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Analysis of Sulfur Compound Types in Asphalt

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Contents

Abstract 1

Executive Summary 3

1. **Phase I**

Introduction 5

Experimental Section 7

Materials

LC Separations

Total Sulfur Analysis

Determination of Sulfoxides

IR-oxidation Method of Determination of Aliphatic Sulfides

UV Determination of Aliphatic Sulfides Via Complexation with Iodine

Determination of Sulfonic Acids and Other Strongly Acidic Types

Determination of Thiols

Determination of Sulfoxides by Titration with Perchloric Acid

Thiophenic Sulfur Types

Results and Discussion 11

LC Separations and Sulfur Balance

Preliminary Evaluation of Analytical Methods

Analysis of Asphalt Fractions

Oxidizable Sulfur in Asphalt

Correlation of Sulfur Type Distributions with Asphalt Performance

Conclusions and Recommendations 28

2. **Phase II. Direct Determinaton of Thiophenic Sulfur**

Introduction 31

Experimental 31

Materials

Oxidation of Thiophenic Sulfur to Sulfone Type

IR Measurement of Sulfones

HPLC Separation of Sulfones

Results and Discussion 33

Conclusions 41

References 43

List of Figures

1-1. Scheme for liquid chromatographic (LC) separation of asphalts 8

2-1. HPLC chromatogram depicting separation of oxidation products (sulfones, ketones) from residual hydrocarbons in oxidized Cerro Negro 200-425° C neutrals 35

2-2. Partial IR spectrum of fraction 4 from HPLC separation of oxidized Cerro Negro 200-425° C neutrals 37

2-3. Sulfone band area versus total sulfur concentration for selected oxidized fractions 38

2-4. Partial IR spectra of oxidized ADD-1 neutral sulfide (A), neutral nonsulfide (B), and whole neutral (C) fractions. 39

List of Tables

1-1. Separation mass balances (fraction yield, wt% whole asphalt) and sulfur contents of fractions (S, wt% fraction) 12

1-2. Separation mass balance, sulfur and nitrogen contents for Wilmington 650-1000° F distillate (NIPER 1693) 14

1-3. HPLC fractionation of Wilmington 650-1000° F neutral subtypes 14

1-4. Analysis of Wilmington 650-1000° F neutral subfractions (wt% S) 15

1-5. Breakdown of sulfur types in Wilmington 650-1000° F neutrals from various methods (wt% S) 18

1-6. Overall sulfur speciation in Wilmington (CA) 650-1000° F distillate (NIPER 1693) fractions (wt% S) 19

1-7. Sulfur speciation in strong acid fractions (wt% S) 20

1-8. Sulfur speciation in weak acid fractions (wt% S) 22

1-9. Sulfur speciation in strong base fractions (wt% S) 22

1-10. Sulfur speciation in weak base fractions (wt% S) 23

1-11. Sulfur speciation in neutral fractions (wt% S) 23

1-12A. Sulfur speciation in whole asphalts (wt% S) 25

1-12B. Relative distribution of sulfur types in whole asphalts (%) 25

1-13. Concentration of amphoteric molecules containing acidic plus sulfoxide groups (wt% of whole asphalt) 27

1-14. Compounds in strong base fractions containing both basic nitrogen and sulfoxide groups 27

2-1. Results from HPLC separation of Cerro Negro 200-425° C neutrals 34

2-2. Sulfur speciation in neutral fractions (wt% S). Phase I and Phase II data 40

Abstract

The project objectives were to evaluate analytical methods for determination of sulfur compound types in asphalt and to obtain results on asphalts from the SHRP Materials Reference Library. Methods were applied to whole asphalts and fractions obtained through liquid chromatographic (LC) separations. The distribution of sulfur types varied with asphalt source and within fractions (acids, bases, neutrals) from a given asphalt. Sulfur types determined were (method in parenthesis): sulfoxides (infrared (IR)), aliphatic sulfides (tetrabutylammonium periodate oxidation, IR), aromatic sulfides (total sulfides - aliphatic sulfides), and thiophenes (by difference; or direct via oxidation with hydrogen peroxide, IR). Sulfur types present at negligible concentrations in the asphalts tested include thiols, sulfones and sulfonic acids.

Executive Summary

Phase I

Sulfur compound types were determined in asphalts from the SHRP Materials Reference Library. Sulfoxides were determined by infrared spectrophotometry (IR); sulfides were measured via oxidation to sulfoxides with tetrabutylammonium periodate followed by IR; thiophenes were determined by difference (total sulfur minus other types). Compound types were determined in whole asphalts as well as for fractions from each asphalt obtained using nonaqueous ion exchange liquid chromatography (NIELC). Results from the individual NIELC fractions were compared against those for the corresponding whole asphalt. In addition, results from this analysis were compared against those obtained by other workers utilizing X-ray (XANES) techniques.

The neutral fraction from NIELC was further fractionated into saturated hydrocarbon, neutral-aromatic (contains thiophenic sulfur types) and sulfide classes using liquid chromatographic (LC) techniques. The distribution of sulfur types obtained from the LC separation of neutrals was compared with that obtained from the above instrumental methods.

Generally, results from the IR-oxidation techniques were in good agreement with those from LC separations and XANES analysis, except that the latter include aromatic or other sulfide types in with total sulfides, whereas the oxidation-IR approach appears to be specific for aliphatic sulfides, *per se*. Considerable variation of sulfur types within NIELC fractions was observed. Compounds with one or more acidic groups plus a sulfoxide group constitute a significant proportion of the total amphoteric compounds present in most asphalts.

Phase II

A rapid method for determination of total sulfur and major sulfur compound types in asphalt was investigated. It was based on oxidation of total sulfur to sulfones followed by IR measurement

of the sulfones produced. Sulfide versus thiophenic sulfones were sufficiently resolved to enable determination of each type.

Agreement between data from this approach versus the more conventional methods used in Phase I was unsatisfactory. However, it is likely that the procedures could be improved to obtain acceptable results.

This approach requires much lower capital investment and per analysis costs than current methods providing equivalent data. Thus, it is much more amenable to use in quality control of asphalts or related products than alternate analytical techniques.

Significance of the findings

The project objectives were to evaluate analytical methods and to obtain results on asphalts in the SHRP Library. Correlation of results with asphalt performance or process history was outside the project scope.

The distribution of sulfur compound types within the asphalts investigated was in fact found to vary, even between asphalts with nearly the same total sulfur content. Given the known differences in chemical behavior between the various sulfur types, the probability of obtaining a significant correlation between asphalt performance versus concentration of a specific sulfur type is much greater than one versus total sulfur content.

Aliphatic sulfides were found to be more susceptible to oxidation than other forms of sulfur present. Their oxidation to sulfoxide groups affects asphalt properties in the following ways: 1) increases levels of amphoteric species, 2) increases basicity, and 3) potentially increases water solubility, viscosity, and strength of asphalt-asphalt and asphalt-aggregate interactions.

1

Phase I

Introduction

Sulfur is typically the most abundant heteroatom in crude petroleum and petroleum-derived asphalt. However, the sulfur content of crude oil varies significantly with source, from about 0.5 to 7 wt%, and that of asphalt products varies not only with a crude source, but with refining conditions as well.

The greatest impact of sulfur on asphalt properties and performance probably relates to air oxidation of the sulfide forms indigenous to crude oil to various sulfur oxide species. For example, conversion of aliphatic sulfides to the corresponding sulfoxide [RS(O)R], occurs during oxidative aging tests for asphalt.[1,2] Further conversion of aliphatic sulfides to sulfones [$RS(O_2)R$] has been demonstrated in the laboratory using hydrogen peroxide/acetic acid,[2] and quantitative conversion of thiophenic forms of sulfur to sulfones has been achieved with m-chloroperbenzoic acid.[3] Whether or not the latter two, or other relatively severe oxidations occur during normal asphalt manufacturing, application, or weathering processes remains to be seen, but formation of sulfoxides from sulfides readily occurs.

The change in physical properties of sulfides with oxidation is dramatic. For example, methyl sulfide (CH_3SCH_3), is a light (p=0.846 g/mL), water-insoluble, low boiling liquid (bp=36° C); whereas methyl sulfoxide [$CH_3S(O)CH_3$] is a heavy (p=1.48), water miscible liquid boiling at 189° C. With regard to asphalts, the sulfoxide group exhibits a significant interaction with most aggregates which is fairly susceptible to water stripping, in contrast to the negligible adsorption of sulfides onto aggregate.[4,5]

Total sulfur may be determined by any of a number of standard methods. Sulfoxide forms of sulfur are typically determined by infrared spectroscopy (IR),[1,2,4-7] utilizing the intense SO band

at 1030 cm^{-1}. Aliphatic sulfide type sulfur can be measured by a UV method based on iodine complexation,[8-11] by oxidation to sulfoxides followed by IR[10] or gravimetric[3] determination, or potentiometric titration.[10,12] Thiophenic sulfur may be calculated by difference, or measured directly via conversion to sulfones.[3] Thiols are usually determined by titration with silver nitrate;[10] strongly acidic species such as sulfonic acids are typically titrated with base.[13] More recent work has utilized x-ray methods including photoelectron (ESCA, XPS)[14,15] and absorption near edge structure (XANES) spectroscopy.[16-18] These methods can simultaneously determine most or all of the sulfur types listed above, but require elaborate data processing techniques to resolve regions of spectral overlap, and utilize hardware available only at a very few facilities world-wide. An NMR method for determination of thiols and sulfides, via their reduction to thiols, was also reported.[19] Thiols were derivatized with organotin agents and ^{119}Sn NMR was employed for detection of the resulting derivatives.

