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Photochemical sample treatment for extracts clean up in PCB analysis from sediments

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ABSTRACT

Sample purification can be considered the most polluting step of the whole analytical process for PCBs determination in sediment samples. The use of photochemical sample treatment represents an alternative methodology for extracts clean up allowing for a reduction of the used amount of organic solvents. The first application of a photochemical sample treatment for the selective removal or reduction of organic substances interfering with PCBs analyses in sediments is reported. The method's efficiency and robustness were compared with currently used chromatographic purification. Quality parameters such as recovery, linearity and reproducibility were studied. The entire procedure was validated by four replicate analysis of certified reference sediment. The quantification limits (LOQ) obtained by us ranged from 1 to 3.1 ng g^{-1}. The RSD for each congener was below 15% and recoveries were in the range 40–130%.

Results based on the analysis of real and certified samples showed similar or improved detection thresholds and pointed out the advantages of the photochemical methodology in terms of costs and environmental friendly conditions.

1. Introduction

Humans are exposed daily to a number of potentially harmful substances of natural or anthropogenic origin [1]. However, while direct exposure to pollutants (by inhalation, ingestion or contact) is obviously a major concern, awareness of indirect exposure (e.g. through contaminated food) [2] is difficult to achieve. This is particularly important for harmful micropollutants from transport or industrial activities [3] whose monitoring represents a major challenge in analytical chemistry.

Electrical installations, industrial outlets and the use of pesticides are the major source of chlorinated organic compounds released in the environment. In temperate regions, these are distributed in several geographical areas through long-range atmospheric transport and deposition. Additionally, chlorinated organic compounds can be introduced in the food chain and reach consumers in very high levels [4].

In this context, polychlorinated biphenyls (PCBs) micropollutants, whose production was banned in Europe in 1985 [5], are still an environmental issue [6]. In fact, this class of persistent organic pollutants, whose world production has been recently estimated at more than $1.3 \cdot 10^6$ t, can lead to significant emissions into the environment [7]. Due to their chemical and thermal stability, low flammability, and electrical insulating properties [8], PCBs have been widely used as dielectric fluids in capacitors and transformers, special lubricants and additives in paints and pesticides [9].

Besides toxicological studies on PCBs, recent research is focusing on more sophisticated analytical methods for PCBs detection [10]. Distribution and dispersion of PCBs mostly occurs through air [11], water, soils and sediments [12]. The latter, are complex matrices whose analysis often involves costly extraction and purification procedures. PCBs are separated from environmental matrices using different techniques, for example solid phases microextraction (SPME) [13,14] (analyta recoveries in the range from 25 to 130% [15] standard deviations from 4 to 17% [16]), and different organic solvents such as dichloromethane, hexane, acetone, or a combination of them [17]. For this reason, sample purification can be considered the most important and polluting step of the whole analytical process for PCBs determination in a sediment sample [18].

Unfortunately, due to strong interactions of PCBs with the natural organic matter present in sediments, problems such as low and variable extraction efficiency are commonly experienced [19]. Additionally, co-extraction of compounds causing interferences during instrumental analysis is also a major issue. Indeed, several interfering substances can be present in PCBs extracts that need to be analyzed by GC–MS methods; these include organic compounds having molecular or fragment mass equal to that of

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the analyte and interfering in SIM-mode GC–MS analysis. In order to resolve these issues, purification procedures of the analytical extracts are required.

Chromatographic purification over silica gel can be utilized for the clean up of extracts of environmental matrices. In fact, currently used methods for extract purification in PCBs analysis in sediments are: EPA method N°3630 (Silica gel clean up) and EPA method N°3620 (Florisil clean up). However, these methods use large amounts of toxic and hazardous solvents [20].

In this context, we decided to develop a new procedure, for the purification of extracts for the analysis of PCBs in sediments, which is also more selective, inexpensive, more robust, and substantially less solvent-consuming than previous methods [21–23]. This procedure allowed good analyta recoveries (40–140%) within the range accepted by EPA, high reproducibility (relative error $<10\%$) and low detection limits comparable to EPA method n. 3620 (Florisil clean up). Modern treatments to degrade chemical and biological contaminants in water and sediments include advanced oxidation processes (AOPs) [24] as well as photochemical and photocatalytic procedures [25–27]. For instance, the unselective photochemical mineralization of organic compounds has been used as a valid alternative to conventional methods for the purification of extracts in the analysis of metals [28]. However, the selective photochemical removal of organic substances interfering in the PCBs gas-chromatographic analysis has never been reported. In this study we report a new photochemical method, which takes advantage of ultraviolet light irradiation to reduce the concentration of organic substances that interfere in SIM-mode GC–MS analysis of PCBs from sediments. The described approach includes the choice of the most appropriate irradiation conditions in order to avoid photochemical degradation of the analyta.

