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TRACE CHEMICAL ANALYSIS METHODOLOGY.

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A method was developed for the analysis of aqueous nitrates and nitrites. In this method, the sample is treated with benzene, hydrogen peroxide (for nitrite ion analysis), and sulfuric acid to produce nitrobenzene which is then detected by electron capture gas chromatography. This analytical method was adapted to determine oxides of nitrogen in air.

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A system to sample and analyze the hydrocarbon portion of jet engine exhaust to assess its environmental consequences was evaluated. Exhaust samples were collected and analyzed from five jet fuels and isooctane. The samples were collected on a combination sorbent trap packed with Tenax GC and Carbosieve B, then desorbed into a gas chromatograph.

This contract was then transferred from the Aerospace Research Laboratories to the Air Force Materials Laboratory. The principal thrust of the contract became the development of methodology to support the Spectrometric Oil Analysis Program, resulting in a two-task program. Task I was designed to assess the role of non-metallic oil indicators in predicting jet engine wear. Valuable baseline data were obtained on the unused lubricants, and changes occurring in the used lubricants were detected by gas chromatography. Computerized pattern recognition techniques were developed for use in comparing subtle differences in gas chromatograms. The goal of Task II was to develop a rapid flight-line method for assessing the iron content in used jet engine lubricating oil. A colorimetric method was developed for this purpose, and six flight-line kits capable of analyzing 1500 samples were designed and built for an Air Force-conducted field test.

SUMMARY

The research performed on Contract F33615-75-C-1130 was done in two widely separated areas of trace chemical analysis. This was due to a major shift in emphasis of the contract work. Originally the "Trace Chemical Analysis Methodology" contract was funded through the Aerospace Research Laboratories (ARL). At that time, the primary emphasis was the development of methods for measuring environmentally significant pollutants related to Air Force operations.

On 30 June 1975 ARL was disestablished. Contract F33615-75-C-1130 was subsequently transferred to the Materials Laboratory (ML) where a new direction was given to the research. The principal thrust became the development of methodology to support the Air Force Spectrometric Oil Analysis Program (SOAP). In response to this redirection, a two-task research plan was developed. Task I was designed to assess the role of nonmetallic oil indicators in predicting engine wear. Task II had as its goal the development of a rapid, semiquantitative flight-line method for assessing the iron content in aircraft lubricating oil.

The work on the ARL portion of the contract was done in two areas. The first area was the development of methodology to analyze for aqueous nitrates and nitrites and gaseous oxides of nitrogen. The method we developed was based on the nitration of an aromatic compound (e.g., benzene) in the presence of concentrated sulfuric acid to form nitrobenzene. The resulting nitrobenzene, which is stable, can be detected with great sensitivity by electron capture gas chromatography (EC-GC). The detection limit of nitrobenzene by EC-GC was found to be ca. 10^{-12} gram. The efficiencies of conversion of nitrate, nitrite, and nitric acid were very good, as borne out by an evaluation of the procedure for aqueous nitrate determination that was made on human urine and city drinking water supply samples. The conversion of nitrogen dioxide to nitrobenzene was studied using a permeation train. Eight samples containing 3 to 5 ppm nitrogen dioxide were analyzed by our method. Recoveries were excellent and the sensitivity was very good at these levels.

The other area of research on the ARL portion of the contract was the development and evaluation of a sampling and hydrocarbon classification system for jet engine exhaust analysis. Due to the complex mixture of organic compounds with varying potentials for affecting the environment, there was a need for an intermediate analytical method that was inexpensive and relatively fast for routine or multiple analysis. Initial invistigations into this analytical problem were conducted by Technology Incorporated at ARL under another contract. Under this phase of Contract F33615-75-C-1130 MRC tested, evaluated, and improved the

existing system, and ran and evaluated analyses of combustion exhaust samples.

Using this dual system (sampling and analysis), the exhaust was sampled by collection on a combination sorbent trap. The analytical system included a tube furnace and heated gas sampling valve for desorbing the sorbent traps into a gas chromatograph equipped with a dual flame ionization detector. The column system consisted of two analytical columns, a four-port switching valve, and a removable subtractor column. The data obtainable from this sytem were divided into the following classifications:

(a) total unreactive hydrocarbons (paraffinic compounds)
(b) olefins (+ acetaldehyde)
(c) oxygenates + aromatics
(d) total reactive hydrocarbons (nonparaffinic compounds)
(e) total hydrocarbons

Exhaust samples for five jet fuels plus isooctane were collected from a T-56 combustor rig at the Air Force Aero Propulsion Laboratory and analyzed by the system described above. The analytical system performed very well on these samples and the precision on replicate samples was good. However, breakthrough occurred in the sampling system and placed serious limitations on the data obtained. Perhaps minor changes such as increasing the trap volumes would eliminate the problem. Such changes could not be explored because of the change in contract direction.

However, subject to the limitations expressed above, some tentative conclusions can be drawn from the analytical data obtained:

(1) The major portion of the hydrocarbon exhaust from all fuels tested is reactive in nature.

(2) For a given fuel, the percentage composition of reactive compounds increases as the power is increased.

(3) There is a general decrease in absolute concentration of all classifications of compounds as the power is increased.

(4) The distribution of hydrocarbon species into the various classifications does not differ appreciably for JP-5 fuel compared to DEL-5 fuel, even though DEL-5 is JP-4 with increased aromatic content.

(5) Greater than 55% of the total hydrocarbons sampled from actual jet fuels was classified as either aromatic or oxygenated.

(6) The pure isooctane showed marked reduction in total hydrocarbons compared with actual jet fuels and had the highest percentage contribution from unreactive compounds.

After transfer of the contract to ML, work began in the area of oil analysis. Task I sought to discover if lubricating oil undergoes some detectable change prior to the onset of inordinate engine wear which can be used as an indicator of impending wear. Of the five analytical techniques examined, gas chromatography was the most promising, and this method was studied more thoroughly.

Initial investigations in this area concentrated on the analysis of MIL-L-23699 lubricant because the oil samples available were from a single manufacturer. The gas chromatograph (equipped with a flame ionization detector and glass column packed with 3% Dexsil 400 on 90/100 mesh Chromosorb W), was capable of eluting all 15 esters from the base stock ester of MIL-L-23699 lubricant without the aid of standards or other confirmatory methods.

Due to the complexity of the chromatogram, the additives used in MIL-L-23699 oil were only partially identified using the flame ionization detector, but they were easily identified when a nitrogen-phosphorus detector was used. Several differences were found between the chromatograms of used and unused MIL-L-23699 oils, but we were unable to correlate these to either lubricant degradation or engine wear.

The jet engine lubricants currently most widely used in the U.S. Air Force are of the MIL-L-7808 type. The problems associated with the analysis of used MIL-L-7808 oils are complicated by the fact that six different manufacturers supply this lubricant and, in general, the compositions vary widely. Every used oil examined by GC was a mixture of two or more manufacturers' formulations. Therefore, we developed a process of visual pattern recognition based on a unique plotting technique that produces a circular plot by condensing the chromatographic data. A computer-assisted pattern recognition method was then developed which is capable of identifying and approximating the contribution of each lubricant in a mixture.

Task II of the oil research sought to develop a rapid, portable flight-line method for assessing the iron content in jet engine lubricating oil. Present procedures call for lubricating oil samples to be sent to a laboratory for detailed SOAP analysis. Such a procedure can produce considerable lag time between sampling, analysis, and action which might be dictated by the analytical results. This creates the possibility that corrective response time may in some cases be too long to prevent engine failure. A simple, on-the-spot test for a major wear indicator such as iron would be of value in eliminating this problem. In some instances it would also serve as a first-line screen for identifying samples which should receive the more detailed SOAP analysis and thus minimize the number of comprehensive analyses performed.

We developed a "solvent extraction-chelation" method to determine the concentration of iron (a major wear indicator) in synthetic jet engine lubricating oils. The concept of analysis by solvent extraction-chelation generally involves four steps:

(1) Extraction of all iron into an immiscible layer,
(2) Conversion of iron to an appropriate oxidation state,
(3) Chelation with a colorimetric indicator, and
(4) Determination of color intensity.

The procedure we developed uses sulfuric acid to extract the iron from the oil phase into the aqueous phase, eliminating interference from the oil. Isoamyl alcohol is used to prevent emulsions and keep the aqueous layer clear. The aqueous phase is buffered to pH 4 with sodium acetate and the iron is reduced to the ferrous (+2) state with hydroxylamine hydrochloride. The indicator, bathophenanthrolinedisulfonic acid, forms a red complex with iron that is indicative of the iron concentration. The iron concentration can be quantitated by measuring the red aqueous layer with a spectrophotometer or colorimeter at 530 mm.

The colorimetric method in its present form is capable of analyzing for iron up to ∿90 ppm in oils containing equal amounts of 12 metals and up to ∿120 ppm if only iron is present. A calibration curve from 0 to 500 ppm iron in oil was obtained by increasing the indicator strength. The indicator is effective if the pH is maintained between 1 and 7.

Twenty-nine used oils were analyzed by the colorimetric, atomic absorption, and particle independent methods. The colorimetric data compared very well with the atomic absorption data. Precision data were obtained on six used and synthetic oil samples which covered a range from ∿4 to ∿48 ppm iron. Standard deviations were acceptable at each level.

The colorimetric method gave lower results than did the particle independent method when synthetic oil samples containing >1 μm pure iron powder were analyzed. The colorimetric method was modified by heating the reaction bottle during the extraction step. This gave improved results but more research is needed on this modification.

Development of a workable colorimetric method led to the design and construction of a successful prototype flight-line kit containing individual analysis packets. Six such portable colorimetric iron kits and 1491 analysis packets were delivered to the Air Force. A detailed operating manual explaining the new procedure we developed was also prepared, and a copy was included in each kit. The Air Force used the kits in a field test designed and administered by the Air Force Materials Laboratory.

PREFACE

This final report, prepared by Monsanto Research Corporation (MRC) under Contract F33615-75-C-1130, "Trace Chemical Analysis Methodology," covers research performed during the period 5 February 1975 through 15 December 1979. The work was performed at MRC's Dayton Laboratory, at the Aerospace Research Laboratories (ARL), and at the Materials Laboratory (ML), with William D. Ross as MRC project leader. From 5 February 1975 to 15 May 1975 the research was sponsored by ARL, with Robert E. Sievers as project engineer. ML then took over sponsorship of the work and assigned two project engineers: Lt. Col. Kenneth Davis from 15 May 1975 to 15 February 1976, and Dr. Kent J. Eisentraut from 15 February 1976 to 15 December 1979.

The authors wish to acknowledge the helpful guidance and coordination of related efforts provided by Dr. Kent J. Eisentraut of AFWAL/MLBT. We also wish to thank the following personnel: Dr. Wendell E. Rhine, for his many valuable comments, particularly for his help in developing chromatographic methods for the analysis of the synthetic lubricants; Dr. Costandy Saba and Charles Tobin, for conducting atomic absorption analyses of the used oil samples; John R. Brown, for developing the particle size independent analytical method; and Patricia Fair, for providing the particle size independent data. We would also like to acknowledge the valuable assistance received from Dr. Karl Scheller on the statistical analysis of the colorimetric and atomic absorption data.