Recent efforts toward isolation of sulfur compounds have largely utilized liquid chromatographic (LC) techniques. Two main approaches have been used: 1) oxidation of the sample followed by liquid-solid LC separation of the resulting sulfoxides/sulfones, and 2) ligand exchange LC utilizing metals with an affinity for sulfur [e.g. Hg(II), Cu(II), Pd(II)]. Work published up to 1987 has been reviewed elsewhere.[20] Since then, the most significant advance in the oxidation approach has been use of more selective agents for stepwise conversion of sulfides to sulfoxides, followed by oxidation of thiophenes to sulfones.[3] Each product is separated on silica gel and reduced to the parent sulfur type with $LiAlH_4$. Recent work in LC separation of sulfides has employed bonded-phase silica packings loaded with Cu(II) or Pd(II).[20,21] Separation of thiophenic sulfur compounds has been attempted with $PdCl_2$-loaded silica,[20,22-25] or a two dimensional system utilizing Cs-treated silica and Ag(I)-loaded cation exchange columns.[20]

Most of the available methods for separation of sulfur compounds have been evaluated in the authors' laboratory.[20] The approach based on oxidation of total sulfur compounds to sulfones appears to work well on lower boiling fractions, but problems with incomplete conversion of sulfur compounds and unwanted oxidation of aromatic hydrocarbons effectively prevent its application to materials boiling above approximately 550° C.[26,27] Separation of sulfides using a Pd(II) chelate (2-amino-1-cyclopentenedithiocarboxylic acid) bonded to silica appears to be generally applicable.[20] Separation of thiophenic sulfur types is successful only for selected structural configurations.[20,25] Asphalt or other similarly complex, wide boiling range, or high molecular weight materials are clearly beyond the capabilities of available methods for thiophenic types.

The ultimate objective of this work is to obtain analytical methods for determination of sulfur types in asphalt which significantly affect its performance in road paving applications. The methods should be suitable for routine use and have defined limits of precision and accuracy. The initial phase of the work, reported here, evaluated available methods for sulfur compound analysis for suitability in asphalt analysis and compared results among alternate methods. In addition, sulfur compound types were determined over acidic, basic, and neutral components within each asphalt. Nonaqueous ion exchange LC (NIELC)[28,29] was employed for separation of acids, bases, and neutrals. Also, due to the recent interest in amphoteric compounds in asphalt,[30] the proportion of compounds containing one or more acid groups and one sulfoxide group (sulfoxides are weakly basic) was calculated for each asphalt examined.

Experimental Section

Materials

Asphalts were obtained from the Strategic Highway Research Program (SHRP) Materials Reference Library.[31] In addition, a nominal 650-1000° F distillate from a Wilmington, CA, crude was employed for evaluation of the performance of selected methods because of the availability of numerous LC fractions and analytical data from this material.[21,32,33] Solvents were obtained from EM Science (Gibbstown, NJ) and were of high purity, OmniSolve®, grade. Other reagents were obtained from Aldrich (Milwaukee, WI).

LC Separations

Each asphalt was separated into strong acid, weak acid, strong base, weak base and neutral fractions via a previously published NIELC procedure.[28,29] Neutral fractions were further fractionated into polar-neutral, sulfide, neutral-aromatic and saturate fractions after the scheme illustrated in figure 1-1. Polar neutrals are adsorbed onto a silica precolumn placed ahead of the Pd(II) 2-amino-1-cyclopentenedithiocarboxylic acid (ACDA) column used to trap sulfide types. Each of those fractions is recovered via backflushing of the appropriate column. Saturated hydrocarbon and neutral-aromatic fractions are obtained through subsequent separation of the polar/sulfide-free neutrals. Detailed procedures for those separations, including preparation of the Pd(II)-ACDA and dinitroanilinopropyl silica column packings, appear elsewhere.[20,29]

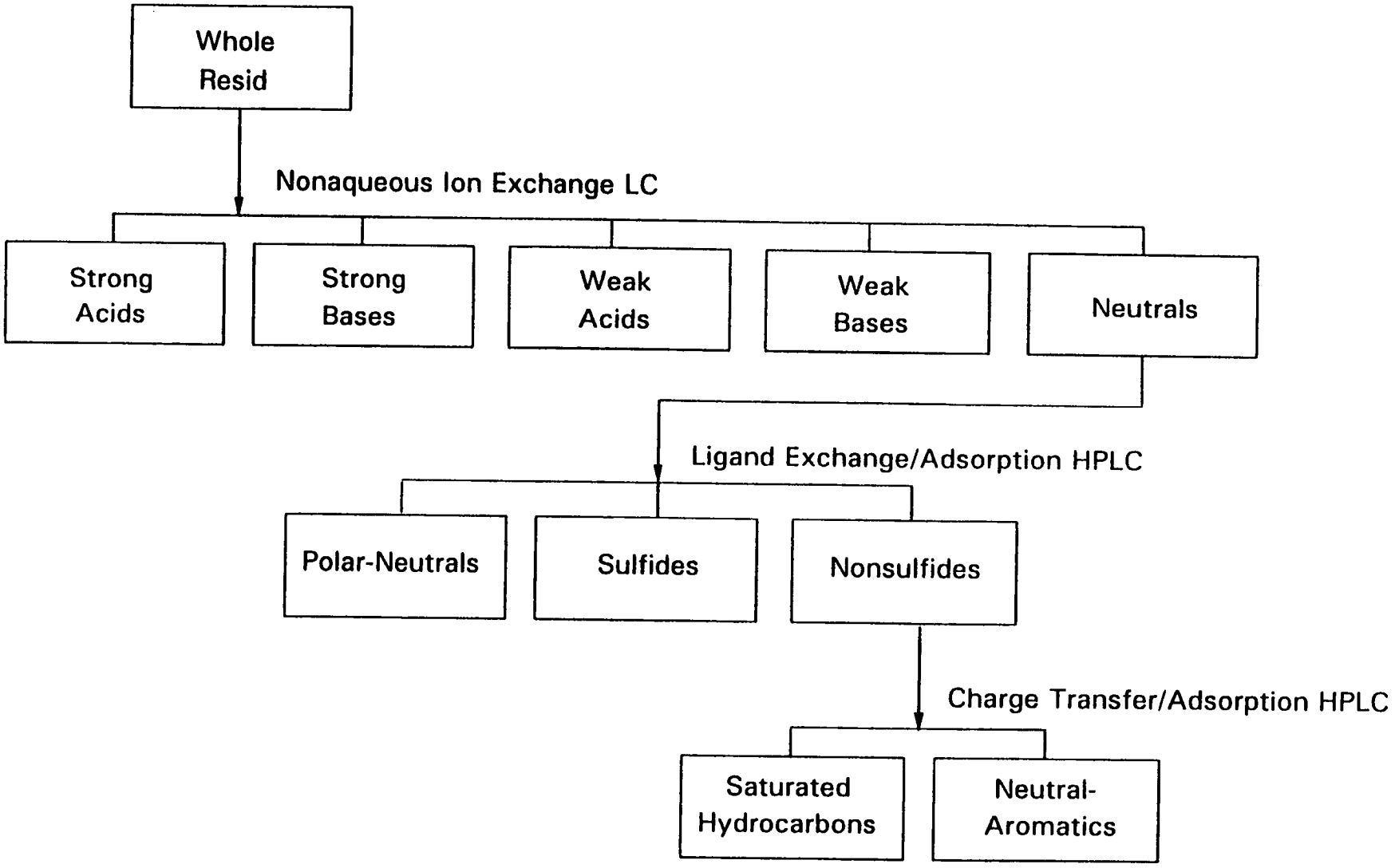

Figure 1-1. Scheme for liquid chromatographic (LC) separation of asphalts.

Sulfoxides were recovered from selected materials using an HPLC procedure developed for subfractionating basic compound types.[21,34-37] With this method, sulfoxides elute well after sulfides, thiophenes or other neutral or weakly polar types. The current version of the method has been described in detail.[37]

Total Sulfur Analysis

The bulk of the total sulfur analyses were performed using a microcoulometric technique (ASTM D 3120). Whole asphalts were also analyzed via combustion followed by IR determination of SO_2 (ASTM D 1552).

Determination of Sulfoxides

Sulfoxides were measured via their maximum IR absorbance near 1030 cm^{-1}. A calibration curve was prepared via dichloromethane dilution of a Wilmington, CA, 700-1000° F weak base fraction previously assayed to contain 81% sulfoxides by weight.[37] The molar absorptivity determined from this curve, 245 L $mole^{-1}$ cm^{-1}, was used to calculate sulfoxides in all asphalts and LC fractions. For comparison, the molar absorptivity of tetramethylene sulfoxide was determined to be 313 L $mole^{-1}$ cm^{-1} in dichloromethane. In the authors' experience, this magnitude of variation between IR absorptivities for a single component versus an actual petroleum fraction is typical. Calibration based on a petroleum fraction is inherently more reliable than use of a pure compound which may be totally nonrepresentative of petroleum-derived species.

All IR measurements were performed with a Perkin-Elmer M283 dual beam (pure dichloromethane reference) dispersive instrument using conventional amalgamated 0.5 mm pathlength KBr liquid sampling cells. Dichloromethane was used to dilute samples to obtain absorbances within the range of 0.04-0.1, which was the optimum range from the standpoint of maximizing signal to noise while remaining within the linear response region. Zero absorbance was defined via baselines drawn manually for each spectrum. Results were expressed as wt% S in the sulfoxide form via the following expression:

$$\text{wt\% S (SO type)} = \frac{32\ A}{abc} \times 100\% \qquad (1$$

A = absorbance

32 = at. wt. S

a = 245 L mole-1 cm-1

b = cell pathlength, cm

c = sample concentration, g/L

IR-oxidation method for determination of aliphatic sulfides

The method employed was based on that of Payzant et al.[3], but with modifications in the quantities of reagents used, and use of IR instead of gravimetric LC methods for product analysis. A known quantity of sample, near 0.2 g, was dissolved into 25 mL toluene plus 5 mL methanol. Then, 0.2 g tetrabutylammonium periodate was added, and the resulting mixture was refluxed for 30 minutes. The reflux apparatus consisted of a 100 mL round bottom flask and a short condenser. The cooled product was extracted three times with about 100 mL high purity water per extraction, rotary evaporated to dryness, and dried an additional 2 hours at 65° C in a vacuum oven. The dried product was dissolved in dichloromethane and its sulfoxide content was measured by IR as described above.