2. Experimental

2.1. Chemicals

Dichloromethane, n-hexane and diethyl ether were purchased from Carlo Erba, (GC pure grade). Standard solutions were purchased from Chemical Research. Twelve compounds were used as internal standards (one for every group of analytes determined by gas chromatography using the same ratios M^{n+}/z). Stock internal standard solutions of PCBs (PCB81, PCB77, PCB123, PCB81, PCB114, PCB105, PCB126, PCB167, PCB156, PC157, PCB169, PCB189) were prepared (100 ppb) in hexane from commercial standard nonane solutions (1 ppm) (Chemical Research WELEPA-1668IS) by drying and re-dilution.

Stock congener solutions of PCBs (100 ppb) were prepared in hexane from commercial standard isooctane solutions (10 ppm) (Chemical Research O2S130111-01) by drying and re-dilution. Both stock internal and commercial standard solutions were stored in a refrigerator (4 °C). PCB congeners were from CEN PCB congener MIX 1 SUPELCO. The certified sediment used in this study was CRM no. 536 PCBs in fresh water harbor sediment. Florisil (60–100 mesh) was obtained from Merck and heated at 130 °C for 16 h prior to use. Extractions were performed using an automated Soxhlet (Büchi Extraction System B-811). Irradiations were carried out in pyrex vessels by using a Rayonet RPR-100 photoreactor equipped with a merry-go-round apparatus and 16 RPR-3500 A Hg lamps (8 W each) irradiating at $\lambda = 350 \pm 25$ nm.

2.2. Samples

Real sediment samples collected from Palermo (Italy) coastal area (Cala station) were used to develop the analytical method. qA total of 3–5 Kg of sample was collected by bucketing 30 cm of the top layer sediments from each site and placed into plastic bags. The samples were initially stored in the dark at −5 °C on site, to inhibit biological activity and avoid exposure to light, and then rapidly transported to the laboratory where they were stored at −18 °C.

2.3. General procedure

According to reported methods [29], the standard procedure for PCBs determination in sediments involves matrix preparation, extraction, purification and analysis steps. These were performed on real samples collected at Palermo coastal area. Matrix preparation was not necessary for the determination of PCBs in the commercial Certified reference material, which was purchased as already sampled, sub-sampled, homogenized, sieved and dried. All analyses were performed in four replicates.

2.4. Matrix preparation

The marine sediment sample was sub-sampled from five different parts of the bucket. These five sub-samples (20–25 g) were unified and homogenized into a single batch. The batch was then air-dried and sieved through a mesh with a grain size of 2 mm. The obtained sediment sample was dried in an oven for 48 h at 60 °C and stirred occasionally to avoid aggregation of the material.

2.5. Method development

In order to evaluate the best extraction and clean up methodologies, we have applied different operating conditions to real spiked samples obtained by adding 250 μL of a 100 ppb PCB congeners solution to a sediment sample (5 g) collected from Cala station. In fact, testing the method on spiked real marine sediment samples is a very important approach to simulate a real analysis and identify optimal conditions.

Figs. 1 and 2 show the percentages of PCBs recovery as a function of solvent mixture and number of extraction cycles, using as blank marine sediment samples from Cala station. The results showed that the best percentage recoveries were obtained using a 1:1 (v/v) n-hexane/dichloromethane solvent mixture for 30 extraction cycles. These parameters have been used for PCBs extraction from sediment sample.

