an air sampling orifice. The purpose of this project at the Salt Lake Technical Center has been to evaluate the utility of the Entech canister sampling system for use in occupational safety and health inspections, as well as in the areas such as indoor air quality and hazardous waste site investigations. The evacuated canisters may offer a number of advantages, including elimination of the need for a sampling pump, avoidance of questions concerning sorbent tube collection efficiency and recovery, and the ability to make replicate injections and dilutions. This technique may also lead to improved analytical methods for a variety of reactive and labile compounds of interest at very low levels.

The system can be run in two modes, one employing a loop injector for introduction of analytes at parts per million levels, and another which makes use of a series of traps to concentrate the sample for analysis at parts per billion levels. Samples from both methods are cryofocused prior to introduction onto the GC/MS column. In this study, the following tests have been conducted on both the loop injector and cryofocuser:

- Canisters and traps cleaning. Can the MiniCans and the traps be effectively cleaned to avoid a carryover?
- Limits of detection. At what levels can a compound be reliably detected?
- Storage stability. Can samples be stored without loss or degradation?
- Precision and accuracy. How reliable is the data produced by the Entech system?

Materials and Equipment

The system we evaluated consisted of Entech 3100 Canister Cleaning System, 4600 Dynamic Dilution System, 7032L 21-Position Loop Autosampler, and 7100 Preconcentrator. The analysis was conducted with a Hewlett Packard 6890 GC connected to an HP 5973 mass selective detector. A standard mixture of propane (18 ppm), *n*-hexane (5.1 ppm), toluene (5.1 ppm), tetrachloroethene (5.0 ppm), and *p*-xylene (5.1 ppm) in nitrogen was obtained from Alphagaz (Cambridge, MD). Liquid nitrogen was obtained from Praxair (Salt Lake City, UT). MiniCans and Summa cans were obtained from Entech. Cali-5-Bond air sampling bag, 10-L capacity, was obtained from Calibrated Instruments (Ardsley, NY). Alicat flow meter H12-10CCM was obtained from Alicat Scientific (Tucson, AZ).

Procedures

Analytical procedure.

Samples in MiniCans were pressurized with nitrogen to twice the original pressure before analysis.

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[1]EPA Method TO-14: Determination of Volatile Organic Compounds in Ambient Air Using Summa Polished Canister Sampling and Chromatographic Analysis, EPA/600/4-89/017, June 1988. EPA Method TO-15: The Determination of Volatile Organic Compounds (VOCs) in Air Collected in Summa Canisters and Analyzed by Gas Chromatography/Mass Spectrometry, 1997. Atmospheric Research and Exposure Assessment Laboratory, Office of Research and Development, U.S. Environmental protection Agency, Research Triangle Park, NC.

Evacuated cans used as blanks were pressurized to 30 psia before analysis. Analysis by loop injection was conducted with Entech 7032-L and 7100. The sample volume was 1 mL. The method was stored in “phfocus.m32.” Analysis by pre-concentration was also conducted with Entech 7032-L and 7100. The sample volume was usually 100 mL. The method was stored in “TO14-2.MPT.”

GC/MS conditions.

GC column	J&W DB-1, 60 m × 320 µm × 1.0 µm
flow rate	1.5 mL/min
GC oven	1 min at 35°C, 10°/min to 270°C, hold 0 min, or 5 min at 35°C, 10°/min to 270°C, hold 10 min
mass range	24 to 270

Cleaning the canisters, the loop, and the traps.

MiniCans were cleaned with the use of Entech 3100 by evacuating to two psia and filling with diluent (nitrogen) to 25 psia repeatedly while heating at 80°C (method “cleancan.m30"). The 6-L Summa cans cannot fit under the heating mantle. They were cleaned without heating (method “noheat3.m30"). The cleaned cans were filled with nitrogen to 30 psia and analyzed by loop injection or by pre-concentration. The cleaning cycles were repeated until a flat baseline was obtained.

