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LIQUID CHROMATOGRAPHY ON SILICA USING MOBILE PHASES CONTAINING ALIPHATIC CARBOXYLIC ACIDS

II. APPLICATIONS IN FOSSIL FUEL CHARACTERIZATION

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SUMMARY

High-performance liquid chromatographic (HPLC) separations on silica columns using medium polarity mobile phases containing normal chain aliphatic carboxylic acids are applied to characterization of acid and base extracts of fuels. Separations performed on an SRC-II coal liquid and a Wilmington, CA, petroleum illustrate the utility of the HPLC method for rapid assessment of functionalities present in acid and base extracts of fuels. The technique is currently limited by the HPLC detectors available; complex samples such as fuels will require more sophisticated detectors.

Separation of base extracts into hydrocarbon (impurity), pyrrole/phenylaniline, aniline/thiazole and pyridine/dinitrogen types as a function of the chain length of the carboxylic acid in the mobile phase is discussed. Similar functional group-type separations of acid extracts are also presented as a function of mobile phase composition. Applications of the technique to assessing purity of fractions obtained from other separation schemes, analyzing high-boiling distillates and residua, and monitoring effects of catalytic hydrogenation are presented.

INTRODUCTION

This paper reports the application of liquid chromatographic (LC) systems developed during work with model compounds[1] to separations of polar extracts of fossil fuel liquids. Correlations developed during the model compound study, including retention time–functional group, retention time–solute basicity, retention time–carboxylic acid chain length, and peak shape–carboxylic acid chain length, will be applied here toward qualitative interpretation of chromatograms of fuel extracts.

Numerous approaches exist for analysis and characterization of polar compounds such as those found in fuels. For example several excellent gas chromatography–mass spectrometry (GC–MS) papers on characterization of nitrogen containing compounds in fuels and environmental samples have been published recently[2–6]. On the other hand, simpler techniques such as non-aqueous titration are also used[7].

Traditionally, this type of problem has been attacked using preparative-scale, gravity-flow LC (mostly on alumina) followed by application of one or more spectroscopic techniques for characterization of the fractions[8–21]. MS and infrared (IR) spectroscopy are used extensively; nuclear magnetic resonance (NMR), UV and fluorescence are employed less often. Size-exclusion (SEC), paper and ion-exchange chromatography are sometimes used in conjunction with adsorption LC. Low volatility of many of the acidic and basic compounds in fuels has limited the use of GC[22,23].

The outstanding disadvantage of the above approaches, perhaps with the exception of non-aqueous titration, is their extensive time and manpower requirements. Clearly, a method which would give at least general qualitative and gross quantitative information in less than one day would be desirable.

Modern high-performance liquid chromatography (HPLC) shows promise as such a method. Both reversed- and normal-phase separations of phenols[24] and azaarenes[25–33] have been reported. SEC has also been used[34–36]. Much of the work has been done on fairly extensively prefractionated materials, however. Also, none of the techniques reported previously has shown sufficient resolution capabilities and/or retention–functional group correlation to serve as a rapid and general method for fuel characterization.

EXPERIMENTAL

Apparatus

Most of the HPLC work was done with the same apparatus used for the model compound study[1]. That setup consisted of two Waters Assoc. M6000 pumps, a Waters Assoc. M660 solvent programer, a Waters Assoc. WISP autoinjector and two variable-wavelength UV–visible detectors connected in series.

In addition, a Spectra-Physics M8000 LC was used for a small portion of the HPLC work reported here. A Waters Assoc. WISP and M440 dual-channel detector completed that system.

HPLC columns were packed in this laboratory after the method of Coq *et al.*[37].

Cheminert® type columns (Applied Science Labs., State College, PA, U.S.A.) and a low-pressure pump (Fluid Metering) were used for isolation of the acid and base extracts of the fuel samples by non-aqueous ion-exchange chromatography. The columns were water jacketed for temperature control.

Materials

Halogenated solvents were Burdick & Jackson Labs. (Muskegon, MI, U.S.A.) "distilled in glass" grade. Heptane was obtained from Phillips Petroleum (pure grade; Bartlesville, OK, U.S.A.) and ethanol from U.S. Industrial Chemical Co. (New York, NY, U.S.A.). Acetic, propanoic and decanoic acids were obtained from Fisher Scientific (Pittsburgh, PA, U.S.A.), Mallinckrodt (St. Louis, MO, U.S.A.) and Aldrich

(Milwaukee, WI, U.S.A.), respectively. The purification of all the above mobile phase components was described earlier[1].

HPLC column packing materials were obtained from E. Merck (Darmstadt, G.F.R.). LiChrosorb Si-60 silica in both 5- and 10-μm sizes was used. Columns were constructed of polished 316 stainless-steel tubing and zero dead volume fittings commonly available from many suppliers.

Macroreticular ion-exchange resins were obtained from Bio-Rad Labs. (Richmond, CA, U.S.A.). The anion resin (AG-MP-1, 200–400 mesh) was purified according to Table I. The cation resin (AG-MP-50, 200–400 mesh) was treated similarly, except that the order of washes No. 1 and 3 (Table I) was reversed. The purification scheme in Table I is similar to the one recommended by McKay[38]. After purification, the resins were transferred as cyclohexane slurries to brown bottles for storage.

TABLE I

PURIFICATION SCHEME FOR MACROPOROUS POLYSTYRENE–DIVINYLBENZENE ION-EXCHANGE RESINS USED IN ISOLATION OF ACIDS AND BASES FROM FUELS

Notes: (1) Since the anion resin is in the OH^- form, exposure to air should be minimized to prevent CO_2 adsorption. (2) Due to the extreme difference in density between dichloromethane and pentane, it is best to manually wash out the majority of the dichloromethane prior to starting the pentane extraction. (3) Sometimes removal of resin fines via aqueous slurrying and decanting is necessary prior to purification. (4) All washing solvents should be "distilled in glass" quality.

Elution order (anion resin)	*Reagent*	*Amount (l)**
1	1–2 *N* Hydrochloric acid	10
2	Water	3
3	1–2 *N* Sodium hydroxide	10
4	Water	5**
5	Methanol–water (1:1)	5–10***
6	Methanol	Recycle in Soxhlet, for 24 h §
7	Dichloromethane	Recycle in Soxhlet, for 24 h §
8	*n*-Pentane	Recycle in Soxhlet, for 24 h §

* Per 454 g resin.

** Test with pH paper.

*** Test effluent by running a UV scan.

§ Alternatively, wash with ≈ 10 l of each in a Buchner funnel.

Cyclohexane (98%, Phillips) used in the ion-exchange work was purified by passing each gallon (3.79 l) through a pair of 2 × 0.025 m columns filled with activated carbon (No. 5-690A; Fisher Scientific) and 1:1 silica–alumina (upper half of column, 400°C activated alumina; lower, 200°C activated silica), respectively.

The samples dealt with in this report were a Wilmington, CA, petroleum and an SRC-II coal liquid. The distillation and hydrocarbon-type characterization of the Wilmington sample has been published[39]. A similar breakdown of the coal liquid, obtained from Pittsburg and Midway Coal Mining (Run No. 77 SR-12; Merriam, KS, U.S.A.), has not yet been reported, although the distillation was similar to that described by Dooley *et al.*[40].

