A COMPARATIVE STUDY OF THE IDENTIFICATION OF MIDRANGE PETROLEUM PRODUCTS BY GAS CHROMATOGRAPHY AND 3-D FLUORESCENCE SPECTROSCOPY

By

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ABSTRACT

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Twenty-two mid-range petroleum-based products, including charcoal lighters, paint thinners, and synthetic solvents, were studied by capillary GC and 3-D fluorescence. It was found that 3-D fluorescence is far better at discriminating among similar products than was GC, which could only put the products into broad classes. When partially or totally evaporated, the 3-D fluorescence plots were altered enough that they could not be matched with those of neat samples. A similar situation exists when they are burned. Also, when burned even under controlled conditions, these compounds did not yield consistent fluorescence patterns.

A blind test on neat samples showed that 3-D fluorescence can be a reliable technique for determining whether or not two neat samples were of the same brand.

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CONTENTS

PRELUDE

Arson investigation has been one of the most challenging subjects in the field of forensic sciences. The detection and analysis of accelerants are always considered one of the central themes in arson investigation, and has been the subject of many books and articles over the past thirty years or so. Numerous kinds of materials can be used as an arson accelerant. The most common ones are petroleum distillates or products. A sub-class are the so-called midrange petroleum products such as charcoal lighters and paint thinners. Because they are commonly found around the home, they have the potential to be used as an accelerant in arson fires. However, it is somewhat surprising that the midrange petroleum products have not been the subject of much research into classification and methods of detection and analysis. Therefore, the author believes that a careful study of midrange petroleum products will contribute to arson investigation in general as well as to petroleum-based accelerant analyses in particular. This is why Dr. Jay A. Siegel suggested the author choose this topic as his Master's thesis.

In Part I of the thesis, the author intends to give a broad but brief picture of arson crime in its legalistic and technical aspects; then change the focus from arson investigation to general laboratory methods of accelerant analysis, and finally to highlight the gas chromatography (GC) and three dimensional

fluorescence spectroscopy techniques which were used in this study.

In Part II, III VI and V, the study involving twenty-two midrange petroleum-based products, including charcoal lighters, paint thinners, and synthetic solvents, is described. All the samples were measured under the conditions of (1) neat state, (2) 50% evaporated state, (3) 100% evaporated state, and (4) totally burned state. In addition, a concentration study and a blind test of neat sample were also conducted. It was found that 3-D fluorescence is superior at discriminating among similar products than was GC for neat samples. When partially or totally evaporated, the 3-D fluorescence plots were altered enough that they could not be matched with those of neat samples. A similar situation exists when they are burned. Also, when burned even under controlled conditions, these compounds did not yield consistent fluorescence patterns.

PART I. INTRODUCTION.

1. ARSON CRIMES IN GENERAL.

No person can argue with the fact that arson is one of the major property crimes in the United States as well as in most other countries in the world. Its seriousness could be viewed from different perspectives. First, in terms of crime rate, although the incidence of arson is not as high as the crime of robbery, auto theft, or breaking and entering, it is comparable in number to the homicides committed each year [1]. Second, in terms of arson occurrence, in 1975, the report from the National Research Committee of Fire Research estimated that perhaps as high as 40% of all fires are caused by arson [2]. Third, in terms of amount of money lost by the victims, the above report has established the annual loss from wrongful setting of fires at between 5 and 6 billion dollars. Fourth, in terms of death rate, it was estimated more than 4,000 deaths from arson occur each year in the United States [3].

In the United States, historically, common law conceptions of arson referred to the "malicious burning of the dwelling of another". However, modern statutes have altered the notion of arson in variety of ways. For example, Massachusetts has expanded the definition by passing legislation defining arson as "the willful and malicious setting fire to, or burning of, any building

or contents thereof even if they were burned by the owner" [4]. According to the Uniform Crime Reports (UCR), which publishes nnually by FBI, arson was assigned as item 8 of the Part I offenses ("crime known to the police and arrests"), and was defined as "any willful or malicious burning or attempt to burn, with or without intent to defraud, a dwelling house, public building, motor vehicle or aircraft, personal property of another". Today, like most other legal concepts, the definitions of arson are not the same in different states. However, in comparison with the common law, the expansion of modern statutes about arson at least could be summarized in three aspects. (1) While arson originally carried the ideas of fire and burning, many jurisdictions now include the use of explosives. (2) Contemporary statutes include not only dwellings, but also other types of buildings, as well as other property like motor vehicles and aircraft as the subject of the arson crime. (3) The property of the arsonist is also included if there is an attempt to defraud an insurer or if the building is occupied [5, 6].

Though the legal definitions of arson vary historically and geographically, it was and is a felony in all jurisdictions. Typically, arson is divided into at least two degrees and sometimes three [7]. In general, if the premises set afire are occupied, the charge will be "first-degree arson". If they are unoccupied, the case will be one of "second-degree arson". A person is guilty of arson in the third degree if the premises burned are his or her own, if they are unoccupied,

and if the purpose is to defraud the insurer.

Arson is a complex crime and often presents difficulties during investigation and prosecution. Take Connecticut State as an example, in the single year of 1980, there were 6820 incendiary and suspicious fires, but only 500 arrests (about 7.3%) were made, and only 72 people (only about 1.1%) were convicted of arson [8].

The complexity of arson cases can be viewed from two major perspectives: legalistic and technical. Viewed from the legalistic perspective, the principal problem is the element of criminal agency, or intent. Studies have shown that the reasons for arson are both numerous and obscure, and sometimes hard to detect. For instance, there are "revenge firesetters", whose crimes result from anger, hatred, or jealousy in personal relationships; there are "excitement firesetters", who simply enjoy watching fires and the operations of fire equipment; there are "insurance-claim firesetters", who incinerate business property for its insurance value; there are "vandalism firesetters", who set building ablaze as part of adolescent peer-group activities; there are "criminal vindication firesetters", who use arson for hiding the evidence of other crimes. There also might be "professional torches", who incinerate buildings for a fee, the "firebomers" of activist and political liberation organizations, the large number of skid row vagrants who seem to be over represented among those

arrested for arson, and the many other types for whom intent and motivation are not altogether clear.

From the technical perspective, a fire can have many accidental causes, including faulty wiring, overheated electric motors, improperly cleaned and regulated heating systems, cigarette smoking, etc.. The ultimate task of fire investigation is to establish the willful or malicious setting of a fire. Therefore, final determination as to the cause of a fire must take numerous factors into consideration and requires an extensive on-site investigation as well as laboratory analysis to characterize the physical evidence which could link the cause(s) of a fire and link the person's intention of setting a fire. This task presents a major challenge with many troublesome circumstances to investigate and analyze. First, arson is likely to be conducted premeditatedly with a thorough plan and is committed in secret; little direct evidences or eye witnesses are normally available. Second, it is ordinarily done at the convenience of a perpetrator who has left the crime scene long before any official investigation is launched. Third, all kinds of potential physical evidence are rendered more difficult to obtain than most other kinds of crimes because of the extensive destruction by the fire. Fourth, the top priorities on a scene of a fire are the fire-fighting and life/property rescuing operations rather than collecting potential crime evidence in a most careful and time-consuming manner. Notwithstanding, the first task definitely and sometimes

devastatingly influences, disrupts, or damages the success of the second task in an irreversible way.

All the above factors indeed attribute to the difficulties of arson investigation, but they do not mean that it is impossible to get physical evidence for prosecution of arson cases. As a matter of fact, modern technologies have demonstrated that by means of well-organized, scientific procedures and a thorough search at the fire scene on the one hand, and by means of well-chosen analyses in crime laboratories on the other hand, various types of physical evidence can still be found and can yield valuable results.

The types of physical evidence at an arson scene depend on the method used by the arsonist to set the fire, and can be placed in two broad categories: (a) physical evidence which may be associated with the suspect but not with the incendiary itself, and (b) residual components of the incendiary. The first category includes fingerprints, shoe impressions, toolmarks, glass fragments, blood, tissues, hairs, fibers, and many kinds of trace materials. Though in a particular case, one of these types of evidence may be collected and be crucial in investigating or in prosecuting procedures, because of the destructive nature of fire itself and the chaotic condition of fire scenes, most evidence in this category is likely destroyed or lost, hence infrequently acquired by scene investigators. The second category -- residual components of an incendiary, in

its broad meaning, includes ignition devices, matches, cigarette lighters, papers, pieces of wood, and a variety of accelerants which can assure the rapid start, the enhanced intensity, and the extent of a fire. Among them, experience has shown that accelerants are involved in most arson cases and are frequently found at arson scenes. Therefore, in suspected arson cases, the forensic scientist's function is primarily concentrated on the detecting, demonstrating and analyzing accelerant. The expert testimony of identification of accelerant is extremely important to the success of the prosecution because the discovery of an accelerant establishes "intent" of the arsonist -- a requirement under most statutes as we discussed above [9].

According to its physical state, accelerant can be classified into three groups: (1) gaseous state, (2) solid, and (3) liquid. Gaseous accelerant consist of coal gas, natural gas, propane, and so forth. Solid accelerant include fireworks, explosives, and so on. In arson investigation, it is well acknowledged that the most commonly encountered accelerant are liquids. They include gasoline, fuel oil, kerosene, charcoal lighter, paint thinner, dry cleaning fluids, wax solvents, methanol, alcohol, turpentine, lacquer thinner, industrial solvents, and numerous types of flammable chemical reagents, or any proprietary products that utilize any of the above as carrier or solvent. Among them, petroleum distillates or petroleum-based products are estimated to occupy more than 95 % of the total, because they are easily available and are highly flammable [10].

In order to correctly analyze a suspicious liquid submitted to a crime laboratory, it is helpful to have some brief knowledge of the nature and classification of most frequently confronted accelerant -- petroleum-based products, or petroleum distillates. They are mixtures of many different hydrocarbons, especially different types of polycyclic aromatic hydrocarbons (PAHs). However, the exact components and the composition of these components of a particular product are often not specified or have not been fully studied. For the purpose of our discussion, it is convenient to categorize them into two classes: straight-run products and mixtures of specially processed ones. The following shows the common accelerantes in each class:

Class I. Straight-run products:

1. Light petroleum distillate; for example, naphtha, lighter fluid, cleaning fluid.
2. Medium petroleum distillate; for example paint thinner, charcoal lighter.
3. Heavy petroleum distillate; for example kerosene, diesel fuel, fuel oil.

Class II. Specially processed petroleum products:

1. Separate aromatic; for example, benzene, toluene, xylene.
2. Blended aromatic and aliphatic; for example, gasoline.

3. Blended or modified products; for example, lubricants and special solvents.

The main points above can be summarized as: (1) Arson involves two major aspects: legal and technical. (2) Physical evidence is the key part of the technical aspect. (3) Among various types of physical evidence, residual materials of incendiary are mostly found. (4) Among various residual materials of incendiary, suspected accelerant are mostly found. (5) Among various suspected accelerant, suspected liquid accelerant are mostly found. (6) Among various liquid accelerant, petroleum-based products are most often found. Therefore, the next section will focus on basic techniques of detection of liquid petroleum-based products in arson investigation.

2. BASIC TECHNIQUES OF ARSON INVESTIGATION.

In the situation of most other criminal investigations, when the detective work starts, though there are a lot of unknown things, at least one thing is clear -- it is a crime. But in most fire cases, when the scene investigator starts his work, the cause of the fire is still likely unknown. Therefore, three questions should be answered through the fire investigation and prosecution, if possible. The first is "HOW", i.e., how the fire started? In other words, was the fire an

accident or was it set intentionally? The second is "WHO", i.e., if the fire was set intentionally, or it was an arson, who started the fire? The last question is "WHY", i.e., if the person who set the fire had been found, why he or she did it? The "HOW" question is mainly answered by scene investigators. The "WHO" question is mainly the result of a joint efforts of scene and laboratory personnel. The "WHY" question is mainly solved through the court inquiry process. This last question, though which is critical in the trial and sentencing process, is out of the scope of our study and will not be discussed in the rest of this paper.

Usually, in the stage of answering "HOW" and "WHO" questions, a suspicious liquid (Sample A) is detected and identified at or around the fire scene. Latter on, in addition to Sample A, a control liquid (Sample B) which is possessed by the suspect(s) is frequently submitted with the request that the laboratory determine if it came from the same source as that identified in the scene. In a case like this, there exist two tests: (1) a necessary two-step detection of Sample A and Sample B, and (2) a potential two-step physical link between the fire scene and an individual.

For the detection task, the first step is to find Sample A at or around the fire scene, and the second step is to find Sample B. Either of these steps could only be performed by experienced professional through a careful and thorough

search, and then be well preserved and delivered.

For the link task, the first step is establishing the link between the liquid and an individual. This is usually the responsibility of the submitting agency and is accomplished by direct possession, fingerprint comparison, and so forth. The second link, that the link between the Liquid A and Liquid B, is more difficult to achieve, and is primarily the responsibility of crime laboratory. The variation of individual products within the pertinent general product classification must be determined before the attempt to establish this second link [11].

2.1. ARSON SCENE INVESTIGATION

As with other types of criminal investigations, the key to successful examination of arson evidence begins with the scene investigator. The final determination of whether a given fire is arson usually depends upon the skill and experience of the fire scene investigator; however, the forensic science laboratory can assume an important backup role by determining the flammability and the identity of an accelerant which is recovered from the fire. Arson-scene investigation, which is often long and tedious, and it generally

includes:

1. Determination of the point of origin of the fire.
2. Examination of electric and mechanical equipments to evaluate the possibility of the fire having been caused by their failures.
3. Examination of the burning patterns.
4. Recognition and collection of the relevant physical evidence.
5. Analysis and reconstruction of the scene.
6. Determination of the cause of the fire.

In all steps of the above procedure, a question about the possibility of arson should always be kept in a scene investigator's mind. Particularly, the above steps 3 and 4 are key processes if the fire is suspected as an arson. When suspected liquid(s) are involved, the following three approaches are needed to be conducted properly in order to get proper samples for laboratory analysis.

2.1.1. Recognition.

Though as it has been emphasized above that arson investigation provides an exceedingly difficult circumstance to recognize and preserve evidence, fortunately, practice shows that only under the most ideal of conditions will combustible liquid(s) be entirely consumed during a fire. For example, when

a flammable liquid is poured over a large area, it is highly likely that a portion of it could seep into porous surfaces nearby, such as cracks in the floor, plaster, upholstery, rags, wall boards, or carpet, where enough of it remains unchanged so that it can be collected by scene investigators. On the one hand, the liquid seeping naturally tends to go downwards by the force of gravity; on the other hand, the center of combustion is in gaseous state, and naturally tends to move upwards because of the effect of hot air causing lower pressure, and tends to sweep over towards a more ventilated direction very rapidly, consequently leaving the original point of fire below or behind. The results of these two opposite movements provide a considerable chance for scene investigator to discover liquid accelerant residues even in the situation where a fire was very serious. In addition, when a fire has been extinguished with water, the rate of evaporation of volatile fluids may have been slowed down because water cools and covers materials through which the combustible liquid may have soaked. Favorably, the presence of water does not interfere with later laboratory methods utilized to detect and characterize flammable liquid residues unless there are huge amounts of water.

Arson with a flammable liquid usually produces a characteristic structural fire pattern which will give the investigator some hints in identifying promising areas, such as the origin of the fire, for evidence collection. If there are some porous or absorbent materials near the origin (such as paper, carpeting, fabric,

book, etc.), these may have retained a substantial amount of volatile accelerant and should be collected even no visible liquid could be found by the naked eye. However, when solid state materials such as paper, pieces of wood, or trash are solely used to start a fire; or when gas phase materials such as natural gas or propane are used as an arson tool, there will usually be little or no residual accelerant for laboratory analysis and the burden of proving incendiary must be borne by the fire investigator on the scene.

In recent years, many scene investigators have begun to use flammable vapor detectors or chemical tests to help in locating trace amounts of accelerant at the area of origin. There are several types of portable flammable vapor detectors available commercially. In general, field tests for accelerant residues can be placed into five categories, according to their principles of detection:

(1) chemical color tests,

(2) catalytic combustion detectors,

(3) flame ionization detectors,

(4) portable gas chromatographs, and

(5) portable infrared spectrophotometers.

The evaluations of these means have not achieved the point to rank them. Nonetheless, it is safe to say that all these techniques are helpful to a certain degree. However, up to now, visual inspection by experienced scene

investigators is still the most productive and reliable means to detect the location of a flammable liquid.

2.1.2. Collection.

Even if any petroleum-based product residues remain after the fire is extinguished, the most valuable and substantial part of them for analysis will evaporate within a matter of hours and certainly within a couple of days. Furthermore, mopping up and the overhauling operations by the fire fighters will dramatically decrease the chance to conduct a meaningful investigation of the fire scene. Therefore, the evidence recognition should be started as soon as the investigator has arrived at the fire scene, and the evidence collection should be launched as soon as the suspected materials have been found provided his work will not influence the major fire-fighting and life-rescuing operations. Unnecessary moving of burned debris, furniture, and other goods, as well as excessive walking around at the scene, will alter the scene and make the investigation more difficult.

In addition to their simple use as accelerant, flammable liquids are used in the construction of firebombs or "Molotov Cocktails". A Molotov Cocktail consists of a flammable liquid, usually one of a low flash point such as gasoline or

charcoal lighter, in a breakable container and fitted with an ignition system. When such a device is used, fragments of the container or portions of the wick may remain around the fire origin and should be collected for laboratory examination.

2.1.3. Packaging and Delivering.

Petroleum-based products are highly volatile. Hence, when suspected liquids or materials which could contain an accelerant are collected, improper packaging and delivering can lead to total loss of fire residues. Some precautions should be in mind of scene investigators:

1. There are three crucial periods of time, one is the time between recovering suspected material(s) and putting them into containers (i.e. packaging time), another is the time between putting them into containers and sending them to crime laboratory (i.e., delivering time), the third is the time between they arriving to the laboratory to conducting the analysis (i.e., the storaging time). All these three periods of time should be as short as possible.
2. If any material which is suspected containing flammable liquid (often called "flammable liquid carrier") is found, it should be cut off from other part of the material, and should be transferred into a tightly sealed, clean, and previously unused glass jar or a metal

can, and marked with a label containing information such as the investigator's name as well as the date, the department, the location, the area from which the sample was taken, case number, and description of the item. Paper bags or envelopes are not suitable due to their porosity. Zip lock plastic bags and most kinds of other plastic containers are also unsuitable because possible chemical reactions can change the nature of petroleum-based products and ruin the whole analysis.

3. Along with the suspected flammable liquid carrier, it is absolutely necessary to get "control evidence" by cutting pieces of the same material from an area which does not contain flammable liquid residues.

4. If the suspected materials can not be examined immediately in the crime laboratory, they should be put into refrigerator at the temperature around 4^0 C as soon as possible.

2.2. GENERAL LABORATORY METHODS FOR ACCELERANT ANALYSIS.

If it is believed that the final determination about whether a given fire is arson depends upon the work of scene investigation, it is also believed that the final

determination about whether Sample A could be linked with Sample B depends upon the work of laboratory analysts. Moreover, the laboratory work is considered more important in terms of the success of case prosecution, and more difficult in terms of the techniques available.

2.2.1. EXTRACTION.

Normally, the suspicious sample which collected by scene investigators (Sample A) is not a pure liquid, but is in a complicated state -- various kinds of porous materials such as rug, paper, cloth, wood, insulation and so forth usually go with it. Therefore, before a meaningful analysis could be carried out, it is necessary to recover a potential accelerant from its matrix in the form of a liquid or gas. This is the first and most critical step of analysis. A variety of means have been developed for this purpose. At least five of them have been implemented in conventional forensic practice: (1) distillation, (2) solvent extraction, (3) water flotation, (4) vapor concentration, and (5) head space. For the small amounts of the residual flammable liquids present in most arson evidence, simple distillation, solvent extraction, vapor concentration or water floatation techniques frequently fail to retrieve sufficient amounts of an accelerant to allow identification. Today, in forensic laboratories, the most

widely used concentration method with arson evidence is the head space technique [12]. Basically, this technique utilize a hermetically sealed system with two parts. The suspicious accelerant with its matrix is put into the first part, it is usually a glass or metal container. In order to minimize the chance of sample loss, the original container submitted by scene investigators can be directly used. Then it is sealed and heated moderately. The possible accelerant will be evaporated, introduced to the second part of the system, and reduced into its liquid state in lower temperature. For some analytical techniques illustrated later (for example, MS or GC), the first part of the system can be directly connected with the sample entrance of the equipment.

2.2.2. ANALYSIS.

After the suspicious sample has been extracted from its carrier, the next and the key stage -- sample analysis -- can be conducted. Traditionally, the analysis of petroleum-based products in the forensic laboratory can be classified into two basic branches -- physical analysis and chemical analysis. Physical analysis includes the determination of flash point, distillation range, reflective index, specific gravity, and so on. These physical parameter measurements have some limitations. First, considerable amounts of sample are required which is usually hard to abtain in real arson cases. Second,

during most of these physical measurements, the sample will be consumed or altered, therefore decrease the possibility of successive work. Third, they are relatively coarse in terms of the discriminatibility among types of petroleum-based products. Hence, though they had been extensively studied and were quite popular twenty or even ten years ago, they are getting less and less employed in routine work of accelerant analyses.

2.2.3. CHEMICAL ANALYSIS.

Chemical analysis of petroleum-based products in arson cases is typically further divided into two major categories -- chemical reaction analysis (for example, color test) and instrumental analysis. Customarily, chemical reaction analysis also needs a relatively large amount of sample, consumed or altered sample during the tests, and have even less discriminating power than physical analysis in general. So, only a few forensic scientists are still routinely using them.

2.2.4. INSTRUMENTAL ANALYSIS.

Instrumental analysis, along with the rapid development of micro-electronics,

precision optics and computer techniques, is continuously changing. Accordingly, though it demands ample investment of both fiscal and human resources, is still drawing more and more attention in nearly all aspects of forensic sciences as well as in accelerant analysis.

A great deal of effort has been devoted to the characterization of petroleum samples by a variety of instrumental techniques. Petroleum-based products have very complicated components, and can be investigated from different aspects of their features. Certain analytical methods inspect certain sets of these characteristics. Consequently, in theory as well as in practice, no one technique can completely take the place of another. By scrutinizing research literature of liquid accelerant analysis, it is found that the following instrumental techniques are frequently employed and can provide complementary and corroborating information:

(1) Gas chromatography (GC).

(2) Liquid chromatography (LC).

(3) Thin layer chromatography (TLC).

(4) Gas-liquid chromatography (GLC).

(5) Mass spectrometry (MS).

(6) Gas chromatography coupled with mass spectrometer (GC-MS).

(7) Infrared spectroscopy (IR).

(8) Ultraviolet spectroscopy (UV).

(9) Fluorescence spectroscopy (FS).

(10) Gas chromatography coupled with infrared spectrometer (GC-IR).

(11) Atomic absorption spectrophotometry (AA).

(12) X-ray diffraction spectroscopy (XRD).

(13) Nuclear magnetic resonance spectroscopy (NMR).

Among the above methods, GC, LC, GLC, and MS are usually utilized for separating and distributing different types of hydrocarbons or certain frictions of hydrocarbons (e.g., by MS) in the mixtural sample.

For improved characterization of a suspected flammable liquid both IR and UV spectroscopy have been explored. A few investigators have claimed success with these techniques but they are not widely used. UV spectroscopy offers little discrimination between types of petroleum distillates, as for example, between kerosene and fuel oil, because both are primarily mixtures of saturated aliphatic hydrocarbons [13]. IR spectroscopy could offer more information, primarily in the detection of aromatics [14], which are found in relatively high concentrations in gasoline as compared to un-cracked products such as kerosene. No doubt, both IR and MS have high sensitivity (whcih is defined as the ability to detect minimum amount of sample) and high selectivity (which is defined as the ablility to distinguish different while

similar samples or components of a sample in terms of certain features which the instrument is targeting), but the production of meaningful spectra requires pure samples. In most arson cases, pure samples are seldom available even after using an extracting procedure. The introduction of GC-IR or GC-MS in recent times, has made it possible to utilize both IR and MS on casework samples. The mixture is first separated by GC, and the components are then individually analyzed by IR spectrophotometry or by MS all in one process.

TLC has been very useful to detect dyes which are usually added in many petroleum products by manufacturers as identification marks of a particular brand or a particular batch of a brand. TLC techniques are uniquely successful to separate, segregate, arrange, compare and identify components of the mixtures of dyes. TLC's are much less expensive and easy-to-manipulate than any other techniques listed above, and it is both sensitive and discriminative to dyes. However, it is not a method which directly probes the components of petroleum-based products, and not all petroleum-based products contain dyes, especially in foreign countries such as in Austria and many Asian countries [15].

Atomic absorption spectrophotometry (AA) and X-ray diffraction spectroscopy (XRD) are valuable in quantitatively detecting the inorganic elements such as lead and bromine in petroleum-based samples, especially in gasolines.

Some of the above techniques have been refined to the point where they can be applied to the typing of unknown petroleum samples. Analytical data employed for petroleum-based product classification include gas chromatography [16-21], infrared spectra [22-27], the combination of the two techniques [28], trace metal concentrations [29,30], luminescence spectrometry [31], field ionization mass spectrometry [32], high pressure liquid chromatography [33], thin-layer chromatography [34], and other methods [35-39]. Several of the analytical methods have been standardized and published as Standard Methods by the American Society for Testing and Materials, including gas chromatography, elemental analysis, fluorescence analysis, and infrared spectroscopy.

