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Chemical Analysis of Aromatics in Diesel Fuels

State of California
AIR RESOURCES BOARD
Research Division

CHEMICAL ANALYSIS OF AROMATICS IN DIESEL FUELS

Final Report
Contract No. A932-125

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ABSTRACT

Diesel engines are major contributors to the emission of toxic substances into the atmosphere. These toxic substances are a vital concern nationwide due to human health and environmental effects. For regulation of exhaust emissions and quality of fuel, improved methods of quantitation and characterization of problem-causing components of diesel fuel are needed.

This program was performed in response to the need for improved chemical analysis of aromatic content in diesel fuel. The analytical techniques used, infrared (IR) analysis and ultraviolet (UV) spectroscopy, are familiar, convenient to run, and readily available. Both methods proved to be fairly rugged in terms of variety of fuels, treatments, and additives of tested materials. The effort included method optimization, correlation to FIA results, and statistical analysis of the quality of measurements possible with the methods.

Results of testing on a large data-base of samples and a round-robin study on the two methods in various laboratories showed repeatability of 0.6 VOL% and reproducibility of 1.7 VOL% in the range of 10% predicted aromatics for the infrared method; with a pooled repeatability of 0.2 WT% ring carbon and reproducibility of 0.8 WT% ring carbon for the UV method for total WT% ring carbon. The UV method also provides values for mono-, di- and tri-ring aromatic species. Both methods are relatively inexpensive and easy to run, and would be amenable to automation.

ACKNOWLEDGEMENTS

Beckman Instruments was very helpful in the program, providing a model DU series 7500 diode array spectrophotometer for the duration of the program, at no charge. Ms. Rose Robledo organized the UV round-robin program and provided invaluable assistance in optimizing the UV method. We would like to thank all of the round-robin participants for their cooperation in running the samples. They included: Nicolet Analytical Instruments, Midac, Perkin-Elmer, Shell Westhollow Research Center, and Pennzoil. Southwest Research staff, including Bill McMahon, Teresa Sauceda, David Herrera, and Mary Gillespie, were also very cooperative in running round robin samples. Dr. Adam Schubert of ARCO was helpful in evaluating the IR method early in the optimization program. LT Industries was very helpful with feasibility studies using the NIR method.

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DISCLAIMER

TABLE OF CONTENTS

LIST OF FIGURES PAGE 44

Figure

LIST OF TABLES

LIST OF APPENDICES

SUMMARY AND CONCLUSIONS

This program, performed in response to the need for improved chemical analysis of aromatic content in diesel fuel, involved optimization of two analytical techniques for the analysis of aromatic content in diesel fuels, one based on infrared spectroscopy, and the other on UV/visible spectroscopy. Both methods are familiar, convenient to run, and readily available. Both methods proved to be fairly rugged in terms of variety of fuels, treatments, and additives of tested materials.

These methods show better repeatability and reproducibility than the Fluorescent Indicator Adsorption (FIA) method, ASTM D-1319, which is currently used in industry. Both methods are inexpensive and quick to run in comparison with other available methods, such as mass spectrometry(MS), supercritical fluid chromatography(SFC), and nuclear magnetic resonance(NMR). Glassware usage is minimal in the two procedures, and each can be run without the necessity for highly trained technical staff. The methods are both based on response factors obtained from a non-empirical method, such as NMR. The methods measure molecular characteristics related to those utilized in NMR measurements, so that they correlate very closely to the weight % ring carbon in fuels. The effort included method optimization, correlation to FIA results, and statistical analysis of the quality of measurements possible with the methods.

Results of testing on a large data-base of samples and a round-robin study on the two methods in various laboratories showed repeatability of 0.6 VOL% and reproducibility of 1.7 VOL% in the range of 10% predicted aromatics for the infrared method; with a pooled repeatability of 0.2 and reproducibility of 1.1 for the UV method for total WT% ring carbon. The UV method also provides values for mono-, di- and tri-ring aromatic species. Both methods are relatively inexpensive and easy to run, and would be amenable to automation.

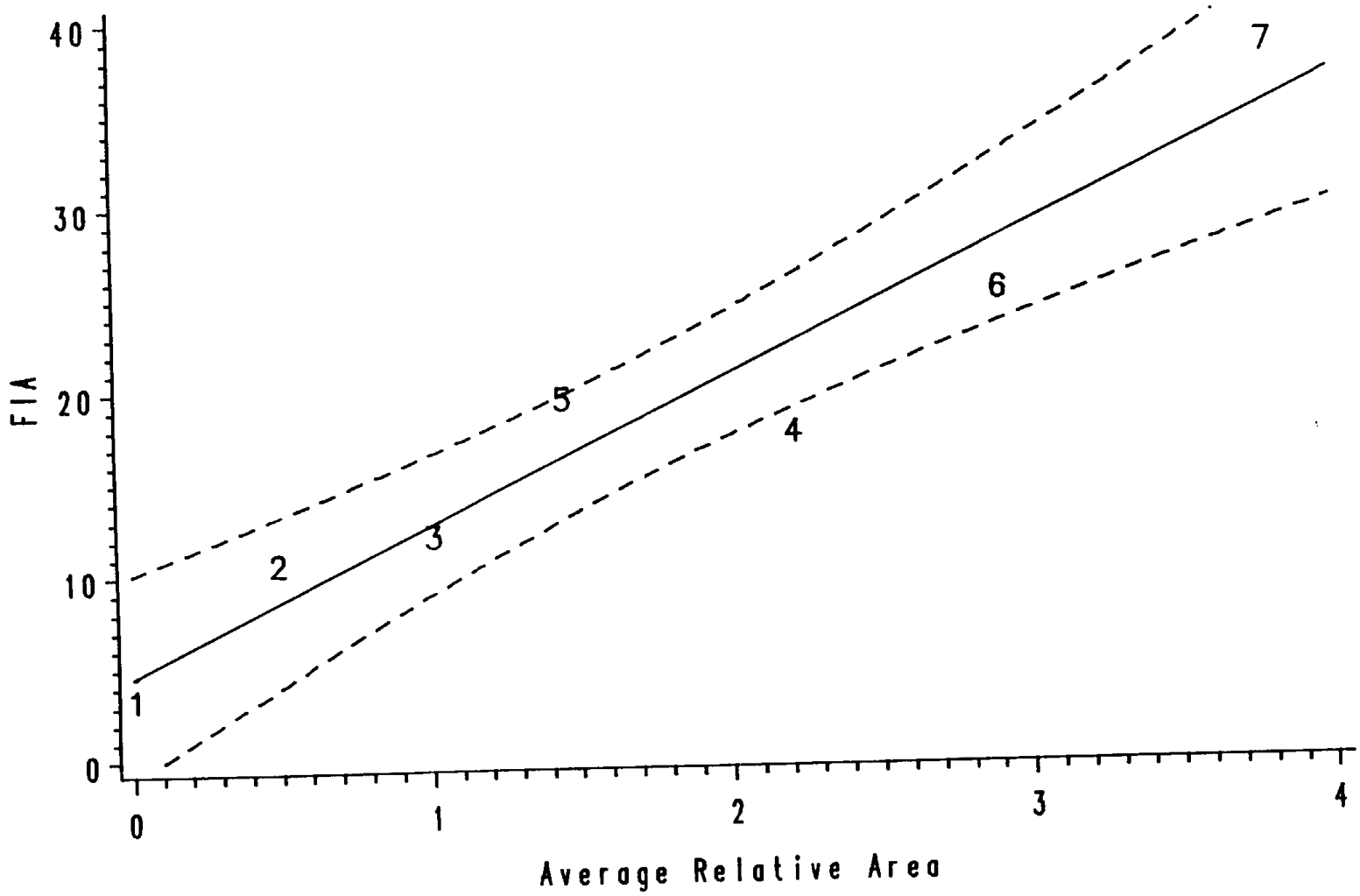
Advantages of the IR method are the lack of sample preparation and the speed of the analysis by FTIR (approximately 3 minutes per sample). The area values measured can be correlated to FIA VOL% data or to ring carbon values. An advantage of the UV method is that it distinguishes ring carbon types: mono-, di-, and tri-ring structures. This information should be valuable in relating to emissions particulates and health concerns. The method also showed very good repeatability and reproducibility in the round robin study. Neither method showed any significant effects from alkyl nitrate type cetane improver.

Correlations of the two methods to FIA values are shown in two plots of the fit of measured values to measured FIA values. For the round-robin data in this program, the equivalent values to a particular FIA value would be given by the following equations:

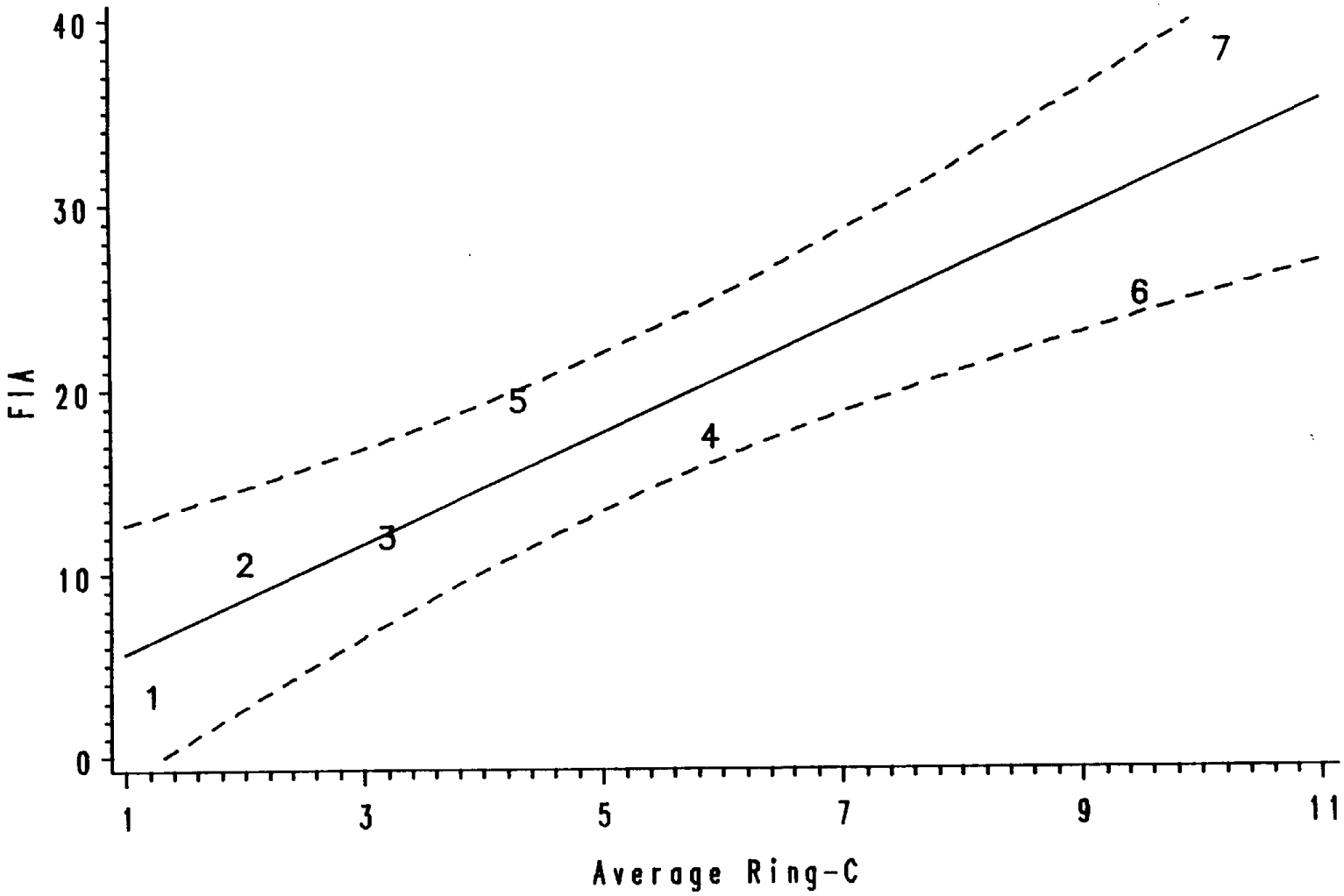
4.57 + IR Relative Area X 8.07 = Predicted Aromatic VOL%

2.67 + UV Total Aromatic X 3.0 = Predicted Aromatic VOL%

IR Method



UV Method



RECOMMENDATIONS

The ultraviolet method would lend itself to a dedicated, low-cost UV instrument designed specifically for aromatics in diesel fuel applications. Further inquiries should be made to the instrument companies to ascertain their interest in developing hardware and software for such an instrument for CARB use. A fixed 0.01 cm cell with a diluter/sipper attachment would allow convenient autosampling.

The infrared (IR) method could be automated with a transmission flow cell device such as that used by Digilab for used oil analysis. Since the samples do not require dilution, this would be a convenient means of sample handling. Duplicate sample runs for each sample would be recommended to prevent cell contamination or bubble effects resulting from the use of a single run.

Near Infrared (NIR) should also be more fully investigated as an option for aromatics analysis. Depending on the quality of the standards which could be assembled to set up the procedure, accuracy equivalent to that achieved with the FTIR method could be possible. If this method is being used for other analyses, such as octane number and oxygenates, it would be convenient to use it for aromatic content of materials as well. An instrument is currently available for octane correlation in the SwRI laboratory, so that such a study is possible.

I. INTRODUCTION

A. SCOPE

In the past, diesel fuel quality has been established through specifications that ensure engine operability and durability. The emission performance of diesel fuel must also be included in the specification requirements to maintain a clean environment. A reduction in the particulate emission profile of diesel fuel has been tied to fuel sulfur and aromatic content.[1] Regulations have been established to limit the content of these components in diesel fuel marketed in California.[2] Sulfur content is relatively easy to measure accurately and thus control; however, the aromatic content of diesel fuel is more difficult to establish, thus hampering regulatory control.

Measurement and regulation of aromatic content in diesel fuels are problem areas due to the lack of a reliable analytical method for quantitation and characterization of aromatics. The method must provide reproducible and non-subjective measurements for use by refineries and by regulatory bodies for monitoring and enforcement of regulations on aromatic content in diesel fuels. Characterization of the aromatic fraction is also necessary for a procedure which will be effective for use in the assessment of health risks, studies of the effects of various classes of aromatics on diesel emissions, and examination of alternative fuels. The ideal method would utilize inexpensive instruments, would be fast, and would not require special operator technique or skill.

The objectives of this program were threefold. First, current methods used to measure aromatic content of diesel fuels were examined and evaluated as far as their accuracy, repeatability, expense, and skill requirements. Second, the most appropriate methods were developed and optimized to provide the best possible analysis of diesels, both for total aromatic content and for characterization of the aromatics. Third, the selected methods were correlated with FIA measurements.

B. CURRENT METHODS

1. FIA

The current method for monitoring and controlling aromatic content of diesel fuel is the fluorescent indicator adsorption (FIA) procedure described in ASTM Method D-1319-88.[3] This method has repeatability of about 1 VOL% and reproducibility of about 2 VOL% around an aromatic content of 10 VOL% in gasolines. The method also states that its scope is limited to petroleum fractions that distill below 600°F (315°C). Most diesel fuels have endpoints that distill above this temperature. The procedure states that narrow boiling petroleum fractions near the 600°F limit "are not eluted properly, and results are erratic."

Reproducibility of aromatic content of diesel fuels measured by the ASTM D-1319 method would therefore be much poorer than that stated above. Most diesel fuels will have end points in the range of 675°F. Repeatability of the method in diesel fuel has been found to be ± 3 VOL% aromatics, reproducibility to ± 6 VOL%.[4] In a CRC program, a diesel fuel in the 10% aromatic range varied from 8.4 to 14.1 VOL% aromatics by the FIA method in well-established laboratories, while a fuel in the 19% range varied from 11.5 to 27.5 VOL% in the laboratories. Clearly, a more precise method is needed to maintain adequate control of diesel fuel aromatic content, but presently, ASTM D-1319 is the only standard available. One aspect of the FIA method which has been examined in relation to diesel aromatic content is the surface area of the silica gel media. Variations in this factor affect diesel aromatic measurements strongly.

The American Society for Testing and Materials (ASTM) has seen the need for an improved method for measuring aromatics in diesel fuel.[5] A round-robin test of four proposed methods was performed to evaluate these options:

1. High Performance Liquid Chromatography using a specially conditioned strong cation exchange column and a dielectric constant detector (HPLC/DCD).
2. Supercritical Fluid Chromatography using a silica column coupled to a flame ionization detector (SFC/FID).
3. Nuclear Magnetic Resonance Spectroscopy examining both carbon-13 and proton spectra (NMR).
4. Open Column Liquid Chromatography following ASTM D-1319 with a heated silica column modification (Heated FIA).

A summary of the average standard deviations for six round-robin samples being tested and the average value for Sample A is given below.

Test Method	Average Standard Deviation (six samples, A - F)	Average Result (sample A)
HPLC/DCD	1.82 VOL%	29.3 VOL%
SFC/FID	1.65 WT%	43.2 WT%
Heated FIA(Activ.)	3.38 VOL%	39.7 VOL%
Heated FIA(Deact.)	3.73 VOL%	39.2 VOL%
Proton NMR	0.90 MOL%	8.8 MOL%
Carbon-13 NMR	1.38 MOL%	26.8 MOL%

It can be seen from the above data that each of the analytical methods produce different values for the aromatic content of sample A of the round-robin. The other samples in the round-robin had similar disparity between results from the several methods. The difference in NMR results and the other methods (which are all chromatographic separations) is expected because the methods detect different chemical phenomena. Carbon-13 NMR detects the fraction of aromatic carbon compared to all carbon in the sample; proton NMR

detects the fraction of aromatic hydrogen compared to all hydrogen in the sample. The chromatographic methods are designed to separate all compounds that have at least one aromatic ring in the structure. Therefore, the chromatographic methods (HPLC/DCD, SFC/FID, and Heated FIA) should produce similar results. Due to differences in column activity and detection methodology, the responses are not equivalent.

The methods selected for the ASTM round-robin represent the two basic approaches for determining the aromatic character of petroleum fractions in the diesel fuel boiling range, chromatographic and spectroscopic. In addition to the chromatographic methods represented by HPLC, SFC, and LC (Heated FIA), gas chromatography is also used for hydrocarbon type determination. This approach is limited to the gasoline boiling range due to inadequate resolution in the higher boiling petroleum fractions such as diesel fuel. Chromatographic separations are dependent on the ability of the separating media to effect a separation. This is an inexact science, particularly in the diesel fuel boiling range. In addition to nuclear magnetic resonance (NMR), other spectroscopic techniques include infrared spectroscopy (IR), mass spectroscopy (MS), and ultraviolet/visible spectrophotometry (UV/VIS). Spectroscopic methods rely on direct measurement of chemical characteristics of the sample and they measure fundamental chemical properties of the sample in question.

2. CHROMATOGRAPHIC METHODS

There are several inherent problems with chromatographic separations in making precise measurements of hydrocarbon type distributions. First, the separating media is difficult to reproduce exactly. This problem causes variations in parallel comparisons of data between labs, and also in series comparisons in the same lab when one tries to reproduce previous results. Another major problem with column activity is the unstable nature of the same column with usage or aging. The separating media will usually deactivate with usage and time and obtaining complete separation between chemical classes is also a source of potential problems. This is a particular problem when trying to separate a material of low relative concentration. To obtain a reliable measure of a given class of compounds, the classes must be completely resolved on the column. If the column is too active, the retention of some of the sample on the column can interfere with accurate results. Problems with column reproducibility in the manufacturing process, and incomplete recovery of retained fractions contribute to difficulties in standardizing a chromatographic procedure to quantitatively determine aromatics in diesel fuel.

In addition to the difficulties in chromatographic separation, due to controlling the activity of the separating media, the detection methods also contribute a source of potential error or bias in the result. The relative response factors between hydrocarbon-types for the given detection system must be known. For the wide range of compound types in a petroleum fraction, this is sometimes difficult to determine. In the HPLC/DCD method in the ASTM round-robin, the dielectric constant detector is a significant advance, as the dielectric constant is nearly uniform across a broad range of compound types covering both saturate and aromatic compounds.[6] The flame ionization detector (FID) response is less uniform across compound types.[7] A direct weight or volume measurement is possible if a preparative scale chromatographic separation is accomplished. Removal of the mobile phase by distillation also introduces error in the final values either due to incomplete removal of the mobile phase or due to loss of light ends of the actual fraction. Preparative scale separations are usually time consuming and not recommended unless further analysis of the separated fractions are required.

3. SPECTROSCOPIC METHODS

Problems in chromatographic methods leave the spectroscopic approaches for consideration. The changing activity of separation media experienced in chromatographic methods is not a problem for spectroscopic techniques. It is true that spectroscopic methods may be subject to minor electronic drift in the instrumentation, but this is held in check by frequent use of standards or internal reference materials. As shown in the most recent results of the ASTM round-robin, the NMR spectroscopic method has the lowest average standard deviation of any of the methods tested. Mass spectrometry, infrared spectroscopy, and ultraviolet spectroscopy are other methods which may be considered for analysis of diesel fuel aromatic character.

A standard method for detailed hydrocarbon type analysis is given in ASTM Method D-2425, "Hydrocarbon Types in Middle Distillates by Mass Spectrometry."[8] This method provides classification of middle distillates into 11 hydrocarbon types. The early work done in analytical mass spectrometry showed that repeatable results could be obtained with mass spectra acquired with 70-eV electron ionization and a fixed magnetic field to separate the ions. With the introduction of bench-top quadruple mass spectrometers, with their fixed analyzing parameters precisely controlled by computer, the way was opened for the development of the necessary inlet systems and software to accomplish hydrocarbon type analyses. The software developed for the modern controlling computers paralleled the requirements shown in ASTM D-2425 for hydrocarbon types in middle distillates, along with other procedures for the MS analysis of hydrocarbon mixtures. Today, the bench-top mass selective detector, coupled to a batch inlet system

with appropriate software, has once again made the analysis of hydrocarbon compound types in petroleum products a practical method yielding results in accordance with ASTM procedures. This method would be more costly than SFC, UV, or IR based analysis.

Infrared spectroscopy is used for analyzing aromatic structure in petroleum fractions. ASTM Method D-4053, "Benzene in Motor Gasoline and Aviation Gasoline by Infrared Spectroscopy," reports reproducibility of 0.18 VOL% for low concentrations of benzene (0-5 VOL%). This method uses the 440 to 690 cm^{-1} region of the spectrum to measure benzene concentration.

Ultraviolet spectroscopy also shows excellent promise for precise measurement of aromatic content of diesel fuels. ASTM Method D-1840, "Naphthalene Hydrocarbons in Aviation Turbine Fuels by Ultraviolet Spectrophotometry," reports reproducibility of 0.11 VOL% for low concentrations of naphthalenes in aviation turbine fuels (0-5 VOL%). A method for measuring one-, two- and three-ring aromatics in fuels and lubricants has been used internally as a characterization tool at SwRI for over ten years.[9] An example of the repeatability of results experienced using this method is illustrated in standard deviations of 0.74, 0.10, and 0.03 WT% for one-, two-, and three-ring aromatics, respectively. With procedure improvements, these repeatability levels can be significantly improved.

Chromatographic methods separate the compounds in a petroleum stream that contain at least one aromatic ring in the structure. The resulting measurement includes the alkyl side chains that may be attached to the aromatic ring structure. The actual aromatic character is therefore not totally divulged. If chromatographic separations of benzene and dodecylbenzene were performed, the results would both be 100% aromatics. This does not disclose important information about the potential combustion performance of these two compounds. The hydrogen-carbon ratio of dodecylbenzene is much higher than that of benzene and improved combustion performance could be expected of the dodecylbenzene with regard to soot or particulate formation.[10] The cetane number of benzene is too low to be measurable while dodecylbenzene has a cetane number of 68, which is well above almost all commercial diesel fuels.[11] If the aromaticity of the two compounds were measured by NMR, IR, or UV, the result would be 100% for benzene and 33% for dodecylbenzene. Clearly, important differences are seen between measuring aromatics by chromatographic methods and measuring aromaticity by spectroscopic methods. Aromaticity provides increased insight into potential performance properties and this connection with performance strongly suggests aromaticity as the better specification parameter.

Spectroscopic methods can aid in assessing the health risk assessment because they directly measure aromaticity, which is more closely related to detrimental health effects in terms of both direct fuel exposure and exposure to exhaust products as compared to aromatics. UV has long been a standard of the U.S. Food and Drug Administration for determining the safety of mineral oils in food and medicines.[12] UV absorbance has also been related to the carcinogenicity of petroleum products.[13]

C. METHODS SELECTED

Eight analytical method requirements have been identified during the initiation of this program. In addition to the main objective of an improved method for measuring total aromatics in diesel fuels, other requirements are:

1. Aromatic type distribution
2. Aid in health risk assessments
3. In-situ or on-site method for refiners
4. Low cost
5. No specialized skills required
6. Applicability to low aromatic diesel fuels
7. Acceptable reproducibility and repeatability
8. Correlation with current FIA standard

Based on the above evaluation of available options, the methods of choice are Infrared and Ultraviolet Spectroscopy. The approach to the analytical problem of measuring aromatic content in diesel fuel consists of two separate analytical procedures. Both IR and UV can provide an improved method for measuring the total aromatics content in diesel fuels. The infrared method will quickly and accurately measure total aromatic content in diesel fuel, while the UV method has the added benefit of providing aromatic ring-type distribution.

Both of these procedures have been used in our facility for several years for measurements of aromatic content on diesel fuels, but have not been widely published or used outside our laboratories. The instrumentation is less costly and more widely available than NMR, MS, or SFC. The IR and UV methods are amenable to in-situ or on-site measurements for use by petroleum refiners in daily production and ARB Staff compliance monitoring. No highly specialized skills or costly equipment will be necessary. IR and UV have excellent precision at low aromatic concentration levels and have reproducibility and repeatability levels that are significant improvements over the current FIA standard. While these methods measure a related but different parameter than FIA, a correlation has been developed. This correlation accounts for the difference in aromatics VS aromaticity in diesel fuels. The aromaticity value measured by IR or UV will be offset from the FIA aromatics value related to the alkyl chain composition of diesel fuel aromatics.

II. PROJECT INITIATION

A. PROJECT PLANNING

A kick-off meeting was held in California on May 24, 1990 to start the Aromatics in Diesel Fuel program. The Air Resources Board group included Dr. Robert Grant, John Courtis, and Paul Rieger, of the Research Division, the Stationary Source Division, and the MLD, respectively. Also present from the compliance group were Tom Wong, Dickman Lum, and Fred Schmidt.

Noteworthy points made during the meeting included specific areas to address during the program and questions to consider while optimizing the methods. These points included addressing errors which could be introduced into the method with vastly differing sizes of substituted aliphatic groups on aromatic structures, with the presence of fuel additives such as cetane improvers or pour point depressants, or with very different densities and refractive indices in fuels. Surface area of the silica gels used in all FIA procedures for the program should be investigated, as ARCO has found this to affect the procedure much more in diesels than in gasolines.

Whether one correlation with FIA and other methods work for all types of aromatics, or whether additional correlations will be required for the case of light cycle oils, highly paraffinic oils or other unusual aromatic compositions will be determined. As a result, samples used in the program include blendstocks from hydrotreaters or hydrosulfation, final blends, and components for blending, as well as several alternative fuels.

The compliance group expressed interest in methods which lend themselves to mobile operation. Because they operate a Greyhound bus lab which checks refineries for compliance with the regulatory tests in effect, they are concerned that the methods be rugged and unaffected by temperature changes in the lab, and with quick enough turn around to run 60 samples in an 8-hr shift if possible. The major requirements for the method include repeatability, reproducibility, and equivalence to the FIA method. The method will serve as a replacement method for FIA, to be used in the regulatory language of the Board, with an equivalent aromatic content by that method to 10% aromatics by FIA.

B. SAMPLE SIZE CONSIDERATIONS

The SwRI statistics group recommended the numbers of samples required for different parts of the program in order to establish repeatability and reproducibility over the range of interest for the two methods and to establish their correlation with FIA results on the samples. The range of concentrations to be covered is 7% to at least 35% aromatics. The following information was formulated for the program.

One objective of the program is to conduct an interlaboratory test program on up to ten different fuel samples and to measure the repeatability and reproducibility of the results. Following ASTM Standard E-691-87, the sample sizes necessary to obtain reasonable estimates of repeatability and reproducibility precision are as follows:

i) Under no circumstances should the final statement of precision of a test method be based on acceptable test results for each sample from fewer than six laboratories.

ii) It is recommended that six or more fuel samples be included in the study. This would increase to seven if only the minimum number of labs is utilized. With the targeted ten samples this goal is easily achievable.

iii) The number of test results on each fuel sample in each laboratory can be a small number given the above restrictions on number of labs and number of fuel samples. The minimum number should normally be three for a chemical test but may be as small as two if there is little danger that questionable test results will be obtained.

