CHROM. 21 140

SEQUENTIAL HYDROCARBON AND NITROGEN DETECTION IN THIN-LAYER CHROMATOGRAPHIC ANALYSIS OF OIL SHALE BITUMEN

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(Received November 4th, 1988)

SUMMARY

Sequential flame ionization detection (FID) and chemiluminescent nitrogen detection (CLD) were used to determine semiquantitatively the hydrocarbon and nitrogen compound types in fossil fuel sources fractionated by thin-layer chromatography (TLC). The design of the TLC–FID/CLD system achieved high specificity for organic nitrogen over a wide dynamic range. The FID mass responses for different hydrocarbon types were near unity except for heteroatom-containing concentrates which were less than unity. A method of TLC adsorbent treatment was used in differential nitrogen-type analysis by CLD. The results from TLC–FID/CLD analysis of high-boiling bitumens from western oil shale indicated that the bitumen composition changes with reaction time during the thermal decomposition of the kerogen.

INTRODUCTION

Chromatographic techniques together with element specific detectors allow complex mixtures to be characterized for compound classes and molecular mass size ranges. Multiple detectors provide characterization data and profiling of chemical species which may differ in physical and chemical properties. This study describes the development and application of an on-line flame ionization detection (FID) and chemiluminescent nitrogen detection (CLD) system for the thin-layer chromatographic (TLC) analysis of fossil fuel bitumens.

Hydrocarbon-type analysis by TLC–FID has been applied to many fossil fuel materials including: coal-derived materials[1,2], tar sand bitumens[3,4], heavy oils[5,6], and products from the combustion of these materials[7]. The TLC–FID analytical technique has been shown to be complementary to the classical liquid chromatographic methods used for compound-class determination and solvent-extraction methods used for the determination of asphaltene content. In addition, the application of TLC–FID in the fields of biology, food science, surfactants, and polymers has been reviewed[8].

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The TLC–FID technique provides for the automated analysis of sample replicates in less than four hours, the reuse of the chromatographic supplies, the semi-quantitation of compound classes in high-boiling (> 250°C) materials, and the versatility in choosing chromatographic conditions. However, the different FID response factors for different compound classes and the susceptibility of the sample to alteration caused by component volatility, thermal lability, oxidation, or photodegradation has limited the accuracy of the data obtained from using this technique.

An extension of the TLC–FID technique was the development of element specific detection modes for TLC analysis. One detection mode of interest is the capability to analyze selectively for nitrogen-containing species. Because nitrogen is concentrated in heavy fractions of bitumens and is detrimental to the processing of these heavy oils[9], information regarding the qualitative and quantitative nature of the nitrogen species is beneficial to the heavy oil processor. The amount and type of organic nitrogen in materials from pyrolysis have been related to the fossil fuel source[10].

An improvement in the design of the TLC–FID together with the development of an on-line flame thermionic ionization detection (FTID) system was reported by Patterson[11]. These modifications allowed both hydrocarbon detection and the detection of nitrogen and halogen compounds such as nitroaromatics and chloro- and nitrophenols. However, FTID does not have the high specificity for nitrogen present at concentrations of less than 0.1–4 wt.% in fossil fuel materials. The interferences from hydrocarbon responses can be significant.

As an alternative to using FTID for nitrogen detection, CLD has been shown to be a highly specific nitrogen detector. McGregor et al.[12] developed a totally specific pyro-chemiluminescent nitrogen detector for gas chromatography that was used successfully in the analysis of nitrogen compounds in jet fuels[13]. The minimum detection limit was in the order of 0.5 ppm nitrogen with a signal-to-noise ratio of 6. Relative response factors were near one for aromatic nitrogen and slightly greater than one for non-aromatic nitrogen. Thus, it appeared that the development of CLD on-line to the TLC–FID system may be applicable in the analysis of fossil fuel material.

The development of a TLC analyzer with sequential FID and CLD is described. High sensitivity over a wide dynamic range for both hydrocarbon and nitrogen species is achieved. One application of the TLC–FID/CLD analyzer is described for determining the composition of oil shale bitumens. The data from this application provide information regarding the reaction mechanisms during a pyrolysis process.

EXPERIMENTAL

Description of the TLC–FID analyzer

An Iatroscan TH-10, MK-IV TLC–FID analyzer from Iatron Laboratories was used in this work. The FID flame was generated with 160 ml/min hydrogen gas flow and 2.5 l/min air flow sustained from compressed gas cylinders. The FID collector was designed for greater collection efficiency for the ionization produced by the flame. Samples were developed under TLC conditions on 5 μm silica gel, Chromarods SII and scanned at 40 s/scan.

