
Formaldehyde and VOC's in Indoor Air Quality Determinations by GCMS

Application Note: 101

Authors

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Abstract

A stainless steel canister based method has been developed to measure both VOCs and light carbonyls in indoor air using a single GCMS analysis. MiniCan stainless steel samplers collect the sample using either a quick five second fill technique (grab sample) or by maintaining a slow constant flow into the canister which gives the average concentration of contaminants in air over time. The vacuum in the MiniCan samplers is used to draw in the sample, eliminating the need for sampling pumps or a source of power (AC or batteries). A new coating called Silonite on the inside of the MiniCan samplers provides an ultra inert surface that prevents the adsorption of analytes. This makes the MiniCan an ideal choice for sampling reactive compounds, and performing site investigations where a more universal technique is needed to detect anything that may be present.

The analysis of MiniCans is performed by GCMS using a preliminary preconcentration step to improve method sensitivity. Up to 100cc of sample

is concentrated down to a few microliters and injected rapidly onto a GC capillary column for analyte separation and detection by a mass spectrometer. Silonite coating throughout the preconcentrator's internal tubing allows a wide range of compounds to be recovered and quantified down to 1-2 PPB(v) in a single analysis.

This application note details the use of MiniCans for sampling and analysis of formaldehyde, light carbonyls, and common VOCs in the concentration range commonly found in indoor air (1-200 PPBv). Included in the study is storage testing in MiniCans, analytical reproducibility, response linearity, and analyte detection limits.

Introduction

Canister methods for whole air sampling have been used for over 20 years to measure the volatile content of air. Polar compounds including formaldehyde and light C2-C3 carbonyl containing compounds have been excluded from canister based methods in the past due either to their instability in the sampling canisters, or to difficulties arising during preconcentration and GC separation. Indoor air quality or other low level testing of these compounds has required the use of a derivitization technique to trap and concentrate these compounds from air. Unfortunately, DNPH derivatizing methods have many limitations. First, the sampling procedure is difficult to perform correctly, as metering pumps are needed and because the flow resistance across the DNPH tubes can change over time, possibly causing errors in volume measurement. DNPH tubes also

suffer from contamination problems, resulting in frequent reporting of “false positives”. The derivitization complex that is formed between the carbonyl and DNPH is not stable in the presence of other oxidants found commonly in air, so changes in concentration of other compounds can affect method accuracy. Finally, there is no way to take a quick sample with a DNPH tube. Instead, several liters of air must be drawn through the tube, requiring from 0.5 to 3 hours. That may not be practical if sampling is being performed in response to a detected odor that may only be present for a few minutes.

The MiniCan method can be used to analyze both polar and non-polar VOCs within a single analysis using GCMS. This simplifies the sampling strategy and reduces time and cost of air monitoring.

Experimental Section

- Sampling

Sample collection and stability testing was performed using 0.4 liter Entech MiniCans (29-MC400L). Quick connect fittings used on the MiniCans facilitate easy connection to field samplers for either quick filling operations (29-RGS-00) or longer duration sampling using constant flow regulators (29-CS12 00P).² Canisters are cleaned using a 21 position heated manifold and automated cleaner (Model 3110) to remove contaminants and restore the vacuum needed to fill the MiniCan in the field.

- Standard Preparation

A five component Carbonyl standard was obtained containing Formaldehyde at 5 PPMv with Acetaldehyde, Acetone, Propanal, and 2-Butanone all at 2 PPMv (Apel-Riemer Environmental, Inc. Denver, Colorado). This mixture was dynamically diluted using a model 4600 6 Channel Diluter (Entech Instruments, Inc.) to concentrations of 5,10,25,50,100, and 200 PPBv for formaldehyde and 2,4,10,20,40, and 80 PPBv for the remaining carbonyls. The 7100 preconcentrator was directly connected to the effluent of the diluter to take the 100 cc aliquot of standard. Alternatively, standards can be prepared into a 6 liter or 15 liter Silonite canister

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so that standards do not have to be prepared daily. Standards are stable for several weeks, although it is important not to add excessive water to the canister because any remaining liquid water will cause substantial loss of formaldehyde. When using the 4600 diluter, nitrogen is already humidified, so no extra water needs to be added. An internal standard, Acetone-d6, was also prepared by static dilution technique starting with neat chemical and diluting to 200 PPBv. The internal standard was prepared dry to avoid putting excessive moisture into the cold trap during analysis.

