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Three Dimensional Fluorescence And Capillary
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Gasoline Samples

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Jay A. Siegel
Major professor

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THREE DIMENSIONAL FLUORESCENCE AND CAPILLARY GAS CHROMATOGRAPHY OF NEAT AND EVAPORATED GASOLINE SAMPLES

by

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Abstract

Three Dimensional Fluorescence Spectroscopy and Capillary Gas Chromatography Of Neat And Evaporated Gasoline Samples

by

Laureen Marinetti-Sheff

Arson is an expensive and dangerous crime in the United States today. Prosecution of this offense depends on locating and placing a suspect at the scene. Most of the physical evidence is destroyed by the fire but usually the accelerant used can be successfully recovered. The common method of analysis of accelerants is capillary gas chromatography.

Capillary gas chromatography and three dimensional fluorescence spectroscopy were used to analyze nine assorted brands and grades of gasolines both neat, 50% and 100% evaporated. Capillary gas chromatography could not distinguish between any of the samples either neat or evaporated nor could it relate an evaporated sample back to its unevaporated form.

Three dimensional fluorescence spectroscopy can distinguish the samples neat and evaporated. It could not relate a totally evaporated gasoline sample back to either the original neat one or the 50% evaporated one. The comparisons were made both visually and with a subtraction program.

ACKNOWLEDGEMENT

First and foremost I would like to thank my husband, Bernard, who always gave his support and instilled in me the confidence I needed to complete this thesis. I would also like to thank my co-workers at the Michigan State Police Crime Lab in East Lansing for their support and help.

In addition I would like to send a special thanks to my parents who greatly simplified this work by providing a personal computer and to my inlaws who happily babysat my son, Benjamin, while I completed this work.

In conclusion I would like to thank Dr. Jay Siegel for his help in getting me "up to snuff" in an area that I had not worked in for a long time. Without his help it would have been impossible for me to finish this thesis.

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Chapter One

Introduction

Arson is a very serious crime in the United States today. It costs Americans billions of dollars each year in damages, not to mention thousands of deaths and injuries. Despite the fact that arson is so widespread, arrests of the perpetrators of these crimes are alarmingly low. Out of 5,497 arson crimes in Michigan in 1987 only 8.9% were cleared by arrests(1). This is due to the nature of arson itself.

Arson involves the malicious destruction of property or material goods by intentionally setting it on fire. This usually involves the deposit of some type of accelerant to start and maintain the fire. The accelerant is placed on, in or around the area or item to be burned. It is then ignited by the perpetrator who usually leaves the scene long before the fire is discovered. Any of the usual types of evidence left at a crime scene such as fingerprints, footprints, hair, fibers or blood may be either destroyed by the fire or by its extinguishing.

Thus in the ensuing investigation, it can usually be determined that a fire is arson but finding and convicting the perpetrator depends on either an eye witness or someone with knowledge of a person or persons who would have something substantial to gain by setting the fire. If a suspect is located, then the investigator must place him at the scene. With most of the usual evidence destroyed this can be a very difficult task.

If the fire was set using a liquid accelerant then there is a good chance that some of it can be recovered. Except in the case of gases or alcohols, rarely does a fire consume 100% of the accelerant. Since the accelerant is a liquid, it will usually soak into any porous material or surface on which it is deposited. The portion of the accelerant that soaks down into a porous surface, where there is little or no oxygen present, will not be consumed in the fire. In addition, even though thousands of gallons of water may be used to put out the fire, a hydrocarbon liquid accelerant will remain since it does not mix with water. For example, gasoline or oil floats on the surface of water.

Taking these facts into consideration and also that a fire scene investigator can determine the origin of a fire hence the prime location of an accelerant if it is present, the investigator knows where to collect evidence. This requires that any porous material present at and around the fire's origin be collected in an air tight container and sent to the forensic science laboratory as soon as possible. If an accelerant is found in the possesion of a suspect and this can be compared to the accelerant found at the scene then, based on the results of the comparison, the suspect may either be ruled out or the case against him strengthened.

Hydrocarbon accelerants are inexpensive and readily available. They can be purchased without raising any suspicion. For instance it is extremely common to buy or posses gasoline, lighter fluid or fuel oil, hence the importance of hydrocarbon analysis by the forensic science laboratory.

Currently, analytical methods used for hydrocarbon analysis can differentiate among classes of petroleum based products such as oils from gasolines or lighter fluids. However, problems may arise when samples within the same class of petroleum based products require differentiation, such as two brands of gasolines.

This thesis addresses the problem of differentiation among gasoline samples. Most forensic science laboratories currently employ capillary gas chromatography to characterize gasoline samples. However, chromatography is inadequate for determining the specific brand or grade of gasoline because the data is not discriminating enough. Therefore a technique that will provide the necessary data would be extremely valuable not only in the analysis of gasolines but other petroleum products as well. Three dimensional fluorescence has been evaluated as a possible analytical technique in helping to provide more information when analyzing gasolines and other hydrocarbons.

Fluorescence is a physical property that some compounds have such that they can be excited to a higher energy level and emit energy when they return to their original energy level. When the compound is exposed to a certain wavelength of light one of its electrons will be energized to a higher energy level than its normal ground state. However, the compound is not stable in this higher energy state so the electron returns to the original ground state. When this occurs a different wavelength of light energy is given off than the original wavelegth. The wavelength required to elevate to a higher energy level is termed the excitation wavelength and the wavelength emitted when the orignal ground state is acheived is termed emission. Both the excitaiton and emission constitute fluorescence. In two dimensional fluorescence spectroscopy, a simple spectrum is derived by either scanning the emission wavelength region while holding the excitation wavelength constant or vice versa. However, in three dimensional fluorescence a more complete picture of the fluorescence characteristics of a sample is possible. This is because a series of emission spectra are scanned over the entire wavelength range of fluorescence while the excitation wavelength is varied by a fixed increment. Each of these spectra are then plotted in a pseudo three dimensional array on the same set of axes. The x-axis represents the emission wavelength, the y-axis represents the excitation wavelength and the z-axis represents the fluorescence intensity.

This thesis will build upon previous work done in this area. It includes the analysis of nine brands and grades of gasoline. They will initially be compared on the basis of their three dimensional fluorescence plots to determine if they can be differentiated by this criterion. A plot subtraction program will be employed when necessary to compare samples. This program subtracts one three dimensional emission stack plot from another and calculates a Pearson's Q coefficient to determine the similarity of the two plots. The closer Pearson's Q is to one the more similar the plots are. Capillary gas chromatograms will also be obtained for the nine samples. Then the gasolines will be evaporated under controlled conditions to observe the effects of weathering on the fluorescence and the chromatograms.

Evaporation will serve to more closely simulate the actual conditions upon which gasolines are encountered in forensic science case work. The evaporation will take place in two steps. First each gasoline will be evaporated to 50% of original volume and finally to dryness. Gas chromatograms will also be obtained. The information generated from the three dimensional fluorescence will be analyzed to determine if gasoline samples are unique when characterized by these methods.

Chapter Two

Literature Review

EARLY CHROMATOGRAPHIC METHODS OF HYDROCARBON ANALYSIS

In the 1960's analysis of gasolines was primarily concerned with characterization of the hydrocarbon component. In an early article by Lucas (2) it was demonstrated how different types of petroleum distillates could be differentiated by gas chromatography. It was shown how gasolines could be distinguished from kerosenes, fuel oils, floor cleaners or varsol. Twenty eight gasolines were studied. All of the samples separated into 26 fractions with 75% of the hydrocarbons in the 0-5 minute retention time range. Point by point comparisons were carried out and it was concluded that gas chromatography had great potential in the identification of petroleum products and the possibility of differentiation of brands within a specific type.

A later study by Sanders et.al.(3) introduced a capillary gas chromatography method that showed detailed compositional data of hydrocarbons in complex gasoline mixtures. They identified many of the 240 peaks that were generated in the two hour run. They also noted a "light end loss" (loss of low boiling point hydrocarbons) from the front end of the chromatograms if the gasoline samples were not kept refrigerated.

Subsequently gas chromatography and infrared spectrometry were used by Ettling (4) for isolation and identification of trace amounts of hydrocarbons in fire remains. He determined that as little as 10mg could be detected with infrared spectrometry. He used gas chromatography as a backup method for further characterization of the hydrocarbons.

Then Ettling et.al. (5) attempted to determine the presence of an accelerant in fire remains by first devising what a "normal level" of hydrocarbons in fire remains would be. This was accomplished by first using headspace gas chromatography followed by extraction of the remains and liquid chromatography performed on the extract. The authors decided that this method was not useful because hydrocarbons could either be destroyed or created by the combustion process of the fire thus making a "normal level" of hydrocarbons an unmeasurable variable.

DEVELOPMENT OF OTHER METHODS OF ANALYSIS FOR HYDROCARBONS

Several different approaches have been studied for the analysis and characterization of petroleum products in the 1970's. Mattson (6) studied the technique of fingerprinting (individualizing) oil samples by infrared spectrometry. He did not find this to be as useful as gas chromatography had been. He determined the best method utilized both gas chromatography and infrared spectrometry.

In two articles by Bentz (7)(8) on the identification of oil samples, a multi-method approach was recommended. When thin layer chromatography, gas chromatography, infrared spectrometry and low temperature luminescence were performed, oil sample identification would occur to greater than 99% if the samples had a common origin.

In another article, Bentz (9) compared several methods of oil spill identification. These were then ranked in order of the most useful results obtained. He concluded that gas chromatography and infrared spectrometry were the best methods followed by fluorescence spectrometry.

Saner et.al. (10) found that thin layer chromatography used in the analysis of waterborne petroleum oils, showed a 0.968 probability of correctly matching an oil spill sample to a suspect oil sample in the sample set he used.

Fortier et.al.(11) explored low temperature luminescence spectrometry for the identification of fuel oils. The samples were identified by comparison to a visual overlay of the sample in question. The advantage of this method is that both phosphorescence and fluorescence are available. However the disadvantage is that a complete picture of the total luminescence (both phosphorescence and fluorescence) cannot be seen because only three excitation wavelengths were used. The extremely low temperatures required for phosphorescence can also cause problems in utilizing this method in that most laboratories do not have the means to cool and maintain a sample at sub-zero temperatures during analysis.

Gas chromatography/mass spectrometry has been utilized for the analysis of characteristic polycyclic aromatic hydrocarbons in gasoline samples under controlled distillation, evaporation and burning conditions by Mach (12). However, mass spectrometry requires that a clean sample be analyzed which is seldom found in evidentiary material. In some cases contaminants are present in such large quantities that they mask the presence of the accelerant. This is especially true for capillary gas chromatography when the accelerant is in some type of partially burned carpet. Unfortunately not only is this the method most crime laboratories use, carpet samples from fires are extremely common as well.

Saner et.al. (13) took the methanol extractable fraction of oil from oil spills and analyzed it by liquid chromatography. This method suffered from pollution and weathering problems that a sample of oil from a spill would undoubtedly expierence. The method could not match the suspect oil to the oil spill sample in all the cases studied.

FURTHER DEVELOPMENT OF FLUORESCENCE IN THE ANALYSIS OF HYDROCARBONS

The 1980's showed increased interest in fluorescence methods for the analysis of petroleum products. A computer controlled instrument for performing multiparametric

fluorescence measurements was devised by Holland et.al.(14). This set the stage to begin exploring this type of methodology.

An early explorer of this idea was Lloyd et.al.(15), who examined a collection of high molecular weight petroleum products by sychronous fluorescence spectroscopy. The objective of this study was to develop and evaluate synchronous fluorescence as a standard technique to be used in the analysis of such evidence. Synchronous fluorescence views the fluorescence of a sample at multiple excitation and emission wavelengths. Eight different samples drawn from forensic science case work were analyzed. The results showed that the same fluorescence characteristics are present in most samples with sample differentiation being dependent on the relative fluorescence intensities. Samples from different sources could be differentiated by visually comparing fluorescence intensities. Samples of common origin looked markedly similar but could not be discounted as having different origins. Samples were reanalyzed over time with the same results. The authors determined that synchronous fluorescence can be successful in that common spectral patterns can be efficiently recognized and retrieved with a low level of error.

Two articles by Kubic et.al.(16)(17) describe variable separation synchronous excitation fluorescence. In this method excitation and emisson wavelengths are scanned simultaneously at different rates thus allowing multiple views of the fluorescence spectra. This creates a simulation of a three dimensional fluorescence spectrum without plotting software. The first article applied this method to the analysis of automobile engine oils (16). In the second article the authors attempted to distinguish used automobile engine oils (17). All but 2 of the 45 oil samples studied could be differentiated.

Blackledge et.al. (18) studied 16 commercial products having a petrolatum base by liquid chromatography and synchronous fluorescence spectrometry. He was able to distinguish all 16 of the samples using as little as 0.5mg. However, interferences from detergents and sizing used on the clothing commonly encountered with this type of evidence could occur. Infrared spectometry and proton magnetic reasonance spectrometry were also used in this study and were determined to have little value for comparison purposes.

Warner et.al. (19) determined that for most pure luminophores the emission spectrum is independent of the excitation wavelength and vice versa. Petroleum products are not pure luminophores, therefore it would be expected that their emission spectra would vary depending on the excitation wavelength used. This fact makes it desirable to devise a method that can view the emission spectrum at various excitation wavelengths thus enabling a more complete picture of the total fluorescence of the sample. As referred to previously Holland et.al.(14) had devised a completely automated system capable of simultaneous absorption and fluorescence measurements, therefore indicating that computer processing of such a multiparametric method could be accommodated.

Siegel (20) proposed such a method called, (by the manufacturer Perkin Elmer), three dimensional fluorescence spectroscopy. Fluorescence properties vary with the relative amounts and different types of polycyclic aromatic hydrocarbons present in the sample. Therefore a method that can view the fluorescence properties of a sample at multiple wavelengths thus characterizing the total fluorescence properties of the sample is valuable in the comparison of two similar samples such as brands of gasoline. Also data processing was introduced that would subtract one three dimensional plot from another to further clarify a comparison of two samples.

Duggan et.al.(21) recognized the need for a multiparametric method to analyze multicomponent environmental samples such as oil spills. His method scanned the excitation and emission wavelength range of interest only. The emission wavelength was scanned between 300 and 600nm while the excitation wavelength was stepped up by 1nm between each scan. This completely characterizes the fluorescence properties of very complex mixtures within the specified excitation and emission wavelength range. A computer with a program capable of plotting and storing all the data collected was interfaced to the fluorimeter.

Three dimensional fluorescence was used to identify major components of crude oil that had come in contact with sea water by Ostgaard (22). Siegel et.al.(23) examined motor oils and lubricants using three dimensional fluorescence. In addition, the resultant three dimensional emission stacked plots were compared by subtracting one from another via computer rather than just by a visual comparison. Ten motor oil and eleven lubricating oil samples were tested. When subtracted, the plots of oils with a common origin resulted in a flat plane indicating no net fluorescence. However, when the plots of samples with different origins were subtracted from each other a net fluorescence was obtained resulting in a plot with "hills and valleys". The authors concluded that the large amount of spectral information generated and the ability to manipulate it by computer, made three dimensional fluorescence an effective method of comparison for motor oils.

Three dimensional fluorescence was also evaluated by Siegel et.al.(24) using gasoline samples. By utilizing the subtraction program developed by Siegel the authors were able to determine if two gasoline samples could have had a common source. The study also addressed whether any common features were present when comparing grades of the same brand of gasoline or a group of gasolines of the same grade.

Siegel et.al.(25) examined petrolatum based products utilizing three dimensional fluorescence. The same subtraction program was used to compare samples. The authors concluded that the petrolatum products studied could be differentiated by this method. In fact this method has been used in actual forensic case work on more than one occasion with successful results.

Mann (26) compared gasoline samples qualitatively and quantitatively using capillary gas chromatography. It was determined that gas chromatograms of neat gasolines demonstrate variability. The authors claim that the ability to discriminate among gasolines depends on resolution in the C4 to C8 region of the chromatogram. Mann concluded that this would be a good technique for differentiating gasolines with different sources. In his second paper Mann (27) discussed capillary gas chromatography as it applies to actual case work. He concluded that the region most important for the comparison of two gasolines is altered before the gasoline is 40-60% evaporated thus making comparison much less meaningful. However it may still be able to be determined if two gasoline samples have a different origin.

Guinther et.al.(28) analyzed gasoline at various stages of evaporation. The authors used capillary gas chromatography to analyze their samples. They concluded that the least volatile components increase dramatically in concentration as the gasoline is evaporated. This change proved to be reproducible thus allowing evaporated gasolines to be isolated and identified as such.

Finally Siegel et.al.(29) studied 22 midrange petroleum products (charcoal lighters, paint thinners and synthetic solvents) by three dimensional fluorescence and capillary gas chromatography. The samples were evaporated and partially combusted. The authors found that three dimensional fluorescence was much better at discriminating among similar products than was capillary gas chromatography, which could only put the products into broad classes. They also found that when the samples were partially or totally evaporated the three dimensional plots could not be related back to the neat plot of the same sample. However the three dimensional results were consistent as long as the sample was evaporated to the same degree. Combusted samples did not yield any useful information by capillary gas chromatography. The combusted samples did have informative three dimensional plots except that the same plots could not be repeated on subsequent burnings. The authors performed a blind test on neat samples, which showed three dimensional fluorescence to be the more reliable technique for determining whether or not two samples were of the same brand.

The current study will further evaluate the combination of the three dimensional fluorescence and capillary gas chromatography methods in the analysis of neat and evaporated gasoline samples. The gasolines were evaluated based on the changes they exhibited in both methods when they were subject to evaporation. Since gasolines are complex mixtures of various multicomponent entities the loss of the most abundant component of the volatile hydrocarbons through evaporation should leave behind the less abundant components that may not be visible. These include the various additives that the manufacturer and refinery add to the different gasolines (30) as well as the higher molecular weight hydrocarbons. These additives would be the most likely component of gasolines to vary significantly between brands, grades and lots. Therefore it may be possible to distingusih brands, grades and lots with capillary gas chromatography and three dimensional fluorescence spectroscopy.

Chapter Three

Materials and Methods

Nine brands and grades of gasolines were chosen for this study. They were obtained from commericial sources and stored in a refrigerator in brown glass screw cap bottles. The samples were as follows: Mobil Unleaded, Mobil Super Unleaded, Shell Regular, Shell Unleaded, Standard Regular, Standard Unleaded, Standard Premium, Total Regular and Total Unleaded. Spectrograde cyclohexane (B&J) was employed as the solvent without further purification. Fluorescence spectra and gas chromatograms of cyclohexane showed no interference.

Glassware Preparation

Non-disposable glassware, including pipettes, volumetric flasks, beakers and quartz fluorescence cuvettes, were prepared using the following procedure to insure that residual fluorescence from a previous sample or from cleaning would not be a problem.

1. Rinse once in fluorescence grade cyclohexane
2. Rinse once in acetone
3. Rinse once in distilled water
4. Rinse once in concentrated nitric acid
5. Rinse again in distilled water
6. Dry in a 60 C oven

Sample Preparation

1. Ten ul of gasoline were placed into a ten ml volumetric flask and diluted to the mark with spectrograde cyclohexane.

2. One ml of the solution prepared in step #1 was placed in a second ten ml volumetric flask and diluted to the mark with spectrograde cyclohexane.

3. Step #2 was repeated using the solution made in step #2. This was the final dilution to a concentration of ten parts per million (ppm).

4. The solution made in step #3 was kept covered to prevent evaporation and was analyzed within twenty four hours.

Sample Analysis

The fluorimeter was a Perkin Elmer MPF-66 Spectrofluorimeter equipped with a Perkin Elmer Model 7300 Data Station and a PR-310 printer/plotter. The software was a Perkin - Elmer "PECLS" data collection and plotting program. Three dimensional spectra were obtained using the "tlsm" software. Each sample was first prescanned using a "scout" program to determine the range of excitation and emission fluorescence and also the excitation and emission maxima (Figures 4.1 and 4.2).

1. Emission was scanned from 250-400nm with the excitation start at 200nm and the increment set at 4nm.

2. Excitation was scanned from 200-300nm with the emission start at 250nm and the increment set at 5nm.

The gas chromatograph was a Varian Model 3300 equipped with a Model 601 Data Station and a Hewlett Packard Thinkjet Printer. The capillary column was a J & W DB-1, 30 meter with a 0.25 micron coating. The chromatographic conditions were as follows:

Initial column temperature - 50 degrees centigrade
Initial hold time - 4 minutes
Final column temperature - 200 degrees centigrade
Program rate - 10 degrees centigrade per minute
Final hold time - 6 minutes
Injector/detector temperature - 250 degrees centigrade
Injection volume - one microliter
Range - 11
DS attenuation - 128
Run time - 25 minutes

Obtaining Fluorescence Spectra

The Perkin Elmer Total Luminescence Spectroscopy III package, PETLS III, was utilized to run, collect and plot the three dimensional spectra. The fluorimetric conditions were as follows:

Entrance slit - 5
Exit slit - 5
Scan speed - 240nm/min.
Response factor - 1
Emission slit - 3
Excitation slit - 3
Mode - ratio
Gain - lo
Emission filter - open

Evaporation of the Gasolines

Ten milliliters of the gasoline sample was placed into a fifty milliliter beaker and placed in the fume hood. The five milliliter point on the beaker was marked prior to putting the gasoline in it. The gasoline was evaporated to the mark for 50% evaporated. For the 100% evaporated sample 10 milliliters of gasoline was placed in the beaker and was allowed to evaporate completely. This residue was reconstituted in spectrograde cyclohexane and analyzed.

Chapter Four

Results

Tables 1 - 3 list three dimensional fluorescence data for each gasoline sample neat, 50% and 100% evaporated.

Figures 4.1 and 4.2 are an example of an emission and an excitation scout spectrum.

Figures 4.3 - 4.11 are the capillary gas chromatograms of the neat gasoline samples.

Figures 4.12 -4.20 are the capillary gas chromatograms of the 50% evaporated gasoline samples.

Figures 4.21 - 4.27 are the capillary gas chromatograms of the 100% evaporated gasoline samples.

Figures 4.28 - 4.36 are the three dimensional fluorescence emission stacked plots of the neat gasoline samples.

Figures 4.37 - 4.45 are the three dimensional fluorescence emission stacked plots of the 50% evaporated gasoline samples.

Figures 4.46 - 4.50 are the three dimensional fluorescence emission stacked plots of the 100% evaporated gasoline samples.

Figures 4.51 - 4.58 are various three dimensional fluorescence subtraction plots.

Table 1

Three Dimensional Fluorescence Data for the Neat Gasoline Samples

Gasoline	Excitation Wavelength	Emission Wavelength	Maximum Intensity
Mobil Unleaded	219	288	16.4
Mobil Super Unleaded	219	286	18.4
Shell Regular	217	285	10.0
Shell Unleaded	219	287	13.8
Standard Regular	219	288	20.2
Standard Unleaded	217	285	11.0
Standard Premium	217	287	14.4
Total Regular	217	289	480.6
Total Unleaded	219	289	20.6
Cyclcohexane Blank	255	276	105.0

Table 2

Three Dimensional Fluorescence Data for the 50% Evaporated Gasoline Samples

Gasoline	Excitation Wavelength	Emission Wavelength	Maximum Intensity
Mobil Unleaded	217	287	18.0
Mobil Super Unleaded	223	287	18.4
Shell Regular	217	287	16.4
Shell Unleaded	227	336	20.4
Standard Regular	221	288	26.8
Standard Unleaded	219	288	20.4
Standard Premium	221	289	20.0
Total Regular	217	288	15.4
Total Unleaded	221	289	21.4

Table 3

Three Dimensional Fluorescence Data for the 100% Evaporated Gasoline Samples.

