GLOBAL ANALYTICAL SOLUTIONS

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AppNote 1/1997

A Fully Automated and Robust LC-CGC Combination for Application in Environmental Analysis

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Summary

A new interface has been developed for the on-line coupling of liquid chromatography (LC) and capillary gas chromatography (CGC). The interface consists of a flow cell from which a sample can be taken by the syringe of a large-volume programmed temperature vaporisation (PTV) injector. The PTV injector is then operated in the solvent venting mode for injection in the capillary column. The fully automated system can be operated and the data handled by one PC. The performance is illustrated with the analysis of some phenylurea pesticides in tobacco leaves.

Introduction

We recently discussed the importance of automated analytical systems in environmental analysis[1]. In this framework, recent research was focused on the construction of a reliable

and versatile interface for the on-line coupling of LC to CGC.

On-line LC-CGC is not new and the first report dates from 1980 [2]. Over the years several groups have developed interfaces to transfer relatively large LC fractions into the GC capillary column and instrumentation became commercially available [3-8].

Interfacing LC and CGC instrumentation can be done in different ways including partial transfer of an LC fraction via a split interface or total transfer via PTV injection with solvent venting or cool on-column (COC) injection applying partial or total concurrent solvent evaporation. An excellent overview of the different possibilities was presented by K. Grob, one of the pioneers of LC-CGC hyphenation [8].

In this contribution, a new fully automated and flexible system based on standard LC and CGC instrumentation is described. The interface consists of a flow cell, a large volume sampler (LVS) and a PTV injector. Transfer of LC fractions, originating from normal phase LC, reversed phase LC or size exclusion LC, can be done totally or partially. Moreover, both LC and CGC instrumentation remain accessible for off-line use [9].

The performance of the system is demonstrated with the analysis of some phenylurea herbicides extracted from tobacco leaves.

System Description

The LC-CGC combination consists of an HP 1100 LC and an HP 6890 GC, both from Hewlett-Packard, Waldbronn, Germany. The LC system contains an automated sample injection device, a binary or quaternary solvent pump, solvent degassing and column thermostating units and a detector (variable UV, multiwavelength or diode array). The GC instrument is equipped with a PTV injector and FID or MS detection. Other detectors like ECD, NPD or FPD can be applied as well. Both systems can be controlled independently or simultaneously from a single PC (Chemstation) using the respective software programs.

The interface between the two chromatographs is a modified large volume sampler (Multipurpose Sampler) from Gerstel GmbH, Mülheim an der Ruhr, Germany. The interface is shown in Figure 1. The mobile phase leaving the LC detector is directed via a capillary tube with well defined dimensions in a T-shaped flow cell. The cell is equipped with a septumless head, through which the needle of the syringe can be introduced. The sampler is controlled by a Model 505 controller and an additional software program.

