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Application of Programmed Temperature Vaporization Large Volume Injection Gas Chromatography (PTV-LVI-GC) to the Analysis of Polycyclic Aromatic Hydrocarbons (PAHs) in Soils

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Abstract. A sensitive, selective and robust method was developed to quantify low levels of polycyclic aromatic hydrocarbons (PAHs) in soils by means of Programmed Temperature Vaporization - Large Volume Injection (PTV-LVI) coupled to gas chromatography with flame ionization detection. Optimal vent pressure and flux at the PTV inlet of the GC system were determined by comparison of peak areas obtained from injection of a standard PAHs mixture at different conditions. Assessment of method performance was carried out with home-made standards prepared by spiking three non-PAH contaminated soils that contained 1.8%, 4.6% and 25% natural organic matter (NOM), with mixtures of six different PAHs at low concentration levels. Detection limits between 9 and 12 ng g^{-1} and variation coefficients below 11% were determined from analysis of spiked samples of the soil with lowest NOM content. PAHs recoveries typically ranged from 61% to 96% for the three studied soils.
Key words: polycyclic aromatic hydrocarbons, PAH; large volume injection, programmed temperature vaporization, solvent vent, soil analysis.

Resumen. Se realizó la determinación de Hidrocarburos Aromáticos Policíclicos (HAPs) en suelos a niveles de trazas, utilizando cromatografía de gases con detector de ionización de llama por medio de la inyección de grandes volúmenes con temperatura de vaporización programada (IGV-TVP). Las condiciones óptimas de flujo y presión del inyector TVP se determinaron por comparación de las áreas de pico obtenidas al inyectar una mezcla estándar de HAPs variando estos parámetros. La evaluación del método desarrollado se realizó usando tres diferentes muestras de suelo con contenidos de 1.8%, 4.6% y 25% de materia orgánica (MO), las cuales fueron fortificadas con mezclas de seis HAPs a bajos niveles de concentración. Se determinaron límites de detección entre 9 y 12 ng g^{-1} y coeficientes de variación menores a 11% en el análisis de muestras fortificadas del suelo con menor contenido de MO. Las recuperaciones de los HAPs en los tres tipos de suelo estudiados estuvieron en general comprendidas en el intervalo de 61 a 96%.
Palabras clave: Hidrocarburos aromáticos policíclicos, HAPs, inyección de grandes volúmenes, temperatura de vaporización programada, venteo de disolvente, análisis de suelo.

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are enlisted as priority environmental pollutants by the United States Environmental Protection Agency (USEPA), due to their high toxicity and proven carcinogenic effects to humans [1]. These compounds are widely spread in the environment and mainly arise from incomplete fuel combustion, associated with vehicular traffic and diverse industrial processes, and from activities related to petroleum extraction and transport, as well as energy generation industries [1, 2]. Thus, contamination of soil with PAHs may occur via atmospheric deposition of PAH-associated particulate matter in air, or due to oil spills at petroleum activity sites [1-3].

Routine analysis is required for assessment of the progress and efficiency of soil remediation strategies and methods. For this, very high sensitivities and low detection limits are desired when applied to PAHs trace analysis. These are often achieved by means of gas chromatography (GC) using splitless injection coupled with mass spectrometry (MS) detection because it provides low detection limits [*ca*. 0.7-28 ng mL^{-1} in full scan mode and 0.8-18 ng mL^{-1} in selected ion monitoring (SIM) mode for a group of 26 PAHs], and allows differentiation of the matrix interferences and a simultaneous identification and quantification of the analytes [4]. However, the costs associated with the acquisition and operations of a CG-MS system and its maintenance are considerably higher than those of the simpler GC with Flame Ionization Detection (FID).

Large volume injection (LVI) is an excellent alternative for use of the latter technique, and in fact may become a prerequisite for determination of trace components because it increases sensitivity and reduces the need to pre-concentrate the extract for analysis [5-9]. Programmed temperature vaporization (PTV) in solvent split mode is one of the most commonly applied LVI methods when the analyte is present in complex matrices because the PTV inlet allows a solvent elimination step and pre-concentration of analytes in the liner, and the transfer of compounds to the analytical column is performed by a vaporizer program [5]. Thus, after an appropriate clean up procedure of the sample, remaining matrix interferences can be readily eliminated. The injector temperature program decreases loss from volatilization of low molecular weight compounds and the discrimination of high molecular weight compounds, also improving focusing at the entrance of the analytical column.