Entech 7100 bakes out the traps after each analysis by heating the #1 trap at 150°C and #2 trap at 190°C for three minutes. When the traps were grossly contaminated, the bake out routine was initiated with a 10 to 60 min heating time. The cleanliness of the traps was checked by running an analysis without injecting any of the sample, calibration standard, or internal standard.

When the loop was contaminated, it was cleaned by setting the sample transfer time to 20 min and injecting 1 µL of water every minute for the first 10 min. The method is stored in the program “loopclen.m32.”

Evaluating the sampling restrictors.

There are five different sampling restrictors available for the MiniCans: 0-min, 5-min, 15-min, 4-h, and 8-h. The first three are for the short-term sampling and the last two, time-weighted-average sampling. For each of the sampling restrictors, flow rates were measured by the Alicat mass flow meter. Flow rate and pressure gauge readings were recorded at regular intervals.

Standard preparation and calibration curve.

A 100 ppm 1,1,1-trichloroethane standard was prepared in a Cali-5-Bond air sampling bag by filling it with 9.2 L of air and injecting three microliters of the neat compound. The concentration was calculated from the density, temperature, and pressure data.

Parts-per-billion level standards were prepared in 6-L Summa cans with use of the Entech 4600 Dynamic Dilution System. A 5.1 ppm standard mixture of propane, *n*-hexane, toluene, tetrachloroethene, and *p*-xylene was diluted with nitrogen 1:100 and 1:1000. Calibration curves were constructed by injecting various amounts (10 to 200 mL) of the two standards. For the external standard calibration, the area counts were plotted against the injected volume (ppb mL or 10^{-9} mL). For the internal standard (ISTD) calibration, the ISTD-adjusted response was plotted against the injected volume (ppb mL). The volume of an analyte in a sample was obtained as “ppb mL” from the calibration curve. The concentration was calculated by the following formula:

where C_1 = concentration in ppb
n = dilution factor
C_2 = ppb mL obtained from the calibration curve
v = injected volume in mL

Detection limits.

Various volumes of a 5 ppb standard gas mixture were injected to determine the lower limit of detection for each of the four test compounds.

Storage tests.

Storage tests were performed at two concentration levels: 100 ppm and 25 ppb. Ten high-level storage samples were each prepared by connecting a MiniCan equipped with a 0-min restrictor to a Cali-5-Bond bag containing 100 ppm 1,1,1-trichloroethane and left open for 10 minutes. They were analyzed by loop injection over a period of 14 days.

The low-level storage samples were prepared with the use of 4600 Dynamic Dilution System which diluted with nitrogen 1:200 a 5 ppm mixture of *n*-hexane, toluene, tetrachloroethene, *p*-xylene, and propane in nitrogen. The MiniCans were filled to 28-30 psia with the diluted standard mixture. Seven samples were analyzed over a period of two weeks.

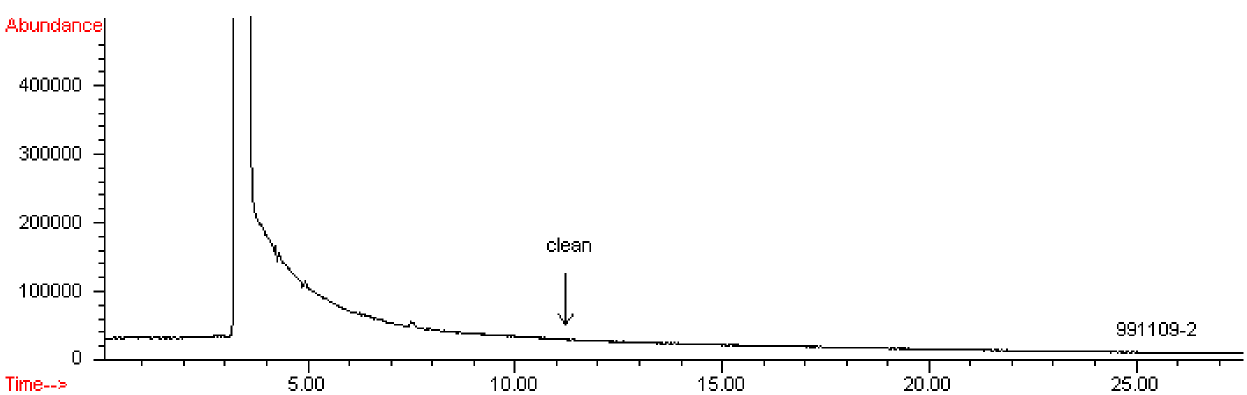
Analysis of indoor air.

