

FIELD IONIZATION AND FIELD DESORPTION MASS SPECTROMETRY
APPLIED TO COAL RESEARCH

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Mass spectrometry offers a unique way to characterize coal liquefaction products. Molecular weight profiles of such complex mixtures of organic materials may be considered as the first step in the understanding of their nature in molecular terms. Molecular weight profiles may be produced by nonfragmenting mass spectrometry, which almost exclusively yields molecular ions. Field ionization produces molecular ions from most organic compounds (1). When a complex mixture is analyzed by this mass spectrometric technique, we obtain a single peak for each constituent or for a group of constituents that shares the same nominal molecular weight. By repeated multi-scanning, we can obtain a quantitative molecular weight profile of complex mixtures (2).

The detailed molecular weight profiles attainable by field ionization mass spectrometry are much more informative than molecular weight profiles obtained by gel permeation chromatography (GPC). Moreover, GPC is subject to artifacts caused by associations of solutes or by solute-solvent complex formations. The average molecular weight profiles obtained by vapor phase osmosis (VPO) contain minimal chemical information and are useful mainly in conjunction with prior chromatographic separation. The cost per mass spectrometric analysis is higher than by these two techniques, but the information obtained on each individual constituent or group of constituents would cost much more if obtained separately by other techniques. The advantage of the mass spectrometric technique is its universality; for the same sample, the same molecular weight profile will be obtained by different investigators using different mass spectrometers.

Low energy electron impact ionization, which induces relatively little fragmentation, has been proposed as an appropriate alternative technique for the analysis of complex organic mixtures (3,4) including fuels(5). However, an excellent systematic study by Scheppele *et al* (6), has shown that field ionization is by far superior for this purpose. This recent study has shown that the relative ionization efficiencies by field ionization of many different classes of organic compounds are very similar, ranging only over a factor of two. This can be compared with a range of over an order of magnitude for low energy electron impact on the same substrates. Moreover, it was shown (6) that once corrected for the small differences in ionization efficiencies, which can be programmed and calculated for known homologous series, the analysis of complex mixtures, like fuels, can produce quantitative results with a significantly lower variance than obtainable with low energy electron impact, following an identical computational correction.

Without such a correction, when dealing with unknown constituents, field ionization is by far a superior technique for obtaining semiquantitative information on the composition of highly complex mixture.

Field ionization is facilitated by the high field gradient that can be produced with very high curvatures. A cathode with a radius of curvature of about 0.1μ requires less than 1000 V to produce field ionization. Such a configuration is readily attainable in a reproducible manner by the appropriate technology. At SRI, we have developed a novel field ionization source, the preactivated foil slit type source (7). This source is superior to the now classical SRI multipoint source (2,8) because of its lower sensitivity to deactivation in the presence of oxygen-, sulfur-, or halogen-containing compounds. The new source comprises an activated tantalum foil on which carbonaceous dendrites are deposited from pyridine vapor at high temperature under a high electrostatic field (7).

The mass analyzer used by us for multicomponent analysis is a 60° sector, 25 cm instrument and has been described before (9). The temperature of the sample can be controlled independently of the temperature of the source. The temperature of the source is maintained constant and higher than the maximum temperature the sample is subjected to; this prevents memory effects and results in more controlled ionization conditions. This ionization source, which may be operated up to 400°C , may thus handle thermally stable compounds of very low volatility (9).

The ionization efficiency of our sources is 5×10^{-4} or higher, (10) which is comparable to that of advanced electron impact sources. However, owing to the relatively large area of our ionization source, the high energy of the ions produced, and their divergence, less than 10^{-4} of the ions produced are detected after mass separation. The overall efficiency of the present generation of field ionization mass spectrometers is about 2×10^{-8} ions/molecule for instruments with a magnetic sector analyzer and a resolution of 700.

Since most organic compounds have similar field ionization efficiencies (6), the molecular weight profile obtained by integrating all the spectra while evaporating the sample to completion truly represents the composition of the mixture. A number of examples of molecular weight profiles of different coal liquefaction products have been presented elsewhere (9). These spectra were obtained on our mass spectrometric system before it was interfaced with a PDP-11 computer. In this mode of operation, the mass range of interest was scanned repeatedly and synchronized with a 4096-multichannel analyzer operating in the multiscaler mode (8). The instrument integrates the spectra produced in each scan into a composite mass spectrum. The integration over time is necessary because the sample is evaporated slowly and the composition of the vapor phase changes because of the wide range of volatility of the different components. This field ionization mass spectrometric system thus facilitates the quantitative analysis of molecular weight profiles of mixtures that may contain constituents varying in their vapor pressure by many orders of magnitude (estimated range, 10^{10}) over a mass range up to 2000 amu with a resolution of $M/\Delta M = 800$.

