Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Gel Chromatographic Isolation of Resins and Asphaltene Material in Crude Oils

A. Aaberg[a]; K. Tjessem[b]
[a] DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BERGEN, NORWAY [b] NORSK HYDRO A/S, SANDVIKA, NORWAY

To cite this Article Aaberg, A. and Tjessem, K.(1982) 'Gel Chromatographic Isolation of Resins and Asphaltene Material in Crude Oils', Separation Science and Technology, 17: 12, 1425 — 1432
To link to this Article: DOI: 10.1080/01496398208055630
URL: http://dx.doi.org/10.1080/01496398208055630

SEPARATION SCIENCE AND TECHNOLOGY, 17(12), pp. 1425–1432, 1982-83

Gel Chromatographic Isolation of Resins and Asphaltene Material in Crude Oils

A. AABERG

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BERGEN
N-5014 BERGEN-U, NORWAY

K. TJESSEM*

NORSK HYDRO A/S
KJ0RBOKOLLEN, 1301 SANDVIKA, NORWAY

Abstract

A new method is described for fast, simple, and quantitative isolation of high molecular resinous and asphaltene material in crude oils without any alteration of the petroleum constituents. The method is based on gel permeation on Sephadex LH-20 using chloroform as the mobile phase which isolates the high molecular weight resins and asphaltene material from the remainder of the crude oil, and a subsequent gel filtration on Sephadex LH-60 separates resins from asphaltenes if required.

INTRODUCTION

Asphaltenes and most resins are complex structural arrangements made of polycyclic aromatic and naphthenoaromatic nuclei characterized by a high heteroatom content and a chemical composition and molecular weight which are highly variable even among samples of the same elemental composition (*1–3*). The average molecular weight is unknown, but it is commonly accepted that it may extend up to several thousands for asphaltenes with a somewhat lower number for resins (*3–5*).

---

*To whom correspondence should be addressed.

Asphaltenes and resins have been found to be present in all crude oils in concentrations which may vary between a few tenths of a percent up to as much as 20% by weight, and much work has been devoted to characterizing asphaltenes with respect to their effect on rheological properties (*3*). The heavy end members of petroleum may also have important geochemical implications, offering a clue to petroleum generation and having been shown to be a useful parameter in the reconstruction of the geology of organic matter found in the geosphere (*2*, *6*). Recent studies have also shown that these components play a crucial role in the weathering of spilled oil in the environment (*7*). It may also prove possible to use these constituents to get a firmer source identification of spilled oil than has previously been the case.

The heavy end members of petroleum are often separated from the remaining part of the oil by distillation, but this process suffers from the disadvantage that chemical changes might occur in the distillate due to high temperatures. Deasphalting and removal of resinous compounds can also be achieved by solvent partitioning in a two-stage process using an excess of the nonpolar solvents *n*-propane and *n*-pentane (*2*), or may be achieved by a combined procedure using solvent partioning and subsequent adsorption chromatography (*2*).

These procedures, which are used extensively today, are also associated with serious drawbacks (*8*).

This paper describes our experience in using gel filtration chromatography with the liphophilic gels Sephadex LH-20 and Sephadex LH-60 to obtain very clean isolates of the high molecular material from petroleum. Gel permeation chromatography circumvents the above-mentioned drawbacks to a high degree insofar as it gives a fractionation depending only on molecular size, whereas all other techniques involve both the functional nature and the molecular weight.

EXPERIMENTAL SECTION

Material Used

The following crude and refined products have been used in this experiment: Ekofisk crude oil, Romanisho crude oil (USSR), Nigerian crude oil, Argull crude oil (North Sea), Iranian crude oil, Saudi Arabian heavy gas oil, and Saudi Arabian light gas oil.

