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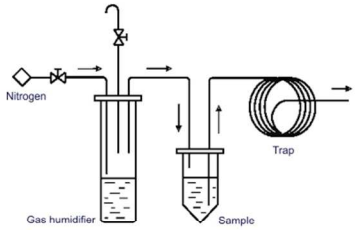
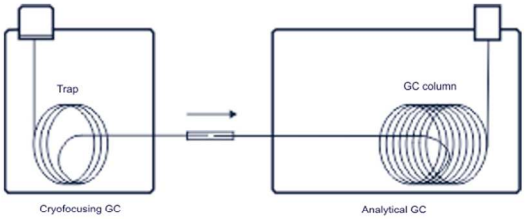


In-tube SPME



Focalization & GC analysis

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ARTICLE

Direct determination of halogenated POPs in aqueous samples by in-tube SPME, focalization and GC-ECD analysis

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A rapid analytical screening method allowing simultaneous analysis of few halogenated persistent organic pollutants (POPs) in water samples at ultra-trace levels was developed. Two-metre long capillary traps with an inner diameter of 320 µm, internally coated with 1.2-µm thick of 5%-diphenyl-95%-dimethylpolysiloxane or 14%-cyanopropylphenyl-86%-dimethyl-polysiloxane stationary phase, were used to extract some chlorinated pesticides (aldrin, heptachlor, heptachlorepoxide, dieldrin, endrin, 4,4'-DDE, α-endosulfan) and polychlorobi-phenyls (PCBs 1, 15, 44, 77, and 180) from aqueous media. Water samples were pushed through the traps at constant velocity using nitrogen. Every trap was installed in a GC oven and connected in series to an analytical column (25-m long, 320-µm I.D. of CP-Sil 8 CB with a 1.2-µm film thickness) installed in a second GC equipped with an ECD detector (GC-GC tandem system). The capillary trap in the first GC was quickly heated from 50 to 280°C to focus the retained analytes into a narrow zone between the trap outlet and the analytical column inlet, temporary kept at room temperature outside the first GC oven. After moving this zone inside the oven of the second GC, focused solutes were thermally desorbed and separated into the analytical column by programming the temperature of the second GC. Extraction recovery was always greater than 70-80% and nearly quantitative for most of the analytes. The sorptive properties of the two stationary phases were independent of sample volume and velocity but was slightly influenced by their polarity. The latter effect was used to investigate the possibility to fractionate the two classes of compounds. For this purpose, a capillary trap containing 14%-cyanopropylphenyl-86%-dimethylpolysiloxane was connected in series to a second capillary trap containing 5%-diphenyl-95%-dimethyl-polysiloxane immediately before the trapping step. Adsorbed solutes were fractioned between the two traps by eluting 0.5 mL of water-methanol 40:60 v/v. Most of the tested compounds were retained exclusively by one of the two stationary phases. Overall, the proposed method proved to be practically insensitive to laboratory contamination, reproducible, and suitable for the determination of halogenated POPs at trace level (LoD in the range 5-50 pg L^{-1}).

1. Introduction

Persistent organic pollutants (POPs) represent a group of anthropogenic organic substances, which have been regulated by the UN Stockholm Convention since 2004 [1]. Owing to their widespread use in the past, resistance to environmental degradation, and long-range transportability, they became ubiquitous in the environment, even in remote areas far away from initial emission sources. Because of their high lipophilicity, such chemicals tend to bio-accumulate in animals and humans, thus contributing to a long-term toxic exposure [2]. Although their determination in solid matrices such as soils, sediments, and biological tissues have been well established, their quantification in aqueous samples is still a demanding task. This is mainly due to extremely low concentrations at

which every compound may be found that require enrichment and clean-up steps prone to a number of interferences in the laboratory environment.

Much effort has been devoted during the last two decades to the development of faster, safer and more reliable pre-concentration techniques for these pollutants. In particular, solvent-less procedures such as solid phase micro-extraction (SPME) and stir-bar sorptive extraction (SBSE) were applied to reduce contaminations and artefacts introduced using classical well-established methods like liquid-liquid (LLE) and solid-phase (SPE) extractions. SPME uses 1-cm extractive fibres externally coated with not more than 100 µm of polymeric sorbent [3, 4]. During extraction, the fibre remains immersed in the aqueous sample for a known amount of time, generally less than 30 min, after which it is desorbed into a conventional heated GC injector. SBSE uses small glass-encapsulated magnetic stir-bars usually covered with 500 µm of polymeric sorbent, which are swirled into the samples for some length of time and then thermally desorbed in a dedicated GC injector [5]. SPME is less concerned with ghost peaks or carryover than SBSE but detection limits are worse than those obtainable by the latter. In both cases, additional band focusing by cold-trapping with column temperature programming or rather external cryofocusing may be necessary to reduce peak tailing.

