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## Application of Size Exclusion Chromatography Coupled with Element-Specific Detection to the Study of Heavy Crude Oil and Residua Processing

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Stimulated by oil shortages of 1974 and 1979, the search for alternative sources of carbonaceous fuels has opened new and fascinating areas of research in the petroleum industry.<sup>1</sup> One particular area, in which several domestic oil companies have invested significant capital, is the conversion of heavy crude oils to transportation fuels.<sup>2</sup> The properties of heavy crude oils differ significantly from the properties of light, conventional refining stocks. Heavy crude oils have high specific gravities, viscosities, heteroatom levels (N, S, O, Ni, V, Fe), coking carbon precursors, and nondistillable materials.

In order to convert heavy crude oils to transportation fuels, these deleterious properties must be upgraded in the refining process. The high concentrations of het-

eroatoms make their removal generally much more difficult than from lighter crude oils, so most traditional refining practices have been found inadequate. To meet the demands of these feeds,<sup>2</sup> new and innovative methods of upgrading have been examined, developed, and, in some cases, commercialized.

The complex chemical nature of these heavy feeds has rendered standard analytical methods inadequate as tools for understanding and predicting the impact of the refining process. As a result, several new analytical techniques have been developed, such as high-performance liquid chromatography coupled directly with specific-element detection.<sup>3-6</sup> This particular combination allows the separation of very complex mixtures by various physical properties (size, polarity, aromaticity) with direct on-line detection of a variety of elements. Because of the extensive use of catalysts in the petroleum industry for upgrading,<sup>7</sup> size exclusion chromatography (SEC) is an attractive and pertinent method of separation. The catalyst pore-molecule size

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relationship is very important in affording the chemical changes generated by catalysts. As an element-specific detector, inductively coupled plasma (ICP) atomic emission spectrometry is particularly suited because its continuous multielement capacity allows simultaneous monitoring of metal and nonmetal heteroatoms. Coupled together, these techniques represent a powerful capability that has led to useful and interesting chemical studies in the alternative fuel research areas.

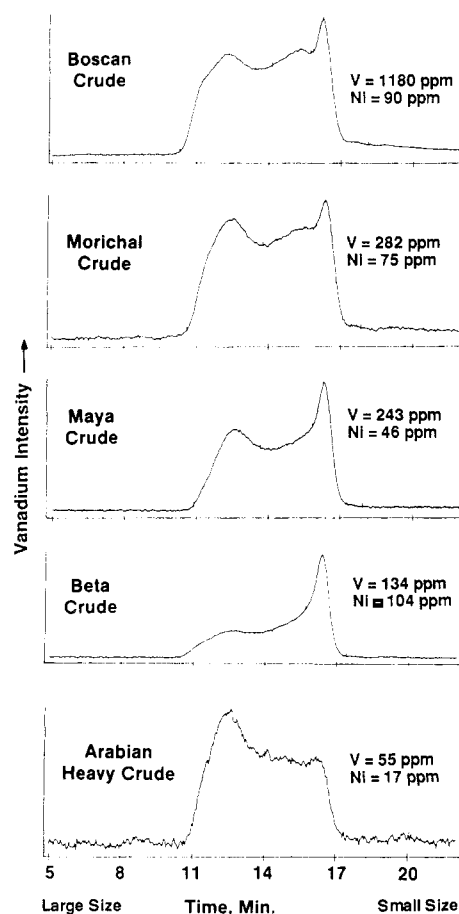
This report summarizes the application of SEC-ICP to the study of the behavior of vanadium, nickel, and sulfur during heavy crude oil conversion processes. We have picked three areas that are considered some of the most important in heavy oil processing, and upon which SEC-ICP has had the greatest impact: (1) thermal hydroprocessing, (2) catalytic fixed-bed hydroprocessing, and (3) solvent deasphalting. This research area is truly an interdisciplinary effort, coupling engineering (petroleum and chemical) with chemistry (analytical, organic, and inorganic). The area is also challenging by virtue of the enormous complexity of the materials (crude oils and processed components) being studied—no one chemical species is dominant enough to be easily identified.

### Techniques

Methods and techniques utilized here have been described in detail elsewhere.<sup>3,8,9</sup> Briefly, the SEC-ICP experiment measures the selected elemental content as a function of elution time. The sample is diluted in the appropriate mobile phase and injected onto the size exclusion column. The column effluent is then directly and continuously injected into the ICP and the concentration of the element is measured by atomic emission. In the experiments below, sulfur, vanadium, and nickel were monitored simultaneously. Calibration by polystyrene standards and model compounds<sup>10-12</sup> can be used to relate elution time to molecular size. In the profiles below, the molecular size increases from right to left. Because the relative distribution is far more important in these studies than absolute changes and the molecular weight (MW) calibrations are at best very difficult in the SEC experiment (particularly in the high-MW range),<sup>11,12</sup> the profiles shown here were not calibrated to absolute MW.