MiniCans were first cleaned, then analyzed to make sure they were clean. Samples of indoor air in the mass spec room were taken with a 0-min restrictor for 10 minutes. The samples were analyzed by pre-concentration. The mass spec room air was also analyzed through the port provided for the calibration standard. The port was left open so that instead of the calibration standard, 100 mL of the ambient air was injected.

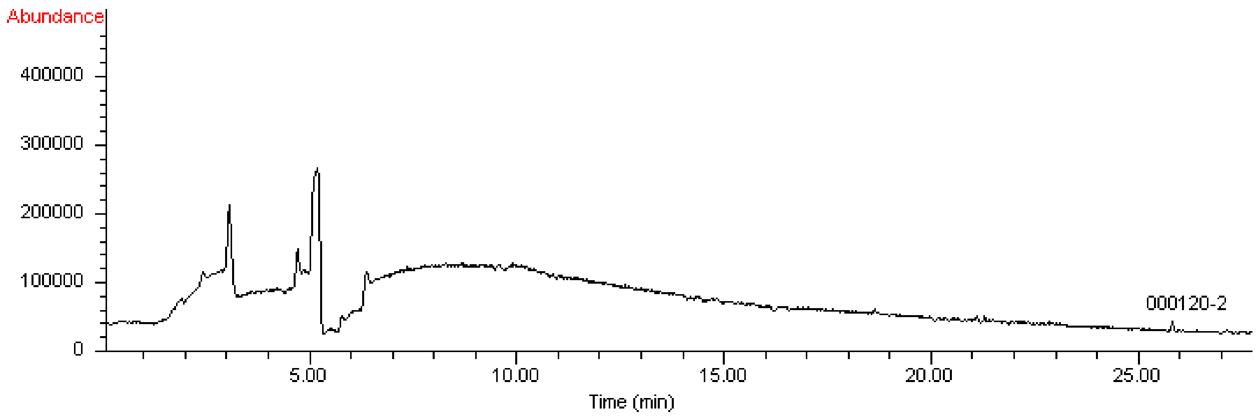
Result and Discussion

Cleaning the canisters and the traps.

1. Cleaning MiniCans for loop injection. Figure 2 shows the chromatogram of a MiniCan that had contained 33 ppm of 1,1,1-trichloroethane, and was then cleaned three cycles. For analysis of parts per million level samples by loop injection, three cycles of cleaning are sufficient.



2. Cleaning Summa cans for analysis by pre-concentration. Figure 3 shows the chromatogram of a cleaned Summa can. The can had previously contained parts per billion levels of organic compounds. It had gone through two sets of three cleaning cycles without heating. We have not exposed the Summa cans to parts-per-million levels of material so we do not know how many cycles of cleaning will be required before they are suitable for ppb level work.



3. Cleaning the MiniCans for analysis by pre-concentration. After the MiniCans have been exposed to parts-per-million-levels of material, it takes many cycles of cleaning before they are suitable for parts-per-billion level work. We found that a MiniCan which had contained 100 ppm 1,1,1-trichloroethane required 100 cycles of cleaning (Figure 4). Later, Entech told us that it is more efficient to clean for three cycles, let the can sit for a few days, then clean for three cycles again, and so on.

4. Cleaning the traps. When we first started operating the instrument, we found the traps to contain gross contamination that took repeated baking to clean. The cleaning had to be repeated many times, because the contaminants would reappear after sitting overnight or over the weekend. The traps should be tested for cleanliness before doing an analysis by pre-concentration.