- Preconcentration and GCMS Analysis

To achieve the detection limits desired (approximately 1-2 PPBv), indoor air samples must be concentrated before injection into a GCMS for analysis. The presence of water vapor and CO₂ at levels 4-8 orders of magnitude higher than the target volatile compounds requires water and CO₂ to be removed prior to GC injection in order to avoid chromatography problems and attenuation of response in the mass spectrometer. The 7100 utilizes 3 stages to manage the water and CO₂ without losses of desired analytes. Using a technique called “Cold Trap Dehydration”, the moisture dew point is lowered to -40 deg.C using an empty 1/8”x14” Silonite coated trap. The target compounds are trapped in a second stage containing 35/60 mesh Tenax TA (0.085”IDx8” bed length) at -30 deg.C. At this reduced temperature, Tenax will trap the lighter compounds of interest, but will allow the CO₂ to purge through. After trapping the sample, the volatiles are further concentrated in a 3rd stage focusing trap using 1/32” OD Silonite coated tubing. Heating of the 3rd trap occurs extremely fast, producing the narrow peaks shown in the chromatogram in figure 1. Peak tailing during transfer to the gas chromatograph is virtually eliminated using the inert 1/32” Silonite coated transfer line.

-Analytical System

GCMS Inlet System: 7100 Preconcentrator and 7032 21 Position Autosampler (Entech Instruments, Inc.)
7100 Mode of Operation: Cold Trap Dehydration

GCMS: Agilent 6890/5973N (Palo Alto, CA)
 Column: DB-5MS, 0.32 mm ID, 60 m, 1 μ m
 Temperature: 35C (5min) to 85C at 10C/min
 (0 hold)
 Scan: T = 0 min: 29-180 amu, 2.46 scans/sec
 T = 6 min: 33-280 amu, 2.97 scans/sec
 Ionization Mode: Electron Impact at 70 eV

Table 1 shows the parameters necessary for proper operation of the 7100 preconcentrator. Note that bakeout is performed after desorption, except for trap 3 where bakeout is not for the purpose of removing any residual analyte, but to remove any excess water. Therefore, this is performed at the beginning of the next run. The GC transfer line is at 20 degrees C, used as another water management tool, this temperature will spread the water out to minimize attenuation of analyte response during first few minutes of the run.

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Table 1.

7100 Temperature Parameters

	Part number	Packing	Trap Temp	Desorb Temp	Bake Temp
Trap 1	04-11310	Empty	-40 C	NA	150 C
Bulkhead 1		NA	30 C	NA	150 C
Trap 2	04-11330	Tenax TA	-30 C	180 C(3.5min)	190 C
Bulkhead 2		NA	30 C	100 C	150 C
Trap 3	06-08050	Empty	-160 C	60 C(2min)	60 C(3min)

Constant Temperature Zones

7100 Rotary Valve	100 C	7032 Transfer Line	100 C
7032 Rotary Valve	100 C	GC Transfer Line	20 C

7100 Flows and Volumes

Medium	Preflush (sec)	Flow Rate (sccm)	Volume (cc)
Internal Standard	5	50	25
Analytical Standard	5	50	100
Sample	10	50	20 - 100
Sweep/Purge	5	50	50