In order to avoid artefacts such as ghost peaks and thermal decompositions caused by heated injectors during the desorption step, a complementary approach to SPME and SBSE, called in-tube SPME, was recently proposed by our research group [6-9] and other authors [10-21]: it is based on the use of capillary extractors made of short pieces (usually 5-30 cm long) of coated capillaries, trimmed from conventional high-resolution GC columns and carrying glass press-fits at their ends. Target analytes are first trapped by the polymeric sorbent inside the capillary extractor while a sample plug is made to flow at constant speed by applying a nitrogen overpressure on the sample surface. After removing water by purging the inert gas at low flow rates, trapped compounds are directly desorbed into the GC column without using any heated injector and subsequently refocused as described previously for SPME and SBSE. By acting on stationary phase thickness, trap length and internal diameter, extraction of analytes from aqueous samples may be non-, partially or completely depletive. In the first case the volume of the stationary phase is low and swelling of the stationary phase is needed prior to sorption. Moreover, mixing conditions in the trap are rather poor and sorption equilibrium cannot be obtained in a single sorption cycle; therefore, several sorption cycles are needed to approach the equilibrium. On the contrary, in the other two cases the quantity of stationary phase inside every capillary extractor is usually sufficient to retain quantitatively, or nearly so, target analyets in one single extraction.

The present article explores the performances of this technique in depletive conditions for the extraction, pre-concentration and subsequent GC analysis of 12 chlorinated POPs (7 chlorinated pesticides and 5 polychlorobiphenyls) using short open tubular capillary columns internally coated with non-polar or medium-polar stationary phases. The effect of experimental conditions on the recovery of the target analytes is examined in details.

2. Experimental

2.1. Reagents

All chemicals and standard products were analytical grade reagents for pesticide analysis. Demineralised water was produced by a Milli-Q system (Millipore, Bedford, MA, USA). Pesticide standards (aldrin, heptachlor, heptachlorepoxide, dieldrin, endrin, 4,4'-DDE, and α-endosulfan) were purchased from Riedel-de Haën (Seelze , Germany), Aroclor 1232 and five individual PCB congeners (2-chlorobiphenyl, 4,4'-dichlorobiphenyl, 2,2',3,3'-tetrachlorobiphenyl, 3,3',4,4'-tetrachlorobiphenyl, and 2,2',3,4,4',5,5'-heptachlorobiphenyl, symbolized respectively as PCB 1, 15, 44, 77, and 180 according to [22]) were acquired from LabService Analytica (Anzola Emilia, Bologna, Italy), while acetone and methanol were provided by Carlo Erba Reagenti (Milan, Italy).

Stock solutions (0.1 g L^{-1}) of pesticides and PCBs was prepared by dissolving every product in acetone. These standards were then diluted with acetone to prepare intermediate mix solutions used to spike aqueous samples. All standard solutions were kept in a refrigerator at 4°C and were stable for 1 month, at least. During the preparation of aqueous samples containing 0.2-240 µg L^{-1} of each target analyte, no more than 10 µL of the appropriate mixture in acetone was introduced per mL of water.

Two different real aqueous matrices (that is, water samples collected from rivers Aniene and Tiber at Rome, Italy) were used to test the matrix effect on analyte recovery. The water samples, respectively containing a total organic carbon (TOC) of 16.7 and 14.6 mg L^{-1} determined in accordance with the American Public Health Association (APHA)'s standard method [23], were filtered through 25-mm diameter, glass-fibre membranes with a pore size of 0.2 µm (Alltech Deerfield, IL, USA) and spiked with an intermediate standard mixture of target analytes directly before capillary extraction.

2.2. Sampling procedure

Capillary traps were prepared by cutting 2-m long pieces from 25-m long fused silica GC columns with an inner diameter of 320 µm and a film thickness of 1.2 µm immobilised Chrompack CP-Sil 8 CB (5%-phenyl-95%-dimethylpolysiloxane) or Chrompack CP-Sil 19 CB (14%-cyanopropylphenyl-86%-dimethylpolysiloxane) supplied by Varian (Palo Alto, CA, USA).

