Determination of Total Hydroxyls and Carboxyls in Petroleum and Syncrudes after Chemical Derivatization by Infrared Spectroscopy

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Oxygen-containing functional groups (hydroxyl and carboxyl) in fuels or crude oils, or fractions thereof, are determined by IR spectroscopy. The approach is based on chemical derivatization followed by measurement of IR bands of the corresponding derivatives. The chemical derivatization procedure involves two steps: (1) esterification of carboxylic acids with 2,2,2-trifluoroethanol and (2) acylation of alcoholic and phenolic hydroxyls with trifluoroacetyl chloride. The aryl trifluoroacetates absorb at 1800 cm^{-1}; the 2,2,2-trifluoroethyl esters absorb in the region 1760–1740 cm^{-1}. Variation of molar absorptivity of the derivatives as a function of structure is determined by using pure compounds and well-defined fractions from actual fuel samples. The overall accuracy, precision, sensitivity, and range of applicability to petroleum and related sample types are discussed.

INTRODUCTION

Chemical derivatization has traditionally been an important organic analytical tool for increasing specificity and sensitivity in the determination of functional groups, compound classes, or individual compounds. In functional group analysis of fuels or petroleum, the typical derivatization approach involves addition of an element or chemical functionality that is absent or present in low abundance, followed by instrumental determination of the introduced element or moiety. The concentration of the added element or moiety is then used to calculate the parent functional group concentration from the stoichiometry of the reaction, with correction for reaction yield in cases of nonquantitative conversion or where losses during product workup occur. For example, ^{19}F NMR was used to determine trifluoroacetyl derivatives of hydroxyaromatics, alcohols, thiols, and amines (*1–5*). Similarly, ^{119}Sn NMR has been used to measure hydroxyaromatics in coal liquids reacted with bis(tri-*n*-butyltin) oxide (*6*), and ^{29}Si NMR has been used in conjunction with silylating agents (*7, 8*). A variety of wet chemical methods based on acylation followed by determination of excess acylating agent (*9*) or hydrolysis and subsequent analysis of acetic or trifluoroacetic acid (*10, 11*) is also available. Results from the latter are typically expressed as total acylatable compounds or in an equivalent manner.

Infrared (IR) spectroscopy in conjunction with chemical derivatization has also been used for functional group determination. IR measurement of trimethylsilyl ethers has been employed (*12*). Also, several researchers (*13–16*) have used acylation techniques for quantitative measurement of hydroxyl content of coals and bitumen. They employed acetic anhydride as the derivatizing agent and measured the band from the resulting acetate esters at 1745–1770 cm^{-1}. Since unaltered coal and other fossil fuels (*17*) typically exhibit significant absorption in that IR region, precise background subtraction to determine net absorption by the acetate derivatives is required. However, measurement of underivatized hydroxyls (3600–3800 cm^{-1}) suffers from even greater disadvantages. For example, Osawa and Shih (*18*) state that OH band intensity is significantly affected by moisture in coal. Therefore, semiquantitative information is obtained only after rigorous drying of the powdered coal, potassium bromide, and of the resulting KBr pellets. Robbins et al. (*19*) point out the possibility of N–H band interference in the determination of hydroxyl content of coal liquids dissolved in tetrahydrofuran. In addition, the frequency, shape, and intensity of OH bands are significantly affected by hydrogen bonding, including interactions involving absorbed water (*11, 20, 21*).

Table I. Band Maxima ($\tilde{\nu}_{max}$) and Molar Absorptivities (ϵ) of IR Bands Corresponding to Underivatized and Derivatized OH and C(O)OH Groups[a]

	underivatized		derivatized	
functional group	$\tilde{\nu}_{max}$, cm^{-1} [b]	ϵ, L mol^{-1} cm^{-1} [c]	$\tilde{\nu}_{max}$, cm^{-1}	ϵ, L mol^{-1} cm^{-1}
	A. From Pure Compounds			
OH (alcoholic)	3610 ± 10	60 ± 10	1785 ± 5	420 ± 40
OH (phenolic)	3590 ± 10	120 ± 10	1800 ± 5	610 ± 50
C(O)OH (aliphatic)	1750 ± 5 (monomer) 1715 ± 5 (dimer)	580 ± 40	1755 ± 5	330 ± 20
C(O)OH (aromatic)	1740 ± 10 (monomer) 1700 ± 10 (dimer)	610 ± 40[d]	1740 ± 5	370 ± 30[d]
	B. From Petroleum Fractions			
OH	3600 ± 10	nd[e]	1800 ± 5	600 ± 40
C(O)OH	1750 ± 5 (monomer) 1710 ± 5 (dimer)	470 ± 40	1760 ± 5	280 ± 14

[a] For dilute dichloromethane solutions, ca. 1–10 mg/mL. [b] Median ± range for petroleum and related pure compounds. [c] Mean ± SD. [d] Results for para alkyl and 2-naphthoic acids were excluded from the mean. ϵ's for para alkyl and 2-naphthoic acids were approximately 50% greater than those of other aromatic acids. [e] Not determined.

The IR spectra of underivatized carboxylic acids in methylene chloride exhibit bands corresponding to monomeric and dimeric species. The carbonyl absorption of the dimeric species occurs at ca. 1710 cm^{-1}; the monomer (free acid) band appears at ca. 1750 cm^{-1}. Helm and Peterson (*22*) found the equilibrium ratio of monomer and dimer as determined by IR to be both solvent dependent and affected by other hydrogen-bonding species present. Cogswell et al. (*23*) utilized this distinctive two-band pattern for qualitative analysis for carboxylic acids in petroleum acid concentrates. Later, McKay et al. (*24*) used an average molar absorptivity obtained from pure compounds for quantitative determination of carboxylic

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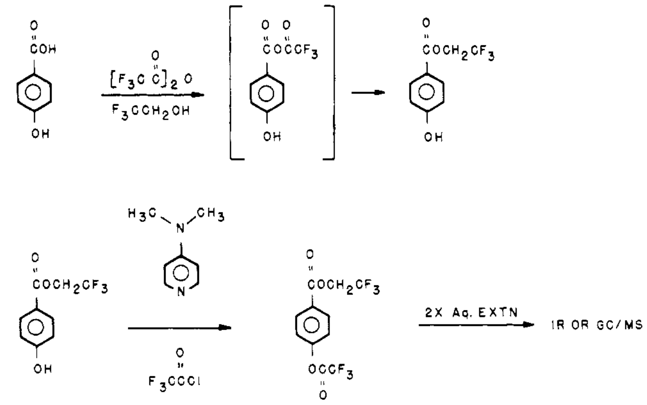
acids in petroleum acid concentrates and pure carboxylic acid fractions. In selected cases, they used tetrahydrofuran as the solvent in order to eliminate the interference from the molecular association between carboxylic acids and amides. Bunger et al. (*25*) found significant overlap in carbonyl bands from carboxylic acids, ketones, and esters in tar sand bitumens. Liotta et al. (*26*) state that free carboxylic acid groups are difficult to detect in IR spectra of coals, but are easily detected after methylation. In general, esterification of carboxylic acids with aliphatic alcohols results in esters with absorption at ca. 1720 cm^{-1} (*27*).