Description of CLD interfaced to the TLC–FID

The Antek Model 771 pyroreactor and Model 720 chemiluminescent digital detector were modified for interfacing to the TLC–FID analyzer. The stand-alone Antek instrument achieved $\pm 3\%$ reproducibility in determining low to high concentrations ($1-10^4$ ppm) of nitrogen in fossil fuel materials. The pyroreactor combustion tube comprised a concentric-designed, quartz tube which allowed make-up oxygen to mix with the combustion gases from the TLC–FID analyzer. The detector response time was decreased by lowering the capacity of the photomultiplier current of the digital detector so that the peak width was 4 s at 10% peak height.

The chemiluminescent nitrogen detector was placed in series with the FID system via a PTFE line which was heated above the dew point to eliminate moisture condensation. The FID tower incorporated a 0.64-cm stainless-steel tube which was connected to the inlet of the PTFE line. The outlet of the PTFE line was connected by a stainless-steel union to the heated inlet of the quartz tube of the pyroreactor. The outlet of the digital nitrogen detector was connected to a mechanical vacuum pump having an in-line air bleed needle valve for vacuum control at the detector of $3.1 \cdot 10^4$ Pa (225 Torr). Make-up oxygen to the combustion tube was 10 ml/min, and oxygen flow to the ozone generator was 100 ml/min. Pumping capability provided a volume displacement of 985 cm^3/min.

The FID and CLD response data were reduced using a Hewlett-Packard 21MX minicomputer equipped with a 3354 B/C Laboratory Automation system. The integration procedures incorporated gas chromatographic software with peak integration every 0.25 s. Data were corrected for the background responses obtained by the scanning of blank chromarods. Component retention times were used to determine R_F values and area percentages were converted to detector mass response factors using known concentrations of compound-type fractions. Each chromarod was scanned twice to ensure complete combustion of the sample material.

Chromatographic conditions

Each analysis run was conducted using a set of ten chromarods (Chromarods SII from Iatron Laboratories). Two different sets of chromarods were prepared, one was unmodified and one was treated with chromic acid. The unmodified set of chromarods was hydrated overnight prior to each day's use. After hydration, the ten chromarods were activated by scanning twice in the TLC–FID analyzer. Modification of a second set of chromarods was achieved by immersing the rods in Pierce RB5-35 cleaning solution for 1 h at 50°C, rinsing them in water, immersing them in chromic acid solution, and rinsing them with distilled water followed by blank scanning. A temperature of about 430°C was experienced by these chromarods during blank scanning which was sufficient for Cr(VI) oxide to decompose to Cr(III) oxide at 197°C.

A microsyringe with a syringe pump was used to deliver accurately 1 μl of a 1–2 vol.% solution of sample in benzene to each chromarod which was then solvent developed. The solvent system used in the TLC work consisted of the development with *n*-heptane to 10 cm, the development with *n*-heptane–toluene (30:70, v/v) to 7 cm, and the development with toluene–ethanol (90:10, v/v) to 3.5 cm. The sample application and TLC development were performed in a laboratory equipped with gold fluorescent bulbs which excluded light below 500 nm to minimize photodegrada-

tion of the sample. Drying of the solvents was accomplished using a nitrogen flow-through oven with mechanical pumping at 90°C for 6 min. Prior to analysis, the developed chromarods were rotated 180° in the holder.

In each set of ten chromarods, samples and calibrants were analyzed in duplicate, and two chromarods were used for background corrections. Model compounds and preparative-sized fractions from an oil shale bitumen were used in the calibration of TLC–FID/CLD. These fractions were generated by using adsorption chromatography on neutral alumina and silica gel[14,15].

Preparation of samples of bitumens from oil shale

Samples of bitumen from western reference oil shale (Colorado-Green River) and from eastern reference oil shale (Kentucky-New Albany) were obtained by the isothermal heating of these shales at different reaction times. The shale particles were sized from −20 to +45 mesh and heated at 400°C at different reactor (reaction) times ranging from 5 to 480 min. The reactor design and tests are described in detail by Miknis *et al.*[16]. Following rapid quenching of the reactor, the heat-treated shales were withdrawn and extracted with benzene for a 24-h period using a Soxhlet extractor. The benzene solutions were filtered through 0.4 μm Nylon-66 filters, and the volume was reduced to approximately 2 vol.% bitumen in benzene. The TLC–FID/CLD analyses of these sample solutions were performed within a week of production to minimize sample alteration. After analyses, the solutions were taken to dryness at 60°C and a pressure of 5 mmHg by using a rotary evaporator. Accurate sample weights were obtained, and the concentrations of the benzene solutions were determined. Product gases and oils were collected separately and are described in other studies.

