Comprehensive two-dimensional gas chromatography using liquid nitrogen modulation: set-up and applications ☆

Matthias Pursch [a,*], Patric Eckerle [a], Juergen Biel [a], Roman Streck [a], Hernan Cortes [b], Kefu Sun [c], Bill Winniford [c]

[a] *Dow Deutschland GmbH & OHG, Analytical Sciences, 77836 Rheinmuenster, Germany*
[b] *The Dow Chemical Company, Analytical Sciences, 1897 Building, Midland, MI 48667, USA*
[c] *The Dow Chemical Company, Analytical Sciences, B-1216 Building, Freeport, TX, USA*

Abstract

An improved modulation system for comprehensive two-dimensional gas chromatography (GC × GC) is presented. It is based on two-jet modulation with liquid nitrogen as cryogen. A valve system was designed to include subsequent re-heating of cooled capillary segments after modulation. It is demonstrated that even volatile components, such as propane or butane, are easily modulated with this system. Thus, the temperature range for GC × GC operation compared to diaphragm valve or liquid CO_2 modulation is extended. The system allows highly efficient analysis of volatile and non-volatile components. Applications include separations of alkenes and gasoline samples. Also sulfur-containing hydrocarbon samples were compared via GC × GC and differences among samples of different producers were observed. Finally, headspace GC × GC investigations of volatiles found in polymer latex-coated papers round out the increasing portfolio of valuable applications.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Gas chromatography, comprehensive two-dimensional; Liquid nitrogen modulation; Hydrocarbons, sulfur-containing; Alkenes

1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) is currently receiving widespread attention for analysis of complex samples. Several review articles have been published in the literature as refinements in the methodology are reported [1–3]. Current studies deal with retention time data of GC × GC measurements [4,5], as well as new applications in food and environmental areas [6,7]. An example for enantiomer analysis with a second dimension chiral column was presented very recently [8]. In addition, research activities include further studies and modifications of modulator systems [9].

The modulation device is the critical part of a GC × GC system. Various strategies have been implemented and are briefly summarized here. Non-thermal modulators have utilized diaphragm valves, in some cases in conjunction with chemometric analysis [10]. Seeley et al. have demonstrated valve modulation with differential flows on first and secondary columns [11]. Up to now, diaphragm valves are operated up to

200 °C, which makes them useful for volatile components, but limitations for high-boiling compounds (>180–200 °C) are apparent. Very recently, the temperature range for valve operation has been extended towards 250 °C by mounting the valve in such a way that the polymeric seals are not subject to the high temperatures [12].

The first modulation devices were thermal modulators and based on resistive heating of metal tubing [13]. Later, such designs have included slotted heaters [14]. Marriott and Kinghorn developed the longitudinally modulated cryogenic system (LMCS) which is based on cryofocusing with liquid CO_2 [15]. Beens et al. proposed a two-jet modulator, which is capable of pulsing alternating streams of liquid CO_2 [16]. Both approaches are very powerful with the additional benefit of the two-jet approach not requiring moving parts in the GC × GC system. Very recently, a new modulator design based on cryotrapping with CO_2 and subsequent remobilization via electrical heating has been presented [9]. Also, modulation with a single-jet, single-stage approach has been proposed and tested for polar and non-polar compounds [17].

Another innovative example comprises the development of a semi-rotating cryogenic modulator based on cryotrapping with CO_2 [18]. This modulator shows similar as the jet modulator [16], but the set-up seems to be a little more complicated due to the rotating device. One general drawback of modulation with liquid CO_2 is the difficulty to trap very volatile components, such as butene, butadiene or acrylonitrile, which are important precursors for polymer synthesis. In general a thick film capillary column could be utilized as the modulation column for these volatile compounds to increase cryotrapping efficiency, but it would become difficult to modulate heavier components in the mixture during the analysis.

