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SUPERCRITICAL FLUID CHROMATOGRAPHY WITH A BACKFLUSH TECHNIQUE

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DETERMINATION OF SATURATES, AROMATICS, AND POLARS IN GAS OILS
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ABSTRACT

Supercritical fluid chromatography (SFC) has been used successfully for determining saturates and aromatics in middle distillates, diesel fuel and heating oils having a high boiling cutpoint up to 440°C. Advantages are fast analysis time, minimum sample preparation and direct quantification using a flame ionization detector.

This paper presents an extension of the method to analyze gas oils (final boiling point = 525°C). The heavier boiling point samples contain polar compounds which cannot be chromatographed directly because of strong adsorption on the column. A model compound study shows how a backflush technique was used to successfully elute strongly adsorbed compounds that were not detected in the regular elution mode. In contrast with middle distillates where the saturates and aromatics were easily quantified, a calibration is needed in the analysis of gas oils. The polar fraction is especially affected presumably because of the presence of heteroatoms.

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DÉTERMINATION DES SATURÉS, AROMATIQUES ET POLAIRES DANS LES GAZOLES
PAR CHROMATOGRAPHIE EN PHASE SUPERCRITIQUE AVEC INVERSION DE DÉBIT

par

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RÉSUMÉ

La chromatographie en phase supercritique (SFC) a été employée avec succès pour la détermination des saturés et aromatiques dans les distillats moyens, carburants diesel et huiles à chauffage ayant un point d'ébullition maximum aussi élevé que 440°C. Les avantages sont un temps d'analyse court, un minimum de préparation d'échantillon et la quantification directe par détecteur à ionisation de flamme.

Nous présentons ici une extension de cette méthode aux gazoles (point d'ébullition maximum = 525°C). Ces distillats plus lourds contiennent des composés polaires qui ne peuvent être chromatographiés directement à cause de leur forte adsorption sur la colonne. Une étude de composés modèle a montré que l'inversion de débit permettait d'éluer ces composés impossibles à détecter avec un mode d'élution normal. De plus, alors que les saturés et les aromatiques sont aisément quantifiés dans les distillats moyens, une calibration est nécessaire avec les gazoles. La fraction polaire est particulièrement affectée probablement à cause de la présence d'hétéroatomes.

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INTRODUCTION

Supercritical fluid chromatography (SFC) has been used successfully to determine aromatics in middle distillates^{1,2,3}. The method requires simple experimental conditions (constant pressure and temperature) and quantification can be done directly. Other advantages are fast analysis time and minimum sample preparation. Gas oils have a higher distillation range than middle distillates, typically 350°C-525°C. For this reason, there is more overlap between the saturates and aromatic peaks in SFC. Their composition is also very different because they contain more condensed aromatic structures and have a higher heteroatomic content. This paper addresses problems encountered in the application of SFC to hydrocarbon type separation of gas oils.

EXPERIMENTAL

A Lee Scientific 600 Series SFC system was used. The mobile phase was carbon dioxide. Two columns were used alone or combined in series: Alltech Microsphere, 50 cm x 1 mm I.D., 10 μ m particles and Alltech Adsorbosphere, 25 cm x 1 mm I.D., 5 μ m particles. A flame ionization detector was used. Other conditions are described in Results and Discussion.

The samples were derived from a synthetic gas oil produced from tar sands. The gas oil (350°C-525°C) was treated to reduce the heteroatom content using an in-house procedure. The samples consisted of the original synthetic gas oil, the polar concentrate and the upgraded gas oil.

Hydrocarbon type fractions were generated by preparative liquid chromatography (LC) using a method derived from the Sawatzky method⁴. A stainless steel column (123 cm x 1 cm ID) was packed with silica and alumina (1:1 volume). The eluant flows upwards through the silica gel then through the alumina. The typical sample size is 1 g. The following solvent sequence was used for eluting the corresponding fractions:

<u>Solvent</u>	<u>Volume (mL)</u>	<u>Eluted components</u>
Pentane	250	→ saturates
5% toluene in pentane	250	→ monoaromatics
15% toluene in pentane	250	→ diaromatics
Toluene	200	→ polyaromatics
60% methanol in toluene	320	→ polars 1
Methanol (backflush)	320	→ polars 2

Some losses are due to strong adsorption on the column and are considered as a third polar fraction.

RESULTS AND DISCUSSION

Separation

Preliminary experiments showed that normal flow did not permit the efficient elution of polar standards. Some took a long time to elute and appeared

as broad peaks. Others were not detected possibly because they were very strongly adsorbed or because the peak was too broad. Because of the polar materials present in the gas oils, these conditions were not acceptable for the quantification of compound types in these samples. For this reason, a backflush technique was considered. As expected, strongly adsorbed compounds were eluted in the backflush mode. Usually it is not recommended to reverse the flow on an HPLC column to avoid packing displacement. However, after more than one year of experimentation, there was no evidence of column damage since peak shapes and retention times are comparable to those of a new column. This is probably due to the low viscosity of the phase and its low linear velocity in the column.

