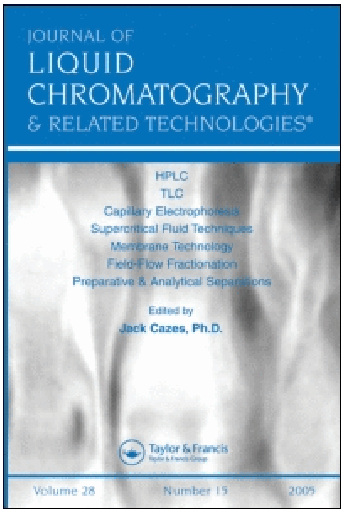

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Separation of Sulfur Compounds from a Diesel Fraction by Ligand Exchange Chromatography

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Abstract: Ligand exchange chromatography is reported as an effective technique for the separation of sulfur compounds from hydrocarbon molecules in a petroleum fraction. Palladium (II) chloride anhydrous, ferric chloride 6-hydrate, copper (II) sulfate 5-hydrate, silver nitrate, and tin (II) chloride 2-hydrate were studied for their effectiveness to separate sulfur compounds present in a Kuwaiti diesel fraction. Tin, silver, and palladium salts were found to be more effective than iron and copper salts for the separation of sulfur compounds from aromatic hydrocarbon molecules present in the fraction by these studies.

Keywords: Sulfur compounds, Ligand exchange chromatography, Diesel fraction

INTRODUCTION

Sulfur is the most abundant heteroatom present in petroleum fossil fuel and is the major cause of atmospheric pollution when petroleum fuels are used as sources of energy. Sulfur emissions from the combustion of a wide range of distillate fuels present an environmental concern, because they contribute to acid rain. Sulfur compounds are catalyst poisons in many processes, such as fluid catalytic cracking (FCC), hydrocracking, and catalytic reforming to produce lighter and cleaner motor or diesel fuels. Also, the sulfur compounds cause poisoning of advanced automotive catalysts that are used to reduce emissions of pollutant hydrocarbons, carbon monoxide, and

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nitrogen oxides from gasoline- and diesel-fueled vehicles. Many polycyclic aromatic sulfur compounds are suspected mutagens and/or carcinogens. Future regulations may mandate that the sulfur level in gasoline be reduced from the current level of 300 ppm to 30 ppm and, in diesel fuel, be reduced from 500 ppm to 15 ppm. Aviation fuel also will likely to be subjected to more stringent sulfur regulations, which currently have a total sulfur limit of 3000 ppm. This has raised concerns, with respect to how the fuel will behave under the high stresses that the fuel typically encounters, as well as the performance of engines that are powered by this fuel. Under the stress of high temperature, jet fuel can form oxidative deposits as the fuel thermally degrades. The formation of thermal deposits is greatly affected by the sulfur concentration of the fuel.[1] Other fuel characteristics, such as lubricity and storage stability, are also affected by the amount of sulfur in the fuel, in both positive and negative ways. The deposit formation has been associated with the presence of reactive sulfur species, such as thiols, sulfides, and disulfides.

Sulfur compounds in petroleum exist in enormous chemical structures and can be classified into two types, aliphatic or aromatic. The aliphatic sulfur compounds include those existing in paraffinic, isoparaffinic, or naphthenic structures, such as thiols, sulfides, or disulfides. The aromatic sulfur compounds include those with sulfur atoms present in aromatic rings or with sulfur atoms present in aliphatic side chains, substituted to aromatic rings. The sulfur atom present in an aliphatic structure, such as thiols, sulfides, or disulfide, is more reactive than the sulfur atom present in an aromatic ring structure, such as thiophenes, benzothiophenes, or dibenzothiophenes. Studies on the reactivity of some individual model sulfur compounds from different groups have shown that the relative reactivity of various sulfur species are considerably different, and fall into the sequence $k_{\text{sulfides}} > k_{\text{mercaptans}} > k_{\text{thiophenes}} > k_{\text{benzothiophenes}} > k_{\text{dibenzothiophenes}}$.[2] This means that during the desulfurization processes in the refinery, sulfides, disulfides, thiols, etc, present in the petroleum feed stocks are more easily desulfurized than the aromatic sulfur compounds. Therefore, the sulfur compounds in the product stream of a desulfurization process are mostly in aromatic form and are considered more refractory towards desulfurization processes. Among these, the substituted benzothiophenes and dibenzothiophenes are the most difficult to remove compared to unsubstituted thiophenes, benzothiophenes, or dibenzothiophenes.

Since it is very important to know the structure of a sulfur compound in a fuel to link it's reactivity towards a reaction, some method must be developed to estimate and identify the individual classes of sulfur compounds. The method should be good enough to determine sulfur components present in trace levels within a large hydrocarbon mixture. Even though the regulatory requirements only mandate the maximum limit for total sulfur content in a fuel, it is clear that speculated information on sulfur compounds is necessary to understand the fuel properties and performance.

BACKGROUND

The analysis of sulfur in transportation fuels has been performed by using gas chromatography with sulfur-specific detectors, such as atomic emission detector, flame photometric detector, hall detector, sulfur chemiluminescence detector, etc. The sulfur-specific detection allows for simplification of the fuel chromatogram by detection of only the sulfur compounds, but the assignment of the peaks in the sulfur chromatogram to individual sulfur containing species is still complicated and laborious, because it requires the comparison of retention times of hundreds of sulfur compound peaks with those of known standards. If the matrix effect from the hydrocarbon components can be eliminated by physical separation to isolate only the sulfur containing compounds, it may be more convenient to use a universal detection method, such as mass spectrometry. The common chromatography methods are not very effective for the separation and isolation of organic sulfur compounds because of the very small differences in polarity of a C-C bond and a C-S bond. Literature is enriched with different approaches for the preparative separation of sulfur compounds in a petroleum sample and most of the procedures used different forms of ligand exchange chromatography and some procedures explored extractions using specific solvent systems as a means of separation. Among the literature, we found that ligand exchange chromatography was the most popular approach, and different metal salts were reported specific for separation of different types of sulfur compounds from the hydrocarbon matrix.

Vogh and Dooley[3] separated alkyl and aryl sulfides from aromatic hydrocarbons by liquid chromatography on a copper loaded carboxylic cation exchange resin (Bio-Rex 70, 200–400 mesh from Bio-Rad Corporation). Gundermann et al.[4] used the complexation property of organic sulfur compounds, by means of copper-, mercury-, palladium-, etc., for the separation and isolation of organic sulfur compounds. The sulfur compounds were eluted according to their lewis-basicity. Cupric chloride ($CuCl_2$) was a good complexing agent for aliphatic thioethers, and palladium chloride ($PdCl_2$) for aromatic heterocycles. A ligand exchange chromatography procedure using cupric chloride ($CuCl_2$) had been developed by Nishioka and Tomich[5] for the isolation of aliphatic sulfur compounds in petroleum samples. Aliphatic sulfur compounds form stronger ligands with $CuCl_2$, because of the higher nucleophilicity, than do aromatic sulfur compounds. After the isolation of the sulfur compounds, they were identified by gas chromatography and mass spectrometry.

Nishioka et al.[6] separated polyaromatic sulfur heterocycles (PASH) having two to six aromatic rings from polycyclic aromatic hydrocarbons (PAH) by ligand exchange chromatography, using palladium chloride coated silica gel (5 wt% $PdCl_2$). Ma et al.[7] identified the sulfur compounds in the non-polar fraction of vacuum gas oil (VGO) of Middle East crude. These sulfur compounds represent 73 wt% of the total sulfur in the VGO.

