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ELUCIDATION OF GEOMATRICES BY LASER PYROLYSIS-GAS CHROMATOGRAPHY AND PYROLYSIS-MASS SPECTROMETRY

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SUMMARY

Present methods for the examination of organics entrained in geological matrices are tedious even if not fallible. Thermal degradative techniques combined with the separatory power of a gas chromatographic column or a quadrupole mass spectrometer operating in the low-voltage electron-impact mode afford rapid access to detailed profiles of such materials. The virtues of these parallel approaches are compared and contrasted in application to the elucidation of Devonian Shale and other geological material.

INTRODUCTION

Although there has been novel advance¹⁻³ in the methodology of latent fossil fuel resource investigations, perhaps the full potential of the methods of analytical pyrolysis or controlled thermal degradation in conjunction with other instrumental techniques has yet to be fully realized. Geological samples are complex mixtures of interrelated organic and mineral components. Maturation processes in these sediments are only partially understood⁴⁻⁶. Organic rich debris, mainly condensed isoprenes, lignin and cellulose, are deposited under reductive conditions and maintained at elevated temperature and pressure. Initially, owing partly to biological action, the debris are converted to complex organic material and methane is released. With continued high pressure the material forms condensed carbonaceous macromolecules and additionally more methane. Continued evolution of lower-molecular-weight species generates a mobile material that can migrate from the source rock. Estimation of production potential of a particular formation requires a measurement of both the total quantity of carbonaceous material per volume of rock and a measurement of the nature of that material.

Standard procedures for these tasks are suggested in the typical separation scheme for organic sediments shown in Fig. 1. Initial sampling requires homogenization of a selected rock sample, then extensive mechanical grinding, then extraction in organic solvents. Frequently the organic fraction is entirely insoluble. The mineral

portion of the matrix is then dissolved in concentrated aqueous acids. There exists a certain potential for alteration of the sample during these several attritions. Although a number of workers claim little evidence for such chemical modifications, it would seem that such a rapid disturbance of an equilibrium gently established over an eon of time could accord change to the organic system.

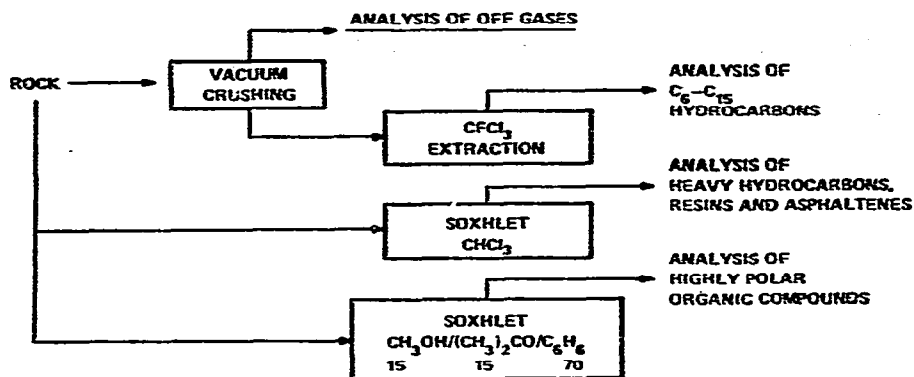


Fig. 1. Typical procedure for organic separation prior to analysis for chemical characterization.

It is also necessary to acquire meaningfully detailed profiles of geologically likely zones at a rate concomitant with that with which samples are actually produced. Consequently improved organic geochemical techniques must consider analysis time as an important component. Sample integrity will be preserved if analyses are completed immediately after removal and rapid results could factor meaningfully into production techniques. It is thus apparent that field processing of drilling chips as they are brought to the surface would not only expedite exploration but also make substantive contribution to the economics of the exercise.

These rapid conditions are approached by modern analytical pyrolysis systems. We describe two techniques and contrast these complimentary fast heating methods for rock characterization.

EXPERIMENTAL

The equipment used for the measurements described below was of two basic types:

(i) Laser pyrolysis in combination with gas chromatography-mass spectrometry (laser-GC-MS)⁷;

(ii) Curie-point pyrolysis in combination with mass spectrometry (Py-MS)⁸. Each will be described sequentially.

