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Inorganic constituents in American lignites

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Both the discrete mineral phases and the ion-exchangeable inorganic constituents of lignites from Texas, Montana, and North Dakota have been studied. The ion-exchangeable cations and the carboxyl groups with which they are associated were characterized by ion exchange methods utilizing ammonium acetate and barium acetate respectively. Na, K, Mg, Ca, Sr, and Ba were found to be present in all three coals, but significant variations in the relative and absolute concentrations of all the cations were observed. It was found that Ca and Mg were the most abundant cations and that 40–60% of the carboxyl groups in the raw coals were exchanged with cations. The discrete mineral phases in these lignites were studied by semi-quantitative X-ray diffraction and infrared spectroscopy. The importance of the cations in this analysis was shown when the mineralogical analyses of the low-temperature ash (LTA) of the coals with the cations removed and the raw coals were compared. Results show that up to 50% of the LTA of these raw coals can be attributed to the existence of metal cations and that fixation of sulphur, carbon, and oxygen to form carbonates and sulphates is the major reason for this contribution.

When lignitic coals are subjected to liquefaction, gasification, and combustion conditions, they exhibit behaviour which is quite different from that of higher-rank coals. One of the major causes of these differences is the nature of the inorganic constituents present. These inorganic constituents can be divided into three classes: discrete mineral phases, organo-metallic compounds, and trace elements. The most significant feature of the inorganic constituents of lignites is the large amount of exchangeable cations. These cations are mainly alkali and alkaline-earth metals associated with carboxyl groups which are in high concentration in lignites.

A number of investigators have shown the effect of these cations on coal utilization processes. United States Bureau of Mines investigators[1] found that the slagging behaviour of low-rank coals in combustion processes is greatly influenced by the amount of ion-exchangeable cations. Walker, *et al.*[2] and Hippo *et al.*[3] have found that exchanged cations can act as active catalysts when lignites are gasified. Wakeley *et al.*[4] investigated the formation of carbonates when low-rank coals are liquefied and related the extent of formation to the quantity of ion-exchangeable calcium. The presence of exchangeable cations can also affect the analysis of lignites. For example, Miller *et al.*[5] showed that the cations present in lignites can form sulphates under the conditions present during low-temperature ashing.

Although these researchers have shown cations to be important in the processes described, satisfactory techniques for the analysis of the cations, the carboxyl groups, and the mineral phases present in American lignites have not been fully developed. The characterization of these constituents is the topic of this paper.

EXPERIMENTAL

The lignites chosen for this study were three whole channel samples from Texas, Montana, and North Dakota. The proximate and ultimate analyses of these samples are given in *Table 1*.

Carboxyl group determination

The determination of the carboxyl group content was modelled after that of Schafer[6,7] and employs exchange of the carboxyl groups with barium acetate. The first step is the demineralization of the coal which serves two functions. First, it puts all the carboxyl groups in the acid form, thereby facilitating complete exchange and permitting a quantification of the total exchange capacity by observing the variation of pH of the solution. Second, demineralization removes minerals which undergo exchange reactions (e.g. clays).

Brooks and Sternhell[8] have shown that demineralization has a negligible effect on the amount of oxygen containing functional groups in coal. In a study of these groups, they found that no significant change in carboxyl group concentration occurred as a result of oxidation of the coal or rearrangement of functional groups existing prior to demineralization.

Table 1 Analyses of lignites studied

PSOC coal	246	623	833
State	North Dakota	Texas	Montana
Seam	Hagel	Darco	Fort Union
	Ultimate analyses (wt % dry basis)		
Ash	9.7	16.6	13.0
C	64.9	60.9	61.0
H	4.4	4.5	4.5
N	1.4	1.1	0.9
Total S	0.6	1.1	0.5
O (by difference)	19.8	15.8	20.1
	Proximate analyses (wt % dry basis)		
Ash	9.7	16.6	13.0
Volatile matter	44.7	44.6	40.9
Fixed carbon	45.6	38.8	46.1

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The demineralization procedure is a modified form of that developed by Bishop and Ward.[9] It entails washing the coal successively with 5N HCl, 29N HF, and 12N HCl for periods of 1 h at 328–333 K. From the results of Bishop and Ward, it is apparent that retention of HCl in demineralized coals is significant. De *et al.*[10] investigated the effect of HCl retention on the determination of the carboxyl group content via ion exchange and found that essentially all of the adsorbed HCl can be removed by refluxing in distilled water. Thus the demineralized coal was refluxed for 2 h. The coal was then washed repeatedly with distilled water until Cl^- was no longer detected with the use of silver nitrate.

