Development of a sensitive methodology for the Analysis of Chlorobenzenes in Air by Combination of Solid-Phase Extraction and Headspace Solid-Phase Microextraction

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Abstract

In this study, a combination of solid-phase extraction and solid-phase microextraction has been used to determine chlorobenzenes in air. Analytes were sampled by pumping a known volume of air through a porous polymer (Tenax TA). Then, the adsorbent was transferred into a glass vial and SPME was performed. The quantification was carried out using GC-ECD or GC-MS. Several SPME coatings (100μm PDMS, 75μm CAR/PDMS, 65μm PDMS/DVB, 65μm CW/DVB and 85μm PA) were evaluated, obtaining the highest responses with CAR/PDMS for the most volatile chlorobenzenes, and with PDMS/DVB or CW/DVB fibers for the semivolatile compounds. To optimize some other factors that could affect the SPME step, a factorial design was used. Kinetic studies of the SPME process were also performed. Concerning the SPE step, breakthrough was studied, showing that 2.5 m^3 of air could be processed without losses of the most volatile compounds. The performance of the method was evaluated. External calibration, which does not require the complete sampling process, demonstrated to be suitable, obtaining good linearity (R^2 >0.99) for all chlorobenzenes. Recovery studies were performed at two concentration levels (4 ng/m^3 and 40 ng/m^3), obtaining quantitative recoveries (>80%). Limits of detection at the sub ng/m^3 were achieved for all the target compounds.

Key words

Air analysis, chlorobenzenes, gas chromatography-mass spectrometry, Solid-phase microextraction, solid-phase extraction, factorial design, volatile compounds.

Introduction

Chlorobenzenes are a family of environmental pollutants that are produced in huge quantities in industrial processes to be used as intermediates in the synthesis of other organic chemicals and in the production of a wide range of consumer and commercial products. The less chlorinated benzenes are widely used in cleaning and degreasing of metal, leather, wool and paper, in dry cleaning and textile dyeing operations, as wood-preserving compounds, in organic synthesis of pesticides and herbicides, as deodorizing agents for garbage and sewage, as air fresheners, as heat transfer mediums in maintenance equipment, and as magnetic coil coolants for the electrical and electronics industries. They are also used in application or removal of surface coatings as solvents for organic materials, waxes, resins, rubbers, oils and asphalts. Pentachlorobenzene is used to make pentachloronitrobenzene, a fungicide and it is currently used as fire retardant. Hexachlorobenzene was used, among other applications, as fungicide, in the production of pyrotechnic compositions for the military, as a plasticizer agent for polyvinyl chloride (PVC), although in many countries its production and use have ceased [1].

Release of chlobenzenes to the environment occurs primary during manufacture, and incineration of chlorobenzenes may lead to the emission of polychlorinated dibenzo-p-dioxins and dibenzofurans. Volatile chlorobenzenes are extensively used as solvents, so large quantities are released to the air. However, atmospheric concentrations are usually very low, often much less than a few μg/m^3. Nevertheless, indoor air concentrations may be from one to three orders of magnitude higher where they are used [2]. Risks of human exposure arising from contaminated indoor air are linked to the use of these compounds as moth repellents and air fresheners [1].

Hexachlorobenzene and 1,4-dichlorobenzene were the first compounds included in the Third and Fifth (repectively) Annual Report on Carcinogens in the U. S. Department of Health and Human Services as reasonably anticipated to be a human carcinogens based on sufficient evidence of carcinogenicity in experimental animals [2]. The Clean Air Act Amendments of 1990 list some chlorobenzenes as Hazardous Air Pollutants (HAPs), so federal agencies and groups may develop recommendations to assist in controlling exposure [3].

Chlorobenzenes are frequently found in air at very low concentrations, so a preconcentration step before the analysis is necessary. Most volatile chlorobenzenes are usually analyzed following general procedures developed for the analysis of volatile organic compounds (VOCs). In most procedures, once the analytes are extracted from air to an appropriate sorbent by solid-phase extraction, a thermal or solvent desorption step is carried out to transfer the target compounds into a standard gas chromatograph. For trapping VOCs, a wide variety of sorbents have been applied, such as carbon-based material [4], Tenax [5] or mixtures of Tenax with other sorbents [6, 7]. Some other trapping materials can also be used [8]. To retain the less volatile chlorobenzenes, the use of more adsorbent materials such as expanded polyurethane foam (PUF), both used as monosorbent or mixtured with other polymeric sorbents in multibed cartridges, were studied, and the retained compounds were extracted using Soxhlet solvent desorption during 12 hours [9, 10]. However, there is currently an increasing demand for simple and cost-effective sampling and analytical methods capable of achieving very low detection limits in real or almost real-time [11]. Benefits of solid-phase microextraction (SPME) in the analysis of air samples include the use of simple instrumentation like lightweight and compact devices, so expensive cryotraps or thermal desorbers are not required, dangerous and toxic organic solvents or reagents are not used, and short extraction times are usually employed [12]. SPME is an equilibrium technique and in consequence, analytes are not quantitatively extracted. Therefore, the main problem in SPME analysis, especially in the case of air, is calibration. Up to now, different strategies have been studied to overcome this drawback of the technique [13-19]. In addition, the working concentration levels for air analysis by SPME are usually in the range of μg/m^3 and mg/m^3 [20, 21]. These levels are suitable for the determination of volatile compounds that can be found at relatively high concentrations in air. Nevertheless, some hazardous air pollutants need to be monitored at very low concentrations and the levels achieved by SPME might be insufficient.

In the present paper, a method based in the combination of SPE and SPME techniques is proposed to determine chlorobenzenes (including the less volatile in the family) in air samples. The optimization of the method was performed using an experimental design approach. External calibration, which does not require the complete sampling process, demonstrates to be suitable. Limits of detection at the sub ng/m^3 were achieved for all the target compounds.

Up to now, the combination of both techniques has only been applied to the analysis of two high volatile organic compounds (toluene and benzene) in air samples [22, 23].

Experimental

Reagents

1,3-dichlorobenzene (1,3-DCB), 1,4-dichlorobenzene (1,4-DCB) and 1,2,4-trichlorobenzene (1,2,4-TCB) were supplied by Fluka (CH, Switzerland), 1,2-dichlorobenzene (1,2-DCB) and 1,2,3-trichlorobenzene (1,2,3-TCB) were purchased from Aldrich Chemie (Steinheim, Germany), 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB), 1,2,3,5-tetrachlorobenzene (1,2,3,5-TeCB) and 1,2,4,5-tetrachlorobenzene

(1,2,4,5-TeCB) were obtained from Riedel-de Haën (Seelze, Germany), pentachlorobenzene (PeCB) and hexachlorobenzene (HCB) were supplied by Supelco (Bellefonte, PA, USA). All organic solvents (isooctane, acetone, methanol and hexane) were of pesticide grade and were obtained from Merck (Mollet del Vallés, Barcelona, Spain).

