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# Fast monitoring of $C_{20}$ – $C_{160}$ crude oil alkanes by size-exclusion chromatography–evaporative light scattering detection performed with silica columns

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## Abstract

Fast (7 and 20 min) size-exclusion chromatography methodologies were developed for monitoring crude oil alkane mixtures derived from solid deposits and asphalts. Microparticulate, highly efficient silica columns operated at 45°C, using a toluene carrier and evaporative light scattering detection were adopted. Applications were assessed for samples containing alkanes within the  $C_{20}$ – $C_{160}$  range. *n*-Alkane standards were adopted for molecular mass calibrations. © 1997 Elsevier Science B.V.

*Keywords:* Oils; Alkanes

## 1. Introduction

The presence of large alkanes in solid deposits from oil production and transportation operations is a problem which has been commonly observed in recent years [1–3]. During the past 5 years, interest has also arisen on the possible role, beneficial and/or detrimental, exerted by alkanes present in residual oil fractions commonly employed for formulation of asphaltic products [4].

Recent work in our laboratory has addressed the analysis of alkane mixtures using a size-exclusion chromatographic (SEC) methodology, which adopted commercial polymeric columns and flame ionization detection (FID) [5]. However, concerns arose with such an approach, among them the long analysis time (1 h), signal asymmetry obtained with the detection device employed, and the non-universal

response shown by different alkane families (normal, branched and cyclic).

The advantages of rigid column packings have been exploited in the past in order to achieve very fast SEC analysis [6], and the exclusion properties of silica stationary phases were described as long ago as the 1970s [7,8]. These facts suggested the adoption of silica columns in order to improve on the time-consuming SEC methodologies routinely performed with polymeric columns. Another reason that supports the change towards the adoption of rigid silica-based columns lies in the fact that adsorption mechanisms were not expected to affect alkanes when using polar stationary phases. Selection of SEC approaches from among the many possible ways to analyze complex alkane mixtures appears to be supported by various facts: (1) pragmatic reasons, i.e., less demanding analytical conditions when com-

pared with mass spectrometry (MS) methods [9,10]; (2) solubility factors when using a CO<sub>2</sub> eluent for very large alkanes in supercritical fluid chromatography (SFC) approaches [11]; (3) concerns over the possibilities of cracking with high-molecular-mass (*MM*) components when using high-temperature gas chromatographic techniques [11–13]; (4) that elution of very large compounds by high-temperature SEC methodologies has already been shown [5,14,15].

Advantages for evaporative light scattering detection (ELSD) devices reportedly describe unitary responses for hydrocarbon families [16–20], and very stable baselines [21–23]. As a consequence of these advantages, interesting applications have been published on fossil fuel-related topics [20,22,24–26]. Nevertheless, precautions must be taken if accurate determinations are required, since many variables affect the operation of these instruments [27]. Variables that affect particle growing in the nebulizer, such as gas flow, sample concentration and nebulizer design, exert marked influence on the response [28–31]. Also, non-linear response is characteristic of these devices [29,30]. These characteristics of ELSD are obvious drawbacks when quantitative analysis is involved. Consequently, simulation models have been proposed to avoid cumbersome construction of calibration curves [27].

The purpose of this work was the development of more rugged and faster SEC methodologies, aimed at the analysis of very large (C<sub>20</sub>–C<sub>160</sub>) alkanes found in crude oil solid deposits and vacuum distillation bottoms. The described combination of rigid silica columns, operated above ambient temperatures with a very stable ELSD device, was the approach selected in order to fulfil these objectives.

## 2. Experimental

### 2.1. Reagents and solvents

Standard alkanes were used as received and came from four different sources: (1) Aldrich (Milwaukee, WI, USA); (2) Alltech (Deerfield, IL, USA); (3) Riedel-de Haen (Seelze, Germany); (4) E. Merck (Darmstadt, Germany). Solvents were purchased from J.T. Baker (Philipsburg, NJ, USA) or Burdick

& Jackson (Muskegon, MI, USA), and were used as received.

Polystyrene standard (*MM* 50 000) was acquired from Arro Laboratories (Joliet, IL, USA). *n*-Alkane C<sub>60</sub> was made by Fluka (Buchs, Switzerland) and, Polywax 655 was provided by Separation Systems (Gulf Breeze, FL, USA).

### 2.2. Samples

Isolated alkane concentrates were exclusively analyzed with the system described in this work. Preparative isolation was performed by high-temperature HPLC on silica columns, as previously described [5]. Isolation from solid deposits, required additional steps, among them liquid–solid extraction procedures already described [1]. Care was taken to extract very large hydrocarbons by an additional extraction with a toluene–2-propanol (95:5, v/v) solvent mixture.