The above sample sizes for laboratories, fuel samples, and test results are common in many interlaboratory studies. Their basis is well explained in the referenced standard. One possible question is whether anything is gained by increasing the sample sizes given above. The answer is that the information on the variability increases slowly beyond these minimums. Enough labs and samples are necessary to obtain some precision in the precision estimates. For example, analyzing the data on a single sample with six labs and three test results per lab would allow five degrees of freedom for the between-lab variation estimate and 12 degrees of freedom for the within-lab variation estimate.

The total number of samples required for the program was not specified, due to the requirements for inclusion of several sources of blendstock, hydrotreated samples, paraffinic oils, etc., but each sample type should be included at several aromatic contents, ranging from the high to the low concentrations of interest. Looking at specific fuel types only at high, low, or medium concentration ranges could give biased correlation data or poor precision across the range. Using this information, plans were made to analyze 20 to 30 samples during the program, with at least 4 or 5 differing aromatic concentrations for each of 4 to 5 sample types. Each of these samples was analyzed by each of the three methods, UV, IR, and FIA, in order to provide correlation data.

C. SAMPLE ACQUISITION

Samples collected for the program include ASTM and other check fuels with FIA data from a variety of laboratories, a small selection of field samples, and samples from a WESPA SFC round-robin program. Pure materials for calibration of the IR and UV methods for WT% ring carbon response factors have also been included.

Diesel fuel samples from the Coordinating Research Council (CRC) Project V1 on diesel fuel effects on exhaust emissions were obtained from the CRC project manager. These samples include a wide range of aromatic contents, from 11.1 to 46.9 by FIA.[1] The samples also provide a great deal of information, including NMR and mass spectroscopic data, which aided in the optimization of the two selected methods.

A group of diesel fuel samples was obtained from the Canadian Combustion Research Laboratory that relate to the SAE paper Number 872142, "Evaluation of a New Chromatographic Method for Aromatics in Diesel Fuels." These samples include an unusually wide range of aromatic contents, from 20.6 to 75.0 by FIA.[2] The samples also have a great deal of information available including NMR and supercritical fluid data.

Diesel fuel samples with a good selection of low aromatic content materials were obtained from the California Air Resources Board. Nine additional middle distillate samples of known processing and crude history were also obtained for use in the project. These samples were collected from refineries across the country to represent a range of processing and crude types used in the U.S. They had been previously characterized by FIA and have a range of 10 to 25 VOL% aromatics.

A total of 55 samples was gathered from various sources, including the Canadian study, the CRC study, a round-robin for aromatics, a group of refinery middle distillates, and CARB provided samples. Each of these selected samples has some sort of data base of previously collected data. We have access to the data for each group except the CARB provided samples. A summary of the selected samples is presented in **Table 1** and shows the sample number designation, crude source, refinery processing history, and the FIA aromatics content from the literature or lab.

TABLE 1. CARB SAMPLE DESCRIPTIONS

Sample	Description
Mineral Oil	A pharmacy grade mineral oil
NEG 794,796,797	ASTM Check fuels, #2 Diesel Fuel Oil
Field A - F	Field samples of diesel with varying FIA based aromatic concentrations
CRC 1 - 9	Blended fuels with varying composition
WX 1 - 7	Round-robin fuels from Aromatics in Diesel Fuel Method Study
CAN A - V	Diesel fuels with wide range of boiling point distributions and different concentrations of aromatics, - Canadian Combustion Research Labs.
CARB 1 - 12	Diesel fuel samples from the Air Resources Board
FL-0416-F	West coast straightrun distillate from naphthenic crude; caustic & clay treated.
FL-0422-F	West coast heavy crude straightrun & hydrocracker blend; antistatic additive.
FL-0429-F	California & Alaska north slope heavy crudes plus coked heavy crude; hydrotreated; antioxidant.
FL-0436-F	Straightrun mixture of Texas & imported crudes, mild hydrotreatment to reduce sulfur.
FL-0464-F	Texas plus some naphthenic crude; salt drying and clay treatments.
FL-0467-F	Hydrocracker distillate from Alaska north slope crude oil.
FL-0468-F	Straightrun distillate from South Texas; no other treatment.
FL-0470-F	Straightrun distillate from Texas and imported crudes; hydrotreated for sulfur reduction.
FL-0502-F	Highly refined east coast distillate.

III. INFRARED METHOD OPTIMIZATION

A. THEORY OF METHOD

For total aromatic content, an infrared method has been described which uses absorbance in the region between 1650 and 1550 wavenumbers to quantitate aromatic content. A large peak at 1600cm^{-1} is due to C=C vibrations, according to Bellamy[13], and in this region, the absorption bands are very little affected by the substitution pattern. Olefins also have an absorption band also due to C=C vibrations, which can occur at 1680-1620cm^{-1}.

The infrared method requires no sample preparation and is effective with dark samples. In the original method, the sample was analyzed in a 0.05 mm NaCl or KBr transmission cell, versus air if run on a dual beam instrument. The initial procedure called for running three solvent blanks, a series of up to ten fuels, then a final solvent blank. The cell is rinsed with hexane or heptane to prevent sample buildup on the salt plates.

The calculation was originally based on a triangulation method of area estimation. The method gave both olefin and aromatic areas using the following equations:

1) Olefin content = 1/2 (B2 x H2)
2) Aromatic content = 1/2 (B1 x H1) + 1/2 (B3 x H1) - Olefin content

Where B1 = width of left baseline to aromatic peak center
B2 = width of left baseline to olefin peak center
B3 = width of left baseline to right baseline
H1 = aromatic peak height
H2 = olefin peak height

Optimization of the method included hardware upgrade to FTIR instrumentation, which may use computer programs to simplify the calculation, and a change to actual area measurements rather than the triangulation approximation.

B. OPTIMIZATION OF METHOD

1. OPTIMIZATION OF HARDWARE

The original method ran on a Perkin-Elmer Model 599B dispersive, dual beam Infrared Spectrophotometer with a work station capable of performing the calculations above. Optimization of the method involved the following:

1. Upgrading the current method to run on a small FTIR.
2. Modification of the calculations to use actual area under the peak for calculations rather than the triangulation method.
3. Modification of the analysis program to a PC compatible program capable of identifying and reporting data in a simple format.
4. Writing a laboratory procedure containing all necessary operating specifications and safety information to obtain good repeatable data in any laboratory.

The instrument used for initial development of the IR method was a Nicolet 8210 analyzer, equipped with a built-in horizontal attenuated total reflectance (ATR) sample unit accessible without opening any sample compartment. The unit utilizes a crystal set horizontally in a trough configuration allowing a sample to be poured on, analyzed, then wiped off. The sample contact area is the surface of the crystal. An infrared beam enters the crystal at an angle and makes numerous passes through the crystal, reflecting each time it encounters a surface. During each of the reflections, the beam penetrates a fraction of a wavelength beyond the reflecting surface, losing energy at wavelengths where the material absorbs. Similar units are available as add-on accessories for various infrared systems from Spectra-Tech for around $2500. Called Contact samplers, they are routinely used as fast, simple and reproducible means of analyzing films, powders, pastes, and liquids. Early investigation also involved the use of an ordinary short pathlength transmission cell to check for any problems or advantages that might occur.

The draft procedure detailed in **Appendix B** was written into a simple macro for the Nicolet ATR system, so that operator calculations are not necessary and plots may be produced as desired for each analysis. Any computer-driven FTIR system could easily handle this type of programming. A large selection of the program samples was analyzed in replicate using this simple method to check for consistency of results.

2. OPTIMIZATION OF PROCEDURE

Initial work on the IR method optimization involved working with ASTM NEG check fuel samples which had interlaboratory results on FIA and other diesel specification tests. When the area between 1683 and 1536cm^{-1} was integrated, olefin content was added to aromatic content. The approach to removing this area from the integrated area was to integrate the area from 1649 to 1627cm^{-1} separately, then subtract that area from the total. This is similar to the approach used in the triangulated calculation of the original method. Additional work in optimizing the infrared method involved analysis of a variety of diesel fuels obtained in the field using both ATR and transmission sample cells. Further work in optimizing the infrared method involved analysis of diesel fuels obtained from the CRC program mentioned earlier, the round-robin samples used by Adam Schubert at ARCO in his study of the supercritical fluid procedure, the Canadian Combustion Research Laboratory, and CARB for comparison of the various test results to FTIR area.

The sample area was modified to approximately 1650 to 1555 wavenumbers, with the olefin area between 1650 and 1635 wavenumbers. These measurements were compared with available data on the samples. Densities were measured for the samples and pure materials were measured for comparison purposes. Development work for each set of samples is outlined below. A round-robin was performed to gain information on repeatability and reproducibility parameters.

Check Fuels - Initial work on the IR method optimization involved working with ASTM NEG check fuel samples that had interlaboratory results on FIA and other diesel specification tests. **Figure 1** shows one of these spectra, the sample NEG796, where the aromatic band at 1600cm^{-1} is apparent. If the area between 1683 and 1536cm^{-1} was integrated, olefin content was included with aromatic content. The approach to removing this area from the integrated area was to integrate the area from 1649 to 1627cm^{-1} separately, then subtract that area from the total. This is similar to the approach used in the triangulated calculation of the original method. **Table 2** shows results for the original check fuels which were used in method optimization.

TABLE 2. CHECK FUEL DATA

SAMPLE NAME	AROMATICS BY FIA	TOTAL AREA	OLEFIN AREA	AROMATIC AREA	BASELINE COR. AREA
NEG794	35.2	3.1038	0.0844	3.0194	1.9557
NEG797	37.9	2.7291	0.0046	2.7245	1.6608
NEG796	33.0	2.9941	0.1570	2.8371	1.7734
50%796	15.5	1.7739	0.0800	1.6939	0.6302
25%796	7.3	1.2672	0.0420	1.2252	0.1615
KEROSENE	3.2	1.0637	0.0000	1.0637	0.0000

Field Samples - Additional work in optimizing the infrared method involved analysis of a variety of diesel fuels obtained in the field. The samples were analyzed according to the procedure above, with integration of total area under the total aromatic and olefin region followed by subtraction of the olefinic band. **Table 3** shows results for the fuels included, with FIA data where it is complete. The samples were run in two FTIR instruments, one the Nicolet 5DXC and one the Digilab FTS-40, in an ordinary short pathlength transmission cell for correlation between the horizontal ATR and transmission data over the same region. **Figure 2** shows a correlation plot between the data shown and the FIA data obtained in our lab for the samples.

TABLE 3. FIELD SAMPLE DATA

Sample ID	Total area	Olefin area	Aromatic area	Aromatic FIA	Olefin FIA
Kerosene	0.0906	0.0014	0.0892	3.2	1.4
Mobil 9014	2.0882	0.0350	2.0532	38.3	
Mobil 9015	1.2605	0.1430	1.1175	34.4	
Field A	1.5513	0.0427	1.5086	32.3	2.3
Field B	0.9652	0.0230	0.9422	23.9	2.8
Field C	1.9271	0.0570	1.8701	34.8	3.9
Field D	1.4283	0.1132	1.3151	35.9	7.2
Field E	1.1789	0.0063	1.1726	29.2	4.9
Field F	1.9786	0.0418	1.9368	41.3	5.8

CRC and WX Samples - Further work in optimizing the infrared method involved analysis of a variety of diesel fuels obtained from the CRC program mentioned earlier and the round-robin samples used by Adam Schubert at ARCO in his study of the supercritical fluid procedure. The samples were analyzed by integration of total area under the total aromatic and olefin region followed by subtraction of the olefinic band. The total integration area selected was that between 1650 and 1555 wavenumbers, with the olefin area between 1650 and 1635 wavenumbers. The Digilab FTS-40 model instrument was run with an ordinary short pathlength transmission cell (0.06 mm, KBr windows) for correlation between the horizontal ATR and transmission data over the same region.

Table 4 shows results for the analyses of these samples, with FIA, SFC and available CRC information.[2] **Figures 3 through 7** show correlation plots between the data shown and FIA, NMR, MS, and SFC data for the samples. The best correlation is with the NMR(C13) data. **Table 5** shows results for samples run in a transmission cell.

TABLE 4. CRC and WX SAMPLE DATA

Sample ID	(ATR crystal) Aromatic area	Aromatic FIA	Aromatic MS	Aromatic SFC	Aromatic NMR(C-13)
Kerosene	0.0892	3.2			
Mineral Oil	0.0280	-			
NEG 794	2.0099	35.2			
NEG 796	1.7143	33.0			
CRC1	0.7224	16.6	16.1		11
CRC2	3.1090	43.9	45.1		28
CRC3	3.0984	46.9	43.2		27
CRC4	0.9008	19.0	16.0		9
CRC6	1.3366	33.5	25.7		13
CRC8	0.3098	11.1	9.0		6
CRC9	2.2403	42.9	41.1		23
WX1	0.7304	26.02	25.62	26.35	
WX2	0.0805	2.22	1.79	2.09	
WX3	0.4787	20.42	19.81	20.34	
WX4	0.1957	8.40	6.22	7.65	
WX5	0.4966	15.23	12.22	14.29	
WX6	0.9149	22.60	22.47	24.81	
WX7	0.6800	21.03	19.19	21.39	

TABLE 5. INITIAL FTIR TRANSMISSION DATA

Sample ID	(Transmission cell) Aromatic area	Aromatic FIA	Aromatic MS	Aromatic NMR(C-13)
Mineral Oil	-0.1480			
NEG 794	5.246	35.2		
NEG 796	4.127	33.0		
CRC4	2.112	19.0	16.0	9
CRC6	3.051	33.5	25.7	13
CRC8	0.833	11.1	9.0	6
CRC9	5.415	42.9	41.1	23

The first draft of the IR procedure, included as **Appendix B**, was forwarded to Adam Schubert of ARCO and Jim Hatchell of Ultramar to test samples used for Adam Schubert's round-robin. The data provided by Adam Schubert's lab is also included in the **Appendix B**. The calculation step was not accurate at this point in the study, but FTIR area versus aromatic concentration shows a linear relationship.

Canadian Samples - An additional group of analyses used in optimizing the infrared method involved a variety of diesel fuels obtained from the Canadian Combustion Research Laboratory. **Figures 8 through 13** show plots of a few of the Canadian samples. The samples were analyzed according to the procedure detailed in **Appendix B**, with integration of total area under the total aromatic and olefin region followed by subtraction of the olefinic band. The total integration area was between 1650 and 1555 wavenumbers, with the olefin area between 1650 and 1625 wavenumbers. **Table 6** shows results for the Canadian analysis group, with FIA, NMR, and SFC data where it is available. **Figures 14 through 17** show correlation plots between the FTIR area data shown and FIA, NMR, and SFC data for the samples, with the best correlation with the UV aromatic data.

TABLE 6. CANADIAN SAMPLE DATA
FIA and other data with IR

Sample ID	(ATR crystal) Aromatic area	Aromatic FIA	Aromatic SFC	Aromatic UV(total)	Aromatic NMR(H)
A	2.2105	35.0	40.3	18.1	28.8
B	1.3547	28.9	30.7	11.4	19.1
C	1.9013	41.8	34.5	12.6	20.9
D	2.0579	46.7	37.1	10.9	24.1
E	2.2209	37.0	42.9	19.6	29.8
F	2.0295	33.3	39.1	12.9	27.2
G	1.1675	25.0	30.4	12.5	21.4
H	2.6929	39.1	46.8	23.6	33.5
I	-.-	63.9	55.2	21.3	35.1
J	1.7941	44.7	46.4	17.6	26.2
K	-.-	74.2	80.8	49.5	59.9
L	-.-	20.6	23.8	7.2	22.4
M	1.0579	24.1	28.4	11.8	18.6
N	-.-	44.9	50.2	22.6	25.1
O	2.8513	43.7	49.5	21.2	33.1
P	2.9896	44.2	51.7	22.9	33.7
Q	5.3371	64.0	69.6	35.3	47.2
R	6.8991	75.0	79.0	41.6	51.9
S	1.5021	33.3	37.6	11.8	14.7
T	-.-	33.0	37.7	14.7	14.7
U	0.8783	-.-	-.-	7.9	-.-
V	1.2245	-.-	-.-	11.8	-.-

CARB Samples - **Table 7** shows FIA, density, and FTIR data for the CARB samples. A correlation graph for the FIA versus FTIR data for these samples is included as **Figure 18**.

TABLE 7. CARB SAMPLE DATA

Sample	Total	Olefin	Aromatic	FIA aromatics		Density
CARB 1	0.2011	0	0.2011	7.1,	9.8	0.8382
CARB 2	0.0045	0	0.0045	2.0,	2.2	0.8304
CARB 3	0.2589	0	0.2589	8.7,	9.4	0.8389
CARB 4	0.7993	0	0.7993	24.1,	24.3	0.8469
CARB 5	0.2349	0.0053	0.2296	8.8,	8.2	0.8372
CARB 6	1.5499	0.5990	0.9509	29.0,	27.1	0.8499
CARB 7	0.0030	0.0006	0.0024	1.8,	1.4	0.7986
CARB 8	0.7903	0.0329	0.7574	16.4,	16.2	0.8246
CARB 9	0.5854	0	0.5854	20.0,	18.2	0.8398
CARB 10	0.7543	0.0145	0.7398	16.0,	16.7	0.8247
CARB 11	0.0000	0	0	1.7,	1.5	0.7998
CARB 12	0.9052	0	0.9052	26.1,	25.7	0.8367

Pure Material Samples - A selection of pure compounds was diluted to 10 or 20 WT% aromatic content in kerosene for analysis. Each sample was analyzed using an ATR crystal with integration of total area under the total aromatic and olefin region followed by subtraction of the olefinic band. The total integration area was between 1650 and 1555 wavenumbers, with the olefin area between 1650 and 1625 wavenumbers.

The WT% ring carbon for each of these mixtures has been calculated, with data shown in **Table 8**. A comparison of FTIR area for each of these nominal 10% aromatic mixtures with the amount of actual ring carbon is given in **Figure 19**. The method definitely correlates to the ring carbon content better than to the total aromatic content, as shown by the distinct relationship here. This correlation ties in with our previous data showing better correlation to NMR data than to chromatographic data for sample groups.

TABLE 8. PURE MATERIALS DATA

Sample Name	FTIR AREA	% Ring Carbon
1-Phenylheptane	0.4376	6.429
SCL Butylbenzene	0.5186	5.809
n-Tetradecylbenzene	0.3010	2.834
Dodecylbenzene	0.2739	3.162
Heptadecylbenzene	0.2604	2.563
i-Butylbenzene	0.4612	5.826
Xylenes	0.8872	7.826
n-Butylbenzene	0.5164	5.812
Dodecylbenzene	0.3280	3.162
Tridecylbenzene	0.3010	2.995
n-Nonylbenzene	0.4030	3.817
Ethylbenzene	0.5419	6.792
n-Hexylbenzene	0.4608	4.820
1-Methylnapthalene	0.7280	9.007
1,4-Dimethylnapthalene	0.7669	8.197

Available samples have been measured for density and analyzed using both transmission and ATR methods in order to ascertain the effects of varied sample density on the ATR method with respect to FIA and transmission data. **Figure 20** shows the correlation between ATR and transmission cell for FTIR work. The variation in density correlates fairly closely with aromatic content in the wide range of samples we have examined. There does not appear to be an observable density effect to bias ATR versus transmission data. **Table 9** gives FIA and density values for the samples, with the regression information on the correlation. A graph of this data is shown in **Figure 21**.

Cetane improver was added in large quantity, 0.30WT%, to one of the CRC samples. The resulting spectra are shown in **Figures 22 and 23**. The cetane improver is almost on top of the olefin band, but only affects the aromatic area to less than 3% area even at high levels.

The sample contained 2 VOL% olefins by FIA analysis.

TABLE 9. DENSITY DATA

SAMPLE	FIA	DENSITY	SAMPLE	FIA	DENSITY
CRC 1	16.6	0.8088	CAN A	35.0	0.8507
CRC 2	43.9	0.8626	CAN B	28.9	0.8488
CRC 3	46.9	0.8797	CAN C	41.8	0.8729
CRC 5	33.5	0.8517	CAN D	46.7	0.8807
CRC 6	33.5	0.8509	CAN E	37.0	0.8528
CRC 7	33.5	0.8513	CAN F	33.3	0.8491
CRC 8	11.1	0.8253	CAN G	25.0	0.8249
CRC 9	42.9	0.8631	CAN H	39.1	0.8536
CARB1	7.1	0.8382	CAN J	44.7	0.8727
CARB2	2.0	0.8304	CAN M	24.1	0.8388
CARB3	8.7	0.8389	CAN O	43.7	0.8736
CARB4	24.1	0.8469	CAN P	44.2	0.8710
CARB5	8.8	0.8372	CAN Q	64.0	0.9241
CARB6	29.0	0.8499	CAN R	75.0	0.9447
CARB7	1.8	0.7986	CAN S	33.3	0.8467
CARB8	16.4	0.8246	WX1	26.0	.8521
CARB9	20.0	0.8398	WX2	2.22	.8085
CARB10	16.0	0.8247	WX3	20.4	.8318
CARB11	1.7	0.7998	WX4	8.4	.8477
CARB12	26.1	0.8367	WX5	15.2	.8558
			WX6	22.6	.8233
REGRESSION DATA:			WX7	21.0	.8463
R SQUARED = 0.7536					

C. GASOLINE FEASIBILITY STUDY

A small selection of gasoline samples with widely varied aromatic content has also been analyzed to check feasibility of the method for other distillate ranges. These FTIR data are compared with FIA results in **Figure 24**, and two of the spectra shown in **Figures 25 and 26.** They do show a correlation, but not the same correlations as those found for the diesel fuel distillate range. We did run by both transmittance and ATR methods for gasoline on the FTIR. This method looks quite feasible for both olefin and aromatic measurements, but would take a little more work to optimize and standardize. The peak locations were a little different for the gasolines than for the diesel samples, with a wider separation between the bands, and large, distinct peaks. The subtraction of olefin values from a total area would probably not be necessary for gasoline analyses.

D. IR ROUND-ROBIN STUDY

The final step in optimizing the infrared method involved round-robin analysis of a variety of diesel fuel samples, on a variety of infrared instruments. Midac, Nicolet, Bio-Rad, and Perkin-Elmer infrared instruments were used by the laboratories to produce this data. Seven samples were selected from our 55 sample database for use in the round-robin portion of the study. These samples were selected to represent the range of interest for the methods, and were drawn from our own sample base, the CARB provided samples, and samples from the CRC study performed at Southwest Research Institute. These samples are shown below.

TABLE 10. SELECTED SAMPLES FOR IR ROUND-ROBIN

Sample identification	FIA aromatic result, VOL%	
	(Literature)	(Measured)
1. FL-0502-F	3.7	3.4
2. CARB 5	8.8	11.4
3. CRC 8	11.1	12.6
4. CARB 10	16.0	18.2
5. CARB 9	20.0	19.5
6. FL-0429-F	24.9	25.5
7. CRC 5	33.5	40.2

Six round-robin participants were selected for comparison purposes using the IR method. A list of these participants is shown below. Two of the laboratories had more than one instrument available, and provided two sets of data each. A second draft of the IR procedure, along with a copy of the cover letter which was sent to each participating laboratory, is included as **Appendix C**. The procedure describes integration of total area under the aromatic and olefin region followed by subtraction of the olefinic band. The total integration area is between about 1650 and 1550 wavenumbers, with the olefin area between approximately 1650 and 1625 wavenumbers. Participants were allowed to vary the background points selected to optimize values in their instrument systems.

TABLE 11. PARTICIPANTS IN IR ROUND-ROBIN STUDY

1. SwRI Chemistry and Chemical Engineering Division
   Contact: Bill McMahon, x2178
   Instrument: Bio-Rad Digilab
2. SwRI Automotive Products and Emissions Research Division
   Contact: Karen Kohl, x2071
   Instrument: Nicolet 8210
3. SwRI Automotive Products and Emissions Research Division
   Contact: Mary Gillespie, x5345
   Instrument: Nicolet 5DXC-ATR
4. SwRI Automotive Products and Emissions Research Division
   Contact: Mary Gillespie, x5345
   Instrument: Nicolet 5DXC-Transmission
5. Midac Instrument, Costa Mesa, California
   Contact: Gary Hancock
   Instrument: Midac
6. Perkin-Elmer, Dallas, Texas
   Contact: Gerald Brooks
   Instrument: Perkin-Elmer
7. Nicolet Instruments, Houston, Texas
   Contact: Tom Hosea
   Instrument: Nicolet 205
8. Nicolet Instruments, Houston, Texas
   Contact: Tom Hosea
   Instrument: Nicolet 710

Round-robin interlaboratory samples were sent out for the area measurements only, with final calculation parameters completed following our statistical analysis for the program. Both transmittance and ATR data were requested, in order to evaluate any effects of density or varied refractive index on the test procedure. No such effects were found in our in-lab studies between the two methods.

Results of the interlaboratory analyses are shown in **Appendix D** of this report. Both transmission and ATR data were received from the labs. Each data set is reported in at least three forms. First, results are given as aromatic area, the integrated area in the peak at 1600 less the olefin contribution. Next, the relative area, obtained by ratio of the aromatic area to the area of the CRC8 sample, which has approximately 10% aromatic content by FIA, is given. This form of the data was presented to give an equivalent area for the different path lengths of cells which were used.

Calculated relative aromatic content is given, in order to predict the FIA result for a sample, based on regression of the relative area VS the FIA aromatic values. This value was obtained by multiplying the relative area by the 8.57 factor found to relate corrected relative areas of the samples to FIA values for 0 to 40% aromatics. This procedure allows the prediction of FIA results for a wide range of samples.

A final value of calculated WT% ring carbon is shown, based on the relation found by regression of relative areas VS ring carbon values measured by NMR for samples FL-0502 and CRC5 as described in section V., part B. The value is relative area multiplied by 4.282.

Repeatability and reproducibility values obtained from the interlaboratory study are shown in **Table 12** for the relative aromatics variable. Repeatability represents the dispersion of measurements made on the same fuel sample in the same laboratory by the same operator using the same apparatus in a short period of time. Reproducibility represents the dispersion of systematic errors associated with the various laboratories and methods. The values obtained are based on the data collected by eight laboratories on the seven different fuel samples. The repeatability and reproducibility values were determined utilizing the statistical techniques described in ASTM Standard E-691-87. Tables of the statistical measurements on the interlaboratory data are given in **Appendix E.** The literature FIA values are the values from sample sources or from measurement on entering the laboratory; the measured FIA values as measured in the laboratory in triplicate in conjunction with the round-robin program.

The reproducibility measures in **Table 12** are larger than the repeatability measures for all seven fuel samples, indicating the existence of larger variation between the laboratories as compared to within each lab. Relative area and relative aromatic averages are given in **Table 13** and **Table 14** for each lab and each fuel sample, as well as over-all labs and samples, as well as the measured FIA values obtained in the SwRI Petroleum Products Research Department lab.

The data were also examined to determine the degree of linear correlation between the proposed method and FIA analysis. The resulting squared correlation value was 92.6%, indicating an excellent linear relationship. A plot of the fit, along with 95% confidence bounds, is illustrated in **Figure 27.** This work serves to establish an equivalent measure, using relative aromatic area, to the value of 10 VOL% aromatics using FIA.

TABLE 12: REPEATABILITY AND REPRODUCIBILITY
(Standard Deviations in VOL% predicted FIA aromatic)

FUEL	Average Level	Repeat-ability	Reproduc-ibility	Lit. FIA	Measured FIA
FL502	-0.4	0.8	1.1	3.7	3.5
CARB5	3.7	0.5	1.6	8.8	11.4
CRC8	8.6	0.4	0.0	11.1	12.6
CARB9	13.9	0.6	1.2	19.1	19.5
CARB10	18.8	2.0	1.9	16.4	18.2
FL429	24.8	1.1	2.5	24.9	25.4
CRC5	32.4	1.6	2.7	33.5	40.2

Calculated WT% ring carbon average values, shown in **Table 15**, were obtained by relating the relative area of the samples to NMR data on two of the samples, CRC5 and FL-0502.

