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A GAS LIQUID-GAS SOLID CHROMATOGRAPHIC METHOD FOR THE IDENTIFICATION OF SOURCES OF OIL POLLUTION

A. E. GEORGE, G. T. SMILEY, D. S. MONTGOMERY AND H. SAWATZKY

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A GAS LIQUID-GAS SOLID CHROMATOGRAPHIC METHOD FOR THE IDENTIFICATION OF SOURCES OF OIL POLLUTION

by

A. E. George*, G. T. Smiley**, D. S. Montgomery*** and H. Sawatzky*

ABSTRACT

A two-step gas chromatographic fingerprinting technique has been developed for the identification of petroleum that may be conveniently applied to oil spills. The first step consists of a gas chromatographic separation on non-polar silicone rubber (SE-30) which separates according to boiling point. Five arbitrary 20° cuts are made then further separated by gas chromatography on columns of lithium chloride supported on diatomaceous silica (Chromosorb A). The advantage of this inorganic packing is its high thermal stability that permits the separation of high-boiling oil components not readily affected by weathering. It also has the added advantage of causing no "bleeding" problems that can complicate further analyses involving mass spectroscopy. The simultaneous use of the flame ionization detector and the Melpar sulphur detector provides highly characteristic fingerprints. This method has been applied to two heavy crude oils, and two fuel oils involved in oil spills from the "Arrow" and "Irving Whale" to demonstrate the potential of the method.

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Direction des mines

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UNE METHODE DE CHROMATOGRAPHIE EN PHASE GAZEUSE ET CHROMATOGRAPHIE GAS SOLIDE POUR L'IDENTIFICATION DE SOURCES DE POLLUTION DU PETROLE

par

A. E. George*, G. T. Smiley**, D. S. Montgomery*** et H. Sawatzky*

RÉSUMÉ

Une technique à deux étapes chromatographiques a été developpée pour l'identification du pétrole. Cette technique peut être pratiquement appliquée pour les échappés du pétrole. La première étape se compose de chromatographie sur le caoutchouc silicone (SE-30) non polaire qui fait la séparation selon le point d'ébullition. Cinq fractions arbitraires ayant des intervalles d'ebullition de 20°C sont recueillies pour rechromatographier sur une colonne qui se compose de silice à diatomées (Chromosorb A) recouverte de chlorure de lithium. L'avantage de ce remplissage inorganique de colonne est sa stabilité thermique élevée qui permet de séparer les composés du pétrole à haut point d'ébullition. Ces composés résistent à la dégradation sous les conditions atmosphériques. Le remplissage inorganique a aussi l'avantage de ne pas causer de problème d'entraînement de la phase stationnaire qui puisse ainsi compliquer les autres étapes d'analyse qu'engage l'usage de la spectroscopie de masse. L'application simultanée du détecteur à ionisation de flamme et du détecteur Melpar de soufre permet d'obtenir des empreintes très caractéristiques du pétrole. La méthode a été appliquée à deux pétroles lourds et à deux mazouts recueillis lors des échappés d'une culbute de "l'Arrow" et de "l'Irving Whale" pour démontrer l'efficacité de la technique proposée.

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INTRODUCTION

Pollution emanates from crude oil or fuel oil as a consequence of ships discharging their tank washings or bilges at sea, but occasionally is the result of collisions or accidental spillages. Leaks from pipelines, storage tanks, and uncontained oil during undersea drilling operations can also be sources of pollution. In the last few years, slicks appeared off the coasts of Nova Scotia, Australia, California, Alaska, England and Florida. These mysteriously appearing slicks could be caused naturally by oil seeping through fissures in the ocean floor or by ships sunk during war time.

The problem of oil spillage in Canadian waters is becoming increasingly serious. According to a report prepared for the federal Department of the Environment, a major oil spill that would seriously affect the coastal environment of western Canada can be expected repeatedly if tankers begin transporting Alaskan oil to United States refineries. The recent oil spillages which drifted to the western coast of British Columbia are early indications of the validity of this forecast.

Work associated with various aspects of oil spillage has been increasing steadily for several years by the major oil companies and government agencies. One problem of growing interest is the identification of pollution samples. In the past the analysis of beach samples of oil has been largely in terms of oil resins and asphaltenes, wax content and elemental analysis. The characteristics that help distinguish one oil from another have been found to include volatility, amount and relative proportion of trace metals and a significant difference in sulphur and nitrogen content. A Canadian association, The Oil Slick Group (consisting of 200 scientists), is exploring the use of neutron activation analysis to establish the origin of an oil slick (1). In the United States, Gulf General Atomic has been investigating a similar neutron activation system since 1968, and work is being done at the University of Lund in Sweden to "tag" tanker loads with isotopes of iodine.

In a previous report (2) it was shown that the positive identification of the crude oil source of an unknown oil washed upon a beach presents many

difficulties when one considers the variety of crude oils trans-shipped throughout the world. The position is further complicated by the effects of exposure on oil from the time of discharge to the arrival of the pollution on the coastal areas. There are various pitfalls in trying to draw conclusions from the conventional methods of oil source identification.

A number of techniques exist for pollutant identification. These have been used with varying degrees of success (3 - 10). All these methods require sample clean-up and sometimes other pretreatment, such as ashing, before analysis. Also, in many cases, comparatively large samples are required for analysis.

Among the analytical methods already known to yield properties significant for the recognition of oil from various pollution sources, the gas chromatographic "fingerprint" method is recommended as the most suitable of the methods already mentioned for a quick examination of a pollutant. This technique can serve to eliminate a considerable number of possibilities. A direct gas chromatographic analysis of an oil sample has several advantages: very small amounts in the order of 50 μl are quite enough for analysis, no sample pretreatment is required, analysis is relatively rapid, and the fingerprinting method is the most dependable among the known procedures.

However, the gas chromatographic procedures that have been used are not sufficiently discerning to distinguish between very similar oils. Also, in general the oil components responsible for the major sharp peaks in the chromatogram are normal alkanes. These normal alkanes are susceptible to attack by micro-organisms and thus the chromatograms become less reliable as the oil ages.

We have developed a two-step gas chromatographic procedure that is superior to the single-step method. Also our method is capable of dealing with very high-boiling materials.

EXPERIMENTAL

Samples

Five samples were investigated:

(1) Lloydminster crude oil;
(2) Lathom crude oil;
(3) Bunker C from the "Arrow" cargo;
(4) Weathered bunker C from the "Arrow" incident collected from the beach on Crichton Island, Nova Scotia on April 21, 1970 (The wreckage was on February 4, 1970): and
(5) Weathered "Irving Whale" bunker C.

The method of fingerprinting comprises two steps:

(a) Simulated Distillation and Preparative Step:

A "Varian Aerograph" Model 2100 gas chromatograph was employed throughout the whole investigation. In the simulated distillation and preparative step a glass column (5 ft x 0.25 in. OD) was used. It was packed with 10 % silicone rubber SE-30 on acid-washed Chromosorb W, Dimethyl dichlorosilane-treated (DMCS), 60 to 80 mesh. The temperature was programmed at 4°C/min from 50°C to 300°C and then held isothermally at this temperature. The chart speed was 0.2" per minute. The carrier gas was helium and the flow rate was 200 ml/min. The effluent was split and 1/3 of it was diverted into the detector and the main stream to collection system.