RESULTS AND DISCUSSION

Performance of the TLC–FID/CLD analyzer

The TLC–FID analyzer was used initially to obtain the hydrocarbon compositional data for bitumens produced under different process conditions. The total nitrogen contents of these bitumens were different for different bitumens. Therefore, nitrogen distributions as well as hydrocarbon distributions in these bitumens were being affected by different process conditions. A CLD unit, offering high sensitivity and specificity for nitrogen, was selected for interfacing to the TLC–FID analyzer (Fig. 1). In general application, the sample material on the chromatographic support is combusted in a hydrogen–air flame, and a mechanical vacuum pump draws the combustion gases through the dual detection system which is placed in series. The vaporized hydrocarbons are ionized in a gas-phase ionization process and detected by the flame ionization detector. Neutral products of this combustion include nitric oxide and chemically bound nitrogen which is converted by oxidative pyrolysis in the 950°C pyroreactor to additional nitric oxide and reacted with ozone in the CLD unit to form NO_2^* in the excited state. The relaxation of NO_2^* to NO_2 causes the emission of photons which are measured.

Both the hydrocarbon and organic nitrogen species in the TLC chromatographed fractions were determined semiquantitatively. By making different sized injections of nitric oxide diluted with air, a linear ($r^2 = 0.995$) dynamic range of 500
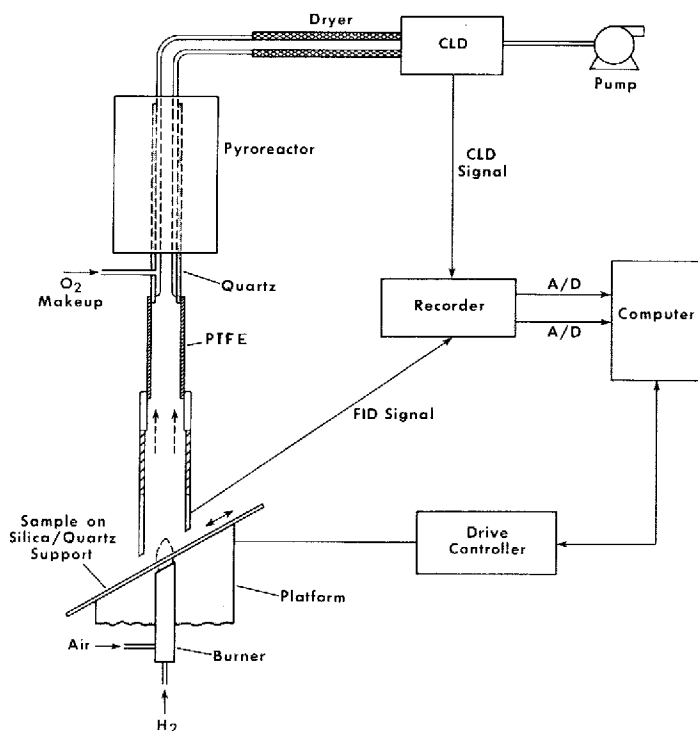
Fig. 1. Schematic of the TLC–FID/CLD system.

ppm to 20 wt.% nitrogen was determined for the CLD. A lower signal-to-noise ratio was observed at concentrations < 500 ppm nitrogen; this lower ratio was caused by gas flow fluctuations. The peak width at 10% peak height for nitric oxide was about 3.6 s compared to 2.4 s for that of pyrene detected by FID. A delay time of approximately 1 s was observed between the FID and CLD responses for the nitrogen-containing organic species. Good reproducibility (relative standard deviation, R.S.D. 2%) for the FID responses was observed for both model compounds and fossil fuel samples. The precision in the quantitation of detector responses for the TLC developed fractions (about 15 μg) was R.S.D. 4% and 5% for the FID and CLD, respectively; however, this compared well with that reported for FID (R.S.D. 10%)[3].

For similar FID responses, the configuration of the dual detectors in the TLC analyzer required considerably less sample than was needed in the TLC–FID analyzer. With the aid of the mechanical vacuum pump, approximately one-half the amount of sample was needed for adequate TLC–FID/CLD analysis. For example, an 1-μl aliquot of a 10–15 mg/ml sample in benzene solution gave the same amount of FID response by TLC–FID/CLD compared with an 1-μl aliquot of a 25–30 mg/ml sample in benzene solution by TLC–FID.

Observed R_F values and detector response factors

Several model compounds and fractions from bitumen were analyzed by TLC–FID/CLD to determine R_F values, retention times, and mass response factors. Model

compounds representing species in fossil fuel materials were selected for this study. Liquid adsorption chromatography was used to generate four preparative-size fractions from a representative oil shale bitumen. These saturate, polyaromatic hydrocarbon (PAH), nitrogen polyaromatic hydrocarbon (NPAH), and polar fractions were analyzed by ultraviolet and infrared spectroscopy and determined to be comprised of numerous compound-type structures. The saturate fraction was comprised of alicyclic and cyclic saturated hydrocarbons. The PAH fraction was comprised of alkyl-substituted compounds of one to five aromatic rings. The NPAH fraction was primarily a concentrate of pyridine derivatives, and the polar fraction consisted of multifunctional, heteroatom-containing aromatic and aliphatic structures.