Though different instrumental analytical techniques can provide complementary information, GC is regarded as the most powerful one in petroleum-based product analysis by most forensic scientists.

3. GAS CHROMATOGRAPHY

Though gas chromatography has been extensively used as a major chemical separation method for years, its mechanism has not been thoroughly understood. Nevertheless, briefly speaking, it involves the segregation of

substances based on their relative affinity for two phases, one is stationary, the other is mobile. Substances or components of a substance which have higher affinities for the mobile phase are moved, or carried along with it faster, and are thus separated from those with higher affinities for the stationary phase. Basically, a GC consists of three portions: separation, detection and recording.

Early GC workers in 1960s mainly relied on packed columns for separation, thermal conductivity detectors, and linear recorders. Their results proved that the **presence** of hydrocarbons could be detected in fire residue [40]. Recent instrumental development has enormously elevated GC's capability in accelerant analysis. For separation portion, capillary columns up to several hundred feet are routinely used and offer a resolution of hundreds of peaks of petroleum-based products. Computerized temperature programming increases the separation range, sharpens peaks and shortens analysis time, particularly with higher boiling hydrocarbon fractions which are often the important part of fire residues. For the detection portion, a variety of detectors have been developed, and a modern GC system is usually equipped with several different types of detectors, such as flame ionization (FID), electron capture (ECD), as well as thermal conductivity (TCD), to optimize different applications. Among them, flame ionization detectors are ideal for arson evidence because they have very high sensitivity to hydrocarbons and hydrocarbon-related products such as alcohols. For the recording portion, log recording techniques have been

developed and applied in petroleum products [41]. It transfers the ordinary linear recording mode of Y-axis (usually represent the intensities of GC peaks) into logarithmic mode, and therefore, tremendously expands the inner-dynamical extent of a gas chromatogram by increasing the area of weak peaks and decreasing the area of strong peaks. In fact, weak peaks usually offer important and substantial information about different samples among a category of petroleum-based products, such as different brands of paint thinners. Based upon these new advancements, later work [42] explored the recovery of many different accelerants from various types of fire residues, though in recent years, with the development of automatic-interpreters, log presentation has lost its popularity. Basic parameters used to distinguish different groups of fire residues include aliphatic and aromatic hydrocarbon content, relative concentration of major versus minor components, and even the presence of additives. GC has also been used to compare petroleum-based products within a given group [43-45]. In these comparisons, the relative peak intensities are used to distinguish products containing the same components but in different quantities. By this approach, products with only a few components will not yield as much comparative information as products containing hundreds of components. Fortunately, in the case of petroleum-based products analysis, modern GC can easily detect hundreds of peaks, which makes the comparisons ready to conduct. Two comparison mechanisms were employed in these exercises [46]. The first is a simple qualitative method

-- the overlay method. In this method, two chromatograms, with the relevant peaks on scale and approximately the same size, are simply superimposed on a light box. Large to moderate differences between peak ratios in the two chromatograms are readily visible. Extra care should be taken when comparing sets of peaks which do not separate completely. A slight increase in separation can cause a significant decrease in peak height. The overlay method provides a rapid screening procedure to determine if it is necessary to proceed to the more precise quantitative comparison. The second method is peak areas comparison which is provided automatically by many new model GCs and can be used to perform quantitative comparisons. Both of the comparison methods were adopted in this study.

In addition to its well-recognized selectivity (the separating ability), high sensitivity is GC's another primary advantage. Petroleum-based product vapor as low as a few parts per million in concentration can be detected and identified quickly and accurately, far surpassing most other techniques known to criminalists. The third advantage of GC is its extensiveness. It can cover the entire range of petroleum distillates -- from the very light fractions of petroleum (e.g., ether), to the middle distillates (e.g., naphthenes and kerosene), to heavier products such as fuel oil and lubricating oils. Each of these is a complex mixture of saturated and unsaturated aliphatic and aromatic compounds.

Due to its peculiar advantages, GC is unparalleled in determining the existence and identifying the type of petroleum-based products in arson cases. In 1967, Bruce V. Ettling et al [42] found the amount of hydrocarbons in the char does not necessarily indicate that accelerant had been added. However, under careful experimental conditions, the GC plots yielded from char with accelerant in it could be distinguished from the plots of residues of wood, paper and textiles without accelerant in them. A year later, the Research Laboratory of Shell Oil Company [47] systemically studied C_3-CO hydrocarbons in full range motor gasolines by capillary GC. Approximately 240 peaks are observed; 180 of them had been specifically identified. This research set up a solid foundation of petroleum-based product analysis by GC. In 1971, Chisum et al. [41] at the first time employed digital log electrometer instead of traditional linear electrometer as a recording approach in arson accelerant analysis covered four decades of signals without a range change and provided a continuous line graph showing all of the weak and strong peaks resolved by the column. Therefore, its chromatographic pattern provided a substantially improved means for identifying and distinguishing hydrocarbons commonly encountered as accelerant in arson cases. In 1976, M. H. Mach [48] utilized a computerized Finnigan GC-MS spectrometer with methane chemical ionization to characterize samples of simulated arson residue derived from gasoline by distillation, evaporation, and combustion. His result showed the more concentrated samples demonstrated the presence of higher polycyclic

aromatic hydrocarbons (PAHs) not seen in the original gasoline or the early distillation residues. He believed that if these materials could be distinguished from compounds derived from their carriers like wood, plastics, etc., routine analytical techniques can be developed, based on the presence of these characteristic PAHs, to determine whether or not gasoline was used as an accelerant in a suspected arson case. In 1977, a comprehensive and comparative study was conducted by I. C. Stone et al [49]. Headspace GC-MS, IR, XRD, GLC, NMR and even TLC were employed, and the conclusion was all the above instrumentations could provide complementary and corroborating information. A study [50] of 80 crude oil GC plots which were yielded from 4 oil types by the pattern recognition technique with 13 descriptors (peak areas of 13 particular components) showed that there are strong similarities between un-weathered and weathered oils of a same type. However, there were also dissimilarities present. They suggested that a more reliable method requires a model for the weathering process. But it is common sense that the more the weathering process is standardized, the further away from the real arson situations the research is getting. In 1979, a study done by P.J. Loscalzo etc. [51] studied an important issue of arson accelerant identification -- the limit of detectibility of gasoline vapor from simulated arson residues, which was operationally defined as the maximum time period allowed for collection and analysis of samples in which a positive result by GLC could be obtained. Their research measured each sample by using various combustion time and

collection delays after the fire was extinguished. They concluded the GLC detectibility is 20 minutes of combustion and 162 hours of delay. In 1986, D. C. Mann's study [52] exhibited that all the 12 neat petroleum products of his study collected at random were easily distinguished by a capillary GC plot comparison method he designed. But he also admitted that when this method was applied to general case work, it is only useful in eliminating the possibility of common origin between samples and much less useful in determining conclusively that two samples could have same origin.

A literature review of petroleum-based product studies shows that though many papers deal with the detection of gasoline residues in arson cases [53-57], only a few cover the identification of the brand, the production plant or lot to lot individualization, or to match Sample B with Sample A. In 1988, Robert Hirz [15] investigated individualizing of gasoline by GLC. According to the results, identification of the refinery is possible for leaded, liquid gasoline samples whereas lot to lot individualization is possible with liquid, slightly-weathered or un-weathered samples. Highly weathered samples, like fire debris from successful arson, can neither be used for identification of the production plant nor for lot to lot individualization.

To sum up, the GC can readily distinguish types of petroleum-based products, for example, it can differentiate gasoline from other types of flammable liquids

such as kerosene, turpentine, and naphtha, or differentiate various groups among each of the above general types, with current instrumentation. It still can not offer satisfied solution however, for the identification of petroleum-based products by brand name by itself, or determines if two samples could have had a common source.

4. THREE DIMENSIONAL FLUOROMETRY.

Starting about three decades ago, criminalists have been nearly unanimous in judging gas chromatography as the most sensitive and reliable instrumentation for detecting and characterizing petroleum-based product residues from arson cases. However, a new technique is becoming more well known during the recent decade. It is fluorescence spectroscopy, especially its new generation techniques -- three dimensional fluorescence spectroscopy.

As pointed out before, there is no single method for the individualization of an oil. For example, the U.S. Coast Guard Research and Development Center used infrared spectroscopy, gas chromatography, thin-layer chromatography, and fluorescence spectroscopy in its basic oil identification protocol [58]. The U.S. Environmental Protection Agency used gas chromatography, fluorescence spectroscopy, and ultraviolet absorption spectroscopy [59]. However, the

possibility of using fluorescence spectroscopy has received increased attention recently. By years of systematic research, both EPA and the Coast Guard believe that fluorescence spectroscopy is singularly the most useful diagnostic tool [59]. Virtually all of the fuels and lubricants derived from petroleum exhibit significant fluorescence due to the presence of various types of PAHs [60].

Along with the birth and growth of quantum mechanics, the phenomenon of luminescence has been thoroughly studied in this century. Superficially speaking, in normal physical conditions (for example, room temperature, atmospheric pressure on the surface of the earth), most electrons rotating around the nucleus of a molecule possess a series of closely spaced energy levels with the lowest being called ground state. However, when external energy is introduced to this ground state molecular system, for example, in the form of optical illumination, these electrons may absorb a certain amount of energy based upon the specific molecular structure of a specific compound, and jump up, or in physical term "transit" to higher energy levels (excited state). This process is called excitation. However, the excited electrons at higher energy levels are very unstable. Spontaneous returning to their original lower energy levels occurs, and causes these electrons to release the extra energy they just got from excitation. This release can take place in two ways. Most of the released energy is in the form of electromagnetic energy, the rest is in

the form of thermal energy. This process is called emission. If the released electromagnetic energy is in the form of either ultraviolet, visible or infrared light, the phenomenon is designated as luminescence. Luminescence can be in the form of either fluorescence or phosphorescence. The former appears at shorter wavelengths and has a faster decay time (10^{-12} - 10^{-6} second) while the latter appears at longer wavelengths and has a longer decay time (10^{-6} to 10 second) [61]. Because the measurement of phosphorescence spectra require much sophisticated instrumentation (for example, linear matrix detector, synchronous shutters to control excitation and detection time sequence, etc.), it has not been commercially developed. On the other hand, normal fluorescence spectrometer has been available for about two decades.

For any one sample, normal fluorescence spectroscopy consists of two spectra: excitation and emission. They are obtained by scanning either the emission or excitation monochromator through the ultraviolet-visible electromagnetic spectrum while holding the other monochromator constant, at a wavelength where significant luminescence is expected to occur. Normal fluorescence spectroscopy yields information about the luminescence properties of a sample under only a single set of instrumental conditions, for example, a fixed emission wavelength with a corresponding excitation spectrum, or a fixed excitation wavelength with a corresponding emission spectrum. In terms of sensitivity, normal fluorescence spectroscopy is superior than many other

instrumental analytical means for samples which are pure compounds and have high quantum yield. This is why it has received wide applications in many areas such as environmental pollution monitoring, biochemical analysis, medical testing and so forth. In terms of selectivity, both fluorescence and phosphorescence spectra are usually characterized by yielding several relatively broad band peaks under the condition of room temperature, whereas UV, IR, MS or AA can offer several dozens or more than a hundred narrow peaks. Therefore, in the presence of complex mixtures, normal fluorescence measurements offer limited analytical application due to at least two reasons: (1) Strongly overlapping and interfering broad peaks are hard to interpret. (2) Normal fluorescence is performed under only a single set of instrumental conditions, this set of conditions could be appropriate to one component in the mixture to get optimum excitation or emission intensity but incompatible with other components. Unfortunately, petroleum-based products are complex mixtures which consist of a number of different kinds of PAHs. Accordingly normal fluorescence is very sensitive and suitable to detect the existence of trace petroleum-based products quantitatively, or classify petroleum-based products between different groups, but not adequate to identify whether two petroleum-based products could have come from the same source.

In the last fifteen years, multidimensional analysis has become an important trend in the whole realm of instrumental analysis. Multidimensional data can

provide chemical information as a function of more than one variable and, hence, is especially useful for the examination of complicated mixtures. Examples of multidimensional, or multi-parametric techniques include gas chromatography/mass spectrometry (GC/MS) [62], gas chromatography-infrared spectrometry (GC/IR) [63], chromatopolarography [64], secondary ion mass spectrometry [65], and fluorometry -- excitation-emission matrix (EEM).

EEM or Three-dimensional fluorescence spectroscopy represents a great improvement over normal fluorescence because it is capable of providing the total luminescence of petroleum-based products instead of a single narrow region. It retains the advantage of normal fluorescence -- high sensitivity while overcomes its disadvantage -- low selectivity. 3-D fluorescence involves the collection of a large number of fluorescence spectra, each taken under different instrumental conditions, for example different excitation or emission wavelengths. This collection of spectra is then plotted on a single graph resulting in a complete picture of the fluorescence characteristics of the sample, far more information than would be available from a single fluorescence plot.

In a spectrofluorescence measurement, there are three intrinsic parameters: the excitation (EX) wavelength, the emission (EM) wavelength, and the fluorescence intensity. They may be readily depicted in a three-dimensional

representation. Instrumentally, 3-D florescence can be accomplished in two ways. One is "video fluorometry", the other is "computerized re-composition fluorometry".

Video fluorometer approach adopts two major innovations comparing to normal fluorescence instrument. The first is the slits of both excitation and emission monochrometor are widened from several nm (e.g, 3 nm) to more than a hundred nm (e.g., 250 nm). This means, first, the electromagnetic energy of the total wavelength range which is intended to measure is projected to the sample simultaneously. And second, the fluorescence emitted by the sample is also transferred to the detector simultaneously. The gratings in EX and EM monochrometors are mounted perpendicularly to each other; consequently, at the optical plane of the detector, EX wavelength will be arranged from high to low along one axis (say, x-axis) and EM wavelength will be arranged from high to low along with another axis (say, y-axis). This forms a matrix at the detector plane. Each element of the matrix represents a pair of EX-EM wavelengths and the value of this element (z-axis) represents the fluorescence intensity. The second innovation of the video fluorometer is that it uses a high resolution/high sensitivity TV camera tube instead of the traditional single element detector. By fast scanning the elements one by one in a line and line by line in the matrix, a frame of fluorescence can be picked up by the electronic beam in the TV camera and further processed by an on-line computer to

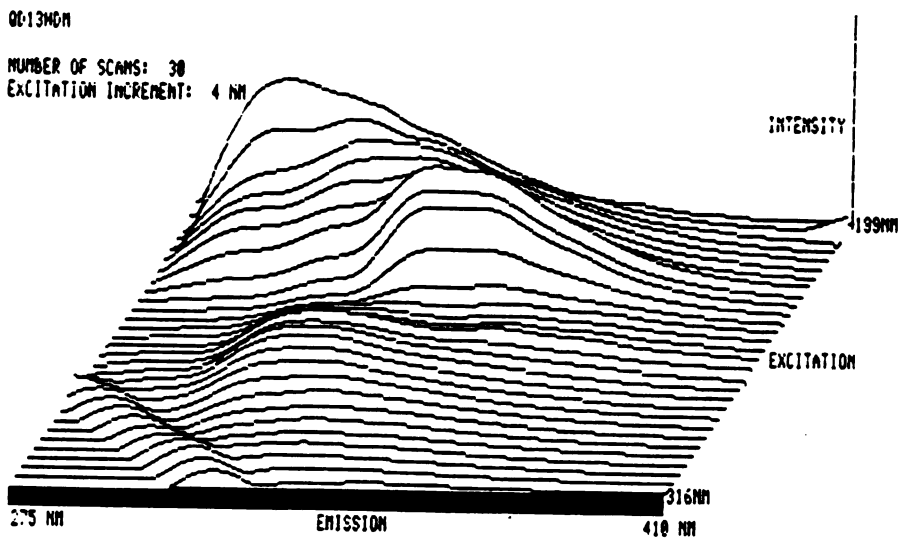
construct 3-D fluorescence in different representations. The advantage of video fluorometry is it can get all the needed information nearly simultaneously (for example, within 1/30 second) and makes it ready to process or printout. This is especially important to the samples which are subject to chemical change under long time luminescence. However, until now, this technique has still at the stage of laboratory experimentation, and not commercially available.

This study adopts computerized re-composition fluorometry to generate 3-D fluorescence, which does not dramatically change the monochromatic system and the detection system. Its innovations are principally in two aspects. The first is the mechanical automation of EX and EM scanning procedures under computer control. The second is the adoption of a powerful computer work station to process the data yielded by the detector under preset scanning conditions. In the case of this study, during each EX or EM scan, the scanning monochromator covered the same wavelength range while the other monochromator was fixed at a certain wavelength. Between different scans of the same wavelength range, the fixed monochrometor incrementally moves to the next fixed wavelength, and stops at this wavelength for the next scan. By this fashion, the fixed monochrometor will incrementally scan several dozen times and over the entire range of luminescence. The process is automated so that the operator need not be present for each scan. The resultant spectra are saved by the computer and then subsequently plotted on a three-dimensional

Cartesian system with the scanning monochromator wavelength on the x-axis, the fixed monochromator wavelength on the y-axis, and the fluorescence intensity on the z-axis. The resultant plot can be presented in two ways. The first way is so called 3-D stacked fluorescence plot. It so obtained is a profile of all of the major areas of fluorescence of the sample. The profile is like the figure used in cubic projective geometry. As many as four different views of the contour plot may be obtained by generating both excitation and emission 3-D fluorescence plots and by plotting the fixed monochromator response from either high to low or low to high wavelength. Figure 1 presents the four views of the 3-D stacked fluorescence plots for a motor sample. The second way is so called contour plot which looks like the isograms used in topography or in meteorology. In this kind of plot, x- and y- axis are represent EX and EM wavelength representatively, or vice versa. The plot consists of many non-intersected and self-closed curves. The highest fluorescence intensity is the highest at the center of the plot and gets lower toward the outside edges. Figure 2 presents a 3-D contour plot of a charcoal lighter sample.

The high sensitivity, high selectivity (discriminating power), nondestructiveness, and informativeness, coupled with its ability to directly dealing with mixed samples, make 3-D fluorescence a very promising method that can be recommended in forensic petroleum-based product analysis [66].

(a)



(b)

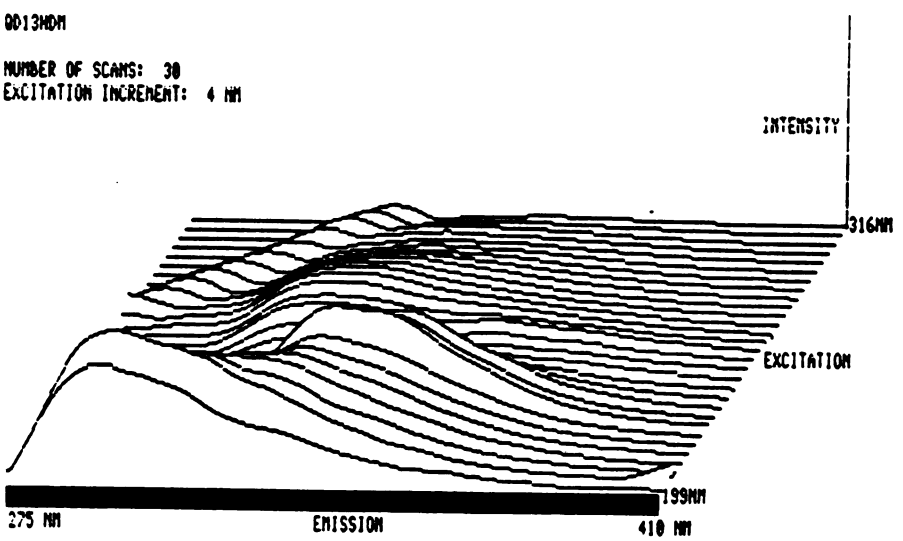
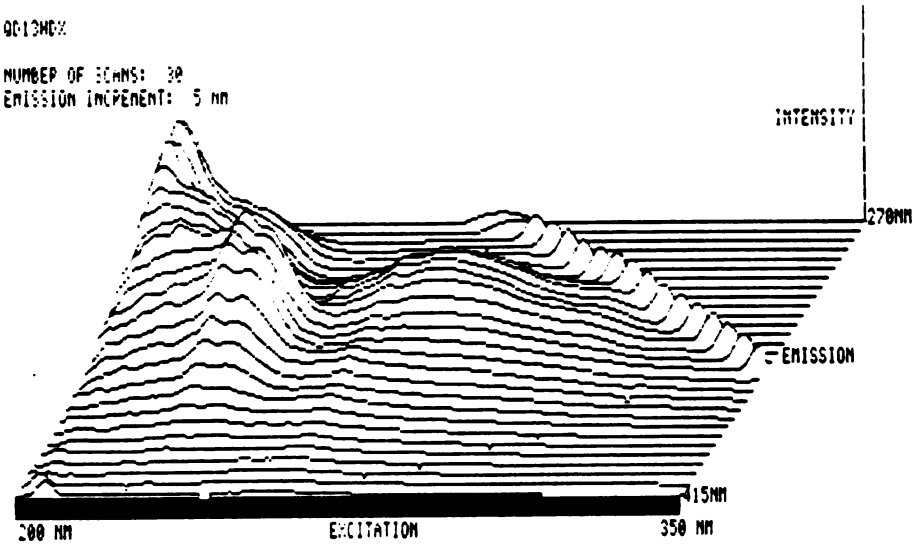


FIG. 1 **Four different views of the 3-D fluorescence stacked plots of a motor oil.**

(c)



(d)

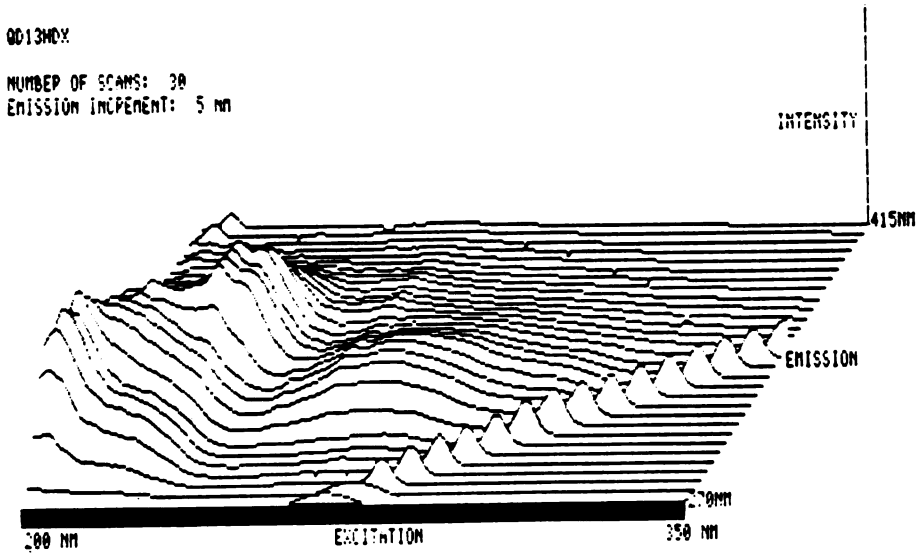


FIG. 1. **Continued.**

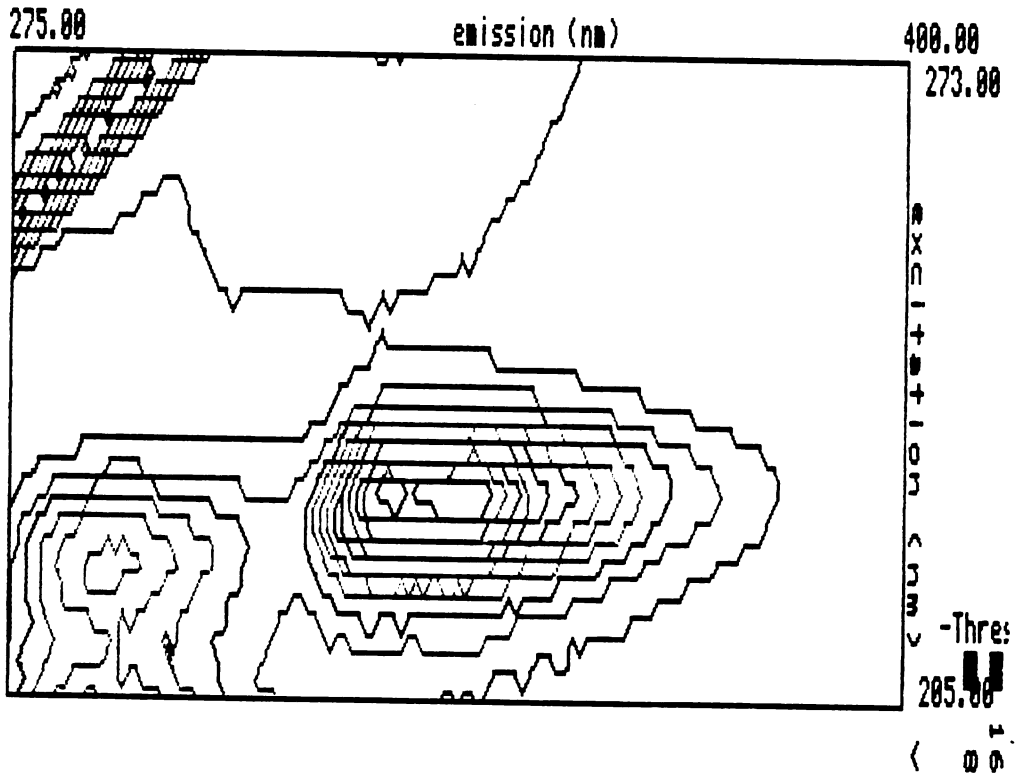


FIG. 2. 3-D fluorescence contour plot of a charcoal lighter sample.