A powerful alternative could be modulation with liquid nitrogen. Much lower modulation temperatures can be applied using liquid nitrogen instead as cryogen of liquid CO_2, where the minimum is reached at about −60 to −30 °C. As a consequence, a wider temperature range would be accessible for GC × GC operation allowing modulation of very volatile components. This paper demonstrates the set-up of a two-jet modulation system, which uses liquid ni-
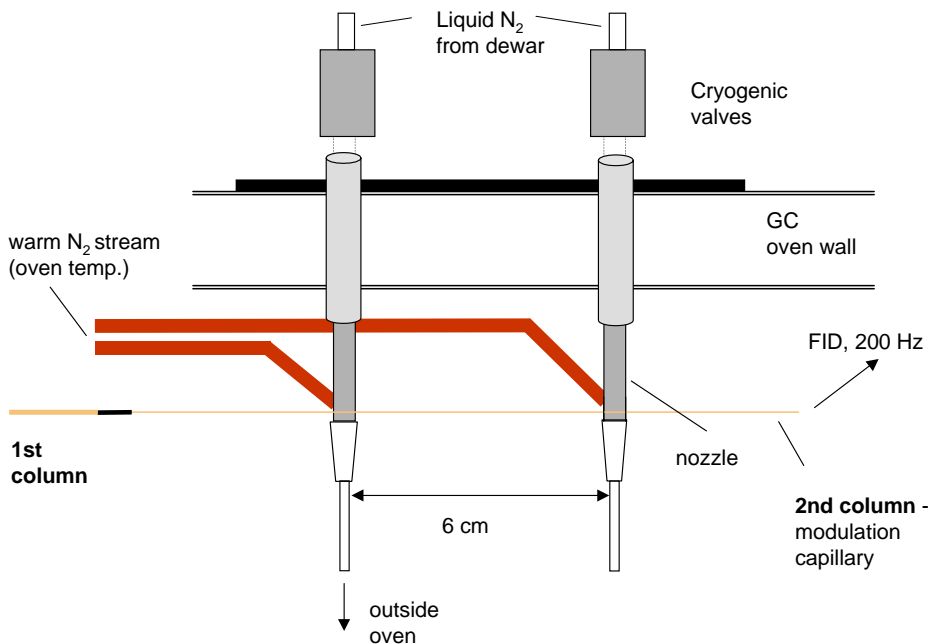

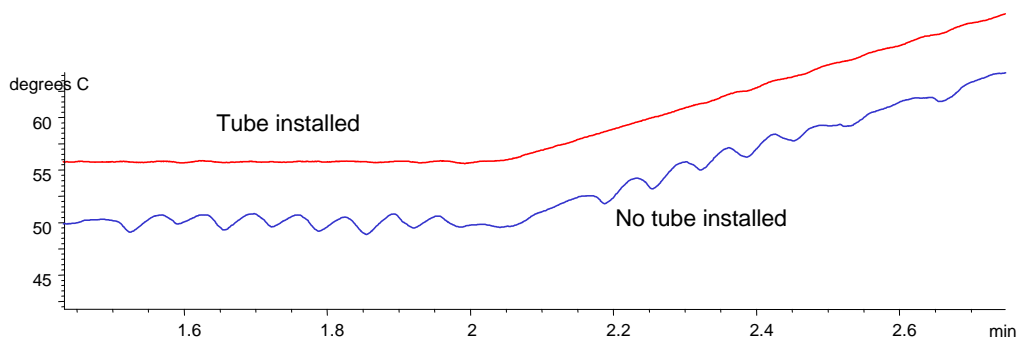Fig. 1. Design of two-jet modulator capable of pulsing liquid N_2 gas.

Fig. 2. Plot of oven temperature during temperature program (heating rate 20 °C/min). Without removal of cold nitrogen, fluctuations are observed (bottom). After doing the set-up as described in Fig. 1, the oven temperature is stable (top).

