Determination of polyaromatic hydrocarbons and some related compounds in industrial waste oils by GPC-HPLC-UV

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The determination of polyaromatic hydrocarbons (PAHs) in industrial waste oils was studied. The optimized procedure consisted in using low pressure gel permeation chromatography to separate the fraction containing PAHs and PCBs from the matrix. Both groups of contaminants were further fractionated on a small column of 3% deactivated alumina, using hexane to elute the PCB fraction and then hexane–dichloromethane (95 + 5) to elute PAHs. The final analysis was carried out by HPLC on a 2(1-pyrenyl)ethyldimethylsilica column with hexane as mobile phase in the isocratic mode and with UV detection at three different wavelengths, to quantify 16 priority PAHs. Recoveries were between 89 and 99%. Four different industrial waste oil samples were analyzed and the results obtained are discussed.

Introduction

Industrial waste oils are classified as toxic residues owing to the presence of toxic chemicals such as heavy metals, PCBs and PAHs, among others. Althougth the PAHs are not included in the legislation for waste oils, either in the USA or in Europe, their study is generally recommended since waste oils can be used in different combustion processes.[1] As the volume of these residues is increasing, some alternatives have been proposed which include the recycling or the combustion approaches. However, the succes of any proposal depends critically on the composition of the waste oils. In this context, analytical methodology for the determination of PCBs and PAHs is necessary.

Previous work has been carried out with heavy metals[2] and PCBs,[3] but very few data exist on PAHs in waste oils, which was the main objective of this work. The determination of organic chemicals in waste oils is not an easy task, mainly owing to the lipidic and oily matrix, which has to be eliminated without modifying the analytes, PAHs in this case. Common methods for this step are saponification with alcoholic KOH, the use of sulfuric acid,[4] gel permeation chromatography[5–7] and the use of solid adsorbents. Saponification is only appropriate for very stable chemicals. Gel permeation is non-destructive, but it is often not efficient enough[8] and usually requires a second clean-up step. The use of solid adsorbents such as silica, Florisil and alumina[9–11] placed in columns (solid phase extraction) is not always appropriate for eliminating high amounts of lipids.

In this work, a systematic study of several procedures applied to the determination of some priority PAHs established by the EPA[12] and naphthalene and biphenyl in industrial waste oils was carried out.

Experimental

Apparatus

A Hewlett-Packard (Palo Alto, CA, USA) HPLC 1050 Series chromatograph equipped with both autosampler and UV detector was used. The analytical column used was a Cosmosil packed with 2-(1-pyrenyl)ethyldimethylsilica (5 PYE), size 250 × 4.6 mm id. Hexane was used as the mobile phase at a flow rate of 1 ml min^{-1}.

A Model 991 diode array detector coupled to the HPLC system was used to identify the PAHs in waste oils.

Gel permeation chromatography (GPC) was carried out with an HPLC pump [Kontron (Zurich, Switzerland) LC-Pump T-414] connected to a manual injector [Rheodyne (Cotati, CA, USA) Model 756], with an injection loop of 2 ml, a glass column of 40 cm × 2 cm id filled with BioBeads SX3 and a Perkin-Elmer (Norwalk, CT, USA) Lambda 3 UV spectrophotometer equipped with a flow cell of 5 μl for detection. The detector response from GPC was monitored with a Perkin-Elmer Model 561 recorder. As the eluent, cyclohexane–dichloromethane (70 + 30) was used at a flow rate of 1 ml min^{-1}.

A stainless steel filter equipped with an internal grid as support, appropriate fittings and a Millipore (Bedford, MA, USA) membrane filter of 25 mm diameter and 0.45 μm pore size was placed between the injector and the column, to prevent damage to the gel by particles carried by the oil. This filter was changed before each injection. All transfer lines were of PTFE capillary tubing.

Reagents

Naphthalene, biphenyl, dibenzofuran, acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, fluoranthene, benz[*a*]anthracene, chrysene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenz[*a*,*h*]anthracene, indene and benzo[*ghi*]perylene were supplied as certified standards by the Environmental Protection Agency, USA.

