



Photochemical sample treatment: A greener approach to chlorobenzene determination in sediments

Salvatore Barreca^{a,b}, Santino Orecchio^{a,*}, Andrea Pace^{a,b}

^a Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e farmaceutiche "STEBICEF", Università Degli Studi di Palermo-Italy, Viale delle Scienze Ed. 17, 90128 Palermo, Italy

^b Istituto Euro Mediterraneo di Scienza e Tecnologia (IEMEST), Via Emerico Amari 123, 90139 Palermo, Italy

ARTICLE INFO

Article history:

Received 25 February 2014

Received in revised form

13 May 2014

Accepted 18 May 2014

Available online 2 June 2014

Keywords:

Chlorobenzene

Photochemical sample treatment

Sediment analysis

Clean up

UV irradiation

ABSTRACT

Due to worker's exposure, solvent and stationary phases' consumption, sample purification is one of the most polluting steps in analytical procedures for determination of organic pollutants in real samples. The use of photochemical sample treatment represents a valid alternative methodology for extracts clean up allowing for a reduction of the used amount of organic solvents.

In this paper we report the first application on the photolytic destruction of organic substances to eliminate some of the interferences in the analysis of Chlorobenzenes in sediment samples.

The method's efficiency and robustness were compared with classic silica column purification process currently used in clean up procedures in sediment analysis. Quality parameters such as recovery, linearity and reproducibility were studied. The entire procedure was validated by three replicate analysis of spiked real sediment sample. The quantification limits (LOQ) obtained by us ranged from 1.0 to 2.3 ng g⁻¹, while the detection limits (LOD) were of 1.0 ng g⁻¹. The RSD for each congener was below 10% and recoveries were in the range 95–130%.

Results based on the analysis of real samples showed similar or improved detection thresholds and pointed out the advantages of the photochemical methodology in terms of costs, use of chemical substances and operator's safety according to *Green Analytical Chemistry* principles.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In the last 20 years some research communities have focused their interest in environmental-friendly techniques with respect to green chemistry principles [1].

In analytical chemistry, *Green analytical chemistry* (GAC) emerged from green chemistry in 2000 [2]. GAC should be recognized as a stimulant to the progress of analytical chemistry. The most important challenge for the future of this discipline is to reach a compromise between the increasing quality of the results and the improving environmental friendliness of analytical methods. These important principles in GAC were summarized in a word: "SIGNIFICANCE" [3]. The key goals to be achieved in green analytical methods are elimination or reduction of the use of chemical substances; minimization of energy consumption; proper management of analytical waste; increased safety for the operator.

In the classic analytical technique, the organic pollutant determinations, involved the use of a large amount of organic solvents and exposure of work during the clean up procedures.

In this context Chlorobenzenes (CBs) analyses represent an important issue.

Chlorobenzenes (CBs) micropollutants are ubiquitous, hydrophobic chlorinated organic compounds. Through substitution in the benzene ring by chlorine atoms it is possible to obtain 12 compounds, monochlorobenzene (MCB), three isomeric forms of dichlorobenzene (di-CB), three isomers of trichlorobenzene (tri-CB), three isomers of tetrachlorobenzene (tetra-CB), pentachlorobenzene (penta-CB), and hexachlorobenzene (hexa-CB).

Chlorobenzenes are used mainly as (a) intermediates in the synthesis of pesticides and other chemicals, (b) byproducts of petro-chemical related manufacturing processes, such as PCBs and pentachlorophenol [4], or of biodegradation of Lindane [5], (c) components of dielectric fluids [the higher chlorinated benzenes (triCBs) and 1,2,3,4-tetraCB], and (d) a functional fluid in external combustion Rankine engines [6] and a component in heat transfer fluids in solar energy collectors (MCB) [7].

Under the anaerobic conditions, usually found in sediment and ground water, chlorobenzenes are very persistent; but many

* Corresponding author.

E-mail address: santino.orecchio@unipa.it (S. Orecchio).

microorganisms from sediments and sewage sludge have been shown to degrade chlorobenzenes (higher chlorinated compounds are less readily degraded and such degradation occurs).

Distribution and dispersion of CBs mostly occurs through air [8], water [9], soils [10] and sediments [11]. The latter, are complex matrices whose analysis often involves costly extraction and purification procedures.

The extraction of chlorobenzenes from the original matrix (i.e., sediment) is particularly difficult because of a large difference in the volatility between the volatile chlorobenzene and the non-volatile hexa-CB. Therefore, the analysis of chlorobenzenes in sediments should not include a sample drying step using drying at a raised temperature ($\sim 100\text{ }^{\circ}\text{C}$), lyophilization (freeze-drying), or drying with a stream of inert gas at room temperature. The recovery of MCB was not quantitative under these conditions [12].

