

Automated in situ gas chromatographic–mass spectrometric analysis of ppt level volatile organic trace gases using multistage solid-adsorbent trapping

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Abstract

A fully automated sampling/injection system for the gas chromatographic–mass spectrometric (GC–MS) analysis of volatile organic compounds at tropospheric background levels was developed. Organic trace gases from air samples up to 100 l were trapped in temperature-controlled solid-adsorbent traps. The instrument utilized a one stage sampling/desorption inlet system designed as a closed device that did not require any replumbing steps between sampling and analysis. For analysis, the adsorbent trap was thermally desorbed and backflushed onto the chromatographic column where organic trace gases were directly cryofocused. Adsorbents tested were Carbotrap, Carbotrap C, Carbosieve S III, Tenax TA, Tenax GR and multistage combinations of these adsorbents. Interferences from blanks and adsorbent artifacts were minimized by backflushing the adsorbent trap, switching valve and transfer line between sampling sequences at temperatures above the levels used during trapping and sample transfer. The high sample volumes that could be concentrated and the low background levels allowed structural identification in GC–MS (electron impact ionization scan mode) at minimum levels of ca. 100 pg per peak (ca. 10^{-12} mol) equivalent to atmospheric concentrations at the lower parts per trillion (v/v) level. The volatility range of organic compounds that could be identified was approximately from pentane to pentadecane. The system was completely computer controlled and could be operated continuously and unattended around the clock for in situ analysis. The instrument was successfully deployed at the Mauna Loa Observatory, Hawaii, USA in July and August 1992.

1. Introduction

Volatile organic trace compounds (VOCs) in the atmosphere play an important role in the formation and transformation of atmospheric oxidants [1–3]. At remote background sites, such as the Mauna Loa Observatory (MLO), Hawaii, USA (elevation 3.4 km), air characteristic of the

free troposphere is often present [4] and the influence of recent anthropogenic emissions is low. Consequently the atmosphere at such a site may be representative of large regions of the remote marine troposphere. The identification and quantification of the VOCs present may provide valuable information about chemical transformations and atmospheric reaction pathways.

For the structural identification of individual

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atmospheric VOCs, several analytical problems have to be considered: sample collection and storage, separation of VOCs of interest, and detection and identification. Ambient air samples can be collected into evacuated stainless-steel canisters (either by opening them to atmospheric pressure or by pressurizing air to a few atmospheres using metal bellows pumps) or by sampling into bags made of PTFE materials [5]. Another approach is the use of solid-adsorbent traps [6,7] or the cryogenic freezeout of the analytes onto inert surfaces [8–11]. Cryogenic freezeout techniques allow the sampling of high volumes but have the disadvantage of concentrating water and carbon dioxide concurrent with the organic trace gases, which can cause interferences in the gas chromatographic (GC) analysis.

Solid adsorbent materials are designed to specifically trap organic vapors from atmospheric samples without enriching water and carbon dioxide. Among solid-adsorbent sampling techniques described, multi-adsorbent traps recently have received increased attention because the advantages of single adsorbents can be combined in one system and the range of compounds to be collected and desorbed is widened [12–18].

For qualitative analysis with individual compound identification, canisters, bags or adsorbent traps are usually transported to the laboratory for GC–mass spectrometric (MS) analysis. One disadvantage of most of the methods listed above is the time delay between the sampling at the site and the analysis. Adjustments in the sampling strategy during field experiments are difficult because of the delay and the physical separation which can occur between the sampling and the analytical site. Also, typical canister sizes allow the sampling of only a few liters of air which poses a limitation for achievable detection limits: For structural identification of VOCs in the electron impact ionization (EI) scan mode, typical MS instruments need compound amounts in the low nanogram range per peak. This is equivalent to a sample volume of approximately 10 to 100 l for atmospheric samples in the lower parts per trillion (ppt; throughout, ppt refers to a v/v ratio) range. Other disadvantages of all of these techniques are the possible instability of certain

analytes in canisters or in traps and possible contamination during transport, storage, handling and the plumbing steps required for capping the containers and reattaching to the analytical device.

