

GRADIENT-BASED HIGH PERFORMANCE THIN-LAYER CHROMATOGRAPHY FOR AN EXPANDED SARA ANALYSIS OF HEAVY PETROLEUM PRODUCTS

Carmen Jarne, Vicente L. Cebolla, Luis Membrado

Instituto de Carboquímica (CSIC), 50018 Zaragoza, Spain
vcebolla@icb.csic.es

Introduction

A complete molecular separation of heavy petroleum products is not feasible for their quality control. They are instead characterized in terms of chemical family composition, using classical Hydrocarbon Group Type Analysis such as SARA (Saturates, Aromatics, Resins, and Asphaltenes). However, SARA does not provide information enough to correlate chemical differences of products with their conversion parameters in the case of heavy products.

High-Performance Thin-Layer Chromatography (HPTLC) has been scarcely used for analyzing heavy petroleum products. The inherent advantages of HPTLC (e.g., high sample throughput, minimal sample preparation, presence of the whole sample on the layer) have been supplemented by those resulting from the development of automated application, development and detection systems. HPTLC is at present a reliable, flexible and cost-efficient quality control-oriented technique [1].

Automated Multiple Development (AMD) is a fully-automated technique for HPTLC development that combines incremental multiple development, solvent gradient in short steps (1-2 mm), and repetition of elemental steps [2]. This provides band focusing and improves sample separation. The use of AMD in combination with a robotic, spray-on sample applicator contributes to improve the repeatability and sensitivity. AMD is especially adequate for samples which comprise a wide range of polarity [3] and therefore appears as an interesting alternative to obtain different separations with increasing level of complexity for heavy petroleum products with regard to those provided by simple SARA [4].

Experimental

HPTLC plates (20 x 10 cm, Merck) were pre-conditioned by developing 90 mm with tetrahydrofuran (THF).

Materials. Asphaltenes, residua, base oils, heavy oils, refining products, vacuum gas oil were provided by TOTAL RM.

Sample application. Samples were dissolved in HPLC-grade DCM and applied using the Automatic TLC Sampler 4 (Camag), as 4 mm-bands. 25 bands of samples were applied on the same plate with a distance of 2 mm between tracks. Two additional tracks were always kept free of application, as blank runs. The first application position was 10 mm (x coordinate), and the distance from lower edge of plate was 10 mm (y coordinate). Typical application volumes for petroleum samples were between 0.2 and 0.8 μL typical effective masses applied were between 0.5 and 3 μg for UV, and between 3 and 10 μg for fluorescence evaluation.

Chromatography. Chromatographic development was performed with an AMD2 system using a 20-step gradient based on THF, DCM and *n*-heptane (Figure 1). Gradient composition in each step; number of steps; distance per step (mm step⁻¹); and total developing distance (mm) are detailed.

UV and Fluorescence Densitometry. A TLC Scanner 3 (Camag) was used in UV and fluorescence modes. First, UV densitometry at different wavelengths was recorded, as well as UV spectra of peaks. Subsequently, HPTLC silica gel plates were post-impregnated with a 60 mg L⁻¹ solution of berberine hemisulphate in

MeOH, using a Camag Chromatogram Immersion Device III. Fluorescence mode was then used for peak detection by excitation at 365 nm. Emission was collected at longer wavelengths than 400 nm. This detection was referred to as FDIC (Fluorescence Detection by Intensity Changes) [5]

Results and Discussion

AMD operates in successive elemental elution steps (of several mm each) which are performed with decreasing solvent strength in combination with increasing developing distance. The composition of the mobile phase in each step is different and usually of lower polarity than that of the previous one, adjusted by mixing of different proportions of up to five solvents. The stepwise gradient formed allows narrow peaks and efficient separations to be obtained in a highly reproducible way (± 0.45 mm). If required, repetition of elemental steps can be performed which provides band refocusing.

Automated Multiple Development (AMD) can be used for semi-detailed chromatographic characterization of heavy petroleum products. An optimized 20-step, THF-DCM-*n*-heptane gradient (Figure 1) has been used for profiling a variety of samples that covers the whole range of petroleum heavy products.

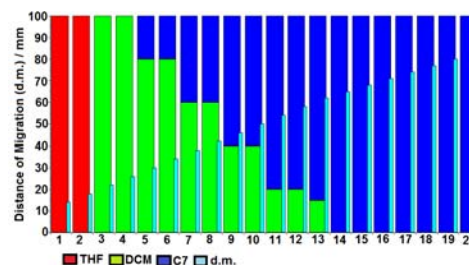


Figure 1. 20-step THF-DCM-*n*-heptane gradient

Figure 2 shows the chromatogram of a vacuum gasoil under these AMD conditions at different wavelengths. The most polar and heaviest compounds remain at the application point (m.d.= 10 mm) and are directly detected on the plate by UV densitometry. The peak in the chromatogram appearing in the 100 vol.% THF development zone (up to 14 mm m.d.; one step) can be considered as Asphaltenes (THF-insolubles).

Peaks eluted in the 18-58 mm m.d. zone (10 steps, from 100 vol.% DCM to 20:80, v/v DCM-*n*-heptane), correspond to Resins. This zone is particularly well resolved using the described gradient conditions and may provide more useful information than that obtained using classical methods.

Peaks eluted in the 58-83 mm zone, from 15:85 (v/v) DCM-*n*-heptane to 100 vol.% *n*-heptane, are usually considered Aromatics and Saturates. Figure 3 shows a detailed view of different chemical groups. Several peaks are coeluted in this zone. Identification of component groups has been possible by using selective detection, direct recording of UV spectrum of each separated peak, and comparing UV spectra of peaks with those of standards which were eluted on the plate under the same gradient conditions.

