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High-Speed Isothermal Analysis of Atmospheric Isoprene and DMS Using On-Line Two-Dimensional Gas Chromatography

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An instrument has been developed that allows rapid measurements of two of the most important volatile organic species in the atmosphere. The method utilizes twodimensional gas chromatography coupled to a programmed temperature vaporization injector used for sample preconcentration and injection. Attention is paid to the determination of atmospheric concentrations of isoprene (the most reactive hydrocarbon species) and dimethyl sulfide (DMS), the major source of sulfur in the marine troposphere and a precursor to cloud formation. A sorbent packed liner placed inside a programmed temperature vaporization injector was held subambiently by means of a Peltier device during sample collection. Thermal desorption is performed and the analytes passed to a primary column, separating with respect to analyte vapor pressure. Selected linear or "heart-cut" transfer is performed to a second column where the final separation is performed with respect to chemical functionality. Both primary and secondary separations are performed under isothermal conditions with carrier pressure programming used to improve speed of analysis. Primary column backflush and concurrent sample acquisition during the secondary analysis are also used to keep analysis cycle times to a minimum. Total time for sample collection and analysis is around 10 min, with an instrument peak power consumption of 400 W and a minimum detectable limit of 5 ppt for isoprene and 25 ppt for DMS.

Introduction

Improvements in chromatographic resolution by the coupling of separation dimensions have been well documented producing increases in peak capacity of the order $n_1 n_2$, where n_1 and n_2 are the mean peak capacity of the individual dimensions *(1,2)*. The coupling of liquid chromatography to gas chromatography has been the most widely applied hyphenation, notably for the analysis of complex fuel, combustion, and environmental samples, reviewed recently by Kelly and Bartle *(3)*. LC-GC typically uses the primary dimension as an advanced on-line sample preparation step, with the selected fraction transferred via heart-cut to the secondary column *(4)*. This linear form of hyphenation has also been applied in coupled GC-GC *(5-7)*, GC-GC-MS *(8,9)*, and LC-LC *(10)*. In the field of atmospheric chemistry, a recent publication by Schrimpf *et al. (11)* has described a methodology using a heart-cut GC-GC method for the analysis of atmospheric PAN.

True two-dimensional GC-GC has also been extensively reported by Philips and Liu *(12)*, where all components from a primary column are transferred to a secondary column, described as orthogonal coupling. This has been shown to produce extremely high-resolution chromatography, producing unique separations of complex mixtures such as fuels and petrochemicals. Most previously reported applications of 2DGC have placed emphasis on the increases in peak capacity that are possible with both linear and orthogonal coupling as the primary aim. In this paper, the focus is shifted to the increase in speed of analysis that is possible with 2D-GC, while retaining large sample capacity. The sample capacity factor is greatly reduced when narrow bore one-dimensional columns are employed for rapid GC analyses, making them unsuitable for coupling to thermal desorption systems.

Gas chromatography has been used widely in the determination of atmospheric species, and very many automated instruments have been described covering not only hydrocarbon species but also permanent gases such as methane, CO and N_2O *(13)*, CFCs/halocarbon species *(14)*, and many others. Automated GC systems are currently integrated into many national scale monitoring programs such as the U.K. Department of the Environment Hydrocarbon Network *(15)*. Some manufacturing development has produced GC ovens that have lower than normal power consumption; however, oven cooling is still a major time constraint even with the most efficient oven.

The application of 2D-GC described in this paper is in the analysis of two of the more reactive organic species in the atmosphere. Dimethyl sulfide (DMS) and isoprene are two of the most reactive species emitted from marine sources, where their presence in the troposphere has an important effect on clean air OH and NO_3 concentrations [for DMS k_{OH} =6.3 x 10^{-12} molecules^{-1}cm^{3}s^{-1}, k_{NO3} = 9 x 10^{-13} molecules^{-1} cm^3 s^{-1}, and isoprene k_{OH} = 1.01 x 10^{-10} molecules^{-1} cm$_3$ s^{-1}, k_{NO3} 6.78 x 10^{-13} molecules^{-1} cm$_3$ s^{-1} *(16)]*. Concentrations of isoprene in the planetary boundary layer can vary from 10 ppb or higher in Mediterranean forest environments to as low as 1-10 ppt in marine air. The presence, however, of only small concentrations of reactive hydrocarbons such as isoprene in clean marine air may lead to significant OH removal and may contribute to production of peroxy radical species. In low-NO, high-OH (>5 x 10^6 molecules cm^{-3}) conditions, the atmospheric lifetime of isoprene is around 20 min. It is therefore vital that any measurement of this species is performed at a temporal resolution approaching its lifetime in the atmosphere.

DMS is released as a byproduct of compounds used by marine algae to regulate cellular osmotic pressure and is transferred to the atmosphere at the water-air interface as a result of a large concentration gradient. The ambient air concentration of DMS is a product of numerous physical parameters such as pressure, temperature, and wind speed. As a result, there are considerable spatiotemporal variations in its distribution in the marine environment which are currently poorly understood. DMS has also been implicated as a key factor in production of cloud condensation nuclei (CCN) and in turn may have an important effect on climate and meteorology.

Methods of determination involve either off-site analysis using sample canisters *(1 7)* or adsorbent tubes or analyses performed *in situ* using automated GC instruments requiring significant apparatus and electricity. Instruments configured for

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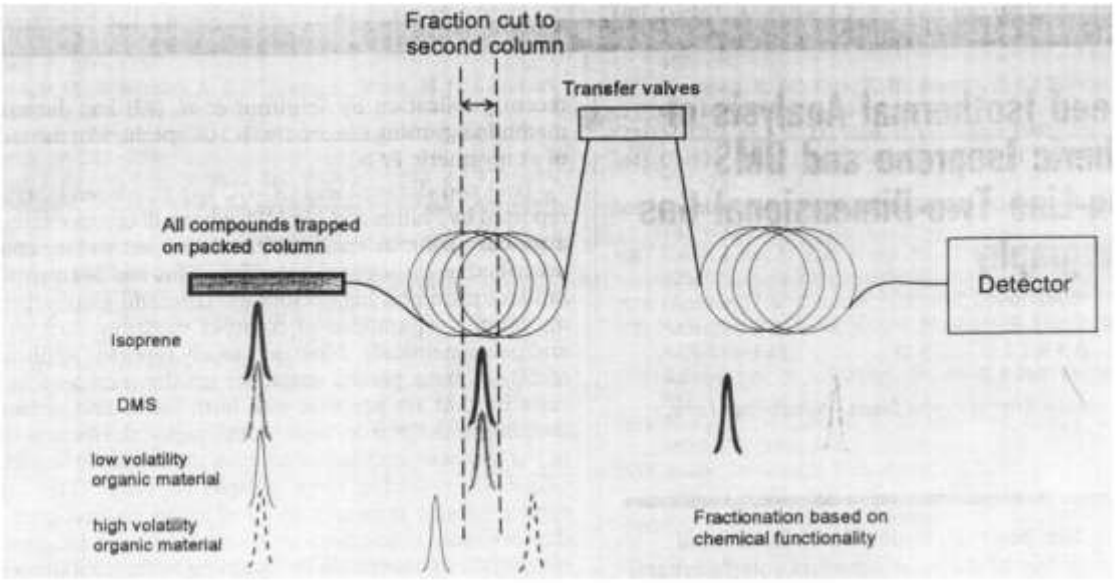


