Application Note No. 027

A Simplified Method for the Determination of Atmospheric Hydrocarbons

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Key Words: Gas chromatography, Programmed temperature vaporisation injection, Volatile organic compounds.

Abstract

An instrument has been developed for the automated *in situ* determination of airborne C_1-C_6 and C_5-C_{10} volatile organic compounds using programmed temperature vaporisation injection from a sorbent tube trap. A single sorbent tube placed as an injection port liner can be repeatedly used to collect samples of air, with the trapped analytes being subsequently desorbed onto either a wide bore dimethyl polysiloxane (C_5-C_{10}) or porous layer open tubular (C_1-C_5) gas chromatography column without use of intermediate cryogenic refocussing. High flow rates of helium used during the analysis result in not only a rapid separation, but also a fast recleaning of the sorbent tube making it ready to reuse following the analytical separation. Examples of analysis of a wide range of urban VOCs are presented demonstrating the possibility to quasi-continuously 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.

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 (NOx) and sunlight is important (4). It has also been demonstrated that some hydrocarbons may contribute to global warming and stratospheric ozone depletion and may also accumulate as persistent organic pollutants in some environments. Urban concentrations of VOCs are influenced directly by the emissions from major anthropogenic sources such as vehicle emissions, solvent and petrochemical evaporative losses, gas leaks and many other forms of emission.

Many methods for analysing airborne VOCs have been proposed, typically using sorbent traps or evacuated canisters. Carbon molecular sieves of differing mesh sizes are particularly effective in trapping VOCs in air and are frequently incorporated into packed sorbent tubes. Analysis is usually then performed by thermally desorbing the collected sample in a stream of helium over a period of several minutes onto a cryogenically cooled intermediate trap (6-8). The sample is refocussed at the intermediate trap prior to subsequent flash heating, thus introducing the collected analytes as a narrow band onto the analytical column. Previously described refocussing methods have included the use of carbon dioxide CO_2 (9) and the Peltier effect (10), however the single most common cryogenic coolant used is liquid nitrogen. A method based on a thermally desorbed adsorption trap and cryo refocussing with liquid nitrogen is currently used in the U.K Department of Environment Hydrocarbon Monitoring Network (11), and uses typically 50 litres of coolant per day. Whilst methods involving the cryogenic refocussing of sample produce effective analytical separations, the equipment required is both complex and expensive, and the unit requires regular user attention to replenish cryogen supplies.

Placing a sorbent tube trap as an injection port liner inside a programmed temperature vaporisation (PTV) 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 the 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 refocussing 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 (12). In addition, Lewis *et al.* (1995) described the use of PTV for *in situ* measurements of biogenic emissions, also using both off and on-line sampling techniques (13,14). In this technical note we describe the use of on-line sorbent tube trap sample collection, with programmed vaporisation injector (PTV) for the analysis of samples ambient air samples collected in a city centre environment. The automation of sample collection and the elimination of the intermediate refocussing step, reduces much of the necessary on-site maintenance required for continuous monitoring, and allows *in situ* analysis in locations where previously this was not previously possible.

Experimental.

Air Sampling and Analyte Trapping.

When using sorbent traps for the collection of air samples it is important to first calculate the maximum amount of sample that can be collected without any analyte breakthrough. This was performed using quantities of zero air (2500 Zero Air Unit, Packard Instruments, CT, USA.) 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.)

The sorbent trap itself consisted of a glass injection port liner (88.1 mm L x 3.5 mm i.d.) filled with one of two different types of adsorbent. For the collection of hydrocarbons with a volatility similar to pentane or less Tenax TA is a very effective trapping material, and has been used extensively previously. At a trap temperature of -10°C Tenax TA proved to be an effective reliable adsorbent and was used in the C_5-C_{10} hydrocarbon analytical system. The desorption temperature of Tenax is limited to around 260°C, and in practice, a maximum temperature of 240°C was used

Effective quantitative trapping of species as volatile as ethane is naturally much harder to achieve than for species like benzene. Previously reported traps have included specialist materials such as Tenax GR, Carboseive, Chromosorb 106 and many others. Activated charcoal is also a very good adsorbent for volatile species, and has been often overlooked since it requires very high temperatures for effective desorption. Programmed temperature vaporisation injection however offers the ability to inject at temperatures of 400°C and above, and coupled to a wide bore GC column, the resulting high carrier flow rates produces a desorption as rapid and efficient as any other type of trap. In the C_1-C_6 analytical system a sorbent trap containing around 0.2g of activated charcoal was used (Phase Separations Ltd, Deeside, U.K). Prior to use the trap was conditioned at 400°C for 24 hours with a purge gas flow rate of 30 mL/min.