The PTV injector is similar to a conventional split/splitless injector because in both systems the sample is injected to a liner placed inside a thermal device. However, the PTV injector is equipped with a very sophisticated temperature control function

and can be rapidly heated or cooled during injection, while the conventional split/splitless injector is isothermal. In LVI, the PTV inlet must be used in solvent vent mode, which allows the solvent excess to be vented out through the PTV split purge, after setting the optimal vent flow, pressure, and time parameters.

A brief principle of the solvent vent injection is as follows: first, the sample is introduced at low temperature (below solvent boiling point); then, solvent is eliminated (at optimal conditions) via split purge while the analytes are retained in the liner; then, the PTV inlet is quickly heated (up to 12 °C s^{-1}) and the retained analytes are transferred to the analytical column in splitless mode, keeping the oven temperature below solvent boiling temperature to refocus the analytes at the front of the analytical column; finally, after the splitless transfer, the split purge is reopened to remove residual solvent vapor and low-volatile matrix compounds from the inlet. This improvement could lead to the complete elimination of preconcentration steps in the analysis of samples containing trace compounds. Although these options of the PTV inlet offer a great advantage and versatility in applications for the trace determination of pollutants, the optimization of parameters is not easy, since the vent flow, vent pressure and vent time must be carefully adjusted in order to obtain reliable and reproducible results in the analysis.

The PTV-LVI-GC method has been applied to a wide range of analytes, including PAHs, in a large number of matrices [5], but to our knowledge only one application of PAH analysis in soils has been previously published using PTV-LVI [6]. However, the GC effluent analysis in that investigation was performed via MS detection, so explicit optimization of the PTV conditions was not required and the work focused more on evaluating the efficiency of the miniature pressurized soil extraction procedure proposed by the authors.

The goal of the present work was to identify and carefully optimize the crucial parameters related to the solvent vent mode in the PTV-LVI method, which is required for its application in the routine analysis of trace concentrations of PAHs in soil extracts using GC-FID. Three non-contaminated soils with different organic matter content, spiked with mixtures of low concentrations of PAHs and allowed to reach sorption equilibrium were employed for the assessment of method performance. Two remediated soil samples were additionally tested with the developed method, which may be applicable as well to other trace organic soil contaminants.

Results and Discussion

Soil characterization and clean up

Results of soils characterization are listed in Table 1. The most important soil parameter for retention of PAHs and organic contaminants in general is the natural organic matter (NOM) content, and as such the three chosen soils span over a wide range representative of low, medium and high NOM contents (1.8%, 4.6% and 25%).

Table 1. Identification and physico-chemical properties of spiked soils

Property	Soil type		
	Luvisol	Acrisol	Histosol[b]
pH[a]	6.7	6.0	Nd
Conductivity (μS/cm)[a]	107	95	Nd
Organic carbon (%)	1.1	2.7	14.7
Organic matter (%)	1.8	4.6	25
Clay (%)	20.8	34.5	Nd
Sand (%)	30.0	29.0	Nd
Silt (%)	49.2	32.0	Nd

[a]25 °C.
[b]Nd = not determined. The crucial property of this histosol for the purposes of our work was its extremely high humic matter content. Other properties were not determined.

Removal of the saponified fraction of the soil during the extraction procedure considerably reduced the background matrix signals in chromatograms (Figs. 1a,b). This procedure only removes saponifiable compounds, such as lipids present in soil, which can be co-extracted with PAHs. Recovery of PAHs after the saponification procedure was evaluated at *ca.* 10-100 times quantification limit levels and showed no negative effects, as compared to recoveries obtained when excluding this step. The procedure was nevertheless required to decrease noise levels and thus detection limits.

A total ion chromatogram (TIC) of a PAH-spiked soil after the clean up procedure (Fig 1c) showed that the proper resolution had been attained between the analytes and the matrix interferences, and thus that FID could indeed be used instead for quantitative analysis. The clean up step was evaluated further as part of the complete procedure by computing the final PAHs recoveries (below).