A solid adsorption sampling method for in situ GC–MS analysis was recently described by Yokouchi et al. [19] and applied for quantitative measurements of organic trace gases at tropospheric background levels. Sample volumes of 200 ml were concentrated on Tenax TA and analyzed by thermal desorption GC–MS in the selected ion monitoring (SIM) mode. With the increased MS sensitivity in the SIM mode, selected organic compounds could be measured down to the low ppt level, but no identifications of unknown species by scan analysis were possible.

To overcome the listed drawbacks we designed a closed solid adsorbent sampling system with thermal desorption injection for automated, unattended on-site GC–MS analysis. All stages of the analysis, including sample loading and injection, as well as the temperature controlling and ramping of individual zones were controlled by a personal computer system. Organic trace gases were separated from air on temperature-controlled solid-adsorbent traps and then directly transferred by thermal desorption onto the chromatographic system. The system allows the sampling of volumes up to 100 l. This provides sufficient detection limits to achieve MS identifications of unknown VOCs in the EI scan mode at low ppt levels. The instrument was successfully employed during the second field campaign of the MLO Photochemical Experiment.

2. Experimental

A diagram of the analytical system is shown in Fig. 1. Ambient air was drawn through a sampling line (6.4 mm O.D. PTFE-lined stainless-steel tubing; Alltech, Deerfield, IL, USA) at a flow-rate of about 5 l min^{-1} from a sampling port located 9 m above ground. A PTFE-coated glass fiber filter (Pallflex T60A20, Putnam, CT, USA) was used as an inlet filter to exclude particulates from air sampled. The sampling line was wrap-

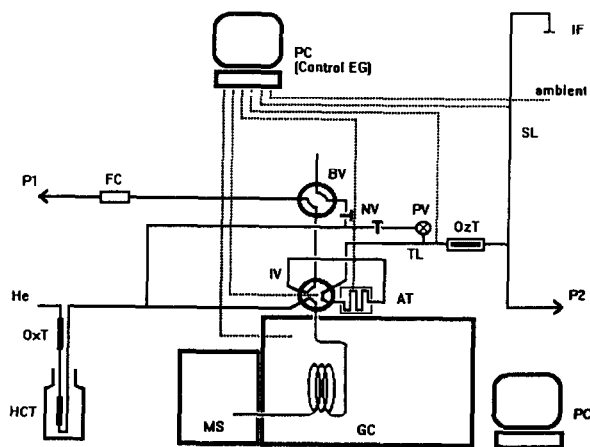


Fig. 1. Plumbing diagram of the automated GC-MS system. AT = Adsorbent trap; BV = backflush/sampling valve (4-port, 0.25 in., Valco, Houston, TX, USA); Control EG = CONTROL EG software; FC = mass flow controller; GC = Hewlett-Packard 5980 gas chromatograph; HCT = hydrocarbon trap (SGE, Austin, TX, USA); He = helium carrier gas and purge gas; IF = inlet filter; IV = injection valve (6-port, 0.125 in., Valco); MS = Hewlett-Packard mass-selective detector 5971A; NV = needle valve; OzT = ozone trap (Baxter, McGaw Park, IL, USA); P1 = sampling pump; P2 = sampling line pump; PC = personal computer; PV = purge valve (0.25 in. stainless-steel bellows shut-off valve, NUPRO, Willoughby, OH, USA); SL = sampling line; TL = transfer line. Monitored temperature zones are indicated by dotted lines. Temperature controlled zones were the adsorbent trap, injection valve and transfer line.

ped with 22-gauge (i.e., cross-section 0.35 mm^2) PTFE insulated wire, ceramic fiber insulation and aluminum foil and heated to 15°C above ambient temperature by passing a low-voltage high current (approximately 10 V/5 A) through the PTFE wire. The heating of the sampling and transfer line reduced possible sample carryover for more sticky compounds.

Part of the main flow was directed through an oxidant scrubber and a 30 cm long transfer line (same material as the sampling line). The oxidant scrubber was used to selectively remove ozone in order to reduce possible artifact formation from reactions occurring on the adsorbent bed during sampling. We used potassium iodide (5 cm \times 6.4 mm O.D. PTFE-lined stainless-steel tubing filled with KI-coated glass wool [20]) in some of our experiments.

