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Development of Analytical Techniques for Hydrocarbons in Mineral Aggregates

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(NASA Contract No. NASw-438)

Final Report

July, 1962 - June, 1963

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SHELL DEVELOPMENT COMPANY

A DIVISION OF SHELL OIL COMPANY

Emeryville, California

S-13893

DEVELOPMENT OF ANALYTICAL TECHNIQUES FOR HYDROCARBONS IN MINERAL AGGREGATES

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Written by: D. P. Stevenson and
A. G. Polgar [1963] refs

SHELL DEVELOPMENT COMPANY
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ABSTRACT

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There is described an extraction-elution chromatography procedure for the recovery of representative samples of small quantities of saturated hydrocarbons of molecular weight greater than ca 200 from mineral aggregates such as sedimentary rocks. Provided the concentration of sought hydrocarbons in the rock, C (ppm) exceeds 1 ppm, and the product $CW \geq 500$, where W is the weight of rock sample in grams, the recovery procedure leads to representative samples suitable for characterization by mass, infrared, and/or ultraviolet spectroscopy.

It is found that for small samples, 0.1 to 1.0 mg, of complex saturated hydrocarbon mixtures, the accuracy of mass spectrometric characterization is such that the relative concentrations of adjacent homologes are determined to ±10%.

AUTHOR

DEVELOPMENT OF ANALYTICAL TECHNIQUES FOR HYDROCARBONS IN MINERAL AGGREGATES

Introduction

This report is concerned with the description of the development and tests of a method for the recovery and characterization of small quantities of C_{14} plus, nominally saturated hydrocarbons, that may be associated with mineral matter, particularly sedimentary rocks. The purpose for which the recovery and characterization method is designed is that of examining the organic chemical content of meteoric or other extra-terrestrial matter for fossilized substances of biochemical origin. The particular features of the method are that it is applicable to relatively small samples of "rock" ($\leq$ 100 grams) with total saturated hydrocarbon content less than 10 parts per million and probably as small as 1 ppm. Furthermore, as an inherent feature of the method, a greater or lesser portion of the organic chemical content of the rock other than saturated hydrocarbon is recovered in form suitable for characterization, and the organic chemicals not recovered, i.e., remaining with the rock, are in no wise modified so that if desired they may be recovered at a later time by more drastic treatment of the rock than is necessary for the recovery of saturated hydrocarbons.

The basic procedure is that of extraction (Soxhlet) with a light petroleum ether (purified n-hexane), evaporation at low temperature to remove the solvent,[a] followed by elution chromatography over siliga gel with isooctane or n-hexane as development solvent to provide a nominally saturated hydrocarbon extract that contains all the C_{14} plus saturated hydrocarbons and a greater or lesser portion of the lightly unsaturated (mono- and possibly diolefins) hydrocarbons if any are associated with the rock. This saturate, or perhaps a better name would be aliphatic-naphthenic extract, is suitable for characterization by the three well developed techniques of spectroscopy, ultraviolet and infrared absorption spectrophotometry and mass spectrometry.

Of the two possible procedures for separating organic substances from rocks for analytical purposes, the solvent extraction procedure was chosen because the alternate vacuum distillation procedure suffers from the following defects: 1): Labile substances may be decomposed, destroying actual constituents and thus producing possibly new constituents with the consequence of unrepresentative analytical data. 2): The essentially destructive character of a distillation procedure results in a residual sample unsuitable for further or later analytical testing. 3): Distillation results in the recovered product containing a major fraction of the water content of the rock, and in the case of low relative organic chemical content, drying, to render the recovered organics suitable for spectroscopic characterization can present major difficulties, particularly in the case

a) Low molecular weight substances extracted from the rocks are also removed and lost.

of small samples. 4): Heating presents the possibility of synthesis of organic substances from inorganic ones as for example the reactions of water and carbon dioxide with iron or iron carbide, again leading to the possibility of an unrepresentative sample for characterization.

Solvent extraction procedures for the recovery of organic chemicals from sedimentary rocks have been extensively employed in studies aimed at elucidating the origin and migration of petroleum. The users of these methods appear to have made the tacit assumption that these procedures yield representative, if not quantitative, samples of the hydrocarbon content of the rocks. Thorough-going testing of the quality of the extractive procedure was deemed necessary for two reasons. These were, 1) it is proposed to apply the method to much smaller samples than are customarily employed, and 2) exploratory studies[a)] of the possible use of solvent extraction procedures as an alternate to pyrolytic ones for the recovery of oil from oil shale have indicated the degree of recovery of organic matter by Soxhlet extraction with chloroform to be of only the order of 30% of the total organic content of the shale and with other solvents even less reocvery is achieved. In order to minimize the problems of drying and type separation in preparation of the sample for spectroscopic characterization it was desired to use a solvent of low polarity in order to minimize water extraction. The oil shale extraction experience indicated that the use of a solvent of low polarity would probably result in incomplete removal of the organic constituents of the rock (as desired), but might entail the hazard of providing a non-representative sample of the sought constituents, the saturated hydrocarbons.

Prior to concluding this introduction, it appears desirable to provide the reader with an explanation of why attention has been focused on the recovery and characterization of saturated hydrocarbons in the search for fossilized biochemical substances, rather than on such more typical biosubstances as amino acids or the closely related nitrogen-containing heterocyclics, and on optical and mass spectroscopy as a means of characterization rather than the essentially definitive evidence of optical activity.

Whitmore[b)] pointed out in 1943 that <u>all</u> living organisms contain hydrocarbons as a part of their chemical constitution, and that a finite portion of these are paraffins and naphthenes. It has been emphasized by Abelson[c)] that paraffinic hydrocarbons as a group are particularly resistant to thermal degradation. Thus the saturated hydrocarbons constitute the group of substances characteristic of both plant and animal life that are perhaps least subject to alteration by unfavorable environments.

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a) Holzman and Archibald, unpublished.
b) F. C. Whitmore, Fundamental Research in Occurrence and Recovery of Petroleum, Am. Pet. Int., New York (1943), page 124.
c) Researches in Geochemistry, P. H. Abelson, ed., J. Wiley and Sons, New York (1959). Chap. entitled "Geochemistry of Organic Substances", pp. 79-103.

Certainly a unique characteristic of the enzyme catalysts of biological systems is that of bringing about synthesis of a remarkable array of substances of both complex and simple structure, at quite low temperature as compared to those employed in the laboratory by chemists. A second unique characteristic is the stereospecific nature of the biologic synthesis reactions that result in optical activity being a very common characteristic of substances so synthesized. Fenske and co-workers[a] have reported the observation of optical activity in the lubricating oil range of a variety of crude oils and found such activity in fractions of molecular weight as low as 220 in a California crude oil. In connection with the present research project the authors have found observable optical activity in the C_7 range (molecular weight ca. 100) of a California gasoline. There appears to be no question but that the detection of optical activity in an organic chemical extract from a mineral aggregate would be the best evidence for biological processes as contributors to the organic substances. The difficulty lies in the quantities of material necessary to make an observation of the optical rotation. A minimum of 2 to 3 grams of liquid is required to permit the reliable detection of optical rotation of the magnitude found by the authors in the California gasoline, while about one-tenth that quantity (0.2 to 0.3 grams) would be required to permit detection of optical activity of the magnitude associated with the heavier fractions of crude oil reported by Fenske et al. These required quantities of sample are at least an order of magnitude greater than one might expect to recover in the most favorable cases from samples of "rock" of the order of 100 grams. In contrast with the requirement of literally hundreds of milligrams of organic extract for the observation of possible optical activity, complete infrared and ultraviolet absorption spectra can be measured on a single sample of the order of one milligram, and a complete high resolution mass spectrum obtained on a sample of the order of 0.1 milligram.

If perchance there should be acquired a meteoric or other specimen of extra-terrestrial matter of sufficient size and/or organic chemical content that hundreds of milligrams of organics were recoverable, search for optical activity could be readily made. The quality of the recovery procedure with respect to representative sampling would be unimportant in such a case because no conventional laboratory extraction procedure is known that would result in separation of optical antipodes accidentally. On the other hand, to be able to infer probable biologic origin of a portion of the organic material extracted from a "rock" from the analytical characterization provided by the infrared, ultraviolet and mass spectrometric techniques requires a high degree of certainty that the sampling or recovery procedure was one that led to a representative recovery of the substances associated with the "rock".

Since one expects that searches for evidence of fossilized chemical substances of biological origin in extra-terrestrial matter will be sample size limited in the foreseeable future, the emphasis in the present

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a) Fenske, Carnahan, Breston, Caser and Rescorla, Ind. Eng. Chem. 34, 638 (1942).

work has been on ascertaining that the recovery procedures lead to representative samples with respect to the three micro characterization methods, infrared, ultraviolet and mass spectrometry.

The program of development and testing the proposed recovery procedure has been the usual one of analytical chemistry, namely, first the application of the method to synthetic "unknowns", modifying the operations as necessary to achieve satisfactory analyses of these synthetic samples. When an overall procedure has been established that yielded satisfactory analyses of the synthetics, the method was tested on actual minerals (subterranean sedimentary rocks from drilling cores) for repeatability of analyses.

Three kinds of synthetic unknown were prepared. First the model solids were impregnated with a single substance, cetane (normal hexadecane). The experiments with these synthetic samples provided a measure of the quantitative character that could be expected of the recovery procedure. In the second series of experiments a light (C_{15}-C_{23}) wax to which cetane had been added was used as the impregnant. These experiments supplied further substantiation of the quantitative character of the recovery provided by the first series of experiments, and in addition indicated what effects could be expected in the way of distortion of the distribution of components in molecular weight for substances in the lower range of molecular weights of interest. In the third and fourth series of experiments a heavy wax (C_{22}-C_{30}) and this heavy wax with added C_{31} and C_{33} alkane (from a plant wax) were the impregnants. In this manner the quantitative and representative character of the recovery of higher molecular weight substances was established.

In the major portion of these studies of synthetics only the extraction and evaporation steps of the complete recovery procedure were employed. The quality of the chromatographic separation or cleanup procedure was tested in separate experiments. However, in several experiments with the heavy wax, the complete procedure, extraction, evaporation, chromatography, evaporation, was employed and thus tested.

Inasmuch as the manner in which the organic matter associated with sedimentary rocks is initially deposited or might have been deposited in a meteorite is unknown, it is most probable that a laboratory-synthesized unknown represents a quite unrealistic test. On the other hand, the lack of real knowledge of the organic content of a real sedimentary rock makes it impossible to evaluate the absolute quality of an analytical procedure. In applying the method to real sediments two criteria of quality have been employed. The first criterion of quality was simply that of repeatability of analyses. As a second test, a further group of analyses was carried out employing a more severe solvent than n-hexane, namely a benzene-methanol azeotropic mixture, that increased by one-half to one order of magnitude the quantity of organic material extracted. The comparison of the quantity and distribution in molecular weight of the saturated hydrocarbons recovered with hexane with that recovered with the benzene-methanol then became the final check on the quality of the procedure and an indication of the confidence level that is to be associated with the determination of relative concentrations of homologous substances.

