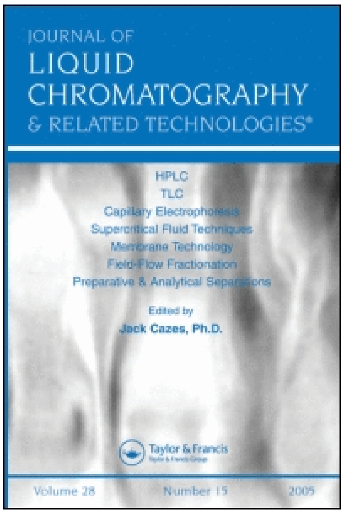

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THE DEVELOPMENT OF LESS HAZARDOUS ELUENT MIXTURES FOR THE LIQUID CHROMATOGRAPHIC SEPARATION OF TOTAL POLYCYCLIC AROMATIC HYDROCARBONS IN HEAVY HYDROCARBON OIL MIXTURES

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ABSTRACT

A safer eluent system was developed for the chromatographic separation of heavy petroleum mixtures into concentrates containing the potentially hazardous polycyclic aromatic hydrocarbons (PACHs) and their heterologues (PSAHs and PNAHs). The eluent system, which originally made use of benzene mixtures to recover these materials, was modified; mixtures of dichloromethane and petroleum spirit (12:88 V/V) and ethyl acetate and methanol (40:60 V/V) now follow the initial non-polar petroleum spirit eluent. The new elutropic series was successfully applied to diesel and gas oils, lube raffinates, brightstocks, aromatic extracts, hydrocracker products, and atmospheric and vacuum resids. The relative precision of the technique was established at +/- 4.6% for a wide range of petroleum mixtures.

INTRODUCTION

The separation of polycyclic aromatic hydrocarbon (PCAHs) concentrates from petroleum oils has been possible for many years, and a range of different procedures is available. Where relatively large quantities of the concentrates are required for further studies, traditional open column chromatography (1-4), and solvent extraction techniques (5) can still have a role to play. When some of these methods were developed, the hazardous nature of benzene (6) was not appreciated, and, unfortunately, several of the elutropic series developed included significant amounts of benzene. Since this laboratory has been concerned with reducing the usage of hazardous materials, work was initiated to find a relatively safe elutropic series for a separation method that had already been well established (3). The study employed the same approach as was followed earlier (7): baseline data are generated using the original eluents; a range of alternative elutropic series are developed based on safety, volatility, stability and solvent strength factors; and, after testing, the most satisfactory series is selected and a range of petroleum oils separated. This paper describes: (i) the development of the new elutropic series; (ii) some modifications to streamline both the original laboratory technique and the calculations; (iii) the separation of a wide range of petroleum oils; and (iv) the precision of the method.

EXPERIMENTAL SECTION

Eluents

The following A.R. grade solvents were used:

1. For the chromatographic separation: petroleum spirit (40-60°C or 60-80°C, free of aromatics), benzene, dichloromethane, methanol, ethyl acetate.
2. For deasphalting residual oils: toluene, n-heptane.
3. Spectrosol n-hexane or 2,2,4 trimethylpentane (iso-octane) for spectrophotometry.

Adsorbent

Fresh alumina (Alcoa F-20 or equivalent), sieved to 100-200 mesh range, activated at 400°C for 4 h, partially deactivated with 3% wt deionized water after cooling, and stored in a sealed container for at least 24 h to ensure equilibration.

Columns

Glass chromatography columns, 1.4 cm x 50 cm, with a 100 ml solvent reservoir at the top and a PTFE keyed tap at the bottom. Normally, 40 g of partially deactivated alumina are packed to form an efficient adsorbent bed, by use of a mechanical vibrator.

Ultraviolet Spectrophotometer

A Perkin-Elmer 330 Ultraviolet Spectrophotometer was used in the rerun mode, over the 190-300 nm range. Solutions of the fractions (normally 0.002-0.005% concentration) were studied in 1 cm path-length cells.

Samples

A wide range of petroleum products boiling above 250°C were studied. These included straight run diesel cuts, hydrocracker products, raffinates, extracts, atmospheric and vacuum residues.