Sampling step was performed with a capillary trap, disconnected from the analytical column, using the equipment shown in Fig. 1 unless otherwise indicated. A known volume of aqueous sample was pushed through the trap at room temperature (18-30°C) by nitrogen humidified with demineralized water to prevent solvent evaporation in the sample reservoir. Sample flow rate was controlled (SD: ±0.1 cm s^{-1}) by acting on course and fine valves while timing liquid front or tail into the capillary trap. After sampling, the trap was washed with 1.0 mL of demineralised water introduced at the maximum speed (near 20 cm s^{-1}) to remove soluble inorganic salts, left by the sample, without significantly altering the profile of adsorbed solutes [7].

Finally, the trap was emptied of residual liquid and dried with nitrogen for 5-10 min.

2.3. GC-GC-ECD analysis

Every trap was subsequently installed in a split/splitless (S/SL) injector within a DANI 3900 gas chromatograph (Monza, Italy) with 5.0 ± 0.5 cm of the outlet outside the oven. The S/SL injector temperature was set at 50°C while the portion of the trap within the oven was heated as follows: 50°C for 1 min, 20°C min^{-1} from 50 to 280°C, 280°C for 10 min. As a result, the thermally desorbed analytes were focused on the short piece of the trap at room temperature outside the oven.

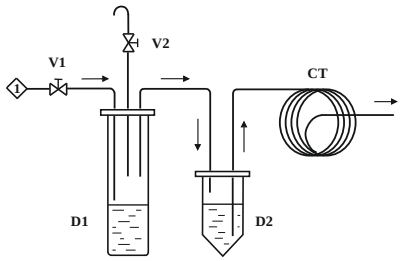

Fig. 1. Sampling apparatus. 1: N_2 99.999%, 3.0 kg cm^{-2}; V1: coarse needle valve; V2: fine needle valve; D1: nitrogen humidifier (10 mL); D2: sample reservoir (1.5-10.0 mL); CT: capillary trap.

In a following step, the focused solutes were thermally desorbed and separated into another 25-m long, 320-µm I.D. GC column internally coated with 1.2 µm of Chrompack CP-Sil 8 CB. This analytical column was permanently installed in a second gas chromatograph (DANI 6500) equipped with a ^{63}Ni electron capture detector (ECD) connected to a personal computer implementing a Chemstation CSW32 v.1.4 software (Data Apex Ltd. 2002, Prague, The Czech Republic). A deactivated press-fit connector (Carlo Erba, Milan, Italy) was used to interface the outlet of the trap to the analytical column. Thermal desorption of the analytes previously focused at the outlet of the trap and the consequent chromatographic separation were started by moving manually the last 20 ± 1 cm of the trap inside the second GC oven and heating the analytical column as follows: 50°C for 1 min, 20°C min^{-1} from 50 to 170°C, 3°C min^{-1} from 170 to 280°C, 280°C for 5 min. At the same time, the first GC oven was set at 50°C.

The ECD temperature was kept at 300°C during the whole operating sequence while nitrogen was made to flow at 30 mL min^{-1} as detector make-up gas. Fig. 2 depicts a schematic representation of the GC-GC-ECD tandem system.

Quantitative results acquired by applying this procedure were compared with the corresponding data obtained after injecting 1.0 µL of a standard solution in the S/SL injector working in splitless mode for 5 min at the temperature of 290°C. During this calibration step, the tandem system was operated in the same way as described above.

Hydrogen at 40 cm s^{-1} was chosen as carrier gas. Every gas chromatographic test was replicated three times.

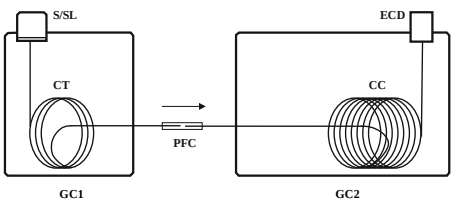

Fig. 2. Scheme of the GC-GC-ECD tandem system assembled in the present study. GC1: gas chromatograph DANI 3900; GC2: gas chromatograph DANI 6500; S/SL: split/splitless injector; CT: capillary trap; CC: analytical capillary column; PFC: press-fit connector; ECD: ^{63}Ni electron capture detector.

