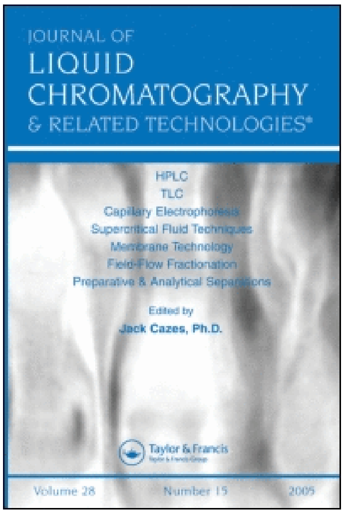

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# SEPARATION OF SULPHUR COMPOUNDS FROM VACUUM GAS OIL DISTILLATES BY LIGAND EXCHANGE CHROMATOGRAPHY

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## ABSTRACT

For characterizing the sulphur components present in vacuum gas oil (VGO) distillates, it is essential to develop and standardize a procedure to separate the sulphur components present in the fraction before applying any techniques for structural elucidation.

Ligand exchange chromatography (LEC) has been reported for the separation of sulphur compounds (SCs) from petroleum distillates and shale oil. Therefore, in the present study, the LEC technique was applied using four metals: $Cu^{++}$, $Ag^{+}$, $Hg^{++}$, and $Pd^{++}$. These metal salts (5 wt%) were impregnated onto grade-12 silica gel in aqueous phase or in dichloromethane. All of them were tested to form complexes with different types of SC in subfractions of VGO from Kuwaiti crude oils. The efficiency of the ions in separating the SCs, was in the order of $PdCl_2$ (aqueous) $< AgNO_3 < HgCl_2 < CuSO_4 < PdCl_2$(dichloromethane).

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Palladium chloride impregnated over grade 12 silica gel in aqueous phase was very effective in separating the SCs from complex mixtures of aromatics. The methodology was optimized, and it was found that a 30 : 1 ratio of the adsorbent to the sample was effective for the separation of SCs.

*Key Words*: Sulphur compounds (SCs); Palladium chloride; Ligand exchange chromatography; Vacuum gas oil (VGO)

## INTRODUCTION

Sulphur compounds (SCs) are the most common heteroatomic components of crude oil. They have been reported as mutagenes and/or carcinogenics, and some of them have an effect on human health. They act as catalyst poisons in many processes and affect the quality of fuels and lubricants. Fossil fuel combination also produces sulphur oxides, which causes acid rain and is considered a major pollutant.[1] It has been known for many years that SCs in crude oil are the single largest cause of corrosion in crude-distillation units. At the same time, petroleum supplies are becoming increasingly sour, and new environmental regulations are requiring fuels with SC distributions. Knowledge of the compositional structure of the SCs in petroleum fractions is essential for adopting the correct methodology and technique for separating SCs from petroleum ends.

SCs can be subdivided into two types: (a) aliphatic and aromatic sulphides, and (b) sulphur aromatics and polyaromatic sulphur heterocycles (PASHs). They may exist in the form of sulphides, di-sulphides, mercaptans, and thiophenes and benzothiophenes and di-benzothiophene derivatives. Common adsorption chromatographic techniques fail to separate as ring size; substituents and electronic properties of sulphur aromatics and PASH are very close to those of polyaromatic hydrocarbon (PAH).[2] Secondly, the structure of these compounds in high boiling distillates is more complex than in the light distillates. They contain many highly branched alkyl groups substituted in different positions of the aromatic ring.[3]

Several methods have been used for the separation of SCs. Early methods were based on the oxidation of sulphur compounds into sulphoxides, and then separation of sulphoxides on silica gel and reduction of the sulphoxides back to their original SCs.[4] It was not very successful, as the yield varied from 0 to 70 wt% depending upon the chemical structure of the selected PASH. Other methods for the separation of aliphatic sulphides are based on the formation of complexes with some metals, although sulphur aromatics are not separated with mercury, zinc,[5] tin, or copper ions, as they elute together with the aromatics. Gundermann[6] and Nishioka et al.[7,8] reported the use of ligand exchange chromatography (LEC) using $PdCl_2$ impregnated over silica gel. They were able to separate two to six rings of PASH compounds from PAHs.