They separated poly aromatic sulfur heterocycles (PASH) from the non-polar fraction of VGO by ligand exchange chromatography, using palladium chloride coated silica gel. Marvin et al.[8] used a multi-dimensional chromatographic procedure for the separation of sulfur compounds and polycyclic aromatic compounds from coal tar. The sample of coal tar was initially separated into four fractions (A1, A2, A3, and A4), using neutral alumina (80–200 mesh) as stationary phase and n-hexane, benzene, dichloromethane, and methyl alcohol, respectively, as eluents. The benzene fraction was separated into two fractions (A2P1 and A2P2) by ligand exchange chromatography using palladium chloride (5% wt) coated silica gel (230–400 mesh). Strand and Cermy[9] described the requirement of silver or palladium ions with silica gel stationary phase for the separation of sulfur aromatics and polyaromatic sulfur heterocycles (PASH) from aromatics and polyaromatics during the high performance liquid chromatographic procedures. The sulfides form stronger complexes than PASH and are irreversibly retained on the column.

The earlier work carried out in this laboratory by Ghaloum et al.,[10] explored ligand exchange chromatography using palladium, copper, mercury, and silver for the separation of sulfur compounds from monoaromatic and diaromatic fractions of vacuum gas oil.

Anderson[11] (1987) listed the problems encountered for the ligand exchange chromatography on silica containing 5% palladium chloride deposited on its surface as: (1) diethyl amine had to be added to destroy the $PdCl_2$/PASH complexes; (2) benzothiophenes partly eluted in through PAH fractions; and (3) compounds with a terminal thiophene ring show low recovery. If the nitrogen atom in diethyl amine could coordinate strongly enough with the palladium ion to destroy the PASH/$PdCl_2$ complex, the primary amino group in aminopropyl-bonded silica (such as LiChrosorb NH_2) should be able to retain all the $PdCl_2$. Anderson et al.[12] claimed a complete separation of polycyclic aromatic sulfur heterocycles (PASH) from polycyclic aromatic hydrocarbons (PAH) using a liquid chromatographic phase that includes palladium ion. Commercial aminopropyl substituted silica gel was derivatized with 2-aminocyclopentene-1-dithiocarboxylic acid (ACDA) and then complexed with palladium (II) chloride to give the stationary phase. The interactions of PASH's with palladium ions were more selective for PASH (vs. PAHs) than the interactions on the palladium chloride phase, especially for compounds with a terminal thiophenic ring. 4,6-Dimethyl dibenzothiophene exhibited longer retention time on Pd-ACDA and was separated from chrysene, a four ring PAH. Similarly, benzothiophene was separated from phenanthrene, which was not possible with PdCl2/silica.

Pyell et al.[13] used a chelating silica gel with immobilized 2-amino-1-cyclopentene-dithiocarboxylic acid (ACDA-SG) loaded with Ag(I) and Pd(II) as sorbent for the fractionation of PASH and PAH by high performance ligand exchange chromatography (HPLEC). The problem of column bleeding (remobilization of the immobilized metal cation) was reduced by chelating sorbents. Their studies proved palladium (II) loaded ACDA-SG to be suitable for the isolation of PASH from the PAH (number of condensed rings less than or equal to three).

Kuzmenko et al.[14] studied the model mixtures naphthalene-benzothiophene, phenanthrene-dibenzothiophene, and naphthalene-benzothiophene-phenanthrene-dibenzothiophene, as well as a high sulfur fraction (200–350°C) of a South Uzbekistan petroleum blend, deresined and deasphalted oil, and a crude oil from West Siberia, using tin tetrachloride ($SnCl_4$) modified silica gel for the separation of sulfur compounds. $SnCl_4$ is a soft acid and is reported more effective in the separation of sulfur compounds. The separation efficiency was determined by the donating ability of sulfur compounds towards $SnCl_4$. The solubility of $SnCl_4$ in hydrocarbons simplified the experimental procedures. The complexes were decomposed by adding 0.1 N sodium hydroxide solution to the fractions, washing with water, drying, and distilling of the solvent. The adsorbability of sulfur compounds on silica gel depends on their structure and decreases in the following order: aliphatic and cyclic sulfides, aromatic and cyclic thiols, aliphatic disulfides, aliphatic thiols, and thiophenes. The stability of sulfur compound-$SnCl_4$ complexes change as follows: $SnCl_4$-arenes $<$ $SnCl_4$-arenothiophenes $<$ $SnCl_4$-sulphides $<$ $SnCl_4$-mercaptans.

Some workers had reported extraction procedures, also, for the separation of sulfur compounds. Ruthenium (II) complex was found effective for the extraction of dibenzothiophenes, benzothiophenes, and thiophenes from petroleum feed stock by McKinley and Angelici.[15] The extraction was not effective for 4,6-dimethyl dibenzothiophene. Willey et al.[16] separated sulfur heterocycles from aromatic hydrocarbons by extraction into dimethyl sulfoxide, and subsequent oxidation to sulfones by hydrogen peroxide. Min and Savinova[17] studied the separation of sulfur compounds in the 200–350°C fraction of South Uzbekistan crude oil, using extraction with solutions of metal chlorides (inorganic electron acceptors) in coordinating organic solvents. They studied solutions of cadmium (II), copper (II), cobalt (II), nickel (II), manganese (II), chromium (II), zinc (II), and lithium (I) chlorides in dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), and propylene carbonate (PC). They discussed the extraction properties from positions of the hard and soft acid base (HSAB) theory. Solvent systems with a soft acid (cadmium chloride) lead to more effective extraction of sulfur compounds (soft bases). The reaction of sulfur compounds in petroleum fractions with hard acids, such as lithium chloride, proved to be less effective by their studies.

EXPERIMENTAL

Identification of the structure and type of sulfur compound using techniques such as nuclear magnetic resonance spectroscopy or mass spectrometry, require a preliminary separation of these compounds to reduce the complexity and interference from other hydrocarbon structures. The literature on the procedures for separation of sulfur compounds from petroleum fractions indicated that a multidimensional approach was required. The most popular approach was by ligand exchange chromatography of a sulfur rich fraction initially separated by elution chromatography using soft acid salts, such as palladium chloride, silver nitrate, copper sulfate, stannous chloride, etc., coated on silica gel as stationary phase. This approach was recently used in this laboratory for the separation of sulfur compounds from the monoaromatic and diaromatic fractions of Kuwaiti vacuum gas oil cuts by Ghaloum et al.[10] Vacuum gas oil was initially separated into saturates, monoaromatics, diaromatics, polyaromatics, and polars. The saturate fraction did not contain appreciable quantities of sulfur. Polyaromatics and polar fractions had high total sulfur contents corresponding to at least one atom of sulfur present in every molecule. The monoaromatic and diaromatic fractions had both aromatic hydrocarbon molecules and aromatic sulfur compounds that required a preliminary separation before applying techniques, such as NMR, IR, etc., to study the average chemical structure of these molecules. Palladium chloride coated (5% w/w) on silica gel was found the most effective stationary phase, when used in a sample to sorbent ratio of 1:30 for optimum separation.

In the case of a diesel sample, the aromatic components are mainly monoaromatic and diaromatic in nature, with a negligible amount of higher ring aromatics (triaromatics, tetraaromatics etc.) or polars. The objective of the present study was to compare the effectiveness of different metal salts during ligand exchange chromatography, to separate the sulfur compounds present in a Kuwaiti diesel fraction. The stationary phases were prepared by simple coating of the metal salts on silica or alumina, even though stationary phases prepared from commercial aminopropyl substituted silica gel derivatized with 2-aminocyclopentene-1-dithiocarboxylic acid (ACDA) and then complexed with metal salts were reported to be more effective for the separation of sulfur compounds in pure form (non-complexed) from a petroleum stream. We avoided the preparation of stationary phases with immobilized metal ions in the present studies since our objective was not an analytical or preparative separation of sulfur compounds in the sample. The experimental studies were conducted using five metal salts, Palladium (II) chloride anhydrous, ferric chloride 6-hydrate, copper (II) sulfate 5-hydrate, silver nitrate, and tin (II) chloride 2-hydrate. All these metal salts, except iron salt, were reported in the literature as effective for the separation of various types of sulfur compounds. The selection of iron salt is based on the fact that iron complexes are used industrially as a redox system to remove hydrogen sulfide from gaseous streams and to recover sulfur. The chromatographic conditions, such as coating media (alumina, different grades of silica gel), solvent polarity, and metal to sulfur ratio, were optimized using palladium chloride. The other metal salts were then compared using these optimum chromatographic conditions for the effective separation of sulfur compounds present in a Kuwaiti diesel fraction.

