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Modulator Design for Comprehensive Two-Dimensional Gas Chromatography: Quantitative Analysis of Polyaromatic Hydrocarbons and Polychlorinated Biphenyls

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A novel cryogenic modulator was constructed for comprehensive two-dimensional gas chromatography (GC×GC). The modulator is based on two-step cryogenic trapping with CO_2 and thermal desorption with electric heating. The GC×GC system included a nonpolar first-dimension column and two semipolar second-dimension columns, one connected to a flame ionization detector and the other one to a electron capture detector. A Matlab-based program, which allowed determination of peak heights and volumes, was written for the data analysis. The GC×GC system was applied for the analysis of polyaromatic hydrocarbons and polychlorinated biphenyls. The functioning of the modulator and the quantitativity of the method were studied with both peak volumes and peak heights from a three-dimensional plot. The separate peak areas from the modulated chromatogram were calculated as a comparison. The quantitative results were compared with those obtained with the same system but without the thermal modulation. The method was found to be repeatable and linear with use of peak volumes as well as peak heights. There was also good agreement with the results obtained by integration of separate peak areas. The developed GC×GC method was applied to the analysis of a Soxhlet extract of a certified sediment sample. The results were compared with the certified values.

Determination of pollutants in the environment possesses a significant challenge to the analyst, as sample matrixes may be complex and the levels of pollutants at ppb or even ppt level. The problem in environmental analysis is that the extract typically contains a large amount of matrix compounds, which if they coelute with the analytes will disturb the quantitation. Many sediment samples, for example, contain relatively high concentrations of hydrocarbons, which may interfere with the GC analysis of analytes of interest. Typically, tedious sample pretreatment is required, followed by GC separation and selective detection by mass spectrometry. Furthermore, different compound groups often must be analyzed separately.

Recently, comprehensive multidimensional gas chromatography (GC×GC) has been shown to be useful for the analysis of complex samples.[1−21] In this technique, the sample zones eluting from the first GC column enter a modulator, which collects small and separate portions of the eluate and then introduces them successively as sharp zones to a second column for further separation. The second separation is very fast (3−10 s), and the whole sample is subjected to 2-D separation in a single run. The resulting modulated one-dimensional chromatogram consists of a series of slices, which represent the second-dimension separation

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of the modulated fractions. The chromatogram is usually converted to three-dimensional presentation and further to a contour plot.

Several different modulation solutions are currently being investigated in detail. The first modulator developed was a thermal desorption modulator, in which the analytes are first trapped in a short piece of capillary, which is coated outside with thin layer of metal, and then thermally desorbed with conductive heating. [22] However, the thermal desorption system was not sufficiently robust for prolonged use. After that, a "sweeper"-type modulator was presented in which the analytes are trapped in a capillary with thick stationary film and then thermally desorbed by a moving heating element.[1,3,4,6,7,10,18] The problem with this solution is that very careful positioning of the GC column is required and the temperature range of the analysis is limited. Modulation can also be done by cryogenic trapping, with thermal desorption by heating with the GC oven air.[9,12,14,15,17,20] Two models of this type have been developed, one based on a longitudinally moving trap[9,14−16,20] and the other consisting of dual-jet cryogenic trapping, where the CO_2 flow is controlled with a valve.[12] In the first model, the capillary positioning is critical, and problems with breakage of the column have been encountered. In addition, to prevent ice formation, which can cause breakage of the column, additional flow of nitrogen is required. There exists also two different valve-based modulator types, which differ from the previously described modulators substantially.[23−25] In a valve-type modulator, part of the sample is wasted during the switching, and the modulated fractions are not concentrated during the modulation.