As a matter of fact, a literature review reveals that the practical application of fluorometry in analyzing petroleum-based products has received much attention within the past decade. Furthermore, unlike GC studies which were primarily focused on detecting the existence of petroleum-based products, fluorescence studies were mainly concentrated on the individualization of petroleum-based products. In 1977, the U.S. Coast Guard Research Center first employed fluorescence for identification [67] purpose and successfully characterized spilled oil samples. Similarly, in 1970s, crude oils have also been subjected to fluorescence [68, 69], as have fuels, and all claimed better discriminating power than other means of instrumental analysis. Several year later, Kubic and his coworkers [61, 66] conducted a remarkable research of engine oil individualization by the means of conventional, synchronous excitation, and variable separation synchronous excitation (VSSE) fluorometry. sixty-one neat and forty-five used automobile engine oil samples were analyzed. The results showed very high degree of individuating ability. Only two samples were considered to be indistinguishable. In 1985, T. M. Rossi and I. M. Warner [70] developed an algorithm for spectral matching of excitation-emission matrices (EEMs). Their "pattern recognition" method operates completely in the "frequency domain after Fourier transformation of unknown and known polynuclear aromatic (PNA) samples. In 1986, a method [71] called constant energy synchronous luminescence spectrometry (CESLS) was reported to be applied in environmental analysis of gasoline and crude oil samples. This

study pointed out that, (1) different dilution is needed for different sample; (2) low temperature (77°K) provided better spectral resolution and enhanced discriminating power of two very similar samples; (3) the sensitivity, selectivity and reproducibility of CESLS could fingerprint polycyclic aromatic hydrocarbons (PAHs) in environmental samples. Due to lack of instrumentation, most of the above studies can not directly yield true 3-D fluorescence plots. Systematic studies of petroleum-based products encountered in criminalistics by a commercial 3-D fluorometer were performed only by J. A. Siegel [60, 72, 73, 74]. In his 1985 research, twenty-one unused samples (ten motor oil samples and eleven lubricating oil samples) were analyzed by 3-D fluorescence. In his 1987's research, ten whole gasoline samples (including leaded and unleaded) were analyzed by 3-D fluorescence. A comparison program was designed to determine if two measured samples come from a common source by subtracting their 3-D plots. The results of these two studies showed 3-D fluorescence provides much more spectral information than is available from conventional forms of fluorescence.

The INTRODUCTION part of this paper can be summarized as the following points:

1. In the United States, A remarkable percentage of fires are not the result of natural or accidental causes, but the result of arson.

2. Arson is a very devastating and costly crime. Therefore, it is an area which is worthwhile to devote research time and effort by law enforcement as well as forensic scientists.
3. Accelerants are often involved in arson cases.
4. The laboratory analysis of accelerants play a very important role in: (1) determining the nature of the fire, (2) case investigations by the law enforcement agencies, (3) prosecution procedures in court.
5. Various types of materials could be used as accelerant.
6. The most common accelerants are petroleum-based products such as gasoline- and kerosene-based materials (kerosene, fuel oils, and so no).
7. The detection and analysis these common accelerants have been the subject of numerous books and articles over the past thirty to forty years.
8. Up to now, among numerous kinds laboratory analysis techniques, gas chromatography is regarded as the most powerful and useful method.
9. Fluorescence spectrometry, especially three-dimensional fluorescence spectrometry is a newly emerging technique in accelerant analysis, but it is still in the stage of developing its potentials.

PART II. RESEARCH OBJECTIVES.

By critically studying the previous research in accelerant analysis mentioned in the introduction, some inferences can be drawn. First, although a variety of studies had dealt with the analysis of arson accelerant by either GC or fluorescence, one class of hydrocarbons have not been given much attention, which is the so called mid-range petroleum products. This group mainly consists of paint thinners, charcoal lighters and certain synthetic turpentine products. In terms of possible arson accelerants, the products in this group have the following characteristics: (1) They are commercially available. (2) They are commonly found around the home. (3) They are highly combustible. (4) A significant percentage of arson cases showed that midrange petroleum products were involved as the accelerant. Therefore, it is somewhat surprising that these materials have not been the subject of much research into their classification and methods of detection and analysis. A detailed examination of the literature turns up little in the way of research specific to this class of products, and the only method reported for the analysis of these materials is gas chromatography, either with packed or capillary columns. Also, as discussed above, the technique of 3-D fluorescence has been employed in the analysis of several types of petroleum-based products including motor oils [60], gasoline and lubricants [73], and, petrolatum products [74]. Second, although

in the field of accelerant analysis, GC is the most accepted technique; 3-D fluorescence shows much potential, the comparison and evaluation between the two techniques have not been performed. The author believes this comparison and evaluation would be helpful for further development of accelerant analysis. Third, the analysis of evaporated and burned accelerant samples had not been conducted very much, especially by the means of 3-D fluorescence.

Recognizing the above three points, the present study designed to employ 3-D fluorescence in conjunction with capillary GC to characterize mid-range petroleum distillates under the conditions of

1. neat samples,
2. evaporated samples, and
3. burned samples.

The objectives of this study were:

1. to determine if midrange petroleum products could be classified in groups according to their fluorescence and gas chromatographic characteristics and to see what extent these two groups correlate,

2. to determine if the 3-D fluorescence spectrum and the gas chromatogram of a given midrange petroleum product are unique with

respect to the other members of its class,

3. to determine if the 3-D fluorescence spectrum and the GC chromatogram of an unknown sample of a midrange petroleum product can be matched to the particular source from which it came,

4. to determine if samples which have been partially or totally evaporated can be matched to a particular source, and

5. to determine the effects of combustion upon the results of 3-D fluorescence and GC of selected midrange petroleum distillates.

PART III. MATERIALS AND INSTRUMENTATION CONDITIONS.

3.1. SAMPLES.

Twenty-two midrange petroleum-based products were selected for the study. Eight of them were bought from local commercial sources during the summer of 1987. The rest were obtained from the Federal Bureau of Alcohol, Tobacco and Firearms National Laboratory, Rockville, Maryland, they are all available mid-range petroleum products samples which the Laboratory had collected on a national base at that time. The code, brand name and manufacturer of each of these samples is listed in Table 1. The code number is created by the author for the sake of research convenience.

TABLE 1. Samples in the Study.

SERIES#	CODE#	BRAND NAME	MANUFACTURER
Paint Thinners:			
1	PT01	Sunnyside	Sunnyside Co.
2	PT02	Tru-test	Cotter & Company
3	PT03	Parks	Parks Co.
4	PT04	Sunnyside (odorless)	Sunnyside Co.
5	PT05	UGL Raizoff	---
6	PT06	NASCA	---

(TABLE 1. Continued.)

SERIES#	CODE#	BRAND NAME	MANUFACTURER
Charcoal Lighters:			
7	CL01	Gulf Lite	Gulf Oil Co.
8	CL02	Poly-start	Midwest Polychem
9	CL03	Northland	Linwo Industries Ltd
10	CL04	Wizard	Boyle-midway Inc.
11	CL05	Farmlite	---
12	CL06	Boron	---
13	CL07	Sparks	---
14	CL08	Chefs Choice	---
15	CL09	Gulf Lite (another batch from CL01)	---
Mineral Spirits and Miscellaneous Others:			
16	MS01	Varsol	---
17	MS02	Parks 100%	---
18	MS03	Hechinger	---
19	TT01	Sears Tirpolene	---
20	LT01	Sears Lacquer Thinner	---
21	ST01	Parks Shellac Thinner	---
22	GT01	GUM Turpentine	---

3.2. Fluorescence Spectrometer and Its Conditions:

The fluorimeter used was a Perkin-Elmer MPF-66 Fluorescence Spectrometer equipped with a Perkin-Elmer Model 7300 Data Station and PR-310 Printer/Plotter. In the initial step of the study, each sample was prescanned to determine:

(1) the maximum excitation and emission wavelengths,

(2) the suitable excitation and emission scanning range,

(3) the suitable excitation and emission slit widths, and

(4) the suitable scanning speed.

For a particular sample, some instrumental conditions such as scanning range (for both EX and EM) can be automatically optimized by the function of prescan. Therefore, by investigating the prescaned EX and EM plots of all the 22 samples, weighing the pros and cons were needed at least in the following three fundamental aspects.

First, the chosen EX and EM scanning ranges of this study had to be a compromise among the samples. It means, the range should be inclusive in terms of covering as many major peaks of each sample as possible; at the same time, it should be exclusive in terms of eliminating as much no-excitation-range and no-fluorescence-range as possible. Therefore, talking about a specific sample spectrum, some minor peaks could be excluded, or some flat range could be included due to the consideration of the features of other samples. But the maximum excitation and emission wavelengths of any of the twenty-two samples should be included.

Second, the chosen end-wavelength of the excitation scanning range and start-

wavelength of the emission scanning range had to be a compromise: (1) The scanning ranges of excitation and emission cannot be overlapped, i.e., the end-wavelength of the EX spectra should be lower than the start-wavelength of EM spectra. Otherwise, within the overlapping range, the scattering electromagnetic energy of excitation caused by the sample liquid scattering will directly pass through the emission monochromator, reach the detector and provoke a very strong interfering response (false signal). (2) The comparison of spectra of different samples was a major part of this study. Consequently, it is appropriate for all samples to have the same EX as well as EM scanning range. (3) Different samples are likely to have different excitation and emission spectral range. So, it was necessary to take the prescan results of all samples into consideration and create a trade-off which sacrifices both less EX and EM spectra of the samples as whole, but may not sacrifice the lowest EX and EM spectra for a particular sample. In other words, for a particular sample, there could be a better choice of the end-wavelength of EX and start-wavelength of EM which could gain a more integrated EX and EM spectra for that sample. But when considering the whole set of the twenty-two samples, that decision could cut off some meaningful parts of either EX or EM spectra of more than one other samples.

Third, the chosen width of either EX or EM slit of monochromator of the fluorometer had to be a compromise of sensitivity and selectivity. This means,

if the slit gets narrower, the selectivity of measurement will increase. In other words, the ability to distinguish two sharp and near peaks in a spectrum will be increased. But at the same time, the electromagnetic energy which could pass through the optical system and be received by the detector will decrease. In other words, the ability to catch weak fluorescent peaks (which could be crucial to differentiate two similar spectra) will be diminished. By the same token, widening the slits will decrease the ability to detect the narrow and near peaks but increase the ability to detect the weak energy peaks. Fortunately, unlike an atomic emission spectrum, which usually occurs at high temperature and gas state conditions, and is characterized by having many sets of very narrow spectral peaks (lines), our samples belong to the category of molecular spectra, which usually occur in low temperature (for example, room temperature or lower) and in liquid or solid states, and is characterized as having relatively broad spectral peaks or bands. Accordingly, it is possible to choose relatively wide slits to guarantee the detection of weak peaks. At the same time, it is unlikely to blur the spectral details.

Based on the above considerations, the instrumental conditions for the analysis, determined empirically in the initial stage were listed in TABLE 2.

TABLE 2. The Instrumental Conditions of MPF-66 Spectrofluorimeter.

Excitation (EX) scanning range			205 to 273 nm		
Emission (EM) scanning range			275 to 400 nm		
EX slit			5 nm		
EM slit			5 nm		
Scan speed			120 nm/min		
Numbers of scans			35		
Signal response			AUTO		
Emission filter			OPEN		
Plotting choice	(1)	Stacked	(a)	EM:	low-high high-low
			(b)	EX:	low-high high-low
	(2)	Contour		THRESHOLD: 8 %	

3.3. Gas Chromatograph and Its Conditions.

All gas chromatography analyses were performed on a Varian Model 3300 equipped with a Model 601 Data Station and a Hewlett-Packard Think Jet printer. The capillary column was a J&W DB-1, 30-M, 0.25-micron coating. The oven was temperature programmed from 50^0 C to 250^0 C. The detailed temperature programming conditions were listed in TABLE 3. Before this study, the experience of Dr. Jay A. Siegel's forensic sciences laboratory had indicated this combination of column and temperature conditions allowed good separation, low baseline, and high signal/noise ratio for hydrocarbons while still permitting a short analysis time (approximately 25 min per sample) for

mid-range petroleum products. The chart speed (1cm/min) used was a trade-off of adequate peak separation and sufficient peak height representation for easier visual evaluation of the peak heights and shapes.

TABLE 3. The Temperature Programming Conditions of Varian Model 3300 Gas Chromatograph.

Initial column temperature	50^0 C
Initial hold time	4 min
Final column temperature	200^0 C
Programming rate	10 deg/min
Final hold time	6 min
Injector and detector temperature	250^0 C
Detector temperature	250^0 C
Run time	25 min
Injection size	0.5 to 2 uL

PART IV. PROCEDURES AND RESULTS.

This study is consist of five stages. They are: neat sample grouping by both GC and 3-D fluorescence, 3-D fluorescence concentration study, blend test to compare the discriminating power of GC and 3-D fluorescence, evaporated sample study and burned sample study.

1. STAGE I. NEAT SAMPLE GROUPING.

"Neat Sample" in this study is defined as (1) the sample which was directly obtained from either retail market or the supplier maintained above; (2) they were well protected by glass or metal containers at room temperature after they were received by Jay A. Siegel's laboratory; (3) they were not contaminated, evaporated or burned before this stage of the study.

The reasons to conduct the "neat sample grouping" were:

1. From the instrumental point of view, most previous studies utilized GC and 3-D fluorescence to identify arson accelerant separately, and both claimed substantial progress. However, few studies had been done to compare the discriminating power of arson accelerant by GC and 3-D fluorescence. As the purpose here is to compare the two instruments,

it is necessary to eliminate other factors which could influence the results as much as possible. A major set of influential factors were "sample variation" by their environment, such as evaporation, weathering, contamination, burning. Only in this way, can the variable of interest -- the difference of the discriminating power between the two means be explored explicitly and undoubtedly. In this regard, neat samples were more suitable than evaporated or burned samples.

2. From a practical point of view, in certain incendiary fires, some of the petroleum-based products used to accelerate the fire may be recovered in unaltered or slightly altered form. For instance, the remains of a Molotov cocktail are recovered partially intact soon after a fire, and it constitutes essential crime scene evidence especially if a suspect is apprehended and has in his possession a container that contains some petroleum-based product which is suspected to be the source of the material found from the crime scene. This kind of sample is similar to the condition of "neat sample".

Neat sample grouping was conducted in two steps. The first step was grouping the twenty-two samples by 3-D spectral plots. The second step was grouping them by gas chromatography.

In the first step, each of the 22 samples was diluted into the solutions with three concentrations: 1000ppm, 100ppm, and 10ppm (v/v) by spectrograde cyclohexane (Burdick & Jackson Co.). T. A. Kubic etc. [61] found that impurities in the solvent can frequently cause false sample fluorescence or can yield spectra that coincide with those of petroleum-based product samples. These effects can only be minimized if high-quality spectral grade solvents or a suitable purification system is used. Therefore, this study chose cyclohexane as the solvent from a possible solvent pool by experimentally determining it has lower fluorescence than others in the wavelength range which were intended to adopt for sample measurement, and chose the highest quality cyclohexane which could be found on the market. Under the experimental conditions of this study, the background fluorescence of cyclohexane was examined and determined that it is not strong enough to contribute any significant distortion to the sample spectra, and thus did not interfere in the analytical results.

Previous experimental experience with fluorescence of petroleum-based products has been that they are likely prone to leave some residues behind in the glassware used in making up the solutions. To guard against any chance of this occurring and to minimize the chance of any residual fluorescence from such residues, two procedures were employed. First, glassware was only used once before a carefully designed and performed washing process. After

preparing a solution for each concentration of each sample, a specific washing process of all glassware was employed: cyclohexane followed by acetone, distilled water, concentrated nitric acid, and then several times by distilled water again. After the final wash with distilled water, the glassware was dried in an oven at 60^0 C. By adopting this process, the residues left from previous sample preparation or from the same sample but different concentration preparation was eliminated enough to the degree which had no influence on later measurement. Second, a "purity test" was conducted after each three runs. This means a background measurement was performed. The "background measurement" is the measurement which only measure the solvent (i.e., cyclohexane) without solute (i.e.,mid-range petroleum-based products) under the same instrumental conditions of sample measurement. If the resulting 3-D spectrum by purity test turned out abnormal -- different from the standard background spectrum which was obtained at the beginning of this step under restricted conditions and showed no residual fluorescence, the above glassware washing process and the whole sample measurements after the last qualified purity test would be redone more carefully, until no residue inference could be observed. This measure was very time consuming, but the author utilized it throughout all stages of this study in order to ensure the reliability of the work.

When it was necessary to compare 3-D fluorescence plots of measured samples

in order to determine if they belong to the same group (i.e., they were similar) in this stage of the study, or if they came from the same source (i.e., they were identical) in the study of later stages, two methods were available.

The first was direct "visual comparison". By this method, the number of peak regions, the maximal EX and EM wavelengths, the relative intensities of major peaks, and the general profile appearances were examined. Though this method could be appraised as somewhat subjective, the 3-D fluorescence plots were so informative and detailed enough to permit an accurate logical judgement, i.e., yes-or-no judgement by an experienced researcher. The other method was a computerized "subtraction algorithm". Software developed by Jay A. Siegel [73] provided an algorithm whereby two 3-D fluorescence plots (not limited to fluorescence plots) can be subtracted spectrum-by-spectrum and the resulting difference plot can be displayed. Strictly speaking, because the fluorometer used was extremely sensitive, even two samples which had the same source would yield some differences caused by the instrumental fluctuation or any random errors introduced during the process of sample preparation. Therefore, the subtracted plot usually did not consist of several dozens of parallel straight lines, instead, some non-zero fluorescence always appears. However, the intensity of the peaks which were subtracted from two samples having a common source would be much lower than those having different sources. More importantly, the software can provide Pearson's Q

algorithm to calculate the peak differences between the samples. In those cases where the samples had a common source, the Q value was typically above 0.9 (1.0 representing perfect correlation). In most of the samples which did not have a common source, Q was less than 0.9. In theory, this method is more objective and accurate than visual comparison. But two concerns exist for adopting the computerized subtraction algorithm. First, a subjective judgement if the subtracted plot of two comparing samples was still needed. Second, if totally turned to objective judgement, i.e., totally relied on the critical value (Pearson's Q is greater or less than 0.9) determination, some practical considerations must be taken into account. Like in many fields of experimental science, during the experimental procedure of yielding 3-D fluorescence plots, a lot of manipulable and variable factors could influence the results. For instance, the sample were all measured at very low concentrations. The preparation of these concentrations was done by hand and by using relatively coarse volumetric flasks. Therefore, concentration fluctuation was inevitable. It is needed to point out that, unlike with some other instrumental approaches, the variation of sample concentrations will not cause the fluorescent intensity of different components (different peaks in plot) to change proportionally, but will usually change the ratios of peak intensities. This change will definitely affect the Q value to some degree. At the time of this study, the algorithm had not yet fully tested to determine the general "rule" can be relied upon in all cases, and in our particular experimental

conditions. Therefore, the author decided to choose "visual comparison" in all stages of this study.

TABLE 4. The Grouping Result of 3-D Fluorescence Plots.

Group	1	2	3	4	5
Sample Code	PT01 PT02 PT04 (100ppm) PT06 (100ppm) CL02 (1000ppm) CL03 CL04 (100ppm) CL07 CL08 MS01 MS03 TT01 GT01	PT03 MS02	PT05 LT01	CL09 (1000ppm) CL01 (1000ppm) CL05 (100ppm) CL06	ST01

By the means of cautious visual comparison, the 3-D fluorescence plots of the 22 samples were classified into one of the five groups. The results are listed in TABLE 4. In the table, if the concentrations of a sample are not noted in parentheses, they were measured at 10 ppm. At this stage of the study,

though each sample was measured at least in three concentrations (1000 ppm, 100ppm, 10ppm) in order to get more understanding of 3-D fluorescence spectra of mid-range petroleum products, the optimum concentration of grouping was chosen when the ratio between the scatter peak and the most intense fluorescence peak intensities were approximately constant. This condition implies that the effects of self-absorption among different components of a sample had been diminished at the lowest level. Accordingly, the fluorescence feature of the sample had been undistortedly exhibited. Figure 3a through e are 3-D fluorescence stacked plot spectra of a representative of each group.

The second step of STAGE I is grouping the twenty-two neat samples by their gas chromatograms. In this step, as well as in all the following stages of this study, all samples for GC measurement were original (un-diluted). It means that they were directly drawn from their original containers by 10 ul syringe (Namilton Co.). The injection volume was 1 ul for first run. If the chromatograms were over-scaled or too weak, the initial plot attenuation and/or the injecting volume of that sample would be adjusted gradually until a suitable chromatogram was obtained. Likewise, "visual comparison" was also adopted as the grouping criterion. The results of GC grouping showed the twenty-two samples fell into nine groups and these presented in TABLE 5. In the table, Group 2 was empty intentionally so that fluorescence spectra and

gas chromatograms which fell into corresponding groups were numbered the same. Figure 4 a though h show representative chromatogram for each of the eight groups.

TABLE 5. The Grouping Results of Chromatogram.

Group	1	2	3	4	5	6	7	8	9
Sample Code	PT01		PT05	CLO5	ST01	PTO4	CL09	GT01	CL01
	PT02		LT01	CL06					
	PT03								
	PT06								
	CL02								
	CL03								
	CL04								
	CL07								
	CL08								
	MS01								
	MS02								
	MS03								
	TT01								

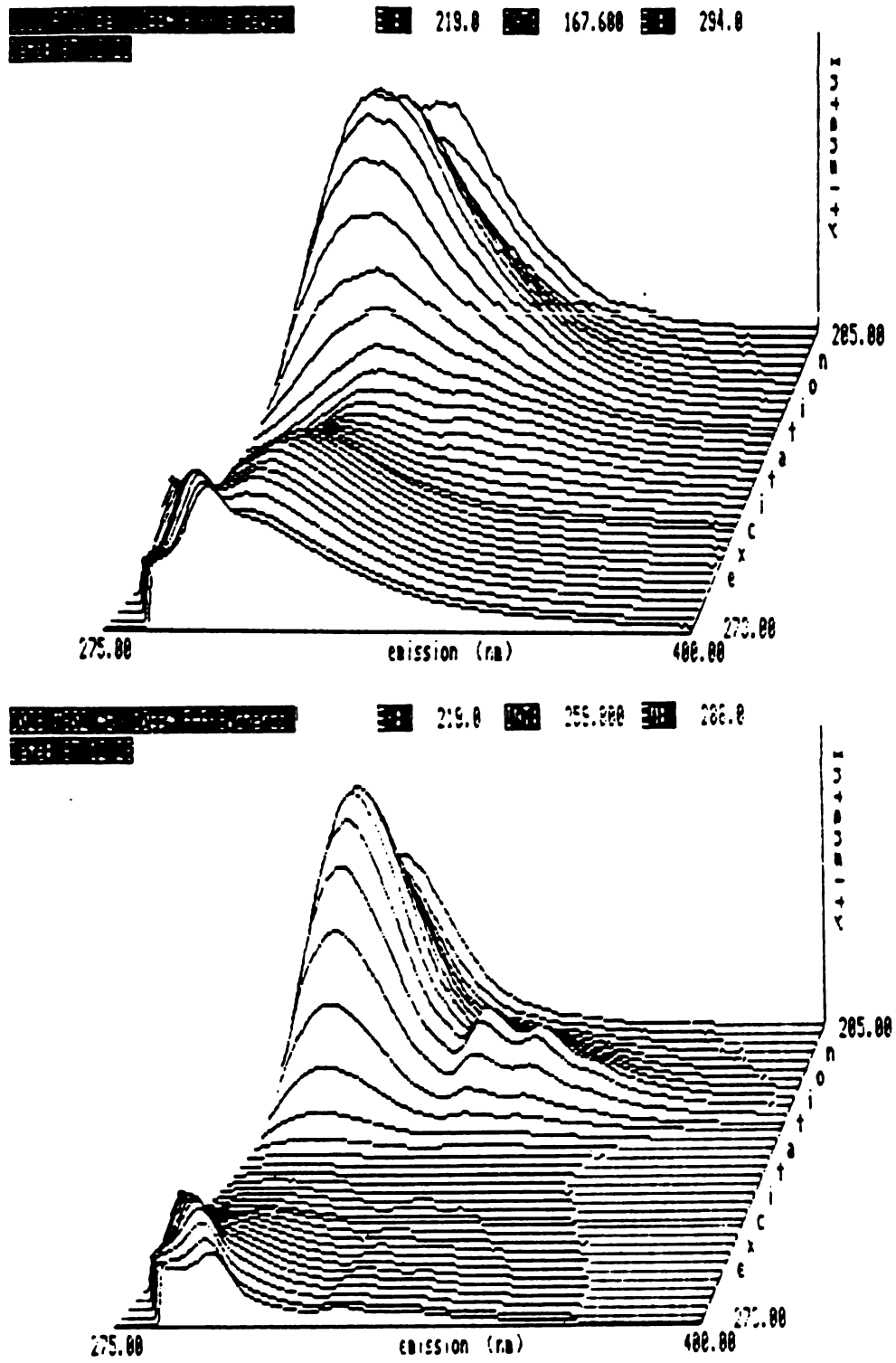
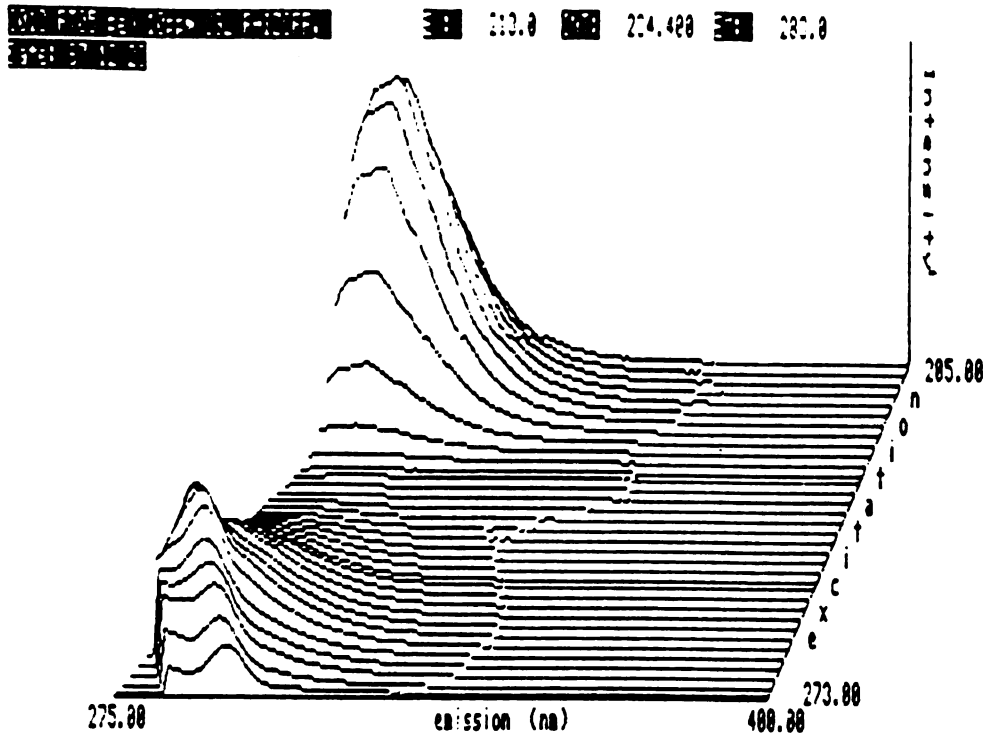


FIG. 3. 3-D stacked emission plot of representative members of each of the five groups in which the midrange products are classified: (a) Group 1, PT01; (b) Group 2, MS02; (c) Group 3, PT05; (d) Group 4, CL06; (e) Group 5, ST01.

