Uncertainty Measurement of Chlorophenols and PCBs Analyzed in Aqueous Media by SPME–GC–ECD

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Abstract

Chlorophenols (CPs) and polychlorinated biphenyls (PCBs) are two of the most important groups of high-priority pollutants, due to their carcinogenicity, toxicity, and mutagenicity. This paper compares the utilization of two solid-phase microextraction (SPME) based extraction procedures, prior to gas chromatography with electron capture detection (GC–ECD), to determine PCBs (PCB 101 and PCB 153) and CPs (2,4,6-TCP and PCP) in aqueous media. Good linearity was observed with the SPME–GC–ECD method for the concentration range studied; detection limits ranged from 0.5 to 1.0 µg/L. Repeatability was between 13% and 31% for the lowest concentration and between 5.6% and 7.8% for the highest concentration. The uncertainty was determined by Thompson and bottom-up approaches. The identification of the compounds was confirmed by GC–MS. The developed procedure has the advantage of simplicity of sample treatment and avoids the use of potentially hazardous organic solvents and the clean-up or pre-concentration steps. Regarding PCBs, this procedure is simpler and faster, but the limits of detection are higher.

Introduction

Chlorophenols (CPs) and polychlorinated biphenyls (PCBs) are organochlorine pollutants which represent a major environmental concern. These compounds can be a public health problem due to their carcinogenic properties, which increase incrementally with chlorination (1). They are also highly toxic, poorly degradable, and are persist in the environment (2–7).

Therefore, the United States Environmental Protection Agency (U.S. EPA) and the European Union (EU) have included them in their list of priority pollutants (3,6,8–12). The EPA has defined a maximum level of 1 µg/L of pentachlorophenol (PCP) and 0.5 µg/L of PCBs in drinking water (13). The EU has set a maximum level of 1–2 µg/L of PCBs for natural water and a 10× lower value for drinking water (9). The EU has also established a maximum legal limit for PCP in 1 mg/L in industrial effluents of PCP-Na industries (14). The recent proposal of the European Commission (15) suggests new environmental quality standards for PCP, expressed as maximum allowable concentration of 1 µg/L and as an annual average of 0.4 µg/L in surface water.

The last edition of Guidelines for Drinking-Water Quality (16) presents health-based guideline values of 0.2 mg/L for 2,4,6-trichlorophenol (2,4,6-TCP) and 0.009 mg/L for PCP. The most evident influence of CPs on drinking water is their organoleptic perception level. The taste thresholds in water for 2,4,6-TCP and PCP are 2 µg/L and 0.03 mg/L, and the odor thresholds are 300 µg/L and 1.6 mg/L, respectively (17,18).

PCP and 2,4,6-TCP are two of the CPs used in several industrial processes and, therefore, they often lead to wastewater and ground water contamination. PCP was detected in water samples, usually with concentrations below 10 µg/L, although much higher concentrations in groundwater may be measured under certain conditions (16). In Portugal, 2,4,6-TCP was detected in surface and treated water, while PCP was only detected in treated water (6). These two CPs were also detected in the Isipingo Estuary (0.1–27 µg/L) and in the Baltic Sea (0.1–6.0 µg/L) (19,20).

While CP use is in decline, the production of PCBs was banned from use many years ago (20). However, PCBs are still widely distributed in environment due to non-intentional sources of persistent contaminants from incomplete combustion of organic matter and chlorine (21). PCBs have been found, in ng/L levels, in the Baltic Sea in the period from 1996–2001 (20).

Most of these environmental contaminants are hazardous at low concentrations, so analytical methods must be very sensitive when providing the detection of small amounts and an enrichment step is needed before the chromatographic analysis. Several works have already reported suitable techniques for the analysis of chlorinated pollutants from various matrices. GC detection methods, mainly used in CPs and PCBs determinations, are electron capture detection (ECD) and mass spectrometry (MS). Most of them couple a clean-up or pre-concentration technique, such as liquid–liquid extraction (LLE) (12) and solid-

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phase extraction (SPE) (12,22,23). Although these conventional extraction methods offer good results, they are relatively solvent- and time-consuming, with use of organic solvents injurious to health, and are highly expensive (4,7,24).