Original Techniques

Two procedures are defined in the BAM-27 methodology (3), differing in the conditions used to define the chromatographic fractions; in all other aspects, the techniques are identical. In the definitive procedure, the oil sample is initially eluted down the column with petroleum spirit (30-40°C boiling range), and the progress of the mono and di-aromatic hydrocarbons followed by ultraviolet (UV) spectrophotometry. Fraction 1 contains the saturates, mono- and di-aromatic compounds (SMD). After these groups of compounds have eluted, the PCAHs are recovered using benzene/petroleum spirit (25/75 V/V), again monitoring with UV. The polar compounds are subsequently eluted with a 50/50 (V/V) mixture of benzene/methanol. Small quantities of PCAHs may elute in the first fraction due to the need to ensure the total elution of the mono- and di-aromatics in the fraction; an iterative correction procedure is applied. In the second, simpler, technique the progress of the elution is not monitored by UV, the first 420 ml of petroleum spirit eluting are collected as fraction 1, where as the PCAHs are recovered in Fraction 2 with 250 ml of benzene/petroleum spirit (25/75 V/V).

Depending upon the total PCAHs content, the optimum sample size varies from 0.5 g to 30 g, for normal oils. However, for highly refined oils, e.g., white oils, samples up to 200 g in size may be required, when dilution in aromatic-free petroleum spirit, and the application of nitrogen pressure (typically 2-3 psig) have to be used initially to achieve satisfactory percolation rates during sample charging.

RESULTS AND DISCUSSION

Selection of the Eluents

The selection of the appropriate eluent is a key task in the formulation of an efficient adsorption chromatography system. In this case, a safer eluent system is required, which will perform similarly to an already established system for the recovery of both PCAHs and polar fractions from a wide range of petroleum samples. The same approach was adopted, as in an earlier study (7). In it, eluent mixtures of the same solvent strengths (ε^{o}) as those used for the original system are identified and tested.

Solvent strengths were calculated by Snyder (8) for a number of pure eluents and several absorbents, and relevant values are plotted in Fig. 1. In the case under study, the alumina used (deactivated with 3% water) was slightly less active, $\alpha = 0.7$, than that in Fig. 1, and aromatic-free petroleum spirit ($\varepsilon^{o} = 0.01$) was substituted for the n-pentane ($\varepsilon^{o} = 0.00$), for cost and year-round availability reasons. These differences are not expected to have any major effects on the performance of the alternative elution system that could not be accommodated by the developmental methodology.

A 12:88 V/V mixture of dichloromethane/pentane has the same ε^{o} (0.18) as a 25:75 V/V mixture of benzene in pentane, and a 40:60 V/V

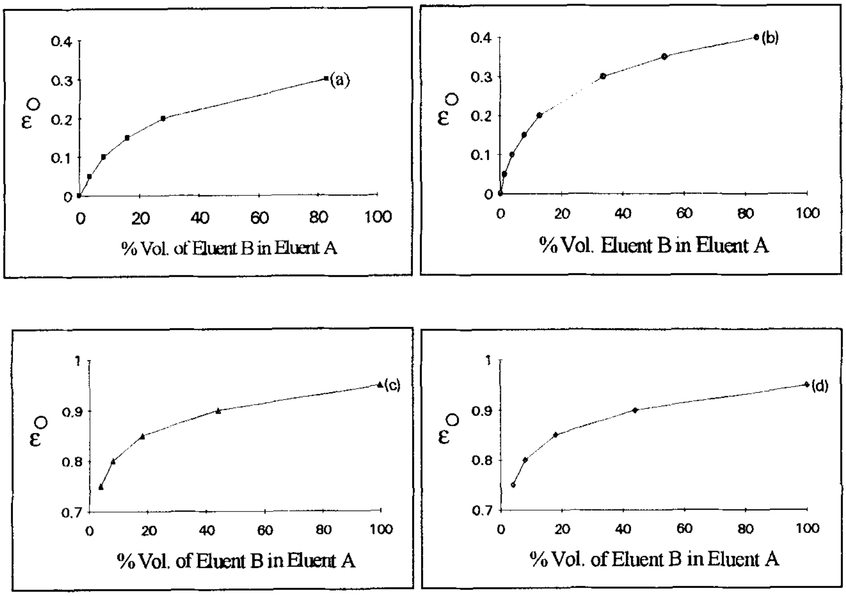

Fig. 1. The relationship between the solvent interaction parameter (ε^{o}) and eluent composition for water deactivated alumina (α = 0.6). (a) ■ -- pentane (A) --benzene (B) mixtures; (b) ⊗ -- pentane (A) -- dichloro-methane (B) mixtures. (c) ▲ -- benzene (A) -- methanol (B) mixtures (d) ◆ -- methyl acetate (A) -- methanol (B) mixtures. (After Snyder, 1968).

