Atmospheric Monitoring of Volatile Organic Compounds Using Programmed Temperature Vaporization Injection

Alastair C. Lewis*, Keith D. Bartle, James B. McQuaid, Michael J. Pilling, and Paul W. Seakins
School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

Peter Ridgeon
Ai Cambridge Ltd., London Road, Pampisford, Cambridge, CB2 4EF, UK

Key Words:

Programmed temperature vaporization injection Volatile organic compounds Isoprene Biogenic emissions

Summary

A method has been developed for the automated determination of C_5-C_{10} and C_2-C_6 volatile organic compounds in urban and rural air, using programmed temperature vaporization injection from a sorbent tube trap. A single activated charcoal sorbent tube was repeatedly used to collect samples of air with trapped VOCs being subsequently desorbed onto either a wide bore dimethyl polysiloxane (C_5-C_{10}) or porous layer open tubular (C_2-C_6) gas chromatography column without use of intermediate cryogenic refocussing. The high flow rates of helium used during the analysis resulted in the sample tube being cleaned and ready to reuse following the analytical separation. Examples of analysis of aromatic VOCs in urban air, and biogenic emissions in rural air, collected in a Sitka Spruce forest are presented. Using this method it is possible to quasicontinuously monitor concentrations of VOCs in locations where high sensitivity *in situ* analysis is required, but where cryogenic coolants may not be readily available or desirable.

1 Introduction

Measurements of atmospheric concentrations of volatile organic compounds are currently required in both urban and rural environments [1,2], where their presence can be directly detrimental to health [3], and their ability to form photochemical oxidants in the presence of NO_x and sunlight is important [4]. Some hydrocarbons may also contribute to global warming and stratospheric ozone depletion and may accumulate as persistent organic pollutants in some environments. Anthropogenic sources of VOCs, which include vehicle emissions, solvent evaporation, and gas leaks, have been extensively studied in an urban environment, and the measurement of UK urban concentrations of VOCs is now performed routinely through the Department of the Environment Hydrocarbon Network. Biogenic emissions of VOCs from plants and trees constitute a significant percentage of all VOC emissions, and are of particular importance when accurate models of the troposphere are to be constructed [5], and information on ambient concentrations and rates of emission are largely unknown for many UK species.

Many methods for analyzing VOCs typically using sorbent traps or evacuated canisters have been proposed, although carbon molecular sieves of differing mesh sizes are particularly effective [6] in trapping VOCs in air and are frequently incorporated into packed sorbent tubes. Analysis is usually performed by thermally desorbing the collected sample from its sorbent trap over a period of several minutes onto a cryogenically cooled intermediate trap [7-9]. The sample is refocused in the intermediate trap prior to subsequent flash heating, thus introducing the collected analytes as a narrow band onto the analytical column. Previously described refocusing methods have included the use of carbon dioxide [10] and the Peltier effect [11]; however, the single most common cryogenic coolant used is liquid nitrogen. A method based on a thermally desorbed adsorption trap and cryorefocusing with liquid nitrogen is currently used in the UK Department of Environment Hydrocarbon Monitoring Network [12]. Whilst manual use of liquid nitrogen can be limited to the order of only a few liters per day, automated systems such as the one described above use typically 50 liters of coolant per day.

Placing a sorbent tube trap as an injection port liner inside a programmed temperature vaporization injector allows rapid desorption of analytes directly into an analytical column. Using a wide bore analytical column it is possible to rapidly transfer analytes from sorbent tube to column, where, at lower temperatures, the initial stages of the separation then produce sufficient refocusing to produce well resolved peaks. Using this method the traditional intermediate refocusing between desorption and separation is no longer required. Denha *et al* (1994) described previously how a PTV injector could be used in conjunction with a porous layer open tubular column for the determination of C_2-C_7 hydrocarbons using off-line sampling methods [13]. Similarly, Lewis *et al* (1995) described the use of PTV for *in situ* measurements of biogenic emissions and oxidation products, also using an off-line sampling technique [14]. This paper describes the use of online sorbent tube trap sample collection, with programmed vaporization injector (PTV) for the analysis of samples collected in both urban and rural environments. The automation of sample collection and the elimination of the intermediate refocusing step, reduces much of the necessary on-site maintenance required for continuous monitoring, and allows *in situ* analysis in locations where this was not previously possible.