Performance of sampling restrictors.

Figure 5 plots the change in flow rate with time for 0-min, 5-min, and 15-min restrictors. The upper limit of our flow meter was 10 mL/min so the readings above this value are not dependable. The 0-min restrictor provided six minutes of high level flow and continued to collect for 11 minutes. The 5-min restrictor had 11 minutes of high level flow and continued sampling for 22 minutes. The 15-min restrictors had high level flow for the first 15-20 minutes and continued to sample for 63 minutes.

The 4-h and 8-h samplers are provided with a regulator that maintains a constant flow until the pressure differential between the inside and the outside of the can approaches zero. Figure 6 plots the flow rate and the gauge reading against time. Although we did not monitor the flow rate for the whole durations, both samplers seem to be able to maintain a constant flow for the length of time monitored. The person doing the sampling would be able to see whether sampling is still continuing by looking at the gauge. Simon and Farant[2] claimed that this type of sampler "was able to maintain a constant flow rate during five consecutive periods of eight hours taken during one week."

Standard preparation and calibration curve.

Table 1 lists the total ion area counts for each of the analytes when 10 to 200 mL volumes of a 5 ppb standard gas mixture were injected.

Table 1. Instrument response of 5 ppb standard

mL	hexane	toluene	tetrachloro ethene	xylene	ISTD

[2] Simon, P.; Farant, J-P. Portable Device for Long Term Integrative Personal Sampling of VOCs and Other Gaseous Air Pollutants. *Measurement of Toxic and Related Air Pollutants*, May 7-9, 1996, Research Triangle Park, NC.

10	446313	271093	564254	128740	871636
10	228035	97245	125554	not integrated	908146
20	530587	148087	374156	not integrated	724094
20	657242	179369	375283	53223	819811
50	2250353	929884	1201465	253742	1152692
50	2127132	716058	1151416	248275	1104386
100	5484113	1977977	2718285	925084	1328787
100	5683572	1883689	2703685	719336	1367106
150	7702801	4798901	4277559	1839520	1186510
150	7171058	3985094	4185104	1380536	1063261
200	9535723	4707200	5907466	2126228	993090
200	10253456	4751766	6043210	2091703	1081397

Table 2 lists the area counts when 5 to 200 mL volumes of the 50 ppb standard were injected. The area counts obtained with 5 mL injection deviated from the others significantly, indicating that 10 mL is the minimum injection volume that can reliably be used.

Table 2. Instrument response of 50 ppb standard

mL	hexane	toluene	tetrachloro-ethene	xylene	ISTD
5	135213	77835	244387	48399	1174510
5	299161	191667	426274	121338	1111884
10	4459700	4534540	6104070	4245197	1318405
10	3690372	3667848	5004722	3339190	1112885
20	12708131	14293658	18675442	13303503	789727
20	12661318	13970257	18132314	12841465	1073221
50	31717802	45084647	64610183	41904604	2195409
50	30678491	43439246	63863835	40392582	1716193
50	30201947	43346349	63159344	40179816	1569277
50	29278081	40377803	58893541	37513228	1636387
50	39971450	38043062	54059640	35324003	834744
100	61064562	126363870	244037259	122562739	2049239
100	56598966	111798212	213612977	109534835	2245114
150	161232524	221738723	451565957	267346044	1743758
150	160587701	213603130	438511070	249931430	1948079
200	109569656	300828355	618466534	346332656	2497457
200	211332078	310746877	617009392	322998984	2033987

For each of the four analytes, two sets of calibration curves were constructed: one by plotting the injected volume versus the TIC areas, and the other, by plotting the injected volume versus the internal standard-corrected responses. The former is presented in Figures 7 and 8.

Figures 9 and 10 show the calibration curves using the internal standard-adjusted responses. They are not as good as the external standard calibration curves.

Table 3 compares the r-square values of these calibration curves. In all cases except one, the external standard calibration gave better correlation than the internal standard calibration.