Gasoline	Excitation Wavelength	Emission Wavelength	Maximum Intensity
Mobil Unleaded	265	361	15.6
Shell Unleaded	265	361	36.6
Standard Unleaded	233	344	15.2
Standard Premium	233	344	10.6
Total Unleaded	227	340	178.4

```
SCOUT    PERKIN-ELMER MODEL MPF-66 EMISSION SURVEY REPORT    REV 4.0
         ==============================================

SAMPLE: standard premium gas 10ppm  DATE: Mar 27 1987   TIME: 10:38:00

                                   EMISSION PEAK TABLE
                 1            2            3            4            5
              -------      -------      -------      -------      -------
WAVELENGTH:  288.6        321.4        336.4        238.6          0.0
 INTENSITY:  12.19         3.30         2.68         0.68         0.00

status y
    Points   Ex wl    Slts(X/M)   From      To       Int      Min      Max     Name
Y:   1011    222.0    5.0/ 3.0   232.0 - 434.0      0.2     0.01    12.20

    Mode/Gain Corr Emfil   Spd/Rsp                      Indicators
    RATIO/LO   NO   OPEN   120.0/1.0                       F          AC1
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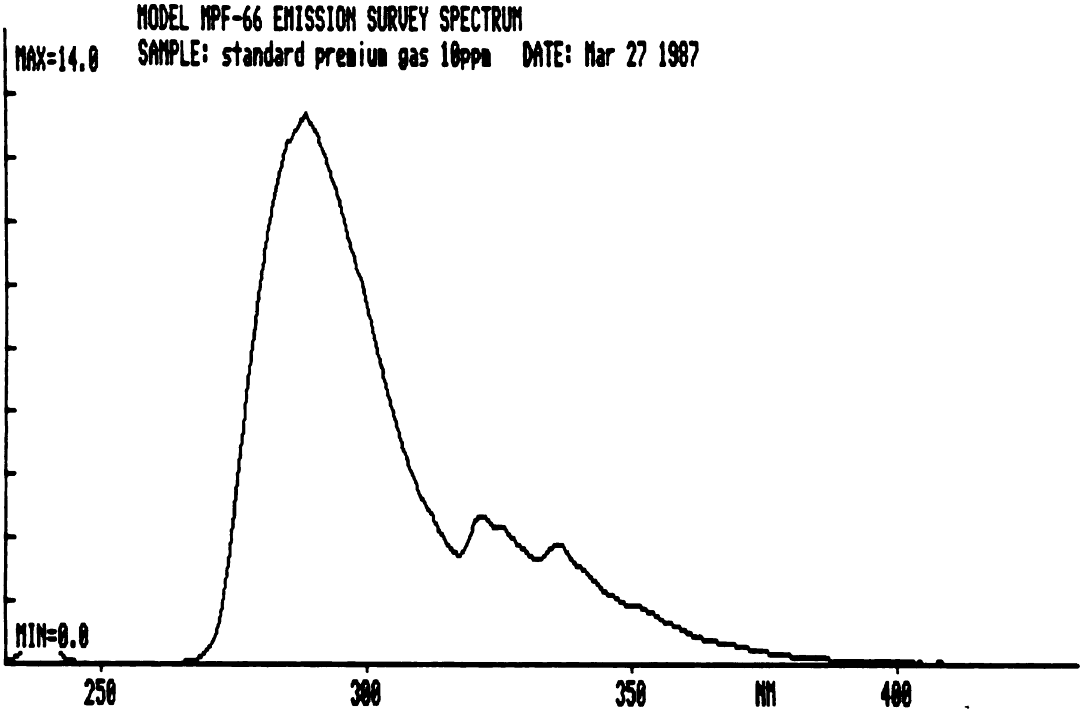

Figure 4.1 Emission Scout Spectrum Of 10ppm Standard Premium Gasoline

```
SCOUT    PERKIN-ELMER MODEL MPF-66 EXCITATION SURVEY REPORT  REV 4.0
         ================================================

SAMPLE: standard premium gas 10ppm  DATE: Mar 27 1987  TIME: 10:41:25

                        EXCITATION PEAK TABLE
              1          2          3          4          5
          --------   -------    -------    -------    -------
WAVELENGTH: 218.0      267.6        0.0        0.0        0.0
 INTENSITY:   14.3       3.3        0.0        0.0        0.0

status z
    Points  Em wl   Slts(X/M)   From      To        Int      Min     Max     Name
z:    371   289.0   5.0/ 3.0  205.0 - 279.0       0.2     0.27   14.31

    Mode/Gain Corr Emfil  Spd/Rsp                       Indicators
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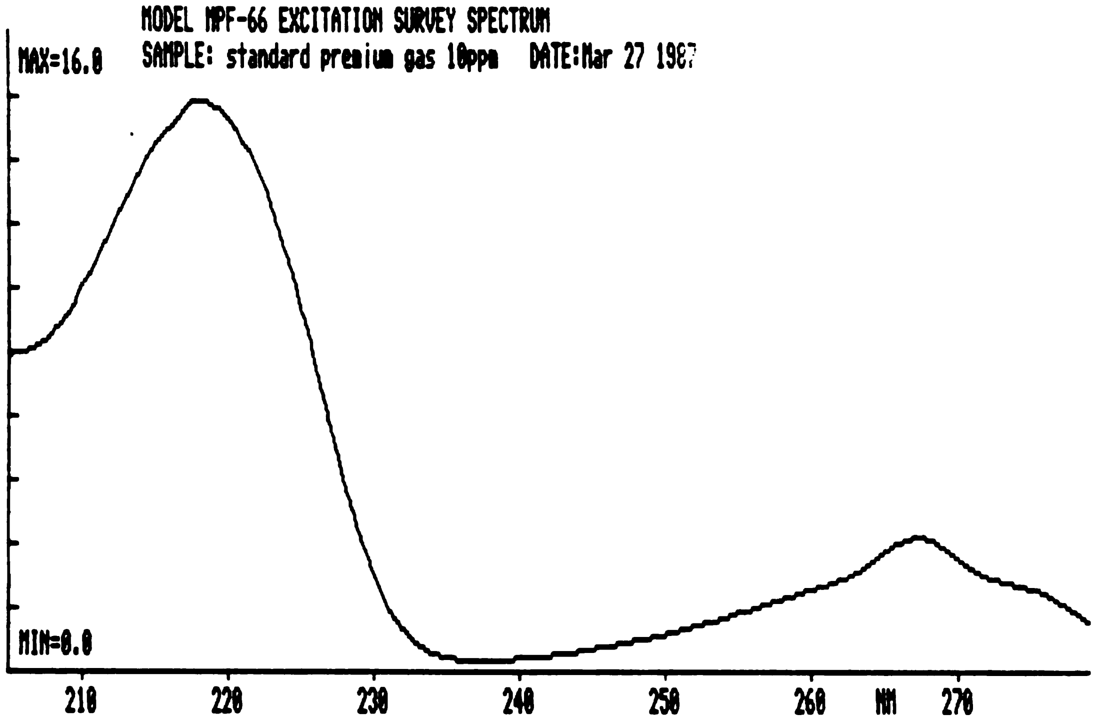