TABLE 13 AVERAGE RELATIVE AREA - IR
(by Laboratory, Areas relative to 10VOL% aromatic fuel)

	A	B	C	D	E	F	G	H	avg
FL 502	0.02	-0.3	0.03	.005	0.13	0.05	0.03	0.00	0.00
CARB 5	0.55	0.26	0.41	0.42	0.79	0.54	0.21	0.75	0.49
CRC 8	1.00	1.02	0.99	1.02	1.02	1.00	1.00	1.00	1.01
CARB 9	1.77	1.55	1.65	1.58	1.84	1.47	1.44	1.86	1.45
CARB 10	2.30	2.23	2.33	2.42	2.41	1.75	1.84	2.42	2.21
FL 429	2.97	2.97	3.22	3.10	3.02	2.51	2.34	3.08	2.90
CRC 5	3.87	4.12	4.07	3.93	3.82	3.29	3.29	3.91	3.79

Table 14. RELATIVE AROMATICS - IR
(From regression of relative area VS FIA aromatic content)

	A	B	C	D	E	F	G	H	avg
FL 502	0.0	-3.0	-.93	0.11	1.57	0.48	0.24	0.0	0.28
CARB 5	4.70	2.52	3.54	3.63	6.69	4.66	3.10	6.40	4.40
CRC 8	8.57	8.70	8.57	8.74	8.74	8.58	8.57	8.57	8.63
CARB 9	15.2	13.3	14.1	13.5	15.8	12.6	12.3	15.9	14.1
CARB 10	19.7	19.1	20.0	20.7	20.7	15.1	15.8	20.8	19.0
FL 429	25.4	25.5	27.6	26.6	25.9	21.5	20.1	26.4	24.9
CRC 5	33.2	25.4	34.9	33.7	32.7	28.3	28.2	33.5	31.2

Table 15. AVERAGE CALCULATED WT% RING CARBON - IR
(From regression of relative area data VS NMR WT% ring carbon data)

	A	B	C	D	E	F	G	H	avg
FL 502	0.00	-1.4	-.49	0.06	0.28	0.24	0.14	0.00	-.14
CARB 5	2.35	1.25	1.76	1.82	3.31	2.33	0.88	3.19	2.11
CRC 8	4.52	4.34	4.28	4.37	4.37	4.28	4.28	4.27	4.34
CARB 9	7.58	6.64	7.06	6.76	7.87	6.31	6.14	10.4	7.34
CARB 10	9.83	9.55	10.0	10.3	10.3	7.56	7.91	10.3	9.47
FL 429	12.7	12.7	13.8	13.3	12.9	10.8	10.0	13.1	12.4
CRC 5	16.6	17.7	17.4	16.7	16.3	14.1	14.1	16.7	16.2

A - ATR
B - ATR
C - Transmission
D - Transmission
E - ATR
F - Transmission
G - ATR
H - ATR

IV. ULTRAVIOLET METHOD OPTIMIZATION

A. THEORY OF METHOD

The analysis of petroleum and petroleum-related materials for aromatic components using ultraviolet spectroscopy (UV) has been a viable procedure since the early 1940's when the synthetic rubber plants used UV to control the styrene content of GRS. During the 1950's, a current staff member at SwRI helped develop a UV method for mono-, di-, and tri-aromatics in recent geological sediments while employed at Shell Development Co. This methodology has since been modified and refined to permit the measurement of one-, two- and three-ring aromatic hydrocarbons in fuels and lubricants to aid in the understanding of fuel and lubricant performance. Aromaticity has been shown to be an important factor in fuel combustion and lubricant research. The WT% ring carbon, independent of side chain composition or quantity, has been found to be the key parameter.

This method involves the dilution of a carefully measured weight or volume of sample with a very high purity aliphatic solvent such as spectro-grade cyclohexane or isooctane to a precisely known selected volume. After careful mixing to obtain uniform concentration, the solution is placed into fixed pathlength UV quartz cells or cuvettes which can be sealed to prevent evaporation losses and concentration changes during the analysis. The cell pathlengths used are in decreasing order of magnitude steps such as 10mm, 1mm, and 0.1mm. The cells must be scrupulously clean with no trace of contaminants, fingerprints, or sample from a prior analysis.

The cells are placed in a recording ultraviolet spectrometer capable of scanning from 350 to 190 nm with a spectral halfband width of 1nm or less. As the absorbance increases in the shorter wavelength regions to values of 1.0 or 2.0 maximum, the shorter path cell is selected to reduce the absorbance to the more accurate measuring range of 0.3 to 0.7 absorbance units. Once the full spectrum has been obtained, the absorbance values at selected maxima for one-, two-, and three-ring aromatics are read, corrected for cell and solvent contribution either automatically (differentially) or based on separate, prior measurements of blank solutions. Inspection of the recorded spectrum is made to ascertain that there are no abnormal components which could cause erroneous values in the analysis.

Based upon the absorbance values of standard components at the selected wavelengths, a three-by-three matrix is solved for the concentration of one-, two-, and three-ring aromatic compounds present in the sample. The complete analysis can be performed by an analyst, using a computer for the calculations, in about one-half hour per determination.

B. OPTIMIZATION OF METHOD
1. OPTIMIZATION OF HARDWARE

A Beckman model DU series 7500 diode array spectrophotometer was received from Beckman Instruments on a loan basis. This spectrophotometer has a flat optical system and passes undispersed light from the sources through the sample. The light is then dispersed by the concave holographic grating onto the diode array detector (**Figure 28**). The diode array consists of 512 elements, each diode reading 1.25nm. Photometric measurements at a particular wavelength are obtained by interpolating the readings at two bracketing diodes.

The DU-7500 diode array spectrophotometer does not scan, but collects simultaneous readings at different wavelengths. This instrument takes a sample reading from the diode array detector by electronically scanning the wavelengths. Spectra were obtained over a wavelength range of 190 to 290nm. The spectrum can be presented either in absorbance or transmittance. Spectral addition, subtraction, and multiplication can also be performed on stored spectra.

To evaluate the DU-7500 Spectrophotometer, its data was compared with that obtained using a Beckman ACTA CIII dispersive Spectrophotometer, to determine the feasibility of using a diode-array instrument such as the DU-7500. The Beckman ACTA CIII is a precision, dispersive instrument and is very accurate. The diode array system has no moving parts, and would be especially desirable for field applications. The diode array system is a very fast system and could analyze samples very rapidly.

Three standard materials were analyzed on both instruments for comparison. The standards chosen were:

Tridecylbenzene--Mono-aromatic
1,4-Dimethylnaphathalene--Di-aromatic
4,5-Methylenephenanthrene--Tri-aromatic

Each of these compounds was analyzed using 1.00, 0.10, and 0.01 cm cells, according to the basic UV procedure outlined in section IV.A. Absorbance was determined for each aromatic compound at each specific wavelength: 195, 225,and 255nm. Sample analysis is relatively fast, using the DU-7500 instrument. The instrument selects peaks at maximum intensity, and lists the peaks and the absorbance values. The point value function lists the absorbance values at selected points of interest.

Spectra of Tridecylbenzene (mono-aromatic), 1,4-Dimethylnaphthalene (di-aromatic), and 4,5-Methylenephenanthrene (tri-aromatic) are shown using the DU-7500, in overlay of 1.00, 0.10, 0.01 cm pathlengths, (**Figures 29 through 31**). The same components were also run in 1.00, 0.10, 0.01 cm pathlengths on the Beckman ACTA CIII.

The Beckman Model DU Series 7500 diode array spectrophotometer selected for use in this procedure was calibrated by the manufacturer in preparation for characterization of standard compounds. The instrument in its present installed condition at SwRI is well within specification operating condition as certified by the Beckman service representative.

2. OPTIMIZATION OF PROCEDURE

The original UV method was applicable to all petroleum-based fuels and lubricants basestocks. The response factors (molar extinction coefficients) were selected to represent an average of those observed for all these products. Limiting the method to diesel fuels, with particular attention to the low aromatic concentration range, allows improved accuracy and reliability in the method. The following steps were taken to optimize the existing UV method in this program.

1. Identify molar extinction coefficients for one-, two-, and three-ring aromatic compounds in the diesel fuel boiling range.

2. Recommend standards to be used in laboratory-to-laboratory calibration and standardization of instrument response.

3. Calculate anticipated responses and establish sample dilution and instrument operational procedure details.

4. Write an optimized procedure for lab development.

In order to select the correct aromatic compounds for calibration purposes, a search for detailed analysis data of "typical fuels" was performed. Since low aromatic diesel fuels are rare, analytical data on such fuels is difficult to obtain. In a report to the U.S. Army, authors Fodor, Bailey, Present, and Kohl,[14] provided detailed analytical data on the four fuels used in the study. **Table 16** shows a compilation of most of the mass spectrometry aromatic data. The CAT 1H fuel is a typical fuel used in performance testing. The EPA fuel is the Phillips 2-D fuel. The REF fuel is a military specification fuel(MIL-F-46162). The LCO fuel is a light cycle oil used as a blendstock in diesel fuels. The data shown as AVG.1 is the average of all four fuels for each component. The data AVG.2 is the average of the first three fuels, excluding the light cycle oil, since its high aromatics content would preclude its use in blending low aromatics diesel fuel.

TABLE 16. AROMATIC COMPOUNDS
(AROMATICS FOUND IN FOUR FUELS, % BY MASS SPEC)

COMPONENT	CAT1H	EPA	REF	LCO	AVG 1	AVG 2
BENZENES						
C3-		0.15			0.04	0.05
C4-		0.20	3.33		0.88	1.18
C5-	0.03	0.57	2.46		0.77	1.02
C6-	0.05	0.18	1.20		0.36	0.48
c-C6-	0.15				0.04	0.05
C7-	0.05	0.13	0.25	0.76	0.30	0.14
c-C7-		0.13			0.03	0.04
C8-	0.21	0.23			0.11	0.15
C9-	0.33	0.34			0.17	0.22
C10-	0.24		0.15		0.10	0.13
C11-	0.33	0.45	0.11	0.48	0.34	0.30
C12-	0.18	0.90	0.23	0.73	0.51	0.44
C13-	0.12	0.27	0.21		0.15	0.20
C14-		0.07	0.45		0.13	0.17
C15-	0.06	0.08			0.04	0.05
C18-			0.24		0.06	0.08
SUBTOTAL	1.75	3.70	8.63	1.97		
TETRALINS	0.04	0.11	0.63		0.20	0.26
C2-	0.17	0.36	0.77	0.30	0.40	0.43
C3-	0.17	0.90	0.10		0.29	0.39
C4-		0.28	0.41		0.17	0.23
C5-			0.20		0.05	0.07
C6-			0.46		0.12	0.15
C7-			0.18		0.04	0.06
SUBTOTAL	0.38	1.65	2.75	0.30		
NAPH-						
THALENES	0.08			0.17	0.06	0.03
C2-	0.57			8.49	2.27	0.19
C3-	1.52		2.65		1.04	1.39
C4-	1.74	0.80	2.13	3.00	1.92	1.56
C5-	0.63	2.50	0.33	5.57	2.26	1.15
C6-	2.05	5.20		0.97	2.06	2.42
C7-	0.16	1.14			0.32	0.43
SUBTOTAL	6.75	9.64	5.11	18.20		

TABLE 16. AROMATIC COMPOUNDS (CONT.)
(AROMATICS FOUND IN FOUR FUELS, % BY MASS SPEC)

COMPONENT	CAT1H	EPA	REF	LCO	AVG 1	AVG 2
BIPHENYLS	0.12		0.30		0.10	0.14
C1-	0.24				0.06	0.08
C3-	0.15				0.04	0.05
C4-				0.26	0.07	0.00
C5-				2.89	0.72	0.00
C6-		0.28		1.19	0.37	0.09
SUBTOTAL	0.51	0.28	0.30	4.34		
PHENANTHRENES						
C2-				3.67	0.92	0.00
C3-	0.29			0.73	0.26	0.10
C4-				1.16	0.29	0.00
C5-		0.35		2.30	0.66	0.12
C6-	0.71	0.15		0.20	0.27	0.29
C7-	0.52	0.14		0.75	0.35	0.22
C8-				0.19	0.05	0.00
SUBTOTAL	1.52	0.64	0.00	9.00		
ANTHRACENES						
C3-				1.49	0.37	0.00
C4-				0.42	0.10	0.00
C5-				0.22	0.06	0.00
C6-	0.21				0.05	0.07
SUBTOTAL	0.21	0.00	0.00	2.13		
FLUORENES						
C2-				1.59	0.40	0.00
C3-	0.13	0.12		0.19	0.11	0.08
C4-	0.15				0.04	0.05
C5-	0.36				0.09	0.12
C6-	0.44		0.23		0.17	0.22
SUBTOTAL	1.08	0.12	0.23	1.78		

Review of these limited data show that anthracenes are nearly absent in the lower aromatic concentration fuels (AVG.2), with only a trace(0.07WT%) of C6-anthracene. However, C5-,C6-, and C7-phenanthrenes are present and should be considered for analysis. Biphenyls do not appear to be of major concern. Naphthalenes with C3-, C4-, C5-, and C6- substituents are of major concern with emphasis on C6-. Tetralins deserve some consideration but mono-aromatics(substituted benzenes) are more important. The C4-, C5-, C6-, C11-, C12-, and C13- are the prime substituents of interest in the benzene family. From this data and other data, a number of aromatic compounds which appear prominently in low aromatic diesel fuels were selected for method optimization.

The measured extinction coefficient for each compound was weighted according to the levels indicated in mass spectrometric analysis to arrive at the proper extinction coefficient conversion factors to be used in the final UV method matrix calculations. Final selection of the compounds to be used was based on mass spectroscopic analyses of diesel fuels used in fuel studies at SwRI (Fodor, Bailey, Present, and Kohl)[14] and also from mass spectroscopic characterization of diesel fuels used in the Coordinating Research Council study of diesel fuel composition on particulate emissions (Ullman)[1]. The selected compounds are listed below.

Aromatic Compounds Prevalent in Low Aromatic Diesel Fuel as Determined by Mass Spectroscopic Analysis

General Class	Substitution
Alkyl Benzenes	C3 through C14
Benzocycloparaffin	C2 through C6
Benzodicycloparaffins	substitution unspecified
Naphthalenes	C3 through C6
Acenaphthenes	C1
Acenaphthylenes	C1
Phenanthrenes	C3,5,6,7
Benzothiophenes	substitution unspecified
Dibenzothiophenes	substitution unspecified

A large group of representative one-ring, two-ring, and three-ring compounds was obtained for evaluation of extinction coefficients at the appropriate wavenumbers for optimization of the UV method around the 10% aromatics range. Other aromatic compounds including anthracenes, biphenyls, naphthobenzothiophenes, and tetraaromatics were not included due to their relative low abundance (typically <0.1 WT%) in the diesel fuel analyses that have been examined.

Following selection, the standard compounds spectra were obtained to give an extinction coefficient for each of the aromatic classes (mono, di, and tri-ring). Once the response factor had been determined, these standards were used to calculate weighted composite standard spectra for each of the aromatic families. Then several diesel fuels were analyzed to test the calculation for aromatics present in the sample.

The procedure used for preparation of single compound standards was as follows:

1. Prepare 8 dram glass vials by acid cleaning overnight in an acid wash solution of NOCHROMIX in sulfuric acid. (NOCHROMIX is a metal-free substitute for dichromates available from Godax Laboratories, Inc., New York, NY.)

2. Rinse vials in deionized water and dry.

3. Weigh 3-4 milligrams of solid standards directly into clean vial. Weigh to plus or minus 0.01 milligram.

4. Weigh 10 microliters of liquid standards into clean vial by weighing syringe before and after injection. Weigh to plus or minus 0.01 milligram.

5. Add 25.00 milliliters of Fisher Scientific Optima Grade Isooctane to the vial and gently swirl to bring standard compound into solution.

6. Cap standard mixture with a Polyseal (polyethylene) sealed closure.

This procedure was used to prepare standards for the determination of extinction coefficients. The isooctane solvent to be used in the UV procedure was obtained and measured in the instrument to confirm purity. Isooctane was supplied by Fisher Scientific with a certified analysis. The Fisher Scientific grade designation is Optima.

The UV absorption spectra were obtained for the single compound standards and extinction coefficients were determined for use in the procedure. The extinction coefficients from the standard spectra were examined to select final optimized method parameters and define the procedures. Calculation of the mass extinction coefficients at a local absorbance maxima, rather than at a fixed wavelength, has lead to greater consistency between coefficients. This result indicates that weighting of mass extinction coefficients to match expected composition was not a critical factor, thus making the UV method a more reliable approach for evaluating low aromatic diesel fuels.

Standard data measurements are given in **Table 17** showing sample weight used, ring carbon weight, absorbance at the primary peak local maxima, and a calculated mass extinction coefficient in units of absorbance per milligrams of ring carbon for the single pathlength cell used. These data include measurements for 29 compounds.

TABLE 17. STANDARD DATA MEASUREMENTS

MONO AROMATICS	SAMPLE WEIGHT	RING CARBON	PRIMARY PEAK	ABS./mg RING C
	mg.	mg.	ABS.	
n-Butylbenzene	3.94	2.29	0.69	0.30
i-Butylbenzene	3.81	2.22	0.64	0.29
t-Butylbenzene	3.76	2.19	0.67	0.31
s-Butylbenzene	3.03	1.76	0.51	0.29
Pentylbenzene	3.21	1.69	0.46	0.27
Tetralin	10.59	5.77	1.53	0.58
Hexylbenzene	4.17	2.01	0.56	0.28
Octylbenzene	3.92	1.61	0.48	0.30
Nonylbenzene	3.93	1.50	0.41	0.27
Decylbenzene	4.28	1.53	0.42	0.28
Dodecylbenzene	2.91	0.92	0.29	0.31
Tridecylbenzene	3.94	1.18	0.38	0.32
Octahydroanthracene	3.60	1.35	0.25	0.28
Pentamethylbenzene	4.32	2.28	0.68	0.30
DI-AROMATIC				
Naphthalene	4.01	4.01	1.34	0.33
Methylnaphthalene	4.33	3.90	1.02	0.26
Ethylnaphthalene	4.12	3.38	0.93	0.28
1,2-Dimethylnaphthalene	6.47	5.31	1.35	0.25
2,3-Dimethylnaphthalene	3.66	3.00	0.89	0.30
1,4-Dimethylnaphthalene	3.45	2.65	0.62	0.32
2,6-Dimethylnaphthalene	4.00	3.28	1.12	0.34
Trimethylnaphthalene	3.91	2.94	1.06	0.36
Diisopropylnaphthalene	3.10	1.87	0.50	0.27
Dinonylnaphthalene	3.10	1.04	0.31	0.29
Acenaphthene	3.23	2.68	0.81	0.30
TRI-AROMATIC				
Phenanthrene	3.04	3.04	0.44	0.15
4,5-Methylenephenanthrene	3.66	2.80	0.52	0.19
Methylphenanthrene	4.33	4.01	0.60	0.15
Dodecylphenanthrene	3.73	1.92	0.25	0.13

UV absorbance responses for the single compound standards were reviewed to determine the most accurate approach for the UV method. Absorbance peak values have occurred within a range of wavenumbers corresponding to the one-, two-, and three-ring standards, respectively. Final selection of either a fixed wavelength, or a local maxima for the UV method depended on consistency among the standards spectra. The local maxima approach was found to be the most favorable.

Comparisons of the single compound standards spectra with full boiling range diesel fuel samples were made to provide input into the selection of final procedure steps. California refinery samples received from CARB and the refinery samples collected by SwRI were measured for UV absorbance response.

Review of the UV mass extinction coefficients for the single compound standards revealed the most accurate approach for the UV method. Absorbance peak values occurred within a range of wavenumbers corresponding to the one-, two-, and three-ring standards, respectively. By selecting a local maxima in the region ranging from 190 - 200 nm for on-ring aromatics, from 220 - 230 nm for two-ring aromatics, and from 250 - 260 nm for three-ring aromatics, the data appeared to be very consistent. The precise wavelengths were determined from weighted composite spectra of the standards.

The 0.01cm fixed pathlength cell was selected as a simplification to the procedure for determination of each of the three aromatic types. The single compound spectra were manipulated to generate a representative mixture of concentrations of the various aromatic species to determine the extinction coefficients. The distribution of various aromatic types determined by mass spectrometry that were used to weight the extinction coefficients is shown in **Table 18**. The extinction coefficients from the compiled composite spectrum were also checked mathematically to confirm the final extinction coefficient selection, and the wavelength of maximum absorption.

Table 18. Aromatic Type Distribution by Mass Spectrometry on 15 Diesel Fuels

Monoaromatics	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	AVG	%
Alkylbenzenes	6.2	10.8	9.2	6.4	7.7	8.2	7.2	11.1	8.2	7.0	7.7	9.7	9.4	8.5	4.8	8.14	32.11
Benzo-cycloparaffins	2.8	11.4	6.7	3.4	5.3	4.6	4.9	11.9	6.8	5.2	5.3	11.5	6.5	14.5	2.7	6.90	27.22
Benzo-dicycloparaffins	0.9	4.1	2.6	1.5	2.1	2.4	2.2	3.7	2.4	1.8	2.3	3.3	3.0	4.8	0.2	2.53	9.97
Diaromatics																	
Naphthalenes	1.3	10.4	3.7	1.7	2.2	4.5	3.8	9.9	3.0	1.7	3.8	9.1	4.8	7.4	0.5	4.52	17.83
C_nH_{2n-14}	0.2	2.9	0.5	0	0	1.7	1.5	2.7	0.4	0	1.3	2.9	1.5	2.8	0	1.23	4.84
C_nH_{2n-16}	0.3	3.9	0.6	0	0.1	2.2	1.8	3.5	0.5	0	1.4	3.7	1.7	2.2	0	1.46	5.76
Triaromatics																	
C_nH_{2n-18}	0.3	1.3	0.2	0	0	0.5	0.5	0.9	0.1	0	0.4	1.1	0.3	0	0	0.37	1.47
C_nH_{2n-22}	0.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.01	0.05
Tetraaromatics	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.00	0.00
Sulfur Aromatics																	
Thiophenes	0	0.1	0	0	0	0	0	0.1	0	0	0	0.1	0	0	0	0.02	0.08
Benzothiophenes	0.1	0.5	0.1	0	0	0.2	0.2	0.4	0	0	0.2	0.4	0.1	0	0	0.15	0.58
Dibenzo-thiophenes	0.1	0.1	0	0	0	0	0	0	0	0	0	0.1	0	0	0	0.02	0.08
Naphtho-benzothiophenes	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.00	0.00
TOTALS	12.4	45.5	23.6	13.0	17.4	24.3	22.1	44.2	21.4	15.7	22.4	41.9	27.3	40.2	8.8	25.35	100.00

C. UV ROUND-ROBIN STUDY

Interlaboratory reproducibility of the method was initiated by selecting six laboratories for analysis of seven samples. Samples and laboratories selected for round-robin testing are identified below in **Tables 19 and 20**. Three of the laboratories, Engine, Fuel, and Vehicle Research; Petroleum Products and Emissions Research; and Belvoir Fuels and Lubricants Research Facility (BFLRF), are part of Southwest Research Institute, but are independent and separate cost center facilities. Samples were prepared and sent to the six laboratories for UV absorbance measurements. The cover letter and instructions sent with the round-robin samples are presented in **Appendix F**.

TABLE 19. Samples selected for the UV Round-Robin

Sample identification	FIA aromatic result, VOL% (Literature)	(Measured)
1. CARB 5	8.8	11.4
2. CARB 9	20.0	19.5
3. CARB 10	16.0	18.2
4. CRC 5	33.5	40.2
5. CRC 8	11.1	12.6
6. FL-0429-F	24.9	25.5
7. FL-0502-F	3.7	3.4

TABLE 20. PARTICIPANTS IN UV ROUND-ROBIN STUDY

1. SwRI Chemistry and Chemical Engineering Division
   Contact: C. David Herrera, x3325
2. SwRI Belvoir Fuels and Lubricants Research Facility
   Contact: Steve Westbrook, x3185
3. SwRI Engine, Fuel, and Vehicle Research Division
   Contact: Rose Robledo, x2024
4. SwRI Automotive Products and Emissions Research Division
   Contact: Karen Kohl, x2071
5. Pennzoil, Houston
   Contact: John Sardisco
6. Shell Westhollow Research Center, Houston, Texas
   Contact: John Warn, 713-493-8331

The weighted extinction coefficients were applied to the absorbance data collected from round-robin testing. Weighting factors had been assigned for each of the single compound standards and the weighted spectra were added. The addition of weighted, single compound spectra resulted in one composite spectrum for each type of aromatic. The addition of the weighted single compound spectra was achieved by storing the spectra in disk storage, applying the weighting factors to each spectrum file, and adding the files.

Data summaries from the six UV round-robin laboratories are presented as **Appendix G**. One item identified in the round-robin testing was the importance of good cell cleaning technique. A commercial cell-washer was inadequate, so a slightly revised procedure has been written to ensure adequate cleaning of the quartz sample cells between analyses. Two laboratories that were not in agreement initially were found to have instrumental and technical problems. One laboratory's instrumentation was found to have a digital volt meter calibration problem such that absorbance was about 20% less than the correct absorbance. The cause of this problem was determined by analyzing the same diluted samples used for the BFLRF instrumentation on two different instruments. Another laboratory encountered difficulty due to the cell washing technique. The cell washer used had too little vacuum, allowing previous sample to dry on the window and skew results. That technique was corrected by using a vacuum flask set-up with an eye-dropper suction tip to clean cells well. Samples were rerun, producing data in good agreement with the rest.

Results of the statistical analysis of the data are shown in **Appendix G** of this report. First results are given as absorbance data for the three aromatic types and the total. Next, the WT% of the types and total are given. Repeatability and reproducibility values obtained from the interlaboratory study are shown in **Table 21** for the total aromatics variable. Repeatability represents the dispersion of measurements made on the same fuel sample in the same laboratory by the same operator using the same apparatus in a short period of time. Reproducibility represents the dispersion of systematic errors associated with the various laboratories and methods. The values obtained are based on the data collected by six laboratories on the seven different fuel samples. The repeatability and reproducibility values were determined utilizing the statistical techniques described in ASTM Standard E-691-87.

The reproducibility measures in **Table 21** are larger than the repeatability measures for all seven fuel samples, indicating the existence of larger variation between the laboratories as compared to within each lab. The WT% ring carbon averages are given in **Table 22** for each lab and each fuel sample, as well as over all labs and samples. Also shown in **Table 22** are the measured FIA values obtained in the SwRI Petroleum Products Research Department lab.

The data were also examined to determine the degree of linear correlation between the proposed method and FIA analysis. The resulting squared correlation value was 92.6%, indicating an excellent linear relationship. A plot of the fit, along with 95% confidence bounds is illustrated in **Figure 32** All the data are within the bounds, indicating a good correlation. This work serves to establish an equivalent measure, using relative aromatic area, to the value of 10 VOL% aromatics using FIA.

A test was conducted to determine the effect of alkyl nitrate cetane improver additive on the method by spiking one of the samples with additive at a relatively high level of 0.30 WT%. The absorption for the cetane improver occurred at 198 nm, with a difference of less than a 0.2 in absorbance at 190-196 nm where the nearest aromatic value is measured. Spectra of the sample with and without the improver are included as **Appendix K.**

TABLE 21: REPEATABILITY AND REPRODUCIBILITY - UV
(Standard Deviations in WT% ring carbon)

FUEL	AVERAGE LEVEL	REPEATABILITY	REPRODUCIBILITY
#1	1.2	0.1	2.5
CARB5	2.0	0.2	1.1
CRC8	3.2	0.4	1.6
CARB10	5.9	0.5	2.0
CARB9	4.3	0.6	2.2
FL429	9.5	0.2	1.8
CRC5	10.2	1.2	3.3

TABLE 22. AVERAGE TOTAL AROMATICS CONTENT - UV

Fuel	A	B	C	D	E	F	FIA
#1	0.9	1.0	1.0	1.1	2.5	1.0	3.4
#2	1.8	1.8	2.0	2.1	2.5	2.0	11.4
#3	2.4	3.0	3.2	3.4	4.0	3.2	12.6
#4	5.6	4.7	6.1	6.5	6.8	6.0	18.2
#5	3.4	3.6	4.4	4.5	5.5	4.2	19.5
#6	6.2	11.5	9.2	9.6	11.0	9.2	25.5
#7	7.8	10.1	9.9	10.7	12.9	10.1	40.2

V. BACKUP INFORMATION

A. FIA WORK

The FIA work for correlation use in the program was performed in the Petroleum Products Research Department laboratory. The silica gel lot used was analyzed for surface area and pH and found to be within specifications for method ASTM D-1319. The surface areas found in batches of silica gel used in the program were 536 and 542 meter^2 per gram, measured in our Emissions Research Laboratory. FIA analyses were run in triplicate in most cases, with an average value reported. We participate in several check fuel programs which measure FIA values for both gasolines and diesel fuels. Our results routinely come near the average for the labs, and are not found to be excessively high or low when compared with other laboratories running the method. **Figure 33** shows the data for the samples used in the round-robin studies.

