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Direct automatic screening of soils for polycyclic aromatic hydrocarbons based on microwave-assisted extraction/fluorescence detection and on-line liquid chromatographic confirmation

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Abstract

An integrated screening-confirmation system for PAHs in soils is presented. The sample screening configuration comprises on-line microwave-assisted extraction of the selected pollutants, followed by continuous preconcentration and sample clean-up on RP-C_{18}. Those samples for which the total concentration is close to or above the threshold limit established (10 μg/g) are subjected to liquid chromatographic separation for confirmation. An evaluation of the qualitative data obtained was also carried out, by calculating the unreliability zone as well as the false positive and false negative rates. The whole method (extraction/determination/confirmation) was validated using industrial soil and harbour sediment certified reference materials (IRMM, European Commission CRM 524 and CRM 535). Application to the screening of solid environmental samples with subsequent confirmation of the results is also presented.

Keywords: Screening; Microwave-assisted extraction; Soils; Polycyclic aromatic hydrocarbons

1. Introduction

The determination of trace pollutants in environmental solid samples involves tedious and multi-steps analytical procedures, being analyte extraction usually regarded as the most difficult step. Polycyclic aromatic hydrocarbons (PAHs) are a widely distributed group of organic pollutants; their great environmental concern comes from their mutagenicity, carcinogenicity and persistence. Both, natural sources (forest fires) and mainly human activity (incomplete combustion of fossil fuels, coke production, industrial processes and motor vehicles), generate them [1]. The US Environmental Protection Agency has included 16 PAHs in its priority pollutant list and they are also considered as priority contaminants by the European Union. There are a variety of analytical methodologies available for the extraction of PAHs from solid environmental samples. Soxhlet extraction can be considered as a standard method for leaching PAHs from solids, however, it requires long extraction times and large volumes of organic solvents. Existing alternatives include supercritical fluid extraction (SFE), pressurised liquid extraction (PLE), microwave-assisted extraction (MAE) and ultrasonication.

SFE appears to be a good alternative to Soxhlet extraction because of the less consumption of time and solvents. The use of conventional supercritical CO_2 has been shown to yield good recoveries for PAHs from soils and fly ashes [2]; static subcritical water extraction with simultaneous solid-phase extraction for determining the target analytes in solid environmental samples has also been proposed [3]. Other methods include binary and ternary supercritical phases with the use of organic modifier [4] as well as in-situ derivatization [5] to evaluate the recovery of PAHs from soils. PLE is based on the use of a solvent or combination of them to extract organic pollutants at elevated pressure (up to 20 MPa) and temperature (up to 200 °C). Different solvents such as toluene [6], 1:1 dichloromethane:acetone [7], 1:1 acetone:hexane [8] and more recently pressurised hot water [9,10] have been

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proposed for the extraction of PAHs from soils and solid wastes. A miniaturised alternative uses 100 μl of toluene for the 10 min static–dynamic PLE of PAHs from 50 mg of soil or sediment [11]. Focused-microwave-assisted methods available for the extraction of PAHs from environmental matrices offer reduced extraction time [12–14]. The potential of the combined use of micellar media and microwave-assistance for the extraction of PAHs from soils into an aqueous media has also been checked [15]. Other alternatives that can be found in the literature refer to the use of ultrasounds [16–18] and focused-microwave-assisted Soxhlet extraction [19]. In the majority of the analytical procedures described additional clean-up/preconcentration step is required prior to the final analysis. For this purpose, hollow microporous membrane liquid–liquid extraction [9,10] and mainly solid-phase extraction (SPE) using styrene–divinyl benzene disks (3) silica [8,14], RP-C_{18} [15,16] or selective materials such as immunosorbents [17] or chemically modified polymeric sorbents [18] can be used. In all cases, identification and individual quantitation of the target analytes involve the use of liquid chromatography (LC) with fluorescence or diode array detection and gas chromatography using either flame ionisation or mass spectrometric detectors.

The aim of this work is to provide a fast response analytical methodology for the screening of solid environmental samples for PAHs. Therefore, MAE of the target analytes with acetonitrile was investigated, using a household microwave oven. Analyte preconcentration/sample clean-up was implemented in a continuous manner before obtaining the global fluorimetric response. Confirmation of the positive responses was systematically carried out by liquid chromatography with both UV and fluorescence detectors.