In both systems, 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 analyse' 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 10 µm i.d. fused silica capillary column so that when the valve was in 'analyse' 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, U.K) regulating CO_2 flow through a stainless steel restrictor.

Separation conditions.

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). Following sample collection, analyte desorption was performed via a rapid Ohmic heating of the port liner, from -10°C to 400°C at 16°C s^{-1}. On reaching maximum desorption temperature, the carrier flow (30 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. The pause before allowing the carrier to flow resulted in much improved peak shape, 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 ionisation detection was used in conjunction with a 60 m, 0.53 mm i.d. 100% dimethyl polysiloxane column with 3 µm film thickness (RTX-1 Thames Chromatography, U.K.) for the separation of C_5-C_{10} species, and with a 50m Al_2O_3 Porous Layer Open Tubular column with 10 µm stationary phase thickness modified with Na_2SO_4 (Chrompack, Belgium) for the separation of C_1-C_6 compounds. The flow rate of carrier gas through sorbent tube and column was established as 30 mL min^{-1} in each case .

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

Sample breakthrough volumes.

The maximum air sample sizes were calculated using selected VOC 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. The results from these tests have been reported elsewhere, however in summary the maximum sample size was established to be around 2000 mL for both Tenax and Activated charcoal traps. Brown and Purnell (15) defined a safe sampling volume as approximately 50% of the retention volume, so for real samples, a maximum sample size of 1000 mL must be applied. In practice. a sampling volume of 400-600 mL was used typically for urban measurements, well inside predicted limits.

With the sorbent trap set at -10 °C pentane and ethane were found to be the most volatile species that could be quantitatively trapped on the Tenax TA and activated charcoal beds respectively.

Methane is unretained by almost all forms of hydrocarbon trap, however can be determined in this system by knowing the volume of port-1iner minus packing material. Since methane concentrations are typically at the ppm level, an injection volume of 1 mL (the volume of the trap) is easily sufficient to give enough analyte for detection.

Sample of urban air.

600mL 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. Analysis of C_5-C_{10} hydrocarbons was performed on the RTX-1 column described earlier. A temperature programme of 5°C for 3 mins followed by 3°C min^{-1} to 115°C, followed by 15°C min^{-1} too 220°C was used for the separation. 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 VG1000) detection. A typical chromatogram is shown in Figure 2, with 38 VOC positively identified in the sample. With a sample size of 600 mL the practical detection limit was typically 30-50 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 re-desorption of the tube following cooling.

With the separation of C_5-C_{10} species taking 40 minutes, 5 minutes for rapid heating to clean the column, 5 minutes for oven cooling, and 10 minutes for actual air sample acquisition, hourly VOC monitoring for 38 species is possible using this instrument.

Analysis of C_1-C_6 hydrocarbons was performed using the same instrument operating with an activated charcoal trap and PLOT column. The analytical temperature program was as follows: 50°C isothermal for 3 mins, 6°C min^{-1} to 195°C, 195°C isothermal for 10 mins. At the end of the analytical program the oven was returned to 50°C and 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 20-30 ppt was established, better than for heavier hydrocarbons due to the narrower peak width produced by the PLOT column.

Using this apparatus it was possible to monitor the concentrations of C_1 to C_6 hydrocarbons on a 45 minute basis. Figure 3 shows a typical chromatogram of urban air in the C_1 to C_6 region.

To check that the desorption is complete, and that there is no residual material remaining on the trap, the sample tube was re-desorbed following the analytical separation. The lower trace on Figure 3, shows the chromatogram produced from the re-desorption of sample tube following the analysis of a normal air sample. The lower trace shows that there is less than 0.1 % of any species remaining on the sorbent tube following initial desorption.

Run to run reproducibility using PLOT columns can prove to be difficult especially if the initial sample contains significant levels of water, which can affect the retention characteristics of the stationary phase. Urban air samples are potentially difficult in this respect, however the inclusion of a 100 cm 1/8" i.d. Nafion permeation drier on the air flow inlet dried the sample sufficiently that even in wet atmospheric conditions, run to run retention time agreement was excellent. From a period of hourly measurements, the chromatograms obtained from the 9am, 1 pm and 6pm samples have been overlaid, and are shown in Figure 4.

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 unsaturated hydrocarbon species such as butanes or isoprene.

The high desorption temperatures available with a programmed temperature vaporisation injector, allows the use of strong adsorptive beds such as activated charcoal, giving increased sample size and less analyte breakthrough. The simplification of the apparatus compared to previously described instruments allows the possibility of continuous unmanned monitoring for periods longer than has been possible previously, and would allow measurements in remote or inaccessible locations. With supply gases of hydrogen and air being supplied by gas generators, the instrument requires few support gases for operation making it also ideal for operating in a mobile laboratory.

