

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597273>

Replacement of Benzene and Carbon Tetrachloride with Less Hazardous Eluants in Chromatography for the Determination of Saturates Content of Hydrocarbon Oils

Z. H. Khan^a; K. Marron^a

^a Petroleum Technology Department Petroleum, Petrochemicals and Materials Division, Safat, Kuwait

To cite this Article Khan, Z. H. and Marron, K.(1988) 'Replacement of Benzene and Carbon Tetrachloride with Less Hazardous Eluants in Chromatography for the Determination of Saturates Content of Hydrocarbon Oils', *Journal of Liquid Chromatography & Related Technologies*, 11: 8, 1605 – 1613

To link to this Article: DOI: 10.1080/01483918808076724

URL: <http://dx.doi.org/10.1080/01483918808076724>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

REPLACEMENT OF BENZENE AND CARBON TETRACHLORIDE WITH LESS HAZARDOUS ELUANTS IN CHROMATOGRAPHY FOR THE DETERMINATION OF SATURATES CONTENT OF HYDROCARBON OILS

Z. H. Khan and K. Marron

*Petroleum Technology Department
Petroleum, Petrochemicals and Materials Division
P. O. Box 24885
13109 Safat, Kuwait*

ABSTRACT

The method for the separation of heavy petroleum hydrocarbons into structural types—saturates, aromatics and polar materials has been modified. The eluants, carbon tetrachloride and benzene that are carcinogenic and toxic, were successfully replaced with dichloromethane and petroleum spirit mixtures (35:65 and 82:18, respectively). The modified method was successfully applied to raffinates, extracts, hydrocracker products, heavy distillates, atmospheric and vacuum bottoms and other deasphalted residues (maltenes).

An improved handling technique was developed for hydrocarbon oils containing asphaltenes utilizing a preliminary deasphalting step with n-pentane.

The precision of the technique was established for the saturates measured at $\pm 0.4\%$ for a wide range of hydrocarbon oils.

INTRODUCTION

High-boiling petroleum cuts have been separated into saturates, aromatics and polar/resin fractions by traditional open-column chromatographic techniques

for many years (1 - 4). These methods are, in general, too time consuming (taking from 4-8 hr) for refinery quality control, and attempts are being made to develop automatable high performance liquid chromatographic (HPLC) techniques to replace them. In the absence of a satisfactory mass-detector, however, response factor variation with crude oil and sample boiling range has proved to be a stumbling block to the HPLC analysis of unknown samples. Prior large-scale separations are still required to obtain calibration materials for the quantification of HPLC separations of routine refinery samples. Work in the last decade (5, 6), led to the development of a compromise in technique (7) whereby preparative scale HPLC is utilised for the initial separation of the sample according to hydrocarbon type, with a subsequent gravimetric finish following solvent evaporation.

Since fully automated HPLC techniques for analysing high-boiling petroleum fractions have not yet been developed, the traditional open-column methods can be expected to be utilized for some years to come. Unfortunately, when some of these methods were developed, the potent carcinogen benzene (8) was utilized in the elutropic series. This laboratory has been concerned with reducing the usage of hazardous materials as much as possible and therefore work has begun on finding a relatively safe elutropic series for the separation method (3) that has already been well established. Initial work was carried out using toluene to replace benzene because of its similar structure. However, it was found that incomplete elution of the aromatics resulted and the toluene was slow to strip from the oil fractions. Therefore, a detailed study was undertaken using a range of more volatile eluant mixtures. An alternative elution system was developed employing solvent mixtures equivalent in solvent strength to those in the original. Baseline data generated using the original method was utilized to show that the separation efficiency was not changed. This paper describes the development of the new elutropic series, mixture of dichloromethane and petroleum spirit, and its subsequent application to a wide range of petroleum products.

EXPERIMENTAL SECTION

Eluants

The following (A.R.), grade solvents were used for the chromatographic separation:

Petroleum spirit (60–80°C), benzene, toluene, dichloromethane, methanol and acetone.

Adsorbents

Fresh Davison 923 silica gel activated at 150°C for four hr, and Alcoa F₂₀ alumina activated at 400°C for four hr were utilized.

Columns

Glass chromatography columns, 1.4 cm x 50 cm, were used in this study.

Samples

A wide range of 250°C + boiling range products were studied. These included straight run diesel oil, heavy diesel oil, gas oil, hydrocracker products, light, medium and heavy aromatic extracts, deasphalted atmospheric and vacuum residues.

