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Volatile organic compounds in air

Method number:	PV2120
Control number:	T-PV2120-01-0305-ACT
Procedure:	A sample is collected by drawing air through an orifice into an evacuated fused silica-lined stainless-steel canister. The canisters are analyzed in the laboratory, where they are first pressurized with nitrogen. Aliquots of the air sample are withdrawn, cryofocused, and analyzed by gas chromatography/mass spectrometry to determine the concentrations of compounds collected.
Recommended sampling volume and sampling time:	The canister volume is approximately 400-mL. Short-term sampling orifices allow the canister to be filled in less than one minute. Long-term area samples or personal air samples may be collected over periods up to 8 hours or longer.
Detection limits:	Detection and reliable quantitation limits will vary with the analyte response factor. Detection limits of low ppb levels are possible for most common analytes.
Status of method:	Partially Validated. This method has been subjected to the established evaluation procedures of the SLTC Methods Development Team.

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Note: OSHA no longer uses or supports this method (April 2025)

1 General Discussion

1.1 Background and History

Evacuated stainless steel canisters with electro-polished inner surfaces, called SUMMA canisters, are widely used in EPA applications when sampling for volatile organic compounds (VOC's) in the environment (1). Canisters have been evaluated for use with a range of volatile organics, including aliphatic and aromatic hydrocarbons, and chlorinated compounds (2). This technique has also been applied to a variety of practical applications, such as indoor air quality problems (3), and other situations involving low levels of volatile contaminants, including the docking of the Russian Priroda module with Space Station Mir (4). The evacuated canisters offer a number of advantages, including elimination of the need for a sampling pump, avoidance of questions concerning sorbent tube collection and recovery, and the ability to make replicate injections and dilutions during analysis.

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. Entech, Inc., Simi Valley, CA, has combined the fused silica coating with the polished canister technology in a smaller MiniCan, 400-mL capacity, for use as a personal sampler in industrial hygiene. This new technique is leading to improved analytical methods for a variety of reactive and labile compounds of interest at very low levels (5, 6).

Short-term area samples are collected by attaching a sampling orifice to the inlet of the MiniCan. Sampling begins immediately, and is completed when the pressure inside the canister is equal to the atmospheric pressure on the outside, or when the sampling orifice is detached from the canister. For personal air samples, a MiniCan is mounted in a holster attached to a belt fastened around the waist of the worker. A sampling orifice with regulator is attached to the inlet of the canister, and a length of inert tubing leading from the breathing zone of the worker is connected to the inlet of the orifice. In the laboratory, the canister is pressurized with nitrogen, and the contents are analyzed by gas chromatography/mass spectrometry.

The data presented in this method were produced during an evaluation study conducted at OSHA's Salt Lake Technical Center (7).

1.2 Limit Defining Parameters.

1.2.1 Detection Limits

Standards of n-hexane (5.3 ppb), tetrachloroethylene (5.2 ppb), toluene (5.3 ppb), and p-xylene (5.3 ppb) were analyzed for determination of detection limits. Lower limits of detection are estimated to be: 0.2 ppb for n-hexane, 0.4 ppb for tetrachloroethylene, 1 ppb for toluene, and 4 ppb for p-xylene. (Section 4.1)

1.2.2 Minimum Injection Volume

Using canisters spiked with standards of 50 ppb of the four analytes listed above, injection volumes from 5 mL to 200 mL were analyzed. Results indicate that a 10 mL injection is the smallest volume which provides acceptable precision. (Section 4.2)

1.2.3 Storage Stability

Canisters spiked with each of the four test compounds at 25 ppb were stored at room temperature for up to 14 days. The average of four replicates was as follows: n-hexane 125%; toluene 97.4%; tetrachloroethylene 89.7%; p-xylene 100%. (Section 4.3)

To test recovery at higher levels, a single test was run by spiking one canister with trichloroethane at 100 ppm. The measured value after 5 days was 102%.

The draft NIOSH method for canister sampling of VOC's indicates 30-day sample stability for most compounds (8). Some compounds have been reported stable for up to 4 months (2).

1.2.4 Precision

Five canister replicates were spiked with the four test analytes each at a level of 50 ppb. The coefficients of variation for the four analytes were as follows: n-hexane 13.4%; toluene 6.7%; tetrachloroethylene 7.3%; p-xylene 6.8%. Data were taken from Table 4.2. Statistical analyses may be found in Tables 4.4.1 through 4.4.4.