Contributions to this research were made by the following MRC personnel: Marilyn S. Black, Gerry W. Buttler, Richard J. Hare, John V. Pustinger, William R. Rehg, Arthur D. Snyder, and Leonard Stamper.

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SECTION 1

GENERAL INTRODUCTION

The research described in this report is in two widely separated areas of trace chemical analysis. This is the result of a major shift in emphasis in the work being performed under Contract F33615-75-C-1130. Originally the "Trace Chemical Analysis Methodology" contract was funded through the Aerospace Research Laboratories (ARL). At that time, the primary emphasis was on developing methods for measuring environmentally significant pollutants related to Air Force operations. Under this charter, two methods were developed: a method for measuring oxides of nitrogen in various matrices, and a method for characterizing the hydrocarbon fraction of jet engine exhaust according to specific compound classifications.

On 30 June 1975 ARL was disestablished. Contract F33615-75-C-1130 was subsequently transferred to the Materials Laboratory (ML) where a new direction was given to the research. The principal thrust became the development of methodology to support the Air Force Spectrometric Oil Analysis Program (SOAP). In response to this redirection, a two-task research plan was developed. Task I, "New Concepts in Predicting Engine Wear Through Oil Analysis," had as its goal the assessment of the role of nonmetallic oil indicators in predicting engine wear. The goal of Task II, "Rapid Techniques for the Analysis of Wear Metal in Lubricating Oils," was to develop a rapid semiquantitative flight-line method for assessing the iron content in used engine lubricating oil.

Appendix A is an extensive bibliography of SOAP related material collected during the course of our study. This bibliography is by no means exhaustive, but it represents a substantial portion of the literature particularly in the area of metal analysis in lubricating oil.

SECTION 2

ANALYTICAL METHODOLOGY FOR AIR FORCE RELATED POLLUTANTS

2.1 ANALYSIS FOR AQUEOUS NITRATES AND NITRITES AND GASEOUS OXIDES OF NITROGEN BY ELECTRON CAPTURE GAS CHROMATOGRAPHY

2.1.1 Introduction

Nitrogen oxide gases and aqueous soluble nitrites and nitrates are all of primary environmental concern because of their toxicity and reactivity as well as the synergistic effects they exhibit with other compounds. Several methods of analysis have been developed and are presently being evaluated by the U.S. Environmental Protection Agency [1-4].

In a preliminary report on an earlier contract [5] we described a gas chromatographic method of analysis which showed promise for gaseous oxides of nitrogen [nitrogen dioxide (NO_2) and nitric oxide (NO)] as well as aqueous soluble nitrate (NO_3^-), nitrite (NO_2^-), and nitric acid (HNO_3). Glover and Hoffsommer [6] have published a note on the analysis of aqueous standard potassium nitrate and potassium nitrite.

The analyses are based on the nitration of an aromatic compound, e.g., benzene (C_6H_6), in the presence of concentrated sulfuric acid to form nitrobenzene ($C_6H_5NO_2$). The reagents used in the Saltzman [2] method form relatively unstable diazo dyes, and analyses must be performed soon after absorption. In contrast,

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[1] Environmental Protection Agency, "National Primary and Secondary Ambient Air Quality Standards," Federal Register, 36:228, 22384-22397 (Nov. 25, 1971).

[2] Saltzman, B. E., "Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere," Anal. Chem., 26, 1949 (1954).

[3] Baumgardner, R. E., Clark, T. A., and Stevens, R. K., "Comparison of Instrumental Methods to Measure Nitrogen Dioxide," Environ. Sci. and Technol., 9, 67 (1975).

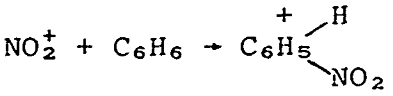
[4] Environmental Protection Agency, "Standards of Performance for New Stationary Sources," Federal Register, 36:247, 24891-24893 (Dec. 23, 1971).

[5] Ross, W. D., "Trace Analysis for Metals in Aerospace Materials by Gas Chromatography," 8th Quarterly Progress Report, Contract F33615-72-C-1304, May 15, 1974.

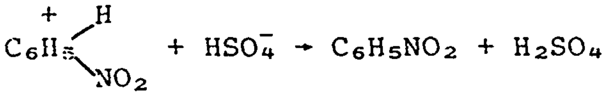
[6] Glover, D. J., and Hoffsommer, J. C., "Gas Chromatographic Analysis of Nitrate and Nitrite Ions in Microgram Quantities by Conversion to Nitrobenzene," J. Chromatogr., 94, 334 (1974).

nitrobenzene is relatively stable (if the organic layer is separated from the aqueous layer). Therefore, field samples can be collected and treated to form nitrobenzene, and then shipped to an analytical laboratory for immediate analysis or storage until the analysis can be performed. The commonly accepted mechanism of nitration with a mixture of nitric and sulfuric acids involves the following sequence of reactions:

$$HONO_2 + 2H_2SO_4 \rightleftharpoons H_3O^+ + 2HSO_4^- + NO_2^+ \qquad (1)$$



$$NO_2^+ + C_6H_6 \rightarrow \overset{+}{C_6H_5}\begin{matrix} \diagup H \\ \diagdown NO_2 \end{matrix} \qquad (2)$$



$$\overset{+}{C_6H_5}\begin{matrix} \diagup H \\ \diagdown NO_2 \end{matrix} + HSO_4^- \rightarrow C_6H_5NO_2 + H_2SO_4 \qquad (3)$$

The resulting nitrobenzene can be detected with great sensitivity by the electron capture detector, and determinations can be made with excellent selectivity even at very low concentrations.

2.1.2 Experimental

2.1.2.1 Reagents

Fisher and Allied Chemical A.C.S. reagent grade sulfuric acids with nominal analysis specifications of 0.00005% and 0.00002% nitrate, respectively, were used. It was necessary to further treat the sulfuric acid (H_2SO_4) with benzene to remove additional nitrate for ultratrace analysis. Furthermore, different lots of sulfuric acid varied considerably in nitrate impurity content. For analysis of low levels of nitrate, it is desirable to check the blank levels in the available bottles of sulfuric acid and select the one with the lowest impurity level. This is not necessary when measuring higher concentrations of nitrate. Exposure of the sulfuric acid to the atmosphere should be minimized to prevent contamination from atmospheric oxides of nitrogen (NO_x). Mallinckrodt nanograde benzene and 0.1 molar hydrogen peroxide (prepared by dilution of 30% Fisher A.C.S. certified reagent grade hydrogen peroxide) were used. Nitrobenzene (Chem-Services, Inc.) and National Bureau of Standards nitrogen dioxide (Standard Reference Material 1629) were employed.

Additional reagents used for the analysis of nitrate, nitrite, and nitric acid samples were potassium nitrate (Fisher, certified reagent), potassium nitrite (Matheson, Coleman and Bell, reagent grade), and nitric acid (Mallinckrodt, A.C.S. reagent grade).

2.1.2.2 Standard Solutions

Nitrobenzene standard solutions were made by dissolving weighed amounts of nitrobenzene in benzene to produce the following concentrations: 2.50×10^{-7} g/mL, 5.00×10^{-7} g/mL, 1.00×10^{-6} g/mL, 5.00×10^{-6} g/mL, and 1.00×10^{-5} g/mL. Standard aqueous solutions were prepared with triply distilled and deionized water at the following concentrations: potassium nitrate, 2.50×10^{-6} g/mL, 5.00×10^{-6} g/mL, 1.00×10^{-5} g/mL, and 2.50×10^{-5} g/mL; potassium nitrite, 1.00×10^{-5} g/mL and 5.00×10^{-5} g/mL; nitric acid, 5.00×10^{-6} g/mL and 2.5×10^{-5} g/mL.

2.1.2.3 Chromatographic Conditions

The gas chromatographs used were Hewlett-Packard Models 402, 810, and 5713, equipped with electron capture detectors (Ni^{63} or titanium tritide). The chromatographic columns were 1-m by 3-mm ID glass or Teflon® packed with 3.8% Union Carbide W98 silicone on 80/100 mesh Diataport S. Isothermal column and injection port temperatures in various experiments ranged from 100°C to 120°C. The argon-methane (90/10) carrier gas flow rate was 60 mL/min.

2.1.2.4 Analytical Procedure for Aqueous Nitrate and Nitrite

a. A 1-mL aliquot of the sample is added to 10.00 mL of benzene in a 125-mL Erlenmeyer flask with a 24/40 Standard taper ground glass neck.

b. For nitrite ion analyses, 1 mL of 0.1M hydrogen peroxide is added to convert the nitrite to nitrate.

c. Ten milliliters of concentrated sulfuric acid is added.

d. The reaction flask is sealed with a ground glass stopper and shaken briefly by hand, then the pressure is relieved by slightly loosening the stopper.

e. The stopper is replaced and secured, and the flask is placed on a wrist-action shaker for 10 minutes.

f. The benzene layer is decanted and a 1-µL aliquot is injected into the gas chromatograph for analysis.

g. The peak height of the nitrobenzene produced from the sample is compared with that of standard nitrobenzene solutions which have been subjected to the identical analysis procedure (see Calibration Procedures, section 2.1.3.4).