There are different extraction methods for removing chlorobenzenes from a sample that depend mainly on the matrix (i.e., air, water, and sediment). The extraction from sediments or soil can be achieved by classic techniques (solvent assisted by ultrasonic bath or shaking or Soxhlet extraction) [13] employing common solvents as dichloromethane, acetone, hexane, or new techniques (ion liquids) [14]. In any cases, the extract is generally purified by silica clean-up column before gas chromatographic (GC) analysis [15].

In sample purification worker's exposures can be considered the most important and polluting step of the whole analytical process for CBs determination in sediment samples and the safety of the operator is one of the most important principles in GAC [16].

Unfortunately, due to strong interactions of CBs with the natural organic matter present in sediments, problems such as low and variable extraction efficiency are commonly experienced [17]. Additionally, co-extraction of compounds causing interferences during instrumental analysis is also a major issue both for analytical procedures and instrument life time.

Photochemical techniques with high intensity ultraviolet light have been used to eliminate the interfering compounds in the analysis of organic [18] or inorganic substances [3].

However, these new practices used in *Green Analytical Chemistry* are in developing states [16].

In this context, we decided to develop a new procedure, for the purification of extracts in CBs analysis from sediments, which is also more selective, inexpensive, more robust, and substantially less solvent-consuming. In this study we report a new photochemical method to reduce the concentration of organic substances in CBs from sediments.

2. Experimental

2.1. Chemicals

Acetone and *n*-hexane were purchased from Carlo Erba, (GC pure grade). Silica (0.05–0.20 mm) was obtained from Carlo Erba and heated at $130\text{ }^{\circ}\text{C}$ for 16 h prior to use as reported in EPA method [19]. Stock CBs congener solution was purchased from Chemical Research. Internal and surrogate solutions were purchased from Sigma Aldrich. Internal standard solutions (Chlorobenzene $-d_5$) were prepared (100 $\mu\text{g/L}$) in hexane from commercial standard methanol solutions (2000 $\mu\text{g/L}$) by drying and re-dilution.

Surrogate standard solutions (Chlorobenzene- $1-^{13}\text{C}$) were prepared (100 $\mu\text{g/L}$) in hexane from commercial standard methanol solutions (1000 $\mu\text{g/L}$) by drying and re-dilution.

Stock CBs congener solutions (1000 $\mu\text{g/L}$) were prepared in hexane from commercial standard Methylene chloride solutions (200 mg/L) by drying and re-dilution. Both stock internal and commercial standard solutions were stored in a refrigerator at $4\text{ }^{\circ}\text{C}$. Silica was obtained from Merck and heated at $130\text{ }^{\circ}\text{C}$ for 16 h

prior to use. Extractions were performed using an automated Soxhlet (Büchi Extraction SystemB-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-3500A Hg lamps (8 W each) irradiating at $\lambda = 350 \pm 25\text{ nm}$ at a distance of 7 cm from the lamps.

2.2. Samples

Real sediment samples collected from Palermo (Italy) coastal area (Cala) were used to develop the analytical method.

A 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 immediately stored in the dark at $-5\text{ }^{\circ}\text{C}$ on site, and then rapidly transported to the laboratory where they were stored at $-18\text{ }^{\circ}\text{C}$.

The 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 $40\text{ }^{\circ}\text{C}$.

2.3. Determination of water

About 2 g of homogenized sample of sediment was dried at $180\text{ }^{\circ}\text{C}$ in an oven for one night. The water content was determined by weight loss and was utilized to correlate all the results with dry weight. The results were expressed as a percentage of total water content.

2.4. Determination of organic matter

An aliquot (2–3 g) of the dried sample was weighed and placed in a platinum crucible. The total organic matter in the soil was measured by determining the loss of weight after combustion at $550\text{ }^{\circ}\text{C}$ in a muffle furnace for 8 h. The results were expressed as a percentage of total organic matter.

2.5. Method

The use of spiked real marine sediment samples in testing method is a very important approach to simulate a real analysis and identify optimal conditions.

To evaluate the best extraction and clean up methodologies, we have applied different operating conditions to real spiked samples obtained by adding 200 μL of a xCBs congeners solution 1000 ppb to a sediment sample (5 g) collected from Palermo Cala station. Figs. 1 and 2 show the percentages of xCBs recovery as a function of solvent mixture and number of extraction cycles, using spiked real marine sediment samples. The results showed that the best percentages recoveries were obtained by using two different extraction steps: the first using 1:1 (v/v) *n*-hexane/acetone solvent mixture for the 15 extraction cycles and the last using 1:2 (v/v) *n*-hexane/acetone solvent mixture for other 15 extraction cycles. These conditions have been used for CBs extraction from sediment sample.

