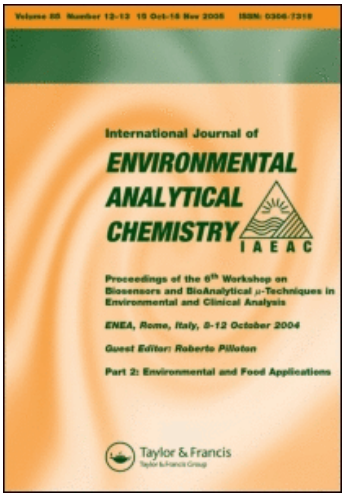

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Almasi, E. , Kirshen, N. and Kern, H.(1993) 'The Determination Of Sub Part-Per-Billion Levels Of Volatile Organic Compounds In Air By Pre-Concentration From Small Sample Volumes', International Journal of Environmental Analytical Chemistry, 52: 1, 39 — 48
To link to this Article: DOI: 10.1080/03067319308042846
URL: http://dx.doi.org/10.1080/03067319308042846

Intern. J. Environ. Anal. Chem. Vol. 52, pp. 39-48
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THE DETERMINATION OF SUB PART-PER-BILLION LEVELS OF VOLATILE ORGANIC COMPOUNDS IN AIR BY PRE-CONCENTRATION FROM SMALL SAMPLE VOLUMES

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(Received, 15 June 1992; in final form, 9 October 1992)

Trace level Volatile Organic Compounds (VOCs) in ambient air are normally determined according to EPA Method TO-14. This method describes the analysis in ambient air of 41 VOCs, ranging in boiling point from -29 to 215°C. It covers a concentration range from 0.2 to 20 parts per billion, volume/volume (ppb), and specifies sample enrichment of a 400 mL air sample on glass beads at -160°C. While this sample volume provides sub-ppb levels of VOC detection for target analytes when using a quadrupole mass spectrometer detector in SIM mode or when using GC detectors, the identification of non-target analytes may only be done in full scan mode for higher concentrations. Also with this sample volume a Nafion dryer is needed for water removal thereby lowering the recovery of polar VOCs.

Because of the very high sensitivity of the ion trap MS, relatively small air volumes (60 mL) are adequate to obtain the required or lower detection levels. An integrated air analysis system based on a GC-ion-trap MS has been investigated and is described. This system has a built-in cryogenic trap and necessary valving, internal standard gas sampling loop, and is controlled from the GC-MS workstation. The linearity, precision, and method detection levels obtainable with this system when using small volumes are reported. In addition, examples of the quantitative and qualitative analysis of ambient air samples are shown.

KEY WORDS: Cryogenic concentrator, ion trap GC-MS, full scan spectra, air, volatile organic compounds.

INTRODUCTION

The determination of basic air pollutants in ambient air is of paramount importance as legislative acts, such as the 1990 amendments to the Clean Air Act (CAA) of the United States, take effect. Federal, state and local actions will ultimately reduce emissions from industrial and mobile sources to meet the requirements of the CAA. The analytical techniques which are used to ensure that allowed emissions are not exceeded must provide sensitive and definitive measurements of volatile organic compounds (VOCs) in ambient air at the sub parts per billion volume/volume (ppb) level.

The United States was quick to initiate experimental guidelines for VOC analysis in air. The resulting EPA method TO-14,[1-5] is the most commonly used method for VOC analysis worldwide and therefore it has been used as a guideline for the following study.

Method TO-14 describes the analysis in ambient air of 41 VOCs, ranging in boiling point from -29 to 215°C (Table 1). It covers a concentration range from 0.2 to 20 ppb, specifies

Table 1 Quantitation Ions, Retention Times, %RSD and Method Detection Limits for Analytes in Method TO-14.