Hexane, cyclohexane and dichloromethane (DCM) (residue analysis grade) were supplied by Merck (Darmstadt, Germany). Individual solutions of each compound were prepared in hexane. Joint standard solutions were obtained gravimetrically from each independent solution and appropriate dilution with hexane. All the standards were gravimetrically controlled.

Samples

Four different samples of waste oils were taken for analysis. All of them were supplied by an authorized manager of industrial

toxic residues. These waste oils were classified according to their origin in automotive, hydraulic, machine and cutting oils.

Elimination of lipids

A sulfuric acid–silica impregnated column was prepared as follows. The silica was first activated at 550 °C in an oven for 5 h. Then, 50% m/m of 98% sulfuric acid was added to the silica and the mixture was shaken for 30 min to homogenize it. A 40 × 2 cm id glass column was carefully filled with this mixture.

The GPC column was prepared as follows. A 50 g amount of BioBeads SX3, (a spherical porous styrene–divinylbenzene copolymer with 3% cross-linking), was placed in a 500 ml flask and mixed with 100 ml of the GPC elution solvent [cyclohexane–dichloromethane (70 + 30 v/v)] and the gel was left to stand for 24 h at 4 °C. The fully swollen gel was then de-gassed by applying a vacuum to the flask, before filling the column with the slurry. Elution solvent was pumped through the column at a flow rate of 1 ml min^{-1} for 1.5 h prior to use.

Quantification

Calibration solutions from 100 to 900 ng g^{-1} were prepared gravimetrically in hexane and 25 μl of each solution were injected into the 5 PYE HPLC column at a 1 ml min^{-1} flow rate with hexane. In this way, a calibration plot for each individual compound was obtained for quantification. Signals were collected and integrated at 250, 320 and 376 nm, according to the procedure reported previously.[13] This system allows the individual quantification of all the compounds under study based on the different absorption ability of each one at the mentioned wavelength. At 250 nm the peak obtained at 3.9 min corresponded to the sum of dibenzofuran and acenaphthylene. The peak at 4.33 min was the sum of phenanthrene and anthracene and the peak at 4.83 min was the sum of pyrene and fluoranthene. The signal obtained at 376 nm corresponded to anthracene (4.33 min) and fluoranthene (4.83 min) when working at 320 nm. The peak obtained at 3.90 min corresponded to acenaphtylene. The same procedure was applied to the clean extracts of waste oils.

Detection limits were calculated by injecting successively diluted standard solutions into the HPLC system until the signal was no longer detected. The values obtained ranged from 0.2 ng for biphenyl to 1.4 ng for chrysene.

Separation of PAHs

A 5 PYE HPLC column was used for separation of individual compounds using hexane as the mobile phase at a flow rate of 1 ml min^{-1}, in the isocratic mode, according to the previous optimization.[13]

Results and discussion

Elimination of the matrix

As mentioned above, the matrix has to be eliminated without altering the composition of the analytes. This elimination can be carried out by chemical treatment using, for example, sulfuric acid or KOH, or by physico-chemical treatment through a size exclusion process.

Chemical treatment has been succesfully applied to the elimination of lipids for the determination of PCBs. As, in principle, PAHs are stable enough to persist through a saponification step, this was the first procedure attempted. However, when a solution of 16 PAHs was added to the sulfuric acid–silica impregnated column and then eluted with hexane–dichloromethane (75 + 25) at 1 ml min^{-1}, the 50 ml fraction collected and analyzed following the recommended procedure showed only two peaks, corresponding to naphthalene and biphenyl. Consequently, these results demonstrate that this procedure cannot be applied to this sample.

A non-destructive method such as GPC was studied. PAHs were recovered in the fraction from 35 to 75 ml when a flow rate of 1 ml min^{-1} of cyclohexane–dichloromethane (70 + 30) was used as the mobile phase and the lipid fraction appeared in the first 35 ml.