Standard stock solutions of 2000-4000 mg/mL of individuals were prepared in acetone or isooctane, and working solutions were obtained by appropriate dilution. All solutions were stored in amber colored vials and stored at –20ºC.

Air sampling and extraction of chlorobenzenes

Using a vacuum pump working at 100 L/min, a known volume of air was pumped through a glass tube containing 25 mg of Tenax TA adsorbent (mesh size 60/80) retained by glass wool (Aldrich, Madrid, Spain). For recovery experiments, the pump was placed in a clean room provided of a laminar flow system, and a V-shaped tube was inserted before the collecting Tenax tube. A solution of the target analytes in hexane was then carefully placed in the V-shaped tube, and a selected volume of air was pumped throughout the system (Figure 1). Thus, the air was enriched in the analytes before reaching the Tenax tube. Only Teflon (PTFE) tubing was used for connections. The adsorbent was then poured into a glass vial sealed with an aluminum cap furnished with a PTFE-faced septum. The vial was placed into a water bath at 50 or 100 °C. Compounds retained by the adsorbent were analyzed by exposing a SPME fiber to the headspace of the vial (HS-SPME). Once finished the SPME process, the fiber was immediately inserted into the injection port of the chromatograph and chlorobenzenes were desorbed to the GC for 4 min. If necessary, vials containing chlorobenzenes adsorbed on Tenax can be stored at –20ºC during a few days to further analysis. SPME manual holders and fibers were obtained from Supelco. Fibers used in this work were: 100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane-divinylbenzene (PDMS/DVB), 75 μm carboxen-polydimethylsiloxane (CAR/PDMS), 65 μm carbowax-divinylbenzene (CW/DVB) and 85 μm polyacrylate (PA).

Gas Chromatographic Analysis

Gas chromatography-mass spectrometry (GC-MS) analysis was performed in a Varian 3400 GC system, equipped with a Saturn 3 ion trap mass detector, operated by Saturn version 5.4 software. A Varian VA-5MS or CP-Sil8 CB Lowbleed/MS (25 m x 0.25 mm i.d. x 0.25 μm) column was used for the separation of chlorobenzenes. Working GC-MS parameters are summarized in Table 1. Mass acquisition ranges were programmed by time segments and centered on the ions characteristic of each group of compounds (Table 2).

Gas chromatography with ECD analysis was performed in a Hewlett Packard 5890 Series II-Plus GC system, equipped with an electron capture detector and a split/splitless injector, operated by HP Chemstation software. A SE-54 (30 m x 0.25 mm i.d. x 0.25 μm) column (Alltech, Deerfield, IL) was used to separate the target analytes. The experimental GC-ECD parameters are shown in Table 1.

Results and discussion

One of the most relevant steps in the sample preparation method is the transfer of the chlorobenzenes from the adsorbent to the SPME fiber. This clearly affects the amount of compound adsorbed by the fiber and hence, the limits of detection and quantification of the method. Therefore, the SPME process was studied before optimization of the sampling step.

Different SPME fiber coatings (85 µm PA, 65 µm CW/DVB, 65 µm PDMS/DVB, 100 µm PDMS and 75 µm CAR/PDMS) were evaluated using the same experimental procedure: 100 mg of clean Tenax were placed in a glass vial and spiked with a standard solution of chlorobenzenes in hexane to obtain 10 ng of each target compound per mg of adsorbent. Tenax TA was the adsorbent selected for the SPE step. Due to its fast desorption kinetics it is suitable to combine with SPME [8]. Solvent is left to evaporate at room temperature and then, vials are closed and immersed in a water bath at high temperature (100ºC) to favor desorption of the analytes. A SPME fiber is exposed to the headspace over the spiked adsorbent for 15 min. In Figure 2, the chromatographic responses obtained for some representative compounds with each fiber are shown. With PA and PDMS fibers, the extraction efficiency was very poor for all compounds. CAR/PDMS fiber was the most efficient in extracting the two and three chlorine substituted compounds, while PDMS/DVB and CW/DVB fibers provided the most efficient extraction for the semivolatile chlorobenzenes (tetra-, penta- and hexa- chlorobenzenes). Therefore, CAR/PDMS and PDMS/DVB fibers were considered for further optimization with other experimental parameters using an experimental design approach. CW/DVB was discarded due to the low stability of its coating.

To simultaneously optimize the experimental factors and to evaluate the parameters that can mainly affect the mass transfer to the SPME fiber, a factorial design was run [24]. Four factors were studied at two levels (extraction temperature, fiber coating, addition of water to the solid, and stirring of the sample) (see Table 3). The design selected was a multifactor screening 3*2(3-1) mixed level fraction, which involves 12 experiments. Extraction time was fixed at 15 min in all cases.

The analysis of the results produced the standardized Pareto charts show in Figure 3. The length of each bar in the graphs is proportional to the absolute value of its associated standardized effect. The standardized effect is obtained by dividing the estimated effect of each factor or interaction by its standard error. The effects are displayed in decreasing order of importance, which allows easy identification of the most important factors. Vertical lines indicate the statistical significance of the effects at a confidence level of 95%. A factor is not significant for a particular chlorobenzene when its bar does not reach the critical line [24]. Figure 4 shows the main effect plots for two selected chlorobenzenes. These plots show the main effects with a line drawn between the low and the high level for the corresponding factors. The length of the lines is proportional to the magnitude of the effect of each factor in the microextraction process, and the sign of the slope indicates the level of the factor that produces the highest response.

As can be seen in Figures 3 and 4, the temperature of extraction and the type of fiber coating were the most relevant factors for the extraction of all chlorobenzenes. Temperature greatly affects the kinetics of extraction. The Pareto charts in figure 3 show that temperature was significant in the extraction of all chlorobenzenes, but for dichlorobenzenes the temperature bar length only slightly exceed the critical value, while the bars length for more chlorinated benzenes exceeds to a great extent the critical value. Figure 4 shows that in all cases the best extraction temperature was the maximum (100ºC).

