

SEPARATION AND ANALYSIS OF HYDROXYAROMATIC SPECIES IN LIQUID
FUELS II. COMPARISON OF ArOH IN SRC-II COAL LIQUID,
WILMINGTON, CA, PETROLEUM AND OSCR SHALE OIL

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INTRODUCTION

Part I of this series, presented in the symposium, "New Applications of Analytical Techniques to Fossil Fuels," describes a general analytical approach for detailed analysis of hydroxyaromatics (ArOH) in fuels (1). An inherent step in development of analytical methods is evaluation of their performance on actual samples. Thus, ArOH concentrates were isolated from a wide spectrum of fuels, chemically derivatized, and analyzed in detail by GC/MS. Results from three of the fuels studied during development of the analytical method are presented here to 1) demonstrate the viability of the analytical methodology and more importantly to 2) contrast the levels and types of ArOH in three distinctly different fuel types: petroleum, shale oil, and liquified coal.

Although numerous compositional studies on one or more fuels of a given type have been published, papers comparing composition of different types of fuels are quite rare. Tomkins and Ho (2) compared levels of selected polycyclic aromatic amines in coal liquids, shale oil and petroleum, and Allen, *et al.* (3), compared overall structural profiles of heavy fractions from a coal liquid, shale oil, petroleum and tar sand. A comparison of the levels of phenol, and C₁- and C₂-phenols in a shale oil and a coal liquid has also been published (4). These three papers are a fairly complete listing of published reports comparing different fuel types.

Prior work on ArOH in individual fuel types has shown coal liquids to contain phenols, indanols/tetralinols, hydroxybiphenyls/hydroxyacenaphthalenes, hydroxyfluorenes, and naphthylphenols (5,6). A study on coal tar cited similar compounds plus dibenzofuranols and pyrenols/fluoranthenols (7). White and Li (8) identified over 20 specific ArOH compounds ranging from 6 to 15 carbons in an SRC-II coal liquid. McClennen, *et al.* (9), studied changes in phenol and indanol distributions induced by hydrotreating, and Scheppele, *et al.* (10), studied ArOH and multihydroxylated aromatics in raw and hydrogenated anthracene oil. Recently, hydroxylated thiophenic compounds and nitrogen heterocycles have also been identified in coal liquids (11,12). Finally, ArOH in coal liquid oils, asphaltenes, and preasphaltenes have been compared (13); the hexane-insoluble fractions contain higher levels of ArOH and generally more polycyclic ArOH.

Shale oil contains mostly phenols, with lesser amounts of naphthols and trace levels of higher-ring ArOH (14-17). Dihydroxyaromatics are also present (16,17).

Petroleum ArOH cover a wide range of structural types and molecular weights from phenol up to highly substituted polycyclic ArOH (18-21). ArOH usually make up less than 10% of the total acidic compound types in petroleum, whereas they are the dominant acidic class in coal liquids and shale oil.

EXPERIMENTAL

Fuels selected for this work were an SRC-II coal liquid from the Fort Lewis pilot plant run 77SR-12 (22,23), an *in situ* produced shale oil, OSCR 76-552, kindly supplied by the Western Research Institute, Laramie, WY, and a Wilmington, CA, petroleum which underwent extensive study during the API-60 project (18,19,24).

The analytical methodology for isolation and analysis of ArOH is described in a separate preprint (1). The results presented here are a composite of the GC/MS analysis of underivatized, silylated and acylated ArOH concentrates; although, as previously explained (1), analysis of acylated ArOH usually gave the most comprehensive data set.

RESULTS AND DISCUSSION

Only qualitative or semiquantitative results are presented, since the relative GC/MS responses of various derivatized ArOH are unknown. The general format for presentation of data is based on the commonly used Z-number convention, where the Z-number of a given ArOH series is defined by its empirical formula: $C_nH_{2n+Z}O$. Although the ArOH were analyzed as either acylated or silylated derivatives, all the tables report ArOH composition on an underivatized basis.

Table 1 shows results from the distillation and liquid chromatographic separations to obtain whole acid and ArOH concentrates. The relative abundance of ArOH is coal liquid > shale oil >> petroleum, as expected. Also, the percentage of total acids attributed to ArOH is greatest in the coal liquid and least in the petroleum.

