

1 Introduction

Although capillary liquid chromatography has matured very rapidly due to new commercially available liquid chromatography systems, the robustness and ruggedness of this technique is still considered a problem. The advantage of capillary liquid chromatography is not only a reduced solvent consumption if the system is able to deliver the mobile phase in the lower $\mu\text{L}/\text{min}$ range. Further benefits of this technique are the low amount of sample material for injection as well as fast analysis times. The hyphenation of capillary liquid chromatography with time-of-flight mass spectrometry should therefore be ideally suited due to the fast scanning rate of these detectors. However, the sensitivity of time-of-flight instruments is often not high enough for trace analysis.

Therefore, the aim of this presentation is to highlight the advantages and drawbacks of coupling capillary liquid chromatography to time-of-flight mass spectrometry if a test solution containing more than 400 pesticides is analyzed.

2 System set-up

All experiments were carried out using a capillary system from Eksigent based on microfluidic flow control (Eksigent ExpressLC-100). This system allows the use of flow rates between 1 and 30 $\mu\text{L}/\text{min}$ without flow splitting and is optimized for 300 μm I. D. columns. A Phenomenex Synergi Fusion-RP column (100 mm, 0.3 mm I.D., 100 Å; particle size 2.5 μm) was used for all experiments. Although the system is equipped with an integrated column thermostat, the connection of the column with the inlet source of the mass spectrometer was achieved by using an external heating system. As column heater the HPLC Mini Column oven from ApuMass, especially designed for LC-MS-systems was used. The connection of the column with the injection port was accomplished by using a PEEKSIL capillary (11 cm, 360 μm O. D.; 30 μm I. D.). The column was connected with the source of the mass spectrometer by using a New Objective standard coated Taper Tip (20 cm, 360 μm O. D., 20 μm I. D.). The system set-up is shown in Figure 1.

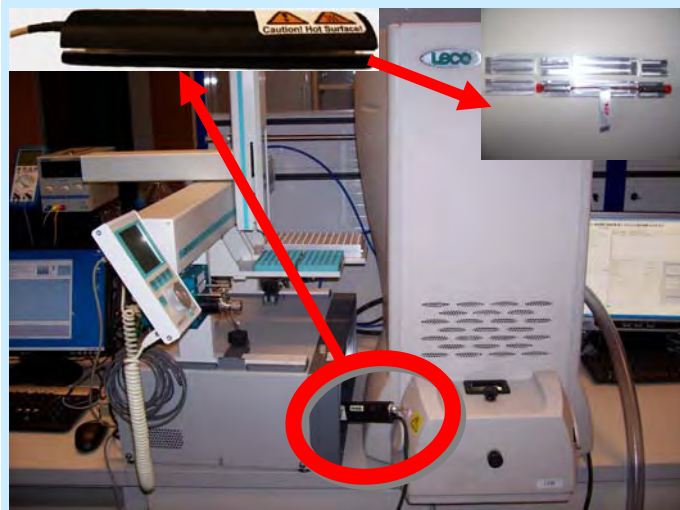


Figure 1: Eksigent ExpressLC-100 system hyphenated to LECO Unique HT TOFMS. The system has been optimized in terms of dead volume by using a column oven specially designed for LC-MS systems (ApuMass, Mini Column oven).

3 Results and Discussion

3.1 Chromatographic performance

The gradient performance in capillary liquid chromatography is often put into question. As becomes evident from Figure 2, the relative standard deviation for the retention time of selected compounds eluting during the gradient is less than 0.7 % which is achieved throughout all runs. This clearly highlights that retention time reproducibility in gradient mode is excellent and can be compared to standard HPLC systems.

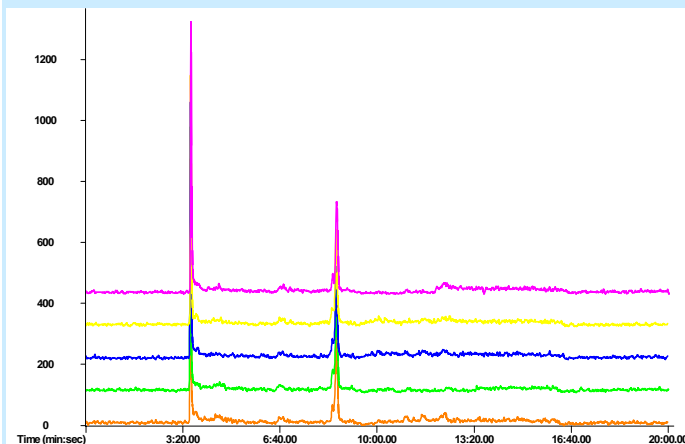


Figure 2: Retention time reproducibility in gradient mode is less than 0.7 %.

