Big Bang: Comprehensive GC x GC

Thermal Modulation combined with the rapid scanning GCMS-QP2010 Plus

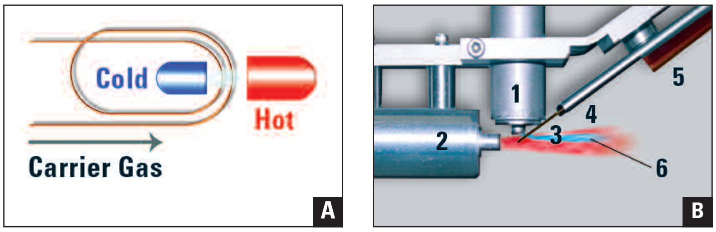


Figure 1: Loop modulator with cold/hot jet assembly.
(A) The loop modulator assembly, shown in accumulation mode, hot jet off.
(B) Components of the modulator: 1) cold jet assembly, 2) hot jet assembly, 3) loop, 4) column holder, 5) Kapton film tensioner, 6) cold gas jet.

GC and GC/MS analysis of complex samples is usually a difficult task as coelutions with matrix are often observed when using just one column. Recent examples have been reported in food analysis such as pesticide screening using the QuEChERS method or the potential allergen determination in cosmetic products. One approach to overcome such problems is comprehensive GC x GC(qMS) which is one of the most innovative developments in chromatography [1,2].

Patented by John Phillips in 1992, this technique first became popular in quality control of petrochemical applications. After the first conference dedicated to this technique in 2003 in Volendam, the Netherlands, a rapidly increasing number of articles was published from year to year followed by the GC x GC Symposium in conjunction with the annual International Symposium on Capillary Chromatography (every 2 years in Riva del Garda, Italy [3]).

This technique uses two columns: one typically non-polar column with 30 m, 0.25 mm, 0.25 µm connected to a typically polar column (Wax), which, however, is very short with about 1 m, 0.1 mm, 0.1 µm. A thermal modulator which can alternately freeze and release the sample molecules is placed between the columns.

Over the years, several types of modulators have been investigated and the technology finally resulted in a very simple and reliable construction referred to as loop modulator (Zoex Corp., USA). Following recent cooperation between Shimadzu and Zoex, a commercial product based on Shimadzu GC and GC/MS systems has been made available from Shimadzu. The advantage of this type of modulator is that only 2 jets (one cold and one hot) are used to modulate the temperature on 2 spots on the column. This is shown in Figure 1.

The column is placed into a holder so that the column passes the cross point defined by the 2 jets twice. The cold jet is produced by feeding nitrogen gas into a dewar already filled with liquid nitrogen whereas the hot jet is produced by nitrogen gas heated by a GC controlled heater cartridge.

The advantage of this thermal modulation over other modulation techniques is that sharp modulation pulses can be produced (Figure 2).

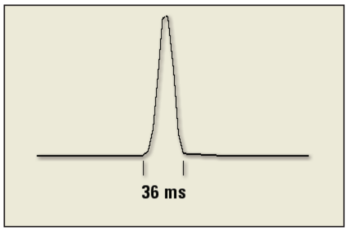


Figure 2: Profile of the thermal pulse for the loop modulator (Zoex Corp.)

Extremely small peak widths

As a result, chromatographic peaks have extremely small peak widths (FWHM) of about 100 ms. The detection system must therefore be able to supply enough data points over the peaks for qualitative and quantitative precision.

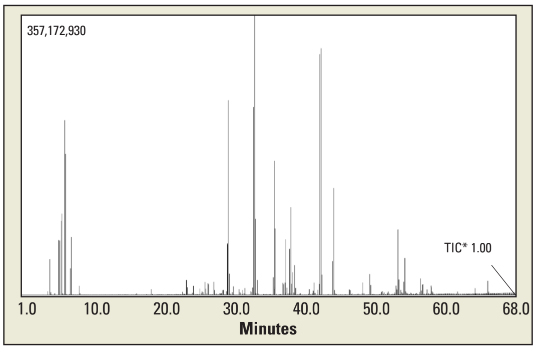
All conventional Shimadzu GC detectors have sampling frequencies up to 250 Hz and filter time constants down to 4 ms, more than sufficient for GC x GC peak shapes. Using MS in the past, time-of-flight (TOF) mass spectrometers were mainly used for quantitative analysis with the drawbacks of limited linear dynamic range and high investment as well as large file sizes.