The emphasis of the several GC×GC methods developed for the analysis of complex samples has been on qualitative analysis; only a few reports have been published on quantitative analysis.[1,3,8,9,16,17,21] Applications involve the characterization of complex hydrocarbon mixtures such as petroleum, jet fuel, and gasoline, [3,5−8] determination of organic compounds in urban air and water;[17,20] separation and identification of the components of essential oils;[2,13,19] determination of pesticides in food extracts; [9] and characterization of fatty acids in biological oils.[4]

In this study, we describe the development of a novel modulator for GC×GC. The modulator is based on two-step cryogenic trapping with CO_2 and thermal desorption by electric heating. A C++ program was written to control the movements and heating cycles of the modulator. The program also recorded the exact times of the movements, which could be used in the construction of the contour plot. A Matlab-based program called Comp, which allowed determination of peak heights and volumes, was written for the data analysis. The functioning of the modulator and the effect of the heating on the peak shapes were studied. A GC×GC method was developed for the analysis of polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). The quantitativity of the method was evaluated by studying peak volumes and heights from the three-dimensional plot. The separate peak areas from the modulated chromatogram were summed and used as a comparison. The quantitative results were compared with those obtained with the same system but without the thermal modulation. The developed GC×GC method was then tested for analysis of a certified sediment sample for PAHs and PCBs.

EXPERIMENTAL SECTION

Reagents and Solvents. All solvents were HPLC quality. Isooctane was purchased from Rathburn Chemicals Ltd. (Walkerbur, Scotland) and toluene from Lab Scan Analytical Sciences (Dublin, Ireland). The PAH standard solution Z-014G-R containing 17 analytes was from AccuStandard Inc. (New Haven, CT). The PCB standard solution PCB-W22 was also from AccuStandard Inc., and it contained 15 congeners. The internal standards, 4,4′-dibromooctafluorobiphenyl and 2,2′-binaphthyl, were from Aldrich (Gillingham, U.K.) and AccuStandard Inc, respectively. The sediment was certified EC-1 sediment (National Water Research Institute, Canada). Standards were prepared in isooctane.

Apparatus. The GC was a HP 6890 with μ-electron capture (μ-ECD) and flame ionization detector (FID) from Agilent Technologies (Palo Alto, CA). For injection, an HP 7683 automatic injector was used with splitless injection of 1 μL at 300 °C. The ECD was held at 325 °C and the FID at 310 °C, with data collection at 100 Hz. Gases and their flow rates for the FID were as follows: hydrogen 35 mL/min, air 135 mL/min, and nitrogen 10 mL/min. For ECD, the nitrogen flow was 30 mL/min.

GC Columns and Conditions. The first-dimension column was a 20 m × 0.25 mm i.d. HP-5MS (Agilent Technologies) with film thickness of 0.25 μm. A short piece of DPTMS-deactivated retention gap (1 m × 0.53 mm i.d, from BGB Analytik) was installed in front of the column. The first-dimension column was connected with a glass press-fit to a 5 cm × 0.1 mm i.d. BGB-Silaren column with film thickness of 0.1 μm (BGB Analytik, Zurich, Switzerland). The BGB-Silaren column was inside the modulating system, and it was further connected with a Y-piece press-fit to two 0.65-m lengths of the same BGB-Silaren column, connected to the FID and the other to the ECD (Figure 1). The connections were made with special press-fits purchased form BGB Analytik.

The temperature program was as follows: 40 °C for 5 min, then 10 °C/min to 179 °C (2 min), 10 °C/min to 214 °C (2 min), 9 °C/min to 268 °C (2 min), and finally to 300 °C at 9 °C/min. Carrier gas was helium and a constant-flow mode was used. The starting pressure was 200 kPa.

Modulator. The modulator was constructed in the laboratory (Figure 1). It consisted of a metal tube (stainless steel 6.3-mm o.d., 4.6-mm i.d., 20-cm length), to which liquid CO_2 was delivered at one end through a flexible PEEK capillary ($^1/_{16}$-in. o.d., 0.25-mm i.d.). The consumption rate of CO_2 was on average 40 mL/min. Two short piece of 5 mm × 0.17 mm i.d. stainless steel capillary were soldered along the tube at a 45° angle to each other, to serve as nozzles for the CO_2 spray. Except for the inlet and the nozzles, the tube was closed. The metal tube was turned with a magnetic actuator, so that the CO_2 flow was directed alternately to one or the other of the two heaters, through which the second-dimension capillary passed. The heaters consisted of coiled wire resistors, heated by electric current. The movements of the CO_2 nozzles and the power of the heaters were computer controlled with a laboratory-written C++ program. With this program, the power profile of the heating cycle was adjusted in such a way