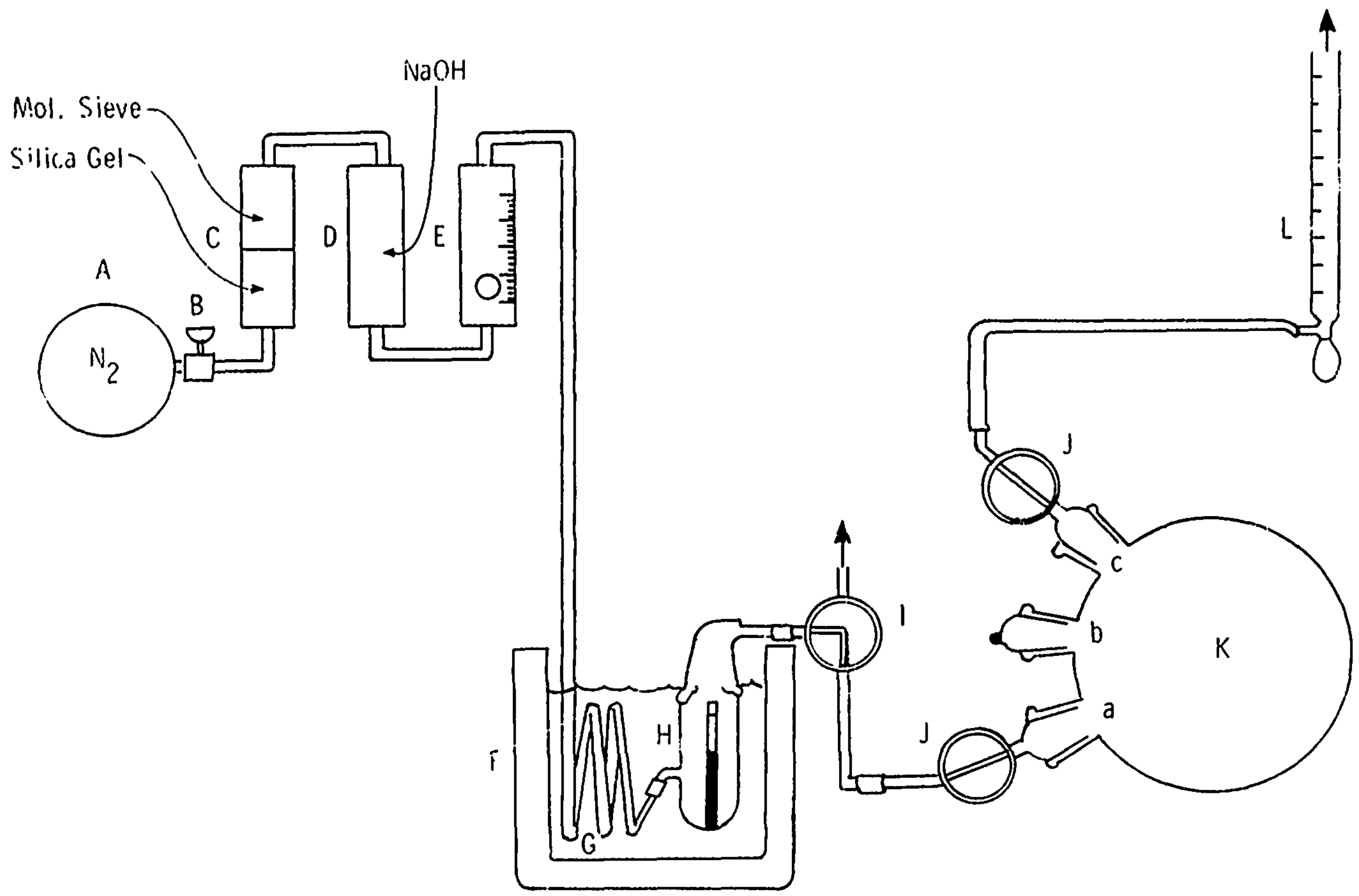


Figure 1. Schematic drawing of the standard gas permeation train and the absorption and reaction vessel.

c. The small silicone rubber stopper is removed from the opening in neck b, and 25 mL of the adsorbing solution used in EPA Method 7 [4] is quickly added.

d. The silicone rubber stopper is replaced, and the flask is briefly shaken by hand, then placed on a wrist-action shaker for 1 hour.

e. The absorbing solution is transferred to a 30-mL sample vial, and an appropriate aliquot (2 to 10 mL) is taken by pipette and placed in a 125-mL Erlenmeyer flask (fitted with a standard taper 24/40 ground glass stopper) containing 10.00 mL of benzene.

f. This absorbing solution aliquot is subjected to the analysis procedure for aqueous nitrate described in section 2.1.2.4 (steps c through g). The amount of concentrated sulfuric acid added in step c of the aqueous nitrate procedure should be five times the volume of the absorbing solution aliquot in order to insure that the final acidity is sufficiently high to cause quantitative conversion to nitrobenzene. CAUTION: Excessive heat may be generated when large volumes of H_2SO_4 are used. Adequate safety precautions should be taken, and sample loss must be prevented.

2.1.3 Results and Discussion

The high sensitivity and selectivity of electron capture gas chromatography (EC-GC) make it an attractive method for determining very low concentrations of compounds which are susceptible to the method. The nonvolatility of nitrates and nitrites, the high reactivity of NO_2, and the low sensitivity of NO to EC detection prohibit the use of this method for the direct analysis of these species at low concentrations. However, the conversion of these species to a compound which is stable, volatile, and sensitive to electron capture detection could provide the basis for a valuable analytical method.

Such a procedure offers several important possibilities:

1. The conversion of highly reactive species such as NO_2 to a more stable compound which can be stored and/or shipped before analysis.

2. The ability to analyze for many different species (NO_2^-, NO_3^-, NO_2, etc.) using the same instrumentation (i.e., EC-GC) and, with minor modifications, the same analytical procedures. In addition, other environmentally significant compounds such as peroxyacyl nitrates (PAN's) can also be determined using the same instrumentation.

3. The recognized sensitivity of electron capture detection, which promises the capability of measuring typical environmental levels of these compounds. Furthermore, since the lower limit of detectability is ca. 10^{-12} g, only very small biological samples are required for analysis.

Consequently, we have investigated a method for converting these species to nitrobenzene which is subsequently measured by electron capture gas chromatography.

2.1.3.1 Analysis for Aqueous Nitrates and Nitrites

Experiments were designed to evaluate the reactivity of benzene with nitrate and of the resulting nitrobenzene in the analytical procedure. Factors studied included efficiency of reaction, solubility of nitrobenzene in benzene, solvent extraction efficiencies, and the efficiency of oxidation of nitrite-containing species. Calibration studies were then made in preparation for the analysis of unknown samples of nitrate in urine and in tap water.

2.1.3.2 Gas Chromatographic Properties of Nitrobenzene

Nitrobenzene has been found to be very sensitive to electron capture detection by other investigators [7]. The detection limit was determined in our study to be ca. 10^{-12} g for a 1-μL sample using the conditions previously described. Figure 2 is a chromatogram of a standard solution of nitrobenzene in benzene. The peak was produced by the injection of 1 μL of benzene containing 5.0×10^{-7} g of nitrobenzene per milliliter.

The chromatograms are remarkably free from interfering peaks (see Figures 2 and 3). At low concentration levels, small peaks sometimes appeared at retention times considerably longer that of nitrobenzene. These peaks only occurred in samples which had been treated with sulfuric acid. The major impurity was tentatively identified by nuclear magnetic resonance spectroscopy (NMR) as benzenesulfonic acid. These peaks were minimized or eliminated by periodic special cleaning of the syringe needle. Normally the syringe was rinsed with benzene after each injection. Periodically it was rinsed with the following sequence of solvents: benzene, acetone, water, acetone, benzene.

2.1.3.3 Solubility Studies

When benzene and sulfuric acid are shaken together with nitrobenzene, the nitrobenzene becomes distributed between the two layers

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[7] Hoffman, D., and Rothkamp, G., "Quantitative Determination of Nitrobenzene in Cigarette Smoke," Anal. Chem., 42, 1643 (1970).

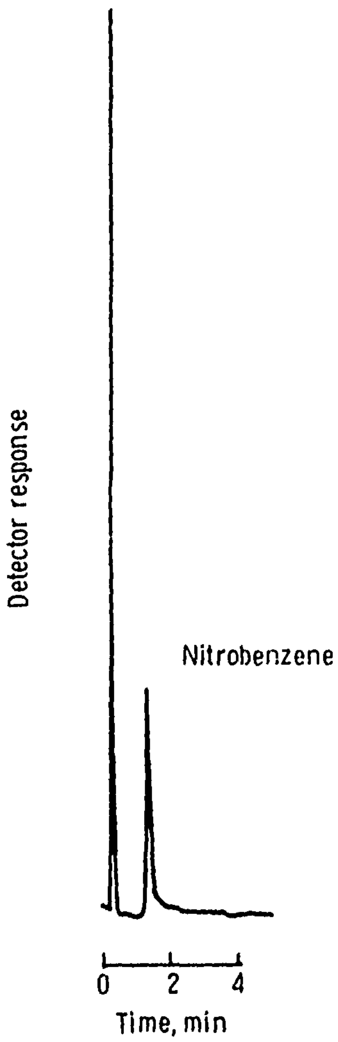

Figure 2. Chromatogram of a standard solution of nitrobenzene in benzene.

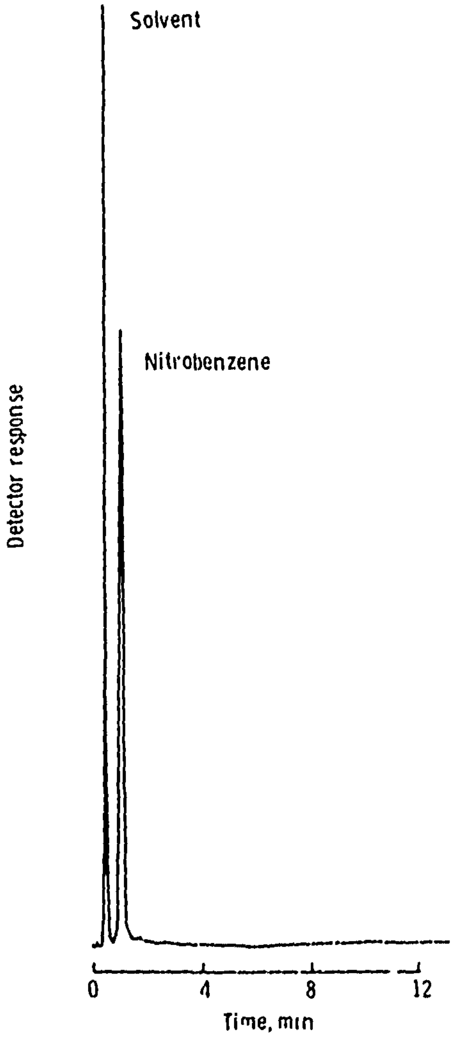

Figure 3. Chromatogram of the product of reaction of nitrate in urine with benzene.

for serious errors can result if this is not taken into account. For example, 25% of the nitrobenzene was lost in the acid layer when 10 mL of a solution containing 2.5×10^{-7} g nitrobenzene per milliliter of benzene was shaken with 10 mL of concentrated H_2SO_4 plus 1 mL of water. In this experiment sample reaction conditions are duplicated. The same percentage was lost in the acid layer when the initial concentration was 1.0×10^{-5} g/mL and at intermediate concentrations as well. Consequently, it is necessary to correct for this loss in the calibration procedure.

2.1.3.4 Calibration Procedures

Four methods of calibration were investigated. When a calibration curve determined from standard solutions of nitrobenzene in benzene was used directly, errors resulted due to the partial solubility of nitrobenzene in the aqueous phase of the reaction mixture. However, a calibration curve determined with nitrobenzene in benzene standards which had undergone the same reaction procedure as unknowns, including the incorporation of a blank (1 mL of distilled-deionized water), accurately depicted the same reaction parameters as the samples themselves experienced. In this manner the consistent loss of nitrobenzene to aqueous solubility (25%) and the increase in signal due to reagent and glassware blanks were automatically corrected. For most determinations, this second method of calibration appears to be most suitable.

In the third method, it was learned that sequential external standards can be used if the detector is less stable than desired (e.g., when detector sensitivity is lowered by successive injections of samples which contaminate the detector cell). The procedure involves bracketing the nitrobenzene peak of the unknown samples with slightly higher and lower concentrations of standard nitrobenzene in a repetitive sequence, and determining the concentration from a two-point calibration. For this calibration method, additional corrections for reagent and glassware blanks, extraction efficiency, and reaction efficiency must be made.