The laser pyrolysis system is shown schematically in Fig. 2. The sample, either small chips or compacted powders, is inserted into a cylindrical quartz chamber. Carrier gas is then fed through the pyrolysis chamber and into a chromatographic column. After the flow conditions have stabilized, the pulsed Nd laser is fired, through a focusing lens, into the sample. Pyrolysis products are transferred directly onto the column and eluted. Carrier gas is stripped by a molecular jet

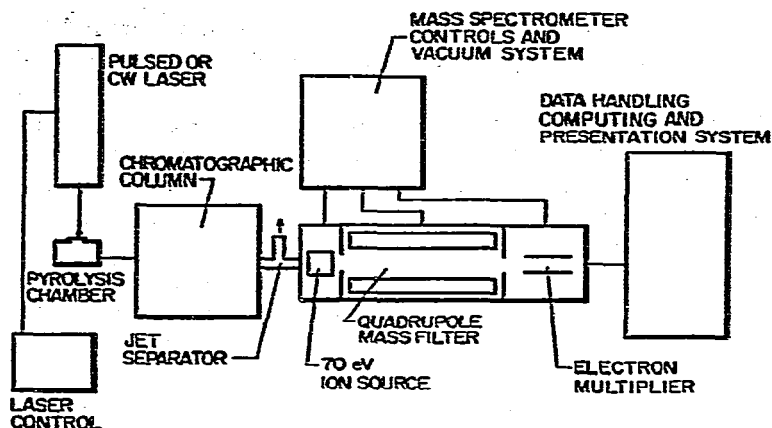


Fig. 2. Schematic of laser-GC-MS instrumentation. Sample is housed in pyrolysis chamber and products are flushed into GC-MS system.

separator and enriched products are introduced into the ion source of a mass spectrometer. There a 70-eV electron beam is used to degrade the sample into characteristic molecular fragments. Data are obtained of normal fragmentation patterns from each characteristic peak. The system is insensitive to changes in carrier gas velocity and sample overloading. Data speed requirements are no more demanding than other high-performance GC-MS systems because data are produced at rates set by column performance.

The Py-MS instrumentation is shown schematically in Fig. 3. This system requires that the sample is finely divided. This powder is then suspended in a volatile organic solvent and the suspension coated on a Curie-point wire. Then the sample-coated wire is inserted into the high-vacuum of a mass spectrometer and positioned within an RF coil. The coil is energized and the wire is heated. Volatile fragments are driven off into a low voltage (14 eV) ion source. These charged fragments are then accelerated through a quadrupole filter and analyzed. Although the pyrolysis event is fast indeed (1-3 msec), products must have sufficient volatility so that they persist in the vacuum system and analyses are completed in much longer times. For instance, in the data presented here, RF energy was used to pyrolyze for 1.0 sec at 510°C. (Sample sizes were of the order 20-25 μg .) Data were recorded

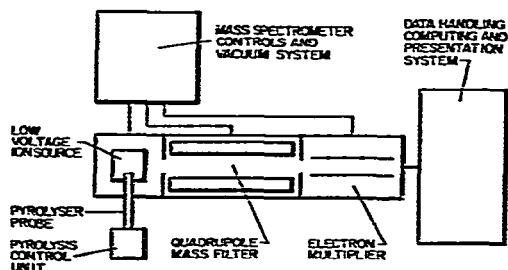


Fig. 3. Schematic of Py-MS instrumentation. Sample, coated on Curie-point wire, is inserted into vacuum system and pyrolyzed into expansion volume.

after 250 repetitive mass scans at a rate of 10 scans/sec. This system requires an expansion volume and a differential pumping to introduce sample into the filter at a continuous rate.

These complimentary techniques are contrasted in Table I. In each case, the intent is to heat a rock sample rapidly enough to minimize secondary reactions. Considerable differences exist for sample procedures. Py-MS techniques require homogenization and grinding of selected rock sections and then that sample is dispersed in an organic solvent. The sample is then suspended on the Curie-point-filament. Pyrolysis utilizes the entire suspended sample although less volatile fragments may remain behind on the filament or precipitate on the walls of the vacuum chamber. Laser-GC-MS is a far more rigorous procedure. Most geomatrices absorb Nd-laser photons (1.06 μm), so the problem of non-absorbing samples is of little concern. The laser "drills" a small section in a larger sample. This sampling procedure permits the direct interrogation of rock chips and other material. For samples chosen to be representative of specific zones, it is possible to grind and blend and then pelletize these materials to a uniform density and convenient shape, usually a cylinder.