The sample air was then passed through the sampling trap, which was filled either with a single solid adsorbent or a combination of different solid adsorbents. Flow-rates through the adsorbent trap depended on the dimensions of the trap and the adsorbent used. Coarse adsorbent grain sizes (20–40 mesh = $420\text{--}840 \mu\text{m}$) were used to allow high sampling flow-rates. Adsorbents used in this study were Tenax TA porous polymer (20–35 mesh = $500\text{--}840 \mu\text{m}$, Alltech), Tenax GR (20–35 mesh, Alltech), Carbotrap (20–40 mesh, Supelco, Bellefonte, PA, USA), Carbotrap C (20–40 mesh, Supelco) and Carbosieve S III (60–80 mesh = $180\text{--}250 \mu\text{m}$, Supelco). The hydrophobic properties of these selected adsorbents prevent the trapping of excess water while they allow the trapping and thermal release of organic gases over a wide volatility range. The capacity of solid adsorbents increases with decreasing temperature. Therefore, cooling the traps during sampling increases the sampling efficiency, particularly for lighter compounds. The lowest possible temperature is limited by the dewpoint of the sampled air, because the trapping of water interferes with the following GC analysis. The sampling-trap temperatures selected were determined empirically and controlled at 5°C below ambient temperature for Tenax GR and Tenax TA. The charcoal-based adsorbents showed a somewhat higher affinity for water and had to be controlled at about 5°C above ambient temperature. Further characteristics of each of the individual adsorbents used in our experiments have extensively been described in the literature [12,16,21–26] and will not be further detailed here. Adsorbent traps were made from 45 cm \times 3.4 mm O.D. and 30 cm \times 6.4 mm O.D. tubing, coiled into a spiral and tightly inserted into a low-mass brass cylinder (7 cm length \times 3.5 cm diameter, 0.5 mm wall thickness). The adsorbent was held in place by small silanized glass wool plugs on either side. Typical maximum flow-rates were in the range of 200 to 400 ml min^{-1} for the 3.2 mm O.D. tubing traps and about 400 to 800 ml min^{-1} for the 6.4 mm O.D. tubing traps. A mass-flow controller downstream of the adsorbent trap insured that the flow through the trap was maintained con-

stant. The flow-rates used to sample ambient air were set to about 80% of the maximum possible flow-rate.

Heating of the adsorbent trap was provided by a 240 W heating wire (Watlow Electric, St. Louis, MO, USA) soldered onto the outside of the brass cylinder. Cryogen (liquid nitrogen) was sprayed into the cylinder through a nozzle made of 0.25 in. (1 in. = 2.54 cm) stainless-steel tubing, in which approximately 40 holes (1 mm diameter) were drilled. A throttle valve was incorporated into the cryogen line to adjust the cryogen flow. The power of the trap heater was regulated by an adjustable resistor. This system allowed the trap temperature to be controlled within a range of about $\pm 2^\circ\text{C}$ at both the cooled and heated setpoints. The controllable temperature range for the sampling trap was from -175 to 325°C .

A purge valve in front of the adsorbent trap allowed purging the trap with helium. The total helium flow was 0.5 l min^{-1} higher than the sampling flow-rate and consequently helium would flow in both directions through the transfer line with the excess flow being backflushed into the sampling line. The helium purge was initiated at the end of the sampling step to remove any oxygen remaining from air sampled prior to the thermal desorption procedure. A backflush valve downstream of the injection valve allowed the backflushing of the entire adsorption system and the transfer line between sampling periods. All tubing and fitting materials in contact with the sample were made either from PTFE, PTFE-lined or -coated stainless-steel or fused-silica-coated stainless steel (Restek, Bellefonte, PA, USA). For additional purification, the carrier, backflush and purge gases (He, 99.9995%) were passed through an oxidant trap and then through a hydrocarbon trap, which was immersed in liquid nitrogen. A Hewlett-Packard 5980 GC system and an HP 5971A mass-selective detector were used for GC separation and detection.