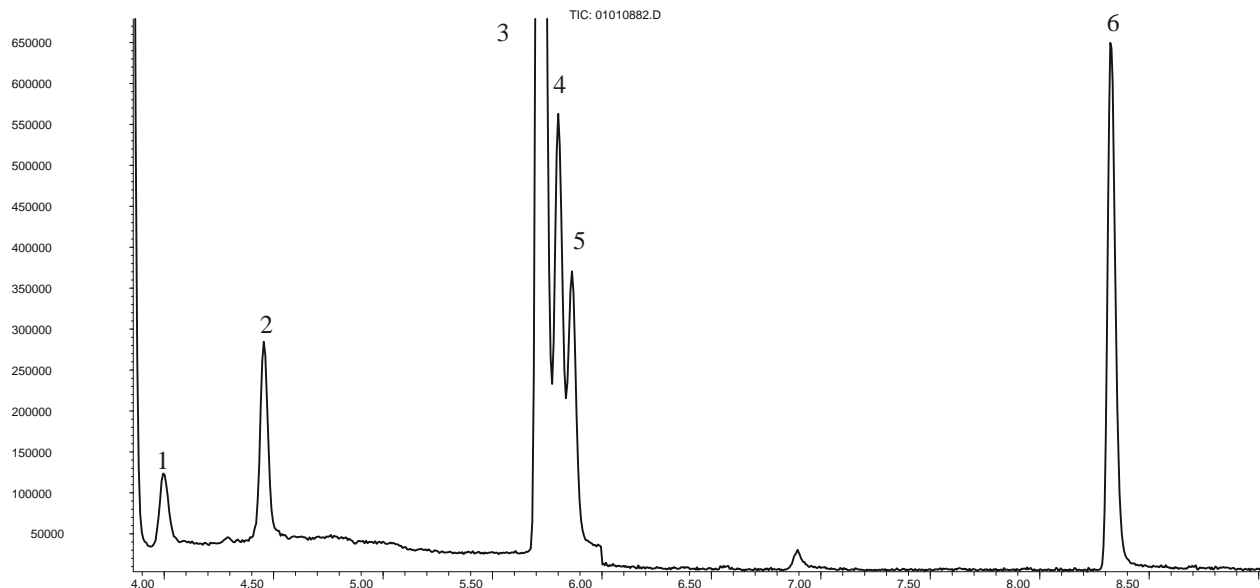


Figure 1. Total Ion Chromatogram containing, 1) 50 PPBv Formaldehyde, 2) 20 PPBv Acetaldehyde, 3) 50 PPBv Acetone-d6, 4) 20 PPBv Acetone, 5) 20 PPBv Propanal, 6) 20 PPBv 2-Butanone.

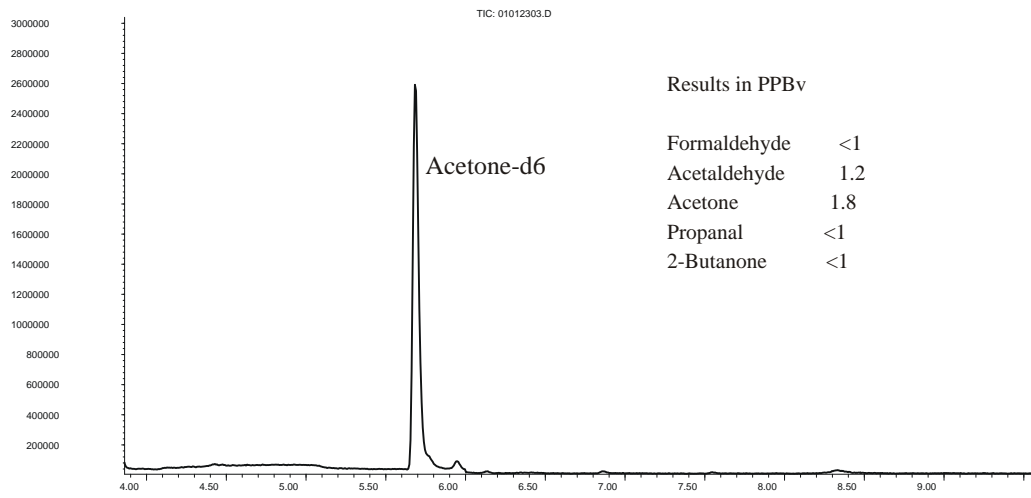


Figure 2. Method blank chromatogram.