Preliminary experiments on the separation of compound types on a 50 cm column showed that the resolution between saturates and aromatics was not as good as for middle distillates. Because the total run time was very long, we switched to a 25 cm column. However, the resolution between saturates and aromatics was very poor for real samples. Additional experiments were conducted with both columns in series. The resolution was improved but the separation between saturates and aromatics was not complete.

Operating conditions were optimized until a reasonable separation was obtained. The separation between saturates and aromatics was still not complete but the quantification of these two fractions was more consistent and closer to the results of the LC separation. The final conditions were the following:

Initial pressure:	300 atm	for 12 min
Pressure gradient:	150 atm/min	for 0.67 min
Final pressure:	400 atm	for 47.33 min
Oven temperature:	50°C	isothermal
Backflush:	valve switched at 30 min	

Figure 1 shows a typical chromatogram obtained under these conditions. Since the gradient is very fast, no difference between a pressure or a density gradient was observed.

In this series of experiments, the sample was injected without any dilution. With the 600 Series SFC instrument, the sample size can be adjusted by using a time-split injection technique in which the injection valve stays in the inject mode during a specified time. This permits the analysis of a liquid sample without dilution. In order to verify that the lack of resolution was not caused by column overloading, the injection time was varied from 0.1 to 1.0 s. During these experiments, the quality of the separation did not change significantly. Table 1 compares the quantification for the two extremes. Results are within the experimental error.

Quantification

Using the above optimized conditions, quantification was checked in order to determine whether hydrocarbon groups were detected proportionally to the injected amount. In middle distillates, direct quantification was possible because response factors were nearly identical for both saturates and aromatics¹⁻³. However, direct quantification was not possible with gas oils (Table 2) presumably because of different structures of saturates and aromatics in gas oil

fractions and because polar compounds contain heteroatoms which add to the mass without adding significantly to the detection.

Individual relative response factors were calculated for combined LC fractions (Table 3). Fraction 6 was omitted because of the very low quantities that were isolated. Higher aromatic response is probably due to long side chains or more substitution on aromatic nuclei combined with more cyclic molecules in the saturates. The polar response was expected to be low because of the high heteroatom content and the cyclic nature of many of the expected components.

Table 4 shows the results from quantification using these relative response factors. Compared to Table 2, results are closer to LC fractionation but still tend to overestimate almost all saturate or aromatic fractions.

In Tables 3 and 4, SFC results are compared to the total LC effluents including the losses, assuming that these losses are polar material. If losses are not included and results are normalized to 100%, then SFC and LC results are much more comparable (within 2%) except for the feed saturate fraction (Table 5). Although it was expected that CO₂ would be strong enough to elute all gas oil fractions, this seems to indicate that the same components are lost by adsorption in the SFC analysis since the solid phase was also silica as the first bed in the LC column.

SUMMARY

The compound type analysis of gas oil samples by SFC is not as efficient as that for middle distillates for the following reasons:

- heavier boiling range results in overlap between the saturate and aromatic fractions,
- polar compounds constitute an important fraction of the sample which necessitate the use of a backflush technique,
- relative response factors are needed to properly quantify the different fractions, especially the polars,
- strong adsorption of some polar compounds.

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Figure captions

Fig. 1 - Typical chromatogram of a gas oil sample. See conditions in text.
'x4' indicates a change in attenuation by a factor of 4.

Table 1 - Variation in injection time (time-split injection)

Injection time s	Area counts		Saturates %	Aromatics %
	Saturates	Aromatics		
0.1	101 794	193 426	34.5	65.5
1.0	679 210	1 410 397	32.5	67.5

Table 2 - Direct quantification by SFC-FID

Sample	Sat.	% LC		Sat.	% SFC	
		Arom.	Pol.+loss*		Arom.	Polars
Original gas oil	52.6	39.5	7.9	42.5	55.4	2.2
Polar concentrate	31.9	44.0	24.1	36.7	58.5	4.8
Upgraded gas oil	46.1	43.4	10.5	46.8	52.8	0.4

* Considered polar compounds

Table 3 - Composition of standard and relative response factors

Compound type	Corresponding LC fractions	Composition (wt %)	Relative response factors
Saturates	Fr 1	27.3	1.00
Aromatics	Fr 2,3,4	48.2	1.25
Polars	Fr 5	24.5	0.27

Table 4 - Quantification using relative response factors

Sample	% LC			% SFC		
	Sat.	Arom.	Pol.+loss*	Sat.	Arom.	Polars
Original gas oil	52.6	39.5	7.9	49.1	43.4	7.5
Polar concentrate	31.9	44.0	24.1	36.2	46.2	17.6
Upgraded gas oil	46.1	43.4	10.5	51.8	46.7	1.6

* Considered polar compounds

Table 5 - Comparison of SFC results with normalized LC

Sample	% LC (normalized)			% SFC		
	Sat.	Arom.	Polars	Sat.	Arom.	Polars
Original gas oil	54.9	41.3	3.8	49.1	43.4	7.5
Polar concentrate	35.6	49.2	15.2	36.2	46.2	17.6
Upgraded gas oil	50.0	47.1	2.9	51.8	46.7	1.6