### 2.3. SEC system

The solvent delivery system was an ISCO 260D syringe pump from ISCO (Lincoln, NE, USA). The injector was a Rheodyne 7010 valve provided with a 5- $\mu$ l sample loop. The column bank was assembled with five columns, the first one being laboratory-made (25 $\times$ 0.4 cm), packed with Nucleosil 100-5 silica particles (5  $\mu$ m and 100 Å pore size), from Macherey–Nagel (Duren, Germany). The following four columns were identical, Spherisorb S3W made by Phase Separations (UK). These columns were packed with 3  $\mu$ m and 80 Å pore size silica particles, their dimensions being 15 $\times$ 0.4 cm. The column bank was thermostated inside a column heater module (TCM) from Waters (Milford, MA, USA). The detector employed was a Varex ELSD IIA (Varex, Burtonsville, MD, USA). Chromatograms were monitored with a strip-chart recorder Model 282 from Cole-Parmer (Vernon Hills, IL, USA) and saved on disk either on a Hewlett-Packard (HPs) diskette unit HP 9153C (HP, Boise, ID, USA) or on an HP 9000/300 data system provided with ChemStation SEC software (HP, Waldbronn, Germany). The A/D interface between the ELSD and the ChemStation was an HP 35900. Additional hardware parts included in the system comprised a solvent

preheater (2-ml stainless steel tubing), rheostats provided with heating stripes, a block heater, a heating water bath and, finally, a digital thermometer used for column oven temperature monitoring (Tegam Model 132C provided with a K-type thermocouple (of unknown origin).

#### 2.4. SEC-ELSD conditions

The selected eluent was toluene and the system was commonly operated at 45°C (column bank) and 60°C (injection valve and transfer lines). Two sets of conditions were chosen, depending on the approach undertaken: (1) a five-column bank (detailed in Section 2.3) employed for experiments identified as a 'slow' approach in the ensuing discussion (20-min run time, 0.5 ml/min toluene flow at an operating pressure between 16 500 and 17 300 kPa); (2) a three-column bank employed for experiments identified as a 'fast' approach during the ensuing discussion (one 100-Å laboratory-made column plus two Spherisorb 80-Å columns i.e., the previous bank after removal of two Spherisorb columns; 7 min per separation and the system operated at 1 ml/min and 25 500 kPa).

Detector parameters were commonly set at 4 l/min for the nebulizer gas ( $N_2$ ) and 70°C for the evaporator tubing. Nebulizer gas was directly supplied from a laboratory cylinder (ca. 6 m<sup>3</sup> at 1 atm; 1 atm=101 325 Pa) in order to avoid baseline changes introduced by shared lines. *n*-Alkanes with 60, 44, 38, 30 and 22 carbon atoms per molecule were used for *MM* calibration. A linear option between those possible with the HP calculation program was chosen, since correlation coefficients ( $r^2$ ) for  $\log MM-t_R$  were found to be greater than 0.995 when selecting this approach.

Sample preparation was performed by simple dilution in the eluent at a concentration of about 0.5–1% (w/v). Sample solutions were maintained in closed vials at approximately 70°C inside the heated water bath. In the eventuality of solid particle contamination in the solutions (visual inspection), removal of the solids was accomplished by filtration through luer tipped 'Maxi-clean CN' cartridges from Alltech. Filtration was performed with gas-tight syringes, rinsing three times with warm solvent, which was subsequently concentrated to near original

sample concentration by micro-*rota*-evaporation with an  $N_2$  sweep. The injection valve was filled with sample solutions by means of gas-tight syringes, maintained at approximately 60°C over the heating block.

In circumstances for which polystyrene internal standard was included for correction of retention times, a sample/standard ratio of 9:1 was adopted and the mixture diluted in the toluene as described previously.

#### 2.5. High-temperature gas chromatography-simulated distillation (HTGC SimDist)

High-temperature gas chromatography was performed on an HP-5890 apparatus provided with oven modifications and SimDist software by Analytical Control (AC TBP 750 system). An HP HT-cross-linked methylsilicone column was employed, its dimensions being 5 m×0.53 mm, 0.09 μm film thickness. The oven temperature was programmed from 40 to 430°C at 10°C/min, and maintained at the final value for 5 min. The injector temperature was programmed from 100 to 430°C at 25°C/min. The FID was maintained at 450°C and the He carrier gas flow was set at 20 ml/min. Sample solution was prepared in  $CS_2$  at 10% (w/v). Closed vials were used and ca. 100-mg samples were weighted to the nearest 0.1 mg; 1.5 μl of sample solution was injected for each run.