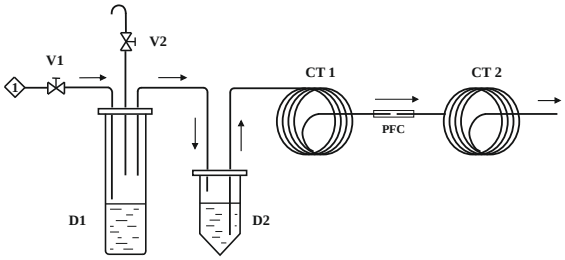

Fig. 3. Sampling apparatus used to fractionate different classes of chlorinated POPs. CT1: capillary trap containing CP-Sil 19 CB as sorbent film; CT2: capillary trap containing CP-Sil 8 CB as sorbent film; PFC: press-fit connector. Other symbols as in Fig. 1.

2.4. Fractionation of different classes of chlorinated POPs

Five mL of an aqueous sample containing a known mixture of chlorinated pesticides and PCBs were sampled as described in 2.2 at the sampling velocity of 1.2 cm s^{-1} using a CP-Sil 19 CB capillary trap connected in series to a CP-Sil 8 CB capillary trap (Fig. 3). Adsorbed solutes were fractioned between the two traps by eluting 0.5 mL of water-methanol 40:60 v/v. After disconnecting the two traps, retained solutes in each extraction device were focused and analysed as described in 2.3.

3. Results and discussion

3.1. Effect of sample volume and polymeric sorbent polarity

Table 1 lists the recoveries of the 12 tested POPs from increasing volumes (1.0-20.0 mL) of demineralized water trapped in the capillary extractors using two different sorbent films. Most of the examined compounds were quantitatively retained by both the stationary phases. For three analytes, namely aldrin, 4,4'-DDE and PCB 180, the recovery was in the range 67-80% when the non-polar silicone sorbent CP-Sil 8 CB was used in the trapping step. By increasing the polarity of the stationary phase, we observed a significant improvement in the trapping efficiency of these three compounds, especially for the chlorinated pesticides that were retained quantitatively. The different behaviours of the 12 POPs on the polymeric film CP-Sil 8 CB was not simply related to the common logarithm of their octanol/water partition coefficient (K_{ow}).

All the tested compounds were not affected by the volume of the aqueous sample introduced in the capillary traps containing one of the two sorbent films examined in the present research. This means that it is possible to sample volumes up to 20 mL, at least, without compromising the retention of the 12 analytes.

3.2. Effect of sampling velocity

Sampling velocity in the capillary traps containing CP-Sil 19 CB as sorbent film did not affect the recovery of the 12 POPs at least in the range 1-5 cm s^{-1} (Table 2). These results confirm the findings obtained in previous studies carried out by our research group [6, 7, 9].

3.3. Effect of POPs concentration

In-tube SPME into CP-Sil 19 CB traps of increasing quantities (1-100 pg) of the 12 POPs dissolved in 20.0 mL of demineralized water did not impair the recovery of each analyte. All peak areas of the retained compounds were

Table 1 Effect of sample volume (mL) and sorbent polarity on the recovery (%) of tested chlorinated pesticides and PCBs.

Compound	Added quantity (pg)	Sample volume eluted inside CP-Sil 8 CB traps				Sample volume eluted inside CP-Sil 19 CB traps			
		1.0	5.0	10.0	20.0	1.0	5.0	10.0	20.0
Heptachlor	10	100	101	100	100	100	100	100	100
Aldrin	10	71	71	76	74	100	100	100	100
Heptachlor epoxide	10	99	100	99	100	100	100	100	100
α-Endosulfan	10	99	101	100	99	100	100	100	100
Dieldrin	10	100	100	100	101	100	100	100	100
Endrin	10	100	100	100	100	100	101	100	99
4,4'-DDE	10	80	77	75	79	100	100	100	100
PCB 1	240	99	101	100	101	100	100	99	99
PCB 15	120	101	100	99	101	100	100	99	99
PCB 44	60	100	100	100	100	100	100	100	100
PCB 77	60	100	100	100	100	100	100	100	100
PCB 180	20	70	69	68	67	82	81	81	78

Sampling velocity: 1.2 cm s^{-1}; standard deviations: 4-6% (three replicates).

proportional to the sampled quantity (coefficient of determination $R^2 \geq 0.9993$). This implies that the linear range for every tested compound was 0.05-5.00 ng L^{-1}, at least.