(c)



(d)

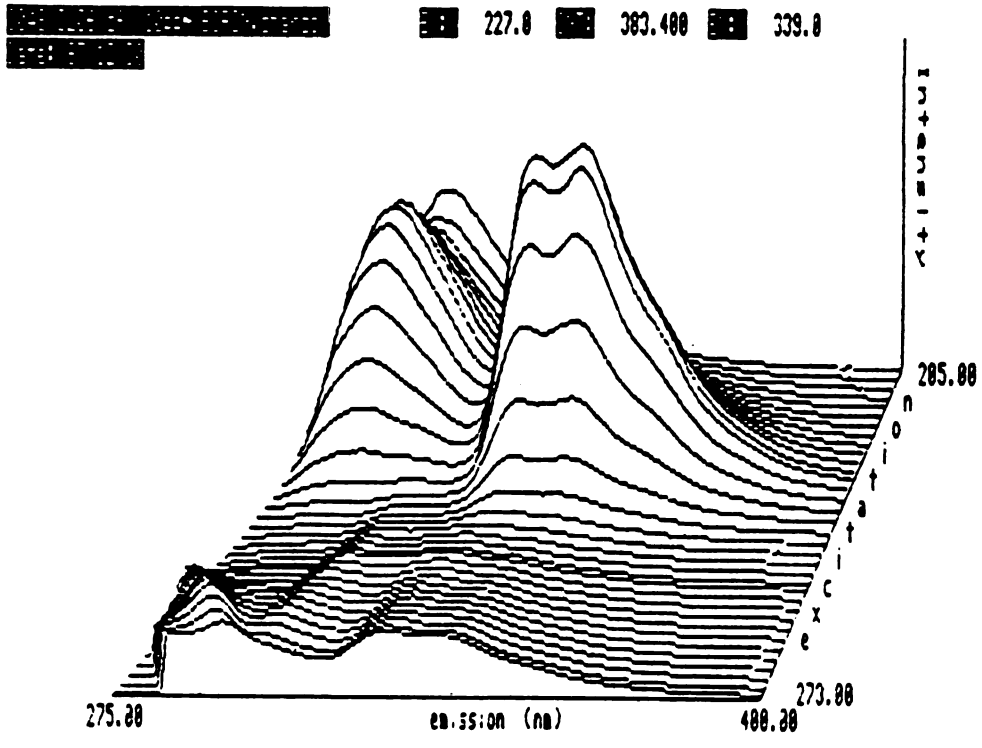


FIG. 3. Continued.

(e)

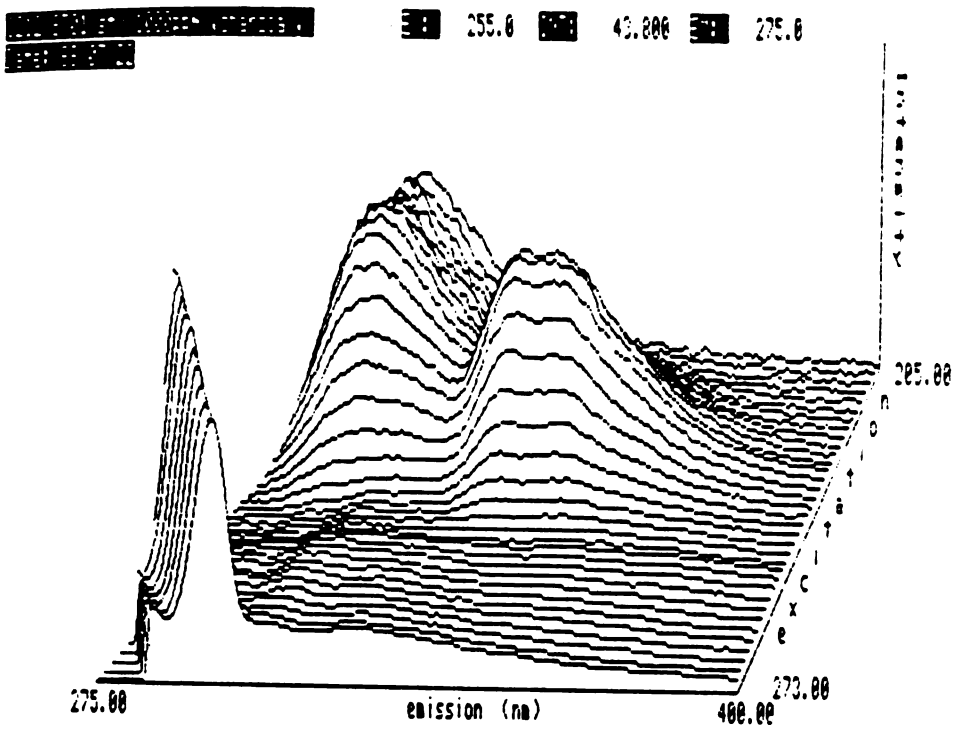
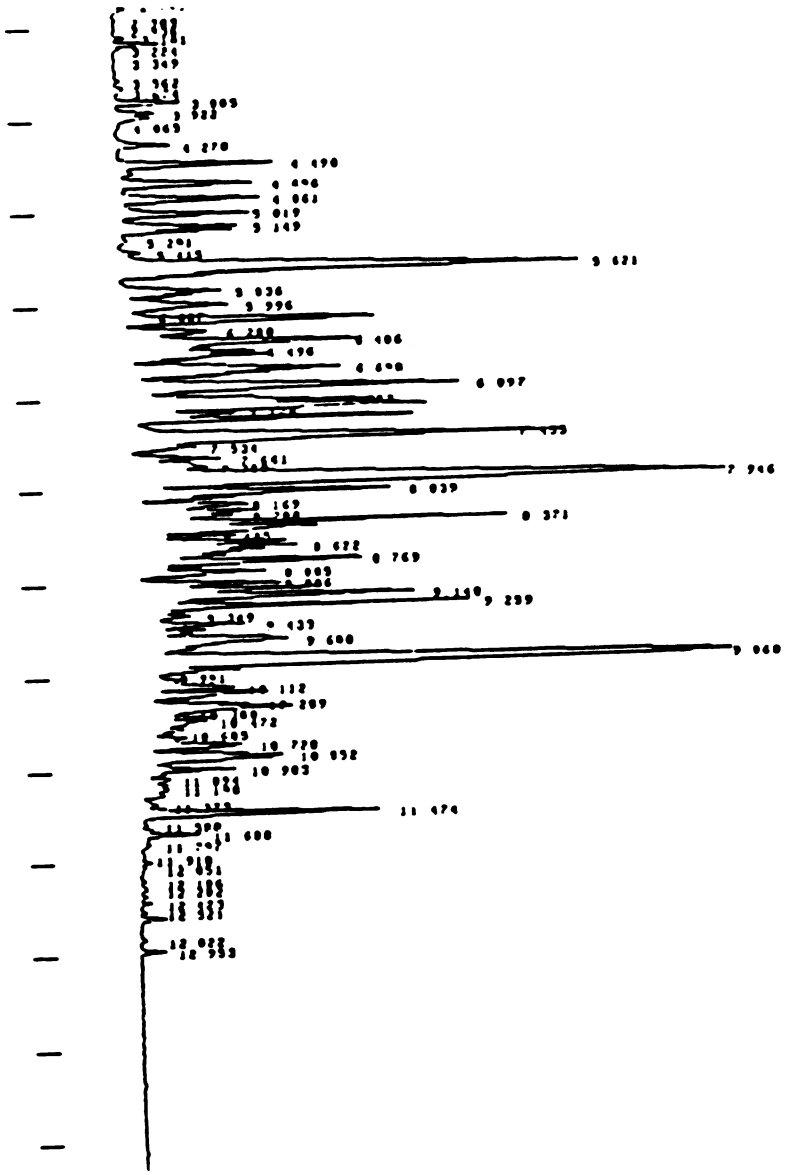
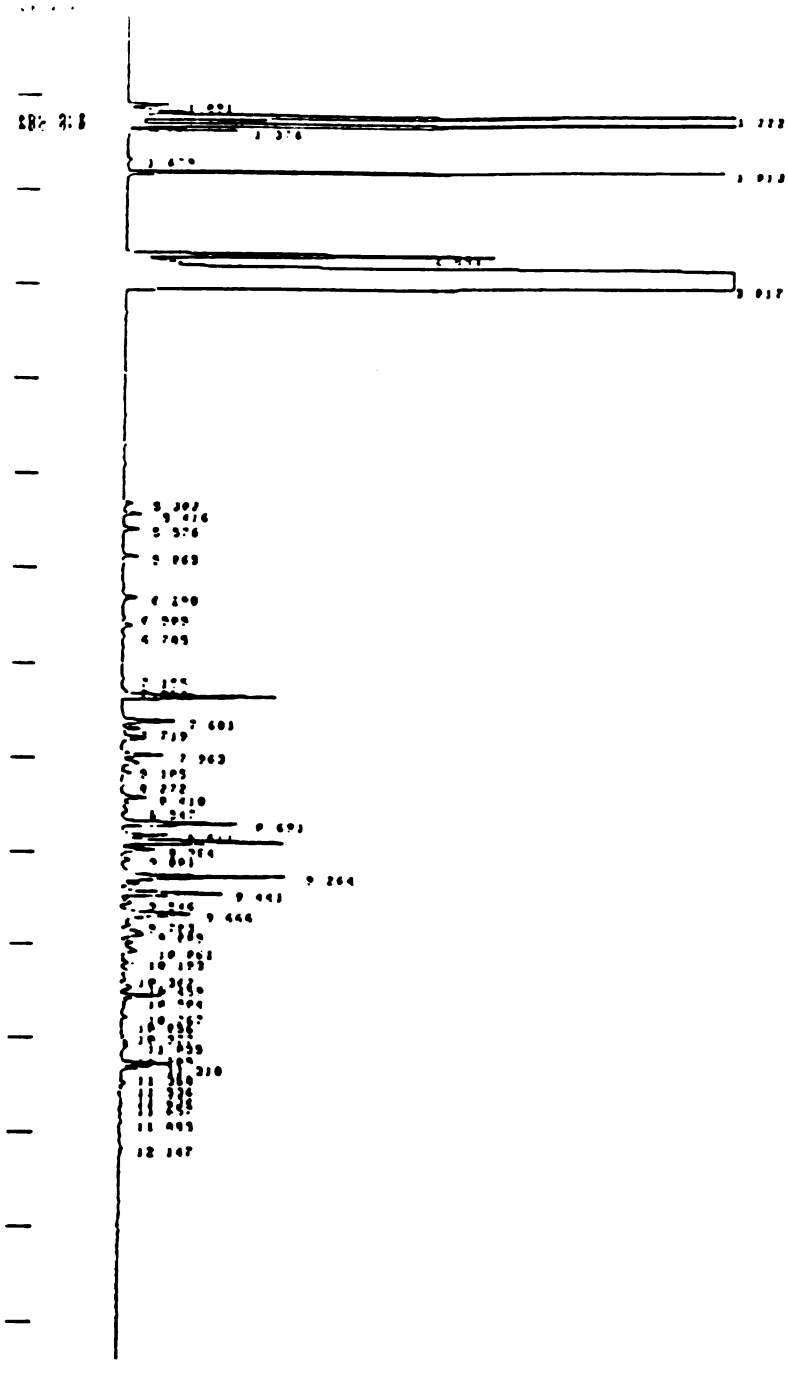


FIG. 3. Continued.



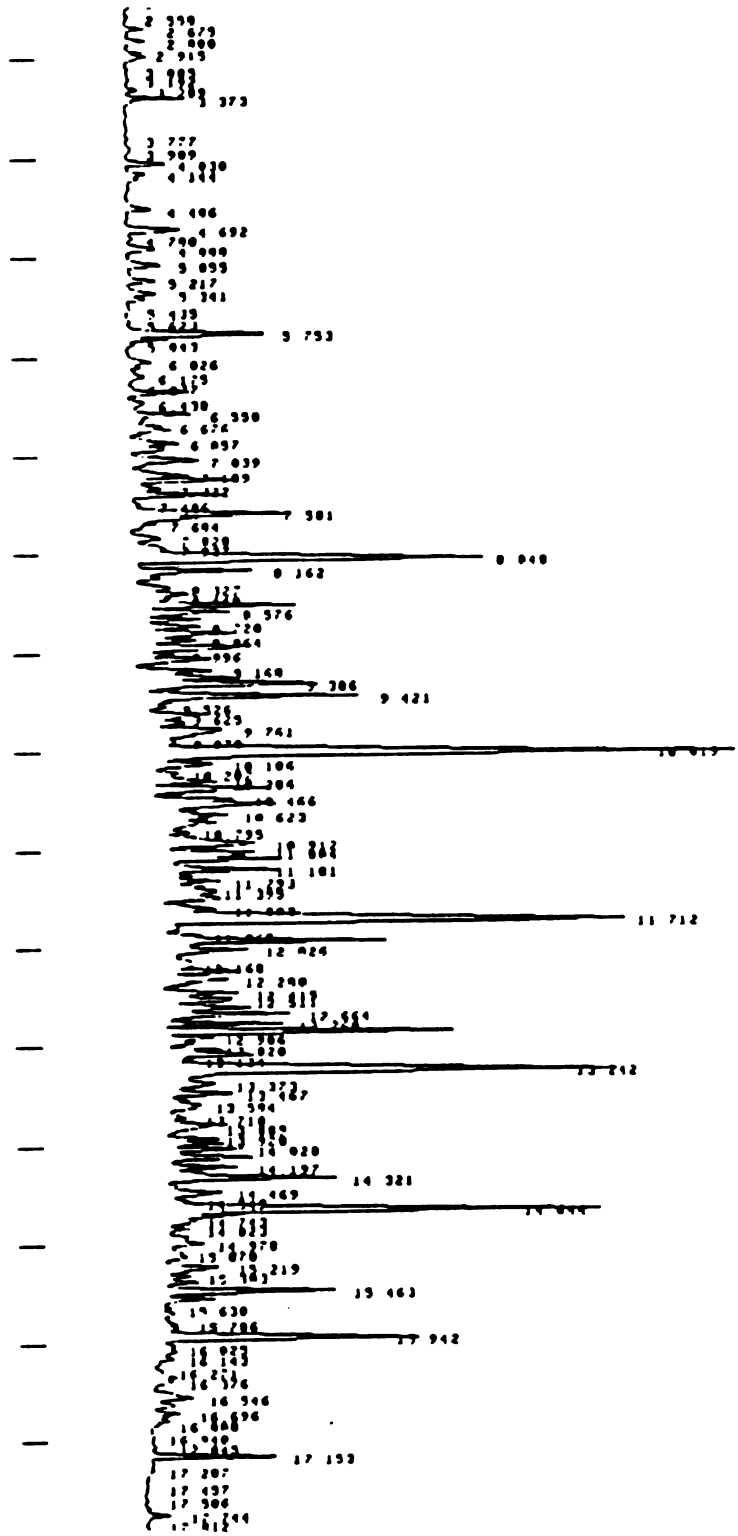
(a)

FIG. 4. Capillary GC plots of representative members of each of the eight groups in which the midrange products are classified: (a) Group 1, MS02; (b) Group 3, PT05; (c) Group 4, CL06; (d) Group 5, ST01; (e) Group 6, PT04; (f) Group 7, CL09; (g) Group 8, GT01; (h) Group 9, CL01.



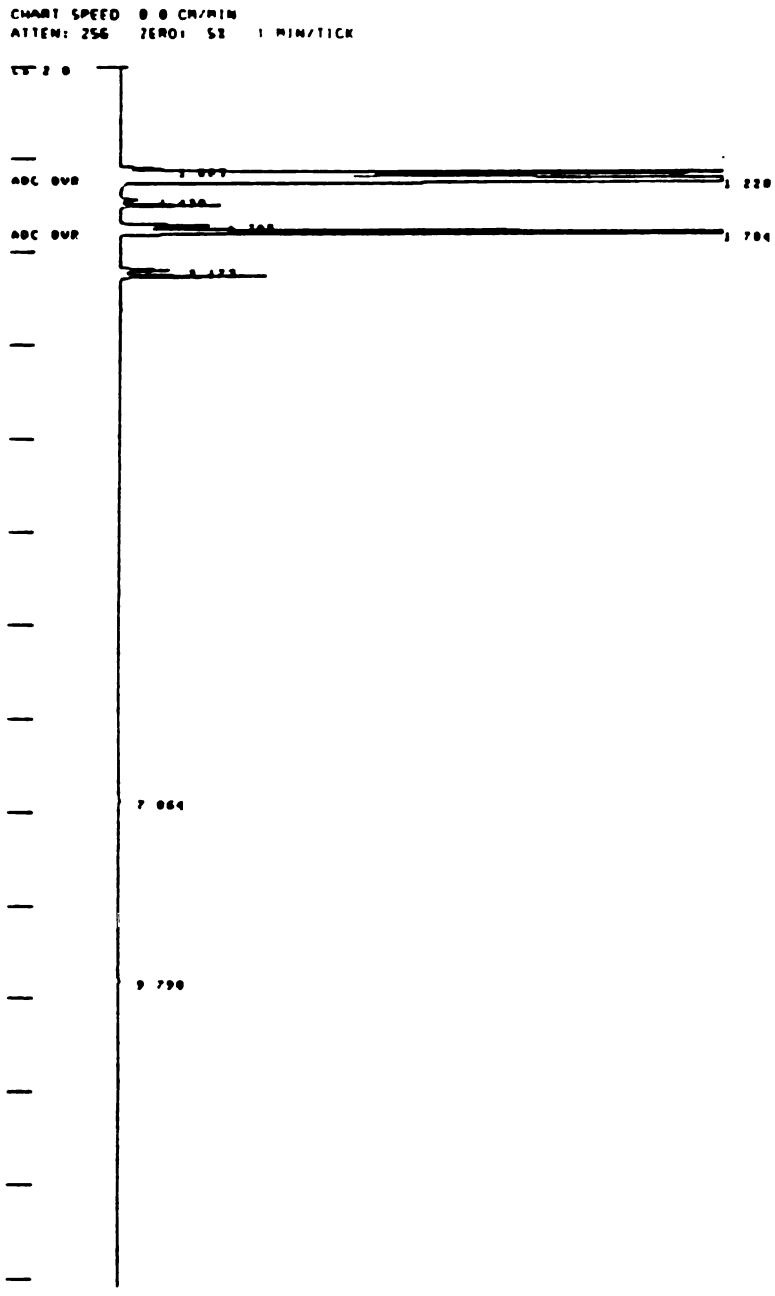
(b)

FIG. 4. Continued.



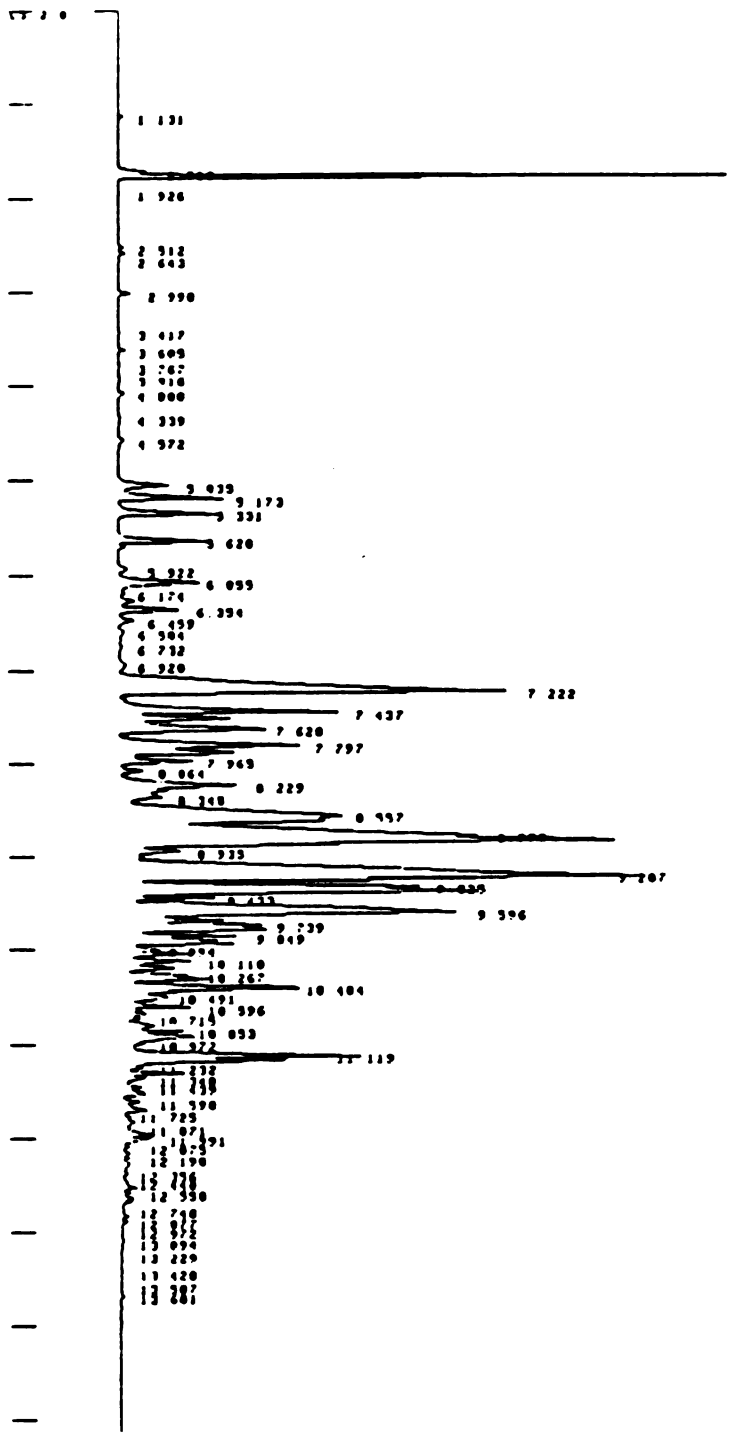
(c)

FIG. 4. Continued.



