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Automated SPE and Fast GC-ECD Analysis of PCBs in Waste Oil

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MACH, Fast GC-ECD, SPE, PCB, waste oil

Abstract
A fast SPE-GC-ECD method for the analysis of PCBs in waste oil was developed. A complete profile was obtained following SPE with a 12 minute GC run-time using a modular accelerated column heater (MACH). Full automation of the sample preparation and analysis (except sample weigh-in) enables a daily throughput of 100 samples. A wide range of concentrations can be determined using a dedicated column and Electron Capture Detection (ECD).

Introduction
The official method for the analysis of PCBs in waste oil (DIN EN 61619) is time consuming and labor intensive (dilutions; extraction, column preparation and cleaning; manual solid phase extraction…) and it requires a long GC run (around 40 min).

Speed of analysis in capillary GC can be increased by using fast and ultra-fast temperature programming. In general, peak resolution will be reduced when the temperature gradient is very fast, but for several applications, some loss of resolution can be accepted. Recently, direct resistive heating of the capillary column resulting in very fast heating rates (> 1800 °C/min) has been introduced [1]. The system available via GERSTEL under the name Modular Accelarated Column Heater (MACH, GERSTEL GmbH, Mülheim an der Ruhr, Germany) is mounted onto the door of a standard GC holding up to four modules containing separate capillary columns

that can be controlled independently. Columns using short transfer capillaries are connected to the injector and detector of choice. The MACH system has previously been used to improve analysis speed by up to a factor 10 and, mainly in combination with split or splitless liquid or headspace injection, for the analysis of mineral oil and residual solvents [2,3].

Solid phase extraction (SPE) is a relatively fast sample preparation method that enables enrichment and/or purification. SPE can be fully automated and is compatible with fast GC, making a high throughput possible.

This work describes the use of automated SPE with the GERSTEL MPS 3 autosampler with SPE option (Figure 1) in combination with fast GC-ECD analysis for the determination PCBs in waste oil.