The second step of the method development involved the verification of the optimal conditions to apply a photochemical clean up methodology for PCB determination in sediment samples. Even though PCBs do not absorb at wavelengths greater than 310 nm, [30] we checked their stability under irradiation for 3 h at $\lambda = 350 \pm 25$. Fig. 3 illustrates the absorbance spectra of a PCB

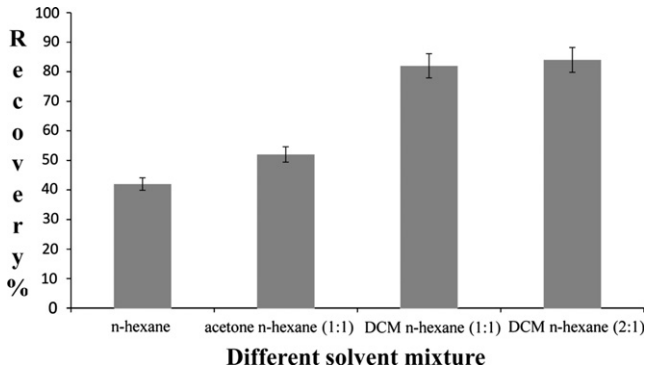

Fig. 1. Recoveries of PCB using different solvent mixtures.

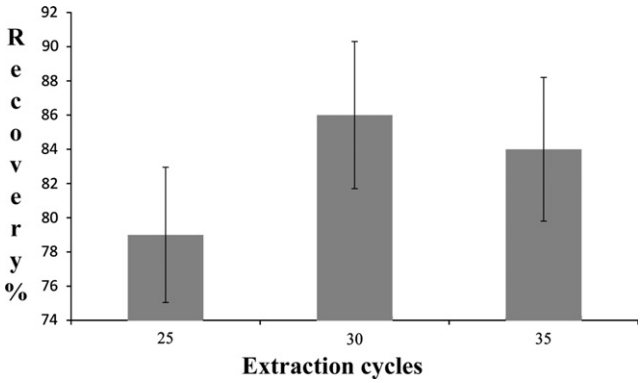

Fig. 2. Recoveries of PCB using different extraction cycles.

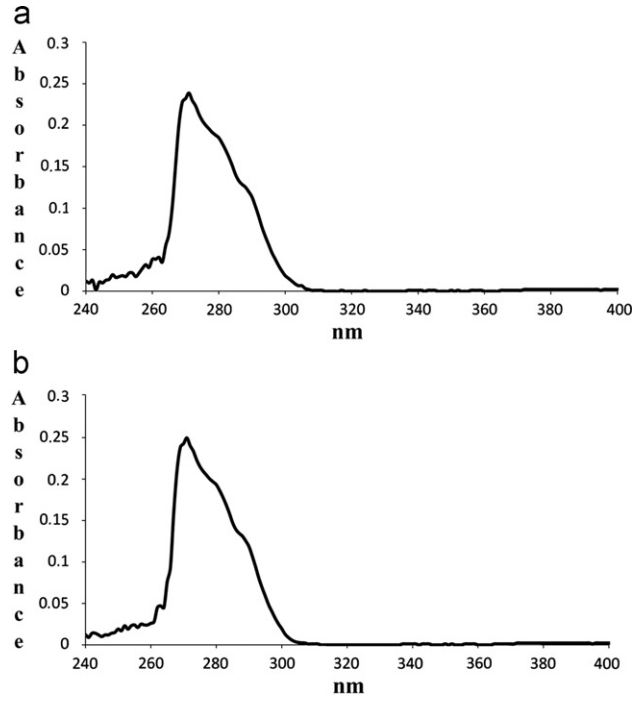

Fig. 3. Absorbance spectra of a PCB mixture solution (CEN PCB congener MIX 1 SUPELCO) at a concentration of 500 ppb (of each PCBs) in a 1:1 (v/v) dichloromethane/n-hexane (a) before and (b) after irradiation.

mixture solution (CEN PCB congener MIX 1 SUPELCO) at a concentration of 500 ppb (of each PCBs) in a 1:1 (v/v) dichloromethane/n-hexane before (Fig. 3a) and after (Fig. 3b) irradiation. The spectra are basically unchanged, confirming that, PCBs are not decomposed at $\lambda = 350 \pm 25$. Therefore, the solutions obtained from the extraction of sediments could be irradiated at 350 nm to reduce the amount of interfering organic substances.