Procedure

Obtaining polar extracts. Approximately 10 g of each distillate were dissolved in 45 ml cyclohexane, filtered (if necessary), warmed to 40°C and pumped (1 ml/min) onto a pair of 0.9 × 74 cm anion (placed first) and cation resin columns maintained at 40°C. Hydrocarbons were eluted by pumping 3 dead volumes of eluting solvent (≈ 160 ml) through the system at 1–2 ml/min. The resins were removed from the columns into Soxhlet thimbles placed inside beakers. Acids were Soxhlet extracted with a formic acid–benzene azeotrope; 10 ml of reagent grade formic acid were added to 200 ml of benzene in the Soxhlet pot. Bases were extracted using $\approx 10\%$ isopropylamine in benzene. To avoid a very exothermic reaction in the Soxhlet thimble, the amine must be added in small increments to the benzene to eventually reach a concentration near 10% (v/v). Soxhlet extractions were usually run overnight. The extracts were filtered through 0.5-μm PTFE membranes, and solvents removed in roto-evaporators. During solvent removal, additional benzene was added to the acid fraction to ensure complete formic acid removal as the azeotrope. Extra benzene was often added to the bases also, to aid in water removal.

Many fuel samples contain cyclohexane-insoluble materials. In these cases, the sample or distillate is dissolved in dichloromethane and run as above (at room temperature). Solvent is removed from the "hydrocarbon" fraction, which is redissolved in cyclohexane and rerun as above. Thus, five fractions are eventually obtained: hydrocarbons, strong acids and bases (dichloromethane run), and weak acids and bases (cyclohexane run). If the sample is not completely soluble in dichloromethane, toluene is substituted. Any toluene insoluble material is reported as "residue". Also, if the sample or distillate is believed to contain over 25% (w/w) of either acids or bases, an extra column of the appropriate type is inserted into the system. Often the percent of the capacity of each column occupied by the sample at a given time during a run can be visually assessed and extra columns inserted if needed.

For comparison with extracts obtained by the above method, some distillates were extracted with solutions of 1 *N* K_2CO_3, NaOH and HCl in water–methanol (1:2) to effect separation of acid and base fractions. Details of the procedure have been outlined elsewhere[40–42].

HPLC

Portions (1–4 mg) of the various extracts were dissolved in 2 ml dichloromethane in vials appropriate for the HPLC autoinjector. Chromatographic conditions using Waters Assoc. equipment were the same as those used in an earlier study with model compounds[1] and are summarized in Table II. Table III summarizes analogous conditions for the Spectra-Physics equipment, which has ternary gradient capabilities.

RESULTS AND DISCUSSION

Comparison of the performance of mobile phases containing acids of different chain length

Fig. 1 shows chromatograms of a base extract of a mid-boiling SRC-II distillate. Gradient 2 (Table II) was used, which means that the greatest resolution was obtained for pyridine-type components. A clear trend exists in the degree of reso-

TABLE II
HPLC CHROMATOGRAPHIC CONDITIONS —TWO-PUMP SYSTEM

Gradient number	1	2
Column length × diameter (cm)	25.0 × 0.46	16.3 × 0.46
Precolumn length × diameter (cm)	7.0 × 0.46	7.0 × 0.46
Column packing (SiO_2, Merck)	Si-60, 5 µm	Si-60, 10 µm
N (average plates/m)	10–15,000	8–10,000
Precolumn packing (SiO_2, Merck)	Si-60, 10 µm	Si-60, 10 µm
Flow-rate (ml/min)	2.0	2.0
Average back pressure (p.s.i.)	1200	1200
Chart speed (cm/min)	0.5	0.5
Gradient conditions:		
Initial %B→ final %B;	1→100	6→100
Gradient time (min), time at 100%B (min), reequilibration time (min)	30, 2, 20	40, 0, 20
Gradient curve	Linear	Linear
Solvent A	Heptane	1,2-Dichloroethane containing 0.0335 M acid*
Solvent B	Dichloromethane containing 0.0268 M acid* and 0.3% (v/v) ethanol	1,2-Dichloroethane containing 0.0335 M acid* and 8.0% (v/v) ethanol

* Either acetic, propanoic, decanoic or no acid.

lution from the acetic acid-containing system to the system without acid. The much improved retention of the substituted pyridines and quinolines in this boiling range with the acetic, and to a slightly lesser degree propanoic acid-containing mobile phases was predicted from work with model compounds. Even the decanoic acid chromatogram is much superior to the one without acid.

TABLE III
HPLC CHROMATOGRAPHIC CONDITIONS–TERNARY GRADIENT SYSTEM
A = Heptane; B = dichloromethane containing 0.2% (v/v) ethanol and 0.0268 M propanoic acid; C = 93% dichloromethane, 7% (v/v) ethanol containing 0.0335 M propanoic acid.

Column	15 cm × 0.46 cm I.D.; 10 µm Si-60 (E. Merck)
Precolumn	7 cm × 0.46 cm I.D.; 10 µm Si-60 (E. Merck)
N (average plates/m)	10,000
Flow-rate	2.0 ml/min
Chart speed	0.5 cm/min
Temperature	25.0°C

Gradient

time (min)	*%A*	*%B*	*%C*
0	99	1	0
28	6.6	93.4	0
30	0	92.0	8.0
65	0	0	100
begin re-equilibration cycle			
66	0	100	0
70	0	100	0
72	99	1	0
90	99	1	0