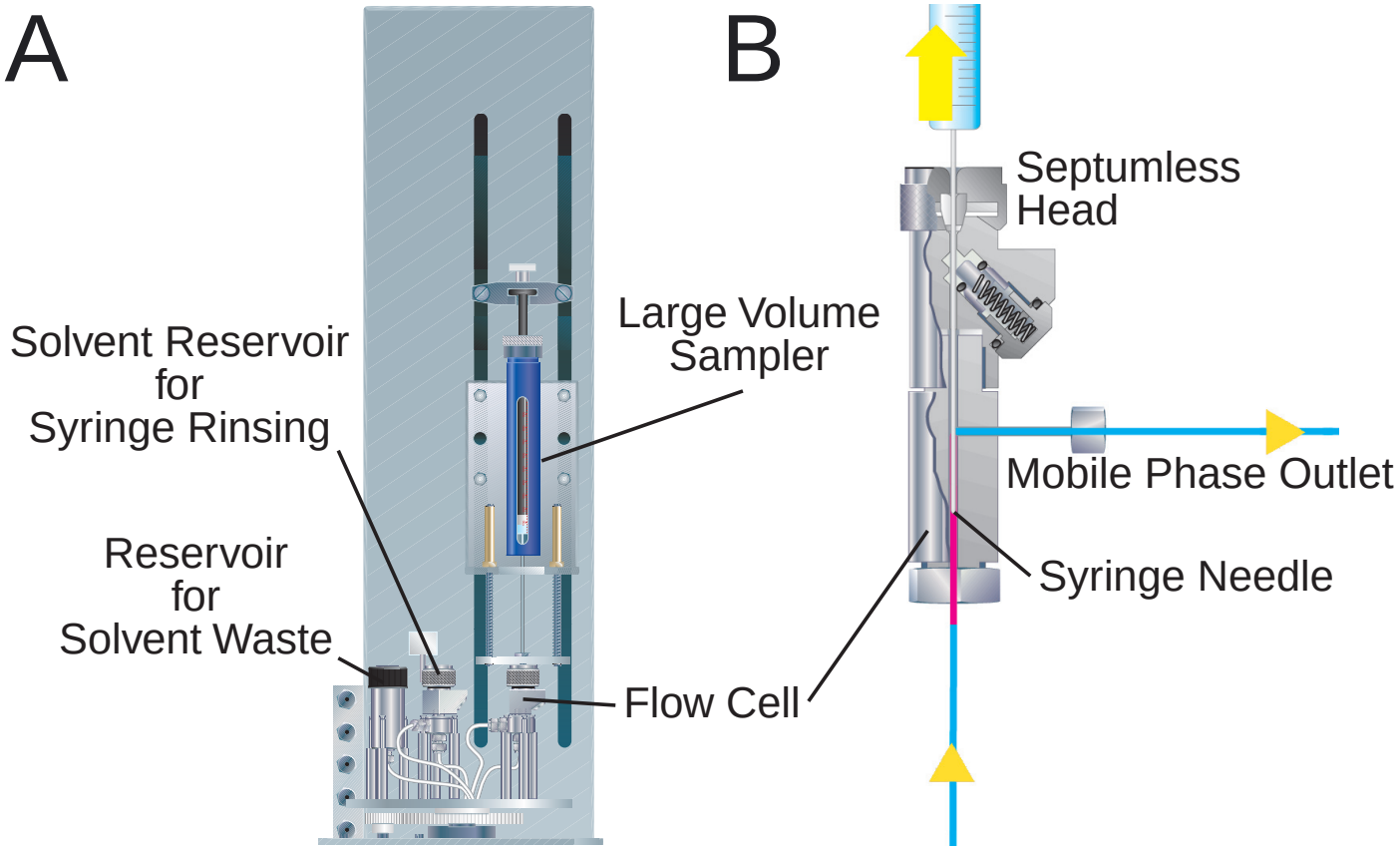

Figure 1. Schematic drawing of the LC-CGC interface (A: General view, B: Detail of the flow cell).

To transfer a selected LC fraction, the heartcut window (start and stop time of transfer) is introduced in the program together with the flow rate applied in the LC analysis and the dimensions of the connecting capillary tube. At the time the fraction passes the flow cell, the syringe needle penetrates the septumless head and samples the LC fraction at a speed equal to the LC flow rate. The LC mobile phase flow and syringe plunger speed of the Multipurpose Sampler are synchronized. The time delay between the LC detector and the flow cell is automatically taken into account by the software program so that the heart-cut times can be directly deduced from the LC chromatogram. Volumes up to 2 ml can be introduced into the PTV syringe. After collection, the needle is withdrawn from the flow cell which rotates away from the PTV inlet and an injection in the solvent venting mode is made. Depending on the fraction volume and solvent type, the sample introduction parameters (injection temperature, injection speed, vent flow, vent pressure, purge delay time, etc.) are determined using the PTV calculator program and introduced in the controller and GC software. During an initial time, the inlet is kept at low temperature while the split vent is open (eventually with increased split flow and reduced inlet pressure). The largest part of the mobile phase is thus evaporated. After solvent venting, the split valve is closed, the pressure is set to the normal head pressure and the injector is heated to evaporate the solutes and to transfer them, in the splitless mode, into the capillary GC column.