The enrichment system was fully automated and computer controlled by an IBM AT personal computer which was equipped with an internal analog input/digital output board (part CIO-DAS08, ComputerBoards, Mansfield, MA,

USA) and an external analog multiplexer (CIO-EXP16) and an external relay board (SSR-Rack24). It was operated by CONTROL EG software (Quinn-Curtis, Needham, MA, USA). A scheme showing the computer-controlled zones and devices is also given in Fig. 1. A total of up to 22 analog input channels are available, six of which were used for temperature measurements. Monitored temperature zones included the ambient air inlet, sample adsorbent trap, GC oven, injection valve, transfer line and the main sampling line. Ten of the possible 24 output channels were used for the control of the backflush valve, injection valve, purge valve, injection valve heater, injection valve cooling (fan), transfer line heater, main sampling line heater, trap heater, trap cryogen valve and remote GC-MS start. Temperature-programmed zones included the adsorbent trap, transfer line and injection valve. The transfer line and injection valve were kept at room temperature during sampling and heated during sample transfer and in the backflush mode to reduce sample carryover.

The sequence and operating parameters of a typical sample and analysis cycle is shown in Table 1. It consists of different stages for sampling preparation, equilibration time, sampling, injection, trap purge and GC analysis-trap backflush. During sampling, the trap temperature was adjusted with respect to ambient temperature. The trap setpoint was recalculated and reset every 1 min using ambient temperature as an input value. For thermal desorption, the gas sampling valve, which contained the sample trap instead of a sample loop, was switched into the inject position to backflush the contents of the trap onto the analytical column. Typically, the trap was heated at a controlled rate of $25^\circ\text{C min}^{-1}$ to allow elution of lower boiling compounds at lower temperatures. Concurrent with the heating of the trap, the injection valve temperature was raised from ambient to 50°C . This strategy allows early eluting compounds to pass through the injection valve while it was at lower temperature, therefore minimizing thermal cracking artifacts. The GC-MS start signal was sent about 6 min before the thermal desorption start to allow cooling of the GC oven (negative

Table 1
Analysis sequence with typical parameters used during the field study (2 h sampling time)

	Analysis step						
	Sampling preparation	Sampling	Analysis preparation	Trap purge	Sample transfer	Analysis	Conditioning
Sampling valve	Sampling/ backflush	Sampling/ backflush	Sampling/ backflush	Sampling/ backflush	Injection	Sampling/ backflush	Sampling/ backflush
Backflush valve	Backflush	Sampling	Sampling	Sampling	Backflush	Backflush	Backflush
Purge valve	Closed	Closed	Closed	Open	Closed	Closed	Closed
Adsorption trap temperature	↓ Ambient ± x ^a	Ambient ± x	Ambient ± x	Ambient ± x	↑ Maximum desorption temperature at 20°C min ⁻¹	Maximum desorption temperature + 25°C	Maximum desorption temperature + 25°C
Injection valve temperature	↓ Ambient	Ambient	Ambient	Ambient	↑ 50°C	50°C	50°C
Transfer line temperature	↓ 25°C	25°C	25°C	25°C	↑ 75°C	75°C	75°C
GC oven temperature	150°C	150°C	↓ -60°C	-60°C	-60°C	↑ 200°C at 6°C min ⁻¹	150°C
Typical time	10 min + 3 min equilibration	115 min	5 min	0.5 min	10 min	45 min	75 min

↓ = Down to; ↑ = up to.

^a The adsorbent trap sampling temperature was kept at a constant offset to ambient temperature (see description in text).

temperature ramping to -60°C) from its standby temperature of 150°C. During the thermal desorption the GC oven was kept at low temperature to cryofocus desorbed VOCs onto the column head. The trap was kept at the maximum desorption temperature (typically 275°C) for 5 min, after which the injection valve was switched back to the backflush position and the temperature program was started.

3. Results and discussion

The enrichment system was employed during a six-week field experiment at MLO in July and August 1992. Atmospheric measurements at the observatory site during nighttime downslope flow are usually characteristic of maritime free tropospheric air and show very low concentrations of VOCs [27]. The analysis of a 22.5-l sample

collected with the GC-MS system is shown in Fig. 2. This sample was collected with a KI ozone trap and using a multiadsorbent trap containing 0.7 ml Carbotrap C, 1.2 ml Carbotrap and 0.3 ml Carbosieve S III. These adsorbents were arranged in order of increasing sampling capacity, with the weakest adsorbent (Carbotrap C) on the trap inlet side. GC separation was performed on a 60 m × 0.32 mm DB-1 (0.25 μm film, J & W) column. The oven temperature was held at -60°C for 10 min during desorption and then raised to 200°C at a rate of 6°C min⁻¹ and then held at 200°C for 5 min. Peak identifications for the illustrated chromatogram are given in the figure caption. The retention time values given represent the time elapsed from the GC-MS start signal and include the time needed for oven cooling and thermal desorption. For comparison the chromatogram of a 22.5-l blank sample is also included in Fig. 2 (plotted at 10 × the