Figure 4.2 Excitation Scout Spectrum Of 10ppm Standard Premium Gasoline

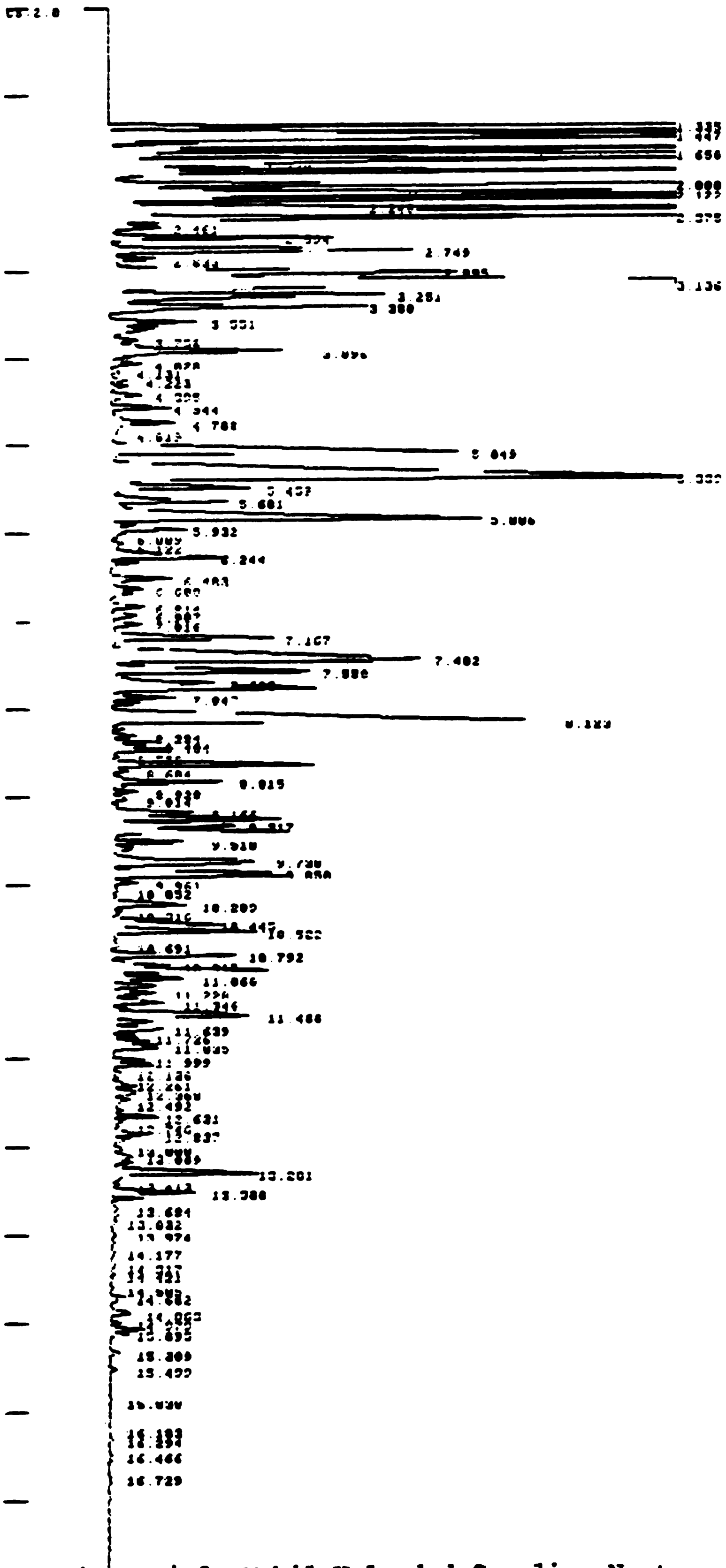

Figure 4.3 Mobil Unleaded Gasoline Neat

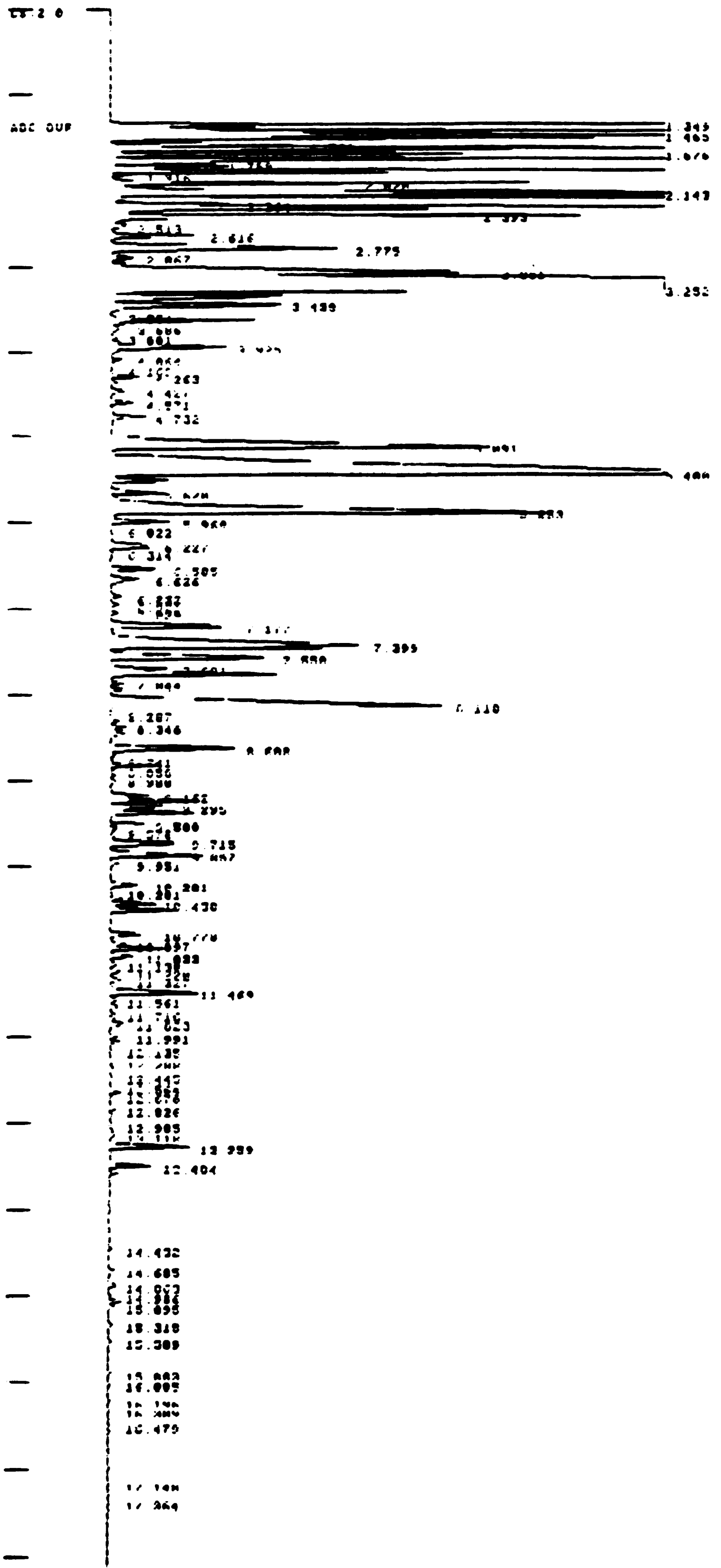

Figure 4.4 Mobil Super Unleaded Gasoline Neat

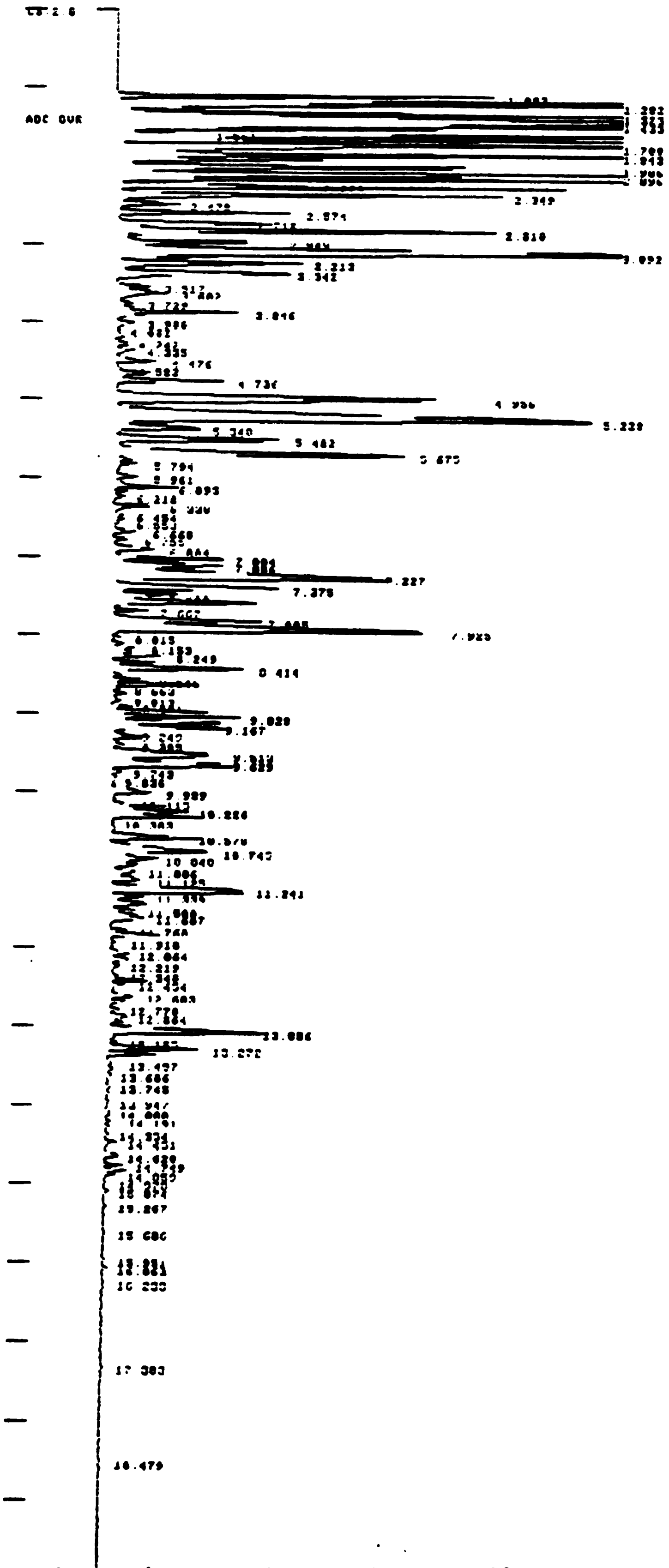

Figure 4.5 Shell Regular Gasoline Neat

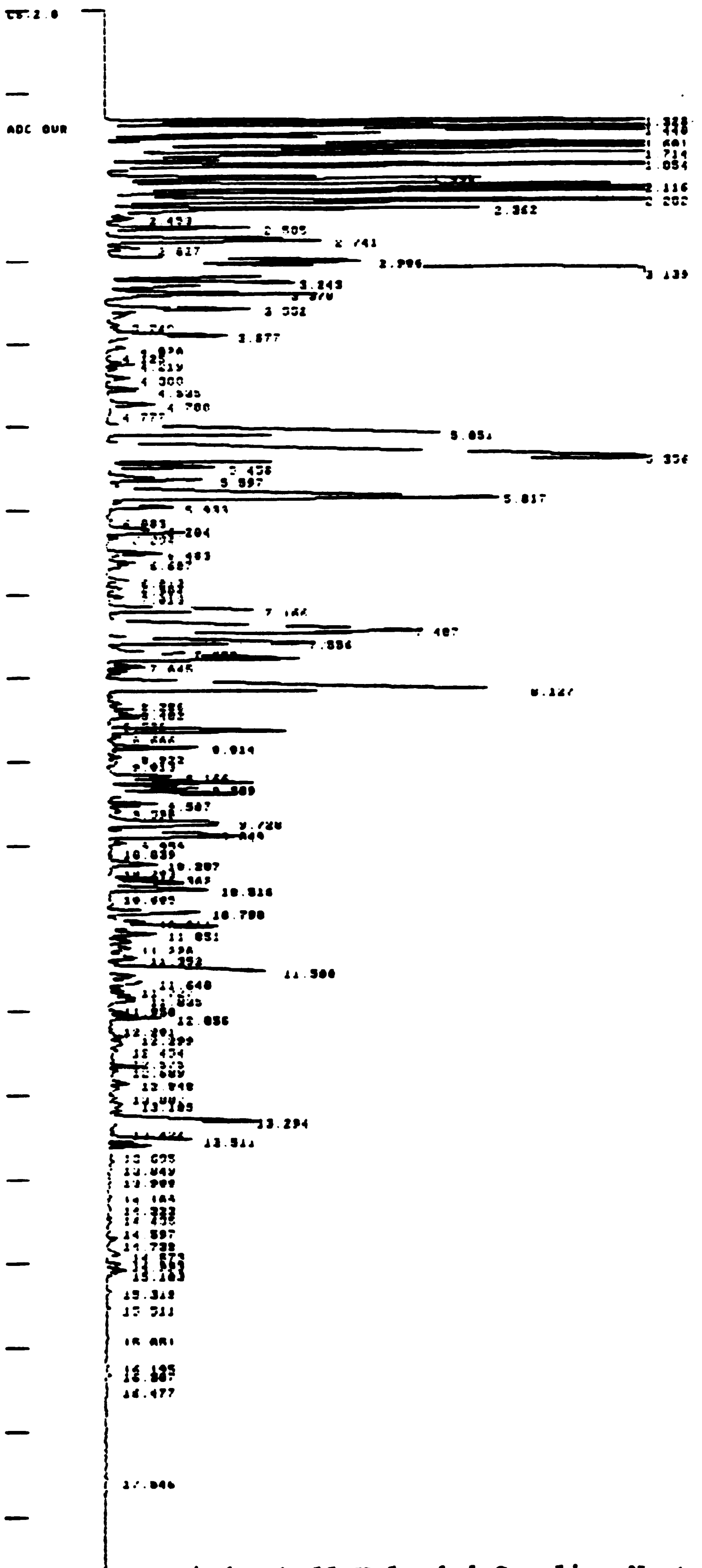

Figure 4.6 Shell Unleaded Gasoline Neat

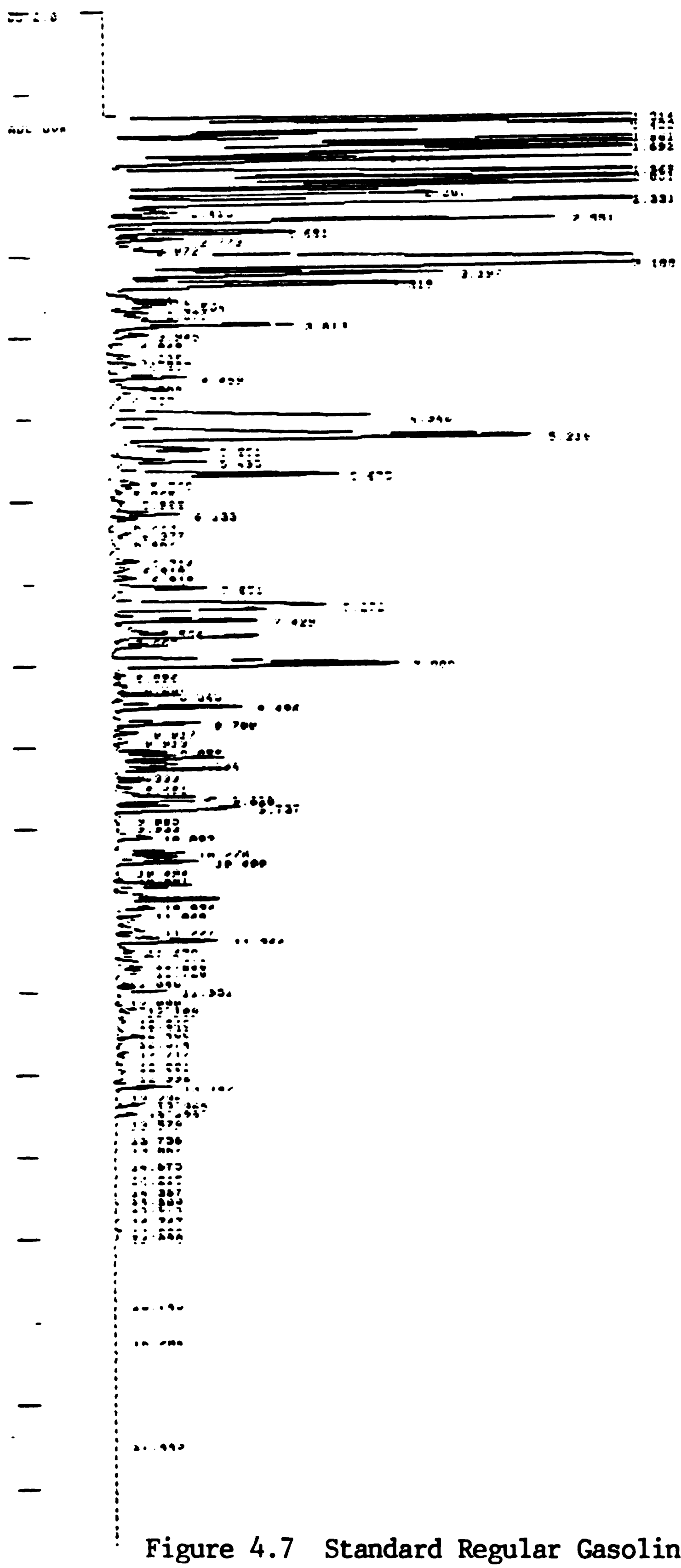

Figure 4.7 Standard Regular Gasoline Neat

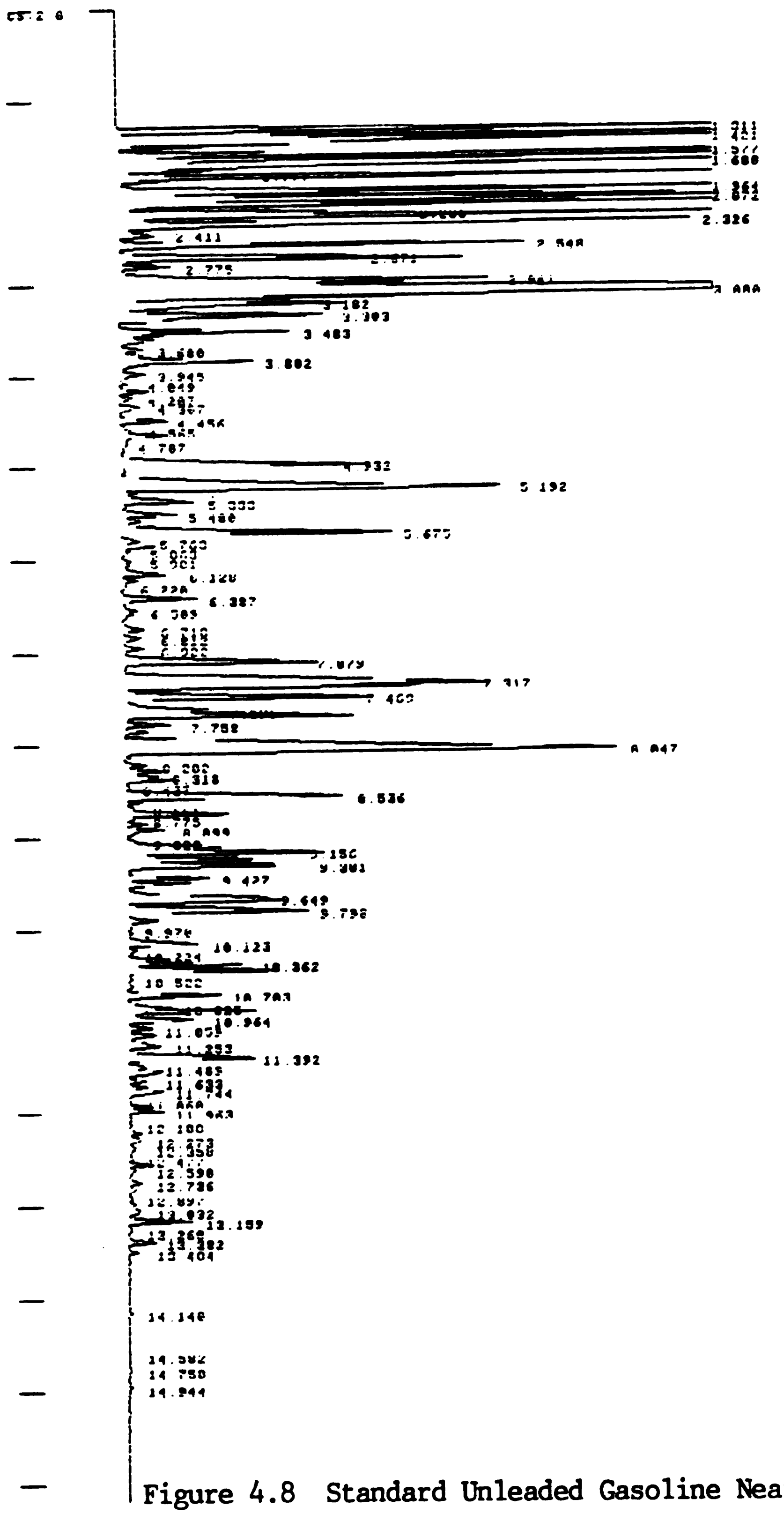

Figure 4.8 Standard Unleaded Gasoline Neat

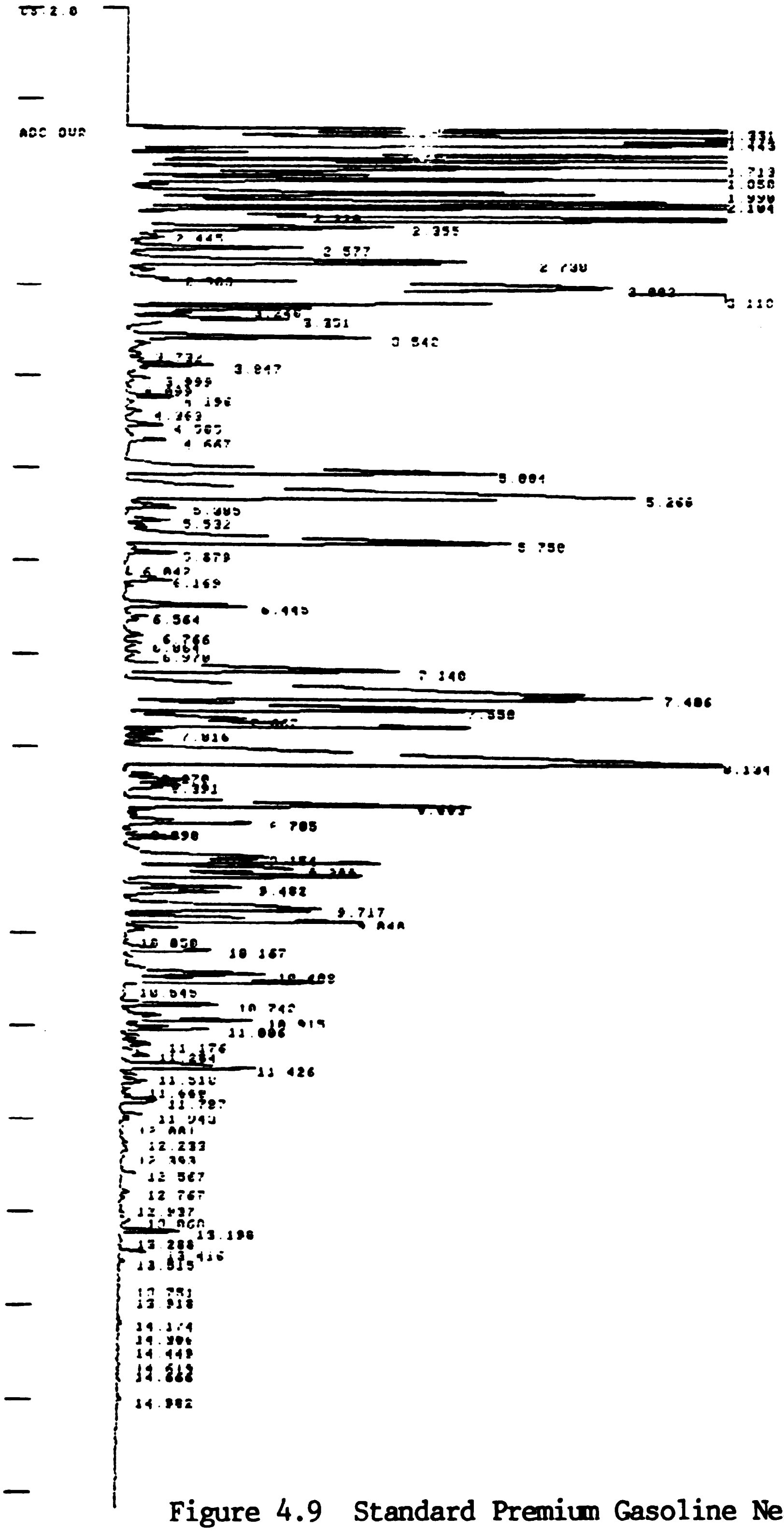

Figure 4.9 Standard Premium Gasoline Neat

Figure 4.10 Total Regular Gasoline Neat

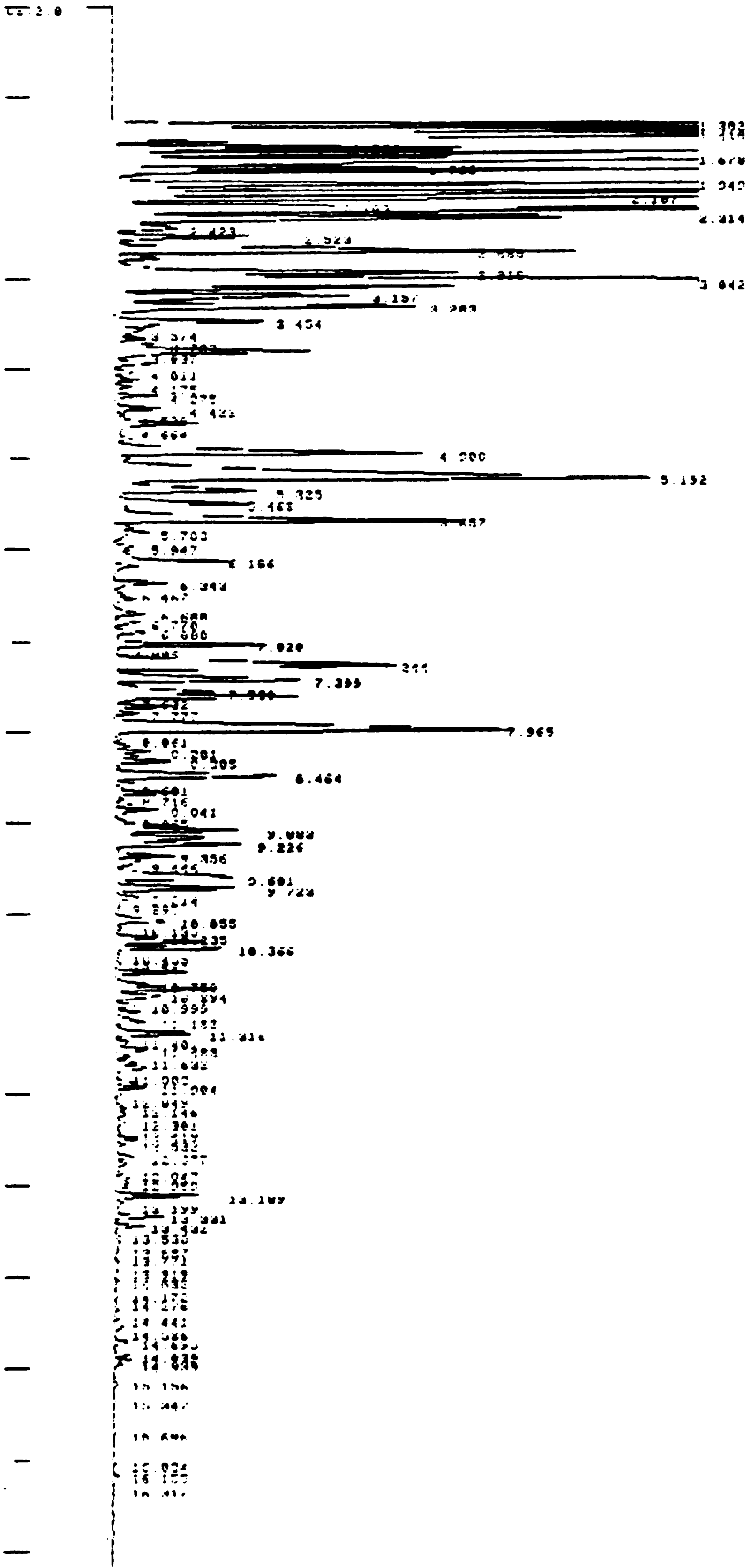

Figure 4.11 Total Unleaded Gasoline Neat