Optimization of PTV conditions and efficiency comparison

LVI in solvent vent mode involves preconcentration of the sample inside the PTV inlet, thus, the solvent excess should be evaporated to avoid liner flooding but taking care of not losing the analytes. In the solvent elimination step, the injector temperature must be below the solvent boiling point [7-11]. The temperature of solvent elimination is important since it must prevent the analytes to be mixed with the solvent vapour. The success of the solvent elimination and analyte preconcentration steps in the PTV inlet depends on the solvent evaporation temperature, vent flow, vent pressure and vent time (solvent evaporation time).

Parameters of the PTV inlet were optimized for use of LVI (50 μL). Considering the boiling point of the solvent used for soil extraction (toluene b.p. 110 °C), the temperature during solvent vent was set to 60 °C (initial inlet temperature), and vent pressure and vent flow were varied at this fixed temperature with a solvent vent time of 1.4 min (time of multiple injection sequence). Figure 2 shows that the GC peak areas

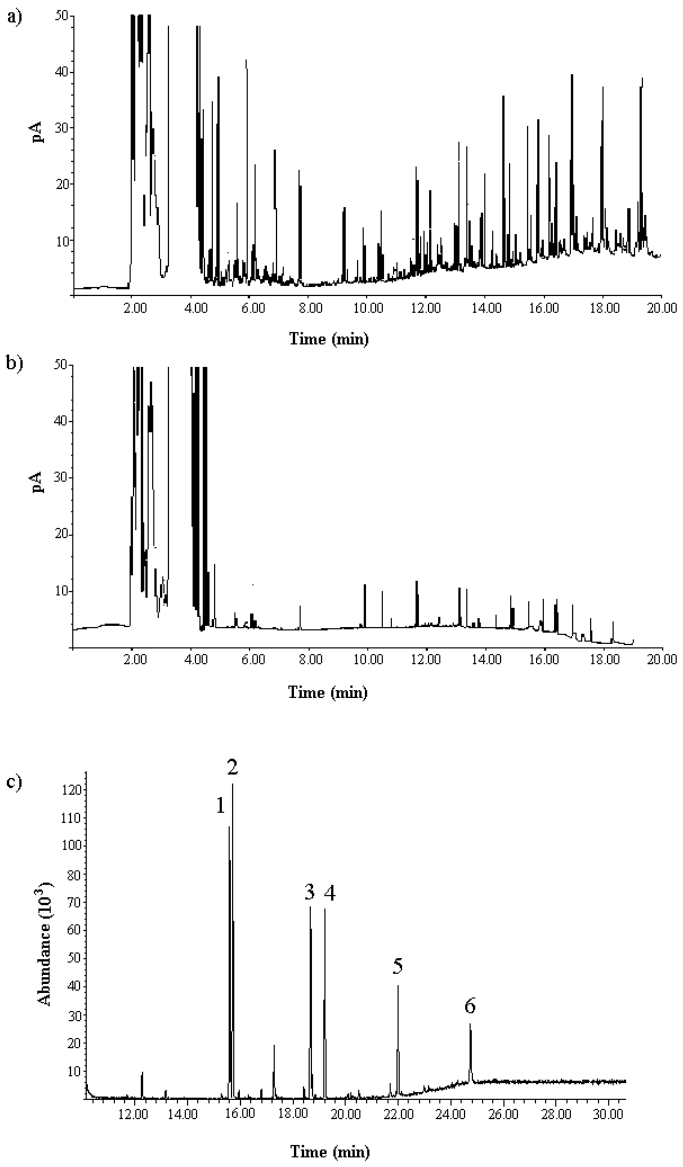

Fig. 1. PTV-LVI-FID chromatogram (50 µL) of blank soil extract (a) before, and (b) after the cleanup procedure; c) total ion chromatogram with splitless injection (1 µL) of spiked soil extract (1 µg mL^{-1}) after the clean up step. The number assignments refer to: 1. Phenanthrene, 2. Anthracene, 3. Fluoranthene, 4. Pyrene, 5. Chrysene and 6. Benzo(a)pyrene.