1.3 Advantages

1.3.1 Problems with collection efficiency and analyte recovery, which may be encountered with sorbents or filters, are avoided. Evacuated canister sampling is a whole-air sampling technique.

1.3.2 When collecting short-term samples, no sampling error is associated with this method.

1.3.3 Sampling pumps are not needed.

2 Sampling Procedure

2.1 Apparatus

2.1.1 Entech Minicans, 400-mL volume (Entech P/N 29-MC400), were used in this study. Sampling canisters may be obtained from a contract laboratory, and returned to the contract lab after samples are collected. Canisters obtained from the contract lab will be certified clean (9).

Figure 2.1.1
Four 400-mL Minicans.

2.1.2 Samples are collected by filling evacuated canisters through a sampling orifice. Orifices are available which provide practically instant grab sampling (Entech P/N 39-QFS). Pressure regulated orifices (Entech P/N CS1200E) offer sampling times as short as 2 minutes, or as long as 8 hours or more. These sapphire orifices are said to provide superior flow stability, compared to needle valve or frit-regulated controllers.

Figure 2.1.2.1
Short-term sampling orifice.

Figure 2.1.2.2
Minican with pressure regulated orifice.

2.1.3 For personal sampling, a holster and belt (Entech P/N 39-35000) can be used to attach the canister to the waist of an employee. An inert inlet line (Entech P/N 39-36010) is used to draw air from the employee's breathing zone.

Figure 2.1.3
Minican with pressure regulated orifice and personal sampling belt and inlet line.

2.1.4 End caps are removed from the canisters prior to attachment of the sampling regulators, and replaced when sampling is complete.

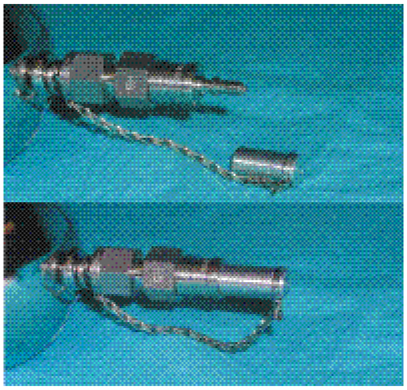

Figure 2.1.4
Minican inlet with end cap removed and in place.

2.2 Reagents

None needed.

2.3 Sampling Technique

2.3.1 Choose the time-release regulator, either short- or long-term, appropriate for the desired application.

2.3.2 Holding the sampling regulator in one hand, slide back the knurled collar with thumb and index finger.

2.3.3 Hold the canister in the other hand, with protective end cap removed, and with tip of canister facing sampling regulator.

2.3.4 Insert the canister tip into the regulator, and release the knurled collar. No gap should be observable between the regulator and the fitting at the end of the canister.

2.3.5 Sampling begins immediately. (Note the time of day.)

2.3.6 Bear in mind that this is a whole air sampling technique. Lack of selectivity is inherent in this method. If for example, the person performing the sampling, or the person being sampled should be wearing perfume or cologne, volatile components of these will also be sampled.

2.3.7 When sampling is complete, reverse above steps to disengage the canister from the regulator. Slide back the knurled collar with thumb and index finger, and separate the canister from the regulator. Release the knurled collar.

2.3.8 Replace the protective end cap onto the canister, and seal each canister with a Form OSHA-21 seal.

2.3.9 Record sampling time. (Note the time of day when sampling is completed.)

2.3.10 No sample blank is necessary if the canisters were assured to be clean at the outset of sampling. A sample collected in a control area may be included if desired.

2.4 Safety Precautions (sampling)

2.4.1 Follow all safety procedures which apply in the work area being sampled.

2.4.2 If personal sampling is being conducted, attach sampling equipment to the employees in such a manner that it will not interfere with work performance or safety.

3 Analytical Procedure

It is possible to conduct sampling using this method even if your laboratory is not equipped with apparatus for cleaning and analysis of canister samples. Contract laboratories will provide loan of cleaned and evacuated canisters followed by GC/MS analysis of your samples (9).