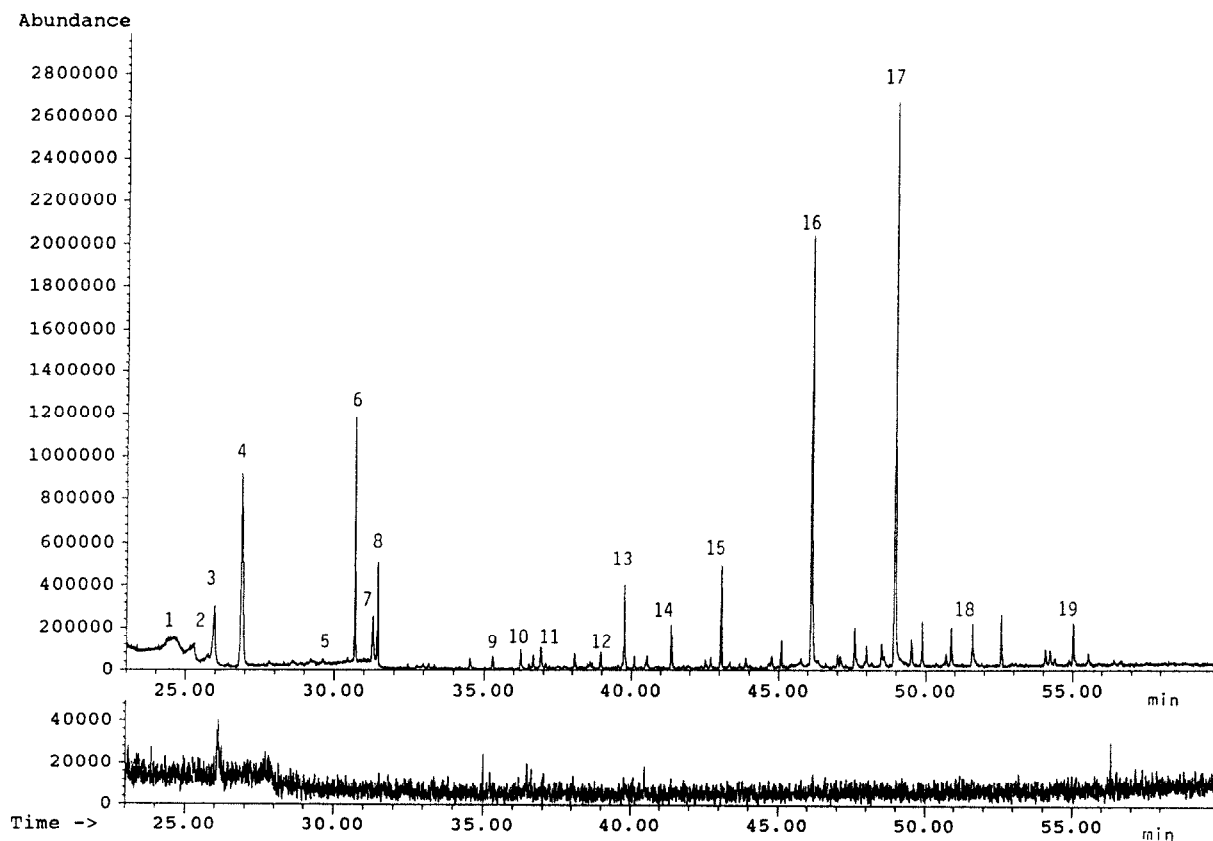


Fig. 2. GC-MS chromatogram of a 22.5-l (normalized to 20°C and 1013 mbar) ambient air sample collected at Mauna Loa Observatory from 14 h 17 min to 15 h 24 min on August 1, 1992. Major peaks: 1 = trichlorofluoromethane (F-11); 2 = acetone; 3 = dichloroethene; 4 = 1,1,2-trichloro-1,2,2-trifluoroethane (F-113); 5 = chloroform; 6 = 1,1,1-trichloroethane; 7 = benzene; 8 = tetrachloromethane; 9 = toluene; 10 = hexanal; 11 = tetrachloroethene; 12 = *m/p*-xylene; 13 = heptanal; 14 = benzaldehyde; 15 = octanal; 16 = nonanal; 17 = decanal; 18 = undecanal; 19 = 6,10-dimethyl-5,9-undecadien-2-one. The trace below the sample chromatogram shows the analysis of a 22.5-l liquid nitrogen blowoff sample (plotted at 10-fold amplification).

