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Extraction of polychlorinated biphenyls from soils by automated focused microwave-assisted Soxhlet extraction

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Abstract

The application of a new focused microwave-assisted Soxhlet extractor for the extraction of polychlorinated biphenyls from differently aged soils is here presented. The new extractor overcomes the disadvantages of previous devices based on the same principle and enables a fully automated extraction of two samples simultaneously. The variables affecting the extraction step (namely, power of irradiation, irradiation time, extractant volume, extractant composition and number of extraction cycles) have been optimized using experimental design methodology. The optimized method has also been applied to a certified reference material (CRM910-050 ‘‘real’’ contaminated soil) for quality assurance validation. Quantification of the target compounds has been performed by GC with ion-trap MS. The mass spectrometer was operated in the electron-ionization mode, with selected-ion monitoring at m/z 152, 186, 292, 326 and 498. The results obtained have demonstrated that this approach is as efficient as conventional Soxhlet but with a drastic reduction of both extraction time (70 min vs. 24 h for the ‘‘real’’ contaminated soil) and organic solvent disposal, as 75–80% of the extractant is recycled.

Keywords: Soil; Focused microwave-assisted Soxhlet extraction; Microwave-assisted extraction; Extraction methods; Polychlorinated biphenyls

1. Introduction

Polychlorinated biphenyls (PCBs) were produced from 1930 to 1983 in the form of complex mixtures for a variety of uses (e.g. dielectric fluids in transformers and capacitors, and plasticizers in paint and rubber sealants). Because of their physical and chemical stability, and also of their lipophilic affinity, they are highly persistent and tend to accumulate in soils, sediments, adipose tissues and aquatic biota [1].

Microwave-assisted extraction (MAE) has been widely used for the extraction of PCBs from several samples including soils, sediments and animal tissues [2–5]. In 1998, a first prototype of a focused microwave-assisted extractor was designed by Luque de Castro et al. and constructed by Prolabo [6].This prototype combined the advantages of the Soxhlet extractor with those of the microwave-assisted processes. The extractor design was based on the same principles as a conventional Soxhlet extractor modified to facilitate accommodation of the sample cartridge compartment in the irradiation zone of a

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microwave device. The use of this device has provided better results than conventional Soxhlet extraction in much shorter periods of time [7–9]. The device, which enabled focused microwave-assisted Soxhlet extraction (FMASE) retained the advantages of conventional Soxhlet extraction (namely, sample-fresh solvent contact during the whole extraction step, no filtration required after extraction, easy manipulation, etc.) while overcoming restrictions such as the long extraction time and non-quantitative extraction of strongly retained analytes due to the easier cleavage of analyte–matrix bonds by interactions with focused microwave energy, and recycling up to 75–85% of the total extractant volume, thus reusing the solvent rather than discarded. In addition, solvent distillation in the FMAS extractor was achieved by electrical heating, which is independent of the extractant polarity, thus avoiding the principal problem of commercial focused microwave devices such as those of the Soxwave series from Prolabo, where the solvent is heated by microwave irradiation. The main drawbacks of this first FMASE prototype were the difficulty of using water or other high-boiling point solvent as extractant owing to the length of the glassware, which considerably slowed the process, and the lack of automation as the user had to switch the magnetron on every extraction cycle.

A new fully automated focused microwave-assisted Soxhlet extractor has been designed and constructed. The new extractor has been applied to the extraction of PCBs from differently aged spiked samples and from a ‘‘real’’ contaminated soil, showing the necessity of different extraction conditions depending on the age of the samples. A comparison of the proposed method with the conventional Soxhlet extraction has also been performed in terms of time needed for total removal of the analytes in the different samples tested.

2. Experimental

2.1. Chemicals and materials

A technical mixture of PCBs, Aroclor 1242, was obtained from Supelco (Bellefonte, PA, USA) and used for preparing the stock standard solutions in chromatographic-grade *n*-hexane (Panreac, Barcelona, Spain). Decachlorobiphenyl was obtained from Supelco and used as internal standard.