System Performance

The performance of the LC-CGC interface has been demonstrated with the analysis of the dibenzothiophene fraction in crude oils [9]. Normal phase LC fractionation on aminopropyl silica was applied. Methylated dibenzothiophenes are very persistent in the environment and can therefore be used as markers of oil pollution. RSDs for five runs on absolute peak areas for 2- and 3-methyldibenzothiophene were in the order of 2%.

An LC-CGC method has also been developed for the determination of phenylurea pesticides in tobacco leaves. The conventional analytical method contains a number of time consuming steps like solvent extraction, column chromatography on silica and florisil, evaporation of large amounts of solvents, etc.

The LC-CGC method implies only an ultrasonic extraction with ethylacetate, filtration, concentration and LC-CGC analysis applying size exclusion chromatography.

Figure 2 shows the SEC chromatogram of tobacco leaves spiked with 100 ppb monolinuron and metobromuron. The SEC analysis was carried out on a 30 cm L x 7.5 mm i.d. column packed with 5 µm SEC particles with 5 nm pores (Phenomenex, Torrance, CA, USA). The mobile phase was acetone-cyclohexane in ratio 2:1 at a flow rate of 1 ml/min. Detection was performed at 245 nm. The fraction containing the phenylurea pesticides elutes between 8.2 and 9.2 min. This fraction was transferred to a capillary column 30 m L x 0.25 mm i.d. x 0.25 µm HP-5MS (Hewlett-Packard).