Several methods for esterification of carboxylic acids (*28–34*) have been reported. Acylation is normally carried out by using the corresponding acid anhydride or chloride (*35*). However, the majority of these procedures are not well suited for IR applications because either the solvent system, residual reagents, or reaction byproducts produce significant background absorption in the IR regions of interest. Basic requirements for chemical derivatization procedures for IR include use of solvents with high IR transparency, quantitative product yields, and suitability for microscale reactions. Since halogenated derivatives frequently exhibit bands at significantly higher wavenumbers than nonhalogenated compounds (*36*), fluorinated acylating or esterifying agents seemed a logical choice for reducing the likelihood of interference in a halogen-free matrix such as petroleum. The overall reaction scheme



shown using *p*-hydroxybenzoic acid as an example was assimilated from prior work on esterification of carboxylic acids in trifluoroacetic anhydride media (*29–33*) and acylation of hydroxyl groups with trifluoroacetyl chloride (*1–3*). Trifluoroacetyl chloride is preferred over trifluoroacetic anhydride because of its greater reactivity (*35*). Use of 4-(dimethylamino)pyridine as the acylation catalyst was suggested by Dorn et al. (*2*). Use of water-soluble derivatization agents throughout enabled cleanup of the crude reaction mixture via aqueous extraction. The inherent hydrophobicity of fluorinated derivatives (*37*) helps to prevent significant product loss during the extraction.

As discussed above, IR measurement of underivatized hydroxyl bands suffers from interference by water, which is typically present in equal or greater molar concentration than organically bound hydroxyls in many crudes and fuels, and hydrogen-bonding effects. The free OH band also exhibits a low molar absorptivity, which makes detection of hydroxyls difficult in virtually all types of crudes except coal liquids, where phenols are typically present at percent levels. Similarly, direct measurement of carboxyls is complicated by interference from other carbonyl types and the presence of both monomeric and dimeric species in solvents typically employed for IR measurements. For these reasons, a derivatization approach such as the one shown above offered significant potential advantages. In addition, hydrogen-bonding effects would be greatly reduced for other bands of interest—e.g., N-H, SO, and other C=O—by the combined esterification–acylation of carboxyls and hydroxyls. Of course, it was essential that chemical moieties added in the reaction yield bands that both were self-resolved and provided minimal overlap with other carbonyl species typically present in fossil fuels.

The objective of the work was to determine the feasibility and practicality of the derivatization approach and compare it with conventional IR analysis of underivatized hydroxyl and carboxyl bands. The inherent simplicity, lower cost, and wide availability of IR compared to that of NMR and other more sophisticated instrumental techniques were major factors in its selection. Conventional sample handling methods and a dispersive instrument were employed. For calibration and verification of the method, whole acid concentrates and subfractions previously isolated from Cerro Negro heavy oil (*38*), SRC-II coal liquid (*39*), Wilmington, CA, petroleum (*40*), and selected commercial refinery streams were employed. The preceding derivatization scheme has also been extensively applied to GC/MS determination of specific hydroxyaromatic compounds in fuels and crudes. That work will be reported separately.

EXPERIMENTAL SECTION

Apparatus. All IR measurements were made with a Perkin-Elmer (Norwalk, CT) Model 283 spectrophotometer. Conventional amalgamated KBr liquid cells, nominal 0.5-mm path length, were employed. The instrument was set up and operated under "normal" scanning conditions suggested by the manufacturer. With the slit program and scans speeds employed, the instrument manual specified a scan rate of 4.2 cm^{-1} s^{-1} and spectral band-pass of 2–2.5 cm^{-1} for the region from 1800 to 1600 cm^{-1}.

Reagents. All solvents were of high-purity grade (OmniSolv, EM Science, Cherry Hill, NJ). Trifluoroacetyl chloride was obtained from SCM (Gainesville, FL); trifluoroacetic anhydride (99+%), 2,2,2-trifluoroethanol (99+%), and 4-(dimethylamino)pyridine (99%) were obtained from Aldrich (Milwaukee, WI). Inorganic reagents were of ACS grade. Organic compounds used for molar absorptivity determinations typically assayed at 97% or better and were obtained from commercial sources.

Procedure. The optimized derivatization procedure was as follows. A known weight of material, typically 5–10 mg, was added to 1 mL of 9:1 (v/v) trifluoroacetic anhydride–2,2,2-trifluoroethanol. Esterification was accomplished by heating this mixture in a 5-mL reaction vial to 60 °C for ca. 15 min. The resulting product was prepared for acylation by addition of 4 mL of a solution of 0.25 M 4-(dimethylamino)pyridine (DMAP) in dichloromethane. Acylation was carried out simply by bubbling the solution with trifluoroacetyl chloride (TFACl) gas for 30 min at room temperature. A short piece of fused silica tubing, ca. 20 cm (length) × 0.25 μm (i.d.), proved ideal for delivery of the TFACl. The cylinder was also fitted with a metering valve for flow control. Excess reagents and trifluoroacetic acid produced as a byproduct were removed via extraction with 20 mL of aqueous 0.167 M Na_2HPO_4–0.083 M NaH_2PO_4 buffer. The extraction process was repeated to ensure complete removal, and the resulting dichloromethane solution was dried by passing it through a 4-mL cartridge of anhydrous Na_2SO_4. Quantitative elution from the cartridge was effected by flushing it with an additional 5–10 mL of dichloromethane. The purified product was taken to near dryness under a stream of nigrogen and diluted to a known volume, typically 1 mL, prior to IR measurements. Evaporation of excess dichloromethane yielded a more concentrated solution for improved sensitivity and removed the relatively volatile 2,2,2-trifluoroethyl trifluoroacetate byproduct, which interfered in the determination of total hydroxyl content.

Absorbance was measured at band maxima relative to a solvent versus solvent base line. In each case, repetitive determinations were performed over a series of dilutions of the stock solution to check linearity of absorbance versus concentration. Molar absorptivities were calculated from regression analysis of the linear portion of these plots, in accordance with Beer's law. Typically, significant deviation from linearity was observed whenever absorbance exceeded 0.3 unit. Band maxima for trifluoroacetate derivatives occurred near 1800 cm^{-1}; those for 2,2,2-trifluoroethyl esters ranged from 1760 to 1740 cm^{-1}. Spectra of underivatized compounds and petroleum fractions were also obtained from dichloromethane solutions and were interpreted in an analogous manner.