A 900 g sample of clayey soil (1.23% organic matter content) was dried and sieved to a size smaller than 1 mm and divided into three portions of 300 g. The first portion (A) was spiked with the PCBs mixture by adding to the soil 200 ml of diethyl ether (Panreac), containing the necessary volume of stock standard solution of Aroclor 1242 to obtain a final concentration in the dry soil of 1 μg/g. Then, the slurry was shaken for 72 h, and after evaporation of the solvent in a rotary evaporator, the soil was completely dried under an N_2 stream and then aged for 24 months. The second portion (B) was spiked in the same manner and aged for 12 months; meanwhile the third portion (C) was also spiked at 1 μg/g and aged for 3 months. The soil did not have detectable levels of the target analytes before spiking.

The certified reference material (CRM) used was CRM910-050 [US Environmental Protection Agency (EPA) Certified Reference Material, Resource Technology Corp., Laramie, WY, USA], a ‘‘real world’’ waste soil produced from a contaminated site in the Eastern United States, in which the concentration of Aroclor 1242 is certified.

2.2. Microwave-assisted Soxhlet equipment

The new prototype, called MIC V (SEV, Puebla, México), is similar to that developed previously by the authors with the addition of some improvements that allow automation of the extraction process. The new device consists of a single unit where the glassware pathway allows reception of the solvent vapor from the distillation flask on a refrigerant connected to the top of the sample-cartridge vessel with minimal heat losses on the way to its subsequent condensation and dropping on the solid sample. The new system operates with two extraction units, which allow the simultaneous processing of two samples. It also includes an optical sensor that is positioned at the desired siphon height to have the magnetron start irradiation of the sample when the solvent reaches the preset level. Finally, a solenoid valve is included in the bottom of the siphon, which is switched on at the end of the irradiation process to empty the sample vessel. The optical sensor can be placed along the siphon, which has a length of 18 cm, but only the first 5 cm are irradiated with microwaves. The higher the position of the optical sensor along the siphon, the higher the extractant volume put into contact with the target sample. Another parameter related with the extractant volume, and thus with the position of the optical sensor, is the unloading time, which is the time during which the solenoid valve remains in its unload position. Eqs. (1) and (2) show the linear relationship between the optical sensor height, the extractant volume put into contact with the sample and the unloading time necessary for total unload of the extractant volume.

$$\text{Extractant volume} = 15 + 10h_s \qquad (1)$$

$$\text{Unloading time} = 10 + 5h_s \qquad (2)$$

where h_s is the increment in sensor height. This value can be modified between 0 (5 cm) and 5 (10 cm).

The equipment operates similarly to a conventional Soxhlet extractor (i.e. the sample is continuously brought into contact with fresh, recycled solvent), the sole difference being that the sample receives microwave irradiation over a preset period when it is in contact with the extractant. The device operates at microwave power between 120 and 300 W. A microprocessor programmer (SEV) was used to control the parameters involved in the microwave-assisted extraction, namely: microwave power, irradiation time, number of extraction cycles and unloading time.

A 50 ml Soxhlet extractor (Selecta, Barcelona, Spain) was used to carry out the conventional Soxhlet extraction and a rotary-evaporator (R-200, Büchi, Switzerland) was used to release the solvent after each conventional Soxhlet extraction.

2.3. Conventional Soxhlet extraction procedure

Subsequently, 2 or 0.5 g of the spiked soil under study or the certified reference material (CRM), respectively, were placed in a cellulose thimble (25×88 mm, Albet, Barcelona, Spain). The overall Soxhlet glassware was fitted to a distillation flask containing 100 ml of an *n*-hexane–acetone (25:75) mixture and two to three boiling glass regulators. After extraction for a preset time, the solvent was released using a rotary-evaporator and the extract was dried under an N_2 stream. Then, the extract was recomposed to 2 ml with chromatographic-grade *n*-hexane and stored in the dark in a sealed vial at −4 °C until analysis.