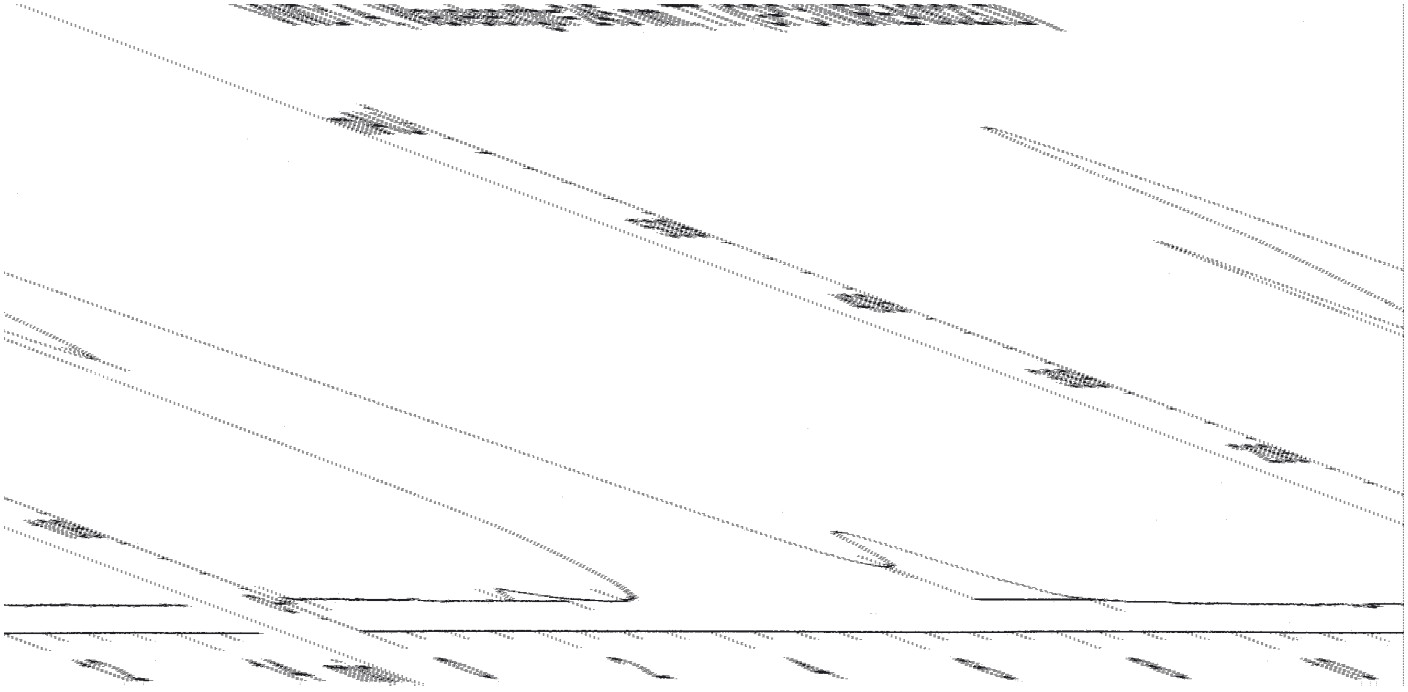

Figure 2. SEC chromatogram of the tobacco extract spiked with 100 ppb monolinuron and metobromuron.

Figure 3 shows the chromatogram recorded with an HP 5973 MSD operated in the full scan mode. The chromatogram is still very complex but by applying ion extraction at m/z 61 both pesticides can easily be elucidated at 16.16 and 17.24 min, respectively (Figure 4). Moreover, the sensitivity of the HP 5973 MSD allows to confirm the identity by library search as illustrated in Figure 5 for monolinuron, eluting at 16.16 min. The robustness of the method is more than acceptable [11] and detectabilities in the order of 1 ppb with RSDs < 10% can easily be reached applying ion monitoring. This is far below the maximum allowable concentration (MACvalue) in tobacco.