The R_F values were determined from the retention times of model compounds and compound-type fractions. As expected, the elution order was saturate (near the n-heptane solvent front), PAH, NPAH, and polar fractions ($R_F = 0.00$ at the origin). In Table I, the well-separated, narrow ranges for both the retention times and calculated R_F values indicate adequate separation of the compound-type fractions.

The TLC–FID/CLD analysis of different nitrogen compound classes in samples of complex mixtures of compound types was demonstrated. Several different nitrogen-containing model compounds had similar R_F values (Table I) which indicated their inadequate separation. However, the separations of the nitrogen species in the compound-type fractions gave distinct R_F values for specific nitrogen-type classes. This suggested that the solubility and association characteristics of nitrogen classes adsorbed on silica gel stongly influence their isolation by TLC. From the R_F values, carbazole derivatives are present in the PAH fraction, pyridine derivatives are in the NPAH fraction, and bifunctional nitrogen/oxygen species are in the polar fraction.

The effect of a sample's concentration on its associative properties was explored

TABLE I

RETENTION TIMES AND OBSERVED R_F VALUES FOR HYDROCARBON AND NITROGEN-CONTAINING SPECIES

Compound-type fraction or model compound	FID		CLD	
	Retention time (s)	R_F	Retention time (s)	R_F
Saturate	11–14	0.65–0.74	–	–
PAH	18–20	0.47–0.53	21–22	0.44–0.47
NPAH	24–28	0.24–0.35	27–29	0.24–0.29
Polar	34–36	0.00–0.06	37–38	0.00
Pyrene	19	0.50	–	–
Ethylcarbazole	20	0.47	21	0.47
Benzocarbazole	26	0.29	27	0.29
Tetrahydrocarbazole	29	0.21	30	0.21
Benzoacridine	30	0.18	31	0.18
Benzoquinoline	30	0.18	31	0.18
Formanilide	30	0.18	31	0.18
Toluamide	31	0.15	33	0.12
Hydroxyquinoline	35	0.00	37	0.00

TABLE II

RELATIVE TLC–FID MASS RESPONSES FOR 1-μg QUANTITIES OF FRACTIONS FROM DIF-
FERENT BITUMENS

Compound-type fraction	TLC–FID[a]		TLC–FID/CLD[b]			
	Oil shale		Tar sand		Oil shale	
	Area	Relative response	Area	Relative response	Area	Relative response
Saturate	6790	0.81	5160	0.41	8560	0.84
PAH	7170	0.85	6040	0.48	8610	0.84
NPAH	8430	1.00	12590	1.00	10190	1.00
Polar	3830	0.45	4700	0.37	4650	0.46

[a] No vacuum pump was used in this configuration.
[b] A mechanical vacuum pump was used in this configuration.

by using pyridine as a solvent. Solutions of different bitumen concentrations were
applied to the Chromarod SII. Pyridine without sample was readily removed in the
drying oven. But, the pyridine could only be removed from samples with less than 4
mg/ml of pyridine using similar drying oven conditions. Greater concentrations re-
sulted in strong intermolecular associations of bitumen, pyridine, and silica gel.

The relative mass responses by the FID were determined for 1-μg quantities of
the saturate, PAH, NPAH, and polar fractions. The FID signals were corrected for
background and integrated. Each area was normalized to the highest chromato-
graphic peak area that was determined to be that for the NPAH fraction (Table II).
These data for the compound-type fractions were dependent upon the composition of
the sample (oil shale or tar sand) and on the configurations of the TLC–FID and
TLC–FID/CLD systems. The FID detector mass responses for the fractions from the
oil shale bitumen ranged from 0.8–1.00 compared with 0.4–1.00 for the fractions from
the tar sand bitumen. The ionization of hydrocarbons was greater than that for
compounds containing large amounts of oxygen, sulfur, or nitrogen which accounted
for the low mass responses of the polar fractions. By varying the hydrogen–air ratio
and therefore changing the flame temperature, it was observed that the volatility of
the polar fractions was less than for the other fraction types. The volatility of the
saturate fraction was the greatest. Because these relative FID mass responses are
dependent upon the composition of the fraction and the configuration of the TLC–
FID/CLD, the correlation of these data with FID data from gas chromatographic
analysis should be limited. It is obvious that the FID calibration for each fossil fuel
source is required.