B. NMR WORK

Ten samples from the CARB data base were initially submitted to the Chemistry and Chemical Engineering Division for aromatic content analysis by carbon 13 NMR. These results were unsuitable for standardization purposes because the integration of the spectra was clearly skewed and inaccurate. The seven round robin samples were then submitted to the University of Utah for NMR analysis. Three of these samples were analyzed including Round-Robin Samples #1 (FL-0502), #6 (FL-0429), and #7(CRC #5).

To provide a standard reference of WT% aromatic carbon for comparison to the UV aromatic results, three of the Round Robin Samples were submitted to the University of Utah Chemistry Department for quantitative Carbon-13 Nuclear Magnetic Resonance (C-13 NMR) analysis. A Varian XL400 400 MHz instrument, which provides greater resolution and much improved integration of the C-13 spectrum, was used to analyze samples diluted in Deutero-chloroform. The resultant spectra and details of instrument operating conditions are given in **Figures 34, 35, and 36.** Integration of the saturate and aromatic regions of the spectra yielded the results given in **Table 23.**

TABLE 23. NMR DATA
(FRACTION OF AROMATIC CARBON DETERMINED BY C-13 NMR FOR SELECTED ROUND ROBIN SAMPLES)

SAMPLE	ALIPHATIC INTEGRAL	AROMATIC INTEGRAL
ROUND ROBIN #1	>99%	0%
ROUND ROBIN #6	87.9%	12.1%
ROUND ROBIN #7	83.3%	16.7%

The results for aromatic content by carbon-13 NMR were used to relate the relative aromatic area by the FTIR method to actual wt% ring carbon. This step allows the FTIR method to give quantitative data which is not based on a correlation to FIA data, but on the response of the instrument to a wt% ring carbon value. A standard pure material, such as N-pentyl benzene or tert-butyl benzene, in kerosene or mineral oil can be used to standardize between instruments and/or cells. The values from the NMR analysis for these round-robin samples give a three point curve for establishing the relationship of FTIR area to wt% ring carbon for the study.

C. NIR STUDY RESULTS

A feasibility study was completed by LT Industries, Inc. to investigate the suitability of Near Infrared Spectrophotometry (NIR) to determine the aromatic content of diesel fuels. A total of thirty samples with ASTM D-1319 FIA analyses of the aromatic content was forwarded to LT Industries, Inc. from Southwest Research Institute. In addition, five unknown samples covering a range of 7 to 25 VOL% aromatics were also forwarded. LT Industries, Inc. developed two correlations based on the NIR spectra of the 30 known samples. From these equations, the aromatic contents of the five unknown samples were predicted.

The standard error of the calibration ranged from 2 to 3 VOL% aromatics. One of the unknown samples, FL-0416-F fell somewhat outside the range of the parameters used to develop the correlations from the 30 known samples. The results of the unknown samples are given below in **Table 24**. **Appendix** I contains the letter sent with samples to LT Industries, and the report presented by LT Industries on the samples.

TABLE 24. NIR FEASIBILITY STUDY FOR DIESEL FUEL AROMATICS

SAMPLE ID	CORRELATION 1	CORRELATION 2	MEASURED VALUE
Fl-0429-F	26.56	27.10	24.9
CARB-1	9.12	11.25	7.1
FL-0416-F	11.64	19.70	9.4
FL-0422-F	15.00	15.90	12.7
CARB-12	23.64	24.00	26.1

D. SFC STUDY PROGRAM

Results from the determination of aromatics in diesel fuels by SFC (Adam Schubert, Lee Scientific, and SwRI) are presented in **Table 25.** The FIA method results are also listed for comparison. The Lee Scientific and SwRI test apparatus specifications are listed below.

	Lee Scientific	SwRI
1. Liquid Injection Valve	0.2μl	0.2μl
2. Column Temperature	40°C	30°C
3. Pump Pressure	115 ATM	115 ATM
4. FID Temperature	350°C	375°C
5. Program Hold Time	30-40 min.	30 min.
6. Restrictor Length/ Inner Diameter/Type	90cm/25μm/ packed silica	25cm/20μm/ packed silica
7. Hydrogen Flow	50 ml/min.	65 ml/min.
8. Air Flow	300 ml/min.	260 ml/min.
9. Make-up Gas Flow	0 ml/min.	0 ml/min.
10. CO2 Flow	40 ml/min.	40 ml/min.
11. Column Length/ Inner Diameter/Type	25cm/2.0mm/5μm packed silica by Chromegasphere SI-60	25cm/2.0mm/5μm packed silica by Phenomenex Lichrosorb 5 Silica 60A

The Lee Scientific and SwRI programs are isothermal, isobaric, and isoconfertic (constant temperature, pressure, and density). Both begin with a 0.1 ms injection of pure sample, followed by a 30 minute hold time. In the Lee Scientific method, it was necessary to increase the hold time to 40 minutes for some samples in order to allow sufficient time for the entire sample to elute. In analyzing the chromatograms, the separation between the saturate and aromatic peaks was not always complete, and a forced baseline drop (or peak split) was necessary in order to integrate peak areas.

TABLE 25. SFC DATA

SAMPLE	FIA	SFC(ARCO)	SFC(LEE)	SFC(SWRI)
WX-1	26.02	26.35	22.42	29.1
WX-2	2.22	2.09	-	-
WX-3	20.42	20.34	17.66	20.2
WX-4	8.40	7.65	6.54	8.8
WX-5	15.23	14.29	11.86	13.1
WX-6	22.60	24.81	20.25	25.5
WX-7	21.03	21.39	17.14	21.3
CRC 5	33.5 - 40.2		26.29	33.2
CRC 8	11.1 - 12.6		9.49	10.6
CARB 5	8.8 - 11.4		5.68	8.3
CARB 9	16.0 - 18.2		12.46	16.4
CARB 10	20.0 - 19.5		12.30	18.1
FL-0429	24.9 - 25.5		21.00	27.6
FL-0502	3.7 - 3.4		2.20	5.3

E. DATA COMPILATION FOR THE PROGRAM

A total of 55 samples was gathered from various sources, including a Canadian study, a CRC study, a round-robin for aromatics, a group of refinery middle distillates, and CARB provided samples. Each of these selected samples has some sort of data base of previously collected data. We have access to the data for each group except the CARB provided samples. **Appendix J** shows a summary of all the available data on the samples for a visual comparison of the methods. FIA values are literature values where available, laboratory measurements in other cases. Only the areas are shown for the FTIR aromatic measurements, as baseline and standard data were not consistent during the whole range of testing for accurate predictions. Each group of samples is internally consistent for comparison of FTIR aromatic area trends with available literature data.

VI. REFERENCES

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2. Adopted by the California Air Resources Board on May 11, 1989.

3. American Society of Testing and Materials Method D-1319-88.

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13. Haas, J.M. et.al., "A Simple Analytical Test and a Formula to Predict the Potential for Dermal Carcinogenicity from Petroleum Oils", Am. Ind. Hyg. Assoc. J. 48(11):935-940 (1987).

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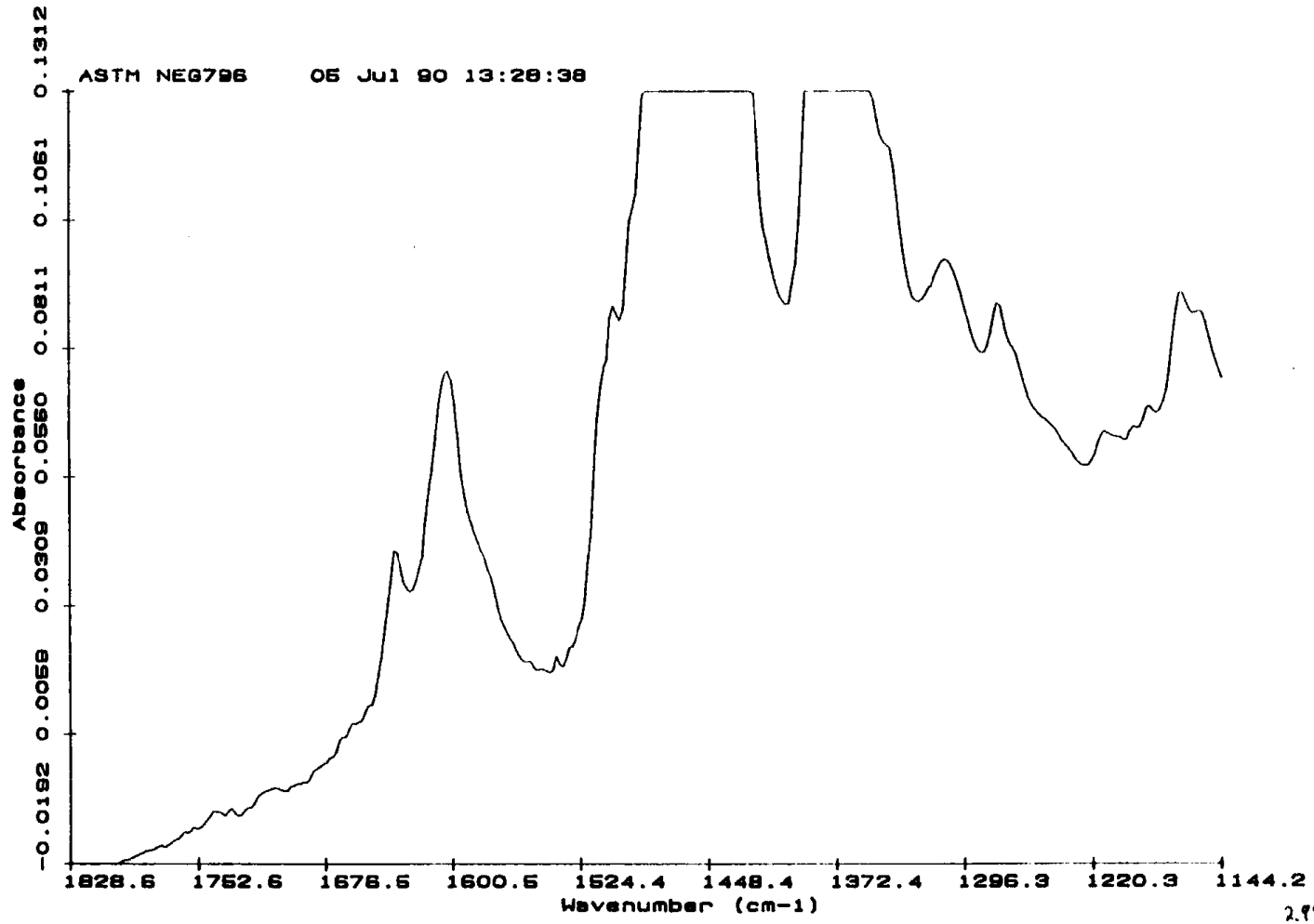
APPENDIX A. FIGURES

FIGURE 1. Infrared Spectrum of NEG 796



2.9941

FIGURE 2. FIA vs FTIR Correlation, Field Samples

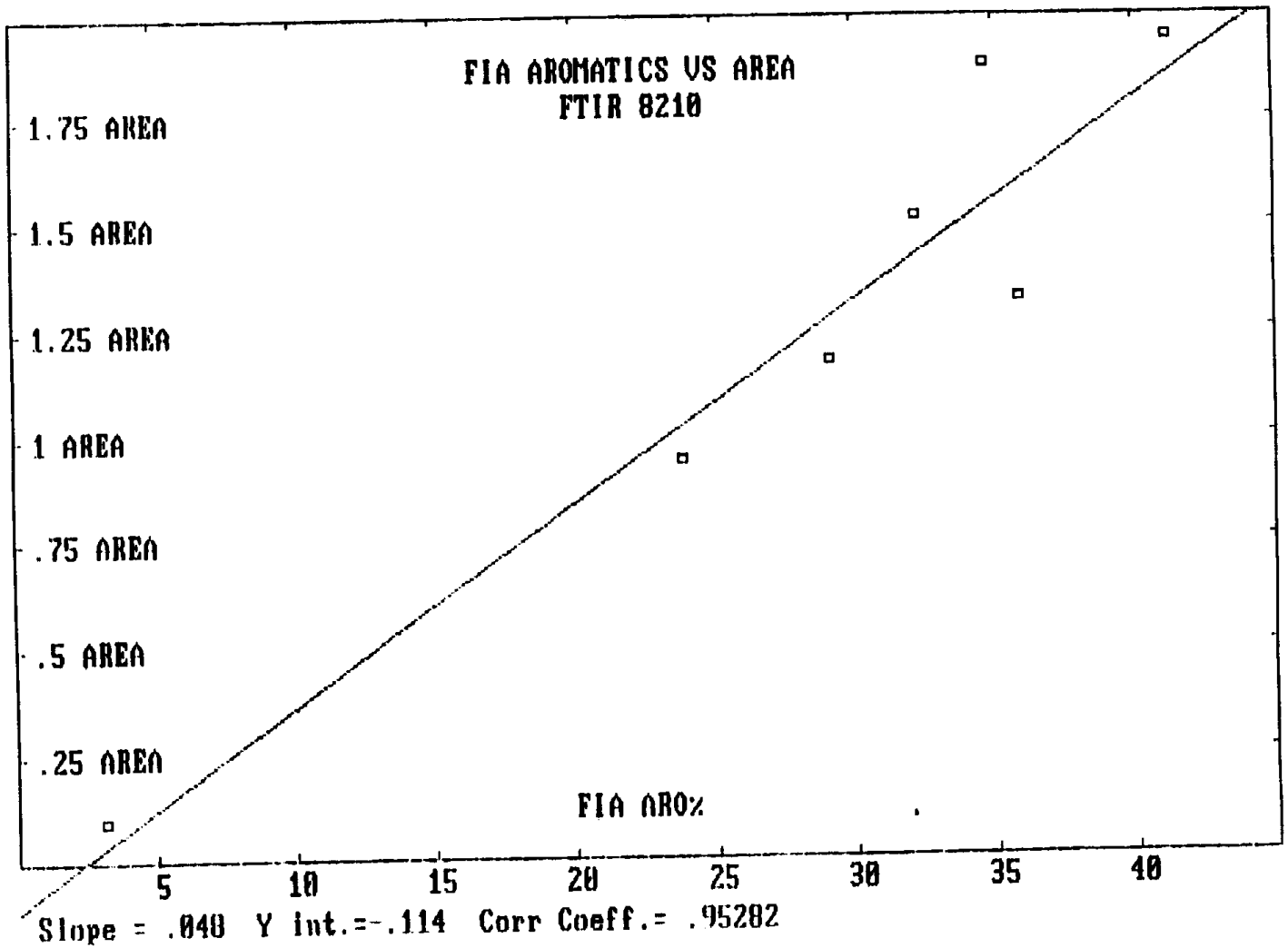


FIGURE 3. Nicolet Data vs Digilab Data

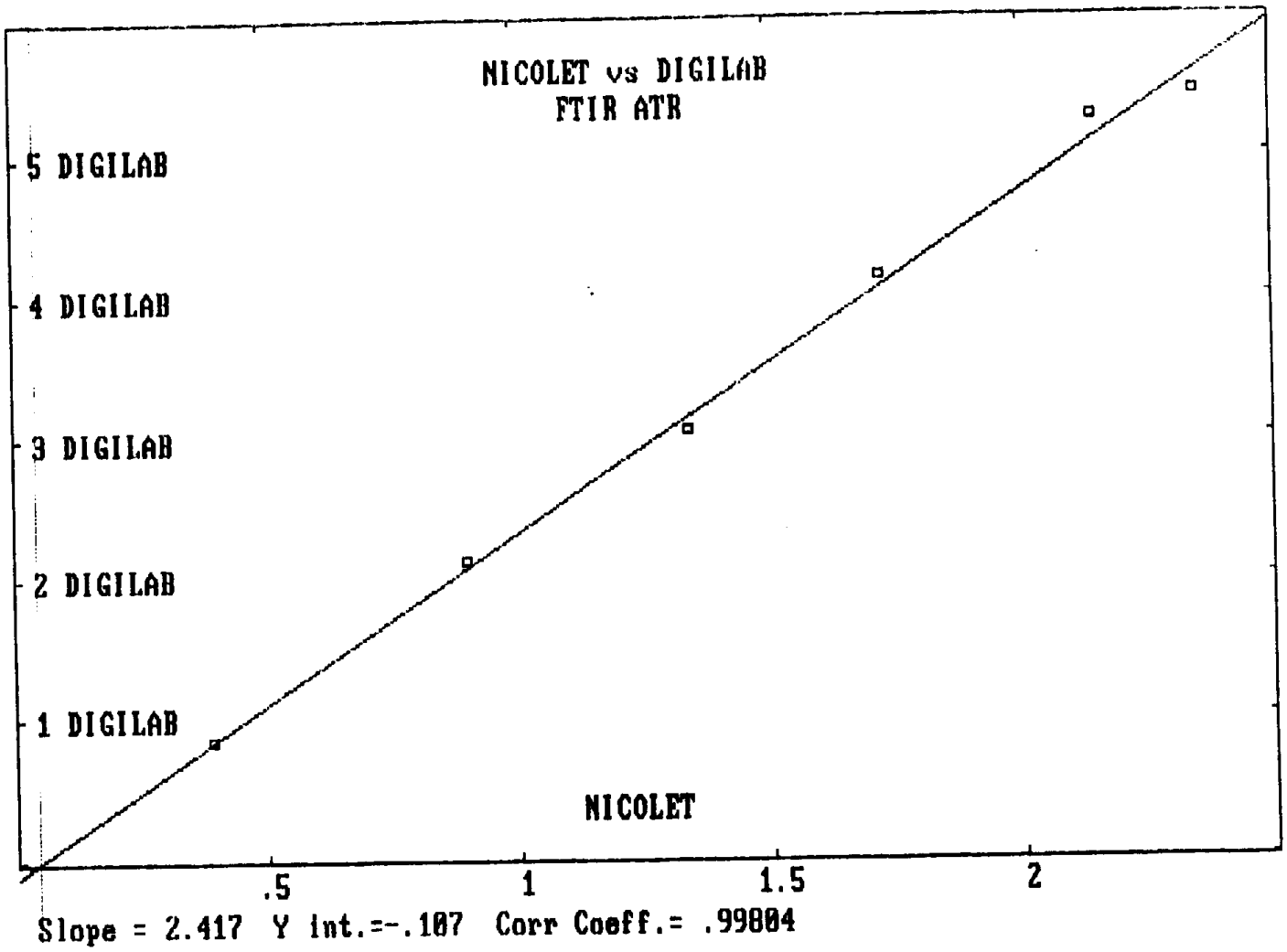


FIGURE 4. FTIR vs FIA, CRC and WX Samples

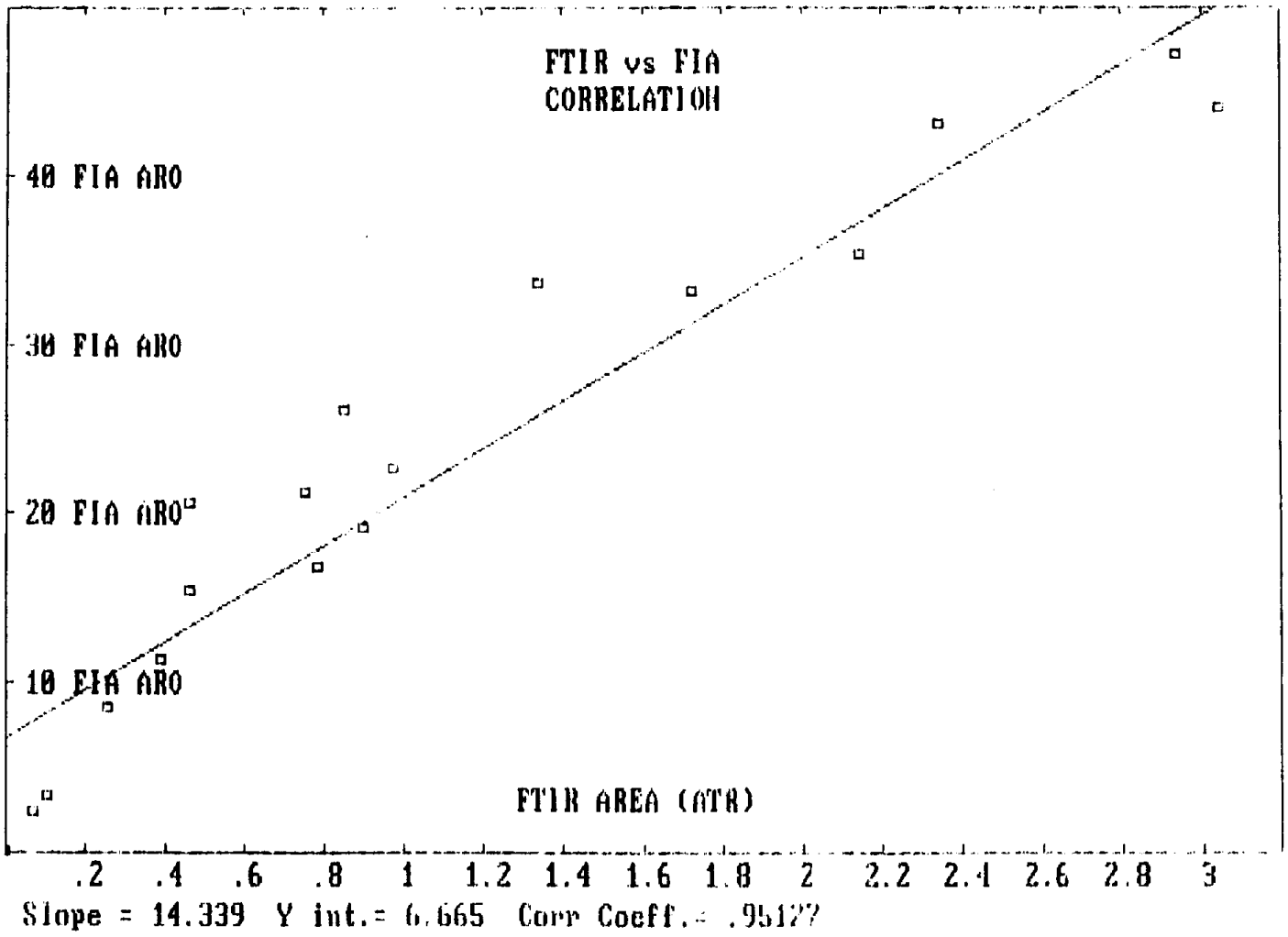


FIGURE 5. FTIR vs MS, CRC and WX Samples

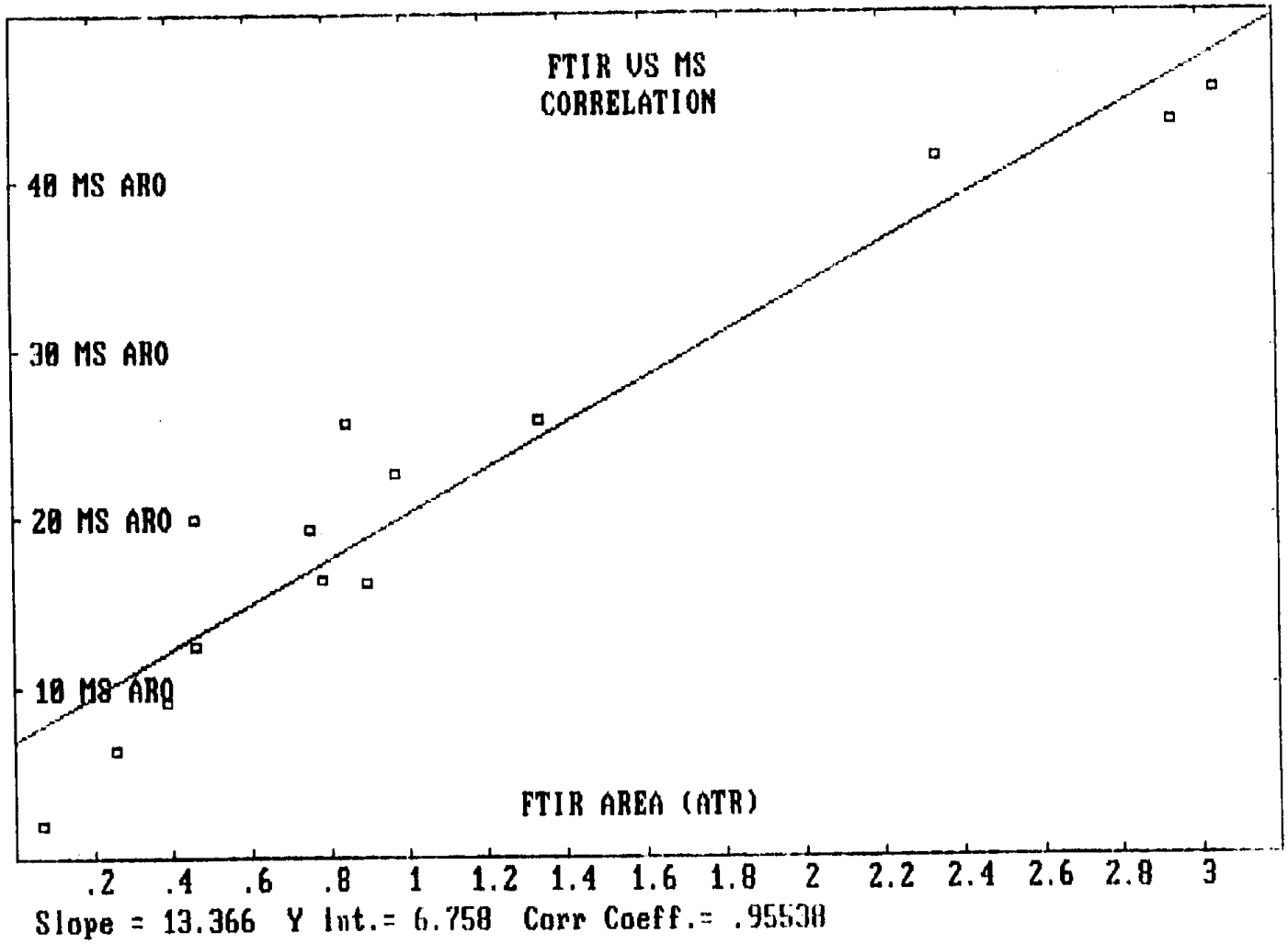
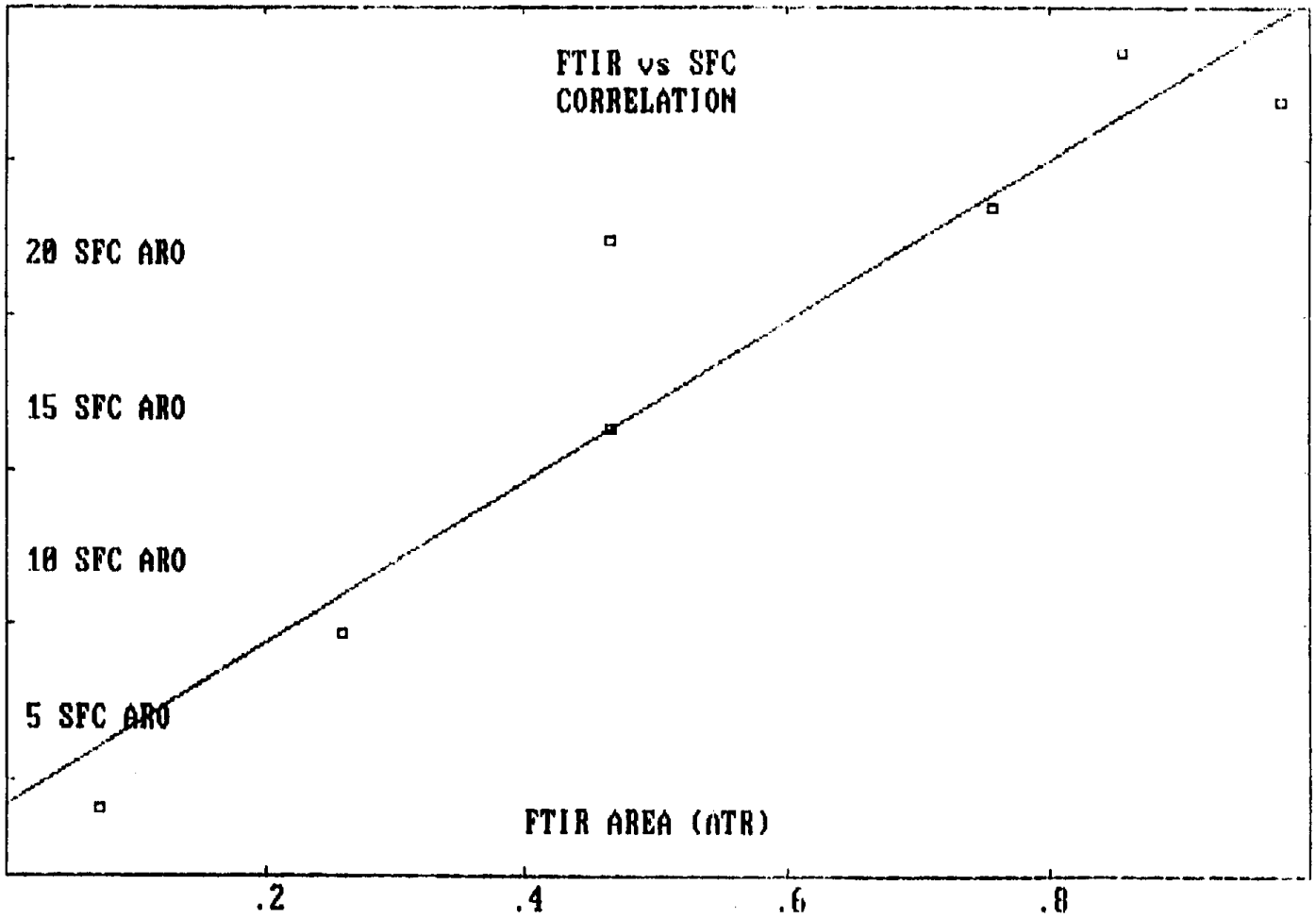