Materials

The diesel sample from a primary processing unit of a Kuwaiti refinery was used as the feed for the separation of sulfur compounds. The sample was characterized according to the procedures of American Society for Testing and Materials (ASTM),[18] and the properties are given in Table 1. The sample had 58.41% wt nonaromatics and 41.59% wt aromatics by elution chromatography (ASTM D 2549). The total sulfur content of the sample was 2.6 wt% (ASTM D 5453) with a total mercaptan sulfur content of only 211 ppm (ASTM D 3237).

The stationary phases used during the chromatographic experiments were silica gel grade 12 (28–200 mesh, Aldrich), silica gel grade 923 (100–200 mesh, Aldrich) and alumina for thin layer chromatography type F-20 (80–200 mesh, Sigma). The metal salts used for coating the stationary phases were palladium (II) chloride anhydrous (Purum, Fluka), ferric chloride hexahydrate (Puriss, Fluka), copper (II) sulfate 5-hydrate (Analar, BDH), silver nitrate (Chem pue, Riedel-de Haen), and tin (II) chloride 2-hydrate (Analar, BDH). Chloroform, n-pentane, diethylether and ethyl alcohol were used as solvents for elution.

Ligand Exchange Chromatography Procedure

An atom (0.0141 g) of the metal salt (palladium chloride, ferric chloride, copper sulfate, silver nitrate, or stannous chloride) was accurately weighed into the flask of a rotary evaporator. Silica gel grade 12 or silica gel grade 923 (50 g), or neutral alumina was also accurately weighed into the flask. Deionized water (100 mL) was added to the flask and shaken well. Water was evaporated with a rotary evaporator under vacuum (500 torr), keeping the flask in a water bath maintained at 95°C. When 95% volume of the water was removed, 50 mL of methyl alcohol was added to the flask and the contents of the flask were mixed well. Methyl alcohol was also evaporated at 95°C using rotary evaporator, but under atmospheric pressure. When most of the methyl alcohol was evaporated off from the flask, one more volume of methyl alcohol (50 mL) was added to the flask and the contents were mixed well before removing the alcohol by a rotary evaporator. The material inside the flask would become a free flowing powder as most of the solvent was evaporated. The final traces of solvent were removed using the rotary evaporator, under vacuum (500 torr) and maintaining the flask temperature at 95°C for 15 minutes. The contents of the flask were transferred to a porcelain crucible and dried to constant weight in an oven at 250°C, for 12 hours.

Table 1. Properties of diesel from refinery stream

Properties	Values	Method
Density	0.8811	D 5002
API	29.09	D 287
R. I. at 20°C	1.493	D 1218
Molecular weight	261	D 2503
Acid number, mg KOH/g	0.109	D 664
Base number, mg KOH/g	0.017	D 4739
Bromine number, g/100 g	2.50	D 1159
Aniline point, °C	73.4	D 611
Cetane index	54.83	D 4737
Mercaptan sulfur, ppmw	211	D 3227
Elemental analysis, %w/w		D 5291
Carbon	84.23	
Hydrogen	13.16	
Nitrogen	0.01	D 5762
Sulfur	2.60	D 5453
Elution chromatography, %w/w		D 2549
Non-aromatics	58.41	
Aromatics	41.59	
Supercritical chromatography, %w/w		D 5186
Non-aromatics	64.51	
Mono-aromatics	17.99	
Poly-aromatics	17.50	
Distillation, D2887, %w/w		D 2887
IBP	229.5	
5	268.5	
10	286.0	
20	305.0	
30	316.5	
40	326.5	
50	337.5	
60	347.0	
70	356.5	
80	367.5	
90	383.0	
95	395.0	
FBP	430.5	

The column chromatographic procedure was similar to the ASTM D 2549 method used for characterizing the feed diesel sample. Two stationary phases were used for these tests, with either silica gel grade 923 or silica gel grade 12 used as the bottom stationary phase, and metal coated medium as the top stationary phase. The bottom stationary phase was packed to a height of 780 mm and the top stationary phase was packed to a height of 360 mm.

The bottom stationary phases weighed in the range of 114 to 120 g and the upper stationary phases weighed in the range of 50 to 53 g in these experiments. The experiments were performed using different "metal to sulfur" ratio and was adjusted by sample sizes. Sample sizes used were 10 g, 5 g, and 2.5 g, corresponding to a sample to sorbent ratio of 1:17, 1:34, and 1:68, respectively. The metal to sulfur ratios were 0.0141:0.0081, 0.0141:0.0040, and 0.0141:0.0020, respectively, in these cases.

There were a total of eleven ligand exchange chromatography experiments. The first seven experiments were conducted to optimize the chromatographic conditions using palladium chloride as the metal salt. Among these, the first three ligand exchange chromatography experiments were conducted to study the effect of three coating media, silica gel 12, silica gel 923, and alumina on the separation of sulfur compounds (Table 2).

Palladium(II) chloride anhydrous (2.5 g) was coated on to these phases to maintain a metal to sulfur atomic ratio of 0.0141:0.0081 when 10 g of the diesel sample was used as the feed. n-Pentane (130 mL) was used for the elution of the first fraction, 20 mL each of diethyl ether was used for the elution of the next five fractions, 20 mL each of chloroform was used for the elution of the subsequent five fractions, and finally, 100 mL ethyl alcohol was used for the elution of the final fraction. A total number of twelve fractions were collected for each experiment. The solvent was removed and the recovery in each fraction was estimated. The fractions were analyzed for sulfur, nitrogen, and molecular weight. The analyses could not be performed on fractions that were negligible.

Ligand exchange chromatography experiment 4 was conducted under identical conditions as ligand exchange chromatography experiment 3, except for the elution order of solvents (Table 3). n-Pentane (130 mL) was used for the elution of the nonaromatic fraction and a mixture of n-pentane and chloroform were used for the elution of fractions 2 to 5. Fractions 6, 7, and 8 were eluted with chloroform, fraction 9 with diethylether, and finally, the fraction with ethyl alcohol.

Ligand exchange chromatography experiments 5 and 6 were conducted to study the effect of sample sizes on the separation of sulfur compounds (Table 3). Sample sizes of 5 g and 2.5 g were used in these experiments to keep the "metal to sulfur" atomic ratios as 0.0141:0.0040 and 0.0141:0.0020, respectively. For both experiments, fractions were eluted using the same elution order of solvents. Fraction 1 was eluted with 130 mL of n-pentane, fraction 2 was eluted using n-pentane and mixtures of n-pentane and chloroform (95:5, 90:10 and 80:20 volume ratios). Fraction 3 was eluted with chloroform, fractions 4 and 5 were eluted with diethyl ether, and fraction 6 and fraction 7 were eluted with ethyl alcohol.

Ligand exchange chromatography experiments 1 to 6 were conducted using silica gel grade 923 as the bottom stationary phase. Ligand exchange chromatography experiment 7 was conducted using silica gel grade 12 as the bottom stationary phase, with a metal to sulfur atomic ratio of 0.0141:0.0020 (Table 4).