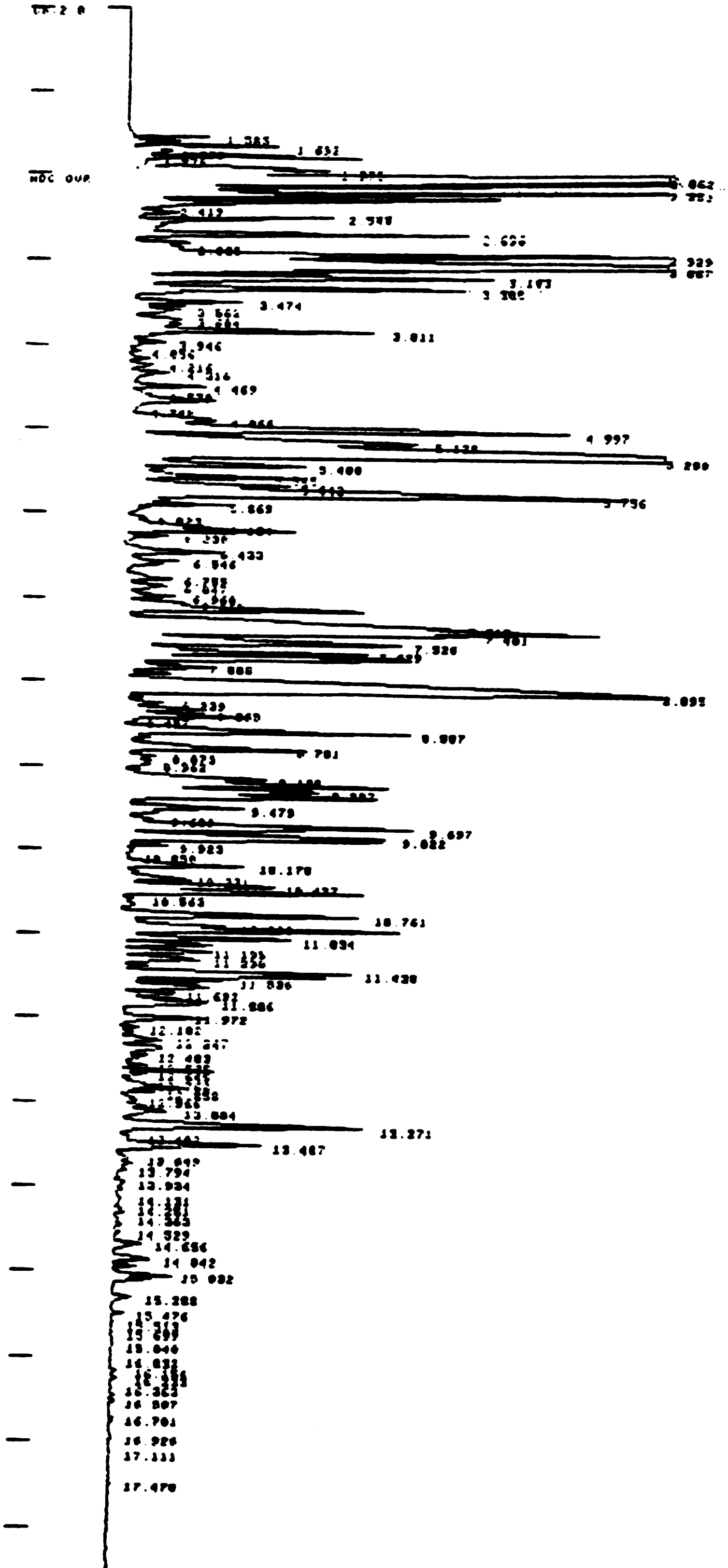

Figure 4.12 Mobil Unleaded Gasoline 50% Evaporated

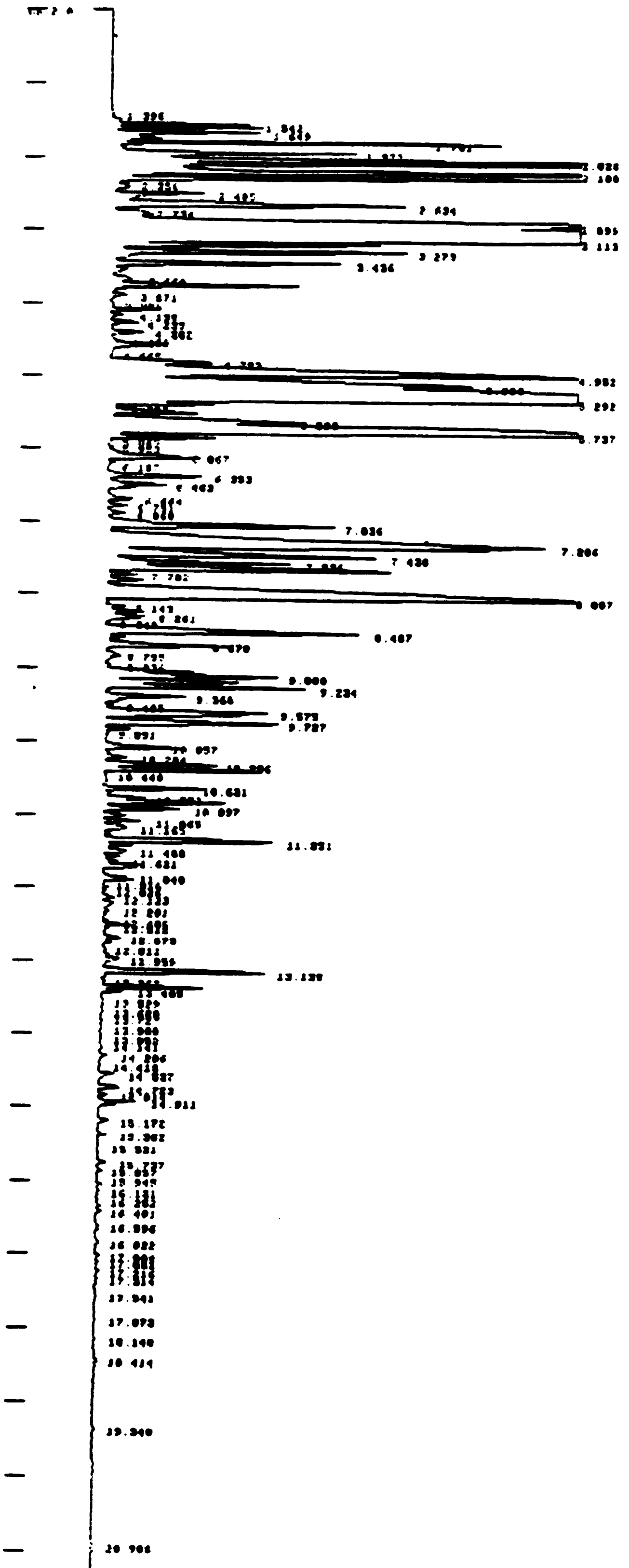

Figure 4.13 Mobil Super Unleaded Gasoline 50% Evaporated

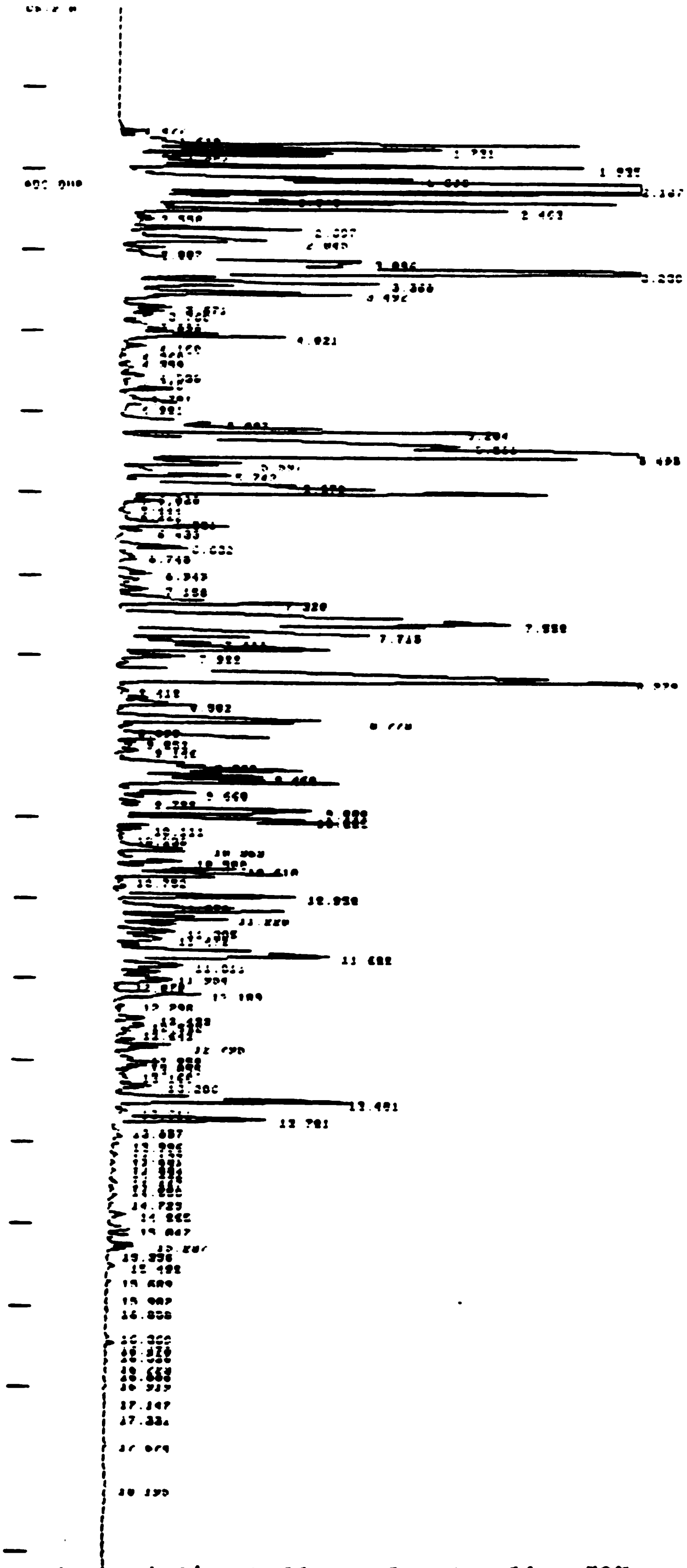

Figure 4.14 Shell Regular Gasoline 50% Evaporated

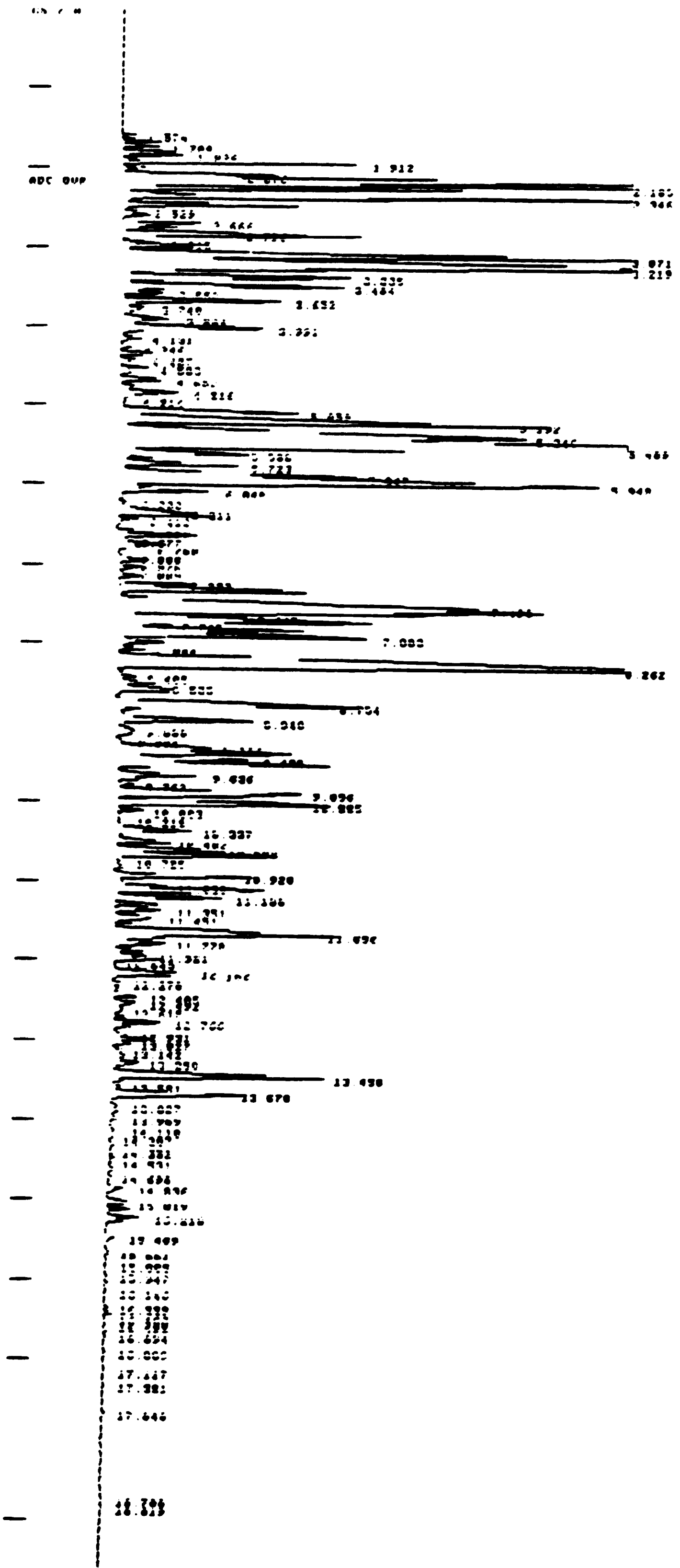

Figure 4.15 Shell Unleaded Gasoline 50% Evaporated

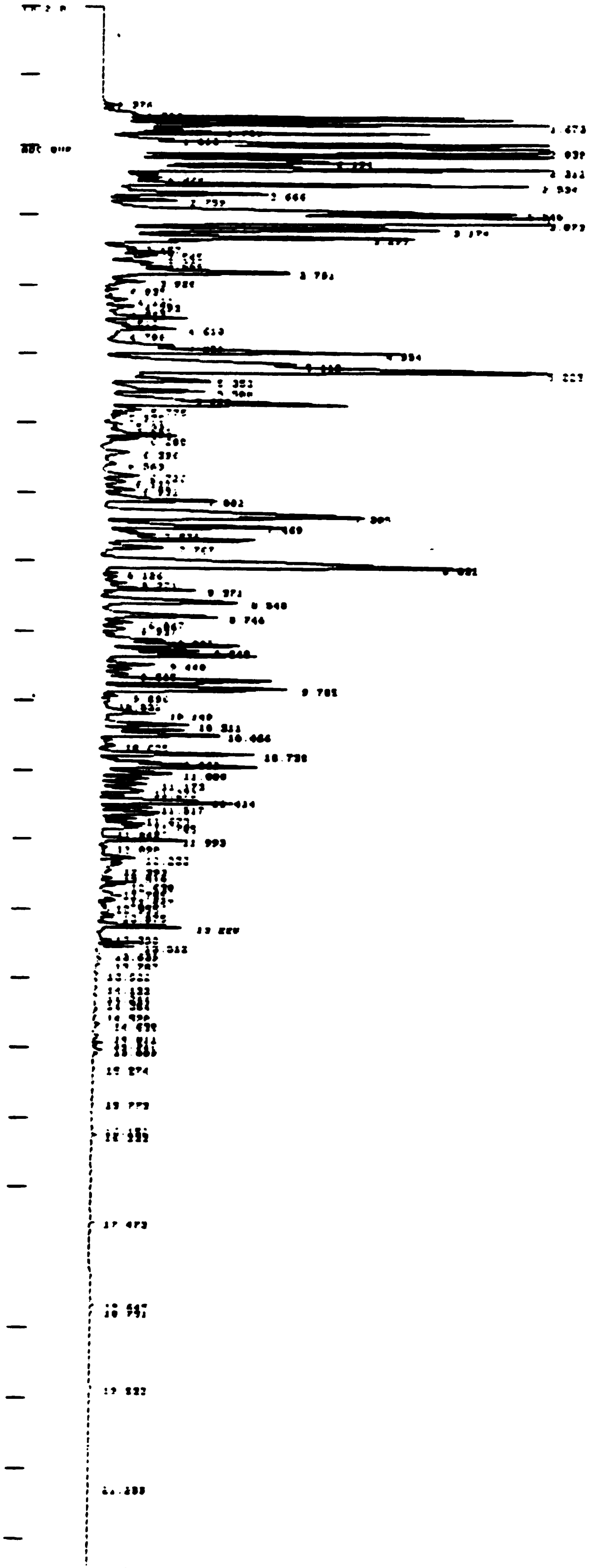

Figure 4.16 Standard Regular Gasoline 50% Evaporated

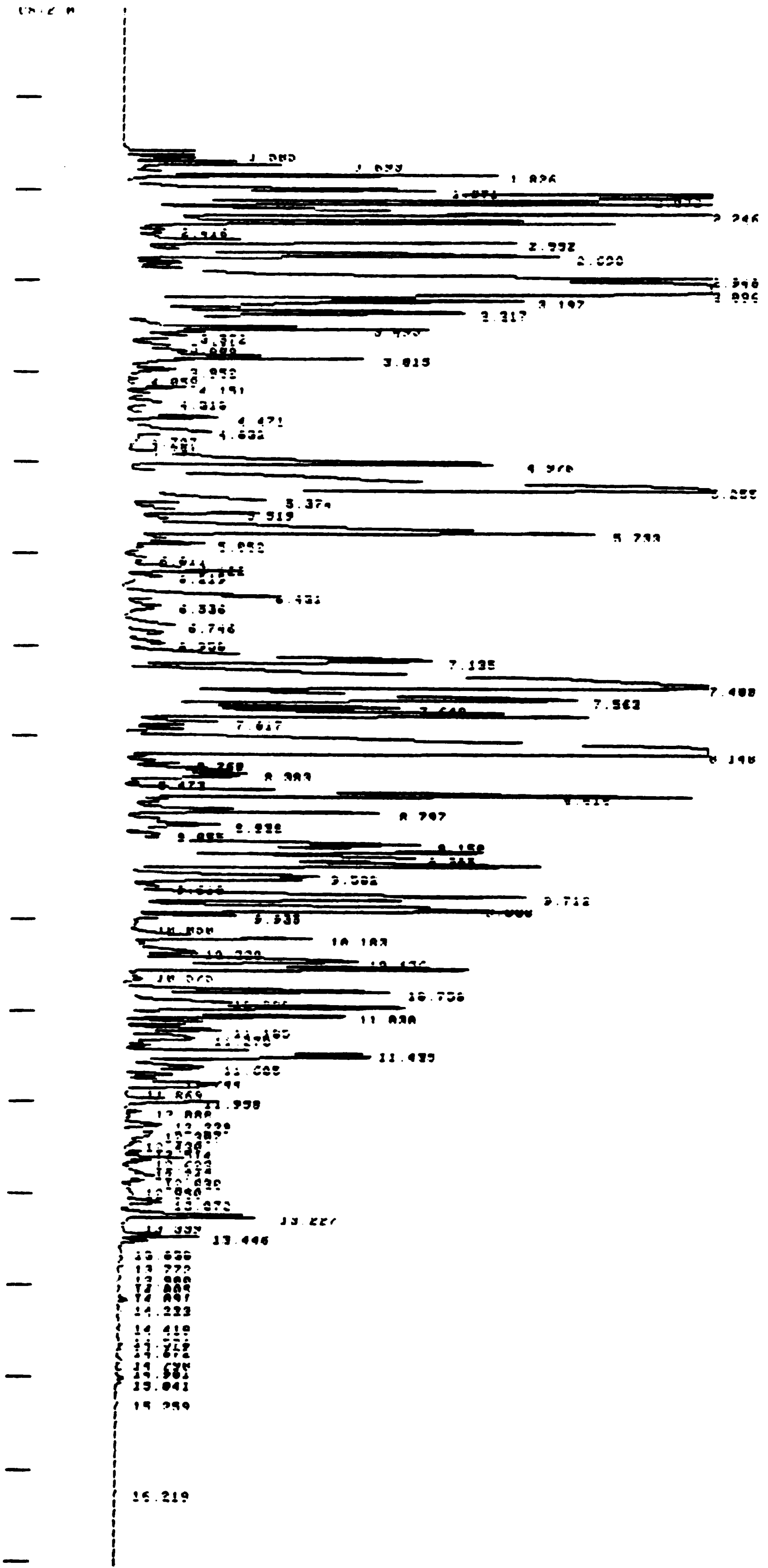

Figure 4.17 Standard Unleaded Gasoline 50% Evaporated

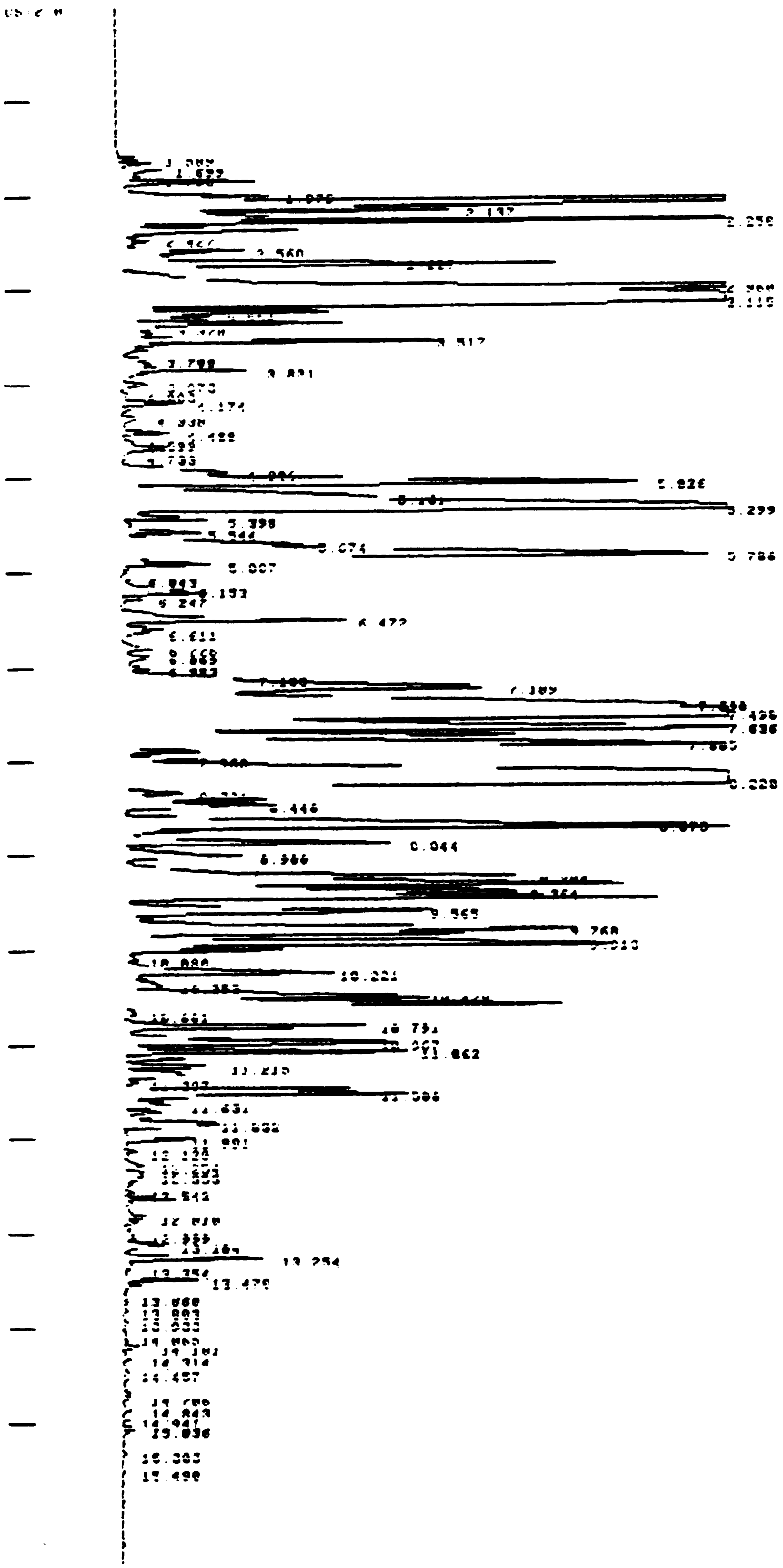

Figure 4.18 Standard Premium Gasoline 50% Evaporated

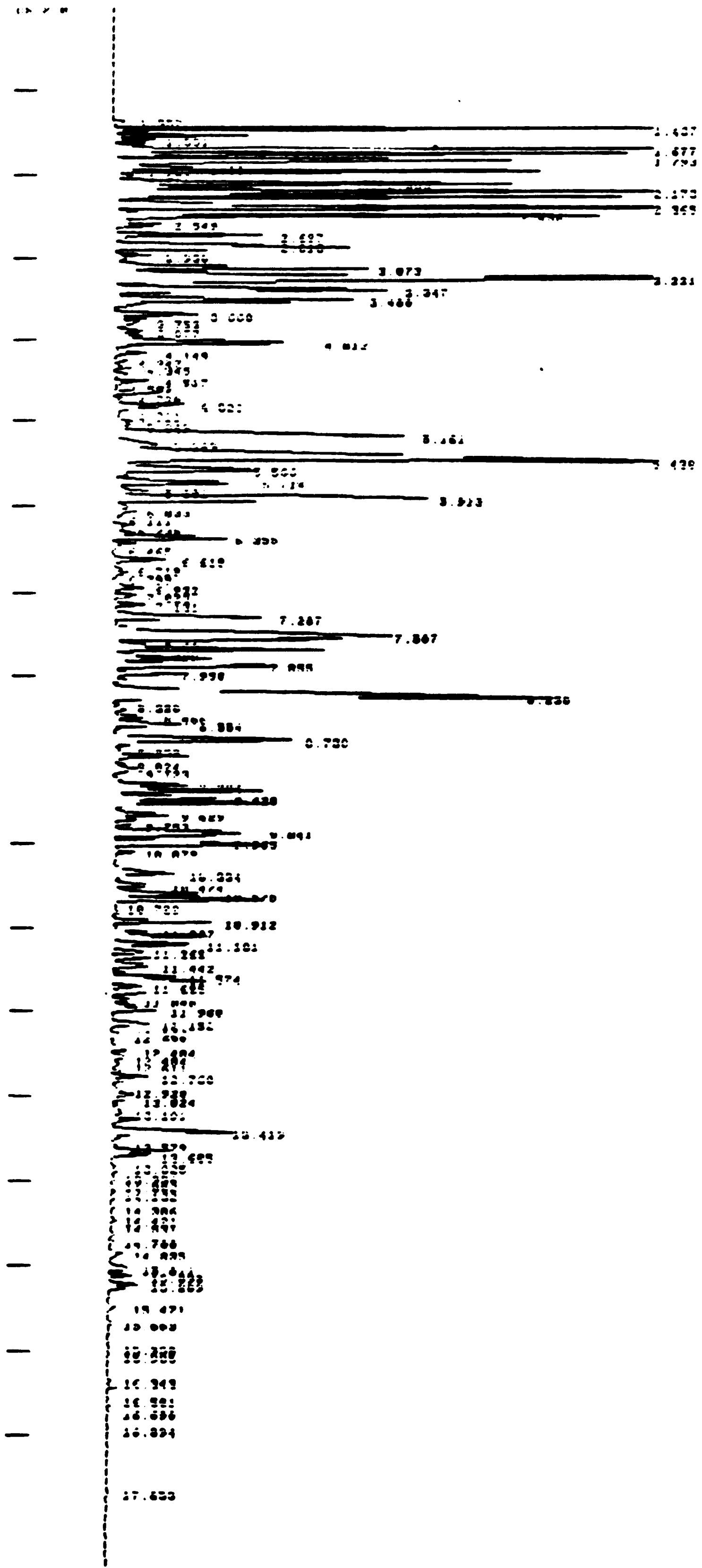

Figure 4.19 Total Regular Gasoline 50% Evaporated

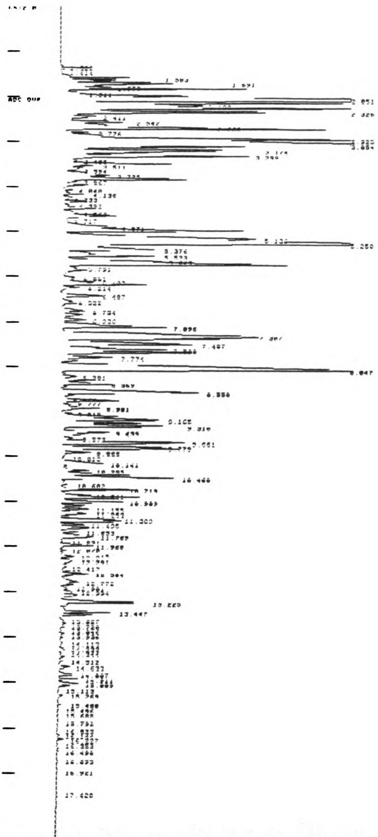

