Application Note No. 021

In-Situ Field Measurements of Isoprene, Its Oxidation Products and Selected Monoterpenes in a Eucalyptus Forest

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Abstract

In-situ field measurements of isoprene, methacrolein (MACR), methyl vinyl ketone (MVK) and selected monoterpenes have been taken in a Portuguese eucalyptus forest. Samples were collected on to a sorbent trap, and analysis was performed on site using a programmed temperature vaporisation injector (PTV) to produce a rapid desorption of analytes from sorbent trap on to a wide bore gas chromatography (GC) column. Using this method no intermediate cryofocusing step is required, eliminating the need for cyrogenic coolants. The high flow rate of helium over the sorbent trap during the GC analysis rapidly reconditions the trap which is ready be to be reused at the end of the analytical programme. Using a single sorbent trap ambient biogenic compound concentrations from the forest canopy were monitored every 70 minutes, over a 5 day period.

1.Introduction

Isoprene and monoterpenes have long been identified as being of considerable atmospheric importance (Fehsenfeld 1992, Jacob 1988) and many systems and methods for collecting and analysing these natural biogenic emissions currently exist (Shreffler 1993, Almasi 1993, Farmer 1994). Isoprene is a major hydrocarbon emission from biogenic sources, and laboratory studies suggest that it is oxidized in the atmosphere to number of products including MVK and MACR (Grosjean 1993). The collection of samples on sorbent traps is widely used as a convenient and easy method for sampling volatile organic compounds (VOC) in ambient air in both urban (Ciccioli 1992, Kruschel 1994) and rural (Ciccioli 1993) environments. Analysis of collected samples is then generally performed by desorption and subsequent sample refocusing on a cryogenically cooled trap (liquid nitrogen, carbon dioxide (Mattinen 1992) or Peltier effect (Woolfenden 1993) before introduction into an analytical column.

For sustained on-site analysis in remote areas however. the use of liquid nitrogen (the most common cryogenic coolant), presents considerable practical difficulties. Storage and transport of samples back to a laboratory for analysis also has inherent problems of sample degradation and formation of by-products. This paper describes on-site field measurements of isoprene, methacrolein (MACR), methyl vinyl ketone (MVK) and selected monoterpenes have been performed in a Portuguese eucalyptus forest. It is demonstrated that the intermediate refocusing step is made unnecessary if the sample is collected on a Tenax TA/Carbotrap sorbent tube, and subsequently desorbed using a programmed temperature vapourisation injector (PTV) on to a wide bore dimethyl polysiloxane gas chromatography column.

The initial results from an intensive 5 day (3/7/94-7/7/94) on-site monitoring program of ambient eucalyptus forest air from the tree canopy via a sampling tower are presented for illustrative purposes. This work was conducted as part of the European Community Field VOC programme of experiments on biogenic emissions and atmospheric chemistry.

2. Experimental

2.1 Air Sampling.

Samples of ambient air from a eucalyptus forest were collected at the tree canopy height of 16m using a specially constructed sampling tower. The samples were collected in a glass tube (Figure 1) packed with sorbent using a battery powered personal air sampler (SKC). The sample tube (glass 8.1 x 0.11 cm i.d.) was packed with 4.8 mg of Tenax TA (Supelco) and 6.4 mg of Carbosieve S-III (Supelco). Air was sampled at a rate of 15 ml min^{-1} for 15 minutes.

Breakthrough experiments were performed on isoprene (the most volatile component) by placing the sorbent tube in a cryogenically cooled GC oven and connecting it directly to a septum injector and a flame ionisation detector. The breakthrough of isoprene was measured at different tube temperatures from -10°C to 30°C. The retention on the tube was found to be maximized when the tube was cooled to -10°C. Experimentally in the field, the sample tube was placed between two cooling blocks and raised to the correct sampling height in an insulated container. This produced an average tube temperature of
-10°C, at which temperature the breakthrough experiments had shown a maximum possible sample size of 500 ml without losses (Denha 1994). In practice a 225 m1 sample was used, well inside the calculated limits.