The integrated areas of the FID responses for each compound-type fraction by
TLC–FID and by TLC–FID/CLD were compared. A more effective analysis of the
fractions was obtained by using the latter system's configuration, which incorporated
a mechanical vacuum pump. By using reduced pressure, an area that was about 20–26
percent larger was obtained for each fraction. Reduced pressure decreased the prob-
ability of ion–ion recombination prior to the ion contact with the anode (collector
electrode). In addition, the off gases from the analyzer are removed by the pump from
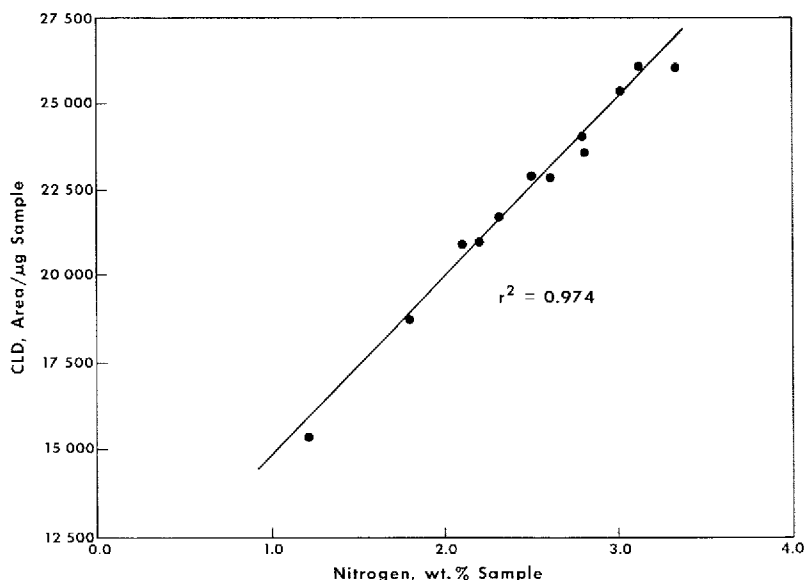
Fig. 2. Correlation for the CLD responses for nitrogen in western shale bitumens (400°C).

the laboratory environment in an acceptable manner. As a consequence of using TLC–FID/CLD, the chromatographic peaks had better resolution. Numerous reuses of the chromatographic support are obtained by using the TLC–FID/CLD configuration.

The CLD mass responses could not be determined for model nitrogen compounds because of the irreproducibility in the integrated areas. This was attributed, in part, to the thermal lability of model nitrogen compounds on the chromatographic support. However, the nitrogen species participating in the intermolecular interactions of complex mixtures such as those found in fossil fuel chromatographic fractions were amenable to TLC–FID/CLD analysis. The CLD measurements for these fractions were reproducible to within 2%.

The amount of organic nitrogen detected by chemiluminescence was independent of the nitrogen compound class. Fig. 2 demonstrates this linearity ($r^2 = 0.974$) for the CLD responses from samples of oil shale bitumens with the wt.% of nitrogen as determined by pyrolytic techniques. The total CLD response for a sample is additive of each CLD response fro the PAH, NPAH, and polar fractions, and the CLD mass response for each fraction from these bitumens was assumed to be unity. The TLC–FID/CLD analysis of a fossil fuel sample provides both the distribution of nitrogen compound types and the semiquantitation of nitrogen by using a calibration curve similar to that in Fig. 2.

Differential nitrogen analysis by TLC–FID/CLD

Differential nitrogen analysis of shale bitumens by TLC–FID/CLD was accomplished by using both unmodified and chromic acid-treated Chromarod SII. The latter allowed the determination of compound types which selectively complexed to

TABLE III

EFFECT OF CHROMIC-ACID TREATMENT ON CHROMAROD SII TO DISTINGUISH COMPOUND-TYPES IN SHALE BITUMENS

Reaction time (min)	Modi-fication	FID (area %)				CLD (area %)			Total nitrogen (Wt.% sample)
		Saturate	PAH	NPAH	Polar	PAH	NPAH	Polar	
5	None	3	6	84	7	–	92	8	1.2
	Acid	6	11	57	26	3	63	34	
30	None	4	6	78	12	<1	90	9	2.1
	Acid	5	5	36	54	(2)^a	(39)	(59)	
60	None	3	5	71	21	<1	77	22	2.3
	Acid	6	2	27	65	(2)	(29)	(69)	
120	None	4	4	64	28	–	67	33	2.8
	Acid	5	2	25	68	1	29	70	
240	None	7	9	77	7	–	94	6	2.6
	Acid	18	8	54	20	1	68	31	
480	None	17	7	68	8	–	90	10	2.2
	Acid	22	3	57	18	3	68	29	

^{a} Values in parentheses were not determined directly on the chromic acid-treated chromarods but were inferred from the FID area %.

positive chromium metal centers. Separate analysis was carried out by using the different sets of chromarods, and the data were compared. The impregnation of Cr in the silica gel allowed ligand exchange/complexation reactions[17] with organics during TLC development. The basic primary amine and pyridinic compound types selectively complexed to cationic metal centers. Also, π-electrons in polyaromatics allowed weak coordination to metal centers. This complexation effectively retarded the movement of such organic species when weakly polar, organic solvents were used as elements.

