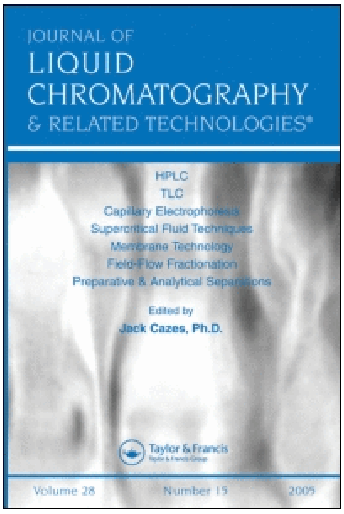

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Fuel Oil Classification by Gel Permeation Chromatography

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FUEL OIL CLASSIFICATION BY GEL PERMEATION CHROMATOGRAPHY

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ABSTRACT

The use of the gel permeation chromatography (GPC) in the petrochemical laboratory is demonstrated by experimental optimization of the separation, detection and results calculation for fuel oil samples. A chromatographic response based on the fuel oil GPC separation and detection is compared with results of Conradson carbon residue (CCR) determination - which is one of the standard petrochemical tests for residue fuel. The linear relationship between the results of both tests was confirmed. The coincidence of the chromatographic method with the CCR determination is better than ±1.5% in the range 7.5 - 18.5% CCR. Comparison of refractive and UV detection for fuel oil classification is presented.

INTRODUCTION

GPC is considered as general method in petroleum analyses (1). The goal of the GPC methods development in petrochemical laboratory is to obtain molecular distribution due to a column separation with consequent detection of the components. Residual fuel contains residues from various processing units that can vary from different refineries and frequently these residues are blended with low viscosity components to meet the requirements of the market. The identification of chemical individuals, even not groups of hydrocarbons in fuel oil is not therefore the reason of the investigation. The chromatographic results presented in form of the petrochemical parameters are more significant for the testing of the fuel quality than the separation and identification of the chemical components. Existing approaches to the fuel oil testing use measures of distillations and pyrolyses residues as described in the D 189 ASTM method - the Conradson carbon residue determination (2).

The essence of the chromatographic information is in molecular weight/size distribution. The high molecular part of a fuel oil is considered as a reason for carbon and coke deposits formed under the combustion. The direct correlation between carbon and coke deposits presence and cylinder wear of the diesel engines was confirmed (3).

Here is reported a GPC method for routine classification of fuel oils. The chromatographic system used in this study comprises an isocratic elution by tetrahydrofurane as mobile phase and styrene-divinylbenzene gel as stationary phase. The correlation between chromatographic results and results of the CCR determination are described.

EXPERIMENTAL

Apparatus

The apparatus consisted of Perkin Elmer models: serie 2/1 Liquid Chromatograph, 7010 septumless syringe injector (6 µl sample loop) and 65 variable wavelength UV detector. The refractive index detector was Showa Denko SE 11 model. A computing integrator system Supergrator (CSI, Austin, TX, U.S.A.) was used for cumulative area measurement and data treatment.

Shodex A 803 S (25cm x 8.0 mm i.d.) analytical column (Showa Denko K.K., Tokyo, Japan) was used in this study.

Standards, reagents and samples

The individual standard solutions were prepared from the Perkin Elmer Standard kit of monodispersed polystyrenes by dissolving in mobile phase. The standards used for the calibration and testing of the column had molecular weights 600: 800: 2200: 4000: 9000 and 1 450 000.

Tetrahydrofurane and acetone, of HPLC grade, were obtained from Rathburn Chemicals Ltd., U.K.

The samples used in this study come from the Veritas fuel quality testing program.

RESULTS & DISCUSSION

Refractive index (RI) and UV detection were attempted to define optimal condition for the correlation between the CCR determination and the results of the GPC separation.

Fig. 1 shows the elution profile detected after elution by tetrahydrofurane (THF) with RI detector. It is noteworthy that compounds of highest/largest molecular weight/size have RI lower than THF and they are detected as an inversion maximum on the chromatogram (peak A-Fig. 1). The area of the inversion peak

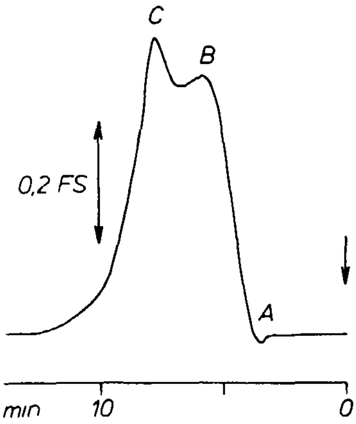

FIGURE 1

Chromatogram of the fuel oil sample, CCR = 14.5%. RI detector: 2 x 10^{-5} RI/FS, room temp. Eluent THF: flow rate 1.0 ml/min. The sample diluted 1:10 by THF(w/w).

is very close to linear function of the CCR. The inversion peak has, unfortunately, very high detection limit and for fuel oils the CCR under 11% is not clearly detectable.