2.2 Gas Chromatography

A gas chromatograph (Carlo Erba GC-8000) was positioned in a shelter at the bottom of the sampling tower. The GC was fitted with an Optic 400 (Ai Cambridge) programmed temperature vaporisation injector (Figure 2) and a CO_2 oven cooling unit. This approach has previously been employed to study C_2-C_7 hydrocarbons in urban air samples (Denha 1994). The analytical column used was a 60m, 0.53 mm i.d. 100% dimethyl polysiloxane column with 3µm stationary phase film thickness. Detection was via a flame ionisation detector, with a helium carrier gas at a high flow rate of around 30 m1 min^{-1}. On setting up on site a full calibration for isoprene response was performed, using varying volumes of isoprene taken from a pre-mixed cylinder of 1 ppm isoprene and nitrogen make-up gas (ECM).

Typically field concentrations of isoprene are of the order 1-20 ppb. For a 225 ml sample, the calibration performed covered the region 0.2 ppb (detection limit)-100 ppb and gave a linear response (Figure 3). Responses were checked regularly and a full end calibration was performed which showed no change in response. Response factors for other compounds were calculated relative to isoprene in the laboratory, and these ratios applied when calculating concentrations in the field. Retention times of the other compounds measured were also checked using headspace samples of standard mixtures drawn onto the sorbent tube.

2.3 Analysis Procedure

Following sample collection, analysis was performed immediately. The sample tube was placed in the programmed injector in the place of the blank glass injection port liner. Desorption was performed using a rapid temperature ramp from 30 °C to 240 °C at 16 °C min^{-1}. The helium carrier flow rate over the sample tube sorbent and through analytical column was 28 m1 min^{-1}, and was checked regularly. The analytical temperature program was as follows: 5°C isothermal for 3 mins, 3°C min^{-1} to 50 °C, 6 °C min^{-1} to 200 °C, 20 °C min^{-1} to 240 °C. At the end of the analytical program both the injector and column were returned to 30 °C. Because of the high flow rate of helium and the high injector temperature, the tube was clean and ready to use again at the end of each run. The cleanliness of the tube was also checked periodically by performing a blank injection, which showed no residual compounds remaining on the tube. Using this procedure it was possible to take samples every 70 mins, and analyse for isoprene, oxidation products and selected monoterpenes. The high carrier gas flow rate, important in producing a rapid analysis and sorbent tube re-conditioning, does lead to a reduction in column efficiency. The reduced column efficiency, coupled with a relatively rapid temperature program, produces a compromised separation of some of the monoterpenes, and as a result only well separated monoterpenes such as á-pinene could be quantified with accuracy. With a less rapid analysis time the monoterpene separation can be considerably improved. With a more rapid temperature program, the sampling and analysis time for isoprene and its products only could be reduced to around 30 minutes.

2.4 Monitoring Data

Using the procedure described, ambient air samples were collected at 16 m height every 70 minutes from early morning to late evening every day over a 4 day period, and then continuously over-night for the final fifth day. All analyses were performed immediately on-site minimising possible further sample degradation. A typical chromatogram of isoprene and its products is shown in Figure 4 and a chromatogram of the monoterpenes in Figure 5. Diurnal variations in isoprene concentrations and in the concentrations of its major oxidation products are clearly visible (Figure 6). On the first 4 days of the monitoring period, considerable cloud cover persisted until around 13:00 local time (GMT +2 hours). The subsequent increase in solar flux led to a very rapid increase in the concentration of isoprene, methacrolein and methyl vinyl ketone. The concentration variations of isoprene and its products agree well with results previously reported by other groups measuring in similar locations (Martin 1993).

2. Conclusions

Frequent on-site analysis of biogenic emissions were successfully performed at a remote sampling site using rapid desorption and no intermediate re-focusing step eliminating the need for liquid nitorogen as a cryrogenic coolant. The small amount of sorbent used, coupled with a high injector temperature and high carrier gas flow rate, leads to a rapid tube re-cleaning, allowing the same tube to be used to collect many samples. This eliminates the cost and preparation time of using a new tube for each sample, as well as eliminating the problem of variability in tube, packing density (and therefore sampling rate) that can occur when a different tube is used for each sample.

Immediate on-site analysis reduces the time between sample collection and sample desorption into the GC (in this case it was less than two minutes), helping to minimise any possible degradation of sample. Using the programmed temperature injector, there is potential to develop an automated sampling and analysis procedure, which would allow continuous un-manned monitoring with the minimum of equipment maintenance.

4.Acknowledgements

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5. References

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Figure Captions

Figure 1
Sorbent trap and air sampling apparatus.

Figure 2
Diagram of programmed temperature vapourisation injector unit (PTV).

Figure 3
Field calibration for isoprene response.