Concentrations (wt %) of hydroxyl-containing compounds and carboxylic acids in crudes, fuels, or their fractions were calculated from the measured intensities of the appropriate bands per unit weight, corresponding measured or estimated average molecular weights, and average molar absorptivities for the respective bands determined from calibration with pure compounds and selected petroleum or synfuel fractions. In cases where average molecular weights were inappropriate or could not be determined or reasonably estimated, the concentration of the functional group proper was reported in lieu of the compound type.

Liquid chromatographic procedures for isolating fractions used in calibration and verification of the method have been described previously (*40–43*). Briefly, whole acid fractions were isolated by using nonaqueous ion-exchange liquid chromatography (*40*). Whole acids were subfractionated via normal-phase HPLC on silica using a mobile phase containing tetramethylammonium hydroxide (*41–43*). In cases where acid fractions or subfractions were used to determine average molar absorptivities, their hydroxyaromatic or carboxylic acid content was independently assayed by using one or more of the following techniques: elemental analysis, nonaqueous titration with potassium dimsyl (*41*), IR (without chemical derivatization (*41*)), and GC/MS (*43*). The resulting molar absorptivities were corrected for the presence of non-hydroxyl or non-carboxyl types as required. Average molecular weights were estimated by nonaqueous titration and/or vapor pressure osmometry techniques (*44*).

RESULTS AND DISCUSSION

Optimization of the Derivatization Procedure. Initial efforts focused on maximizing product yields and recoveries, minimizing interferences, and improving practical aspects of the derivatization procedure.

In the case of acylation, obtaining quantitative product yields presented little difficulty, except in cases of severely hindered hydroxyaromatics like 2,6-di-*tert*-butylphenol—which is essentially nonreactive. Substitution of DMAP as the acylation catalyst significantly decreased reaction time and improved yields of products from partially hindered hydroxyaromatics, such as 2-*tert*-butyl-6-methylphenol, over those obtained with an earlier procedure utilizing triethylamine (*43*). An appreciable excess of catalyst is required, since it also acts as a scavenger for HCl produced during acylation (*1*). In GC/MS analysis of pure hydroxyaromatic compounds or actual samples, detection of non-acylated species was rare, and their relative concentration very seldom exceeded 1% of the total present.

The corresponding situation for esterification of carboxylic acids may have been similar, but was much more difficult to ascertain. The main difficulty arose from the poor GC characteristics of free carboxylic acids, which made GC/MS detection of unreacted pure carboxylic acids difficult, and virtually impossible in the case of actual petroleum fractions. Since Smith and Tsai (*29*) reported yields in excess of 98% using 2,2,2-trichloroethanol, initial reaction conditions were identical with their procedure. Systematic variation of reaction conditions and molar ratios of reagents/reactant in order to maximize IR response led to only a slight modification of the Smith and Tsai procedure: a 60 °C versus 100 °C reaction temperature. The lower temperature was largely employed for practical convenience and because reagent loss from evaporation was less. Reaction time was extended slightly to compensate for the lower temperature.

Aqueous extraction was found to be effective for removal of excess reagents and reaction byproducts from the crude reaction product. The pH of the aqueous buffer was optimized to yield the highest recovery of product and to be consistent with complete trifluoroacetic acid removal. Trifluoroacetic acid exhibits carbonyl absorption in the same region of the IR as trifluoroacetate esters, thereby necessitating its quantitative removal. Further details of the optimization of reaction conditions are reported elsewhere (*45*).

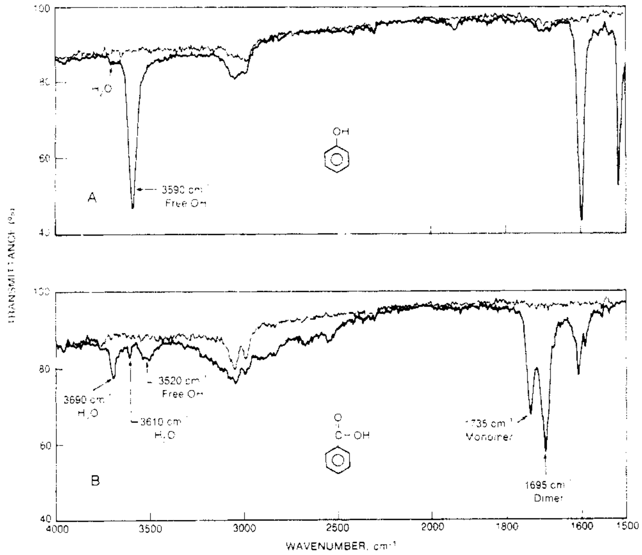


Figure 1. IR spectra of phenol and benzoic acid. Concentrations are 5.58 and 1.45 mg/mL of CH_2Cl_2, respectively. Dashed line is the solvent versus solvent base line.

Direct acylation of petroleum fractions, or other sample types containing carboxylic acids, proved infeasible owing in part to formation of mixed anhydrides, which interfered with the IR determination of trifluoroacetate esters. Mixed anhydride formation during reaction of trifluoroacetic anhydride with a variety of carboxylic acids is well documented (*33*). This apparently also occurs during direct acylation with TFACl. In addition, GC/MS analysis of *o*-toluic acid that had been exposed to TFACl revealed significant amounts of the corresponding acid chloride. Furthermore, many of these interfering species are stable to hydrolysis during the aqueous extraction. Thus, the initial esterification of carboxylic acids with 2,2,2-trifluoroethanol is required to prevent subsequent formation of anhydrides/acid chlorides in the acylation step that interfere in the determination of hydroxyl compounds as their trifluoroacetates. Unless a given fraction is certifiably free of carboxylic acids, it is recommended that the complete reaction sequence be performed, even though only the hydroxyl compounds may be of interest.

General Characteristics of Spectra before and after Derivatization. Figure 1 shows portions of the IR spectrum of phenol and benzoic acid where OH and carbonyl stretching bands occur. Because neither compound was dried prior to obtaining its spectrum, both show water-derived contributions to OH stretching (3690, 3610 cm^{-1}) and bending (1610 cm^{-1}) bands. Aromatic C=C vibrations also contribute to the band observed near 1600 cm^{-1}. Since the free carboxyl OH band occurs at a lower wavenumber (3520 cm^{-1}) than that of the OH band of phenol (3590 cm^{-1}), both water-derived OH stretching bands are apparent in the benzoic acid spectrum, while the phenolic OH band overlaps the lower wavenumber water band in its spectrum. In quantitative IR determination of phenolic/alcoholic hydroxyls, the intensity of the combined OH band at ca. 3600 cm^{-1} is corrected for water contribution by subtracting 41% of the absorbance of the resolved H_2O band (3690 cm^{-1}). The approximate 2.5:1 ratio of the 3690/3600 cm^{-1} H_2O band intensities is evident in the benzoic acid spectrum. Carbonyl bands representing monomeric versus hydrogen-bonded benzoic acid dimers are clearly resolved. Corresponding carbonyl absorption patterns for saturated carboxylic acids are similar, except the wavenumber