Therefore, every improvement of these methods and validation of new methods are important. Solid-phase microextraction (SPME), a highly sensitive and selective extraction/concentration technique, is considered an advantageous alternative, because it greatly reduces or eliminates the need for solvents. In addition, SPME is faster and requires fewer steps than those techniques, because it integrates sampling, extraction, concentration and sample introduction into a single step, which can greatly decrease the uncertainty of the sample preparation. Finally, SPME often allows equal or better sensitivities than LLE and SPE for a wide range of compounds (6,11,25).

In this decade, microwave energy has been widely applied as an extraction technique (7,24). Microwave-assisted headspace (MA-HS)-SPME has already been reported as an extraction procedure of PCBs and PAHs in landfill leachates and sediments (3), organochlorine pesticides in water (24), and CPs in soil samples (7) prior to gas chromatography (GC).

Besides the cited advantages, it should be noted that SPME provides generally low extraction efficiency, carryover problems on stir bars and incomplete desorption from used SPME fibers (20). During the analytical process, analyte losses may happen, mainly during sampling, transport, and storage. For example, the stir bar and fiber carryover can achieve losses of 5% and 20%, respectively (7). Therefore, it is very important to identify the sources of analytic uncertainty.

Two of the most used approaches to assess global uncertainty of analytic results are the bottom-up, adopted by EURACHEM/CITAC Guide (26), and the top-down (27). The first one is an overestimation of the uncertainty, but it allows a good knowledge of each individual uncertainty source and the detection of the most significant (27). This approach also provides information about the variation of uncertainty and, thus, allows corrective actions on critical steps. The top-down approach constitutes a simpler way of uncertainty estimation, based on inter-laboratory results. Horwitz reported an empiric equation to estimate the inter-laboratory precision (27). However, later, Thompson (28) suggested some modifications for the highest and lowest concentration ranges.

In the current work, an analytical method was adapted from previously described ones (2,5) to determinate four environmental pollutants in aqueous media, because the contamination of water supplies is a global problem. The selected compounds (2,4,6-TCP, PCP, PCB 101, and PCB 153) comprise the most hazardous compounds of their groups and have different steps of chlorination.

Although the use of SPME or HS-SPME techniques for the analysis of PCBs or CPs in water have already been reported (2,6,25), to our knowledge, none reported the simultaneous extraction and concentration of the selected CPs and PCBs in the SPME fiber allowing direct analysis by GC–ECD. Thus, the present paper describes the validation of a simple extraction procedure of the investigated pollutants, as well as the assessment of the global uncertainty associated with the results for all of the range of linearity covered by the analytical methodology.

Experimental

Chemicals

The studied CPs (2,4,6-TCP and PCP, both 98%) were obtained from Supelco (Bellefonte). The two PCB congeners used (2,2',4,5,5'-pentachlorobiphenyl, PCB 101, 99%, and 2,2',4,4',5,5'-hexachlorobiphenyl, PCB 153, 97.5%) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Isopropyl alcohol (99.8%) was acquired from Riedel-de-Haën (Seelze, Germany) and sulphuric acid (95-97%) from Fluka (Buchs, Switzerland).

Standard solutions

Individual stock solutions (~ 500 mg/L for CPs and 200 mg/L for PCBs) and intermediate standard solutions (around 5 mg/L) were prepared by dissolving standards in isopropyl alcohol. Appropriate volumes of each intermediate standard solution were diluted in deionized water to prepare calibration standard solutions, containing 1.1% of isopropyl alcohol, in order to reach final concentrations of 0.5–5.0 µg/L for both CPs; 1.0–20.2 µg/L for PCB 101; and 1.0–15.2 µg/L for PCB 153. These solutions were stored at 4°C in the absence of light. All standards were acidified to pH 2, with sulphuric acid 0.1M, to ensure that all chlorophenolic compounds were in their non-ionized form.

Instrumentation

Chromatographic separation and detection of the studied compounds were performed using a Finnigan 9001 GC from Finnigan Corporation (Austin, TX), equipped with a split-splitless injector and 63Ni Electron Capture Detector. The analytical column was a DB-5MS, with a length of 30 m × 0.53 mm i.d., 1.5 µm film thickness, from J&W Scientific (Folsom, CA). Borwin software was used for data acquisition and analysis. Carrier and make-up gas was nitrogen 5.0 (99.999%) from Air Liquide (Maia, Portugal).