TABLE I

COMPARISON OF PYROLYSIS CONDITIONS BETWEEN Py-MS AND LASER-GC-MS

	<i>Py-MS</i>	<i>Laser-GC-MS</i>
Heating method	Magnetic wire in RF field	Photon absorption and plasma radiation
Heating geometry	Back sample surface	Front surface
Sample properties	Powder dispersed in organic solvent	Compacted powders; rock chips; whole rocks
Heating rate	10^5 °K/sec	10^7 °K/sec
Cooling rate	-10^4 °K/sec	-10^6 °K/sec
Pyrolysis conditions	Vacuum	Variable pressure and reactant conditions
Time	1-100 msec	0.1-1 msec
Limitations	Volatile samples; catalytic influences metal surfaces; back-heating blow off	Transparent materials; variable energy input; plasma complications; photoysis
Separation of products	Quadruple	Chromatographic column
Separator	Differential pressure	Molecular jet
Ionization	14 eV*	70 eV*

* These experiments.

Typically pyrolysis is done under inert conditions. Py-MS is performed in a vacuum while laser-GC-MS can be accomplished under a variety of inert (including vacuum) and reactive conditions. In these experiments the laser-GC-MS experiments were accomplished in the flowing carrier gas stream, helium⁷.

THE NATURE OF CARBONACEOUS SEDIMENTS

There is considerable literature on the pyrolysis of carbonaceous sediments^{1,2}. Clearly these insoluble, condensed materials are challenging. Although *in situ*

measurements may reveal labile, low-molecular-weight compounds in sediments, typically unless special techniques are used, by the time measurements are made, such species are lost. The geomatrices consist of cross-linked, three-dimensional condensed polymeric material. Thermal treatment, like *in situ* maturation, leads to bond cleavages between the carbon-rich, semiaromatic polymeric backbone and pendant groups. Typically these cleavages involve the formation of free radicals. Unpaired electrons are formed both on the parent species and on the newly separated pendant. The cleaved section then couples with other radical species to form lower (than the parent) molecular weight products. Should geometries be suitable, two adjacent free radicals in the backbone can couple to form more condensed residue. This sort of scheme has been identified in the coal literature, for instance, where it is well known that coal, when heated, forms "volatiles" and "char", both products from the same starting material⁹. It is important to recognize that such phenomena are general during carbonaceous pyrolysis. It is also important to recognize that only the volatile materials are detected. The residual compounds are aromatic in nature, carbon-rich graphitic compounds of vanishingly small volatility, char.

This sort of behavior is paralleled in polymer pyrolysis. For instance, vinyl chloride polymers give only a small pyrolysis yield of the monomer. Rather, when pyrolyzed, product HCl and condensed "char" are formed. This result is quite different from that in systems with aromatic pendant groups like polystyrene, that degrade preferentially to yield monomeric species, like styrene¹⁰.

The implications are that during rapid pyrolysis the only discernible products will be those cleaved from the parent species. That such radical species can couple to form stable compounds is unquestioned and such coupling must be an important step in petroleum genesis.

PYROLYSIS MECHANISMS

Rapid heating of these sediments is essential. If slow heating techniques are used, solid condensation reactions can concurrently produce different types of materials that will, in turn, produce other fragment types. Py-MS, in a vacuum is fairly well understood although free radical coupling is not impossible. Although the average chamber pressure may be low enough to lower collision rates, pressures are high enough in the vicinity of the filament to promote coupling and other interactions involving energy exchange between the primary molecular fragments.

Laser pyrolysis is complicated because of plasma interactions⁷. Initially, during the early part of the laser pulse, elements on the surface are ionized by the intense photon flux. Ions and electrons are pumped into a dense, hot gas. This plasma then grows between the laser source and the sample. Since photon absorptivities for free electrons are far more probable than for atoms, the electrons continue to absorb energy and rapidly re-radiate this energy to the sample. The sample, then, during the later part of the pulse is subjected to a black-body radiative flux that heats the surface. The plasma state is kinetically isothermal during the pulse life since unbound electrons have sufficient velocity to rapidly distribute energy. Shortly after the termination of the pulse, electrons re-enter atomic manifolds; once this happens, heat transfer becomes less efficient and a high-temperature "equilibrium" distribution of matter is frozen from the plasma. In carbon-rich systems, a significant species in this

distribution is the acetylene radical, C_2H^+ . There is ample evidence that this species plays a major role in the formation of pyrolysis products.