2.6. Extraction

Based on the optimized extraction procedure, a 5 g sample of CRM sediment was placed into a 33 mL cellulose thimble together with 0.5 g of anhydrous Na_2SO_4. The cellulose thimble was then placed in an automated Soxhlet extractor, which was fitted to a distillation flask containing 150 mL of a 1:1 (v/v) n-hexane/dichloromethane mixture and the sample was extracted for 30 cycles (3 h) in warm mode. A similar extraction procedure was followed for real sediments samples to which 250 μL of a 100 ppb PCBs congener standard solution was added before the extraction (spiked samples).

2.7. Purification

The photochemical purification of the organic extracts was performed under various conditions (Table 1) and its efficiency was compared with the Florisil chromatographic clean up (EPA method N° 3620) used as reference method (Table 2). The organic extracts (50 mL) were transferred into a Pyrex glass photolysis tube, and either directly irradiated at $\lambda = 350 \pm 25$ nm for a total of 3 h (sample a), or purged with argon (sample b) or oxygen (sample c) for 10 min prior to irradiation (Table 1). In order to monitor the effect of the irradiation as a function of time, samples were collected at 1, 2 and 3 h during and after irradiation. As blank experiment, sample d was analyzed without previous purification. Each sample was reduced in volume using a rotary-evaporator and dried under a N_2 stream. Residues were then recomposed to 250 μL with internal standard solutions of PCBs (100 ppb) and analyzed by GC–MS.

2.8. GC–MS analysis

Analysis of purified solutions and were carried out using a gas chromatograph coupled with a mass spectrometer (Shimadzu, mod. GCMS-QP2000) equipped with an Equity-5 (30 m × 0.25 mm I.D., 0.25 μm film thickness) fused-silica capillary column from Supelco SLBTM-5 ms, lot. 41579-03A. Ultra pure (99.999%) helium was used as a carrier gas and the flow rate was maintained at 1.7 mL/min. 1 μL of each concentrated solution was injected by the Shimadzu Auto Injector AOC-20I, in splitless mode with a 0.61 min split delay. The injector temperature was maintained at 250 °C and detector at 270 °C. The GC temperature ramp increased: from 60 °C (1 min) to 170 °C (1 min) at a 30°/min heating rate, from 170 °C to 300 °C at a 5°/min rate, and then from 300 °C to 330 °C (5 min) at 20°/min rate. The calibration was performed weekly. The data were acquired operating in single-ion monitoring mode (SIM). Identification of the

Table 1
Operating conditions for real sediment sample.

Sample	λ irradiation (nm)	Time irradiation (h)	Gas bubbling
a	350 ± 25 nm	3	No gas bubbling
b	350 ± 25 nm	3	O_2
c	350 ± 25 nm	3	Ar
d	No irradiation	No irradiation	No gas bubbling

Table 2
Comparison of the results for PCB analysis from CRM marine samples using the different clean up procedures.

PCB	μg Kg^{-1} Real	Repeatability	Repeatability		
	Absolute concentration	Recovery (%) (RSD%)[a]	Recovery (%) (RSD%)[b]	t_{cal} test	t_{crit} test
PCB 28	44	130 ± 2	145 ± 2	1.150	3.182
PCB 52	38	63 ± 1	75 ± 1	1.777	3.182
PCB 101	44	89 ± 1	100 ± 3	1.791	3.182
PCB 149	49	51 ± 1	60 ± 1	2.368	3.182
PCB 118	28	53 ± 1	61 ± 1	1.736	3.182
PCB 153	50	59 ± 1	69 ± 1	2.213	3.182
PCB 105	4	64 ± 3	69 ± 1	1.111	3.182
PCB 138	27	48 ± 6	69 ± 6	1.268	3.182
PCB 128	5	41 ± 9	54 ± 9	1.231	3.182
PCB 156	3	84 ± 15	54 ± 3	0.746	3.182
PCB 180	22	56 ± 1	70 ± 1	2.720	3.182
PCB 170	13	46 ± 2	74 ± 2	1.303	3.182

[a] Photochemical purification process.
[b] Florisil purification process.

components of the standard mixture was carried out by comparing retention times for each component in the mixture with those of the corresponding pure compounds, analyzed under the same experimental conditions. Identification was confirmed by comparing the corresponding MS spectra. The identification of PCBs in the solutions extracted from sediments was carried out on the basis of previously determined retention times and confirmed by using mass spectra.

Response factors for different compounds were measured by injecting a mixture containing standard compounds and having the same concentration of internal standard solutions of PCBs as that used for spiking the samples. The most abundant ion was used for quantification and two other ions were additionally used for confirmation.