FIGURE 1. Schematic of the PTV-GC-GC separation process.

automated determination of sulfur, based on use of the flame photometric detector (FPD) *(18)*, have been described, however, they give no information on hydrocarbon concentrations. Time resolution is a critical factor when performing these types of measurements since the lifetime of isoprene in the atmosphere may be only 10-15 min under certain high OH concentration conditions. With current one-dimensional temperature programmed automated GC instruments, the best *in situ* time resolution is only around 1 sample/h. Working with this temporal resolution results in measurements being performed on a time scale slower than that of the kinetics of reaction in the atmosphere. For remote site measurements, power consumption is also an important factor, and traditional laboratory GC ovens typically use around 2 kW ac power.

In this paper, a 2D-GC system coupled to a programmed vaporization injector (PTV) is used to perform *in situ* analysis of isoprene and DMS. A primary column is used for a crude vapour pressure/boiling point fractionation of sample. Transfer by heart-cut passes analytes to a secondary column with separation selectivity based on chemical functionality.

Figure 1 shows a schematic of the described separation process. Both columns are held isothermally throughout the separation reducing power consumption by a factor of 10 over temperature-programmed bench top GC. To reduce analysis time, carrier gas pressure programming is used to elute the compounds from the secondary column in minimum time. The primary column is backflushed following the heart-cut, and sample acquisition occurs concurrently during the final stage of the secondary separation. In this way it was possible to perform a complete isothermal analysis/sample acquisition cycle in around 12 min.

Experimental Section

Two in-house-built electric ovens were used for holding primary and secondary columns at independent temperatures. Both were housed inside a single 19 in. equipment rack. The ovens were internally fan circulated and had a set point accuracy of ± 0.2°C. Column outlet from the second oven passed to a home-built flame ionization detector, with connection to a Carlo Erba EL580 electrometer. An in-housebuilt detector heater was used and held the detector body at 250°C.

Sample injection was by programmed temperature vaporization (pm injector (OPTIC 2, ATAS Cambridge, U.K.). The use of PTV injectors to house adsorbent tube traps for online air sample preconcentration has been described elsewhere *(19, 20)*. Activated charcoal packing (200 mg of coconut husk activated charcoal, surface area 1064 m^3/g, Phase Separations, Deeside, Wales) was used inside a wide bore (4.2 mm i.d.) glass liner (80 mm L) as the preconcentration trap. Both ends of the trap were plugged using deactivated glass wool.

Previous studies have shown that sample retention volumes for compounds such as ethane and ethene are limited to around 1.5 L for this type of activated charcoal trap *(21)*. The breakthrough of compounds such as isoprene and DMS, however, is considerably larger than this value due to the In [retention volume] versus carbon number relationship. By holding the sample trap at subambient temperatures coupled to large volumes of adsorbent, large air samples are allowed to collected at high flow rates with no losses.

In sample acquisition modes, flow rates of air as high as 400 mL/min can be passed over the adsorbent trap for periods up to 6 min with no sample breakthrough of isoprene, the most volatile component. Analyte desorption was performed at 400°C.

The PTV outer body was silicon bonded into a heat sink housing which could be cooled by either Peltier device, or by circulating ethylene glycol coolant from a chiller bath. In both instances the cooling systems ran permanently, with the PTV injector being used to heat for short periods against the cooling capacity of the block.

The desorption from the preconcentration trap to the primary column when performed by PTV is sufficiently fast that no analyte refocusing step is required. With 2D-GC where the individual columns are held isothermally, there is no possibility of phase ratio refocusing, and thus it is important to pass analytes as quickly as possible from trap to the primary analytical column. This is achieved by coupling a high flow rate of carrier gas with a very rapid heating time. Helium flow is delayed for a few seconds in order that all analytes are in the gas phase and that the peak width achieved on transfer is not desorption limited.

A schematic showing experimental apparatus is shown in Figure 2, and a schematic of valve connections is shown in Figure 3. Valves used in the interlace were low dead volume