2 Experimental

2.1 *Air Sampling and Analyte Trapping.*

Quantities of zero air (2500 Zero Air Unit, Packard Instruments, CT, USA) were spiked with known amounts of selected VOCs and held in Tedlar bags (SKC Inc., PA, USA). These samples were used as standards for calibration, and calculation of breakthrough volume along with a 27 component pre-mixed cylinder of VOCs at the ppb level (NPL, Middlesex, UK). Neither source

of standard showed any sign of degradation over the 2 week period required for calibration.

A glass injection port liner (88.1 mm L x 3.5 mm i.d.) was filled with 30-60 mesh activated charcoal produced from coconut husks (Phase Separations Ltd., Deeside, UK). This type of adsorbent has been reported previously [15] to have a surface area of roughly 1070 m^2g^{-1}.

The sorbent tube was held inside the PTV injector, with a glass lined capillary T-piece placed at the outlet of the sorbent tube, providing a split to either analytical column or sampling line. **Figure 1** shows the analytical apparatus used, set in 'sample analyze' position. Samples of air were drawn either from the atmosphere or from standard bags at a flow rate of 60 ml/min, using a personal air sampler pump (SKC, USA). The pump reduced the pressure at the head of the sorbent tube, resulting in the sampled air being drawn up through the sorbent trap. On completion of sampling a pneumatically actuated 6 port valve (Valco, USA) was used to switch the air flow from the sorbent tube leaving it isolated ready for desorption. The sample inlet line was connected to a length of 1 0 µm i.d. fused silica capillary column so that when the valve was in 'analyze' position, a positive flow of carrier out of the sample line was maintained. To improve trapping retention of volatile species during sampling, the sorbent trap was cooled using small quantities of CO_2, the temperature being thermostatically controlled by the PTV unit using a pneumatically actuated needle valve (SGE, Milton Keynes, UK) regulating CO_2 flow through a stainless steel restrictor. Using this apparatus it was possible to regulate the trap temperature down to temperatures as low as -50 °C.

2.2 *Analysis*

Analysis was performed by desorbing the collected analytes from the sorbent tube into the analytical column using an OPTIC 400 PTV injector (Ai Cambridge, UK). With the trap at -10 °C, the air was purged from the trap using the carrier gas for 30 s, following this the carrier flow was diverted away from the trap as before. Desorption took place via rapid heating of the port liner, from -10 °C to 400 °C at 16 $°s^{-1}$. On reaching maximum desorption temperature, the carrier flow (20 mL min^{-1} helium (6.0 Grade, Distillers MG, UK)) was diverted through the tube via a second pneumatically actuated 6 port valve (Valco, USA). The second switching valve controlling carrier flow also contained an internal standard loop and injection port. Known volumes of calibration could be added to the internal standard loop between runs for quantitative validation. Volatile calibration species, gave the best peak shape on desorption, whereas heavy species added to the top of the tube were often significantly broadened. The pause before allowing the carrier to flow resulted in much improved peak shape, particularly for C_{6}-C_{10} species due to desorption being eliminated as a limiting step for the introduction of a narrow sample band into the analytical column-

A Carlo-Erba GC8000 with flame ionization detection was used in conjunction with a 60 m, 0.53 i.d. 100% dimethyl polysiloxane column with 3 µm film thickness (RTX-1 Thames Chromatography, UK) for the separation of C_5-C_{10} species, and with a 50 m x 0.53 mm i.d. Al_2O_3 Porous Layer Open Tubu1ar (Chrompack, Belgium) column doped with Na_2SO_4 and 10 µm film thickness, for the separation of C_2-C_6 compounds. The flow rate of carrier gas through sorbent tube and