In the various sections of this report that follow, there is first described the chromatographic procedure and the results of the separate tests of this procedure. We then briefly indicate what mass spectrometers were used and why changes in instruments were made during the course of the program. No discussion of the mass spectrometric method of analysis is given since the procedures are readily available in the literature. In the section entitled "Impregnation Experiments", there are described in detail the model solids and the model impregnants as well as the procedure of preparation of the synthetic unknowns, the method of extraction and recovery and the results of the various experiments. There are given then the results of the various analyses of the sedimentary rocks, a sample of garden earth and the leaf waxes of two common decorative shrubs or trees. In the final section of the report proper there are given the results of some observations on optical activity of saturated hydrocarbons in the C_7 range of a straight run gasoline from a mixed California crude oil. These latter experiments were carried out to provide the authors with background for evaluating the potential of such measurements in tests for biological origin of fossilized organic substances. In the Appendix there is summarized the details of the recommended analytical recovery method.

The conclusions we draw from the various experiments may be stated as follows: If C is the concentration (ppm) of hexane-soluble organic matter in a sample of mineral matter of weight W grams, the relative concentration of adjacent members of a homologous series of the saturated hydrocarbon recoverable from the mineral can be determined to ±10% $CW \geq 500$ and $C \geq 1$, if there is available a CEC 21-110 mass spectrometer or one of similar sensitivity. If only conventional mass spectrometers such as the CEC 21-103 are available, the condition for similar reliability becomes $CW \geq 2000$ and there still obtains $C > 1$.

Chromatography

Silica gel is generally considered the most suitable adsorbent for the separation of saturated hydrocarbons from aromatics and non-hydrocarbons. Employing a moderately high gel/oil ratio and using a low-boiling saturated hydrocarbon as developer, it is usually possible to collect all of the sample saturates in a small filtrate portion without desorbing any of the aromatics. This fraction is expected to contain also the olefinic sample components. The aggregate of the sample aromatics may be produced by continuing the development with benzene; then forcing a strong polar solvent, such as alcohol, through the column permits the collection of the non-hydrocarbons in a third filtrate portion.

The column designed for this investigation has a 2.2-g gel capacity (Davison's grade 923) that permits the chromatography of 5 mg or smaller samples with gel/oil ratios of 400 or higher. The bed volume of this column is 2.1 ml. Grade 923 gel is nearly neutral as received and considered inert toward sample components expected to be encountered in this project; it must not be calcined before use because this treatment may introduce undesirable acid sites.

The upward flow arrangement of the column is to produce more uniform fronts especially by preventing channeling.

The assembly and operation of the equipment (Figure 1) is described in the Appendix. Results of checking column performance are given below.

1. n-Hexadecane (1.34 mg) was chromatographed from n-hexane or isooctane solutions in a few preliminary experiments with recoveries (mass spectrometric) of 107, 99, 71 and 127%.

2. It was established that n-hexadecane developed with isooctane proceeds through our column with no appreciable retention and may be recovered quantitatively from the prewetted column in the second bed volume of effluent. The separation of n-hexadecane (0.67 mg) from decylbenzene (0.50 mg) was complete, the latter appearing toward the end of the third bed volume of effluent; its emergence was complete in the fifth bed volume. Recoveries were 87% for n-hexadecane (by MS) and 99% for decylbenzene (by UV).

3. A 1.23 mg sample of gas oil range waxes (enriched with n-hexadecane) was recovered in satisfactory yield (84%) with no change in carbon number distribution.

4. The chromatographic resolution of a blend of the gas oil waxes (1.26 mg) and n-decylbenzene (0.50 mg) is shown in Figure 2. Following 1 bed volume of isooctane, added ahead of the charge to completely wet the column, the sample paraffins were desorbed in 1/2 bed volume of effluent. This was followed by a full bed volume of clean developing solvent, then the elution of decylbenzene started and became complete in three bed volumes of isooctane.

5. Parowax (1.26 mg) and Parowax enriched with paraffins from Candelilla wax (1.29 mg) were recovered quantitatively (133 and 135%, respectively) in one bed volume of isooctane effluent.

These experiments show that paraffins of the C_{15} and C_{35} range may be desorbed from our silica gel column with one-half to one bed volume (1.1 to 2.1 ml) of isooctane. This volume will be smaller, and consequently the separation of saturates and aromatics will be accomplished by a wider solvent barrier, the smaller the volume of the charge solution. The break-through of the aromatics could only be expected in the second half of the third bed volume of effluent.

Mass Spectrometry

During the course of the present work there were employed three different mass spectrometers. In the experiments involving the recovery of cetane and cetane-spiked catalytically cracked gas oil wax from the various solids, silica gel, bentonite, molecular sieve and olivine, a Westinghouse, Type LV, mass spectrometer modified in these laboratories for work with materials of low volatility and with an effective resolving power of about 1/250 a.m.u. was employed. In the experiments on the recovery of synthetic samples involving Parowax and Candellila-spiked Parowax from the defined