Firstly, to establish a calibration curve, a 0.9-μl sample of n-paraffin mixture C_{10} - C_{36} (10 % solution in ethylbenzene) was chromatographed starting from 50°C up to 300°C of column temperature. Calibration of the column was repeated three times to ensure that the column did not change during the course of investigation. The calibration curve is shown in Figure 1.

The same column, without changing any of the conditions was used for direct chromatography of each of the three crude oils under investigation. In this case the dual detector Melpar-Flame Ionization was used. A 30-μl sample of the crude oil was directly injected, using a 100-μl Hamilton syringe, without overloading the SE-30 column. The injection port temperature was kept at 300°C and the initial 3 inches of the columnwere filled with acid-washed Chromosorb W

to trap out heavy residue and material boiling above 500°C, and thus protect the column. The effluent not passing into the detector was led into traps; each containing 60 mg of acid-washed Chromosorb W, 60 to 80 mesh. This amount of Chromosorb W was used to maintain the pressure differential needed to get the required split ratio. Five cuts were collected in the boiling ranges of 250 to 270°C; 270 to 290°C; 290 to 310°C; 310 to 330°C; and 330 to 350°C. These fractions boiling in the 250 to 350°C range were then rechromatographed on the analytical lithium chloride-diatomaceous earth column to obtain the fingerprints.

(b) Separation According to Type:

An inorganic column was used in this step. It consisted of a glass U-tube (5 ft x 0.25 in. OD) packed with 50 % lithium-chloride on diatomaceous silica (Chromosorb A) of 60 to 80-mesh size. The packing was prepared by covering the chromosorb with an aqueous solution of the salt and evaporating the mixture to dryness. The dry mixture was then fired at 700 to 750°C for 30 minutes in a muffle furnace. The chromatograph used was a Varian 2100 fitted with both flame ionization and Melpar sulphur detectors. The flow rate was 85 ml/min of helium.

The Chromosorb W from each collection tube that contained a fraction was packed into a glass capillary tube under nitrogen. The capillary tubes and their contents were then injected with a Hewlett-Packard solid injector on to the salt-containing column at room temperature. The column oven was heated to 50°C and then programmed at 4°C/min. The column was calibrated with amounts of normal alkane mixture that gave detector responses comparable to the responses obtained during the chromatography of the petroleum fractions.

Detectors

In this investigation the flame photometric detector with a sulphur-selective filter (394 μ) was used in conjunction with the flame ionization detector to obtain two fingerprints simultaneously and in this way to affect a significant improvement in the identifying power of the method.

Assigning Kovat's Indices to the Chromatograms

To compensate for fluctuations in chromatographic conditions, and make the results from the analytical step comparable in different laboratories, the retentions were expressed in terms of Kovat's indices. Retentions on the oil chromatogram were expressed relative to the retentions of n-alkanes as reference compounds. The Kovat's index of an n-alkane is by definition its number of carbon atoms mulitiplied by one hundred. Thus, a material eluting after decane but before undecane would have a retention, in terms of Kovat's index units, between 1000 and 1100 (10 plus linearily interpolated decimal fraction multiplied by one hundred) (11).

DISCUSSION

Critical Review of Methods of Oil Spill Characterization

In the past, attempts at characterizing oil spillages have relied on the usual process control or specification parameters such as distillation range, hydrocarbon type distribution, difference in sulphur and nitrogen content, and on physical properties such as density, viscosity, and aniline point. These attempts were not very successful, principally because the data the methods provide are not sufficiently precise to distinguish several alternatives.

The asphaltene content has also been used as a method of identifying the origin of an oil spill. It is well known that one of the first effects of exposure on an evaporated crude is an increase in its asphaltene content, which makes this type of analysis somewhat questionable.

The Ni/V ratio has been widely recognized as a useful parameter for crude oil identification purposes. Some suggest that, because the concentrations of both metals will be similarly affected by the evaporation losses of volatile materials, the Ni/V ratio will frequently provide identification by comparison with data for known crude oils. But the Ni/V ratio alone, except under rather special circumstances, is not sufficient to actually identify an individual crude oil. It should be borne in mind that the values obtained for V and Ni for certain crudes are very small and that any error in measurement will affect

the ratio considerably. An examination of the Ni and V contents of samples believed to be from the Torrey Canyon (12) and the Arrow (13), shows that the results fluctuate very substantially. Because these metals are contained in porphyrin or porphyrin-like structures that are hydrophylic, it is likely that portions of these might be lost from the oil by dispersion in water. Moreover, metals may be displaced from the porphyrin structures by other metals in the water. It is also known that the porphyrins are subject to photo-oxidation reactions which lead to oxidation products that may be more readily dissolved or dispersed. However, the analysis for inorganic trace constituents in an oil as a means of identification is questionable because it is not always certain that the trace elements present were initially contained by the oil.

A number of other techniques exist for pollutant identification which may be applied to oils. One of the most promising of these methods based on the inorganic elements appears to be trace-element analysis by either neutron activation (15) or emission spectrometry. The problem associated with this type of analysis is that the trace elements either may be introduced from or lost to water. The facilities required for neutron activation analysis are extremely expensive and not widely available, whereas those for emission spectrometry are relatively cheap and widely available.

Infra-red attempts to fingerprint oil spills employed extraction by chloroform (14) of oils and asphaltenes from beach sands. Direct infra-red heating was recommended to get rid of the solvent. This direct heating of crude oil will change the absorbance and thus the validity of the absorbance ratios becomes questionable. It was noticed that the absorbances of all the bands decreased non-uniformly from 20 to 100 % over a period of 30 minutes. The non-destructive techniques (7, 8) for infra-red identification of crude oils are not as sensitive to minor compositional changes as gas chromatography, which limit their use to oils with conspicuous compositional differences.

By its nature petroleum contains a very large number of hydrocarbons not to mention, oxygen, nitrogen, and sulphur-containing compounds which should, if they could be resolved, provide an excellent fingerprint.

Gas Chromatography as a Means of Oil Spill Identification

Though gas chromatography is, in principle, the best and most promising tool in the field of oil spill identification, all previous attempts to obtain identification chromatograms for crude and fuel oils suffered from the following disadvantages:

1. The polar stationary phases have been unable to stand high column temperatures. This difficulty precludes the possible use of the heavy residue for a dependable fingerprint. Usually these heavy ends are the least affected by evaporation conditions, contain the most stable compounds, and thus are most promising for providing characteristics least changeable under weathering conditions.
2. In some cases single chromatograms, obtained by using non-polar relatively thermally stable chromatographic columns, can be used to establish the source of spillage. However, if the oils are quite similar and overlapping between a large number of fingerprints occurs, this one-step analysis will not be adequate. In many paraffinic oils (16), the chromatogram consists of a number of peaks standing out on a broad "envelope" representing abundant numbers of incompletely separated components. More efficient separation is a necessity for a dependable fingerprint.
3. The peaks representing the profiles of normal paraffins have been used (17) as the main criteria in the chromatograms to differentiate between oil spills and to identify them. Normal paraffins are known for their susceptibility to biodegradation (24, 25) and more stable compounds would be more useful for identification purposes.