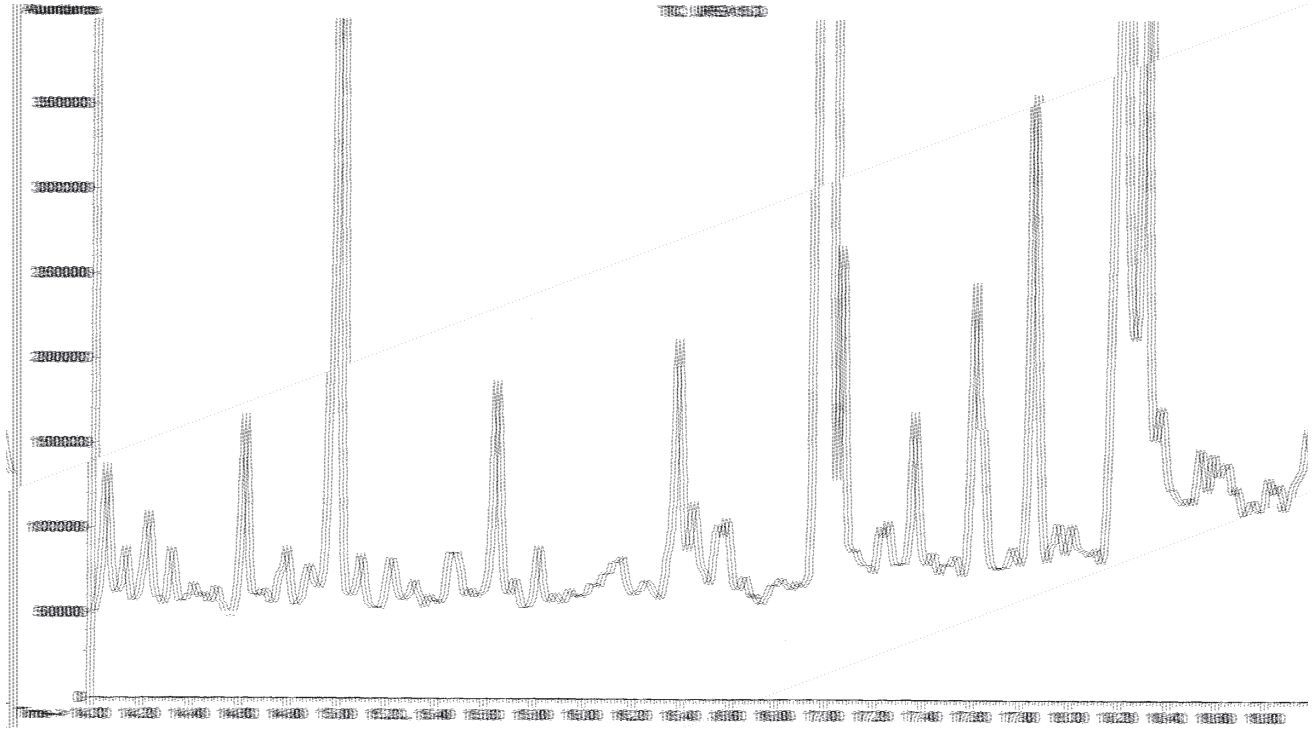

Figure 3. Total ion chromatogram of the transferred phenylurea fraction.

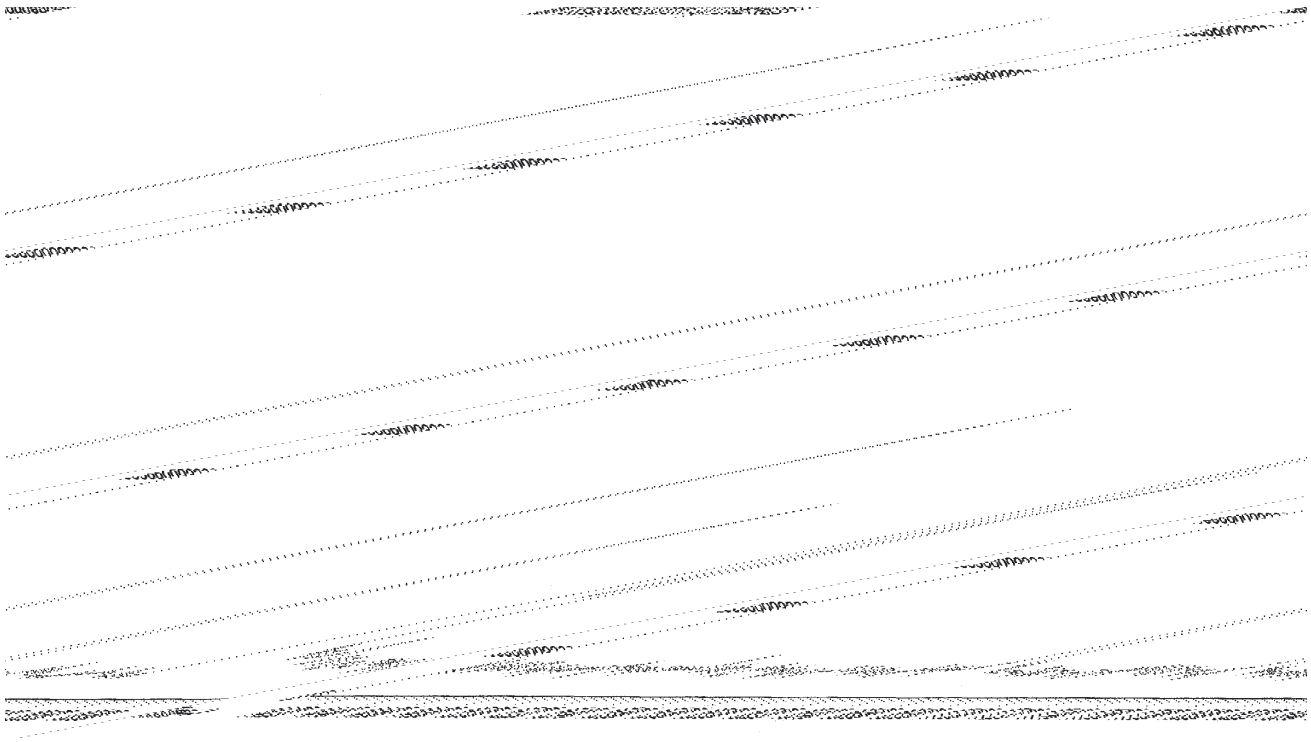

Figure 4. Extracted ion chromatogram (m/z 61) of the transferred phenylurea fraction, monolinuron (peak 1), metobromuron (peak 2).