Compound	*Quan Ion*	*RT* (min)*	*%RSD** (area)*	*MDL (ppb)*
Dichlorodifluoromethane	85	13:05	3.8	0.01
Chloromethane	50	14:11	8.5	0.03
1,2-Dichloro-1,1,2,2-tetrafluoroethane	85	15:11	3.5	0.01
Vinyl Chloride	62	15:30	6.0	0.02
Bromomethane	94	16:56	4.7	0.01
Chloroethane	49	17:36	9.0	0.03
Trichlorofluoromethane	101	19:23	3.2	0.01
1,1-Dichloroethylene	61	20:25	5.6	0.02
Dichloromethane	49	20:42	3.9	0.01
1,1,2-Trichloro-1,2,2-trifluoroethane	101	21:07	3.8	0.01
1,1-Dichloroethane	63	22:10	4.8	0.01
c-1,2-Dichloroethene	61	23:08	4.4	0.01
Chloroform	83	23:28	3.7	0.01
1,2-Dichloroethane	62	24:14	4.1	0.01
1,1,1-Trichloroethane	97	24:30	4.6	0.01
Benzene	78	24:59	3.4	0.01
Carbon Tetrachloride	117	25:08	3.4	0.01
1,2-Dichloropropane	63	25:50	2.9	0.01
Trichloroethene	130	26:05	3.8	0.01
c-1,3-Dichloropropene	75	26:59	4.7	0.01
t-1,3-Dichloropropene	75	27:32	5.7	0.02
1,1,2-Trichloroethane	97	27:43	3.9	0.01
Toluene	91	28:03	2.4	0.01
1,2-Dibromoethane	107	28:47	2.9	0.01
Tetrachloroethene	166	29:19	3.5	0.01
Chlorobenzene	112	30:06	3.8	0.01
Ethylbenzene	91	30:33	4.6	0.01
m,p-Xylene	91	30:47	2.9	0.01
Styrene	104	31:12	5.2	0.02
1,1,2,2-Tetrachloroethane	83	31:19	4.7	0.01
o-Xylene	91	31:21	5.0	0.02
4-Ethyltoluene	105	33:02	7.0	0.02
1,3,5-Trimethylbenzene	105	33:09	8.9	0.02
Benzylchloride	91	33:15	10.1	0.03
1,2,4-Trimethylbenzene	105	33:45	10.3	0.03
m-Dichlorobenzene	146	33:58	3.2	0.01
p-Dichlorobenzene	146	34:05	4.3	0.01
o-Dichlorobenzene	146	34:37	4.8	0.01
1,2,4-Trichlorobenzene	180	37:56	9.3	0.03
Hexachlorobutadiene	225	39:11	8.0	0.03

*RT includes the concentration step also, column DB-1

**%RSD calculated from area responses of 9 replicate runs.

sample enrichment (400 mL) on glass beads at -160°C, thermal desorption, separation on a capillary column, and detection with a mass spectrometric detector. The first draft of the Contract Laboratory Program (CLP) method[6] was published in February 1991 employing a similar technique. The samples to be analyzed by the CLP method are from known or suspected hazardous waste sites, therefore the concentration range is from 2 to 100 ppb, higher than required for ambient air monitoring.

Previous work with TO-14 systems based on GC detectors[7,8] has confirmed that volumes of approximately 400 mL are required to obtain sensitivities of 0.2 ppb. The same requirements apply to quadrupole mass spectrometers. Because of the very high sensitivity of the ion-trap MS, relatively small air volumes (60 mL) are required to obtain these or lower detection levels. An integrated air/soil gas analysis system based on a GC-Ion-trap MS has been investigated and is described here. This system has a built-in cryogenic trap, internal standard gas sampling loop, sixteen sample automation and is controlled from the GC-MS workstation. The linearity, precision, and method detection levels obtainable with this system when using small volumes are reported. In addition, examples of the quantitative and qualitative analysis of ambient air samples are shown.

EXPERIMENTAL

System description

The schematic of the GC-Ion-trap MS system is shown in Figure 1. The built-in trapping and preconcentrating device, the Variable Temperature Adsorption Trap (VTAT, Figure 2) is capable of trapping and preconcentating VOCs from air on glass beads at -160°C or on an adsorbent such as Carbosieve™/Carbotrap™ at ambient temperatures. In the present