The approach used in this investigation to offset these disadvantages was to first use gas chromatography to obtain speed and the advantage of being able to use small samples of oil spills without any pretreatment. To increase the resolving power of the method an analytical step — which separates according to type — on inorganic columns of lithium chloride on diatomaceous silica was added to the chromatography on non-polar silicone rubber columns as used

by most investigators. The latter chromatographic separation according to boiling point, referred to as simulated distillation, was used as a preparative step during which arbitrary cuts 20°C wide in boiling range were collected. These cuts were further resolved on the salt column using two types of detector to give both the carbon and sulphur traces simultaneously. These steps will now be discussed in somewhat greater detail.

Simulated Distillation

The backbone of any analytical study of a petroleum sample is distillation. However, the time required for true boiling point (TBP) distillation - 6 to 100 hr - precludes its use for quick examination of a pollutant. Also the conventional distillation methods fail to establish initial or final boiling points with precision for high-boiling fractions. Gas chromatography is gaining wide acceptance (18, 19) as the most reproducible method of distillation and the most accurate method of determining initial and final boiling points of hydrocarbon materials. Gas chromatographic separations according to boiling points can be made on materials boiling up to 600°C on a number of non-polar thermally stable stationary liquid phases. Using 20-μl or smaller samples, a simulated gas chromatographic distillation was performed on each of the oil samples used to evaluate the method, as a preliminary step before actual fingerprinting (Figures 1 to 6).

It has been demonstrated in the proposed method of analysis that fingerprint chromatograms, obtained solely on a silicone rubber column, are not sufficiently discriminating to be useful in screening oil samples that are potential pollutants of the environment. The differentiating power of the method is greatly improved by using inorganic salt columns of which lithium chloride-Chromosorb A and lithium chloride-Porasil F are, so far, the best combinations tested in our laboratory.

Gas-Solid Chromatography

In previous publications (20, 21 22), we have shown that high-boiling hydrocarbons and sulphur compounds can be separated according to type on porous silica, coated with lithium chloride, at temperatures no higher than for comparable separations on gas-liquid chromatography. From the results obtained we

recommended the use of salt columns for efficient chromatographic characterization of oil spills. The fact that these inorganic column packings allow characterizations at the high boiling ranges should considerably improve the fingerprinting technique because these ranges are least affected by changes caused by evaporation. Also the inorganic gas chromatographic columns have the added advantage that there are no "bleeding" problems that can complicate mass spectroscopy, hydrodesulphurization, and various new detectors. Efficient separations can be achieved on salt columns as evidenced by mass spectrometry. The analysis of a distillate fraction of Athabasca bitumen separated isomers of both the benzothiophenes and the naphthalenes (20).

Dual-Trace Fingerprinting

In addition to containing a wide boiling range of hydrocarbons, most crude oils contain a wide boiling range of organic-sulphur compounds, therefore, by using a sulphur-selective gas chromatographic detector such as the Melpar flame photometric detector (FPD), it was possible to obtain a sulphur "fingerprint' for each oil in a manner analogous to the carbon "fingerprint" obtained with the flame ionization detector (FID). Becuase the FPD response varies for different types of sulphur-containing compounds and is affected by the nature of the hydrocarbon components, this detector gives unique and reproducible chromatograms for different oils even, in many cases, for those of very similar sulphur content. The latter can be true even when the FID carbon traces are very similar. For these reasons, the Melpar detector is valuable in fingerprinting oils and surpasses the quantitative micro-coulometric sulphur detector. In some cases, the sulphur compounds are largely absent from the lower-boiling fractions of crude oil so that evaporative weathering has a smaller effect on the FPD fingerprint than on the FID fingerprint.

Although there was some loss of sulphur due to exposure, e.g., the "Torrey Canyon" spill, oils contain many types of sulphur compounds that are very resistant to degradation. The aromatic sulphides, benzothiophenes, dibenzothiophenes, and other thiophenes are very stable (24). Because these compounds vary considerably for different oils in both type and amount, they should be ideal for identification purposes.

The micro-organisms which digest oil attack normal paraffins preferentially. Consequently, we are inclined to think that the FID chromatogram of a biologically aged paraffinic crude oil will become like a naphthenic oil but that the Melpar sulphur chromatogram will remain relatively unchanged (23).

Specific and Non-Specific Interactions

The boiling ranges of the arbitrary simulated distillation cuts chosen for fingerprinting and their corresponding Kovat's indices are shown in Table 1. The width, in terms of Kovat's indices, of the particular arbitrary cut that is rechromatographed on the supported lithium chloride column is shown in Figures 7 to 26 by two dashed lines to indicate the limits of the non-specific interaction region. We have discussed specific and non-specific interactions on the salt columns in detail in a previous report (22). The material eluting before the lower limit of the non-specific interaction region is believed to contain non-planar cyclic saturates, that within the limits mainly saturated alkanes, whereas the region that lies beyond the higher limit represents the specific interaction caused by aromatic structures or heteroatoms.

Fingerprints of the Lathom and Lloydminster Crude Oils

All of the flame ionization traces of the Lathom fractions (Figures 7 to 10) show two envelopes of peaks. The first envelope of peaks generally ends fairly abruptly near the limit of the non-specific interactions. Then there is a valley between the two envelopes. If the boiling ranges were narrower, the valleys probably would be nearer to the base line.

In all the chromatograms of the Lathom fractions, there is considerable material with negative specific interaction which indicates the probable existence of substantial amounts of non-planar saturated cyclic hydrocarbons. It seems that, as the boiling points of the fractions increase, the initial materials that elute involve greater negative specific interaction. Possible substitution on the cyclic structures explains this observation.

In Figure 9, normal hexadecane and heptadecane appear quite prominent. In Figure 10, normal octadecane and, to a much lesser extent, nonadecane are very evident. The second envelope of peaks in the chromatograms of these Lathom

fractions is due to aromatic hydrocarbons and sulphur compounds. Probably the sulphur compounds are mostly substituted benzothiophenes. The tail on the sulphur chromatograms might be due to dialkyl and alkyl aryl sulphides.

As can be seen in Figures 11 to 14, the Lloydminster fractions differ considerably from the Lathom fractions. The first envelope of peaks declines much sooner in the Lloydminster fractions. In fact, octadecane appears to be in the second envelope in the 290 to 310°C fraction. In general, the Lloydminster chromatograms are more spread out than the Lathom for both the flame ionization and the Melpar sulphur traces. As the boiling point of the fractions increase, there appears to be considerable sulphur-containing material with specific interaction lower than for the Lathom fractions. Also the amount of material involving negative specific interaction increases.

Chromatography of the "Arrow" and "Irving Whale"
Samples on the Silicone Rubber (SE-30) Column

The chromatographic FID traces obtained during simulated distillation on the non-polar silicone rubber column are shown in Figures 4 to 6. It can be seen that the major peaks from the weathered samples still match the ones from the cargo oil. However, the lower-boiling material has been reduced by evaporation and the peaks have been quite subdued. Even in the high-boiling region, where losses by evaporation are not as significant and material would be more suited for comparison, the peaks are still subdued. In fact the main part of the chromatogram of the weathered "Irving Whale" Bunker C is more similar to the "Arrow" cargo (Figures 4 and 6) than to the weathered "Arrow" Bunker C. Thus, it is clear that a single chromatographic separation according to boiling point is not sufficient for dependable fingerprinting. However, if comparisons are made with chromatograms obtained from the salt column, the situation becomes quite different.