In the same experimental conditions, the limit of detection (LoD) estimated according to Knoll's definition (analyte concentration that produces a chromatographic peak equal to three times the standard deviation of the baseline noise) [24] was 9 pg L^{-1} for heptachlor, 14 pg L^{-1} for aldrin, 8 pg L^{-1} for heptachlor epoxide, 9 pg L^{-1} for α-endosulfan, 12 pg L^{-1} for dieldrin, 13 pg L^{-1} for endrin, 14 pg L^{-1} for 4,4'-DDE, 50 pg L^{-1} for PCB 1, 32 pg L^{-1} for PCB 15, 15 pg L^{-1} for PCB 44, 12 pg L^{-1} for PCB 77, and 5 pg L^{-1} for PCB 180. These values are sufficiently low to enable the direct determination of chlorinated POPs at the concentration levels found in most of polluted natural waters (Table 3).

Table 2 Effect of sampling velocity (cm s^{-1}) on the recovery (%) of tested chlorinated pesticides and PCBs using capillary traps coated with CP-Sil 19 CB.

Compound	Added quantity (pg)	Sampling velocity			
		1.2	2.4	3.6	5.2
Heptachlor	10	100	100	101	100
Aldrin	10	101	100	100	101
Heptachlor epoxide	10	100	100	100	100
α-Endosulfan	10	99	99	100	100
Dieldrin	10	101	99	100	100
Endrin	10	100	100	100	100
4,4'-DDE	10	101	100	100	101
PCB 1	240	101	100	99	100
PCB 15	120	101	99	100	100
PCB 44	60	100	100	100	100
PCB 77	60	100	100	100	100
PCB 180	20	82	83	85	82

Sample volume: 5.0 mL; standard deviations: 3-5% (three replicates).

Table 3 Occurrence of chlorinated pesticides (OCPs) and polychlorobiphenyls in natural waters.

POPs	Aqueous matrix	Individual POP concentration range (ng L^{-1})	Reference
OCPs	Chao river (China)	n.d.-1.8	[25]
PCBs	Chao river (China)	n.d.-0.01	[25]
OCPs	Selangor river (Malaysia)	0.6-25	[26]
OCPs	Pangani river (Tanzania)	n.d.-4.5	[27]
PCBs	Khour-e-Mousa, Persian gulf (Iran)	n.d.-120	[28]
OCPs	Densu river (Ghana)	n.d.-260	[29]
PCBs	North West Persian gulf (Iran)	n.d.-100	[30]
OCPs	Coastal marine environment (Singapore)	n.d.-1.7	[31]
PCBs	New York / New Jersey WPCP (USA)	n.d.-29	[32]

n.d.: lower than detection limit, WPCP: water pollution control plant.

Table 4 Effect of aqueous matrix and sample volume (mL) on the recovery (%) of tested chlorinated pesticides and PCBs using capillary traps coated with CP-Sil 19 CB.

Compound	Added quantity (pg)	DW volume		RA volume		RT volume	
		1.0	5.0	1.0	5.0	1.0	5.0
Heptachlor	1	100	100	97	97	98	97
Aldrin	1	100	100	97	97	97	97
Heptachlor epoxide	1	100	100	98	97	98	98
α-Endosulfan	1	100	100	99	97	98	98
Dieldrin	1	100	100	97	97	98	99
Endrin	1	100	101	97	96	97	97
4,4'-DDE	1	100	100	97	98	98	98
PCB 1	240	100	100	99	99	99	98
PCB 15	120	100	100	99	99	99	99
PCB 44	60	100	100	100	100	100	100
PCB 77	60	100	100	100	100	100	100
PCB 180	20	82	81	79	78	78	78

DW: demineralized water; RA: aliquot of the river Aniene; RT: aliquot of the river Tiber; standard deviations: 4-6% (three replicates).

3.4. Effect of aqueous matrix

Recovery tests carried out by sampling aliquots (1.0 and 5.0 mL) of river waters spiked with known amounts of 6 POPs resulted in no loss in performance of the capillary traps containing CP-Sil 19 CB as sorbent film (Table 4). The results obtained from this check seem to confirm the general belief that well-immobilised polysiloxane phases are practically unaffected by the contact with aqueous matrices even when they contain a non-negligible load of organic substances.

Fig. 4A shows a typical chromatogram produced after sampling 1.0 mL of water collected from the river Tiber, filtered and spiked with 20 ng of Arochlor 1232 immediately before the trapping step. The resulting profile may be compared with the chromatogram obtained by injecting the same amount of the PCB mixture in the GC column through the conventional split/splitless injector (Fig. 4B). Every chromatogram is made up of two signal profiles: the first one (GC1) represents the ECD response recorded during the preliminary focalization of the trapped analytes at the end of the capillary trap while the second one (GC2) represents the signal produced by the following gas chromatographic separation. By comparing the two GC2 profiles it can be seen that the inevitable loss of chromatographic resolution due to the sampling technique was almost efficiently contrasted by the well-known re-focusing action at the end of the trap operated by programming the temperature in the first GC.