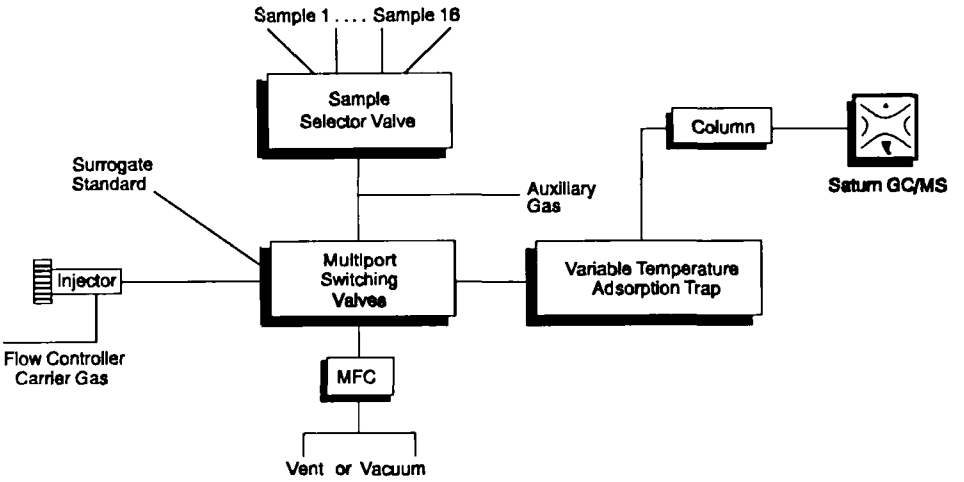

Figure 1 Schematic of a GC/Ion-trap MS System for VOCs

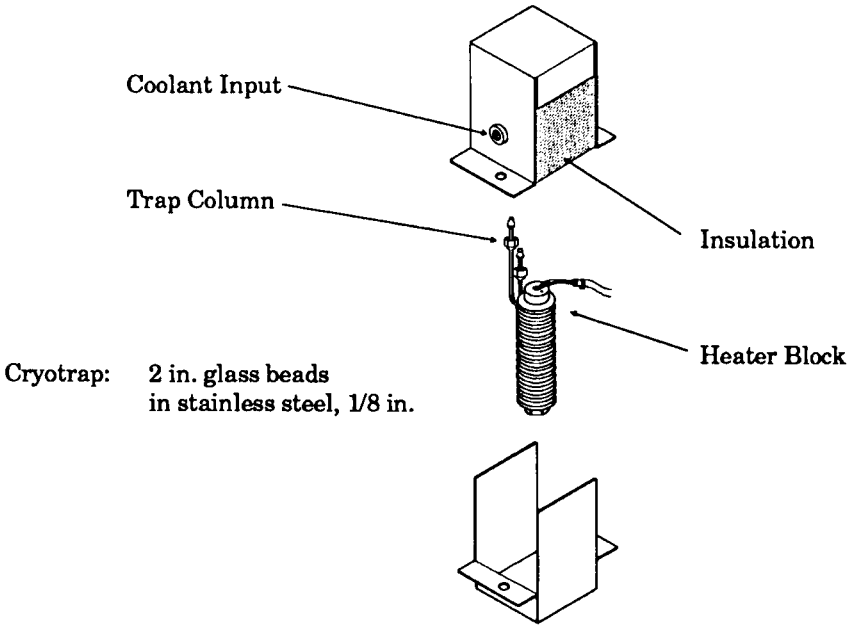

Figure 2 The variable temperature absorption trap (VTAT)

study only the subambient mode was used and the glass bead trap was cooled with liquid N_2 to -160°C. (Liquid CO_2 can be used also if the application requires -60°C or higher trapping temperature.)

Instrumentation and conditions

Cryogenic concentrator:

- Variable Temperature Adsorption Trap (VTAT), 5 cm of 60/80 mesh silanized glass beads
- Two automated valves, 4- and 10-port; capable of sample and internal standard (I.S.) introduction
- Electronic mass flow controller, 0–100 mL/min, with readout box
- Vacuum pump (metal diaphragm)

Pneumatics:

Air sample flow rate:	20 mL/min
Column flow rate:	1 mL/min He
Auxiliary flow rate:	20 mL/min He

Temperatures:

VTAT:	-160°C for 4 min, 180°C/min to 120°C, hold
Valves:	160°C
Column:	-50°C for 6 min, 8°C/min to 160°C, hold

Columns:
DB-1 (J&W), 60m × 0.32 mm I.D., 1 μm film or
DB-624 (J&W), 60m × 0.32 mm I.D., 1.8 μm film

Ion-trap MS (Varian Saturn II):
Scan Range: 47–260 u
Scan Rate: 0.8 sec/scan (3 μscan/analytical scan)
RF storage Level: 210 DAC Steps; background Mass: 45 u
Segment Breaks: 70/78/150; Tune factors: 120/70/100/70
Automatic Gain Control (AGC) Target: 20000
Emission Current: 30μA (Optimized parameters might vary instrument to instrument)