However, when the waste oil was injected into the GPC column, the bed became gray owing to the small particles carried by the oil and a new column was required. To avoid this problem, a removable membrane filter of 0.45 μm was placed between the injector and the GPC column to remove the particles. This filter was changed after each injection of waste oil. To study the recoveries on the GPC column, a standard solution containing about 400 ng g^{-1} of each compound was used. Table 1 gives the recoveries obtained. It can be seen that only benzo[*ghi*]perylene has a recovery lower than 75%. This low value could be attributed to adsorption effects on the gel column.

Clean-up

The fraction eluted by GPC still contains a small amount of lipids and co-extracted materials which have to be eliminated. Furthermore, waste oils also contain PCBs which are eluted from the GPC column together with the PAHs and a further fractionation step is necessary, since some PCBs and PAHs are also co-eluted in the 5 PYE analytical column used.[13]

We studied 3% deactivated silica and alumina beds filled in glass columns of 20 × 0.6 cm id. Hexane was used as the mobile phase to elute the PCBs and hexane–DCM (95 + 5) to elute PAHs. A study of the elution profiles showed that PCBs were eluted with 10 ml of hexane from the silica column and with 15 ml from the alumina column. PAHs were eluted with hexane–DCM (95 + 5); 25 ml were necessary for the silica column and 20 ml for the alumina. In both cases, PCBs were eluted with a less polar solvent than PAHs, which were efficiently trapped by the adsorbents and were only released from the bed by increasing the polarity of the mobile phase.

Table 1 Recoveries of 16 PAHs obtained after GPC separation. Standard solution in hexane of 400 ng g^{-1} for each PAH

Compound	Mean concentration[a]/ ng g^{-1} (n = 4)	Recovery (%)
Naphthalene	350 ± 9	80
Biphenyl	325 ± 10	78
Dibenzofuran	385 ± 7	82
Acenaphthylene	373 ± 3	89
Fluorene	446 ± 6	90
Phenanthrene	386 ± 2	95
Anthracene	350 ± 3	92
Pyrene	328 ± 4	90
Fluoranthene	326 ± 2	89
Benz[*a*]anthracene	362 ± 4	91
Chrysene	376 ± 2	93
Benzo[*k*]fluoranthene	375 ± 4	92
Benzo[*b*]fluoranthene	376 ± 3	93
Benzo[*a*]pyrene	348 ± 3	91
Dibenz[*a,h*]anthracene	356 ± 3	94
Indene	334 ± 2	91
Benzo[*ghi*]perylene	279 ± 5	65

[a] $\bar{x} \pm \sigma f$, σ = standard deviation, f = 1.6 (n = 4) at the 95% confidence level.

Table 2 Recoveries of PAHs in silica (3%) and alumina (3%) clean-up procedures. Standard solution in hexane of 300 ng g^{-1} for each PAH

Compound	Mean recovery[a] (%)	
	Silica	Alumina
Naphthalene	89 ± 5	90 ± 6
Biphenyl	91 ± 9	92 ± 7
Dibenzofuran	90 ± 7	93 ± 9
Acenaphthylene	88 ± 8	89 ± 10
Fluorene	92 ± 9	91 ± 11
Phenanthrene	97 ± 3	98 ± 4
Anthracene	98 ± 4	99 ± 5
Pyrene	95 ± 6	97 ± 7
Fluoranthene	94 ± 7	98 ± 6
Benz[*a*]anthracene	87 ± 4	95 ± 5
Chrysene	97 ± 7	101 ± 8
Benzo[*k*]fluoranthene	85 ± 10	95 ± 11
Benzo[*b*]fluoranthene	80 ± 9	94 ± 12
Benzo[*a*]pyrene	78 ± 9	98 ± 8
Dibenz[*a,h*]anthracene	76 ± 7	94 ± 6
Indene	81 ± 11	91 ± 9
Benzo[*ghi*]perylene	74 ± 9	89 ± 11

[a] $\bar{x} \pm \sigma f$; σ = standard deviation, f = 1.6 (n = 4) at the 95% confidence level.