Computer Controlled FI Multicomponent Analysis

The published field ionization spectra of coal liquefaction products (9) are just the first step in the full utilization of field ionization mass spectrometric multicomponent analysis. These are chart recordings from a 4096-channel analyzer and, although the information in each channel is digitized, these spectra give us only a means of visual inspection of the gross feature of the spectra. Accurate mass assignment and the integrated ion counts under each peak are lacking, and these are necessary for any detailed quantitative interpretation of these complex spectra.

We would also like to know the "history" of each peak--the actual rate of accumulation of the ions of a given nominal molecular weight as a function of time and temperature of the analyzed sample. This information is necessary for estimating the number of materials of the same nominal molecular weight that contributed to a given peak. Moreover, from the temperature profile of a given peak, it may be possible to deduce whether some of the contributing ions originate from a chemical process (e.g., pyrolysis, dehydrogenation) that took place in the sample while the sample probe was being heated. Obtaining, for instance, a material with a molecular weight of only 150 when the probe temperature reaches 300°C suggests that it may be a secondary pyrolytic decomposition product. The temperature profile analysis may help us to distinguish between these two possibilities and even determine the activation energy for the appearance of the given species.

To achieve these goals, we have interfaced our mass spectrometric system with a PDP 11/10 dedicated computer (Fig. 1). The computer controls the magnet scan of the mass spectrometer by means of the 12-bit digital-to-analog converter (DAC). The data acquisition program increments the input to the DAC at precisely controlled time intervals so that each channel is receiving ions counted for exactly the same amount of time. At the end of each time interval, the computer causes the ion counts accumulated by the 10-MHz counter to be transferred to the 12-bit buffer register. The counter is cleared and restarted in less than one microsecond, so the interface has a negligible dead-time and no ion counts are missed. The DAC input is incremented by one unit, and the ion count in the buffer is transferred to the computer and added to the previous ion counts for that channel. The time spent at each channel, or in other words, the scan rate of the mass spectrometer, is variable and is controlled by the operator through the data acquisition software. Actual time intervals are measured within the computer by a programmable clock based on a very stable quartz crystal oscillator.

The output from the DAC is a linear voltage ramp, since each of the 4096 possible channels is active for an equal amount of time. Since the mass of the ions focused on the mass spectrometer's detector varies as the square root of the magnet current, the magnet scan control unit is used to convert the linear voltage ramp into a signal that drives the magnet power supply to produce a linear mass scan.

The 12-bit analog-to-digital converter (ADC) is connected to a temperature programmer for the solids probe. At the end of each mass spectrometer scan, the temperature of the probe is recorded for later use in the printed reports or data analysis. Since the temperature programmer is digitally driven, a given temperature program can be very precisely reproduced to allow meaningful comparisons between samples. Our experience indicates that most pure compounds are volatilized over a narrow temperature range of 10-30°C. Thus, separate peaks will be observed in

the temperature profile of a single mass if there is more than one component of the sample with that particular molecular weight. It is possible to distinguish between genuine low molecular weight components of a sample and those resulting from the thermal decomposition of much larger molecules because these two different types of species appear at very different temperatures. Our experiments show no indication of significant pyrolysis of coal liquefaction products or of crude oils.

The report program produces reports listing the masses and total ion counts for each peak in the spectrum. Two different formats are available: one is a simple table of the peak mass and intensity, and the other is the same information arranged in a fixed format with 14 masses in each row. The advantage of this second format is that homologs are all listed in the same column, making it easy to pick out groups of peaks that may have similar chemical structures.

The plotting program produces simple bar graphs of the mass spectra on the X-Y recorder. Full-scale intensity is arbitrarily chosen as 50 and the entire spectrum is automatically scaled, if necessary, by dividing all peak intensities by an integer. Figure 2 is an example of a spectrum plot obtained in this manner. These spectra are evidently superior in quality to those obtained with the multi-channel analyzers (9).