Table 2. Details of ligand exchange chromatography experiments 1, 2 and 3

Experiment no	1	2	3
Metal salt	$PdCl_2$	$PdCl_2$	$PdCl_2$
Coated phase	Silica gel 12	Silica gel 923	Alumina
M:S (g atoms)	0.0141:0.0081	0.0141:0.0081	0.0141:0.0081
Bottom phase	Silica gel 923	Silica gel 923	Silica gel 923
Feed weight, g	10.0019	10.0009	10.0009
Fraction 1	130 ml n-pentane	130 ml n-pentane	130 ml n-pentane
Yield, %wt	53.58	57.39	57.77
Sulfur, %wt	0.03	0.03	0.01
Molecular weight	271.70	272.5	273.9
Fraction 2	20 ml DEE	20 ml DEE	20 ml DEE
Yield, %wt	5.94	8.33	10.69
S, %wt	5.11	5.69	4.22
Molecular weight	246.9	307.1	253.5
Fraction 3	20 ml DEE	20 ml DEE	20 ml DEE
Yield, %wt	16.16	18.07	17.08
S, %wt	4.35	4.73	4.64
Molecular weight	247.7	311.1	273.6
Fraction 4	20 ml DEE	20 ml DEE	20 ml DEE
Yield, %wt	12.17	11.62	8.06
S, %wt	4.93	5.04	4.40
Molecular weight	255.9	290.6	253.4
Fraction 5	20 ml DEE	20 ml DEE	20 ml DEE
Yield, %wt	4.90	4.30	1.70
S, %wt	4.60	4.91	4.38
Molecular Weight	255.0	296.8	272.3
Fraction 6	20 ml DEE	20 ml DEE	20 ml DEE
Yield, %wt	0.47	0.23	0.26
S, %wt	5.75	4.99	6.17
Molecular weight	495.5	603.6	855.60
Fraction 7	20 ml $CHCl_3$	20 ml $CHCl_3$	20 ml $CHCl_3$
Yield, %wt	0.25	0.13	0.10
S, %wt	5.29	ND	ND
Molecular weight	464.3	ND	ND
Fraction 8	20 ml $CHCl_3$	20 ml $CHCl_3$	20 ml $CHCl_3$
Yield, %wt	0.18	0.05	0.06
S, %wt	3.60	ND	ND
Molecular weight	575.5	ND	ND
Fraction 9	20 ml $CHCl_3$	20 ml $CHCl_3$	20 ml $CHCl_3$
Yield, %wt	0.26	0.02	0.04
S, %wt	5.72	ND	ND
Molecular weight	546.9	ND	ND

(*continued*)

Table 2. Continued

Experiment no	1	2	3
Fraction 10	20 ml $CHCl_3$	20 ml $CHCl_3$	20 ml $CHCl_3$
Yield, %wt	0.19	0.02	0.03
S, %wt	5.69	ND	ND
Molecular weight	592.1		
Fraction 11	20 ml $CHCl_3$	20 ml $CHCl_3$	20 ml $CHCl_3$
Yield, %wt	0.14	0.04	0.32
S, %wt	5.46	ND	ND
Molecular weight	680.9	ND	ND
Fraction 12	100 ml EA	100 ml EA	100 ml EA
Yield, %wt	4.97	6.97	4.64
S, %wt	ND	ND	4.09
Molecular weight	ND	ND	ND
Total recovery, %wt	99.21	107.18	100.77
Total S recovery, %wt	74.15	82.89	72.54

$PdCl_2$ = Palladium chloride anhydrous; M:S = Metal:Sulfur; S = Sulfur; DEE = Diethyl ether; $CHCl_3$ = Chloroform; EA = Ethyl alcohol; ND = Not determined.

Only five fractions were collected, the first fraction using n-pentane, the second fraction using mixture of n-pentane and chloroform (95:5 and 80:20 volume ratios), the third fraction using chloroform, the forth fraction using diethyl ether, and the last fraction using ethyl alcohol.

Ligand exchange chromatography experiments 1 to 7 were conducted using palladium chloride as the metal salt for coating the upper stationary phase. Ligand exchange chromatography experiments 8 to 11 were performed using ferric chloride hexahydrate, copper (II) sulfate 5-hydrate, silver nitrate, and tin (II) chloride 2-hydrate, respectively, as metal salts (Table 4). The "metal to sulfur" atomic ratios for these experiments were kept the same as in ligand exchange chromatography experiment 7 (0.0141:0020). Five fractions were collected in each of these experiments, keeping the same solvent quantity and elution order as in experiment number 7. Also, silica gel grade 12 was used as the bottom stationary phase in these experiments.

RESULTS AND DISCUSSIONS

Ligand exchange chromatography experiments 1, 2, and 3 are compared for the yield, sulfur content, sulfur recovery, and molecular weight of fractions in Figures 1 to 4. These experiments were conducted to compare the effectiveness of three stationary phases, silica gel grade 12, silica gel grade 923, and alumina, as coating medium for metal salts to separate sulfur compounds by ligand exchange chromatography. Figures 1 to 4 show a similar trend for

Table 3. Details of ligand exchange chromatography experiments 4, 5 and 6

Experiment no	4	5	6
Metal salt	$PdCl_2$	$PdCl_2$	$PdCl_2$
Coated phase	Alumina	Alumina	Alumina
M:S (g atoms)	0.0141:0.0081	0.0141:0.0040	0.0141:0.0020
Bottom phase	Silica gel 923	Silica gel 923	Silica gel 923
Feed weight, g	10.0835	5.0287	2.5066
Fraction 1	130 ml n-pentane	130 ml n-pentane	130 ml n-pentane
Yield, %wt	57.55	57.39	57.39
S, %wt	0.01	0.00	0.00
Molecular weight	279.70	274.10	279.20
Fraction 2	100 ml A	100 ml n-pentane, 200 ml A, 100 ml B, 300 ml C	100 ml n-pentane, 200 ml A, 100 ml B, 300 ml C
Yield, %wt	0.72	24.62	19.76
S, %wt	0.95	3.59	2.24
Molecular weight	278.30	239.40	246.30
Fraction 3	100 ml D	100 ml $CHCl_3$	100 ml $CHCl_3$
Yield, %wt	22.48	8.57	11.10
S, %wt	3.40	9.93	8.30
Molecular weight	244.20	230.00	223.90
Fraction 4	100 ml D	20 ml DEE	20 ml DEE
Yield, %wt	5.22	1.99	1.36
S, %wt	5.91	3.67	2.78
Molecular weight	218.10	482.9	424.3
Fraction 5	100 ml E	80 ml DEE	80 ml DEE
Yield, %wt	2.76	2.10	1.05
S, %wt	7.00	6.40	2.46
Molecular weight	220.00	662.70	958.50
Fraction 6	200 ml $CHCl_3$	20 ml EA	20 ml EA
Yield, %wt	0.85	2.28	2.76
S, %wt	9.76	3.66	3.22
Molecular weight	225.2	965.4	934.2
Fraction 7	100 ml $CHCl_3$	100 ml EA	100 ml EA
Yield, %wt	0.50	5.23	9.44
S, %wt	9.76	3.66	3.22
Molecular weight	219.60	893.60	980.50
Fraction 8	90 ml $CHCl_3$		
Yield, %wt	0.35		
S, %wt	9.64		
Molecular weight	219.70		

(*continued*)

Table 3. Continued

Experiment no	4	5	6
Fraction 9	100 ml DEE		
Yield, %wt	6.37		
S, %wt	10.21		
Molecular weight	451.30		
Fraction 10	100 ml EA		
Yield, %wt	4.81		
S, %wt	7.02		
Molecular weight	ND		
Total sample recovery, %wt	101.61	102.20	102.87
Total sulfur recovery, %wt	80.31	87.62	72.56

$PdCl_2$ = Palladium chloride anhydrous; M:S = Metal:Sulfur; S = Sulfur; A = n-Pentane:chloroform (95:5); B = n-Pentane:chloroform (90:10); C = n-Pentane:chloroform (80:20); D = n-Pentane:chloroform (75:25); E = n-Pentane:chloroform (50:50); $CHCl_3$ = Chloroform; DEE = Diethylether; EA = Ethyl alcohol; ND = Not determined.