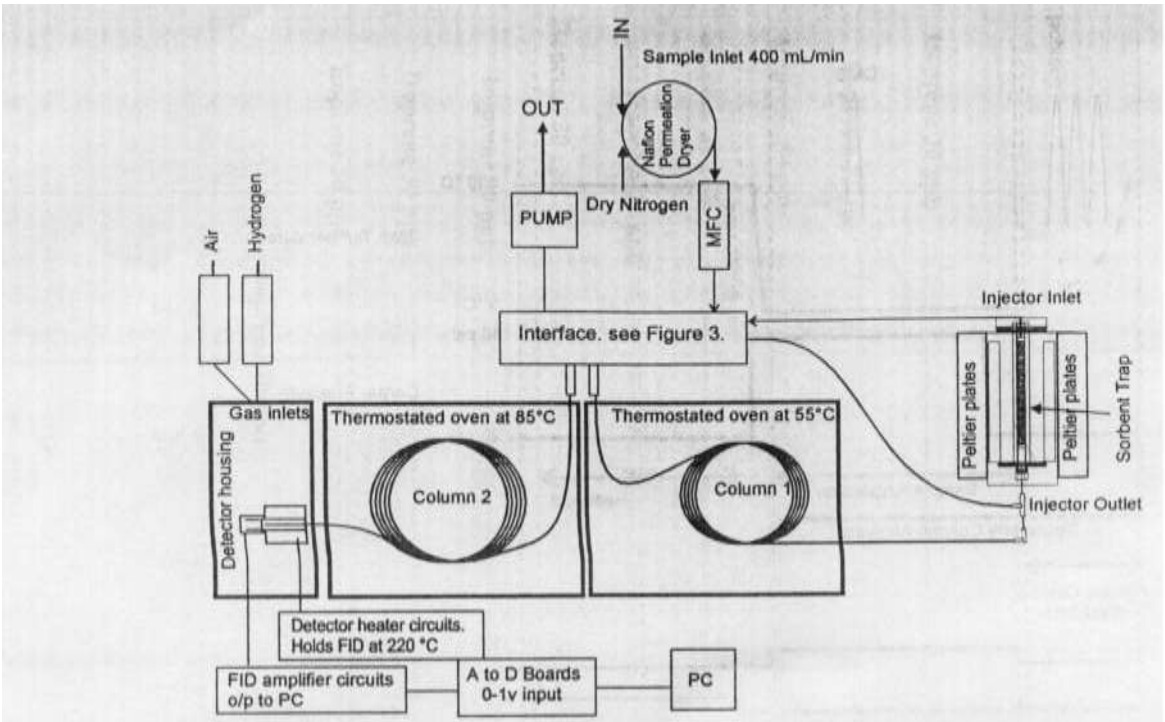
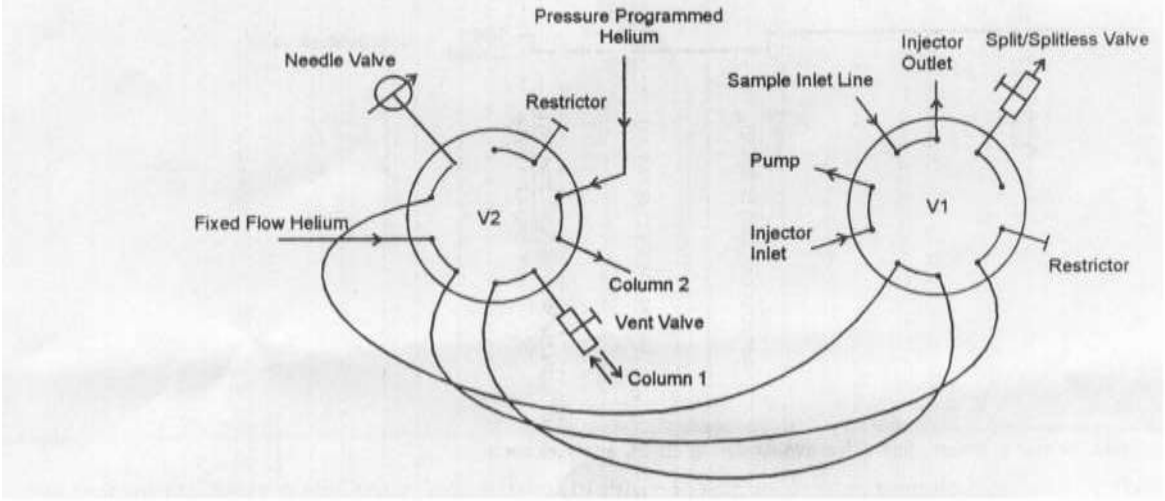


FIGURE 2. Experimental apparatus.



Interface set in sample acquire / secondary column analysis position. V1 position 1, V2 position 0

FIGURE 3. Valve configuration for GC-GC.

1/16 in. 10 port pneumatically driven (Valco VICI. Houston, TX). Carrier gas flow rate through the secondary column was determined by helium pressure programming controlled by the PTV injector. Helium flow through the primary column in both forward and backflush modes was controlled independently by mass flow controller. All external valve events were controlled via the PTV injector, along with internal split/splitless valve control.

Figure 4 shows the carrier pressure, temperature, and external and internal valve event for an analytical cycle. This can be described as follows.

Stage 1: Sample Acquisition/Secondary Separation Part Two. V1 switches to the sample acquisition position routing air sample flow through the adsorbent trap. Helium flow to column 1 is routed via a restrictor. The secondary column is in the second high pressure stage of the separation, with carrier pressure controlled by PTV injector, with DMS eluting after around 5 min.

Stage 2: Desorb.V1 switches to the sample desorb position with PTV heating trap to 400°C at 16°C is. At this stage, helium flow through the column has yet to be established, in order that all compounds pass into the gas phase prior to transfer to column 1. The helium flow to column 1 during this static desorption is routed in the reverse direction down column 1, however, the tee at the PTV outlet is connected to a split/splitless line which was open to split, passing carrier out of the system without flushing any sample away from the trap.

Stage 3: Desorb/Transfer/Primary Separation. After 10 s of static desorption, V2 switches to the transfer position, establishing carrier flow to the PTV trap, sweeping analytes onto column 1. During this transfer stage the split/splitless valve was closed. A vent valve at the outlet of column 1 and prior to column 2 was opened in order to vent lightweight analytes away to waste. Following a preset vent time, this valve is closed and eluting analytes pass directly onto column 2.

Stage 4: Backflush/Secondary Separation Part One. Following transfer of sample for preset time, valve V2 switches to provide independent pressure controlled carrier to column 2