The complete identification of the separated PASHs is also a difficult task, as they are highly complex mixtures, due to the presence of highly alkylated substituents in the ring;[9] we identified 32 SCs in coal liquids and shale oils using flame photometric detection and mass spectral data.

LEC is based on the principle of a complex formation between SCs, which can donate a lone pair of electrons, and a metal atom, which has got a vacant “d” orbital to accept those lone pairs of electrons. The stationary phase coated with metal ions, tends to slow down the sulphur-containing compounds in relation to other molecules as they move ahead in the mobile phase.

In the present work, four metal salts (copper, silver, mercury, and palladium) were used to coat the silica-gel stationary phase in order to study their effectiveness in the separation of SCs. A preliminary separation of Vacuum Gas Oil (VGO) distillates into saturates, and mono-, di-, polyaromatics, and polar compounds was considered to be essential before applying LEC prior to the removal of SCs. The total aromatic fraction was used for the development of the methodology and to check the efficiency of different ions in the separation of SCs from aromatic hydrocarbons. The aim of this study was to establish a methodology to separate the SCs from Kuwaiti VGO distillates, and to implement the modified methodology on different fractions separated from VGO distillates, e.g., mono-, di-, and poly aromatics. No work has been reported on the separation of SCs from Kuwaiti VGO distillates.

## EXPERIMENTAL

### Materials

Fresh alumina (Alcoa F-20, 100–200 mesh) activated at 400°C for 16 h and silica gel (Davison Chemical Co., grade 12, 12–200 mesh) activated at 265°C for 16 h, were used as adsorbents (stationary phase) in all the chromatographic separation experiments. VGO distillates from different crudes were separated into saturates, monoaromatics, diaromatics, polyaromatics, and polar hydrocarbons according to the scheme established by Petroleum Refinery. Copper sulphate 5-hydrate (Analar), anhydrous palladium chloride (Fluka), silver nitrate (Riedel-de Hean), and mercuric chloride (Fluka) were used for the preparation of metal-impregnated silica gel. Petroleum ether (40–60°C), dichloromethane, and ethyl acetate were used as solvents for elution.

### Elemental Analysis

Elemental analysis was carried out on elemental analyzer, model EA 1110 CHNS. An ANTEK 7000 analyzer was used for determination of total nitrogen and sulphur in low concentrations. Appropriate standard reference samples were used to prepare the calibration curves.

### Preparation of Impregnated-Metal on Silica Gel

First, 5% metal salt was impregnated over silica gel (grade 12) in aqueous solution or in dichloromethane. The metal-impregnated silica gel was then dried in an oven at 95°C overnight. For the next 24 h, or longer, the dried metal-impregnated silica gel was maintained at 200°C in the oven, before it was cooled in a dessicator overnight. The gel was then transferred to a glass bottle that was kept closed prior to use of the gel. Although $PdCl_2$ is insoluble in water and dichloromethane, this procedure facilitated uniform distribution on the surface of the silica gel.

### General Procedure for the Separation

A slurry (30 g) of silica gel, or resin, impregnated with metal salts was wet-packed in a column. The column was prewet with 5 mL of petroleum ether