Table 3. Comparison of calibration curves using external and internal standards

	high standards (50 ppb)		low standards (5 ppb)	
	external standard	internal standard	external standard	internal standard
n-hexane	r^2 = 0.8652	r^2 = 0.7334	r^2 = 0.9900	r^2 = 0.9944
toluene	r^2 = 0.9844	r^2 = 0.9497	r^2 = 0.9513	r^2 = 0.9478
tetrachloroethene	r^2 = 0.9737	r^2 = 0.9497	r^2 = 0.9934	r^2 = 0.9653
p-xylene	r^2 = 0.9693	r^2 = 0.9332	r^2 = 0.9593	r^2 = 0.9457

Detection limits.

Chromatograms of 20-mL and 10-mL injections of the 5 ppb standard are shown in Figure 11. Detection limits are estimated to be 0.2 ppb for *n*-hexane, 0.4 ppb for tetrachloroethene, 1 ppb for toluene, and 4 ppb for *p*-xylene. These are based on 100-mL sample volume and 2-fold dilution.

Storage tests.

1. Storage test at parts per million level.

Table 4 summarizes the results of a storage test for 100 ppm 1,1,1-trichloroethane. The results are plotted in Figure 12

Table 4. Storage test for 1,1,1-tricholoroethane at 100 ppm level

time (days)	recovery (%)	
0	102.0	98.0
3	100.4	93.3
5	107.2	96.1
7	96.8	90.0
12	91.4	80.3
13	91.3	80.3
17	98.3	120.7

2. Storage tests at parts per billion levels.

Table 5 summarizes the storage data for *n*-hexane and toluene at 25 ppb level. The data are plotted in Figures 13 and 14.

Table 5. Storage data for *n*-hexane and toluene at 25 ppb level

time (days)	n-hexane recovery (%)				toluene recovery (%)			
0	98.4	102.1	101.6	98.0	99.7	104.3	100.4	95.5

3	98.5	99.5			99.8	101.3		
9	109.6	112.6	98.7	97.8	101.1	102.4	100.9	102.7
14	119.8	115.3	134.3	131.2	95.3	91.3	102.7	100.3

Table 6 summarizes the storage data for tetrachloroethene and *p*-xylene at 25 ppb level. The data are plotted in figures 15 and 16.

Table 6. Storage data for tetrachloroethene and *p*-xylene at 25 ppb level

time (days)	tetrachloroethene recovery (%)				p-xylene recovery (%)			
0	98.9	104.9	100.8	95.4	98.9	105.1	100.4	95.6
3	101.8	105.3			100.4	103.2		
9	81.9	80.0	87.3	94.0	96.3	99.4	102.7	102.4
14	93.4	87.5	89.9	88.1	96.5	93.1	106.1	104.2

Precision and accuracy.

The 95% confidence limits obtained from the storage tests are ±15.9% for *n*-hexane, ±7.0% for toluene, ±11.8% for tetrachloroethene, and ±7.9% for *p*-xylene. There is no sampling error involved with the use of this system.

The accuracy of the Entech system was not evaluated in this study due to the time constraint. The accuracy will be dependent on the accuracy of the certified standard gas mixture, as well as on the accuracy of the mass flow meters that measure the gas volume. The Entech manuals provide procedures for calibrating the mass flow meters.

Analysis of indoor air.

Figure 17 shows the chromatograms of a sample of ambient air taken in the mass spec room (100 mL, diluted 2-fold). The MiniCan before sampling had been shown to be clean (0224-8). Figure 18 shows the chromatogram of a sample of mass spec room air taken through the calibration standard port of Entech 7100 (100 mL, not diluted). Compounds found in these samples are summarized in Table 7 and compared with the results obtained previously from the mass spec room air sampled with a thermal desorption tube. Since the time of these analyses, we have been informed by Entech that the air peak seen in both chromatograms is the result of an air leak.

Table 7. Comparison of mass spec room air sampled on two different days with the Entech System, and a sample taken using a thermal desorption tube.