The SPME device (fiber and holder) was purchased from Supelco (Bellefonte, PA). The fiber used was an 85 µm polyacrylate (PA). SPME was performed on a heater-stirrer plate (Corning, NY). Samples were extracted in 5-mL amber vials with magnetic stir bars (8 × 3 mm), PTFE coated, ensured stirring.

GC–mass spectrometry (MS) was performed on a Varian (Walnut Creek, CA) CP-3800 GC, equipped with a split/splitless injector. A Varian 4000 MS ion trap detector was used. The analytical column was a Varian FactorFour Capillary Column VF-5MS, 30 m × 0.25 mm i.d. (0.25 µm film thickness).

Chromatographic conditions

GC–ECD

The injector and ECD temperatures were held constant at 280°C and 350°C, respectively. The splitless time for desorption was set to 5 min.

According to the optimized program, the oven temperature was initially held for 1 min after injection at 130°C, and then increased at a rate of 12°C/min to 235°C and afterwards increased to the final temperature of 280°C at 2°C/min. The total run time was 33 min.

The carrier and make-up gas flow rate were 2 and 15 mL/min, respectively.

GC–MS

The chromatographic oven-temperature was as follows: the initial temperature of 130°C was held for 1 min after injection, then ramped to 280°C at a rate of 12°C/min and held for 1 min. Helium at 1 mL/min (constant flow) was used as carrier gas. The transfer line, manifold, and trap temperatures were 300°C, 50°C, and 220°C, respectively. The injection temperature was 280°C. Detection was made in the selected ion storage mode (SIS). The selected quantitation ions and the retention times, under the given experimental conditions, are summarized in Table I. The ionization was performed with a kinetic energy of impacting electrons. The emission current was set to 50 µA for all segments.

Conventional SPME

The PA fibers were conditioned prior to use by heating, at 300°C, in the injection port of the GC for 2 h, according to the instructions recommended by the manufacturer. Whenever needed, the conditioning step was repeated for fiber cleanup. Moreover, blank runs were performed periodically during the analysis to look for possible fiber contamination or carryover, avoiding quantitative errors.

For CP extraction, the use of PA fibers, by immersion mode, is very usual, but for PCBs, PDMS fibers are advisable, mainly in the mode of headspace (5,6,10,25). Ribeiro et al. (5) reported the optimized extraction conditions for CP analysis as an 85 µm PA fiber immersion at 40°C for 60 min and stirring (750 rpm), with saturated sal conditions sample pH < 2 and desorption for 3 min at 280°C. These conditions were adapted for the simultaneous CP and PCB analysis. However, because one GC run lasted 33 min and SPME of a new sample can be performed simultaneously with GC analysis of a previous sample, a shorter extraction time can decrease the total time of the SPME-GC process. Therefore, a 35-min sampling time (~ the same for the chromatographic separation) was used. To avoid damage of the fibers, the extraction was performed without salt. Thus, SPME was carried out by introducing 4 mL of standard (pH 2, adjusted with sulfuric acid) into glass vials, with a stir bar, placed on a hot/stirring plate at 40°C. A homemade system was used to control the temperature. After extraction, the fiber was immediately inserted in GC injector for desorption. The fiber remained in the injector at 280°C for 3 min after run start, with the split valve closed, for desorption of all the analytes. After each extraction, stir bars were substituted and rinsed with acetone and distilled water to prevent carryover between samples.

Table I. Method Parameters for Each Segment of the GC–MS Method

Segment	Compound	Start time (min)	End time (min)	Retention time (min)	Quantification ions (*m/z*)
Solvent delay	–	0	2	–	–
2	2,4,6-TCP	2	9.5	4.32	196, 198
	PCP			8.00	265, 266
3	PCB 101	9.5	13.5	11.01	326, 324
	PCB 153			12.33	360, 362

Uncertainty measurement

In this work, two different approaches were used for the estimation of uncertainty: the bottom-up and the modified top-down reported by Thompson (28).