***Table 1.*** Ligand Exchange Chromatography of Total Aromatic Fraction with Different Metals

| | | Recovery % Wt | | | | |
|---|---|---|---|---|---|---|
| Fraction | Eluent | $AgNO_3$ | $CuSO_4$ | $HgCl_2$ | $PdCl_2$ (DM) | $PdCl_2$ (Aq) |
| 1 | A | 5.04 | 6.11 | 2.20 | 0.70 | 0.81 |
| 2 | B | 0.20 | 7.67 | 7.20 | 2.63 | 2.81 |
| 3 | C | 4.99 | 20.43 | 20.97 | 29.41 | 8.85 |
| 4 | D | 18.88 | 15.00 | 27.52 | 32.45 | 7.72 |
| 5 | E | 25.91 | 16.94 | 8.59 | 10.64 | 9.73 |
| 6 | F | 7.88 | 3.86 | 4.05 | 6.00 | 7.44 |
| 7 | G | 9.81 | 4.46 | 6.97 | 5.26 | 11.73 |
| 8 | H | 10.66 | 9.10 | 21.02 | 5.54 | 33.94 |
| 9 | I | 20.52 | 10.01 | 10.24 | 9.80 | 26.86 |
| Total recovery | | 101.37 | 93.58 | 85.74 | 102.40 | 109.80 |

A. PE (300 mL); B. PE : DM (97.5 : 2.5, 70 mL); C. PE : DM (95 : 5, 70 mL); D. PE : DM (90 : 10, 70 mL); E. PE : DM (80 : 20); F. PE : DM (75 : 25, 70 mL); G. PE : DM (50 : 50, 70 mL); H. PE : DM (0 : 100, 100 mL); I. PE : DM (0 : 100, 150 mL).
(PE = Petroleum ether, DM = Dichloromethane, EA = Ethyl acetate).

***Table 2.*** Ligand Exchange Chromatography of Total Aromatic Fraction

| | | Distribution of SC % Wt | | | | |
|---|---|---|---|---|---|---|
| Fraction | Eluent | $AgNO_3$ | $CuSo_4$ | $HgCl_2$ | $PdCl_2$ (DM) | $PdCl_2$ (Aq) |
| 1 | A | 2.14 | 4.44 | 0.20 | 0.12 | 0.00 |
| 2 | B | 0.00 | 11.88 | 8.65 | 2.80 | 0.60 |
| 3 | C | 5.04 | 24.64 | 23.88 | 34.04 | 4.80 |
| 4 | D | 21.23 | 11.41 | 32.74 | 31.54 | 1.58 |
| 5 | E | 25.72 | 18.61 | 6.15 | 14.92 | 6.15 |
| 6 | F | 6.74 | 2.59 | 2.76 | ND | 7.55 |
| 7 | G | 11.80 | 3.30 | 4.06 | 3.85 | 16.24 |
| 8 | H | 8.48 | 4.97 | 4.11 | 5.46 | 63.01 |
| 9 | I | 15.61 | 5.63 | 5.29 | 7.92 | 6.56 |
| Total recovery | | 95.6 | 87.48 | 87.85 | 100.64 | 100.77 |

ND = not determined.

(40–60°C). A known amount of sample (1–1.2 g) was dissolved in 5 mL of petroleum ether and transferred to the top of the column very carefully, without disturbing the surface of the gel. The first fraction was eluted with petroleum ether, and then the elution was continued with a mixture of petroleum ether and dichloromethane, with the polarity being gradually increased by using an increasing ratio of dichloromethane. Then, the column was washed with ethyl acetate. The solvent was removed from the fractions using a Rotavapor, and taken to a constant weight. The sulphur content was determined using an ANTEK analyzer. The sulphur percent weight and distribution of total S in the fractions were calculated.

All experiments were carried out under identical conditions. The fractions were collected in the usual way. The mass yield, sulphur percent-weight, and the distribution of total sulphur were calculated and are reported in Tables 1 and 2.

## RESULTS AND DISCUSSION

The distribution of SCs between the fractions varies with the type of metal salt coated on the silica gel. The total aromatic fraction was used for the development of the methodology. Total aromatics were separated from a crude oil using column chromatography on silica gel grade 12. The elution of the fractions was carried out by gradually increasing the polarity of the solvents. The recovery of the material was from 93.6–110.9 wt%. The increase in the percent weight yield was due to the metal complex formation with SC. The low recovery can be attributed to the irreversible adsorption of some of the SCs on the adsorbent. The best separation of SCs was achieved with $PdCl_2$ prepared in aqueous phase. This is shown in Figures 1 and 2.