Chromatographic Procedure

Gel chromatography on Sephadex LH-20 and Sephadex LH-60 (Pharmacia Fine Chemicals, Sweden) with chloroform as the mobile phase was performed in the following way. The gels were allowed to swell overnight in a mixture of chloroform/cyclohexane (3:1) and then packed in a 1.27 × 109 cm glass Cheminert LC column (Laboratory Data Control 1, Riviera Beach, Florida) as a slurry. The gel was settled and packed downward through the bed at a flow rate of 5.0 mL/min with pure chloroform to elute all the cyclohexane by using a Constametric L solvent delivery system. The system was equipped with a filter photometer detector Model 1203 from LDC operating at 254 nm. The operating flow rate was set at 2.0 mL/min for chromatography on Sephadex LH-20 and 0.67 mL/min for chromatography on Sephadex LH-60.

RESULTS AND DISCUSSION

A general elution profile as illustrated in Fig. 1 for Romanisho crude oil, Iranian heavy crude oil, and Argull crude oil, all containing appreciable amounts of resinous and asphaltene material; Ekofisk crude oil and Nigerian

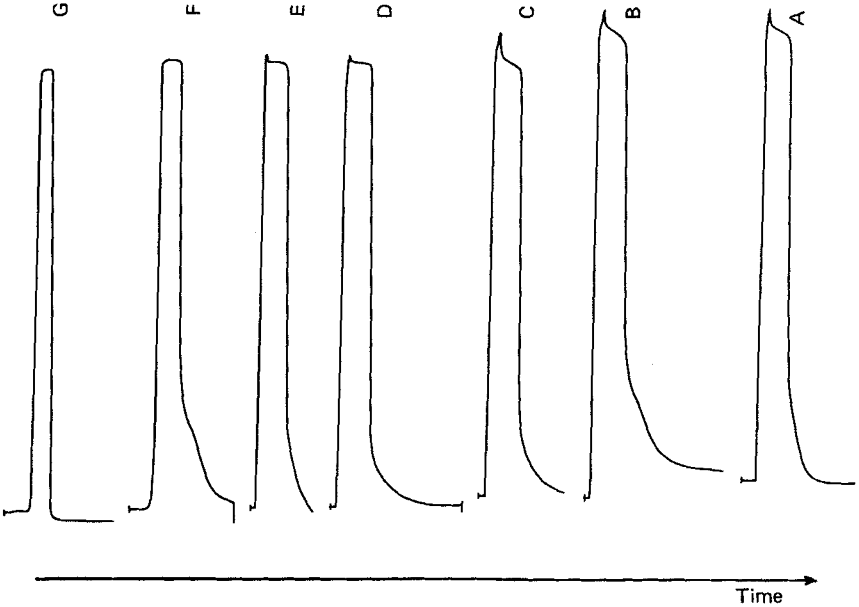

FIG. 1. Gel chromatographic trace on Sephadex LH-20 with chloroform as the mobile phase of (A) Romanisho crude oil (USSR), (B) Iranian crude oil, (C) Argull crude oil (North Sea), (D) Ekofisk crude oil (North Sea), (E) Nigerian crude oil, (F) Saudi Arabian heavy gas oil, (G) Saudi Arabian light gas oil. Injected amount 200 μL of a 1:1 mixture oil dissolved in chloroform.

crude oil, which are rather lean in the same constituents, especially asphaltenes; and Saudi Arabian heavy and light gas oil (refined products containing no resins and asphaltenes) constitute typical examples of chromatograms for petroleums studied in our laboratory.

The rather unusual sharp peak eluting close to the solvent front has been found to be very characteristic for crude oils containing resins and asphaltenes and could not be observed with refined oils lacking these components. The observed peak shape can be explained by virtue of size exclusion of resins and asphaltenes existing as agglomerates in rather concentrated solutions (*8*), resulting in a very narrow band which can easily be visualized in gel filtration chromatography with glass columns. This allows easy monitoring of the separation in progress and the collection of peaks of interest. By careful inspection of the chromatogram a small peak eluting in the front of the asphaltene/resin peak is also apparent.

The separation efficiency has been found to be fairly independent of flow rates between 2.0 and 0.25 mL/min as well as the amount of sample loaded onto the column as long as it is not overloaded.