Acknowledgements.

The authors wish to thank Ray Perkins and Peter Ridgeon of Ai Cambridge Ltd for much helpful advice and Peter Mertens of Packard Instruments Inc for the loan of gas generators,

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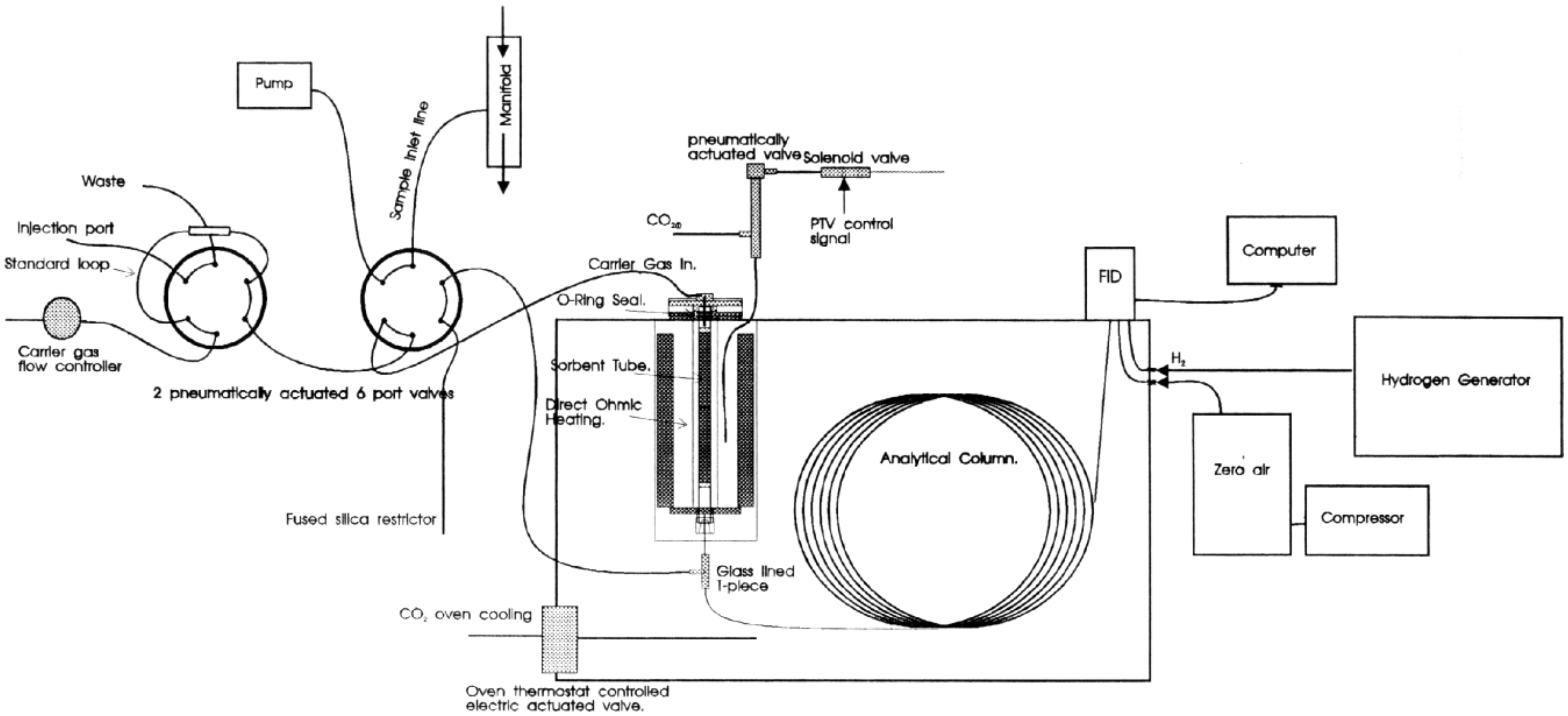

Figure 1. Experimental Apparatus

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Sample : 15C 5sec del
Analysed : 02-06-95 17:31:53

Filename : DELAY3.DAT
Printed : 06-02-1995 17:33:39

[redacted]

1. Methane, 2. Ethane, 3. Ethene, 4. Propane, 5. Propene, 6. 2-Methyl propane, 7. Ethyne, 8. n-Butane, 9. Trans-2-butene, 10. 1-Butene, 11. Iso-butene, 12. Cis-2-Butene, 13. 2-Methyl butane, 14. n-Pentane, 15.1,3 Butadiene, 16. Pentenes, 17. 2-Methyl pentane, 18. 3-methyl pentane,19. n-Hexane, 20. Methyl hexanes and hexenes, 21. Heptane, 22. Methyl cyclopentane, 23. benzene, 24. Toluene.

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