In the fourth method of calibration evaluated, standard solutions of potassium nitrate in water were subjected to the same treatment as unknowns and the results were compared. Glover and Hoffsommer [6] used yet another method of calibration: internal calibration with added nitrotoluene. However, this method has the disadvantage that losses of nitrobenzene to the acid layer are harder to assess.

2.1.3.5 Efficiency of Reactions

The efficiencies of conversion of nitrate, nitrite, and nitric acid to nitrobenzene were determined by the analyses of 1-mL aliquote of standard potassium nitrate (KNO_3), potassium nitrite (KNO_2), and HNO_3 solutions. The analyses were performed by the previously described procedures for aqueous nitrates and nitrites. The results of this study, listed in Table 1, showed mean efficiencies of conversion of 90.3% for KNO_3, 99.9% for HNO_3, and 100.4% for KNO_2.

TABLE 1. EFFICIENCIES OF CONVERSION TO NITROBENZENE

Solution	Concentration, g/mL	Average[a] percent conversion	Mean[b]
KNO_3	2.5×10^{-6}	87.6 ± 8.8	90.3 ± 7.9
	5.0×10^{-6}	90.4 ± 9.2	
	1.0×10^{-5}	86.7 ± 3.7	
	2.5×10^{-5}	96.4 ± 6.8	
KNO_2	1.0×10^{-5}	103.4 ± 3.9	100.4 ± 4.2
	5.0×10^{-5}	97.3 ± 1.3	
HNO_3	0.5×10^{-5}	97.0 ± 4.6	99.9 ± 5.2
	2.5×10^{-5}	102.9 ± 4.4	

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[a] Mean of five reactions. Standard deviation of 25 chromatographic determinations (5 aqueous sample aliquots, 5 injections from the reaction of each).

[b] Calculated using all percent conversion values (i.e., five values for each concentration).

By adding the reagents in the concentrations and order described in section 2.1.2, Experimental, it is possible to take advantage of the heat generated upon mixing to effect quantitative conversion without the addition of external heat.

2.1.3.6 Analysis for Nitrate in Urine and Drinking Water

An evaluation of the procedure for nitrate determination was made on two types of samples: human urine, and drinking water from a city water supply. Five samples of each type were analyzed. The samples were taken over a period of 1 month; i.e., each value in Table 2 represents the nitrate level on a different day. It was found that the nitrate levels were relatively constant over a 1-month period of time, both in the urine from a single individual and in the Dayton city water supply. The mean concentration of nitrate in the water supply was 1.16 ppm. The relative standard deviation over the 1-month period was

13.8%. The meam concentration of nitrate in the urine of an adult male donor was 33.2 ppm, with a relative standard deviation over 1 month of 13.6%. Figure 3 is a chromatogram of nitrobenzene formed from the reaction of the nitrate in urine.

TABLE 2. ANALYSIS OF NITRATE IN DRINKING WATER AND URINE

Sample type	Concentration of NO_3^-, ppm	Standard deviation[a]
Drinking water	1.29	±0.04
	1.20	±0.09
	1.29	±0.14
	1.15	±0.08
	0.88	±0.07
Human urine	33.3	±4.5
	37.8	±2.1
	37.3	±2.4
	30.2	±2.8
	27.6	±1.4

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[a] Standard deviation of five replicate chromatographic injections of the same sample.

2.1.3.7 Studies of the Conversion of Nitrogen Dioxide to Nitrobenzene

The highly reactive nature of NO_2 causes major problems in both sampling and analysis. For this reason, in the generally accepted methods [1, 2, 4] NO_2 is converted into other species before analysis. In the phenoldisulfonic acid method (EPA Method 7 [4]) an absorbing solution consisting of dilute sulfuric acid and hydrogen peroxide is employed to convert oxides of nitrogen to aqueous nitrate. We reasoned that a similar approach could be used to convert NO_2 to nitrate ion in aqueous solution with subsequent conversion to nitrobenzene and analysis by the EC-GC procedure described above.

To investigate this possibility, we conducted preliminary experiments on samples of NO_2 in nitrogen. The samples were prepared with known concentrations of NO_2 using the permeation train described in the Experimental section. Using the method outlined above, determination of NO_2 concentrations were made on eight samples calculated from permeation data to contain 3 to 5 ppm NO_2. Recoveries were 98%, 100%, 97%, 100%, 99%, 100%, 103%, and 98%. There is more than adequate sensitivity to make measurement at these levels.

2.2 DEVELOPMENT AND EVALUATION OF A SAMPLING AND HYDROCARBON CLASSIFICATION SYSTEM FOR JET ENGINE EXHAUST ANALYSIS

2.2.1 Introduction

The incomplete combustion of nonhomogeneous hydrocarbon based fuels produces an exhaust which contains a complex mixture of organic compounds. As an illustration of the complexity of this mixture, Table 3 contains a partial list of compounds identified in the exhaust from the combustion of JP-4 fuel by the Air Force School of Aerospace Medicine (AFSAM) [8]. Each of these compounds is of environmental significance depending upon the degree to which it exhibits properties that are detrimental to the environment or harmful or irritating to the public. Toxicity, smog producing capability, odor, and eye irritability are examples of environmentally significant properties. More generally, certain of these properties have been associated with particular reactivity classes of compounds. As examples, olefins are known to be important links in the reaction sequence which produces smog [9], and oxygenated and aromatic compounds are recognized as being among the more odorous [10] and toxic compounds [11]. By comparison, the paraffins are relatively innocuous.

Since these compounds have different potentials for affecting the environment, total hydrocarbon analyses do little to provide useful information concerning the environmental consequences of hydrocarbon exhaust. On the other hand, a quantitative compound-by-compound determination, which is the most complete type of analysis for this purpose, is expensive and time consuming, and requires instrumental sophistication beyond the capability of many analytical laboratories. The need for an intermediate analytical capability (one that could provide enough detail to reasonably assess the environmental consequences of the hydrocarbon portion of exhaust, and yet be relatively inexpensive and fast for routine or multiple analyses) spurred several attempts

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[8] Conkle, J. P., Lackey, W. W., and Miller, R. L., "Cryogenic Sampling of Turbine Engine Exhaust," School of Aerospace Medicine Technical Report. SAM-TR-75-8, March 1975.

[9] Kerr, J. A., Calvert, J. G., and Demerjian, K. L., "The Mechanism of Photochemical Smok Formation," Chem. in Brit., 8, 252 (1972).

[10] A. D. Little Co., "Chemical Identification of the Odor Components in Diesel Engine Exhaust," CRC Project CAPE-7-68, HEW Contract EHSD 71-18, Final Report, June 1971.

[11] Olsen, D. A., and Haynes, J. L., "Air Pollution Aspects of Organic Carcinogens," NAPCA Report for HEW Contract PH-22-68-25, September 1969.

TABLE 3. COMPOUNDS IDENTIFIED IN JP-4 EXHAUST BY USAF SCHOOL OF AEROSPACE MEDICINE [8]

Paraffins

- Methane
- 2,2,3-Trimethylbutane
- 3-Methylhexane
- 2,3,4-Trimethylpentane
- 3,4-Dimethylhexane
- 2,4-Dimethylhexane
- 3,4-Dimethylheptane
- n-Octane
- n-Nonane
- 4-Methyloctane
- 2-Methyl-4-ethylhexane
- n-Decane
- 2-Methyl-5-ethylheptane
- Isopropylcyclopropane
- Methylcyclohexane

Ethers

- Furan
- 3-Methylfuran
- 2,3-Epoxybutane
- Isooctyl vinyl ether

Olefins

- Ethylene
- Acetylene
- Propylene
- Propyne
- 2-Methylpropene
- 1-Butene
- 2-Butene-cis
- 2-Methyl-1-pentene
- 1-Hexene
- 3-Heptene-trans
- Allene

Alcohols

- Methanol
- Cyclohexanemethanol
- 2-Propylheptanol

Esters

- n-Amyl acetate

Aromatics

- Ethylbenzene
- 1,4-Dimethylbenzene
- 1,2,3-Trimethylbenzene
- n-Propylbenzene
- 1,2,4-Trimethylbenzene
- 1,3-Diethylbenzene

Aldehydes

- Acetaldehyde
- Propionaldehyde
- Crotonaldehyde
- Butyraldehyde

Ketones

- 2-Butanone
- Methylpropylketone
- 3-Hexanone
- 5-Methyl-2-hexanone
- Propylbenzylketone
- 3-Heptanone

at developing analysis schemes which divide organic exhaust products into various classifications based on reactivity or compound type [12-16]. The goal of research conducted at the Aerospace Research Laboratories by ARL and MRC personnel was to investigate methods of accomplishing such an analysis and applying this technology to real-world samples from the combustion of various fuels under selected conditions.

2.2.2 Experimental

2.2.2.1 Analytical System

Work to develop the analytical system used for the analyses described in this report was conducted primarily by Technology Incorporated personnel at ARL. The work conducted by MRC in this phase of Contract F33615-75-C-1130 was in the areas of testing, evaluating, and improving, where possible, the existing system, and conducting and evaluating analyses of combustion exhaust samples. A brief discussion of the analytical system is included for completeness.

The instrumentation used in the analytical system includes:

(a) A Hewlett-Packard Model 5750B research gas chromatograph equipped with a dual flame ionization detector (FID)

(b) An Autolab System IV computing integrator

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[12] Haken, J. K., Ho, D.K.M., and Withers, M. K., "The Identification of Peaks in Gas Chromatography by the Use of Subtractor Columns. Part 1: The Removal of Aldehydes and Ketones," J. Chromatogr. Sci., 10, 566 (1972).

[13] Seitzinger, D. E., and Dimitriades, B., "Oxygenates in Exhaust from Simple Hydrocarbon Fuels," J. of Air Pollution Control Assoc., 22, 47 (1972).

[14] Withers, M. K., "The Identification of Peaks in Gas Chromatography by the Use of Subtractor Column. Part II: The Action of Free Fatty Acid Phase on Aldehydes," J. Chromatogr., 66, 249 (1972).

[15] Martinu, V., and Janak, J., "Selective Chromatographic Separation of Aromatic Hydrocarbons and their Hydrogenated Derivatives on Porapak T," J. Chromatogr., 65, 477 (1972).

[16] Bellar, T. A., and Sigsby, J. E., Jr., "Direct Gas Chromatographic Analysis of Low Molecular Weight Substituted Organic Compounds in Emissions," Environ. Sci. and Technol., 4, 150 (1970).

(c) A Hewlett-Packard Model 19021A heated gas sampling valve modified to accommodate solid sorbent sampling tubes

(d) A specially designed tube furnace for desorbing samples from sorption tubes

The heart of the analytical system is the column arrangement shown in Figure 4. The essential components are:

(a) A 1-m analytical column packed with 60/80 mesh Chromosorb P coated 30% by weight with 1,2,3-tris(2-cyanoethoxy)propane (TCEP)

(b) A four-port switching valve

(c) A removable subtractor column consisting of two sections: (1) Ag_2SO_4/H_2SO_4 on 60/80 mesh Chromosorb W, and (2) $PdSO_4/H_2SO_4$ on 60/80 mesh Chromosorb W

(d) An analytical column packed with 13 cm of Chromosorb 105.