### Heavy Crude Oils

"Heavy" crude oil has somewhat of an arbitrary definition, referring to a crude oil that has more than 0.934 specific gravity. While poor flow properties of heavy crude oils can cause problems, heteroatom removal—particularly nickel, vanadium, and sulfur—is the biggest challenge for upgrading. Nickel plus vanadium concentrations typically range from 100 to over 1300 ppm, while sulfur concentrations are around 4–6 wt %. Nitrogen is also a particularly costly and difficult element to remove when in sufficient concentration to



**Figure 1.** Vanadium SEC-ICP profiles of selected crude oils. Reproduced from ref 3 with permission. Copyright 1985, Marcel Dekker, Inc.

cause problems, but will not be discussed here.

As the light or heavy crude oil enters the refinery,<sup>13</sup> the volatile materials are continuously distilled at either an approximately 343 or 565 °C atmospheric equivalent cut point, yielding nondistillable residues, called "atmospheric" (AR) or "vacuum" (VR) residua, respectively. This further concentrates the metal levels (metals are nonvolatile at these distillation conditions).<sup>14</sup> In general, the nondistillable content runs from 35 to 60 wt % for AR and 90+ wt % for VR. For most heavy crude oil processing, the AR or VR is the actual feed. From these properties, the impetus in heavy crude oil processing is apparent—how to utilize the large quantity of nondistillable material that is high in undesirable elements.

**Molecular Characterization.** Bulk elemental analyses have been the petroleum industry standard to evaluate feeds and predict process performance. For heavy crude oils and residua, these techniques have been less than adequate when predicting catalyst life and performance. SEC-ICP, however, is solving problems where standard methods fail.

For all three process options mentioned in the introduction, size behavior of the molecules is crucial in understanding process fundamentals. Figure 1 shows the vanadium SEC-ICP profiles for selected heavy crude oils (included also are metal concentrations).<sup>3</sup> The profiles exhibit a bimodal distribution with maxima

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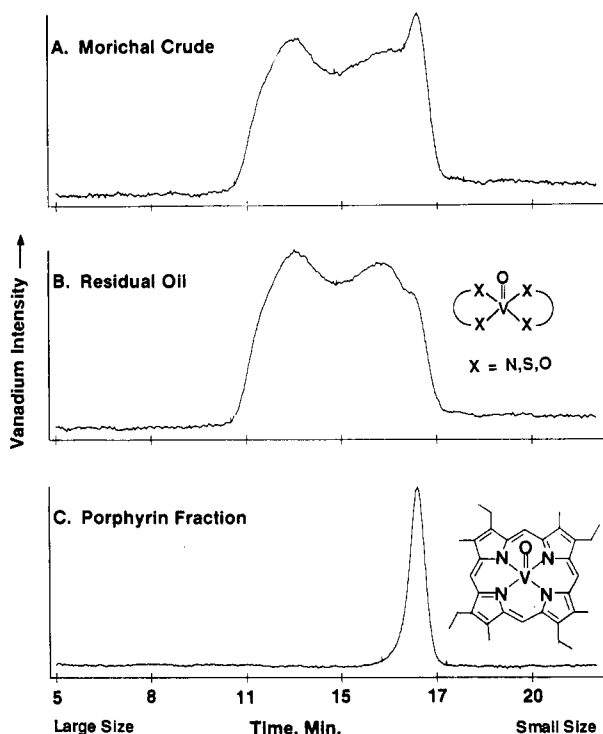
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**Figure 2.** Vanadium SEC-ICP profiles of Morichal: (A) crude; (B) residual oil (nonporphyrins); (C) extracted petroporphyrins. Reproduced from ref 3 with permission. Copyright 1985, Marcel Dekker, Inc.

at MW 800 and 9000 assigned to extractable petroporphyrins and metallo-nonporphyrins, respectively.<sup>3,15,16</sup> The profiles all have the same general shape, but each profile has individual characteristics and may have geochemical significance, such as for reservoir geology.<sup>5</sup>