Fingerprints of the "Arrow and Irving Whale"
Samples on the Salt Column

Though having similar chromatograms on the silicone rubber column, the weathered "Arrow" and "Irving Whale" Bunker C oils show significant differences on the salt column. A large portion of the FID trace of the "Irving Whale"

fractions lie in the negative interaction range (Figures 23 to 26), indicating a stronger naphthenic nature than the "Arrow" fractions. The latter, on the other hand, show prominent straight-chain paraffin peaks, e.g., normal hexadecane (Figure 16), normal heptadecane (Figure 18), normal octadecane and normal nonadecane (Figure 20), then normal eicosane (Figure 22) which are missing in the equivalent cuts of the "Irving Whale" sample. In both samples, however, the non-planar saturated cyclic content gradually rises with boiling point.

The weathered "Arrow" fractions (Figures 16, 18, 20, 22) show two groups of peaks on the FID trace, the first of which ends near the upper limits of the non-specific interaction range. This tendency is less noticeable in the "Irving Whale" chromatograms (Figures 24 to 26) with the exception of the 250 to 290°C fraction (Figure 23).

Also the FPD trace shows no sulphur in the area between the dashed lines over the whole boiling range of the weathered "Arrow" samples. In the "Irving Whale" fractions, sulphur is represented in this region and increases considerably from 290°C up to the end of the fingerprinting range (Figures 24 to 26). Thus, this two-step method can clearly differentiate between two weathered bunker fuel oils which would have appeared similar after one-step chromatography.

On the other hand, the cargo samples and weathered (for 10 weeks) samples of the "Arrow" Bunker C oil show considerable differences on the silicone rubber chromatograms due to weathering as discussed before, but their salt column fingerprints are very similar (Figures 15 to 22) giving all the peaks at the same retentions as expressed by Kovat's indices. The minor differences present do not affect the high efficiency of the method for identification purposes.

Reproducibility

The whole procedure (simulated distillation, collecting fractions, and rechromatography according to type on the salt column) was repeated for both the cargo and weathered samples of the "Arrow" Bunker C oil. Chromatograms were reproducible for both the carbon and sulphur traces.

Automating the Method

The procedure can be automated to a large extent to facilitate the handling of a large number of pollutant samples at the same time. This would allow wider and faster comparisons and identifications.

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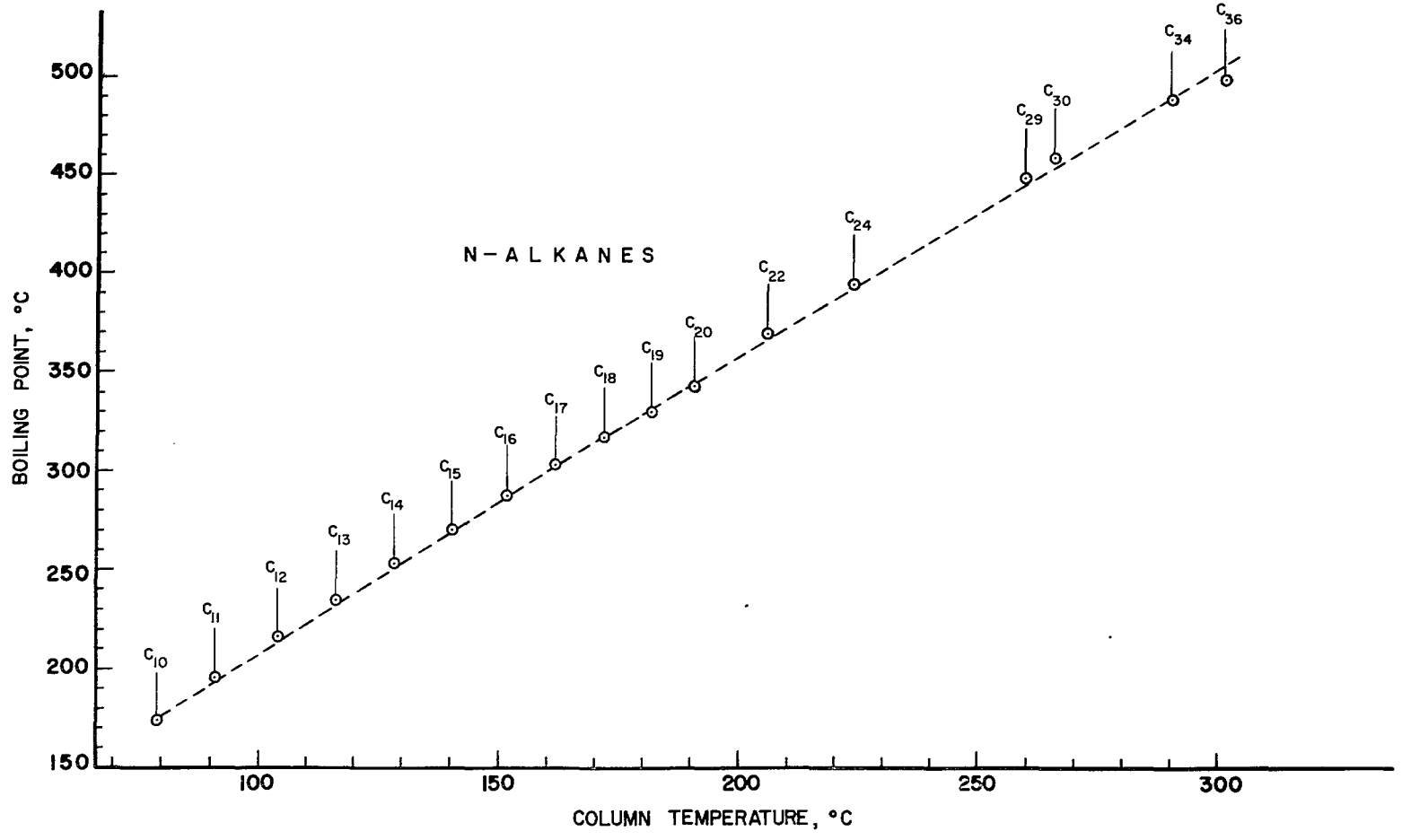
Table 1