## Optimization of the Methodology

Preliminary experiments were conducted using silica gel coated with $PdCl_2$ in aqueous medium, as well as in dichloromethane. The experiments showed that wet coating of $PdCl_2$ on silica gel (Tables 1 and 2) gives better results. Therefore, the subsequent experiments were carried out using the same procedure. The procedure was optimized by gradually increasing the ratios of the adsorbent to the sample (10 : 1, 20 : 1 and 30 : 1). There was an improvement of separation between SCs and aromatics with the increase of the ratio of silica to sample. The ratio 30 : 1 gave the best result, and it was selected for all other experiments (Figure 3).

## Repeatability

Two parallel experiments were conducted to separate the SCs. The distributions of total sulphur among the fractions were plotted for both runs. Excellent repeatability was obtained (Figure 4).

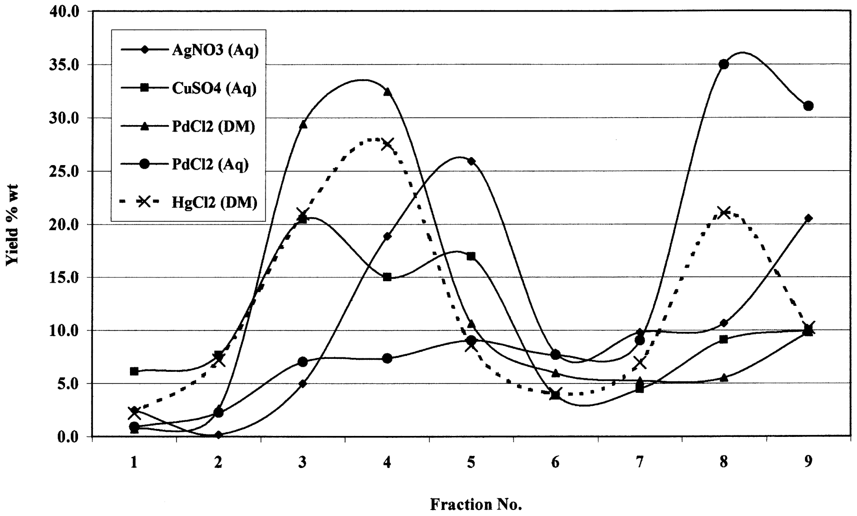

*Figure 1.* Ligand exchange chromatography fractions from the total aromatic fraction using different metal salts.

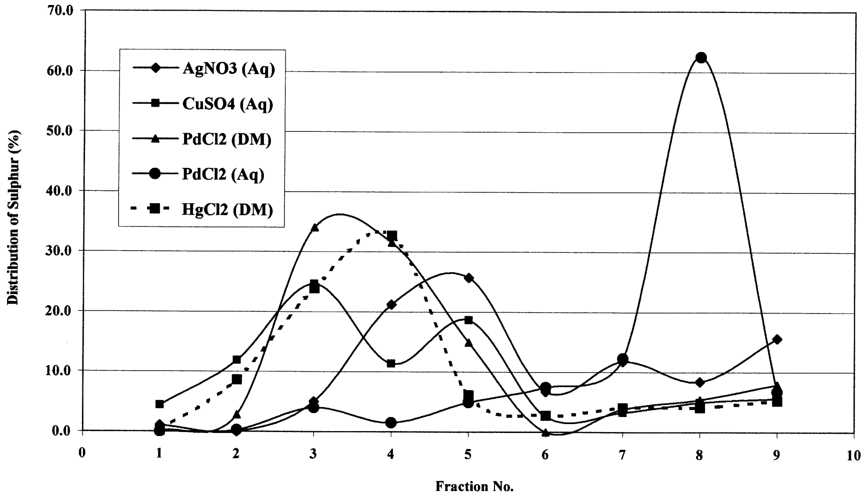

*Figure 2.* Comparison of sulphur distribution between fractions for different metals.