As has been shown previously, laser pyrolysis results in a series of product types. The plasma quenches to an ensemble of low-molecular-weight gases, including acetylene. Then higher-molecular-weight fragments, pyrolysis fragments and condensed fragments result. Such results are shown in Fig. 4 and Table II obtained with a sample of Gilsonite removed from the Independence Vein. It is thought that Gilsonite is composed of a complex mixture of porphyrins¹¹. Fig. 4 shows a tracing of the total ion current following the laser pulse. As each peak is eluted into the mass spectrometer, the data system is activated and an electron-impact mass spectrum is recorded. Table II lists the relevant data as well as suspected identification of major peaks.

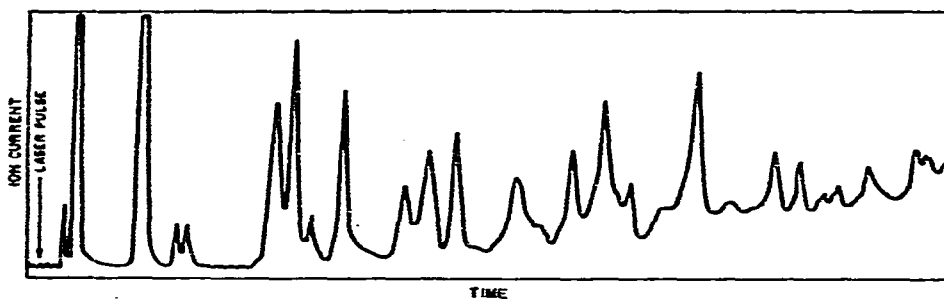


Fig. 4. Pyrogram from Gilsonite (Independence) sample. Tracing of total ion current during column elution. Column, Tenax, 2 m \times $\frac{1}{8}$ in. I.D. stainless steel; Carrier gas, helium; flow-rate 15 cm³/min; temperature program, 100–225 °C, 10 °C/min; laser, Nd (1.06 μ m), 2.5 J, 0.001 sec.

The first peaks are low-molecular-weight gases. As expected, acetylene (plasma) results in an intense peak. The fourth peak is propylene, the first of a series of terminal acetylenic compounds. For instance, acetylene derivatives of methyl (propyne), ethyl, isopropyl, *n*-propyl, etc. are apparent. Lastly, higher-molecular-weight fragments such as $C_7H_{12}O_2$, apparently molecular fragments from cleavage across the substituted back of the pyrrole ring, appear. Interestingly, there is little evidence of nitrogen-containing product compounds. Neither do we observe any compounds of molecular weight in excess of, approximately, 150.

From this behavior, we conclude that free-radical products are tagged with acetylenic fragments. The sediment is rapidly heated, forming, in part, an intense, carbon-rich plasma. This plasma radiates an intense thermal flux on the surface. At the termination of the event, the collapsing plasma, rich in the acetylene radical, merges into the hot surface and into short-lived radical species. Owing to the triple bond, the acetylene moiety is an effective quenching agent. Consequently, stable, terminal acetylene species are formed, typified by $HCC-CH_3$, from methyl radicals. Interestingly we observe little ethane, a compound which should form from dimerization of two methyl radicals. This compound cannot result when the acetylene species is present in high enough concentration that the radical-radical coupling reactions are dominated by acetylene.