3.2 Detection performance and deconvolution of spectra

In order to evaluate the performance of the cap-LC-TOF-system, a mixture containing approximately 400 pesticides was injected and analyzed. The data analysis was done by the LECO® ChromaTOF® 4.0 software for LC-TOFMS. The ChromaTOF software platform offers a suite of automated processing tools, including automated peak find, True Signal Deconvolution®, library searching, and sample comparison. In order to obtain accurate mass spectra of specific compounds even in coeluted peaks, the peak find and True Signal Deconvolution® algorithm of the software was used. Figure 3 shows a typical chromatogram which was obtained when using the system set-up as described above.

The black curve represents the Total Ion Chromatogram. If the data is processed automatically, the software is able to find the majority of all compounds which are present in the sample. In the insertion of Figure 3, a detail of the chromatogram of Figure 2 is shown. Within the time interval between 9:20 minutes and 10:40 minutes in the chromatogram, it was possible to detect 50 pesticides within 90 seconds. Every analyte which has been automatically detected by the software is highlighted by a peak marker (in grey). The peak width of each compound is around 10 seconds. Using a scan speed of eight spectra per second in average 80 data points across a peak are obtained which allows accurate quantification.

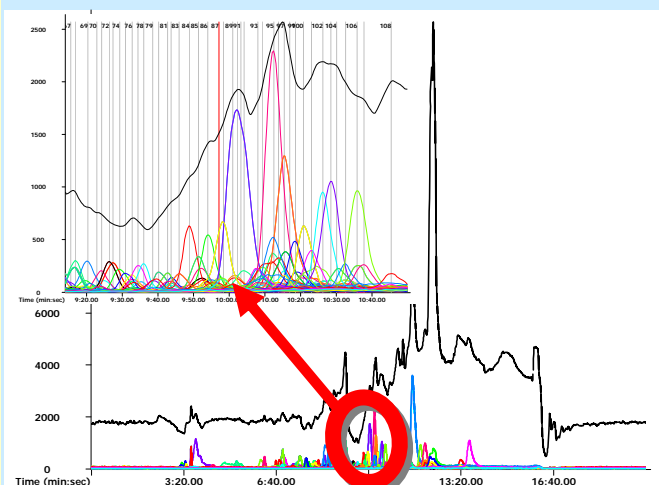


Figure 3: Automatic peak identification using the LECO® ChromaTOF® 4.0 software.

Figure 4 displays the extracted ion chromatogram of the coeluting pesticides heptenephos and isotropuron. Using the True Signal Deconvolution® algorithm the caliper spectra, which is the summarized spectra between 8:30 min and 8:45 min is extracted into the peak true spectra of both pesticides. The peak true spectra could be used for identification by mass delta or isotopic pattern matching.

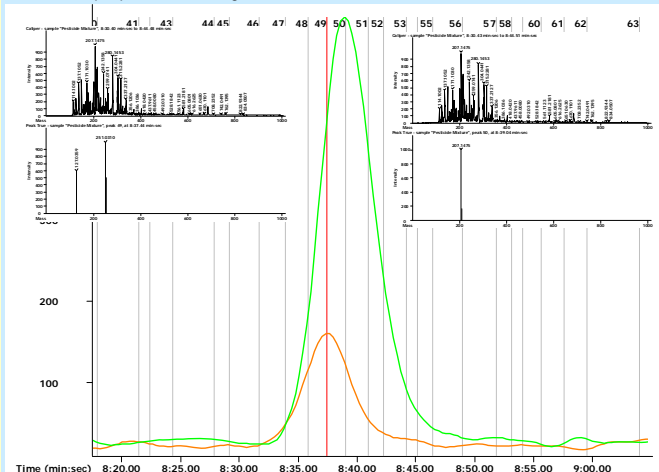


Figure 4: Automatic peak identification by using the deconvolution algorithm of the LECO® ChromaTOF® Software.

4 Conclusions

Although capillary liquid chromatography is usually thought of as a method with poor reproducibility, the results we presented for the separation of a pesticide mixture using capillary liquid chromatography coupled to time-of-flight mass spectrometry revealed that excellent chromatographic performance and detection sensitivity were achieved.

5 Acknowledgements

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