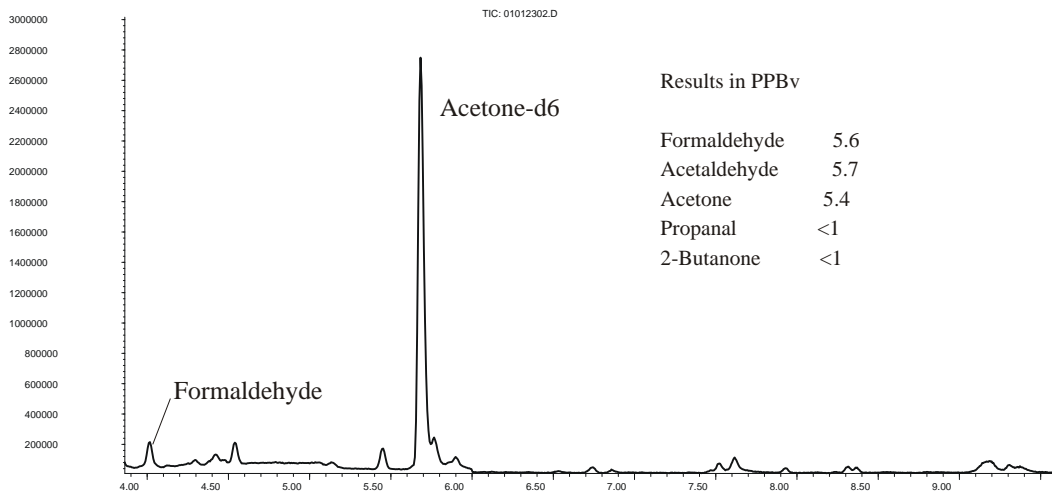


Figure 3. Chromatogram of ambient air.

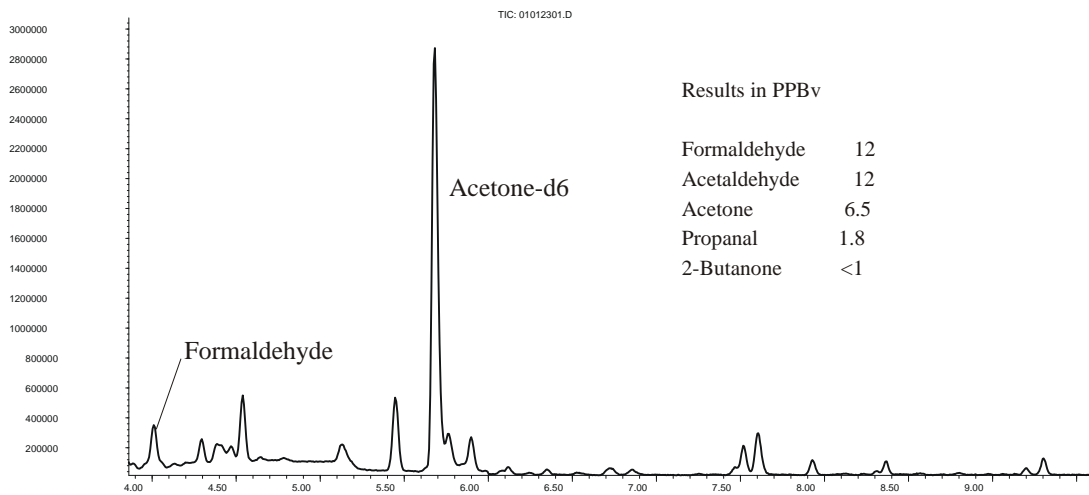


Figure 4. Chromatogram of indoor air.

Results and Discussion

Six point calibration curves were generated for the carbonyl standard with all compounds yielding low percent Relative Standard Deviations (%RSD's in table 2 and figure 5). Single ion quantitation is performed using m/z 30 for Formaldehyde, 29 for Acetaldehyde, 46 for Acetone-d6, 43 for Acetone, 29 for Propanal, and 72 for 2-Butanone. The chromatogram in figure 1 does not show baseline resolution for the middle three analytes, but their selected ion chromatograms used in quantitation are base line resolved. Detection limit studies were performed with seven replicate analyses resulting in limits of 1 PPBv or less with only a 100 cc sample size (table 3). Figure 6 shows a single ion chromatogram of m/z 30 for formaldehyde at 10 PPBv. Although the 0.4 liter MiniCan allows up to 200 cc's to be withdrawn during preconcentration, a sample size of 100 cc's was chosen to allow a repeat analysis if necessary. Method blank concentrations are at the targeted quantitation levels of 1 - 2 PPBv or lower (figure 2).