2. Experimental

2.1. Reagents and standards

All chemicals used were of analytical grade or better. Polycyclic aromatic hydrocarbons [naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, dibenzo(*a*,*h*)anthracene, indeno(1,2,3-cd)pyrene, benzo(*g*,*h*,*i*)perylene] and octadecyl-bonded silica (RP-C_{18}) were purchased from Sigma–Aldrich Química (Madrid, Spain). HPLC-grade acetonitrile solvent (Scharlau, Barcelona, Spain) filtered through a Nylon 66 filter (0.45 μm pore size) were used to prepare both the eluent and the mobile phase. Methanol, acetone and nitric acid were obtained from Merck (Darmstadt, Germany).

Stock standard solutions of each PAH at a concentration of 1 mg/ml were prepared in methanol and stored at 4 °C in the dark. Working solutions at the microgram per millilitre level were prepared by appropriate dilution of the stocks in acetone or 1 M HNO_3.

Two standard reference materials of dried contaminated industrial soil (CRM 524) and harbour sediment (CRM 535) with certified concentrations of several PAHs were obtained from the European Commission (IRMM, Geel, Belgium) and used to verify the efficiency of the screening and confirmatory methods with real polluted samples.

As the PAHs studied are suspected carcinogents, caution must be taken with them. All the solutions should be handled in a ventilated hood and the operator must wear gloves and avoid inhalation or skin contact.

2.2. Apparatus

The continuous flow system designed for screening of soil for polycyclic aromatic hydrocarbons was constructed by using a low-pressure Gilson (Villiers-le-Bel, France) Minipuls-3 peristaltic pump fitted with Solvaflex pumping tubes, a Rheodyne (Cotati, CA, USA) 5041 injection valve and PTFE tubing (0.5 mm i.d.) for connector and coils. A laboratory-made sorbent column was constructed by packing a commercial Omnifit glass column (2.5 cm × 3 mm i.d.) with ca. 50 mg of octadecyl-bonded silica (RP-C_{18}) sorbent material; small cotton beads were used to prevent material losses. A glass column with cotton wool was used as filter. The extraction system comprised a household microwave oven equipped with a magnetron of 2450 MHz with a nominal maximum power of 800 W as marketed; a piece of PTFE tubing of 0.5 mm i.d. for sample aspiration was inserted into the microwave oven through the vent holes in order to avoid drilling of the walls.

The chromatographic system consisted of an Hewlett-Packard 1050 high-pressure quaternary gradient pump for delivery of the mobile phase, a tandem-Nova-Pack® RP-C_{18}LC cartridge columns (2 mm × 150 mm × 3.9 mm, 4 μm, Waters, Barcelona, Spain) and a UV–vis detector. A Waters 470 scanning fluorescence detector equipped with a high-pressure flow cell of 16 μl was coupled in serie to the UV–vis detector. Stainless steel tubing of 0.5 mm i.d. was used for all connections. The elution program was: 0–5 min acetonitrile–water 75:25 (v/v) and then a linear gradient elution: from 75% acetonitrile at 5 min to 85% acetonitrile at 10 min and then to 100% acetonitrile at 20 min, followed by isocratic elution with acetonitrile for 5 min. Finally, 5 min were necessary to re-establishing the initial conditions. Separation was done at room temperature using a constant flow-rate of 1 ml/min and the mobile phase was degassed during analysis by using and helium stream.

The flow injection (FI) and the LC systems were interfaced by means of a six-port high-pressure injection valve (Knauer 63320000) and the signals were registered on a Radiometer REC-80 Servograph recorder (Copenhagen, Denmark).