UV determination of aliphatic sulfides via complexation with iodine

This analysis was performed after the procedure of Saetre and Somogyvari.[10] The UV response of aliphatic sulfide sulfur was based on that of 5-thianonane, as specified therein. Its absorptivity was determined to be 517 L $g(S)^{-1}$ cm^{-1}, which compares well with the literature value of 501.[10]

Determination of sulfonic acids and other strongly acidic types

Strong and weak acid fractions were titrated potentiometrically with potassium dimsyl, the potassium salt of dimethyl sulfoxide. Details of the procedure are described elsewhere.[38] Sulfonic acids and other species of similar acidity titrate at half-neutralization potentials from +300 to +200 mV, which is well above those for carboxylic acids (-50 to -150 mV) or other weak acids present. The proportions of acidic groups consisting of sulfonic acids or related types was

determined from the equivalence point attributable to those species divided by the total neutralization equivalent for all acidic groups. The latter quantity was also used to calculate the equivalent weight for each acid fraction.

Determination of thiols

IR was employed to screen for presence of significant quantities of SH groups in either strong or weak acid fractions. The SH stretching band generally occurs in the range from 2600 to 2400 cm^{-1}. In addition, whole asphalts were analyzed for total mercaptans via UOP method 163.[39]

Determination of sulfoxides by titration with perchloric acid

Strong and weak base fractions were titrated with dilute perchloric acid as described elsewhere.[37] The second equivalence point obtained whenever a 1:2 mixture of toluene:acetic anhydride is used for sample dissolution can be used to estimate sulfoxide content. However, selected weakly basic nitrogen compounds may interfere.

Thiophenic sulfur types

Thiophenic sulfur was usually calculated as the difference between total sulfur and all other types. Where possible, it was also determined directly from the sulfur content of the neutral-aromatic fraction (yield of neutral-aromatics multiplied by their sulfur content).

Results and Discussion

LC separations and sulfur balance

Table 1-1 summarizes mass balances from the NIELC separation of whole asphalts and the additional LC fractionation of neutral subtypes. Sulfur contents of fractions are also indicated in the table. Recoveries from the NIELC separation ranged from 96.3 - 100.6 wt %. Relative recovery of

Table 1-1. - Separation Mass Balances (fraction yield, wt% whole asphalt) and Sulfur Contents of Fractions (S, wt% fraction)

Sample No.	AAA-1		AAD-1		AAG-1		AAK-1	
Origin	Lloydminster		CA Coastal		CA Valley		Boscan	
	Yield	S	Yield	S	Yield	S	Yield	S
Whole Asphalt	100	4.04	100	5.29	100	0.85	100	4.81
		(4.6)[a]		(5.9)		(1.0)		(5.6)
Strong Acids	14.8	4.91	18.1	4.88	16.3	0.78	16.7	4.73
Weak Acids	7.4	3.82	12.6	4.29	13.4	0.61	9.5	3.95
Strong Bases	8.1	5.06	14.2	5.70	12.8	0.76	12.1	5.04
Weak Bases	2.2	5.47	5.2	7.52	4.0	1.03	3.4	5.28
Neutrals	63.9	4.01	50.5	5.50	53.5	1.17	54.6	4.86
Polar-neutrals	7.1	7.77	5.8	9.09	3.0	2.80	5.9	6.32
Sulfides	10.4	7.32	10.4	7.71	5.8	4.65	10.3	7.17
Saturates	12.8	0.02	11.6	0.02	12.7	0.01	4.3	0.04
Neutral-aromatics	29.6	4.28	24.9	3.61	32.5	0.83	32.6	4.24
Total, Neutral Subtypes	59.9	4.31	52.7	4.23	54.0	1.15	53.1	4.70
Total, Acids & Bases & Neutrals	96.4	4.26	100.6	5.37	100.0	0.97	96.3	4.79

[a] Data in parentheses measured using an alternate technique (D 1552).

neutral subtypes (compared with whole neutrals) was similar. The mass balance data in Table 1-1 correspond reasonably well with those published by Branthaver, et al.[40] In general, yields of strong base fractions reported here are higher than those of Branthaver, et al., but the present weak base yields are proportionately lower to provide an overall base content which agrees well with their data. The situation with acid fraction yields is similar to that of base yields; yields of neutrals correspond closely. Results for sulfur content show that, except for the saturated hydrocarbon fraction which is essentially sulfur-free, sulfur is widely distributed throughout all compound classes. Relative recovery of sulfur over the separations was comparable to that of total mass, except that recovery of AAD-1 sulfur over the neutral subtypes was notably low. As evident in the table, asphalt AAG-1 and its fractions contain much lower levels of sulfur than any of the others selected.

Preliminary evaluation of analytical methods

Table 1-2 lists separation data as well as sulfur and nitrogen contents of fractions from the Wilmington 650-1000° F distillate used as a test sample in preliminary evaluations of sulfur analysis methods. Unlike the asphalts, both the acid and base fractions from the Wilmington distillate are deficient in sulfur relative to either the whole distillate or neutral fraction. Nitrogen is highly enriched in the acid and base fractions.

Table 1-3 shows results from HPLC subfractionation of neat polar-neutral and sulfide fractions from Wilmington, as well as for the sulfide fraction after oxidation with tetrabutylammonium periodate. As indicated in the table, sulfoxides are the predominant sulfur type in the polar-neutral fraction, whereas sulfides predominate in the sulfide fraction. Oxidation converts a substantial quantity of sulfides to sulfoxides. Compounds listed as "other" do contain some sulfur, but are predominantly carbonyl oxygen and nitrogen types. The very modest increase in this category for the oxidized versus neat sulfide fractions indicates minimal formation of side products from the periodate oxidation.

Table 1-4 compares analytical results for HPLC subfractions in Table 1-3 with those for whole sulfide and polar-neutral fractions listed in Table 1-2. In addition, results from different analytical methods are listed. Assays of the sulfide fraction for aliphatic sulfide forms of sulfur indicated a range of 4.11 to 4.96 wt % S, depending on the method employed. The balance of the sulfur in that fraction is assumed to be aromatic sulfide (Ar-S-R or Ar-S-Ar) types. The relatively small proportion of sulfoxide sulfur present in the sulfide fraction (0.44 wt % S)

Table 1-2. Separation Mass Balance, Sulfur and Nitrogen Contents for Wilmington 650-1000°F Distillate (NIPER 1693)

Fraction	Yield, wt% distillate	S, wt% fraction	N, wt% fraction
Whole distillate	-	1.97	0.50
Acids	10.4	0.94	2.14
Bases	4.7	1.40	3.90
Neutrals	85.4	2.05	0.093
Polar-neutrals	2.6	4.9	0.16
Sulfides	12.9	7.5	0.12
Nonsulfides	69.8	0.95	0.064
Total, Neutral Subtypes	85.3	2.06	0.075
Total, Acids & Bases & Neutrals	100.5	1.91	0.48

Table 1-3. HPLC Fractionation of Wilmington 650-1000°F Neutral Subtypes

	Normalized Yield, wt% Starting Material		
Starting Material	Sulfides	Sulfoxides	Other
Polar-neutrals	8.9(PN1)[a]	84.0(PN2)	7.1(PN3)
Sulfides	85.0(SUL1)	7.2(SUL2)	7.8(SUL3)
Oxidized Sulfides	44.8(OXS1)	46.6(OXS2)	8.6(OXS3)

[a] Fraction designations shown in parentheses.

Table 1-4. Analysis of Wilmington 650-1000°F Neutral Subfractions (wt% S)

Fraction	Total	Aliphatic Sulfide IR-ox	Aliphatic Sulfide HPLC	Aliphatic Sulfide UV	Sulfoxide	Aromatic Sulfide
Sulfides	7.5	4.96±0.09[a]	4.11	4.35±0.25	0.44±0.05	2.1
Polar-neutrals	4.9	-	0.51	0.55±0.01	4.47	ND[b]
SUL1	7.6	5.40	-	4.18±0.08	ND 2.2	
SUL2	6.7	-	-	-	6.22	-
OXS2	7.6	-	-	-	7.53	-
PN2	6.9	-	-	0.84±0.07	6.60	-
OXS1	6.6	2.36	-	2.04	ND4.2	

[a] Uncertainties shown are average deviations from duplicate determinations.
[b] None detected.

probably reflects air oxidation of aliphatic sulfides during storage of this fraction, which was prepared in 1987. Analysis of the purified sulfide subfraction (SUL1, Table 1-4) yielded results similar to that of the whole sulfides.

Consistent with HPLC data in Table 1-3, IR shows the bulk of the polar-neutral sulfur to be present in the sulfoxide form. The residual sulfides present in the polar-neutrals (0.5 wt % S) may reflect chromatographic overlap during the LC separation, or presence of sulfides containing other polar functional groups which would have caused them to partition into the polar-neutral, rather than into the sulfide fraction. Sulfur present in the three sulfoxide concentrates isolated by HPLC (SUL2, OXS2, PN2) consists almost entirely of sulfoxide type.

A substantial proportion (>2 wt % S) of sulfides left over from the initial oxidation of the sulfide fraction (OXS1) were found to be of aliphatic sulfide type upon reoxidation and subsequent IR analysis. This finding led to modification of the procedure of Payzant, et al.,[3] which was followed verbatim in this case, to the modified one recommended in the Experimental Section. The modified procedure was applied in all subsequent work, including the analysis of asphalts reported below.

Comparison of IR-determined sulfoxide S versus total S present in sulfoxide concentrates revealed very good agreement in all cases (SUL2, OXS2, PN2). This observation provides a high degree of confidence in the IR response factor employed here for sulfoxide determinations,

as well as in the overall method itself. The combination of tetrabutylammonium periodate oxidation followed by IR determination of sulfoxides generally yielded higher results for aliphatic sulfides than the UV method. Since the probable error lies toward obtaining low results with either method, the IR-oxidation data are believed to be the more accurate. A major source of inaccuracy in the UV method is very likely its reliance on the response of 5-thianonane as being representative of that for all aliphatic sulfides in petroleum. The HPLC result for aliphatic sulfides listed in Table 1-4 is known to be too low because of the previously mentioned incomplete oxidation obtained with the preliminary procedure employed.

The UV method for determination of aliphatic sulfides was dropped from further consideration because of the following factors: 1) the unavailability of a petroleum-derived aliphatic sulfide fraction for use as a calibration standard, 2) the rapid change in absorbance of the I_2-sulfide complex with time, which necessitated careful timing of all mixing and measuring operations, 3) the tedious nature of the method, especially with regard to correcting for reagent and sample-related blanks, and 4) the high probability of interference from nitrogen compounds or other types capable of complexation with iodine, which limits its application to nonpolar samples (neutral fractions).