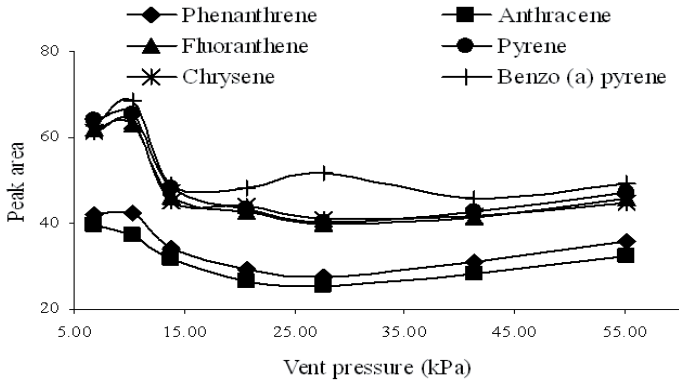

Fig. 2. Optimization of vent pressure in PTV-LVI for 1 µg.mL^{-1} mixed PAHs standard solution in toluene. The vent flow was set to 50 mL min^{-1}.

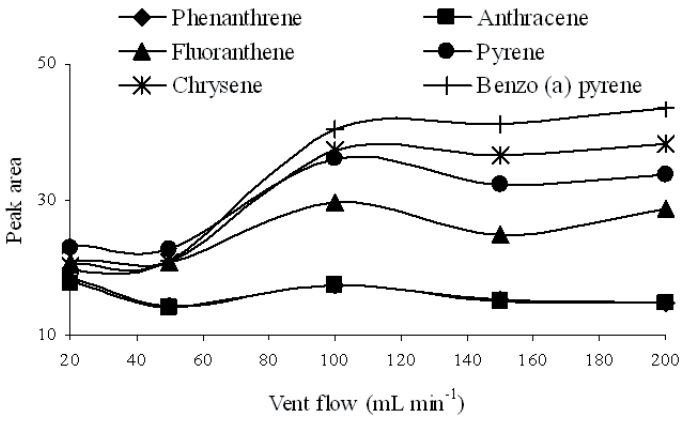

Fig. 3. Optimization of vent flow in PTV-LVI for 500 ng.mL^{-1} mixed PAHs standard solution in toluene. The vent pressure was set to 10.3 kPa.

of analyzed PAHs were highly sensitive to the vent pressure imposed, except for phenanthrene and anthracene. An optimal pressure of 10.3 kPa was selected, in accordance with the largest peak area obtained for all PAHs. Peak areas were also highly sensitive to vent flow but only when transitioning from a region below 60 ml min^{-1} to *ca*. 100 ml min^{-1}, again except for phenanthrene and anthracene (Fig. 3). Optimal vent flow was considered at 100 mL min^{-1} for all analyzed PAHs. These conditions were thus used henceforth to analyze PAHs at trace levels.

Figure 4 shows a comparison of chromatograms obtained from analysis of a 500 ng mL^{-1} mixed PAHs standard solution using splitless injection of 1.0 µL (Fig 4.a) and PTV-LVI of 50 µL (Fig. 4.b), both under the same chromatographic conditions. The increase in sensitivity with LVI, as compared to splitless injection, is evident from the larger peak heights and areas, as well as a decrease in the height of the solvent peak. Thus, adequate preconcentration of the compounds of interest in the liner before being transferred to the analytical column and a decrease in analyte discrimination may be inferred.

PTV injection in solvent vent mode allows large volume injections without flooding the chromatographic system since the solvent vapour volume that transfers to the analytical column is smaller than in splitless injection. Furthermore, the PTV inlet is quickly heated and analytes are transferred to the analytical column, while keeping the oven temperature below solvent boiling temperature to refocus the compounds of interest at the beginning of the analytical column. Overall chromatographic efficiency was improved with PTV-LVI as shown in Table 2, since peak areas were larger for all six compounds and their calculated plate heights (H) and peak widths were smaller than for splitless injection. Finally, reproducibility for PTV-LVI despite being lower than for splitless injection, was

Table 2. Chromatographic efficiency comparison of PTV-LVI and splitless injection for a mixed PAHs standard solution of 500 ng mL^{-1}*.