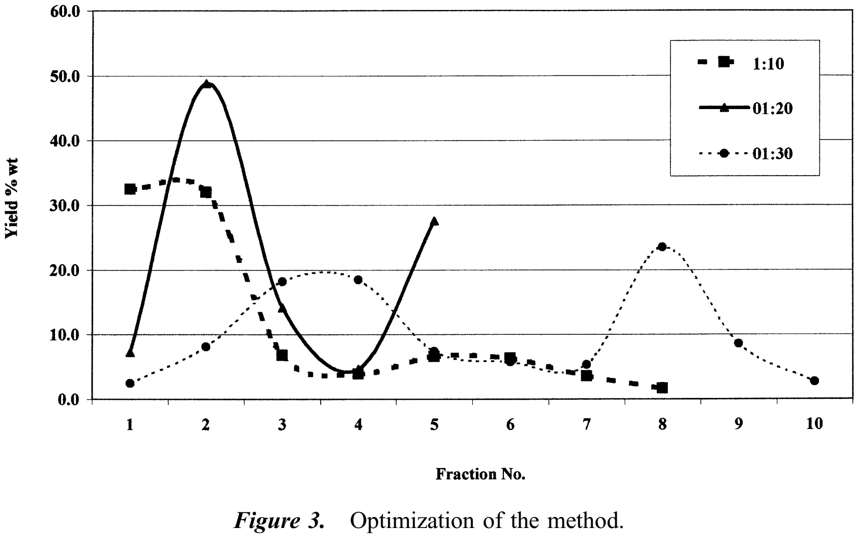

*Figure 3.* Optimization of the method.

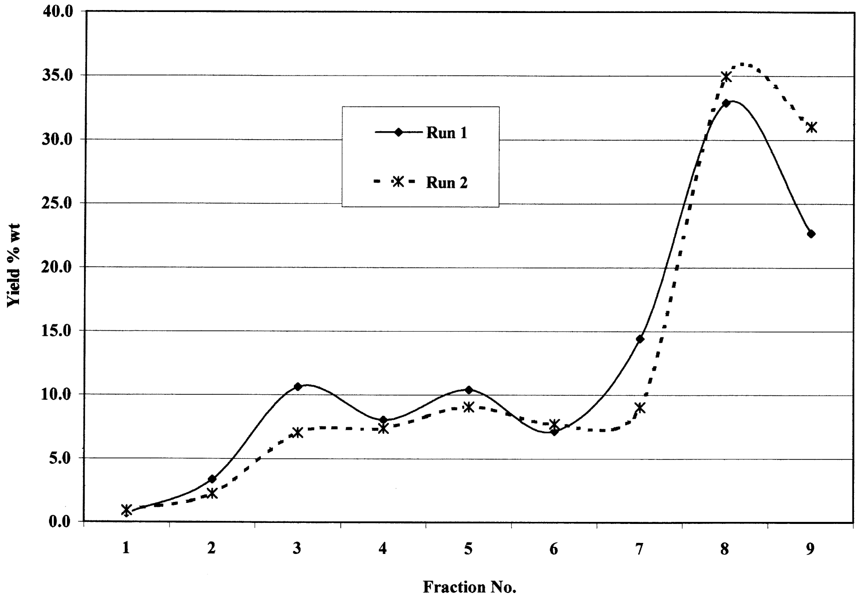

***Figure 4.*** Repeatability of the ligand exchange chromatography using $PdCl_2$ over silica gel.

## Application of the Optimized Method on Different Fractions from VGO Distillate

VGO distillate was separated into monoaromatic, diaromatic, polyaromatic, and polar fractions according to the procedures of API project 60 and a modified project entitled "Non-destructive analysis of crude oils by gel permeation chromatography".[10] The total sulphur content in these fractions ranged from 2.52 to 8.02 wt%. The optimized procedure for the separation of SCs was applied to the monoaromatic and diaromatic fractions from the VGO distillate of one crude. The yields of material in the low sulphur and high sulphur fractions were about 80 and 20 wt%, respectively.