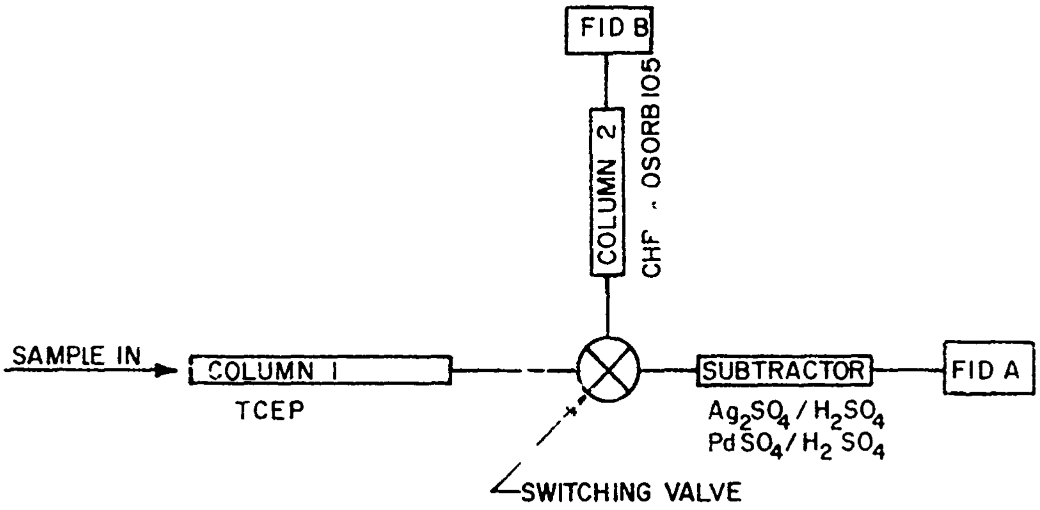

Figure 4. Column system for hydrocarbon characterization studies.

The functions of the various components of the column system are described in the following subsections.

a. TCEP Column

The function of the TCEP column is to retard water and oxygenated and aromatic compounds while allowing paraffinic and olefinic compounds to elute relatively quickly [13]. The column was maintained at 80°C during the analyses. The effectiveness of this column is illustrated by the retention data in Table 4. Particular attention should be given to the retention time of n-decane (81 s) because previous studies by AFSAM [8] identified this compound as the highest molecular weight saturated compound found in JP-4 exhaust. Consequently, a time corresponding to that required for the elution of n-decane was chosen for switching the effluent from the TCEP column onto the Chromosorb 105 column. Figure 5 is a chromatogram of a synthetic mixture of representative organic compounds on the TCEP column.

TABLE 4. RETENTION DATA FOR REPRESENTATIVE COMPOUNDS ON TCEP COLUMN

Temperature = 80°C
Flow rate = 60 mL/min
Weight percent coating of TCEP = 30

Compound	Retention time, s	r¹[a]
Methane	14	1.0
Methylcyclopentane	31	2.2
n-Hexane	22	1.6
n-Octane	37	2.6
n-Decane	81	5.7
n-Dodecane	222	15.8
Propionaldehyde	128	9.1
Butyraldehyde	196	14.0
Valeraldehyde	323	23.1
Benzaldehyde	375	26.8
Allyl ether	168	12.0
Methyl furan	118	8.4
Methanol	258	18.4
Acetone	187	13.4
Methyl ethyl ketone	273	19.5
Benzene	241	17.2
Acetylene	16	1.1
2,2,4-Trimethyl-pentene-1	30	2.1
Nonene-1	60	4.3
Decene-1	92	6.6

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[a] r¹ = retention time of compound divided by retention time of methane.

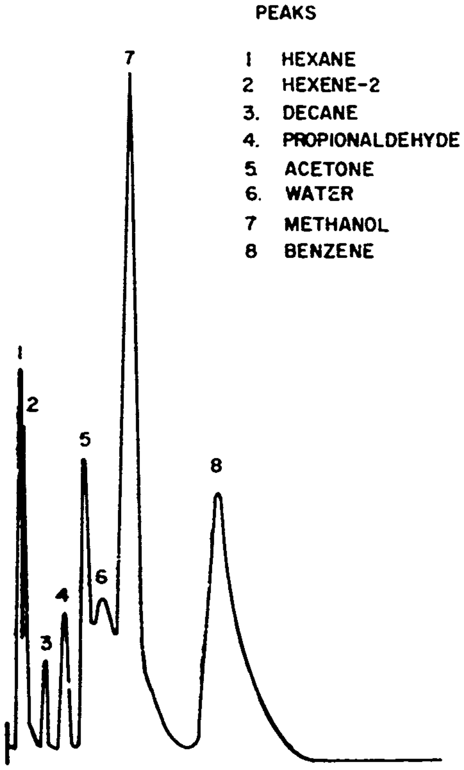

Figure 5. Chromatographic separation of synthetic hydrocarbon mixture on TCEP column.

b. Switching Valve

The function of the switching valve is to direct the effluent from the TCEP column either into the subtractor (or directly into the FID if the subtractor is not in the system) or into the Chromosorb 105 column. The valve was switched at a predetermined time after injection of a sample. As explained above, this switching time corresponded to total elution of the n-decane peak. In the chromatogram shown in Figure 5, the proper switching time was after peak 3 had passed from the TCEP column. Performing the valve switch in this manner caused olefinic and paraffinic compounds to pass directly into FID A (or into the subtractor if it was in the system), and water and oxygenated and aromatic compounds to pass into the Chromosorb 105 column. Oxygenated compounds, which have shorter retention times than propionaldehyde on the TCEP column, probably passed through with the olefins and paraffins before the valve was switched. Acetaldehyde was identified by AFSAM in JP-4 exhaust and is probably the only compound which need cause any concern in this respect. Provisions were made for the removal of any light oxygenates which may have been eluted before the valve was switched (see discussion of subtractor).

c. Subtractor Column

The function of the subtractor column is to efficiently remove olefinic and light oxygenated compounds from the effluent coming from the TCEP column before the valve is switched. Ag_2SO_4/H_2SO_4 is an efficient subtractor for the olefinic compounds [17], and $PdSO_4/H_2SO_4$ serves as a subtractor for any light oxygenated compounds (particularly acetaldehyde) [17]. The olefinic subtracting efficiency of the Ag_2SO_4/H_2SO_4 subtractor is illustrated by the data in Table 5 and the chromatogram in Figure 6. The efficiency of the $PdSO_4/H_2SO_4$ subtractor for removing oxygenated compounds is illustrated by the data in Table 6. Particularly important is the fact that paraffins are essentially unaffected by the subtraction process (see Tables 5 and 6).

TABLE 5. EFFICIENCY OF Ag_2SO_4/H_2SO_4 ABSORBENT (80°C)

Compound	Concentration, μg	Efficiency, percent of compound removed
n-Pentane	90	0
n-Heptane	19	1.11
n-Decane	2	3.07
Methylcyclopropane	37	1.41
2,3-Dimethylbutane	56	0.39
Acetylene	5,780	100
Ethylene	1,273	99.4
2-Ethyl-butene-1	123	100
4-Methyl-pentene-1	121	100
Hexene-1	47	100
Octene-1	10	100
Decene-1	2	100
Benzene	78	100
Ethylbenzene	48	100

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[17] Klosterman, D. L., and Sigsby, J. E., Jr., "Application of Subtractive Techniques to the Analysis of Automotive Exhaust," Environ. Sci. and Technol., 1, 309 (1967).

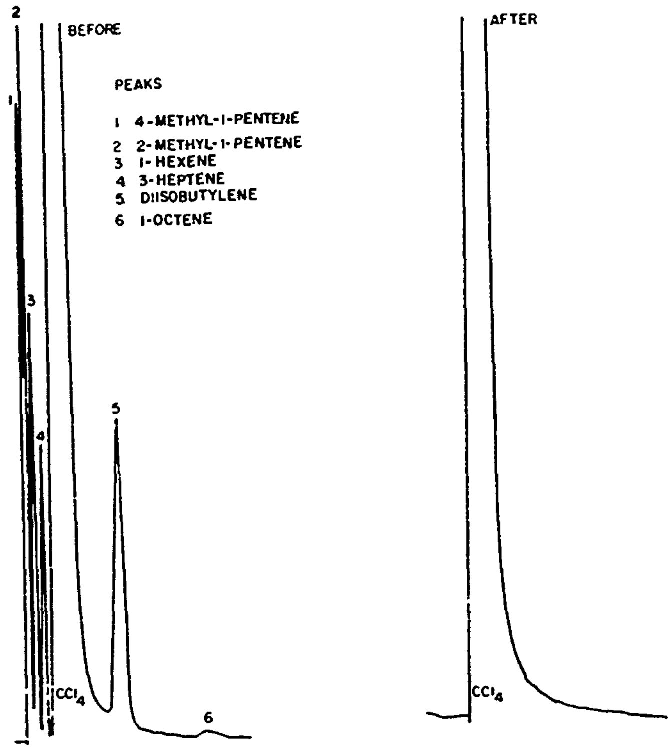

Figure 6. Chromatograms of olefin mixture before and after subtracting with Ag_2SO_4/H_2SO_4.

TABLE 6. EFFICIENCY OF $PdSO_4/H_2SO_4$ ABSORBENT (80°C)

Compound	Concentration, µg	Efficiency, percent of compound removal
Acetaldehyde	100	99.1
n-Propionaldehyde	67	100
n-Butyraldehyde	22	100
Allyl ether	98	100
2-Methyl furan	125	100
Methyl acetate	53	100
Acetone	25	100
Methanol	19	100
n-Pentane	90	0
n-Heptane	19	0
n-Decane	2	0.1
Methylcyclopropane	37	0.24
2,3-Dimethylbutane	56	0.19

d. Chromosorb 105 Column

Chromosorb 105 is a hydrophobic porous polymer which performs the function of allowing the water to pass quickly through the column while retarding the oxygenated and aromatic compounds. This functions was considered important since it was feared that water, a major product of the combustion process, might adversely affect the analyses if it were allowed to elute at the same time as the peaks of interest. The Chromosorb 105 column was connected exterior to the oven by passing lines from the switching valve through the oven wall. It was wrapped with heating tape to allow individual temperature control through a Variac transformer. The column was maintained at ambient temperature until the water eluted, then heated to ∿150°C to facilitate the elution of the aromatic and oxygenated compounds. Typical operation of the Chromasorb 105 column is illustrated by the chromatogram in Figure 7. The injection sequence used for this chromatogram simulates the order of elution from the TCEP column. Note that the very small response associated with the elution of water is the first to appear in the chromatogram.