Compound name	Entech on 02/03/2000	Entech on 02/25/2000	Thermal desorption tube on 04/01/1998, E63192
isobutane	8 ppb	5 ppb	aliphatics, C5 - C12
isobutene	3 ppb		
n-butane	6 ppb	4 ppb	
n-pentane	3 ppb		
2-methylpentane	2 ppb		
3-methylpentane	2 ppb		
n-hexane	2 ppb	1 ppb	
2,3-dimethylpentane	1 ppb		
3-methylhexane	1 ppb		
2,2,3,3,-tetramethylbutane	2 ppb		
n-heptane	1 ppb		
methylcyclohexane	1 ppb		
2,3,4-trimethylpentane	1 ppb		
n-octane	1 ppb		
2,4-dimethylpentane	1 ppb		
dichlorodifluoromethane	10 ppb		
fluorotrichlormethane	1 ppb		
dichloromethane	1 ppb	2 ppb	
Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane)	1 ppb	2 ppb	

tetrachloroethene (perchloroethylene)	1 ppb		found
carbon disulfide	3 ppb	4 ppb	
acetonitrile	4 ppb	2 ppb	
THF		2 ppb	
ethanol	3 ppb	3 ppb	
2-propanol	3 ppb	1 ppb	
n-butanol			found
acetone	9 ppb	9 ppb	
MEK	1 ppb		
MIBK			found
benzene	2 ppb	trace	found
toluene	5 ppb	2 ppb	found
ethylbenzene	1 ppb		found
xylenes	3 ppb		found
styrene			found
methylethylbenzene	1 ppb		C3, C4-alkyl-benzenes found
dichlorobenzene			found
phenol			found
limonene	3 ppb		found, also α-pinene, myrcene
acetophenone	1 ppb		
siloxanes	found	found	found
isobutyl acetate		trace	
butyl butyrate			found
C4 - C10 aldehydes			found

Conclusion and Recommendation

In this study we have shown: (1) that the MiniCans, the traps, and the sample loop can all be effectively cleaned, and that the danger of carryover can be eliminated, (2) that the Entech system can detect down to 1 ppb of volatile organic vapors, which is adequate for indoor air, hazardous waste, and other low-level applications, (3) that samples in the MiniCans are stable for at least two weeks (for the compounds tested), and (4) that the system's precision is satisfactory. One of the advantages of the Entech system is that there is no sampling error such as is seen in active sampling. It is also very convenient to use because there is no sampling pump to calibrate and to carry around.

The Entech system presents instrumentation and technology with which we have very limited experience. Since the conclusion of our experiments, the company has informed us that some of the problems we experienced were caused by instrument malfunctions which we did not recognize. We must still learn a lot in order to obtain optimum performance from the system. Issues to be considered and problems to be resolved include the following: (1) Our understanding of instrument maintenance is inadequate. (2) At times we have not felt that the company was sufficiently responsive to our questions and problems. (3) The Entech operating software is not compatible with Windows NT, which is the software system operating all other instrument PCs at SLTC. (4) For field sampling, two sets of canisters must be maintained. One set would be used for ppm-level samples, and a separate set must be kept for use in trace level applications. (5) At this point, analysis of canister samples is more time consuming than many other types of samples. Canisters must be checked for cleanliness before being sent out for sample collection, and protocols must be established for preparation and analysis of standards.

Some further work, including some application specific work, using the Entech system is recommended for consideration. The applicability of the system to sampling of reactive and labile compounds such as chloroprene, formaldehyde, and mercaptans, should be investigated. Also, a canister sampling orifice for collection of breath samples has been developed by Entech, and should be considered as a potentially useful tool in the assessment of employee exposure to volatile chemicals.

In summary, we consider the Entech system a valuable tool for sampling and analysis of volatile organic compounds. Most of the problems that we encountered could be resolved with proper training and with enough hands-on experience. In certain cases, the system has distinct advantages over current air sampling methods recommended by SLTC such as sorbent tubes with personal sampling pumps or diffusive sampling badges.