For highly volatile compounds, best results were achieved with CAR/PDMS coating (labeled as low level in Table 3, and in the main effects graph shown in Figure 4), while semivolatile compounds showed higher affinity for the PDMS/DVB fiber (the high level for this factor in Table 3 and in Figure 4). Nevertheless, the responses for semivolatile compounds were lower than the responses for the volatile ones, regardless of the fiber used. As the aim of this work was to develop a method to determine both volatile and semivolatile chlorobenzenes, PDMS/DVB fiber was finally adopted as the best option. Furthermore, this decision was supported by some memory problems detected when CAR/PDMS fiber was used.

Both stirring and water addition were non-significant factors for the chlorobenzenes extraction (Figure 3). Nevertheless, the stirring of the adsorbent during SPME in general favored the extraction of all the analytes.

To evaluate the efficiency of the SPME with the extraction time, kinetic studies were performed with all the target analytes. The exposition times were between 5 and 60 min (Figure 5). VOCs (dichlorobenzenes and trichlorobenzenes) reached the equilibrium state after short periods of extraction, while semivolatile organic compounds (SVOCs) did not reach equilibrium even after 60 min of extraction. Pentachlorobenzene and hexachlorobenzene showed the slowest kinetics, with a linear increase in chromatographic response. Hence, the selection of a short practical extraction time of 15 min allows obtaining an adequate response for all chlorobenzenes. The sensitivity in the extraction of the less volatile compounds could be improved by conveniently increasing the extraction time.

After demonstrating that chlorobenzenes could be transferred from the adsorbent to a SPME fiber, the sampling step using Tenax as adsorbent was studied. To evaluate if breakthrough occurred for the target analytes, initial experiments were performed by forcing 1 m^3 air to pass through a V-tube containing 100 ng of each compound placed before the Tenax collecting tube. In these experiments, a second tube with adsorbent was placed consecutively. Results showed that analytes were not recovered in the second adsorbent portion. Then, different volumes of air (from 1 m^3 to 10 m^3) were spiked with the compounds as described in the Experimental section. In Figure 6 can be showed that breakthrough did not occur for any chlorinated benzene when volumes of air sampled were as much as 2.5 m^3 . After sampling 5 m^3 air, a decrease in response was only observed for dichlorobenzenes (<20%). Hence, 2.5 m^3 was selected as a practical air volume to be sampled. For the remaining compounds, no breakthrough was observed even after sampling 10 m^3. Thus, sensitivity of the method for these compounds could be improved by sampling more than 2.5 m^3 of air.

The amount of adsorbent used to retain the compounds during the sampling step was also investigated. Different amounts of Tenax ranging from 5 to 200 mg were used, and results demonstrated that for all chlorobenzenes the SPME response decreased exponentially with the amount of Tenax (see Figure 7). However, the repeatability of the response was poor when the amount of adsorbent used was less than 25 mg. Therefore, this amount of adsorbent was finally chosen (see Experimental section).

In summary, a general method can be proposed for the determination of chlorobenzenes in air, pumping 2.5 m^3 air through 25 mg Tenax, pouring the adsorbent in a vial and desorbing the target analytes at 100ºC for 15 min to a PDMS/DVB fiber.

Figure 8a shows the chromatogram obtained for an air sample contaminated with 40 ng/m^3 of chlorobenzenes using the proposed method based on SPME analysis and Figure 8b shows the chromatogram obtained for a similar air sample in which the analytes were desorbed from the Tenax using 1 mL of hexane (injection of 2 μL of the extract). As can be seen, the chromatographic responses obtained using SPME are considerably higher than those obtained using solvent extraction, especially for the less chlorinated compounds, demonstrating the sensibility of the method based on SPME. In addition, it can be seen that with SPME the chromatographic peaks are narrower, leading in this case to the resolution of 1,2,3,5- and 1,2,4,5-tetrachorobenzenes.

Validation of the method

Air blanks as well as adsorbent blanks were analyzed for the target chlorobenzenes every set of experiments. To assure blank air samples, sampling was carried out in a clean room provided with a laminar flow system.

The apparent recoveries (found/added concentration expressed as a percentage) [25] were calculated for each compound comparing the responses obtained by sampling spiked air with the responses obtained when compounds were spiked directly on Tenax. Experiments were carried out at two concentration levels. Table 4 shows that recoveries ranged from 86% to 133% (%RSD values ranging from 4% to 11%) for the low concentration level (4 ng/m^3), and from 77% to 116% for the high concentration level (40 ng/m^3) with %RSD values of 4-11%. Therefore, recovery can be considered quantitative for all chlorinated benzenes.

The linearity of the method was evaluated by external calibration spiking the adsorbent with known amounts of analytes in the range 0.04-10 ng$_{\text{chlorobenzene}}$/mg$_{\text{Tenax}}$ (equivalent to 0.4-100 ng/m^3 sampling 2.5 m^3 air). The correlation coefficients (R^2) were higher than 0.99 for all chlorobenzenes (Table 5). In addition, to validate the regression data an analysis of variance (ANOVA) was performed. The lack-of-fit test is designed to determine whether the model is adequate to describe the observed data, or whether a more complicated model should be used. The test is performed by comparing the variability of the current model residuals to the variability between observations at replicate values of the independent variable. If the lack-of-fit variance is not significantly higher to the variance associated to the pure error, then the selected model is valid. In Table 5 the results of the F-test and the P-values obtained for the target compounds are presented. Since P-values are higher than 0.05, models are adequate for the observed data.

Precision of the method was evaluated and results are also shown in Table 5. %RSD values ranged from 6.0 to 13% using directly spiked Tenax samples extracted by SPME (n= 6), and from 8 to 12% using the complete procedure of SPE-SPME (n= 4), indicating that the SPE sampling step do not contribute with more variability to the results.

The detection limits (signal-to-noise ratio of 3) and the quantification limits (signal-to-noise ratio of 10) are also presented in Table 5. LOQ values were between 0.011 and 0.238 ng/m^3. These limits are at least one order of magnitude lower than that reported by other authors for some of the target chlorobenzenes and other volatile organic compounds [4, 17, 26].

Conclusions

A method based on the association of solid-phase extraction and solid-phase microextraction (SPE-SPME) was optimized for the rapid analysis of polychlorinated benzenes in air samples. Optimization of the experimental parameters included the use of an experimental design strategy. One of the best attainments of the proposed method is that calibration can be performed by direct spike of the adsorbent with the target compounds. The sensitivity of the method was demonstrated since limits of detection were well below 0.1 ng/m^3 for the majority of the target compounds. The SPE-HSSPME method proposed is simple and fast, and can represent a good alternative to methods based on thermal or solvent desorption, in particular for non-specialized laboratories that perform air monitoring sporadically. In addition, the SPME technique can be automatized, allowing high throughput analysis of chlorobenzenes.