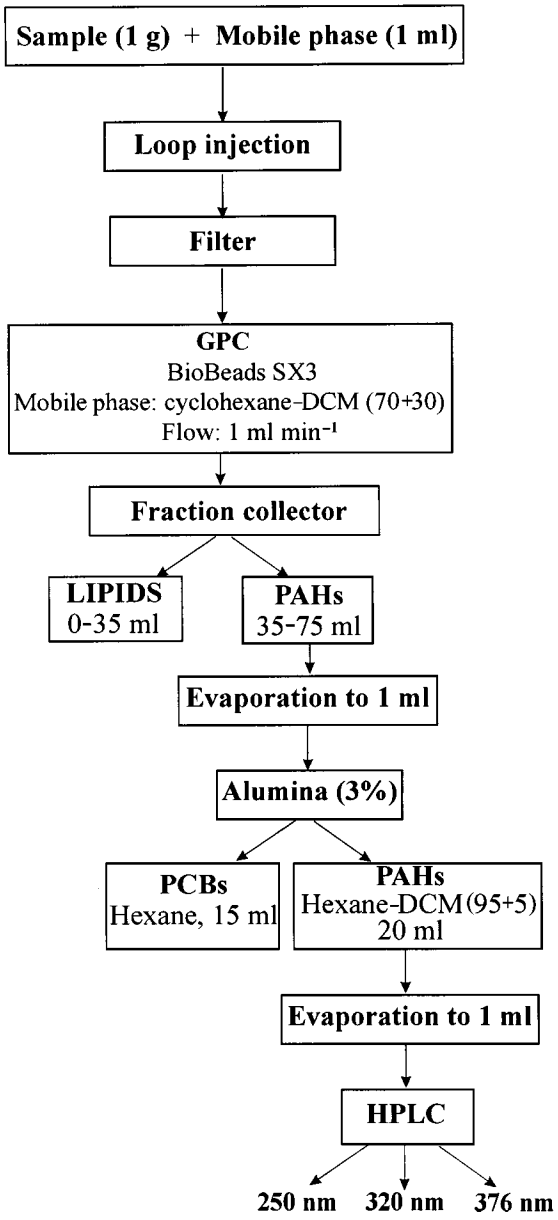

Fig. 1 Schematic diagram of the overall analytical procedure.

A recovery study with both columns (3% alumina and 3% silica) was carried out with standard solutions containing 300 ng g^{-1} of each of the 16 PAHs. Table 2 gives the results obtained for all the PAHs under study.

Comparing the chromatograms obtained with the fraction eluted from both silica and alumina columns, a better baseline was observed from the alumina column and consequently this was selected for further studies.

Fig. 1 shows a general scheme of the whole analytical procedure.

Determination of PAHs in waste oils

Four different samples of industrial waste oils were treated and analyzed using the optimized procedure described above. Individual PAHs in the oil samples were identified through the UV spectrum obtained using a diode array detector connected to the 5 PYE column. The study carried out with diode array detection showed that other co-eluted compounds were not present with the mentioned PAHs and no other unknown PAHs appear. The identification was confirmed by GC-MS of the fraction collected from the alumina column. Table 3 gives the results obtained. As can be seen, naphthalene is the most concentrated in all the waste oils. These results agree with the

Table 3 Slope of calibration plot for each PAH

Compound	Slope/mV g ng^{-1}
Naphthalene	0.603
Biphenyl	3.394
Dibenzofuran	3.432
Acenaphthylene	27.833
Fluorene	2.682
Phenanthrene	9.239
Anthracene	18.173
Pyrene	1.289
Fluoranthene	4.163
Benz[*a*]anthracene	3.607
Chrysene	3.446
Benzo[*k*]fluoranthene	4.163
Benzo[*b*]fluoranthene	3.130
Benzo[*a*]pyrene	2.736
Dibenz[*a,h*]anthracene	0.382
Indene	6.270
Benzo[*ghi*]perylene	0.756

