

RAPID DETERMINATION OF RECOVERABLE OIL IN OIL SHALE BY THERMAL ANALYSIS

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INTRODUCTION

Determination of recoverable oil in Green River oil shale and separation and analysis of bitumen and kerogen components was accomplished with the MP-3 thermal chromatograph. Recoverable oil in Green River oil shale determined with the MP-3 correlated well with Fischer assay results. Chromatographic data confirmed that it is possible to separate bitumen and kerogen thermally.

INSTRUMENTATION

The MP-3 combines both evolved gas analysis and chromatographic techniques in one piece of instrumentation. A thermogram (EGA curve) of the substance was obtained by heating it as a solid or liquid in a programmed manner. The gases evolved generated a curve as a function of temperature as they passed through the detector. A gas chromatogram of the volatiles was obtained by trapping, then backflushing them through a GC column.

A flow diagram of the MP-3 is shown in figure 1. A sample, in the solids chamber, could be heated programmably from 4 to 40°C/min to a maximum of 800°C. Other possible modes were ballistic heating and isothermal controlled heating.

Following the flow path in figure 1, volatiles from the sample chamber pass through valve number 1, valve number 2, the detector, and valve number 3. About half the sample is split to the flame ionization detector (FID). Emerging from the thermal conductivity (TC) detector, the remaining half is trapped in a sampling loop filled with Porapak Q and SE-30 on Chromosorb G. For the typical sample, the trap is backflushed to the GC column and ballistically heated to 250°C in less than one

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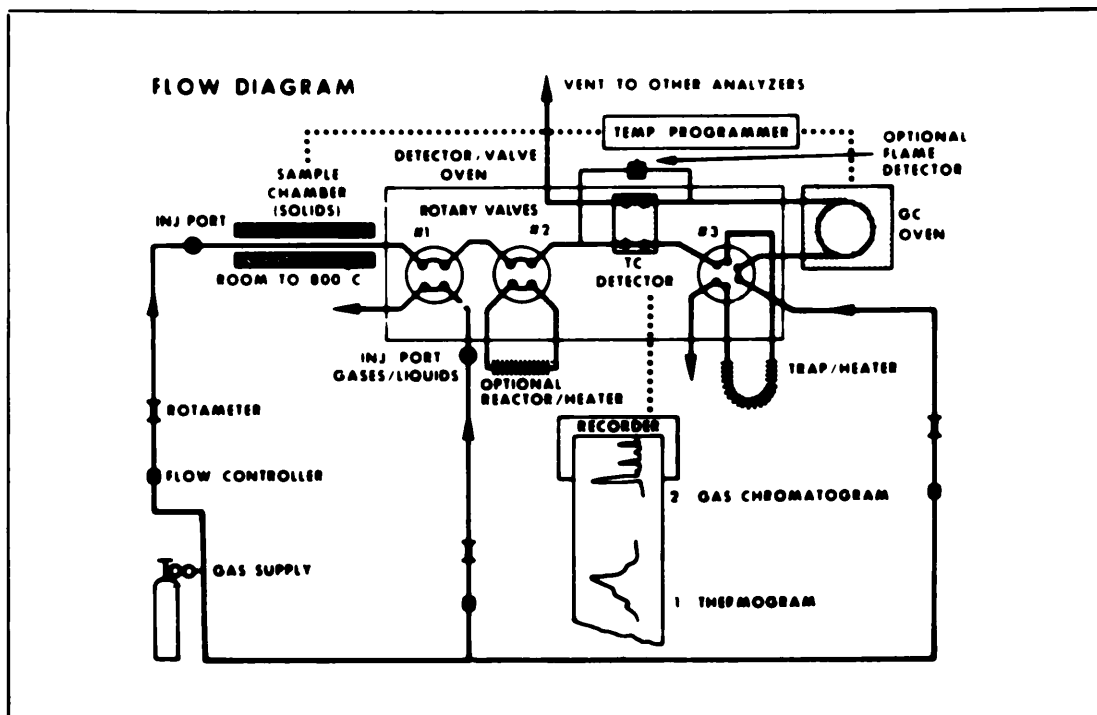


FIGURE 1.—The MP-3 contains a unique valve system. The same TC and FID detectors are used for both the thermogram and chromatogram. The valve system permits the operator to pass a variety of carrier gases over the sample as it is heated. By switching valve Number 3, the operator can record only the thermogram or collect only those thermal fractions wanted for further analysis.

minute; as a means of identifying constituents in the chromatogram, the trapped volatiles can be spiked with known substances through the liquid injection port. Rapid heating sends the adsorbates to the column as a "slug." The GC column heat is programmable to a maximum of 400°C with the same programmer used for the thermal section. The TC and FID detectors used for the thermogram also measure the column elutants.