Bottom-up approach

Following the bottom-up approach, according to the EURACHEM/CITAC guide (26), there are four main individual sources of uncertainty that must be taken into account, namely the uncertainty associated with the standard preparation (U1), the uncertainty associated with the calibration curve (U2), the uncertainty associated with the precision (U3), and uncertainty associated with the accuracy (U4) (25,27).

Ratola et al. (27) summarizes the calculation procedure of these individual uncertainties and the estimation of the global uncertainty. This uncertainty allows one to achieve the expanded uncertainty (U) of an analytical result, for a confidence level of approximately 95% (26), using a coverage factor (k) of 2. The expanded uncertainty provides an interval within which the measured value is believed to lie.

Modified top-down approach

Thompson (28) established a simpler method, based in interlaboratory studies, to approach almost immediately the global uncertainty. This estimation is completely independent from the type of analyte, the matrix studied, and of the methodology employed. The suggested functions are only dependent of the analyte concentration.

Results and Discussion

Validation of the analytical method

An in-house validation of the proposed analytical method was performed in order to establish the essential parameters (linearity range, detection limits, precision, and accuracy) and to assess the global uncertainty associated with the results.

Chromatographic separation

The chromatographic conditions used yielded an adequate resolution of the target compounds in less than 35 min. Figure 1 shows a SPME–GC–ECD chromatogram of a 4 mL water sample, containing a mixture of the studied CPs and PCBs with a concentration of 1.5 µg/L for 2,4,6-TCP, 1.0 µg/L for PCP, and 5.1 µg/L for PCBs, under the chromatographic conditions described in the experimental section.

The method validation is an important issue of overall quality associated with analytical data. The following parameters are those currently considered more important in quantitative analytical methods validation.

Linearity

In the present work, five calibration standards were analyzed in duplicate for the calibration of each selected CP and PCB. Linear relationships were checked, plotting concentration against peak areas, within the concentration range considered

(0.5–5.0 µg/L for both CPs, 1.0–20.2 µg/L for PCB 101, and 1.0–15.2 µg/L for PCB 153). The highest coefficient of determination (R^2) was 0.983 (PCB 153) and the lowest was 0.940 (PCB 101), as can be seen in Table II.

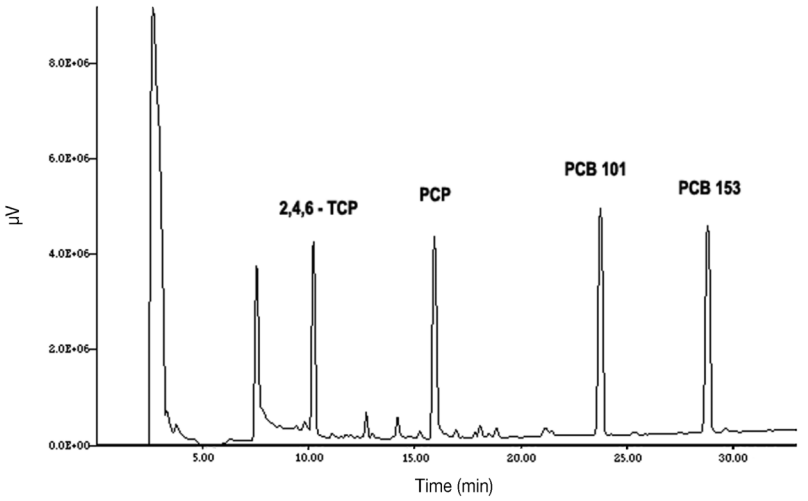

Figure 1. SPME–GC–ECD chromatogram of a CPs and PCB mixture (1.5 µg/L for 2,4,6-TCP, 1.0 µg/L for PCP, and 5.0 µg/L for PCBs) in water under SPME conditions. Chromatographic conditions specified in the text.

Table II. Linearity and Detection Limits of the Method*

Compound	Linearity range (µg/L)	R^2*	LOD (µg/L)
2,4,6-TCP	0.5–5.0	0.957	0.5
PCP	0.5–5.0	0.967	0.5
PCB 101	1.0–20.2	0.940	1.0
PCB 153	1.0–15.2	0.983	1.0

* R^2 = coefficient of determination; LOD = detection limits.