2.4. Focused microwave-assisted Soxhlet extraction procedure

The focused microwave-assisted Soxhlet extractor is shown in Fig. 1. Subsequently, 2 or 0.5 g of the corresponding spiked soil or the CRM, respectively, was weighed into a cellulose extraction cartridge, which was capped with cotton wool and placed into the sample cartridge vessel located in the zone of microwave irradiation. Then, 150 ml of an *n*-hexane–acetone (25:75) mixture was poured into the distillation flask and two or three glass boiling regulators were also added. The isomantle rheostat was set at 100% in order to reach a continuous flow of extractant from the distillation flask to the sample cartridge vessel. The extraction program, which started when this vessel had been filled, consisted of a numbers of cycles that depended on the extraction kinetics of the target sample. Each cycle involved three steps:

1. Filling of the sample cartridge vessel by the extractant (35 ml) evaporated from the distillation flask, condensed from the refrigerant, and dropped on the sample.
2. Microwave irradiation of the cartridge for 90 s at 150 W after the solvent reached the optical sensor height (7 cm).
3. Unloading of the extraction vessel by switching on the solenoid valve automatically, just after microwave irradiation, to its unload position (during 30 s), thus delivering the vessel extract to the distillation flask.

After the last cycle, the optical sensor was disconnected and the remaining solid was removed from the extraction vessel. Then, only step (1) was carried out again in order to reduce the volume of the extract contained in the distillation flask. After the extract was evaporated to dryness with an N_2 stream, the extract was recomposed to 2 ml with chromatographic-grade *n*-hexane and storage in the dark in a sealed vial at −4 °C until analysis.

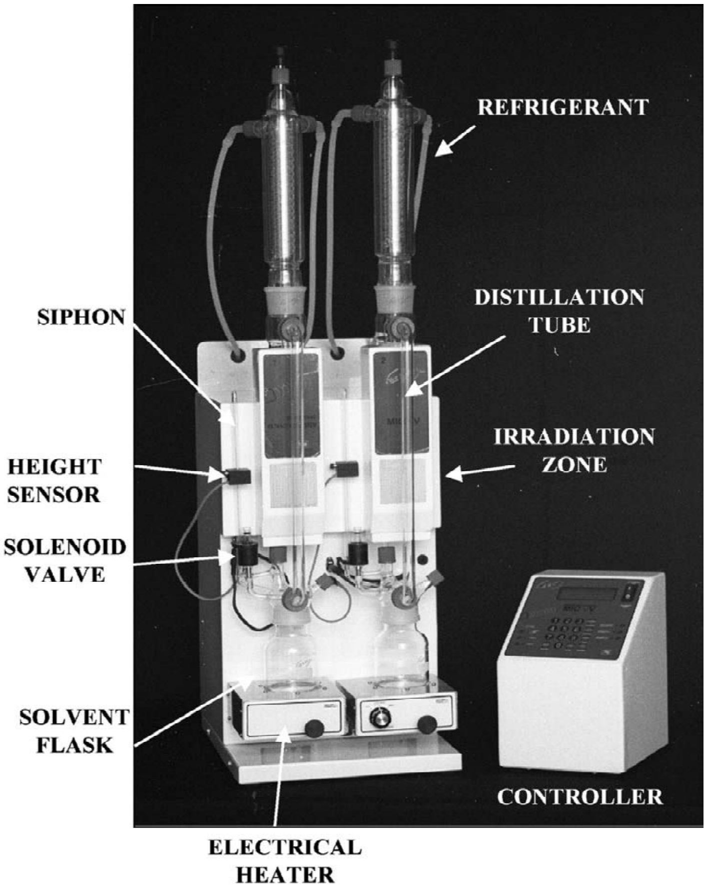

Fig. 1. Picture of the new dual automated focused microwave-assisted Soxhlet extractor.