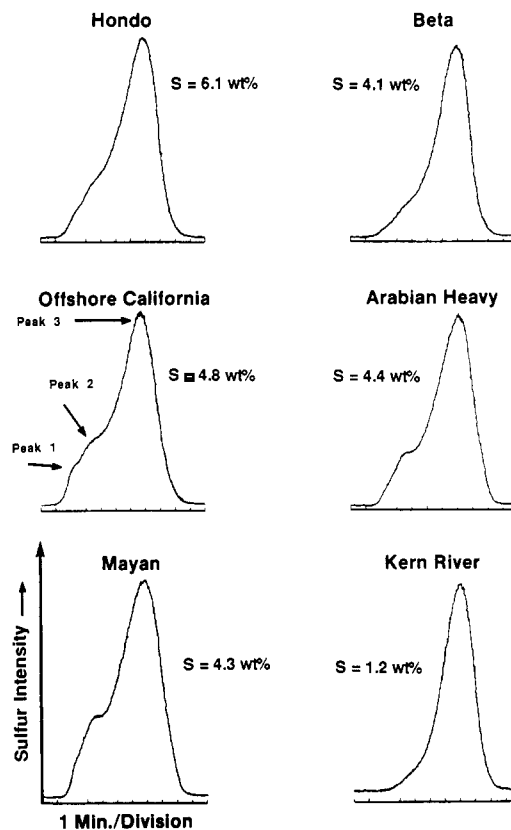
To better understand the reactivity of the metals on a molecular level, attempts have been made to identify individual or classes of metal-containing compounds. For vanadium and nickel, the compounds have been broadly divided into two types: the petroporphyrins and the metallo-nonporphyrins.<sup>3,15,16</sup> Extraction techniques have been developed and applied to separate extractable petroporphyrins from metallo-nonporphyrins.<sup>3</sup> Figure 2 shows the vanadium SEC-ICP profiles for Morichal crude oil and extractable petroporphyrin and nonporphyrin separated fractions. The extractable petroporphyrins are a well-studied class of compounds,<sup>17</sup> and several different types have been identified in carbonaceous materials. An exemplary structure of vanadyl petroporphyrins is inset in Figure 2C. The principal structural differences among the extractable petroporphyrins are in the attendant side chains, which essentially vary in alkyl substitution, position, length, and size.

The metallo-nonporphyrins, on the other hand, are not nearly so well characterized. Several attempts to elucidate these structures by inorganic modeling have been made, but only partial details can be resolved. A generalized structure for vanadyl nonporphyrins is shown in Figure 2B, where the first coordination sphere

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(17) Gallegos, E. J.; Sundarman, P. *Mass Spectrom. Rev.* 1985, 4, 55-85 and references within.



**Figure 3.** Sulfur SEC-ICP profiles of selected atmospheric residua. Reproduced from ref 26 with permission. Copyright 1988, Marcel Dekker, Inc.

can have combinations of N, S, and O. The evidence comes from various studies—reversed-phase chromatography,<sup>5,10</sup> electron paramagnetic resonance spectroscopy (EPR),<sup>8,18-21</sup> and mass spectrometry (MS).<sup>22</sup> In addition, initial MS results indicate some fraction of the nickel is bound by carboxylic acids in at least one heavy crude oil.<sup>23</sup>

The important findings determined by SEC-ICP pertinent to characterization and processing are (1) the extractable petroporphyrins are small in molecular size compared to the majority of the metallo-nonporphyrins, (2) the metallo-nonporphyrins are the majority of the metals, and (3) the extraction procedure leaves the size distribution of the metallo-nonporphyrins virtually unchanged. This technique has been also used to quantitate the amount of extractable petroporphyrins in various feeds, products, and separated fractions. Examples of these values are as follows (feed, % of total vanadium): Boscan crude, 25%; Beta crude, 28%; Morichal crude, 21%; Maya crude, 13%; Arabian heavy crude, 6%; California AR no. 1, 35%; California AR no. 2, 28%.

Molecular or DISTACT distillation has also proven to be a method to separate and characterize petroporphyrins from metallo-nonporphyrins.<sup>14,24</sup> This tech-

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nique distills much higher boiling material than conventional vacuum distillation. The petroporphyrins are found in the volatile fraction (454–677 °C), and SEC-ICP again shows them to be small in molecular size. The nonvolatile (677 °C+) fraction contains the metallo-nonporphyrins with virtually no extractable petroporphyrins (2% of the remaining vanadium).<sup>15,16</sup>

Sulfur removal is important in the processing of residua. Size characterization would be appropriate because the major removal method is catalytic.<sup>13</sup> Figure 3 shows the sulfur SEC-ICP profiles and sulfur concentrations for several residua.<sup>25,26</sup> In general (cf. Offshore California), the profiles exhibit a prominent maximum (peak 3) that elutes at approximately the same relative time in all the residua. Also observed is an asymmetry on the large molecular size side of this maximum due to partially resolved shoulders (peaks 1 and 2). The molecular nature of the compounds constituting these three peaks is not well characterized; but preliminary evidence suggests peaks 1 and 2 are related to the same compounds that make up the asphaltenes (alkane-insoluble portion of the residuum) and also may be directly related to some of the vanadium compounds.<sup>25,26</sup>

Closer inspection of these profiles indicates differences exist in the relative size distribution. For example, the Kern River AR profile is relatively narrow, while the Hondo AR profile is much broader. Offshore California AR exhibits two reasonably well-defined shoulders, while Arabian heavy AR has only one.