Compound	Splitless				PTV-LVI			
	Peak Area (±SD)	RSD (%)	H (μm)	Peak width (min)	Peak Area (±SD)	RSD (%)	H (μm)	Peak width (min)
Phenanthrene	11.7 ± 0.27	2.3	52	0.038	196 ± 16.5	8.4	12	0.017
Anthracene	11.2 ± 0.25	2.2	44	0.035	214 ± 18.8	8.8	12	0.018
Fluoranthene	10.7 ± 0.36	3.4	33	0.034	213 ± 16.2	7.6	9.4	0.017
Pyrene	11.0 ± 0.32	2.9	36	0.036	253 ± 22	8.7	9.1	0.017
Chrysene	9.6 ± 0.33	3.4	23	0.032	222 ± 18.6	8.4	6.9	0.017
Benzo a pyrene	8.2 ± 0.26	3.2	15	0.029	200 ± 16.2	8.1	8.9	0.021

*10 injections of 5 μL each for PTV-LVI and 1injection of 1 μL for splitless were performed (n = 3).

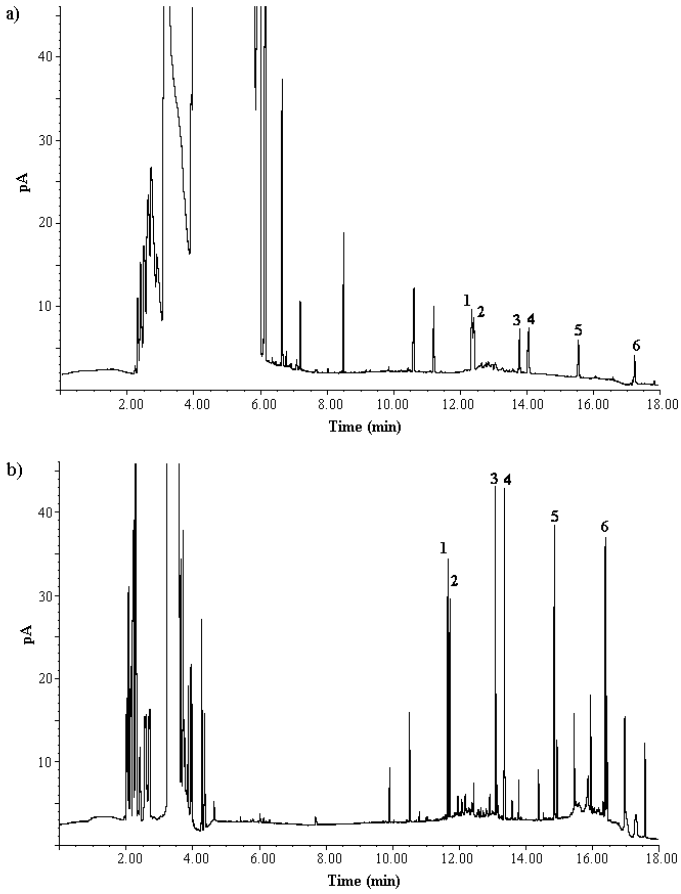

Fig. 4. Chromatograms of 500 ng mL^{-1} mixed PAHs standard solution in toluene by (a) splitless injection (1 μL), and b) solvent vent mode (50 μL). Peak assignments as shown in Figure 1.

quite acceptable (% RSD < 10% for all compounds), given the many variables involved in PTV performance.

Detection limits of PTV-LVI-GC/FID system

Precision of the developed PTV-LVI method was not greatly affected when diluting ten times the previous mixed PAHs solution (50 μg L^{-1}). RSD values obtained from seven replicate injections in the GC system (peak area variability) and standard deviation (SD) in concentration units are reported in Table 3. Calculated detection and quantification limits for each investigated PAH were quite favourable and ranged from 13-27 μg L^{-1} and from 44-92 μg L^{-1}, respectively, in the GC analysis only. The overall detection limits for PAH soil analysis will be discussed in the following section.