After setting the best extraction procedures, the method of development involved the finding of the optimal photochemical conditions to apply a clean up methodology. From literature data, CBs do not absorb at wavelengths greater than 310 nm [20]. However, we tested their stability under irradiation for 6 h at $\lambda = 350 \pm 25\text{ nm}$ and in Fig. 3 are reported the absorbance spectra of CBs mixture solution at a concentration of 1000 ppb (of each CBs) in extraction mixture before (Fig. 3a) and after (Fig. 3b) 6 hours of irradiation.

The spectra confirm that CBs are not decomposed after 6 h of irradiation at $\lambda = 350 \pm 25\text{ nm}$.

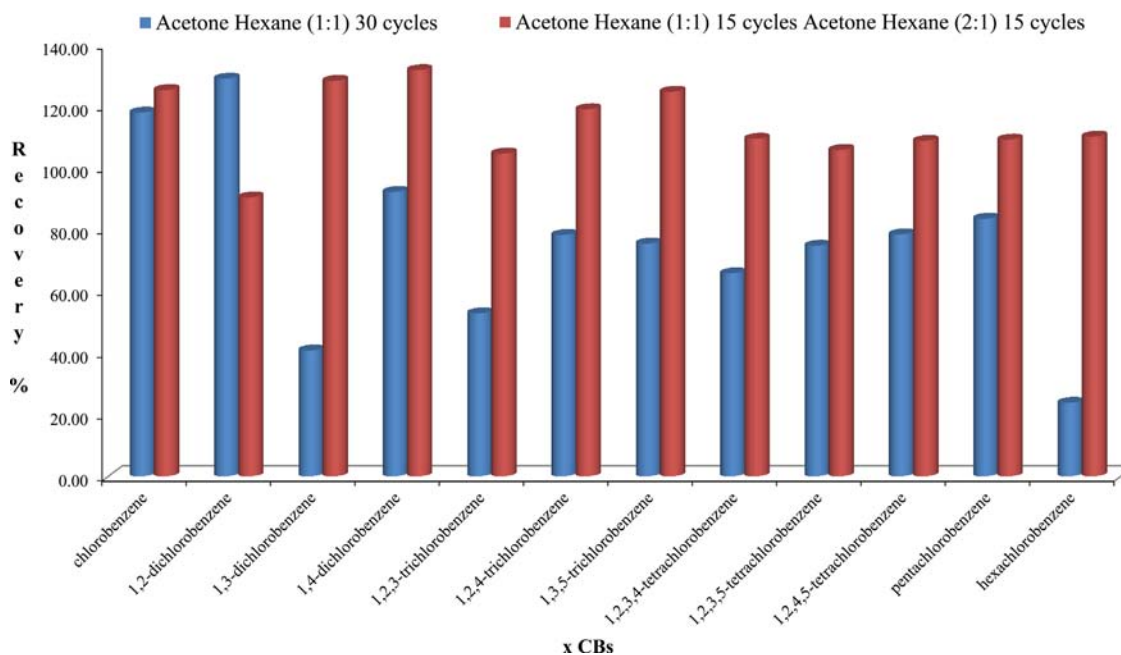


Fig. 1. Percentage recovery of xCBs using different solvent mixtures.