2.3. Sample preparation

Uncontaminated agricultural soils (blank samples, previously analysed), with averages organic carbon and clay con-

tents of 1.3 and 50%, respectively, were spiked with the PAHs 1 month before treatment in order to simulate weathering and allow for analyte–matrix interactions to occur and following reported recommendations [20]. For this purpose, the soil samples were air-dried at room temperature for 1 week, grounded, and sieved to a size smaller than 2 mm. Aliquots of 0.1–1 g of soil were spiked with 1 ml of acetone containing between 0.2 and 25 μg of the 16 priority EPA PAHs in order to study the influence of the concentration on the sorption process. After spiking, the samples were allowed to air-dry (ca. 10 h) in the dark at room temperature, protected from draughts with shaking every 30 min at the beginning and 1 h at the end. The samples were then stored in amber glass-stoppered bottles at 4 °C at least 1 month before their first extractions. The PAHs were to be assumed uniformly distributed in the aliquots of sample. Any analyte–matrix interactions were assumed to have occurred over the weathering period and to an extent similar to that in actual contaminated soil of similar properties.

2.4. Procedure

The integrated FI–FD arrangement designed for direct screening of contaminated soil for PAHs and further confirmation of the positive results by FI–LC–FD/UV is depicted in Fig. 1.The soil samples (0.1–1 g) were weighed inside 10 ml PTFE bottles to which 3 ml of acetonitrile were added. The bottle cap was drilled for insertion of the aspiration tube of the sample channel and the bottle was then placed in the microwave oven, in front of the magnetron; the extraction was performed at a power of 425 W for 10 min. After the extraction, the pump was started and 2 ml of the organic extract was aspirated and cooled by immersion in an ice beaker for complete vapour condensation, and then filtered. The filtered organic solution was continuously transferred to a vial containing 3 ml of 1 M HNO_3. Then, the low pressure pump started the aspiration of the acidic mixture through the RP-C_{18} sorbent column (located in the loop of the low pressure injection valve) at a flow-rate of 0.5 ml/min; PAHs were retained