In view of the importance of interaction problems in asphaltenes and resins, it was considered desirable to study the influence of concentration of the injected solution on the shapes of the chromatograms for a couple of the crude oils studied.

The shapes of the chromatograms as a function of the amount of material injected is shown in Fig. 2 as illustrated by Romanisho and Ekofisk crude oils.

Apparently the detector does not respond in a linear way to concentrations over a critical range. This is clearly illustrated in Fig. 2 for chromatograms A and B, which should exhibit a similar appearance to the one illustrated by C. The same phenomenon can also be observed in chromatogram A for Ekofisk crude oil.

These investigations have revealed that for both types of crude oils there is a pronounced change in appearance as a function of concentration. The most pronounced change is the disappearance of the peak eluting in the front of the resin/asphaltene peak and a subsequent buildup of a second peak of increasing concentration and retention time with decreasing concentration of the sample injected.

These peaks have been subjected to GC screening with glass capillary columns. No peaks were evident on programming up to 320° C with hydrogen as a carrier gas. This strongly indicates that the peaks cannot be of low molecular weight. The most likely explanation for this phenomenon is a dissociation of the asphaltene and resins agglomerates into micelles by simple dilution, the intensity of this process being reflected by the force of the interactions.

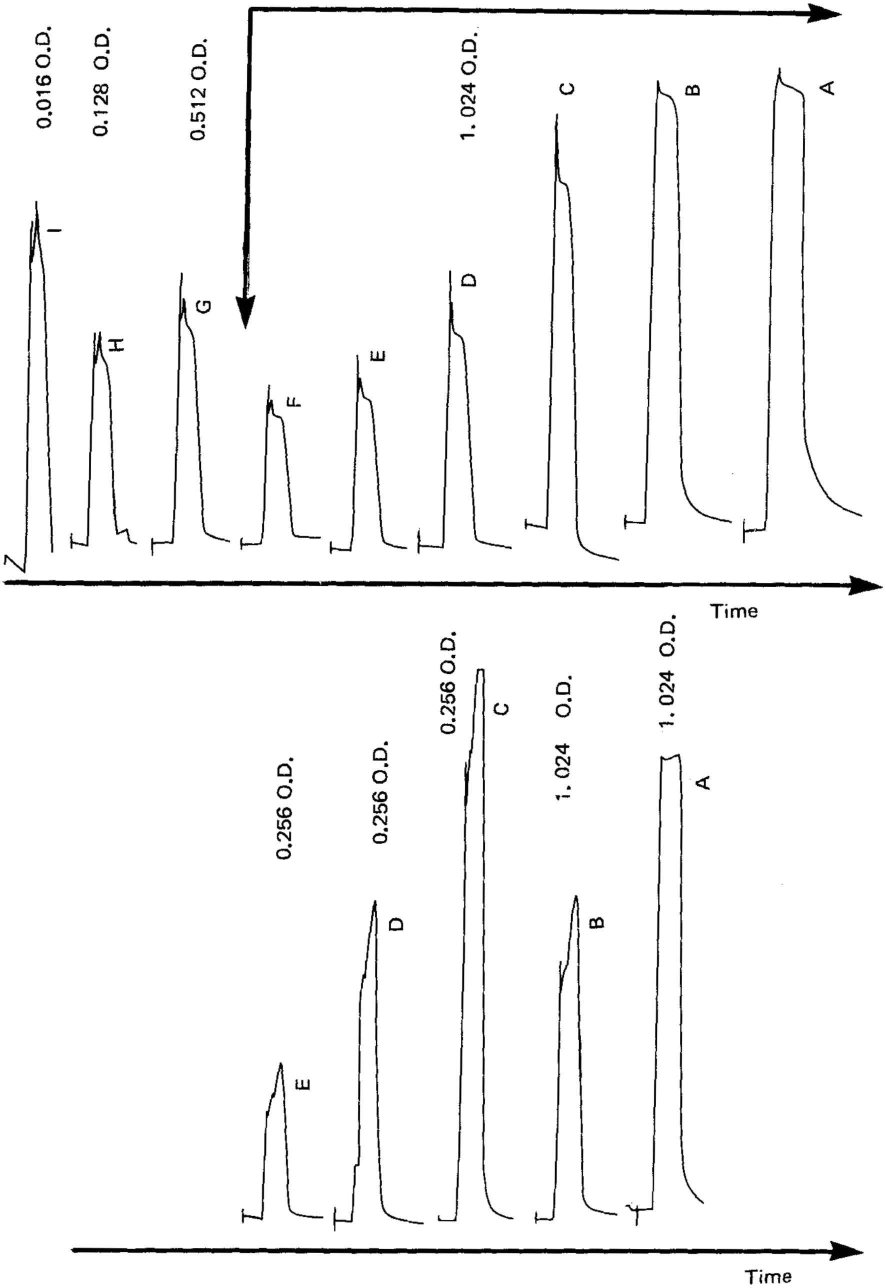

FIG. 2. Effect of concentration on the gel chromatographic trace of Romanisho crude oil (USSR) and Ekofisk crude oil (North Sea). Top: Injected amount of 100 μL of various mixtures of the Russian crude oil dissolved in chloroform. A (1:1), B (1:3), C (1:7), D (1:15), E (1:23), F (1:37), G (1:39), H (1:199), I (1:999). Attenuation used indicated on the figure. Bottom: Injected amount of 100 μL of various mixtures of Ekofisk crude oil dissolved in chloroform. A (1:2), B (1:9), C (1:24), D (1:49), E (1:99). Attenuation used is indicated on the figure.