Additional programs are available for performing simple but useful data handling tasks. These include programs for listing on the terminal the ion counts in each channel of a raw data file and a program for summing the data in several files into a composite spectrum. The latter program is useful for obtaining the molecular weight profile of a complex multicomponent mixture by adding together all the spectra obtained from a sample.

Additional examples of the types of information currently available from the combination of FIMS and the PDP 11/10 computer are shown in Figs. 3a and 3b. The sample was fractions 1 and 2 of basic compounds from an H-coal product and was provided to us by the Atlantic Richfield Company. The evolution of this spectrum as a function of temperature is presented in Figs. 3a and 3b. This figure presents the plotted spectra integrated within the different temperature ranges during the evaporation of a single sample.

The first three spectra in Figure 3a show volatile components of the sample that came off as soon as the sample was introduced into the mass spectrometer. When the signal produced by these volatile materials began to decrease, the operator started the temperature program, heating the sample at about 2°C per minute. The heating rate was increased twice during the run to maintain a reasonably high signal as the less volatile components were being analyzed. Finally, three spectra were recorded at 325°C, (Figure 3b) which was the final probe temperature for this sample. Weighing the sample before and after analysis showed that 94% of this material was volatilized.

These results illustrate the vast amount of information to be obtained by combining chemical separations with nonfragmenting FIMS in the analysis of coal liquefaction products.

Figure 4 is an example of a spectrum of a crude oil analyzed by the computer in the same manner as the samples presented in Figures 2 and 3. The only difference was that the crude oil sample was "weathered" in the probe at room temperature to remove the most volatile constituents. The same sample was analyzed 5 times to assess the variance of the analytical procedure. Figure 5 presents the standard deviation of each of the mass peaks as a function of molecular weight. One can see here that the constituents below 250 amu have a high variance due to irreproducible preevaporation ("weathering") but in the mass range 250 to 550, the standard deviation is in the range of 3 to 6%, which is very satisfactory for such a complex analysis. It should be noted that even the most abundant constituents in our complex mixture amount to just about 0.6% of the total. At higher molecular weights, there is an increase in the variance predominantly because of the lower abundance of these constituents and possibly also because of some irreproducible pyrolysis or polymerization of such minor components. The effect of abundance on the variability of the individual constituents can be seen in Figure 6 which also presents the theoretical lower limit of variance due to statistical fluctuations of the ions counted. The two lines "200" and "800" designate the theoretical limit for these two extreme cases of molecular weights. The limits are different because of the difference in the monitoring time per amu during the magnetic scanning. The actual variance is about 2 to 3 times higher than the theoretical lower limit. This is fairly satisfactory in view of the complexity of the sample and the analytical procedure.

Field Desorption Experiments

Two years ago, we developed at SRI a novel type of field desorbing source that used a broken metal tip (11). We have also shown that ionic and other polar substances field desorb more readily when dissolved in an appropriate nonvolatile matrix. Our preliminary tests on low molecular weight hydrocarbon polymers were highly encouraging (9). Recently, we have extended our experiments, using broken graphite rods and bundles of graphite rods and bundles of graphite fibers as field desorbing sources, with even greater success. We applied these sources to the analysis of asphaltenes. Figure 7 shows a field desorption spectrum (obtained on a multichannel analyzer) of the asphaltenes of SRC produced from Illinois No. 6 coal. The spectrum was obtained from a graphite fiber field desorbing bundle at 205°C.

An example of a computer handled FD spectrum of asphaltenes (produced from Kentucky coal) is presented in Fig. 8. In order to provide a direct comparison of the characteristics of FD and FI spectra currently available, Figures 8-12 show the raw data as it was acquired by the computer, rather than the normal bar-graphs. The resolution of the FD spectrum is inferior to that obtained by FI of the same sample (Fig. 9), probably due to the wider energy spread of the field desorbed ions, as well as to the fluctuating nature of the FD ion beam. Note, however, the significant mass peaks at about 395 amu in the FD spectrum which are absent in the FI spectrum. This feature appears again at somewhat higher temperatures (157-158°C) as shown in Figure 10. Figure 11 a-d present FD spectra in the temperature range 160 to 187°C. Comparison of these spectra with the FI spectrum over the same temperature range (Fig. 9) and over a higher temperature range (Fig. 12) shows that under FD, one ionizes the same constituents, or other compounds of comparable molecular weight, at significantly lower temperatures. The reproducibility and resolution obtained by FD are, however, major limiting factors in the application of

this technique as a quantitative way to characterize coal products. Some of these limitations could be overcome by focal plane simultaneous ion collection techniques (e.g., photoplate mass spectrography).