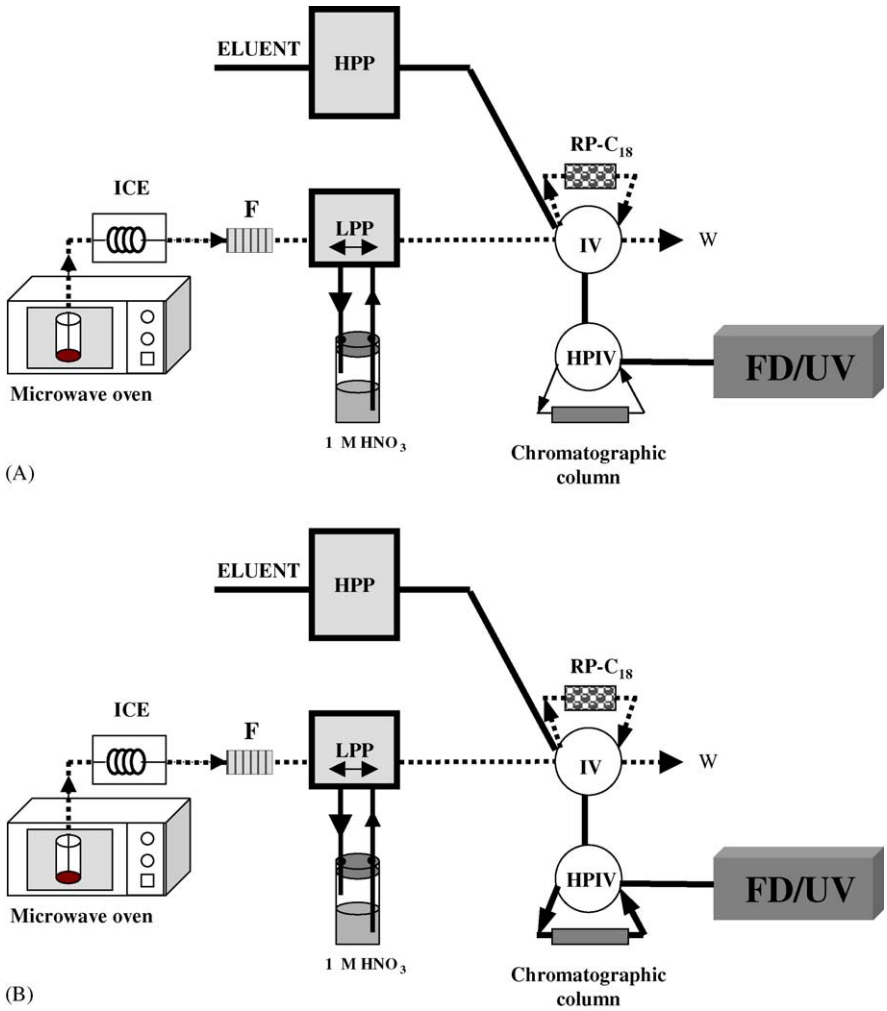

Fig. 1. Integrated FI–LC–FD/UV system proposed for the screening (A) and confirmation (B) of soil samples for PAHs using on-line microwave-assisted extraction. HPP, high-pressure pump; F, filter; LPP, low pressure pump; IV, injection valve; W, waste; HPIV, high-pressure injection valve; FD, fluorescence detector; UV, UV–vis detector.

and the majority of the concomitants wasted. The column was washed with 2 ml of 1 M HNO_3. PAHs were eluted by means of an acetonitrile stream, pumped by the high-pressure pump at a flow-rate of 1 ml/min. In this step, the high-pressure line was directly connected to the spectrofluorimeter working at λ_{ex} = 365 nm and λ_{em} = 470 nm as a compromise to obtain the maximum PAHs global signal. Peak height was used as analytical signal and a global response for the total PAHs content in the soil sample therefore obtained. In the confirmatory method, the FI and the LC were connected by switching the HPIV to the injection position 1 min after elution from the RP-C_{18} sorbent column started. Therefore, PAHs were loaded onto the LC cartridges. The mobile phase gradient started at a flow-rate of 1 ml/min and the separated analytes were individually detected and quantified. The fluorescence excitation and emission wavelengths were changed during the chromatographic separation in order to obtain better sensitivity. The excitation/emission wavelengths were set as follows: 257/347 at 0 min; 284/405 at 8 min and 365/470 at 16.5 min until the end of the chromatogram. The UV–vis detector wavelength was fixed at 254 nm. Peak area was used for the preparation of the 16 PAHs calibration curves and analyte quantitation in soil samples.

3. Results and discussion

3.1. Selection of the solid-phase extraction unit

The SPE unit permits the isolation of the analytes from interfering compounds potentially present in the soil samples as well as preconcentration of the target pollutants as they can be present at low concentration in such matrices (screening step). Moreover, it acts as an introduction system to the LC for analysing those samples providing an overall concentration higher than the legislated limits. According to the literature [15,16] RP-C_{18} was selected as sorbent material and the optimum chemical and flow variables were established for the preconcentration of the PAHs using a flow configuration similar to that depicted in Fig. 1 and acetonitrile as eluent. For this study, the excitation and emission wavelengths were fixed at 365 and 470 nm as a compromise in order to obtain a global response for the 16 selected PAHs. The efficiency of the retention process was studied by using 5 ml of standard solutions containing the analytes at a global concentration of 15 mg/ml at different percentages of acetonitrile in 1 M HNO_3 (20–100%). Retention of analytes was maximum within the interval 30–50% and decreasing over this value; therefore a percentage of 40% acetonitrile was used for the optimisation of the amount of sorbent material. It was studied by varying the length of the column between 30–80 mg. The analytical signal increased with increasing amount of sorbent, reaching a steady state between 40 and 60 mg and decreasing over this value. A working column packed with 50 mg of RP-C_{18} was selected for further experiments.

The effect of the sample flow-rate through the sorbent column during the preconcentration step was studied between 0.2 and 1.0 ml/min. Signals remained almost constant up to 0.7 ml/min, decreasing over this value. The effect of the eluent was optimised between 0.2 and 1.5 ml/min. The signal increased as the flow-rate was increased to 0.8 ml/min, remaining constant up to 1.2 ml/min and decreasing when this value was exceeded, probably because of incomplete elution of the PAHs at higher flow-rates. Thus, flow-rates of 0.5 and 1.0 ml/min were selected for sample and eluent, respectively.

