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PYROLYSIS-GAS CHROMATOGRAPHY

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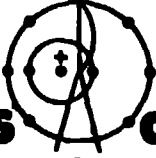
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CHARACTERIZATION OF DEVONIAN SHALES USING  
LASER PYROLYSIS-GAS CHROMATOGRAPHY

by

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TECHNICAL UTILIZATION OF THE DEVONIAN SHALE RESOURCE FOR HYDROCARBON SUPPLIES REQUIRES INCREASED UNDERSTANDINGS OF THE SOURCE ROCKS AND OF MECHANISMS THAT LEAD TO GAS AND/OR OIL PRODUCTION. ALTHOUGH SOME CONCEPTS NOW ACCOUNT FOR THE PRODUCTION OF METHANE FROM THESE MATERIALS, LESS IS KNOWN ABOUT THE NATURE OF THE SOLID ORGANIC CONSTITUENTS AND THE BEHAVIOR OF THESE MATERIALS DURING THERMAL PROCESSING.

PULSED LASER HEATING RESULTS IN A RAPID DEPOSITION OF PRECISE QUANTITIES OF THERMAL ENERGY INTO SELECTED SHALE VOLUME SEGMENTS. THE LASL PROGRAM, PART OF MERC'S EGSP, TO UTILIZE LASER INDUCED PYROLYSIS FOR THE RAPID DETERMINATION OF THE TYPES AND AMOUNTS OF ORGANIC CONSTITUENTS IN VARIOUS SHALE SAMPLES WILL BE DESCRIBED.

INTRODUCTION

Enhanced technical utilization of the natural gas resource contained with the Devonian shales underlying much of the Eastern United States requires new understandings of these source rocks and of mechanisms that eventually lead to gas and oil production. It is generally agreed that these formations consist of an organic fraction, thought to be a coaly type material (1), dispersed throughout a silicate matrix. Methane and other low-molecular weight gases are contained, probably dissolved, in the organic fraction. Drainage of gas from this type of system may require not only the creation of new flow paths, but also methods to promote gas dissolution. Because of this fact, studies of the organic constituents of these shales have begun using the method of laser pyrolysis (2).

Pyrolysis chromatography, heating a solid material to degrade it into smaller fragments and then separating these using chromatographic techniques, is a well described approach to analyzing samples which exhibit low vapor pressures at usual temperatures. Pyrolysis processes of large organic moieties are complicated. Typically, during pyrolysis, different regions of the sample experience different temperatures. These temperature variances lead to different product distributions emanating from discrete regions at distinct temperatures. The overall result is

a highly complicated fragmentation pattern. The distributions of various pyrolysis fragments depend markedly upon sample size and geometry. To circumvent this type of problem, several analytical pyrolysis approaches have been proposed (3). Laser pyrolysis is one of these newer methods (2).

Pulsed lasers offer a convenient power source to deliver intense, short bursts of power into well defined sample regions. In the experiments described here, a focused laser beam is used to rapidly heat a small volume of sample. This heating (the pulse width of the laser event is, approximately  $10^{-3}$  s.) leads to a rapid temperature rise and, then, a high temperature degradation. Depending upon the degree of focus, very high temperatures can be obtained. If these elevated temperatures are reached (temperatures in excess of 5,000K), part of the sample is converted into a high temperature plasma. Such a high temperature ensemble mirrors the atomic composition of the sampling volume (4). Upon the termination of the laser event, this atomic ensemble quenches into a series of low molecular weight gases. Those components of the pyrolysis pattern are called the plasma products. Other parts of the sample see less vigorous conditions. Products emanate from those regions through several processes. Probably the most important of these is degradation resulting from the acoustical shock wave generated by the laser burst. Attenuation of this wave results in the rupture of certain bond types. This bond rupturing process then leads to a series of higher-molecular weight products. This portion of the pyrolysis pattern is called the thermal shock products. It should be emphasized that this type of thermal processing is quite different from more conventional pyrolysis-chromatography (2).