Figure 4.20 Total Unleaded Gasoline 50% Evaporated

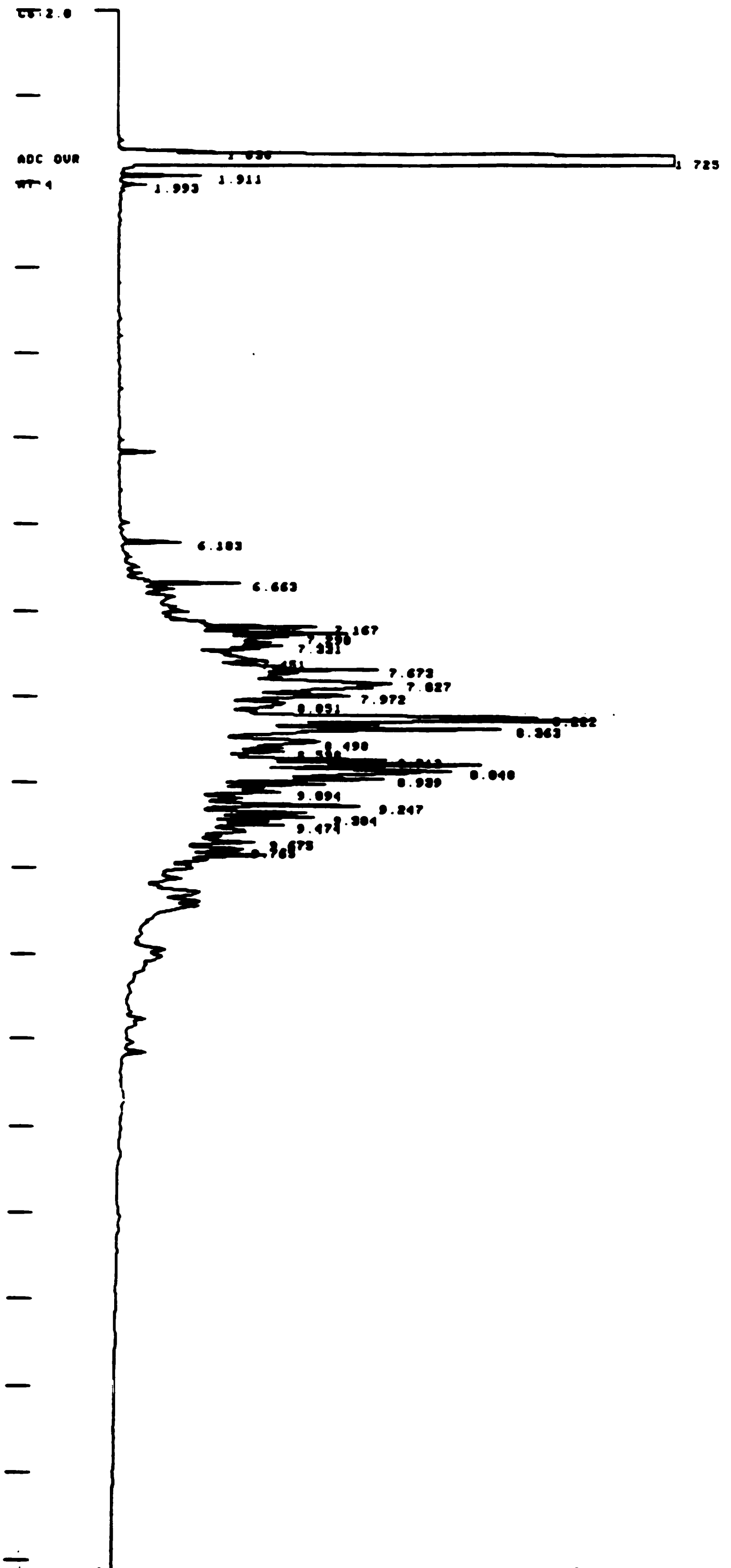

Figure 4.21 Mobil Unleaded Gasoline 100% Evaporated

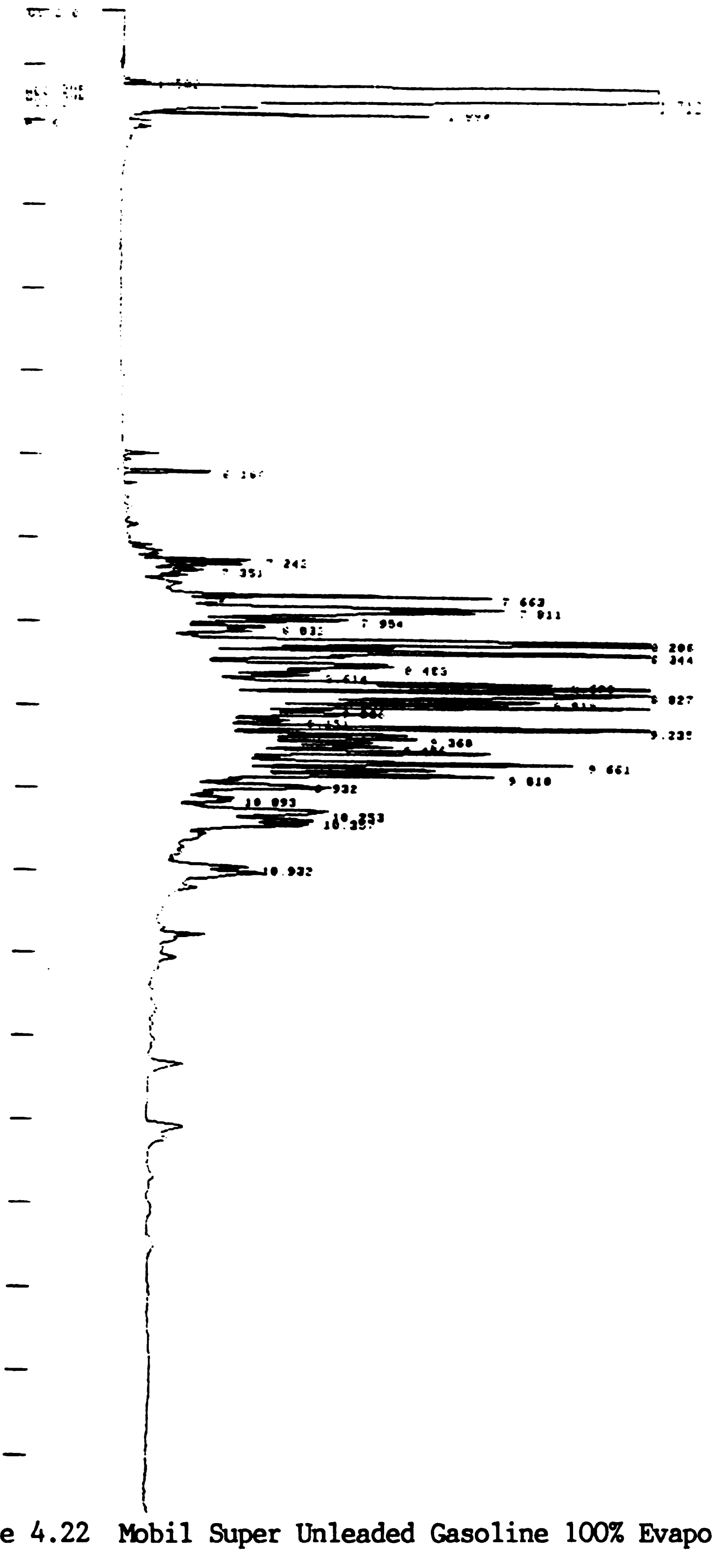

Figure 4.22 Mobil Super Unleaded Gasoline 100% Evaporated

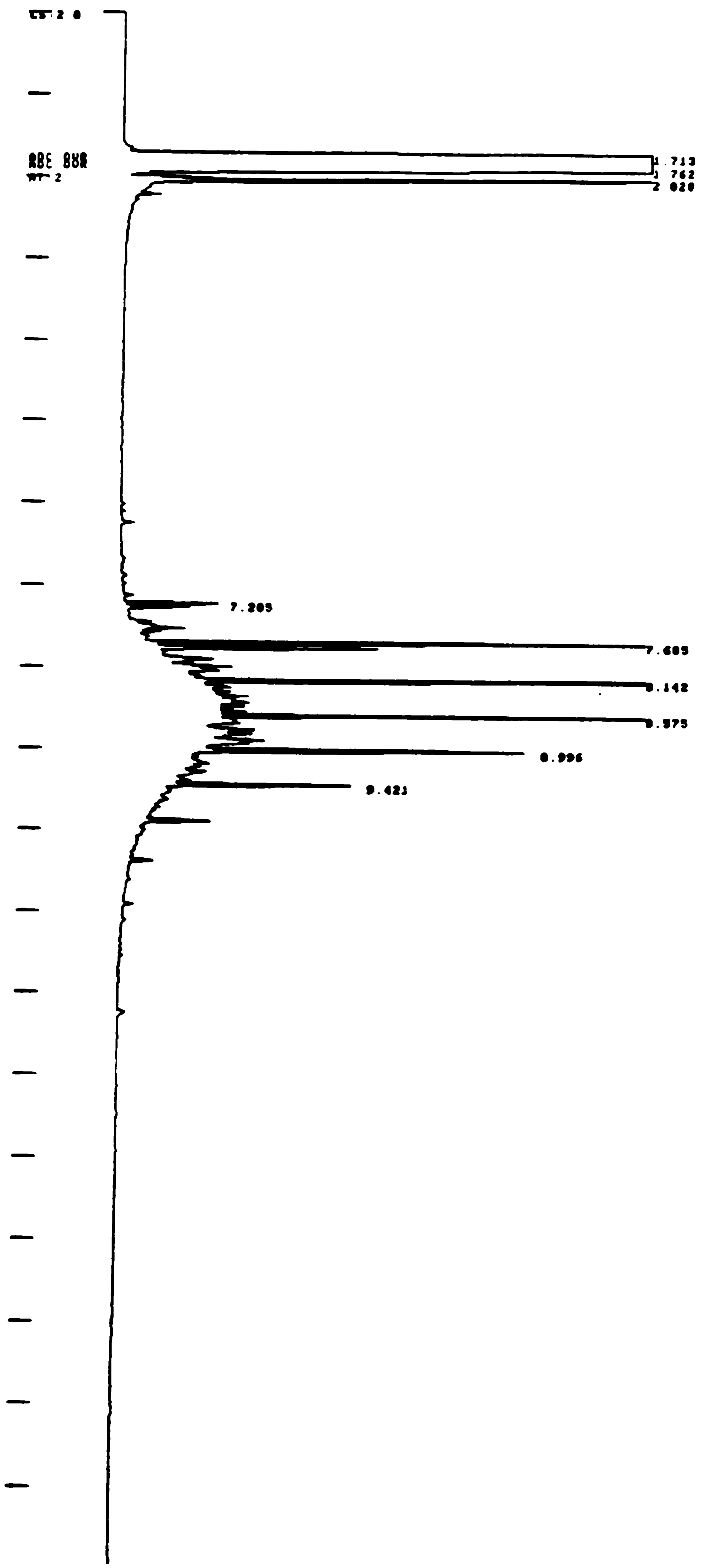

Figure 4.23 Standard Regular Gasoline 100% Evaporated

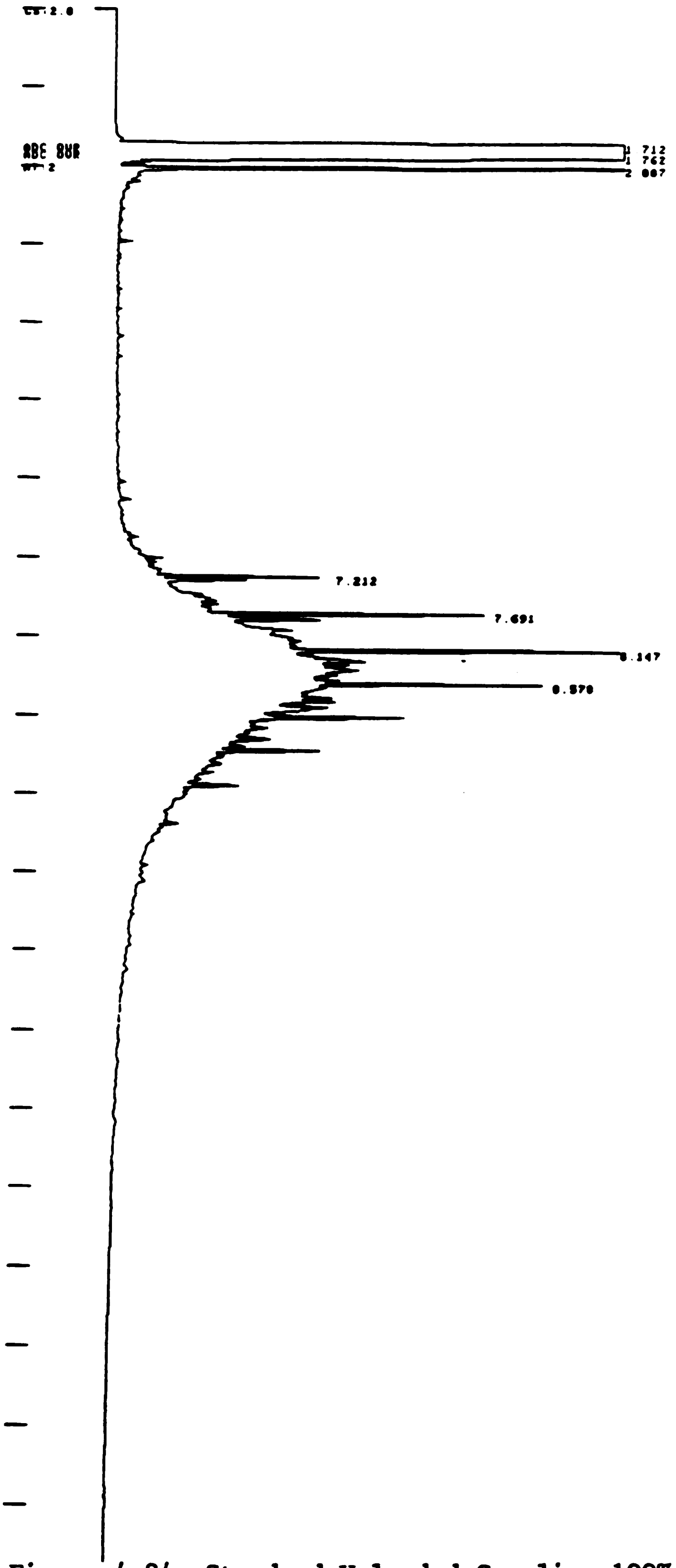

Figure 4.24 Standard Unleaded Gasoline 100% Evaporated

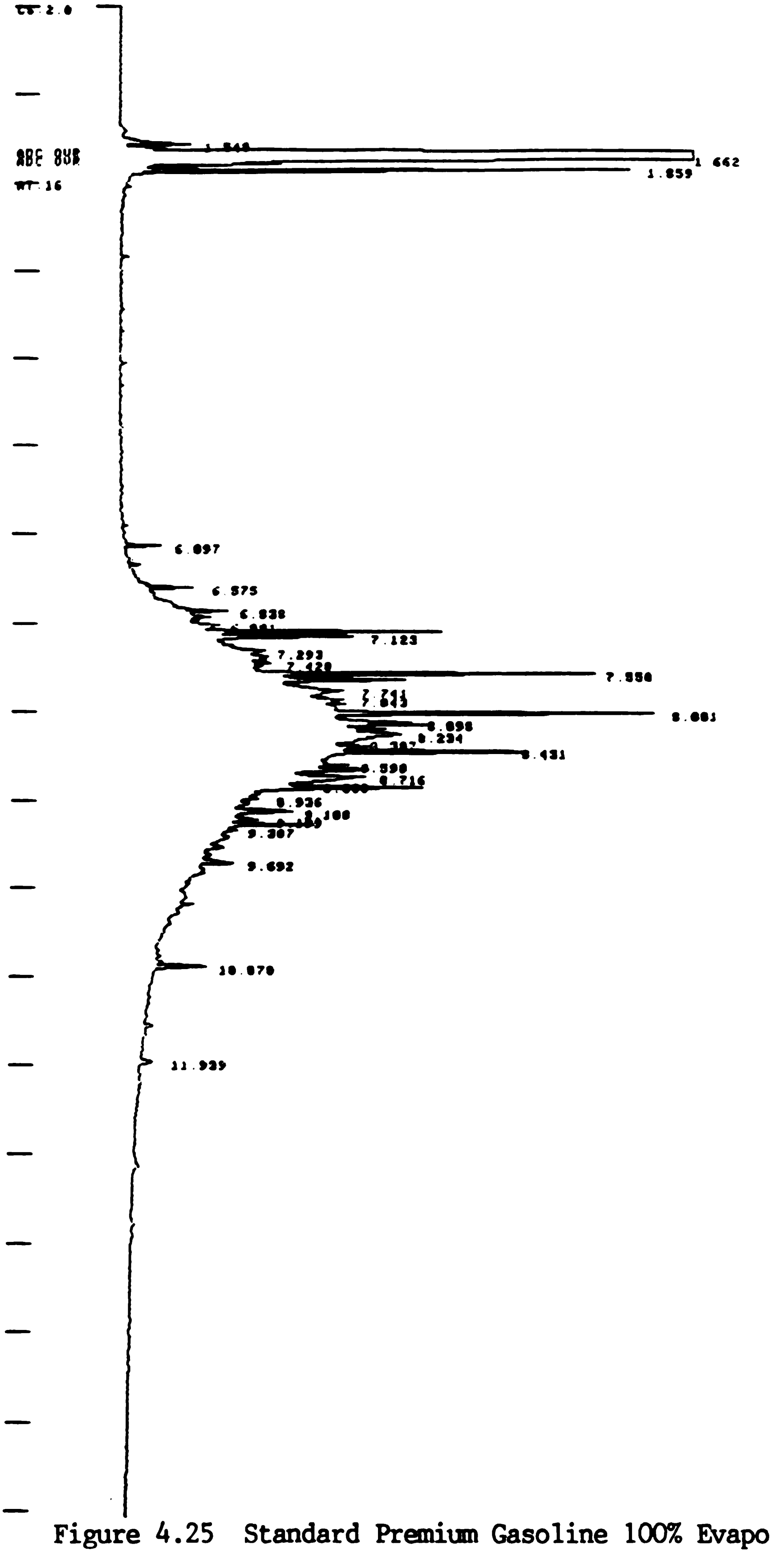

Figure 4.25 Standard Premium Gasoline 100% Evaporated

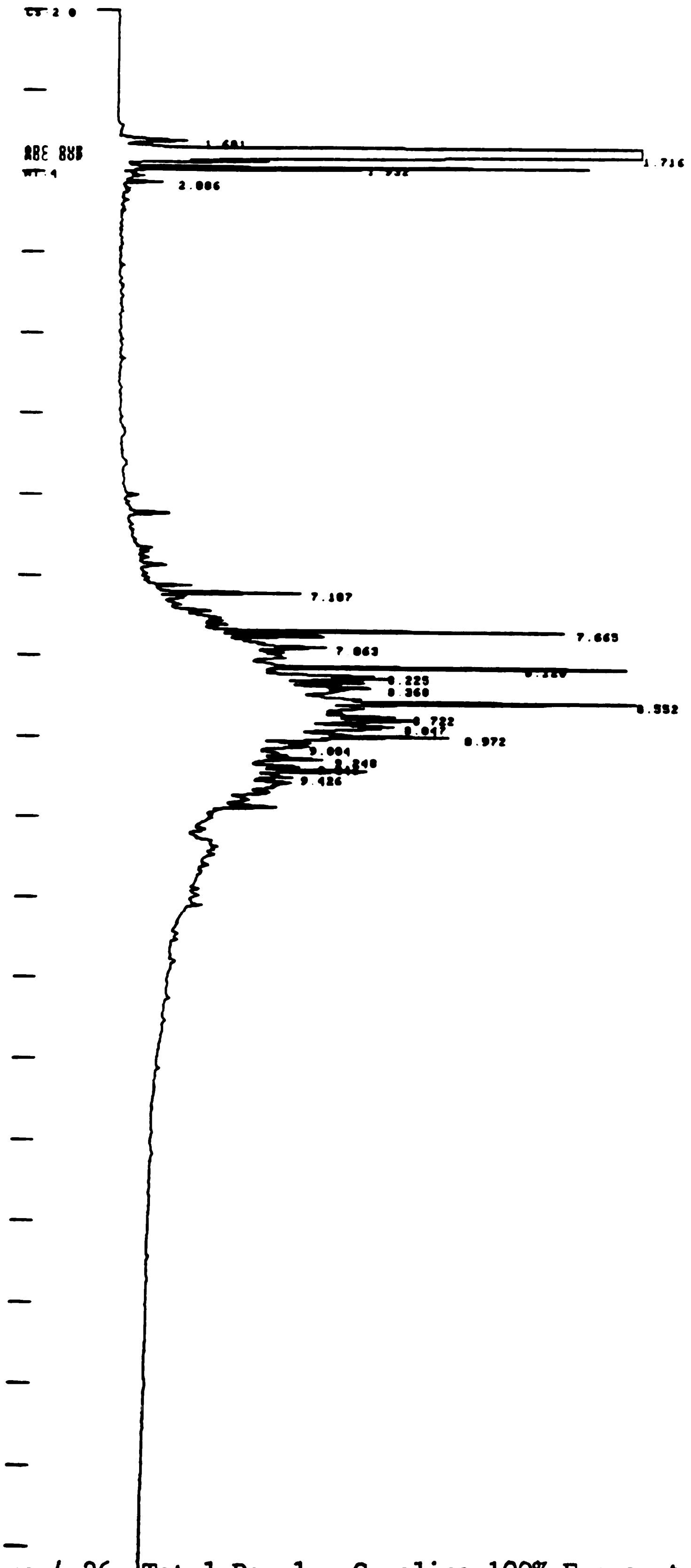

Figure 4.26 Total Regular Gasoline 100% Evaporated

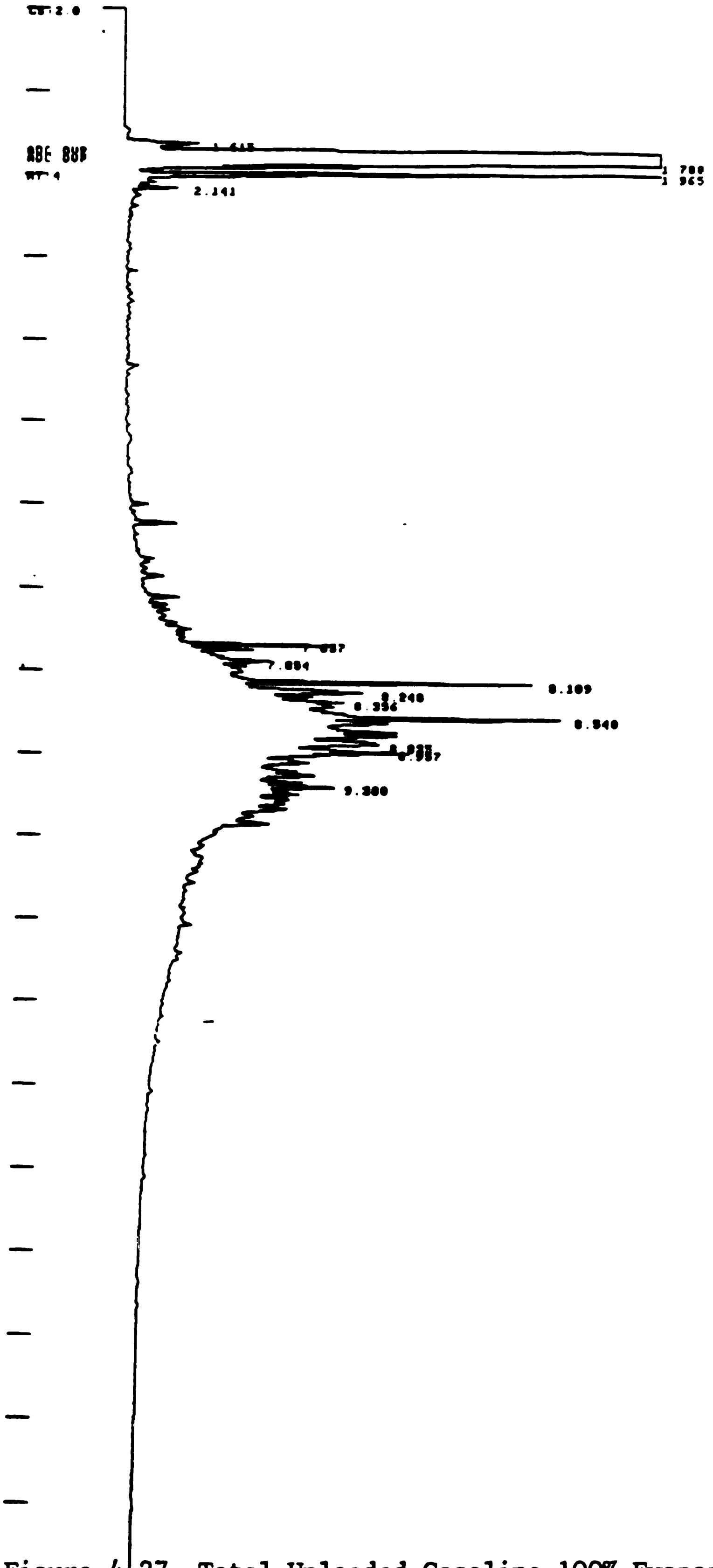

Figure 4.27 Total Unleaded Gasoline 100% Evaporated

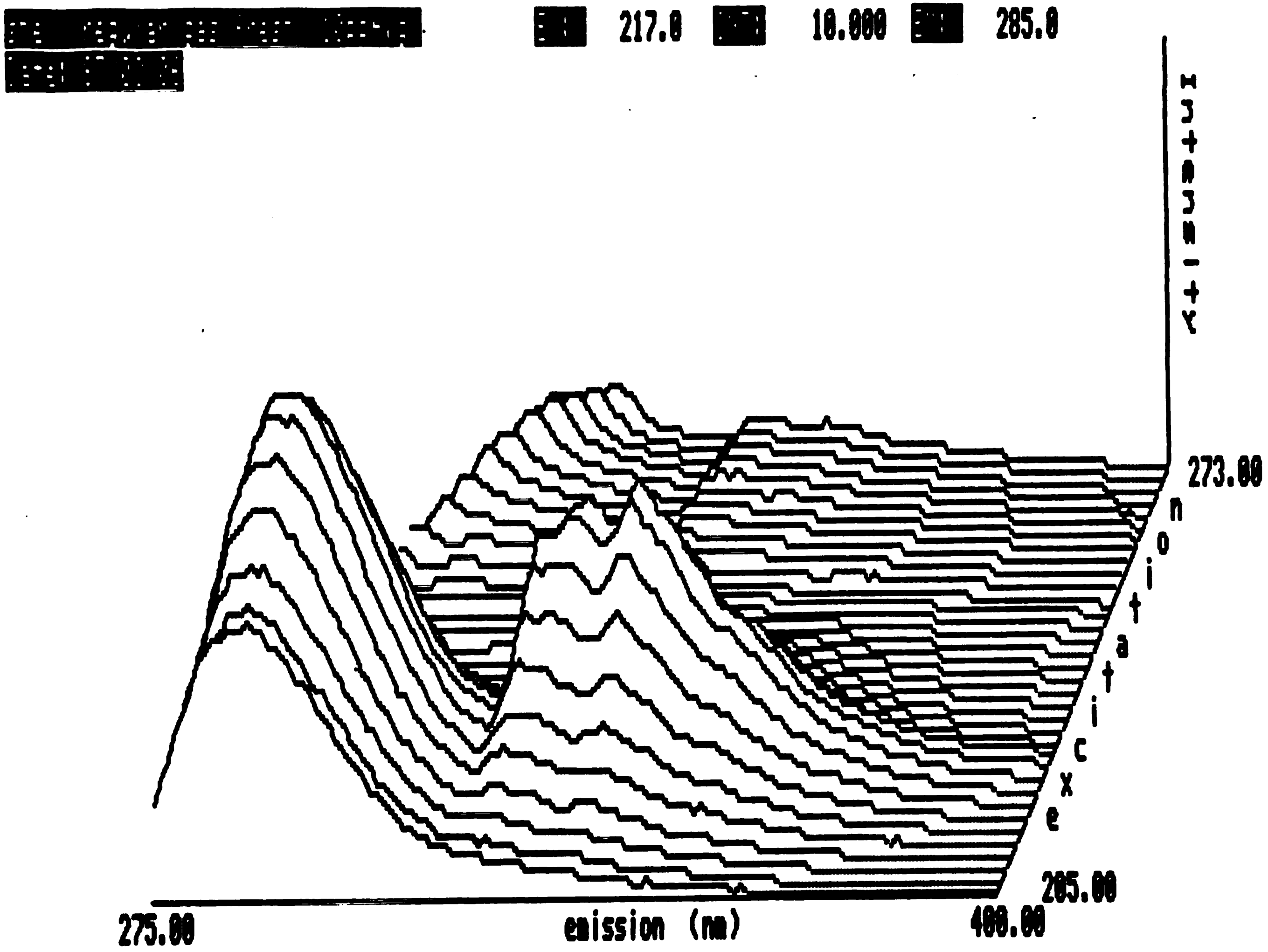

Figure 4.30 Shell Regular Gasoline Neat

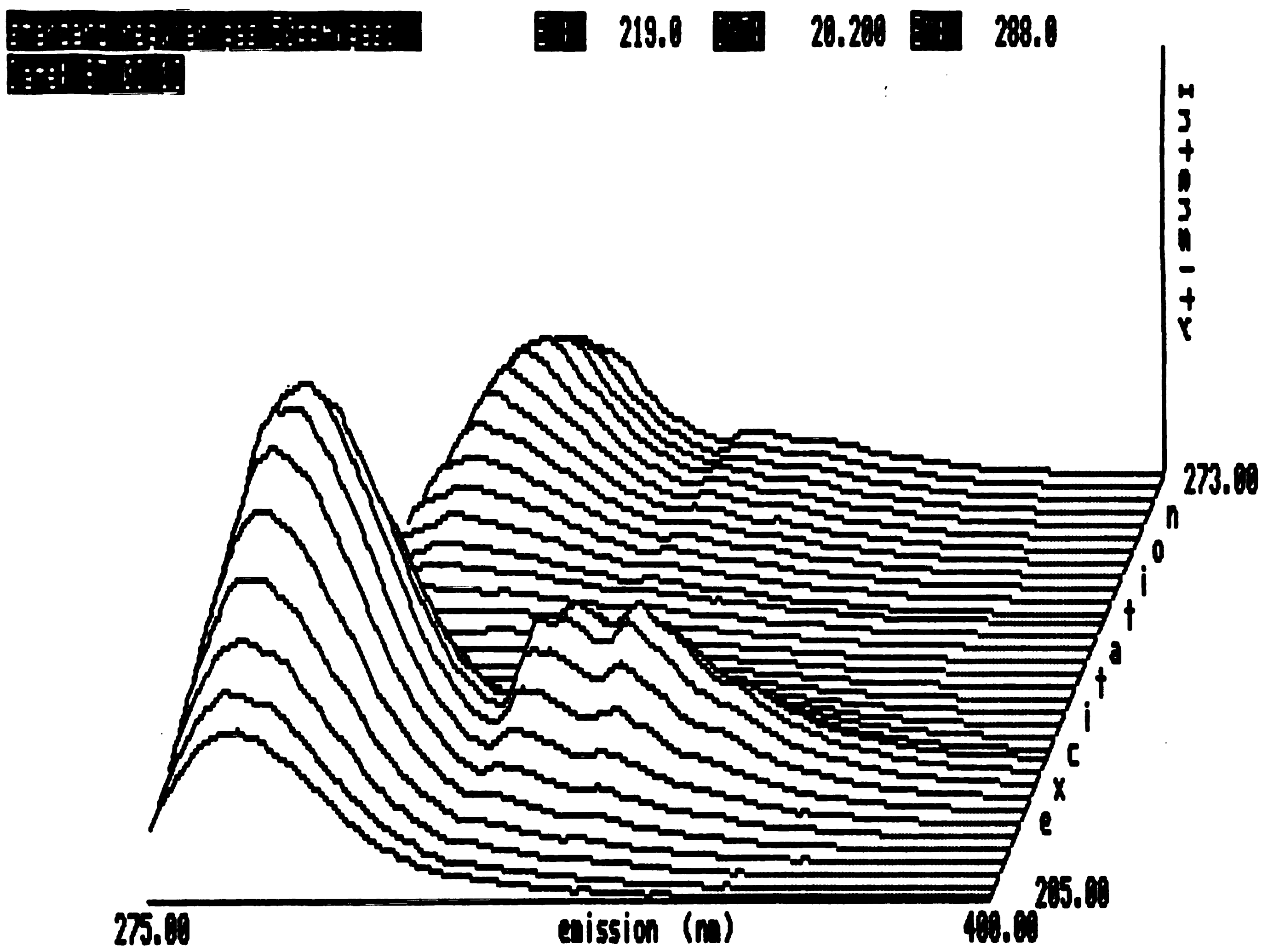