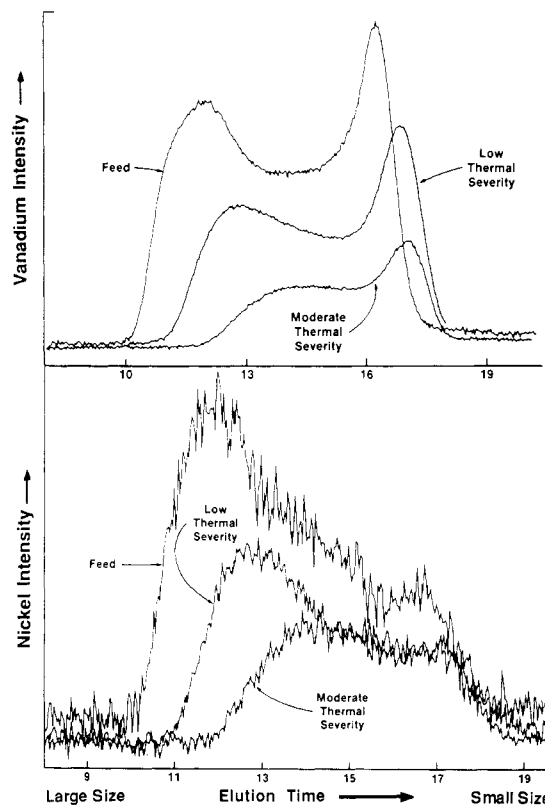
No further sulfur speciation using SEC-ICP has been performed. However, specific examples of homologous series containing sulfur exist, such as pentacyclic C<sub>30</sub> to C<sub>35</sub> hopane type sulfides and bi- (C<sub>12</sub> to C<sub>26</sub>), tri- (C<sub>17</sub> to C<sub>31</sub>), and tetracyclic (C<sub>22</sub> to C<sub>40</sub>) terpenoid sulfides.<sup>27,28</sup> Homologous series type structures such as these could easily account for some of the size variations shown in the figure.

While no explicit molecular species have been correlated with portions of the sulfur SEC-ICP profiles, size characterization is still important in terms of mechanistic studies of how a particular class of compounds behave during removal.

### Applications to Petroleum Processing

The reason for upgrading residuum is simple—increasing the hydrogen-to-carbon ratio and lowering the molecular weight generate marketable distillable products. To correct this hydrogen imbalance, various processes (called residuum conversion processes) either add hydrogen or reject carbon. Currently, there are several types of residuum conversion processes. Thermal and extractive processes generally reject carbon while hydroconversion processes add hydrogen. The more realistic view is a combination of two or more options.

The residuum conversion process treats the large quantity of nondistillables from the crude distillation



**Figure 4.** Top: Vanadium SEC-ICP profiles of California AR no. 1 and products from treatment at low and moderate thermal severity. Bottom: Nickel SEC-ICP profiles of California AR no. 1 and products from thermal treatment at low and moderate thermal severity. Reproduced from ref 16 with permission. Copyright 1986, Marcel Dekker, Inc.

units.<sup>29</sup> Typically, residuum feedstock is partially converted to C<sub>4</sub><sup>+</sup> distillable liquids and C<sub>1</sub>–C<sub>4</sub> gases. The hydrogen necessary for hydrogen conversion reactions (hydroconversion) is supplied from an outside source. The hydroconversion reaction system may consist of a series of thermal and/or catalytic steps with process severity defined by operating conditions, catalysts, and process schemes.<sup>30</sup>

The following are very practical residuum conversion processes that have been studied by SEC-ICP while adapting them to heavy crude petroleum upgrading: (1) thermal hydroprocessing, (2) catalytic hydroprocessing, and (3) solvent deasphalting. The first two utilize hydroconversion reactions, while the latter is simply a physical separation method. All three process types have been commercialized in some form.

**Thermal Hydroprocessing.** Heavy crude oils have substantial amounts of nondistillable material having little direct use in making transportation fuels. Thermal hydroprocessing reduces the quantity of residuum by cracking organic molecules to lower boiling ranges. High hydrogen pressure is used to suppress coke and gas formation and increase the H/C. The temperatures selected for this type of processing are generally above 404 °C (760 °F), on the lower edge of the thermal reaction regime for petroleum materials. Using California AR no. 1 as an example, the thermal step (1) reduces the residuum content (1000 °F+) by 80%, generating