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Figure captions

Figure 1. Schematic diagram of the air-sampling device. 1: vacuum pump, 2: PTFE connectors, 3: flow meter, 4: Tenax TA, 5: glass wool, 6: V-shaped glass tube to contain the analytes in the recovery experiments.

Figure 2. Comparison of different fiber coatings on the extraction of some representative chlorobenzenes.

Figure 3. Pareto charts for main effects. Vertical lines indicate the statistical significance of the effects (95% confidence level).

Figure 4. Graphics showing the influence of main effects on the extraction of two chlorobenzenes: low level (-), high level (+).

Figure 5. Extraction time profiles obtained in the optimal SPME conditions.

Figure 6. Variation of the response (expressed as area counts) with the volume of air sampled for two selected chlorobenzenes.

Figure 7. Variation of the response (expressed as area counts) with the amount of adsorbent for chlorobenzenes.

Figure 8. Mass chromatograms obtained by a) SPME extraction at the optimal experimental conditions, and b) 2 μL injection of a 1 mL n-hexane extraction of the

target chlorobenzenes adsorbed onto Tenax. The concentration of each compound in the air samples was 40 ng/m^3.

Table 1. Experimental GC-MS and GC-ECD conditions

GC-MS	
Oven temperature program	60ºC (2 min) 100ºC (10ºC/min) 120ºC (3ºC/min) 210ºC (10ºC/min, 2 min))
Injection	Splitless mode (2 min) 260-300ºC (depending on the fiber used)
Transfer line	260ºC
Carrier gas	He, 8 psi at 60ºC
Ionization mode	EI (70eV)
Manifold temperature	200ºC
GC-ECD	
Oven temperature program	50ºC (1 min) 250ºC (10ºC/min, 5 min)
Injection	Splitless mode (1 min) 260ºC
Detector temperature	250ºC
Carrier gas	Nitrogen, 1 mL/min
Make-up gas	Nitrogen, 40 mL/min

Table 2. Quantification ions, mass acquisition ranges, and time segments selected for the determination of each group of chlorobenzenes using an ion trap mass detector.

Compound	Quantification ions	Mass acquisition range (m/z)	Time (min)	Segment time length (min)
DCBs	146	144-148	0.00 to 8.00	8.00
TCBs	180+182	178-184	8.00 to 13.00	5.00
TeCBs	216	214-218	13.00 to 16.50	3.50
PeCB	248+250	246-252	16.50 to 19.00	2.50
HCB	280-288	280-290	19.00 to 22.66	3.66

Table 3. Factors and levels considered in the experimental design.

Factor	Low level	High level	Continuous
Water (μL)	0	300	Yes
Temperature (ºC)	50	100	Yes
Fiber	CAR/PDMS	PDMS/DVB	No
Agitation	No	Yes	No

Table 4. Collection efficiency of chlorobenzenes at two concentration levels.

	4 ng/m^3		40 ng/m^3	
	Apparent recovery (%)	%RSD	Apparent recovery (%)	%RSD
1,3-DCB	86	6	84	5
1,4-DCB	133	4	97	4
1,2-DCB	99	7	77	5
1,2,4-TCB	100	9	118	11
1,2,3-TCB	95	11	97	11
1,2,3,5-TeCB	98	9	88	8
1,2,4,5-TeCB	100	7	89	6
1,2,3,4-TeCB	105	9	82	7
PeCB	126	10	87	9
HCB	-	-	116	-

Table 5. Linearity, repeatability (%RSD), and limits of detection and quantification of the method (see text for more details).

Compound	Linearity			Repeatability (%RSD)		Detection limits (S/N=3, ng/m^3)	Quantification limits (S/N=10, ng/m^3)
	Correlation coefficient (R^2)	F-test	P-value	SPME of spiked Tenax (n=6)	SPE-SPME (n= 4)		
1,3-DCB	0.9973	1.52	0.3256	12	10	0.022	0.062
1,4-DCB	0.9962	1.84	0.2582	13	10	0.012	0.033
1,2-DCB	0.9971	2.10	0.2187	13	12	0.011	0.029
1,2,4-TCB	0.9968	0.66	0.6434	11	9	0.007	0.018
1,2,3-TCB	0.9970	0.56	0.7025	11	9	0.004	0.012
1,2,3,5-TeCB	0.9971	0.34	0.8407	9	11	0.019	0.042
1,2,4,5-TeCB	0.9986	0.21	0.9249	6	10	0.005	0.011
1,2,3,4-TeCB	0.9983	0.64	0.6549	8	11	0.015	0.041
PeCB	0.9920	0.41	0.7989	8	8	0.035	0.075
HCB	0.9980	0.25	0.8987	9	8	0.108	0.238

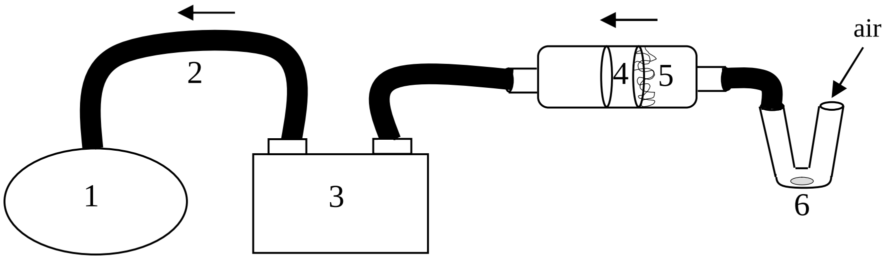
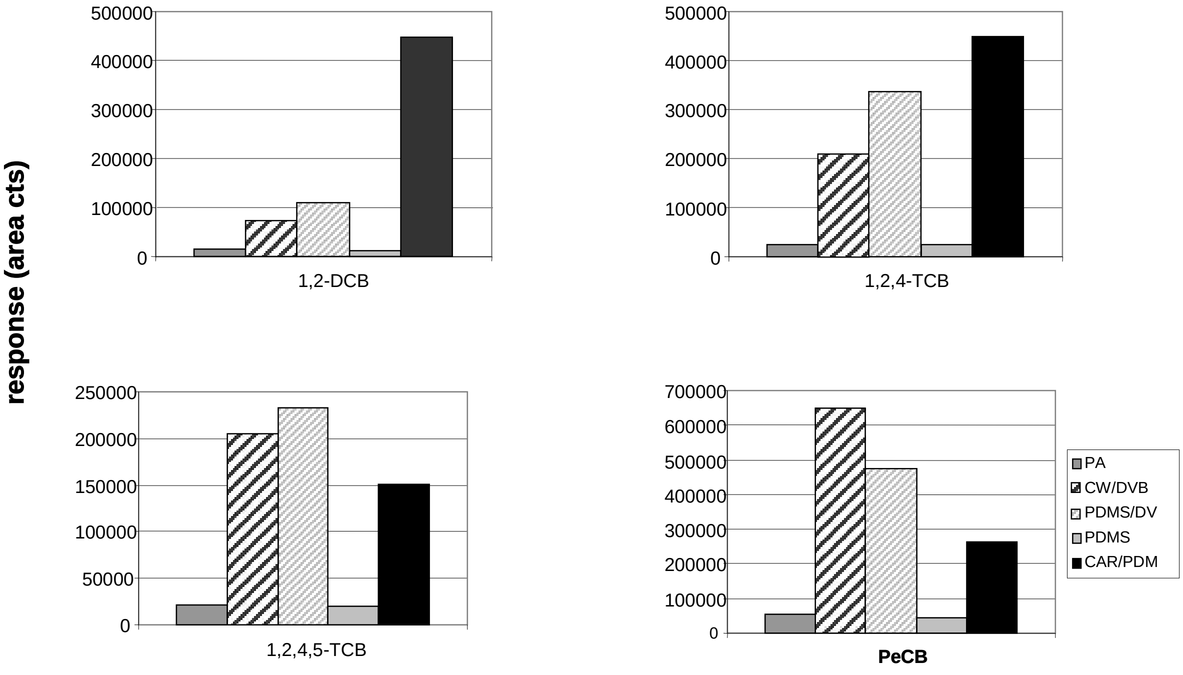