Several oil shale bitumens which were produced at different reactor residence (reaction) times at 400°C were analyzed using the unmodified and the chromic acid-treated Chromarod SII. The CLD area percentages for the NPAH fractions decrease as the area percentage for the polar fractions increase upon using the chromic acid-treated chromarods compared to using the unmodified chromarods (Table III). Similar trends are indicated for the FID area percentages. Because the R_F values of some carbazole derivatives are similar to pyridinic derivatives (Table I) using unmodified chromarods, the selective retardation of pyridinic derivatives on the chromic acid-treated chromarods will enable these species to be concentrated in the polar fraction. The carbazole derivatives will remain in the NPAH fraction. The summation of the CLD area percentages for the PAH and NPAH fractions using chromic acid-treated chromarods represents the relative amount of nitrogen in carbazole derivatives. The relative amounts of nitrogen in pyridinic derivatives were determined as the differences in the CLD area percentages of polar fractions using chromic acid-treated chromarods and that in the polar fractions using the unmodified chromarods. The CLD area percentage of the polar fraction determined by using only the unmodified chromarods represents the relative amount of bifunctional nitrogen compounds, which include amidic derivatives.

For maximum oil shale bitumen production between the 30 and 60 min reaction times, the relative distributions of nitrogen are in the range 31–41% carbazole, 47–50% pyridinic, and 9–22% bifunctional or amidic derivatives (Table III). These data compare favorably with the results from liquid chromatographic analysis of a retorted western shale oil having 2.2 wt.% total nitrogen: 36% carbazole, 50% pyridinic, and 14% amidic nitrogen[18].
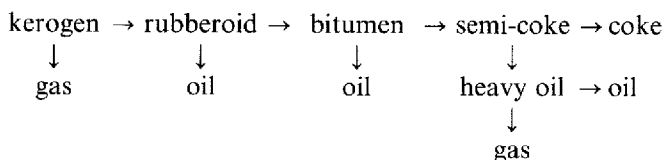
The results from differential nitrogen analysis of eastern oil shale bitumens indicated only negligible differences in the compositional distributions by using either type of chromarod. There was less complexation of the compound types in the eastern oil shale bitumens compared with that of in the western oil shale bitumens. In a retorted eastern shale oil, there was only 28% pyridinic nitrogen but 54% carbazole nitrogen[18]. The character of the nitrogen in the bitumen and the soil from eastern oil shale was considerably more aromatic and less basic than that from the western oil shale. Less complexation of the nitrogen compound types in eastern shale bitumen was expected.

Relative FID area percentages for the PAH and saturate fractions were erroneously measured using chromic acid-treated chromarods. Impregnation of metals in the chromarods may block the pore structure of the silica gel as well as inactivate the Si–O–Si and Si–OH active sites needed to retard the elution of aromatic structures. This would cause the PAHs to elute with saturates on chromic acid-treated chromarods, and the measured saturate content would be exaggerated. Therefore, the amounts of saturates and PAHs should be determined from the calibrated FID mass responses using unmodified Chromarod SII.

Cleaning Chromarod SII with chromic acid cleaning solution is not recommended. The previous work suggested that metal impregnation occurred when chromic acid was used. It was found that the chromic acid-treated chromarods could not be reconverted to the unmodified character of the TLC adsorbent. Because multiple sample analyses on Chromarod SII reduced cost and allowed consistency in measurements, the reuse of unmodified Chromarod SII was achieved by cleaning with 4 M nitric acid followed by copious washing with distilled water[8]. Nitric acid was used for cleaning without modifying the TLC adsorbent. This suggested that the chromatographic process is one of complexation and not necessarily acid–base interaction with the chromic acid-treated materials.

TLC–FID/CLD analysis of reaction intermediates

By understanding the kinetics of the thermal decomposition of shale, the efficiency of conversion processes can be improved and novel approaches to shale pyrolysis can be developed. Various models of decomposition processes have been proposed in attempts to predict the product yields for different types of oil shale. Several models have indicated that the bitumen is an intermediate in the pathway of kerogen decomposition to oil and gas as shown below[19]

$$
\begin{array}{ccccccc}
\text{kerogen} & \to & \text{rubberoid} & \to & \text{bitumen} & \to & \text{semi-coke} & \to \text{coke} \\
\downarrow & & \downarrow & & \downarrow & & \downarrow & \\
\text{gas} & & \text{oil} & & \text{oil} & & \text{heavy oil} & \to \text{oil} \\
& & & & & & \downarrow & \\
& & & & & & \text{gas} &
\end{array}
$$

Kerogen is defined as that portion of organic matter in oil shale that is insoluble in common organic solvents. Bitumen is defined as unvaporized benzene-soluble organic matter that is formed during the heating period and that remains in the shale sample. However, bitumen formation may depend on the kerogen structure, and there may be a variety of intermediate products[20]. Because certain physicochemical properties of the bitumen changed with temperature and reaction time, Turner *et al.*[21] have suggested that the varying bitumen composition was responsible for the lack of fit of the bitumen data to the kinetic model of kerogen decomposition shown above.