Figure 4
Chromatogram showing isoprene MACR and MVK from a sample of ambient air taken from forest canopy.

Figure 5
Chromatogram showing selected monoterpenes, from a sample of ambient air taken from the forest canopy.

Figure 6

Variation of ambient isoprene and its products over a five day period.

Figure 1

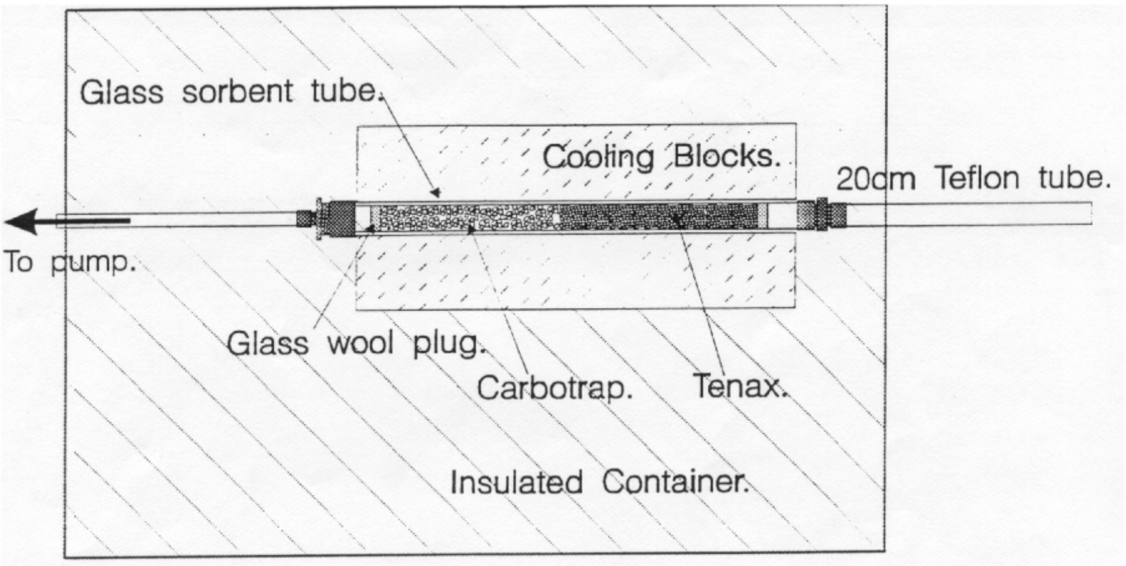


Figure 3

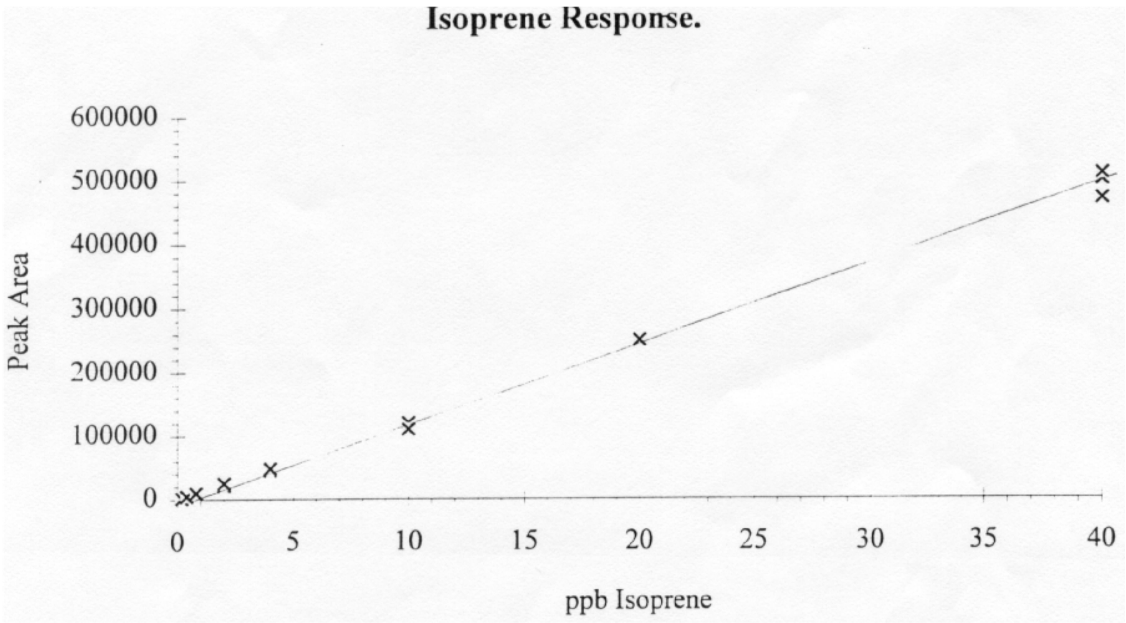
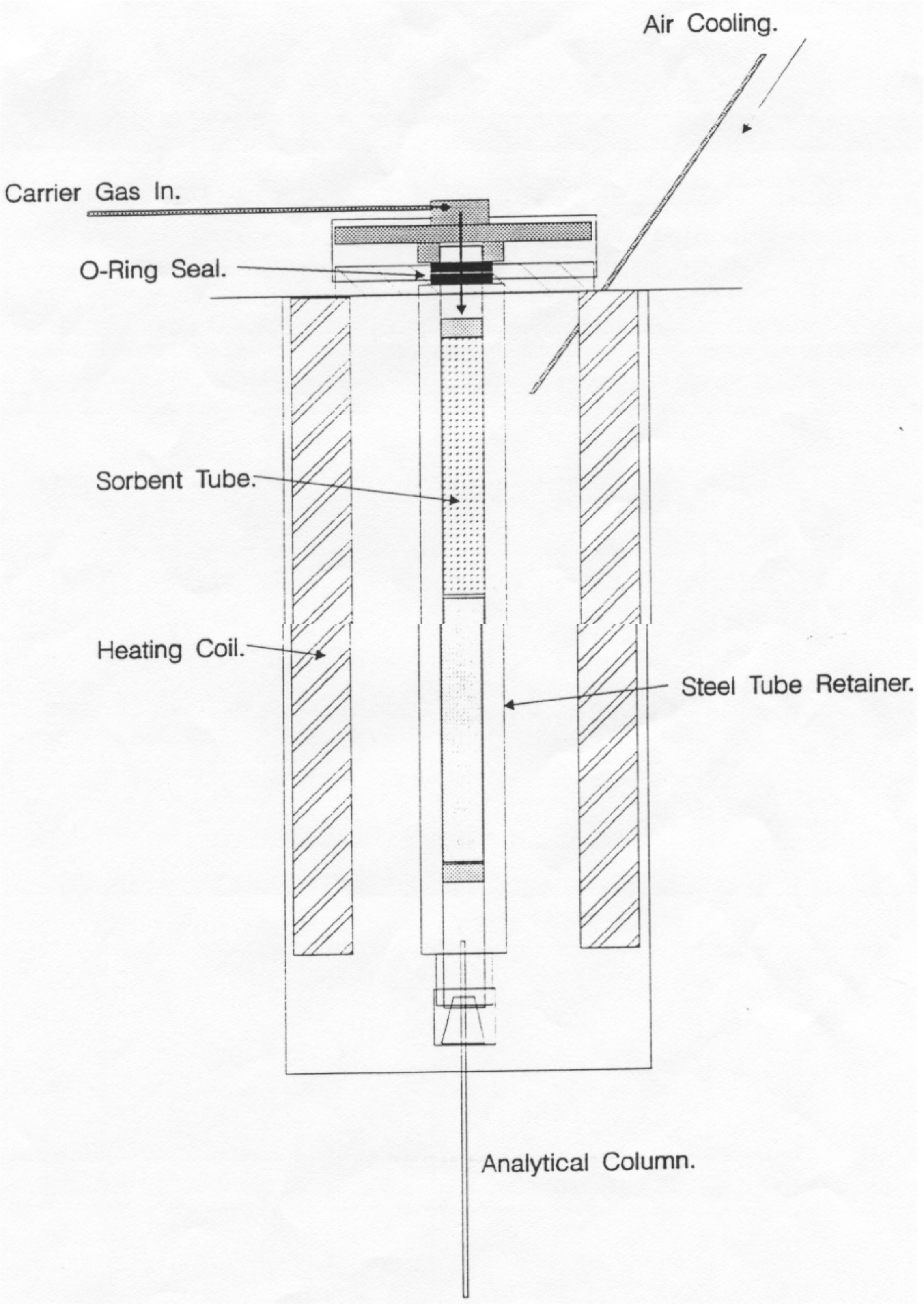