3.1 Apparatus

3.1.1 Entech Canister System consisting of a Model 7032L 21-Position Loop Autosampler and Model 7100 Preconcentrator, connected to a GC/mass spectrometer system. A Hewlett-Packard 5973 GC/mass spectrometer was used in this evaluation.

3.1.2 Entech Model 4600 Dynamic Dilution System.

3.1.3 Entech Model 3100 Canister Cleaning System.

3.1.4 Summa Canisters 6-liter volume, Silonite coated.

3.1.5 A GC column capable of providing adequate separation of the analytes of interest must be chosen. A 30-m x 0.32-mm i.d. (0.25 µm d_f DB-1-MS) capillary column (J&W Scientific, catalog #1230132) was used in this study.

3.2 Reagents

3.2.1 Standard gas mixture according to the compounds to be analyzed.

3.2.2 Liquid nitrogen.

3.2.3 Helium (ulta high purity).

3.3 Canister Cleaning

3.3.1 The Entech Model 3100 is used to clean canisters prior to sampling. Canisters are evacuated to 13 kPa (2 psi), and then filled with clean, humidified nitrogen to 172 kPa (25 psi), while heated to 80 °C.

3.3.2 This process is repeated until no residual contaminants remain. Canisters are pressurized to 207 kPa (30 psi) with nitrogen, and an aliquot is withdrawn for analysis (Section 3.6) to ascertain cleanliness.

3.3.3 Canisters which are to be used to sample relatively high (ppm) concentrations of analytes are usually adequately cleaned after 3 cleaning cycles. If a canister, which has previously been used for sampling of ppm-level contaminants is to be used to sample low (ppb) concentrations of analytes, more rigorous cleaning will be required. Up to 100 cleaning cycles may be necessary. An effective and more efficient approach, however, is to put the contaminated canisters through 3 cleaning cycles, allow the canisters to sit for a couple of days, then repeat cleaning through three cycles, and check for cleanliness. Repeat this clean, store, and clean sequence as many times as necessary.

3.3.4 Canisters should be evacuated to a pressure of 6.7 Pa or less prior to sampling. It is recommended that cleaning and evacuation be conducted as near to the time of use as practical.

3.3.5 Canisters may be checked for leaks by pressurizing with clean nitrogen to 207 kPa, rechecking pressure after 24 hours. A pressure drop greater than 14 kPa indicates a leak.

3.4 Standard Preparation

3.4.1 Using nitrogen as the diluent gas, standards of the desired analytes plus internal standards are prepared in 6-liter Summa canisters using the Entech Model 4600 Dynamic Dilution System.

3.4.2 If electropolished Summa canisters are used, be sure to use humidified nitrogen as diluent gas, especially if polar compounds are being analyzed. When using fused silica-coated canisters, the requirement for humidity is not critical, since contaminant molecules have lower affinity for the silica-coated surface than for bare stainless steel surfaces.

3.5 Sample Preparation

Prior to analysis, the pressure in each sample canister is increased to twice its original value, using zero-grade nitrogen as the diluent gas. After equilibration, this elevated pressure allows measured aliquots of the sample gas to be easily withdrawn for analysis.

3.6 Analysis

3.6.1 For samples expected to contain relatively high levels of contaminants (e.g., ppm levels); the Entech Model 7032L Loop Autosampler is used to withdraw approximately 1-mL aliquots of the sample air, diluted with nitrogen. This aliquot is cryofocused prior to introduction on to the GC/MS column.

3.6.2 For samples expected to contain levels of contaminants less than 1 ppm, the Entech Model 7032L Loop Autosampler, is used to withdraw 10 to 100-mL aliquots of the sample air, diluted with nitrogen. These aliquots are drawn into a sampling loop, then concentrated and cryofocused prior to introduction on to the GC/MS column.

3.6.3 Replicate analyses or subsequent aliquots of a different size may be drawn from a sample canister.

3.6.4 Mass spec conditions

GC Column	30-m x 0.32-mm i.d. (0.25-µm d_f DB-1-MS) capillary column
Initial temperature:	35 °C, hold for 5 minutes
Program rate:	10 °C/minute
Final temperature:	280 °C
zone temperatures	
GC injector:	250 °C
Transfer line:	280 °C
Source:	230 °C
Analyzer:	150 °C
Electron energy:	70 eV
Scan range:	24-250 amu

4 Back-up Data

4.1 Detection Limits

Figure 4.1 shows chromatograms of 20-mL and 10-mL injections of a standard of approximately 5 ppb each of the four test compounds. Based on a 100-mL injected sample volume and a two-fold dilution, the estimated limits of detection are: n-hexane 0.2 ppb; tetrachloroethylene 0.4 ppb; toluene 1 ppb; and p-xylene 4 ppb. Detection limits were calculated based on peak heights which are three times the baseline noise.