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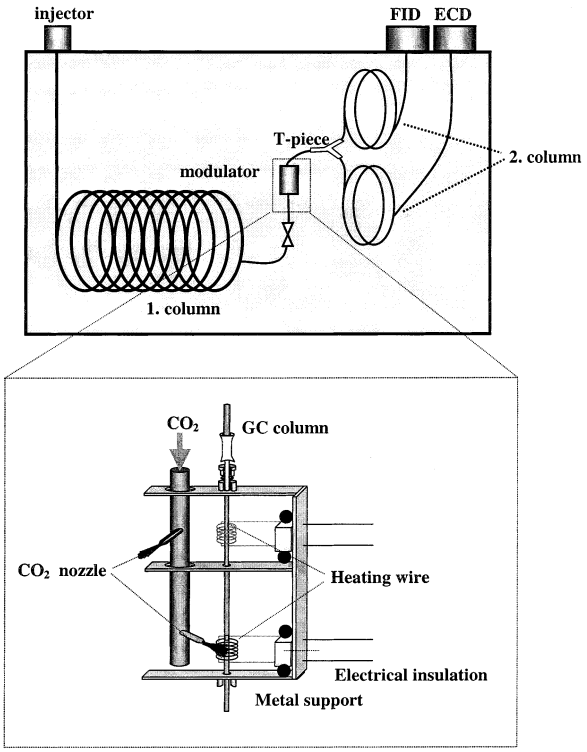

Figure 1. Schematic view of the GC×GC apparatus and thermal modulator.

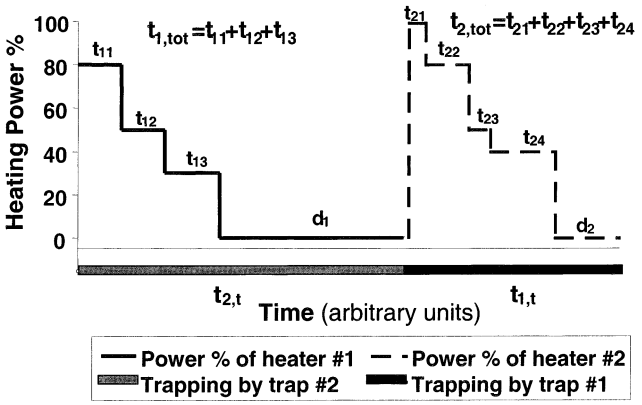

Figure 2. Time program for the trap heater (an example). See the section Time Programming of the Heating Power for the details.

that high power could be used at the start of the heating cycle, after which the power was gradually lowered. This offered a very high heating rate and thus fast desorption of the trapped compounds. The heating power was adjusted by applying the pulse width modulation technique.

The GC capillary was secured to the metal frame of the modulation system with two nuts (Valco Instruments Co. Inc., Houston, TX) and two vespel ferrules to avoid any vibration of the column due to the cooling gas flow, as shown in Figure 1. The metal frame of the modulator was further connected to the wall of the GC oven.

During the modulation, the CO_2 stream was first directed to the upper heating coil and the column for a predetermined time. Then the modulator was rotated so that the CO_2 stream was directed to the lower heating wire. At the same time, the upper heating wire was heated to enhance the thermal desorption. The analytes released from the upper trap were trapped in the lower cold trap, from which they were desorbed through rotation of the modulator to the original position and heating of the second wire.