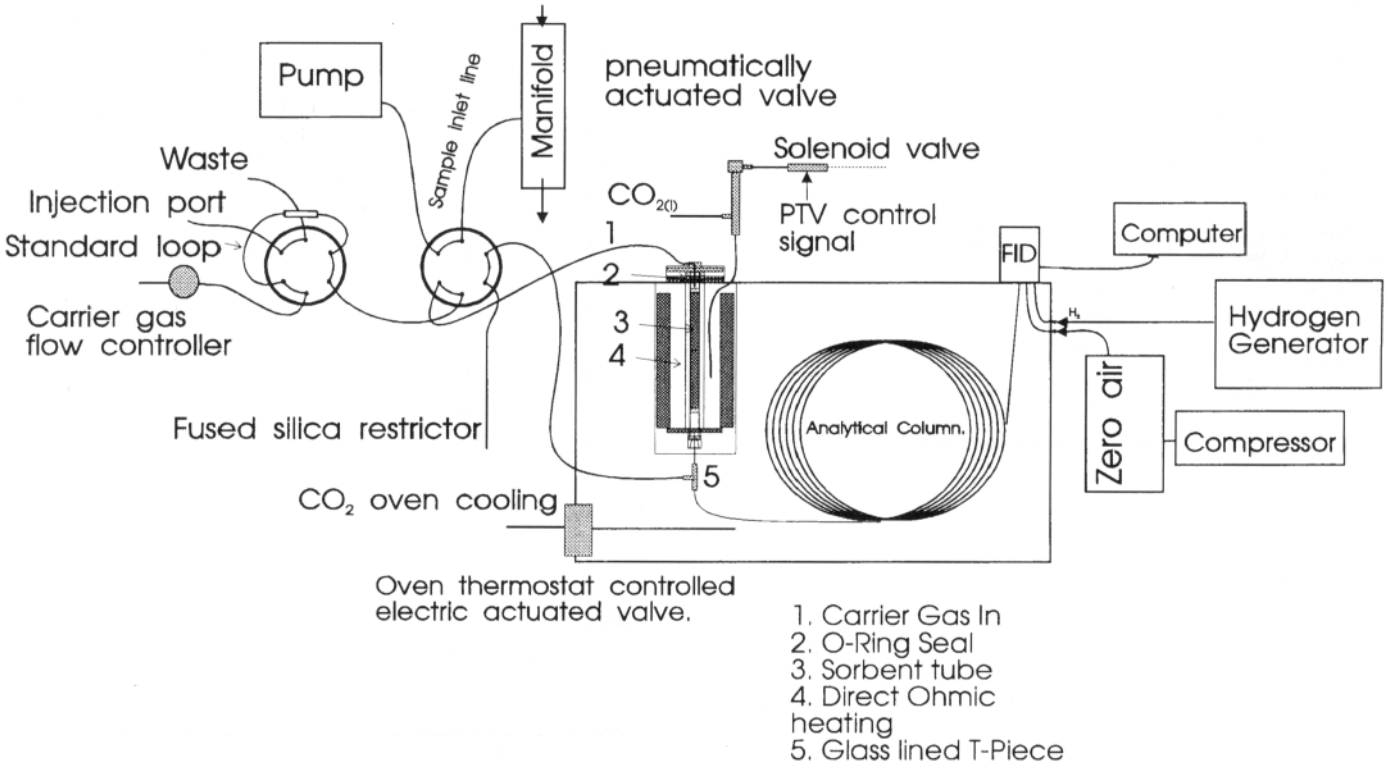

Figure 1. Auto PTV in 'analyze' configuration.

column was established as 20 mL min^{-1}. Whilst this high flow rate is beyond the Van Deemter optimum, it produces a sufficiently good separation and at the same time is high enough to clean the trap ready for the next sample.

Detection was by a flame ionization detector (FID), with compressed air supply (Jun-Air 200, Norresundby, Norway) cleaned using a zero air unit, (Mode1 2500 Packard, USA) and hydrogen produced by gas generator (Model 9200 Packard Instruments, USA).

2.3 *Sample Breakthrough Volumes*

Maximum sample sizes were established for selected VOCs using standard mixtures in zero air, held in Tedlar bags. Samples of differing volumes were drawn onto the sorbent trap via the process described above, and the maximum sample size established from the point where increases in trapped analyte ceased to be linear. **Figure 2** shows the effectiveness of trapping ethane, propane, butane, pentane, and hexane for increasing volumes of 100 ppb spiked zero air, sampled at 60 mL/min, with the sorbent trap held at -10 °C. The plot clearly shows that the quantities of all species trapped on the sorbent bed remain close to the theoretical values up to sample volumes of around 1200 mL for the most volatile species ethane. At this point it is clear that the trap is no longer retaining 100% of the ethane being loaded, and by 1800 mL the quantities of ethane retained on the tube have almost reached an equilibrium. Brown and Pumell [16] defined a safe sampling volume as approximately 50% of the retention volume, so for real samples, a maximum sample size of between 500 and 1000 mL must be applied. In practice, a sampling volume of 600 mL was used typically for urban measurements, well inside predicted limits.