FIG. 1


response (area cts)
500000
400000
300000
200000
100000
0
1,2-DCB
500000
400000
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200000
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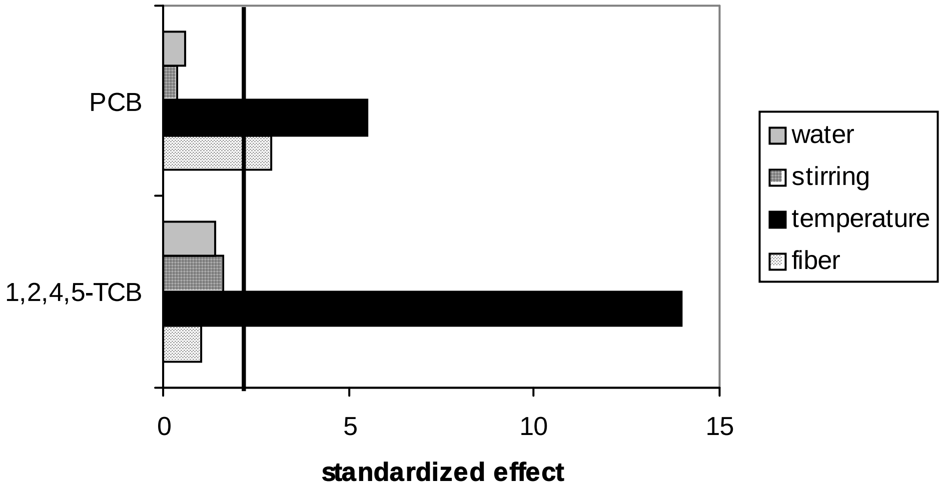
0
1,2,4-TCB
250000
200000
150000
100000
50000
0
1,2,4,5-TCB
700000
600000
500000
400000
300000
200000
100000
0
PeCB
PA
CW/DVB
PDMS/DV
PDMS
CAR/PDM