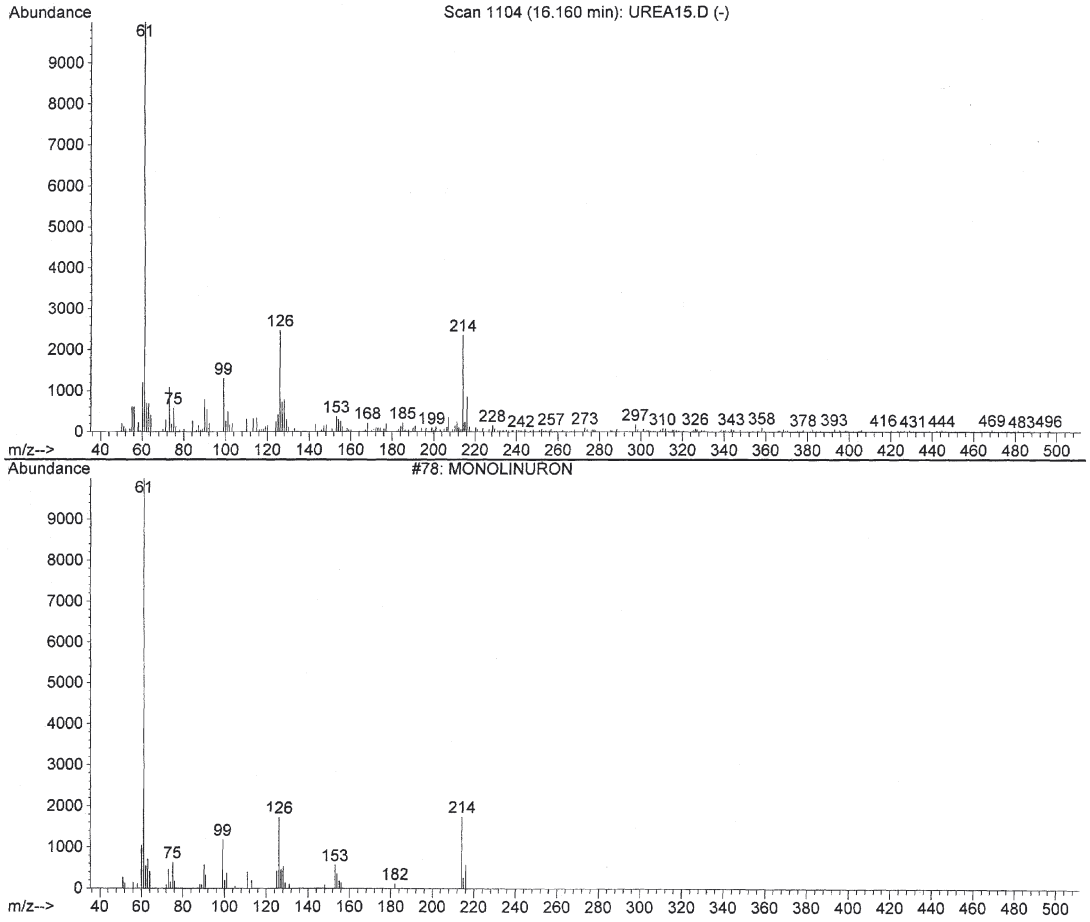

Figure 5. MS spectrum at 16.16 min (top) and the library spectrum (bottom).

Conclusion

The described automated on-line LC-CGC system, based on a flow cell from which eluting LC fractions can be sampled and on large volume injection using a PTV inlet operated in the solvent vent mode, offers a very flexible and robust analytical tool and this, not only for improved sample preparation but also to enhance on resolution for complex mixtures by combining LC and CGC selectivities.

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