The fact that these data show few nitrogenous compounds is interesting

TABLE II

LASER-GC-MS DATA ON GILSONITE REMOVED FROM THE INDEPENDENCE VEIN

Peak No.	Intensity	Retention time (min)	Base peak (a.m.u.)	Abundance	Highest intensity fragments				Peak identity
					1	2	3	4	
1	1330	1.4	28	313	28.0	16.2	15.2	14.2	CH ₄ /CO
2	8566	1.6	26.1	3167	26.1	28.1	25.1	44.1	C ₂ H ₂ /CO ₂
3	6481	2.9	41.1	1636	41.1	39.2	42.2	40.1	CH ₃ -CH=CH ₂
4	12251	3.6	40.1	208	40.1	39.1	38.1	28.1	Mixture
5	1199	3.9	40.1	188	40.1	39.1	28.0	44.0	C ₂ H · CH ₃
7	2749	5.6	41.1	596	41.1	39.1	56.0	55.0	CH ₃ CH ₂ CH=CH ₂
8	3487	5.9	54.0	539	54.0	39.2	53.0	50.0	C ₂ H · C ₂ H ₅
9	1267	6.3	52.1	160	52.1	51.1	28.0	50.1	C ₂ H · CH ₂ OH
10	2778	6.9	50.0	931	50.0	49.1	44.0	28.1	C ₂ H · C ₂ H
11	1629	8.2	55.1	184	55.1	42.2	39.1	28.0	C ₂ H · CH(CH ₃) ₂
12	2034	8.6	57.1	183	67.1	55.1	53.0	39.2	1-Pentene
13	2431	9.2	66.0	247	66.0	67.1	39.1	65.1	C ₂ H · CH ₂ CH ₂ CH ₃
14	1862	10.9	41.1	165	41.1	56.0	39.2	28.1	C ₂ H · CH ₂ COOH
15	2237	11.4	79.0	294	79.0	80.0	77.0	67.1	C ₂ H · nC ₄ H ₉
16	2855	12.1	78.1	548	78.1	77.0	50.1	51.1	C ₂ H · CH ₂ CHCHCH ₃
21	3212	14.0	91.1	552	91.1	92.1	44.1	39.1	C ₂ H · C ₅ H ₉
22	1669	15.3	44.1	178	44.1	91.1	55.1	41.1	C ₂ H · C ₅ H ₁₀
23	2280	15.6	91.1	297	91.1	44.1	28.0	106.1	C ₈ H ₁₀
28	2076	17.5	44.1	254	44.1	117.0	118.0	28.6	R-COOH
30	2420	19.6	44.1	360	44.1	28.1	115.0	130.1	R-COOH
31	2397	20.4	44.1	407	44.1	128.1	28.0	55.1	C ₇ H ₁₂ O ₂

and still only partially understood. This fact suggests that the nitrogen is left behind in the char, an observation that might have application in high-temperature fossil fuel processing.

Py-MS data were determined for a series of carbonaceous shales dating from the Devonian period. These samples were removed from a section of core cut from Hazard, Ky., U.S.A. — well No. 7239¹². Core sections were examined and geometric samples of 15 cm were ground and carefully homogenized. Standard geochemical measurements were made on those samples (Table III). Results show that these samples contain both mineral carbon and organic carbon. The color of these samples was from white-grey to dark brown. The color is, perhaps, a measure of

TABLE III

STANDARD ANALYSES OF POWDERED SAMPLES OF DEVONIAN SHALE (HAZARD, KY., U.S.A. —WELL 7239)

Sample	Color	Average depth (m)	%C	%H	%N	%CO ₂ *	%C _{org} *	%S*	%S _{pyr} *
A	White-grey	742.2	0.45	0.43	0.29	0.40	0.34	3.12	2.95
B	Light brown	749.9	5.78	0.76	0.23	0.60	5.61	3.00	2.75
C	Brown	761.8	3.67	0.61	0.22	0.80	3.45	3.20	3.03
D	Dark brown	765.0	4.62	0.66	0.22	1.31	4.26	3.04	2.95
E	Dark brown	792.5	7.78	0.90	0.30	0.94	7.52	4.38	4.11
F	Grey	813.1	0.61	0.39	0.10	1.35	0.24	1.31	1.16

* Analysis data supplied by Morgantown Energy Technology Center¹².

pyrite concentration. Some of the samples, like that from 742.2 m, have very low quantities of organic carbon (0.3%) while the sample removed at 792.5 m has 25 times as much. These sediments are known to be matured and produce only small quantities of low-molecular-weight gases when heated.

The Py-MS sampling technique offers methodology to deal with such materials. First, the sample size can be readily adjusted for optimum product delivery rates to the quadrupole filter. This is done by first using a trial suspension loading and then increasing or decreasing the sample size depending upon initial results. In that way, larger samples for low carbon content rocks are used than for rocks that have a high carbon content. Low electron-impact conditions are used. The intent is to charge gently the various fragments so that the possibility of additionally fragmenting pyrolysis products is minimized. This is essential since all products are analyzed concurrently.

