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TITLE: PHYSICAL AND CHEMICAL CHARACTERIZATION AND COMPARISON OF SOLIDS, LIQUIDS, AND OILS DERIVED FROM ESTONIAN AND GREEN RIVER FORMATION SHALES

AUTHOR(S): E. J. Peterson, CMB-8, Chemistry and Material Sciences Division
W. Dale Spall, LS-5, Life Sciences Division

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University of California

LOS ALAMOS SCIENTIFIC LABORATORY
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## INTRODUCTION

Estonia has had a producing oil shale industry since the 1920's. A United States oil shale resource has been recognized since the early 1900's, but commercialization has been postponed by the lower cost of petroleum products. The decreasing world supply of oil promises to bring about an expansion of the Estonian production and the growth of a United States industry. Samples of Estonian and Green River shale have been made available under a joint US/USSR environmental protection agreement dealing with the biological and genetic effects of pollution (project number 0.-[illegible]-11). The characterization of these two shales and products derived from them is the subject of this paper, and is an integral part of the biological study.

Specific samples investigated include Estonian raw and spent shales obtained from the EPA/DOE Fossil Fuel Repository, samples of raw shale feed stock and spent shale from the Paraho demonstration facility located at Anvil Points, Colorado, and a raw shale sample retrieved from the Mahogany zone of the Green River formation in Garfield County, Colorado. The Estonian raw shale sample, and both Paraho shale samples are the subject of animal inhalation studies being carried out at the Los Alamos National Laboratory.

## EXPERIMENTAL TECHNIQUES

### A. Solids

1. Neutron Activation Analysis. Neutron activation analysis (NAA) is one of the most accurate and reliable methods of analyzing for trace elements in natural materials. The method relies on production of unstable nuclides by neutron irradiation and subsequent emission of gamma radiation during decay to a stable state. Gamma-ray detection and measurement are accomplished with a Ge(Li) detector. It is a nondestructive technique in most applications, and has the advantage that many elements can be observed simultaneously. However, the method is not sensitive to some elements, such as carbon, oxygen, silicon, and lead, but this is often an advantage.

A split of each sample is transferred to a clean 1/2 in. diam. 4 ml. polyethylene rabbit vial. After weight and sample number are computer-filed, the rabbits are pneumatically sent to an irradiation position with approximate neutron flux of 6 x $10^{12}$ n/cm$^2$·s for 20 s. The sample is then blown into a large delayed-neutron detector if uranium analysis is desired, and after a 20-min delay, it is transferred pneumatically to a position in front of a Ge(Li) gamma-ray spectrometer. The spectrometer measures the gross gamma-ray spectrum emitted by the sample. The counting time is normally 8 min, after which the accumulated 4096 channel spectrum is recorded on magnetic tape for later computer analysis. In this initial Ge(Li) scan, short-lived isotopes of sodium, magnesium, aluminum, chlorine, potassium, strontium, iodine, barium, and dysprosium are identified and quantified

To observe long-lived isotopes of various elements by Ge(Li) counting, the gamma-ray spectrum must be recorded for longer times. The timing parameters used to assay natural materials are given below.

| Half-Life | Irradiation (Δt) | Delay Time | Count Δt |
|---|---|---|---|
| Short | 20 s | 20 min | 8 min |
| Intermediate | 200 s | 4 d | 1 h |
| Long | 200 s | 24 d | 1 h |

The elements observable [illegible] include gallium, arsenic, bromine, antimony, lanthanum, samarium, tungsten, and gold. Additional elements observable [illegible] include scandium, chromium, iron, cobalt, zinc, selenium, rubidium, cesium, [illegible], europium, terbium, lutetium, hafnium, tantalum, mercury, and thorium. The limit of detection for a given element is not a fixed value, but is sample-dependent.

C. Infrared and X-Ray Diffraction Methods. Infrared spectra were recorded on a Perkin-Elmer Model [illegible] spectrometer in the range of [illegible] cm⁻¹, in KBr pellets. Comparison [illegible] was employed to determine the relative amount of [illegible] contained in the samples. [illegible]

X-ray diffraction [illegible]

1/4° and/or 1/8° per minute, together with selected combinations of scale factors and time constants, permitted excellent sensitivity of peak detection. In reading the diffraction patterns, all peaks were recorded which exhibited consistent intensities greater than two standard deviations above background. Critical overlapping peaks were resolved with the aid of a DuPont curve resolver. All indexing was accomplished by reference to the mineral subfile of the general JCPDS powder diffraction file. All reflections within the patterns were identified, except the occasional weak or trace phases. For those mineral constituents which were obviously members of an isomorphous series, the lattice parameters were also obtained to establish the relative positions of these phases within the series. Estimates were made of the relative abundances of the mineral constituents by comparing the background normalized intensities of the stronger reflections from each phase.

[illegible]. Optical Microscopy, Scanning Electron Microscopy, and Electron Microprobe Analysis. Shale samples are partially cut with an abrasive saw, and then broken through the saw cut to minimize saw kerf material loss. The samples are placed in 1 in. diam. molds, and vacuum-epoxy-potted. The samples are then pressurized to [illegible] psi to fill surface-connected voids with epoxy. The samples are then given a metallographic polish and a [illegible] min. [illegible] etch. Scribe marks are placed on the sample to help identify layers and interesting areas. The samples are examined with a metallograph and photomicrographs and macrographs are taken. The samples are then SEM-EDS examined with a Coates-Welter Field Emission Scanning Electron Microscope equipped with an Ortec Energy Dispersive Spectrometer. A [illegible] kV accelerating voltage is used with a beam diameter of ~[illegible] A. The SEM resolution is [illegible] A and the EDS spatial resolution is ~1 μ, depending on the Z number of the element. The EDS energy resolution is 155 eV full width at half maximum (FWHM) on the Mn Kα line. Field emission SEM does not permit quantitative analysis because the electron beam is not stable; however, point counts can provide useful information. A small particle in a matrix of different composition will not be quantitatively analyzed even with a stable beam. Electron excitation of characteristic x rays also produces a large bremsstrahlung background and, thus, very long counts are required to obtain peaks from elements present at less than 1/2%.

Sediment layers of the oil shale were examined at magnifications of 5000-10 000X because many of the trace elements are present as discrete submicron particles. EDS analysis are made of a particle and its immediate environment. Low-magnification EDS analyses of typical layers are also obtained.

4. Fischer Assay. The raw Estonian shale and the Green River shale were assayed for [illegible] content by the modified Fischer assay[1]. The Estonian shale contains [illegible] gallons per ton and the Green River shale assayed at 26 gallons per ton. These values compare well to reported values[2].

B. Liquids

1. Leaching Experiments. Leaching experiments were utilized to determine the solubility of major, minor, and trace elements as a function of mineralogical and chemical properties of the raw and spent shales. These experiments consisted of a [illegible] shaker leaching [illegible] material with [illegible] volume ratio [illegible]. The [illegible] were separated from the solid phase by centrifugation and filtration through 0.45 μm millipore filters. Analytical data were obtained by Direct Current Arc Plasma Emission Spectrometry (DCAPES) and [illegible] selective electrode [illegible]. [illegible] generated by this procedure may approach maximum concentrations of most elements because of the particle size distribution of the solid material.

2. Direct Current Arc Plasma Emission Spectrometry. To provide [illegible] complementary to [illegible] capabilities, direct current plasma emission spectrometry (DCAPES) [illegible] trace element analysis of [illegible] waters. Results obtained are acceptable [illegible] sensitivity, selectivity, accuracy, speed, economy [illegible] of the elements of interest [illegible] water. [illegible] samples that are [illegible].

[illegible]

that allows only certain atomic emission wavelengths to impinge on the instrument's photomultiplier tubes. One multielement standard is used for all calibrations. The analyses are made by standard analytical procedures. If an element of interest is not included on any cassette, the instrument can be operated in a single-element sequential mode.

Typically, three replicates of each analyte are obtained with the error in the measurement being the root mean square deviation. Of course, the limit of detection of each element depends on such variables as sample composition, but representative detection limits range from 1 to 100 ppb for elements determined.

4. Gas Chromatography-Mass Spectroscopy (GC-MS). The GC-MS method discussed in the next section was used to characterize organic constituents of the aqueous leachates.

[illegible]. Oils

1. Chemicals. Reference compounds were obtained from commercial sources and were purified as required. Solvents used in the extraction study were obtained from two sources. Cyclohexane, tetrahydrofuran, methylene chloride, methanol, hexane and acetonitrile were obtained from Burdick and Jackson (distilled in glass). All other solvents were Eastman White Label grade, except ethanol, which was 200 proof (U.S. Industrial Chemicals Co., New York). The dimethyl sulfoxide was Aldrich gold label and was dried over Linde 4A molecular sieves before use. Reagent grade [illegible] isobutane, helium and nitrogen were dried by passage through Linde 13X molecular sieves before use.