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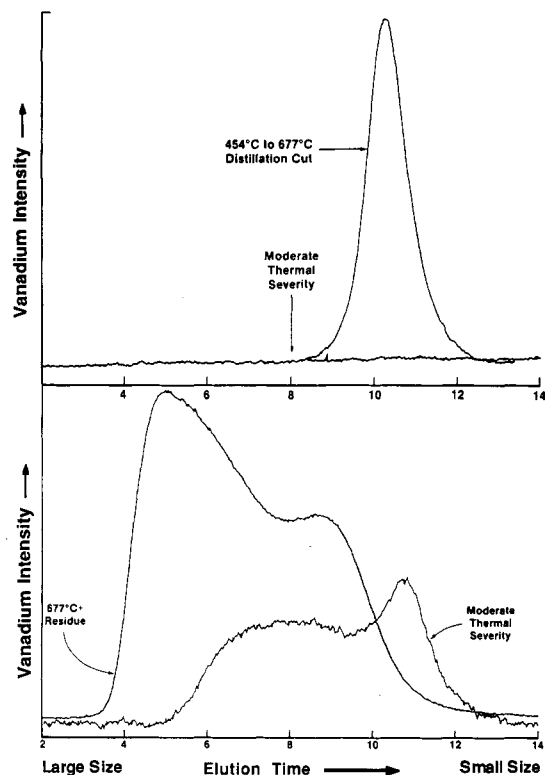
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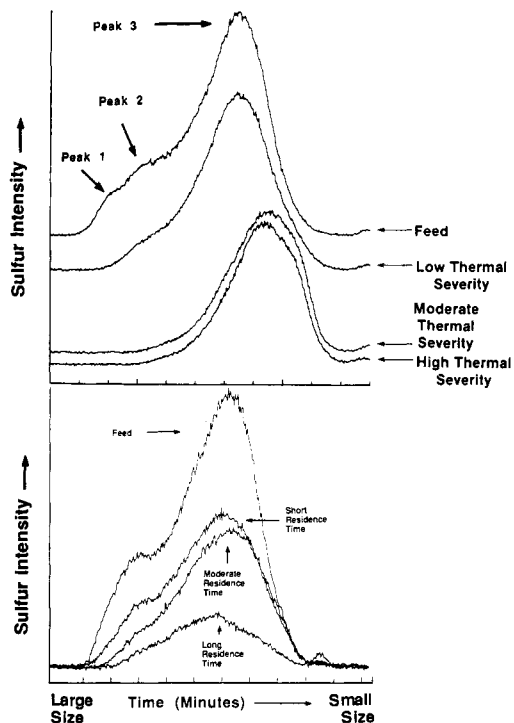


**Figure 5.** Top: Vanadium SEC-ICP profiles of the 454–677 °C distillation cut fraction of California AR no. 1 and moderate thermal severity product. Bottom: Vanadium SEC-ICP profiles of the 677 °C+ fraction of California AR no. 1 and moderate thermal severity product. Reproduced from ref 16 with permission. Copyright 1986, Marcel Dekker, Inc.

distillate with only 5.8% yield loss to gas formation, (2) lowers specific gravity by 0.078, improving viscosity, and (3) reduces sulfur, vanadium, and nickel contents 50–70%. The amount of reduction is a function of the thermal processing conditions. Lower temperatures give less distilled product, metal and sulfur removal, and gas production. Higher processing temperatures yield more distillate and purer products but greater gas production.

Figure 4 shows the vanadium (top) and nickel (bottom) SEC-ICP profiles of products generated from the thermal hydroprocessing of California AR no. 1 in a tubular flow reactor at low (38% vanadium and 35% nickel removal) and moderate (78% vanadium and 65% nickel removal) process severities.<sup>15,16</sup> A high process severity product was also examined, but the metal concentrations were too low to study. Three process pertinent trends are evident in both the vanadium and nickel profiles with increasing severity: (1) the large-size components (nonporphyrins) disappear, (2) the remaining components shift to smaller molecular size, and (3) small metal-containing molecules, nonexistent in the feed, are being formed.

Fractions generated by the DISTACT distillation and processed at moderate thermal severity condition<sup>15,16</sup> were also examined by SEC-ICP to better understand the differences in demetalation reactivity and mechanisms.<sup>31–36</sup> The top profile set in Figure 5 shows the



**Figure 6.** Top: Sulfur SEC-ICP profiles of processing of California AR no. 1 at low, moderate, and high thermal severities. Bottom: Sulfur SEC-ICP profiles of the fixed-bed catalytic processing of California AR no. 7 over a low-severity catalyst. Reproduced from ref 26 with permission. Copyright 1988, Marcel Dekker, Inc.

vanadium SEC-ICP profile of the feed petroporphyrin fraction (454–677 °C) and the processed product profile. Obvious in the product profile is the complete lack of the petroporphyrins (as well as any other vanadium compounds). The bottom profile set shows the nonporphyrin fraction (677 °C) before and after moderate thermal processing. Moderate demetalation occurs, but the most prominent features are the extent of size reduction and the formation of vanadium compounds not present in the original feed. The behavior of this profile set is similar to that of the undistilled residuum and indicates the whole product profile (Figure 4) is all metallo-nonporphyrins. The results of UV-vis analysis<sup>37</sup> of this product and the top profile set of Figure 5 are consistent with complete petroporphyrin removal at moderate thermal severity.