Figures 1 and 2 follow

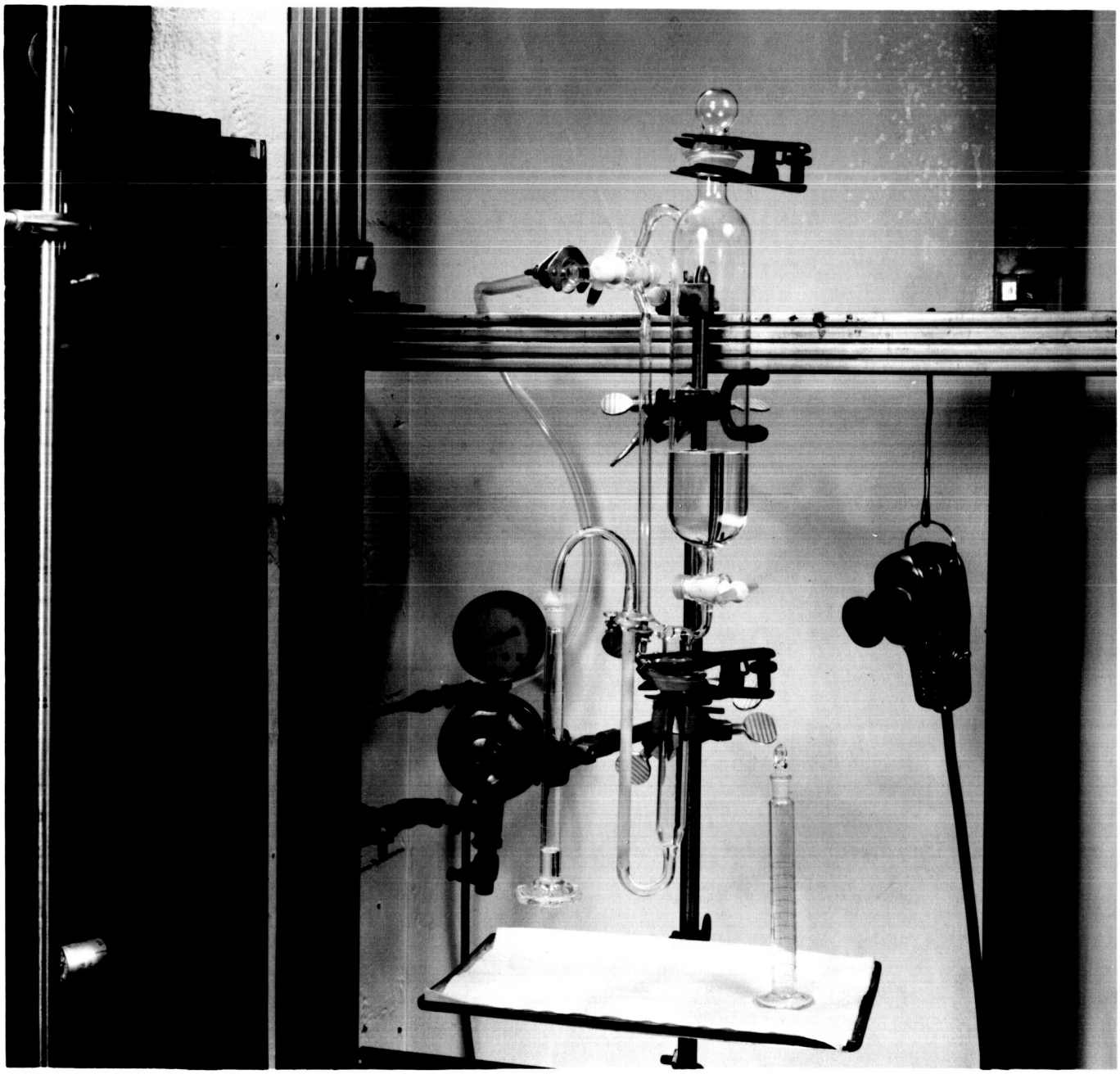

Figure 1. CHROMATOGRAPHIC COLUMN ASSEMBLY

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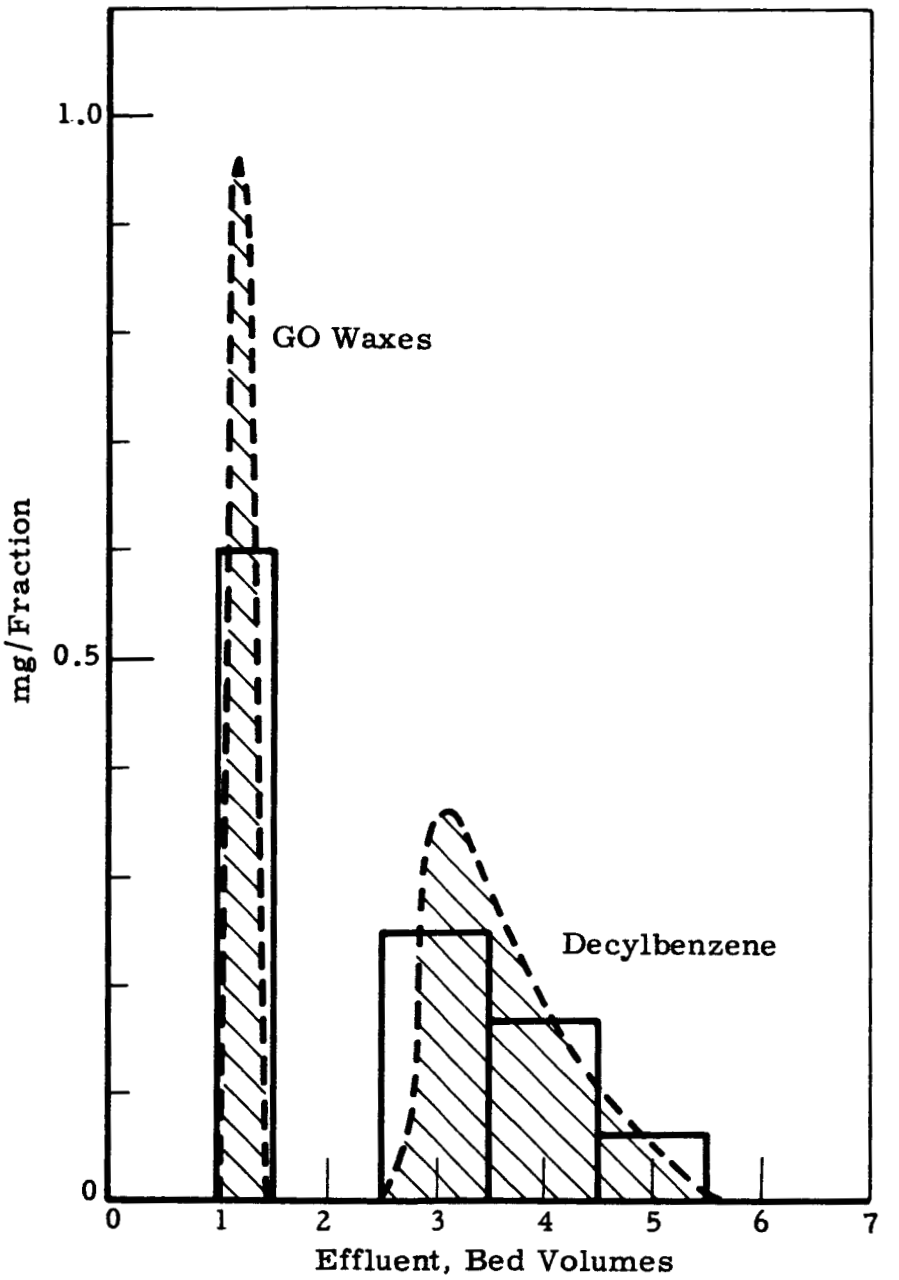

Figure 2. CHROMATOGRAPHIC SEPARATION OF GAS OIL WAXES FROM DECYLBENZENE

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solids it was necessary to employ an instrument of higher resolving power and thus a CEC 21-103 mass spectrometer with heated inlet system was employed. For both of these instruments the effective sensitivity of detection of C_{14}-C_{30} n-alkanes is ca 2 micrograms. The inherently better efficiency of the Westinghouse instrument and the lower operating temperature of its ion source, that should result in higher sensitivity, are offset by the fact that the ion detector is primitive by present day standards, and the use of a vibrating reed electrometer as a preamplifier with the CEC 21-103 compensates for its deficiencies in ion optics and ion source temperature. The CEC 21-103 was also employed in preliminary examination of the extracts from the sedimentary rocks. However, at about this time in the program an electron multiplier detector was installed on the relatively recently acquired, very high resolving power, CEC 21-110 double focusing mass spectrometer. With this very high gain detector the effective sensitivity of the instrument for C_{20}-C_{30} alkanes is of the order of 0.02 to 0.05 micrograms. This large gain in sensitivity makes it possible to reduce the sample requirement for mass spectrometric characterization by over one order of magnitude. In view of the ultimate objectives, namely the analyses of extra-terrestrial material that may be expected to be available in very limited quantity, it was deemed desirable to concentrate all further work on the use of the CEC 21-110 mass spectrometer.

As might be expected it is necessary to pay for the increased sensitivity that is realized with the use of the electron multiplier detector. The payment is made in a significant loss in precision of measurement of the ion intensities. The magnitude of this loss in precision is such that the reliability of the relative intensities of "peaks" corresponding to C_{20}-C_{30} alkanes as measured on a 0.1 mg sample with the 21-110 is about the same as when a 0.5 to 1.0 mg sample is used with the 21-103. In the case of the 21-103 the limit on the precision is set by the accuracy of measurement of deflections on the recorder chart, while in the case of the 21-110 it is set by the fluctuations in sensitivity of the detector.

In the various tables in later sections of this report the relative concentrations of alkanes are reported as nominal volume percent. That is, there are given the relative intensities of the isotope-crrrected alkane parent peaks (mass to charge rations in the series, $14n+2$, $n = 14, 15$, etc.) on a scale such that their sum is 100 or 1000. For the Type LV and the CEC 21-110 mass spectrometers with relatively low temperature ion sources and small mass dependent discrimination due to magnetic scanning of the spectra, this is a good approximation. It is a very poor approximation in the case of the CEC 21-103 mass spectrometer. However, in all cases the interest is in the comparison of the mass spectra of samples obtained with a single mass spectrometer and thus the fact that nominal concentrations are not true concentrations is without significance. This approximation is the cause of apparently different compositions of a particular sample as measured with different mass spectrometers. In a single table the data are in all cases from a single mass spectrometer.

Impregnation Experiments

Mineral Aggregates

The list of model minerals used in the impregnation experiments is given in Table 1. These mineral or mineral-like materials were selected to provide a representative range with respect to specific surface area (from less than 1 to 500 m^2), porosity (from less than 0.01 to 1 ml/g and pore opening 5 A and larger), and chemistry of surface.

Hydrocarbon Aggregates

The hydrocarbon aggregates employed in the impregnation experiments range in carbon number from C_{15} to C_{33} and include cetane, the paraffinic aggregate of a light gas oil, a commercial household wax (Parowax), Candelilla wax and their blends.

The isolation and purification of these materials is given below.

1. Cetane. Two samples from commercial sources have been used without further purification. By mass spectrometric analysis, both were approximately 99% pure n-hexadecane, the remainder being n-$C_{15}H_{32}$, n-$C_{17}H_{36}$ and iso-$C_{16}H_{34}$.

2. Gas Oil Wax. One liter of pale yellow colored, catalytically cracked light gas oil (from the Wood River Refinery of Shell Oil Company) with an approximate composition of 50% saturates, 40% aromatics and 1.0% olefins in the 240 to 310°C boiling range was treated as follows: Repeated extractions with 87%, 98%, 100% sulfuric acid and finally with Kattwinkel acid (30%w phosphorous pentoxide in 100% sulfuric acid) produced a colorless product that contained only traces of unsaturation. Fractional crystallization from methyl ethyl ketone solution (10%) at -20°C gave a snow white solid from which some residual methyl ethyl ketone solvent and traces of other impurities were removed by thermal distillation and by chromatography through silica gel and activated alumina. Carbon number distribution of this material is given in Table 2.

3. "Parowax". Commercial "Superla Parowax-USP Paraffin" was fractionally distilled (rotary spinning band column, 1 mm pressure) and, to obtain a more even distribution of alkanes, the last 25% of the distillate was rejected. Next the re-distilled material was dissolved in hot methyl isobutyl ketone (10% solution) and the fluffy, white crystalline product, formed at room temperature, was separated. This latter step eliminated nearly all of the cyclic components present in the commercial Parowax sample (Table 2).

4. Candelilla Wax. Commercial Candelilla wax is approximately a 50/50 mixture of paraffins and higher acids, alchols and their esters. Our sample, purchased from Distributing and Trading Co., New York, was designated as "extra light" and "double refined"; it was brittle and light brown in color. Neither treatment with sulfuric acid, the standard procedure for the isolation of plant waxes, nor extraction with some oxygenated solvents, recommended in the literature, gave reasonable removal of the

Table 1. REPRESENTATIVE "MINERALS" FOR IMPREGNATION EXPERIMENTS

Materials	Physical Characteristics	Chemical Characteristics	Source and Additional Comments
Fused quartz	ca 150 mesh; no porosity (less than 0.01 ml/g) very low specific surface (0.1 m^2/g)	Pure SiO_2; neutral	"Vycor", water elutriated, caustic and acid treated, calcined 6 hrs at 565°C
Silica gel	60-200 mesh; avg. pore diam. 140 A, pore volume 1.07 ml/g; specific surface, 260 m^2/g	SiO_2 with 0.07% Al_2O_3; nearly neutral	Davison Chemical Co.'s grade 62 gel
Synthetic "molecular sieve"	30-60 mesh; pore openings, 5A; pore volume, 0.26 ml/g; specific surface, 480 m^2/g	Metal-alumino silicates; slightly acidic	Linde Co.'s 5A molecular sieve ground and packaged by Coast Engineering Laboratory, Hermosa Beach, Calif.
Bentonite	60% below, 40% above 325 mesh; pore vol. 0.06 ml/g; specific surface, 31 m^2/g	Metal(Na)-alumino silicates; acidic	Montmorillonite clay from Wyoming; Standard Volclay Bentonite No. 32, American Colloid Co., Chicago
Olivine	Crystalline; no porosity and very low specific surface	Magnesium-iron orthosilicate	From Jackson County, N.C. (Ward's Nat. Sci. Establ., Rochester, N.Y.)

Table 2. HYDROCARBON AGGREGATES FOR IMPREGNATION EXPERIMENTS

n-Alkanes Distribution, Apparent Volume Percent*

Carbon No.	Gas Oil Wax	Gas Oil Wax Enriched with n-C_{16}	"Parowax"	Candelilla Wax	Parowax enriched with Candelilla Wax
15	4.4	3.4			
16	9.6	24.0			
17	21.4	17.7			
18	21.3	18.2			
19	22.5	19.5			
20	12.9	10.5			
21	5.7	4.9			
22	2.1	1.9	2.3		2.3
23			5.9		4.8
24			14.7		11.8
25			20.8		17.7
26			21.3		18.8
27			16.4		16.6
28			11.5		13.2
29			6.3	4.1	8.7
30			0.9	0.9	1.8
31				83.2	4.3
32				1.5	
33				10.3	

*In this and following tables the alkane parent peak sensitivities were taken to be independent of carbon number. This is a good approximation for the $\pi/2$-sector mass spectrometer but not for the 180° analyzer instrument. Hence analyses made with the CEC 21-103 are not directly comparable with those made with the Type LV and/or CEC 21-110.

non-hydrocarbons. However, percolation through a column of activated alumina with isooctane development produced a colorless fraction which after readsorption on a column of silica gel and recrystallization from warm methyl isobutyl ketone gave the composition shown in Table 2.

Solvents

1. n-Hexane, Phillips Petroleum Co.'s "pure grade" (99% min.) material was redistilled. The residue of 100 ml of this product was 0.1 (±0.1) mg or approx. 1.5 ppm under the conditions of our evaporation procedure (see Appendix).

2. Cyclopentane, Phillips Petroleum Co.'s "pure grade" (99% min.) material was redistilled to the same purity as that of n-hexane above (approx. 1.5 ppm heavy ends).