The commonly accepted structural model for asphaltenes is thought to consist of asphaltene particles grouping together to form agglomerates (*9, 10*).

Asphaltenes and resins have been found to coelute by gel filtration chromatography on Sephadex LH-20 using chloroform as the mobile phase. This is the result of injecting separate solutions of resins and asphaltenes obtained by a tedious procedure modified after Pozydysnev et al. (*11*).

A further fractionation of the sharp peak isolated by gel chromatography on Sephadex LH-20 according to molecular size can be accomplished by gel chromatography on Sephadex LH-60 using chloroform as the mobile phase. This fractionation leads essentially to a separation of asphaltenes and resins although a shoulder can be seen to elute in the front of the resin peak. Strangely, the position of this peak is rather dependent on the composition of the mobile phase. Inclusion of a small amount of ethanol (0.8%) in the mobile phase results in a substantial reduction in retention time for this peak as illustrated in Fig. 3.

The most likely explanation for this phenomenon is retardation of some portion of the asphaltenes containing strongly polar groups with pure chloroform as the mobile phase. Addition of ethanol to the mobile phase makes this adsorption effect less pronounced.

Confirmation of the elution behavior of asphaltenes and resins has been done by injecting separate solutions of resins and asphaltenes obtained by the method described earlier in this paper.

The most important advantage with this isolation procedure is its simplicity and the fact that it makes possible a complete isolation of asphaltenes and resinous constituents without influencing the other constituents in any way. This is not the case with the other deasphalting methods being used. Petroleum is a delicately balanced mixture of compounds that depend on each other for solubility. When this composition is changed by adding an excess of a low molecular weight hydrocarbon solvent, the balance is upset so that low molecular weight polar constituents and the higher molecular weight components are no longer soluble. The result is that these compound classes precipitate.