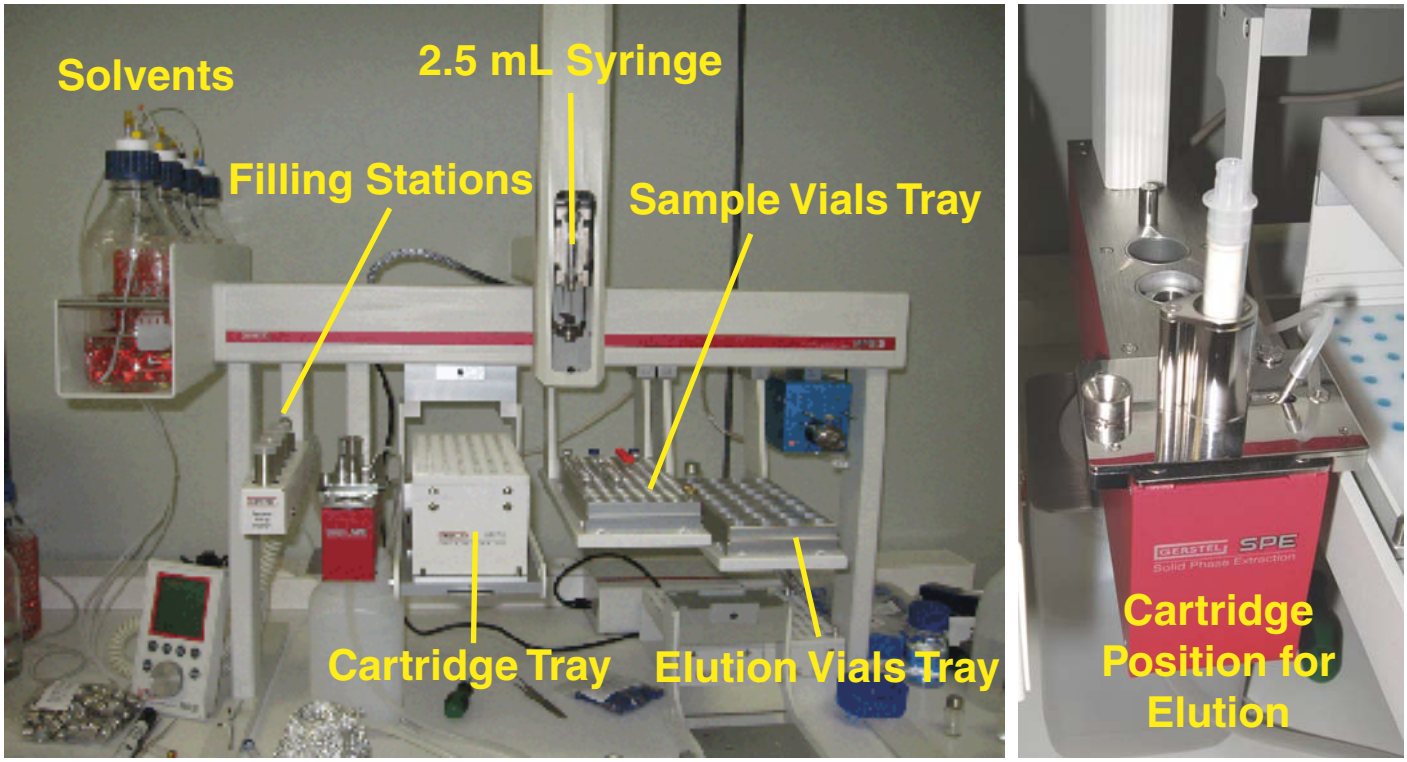

Figure 1. Gerstel MPS3 with integrated SPE option.

Experimental

Sample preparation by SPE. The following SPE method is based on a Macherey-Nagel procedure [4].

A standard 3 mL SA/SiOH SPE cartridge (No. 730132, MACHEREY-NAGEL GmbH & Co. KG, Düren, Germany) with 500 mg solid phase was used. The cartridges are capped in such a way that no dead volume is left between the packing and the cap itself. The sample and solvent are loaded onto the cartridge under positive pressure using a syringe, ensuring optimal control over the automated elution steps.

All required steps are selected by mouse-click from a pull-down menu using the PrepBuilder function of the GERSTEL MAESTRO software.

160 mg samples were weighed in 2 mL vials and 1 mL hexane was added. The samples were homogenized and placed in the SPE station (figure 1).

The SPE process was set up as followed:

1. Condition the SPE cartridge with 1.5 mL hexane
2. Add 250 µL sample
3. Rinse the SPE cartridge with 0.5 mL hexane
4. Elute the analytes with 2 x 2.5 mL hexane (collected in 10 mL vial)

Optionally, 50 µL of an IS solution (octachloronaphthalene, 1 ppm in hexane) could be automatically added to the sample prior to SPE.

Instrumental conditions

A Modular Accelerated Column Heater (MACH™) was mounted on the oven door of an Agilent 6890 gas chromatograph (Agilent Technologies, Little Falls, DE, USA), which was configured with an Agilent electron capture detector (ECD). The system was equipped with a 6890 ALS for automated injection. The MACH

column oven module contained a 20 m x 180 µm I.D., 0.18 µm Rtx-PCB (Restek Corporation, Bellefonte, PA, USA) capillary column. The inlet of the column was connected to a split-splitless injector using 20 cm of a deactivated fused silica capillary of 180 µm I.D. The outlet of the column was coupled with a deactivated fused silica capillary (20 cm x 180 µm I.D.) to the ECD. Both transfer capillaries were connected to the analytical column using low dead volume connectors. The injector was used in splitless mode, the injector temperature was set to 300°C. Hydrogen was used as carrier gas at a constant flow of 1.5 mL/min. The MACH oven module was programmed from 100°C (1 sec) to 200°C (0 sec) at a rate of 100°C/min, and to 300°C (60 sec) at a rate of 10°C/min. The Agilent GC oven served only to keep the transfer capillaries heated and was set to a constant temperature of 320°C. The ECD temperature was set to 330°C and the data acquisition frequency was 50 Hz.

Results

The separation of a PCB congener mixture (M-8082 from AccuStandard, 100 pg/µL in hexane) on the MACH-GC-ECD is shown in figure 2.