On the other hand, the IR-oxidation procedure has the following positive features: 1) ease in obtaining petroleum-derived sulfoxide concentrates for use in IR calibration, 2) stability of sulfoxide products with time, 3) decreased structural dependence of IR response compared to UV response, 4) lack of spectral interferences, and 5) relatively low analysis time required (1-2 man-hours).

The Pd(II)-ACDA LC separation method enables determination of additional sulfide types, believed to be largely aromatic sulfides, which are not detected by either the IR-oxidation or UV methods. However, alkyl phenyl disulfides, such as those identified in Wilmington, CA, crude oil,[24] or other unknown sulfide/disulfide types may also be included in this category. Thus, although the difference between total (LC) versus aliphatic sulfides (IR-oxidation or UV) is referred to simply as "aromatic sulfides" in Table 1-4 and subsequent tables, the potential inclusion of alternate sulfide/disulfide types should be kept in mind. In addition, the possibility that nonsulfide sulfur compound types, including thiophenic species, potentially contribute to the Pd(II)-ACDA sulfide yield cannot be ruled out from the present data. However, as discussed later in connection with results on asphalts, correlation between total sulfides from the Pd(II)-ACDA method correlated well with those from the XANES technique.

Table 1-5 expresses data provided in Table 1-4 and elsewhere on a whole neutrals basis to provide a quantitative breakdown of the Wilmington 650-1000° F neutrals. Table 1-6 combines average results for neutrals in Table 1-5 with those for other fractions to provide a summary of sulfur compound types in the whole distillate. As shown in Table 1-5, results obtained from analysis of the whole neutrals are generally consistent with those calculated from neutral subfractions. Also, results from the various analytical methods agree acceptably well.

The proportion of sulfur present as sulfides exceeds thiophenic forms in the case of neutral fraction; but, the two types are approximately equivalent in the whole distillate. On the other hand, thiophenic sulfur predominates in the acid fraction, but is essentially absent in the bases, thereby demonstrating a distinctly different sulfur compound distribution in each general compound class. Overall results for sulfoxide and total sulfide types calculated over the acid, base and neutral fractions are somewhat higher than those from direct analysis of the whole distillate. The bulk of the discrepancy in total sulfide results is derived in turn from the higher level of sulfoxides calculated from analysis of the LC fractions. Sulfoxides are included in the total sulfide balance on the premise that they are derived via oxidation of sulfides during storage and handling.[6,7]

The performances of the IR method for determination of sulfoxides, IR-oxidation procedure for aliphatic sulfides, and PD(II)-ACDA separation of total sulfides on the Wilmington distillate were judged to be sufficient to warrant their extension to asphalt.

Analysis of asphalt fractions

Table 1-7 shows absolute (wt% S in a given form) and relative (percent of sulfur present) distributions of sulfur types in the asphalt strong acid fractions. Given the absence of detectable levels of thiol (SH) and sulfonic (SO_3H) or other strongly acidic groups, the bulk of the sulfur must be contained within the hydrocarbon skeleton of each fraction. As was found for the Wilmington total acid fraction, thiophenic or other nonoxidizable forms of sulfur predominate in all of the asphalt strong acid concentrates. Only the CA Coastal asphalt fraction (AAD-1) contains aliphatic sulfide forms of sulfur in excess of 1 wt % S. It should be noted that in the case of strong acid and other acid/base fractions in subsequent tables, thiophenic and aromatic sulfide sulfur types are lumped together, since they are calculated as the difference between total sulfur and measured sulfur types.

Table 1-5. Breakdown of Sulfur Types in Wilmington 650-1000°F Neutrals From Various Methods (wt% S)

Parameter	Results	Methodology/Fraction
Sulfoxide	0.28	IR/whole neutrals
	0.20	Polar-neutrals + IR/sulfides
	0.24±0.04[a]	Average of all methods
Aliphatic Sulfide	0.65±0.03	IR-ox/whole neutrals
	0.75±0.02	IR-ox/whole sulfides
	0.62	IR-ox/(OXS1) + (OXS2) - (PN2)
	0.66±0.04	UV analysis/whole sulfides
	0.67±0.04	Average of all methods
Aromatic Sulfide	0.31	Whole sulfides - IR-ox/whole sulfides
	0.29	IR-ox/OXS1
	0.28	IR-ox/SUL1
	0.29±0.02	Average of all methods
Total (sulfide + sulfoxide)	1.20±0.10	Sum of averages
Thiophenic	0.85	Total S - Total (sulfide + sulfoxide)

[a] Uncertainties shown are average deviations.

Table 1-6. Overall Sulfur Speciation in Wilmington (CA) 650-1000°F Distillate (NIPER 1693) Fractions (wt% S)

Fraction	Acids	Bases	Neutrals[a]	Whole	
				Direct	Calculated
Sulfoxide	0.22	1.22	0.24±0.04	0.13±0.01	0.28
Aliphatic Sulfide	ND[b]	0.25	0.67±0.04	0.54±0.01	0.58
Aromatic Sulfide	-	ND	0.29±0.02	-	0.25
Total Sulfide Types	0.22	1.47	1.20±0.10	0.92±0.01[c]	1.11
Thiophenic	0.72	ND	0.85	1.05	0.86
Total S	0.94	1.40	2.05	1.97	1.97

[a] From table V.
[b] None detected.
[c] The result for aromatic sulfide calculated from the fractions was included in this subtotal.

Table 1-7. - Sulfur Speciation in Strong Acid Fractions (wt% S)

Sample No.	AAA-1		AAD-1		AAG-1		AAK-1	
Sulfonic Acid (RSO_3H)	ND[a]	(ND)[b]	ND	(ND)	ND	(ND)	ND	(ND)
Sulfoxide (R_2SO)	0.19	(4)	0.48	(10)	0.23	(29)	0.23	(5)
Aliphatic Sulfide (R_2S)	0.40	(8)	1.28	(26)	ND	(ND)	0.22	(5)
$R_2S + R_2SO$	0.59	(12)	1.76	(36)	0.23	(29)	0.45	(10)
Thiophenic + Aromatic Sulfide	4.32	(88)	3.12	(64)	0.55	(71)	4.28	(90)
Thiol (RSH)	ND	(ND)	ND	(ND)	ND	(ND)	ND	(ND)
Total S	4.91	(100)	4.88	(100)	0.78	(100)	4.73	(100)

[a] None detected.
[b] Data in parentheses refer to the relative distribution of sulfur types.

Table 1-8 indicates sulfur speciation in weak acid fractions. As with strong acids, a predominance of thiophenic sulfur forms was typically observed. However, in the case of AAG-1 weak acids, sulfoxides were the major sulfur type; yet, the absolute concentrations of all sulfur species were quite low in that fraction.

Table 1-9 shows sulfur type distributions in strong base fractions. Unlike the Wilmington bases (Table 1-6) the asphalt strong base fractions contain major quantities of thiophenic forms of sulfur.

Table 1-10 lists sulfur type distributions for weak base fractions. Variations in distributions of sulfur types between asphalts are greater for this fraction than others cited above. A prevalence of sulfoxide sulfur, such as that observed in AAD-1 weak bases, is common for this fraction since sulfoxides present in the original whole material typically partition into this fraction during the NIELC separation process.[37] Owing to the anticipated abundance of sulfoxides in this fraction, an alternate method (besides IR) was attempted for their determination. However, as indicated in the table, titration with perchloric acid generally over-estimates sulfoxides, even when they are quite prevalent, because of interference from weakly basic nitrogen compounds. Thus, this technique was judged to be unsatisfactory for sulfoxide determinations.

Table 1-11 provides sulfur distributions for asphalt neutrals. Since the Pd(II)-ACDA technique for separation of total sulfides was applied to the neutrals, aromatic sulfides could be calculated separately in this case instead of being lumped in with thiophenes, as done in Tables 1-7 through 1-10. Also, since the yields of neutral-aromatics and their sulfur contents were known, the concentration of thiophenic sulfur could be calculated directly from those parameters.

IR versus LC measurements of sulfoxide contents differed significantly for AAA-1 and AAK-1. This difference is attributed to oxidation of aliphatic sulfides to sulfoxides during separation and handling of those two samples. Apparently, the aliphatic sulfides contained therein are quite susceptible to air oxidation. The concentrations of thiophenic sulfur calculated from the neutral-aromatic fractions agreed well with those calculated by difference in all cases except for asphalt AAD-1. As noted earlier in conjunction with Table 1-1, a significant proportion of sulfur was not recovered during LC separation of subtypes from the AAD-1 neutrals. Since the sulfur content of the neutral-aromatic fraction obtained from AAD-1 appears disproportionately low compared to that of the whole neutrals, the thiophene content calculated by difference is believed to be the more reliable estimate in that case.

Table 1-8. - Sulfur Speciation in Weak Acid Fractions (wt% S)

Sample No.	AAA-1		AAD-1		AAG-1		AAK-1	
Sulfoxide (R_2SO)	0.49	(13)[b]	0.83	(19)	0.38	(64)	0.73	(18)
Aliphatic Sulfide (R_2S)	0.50	(13)	0.45	(11)	ND[a]	(ND)	0.28	(7)
$R_2S + R_2SO$	0.99	(26)	1.28	(30)	0.38	(64)	1.01	(25)
Thiophenic + Aromatic Sulfide	2.83	(74)	3.01	(70)	0.23	(36)	2.94	(75)
Total S	3.82	(100)	4.29	(100)	0.61	(100)	3.95	(100)

[a] None detected.
[b] Data in parentheses refer to the relative distribution of sulfur types.

Table 1-9. - Sulfur Speciation in Strong Base Fractions (wt% S)

Sample No.	AAA-1		AAD-1		AAG-1		AAK-1	
Sulfoxide (R_2SO)	0.59	(12)[b]	0.92	(16)	0.37	(49)	0.39	(8)
Aliphatic Sulfide (R_2S)	0.65	(13)	1.13	(20)	ND[a]	(ND)	0.54	(11)
$R_2S + R_2SO$	1.24	(25)	2.05	(36)	0.37	(49)	0.93	(19)
Thiophenic + Aromatic Sulfide	3.82	(75)	3.65	(64)	0.39	(51)	4.11	(81)
Total S	5.06	(100)	5.70	(100)	0.76	(100)	5.04	(100)

[a] None detected.
[b] Data in parentheses refer to the relative distribution of sulfur types.