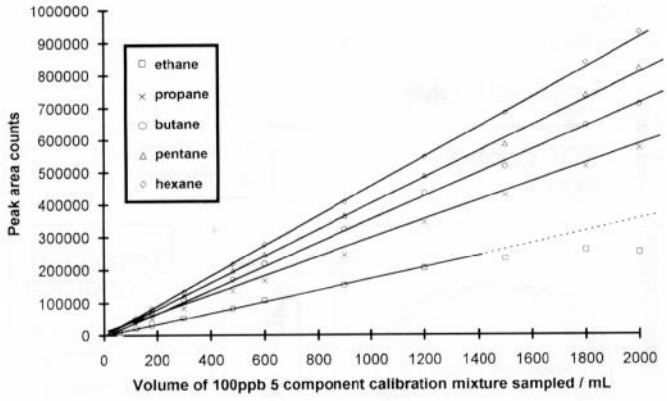

Figure 2. Sampling loading curves @ -10 °C.

With the sorbent trap set at -10 °C ethane was found to be the most volatile species that could be quantitatively analyzed. By lowering the trap temperature further, it is possible to increase the maximum safe sampling volume, particularly for the most volatile species; however water vapor traps must then be used.

Alternative adsorbents to activated charcoal can be used for the quantitative trapping of the C5-C10 species, with Tenax TA in particular having been used successfully with this system for analysis of these species.

2.4 *Samples of* C5-C10 *Hydrocarbons in Urban Air*

600 mL samples of urban air were collected directly from a University building overlooking a busy road, using an inlet manifold connected to the sampling device described earlier. Separation was performed on the RTX-l column described earlier. A temperature program of 5 °C for 1 min followed by 3 ° min^{-1} to 130 °C, followed by 15 ° min^{-1} to 220 °C was used for the separation. The low start temperature used for this program was to enable isoprene to be analyzed successfully. Using a start temperature of 35 °C and a similar ramping rate hexane was found to be the first compound that could be successfully separated.

Compound identification was via a combination of information gained by direct injection of standard mixtures, use of the multi-component standard cylinder and identifications made by the desorption of similar samples (Fisons TD5000) into a 0.33 *μm* i.d. 100% dimethyl polysiloxane column, with quadrupole mass spectrometer (Trio VG 1000) detection. A typical chromatogram is shown in **Figure 3,** with 38 VOCs positively identified in the sample. With a sample size of 600 mL the practical detection limit was typically 50-100 ppt for each species. Due to the high flow rate of helium and high injector temperature the tube was clean and ready to reuse after each analytical separation; this cleanliness was checked periodically by the redesorption of the tube following cooling.

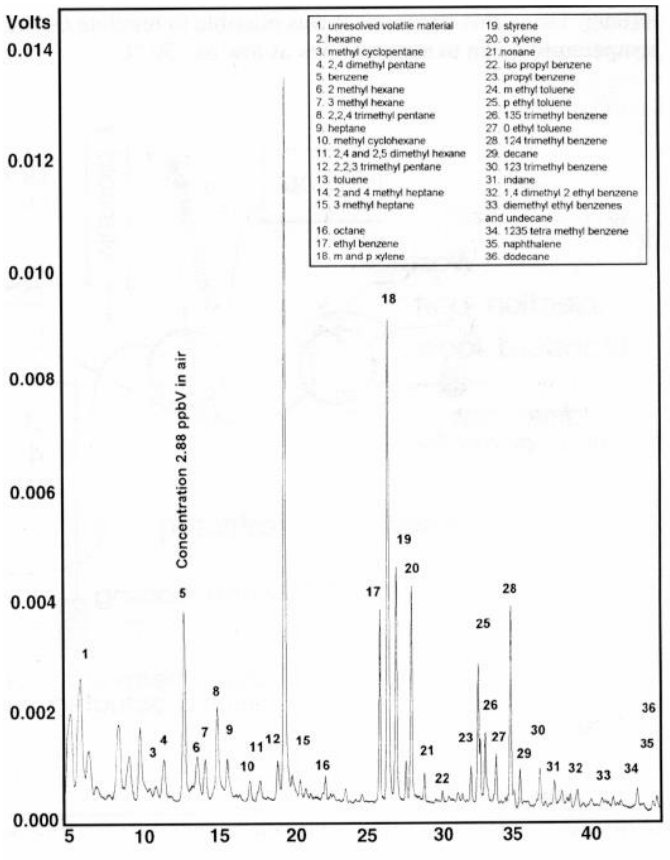

Figure 3. C5-C10 species in urban air.