The Paraho crude shale oil (Paraho [illegible]) is a composite sample of an [illegible] barrel demonstration run from the Development Engineering Inc. pilot plant facility operated at Anvil Points near Rifle, Colorado. The sample was obtained from the EPA/DOE Fossil Fuel Repository at Oak Ridge National Laboratory (ORNL). The Estonian raw and spent shales were also obtained from the ORNL Repository.

The Estonian raw shale was retorted using the modified Fischer assay[1], and the oil produced from that retorting is designated as Estonian Fischer oil in this paper.

2. Equipment. The GC-MS used for identification and quantitation was a Hewlett-Packard model [illegible] GC-MS. Simulated distillations on normal

alkane distributions of the oils were made on a Hewlett Packard 5710A gas chromatograph equipped with flame ionization detectors.

3. Compound Identification. The GC-MS was operated in the electron ionization mode. A 30 m. x 0.25 mm WCOT fused silica column coated with SP-54 (J & W Scientific, Grade AA) was interfaced to the mass spectrometer by insertion through graphite ferrules in the GC oven compartment into the ion source. The fused silica column vented directly into the ion source for maximum sensitivity. The mass spectrometer was controlled to scan from 25 amu to 350 amu in 0.8 sec. The gas chromatograph was temperature programmed from 30° C to 270° C at 4° C/min. Column inlet pressure was maintained at 17.5 psi, which gave a column linear flow velocity of 21.6 cm/sec, measured by the retention time of argon.

Spectra were collected, corrected for background by computer subtraction of adjacent spectra. Initial compound identifications were verified by comparison of the unknown spectrum to reference spectra in either the EPA NIH mass spectra library, or the Aldermaston mass spectral library. Retention times for some compounds were converted to Kovats indices which were compared to published compilations of Kovats indices. In some cases, authentic compounds were added to the sample, and the sample run for verification of identification.

4. Compound Quantitation. Using the GC-MS conditions described above, it was possible to use isobutane chemical ionization, coupled with selected ion monitoring and standard additions of authentic compounds to quantitate selected compounds. The details of the method may be found elsewhere[2].

5. Organic Extraction Procedure. A [illegible] sample of the material passing a [illegible] mesh screen was weighed into a [illegible] mL screw top vial. Twenty-five mL of the appropriate solvent was added, the vial sealed, and the contents placed in an ultrasonic water bath for [illegible] h. The slurry was allowed to settle for [illegible] h, and was then filtered through a [illegible] Millipore filter. Ten mL of the filtrate was pipetted into a tared beaker, and allowed to evaporate at room temperature. The evaporation was considered complete when constant weight was achieved. The residue was computed by difference and used to calculate the percent of the raw shale extracted.

## III. RESULTS AND DISCUSSION

### A. Analytical and Physical Characterization of Solids

1. **Neutron Activation Analysis.** Analytical results for solid samples of raw and spent Estonian shale, a typical Green River formation raw shale, Paraho spent shale*, Tosco spent shale* and Occidental spent shale* are listed in Table I. Elemental abundances in the raw shales indicate some major differences in the Estonian shale compared to the Green River shale. These differences appear to be correlated with differences in mineralogy (to be discussed) of the materials, that is ultimately traceable to differences in the depositional environment of the sediments.

Examination of the major elements indicates lesser amounts of aluminum, magnesium, and sodium in the Estonian shale compared to the Green River shale, while there are comparable amounts of calcium and iron. These results are consistent with the mineralogy to be discussed. In addition to the smaller quantity of magnesium, the Estonian shale contains no detectable quantities of the alkaline earths, barium and strontium, in contrast to the Green River shale which contains approximately 800 μg/g of these elements. Other elemental deficiencies in Estonian shale compared to Green River shale occur for arsenic, cobalt, rare earth elements, uranium, vanadium, and zinc. The only elements with increased abundances compared to Green River shale are the halogens, chlorine and bromine, indicating the marine nature of the depositional environment.

From these data, a measure of the effect of processing on the elemental abundances in the spent shale compared to the raw shale can be determined by examining the ratio of the abundance of an element in the spent material to the abundance of that element in the raw material,

$$R = \frac{\mu g/g\ \text{Spent}}{\mu g/g\ \text{Raw}}$$

This parameter is an indication of the weight loss of the shale due to retorting, and is associated with the organic extraction and carbonate decomposition. The average R value for all elements determined by neutron activation analysis was 1.[illegible] for Estonian shale, 1.20 for Paraho shale, and 1.[illegible] for Occidental shale processed by vertical modified *in situ* retorting

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*Paraho and Tosco processes are above ground retorting processes, while Occidental Oil Shale Inc. process is a vertical modified *in situ* method.

(VMIS). It is difficult to determine whether the similarity in R values for Estonian and Occidental materials are a consequence of retorting process similarities or the larger weight percent of organic material in the Estonian shale.

2. Infrared Spectroscopy. The major infrared absorption peaks are listed in Table II. The infrared spectra of the Estonian raw shale and Paraho raw shale exhibit similarities expected of two carbonate matrices. Both spectra contain C-H stretching frequencies indicating the oil bearing nature of the solids. In addition, both spectra contain peaks that can be assigned as C-O stretching and bending modes. Both spectra also exhibit a broad peak centered around 1000 $cm^{-1}$ that is assigned as Si-O stretching frequency, due to the variety of silica containing minerals in both types of shales.

Comparison of the Paraho raw shale spectrum with the Paraho spent shale spectrum indicates that major disruption of the carbonate matrix did not occur for this sample as a result of Paraho direct mode retorting. On the basis of Laboratory work accomplished with Green River shales(8,9), studying carbonate decomposition reactions, temperatures in excess of 600° C were not experienced by this sample. Frequency shifts for C-O vibrational modes were not noted and intensity changes were minimal. Infrared spectra of Estonian raw and spent shale, however, exhibit obvious differences suggesting major alteration of the original mineral matrix. The C-O stretching frequencies have decreased in intensities but have not disappeared completely. The region of the Si-O stretching frequencies has broadened, suggesting more variation in the minerals containing this moiety. The Estonian spent shale also has a very large, broad peak in the O-H stretching region indicating rehydration of minerals after processing. These data correlate with x-ray diffraction information to be discussed.

3. X-Ray Diffraction Studies. X-ray diffraction data has been obtained for the Estonian raw and spent shale and can be compared with the average mineral composition of shale from the Green River formation. Table III lists the major and minor phases identified in Estonian raw and spent shales and the average composition of Green River shale. Comparison of the raw shales indicates that there are substantial differences in the individual minerals present, although the major rock matrix in both cases is carbonate based. The Estonian shale mineral matrix is essentially

calcite with $\alpha$-quartz being the next predominant mineral. In contrast, the Green River shale is predominantly the mineral carbonate dolomite, with lesser amounts of calcite, although the relative amounts are variable throughout the resource. After the carbonate minerals, the next most abundant mineral in Green River shales is $\alpha$-quartz. A rough estimate of the relative abundance of this mineral in the Green River shale compared to the Estonian raw shale can be made by peak height comparisons of the $\alpha$-quartz (101) reflection. Based on experience in this laboratory there is two to three times as much $\alpha$-quartz in Green River shales compared to the Estonian shale that has been examined. In addition to these major mineral phases, both shales have minor amounts of clay minerals, feldspars and other silicates, and pyrite. The major specific differences are greater quantities of feldspathic minerals in the Green River shale compared to the Estonian shale, including the absence of sodium feldspars in the Estonian material. There also appears to be a greater quantity of clay minerals in the Green River shale compared to the Estonian shale.

The composition of the Estonian spent shale provides insight into the processing conditions experienced by this material. The mineral content of this material suggests retorting temperatures that are higher than optimum temperatures for surface retorts (Paraho, Tosco, Lurgi) used in the United States. Major disruption of the original mineral matrix is indicated. The occurrence of portlandite as the major phase, the appearance of minor amounts of akermanite/gehlenite and diopside/augite solid solutions, and the relative disappearance of calcite and quartz indicate retorting conditions that resemble Occidental Oil Shale, Inc. modified *in situ* (MIS) process. In Green River shales processed by MIS technology, calcite decomposition occurs above 1075 K along with a competing reaction(4,9). It has also been recognized that calcite reacts with $\alpha$-quartz to form calcium silicates or, perhaps with feldspars, to form calcium aluminum silicates (akermanite/gehlenite or diopside/augite solid solutions). It is apparent that the disappearance of minerals during processing can be accomplished through a variety of reaction pathways, which are determined by process variables such as maximum temperature, time at maximum temperature, heating rate (kinetics of solid state reactions), and retort atmosphere.