Tables 2(A-I) show the number of isomers separated and detected by GC/MS at each carbon number of the major ArOH Z-series for the three fuels. If a given distillate contained no members of a given series, it is omitted from that section of Table 2.

Results for the Wilmington 370-535° C ArOH are not included in Table 2. Current GC/MS profiles of this fraction do not show sufficient chromatographic resolution to obtain more than a superficial analysis of ArOH present. Acylation did decrease the retention of ArOH present, as expected, but did not improve chromatographic resolution enough for detailed analysis. The few peaks which were resolved corresponded to Z-series ranging from -16 O to -24 O. Fragment ions from these series do not correspond with those present in synfuel ArOH--probably because the Wilmington ArOH are primarily less condensed structures with naphthene rings attached to 1- and 2-ring aromatic nuclei.

Table 3 compares the overall composition of ArOH in the three fuels. All three fuels contain phenols, indanols/tetralinols and members of the -14 O and -16 O series of ArOH. The major differences between the fuels lie in the relative abundances of these series and in the individual structures of ArOH in these and the other series present. These differences are discussed below for each ArOH series.

-6 O

The coal liquid contains the largest overall abundance of phenols as seen by the large proportion (10.3% of the whole oil) of ArOH in the 200-325° C distillate (Table 1) and by the fact that they are the major ArOH type in that distillate (Table 3). The coal liquid GC/MS profile showed large peaks corresponding to individual C₂-C₄ phenol isomers, which in total probably accounted for nearly half of the ArOH present. C₅- and C₆-phenols were relatively minor components in the coal liquid and no C₇- or higher homologs were detected.

The distribution of phenolic homologs in the Wilmington petroleum was similar to that of the coal liquid (Table 2A). However, their overall abundance was lower by about three orders of magnitude, as estimated by the total ArOH present (225-370° C ArOH were 0.03% of the whole crude, Table 1) and the intensity of phenolic GC/MS peaks observed.

On the other hand, the distribution of phenols in the shale oil was markedly different than the other fuels. Species with a total alkyl carbon number up to C₁₇ were observed, and mass spectral fragmentation patterns indicated predominantly straight-chain alkyl substituents or substituents with one or two methyl-branches. In total, phenolic species probably accounted for two-thirds of the shale oil ArOH.

-8 O

Indanols/tetralinols were present in all fuels, but were not a dominant series in any fuel. Their abundance was highest in the coal liquid, since they were the second most prevalent type in the 200-325° C ArOH concentrate which comprised 10.3% of the whole SRC-II oil. Based on mass spectral fragmentation patterns (1), indanols dominated tetralinols in all fuels. The predominance of indanols over tetralinols has been reported previously (5,9). Due to the relatively low amounts of naphthols observed in all fuels, especially the coal liquid, it seems likely that this series may be largely derived from hydrogenation of naphthols during coal liquifaction, shale retorting and petroleum maturation processes.

-10 O

This series was not conclusively identified in any fuel. McClennen, *et al.* (9), alluded to the presence of hydroxytetrahydroacenaphthalenes in their study of coal liquid ArOH, and the authors have tentatively identified a -10 O ArOH series of compounds in a marine diesel fuel. Overall, -10 O ArOH compounds appear to be present at low levels or nonexistent in most fuels.

-12 0

Naphthols were positively identified in the petroleum and shale oil ArOH concentrates, but they were not major components in either fuel. Based on the intensity of the GC/MS peaks and overall amount of ArOH present, naphthols comprised a much more significant percentage of the shale oil than any other fuel. Minor amounts of a higher molecular weight -12 0 series, corresponding to tricycloalkylphenols, have tentatively been identified in the SRC-II >325° C ArOH concentrate.