3. Results and discussion

The linearity of the method for PCBs analysis in CRM was evaluated over a range of concentrations (6.00–500 ng mL^{-1}) finding a linear response (see correlation coefficients in Table 3) for all analytes.

Table 3
Calibration data, linear range, correlation coefficient, LOD and LOQ analysis of PCBs.

PCB	Calibration range (ng mL^{-1})	Correlation coefficient (r^2)	Limit of detection (LOD; ng g^{-1})	Limit of quantification (LOQ; ng g^{-1})
PCB 28	6–500	0.987	1.0	3.1
PCB 52	6–500	0.990	1.0	2.7
PCB 101	6–500	0.997	1.0	1.0
PCB 149	6–500	0.999	1.0	1.0
PCB 118	6–500	0.993	1.0	1.0
PCB 153	6–500	0.992	1.0	1.0
PCB 105	6–500	0.994	1.0	1.0
PCB 138	6–500	0.999	1.0	1.0
PCB 128	6–500	0.997	1.0	1.0
PCB 156	6–500	0.992	1.0	1.0
PCB 180	6–500	0.994	1.0	1.0
PCB 170	6–500	0.994	1.0	1.0

Since PCB 28 has major organic interferences in the determination from sediment samples through the GC–MS analyses, we decided to test the efficiency of the proposed photochemical sample purification in the chromatographic analysis of PCB28.

SIM-mode (256 amu) representative chromatograms of PCB 28 analysis for the four a–d samples from real sediments treated as summarized in Table 1 are shown in Fig. 4 a–d. Results pointed out that oxygen purging of the organic extracts followed by irradiation at 350 nm for 3 h were the best purification conditions for the detection of PCB 28 (mass 256 amu, RT = 11.50 min) in real sediments (Fig. 4b). In fact, no PCB 28 was detectable in not purified sample extracts (sample d), since the baseline was covering the corresponding peak at around 11.50 min, due to the presence of interfering organic matter from the matrix. Indeed, in SIM mode, interferences could arise not only from single compounds but from all possible matrix compounds fragments at the detected mass, thus appearing as an up shifted baseline.

On the other hand, PCB 28 was barely detectable in argon purged (sample c) or not purged (sample a) irradiated extracts.

Results from the analysis of samples a–d show the role of molecular oxygen in the photodegradation of the interfering organic compounds. In particular, comparison of data from samples a (not purged extract) and c (deoxygenated extract) with untreated extract (sample d), pointed out the occurrence of an oxygen-independent photochemical degradation of the organic compounds interfering with PCB analysis. On the other hand, improved analyses achieved by saturating the extract with oxygen prior to irradiation (sample b) indicate that a photo-oxygenation process is also promoted under the used irradiation conditions. By considering the qualitative absorption spectrum of a typical extract (Fig. 5), it is likely that irradiation at 350 nm promotes one or more of the following degradation processes: (i) a direct photochemical reaction of the excited interfering organic compounds, (ii) a photo-oxidation of the interfering organic compounds involving the direct interaction between their excited states with molecular oxygen, (iii) a sensitized singlet oxygen photooxidation of the interfering organic compounds by the Kautsky mechanism [31]. Particularly in the latter case, the electrophilic character of singlet oxygen would prevent its attack to electron poor PCBs, which remain preserved in the purification procedure.