Summary

We have shown that mass spectrometric multicomponent analysis techniques are ideal for the characterization of coal liquefaction and fuel products. These include the capability of determining molecular weight profiles up to 1000 amu with unit amu resolution and the ability to obtain and record molecular weight profiles as a function of sample temperature during a temperature programmed evaporation of the analyzed sample.

Combined with appropriate liquid chromatographic separation techniques or certain fast and quantitative derivatization procedures to separate coal liquefaction products into families of compounds, advanced FIMS offers an unprecedented, precise and meaningful analytical methodology for the characterization of coal products.

The field ionization technique described in this paper is not yet perfect, and it requires some further development in the areas of instrumentation, sample pretreatment, and data handling. However, there is sufficient evidence that this technique can provide the basis for one of the most comprehensive analytical methodologies ever available to coal research.

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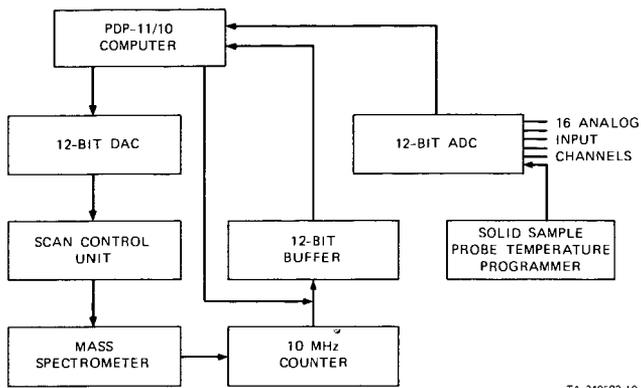


FIGURE 1 MASS SPECTROMETER-COMPUTER INTERFACE

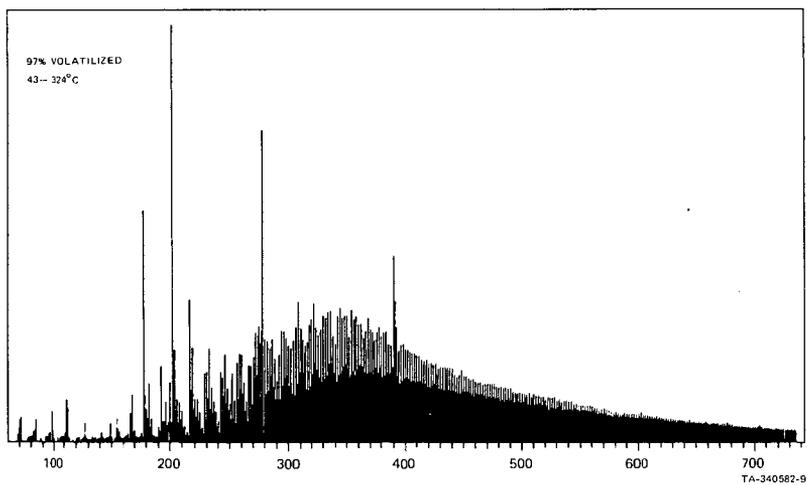


FIGURE 2 KENTUCKY 9/14 SRC, OILS FRACTION (SOURCE: ARCO)

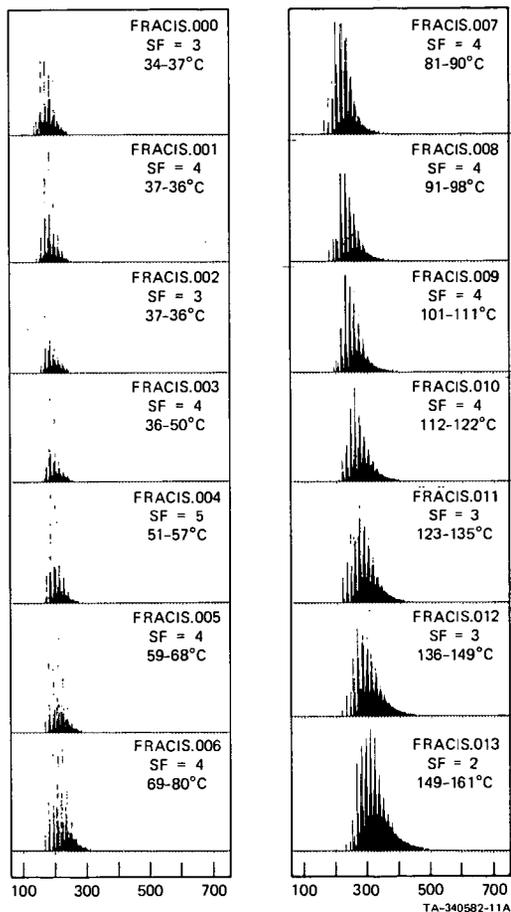


FIGURE 3A FRACTIONS 1 AND 2 FROM H-COAL PRODUCT 177-57-49 BY COLUMN CHROMATOGRAPHY (SOURCE: ARCO)