The compound-type characterization of these high-boiling, high-molecular-weight bitumens by TLC–FID/CLD allowed the investigation of bitumen composition changes caused by the reaction conditions in kerogen decomposition. The 400°C isothermal pyrolysis tests of western oil shale samples at 5–480 min reactor residence times were performed. The amounts of bitumen recovered on the basis of dry shale sample from each test ranged from 1.35 wt.% (5 min) to 6.26 wt.% (60 min). Average molecular weights determined by vapor phase osmometry of these bitumens ranged from 1030 (5 min) to 500 (360 min). By using the TLC–FID/CLD mass response factors (Table II) for the different compound-type fractions and weighting each fraction on the basis of weight percentage of recovered bitumen, the relative amounts of saturate, PAH, NPAH, and polar compound-type fractions were determined. The weight percentage of each fraction of the oil shale was plotted *versus* the $\log_e$ of the reaction time (Fig. 3). Significantly different bitumen compositions are indicated at the different reaction times. In particular, different amounts of the NPAH and polar fractions were recovered in the bitumen at different reaction times, whereas the amounts of saturated compounds and PAHs were generally constant. The amounts
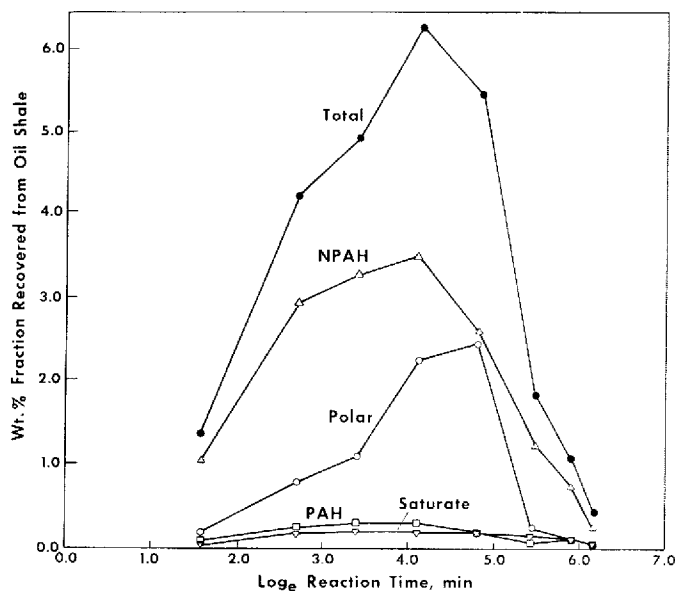

Fig. 3. Hydrocarbon distributions in bitumen recovered from oil shale at different reaction times at 400°C.
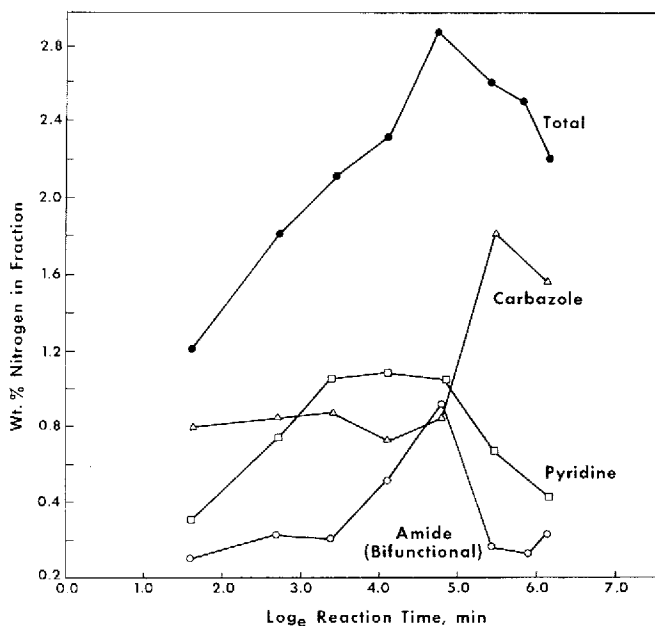
Fig. 4. Nitrogen distributions in shale bitumens produced at different reaction times at 400°C.

of the recovered NPAH fractions increased steadily from 5 min to 60 min (maximum bitumen recovery) at 400°C; the NPAH amounts decreased sharply at longer reaction times. The amounts of polars increased slowly from 5 to 30 min, rapidly increased from 30 to 120 min, and decreased sharply after 120 min.