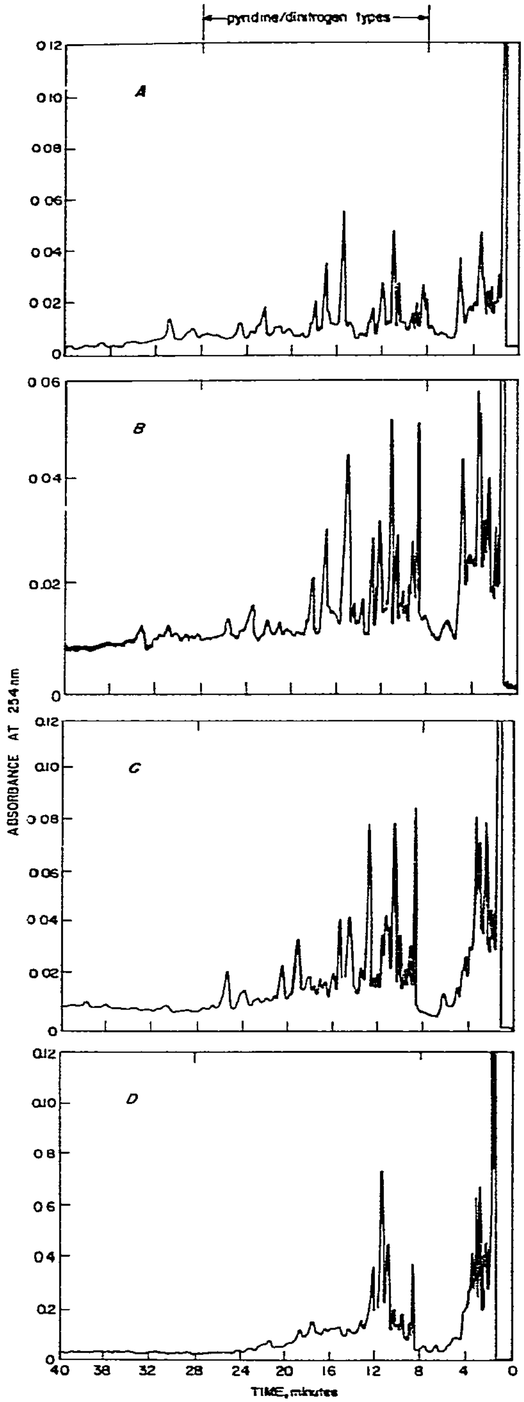

Fig. 1. Gradient 2 chromatograms of a base extract of the SRC-II 200–325°C distillate. A–D were run with acetic, propanoic, decanoic and no acids, respectively. Amounts injected in A–D: 35, 35, 52 and 35 μg, respectively.

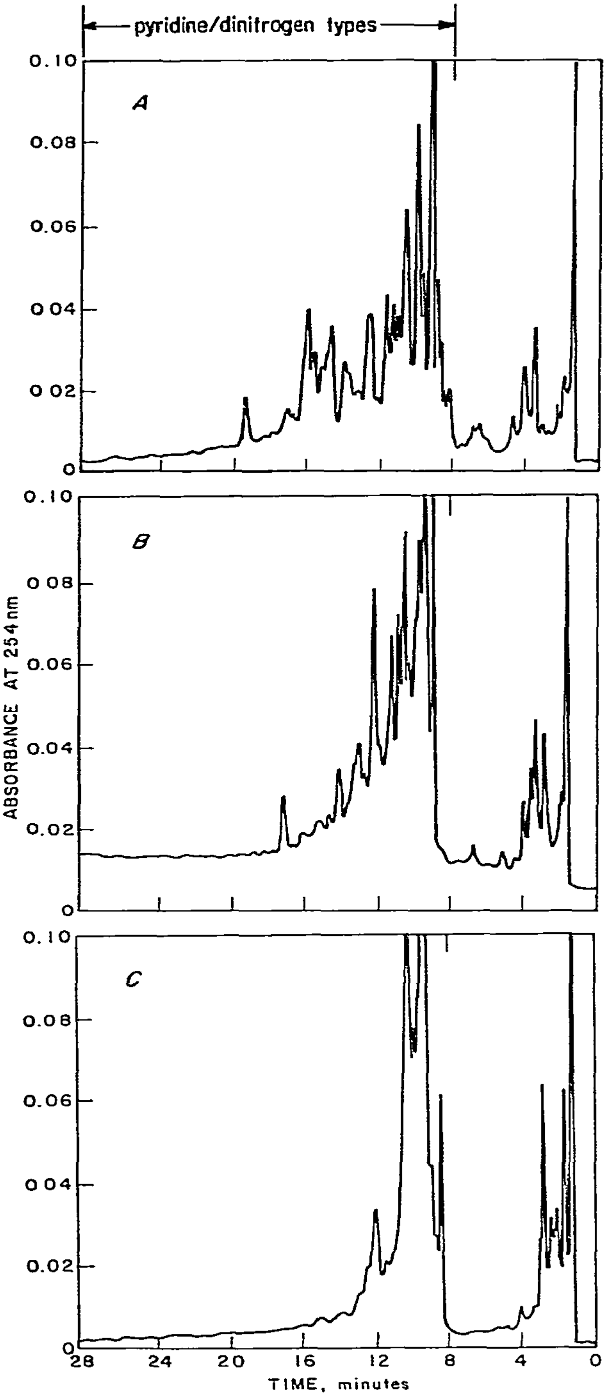

Fig. 2. Gradient 2 chromatograms of a base extract of the SRC-II 325–425°C distillate. A–C were run with acetic, decanoic and no acids, respectively. The amount injected in A–C was 9.6 μg. The chromatogram obtained using propanoic acid was very similar to A.

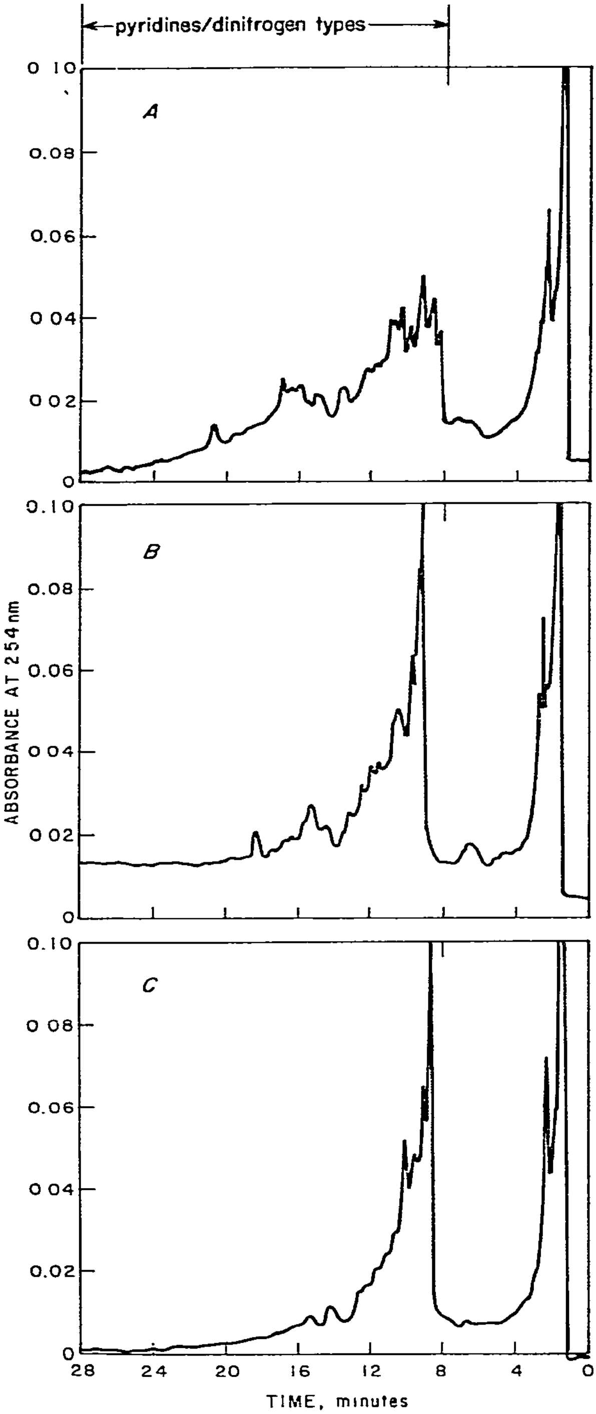

Fig. 3. Gradient 2 chromatograms of the strong bases in the SRC-II 425°C+ residue. A–C were run with acetic, decanoic and no acids, respectively. For each chromatogram 9.4 μg was injected. The chromatogram obtained using propanoic acid had slightly less resolution than A.