Figure 2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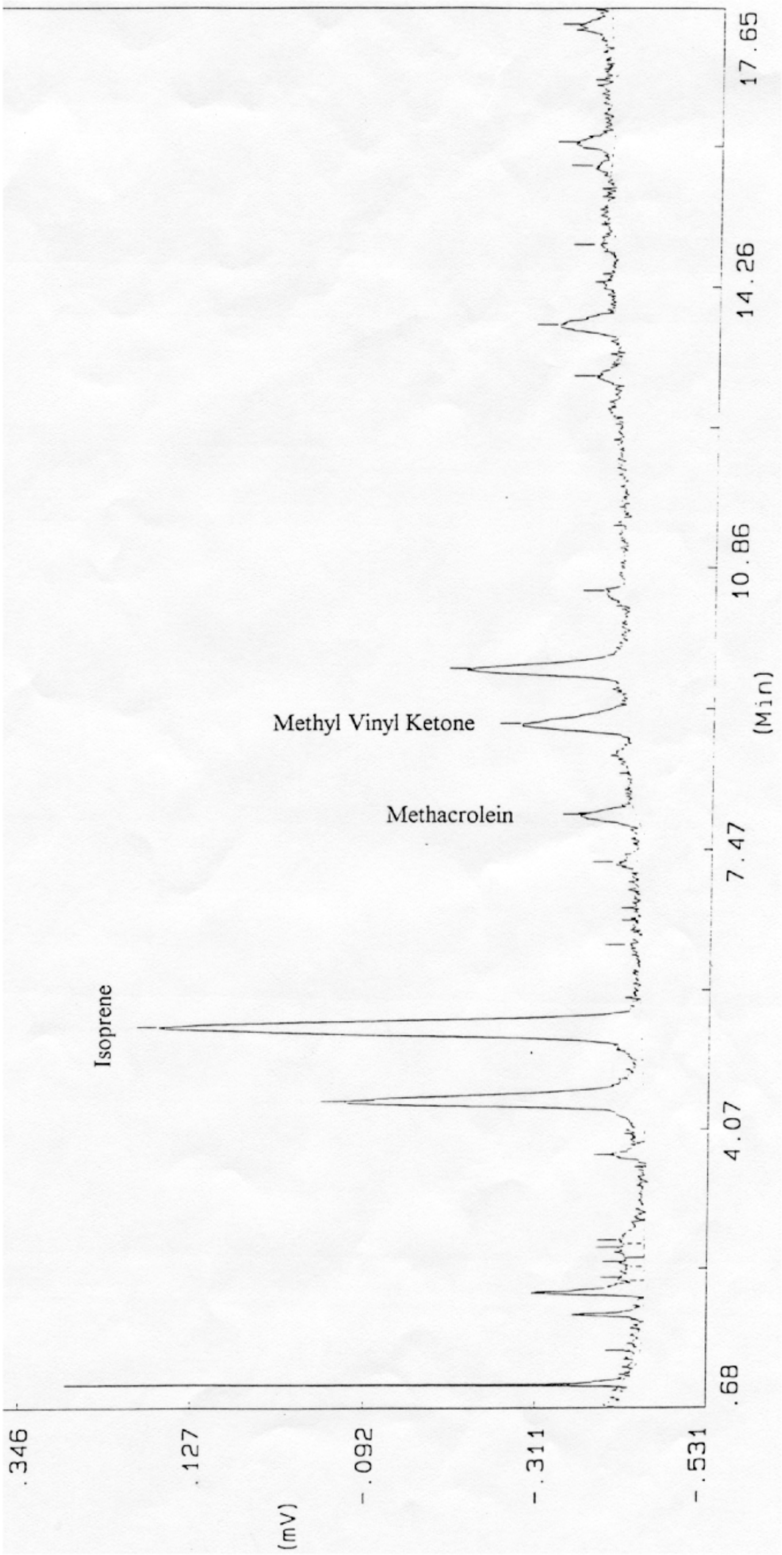
Carrier Gas In.
O-Ring Seal.
Sorbent Tube.
Heating Coil.
Steel Tube Retainer.
Analytical Column.