These profiles, and those of other residua and petroporphyrin/nonporphyrin fractions subjected to similar processing conditions, have yielded the following thermal hydroprocessing information: (1) demetalation is a function of temperature, (2) profile shape of the metal-containing compounds in the product is a function of temperature, but not reaction time, and (3) petroporphyrins react preferentially over metallo-nonporphyrins. The results of these studies have also indicated (1) the petroporphyrin demetalation mechanism goes through hydrogenative intermediates,<sup>37</sup> (2) downstream processing may be more amenable to catalytic upgrading because of the removal and size reduction of the metal-containing molecules (thermal treatment

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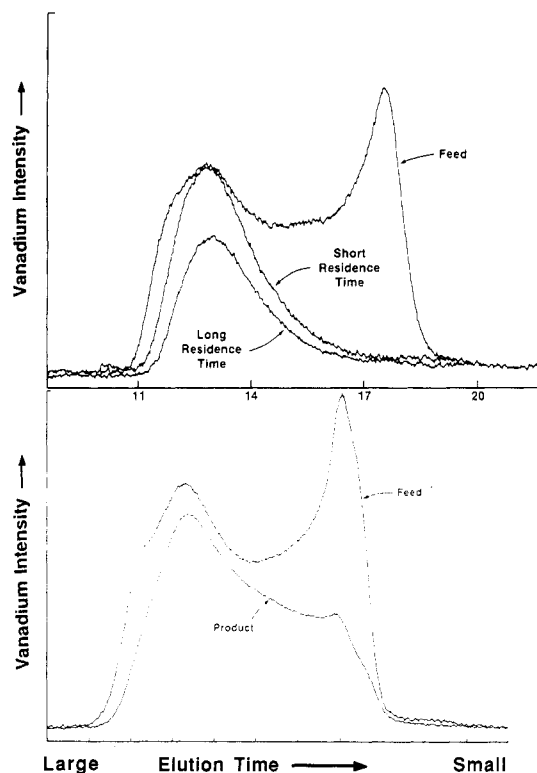
may be a very effective residuum conversion step), and (3) the demetalation mechanism going from feed metals to  $VS_x$ <sup>38</sup> on the catalyst surface may go through vanadium-sulfur intermediates.<sup>25,26</sup> These insights show the process effectiveness of thermal hydroconversion.

Thermal hydroprocessing was not specifically developed for desulfurization but affords a moderate amount (approximately 50%), and therefore is considered in desulfurization process schemes. The top profile set of Figure 6 shows the sulfur SEC-ICP profiles for California AR no. 1 and processed products generated under the same thermal severity conditions described for the metals.<sup>25,26</sup> In addition to overall sulfur removal, the three thermal processing products exhibit the following trends: (1) disappearance of the larger size molecules (peak 1 and peaks 1 and 2 in the lower and moderate severity profiles, respectively), (2) shift in the profiles to smaller molecular size (all severities), and (3) appearance of molecules not present in the feed (moderate and high severity). The extent of these trends, like total sulfur removal, appears to be a function of the thermal severity, identical with the behavior of the metal-containing molecules (see above) at corresponding conditions.<sup>15,16</sup>

Chain scission can explain the thermal processing behavior of at least some of the sulfur-containing compounds detected in the sulfur SEC-ICP profiles. Feed structural size differences can be accounted for, in part, by variation in chain lengths of alkyl substituents.<sup>27,28,39,40</sup> Thermal processing conditions are adequate to sever these side chains, causing size reduction. The scission of these chains then allows easier access of hydrogen to afford hydrodesulfurization. The remaining smaller-sized sulfur compounds could also be more amenable to downstream catalytic processing.

**Catalytic Hydroprocessing.** Another residuum process option is catalytic hydroprocessing,<sup>2,41-43</sup> which is designed to remove a substantial amount of heteroatoms by hydroprocessing over a fixed-bed catalyst. For example, very mild treatment of Maya AR by a commercially available hydroprocessing catalyst yielded 43, 40, and 27% sulfur, vanadium, and nickel removal, respectively.<sup>44</sup> But due to much lower process temperatures for catalytic hydroprocessing, much less cracking occurred (15% 1000 °F+ reduction and 0.92 wt %  $C_1$ - $C_4$  gas formation). The hydrogenative aspect of this type of processing was also evident in the improved specific gravity by 0.036.

Several types of catalysts have been recently developed to deal with different aspects of upgrading that are endemic to heavy crude oils and residua<sup>45</sup>—for example, large-pore demetalation catalysts. The success of these catalysts is intimately associated with the pore characteristics, and, in particular, pore size, because of pore deactivation by metals.<sup>46,47</sup> SEC-ICP has helped



**Figure 7.** Top: Vanadium SEC-ICP profiles of California AR no. 1 processed over a high-activity, small-pore fixed-bed catalyst at short and long residence times. Bottom: Vanadium SEC-ICP profiles of California AR no. 3 processed over a low-activity, large-pore fixed-bed catalyst. Reproduced from ref 6 and 37.

determine the nature of interactions between nickel and vanadium components and fixed-bed catalysts. Two catalyst types are shown as examples: (1) a high-activity, small-pore desulfurization catalyst and (2) a low-activity, large-pore demetalation catalyst.