The versatility of this flow system increases the utility of the MP-3 for oil shale samples and saves operating time. For example, to study re-torting, oxygen or other active gases at various flows and pressures can be swept through the sample chamber provided the TC detector is turned off. The liquid injection port at the sample furnace provides a means of adding a reactant to a heated sample. Also, solvents or water are removed by switching valve number 1 to the vent position and heating the sample.

Alternatively, solvents or H_2O removal can be monitored by switching valve number 3 to the vent position. During a sample run, valve number 1 or valve number 3 can be switched to collect or reject selected thermal fractions for identification. An optional valve can be added to the system to bypass volatiles to a stripper or catalyst bed.

EXPERIMENTAL CONSIDERATION

The format of the data for oil shale samples was usually a smooth, single-phase thermogram and a rich chromatogram as shown in figures 2 and 3, respectively. The ordinates correspond to signal intensity while the abscissa correspond to temperature or time. Flame ionization detection (FID) is the preferred method of detection for oil in oil shale, because it is insensitive to H_2O , CO , CO_2 , NH_3 , H_2S , SO_2 , NO_2 relative to its high sensitivity toward hydrocarbons.

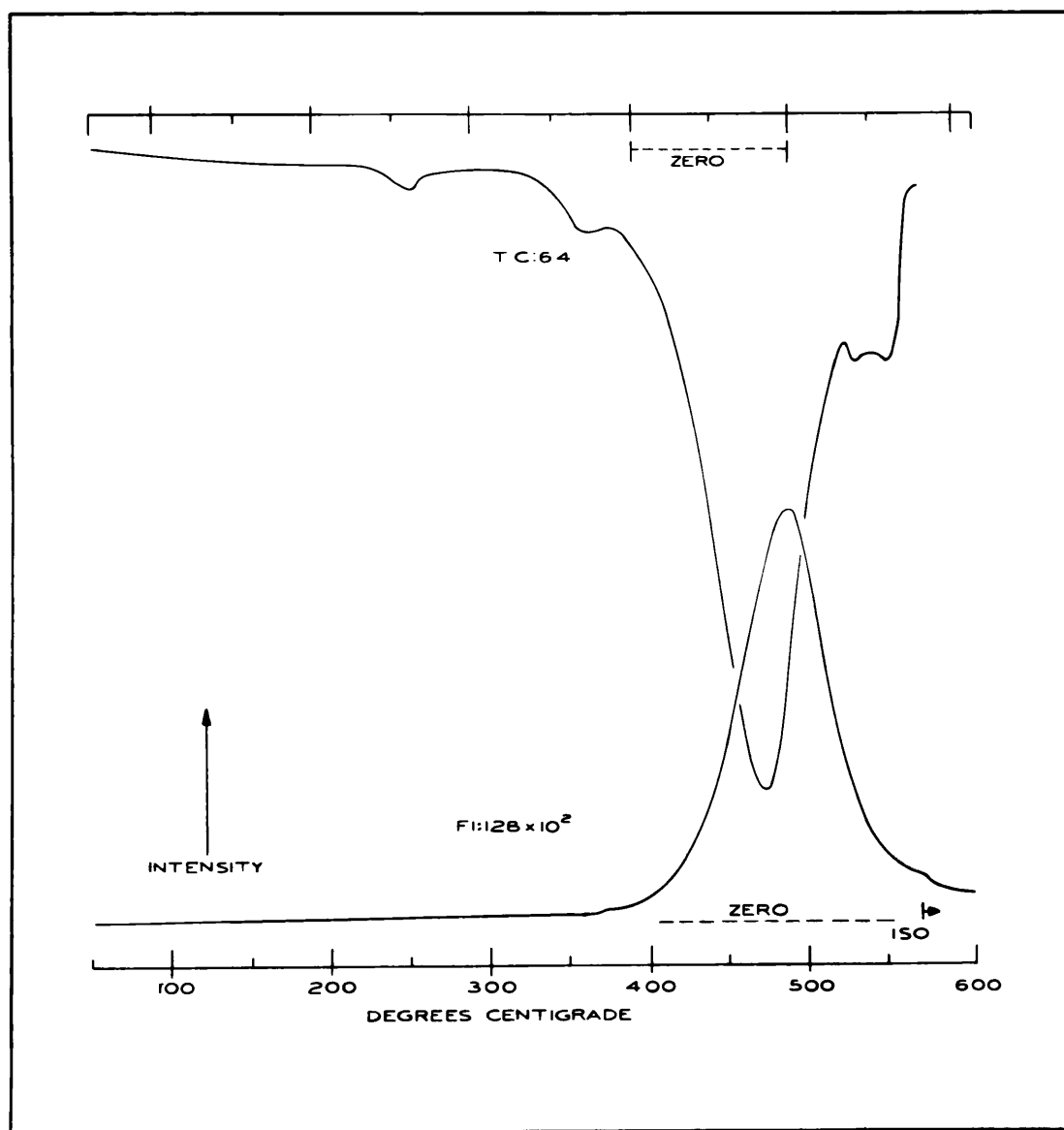


FIGURE 2.—Thermogram of oil shale, 34.7 gal/ton. The upper and lower traces were recorded simultaneously with TC and FID detection, respectively. That the TC “sees” everything and the FID “sees” only organic materials is corroborated by additional peak in the upper trace, probably due to water, CO_2 , CO , NH_3 and other inorganics. Heating rate was $28^\circ C/min$.