In the carboxyl group determination, exchange of the acid form carboxyl groups can be represented as:

$$2(R-COOH)+Ba(CH_3COO)_2 \rightleftharpoons Ba(R-COO)_2 + 2(CH_3COOH)$$

The exchange of two carboxyl groups with each divalent barium ion has been substantiated by evidence presented by Schafer[6]. The release of acetic acid results in a decrease in pH of the solution, and the quantity of released acetic acid can be determined by titration.

Specifically, 0.5 g of demineralized coal, ground to <200 US mesh under N_2 (to preclude significant oxidation), was mixed with 250 ml of 1N barium acetate (pH of 8.25–8.30) in a refluxing apparatus. Schafer[6,7] has shown that the use of 1N barium acetate at a pH of 8.25–8.30 achieves complete exchange of the carboxyl groups. Refluxing was performed under purified N_2 to prevent oxidation of the coal during refluxing which would result in the precipitation of barium carbonate and a decrease in the pH. The coal–barium acetate slurry was refluxed for 4 h. At the end of this period it was cooled to room temperature and the pH recorded. Barium hydroxide (0.05N) was then added to the solution until the pH was restored to the original value. The quantity of barium hydroxide utilized could be used to calculate the number of carboxyl groups exchanged. This cycle of refluxing and titration was repeated for two additional 4 h periods.

Carboxyl contents are reported on a dry, mineral matter-free basis (dmmf). Moisture content was determined by heating the lignite for 1 h at 378–383 K. The residual mineral matter content was determined by low-temperature ashing of the demineralized coal.

To check the carboxyl group determination, the amount of Ba exchanged onto the coal was determined by back exchanging with 0.2N perchloric acid. First, the coal was washed with 1N sodium acetate (pH of 8.25–8.30) to remove any barium acetate remaining on the coal after filtration. The choice of the proper wash solution is critical since all the excess barium acetate must be removed without hydrolysing or exchanging the barium carboxylates. The pH of 8.25–8.30 minimizes hydrolysis and the use of sodium acetate minimizes exchange due to the low affinity which sodium has when compared to barium in ion exchange reactions. Thus the coal was washed twice with a total of 25 ml of wash solution under flowing N_2. The exchanged and washed coal was then mixed with 50 ml of 0.2N perchloric acid and the slurry stirred and boiled for 20 min. The solution was then analysed for barium by emission spectrometry, and the carboxyl content calculated by assuming two carboxyl groups to be exchanged with each barium ion.

Exchangeable cation determination

The determination of exchangeable cations in the raw coal also utilizes ion exchange. For this determination, 1N ammonium acetate (pH of 7.0–7.2) was employed, because of the absence of ammonium ions in the raw lignites. A pH of 7.0–7.2 is considered to be sufficient because groundwaters found in association with coal ar acidic.

Specifically, 0.5 g of as recieved coal, ground to <200 mesh, was mixed with 50 ml of 1N ammonium acetate. This slurry was stirred at room temperature for 3 h, filtered and washed with a total of 25 ml of 1N ammonium acetate. Next, the coal was transferred back to the beaker with 1N ammonium acetate and the slurry diluted to 50 ml. The procedure of extraction and filtration was repeated for four more 3-h periods, followed by an overnight extraction period and an additional 3-h period in the morning. Each filtrate was acidified with 5 ml of glacial acetic acid, further diluted with 1N ammonium acetate, and stored to await analysis. After 27 h, the extracts were analysed for Ca, Mg, Na, K, Sr, and Ba by emission spectrometry.