2.5. GC–MS procedure

The extracts were analyzed using a Varian CP 3800 gas chromatograph coupled to a Saturn 2200 ion trap mass spectrometer (Sugar Land, TX, USA). Separations were conducted on a CP-Sil 8 CB-MS wall-coated open tubular (WCOT) fused-silica capillary column, 30 m×0.25 mm I.D., 0.25 μm (Varian, Walnut Creek, CA, USA).

The analyses of the Aroclor 1242 extracts were carried out using helium as carrier gas at a constant flow-rate of 1 ml/min. The column temperature program was 55 °C, held for 2 min, then increased at 25 °C/min to 150 °C, held for 2 min, and finally increased at a rate of 10 °C/min to 300 °C and held for 5 min. The injections (2 μl each) were of the splitless mode with the injector temperature set at 250 °C.

The ion trap mass spectrometer was operated in electron impact ionization (EI) positive-mode using automatic gain control. For EI experiments, the instrumental parameters were set at the following values: a filament emission current of 190 μA, an electron multiplier voltage of 1400 V, and a modulation amplitude of 4.0 V, using perfluorotributylamine (FC-43) as reference. The transfer line, the ion trap and the manifold temperatures were kept at 280, 200 and 50 °C, respectively. The storage window was set between *m*/*z* 130 and *m*/*z* 500 and selected-ion monitoring (SIM) ion preparation mode was used. The scan time during data acquisition was set at 1.0 s with four microscans per second. Quantification of the target compounds was performed considering the chromatogram as a group of peaks where the ions m/z 152, 186, 292, 326, and 498 where monitored and used for quantification. These ions were selected considering the parent ions of the group of PCBs present in Aroclor 1242. Calibration curves were built by injection of standard solutions of Aroclor 1242 ranging from 0.1 and 20 μ/ml. The total analysis time was 30 min. The chromatographic ‘‘fingerprint’’ of the standard Aroclor 1242 solution matched up well with the fingerprint of the extract from either conventional Soxhlet or microwave-assisted Soxhlet extraction.

3. Results and discussion

3.1. Optimization of the conventional Soxhlet extraction

Optimization of both extractant composition and extraction time was performed as great differences between these variables were found in the literature. Concerning the extractant composition, solvents such as toluene [10,11] or *n*-hexane [12,13] as well as binary mixtures such as *n*-hexane–acetone [14,15], *n*-hexane–dichloromethane [16] and cyclohexane–ethylacetate [17] have been used. In this case, the *n*-hexane–acetone mixture was selected as good results were obtained by other authors [14,15]. This mixture was tested at different proportions ranging from 100:0 to 0:100 (*n*-hexane–acetone) using an extraction time of 2 h and soil B (aged for 12 months). The results obtained are shown in Fig. 2. As can be seen, the optimum extractant composition was *n*-hexane–acetone (25:75).

The extraction time used by the different authors ranges from 4 to 24 h, but most of them did not optimize this variable. In this study, different aged soils and a natural contaminated soil (CRM) have been used. In order to compare the difference between the extraction time depending on the age of the soils or if a spiked or a natural contaminated soil is used, different times ranging from 15 min to 24 h were tested. The results obtained are shown in Table 1. As can be seen, the time necessary for total removal of the target compounds strongly depended on the age of the soil. Thus, 4 h were necessary for soil B (aged for 12 months); while only 2 h were necessary for soil C (aged for 3 months), but 8 h were needed for total removal of Aroclor from soil A (aged for 24 months). For the certified reference material, 24 h of Soxhlet were necessary for obtaining a value similar to the certified one.

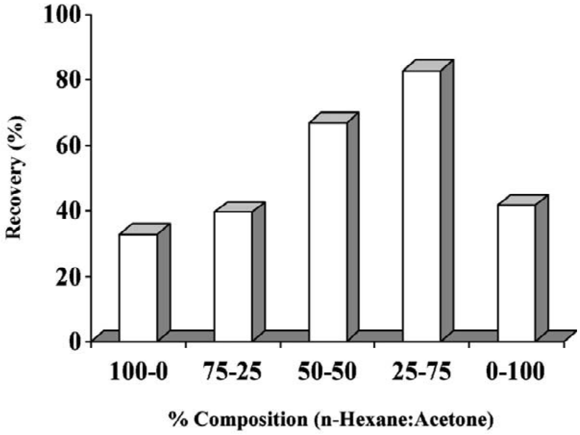

Fig. 2. Optimization of the extractant composition for the conventional Soxhlet method.