3.2. Optimisation of the microwave-assisted extraction conditions

The optimal conditions for the extraction of PAHs from soils were established by using a blank soil sample spiked with 25 μg of the 16 PAHs per gram of soil as described in the section 2.3 and stored for 1 month. The variables affecting

Table 1
Analytical features of the integrated FI–LC–FD/UV method used for the confirmation

PAH	Fluorescence detection			UV–vis detection		
	Linear range (μg/g)	DL (μg/g)	R.S.D. (%)	Linear range (μg/g)	DL (μg/g)	R.S.D. (%)
Naphthalene	0.006–1.25	0.002	4.1	0.03–0.3	0.01	3.9
Acenaphthylene	–	–	–	0.05–0.6	0.02	4.6
Acenaphthene	0.004–0.40	0.001	3.7	0.005–0.06	0.002	2.9
Fluorene	0.006–1.25	0.002	4.6	0.10–1.2	0.04	4.8
Phenanthrene	0.003–0.50	0.001	3.2	0.01–1.0	0.003	3.0
Anthracene	0.006–1.25	0.002	4.8	0.005–0.05	0.002	2.5
Fluoranthene	0.003–0.50	0.001	3.5	0.02–0.2	0.01	3.9
Pyrene	0.006–1.25	0.002	5.1	0.04–0.4	0.02	4.2
Benzo(*a*)anthracene + chrysene	0.002–0.30	0.0005	2.8	0.005–0.06	0.002	2.7
Benzo(*b*)fluoranthene	0.003–0.50	0.001	4.0	0.01–0.1	0.003	2.4
Benzo(*k*)fluoranthene	0.001–0.20	0.0003	2.5	0.01–0.1	0.003	2.9
Benzo(*a*)pyrene	0.002–0.30	0.0005	2.6	0.01–0.1	0.003	3.2
Dibenz(*a*,*h*)anthracene	0.003–0.50	0.001	4.6	0.10–1.0	0.04	4.5
Indeno(1,2,3-cd)pyrene	0.006–1.25	0.002	5.4	0.01–0.1	0.003	3.3
Benzo(*g*,*h*,*i*)perylene	–	–	–	0.05–0.6	0.02	5.6

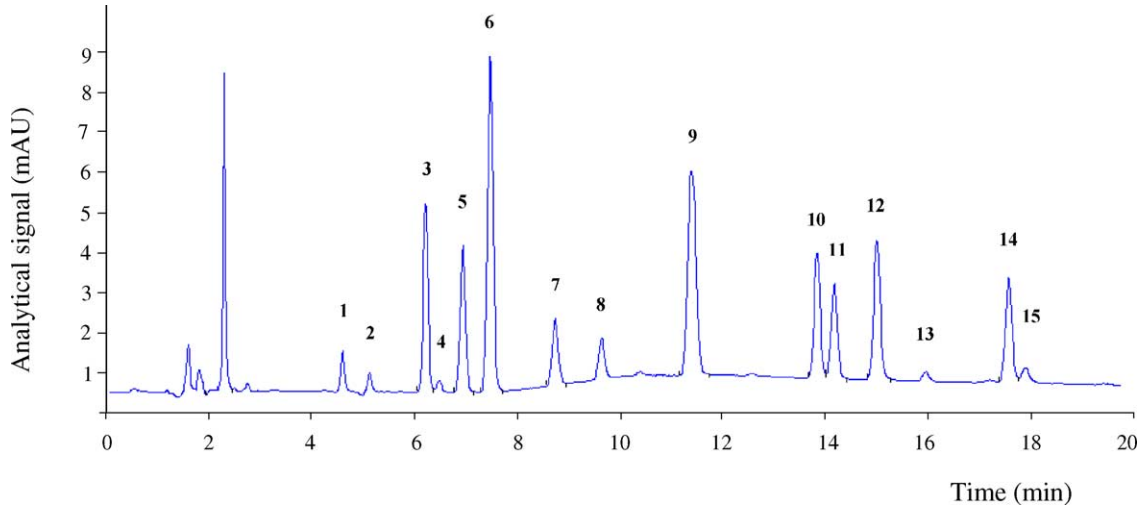

Fig. 2. LC chromatogram of a standard PAH mixture spiked to a soil sample. Peaks: (1) naphthalene; (2) acenaphthylene; (3) acenaphthene; (4) fluorene; (5) phenanthrene; (6) anthracene; (7) fluoranthene; (8) pyrene; (9) benzo(*a*)anthracene + chrysene; (10) benzo(*b*)fluoranthene; (11) benzo(*k*)fluoranthene; (12) benzo(*a*)pyrene; (13) dibenz(*a*,*h*)anthracene; (14) indene(1,2,3-cd)pyrene; (15) benzo(*g*,*h*,*i*)perylene.