Standard:
Alphagaz TO-14 standard, 41 component, 2 ppm

Procedure

In Method TO-14 a critical part of the analysis is the preconcentration step. In the first stage of this enrichment process the sample (generally VOCs present in low or sub ppb concentrations) is flushed through the lines with a flow set by the electronic mass flow controller, while the loop (0.25 mL) is filled by the internal standard. While Method TO-14 is based on external standard calibration, the CLP method suggests bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5, as internal standards. In addition to these, other compounds such as octafluorotoluene, 1-bromo-4-fluorobenzene and 1,4-dichlorobenzene-d_4 have been used as internal standards (Figure 7). After the initial column and VTAT temperatures are equilibrated, the air sample and internal standard are directed to the -160°C VTAT and the VOCs are deposited onto the glass beads.

The duration of this "trapping" time can be varied and the volume of the analyzed sample changed accordingly. The sample flow during this step, usually 20 mL/min, is held constant by the mass flow controller. In this study the trapping time was 3 minutes resulting in a 60 mL sampled volume. After the sample VOCs are deposited, the residual air is removed from the VTAT by the auxiliary flow. Then the VTAT is heated to 120°C and the analytes are backflushed to the capillary column where they are focussed, separated, and detected. Later the VTAT is cooled down in preparation for the next analysis.

The main difference between the experimental parameters used in this work and those specified in the TO-14 method is the sample size. The method specifies a sample volume of 400 mL. This volume of air can introduce a significant amount of water that might either plug the VTAT or capillary column. Elimination of this residual water is possible with a semipermeable membrane dryer such as a Nafion™ dryer. The removal of water with this type of dryer results in the loss of any trace polar organics that might be in the sample. The sensitivity of the GC-Ion-trap MS allows trace level VOC detection by preconcentrating only 60 mL of sample. This small sample reduces the interference of water and eliminates the need for a Nafion dryer.

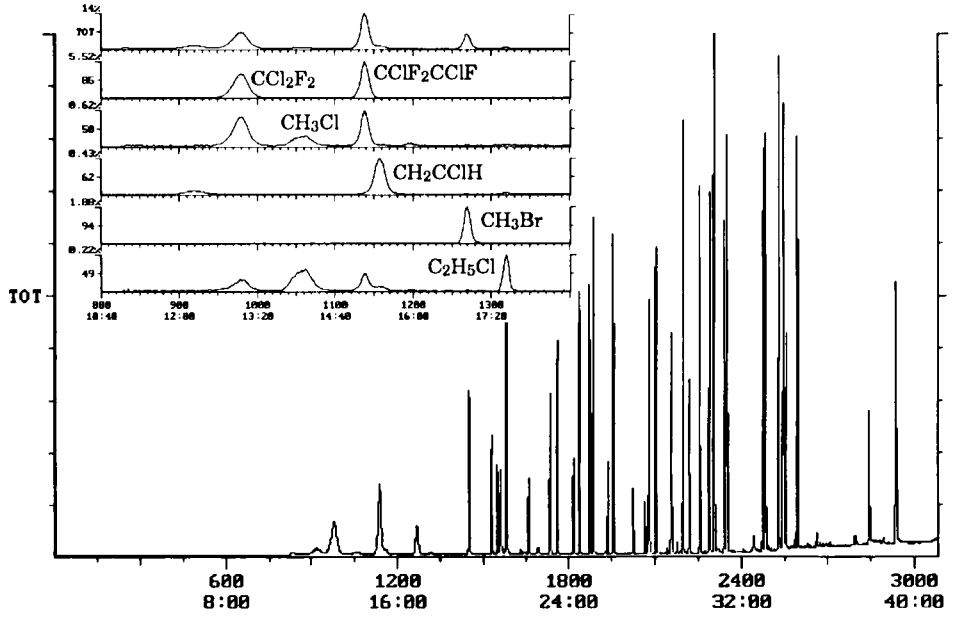

Figure 3 RTICC of 41 VOC compounds, 60 mL, 2 ppb v/v and mass chromatogram of the gases.