mixture of methyl acetate in methanol has the same ε^{o} (0.91) as a 50/50 V/V mixture of benzene and methanol. To study the sensitivity of the chromatographic separation to the dichloromethane ratio, three eluent mixtures (10:90, 12:88 and 15:85 V/V) centering on the ε = 0.18 value were used to replace the first benzene-containing eluent. Due to availability, ethyl acetate rather than methyl acetate was selected for mixing with methanol to elute the polars. By this stage of the separation, the requirement is to elute the materials remaining on the column to give a good recovery, hence the minor differences in solvent strength (methyl acetate ε^{o}= 0.60, ethyl acetate ε^{o}= 0.58) (Snyder, 1968) were not expected to effect the results obtained.

Establishment of Baseline Data

A straight-run vacuum gas oil from an intermediate-type crude oil was selected for the baseline study. Work was carried out according to the original BAM-27 procedure (3) to establish baseline data for separations involving both the UV monitoring and constant elution volume procedures. Subsequently, chromatographic runs were carried out using the three new eluent systems selected (Table 1); again, work was carried out using both fraction cut-point identification techniques.

For both procedures, the results of all three new solvent mixtures were comparable with those generated using the benzene-containing eluents. The recoveries were good (all >99%), demonstrating the satisfactory nature of the final eluent, and the yields of the individual fractions obtained were well within the repeatability limits of the original method. The central (12:88 V/V) dichloromethane/petroleum spirit mixture was selected, since any minor fluctuations in its preparation would not affect the separation.

Application of the Techniques to Other Petroleum Oils

The range of applicability of the new solvent system was tested by separating a number different petroleum oils, including gas oils, aromatic extracts, hydrocracker products and a raffinate (Table 2). Excellent agreement is apparent between the data generated for the original and the new solvent systems. Since there were no significant differences between the results generated by the two techniques, the simpler approach with the new eluent systems (no UV monitoring) was adopted for the routine separation of PCAHs concentrates.

Application to Residual Oils

As with our earlier study (7), it was found essential to deasphalt residual oils before taking them up in petroleum spirit for separation on alumina column. In this present study, a long resid from a wax-bearing intermediate crude was deasphalted with pentane (at a 30:1 pentane to oil ratio), and both the asphaltenes and the deasphalted oil (DAO) recovered quantitatively. The DAO was separated by both the original (benzene-containing) and the newly developed eluent systems (Table 3).

TABLE 1.
Alternative Eluent Systems for Separating PCAHs Fractions from a Vacuum Gas Oil

Eluent Sequence*	Number of Runs	Sample Loading (g)	SMD Fraction (% wt)	PCAH Fraction (% wt)	PCAH Fraction R.I.**	Polars (% wt)
Runs Monitored by UV:						
A***	4	2.1	79.4	16.3	1.6130	4.3
B	4	2.0	80.1	15.0	1.6012	4.9
C	7	2.2	80.5	15.1	1.6292	4.4
D	4	2.1	80.2	15.8	1.6072	4.0
Runs Performed Without UV Monitoring						
A***	9	2.5	79.4	16.2	1.6122	4.4
B	2	2.1	80.7	15.1	1.6069	4.2
C	4	2.0	80.0	16.0	1.6060	4.0
D	2	2.2	80.3	16.5	1.6091	3.2

* Sequences following the initial petroleum spirit percolation:
A - (i) benzene and petroleum spirit (25:75 V/V), (ii) benzene and methanol (50:50 V/V), (baseline data);
B - (i) dichloromethane and petroleum spirit (10:90 V/V)
(ii) methanol and ethyl acetate (40:60 V/V);
C - (i) dichloromethane and petroleum spirit (12:88 V/V),
(ii) methanol and ethyl acetate (40:60 V/V)
D - (i) dichloromethane and petroleum spirit (15:85 V/V),
(ii) methanol and ethyl acetate (40:60 V/V);

** Refractive index measured at 65°C.
*** Original sequence, generating baseline data.

Again, results well within the repeatability limits were obtained for both solvent systems, whether or not UV monitoring was employed. One pair of separations, without prior deasphalting of the sample, are also shown (Table 3). Considerable handling problems were experienced during charging the column with this oil, and a slow elution took place due to partial clogging of the column by flocculated asphaltic moieties. The