trogen. Thus far, to our knowledge, liquid nitrogen has only been used to pre-cool gaseous nitrogen for modulation. ZOEX Corporation and LECO have commercialized such systems. Our set-up, however, is based on liquid N_2 modulation with the nitrogen being supplied directly from the dewar. This paper details the changes that are necessary for successful operation and illustrates the benefits for modulating of
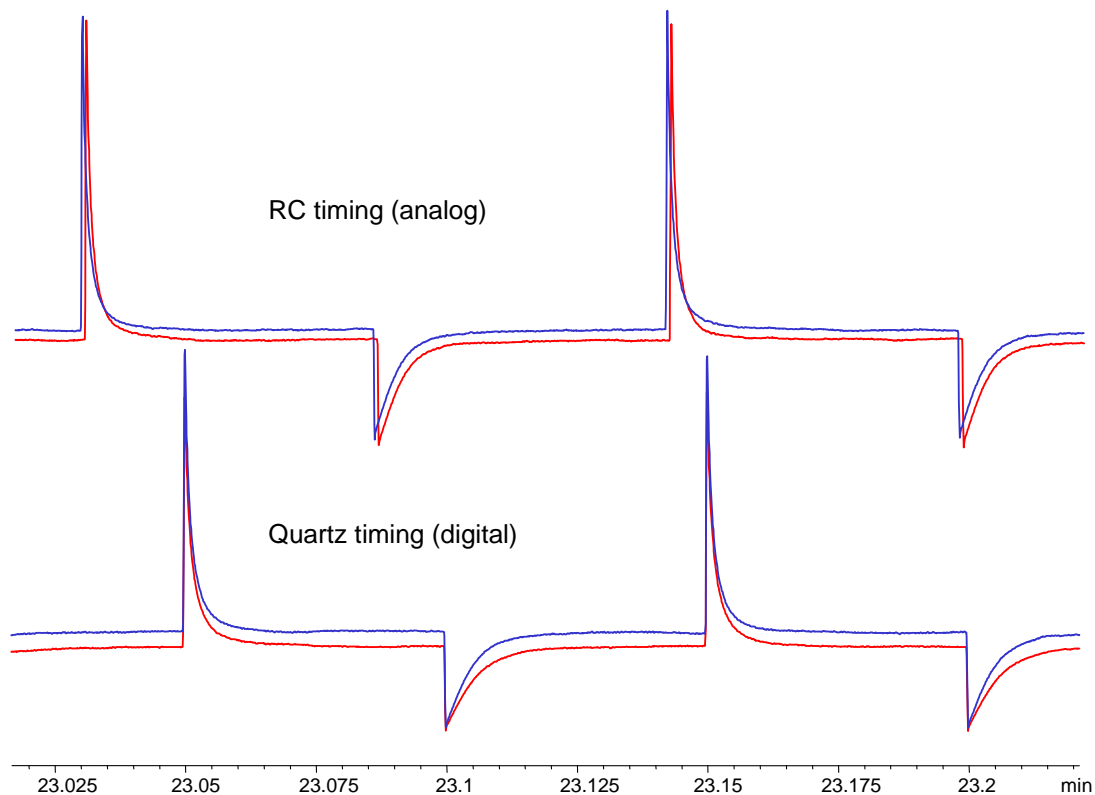

Fig. 3. Electronic modulation signal of valves with analog (top) and digital (bottom) valve timer.

volatile and non-volatile components. A wide range of applications is presented, including separations of gasolines, alkene monomers, sulfur-containing hydrocarbons, as well as volatiles in polymer-coated samples.

2. Experimental

An Agilent (Waldbronn, Germany) 6890 GC oven was retrofitted to accommodate two jets similar as described in the literature [16], but capable of pulsing liquid nitrogen. Stainless steel tubing of approximately 0.9 mm i.d. was attached to the brass jets to accommodate sufficient N_2 flow for cooling. A tank of liquid nitrogen was installed in vicinity of the GC system, and nitrogen pressure was set to 100–130 kPa. Cryogenic valves suited for N_2 operation were obtained from Gerstel. The modulation system is shown in Fig. 1.

Following column configuration was chosen: column 1, BP-5 (25 m × 0.25 mm i.d. × 0.25 μm film thickness); column 2, CP-52-Wax (1.2 m × 0.1 mm × 0.2 μm). Hydrogen was used as carrier gas (flow rate 0.5 ml/min) and FID detection was set to 200 Hz acquisition rate. Modulation was controlled with a home-built valve timing system (individual parts were received from Conrad Elektronik, Germany) that is remote-controlled by Agilent Chemstation. Two different versions of valve timers were built. The initial model is based on RC timing, where timing errors of about 0.1% are inherent. As shown in the discussion, this precision was not high enough. The second model is based on quartz timing, which provides the accuracy needed. Modulation periods of 2.5–6 s were applied. Using a three-way valve, warm nitrogen (oven temperature) was actuated to immediately re-heat the cooled capillary segments. A typical temperature program consists of following profile: 50 °C (4 min hold), 250 °C (10 °C/min), and 250 °C (5 min hold). The modulator was synchronized with the start of each GC run at 3 min upon injection using the Chemstation software.