The low sulphur fractions were combined all together using a solvent system from A + B + C + D + E + F, and the high sulphur fractions were also combined using a solvent system from G + H + I. The trend was the same for both the mono- and diaromatic fractions. On the other hand, 70–80% of the total SCs were enriched into the high sulphur fraction, and 20–30 wt% of the material distributed into the low sulphur fraction. The total sulphur content in the monoaromatic fraction was 2.87 wt%, and in the diaromatic fraction it was 3.95 wt%. The sulphur content in low sulphur fraction reduced to 0.5 wt% in both cases (Figures 5 and 6).

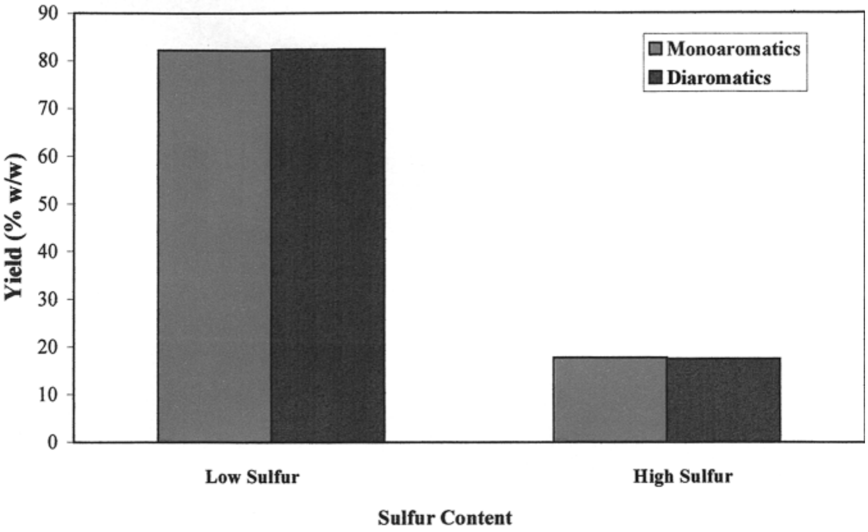

*Figure 5.* Yields of low and high sulfur fractions.

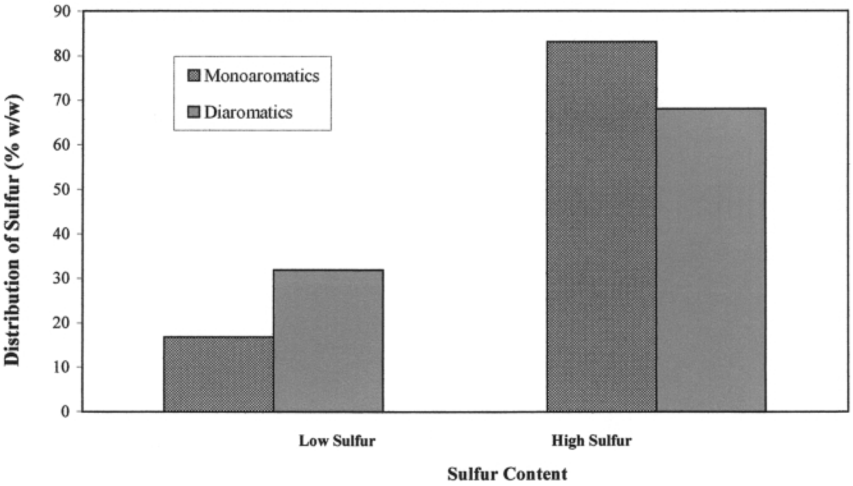

*Figure 6.* Distribution of SCs into low and high sulfur fractions.

### Recovery of Fractions vs. Polarity of Solvent System for Aromatic Fractions

The yields of the lower sulphur fractions were lower, and more samples were retained in the columns, in descending order, from the mono, di-, to polyaromatic fractions. The yield of the low sulphur fraction was far lower for polyaromatics indicating that almost all molecules in the polyaromatic sample had a minimum of one sulphur atom per molecule. Any fraction with a total sulphur content of 8.0% w/w and an average molecular weight of around 400, must contain a minimum of one sulphur atom per molecule. The procedure for the separation of SCs may not be required for polyaromatic and polar fractions (Figure 7).