Within the context of the potential solid state decomposition and silication reactions, the mineral composition of the Estonian spent shale is consistent with the mineralogy of the raw material. The mineral portlandite, $Ca(OH)_2$, is probably the result of weathering or leaching of lime, CaO. The CaO is the product of $CaCO_3$ decomposition. The calcite could be a survivor of the retorting process or a regeneration product also resulting from the weathering of lime. The minor phases, akermanite/gehlenite and diopside/augite solid solutions, indicate that some of the calcite and α-quartz have reacted to form silicates. This definitely suggests temperatures in excess of 1110 K for the retorting of this material. The mineral ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$, was the only identified sulfur containing mineral in the Estonian spent material. This is in contrast to surface and in situ spent shales from processing of Green River shale where anhydrite and gypsum, $CaSO_4$ and $CaSO_4 \cdot 2H_2O$ respectively, are the major sulfur minerals. The predominance of the more complicated calcium aluminum sulfate hydroxide hydrate may also be a consequence of weathering or leaching processes. Because historical documentation of the studied material was not available, suggestions regarding the occurrence of minerals in the Estonian spent shale are speculative.

4. Scanning Electron Microscopy/Energy Dispersive Spectrometry. Unretorted shale samples from the Mahogany zone retrieved from Garfield County, CO, were examined by SEM-EDS. Low magnification scans of specimens indicated silicon and calcium as the most common elements present. Aluminum, magnesium, potassium, and iron were also fairly abundant, and sodium and sulfur were present in most specimens. The sodium was probably present to a greater degree than indicated because its detection efficiency is poor. The sulfur detected in low magnification scans was probably from its presence in the [illegible] of [illegible] and sulfur as the most prominent element. The only trace material found in all the specimens contained iron and sulfur ($FeS_2$). Generally the $FeS_2$ existed as small particles within a mineral matrix, but some massive nodules were located. The next most common trace material found, although much less common than $FeS_2$, was Ti, probably as rutile. A few small particles of Cu, Fe and S (chalcopyrite?), Zn and S (sphalerite?), and rare earth phosphates (monazite?) were found. Figure [illegible] shows an area of a sample with major mineral phases and three areas (1, 2, and 3) of minor trace element residence. The intimacy of the major mineral phases on the micron level is

illustrated in this photomicrograph. Relative amounts of trace elements in regions 1, 2, and 3 are indicated by x-ray intensities from EDS. Figure 2 shows the identities of the major minerals in the matrix surrounding some kerogen material. No elevated trace element concentrations were noted in this area.

The Estonian raw shale sample that was examined has a much higher kerogen content than most Green River shales and this fact was obvious during SEM scans. The Green River raw shale is essentially a rock matrix with small pockets of organic material interspersed. On the other hand, the Estonian raw shale on the microscopic level appears to be organic material with mineral matter dispersed throughout. The low magnification scans, an example is given in Figure 3, indicated that calcium, silicon, aluminum, and potassium are the most abundant elements. No sodium was detected in these scans. The sulfur detected in the low magnification scans was undoubtedly due to kerogen. The dark areas in Figure 3 are kerogen and are much more abundant than in Green River shales (e.g. Fig. 1). Trace materials found generally contained Fe and S ($FeS_2$), and usually occurred as small nodules. Very small areas of dolomite, always associated with the calcite, were detected. Figure 4 identifies some typical areas of a 1000 x magnification scan and the abundance of kerogen is again evident. Figure 5 is a photomicrograph of an area abundant with kerogen, but with very thin, wispy looking, areas of mineral matter separating the kerogen areas. The EDS analysis of these areas gives elemental abundances that suggest that thin threads of clay minerals are interwoven through the organic material. Further work is in progress to substantiate this observation as a general phenomenon.

In general, the SEM-EDS information corroborates the mineralogic data. From these data, it is obvious that there are important differences in the mineral composition of these shales, probably indicative of different depositional environments. There are also differences on the microscopic level that arise mainly due to the wide variation in kerogen content of these raw shales. The minerals in the Green River shale enjoy intimate contact as the major part of the shale matrix, while the minerals in the Estonian shale are widely dispersed through the organic matter. These differences on the microscopic level impact the extent of solid state reactions which occur during processing. The more intimate mineral matrix associated with the Green River shale should favor solid state reactions in addition to carbonate decomposition reactions, compared to the Estonian shale where solid state reactions would be more difficult.

### B. Leachate Characterization

1. Inorganics. Analytical results for Estonian raw and spent shales and Paraho raw and spent shales are listed in Table IV. Comparison of leachates generated from Estonian raw and Paraho raw shale indicate little difference in specific conductance and pH values. The major difference in elemental analysis is that the major cation in the Estonian leachate is calcium, while the major cation from the Paraho shale is sodium. The difference reflects the lack of sodium minerals in the Estonian shale compared to the Paraho shale. The high inorganic carbon content of the Paraho leachate suggests that this leachate is essentially a sodium carbonate/bicarbonate solution. Other differences in raw shale leachates are exhibited in several trace element concentrations. Boron and molybdenum solubilities are greater from the Paraho raw shale compared to the Estonian raw shale. Most other major and trace element concentrations are comparable for the two raw shale leachates.

Examination of the spent shale leachate compositions suggests differences in processing conditions that correlate with the mineralogy of the shales. The higher conductivity of the Estonian spent shale leachate compared to the Paraho spent shale leachate indicates probable greater disruption of the mineral matrix during retorting for Estonian shale. The extent of carbonate decomposition is also suggested by calcium ion concentrations, which are much higher in the Estonian spent shale leachate. Processing of both spent shales appears to have had very little effect on the other major or minor cations. For example, boron and molybdenum concentrations were relatively unaffected in the Paraho materials. The only exception is the lead concentration which increases in the Estonian spent shale leachate compared to the raw shale leachate. Because of the health and environmental water quality effects associated with lead mobility, this concentration is undesirably high. However, from the leachate composition this is the only potential water quality environmental impact indicated for the Estonian materials.

2. Organics. Gas chromatography mass spectrometry was applied to the leach waters to identify the major organic components present. The organic

material was concentrated by passage through a reverse phase chromatography column. The column (C18 Sep-pak, Waters Associates, Milford, Mass.) was eluted with 2 mL of ethyl acetate, and the ethyl acetate concentrated by evaporation to 50 μL. Five microliters of the concentrate were used for the identification. The compounds identified in the leachates are shown in Table V.

Phenolic compounds are the predominant species in both the Estonian raw and spent leachates. The spent shale leachate contains more phenolic compounds than the raw shale leachate. Most compounds are present at the 10 to 50 parts per billion (ppb) level, the exceptions being phenol, 5-methylresorcinol and resorcinol which are present in the 500-1000 ppb range. These waters are characterized by very few nitrogen or sulfur containing organic compounds.

By comparison, the organic portion of the Green River spent shale leachate is predominately aliphatic acid compounds from acetic acid through hexanoic acid. Phenolic compounds are of little consequence in this leachate. Nitrogen containing compounds are the second most important class of compounds, with the amides having nearly as high a concentration as the carboxylic acids. Aliphatic hydrocarbons are the third most concentrated class of compounds followed by alkyl substituted pyridines. Both of these classes of compounds are of low concentration in the Estonian leachates. The differences between organic components of the leach waters of the Estonian and Green River shales appear to reflect a basic difference in the organic structure of the kerogen involved, and do not appear to reflect differences in retorting procedures. Further work is required to verify this assumption.

### C. Oils

1. Qualitative Characterization. Experience has shown that extraction of raw shale with various organic solvents can show differences in kerogen structure between the shales[5]. A suite of fifteen organic solvents were used to extract both Estonia and Green River raw shales. The results of that extraction are given in Table VI. The primary difference between the shales is the inability to solvent extract any significant portion of the Estonian shale, as compared to the Green River shale.

Fischer assays of the two oils shows the Green River shale to have an oil yield of 26 gallons per ton compared to 93 gallons per ton for the

Estonian shale. This means that the Green River shale contains about 9 weight percent retortable kerogen, and the Estonian about 32%. The maximum weight percent of the Green River extracted by tetrahydrofuran (THF) is 5.4% or 60% of the kerogen present, assuming no inorganic species were soluble. The Estonian shale, on the other hand, is only 3.8% soluble, or about 12% of the kerogen is soluble in THF. This would seem to indicate a different form of both kerogen structure and kerogen bonding between the two shales.