For headspace (HS) injection, a Perkin-Elmer HS-40-XL instrument was utilized. Two hundred milligrams sample were weighed into HS vial and sealed. Equilibration time was 2 h at 120 °C, and injection period amounted to 0.08 min. Experiments were run at constant flow using helium as carrier gas.
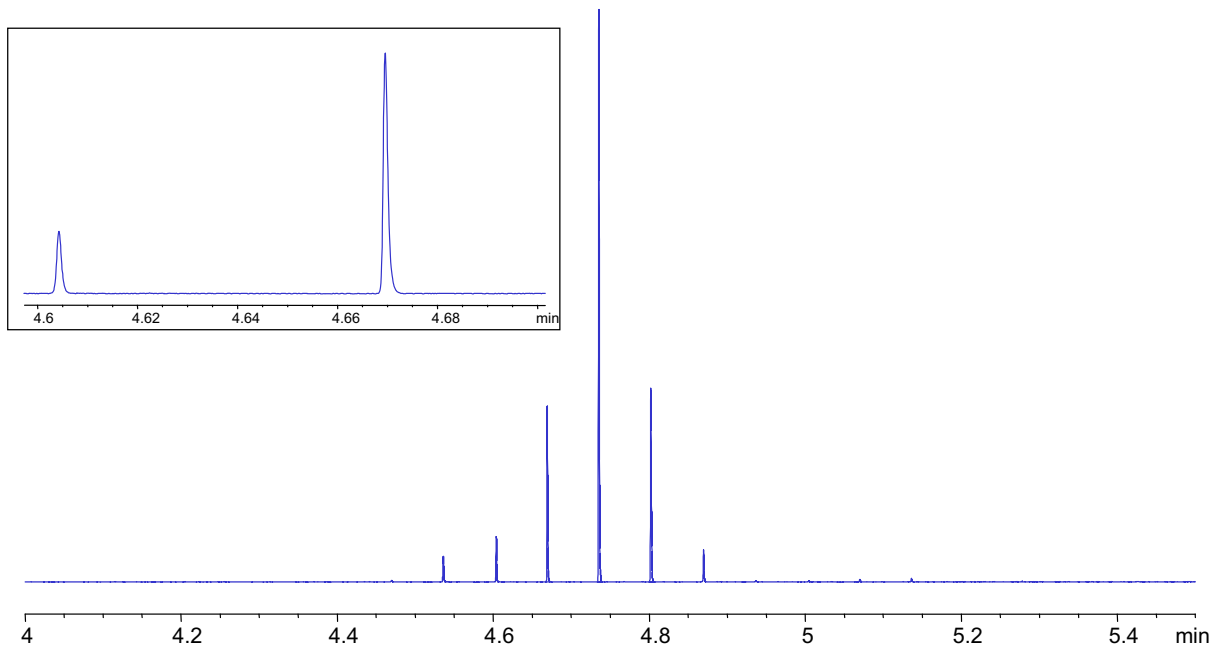

Fig. 4. Modulation pattern of a propane–butane gas mixture.

3. Results and discussion

3.1. Modulator performance

Initial observations after set-up of the new modulator showed that oven temperature was not stable during modulation with liquid N_2. This is attributed to an increased amount of cool nitrogen gas that is introduced into the oven chamber during modulation process. This problem was solved after Teflon tubes were installed underneath the nozzles. The tubes lead outside the GC oven and therefore allow for fast removal of cold gas out of the oven environment. Initially, the cryogen removal was assisted by vacuum pumps but it was experienced that these pumps were not absolutely necessary. It needs to be ensured that the particular grade of Teflon can withstand temperatures up to 320 °C. Fig. 2 illustrates the variance in oven temperature that can reach up to 4 °C, if cold nitrogen gas pulses are not constantly being removed. It should be noted here that either reduced amounts of liquid nitrogen introduced into the oven or slower heating rates (<15 °C/min) cause less temperature fluctuations.