FIGURE 6. FTIR vs SFC, WX Samples



Slope = 26.172 Y Int.= 2.26 Corr Coeff.= .94479

FIGURE 7. FTIR vs NMR, CRC Samples

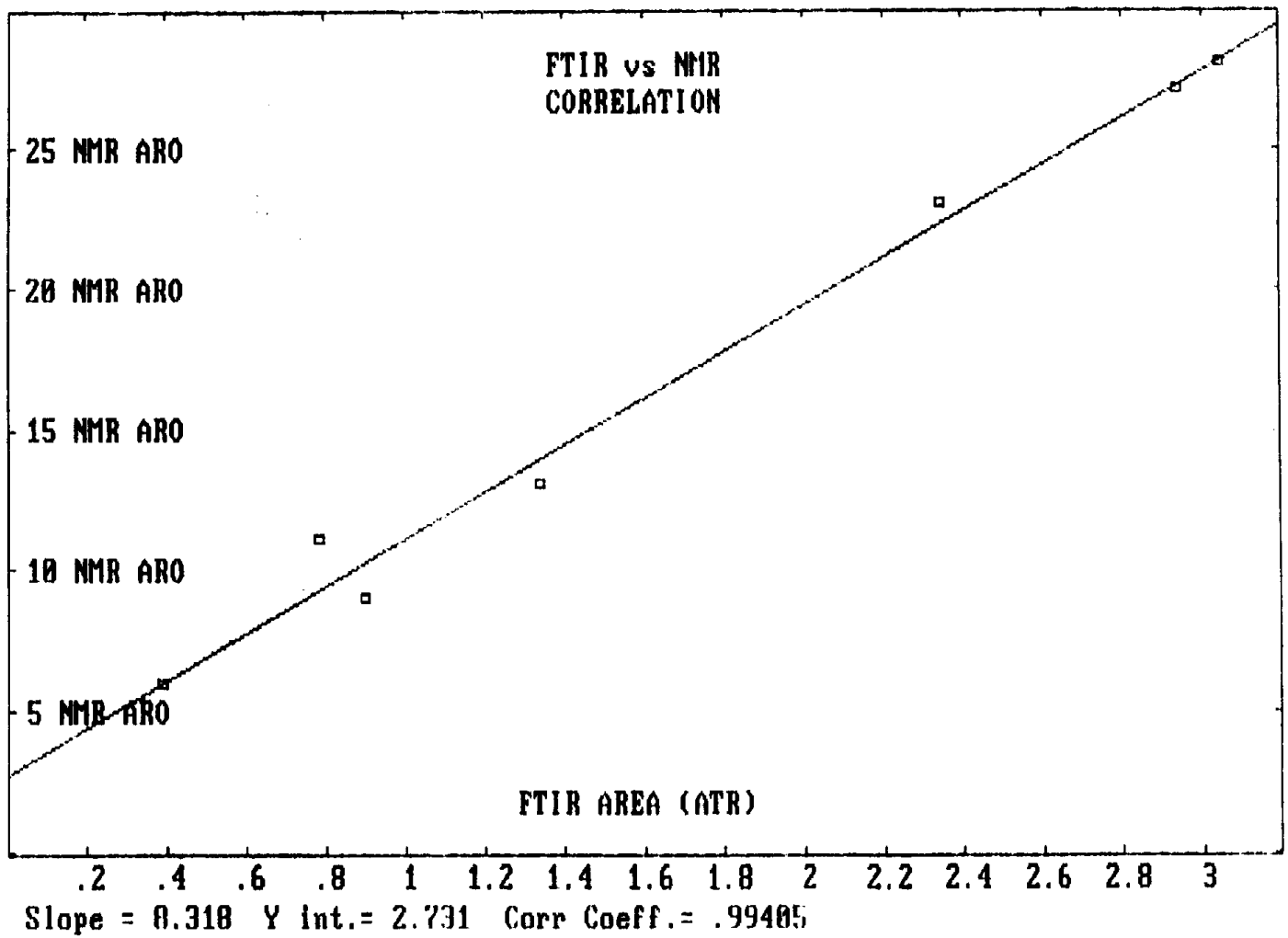


FIGURE 8. Infrared Spectrum of Canadian Sample A

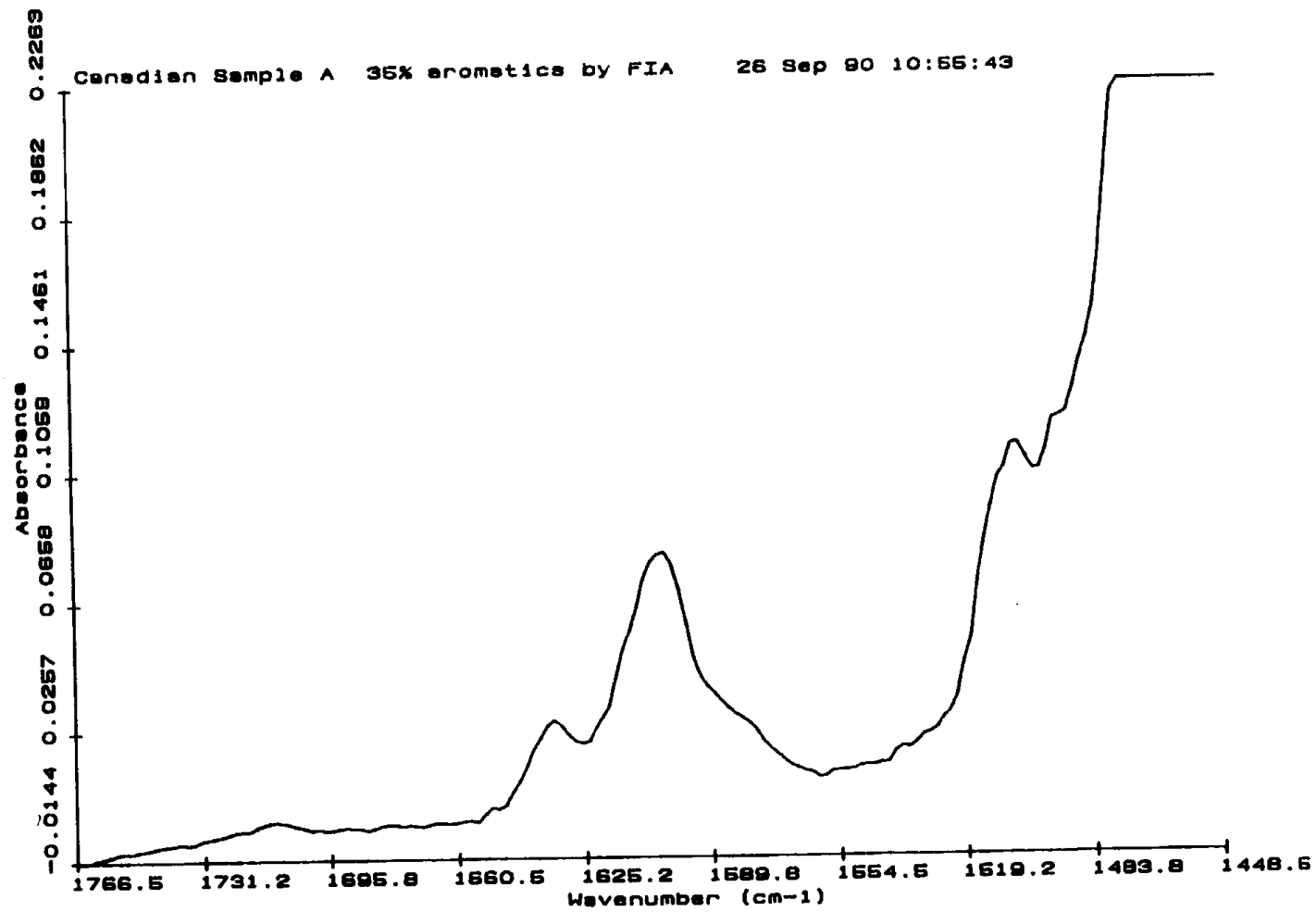


FIGURE 9. Infrared Spectrum of Canadian Sample E

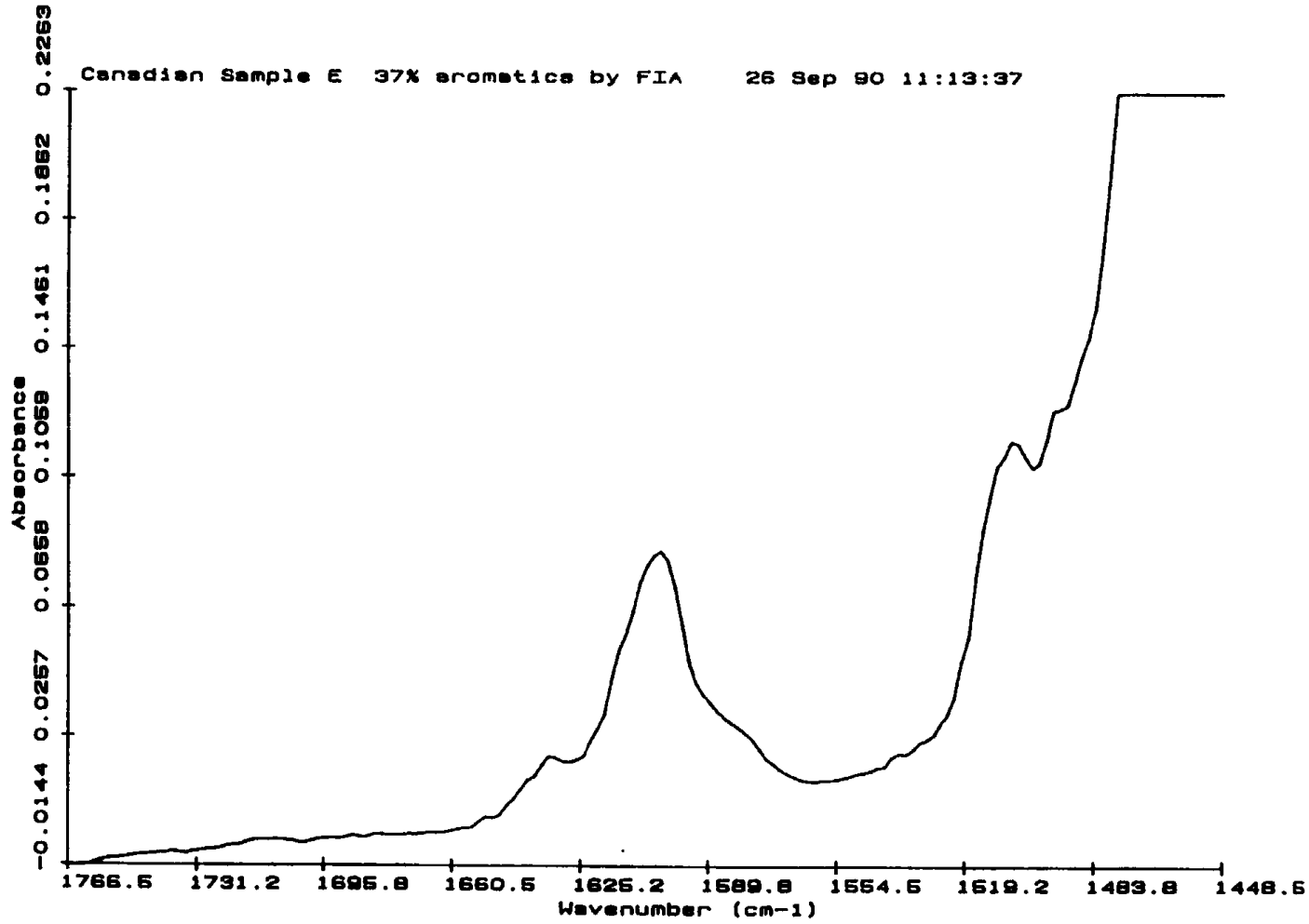


FIGURE 10. Infrared Spectrum of Canadian Sample G

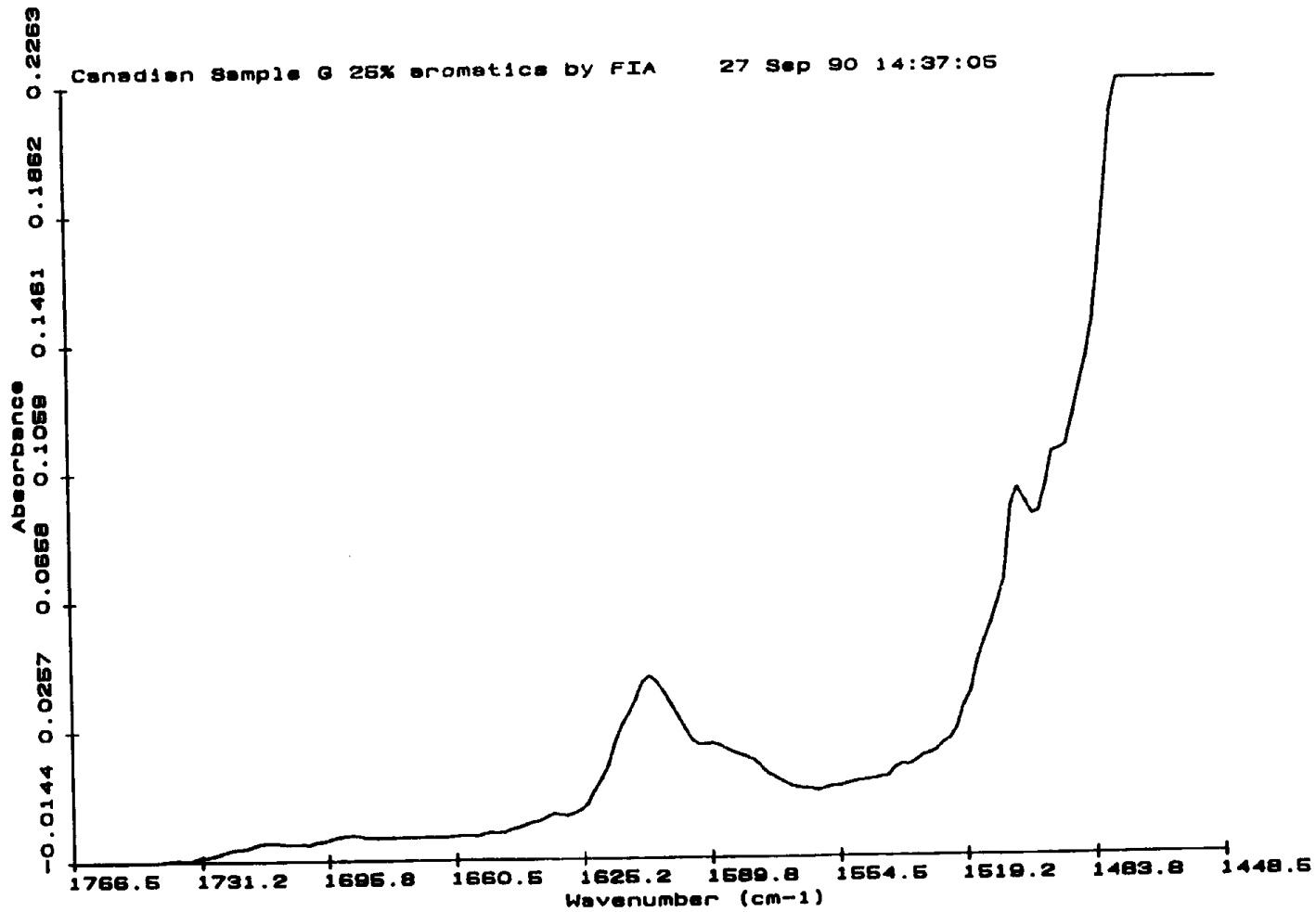


FIGURE 11. Infrared Spectrum of Canadian Sample M

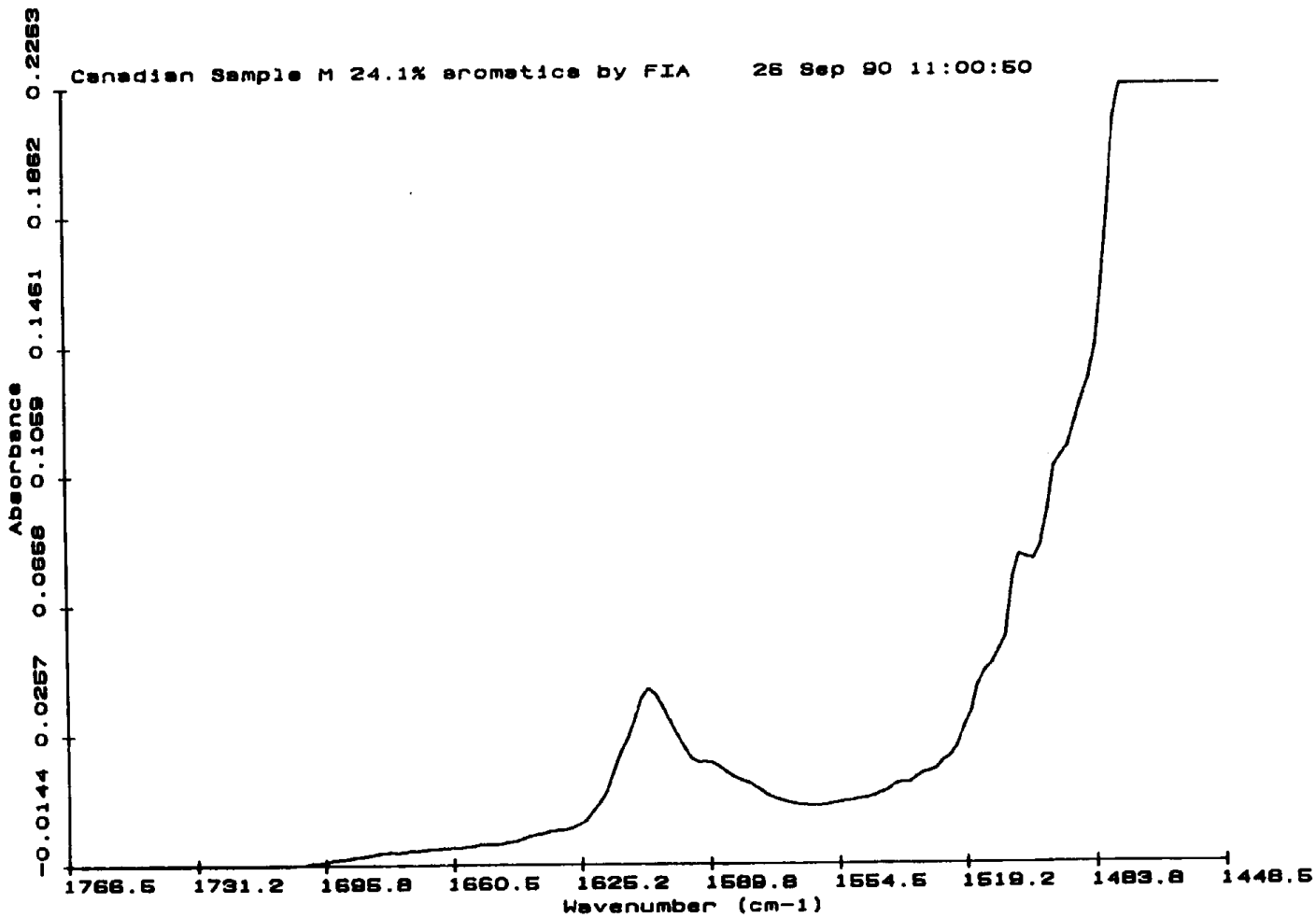


FIGURE 12. Infrared Spectrum of Canadian Sample O

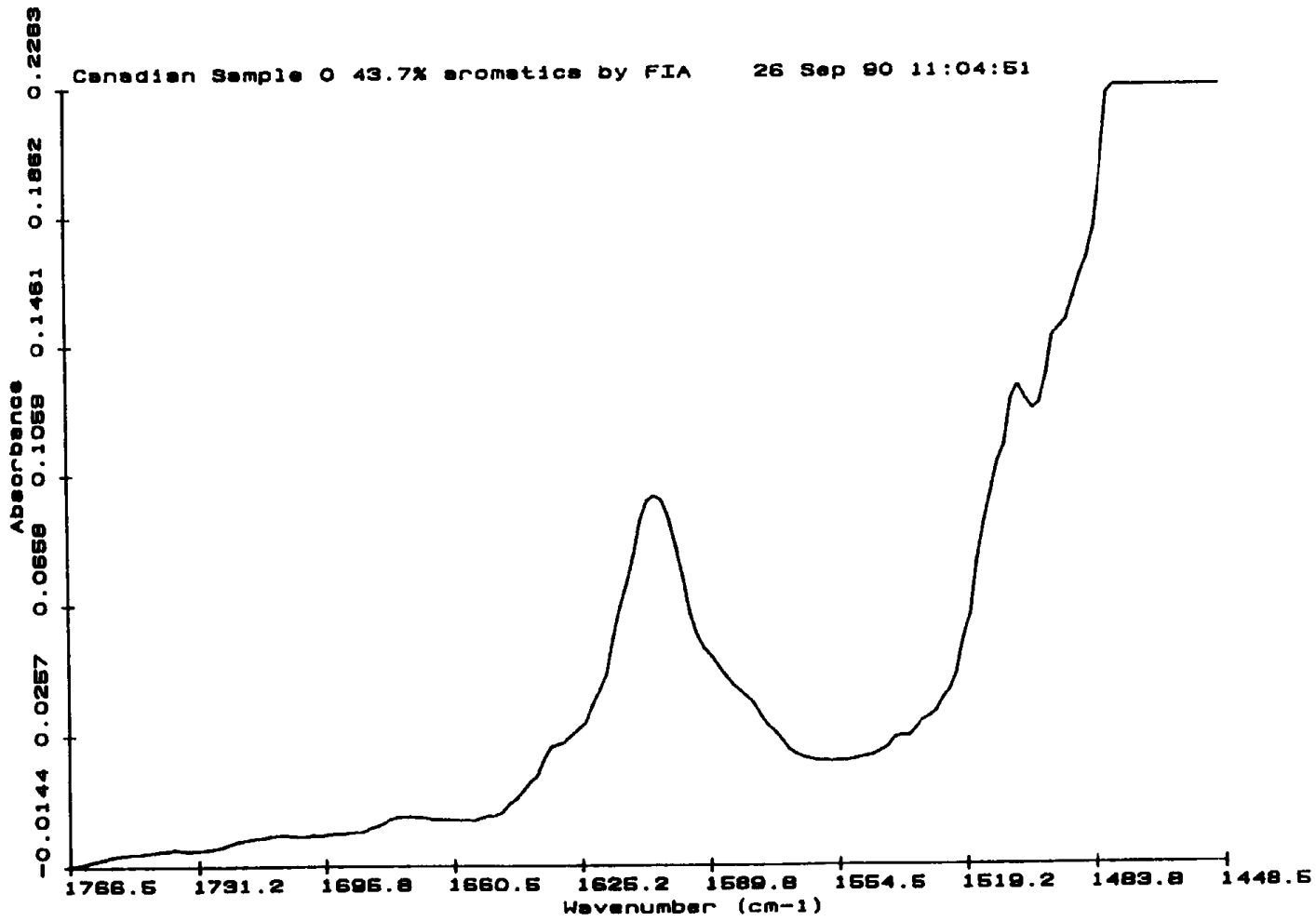


FIGURE 13. Infrared Spectrum of Canadian Sample R

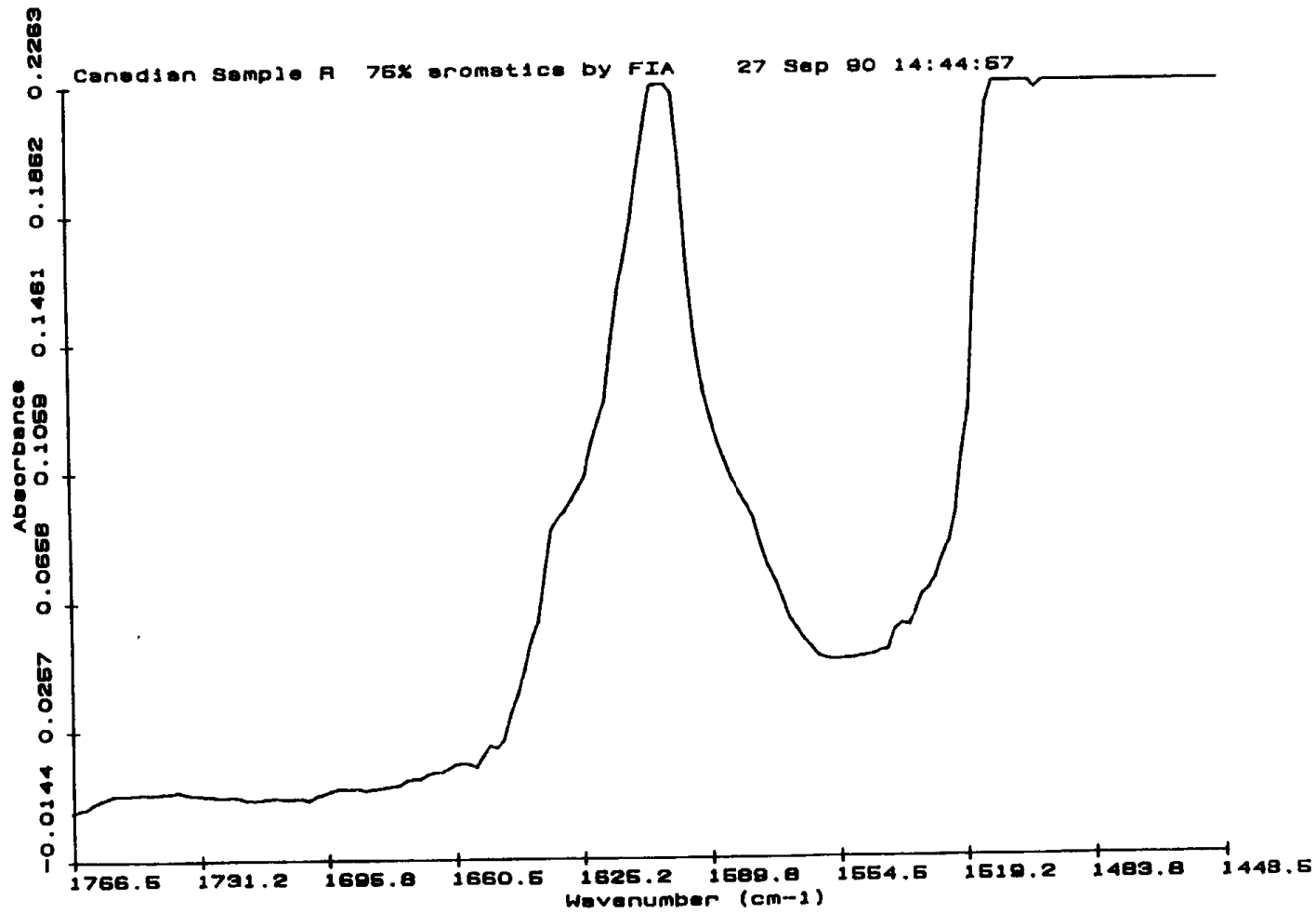