Peak eluted at 83.3 mm with the front of solvent is due to saturated hydrocarbons. This peak has no UV response and is detected by FDIC-berberine [5]. An ion-induced dipole interaction between *n*-alkanes and berberine cation is responsible of an increase in berberine emission in the presence of alkanes [5]. The shoulder at 81 mm in the FDIC-berberine chromatogram, which coelutes with saturated hydrocarbons and has a response in the presence of berberine, may be attributed to naphthenes. This shoulder is encompassed in the peak eluted at 80.3 mm which has been

selectively detected by UV at 201 nm. UV spectrum suggest that this peak consists of naphthenic and naphthene-aromatic structures.

The inspection of the chromatogram obtained by UV detection at 228 nm, and the UV spectrum of the peak eluted at 78.2 mm are coherent with the presence of alkyl-aromatic structures in this peak. Likewise, the chromatogram obtained by UV at 273 nm together with UV spectra of peaks eluted at 73.2, 68.5, and 64.3 mm suggest the presence of aromatic structures, probably with different degrees of condensation.

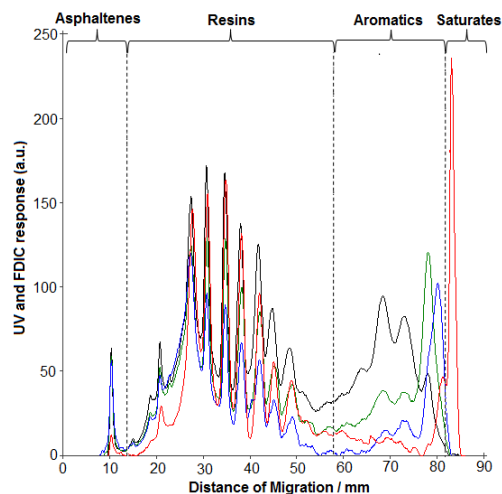


Figure 2. Chromatogram of a vacuum gasoil under the AMD conditions (Figure 1) at different wavelengths: UV-273nm (---), UV-228nm (---), UV-201nm (---) and FDIC-365nm (---)

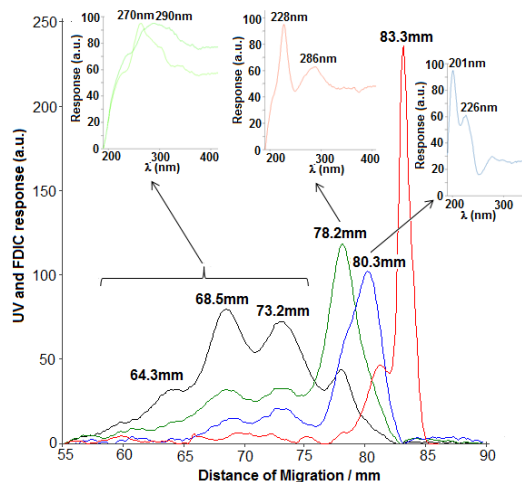


Figure 3. Detail of apolar zone

In a general AMD practice, an unresolved chromatogram can be superimposed with the corresponding diagram of the gradient employed. Thus, inefficient zones with regard to separation can be identified. Likewise it is possible to make changes in solvent composition (or steps number) with predictable effects on separation. In this way, the gradient conditions can be modified to improve or optimize sample separation on the plate. Separation can be fine-tuned and amplified for each segment of the chromatogram. Thus, an expansion of the asphaltenic-resinic or the apolar chromatographic zones can be obtained

AMD chromatographic zones can be related to Hydrocarbon groups in classical SARA. The AMD instrument can also be used with a sequence of several elution solvents in order of growing or decreasing polarity, as when using a conventional developing chamber. In this way, a simple SARA can also be obtained from AMD.

Figure 4 shows that the application of this gradient sequence to different heavy products provides qualitatively different chromatograms. Although this separation does not provide a complete molecular resolution of heavy petroleum products, the resulting profiles adequately represent the complexity of the analyte, and can provide a useful information for identification, comparison purposes, or for evaluating the effect of process variables on a crude oil.

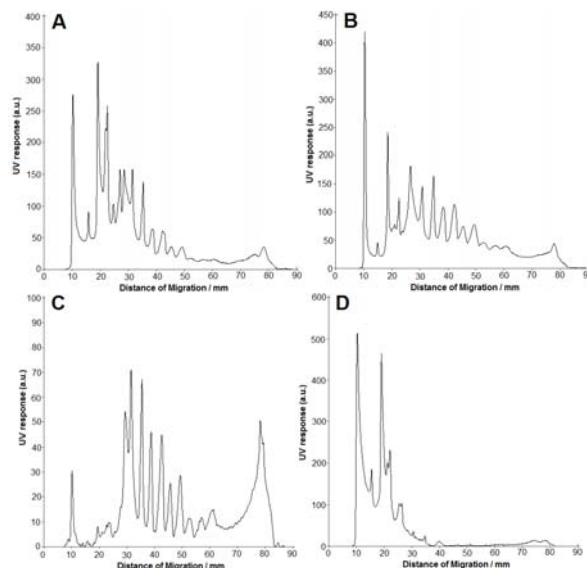


Figure 4. AMD of a bitumen (A), refining products (B,C) and an asphaltene (D)

Conclusion

Extended SARA of a high number of samples on the same plate (up to 28) can be obtained by using AMD, in a reasonable time, under strictly identical conditions, with minimal solvent requirements, reduced labour times, and important cost savings. Expansion of separation and or scanning of desired zones of the chromatograms can be obtained

Acknowledgement. Authors thanks TOTAL RM for financial support.

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