Table 1-10. - Sulfur Speciation in Weak Base Fractions (wt% S)

Sample No.	AAA-1		AAD-1		AAG-1		AAK-1	
Sulfoxide[a] (R_2SO)	1.12	(20)[c]	4.34	(58)	0.60	(58)	1.19	(22)
Sulfoxide[b] (R_2SO)	2.18		4.74		1.13		1.92	
Aliphatic Sulfide (R_2S)	1.13	(21)	1.73	(23)	ND[d]	(ND)	1.99	(38)
$R_2S + R_2SO$[a]	2.25	(41)	6.07	(81)	0.60	(58)	3.18	(60)
Thiophenic + other	3.22	(59)	1.45	(19)	0.43	(42)	2.10	(40)
Total S	5.47	(100)	7.52	(100)	1.03	(100)	5.28	(100)

[a] From IR.
[b] From titration with $HClO_4$.
[c] Data in parentheses refer to the relative distribution of sulfur types.
[d] None detected.

Table 1-11. - Sulfur Speciation in Neutral Fractions (wt% S)

Sample No.	AAA-1		AAD-1		AAG-1		AAK-1	
Sulfoxide[a] (R_2SO)	0.34	(8)	0.64	(12)	0.25	(21)	0.27	(6)
Sulfoxide[b] (R_2SO)	0.92		0.69		0.16		0.70	
Aliphatic Sulfide (R_2S)	0.45	(11)	1.00	(18)	0.19	(16)	1.76	(36)
Aromatic Sulfide	1.40	(35)	0.63	(11)	0.22	(19)	0.06	(1)
Total Sulfide Types[c]	2.19	(54)	2.27	(41)	0.66	(56)	2.09	(43)
Thiophenic[d]	1.82	(46)	3.23	(59)	0.51	(44)	2.77	(57)
Thiophenic[e]	1.98		1.78		0.50		2.53	
Total S	4.01	(100)	5.50	(100)	1.17	(100)	4.86	(100)

[a] From IR.
[b] From LC (yield of polar neutrals x sulfur content of polar neutrals).
[c] Sulfoxide (IR) + aliphatic sulfide + aromatic sulfide.
[d] By difference.
[e] From LC (yield of neutral-aromatics x sulfur content of neutral-aromatics).
[f] Data in parentheses refer to the relative distribution of sulfur types.

Neutral sulfur is split approximately 50/50 between sulfide and thiophenic forms for all asphalts. However, considerable variation among sulfide subtypes (sulfoxide, aliphatic sulfide, aromatic sulfide) was observed. Detailed evaluation of thiophenic subtypes (benzothiophenes, dibenzothiophenes, etc.) may reveal a similar disparity between asphalts for that family of compounds as well. Of particular interest is the high concentration of aromatic sulfides in AAA-1 versus their virtual absence in AAK-1. The comparable sulfur contents (Table 1-1) of sulfide fractions from those two asphalts suggests that AAA-1 contained aromatic sulfides, rather than disulfides or other polysulfur species, since the latter would increase the sulfur content of the sulfide fraction appreciably.

Table 1-12A summarizes directly determined data as well as results calculated over LC fractions for whole asphalts. Table 1-12B shows data from 1-12A converted to a relative basis and compares them with results obtained at the University of Kentucky using the XANES technique.[41] Direct versus calculated data from the present work generally corresponded well. However, partial conversion of aliphatic sulfides to sulfoxides over the course of LC fractionation was indicated by generally higher calculated sulfoxide concentrations, coupled with a corresponding decrease in calculated levels of aliphatic sulfides. Agreement between relative sulfur types determined here compared to those obtained by XANES is generally quite satisfactory. The largest discrepancy in data occurred with sample AAG-1, which contained the least sulfur, by far, of the asphalts investigated. The XANES technique did not detect sulfoxides in whole as-received asphalts, except for AAG-1; whereas, a minimum of 3.4 % of sulfur present was classified as sulfoxide type in the present work. Because of the curve fitting and data manipulation required in the XANES analysis, it probably has difficulty in detecting lower levels of selected sulfur types.

The results in Tables 1-12A and 1-12B and the preceding tables demonstrate the viability of the IR method for determination of sulfoxides, the IR-oxidation method for aliphatic sulfides, and the Pd(II)-ACDA method for separation of total sulfides in asphalts. One limitation of the present scheme is the restricted applicability of the Pd(II)-ACDA separation method to neutral species. This prevents calculation of aromatic sulfide types in acid or base fractions, which in turn may lead to a low estimate for this type in whole asphalts. Another is the necessity of calculating thiophenic types by difference in most cases.

Table 1-12A. - Sulfur Speciation in Whole Asphalts (wt% S)

Sample No.	AAA-1		AAD-1		AAG-1		AAK-1	
	Direct	Calc.	Direct	Calc.	Direct	Calc.	Direct	Calc.
Sulfonic Acid	-	ND[a]	-	ND	-	ND	-	ND
Thiol	ND[b]	ND	0.014	ND	ND	ND	ND	ND
Sulfoxide	0.22	0.37	0.18	0.87	0.26	0.31	0.18	0.36
Aliphatic Sulfide	0.57	0.48	1.71	1.03	0.15	0.09	1.15	1.20
Aromatic Sulfide	-	0.93	-	0.32	-	0.12	-	0.03
Total Sulfide Types[c]	1.72[d]	1.78	2.21	2.22	0.53	0.52	1.36	1.59
Thiophenic	2.54	2.48	3.16	3.15	0.44	0.45	3.43	3.20
Total S	4.26	4.26	5.37	5.37	0.97	0.97	4.79	4.79

[a] None detected.
[b] Via UOP Method 163.
[c] Sulfoxide + aliphatic sulfide + aromatic sulfide.
[d] Calculated result for aromatic sulfide included in Direct subtotal for total sulfide types.

Table 1-12B. - Relative Distribution of Sulfur Types in Whole Asphalts (%)

Sample No.	AAA-1				AAD-1				AAG-1				AAK-1			
	This work		XANES[e]		This work		XANES		This work		XANES		This work		XANES	
	Direct	Calc.	Neat	Ox.	Direct	Calc.	Neat	Ox.	Direct	Calc.	Neat	Ox.	Direct	Calc.	Neat	Ox.
Sulfonic Acid	-	ND[a]	ND	ND	-	ND	ND	-	-	ND	ND	ND	-	ND	ND	ND
Thiol	ND[b]	ND	ND	ND	0.26	ND	ND	-	ND	ND	ND	ND	ND	ND	ND	ND
Sulfoxide	5.2	8.7	ND	6	3.4	16	ND	-	27	32	8	25	3.8	7.5	ND	7
Aliphatic Sulfide	13	11	}40	}27	32	19	}46	}-		15	9	}33	}15	24	25	}36	}31
Aromatic Sulfide	-	22			-	6.0				-	12			-	0.6		
Total Sulfide Types[c]	40[d]	42	40	33	41	41	46	-		54	53	41	40	28	33	36	38
Thiophenic	60	58	60	67	59	59	54	-		46	47	59	60	72	67	64	62

[a] None detected.
[b] Via UOP Method 163.
[c] Sulfoxide + aliphatic sulfide + aromatic sulfide.
[d] Calculated result for aromatic sulfide included in direct subtotal for total sulfide types.
[e] From reference 41. Ox. = air oxidized sample.

Oxidizable sulfur in asphalt

One advantage of the IR and IR-oxidation procedures is that they measure sulfide species which have already oxidized to sulfoxides as well as those which could easily oxidize, respectively. In other words, they determine reactive sulfur types. The ready conversion of aliphatic sulfides to sulfoxides is demonstrated from the significant occurrence here during LC fractionation and workup, as well as from the XANES analysis of oxidized asphalts (Table 1-12B).

Asphalts AAD-1 and AAK-1 contain significantly higher absolute levels of oxidizable (see results for aliphatic sulfide, Table 1-12A) sulfur than the other two asphalts; that in AAD-1 appears to be the most easily converted, based on the observed high degree of conversion during LC separation. Surprisingly, air oxidation appears to be generally less efficient at converting sulfides to sulfoxides than simply subjecting asphalt to LC separations.

Oxidizable (aliphatic sulfide) sulfur in acidic fractions was of particular interest since introduction of a sulfoxide group (weakly basic) onto a molecule possessing one or more acidic groups creates an amphoteric species. As mentioned in the Introduction, the latter have been identified as particularly important constituents of asphalt in other SHRP-supported research projects. Table 1-13 shows results of calculations of acidic-sulfoxide type amphoterics in strong and weak acid fractions. The equivalent weight of each fraction, determined by titration with potassium dimsyl, was employed in the respective calculations. As indicated in the table, asphalt AAD-1 contains the greatest existing and potential concentrations of this compound type.

Prior work by Plancher, et al.,[4] indicated that sulfoxide-aggregate bonds were more susceptible to water displacement that those involving nitrogen compounds. In this vein, the proportion of compounds in strong base fractions, which are comprised largely of nitrogen bases, containing a sulfoxide group in addition to a nitrogen atom was calculated. Furthermore, the proportion of strong bases containing sulfoxide groups after conversion of aliphatic sulfides to sulfoxides was also determined. These data are summarized in Table 1-14.

Table 1-13 Concentration of Amphoteric Molecules containing Acidic Plus Sulfoxide Groups (wt% of Whole Asphalt)

Sample No.	AAA-1	AAD-1	AAG-1	AAK-1
Equivalent wt (g/equ)[a]				
Strong Acids	840	515	417	877
Weak Acids	641	654	529	621
Amphoterics (wt%)				
As received				
Strong Acids	0.74	1.4	0.49	1.0
Weak Acids	0.74	2.1	0.94	1.3
Total	1.5	3.5	1.4	2.3
Fully Oxidized				
Strong Acids	2.4	5.1	0.49	2.0
Weak Acids	1.5	3.3	0.94	1.8
Total	3.9	8.4	1.4	3.8

[a] From titration with potassium dimsyl.