Table III. Recovery and Precision (n = 5 Injections) for CPs and PCBs with the Proposed Method*

Compound	C (µg/L)	Precision (% CV)	Recovery (%) Average ± SD	Min.	Max.
2,4,6-TCP	0.5	12.66			
	1.5	3.26	93.01 ± 17.77	81.13	112.37
	5.0	5.63			
PCP	1.0	7.28			
	2.5	7.80	106.74 ± 12.14	97.35	116.13
PCB 101	1.0	14.52			
	5.0	3.90	100.18 ± 52.82	54.59	169.82
	15.1	6.42			
PCB 153	1.0	30.91			
	5.1	4.61	109.69 ± 39.75	74.68	159.69
	15.2	6.96			

* CV = coefficient of variation.

Detection limit

Although other methods to calculate the detection limits (LODs) were available, these parameters were evaluated based on the signal-to-noise ratio (S/N). The peak area of analyte should be at least three times higher than the noise. The LOD ranged from 0.5 for CPs to 1.0 µg/L for PCBs, making this methodology suitable to comply the requirements of PCP in drinking water according to U.S. EPA, as well as PCBs in natural water defined by European Union Directives.

These results are comparable with those obtained by other authors using similar techniques, showing similar or better characteristics, namely in terms of LOD, analysis time, and solvent consumption. Estevinho et al. (2) employed calibration ranges between 1 and 25 µg/L of PCP and reached detection limit of 0.96 µg/L. Logically, it is possible to improve selectivity and to reach lower LODs using, for example, other extraction procedure or other detection methods like MS, but ECD is a cheaper equipment and is still widely used (27). Simões et al. (6) obtained LODs limits of 0.06 and 0.20 µg/L for 2,4,6-TCP and PCP, respectively, by SPME–GC–MS. Other new techniques for the extraction of CPs from aqueous samples like simultaneous dispersive liquid–liquid microextraction and derivatization (DLLME) (1) and SPME with micellar desorption (SPME–MD) (11) were subject of current scientific work. Lower LODs than those obtained in this research, were achieved by DLLME–GC–ECD (0.010–0.015 µg/L); however, this technique requires solvent consumption (1).

Some reported methods (4,25) for PCB extraction and analysis obtained LODs in the ng/L level, however, the overall analysis runtime was much longer.

Precision

In the present case, the precision of the developed method was obtained by repeatable standard deviation, expressed as the coefficient of variation (CV %), performing five repeated analysis of the same standard on the same day. Two concentration levels for PCP and three concentration levels for the other compounds were studied: 0.5, 1.5, and 4.9 µg/L for 2,4,6-TCP; 1.0 and 2.5 µg/L for PCP; and 1.0, 5.1 and 15.2 µg/L for PCBs (Table III). All values are below 15%, except for the first concentration level of PCP and PCB 153 by GC–MS.

Nowadays, the other compounds, 2,4,6-TCP and PCB 101, showed better precision. Hartley's test (29) was applied to check if the obtained CV values were statistically similar. According to this test, the results were considered similar, except for PCB 101.

Accuracy

Accuracy, expressed through analytical recovery assays (the observed value divided by the expected value after standard addition), was determined by five independent extractions at three different standard levels. The standard concentrations used were

the same as those for precision studies. The results, displayed as average, minimum, and maximum recoveries (%), are presented in Table III. The results reported provide evidence that the optimized method achieves for acceptable repeatability (RSD ≤ 20%), in line with criteria sets by EU guidelines (30) nearly all analytes.

Confirmation of peak identity by GC–MS

Nowadays, the use of GC–MS is accepted to be one of the best ways for unequivocal confirmation of peak identity (21). Therefore, the identification of the analytes was achieved using GC–MS, by extracting the characteristic ions of each studied compound, monitored at the specific retention time. Figure 2 represents the chromatogram of a sample with selected PCBs and CPs.

Uncertainty evaluation

Bottom-up approach

A validation-based approach, proposed by EURACHEM, was used to identify and quantify the main uncertainty sources of the method. Table IV shows, as an example, the variation of each individual source of uncertainty for each standard concentration of 2,4,6-TCP.