Figure 4.32 Standard Regular Gasoline Neat

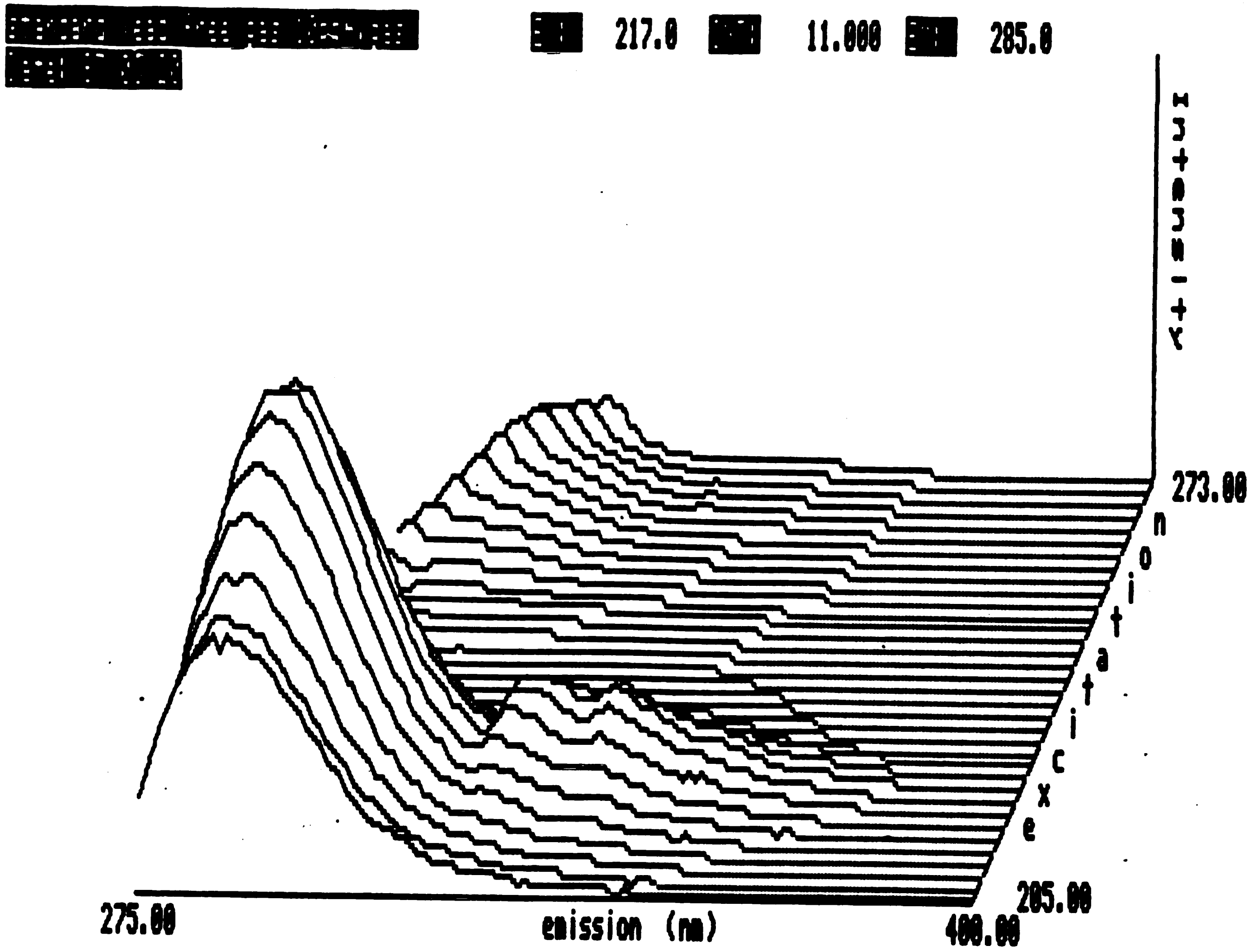

Figure 4.33 Standard Unleaded Gasoline Neat

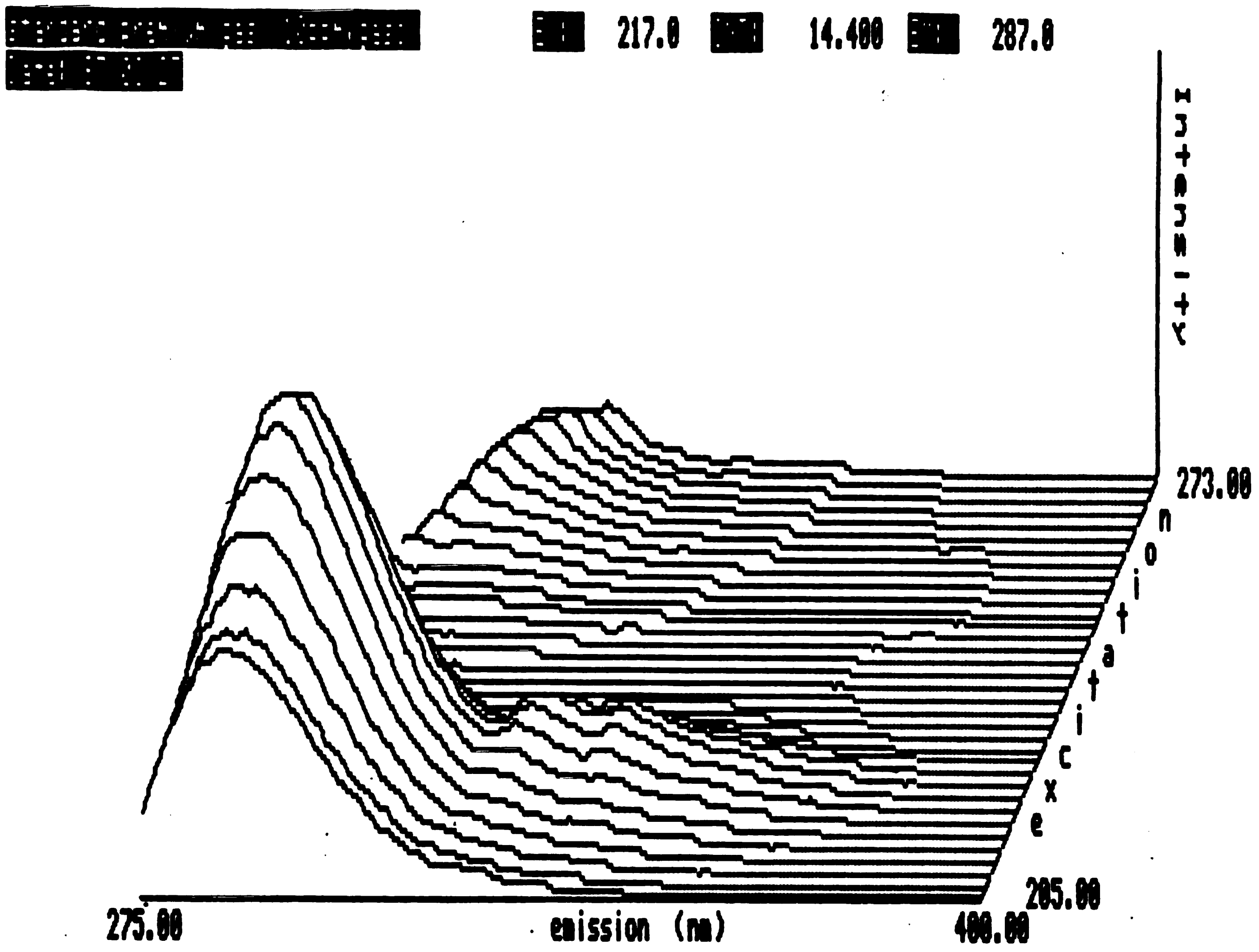

Figure 4.34 Standard Premium Gasoline Neat

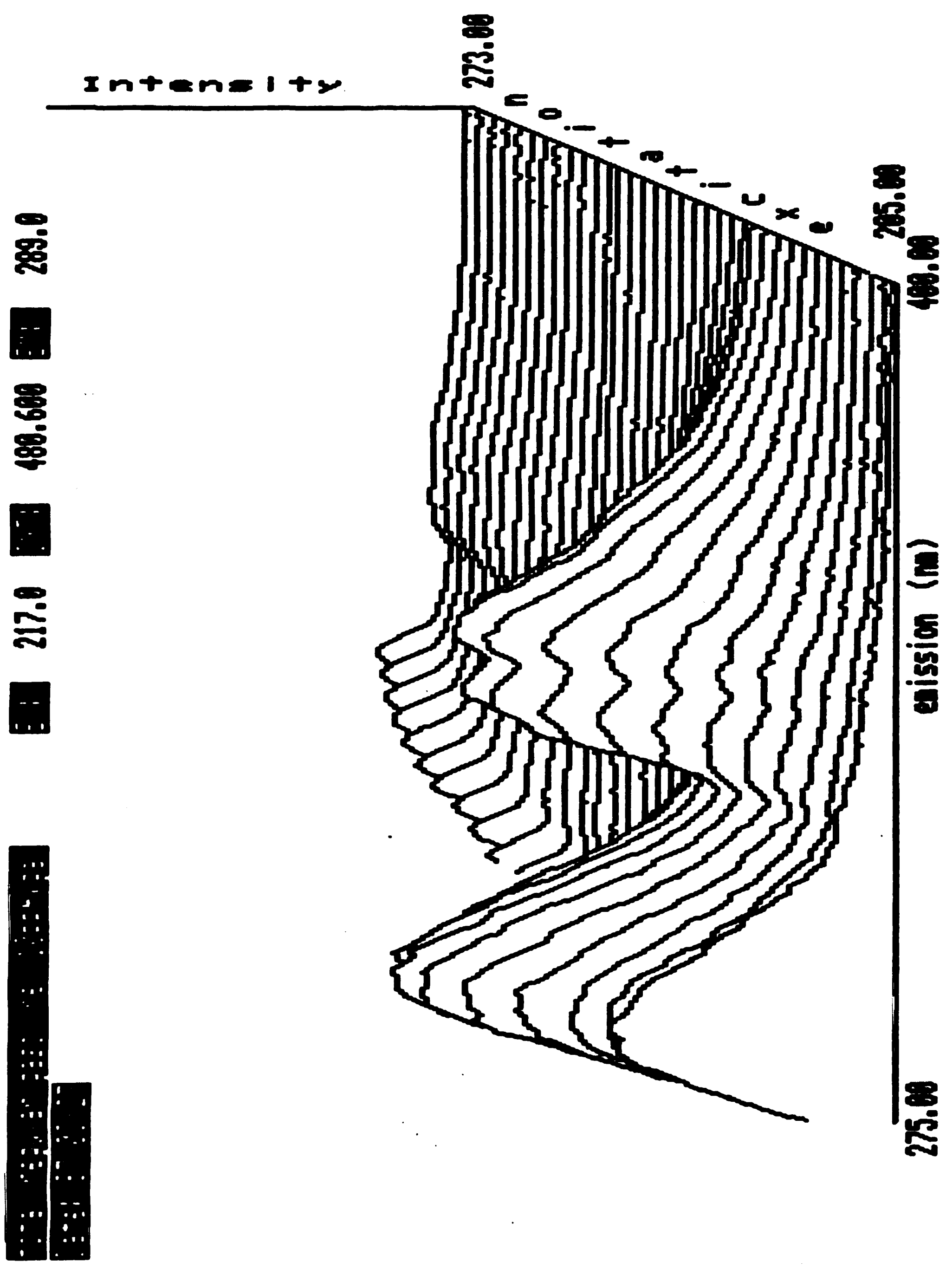

Figure 4.35 Total Regular Gasoline Neat

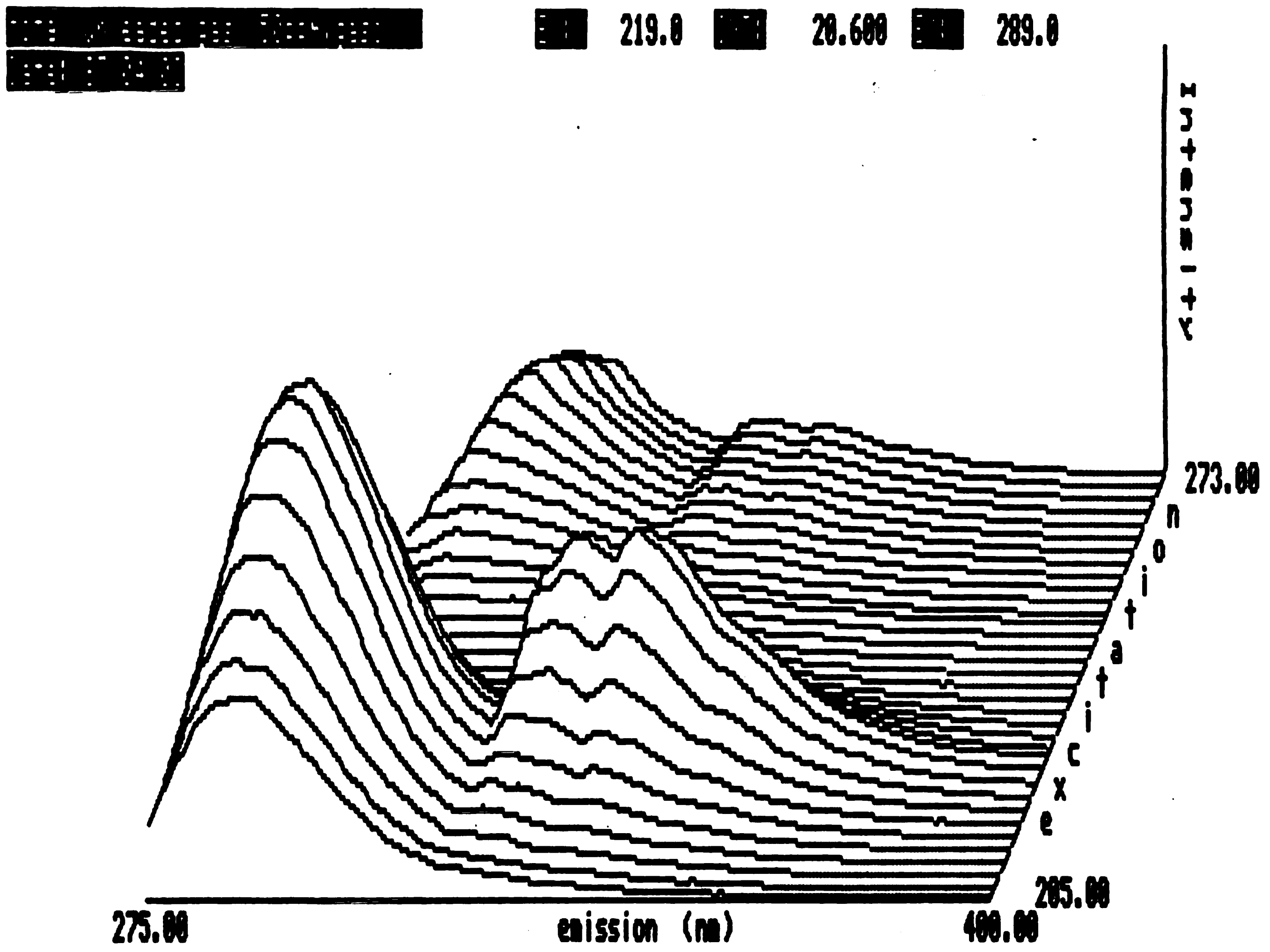

Figure 4.36 Total Unleaded Gasoline Neat

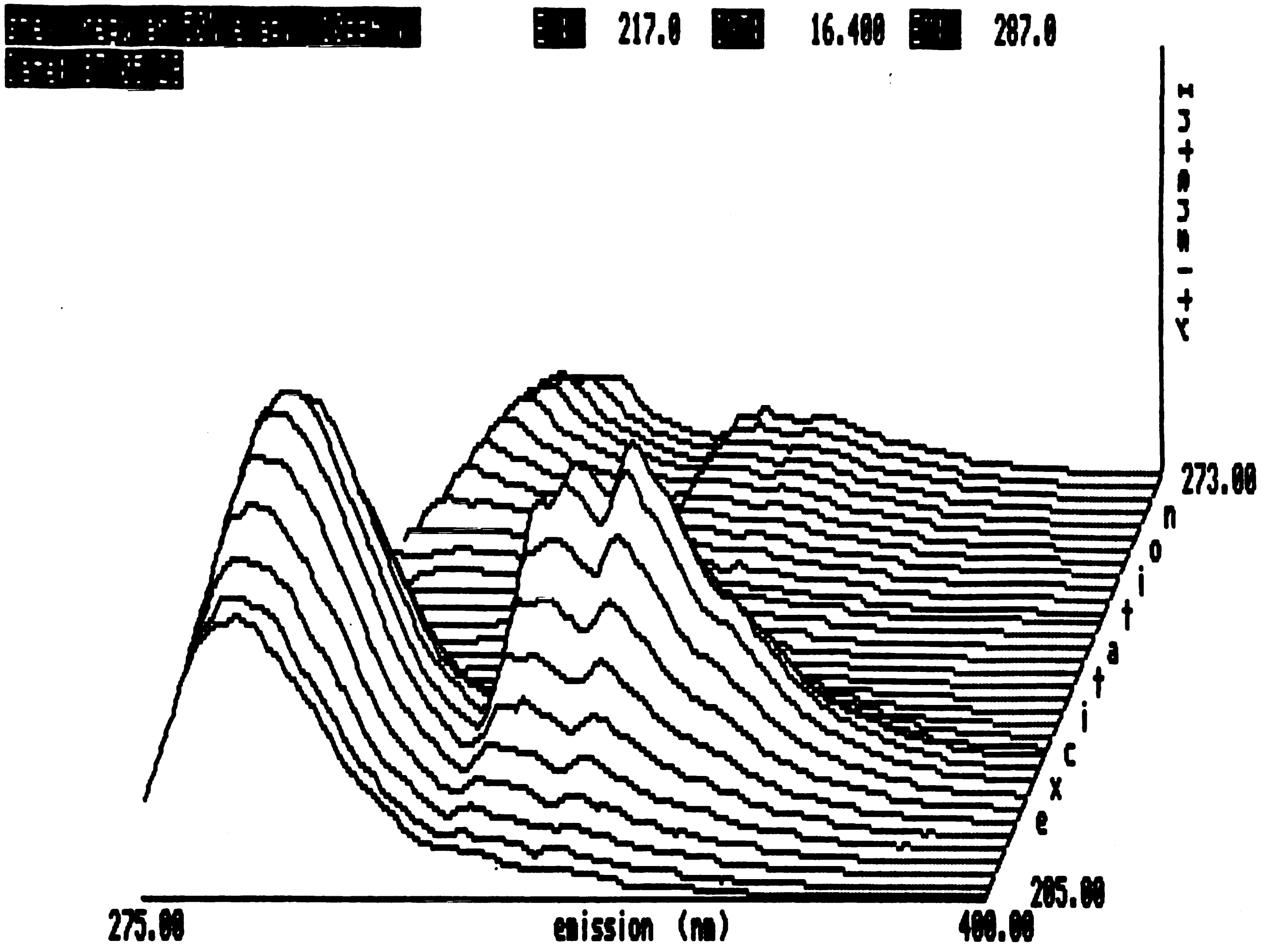

Figure 4.39 Shell Regular Gasoline 50% Evaporated

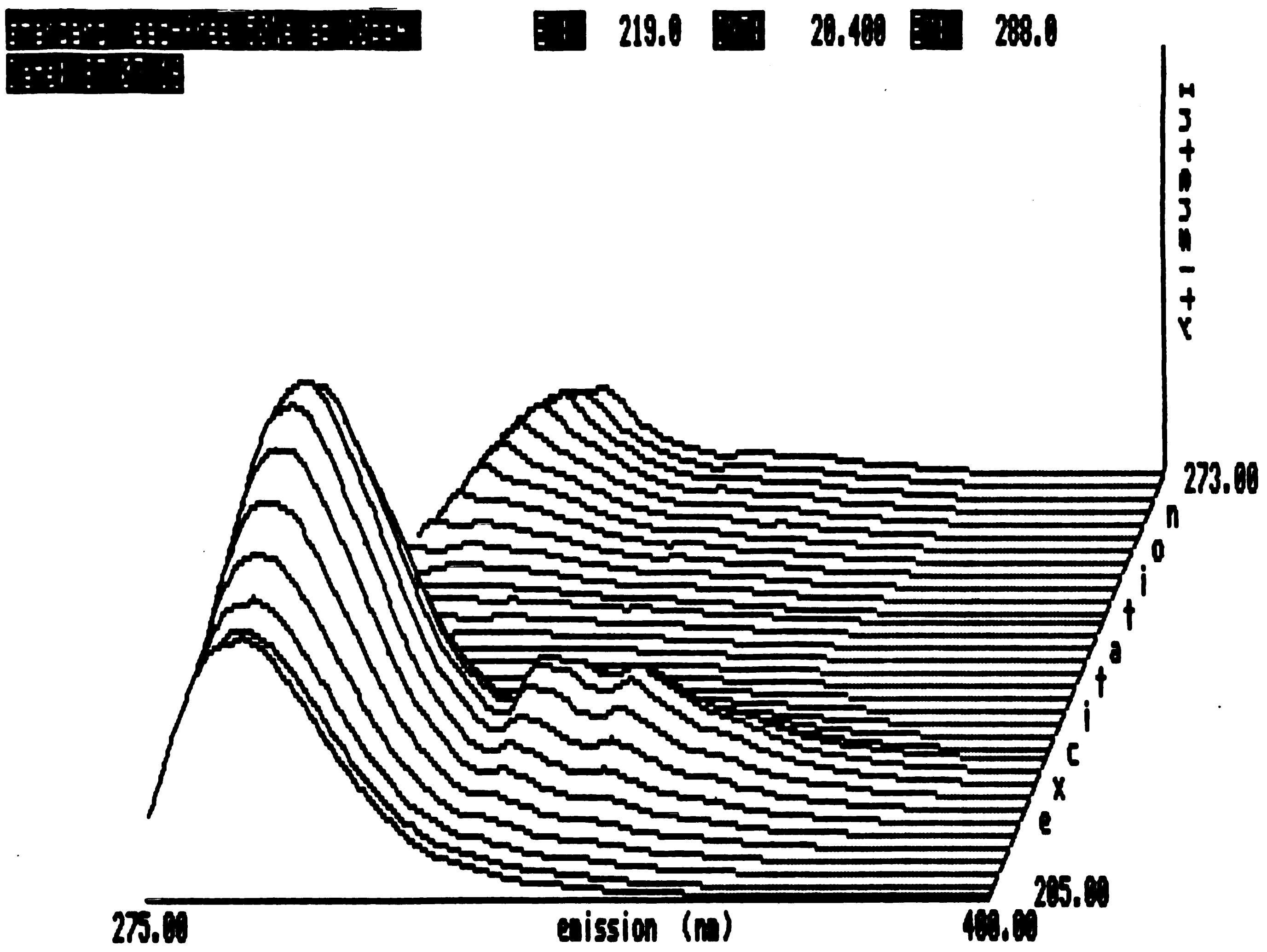

Figure 4.42 Standard Unleaded Gasoline 50% Evaporated

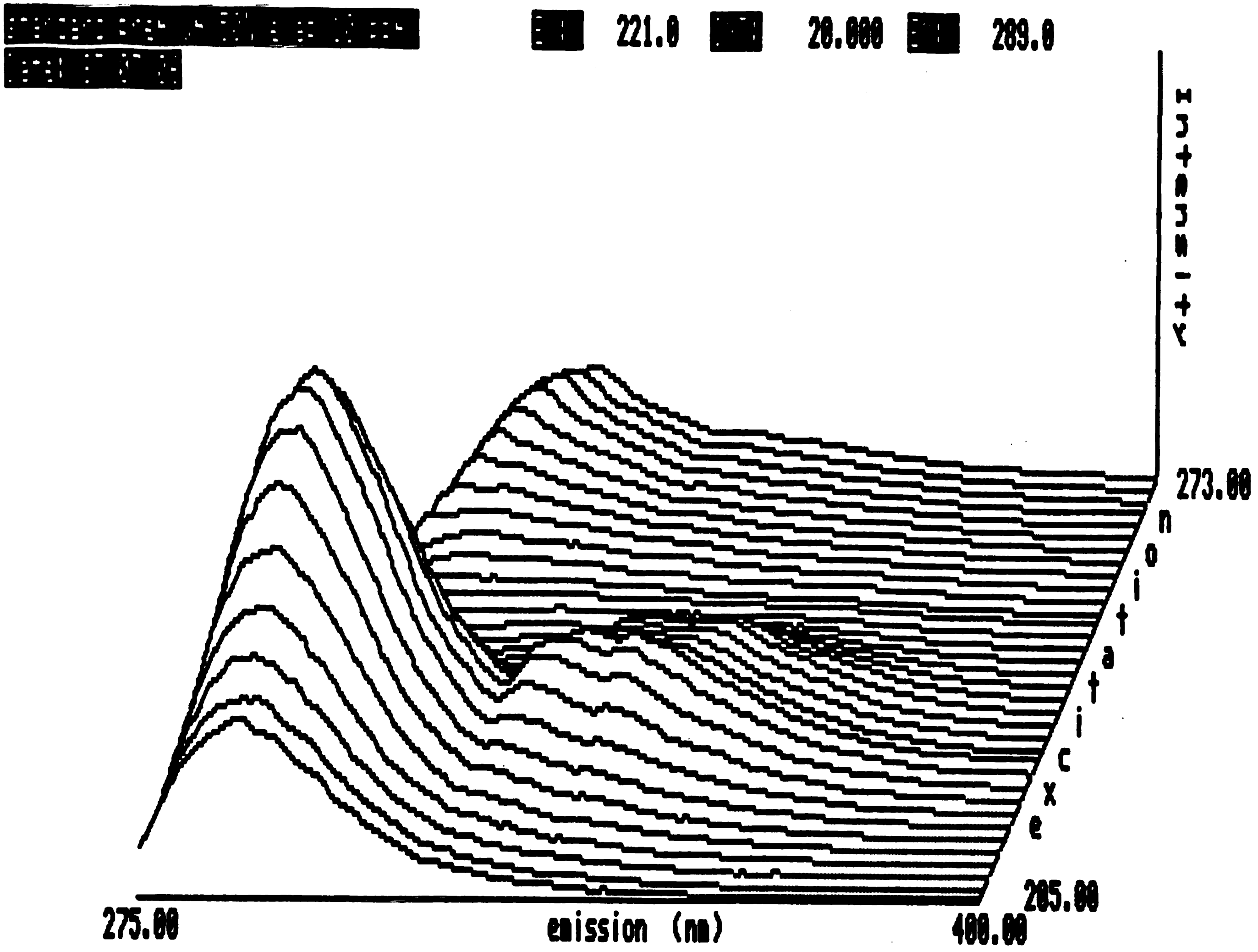

Figure 4.43 Standard Premium Gasoline 50% Evaporated

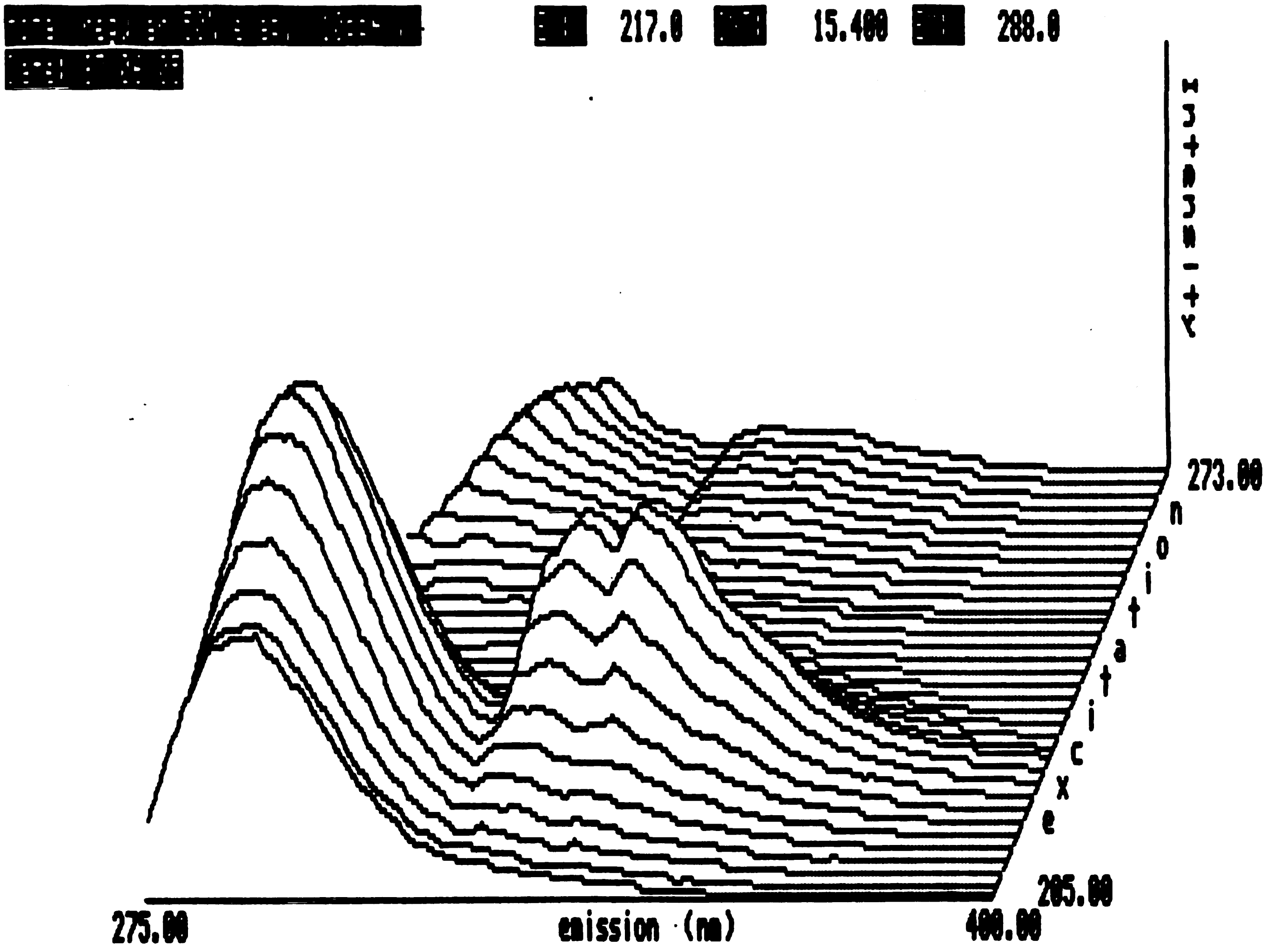

Figure 4.44 Total Regular Gasoline 50% Evaporated

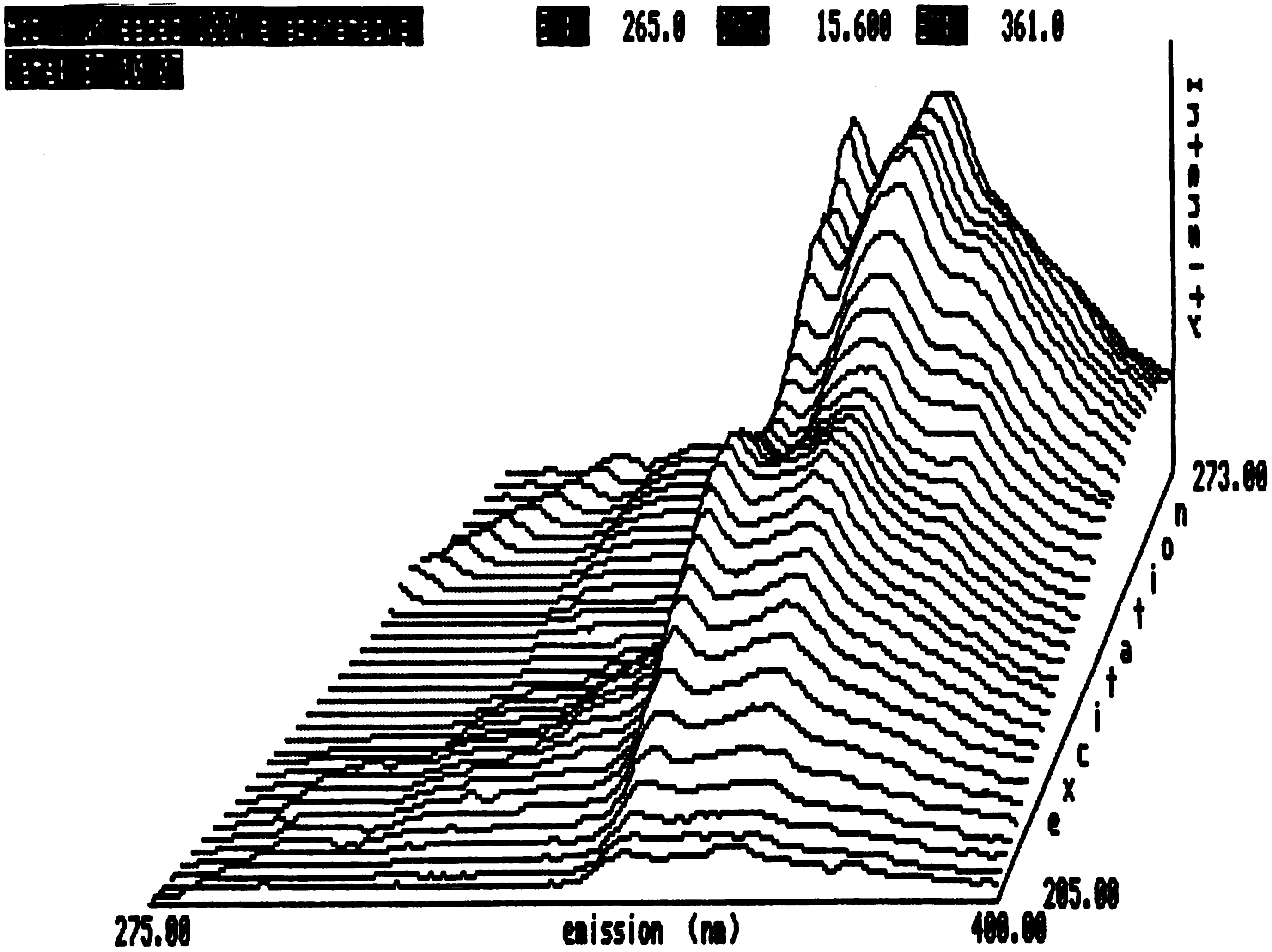