3. Benzene-methanol azeotrope (60.5/39.5 by wt) was distilled from a blend of the C.P. grade components. This material contained 2.4 ppm heavy ends.

Stock Solutions

Stock solutions of cetane, gas oil wax enriched with 10% cetane, Parowax and the latter enriched with 10% Candelilla wax paraffins were prepared to concentrations of approx. 5 or 10% by wt. in redistilled n-hexane and used for calibration of the mass spectrometer.

Dilutions of these solutions with n-hexane to a level of 0.25 or 0.5 mg/ml were used in the impregnation experiments.

Impregnations of Mineral Aggregates

10 to 50 g of mineral material was layered with redistilled cyclopentane, then 1 to 2 ml of "diluted" stock solution, containing 0.5 to 1.5 mg hydrocarbon aggregate, were added to produce levels of impregnation in the range of 10 to 100 μg/g. The glass dish containing this slurry was placed in a vacuum oven and kept at 40°C and 500-600 mm vacuum for a few hours. Laboratory air entered the oven through a silica gel trap to filter out hydrocarbon impurities.

Compression of Impregnated Mineral Aggregates

An Applied Research Laboratories (Glendale, California) hydraulic press, equipped with a dye to press potassium bromide plates for infrared analysis, was utilized. Approximately 1 g portions of the impregnated, vacuum-dried mineral aggregate were placed in the dye of the press and subjected to 100,000 psi pressure for one minute. The plates formed were crushed to a fine powder in an agate mortar for extraction.

Extractions and Evaporations

Impregnated mineral aggregates were extracted with n-hexane and the extracts were evaporated according to the procedure described in the Appendix.

Transfer of Extract to the Mass Spectrometer

The dry extract was weighed, then re-distilled n-hexane was added to provide a 5 to 10% solution. After centrifuging at 3000 rpm, this solution was introduced into the mass spectrometer by means of a calibrated "dipper". Calibrated standard bore glass capillaries of a few microliters volume ("Microcaps", manufactured by Drummond Scientific Co., Philadelphia, Pa.) were also used for this purpose. The most convenient size glass capillary had a length of 72 mm and a volume of 5 microliters. When a 1- to 2-microliter charge was tapped to the center of this tubing, the two ends could be sealed without damage to the sample and the charge preserved, if desired, for later analysis. The weight of neat charge was calculated from the weight increase of the capillary, or from the known volume of the dipper, the length of solution thread in the capillary and the assumed density of the charge solution.

It is recognized that the actual concentration of the charge solution is somewhat higher than the one calculated with the weight of solvent added because at room temperature approximately 4 mg of n-hexane will be in the gas phase of the flask.

Results

Recoveries were calculated by comparing intensities of selected parent peaks in the mass spectrum of the sample with those of the mass spectrum of the stock solutions. In this manner the mass spectrometer is employed as a selective microbalance with a sensitivity for individual n-alkanes of approximately 2 micrograms under conventional operating conditions. In addition, any distortion of the envelope of the apparent carbon number (molecular weights) distribution of the sample is an indication of selective loss in the recovery process. Results are tabulated in Tables 3 to 9.

Table 3. MASS SPECTROMETRIC RECOVERIES OF ADDED HYDROCARBONS FROM SOME "MINERALS"

Percent Recovery

"Minerals"	Hydrocarbons				
	n-Hexadecane	n-Hexadecane + Sats ex CCGO		Parowax	Parowax + Sats ex Candelilla
	100 μg/g	100 μg/g	10 μg/g	25 μg/g	25 μg/g
Impregnations					
Fused quartz	128, 66				
Silica gel	162			104	101
Olivine sand	173, 50		73, 115		
Bentonite	157		101	118	154
Molecular sieve	114, 134, 4.5	79	39, 40	62	37
Impregnation Compressions					
Silica gel	35	114			
Molecular sieve	16, 7	104			
Blanks					
Evaporated stock solutions	135		151	117	122

Table 4. DISTRIBUTION OF n-ALKANES IN EXTRACT AFTER IMPREGNATION WITH GAS OIL WAX ENRICHED WITH CETANE

Mass Spectrometer: Westinghouse, Type LV
Apparent Volume Percent

Carbon No.	Stock Solution I	Chromatographed Through Silica Gel	Recovered From Impregnated			
			Olivine[a)]	Bentonite[a)]	Mol. Sieve[a)]	Mol. Sieve[b)]
15	1.3	3.2	5.6	4.0	1.2	0.5
16	19.2	18.6	18.7	15.2	17.3	10.6
17	18.4	18.1	17.5	16.2	18.5	16.1
18	20.7	20.2	18.5	21.2	23.4	22.4
19	20.7	20.5	19.4	20.1	25.8	25.1
20	12.3	12.0	11.2	12.6	13.6	14.9
21	5.4	5.5	6.1	7.1	-	7.0
22	1.9	1.9	3.0	3.6	-	3.2

a) Impregnation level: 10 μg/g.
b) Impregnation level: 100 μg/g.

Table 5. DISTRIBUTION OF n-ALKANES IN EXTRACT AFTER IMPREGNATION WITH GAS OIL WAX ENRICHED WITH CETANE

Mass Spectrometer: CEC 21-103
Level of Impregnation: 10 μg/g
Apparent Volume Percent

Carbon No.	Stock Solution	Recovered From Impregnated	
		Olivine	Molecular Sieve
15	3.4	1.4	6.7
16	24.0	16.2	10.1
17	17.7	15.1	13.4
18	18.2	20.7	20.2
19	19.5	24.4	21.8
20	10.5	13.5	12.6
21	4.9	6.2	10.1
22	1.9	2.5	5.0

Table 6. DISTRIBUTION OF n-ALKANES IN EXTRACT AFTER IMPREGNATION-COMPRESSION WITH GAS OIL WAX ENRICHED WITH CETANE

Mass Spectrometer: Westinghouse, Type LV
Level of Impregnation: 100 μg/g
Apparent Volume Percent

Carbon No.	Stock Solution I	Recovered From Impregnated/ Compressed	
		Silica Gel	Molecular Sieve
15	1.3	1.2	0.8
16	19.2	14.8	14.8
17	18.4	16.0	16.9
18	20.7	21.6	21.7
19	20.7	24.7	23.5
20	12.3	13.4	13.2
21	5.4	5.9	6.8
22	1.9	2.3	2.1

Table 7. DISTRIBUTION OF n-ALKANES IN EVAPORATION BLANK OF GAS OIL WAX ENRICHED WITH CETANE

Mass Spectrometer: CEC 21-103
Apparent Volume Percent

Carbon No.	Neat Enriched Wax II	Stock Solution II	Evaporation Blank
15	3.8	3.5	2.7
16	24.1	22.6	22.6
17	18.1	17.8	18.2
18	17.9	18.7	18.8
19	19.2	19.1	19.9
20	10.5	11.3	11.3
21	4.7	5.1	4.8
22	1.8	1.9	1.8

Table 8. DISTRIBUTION OF n-ALKANES IN EXTRACT AFTER IMPREGNATION WITH PAROWAX

Mass Spectrometer: CEC 21-103
Impregnation Level: 25μg/g
Apparent Volume Percent

Carbon No.	Neat Parowax		Stock Solution		Blank	Chromatographed Through Silica Gel	Recovered From Impregnated		
							Silica Gel	Mol. Sieve	Bentonite
22	1.6	2.3	1.1	1.5	1.7	2.1	4.3	2.1	4.6
23	6.7	5.9	6.8	5.9	6.0	5.6	8.0	5.4	7.6
24	13.5	14.7	12.4	12.9	14.6	13.8	15.6	12.4	14.2
25	18.3	20.8	19.5	18.7	21.0	18.5	20.6	19.1	19.2
26	20.0	21.3	20.7	20.2	21.6	20.2	20.6	20.3	19.5
27	17.2	16.4	17.7	17.6	16.3	16.7	15.0	17.0	15.9
28	13.0	11.5	13.2	13.2	12.6	13.2	10.0	13.7	11.5
29	8.6	6.3	7.5	8.5	5.7	8.2	5.0	8.7	6.5
30	1.6	0.9	1.1	1.5	1.0	1.8	0.9	1.2	1.5

Table 9. DISTRIBUTION OF n-ALKANES IN EXTRACT AFTER IMPREGNATION WITH PAROWAX ENRICHED WITH CANDELILLA WAX SATURATES

Mass Spectrometer: CEC-21-103
Impregnation Level: 25μg/g
Apparent Volume Percent

Carbon No.	Stock Solution		Blank	Chromatographed Through Silica Gel	Recovered From Impregnated		
					Silica Gel	Mol. Sieve	Bentonite
22	2.3	1.7	1.2	1.4	4.7	2.9	5.4
23	4.8	4.6	5.4	5.7	8.0	5.0	9.2
24	11.9	11.9	12.1	12.6	12.4	11.4	15.5
25	17.7	17.5	17.8	18.1	17.1	17.9	16.2
26	18.7	18.9	19.5	19.2	18.1	18.6	16.7
27	16.6	16.6	16.1	16.6	15.0	17.1	13.8
28	13.1	13.2	12.8	12.3	12.4	13.6	10.6
29	8.7	8.9	8.3	7.7	5.7	7.9	7.8
30	1.9	2.0	1.7	3.0	2.3	1.4	1.2
31	4.4	4.6	5.0	4.3	4.1	4.3	3.4

Sedimentary Rocks

Samples

The four sedimentary rock samples examined included two shales and two limestones with reported benzene-methanol extractables contents of 20 to 180 ppm, and CO_2 and non-carbonate carbon concentrations as shown below:

	CO_2 as $CaCO_3$, %	Non-carbonate carbon, %
Shale A	3	0.41
Shale B	4	0.16
Limestone A	87	0.69
Limestone B	99.6	0.34

These samples were first broken up into < 1-1/2 cm pieces, then ground in a hammer type laboratory pulverizing mill (Weber Brothers Metal Works) equipped with a Tyler mesh 16 (1 mm openings) sieve.

Extractions and Chromatography

Two approximately 125-gram batches of each of the four ground rock samples were extracted with n-hexane according to the procedure described in the Appendix. The yellow colored residues ranged from 32 to 100 ppm (see Table 10). Elution chromatography (see Method in Appendix) of these materials yielded 18 to 62 ppm waxy "saturates", representing 57 to 77%w of the extracts (see Table 11).

Extraction of all four samples and isolation of the saturates by chromatography were repeated with 10-gram samples. In addition, one shale and one limestone were also extracted with benzene-methanol azeotrope and the saturates were separated chromatographically. Yields of these operations are included in Table 11.