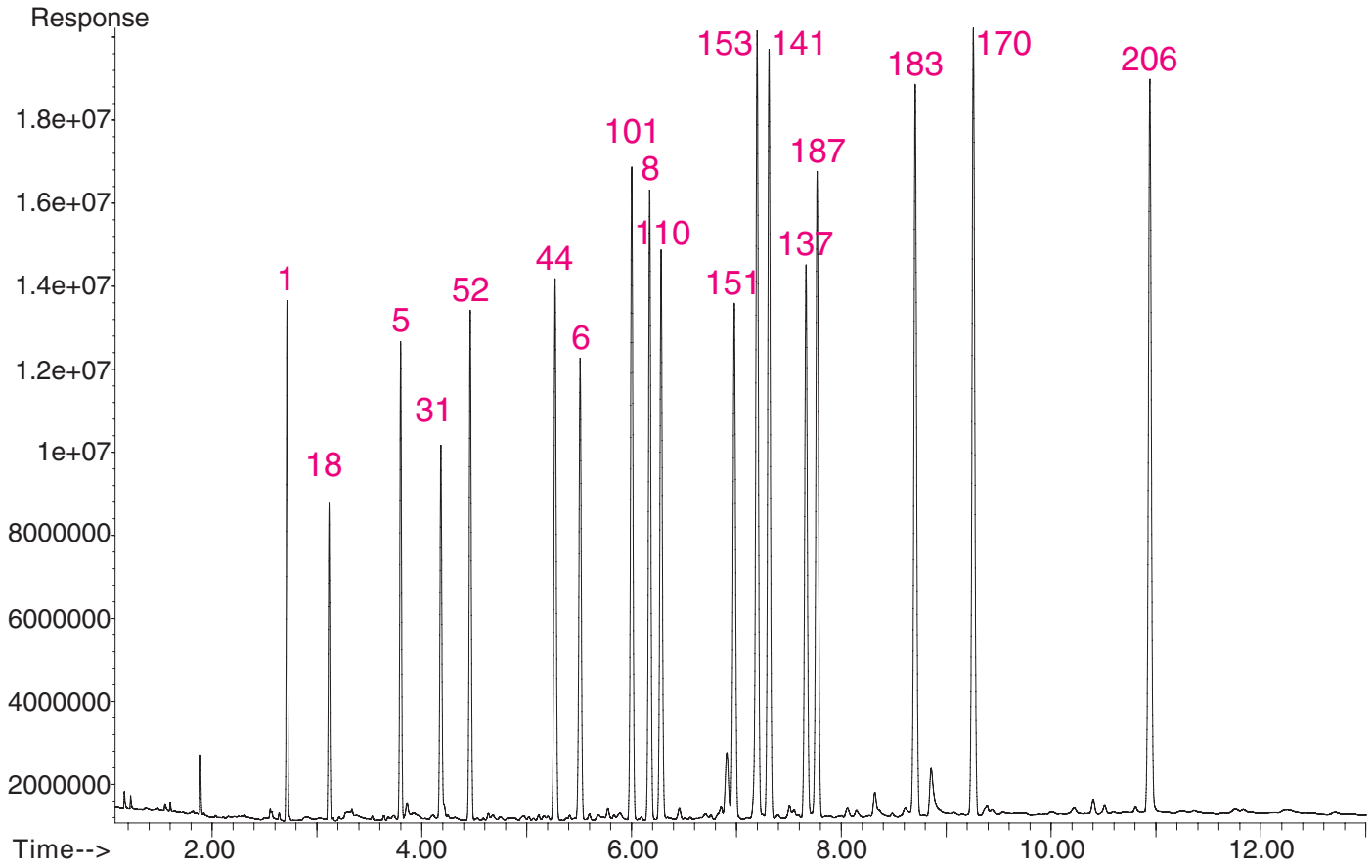

Figure 2. Chromatogram of PCB congener mixture, M-8082 from AccuStandard, 100 pg/µL in hexane.

SPE was subsequently performed on a certified waste mineral oil with high levels of PCBs (BCR-449, IRMM). The chromatogram is shown in figure 3, the PCB concentrations are listed in table 2.