Figure 4.46 Mobil Unleaded Gasoline 100% Evaporated

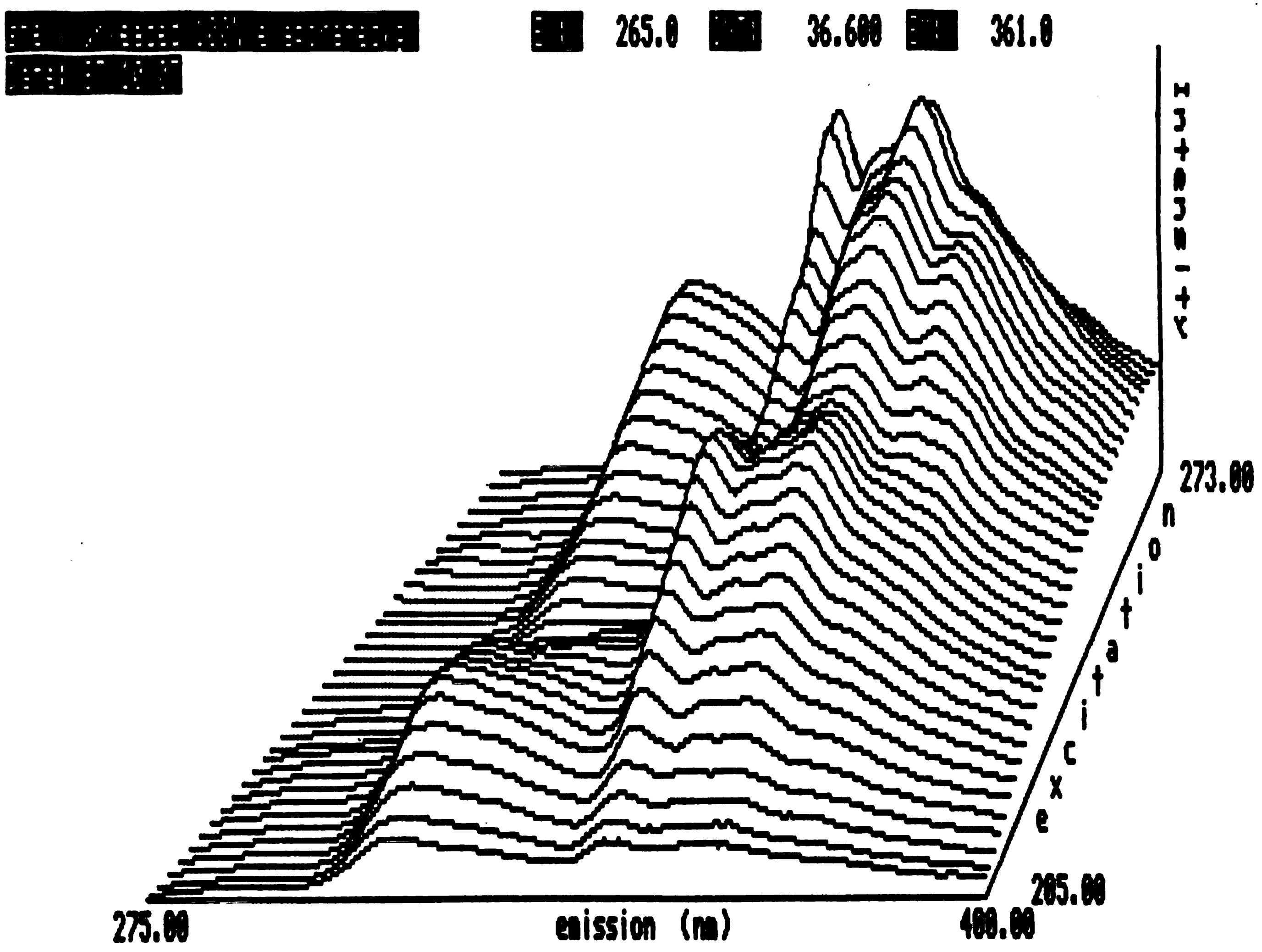

Figure 4.47 Shell Unleaded Gasoline 100% Evaporated

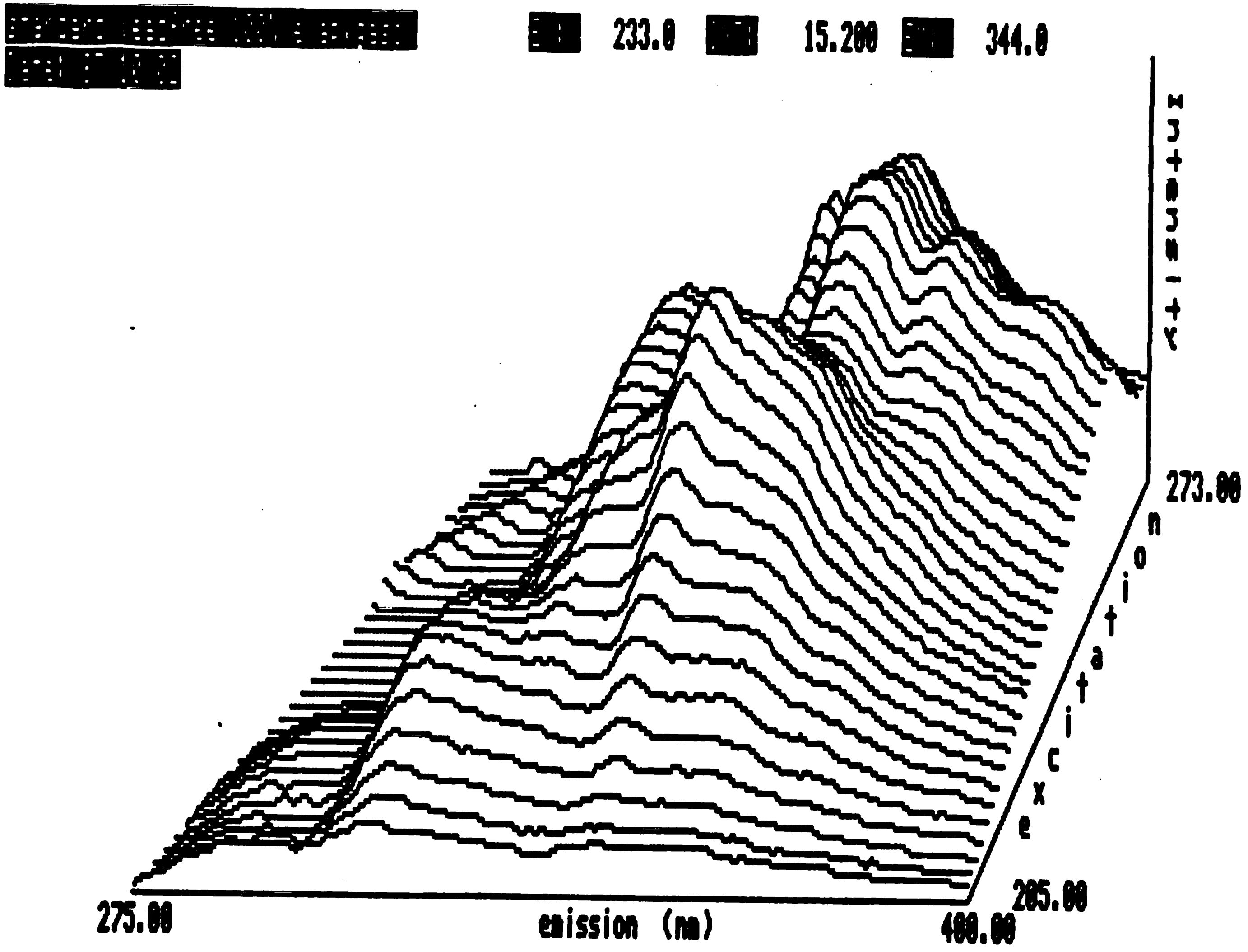

Figure 4.48 Standard Unleaded Gasoline 100% Evaporated

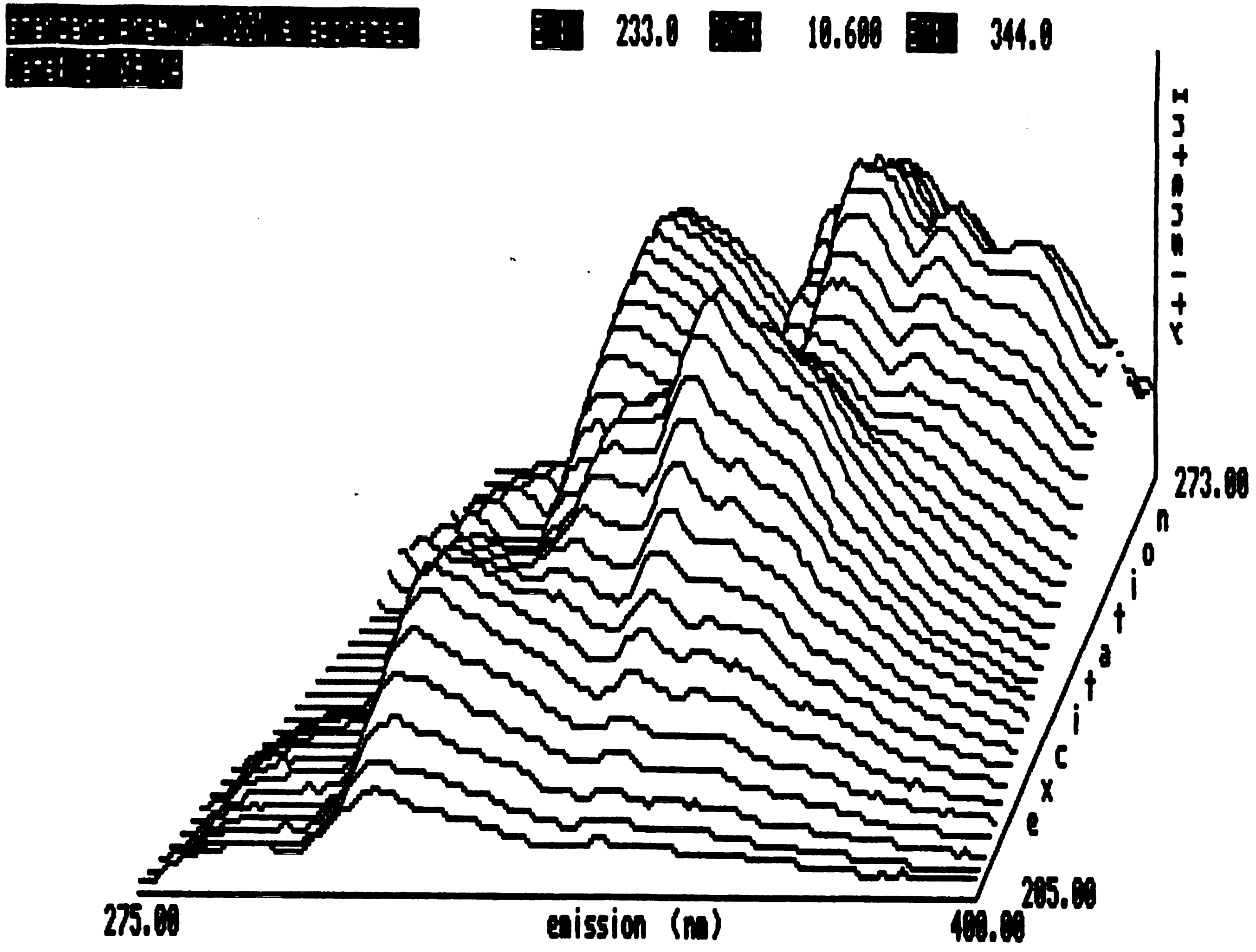

Figure 4.49 Standard Premium Gasoline 100% Evaporated

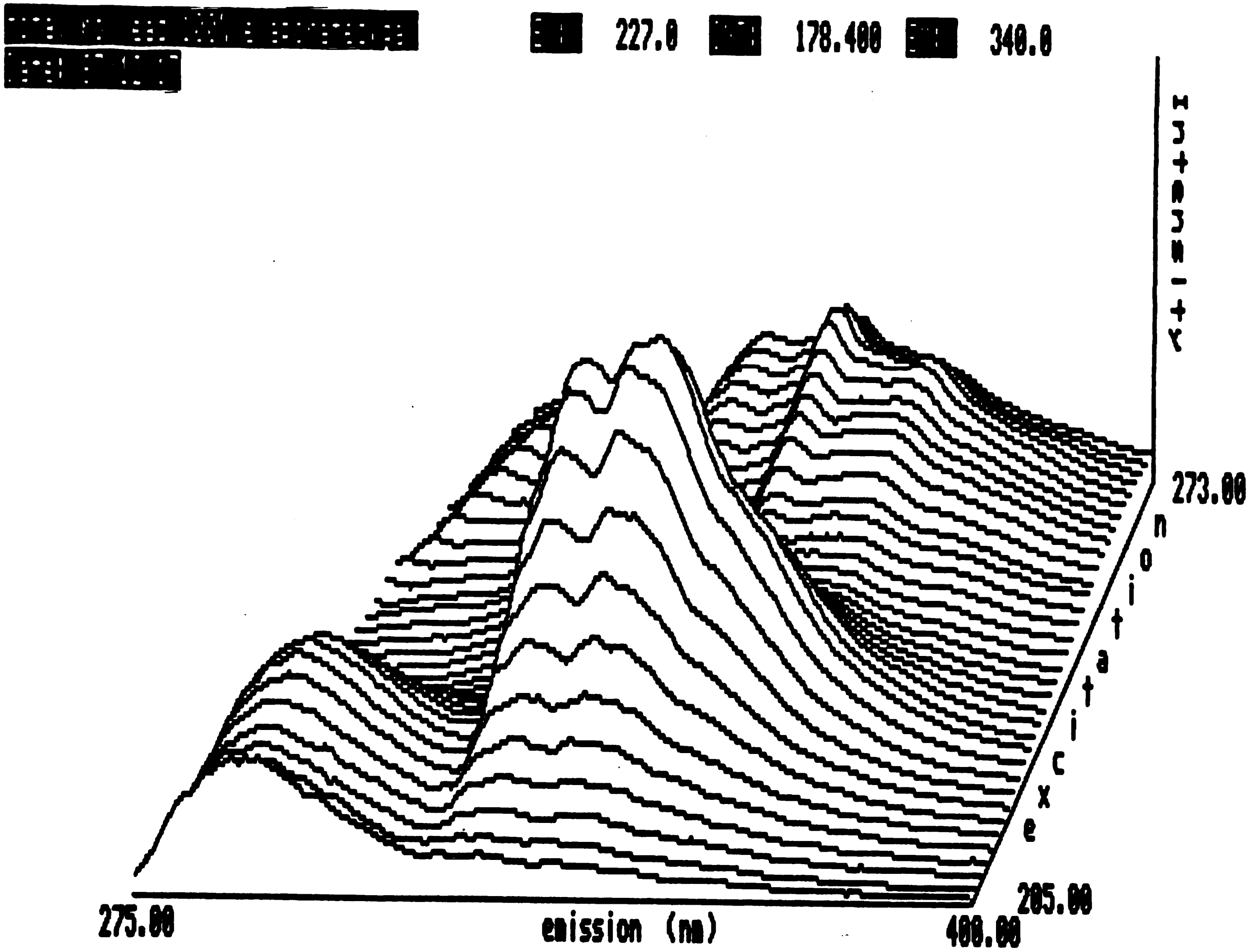

Figure 4.50 Total Unleaded Gasoline 100% Evaporated

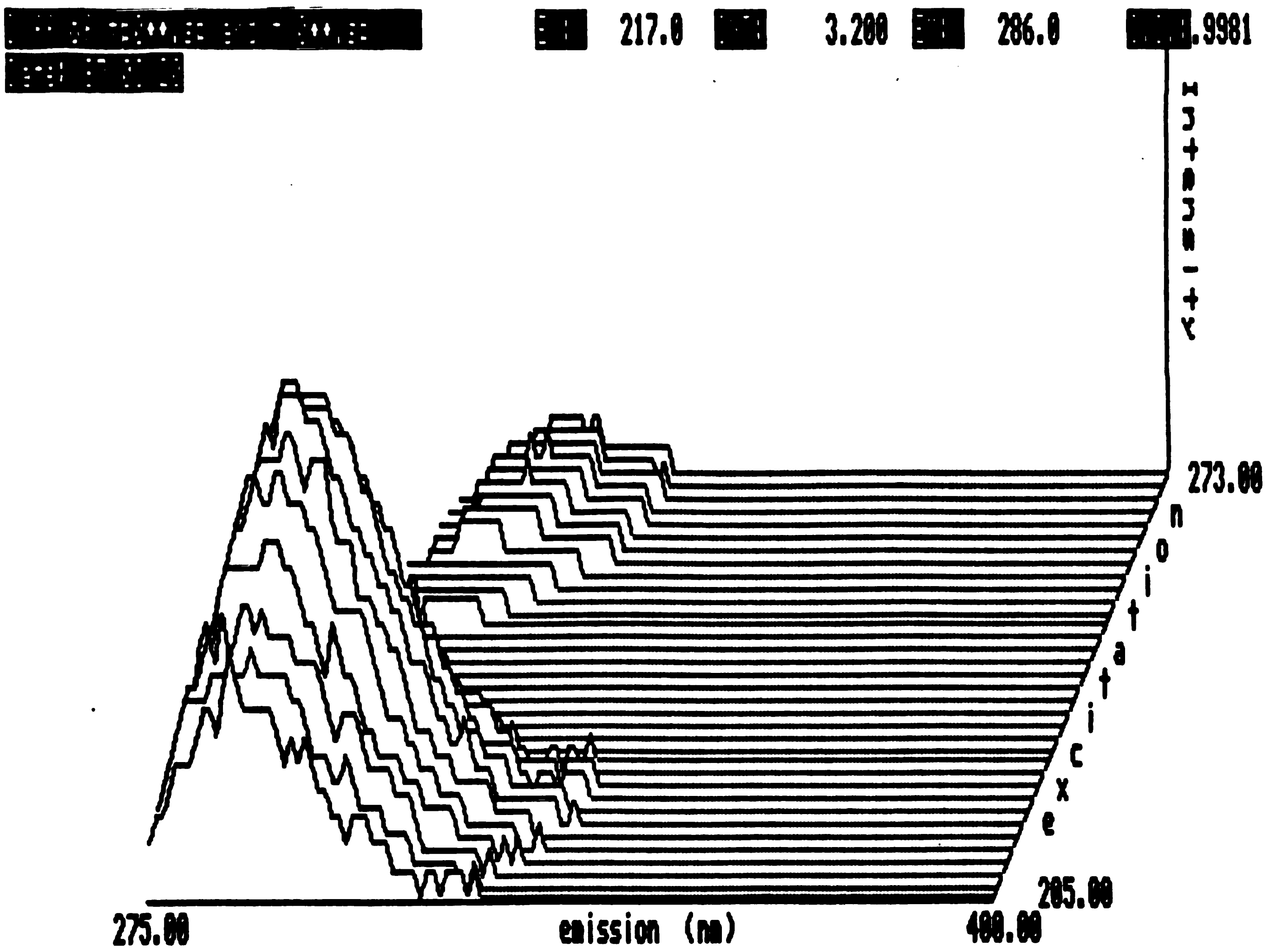

Figure 4.51 Standard Premium Neat Minus Standard Unleaded Neat

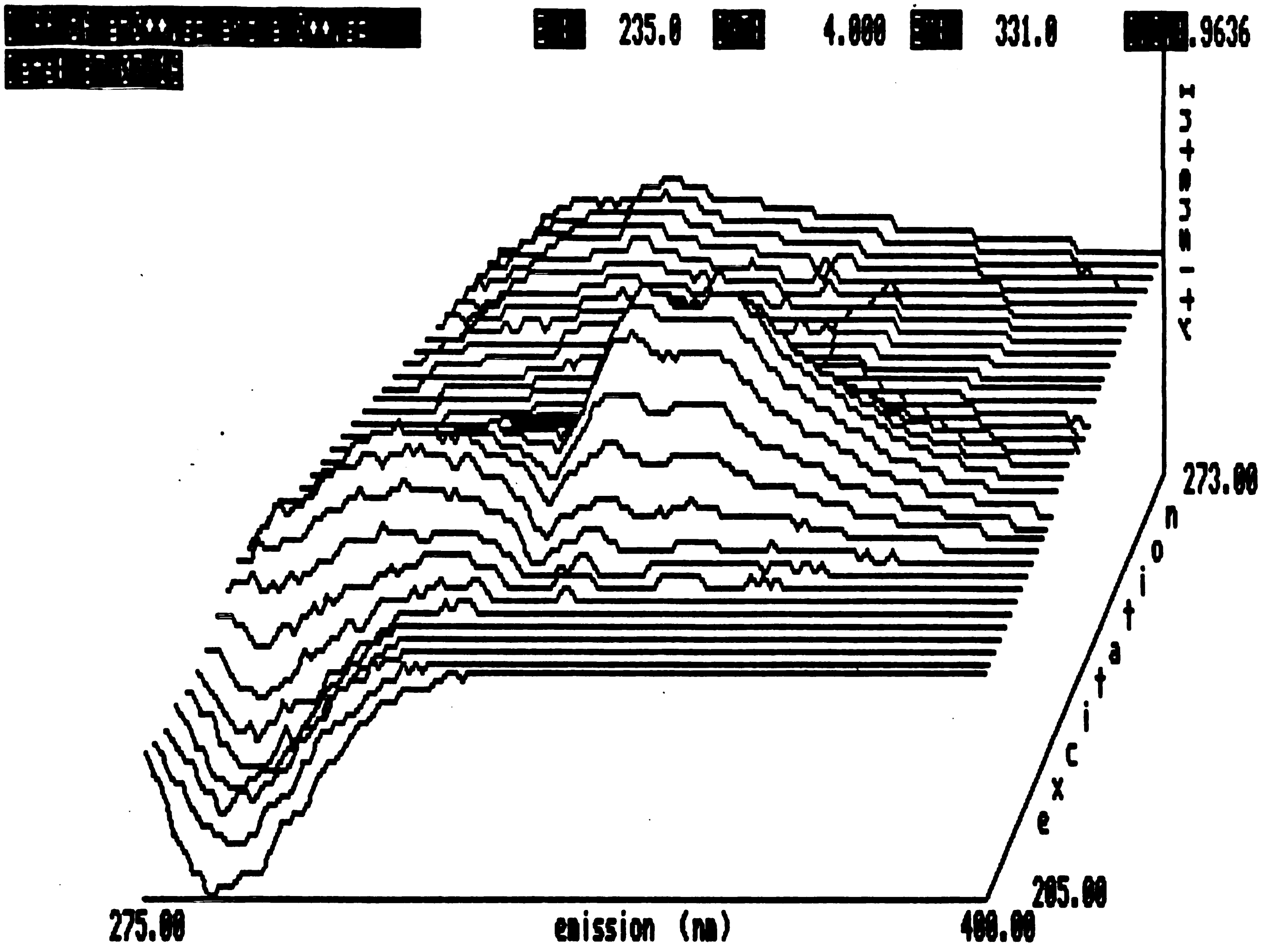

Figure 4.52 Standard Premium 50% Evaporated Minus Standard Unleaded 50% Evaporated

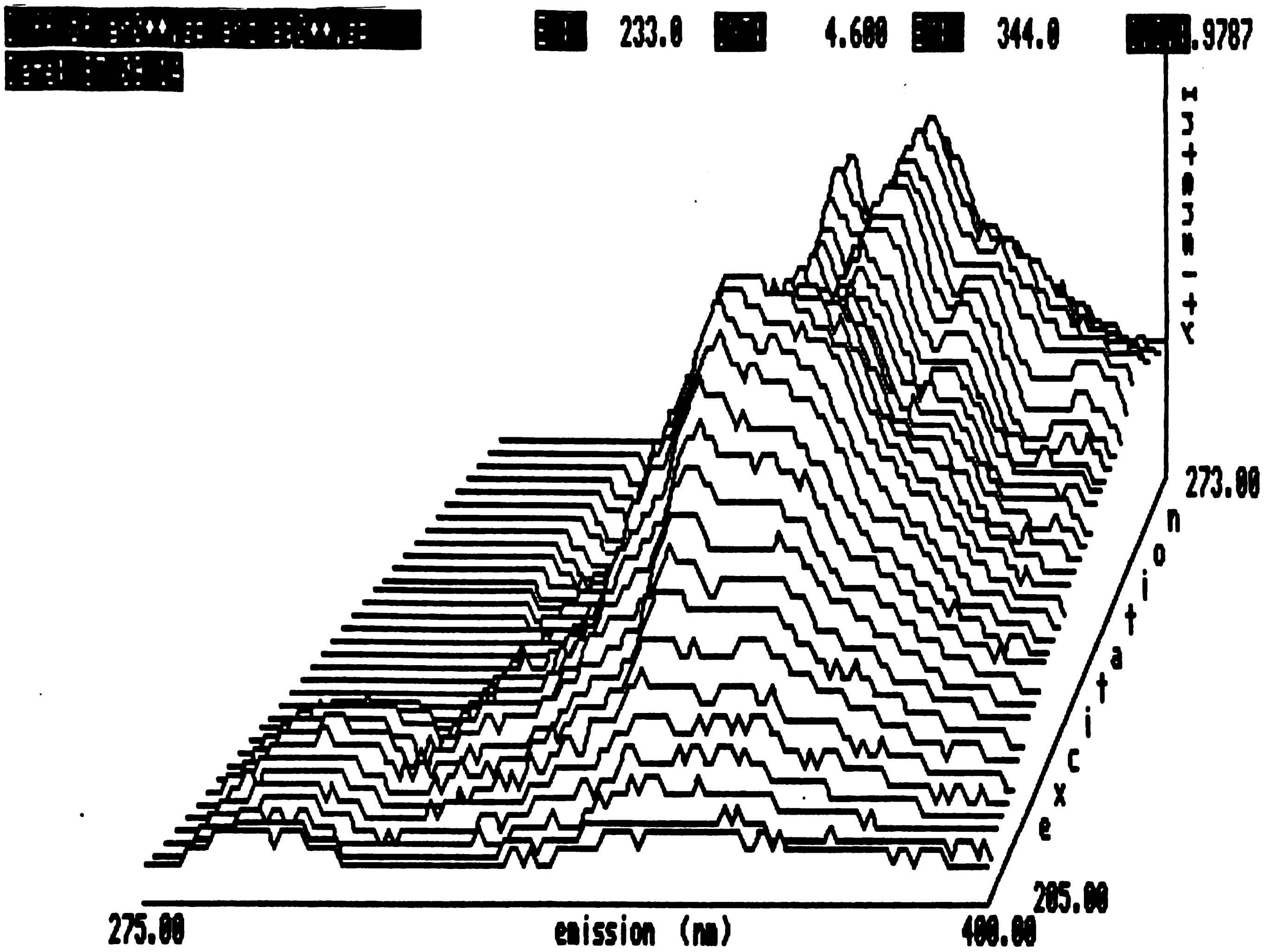

Figure 4.53 Standard Unleaded 100% Evaporated Minus Standard Premium 100% Evaporated

