Comprehensive GC×GC(qMS)

Qualitative and Quantitative Analysis of PCBs using EI and NCI Mode with a Rapid Scanning Quadrupole Mass Spectrometer

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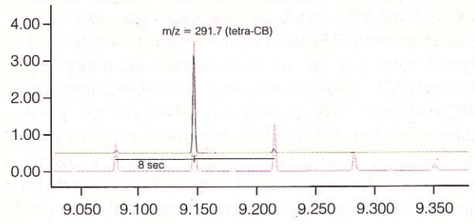
Comprehensive GC×GC, invented by J. Phillips in 1989,[1] has experienced rapidly increasing interest in the last years. The original application area in the petrochemical field has been extended to many different topics. Very often coelutions with matrix peaks are observed and a high separation power is needed. Next to the enhanced GC×GC peak capacity, the hyphenation of GC×GC to mass spectrometry gives an extra dimension for easy identification of the compounds hiding under contour plot displays used in GC×GC.

Figure 1: Three fractions (modulation 8s) of tetra-CB for a standard (top) and the QC sample (bottom).



Most reports are based on thermal modulation, especially when using MS as a detector. In this work a loop modulator (Zoex Corp., USA) was used where a two stage hot/cold jet modulation was achieved with one cold and one hot jet. In the first dimension a 30 m BPX-1 (0.25 mm i.d. × 0.25 µm df) was used coupled with a 1 m BPX-50 (0.15 mm i.d. × 0.15 µm df) in the second dimension. The modulation period was set to 8 seconds. As the peak width of subsequent modulated peaks is about 350 ms at the base, the detector needs a high acquisition speed to supply enough data points across the peak. Furthermore, a high-speed quadrupole MS (Shimadzu GCMS-QP2010 Plus) was used and the sampling frequency in full scan mode was set between 25 and 50 scans/s at a scanning speed of 10000 amu/s.

The analysis of PCBs has been performed using EI and NCI ionization. In EI mode full scan and selected ion monitoring were performed. The quantitative accuracy of the method was tested by measuring a QC sample [bovine fat extract spiked with PCB and dioxins, 10–250 pg (PCB)/g fat)] which was prepared using an accredited procedure including preparative multi-stage LC. In Figure 1 the SIM raw data of a standard (140 ppm) and the QC sample for tetra-CB is shown. For SIM four ions and 10–13 data points were recorded across each of the modulated fractions.

Figure 2: GC×GC(qMS) calibration curves for PCB-28 and PCB-114, EI SIM Mode

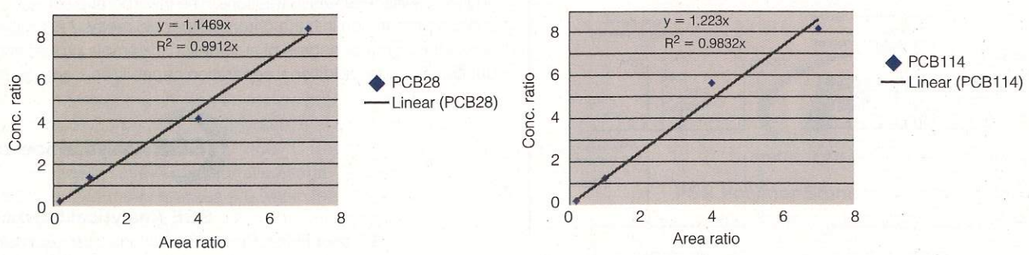


Figure 3: EI-TIC image of the QC sample (35–500 amu)

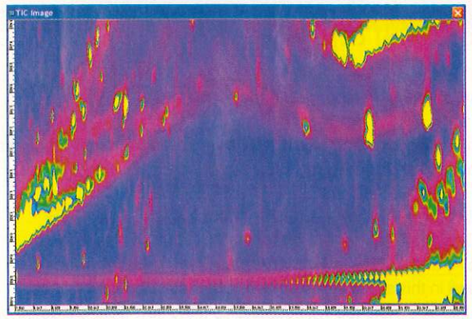
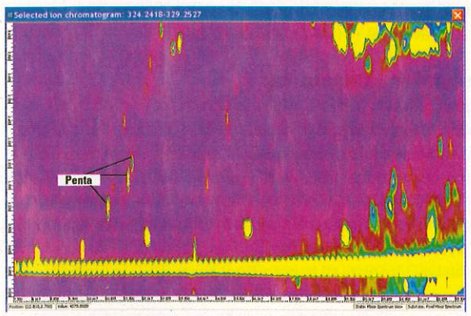


Figure 4: Extracted ion image (324–329 amu) from the EI-TIC data to locate penta-CB.

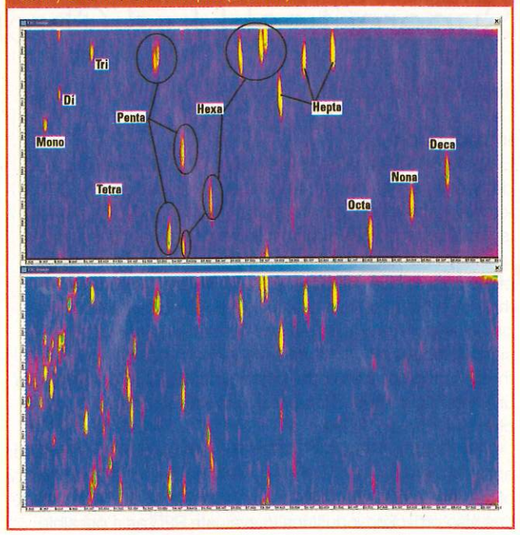


This is sufficient for reliable quantitative GC×GC(qMS) work, as proven by the data of Figure 2 where calibration curves are shown for PCB-28 and PCB-114 with good linearity (4–140 ppm). The area is the sum of the modulated fractions per compound. In EI full scan mode a mass range of 34–500 amu was selected with a minimum of 10 data points (scans) across each peak. The TIC image of the QC sample is shown in Figure 3.

The whole image is dominated by matrix signals. To identify the PCBs an extracted mass ion has to be calculated by the image software used. This is shown in Figure 4 for penta-CBs. Negative chemical ionization (NCI) is very popular as an alternative to ECD detectors for electrophilic compounds. The NCI/GC–MS sensitivity is comparable to ECD response for PCBs. Low chlorinated PCBs show a dominant 35 fragment indicating dissociative electron capture processes. For higher chlorinated PCBs resonance electron capture becomes more dominant.

Figure 5 shows the NCI-TIC (34–500) image of the QC sample together with the image of a PCB standard. The signals relative to PCBs can be identified very easily by comparison. The difference of the GC×GC(qMS) images in EI and NCI mode recorded in full scan indicate the power of the selectivity in NCI mode. Very small signals

Figure 5: NCI-TIC images of a PCB standard (top, 140 ppm each) and the QC sample (bottom)



can be seen from the matrix whereas in NCI mode PCBs show a strong signal response.

As a result GC×GC(qMS) with a rapid scanning quadrupole instrument offers an alternative to a TOF-MS when the mass range is adjusted for target analysis. The easy switching between the ionization techniques allows high selectivity.

References

1. (a) John B. Phillips and Zaiyou Liu. "Chromatographic Technique and Apparatus", US Patent No. 5135549, August 4 (1992).
(b) John B. Phillips and Zaiyou Liu. "Apparatus and Method for Multi-dimensional Chemical Separation", US Patent No. 5196039, March 23 (1993).