Figure 2. Sampling loading curves @ -10 °C.

With the separation of C_{6}-C_{11} species taking 40 min, 5 min for rapid heating to clean the column, 5 min for oven cooling, and 10 min for actual air sample acquisition, hourly VOC monitoring for 38 species is possible using this instrument.

2.5 *Samples of C_{2}-C_{6} in Biogenic Emissions*

Possibly the single most important biogenic species is 2-methyl-1,3 butadiene (isoprene), which is emitted by many species of trees such as oak, poplar, cotton wood, eucalyptus, and many pine species. The measurement of this compound and its oxidation product much current research effort is focused on [17-19]. Many methods for collecting ambient rural air samples exist, some based on the collection of compounds on a sorbent bed, others using evacuated canisters, however almost all involve the storage and transport of samples back to the laboratory, for analysis [20]. The reactivity of isoprene however, makes any delay between sampling and analysis extremely undesirable, and *in situ* analysis is the ideal method for monitoring biogenic concentrations.

Kielder forest is one of the largest expanses of woodland in Britain covering 50000 hectares stretching from Northumberland into the Scottish borders. Over 70% of the forest is Sitka Spruce, a non-indigenous species originating from Alaska and North America. This species of tree is known to emit isoprene in its native environment; however levels of emission in the UK climate are unknown. The sampling site was situated in the east of the forest (grid ref. NY 740895) on a raised elevation at 320 m. The trees surrounding the site were between 8-12 years old and of the Sitka spruce variety. The site was some 3 km from the nearest road, and there was no significant habitation in the surrounding area.

Samples of ambient air were collected at a height of 10 m using a specially constructed sampling tower and manifold system. The manifold was constructed from 16 mm i.d. glass tubing, connected to a vacuum pump (Edwards 1.5). At the bottom of the manifold, sample nozzles were placed into the air stream, and from here connected to each instrument by Teflon tubing. Concentrations of NO, NO2, CO, and ozone were monitored using commercial analyzers (Advanced Pollution Instrumentation, USA) to measure the extent of anthropogenic emissions in the area, and their data logged by RAM cartridge. Meteorological data was obtained at a height of 16 m using a Vector Instruments meteorological station, the data also being logged on a RAM cartridge.

The gas chromatograph system described earlier was housed in a vehicle at the bottom of the sampling tower, and connected to the sample manifold via Teflon tubing. The sample was dried of water vapor prior to passing through the adsorption bed by a 100cm L, 1/8' i.d. Nafion drier (Perma-Pure Inc, USA). Compared to the relatively robust nature of the RTX-1 column, adsorption of water onto the PLOT column radically affects the retention characteristics of the stationary phase, and has to be eliminated as much as possible. A PLOT column was used for the separation of C_{2}-C_{6} hydrocarbons. Sample collection was performed at -10 °C, and desorption took place by an increase in trap temperature from -10 to 400 °C at 16 ° min^{-1}. The analytical temperature program was as follows: 50 °C isothermal for 3 min, 60 C min^{-1} to 200 °C, 200 °C isothermal for 10 min. At the end of the analytical program the oven was returned to 50 °C and