Table 10. EXTRACTS OF SEDIMENTARY ROCKS WITH n-HEXANE

Sample size: 250 g

Sedimentary Rock	Extract, ppm	Saturates Fraction ppm	Saturates Fraction %w of extract
Shale A	36	28	78
Shale B	32	18	58
Limestone A	100	62	62
Limestone B	42	24	57

Table 11. EXTRACTS OF TWO SEDIMENTARY ROCKS WITH n-HEXANE AND BENZENE-METHANOL AZEOTROPE

Extract, ppm	Shale A		Limestone A	
	250 g	10 g	250 g	10 g
Benzene-Methanol Extract				
Total	-	228, 204 (± 20)		330, 370 (± 20)
Saturates Fraction	-	24, 20 (± 20)		50, 120 (± 20)
n-Hexane Extract				
Total	36 (± 2)	30, 50 (± 20)	100 (± 1)	580,[a] 90, 130 (± 20)
Saturates Fraction	27 (± 2)	50, 30 (± 20)	62 (± 2)	70, 50, 60 (± 20)

a) Residue not dry.

Analyses

Ultraviolet spectra of all chromatographic fractions from the 250-gram extractions were recorded from 3500 A down to the limit of the instrument (~2100 A) in a Cary Model 14 spectrophotometer. A Cary Model 15 recording spectrophotometer was used to obtain the spectra of chromatographic fractions from the 10-gram extractions. Extensively purified isooctane was the solvent for both sets of extracts.

The spectra obtained for the "saturates" from the extraction of each of the 10-g rock samples and for one of the 250-g rock samples are shown in Figure 3. The magnitude of the absorbance at 2600 A corresponds to these samples containing the order of 1-2% (molal) conjugated cyclic dienes. It will be noted that there is quite reasonable agreement between the spectra obtained for the saturates recovered from the two scales of extraction of the Limestone A.

Mass spectra of the saturates fractions isolated in the various experiments were recorded with the CEC 21-103 and 21-110 spectrometers. Hydrocarbon type compositions of these fractions were calculated employing the total ion current-parent peak method developed in These Laboratories, as shown in Tables 12 and 13. These calculations provide an indication of the overall repeatability of the analytical experiment, separation and mass spectrometric characterization. We see that with respect to the apparent distribution of hydrocarbons in empirical formula, the repeatability is about ±10% of the quantity present.

The apparent distribution of alkanes in carbon number, as indicated by the intensities of the ions of mass number 14n + 2 in the spectrum adjusted to their sum equal to 1000, after correction of the mass spectrum for C^{13} content, over the indicated range of n are given for the various saturates from the four rocks in Tables 14 and 15. Examination of these data reveals that the gain in sensitivity that results from the use of the ultrahigh resolution mass spectrometer (21-110) that enables complete spectra to be recorded from 0.1 mg samples results in a very significant loss in repeatability. It would appear from these data that it would be quite rash to attempt to interpret differences in apparent concentrations of successive homologues of less than 10% of the quantity present. Thus for example in the case of the alkanes in the extract from the Linestone A, there appears to be a bimodal distribution with maxima at 19 and 22 carbon atoms. However, the precision indicated in Table 15 shows that the magnitude of the apparent minimum at 21 carbon atom is less than the uncertainty.

Similarly, comparing the distributions in carbon number of the alkanes found for Shale A (Table 14) with that of Limestone A in the light of the precision indicated in the data of Table 15 indicates these distributions to be essentially indistinguishable. However, one can conclude that there are real differences between the alkane distributions of Shale B and Limestone B and that these distributions are both different from the distribution of the A samples.

Figure 3 follows

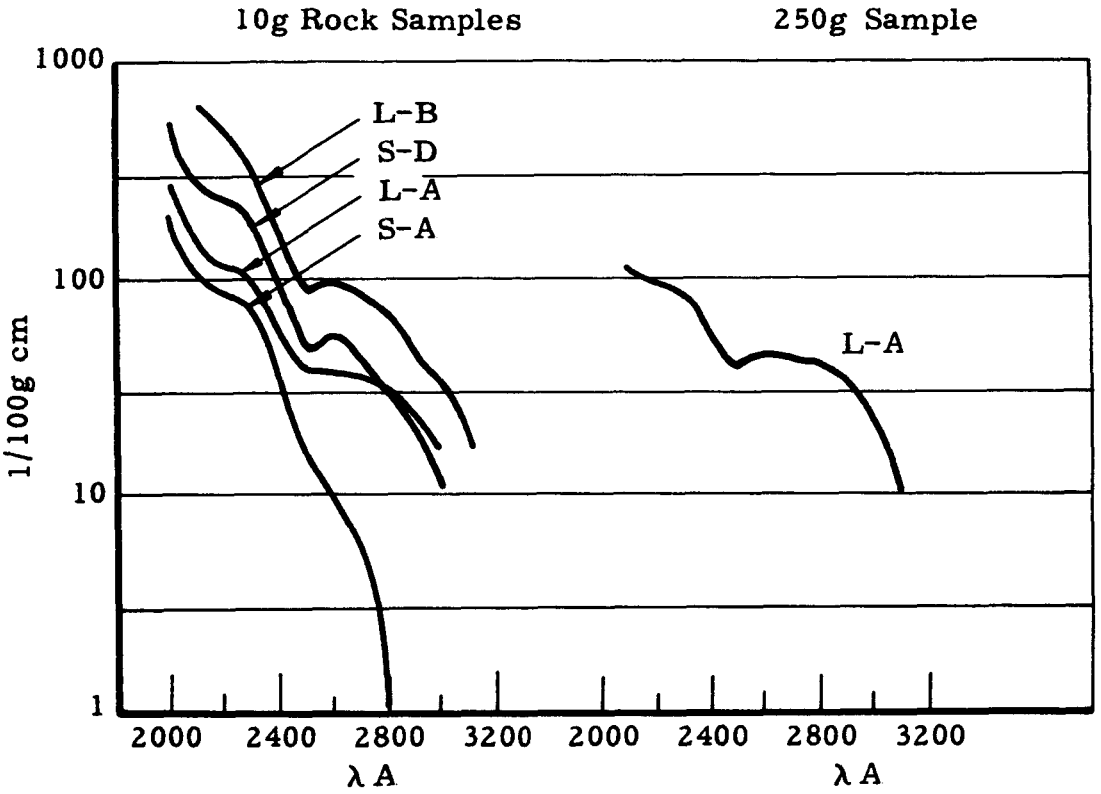

Figure 3. ABSORPTION SPECTRA OF "SATURATED-HYDROCARBONS" RECOVERED FROM SHALES, S-A, S-B AND LIMESTONES L-A AND L-B

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Table 12. HYDROCARBON TYPE ANALYSES

Mass Spectrometer: CEC 21-103
Volume Percent

"z No."*	Shale A 250 g Hexane	Shale B 250 g Hexane	Limestone A 250 g Hexane	Limestone A 10 g Hexane	Limestone B 250 g Hexane
+ 2	32.6	22.3	33.8	32.2	26.5
0	23.7	26.9	21.8	21.6	25.6
- 2	21.6	24.6	18.2	18.9	25.0
- 4	12.3	14.0	10.9	11.6	11.7
- 6	3.8	7.6	9.5	10.0	7.0
- 8	4.0	3.2	4.2	4.0	2.9
-10	2.0	1.3	1.7	1.8	1.2

* The z-Number in the expression C_nH_{2n+z} defines the nominal homologous series of the hydrocarbons.

Table 13. HYDROCARBON TYPE ANALYSES

Mass Spectrometer: High Resolution CEC 21-110
Volume Percent

"z No."	Shale A			Limestone A				
	250 g Hexane	10 g Hexane	10 g φH-MeOH	250 g Hexane	10 g Hexane	10 g Hexane	10 g φH-MeOH	10 g φH-MeOH
+ 2	32.3	28.8	28.8	37.4,33.3	37.1	34.4	34.2	34.3
0	33.9	30.2	32.7	31.9,31.4	29.1	30.9	27.9	28.8
- 2	18.0	21.5	19.3	15.2,17.3	14.8	17.0	17.1	17.0
- 4	9.5	10.4	10.4	7.8,9.2	8.7	8.8	10.0	9.0
- 6	5.2	7.2	7.0	7.1,7.7	9.3	7.9	9.1	9.4
-10	1.0	1.9	1.9	0.6,1.1	1.0	1.0	1.7	1.5
LR-7648-*	81-7	98-4	98-7	68-1,95-8	79-6	96-7	96-5	96-2

"z-No."	Shale B	
	250 g Hexane	10 g Hexane
+ 2	23.0	18.5
0	34.2	33.1
- 2	23.0	21.8
- 4	10.8	13.2
- 6	5.7	7.8
- 8	2.3	3.9
-10	0.9	1.7
LR-7648-*	80-4	79-8

Limestone B	
250 g Hexane	10 g Hexane
24.5	24.3
35.6	32.5
20.7	19.4
10.4	11.6
5.7	7.7
2.2	3.2
1.1	1.4
81-5	77-5

*Experiment number.

Table 14. APPARENT DISTRIBUTION OF ALKANES, C_nH_{2n+2}, FROM SEDIMENTARY ROCKS, IN CARBON NUMBER

Mass Spectrometer: High Resolution CEC 21-110

n	Shale A			Shale B		Limestone B	
	Experiment Number						
	98-4	98-7	81-7	79-8	80-4	77-5	81-5
14	1	10	23	0	19	0	0
15	24	14	82	27	57	0	4
16	74	48	109	61	114	1	15
17	105	87	126	145	161	29	8
18	132	118	108	155	143	39	33
19	152	144	101	80	114	51	42
20	122	128	98	83	82	60	45
21	81	113	58	77	66	33	40
22	106	112	67	92	66	89	64
23	85	80	61	105	61	139	98
24	30	49	28	69	47	118	109
25	27	34	39	50	32	80	113
26	15	25	14	18	13	88	107
27	19	16	23	15	2	62	87
28	4	10	20	12	7	47	44
29	8	8	10	9	5	41	45
30	2	4	10		3	27	33
31	0	2	4		2	28	37
32					2	18	21
33						14	5
34						14	8
35						5	10

Table 5. ALKANE C_nH_{2n+2} AND C_nH_{2n-6} DISTRIBUTIONS FROM LIMESTONE A, IN CARBON NUMBER

Mass Spectrometer: High Resolution CEC 21-110

n	Experiment Number						Average	C_nH_{2n-6}	
	68-1	95-8	96-7	96-2	96-5	79-6		96-7	96-5
14	36	31	13	2	21	2	18 ± 12	42	46
15	51	55	20	15	21	0	27 ± 20	32	44
16	56	77	43	13	43	28	43 ± 20	62	78
17	80	97	91	50	81	60	76 ± 18	50	67
18	100	100	109	84	107	117	103 ± 10	31	46
19	101	112	123	92	110	95	105 ± 11	43	52
20	86	100	96	106	117	109	102 ± 10	37	52
21	75	84	104	115	98	96	97 ± 13	44	50
22	112	114	137	137	130	125	126 ± 10	31	50
23	104	97	107	124	99	125	110 ± 11	32	52
24	78	56	71	91	69	94	78 ± 13	21	27
25	45	31	37	74	38	45	45 ± 14	21	23
26	25	19	20	33	17	31	24 ± 6	18	21
27	27	11	13	18	19	24	17 ± 6	43	66
28	8	7	8	12	10	20	11 ± 4	31	36
29	9	4	8	14	11	16	10 ± 4	34	46
30	3	3	3	8	6	8	5 ± 2	12	19
31	2	2	2	6	1	4	3 ± 2	5	11
32	2	1	1	2	2	3	2 ± 1	2	4
Wt. rock	250 g	250 g	10 g	10 g	10 g	10 g		10 g	10 g
Solvent	Hex	Hex	Hex	φH-MeOH	φH-MeOH	Hex		Hex	φH-MeOH