The differential TLC–FID/CLD analysis of the bitumens was used to determine the relative amounts of nitrogen in carbazole, pyridinic, and amidic derivatives. The total nitrogen content increased from 1.2 wt.% (5 min) to 2.8 wt.% (120 min) and decreased to 2.2 wt.% (480 min). These data (Fig. 4) indicate that different bitumen compositions were obtained at different reaction times, which suggested multiple bitumen intermediates during kerogen decomposition. For each nitrogen type, the maximum concentration was observed at different reaction times: pyridinic nitrogen (60 min), amidic nitrogen (120 min), and carbazole nitrogen (240 min). Carbazole derivatives have been generally considered the most refractory (unreactive) nitrogen species, and as expected at long reaction times, these refractory species were noted to have survived isothermal heating. Lesser amounts of bifunctional species including amides and hydroxypyridine derivatives resulted from their susceptibility to thermal decomposition. Also, interconversion of nitrogen functionalities may occur during the decomposition of kerogen.

Western oil shale bitumens contained more aromatic carbons and correspondingly less aliphatic carbons as the pyrolytic reaction times increased. This was attributed to the aromatization of aliphatic carbons as thermal decomposition proceeded[16]. These TLC–FID/CLD data suggested that at times longer than 60 to 120 min, the increase in aromatization resulted, in part, from the presence of relatively large amounts of carbazole compounds and other dealkylated aromatic ring systems.

The TLC–FID/CLD analysis of bitumens produced by the 400°C pyrolysis of eastern oil shale indicated a more aromatic but less polar bitumen composition compared to the western oil shale bitumens. The maximum production of eastern oil shale bitumen occurred at 15 min rather than at 60 min as for the western oil shale bitumen. Again, the TLC–FID/CLD data provided compound-type information consistent with the observation that the bitumen composition was dependent on the reaction time. From the thermal decomposition of kerogen, a bitumen intermediate as a single entity was not indicated. These data suggest that bitumen and thermal decomposition formation were also dependent on the different kerogen structure for the two different shales.

Presumably, at long reaction times, secondary reactions such as the cracking and coking of the organic material occurred; these reactions effectively decreased the amounts of NPAHs and polar compounds recovered from the bitumen. The amounts of saturated compounds in the bitumen were either unaffected by the pyrolysis process or were formed as products from these secondary reactions. Also, the amounts of the recovered PAH and NPAH fractions at these reaction conditions generally increased and decreased at similar rates.

Low amounts of polar components at long reaction times result from coke formation on the spent shale as well as increased gas production. The different bitumen compositions are affected by the original components in the kerogen being converted at different times to bitumen. Because thermal decomposition of the components comprising the bitumen result in gas, oil, and coke products, the different components of the bitumen have different susceptibilities to product formation. In kerogen decomposition both a reaction time and temperature dependence is observed and a range of activation energies must be considered.

CONCLUSIONS

The TLC–FID/CLD analyzer was shown to be a versatile analytical tool. The sequential TLC–FID/CLD analysis of high-boiling, high-molecular-weight fossil fuel materials provided hydrocarbon and nitrogen compound-type distributions. The reaction mechanisms ongoing in bench-scale process studies were investigated by relating the compound-type distributions of the reaction intermediates with process conditions. In the present study of the thermal decomposition of kerogen, the TLC–FID/CLD demonstrated that the composition of the bitumen as a reaction intermediate is dependent on the source of the shale and reaction time.

The FID mass response factors were shown to depend on the configurations of the hydrogen-air flame, the detector, and the TLC support. Mass response factors were dependent on heteroatom content and component volatility. The different mass response factors for tar sand bitumen and for oil shale bitumen indicated that the FID must be calibrated for different source materials. The lower mass responses for saturates and PAHs compared to NPAHs suggested that the associations and interactions of these components on the silica gel were different. The TLC support affected elution behavior as demonstrated by the impregnation of chromium ions on the Chromarod SII. This particular Chromarod SII treatment was shown to provide a differential nitrogen-type analysis.

An advantage of TLC–FID/CLD analysis was the ability to characterize very

small quantities of material containing large amounts of high boiling material. The vacuum-assisted analysis allowed improvement in the FID response detection by increasing the samples' ionization with lower pressures. This requirement of less sample improved the resolution of the components. The rapid analysis of hydrocarbon and nitrogen species (four samples in duplicate done in less than 4 h) was performed with fair reproducibility (R.S.D. 4 and 5%, respectively). The nitrogen-specific CLD was found to be the nitrogen detector of choice with high sensitivity over a wide dynamic range.

ACKNOWLEDGEMENTS

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