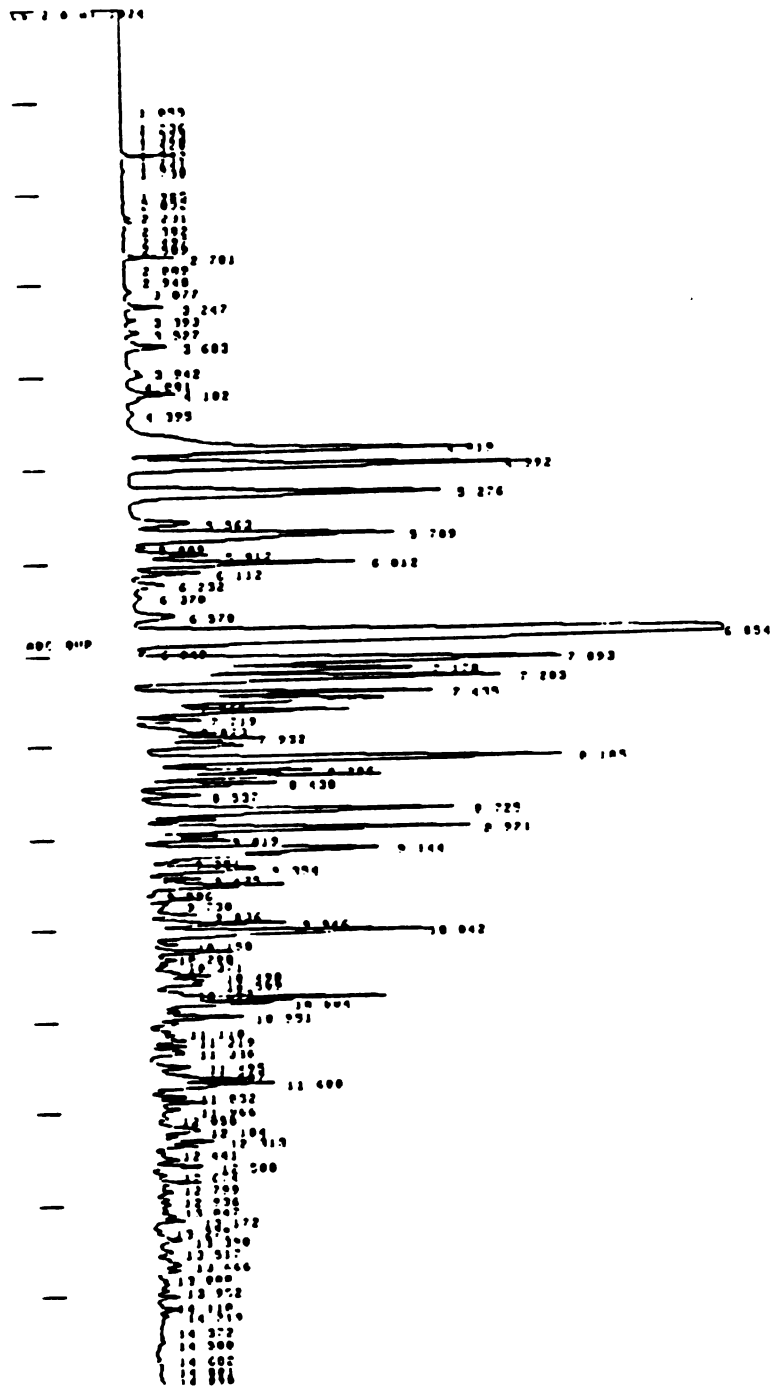
(d)

FIG. 4. Continued.



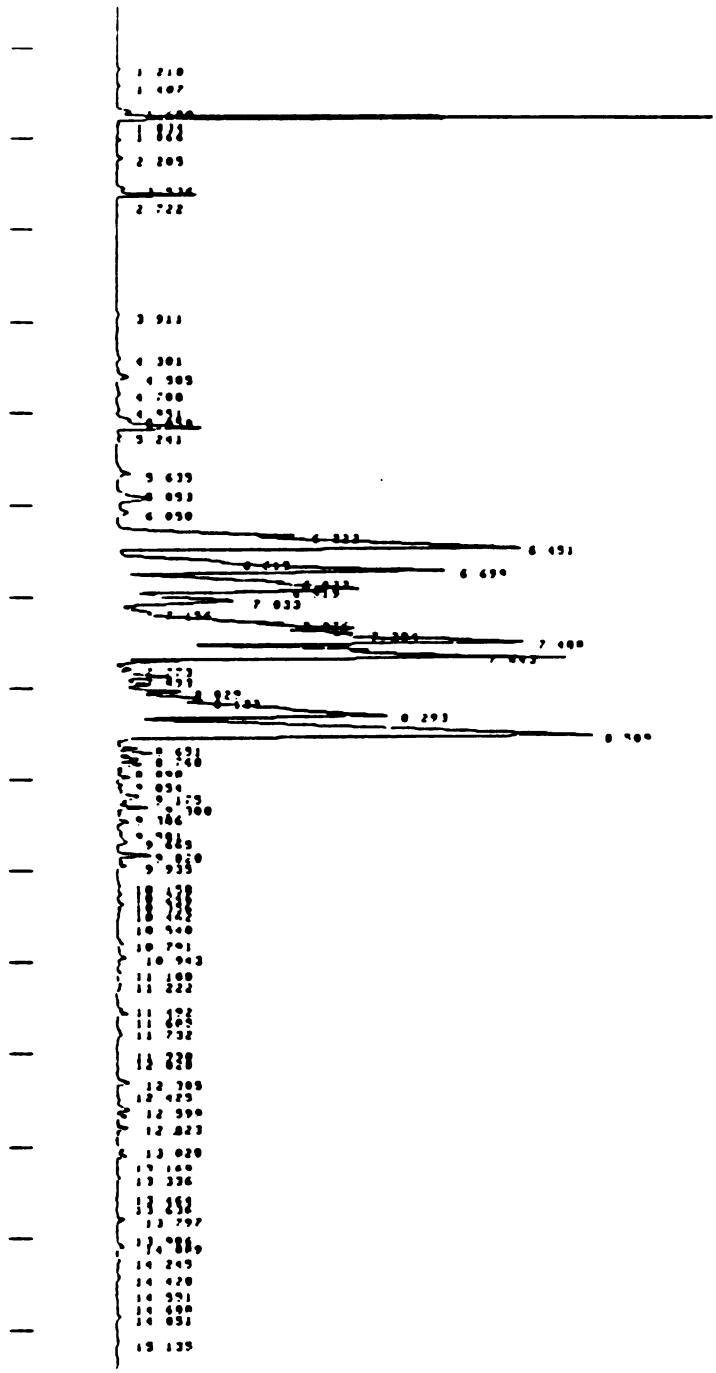
(e)

FIG. 4. Continued.



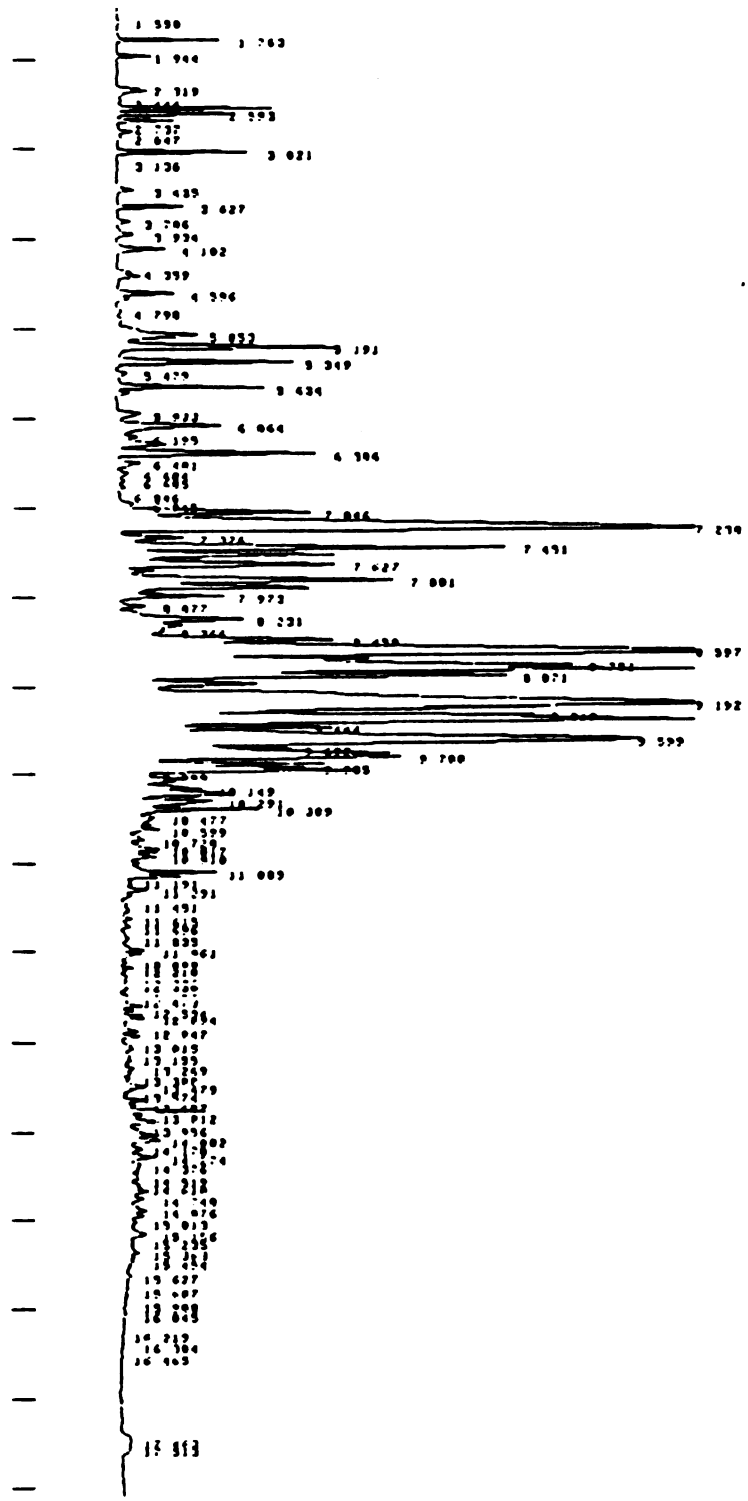
(f)

FIG. 4. Continued.



(g)

FIG. 4. Continued.



(h)

FIG. 4. Continued.

When the two sets of groups are compared, it is found that many of the samples fall into the same fluorescence and GC group. These are represented in TABLE 6.

TABLE 6. The Samples Which Fall Into Same Groups By 3-D Fluorescence and GC Plots.

Group	1	2	3	4	5
Sample Code	PT01 PT02 PT06 CL02 CL03 CL04 CL07 CL08 MS01 MS03 TT01		PT05 LT01	CL05 CL06	ST01

TABLE 6 shows that, at the concentrations chosen, 16 out of the 22 samples (about 72.7%) can be grouped the same way by both 3-D fluorescence and GC plots, though the mechanism of the two instruments and the nature of the features the two approaches are totally different. Thus, merely by running the GC and 3-D fluorescence, one can immediately identify the samples that do not fall into the corresponding groupings (assuming that the samples came from the pool of 22 used here).

By comparing TABLE 4, TABLE 5 and TABLE 6, some inferences can be deduced: (1) though the physical and chemical characteristics targeted and instrumental mechanism employed by 3-D fluorescence and GC are totally different, both of them yielded a biggest group -- Group 1, which occupied about half of the total samples of this study. (2) the discriminability of the two approaches are mutually compensatory. For example, 3-D fluorescence could distinguish PT03 and MS02 from the same GC group (Group 2); on the other hand, GC could distinguish PT04 and GT01 from a same 3-D fluorescence group (Group 3), and distinguish CL09 and CL01 from a same 3-D fluorescence group (Group 4). Therefore, solely based on the results of this stage, there was no basis to say which of the two approaches has higher discriminatory power.

In order to test reliability and repeatability of 3-D fluorescence, under the exactly same experimental conditions described above, each sample ran twice on GC and three times on the fluorimeter. After careful examination of more than a hundred graphs, some tentative conclusions can be reached.

First, in each gas chromatogram of mid-range petroleum products, there were usually more than a hundred peaks. If taking retention time, peak area of all these peaks, and their relative ratios of peak intensities between peaks into consideration, even by visual examination, it was obvious that these

parameters vary not only from one sample to another, but also from one run to another run of a same sample under the conditions researchers could control. In other words, the chromatograms of different runs of one sample could show some easy-to-find data or visual differences. Hence, the data or profile fluctuations prohibit us to firmly ascertain if the differences between two chromatogram indeed mean they are the results from two different samples. This was why the author had to put the samples into a group though there were always some chromatogramic differences among any two GC plots within any group. However, our judgement was not based on retention times and relative intensity ratios of all peaks, but based on some so called "intrinsic peaks" and their relative intensities as well as the profile configuration of a GC plot. These characteristics were stable and repeatable, and were the foundation for the grouping of samples.

Second, contrary to the considerable fluctuation of gas chromatograms, repeated run of 3-D fluorescence of a same sample revealed that under carefully controlled experimental conditions, the resultant 3-D fluorescence plots of one sample were stable. In addition, under the chosen concentration conditions presented in TABLE 4, the differences of profile configurations, maximum fluorescence intensities, maximum EX and EM wavelength positions of different samples among any 3-D fluorescence group, though maybe quite subtle, were stable and repeatable by different runs. So, these differences

could be used to distinguish samples within a 3-D fluorescence group. By this further within-group examination, about two thirds of the samples in the same 3-D fluorescence groups could be readily differentiated, and therefore, one could conclude that they came from different sources.

Third, when conducting 3-D fluorescence visual comparison within a group, contour plots possessed higher discriminating power than stacked plots. This can be explained by the fact that in stacked 3-D fluorescence plots, some profile configuration features are always blocked by the higher and/or broader curves in front of them. Therefore, from any single view (either EX or EM, either hi-lo or lo-hi), i.e., from any single stacked 3-D fluorescence plot, some set of spectra -- maybe a crucial set of spectra for distinguishing similar samples -- could be blocked by other higher and/or wider spectra in front of them. Though the data or information of this set of spectra had been detected by the fluorimeter and stored in the computer, they could not be fully displayed by a stacked plot. Contour plots, on the other hand, create a x-y coordinate for each fluorescence sample data, within which, a closed curve represent a same intensity (isogradient), and a pair of x and y values of any point on an isogradient represent the corresponding EX and EM wavelengths. In this way, a single contour plot, in theory, losses less information than a single stacked plot.

The results of STAGE I can be summarized as: GC grouped the 22 samples into 8 groups, 3-D fluorescence grouped them into 5 groups. It was difficult to identify most samples within a group by GC plots due to their higher complexity and less repeatability; two thirds of the samples within groups by 3-D fluorescence plots could be reliably distinguished.

2. STAGE II. CONCENTRATION STUDY.

It is well-known that the intensities and shapes of oil fluorescence spectra depend significantly on concentration [75]. If the concentration is too high, the inner filter effect (self-absorption) could suppress some strong fluorescence of certain component(s) in the sample; if the concentration is too low, some weak fluorescence of certain component(s) could not be received by the detector of fluorimeter [76]. Accordingly, it is reasonable to assume that if a sample is a mixture, the fluorescent feature at a specific concentration mainly reflects the features of certain components in the sample; the fluorescent features at different concentrations could probably reflect different components in the sample. This presumption infers that comparing 3-D fluorescence at different concentrations could increase the discriminating power of the technique.

In STAGE I, there were still approximately one third of the samples within either of the five groups which could not be distinguished by 3-D fluorescence, because they were too similar at the concentration listed in TABLE 4. Stage II of this study was an attempt to enhance the discriminability of 3-D fluorescence by running samples at different concentrations. This stage was performed in two steps.

The first step was to ascertain the variability and stability of 3-D fluorescence yielded from mid-range petroleum product samples at different concentrations. It is well known that in theory, during a sample preparation procedure, "experimental error" always exists. In the present study, for example, sample dilutions were made by, first, drawing the original sample by a syringe; then, diluting it by a set of glass graduated cylinders and measuring flasks. All these procedures were done by hand. Therefore, the degree of precision was objectively limited by the accuracy of graduation of the cylinders or flasks available on the one hand; and also subjectively limited by technical fluency and psychological state of the operator on the other hand. According to a theory of scientific experimentation, results are always subject to systematic errors, (e.g., caused by the deficiency of experimental tools) as well as random errors (e.g., caused by operator's errors in sample preparation). Because fluorometry is very sensitive technique, and mid-range petroleum products are

very complex mixtures, it is necessary to evaluate the interference of experimental errors before conducting the actual concentration study.

By doing this error evaluation, two samples were randomly chosen from Group 1 and Group 4 (see TABLE 4). They were: PT02 and CL05. Each of the two samples was measured at various concentrations. They are listed in TABLE 7.

TABLE 7. The Concentrations Used to Test the Variability and Stability of 3-D fluorescence at Different Concentration.

Concentration	1:	Original (without any dilution)
Concentration	2:	2000 ppm
Concentration	3:	1000 ppm
Concentration	4:	500 ppm
Concentration	5:	100 ppm
Concentration	6:	50 ppm
Concentration	7:	10 ppm
Concentration	8:	5 ppm
Concentration	9:	1 ppm

In this step, all concentrations of each sample were measured two times. This means, for any of the 36 measurements (i.e., 2 samples x 9 concentrations of each sample x 2 measurements of each concentration = 36 runs), each preparation began right from a totally separate solution. In other words, each of the two samples were run two times at all nine concentrations from two sets of independently prepared solutions.

The results of this test displayed, first, one sample at different concentrations showed different fluorescence features in terms of the 3-D fluorescence patterns, the relative maximum intensities of EX or EM wavelengths, the value of maximum EX or EM wavelengths, etc.. Second, all the above features of two separately prepared runs of one sample at any of the nine concentrations showed no substantial distinctions. This indicated that either the systematic or random errors, or objective or subjective errors were not significant enough to cause interference to the 3-D fluorescence results from the available measurementation. The characteristics of 3-D fluorescence plots under different concentrations were stable, repeatable and therefore reliable.

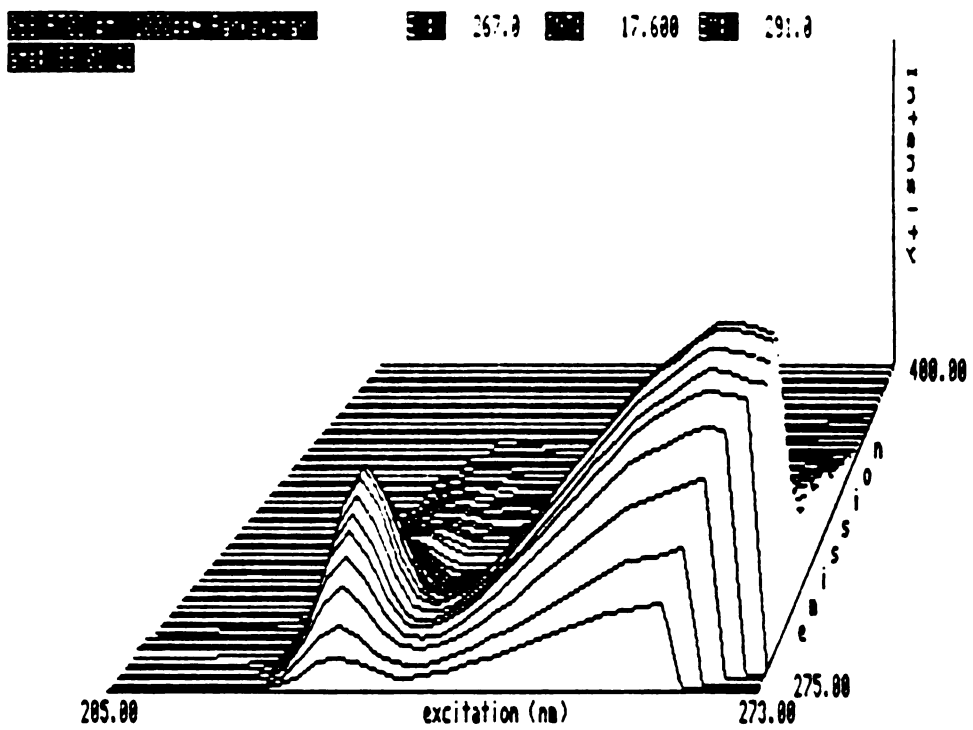
The second step was an actual concentration study. In this step, six samples were utilized. They are listed in TABLE 8.

TABLE 8. The Samples Used in Concentration Study.

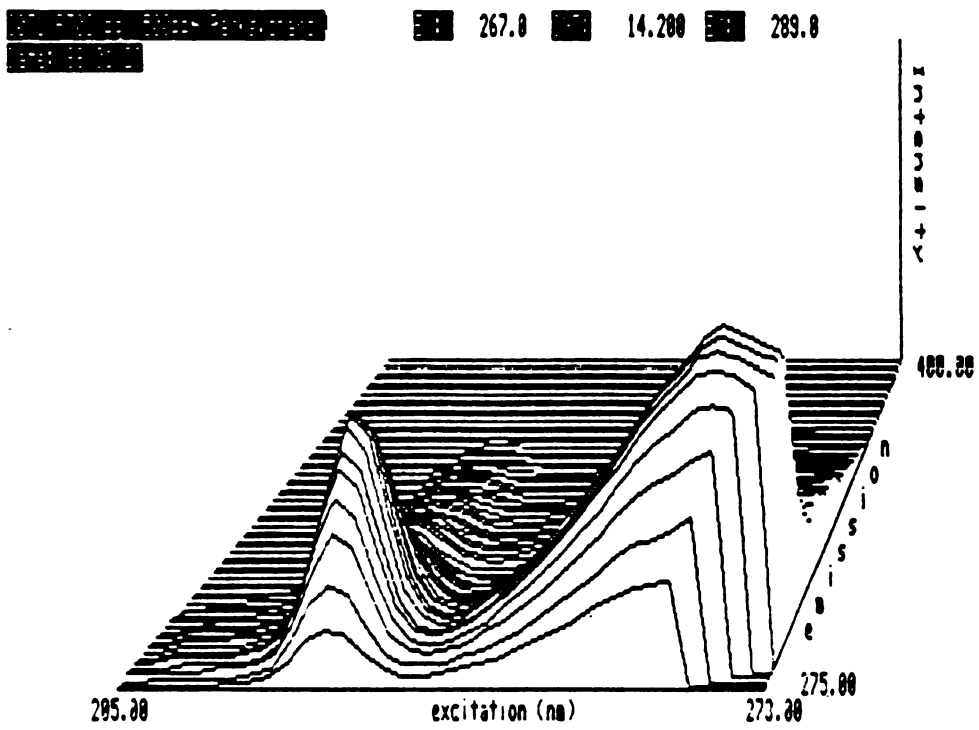
3-D Group	**1**	**2**	**3**	**4**
Sample Code	CLO3 PT01 PT02	PT03	LT01	CL05

In this step of STAGE II, because of an extremely strong self-absorption effect

at very high concentrations and too weak fluorescence intensities at very low concentrations, three concentrations used in the last step were excluded. They were: original (undiluted), 2000ppm, and 1ppm. So, for each sample, 3-D fluorescence measurements were taken at six concentrations: 1000ppm, 500ppm, 100ppm, 50ppm, 10ppm, and 5ppm. The stacked (both EM lo-hi and EX hi-lo) and contour plots were obtained for each sample at each concentration. The results of this study showed that the spectra for a single sample at different concentrations differed markedly. This can be seen from Figure 5a through f for the stacked plot spectra of a sample at different concentrations. Another more significant outcome was, when the three sets of plots in 3-D Group 1 were examined, it could easily be seen that at the concentration of 10ppm, all features of CL03, PT01 and PT02 were quite alike and could not be distinguished. But if examining them at other concentrations, for example, in this case, at 100ppm, the features of their stacked and contour plots showed very substantially differences (see FIG. 6). This result shows that a new approach which has not pursued in previous 3-D fluorescence studies, that is, when the task is to determine if two samples (not limited to mid-range petroleum products) coming from the same source, in the situation when it is difficult to distinguish two samples from 3-D fluorescence plots at one concentration as the results in STAGE I demonstrated, obtaining spectra at other concentration(s) could substantially increase the discriminating power of the tests.



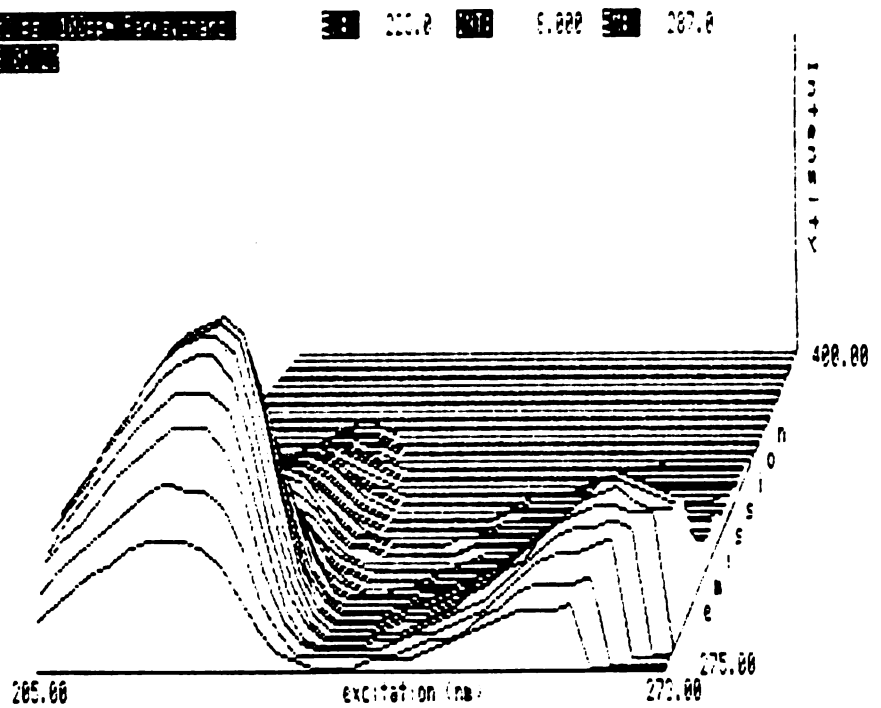
(a)



(b)

FIG. 5. 3-D fluorescence stacked plots of sample PT03 at different concentrations: (a) 1000 ppm; (b) 500 ppm; (c) 100 ppm; (d) 50 ppm; (e) 10 ppm; (f) 5 ppm.