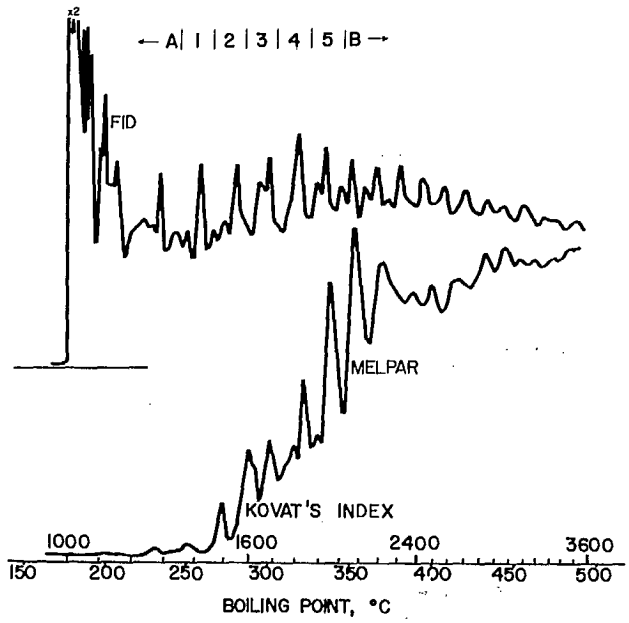
Boiling Ranges and Kovat's Indices
Corresponding to the Fingerprinting Fractions

Fraction No.	Boiling Range, °C	Kovat's Index Range
1	250 - 270	1383 - 1495
2	270 - 290	1495 - 1620
3	290 - 310	1620 - 1760
4	310 - 330	1760 - 1905
5	330 - 350	1905 - 2060