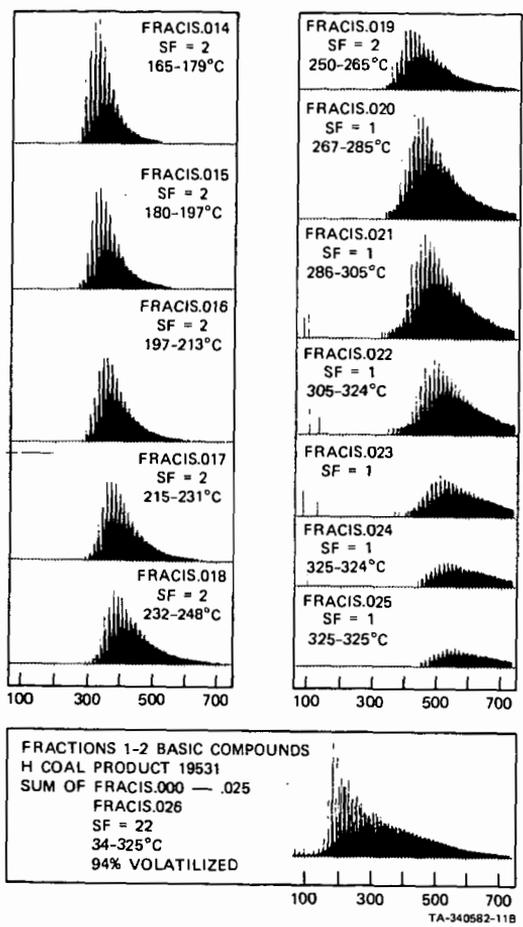
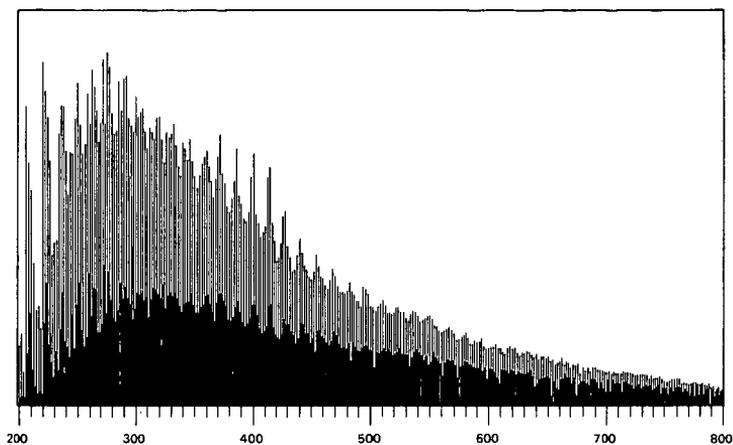
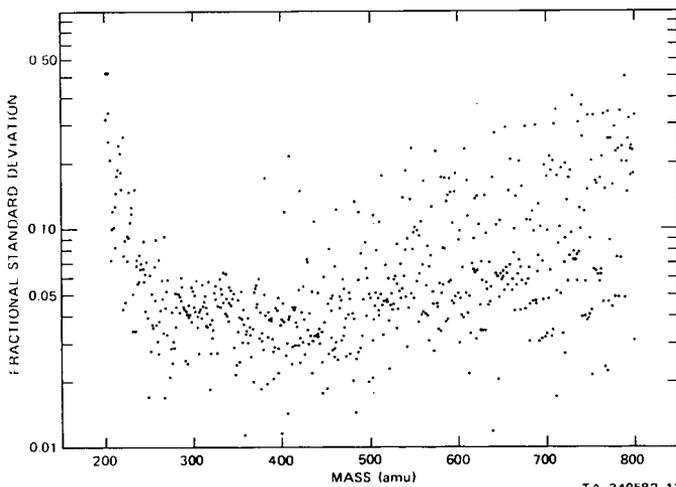