Table 1-14. Compounds in Strong Base Fractions Containing Both Basic Nitrogen and Sulfoxide Groups

Sample No.	AAA-1	AAD-1	AAG-1	AAK-1
Equivalent wt (g/equ)[a]	1225	1140	770	1285
N-S(O) Compounds (wt% Whole Asphalt)				
As-received	1.9	4.7	1.2	1.9
Fully Oxidized	3.8	10.4	1.2	4.5
Percent Strong Bases Containing an S(O) Group				
As-received	23	33	9	16
Fully Oxidized	47	73	9	37

[a] From titration with perchloric acid in acetic anhydride.

Compounds containing both a basic nitrogen and sulfoxide group are most prevalent in asphalt AAD-1, but significant in all except perhaps sample AAG-1. Reconciliation of the data in the table with those of Plancher, et al., suggests that the bulk of the sulfoxides removed via water displacement are probably those within the neutral fraction which lack other polar functionalities to enhance adhesion to aggregate in the presence of water.

Correlation of sulfur type distributions with asphalt performance

Oxidation of sulfides to sulfoxides would be expected to increase asphalt hardness/viscosity, and to increase the concentration of amphoteric species. It would also potentially increase susceptibility to water stripping and strength of asphalt-aggregate adhesion.

CA Coastal (AAD-1) and Boscan (AAK-1) asphalts are perceived to perform poorly with respect to one or more types of pavement distress.[31] In this work, these asphalts were determined to contain significantly higher concentrations of aliphatic sulfide (oxidizable) type sulfur than the other two asphalts, which generally have good performance histories. Thus, a negative correlation of performance with oxidizable sulfur content is indicated.

Conclusions and Recommendations

The IR method for determination of sulfoxides, IR-oxidation method for aliphatic sulfides, and Pd(II)-ACDA LC method for separation of total sulfides performed well in this initial evaluation. The IR and IR-oxidation analysis methods are suitable for routine use on whole asphalts. Comparable methods for determination of aromatic sulfides and thiophenic forms of sulfur should be developed. The m-chloroperbenzoic acid oxidation suggested by Payzant, et al.,[3] should certainly be evaluated for its suitability towards converting the above to sulfones or other species suitable for spectroscopic measurement. The LC methods utilized here can be used to provide fractions for development of further oxidation procedures and to check the accuracy of results.

The best assurance of accuracy of any of the reported data comes from agreement in results from independent methods. For example, acceptable agreement was obtained between IR-oxidation and iodine-complexation UV methods for aliphatic sulfides in the Wilmington distillate (the ratio of UV/IR was typically 0.9) Also, IR estimates of sulfoxide concentrations corresponded well

with results obtained from HPLC subfractionation of Wilmington neutral subtypes. Relative proportions of sulfide versus thiophenic types of sulfur from the XANES analysis typically agreed within five percent of the data on asphalts obtained from this work, which is within the estimated precision for either approach. Comparison of results on a wider range of samples would be useful toward further definition of the limits of accuracy, sensitivity, and precision of each method.

The oxidized (sulfoxides) and oxidizable (aliphatic sulfides) sulfur probably impact asphalt performance to a much greater extent than the more inert forms (aromatic sulfides, thiophenes). From the very limited data available, a negative correlation of oxidized plus oxidizable sulfur with asphalt performance is suggested. Considerable variation in concentrations of these forms of sulfur occurs even among asphalts with similar total sulfur contents.

Analysis of LC fractions provides fairly detailed information on the distribution of sulfur types as a function of compound class (acidic, basic, or neutral) and on the nature of multifunctional species (e.g., amphoteric compounds, nitrogen bases containing sulfoxide groups). This information should be carefully evaluated in regard to obtaining correlations with physical properties and performance of asphalts. Extension of the complete analysis scheme to additional asphalts is recommended.

The asphalts examined here contain negligible quantities of thiol, sulfonic acid, or sulfone types of sulfur. Unless asphalts have received unusual treatment which could result in formation of any of these types, analysis for these species should receive only limited consideration in future work.

The four asphalt samples analyzed exhibit distinctly different sulfur compound type distributions. The Lloydminster asphalt (AAA-1) contains unusually high levels of aromatic sulfides, but only moderate levels of oxidizable sulfur. The CA Coastal asphalt (AAD-1) contains the highest level of oxidizable sulfur, and exhibits the highest potential for forming amphoterics and nitrogen compounds containing sulfoxide groups. It is also the only asphalt with detectable levels of thiols. The CA Valley asphalt (AAG-1) contains the highest proportion of oxidizable sulfur, but the lowest absolute concentration due to its low total sulfur content. The Boscan (AAK-1) asphalt possesses a high concentration of potentially oxidizable sulfur, but low conversions to oxidized forms were observed during either LC separations or air oxidation. Apparently, the aliphatic sulfides contained therein are slow to convert to sulfoxides under those conditions. Also, the level of aromatic sulfides in Boscan is extremely low; it is even lower than

that of the CA Valley asphalt, which contains only one percent total sulfur compared to over five percent in Boscan.

2

Phase II. Direct Determination of Thiophenic Sulfur

Introduction

As noted in the Phase I Section of this report, a major deficiency in existing methodology for determination of sulfur types in asphalt is the lack of a convenient method for direct measurement of thiophenic sulfur. Work in Phase II of this project addresses this need by attempting to combine existing procedures for converting thiophenic sulfur to sulfone type with infrared (IR) techniques for measuring the resulting sulfones, in order to obtain a direct result for thiophenic sulfur. The apparatus required in these procedures is relatively simple and available in most laboratories. The time and effort needed to carryout the oxidation is minimal. Therefore, the approach is suitable for routine analysis. The data obtained for whole asphalts and liquid chromatographic (LC) fractions thereof in Phase I provide an excellent basis for evaluating prospective methods for determination of thiophenic sulfur.

Experimental

Materials

The whole asphalts and their LC fractions are described in the Phase I Section of this report. Reagents employed in oxidations and infrared analysis were obtained from Aldrich Chemical, Milwaukee, WI.

Oxidation of Thiophenic Sulfur to Sulfone Type

Initially, oxidation with m-chloroperbenzoic acid after the procedure of Pazant, et al.,[3] was attempted. However, this method was subsequently abandoned because of interference from the m-chlorobenzoic acid reaction byproduct with IR measurement of sulfones. Attempts at removal of m-chlorobenzoic acid via solvent extract, etc., were not successful.

Use of hydrogen peroxide in conjunction with acetic acid proved more satisfactory. The procedure was similar to that of Drushel and Sommers.[42] A known quantity of sample (0.2 - 0.3g) was refluxed for 3 hours with 2.5 mL 30% hydrogen peroxide, 2.5 mL acetic acid, and 25 mL toluene. After reflux, the remaining hydrogen peroxide and acetic acid were removed after cooling via water extraction. The extracted sample was taken to dryness in a rotary evaporator.

IR Measurement of Sulfones

Aliquots of oxidized materials prepared as above were dissolved in carbon tetrachloride to obtain concentrations near 10 mg/mL. Sulfones from aromatic sulfur types (thiophenes) were determined from the area of IR bands centered near 1150 cm^{-1}; sulfides from aliphatic sulfur types were determined via the area of the band near 1120 cm^{-1}. Whenever both types of sulfones were observed, as was typically the case, the areas of the two types were split according to the valley between the two partially resolved bands (1120 cm^{-1}: right of valley, 1150 cm^{-1}: left of valley). The baseline (zero absorbance) was defined by a line extending from about 1180 cm^{-1} to 1100 cm^{-1}.

IR spectra were obtained using a conventional dual beam dispersive instrument (Perkin Elmer M283) set at medium scan rate in the absorbance mode. Liquid sampling cells (KBr windows, 0.5 mm path length) were employed (pure CCl_4 reference). IR band integration was performed using Nelson Analytical (chromatography) software and an IBM AT computer.

HPLC Separation of Sulfones

In order to obtain sulfone concentrates for IR calibration, a neutral fraction from the 200-425° C boiling range of Cerro Negro (Venezuelan heavy crude oil) was oxidized as above and the product fractionated via HPLC. A 30 x 2.5 (i.d.) cm silica column, Spectra Physics M8000

instrument, and UV detector (254 nm) were employed. A Ternary solvent gradient was used for sample elution; it is specified below.

Time (min)	Volume Percent		
	Pentane	CH_2Cl_2	CH_3OH
0	90	10	0
8.0	90	10	0
40.0	0	100	0
50.0	0	0	100
51.0	0	100	0
55.0	90	10	0
60.0	90	10	0

The column temperature was 30.0° C. Fractions were collected at the following times (min): F1 (0-16.4); F2 (16.4-27.2); F3 (27.2-30.5); F4 (30.5-42.6). Material eluting after 42.6 min was diverted to waste. Repetitive separations were performed until a total of 2g oxidized neutrals had been injected (ca. 0.3g/injection).

Results and Discussion

Figure 2-1 shows a chromatogram from HPLC separation of oxidized Cerro Negro 200-425° C neutrals. Sulfones and hydrocarbon oxidation products (ketones, diones, etc.) are clearly resolved from unoxidized materials eluting in fraction 1. The oxidized materials eluting in the middle of the chromatogram were arbitrarily cut into three fractions (F2-F4), as indicated. Highly oxidized materials eluting near the end of the chromatogram were not collected.

Table 2-1 lists the yields and sulfur contents of HPLC fractions F1-F4. The sulfur content of F1 was quite low (0.04 wt%), thereby indicating quantitative oxidation of sulfur present in the starting material (unoxidized sulfur compounds would elute in F1). Quantitative oxidation of this same material was also reported earlier using similar conditions.[26] Sulfone contents of later eluting fractions ranged from 44 to 80 wt%. The fraction with the highest sulfone content (F4) coincided with the elution of dibenzothiophene sulfone (see figure 2). Since the starting neutrals contained 74 wt% hydrocarbons (41.2% saturates, 32.8% aromatics), while F1 accounted for only 51.6 wt% of the oxidation product, significant oxidation of hydrocarbons obviously occurred. Also, since recovery of sulfur was less than quantitative even after correction for

Table 2-1. Results from HPLC Separation of Oxidized Cerro Negro 200-425° C Neutrals

Fraction	Yield (wt%)	Sulfur Content (wt%)	Compound Type (wt%)
Whole neutrals	100	2.93	41.2% Saturated hydrocarbons 32.8% Aromatic hydrocarbons 26.2% Sulfur compounds[a]
1	51.6	0.04	Hydrocarbons
2	5.0	4.81	56% Ketones + 44% Sulfones
3	6.7	8.14	75% Sulfones[b]
4	11.6	8.80	80% Sulfones[b]
Total	74.9	1.83 (2.44 normalized)	

[a] See ref. 29.
[b] Sulfone assay based on sulfur content (100% sulfones = 11.0 wt% S).