RESULTS AND DISCUSSION

Selection of the Eluants

The selection of the correct eluant is a major task for a suitable adsorption chromatographic separation system. Three basic factors contribute to eluant strength: (a) interaction between eluant molecules and a sample molecule in solution; (b) interaction between eluant molecules and a sample molecule in the adsorbed phase; and (c) interaction between an adsorbed eluant molecule and the adsorbent (9). To achieve the separation, the sample molecules already adsorbed have to be displaced with a suitable eluant. The thermodynamics of adsorption have been dealt with in detail by Synder (9). The interaction between the eluant and the adsorbent, the solvent strength denoted by ϵ^0 is the adsorption energy per unit area of standard activity surface. By convention, ϵ^0 is taken as zero for pentane and this leads to positive values of ϵ^0 in the range 0–1.0 for other more polar eluants.

The solvent strength parameter ϵ^0 was calculated by Synder (9) for a variety of pure eluants and several adsorbents, and relevant values are shown in Fig. 1. A 82:18 V/V mixture of dichloromethane pentane has the same ϵ^0 as

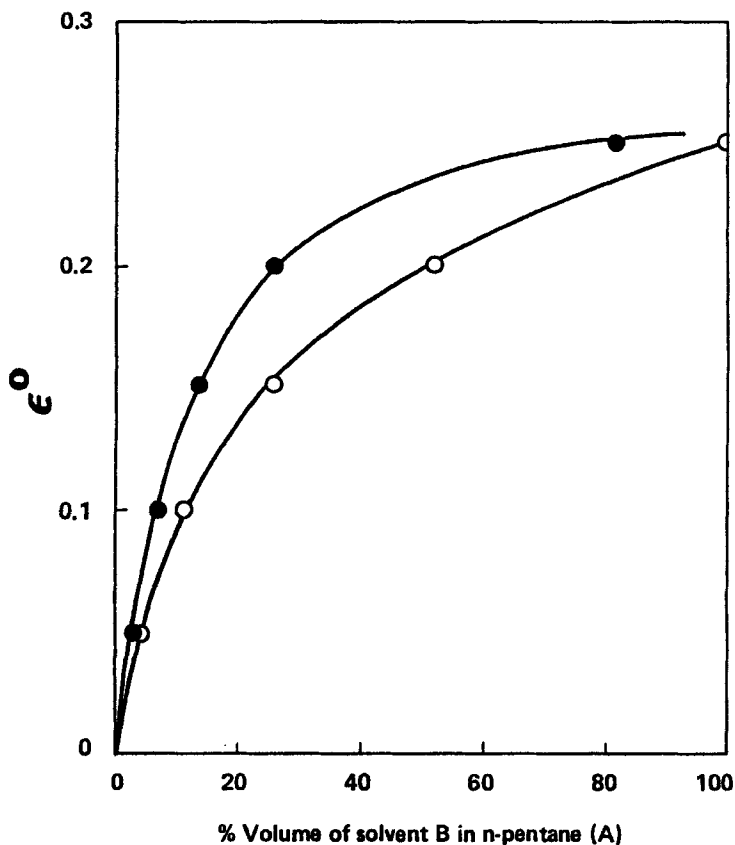


Fig. 1. The relationship between the solvent interaction parameter (ϵ^0) and eluent composition for water deactivated silica ($\alpha = 0.7$). \circ — pentane (A)-benzene (B) mixtures; \bullet — pentane (A)-dichloromethane (B) mixtures. (After Snyder, 1964)

benzene (0.25). To study the sensitivity of the chromatographic separation to the dichloromethane ratio, three eluant mixtures (85:15; 82:18; 80:20) centering on the $\epsilon^0 = 0.25$ value were used to replace the benzene.

Establishment of Baseline Data

A hydrocracker product with a relatively high content of aromatics and high-boiling range was selected for the baseline study. This material was of

very low sulphur and nitrogen content and would result in negligible chromatographic interference by heterocyclic materials. Work was carried out according to the original BAM 74 procedure (3) to establish the baseline data and then separations were made using the three systems (Table 1).

The results of all three solvent mixtures are comparable with the results obtained using benzene as an eluant (Table 1). Recoveries are good and the yields of saturates, aromatics and polar hydrocarbons are within the repeatability limits. The dichloromethane/petroleum spirit mixture 82:18 V/V was selected, since any minor fluctuations in its preparation would not affect the separation results.