FIGURE 3B FRACTIONS 1 AND 2 FROM H-COAL PRODUCT 177-57-49 BY COLUMN CHROMATOGRAPHY (SOURCE: ARCO)



TA-340582-14

FIGURE 4 VENEZUELAN OIL WEATHERED IN MASS SPECTROMETER



TA-340582-13

FIGURE 5 STANDARD DEVIATION OF EACH OF THE MASS PEAKS AS FUNCTION OF MOLECULAR WEIGHT

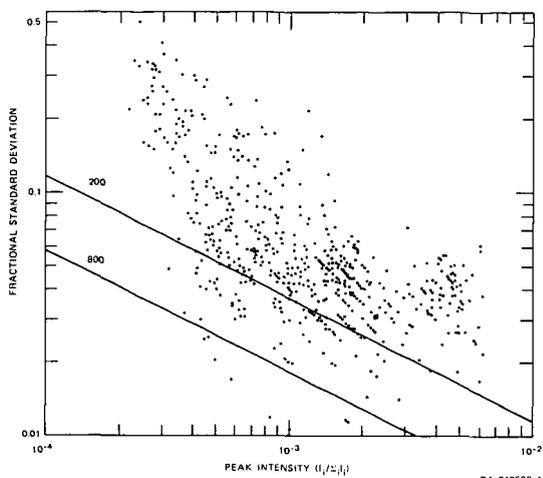


FIGURE 6 EFFECT OF ABUNDANCE ON VARIABILITY OF INDIVIDUAL CONSTITUENTS

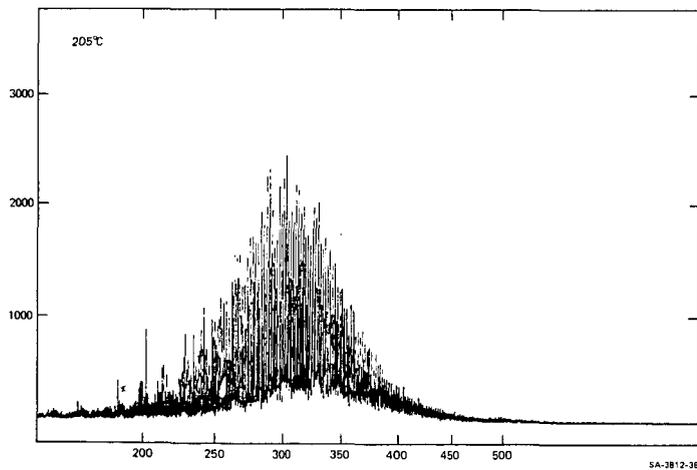


FIGURE 7 ASPHALTENES FROM ILLINOIS NO. 6 COAL, SRC PRODUCT, ARCO SAMPLE NO. 9634, GRAPHITE FIBERS SOURCE - FDMS

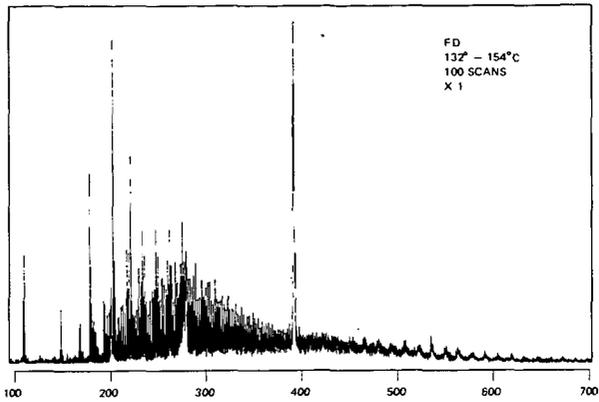