Another reason for using tubes is to have a guide for liquid nitrogen. With open nozzles alone, very heterogeneous spraying of N_2 was observed. This leads to irreproducible modulation, since not all of the cryogenic liquid hit the capillary segments. With the modulation capillary segments embedded in the tubes, cryocooling occurs much more reproducible, i.e. the same amount of cryogen is constantly being sprayed onto the capillary. Liquid nitrogen consumption is rather low and amounts to about 30–40 l per day. In contrast, the ZOEX loop modulator consumes about 100 l liquid nitrogen per day as experienced in one of our labs.
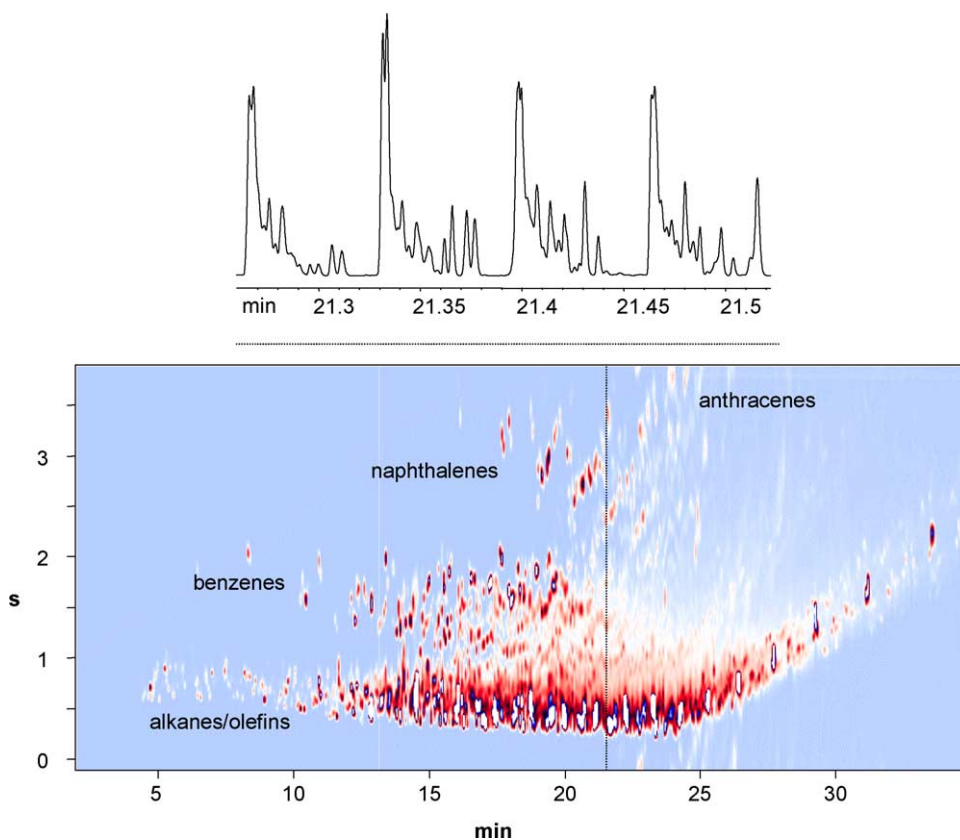

Fig. 5. GC × GC separation of gasoline using liquid nitrogen as cryogen. Top: extracted region of one-dimensional chromatogram illustrating four consecutive secondary column separations; bottom: two-dimensional contour map.

It was also apparent that a non-digital valve timer (RC-based) did not give reproducible data with regard to retention time on the second dimension. Variations in modulation time occurred and made evaluation of GC × GC contour plots very difficult. Significant peak shift up to 2 s was observed during a GC × GC separation. The electronic signals of both non-digital and digital timed valves were recorded and are shown in Fig. 3. Stable and reproducible modulation was achieved with a digital valve timer based on quartz timing.

Volatiles in urban air or residual monomers in synthetic polymers can contain molecules of high vapor pressure. In polymers such species include for example alkenes or acrylonitrile. These fragments are also produced during pyrolysis of respective (co-)polymers. Modulation based on liquid CO_2 is not able to trap these components effectively, hence

qualitative and quantitative evaluation would be very difficult. Fig. 4 shows GC × GC analysis of a propane–butane gas mixture. These components are nicely modulated and confirm the superiority of liquid N_2-based modulation in comparison with CO_2. Peak widths for butane modulated peaks are 66 ms at half height and 240 ms at base. Symmetry factors amount to 0.8 indicating some tailing. It should be noted here that separation was not optimized in terms of temperature programming—the main purpose was to demonstrate the ability to trap/remobilize very volatile components.