Mineral matter determination

Low-temperature ashing was used to separate the mineral matter from the organic matter. Although this technique has been found to be suitable for use with high-rank coals, the existence of cations in low-rank coals can lead to spurious results.[5] To observe the effect of cations, both raw and ammonium acetate treated lignites were subjected to low-temperature ashing, using the procedure recommended by Miller *et al.*[5]

After low-temperature ashing of the coal, the residue was subjected to both qualitative and quantitative mineralogical analyses. The qualitative analysis was performed with the use of infrared spectroscopy, X-ray diffraction and optical microscopy. Quantitative analysis of calcite, pyrite and quartz was performed by using X-ray diffraction. The amounts of these phases present in the LTA was determined by the internal standard technique outlined by Rao and Gluskoter[11] and Jenkins and Walker.[12] By this technique, the ratio of the mineral peak area to that of the internal standard (calcium fluoride) is related to the quantity of the mineral present. Calibration curves were prepared by analysing a series of mixtures containing various proportions of calcite, quartz, pyrite, and a clay mixture (1:1 kaolinite:montmorillonite). The use of peak areas in the preparation of the calibration curves as opposed to peak heights results in less error due to differences in crystallinity between the minerals in the coal and the calibration standards. The sample preparation included: grinding the mineral to <325 mesh; mixing the calibration mixture with calcium fluoride, in the proportions 1:0.2, in a Spex mixer/mill for 30 min; and mounting the sample by the cavity mount technique.[11,12] The peaks used in this analysis from diffraction of CuK_α were: quartz, 26.7°; calcium fluoride, 28.3°; calcite, 29.4°; and pyrite, 33.0° (2θ). In the case of the raw coal LTA, additional treatment was necessary because of the presence of bassinite. Gypsum ($CaSO_4 \cdot 2H_2O$) is the sulphate form found in raw lignites, but bassinite ($CaSO_4 \cdot 1/2\ H_2O$) and anhydrite ($CaSO_4$) are the only forms of the mineral found in the LTA of the lignites studied. The 29.8° peak of bassinite overlaps the 29.4° peak of calcite. Therefore the LTA was heated to 773 K in flowing N_2 for 2 h to dehydrate the bassinite present, converting it to anhydrite which has no peak around 29°.

Kaolinite and anhydrite are analysed by infrared spectroscopy. The pellets were composed of 200 mg of KBr and 1 mg of sample, and were prepared by a double press method in a vacuum die. Calibration mixtures in the form of pellets were prepared with varying amounts of pure kaolinite and anhydrite. The absorbance, calculated by the baseline method,[13] was then compared to the quantity of the mineral present. Peaks utilized in the quantitative analysis were 670 cm^{-1} for anhydrite and 910 cm^{-1} for kaolinite. The spectrum of both bassinite and anhydrite have a 670 cm^{-1} peak; therefore, it was necessary to convert bassinite to anhydrite by heating to 773 K. As this treatment alters the clay structure, the amount of kaolinite present in the LTA was determined in a sample of the untreated LTA.

After analysis of these five minerals was completed, a significant portion of the LTA was still unaccounted for. The amount of clays other than kaolinite was determined by a normative method. To perform the normative analysis one must have a measure of the percentage Si and Al and a semi-quantitative analysis of the amounts of kaolinite and quartz in the LTA. When these values have been determined, the amount of SiO_2 and Al_2O_3 accounted for by the quartz and kaolinite present can be calculated. The amount of total other clays (i.e. illite, montmorillonite, and mixed-layer clays) can now be calculated by assuming a reasonable figure for the amounts of SiO_2 and Al_2O_3 in these clays (25% Al_2O_3 and 50% SiO_2[14]). After the quantity of other clays was calculated, the unaccounted for portion of the LTA was calculated by difference.

Table 2 Carboxyl contents of lignites

	Carboxyl contents, meq g^{-1} (dmmf)	
PSOC coal	Titration	Ba^{++} Released
246	3.13 ± 0.05	3.24
623	2.11 ± 0.08	2.22
833	3.00 ± 0.07	3.07

Table 3 Amount of carboxyl groups exchanged *versus* time

	Carboxyl group content (meq g^{-1}, dmmf)			
Cumulative time (h)	PSOC 246 <200 mesh	PSOC 623 <200 mesh	PSOC 623 <80 mesh	PSOC 833 <200 mesh
4	2.51	1.75	1.76	2.52
8	2.96	2.02	2.04	2.91
12	3.13	2.11	2.11	3.00