A typical tracing from the Py-MS instrumentation is shown in Fig. 5. This result is the analog output of the data system that displays peak heights for each a.m.u. channel from 10 through 160. (No peaks were apparent at higher a.m.u. values.) Suspensions were made in methanol. Although the solvent was evaporated, residual methanol may appear at a.m.u. = 32. These data were run, once the proper sample loading was determined, in duplicate. Peak intensities depend on sample quantities. Moreover, the filament-sample interface complicates heat transfer. However, the ratios of particular components are a measure of replication. We chose to measure the ratio of the alkene/alkanes for C_3 through C_7 . Data are presented in Table IV showing the two sets for each of the six shale samples. As can be seen, the repeatability of these product ratios is adequate and suggests that sampling from such a liquid suspension does sufficiently homogenize the sample to obtain representative results.

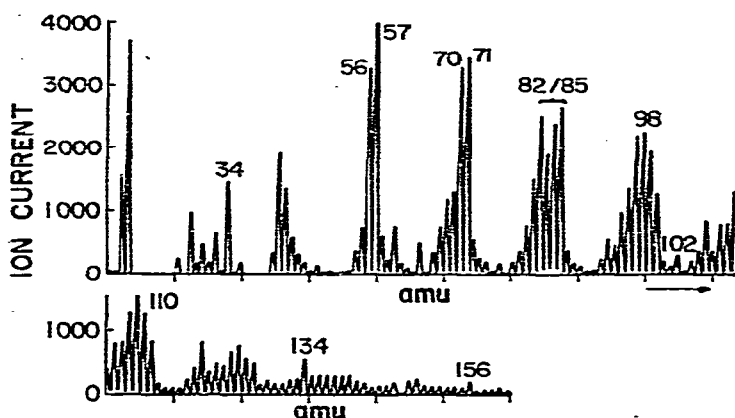


Fig. 5. Py-MS result from Devonian Shale sample. Pyrolysis, 1 sec at 510 °C; data acquisition, 250 scans; sample, Core 7239 Hazard, Ky., U.S.A., removed at depth of 792.5 m.

Py-MS data in Fig. 5 show a variety of possible product types. It follows that unambiguous identities can be assigned to certain masses but tentative identification can only be made in those other cases where a number of possibilities

TABLE IV
TYPICAL REPEATABILITY OF Py-MS ON POWDERED ROCK SAMPLES

Sample	Ratio of peak intensities (alkene alkane)				
	C ₃	C ₄	C ₅	C ₆	C ₇
A	1.71	1.92	2.03	1.67	4.00
	1.65	1.37	1.62	1.45	4.64
B	1.39	0.86	1.01	1.03	2.00
	1.37	0.89	1.12	1.16	3.00
C	1.30	1.01	1.06	1.02	2.67
	1.19	1.03	1.02	1.19	2.42
D	1.39	1.10	1.04	1.12	2.21
	1.42	1.08	1.15	1.08	1.64
E	1.37	0.82	0.95	0.90	1.56
	1.35	0.87	0.98	1.01	1.71
F	1.21	1.06	2.23	1.84	4.20
	1.89	1.47	2.07	1.77	4.14

TABLE V
MAJOR FRAGMENTS FROM LOW-VOLTAGE Py/MS
Data are percentage of total ion current

Compound	Mass (a.m.u.)	Depth(m)					
		742.2	749.9	761.8	765.0	792.5	813.6
NH ₃	17	2.88	1.86	2.25	2.00	1.49	1.89
H ₂ O	18	7.14	5.52	6.21	5.23	4.11	8.26
HC≡CH	26	0.51	0.48	0.40	0.46	0.33	0.66
CH ₃ OH	32	0.42	0.42	0.51	0.76	0.78	1.07
H ₂ S	34	0.58	1.33	1.10	1.16	1.84	0.89
C ₂ H ₅ OH	46	0.19	0.17	0.20	0.28	0.22	0.32
CH ₃ SH	48	0.07	0.08	0.10	0.10	0.13	0.05
SO ₂	64	0.52	0.36	0.40	0.30	0.58	0.71
Pyrrole	67	0.64	0.85	0.78	0.82	0.89	0.61
C ₅ (Ali)	70-72	8.51	8.64	8.82	8.23	8.64	9.18
CS ₂	76	0.06	0.08	0.10	0.10	0.17	0.07
Benzene	78	0.67	0.38	0.35	0.31	0.26	0.81
Pyridine	79	0.32	0.43	0.39	0.41	0.41	0.32
MeSSH	80	0.61	0.82	0.81	0.82	0.89	0.62
C ₂ H ₅ N	81	1.15	1.66	1.65	1.65	1.80	1.11
C ₆ (Ali)	84-86	5.19	6.32	6.35	6.16	6.46	5.39
Toluene	92	0.43	0.73	0.61	0.59	0.58	0.44
Picoline	93	0.37	0.51	0.47	0.51	0.55	0.36
Phenol	94	1.10	1.25	1.22	1.27	1.27	1.10
Furfural	96	1.98	2.62	2.68	3.08	2.82	1.96
Thiophene	97	2.30	2.58	2.68	2.59	2.70	2.20
C ₇ (Ali)	98-100	8.28	5.31	5.63	5.43	4.64	6.96
Styrene	104	0.54	0.23	0.23	0.26	0.22	0.42
Xylenes	106	0.37	1.00	0.86	0.87	0.90	0.39
C ₈ (Ali)	112-114	5.21	2.94	3.30	3.08	2.66	0.89
C ₉ (Ali)	126-128	1.52	1.12	1.18	1.12	1.21	0.89