the above mentioned parameters, by fractions separated during ligand exchange chromatography using palladium coated on three different stationary phases. The first fractions eluted with n-pentane were nonaromatic in nature and had negligible sulfur content. Most of the sulfur recovered was distributed in the second, third, fourth, and fifth fractions in these experiments. The sulfur content of around 5% wt and a molecular weight of around 250 for these fractions correlated to two sulfur containing molecules for every three hydrocarbon molecules without sulfur. It was also assumed that the sulfur containing molecules were having only one sulfur atom per molecule. The sixth fractions eluted with diethyl ether were in complex forms with the metal ions, as indicated by the molecular weights, and the recoveries of these fractions were much less in these experiments. The recoveries of chloroform fractions were less and only for experiment number 1 could the fraction be analyzed for sulfur content and molecular weight. The molecular weight of the fraction indicated that the sulfur compounds in the fraction were in complex structures with palladium. The sulfur content of the complex fraction related to an average of one sulfur atom per molecule. For the rest of the experiments alumina was selected as the media to coat metal salts, since the three phases (silica gel grade 12, silica gel grade 923, and alumina) did not show much difference in the results. The ASTM 2549 method for the separation of nonaromatics and aromatics uses alumina as the upper stationary phase, along with silica gel grade 923 as the bottom stationary phase. The alumina retains the polar compounds that are eluted in the ethyl alcohol fraction.

Ligand exchange chromatography experiment 4 was conducted to study the effect of the solvent elution order on the type and recovery of fractions.

Table 4. Details of ligand exchange chromatography experiments 7, 8, 9, 10 and 11

Experiment no	7	8	9	10	11
Metal salt	$PdCl_2$	$FeCl_3 \cdot 6H_2O$	$CuSO_4 \cdot 5H_2O$	$AgNO_3$	$SnCl_2 \cdot 2H_2O$
Coated phase	Alumina				
M:S (g atoms)	0.0141:0.0020				
Bottom Phase	Silica gel 12				
Feed weight, g	2.5052	2.5002	2.5005	2.5002	2.5007
Fraction 1	130 ml n-pentane				
Yield, %wt	57.08	50.98	53.26	52.84	51.82
S, %wt	0.00	0.002	0.002	0.003	0.004
Molecular weight	280.0	303.4	268.10	268.6	267.6
Fraction 2	100 ml A, 100 ml B				
Yield, %wt	10.28	28.34	27.28	15.09	9.45
S, %wt	1.21	5.73	6.15	4.12	3.33
Molecular weight	269.2	247.5	235.1	223.1	244.5
Fraction 3	100 ml $CHCl_3$				
Yield, %wt	22.12	8.58	10.42	16.88	26.31

S, %wt	4.76	7.82	8.75	7.53	7.61
Molecular weight	246.4	254.8	229.9	216.4	231.7
Fraction 4	100 ml DEE				
Yield, %wt	5.59	1.26	0.75	2.77	2.61
S, %wt	4.17	4.21	2.46	8.46	10.56
Molecular weight	810.1	455.3	690.6	251.2	252.5
Fraction 5	100 ml EA				
Yield, %wt	9.85	0.33	0.23	2.12	0.60
S, %wt	2.69	3.94	0.92	8.95	1.43
Molecular weight	ND	952.9	1615.3	506.1	1103.8
Total sample recovery, %wt	104.92	89.48	91.94	89.69	90.79
Total S recovery, %wt	64.44	90.82	100.51	89.17	100.06

$PdCl_2$ = Palladium (II) chloride anhydrous; $FeCl_3 \cdot 6H_2O$ = Ferric chloride hexahydrate; $CuSO_4 \cdot 5H_2O$ = Copper (II) sulfate pentahydrate; $AgNO_3$ = Silver nitrate; $SnCl_2 \cdot 2H_2O$ = Tin (II) chloride 2-hydrate; M:S = Metal:Sulfur; S = Sulfur; A = n-Pentane:chloroform (95:5); B = n-Pentane:chloroform (80:20); $CHCl_3$ = Chloroform; DEE = Diethylether; EA = Ethyl alcohol; ND = Not determined.

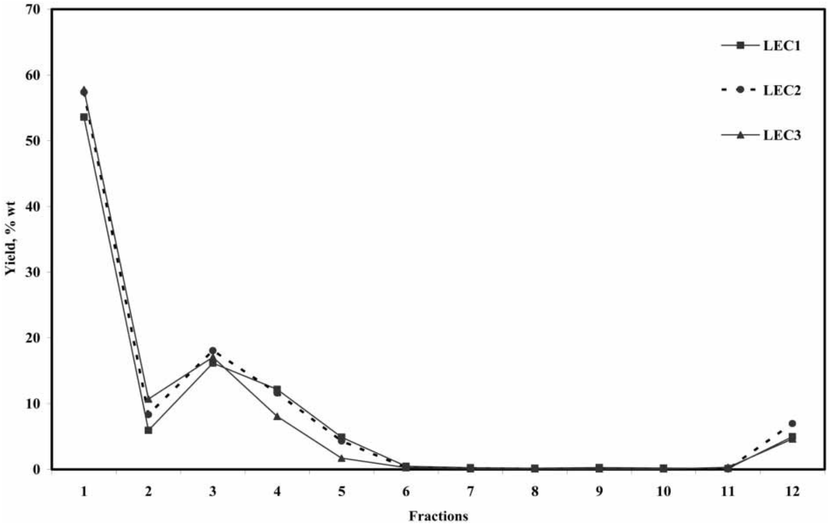

Figure 1. Yield of fractions of ligand exchange chromatography (LEC) experiments 1, 2, and 3 with palladium coated on different stationary phases.

The first fraction eluted with n-pentane composed of nonaromatic hydrocarbons with no sulfur compounds as in the previous experiments. For the elution of the second, third, forth, and fifth fractions, a mixture of n-pentane and chloroform were used in different volume ratios. The sixth, seventh, and eighth fractions were recovered with chloroform, the ninth fraction with

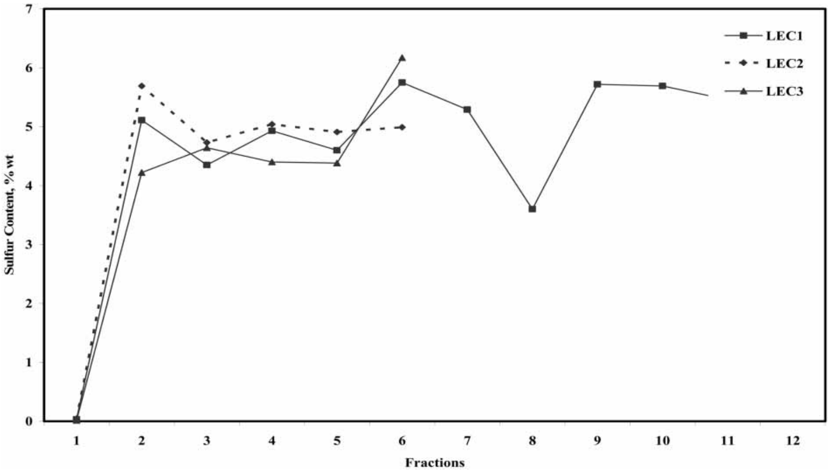

Figure 2. Sulfur content in fractions of ligand exchange chromatography (LEC) experiments 1, 2, and 3 with palladium coated on different stationary phases.