RESULTS AND DISCUSSION

Carboxyl group determination

Table 2 presents the results of the carboxyl group analysis. Each value, calculated from the titration results, represents the average of six to eight determinations with the value of one standard deviation also given. The barium released values are for one determination, and are presented as a check on the titration measurements. The values of the standard deviations and the agreement of the two techniques display the precision of the determination. The good agreement between the two methods also substantiates the assumption that approximately two carboxyl groups are exchanged with each divalent barium ion. The oxygen contained in the carboxyl groups accounts for a significant portion of the total oxygen (by difference) values for the lignites. The percentage of the total oxygen contained in these groups is 46% (North Dakota), 37% (Texas), and 42% (Montana).

Schafer[6,7] suggested that there is an optimum number of 4-h refluxes. That is, one reflux is not sufficient for complete exchange, but excessive refluxes will lead to physical adsorption of barium acetate and barium hydroxide. The rationale behind the use of three 4-h refluxes is shown in *Table 3* where the cumulative amounts of carboxyl groups exchanged *versus* time are shown. Each value is the average of six to eight determinations. In each case, 5% or less of the total exchange occurred in the final 4-h period, which demonstrates the completeness of exchange. Agreement between the titration and barium released values illustrates the absence of significant amounts of barium adsorption.

The effect of particle size for the <80 and <200 mesh fraction of PSOC 623 can also be seen in *Table 3*. The fact that no significant difference exists suggests that essentially all of the pore surface area containing carboxyl groups was available to the barium ions for exchange.

Amounts of carboxyl groups reported here are in good agreement with values found in the literature. Schafer[6] studied a suite of low-rank coals from the United States, Australia, Thailand and Hungary. He found a range of 1.0 to 3.4 meq g^{-1} of carboxyl groups on his samples. Of the samples he studied, he found a North Dakota and a Texas lignite to contain 2.2–2.3 meq g^{-1}. Cronauer and Ruberto[15] found an American lignite (origin not reported) to contain 1.1 meq g^{-1} of carboxyl groups.

Exchangeable cation determination

Table 4 summarizes the results of the exchangeable cation analysis, and shows that Ca and Mg are always the predominant cations. The other four cations (Na, K, Sr, and Ba) vary in both relative and absolute amounts. In *Table 4*, the average value for one standard deviation of each of the elements is also shown. Deviation is acceptable

Table 4 Cation contents of lignites associated with carboxyl groups

PSOC coal	Cation concentrations, 10^{-4} (g/g, dmmf)						
	Mg^{++}	Ca^{++}	Na^{+}	K^{+}	Ba^{++}	Sr^{++}	Total
246	34.4	171	27.8	1.89	6.51	3.30	244.9
623	22.6	129	8.69	3.42	3.36	2.38	169.5
833	59.8	212	10.0	5.30	10.9	3.34	301.3
1 S.D	2.4%	3.3%	8.5%	44%	5.0%	3.3%	

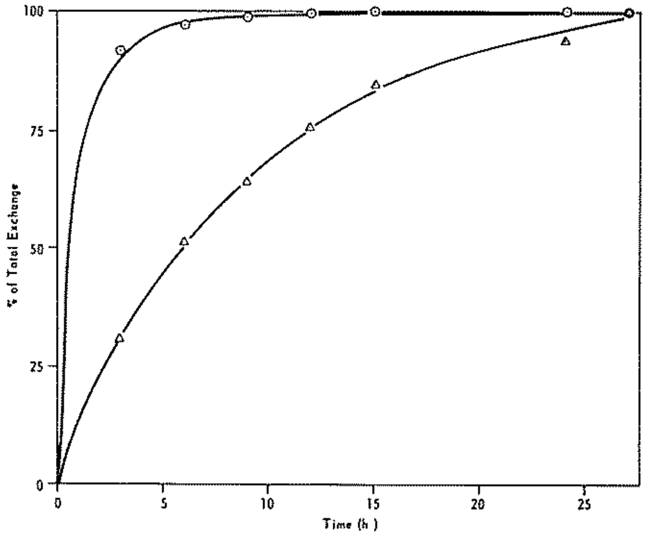

Figure 1 Release of magnesium (○) and barium (△) from PSOC 246 during ammonium acetate treatment

with the exception of K, which tended to be difficult to analyse because of a drift in the K emission intensity owing to consumption of the spectrometer electrode which resulted in an increase in the plasma temperature. The cations present are exchanged on a significant portion of the total carboxyl groups. Assuming two carboxyl groups to be associated with divalent cations and one with monovalent cations, the coverage of carboxyl groups by cations is estimated to be 43% (North Dakota), 44% (Texas), and 54% (Montana).