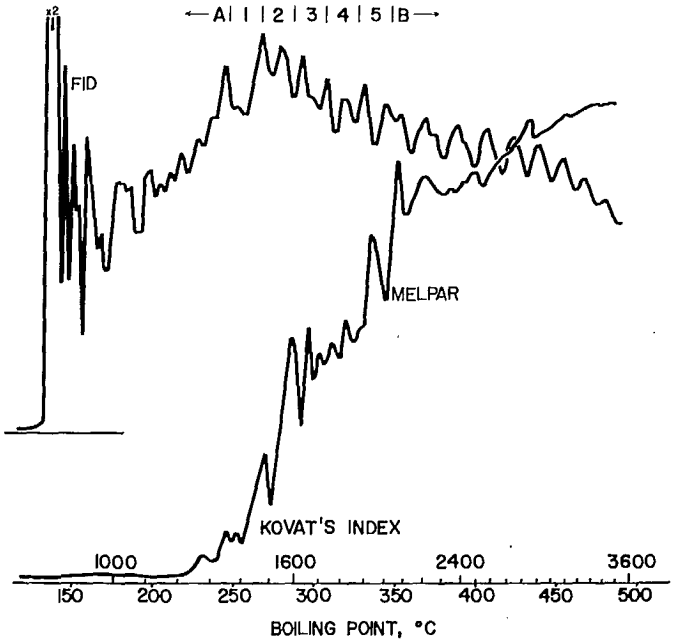
CALIBRATION CURVE FOR SIMULATED DISTILLATION

Figure 1



SAMPLE: LATHOM CRUDE OIL
COLUMN: SILICONE RUBBER (SE-30) ON CHROMOSORB W

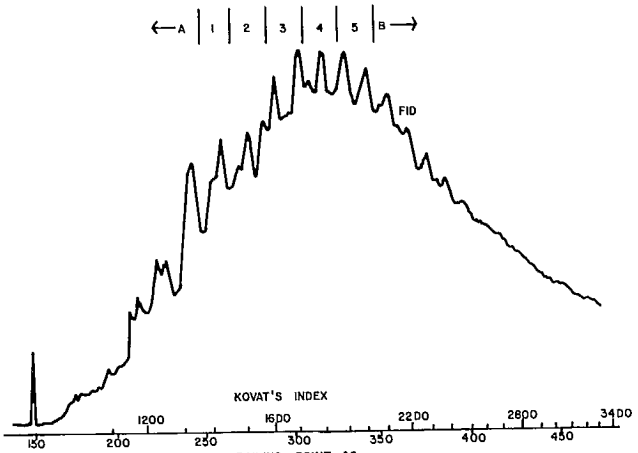
Figure 2



SAMPLE: LLOYDMINSTER CRUDE OIL
COLUMN: SILICONE RUBBER (SE-30) ON CHROMOSORB W

Figure 3

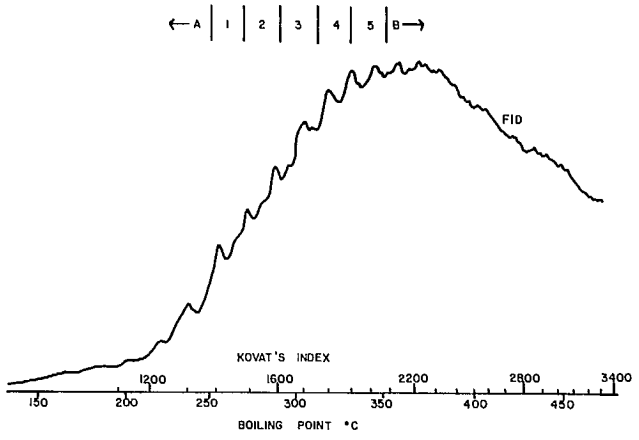
Figure 4



SAMPLE: ARROW CARGO

COLUMN: SILICONE RUBBER (SE-30) ON CHROMOSORB W

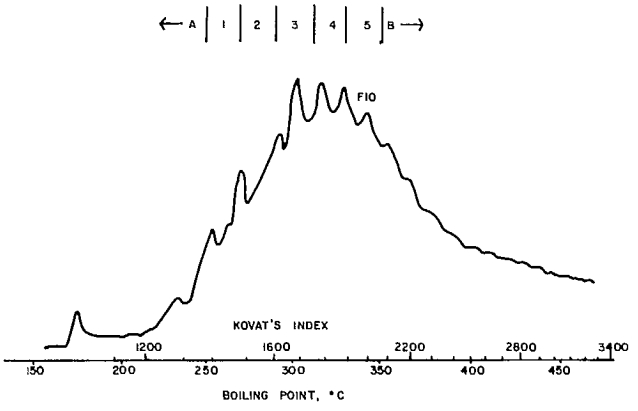
Figure 5



SAMPLE: WEATHERED ARRDW

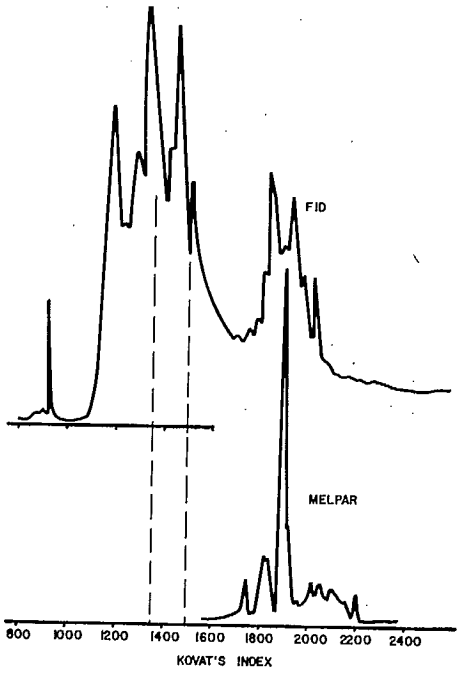
COLUMN: SILICONE RUBBER (SE-30) DN CHRDMOSDRB W

Figure 6



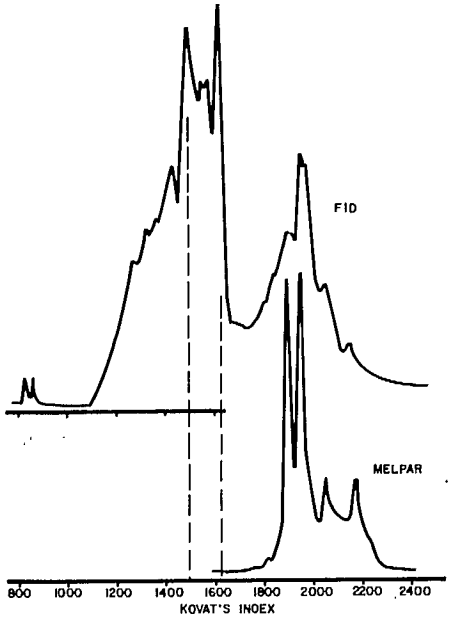
SAMPLE: WEATHERED IRVING WHALE

COLUMN: SILICONE RUBBER (SE-30) ON CHRDMOSORB W



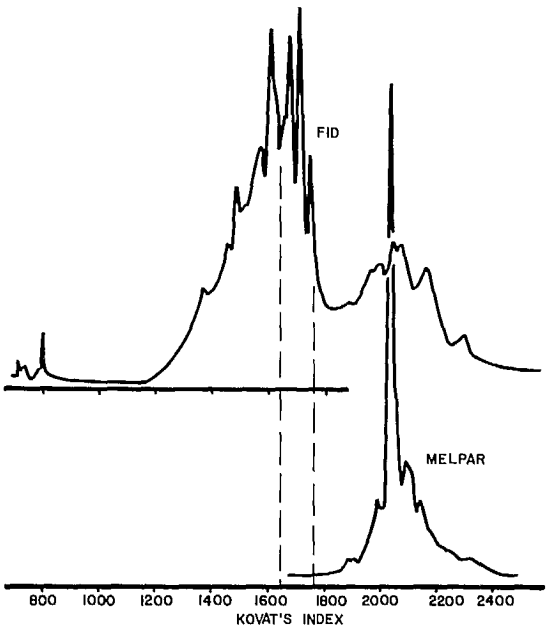
LATHOM, b.p. 250-270 °C, LiCl-CHROMOSORB A

Figure 7



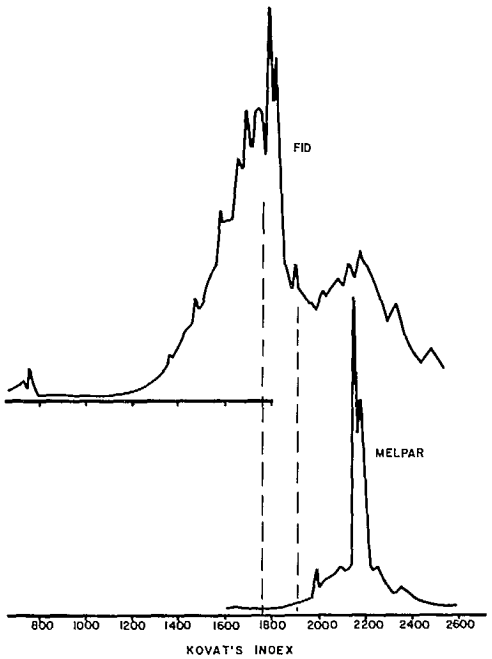
LATHOM, b.p. 270-290 °C, LiCl-CHROMOSORB A

Figure 8



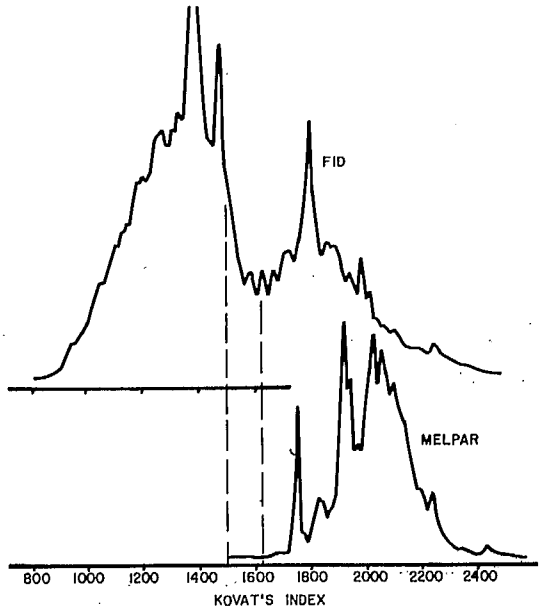
LATHOM, b.p. 290-310 °C, LiCl-CHROMOSORB A

Figure 9



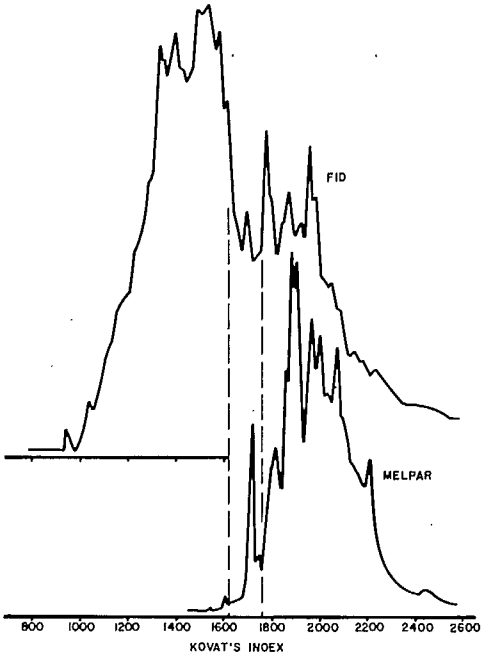
LATHOM, b.p. 310-330 °C, LiCl-CHROMOSORB A

Figure 10



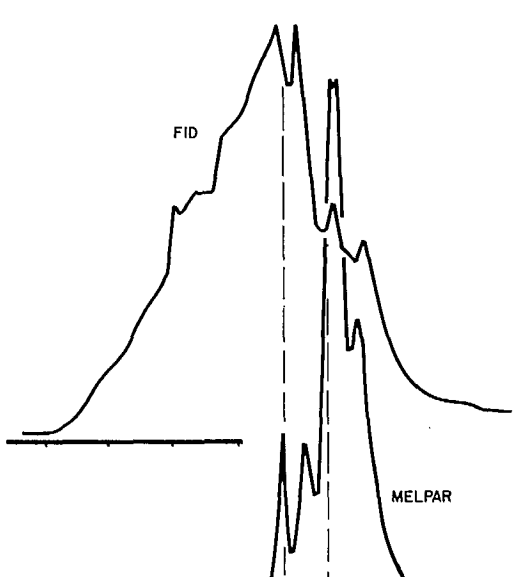
LLOYDMINSTER, b.p. 270-290 °C, LiCl-CHROMOSORB A