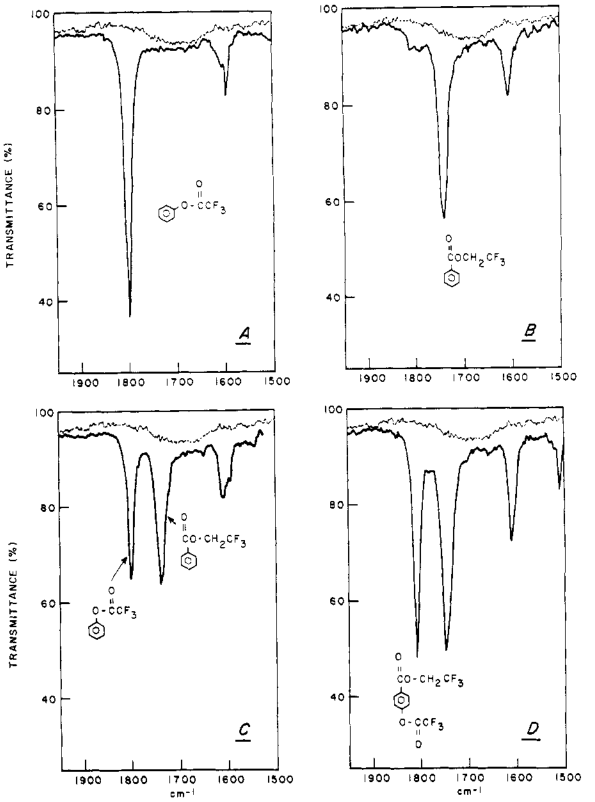


Figure 2. Partial IR spectra showing carbonyl absorption from derivatized phenol (A), benzoic acid (B), a 1:1 mixture of phenol and benzoic acid (C), and 4-hydroxybenzoic acid (D). Concentrations of A–D are 1.20, 1.50, 0.90/1.07, and 1.77 mg/mL of CH_2Cl_2, respectively.

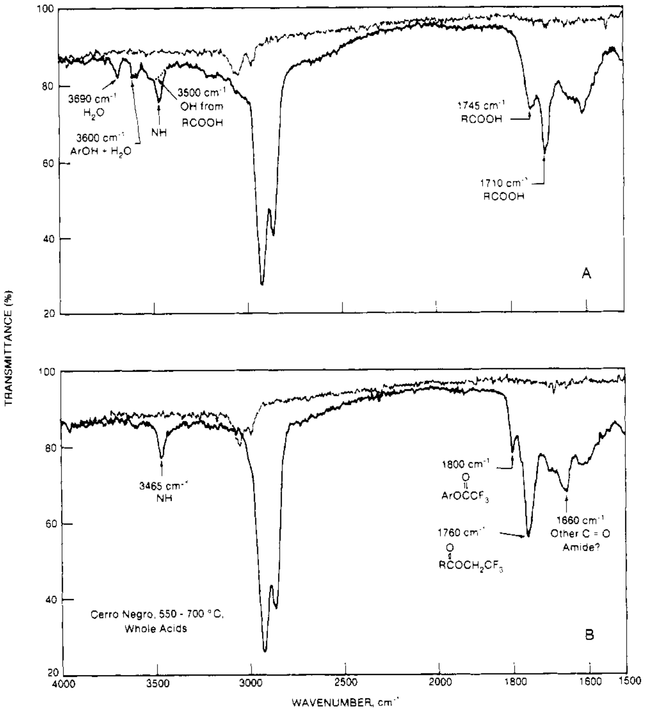


Figure 3. IR spectra of underivatized (A) and derivatized (B) Cerro Negro 550–700 °C acids. Concentrations are 14.0 (A) and 19.1 (B) mg/mL of CH_2Cl_2. See text.

of each band is typically 15 cm^{-1} higher.

Figure 2 shows portions of IR spectra containing carbonyl bands from the corresponding derivatives of phenol and benzoic acid, as well as derivatized 4-hydroxybenzoic acid. The only OH bands evident in any of those spectra were from small amounts of water carried over from the aqueous extraction. The carbonyl bands from trifluoroacetate and 2,2,2-trifluoroethyl esters are easily resolved and, in the case of the compounds shown, of nearly equal intensity. The small doublet at ca. 1800 cm^{-1} in the spectrum of 2,2,2-trifluoroethyl benzoate (Figure 2B) is characteristic of trifluoroacetic acid (monomer, 1810 cm^{-1}; dimer, 1790 cm^{-1}), which was incompletely removed in that case.

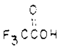
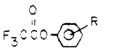
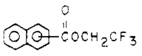
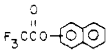
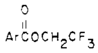
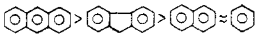
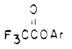
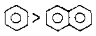
Figure 3 compares spectra of a whole acid fraction from a high-boiling petroleum distillate before (A) and after (B) derivatization. The following features are apparent in the spectrum of the underivatized acids: (1) the weak intensity of the OH band at 3600 cm^{-1}, which is typical for petroleum fractions, (2) the significant contribution by water to the 3600-cm^{-1} band indicated by the intensity of the 3690-cm^{-1} band, due to water alone, and the assumption of a 2.5:1 intensity ratio for 3690/3610-cm^{-1} bands from water, (3) significant overlap between the OH band from carboxyl groups (3500 cm^{-1}) and the N–H stretching band from pyrrolic benzologues present, (4) distinct bands for carboxylic acid monomers and dimers, and (5) the presence of other carbonyl types indicated by broad absorption near 1650 cm^{-1}. In contrast, only the N–H band is observed in the upper region of the derivatized acid spectrum. In addition, well resolved carbonyl bands representing absorption by trifluoroacetate and 2,2,2-trifluoroethyl esters are observed, along with an unidentified carbonyl band at 1660 cm^{-1}, which may represent amides analogous to 2-quinolone. The wavenumber (1760 cm^{-1}) of the 2,2,2-trifluoroethyl esters is typical of aliphatic carboxylic acids; aromatic acids, i.e. where the carboxyl group is directly substituted onto the aromatic ring, typically absorb near 1740 cm^{-1} (see Figure 2). Due to their predominantly aliphatic nature (*46*), a single band at ca. 1760 cm^{-1} is normally observed for petroleum carboxylic acids.

Table I summarizes wavenumbers corresponding to band maxima ($\tilde{\nu}_{max}$) and average molar absorptivities (ϵ) at $\tilde{\nu}_{max}$ for plain and derivatized hydroxyl and carboxyl groups. Determination of these parameters is discussed in detail in the next section. The range given for $\tilde{\nu}_{max}$ represents that normally encountered in spectra of petroleum, synfuels, and representative pure components. The variation of ϵ with structure, approximated in the table by the standard deviation of ϵ's for individual compounds, was approximately ±10% relative for each band measured, regardless of type. Good agreement between ϵ for derivatized pure phenols (610 ± 50) and petroleum hydroxyls (600 ± 40) was obtained. However, petroleum carboxyls yielded lower ϵ's than any of the pure compounds investigated. As noted previously, trifluoroacetate esters of hydroxyl groups exhibit a much greater IR response (5–7:1) than plain OH groups. At first glance, the corresponding situation for 2,2,2-trifluoroethyl esters versus plain carboxyls appears reversed, with an average decrease in ϵ of nearly 50% after esterification. However, since carboxyls give rise to two bands and esters only one, their practical IR sensitivities are about equal.