### 3. Results and discussion

Long analysis time and peak asymmetry were the driving forces behind the search for better SEC alternatives for the determination of the *MM* and molecular mass distributions (MMD) of alkanes [5]. The exclusion properties of silica stationary phases [7,8], and the possibility to perform very fast analysis with such rigid packings [6] suggested the adoption of these materials in order to overcome the cited inconveniences. The availability of a great variety of conventional silica columns (4 and 7 mm I.D.) packed with 5–10-μm stationary phases, dictated the evaluation of these as a first alternative. However, such attempts proved unsuccessful since the measured resolutions ( $R_s$ ) for a pair of standard

compounds used for this phase of the study were less than 0.6. The selected compounds were squalane and *n*-octadecane. In spite of pressure inconveniences expected from adoption of 3- $\mu\text{m}$  columns, trial and error experiments showed that improved  $R_s$  values were possible with these columns. Measured  $R_s$  values for the pair of selected analytes were 0.8 and 1.0 in experiments performed with two or four commercial Spherisorb S3W columns in series. Consequently, a column bank was assembled with four of these columns, but addition of one 100- $\text{\AA}$ /5- $\mu\text{m}$  column was deemed necessary since very large alkanes have been detected during previous studies [5]. The assembled column bank permitted good  $R_s$  values for standard *n*-alkane mixtures used for calibration purposes (Fig. 1). In the same figure it is also possible to ascertain that separation of alkanes with the same carbon number was achieved with this

approach, as illustrated for the  $\text{C}_{10}$  included in the example shown.

The aim of the desired SEC methodology was the analysis of alkanes greater than  $\text{C}_{20}$ , which are the compounds commonly found in solid deposits and crude oil residua. With this in mind, some adjustments were performed for optimization of the main parameters that govern the detector operation, namely evaporator tube temperature and nebulizer gas flow. Temperature was evaluated within the range of 70–120°C, and it was found that the signal for *n*- $\text{C}_{22}$  gradually decreased and, above 100°C it disappeared. Nebulizer gas flows were varied between 1.5 and 4.5 l/min, and it was observed that settings lower than 4 l/min produced signals tailing, which was severe under 2 l/min. The best conditions found, to get symmetric peaks and to detect components in the desired interval ( $>\text{C}_{20}$ ), were 70°C and 4 l/min.

Experiments not shown in this paper showed that, under the selected detector settings, *n*- $\text{C}_{19}$  was the first alkane detected, and that the full detector response was obtained beginning at *n*- $\text{C}_{24}$ . Volatile compound losses were typical for ELSD, as previously shown by others [24,26,32]. The fact that a relatively low temperature was adopted for toluene carrier removal (70°C), is explained by the low evaporation heat of this solvent, which is reportedly the important parameter governing solvent removal within the detector [29,33].

High temperature has been recognized as necessary or, at least, convenient for elution of solid alkane mixtures (waxes) from chromatographic columns [5,14,34]. However, no correlation has been proposed in these works in order to select a defined temperature as a function of molecular masses spanned by the sample mixtures. In principle, a lower temperature would be better in order to extend the lifetime of the column and chromatographic hardware. From previous work [5], it was assessed that chromatography carried out under dilute conditions permitted the elution of solid  $\text{C}_{18}$ – $\text{C}_{36}$  *n*-alkanes at ambient temperature. In order to shed some light on this topic, SEC separations were carried out at three different temperatures: 45, 60 and 100°C. The samples employed for these experiences were chosen taking care that the selected ones possessed significant amounts of alkanes larger than  $\text{C}_{60}$ . The criteria adopted in order to differentiate

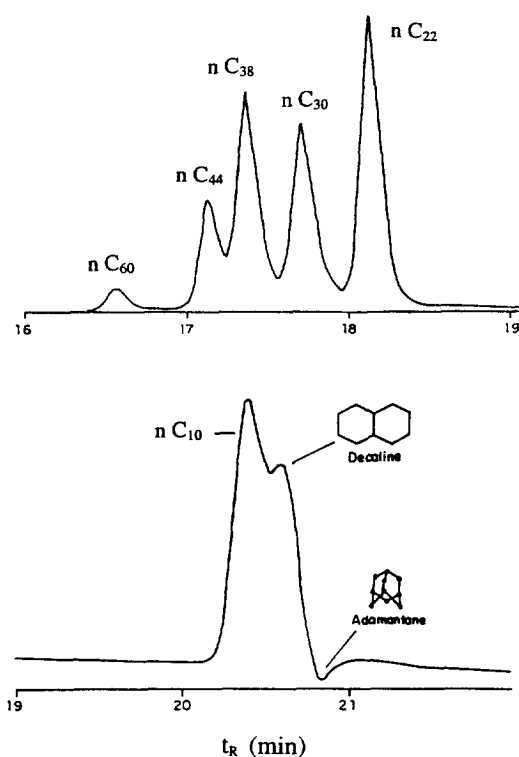


Fig. 1. Resolution of *n*-alkane standards and  $\text{C}_{10}$  hydrocarbons with the five-column bank SEC system. ELSD employed for *n*-alkane monitoring. Differential RI detector used for volatile  $\text{C}_{10}$ . Separations performed at 45°C.

between samples will be discussed later on this work.

Results from these experiments can be seen in Fig. 2. It is to be emphasized that the multimodal distributions displayed by the studied samples, did not change when temperature was varied in the cited interval. These findings suggested two things: (1) under the dilute conditions employed during the described chromatographic separations, the largest compounds were eluted independently of temperature in the range 45–100°C; (2) large detected components ( $>C_{60}$ ) are real, i.e., they can still be observed at 100°C, which is proof of their intrinsic molecular nature and not of an aggregation phenomenon. However, as previously cited [5,8], decreasing retention times can be observed as the temperature is raised. All the previous findings indicate 45°C as being a suitable temperature for the rest of this work.

One of the features of the chromatographic system is considered to be worth brief description. This feature is related to the heat exchange observed when the system was thermostated under dynamic (elution) conditions. After setting the desired operating temperature to 45°C, during the first hour of operation this parameter was observed to increase from ambient to ca. 52°C inside the column oven. The phenomenon was explained by heat transfer from the heated injection valve and connecting tubing, which

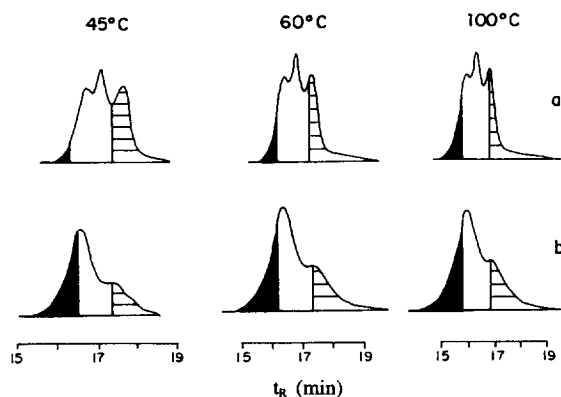


Fig. 2. SEC-ELSD for selected samples, performed under diverse temperatures. Toluene carrier used for the experiments carried out at the lower temperatures. *o*-Xylene employed for 100°C operation. (a) SRC71 microcrystalline fraction. (b) M12FS72 fraction from storage deposit. (■) Alkanes  $>C_{60}$ ; (▨) alkanes  $C_{60}-C_{30}$ ; (□) alkanes  $<C_{30}$ .

were maintained at a higher setting (60°C). It was important to take this into account, in order to make the proper temperature adjustment: the set value being 38°C and the real column bank temperature being 45°C. It was also important to avoid acquiring data during the equilibration period (first hour), since retention times were observed to continuously vary along such interval. After equilibration, the system was observed to maintain temperature constancy to  $\pm 2^\circ\text{C}$ , a fluctuation that was also attributed to heat exchange between different components of the chromatograph.

Two topics were evaluated during this work in order to ascertain the accuracy of results obtained by SEC-ELSD performed on silica columns. The first one concerns universality for SEC calibrations when alkanes from diverse families (normal, branched or cyclic) are used as standards. Low-*MM* alkanes ( $<C_{36}$ ) and refractive index (RI) detection were employed during these experiments. The results showed that, exactly in the same way as previously found with polymeric columns [5], SEC retention for cyclic alkanes is greater than for linear and branched compounds. Consequently, calibration performed with *n*-alkanes (commercially available in a wide molecular mass range), can generate smaller *MM* components than real ones when cyclic compounds are present in the samples. This is a significant quantitation drawback that is currently being investigated for the purpose of understanding and control.

The second topic evaluated was related to ELSD response constancy for diverse alkane mixtures and/or samples with diverse average molecular masses. According to previous publications related to particular hydrocarbon groups or families [16–20], response constancy was in principle expected for 'alkanes'. On the other hand, universality was not expected for fractions differing widely in molecular mass, since there is the possibility to generate aerosols with diverse properties due to changes in melting points, refractive indexes, and diverse light absorption properties [24,30,35]. The results shown in Fig. 3 revealed that samples can be grouped into two categories: standard hydrocarbons plus macrocrystalline commercial paraffin waxes, which showed a response almost double that of the other group. The second group comprised complex poly-disperse samples originating from crude oil residua

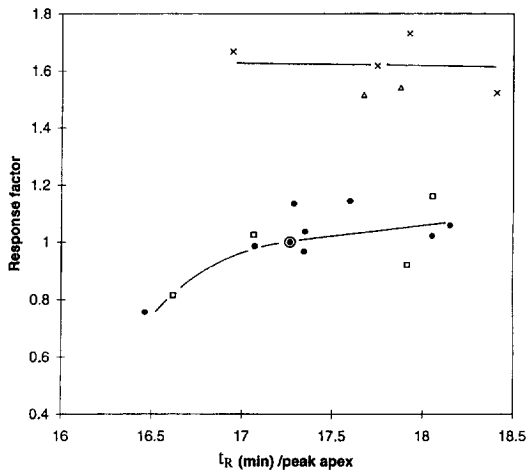


Fig. 3. ELSD response factors for alkane mixtures. A commercial microcrystalline wax was selected as reference ( $\odot$ ,  $rf=1$ ). Origin of the samples: ( $\bullet$ ) paraffinic crudes; ( $\square$ ) naphtho-aromatic crudes; ( $\triangle$ ) commercial macrocrystalline waxes; ( $\times$ ) standard hydrocarbons.

and solid deposits. The response of the second group was observed to be almost half that of the previous group. Within the second group, differentiation was made with regard to the nature of the referred fraction, i.e. paraffinic or naphtho-aromatic origin. From our particular point of view, this whole group comprises the important samples currently under study and its response is reasonably constant.

The results shown in Fig. 3 for the significant samples (second group), suggested that the response obtained was nearly constant. However, a slight tendency to get smaller responses for high *MM* components was already noticeable. This tendency was confirmed in greater detail by determining the response of subfractions separated from a sample and comparing these with the corresponding response for the original common source. The comparisons were performed at two temperatures: 45 and 65°C. Results obtained in both cases were equivalent, and those obtained at the higher temperature are shown in Fig. 4. Computed areas for the chromatograms displayed in this figure showed that for fractions varying widely in MMDs, the response of high-*MM* components is lower than the corresponding one for low-*MM* compounds. This behavior contradicts previous studies in which solid high-*MM* components

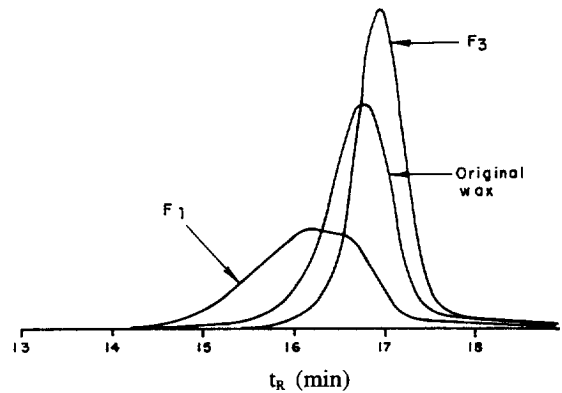


Fig. 4. ELSD response for fractions differing in MMD, separated from a commercial microcrystalline wax. Experiments were carried out at 65°C. Computed area counting: F1, 207; F3, 300; original wax, 273.

usually gave higher responses [24,30]. Different aerosol growing mechanisms were probably involved in these studies. Another interesting observation can be deduced from the chromatograms included in Fig. 4. Preparative SEC fractionation of the sample allowed to observe high-*MM* components that partitioned into the first eluted fraction. These went otherwise undetected in the original sample, and it is to be presumed that this was partially due to the lower response already discussed.

The former observations on calibration and detector response are important with regard to quantitatively accurate analysis. The combined effects of these parameters suggest that SEC-ELSD results for complex-polydisperse samples must be viewed with caution. In principle, the results were deemed valid for monitoring purposes but not for accurate *MM* determinations. However, some examples discussed in the ensuing discussion, will illustrate that, in general, agreement of the results from this system with those using another technique (HTGC SimDist) was better than presumed. However, this agreement was only possible for verification of components smaller than ca.  $C_{120}$ , since the GC technique was restricted to this range. It is to be presumed that an unknown compensation is taking place in the SEC-ELSD separation in order to explain the matching.

Comparison of MMDs can be seen in Fig. 5 for two samples, from both SEC-ELSD and HTGC SimDist. The sample described as M12F was sepa-

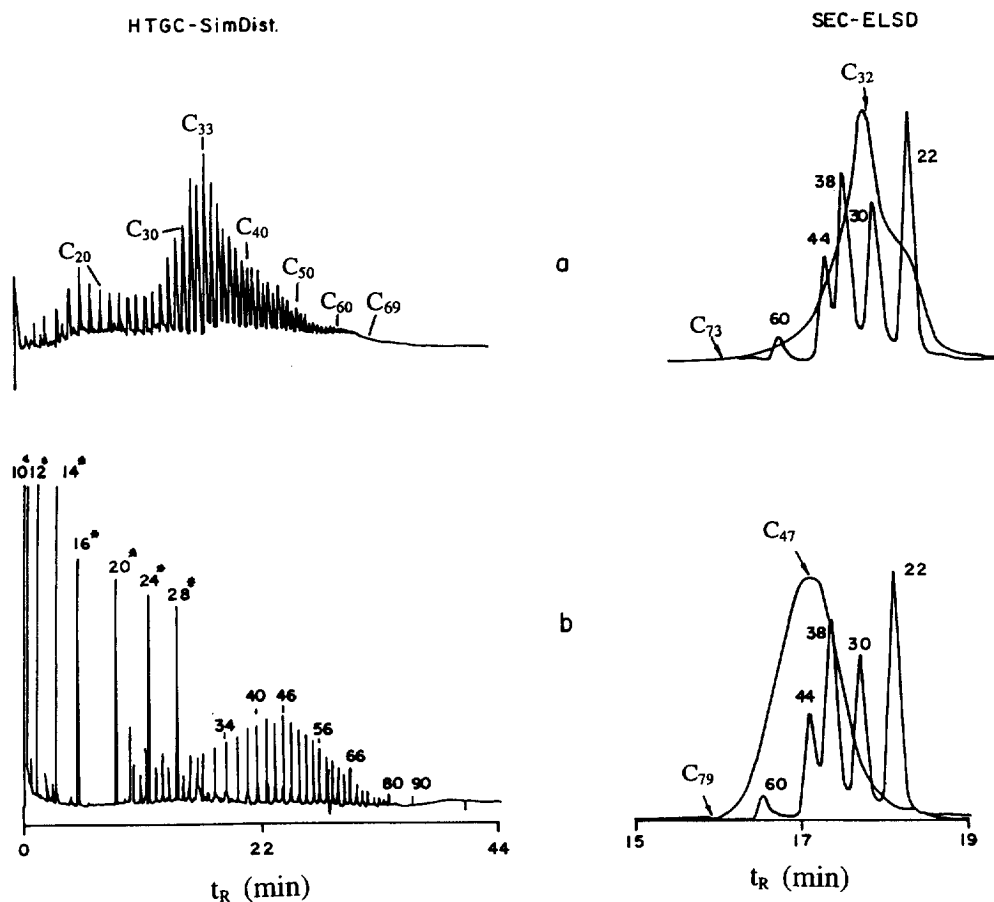


Fig. 5. MMD determined by SEC-ELSD and HTGC SimDist. (a) Alkane fraction from deposit M12F. (b) Polywax 655 synthetic polyethylene wax. SEC-ELSD chromatograms were superposed on calibration standards for comparison purposes. \*Polywax 655 was enriched with small *n*-alkanes.

rated from a deposit generated within a paraffinic medium oil, stored at ambient conditions for 4 years. The maxima correspond to C<sub>33</sub> by HTGC and C<sub>32</sub> by SEC-ELSD. The measured carbon range spanned was C<sub>15</sub>–C<sub>70</sub> by GC and C<sub>19</sub>–C<sub>73</sub> by SEC-ELSD. The other sample displayed in Fig. 5 was a commonly used calibration standard for HTGC SimDist analysis: a polyethylene carbon synthetic wax [11,13]. The maxima were found at C<sub>46</sub> by GC and at C<sub>47</sub> by SEC-ELSD. The carbon range spanned was determined to be C<sub>22</sub>–C<sub>86</sub> by GC and C<sub>20</sub>–C<sub>79</sub> by SEC-ELSD.

The previous findings showed, as previously stated, that agreement for MMDs obtained by the two chromatographic techniques compared was bet-

ter than expected for samples containing components smaller than C<sub>120</sub>. However, as shown in Fig. 6, the same agreement was not verified for samples containing larger compounds, since HTGC SimDist, performed under routine conditions, was found to be unsuitable for the analysis of these components, which were not eluted under the analytical protocol employed. For these cases, SEC techniques are considered better alternatives. This choice was also supported by the fact that the milder conditions employed in this work, as well as others [5,14,15], suggest that the risk of molecules cracking was easily avoided [36]. However, the same can be said regarding SFC techniques, if the adoption of other operating parameters and/or eluents than formerly

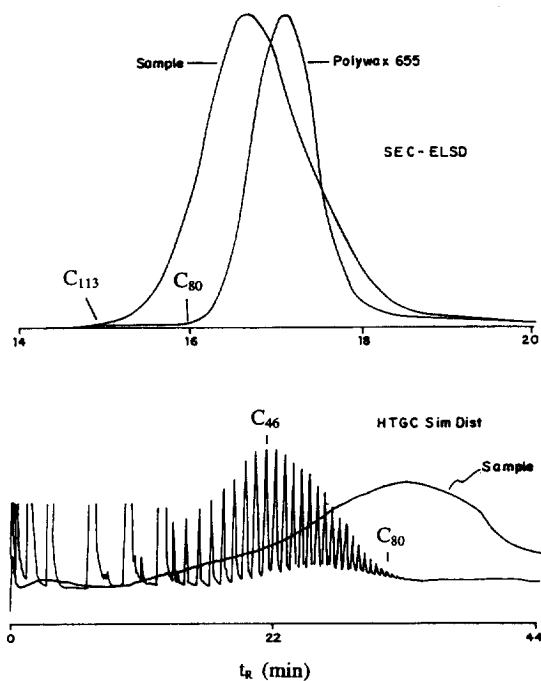


Fig. 6. MMD determined by SEC-ELSD and HTGC SimDist for the wax separated on cooling from L3B vacuum distillation residue; 16% (w/w) sample was computed to remain inside the HTGC column. Chromatograms are shown superposed on Polywax 655 for comparison with a known standard.

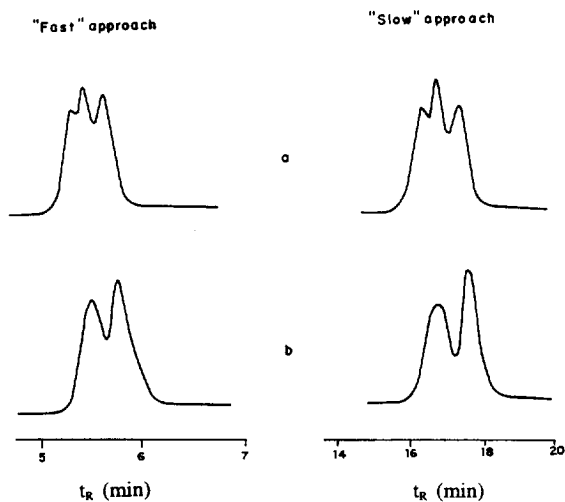


Fig. 7. SEC-ELSD performed with 'slow' (five columns bank) and 'fast' (three columns bank) approaches. (a) SRC71 microcrystalline fraction, separated from clay at 71°C. (b) M12FC71 storage vessel fraction, separated from clay at 71°C.

reported [11] will enable detection of such compounds.

Results discussed in previous paragraphs, showed that it was possible to reduce SEC analysis time from 1 h [5] to 20 min, by adoption of rigid silica packing materials instead of polymeric stationary phases. Previous publications based on this approach have shown remarkable achievements [6]. Experiments have since been undertaken in order to improve analysis time, by adoption of the principles of high-speed liquid chromatography (HSLC) [37]. In this work a column bank was assembled with three columns, as described in the Section 2. Flow was set in such a way as to produce a pressure which was not excessively high, in order not to compromise column life, and also in order not to greatly impair the chromatographic resolution. Examples included

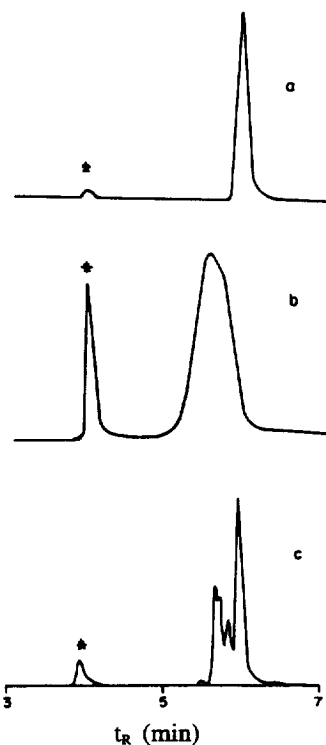


Fig. 8. SEC-ELSD chromatograms for selected samples calibrated with the aid of internal standardization. (a) Commercial Venezuelan macrocrystalline wax. (b) High-MM fraction separated from a commercial microcrystalline wax. (c) Calibration standards (*n*-alkanes  $C_{60,44,38,30,22}$ ). \*Internal standard (polystyrene, *MM* 50 000).



in Fig. 7 show that comparable results were possible both by the 'slow' and 'fast' techniques (described earlier). This important result demonstrated that significant time savings were possible using the 'fast' technique. In spite of the short analysis time, the 'fast' technique could not be considered typical HSLC, because of the relatively low flow and long column (bank) used.

In order to estimate analysis precision for the described SEC–ELSD techniques, repeatabilities were determined for some samples. A retention time variation of 0.05 min was typically found, and was considered as the main drawback for adopting external *MM* calibration with *n*-alkane standards. Nevertheless, results not included in this paper showed that R.S.D. was less than 3% for analyses performed adopting this calibration procedure and the 'slow' SEC–ELSD approach. When the analysis was performed with the 'fast' approach, the precision was worse, since the absolute retention time variability proved to be of the same magnitude, but within a time-span three times smaller. Flow-rate constancy is vital for accurate MMD by SEC analysis with

external calibration [38]. In order to improve this negative finding, an internal standardization was introduced, as discussed in the following.

The internal standardization was possible by addition to the samples of a spike of a polystyrene with a reported average *MM* of 50 000. The standard was selected after verifying that resolution was always possible from sample components. Fig. 8 illustrates this for oil-derived samples which were estimated to represent extreme cases concerning MMDs. This figure permitted also to assess the impairment of resolution when results were obtained by the 'fast' technique instead of the 'slow' technique (see Fig. 8c and Fig. 1). However, this impairment did not preclude the adoption of *n*-alkanes for *MM* calibration. Analysis repeatability was greatly improved with internal standardization, as shown by the data included in Table 1. R.S.D.s were then comparable for the two SEC–ELSD approaches described in this work. After this was assessed, the 'fast' technique was subsequently selected for routine analysis.

Finally, an example is shown in Fig. 9 which illustrates the applicability of SEC–ELSD for very

Table 1  
Precision in the SEC–ELSD analysis for a commercial microcrystalline wax, using the 'fast' approach<sup>a</sup>

Calibration method <sup>b</sup>	$M_n^c$	$M_w^c$	$M$ (peak apex)	$M$ (1% initial) <sup>d</sup>	
External	510	557	502	1000	
	484	528	475	943	
	461	500	457	847	
	506	549	495	929	
	507	551	657	921	
	661	722	513	1201	
	522 ± 71	568 ± 78	513 ± 73	974 ± 122	
	(14) <sup>f</sup>	(14) <sup>f</sup>	(14) <sup>f</sup>	(13) <sup>f</sup>	
	Internal standardization <sup>e</sup>	514	582	506	1056
		513	582	504	1018
525		588	520	963	
552		588	540	1013	
523		588	510	952	
543		587	532	996	
528 ± 16		586 ± 3	519 ± 15	1000 ± 38	
(3) <sup>f</sup>		(0.5) <sup>f</sup>	(3) <sup>f</sup>	(4) <sup>f</sup>	

<sup>a</sup>Replicas performed on different days.

<sup>b</sup>Linear option, *n*-alkanes C<sub>60,44,38,30,22</sub>.

<sup>c</sup>For definitions see Ref. [8].

<sup>d</sup>Mass at the point where 1% area was computed.

<sup>e</sup>Polystyrene *MM* 50 000.

<sup>f</sup>In parenthesis R.S.D. (%).

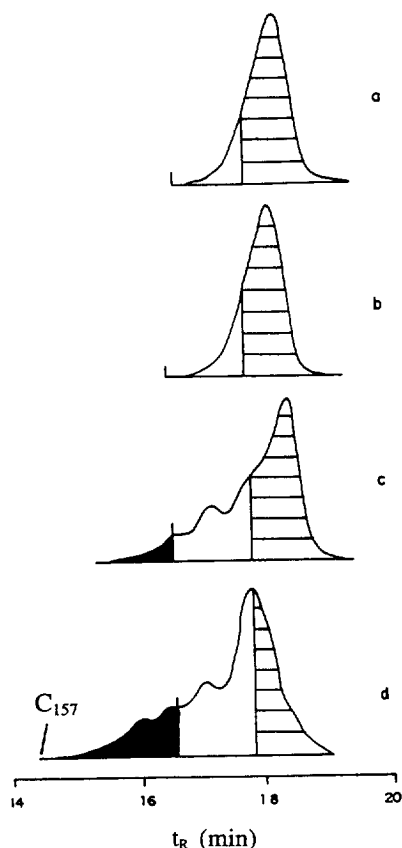


Fig. 9. SEC-ELSD for alkane fractions separated from a medium crude oil. (a) M12S-whole crude  $>C_{20}$  alkanes. (b) M12SC24 fraction separated from clay at 24°C. (c) M12SC46 fraction separated from clay at 46°C. (d) M12SC75 fraction separated from clay at 75°C. (■) Alkanes  $>C_{60}$ ; (□) alkanes  $C_{60}-C_{30}$ ; (=) alkanes  $<C_{30}$ .

large alkanes found in solid mixtures separated from crude oils. This topic is currently under study and will be published in the near future. Alkane multimodality is typical of 'problematic' fractions, as previously suggested by others [39]. There are two points to be stressed: the absence or non-detectability of large molecules in the original crude (Fig. 9a); and the fraction separated from clay at ambient temperature (Fig. 9b). Poor detectability was previously discussed in relation to the lower response of high-*MM* components. The second point refers to the determination of very large components within fractions from the same crude, separated under the combined effects of temperature and porous minerals

(Fig. 9c,d). The relative proportion of extracts obtained was 86/11/1% (w/w) for corresponding temperatures of 24/46/75°C. If the response factor is considered to be unitary, calculations suggest that the amount for each carbon fraction above  $C_{60}$  is in the ppm range. Adoption of linear  $\log MM-t_R$  calibrations obtained with *n*-alkane standards, permitted to estimate *MM* for the larger detected molecules in the vicinity of  $C_{160}$ , as illustrated for one of the cases included in Fig. 9d, for which the initial computed *MM* was 2200 ( $C_{157}$ ). The origin of such large alkanes was recently suggested as an interesting research field [12,40]. In the past, these compounds were not described very often, but their existence has been clearly established by others [9].

#### 4. Conclusions

A fast SEC methodology was developed, based on rigid silica columns and the use of a very stable ELSD system. Applicability to alkane mixtures derived from oil distillation bottoms and solid deposits was shown. These samples typically spanned the carbon range between  $C_{20}$  and  $C_{160}$ . Problems confronted on calibration and detection response for samples covering diverse alkane families and molecular mass intervals, suggested the method as best suited for monitoring of operations involving alkane mixtures. However, fair agreement in MMD was verified with HTGC techniques for samples smaller than  $C_{120}$ , and advantages were shown for SEC in cases for which the analysis concerns larger components. Analytical R.S.D. was less than 3%, and internal standardization with polystyrenes proved of help for the improvement of repeatability.

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