To investigate the quantity of cations which originate from the mineral matter, an experiment was performed in which 1 g of various mineral standards (< 325 mesh) was stirred overnight at room temperature in 100 ml of 1N ammonium acetate. The minerals studied were calcite, dolomite, gypsum, illite, kaolinite, montmorillonite, pyrite, and quartz. Gypsum was totally soluble in the ammonium acetate and it was the only mineral that was significantly soluble. Gypsum is also soluble in 1N NH_4OH (50% wt loss). Despite this lower weight loss, highly basic conditions raise the problem of humic acid extraction. Acidic exchange mediums will solubilize carbonates and clays. Since gypsum is usually reported as a minor or trace mineral phase in lignites, the choice of 1N ammonium acetate treatment seems appropriate. The amount of Ca contributed in this manner can be estimated if the following assumptions are made: gypsum percentage of mineral matter is less than 5%, lignite contains 10% mineral matter, and 1.5% exchangeable Ca. Using these assumptions, one can calculate that less than 10% of the reported values for exchangeable Ca concentration is derived from solubilized gypsum.

Although clays possess relatively high ion-exchange capacities,[16] the amount of cations extracted from this source can be shown to be relatively small. If one assumes that the lignite contains 10% mineral matter and 25% of this is the clay in question, it can be calculated that the highest contribution of cations is from montmorillonite: and it is always less than 0.5% of the cations detected from the lignites in this study.

Figure 1 shows the release *versus* time behaviour for Mg and Ba in PSOC 246. In all three coals Mg was released rapidly and Ba slowly. The difference is a function of the affinity and mass transport porperties of the cations. *Figure 1* shows the need for a 27-h exchange period. This exchange period was felt to be sufficient because the average wt % of the total cation contents extracted in the final 3-h period was (average over all three lignites): Mg, 0.2; Ca, 0.7; Na, 3.0; K, 5.9; Ba, 4.6; and Sr, 0.4%.

The cations extracted by ammonium acetate are a significant portion of the total amounts of these elements present in the raw lignites (i.e. both exhanged on carboxyl groups and present in minerals). *Table 5* presents the percentage of the total quantities of Ca, Mg, Ba, and Sr which was extracted by ammonium acetate. Unfortunately, the technique used to quantify the total amounts of these elements[17] appears to lead to loss of K and Na; and, therefore, the results for these elements are not presented.

The concentrations of exchangeable cations are in good agreement with the limited amount of data in the literature. Wakeley *et al.*[4] used extraction with barium acetate to study the cations in a Wyoming subbituminous coal. They found it to contain 0.99 wt% Ca (dry basis). Murray[18] studied a Victorian brown coal from Australia and estimated the quantities of exchangeable cations to be: Ca, 0.39; Mg, 0.55; Na, 0.48%, on a dry coal basis. Similar results were found by Durie[19] on a Morwell brown coal.

Mineral matter determination

The results of the mineralogical analysis are given in *Table 6*. Total LTA contents in the lignites along with the values for one standard deviation over 4–6 determinations are given. Also listed are percentages of the minerals quantified, 'other clays', and 'unaccounted for' (by difference) values. The quantitative analyses of the specific minerals are the average of three runs, and the precision of the values is estimated to be ±1–2%. Both measures of precision are on an absolute basis. That is, a value of 25±2% means the values can vary from 23–27%.