All individual sources of uncertainty, mainly U2, are highly dependent on the calibration levels for concentrations below 1.5 for 2,4,6-TCP, 1 for PCP, and 5 µg/L for PCBs. Above these values, the expanded uncertainties remain approximately constant. As concentration values approach the LODs, the values rise exponentially, and, for the lowest calibration levels, the expanded uncertainties are higher than 100%. Thus, uncertainties in the neighbourhood of the LODs require careful consideration due to an extremely high uncertainty associated to any quantitation of these compounds. Nevertheless, all the individual uncertainty components had the highest values for the lower concentrations; the main contribution came from the uncertainty associated with the calibration curve (U2). The patterns stated, relating the dependence of the uncertainties with the calibration levels, were observed by other authors using similar analytical methods or target analytes (25,27).

Figure 3 shows the contribution of each uncertainty sources for one of the calibration levels. The sources of these uncertainties could be analyte losses during analytical steps, carryover problems, and different responses to each pollutant by electron capture detector. It has also been reported that a 3% change in detector temperature can result in a 10% error in the evaluation of the response (27).

These values were in accordance with those already reported by other authors (25,27). If the expanded uncertainties are applied for PCP concentrations higher than the maximum level defined by EPA for drinking water (1 µg/L), it can be seen that they vary from 32% to 15% for a concentration range of 1.0–5.0 µg/L.

Modified top-down approach

According to Thompson (28) and for the concentration ranges studied, the expanded uncertainties are 44% with a confidence

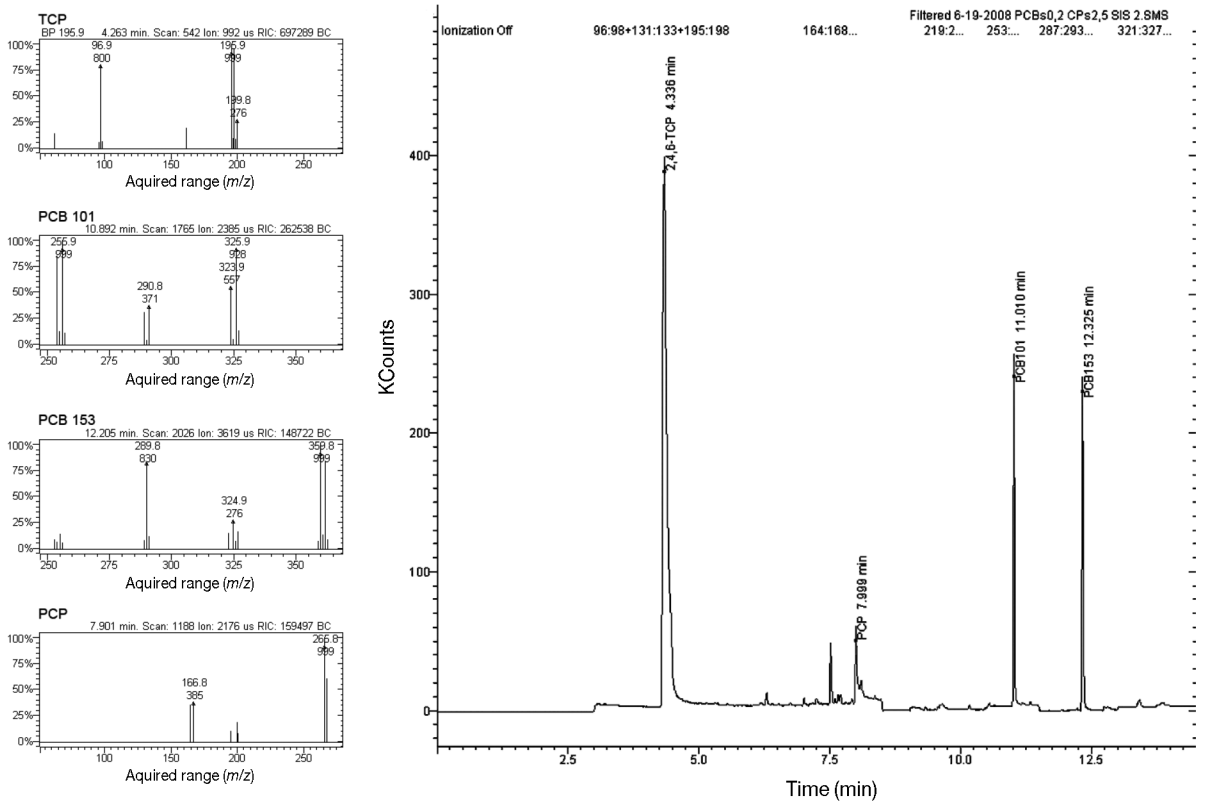

Figure 2. Selected ion chromatogram and mass spectrum of a sample with PCBs (200 ng/mL), 2,4,6-TCP (2.84 µg/mL), and PCP (2.62 µg/mL). Program temperature used in GC: 130°C (1 min), 12°C/min to 280°C with a final hold for 1 min.