Significance and Variability of ϵ. Results for $\tilde{\nu}_{max}$ and ϵ of individual hydroxyl and carboxyl compounds appear elsewhere (*45*). In general, the results obtained for ϵ at $\tilde{\nu}_{max}$ or other wavenumbers are highly dependent on instrumental parameters—especially effective slit width, grating or inferometer performance, and other factors affecting the monochromatic quality of the IR radiation (*47*). Because of the dependence of IR response on other factors such as cell characteristics, detector performance, and operator technique, at least a limited recalibration would be necessary for application of this work in another laboratory, regardless of efforts taken to obtain "ultimate" intensity data.

Empirical correlations of carbonyl intensities with structure are shown in Table II. Although it is known that the magnitude of ϵ depends on the dipole change produced by a given

Table II. Summary of Structural Effects on Carbonyl Intensities

Basic Structure	Variation	Effect on ε
 $RC(=O)OH$	replace H with CH_2CH_3	~30% decrease
	replace H with CH_2CF_3	~40% decrease
	replace R with Arene	NC[a] (non-p-substituted) ~50% increase (p-substituted)
	replace R with CF_3	~25% decrease
 $F_3CC(=O)OH$	replace H with alkyl group	NC[a]
	replace H with Arene	~40% increase
	increase alkyl chain length	o-substituted (CH_3>iso-C_3H_7>n-C_3H_7>C_2H_5) m-substituted (iso-C_3H_7>CH_3>C_2H_5) p-substituted (iso-C_3H_7>n-C_6H_{13}>C_2H_5>CH_3)
	substitution at 1 vs 2 naphthyl position	2 > 1
	substitution at 1 vs 2 naphthyl position	1 > 2
 $ArC(=O)OCH_2CF_3$	increase aromaticity of Ar	
 $F_3CC(=O)OAr$	increase aromaticity of Ar	

[a] NC represents no change.

vibration, correlating this effect with structure presents a considerable challenge. It is interesting to note that in the case of esters, a given substituent or structural modification generally exhibited opposite effects at the carbonyl carbon versus the single bonded oxygen positions. For example, the effects of α- versus β-naphthyl substitution and increasing aromaticity of substituted arene groups are noted in the table. Also, para alkylation dramatically increased ϵ over that of ortho- and meta-substituted 2,2,2-trifluoroethyl alkylbenzoates. However, in the case of phenyl trifluoroacetates, para alkylation usually decreased ϵ compared to meta and especially ortho alkyl isomers.

The higher response of aromatic versus aliphatic acid esters corresponds to that observed for alkylaryl versus dialkyl ketones (*48*). Similarly, the greater carbonyl intensity of carboxylic acids compared to that of esters has also been noted (*48*). The dependence of ϵ on detailed structural effects such as alkyl chain length and degree of branching was not investigated in detail here or in the literature, but the available data suggest a complex relationship. Since the repeatability of ϵ ranged from 2 to 5% (RSD), the differences in ϵ's of structurally related compounds were usually not considered significant unless they exceeded 10%.

Variations in instrument performance and IR transmission quality of sample cells limited the long-term repeatability of ϵ and of IR measurements in general. Other variables such as solvent quality may also have impacted repeatability. Variation in product yield and recovery did not generally control precision in the determination of ϵ for derivatives. For example, repetitive determination of ϵ for commercially prepared (Pfaltz and Bauer, Waterbury, CT) phenyl trifluoroacetate (97%) over a 2-year period yielded the following results: 627, 614, 622, 626, and 689 L mol^{-1} cm^{-1}, $\bar{X}$ = 636; SD = 30, RSD = 4.7%. Corresponding data for derivatives yielded representative RSD's of 4.2% (decanoic acid), 1.8% (2-phenylbenzoic acid), 3.1% (2-naphthol), and 5.5% (phenylacetic acid). Although rejection of the 689 result for phenyl trifluoroacetate improves its RSD to 1.0%, analogous treatment of data for derivatives improves their RSD's as well. Overall, data fluctuation correlated better with chronology and cell use patterns than with whether or not derivatization was performed prior to determination of ϵ.

Table III. Band Maxima ($\tilde{\nu}_{max}$) and Molar Absorptivities (ϵ) of Underivatized and Derivatized Hydroxyaromatic Concentrates from Fuels

		underivatized		derivatized	
fuel	boiling range, °C	$\tilde{\nu}_{max}$, cm^{-1}	ϵ, L mol^{-1} cm^{-1}	$\tilde{\nu}_{max}$, cm^{-1}	ϵ, L mol^{-1} cm^{-1}
raw SRC-II coal liquid[a]	200–325	3600	110	1800	539 ± 30
hydrotreated SRC-II[a,b]	200–325	3600	118	1800	623 ± 11
petroleum-derived JP-5					
as received	170–280	nd[e]		1800	631
thermally stressed[c]		nd		1800	608
LCO[d]	200–325	3600	71	1800	576
LCO[d]	153–325	3600	59	1800	610
$\bar{X}$ ± SD			nd		598 ± 34

[a] For sample documentation, see ref 39 and 50. [b] NiMo catalyst, 310 °C, 0.5 LHSV, 980 SCF H_2/bbl. [c] JFTOT thermal stability test, ASTM D 3241. [d] Light cycle oil from commercial-scale catalytic cracking unit. [e] Not determined.

Although preceding results indicate that the compound to compound variation in ϵ from structural effects is only 2–3 times the RSD for individual ϵ's, further investigation of ϵ on actual petroleum fractions was warranted for the following reasons: (1) Only a limited set of ϵ data was available for each compound type; (2) within a given type, selection of individual compounds was based more on availability than on anticipated concentration in petroleum; (3) at least in the case of carboxylic acids, structures of the available pure compounds differed significantly from those previously identified in petroleum; and (4) additivity of ϵ's and other phenomena potentially affecting results obtained on gross mixtures versus single compounds had not been investigated. Furthermore, inherent structural differences in various types of crudes (*49*) could cause systematic variations in ϵ with crude type. The limiting factors in the determination of ϵ on actual petroleums were (1) isolation of fractions of sufficient purity and (2) obtaining reliable assays for either hydroxyl or carboxyl content in those fractions.

Tables III and IV show results obtained on hydroxyaromatic (ArOH) and carboxylic acid concentrates, respectively. In general, ϵ's for ArOH concentrates compare favorably with the average for pure compounds, while those for carboxylic acids are significantly lower. Precision of ϵ data was comparable to that of pure compounds in cases where multiple determinations were made.