exist. The significance of the chemistry of a particular situation must assist in limiting choices only to sensible possibilities. By intelligent appraisal one can arrive at a completely meaningful interpretation.

The present series of samples derived from this Devonian Shale core show a rather uniform picture of the organic constituents. There is also clear definition of the way that the distribution of these organic presences changes over the depth of the core section examined. Table V summarizes results of aliphatic and aromatic hydrocarbon presences along with some important derivatives. These data are plotted in Fig. 6 to correlate the distribution of "organics" with depth and indeed present a supportingly homogeneous picture. These results are in complete contrast to those emanating from classical geochemical methods which are to be seen in Table III and imply a far more heterogeneous situation¹². The C, H and N analyses (Table III) tend to support the Py-MS data. The interplay between the relative yields of aliphatics and aromatics/heterocyclics is immediately apparent and could well be due to some directive element within the matrix that increases the tendency for cross linking and hence of formation and evolution of aliphatic species in the cases of samples B, C, D and E. Although the two out-lying samples are low in carbon, these two samples show the same general maturation extent with subtle differences mentioned above.

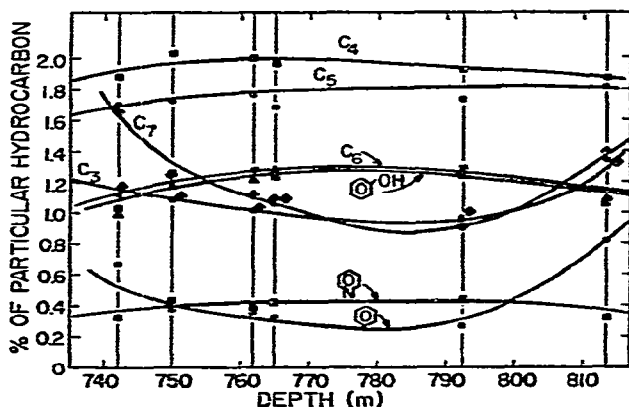


Fig. 6. Variation of selected parameters with depth of Devonian Shale core. Data show uncorrected channel counts (% of total) for several species as a function of depth.

Laser-GC-MS on these similar samples showed a series of low-molecular-weight compounds predominantly due to quenching of the high temperature plasma. The most intense high-molecular-weight compound was CS_2 . This stable compound should indeed form from pyrolysis of carbon rich pyrite systems. Most probably the acetylene radicals are efficiently quenched by the dominant sulfur in the pyrolysis environment.

CONCLUSIONS

There is every indication that both these approaches to problems inherent in the elucidation of carbonaceous geomatrices have merit. Data suggest a subtle

equilibrium between various carbon types and may point to the necessity for direct *in situ* sampling, and, possibly, analyses. High-energy laser pyrolysis in conjunction with GC-MS reveals interesting free-radical reactions that could be feasibly promoted in a system under controlled conditions. Py-MS can be viewed more as indicative of the direct excision of organics from a geomatrix by simple, perhaps serial, low-energy bond ruptures occurring under nearly ideal conditions. Here we probably approach the isolation of primary events.

Considerable more work is necessary before it would be wise to speculate upon the full significances of these results. It may be claimed, however, that we stand on the threshold of a new understanding of the interrelated processes of maturation and, perhaps, with that understanding a new appreciation of the energy potential of abundant fossil fuel resources.

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