Time Programming of the Heating Power. The modulation cycle consisted of the two steps described above. The timing of the heating phase for the trap 1 heater can be specified as p_{11}, t_{11}; p_{12}, t_{12}; ..., p_{1n}, t_{1n}, where p_{11} denotes the heating power to be used for time period t_{11} (Figure 2). The listed values for p and t are consecutively applied until the total heating time ($t_{1,\mathrm{tot}} = t_{11} + t_{12}...t_{1n}$) has elapsed. After the heating phase, a delay time d_1 is applied, after which the modulator is rotated and the desorption from trap 2 (trapping phase by trap 1) commences. Since trap 2 is in trapping phase while trap 1 is in desorption phase, $t_1 + d_1$ also represents the trapping time ($t_{2,\mathrm{tr}}$) of trap 2, and correspondingly, $t_2 + d_2$ represents the trapping time ($t_{1,\mathrm{tr}}$) of trap 1. An arbitrary number of power steps can be included in the heating phases, and individual heating power programs can be designed for the two heaters. An example of a heater power program is shown in Figure 2.

Data Handling. A Hewlett-Packard Chemstation performed the data acquisition. The data files were then converted to the csv format. From the C++ program controlling the modulator, a file containing exact times for modulation was obtained. For analysis of the acquired data, a program called Comp was written for use with Matlab 5.3 software (The MathWorks, Natick, MA).[26] The program used both the actual data file and the modulation time file to generate a matrix presenting the 2-D separation achieved, and it also allowed automatic and manual baseline adoption, peak recognition, and determination of peak heights, volumes, and retention times. From the matrix obtained, contour and three-dimensional plots were generated, and the peaks were integrated. Integration of the peak was done by summing the volume elements under each peak point. The volume elements were calculated simply by multiplying the data point heights by the underlying areas, which were governed by the data acquisition speed and the trap time. Matlab and the data analysis program were run on a Pentium III-type computer with a CPU speed of 750 MHz.

Soxhlet Extraction. The sediment sample was extracted with 80 mL of toluene for 20 h. The sample size was 1 g. Copper (2 g) and sodium sulfate (2 g) were mixed with the sample before extraction for sulfur removal and to give more homogenate sample, and the first internal standard (4,4′-dibromooctafluorobiphenyl) was added. After the extraction, the second internal standard (2,2′-binaphthyl) was added to the sample, and the sample was concentrated in a Rotavapor to 1 mL. The concentrations of internal standards in the final extract were 10 and 0.1 μg/mL. The concentrated extracts were purified in a column packed with 5 g of Florisil (Fluka, Buchs, Switzerland) sandwiched between layers of $NaSO_4$, using 10 mL of isooctane for the elution. After this, the samples were concentrated to 1 mL with a gentle flow of nitrogen.

RESULTS AND DISCUSSION

The goal of our study was to develop a GC×GC system with a rugged modulator and to study the quantitativeness of the method. A study was made of parameters affecting the perfor-

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mance of the system, such as effect of heating on the thermal desorption and the steps of the modulation cycle. A GC×GC method was developed for PAHs and PCBs in environmental samples using a dual-column system in the second dimension with FID and ECD detection for the PAHs and PCBs, respectively. The quantitativeness of the method was studied in detail.

The quantitativity was studied by determining peak volumes and heights for the three-dimensional GC×GC plot and comparing the results with the peak areas of the analytes summed from the modulated chromatogram. The same runs were also made without modulation. The linearity of the method was studied, and the developed method was then applied to the analysis of a certified sediment sample.

Modulator. The modulator was designed so that it could be fitted to the second injection port of the GC system. Instead of an on−off valve to control the CO_2 jet, our modulator was designed to provide a constant flow of CO_2 to both nozzles. The benefit of this solution is that the CO_2 flow is immediately turned on and off, with no delay. In the other modulator solutions with dual cryogenic trapping,[12] even if short tubings are used between the on−off valve and the CO_2 nozzle, the CO_2 stream is not turned on and off immediately after switching the valve because of the dead volume in the tubing. In this system, after the valve is opened, liquid CO_2 flows into a relatively hot tubing and therefore the liquid at the front of the stream vaporizes and only gaseous, poorly cooling CO_2 emerges from the nozzle until the liquid finally reaches the nozzle opening. After the valve is closed, the tubing is still filled with liquid CO_2 and thus the cooling effect is not finished immediately. The drawback of our system, on the other hand, was the relatively high consumption of cooling CO_2. In addition to heating in the oven, heating wires were placed around the trapping part of the column to enhance the thermal desorption of the analytes.