The ArOH concentrates employed for determination of ϵ were also analyzed in detail by GC/MS. Correlation of ϵ's in Table III with composition yielded some interesting results. For example, meta and para alkylphenols predominated in the raw SRC-II coal liquid fraction, whereas ortho alkylphenols were much more enriched in the hydrotreated SRC. The relative abundance of other ArOH paralleled that of the phenols; e.g., the ratio of 4-indanol to 5-indanol was <0.5 before and 4.7 after hydrotreating. Thus, the higher result for ϵ in the case of the derivatized hydrotreated SRC fraction is consistent with the generally higher ϵ's of pure ortho alkylphenol derivatives (*45*), and the result for the raw SRC was comparable to that of compounds present in high abundance such as 3-ethylphenol, 4-ethylphenol, and 5-indanol (*45*). The petroleum-derived JP-5 fraction exhibited a much higher degree of alkylation than either SRC fraction, with easily detectable levels of alkylphenols containing up to 11 carbons

Table IV. Band Maxima ($\tilde{\nu}_{max}$) and Molar Absorptivities (ϵ) of Underivatized and Derivatized Carboxylic Acid Concentrates from Virgin Petroleum Distillates

		underivatized			derivatized	
		$\tilde{\nu}_{max}$, cm^{-1}				
crude	distillate boiling range, °C	monomer	dimer	ϵ, L mol^{-1} cm^{-1} [a]	$\tilde{\nu}_{max}$, cm^{-1}	ϵ, L mol^{-1} cm^{-1}
Cerro Negro[b]	200–425	1750	1715	476	1755	266
	425–550[c]	1745	1710	479	1755	266
		1750	1710	468	1755	279
	550–700	1745	1710	407	1760	159
Wilmington[d]	225–370	1750	1715	643	1760	298
	370–535	1750	1710	514	1760	290
$\bar{X}$ ± SD[e]				469 ± 39		280 ± 14

[a] Combined ϵ for monomer plus dimer. [b] For sample documentation, see ref 36 and 42. [c] Separations were performed in duplicate. Results shown are for respective fractions. [d] For sample documentation, see ref 22 and 38. [e] Wilmington 225–370 °C (underivatized) and Cerro Negro 550–700 °C (derivatized) results were excluded from their respective means.

in alkyl groups. Its relatively high ϵ value is consistent with the probability of a substantial percentage of ortho-substituted compounds, given the degree of alkylation observed. Also, the main structural change observed after thermal stressing was a net lowering in the degree of alkylation, which is consistent with the lower ϵ obtained on the ArOH fraction from the stressed fuel. Although they are petroleum-derived, the distribution of ArOH in light cycle oils (LCO) is quite different from that of virgin petroleum distillates. Significant proportions of plain and alkylated polynuclear species such as naphthols and fluorenols are present in addition to phenols and hydroxybiphenyls. Nevertheless, molar absorptivities for the two derivatized LCO concentrates examined were comparable to those of the other fuels. The LCO fraction yielding the smaller value of ϵ (576) contained a higher proportion of polynuclear ArOH; the trend of lower ϵ's for those types relative to phenols was noted earlier in Table II.

The exceptionally low ϵ's obtained for underivatized LCO ArOH concentrates probably resulted from hydrogen-bonding interactions with nitrogen compounds present as comtaminants. Although ϵ's for both underivatized and derivatized fractions were corrected for their dilution effect, the nitrogen compounds apparently effected a net lowering in the ϵ observed for free hydroxyls beyond that accountable for by simple dilution. This effect appeared to be negligible after derivatization. Conversely, ϵ's consistent with pure ArOH were obtained for both underivatized SRC fractions, which were relatively free of other types.

ϵ's obtained for both underivatized and derivatized petroleum carboxylic acid concentrates (Table IV) were generally lower than those of pure saturated carboxylic acids (*45*). Since repeated attempts at assaying these fractions indicated essentially 100% carboxylic acid content in all cases, this lower response in all boiling ranges has tentatively been attributed to structural effects. Carboxylic acids from Wilmington and other California crudes have been studied extensively by Seifert and co-workers (*51*) and by others (*44*); they are predominantly based on polycyclic alkane structures. Corresponding data are not available for Cerro Negro acids. In all probability, the pure compounds used to determine ϵ for aliphatic acids inadequately represent either petroleum both in terms of structure and IR response.

Considering their complex and variable composition, the agreement obtained between ϵ's for the various fractions and, in the case of ArOH, their correspondence to data for pure compounds were surprisingly good. Although the variability of ϵ with composition could be rationalized in the case of ArOH concentrates, this is not generally possible in routine IR applications where measurements are typically performed on whole fuels of essentially unknown composition. In those cases, nominal values of ϵ, e.g., 600 for ArOH and 280 for carboxylic acid derivatives, must be assumed and the corresponding limits on accuracy of the results, ca. ±10% relative, recognized.

Table V. Reactivity and Degree of Interference from Representative Nitrogen Compounds and Ketones

compound	% reacted	product(s) $\tilde{\nu}_{max}$, cm^{-1}	deg of interference, mol %
indole	78	1800	16
		1740	≪62
1,2,3,4-tetrahydrocarbazole	100	1720	0
carbazole	63	1720	0
benzamide	100	1800	100
		1740	≪100
4-methyl-2-quinoline	0		
p-ethylaniline	>100	1730	~0
4-methyl-1-tetralone	10	1800	10
1-indanone	75	1800	75

Interferences. The probability of interference from other carbonyl species present in petroleum and syncrudes is low, since types normally encountered, e.g., ketones and amides, normally exhibit minimal absorption in the IR regions corresponding to the derivatives. Interference from acylation of types other than ArOH, the most probable source of error, was investigated.

Table V lists results from attempted derivatization of selected nitrogen- and oxygen-containing compounds. Pyrrolic benzologues react to varying degrees to yield N-acyl derivatives (ca. 1720 cm^{-1}); in the case of indole, a minor aromatic ring-acylated product was also observed. The carbonyl band from trifluoroacetamides typically poses negligible interference toward the determination or carboxyls; the ring-acylated product from indole directly interferes with hydroxyl determinations to the extent of its formation (16 mol %). Acylation of benzamide resulted in 100% conversion to its monotrifluoroacetamide, with one carbonyl band directly overlapping that of hydroxyl derivatives (1800 cm^{-1}) and the other (1740 cm^{-1}) contributing to a lesser extent to carboxyl absorption (1760 cm^{-1}). Fortunately, benzamide and other diprotic amides are absent from or at least uncommon to petroleum. Monoprotic amides, represented by 4-methyl-2-quinolone, were unreactive. Anilines react to give a mixture of mono- and diacyl products. For example, 2-methylaniline yielded 70% of the diacyl derivative with the current derivatization procedure. Because of their relatively low $\tilde{\nu}_{max}$, acylated aniline derivatives also present little interference with the determination of carboxyls.