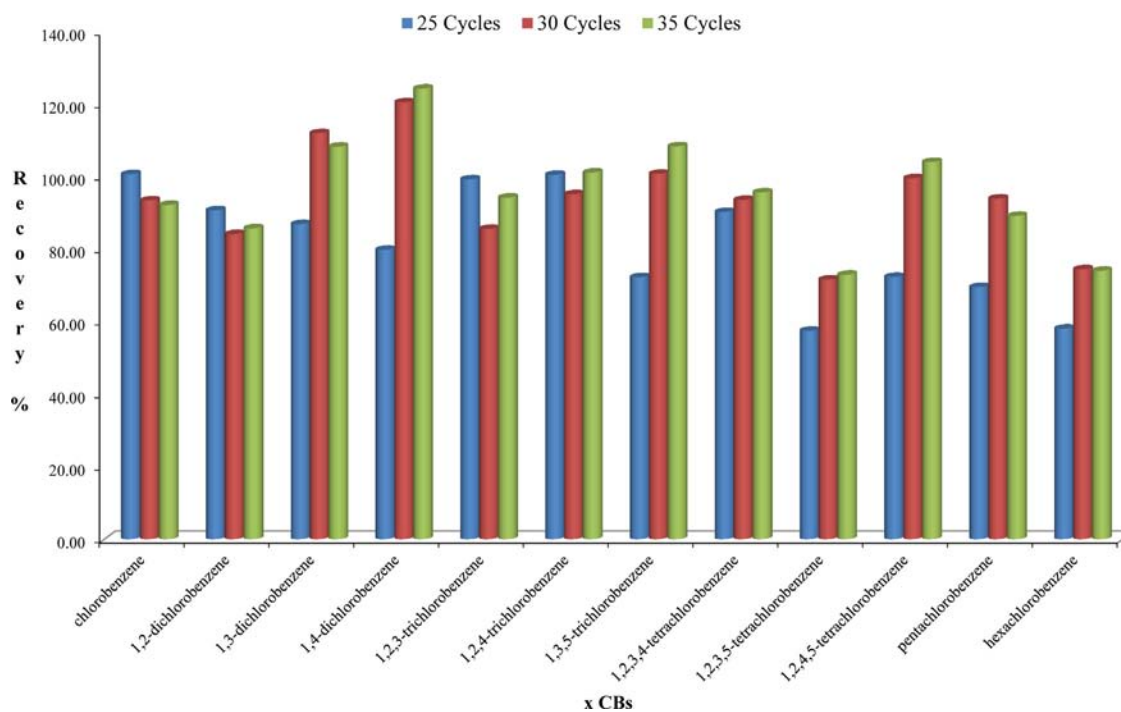


Fig. 2. Recoveries of xCBs for different extraction cycles by using acetone–hexane mixture.

2.6. Extraction

5 g of spiked real sediment sample with 0.5 g of anhydrous Na_2SO_4 was placed into a 33 mL cellulose thimble and extracted by an automated Soxhlet extractor with 100 mL of a 1:1 (v/v) *n*-hexane/acetone mixture before for 15 cycles (1 h) and after with 100 mL of a 1:2 (v/v) *n*-hexane/acetone mixture. The extraction procedures were carried out in warm mode.

2.7. Purification

The photochemical purification of the organic extracts was performed under various conditions (Table 1) and the best result was compared, in term of efficiency, with the silica chromatographic clean up (EPA method no. 3600). The organic extracts (50 mL) were transferred into a Pyrex glass photolysis tube, and directly irradiated at $\lambda = 350 \pm \pm 25$ nm at different irradiation times (Table 1). In order