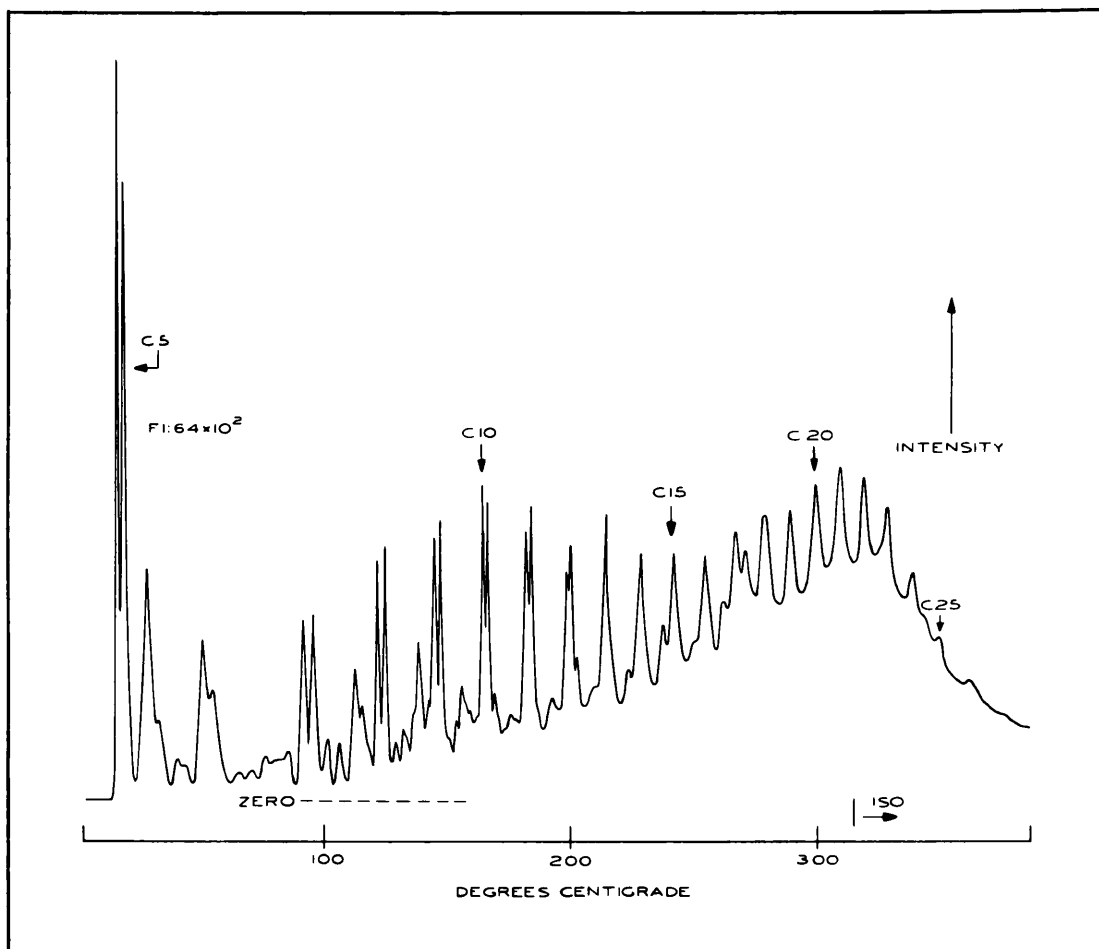


FIGURE 3.—Chromatogram of volatiles formed by thermalizing oil shale. Materials observed here were collected on the MP-3 trap, then backflushed to the GC. The temperature program rate was $8^{\circ}\text{C}/\text{min}$. Hydrocarbons with retention indices as high as 3800 can be backflushed through the system.

SAMPLE PREPARATION

Representative Green River oil shale samples were obtained from the U. S. Bureau of Mines. According to Fischer assay, the samples assayed between 10 and 70 gal/ton of oil to oil shale.* The total weight of each sample was approximately 100 g with particle size ranging from $\frac{1}{2}$ inch to -200 mesh. The entire sample was pulverized for two minutes in a Spex Shatter Box,** a high impact grinding mill. No drying or other sample preparation was necessary. Particle sizes were separated with a Spex sieve set to investigate the effects of mesh size. A bituminous fraction of 34.7 gal/ton Green River oil shale was prepared by benzene extraction for 36 hours.