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It would be very difficult to adduce statistical support for the generally accepted concept of the biologic origin of organic compounds found in sediments from the alkane distributions in carbon number found in the extracts from the four sedimentary rocks.[a] This is in marked contrast to the situation that obtains for the extract of garden earth described in a later section of this report. However, the statistical evidence of biologic origin of the hydrocarbons can be found in the mass spectra of the extracts in comparison of the distribution in carbon number shown by the homologous series of empirical formula C_nH_{2n-6} with that of the alkanes. As may be seen in the last two columns of Table 15, the distribution in intensity of ions of empirical formula, C_nH_{2n-6}, in the mass spectra of the "saturates" from the Limestone A extract shows a well defined maximum at n = 16 and a second maximum for $27 \leq n \leq 30$. From observations of mass spectra of hydrocarbons separated from various crude oils in large scale separation experiments it is known that the C_nH_{2n-6} hydrocarbons with 27 through 30 carbon atoms all have intense fragment ions in their spectra at n = 16, thus the former maximum is most probably related to the presence of the latter. From the point of view of the origin of the hydrocarbons the important point is the marked difference in carbon number of the maxima of the distribution functions for the two series, C_nH_{2n+2}, ca C_{18}-C_{22} and C_nH_{2n-6}, ca C_{27}-C_{30}, and particularly the marked four carbon atom range of the intensity distribution anomaly of the C_nH_{2n-6}.

It is probably no coincidence that Fenske et al found a strong maximum in the optical rotary power of lubricating oil distillation fractions for molecular weights near 370. The molecular weight of $C_{27}H_{48}$ is 372 amu. When a narrow molecular weight (ca 370) range fraction of saturated hydrocarbons from lubricating oil stock is separated according the the "z-number" by the thermal diffusion technique, it is found that the optical activity of the fraction is concentrated in the bottom sections of the thermal diffusion column, i.e., those with z values between 4 and 10.

As a test of the quality of the recovery of the complex mixture of non-saturated substances extracted from the rocks and separated from the saturated hydrocarbons by elution chromatography over silica gel, there were compared the ultraviolet adsorption spectra of the total extracts with the recovered non-saturates. There are shown the absorbances (cm^{-1} for total material dissolved in 5 ml of isooctane) of extracts and recovered non-saturates at selected wavelengths for the cases of extraction of 10 gram samples of each of the four rock samples with hexane in Table 16. It is seen that for the substances contributing to the absorption spectra at wavelengths shorter than ~2800 A, the recovery is $\geq$ 90%.

A high resolution mass spectrum of the non-saturate aggregate for the Limestone A was recorded. This indicated the non-saturate aggregate to be an extraordinarily complex mixture. Not only does this aggregate contain hydrocarbons in each of the following homologous series, C_nH_{2n-6}, C_nH_{2n-8},

a) K.Rankama and Th. G. Sahama, "Geochemistry", Univ. of Chicago Press (1950), particularly pages 535-542.

Table 16. ULTRAVIOLET ABSORPTION SPECTRA, ROCK EXTRACTS

Absorbances cm^{-1}, in 5 ml isooctane solution

λ A°	Limestone A		Limestone B		Shale A		Shale B	
	Extract	Non-Saturates	Extract	Non-Saturates	Extract	Non-Saturates	Extract	Non-Saturates
3000	0.542	0.453	0.266	0.243	0.169	0.150	0.900	0.821
2800	0.824	0.731	0.400	0.377	0.290	0.263	1.284	1.173
2500	1.585	1.410	0.673	0.642	0.723	0.635	2.13	1.90
2300	3.26	3.14	1.128	1.122	1.228	1.170	2.74	2.46
2100	3.44	3.46	1.395	1.358	1.753	1.636	2.94	3.01

C_nH_{2n-10}, C_nH_{2n-12}, C_nH_{2n-14}, C_nH_{2n-16}, C_nH_{2n-18} and C_nH_{2n-20}, but there was certainly identified the presence of substances in the homologous series, $C_nH_{2n-10}S$, $C_nH_{2n-16}S$, $C_nH_{2n-8}O$, $C_nH_{2n-10}O$, $C_nH_{2n-12}O$, $C_nH_{2n-14}O$, $C_nH_{2n-16}O$, $C_nH_{2n-12}O_2$ and at least one substance with three oxygen atoms, $C_8H_6O_3$. Interestingly enough, we have also found in the mass spectrum of a kelp extract evidence of the presence of a substance of empirical formula $C_8H_6O_3$. There was no evidence in the mass spectrum of this aggregate of the presence of substances with nitrogen atoms.

Garden Earth

This sample was collected in October 1962, in Contra Costa County, California, 24 inches from the trunk of a 9-year old Monterey pine tree (Pinus Radiata) after the top 1/2 inch layer of soil (not disturbed since the planting of the tree) was cleared away. It was broken up in a mortar, any vegetable matter (roots, bark pieces) evident under a magnifying glass was picked out, then placed in an oven and kept at 80°C and 430 mm vacuum for 2-1/2 hours.

Two approximately 100 gram portions of this material were extracted with n-hexane, and the extracts chromatographed, according to procedures described earlier. Recoveries and mass spectrometric type analysis of the saturates are shown in Tables 17, 18 and 19.

Table 17. EXTRACTION AND CHROMATOGRAPHY OF GARDEN EARTH

Extraction	A		B
Sample wt, g	136.77		114.35
Extract, ppm	37		38
Chromatography	**A-I**	**A-II**	**B**
Saturates, ppm	39	23	26
Non-saturates, ppm	-	-	6
Recovery, %	-	-	84

Table 18. HYDROCARBON TYPES

Garden Earth

"Z-No."	% v
+ 2	26.4
0	35.0
- 2	19.9
- 4	9.6
- 6	6.0
- 8	2.3
-10	0.8

Table 19. APPARENT ALKANE, C_nH_{2n+2}, DISTRIBUTIONS FROM GARDEN EARTH, COPROSMA AND PRUNUS ILLICIFOLIA WAXES

n	G.E.	C	PI
14	6	2	5
15	14	6	3
16	2	11	8
17	14	9	3
18	11	15	5
19	61	18	5
20	62	25	2
21	57	21	10
22	37	6	9
23	39	21	9
24	20	13	3
25	50	41	10
26	29	0	10
27	95	155	65
28	38	18	35
29	287	339	492
30	23	15	28
31	128	214	263
32	4	10	11
33	13	25	23
34	7		
35	2		

In the last of these three tables there are shown the apparent distributions in alkanes in the nominally saturated hydrocarbon aggregates separated from waxes obtained by hexane extraction of the leaves of two common decorative plants or trees, namely, Coprosma and Prcnus Illicifolia. It will be noted that in the three samples the dominant alkane constituents are the C_{27}, C_{29} and C_{31} alkanes. The shape of the distribution of intensity of the fragment ions, $C_nH_{2n+1}^+$, in carbon number n in the range $20 \leq n \leq 30$ indicates these alkanes to be almost exclusively normal alkanes. In the case of the garden earth aggregate, the intensities of the $C_nH_{2n+1}^+$ ions for $15 \leq n < 20$ strongly suggest the lower molecular weight (C_nH_{2n+2}, $n < 25$) alkanes to be largely of branched structure.

Optical Activity of Gasoline Hydrocarbons

In a recent paper, Friedel and Sharkey,[a] have noted the similarity in the relative quantities of certain alkane isomers in the C_4-C_7 range of Fischer-Tropsch and petroleum gasolines. It could be implied from the data of Friedel and Sharkey that a significant fraction of the saturated hydrocarbon content of petroleum could be primordeal hydrocarbon resulting from purely physical or inorganic synthesis reactions rather than of biogenic origin as is mostly commonly believed by geochemists.

If, as seems more reasonable to the present authors, the major source of the low molecular weight compounds of petroleums has been the physico-chemical degradation of large molecules, it seems probable that a finite fraction of the optically active centers should be able to resist racemization and endow the low molecular weight range hydrocarbons with measurable optical activity. Hence it seemed of interest to make a cursory search for evidence of low molecular weight optical activity in a typical gasoline from petroleum. Inasmuch as the lowest molecular weight fraction (M.W. 220) in which Fenske et al found optical activity in their survey of lubricating oil stocks was a California petroleum, it appeared gasoline from such petroleum would be most suitable for the preliminary survey.

There was available in These Laboratories a sample of saturated hydrocarbons separated some years ago from a straight run gasoline manufactured at the Shell Oil Company Martinez Refinery from a mixed California Central Valley crude oil. It was found that this C_6^+ mixture of hydrocarbons showed a small but real optical activity. Since this was a quite wide range gasoline, it then seemed of interest to determine whether optical activity existed at the lowest possible molecular weight, i.e., in the C_7 hydrocarbons.[b] To this

a) Friedel and Sharkey, Science 139, 1203 (1963)

b) Among the various classes of hydrocarbons that have been identified in petroleum, 3-methylhexane, 2,3-dimethylpentane, and the 1,trans-2- and 1,trans-3-dimethyl cyclopentanes are the lowest molecular weight hydrocarbons with either an asymetric carbon atom or lacking a plane of symmetry. Lower molecular weight hydrocarbons such as trans-dimethyl cyclopropanes and butanes can be optically active but members of these classes of hydrocarbon have never been detected in petroleum to the knowledge of the authors.

end the gasoline range saturated hydrocarbon aggregate was subjected to fractional distillation (20 theoretical plates, 2% reflux ratio) and a series of fractions collected at temperatures between 75° and 100°C. The optical rotations (20-cm cell, sodium-D light) of the fractions were measured[a] and the hydrocarbon composition determined by gas-liquid chromatography.

There are shown in Table 20 the specific rotations of the successive fractions and concentrations of potentially optically active substances in the distillation fractions. It will be seen that there is essential parallelism between the optical rotation profile and the profiles of concentration of these substances with potential optical activity. The specific rotary powers of the optically active C_7 hydrocarbons are reported to be ca 5°, and the upper limit to the concentration of potentially optically active substances in the distillation fractions 8 to 12 is about 40%. Hence we conclude that at least 2.5-3.0% of the potentially optically active C_7 hydrocarbons in this gasoline are optically active.