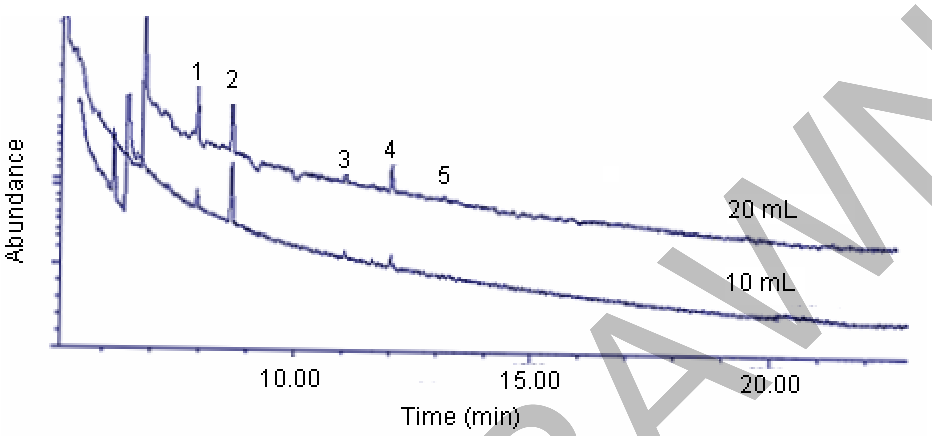

Figure 4.1 Chromatograms of 20 mL and 10 mL volumes of standard 2 (5 ppb). 1 = n-hexane (5.3 ppb), 2 = internal standard (1,1,1-trichloroethane), 3 = toluene (5.3 ppb), 4 = tetrachloroethylene (5.2 ppb), 5 = p-xylene (5.3 ppb)

4.2 Minimum Injection Volume

Table 4.2 shows the results of injections of a standard of approximately 50 ppb of each of the four test compounds, with injection volumes varying from 5 to 200 mL. Due to lack of acceptable reproducibility of the results from injections of 5 mL, it was concluded that 10 mL is the minimum injection volume which produces reliable results.

Table 4.2
Instrument Response of 50-ppb Standard (Area Counts)

mL	n-hexane	toluene	tetrachloroethene	p-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

4.3 Storage Stability

For storage stability studies, canisters were spiked with standards at approximately 25 ppb of each compound and stored at ambient temperatures. Two canisters were spiked with n-hexane and toluene, and two with tetrachloroethylene and p-xylene. Aliquots were analyzed on day 0, and subsequently on days 3, 9, and 14. Table 4.3.1 shows the results, in percentages of theoretical amounts, for n-hexane and toluene. Similar data for tetrachloroethylene and p-xylene are shown in Table 4.3.2. These results are represented graphically for n-hexane in Figure 4.3.1.1, for toluene in Figure 4.3.1.2, for tetrachloroethylene in Figure 4.3.2.1, and for p-xylene in Figure 4.3.2.2.

Table 4.3.1
Storage data for n-Hexane and Toluene at 25 ppb

time (days)	% recovered n-hexane				% recovered toluene			
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 4.3.2
Storage data for tetrachloroethylene and p-xylene at 25 ppb

time (days)	% recovered tetrachloroethylene				% recovered p-xylene			
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