Ambient and Indoor air samples were analyzed for the carbonyl compounds. Formaldehyde concentrations were found to be in the low PPBv range for both samples but notably higher in indoor air (figures 3 and 4).

Formaldehyde is extremely soluble in liquid water

which creates a unique challenge in its analysis. Cold Trap Dehydration makes the separation of formaldehyde and water possible because water goes directly from its vapor state to its solid state. Because of the high solubility, pressurized sampling in the field should be avoided because liquid water will condense and cause formaldehyde to fall out. Alternatively, if an ambient pressure sample is collected and then pressurized in the laboratory with surrogate in dry nitrogen, no liquid water will form in the canister. Although this dilutes the sample, the sensitivity is still sufficient for indoor air quality investigations.

Proper sample collection is just as important as accurate analyses, so studies were performed on the stability of volatile analytes in Silonite coated MiniCans. Eight cans were filled with 50 PPBv formaldehyde and 20 PPBv for the other carbonyls. These cans were analyzed after 3 days and again after 7 days. In addition, 6 cans sampled with ambient air were spiked with the same carbonyl concentrations as above to examine the effects of a real air matrix on formaldehyde recovery. Although figure 7 shows some loss of formaldehyde, figure 8 has no loss of formaldehyde in a real air matrix. A 41-day recovery study is shown in table 4 (compliments of Apel-Riemer Environmental, Inc).

	RF1	RF2	RF3	RF4	RF5	RF6	AVG.RF	%RSD
Formaldehyde	.041	.045	.037	.041	.040	.045	.042	7.1
Acetaldehyde	.171	.163	.151	.151	.146	.160	.157	5.9
Acetone	.699	.686	.662	.646	.664	.708	.678	3.6
Propanal	.277	.241	.247	.226	.226	.239	.243	7.8
2-Butanone	.375	.327	.319	.332	.352	.388	.349	8.0

Table 2. 6 point calibration summary showing percent relative standard deviations of less than 10 for carbonyl compounds..

	1	2	3	4	5	6	7	Average	SDV	MDL (PPBv)
Formaldehyde	2.13	1.93	1.88	2.08	1.73	1.76	1.57	1.9	0.199	0.63
Acetaldehyde	2.01	2.12	1.70	1.67	1.43	1.55	2.34	1.8	0.331	1.0
Acetone	1.06	0.98	0.97	0.92	0.98	0.97	0.95	1.0	0.043	0.14
Propanal	0.77	0.84	0.74	0.75	0.69	0.69	0.67	0.7	0.059	0.19
2-Butanone	0.94	0.73	0.71	0.73	0.73	0.74	0.67	0.8	0.087	0.28

Table 3. Method detection limit study for carbonyl compounds with results of 1 PPBv or less using a 100 cc sample size.