The technique of laser heating leads to several different possibilities. First, sampling is simplified since thin sections and solution-deposited films, required for contemporary hot-wire pyrolysis, are not necessary. Also, sampling can be done in a variety of differing sampling environments. Measurements could be made down-hole, for instance. Second, analysis of surface conditions is straightforward. In fact, unless special care is taken to penetrate the surface, this technique emphasizes chemical states of surfaces of solids (2). Third, one can examine unique regions through regions of known inhomogeneities of a geological sample. For instance, one can investigate the nature of organic material either along a core section or into a core sample. None of these possibilities exist with more conventional pyrolysis-GC.

#### EXPERIMENTAL

A schematic of the apparatus designed for these Devonian shale studies is shown in Figure 1. The pyrolysis is done using a pulsed laser device (shown in the center of the Figure) that deposits energy into a sample contained within a chamber connected directly to the necessary analytical instrumentation. This "on line" configuration permits the direct recovery of very small amounts of pyrolysis fragments. The laser event serves as

a rapid injection of the sample into the chromatograph. Following separation on the chromatographic column, analysis is completed by a mass spectrometric determination of each component. This system will give both qualitative (identification of the type of fragment) and quantitative (identification of the amount of fragment) information. Also, the mass spectrometer will permit measurement of similar chemical species that contain different isotopic composition. For instance, normally occurring methane could be readily distinguished from methane containing the carbon isotope of mass number 13. This type of distinction will be important in experiments that examine adsorption-dissolution phenomena.

Initial studies, reported here, utilize much of this instrumentation. A photograph of the experimental arrangement is shown in Figure 2. The laser power supply is shown to the left of the laser-gas chromatograph. Laser light, generated with a Nd pulsed laser, is directed through a quartz focusing lens (50 mm focal length) and onto a sample contained in the sampling chamber. (The laser is positioned horizontally, unlike the vertical orientation shown in Figure 1.) The pyrolysis products are then led into the gas chromatograph. This instrument utilizes a digital data analysis system (not shown).

Figure 3 shows the focusing lens holder. This device positions the quartz lens to steer the beam onto a discrete region of the sample. The lens can be moved precisely and reproducibly in three dimensions. The location of the sampling volume (to within a spatial distinction of 0.05 cm) is indicated by using a second, low-power laser. This source, 3.0 mw, HeNe, CW, is positioned to the rear of the main laser optical train. Generated light is fed through the optics of the main laser optical train and then through the focusing lens. In this way a focused spot illuminates the exact region that will be interrogated by the pulsed laser beam. It is this aspect of sampling that makes laser-induced pyrolysis a unique technique.

The sampling chamber for these initial studies consists of a short segment of quartz tubing. (Quartz is more resistant to fracturing than is glass.) A photograph of the sample assembly is shown in Figure 4. This top view shows the same lens assembly (Figure 3) to the left of the quartz tube. Carrier gas enters the chamber through the 1/8 in. tubing (top of figure) and exhausts into the gas chromatograph through the 1/16 in. stainless steel tubing (bottom). Specially modified fittings are utilized to minimize the dead volume of the chamber. The 1/16 in. transfer line is normally heated to 250°C during measurements to prevent the condensation of pyrolysis fragments within the transfer line. (Heat tapes have been removed for this photograph.)

Analysis consists of packing a sample fragment into the quartz tube. Either fragments (chips) or consolidated powders can be utilized. The hydraulic connections are re-established; leaks are readily determined by the absence of pressure in the sampling chamber. The laser is then prepared for firing. Final focusing and power adjustments are made and

required safety procedures are carried out. Simultaneously, the laser is fired, the chromatographic data system is initiated and the temperature programming is begun. Using valving, not shown, the carrier gas can be routed around the sample chamber so that another sample can be made ready for analysis while the first is still being processed.