The modulator frame was constructed so that the capillary was secured to it but there was not any direct contact with the metal and the silica capillary. The CO_2 tube was not in a direct contact with the frame either, and only a very small proportion of the CO_2 flow reached the frame. Thus, there was no substantial cooling of the frame, which could have caused problems due to different heatcapacities of the silica capillary and metal. There were no problems of vibration or breaking of the second-dimension column. The flow of CO_2 did not have any adverse effect on the heating of the GC oven either.

1. Modulation Cycle. The modulation cycle was optimized for the PAHs and PCBs to obtain as sharp peaks as possible. The cycle consists of the two-stage cryogenic trapping and the thermal desorption with heating, and the total time of the cycle is determined by the duration of the cold trapping step. Modulation cycles varying from 2 to 12 s were tested, with different durations of the first and second trapping step. The optimal trapping cycle lasted in total 4 s, the first step taking 2.8 s and the second 1.2 s. The optimum time and heating power for the desorption were also studied. At the beginning of the desorption, the heating coils were cold due to the CO_2 flow. Therefore, in the beginning of the desorption step, more efficient heating was used, i.e., more power. After this, the heating power was decreased to a lower level to avoid burning of the GC column. Different heating times were studied, namely, from 0.1 to 2.8 s in the first trap and from 0.1 to 1.2 s in the second trap. Accordingly, various heating powers were tested. The best results were obtained with heating time of 0.8 s in both steps, with the heating power of 50 (0.4 s) and 20% (0.4 s) of the maximum power (5 W).

The movements of the CO_2 tube were controlled with a computer. The program recorded the exact times of the movements, which were then used in the construction of the contour plot. This made the retention times in the second dimension of the plot more reliable compared to the case of simple slicing of the acquired data file with fixed cycle time (e.g., 4 s). During a test period of two weeks, the retention times for PAHs and PCBs in both dimensions were very reproducible; according to the *t*-test, the differences in the retention times were unsignificant (*t*-test <0.01).

2. Effect of Heating on Peak Heights and Widths. To study whether the heating had an effect on the desorption, two series of modulated runs were done, with and without heating ($n = 6$ for both series). For PAHs, the difference was clear and statistically significant (*t*-test >0.01): the peaks were on average 25% higher (17−45%) and on average 20% narrower (36−13%) with heating. The difference was less evident for PCBs, but heating also clearly improved their peak shapes, which could be seen by their improved symmetry factors. Apparently, the effect of heating is dependent on the analytes and on their interaction with the stationary phase.

The peak widths (at half-height) with the GC×GC system were on average 215 ms for PAHs (168−300 ms) and 400 ms for PCBs (390−460 ms). The T-piece used for splitting the second-dimension column to the two detectors caused peak broadening due to its dead volume, even though the T-piece was specially designed for this column configuration. Without the T-piece, the peak widths were for PAHs on average 145 ms at half-height and on average 260 ms when measured from the peak base (10% of the peak height). For alkanes, the corresponding peak widths were on average 95 ms at the half-height and on average 200 ms at the peak base. Direct comparison of peak widths produced by our system with those obtained with other modulator types is not prudent, because the width is dependent not only on the modulator type but also on the gas flow rate, column length, and inner diameter as well as on the analytes and their retention in the second-dimension column. In a recent study, however, thermal sweeper and cryogenic modulator were compared in the analysis of semivolatile aromatics, including several PAHs.[27] Also, the column system was quite similar to that in our study, and therefore, a relevant comparison can be made. Peak base widths (measured at 10% peak height) varied from 330 to 600 ms, which are slightly larger than the values obtained in our study.

The new nonmoving cryogenic modulator has been tested with alkanes, for which the peak widths in half-height have been reported to be ∼30 ms and at base ∼85 ms.[12] These compounds elute from the polar second column very fast, so they are expected to be clearly sharper than the more polar analytes, such as PAHs. By comparing the peak widths, and taking into consideration the limitations in the comparison, it can be concluded that the performance of our modulator is at the same level with the other modulator types.