(c)



(d)

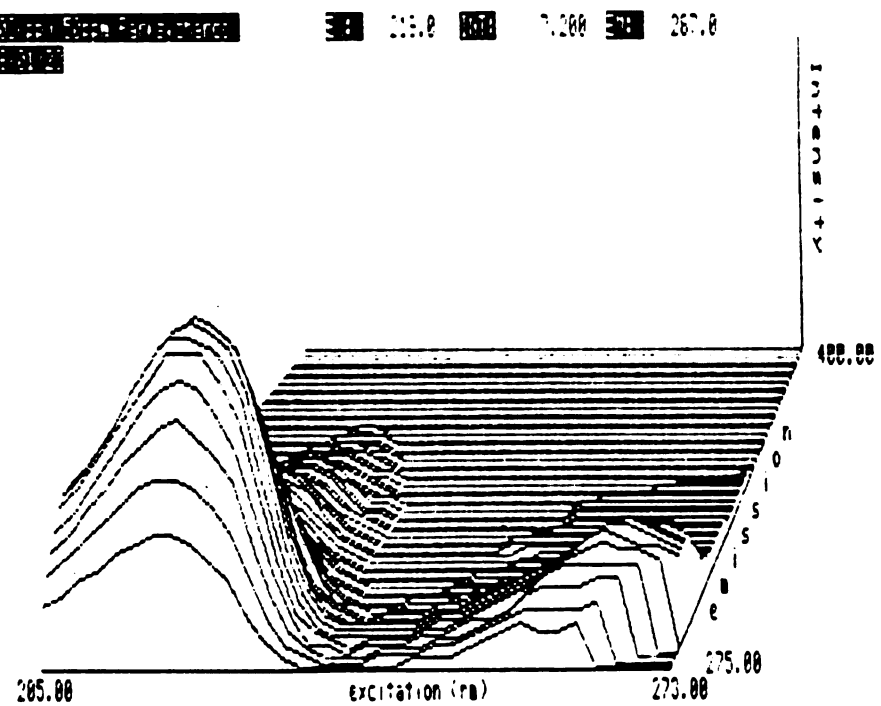
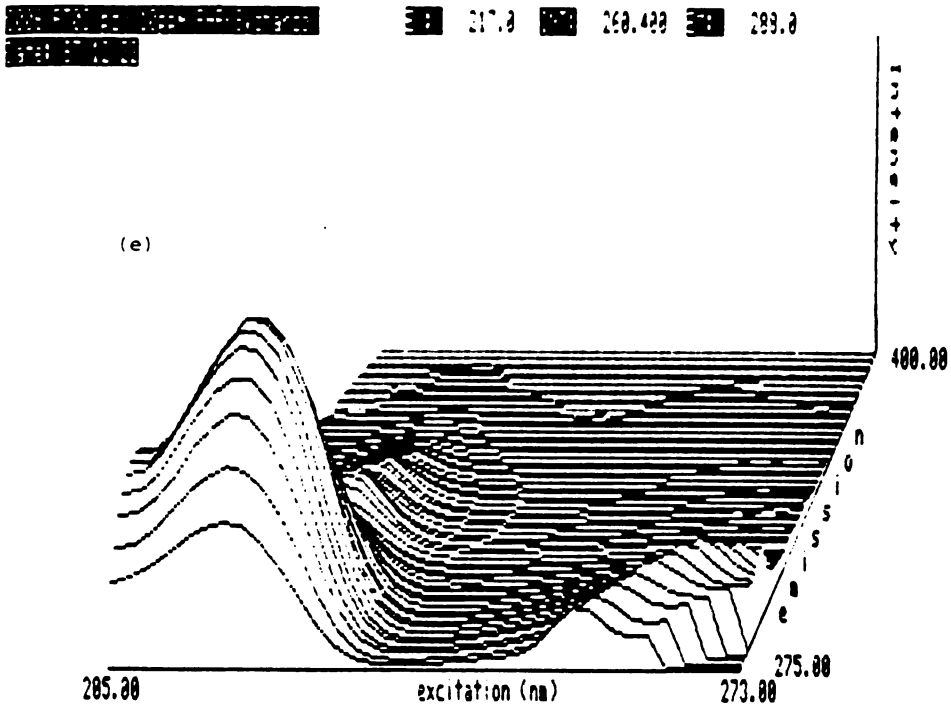


FIG. 5. Continued.

(e)



(f)

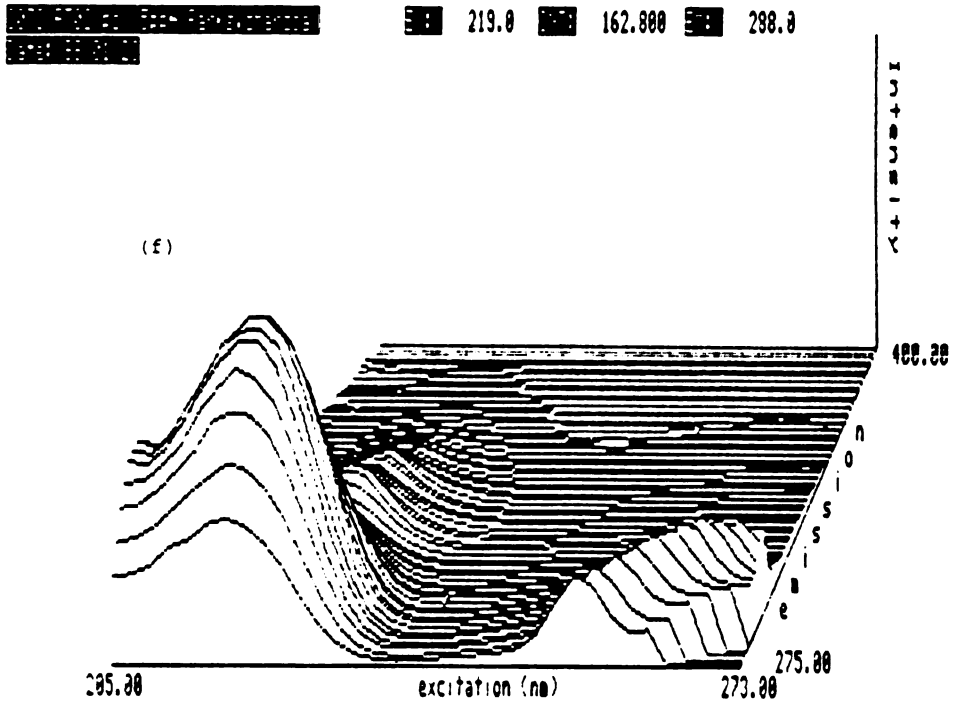


FIG. 5. Continued.

3. STAGE III. BLIND TEST TO COMPARE TWO SAMPLES.

Scientific analysis can be divided into two major branches. One is so called the "rational approach", which is often pursued to answer questions like: "What are they?" "What is the value of a certain parameter this substance has?" "What components are in it?" "What proportions of each component?" In general, conclusions of this kind of approach usually comes from: (1) quantitative observations, and (2) objective measurement done by instruments. In criminalistic, the determination of refraction index of glass, and blood-alcohol analysis are examples of this branch. Traditionally, instrumental analysis in chemistry as well as in criminalistic belong to this category.

Another branch of scientific analysis is the so called "phenomenal approach", which is often pursued to answer questions like: "Do two or a set of things come from a same source?" "Is object A related to object B in terms of certain features?" Conclusions of this kind of analysis are usually yielded from: (1) qualitative observations, and (2) subjective judgements by experienced experts. In forensic science, phenomenal approaches have been extensively employed and overwhelmingly approved in fields such as personal identification by fingerprints, hand-writing documents examination, toolmark comparisons, bullet and cartridge comparisons, and forensic dentistry. Traditionally, pattern recognition belongs to this category. Recently, forensic science has been

blurring the boundary of the two branches by combining the advantages of the two to create a better result. Computerized fingerprint categorization and identification, and voiceprint individualization are two examples of this trend. The above concept may also be applied to arson cases by looking at necessity and possibility.

In terms of necessity, in many cases involving scientific evidence, the goal of the analysis is not to answer the question "what are they", or is not to identify something (e.g., to identify a motor oil as Quaker State 10W-40), but to compare a sample of unknown origin (Sample A) to one whose source is known (Sample B). In common arson cases, the central forensic issue is to confirm if the suspicious substance (usually in liquid state) found at an arson scene and the substance possessed by a suspect came from the same source or one related to the other in certain features. Prosecutors, judges, jurors, and even forensic scientists do not really care about the composition of the liquids, or their physical and chemical parameters, provided the conclusion of "sharing a same source" could be drawn by whatever means.

In terms of possibility, as we know, all petroleum-based products are extremely complex organic mixtures. By employing modern techniques, it is possible to quantitatively determine their major components and put them into more and more detailed groups. However, in spite of its costliness and consumption of

time, present instrumental analysis has not reached the point to quantitatively determine all of the components of petroleum-based products in sufficient degree, and to individualize any two commercial petroleum-based products based on this rational result.

Therefore, one of the goals of this study was to test the discriminating power of 3-D fluorescence and GC by combining the rational and phenomenal approaches. That means, using analytical instruments to get objective plots and using subjective judgement to derive the "yes" or "no" conclusion.

As discussed above, the conventional task of a forensic laboratory for arson evidence is endeavoring to match a liquid found at arson scene with a liquid obtained from the suspect. To imitate this process, the author's supervisor -- Dr. Jay A. Siegel prepared seven pairs of samples (14 single samples) from the twenty-two samples listed in Table 1. They were all approximate 30 ml in volume. Each was put into a small glass container, well sealed by a rubber cap and respectively labelled as: 1A, 1B; 2A, 2B; 3A, 3B; 4A, 4B; 5A, 5B; 6A, 6B; 7A, 7B. The two samples in any of the seven pairs were chosen from same 3-D fluorimetry group, but they may or may not came from the same original sample. In other words, the two samples in each pair were all similar, but might or might not have been the same. The author -- the examiner received labelled containers with samples, but did not know which pairs were from the

common source. His task was trying to determine the "sames" from the "similars" by the methods and conditions developed in early stages.

The GC instrumental conditions used here were same as listed in TABLE 3. The criterion to conclude the two samples in a pair were from a same source was: all the retention time values of characteristic peaks and the intensity relationships among these peaks for the two samples ought to be matched (means they are same brand); otherwise, the two samples would be regarded as coming from different sources. The determination of which peaks were "characteristic" was based on experience and other research results.

The 3-D fluorescence instrumental conditions were the same as listed in TABLE 2. All the samples were first diluted to 10ppm, if no substantial differences could be found between the two plots in a pair at this concentration, additional measurements were taken at higher concentrations in the sequence 50ppm, 100ppm, 200ppm, 500ppm, 1000ppm. At the concentration where substantial differences between the two were confirmed, the matching procedure stopped. The criterion used for reaching the "same source" conclusion was: only if the pairs of spectra showed no substantial differences at all the six concentrations would they be declared to be of the same source. Figure 6a through d demonstrated that at 10 ppm sample 7A and 7B could not be distinguished. However, a cautious comparison at the

concentration of 100 ppm of these two samples showed substantial differences. Accordingly, it is reasonable to conclude 7A and 7B came from different sources.

The results of the blind test are in TABLE 9. In this table, "different" denotes that by the means of that instrumentation, the resultant plots showed substantial differences; "same" denotes by the means of that instrumentation, the resultant plots showed no substantial differences. "Conclusion" means what the Dr. Siegel really did about that pair of the two samples.

TABLE 9. The Comparative Results of GC and TLS Blind Test.

Code of Sample Pair	GC Judgment	Fluorimetry Judgment	Actualities
1	same	different	different
2	different	different	different
3	same	same	same
4	different	different	different
5	different	different	different
6	same	same(?)	same(?)
7	same	different	different

Because Group I of either GC or 3-D fluorescence contained about half of the 22 samples, and either the GC or 3-D fluorescence plots in Group I were very similar, six pairs of the samples were chosen from this group. The actual compositions of the pairs of samples is given in TABLE 10.

TABLE 10. The Samples Used In Blind Test.

Code of Sample Pair	Sample A	Sample B
1	PT03	MS02
2	CL03	CL08
3	PT02	PT02
4	MS03	TT01
5	CL05	CL06
6	CL04 (*)	CL04
7	PT01	PT02

The results of blind test showed that GC was correct in 57.1% of the cases, whereas 3-D fluorescence was correct 100% of the time.

It is worthwhile to explain the meanings of two question marks appeared in TABLE 9 and an asterisk mark appeared in TABLE 10. The GC measurements of the pair 6A and 6B showed exactly same plots in all criteria maintained above (see figure 7a through b). But the results of 3-D fluorescence contour plots of the two samples at 10 ppm exhibited very substantial differences (see figure 8a through b). From experience and careful inspection

of 3-D fluorescence plots of figure 8a and b, the examiner speculated that the majority components of sample 6A and 6B were same but an additional substance was in 6A. This guess was confirmed later by Dr. Siegel that he intentionally added less than 0.1 ppm of another reagent in sample 6A to test the sensitivity and discriminating power of the GC and 3-D fluorescence. The result evidently exhibited that in the case where some low percentage of a minority component exists, or some subtle differences exist among samples, 3-D fluorescence technique could detect this.

4. STAGE IV. EVAPORATED SAMPLES.

One of the notable properties of many petroleum-based products is their high volatility even at room temperature. As evidence found at a crime scene, this kind of material is usually in a well ventilated environment and may be taken out from its original container for a long time period (commonly, from several minutes to several days). Accordingly, partially or totally evaporated accelerant are often encountered in forensic scientific labs. Though it is often necessary to match evaporated unknown samples with whole knowns, there is little in the literature to contribute to this question. So, the purpose of this stage was to determine what effects, if any, there would be on the 3-D fluorescence and GC of the mid-range petroleum products when they are

partially or totally evaporated. It is expected that the GC plots would, of course, be altered significantly, losing much of their volatile fractions even with partial evaporation. Changes in 3-D fluorescence plots are more difficult to predict. The components in protrolem products responsible for fluorescence are presumably the aromatic and polycyclic compounds presented in these products. They would be expected to be among the less volatile fractions and would therefore not be much affected by partial evaporation.

Because the amounts of samples supplied by the Bureau of Alcohol, Tobacco and Firearms National Laboratory were not enough to be evaporated under the evaporation conditions designed for this study, only the eight samples directly obtained from stores were employed. They are listed in the first column of TABLE 11.

TABLE 11. The Comparative Results of Neat Sample And 50% Evaporated Sample Grouping.

Sample Code	Group Numbers From Neat Sample Grouping	Group Numbers From Evaporated Sample Grouping
PT01	1	1
PT02	1	1
PT03	1	1
PT04	6	6
CL01	9	9
CL02	1	1
CL03	1	1
CL04	1	1

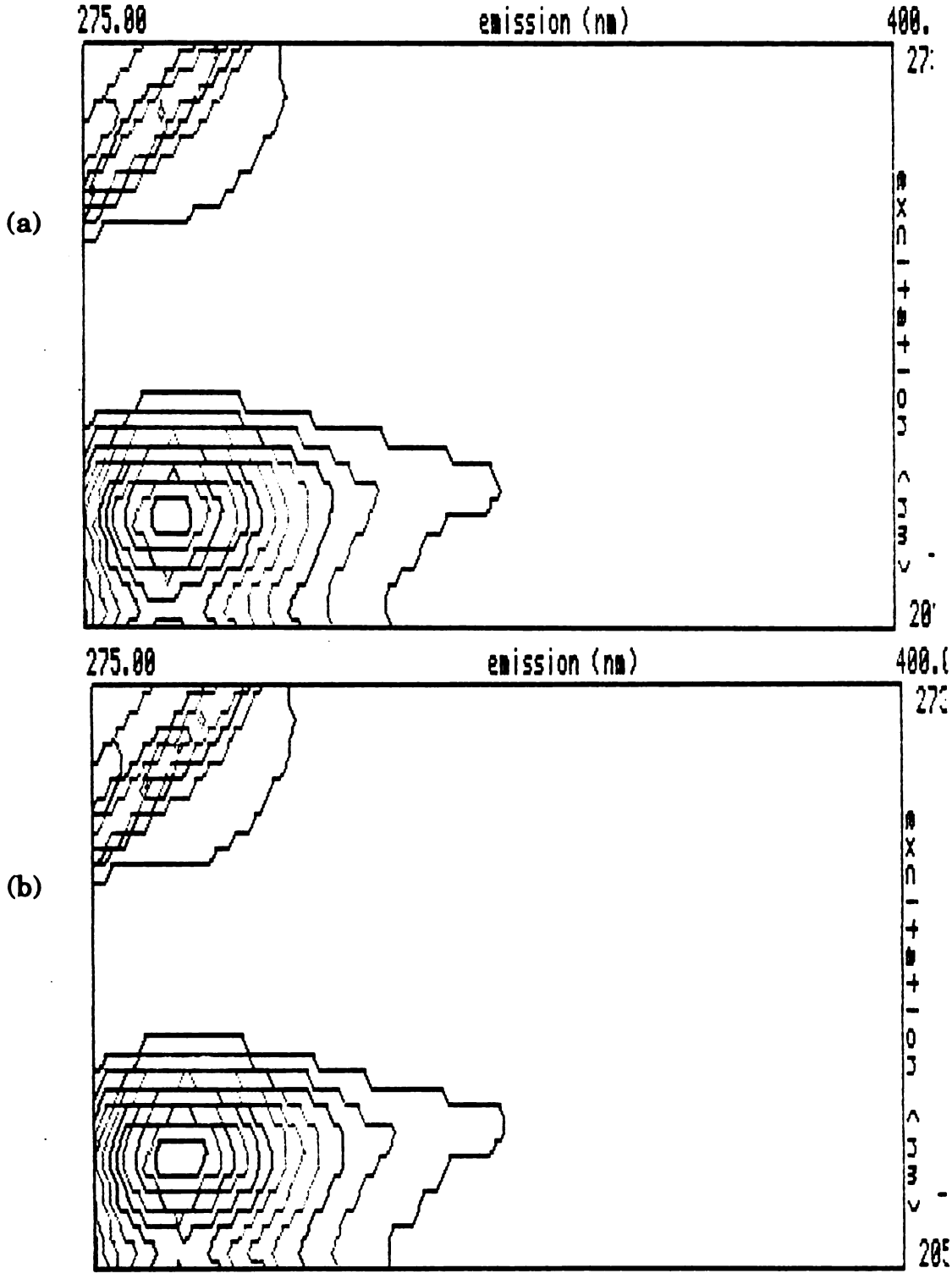
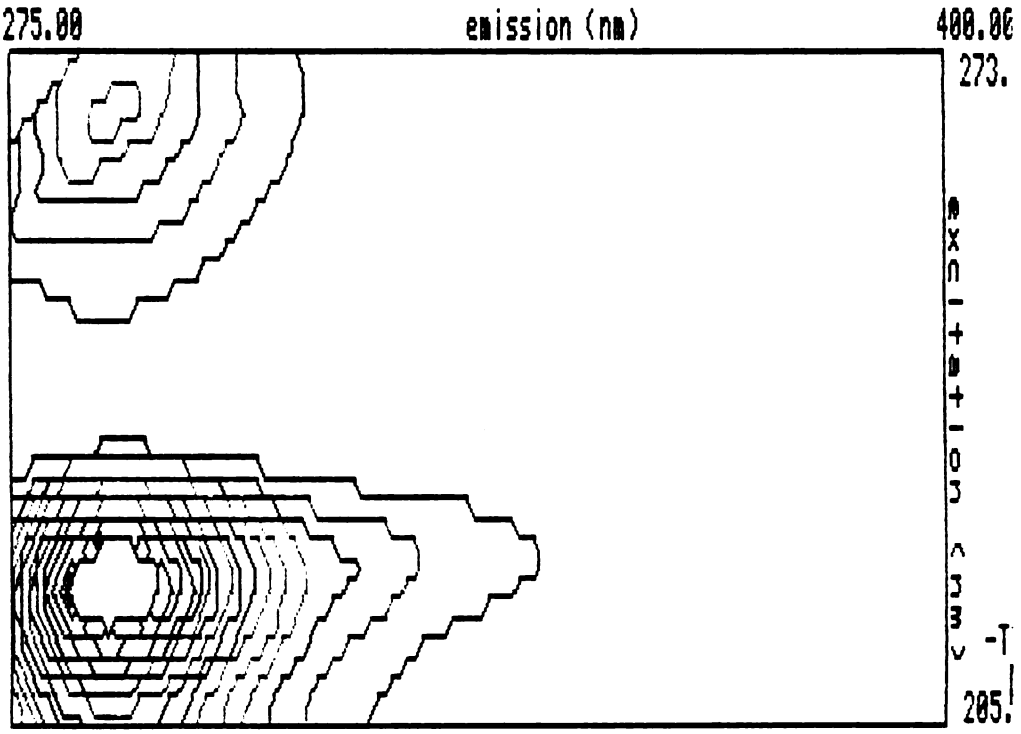


FIG. 6. Concentration studies. At concentration of 10 ppm, Sample 7A (a) and 7B (b) con ont be distinguished; at concentration of 100 ppm, Sample 7A (c) and 7B (d) can be distinguished.

(c)



(d)