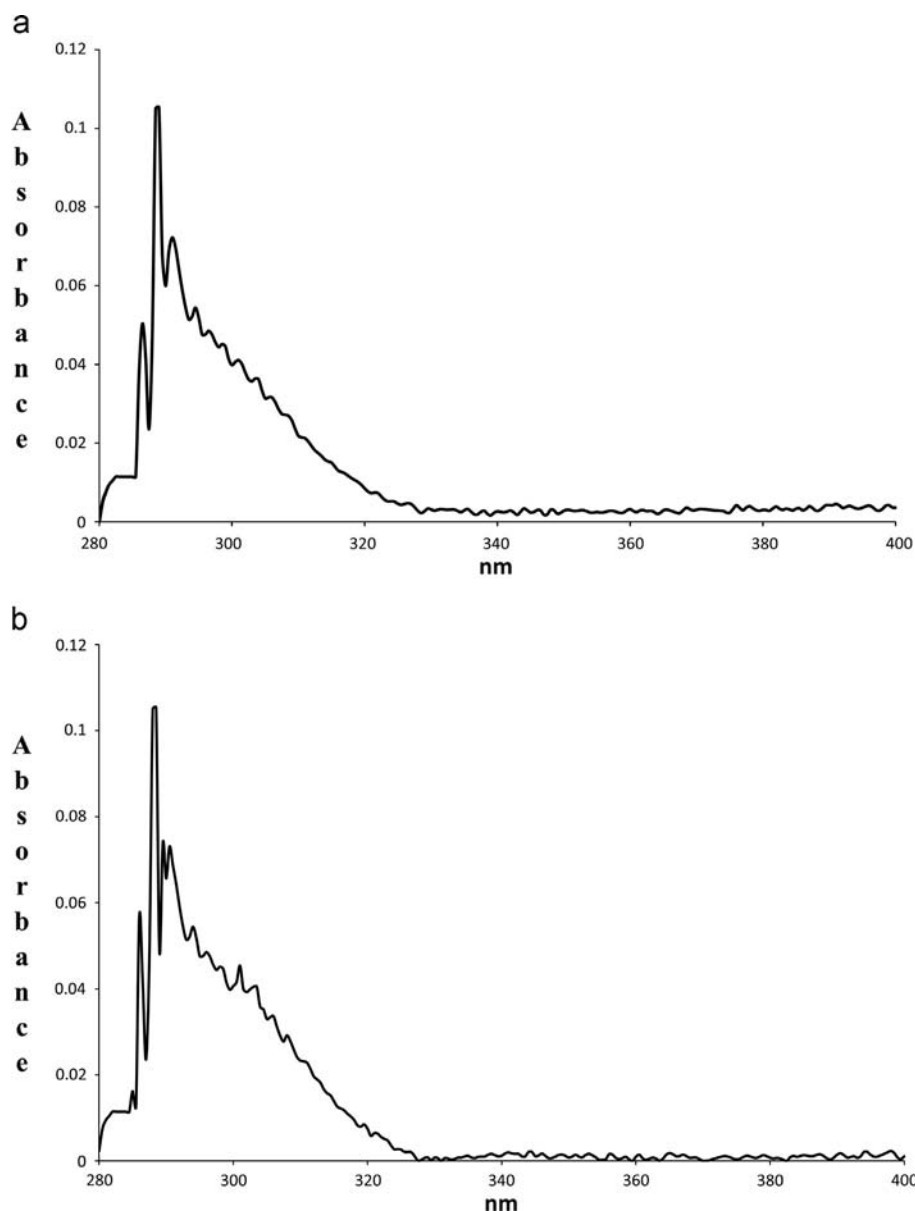


Fig. 3. Absorbance spectra of a CB mixture solution at a concentration of 500 ppb (of each CBs) in a 2:1 (v/v) Acetone/Hexane (a) before and (b) after irradiation.

Table 1
Operating conditions for spiked real sediment sample.

Sample	λ irradiation (nm)	Time irradiation (h)	Oxygen gas bubbling
1	No irradiation	No irradiation	No gas bubbling
2	350 \pm 25 nm	1	10 min
3	350 \pm 25 nm	3	10 min
4	350 \pm 25 nm	6	10 min
5	350 \pm 25 nm	6	No gas bubbling
6	Column purification process	No irradiation	No gas bubbling
7	350 \pm 25 nm	12	No gas bubbling
8	350 \pm 25 nm	24	No gas bubbling

to monitor the effect of the irradiation as a function of time, samples were collected at 1, 3, 6, 12 and 24 h after irradiation. As a blank experiment, a sample was directly analyzed without previous purification. The volume of each sample was reduced using a rotary-evaporator and dried under a N_2 stream. Residues were then

recomposed to 1000 μ L with internal standard solutions of CBs (100 ppb) and analyzed by GC–MS.

2.8. GC–MS analysis

Analysis of purified solutions was carried out using a gas chromatograph coupled with a mass spectrometer (Shimadzu, mod. GCMS-QP2000) equipped with an *SLB-5ms* fused-silica capillary column from Supelco (30 m \times 0.25 mm I.D., 0.25 μ m film thickness). Ultra pure (99.999%) helium was used as a carrier gas and the flow rate was maintained at 1.7 mL/min. 1 μ L of each solution was injected by the Shimadzu *Auto Injector AOC-201*, in splitless mode with a 0.61 min split delay. The injector temperature was maintained at 250 $^{\circ}$ C and detector at 270 $^{\circ}$ C. The GC temperature ramp increased: from 40 $^{\circ}$ C (2 min) to 240 $^{\circ}$ C (0 min) at a 22 $^{\circ}$ /min heating rate; from 240 $^{\circ}$ C to 300 $^{\circ}$ C at a 10 $^{\circ}$ /min rate (5 min). The calibration was performed weekly. The data were acquired operating in selected ions monitoring mode (SIM). Identification of the 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 CBs 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 of CBs 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

Prior to conducting the photochemical purification process, in order to obtain comparable data about the effects of photochemical purification on organic matter concentration, we have characterized the samples for water and organic contents, and the results are reported in Table 2.

The real sediment sample, used to carry out the photochemical purification process, showed higher percentages of water and organic matter than typical sediments from Mediterranean area [21].

Regarding method validation, the linearity of the method for CBs analysis was evaluated over a range of concentrations (from 10 to 500 ng mL⁻¹) finding a linear response (see Correlation coefficients in Table 3) for all analytes. The detection limits (LODs) were estimated as 3σ (three times the background noise) (IUPAC criterion) and as reported in previous papers [22–25] and were similar for all analyzed compounds (1.0 ng g⁻¹). Quantification limits (LOQs) were estimated as 10σ (10 times the background noise) (IUPAC criterion). LOD and LOQ were estimated in selected ion monitoring (SIM) mode as reported in literature [26–28].