3.2. Optimization of the focused microwave-assisted Soxhlet extraction

The variables necessary for optimization in FMASE are the irradiation power, the irradiation time, the extractant composition, the extractant volume and the number of cycles needed for total extraction of the target compounds.

A screening study of the behavior of the main variables affecting the extraction efficiency was performed by means of the experimental design methodology [18]. Table 2 shows the upper and lower values given to each factor. Such values were selected from the available data and experience gathered in the preliminary experiments.

The conclusions were that both, the number of cycles and the extractant composition were the most influential factors on the extraction efficiency. The increased proportion of *n*-hexane in the extractant composition had a negative effect on the analytes removal, so a mixture with a higher proportion in acetone should be tested. The number of cycles had a positive effect so higher values should also be tested.

Table 1
Recoveries obtained by conventional Soxhlet (expressed as percent) as a function of time

Soil	Extraction time								
	15 min	30 min	45 min	1 h	2 h	4 h	8 h	16 h	24 h
A	8.8	25.4	37.4	49.9	68.9	85.8	98.8	99.7	99.4
B	16.8	41.4	55.4	59.6	82.0	95.8	99.0		
C	25.2	54.2	67.4	80.2	99.3	101.2	99.4		
CRM	5.4	11.2	16.2	24.3	41.3	55.3	67.5	76.3	99.4

However, as the recoveries obtained were close to 90% under the best conditions, a higher number of cycles was not tested as it was supposed that only by changing the extractant composition, the recoveries ought to be close to 100%.

The irradiation time, the irradiation power and the extractant volume were not statistically significant factors under the ranges tested. However, the recoveries improved when the longest value of irradiation time and the lowest irradiation power tested were used. Thus, these values (90 s of irradiation time and 150 W of microwave power) were used for subsequent experiments. Good recoveries were obtained using 35 or 55 ml of extractant, so 35 ml were selected for further experiments in order to shorten the time required for each cycle.

In order to optimize both the number of cycles and the extractant composition, a second experimental design was performed (see Table 2). Analyzing this design an estimated response surface was obtained. The optimal values, *n*-hexane–acetone (25.38:74.62) and 3.7 cycles, were obtained by equalizing to zero the first derivatives of the polynomial, solving the resulting equations system, and decodifying the results.

3.3. Study of the extraction kinetics: comparison with the conventional method

Three spiked samples differently aged were used in order to demonstrate the dependence of the ageing of the soil on the time necessary for total removal of the target compounds. The CRM used for validation of the proposed method was also used in the study of the extraction kinetics. Fig. 3a shows the focused microwave-assisted extraction kinetics of the Aroclor 1242 in the different samples tested. As can be seen, the kinetics strongly depended on the ageing of the soils. Seven cycles were necessary for quantitative removal of Aroclor from the certified reference material; meanwhile six cycles were needed for the soil aged for 24 months (A). However, only four and three cycles were required for total extraction of the PCBs mixture from the soil B (aged for 12 months) and C (aged for 3 months), respectively. Fig. 3b shows the conventional Soxhlet extraction kinetics of

Table 2
Experimental values tested for the optimization of the FMASE process (optimal values in italics)

	Extractant composition	Extractant volume (ml)	Irradiation time (s)	Irradiation power (%)	Number of cycles
Screening design					
Upper value	95:5[a]	55	90	100	5
Lowest value	55:45	15	30	50	1
Second factorial design					
Upper value	45:55	*35*	*90*	*50*	5
Lowest value	5:95	*35*	*90*	*50*	1

[a] *n*-hexane–acetone.