When quadrupole instruments were used in the past, the results were restricted mainly to qualitative analysis due to the lack of acquisition speed. However, the GCMS-QP2010 Plus can acquire up to 50 and 100 data points per second in scan and selected ion monitoring (SIM) respectively with a scanning speed at a maximum of 10,000 amu/s. Having used this high speed quadrupole MS, publications on quantitative analysis have been available since 2005 [4,5].

Lavender oil sample data

This article describes an example of lavender oil sample data obtained with the GCMS-QP2010 Plus. This type of sample was first measured using GC x GC by Shellie et al. [6].

Figure 3 shows the TIC of a commercial lavender oil sample diluted 1:10 in ethanol. The



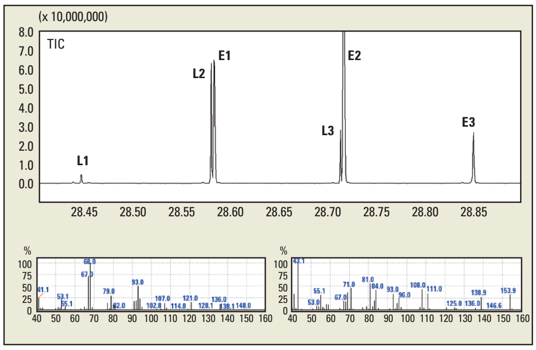


Figure 3: Modulated TIC of a lavender oil sample

Figure 4: Zoom into the retention time window between 28.4 and 28.95 minutes. The spectra indicate the peaks labelled L1-L3, and E1-E3 refer to the compounds limonene and cineole (eucalyptol).

(qMS)

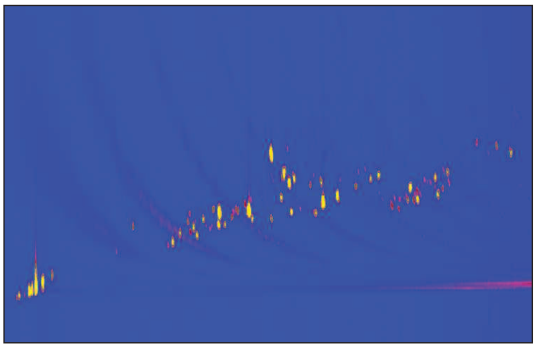


Figure 5: Contour plot of the lavender oil sample

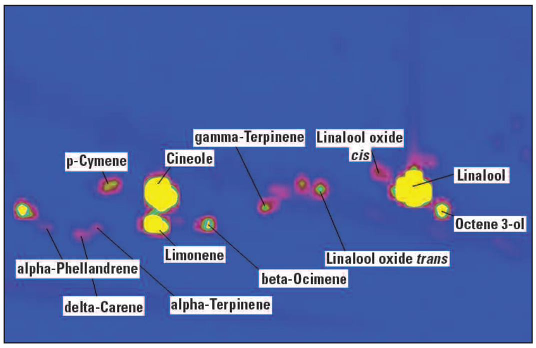


Figure 6: Zoom into Figure 5 (first dimensional retention range of between 26.255 and 34.255 min)

injection volume was 0.2 µL. Modulation frequency was set to 8 s. GC conditions were: column oven 40 °C for 1 minute, then 2.5 °C/minute to 250 °C for 5 minutes. The split ratio was set at 1:100 and pressure was selected to be 150 kPa. The injector and interface temperature were both set to 250 °C. The mass spectrometer acquired data in full scan mode (40 - 350 amu) at 25 Hz resulting in a scan speed of 10,000 amu/s. In Figure 4 a zoom between 28.4 and 28.95 minutes is shown. Two compounds – limonene and cineole (eucalyptol) – are separated in that time range with 3 peaks/compound. The separation in the second column can be seen by the separation of closely eluting pairs of peaks with retention time differences of about 0.3 s.