The top of Figure 7 shows the vanadium SEC-ICP profile of California AR no. 1 upgraded over a high-activity desulfurization catalyst at two severities.<sup>15,16,37</sup> The short residence time profile (50% vanadium removal) exhibits a conspicuous lack of petroporphyrins and similar size nonporphyrin components which were in the feed. The longer residence time profile (70% vanadium removal) shows little difference from the short residence time profile, other than the disappearance of additional vanadium nonporphyrin compounds. This indicates high-activity desulfurization catalysts efficiently and completely remove the metal-containing molecules that fit in the catalyst pore. Larger metal species falling outside the range of the catalyst pore require another mechanism(s) for removal, for example, a thermal step to produce appropriately sized material for penetrating the pores.

The bottom profile set in Figure 7 shows the vanadium SEC-ICP profile for the fixed-bed processing of California AR no. 3 over a low-activity, large-pore demetalation catalyst.<sup>37</sup> This feed has the typical bimodal distribution, where the maximum at small molecular size has been assigned as petroporphyrins (15% of vanadium) by extraction techniques. The product profile (40% vanadium removal) indicates metal re-

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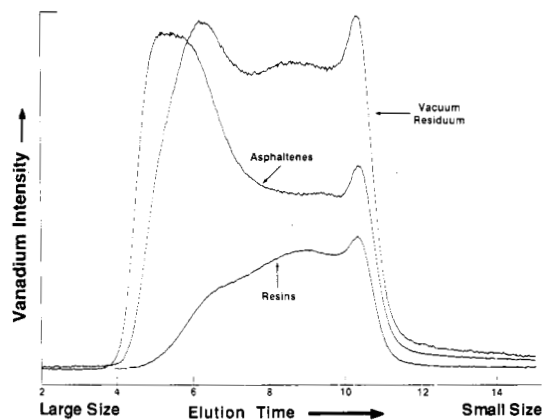
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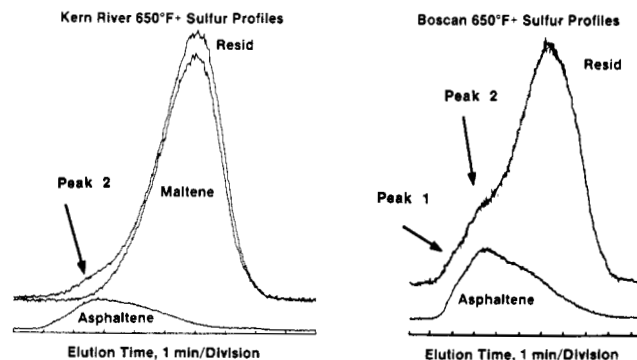
**Figure 8.** Vanadium SEC-ICP profiles for Boscan VR, isooctane insolubles (asphaltenes), and isooctane-soluble resins. Reproduced from ref 54 with permission. Copyright 1986, Marcel Dekker, Inc.

removal from all size ranges, with some preference for smaller size components. This preference is explained by a higher density of small pores, rather than an inherent greater reactivity of the small molecular size components. This density contrasts the desulfurization catalyst, which has a much smaller average pore size. At approximately the same demetalation level, the low-activity catalyst removes a much broader size range of metals, and is also not as effective in removing the metals in the small molecular size range (petroporphyrin content reduced one-half), than the small-pore, desulfurization catalyst (complete petroporphyrin removal).

The general behavior of the metal-containing molecules in catalytic hydroprocessing has been elucidated from studies of these and other catalysts: (1) compounds fitting into the catalyst pores are the easiest to remove, (2) compounds larger than the catalyst pores require different and/or additional demetalation mechanism(s), and (3) petroporphyrin/metallo-nonporphyrin removal selectivity is probably dependent on pore size and not differences in demetalation mechanisms. These observations are extremely important when selecting or developing a catalyst to process a specific feed (see the differences in feed profiles in Figure 1).

Although not specifically the function for larger pore demetalation catalysts, some sulfur removal is also observed. The bottom profile set of Figure 6 shows the sulfur SEC-ICP profiles for the fixed-bed treatment of California AR no. 7 over a low-activity, large-pore catalyst.<sup>25,26</sup> As in the demetalation study, the large-pore catalyst removes sulfur in all size ranges. The amount of removal appears simply a function of reaction time and not of specific molecular types.