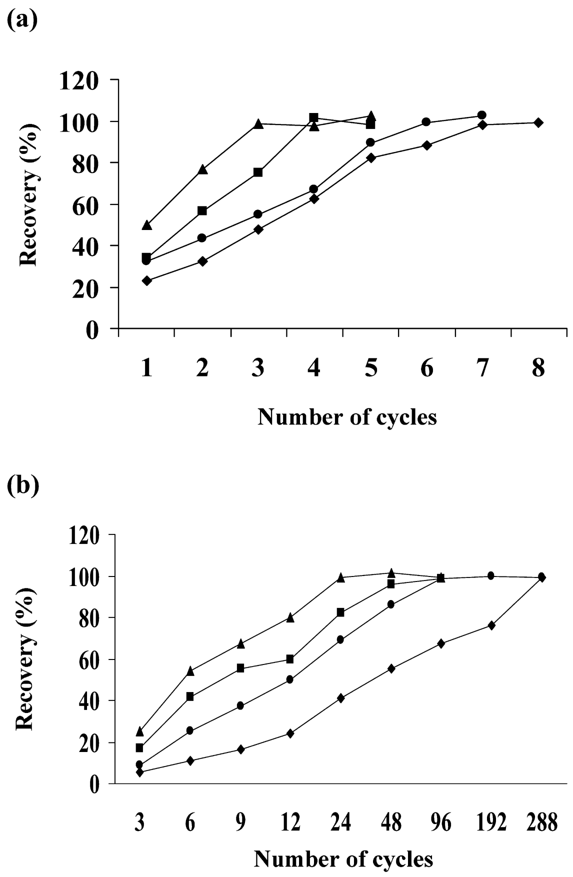

Fig. 3. Kinetics of FMASE and conventional Soxhlet extraction for the different soils tested. (a) FMASE; (b) Conventional Soxhlet extraction. (For details see text). ♦, CRM; ●, soil A; ■, soil B; ▲, soil C.

the target compounds from the different samples used. As can be seen, the behavior is similar to FMASE, as longer the ageing time of the sample, as higher the number of cycles needed for quantitative extraction. However, the cycles needed in this case are much more than those required using FMASE and thus the time required in the extraction process—although the total duration of each FMASE cycle was 10 min vs. 5 min corresponding to each conventional Soxhlet extraction cycle. This fact pointed out the high acceleration of the extraction process caused by the application of microwaves during each extraction cycle. The most remarkable case is that of the CRM where only seven cycles are necessary in the FMASE; meanwhile 288 are needed when microwaves are not applied. Expressed as time, 70 min were required in the FMASE proposed approach vs. 24 h needed by the conventional Soxhlet method.

3.4. *Method validation*

To confirm that the method is suitable for its intended use, a validation process was carried out by establishing the basic analytical requirements for the performance to be appropriate for quantitative determination of PCBs in soils. Accuracy, precision, linear dynamic range and both instrumental and method detection limits were evaluated for the analytical approach developed.

3.4.1. *Accuracy*

The accuracy of the method was assessed by analyzing a natural matrix certified reference material (CRM910-050, EPA), comparing the measured value with the reasonable estimation of the true value (C_{CRM}) as supplied with the material and following the guidelines of the EURACHEM [19]. Six parallel extractions (under the optimal conditions) of the CRM were carried out. The mean value (C_{measured}) and the standard deviation (S_{measured}) were calculated. Whether the method is accurate or not, the following two equations must be fulfilled:

$$S_{\mathrm{measured}} n^{-0.5} < \mu_{\mathrm{CRM}} \tag{3}$$

$$C_{\mathrm{CRM}} - \mu_{\mathrm{CRM}} < C_{\mathrm{measured}} < C_{\mathrm{CRM}} + \mu_{\mathrm{CRM}} \tag{4}$$

where C_{CRM} is the concentration of the certified reference material, μ_{CRM} is the uncertainty (based on the 95% confidence interval) of the CRM, C_{measured} is the mean concentration of the measured samples, S_{measured} is the standard deviation of the measured samples and n is the number of measurements.