About oxidation processes of organic interferent substances 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.

Moreover, from the comparison of extract sediment sample irradiated at 350 nm, in the presence or not of oxygen (see sample 4, 5 and 6 in Fig. 4), it is possible to assert that oxygen bubbling for 10 min does not have effect on organic interferences oxidation for long time irradiations (from 3 to 6 h).

Based on this consideration, it is possible to assert that the principal mechanism in photochemical clean up procedures is the direct photochemical reaction of the excited interfering organic compounds.

The results of sediment samples irradiated for 6 h at 350 nm were used for a comparison between the photochemical clean up and the chromatographic column purification on silica. In particular percentage of recovery and relative standard deviations (SDs) were used to data compare, while *t* test (Table 4) was carried out to value the possible differences among the different methods used.

The *t* values reported in Table 4, show similar efficiencies of the two methods for CBs analysis when $t_{cal} \leq t_{crit}$. This data confirm that, the two methods used, in the range of experimental errors, are similar.

In Fig. 5 percentage recovery of the individual Chlorobenzene congeners in spiked sediment sample obtained by classic Silica purification is compared with those obtained through the photochemical clean up.

CB's percentage recovery determined after photochemical purification is very similar with respect to silica column clean up and the differences are not significant (see *t* values in Table 4). Moreover, in all the cases, CBs recoveries after photochemical clean up were in the range (from 95 to 130%) of those accepted by the Environmental Protection Agency [29].

Table 2

Percentage of water and organic matter in real sediment sample collected in Palermo harbor (Cala).

Sample replicates	% H ₂ O ₂	% Organic matter
Replicate1	61	5.6
Replicate 2	65	6.2
Replicate3	63	5.5
Average	63	5.7
Standard deviation (STD)	± 2	± 0.02

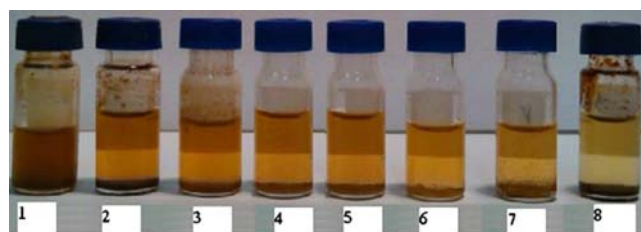


Fig. 4. Extract sediment samples not purified and purified using different conditions; (1) not purified; (2) irradiated for 1 h after O₂ bubbling for 10 min; (3) irradiated for 3 h after O₂ bubbling for 10 min; (4) irradiated for 6 h after O₂ bubbling for 10 min; (5) irradiated for 6 h not O₂ bubbling; (6) silica column purification; (7) irradiated for 12 h not O₂ bubbling; (8) irradiated for 24 h not O₂ bubbling.

Table 3

Calibration data, linear range, correlation coefficient, LOD and LOQ analysis of CBs.

xCBs	Calibration range (ng mL ⁻¹)	Correlation coefficient (R ²)	Limit of detection LOD (ng g ⁻¹)	Limit of quantification LOQ (ng g ⁻¹)
Chlorobenzene	10–500	0.996	1.0	1.0
1,2-Dichlorobenzene	10–500	0.996	1.0	1.0
1,3-Dichlorobenzene	10–500	0.997	1.0	1.0
1,4-Dichlorobenzene	10–500	0.996	1.0	1.0
1,2,3-Trichlorobenzene	10–500	0.993	1.0	1.0
1,2,4-Trichlorobenzene	10–500	0.992	1.0	1.0
1,3,5-Trichlorobenzene	10–500	0.993	1.0	1.0
1,2,3,4-Tetrachlorobenzene	10–500	0.998	1.0	1.0
1,2,3,5-Tetrachlorobenzene	10–500	0.997	1.0	1.0
1,2,4,5-Tetrachlorobenzene	10–500	0.994	1.0	1.0
Pentachlorobenzene	10–500	0.993	1.0	1.0
Hexachlorobenzene	10–500	0.986	1.0	2.3

Table 4

Comparison of the results for CBs analysis from spiked real sediment samples using the different clean up procedures: (a) silica column purification and (b) photochemical purification.