Quantification of PAHs in soils

Quantification of PAHs in the spiked soil samples and in the remediated soil samples was carried out with the optimal conditions for PTV-LVI. The Luvisol sample spiked at 50 ng g^{-1} of each PAH was used to determine the method detection limits. Table 4 shows recoveries and detection limits for each PAH in a seven-replicate experiment at this soil-spike level. Recovery was lowest for pyrene (76%) and highest for anthracene and phenantrene (96% and 92%, respectively), and the detection limits were quite satisfying, in some cases reaching levels down to <10 ng g^{-1}.

Table 5 shows the precision and recovery values for the other two soils at different spike levels. The relative standard deviation of concentration measurements in the Acrisol soil was higher than in the Luvisol sample, despite a twice-fold spike level for the former. On the contrary, precision was simi-

Table 3. Precision and sensitivity of the optimized PTV-LVI method using a 50 μg L^{-1} mixed PAHs standard solution.*

Compound	RSD (%)	SD (μg L^{-1})	LOD# (μg L^{-1})	LOQ† (μg L^{-1})
Phenanthrene	8.7	4.35	13	44
Anthracene	15.8	7.9	24	79
Fluoranthene	14.7	7.35	22	74
Pyrene	13.3	6.65	20	66
Chrysene	16.8	8.4	25	84
Benzo a pyrene	18.3	9.15	27	92

*From 7 injections of 50 μL.
#Limit of detection, calculated from three times the absolute standard deviation.
†Limit of quantification, calculated from ten times the absolute standard deviation.

Table 4. Quantification of PAHs in 50 ng g^{-1}-spiked Luvisol soil samples equilibrated for 9 days using PTV-LVI-GC (n = 7).

Compound	Concentration (ng g^{-1} soil)	Recovery (%)	LOD* (ng g^{-1} soil)	LOQ# (ng g^{-1} soil)
Phenanthrene	46 ± 3	92	9	30
Anthracene	48 ± 4	96	12	40
Fluoranthene	44 ± 3	88	9	30
Pyrene	38 ± 4	76	12	40
Chrysene	43 ± 3	86	9	30
Benzo a pyrene	41 ± 4	82	12	40

*Limit of detection.
#Limit of quantification.

Table 5. Quantification of PAHs in spiked Acrisol and Histosol soil samples using PTV-LVI-GC (n = 3).

Compound	Acrisol*		Histosol#	
	Concentration (ng g^{-1} soil)	Recovery (%)	Concentration (ng g^{-1} soil)	Recovery (%)
Phenanthrene	84 ± 23	84	926 ± 108	93
Anthracene	71 ± 17	71	813 ± 15	81
Fluoranthene	73 ± 19	73	750 ± 20	75
Pyrene	61 ± 16	61	609 ± 5	61
Chrysene	68 ± 20	68	364 ± 36	36
Benzo(a)pyrene	76 ± 24	76	732 ± 76	73

*100 ng g^{-1} mixed PAH spike, equilibrated for 5 days.
#1000 ng g^{-1} mixed PAH spike, equilibrated for 7 days.

lar or even better for Histosol as compared to Luvisol which is certainly due to the twenty times higher spike concentration in the former. PAH recoveries from both, Acrisol and Histosol samples, were somewhat lower than those from Luvisol (excepting phenanthrene in Histosol). Pyrene recovery was again lowest in Acrisol and second lowest in Histosol (61% for both), whereas phenantrene recovery was highest in these soils. A particular case was that of chrysene, whose recovery from Histosol decreased to a low 36%, probably due to specific interactions with some components of the soil matix. In general, recovery trends seem to be more or less dependent on PAH's hydrophobicity, however, a relation with the carbon content of soils is not apparent.

From independent experiments separating the different steps of the procedure it is safe to state that the lack of 100% recoveries of PAHs in soils was almost exclusively due to incomplete extraction, and not to problems associated with subsequent steps of the procedure.

Analyses of remediated soils

The analytical method developed and tested with standards made from artificially-contaminated soils of different NOM content, was applied to the analysis of two remediated soil samples originally contaminated from oil spills. Table 6 shows that levels approaching quantification limits were found for fluoranthene, pyrene and benzo(a)pyrene in one soil, and for fluoranthene and chrysene in the other soil. These results bear proof that the proposed method can be successfully applied to and made to be effective in real contaminated soil scenarios.