Table 3 presents the concentrations and the results of the accuracy test for the PCBs determined in the CRM showing that the method is accurate as both equations are fulfilled.

3.4.2. *Precision*

In order to evaluate not only the extraction efficacy of the proposed method but also the preci-

Table 3
Concentrations and results of the accuracy test for the PCBs determined in the CRM910-050

C_{measured} (mg/kg)	S_{measured} (mg/kg)	C_{CRM} (mg/kg)	μ_{CRM} (mg/kg)	$S_{\mathrm{measured}}/n^{0.5}$	$C_{\mathrm{CRM}}-\mu_{\mathrm{CRM}}$	$C_{\mathrm{CRM}}+\mu_{\mathrm{CRM}}$
41.4[a]	3.2[a]	39.4	8.7	1.3	30.7	48.1

[a] $n=6$.

sion as well as the similar behavior of the two focused microwave-assisted Soxhlet extraction units, within laboratory reproducibility and repeatability were estimated for each method in a single experimental set-up with duplicates [20].The experiments were carried out using 2 g of soil B (as in the optimization procedure). In all the experiments the optimal values obtained for the variables were used. Two extractions and measurements of the target compounds per day were carried out on 7 days. The repeatability, expressed as percent relative standard deviation, was 3.27 and 2.97 for the FMASE units 1 and 2, respectively; meanwhile 2.14% was obtained for the conventional Soxhlet extraction. The within-laboratory reproducibility was 4.00% and 4.32% for the FMASE units 1 and 2, respectively; and 2.95% for the conventional Soxhlet extraction. These results shown that both FMASE units worked in the same way and with a precision estimated as repeatability and within-laboratory reproducibility similar to that of the conventional Soxhlet extraction method.

3.4.3. Linear dynamic range and instrumental detection limit

The calibration graph was run using standard solutions of the Aroclor 1242 in chromatographic grade *n*-hexane. The concentration of the standards fitted within the linear portion of the calibration graph ranged between 0.1 and 20 μg/ml with a correlation coefficient of $r^2=0.9989$. The instrumental limit of detection (LOD) expressed in units of analytes nanograms on-column (reaching the detector), which gives a signal that is 3σ above the mean blank signal (where σ is the standard deviation of the blank signal) was 0.056 ng.

3.4.4. Method detection limit

The method detection limit (MDL) was estimated from LOD multiplied by the final volume and divided by the sample weight and the injection volume (MDL = LOD × final volume)/(sample mass × injected volume). The sample mass is the only parameter which connects the MDL and the extraction method. Therefore, to achieve a ‘‘good’’ MDL, as much sample as possible should be extracted. In this case, when a spiked sample was extracted, 2 g of sample was used and an MDL = 28 ng/g (0.028 ppm) was obtained; for the extraction of the CRM where only 0.5 g was extracted, an MDL = 112 ng/g (0.112 ppm) was obtained.

4. Conclusions

An automated approach based on the use of a new focused microwave-assisted Soxhlet extractor is proposed for the extraction of PCBs from soil.

The use of this new method allowed the extraction of Aroclor 1242 (a mixture of PCBs isomers) from differently aged soils and from a ‘‘real’’ contaminated soil obtaining similar results to those provided by conventional Soxhlet but in much shorter times (70 min vs. 24 h for the CRM) and recycling 75–80% of the organic solvent used as extractant.

A study of the extraction kinetics has shown the dependence of the extraction conditions on the ‘‘real’’ or spiked nature of the sample and also on the ageing of the samples in the latter case.

The results of the method validation following the guidelines of the EURACHEM have shown that the method is as accurate and precise as the conventional one demonstrating the suitability of the proposed approach for its intended use.

The use of GC–MS as separation/detection system allowed MDLs between 0.028 and 0.112 ppm of Aroclor 1242 in soil, depending on the amount of sample extracted.

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