-14 0

Compounds in this series were quite prevalent in the coal liquid and petroleum, but relatively minor in the shale oil. As discussed earlier (1), distinguishing between the various isomers of this series on the basis of mass spectral fragmentation patterns is quite difficult. Possible structures include hydroxybiphenyls, hydroxyacenaphthalenes, benzindanols and benztetralinols. Taking into account the uncertainties in mass spectral interpretation, the petroleum and coal liquid are nevertheless believed to contain all of the possible -14 0 isomers, with hydroxybiphenyls being the dominant species. Figure 1A shows evidence for presence of benztetralinols in the Wilmington petroleum ArOH concentrate. Thus, one or both of the acylated parent (M+) -14 0 species, represented by ions at m/e 364 and 350, give rise via loss of 42 or 28 mass units respectively to the fragment ion at m/e 322. Although it is possible that the m/e 322 ion is a parent (M+) ion resulting from some abnormally high-boiling -14 0 isomer, its production via retro-Diels-Alder loss of propylene or ethylene is much more likely. This fragmentation behavior is characteristic of cyclohexylaromatic systems (25), and thus indicates a benztetralinol structure. The intense ion at m/e 225 in Figure 1A occurs from loss of $CF_3C(O)^+$ from the m/e 322 ion; the ion at m/e 344 is a molecular ion from a coeluting -20 0 species. Also, this and other spectra in Figure 1 indicate the complexity of spectra from later eluting GC/MS peaks.

-16 0

In the coal liquid and shale oil, this series consists largely of hydroxyfluorenes. In the petroleum, the major structural types are probably phenylindanols/phenyltetralinols. Next to -14 0 compounds, -16 0 compounds were the second most prevalent type in the SRC-II >325° C ArOH. On the other hand, the -16 0 series was a very minor one in the shale oil, and intermediate in the petroleum. The -16 0 series was the most condensed ArOH species found in shale oil.

Besides hydroxyfluorenes, the coal liquid contains -16 0 compounds which produce retro-Diels-Alder fragmentation patterns similar to those discussed for -14 0 compounds. Figure 1B shows an example where the parent (M+) ion at m/e 334 gives rise to a 306 fragment. This pattern is consistent with either a phenyltetralinol or dicycloalkynaphthol (e.g., hexahydropyrenol) structure.

-18 0

Only the >325° C coal liquid ArOH concentrate showed easily detectable amounts of this series. Based on its mass range (Table 2F) and the prevalence of phenanthrenes/anthracenes in coal liquids, this series is believed to be hydroxylated phenanthrenes/anthracenes.

-20 0

This series was found in both the coal liquid and petroleum, but was more prevalent in the coal liquid. Possible structures include phenylnaphthols, cycloalkylphenanthrols and dihydropyrenols. Figures 1 (D-F) show example acylated -20 0 series spectra representing the different types present in the coal liquid >325° C residue. Figure 1D shows a fragmentation pattern most likely produced from a C₁-phenylnaphthol. The relatively large M-69 ion (m/e 261) from loss of CF₃ is also exhibited by hydroxybiphenyls--which would be expected to give spectra analogous to phenylnaphthols. Biphenyls also show a pronounced tendency to form another carbon-carbon bridging bond yielding a m/e 152 ion (26); analogous behavior by phenylnaphthols would yield fluoranthene. Thus, the m/e 218 ion in figure 1D should have a structure analogous to an oxyfluoranthene, and the m/e 202 ion a structure similar to fluoranthene itself.

Figure 1E shows a fragment corresponding to loss of 28 (C₂H₄) from the parent ion at m/e 358. This pattern is typical of a C₁-cyclohexylphenanthrol compound type. No M-69 ion is apparent, but the M-97 (m/e 233) fragment is fairly intense.

Figure 1F shows a large parent ion (m/e 330) relative to fragment ions as well as a long GC retention time relative to its molecular weight. For example, the retention of the compound of equal mass in Figure 1D was only 22.5 min, and the retention of the compound 28 mass units heavier in Figure 1E was only 0.3 min longer than that in Figure 1F. These facts all point to a highly condensed species such as C₁-dihydropyrenol. A dihydropyrene species would be expected to form pyrene (m/e 202) during fragmentation (25), as observed in Figure 1F. Also, Figure 1F correlates closely with Figure 1C, which is believed to be a pyrenol. Both figures show a fragment at m/e 189 corresponding to loss of CO from the m/e 217 fragment. Phenol shows this same fragmentation pattern (27); thus a 1- or 2-pyrenol structure is the most logical for Figure 1C, and a 1- or 2-hydroxy-4,5-dihydromethylpyrene structure is the best choice for Figure 1F. For example, 4-hydroxypyrene or 9-hydroxy-4,5-dihydropyrene would not be expected to give rise to a fragmentation pattern promoting loss of CO to form a cyclopentadienyl-type cation.

Structures for -20 0 ArOH in the petroleum could not be defined as well as those from the coal liquid because of coelution of -14 0 and -16 0 compounds which complicated the resulting spectra.