the efficiency extraction of PAHs from soil were the volume of extractant, the microwave energy and the extraction time and were optimised using a continuous configuration similar to that depicted in Fig. 1. For this purpose, 1 g of soil spiked with a global concentration of 25 μg of the selected PAHs was manually extracted with variable volume of acetonitrile (between 2 and 10 ml), at variable microwave power for 10 min. The whole extract was then continuously aspirated and transferred to the vial containing the acidic solution for optimum retention of the PAHs on the RP-C_{18} sorbent column. The signals obtained were compared with those provided by a standard solution containing the same amount spiked to the soils. Above 3 ml, quantitative extraction was achieved and, therefore, this volume was selected as optimum. To prevent solid particles form clogging the filter, only 2 ml of the extract were aspirated into the flow system. Regarding the microwave power, the highest signals were obtained working at 425 W.

3.3. Sensitivity, precision and method validation

The manifold depicted in Fig. 1 was used to establish the analytical figures of merit of both, screening and confirmatory methods. The calibration graph (screening method) for the global response of the 16 PAHs assayed was constructed by extraction 1 g of contaminated soil, containing different concentrations of the analytes (0.1–25 μg/g), using a three replicates for each concentration and 10 concentrations for the calibration graph. The regression curve obtained was $Y = 300X + 1.4$ ($r = 0.999$), where Y is the analytical signal (fluorescence intensity) and X the total concentration of the PAHs (μg/g). As no blank signal was obtained, the limit of detection was calculated as three times the standard deviation of the peak height for 10 determinations of the same sample at the lowest concentration within the linear range up to 0.25 μg/g; it resulted to be 0.03 μg/g. The precision of the method as repeatability, expressed as relative standard devia-

Table 2
Analysis of CRMs 524 and 535 using the proposed screening and confirmatory methods

Sample	PAH	Screening method (μg/g)	Confirmatory method (μg/g)	Certified value (μg/g)
CRM 524	Total concentration	247 ± 12	234 ± 11	
	Pyrene		180 ± 10	173 ± 11
	Benzo(*a*)anthracene		22.1 ± 0.9	22.5 ± 1.8
	Benzo(*a*)pyrene		7.9 ± 0.6	8.6 ± 0.5
	Benzo(*b*)fluoranthene		12.1 ± 0.9	13.5 ± 1.6
	Benzo(*k*)fluoranthene		6.7 ± 0.4	6.2 ± 1.6
	Indeno(1,2,3-cd)pyrene		5.6 ± 0.3	5.1 ± 0.4
	Benzo(*e*)pyrene		–	10.6 ± 1.4
CRM 535	Global response	11.9 ± 0.5	10.7 ± 0.3	
	Pyrene		2.5 ± 0.1	2.52 ± 0.18
	Benzo(*a*)anthracene		1.6 ± 0.1	1.54 ± 0.10
	Benzo(*a*)pyrene		1.1 ± 0.1	1.16 ± 0.10
	Benzo(*b*)fluoranthene		2.6 ± 0.1	2.29 ± 0.15
	Benzo(*k*)fluoranthene		1.1 ± 0.1	1.09 ± 0.15
	Indeno(1,2,3-cd)pyrene		1.8 ± 0.1	1.56 ± 0.14
	Benzo(*e*)pyrene		–	1.86 ± 0.13

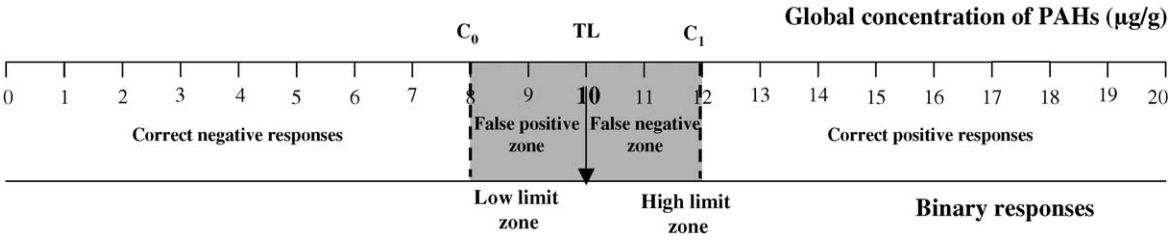

Fig. 3. Graph showing the different regions that characterise the binary response based on the analytical property unreliability.

tion, was checked on 11 individual samples containing a total analyte concentration of 2 μg/g and was found to be 3%.