amplification of the sample chromatogram). The blank sample was simulated by collecting the blowoff of a liquid nitrogen cryogen dewar. The cryogen blowoff was cleaner than available zero air and was therefore also used in addition to zero air as a test gas for blank experiments. The blank sample was collected through the inlet stack and analyzed under the same conditions as the sample.

From the comparison of concurrent quantitative measurements of selected hydrocarbons by GC-flame ionization detection (FID) [28] and halogenated compounds by GC-electron-capture detection (ECD) [29,30] made at the same site, the achievable detection limit can be estimated.

Measurements made near the time of the sample collected in the chromatogram illustrated in Fig. 2 gave ambient air concentrations of approximately 274 ppt trichlorofluoromethane (F-11), 9.7 ppt chloroform, 146 ppt 1,1,1-trichloroethane, 8.3 ppt benzene, 105 ppt tetrachloromethane, 1.8 ppt toluene and 2.9 ppt tetrachloroethene. Assuming no compound loss during sampling, thermal desorption, sample transfer and chromatographic separation, these concentrations at the collected sample volume of 22.5 l for the GC-MS sample correspond to compound amounts in this sample of approximately 38 ng ($270 \cdot 10^{-12}$ mol) F-11, 1.2 ng ($9.7 \cdot 10^{-12}$ mol) chloroform, 20 ng ($150 \cdot 10^{-12}$ mol)

1,1,1-trichloroethane, 0.65 ng ($8.3 \cdot 10^{-12}$ mol) benzene, 16 ng ($110 \cdot 10^{-12}$ mol) tetrachloromethane, 0.17 ng ($1.8 \cdot 10^{-12}$ mol) toluene and 0.48 ng ($2.9 \cdot 10^{-12}$ mol) tetrachloroethene. The mass spectra of all listed compounds showed sufficient signal-to-noise ratios for peak identification in the scan mode. Fig. 3 shows as an example the mass spectrum of the toluene peak at a concentration of about 1.8 ppt from the sample chromatogram. The computerized library search for this spectrum gave toluene as the best fit with an agreement quality of 78%. From this comparison it can be concluded that this enrichment/injection GC-MS system allows MS identifications of certain VOCs down to ca. 10^{-1}

ng or ca. $1 \cdot 10^{-12}$ mol. For sample sizes of up to 100 l this is equivalent to ambient concentrations of sub-ppt levels. In practice, however, detection limits of individual compounds depend on a number of parameters including trapping efficiency, recovery during thermal desorption and sample transfer and possible compound losses through decomposition. Also, with our instrument, which did not have flow-controlled carrier gas, the MS sensitivity changed during the temperature programmed chromatographic run because of the decrease in source pressure at higher oven temperatures. Further important parameters affecting the sensitivity are the ionization yield and the fragmentation pattern.