Figs. 2 and 3 show gradient 2 chromatograms for the base extracts of the other boiling ranges for the SRC-II coal liquid. The chromatograms of the <200°C bases are omitted because they contained only 3–4 peaks. Also, chromatograms obtained with the propanoic acid-containing mobile phase system are omitted because of their close similarity to those of the acetic acid-containing system.

Even more than in Fig. 1, Figs. 2 and 3 show the dramatic increase in resolution of basic components with the use of short chain acids in the mobile phase. The greater degree of condensation found in aromatic ring systems containing nitrogen atoms as boiling point increases results in an overall decrease of basicity (and hence retention) of the pyridine benzologs. Thus, use of a short chain carboxylic acid in the mobile phase magnifies the slight differences in basicity of these condensed ring compounds which results in much improved resolution.

Fig. 4 shows similar effects for the weakly retained components in the 325–425°C base extract using gradient 1 (Table II). The chromatogram of the system containing no acid was not shown in Fig. 4 because it was similar to the one where decanoic acid was used, except that use of decanoic acid resulted in improved peak shape. As discussed earlier[1], gradient 1 is essentially an expansion of all the components eluting in the first 3–4 min of gradient 2. Here, a clear difference is evident between even the acetic and propanoic acid-containing systems. The number of components eluting in the retention region typical of anilines clearly increases in the order decanoic > propanoic > acetic. This is consistent with model compound work which showed that acetic acid enhances the retention of anilines to such a great extent that some of the more basic anilines are not eluted in gradient 1. Also, enhancement was greatest for N-alkylated anilines, which were comparatively weakly retained in the no-acid system. Thus, their presence is implied by the observed retention behavior with varying mobile phase acid chain length.

In summary, Fig. 4 shows: (1) that short chain acids can have an even greater effect in weak, moderately polar mobile phases than in strongly polar phases, (2) that propanoic acid gives a good compromise of adequate retention without much danger of anilines being retained long enough to co-elute with the pyridine types and (3) that the SRC-II sample contained relatively few anilines. Finally, it should be noted that the pyrrolic and/or diphenyl amine nitrogen types which escaped retention on the anion column during isolation of the gross base extract are resolved better in the decanoic acid-containing solvent system than in the shorter chain systems, as is typically the case for weakly acidic or neutral solutes.

Gradient 1 chromatograms of SRC-II base extracts in other boiling ranges lead to similar conclusions; hence they are not shown.

Fig. 5 shows gradient 1 chromatograms of an SRC-II 325–425°C acid I extract. As described in the Experimental section, samples containing excessive amounts of either acids or bases were run with additional ion-exchange columns inserted to increase system capacity. Thus, acid I denotes acids extracted by the first column and acid II (Fig. 6) acids obtained from the second anion-exchange column.

As predicted from model compound work, the decanoic acid-containing system yields superior chromatograms for acidic solutes. Conversely, the quality, in terms of resolution and peak shape, of the non-acid-containing system is poor. The peak shape of the acetic acid-containing system is adequate, but use of the stronger, short-chain acids (acetic or propanoic) usually causes acidic solutes to elute too

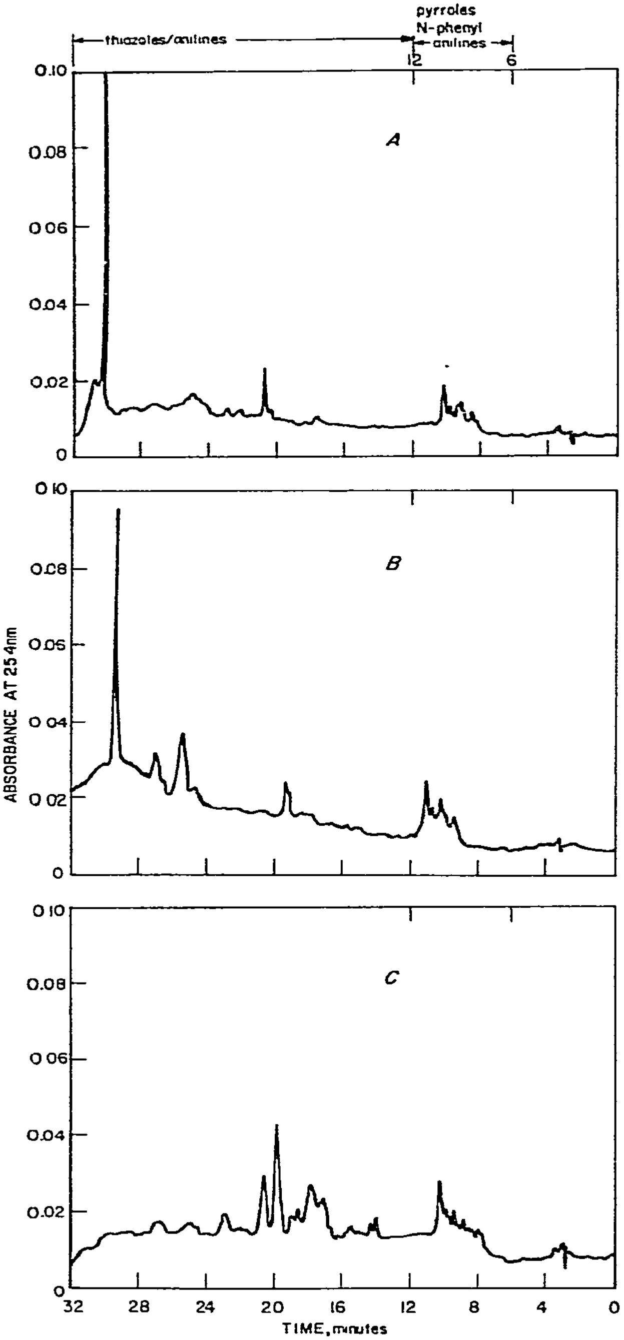

Fig. 4. Gradient 1 chromatograms of the same SRC-II 325–425°C base extract shown in Fig. 2. A–C were run with acetic, propanoic and decanoic acids, respectively. Amounts injected in A–C: 15, 20 and 19 μg, respectively. The chromatogram obtained from the system without added acid was similar in retention to C, but had poorer peak shape.