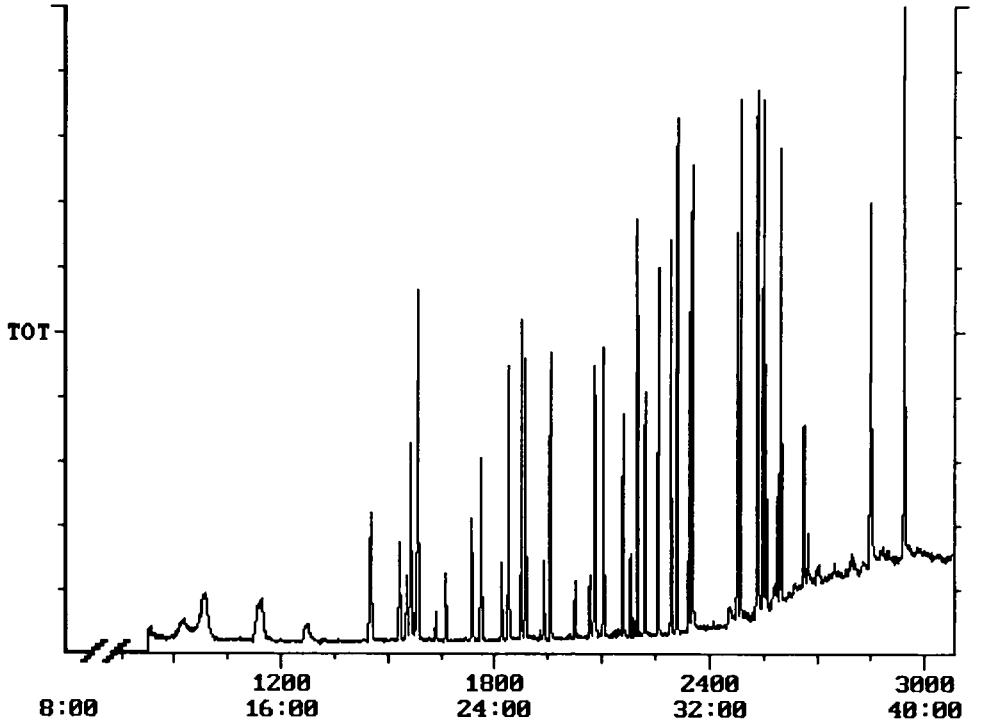

Figure 4 RTICC of 41 VOC compounds, 60 mL, 0.25 ppb v/v

RESULTS

The standard and samples were introduced to the system from stainless steel SUMMA® polished canisters. The standard used was a 41 component, 2 ppm VOC mixture (Alphagaz) diluted with air to the desired concentrations. RTICCs of 2 ppb and 0.25 ppb v/v standards are shown in Figures 3 and 4. Gaussian peak shapes are exhibited by all the compounds including the "gases" (the six most volatile compounds) as shown by their mass chromatograms in the Figure 3 insert. For the quantitation of the gases a peak smoothing algorithm was used, allowing precise quantitation of these components even at low concentrations.

The precision and MDL were determined by multiple injections of a 60 mL, 0.1 ppb standard. Standard deviations of the single ion areas were calculated for nine runs and were between 2–9%, the average of the 41 compounds being 5%, Table 1. The MDL was calculated from integrated areas of single quantitation ions (nine replicate runs) with the following formula:

$$MDL = s \times t$$

where s is the standard deviation of the replicate analyses and t is the student's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. The calculated MDLs were between 0.01–0.03 ppb.

Linearities of the quantitation ion responses versus concentration for the 41 components were examined over the range required in the method, 0.1 to 20 ppb v/v, and were found to be very good, the standard deviation of five representative RF values in the 0.2–20 ppb concentration range was 6.3% for vinyl chloride, 3.8% for chloroform, 4.9% for ethylenedibromide, 8.6% for 1,2,4-trimethylbenzene.