-22 0, -24 0

As discussed previously, the coal liquid contained -22 0 compounds believed to be pyrenols. The possibility of other types of ArOH in this series could not be definitely confirmed or ruled out. -24 0 Species in the coal liquid appear to be cycloalkylpyrenols rather than chrysenols or some

other condensed species based on the mass range observed. Again, because of the complexity of the petroleum ArOH spectra, no definite structures for -22 O species were assigned. Based on the mass range of -22 O ArOH in the petroleum, loosely condensed structures such as naphthylindanol, naphthylteralinols or hydroxytriphenyls seem the most probable.

Non-ArOH species

In contrast to earlier reports citing no or only trace amounts of carboxylic acids in shale oil (14-17), a major series of aliphatic acids ranging from 5 to 27 carbons was observed here. From C₁₄ to C₂₀, 2-3 isomers were observed at every carbon number; only one isomer was found at most of the other carbon numbers. Silylated fatty acids yielded characteristic fragment ions at m/e 117, 129, 132, 145, and M-15. During liquid chromatographic separation of the shale oil strong acid fraction, the retention region corresponding to carboxylic acids was not cut as a separate fraction but simply lumped into the ArOH fraction (1). Since previous work had not shown presence of significant amounts of carboxylic acids in shale oil and since their presence in the authors' sample could not be detected by the UV (280nm) detector employed for the HPLC separation, there was no apparent reason for cutting a separate carboxylic acid fraction. Based on total ion intensities of silylated carboxylic acids vs. silylated ArOH, carboxylic acids accounted for nearly 50% of the total "ArOH" concentrate. Thus, the result given in Table 1 for concentration of ArOH in shale oil may be high by a factor of two. Figure 2 shows GC/MS total ion chromatograms for underivatized, acylated and silylated shale oil ArOH concentrate. The later eluting, evenly spaced, peaks in the silylated (2C) sample are all aliphatic acids. Since underivatized carboxylic acids chromatograph poorly, they are not evident in the underivatized or acylated samples. The shale oil investigated in this work was retorted *in situ*; carboxylic acids present in oil shale (28) apparently survived temperatures reached during that type of oil recovery process.

Small amounts of nitrogen compounds (1) and carboxylic acids were present in petroleum ArOH concentrates, largely from chromatographic overlap usually encountered in liquid chromatographic separations. Coal liquid ArOH concentrates were virtually free of non-ArOH compounds.

CONCLUSIONS

The two most distinguishing features of coal liquid ArOH are their high concentration in the whole oil and presence of condensed ring species such as pyrenols and partially hydrogenated pyrenols. Shale oil ArOH are predominantly phenols, some which possess alkyl side chains up to nearly 20 carbons. Petroleum contains relatively low amounts of ArOH but has the greatest diversity of types and isomers present.

The methodology used for analysis of ArOH generally performed well on the wide range of samples examined, except in the case of the 370-535° C petroleum ArOH concentrate. Further improvements including more liquid chromatographic separations, higher resolution GC columns, etc., will be needed for analysis of that sample or one of similar complexity.

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TABLE 1. - Results from distillation and liquid chromatographic separations

Fuel	Distillate Boiling Range (°C) ¹	Distillate Yield (Wt%)	Total Acids (Wt%)		AroH (Wt%)		Whole Fuel Basis
			Distillates Basis	Whole Fuel Basis	Distillate Total Acid Basis	Distillate Basis	
Coal liquid	200-325	66.3	25.1	16.6	62	15.5	10.3
	325	16.0	30.9	4.94	40.0	12.4	1.98
Shale oil	>200	89.8	16.3	14.6	34.3	5.57	5.00
Petroleum	225-370	25.2	2.24	0.56	5.7	0.13	0.03
	370-535	24.7	10.1	2.49	4	0.4	0.1

¹ Phenol b.p. = 182° C, p-creso1 b.p. = 202° C.