FIGURE 14. FTIR vs FIA, Canadian Samples

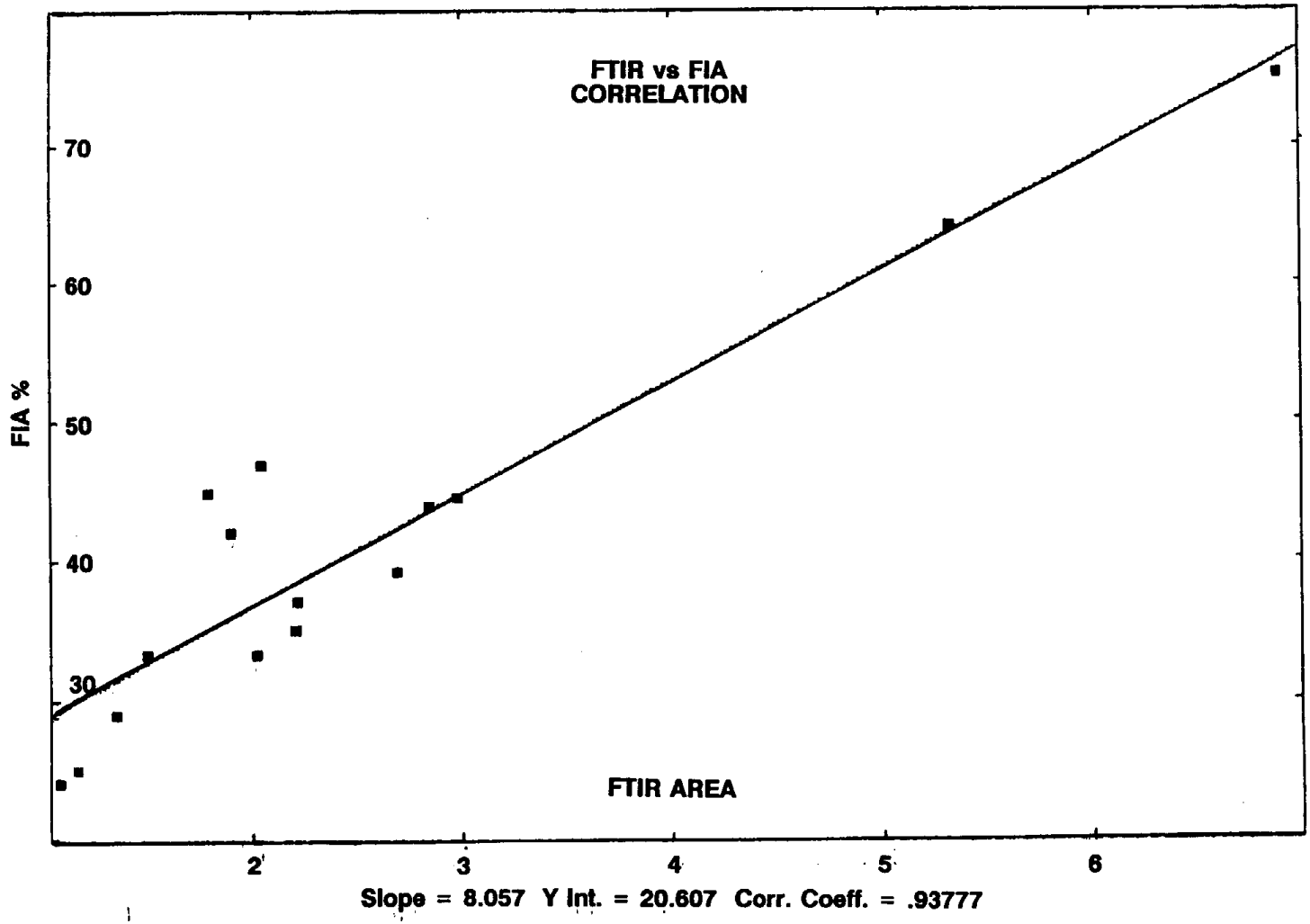


FIGURE 15. FTIR vs SFC, Canadian Samples

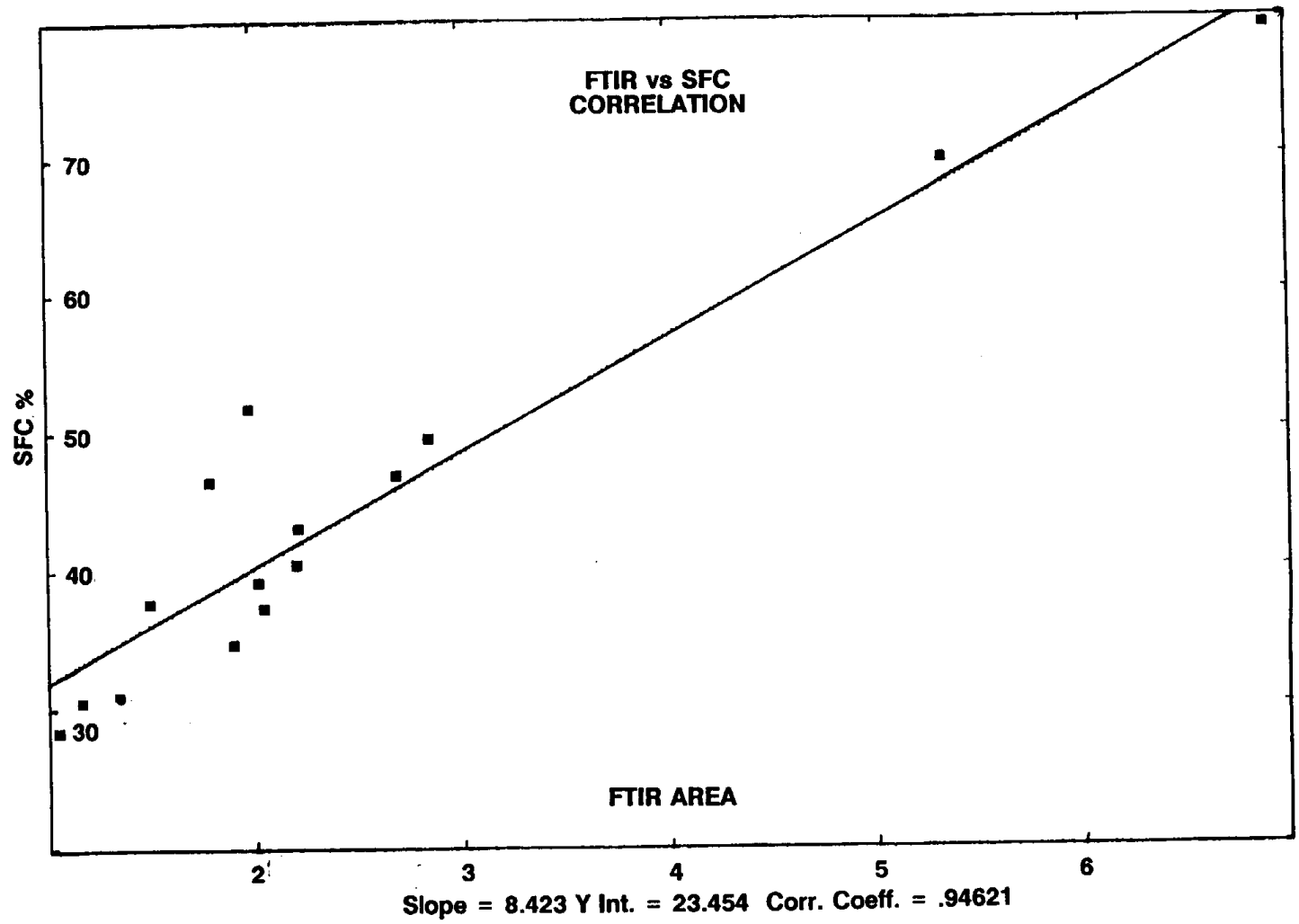


FIGURE 16. FTIR vs UV (TOTAL), Canadian Samples

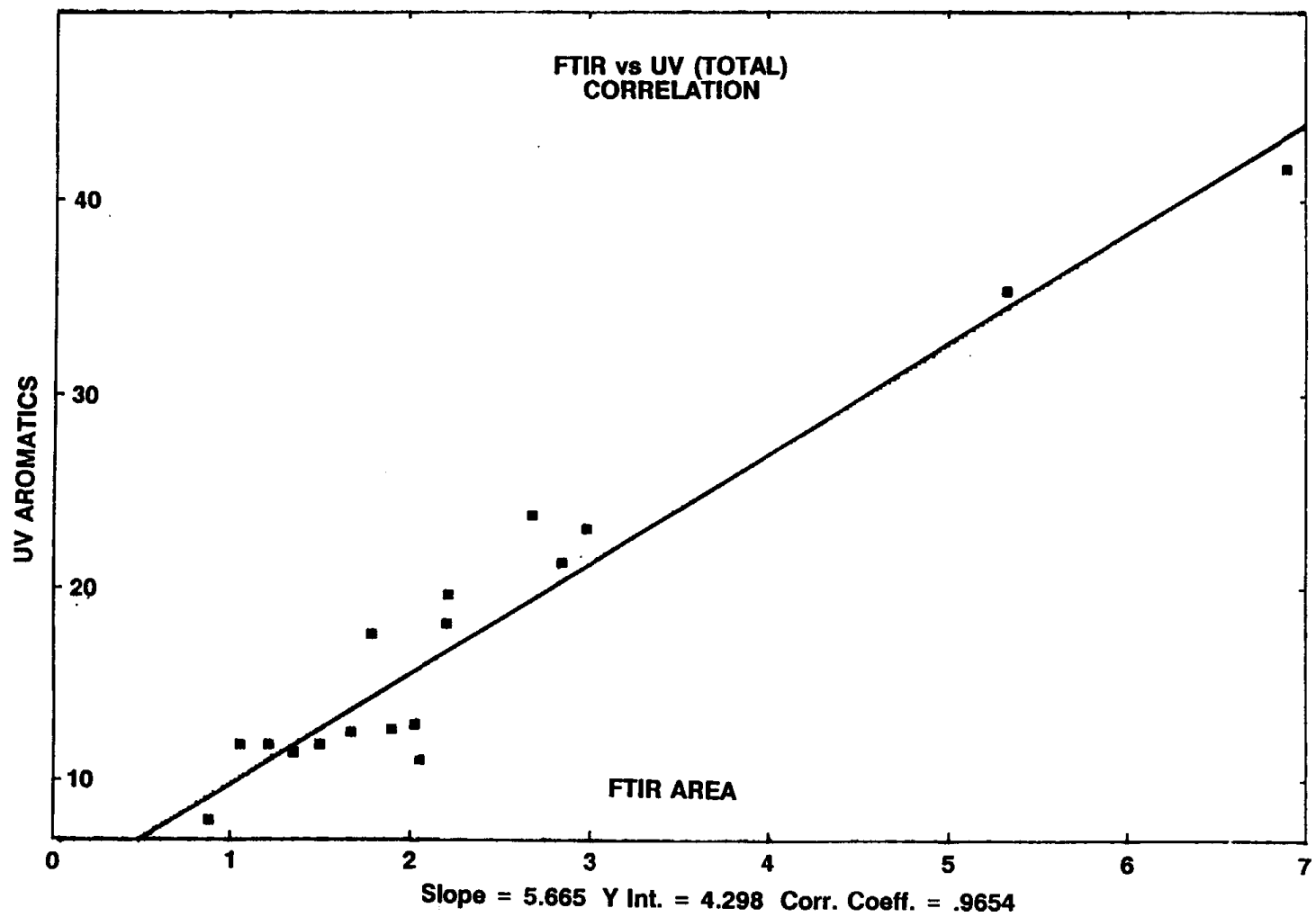


FIGURE 17. FTIR vs NMR, Canadian Samples

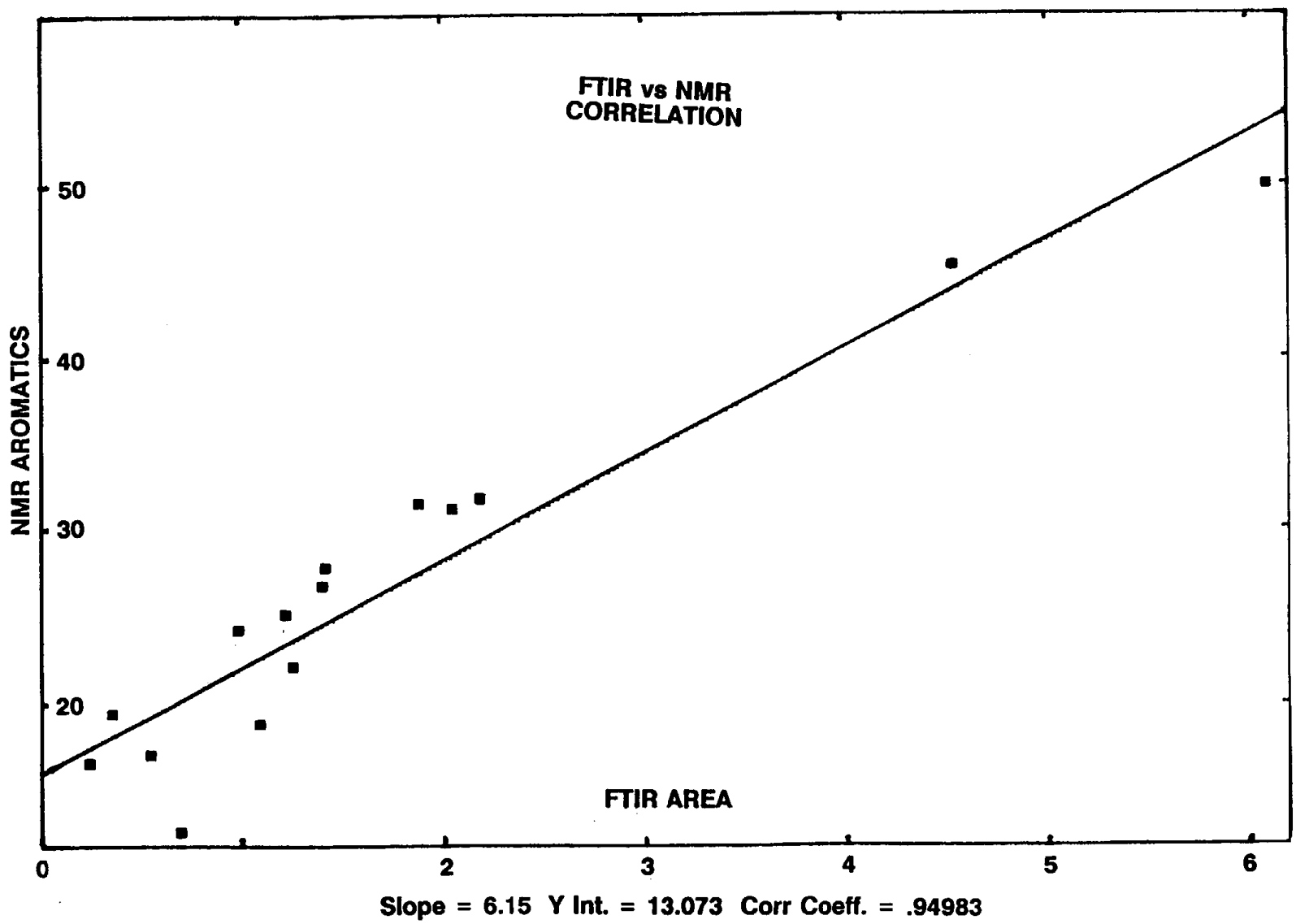
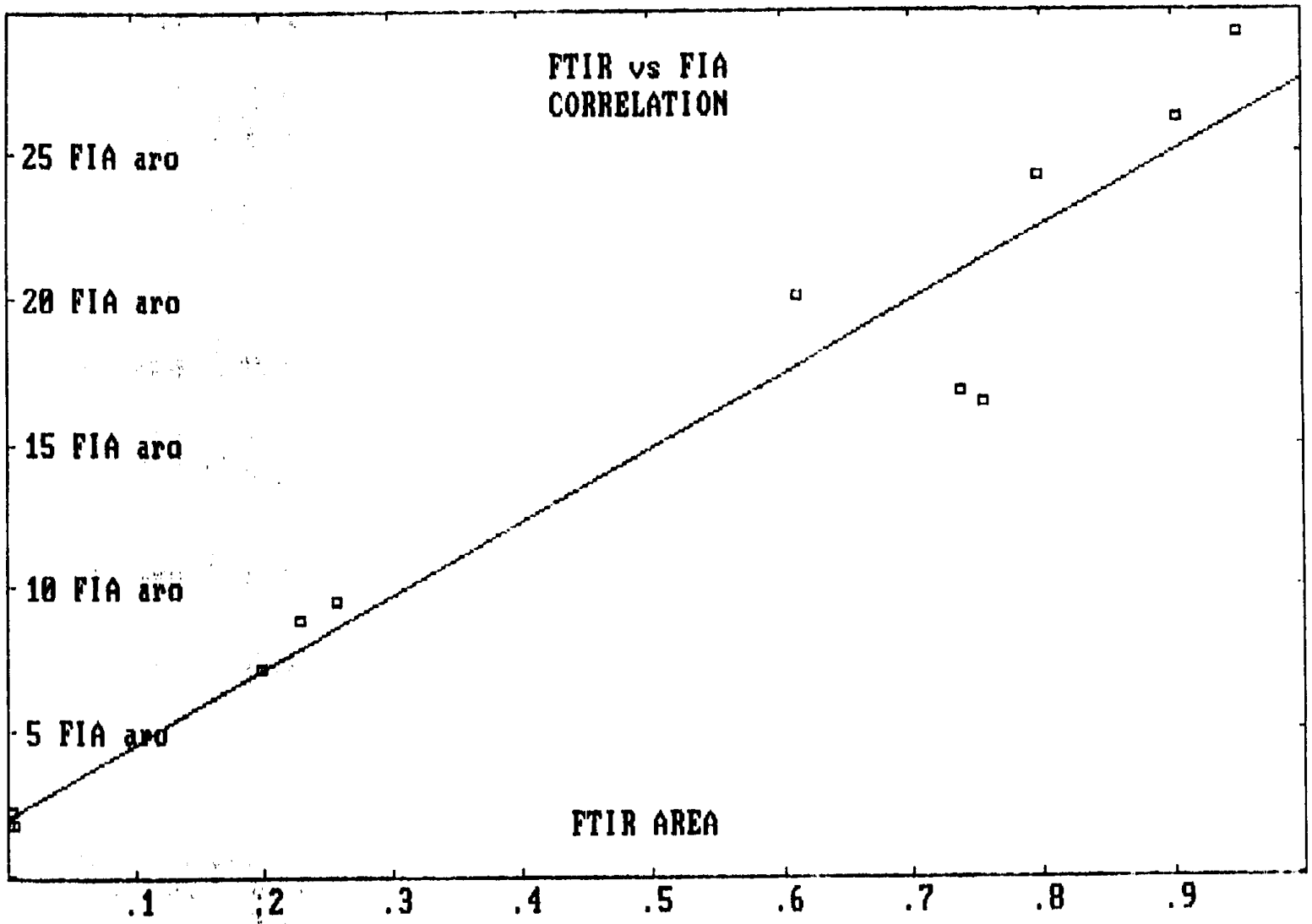
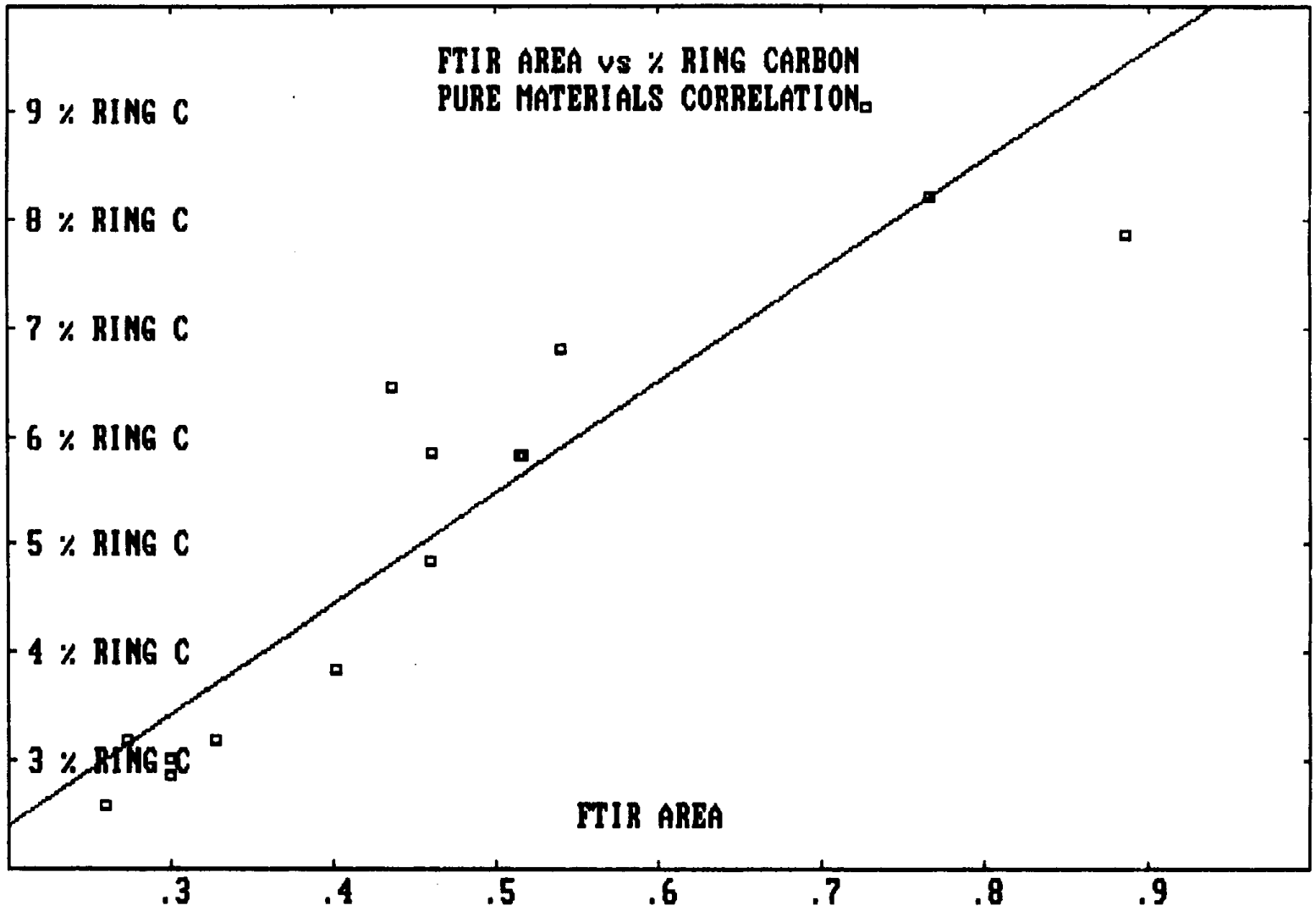


FIGURE 18. FTIR vs FIA, CARB Samples



Slope = 25.527 Y Int.= 1.975 Corr Coeff.= .97095

FIGURE 19. FTIR vs Ring Carbon, Pure Materials



Slope = 10.337 Y Int.= .318 Corr Coeff.= .92146

FIGURE 20. FTIR (ATR) vs FTIR (TRANS)

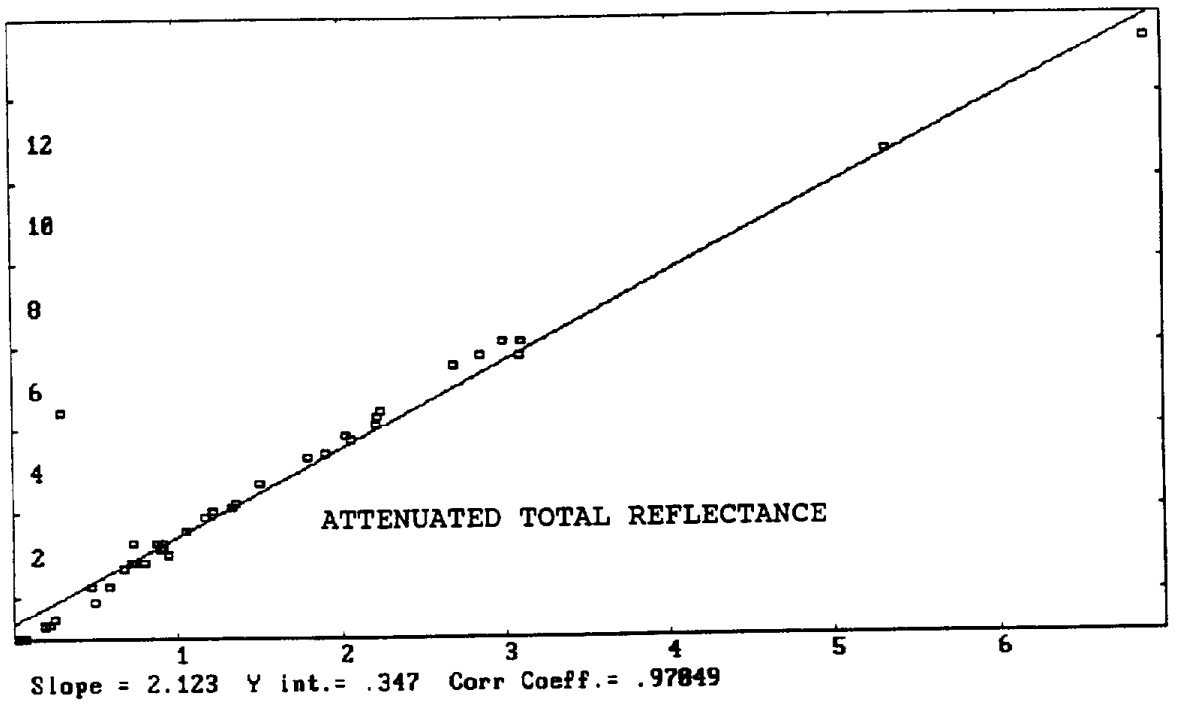


FIGURE 21. Density vs Aromatics (FIA)