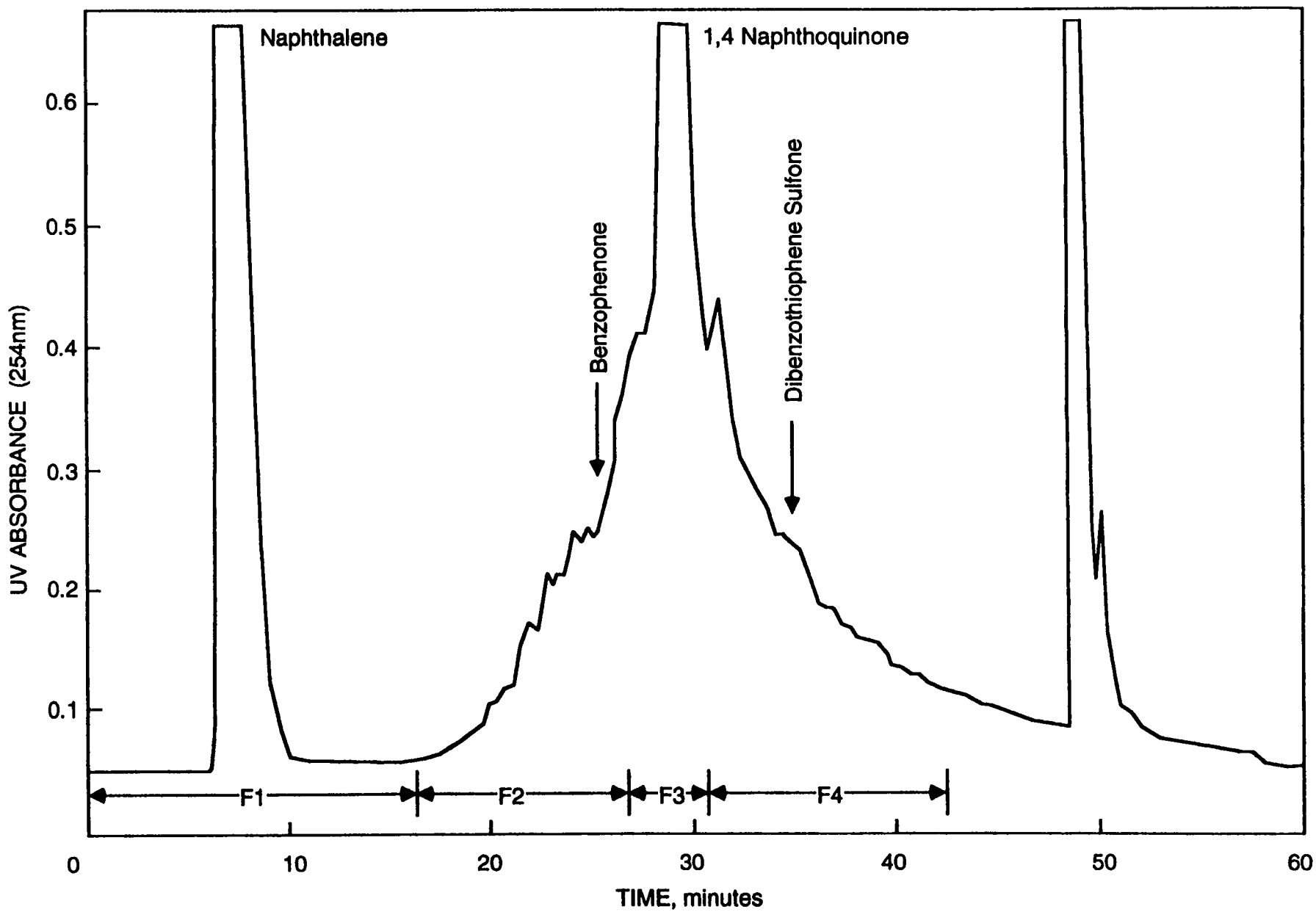

Figure 2-1. HPLC chromatogram depicting separation of oxidation products (sulfones, ketones) from residual hydrocarbons in oxidized Cerro Negro 200-425° C neutrals. Retention of selected pure components and fraction collection intervals are noted.

percent mass recovery (normalized value), a significant proportion must have been lost to the highly oxidized material not recovered in the separation. Both the appreciable oxidation of hydrocarbons and loss of sulfur to highly oxidized materials indicate that the reaction conditions were too severe in this case.

Simple IR response curves (absorbance versus concentration) of fractions F2-F4 from the oxidized Cerro Negro neutrals exhibited poor linearity at higher concentrations, owing to significant band broadening. Plots of band area versus concentration were much improved. Figure 2-2 illustrates sulfone bands at 1310, 1150, and 1120 cm^{-1} for fraction 4. Since both aliphatic and thiophenic sulfones contributed to the 1310 cm^{-1} band, it was not used for quantitation. Thiophenic and sulfidic sulfones were determined via the indicated band areas at 1150 and 1120 cm^{-1}, respectively.

Figure 2-3 illustrates the relation between sulfone band area versus total sulfur content obtained for selected oxidized fractions. Because they were specifically isolated as sulfone fractions via HPLC, the relationship for Cerro Negro fractions F2-F4 should have been definitive. Thus, the correspondence between points for the other materials (Wilmington 650-1000° F sulfides, AAD-1 sulfides and nonsulfides) with those of the Cerro Negro fractions indicates complete conversion of sulfur to sulfones in all cases, as well as approximately equal IR response for various sulfur species present.

Figure 2-4 demonstrates the correspondence between intensities of bands at 1120 versus 1150 cm^{-1} with anticipated sulfur types present in an oxidized sulfide fraction (mainly 1120 cm^{-1}), a neutral nonsulfide fraction (mostly 1150 cm^{-1}), and a whole neutral fraction (both bands). The degree of correspondence observed confirms both the IR band assignments made and the quality of separations performed in Phase I for each asphalt.

The average response curve in figure 2-3 was used as the basis for determination of sulfide and thiophenic forms of sulfur in neutral fractions from each of the asphalts investigated in Phase I. The results are shown in Table 2-2 along with Phase I data reprinted for the reader's convenience.

Agreement between the two sets of data was generally poor. Problems with the present method evident from this comparison include: 1) generally low overall estimation of total sulfur present, 2) typically, underestimation of sulfide types present, and 3) severe underestimation of thiophenic sulfur in the case of asphalt AAK-1. These errors may be potentially attributed to 1)

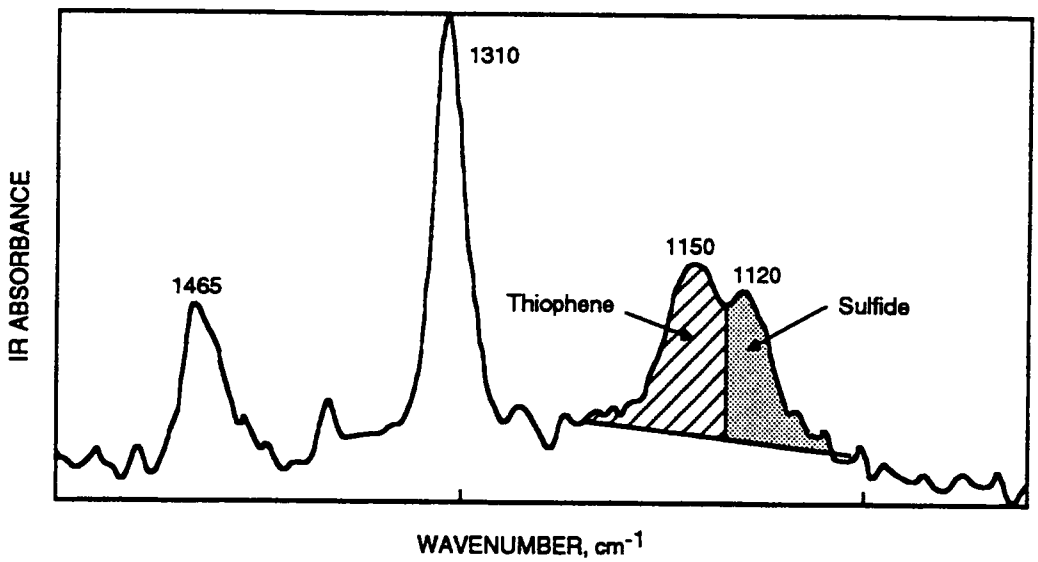

Figure 2-2. Partial IR spectrum of fraction 4 from HPLC separation of oxidized Cerro Negro 200-425° C neutrals showing positions of superimposed baseline and dropline dividing thiophenic versus sulfidic sulfones.