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Table 1. Correlation Coefficients for Selected PAHs and PCBs in GC×GC Analyses of Standard Solutions[a]

	GC×GC				normal GC
compound	volume	height	summed area[b]	summed height[b]	area
fluoranthene	0.9996	0.9912	0.9997	0.9993	1.0000
pyrene	0.9997	0.9857	0.9997	0.9995	1.0000
benzo[*a*]pyrene	0.9954	0.9957	0.9951	0.9964	0.9999
PCB 44	0.9993	0.9966	0.9989	0.9985	0.9997
PCB 101	0.9995	0.9799	0.9986	0.9991	0.9997
PCB 138	0.9956	0.9967	0.9953	0.9994	0.9997

[a] Calculated for peak volumes and heights from the three-dimensional plot, and correlation coefficients for normal GC runs of the same Solutions (c [PAH] = 1−50 μg/mL, c[PCB] = 0.01−0.5 μg/mL). Detection for PAHs was done with FID and for PCBs with ECD. [b] Calculated from the modulated GC chromatogram as sum of peaks.

Quantitativity. As mentioned previously, most of the GC×GC applications in the literature have been of a qualitative nature. In the quantitative GC×GC applications, summed peak heights,[16] summed peak areas,[8,9,16,18] and peak volumes[1,3] have been used. Good linearity has been obtained with all the methods; generally, correlation coefficients of calibration curves have been better than 0.990. In most cases, repeatability of the analyses has been determined only for standard samples, RSD values being typically below 10%.

To evaluate the applicability of the GC×GC system to quantitative analysis, a study was made of the linearity and repeatability of the method. Runs were made with standard solutions of PAHs and PCBs with and without modulation using FID and ECD. The makeup flow for ECD can be critical. According to the manufacturer, the optimum flow rate of the makeup flow is 20−60 mL/min. The best sensitivity was obtained with 30 mL/min, and accordingly, this was chosen for further studies. In the three-dimensional plot, used for quantitation of a GC×GC peak, the integral was taken in both separation dimensions to give a peak volume. Integration of the peak was done by summing the volume elements under each peak point. The volume elements were calculated by multiplying the data point heights by the underlying areas. Also, peak heights were calculated from the three-dimensional plots. In addition, for comparison, peak areas and peak heights of selected analytes were summed from the modulated chromatogram. Peak areas and heights were also calculated for the unmodulated runs.

Selected results for PAHs and PCBs are shown in Table 1. The GC×GC method was linear over the tested range (1−50 μg/mL for PAHs and 0.01−0.5 μg/mL for PCBs). Correlation coefficients were excellent for peak volumes (PAH, 1.000−0.9983; PCB, 0.9999−0.9956) and good but slightly lower for peak heights (PAH, 0.9989−0.9570; PCB, 0.9998−0.9799). This was as expected since the peak height is more dependent on the modulation cycle than is the total volume. The peak height is dependent on the exact timing of the modulation. Even small changes in the retention in the first dimension will result in slightly different time of the modulation and, accordingly, in different peak height in the second dimension. Therefore, we selected peak volumes for the quantitation. The results of the GC×GC analyses were in good agreement both with the results of the summed peak areas of the modulated chromatogram and with the results of the conventional GC analyses (Table 1). The RSD values for the PAHs were on average 1.3% for peak volumes and 20% for peak heights (c = 1−50 ppm). For PCBs, the RSD values were on average 1.5 and 24.4%, for peak volumes and heights, respectively (c = 0.01−0.5 ppm). Thus, the quantitative results are in accordance with other quantitative GC×GC methods.[1,3,8,9,16,18] The accuracy of the method was also tested, and the accuracy was on average 12.5% for PAHs and on average 8.7% for PCBs (c = 10 and 0.1 ppm, respectively).