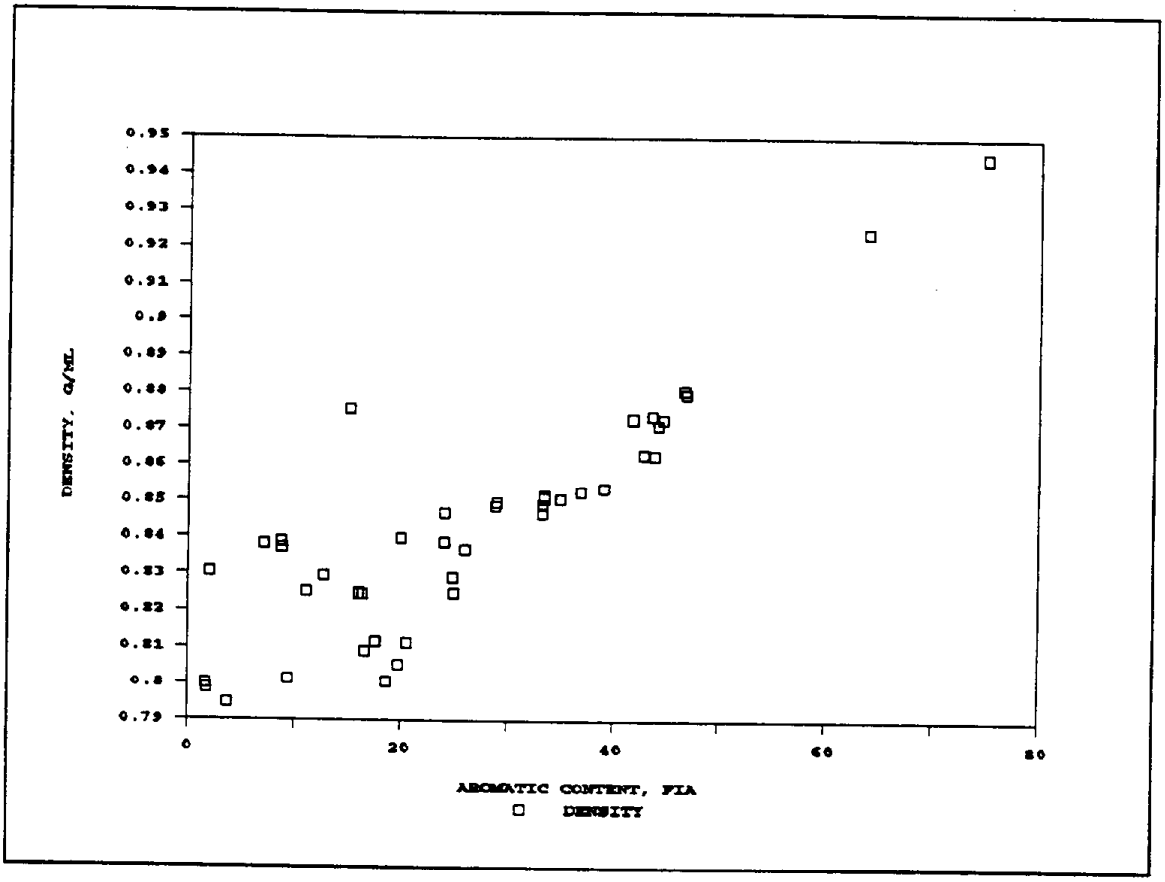


FIGURE 22. IR Spectrum of 44% Aromatic, No Cetane Improver

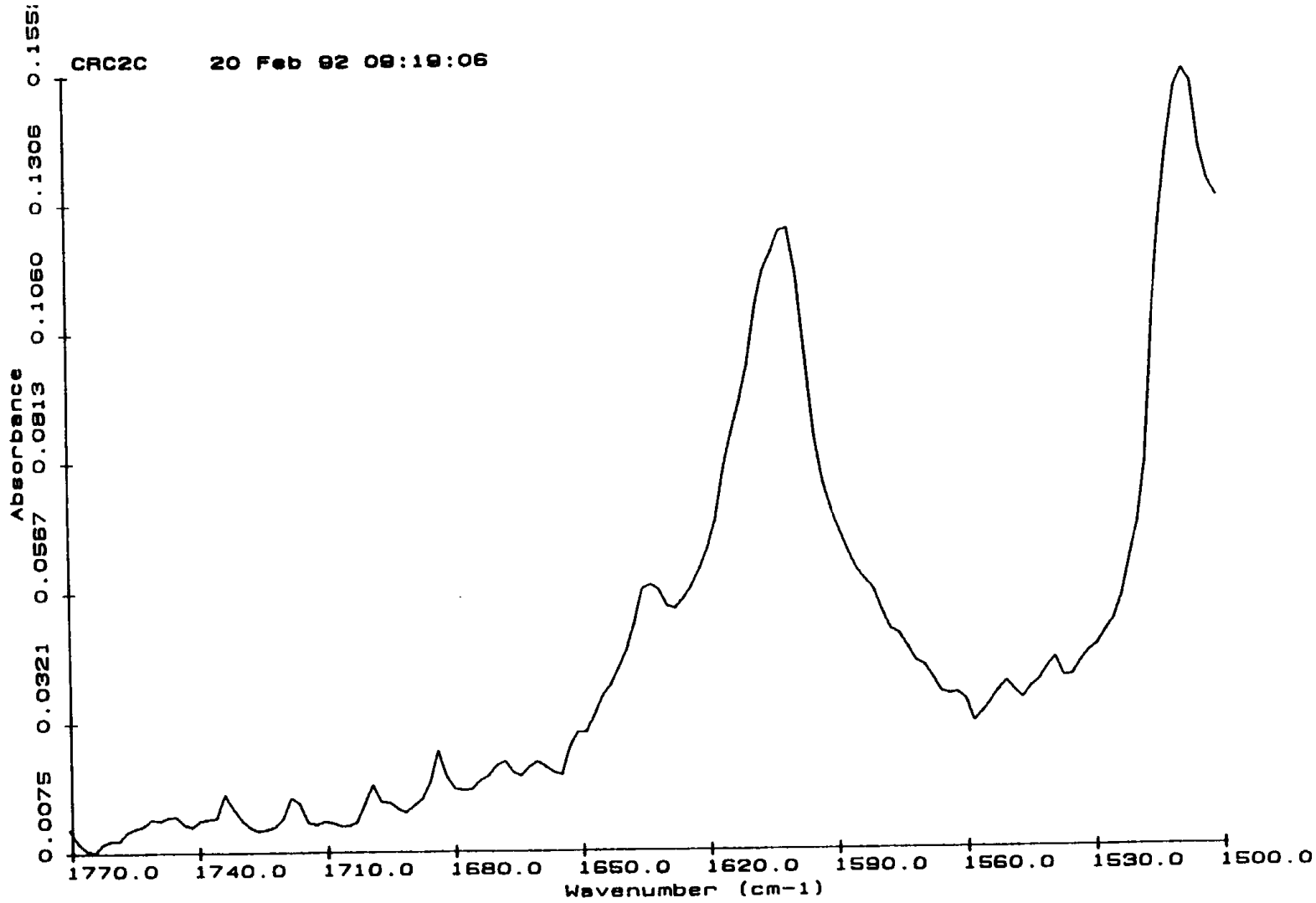


FIGURE 23. IR Spectrum of 44% Aromatic, 0.30wt% Cetane Improver

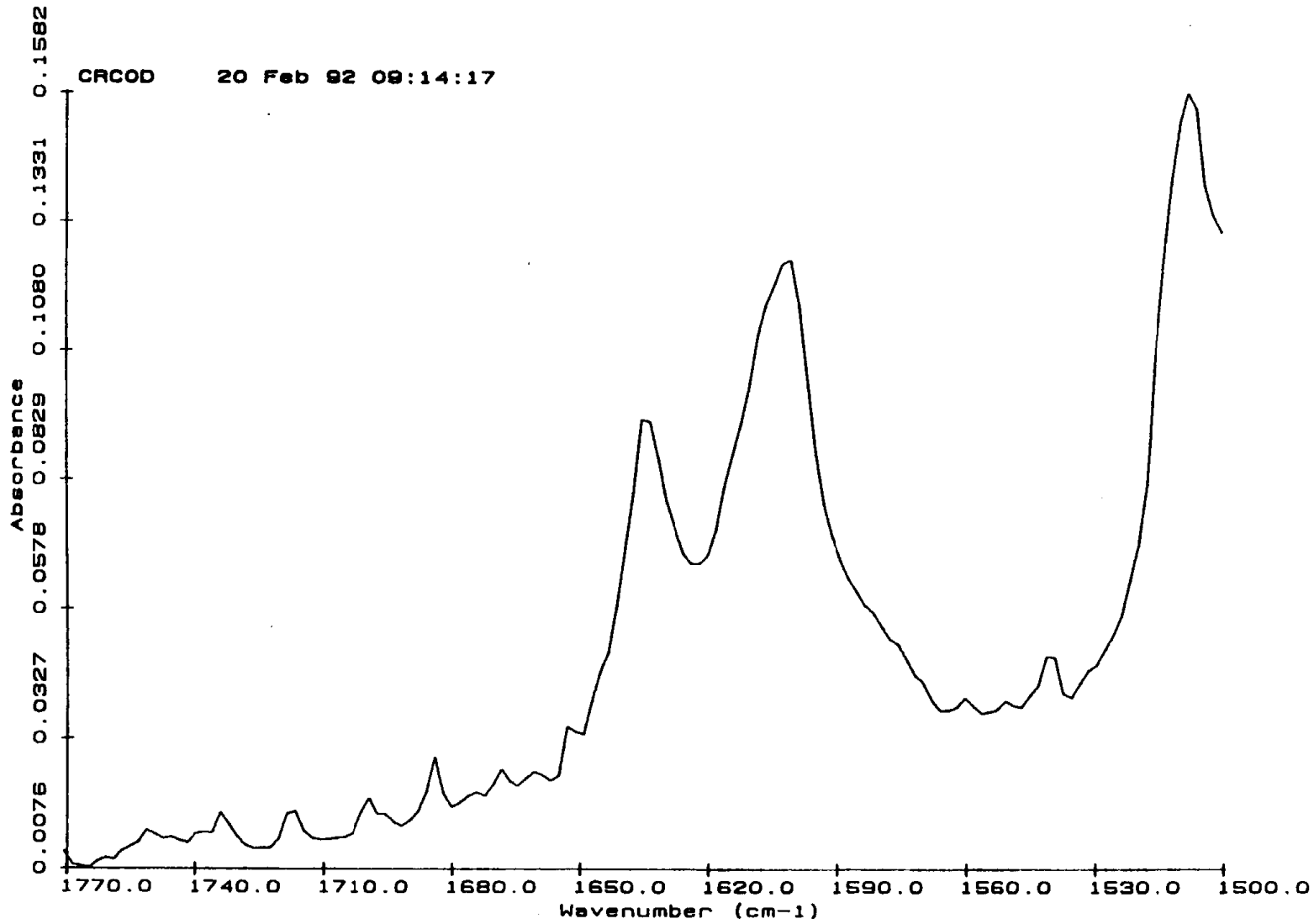


FIGURE 24. FTIR vs FIA, Gasoline Samples

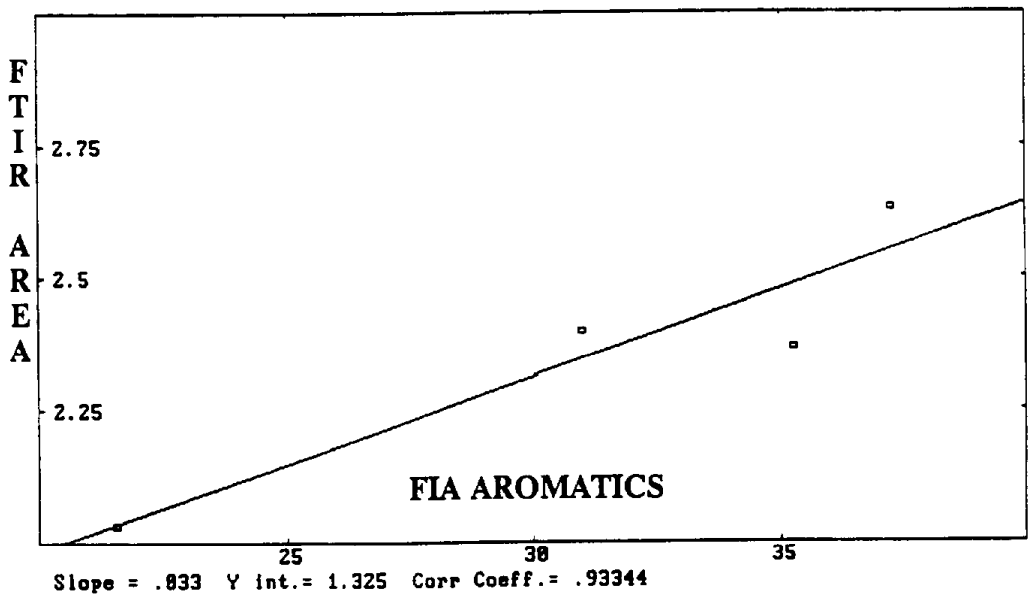


FIGURE 25. IR Spectrum of
Gasoline with 21.6% Aromatics, 24.9% Olefins

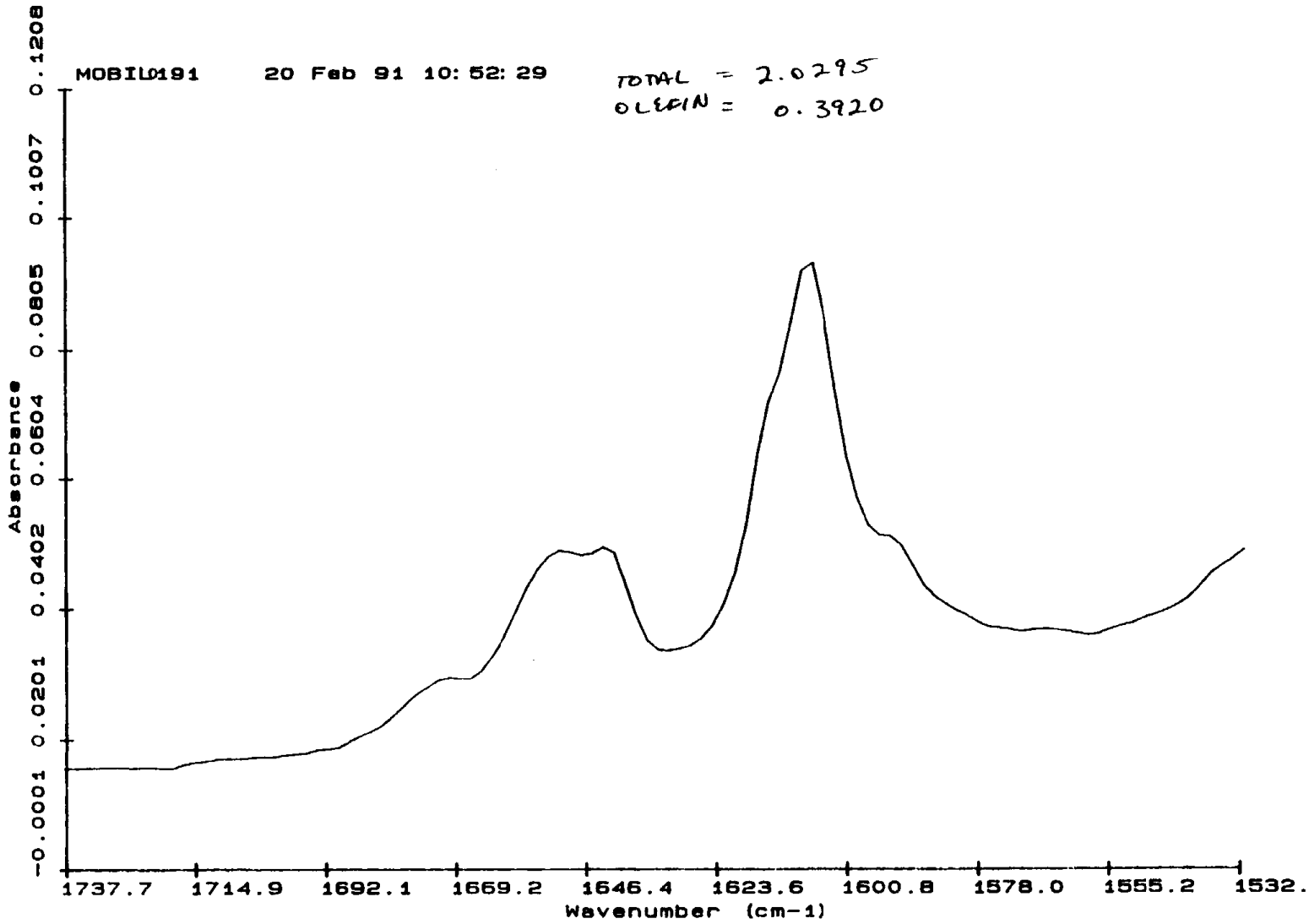


FIGURE 26. IR Spectrum of Gasoline, 37.3% Aromatic, 4.9% Olefin

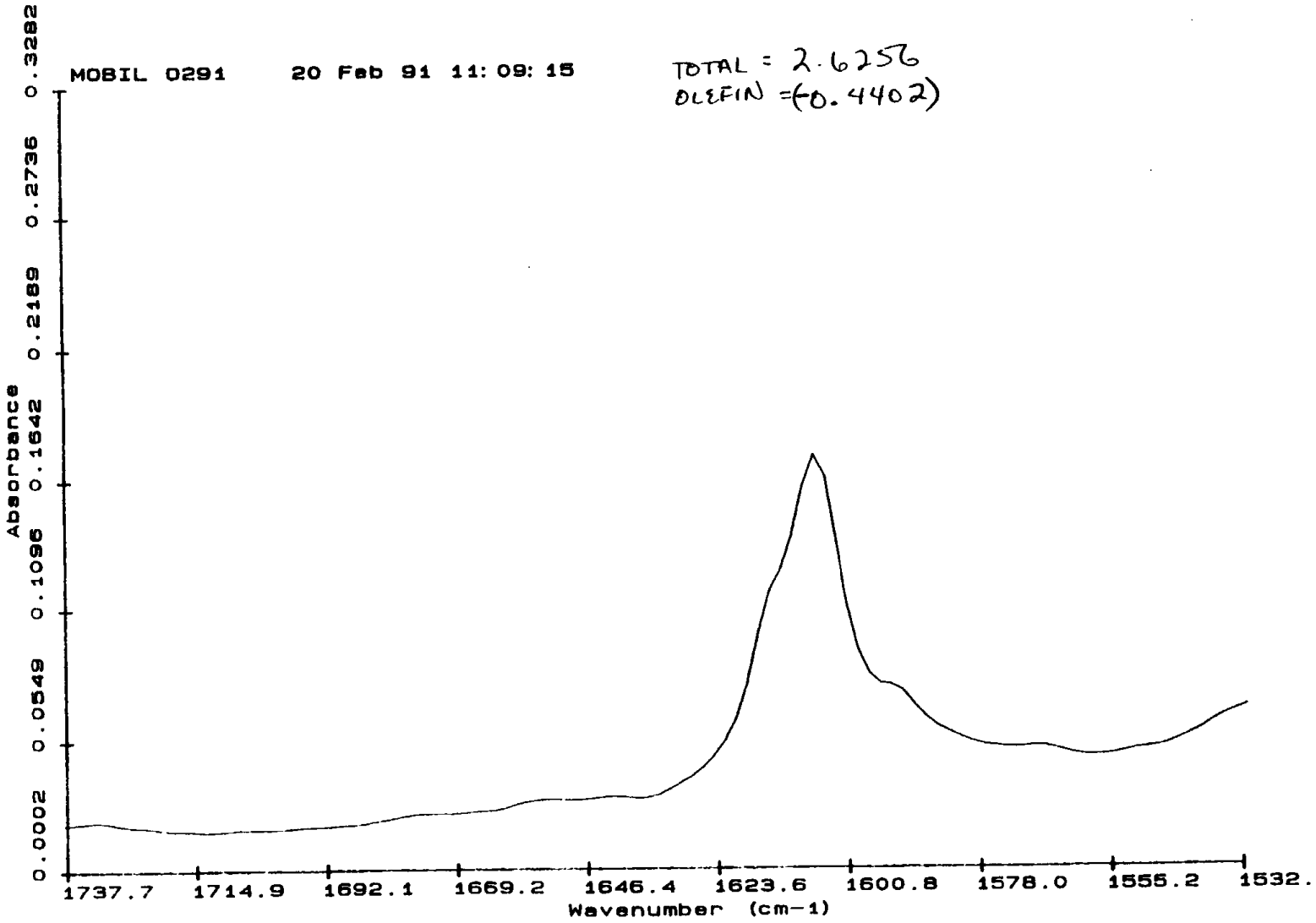
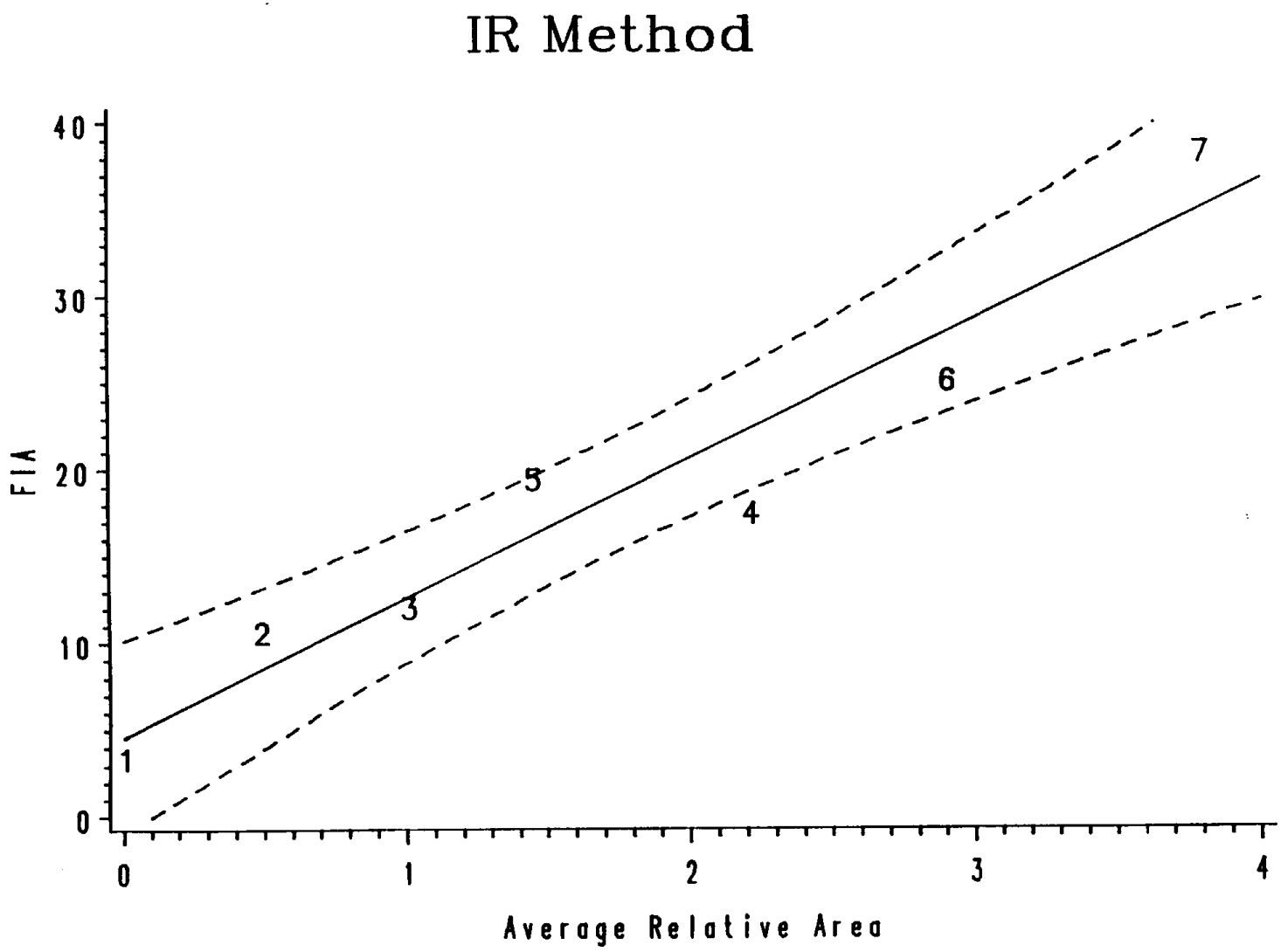


FIGURE 27. Correlation of IR Relative Area to FIA



Optical Principle

The optical diagram of the DU Series 7000 Spectrophotometer is shown in

FIGURE 28. UV Instrument Schematic

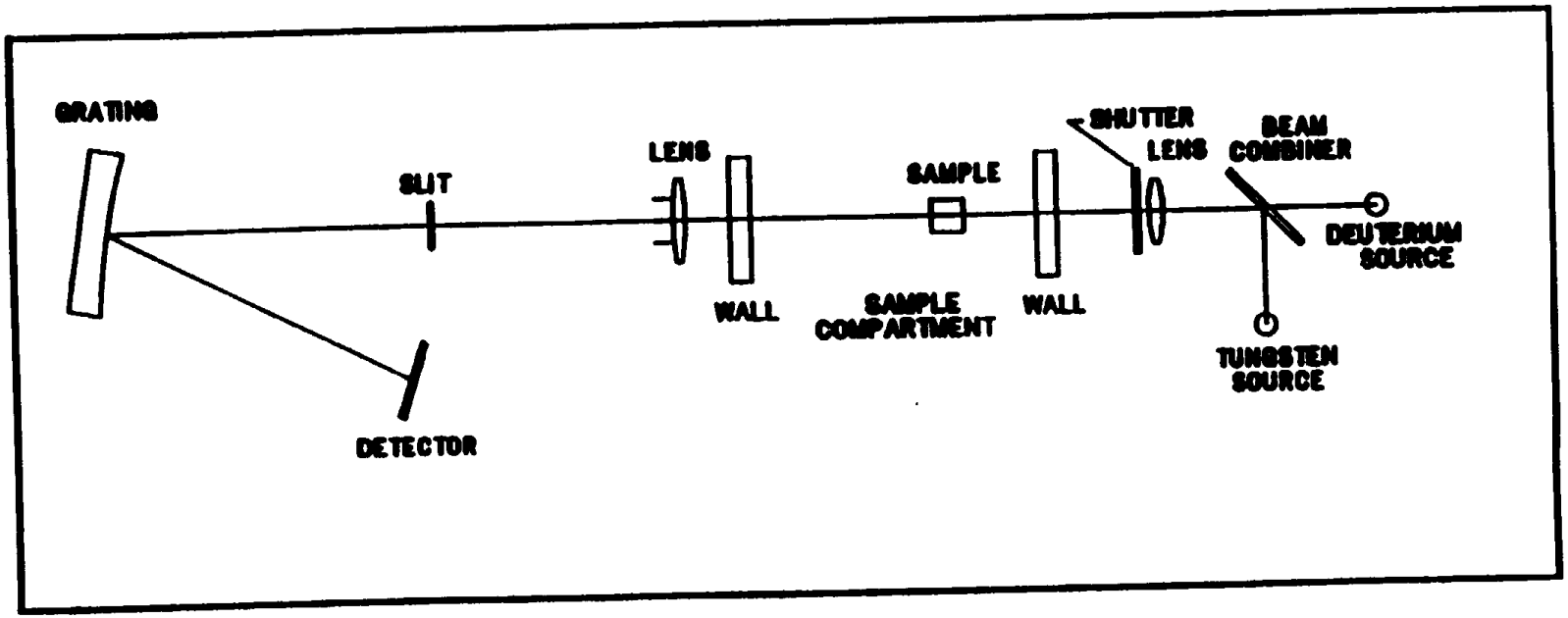


FIGURE 29. UV Spectrum of Tridecylbenzene

Wavelength Scan HELP

ReadSamples Tabulate +-*Scans Scatter Method SaveClear Print Quit

Scan directory: VIEW
Start wl: 190.0 nm
End wl: 290.0 nm
Overlay scans: [Yes]

Autoprint: [No]
Autosave: [Yes]
Scans per sample: 1
Interval: 30.00 [sec]

Method name: A:\UV
Autosave name: [A:\]TRI45
Sampling device: None
Read average time: 1.50 sec

A:\M3106006 A:\M3106008 A:\M3106005

Print ↓ ↑ ← → Exit

A:\M3106006 Scan

wl	Abs	Pick
195.0	1.6789	pt
196.0	1.8333	pk
209.0	1.3080	pk
225.0	0.1051	pt
255.0	0.0561	pt
261.0	0.0592	pk