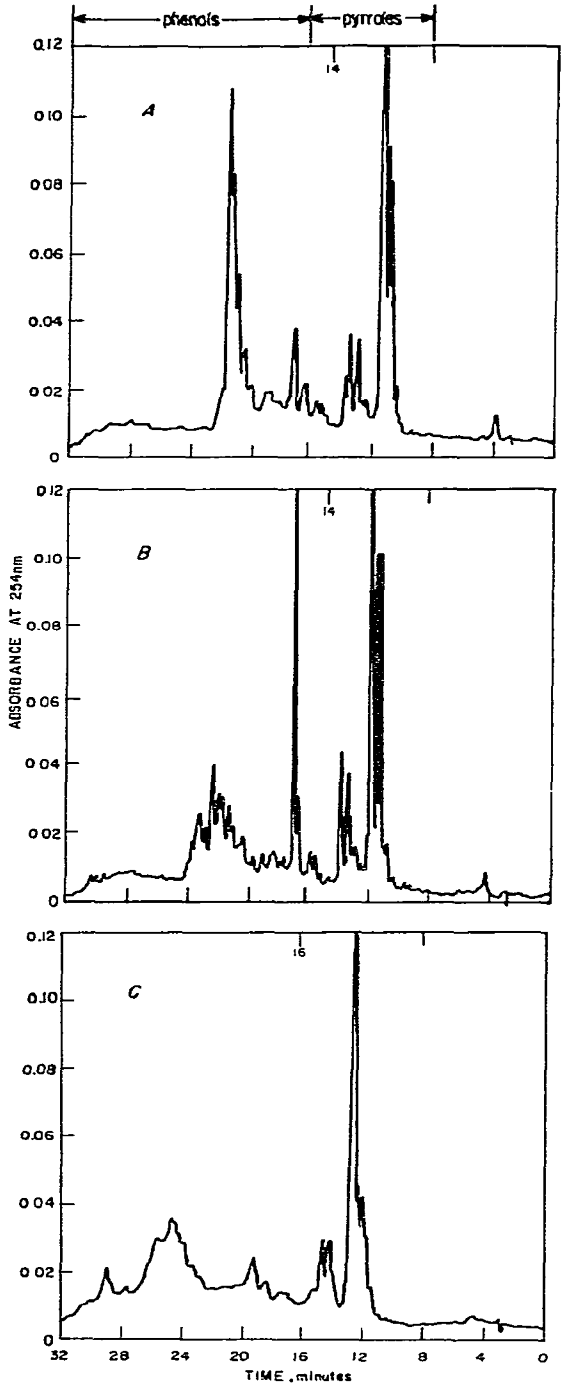

Fig. 5. Gradient 1 chromatograms of 11 μg of the acid-I extract from the SRC-II 325–425°C distillate. A–C were run with acetic, decanoic and no acids, respectively. Resolution of acids obtained using the propanoic acid system was intermediate between that of A and B.

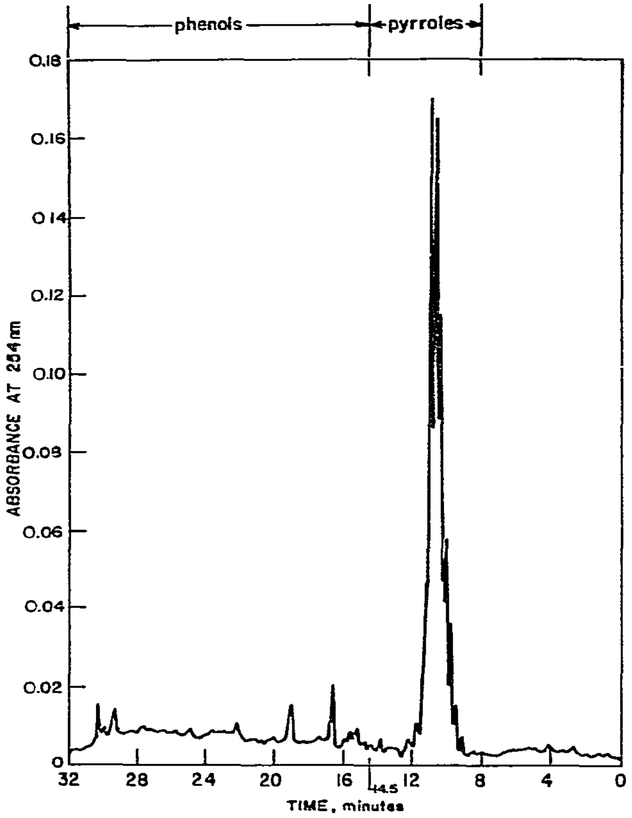

Fig. 6. Gradient 1 chromatogram of 9.3 μg of acid-II extract from the SRC-II 325–425°C distillate obtained with the decanoic acid spiked mobile phase system. The extract obviously contains mostly weak pyrrolic acids.

rapidly for good resolution (see Fig. 5A). Improved results (but not equivalent to those obtained using decanoic acid) can be obtained using more dilute acetic acid. All chromatograms in Fig. 5 indicate prevalence of phenolic and pyrrolic compounds in this extract.

Fig. 6 shows the gradient 1 decanoic acid system chromatogram of the SRC-II 325–425°C acid-II extract. This material contains largely pyrrolic and, as shown later, amide types. Trends in peak shape and resolution with different mobile phases are analogous to those discussed with Fig. 5, thus only the decanoic acid system chromatogram is shown in Fig. 6.

Fig. 7 shows results of running the same SRC-II 325–425°C acid-I and -II extracts using the stronger gradient 2 (Table II). The pyrrolic and phenolic components, of course, elute quite rapidly and are poorly resolved. However, a more strongly retained family, possibly multihydroxyarenes, can be seen using the more polar gradient 2. Interestingly, this retained group of peaks in the acid-I fraction shows different patterns in each of the four solvent systems. Shorter-chain acids cause some components to elute earlier and thus give a well-resolved pattern. Conversely, the same components tend to elute as one peak in the decanoic acid system, and either

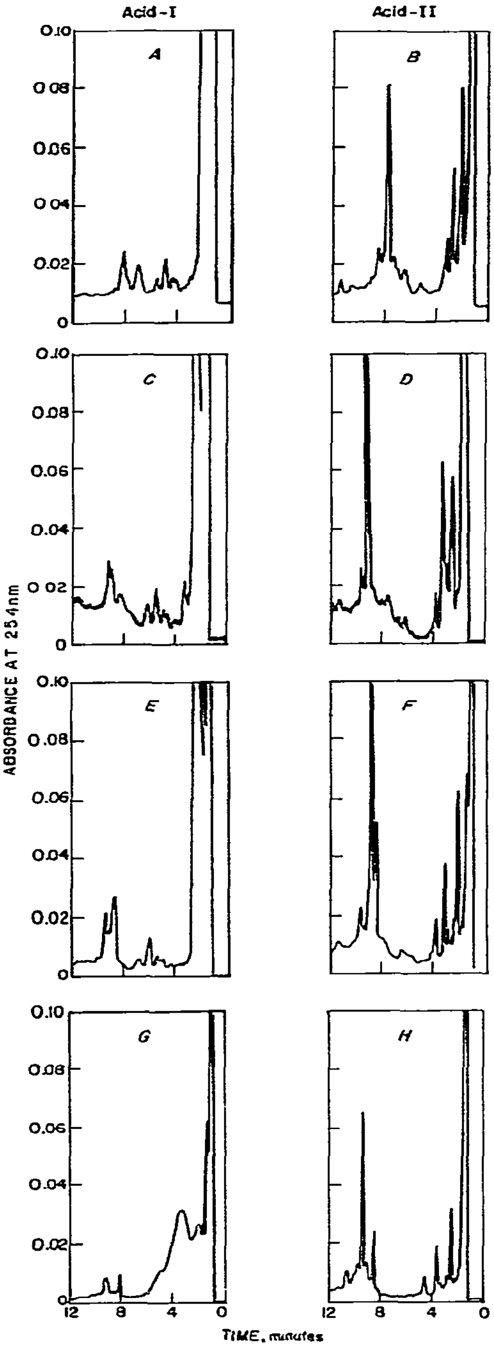

Fig. 7. Gradient 2 chromatograms of SRC-II 325–425°C distillate acid-I (A, C, E, G) and acid-II (B, D, F, H) extracts. A–B, C–D, E–F and G–H were obtained with mobile phases containing acetic, propanoic, decanoic and no acids, respectively. Amounts injected were 17.5, 18.5, 8.2, 9.2, 17.5, 18.5, 8.8 and 9.3 μg for A–H, respectively.

do not elute at all or as a very broad peak in the non-acid-containing systems. On the other hand, the more retained components in the acid-II extract show approximately constant retention in all four systems. Model compound work indicates the latter behavior to be more characteristic of amides.