Fig. 2 shows the elution profile with mobile phase consisting of THF-acetone (9:1: v/v). In this experiment the response for the compounds of high/large molecular weight/size on the positive side of the record was obtained. The maximum A (Fig. 2) is eluated with higher retention time and even the response is well detectable, the correlation between this response and the CCR is not linear. The maximum B and C monitored by RI detector are eluated for both presented chromatographic systems with the same retention time.

Table 1 illustrates the role of different wavelengths (220-400 nm) on the detection in UV region. The highest absorp-

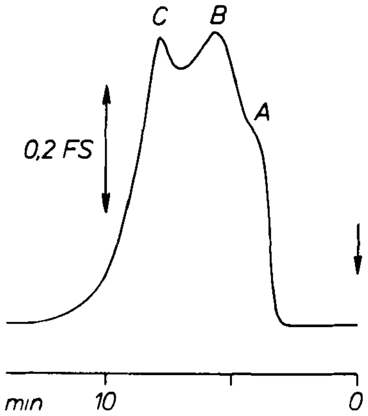

FIGURE 2

Chromatogram of the fuel oil sample (see Fig. 1). RI detector: 2 x 10^{-5} RI/FS, room temp. Eluent 9:1, THF: acetone (v/v), flow rate 1.0 ml/min. The sample diluted 1:10 by mobile phase(w/w).

tion for the high/large molecular weight/size compounds of fuel oils is obtained using the detection at 220 m.

Fig. 3 shows the chromatogram of the fuel oil sample eluated with THF and detected at 220 nm. 50 fuel oil samples were analyzed by this procedure. A linear relationship $y = a + bx + ix$ $(a = 1.3$: $b = 10.2$: $i = 0.4)$ of the cumulative area (area for $t_R < 5.5$ min corresponds to molecular weight over 2500 following polystyrenes standards calibration on the CCR determination exists for the fuel oils with 7.5 - 18.5% CCR. The precision expressed as coincidence of both methods is in range 7.5 - 14.5% CCR ±1.5%. The coefficient of variation for chromatographic procedure is 7% (7.5 - 13.0% CCR) and 5% (13.0 - 18.5% CCR).

In conclusion, the GPC procedure was found to be a valuable method for analyzing and classifying residual fuel oils. Using

Table 1

Absorbance at retention time corresponds to molecular weights (MW) 4000: 2500 and 2000 for the fuel oils (n=5) with CCR = 14.2% ±0.1.

	Absorbance		
λ	at MW		
nm	4000	2500	2000
220	.307	.533	.737
230	.256	.451	.645
240	.287	.471	.626
250	.256	.405	.533
254	.297	.502	.645
260	.205	.405	.522
280	.338	.471	.579
300	.266	.445	.543
350	.133	.220	.261
400	.072	.135	.149

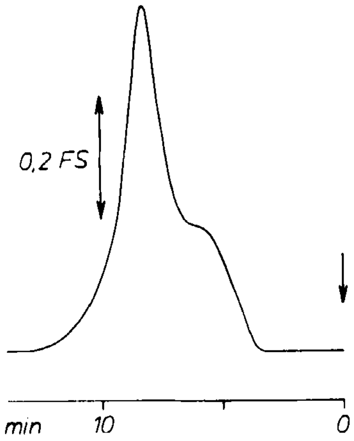

FIGURE 3

Chromatogram of the fuel oil sample (see Fig. 1) monitored by UV variable wavelength detector at 220 nm: 1: 256 AUFS, room temp., eluent THF, flow rate 1.0 ml/min. The sample diluted 1:50 by THF (w/w).

UV absorption at 220 nm rather than RI detection gave a reliable correlation of chromatographic results with CCR determination for the 50 fuel samples tested. The described method is especially attractive since it can be made fully automatic and the time required is very short, 12 minutes, compared with the CCR test which takes 40 minutes.

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REFERENCES

1. Altgelt, K.H., Gel Permeation Chromatography, in Chromatography in Petroleum Analysis. Altgelt, K.H. and Gouw, T.H., eds., Marcel Dekker, New York, p. 287 (1979).

2. Conradson carbon residue of petroleum products, standard test method D 189, in Annual book of ASTM standards, Am. Soc. Test. Mats., part 23, Philadelphia, pp. 123-129 (1980).

3. Wiborg, T.C., Wear problems - experience with how fuel quality parameters influence wear and malfunction in diesel engines, Technical report No. 81 P005, Jan. 1981, Det norske Veritas, N-1322 Høvik, Norway.