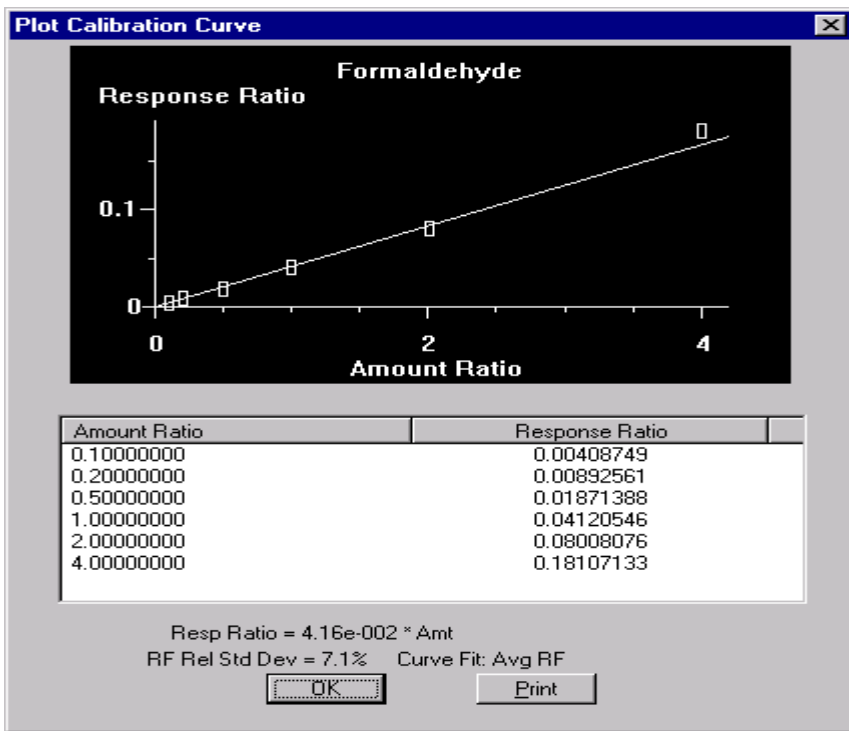


Figure 5 . 6 point calibration plot of formaldehyde.

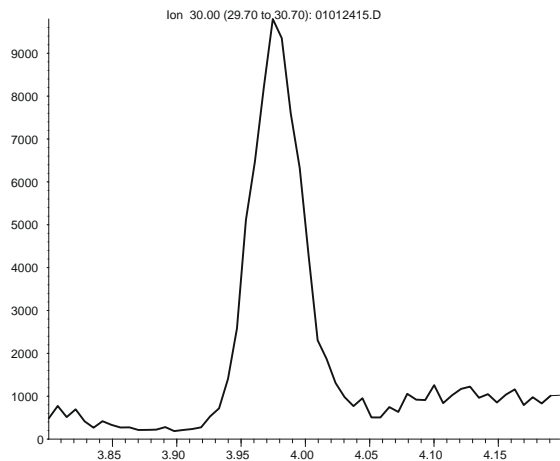


Figure 6. Single ion chromatogram (m/z=30) of formaldehyde at 10 PPBv.

Days in Can	Run 1	Run 2	Average	% Decrease
0	2.56	2.44	2.50	
0	2.57	2.56	2.57	
41	2.46	2.53	2.50	0
41	2.37	2.47	2.42	5.7

Table 4. 41-Day Minican stability results for Formaldehyde. Concentrations are in PPMv.

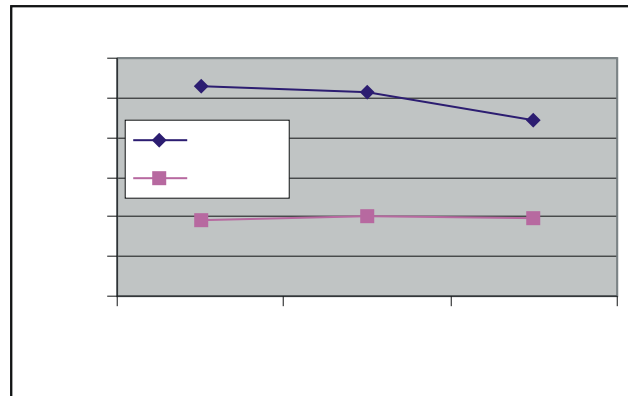


Figure 7. Minican stability data for formaldehyde at 50 PPBv and acetaldehyde at 20 PPBv in nitrogen. Formaldehyde is about 80 percent recovered after 7 days.

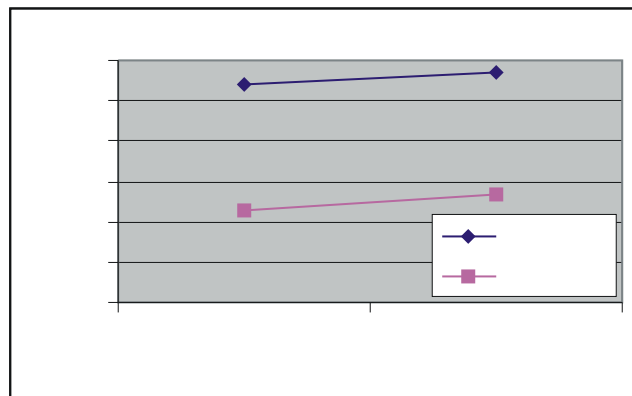


Figure 8. Minican stability data for formaldehyde spiked at 50 PPBv and acetaldehyde spiked at 20 PPBv in ambient air. Recoveries are slightly above 100 percent.