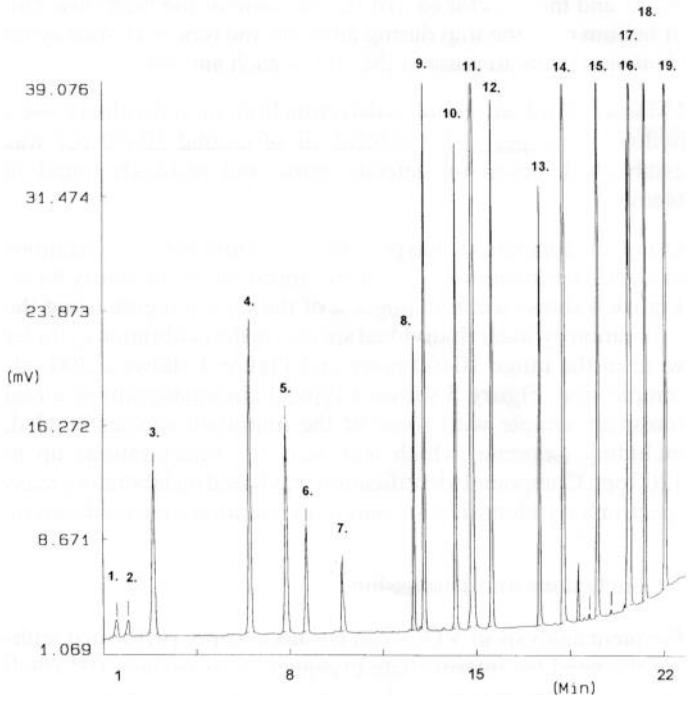

Figure 4. Ethane to isoprene, from 27 component VOC standard cylinder. 1. Ethane, 2. Ethene, 3. Propane, 4. Propene. 5. 2-Methylpropane, 6. Ethyne, 7.n-Butane, 8. *trans-2*-Butene, 9. 1-Butene, 10. cis-2-Butene, 11. 2-Methybutane, 12. n-Pentane, 13.1,3-Butadiene, 14. *trans-2*-pentene, 15. cis-2-Pentene, 16. 2-Methyl pentane, 17. 3-Methylpentane, 18. n-Hexane, 19. Isoprene.

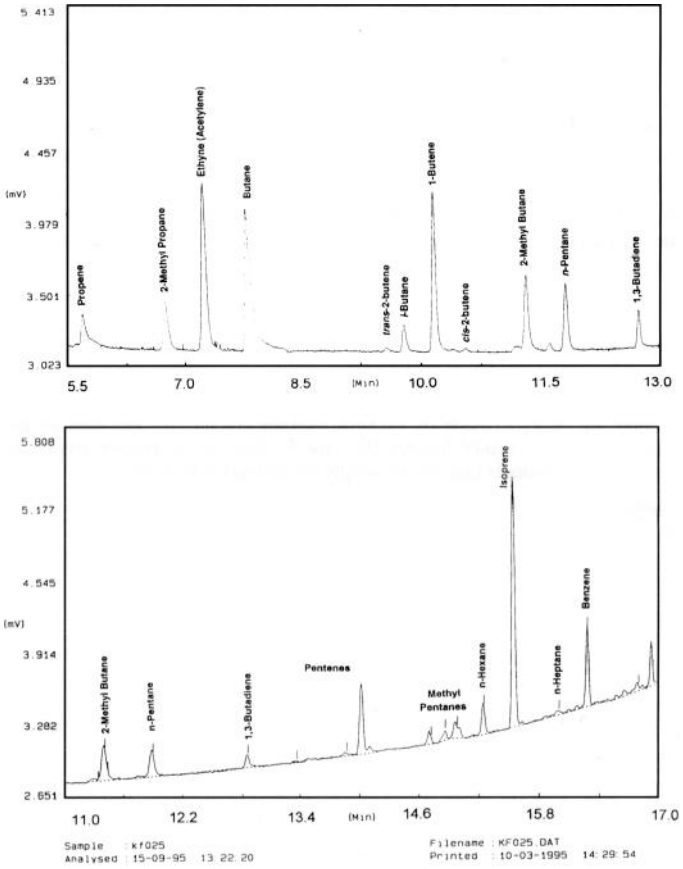

Figure 5. Chromatogram of Sitka Spruce forest air.

the injector to -10 °C. Because of the high flow rate of helium over the trap during analysis, the tube was once again clean and ready to reuse at the end of each analysis.

Using a 600 mL air sample a detection limit for individual C_2-C_6 hydrocarbon species in ambient air of around 50-70 ppt was established, based on detector noise and residuals found in blanks.

Using this apparatus it was possible to monitor the concentrations of C_2-C_6 hydrocarbons in ambient forest air on an hourly basis. **Figure 4** shows a chromatogram of the C_2-C_6 region using the calibration cylinder. Individual species in the calibration cylinder were in the range 10-60 ppbv and Figure 4 shows a 200 mL sample size. **Figure 5** shows a typical chromatogram of a real forest air sample with some of the important species labeled, including isoprene, which was seen in concentrations up to 1200 ppt. Compound identification was based on laboratory mass spectrometry identification and field retention time calibration.