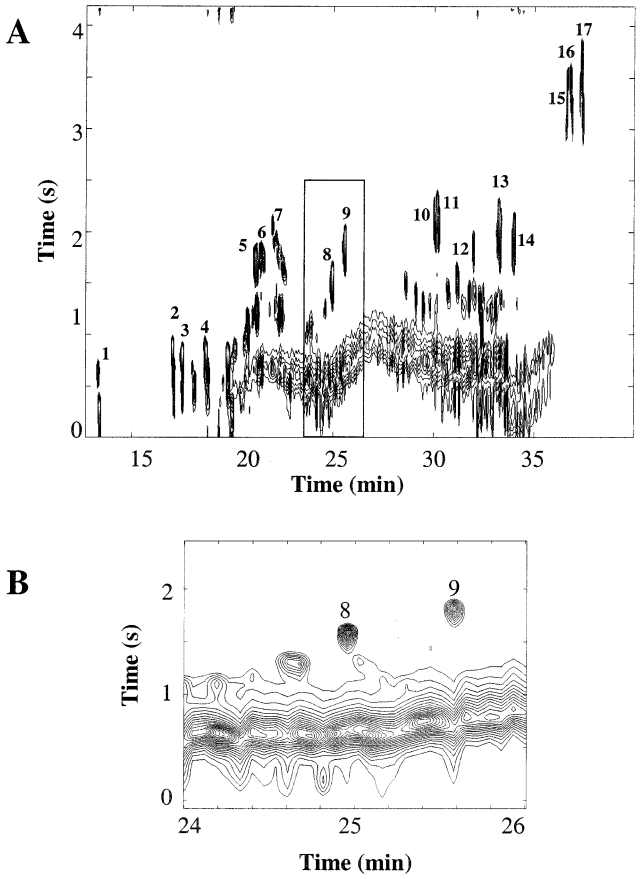

Figure 3. Contour plot of (A) a spiked sediment sample and (B) an enlarged section of an authentic sediment sample. Peaks: (1) naphthalene, (2) acenaphthene. (3) acenaphthylene, (4) fluorene, (5) phenanthrene, (6) anthracene, (7) carbazole, (8) fluoranthene, (9) pyrene, (10) benzo[*a*]anthracene, (11) chrysene, (12) ISTD, (13) benzo[*b*/*k*]fluoranthene (14) benzo[*a*]pyrene, (15) indeno[1,2,3-*cd*]-pyrene, (16) dibenzo[*a,h*]antracene, and (17) benzo[*ghi*]perylene.

The developed method was tested in the analysis of a Soxhlet extract of a certified sediment sample (Figure 3). Cleaning was necessary before injection of the extract to the GC×GC system because the extract contained high-boiling compounds that would not have eluted from the column system. A modification of a published cleanup procedure developed for PCBs[28] was applied. The cleanup was effective for PCBs, where the recoveries were on average 119%, but the larger PAHs were retained too strongly on the adsorbent used for the cleanup. Thus, three of the largest PAHs in the sediment could not be quantified. For other PAHs, the average recovery was 87%. In further studies, the cleanup procedure will need to be better optimized for the PAHs.

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Table 2. Quantitative Analysis of PAHs in Soxhlet Extracted EC-1 Sediment (μg/g ± SD), $n = 5$ (Detection with FID)

	GC×GC			
	volumes	summed areas	normal GC	certified values
phenanthrene	10.6 ± 0.2		125 ± 7.0	15.8 ± 1.2
anthracene	3.5 ± 0.8		33 ± 2.0	1.2 ± 0.3
fluoranthene	18 ± 2	26 ± 4	14 ± 2.0	23.2 ± 2.0
pyrene	14.4 ± 0.7	193 ± 2	12.4 ± 0.9	16.7 ± 2.0
benzo[*a*]-anthracene	3.5 ± 1.1			8.7 ± 0.8
chrysene	5.2 ± 0.9		19.2 ± 1.4	9.2 ± 0.9[a]
benzo[*b*/*k*]-fluoranthene	5.0 ± 2		15.6 ± 1.4	12.3 ± 0.9
benzo[*a*]pyrene	2.3 ± 1.0	2.4 ± 1.1		5.3 ± 0.7

[a] Value not certified.