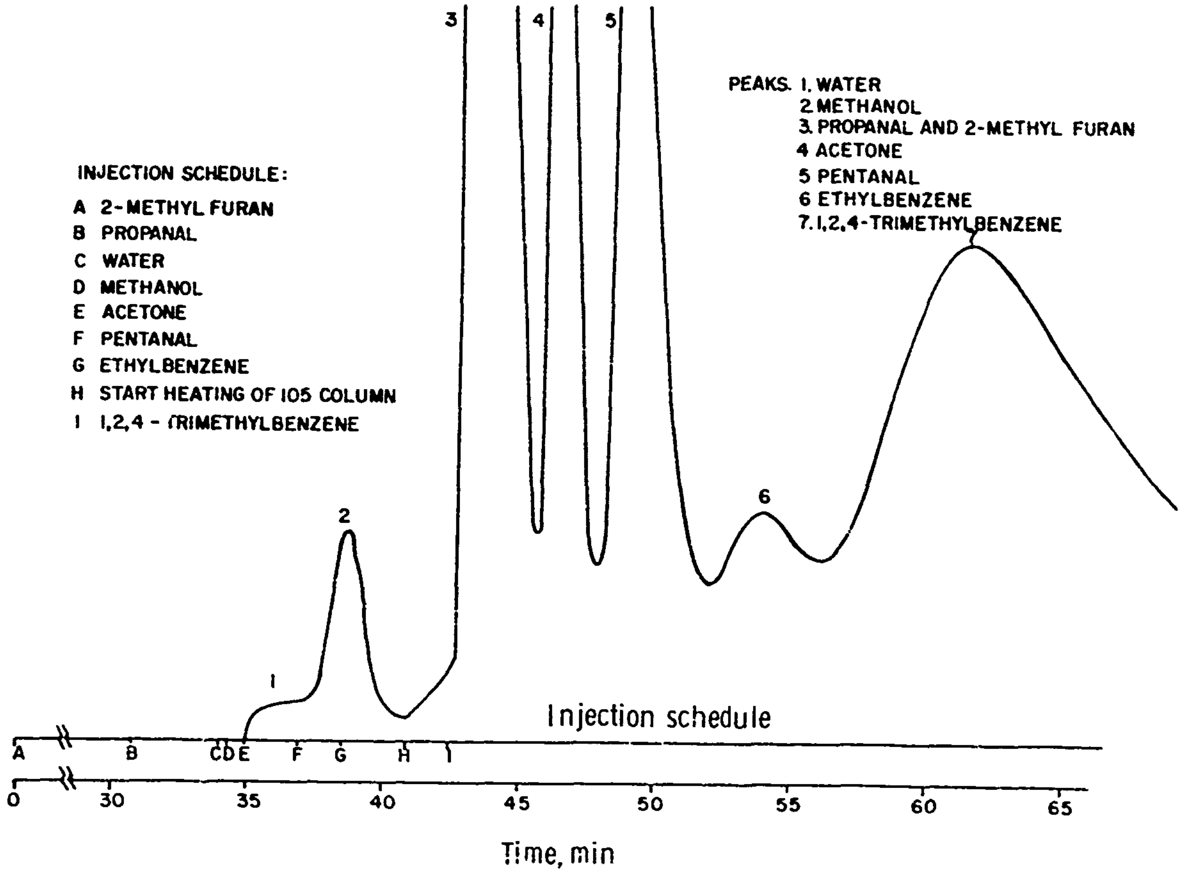

Figure 7. Chromatographic separation of synthetic hydrocarbon mixture on Chromosorb 105 column.

c. The Total System

Figure 8 is a chromatogram illustrating the operation of the complete system on a synthetic mixture of representative compound types. The shift in baseline occurring after peak 2 (n-decane) corresponds to the switching of the valve. Therefore, hexane and decane pass through the TCEP column and are detected at FID A. Water, propionaldehyde, acetone, methanol, and benzene pass through the TCEP column and the Chromasorb 105 column and are detected at FID B. The data obtainable from this system are divided into the following classifications:

- (a) Total unreactive hydrocarbons (paraffinic compounds)
- (b) Olefins (+ acetaldehyde)
- (c) Oxygenates + aromatics
- (d) Total reactive hydrocarbons (nonparaffinic compounds)
- (e) Total hydrocarbons (THC).

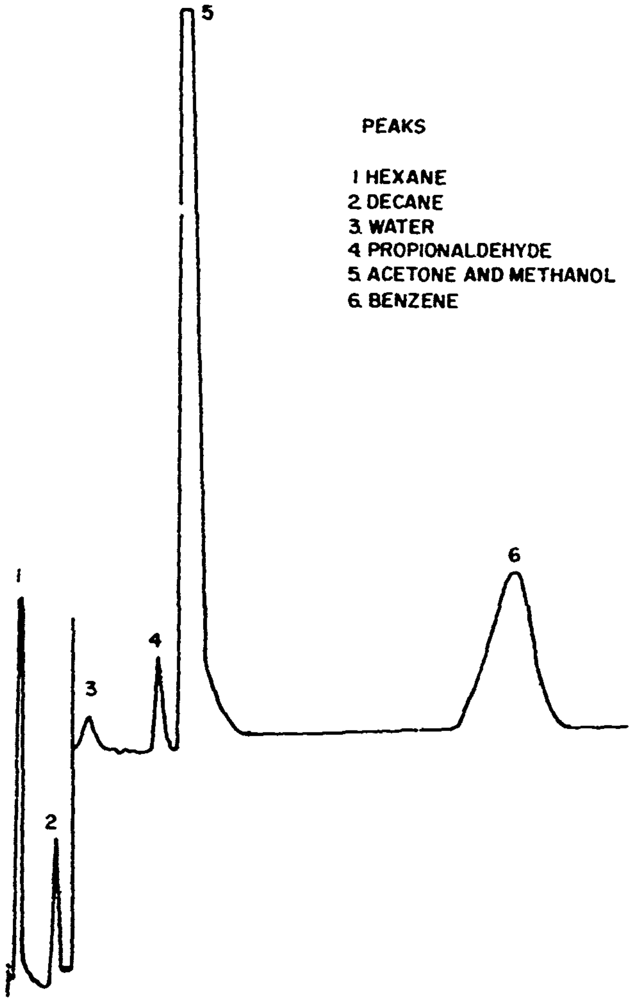

Figure 8. Chromatographic separation of synthetic hydrocarbon mixture on the complete system.

To obtain the complete analysis, it is necessary to have two samples of known sample volumes taken under identical conditions. The first sample is analyzed without the subtractor in the system and yields the following data (see Figure 4).

(a) FID A response = paraffins + olefins (+ acetaldehyde)
(b) FID B response = oxygenates + aromatics.

The second sample is analyzed with the subtractor in the system and yields the following data:

(a) FID A response = paraffins (total unreactive)
(b) FID B response = oxygenates + aromatics.

Olefins (+ acetaldehyde) are obtained by difference by subtracting the FID A response of the second sample from the FID A response of the first sample. The total reactive hydrocarbon value is obtained by summing the values for olefins (+ acetaldehyde) and oxygenates + aromatics. A THC value is obtained by combining the total reactive and total unreactive hydrocarbon values. Note that for each analysis (either with or without the subtractor) a value is obtained for the oxygenate + aromatic content. Thus, in general, this value is more precisely determined than other values.

2.2.2.2 Sampling System

a. Adsorption Tube

Exhaust samples were collected on the combination sorbent trap illustrated in Figure 9. The trap was constructed from 1/4-in. OD, 2-mm ID glass tubing and packed with ∿5 cm of 60/80 mesh Tenax GC and ∿7 cm of 60/80 mesh Carbosieve B. The Tenax GC was used to trap the higher molecular weight organic compounds [18-20] while the Carbosieve B [21] captured the lower molecular weight

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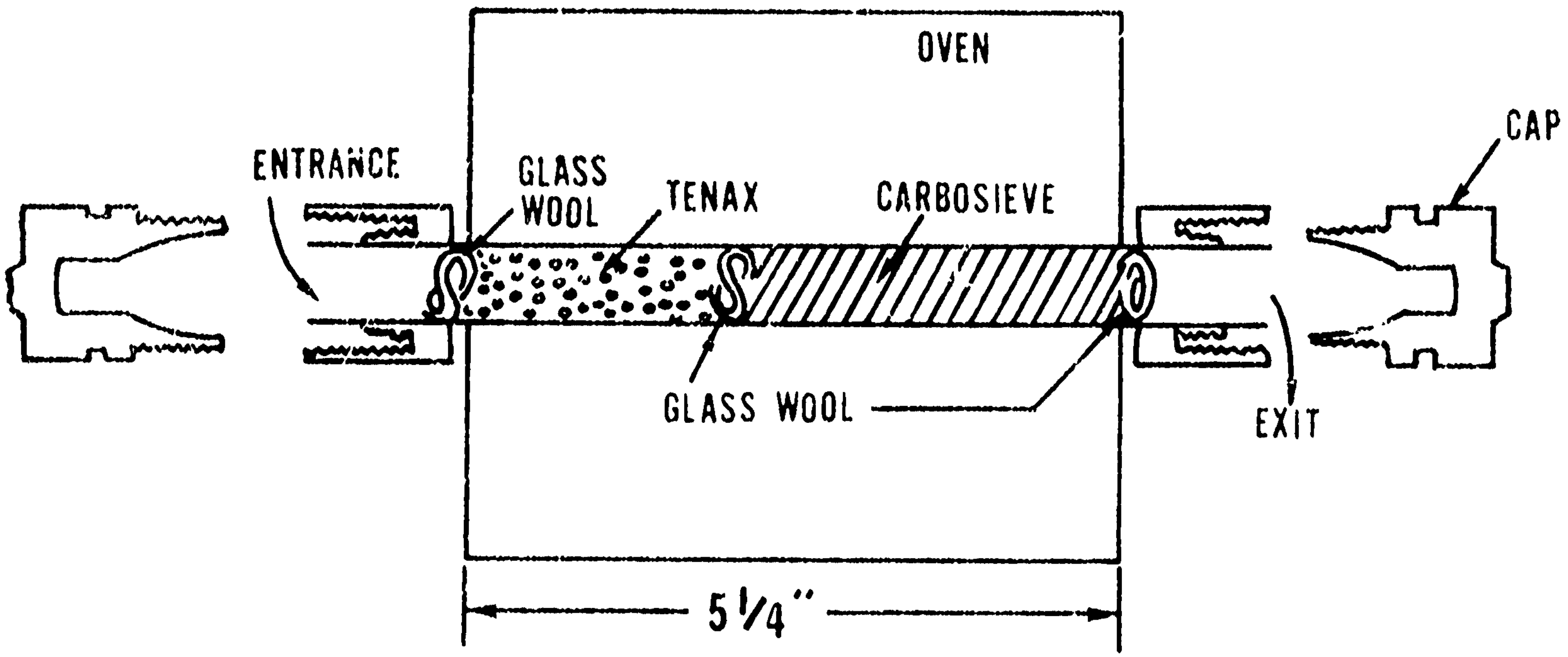
[18] Bertsch, W., Zlatkis, A., Leibich, H. M., and Schneider, H. J., "Concentration and Analysis of Organic Volatiles in Skylab 4," J. Chromatogr., 99 673 (1974).