TABLE 2.
Application of the New Eluent System to Range of Hydrocarbon Oils

Sample Type	Eluent* Sequence	UV Monitoring	Number of Runs	SMD Fraction (% wt)	PCAH Fraction		Polars (% wt)
					(% wt)	R.I.**	
Straight-run VGO (Intemediate Crude)	A	-***	9	79.4	16.2	1.6122	4.4
	C	-	4	80.0	16.0	1.6060	4.0
	A	+	4	79.4	16.3	1.6130	4.3
	C	+	7	80.5	15.1	1.6242	4.4
Straight-run VGO (Naphthenic Crude)	A	-	2	85.2	13.0	1.6087	1.8
	C	-	2	85.0	12.7	****	2.3
	C	+	2	85.9	12.3	****	1.8
Straight-run Light Diesel	A	-	2	90.8	7.4	1.6220	1.8
	C	-	2	91.5	7.0	1.6345	1.5
	A	+	2	91.0	7.3	1.6342	1.7
	C	+	2	90.6	7.6	1.6331	1.8
Bright-stock Extract (Intermediate Crude)	A	-	3	40.1	47.7	1.5562	12.2
	C	-	2	41.5	46.5	1.5597	12.0
	C	+	2	40.0	48.0	1.5562	12.0
Heavy lube Extract	A	-	4	52.2	36.5	1.5972	11.3
	C	-	2	49.9	37.9	1.5905	12.2
	C	+	2	52.4	35.6	1.5887	12.0
Medium lube Raffinate	A	-	3	90.7	7.8	1.6296	1.5
	C	-	2	90.2	8.1	1.6216	1.7
Hydrocracker gas oil A	A	-	5	98.4	1.2	1.6287	0.4
	C	-	2	98.3	1.1	1.6223	0.6
Hydrocracker gas oil B	A	-	3	99.5	0.4	****	0.1
	C	-	2	99.4	0.4	****	0.2

* Sequences following the initial petroleum spirit percolation:
A - (i) benzene and petroleum spirit (25:75 V/V), (ii) benzene and methanol (50:50 V/V) (baseline data)
C - (i) dichloromethane and petroleum spirit (12:88 V/V).
(ii) methanol and ethyl acetate (40:60 V/V) (new eluent sequence).

** Refractive index measured at 65°C.

*** The presence (+) or absence (-) of UV monitoring during the elution is indicated.

**** Signifies the parameter was not determined.

TABLE 3.
Application of the New Eluent System to Residual Oils

Sample Type	Asphaltenes* Separated	Eluent** Sequence	UV Monitoring	Number of Runs	SMD Fraction (% wt)	PCAH Fraction		Polars (% wt)	Recovery (% wt)
						(% wt)	R.I. ***		
Long Resid	0.0****	C	-*****	2	52.1	23.9	1.5697	24.0	94.7
	9.3	A	-	6	50.1	22.3	1.5695	18.3	99.5
	9.3	C	-	2	50.1	23.0	1.5699	17.6	100.1
	9.3	A	+	2	50.8	22.2	1.5715	17.7	99.4
	9.3	C	+	4	50.6	22.4	1.5707	17.7	100.0
Short Resid A	25.9	A	-	2	29.7	25.3	1.5746	19.1	98.4
	25.9	C	-	2	30.0	25.0	1.5776	19.1	98.5
	25.9	C	+	2	29.4	25.7	1.5740	19.0	98.2
Short Resid B	22.7	A	-	2	36.0	25.3	1.5865	16.0	99.7
	22.7	C	-	2	36.3	25.6	1.5883	15.4	99.5

* Asphaltenes flocculated with n-pentane, at a 30:1 pentane to oil ratio.

** Sequences following the initial petroleum spirit percolation.

A - (i) benzene and petroleum spirit (25:75 V/V), (ii) benzene and methanol (50:50 V/V) (baseline data):

B - (i) dichloromethane and petroleum spirit (12:88 V/V), (ii) methanol and ethyl acetate (40:60 V/V) (new eluent sequence)

*** Refractive index at 65°C.

**** The asphaltenes and maltenes were not separated prior to the elution.

***** The presence (+) or absence (-) of UV monitoring during the elution is indicated.

rather unusual results obtained are caused by normalizing such a low recovery, the asphaltenes appear to be spread mainly amongst the PCAHs and polars fractions.