Table 3. Quantitative Analysis of PCBs in Soxhlet Extracted EC-1 Sediment (ng/g ± SD), $n = 5$ (Detection with ECD)

	GC×GC			
	volumes	summed areas	normal GC	reference values[a]
PCB 18	33 ± 15		45 ± 18	47.4 ± 16.0
PCB 31/28	91 ± 8		88 ± 4	
PCB 52	214 ± 5	100 ± 20	101 ± 8	99.4 ± 43.2
PCB 44	79 ± 11	70 ± 20	63 ± 3	64.7 ± 31.4
PCB 101	124 ± 14		112 ± 5	109.4 ± 74.4
PCB 149/118	142 ± 7		114 ± 3	79.8 ± 37.1
PCB 153	48 ± 8		78 ± 6	68.2 ± 22.1
PCB 105	40 ± 20		31 ± 2	34.2 ± 13.5
PCB 138	95 ± 5	80 ± 20	84 ± 7	72 ± 26.3
PCB 180	62 ± 8		45 ± 3	44.9 ± 23.2
PCB 170	22 ± 3		19.1 ± 1	16.8 ± 7.6
PCB 194	12 ± 3		6.9 ± 0.5	13.1 ± 5.6

[a] Values not certified.

The analytes were analyzed with both the unmodulated method and the modulated GC×GC system. The results are shown in Tables 2 and 3 along with the certified reference values. As can be seen, the unmodulated runs gave too high results for phenanthrene, anthracene, and chrysene, probably due to the coelution of some matrix compounds, which were better separated with GC×GC (Figure 3). The GC×GC results for PAHs are slightly lower than the certified values, probably due to the losses during the cleanup step. It is also worth to mention that the separation techniques used in the certification process have not necessarily been better than in GC×GC used here. It can be seen from Figure 3A, that some separation of critical peak pairs 5/6, 10/11, and 15/16 can be achieved with the second dimension. Total run time here is only ~40 min, which is typically longer for similar one-dimensional separations. Another example of the advantage of the GC×GC over one-dimensional separation can be seen in Table 2, where the error for the later-eluting peak (anthracene) in quantitation is clearly decreased due to better separation from the preceding peak. For PCBs, the modulated and unmodulated values are at the same level of magnitude, and both are comparable to the reference values. Some differences obtained for the PCBs between modulated and unmodulated runs just demonstrate the importance of the quantitation (integration) method used. Also higher or lower values with unmodulated run can be due to different selectivity of the second column, which can either nullify or increase the separation of the first column, respectively.

For PAHs and PCBs, repeatability was generally good with the GC×GC method and with normal GC. The repeatability for PCBs (RSD on average 18%) was clearly better with the GC×GC system in comparison with the reference values (RSD on average 44,4%) and on similar level for PAHs (15.3 versus 12,0%). The benefit of the GC×GC analysis is that there was no need to remove hydrocarbons from the sample for PAH analysis, even when FID was used for the detection. The nonpolar hydrocarbons were well separated from the more polar PAHs in GC×GC. Therefore, it would be possible to analyze PCBs, PAHs, and total amount of hydrocarbons in a single run. Further benefit of the GC×GC over conventional GC was the increased sensitivity due to concentrative modulation; the peaks were on average 17 times higher with the modulation for the PAHs and 11 times higher for the PCBs.

CONCLUSIONS

The modulator worked well and proved to be rugged and user-friendly. The modulator system was easily installed onto the injection port of a commercial GC instrument. Likewise, the data analysis program worked well and was user-friendly and also readily modifiable. However, it required a powerful computer to run smoothly. Due to the exact modulation times used in the data handling, more accurate second-dimension retention times were obtained. The GC×GC system gave quantitative results with the most repeatable results obtained with use of the peak volumes. PAHs and PCBs present in a sediment sample could be separated and quantified in a single run, and the results obtained were in good agreement with the certified values.

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