Figure 11



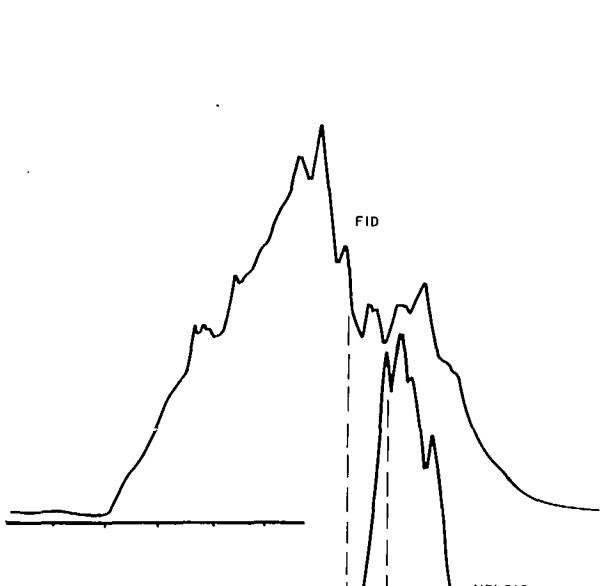
LLOYDMINSTER, b.p. 290-310 °C, LiCl-CHROMOSORB A

Figure 12



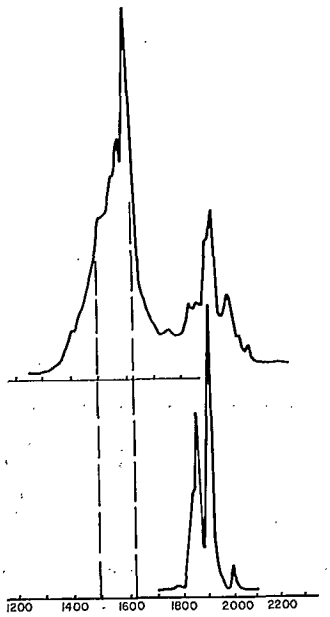
LLOYDMINSTER, b.p. 310-330 °C, LiCl-CHROMOSORB A

Figure 13



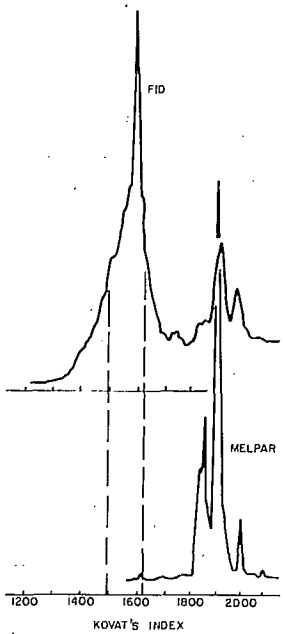
LLOYDMINSTER, b.p. 330-350 °C, LiCl-CHROMOSORB A

Figure 14



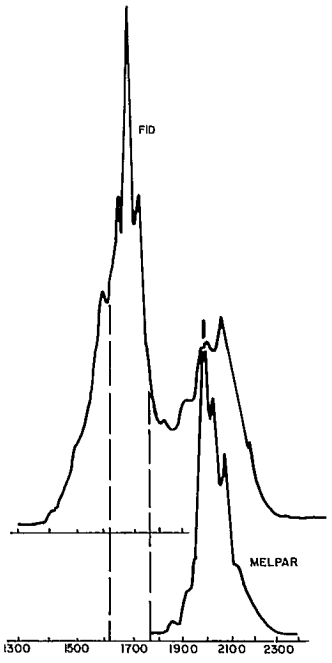
ARROW (CARGO), 270-290° C LiCl ON CHROMOSORB A

Figure 15



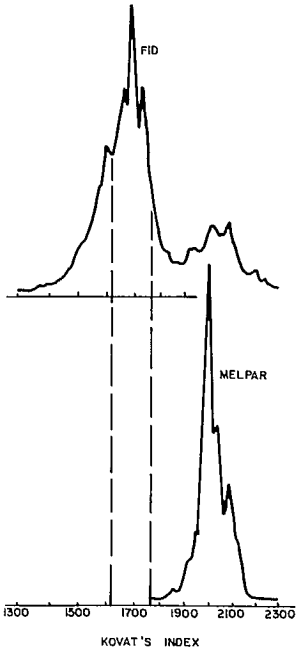
ARROW (WEATHERED), 270-290°C LiCl ON CHROMOSORB A

Figure 16



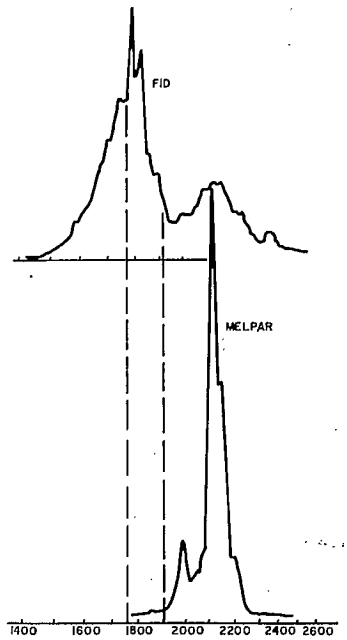
ARROW (CARGO), 290-310°C LiCl ON CHROMOSORB A

Figure 17



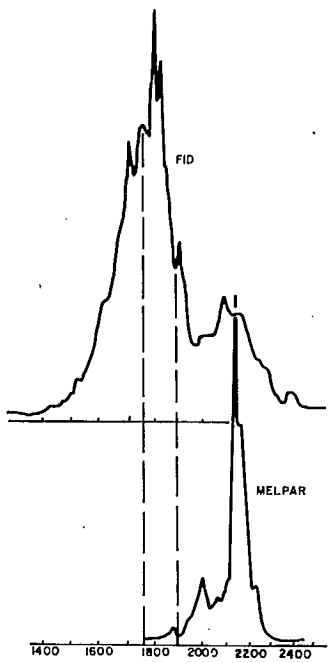
ARROW (WEATHERED), 290-310°C LiCl ON CHROMOSORB A

Figure 18



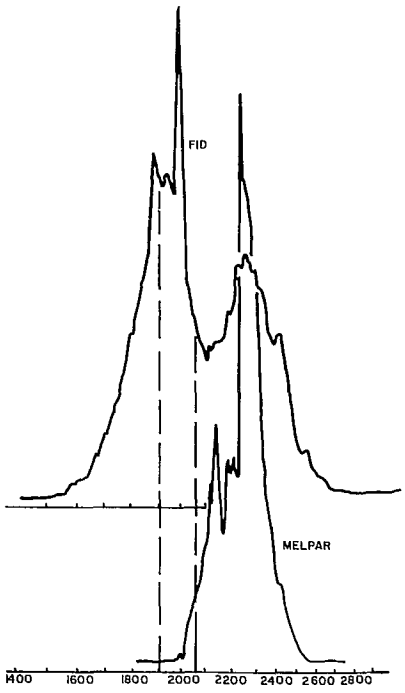
ARROW (CARGO), 310-330° C LiCl ON CHROMOSORB A