Reactivity of ketones correlated with the acidity of their corresponding enol forms. Aliphatic ketones were unreactive, but cyclic/benzylic types such as 1-indanone and 1-tetralone formed significant amounts of enolic trifluoroacetates. By comparison, independent studies of keto–enolate equilibria

Table VI. Comparison of Results Obtained on Derivatized Acid Fractions versus Those from Whole Fuels or Distillates[a]

fuel/distillate	boiling range, °C	total acids,[b] wt %	hydroxyl compounds, wt %		carboxylic acids, wt %	
			from acids[c]	from whole fuel	from acids[c]	from whole fuel
hydrotreated SRC-II coal liquid	200–325	12.8	11.2	11.4	ND[d]	ND
JP-5	175–240	0.11	0.04	0.07	ND	ND
No. 2 diesel (straight run)	200–350	0.47	0.31	0.19	0.17	0.15
No. 2 diesel (straight run)	250–350	0.45	0.15	0.17	0.18	0.15
LCO	225–350	1.30	0.19	0.14	ND	ND
gas oil from Wilmington crude	370–535	10.4	1.69	1.64	2.9	2.7

[a] Nominal values of 600 (OH) and 280 (RCOOH) were assumed for ϵ in the calculation of weight percent. [b] Gravimetric yield from nonaqueous ion-exchange LC separation. [c] Results from analysis of acid fractions are expressed on a whole distillate basis. [d] ND means none detected.

indicated the acidity of 2-indanone (pk_a 12.21) to be $10^{0.7}$ greater than that of 2-tetralone, 10^3 greater than that of benzyl methyl ketone, and 10^7 greater than that of acetone and other simple aliphatic ketones (*52, 53*). Thus, the tendency of indanones, tetralones, and analogous ketones to behave like ArOH in the current procedure arises from their comparable acidities.

Thiophenol trifluoroacetates exhibit $\tilde{\nu}_{\max}$'s in the same region as the bulk of the trifluoroacetamides, ca. 1720 cm^{-1}. No aliphatic thiols were investigated, but based on the correspondence between $\tilde{\nu}_{\max}$ of alcohols versus phenols, their trifluoroacetates should exhibit $\tilde{\nu}_{\max}$ in the region 1720–1700 cm^{-1}. Most petroleum fractions exhibit a band at 1720 cm^{-1} after derivatization which, based on a corresponding decrease in the intensity of the free N–H band at 3460 cm^{-1}, probably represents trifluoroacetamides from pyrrolic benzologues. Current research is aimed at improving the yield from acylation of that type so as to extend the current approach to their estimation as well. Although thiols would theoretically interfere, their concentration relative to N–H types is negligible in most petroleums.

In general, the compound by compound approach for studying interfernces was less than satisfactory because of the real possibility of overlooking significant interference from unknown or unanticipated types, the limited availability of pure compounds representative of those in petroleum, and the likelihood of overestimating the importance of known interferences such as those from cyclic ketones. For these reasons, a more global approach involving comparison of results from whole fuels versus those from acidic fractions was adopted. In that case, significant interference from basic or neutral components would lead to much higher results obtained on the whole sample compared to those obtained on the acid fraction proper. Those data are described in the next section in conjunction with other data obtained to demonstrate the general applicability of the method.

Applications, Sensitivity, Accuracy. Table VI compares results obtained from analysis of acid fractions to those from analysis of whole distillates. In the case of kerosines, jet fuels, most diesel fuels, and other products containing low levels of acidic compounds, 0.5 g of the fuel was diluted approximately 1:1 with dichloromethane and carried through the derivatization procedure. Absorbance of the derivatized fuel was measured against a reference containing an equivalent concentration of fuel in dichloromethane. Use of an equivalent fuel/solvent mixture in the reference cell prevented base-line shifting from low-intensity bands such as those from aromatic substitution, etc.

The results from analysis of the whole fuels were generally equivalent to those obtained from acid fractions, thereby indicating the lack of interference from neutral or basic fuel components. Interestingly, several of the whole petroleum distillates exhibited an additional band at 1780 cm^{-1}. Of the pure compounds investigated, only trifluoroacetates of 1- and 2-indanol exhibited bands in this IR region. This band was approximately 50% resolved from the main trifluoroacetate band at 1800 cm^{-1} and apparently caused minimal interference in the determination of ArOH. The origin of the 1780-cm^{-1} band is currently being investigated; it definitely arises from neutral rather than basic components. Since results for total OH in acid fractions were typically equal to or greater than those obtained on whole distillates, the 1800-cm^{-1} band must represent predominantly ArOH rather than alcohols, which normally partition into the neutral fractions. On the other hand, the occurrence of the 1780-cm^{-1} band in the whole distillate spectrum, coupled with its virtual absence in that of the acid fraction, is consistent with an alcoholic structure.

The sensitivity of the method cannot be rigorously established, since it depends significantly on individual sample characteristics. However, the result obtained for OH compounds in the JP-5 fuel in Table VI was used to estimate an approximate detection limit. Based on the signal-to-noise (S/N) ratio obtained in that case, a detection limit ($S/N = 2$) of 0.007 wt % hydroxyl compounds in the neat fuel, or 0.0005 wt % O as OH, was calculated. This relatively low limit of detection achievable, relative to most IR determinations, results from the narrow bandwidth and high molar absorptivity of the trifluoroacetate carbonyl absorption. The corresponding limit for 2,2,2-trifluoroethyl esters is 5–10 times higher, owing to their lower ϵ's, greater bandwidth, and the typically higher level of base-line fluctuation present in their spectral region.

Accuracy is limited by structural dependence of ϵ, as discussed previously. Nevertheless, it was felt that some independent corroboration of the IR–chemical derivatization method was needed to assess any systematic bias in results aside from uncertainties in ϵ. Table VII compares hydroxyl (effectively ArOH) and carboxyl content of selected petroleum acid fractions for which ϵ's of individual carboxyl concentrates had been previously determined (Table IV). Thus, although nominal ϵ's were employed in the calculation of ArOH, fraction-specific ϵ's were employed for carboxyl determinations for both underivatized and derivatized fractions. Those results are compared against gravimetric yields from high-performance liquid chromatographic (HPLC) isolation of carboxylic acids and nonaqueous titration results for carboxylic acid content.