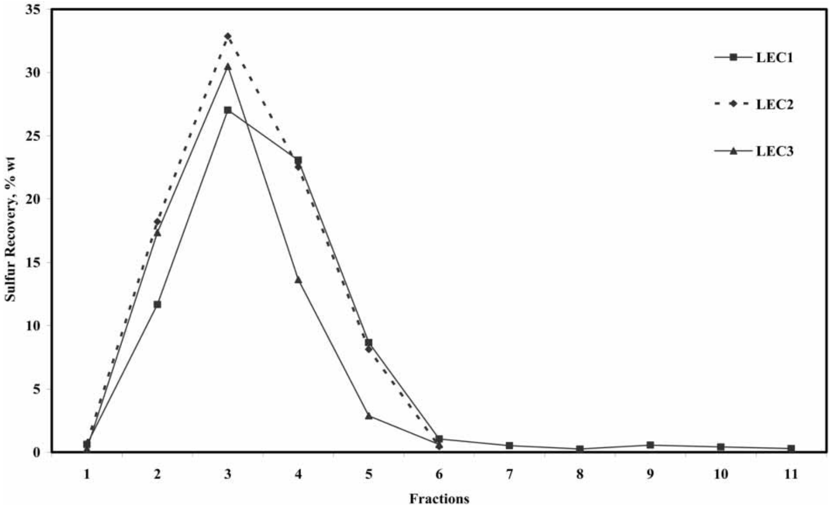

Figure 3. Sulfur recovery in fractions of ligand exchange chromatography (LEC) experiments 1, 2, and 3 with palladium coated on different stationary phases.

diethyl ether, and finally, the last fraction with ethyl alcohol. Most of the sulfur was recovered in the third, forth, fifth, and sixth fractions. Sulfur recoveries in chloroform fractions were much less because of the lower yields of these fractions. The sulfur recovered in diethyl ether (fraction 9) and ethyl

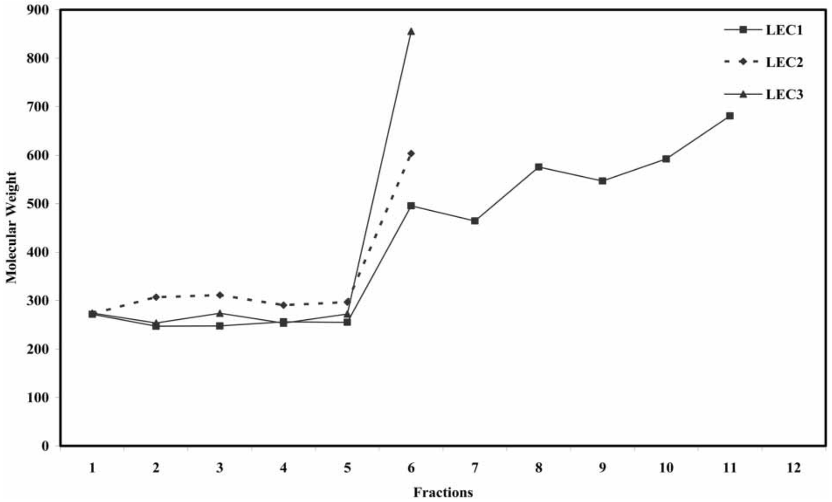

Figure 4. Molecular weight of fractions of ligand exchange chromatography (LEC) experiments 1, 2, and 3 with palladium coated on different stationary phases.

alcohol (fraction 10) fractions were 17.20 wt% and 7.02 wt%, respectively (Fig. 5). The molecular weight of ether fraction indicated that it was in a complex form with palladium salt (Fig. 6). The molecular weight of the ethyl alcohol fraction could not be done by vapor pressure osmometry because of the insoluble nature of the fraction in toluene.

Ligand exchange chromatography experiments 5 and 6 were performed to study the effect of sample size in getting an effective separation for sulfur compounds using palladium chloride. Seven fractions were eluted and most of the sulfur was recovered in the second and third fractions. Metal to sulfur atomic ratios of 0.0141:0.0040 and 0.0141:0.0020, respectively, were used in these experiments, and the recoveries of sulfur (Fig. 7) indicated more enrichment of sulfur compounds in the third fraction (35.43% wt) for experiment 6, effecting a better separation between aromatic hydrocarbons and sulfur compounds compared to experiment 5. The yield and recovery of sulfur in ether fractions were much less. The yield and recovery of sulfur in ethyl alcohol fractions were higher than in the ether fractions. The high molecular weight of fractions separated using ether and ethyl alcohol indicated the compounds were in a complex structure (Fig. 8).

Ligand exchange chromatography experiment 7 was performed using silica gel grade 12 as the bottom stationary phase. The first fraction eluted with n-pentane was nonaromatic in nature with negligible sulfur content. The high molecular weight of the diethyl ether fraction (fraction 4) indicated that the fraction was separated as a metal complex, and the fraction accounted for 8.97% wt of sulfur recovered. The ethyl alcohol

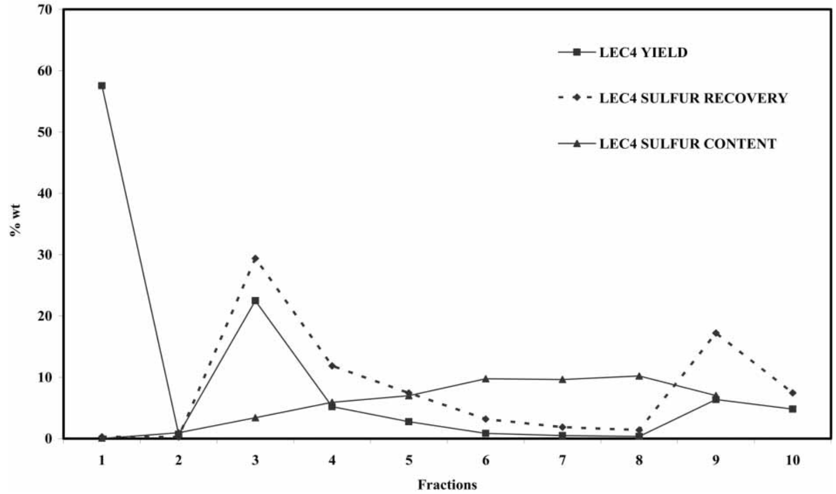

Figure 5. Elution solvent vs yield, sulfur recovery and sulfur content of fractions of ligand exchange chromatography (LEC) experiment 4.

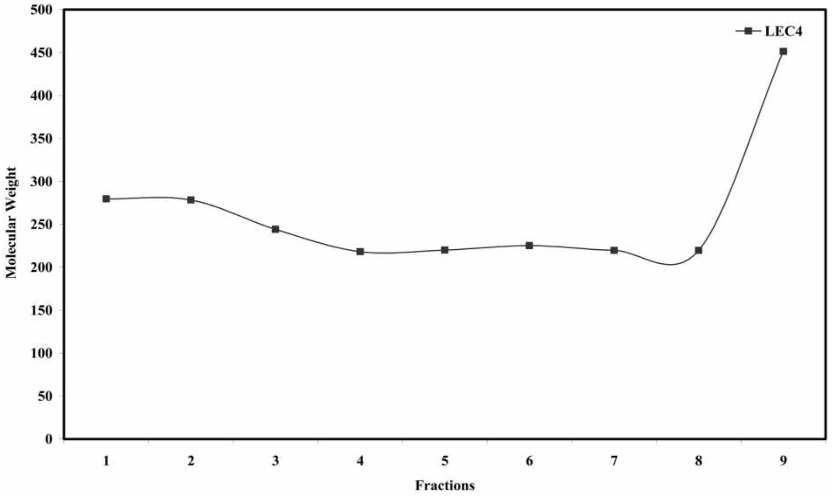

Figure 6. Elution solvent vs molecular weight of fractions of ligand exchange chromatography (LEC) experiment 4.

fraction (fraction 5) was insoluble in toluene and the molecular weight could not be estimated by vapor pressure osmometry, and the fraction recovered 10.19% wt of total sulfur in the sample. The percentage sulfur recoveries in fractions 2 and 3 during ligand exchange chromatography experiment 6 were 17.03% wt and 35.43% wt, respectively, (Fig. 7) while the percentage