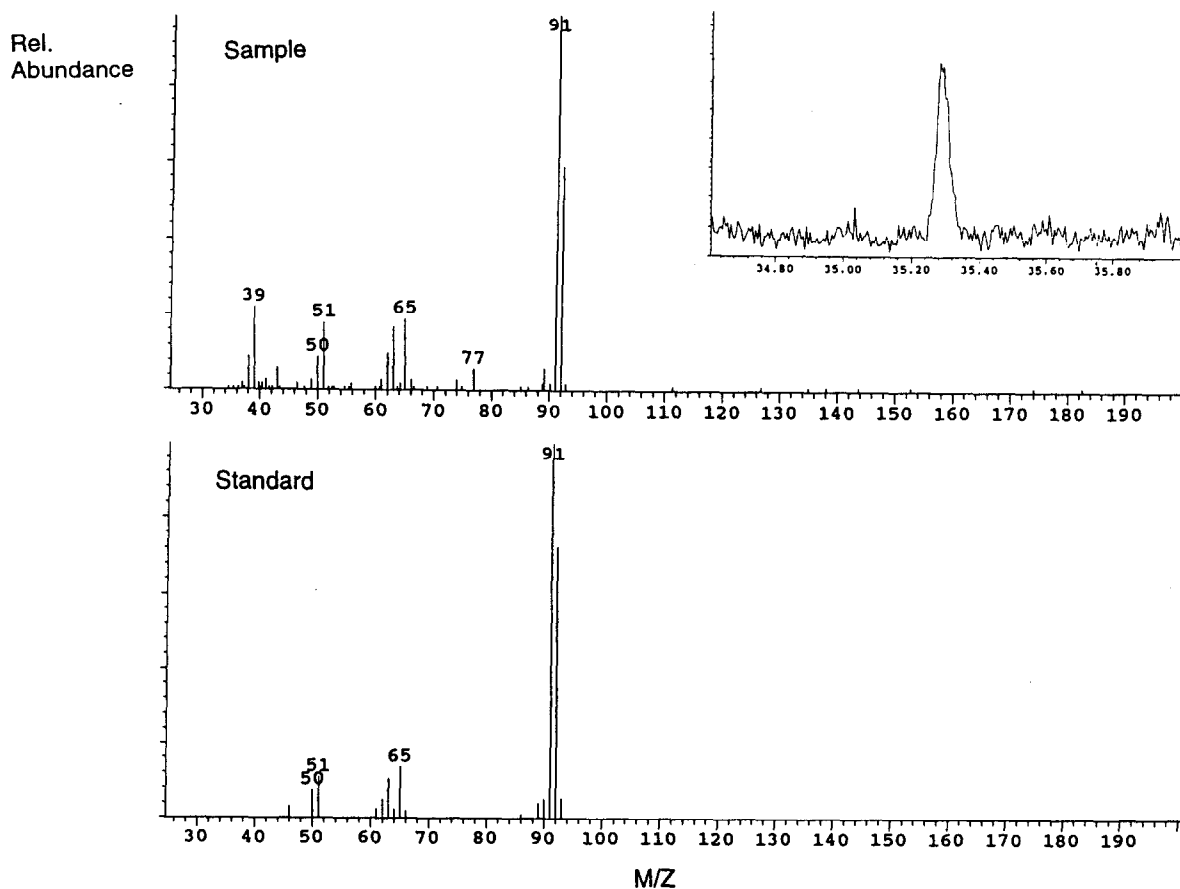


Fig. 3. Mass spectrum obtained from the toluene peak at an ambient concentration of ca. 1.8 ppt (peak number 9 in Fig. 2). The upper spectrum is the sample spectrum and the average of 3 scans around the peak maximum after background subtraction. The insert in the upper spectrum is an enlargement of the total ion current peak. For comparison the toluene standard spectrum from the National Bureau of Standards Library is plotted underneath. Signals below m/z 45 are not included in the standard spectrum.

Chlorofluorocarbons (CFCs), for example, show very distinct mass spectra and can generally be identified with higher sensitivity than hydrocarbons such as alkanes or alkenes. Depending on the scan range (usually above m/z 32 or 44 to reduce signals from air leaks) compounds with low mass fragmentation signals, such as methanol, acetaldehyde or acetone cannot be identified as sensitively because of the lack of or low intensity of molecular ions and fragmentation signals above the lower scan threshold.

The experimental design successfully avoided several common sampling and chromatographic problems. System contaminants were efficiently removed and sample carryover from previous runs was minimized by having the sample trap and transfer line backflushed between samples at higher temperatures than during sampling and desorption. The sample had to pass through only one switching valve, which reduced potential sources of contamination and kept sample loss to a minimum. Oxidant traps reduced artifacts, which can be formed during sampling by reactions with prior adsorbed compounds or with the solid adsorbent itself. KI traps used for ozone removal have been shown to be efficient O_3 scrubber. We found evidence for possible artifact formation (alkyl iodides) from the use of these traps during some of our experiments. These results and alternative ozone trap systems will be discussed elsewhere [31].