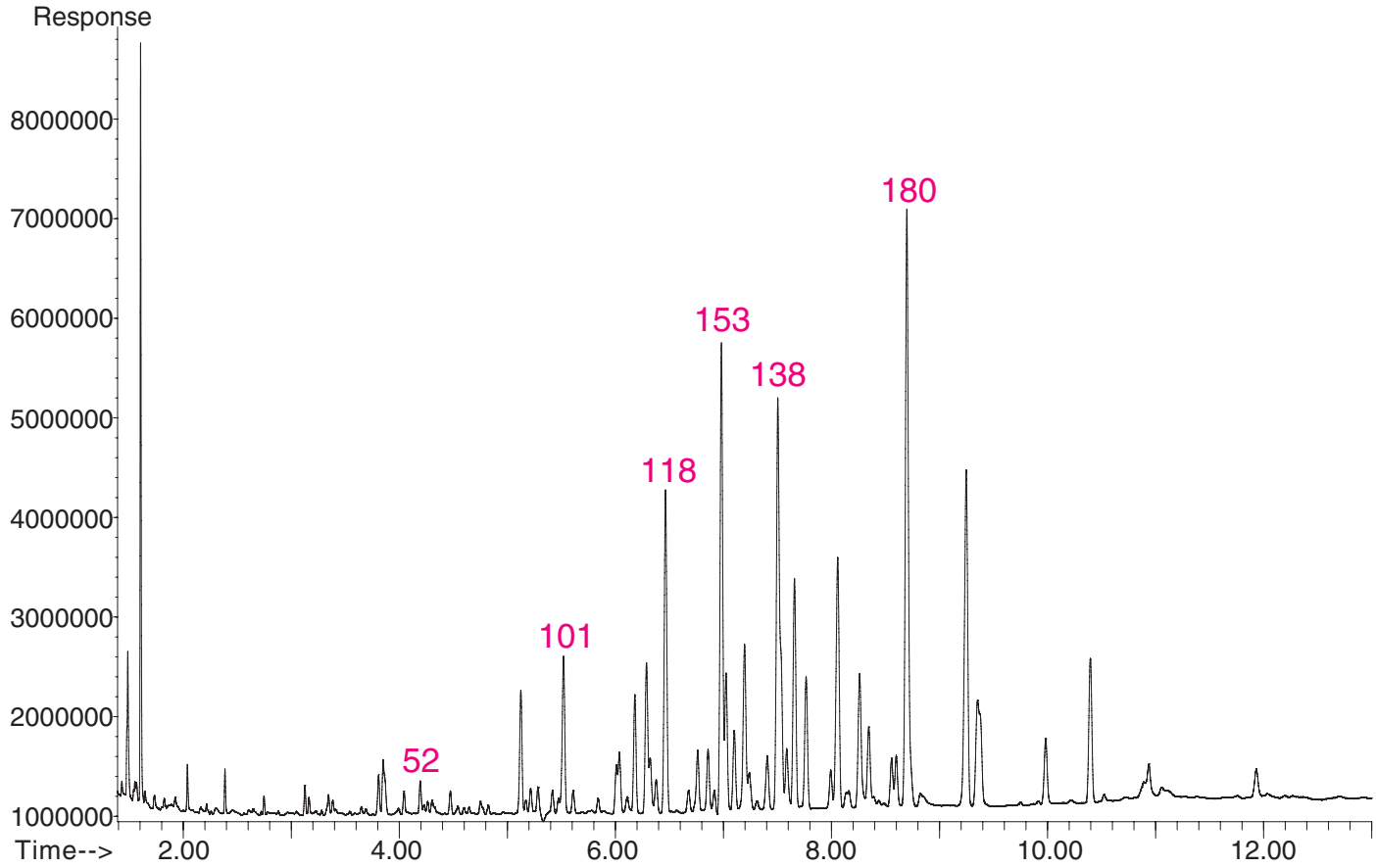

Figure 3. Chromatogram of the BCR standard, waste mineral oil.

SPE was also performed on a customer sample of waste oil, highly contaminated with PCBs.