Fig. 8 contrasts the elution of pyrrolic and carboxylic functions in acetic,

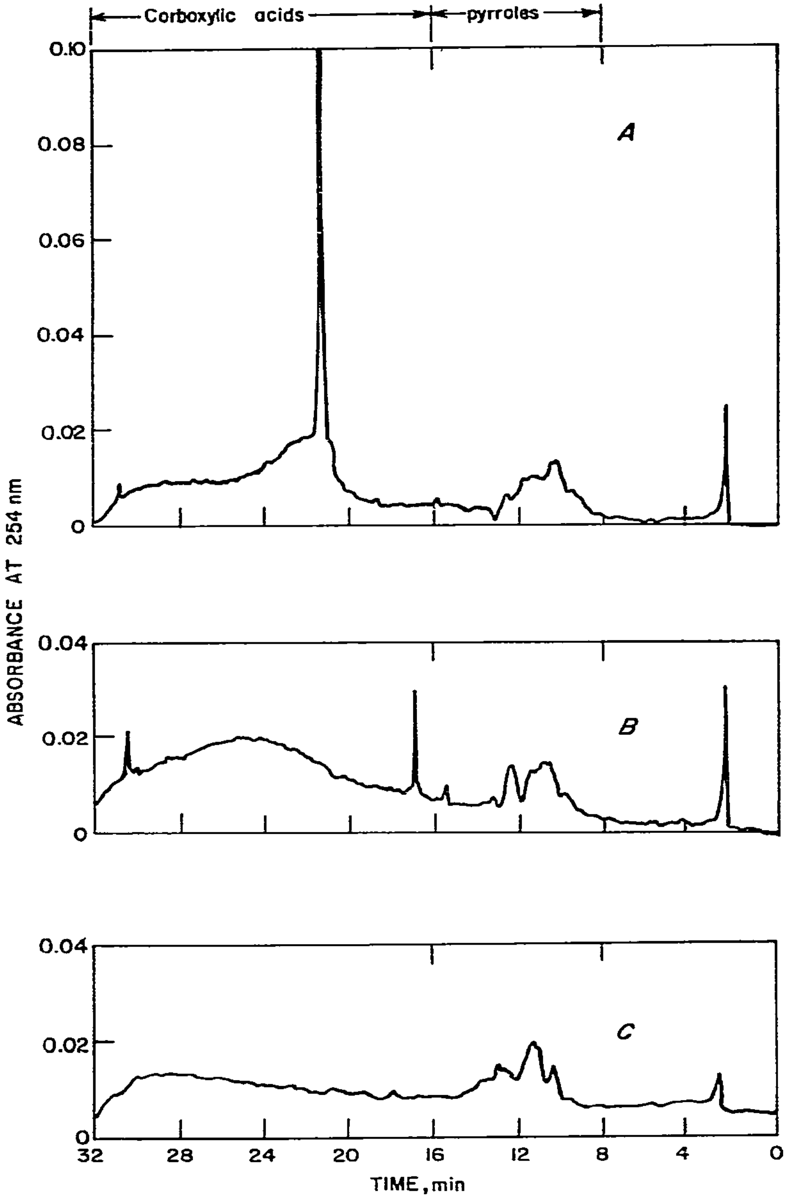

Fig. 8. Gradient 1 chromatograms of a Wilmington 370–535°C 1 F K_2CO_3 extract. A–C were run with acetic, decanoic and no acids, respectively. Amount injected in A–C: 40, 40 and 31 μg, respectively. Note shift in carboxylic acid retention in A–C.

decanoic, and non-acid-containing gradient 1 systems. The sample is the product of a 1 *F* potassium carbonate extraction of the Wilmington 370–535°C distillate. As shown in work with model compounds, pyrrolic nitrogen compounds change retention little with the addition of carboxylic acids to the mobile phase, but carboxylic acid solutes shift retention greatly. Thus, the carboxylic acids in the petroleum elute all together in the acetic acid system, as a broad band in the decanoic acid system, and not at all in the non-acid-containing system. The behavior in the propanoic acid-containing system is intermediate between that of the acetic and decanoic systems. Behavioral patterns such as this greatly enhance the usefulness of separations as qualitative identification tools.

Example applications of carboxylic acid system separations

Fig. 9 contrasts hydrocarbon fractions obtained after aqueous-alcoholic extraction *vs.* non-aqueous ion-exchange chromatographic removal of acids and bases from the SRC-II 325–425°C and Wilmington 370–535°C distillates. Chromatograms obtained using propanoic acid in a gradient 1 system are shown, but those of other acid and non-acid-containing systems are similar due to the fact that the presence of carboxylic acids in the mobile phase only slightly affects retention of neutral molecules such as hydrocarbons and pyrroles. Fig. 9 shows how the LC technique can quickly evaluate the quality of other fractionation procedures. In this case, the superiority of the ion-exchange method for removing pyrrolic nitrogen (into the acid fraction) is obvious.

Ternary gradient instrumentation has the capability to combine gradients 1 and 2 shown in Table II into a single run. Fig. 10 shows chromatograms of the base extracts of the Wilmington, CA, crude petroleum run under conditions specified in Table III. The chromatograms show the applicability of the gradient method to very high molecular weight petroleum fractions such as the Wilmington 675°C+ residue. As is often the case with high boiling residue samples, the 675°C+ material was run through ion-exchange columns first in dichloromethane and then in cyclohexane as described in the Experimental section. This procedure resulted in the weak and strong base extracts shown in Fig. 10D and E. The great complexity of the higher boiling fractions results in rather broad peaks representing collections of many individual components in the major chemical classes indicated on the figure. Clearly, columns with much higher resolving ability would be necessary in order to see individual components in the high boiling materials. However, the surprising similarity of the group type distributions in the different boiling ranges of this sample is evident even from the chromatograms obtained from the relatively low resolution columns used here.