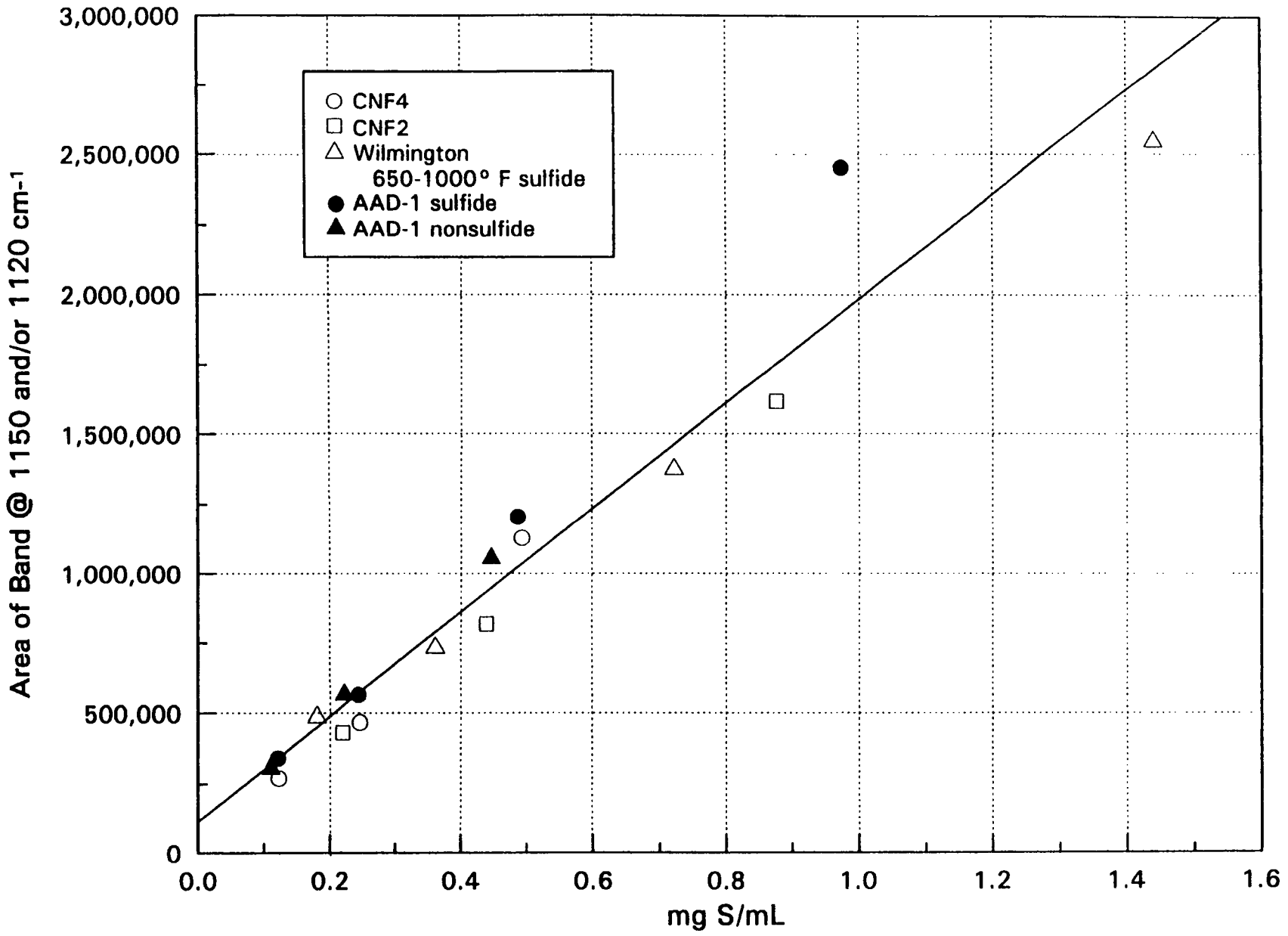

Figure 2-3. Sulfone band area versus total sulfur concentration for selected oxidized fractions.

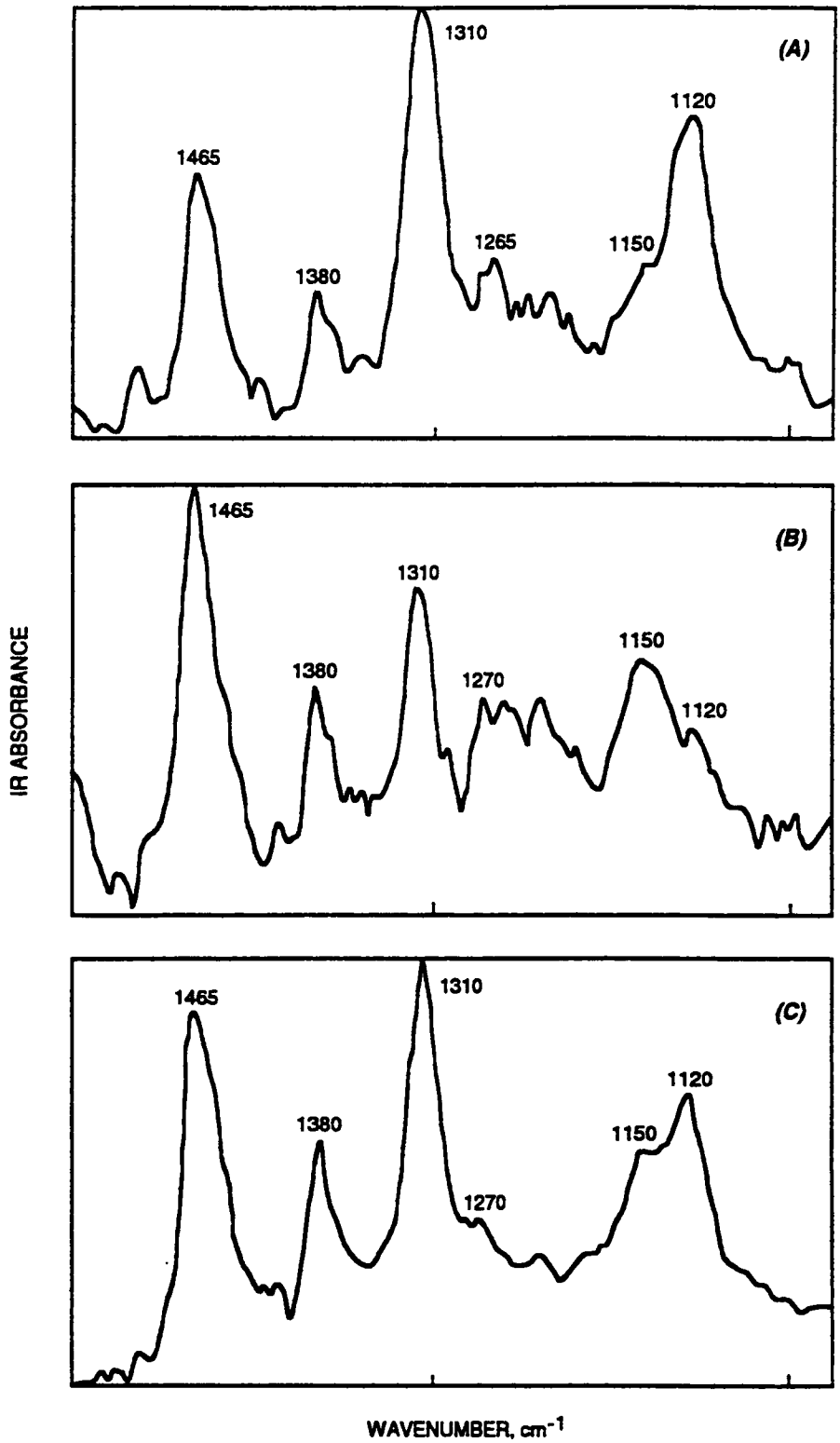

Figure 2-4. Partial IR spectra of oxidized AAD-1 neutral sulfide (A), neutral nonsulfide (B), and whole neutral (C) fractions. Bands at 1310, 1150 and 1120 cm-1 are derived from sulfones. Note prominence of 1120 cm^{-1} band for sulfides and 1150 cm^{-1} for nonsulfides (thiophenics).

Table 2-2. - Sulfur Speciation in Neutral Fractions (wt% S)
A. Phase I Data

Sample No.	AAA-1		AAD-1		AAG-1		AAK-1	
Sulfoxide[a] (R_2SO)	0.34	(8)[f]	0.64	(12)	0.25	(21)	0.27	(6)
Sulfoxide[b] (R_2SO)	0.92		0.69		0.16		0.70	
Aliphatic Sulfide (R_2S)	0.45	(11)	1.00	(18)	0.19	(16)	1.76	(36)
Aromatic Sulfide	1.40	(35)	0.63	(11)	0.22	(19)	0.06	(1)
Total Sulfide Types[c]	2.19	(54)	2.27	(41)	0.66	(56)	2.09	(43)
Thiophenic[d]	1.82	(46)	3.23	(59)	0.51	(44)	2.77	(57)
Thiophenic[e]	1.98		1.78		0.50		2.53	
Total S	4.01	(100)	5.50	(100)	1.17	(100)	4.86	(100)

[a] From IR.
[b] From LC (yield of polar neutrals x sulfur content of polar neutrals).
[c] Sulfoxide (IR) + aliphatic sulfide + aromatic sulfide.
[d] By difference.
[e] From LC (yield of neutral-aromatics x sulfur content of neutral-aromatics).
[f] Data in parentheses refer to the relative distribution of sulfur types.

Table 2-2. - Sulfur Speciation in Neutral Fractions (wt% S)
B. Phase II Data

Sample No.	AAA-1	AAD-1	AAG-1	AAK-1
Total Sulfide Types	1.96	2.95	0.32	1.67
Thiophenic	2.43	1.77	0.50	0.88
Total S	4.39	4.72	0.82	2.55

overoxidation of sulfides (beyond the sulfone stage), 2) losses during water extraction of acetic acid/H_2O_2 and 3) underoxidation of selected thiophenic types, especially in AAK-1 neutrals. Some or all of these deficiencies may be correctable with further optimization of the experimental procedure.

Some positive aspects of the Phase II data were also noted. For example, aromatic sulfides appear to be correctly determined as sulfides rather than thiophenes. Based on prior IR frequency correlations,[42] it was feared that aromatic sulfides would give rise to sulfone bands which would overlap those of thiophenic sulfones, instead of coinciding with sulfide sulfones. In addition, the Phase II data may be more accurate than Phase I data in selected cases. In particular, the agreement between thiophenic sulfur obtained for AAD-1 neutrals from the Phase I LC separation of neutral-aromatics (1.78) and the Phase II result (1.77) suggests that the Phase I determination of thiophenic sulfur by difference (3.23) may be in error, and hence the Phase I estimate for sulfides too low in that case.

Conclusions

Oxidation of sulfide and thiophenic sulfur types to sulfones followed by IR has the potential of developing into a rapid, inexpensive method for determination of sulfur compound types in asphalt. If combined with an initial IR measurement of sulfoxide content, total sulfur and all major sulfur types could be determined, except that aromatic and aliphatic sulfides would not be differentiated. The prototype procedure used here provides a basis for further development of the method.

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