Following such good results for the DAO from a long resid, two short resids were studied (Table 3): Resid A was from a wax-free, naphthenic crude, whereas Resid B originated from a wax-bearing intermediate crude oil. The excellent results obtained confirmed the equivalence of the two eluent systems, even for such difficult materials as these short (vacuum) resids. It was found that the slightly reduced recoveries found here (98-99.5%), were reflected in data generated during the later routine application of the technique to residual oils. This was attributed, in part, to the poor solubility of a proportion of the polar/asphaltic materials in the final ethyl acetate/methanol (EA/M) eluent. This was successfully countered by the elution with pure dichloromethane both prior to, and immediately after, percolation of the EA/M eluent mixture.

General Improvements

As would be expected, it was found that the mesh range of the adsorbent was important: the presence of significant fines (< 200 mesh) reduce the interstitial void volume, resulting in an undesirably slow percolation, whereas the efficiency of the adsorbent is reduced if too great a proportion of coarse (>100 mesh) particles are present. It was decided, therefore, to sieve all alumina received for chromatographic use, and this contributed to improved precision. It was found that some batches of nominal 100-200 mesh alumina contained as little as 40% in the 100-200 mesh range, the remainder being approximately equally split between fines and coarse particles.

To check whether the eluents contributed at all to the weights of any of the fractions recovered, appropriate volumes of each were evaporated to dryness on a hot water bath, both before and after percolation down a normal partially deactivated alumina column. In all cases except one, the eluents were free of deposits; the single exception was the percolated methanol, which yielded 2-4 mg brownish-grey residue for every 50 ml eluent. The effect was also observed earlier for methanol percolated through microporous silica (9). To put this in perspective, for a 1 g sample, this methanol residue will contribute 0.2-0.4% to the overall recovery, whereas for a 10 g oil sample, the contribution will be 0.02-0.04%. Thus, the components of the new eluent system would not be expected to cause anomalous recoveries.

The UV spectrophotometric correction for the PCAHs eluted in cut 1 in the original procedures used the absorbances at 205 nm, 230 nm and 260 nm in an iterative procedure to ascertain the contribution of the PCAHs in the Cut 1 to the absorbance of the cut at 260 nm. Some rearrangement of the original expression and the elimination of the contribution of the A_{205} term allowed the expressions used to be simplified. Application of this simpler procedure led to negligible changes in the corrections, e.g., at PCAHs levels up to 5%, the differences caused by the simplification were found to be <0.25%.

Procedures Developed

1. Separation Monitored by UV.

Approximately 0.4-30 g of oil sample, depending upon the expected PCAHs content (1-90 %, by weight), are dissolved in 5-50 ml of petroleum spirit in a beaker, and charged to the alumina column. The minimum volume of petroleum spirit is used to ensure the transfer is quantitative, and elution is continued with petroleum spirit. The column effluent is sampled every 30 ml from 300 ml onwards, to monitor the progress of the separation by UV spectrophotometry. The procedure involved injecting 25 µl of eluent into a 1 cm path length, PTFE-stoppers UV cell, evaporating the solvent under a vacuum, redissolving the sample in spectrosol n-hexane, and determining the spectrum between 190 and 300 nm. The UV cell contents are collected, consolidated together and added to the appropriate chromatographic fraction after solvent stripping.

The collection of fraction 1 (SMD) is continued while the following criteria all to be met:

1. the UV absorptions near 205 and 230 nm continue to decrease with increasing eluent volume;
2 the UV absorption at 260 nm does not increase with increasing eluent volume;

3. the absorbance at 230 nm remains above 0.10 absorbance unit.

Subsequently, the collection of fraction 2 is commenced and the next eluent (dichloromethane/petroleum spirit 12:88 V/V) is added to the column; UV monitoring is continued every 25 ml until either of the two following criteria are met, when fraction 2 collection is terminated:

1. the UV absorptions at 205 and 260 nm pass through maxima and then decrease to minimum values; or
2. the absorbance at 260 nm decreases to below 0.10 absorbance units.