One significant feature of the results is the comparison of the total LTA obtained from the raw and ammonium acetate treated coals. In every case ammonium acetate treatment of the raw coals sharply reduced the LTA subsequently obtained, with reductions of over 50% seen for PSOC 246 and 833. This result combined with the quantitative analyses of the phases present displays the problems in obtaining unaltered LTA samples from lignites. In general, an increase in the percentages of quartz and clays is seen when comparing the LTA of the ammonium acetate treated and raw lignite samples. This is due to a concentrating effect; i.e., the amounts of clays and quartz are the same, but the total LTA is less. However, calcite and anhydrite show the opposite behaviour. Significant quantities of these minerals exist in the LTA of the raw coal, but little exists in the LTA of the ammonium acetate treated samples. This behaviour suggests that calcite and anhydrite are artefacts of the low-temperature ashing process and that they are formed by

Table 5 Percentage of elements in raw lignites extracted by ammonium acetate

	PSOC 246	PSOC 623	PSOC 833
Ca	70	79	79
Mg	60	62	84
Ba	100	68	71
Sr	78	82	74

Table 6 Mineral matter in LTA residues of lignites

LTA (wt % dry coal)		Mineral matter (wt % LTA)						
		Kaolinite	Quartz	Pyrite	Calcite	Anhydrite	Other clays	Unaccounted for
					PSOC 246			
.aw	11.5 ± 1.3	5	9	Nil^a	11	21	17^b	37^c
NH_4AC	4.6 ± 1.0	8	15	Nil	Nil	1	57^b	19
					PSOC 623			
Raw	20.5 ± 0.3	41	12	Nil	2	14	7^b	14
NH_4AC	16.9 ± 0.4	41	12	Nil	Nil	1	24^b	32
					PSOC 833			
Raw	17.4 ± 0.4	20	19	Nil	16	10	8^b	27^c
NH_4AC	8.2 ± 0.8	41	26	Nil	Nil	4	24^b	5

[a] Nil refers to minerals detected but in amounts too small to quantify

[b] Characteristic clay peak (19.9° 2θ) found but not enough information to determine which variety

[c] Characteristic peak of dolomite and ankerite (30.8–30.9° 2θ) found but not enough information to distinquish between the two

the interaction of exchangeable Ca with oxides of carbon and sulphur.

There is a problem in measuring the amount of anhydrite formation during low-temperature ashing of the raw lignite, because ammonium acetate was found earlier to solubilize gypsum. However, gypsum is not usually found in large quantities in raw lignites. This was confirmed for the samples in this study from results of an optical microscopy analysis.

In view of the preceding evidence, it appears that both calcite and anhydrite were formed in the low-temperature asher. It seems logical that carbonates and sulphates other than these two should have also been formed. However, with the amounts of the other cations in the lignites being in much lower concentrations, it is not surprising that their carbonates and sulphates have not been observed.

These results display the difficulties involved with mineralogical analyses of lignites. This problem is related to the presence of exchangeable cations in the lignites. It is very difficult, if not impossible, to remove the cations without affecting other parameters. In this study, the gypsum was removed by ammonium acetate. However, it is believed that the the amount removed is significantly less than the amount reported in the mineralogical analyses of the raw coal LTA. Therefore, it is certain that any comprehensive technique to analyse the mineral matter present in lignites will entail a significant amount of work which is not necessary in coals where exchangeable cations are not present.

CONCLUSIONS

This study was conducted to develop methods for characterization of the major inorganic phases present in American lignites. The ion exchange techniques utilized to define the number of carboxyl groups and the amounts of exchangeable cations have been shown to be relatively precise, simple, and suitable for lignite characterization. The results of these analyses show that carboxyl groups and exchangeable cations exist in significant quantities in lignite deposits from Texas, North Dakota, and Montana. The fact that Ca and Mg are always the dominant cations is also significant. The mineralogical analysis displays some interesting effects of the exchangeable cations on such analyses, namely, the formation of relatively large quantities of carbonates and sulphates when lignites are subjected to low-temperature ashing. There are some problems with the mineralogical analysis procedure described, but it does provide insight into the amounts of major minerals present in lignites. Finally, the significance of exchangeable cations in lignite utilization and analysis displays the need for routine determination of the cation–carboxyl system present in these coals.