The spectra qualities over the narrow modulated peaks are very well proven by similarity indices SI larger than 95. The peak widths at the base are about 180 ms in this experiment resulting in 6 data points/peak or about 18 data samples per compound.

Usually comprehensive GC x GC and GC x GC(qMS) data are plotted in a three-dimensional plane where the x-axis is the one-dimensional retention time, the y-axis is the retention time in the second dimension and the z-axis represents the intensity. The compound peak in such a plot has a volume (called blob instead of peak) and is proportional to the concentration of that compound.

85 compounds detected in lavender oil

Figure 5 shows a plot of the lavender oil sample. The intensity here is visualized by the color of the blobs. The minimum and maximum signal values can be scaled freely to the corresponding color distribution in order to customize the appearance of the image. In this example blobs of very high intensity are yellow whereas compounds with relatively small concentrations are purple. More than 85 compounds were detected.

As an example, the region is discussed where limonene and linalool have been detected. In Figure 6 a zoom into the map is shown. The blobs detected and identified are labelled. All similarity indices were greater than 95. For confirmation of compounds having similar mass spectra the concept of linear retention index may be used in combination with a corresponding library. A library dedicated to flavor and fragrance compounds containing linear retention indices is available from Shimadzu Europa (FFNSC 1.2).

In order to assess the signal-to-noise ratio for low intensity peaks, the one dimensional fraction of the TIC of alpha-phellandrene is shown in Figure 7 which appears to be weakly colorized due to the large intensities of the other components. Even for this peak the signal-to-noise ratio for that fraction at the mass trace of m/z = 93 is larger than 300:1 in full scan mode.

As the peaks in comprehensive GC x GC have smaller widths when compared to conventional GC analysis they are taller, resulting in a drastically enhanced sensitivity. This effect can be also seen when comparing standard GC with fast GC data [7].

Conclusion

Comprehensive GC x GC and GC x GC(qMS) are approaches to overcome separation problems in complex samples. The hardware and software available from Shimadzu supply ready-to-use tools for both qualitative and quantitative routine work. Workshops and seminars will be offered by Shimadzu on this topic.

Further details at www.shimadzu.eu

Literature

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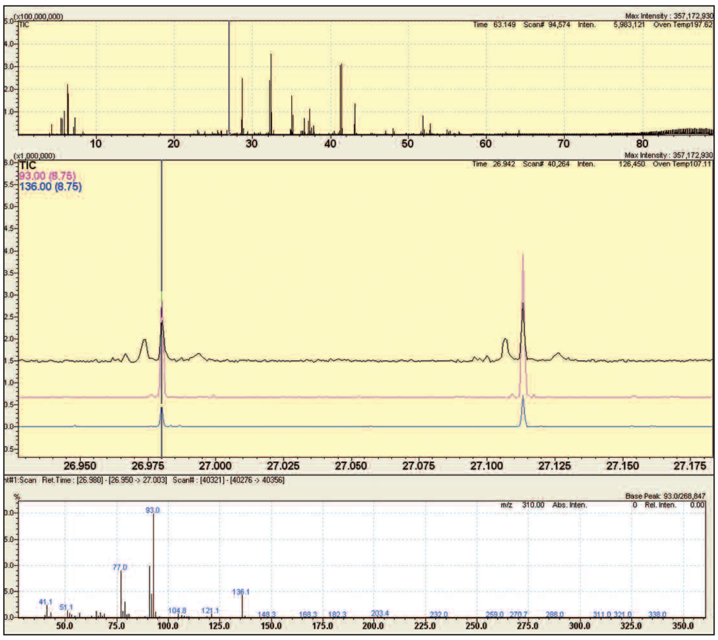

Figure 7: Raw data (TIC) of fractions of alpha-phellandrene