3.2. Applications

The power of the N_2 modulator is demonstrated for separation of diesel as a well-known test application. Fig. 5 (bottom) shows a two-dimensional contour
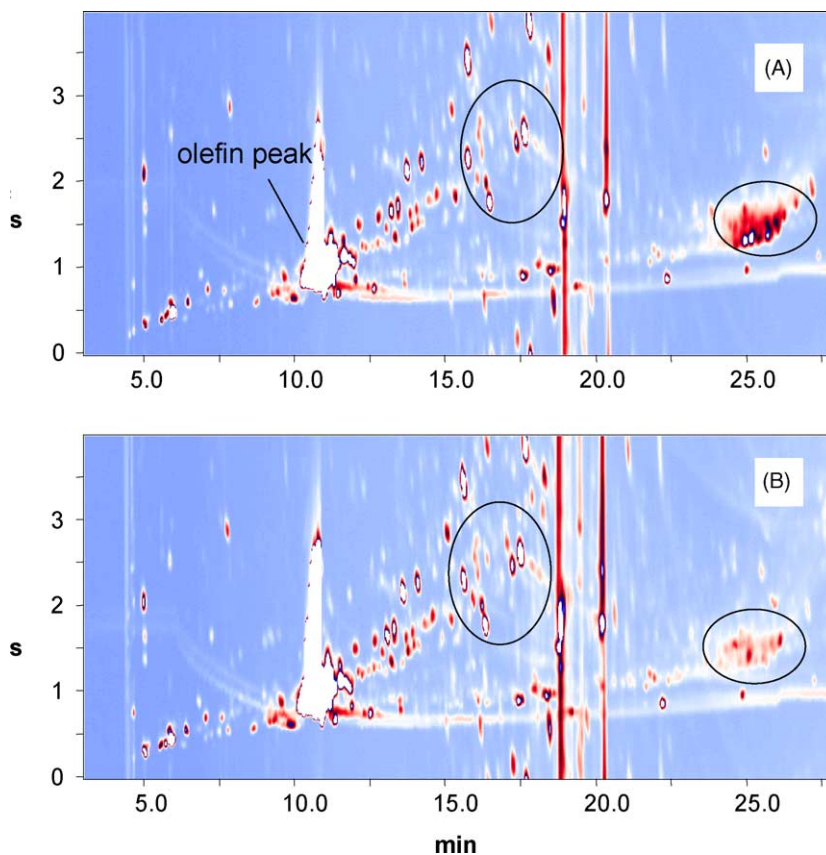

Fig. 6. Contour maps of two alkene lots. Differences in more polar trace levels were observed.

map of the GC × GC separation. As typical for comprehensive GC plots, the horizontal axis represents the separation on the first column (in minutes). The vertical axis represents secondary column separations (in seconds), which are governed by differences in polarity.

Sharp peaks are obtained across the full separation range. For late eluting components, peak widths of 57 ms at half height and 210 ms at base were determined. The one-dimensional trace in Fig. 5 (top) shows four consecutive secondary column separations and illustrates the high number of components with similar boiling points, but different polarities. Up to 11 different components can be observed in one secondary column "injection". It is apparent that even under these conditions peak overlap
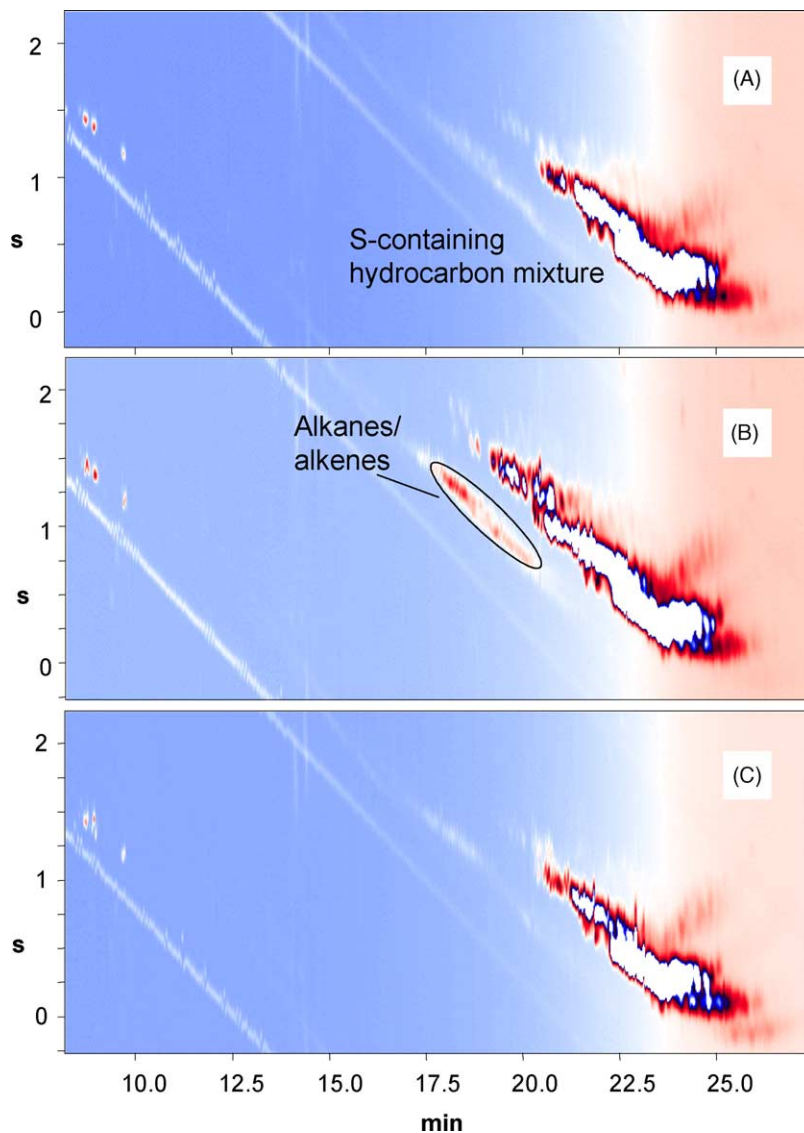