On the positive side, no systematic bias in carboxyl content was observed for the IR–chemical derivatization method, or any of the others for that matter. However, the results largely reveal the inexact nature of compound type analysis of petroleum in general. IR analysis without derivatization suffers positive interference from other carbonyl types, which may explain the somewhat higher results obtained without, compared to those obtained with, derivatization. HPLC data are affected by errors in fraction handling and incomplete separation. These factors can result in either high or low results, in agreement with the random variation observed for those data. Errors in nonaqueous titration are largely positive, either from co-titration of noncarboxylic species or from incomplete

Table VII. Comparison of IR Results Obtained on Petroleum Acid Fractions with Those from Other Techniques

		wt % of acid fraction					
		hydroxyl compounds		carboxylic acids			
crude[a]	distillate boiling range, °C	IR (wo/deriv)[b]	IR (w/deriv)[c]	IR (wo/deriv)[d]	IR (w/deriv)[d]	HPLC[e]	NAT[f]
Cerro Negro	200–425	9.7	10.0	64 ± 2[g]	55	63 ± 2	57
	425–550	6.7	6.8 ± 0.1	58 ± 2	51 ± 1	56 ± 1	56 ± 1
	550–700	5.4	6.5	47	41	36	42 ± 2
Wilmington	225–370	nd[h]	24	56	46	46	61
	370–535[i]	nd	26	57	54	47	55 ± 1

[a] Same crudes as in Table IV. [b] Results based on ϵ = 120 L mol^{-1} cm^{-1}. [c] Results based on ϵ = 600 L mol^{-1} cm^{-1}. [d] Individual ϵ's in Table IV were used to calculate weight percent. [e] Gravimetric yield of acid subfraction containing carboxylic acids. [f] Nonaqueous titration with potassium dimsyl. [g] Uncertainties are average deviations from duplicate determinations. [h] Not determined. [i] Strong acid fraction (4.97 wt % of distillate). Results in Table VI were obtained on a total (strong plus weak) acid fraction (10.4 wt %).

neutralization of weaker acids. The latter effect causes results for carboxylic acids to be high, since carboxylic acid content is computed from the ratio of the first equivalence point (assumed to be carboxylic acids) to the total neutralization factor. Without a petroleum with certified carboxylic content, a more precise assessment of accuracy is not possible.

On the other hand, the agreement between hydroxyl content determined with and without derivatization was surprisingly good, considering that nominal values of ϵ were employed in each case. An independent method for assessing hydroxyl content was not available; several published NMR methods for determining ArOH are currently undergoing evaluation in the authors' laboratory for their applicability to petroleum.

CONCLUSIONS

The highly alkylated nature and generally low concentration of hydroxyl and carboxyl compounds in petroleum, plus the sensitivity of IR to any carbonyl-containing byproducts, place stringent requirements on any derivatization method employed in conjunction with IR analysis of petroleum. The derivatization procedure developed here comes much closer to meeting these requirements than prior methods.

The main advantages of performing chemical derivatization prior to IR analysis are improved sensitivity and elimination of the interference from water in the determination of hydroxyls, decreased interference from other carbonyl compounds in the determination of carboxylic acids, and an overall reduction in the effects of hydrogen bonding in analysis of other types. These advantages become more significant as the average boiling point of the analytes increases—reaching the point of virtual necessity for distillation residues and very heavy crudes. The main disadvantage is the extra time and effort involved.

Precision in IR analysis was similar for derivatized and underivatized samples or pure compounds. Thus, variation in product yields and recoveries or other errors attributable to the derivatization, per se, were negligible compared to those normally encountered in IR measurements. Results from the present method applied to acid fractions generally were comparable to those from other techniques, including IR without derivatization, and often were slightly lower, which is consistent with a lower degree of interference from other acidic compound classes. A comparison of results obtained on derivatized whole fuels/distillates versus those from their respective acid fractions indicated negligible interference from neutral or basic components as well.

The relative dependence of IR response on structure for derivatives was comparable to that normally encountered for other functional groups—ca. ±10%. Trifluoroacetates of 3-methylphenol and 3- or 4-isopropylphenol yield "typical" molar absorptivities and are suitable for calibration of ArOH response. The response of alcohol derivatives is about two-thirds that of ArOH. 2,2,2-Trifluoroethyl esters of petroleum-derived carboxylic acids yield a significantly lower molar absorptivity than that of any of the pure compounds investigated. At present, an authentic petroleum carboxylic acid concentrate is recommended for calibration of carboxyl response. Although the accuracy obtainable in functional group analysis of unknown, complex mixtures like petroleum is inherently limited by their variable composition, which in turn affects their average IR response, it is nevertheless adequate for the vast majority of potential applications. IR is more cost effective than many competing techniques.

Future work is aimed at extending this approach to analysis of acidic nitrogen compounds and to determination of hydroxyls and carboxyls in distillation residues. In the case of very high boiling materials, the main limitations are deficiencies in separation methods and independent analytical methods needed for verification of results from the current method, rather than inadequacies of the method itself.

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Universal Sulfur Detection by Chemiluminescence

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A universal sulfur detector (USD) capable of measuring both reduced and oxidized sulfur compounds in the low picogram range is described. Products of a hydrogen flame are drawn through a critical orifice into a low-pressure flow system and then mixed with ozone. Sulfur compounds entering the flame produce sulfur monoxide which undergoes a chemiluminescent reaction with ozone. The excited state of sulfur dioxide produced emits light with a peak wavelength of 350 nm. The USD, which has been tested in the real-time mode, has a linear response from sub part per billion by volume (ppbv) to sub part per million by volume S, and has a detection limit of about 0.13 ppbv ($\approx$1 pg of S$\cdot$s^{-1}) with a time constant of 2 s. The molar response to sulfur was found to be identical for the five low molecular weight compounds tested. The USD has no interferences from water vapor or CO_2. Hydrocarbon interference is minimized by adjustment of the residence time of the sample in the flame. The base line signal drift is typically undetectable over 24 h of continuous use.

INTRODUCTION

Sensitive and selective detection of sulfur compounds is of considerable interest in a number of widely diverse fields (*1–3*). Nearly as diverse are the methodologies and detectors reported (*4–9*). By far the most widely used sulfur-selective detector is the flame photometric detector (FPD), which has been reviewed thoroughly by Farwell and Barinaga (*10*). Chemiluminescence detection schemes have also been reported for reduced sulfur species with O_3 (*9*), ClO_2 (*11*), and F_2 (*7*). These have not gained wide acceptance because of interference problems, difficulties in handling reagents such as ClO_2, drastic differences in sensitivity to different species, or lack of detection for oxidized species.

The FPD is based on the production of sulfur atoms in a H_2/O_2 flame, which combine to form electronically excited S_2*. The S_2* has chemiluminescence emission bands at 384 and 394 nm (*10*). The intensity of the emission is fundamentally nonlinear in sulfur concentration and has significant interferences from other species, which can be either in the positive or negative direction (*10*). The addition of sulfur compounds at a constant background concentration has been used to linearize the FPD output and decrease the detection limit but decrease the dynamic range. When used as a real-time detector for atmospheric monitoring, the FPD suffers from H_2O and CO_2 interference (*12*). Hydrocarbons are the major source of interference in gas chromatographic uses (*10*).

Theoretical and experimental studies have shown that a large portion of sulfur entering a flame produces SO (*2, 13, 14*). In fact, the SO is present at concentrations about 10 times higher than that of atomic sulfur. Even though SO is a free

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