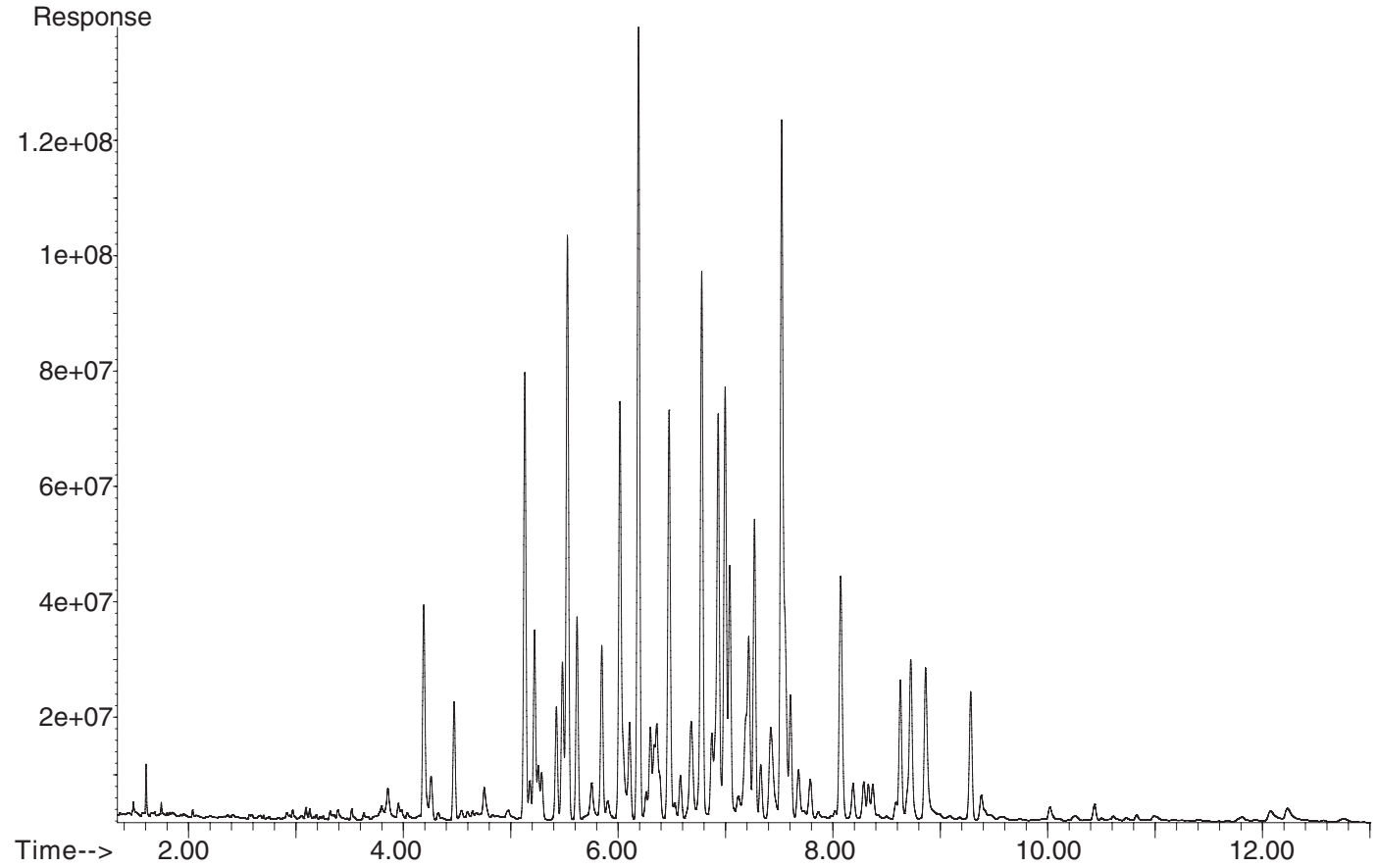

Figure 4. Chromatogram of a highly contaminated customer sample of waste oil.

Repeatability and recovery studies were done on the BCR standard using an internal standard for quantification (tables 1 and 2).

Table 1. Repeatability (from relative areas).

	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 180
Rep1	17.4	15.9	21.1	13.9	21.0	21.4
Rep2	16.9	16.4	20.8	13.3	21.6	21.1
Rep3	16.0	14.8	21.7	13.7	19.5	20.9
Rep4	17.5	15.4	22.1	14.0	21.6	21.5
Rep5	15.7	14.5	20.1	12.5	20.8	20.1
RSD%	5.0	5.0	3.7	4.7	4.1	2.7

Table 2. Recovery (calculated on average concentrations).

PCB	Reference concentration [ppm]	Found concentration [ppm]	Recovery [%]
28	0.8	0.8	95
52	31.4	28.3	90
101	57.2	51.8	91
118	46.6	39.7	85
153	39.0	35.9	92
180	10.4	8.8	85

Conclusion

The full analysis (sample preparation and GC analysis) of waste oils containing complex mixtures of PCBs over a wide range of concentrations (from < 1 ppb to more than 50 mg/mL) is possible with good repeatability and high recovery in less than 15 min using a SPE - fast GC - ECD system.

References

[1] R. Mustacich et al, US patents 6 217 829 (2001), 6 209 386 (2001) and 6 530 260 (2003)

[2] A. Hoffmann, B. Tienpont, F. David and P. Sandra, Gerstel application note 6/2006.

[3] F. David, R. Szücs, J. Makwana and P. Sandra, J. Separation Science 29 (2006) 695-698.

[4] Solid Phase Extraction Application Guide, Macherey-Nagel (MN Appl. No. 301390)

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