Table 1 summarises the figures of merit for the confirmatory method, obtained under the optimum established conditions, using both, the fluorescence and the UV detectors. PAHs can be quantified from 0.001 to 1.25 μg/g using the fluorescence detector and within 0.05–1.2 μg/g using the UV–vis detector. The precision, expressed as relative standard deviation, was calculated for 11 standards containing PAHs at an individual concentrations of 0.02 μg/g, was acceptable in all instances. As can be seen, the determination of PAHs using fluorescence detection is advantageous as it provides wider linear ranges and lower detection limits, being the precision similar in both cases. In addition, peaks corresponding to benzo(*a*)antracene and chrysene overlapped under the chromatographic conditions established so they can not be individually quantified. Finally, no signal for acenaphthylene and benzo(*g*,*h*,*i*)perylene were obtained in the fluorescence detector and they were quantified using the UV–vis detector. By way of example, Fig. 2 shows the chromatogram obtained after the analysis of a soil sample spiked with the 16 PAHs studied at concentrations within the middle of the linear ranges listed in Table 1, using UV detection at 254 nm.

The proposed screening and confirmatory methods were validated using two certified reference materials, contaminated industrial soil (CRM 524) and a harbour sediment (CRM 535) containing certified amounts of some of the PAHs included in this work. The global contents were firstly determined using the screening configuration and then, the individual concentrations were calculated after liquid chromatographic separation using the two detectors proposed. The results obtained are summarised in Table 2. As can be seen, the results obtained in both cases are quite consistent with the certified values which testifies to the applicability of the proposed method for screening and confirmation purposes of the selected analytes in solid environmental samples.

3.4. Reliability and application of the proposed method

The confidence level of the proposed sample qualification/classification method was established by the sequential determination of the reliability zones (first step) and the false positive and false negative rates at different global concentration of the analytes (second step). The threshold limit (TL) was previously set at a global PAHs concentration of 10 μg/g (reference value established by EPA, method 8310 PAHs). In both steps, 10 replicates of 6 blank samples spiked at 12 different concentration of the 16 selected PAHs (6 higher and 6 lower than the TL) were analysed following both, the screening and the confirmatory methods. A false negative arises when a soil sample spiked with a concentration of analytes higher than the TL value gives a signal lower than that of the TL. On the contrary, a false positive is produced when a soil sample spiked with a concentration of analytes lower than the TL value gives an analytical signal higher than that assigned to the TL.

Table 3
Results provided by the proposed screening method for the estimation of the uncertainty zone and the false positive and false negative rates

Replicates	Concentration (μg/g)	Correct result	Result of the method		False	
			Yes	No	Positives	Negatives
7	8.0	No	0	7	0	0
7	8.3	No	1	6	1	0
7	8.5	No	2	5	2	0
7	9.0	No	2	5	2	0
7	9.2	No	2	5	2	0
7	9.5	No	3	4	3	0
7	10.5	Yes	5	2	0	2
7	10.8	Yes	6	1	0	1
7	11.0	Yes	7	0	0	0
7	11.5	Yes	7	0	0	0
7	11.7	Yes	7	0	0	0
7	12.0	Yes	7	0	0	0

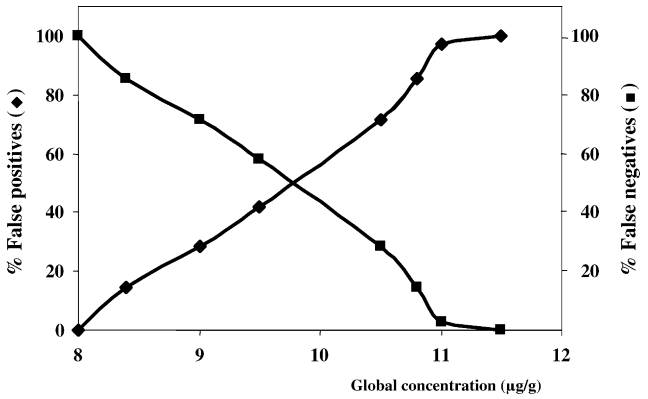

Fig. 4. Estimation of false positive and false negative rates of the proposed sample qualification/classification method based on a threshold limit. For details, see text.