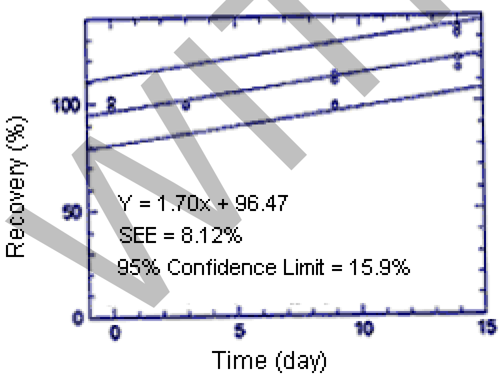

Figure 4.3.1.1
Storage test for 25 ppb of n-hexane

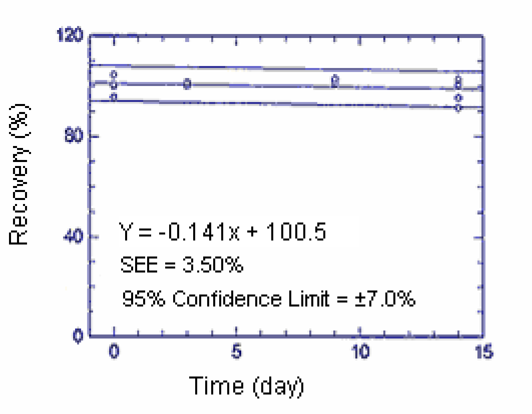

Figure 4.3.1.2
Storage test for 25 ppb of toluene

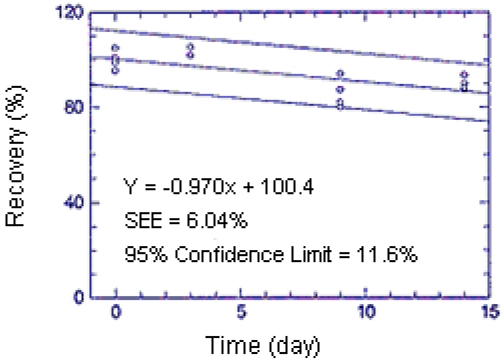

Figure 4.3.2.1
Storage test for 25 ppb of tetrachloroethane

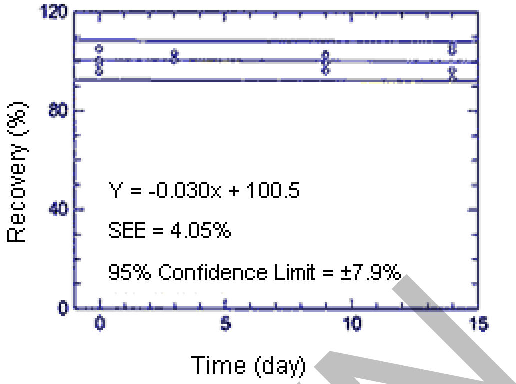

Figure 4.3.2.2
Storage test for 25 ppb of p-xylene

A single canister was spiked with 100-ppm 1,1,1-trichloroethane. This was analyzed immediately, and after storage up to 13 days. Results are tabulated in Table 4.3.3, and shown graphically in Figure 4.3.3.

Table 4.3.3
Storage test for 100 ppm
1,1,1-Trichloroethane

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

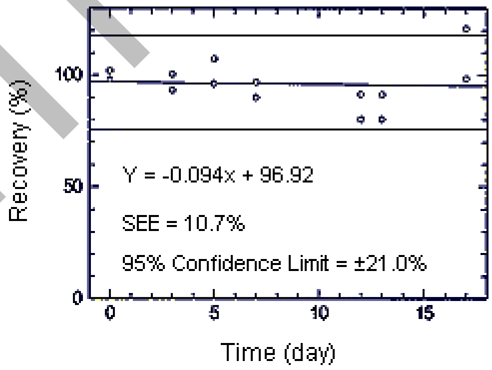

Figure 4.3.3
Storage test for 100 ppm of 1,1,1-trichloroethane.

4.4 Precision

The data in Section 4.4 were extracted from Table 4.2, and show the results of five replicate analyses of a canister spiked with 50 ppb of each of the 4 test compounds. Table 4.4.1 shows results for n-hexane along with statistical analysis. Table 4.4.2 shows similar results for toluene, Table 4.4.3 for tetrachloroethylene, and Table 4.4.4 for p-xylene.