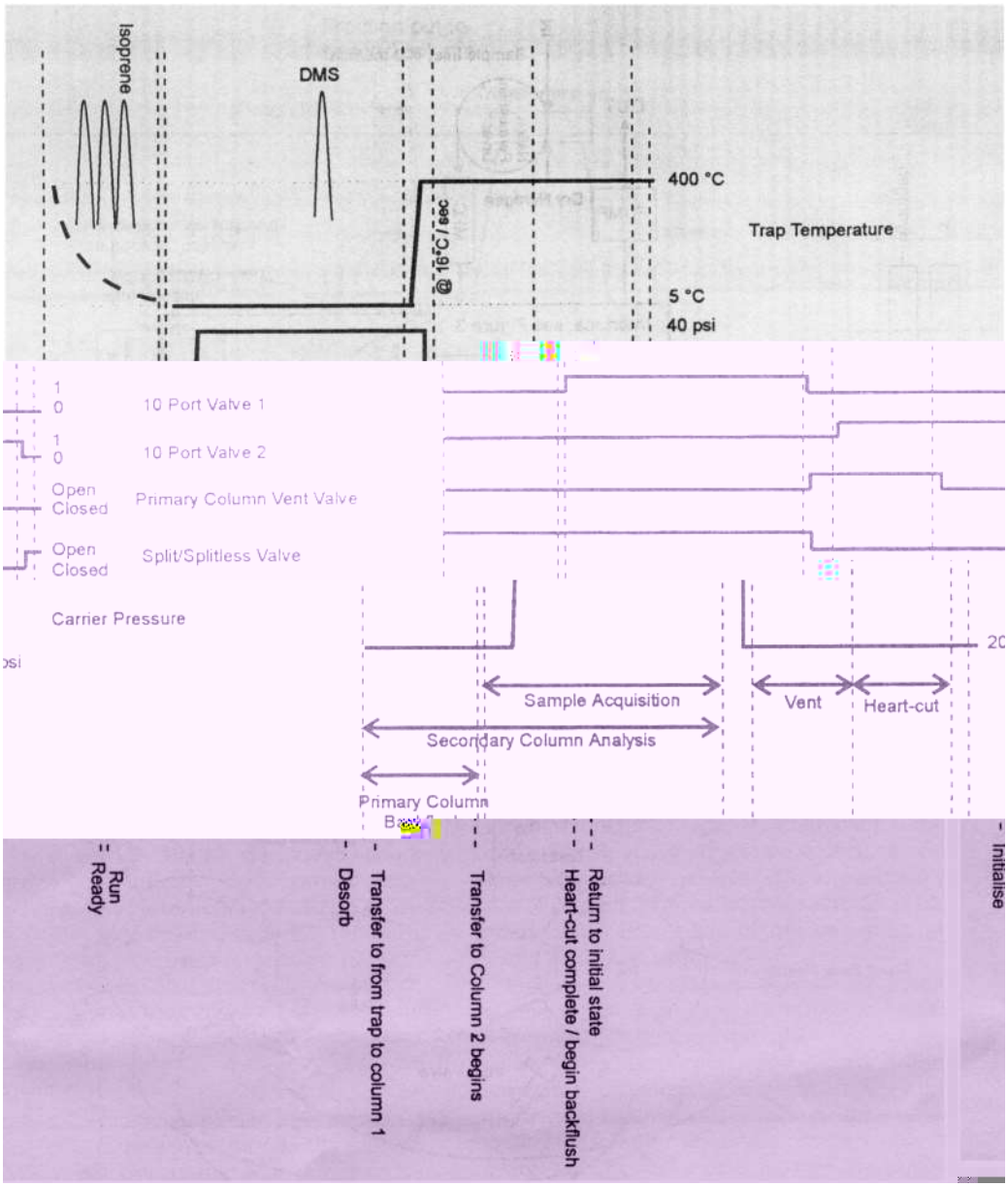


FIGURE 4. Temperature, carrier pressure, and valve events during 2D-GC analysis cycle.

controlled by the PTV injector. Column 1 enters backflush mode; however, to prevent the backflush peak from passing over the trap the split/splitless valve is opened to allow the backflushed compounds to pass to waste. The PTV injector is returned to trapping temperature by heat transfer to cold block during this period.

The secondary separation is performed in two stages: the initial low pressure stage is used to elute isoprene as a single peak, separated from similarly retained interference compounds. From one-dimensional separations of atmospheric samples it has been seen that the nearest eluting compounds to isoprene are 2 and 3 methyl pentane and hexane. Following this low-pressure separation, the carrier flow is increased to elute the remaining DMS from the column. The analytical program at this stage loops back to Stage 1.

Analytical Conditions. A 16 m 0.32 mm film thickness d.f. 5 µm 100% methyl polysiloxane column (Chrompack, Netherlands) was used for the primary separation, held at 55°C. Sample transfer from PTV trap to primary column was performed with a carrier flow rate of 17 mL/min. During transfer from primary to secondary column, a carrier flow rate of 14 mL/min was used. Backflush flow rate through column 1 was determined to be 24 mL/min.

The secondary column was a 15 m 0.53 mm i.d. Al_2O_3 / $NaSO_4$ (Chrompack, Netherlands) layer open tubular column with 10 µm stationary phase held at 85°C. During the lowpressure phase of the separation, a carrier flow rate ramped from 65 to 85 mL/min was used. For the high-pressure phase of the secondary separation, a carrier flow rate of 160 mL/min was used.

In many previous applications of 2D-GC, attention has been paid to the potentially detrimental band-broadening effects that can occur during the interface stage *(22)*. Deans switching (or live switching) has been generally used rather than via a more simple mechanical switching valve approach. In this application, however, the very high flow rates of carrier gas used resulted in a negligible level broadening, and therefore allowed the successful use of mechanical rotor valve switching.

Calibration. To confirm that no sample breakthrough was occurring at high sample flow rates, an instrument calibration was performed using premixed high-pressure cylinders containing parts per billion level hydrocarbon species in a nitrogen balance gas. An example calibration is shown in Figure 5, using 30 ppb isoprene in nitrogen balance (Air Products U.K., Special Gases Division, Crewe, U.K.). A large number of sequential analyses are shown on a single chromatogram. The low concentration obtained during the first sample is attributed to the inlet lines and drier stages having not fully purged with calibration gas. Calibration using premixed standards showed a relative standard deviation of 5.5% based on peak area integration.