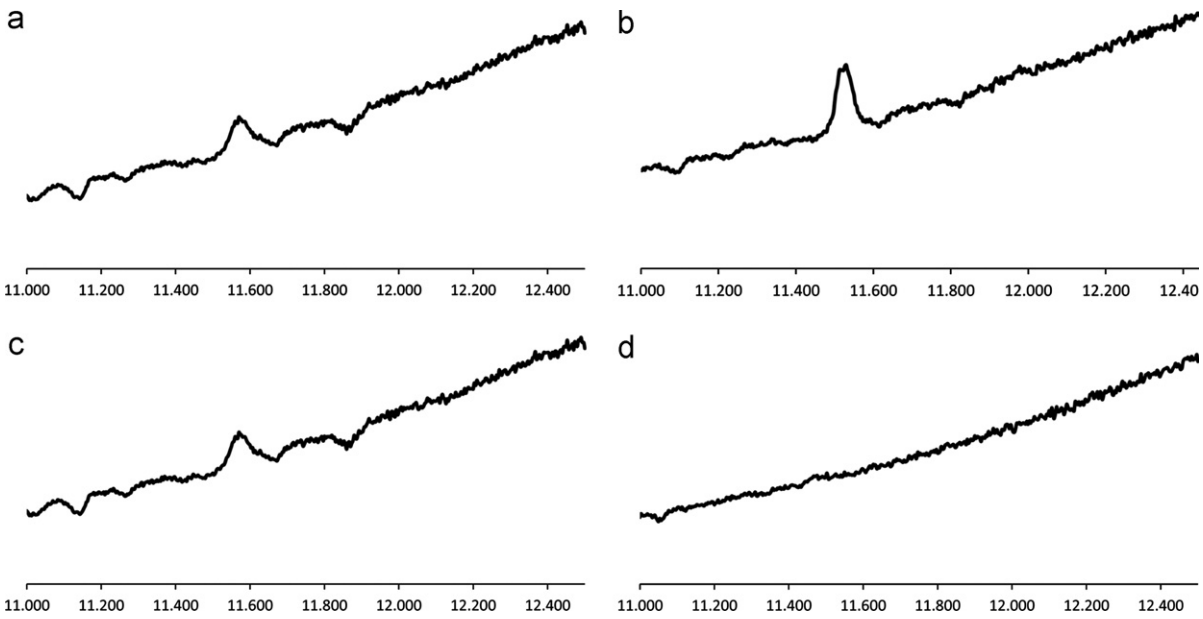

Fig. 4. Chromatograms for PCB 28 (mass 256 amu, RT 11.50) in real sediment sample in different operating conditions.

The best conditions for the photochemical purification were also applied to the analysis of Certified Reference Material (CRM)

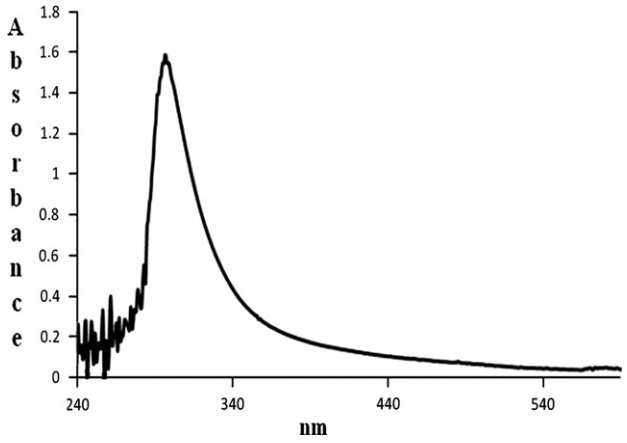

Fig. 5. Absorbance spectrum of organic extract from sediment in dichloromethane/n-hexane 1:1.

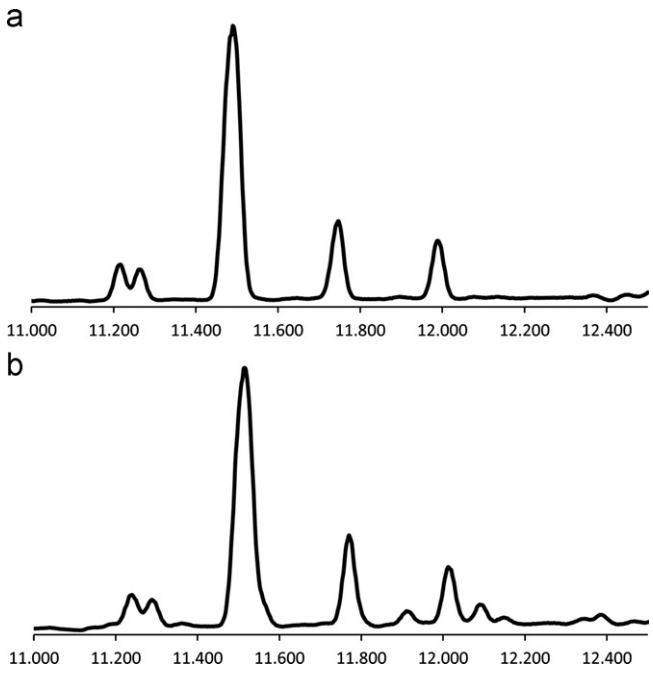

Fig. 6. Comparison of chromatograms for PCB 28 (mass 256 amu, RT 11.50) in CRM Florisil clean up (a) and CRM Photochemical clean up (b).

for the validation of the methodology. The method's precision was evaluated through the analyses of four CRM replicates.