Figure 4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Methyl Vinyl Ketone
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-.092
-.311
-.531
(mV)
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4.07
7.47
10.86
14.26
17.65
(Min)

Figure 5

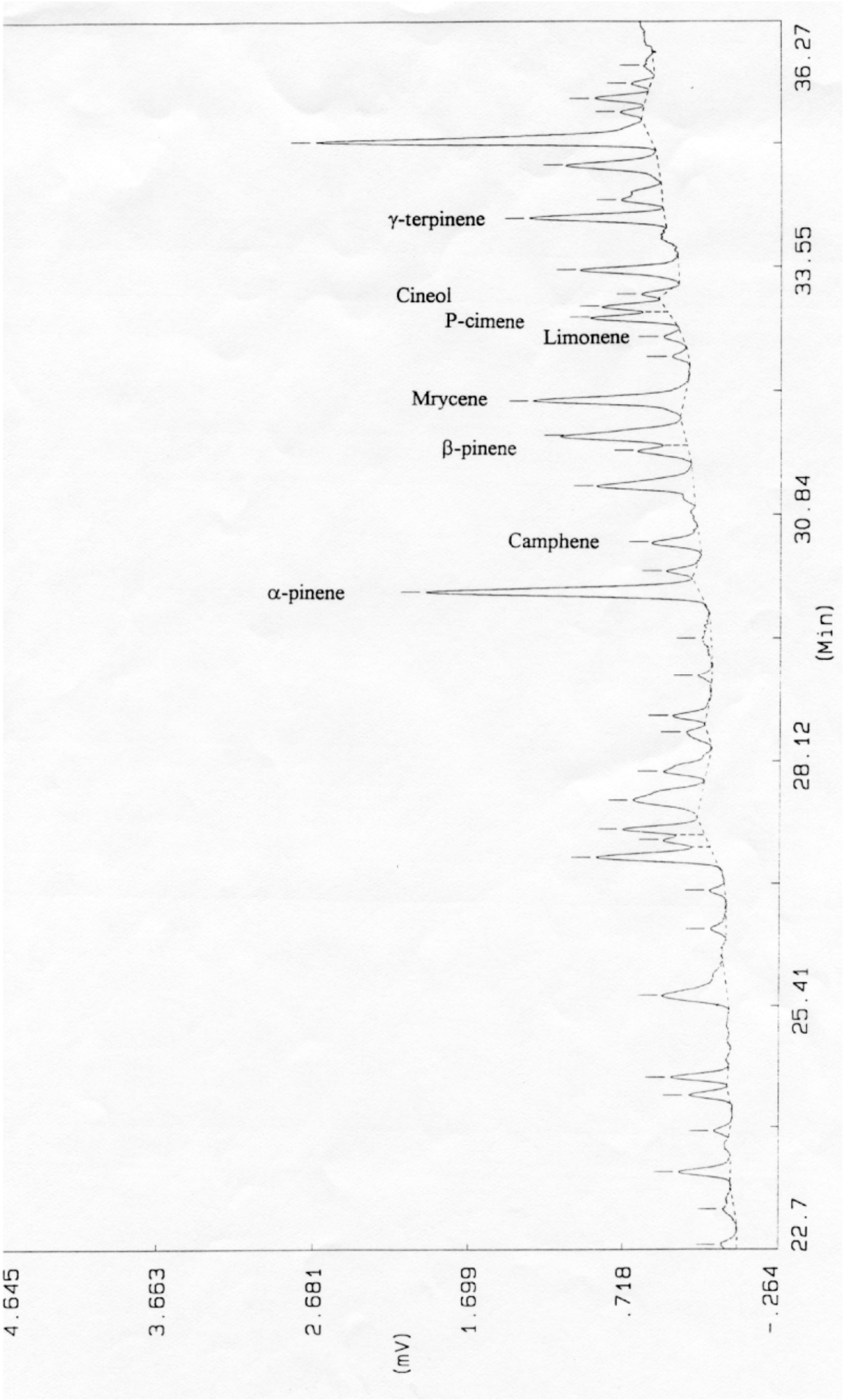
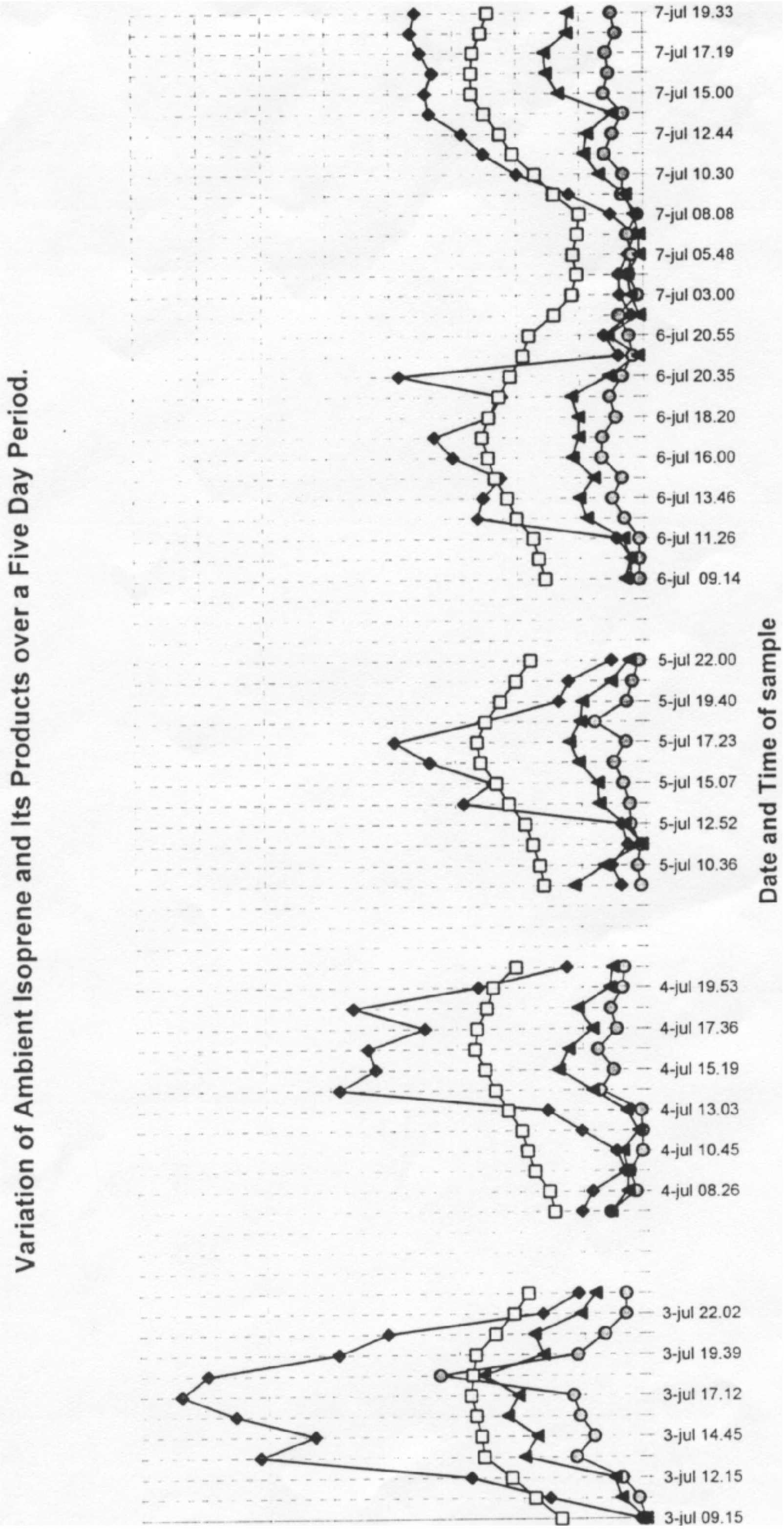

γ-terpinene
Cineol
P-cimene
Limonene
Mrycene
β-pinene
Camphene
α-pinene
36.27
33.55
30.84
28.12
25.41
22.7
(Min)
4.645
3.663
2.681
1.699
.718
-.264
(mV)

Figure 6


Variation of Ambient Isoprene and Its Products over a Five Day Period.
Date and Time of sample
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7-jul 17.19
7-jul 15.00
7-jul 12.44
7-jul 10.30
7-jul 08.08
7-jul 05.48
7-jul 03.00
6-jul 20.55
6-jul 20.35
6-jul 18.20
6-jul 16.00
6-jul 13.46
6-jul 11.26
6-jul 09.14
5-jul 22.00
5-jul 19.40
5-jul 17.23
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5-jul 12.52
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4-jul 19.53
4-jul 17.36
4-jul 15.19
4-jul 13.03
4-jul 10.45
4-jul 08.26
3-jul 22.02
3-jul 19.39
3-jul 17.12
3-jul 14.45
3-jul 12.15
3-jul 09.15