TABLE 2A. - Results for -6 0 series of ArOH (C_nH_{2n-6}O)¹

C _x ²	Molecular Weight	Fuel (Distillate Boiling Range, °C)		
		Coal Liquid (200-325)	Shale Oil (>200)	Petroleum (225-370)
		Number of Isomers ³		
C ₀	94	0	1	1
C ₁	108	2	3	3
C ₂	122	6	6	5
C ₃	136	9	11	4
C ₄	150	4	12	5
C ₅	164	4	12	5
C ₆	178	2	9	2
C ₇	192		9	1
C ₈	206		11	1
C ₉	220		7	
C ₁₀	234		7	
C ₁₁	248		7	
C ₁₂	362		4	
C ₁₃	376		3	
C ₁₄	290		1	
C ₁₅	304		2	
C ₁₆	318		2	
C ₁₇	332		2	

¹ All -6 0 compounds were phenols.

² C_x = total number of carbons in alkyl substituents.

³ Number of isomers detected at each alkyl homolog.

TABLE 2B. - Results for -8 O series of ArOH (C_nH_{2n-8})¹

C_x	Molecular Weight	Fuel (Distillate Boiling Range, °C)		
		Coal Liquid (200-325)	Shale Oil (>200)	Petroleum (225-370)
		Number of Isomers		
C ₀	134	2	2	1
C ₁	148	7	6	4
C ₂	162	8	10	7
C ₃	176	4	11	6
C ₄	190	4	12	4
C ₅	204		7	1

¹ The dominant structure based on GC/MS fragmentation patterns was indanol for all fuels. Some tetralinols (C₀-tetralinol corresponds to C₁-indanol in mass) were detected in all fuels, however.

TABLE 2C. - Results for -12 O series of ArOH (C_nH_{2n-10})^{1,2}

C_x	Molecular Weight	Fuel ³ (Distillate Boiling Range, °C)	
		Shale Oil (>200)	Petroleum (225-370)
		Number of Isomers	
C ₀	144	2	1
C ₁	158	4	1
C ₂	172	6	2
C ₃	186	6	2
C ₄	200	2	2
C ₅	214	1	

¹ No appreciable amounts of -10 O ArOH were detected in any fuel.

² All -12 O compounds were naphthols.

³ Ions corresponding to naphthols were detected in SRC-II, but they were small in intensity and not definitive enough for a positive identification. A -12 O series corresponding to octahydropyrenols or some similar structure has tentatively been identified in SRC-II >325° C ArOH.

TABLE 2D - Results for -14 0 series of ArOH ($C_nH_{2n-14}O$)

C_x ¹	Molecular Weight	Fuel (Distillate Boiling Range, °C)			
		Coal Liquid (200-325)	(>325)	Shale Oil (>200)	Petroleum (225-370)
C ₀	170	2	0	2	2
C ₁	184	5	10	4	3
C ₂	198	2	19	8	5
C ₃	212		20	8	10
C ₄	226		15	6	12
C ₅	240		11	2	11
C ₆	254		5	1	8
C ₇	268				4
C ₈	282				4
C ₉	296				2

¹ Unsubstituted hydroxybiphenyls and hydroxyacenaphthalenes have molecular weights of 170. C₀-benzindanol has molecular weight of 184, and C₀-benztetralinols have molecular weights of 198. Hydroxybiphenyls are believed to be the dominant -14 0 structure, but all other isomers are also believed to be present.

TABLE 2E. - Results for -16 0 series of ArOH ($C_nH_{2n-16}O$)

C_x ¹	Molecular Weight	Fuel (Distillate Boiling Range, °C)		
		Coal Liquid ^{1,2} (>325)	Shale Oil ¹ (>200)	Petroleum ³ (225-370)
		Number of Isomers		
C ₀	182	4	1	0
C ₁	196	12	3	0
C ₂	210	19	5	0
C ₃	224	19	3	1
C ₄	238	15	2	5
C ₅	252	6		6
C ₆	266	1		4
C ₇	280			2
C ₈	294			1

¹ Predominantly fluorenols. MW C₀-fluorenol = 182.

² Compounds analogous to hexahydroxyrenols and phenyltetralinols are also present. MW C₀-hexahydroxyrenol = 224.

³ Based on mass, predominantly phenyltetralinols.
MW C₀-phenyltetralinol = 224.

TABLE 2F. - Results for -18 0 series of ArOH ($C_nH_{2n-18}O$)¹

C_x	Molecular Weight	Fuel (Distillate Boiling Range, °C)
		Coal Liquid (>325)
		Number of Isomers
C ₀	194	4
C ₁	208	5
C ₂	222	9
C ₃	236	5
C ₄	250	3

¹ Presumably hydroxyphenanthrenes/anthracenes. (MW C₀ = 194)
A spectrum of a -18 0 compound free of other types was not obtained, so positive identification was not possible.