Concluding remarks

Routine analysis of low levels of PAHs sorbed to the complex organic matrices of soils poses an analytical challenge if cost reduction is desired. In the present work it was shown that it is possible to analyze PAHs in soils down to 40 ng g^{-1} levels by using PTV-LVI coupled with GC-FID detection, but the extracted samples require a preliminary clean up step through a simultaneous saponification procedure. Proper PTV injection allows co-extracted interferents to remain in the liner and separate adequately from the analytes. Volumes of 50 μL final toluene extracts were injected at the PTV inlet and an optimal vent pressure of 10.3 kPa and vent flow of 100 mL min^{-1} were found to yield the highest PAHs sensitivities. The proposed method showed recoveries from artificially PAH-contaminated soils (with different organic matter contents) that ranged from 61% to 96% depending on the particular PAH and soil investigated, except for one outlier of 36%.

Table 6. Quantification of PAHs in remediated soil samples using PTV-LVI-GC (n = 3)*

Compound	RS 1 (ng g^{-1} soil)	RS 2 (ng g^{-1} soil)
Phenanthrene	N.D.	N.D.
Anthracene	N.D.	N.D.
Fluoranthene	54 ± 4	63 ± 6
Pyrene	65 ± 3	N.D.
Chrysene	N.D.	56 ± 5
Benzo(a)pyrene	60 ± 5	N.D.

*N.D. = Not detected.

As such, automated injection of large volume samples using solvent vent mode in PTV proved to be a robust technique in GC-FID analysis of PAHs in soils, and may be applicable to the analysis of trace pollutants in dirty matrices of environmental samples in general, and thus aide in the assessment of environmental remediation efforts for organic contaminants.

Experimental

Chemicals

The following six PAHs were chosen for development of a PTV-LVI-GC method with application to soil analysis: Phenanthrene, Anthracene, Fluoranthene, Pyrene, Chrysene and Benzo(a)pyrene. These were selected to represent PAHs composed of a range of 3-5 rings and of high toxicity, notably benzo(a)pyrene. Standard solutions of individual PAHs, at 500 ng mL^{-1} and 50 ng mL^{-1} each, were prepared in toluene for determination of analytical parameters. Mixed solutions composed of identical concentrations of the six PAHs were additionally prepared to spike soil samples at different ratios. All standard reagents were supplied by Sigma-Aldrich (USA). Toluene 99.98% and methanol 99.99%, and calcium chloride 99.5% and anhydrous sodium sulphate 99.4 % were supplied by J.T. Baker (USA). Toluene was distilled three times in order to reduce impurities that could interfere in the analysis. Potassium hydroxide 87.9% was supplied by Mallinckrodt Baker (Mexico).

Sample preparation and general soil analyses

Three non PAH-contaminated soil samples were used as homemade standard materials to evaluate method performance. These soils were spiked with accurate concentrations of mixed PAH solutions and left to reach sorption equilibrium to the soil humic material. One of the soils (Luvisol) was collected from Nanchital, Veracruz, Mexico, a near-coastal region on the Gulf of Mexico with an important industrial and oil activity; the other two sampled soils (Acrisol and Histosol) were collected from the State of Tabasco, East of Veracruz and also on the Gulf of Mexico Coast. The soil samples were air-dried, disaggregated, and sieved through a 2-mm mesh, and stored dry until analysis.

The soil samples were characterized by type of soil, pH, electrical conductivity (EC), organic matter (OM) content, and size fractions of clay, silt and sand. The pH and EC measurements were performed in 5:1 (v/m) water-soil suspensions using deionized water and the appropriate electrode for each determination. The size fractions of clays, silt and sand were obtained by the Bouyoucos method [12, 13], which is based on their differential sedimentations rates in aqueous suspension columns. The OM content was determined with a total organic carbon analyzer for solids (TOC, Teledyne-Tekmar, USA).

The soil samples were analyzed to verify that they did not contain PAHs. Then, they were prepared for use as standard materials according to the following procedure: 10 g of soil were spiked with 5 mL of the next aqueous solutions, 0.01 M calcium chloride [14-17], 200 μg mL^{-1} mercury chloride (as microbial inhibitor) and 100 μg L^{-1}, 200 μg L^{-1}, or 2000 μg L^{-1} of mixed PAH solutions in replicates of seven, three, and three for the Luvisol, Acrisol, and Histosol, respectively. All soil samples were maintained at constant temperature and pressure (23 °C and 78 kPa) for a period of time in large excess of that determined in previous preliminary experiments to reach sorption equilibrium. The times were nine, five and seven days for the Luvisol, Acrisol and Histosol, respectively.