FIG. 2


PCB
1,2,4,5-TCB
0
5
10
15
standardized effect
water
stirring
temperature
fiber

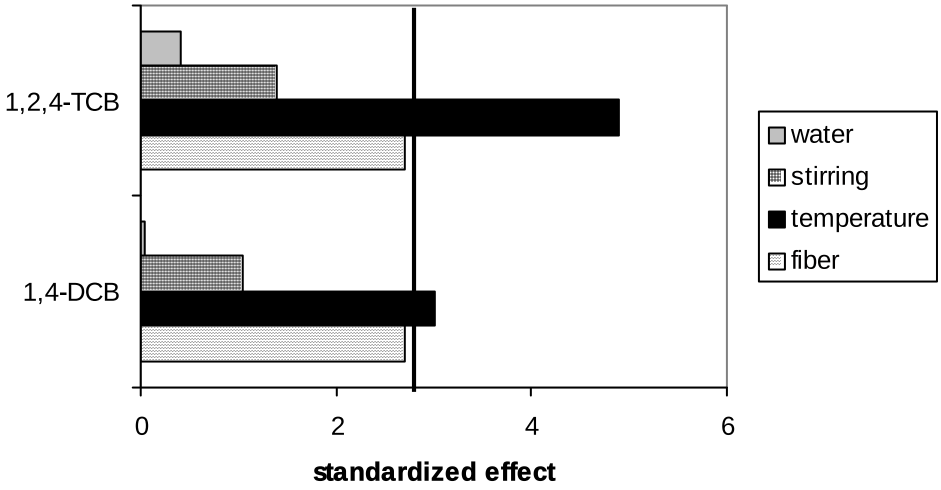

1,2,4-TCB
1,4-DCB
0
2
4
6
standardized effect
water
stirring
temperature
fiber

FIG.3

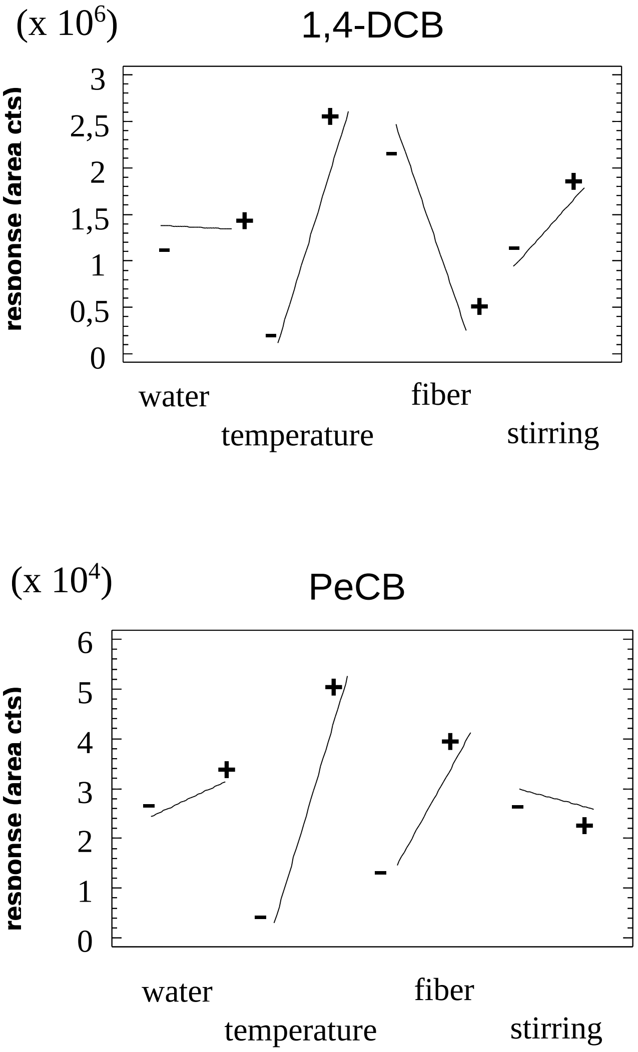

(x 10^6)
1,4-DCB
response (area cts)
3
2,5
2
1,5
1
0,5
0
-
+
water
temperature
fiber
stirring
(x 10^4)
PeCB
response (area cts)
6
5
4
3
2
1
0
water
temperature
fiber
stirring

FIG. 4

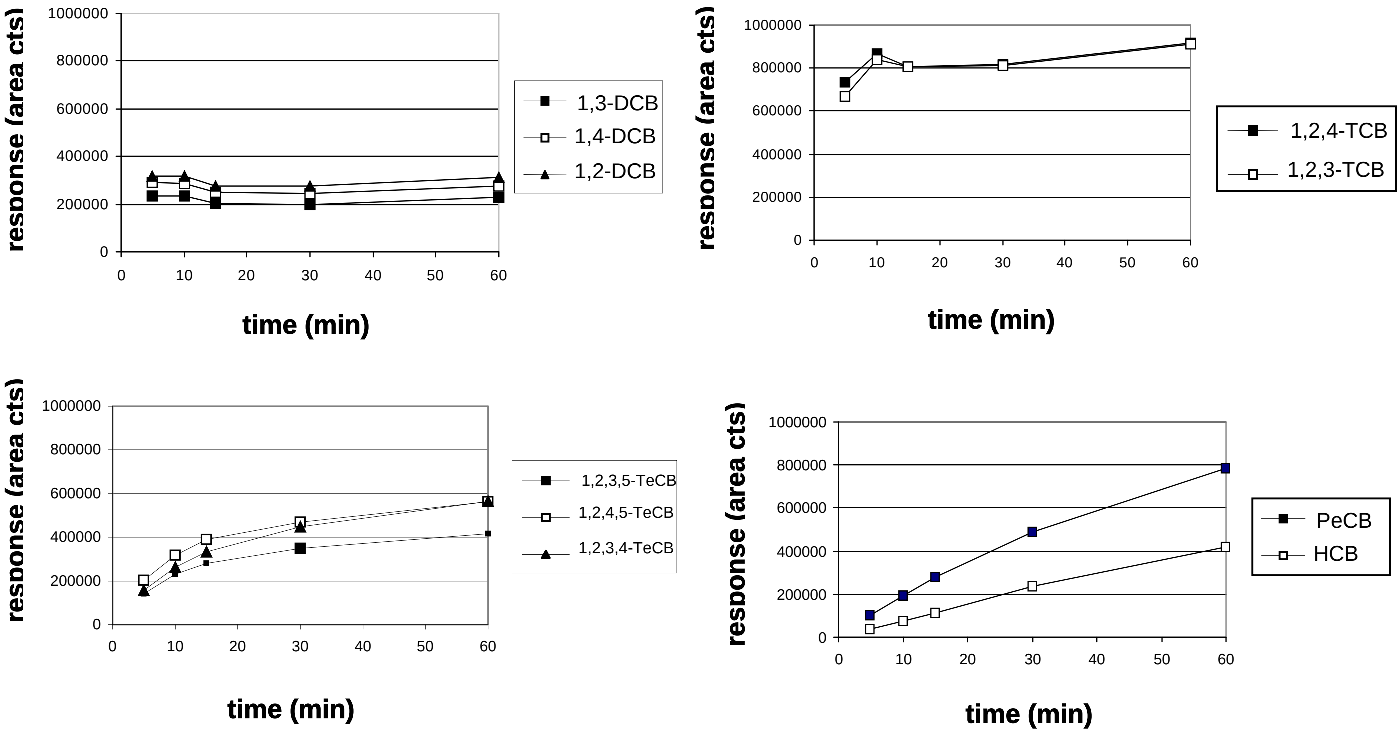

response (area cts)
time (min)
0
200000
400000
600000
800000
1000000
0
10
20
30
40
50
60
1,3-DCB
1,4-DCB
1,2-DCB
1,2,4-TCB
1,2,3-TCB
1,2,3,5-TeCB
1,2,4,5-TeCB
1,2,3,4-TeCB
PeCB
HCB

FIG. 5

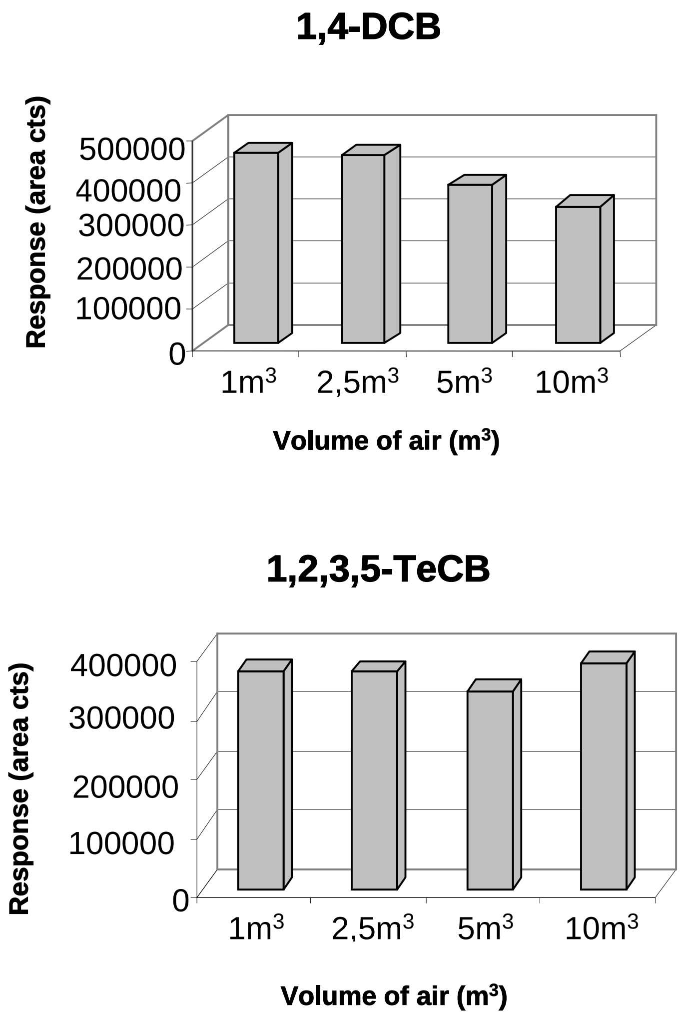

1,4-DCB
Response (area cts)
500000
400000
300000
200000
100000
0
1m3
2,5m3
5m3
10m3
Volume of air (m3)
1,2,3,5-TeCB
Response (area cts)
400000
300000
200000
100000
0
1m3
2,5m3
5m3
10m3
Volume of air (m3)