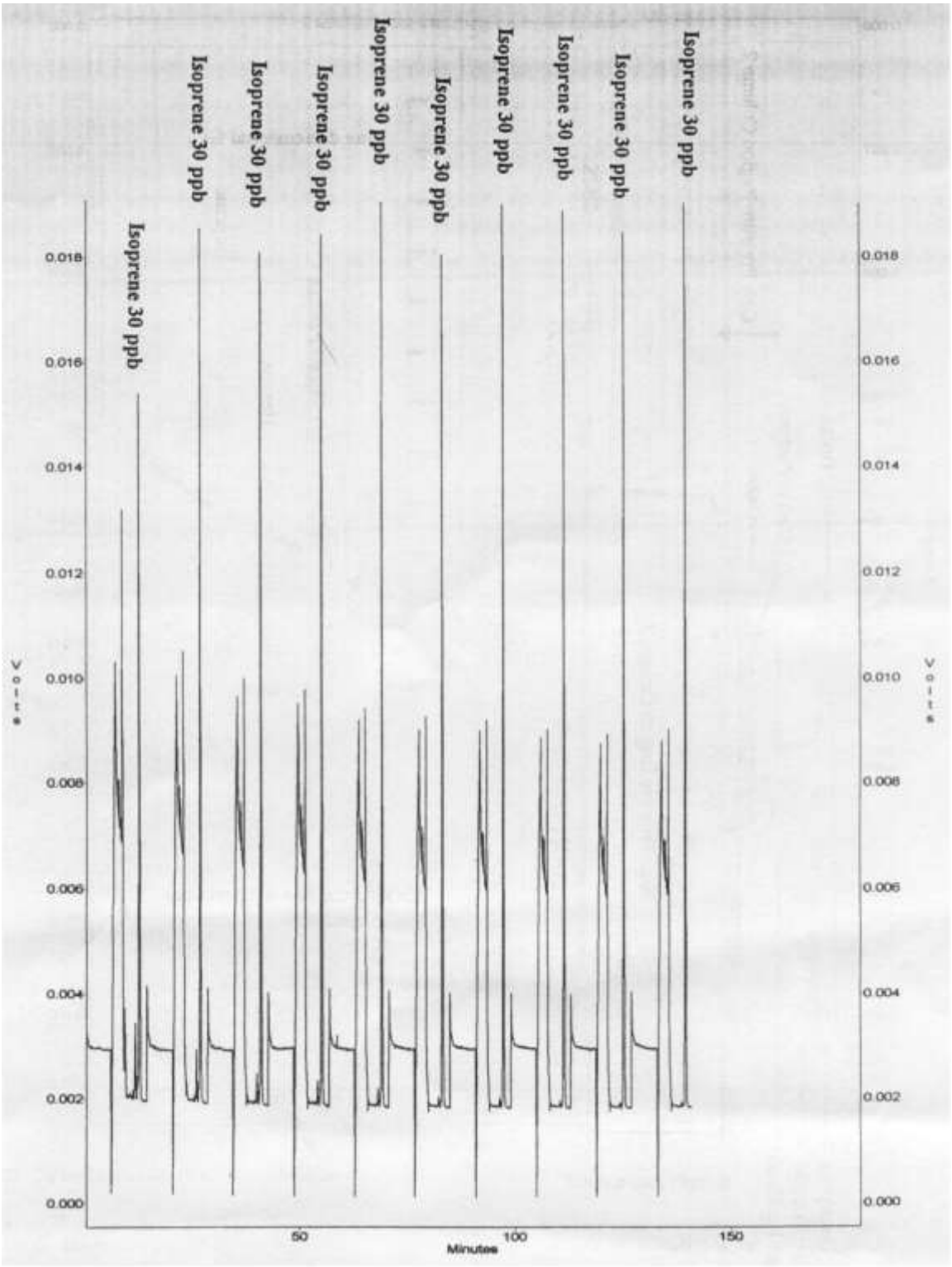


FIGURE 5. Calibration cycles using 30 ppb isoprene in nitrogen balance gas.

Results

Trapping of isoprene and DMS can be performed at flow rates up to 400 mL/min, dependant on pump size; however, the capacity of any water scrubbing stage becomes an important consideration when setting sample flow rates. With a cooled trap there is considerable collection of water vapor onto the activated charcoal. This not only alters trap performance, but may lead to a complete blockage of sample lines if trapping is performed at sub 0°C temperatures. A further effect of water trapped onto the adsorbent is that on desorption some water will be passed to the secondary PLOT column despite the heart -cutting method. Adsorption of water onto the PLOT column stationary phase leads to a considerable change in affinity and shifting in retention times. Since the described system operates isothermally, there is little opportunity to remove water by baking out the column at high temperatures. Where a low sample volume (flow rate < 150 mL/min) was sufficient for analysis. a Nafion permeation drier with a counter current of dry nitrogen was used to remove water from the sample.