### Average Molecular Formulae for the Low and High Sulphur Fractions

The average molecular formulae for the low and high sulphur fractions were estimated using the results of the average molecular weight (gel permeation chromatography) and elemental analysis (C, H, and S using an elemental analyzer).

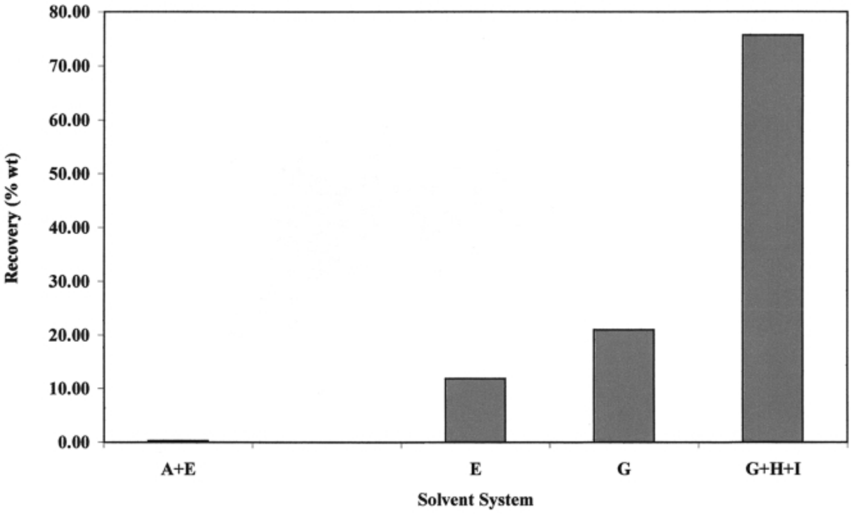

*Figure 7.* Recovery vs. solvent system of polyaromatic fraction from VGO distillate.

The low-sulphur, monoaromatic fraction had an average of 33 carbon atoms per molecule. There was only one molecule with a sulphur atom for every ten sulphur-free molecules. The high-sulphur monoaromatic fraction had an average of 31 carbon atoms per molecule (low molecular weight). This was because, for a fraction with a given boiling point, the molecular weight of the polar molecules will be lower than that of the non-polar molecules. This fraction also had a sulphur atom in each molecule.

In the low-sulphur, diaromatic fraction with an average molecular weight of 430, for every third or fourth molecule, there was one molecule with a sulphur atom attached to it. The average carbon number in the high-sulphur diaromatic fraction was the same as that estimated for the high-sulphur monoaromatic fraction. The relatively high sulphur content in the low sulphur diaromatic fraction, compared to that in the low-sulphur monoaromatic fraction, could be attributed to the steric hindrance on sulphur atoms by substituted alkyl groups in some of these diaromatic molecules. This resulted in poor separation of these molecules by LEC.

## CONCLUSIONS

The efficiency of the ligand compounds in separating SCs was in the order of $PdCl_2(Aq) < AgNO_3 < HgCl_2 < CuSO_4 < PdCl_2(DM)$.

The best separation was obtained with 5% of $PdCl_2$ (Aq) coated on silica gel, and the best ratio of the sample to adsorbent was 1 : 30. VGO distillates were separated successfully into low and high sulphur fractions.

In fractions with a total sulphur content of $\approx 1.0$ wt/wt% and an average molecular weight $\approx 400$, there was one molecule with a sulphur atom for every seven molecules without a sulphur heteroatom. Similarly, for fractions with a total sulphur content of $\approx 8.0$ wt% and an average molecular weight $\approx 400$, every molecule had one sulphur atom. This situation was true only if we assumed that most of the molecules with sulphur heteroatoms did not contain more than one sulphur atom in their molecular structure.

The SC separation scheme is not applicable for polyaromatic and polar fractions, as every molecule in these fractions may contain a sulphur heteroatom.

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