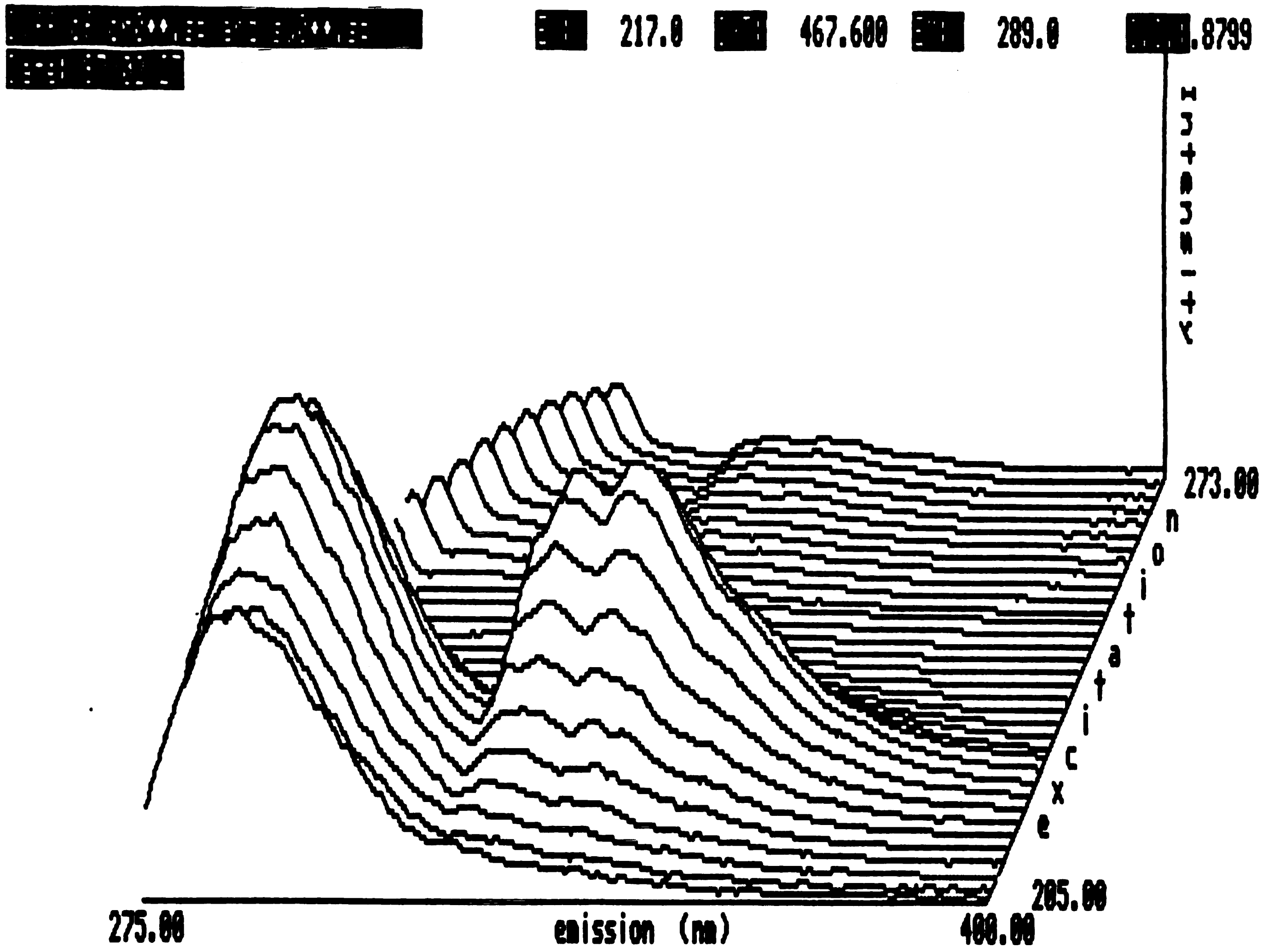

Figure 4.54 Total Regular Neat Minus Shell Regular Neat

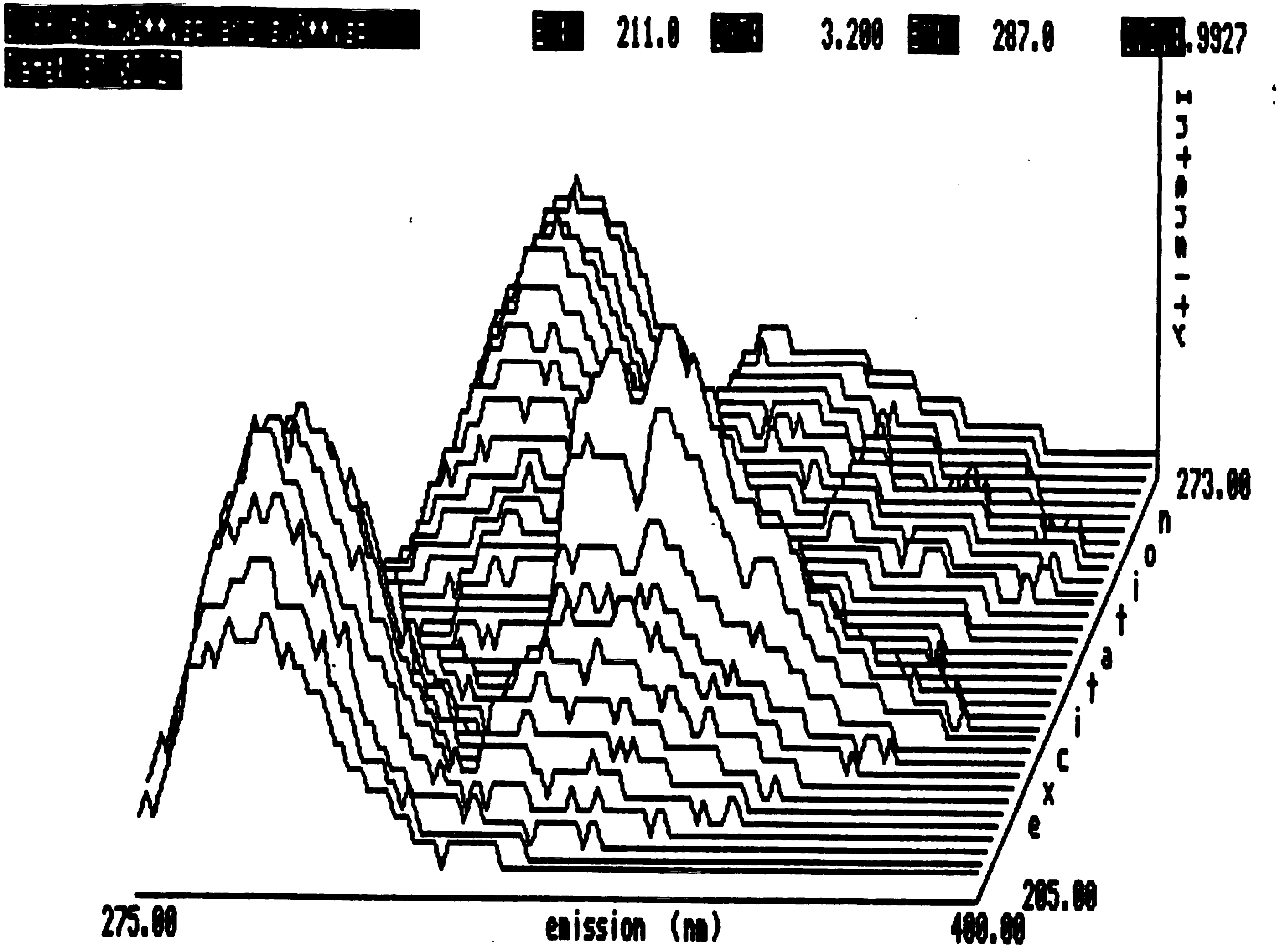

Figure 4.55 Mobil Unleaded Neat Minus Shell Unleaded Neat

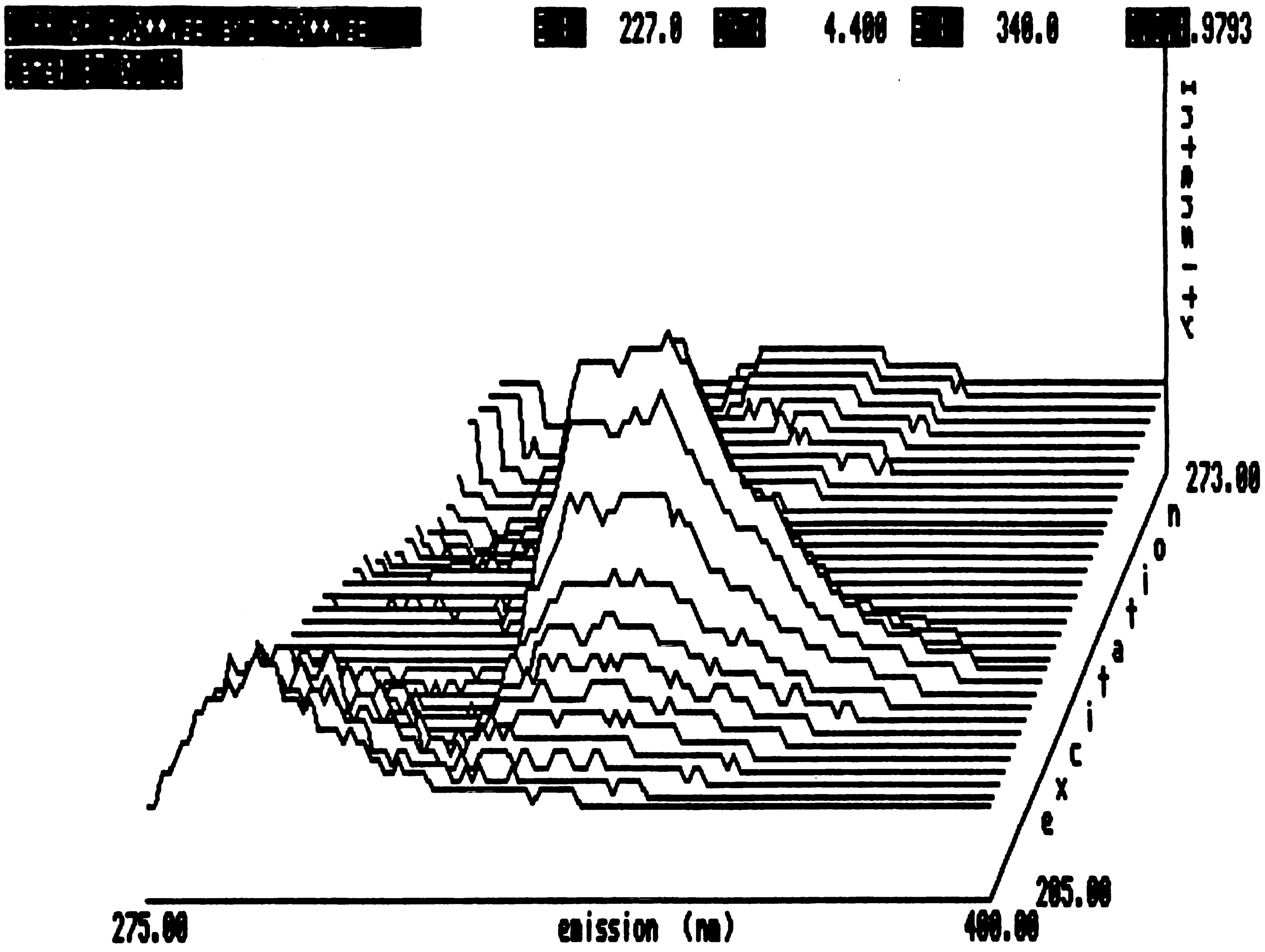

Figure 4.56 Total Unleaded Neat Minus Shell Regular Neat

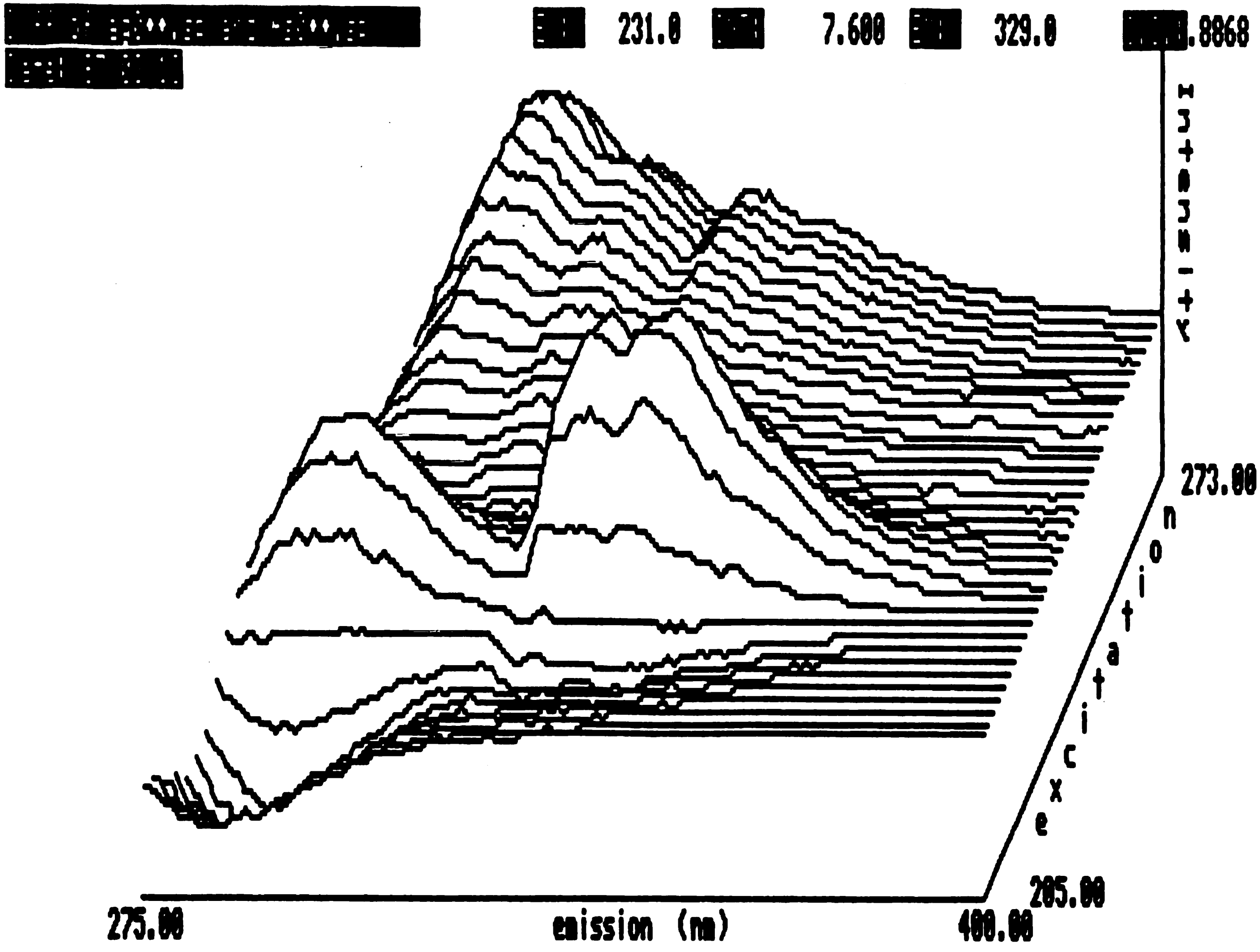

Figure 4.57 Mobil Super Unleaded 50% Evaporated Minus Mobil Super Unleaded Neat

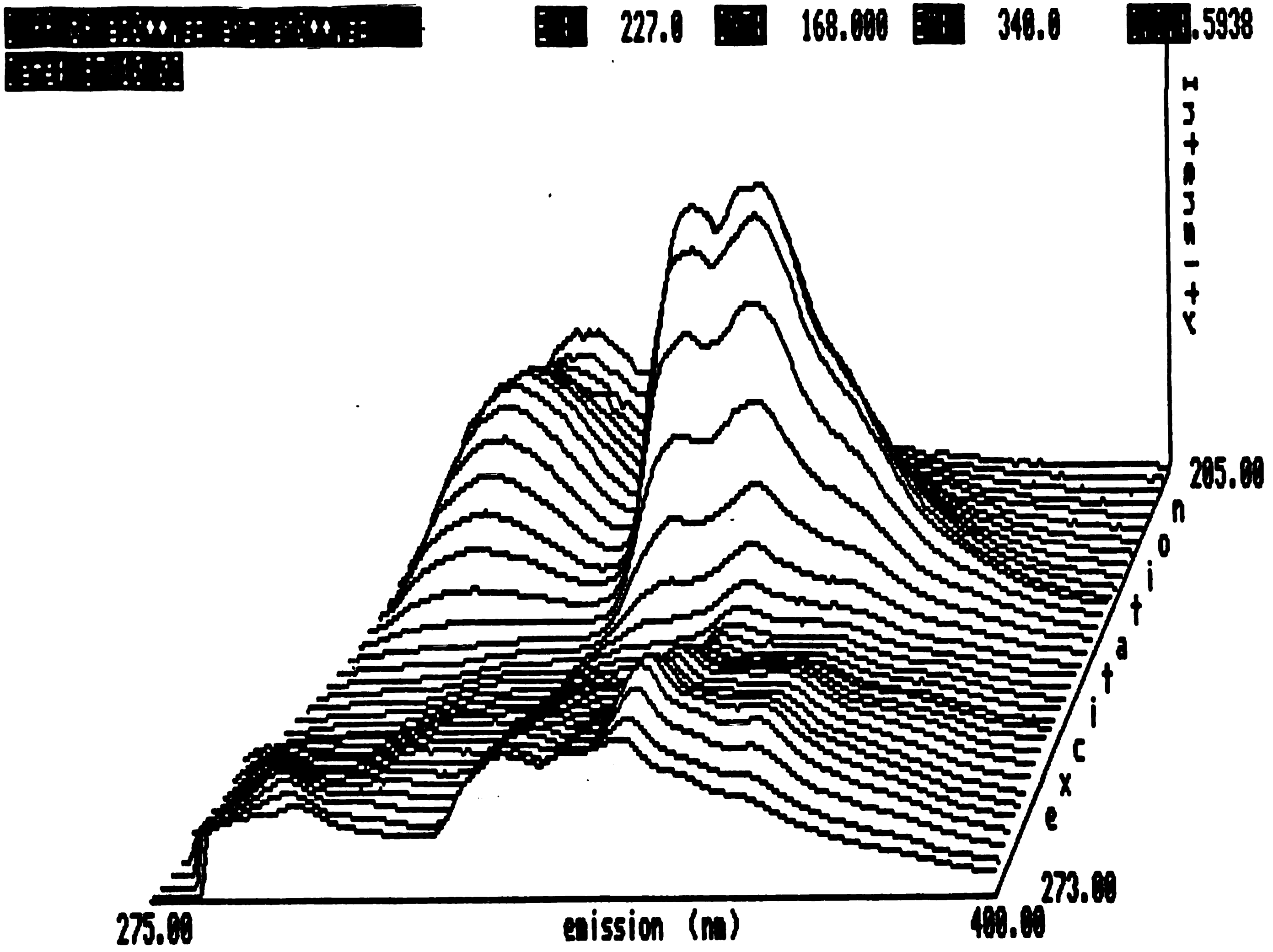

Figure 4.58 Total Unleaded 100% Evaporated Minus Standard Unleaded 100% Evaporated

Chapter Five

Discussion And Conclusion

CAPILLARY GAS CHROMATOGRAPHY

In comparing capillary gas chromatograms of the neat gasoline samples (Figures 4.3-4.11) it becomes immediately apparent that all of the gasoline samples look very similar. In addition to this there are several peaks in each chromatogram which would make a peak by peak comparison very tedious and time consuming. Even if a computer program was designed to do a peak by peak comparison, the major groups of peaks elute at approximately the same time from the column. There are major groups of peaks with the following retention times on the chromatograms of all the gasoline samples: 1-3 minutes, 5-6 minutes, 7-8 minutes and several small peaks having similar retention times greater than 8 minutes. Clearly, in this comparison the gasolines cannot be differentiated by capillary gas chromatography.

The capillary gas chromatograms of the 50% evaporated gasoline samples (Figures 4.12-4.20) also look very similar. The mid range peaks appear to have gotten stronger due to the loss of the lower boiling point fraction at the front end of the chromatogram. Unfortunately these losses are seen in all the gasoline samples with the major peak groups still present at the same retention times that they were prior to evaporation. There also still remains several peaks giving several points of comparison. Although some of the unleaded and premium grade gasolines show more intense peaks in the 7-8 minute retention time range, the 50% evaporated Shell unleaded gasoline (Figure 4.15) does not look any different in this area than does the 50% evaporated Shell regular gasoline (Figure 4.14). Therefore even in such a small sample size as this no common patterns are observed when looking at gasoline samples of the same grade. Again the gasoline samples cannot be differentiated by capillary gas chromatography.

After total evaporation the capillary gas chromatograms of the gasoline samples, (Figures 4.21-4.27), still look very similar within the same brand. For example Total unleaded (Figure 4.27) and Total regular (Figure 4.26) look very similar. However, they look different from the Mobil brand (Figures 4.21 and 4.22) or the Standard brand (Figures 4.23-4.25). Whether brands could be differentiated when they are 100% evaporated by this technique routinely cannot be determined by this study. However, differentiating between grades within a brand is not possible in the samples studied here. Capillary gas chromatography appears to be a useful technique in distinguishing different types of petroleum products. Also the possibility exists in the analysis of the totally evaporated gasoline samples of distinguishing brands as well.

THREE DIMENSIONAL FLUORESCENCE SPECTROSCOPY

Comparison of the three dimensional emission stacked plots of the neat gasoline samples, (Figures 4.28-4.36), were accomplished by direct visual comparison, the subtraction program and by Tables 1-3 which show each gasoline's excitation and emission wavelength at maximum intensity. Simply by viewing the tables it is apparent that the gasolines are very similar in that several have the same excitation and emission wavelengths or wavelengths that only differ by one or two nanometers. This is why the direct visual comparison is necessary to distinguish the samples by being able to view the entire range of fluorescence not just the wavelenghts at maximum intensity. This is especially so in the case of some of the 100% evaporated samples, even though their wavelengths are identical the total fluorescence emission stacked plots are completely different by visual comparison.

Clearly from these observations the neat gasolines can easily be differentiated from each other. However, there does not seem to be any similarity between the same grades of different brands in their fluorescence properties such that one could say, for example, that all the unleaded gasolines showed a certain characteristic fluorescence peak that the other grades did not. This same conclusion was reached by Siegel et.al. (24) in their study of the analysis of neat gasoline samples by three dimensional fluorescence.

The three dimensional fluorescence emission stacked plots of the gasoline samples after 50% evaporation (Figures 4.37-4.45), could easily be related to their corresponding neat plot. This was accomplished by simple visual comparison. In some cases the 50% evaporation made two samples easier to distinguish, Mobil and Shell unleaded for example (Figures 4.37 and 4.40) but in other samples the 50% evaporation made them more difficult to distinguish such as Mobil unleaded and Shell regular (Figures 4.37 and 4.39) or Mobil unleaded and Total regular (Figures 4.37 and 4.44).

The three dimensional emission stack plots of the totally evaporated gasoline samples (Figures 4.46-4.50) looked dramatically different from either their neat or 50% evaporated counter parts. All of the totally evaporated gasoline samples were readily differentiated from each other by direct comparison of their three dimensional emission stacked plots. However, they could not be compared back to their respective neat or 50% evaporated plots. These agree with the findings of Siegel et.al. (29) on the partially and totally evaporated mid-range petroleum products they analyzed by three dimensional fluorescence.

The gasoline samples studied here did not show consistent patterns of fluorescence characteristics within the same brand or grade.

The theory behind the three dimensional fluorescence analysis of totally evaporated gasoline samples is that the components left behind that fluoresce after the lighter volatile hydrocarbons are evaporated off are the high molecular weight polynuclear compounds which contain the most fluorescence. The fluorescence of these compounds seem to be hidden by the fluorescence of the lighter volitle hydrocarbon fraction as is illustrated by the fact that the 100% evaporated three dimensional fluorescence plots look so dramatically different from either the neat or the 50% evaporated plots.

The following examples illustrate how, by the use of all the data generated by this study, it is possible to distinguish these gasoline samples. Standard premium and Standard unleaded were the most similar of all the samples studied. They looked similar chromatographically and in their three dimensional fluorescence emission stacked plots both neat (Figures 4.33 and 4.34) and 50% evaporated (Figures 4.42 and 4.43). However, even though they had the same excitation and emission wavelengths at maximum intensity when 100% evaporated their three dimensional emission stacked plots were visually different. Even when these samples' three dimensional emission stacked plots were subtracted neat, 50% and 100% the resultant plots showed no substantial differences (Figures 4.51-4.53) with the Pearson's Q being very close to one. For the other samples either direct visual comparison or the subtration program or both could distinguish them.

For example, Total regular and Shell regular had very similar three dimensional emission stacked plots both neat (Figures 4.35 and 4.30) and 50% evaporated (Figures 4.44 and 4.39). However, when the neat plots were subtracted from each other the resultant plot showed substantial differences and a lower Pearson's Q (Figure 4.54). In the case of Mobil unleaded and Shell unleaded, the resultant subtration plot of the neat three dimensional fluorescence emission stacked plots (Figure 4.55) showed these samples to be very similar with a high Pearson's Q. However, when their 50% (Figures 4.37 and 4.40) and 100% (Figures 4.46 and 4.47) evaporated three dimensional emission stacked plots are visually compared, they do not look similar at all. The Total unleaded and Shell regular gasolines showed no major differences when their neat three dimensional emission stacked plots were subtracted (Figure 4.56) but upon visual comparison of the neat (Figures 4.36 and 4.30) and 50% (Figures 4.45 and 4.39) evaporated plots these samples do not look similar. Similarly the subtraction plot of the neat Mobil super unleaded and the 50% evaporated Mobil super unleaded (Figure 4.57) shows enough differences and a low enough Pearson's Q that one may conclude that they have a different source. However, upon visual comparison of the three dimensional fluorescence emission stacked plots it is obvious that they are very similar (Figures 4.29 and 4.38). When two samples that have completely different three dimensional fluorescence emission stacked plots are subtracted, such as 100% evaporated Total unleaded (Figure 4.50) and 100% evaporated Standard unleaded (Figure 4.48), the resultant plot shows major differences and a very low Pearson's Q (Figure 4.58). These examples serve to illustrate that one piece of information is not enough to characterize a multicomponent mixture such as gasoline. All of the information generated must be evaluated in order to reach the proper conclusion.

CONCLUSION

This thesis shows promise in characterizing neat, 50% and 100% evaporated gasoline samples by three dimensional fluorescence spectroscopy. Each of the samples analyzed showed dramatically different fluorescence characteristics not only from each other but also from themselves after evaporation. It is certainly a much more powerful technique in this regard than is capillary gas chromatography as is illustrated here. Further study is required to establish the reproducability of three dimensional fluorescence analysis of evaporated gasoline samples. Furthermore, more different brands and their respective grades require analysis by this technique to establish or discount any fluorescence patterns that may or may not be present in a specific brand or grade.

A study which focuses on the reproducability of the analysis conducted here would be a logical progression of this work. If the methods and results cannot be duplicated then their use in the analysis of neat and evaporated gasolines must be seriously questioned. Furthermore, this study involved only nine different brands of gasolines. There are certainly more than that in the United States alone, hence more brands need to be analyzed as well.

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