After equilibration of the spiked sample replicates, extraction and clean up of samples were performed as follows: 1) the solid components were separated by filtration (0.45 μm nylon membranes), 2) they were transferred to the Soxhlet apparatus in a cellulose thimble and extracted for 16 h with 20 mL of a toluene-methanol mixture (6:1 v/v) [18] and 10 mL of KOH solution in 10% methanol-water, 3) the aqueous phase was separated to remove the saponified fraction, thus, reducing interferences from the soil matrix, the organic extract was washed with distilled water to eliminate excess KOH, and dried with anhydrous sodium sulphate, 4) the extract was then evaporated under a low nitrogen stream and reduced to 5 mL in a volumetric flask. The final extract was injected in solvent vent mode in the PTV-GC at optimal conditions. Quantification of target compounds in soil extracts was carried out by external standardization, using calibration curves obtained from analysis of standard PAHs mixtures directly injected (50 μL) in the PTV-GC/FID system. Regression analysis of calibration data confirmed linear behaviour in the concentration range 50-2500 ng mL^{-1} for all PAHs, with r^2 values higher than 0.990.

Two additional PAH-contaminated soil samples that had been previously remediated by a thermal procedure were obtained from Veracruz, Mexico, and prepared for analysis as described for the non-contaminated soils. The remediated soil samples were analyzed in triplicate using the external standard calibration method for quantification.

Gas chromatography

GC analyses were performed with an Agilent Technologies 6890N gas chromatograph equipped with an Agilent 7683B Series autosampler, FID detector and PTV inlet. The chromatograph was fitted with a Zebron ZB-5, 30 m × 0.25 mm I.D. × 0.25 μm F.T. fused silica capillary column. Data were collected

in an Agilent Chem Station A.10.01. The initial column temperature was held at 60 °C for 2 min, then programmed at 10 °C min^{-1} to 90 °C, and finally at 20 °C min^{-1} to 320 °C, which was held for 8 min. Hydrogen (99.98%) at 1.4 mL min^{-1} was used as carrier gas.

GC-MS analyses were performed with a Hewlett Packard 5890 gas chromatograph equipped with a Hewlett Packard 5971 mass selective detector and split/splitless injector. The acquisition of MS data was done in scan mode by electron impact at 70 eV (50-550 m/z). The chromatograph was fitted with a Zebron ZB-5, 30 m × 0.25 mm I.D. × 0.25 μm F.T. fused silica capillary column. The oven temperature program was the same as the one used in GC-FID, previously described. Helium (99.999 %) at 1.3 mL min^{-1} was used as carrier gas. Splitless mode (2 min) at 280 °C was used for injection of samples. The interface temperature was maintained at 280 °C.

PTV inlet conditions and efficiency evaluation

PTV-LVI was performed with an Agilent PTV inlet equipped with a deactivated liner multi baffles. The sample (50 μL) was introduced in the injector using a multiple injections sequence. Ten replicate 5 μL injections of each extract were carried out with an auto sampler equipped with a 10 μL syringe and delay between injections of 1 s. The PTV inlet initial temperature was 60 °C for 1.5 min. The vent flow was varied from 10 mL min^{-1} to 210 mL min^{-1}, and the vent pressure from 7 to 55 kPa to evaluate the GC detection response. The vent flow and pressure were held for 1.4 min, and the flow split purge was held at 50 mL min^{-1} for 1.5 min; afterwards, the split valve was closed and the liner was flash heated at 8.3 °C s^{-1} to 350 °C, which was held for 3 min. The chromatographic efficiency of PTV-LVI and traditional splitless injection was compared by calculating the plate height count (H) for each analyte peak; a standard solution of PAHs (500 ng mL^{-1}) was injected in both injection modes using the same chromatographic conditions (gas carrier, flow in analytical column, oven temperature program and FID temperature).

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