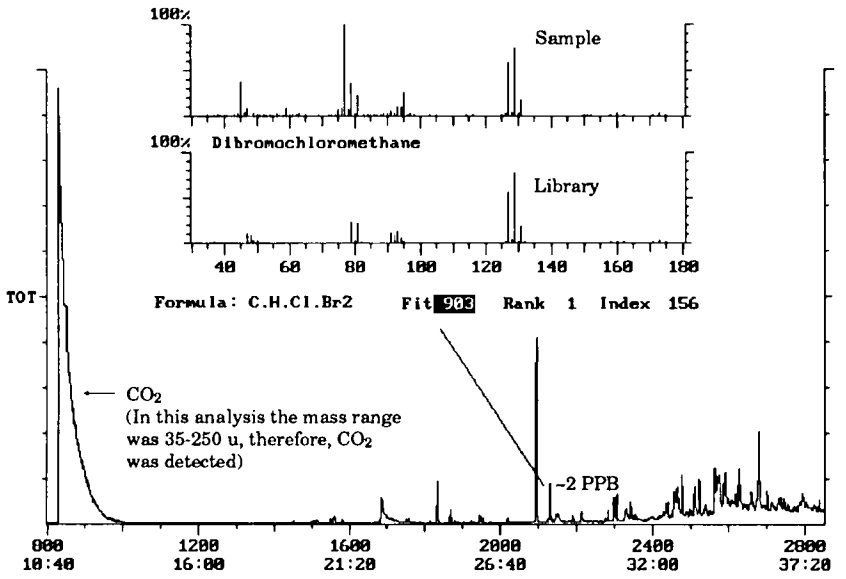

Figure 5a RTICC of 60 mL air sample collected above the surface of a 60°C water bath; dibromochloromethane, a non-target analyte is identified (fit 903/1000), estimated concentration 2 ppb.

Sorted via: Calc Amount(A) ↓

Cal	Name of Compound	Fit S/N	R Time	Me	Calc Amt(A)	Units
23	Toluene	982	27:55	VB	5.220	PPB/V
15	1,1,1-Trichloroethane	829	24:26	BV	1.861	PPB/V
36	Benzylchloride	949	33:51	VV	0.793	PPB/V
2	Chloromethane	821	13:59	BB	0.655	PPB/V
16	Benzene	983	24:54	VV	0.605	PPB/V
33	1,3,5-Trimethylbenzene	987	33:39	VV	0.593	PPB/V
34	1,2,4-Trimethylbenzene	989	33:39	VV	0.587	PPB/V
39	1,2,4-Trichlorobenzene	937	37:51	BB	0.510	PPB/V
9	Dichloromethane	941	20:40	BV	0.499	PPB/V
31	o-Xylene	985	31:15	BV	0.458	PPB/V
29	Styrene	990	31:06	BB	0.362	PPB/V
27	Ethylbenzene	983	30:27	VB	0.347	PPB/V
35	m-Dichlorobenzene	939	33:53	BV	0.304	PPB/V
28	m,p-Xylene	987	31:15	BV	0.252	PPB/V
7	Trichlorofluoromethane	994	19:21	BV	0.248	PPB/V
21	t-1,3-Dichloropropene	776	27:26	VV	0.243	PPB/V
5	Bromomethane	984	16:53	BB	0.217	PPB/V
13	Chloroform	971	23:26	BV	0.194	PPB/V
10	1,1,2-Trichloro-1,2,2-	979	21:06	BB	0.165	PPB/V
1	dichlorodifluoromethan	937	12:57	BB	0.149	PPB/V
26	Chlorobenzene	877	29:59	BB	0.143	PPB/V
32	4-Ethyltoluene	985	33:19	BV	0.143	PPB/V
25	Tetrachloroethene	764	29:27	BB	0.133	PPB/V
24	EDB	850	28:40	BV	0.079	PPB/V
22	1,1,2-Trichloroethane	784	27:19	BB	0.071	PPB/V
14	1,2-Dichloroethane	838	24:10	BV	0.043	PPB/V

Figure 5b Quantitation Report of the Sample Shown in Figure 5a.

In addition to identifying and quantitating target components in a sample it is often necessary to identify and estimate the quantities of non-target analytes. For example, dibromochloromethane, a non-target analyte is identified and its concentration estimated at 2 ppb in Figure 5a.

INTERFERENCES

In ambient air some components are present at much higher concentrations than the VOCs. The two most significant components which are concentrated together with the VOCs from the air are water (mentioned above) and CO_2. The reduced sample volumes used here suppress the problems caused by these components. For example, to represent a very humid sample, an air sample was collected just above the surface of a 60°C water bath. At this temperature the vapor pressure of water is 0.2 atmospheres. The chromatogram and results shown in Figures 5a and 5b indicate that the preconcentration process was not affected by the high level of moisture.

Carbon dioxide which is also present in air at high concentrations ($\approx$ 400 ppm, v/v) can be eliminated as an interference by choosing the scanning range from 47 to 250 u and setting the background mass at 45 u. Then CO_2 (44 u) is not stored or detected by the Saturn mass spectrometer and the detection of the early eluting VOCs is enhanced.