[19] Janak, J., Ruzickova, J., and Novak, J., "Effects of Water Vapour in the Quantitation of Trace Components Concentrated by Frontal Gas Chromatography on Tenax-GC®," J. Chromatogr., 99, 689 (1974).

[20] Zlatkis, A., Lichtenstein, H. A., Tishbee, A., Bertsch, W., Shumbo, F., and Liebrich, H. M., "Concentration and Analysis of Volatile Urinary Metabolites," J. Chromatogr. Sci., 11, 299 (1973).

[21] Brunner, R., Ciccioli, P., and diNardo, F., "Use of Graphitized Carbon Black in Environmental Analysis," J. Chromatogr., 99, 661 (1974).

ADSORPTION TUBE IN OVEN
1/4" OD GLASS



60/80 Mesh Tenax : For heavier Compounds
60/80 Mesh Carbosieve : For Light Compounds

Figure 9. Diagram of sorbent sampling tube.

compounds not retained by the Tenax GC. The tube was fitted with 1/4-in. Swagelok nuts so that it could be directly connected to the sample line and desorption system. A standard 1/4-in. Swagelok back ferrule was reversed and silicon rubber rings were placed on the tube ends to seal the connections of the trap in the sampling and desorption systems. Standard 1/4-in. Swagelok caps were used to seal the tubes during transport and storage.

b. Cryogenic System

The sorbent traps were cooled to -78°C with crushed solid carbon dioxide (CO_2) during sampling and storage. Cooling was accomplished by placing modified styrofoam cups around the traps to contain the dry ice. This system proved to be reasonably effective and inexpensive.

c. Sampling

Figure 10 illustrates the actual sampling arrangement used to collect exhaust samples from a T-56 combustor rig at the Air Force Aero Propulsion Laboratory (AFAPL). The valving system made possible the accommodation of two adsorption tubes. One tube served as a dummy for regulating the flow rate to 50 to 100 cm^3/min. The flow rate was continually monitored so that the total sample volume could be determined. The exhaust sample line was heated to ∿300°F. The adsorption tubes were connected so that the sample passed first through the Tenax GC, then through the Carbosieve B. While the actual samples were being collected, a Beckmann Model 402 total hydrocarbon analyzer provided continuous on-line THC data.

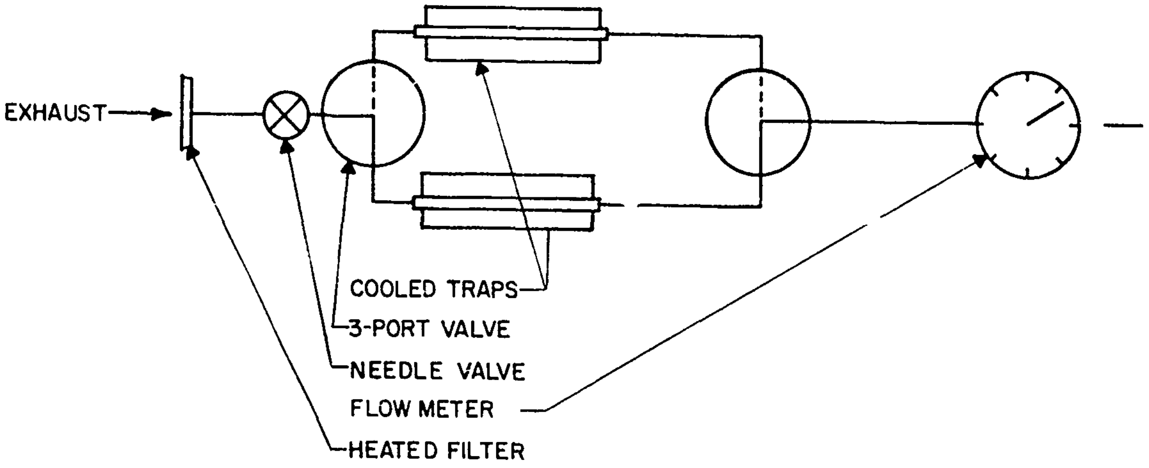


Figure 10. Arrangement of sorbent sampling tubes in sample collection system.

d. Desorption

The exhaust samples were desorbed into the chromatographic system by means of a modified Hewlett-Packard Model 19021A heated gas sampling valve. One of the sampling valve loops was cut and fitted to accommodate the 1/4-in. Swagelok connection of the adsorption traps. This made possible the switching of the sample trap into the system as shown in Figure 11. The desorption was facilitated by means of the specially designed tube furnace detailed in Figure 12. The sorbent traps were heated to 350°C to 400°C during the desorption cycle.

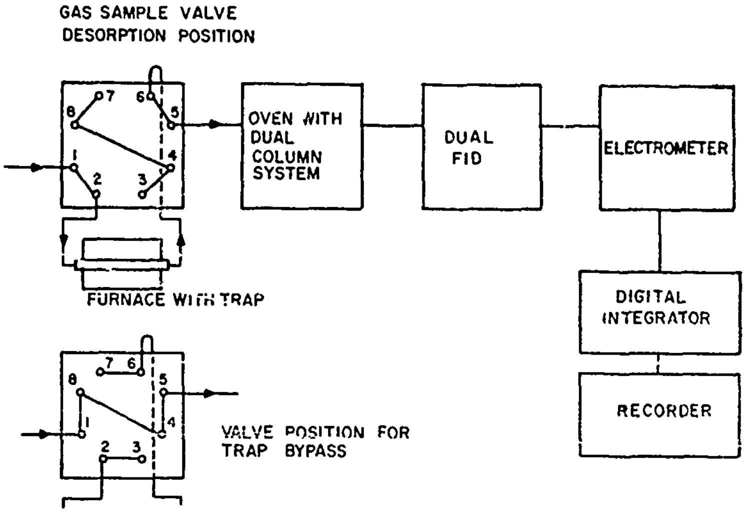


Figure 11. Analytical system with modified gas sampling valve for sorbent tube desorption.

2.2.2.3 Analytical Results

a. Description of Tests

Exhaust samples were collected from a T-56 combustor rig at the Air Force Aero Propulsion Laboratory during the week of 3-7 March 1975. The fuels tested and combustion conditions used are shown in Table 7.

TABLE 7. FUEL AND INLET PRESSURE MATRIX

	Inlet pressure, psia			
Fuel	15	33	50	75
JP-4	5	6	4	
JP-5		2		0
JP-8		2		
Isooctane		4		
DEL-5 blend		6		
JP-5 + Ferrocene				0

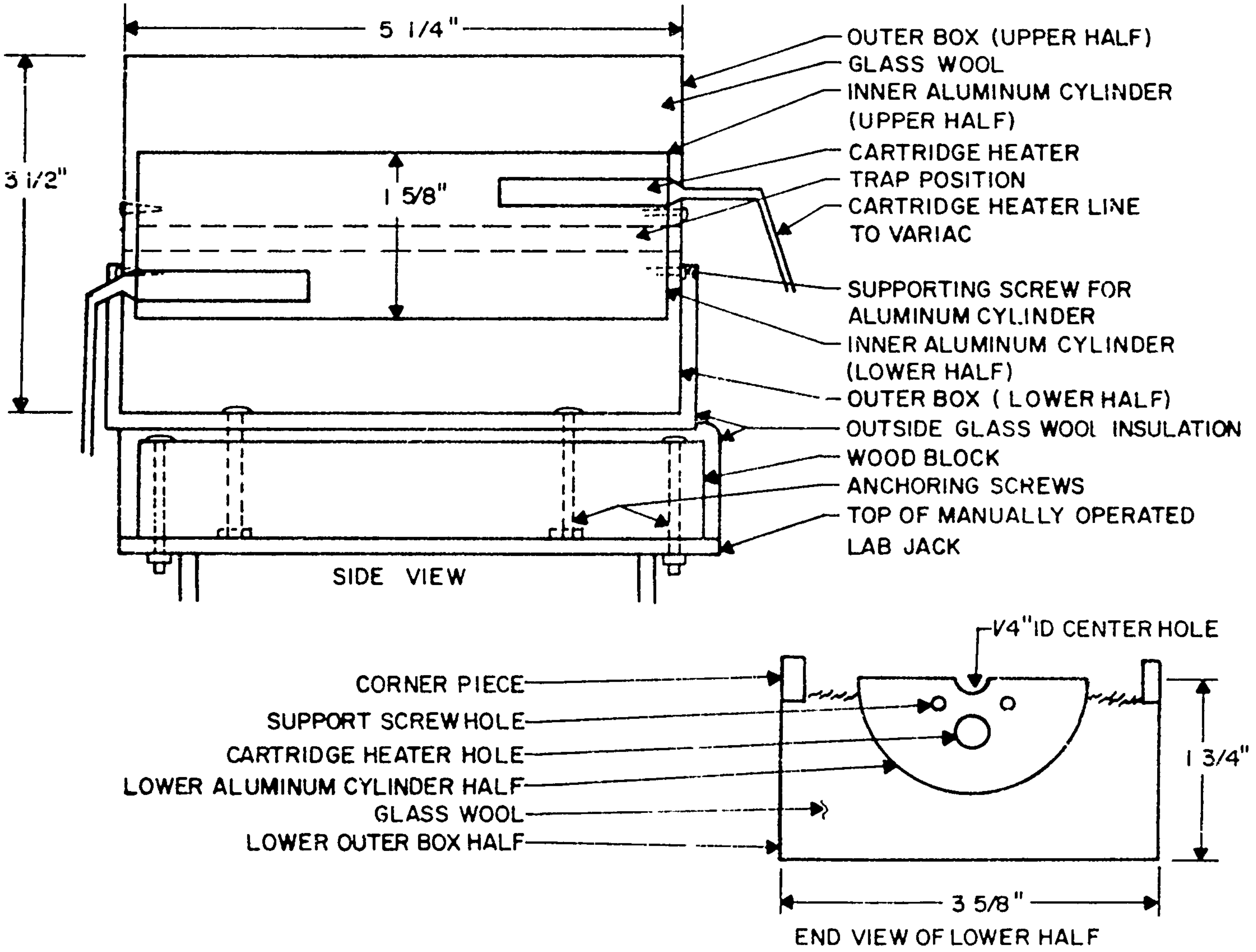


Figure 12. Schematic of desorption furnace.

Only those matrix points (Table 7) which contain entries were run during the week of tests. The numbers in the matrix indicate the number of samples collected at each test point. JP-4, JP-5, and JP-8 are standard military blends used by DOD aircraft. Iso-octane was run to compare a pure fuel with the nonhomogeneous fuels. DEL-5 is a specially blended fuel made by adding 1.6 wt % pyridine to the stock JP-4 fuel and additionally increasing the aromatic content of the fuel from ∿12% to 25%. The DEL-5 was prepared to simulate more closely fuels which may be obtained from alternative sources such as shale oil. The final fuel type was JP-5 with the smoke reducing compound ferrocene added.