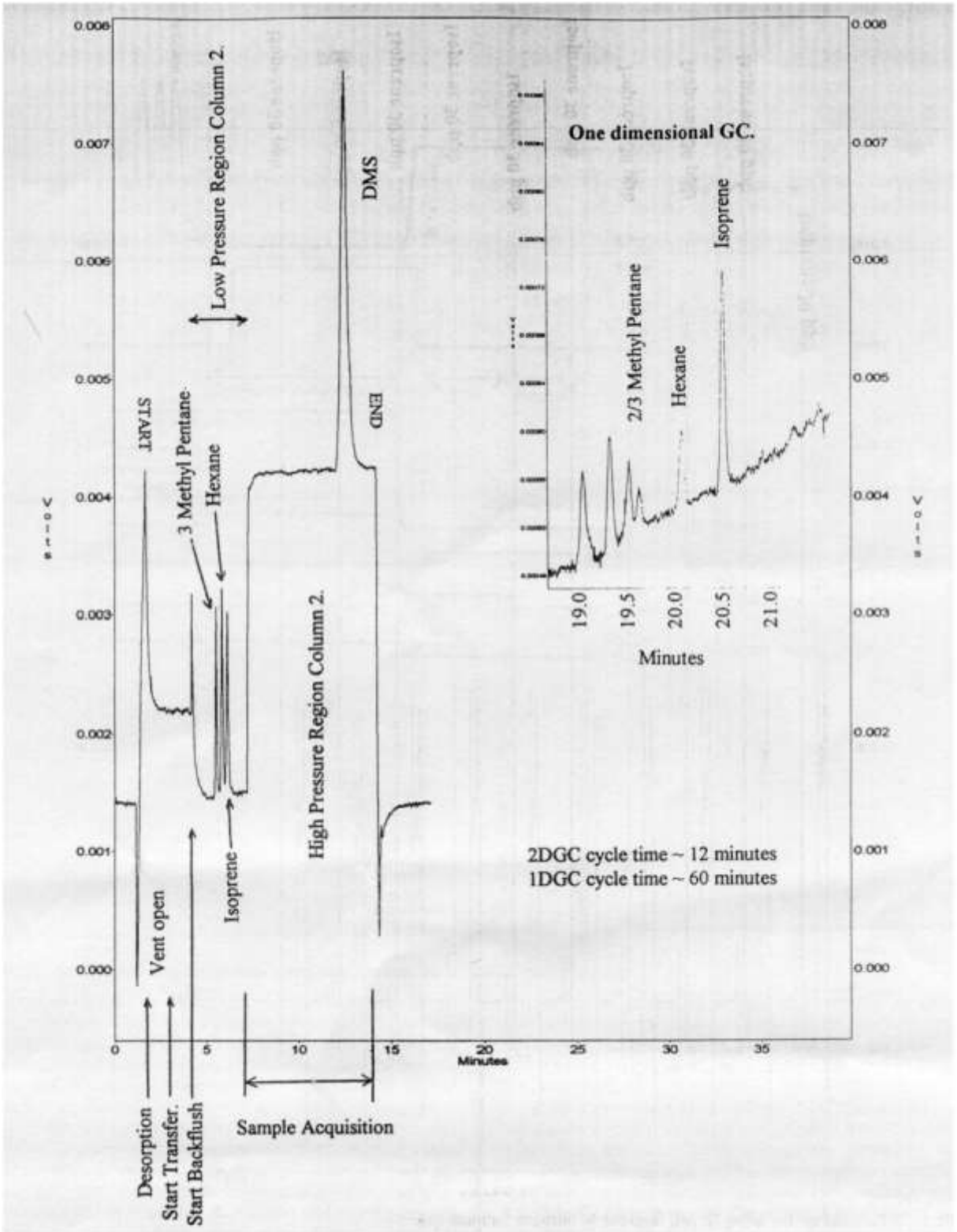


FIGURE 6. 20-GC chromatogram of isoprene, interference hydrocarbons, and DMS. (Inset) One-dimensional separation of isoprene and interference hydrocarbons.

When higher flow rates (150-400 mL/min) are required, to obtain maximum sensitivity, the most efficient method of water removal was found to be flowing sample air through a glass Drescher flask placed in 0°C ethylene glycol. This first stage drying is followed by a second stage adsorbent scrubbing using potassium carbonate. The potassium carbonate was also seen to remove up to 95% of ambient ozone. All instrument calibration was performed with the dryer stages in place and by pumping sample into the system from atmospheric pressure so as to best mimic the acquisition of a real sample.

As described earlier, the lowering of trap temperature may increase maximum sample size; however, a compromise temperature will generally be used that balances large sample capacity with a relatively fast cooling time. In the case of the described instrument, a trapping temperature of 5°C was found to be most ideal. Trap cooling to 5°C from 400°C was complete in around 210 s using a liquid coolant system holding the inj ector block at - 13°C. Minimum trapping temperature

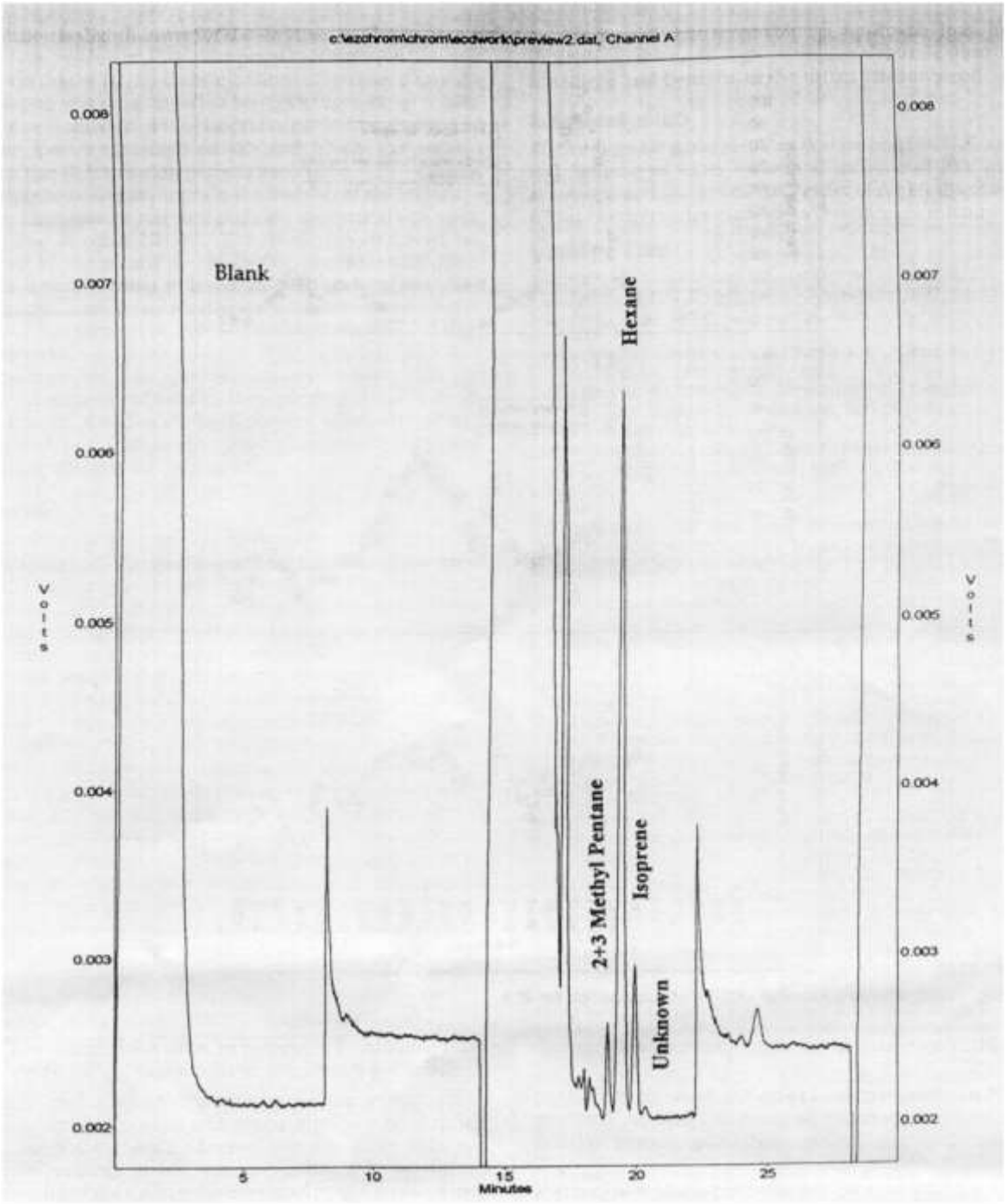


FIGURE 7. Chromatogram obtained during field testing.

using this configuration was found to be -7°C. The use of a direct current driven Peltier device allowed the injector block temperature to be lowered to -45°C with a resulting faster cooling time to 5°C of 170 s. With this mode of cooling, a minimum trap temperature of -25°C was possible; however, the time taken to reach this point was on the order of 10 min.