Pyrolysis products consist of a wide range of differing-molecular-weight products. These can range from H<sub>2</sub> (2) or CH<sub>4</sub> (16) to high molecular weight fragments (>300), limited by the requisite vapor pressure need for chromatographic separation. Analysis has been successful using a high performance column of C<sub>18</sub> on Porasil C. This column is first maintained at -10°C for the separation of low molecular weight compounds and then temperature programmed to 220°C for the eventual separation of higher molecular weight fragments. Presently the analysis system does not include mass spectrometric instrumentation. That will be added during the coming months.

### RESULTS AND DISCUSSION

The sampling of complex geological material such as Devonian shales for organic compounds is not straightforward. Assuming one is dealing with core samples, two techniques are generally possible. One can grind and blend a sample, and then, after pressing to obtain a uniform density, pyrolyze the pelletized sample. This method has certain advantages, the principal of these is that a more representative sample may be available since various averaging procedures can be utilized during preparation. However such extensive sample handling could lead to a severe loss of low molecular weight compounds. The other method is to work with segments removed from larger samples (cores, for instance) using a minimum amount of grinding and, in general, using conditions that would lead to the smallest removal of potentially labile organic species. Both of these approaches are under investigation and additional work will be necessary to define adequate sampling procedures.

A representative laser program obtained by the deposition of 5 J of laser energy into a small section of Devonian shale is shown in Figure 5. The sample was taken from a core removed from Lincoln County, W. Va. at a depth of 1093 m. (Columbia Gas Well 20402). These data were taken with a flame ionization detector and consequently emphasize hydrocarbon products. The experimental conditions are listed in the legend to Figure 5.

There is strong evidence that other compounds (CO and CO<sub>2</sub>, for example) do result from the laser degradation of these shales. Data taken under somewhat similar conditions using a thermal conductivity detector showed a variety of products. This product distribution included only a small fraction of the total as hydrocarbon compounds. Although the qualitative nature of each of the thermal-conductivity-pattern fragments is not certainly known, one can deduce that these species must consist of CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O and, possibly, hydrosulfur compounds. Consequently,

it must be emphasized that Figure 5 only shows hydrocarbons resulting from laser pyrolysis in these shale samples. We shall return to investigate the exact nature of these other compounds when mass spectrometric instrumentation is operational.

It is possible to determine the nature of several of the peaks shown in Figure 5. The first represents the quantity of methane produced by the pyrolysis event. Thermodynamic predictions suggest (6) that little methane should be produced from the quenching of a plasma with the expected carbon to hydrogen ratio. Consequently, we assume that this methane most probably results as a thermal blow off product which is thermally degraded from the shale volume under consideration. This quantity of gas could result from both the release of desorbed methane and from methane produced by several pyrolysis products.

The major peak, Peak 3, contains approximately 1/2 of the total integrated area and represents a C<sub>2</sub> hydrocarbon. We tentatively assign this peak to ethane although, at this writing, we cannot completely eliminate the possibility that this peak may also contain some ethene (ethylene). The second-peak, Peak 2, apparently represents ethyne (acetylene). (All of these assignments are made from the comparison of measured retention times with those found using standard compounds under the same conditions. Mass spectrometric measurements will lead to less ambiguous assignments.) One predicts that acetylene would be the dominant plasma product since a high temperature ensemble containing carbon and hydrogen should result in a distribution rich in C<sub>2</sub>H<sub>2</sub> over wide ranges of carbon hydrogen ratio. Clearly, in these studies acetylene is not the dominant low molecular weight gas. We must initially conclude that the elevated ethane yield results from thermal penetration into the sampling volume. Additional experimentation is needed to verify this assumption although laser defocusing experiments tend to support this theory.