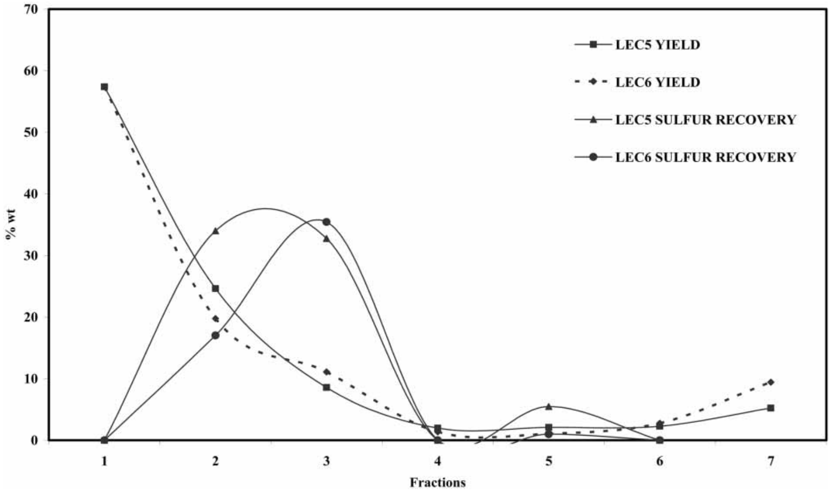

Figure 7. Effect of sample size on yield and sulfur recovery of fractions of ligand exchange chromatography (LEC) experiments 5 and 6.

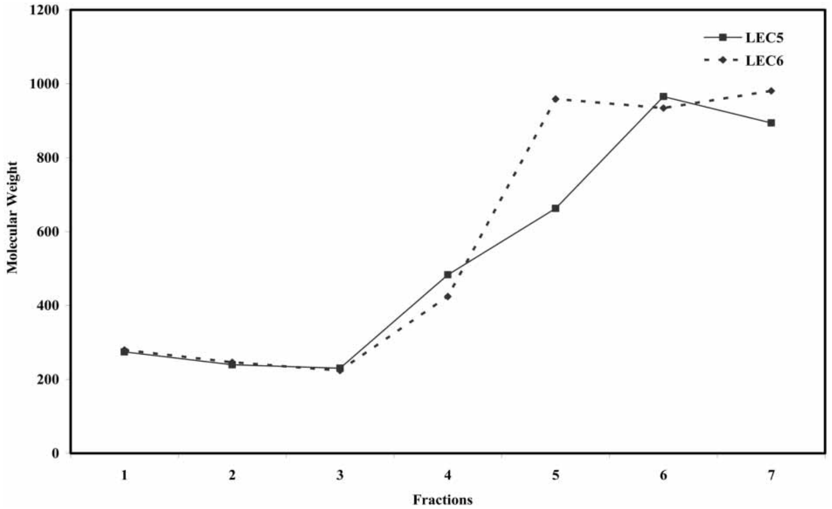

Figure 8. Effect of sample size on molecular weight of fractions of ligand exchange chromatography (LEC) experiments 5 and 6.

sulfur recoveries in these fractions during ligand exchange chromatography experiment 7 were 4.78% wt and 40.50% wt, respectively, (Fig. 11). As our objective was to get a second fraction composed of only aromatic hydrocarbons with out any sulfur compounds, and a third and subsequent fractions enriched with sulfur compounds, we may assume that silica gel grade 12 was equally, or more, effective than silica gel grade 923 as the bottom stationary phase for the separation.

Silica gel grade 12 was used as the bottom stationary phase and metal coated alumina was used as the upper stationary phase, maintaining a metal to sulfur ratio of 0.0141:0020 for experiments 8, 9, 10, and 11 for the comparison of different metal salts. The metal salts used were ferric chloride hexahydrate, copper(II) sulfate 5-hydrate, silver nitrate, and tin(II) chloride 2-hydrate. Experimental parameters were kept identical to experiment number 7 using palladium chloride. The comparison of recovery of samples in different fractions show that there was a gradual decrease in recovery of fractions for experiments with iron and copper salts from fractions 1 to 5, while for experiments with palladium, silver, and tin there was a decrease in recovery from fraction 1 to 2, then an increase from fraction 2 to 3, and then decrease from 3 to 5 (Fig. 9). Sulfur, 62.45% wt and 64.59% wt, respectively, were recovered in fractions 2 using a mixture of n-pentane and chloroform as the elution solvent during experiments with iron and copper salts (Fig. 11). The sulfur compounds and aromatic hydrocarbons eluted together in this fraction without separation. Experiments with palladium (experiment number 7), silver (experiment number 10), and tin (experiment number 11)

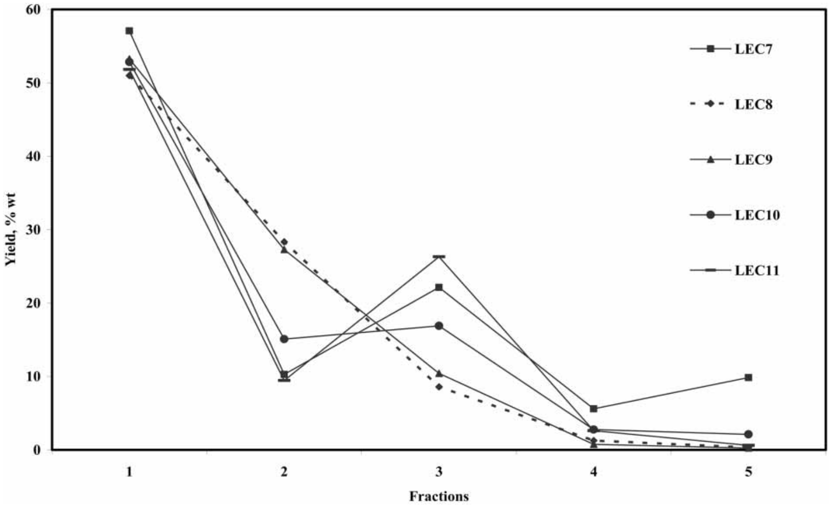

Figure 9. Comparison of yields of fractions of ligand exchange chromatography (LEC) experiments 7, 8, 9, 10, and 11 using palladium, iron, copper, silver, and tin salts.

recovered 40.50, 48.92, and 76.95% wt, respectively, of total sulfur in chloroform (fraction 3) fractions. The recovery of sulfur was highest for tin, followed by silver, and then palladium in the chloroform fractions (Fig. 11). Between these three metals, the sulfur content of the chloroform fraction was the highest for LEC, with tin indicating more enrichment of sulfur molecules in the fraction (Fig. 10). The fractions of 2 eluted with a mixture of n-pentane and chloroform, had less recovery of sulfur for LEC using tin, silver, and palladium and indicated a more effective separation of aromatic hydrocarbons from sulfur compounds. The nitrogen contents of the ether and alcohol fractions were comparatively higher, except for LEC with palladium. The alcohol fractions had less nitrogen content than ether fractions for LEC with copper and iron. Silver and tin showed an opposite trend with alcohol fractions and had a higher nitrogen content than ether fractions (Fig. 12). The molecular weight of ether and alcohol fractions of LEC with these metals showed higher values, indicating the fractions were eluted as metal complexes, with the exception of ether fractions separated during LEC using tin and silver (Fig. 13).