Finally, Fig. 11 shows an example of major changes in functional group distribution induced via catalytic hydrogenation of the SRC-II coal liquid.[43] The acid extracts of the reactor feed material contain major amounts of pyrroles and phenols as indicated in Fig. 11A and B. However, as seen in Fig. 11C, hydrogenation destroys nearly all of the original phenols and pyrroles, with most of the remaining acids being made up of an as yet unidentified group of compounds eluting very early in the chromatogram. The chromatograms in Fig. 11 were run using the ternary gradient system (Table III) as part of an ongoing study of the structural changes occurring during upgrading of crude liquid fuels.[43]

Further work

As the reader may have gathered from the rather pictorial display of results in the previous section, methods for HPLC separations of fuel extracts are relatively far

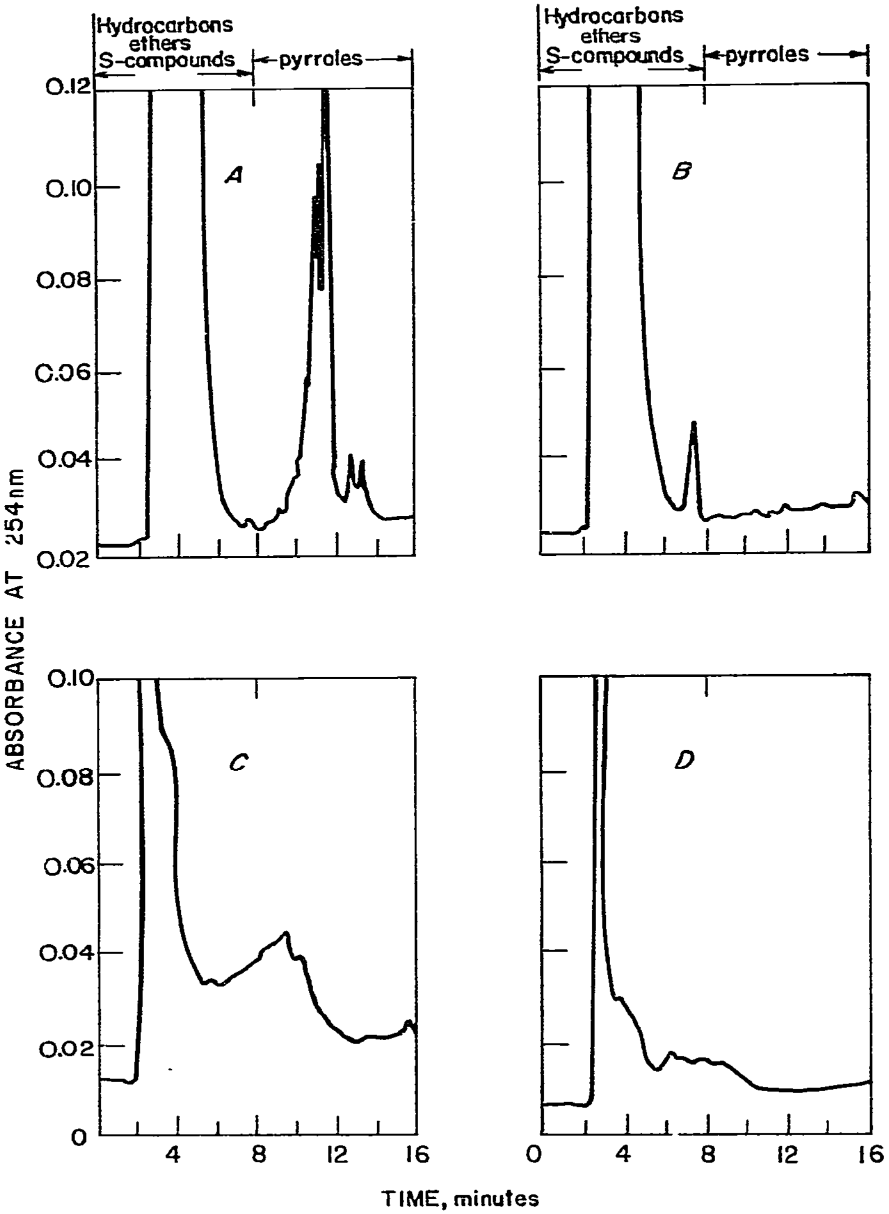

Fig. 9. Gradient 1 chromatograms using propanoic acid of SRC-II 325–425°C (A, B) and Wilmington 370–535°C (C, D) distillate "hydrocarbon" fractions. A and C were isolated via HCl–NaOH solvent extraction procedures, and B and D via non-aqueous ion-exchange chromatography. Amounts injected in A–D: 26, 17, 54 and 23 μg, respectively. Note the decreased amounts of pyrroles in the ion-exchange isolated hydrocarbons.

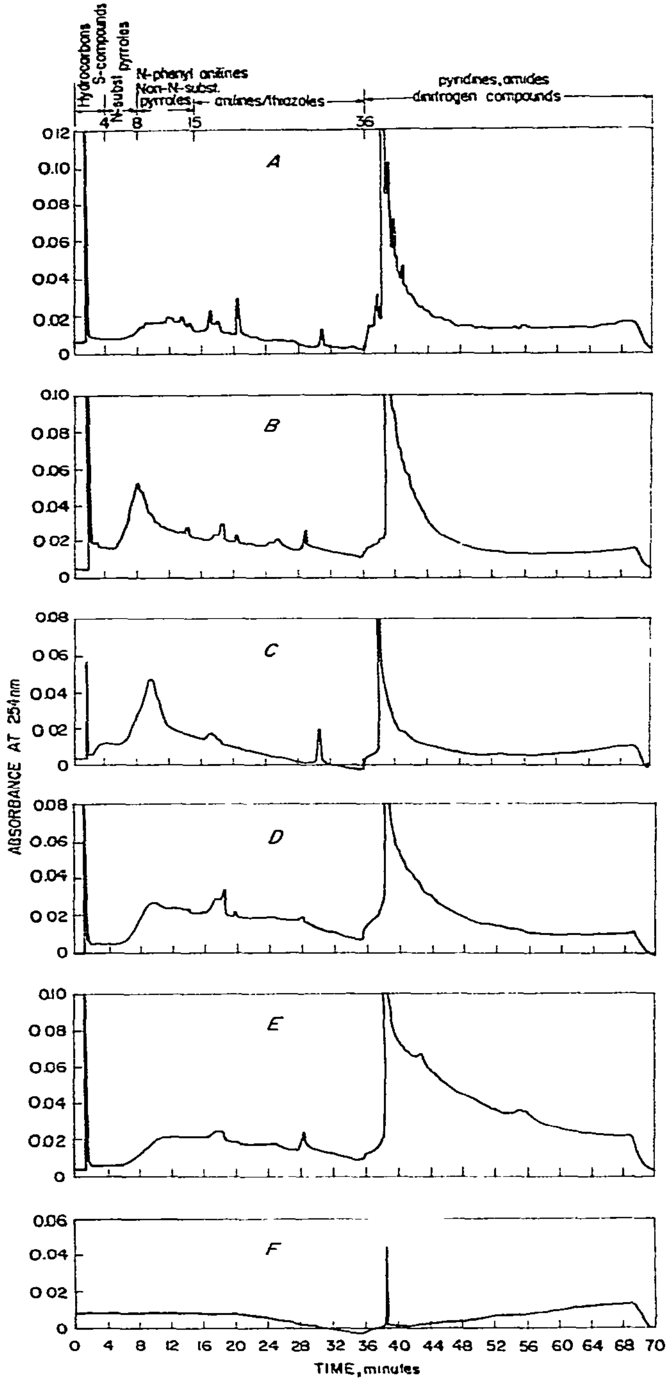

Fig. 10. Ternary gradient chromatograms (Table III) of Wilmington base extracts. A, <370°C; B, 370–535°C; C, 535–675°C; D, 675°C+ (weak); E, 675°C+ (strong); F, blank run. Amounts injected in A–F 160, 98, 52, 97, 98 and 0 μg, respectively.