For short-term measurement exercises or where a very fast cooling time is required, carbon dioxide may be used, delivered to the area surrounding the adsorbent tube via pneumatically actuated needle value, controlled via feedback mechanism from the injector unit.

Figure 6 shows a standard chromatogram obtained using the described method. The sample contains isoprene and major interference compounds 2-methyl pentane (2- and 3-methyl pentane coelute using this system) and hexane spiked at the 1 ppb level. DMS in this sample was spiked at the 10 ppb level.

The inset chromatogram shows a one-dimensional separation of an air sample taken in clean westerly Atlantic air at Mace Head Observatory Co., Galway, Eire. The method of analysis used in this one-dimensional mode was PTV trapping and desorption onto a similar PLOT column with a total cycling time of 1 h.

The one-dimensional separation is included to demonstrate that there are no interfering compounds present other than hexane and 2- or 3-methyl pentane in the clean marine environment. The described two-dimensional method, which baseline separates isoprene from methyl pentane and hexane, therefore, has sufficient resolution for confident identification and quantitation of the isoprene peak.

Peak width W_b of isoprene was determined to be 12 s, a value equivalent to that obtained previously using PTV injection onto 50 m 0.53 µm film thickness 10 µm $^{A}l_2O_3$ / NaS

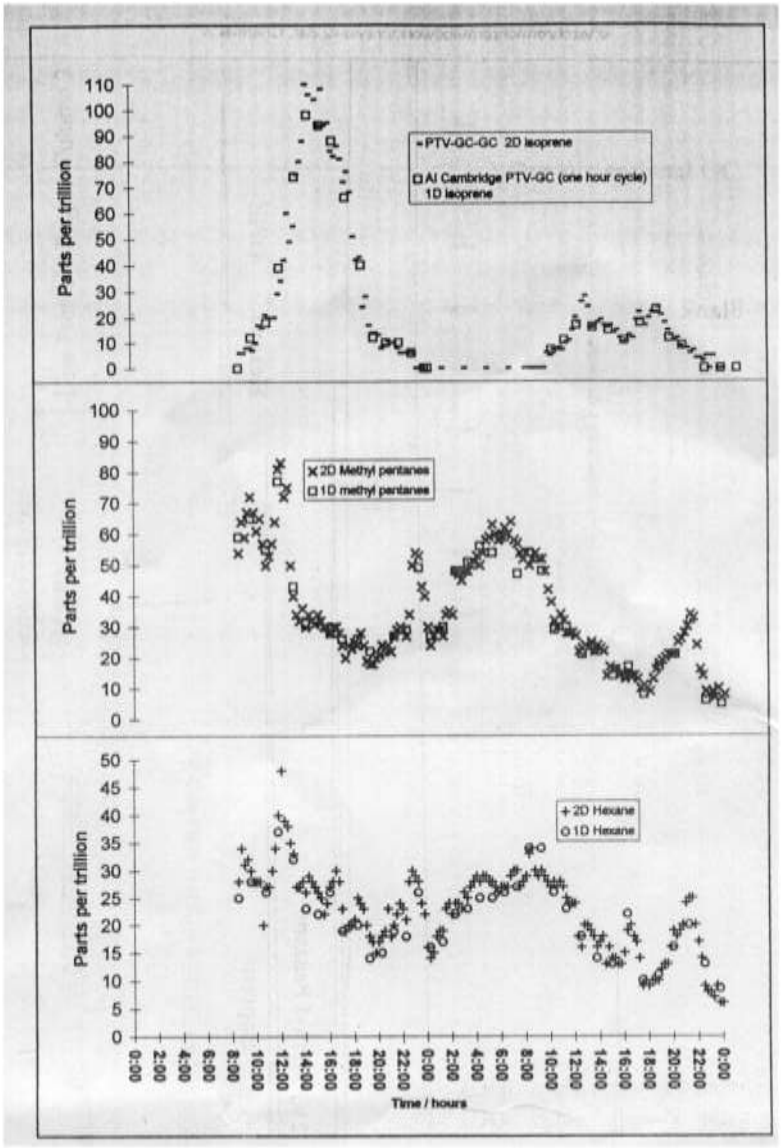


FIGURE 8. Intercomparison exercise with 10 chromatograph for 48 h.

O_4PLOT column temperature programmed over the range 40-175°C.

DMS W_b was determined to be 35 s, wider than obtained with a single temperature programmed column, however, narrower than can be obtained using packed column methods.

With a 2 L air sample, the detection limit for isoprene is estimated at 5 ppt and 25 ppt for DMS, based on backextrapolated calibration against certified parts per billion level gas standards supplied by National Physical Laboratory (Teddington, U .K.) and Air Products (Special Gases Division Crewe, U.K.).

Instrument Intercomparison. To evaluate the performance of the described 2D-GC instrument against currently operating *in situ* analysis single dimension chromatographs, the 2D-GC was deployed at the Mace Head Observatory, Eire, as part of the U.K. NERC ACSOE (Atmospheric Chemistry Studies in the Oceanic Environment) program during April/ May 1997. The site is well characterized for hydrocarbons species through long-term canister monitoring by Penkett *et al. (23)* and continuous hourly monitoring by Lewis *et at. (24)*.

The instrument used for the comparison purposes was based around a similar PTV injector unit housing an activated charcoal trap. Sample collection was performed over a 15 min period followed by desorption onto a 50 m 0.53 mm i.d. PLOT column. Calibration of both instruments was performed using a common 27 compound gas standard.

A period of westerly air flow where a final short period of transit time southerly across Eire coastal regions occurred was chosen as the test period. These conditions were considered ideal since they resulted in elevated isoprene concentrations from local emissions plus a low but detectable concentration of anthropogenic species including 2- and 3-methyl pentane and hexane. Figure 7 shows a chromatogram obtained during the intercomparison exercise. The timing of the exercise was prior to the Atlantic aigael bloom, and as a result, DMS concentrations on both instruments were below detection limits so the intercomparison was not validate the DMS.