The stability of the supermolecular formation formed is determined under these conditions not only by the donor-acceptor interactions with partitioned heteroatoms, but also by the similarity of the structures of the hydrocarbon fragments of the moieties enriched in condensed aromatic and naphthenoaromatic rings. Nor can one exclude the role of the formation of clathrate compounds by a variety of lower molecular weight components with these macromolecules, the former being enclosed in hollow cells of the latter. Recent studies have established noticeable amounts of C_{30}–C_{40} *n*-alkanes

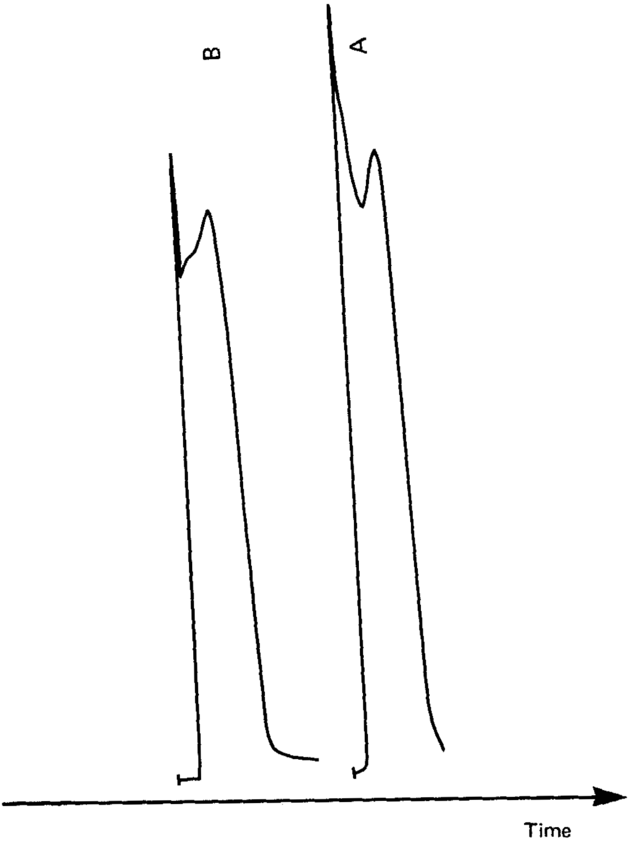

FIG. 3. Gel chromatographic separation of resins and asphaltenes on Sephadex LH-60 using different mobile phases. A: Chloroform containing 0.8% ethanol. B: Purified chloroform containing only traces of ethanol.

entrapped within the higher molecular weight asphaltenes precipitated by adding an excess of a low boiling hydrocarbon solvent. These entrapped constituents, however, can be removed by chromatography prior to solvent partitioning (*6*).

REFERENCES

1. T. Ignasiak, A. V. Kemp Jones and O. P. Strausz, in *Oil Sands and Oil Shale Chemistry* (O. P. Strausz and E. M. Lown, eds.), Verlag Chemie, New York, 1978, pp. 211–222.

2. B. P. Tissot and D. H. Welte, in *Petroleum Formation and Occurrence,* Springer, Berlin, 1978, pp. 361–363.
3. T. F. Yen, *Energy Sources, 1,* 447–463 (1973).
4. T. F. Yen, C. S. Wen, J. T. Kwan, and E. Chow, *Am. Chem. Soc., Div. Fuel. Chem. Prepr., 22*(3), 118–125 (1977).
5. J. F. McKay, P. J. Amend, T. E. Cogswell, P. M. Harrisberger, R. B. Erickson, and D. R. Latham, *Ibid., 21,* 708–715 (1977).
6. I. Rubenstein, C. Spyckerelle, and O. P. Strausz, *Geochim. Cosmochim. Acta, 43,* 1–6 (1979).
7. K. Tjessem, A. Aaberg, and T. Barth, Unpublished Results.
8. G. D. Galpern, *Russ. Chem. Rev., 45*(8), 701–720 (1976).
9. J. P. Dickie and T. F. Yen, *Anal. Chem., 39,* 1847–1852 (1967).
10. T. F. Yen, *Am. Chem. Soc. Meeting Prepr., F,* 102–114 (1972).
11. G. N. Pozdyshev, A. A. Petrov, and A. M. Makarova, *Khim. Tekhnol. Topl. Masel, 1,* 18–23 (1969).

Received by editor March 3, 1982