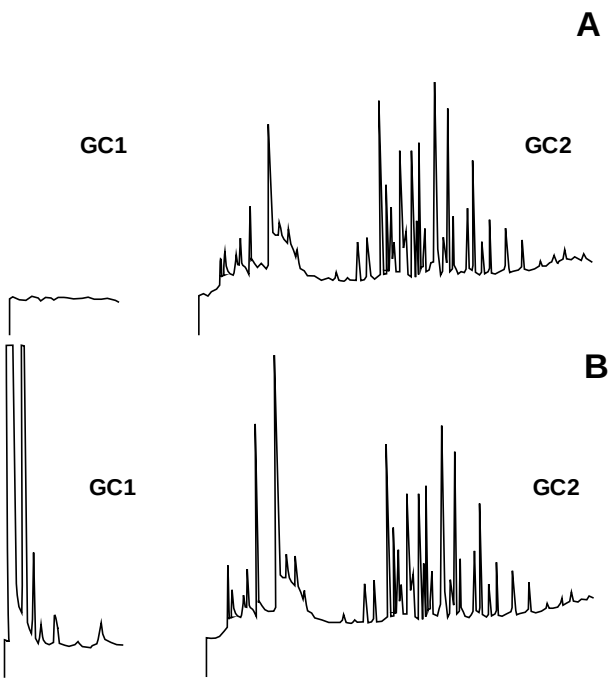

Fig. 4. GC-GC-ECD chromatograms of 20 ng of Arochlor 1232 obtained by: A) sampling 1.0 mL of water collected from the river Tiber, filtered and spiked with the PCB mixture; B) directly injecting 1 µL of the PCB mixture in acetone into the tandem assembly through the conventional split/splitless injector. GC1: signal produced by little retained organics (e.g., injected solvent) during the focalization step by heating the first GC; GC2: signal produced by trapped compounds during the following gas chromatographic analysis by heating the second GC.

3.5. Performance of the fractionating procedure

A preliminary investigation on the possibility of separating compounds belonging to different classes of POPs using in-tube SPME was undertaken by connecting in series two traps containing different sorbent films (Fig. 3). This new configuration was adopted during both the preliminary trapping step and the following fractionation attempted with the elution of a small volume of an aqueous solution of methanol. Table 5 lists the recoveries of the 12 POPs from the two capillary traps after their disconnection. Most of the chlorinated pesticides were retained exclusively by the second trap allowing for a partial separation from the PCBs mainly recovered from the first trap.

A better separation of the two classes of compounds could be achieved by acting on the percentage of the methanol in water, the overall volume of the fractionating solvent as well as the relative order of two traps with respect to the flow direction. These aspects will be investigated thoroughly in the near future.

4. Conclusions

The sampling technique examined in the present study proved to be completely adequate for the determination of chlorinated POPs in aqueous samples. The simplicity of the described operations allowed dosing these toxic chemicals at very low levels without introducing artefacts and contaminations. The recovery of the tested analytes was almost quantitative and independent of many experimental conditions set in the trapping step. Among the different factors that may affect the trapping efficiency, only the polarity of the capillary extractors affected the recovery of few analytes. A preliminary test made coupling two different traps in series suggested that this approach may be adopted to separate different classes of chlorinated POPs before the following GC-GC analysis.

Table 5 Recovery (%) of tested chlorinated pesticides and PCBs from CP-Sil 19 CB and CP-Sil 8 CB traps after fractionation with 0.5 mL of water-methanol 40:60 v/v and disconnection of the two traps.

Compound	Added quantity (pg)	Recovery from CP-Sil 19 CB	Recovery from CP-Sil 8 CB	Total recovery
Heptachlor	5	0	100	100
Aldrin	5	0	100	100
Heptachlor epoxide	5	0	100	100
α-Endosulfan	5	0	100	100
Dieldrin	5	0	100	100
Endrin	5	20	80	100
4,4'-DDE	5	0	100	100
PCB 1	150	0	0	0
PCB 15	100	45	55	100
PCB 44	35	65	35	100
PCB 77	30	97	3	100
PCB 180	10	82	18	100

Sample volume eluted during the trapping step: 5.0 mL; sample and fractionating eluent velocity: 1.2 cm s^{-1}; standard deviations: 3-4% (three replicates).

Notes and references

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