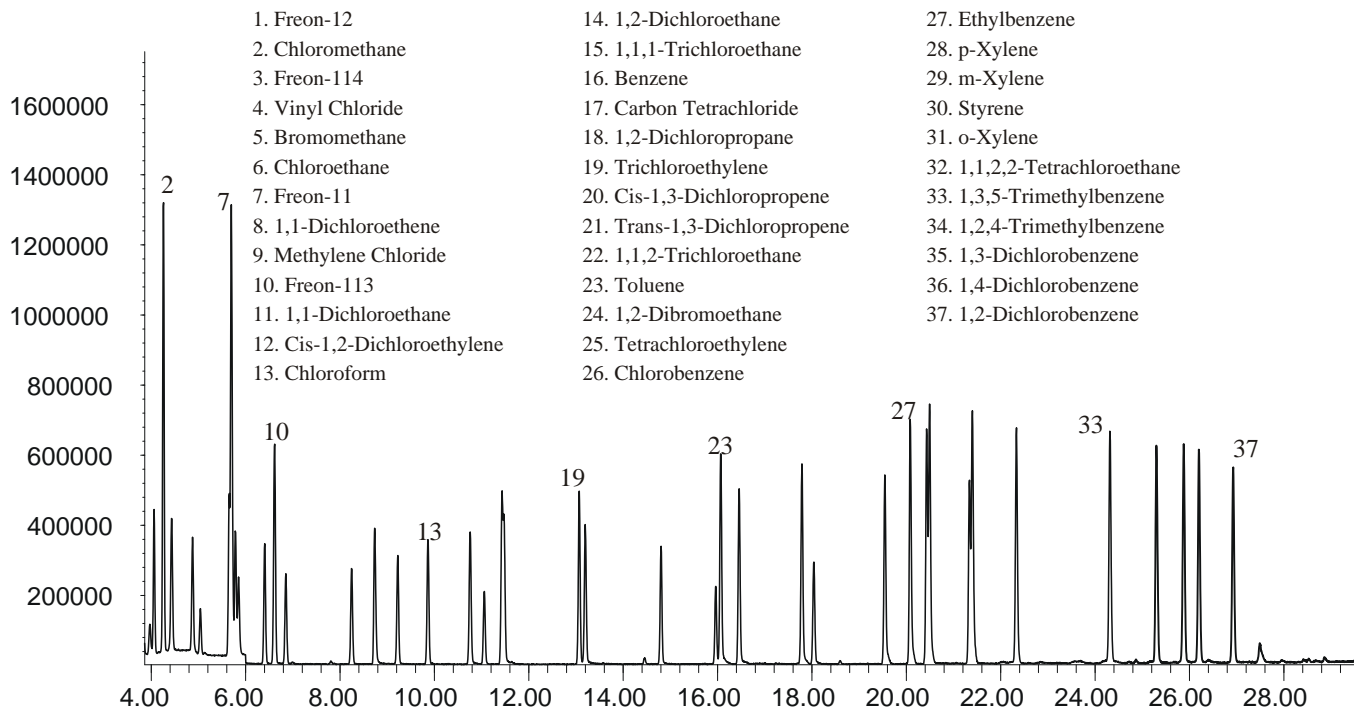


Figure 9. 100 cc's of 10 PPBv 37 component standard by Cold Trap Dehydration.

Conclusion

A new method has been developed for performing the analysis of formaldehyde in indoor air as well as other VOC's by GCMS using Silonite coated sampling canisters. Peak tailing typical of polar compound analysis has been eliminated using Silonite coated transfer tubing. This method replaces the costly and complicated DNPH derivatizing/HPLC procedure.

References

1. K.D. Oliver, J.D. Pleil, and W.A. McClenny, "Sample Integrity of Trace Level Volatile Organic Compounds in Ambient Air Stored in SUMMA Polished Canisters" Atmospheric Environmental, 20:1403, 1986.
2. D. Cardin, K. Langford, V. Shetty, "Improving the Performance of Time Integrated Sampling of TO14 Compounds into Stainless Steel Canisters" Entech Instruments, Inc. Application Note 902, 1999.
3. Compendium Method TO15 "Determination of Volatile Organic Compounds in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)" Center of Environmental Research Information Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268, January 1999.