Upon the successful replacement of the benzene, two mixtures of methylene chloride-petroleum spirit (35:65 and 10:90) were used as potential replacements for carbon tetrachloride, and separations were made for a range of petroleum products (Table 2). The results were comparable and the carbon tetrachloride was replaced with the 35:65 V/V mixture of dichloromethane/petroleum spirit due to the possible higher overall recoveries.

Procedure Developed

Approximately 1 g of sample in 5 ml aromatic-free petroleum spirit (60–80°C) was adsorbed on a silica gel (40 g) column and elution was continued with the petroleum spirit. The first two fractions (40 and 20 ml) were collected. The elution was then continued with 50 ml of dichloromethane – petroleum spirit (35:65 V/V) and 50 ml of dichloromethane– petroleum spirit (82:18 V/V) to elute total aromatic hydrocarbons. Polar hydrocarbons were eluted with 150 ml of acetone. Each volume of the solvent was added when the previous solvent level was just disappearing into the silica gel. After the evaporation of the solvents, the weights of the hydrocarbon cuts eluted were determined. The correction for the aromatic hydrocarbon contaminants in the first two fractions was again made by measuring the adsorbance at 220 nm in iso-octane solution, as in the original procedure. For deasphalted residues, a pad of alumina (5 g) was placed on top of the silica gel and the polar hydrocarbons were eluted with methanol.

Application of the Technique to Other Hydrocarbon Oils

The application of the technique was tested and extended by using a variety of samples ranging from light diesel to extracts, and short and long

TABLE 1
Alternative Solvent Systems for Separating Saturates from a
Hydrocracker Oil

Solvent* System for the Aromatics	Runs	Satura- tes** (% wt)	Aroma- tics (% wt)	Polars (% wt)	Recovery (% wt)	Standard Deviation for Saturates
A	8	77.4	22.2	0.4	99.7	0.3
B	4	76.5	23.0	0.5	99.5	0.2
C	6	76.8	22.6	0.6	99.7	0.4
D	4	76.9	22.7	0.4	99.9	0.3

- * A: Carbon tetrachloride and benzene (baseline case)
 B: Carbon tetrachloride followed by dichloromethane-petroleum spirit (80:20)
 C: Carbon tetrachloride followed by dichloromethane-petroleum spirit (82:18)
 D: Carbon tetrachloride followed by dichloromethane-petroleum spirit (85:15)

** Eluted by petroleum spirit.

TABLE 2
The Replacement of the Carbon Tetrachloride in the Elutropic
Series.

Sample	System*	Runs	Satura- tes ** (% wt)	Aro- matics (% wt)	Polars (% wt)	Recovery (% wt)
Heavy aromatic extract	Y	1	7.8	87.4	4.8	97.7
	Z	2	7.9	87.7	4.4	98.0
Medium aromatic extract	Y	2	10.0	85.6	4.4	98.9
	Z	2	10.1	85.2	4.7	99.6
Light aromatic extract	Y	2	7.4	88.1	4.5	99.0
	Z	2	7.3	88.6	4.1	99.4

* Y: Dichloromethane petroleum spirit (10:90) followed by dichloromethane/petroleum spirit (82:18).

Z: Dichloromethane petroleum spirit (35:65) followed by dichloromethane/petroleum spirit (82:18).

** Eluted with petroleum spirit.

residues. The data obtained were compared with recoveries obtained using carbon tetrachloride and benzene as an eluant (Table 3). All the results, without exception, were comparable with those obtained with the original elutropic series. The low recovery (95%) obtained for the straight-run light diesel oil (boiling range between 166° and 382°C) was due to the volatilization of light end materials. These light end losses could be significantly reduced by stripping the solvent at a lower temperature (40°C), but this was not considered or tested in the present study.

It was found necessary to introduce an initial deasphalting step with an appropriate solvent when residual materials were to be separated. In the present study, an atmospheric residue (>400°C) was deasphalted at a 1:30 ratio with n-pentane, n-hexane and n-heptane giving 12.0%, 7.8% and 6.2% by weight of asphaltenes, respectively. These results show that the co-precipitation of other crude components is an important effect and solvent should be noted when reporting the yields of asphaltenes. This is in accordance with the findings of Cotte and Calderon (10). The removal of the maximum quantity of asphaltenic materials was found to be most convenient for sample charging to the column during the saturates content determination. However, even with deasphalted samples, low recoveries were obtained due to irreversible adsorption. Similar effects were observed by Sawatzky et al., (11) who had to use hot pyridine to elute the final polar, heterocyclic materials during the chromatographic separation of residual materials.