FIGURE 8 FIELD DESORPTION MASS SPECTRUM OF KENTUCKY SRC ASPHALTENES, 132°-154°C

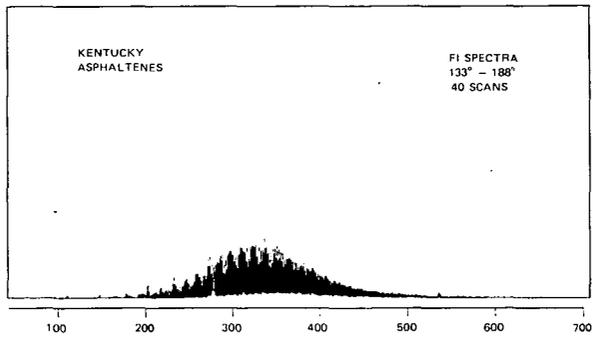


FIGURE 9 FIELD IONIZATION MASS SPECTRUM OF KENTUCKY SRC ASPHALTENES, 133°-188°C

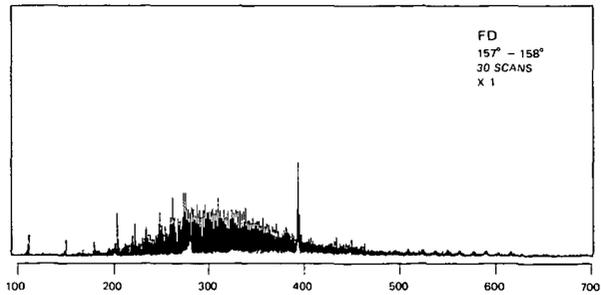


FIGURE 10 FIELD DESORPTION MASS SPECTRUM OF KENTUCKY SRC ASPHALTENES, 157°-158°C

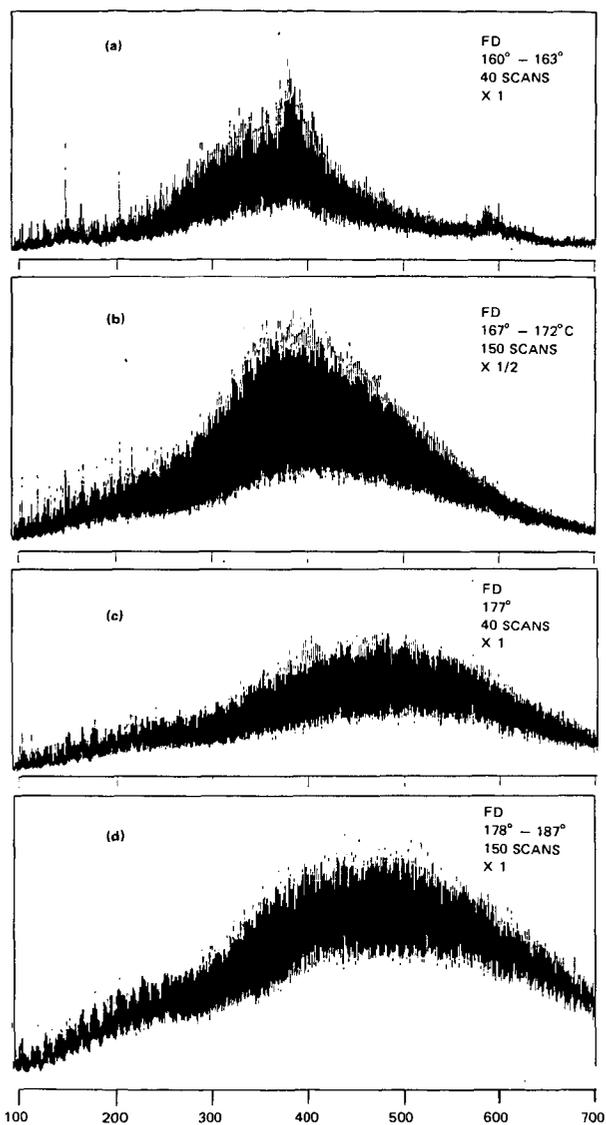


FIGURE 11 FIELD DESORPTION MASS SPECTRA OF KENTUCKY SRC ASPHALTENES, 160°-187°C

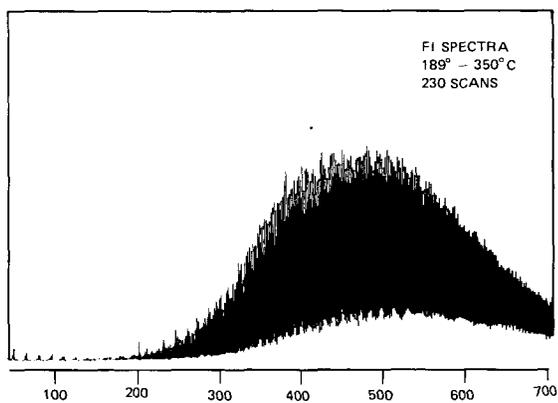


FIGURE 12 FIELD IONIZATION MASS SPECTRUM OF KENTUCKY SRC ASPHALTENES, 189°-350°C