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Method for determining the olefinic content of the saturated and aromatic fraction of petroleum distillates by hydroboration

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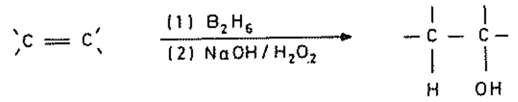
This study was prompted by a perceived need for a reliable method for determining olefin content in petroleum distillate fractions. An improved analytical method for the determination of olefin content in naphtha and higher boiling distillate fractions is described. The procedure comprises quantitative addition of diborane that specifically converts the olefins in the saturated and aromatic portion of the petroleum to alcohols. The reaction mixture is chromatographed on alumina, and alcohols are eluted with dichloromethane. The procedure was applied to two hydrocarbon mixtures of 20 saturated, olefinic and aromatic hydrocarbons in the investigated boiling range. Naphtha (ibp–200°C) and light gas oil (200–350°C) fractions from the Lloydminster oil were also analysed. Results are compared with the standard FIA method, and a method utilizing both the FIA and proton magnetic resonance spectrometry.

Several methods have been used for the determination of olefin content in petroleum fractions[1-5]. Results of the fluorescent indicator adsorption (FIA) method,[1] which uses silica gel chromatorgaphy, are highly dependent upon interpretation by the analyst, and the method is not applicable to petroleum fractions higher than the naphtha boiling range. Because of the subjective judgements that have to be made in this and other methods, e.g., bromine number method[2] and a method utilizing FIA and proton magnetic resonance[3] (p.m.r.), it is very difficult to obtain accurate results. There is a large deviation between experimental and theoretical bromine number values because of the presence of dienes, S- and some N-containing compounds in petroleum samples. Hydroboration of olefins in hydrocarbon mixture distillates was first investigated by Jackson *et al.*[4,5] in shale oil. To determine olefin content they used a lengthy procedure which involves determining the saturates and aromatic content by different standard methods, then hydroborating the olefins and calculating their content by difference. The procedure is not applicable to hydrocarbon mixtures in boiling ranges lower than 200°C.

The application of heat to petroleum in the course of refining frequently produces olefins. These compounds greatly complicate the analysis of the saturated and aromatic fractions of petroleum by mass spectrometry. This paper describes a method designed to eliminate the olefins from the saturated and aromatic fractions of petroleum distillates so that these fractions may be analysed by mass spectrometry to determine the number of rings present. In addition, a quantitative estimate of the olefinic material may be obtained.

This method is based upon the specific and quantitative addition of diborane to olefins which are converted to alcohols after oxidation with a basic peroxide solution. This is illustrated by the equation:



$$>C=C< \xrightarrow[(2)\ NaOH/H_2O_2]{(1)\ B_2H_6} -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-$$

The hydroboration reaction of the distillate leads to a mixture of saturates, aromatics and alcohols. The alcohols are separated from the hydrocarbon mixture by chromatography on alumina. The quantitative recovery of the alcohols gives a more precise estimate of the actual amount of olefins. The amount of olefins in the sample is determined directly from simple calculations of 3 weighings: weight of oil sample, weight of hydroboration product mixture and weight of alcohols recovered from the reaction mixture. This procedure is applicable to the whole boiling range of petroleum distillate. Detailed derivation of the equation leading to the determination of olefin content is described in the Experimental section. The overall time required for an analysis is ≈4 h. The method was first tested on two synthetic mixtures of saturated, olefinic and aromatic hydrocarbons in the range ibp–200°C and 200–350°C (*Table 1*). The total conversion of olefins to alcohols was monitored by p.m.r. The hydroboration procedure was carried out in ether because of the ease of removing this solvent from the volatile hydrocarbons in naphtha without any appreciable losses.[6] Only the lighter C_5 paraffins in the naphtha can present a source of negligible error in the results. The accuracy of the determinations was approximately ±7% for the samples investigated.

Table 1 Saturated, olefinic and aromatic hydrocarbons used in synthetic mixtures

Mixture I (ibp–200°C)	Boiling point (°C)	Mixture II (200–350°C)	Boiling point (°C)
4-methyl-1-pentene	53	dodecane[a]	216
2-methyl-1-pentene	62	tridecane[a]	235
1-hexene	64	1-tetradecene	251
2-ethyl-1-butene	64	tetradecane[a]	253
hexane[a]	68	biphenyl	255
1-heptene	94	pentadecane[a]	270
heptane[a]	98	1,1-diphenylethylene	270
isooctane	99	1-hexadecene	274
toluene	110	hexadecane[a]	286
B-pinene	165	2-nonadecene	328

[a] Straight-chain

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