**SDA Separation.** A very cost-effective, practical method of utilizing heavy crude oil is solvent deasphalting separation (SDA).<sup>13,48</sup> This method, commercial to many refineries, extracts very large waxy saturates, highly conjugated aromatics, and smaller polar organics (containing heteroatoms) from the oil by adding large volumes of alkanes (usually propane to butane).<sup>49-53</sup> Two fractions are generated: (1) a low-



**Figure 9.** Left: Sulfur SEC-ICP profiles for Kern River 650 °F+ residuum, isooctane solubles (maltenes), and isooctane insolubles (asphaltenes). Right: Sulfur SEC-ICP profiles for Boscan 650 °F+ residuum and isooctane insolubles (asphaltenes). Reproduced from ref 26 with permission. Copyright 1988, Marcel Dekker, Inc.

metals-content deasphalted oil (DAO), which is recycled back into the refinery (for catalytic upgrading), and (2) high-metals-content asphaltenes, which usually end up as asphalt or coke.

Figure 8 shows vanadium SEC-ICP profiles of fractions from Boscan VR generated by a modified ASTM D 2007-80 procedure,<sup>54,55</sup> simulating an SDA separation. Note that Boscan VR has a bimodal distribution very similar to that of the whole crude oil (see Figure 1), indicating vacuum distillation has little effect on the size distribution of the metal-containing compounds. The asphaltene profile clearly indicates changes in the molecular size of the vanadium compounds, exhibiting large molecular size which are not present in the starting feed. The real benefit of this processing is seen (Figure 8) in the metals concentration and size distribution in the DAO (resins): (1) the metals concentration is reduced (57 and 47% of the feed vanadium and nickel, respectively), (2) the metal-containing compounds are of small molecular size, and (3) no agglomeration is seen as in the asphaltene profiles. This is important for downstream processing of the DAO, decreasing the process severity required to remove heteroatom-containing materials. In addition, the metal-containing species are of smaller size, so smaller pore, more active catalysts may be used for upgrading (see above).

Figure 9 shows the weight-balanced sulfur SEC-ICP profiles for the Kern River AR and Boscan AR and the corresponding isooctane-insoluble asphaltenes, simulating the SDA separation. Both Kern River AR and Boscan VR asphaltene profiles show a broad asymmetric peak with the elution at approximately the same time as peak 2 in the corresponding residuum profile. Assuming roughly a Gaussian shape, the areas of peak 2 match very well with the areas of the corresponding asphaltene profile (relative areas of peak 2: Kern, 8%; Boscan, 30%). Evident for Boscan asphaltenes is a shoulder at larger molecular size, with the same elution times as peak 1 in the residuum profile.

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The DAO (maltenes) is also shown in the Kern River profile set. The prominent maximum seen in the feed profile (peak 3) is also seen here. This is also the maximum for smaller-sized sulfur-containing compounds and accounts for the majority of the sulfur-containing molecules.

The SDA separation process separates the very large sulfur-containing components from the smaller sulfur-containing compounds, similar to the effect on the metal-containing compounds. But unlike the metal compounds, the majority of the sulfur is found in the DAO fraction. This is not necessarily a disadvantage because these molecules are very amenable to catalytic removal. Desulfurization is one the easiest aspects of refining. It should be noted, however, the distribution of compounds and heteroatoms in this type of processing can be greatly feed dependent,<sup>8</sup> as well as separation solvent dependent.<sup>56</sup> To provide the process with flexibility, several commercial and proposed processes use two-stage or multistage asphaltene removal,<sup>48</sup> with multiple alkane solvents of different solubility parameters. The end result is various grades of DAO

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that will be treated in different parts of the refinery depending upon the quality of the product.

## Conclusions

SEC-ICP has opened up several new areas of petroleum process analysis, showing the size behavior of nickel, vanadium, and sulfur in heavy crude oils and during thermal, catalytic, and SDA processing. It has offered insight into new and innovative ways of processing heavy crude oils and residua derived from them as well as helped explain the success of existing processing methods. This has only come about because of a combined, interdisciplinary effort from several fields of science—analytical, inorganic, and organic chemistry, along with chemical and petroleum engineering.

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# How Bromate Oscillators Are Controlled

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## An Introduction to Chemical Oscillators

A solution containing potassium bromate, malonic acid, and a small amount of cerium sulfate in dilute sulfuric acid is a reaction system that probably exhibits the richest and most complex phenomenology of any known nonliving collection of chemicals!<sup>1</sup> One of the remarkable observations is that in stirred homogeneous systems the  $[Ce^{4+}]/[Ce^{3+}]$  ratio, which can be easily followed by a platinum electrode, shows practically undamped oscillations over a considerable period of

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time, even in closed systems. This reaction is only one example of a class of processes, generally described as *chemical oscillators*, in which some composition variable exhibits regular periodic variations in time or space.<sup>2</sup> A whole family of chemical oscillators with bromate ion as an essential component is now known, and members of this family are often referred to as *bromate-driven oscillators*. More exotic behaviors of bromate-driven oscillators are "trigger waves" in unstirred systems,<sup>3</sup> "facilitation-like behavior",<sup>4</sup> "bistability",<sup>5</sup> or "excitability",<sup>6</sup> which show analogies to propagation of nerve impulses or to dynamic behaviors observed in synapses.<sup>7,8</sup>

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