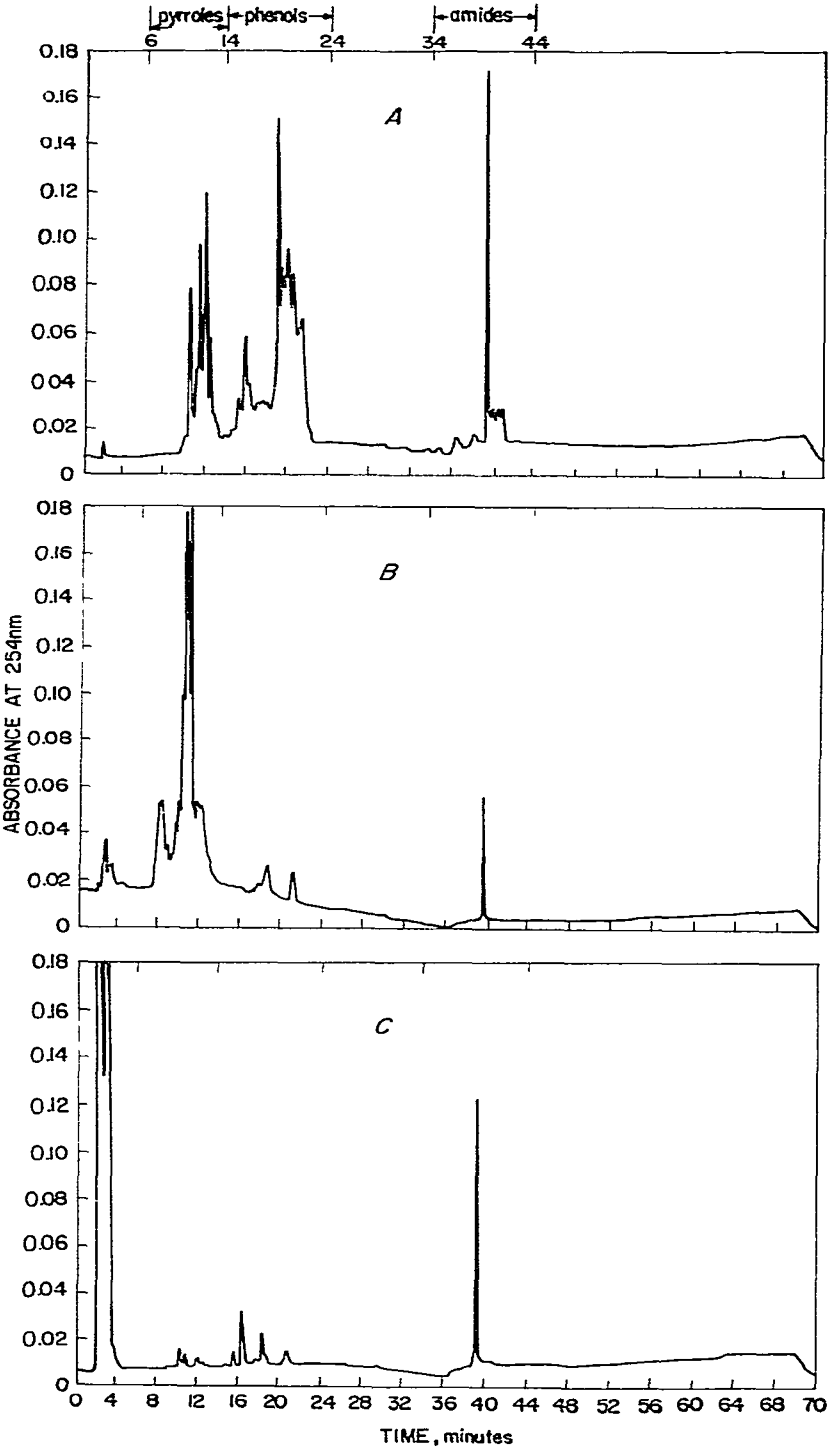

Fig. 11. Ternary gradient chromatograms (Table III) of acid extracts of hydrotreater feed SRC-II 325°C+ residue and extensively hydrotreated SRC-II 325°C+ residue. A, strong acids in feed; B, weak acids in feed; C, total acids in hydrotreated product. Amounts injected in A–C: 20, 10 and 24 μg, respectively. See Fig. 10 for solvent blank trace. Note the effectiveness of catalytic hydrogenation in removing most of the original pyrrolic and phenolic material.

advanced over methods of peak identification and quantification. At present, heavy reliance on retention time correlations and UV absorbance ratios at different wavelengths are the primary methods of qualitative analysis. Quantitation is usually performed via preparative scale separation and weighing of the fractions. Also, MS, IR and other spectroscopic techniques have been used to characterize fractions from preparative runs.

However, the objective of this work is to characterize at least semiquantitatively polar materials from fuels directly by HPLC. For example, IR HPLC detectors show good selectivity and fairly uniform response over members of a given chemical family. However, most common solvent systems including those studied here are IR-incompatible. LC–MS is a very promising solution, but it is expensive and, at present, incompletely developed[44]. Current research in this laboratory is aimed at using packed microbore columns[45] for analytical scale separations because of their inherent ease in interfacing with mass spectrometers[46]. Rapid scanning or diode array type fluorescence and UV–visible detection systems will always suffer from the requirement that standards must be available for spectral matching. Especially for higher boiling fuel components, appropriate standards are simply unavailable. Also, response factors for compounds in a given class can vary over orders of magnitude, making even semiquantitative analysis questionable with UV–visible or fluorescence detectors. However, these detectors do not have solute volatility requirements as do mass spectrometers, and have nearly universal application to any aromatic solute.

Clearly, detection of the HPLC effluents is the major area of future research to improve the applicability of HPLC to complex samples. However, there is room for improvement in the separations also. For example, the separation between pyrrolic and phenolic compounds is relatively poor in the solvent systems reported here. Current research in this laboratory with solvent systems containing bases indicates that considerable improvement can be obtained for separations of acidic samples. Also, base-containing solvents exhibit much different selectivity on silica than acid-containing solvents; for example, pyridine homologues co-elute with hydrocarbons.

CONCLUSIONS

HPLC has good promise as a rapid fuel characterization tool if detectors can be developed with improved qualitative and quantitative capabilities for complex mixtures. In general, solvent systems containing short alkyl-chain acids work best on basic solutes. Also, adequate resolution of acidic solutes can be obtained if the mobile phase contains an acid of relatively long chain length. Quite often, running the same sample in two or more systems containing acids of different chain length yields useful qualitative information on different chemical types in the sample. In any case, acid-containing mobile phases far outperform non-acid-containing mobile phases for separation of fuel samples.

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