About 60 organic trace gases were identified in the course of this experiment using a variety of different solid adsorbents and sampling conditions [32]. The range of compounds that could be analyzed depended on the adsorbents used and the chromatographic conditions. The earliest eluting compounds identified from all adsorbents were F-11, acetone and isoprene, with GC retention indices near 500 (DB-1). The heaviest compounds identified were in the elution range of pentadecane (retention index 1500). The charcoal-based adsorbent traps used showed significantly higher trapping efficiency for lighter compounds than Tenax TA and Tenax GR (elution range approximately from acetone to methylchloroform). The breakthrough volumes of compounds in this elution range are too low to

allow quantitative trapping on Tenax at the temperatures and sample volumes used. The widest range of compounds could be analyzed using the multi-adsorbent trap system described above.

The lower compound range is also limited by the parameters used during thermal desorption and sample transfer: the relatively slow heating rate during the thermal desorption causes individual species to be eluted onto the column over a period of several minutes. At -60°C oven temperature compounds more volatile than F-11 are, therefore, not cryofocused as a sharp band on the GC column used in this study. Peak broadening, as observed for the earliest eluting peaks in Fig. 2, reflects this effect. In order to widen the compound range for lighter compounds a stronger column phase or a second stage trap, kept at lower temperatures until flash heated, is required. The inclusion of a rapidly heated second stage, however, has the potential of introducing blanks and artifacts through compound decomposition during the fast heatup and from contamination by the additional components. We are currently developing a two-stage injection system, where the sample is transferred from the solid adsorbent trap to a cryogenically cooled, low-volume freezeout trap (deactivated 0.53 mm I.D. fused-silica tubing), which then is rapidly heated for sample injection onto the GC column. We have already found that, using the multi-adsorbent trap system, compounds down to the range of propane can be analyzed with this arrangement.

Among the tested solid adsorbents, Carbotrap, Carbotrap C and Carbosieve S III were found to be the most resistant to degradation artifacts from the adsorbent itself. Signals identified in blank runs were from hexamethyltrisiloxane (column bleed) and occasionally small amounts of F-11. The Tenax TA/GR adsorbents showed some significant artifact formation. Major artifacts identified here were benzaldehyde, acetophenone, phenol and benzonitrile. Also, small amounts of *n*-aldehydes (C_9 and C_{10}) and occasionally compounds with signals at m/z 220/205 (tentatively identified as alkylated phenols) were identified in zero air

blank runs, but it could not be determined if these compounds were residual contaminants in the zero air or if they were formed on the adsorbent. The identified Tenax artifacts are consistent with previous reports in the literature. These reports indicate that Tenax is prone to chemical degradation and aging effects [6,33–38].

The sample chromatogram shows relatively high levels of *n*-aldehydes. A series of experiments were performed to confirm the compound identity (determination of retention indices on three different column phases and analysis of *n*-aldehyde standards) and also to investigate whether or not these *n*-aldehydes were system contaminants (blank runs with liquid nitrogen blowoff and purified zero air). It has previously been shown that *n*-aldehydes can be formed artificially on Tenax, in particular during the sampling of ozone-enriched air [35,36]. However, we found *n*-aldehydes in approximately equal relative abundance and distribution from all adsorbent systems we tested. Furthermore, we did not find a substantial change in the pattern during removal of the ozone trap. The GC–MS measurements were also consistent with parallel measurements on a separate GC–FID instrument. On the GC–FID instrument sample preconcentration was performed by cryogenic trapping on glass beads and the same aldehyde species and the same pattern and relative abundances were observed [28]. From these observations we conclude that it is unlikely that the aldehydes observed were adsorbent or system contaminants. The measurements made here are also consistent with reports in the literature, where the same *n*-aldehyde species and similar relative abundances were observed [39,40]. We are planning more future research on the occurrence of the *n*-aldehydes and will detail this discussion more extensively in a following publication.

The experiments performed at MLO were solely of a qualitative nature and compound quantifications were performed with two GC–FID systems operated at the same site [28]. No quantitative GC–MS measurements were performed due to the lack of low-concentration

calibration standards for most of the identified species. Among the different trapping systems tested, the multi-adsorbent trap containing Carbotrap C, Carbotrap and Carbosieve S III gave the best results because of the wide compound range that could be trapped and analyzed and the low levels of observed blanks and artifacts.

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