CONCLUSIONS

Different types of metal salts are reported in the literature for the separation of sulfur compounds in petroleum fractions, because of their ability to form

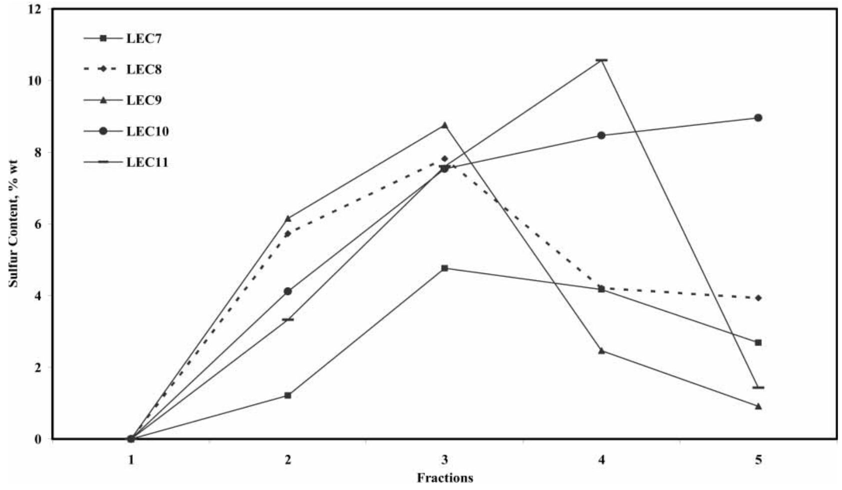

Figure 10. Comparison of sulfur content in fractions of ligand exchange chromatography (LEC) experiments 7, 8, 9, 10, and 11 using palladium, iron, copper, silver, and tin salts.

complexes with them. Depending on the type of sulfur compounds present in petroleum fractions, the metal's ability to form complexes is specific. The objective of our study was to compare the effectiveness of some of the metal salts already reported in the literature, to separate the sulfur

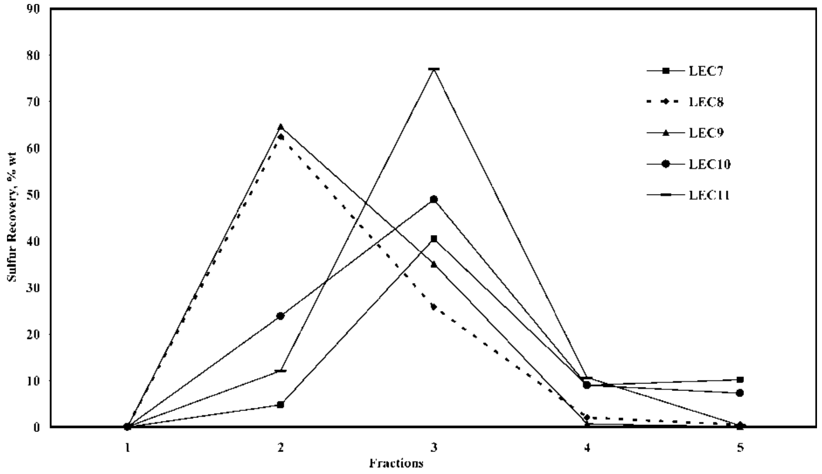

Figure 11. Comparison of sulfur recoveries in fractions of ligand exchange chromatography (LEC) experiments 7, 8, 9, 10, and 11 using palladium, iron, copper, silver, and tin salts.

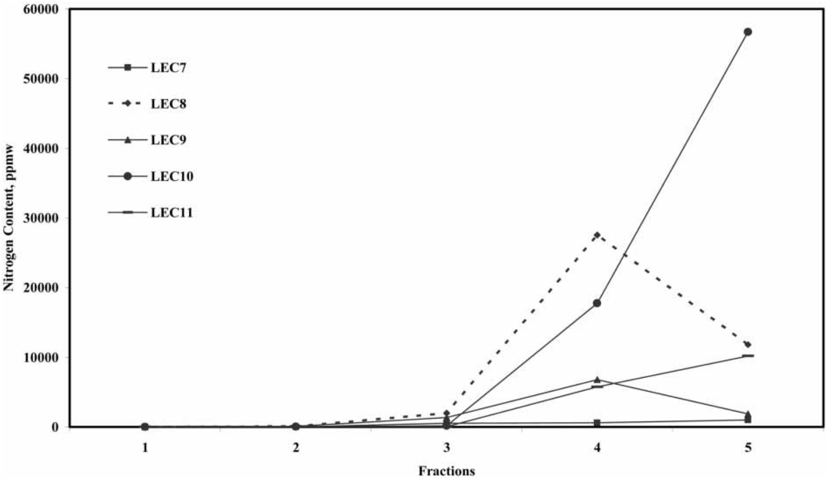

Figure 12. Comparison of nitrogen content in fractions of ligand exchange chromatography (LEC) experiments 7, 8, 9, 10, and 11 using palladium, iron, copper, silver, and tin salts.

compounds from hydrocarbon molecules present in a Kuwaiti diesel fraction. An effective separation of the sulfur containing molecules were required for their characterization and structural elucidation, applying advanced techniques such as nuclear magnetic resonance spectroscopy, mass spectroscopy,

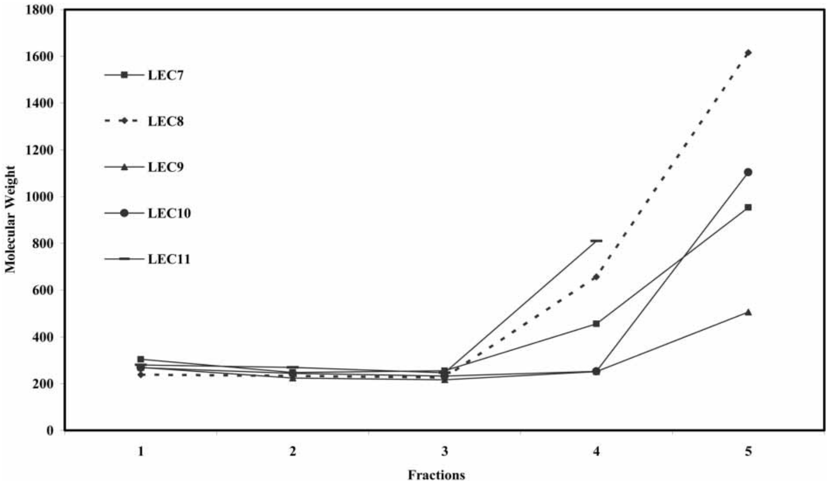

Figure 13. Comparison of molecular weight of fractions of ligand exchange chromatography (LEC) experiments 7, 8, 9, 10, and 11 using palladium, iron, copper, silver, and tin salts.

etc. Among the five metal salts studied, tin, silver, and palladium were found to be more effective than iron and copper for the separation of sulfur compounds from aromatic hydrocarbon molecules present in a Kuwaiti diesel fraction. Alumina coated with the metal salt was used as the upper stationary phase. Silica gel grade 12 was the bottom stationary phase. Metal to sulfur atomic ratio of 0.0140:0.0020 was maintained.

Fractions 1 eluted with n-pentane were nonaromatic in nature having no sulfur compounds irrespective of the metal used. Fractions 2 eluted with a mixture of n-pentane and chloroform recovered less sulfur compounds for LEC using tin, silver, and palladium; while using iron and copper these fractions recovered most of the sulfur compounds. The major portions of sulfur were recovered in the chloroform fractions (fractions 3) during LEC with tin, silver, and palladium and these fractions were not separated as metal complexes.

The weak interaction between metal atoms and sulfur atoms of the sulfur compounds eluted in chloroform fractions resulted in longer retention of these molecules in the column, effecting the enrichment of sulfur compounds in chloroform fractions. The sulfur compounds that formed strong complexes with metal atoms were eluted in more polar solvents like diethyl ether and ethyl alcohol as metal complexes. The ether fractions of LEC with tin and silver were exceptions and were not separated as metal complexes, as indicated by the molecular weights of these fractions. We hope that the observations made during the present study will lead us to develop a high performance liquid chromatographic procedure (analytical and preparative) for the separation of sulfur compounds directly from the sample, without a preliminary separation into aromatics and non aromatic fractions.

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