FIG. 6

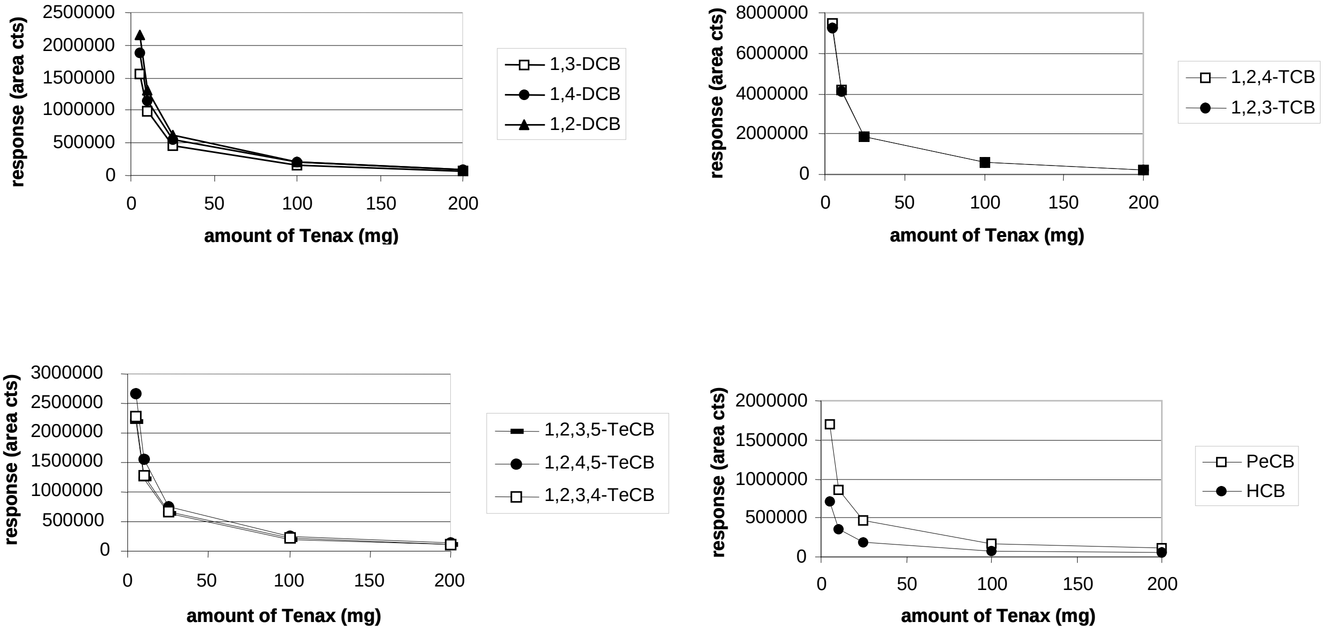

2500000
2000000
1500000
1000000
500000
0
response (area cts)
0
50
100
150
200
amount of Tenax (mg)
1,3-DCB
1,4-DCB
1,2-DCB
8000000
6000000
4000000
2000000
0
response (area cts)
0
50
100
150
200
amount of Tenax (mg)
1,2,4-TCB
1,2,3-TCB
3000000
2500000
2000000
1500000
1000000
500000
0
response (area cts)
0
50
100
150
200
amount of Tenax (mg)
1,2,3,5-TeCB
1,2,4,5-TeCB
1,2,3,4-TeCB
2000000
1500000
1000000
500000
0
response (area cts)
0
50
100
150
200
amount of Tenax (mg)
PeCB
HCB