After the analysis of the above mentioned samples, a rough estimation of the unreliability zone was obtained, which is shown in Fig. 3. As can be seen, two regions were established. One corresponds to the concentration zones were 100% reliable results are obtained (values lower than 8 μg/g and higher than 12 μg/g). The other region is the unreliability zone, where false positives and false negatives are produced and includes the concentration range from 8 to 12 μg/g. More precise boundaries of the reliability zone were calculated by performing a new set of experiments using seven replicates of blank samples spiked with variable global concentration of the PAHs within the unreliability zone [between 8 and 12 μg/g (C_0 and C_1, respectively)]. The estimation of the qualitative error rates was carried out by using the false positive rate [(number of false positives/total known negatives) × 100] and the false negative rate [(number of false negatives/total known positives) × 100]. Numerical results are summarised in Table 3 and graphically depicted in Fig. 4. As can be seen, the unreliability zone is narrower than that defined with the first experiments. The two error zones (false positives and false negatives) are not symmetric as the proposed sample qualification/classification method provides lower percentage of false negatives than false positives. It is rather important, as samples giving a negative response in the screening step are no subjected to a confirmatory assay.

To demonstrate the applicability of the sample screening system developed, six contaminated soils were screened. Two of them, obtained from an industrial area (organic carbon and clay contents of 0.6 and 0.3–0.6%, respectively), gave positive response in the screening system, although the global concentration was lower than the previously established limit. No detectable concentration of the 16 priority PAHs selected was found for the other four samples. The results obtained for the two positive soil samples are listed in Table 4. Moreover, two of the soil samples giving a negative response in the screening system were also analysed following the complete chromatographic procedure for quality control purposes. As expected, no chromatographic signal for none of the PAHs included in this study was obtained neither in the fluorescence nor the UV–vis detectors. This also corroborated the high reliability of the proposed integrated FI system. Taking into account that all the samples assayed contained the target pollutants at concentrations lower than those identified by environmental organisms as potentially dangerous for the operator, no special security precautions should be taken in handling these samples.

Additional recovery experiments were carried out on real soil samples in order to test the accuracy of the procedure. Aliquots of spiked soil containing 5 and 15 μg/g total PAHs

Table 4
Application of the proposed screening and confirmatory method to the analysis of two real contaminated soils samples

Sample	PAH	Screening method (μg/g)	Confirmatory method (μg/g)
Soil 1	Total concentration	3.6 ± 0.2	3.5 ± 0.2
	Acenaphthene		0.16 ± 0.01
	Phenanthrene		0.12 ± 0.01
	Anthracene		0.34 ± 0.02
	Fluoranthene		0.30 ± 0.02
	Pyrene		0.85 ± 0.06
	Benzo(*a*)anthracene + chrysene		0.11 ± 0.01
	Benzo(*b*)fluoranthene		0.19 ± 0.01
	Benzo(*k*)fluoranthene		0.57 ± 0.04
	Indene (1,2,3-cd)pyrene		0.90 ± 0.06
Soil 2	Total concentration	2.3 ± 0.1	2.4 ± 0.1
	Acenaphthylene		0.19 ± 0.01
	Acenaphthene		0.081 ± 0.005
	Phenanthrene		0.28 ± 0.02
	Anthracene		1.0 ± 0.5
	Fluoranthene		0.073 ± 0.005
	Pyrene		0.21 ± 0.01
	Benzo(*a*)anthracene + chrysene		0.30 ± 0.02
	Benzo(*b*)fluoranthene		0.062 ± 0.004
	Benzo(*k*)fluoranthene		0.052 ± 0.004
	Indene (1,2,3-cd)pyrene		0.18 ± 0.01

were processed according to the proposed procedure. The results found were compared with the concentration added and the average recoveries varied between 98 and 99%.

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