Fig. 7. GC × GC plots of separations of various sulfur-containing hydrocarbon samples: (A) good sample; (B) old sample; (C) sample to be qualified.

occurs, but separations are significantly improved over one-dimensional experiments.

Trace level analysis is an important area for GC applications. It is facilitated considerably with a GC×GC system using cryogenic modulation. Since signal intensities can be increased by a factor up to 50, species in the ppb range can easily be analyzed. An example is the characterization of trace level components in commercially available alkenes as shown in Fig. 6. This methodology could be very helpful for determination of impurities in precursors used in polymer synthesis. In this example, additional fractions of higher weight are observed in the range C_{10}–C_{13}. These components possess higher polarity than alkenes or alkylbenzenes. Also, a group of C_{16}–C_{18} species is found in the GC × GC plot, they are more polar than alkanes but less polar than alkylbenzenes, which were used as standard references. Also, traces of lower weight components, such as C_5–C_6 alkenes, were observed and appear as sharp signals in the range 5–7 min, under-

lining the good trapping/release efficiency of the modulator. Concentration levels for some species are estimated in the low ppb level. As can be seen in the plot the two olefin lots differ significantly with regard to these components discussed above, so GC × GC data can provide valuable information even if they were used only as screening tool.

Another powerful example includes GC × GC analysis of sulfur-containing hydrocarbons supplied by various producers. A product from a new supplier had to be tested for its suitability. GC × GC was applied to investigate whether differences compared to other samples are apparent. Speed, high sensitivity and enhanced chromatographic resolution were required. Fig. 7 illustrates contour plots of some of these samples. Based on the information content derived from GC × GC, it is obvious that the 'old' sample contains additional species. These are either alkanes or alkenes based on relative retention times on the second column. Also, the hydrocarbon range is greater for this
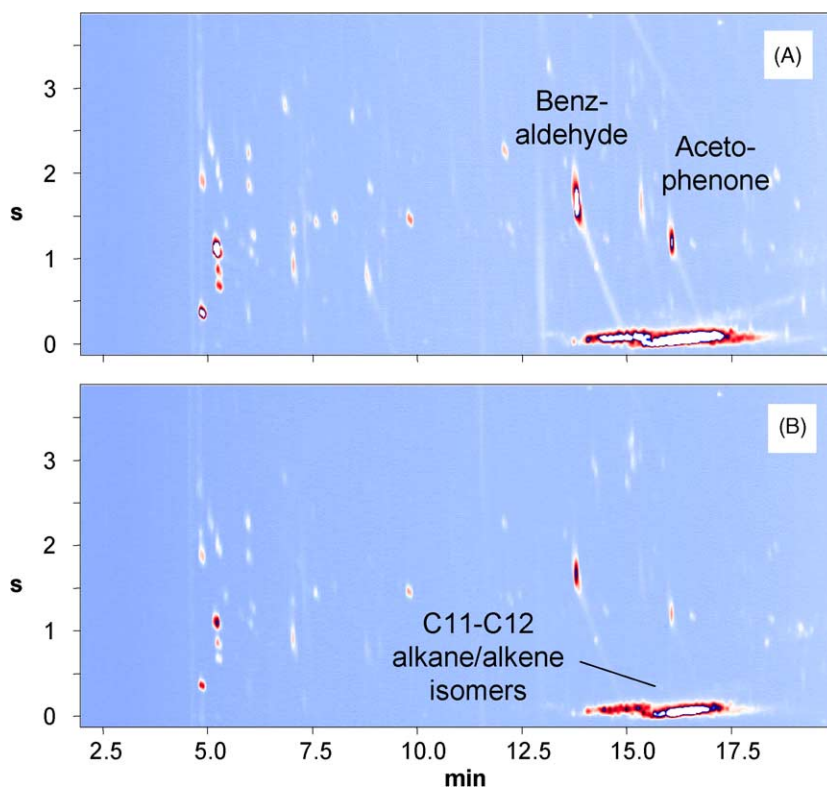

Fig. 8. Two-dimensional GC contour plots of volatiles released from coated substrates.

particular sample (greater heterogeneity). Some separation is indicated for the main peaks of all samples in the second dimension, which is due to presence of alkylated and alkenylated thiols in the mixture. The hydrocarbon chains are linear and branched adding to the complexity of the mixture.