Zoom ZoomOut Trace Function Autoscale Annotate Print

Functions: Scan

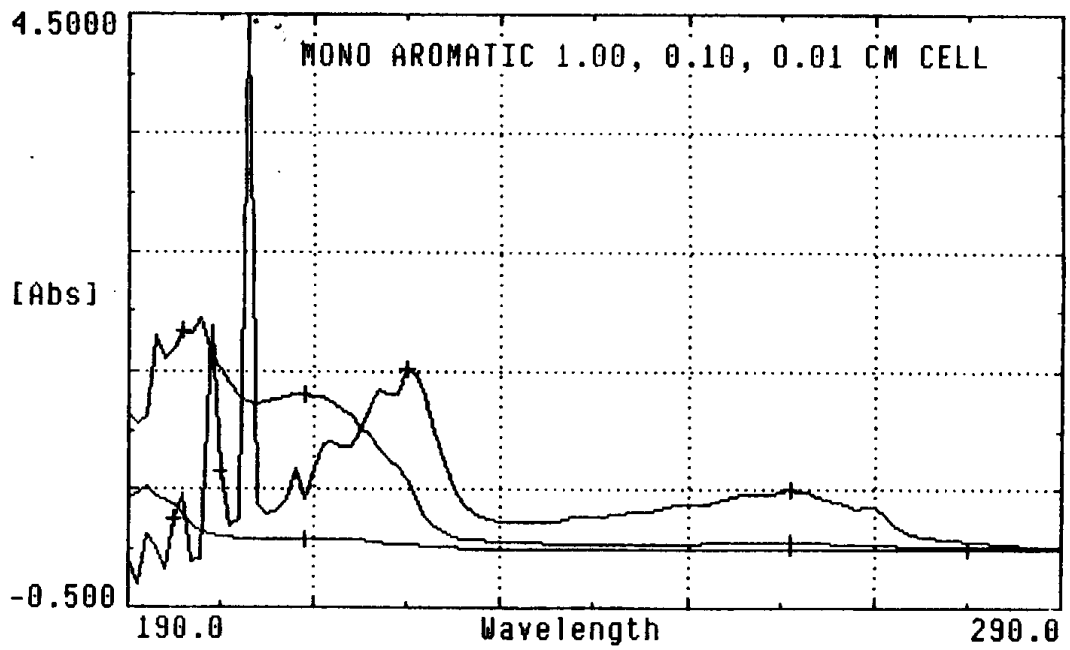


FIGURE 30. UV Spectrum of Dimethylnaphthalene

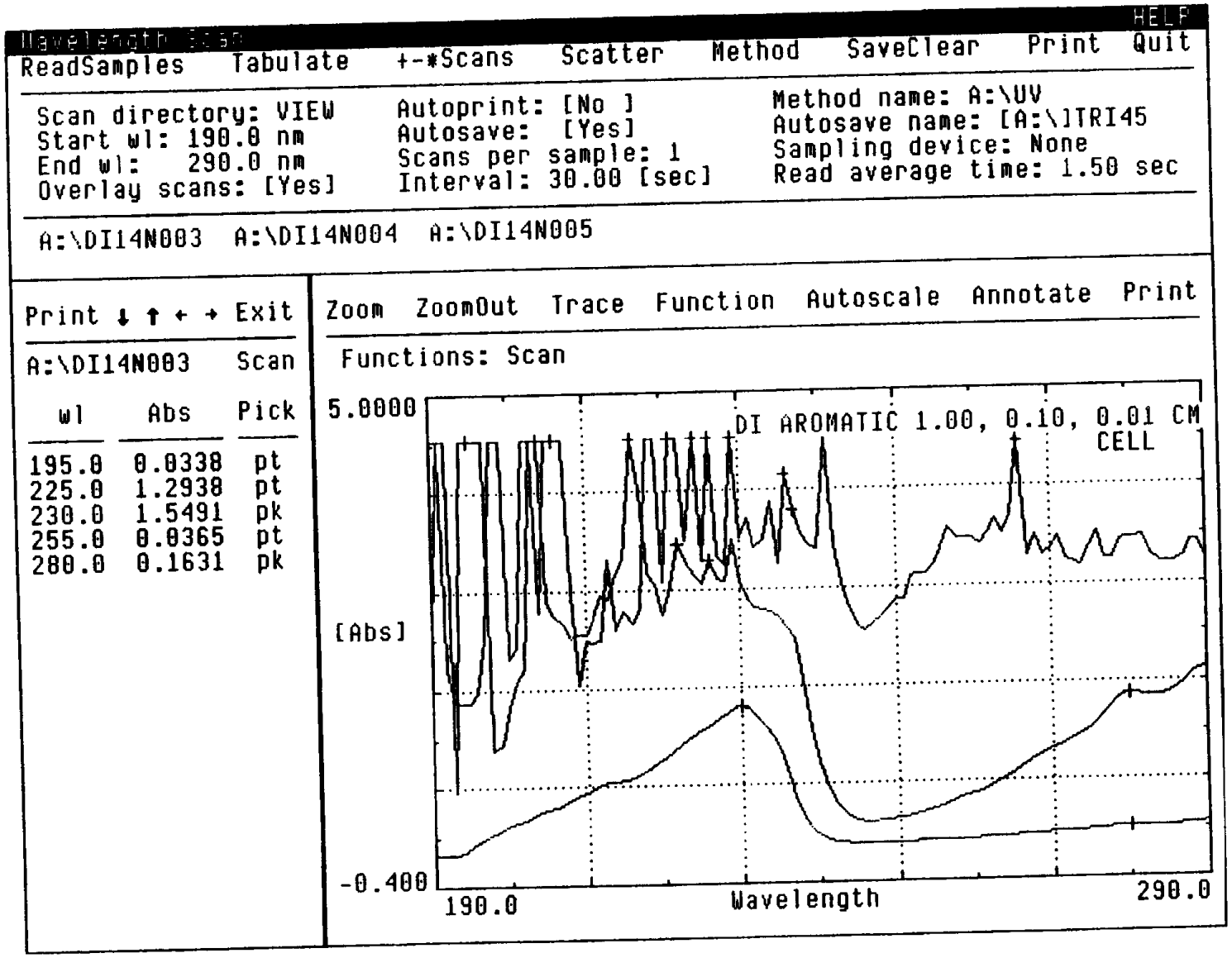


FIGURE 31. UV Spectrum of Methylenephenanthrene

Wavelength Scan HELP

ReadSamples Tabulate +-*Scans Scatter Method SaveClear Print Quit

Scan directory: VIEW
Start wl: 190.0 nm
End wl: 290.0 nm
Overlay scans: [Yes]

Autoprint: [No]
Autosave: [Yes]
Scans per sample: 1
Interval: 30.00 [sec]

Method name: A:\UV
Autosave name: [A:\]TRI45
Sampling device: None
Read average time: 1.50 sec

A:\TRI45016 A:\TRI45017 A:\TRI45019

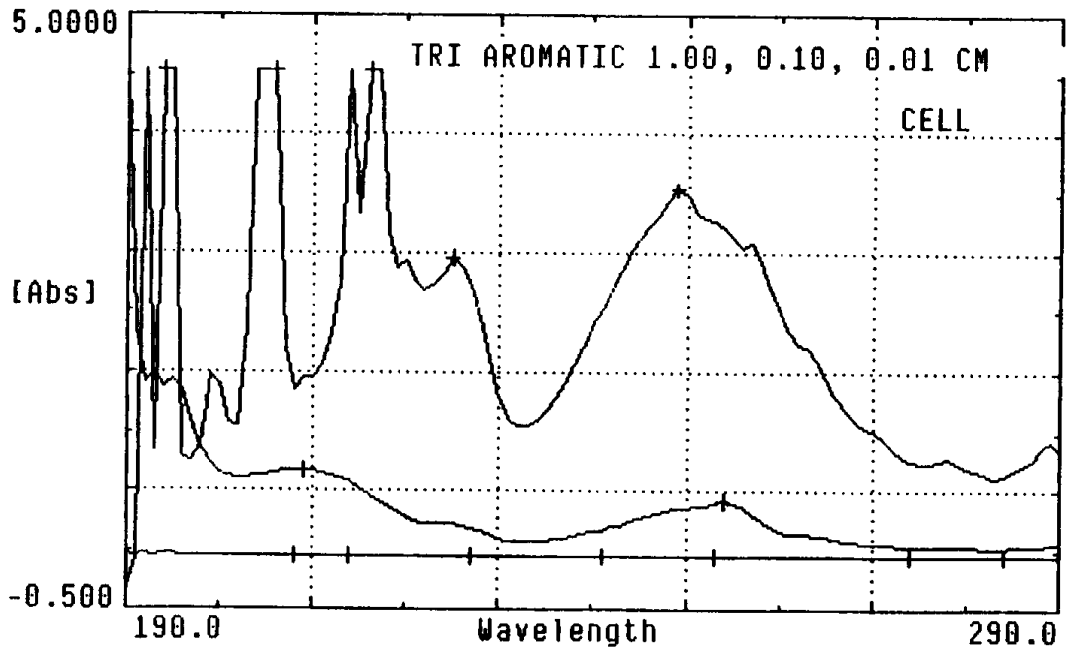
Print ↓ ↑ ← → Exit

A:\TRI45016 Scan

wl	Abs	Pick
194.0	4.5000	pk
195.0	4.5000	pt
206.0	4.5000	pk
216.0	4.5000	pk
225.0	2.7489	pk
225.0	2.7489	pt
249.0	3.3888	pk
255.0	2.9237	pt

Zoom ZoomOut Trace Function Autoscale Annotate Print

Functions: Scan



UV Method

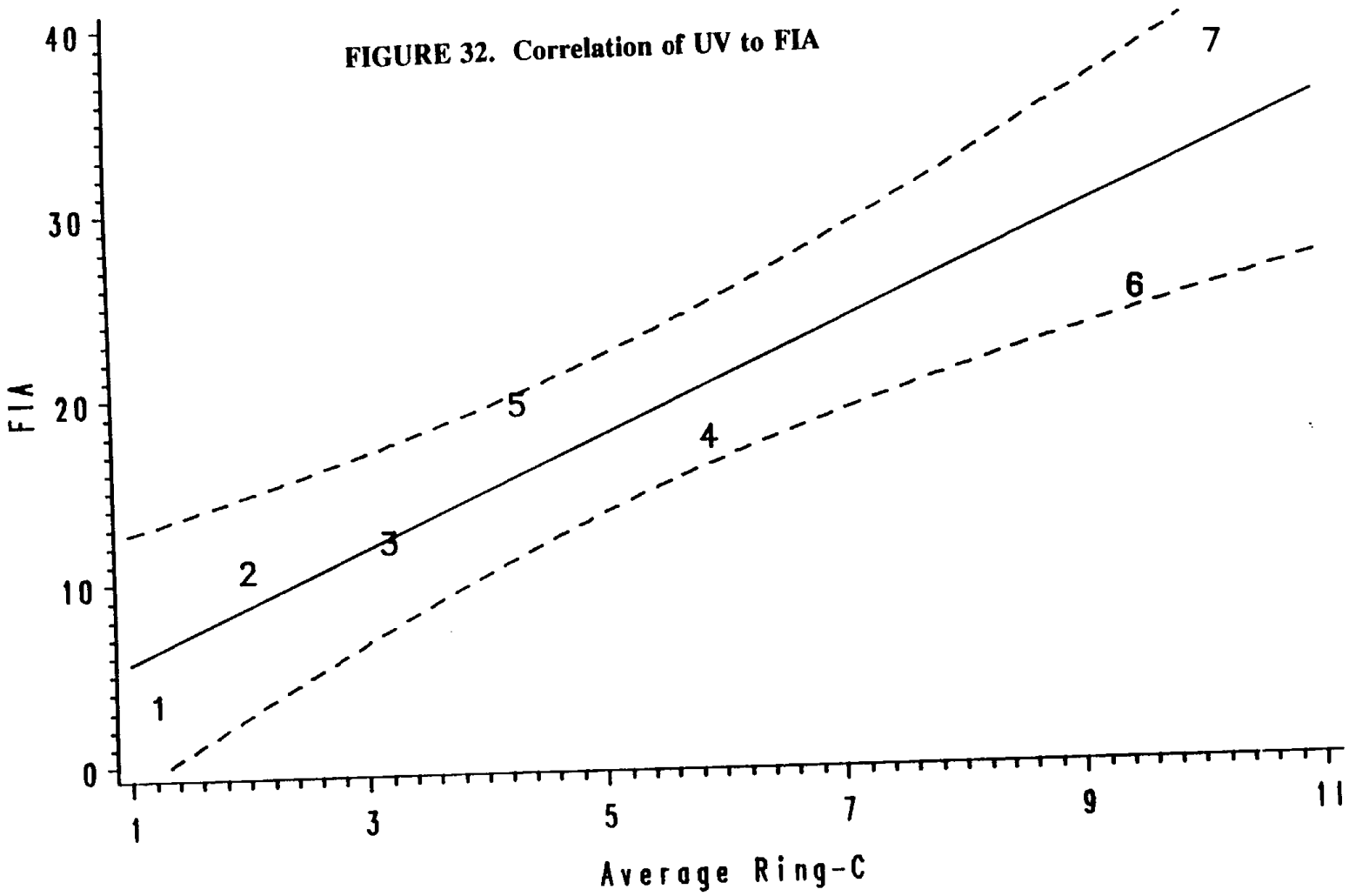


FIGURE 32. Correlation of UV to FIA
FIA
40
30
20
10
0
1
3
5
7
9
11
Average Ring-C
1
2
3
4
5
6
7

AVERAGE FIA BY FUEL SAMPLE

FIGURE 33. FIA Data for Round-Robin Samples

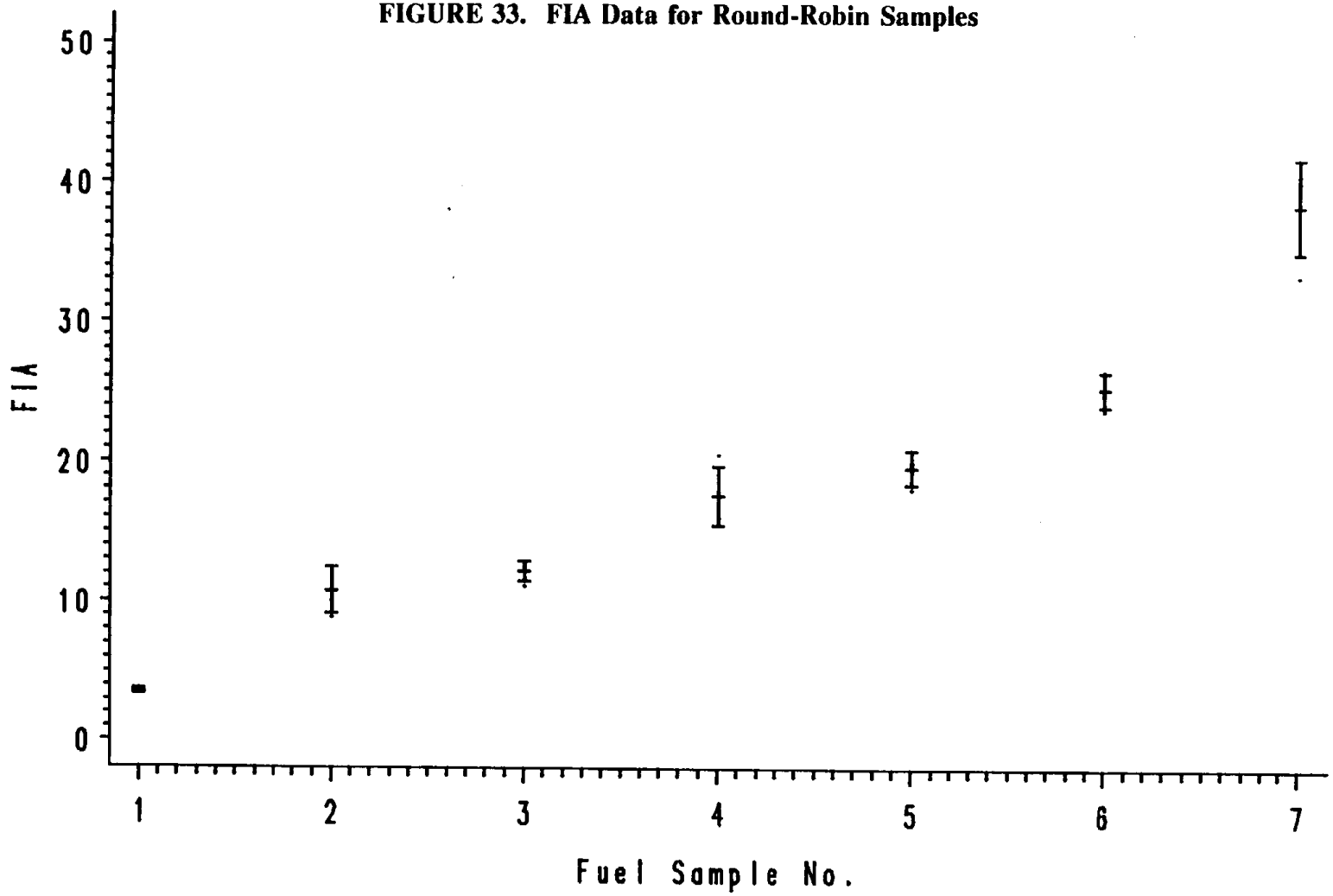
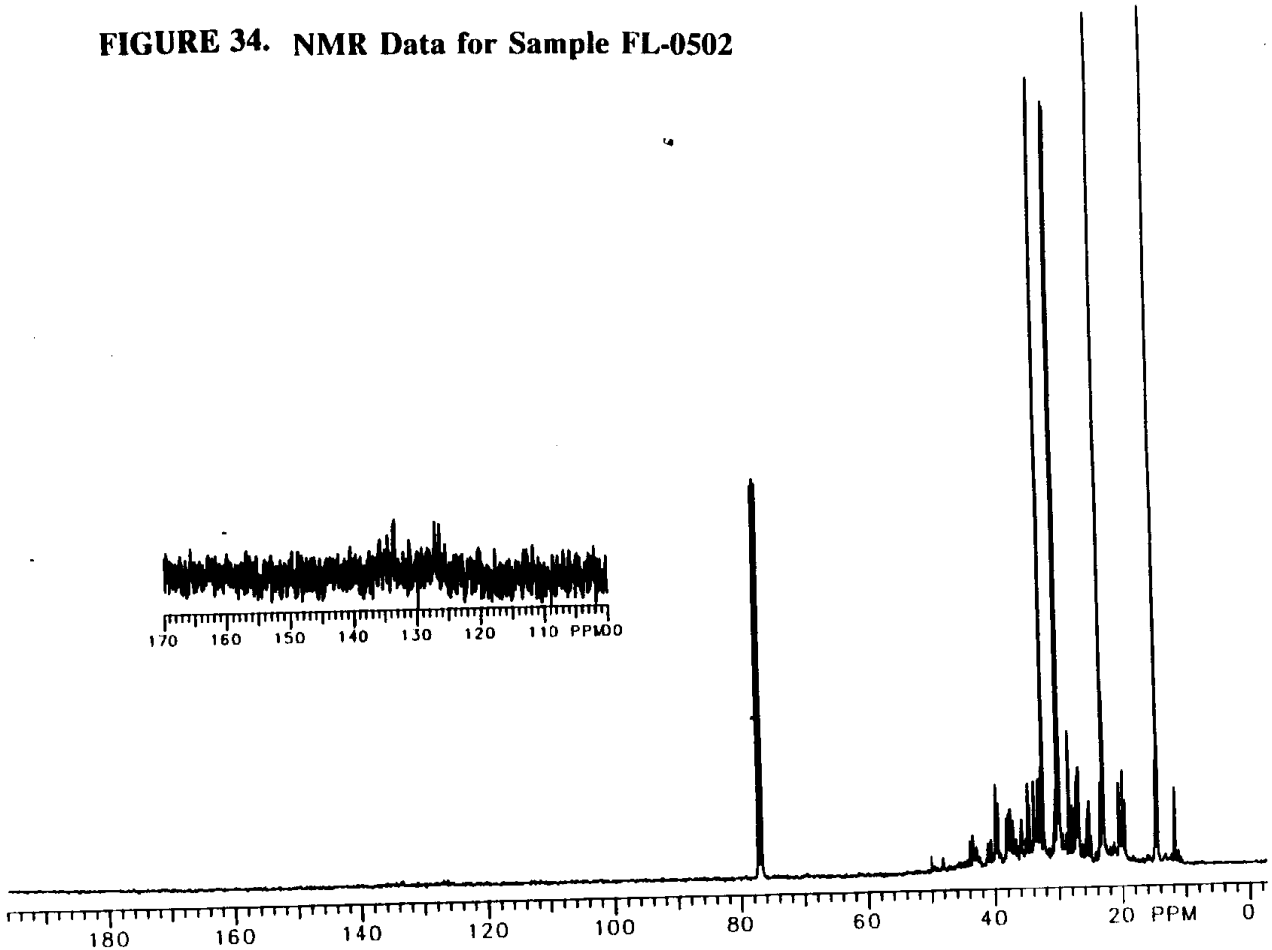


FIGURE 34. NMR Data for Sample FL-0502



ROUND ROBIN 11
PROGRESSIVE STA T1
CDCL3
TEMP=+18 5

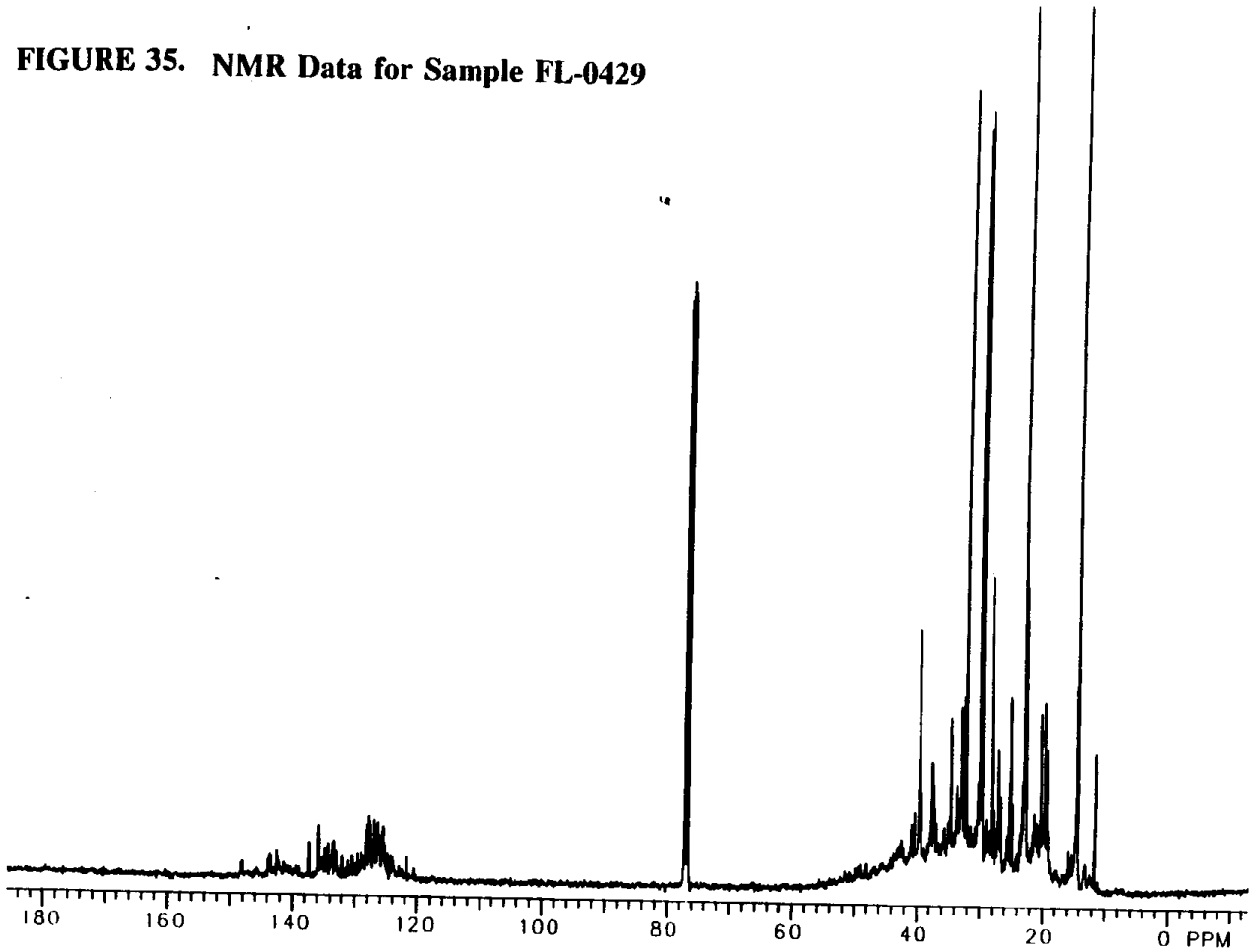
EXP7 PULSE SEQUENCE STD13C
DATE 04-30-91
SOLVENT CDCL3
FILE C
INDEX 5 1. 1

ACQUISITION		DEC & VT	
TN	13 750	DN	1 750
SW	20000.0	DO	0
AT	1 501	DM	NNY
NP	60032	DMM	S
PW	10 0	DMF	9900
P1	0	DHP	N
D1	ARRAY1	DLP	6
D2	0		
TO	0	PROCESSING	
NT	320	SE	0 127
CT	320	LB	2 500
PW90	13.5	MATH	F
BS	16		
SS	0	DISPLAY	
IL	Y	SP	-280 4
IN	N	WP	2000 0
DP	N	VS	129
HS	NN	SC	200
		WC	300
		IS	375
		RFL	8024 5
		RFP	7744 1
		TH	20
		INS	1 000
		AI DC	

D1 ARRAY

INDEX	VALUE	INDEX	VALUE
1	3.500	4	38 500
2	8 500	5	78 500
3	18 500		

FIGURE 35. NMR Data for Sample FL-0429



ROUND ROBIN 16
CDCL3
TEMP=+18 5
PROGRESSIVE SAT T1

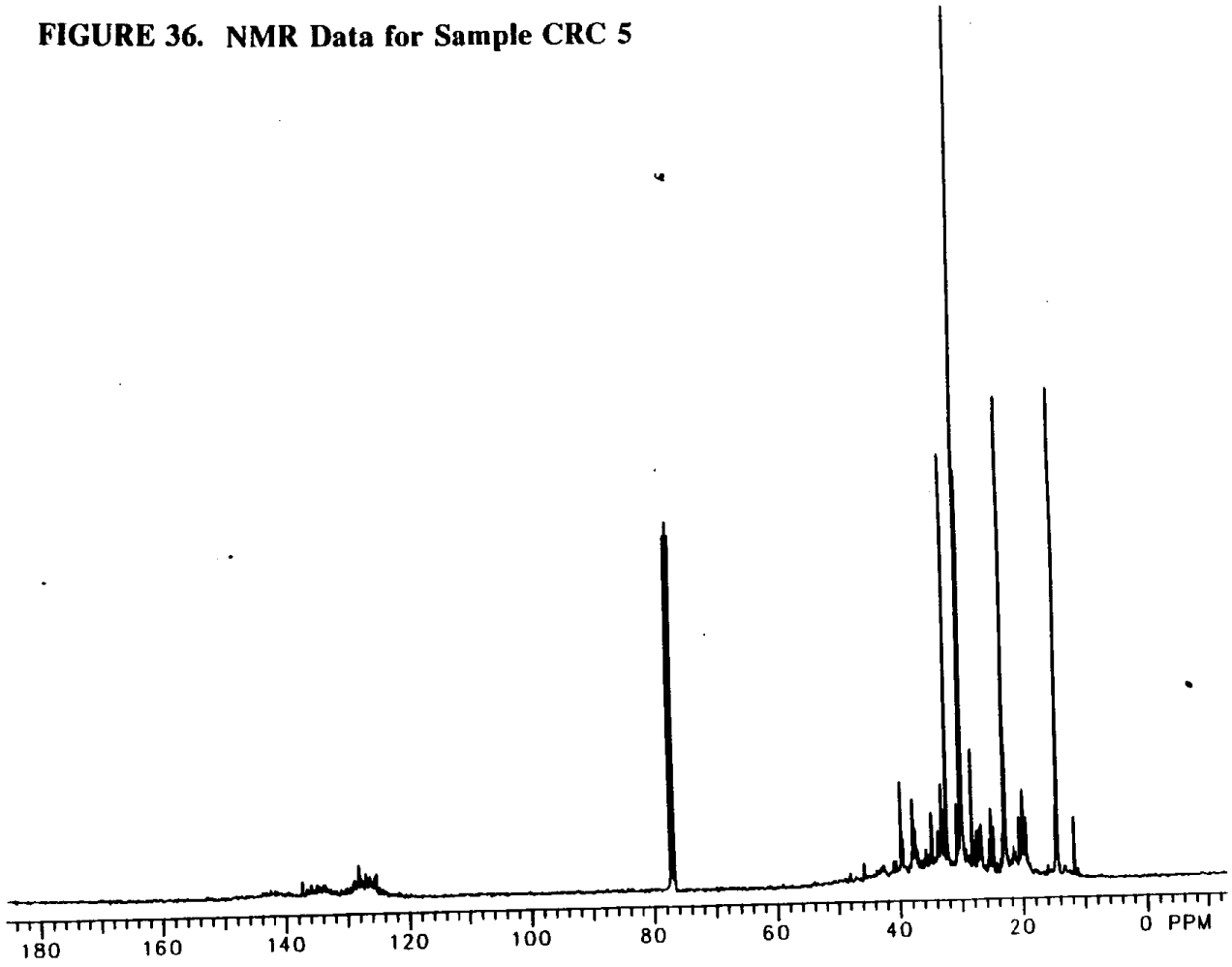
EXP8 PULSE SEQUENCE: S1D13C
DATE 05-01-91
SOLVENT CDCL3
FILE C
INDEX: 4 1 1

ACQUISITION		DEC & VT	
TN	13.750	DN	1 750
SW	20000 0	DO	0
AT	1.501	DM	NNY
NP	60032	DMM	S
PW	10 0	DMF	9900
P1	0	DHP	N
D1	ARRAY1	DLP	6
D2	0		
TO	-1000	PROCESSING	
NT	320	SE	0 127
CT	304	LB	2 500
PW90	13.5	MATH	F
BS	16		
SS	0	DISPLAY	
IL	Y	SP	-1316 2
IN	N	WP	20000 0
DP	N	VS	230
HS	NN	SC	200
		WC	300
		IS	1923
		RFL	9060 3
		RFP	7744 1
		TH	20
		INS	1 000
		AI DC	

D1 ARRAY

INDEX	VALUE	INDEX	VALUE
1	8 500	3	38 500
2	18 500	4	78 500

FIGURE 36. NMR Data for Sample CRC 5



ROUND ROBIN 17
CDCL3
TEMP=20 0

EXP1 PULSE SEQUENCE STD13C
DATE 05-02-91
SOLVENT CDCL3
FILE C

ACQUISITION		DEC & VT	
IN	13.750	DN	1.750
SW	20000.0	DO	0
AT	1.501	DM	NNY
NP	60032	DMM	S
PW	10 0	DMF	9900
P1	0	DHP	N
D1	80 000	DLP	6
D2	0		
TO	-1000	PROCESSING	
NT	1000	SE	0.127
CT	420	LB	2.500
PW90	13.5	MATH	F
BS	40		
SS	0	DISPLAY	
IL	Y	SP	-1318 1
IN	N	WP	20000.0
DP	N	VS	52
HS	NN	SC	200
		WC	300
		IS	200
		RFL	9062 2
		RFP	7744.1
		TH	20
		INS	1 000
		AI	DC