The chromatogram for PCB 28 (mass 256 amu RT = 11.50 min) in the CRM sample is illustrated in Fig. 6, showing the absence of interfering substances after either Florisil (Fig. 6 a) or photochemical (Fig. 6 b) clean up.

The analysis of various CRM samples has been used for a comparison between the photochemical clean up and the chromatographic purification on Florisil. Percentage of recovery, standard deviations (SDs) and t test are reported for both procedures in Table 2, showing similar efficiencies of the two methods for PCBs analysis when $t_{calc} \leq t_{crit}$.

In Fig. 7, percentage recovery of the individual PCB congeners in CRM obtained by Florisil purification are compared with those obtained through the photochemical clean up. In almost all the cases, PCB's percentage recovery determined after photochemical purification is slightly lower than that determined after Florisil clean up ($< 10\%$).

Nevertheless, these differences are not significant (see t values in Table 2). In the case of PCB 156, instead, the photochemical purification allows a higher recovery of the analyta with respect to Florisil procedure. This could be ascribed either to a different partition between the PCB156 analyta and the Florisil stationary phase with respect to the other PCBs, or to the low absolute concentration of PCB 156 in the CRM (see Table 2). In all the cases, PCBs recoveries after photochemical clean up were in the range (from 40 to 140%) of those accepted by the Environmental Protection Agency.

4. Conclusions

The classic clean up process for PCBs determination uses large amounts of toxic solvents and stationary phases. This purification process has a very high impact for the environment and is potentially harmful for the analyst. In this study, we report the development of an alternative photochemical methodology to reduce the concentration of organic substances that interfere with GC–MS analysis of PCBs.

Optimized photochemical purification conditions consisted of a preliminary oxygen saturation of the Soxhlet organic extracts followed by their irradiation at 350 nm for 3 h.

This procedure allowed for good analyta recoveries (40–140%) within the range accepted by EPA, high reproducibility (relative error $< 10\%$) and low detection limits comparable to EPA method n. 3620 (Florisil clean up).

By considering good linearity range (from 6 to 500 ng mL^{-1}), high reproducibility (relative error $< 10\%$), lower limits of detention (1 ng g^{-1}), lower limits of quantification (from 1 to 3.1 ng g^{-1}) and acceptable analyta recoveries (from 40 to 130%)

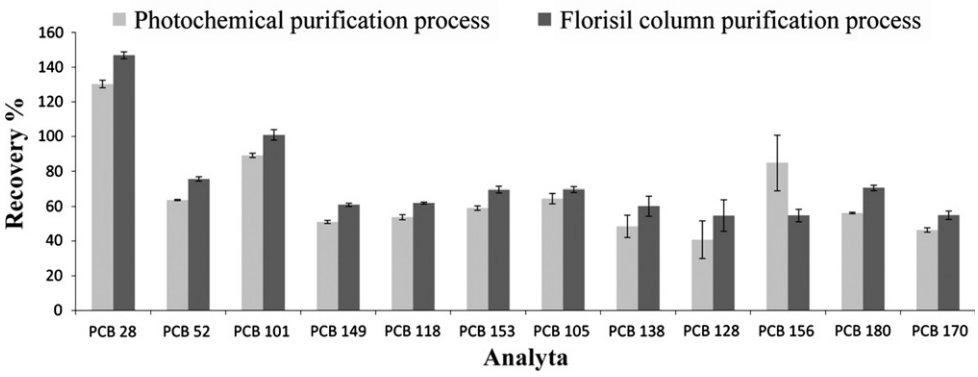

Fig. 7. Comparison of recoveries by Florisil column purification and photochemical purification processes.

the method was demonstrated to be successfully applicable also to real sediment samples.

The photochemical clean up is highly selective and efficiently leads to a final sample containing very low concentrations of interfering compounds. If compared to classical chromatographic purification, the proposed photochemical method for the clean up of organic extracts for the analysis of PCBs in sediments allows a reduction in the use of harmful solvents and benefits analysis time, cost, and health risks.

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