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Laser pyrolysis of oil shales

In order to evaluate the hydrocarbon content of different oil shales, a rapid laser pyrolysis gas chromatographic technique has been developed. A pulsed ruby laser was used to pyrolyse the samples in a specially designed on-line cell. The results obtained show that the technique is reliable and can provide in a few minutes the total amount of hydrocarbons contained in the shale and additional information not accessible by other techniques presently used.

Pyrolysis units have been used[1] for other purposes and even coupled directly to gas chromatographs[2,3]. Hot wires, heated tubes and cups or heated chambers are often reported[4-6] on these techniques. A high voltage electric discharge pyrolysis has also been tried[7]. A common disadvantage of all these techniques is that they are not very reproducible. A pulsed laser is probably the best available source of energy for analytical pyrolysis. Its output, in conventional mode, can be made stable to within 1% and can be concentrated on any desired area of the sample by simply changing the distance from the focusing lens to the sample.

The laser and pyrolysis cell

We have chosen a water cooled ruby laser for our experiments. The ruby crystal (4 × 9/16 in. of Superior Internal Quality from Union Carbide) is optically pumped by a helical flash lamp surrounded by ceramic reflectors. A quartz roof prism and a sapphire etalon completed the optical cavity. Up to 5,000 J under 5 kV are available from a voltage regulated power supply. Although the ruby could produce 30 J output, energies in the range of 5 to 10 J were found to be sufficient for this investigation. The atmosphere was dry during these experiments; the laser head was maintained at a constant temperature of 16°. The laser shots were separated by exactly 6 min, the time needed to analyze the produced gases. The coupling to the gas chromatograph is such that a new sample was ready by the time the separation was achieved by the column.

The on-line pyrolysis cell required several improvements. The latest model, after three previous prototypes, is shown in the insert of Fig. 1. Cells previously de-

scribed in the literature[8-10] are simple but quite impractical. They have to be dismantled, while often the carrier gas is shot down, in order to replace the sample. Also glass or quartz surfaces through which the laser is focused into the cell, are too close to the sample. As soon as the sample starts to be evaporated, the window fogging renders the laser sampling not reproducible enough for quantitative analysis without mentioning the cleaning of the cell after each shot and the frequently required cell replacement.

The cell we have built and the system described on Fig. 1 present several advantages:

The cell is all metal with the exception of one quartz window. It is reliable with easy maintenance and very simple to use.

The quartz window, which is 6 in. from the sample, never becomes contaminated by pyrolysis products or deteriorated by the laser beam.

An electromagnetic valve closes within few milliseconds after the laser pulse
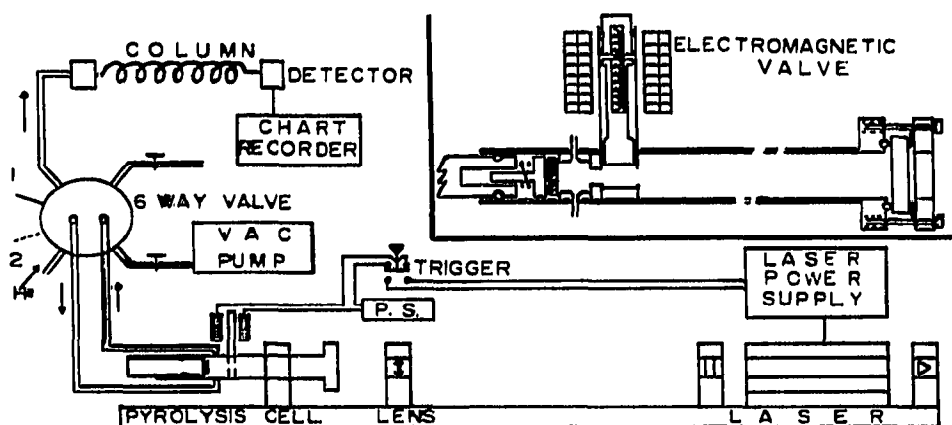

Fig. 1. Diagram of laser pyrolysis system. The sample can be replaced while the separation is achieved in the column. The electromagnetic valve provides sharp and reproducible peaks.

preventing the pyrolysis products from expanding into the total volume of the cell, thus providing sharp enough peaks through the chromatograph.

Because the laser pulse energy is constant it is likely that the volume of shale sampled at each shot is the same as well as the amount of gases expanding toward the window when the electromagnetic valve is closing. These gases trapped between the valve and the window are not analyzed to avoid a large tailing of the peaks. They are removed by pumping for the next cycle.