This hypothesis is further supported by specific compounds derived from the shales as discussed below, and the observations of different relative orders of organic solubility for the two shales. If the solubilities of the shales in the various solvents are ranked from highest weight percent soluble to lowest weight percent soluble, the changes in solubility as a function of shale become more apparent. For example, acetone is a relatively good solvent for Green River shale, ranking fourth, while for the Estonian shale it ranks thirteenth. The identification of specific compounds extracted by each solvent is yet to be completed.

The oils obtained from Fischer assay of raw shale are generally recognized as not typical of process derived oil[1], but are reasonable approximations of oil obtained from direct mode retort processes such as the Paraho or Kiviter processes. Several different characterization procedures were applied to the oils, including elemental analysis for carbon, hydrogen, and nitrogen (Table VII), fingerprinting by glass capillary gas chromatography (GC) (Fig. 6), determination of normal alkane distribution (Figs. 7,8), and GC simulated distillation (Fig. 9).

The elemental analysis for C, H, and N are a characteristic of oils useful for many engineering process computations as well as basic chemical information. The two oils are quite different in carbon/hydrogen ratios. The dry Estonian Fischer oil has a C/H ratio of 8.6, while the Paraho 601 oil is 7.6. This difference in C/H ratios is probably due to differences in degree of saturation, as evidenced by the normal alkane distributions and the specific compound concentrations discussed below.

The glass capillary GC chromatograms for the two oils shown in Figure 6 graphically illustrates the differences between the two oils. The n-alkanes in the Paraho sample are distributed throughout the scan while those in the Estonian are concentrated in the lower boiling portions of the chromatogram. The peak at ∼ 21 minutes in both scans is an artifact (t-butylphthalate) from the solvent. Both oils are at nearly the same concentration so that peak height is a measure of relative concentration in these samples. It is apparent that the Paraho oil is a higher boiling oil and contains a greater concentration of high molecular weight n-alkanes as compared to the Estonian oil. This difference is reflected in the n-alkane distributions (Figs. 7 & 8) and the simulated distillation curves[6] (Fig. 9) for the two oils.

2. Quantitation of Specific Organic Compounds. Tables VIII and IX contain concentrations of selected compounds in the two oils. These compounds have been determined in a number of oils, and are not intended to be inclusive, but rather indicative of selected compound classes.

There is little difference between the two oils for the PAH's and the nitrogen heterocyclic compounds determined. In general, the concentrations in the Estonian Fischer oil are slightly higher than for the same compounds in the Paraho oil. The major difference is to be found in the phenolic compounds, which are major constituents for the Estonian oil, and minor in the Paraho oil. The preponderance of phenolic compounds found may account for the greater degree of unsaturation found for the Estonian oil.

It is difficult to infer structural differences in kerogen from analysis of the derived oil, but it would seem likely that the kerogen in the Estonian shale contains a large amount of oxygen bridges. Further characterization of the oils is necessary to verify this hypothesis.

## IV. SUMMARY

Although only a single Estonian raw shale sample with an unknown history has been examined, physical and chemical characterization of this material has been accomplished. A comparison with a representative Green River formation raw shale has been made. The results suggest the following:

- Elemental analysis indicates that the major elements, aluminum, magnesium, and sodium are deficient in Estonian shale compared to Green River shale. The minor elements, barium and strontium, and the trace elements, arsenic, cobalt, rare earths, uranium, vanadium, and zinc are also deficient in the Estonian shale compared to the Green River shale.

- Green River shales contain greater quantities of clay minerals (mainly illite) compared to the Estonian shale. Illite is a suspected residence of many of the environmentally sensitive trace elements such as fluorine[7], boron[8], and vanadium[9].

- X-ray diffraction data suggests that $\alpha$-quartz concentration in the Estonian material is two to three times less than in typical Green River shales.

- The suite of minerals in the Estonian spent shale suggests extreme processing conditions. Major disruption of the mineral matrix (carbonate decomposition) and solid state reactions (silication reactions) require temperatures in excess of 1100 K.

- The presence of portlandite and ettringite in the Estonian spent shale indicates rehydration of mineral phases from leaching or weathering. This probably impacts the results of aqueous leaching experiments.

- SEM-EDS results indicate the intimate contact of the minerals on the micron level in the Green River shales. Mineral grains in the Estonian shale are dispersed throughout the organic material. This is reflected in the relative lack of silication products (akermanite/gehlenite and diopside/augite solid solutions) and predominance of carbonate decomposition products in the Estonian spent material. Solid state mineral reactions are probably difficult in the Estonian matrix.

- Aqueous leaching experiments indicate lead mobility from the Estonian spent material result in concentrations that are unacceptably high. This behavior has been recognized in other shales where major disruption of the mineral matrix has occurred. This could be a consequence of carbonate decomposition ($PbCO_3$ naturally occurs with alkaline earth carbonates) and the lack of silication reactions which would tend to immobilize the lead. The elucidation of this result is being pursued.

- Phenolic compounds, specifically phenol, resorcinol and 5-methylresorcinol, are the most concentrated organic species present in the aqueous Estonian leachates. By comparison, carboxylic acids from acetic acid through caproic acid are the most concentrated species in the Green River leachates.

- Concentrations of individual organic compounds are generally in the range [illegible] ppb for the aqueous leachates of either shale.

- The Estonian raw shale sample has a Fischer assay of [illegible] barrels per ton, and the Green River an assay of [illegible] barrels per ton.

- Organic solvent extraction of the raw shales with [illegible] different solvents show that approximately [illegible] of the kerogen in the Green River shale is extractable and only [illegible] of the Estonian shale is extracted under the same conditions.

- Carbon/hydrogen ratios for the two oils suggests the Estonian Fischer oil to be more unsaturated than the Paraho oil.

- Normal alkane distributions for the two oils show that the Paraho oil contains relatively more n-alkanes than the Estonian Fischer oil. These n-alkanes in the Paraho oil are distributed over a wider number of carbon atoms.

- Simulated distillation curves clearly show that the Estonian oil is a much lower boiling oil than the paraho oil.

- The concentrations of 54 selected compounds in the two oils are similiar except for the phenolic compounds. In the Estonian oil, phenols are major constitutents, while they are minor in the Paraho oil.

- The concentrations of 16 selected PAH's are similiar in the two oils, with the exception of benzo[a]pyrene, which is over 10 times more concentrated in the Estonian oil.

# TABLE I

## Major, Minor, and Trace Elemental Abundances (µg/g) for Estonian and Green River Raw and Spent Shale Solids[a]

| SAMPLE | SHALES<br>Estonian Raw | Estonian Spent | Green River Raw | Paraho Spent | Tosco Spent | Occidental Spent |
|---|---|---|---|---|---|---|
| Al | 1694 | 2069 | 39450 | 451.0 | [illegible] | [illegible] |
| Sb | .31 | .37 | 2.44 | 2.06 | 2.7 | [illegible] |
| As | 4.2 | 11.0 | 42.65 | 41.4 | 66.9 | 31.9 |
| Ba | <156 | <188 | .042 | 7949 | <155 | 658 |
| Br | 117 | 158 | <.7 | <1.0 | 2.3 | <4.5 |
| Ca | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | 161800 |
| Ce | [illegible] | 29.4 | 3.5 | 4.0 | 39.8 | 59 |
| Cs | 1.9 | 2.5 | 4.5 | 2.9 | 4.8 | [illegible] |
| Cl | [illegible] | 1644 | <113.6 | <124 | 62.8 | <120 |
| Cr | [illegible] | 29.4 | 35.75 | 47.5 | [illegible] | 55 |
| Co | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Cu | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | <310 |
| Dy | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Eu | [illegible] | .44 | .7 | .77 | .61 | [illegible] |
| Ga | [illegible] | [illegible] | <12.6 | <13.8 | [illegible] | <40 |
| Au | [illegible] | [illegible] | <.0006 | [illegible] | $<1.4\times10^{-5}$ | - |
| Hf | 1.3 | 1.5 | 1.7 | 2.1 | 1.5 | [illegible] |
| I | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Fe | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| La | [illegible] | [illegible] | [illegible] | 24.8 | 4.4 | [illegible] |
| Lu | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Mg | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Mn | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Hg | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| K | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Rb | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Sm | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Sc | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Se | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Ag | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | - |
| Na | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Sr | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Ta | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Tb | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Th | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Ti | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| W | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| U | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| V | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Yb | [illegible] | [illegible] | 1.1 | [illegible] | 1.1 | [illegible] |
| Zn | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |

[a] All values are in µg/g.

# TABLE II

## Infrared Absorption Peaks for Raw and Spent Shales (in cm$^{-1}$)[a]

| Estonian Raw | Estonian Spent | Paraho Raw | Paraho Spent |
|---|---|---|---|
| | 3620 sh | | |
| 3300 w,br | 3300 vs, br | 3300 vw | |
| 2900 sh | | 2920 m | |
| 2840 m | | 2850 w | |
| | | 2500 w | |
| [illegible] w, br | 1600 sh | 1800 w | |
| [illegible] s, br | 1400 m | 1430 s, br | 1400 s, br |
| [illegible] s | 1000 s, br | 1070 s, br | 1050 s, br |
| 865 w | | 870 s | 870 m |
| 760 w | | 770 w | 770 w |
| 705 w | | 725 m | 720 w |
| | | 640 w | 640 sh |
| | | 580 m | 570 w |

---

[a] Legend: s = strong, m = moderate, w = weak, vw = very weak, sh = shoulder, br = broad.

## TABLE III
## X-Ray Diffraction Results for Estonian Shale Samples

| Estonian[a]<br>Raw | Estonian<br>Spent | Green River[b]<br>Raw |
|---|---|---|
| Calcite(s) | Portlandite(s) | Dolomite (32) |
| $\alpha$-Quartz(m) | Calcite(w-m) | Calcite (16) |
| Microcline(w) | $\alpha$-Quartz(w) | Quartz (15) |
| Pyrite(vw) | Gehlenite/Akermanite(w) | Illite (19) |
| Mica(vw) | Ettringite(w-m) | Albite (10) |
| Unidentified(t-vw) | Diopside-Augite(vw) | K feldspar (6) |
|  | Unidentified(vw) | Pyrite (1) |
|  |  | Analcime (1) |

---

[a] legend (relative phase content): s = major, m = moderate, w = minor, vw = very minor, t = trace.

[b] Numbers in parentheses indicate average weight percent composition.

# TABLE IV
## Analytical Results for Leachates Generated by Raw and Spent Shales

| | Estonian Raw | Estonian Raw | Paraho Raw | Paraho Spent |
|---|---|---|---|---|
| Spec. Cond. | 1,000 | 10,000 | 1450 | 3750 |
| pH | 8.69 | 12.62 | 8.86 | 11.97 |
| | | | | |
| Inorg. C. | 2 | 1 | 114 | 1 |
| Org. C. | 10 | 53 | 50 | 12 |
| | | | | |
| Al | 0.163 | 0.577 | 0.510 | 0.233 |
| Ba | 0.045 | 0.770 | 0.514 | 0.368 |
| B | 0.47 | 0.04 | 1.37 | 0.93 |
| Cd | <0.015 | <0.015 | <0.024 | <0.012 |
| Ca | 250 | 1678 | 19.3 | 370 |
| Co | 0.04 | 0.05 | <0.012 | 0.022 |
| Cu | 0.003 | 0.006 | 0.061 | 0.003 |
| Fe | 0.04 | 0.08 | 0.017 | 0.027 |
| Pb | 0.19 | 0.80 | 0.06 | 0.28 |
| Li | 0.312 | 0.857 | 0.178 | 1.04 |
| Mg | 26.1 | 0.324 | 19.5 | 0.125 |
| Mn | <0.006 | 0.011 | 0.011 | 0.010 |
| Mo | 0.044 | 0.168 | 1.60 | 1.24 |
| Ni | <0.024 | <0.024 | <0.02 | <0.02 |
| K | 16.5 | 16.5 | 10.1 | 65.8 |
| Si | 1.77 | 0.37 | 1.90 | 1.87 |
| Sr | 0.78 | 7.62 | 0.700 | 4.54 |
| Na | 3 | 36 | 293 | 180 |
| Ti | 0.009 | 0.012 | 0.002 | 0.005 |
| V | 0.015 | 0.044 | 0.008 | 0.029 |

## Table V
## Organic Compounds Identified in Estonian Leach Waters

### Phenols

Phenol
5-methylresorcinol
resorcinol
catechol
2,5-dimethylresorcinol
4,5-dimethylresorcinol
ethylresorcinol
n-propylresorcinol
m-xylenol
p-xylenol
2-napthol
o-xylenol
1-napthol

### PAH

naphthalene
phenanthrene
anthracene
fluorene

### Amides

acetamide
butamide
propionamide
acrylamide
benzamide

### Acids

caproic acid
propionic acid
lineoleic acid
steric acid
oleic acid
heptanoic acid

### Other Compounds

1-octanol
thiophene
quinoline
1-decanol
isoquinoline
pyridine
m-methylpyridine
o-methylpyridine
carbazole
acridine
p-methylacridine

*Compounds within each class are listed in order of decreasing concentration.

## TABLE VI
## Organic Extraction of Raw Shale

| Solvent | Anvil* Points Raw Shale | Estonian* Raw Shale |
|---|---|---|
| Acetone | 20.46 | 1.14 |
| Acetonitrile | 9.73 | 1.73 |
| Benzene | 20.78 | 2.44 |
| Carbon Disulfide | 42.64 | 9.83 |
| Carbon Tetrachloride | 17.34 | 8.27 |
| Chloroform | 16.84 | 2.62 |
| Cyclohexane | 14.40 | 2.12 |
| Dimethoxymethane | 18.59 | 17.72 |
| Ethyl acetate | 13.16 | 2.91 |
| Ethyl alcohol | 13.92 | 1.14 |
| Hexane | 11.31 | .17 |
| Methanol | 16.18 | 2.94 |
| Methylene chloride | 17.96 | 1.74 |
| Tetrahydrofuran | 54.07 | 37.78 |
| Toluene | 17.28 | 3.14 |

*Results are in parts per thousand total shale extracted.

## TABLE VII

### Elemental Carbon, Hydrogen and Nitrogen Content of Estonian Fisher Assay Oil and Paraho Crude Oil

| | Estonian Fisher | Paraho 601 |
|---|---|---|
| wt.% C | 75.58 | 84.46 |
| wt.% H | 9.22 | 11.15 |
| wt.% N | .44 | 2.21 |

## TABLE VIII
## Polycyclic Aromatic Hydrocarbons in Crude Oils

| Compound | Estonian Fisher | Paraho 601 |
|---|---|---|
| 2-Ring | | |
| Naphthalene | 672 | 397 |
| 3-Ring | | |
| Acenaphthylene | 147 | 693 |
| Anthracene | 986 | 480 |
| Fluorene | 114 | 203 |
| Phenanthrene | 842 | 526 |
| 4-Ring | | |
| Chrysene | 52 | 33 |
| 7,12-Dimethylbenz[*a*]anthracene | 2.7 | 4.7 |
| Fluoranthene | 43 | 57 |
| Naphthacene | 6.8 | 1.2 |
| Pyrene | 177 | 200 |
| 5-Ring | | |
| Benzo[*a*]pyrene | 192 | 13.6 |
| Benzo[*e*]pyrene | 61 | 3.1 |
| Dibenz[*a,h*]anthracene | 1.4 | 1.1 |
| 3-methylcholanthrene | 1.1 | 1.3 |
| Perylene | 68 | 57 |
| 6-Ring | | |
| Benzo[*g,h,i*]perylene | 3.6 | 2.0 |

## TABLE XI

## OTHER COMPOUNDS IN CRUDE OILS

| N-HETEROCYCLE | Estonian Fisher | Paraho 601 |
|---|---|---|
| 1 RING | | |
| pyridine | 132 | 37 |
| 2-methyl pyridine | [illegible] | 35 |
| 3-methyl pyridine | 432 | 23 |
| 4-methyl pyridine | 331 | [illegible] |
| 2,4,6-trimethyl pyridine | 2164 | 1573 |
| 2 RING | | |
| isoquinoline | 2021 | 1321 |
| quinoline | 3931 | 2714 |
| 3 RING | | |
| acridine | 214 | 3.6 |
| 4-azafluorene | 132 | 37 |
| benzo(f)quinoline | 147 | 27.8 |
| benzo(h)quinoline | 111 | 36.3 |
| carbazole | 35 | 14.7 |
| phenanthridine | 82 | 622 |
| 4 RING | | |
| 1-azapyrene | 1.6 | 0.5 |
| S-HETEROCYCLE | | |
| benzo(b)thiophene | 414 | 513 |
| 2-methylthiophene | 922 | [illegible] |
| 2-methyl-5-ethylthiophene | 877 | [illegible] |
| thiophene | 9148 | 217 |

| PHENOLS | Estonian Fisher | Paraho [illegible] |
|---|---|---|
| m-cresol | [illegible] | [illegible] |
| o-cresol | [illegible] | [illegible] |
| p-cresol | [illegible] | [illegible] |
| m-ethylphenol | [illegible] | [illegible] |
| o-ethylphenol | [illegible] | [illegible] |
| p-ethylphenol | [illegible] | [illegible] |
| 1-naphthol | [illegible] | [illegible] |
| 2-naphthol | [illegible] | [illegible] |
| phenol | [illegible] | [illegible] |
| resorcinol | [illegible] | [illegible] |
| catechol | [illegible] | [illegible] |
| OTHER HYDROCARBONS | | |
| biphenyl | [illegible] | [illegible] |
| decalin | [illegible] | [illegible] |
| indane | [illegible] | [illegible] |
| indene | [illegible] | [illegible] |
| 1-methylnaphthalene | [illegible] | [illegible] |
| 2-methylnaphthalene | [illegible] | [illegible] |
| tetralin | [illegible] | [illegible] |

## Literature Cited

1. L. Goodfellow, M. T. Atwood, Fischer Assay of Oil Shale: Procedures of the Oil Shale Corporation, presented at 7th Oil Shale Symposium, Colorado School of Mines and American Institute of Mining, Metallurgical and Petroleum Engineers, Golden, Colorado, 1974.

2. C. H. Prien, Survey of Oil-Shale Research in the Last Three Decades, in "Oil Shale," ed. T. F. Yen and G. V. Ghilingarian, Elsevier, New York, 1976.

3. W. D. Spall, Determination of Polycyclic Aromatic Hydrocarbons and other selected Compounds in shale oil and other Materials, Anal. Chem., in press.

4. W. C. Park, A. E. Lindemanis, and G. A. Roah, "Mineral Changes During Oil Shale Retorting," In Situ, 3(4) (1977) pp. 353-381.

5. W. E. Robinson, "Compositional Variations of the Organic Matter in Green River Oil Shale - Colorado No. 1 core," United States Bureau of Mines Report of Investigations, #7492, 1971.

6. American Society for Testing and Materials, Method D2887-73, "Boiling Range Distribution of Petroleum Fractions by Gas Chromatography," 1978.

7. O. M. Saether and D. D. Runnells, "Geochemistry of Fluorine in Oil Shale Leachates," in 13th Oil Shale Symposium Proceedings, J. H. Gary, ed., Golden, CO, (1980) pp. 362-368.

8. E. J. Peterson, unpublished results.

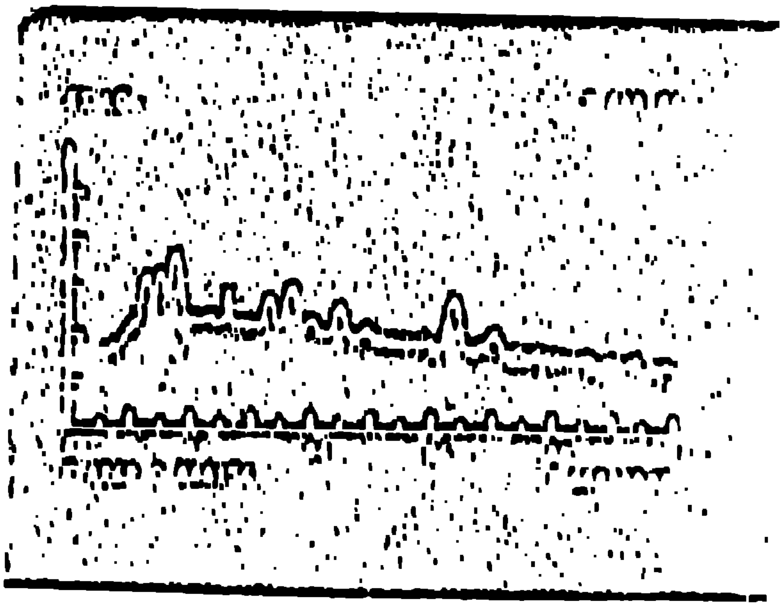
9. J. H. Campbell, "The Kinetics of Decomposition of Colorado Oil Shale: II. Carbonate Minerals," Lawrence Livermore National Laboratory report UCRL-52089 (March 1978).

LEGEND

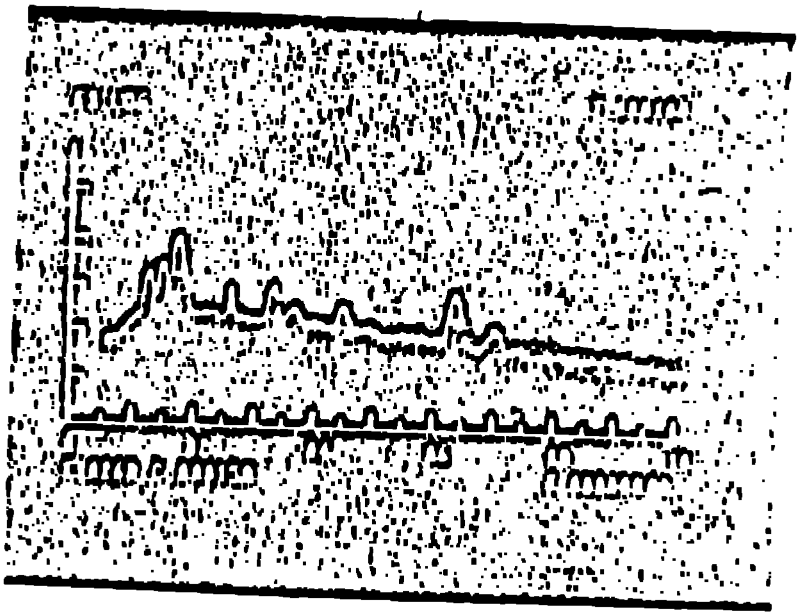
D = Dolomite
C = Calcite
F = Feldspathic
Material
Si = Silica

FIGURE 1. Scanning Electron Micrograph of an Area of Raw Shale Showing Major Mineral Constituents and Trace Element Containing Constituents. Trace Element Analyses of Areas 1,2,and 3 are Given Below (PS2 1, PS2 2, and PS2 3).

```
SAMPLE    :
ID: PS2 1

TIME:    100 SEC

ELEMENT   INTENSITY    BACKGROUND
             CPS           CPS
-------  -----------  ----------
NA          0.0000       16.2161
MG         45.3977       14.1223
[illegible]  [illegible]  [illegible]
[illegible]  [illegible]  [illegible]
[illegible]  [illegible]  [illegible]
[illegible]  [illegible]  [illegible]
[illegible]  [illegible]  [illegible]
[illegible]  [illegible]  [illegible]
[illegible]  [illegible]  [illegible]
[illegible]  [illegible]  [illegible]
[illegible]  [illegible]  [illegible]
[illegible]  [illegible]  [illegible]
[illegible]  [illegible]  [illegible]
[illegible]  [illegible]  [illegible]
[illegible]  [illegible]  [illegible]
[illegible]  [illegible]  [illegible]
```



```
SAMPLE    2
ID: P32 2

TIME:   100 SEC

ELEMENT    INTENSITY     BACKGROUND
              CPS            CPS
-------    ----------    ----------
NA             0.0000       16.5930
MG            39.7989       17.4611
[illegible]                 14.3526
AL            74.2136       17.6164
SI           265.5315       17.7785
P              0.0000       16.1182
[illegible]    0.0000       11.0091
[illegible]    0.0000        9.6776
[illegible]   26.2853        7.3047
CA                           6.6720
TI            10.2830        4.5470
V                            3.8302
FE            23.4422        3.4573
NI             0.0000        2.5531
[illegible]    0.1499        1.6902
[illegible]    0.2499        1.7005
```



```
[illegible]MPLE    3
[illegible]: P32 3

TIME:   100 SEC

ELEMENT    INTENSITY     BACKGROUND
              CPS            CPS
-------    ----------    ----------
[illegible]    0.0000       16.0399
[illegible]   20.7290       16.4307
[illegible]                 13.5334
[illegible]   55.9992       16.7248
[illegible]  161.9104       16.9744
[illegible]  [illegible]    [illegible]
[illegible]    0.0000       11.[illegible]
[illegible]    0.0000       10.6257
[illegible]   17.4121        9.1273
[illegible]   13.5040        9.1[illegible]
[illegible]   99.[illegible]  6.7091
[illegible]                  5.5[illegible]
[illegible]   15.2102        3.4912
[illegible]    0.0000        2.1227
[illegible]    0.2120        2.2879
[illegible]    0.1003        2.1111
```

FIGURE 1 (contd.)

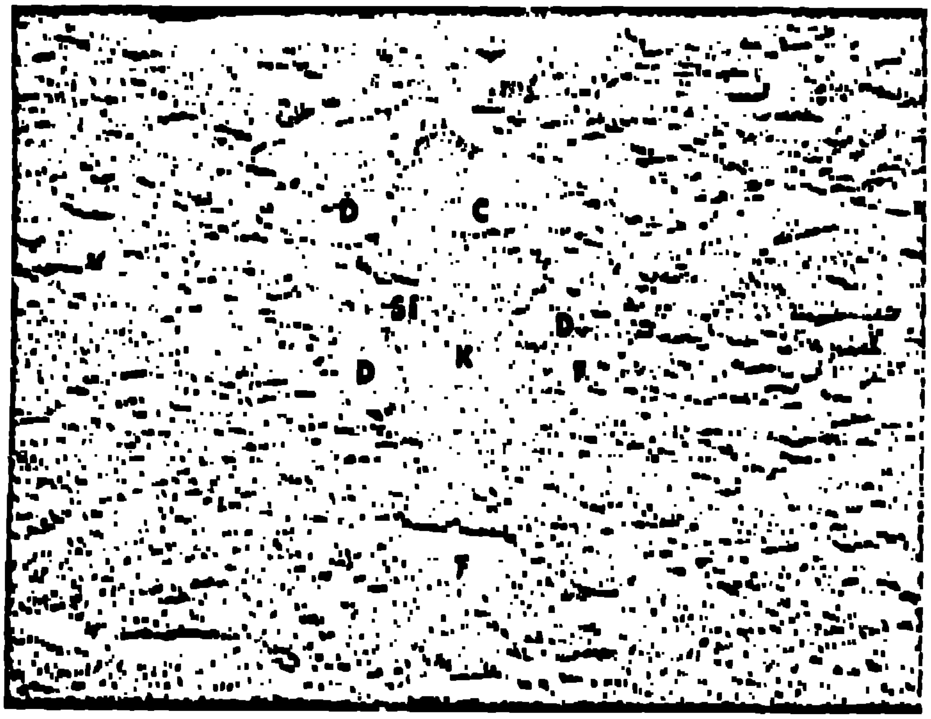


FIGURE 2. Major Mineral Environment in the Vicinity of Kerogen Material. (Legend the same as Fig. 1)

FIGURE 3. Scanning Electron Micrograph of a Typical Area in Estonian Raw Shale Indicating Major Mineral Constituents. Elemental Analysis of the Area Is Given Below

SAMPLE 9
[illegible]

TIME 40 SEC

| ELEMENT | INTENSITY (CPS) | BACKGROUND (CPS) |
|---|---|---|
| [illegible] | 0.0000 | 14.2566 |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |

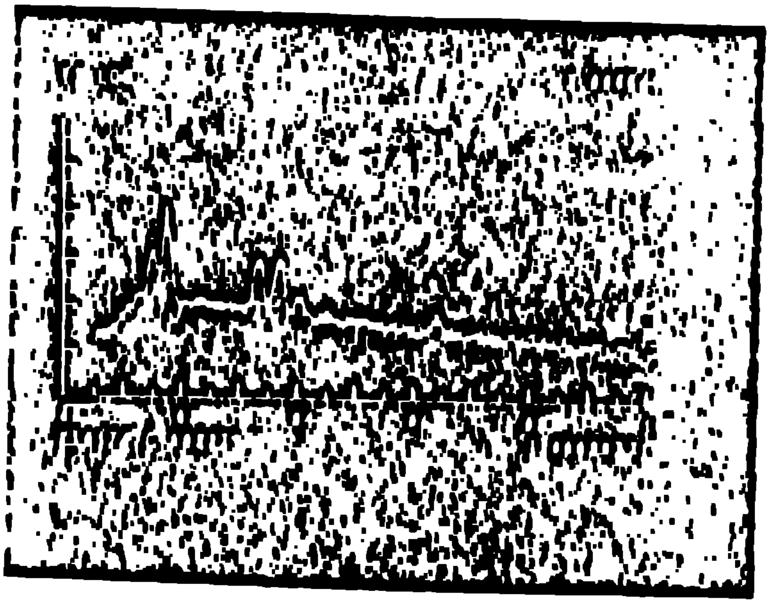
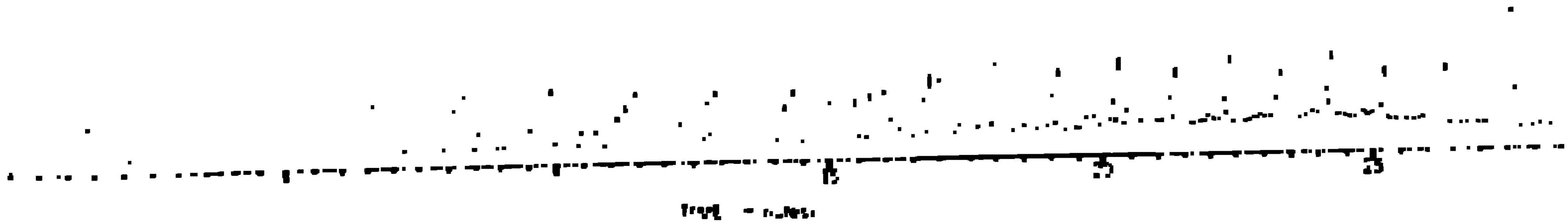


FIGURE 4. Major Mineral Environment in the Vicinity of Kerogen In Estonian Raw Shale. (Legend the same as Fig. 1)

FIGURE 5. Scanning Electron Micrograph of Mineral Feldspar Interweaving Kerogen Material.

# FIGURE 6

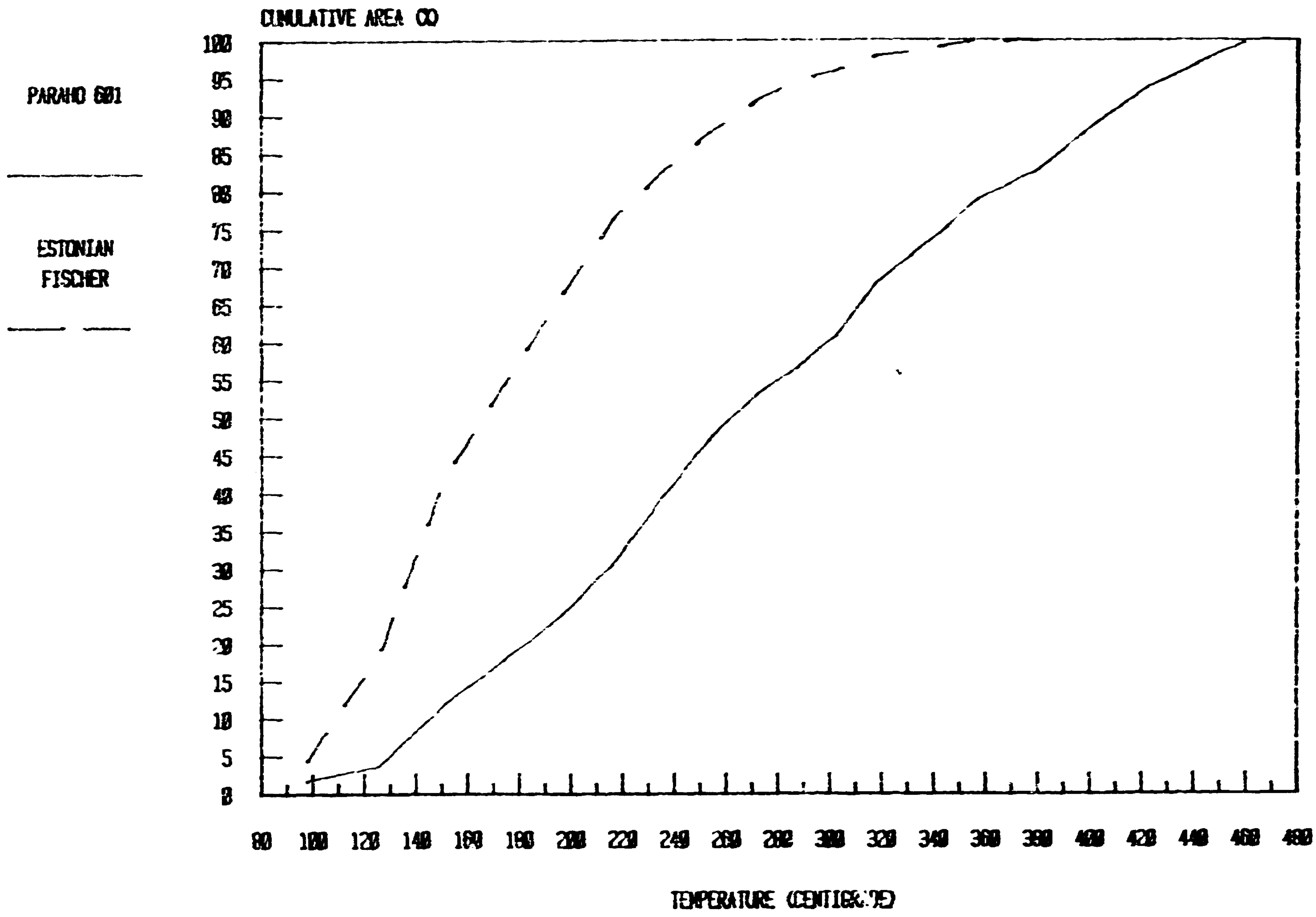
[illegible]



[illegible] FISCHER

FIGURE 9

SIMULATED DISTILLATION CURVES



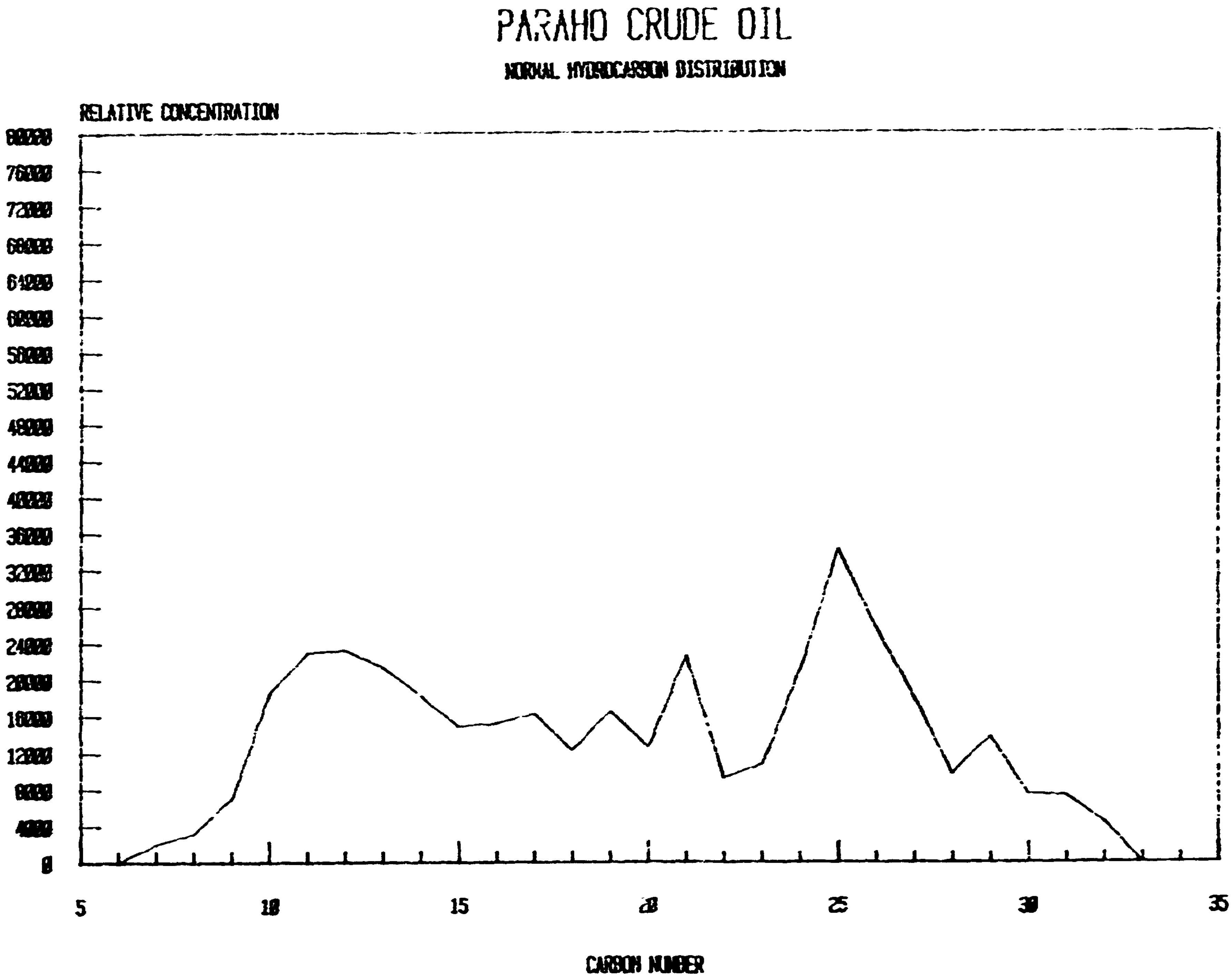

PARAHO CRUDE OIL
NORMAL HYDROCARBON DISTRIBUTION
RELATIVE CONCENTRATION
80000
76000
72000
68000
64000
60000
56000
52000
48000
44000
40000
36000
32000
28000
24000
20000
16000
12000
8000
4000
0
5
10
15
20
25
30
35
CARBON NUMBER

FIGURE 7

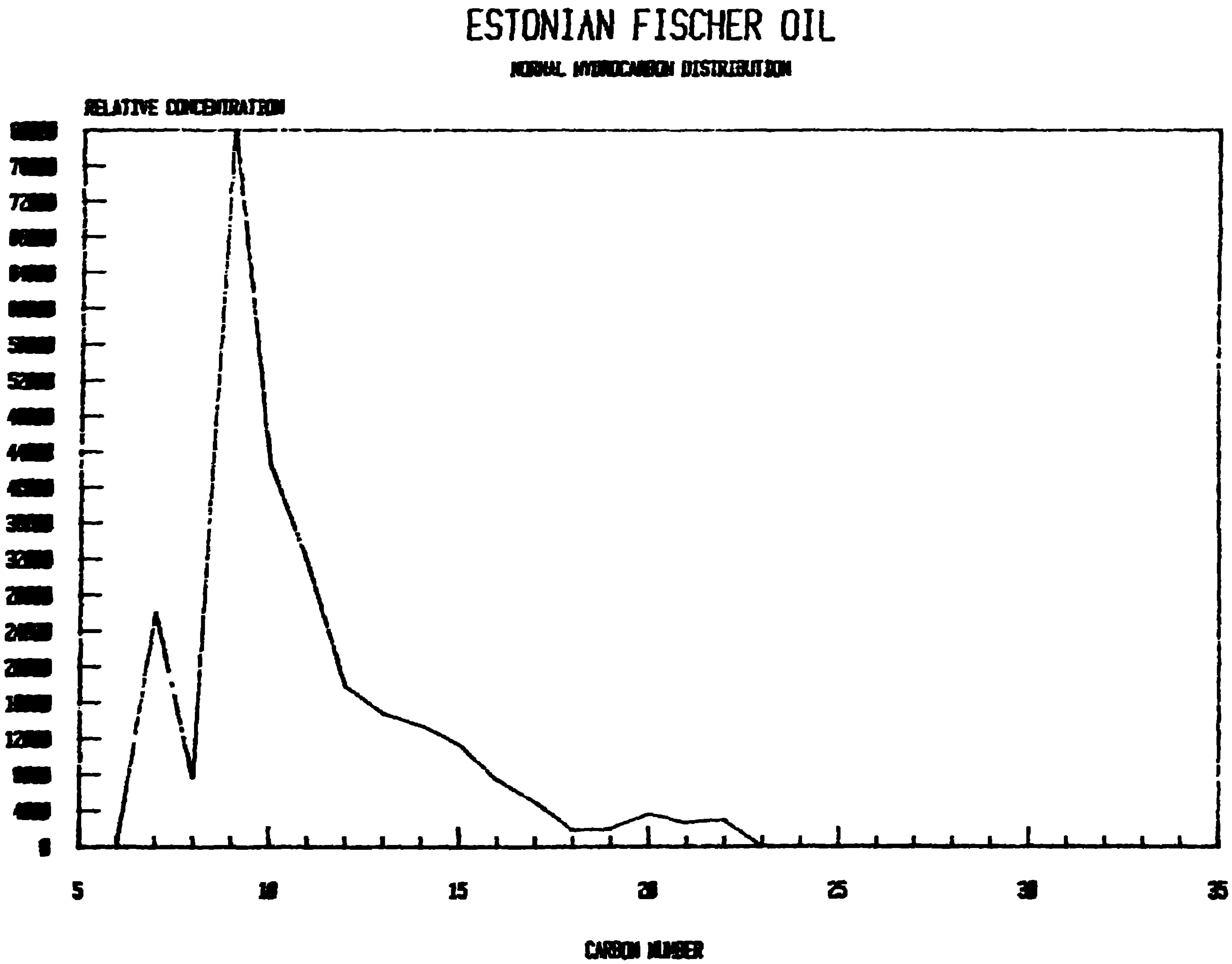

ESTONIAN FISCHER OIL
NORMAL HYDROCARBON DISTRIBUTION
RELATIVE CONCENTRATION
80000
76000
72000
68000
64000
60000
56000
52000
48000
44000
40000
36000
32000
28000
24000
20000
16000
12000
8000
4000
0
5
10
15
20
25
30
35
CARBON NUMBER

FIGURE 8