Table 4.4.1
Precision data for n-hexane
50-mL injection, 50 ppb

area counts x 10^7	statistics
3.1718	
3.0678	mean = 3.2370
3.0202	SD = 0.4339
2.9278	CV = 13.40%
3.9971	

Table 4.4.2
Precision data for toluene
50-mL injection, 50 ppb

area counts x 10^7	statistics
4.5085	
4.3439	mean = 4.2058
4.3346	SD = 0.2814
4.0378	CV = 6.69%
3.8043	

Table 4.4.3
Precision data for tetrachloroethylene
50-mL injection, 50 ppb

area counts x 10^7	statistics
6.4610	
6.3864	mean = 6.0917
6.3159	SD = 0.4429
5.8894	CV = 7.27%
5.4060	

Table 4.4.4
Precision data for xylene
50-mL injection, 50 ppb

area counts x 10^7	statistics
4.1905	
4.0393	mean = 3.9603
4.0180	SD = 0.2690
3.7513	CV = 6.79%
3.5324	

4.5 Canister cleaning.

4.5.1 Figure 4.5.1 shows a chromatogram after 3 cleaning cycles of a canister which had contained 33 ppm 1,1,1-trichloroethane. A 1 mL aliquot was sampled by loop injection without pre-concentration. The canister is adequately clean for sampling and analysis at the ppm level.

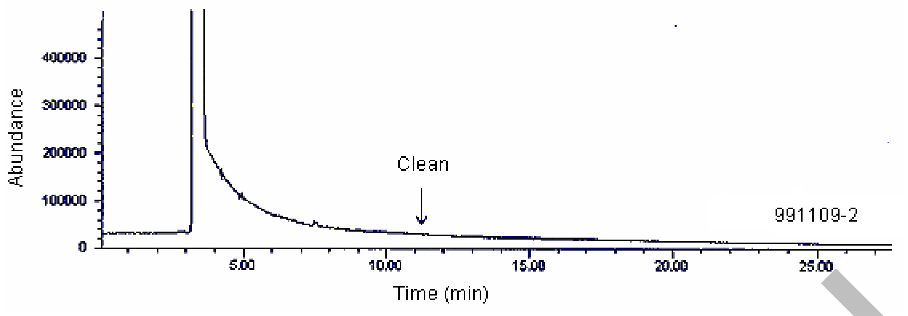

Figure 4.5.1 Total ion chromatogram of a MiniCan that had contained 33 ppm of 1, 1,1-trichloroethane and then was cleaned 3 cycles. Analysis by loop injection. Arrow shows the retention time of 1,1,1-trichloroethane.

4.5.2 Figure 4.5.2 shows a chromatogram after 100 cleaning cycles of a canister which had contained 100 ppm of trichloroethane. A 100 mL aliquot was sampled for pre-concentration prior to injection. The canister is adequately clean for sampling and analysis at the ppb level. It is recommended that highly contaminated canisters be cleaned for 3 cycles, allowed to sit for several days, then cleaned for 3 more cycles and tested for cleanliness. Repeat this sequence until acceptable cleanliness is achieved.

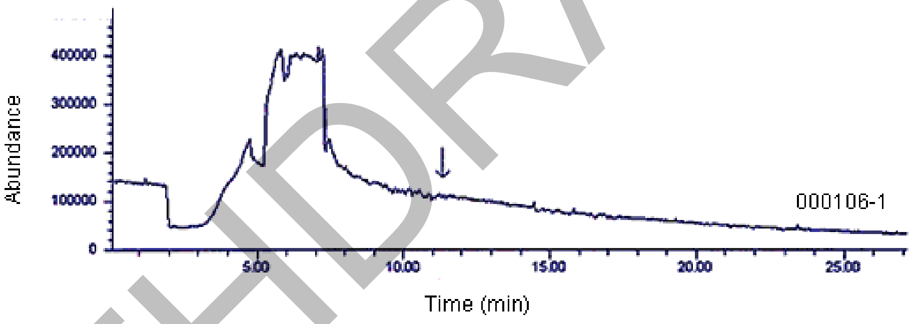

Figure 4.5.2 Total ion chromatogram of a MiniCan that had previously contained 100 ppm of 1,1,1-Trichloroethane and had been cleaned 100 cycles. 1,1,1-trichloroethane elutes at 11.4 min.

5 REFERENCES

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5.7 Chan, Y., and Hearty, P. Evaluation of the Entech Canister System, 2000. Unpublished.

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5.9 Certified laboratories which will analyze Entech Canisters on a fee-for-analysis basis include Galson Laboratories, East Syracuse, NY, and Aerotech Laboratories, Inc., Phoenix, AZ.