As soon as the pyrolysis products have reached the entrance of the column, the six way valve is turned to the position 2 placing the cell out of the He gas carrier circuit without interrupting the chromatogram in progress. The sample is then replaced, the cell evacuated and reconnected to the He flow by turning the six way valve to the position 1. The system is ready for a new laser shot as soon as the last peak is recorded.

The sample replacement can be achieved mechanically because the sample holder is designed to be an hydraulic piston. With all the valves being electromagnetic the entire system can be programmed to run automatically a large number of samples.

Gas chromatograph and shale samples

The gas chromatograph is a Perkin Elmer Model 800 with a hydrogen flame

ionization and a hot wire detector. The data presented here are obtained with the hydrogen flame detector at an attenuation of 500. Besides the hydrocarbon peaks the hot wire detector shows nitrogen, oxygen, carbon dioxide and water peaks. The data of Figs. 2 and 3 are obtained with a silica gel packed column 1/8 in. in diameter and 3 ft. long, maintained at a constant temperature of 80°.

The present samples were obtained from a core drilled at Washakie Basin in Green River, Wyoming. They represent shale layers in which a Fischer assay estimated a hydrocarbon content capable of producing from 5 to 43 gallons of oil per ton of shale. Fischer assay (F. A.) consists of distilling the sample at a temperature of about 500° and measuring the amount of oil produced; this operation takes up to 6 h. Our samples were first ground with a typical mesh size distribution: $-8 + 100$, 3%; $-100 + 200$, 30%; $-200 + 325$, 46%; -325, 21%. The powder was next pressed into a pellet of 1/2 in. diameter and 1/8 in. thickness.
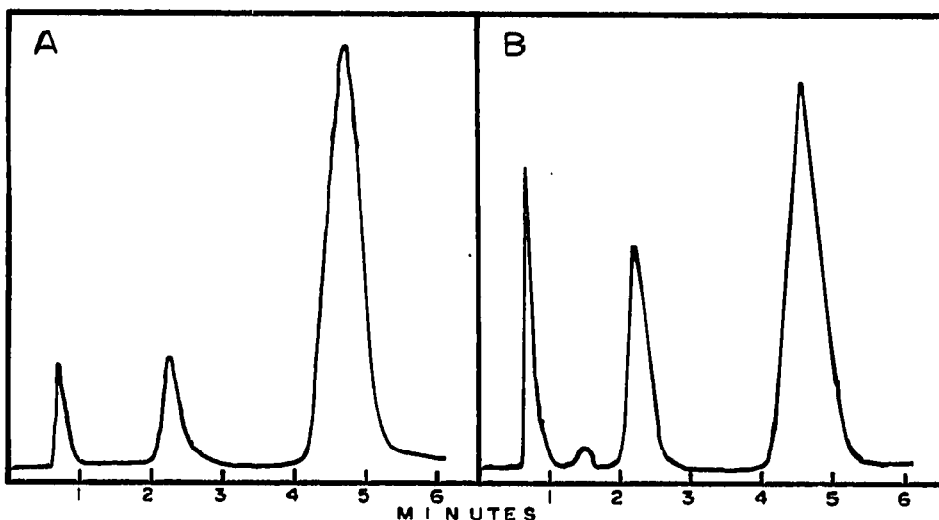

Fig. 2. Typical chromatogram of laser pyrolysed oil shales. (A) Methane, ethylene and acetylene obtained from a sample having a 25.8 Fischer assay yield. (B) Output under identical conditions of a sample having 30.2 Fischer assay yield. While the acetylene peak decreases the methane and ethylene output increase and a new product, ethane, appears.