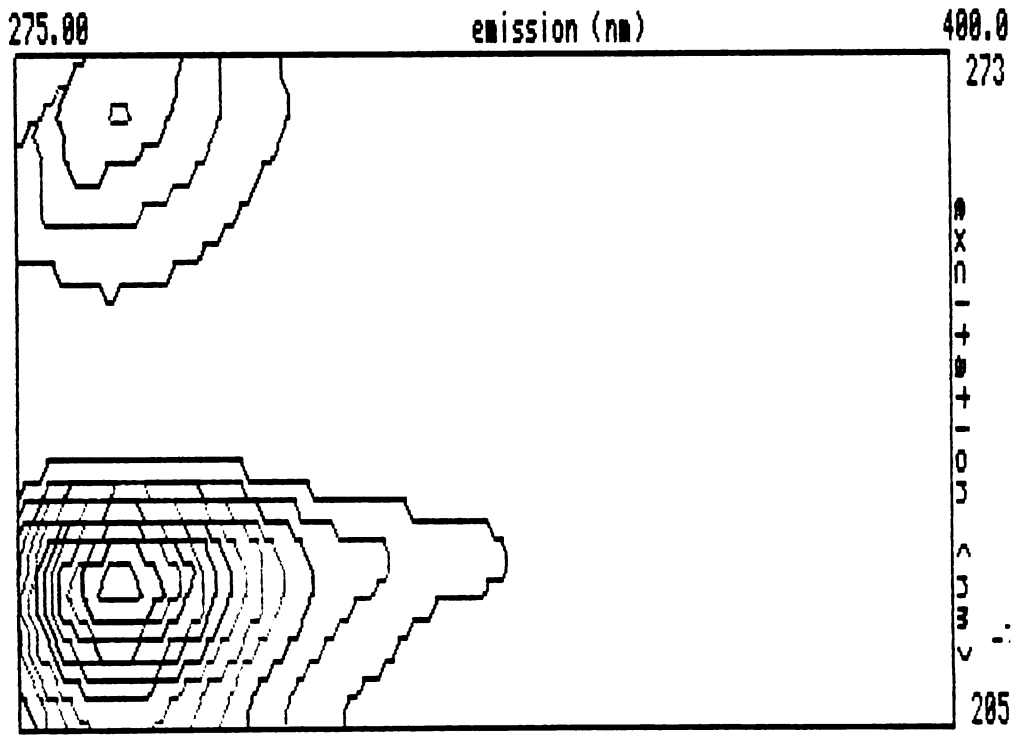
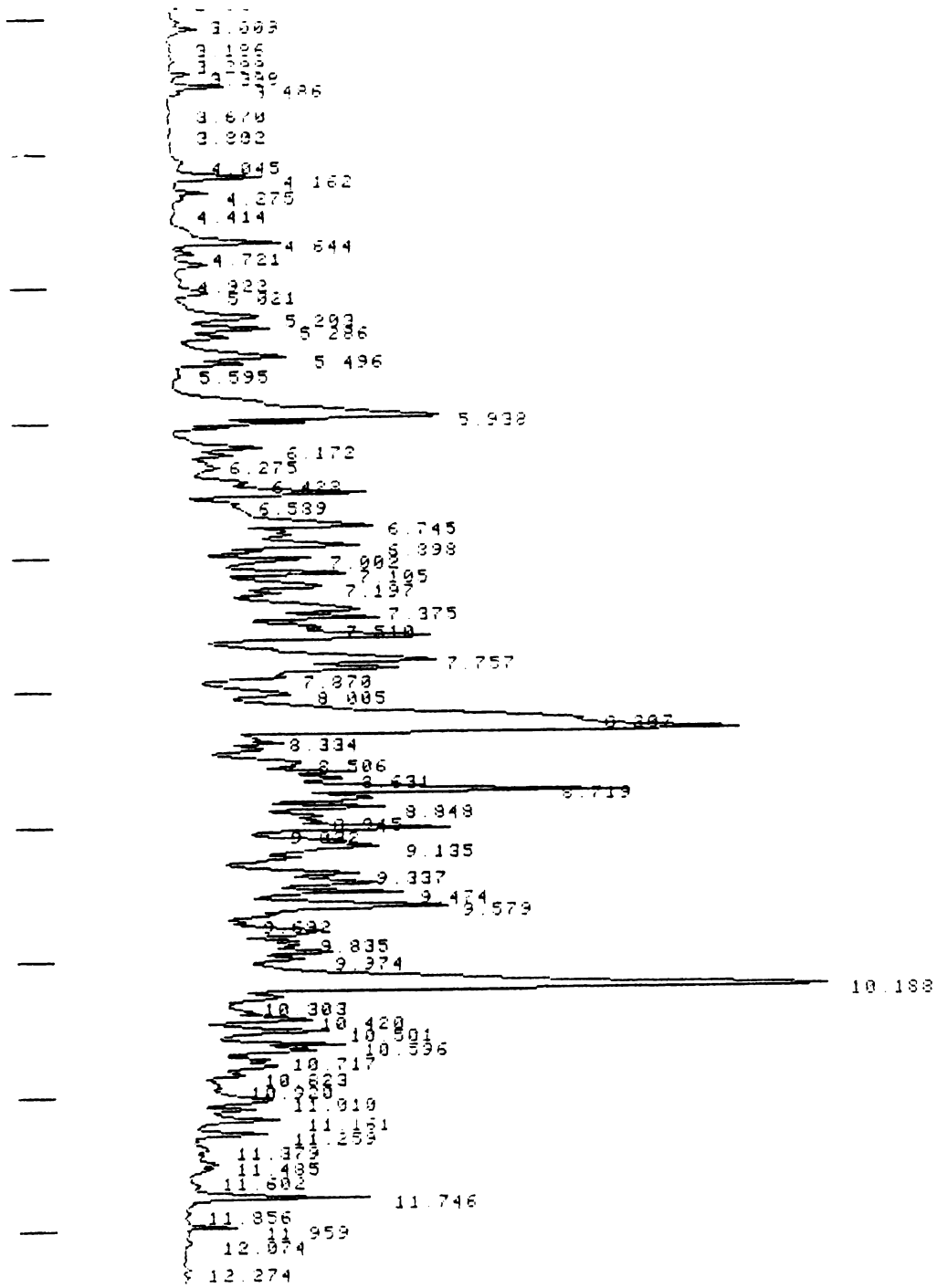
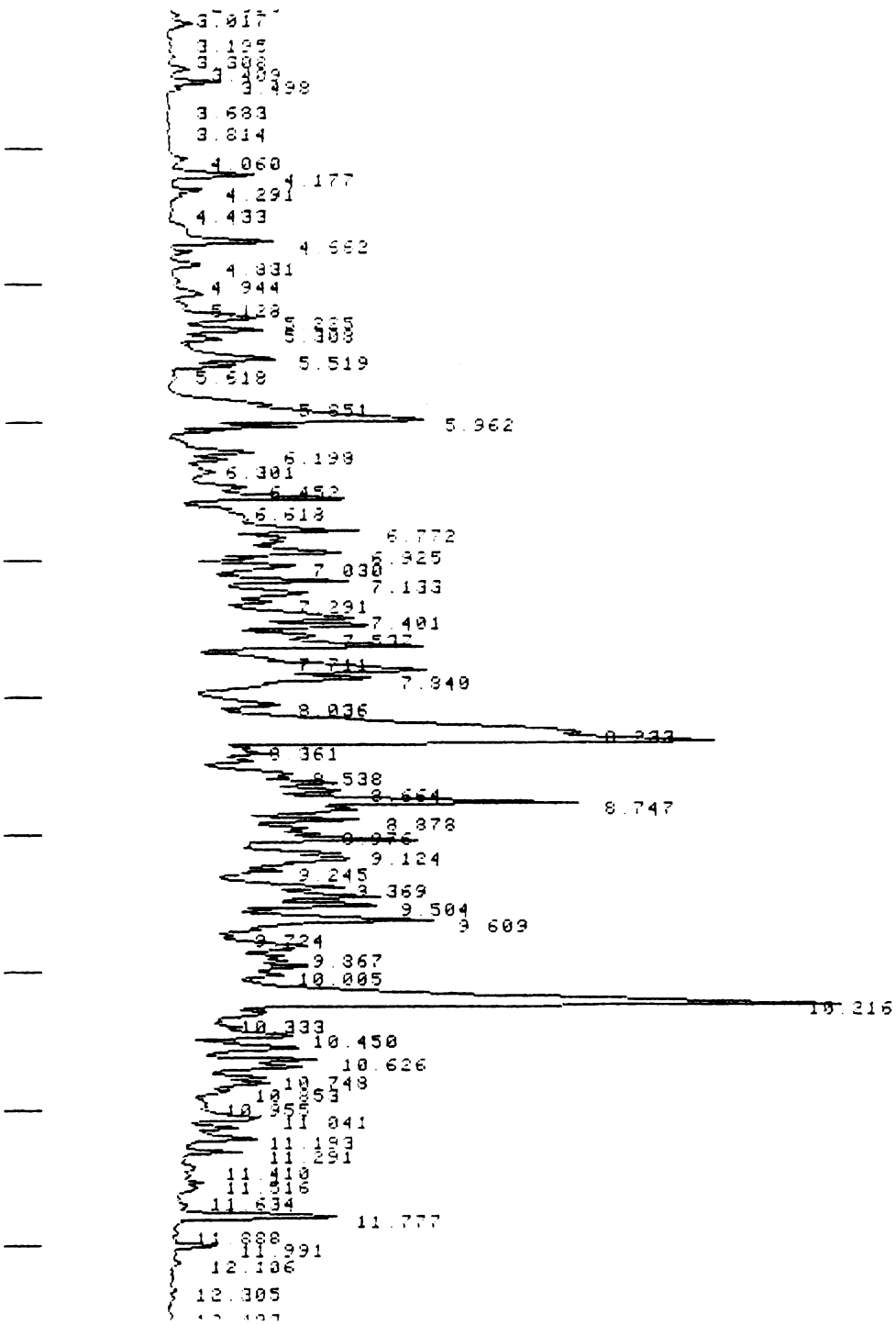


FIG. 6. Continued.



(a)

FIG. 7. **Concentration studies. The GC plots of Sample 6A (a) and Sample 6B (b) show no substantial differences.**



(b)

FIG. 7. Continued.

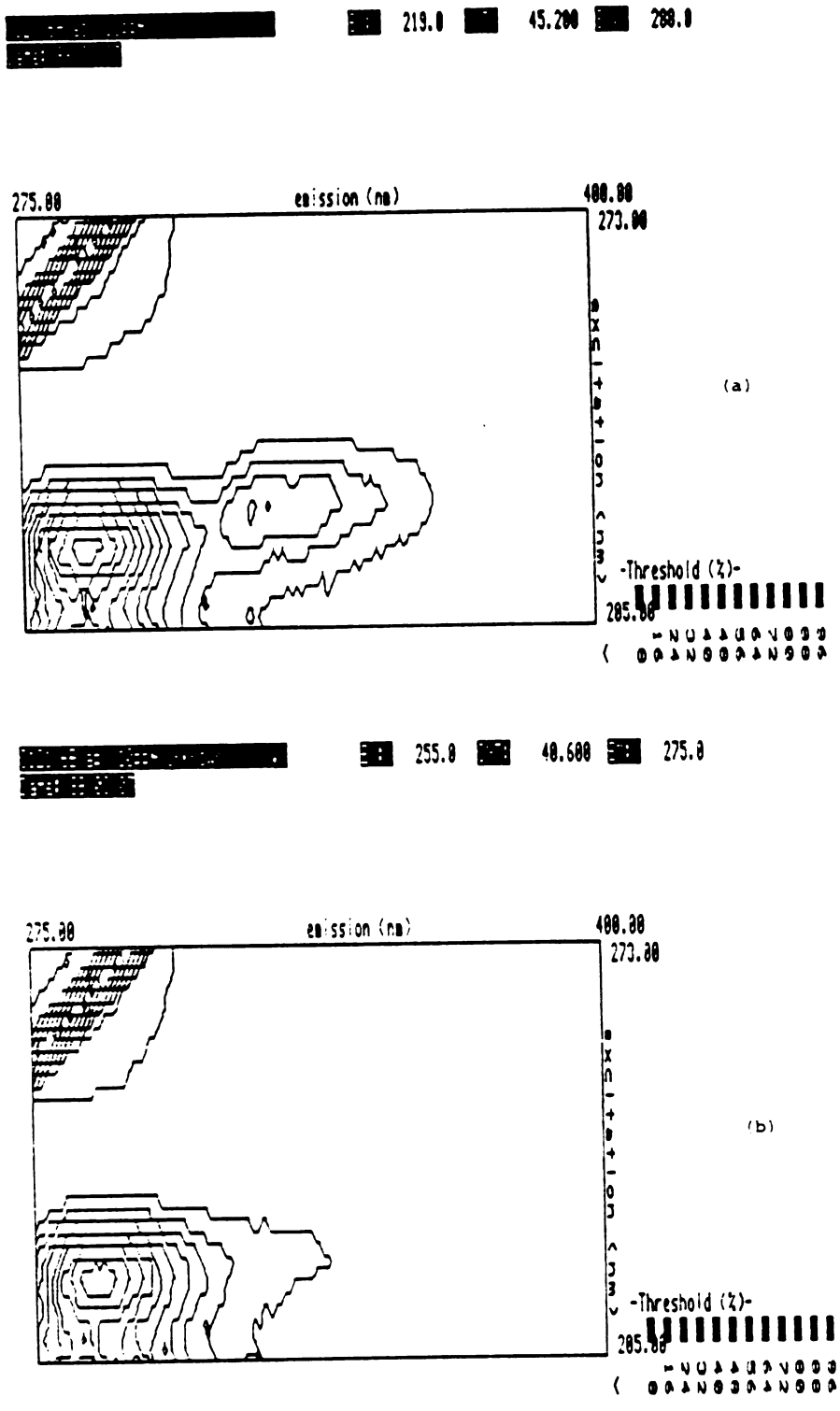


FIG. 8. Concentration studies. The 3-D fluorescence of Sample 6A (a) and Sample 6B (b) show substantial differences.

The preparation of evaporated samples employed the following process:

(1) Put 40 ml original sample into a 100 ml beaker.

(2) Leave the beaker with sample until the sample evaporated to 20 ml at room temperature (25^0 C). It took from about one to six hours depending on the nature of the sample used. These samples were used to conduct the "half evaporation" experiment.

(3) Then let the samples further evaporate until there was no liquid left.

(4) Put about 4 ml cyclohexane into a dried beaker, and thoroughly shake.

(5) Wait about 5 minutes, then pour the solution into a sample cell for 3-D fluorescence measurement.

(6) After fluorescence measurements, further condense the rest of the solution in the sample cell at room temperature until about 0.1 ml is left for the GC injection.

(7) In order to prevent possible mutual contamination between samples, all the glassware used was subjected to the sample cleaning procedure described in STAGE I.

For the half evaporated sample results, all of the eight GC plots were meaningful, but their features such as overall profile, retention time of characteristic peaks, and intensity relations among peaks were all considerably changed from those of the neat sample results. Therefore, it was nearly impossible to trace a half-evaporated sample back to its original sample by

examining the two corresponding GC plots, if there were no systematically evaporated GC plots available as standard. However, when the eight samples were grouped and same group numbers were assigned as did for the neat samples, same grouping pattern appeared. This can be seen in TABLE 11. The above results revealed that at least until half-evaporation, though evaporation affect all GC plots significantly, it does not affect their grouping patterns. In other words, the half-evaporation process has similar influences to the samples in the same groups.

With the totally evaporated samples, it would appear that there was some non-volatile residue left, but GC plots were quite non-descriptive and would not be suitable for any identification purpose. This is different from the results that one gets with gasoline or wherein a nonvolatile residue is left after all of the visible liquid is evaporated. This outcome can be explained that unlike gasolines, which are used as car fuel, both charcoal lighters and paint thinners are more thoroughly refined to decrease the amount of solid residues and impurities. The results imply that, in real cases, if charcoal lighters or paint thinners were used as an accelerant and had been totally evaporated before collection of evidence, it would be hard to identify the existence of accelerant by GC, even if the residue could be identified and collected. Figure 9a through c show GC's of a neat sample and the same sample at half and total evaporation.

In the case of 3-D fluorescence, the spectra were obtainable for both half and totally evaporated samples. However, characteristics such as overall profile configuration, positions of maximum EX and EM wavelengths, intensity of EX and EM peaks of these plots were dramatically different from those of the corresponding neat samples. Like in the case of GC plots, this means that a heavily "weathered" sample could probably not be matched back to a neat sample of the same materials unless the degree of evaporation was known, a rare situation in a real case.

Unlike petroleum-based product studies done by GC, 3-D fluorescence technique is relatively new and less often found in the literature. Therefore, all half and totally evaporated measurements were repeated three or four times to enhance their reliability. Their results clearly showed the following features. First, the spectra of a given sample at both half and total evaporation conditions were stable, i.e., the spectra were the same when each time a given sample was evaporated to the same degree. Second, in the situation of total evaporation, different from GC measurements, by which no meaningful plots could be procured, 3-D fluorescence measurements could produce meaningful and stable spectra. It could provide a possibility to identify the existence of totally evaporated accelerant by this technique, though further study to determine better technical conditions is needed. Figures 10a

through c show the 3-D fluorescence contour plots under the conditions of neat, half evaporation and total evaporation.

5. STAGE V. BURNED SAMPLE EXPERIMENT.

It is always an aspiration for an arson investigator to show that the presence of an accelerant could be found from totally burned fire residues, and a common source confirmation could be established between totally burned Sample A and unburned Sample B. There have been several studies of analysis of fire debris in order to answer this question [51, 75, 76, 77]. The conclusion of P. J. Loscalzo's [75] study represents the primary opinions of studies dealing with this issue:

> Unfortunately, a controlled study ... can not take into account the factors affecting the same accelerant under the conditions of a full-scale dwelling fire. In such a fire the accelerant may be either entirely consumed or altered in such a way that the usual analytical method commonly employed today would fail to produce any positive results.

However, it is the common situation of real arson cases that the materials which contain suspected burned accelerant are often submitted to forensic laboratories. It is known that combustion is an extremely complex process, and even the most rigorous attempts to control the conditions of a combustion

often lead to inconsistent results. Nevertheless, it was felt necessary to study GC and 3-D fluorescence behavior of the mid-range petroleum products under controlled combustion conditions to get a more complete picture of these materials in actual fire situations.

Because a large amount of sample had to be consumed in this stage of the study, only the same eight samples (see TABLE 11) were chosen as in the evaporation experiment. Of each original sample, 50 ml was put into a clean 1 gal (3.8 L, 16.5 cm in diameter, and 19 cm in height) paint can with a 4.4 cm by 20 cm piece of cheesecloth which was folded into a 7.5 cm by 7.5 cm square. The can was located on the platform of a fume hood. The distance between the edge of the front door of the hood and the can was 6 cm. The 50 ml sample was ignited by a match. The electric ventilation system of the hood was then turned on, the interval between two doors of the hood was narrowed to 10 cm, and located, the slit of the doors directly facing the burning can in order to ensure a sufficient and complete combustion. Within 5 to 7 minutes all of the liquid sample was burned out and the fire died out. The can was allowed to cool to normal room temperature, and then 100 ml of cyclohexane was poured in, and the can was shaken. After 10 minutes, the solution was filtered by gravity and evaporated to dryness at room temperature; the residue was then reconstituted in 3.5 ml of cyclohexane, and 3-D fluorescence measurements were taken. Then, the residue solution from the fluorescence sample cell was

put into a 10 ml glass container, and evaporated until about 20 ul residue solution was left for GC analysis.

By the above sample preparation, the mid-range petroleum products were totally burned out and the residue solutions were evaporated to dryness so as to approximate the burning process and the weathering process as closely as possible and to use a worst-case scenario. In the case of these samples, "burned out" meant the all original samples were consumed by combustion under the conditions of sufficient supply of oxygen and ventilation, and "dryness" meant that there was no visible liquid left. However, "burned out" did not mean that there was no any solid residual left by combustion, and "dryness" did not mean that there was no any residue left by evaporation. In almost all cases, some solid combustion products and some nonvolatile residue could be left, as is generally the case with products derived from petroleum. This residue gave rise to the weak fluorescence and resulted in the very weak chromatogram.

As in the GC plots of the total evaporated samples, the plots of these burned samples were quite non-described, and the resultant chromatogram were neither able to prove the existence of accelerant, nor imply the type of accelerant. This indicated that the combustion consumed nearly all of the hydrocarbons. A possible explanation of this result is: on the one side, the

burning temperature of all samples under the conditions of the study were higher at least than 500^0 C; on the other side, the highest programming temperature of GC for detecting the burned residue was 250^0 C. Therefore, if during the burning process, the temperature of more than 500^0 C was held long enough (several minutes is long enough), most components with the decomposition temperature lower the 500^0 C would be split and further burned away. So, it is no wonder that the resultant chromatogram were non-descriptive.

It was possible to obtain 3-D fluorescence plots for all samples after the burning process described above. But they were significantly different than either the plots for neat samples or half evaporated or totally evaporated samples. No configuration profile patterns, positions of maximum EX or EM wavelengths, or intensity of maximum EX or EM wavelengths could permit tracing back to a particular sample, or for that matter, the mid-range petroleum products as a whole. Combustion involves extremely complicated chemical reactions, so it is understandable that a resultant 3-D fluorescence spectrum was dissimilar comparing with its neat or evaporated 3-D fluorescence spectrum. In addition, when the burning was repeated on the same sample a number of times under the same burning conditions, the 3-D fluorescence spectra were all different, indicating that the combustion was somewhat different each time. The combustion conditions could not even be

known, let alone reproducible. Hence, combusting a known sample suspected to be involved in a fire and comparing the spectrum to that of the unknown would probably be futile.

It is possible that, had the combustion been cut short by putting out the fire with water or by smothering it, more of the residue of the hydrocarbon would have remained, perhaps increasing the changes for reproducibility. There are, however, reasons to believe that this would not be the situation in a real case. First, introducing water to the mixture increases the chance for contamination of the fluorescence owing to impurities in the water. Although this will be the case for most real fires, it was not desirable to add this set of variables in this initial study. Second, smothering the fire by cutting off oxygen would not introduce any contamination, but at the same time, is not the way real fires are generally extinguished. Finally, the evaporation study showed that, when a portion of the sample is lost, the 3-D fluorescence plot changes and can no longer be matched to the neat sample. Figure 9 shows a 3-D fluorescence contour plot for a sample after total combustion.

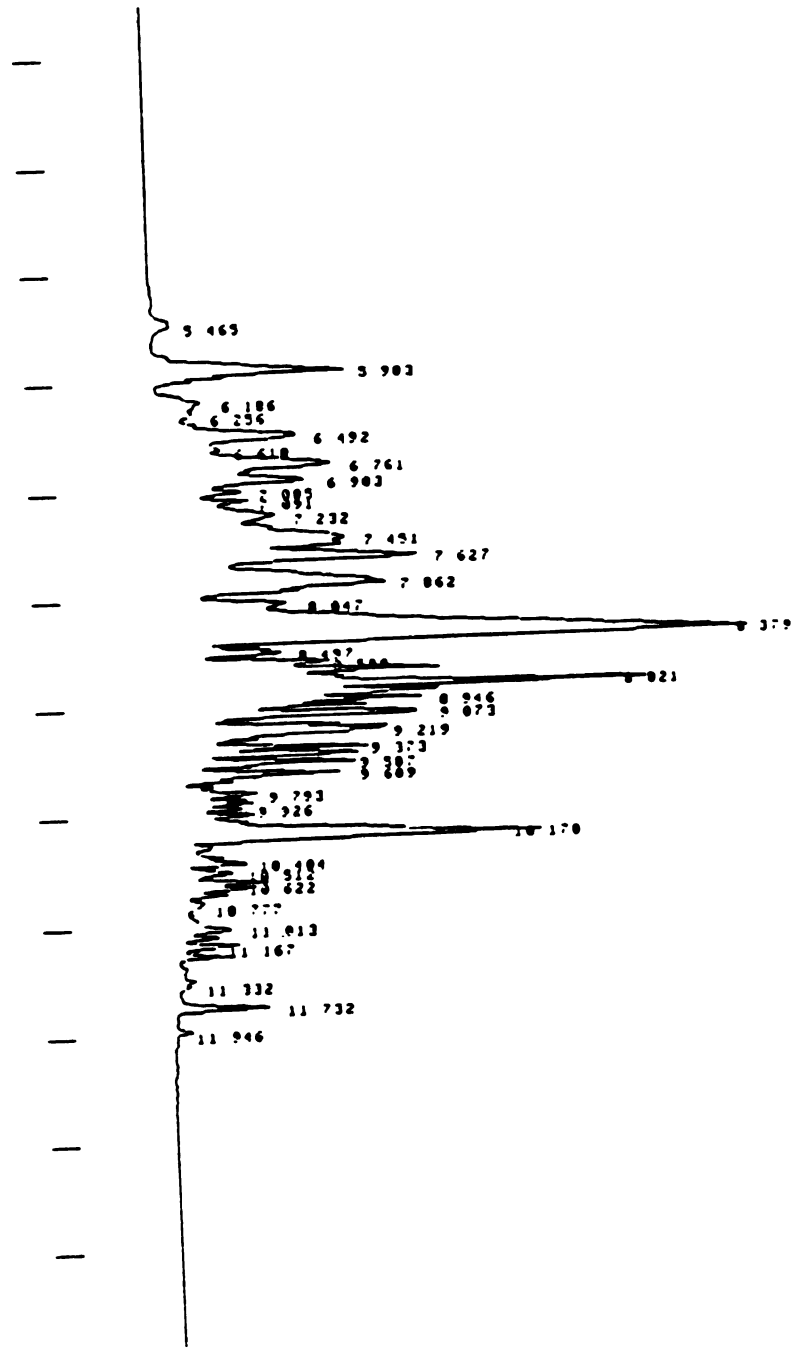
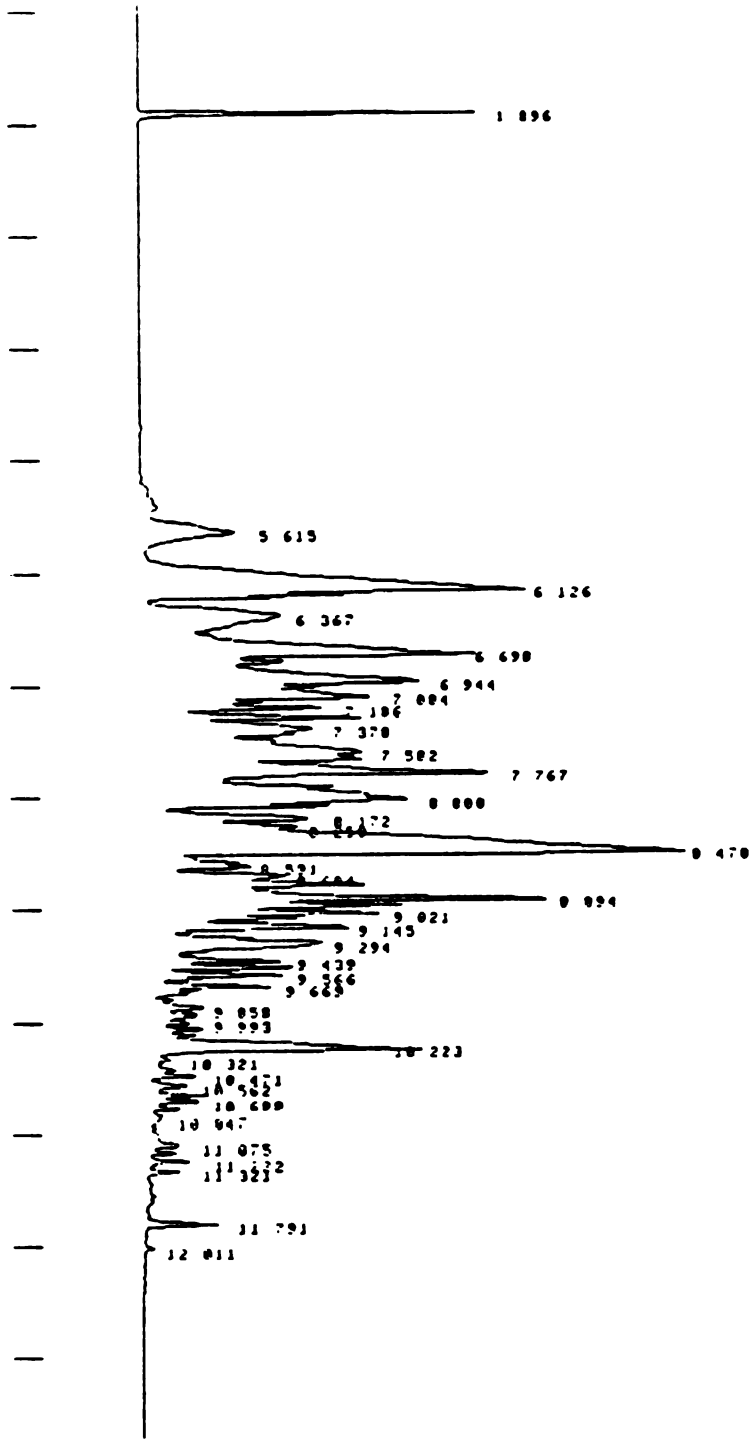
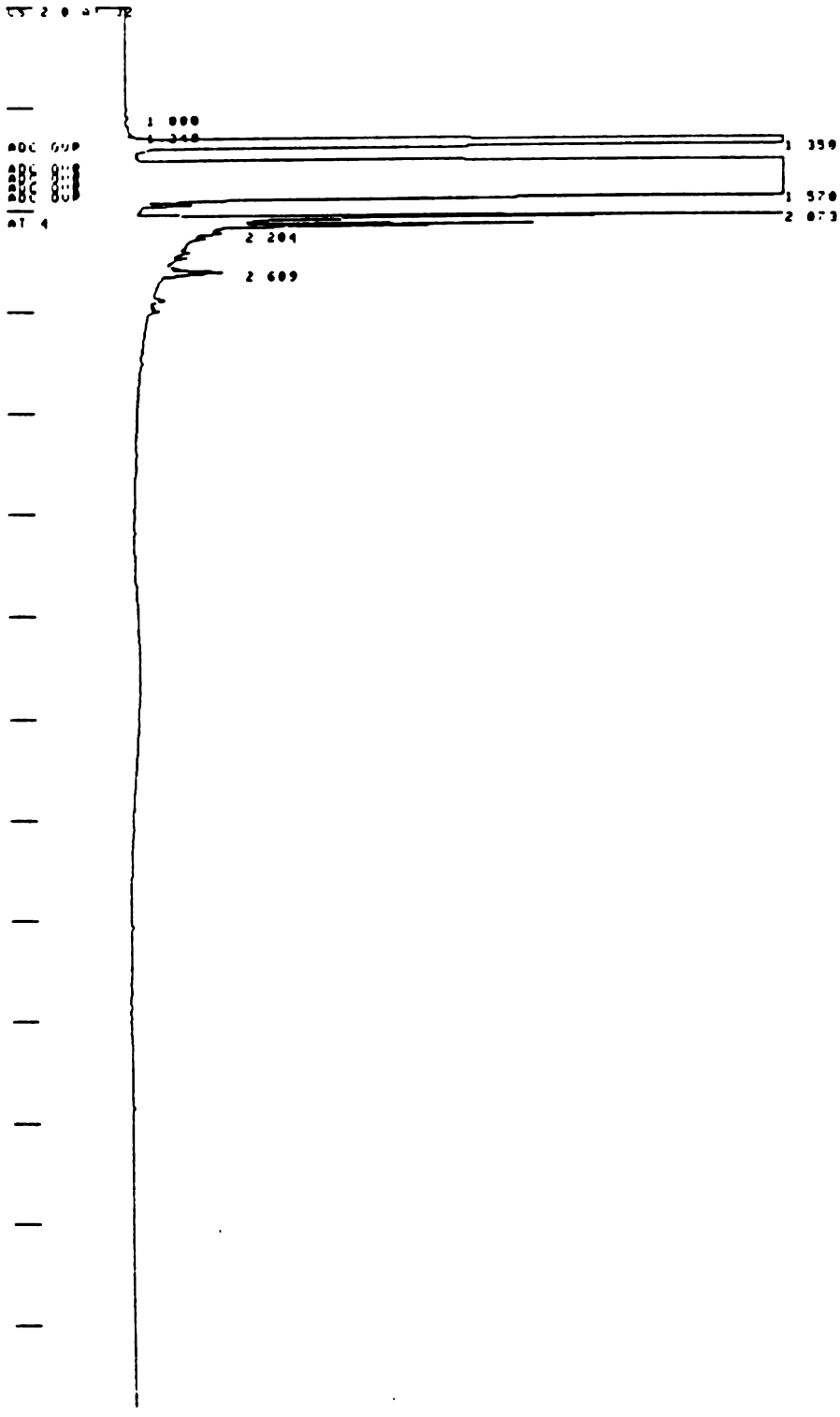


FIG. 9. Evaporation studies. Capillary GC plots of CL02: (a) unevaporated; (b) 50% evaporated; (c) 100% evaporated.