Sensitive methods are always required for volatiles or odor analysis in the low ppm and even ppb level. Due to signal enhancement via cryogenic modulation, GC × GC in combination with headspace injection could be a powerful methodology in this area. As illustrated below, HS-GC × GC was utilized for investigation of volatiles in polymer-coated substrates.

Fig. 8 reveals that the coated samples differ in volatiles content. Sample A shows the highest amount of volatile organics and in sample B volatiles are significantly reduced to 50% and more. Some non-polar species, such as C_{11}–C_{12} alkanes, are detected. Among the odor specific components, acetophenone and benzophenone were identified. The contour plots show that even for these samples, which are not that complex but contain species that possess similar boiling points and different polarities, comprehensive two-dimensional GC is a very nice application. Ideally, TOF/MS detection would allow obtaining structural information of all volatiles present in the coating.

4. Conclusions

The temperature range for GC×GC applications has been extended to low temperatures via an improved modulator design using liquid nitrogen. High separation efficiency is observed, if the cooled capillary segments are subject to immediate heating with warm gas stream. The system was found to be very stable with reproducible secondary retention times.

The liquid N_2 modulator is suited for a wide range of applications including trace level analysis for various analytical problems, such as impurities in olefins or odor components in polymer coating. GC × GC data are powerful even for mixtures of less complexity but having constituents of different polarity at similar boiling points.

References

[1] W. Bertsch, J. High Resolut. Chromatogr. 23 (2000) 167.
[2] M. Pursch, K. Sun, B. Winniford, H.J. Cortes, A. Weber, T. McCabe, J. Luong, Anal. Bioanal. Chem. 373 (2002) 356.
[3] P.J. Marriott, R. Shellie, Trends Anal. Chem. 21 (2002) 573.
[4] R.A. Shellie, L.L. Xie, P.J. Marriott, J. Chromatogr. A 968 (2002) 161.
[5] J.V. Seeley, J. Chromatogr. A 962 (2002) 21.
[6] J. Dalluge, M. van Rijn, J. Beens, R.J.J. Vreuls, U.A.Th. Brinkman, J. Chromatogr. A 965 (2002) 207.
[7] P. Korytar, P.E.G. Leonards, J. de Boer, U.A.Th. Brinkman, J. Chromatogr. A 958 (2002) 203.
[8] R.A. Shellie, P.J. Marriott, Anal. Chem. 74 (2002) 5426.
[9] T. Hyötyläinen, M. Kallio, K. Hartonen, M. Jussila, S. Palonen, M.-L. Riekkola, Anal. Chem. 74 (2002) 4441.
[10] C.A. Bruckner, B.J. Prazen, R.E. Synovec, Anal. Chem. 70 (1998) 2796.
[11] J.V. Seeley, F. Cramp, K.S. Sharpe, J. Sep. Sci. 24 (2001) 444.
[12] A.E. Sinha, K.J. Johnson, B.J. Prazen, S.V. Lucas, C.G. Fraga, R.E. Synovec, J. Chromatogr. A 983 (2003) 195.
[13] Z. Liu, J.B. Phillips, J. Chromatogr. Sci. 29 (1991) 227.
[14] J.B. Phillips, E.B. Ledford, Field Anal. Chem. Technol. 1 (1996) 23.
[15] P.J. Marriott, R.M. Kinghorn, Anal. Chem. 69 (1997) 2582.
[16] J. Beens, M. Adahchour, R.J.J. Vreuls, K. van Altena, U.A.Th. Brinkman, J. Chromatogr. A 919 (2001) 127.
[17] M. Adahchour, J. Beens, U.A.Th. Brinkman, Analyst 128 (2003) 213.
[18] M. Kallio, T. Hyötyläinen, M. Jussila, K. Hartonen, S. Palonen, M. Shimmo, M.-L. Riekkola, Anal. Bioanal. Chem. 375 (2003) 725.