*Samples were obtained from J. W. Smith, U. S. Bureau of Mines, Laramie Energy Research Center, Laramie, Wyoming 82070.

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THERMAL CONDITIONS

Randomly selected samples ranging from 10 to 60 mg in size were contained in a 6 x ¼ in. OD quartz tube with heat-treated glass wool. With helium flow at 20cc/min at 40 psig, each sample was heated 28°C/min from 50 to 600°C. TC detector current was 150 ma at 250°C. Detector sensitivities are indicated. For oil yield determinations, valve number 3 was in the "BACKFLUSH" or vent position, so that only a thermogram was recorded. Each measurement required 15 to 30 minutes.

CHROMATOGRAMS

Chromatograms were recorded with temperature programming at 8°C/min from 25 to 320°C in the "HOLD AT LIMIT" mode. Helium carrier gas flow was 20 cc/min. The column was 6 ft x ⅛ in. stainless steel, packed with 4 percent SE-30 on Chromosorb G, H.P., 80/100 mesh. TC and FID sensitivities are indicated in figures.

MEASUREMENT OF DATA

The response of the MP-3 as a function of sample loading was determined by peak height or peak area per milligram of oil shale. Peak area was measured by triangulation. Errors arising from instrumentation and integration techniques were expected to be 3 percent or less based on previous experience. The error in weighing, detector response, plus recording were less than 0.75 percent, while integration errors could be as large as 2 percent. The error due to sample inhomogeneity depends on the nature of oil shale which is not well documented. Inorganic materials, such as calcite, dolomite, clay, feldspar, quartz, pyrite and water, when heated, yield only inorganic gases which do not interfere with flame ionization detection (Littlewood 1972).

ASSAY RESULTS

Both peak height and peak area of the thermogram were measured for weighed samples with known Fischer assays. The correlation of the MP-3 peak area per milligram as a function of Fischer assay is shown in figure 4. The mean deviation for each data point was 1.8 percent for area and 3.8 percent for peak height. Both were somewhat larger deviations than anticipated on 10 determinations per sample.

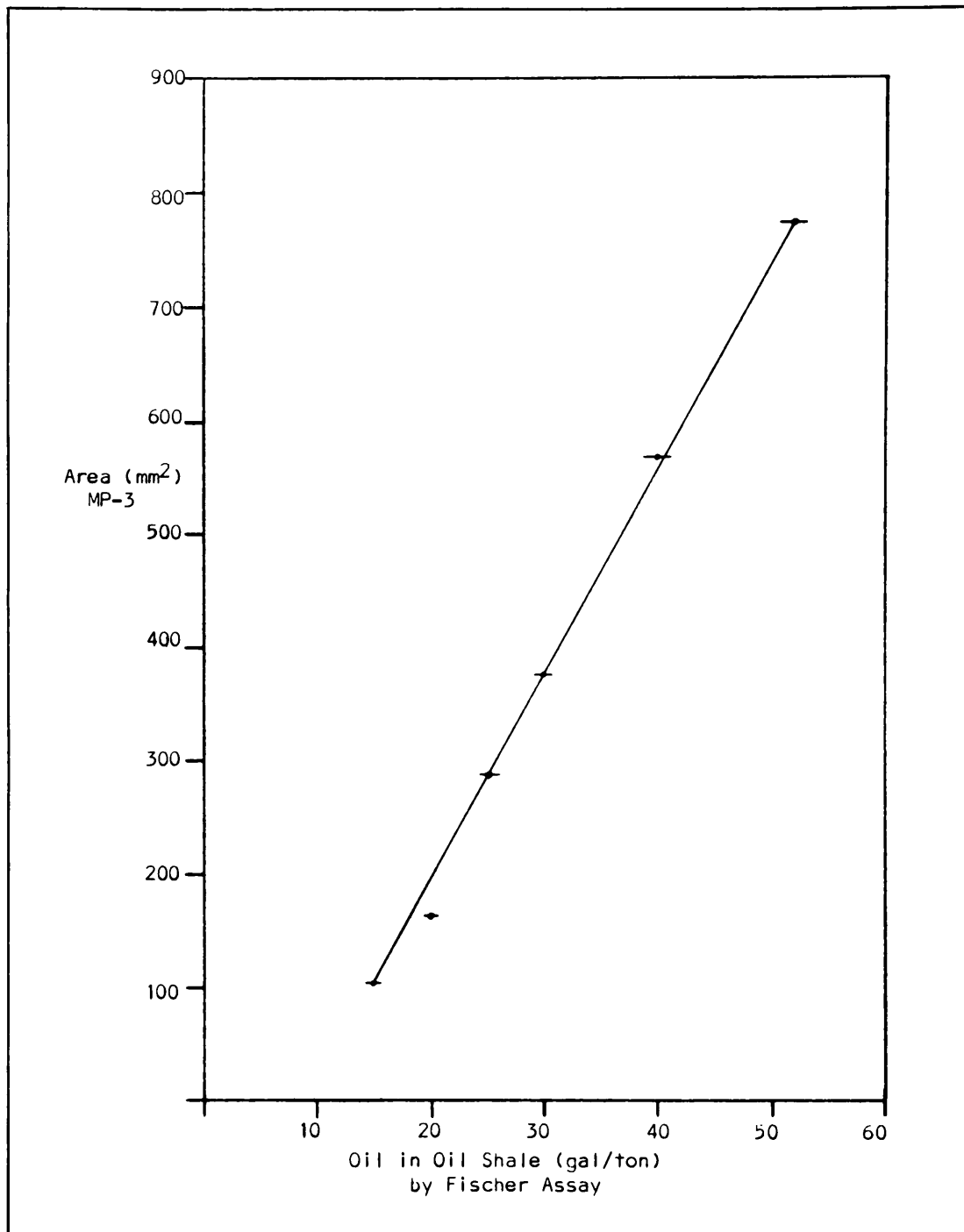


FIGURE 4.—MP-3 response as a function of oil in oil shale. Peak areas for the MP-3 response were determined by triangulation. The horizontal line through each point indicates the 95 percent confidence range for the Fischer assay.

An increase in oil yield with increasing particle size was observed as shown in figure 5. A sample of crushed shale with random distribution of particle size was separated into various fractions with a sieve set. The mesh sizes were -200 , -100 , $+200$, $+100$. A similar effect was observed by L. Goodfellow et al. (1968).

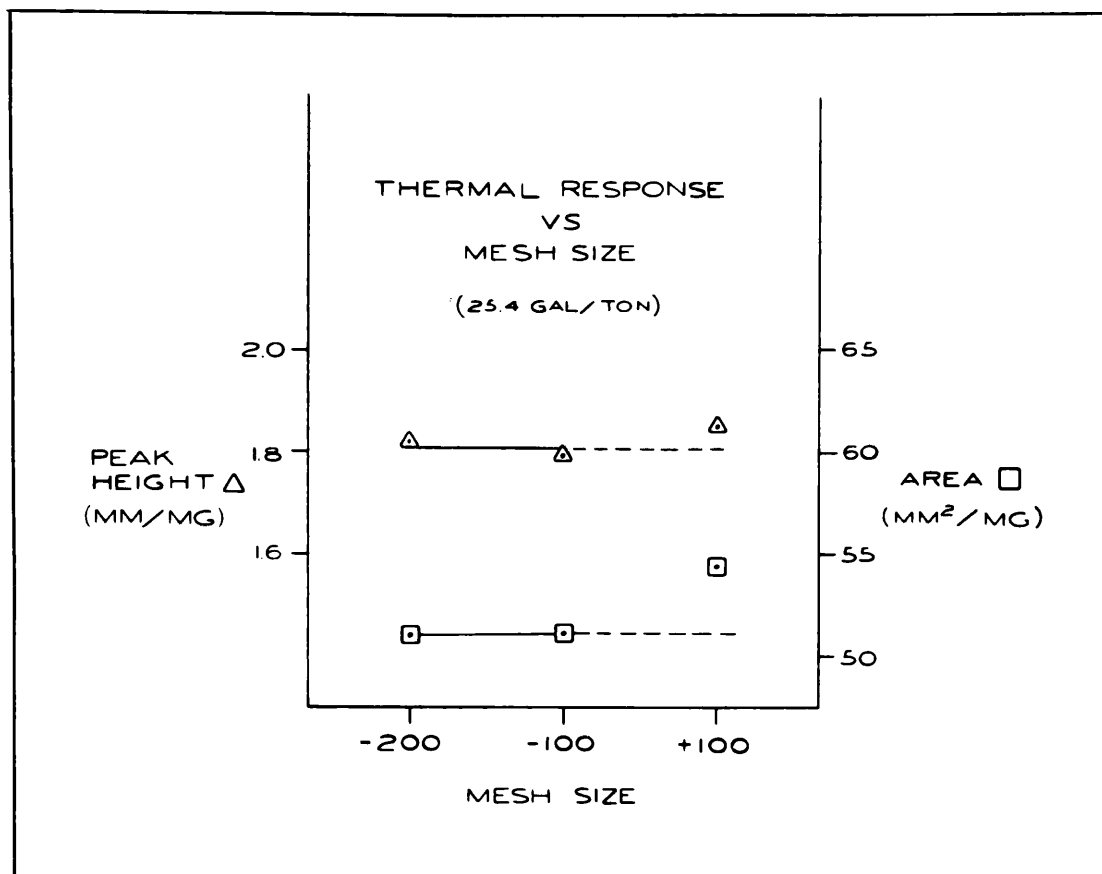


FIGURE 5.—Thermal response as a function of mesh size. As with the Fischer assay (Goodfellow, Haberman, and Atwood 1968), an increase in oil yield with increasing particle size was observed.

THERMAL SEPARATION IN OIL SHALE

A thermal fraction from oil shale was generated by temperature programming the sample in the MP-3 solid furnace to the desired maximum temperature and holding for 10 minutes. A gas chromatogram was obtained by backflushing the volatiles collected through a temperature programmed gas chromatograph. Similarities appeared in the chromatograms of a low temperature fraction and the benzene extract of oil shale. Chromatographic information also indicated that the light hydrocarbons are formed from kerogen decomposition, and heavier hydrocarbons make up the bituminous fraction.

A 22 mg sample of 34.7 gal/ton Green River oil shale was separated in three thermal fractions as follows: (1) 25 to 300°C (fig. 6); (2) 300 to 375°C (fig. 7); (3) 375 to 475°C (fig. 8). The first fraction, compared to the chromatogram of the bitumens (fig. 9), showed numerous coincidences as indicated by the dots. The arrows indicate pristane and phytane,

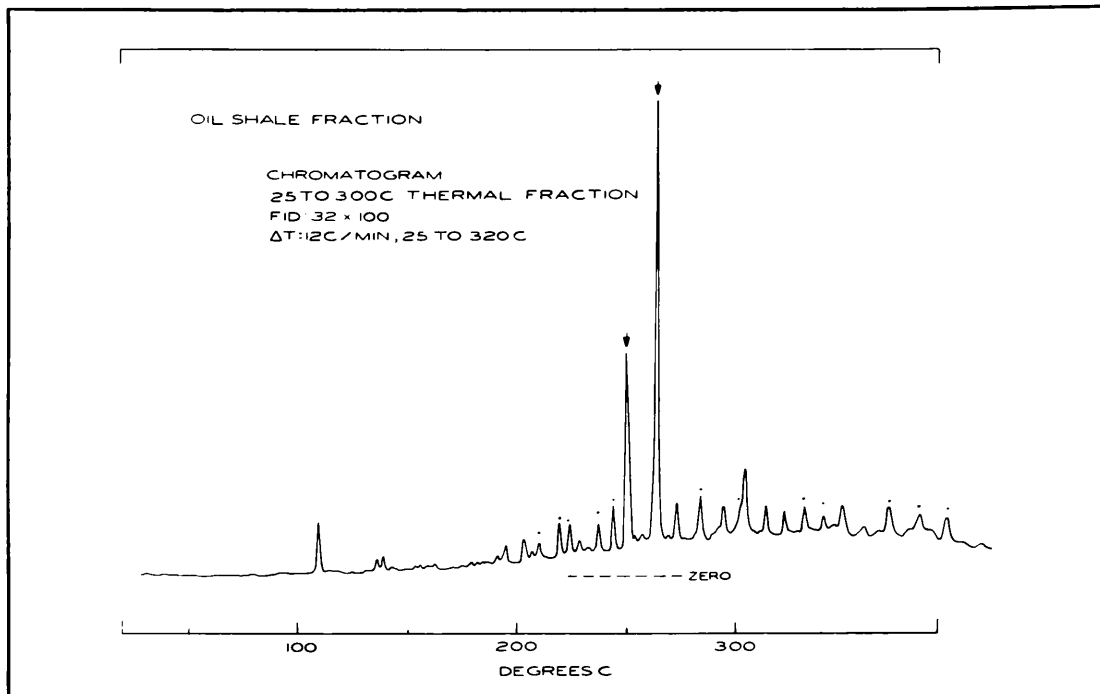


FIGURE 6.—Chromatogram of 25 to 300°C thermal fraction of 34.7 gal/ton oil shale. The first fraction chromatographically resembles the bitumen extract (fig. 9). The arrows mark pristane and phytane, left to right.

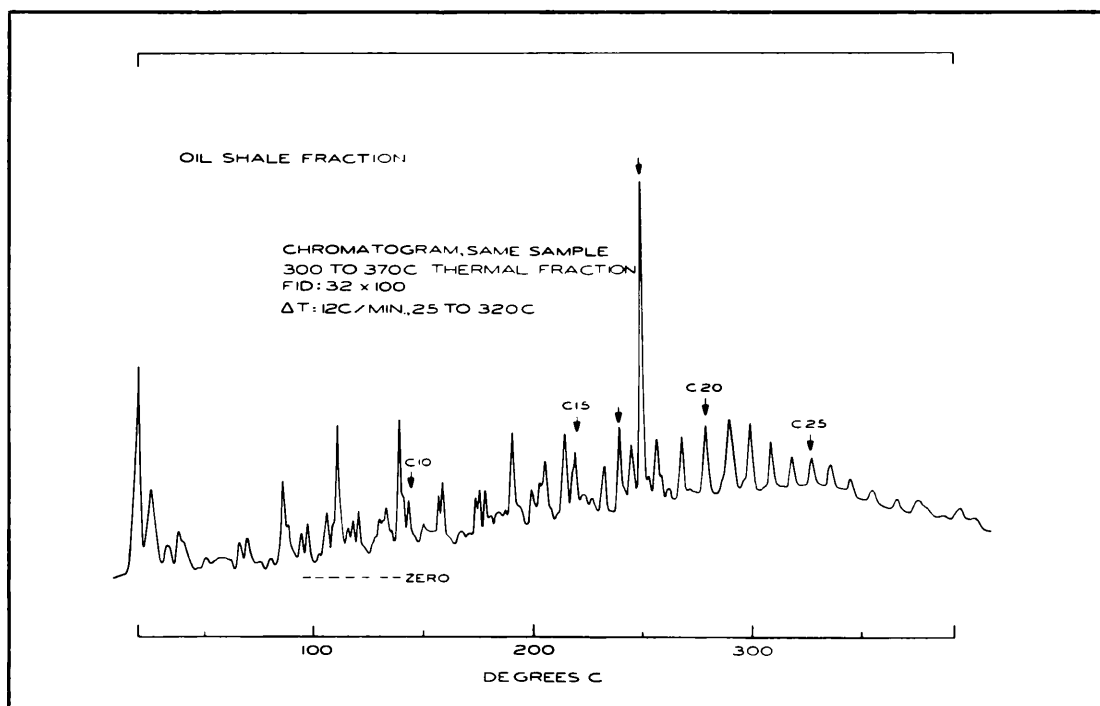


FIGURE 7.—Chromatogram of 300 to 375°C thermal fraction of 34.7 gal/ton oil shale. This was recorded from the remains of the sample used for figure 6. Note the increased abundance of the lower molecular weight materials. Phytane is the right shoulder on C_{18} , much of which was removed with pristane in the first thermal fraction.

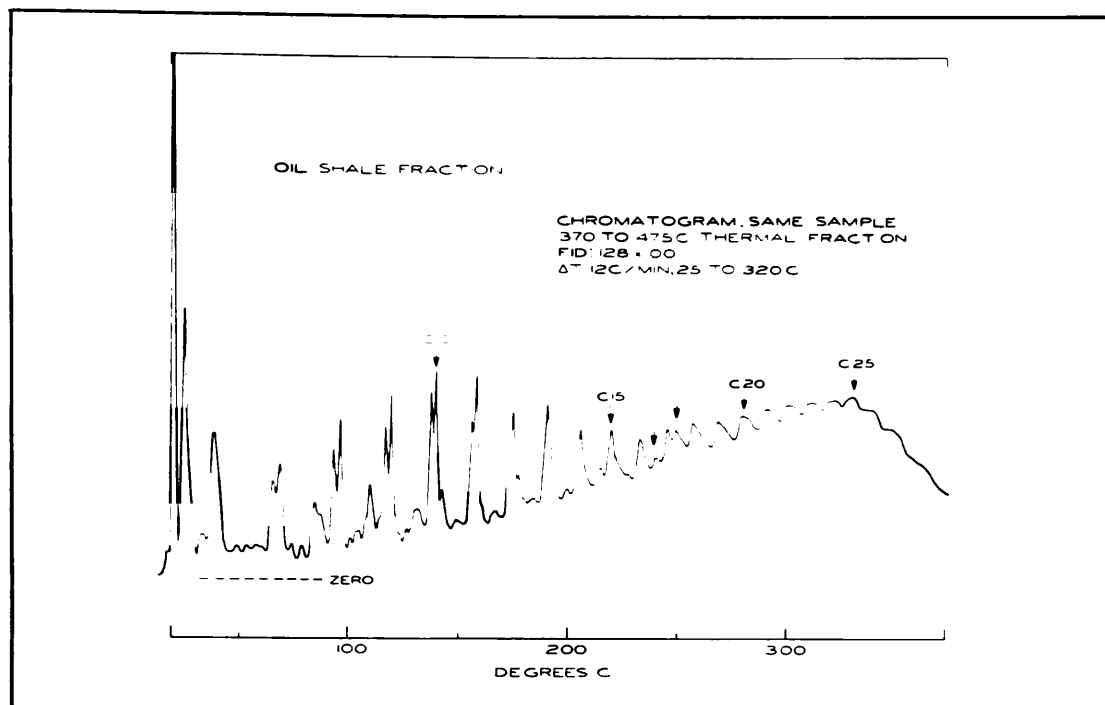


FIGURE 8.—Chromatogram of 375 to 475°C thermal fraction of 34.7 gal/ton oil shale. This chromatogram, recorded from the remains of the sample used for figure 7, shows primarily the decomposition of kerogen. Much of light hydrocarbon fraction from retorted oil shale results from the cracking of kerogen.

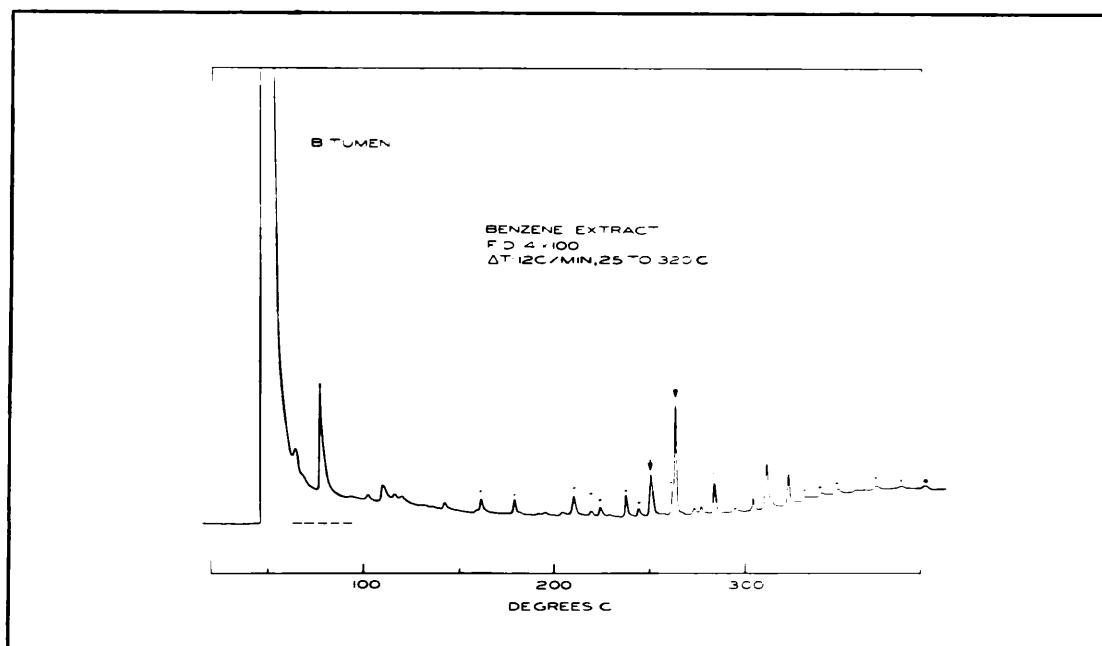


FIGURE 9.—Chromatogram of the benzene extract of oil shale. The dots and arrows mark peaks coincident with those in the first thermal fraction (fig. 6). Except for the first two solvent peaks, phytane is the most prominent peak. C_{18} is the left shoulder of phytane. Pristane and C_{17} have similar retention indices.

respectively, in order of increasing retention index. A subsequent investigation* conclusively demonstrated that the 25 to 300°C thermal fraction is equivalent to the benzene extract. Relative to subsequent thermal fractions, there was an abundance of hydrocarbons C₁₅ and greater in this fraction.

The second thermal fraction from 300 to 375°C was obtained by heating the same sample used for the first thermal fraction. The two prominent peaks were unidentified. They were not pristane and phytane as confirmed by retention indices and spiking with linear hydrocarbons. Furthermore, the low molecular weight materials which were relatively more prominent in this fraction were not linear hydrocarbons. Based on the information available, they appeared to arise from the decomposition of phytane or pristane or preliminary decomposition of the kerogen.

The third thermal fraction from 375°C to 475°C was obtained by heating the same sample again. Low molecular weight hydrocarbons are the most prominent features in this fraction, indicating they arise primarily from the decomposition of kerogen.

DISCUSSION

Experimentally, it was demonstrated that determination of oil in oil shale with the MP-3 is faster and at least as accurate as the Fischer assay. The MP-3 technique resembles the Fischer method in that the sample is programmably heated. However, once calibrated, the MP-3 can give more complete, hence more accurate, information as it measures the hydrocarbon gases evolved, whereas the routine Fischer assay does not. Electronic integration of the thermal output would improve the accuracy and decrease calculation time considerably.

Since the organic carbon to hydrogen ratio and the kerogen hydrocarbon framework are consistent throughout the Green River oil shale bed (Cook 1974), the MP-3 technique can be applied to all Green River shales. Consequently, thermal analysis is a relatively inexpensive, fast method that can be used on-site to supplement other techniques in the oil shale industry where many samples must be assayed.

*D. Scrima and P. Warren, results to be published.

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Littlewood, A. B., 1972, *Gas chromatography: principles, technique and application*: New York, Academic Press.

Goodfellow, Lawrence, Haberman, C. E., and Atwood, M. J., 1968, Modified Fischer assay—equipment, procedures and product balance determinations: *Am. Chem. Soc., San Francisco Mtg., Apr.*