Measurement of Optical Rotations

The polarimeter currently available in This Laboratory is an old instrument that has not been kept in first class condition. As a consequence considerable effort is required to obtain measurements of significance on samples of low optical activity. The procedure employed in the case of the series of gasoline saturates distillation fractions was the following: A series of four readings were made on a sample, the tube was turned end-over-end and a second series of readings was then made. The average rotation from the eight readings was then taken as the apparent rotation of the sample. The zero correction of the instrument was determined by using spectroscopic solvent isooctane as an alternate sample, i.e., an apparent rotation was measured for the isooctane, then for a gasoline fraction, then for isooctane, etc. The standard deviations of the individual measurements in a series from their average ranged from 0.01_6 to 0.03_0°. The averages of the apparent rotations of sets of 7, 5 and 5 series on isooctane were, $0.03_6° \pm 0.01_0$, $0.03_2° \pm 0.00_8$ and $0.02_1° \pm 0.00_6$, respectively. The specific rotations of the gasoline fractions given in column 6 of Table 20 are the differences between the apparent rotations of the sample and the appropriate average of apparent rotations of isooctane for the measurements made on a given day. The uncertainties indicated in Table 20 for the specific rotation (2.0 decimeter tube) of the gasoline fractions are:

$$\epsilon_s = \sqrt{\sigma_s^2 + (0.10)^2}$$

where σ_s is the standard deviation of the apparent rotation of the gasoline sample.

a) See below for the method of measurement and the significance of the measures of accuracy.

Table 20. SELECTED COMPONENTS(%w) AND ROTATIONS OF GASOLINE FRACTIONS

Table 20. COMPOSITION AND ROTATIONS OF GASOLINE FRACTIONS

Cut No.	3MH+1c3DMCP	2MH + 2,3DMP	1t3DMCP	1t2DMCP + 3EP	$[2\alpha]_D^{25°}$
1	0.0	0.1	0.0	0.1	$+ 0.01_4° \pm 0.02_6$
2	1.9	1.3	0.3	1.5	$+ 0.02_6° \pm 0.03_2$
3	4.7	3.3	0.9	3.9	$+ 0.04_8° \pm 0.02_0$
4	8.9	6.4	2.1	7.2	$\pm 0.014° \pm 0.02_2$
5	15.0	9.6	2.9	12.8	$+ 0.03_2° \pm 0.01_9$
6	19.7	9.1	6.1	16.1	$+ 0.03_2° \pm 0.01_8$
7	24.8	13.2	6.6	16.3	$+ 0.05_6° \pm 0.02_3$
8	29.4	14.0	8.4	14.9	$+ 0.08_4° \pm 0.02_2$
9	29.0	15.5	8.3	19.1	$+ 0.08_8° \pm 0.03_1$
10	32.2	12.8	8.7	17.3	$+ 0.06_0° \pm 0.02_5$
11	31.6	13.7	10.8	14.2	a)
12	29.6	11.9	11.3	14.6	$+ 0.08_0° \pm 0.02_2$
13	28.4	10.5	8.7	19.0	$+ 0.08_3° \pm 0.02_2$
14	23.1	8.0	6.7	25.0	$+ 0.07_4° \pm 0.02_3$
15	19.8	6.1	7.3	20.2	$+ 0.07_0° \pm 0.01_9$
16	17.1	4.0	6.3	17.4	$+ 0.02_7° \pm 0.02_0$
17	13.2	2.8	3.8	17.9	a)

a) Sample size was not sufficient for polarimetric measurement.

APPENDIX

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Part 1. Recovery of Organic Matter from Mineral Aggregates. 33

Part 2. Chromatographic Method for the Fractionation of Mineral Aggregate Extracts. 35

APPENDIX

Part 1. RECOVERY OF ORGANIC MATTER FROM MINERAL AGGREGATES

Solvent Extraction Method

Scope

1. This method describes a procedure for the recovery of small (milligram range) quantities of C_{14} and heavier hydrocarbons associated with mineral matter, and preparation of the residue for subsequent mass spectrometric examination.

> Note 1. Sample components other than hydrocarbons, soluble in the extracting solvents, are also recovered but may be separated chromatographicly (see Appendix, Part 2)

Outline of Method

2. The finely ground sample is extracted in a Soxhlet apparatus with n-hexane or benzene-methanol azeotrope. The extract is then evaporated and the residue taken up in n-hexane for transfer to the mass spectrometer.

Apparatus

3(a) Laboratory Pulverizing Mill, hammer type (such as manufactured by Weber Brothers Metal Works, Chicago, Ill.) equipped with sieves in the 16 to 32 mesh (Tyler) range.

(b) Alundum Thimbles of RA98 porosity in two sizes, 40 ml (30 x 80 mm) and 150 ml (45 x 127 mm). Thimbles should be cleaned after each use by extraction with benzene-isopropyl alcohol azeotrope and/or by heating in a muffle oven at about 600°C for a few hours.

(c) Soxhlet Extractors, in two sizes, capable of accomodating the 40-ml and the 150-ml thimbles.

(d) Distillation Assembly, as shown in Figure 4. This assembly consists of a two-part distilling flask to which a short Vigreux column and a water cooled condenser are attached through glass joints. The bottom heart-shaped flask (volume, 6.5 ml) is coupled to the upper part (volume, 110 ml) of the distilling flask with an O-ring joint ("HVS" joints, Scientific Glass Apparatus Co., Bloomfield, N.J.). The O-ring should be of Viton, a synthetic elastomer resistant to all common organic solvents.

(e) Clinical Centrifuge with cups of 25 to 30 mm I.D.

Figure 4 follows

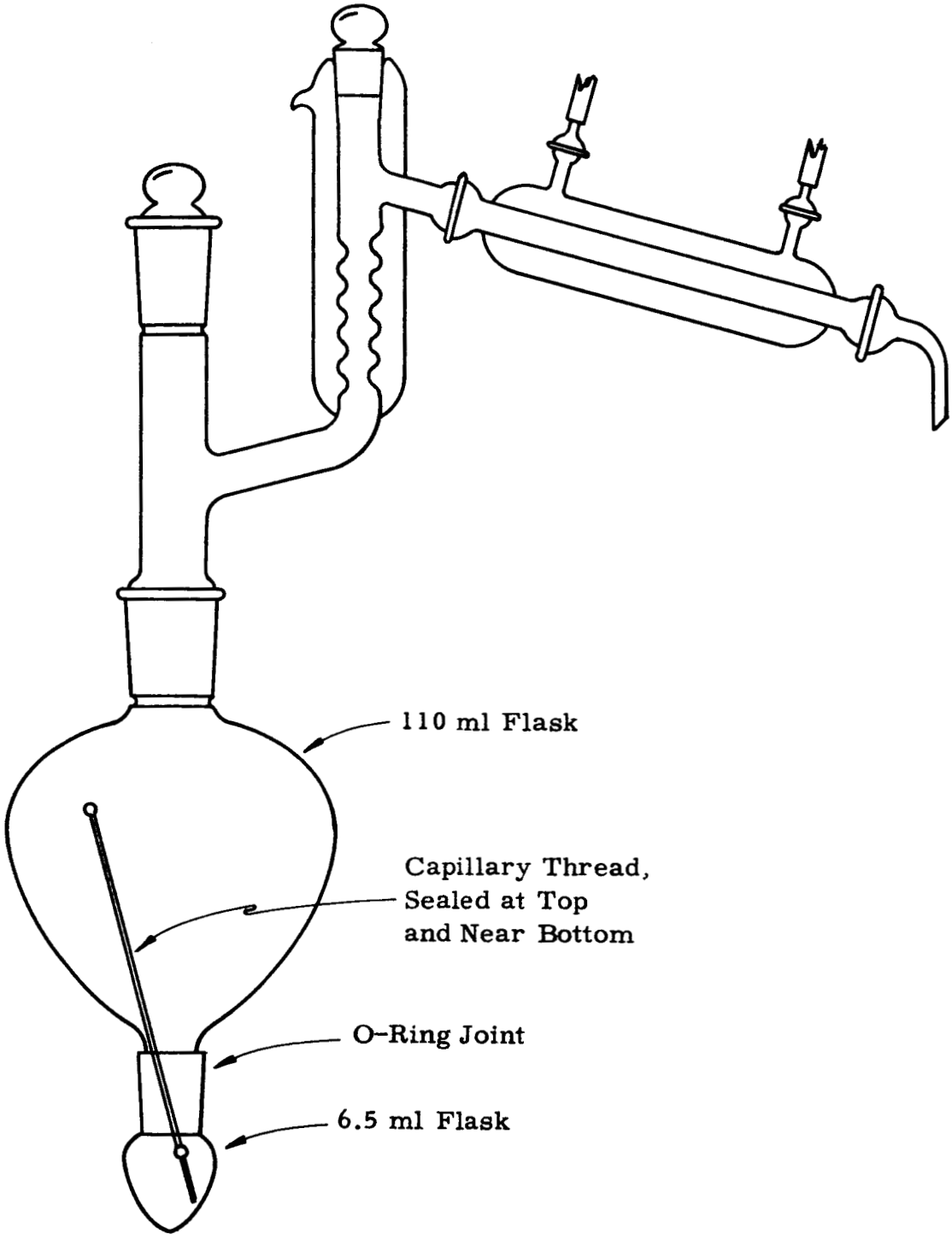

Figure 4. DISTILLATION ASSEMBLY

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Materials

4(a) n-Hexane, 99% min. purity, redistilled. The residue of 100 ml of this material should not exceed 0.2 mg under the conditions of the evaporation procedure below (Section 5).

(b) Benzene-Methanol Azeotrope (60.5/39.5 by wt) should be distilled from a blend of the C.P. grade components. The heavy ends content of this material should be checked as under Section (4a) above.

(c) Benzene-Isopropyl Alcohol Azeotrope (66.7/33.3 by wt) may be blended from the C.P. components.

(d) Boiling Threads. Fine glass capillaries, about 14-cm long, sealed at one end and at about one centimeter from the other.

(e) Nitrogen, filtered through a bed of silica gel.

(f) "Microcaps", calibrated standard bore capillaries of 5-microliter size, manufactured by Drummond Scientific Co., Philadelphia, Pa.

Procedure

5(a) Break the mineral sample into approx. 1-cm pieces, then grind in the laboratory pulverizing mill through Tyler mesh 16 sieve.

(b) Weigh a portion of the ground sample, estimated to contain a few milligrams of extractables, into an alundum thimble and place the thimble into the Soxhlet extractor. If the recovery of the saturated hydrocarbons only is required, extract with n-hexane. Use benzene-methanol azeotrope, if the recovery of a greater portion of the organic chemical content of the mineral sample is desired. Regulate the rate of extraction so that the thimble drains about every six minutes. Assume the extraction complete after 50 to 35 drainings.

> Note 2. The smaller extractor with the 40-ml thimble requires 125 ml of solvent, the larger apparatus with the 150-ml thimble about 175 ml.

(c) Transfer the extract into the distillation assembly, add a boiling thread and immerse the flasks in a hot water bath. Interrupt the distillation by lowering the bath, and detach the bottom flask when the level of the extract is below the O-ring joint.

(d) Complete the evaporation by means of a gentle stream of nitrogen, filtered through a short bed of silica gel, while the flask is immersed in a beaker of warm water. Terminate this phase of the evaporation when the last drop of extract in the tip of the flask is just dissipated.

Note 3. Continuing the nitrogen-blowing beyond this point may result in the selective loss of components at the light end of the extract. The solvent content of this "dry" residue is below 0.2 mg.

(e) Weigh the dried residue, then add n-hexane to provide a 5 to 10% solution. Centrifuge at 3000 rpm and reweigh.

(f) Introduce this solution into the mass spectrometer by means of a standard calibrated dipper. Alternatively use "Microcaps" which accomodate charge sizes up to 5 microliters. "Microcaps" containing 1 to 2 microliter charges may be sealed at both ends if the extract is to be preserved for later analysis.

Part 2. CHROMATOGRAPHIC METHOD FOR THE FRACTIONATION OF MINERAL AGGREGATE EXTRACTS

Scope

1. This method describes a procedure for the fractionation of milligram amounts of high molecular weight (> 200) organic materials into saturated hydrocarbons, aromatic hydrocarbons and non-hydrocarbons. Olefinic hydrocarbons appear in the saturates portion, and some sulfur or nitrogen-containing compounds together with the aromatics.

Outline of Method

2. A small glass adsorption column is packed with fine activated silica gel. This column is prewetted with isooctane, the sample solution introduced and developed with isooctane under pressure to produce first an effluent fraction containing the saturated hydrocarbon portion of the sample and next a fraction containing the aromatics. The rest of the sample, comprised of non-hydrocarbons, is desorbed with benzene-isopropyl alcohol azeotrope. Solvents are evaporated, if needed, before further examination of the fractions.

Apparatus

3. It is very desirable to mount the apparatus assembly described below in a darkroom to facilitate observation, under ultraviolet light, of fluorescent zone boundaries.

(a) The chromatographic column, shown in Figure 5, is made of glass and consists of a solvent reservoir with Teflon stopcock plug, a charger section connected to the separator section by a capillary (2 mm) U-tubing, and a capillary take-off bend. To avoid contamination of sample, the spherical joints are assembled dry. The take-off bend is secured with a screw-type clamp (such as Ace Glass, Inc. Catalog No. 7665); for the other two spherical joints,where absolute tightness is not essential, the conventional pinch-type clamps are satisfactory.

Figure 5 follows

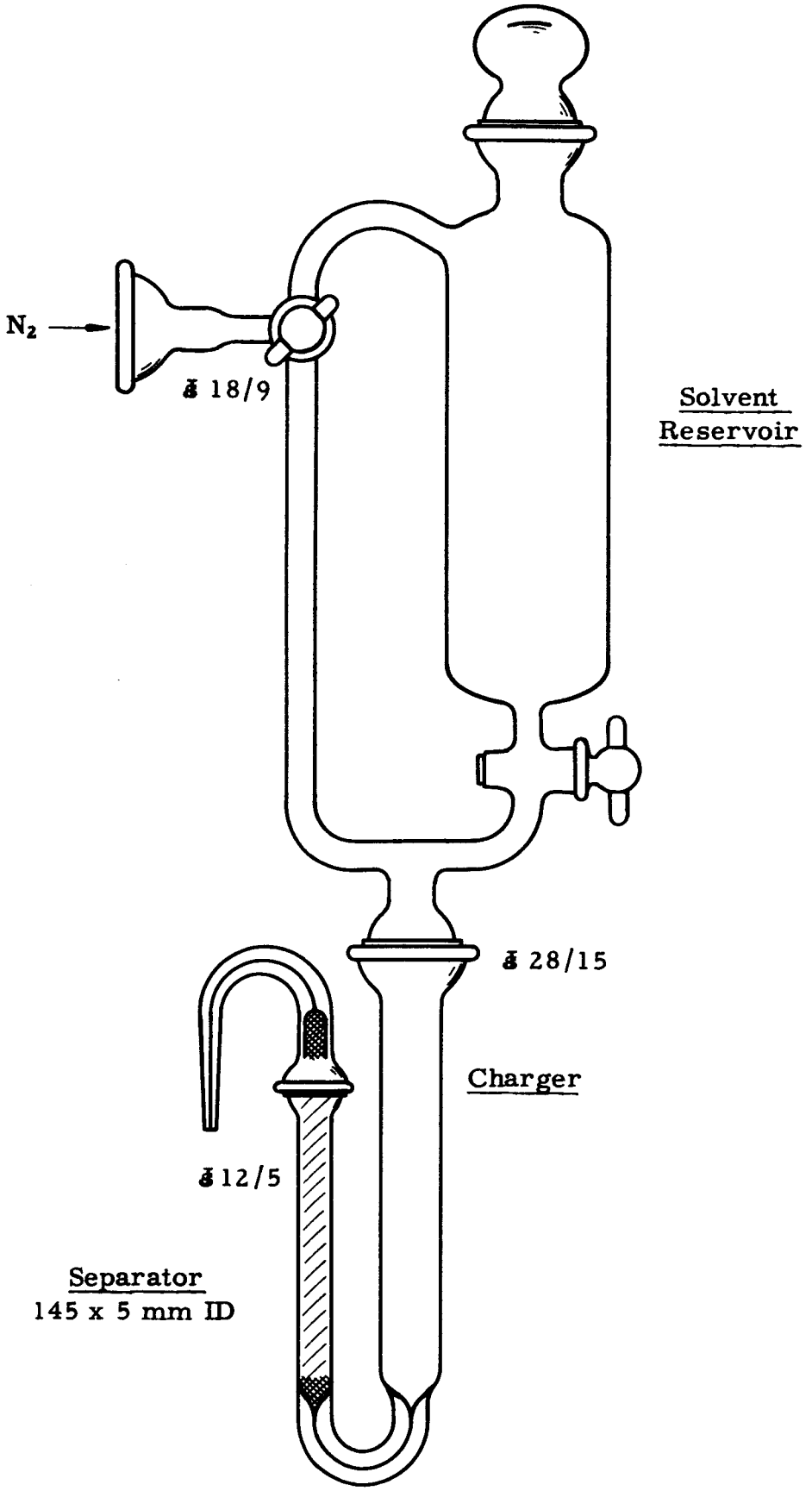

Figure 5. CHROMATOGRAPHIC COLUMN ASSEMBLY

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(b) Ultraviolet Light Source, with radiation predominantly at 3650 A is required. The ordinary "mineral lamp" or any commercial "black light" source is satisfactory.

(c) Vibrator, for packing of the silica gel. A small rubber padded electric massage machine is recommended.

Materials

4.(a) Silica Gel, grade 923 (100-200 mesh), available from Davison Chemical of N. R. Grace and Co., Baltimore 3, Md. Since the gel is received from the manufacturer in hermetically sealed containers, it is not necessary to dry the gel before use, provided it is protected from atmospheric moisture.

(b) Isooctane, spectroscopic grade, free of heavy ends.

(c) Benzene, redistilled, free of heavy ends.

(d) Benzene-isopropyl alcohol azeotrope (66.7/33.3 by wt), free of heavy ends.

(e) Pressuring gas. Nitrogen delivered to the chromatographic column, controllable over the range 0 to 3 psig.

(f) Glass wool, chemically pure.

Procedure

5.(a) Clamp the charger section of the apparatus, and tamp a small wad of glass wool into the capillary lower end of the separator. Pour the silica gel into the separator section through a small glass funnel and pack by running the vibrator up and down the tubing. Add more gel until it is packed all the way up into the spherical joint.

(b) Pack some glass wool into the well of the spherical joint on the take-off bend, then secure the take-off bend onto the separator section with a screw-type spherical joint clamp, without applying any lubricant. Place the solvent reservoir over the charger section, connect the nitrogen line using pinch clamps (no lubricant) to secure these joints.

(c) Make up the charge solution by dissolving the sample in minimum amount of isooctane. Prepare to charge to the column a volume of less than 1 ml containing not more than 5 mg of sample, not more than 2 mg of which may be non-saturates.

Note 1. The more concentrated the charge solution is, the more efficient fractionation of the sample may be expected. Under no circumstances should the sum of the volume of charge solution plus solvent portions used to rinse sample

container and charger section of the chromatographic assembly exceed the bed volume (approx. 2.1 ml) of the gel column.

Note 2. Bed volume is the amount of isooctane needed to completely wet the silica gel column. It is convenient to include in this measurement the volume of solvent needed to fill the capillary take-off bend and the capillary connection between the charge and separator.

(d) Place a small graduated cylinder under the take-off bend. Add some isooctane to the solvent reservoir, then let approx. 5 ml into the charger section. Force this solvent volume into the separator section by connecting the compressed nitrogen line through the 3-way stopcock of the charger section. This prewetting of the column should be done slowly to permit an effective displacement of the air in the gel.

(e) When the last of the isooctane just disappears into the capillary connection, turn off the nitrogen pressure, disconnect and raise the solvent reservoir and introduce the charge (Section 5(c)) to the bottom of the charger section. Change receiver, reconnect the solvent reservoir and turn on the nitrogen pressure (approx. 1-1/4 psig) to move the charge solution into the silica gel column at a rate of 0.3 ml/min. When all of the charge has entered the capillary connection to the separator, rinse the wall of the charger section with two small portions of isooctane (see Note 1), then continue adding isooctane until two bed volumes of effluent (see Note 2, approx. 4.2 ml) are collected. This fraction, which should be completely free of fluorescence, contains the saturates portion of the sample.

Note 3. Continued development with isooctane will desorb a portion of the aromatic hydrocarbon content of the sample (mainly benzene homologs) in the few bed volumes of effluent following the saturates. If isooctane is replaced with benzene, the desorption of the aromatics is more rapid and complete. The progress of this step may be followed under ultraviolet light.

(f) Elute the balance of the sample with benzene-isopropyl alcohol azeotrope. At the completion of the desorption, the effluent and the column should be free (or nearly free) of fluorescence. Maintain the 0.3 ml/min flow rate which will require a somewhat increased nitrogen pressure.

(g) If needed, recover the sample fractions in effluent portions by evaporating the solvent with a gentle stream of nitrogen at elevated temperature.