TABLE 2G. - Results for -20 0 series of ArOH ($C_nH_{2n-20}O$)

C_x	Molecular Weight	Fuel (Distillation Boiling Range, °C)	
		Coal Liquid ¹ (>325)	Petroleum ² (225-370)
C_0	220	8	1
C_1	234	20	1
C_2	248	16	4
C_3	262	10	4
C_4	276	3	4
C_5	290	1	1

- ¹ Dihydroxyrenols, phenylnaphthols, and cycloalkylphenanthrols/anthracenols. MW C_0 -dihydroxyrenol, C_0 -phenylnaphthol and C_0 -benzacenaphthalenol = 220.
² Unknown structure.

TABLE 2H. - Results for -22 0 series of ArOH ($C_nH_{2n-22}O$)

C_x	Molecular Weight	Fuel (Distillation Boiling Range, °C)	
		Coal Liquid ¹ (>325)	Petroleum ² (225-370)
C_0	218	2	0
C_1	232	3	0
C_2	246	2	0
C_3	260	3	2
C_4	274	3	2
C_5	288	1	1

- ¹ Pyrenols/fluoranthenols. MW C_0 = 218.
² Unknown. Possibly naphthylindanol, naphthyltetralinols and/or hydroxytriphenyls. (MW of C_0 homologs = 260, 274, and 246, respectively.)

TABLE 2I. - Results for -24 O series of ArOH ($C_nH_{2n-24}O$)

<u>C_x</u>	<u>Molecular Weight</u>	<u>Fuel (Distillation Boiling Range, °C)</u>	
		<u>Coal Liquid¹</u> (>325)	
		<u>Number of Isomers</u>	
C ₀	258	4	
C ₁	272	3	

¹ Probably cycloalkylpyrenols/cycloalkylfluoranthenols. MW C₀-cyclopentylpyrenol = 258. MW C₀-chrysenol = 244 (not observed).

TABLE 3. - Summary of ArOH in the three fuel types

	Fuel (Distillation Boiling Range, °C)		
	Coal Liquid (200-325)	Shale Oil (<200)	Petroleum (225-370) (370-535)
Major ArOH compound type Present	phenols	phenols	-14 0 Z-series ≥ -16 0
Other important ArOH types	indanois/ tetralinois	indanois/ tetralinois, naphthois	phenols, -16 0, -20 0
Unique structural features	lack of naphthois	long chain C ₁₀ -C ₁₇ phenols	cycloalkyl ArOH
Non-ArOH compounds present	pyrenois and partially hydro- genated pyrenois	none	cycloalkyl ArOH
Overall complexity of concentrate	simple	intermediate	carboxylic acids complex very complex