Table IV. Example of the Contribution of Each of the Four Uncertainty Components, Global, and Expanded Uncertainties (bottom-up approach and EURACHEM) for 2,4,6-TCP Analysis by SPME–GC–ECD for all Standard Concentrations

[2,4,6-TCP] (µg/L)	U1 (%)	U2 (%)	U3 (%)	U4 (%)	U (%)	$U_{expanded}$ (%)
0.5	5.3	92.7	5.7	8.3	93.4	186.7
1.0	5.3	23.2	5.7	8.3	25.8	51.6
1.5	2.4	14.2	1.5	1.9	14.6	29.3
2.5	4.4	10.2	2.5	2.2	11.6	23.2
5.0	2.6	7.9	2.5	2.2	9.0	17.9

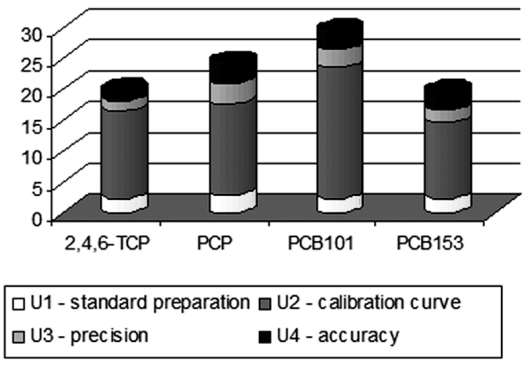

Figure 3. Contribution of each uncertainty sources, for one of the calibration levels (1.5 µg/L for 2,4,6-TCP, 1.0 µg/L for PCP, 10.1 µg/L for PCB 101 and 5.1 µg/L for PCB 153).

level of approximately 95%. The comparison of the uncertainties by the two approaches for each concentration shows that for the higher calibration levels, the modified top-down approach produces uncertainty levels much higher than bottom-up. On the other hand, as the concentration levels are approximates of the LODs, the bottom-up approach provides higher uncertainty levels.

A similar approach was used by Ratola et al. (27), but for different compounds, and it concluded that for bottom-up, the expanded uncertainty was below 25% for most of the calibration ranges studied, except for the lowest ranges. For modified top-down, the expanded uncertainty was 44% for all calibration ranges.

Conclusions

The aim of this study was to implement and validate a method for the analysis of two selected PCBs and two CPs in aqueous media. The use of SPME followed by GC–ECD proved to be a viable and environmentally friendly method to determine PCBs and CPs in aqueous matrix. The method allows the determination of CPs and PCBs, achieving LODs at sub-µg/L levels with sample volume of only 4 mL. Repeatability was between 13% and 31% for the lowest concentration and between 5.6% and 7.8% for the highest concentration.

The expanded uncertainties at µg/L levels were acceptable. For bottom-up/EURACHEM, expanded uncertainty below 50% was found for most of the calibration ranges in each case. However, when concentrations approach the LODs of the analytical method, assessed global uncertainties increase and represent more than 100% of the stated value. For modified top-down, a value of 44% was found for all compounds in the calibration ranges studied. This approach does not reflect the uncertainty dependence on concentration.

The results have proven the applicability of the proposed method to analyzing PCBs and CPs in water with the advantages of low-cost, convenience, simplicity, and freedom from use of toxic organic solvents. However, the developed method cannot achieve LODs of PCBs as low as those described by other methods.

Acknowledgments

The authors wish to thank the Fundação para a Ciência e a Tecnologia (FCT), Portugal, for financial support (SFRH/BD/32355/2006).

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Manuscript received April 17, 2008;
revision received September 18, 2008.