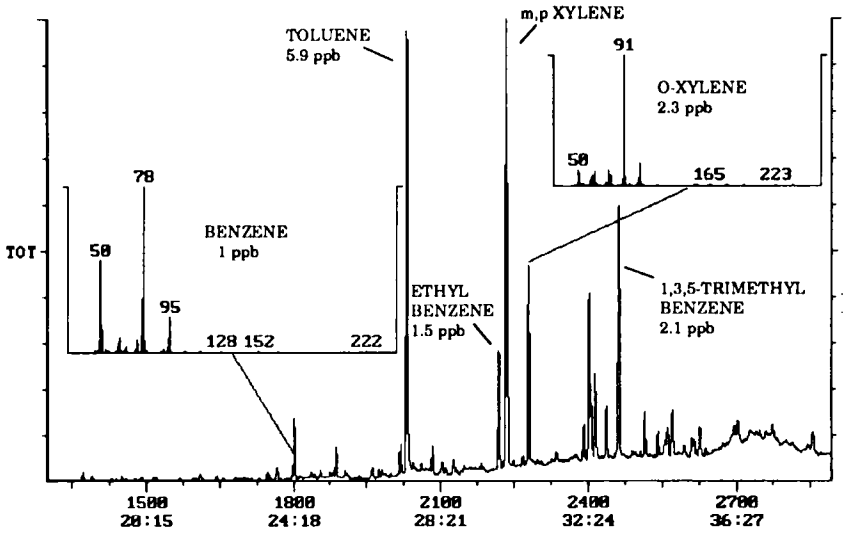

Figure 6 RTICC of 60 mL air sample collected in Walnut Creek, California on a rainy day in heavy traffic. (Spectrums are not background subtracted.)

APPLICATIONS

Two sample applications are shown using the same conditions. The first sample shows a chromatogram of an ambient air sample collected in Walnut Creek, California on a rainy day in rush hour traffic (Figure 6). The aromatics which are the major components of exhaust gas emissions found under these conditions are evident. The second sample was collected at an industrial site to screen for several polar organics. The RTICC and the mass chromatograms at 31 and 45, characteristic mass ions used to quantitate methanol and ethanol, respectively, are shown in Figure 7.

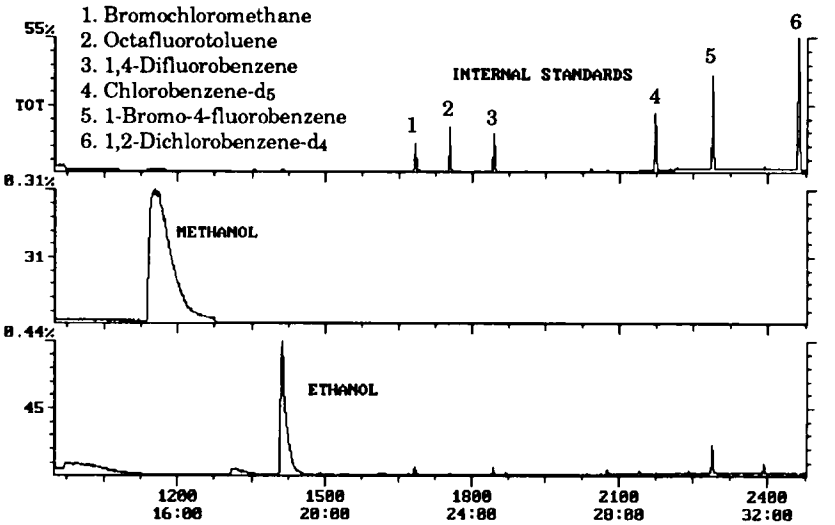

Figure 7 RTICC and characteristic ions for methanol and ethanol from a 60 mL air sample collected at an industrial site. Courtesy of Air Toxics, Ltd., Rancho Cordova, California.

CONCLUSIONS

An integrated air/soil gas analysis system based on a GC-Ion-trap MS has been investigated and applied to the analysis of VOCs following EPA Method TO-14. The very high sensitivity of the ion-trap MS allows the use of relatively small air volumes (60 mL) to obtain both qualitative confirmation (full scan spectra) and quantitative determination of sub ppb levels of VOCS. MDLs of 0.01–0.03 ppb have been calculated from multiple runs at 0.1 ppb.

Since water interference is minimized using this small air volume, the use of Nafion dryers has been eliminated allowing the determination of polar as well as non polar organic compounds.

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