Then, the eluent is changed to the polars sequence and the UV monitoring is terminated. The contents of the UV cell are consolidated with fraction 2, in similar fashion to fraction 1. For this, 50 ml of dichloromethane, 100 ml of ethyl acetate/methanol (60:40 V/V) followed by a last 50 ml portion of dichloromethane and then sufficient petroleum spirit to elute the whole of the dichloromethane. In all cases, fresh eluent is added to the column when the previous is on the point of disappearing into the top of the adsorbent; care is taken not to disturb the top of the adsorbent during the addition of fresh eluent.

The solvents are evaporated from the fractions on a hot-water bath, and the resulting cuts taken to constant weight in an oven at 110°C. The percentages of each cut are normalised to 100%, to take account of handling losses and refractive indexes and UV spectra recorded for both cuts 1 and 2. An iterative procedure is used to correct for the PCAHs contamination of cut 1. This involves absorbances at 230 nm and 260 nm for cut 1, and the absorbance at 260 nm for cut 2. The calculations are shown below. This correction procedure is based upon typical, average UV absorbances for mono-, di-, and polycyclic aromatic concentrates determined earlier (3).

The above absorbances are denoted as A_1, A_2, and A_3, whereas the concentrations of cuts 1 and 2 are C_1 and C_2, respectively.

For cut 1, the first approximation for the contribution of the PCAHs to the absorbance at 260 nm is given by equation (i):

$$(A_P)_1 = A_2 - 0.20\,(A_1)_1 \qquad \text{(i)}$$

If the value of $(A_p)_1$ found is zero or negative, there is no correction to be applied. However, if $(A_p)_1$ is positive, then the following iterative procedure has to be undertaken, since the PCAHs materials also contribute to the UV absorbance at 230 nm.

Due to this contribution, it is necessary to correct the absorbance of the diaromatics according to expression (ii):

$$(A_1)_2 = A_1 - (A_p)_1 \qquad \text{(ii)}$$

This value of $(A_1)_2$ is fed into expression (iii), where an improved estimate of (A_p) is then generated, $(A_p)_2$;

$$(A_p)_2 = A_2 - 0.20\,(A_1)_2 \qquad \text{(iii)}$$

This value of $(A_p)_2$ is back-substituted into expression (ii), resulting in an improved estimate for $(A_1)_1$ for resubstitution into (iii). Iteration is continued until two successive values of $(A_p)_1$ differ by less than 0.5%. Usually, no more than 4 or 5 iterations are needed. The PCAHs eluting in Cut 1 can now be estimated from (iv):

$$P = \frac{(A_p)_1 \cdot C_2 \cdot 100}{C_1 \cdot A_3} \,\% \qquad \text{(iv)}$$

The value of P is used to correct the yields of both Cuts 1 and 2 for the PCAHs eluting in Cut 1, caused by its slightly extended elution volume, the objective of which is to eliminate the di-aromatics from Cut 2.

2. *Separation with Constant Elution Volume Cut-Points.*

In this simplified procedure, the sample is charged to the adsorbent column as described above. Subsequently, the first 420 ml petroleum spirit eluting are collected as the first (saturates plus mono- and di-aromatics) fraction; in the event that more than 10 ml are used to dissolve the sample and transfer it to the column (i.e., x ml), then the volume collected for the first fraction should be (410 + x) ml. Subsequently, the PCAHs are eluted with 250 ml of dichloro-methane/petroleum spirit, and the polars with (in sequence) 50 ml dichloromethane, 100 ml ethyl acetate/methanol (60:40 V/V) and 50 ml dichloromethane. Care has to be taken during fraction collection to ensure that the receiver change-over occurs between 5 and 10 ml before the next eluent begins to exit the column. Progress of the eluent fronts can normally be monitored by following movement of either the colour boundary or the warm band caused by interaction of the new, more polar, eluent with the alumina. The fractions are stripped of solvent, quantified and any corrections made for the presence of PCAHs in the first fraction, as in the above detailed procedure.

Precision

The precision of the method was established from the standard deviation for duplicate analyses of the eleven different oils and residues studied, with PCAHs contents in the range 0.4 to 48.0% wt. The data were evaluated statistically, employing the Student's t approach (10), and the repeatability of the PCAHs fraction separated was established as +/- 4.6%, relative, at the 95% confidence limits, superior to that for the original procedure (+/- 6.9%, relative).

Conclusions

A safer elutropic system using volatile solvents was established for separating the PCAHs and polar concentrates from hydrocarbon oils boiling above 250°C. The method is applicable to a wide range of different petroleum oils and resids, and yields results comparable with the original procedure.

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