CBs	Real spiked sample, $\mu\text{g kg}^{-1}$	Repeatability recovery ^a % RSD %	Repeatability recovery ^b % RSD%	t_{cal}	t_{crit}
Chlorobenzene	200	95 ± 7	103 ± 9	0.5692	2.776
1,2-Dichlorobenzene	200	90 ± 7	103 ± 2	0.3143	2.776
1,3-Dichlorobenzene	200	128 ± 5	111 ± 4	2.2016	2.776
1,4-Dichlorobenzene	200	131 ± 5	105 ± 6	0.8942	2.776
1,2,3-Trichlorobenzene	200	104 ± 9	95 ± 9	0.3168	2.776
1,2,4-Trichlorobenzene	200	104 ± 2	95 ± 10	0.3906	2.776
1,3,5-Trichlorobenzene	200	124 ± 4	111 ± 9	0.8687	2.776
1,2,3,4-Tetrachlorobenzene	200	109 ± 8	113 ± 8	0.2468	2.776
1,2,3,5-Tetrachlorobenzene	200	105 ± 8	95 ± 8	0.3613	2.776
1,2,4,5-Tetrachlorobenzene	200	108 ± 7	125 ± 4	2.3884	2.776
Pentachlorobenzene	200	109 ± 10	130 ± 7	0.5791	2.776
Hexachlorobenzene	200	110 ± 7	96 ± 5	0.0905	2.776

^a Silica column purification.

^b Photochemical purification.

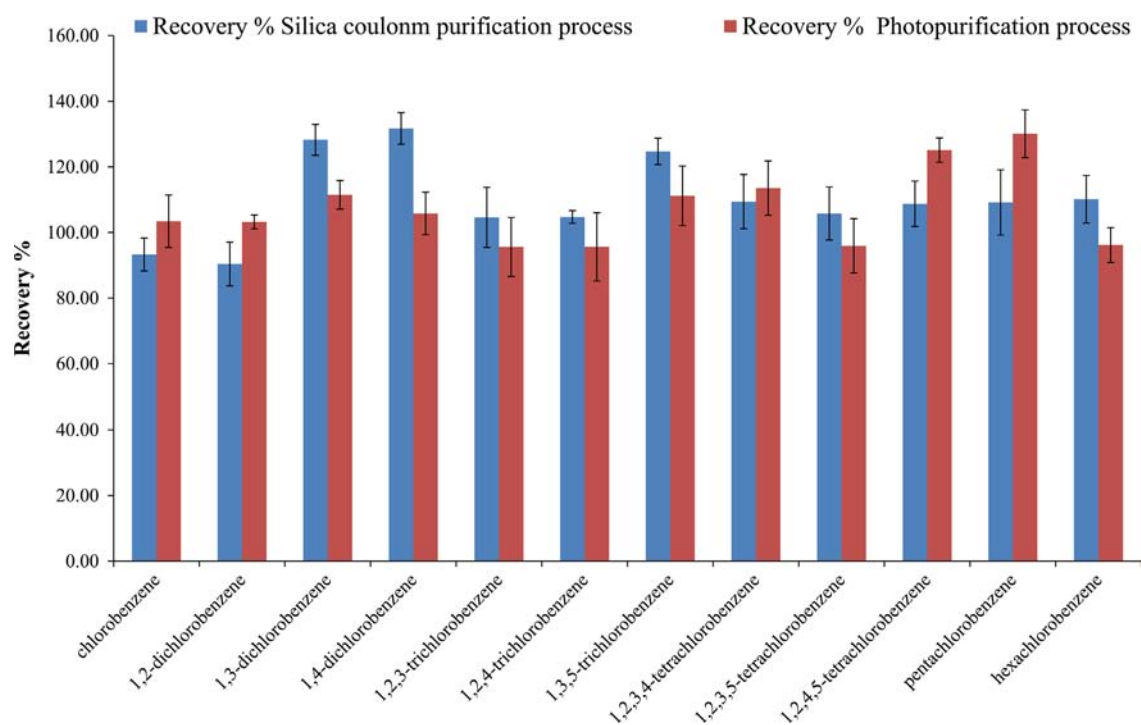


Fig. 5. Comparison of recoveries by Silica column purification and photochemical purification processes.

4. Conclusions

In the present study, a new purification process based on photochemical sample treatment procedure has been developed for the determination of chlorobenzenes in sediment samples with subsequent analysis by GC–MS. After data comparison, optimized photochemical purification conditions consisted in irradiation at 350 nm for 6 h.