FIG. 7

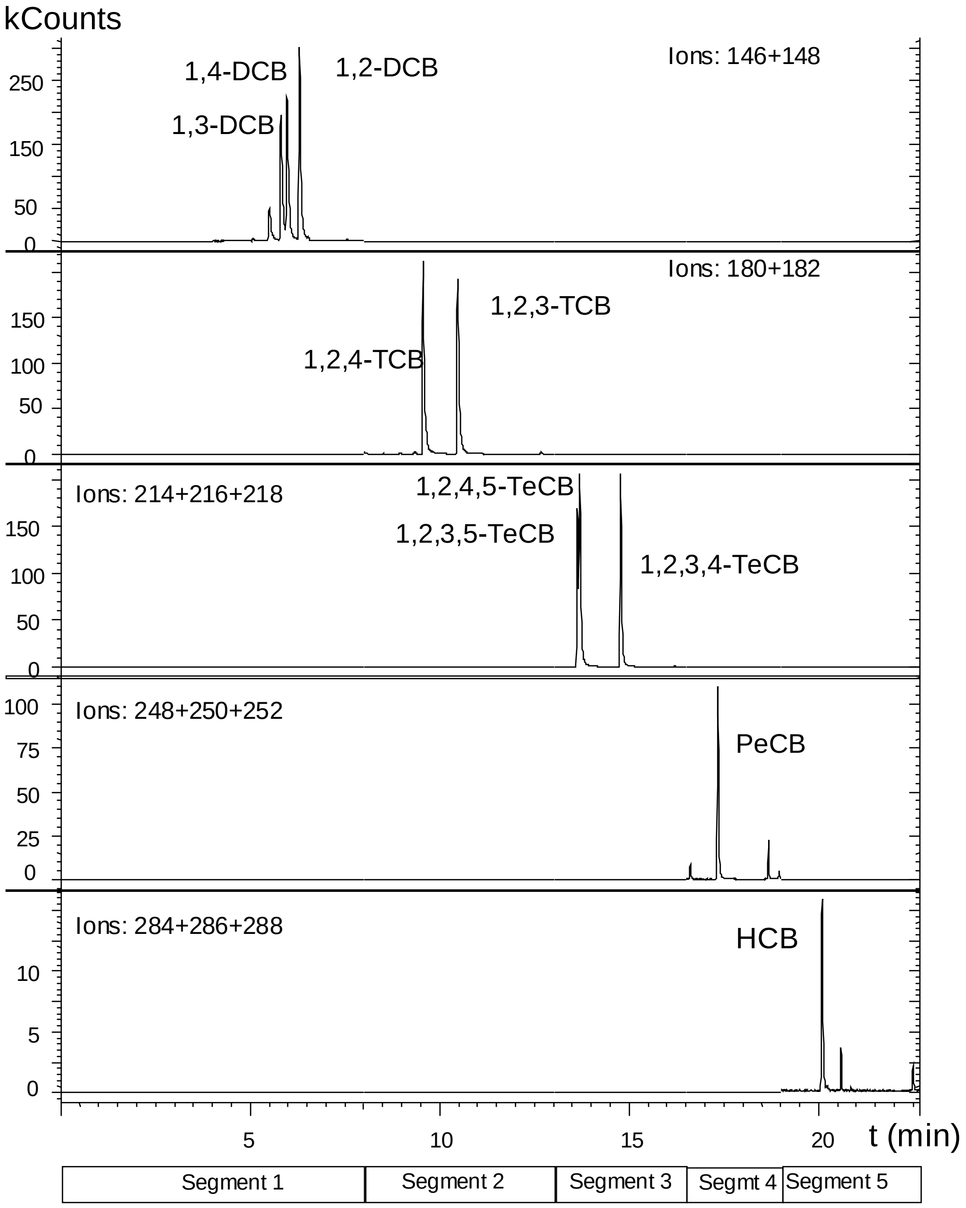

kCounts
1,4-DCB
1,2-DCB
1,3-DCB
Ions: 146+148
250
150
50
0
Ions: 180+182
1,2,3-TCB
1,2,4-TCB
150
100
50
0
Ions: 214+216+218
1,2,4,5-TeCB
1,2,3,5-TeCB
1,2,3,4-TeCB
150
100
50
0
Ions: 248+250+252
PeCB
100
75
50
25
0
Ions: 284+286+288
HCB
10
5
0
5
10
15
20
t (min)
Segment 1
Segment 2
Segment 3
Segmt 4
Segment 5

FIG. 8a

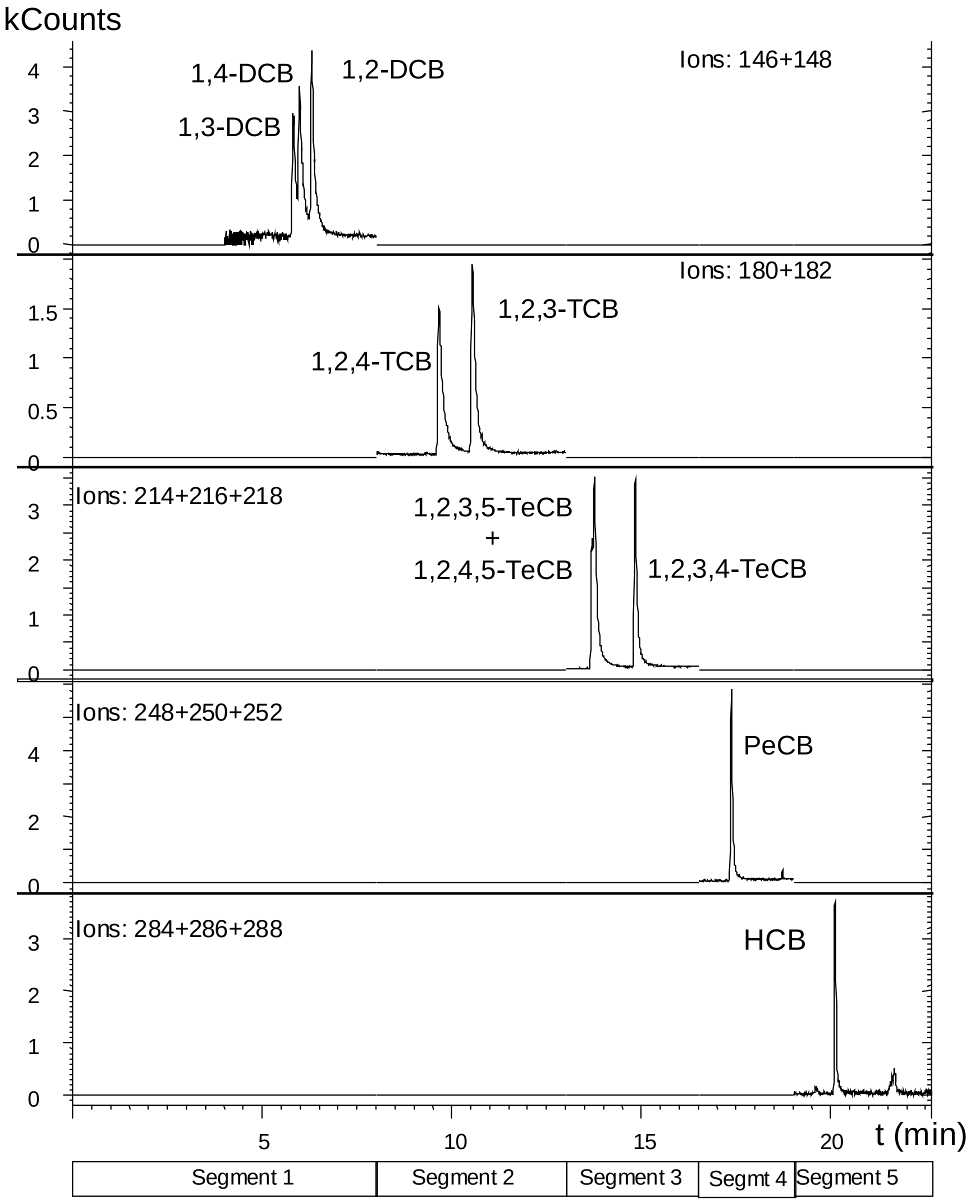

kCounts
4
3
2
1
0
1,4-DCB
1,2-DCB
1,3-DCB
Ions: 146+148
1.5
1
0.5
0
Ions: 180+182
1,2,3-TCB
1,2,4-TCB
3
2
1
0
Ions: 214+216+218
1,2,3,5-TeCB
+
1,2,4,5-TeCB
1,2,3,4-TeCB
4
2
0
Ions: 248+250+252
PeCB
3
2
1
0
Ions: 284+286+288
HCB
5
10
15
20
t (min)
Segment 1
Segment 2
Segment 3
Segmt 4
Segment 5

FIG. 8b