Figure 19



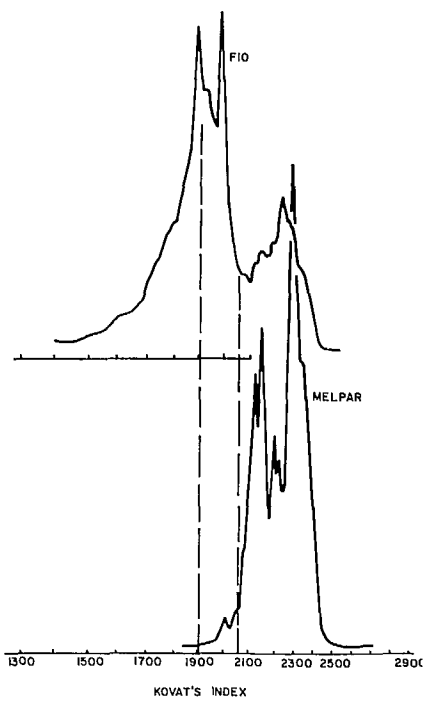
ARROW (WEATHERED), 310-330°C LiCl ON CHROMOSORB A

Figure 20



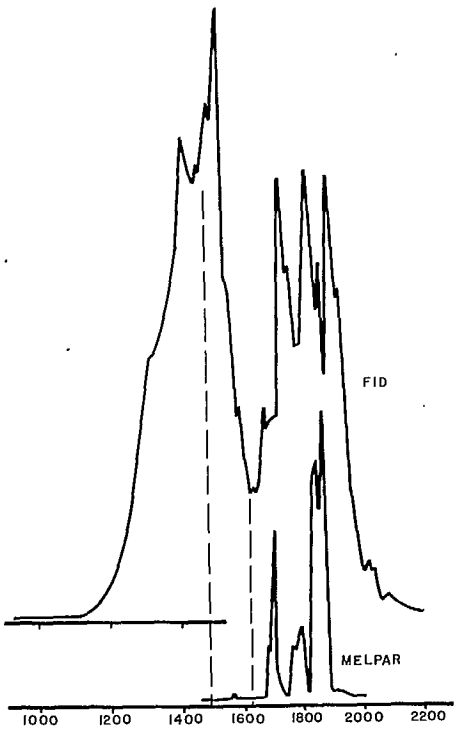
ARROW (CARGO), 330-350°C LiCl ON CHROMOSORB A

Figure 21



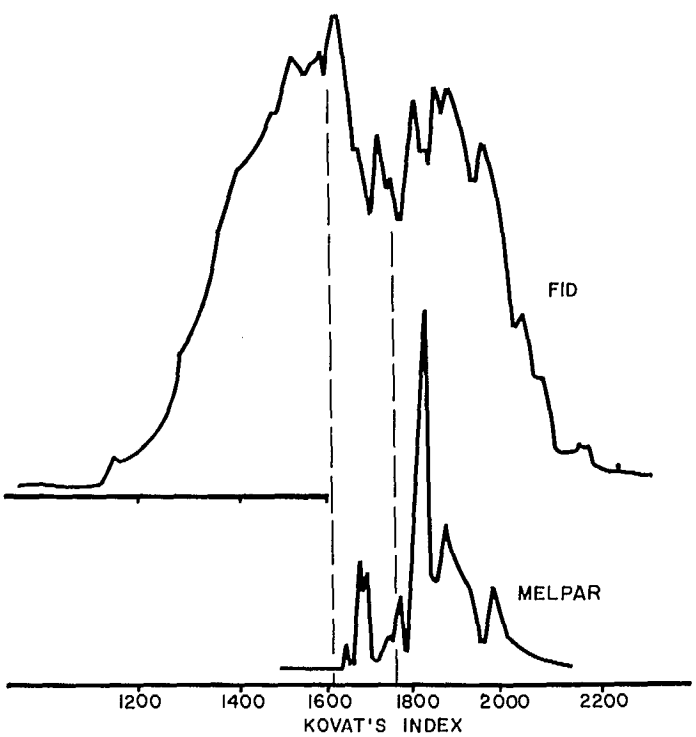
ARROW (WEATHERED), 330-350°C LiCl ON CHROMOSORB A

Figure 22



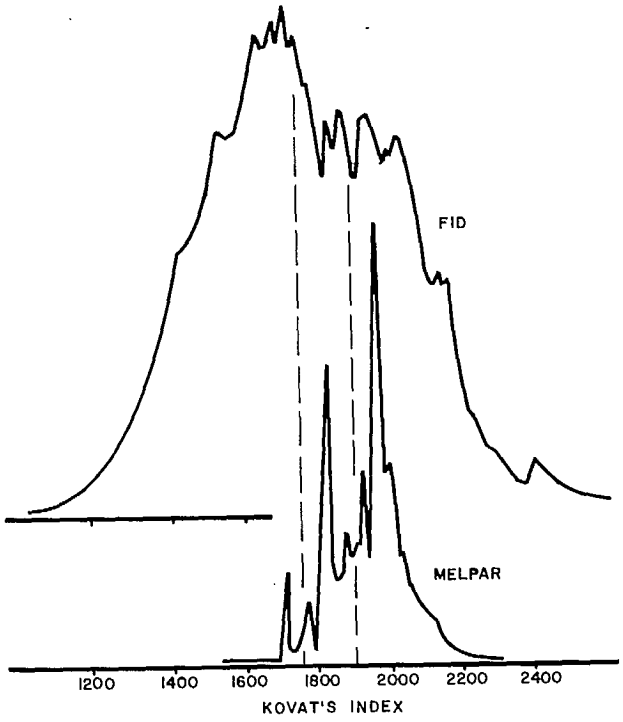
WEATHERED IRVING WHALE, b.p. 270-290 °C
LiCl-CHROMOSORB A

Figure 23



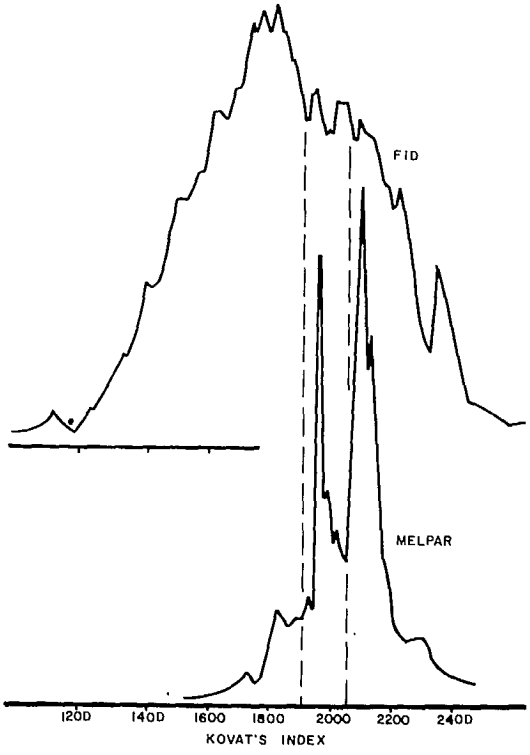
WEATHERED IRVING WHALE, b.p. 290-310 °C
LiCl-CHROMOSORB A

Figure 24



WEATHERED IRVING WHALE, b.p. 310-330 °C
LiCl-CHROMOSORB A

Figure 25



WEATHERED IRVING WHALE, b.p. 330-350 °C
LiCl- CHROMOSORB A

Figure 26