(b)

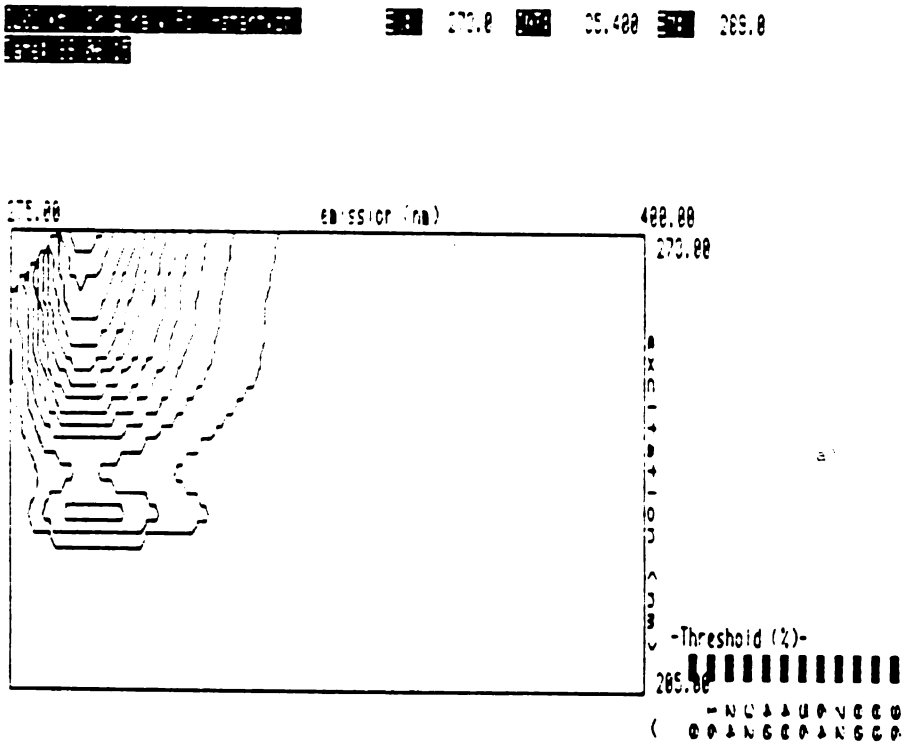
FIG. 9. Continued.



(c)

FIG. 9. Continued.

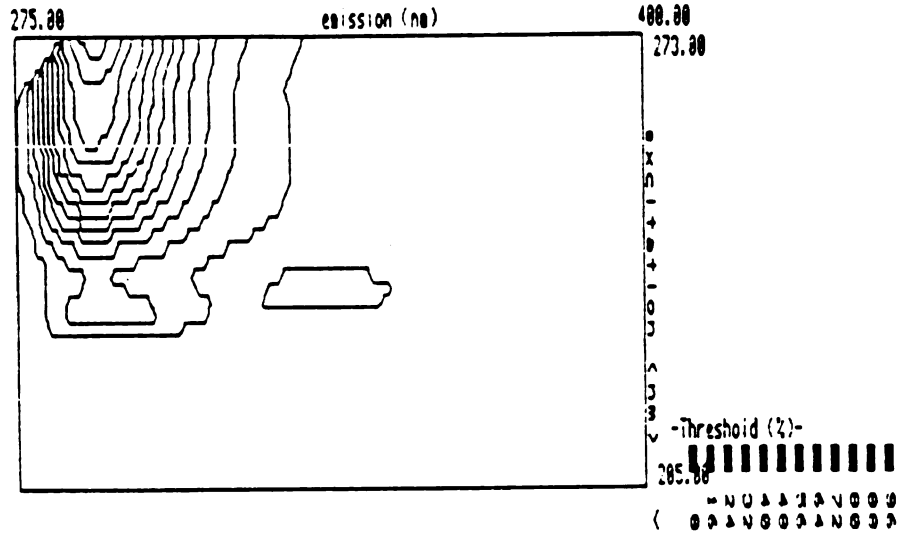
(a)



(a)

FIG. 10. Evaporation studies. 3-D fluorescence plots of Sample LC02: (a) unevaporated; (b) 50% evaporated; (c) 100% evaporated.

(b)



(c)

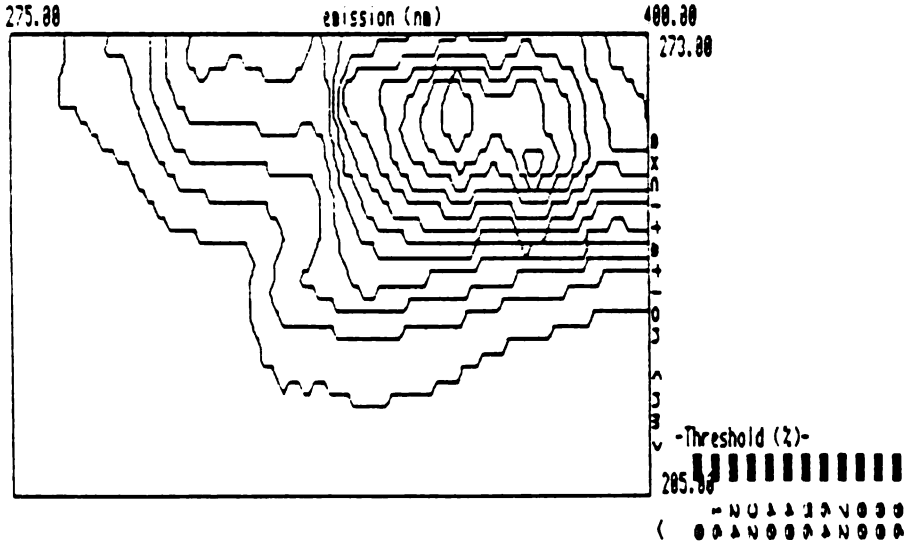


FIG. 10. Continued.

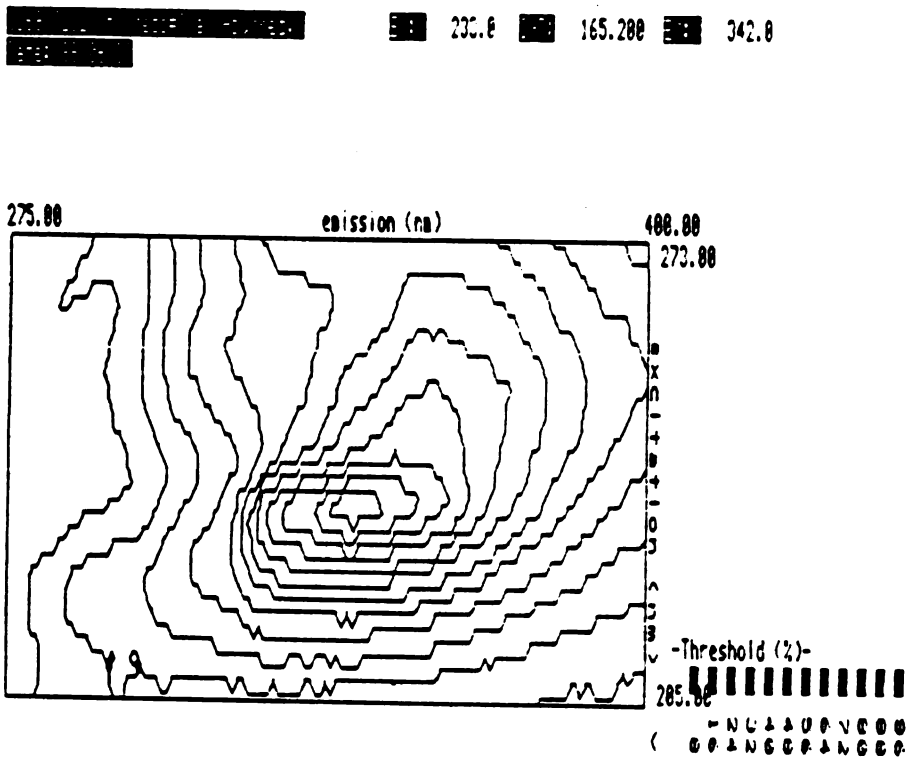


FIG. 11. 3-D fluorescence contour plot of Sample CL02 after combustion.

PART V. SUMMARY

Twenty-two mid-range petroleum-based products, including charcoal lighters, paint thinners, and synthetic solvents, were studied by capillary GC and 3-D fluorescence. It was found that 3-D fluorescence is far better at discriminating among similar products than was GC, which could only put the products into broad classes. When partially or totally evaporated, the 3-D fluorescence plots were altered enough that they could not be matched with those of neat samples. A similar situation exists when they are burned. Also, when burned even under controlled conditions, these compounds did not yield consistent fluorescence patterns. A blind test on neat samples showed that 3-D fluorescence can be a reliable technique for determining whether or not two neat samples were of the same brand.

This study is a continuation of Dr. Siegel's serial studies of 3-D fluorescence, it is also a preliminary study on mid-range petroleum-based products as potential accelerants by the means of both gas chromatography and 3-D fluorescence. It has its limitations like all this kind of studies. First, though the twenty-two samples were the all that the author could get at that time, he is still not very confident about the representativity in terms of the whole population of mid-range petroleum products. Second, no doubt the neat sample grouping has its theoretical meanings, however, pure liquid samples are not

frequently encountered in practical arson cases. Third, 3-D fluorescence approach usually needs larger sample amount for measurement than gas chromatography does, this could be limited its applications in some arson cases.

In spite of the limitations mentioned above, this study does have a few important implications in its technical and legal aspects. First, in accelerant identification of arson cases, 3-D fluorescence has some advantages in terms of either sensitivity or discriminating power comparing to GC. Therefore, it is worthwhile to add this technique as a routine approach in crime laboratories to get complementary information if the financial condition permits to do so. Second, because large percent of organic substances have the property to emit fluorescence under certain conditions, this study could enhance the status of 3-D fluorescence not only in arson analysis, but also in other aspects of forensic sciences as well as in instrumental analysis at large. Third, it is particular interesting that 3-D fluorescence can identify small amount of components under the condition of the existence of other large amount of strong fluorescent substances, like the situation of distinguishing Sample A and B in blend test of this study. Fourth, from the legal aspect, even the proving of the existence (if it is not possible to identify the sample) of an accelerant is helpful to determine the nature of the fire, accordingly, helpful to the process of further police investigation and court prosecution.

REFERENCES

[1] Benett, G. D., Journal of Criminal Law, Criminology and Police Science, Vol. 49, 1968, pp. 172-177.

[2] Horn, J., Journal of Individual Psychology, Vol. 31, 1976, pp. 205-210.

[3] Robison, M. M., and Wagner, P. E., Fire Technology, Vol. 8, No. 4, Nov. 1972, pp.278-290.

[4] Boudreau, J. F., "Arson and Arson Investigation: Survey and Assessment, "Washington, D. C., Government Printing Office, 1977, p.1-5.

[5] Inciardi, J. A., "The Adult Firesetter: A Topology," Criminology: An Interdisciplinary Journal, Vol. 8, August 1970, pp. 145-156.

[6] Inciardi, J. A., "Reflections On Crime," New York: Holt, Rinhart and Winston, 1978, pp. 127-128.

[7] Ferrall, R. T., "Arson Information: Who What Where," Law Enforcement Bulletin, May, 1981.

[8] DeForest, P. R., and Lee, H., "Forensic Science", 1983, McGraw-Hill, New York.

[9] Nicol, and Joseph, D., Fire Eng., Vol. 114, 1961, p. 550.

[10] See [42].

[11] Midkiff, C. R. "GC determination of Traces of Accelerant in Physical Evidence," Journal of the Association of Official Analytical Chemists, Vol. 55, No. 4, 1972, pp. 840-845.

[12] Midkiff, C. R., "Arson and Explosive Investigation", Chapter 6 of "Forensic Science Handbook, Prentice-Hall, Inc. 1982.

[13] Zieba, J., Forensic Science Interna., 1985, Vol. 29, No.3, pp.269.

[14] Zieba, J., Forensic Science Interna., 1986, Vol. 30, No.1, pp.45.

[15] Robert, H., "Gasoline Brand Identification and Individualization of gasoline lots," JFSS, Vol. 29, No. 2, 1989, pp. 91-101.

[16] Zafiriou, O. C., Anal. Chem., 1973, Vol.45, pp. 249.

[17] Garza, M. C. Jr., and Muth, J., Environ. Sci. Technol., 1975, Vol.8, pp. 249.

[18] Dell'Acqua, R. R., Egon, J. A., and Bush, B., Environ. Sci. Technol., 1975, Vol. 9, pp. 38.

[19] Pym, D. G., Ray, J. E., and Whitehead, V. Analy. Chem. 1975, Vol. 47, pp.1617.

[20] Rasmussin, D. V., Anal. Chem., 1976, Vol. 48, pp.1562.

[21] Kawahara, F. K., Environ. Sci. Technol., 1976, Vol. 10, pp. 761.

[22] Goldberg, M. C., and Devonald, D. H., J. Res. U.S. Geol. Sur., 1973, Vol. 1, pp. 709.

[23] Lynch, P. F., and Brown, C. W., Environ. Sci. Technol., 1973, Vol. 7, pp. 1123.

[24] Brown, C. W., and Ahmadjian, M., Environ. Sci. Technol., 1974, Vol. 8, pp. 669.

[25] Brown, C. W., and Lynch, P. F., Anal. Chem., 1976, Vol. 48, pp. 191.

[26] Kawahara, F. K., and Yang, Y. Y., Anal. Chem., 1976, Vol. 48, pp. 651.

[27] Mattson, J. S., and Starks, S. A., Anal. Chem., 1977, Vol. 49, pp. 297.

[28] Kawahara, F. K., J. CHromatogr. Sci. 1972, Vol. 10, pp. 629.

[29] Duewer, D. L., and Shatzki, T. F., Anal. Chem., 1975, Vol.47, pp. 1573.

[30] Ludens, H. R., Prog. Nuci. Eng. Anal. Chem., 1975, Vol. 12, pp. 1.

[31] Fortier, S. H., and Eastwood, D., Anal. Chem., 1978, Vol. 50, pp. 334.

[32] Anbar, M., and Aberth, W. H., Anal. Chem., 1974, Vol.46, pp. 59A.

[33] Shultz, W. W., "Application of High pressure Liquid Chromatography to the Identification of Oil Spills in the Marine Environment", 26th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March, 1975.

[34] Saner W. A., and Fitzgerald II, G. E., Environ. Sci. Technol., 1976, Vol. 10, pp. 893.

[35] Oil Identification Symposium, 27th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, 1976.

[36] Frankerfield, J. W., "Weathering of Oil at Sea", AD 789, 1973.

[37] Miller, J. W., "A Mutilparameter Oil Pollution Source Identification System". EPA-R2-73-221, July, 1973.

[38] Proceedings, Workshop on Pattern Recognition Applied to Oil Identification, Coronado, Calif., November, 1976, IEEE Catalog No. 76, CH 1247-6 C.

[39] Symposium on Oil and Other Organic Pollutants Analysis, 29th Pittsburgh conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, 1978.

[40] Park, B. P., and Kirk, P. L., Microchemical Journal, Vol.6, Jan, 1962, pp.31-38.

[41] Chisum, W. J., "Identification of Arson Accelerant by Gas Chromatographic Patterns Produced by a Digital Log Electrometer", Journal of Forensic Sciences, 1971, Vol. 43, pp.280-291.

[42] Ettling, B. V., and Adams, M. F., Journal of Forensic Science, Vol. 13, No. 1, Jan, 1968, pp. 76-79.

[43] Cain, P. M., "Comparison of Kerosene Using Capillary Column Gas Liquid Chromatography," Journal of Forensic Science Society, Vol. 15, 1975, pp. 301-308.

[44] Dell'Acqua, R., "Identification of Gasoline Contamination of Groundwater by Gas Chromatography," Journal of Chromatography, Vol 128, 1976, pp271-280.

[45] Flanigan, G. A., "Oil Spill 'Fingerprinting' with Gas Chromatography," Research/Development, Sept, 1977, pp. 28-36.

[46] Mann, D. C., "Comparison of Automotive Gasolines Using Capillary Gas Chromatography I: Comparison Methodology," Journal of Forensic Sciences, Vol. 34, July, 1986, pp.606-615.

[47] Sanders, W. N., and Maynard, J. B., "Capillary Gas Chromatographic Method for Determine the Hydrocarbons in Full-Range Motor Gasolines," Anal. Chem. Vol. 40, No. 3, March 1968, pp.527-535.

[48] Mach, M. H., "Gas Chromatography-Mass Spectrometry of Simulated Arson Residue Using Gasoline as an Accelerant," Journal of Forensic Sciences, Vol. 17, 1976, pp. 348-357.

[49] Stone I. C., Lomonte, J. N., "Accelerant Detection in Fire Residues," Journal of Forensic Sciences, Vol. 18, 1977, pp. 78-83.

[50] Clark, H. A., and Jurs, P. C., "Classification of Crude Oil Gas Chromatogram by Pattern Recognition Techniques," Anal. Chem., Vol. 51, No.6, May, 1979, pp. 616-623.

[51] Loscalzo, P. J., and DeForest, P. R., "A Study to Determine the Limit of Detectibility of Gasoline Vapor From Simulated Arson Residues." Journal of Forensic Sciences, Vol. 22, June 1979, pp. 162-167.

[52] Mann, D. C., "Comparison of Automotive Gasolines Using Capillary Gas Chromatography II: Limitations of Automotive Gasoline Comparison In Casework," Journal of Forensic Sciences, Vol. 32, July 1986, pp.616-628.

[53] Saferstein R. and Park S. A., "Application of Dynamic Headspace Analysis to Laboratory and Field Arson Investigations." Journal of Forensic Sciences, Vol. 27, 1982, pp. 484-494.

[54] Russell L. W., "The Concentration and Analysis of Volatile Hydrocarbons in Fire Debris Using Tenax GC," Journal of Forensic Science Society, Vol.21, 1981, pp.317-320.

[55] Twibell J. D., "A Comparison of the Relative Sensitivities of the Adsorption wire and Other Methods for the Selection of Accelerant Residues In Fire Debris," Journal of Forensic Science Society, Vol. 22, 1982, pp. 155-160.

[56] Tontarski, R. E., and Strobel R. A., "Automated Sampling and Computer Assisted Identification of hydrocarbon Accelerant," Journal of Forensic Sciences, Vol. 27, 1982, pp. 710-714.

[57] Andrasko, J., "The Collection and Detection of Accelerant Vapors Using Parous Polymers and Curie Point Pyrolysis Wires." Journal of Forensic Sciences, Vol. 28, 1983, pp. 330-334.

[58] Bentz, A. P., Analytical Chemistry, Vol. 48, No. 6, May, 1976, p. 454.

[59] Gruenfeld, M. and Frank, U., "Prevention Behavior, Control, Cleanup," Oil Spill Conference, May, 1977.

[60] Siegel, J. A., "Solving Crimes with 3-D Fluorescence Spectroscopy," Anal. Chem., Vol. 57, 1985, p.934A.

[61] Kubic, T. A., and Dwyer, J., "Individualization of Automobile Engine Oils I: The Introduction of Variable Separation Synchronous Excitation Fluorescence to Engine Oil Analysis," Journal of Forensic Sciences Vol. 28, No.1, Jan. 1983, pp186-199.

[62] Holand, J. F., Anal. Chem., Vol. 55, 1983, p. 997A.

[63] Griffiths, P. J., Anal. Chem., Vol. 55, 1983, p. 1361A.

[64] Samuelsson, R, DeHaseth, J. A., and Azzaraga, L. V., Anal. Chem., Vol. 52, 1980, p.2215.

[65] Chrestie, W. H., Anal. Chem., Vol. 53, 1980, p.13.

[66] Kubic, T. A., "Individualization of Automobile Engine Oils II: Application of Variable Separation synchronous Excitation Fluorescence to the Analysis of Used Automobile Engine Oils," Journal of Forensic Sciences, Vol. 28, No. 2, April 1983, pp. 345-350.

[67] "Oil Spill Identification by Fluorescence Spectroscopy", Oil Spill Identification System, U.S. Coast Guard Research Center, Groton, CT, June 1977, pp E1-E13.

[68] Thrusto, A. D., "Characterization of Crude and Residual Oils by FS," Environ. Sci. Technol., Vol. 5, Jan. 1971, pp. 64-69.

[69] Smith, H. F., "Identification of Crude Oils by SES," Anal. Chem., Vol. 48, No.3, March 1976, pp.520-524.

[70] Rossi, T. M., and Warner, I. M., "Pattern Recognition of Two-Dimensional Fluorescence Data Using Cross-Correlation Analysis," Applied Spectroscopy, Vol. 39, No.6, 1985, pp.949-959.

[71] Files, L. A., "Gasoline and Crude Oil Fingerprinting Using Constant Energy Synchronous Luminescence Spectrometry," Microchemical Journal, Vol. 35, 1987, pp.305-314.

[72] Siegel, J. A., "Fluorescence of Petroleum Products I. Three Dimensional Fluorescence Plots of Motor Oils and Lubricants," Journal of Forensic Sciences, Vol. 30, No.3, July 1985, pp. 741-759.

[73] Siegel, J. A., "Fluorescence of Petroleum Products II. Three Dimensional Fluorescence Plots of Gasolines," Journal of Forensic Sciences, Vol. 32, No. 1, pp. 72-86.

[74] Siegel, J. A., "Fluorescence of Petroleum Products III. Three Dimensional Fluorescence Plots of Petroleum based Products," Journal of Forensic Seines, Vol. 33, No.6, Nov. 1988, pp. 1405-1414.

[75] Wittkower, R. S., "Identification of Accelerant in Fire Residues by Capillary Column GC," Journal of Forensic Sciences, Vol. 23, March 1978, pp.662-671.

[76] Lucas, D. M., Journal of Forensic Sciences, Vol. 5, No.2, April 1960, pp. 236-247.

[77] Cadman, W., Journal of Forensic Sciences, Vol. 5, No. 3, July 1960, pp. 369-385.