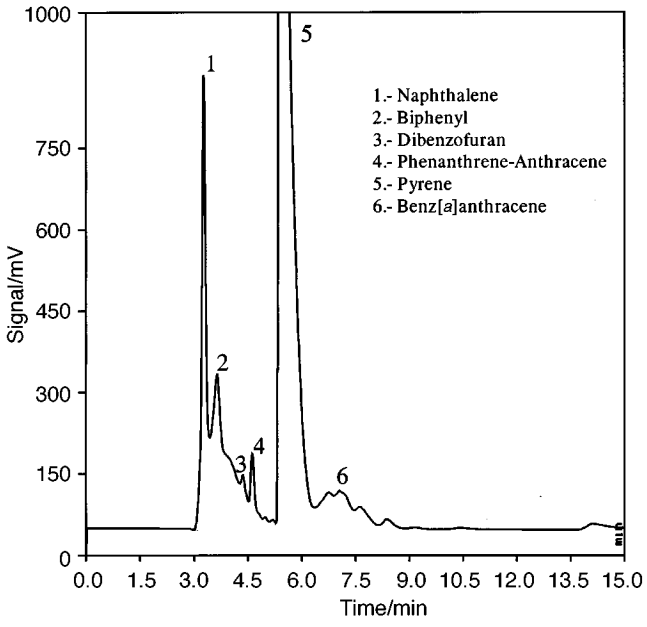

Fig. 2 Chromatogram of a real waste oil sample (automotive oil).

Table 4 Concentrations of PAHs found in real waste oils

Oil	PAH	Concentration/ μg g^{-1}	RSD (%) (n = 4)
Cutting oil	Naphthalene	659	7
	Dibenzofuran	51	9
	Phenanthrene	13	8
	Benzo[*k*]fluoranthene	2	9
	Benzo[*b*]fluoranthene	2	5
Hydraulic oil	Naphthalene	1930	7
	Acenaphthylene	0.9	3
	Anthracene	0.2	7
Automotive oil	Naphthalene	1681	11
	Biphenyl	154	7
	Dibenzofuran	191	9
	Phenanthrene	28	7
	Anthracene	0.1	6
	Pyrene	61	8
	Benz[*a*]anthracene	5	7
Machine oil	Naphthalene	1854	6
	Dibenzofuran	316	10
	Phenanthrene	27	9
	Anthracene	0.5	7
	Fluoranthene	0.07	11
	Benz[*a*]anthracene	6	8
	Benzo[*k*]fluoranthene	7	8
	Benzo[*a*]pyrene	3	8

study of Ouzzani *et al.*[14] which established that industrial virgin oils contain naphthalene. Fig. 2 shows the chromatogram of a sample of automotive waste oil.

Clear differences can be pointed out within the samples. Hydraulic oil is the least contaminated by PAHs, as expected since this application does not require a heating process at high temperature and it is well known that PAHs are mainly formed in high temperature applications where organic compounds are involved. In contrast, the machinery oil is the most contaminated, with a higher number of PAHs than the other oil samples.

The only sample containing benzo[*a*]pyrene, one of the most toxic PAHs,[15] is the machinery oil. Automotive oil shows a high concentration of pyrene, as expected since it has been identified in the exhaust gases from cars.[16] From an environmental point of view, the most dangerous samples are both the machinery and automotion oils.

Conclusions

The determination of PAHs in waste oils requires the elimination of the oily matrix and the isolation and fractionation of the different groups of organic chemicals such as PCBs and PAHs.

In the case of PAHs, the elimination of the oily matrix cannot be carried out with sulfuric acid because most of PAHs are chemically degraded, and GPC with cyclohexane–DCM (70 + 30) as the mobile phase was shown to be an efficient procedure. Further fractionation of the eluted fraction to separate PCBs and PAHs is necessary and the best system is to use solid phase extraction with 3% deactivated alumina column. The elution of PAHs from this column requires a slightly polar solvent such as hexane–DCM (95 + 5) whereas PCBs are eluted with hexane in the first 15 ml fraction.

Several differences in the nature and concentration of PAHs can be found when waste oils of different origin (automotive, hydraulic, machine, lamination) are analysed and these differences can be attributed to the previous use of the oil.

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