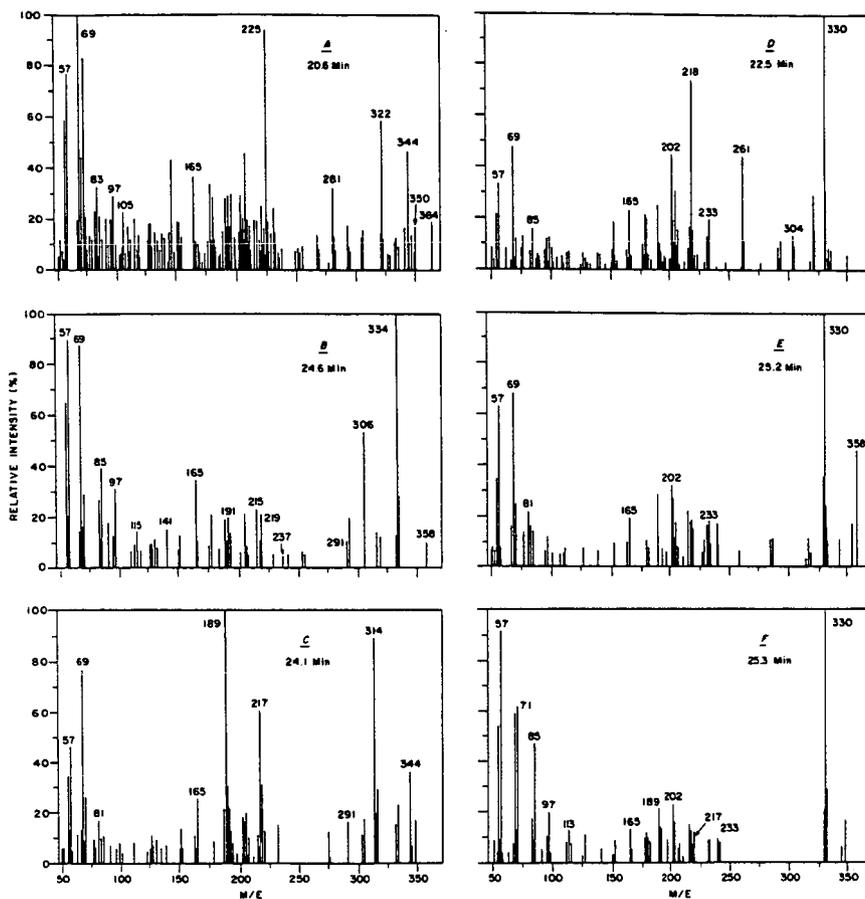


Figure 1 - Mass spectra from GC/MS analysis of acylated Wilmington 225-370°C (A) and SRC-II >325°C (B-F) ArOH concentrates. The GC retention times are noted on each. (A) shows primarily -14 O compounds (m/e 344 is -20 O) (B) shows primarily -16 O (m/e 314 is -20 O) (C) shows -22 O (m/e 314) with minor amounts of other series and (D-F) shows different types of -20 O compounds. For details, see text.

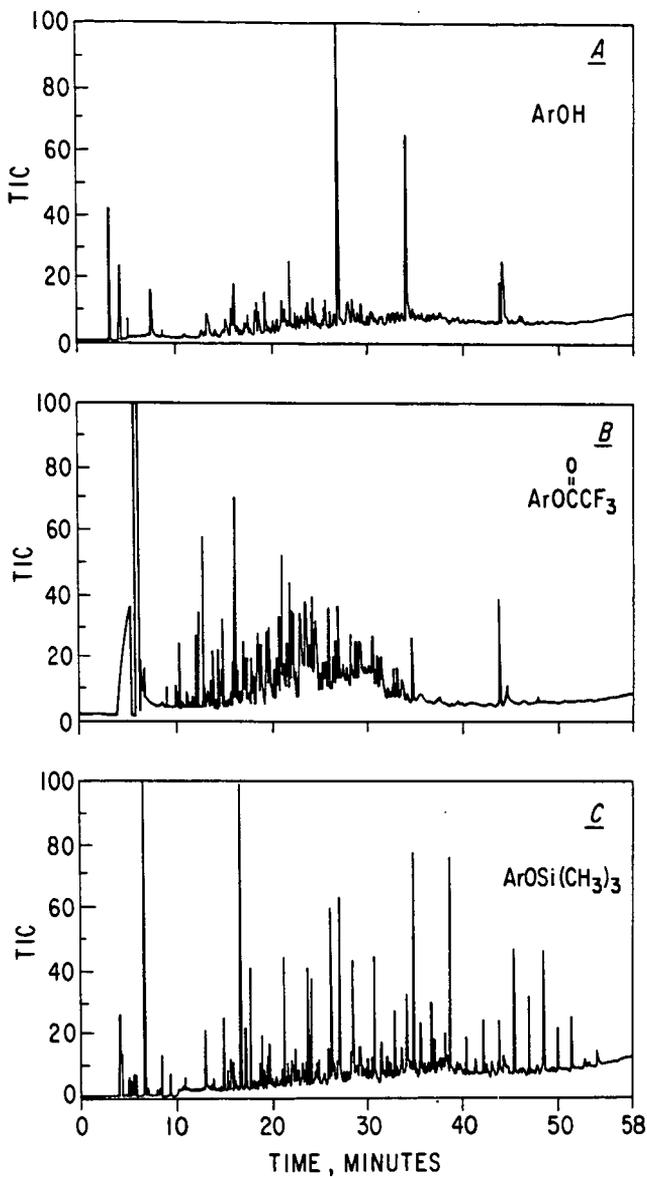


Figure 2 - Total ion GC/MS traces of plain and derivatized >200° C OSCR shale oil ArOH concentrate. Later eluting peaks in (C) are silylated aliphatic acids. Note the high degree of resolution obtained via acylation (B).