Precision

The precision of the method was established from the standard deviation for duplicate analyses of ten different oils, including residues, with saturates contents ranging from 7 % to 77 %. The data were evaluated statistically, employing the Student's t approach (12), and the repeatability of the saturates was established as $\pm 0.4\%$, at the 95% confidence level, identical to that of the original elutropic series.

In summary, a safe elutropic system utilizing volatile solvents was established for separating and quantifying the saturates and aromatics in hydrocarbon oils boiling above 250°C. This revised method yields precise results comparable with the original procedure.

TABLE 3
The Application of the Revised Elutropic Series to a Range of
Petroleum Products

Sample	Solvent system for Aromatics*	Runs	Satura- tes** (% wt)	Aroma- tics (% wt)	Polars (% wt)	Recovery (% wt)
Hydrocracker oil	A	8	77.4	22.2	0.4	99.7
	Z	8	76.5	23.2	0.3	99.1
Straight run diesel oil	A	2	50.7	48.1	1.2	94.8
	Z	2	51.7	47.8	1.1	95.0
Straight run heavy diesel oil	A	2	43.1	54.2	2.7	99.5
	Z	2	43.5	54.2	2.3	100.0
Aromatic extract from deasphalted bright stock	A	2	7.8	85.5	6.7	97.4
	Z	2	7.9	87.7	4.4	98.0
Aromatic extract from medium distillate	A	2	10.2	84.2	5.6	100.1
	Z	2	10.1	85.2	4.7	99.6
Aromatic extract from light distillate	A	2	7.5	87.5	5.0	99.5
	Z	2	7.3	88.6	4.1	99.4
Deasphalted*** long residue	A	2	26.1	55.9	6.0	92.1
	Z	2	26.4	57.5	4.1	93.7
Deasphalted**** short residue	A	2	11.9	59.0	6.5	91.0
	Z	2	12.1	58.8	6.5	90.3

* A: Carbon tetrachloride and benzene

Z: Dichloromethane/petroleum spirit (35:65) followed by
dichloromethane/petroleum spirit (82:18)

** Eluted with petroleum spirit

*** Originally 12.0% asphaltenes

**** Originally 22.6% asphaltenes

ACKNOWLEDGEMENT

The authors thank the management of the Kuwait Institute for Scientific Research for the financial support and encouragement given during this work and for permission to publish this paper.

The authors thank Mr. Thamir A. Majeed for carefully performing the experimental work.

REFERENCES

- (1) ASTM D-2007-80. "Annual Book of ASTM Standards", Part 24; American Society for Testing and Materials: New York, 1985; pp. 155-163.
- (2) ASTM D-2549. "Annual Book of ASTM Standards", Part 24; American Society for Testing and Materials: New York 1985; pp. 464-468.
- (3) Marron, K. In "*Recent Analytical Developments in the Petroleum Industry*". Ed. ECIT. D.R. Hodges; Applied Science: London, 1974; pp. 120-135.
- (4) Snyder, L.P.; Roth, W.F. *Analytical Chemistry*. 1964, 36, pp.128-131.
- (5) Suatoni, J.C.; Swab, R.E. *Journal of Chromatographic Science*. 1976, 14, pp. 535-537.
- (6) Lynes, A.; Gadsby, T.W. In "Petroanalysis '81", Ed. C.B. Crump; John Wiley and Sons: Chichester; 1982; pp. 286-200.
- (7) IP 368-84. *Methods for Analysis and Testing*. Institute of Petroleum. 1986 (1): 368. 1-368.4.
- (8) Sittig, M. "Handbook of Toxic and Hazardous Chemicals", Noyes Publication: New Jersey, 1981; pp. 395-399.
- (9) Snyder, L.R. "Principles of Adsorption Chromatography. The Separation of Non-Ionic Organic Compounds". Edward Arnold: London, 1968.
- (10) Cotte, E.A.; Calderon J.L. 1981, "Preprints - ACS Div. Petroleum Chemistry". American Chemical Society, pp. 538-547.
- (11) Sawatzky, H.; George, A.E., Smiley G.T.; Montgomery D.S. *Fuel*. 1979; 55, pp. 16-20.
- (12) Weast, R.C.; Astle, M.J. "Handbook of Chemistry and Physics", 2nd ed.; CRC Press Inc: Florida, 1981-1982.