The intercomparison demonstrated that there was good agreement both qualitatively and quantitatively between the two instruments. In general, the 2D-GC instrument was found to give marginally higher peak concentrations than those reported using the ill instrument with a wider scatter of data. This marginally higher value has been attributed to the considerably shorter sampling period used by the 2D-GC. The inhomogeneous nature of the air passing over the sampling site results in rapid fluctuation in hydrocarbon concentrations when determined using short sampling periods. Correlations between data sets show a 0.985 correlation for lD/2D isoprene (n_1 = 48,

n_2 = 158). The correlation is slightly lower for the summed methyl pentanes at 0.974 (n_1 = 48, n_2 = 158). The poorest correlation between data was that of 1D/2D determinations of hexane, where the correlation was determined to be 0.949 (n_1 = 48, n_2= 158).

Figure 8 shows a plot of isoprene, methyl pentanes, and hexane species measured on 1D- and 2D-GC instruments during the 48 h intercomparison exercise.

Isoprene concentrations on the first day of the intercomparison are seen to rise to significant concentrations when compared to other NMHC. The maximum concentration reached on the second day of testing is considerably lower due to a combination of lower air temperature, increased cloud cover, and higher wind speeds. Night time concentrations of isoprene were below the detection limit of both instruments.

The anthropogenic species measured (the sum of 2- and 3-methyl pentane and hexane) show good agreement on both instruments. Once again, peak concentrations determined using the 2D-GC instrument is marginally higher than those obtained with the 1D instrument.

Discussion

It has been shown that two-dimensional chromatography offers a potentially powerful method for the rapid analysis of target trace species in the atmosphere. The instrument described has the ability to perform high-resolution determinations of isoprene and DMS with detection limits as low as 5 and 25 ppt, respectively. The two-dimensional system described has the ability to perform chromatography at a speed comparable with narrow bore capillary columns but without the associated loss in sample capacity.

2D-GC coupling to a packed adsorbent bed placed in a programmed temperature vaporization liner has proved an effective method for on-line sample reconcentration/desorption and transfer to primary column. The ability to operate under isothermal conditions dramatically reduces the power consumption of the instrument, making it suitable for operation in remote environments or on sampling platforms such as aircraft where electrical supply is limited. Intercomparison between the described 2D-GC instrument and a traditional single-dimension GC system has shown a good qualitative and quantitative agreement over a 48 h continuous test.

The current application has demonstrated the analysis of species important in the marine environment, isoprene and DMS, although any group of similar boiling point species may be isolated and determined using this two-column approach. With the introduction of two differing secondary columns, it may prove possible to tailor rapid analyses for dissimilar species where the secondary column in each case is optimized for isolation of one compound only. A potential application of this three-column approach may lie for example, in the rapid high-resolution determination of 1,3-butadiene and benzene in the urban environment.

Acknowledgments

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Literature Cited

(1) Davis, J.M.; Giddings, J.C. Labor Praxis **1983,** *10,* 328.
(2) Giddings, J.C. *J. High Resol. Chromatogr.* **1987,** *10,* 319-323.
(3) Kelly, G.A.; Bartle, K.D. *J. High Resol. Chromatogr.* **1994,** *17,* 390-397.
(4) Lewis, A.C.; Robinson, R.E.; Bartle, K.D.; Pilling, M.J. *Environ. Sci. Technol.* **1995,** *29,* 1977-1981.
(5) Ligon, W.V.; May, R.J. *J. Chromatogr. Sci.* **1986,** *24,* 2-6.
(6) Liu, Z.; Sirimanne, S.R.; Patterson, D.G.; Needham, L.L. *Anal. Chem.* **1994,** *66,* 3086-3092.
(7) Casabianca, H.; Graff, J.-B.; Jame, P.; Perrucchietti, C.; Chastrette. M.*J. High Resol. Chromatogr.* **1995,** *18,* 279-285.
(8) Elder, J.F., Jr.; Gordon, B.M.; Uhrig, M.S. *J. Chromatogr. Sci.* **1986,** *24,* 26-32.
(9) Nishimura, O. *J. High Resol. Chromatogr.* **1995.** *l8,* 699-704.
(10) Bushby, M.M.; Jorgenson, J.W. *Anal. Chem.***1990**, *62,* 978-984.
(11) Schrimpf, W.; Muller, K.P.; Johnen, F.J.; Lienaertz, K.; Rudolph, J. *J. Atmos. Chem.* **1995,** *22,* 303-317.
(12) Liu, Z.; Phillips, J.B. *J. Chromatogr. Sci.* **1991,** *29,* 227-231.
(13) Derwent, R.G.; Simmonds, P.G.; Collinds, W.*J. Atmos. Environ.* **1994,** *28,* 2623-2637.
(14) Simmonds, P.G.; O'Doherty, S.; Nickless, G.; Sturrock, G.A.; Swaby, R.; Knight, P.; Gicketts, J.; Woffendin, G.; Smith, R. *Anal. Chem.* **1995,** *67,* 717-723.
(15) Derwent, R.G.; Dumitrean, P.; Chandler, J.; Davies, T.J.; Dollard, G.J.; Delaney, M.; Jones, B.M.R.; Mason, P.D. Report No. AEA/CS/18358030/005, AEA Technology Culam, U.K.
(16) Atkinson, R.; Aschmann, S.M.; Winer, A.M.; Pitts, J.N., Jr. *J. Int. Chem. Kin.* **1982,** *14,* 507.
(17) Penkett, S.A.; Blake, N.J.; Lightman, P.; Marsh, A.R.W.; Anwyl. P.; Butcher, G.*J. Geophys. Res.* **1993,** *98,* 2865-2885.
(18) Davison, B.; Hewitt, C.N.*J. Geophys. Res.* **1992,** *97,* 2475.
(19) Lewis, A.C.; Seakins, P.W.; Denha, A.M.; Bartle, K.D.; Pilling, M. J. *Atmos. Environ.* **1995,** *29,* 1871-1875.
(20) Lewis, A.C.; McQuaid, J.B.; Pilling, M.J.; Bartle, K.D.; Ridgeon, P.*J. High Resol. Chromatogr.* **1996,** *19,* 686-690.
(21) Lewis, A.C.; Bartle, K.D. *LC-GC Int.* **1996,** *9,* 297-304.
(22) Adam, S.T. *J. High Resol. Chromatogr.* **1988,** *11,* 85-89.
(23) Penkett, S.A.; Burgess, R.A. Unpublished results.
(24) Lewis, A.C.; Bartle, K.D.; Heard. D.E.; McQuaid, J.B.; Pilling, M.J.; Seakins, P.W.*J. Chem. Soc., Faraday Trans.* **1997,** *93.*

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