As one, maintaining constant laser energy, defocuses the laser beam, a smaller fraction of high-temperature products result. One, therefore, can change the thermolysis product distribution from one that is dominated by plasma products (high degree of focus) to one that is dominated by thermal shock products (low degree of focus). Typically, a fine degree of focus (enhanced power density) results in a more emphasized distribution of lower molecular weight compounds. Data in Table 1 illustrate this type of behavior. Here we see 11 significant peaks, peaks accounting for less than 1% of the total area are ignored. The first three peaks represent methane, acetylene, and ethane-ethene, respectively. One can readily see that focusing the beam leads to a rapid increase in Peak 3. This most probably results from a deeper penetration into the sample with a focused beam. If this were not the case, a higher temperature should produce larger relative quantities of acetylene. This data also show that methane does not increase at the same time as one sees significant increases in ethane concentration. This may suggest that methane is preferentially depleted within the sample

volume. This behavior is entirely different from that found with coal samples (5).

#### CONCLUSIONS

1. Pulsed Nd pyrolysis with minimum sample pretreatment generates adequate quantities of products for analytical determinations.
2. Significant quantities of pyrolysis products apparently result from methane and ethane released by thermal degradation.
3. Focused power deposition leads to increased ethane production. This may result from a deeper penetration into the sample exploring regions removed from the surface that are less depleted in naturally occurring low molecular weight gases.
4. Higher molecular weight components are readily apparent. These compounds may serve both as useful chemical markers and as component sections of the larger molecular weight species that contain the candidate gaseous fuels.

#### ACKNOWLEDGMENT

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Devonian Shale Pyrolysis- Effects of Defocusing Nd Laser Beams Maintaining Constant  
Five J Pulse

PEAK NUMBER	DEFOCUSED BEAM		PARTIALLY FOCUSED		FOCUSED BEAM	
	T <sub>R</sub>	%	T <sub>R</sub>	%	T <sub>R</sub>	%
1	0.24	2.00	0.25	2.54	0.25	3.66
2	0.45	2.10	0.46	2.46	0.46	3.25
3	0.61	24.0	0.62	26.5	0.59	47.1
4	8.71	1.30	8.57	1.21	8.51	2.97
5	10.40	1.77	10.36	1.59	10.32	0.80
6	12.02	11.4	11.98	14.2	12.02	9.60
7	12.57	1.03	12.55	1.96	12.56	0.53
8	13.75	26.3	13.74	25.3	13.73	13.4
9	15.25	4.51	15.24	3.66	15.22	2.13
10	16.58	1.20	16.61	0.29	16.60	0.22
11	18.28	15.3	18.26	16.6	18.26	15.5

Retention times, T<sub>R</sub>, are given in minutes.

Chromatographic Conditions- Column, 1 m, 120-150 mesh, C<sub>18</sub> on Porasil C;  
Temperature, -10°C for 4 minutes, then 16°/minute to 220°C.  
Nitrogen carrier, 20 ml/min.

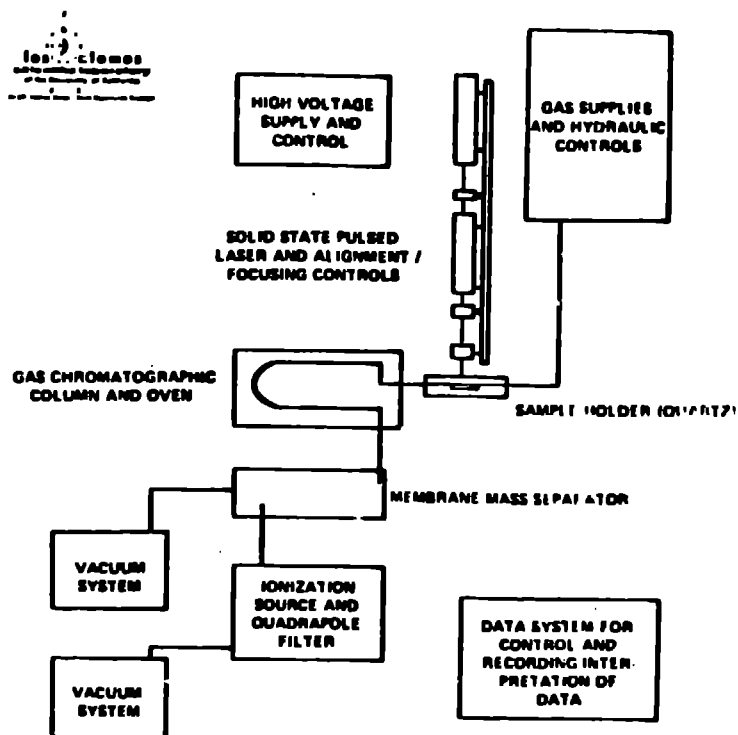


Figure 1: Laser Pyrolysis-Gas Chromatographic-Mass Spectrometric Instrumentation for Rapid Characterization of Devonian Shales



Figure 2: Overall view of laser pyrolysis-gas chromatographic instrumentation. The pulsed laser (Apollo Lasers) deposits energy into the sample contained in

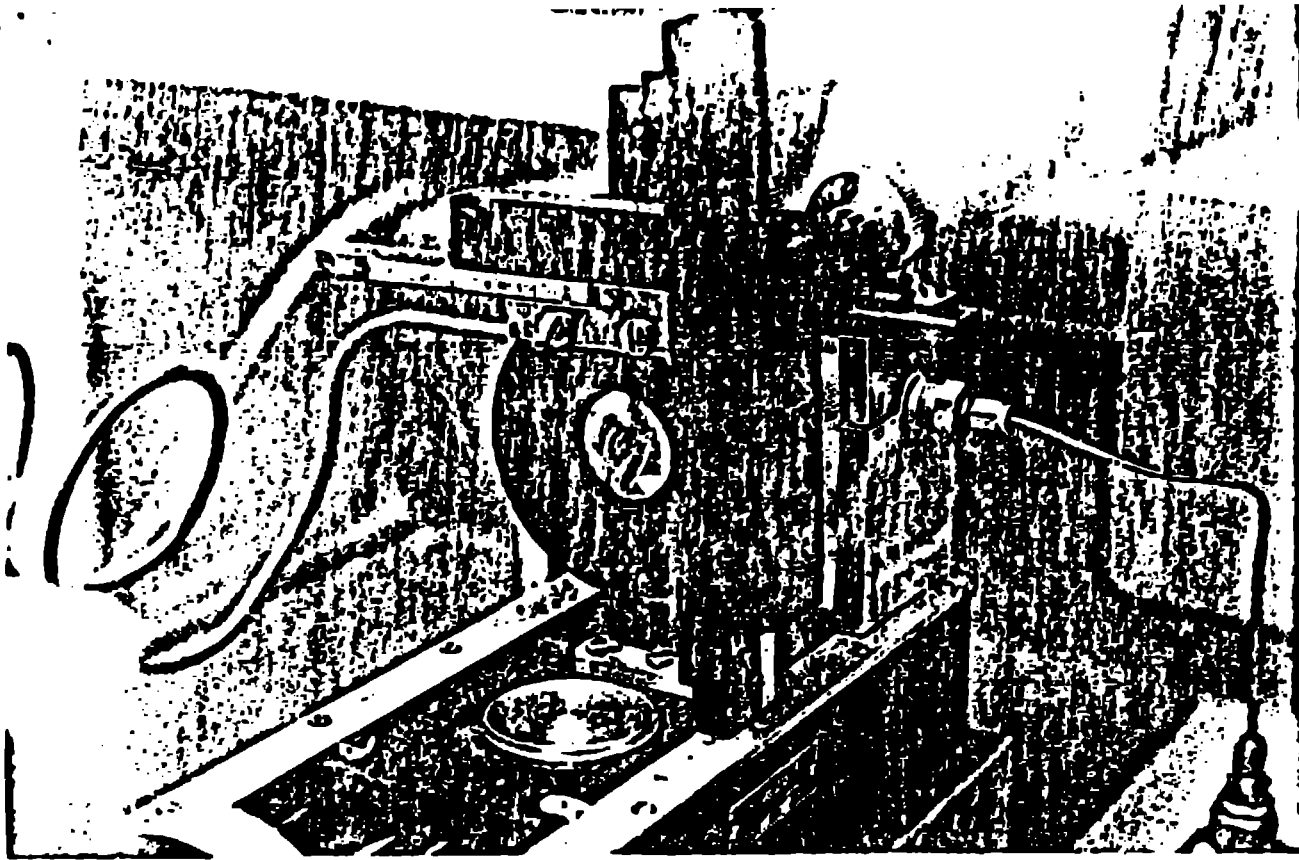


Figure 3: Close-up view of focusing lens. Quartz lens (2.54 cm diameter, 50 mm FL) is used to steam beam onto sample located in chamber behind lens.

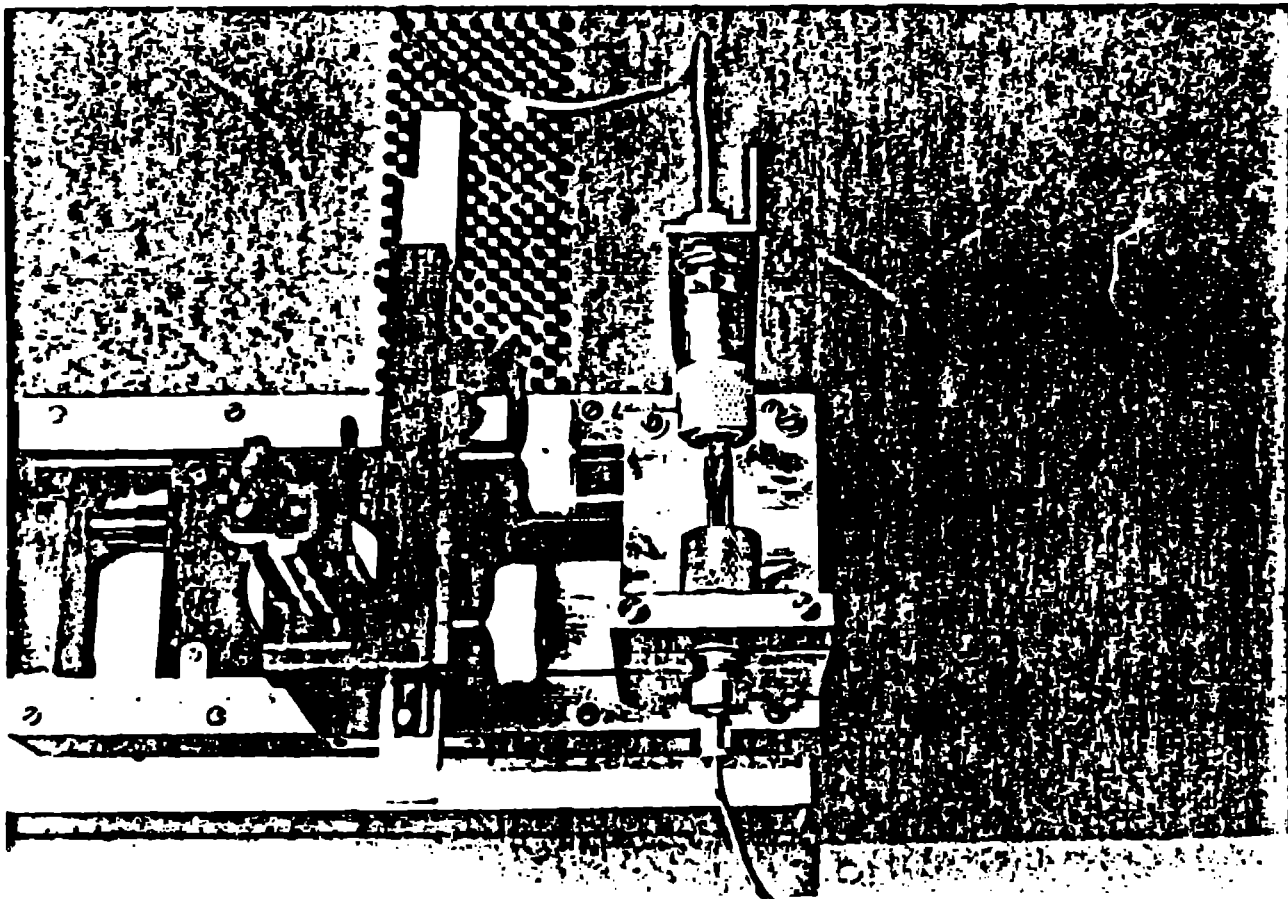


Figure 4: Sample chamber. Tube (6 mm OD) is connected to the gas hydraulic system using Viton O-rings. Sample in place is a polymer calibration standard.

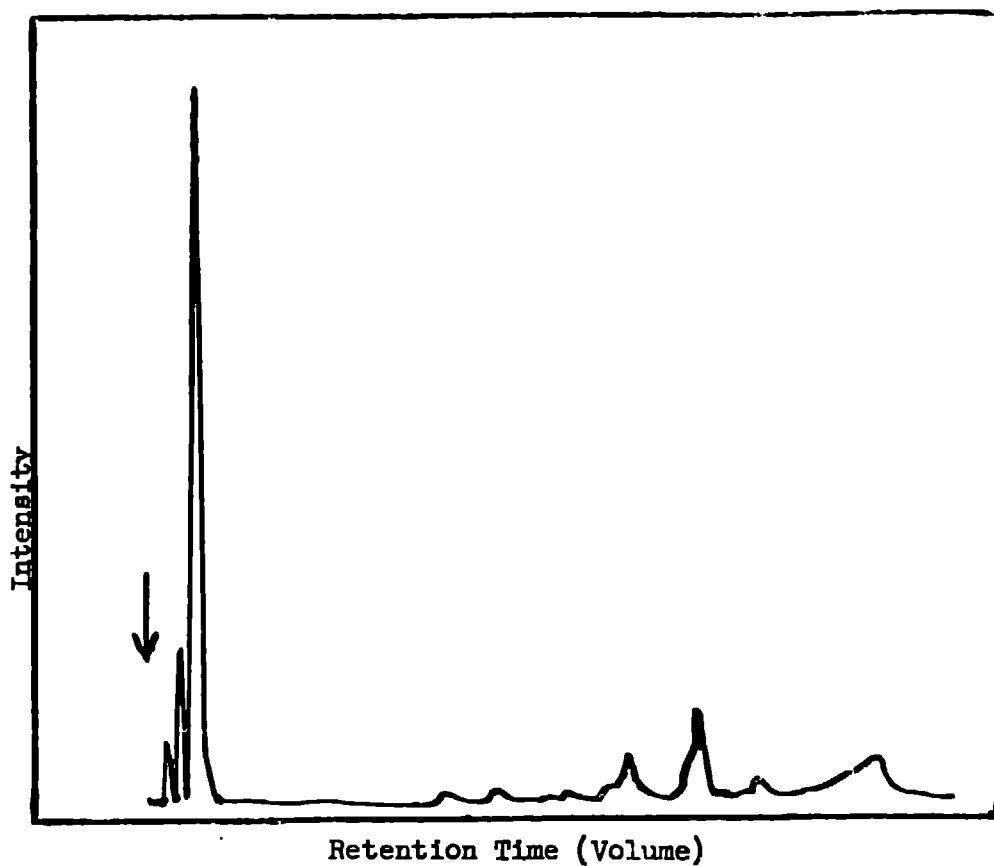


Figure 5: Laser Pyrogram emanating from a 5 J Deposition into a Devonian Shale Sample. Time of firing is shown by the arrow- time then moves from left to right. Chrometographic conditions are listed under Table 1.