Experimental results

A laser beam of approximately 6 J, in conventional mode, was focused by a quartz lens of 10 in. of focal length on the surface of the sample placed at 9.75 in. from the lens. The laser output was stable from shot to shot within 1%. Fig. 2A shows a typical chromatogram obtained from the oil shales. The first peak is methane; the second ethylene and the third acetylene. Natural gas contains mainly methane and small quantities of ethane and propane. Under laser pyrolysis, mainly acetylene is produced because of the high temperatures obtained. In Fig. 3 the acetylene output is plotted vs. the Fischer assay yield. One laser shot was focused in each side of each pellet giving an acetylene output almost the same. The acetylene output vs. Fischer assay yield of the first four samples is a straight line within experimental errors. After absolute calibration this curve can be used to rapidly characterize oil shales. It is interesting to note that this straight line does not go through the origin meaning that the Fischer assay underestimates the hydrocarbon content of the shale, because it is
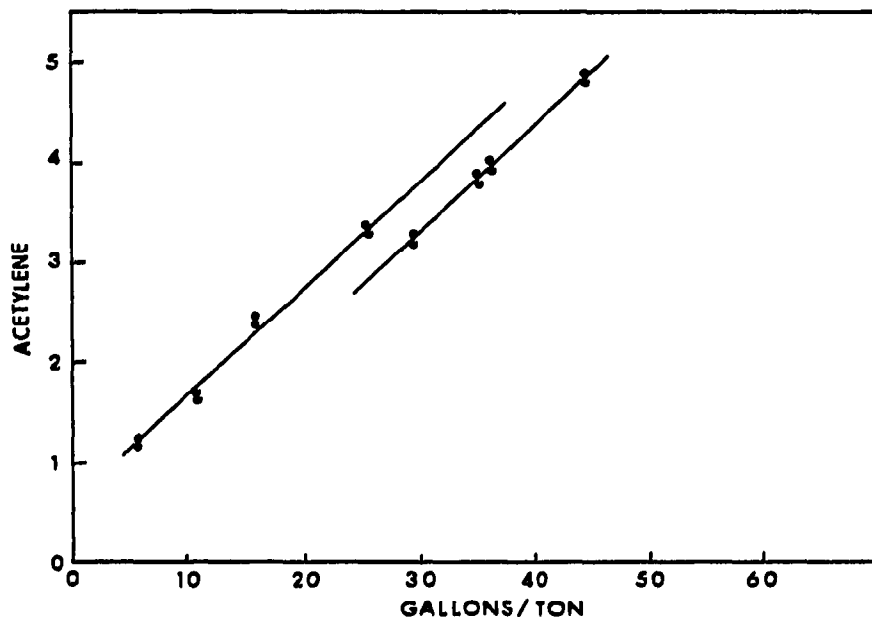
Fig. 3. Acetylene output *vs.* Fischer assay yield of samples obtained from the same core. A characteristic break of the straight line is obtained between 25 and 30 Fischer assay yield.

done at a low temperature compared to the laser pyrolysis and does not recover the distillation gases. Other total organic carbon content tests of the same samples also show the same underestimation by the Fischer assay.

Totally unpredicted was the slight decrease of the acetylene output for the last four samples. The variation seems, however, to be larger than experimental errors. The acetylene output is again proportional to the Fischer assay yield. The two straight lines of the graph 3 have the same slope. This break on the acetylene output does not mean that the laser pyrolysis now underestimates the hydrocarbon content of the sample. The decrease of acetylene peak is compensated by the increase of methane and ethylene peaks. Fig. 2 clearly shows this phenomenon. Fig. 2A is the chromatogram of a sample of 25.8 gallons/ton F. A. yield while Fig. 2B is the output of a sample of 30.2 gallons/ton F. A. yield where not only the methane and ethylene output is increased to compensate for the acetylene decrease but also a new product, ethane, appears between methane and ethylene peaks. When one is only interested in the total hydrocarbon content of the shales, it is more simple to measure the total output of all hydrocarbon gases all together without separating them, which is easy to do with a very short column and higher temperatures. In this case the analysis can be made in less than 1 min.

In addition to this total testing we think that the investigation of individual lines as shown in Fig. 3 can provide interesting new information for oil shales. The methane–ethylene increase at the expense of acetylene means there is a physicochemical variation of the samples not seen by other testing techniques as Fischer assay. For the same laser energy the average temperature reached during the pyrolysis could have been lowered by the variation of some sample parameters: texture of sample, mineral organic ratio, easily available carbon hydrogen ratio, etc.

Another advantage of the laser pyrolysis is that the sampling can be done direct-

ly on the shale. Microsampling of a shale cut perpendicular to the geological layers can provide hydrocarbon content data on layers separated by about 1 mm. Another microsampling we have done is to shoot the laser in the same spot perpendicular to the sedimentation layers. It shows large output variations at some specific layers.

Conclusion

It is clear that a laser pyrolysis gas chromatograph technique can do much for the characterization of oil shales. The output of all hydrocarbons together can very simply be related to the hydrocarbon content of the sample. This analysis can be done in less than 1 min compared to several hours required now by Fischer assay or organic carbon test technique. The analysis of the relative variations of individual peaks like acetylene, ethylene or methane could be related to the easiness of recuperation of the hydrocarbons from the shale which is not accessible to other tests. Information of the oil output of different retort processes and different shales is needed in order to make a correlation with the individual line laser pyrolysis data.

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