3 Conclusions and Discussion

Frequent analysis of VOCs can be successfully performed without the need for intermediate cryogenic refocussing. The small amount of sorbent used for the trap coupled with the high injector temperature and carrier flow rate leads to a rapid recleaning of the sorbent tube, allowing the same tube to be used to collect many samples. This eliminates the considerable 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. The immediate *in-situ* analysis helps to minimize any possible degradation of sample, a particular problem when sampling for reactive species such as isoprene. The simplification of the apparatus compared to previously described instruments allows the possibility of continuous un-manned monitoring in remote or inaccessible locations. With supply gases of hydrogen and air being supplied by gas generators, the instrument requires only cylinders of CO_2 and He for operation making it also ideal for operating in a mobile laboratory .

Acknowledgments

We would like to thank Mr G. Gill of Forest Enterprise UK for forestry access permission, Dr P. Mertens of Packard Instruments Inc. for the loan of gas generators, Mr J. Torp of Jun-Air USA Inc for loan of compressor and Dr G. Ferrier of Air Products Ltd. for the supply of calibration mixtures.

References

[1] C.W. Sweet and S.J. Vermette, Environ. Sci. Techno1. 26 (1992) 165.

[2] R.A, Hadey, and G.R., Cass, Environ. Sci. Technol. 28 (1994) 88.

[3] EPAQS, Expert Panel on Air Quality Standards. Benzene. HM Stationary Office (1993).

[4] PORG, Ozone in the United Kingdom, Department of the Environment, London, UK (1993)

[5] M.E. Jenkin, I.R. Pomeroy, R.G. Derwent, S.M Saunders,. and M.J. Pilling, Tropospheric Chemistry Modelling. AEA report no. AEA/CS/18360008/002 (1995).

[6] S.J. O'Doherty, P.G. Simmonds, and G. Nickless, J. Chromatogr. 630 (1993) 264.

[7] C. Ciccoli, A. Cecinato, A. Brancaleoni, M. Frattoni, and A.Liberti, J. High Resol. Chromatogr. 15 (1992) 75.

[8] B.D. Kruschel, R.W. Bell, R.E. Chapman, M.J. Spencer, and K.V. Srnith, J. High Resol. Chromatogr. 17 (1994) 187.

[9] S.A. Montzka, M. Trainer, P.D. Goldan, W.C. Kuster,andF.C. Fehsenfeld, J. Geophys. Res 98 (1993) 1101.

[10] M.L. Mattinen and 0. Maria, Proc. 14th Int. Symp. on Cap. Chromatogr., Baltimore, Maryland, USA (1992), pp. 307-314.

[11] E.A. Woolfenden, G.M. Broadway, P. Higham, and I. Seely, Proc. Int. Conf. on VOC in the Environment, London, UK, October (1993), pp. 321-329.

[12] J. Derwent, P. Durnitrean, J. Chandier, T.J. Davies, R.G. Derwent, G.J. Dollard, M. Delaney, B.M.R. Jones, and P.D. Nason, AEA Technology, Culham, UK Report No. AEA/CS/I 8358030/005 (1994).

[13] A.M. Denha, K.D. Bart1e, and M.J. Pilling, Anal. Proc. 31 (1994) 297-300..

[14] A.C. Lewis, P.W. Seakins, A.M. Denha, K.D. Bartle, and M.J. Pilling, Atmos. Environ. 29 (1995) 1871-1875.

[15] B. Camel and M. Caude, J. Chromatogr. 710 (1995) 3-19.

[16] R.H. Brown and C.J. Purnell, J. Chromatogr. 178 (1979) 79

[17] D. Grosjean, E.L. Williams II, and E. Grosjean, Environ. Sci. Technol. 27 (1993) 830-840.

[18] R.S. Martin, H. Westberg, E. Allwine, L. Ashman, J. Farmer, and B. Lamb, J. Atmos. Chem. 13(1991) 1-32.

[19] F. Fehsenfeld, J. Calvert, R. Fall, P. Goldan, A.B. Guenther, C.N. Hewitt, B. Lamb, S. Liu, M. Trainer, H. Westberg, and P. Zimmerman, Global Biogeochem. Cycles 6 (1992) 389-430.

[20] B.D. Kruschel, R.W. Bell, R.E. Chapman, M.J. Spencer, and K.V. Srnith, J. High Resol. Chromatogr. 17 (1994) 187-190.