By considering good linearity range (from 10 to 500 ng mL^{-1}), high reproducibility (relative error < 10%), lower Limits of Detection (1 ng g^{-1}), lower Limits of Quantification (from 1 to 3.1 ng g^{-1}) and good recoveries (from 95 to 130%) the method was demonstrated to be successfully applicable also to real sediment samples. Moreover it is possible to assert that the develop clean up procedure is in accord with EPA criteria for CBs analysis in sediment samples

If compared to classical chromatographic purification, the proposed photochemical method for the purification of organic extracts for CBs analysis in sediment samples allows a reduction in

the use of harmful solvents and benefits analysis time, cost, and health risks for workers.

Acknowledgments

This study was made possible by the financial support of Palermo University that has funded the author (Grants ex 60% 2007) and by the financial support PON02_00451_3362185.

References

- [1] P.T. Anastas, J.C. Warner, *Green Chemistry, Theory and Practice*, Oxford University Press, Oxford, 1998.
- [2] J. Namiesnik, *Crit. Rev. Anal. Chem.* 30 (2000) 221–269.
- [3] A. Gałuszka, Z. Migaszewski, Jacek Namiesnik, *Trends Anal. Chem.* 50 (2013) 78–84.
- [4] Q. Wu, C.E. Milliken, G.P. Meier, J.E.M. Watts, K.R. Sowers, H.D. May, *Environ. Sci. Technol.* 36 (2002) 3290.

- [5] V. Elango, J.M. Cashwell, M.J. Bellotti, R. Marotte, D.L. Freedman, *Bioremediat. J.* 14 (2010) 10–27.
- [6] H.M. Curran, *J. Energy* 5 (1981) 218–223.
- [7] J.L. Boy-Marcotte, *Electr. Power Syst. Res.* 3 (1980) 41–51.
- [8] M.R. Ras-Mallorqui, R.M. Marce-Recasens, F. Borrull-Ballarín, *Talanta* 72 (2007) 941–950.
- [9] Mostafa Khajeh, Yadollah Yamini, Jalal Hassan, *Talanta* 69 (2006) 1088–1094.
- [10] L. Wanga, L. Wang, J. Chen, W. Du, G. Fan, X. Lu, *J. Chromatogr. A* 1256 (2012) 9–14.
- [11] K. Pozoa, R. Urrutia, M. Mariottini, A. Rudolph, J. Banguera, Katerine Pozo, Oscar Parra, S. Focardi, central Chile (2013), <http://dx.doi.org/10.1016/j.marpolbul.2013.11.031>.
- [12] C.L. Lee, M.-D. Fang, *Chemosphere* 35 (2007) 2039.
- [13] C.L. Lee, H.J. Song, M.D. Fang, *Chemosphere* 58 (2005) 1503–1516.
- [14] F. Kamarei, H. Ebrahimzadeh, Y. Yamini, *Talanta* 83 (2010) 36–41.
- [15] L. Wolska, P. Konieczka, A. Jastrzebska, J. Namiesnik, *J. Chromatogr. Sci.* 41 (2003) 53–56.
- [16] C. Bendicho, F. Pena, M. Costas, S. Gil, I. Lavilla, *Trends Anal. Chem.* 29 (2010) 681–691.
- [17] W. Chen, L. Duan, D. Zhu, *Environ. Sci. Technol.* 41 (2007) 8295–8300.
- [18] S. Barreca, S. Orecchio, A. Pace, *Talanta* 103 (2013) 349–354.
- [19] EPA Method 8121, Chlorinated Hydrocarbons by Gas Chromatography: Capillary Column Technique. (www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8121.pdf).
- [20] National Institute of Standards and Technology (<http://webbook.nist.gov/cgi/cbook.cgi?ID=C108907&Mask=400#UV-Vis-Spec>).
- [21] H. Papaefthymiou, G. Papatheodorou, D. Christodoulou, M. Geraga, A. Moustakli, J. Kapalos, *Microchem. J.* 96 (2010) 269–276.
- [22] S. Orecchio, *J. Hazard. Mater.* 176 (2010) 339–347.
- [23] S. Orecchio, *J. Hazard. Mater.* 180 (2010) 590–601.
- [24] S. Orecchio, D. Amorello, *Microchem. J.* 99 (2011) 283–288.
- [25] S. Orecchio, *Atmos. Environ.* 41 (2007) 8669–8680.
- [26] A. Gianguzza, L. Culotta, S. Orecchio, *Environ. Res.* 107 (2008) 371–379.
- [27] A. Gianguzza, S. Orecchio, *Polycycl. Aromat. Compd.* 26 (2006) 37–57.
- [28] S. Orecchio, *Atmos. Environ.* 45 (2011) 1888–1895.
- [29] EPA method 8260 B, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry.