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SELECTION OF CONDITIONS FOR THE MOLECULAR SIZE SPECIATION OF VANADIUM AND NICKEL COMPLEXES IN OIL BY SIZE-EXCLUSION CHROMATOGRAPHY COUPLED WITH INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

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SUMMARY

The applicability of size-exclusion chromatography (SEC) with on-line inductively coupled plasma-atomic emission spectrometric (ICP-AES) detection for the determination of nickel and vanadium compounds in oil samples was examined. Four mobile phases, tetrahydrofuran, chloroform, xylene and xylene–methanol, in combination with two stationary phases, a polystyrene–divinylbenzene and a silica-based diol column packing, were characterized with regard to the shapes of the nickel and vanadium elution profiles and overall recoveries. Tetrahydrofuran and chloroform could successfully be introduced into the ICP at conventional flow-rates by the application of an aerosol cooling setup in the SEC-ICP interface. The recoveries on the diol-modified silica gel packing were significantly smaller than those found with the polystyrene–divinylbenzene packing. With tetrahydrofuran and xylene–methanol nearly complete recoveries and similar elution profiles were obtained with the polystyrene–divinylbenzene packing, whereas for chloroform and xylene adsorption of high-molecular-weight components hampered the interpretation.

INTRODUCTION

Heavy oils contain considerable amounts of vanadium and nickel, complexed with porphyrins or porphyrin-like structures[1–6]. The presence of these metals seriously hampers the processing of oils, because they deactivate the catalysts used in hydrotreating and fluid catalytic cracking[1,2]. For this reason, vanadium and nickel are removed from the oil prior to further processing. This is usually done via thermal or catalytic treatment[1,2,6].

In order to optimize the demetallation process, an analytical method is required that not only monitors the vanadium and nickel levels in the original and treated oils,

but also discriminates the metal complexes on the basis of their molecular size[6–8]. Size-exclusion chromatography (SEC) combined with element-specific detection has been shown to be a promising technique for this purpose[3–6], in particular when on-line inductively coupled plasma-atomic emission spectrometric (ICP-AES) detection is used[9–11].

So far, little attention has been paid to the choice of mobile and stationary phases especially with regard to metal speciation, partly because of the difficulties encountered with element-specific detection techniques. The laboriousness of off-line atomic absorption spectrometric (AAS) techniques makes them impractical for routine applications, whereas the use of volatile solvents in ICP-AES often leads to unstable plasmas. In this paper the results are presented of an investigation aimed at the selection of suitable chromatographic and experimental conditions for the determination of vanadium and nickel in oil fractions by SEC–ICP-AES. The role of the type of column packing and the mobile phase on the elution profiles and recovery of nickel and vanadium from the SEC column is discussed, including the effect of these parameters on the calibration graphs as measured with linear polystyrene standards.

The application of aerosol cooling, previously developed in our laboratory[12,13], to the SEC–ICP interface, eliminates the limitations that were previously experienced in the choice of mobile phases for on-line coupling of SEC and ICP-AES.

EXPERIMENTAL

Equipment

The liquid chromatograph consisted of a high-pressure pump (Model 300C; Gynkotek, Germering, F.R.G.), an injection valve (Model 7120; Rheodyne, Berkeley, CA, U.S.A.) equipped with a 20- or 100-μl sample loop, a variable-wavelength UV–VIS spectrophotometer (Spectroflow 757; Kratos, Ramsey, NJ, U.S.A.) and a recorder (Model BD-7; Kipp & Zonen, Delft, The Netherlands). A refractive index (RI) detector (Model R401, Waters Assoc., Framingham, MA, U.S.A.) was occasionally used.

The spectrometer was an AtomComp Model 975 ICAP multi-channel system, including an additional monochromator (Jarrell-Ash, Waltham, MA, U.S.A.). The specifications of the main characteristics of this system have been given elsewhere[14].

Nebulization was performed with a cross-flow nebulizer (Jarrell-Ash Model 90-790). When chloroform or tetrahydrofuran (THF) was used as the mobile phase, a laboratory-made aerosol cooling coil[12] was inserted between the nebulizer and the torch assembly. The coil was immersed in a thermostated ethanol bath (Haake, Berlin, G.D.R.), which was cooled by an immersion cooler (Model EK 11; Haake).

As the tubing materials for peristaltic pumps are not resistent to THF, a high-performance liquid chromatographic HPLC pump (Eldex, San Carlos, CA, U.S.A.) equipped with PTFE tubing was used to carry the condenser drain to waste. For the same reason the spray chamber was modified with a U-shaped glass syphon (see Fig. 1, component 9).

The multi-channel spectrometer was adapted in-house for continuous readout of the photomultiplier signals. For this purpose the data acquisition system of the spectrometer was replaced with a laboratory interface (Model 1401; Cambridge Electronic Design, Cambridge, U.K.) including 12-bit A/D converters, which was oper-
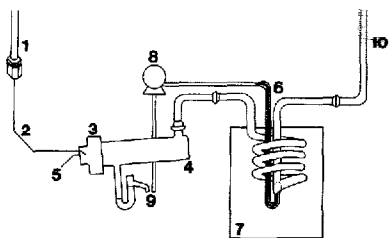
Fig. 1. Experimental setup for the SEC–ICP-AES interface. 1 = SEC column; 2 = PTFE capillary tubing; 3 = nebulizer; 4 = spray chamber; 5 = argon inner-gas inlet; 6 = condenser; 7 = cryostat bath; 8 = drain pump; 9 = drain; 10 = inner tube of ICP torch.

ated under the control of a BBC Master microcomputer (Acorn Computers, Cambridge, U.K.). The 1401 instrument was interfaced to the photomultiplier tubes by means of custom-made current–voltage converters and an eight-channel amplifier-filter system. The data obtained were initially stored on disk on the BBC microcomputer and subsequently sent to a minicomputer (Model HP 1000; Hewlett-Packard, Palo Alto, CA, U.S.A.) for the actual data processing.

Electrothermal atomization AAS (ETA-AAS) measurements were performed with a graphite furnace system (Model HGA 500; Perkin-Elmer, Norwalk, CT, U.S.A.) in combination with an atomic absorption spectrometer (Model 560, Perkin-Elmer).

Materials and chemicals

The solvents were of analytical-reagent grade and were filtered through 0.5-μm Fluoropore filters (Millipore, Bedford, MA, U.S.A.).

Vanadyl mesotetraphenylporphine (VOTPP) was obtained from Strem Chemicals (Newburyport, MA, U.S.A.) and nickel mesotetraphenylporphine (NiTPP), 2,7,12,17-tetraethyl-3,8,13,18-tetramethyl-21H, 23H-porphine dihydrobromide (Etio), 2,3,7,8,12,13,17,18-octaethylporphine (OEP) and its nickel(II) complex (NiOEP) from Aldrich (Brussels, Belgium). Polystyrene standards were obtained from Merck (Darmstadt, F.R.G.).

The SEC columns used were commercially available prepacked columns: a 300 × 7.5 mm I.D. PL-GEL column (Hewlett-Packard, Waldbronn, F.R.G.), containing a polystyrene–divinylbenzene (PS–DVB) packing with a mean pore diameter of 500 Å and a 250 × 9.5 mm I.D. GF-250 column (DuPont, Wilmington, DE, U.S.A.) containing a 5-μm zirconia-stabilized, diol-modified silica gel with a mean pore diameter of 150 Å.

Chromatography

The SEC experiments were carried out on the two types of column packings described above. Four mobile phases, THF, chloroform, p-xylene and a mixture of p-xylene and methanol, which are frequently used for the SEC of oils, were applied throughout the study. In all experiments the columns were equilibrated by pumping through at least 100 ml of the mobile phase (about six column volumes) at a flow-rate of 1 ml/min. The injection volume was usually 100 μl and the chromatograms were

TABLE I

ETA-AAS OPERATING CONDITIONS

Parameter	Nickel	Vanadium*
Sample volume	20 μl	20 μl
Drying**	200°C/5s/5s	200°C/5s/5s
Ashing**	800°C/5s/10s	–
Atomization**,***	2700°C/1s/5s	2660°C/1s/5s
Cleaning**	2700°C/1s/2s	2700°C/1s/2s

  * For vanadium the entire programme was repeated once between consecutive analyses.
  ** Values given are temperature (°C)/ramp time (s)/hold time (s).
  *** The argon purge flow-rate, 300 ml/min during the complete cycle, was reduced to 30 ml/min during atomization.

recorded by UV measurement at 254 nm, visible-range measurement at 405 nm (Soret absorbance) or by refractive index (RI) or ICP-AES detection.

The molecular weight calibration graphs on the SEC columns were obtained by injecting polystyrene standards of known molecular weights. These standards were dissolved in the mobile phase and their retention volumes were measured using UV or RI detection.

Chromatographic recovery studies

The recovery of V and Ni from the SEC column was determined by analysing both the original sample and a defined collected fraction of the effluent. After injection of 100 μl of sample, the effluent fractions between 1.0 and 2.5 times the exclusion volume of the column were collected and adjusted to a volume of 10 ml. Next, the solvent was evaporated to dryness by means of a stream of nitrogen. The residue was dissolved in 0.4 ml of *p*-xylene and this solution was analysed by ETA-AAS.

In order to analyse the original sample under conditions identically to the SEC fractions, the column was disconnected from the injection valve and the same volume of original sample as used in the SEC procedure was directly injected, via the injection valve, into a measuring bottle and then adjusted to a volume of 10 ml. This solution was similarly treated as described for the SEC fractions. All measurements were carried out in duplicate. After each experiment the columns were eluted with about 100 ml of THF before injecting the next sample.

The experimental conditions for the ETA-AAS measurements are given in Table I.

SEC–ICP coupling

SEC–ICP coupling was accomplished by connecting the outlet of the column to the inlet of the nebulizer by means of PTFE tubing with dimensions of 300 × 0.3 mm I.D. For reasons discussed under Results and Discussion, a setup for aerosol cooling was installed between the nebulizer and the torch assembly, as shown schematically in Fig. 1. By means of a cryostat, cooling temperatures could be adjusted down to −20°C.

TABLE II

ICP-AES OPERATING CONDITIONS
Nebulizer feeding rate corresponds to mobile phase flow-rate.

Parameter	Solvent			
	THF	Chloroform	Xylene	Xylene–methanol
Forward power (kW)	1.75	1.75	1.75	1.75
Reflected power (W)	< 10	< 25	< 15	< 10
Observation height (mm above load coil)	20/16	20	20	20
Outer gas flow-rate (l/min)	25	25	22	22
Inner gas flow-rate (l/min)	0.7	0.7	0.7	0.7
Intermediate gas flow-rate (l/min)	1.2	1.2	1.4	1.4
Condenser temperature (°C)	− 20	− 20	20	20

The ICP-AES operating conditions are summarized in Table II. Emission intensities were monitored at 309.311 nm (vanadium/ionic emission) and 341.476 nm (nickel/atomic emission). When both UV and ICP-AES detection were used, the UV detector was placed in series between the column and the nebulizer.

Sample preparation
The oil samples were prepared by dissolving 3% (w/v) of the oil in the applied mobile phase, followed by filtration of this solution through 0.5-μm PTFE filters (Alltech, Deerfield, IL, U.S.A.). Filtered samples were considered to be identical with the original samples as no loss of nickel and vanadium could be detected by ETA-AAS.

RESULTS AND DISCUSSION

Conditions of coupling of SEC with ICP-AES
When using non-aqueous solvents in ICP-AES, special care has to be taken to obtain plasmas that are stable over prolonged periods of time. Compared with water, organic solvents cause a decrease in the plasma excitation temperature and an increase in the background emission intensity[15]. Depending on the type of organic solvent, the deterioration of the excitation conditions may even lead to complete breakdown of the plasma.

It has been found that the plasma becomes unstable when a certain mass flow of organic solvent is exceeded, the so-called maximum tolerable solvent load[12]. This quantity varies with the type of organic solvent and has to be determined experimentally.

The mass flow of organic solvent entering the plasma can either be controlled by application of aerosol introduction rates that have been adapted to the nature of the solvent[16] or by thermal regulation of the plasma loading[12,13]. The latter method
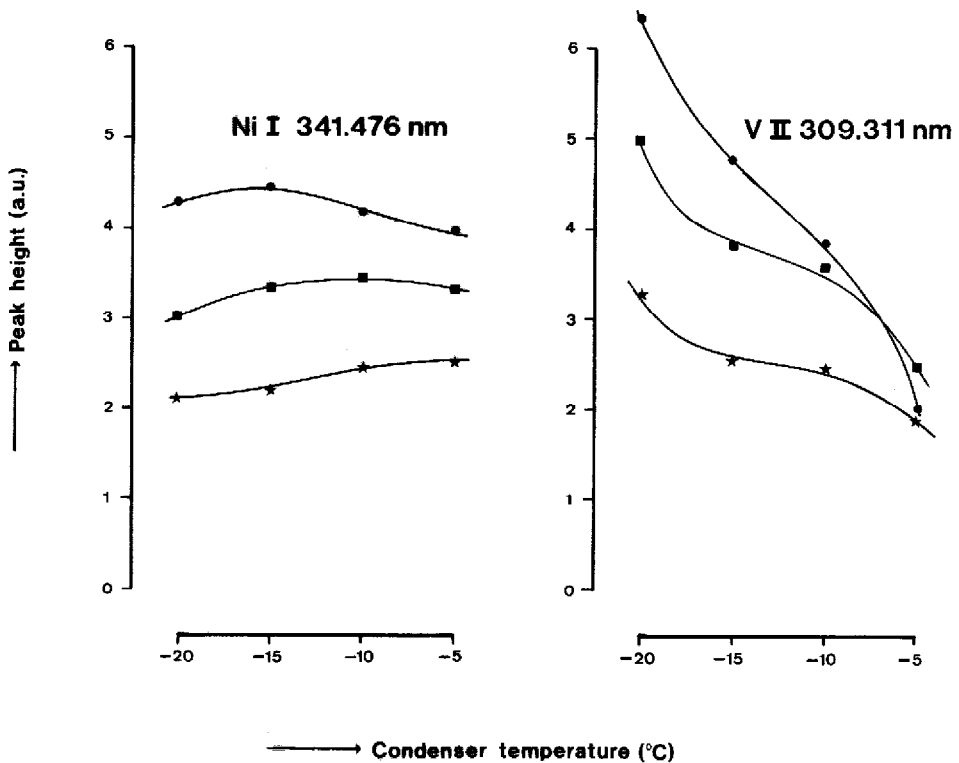
Fig. 2. Peak height of the transient emission intensity signal for a 100-μl injection of nickel and vanadium tetraphenylporphyrin standards in SEC–ICP-AES as a function of condenser temperature for various measuring heights in the plasma: (●) 16 mm, (■) 20 mm and (★) 24 mm above the load coil.

is best suited for liquid chromatography with ICP-AES detection because it does not impose limitations on mobile phase flow-rates. Therefore, a condenser was installed between the nebulizer and the torch assembly (see Fig. 1). The purpose of the cooling unit is to condense a fraction of the organic vapour, via adjustment of the cooling temperature, such that the residual mass flow of organic solvent is kept below the maximum tolerable solvent load of the plasma, while the analyte mass flow is essentially unaffected. The condenser temperature required to accomplish this depends mainly on the volatility of the solvent.

Fig. 2 shows the effect of the condenser temperature on the peak height of the transient emission intensity signals from some standard porphyrins for different observation heights in the plasma and for THF as the solvent. For peak area as a function of the condenser temperature similar results were obtained. It must be noted that the plasma becomes unstable when for THF cooling temperatures above − 5°C are applied. As shown in Fig. 2, a decrease in the condenser temperature, and hence of the mass flow of organic vapour, has a favourable effect on the detector response only for vanadium. The reason for the different behaviour of the spectral lines considered on reduction of the solvent loading of the plasma is that the intensity of ionic lines

(V II) is more susceptible to a decrease in the excitation temperature than the intensity of the atomic lines (Ni I)[17].

As the noise levels of the analytical signals do not differ significantly for the various condenser temperatures, the analytical performance of the condenser setup is determined primarily by the net signal intensity. Accordingly, from Fig. 2 it can be concluded that a condenser temperature of $-20°C$ combined with an observation height in the plasma of 16 mm above the load coil makes a good experimental compromise. Optimum ICP-AES experimental conditions for some other solvents, such as chloroform, can be found in refs. 12 and 13.

The use of a condenser introduces additional peak broadening and consequently affects the chromatographic resolution. The magnitude of this peak broadening was determined by measuring the peak widths resulting from 20-μl injections of a standard porphyrin solution directly (column removed) into the ICP with and without the condenser, at a nebulizer feeding rate of 1 ml/min. From these measurements the peak broadening caused by the condenser, expressed as the volume standard deviation, σ_V, was calculated to be 34 μl. The total external peak broadening introduced by the ICP-AES system amounts to 45 μl. This causes about a 35% decrease in column efficiency (i.e., the plate number N) and about a 20% loss in resolution for the two columns under investigation.

Selection of SEC conditions

SEC has been used frequently for the determination of the molecular weight distributions of oils and oil fractions[18–23] and coal-derived liquids[24–27]. The technique has also been shown to be suitable for the molecular speciation of nickel and vanadium complexes in oil, using off-line ETA-AAS or on-line ICP-AES element-specific detection[3–11]. In most instances polystyrene-based SEC packings with pore sizes in the range 50–1000 Å are used. THF, mixtures of benzene and methanol, xylenes, mixtures of xylenes, cresols and pyridine and, to a lesser extent, chloroform usually serve as the mobile phase.

When employing liquid chromatography with ICP-AES detection, xylenes are generally used as the mobile phase, because they can be introduced into the ICP without the need for precautions regarding plasma overloading[16]. However, in addition to the required matching of the organic mobile phase to the ICP, two other requirements have to be fulfilled: (i) the recovery of the metal complexes from the column must be complete and (ii) the chromatographic system has to discriminate the metal complexes solely on the basis of their molecular size. Both requirements may not be met when the metal complexes interact with the column packing material in the presence of the selected mobile phase[18].

Recoveries of V and Ni in the SEC fractionation

For a meaningful interpretation of SEC results in terms of a molecular weight distribution of the oil, forms of retention of the solutes other than sole exclusion, such as adsorption, must be absent and the metal complexes must be stable during the chromatography. If exclusion is the only retention mechanism all metal species will elute from the column within the exclusion limits, i.e., all injected metal compounds are completely recovered in the eluent volume collected between the total exclusion and total permeation volume. Measurement of the recovery of the injected amount of

metal compounds in this collected eluent fraction (defined as the SEC recovery) is therefore an indication of the occurence of retention phenomena other than size exclusion. We therefore determined the V and Ni content in a collected volume between 1 and 2.5 times the total exclusion volume and calculated the SEC recovery from the total metal content in the injection volume. It must be noted that only for a 100% SEC recovery can a reasonably pure exclusion mechanism be assumed; for smaller SEC recoveries this certainly does not hold.

Little is known about the nature and stability of the metal complexes in oil. Ni and V porphyrins appear to be fairly stable under vigorous conditions such as refluxing at increased temperature in trifluorophosphoric or sulphuric acid[28] and it is therefore reasonable to assume that these compounds are stable in the mobile phases applied in this study. However, it has been shown that V and Ni porphyrins form reversible complexes with nucleophiles such as ethanolamine[28,29]. As many nucleophilic compounds are present in oil, the appearance of multi-ligand metal complexes cannot be excluded. However, when dissolving 3% (v/v) of oil in the mobile phase, the sample is so dilute that the possibly formed multi-ligand metal complexes dissociate into the most stable configuration and most probably will remain stable during the chromatography. The same arguments can be assumed to hold for the non-porphyrin-like metal complexes.

The SEC recoveries of Ni and V on the polystyrene and diol-modified silica gel packings as found with THF, chloroform, p-xylene and p-xylene–methanol (80:20,
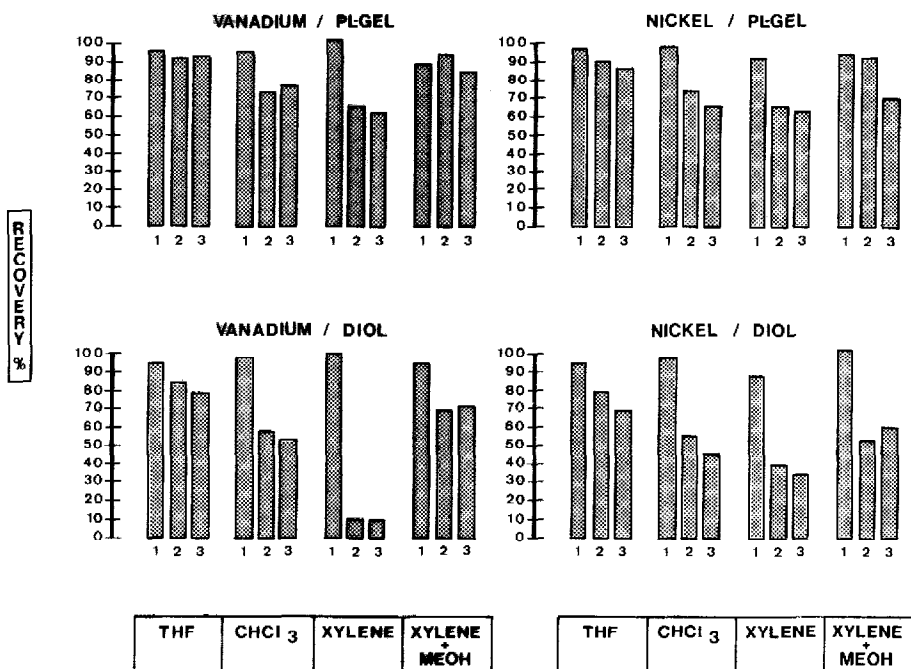

Fig. 3. Recovery of nickel and vanadium in SEC of different samples on PS–DVB and diol-type columns with selected mobile phases. Samples: (1) tetraphenylporphyrin standards; (2) Gach Saran Atmospheric Residue; (3) Arabian Heavy. MeOH = Methanol.

v/v) as mobile phase are shown in Fig. 3. The last mixture was chosen as the addition of methanol to the mobile phase has been reported to result in a better suppression of adsorption effects[3,18]. A methanol concentration of 20% was chosen to obtain the maximum increase in polarity without imposing the need for aerosol cooling. From Fig. 3 it can be seen that, within the experimental error, which is about 5%, in all instances a nearly complete SEC recovery was obtained for the tetraphenylporphyrin standards. With regard to the oil samples, two significant conclusions can be drawn. First, the SEC recoveries of both Ni and V are higher on the polystyrene packing than on the diol-modified silica gel packing. Second, the SEC recoveries decrease substantially with decreasing polarity of the mobile phase according to the sequence THF > chloroform > p-xylene. As expected[3,18], the SEC recoveries are significantly increased by the addition of methanol to p-xylene. The observed effects can be attributed to the interaction of metal complexes with the packing material. The diol-modified silica gel has a significantly more polar surface than the polystyrene packing and, as a result, the former packing shows greater adsorptive properties for (polar) metal complexes. The greater is the adsorption the weaker is the elution strength (polarity) of the mobile phase. In order to investigate whether the Ni and V compounds irreversibly adsorb on the packings, fractions of the mobile phase eluting after 2.5 times the total exclusion volume were collected and analysed by AAS. From the mass balance it appears that on the polystyrene column with THF all metals could be recovered in a volume fraction between 1 and 3.5 times the total exclusion volume. For p-xylene–methanol (80:20), 95% of the metals were found to elute in the volume fraction between 1 and 5 times the total exclusion volume. However, with chloroform and p-xylene it appears that a part of the metal compounds absorb strongly on the packing and only about 80% of the metals were recovered in a collected fraction between 1 and 20 times the total exclusion volume. With the diol column and THF as mobile phase all metals could be recovered within an elution volume of 6 times the total exclusion volume. With p-xylene–methanol (80:20) as mobile phase the recoveries in the same fraction as with THF were about 85% for V and 70% for Ni. Very strong adsorption of the metals was found with chloroform and in particular of V with p-xylene as mobile phase. The recoveries of V and Ni in a fraction of 20 times the exclusion volume ranged between 55 and 65% for chloroform and between 15 and 45% for p-xylene.

From the results depicted in Fig. 3 and from the adsorption data, it can be concluded that for the SEC of vanadium and nickel complexes in oil a polystyrene column packing and a medium-polarity solvent have to be used in order to obtain unambiguous results. In particular, the application of weakly eluting solvents, such as chloroform and p-xylene, should be avoided because with these solvents a substantial part of the metal complexes adsorbs strongly on the column packing material.

In order to investigate whether the metal compounds adsorb irreversibly on the column packing, in all experiments the mobile phase was changed to THF, after collection of the SEC fraction, and 6 (PS–DVB column) to 10 (diol column) times the total exclusion volume were collected and analysed by AAS. The total recovery from the column was then determined from the mass balance. In all experiments the total recovery of the metal compounds ranged between 95 and 105%, which can be considered as complete within the experimental error of the AAS measurements.

Elution profiles

The effect of the type of mobile phase on the elution profiles as recorded with visible-range and ICP-AES detection is shown in Figs. 4–7. In order to facilitate the comparison of the profiles a bar has been drawn at the maximum of the THF elution curve. The figures show that the profiles differ significantly when different mobile phases are used.

The elution patterns recorded with visible-light detection for tetrahydrofuran and chloroform have similar shapes, although the pattern for chloroform seems to be compressed in comparison with the THF curve. For the xylene-based mobile phases
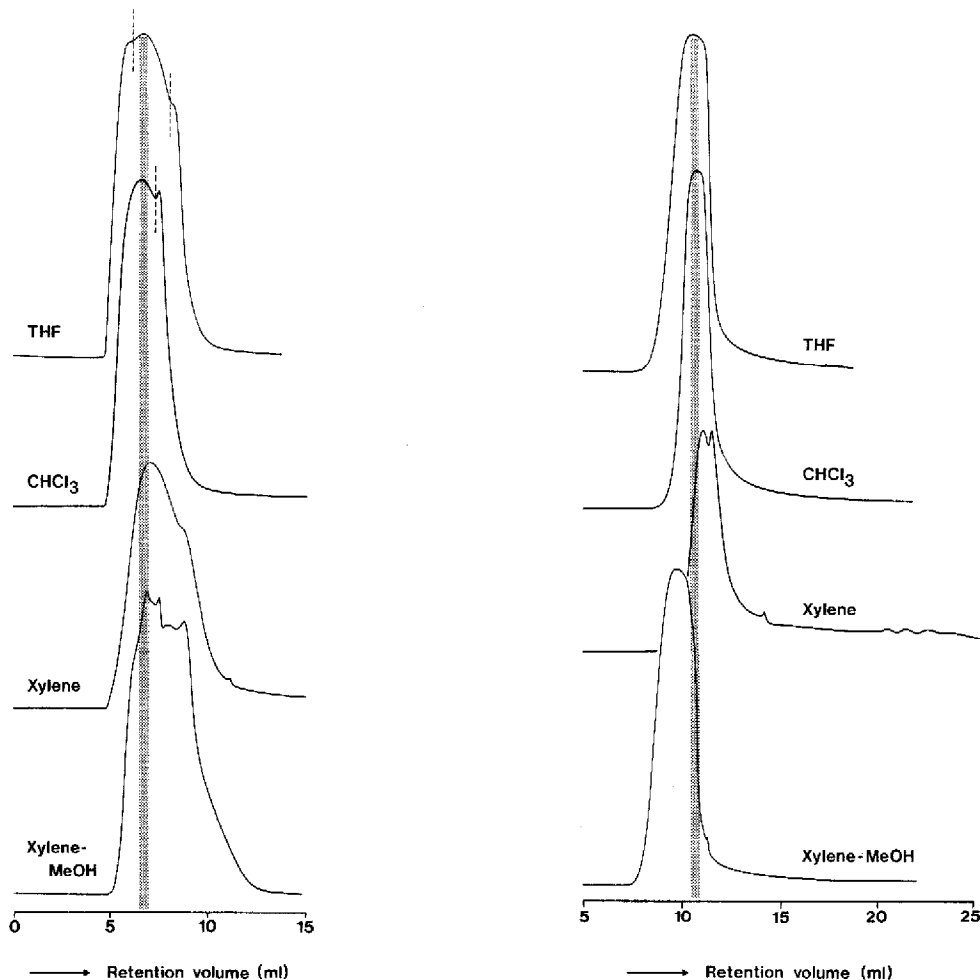

Fig. 4. SEC elution profiles for Gach Saran Atmospheric Residue (3%, w/v) on the PS–DVB column for different mobile phases. Detection, VIS, 405 nm; mobile phase flow-rate, 1 ml/min. The dashed lines refer to fractionation experiments described in the text. MeOH = Methanol.

Fig. 5. SEC elution profiles for Gach Saran Atmospheric Residue (3%, w/v) on the diol-type column for different mobile phases. Detection, VIS, 405 nm; mobile phase flow-rate, 1 ml/min.
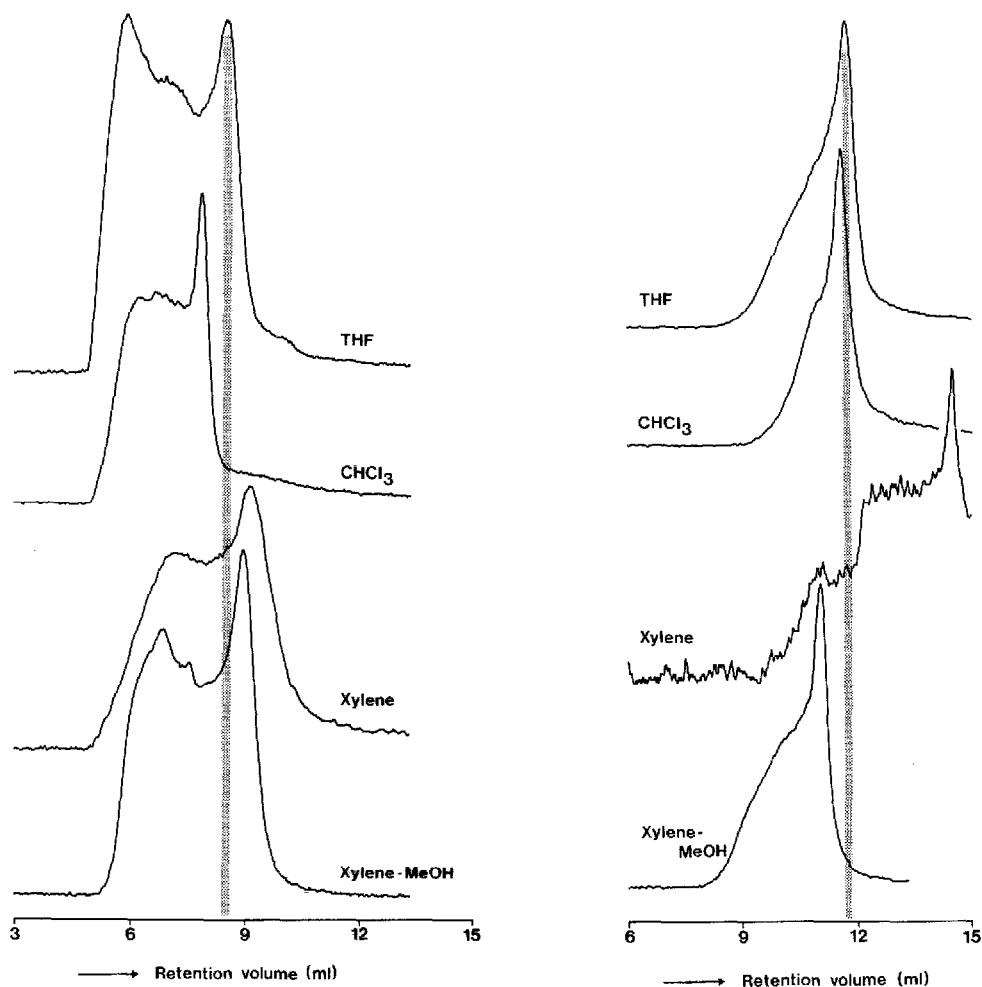
Fig. 6. Elution profiles for vanadium using ICP-AES detection for Gach Saran Atmospheric Residue (3%, w/v) on the PS–DVB column for different mobile phases. Detection wavelength, V, 309.311 nm; mobile phase flow-rate, 1 ml/min. For ICP operating conditions, see Table II.

Fig. 7. Vanadium elution profiles using ICP-AES detection for Gach Saran Atmospheric Residue (3%, w/v) on the diol-type column for different mobile phases. Detection wavelength, Ni, 341.476 nm; mobile phase flow-rate, 1 ml/min. For ICP operating conditions, see Table II.

the chromatogram is broadened and severe tailing is observed, especially for combinations of xylene with the diol-type column and xylene–methanol with the PS–DVB column. The corresponding peak patterns are distinctly different from those obtained using THF or chloroform as the mobile phase.

    With respect to the interpretation of the vanadium ICP profiles shown in Figs. 6 and 7, the following comments can be made. Although xylene and xylene–methanol do not require aerosol thermostatting, the experimental setup shown in Fig. 1 was applied so as to make comparison between the profiles more straightforward. Be-

cause of the lower nickel concentration levels in oil samples, in combination with poorer ICP-AES detection limits, the elution patterns for nickel are much more "noisy' than those for vanadium. As the changes in peak profiles were found to be similar for nickel and vanadium, only those for vanadium are shown. As the ICP-AES detector response is dependent on the plasma excitation conditions and therefore on the mobile phase used in the SEC separations, peak heights and areas cannot be compared directly from the diagrams. However, a comparison of signal-to-noise ratios, in combination with the recoveries shown in Fig. 3, leads to the conclusion that the detection capabilities of ICP-AES do not show gross variations with the mobile phases used.

As can be seen from Figs. 6 and 7, the vanadium profiles differ considerably from those recorded with visible-range detection. Compared with the profile obtained with THF on PS–DVB, the chromatogram for chloroform is compressed and that for xylene is broadened. Both profiles lack the maximum at the high-molecular-weight end of the chromatogram. In contrast, the profile for xylene–methanol more closely resembles that for THF, although its visible-range pattern was distinctly different from the profile for THF. The peak positions for the PS–DVB column depend strongly on the mobile phase used.

Except for xylene, the elution profiles on the diol-type column are nearly identical, although the peak positions are different for the different solvents. The large retention and the poor signal-to-noise ratio for xylene suggest strong adsorption on the diol-type column. This is consistent with the 10% recovery shown in Fig. 3. None of the elution patterns for the diol-type column shows a maximum in the high-molecular-weight region.

Molecular weight calibration of the SEC columns

The effect of the type of mobile phase on the calibration of the SEC columns was determined with a standard set of polystyrenes and benzene and is shown in Figs.
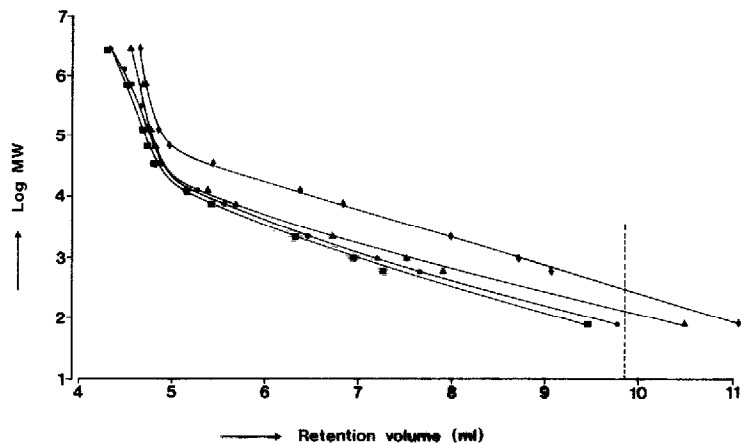

Fig. 8. Molecular weight (MW) calibration graphs for polystyrene standards and benzene on the PL-GEL column using different mobile phases: (●) THF; (■) chloroform; (▲) xylene; (◆) xylene–methanol. Dashed line: total permeation limit.
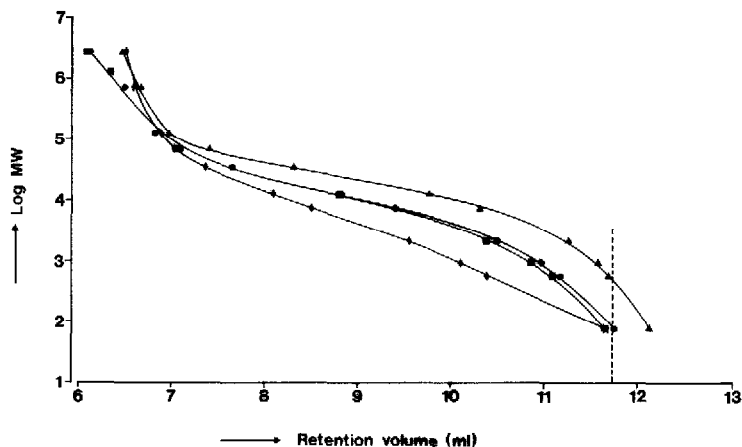
Fig. 9. Molecular weight (MW) calibration graphs for polystyrene standards and benzene on the GF-250 column using different mobile phases: (●) THF; (■) chloroform; (▲) xylene; (◆) xylene–methanol. Dashed line: total permeation limit.

8 and 9. The total permeation limits, as determined by weighing of the column with different solvents, were found to be 9.85 ml for the PL-GEL column and 11.73 ml for the diol column. The elution behaviour of the PS standards on the PL–GEL column with THF and chloroform is nearly identical, except for a constant slight shift in retention volume for the chloroform curve. These small differences in retention can be attributed to the difference in the pore swelling of the gel in chloroform and THF. The lower swelling of the gel in chloroform impairs the resolving power of SEC with this solvent[30]. For xylene there is a small shift towards higher elution volumes, and probably sorption into or on to the packing material will play a part, as is demonstrated by the elution of benzene at a retention volume larger than the total permeation limit.

TABLE III

MOLECULAR WEIGHTS FOR SELECTED MODEL PORPHYRINS DETERMINED EXPERIMENTALLY BY SEC USING THE POLYSTYRENE CALIBRATION GRAPHS

Column	Solute*	Real MW	MW determined by SEC			
			THF	Chloroform	Xylene	Xylene–methanol
PS–DVB	VOTPP	679.7	372	440	237	395
	Etio	640.5	337	409	241	472
	OEP	534.8	397	474	397	714
Diol	VOTPP	679.7	240	248	N.D.**	458
	Etio	640.5	330	153	N.D.	355
	OEP	534.8	426	262	N.D.	433

* Model porphyrins: VOTPP = vanadyl mesotetraphenylporphine; Etio = 2,7,12,17-tetraethyl-3,8,13,18-tetramethyl-21H, 23H-porphine dihydrobromide; OEP = 2,3,7,8,12,13,17,18-octaethylporphine.
** N.D. = Not determined (outside calibration range).

The elution volumes for PS standards in xylene–methanol are larger than those in THF; this difference can be as large as 1.5 ml. Probably a reversed-phase type of distribution towards the packing occurs in the presence of methanol. It can further be noted that the retention of polystyrene standards when using THF as the mobile phase was the same on injecting the standards dissolved in THF or dissolved in the oil samples [3% (w/v) in THF]. This indicates that the sample is sufficiently diluted to avoid the influence of mutual interaction on the retention of the solutes in oil.

For the diol-type column the calibration graphs for THF and chloroform coincide well, but those obtained for the xylene-based mobile phases deviate significantly. With xylene there is an additional retention of the solutes by adsorption on the column packing material. In the presence of methanol the calibration graph is shifted in the opposite direction for unknown reasons.

Molecular weight distributions of oil samples

To examine the suitability of molecular weight calibrations based on PS standards for metal compounds present in oil samples, two different routes were followed. First, the calibration of both columns was checked with a number of model porphyrins. As most of the commercially available metal porphyrins cover only a small molecular weight range, this experiment was performed with both metal-containing and metal-free porphyrins. A selection of results is presented in Table III. For all the solvents used, the molecular weights determined from the PS calibration graphs are much smaller than the real molecular weights. Thus calibration with polystyrenes is insufficient for the determination of the molecular weights of these model porphyrins. However, porphyrins constitute only a minor part of the metal complexes present in oil[1]. Therefore, a second approach involving computerized manipulation of the chromatograms in order to convert the volume axis to a log(molecular weight) axis was adopted. This was done by means of the PS calibration graphs. In the ideal case, this approach would rule out the effects of the mobile phases on the column packing.

The procedure involves a smoothed spline interpolation[31] through the experimental data from the PS calibration graphs. In the present instance the use of the spline interpolation is convenient as it does not require a physical model to fit the data. By means of this interpolation, files were generated that correlate each retention volume data point with a corresponding PS molecular weight value. Subsequent combination of these files with the chromatogram files resulted in profiles of vanadium content *versus* polystyrene-based molecular weights (Fig. 10). It should be noted that the differences in signal height between the converted and the original profiles arise from scaling with the reciprocal slope of the calibration graph, which is necessary for consistency of the distribution[18].

A comparison of Figs. 10 and 6 shows that when the column calibration data are included in the diagrams, there is a better agreement for the elution profiles recorded with THF, chloroform and xylene. The profile for xylene–methanol is "over-compensated". This is probably due to a specific effect of methanol on the polystyrene standards, rather than the result of an overall effect of the mobile phase on the column packing. Except for xylene–methanol, the conversion procedure appears to align the profiles. This could indicate a similar behaviour for solutes present in oil samples and polystyrene standards in three of the mobile phases used.
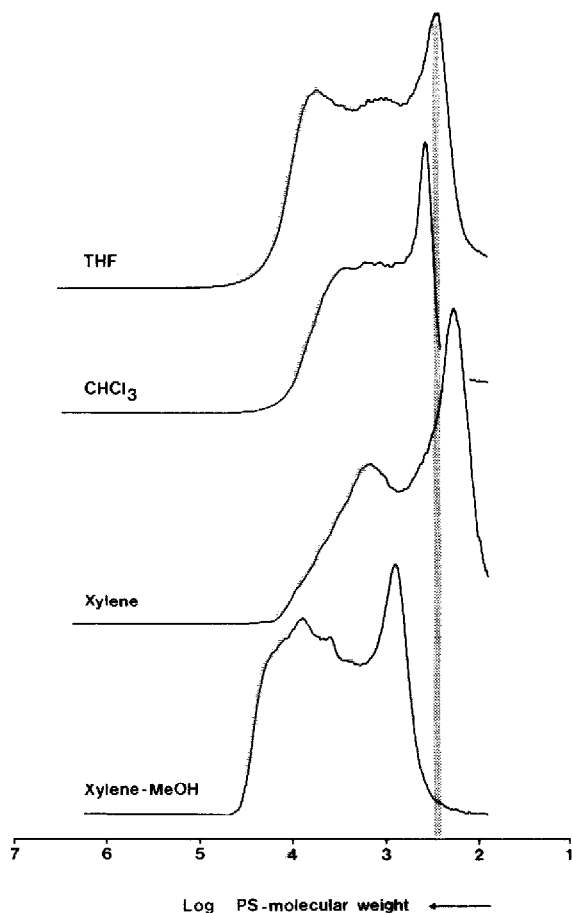
Fig. 10. Vanadium SEC–ICP-AES profiles for Gach Saran Atmospheric Residue on PL-GEL after computerized conversion of the volume axis to a log(PS) molecular weight axis.

Adsorption/association effects

Apart from differences arising from changes in the gel packing, SEC profiles may be affected by solute–solute and solute–solvent associations and by adsorption of solutes on to the gel surface[30]. Although THF and chloroform are reported to be the most compatible solvents for polystyrene stationary phases, with size exclusion being the predominant separation mechanism[20,27,32–34], differences in recoveries (*cf.*, Fig. 3) and the differences in the vanadium profiles for oil samples reveal the occurence of additional interaction mechanisms. The profile in THF, for instance, could indicate that for chloroform and xylene adsorption of high-molecular-weight compounds on to the stationary phase has occurred. This is consistent with the lower recoveries for chloroform and xylene shown in Fig. 3. On the other hand, it is known that in concentrated solutions of asphaltenes in THF self-association can occur[26], which brings about an apparent increase in the molecular weights of these compounds. However, it self-association had occurred, it would be expected to appear

more pronounced in a poorer solvent such as xylene. The lack of a maximum at the high-molecular-weight end of the chromatogram for xylene is not conclusive in this instance because of the simultaneous occurence of adsorption effects.

In order to investigate the role of association effects in more detail, the effluents from the PS-DVB column using THF and chloroform as the mobile phases were collected in three and two fractions, respectively, according to the dashed lines in Fig. 4. After evaporation to dryness, the fractions collected in THF were dissolved and analysed by SEC with chloroform as the mobile phase. The fractions collected in chloroform were treated similarly using THF as the mobile phase. If association had occured in THF, and chloroform were capable of breaking up these associates, the high-molecular-weight fraction collected in THF should reveal the presence of lower molecular weight compounds when analysed in chloroform. In addition, the first fraction collected in chloroform should show a shift towards lower elution volumes (and higher molecular weights) when analysed in THF. However, neither of these effects has been observed. This supports the suggestion that adsorption rather than association is involved. Consequently, the appearance of the high-molecular-weight maximum on the addition of methanol to the xylene mobile phase indicates a significant decrease in the adsorption of the high-molecular-weight compounds.

Detection limits, sample concentrations and matrix effects

The detection limits of nickel and vanadium, based on signals from tetraphenylporphyrin standards equal to three times the standard deviation of the noise and using THF as the mobile phase, were found to be 3.5 and 0.5 ng, respectively. This corresponds to concentration detection limits of 35 and 5 ng/ml for 100-μl injections.

Considering the 30-fold dilution step applied for crudes and derived products, this leads to detection limits in the original sample of 1.2 μg/g for nickel and 0.17 μg/g for vanadium. As the nickel and vanadium levels in crudes range from 4 to 150 and from 8 to 1200 μg/g, respectively[1], and the metal compounds are in general distributed over a large molecular-weight range, the determination of nickel will be limited to samples with a relatively high concentration. The situation is better with vanadium because of the lower detection limits and higher concentration levels in crudes.

As will be clear from the above, relatively high sample concentrations have to be used. This is in agreement with values of 1–10% (w/v) reported by other workers[3,9,10]. As elution anomalies such as association effects tend to increase with increasing sample concentration[20,26], one has to be careful in the interpretation of the SEC patterns and molecular-weight distributions obtained.

SEC–ICP-AES experiments with oil samples spiked with tetraphenylporphyrin standards show that in the presence of an oil matrix the detector response for the tetraphenylporhyrins decreases. The decrease is more pronounced for vanadium (ionic emission) than for nickel (atomic emission), suggesting an effect of the oil matrix on the plasma excitation conditions. Although there is no dramatic decrease in signal intensities (about 10–20% for a 1 ppm NiTPP or VOTPP standard), its occurrence again stresses the potential pitfalls in the interpretation of SEC ICP-AES results. This holds in particular when the matrix composition differs for different sample types and, moreover, when even in a single chromatogram response factors may vary as a result of changes in the matrix composition due to the separation process.

Recommendations for the SEC–ICP-AES of oil samples

As the number of compounds present in oil samples is enormous, and these compounds have a wide variety of different configurations, it is obvious that no specific combination of column, mobile phase and calibration standards can be recommended for all situations. From this work, it can be concluded that THF and xylene–methanol in combination with a PS–DVB column show the best behaviour in terms of overall recoveries for nickel and vanadium and in revealing the high-molecular-weight part of the SEC profiles. Xylene–methanol would be preferable in SEC–ICP, because no special precautions are required. Nevertheless, preference should be given to THF, because for the polystyrene-type columns its interactions with various types of solutes are well documented [20–23,26,27,30,35–39]. However, the complexity of the separation mechanisms, which are complicated by solute–solvent, solute–gel and solute–solute interactions, requires additional experiments with independent analytical techniques to test the SEC results. Especially with regard to the molecular-weight distributions additional calibrations should be performed, preferably with narrow preparative SEC fractions of materials similar to those under study, with known molecular weights as determined, for example, by vapour-phase osmometry or ultracentrifugation[25,26].

Application of SEC–ICP-AES in catalyst research

An important field of application of the SEC–ICP-AES analysis of oil samples involves monitoring of the hydrodemetallation process. Fig. 11 shows the vanadium and nickel profiles of Gach Saran Resid, a heavy Iranian atmospheric residue, and its products. The properties of the feed are given in Table IV. The resid was treated with two different hydrodemetallation catalysts under the conditions given in Table V. As can be seen from Fig. 11, both nickel and vanadium are removed mainly from the smaller molecules. The selectivity of demetallation for different molecular weights is the same for both catalysts.
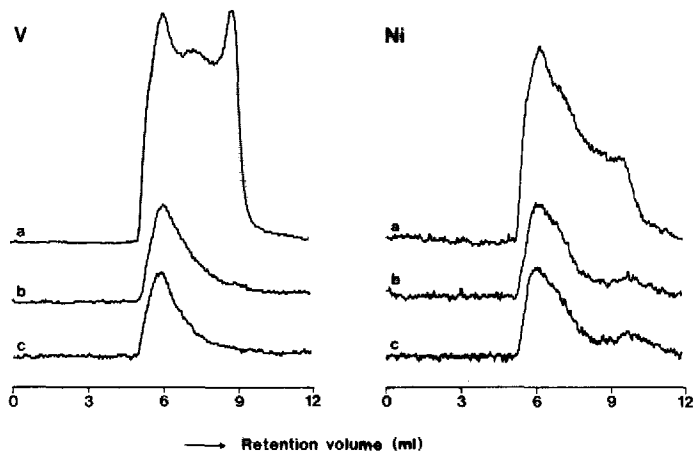

Fig. 11. Vanadium and nickel SEC–ICP-AES profiles for (a) Gach Saran Atmospheric Residue and (b and c) two of its products that followed different hydrotreatment schemes. Sample concentration for nickel analyses: 10% (w/v).

TABLE IV

PROPERTIES OF THE FEEDS USED

Component	Gach Saran Atmospheric Residue (density 0.9751 g/ml)	Kuwait Atmospheric Residue (density 0.9658 g/ml)
Sulphur (%, w/w)	3.05	3.98
Nitrogen (ppm)	4400	2230
Conradson carbon residue (%, w/w)	11.46	10.18
Nickel (ppm)	70	16
Vanadium (ppm)	229	63

TABLE V

PROCESS CONDITIONS OF CATALYTIC HYDROTREATMENT

Parameter	Gach Saran Resid		Kuwait Atmospheric Resid		
	Fig. 11b	Fig. 11c	Figs. 12d–14	Figs. 12b–14	Figs. 12c–14
LHSV*	0.50	0.50	0.95	0.95	0.95
Temperature (°C)	372	372	370	370	370
H_2 pressure	106	106	136	136	140
Catalyst type	HDM**	HDM	HDM	HDS*** (cat. 1)	HDS (cat. 2)

 * LHSV = Liquid hourly space velocity.
 ** HDM = Hydrodemetallation catalyst.
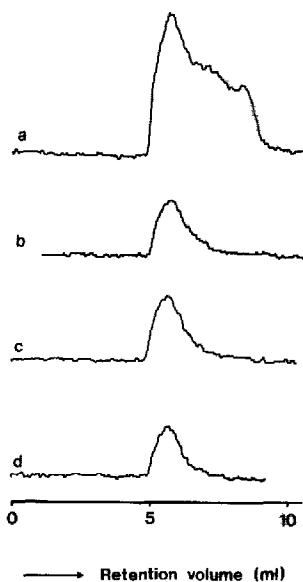 *** HDS = Hydrodesulphurization catalyst.

Fig. 12. Vanadium SEC–ICP-AES profiles for (a) Kuwait Atmospheric Residue, (b and c) products formed when the resid is hydrotreated using two different hydrodesulphurization catalysts and (d) a hydrodemetalation catalyst.
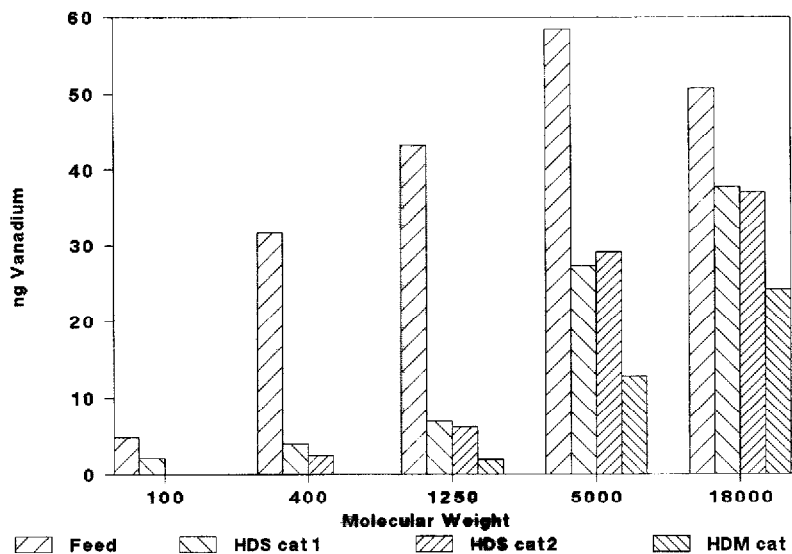
Fig. 13. Vanadium content of five molecular-weight fractions of Kuwait Atmospheric Residue before and after hydrotreatment with different catalysts (cat). The fractions originate from 3 mg of the feed and the products.

Fig. 12 shows the vanadium profiles of Kuwait Atmosperic Resid and different products resulting from treatment with two types of catalysts, *viz.*, two different resid hydrodesulphurization catalysts (Fig. 12b and c) and a hydrodemetallation catalyst
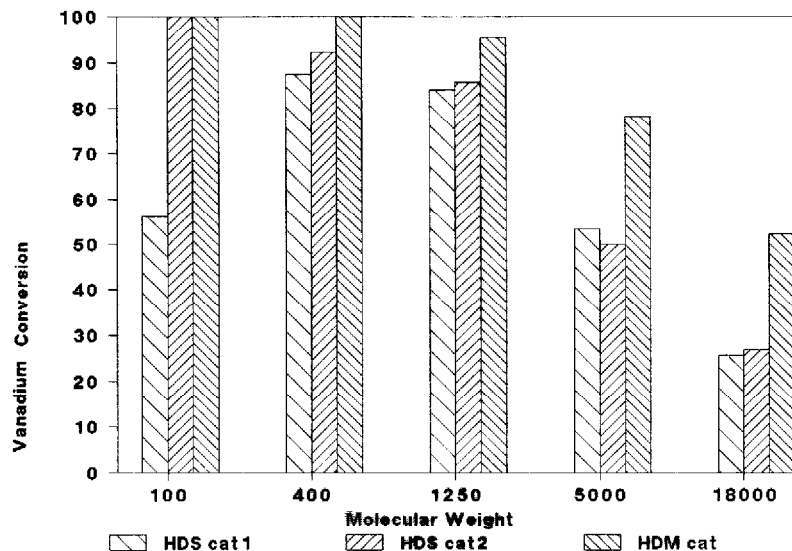

Fig. 14. Conversion of vanadium (in %) of Kuwait Atmospheric Residue as a function of molecular weight for three different hydrotreatment catalysts.

(Fig. 12d). The characteristics of the feed are given in Table IV and the process conditions in Table V. The chromatograms were treated as follows. The area percentages of five fractions of the chromatogram were determined and multiplied by the total amount of vanadium present in the sample (Fig. 13). In doing this, the small changes in signal response that could arise from differences in matrix composition with changing molecular weight are ignored. From Fig. 13 the conversion of vanadium was calculated by dividing the amount of vanadium present in the products and feed in the different fractions.

The difference in performance between the two types of catalysts is clearly shown in Fig. 14. The desulphurization catalysts remove about 20% of the vanadium incorporated in the high-molecular-weight molecules, whereas the conversion of the demetallation catalyst, with larger pores, is about 50%. The difference in performance of the hydrodesulphurization catalysts in the low-molecular-weight region is not considered significant. It can be explained from the less favourable signal-to-noise ratio in this part of the chromatogram. In the other molecular-weight regions the performances of the experimental hydrodesulphurization catalysts are comparable.

This application shows that the SEC–ICP-AES method can indeed be applied to products of low metal level feeds such as Kuwait Atmospheric Resid.

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