Simultaneous sampling was conducted using (1) the on-line THC, NO_x, carbon monoxide (CO), and CO_2 analyzers at the Aero Propulsion Laboratory, (2) a cryogenic system used by the Air Force School of Aerospace Medicine, (3) the sorbent system developed by ARL and MRC and described in this report, (4) an impinger train used for another MRC effort, and (5) sorbent traps provided by A. D. Little Company.

b. Total Sample Volume

To determine concentrations of hydrocarbons in the samples collected, it was necessary to determine the total volume of exhaust which passed through the trap. Because a total volume flow meter which is accurate at the flow rates used was not available, the flow rate was continually monitored throughout sampling. Table 8 contains typical flow rate data obtained during sampling.

TABLE 8. TYPICAL FLOW RATE DATA

Elapsed time, s	Time/10 mL flow, s	Flow rate, mL/min
90	9.0	66.7
120	9.0	66.7
180	9.0	66.7
300	9.5	63.2
340	9.4	63.8
400	9.5	3.2
520	9.5	63.2
600	9.7	61.9
680	9.8	61.2
700	9.9	60.6
760	10.0	60.0
783[a]		

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[a] Total sample time.

The method used to obtain the total sample volume from the flow rate data is illustrated graphically in Figure 13. The cascading line connects the points representing the flow rates recorded during sampling. The area under this curve can be related to the total volume sampled. A convenient way of arriving at this area is illustrated by the rectangular areas on the graph. When two consecutive flow rates differ, the arithmetic mean of these two flow rates is considered to be the flow rate over the period of time covered, and a horizontal line is constructed at the mean value. The sample volumes represented by the areas of the rectangular boxes are summed to obtain the total sample volume as illustrated.

c. Chromatographic Analysis

A chromatogram typical of the actual exhaust sample analyses is shown in Figure 14. The important events in the analytical sequence are noted on the chromatogram. The first peak is labeled "paraffins," signifying that this particular analysis was performed with the subtractor in the system. The "column switch" designation corresponds to the time at which the effluent from the TCEP column was directed into the Chromosorb 105 column. The area of the chromatogram labeled "reconcentration period" represents the period of time during which the Chromosorb 105 column was maintained at ambient temperature to allow the water to pass through. The point at which heating of the Chromosorb 105 column began is indicated on the chromatogram. After this, the oxygenates and aromatics were eluted as shown by the labeled area of the chromatogram. The final peak of the chromatogram, labeled "excess area," is an impurity peak that appears in the baseline when the Chromosorb 105 is heated. This area is routinely discarded from the chromatogram by dropping a perpendicular in the manner indicated.

All samples were subjected to the analytical sequence described above, and the areas corresponding to the different portions of the chromatogram were automatically recorded by the Autolab System IV integrator. These raw data were reduced by a series of corrections and calibrations to yield concentration values for the various hydrocarbon classifications described in this report.

d. Data Corrections

To obtain concentration values from the raw data, it was necessary to subject the data to various corrections and manipulations. Appendix B details the correction sequence for the data obtained from the chromatogram in Figure 14. The raw integrator data are first converted to a common attenuation scale (10^3 x 8) corresponding to the scale used in the calibration curve for hexane (Figure 15). The area under the trace of the chromatogram is

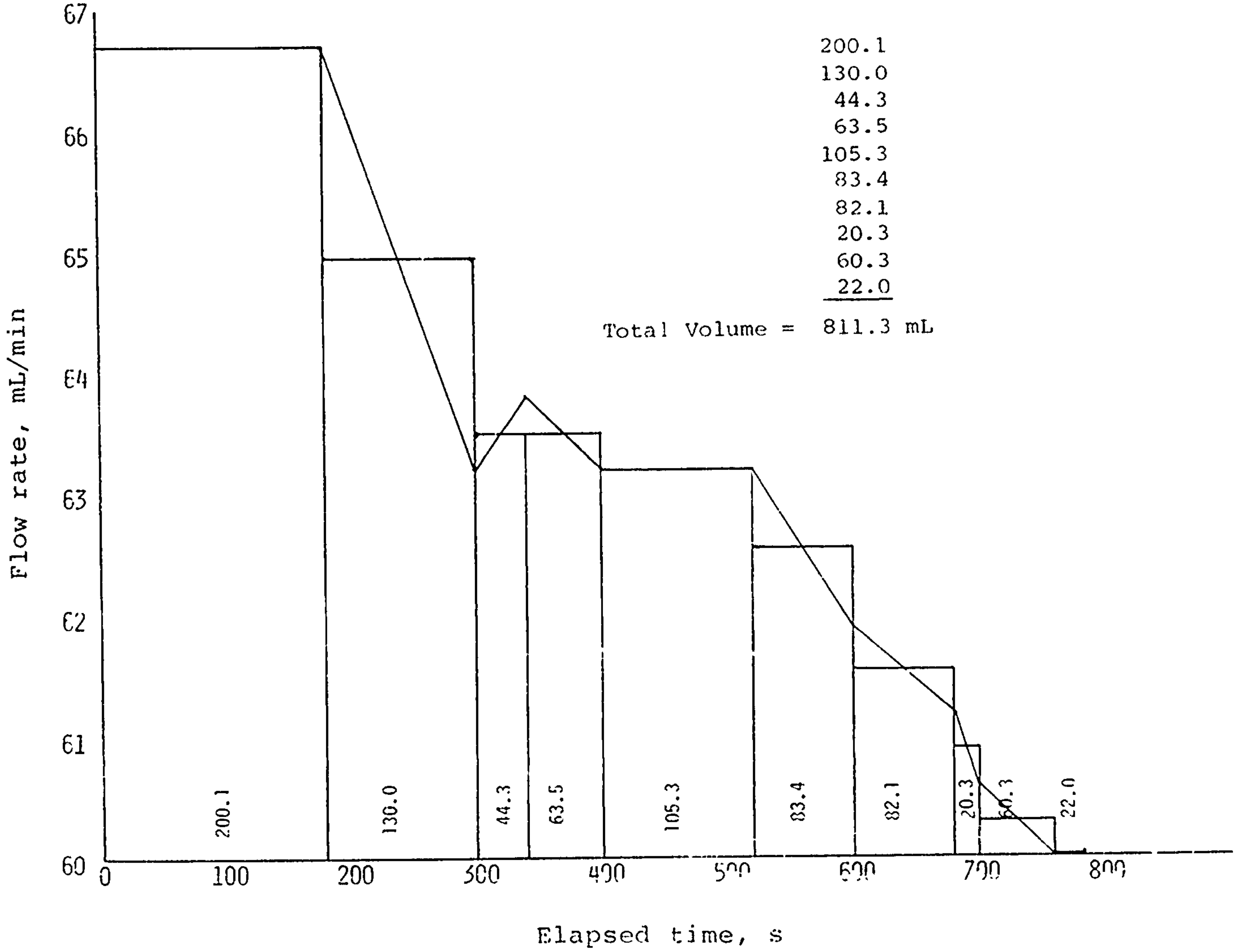

Figure 13. Graphical determination of total sample volume.

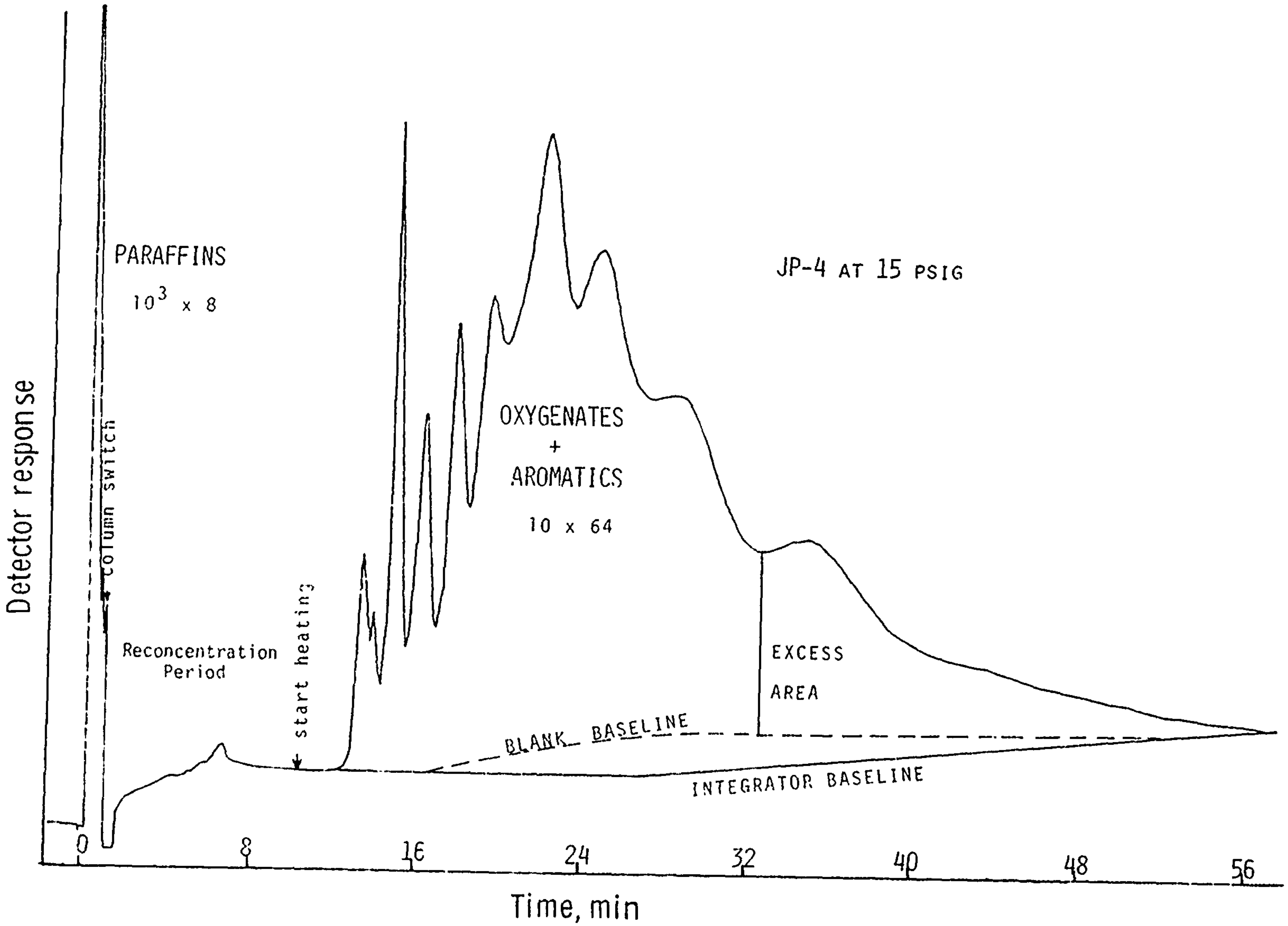

Figure 14. Typical chromatogram of exhaust analysis.

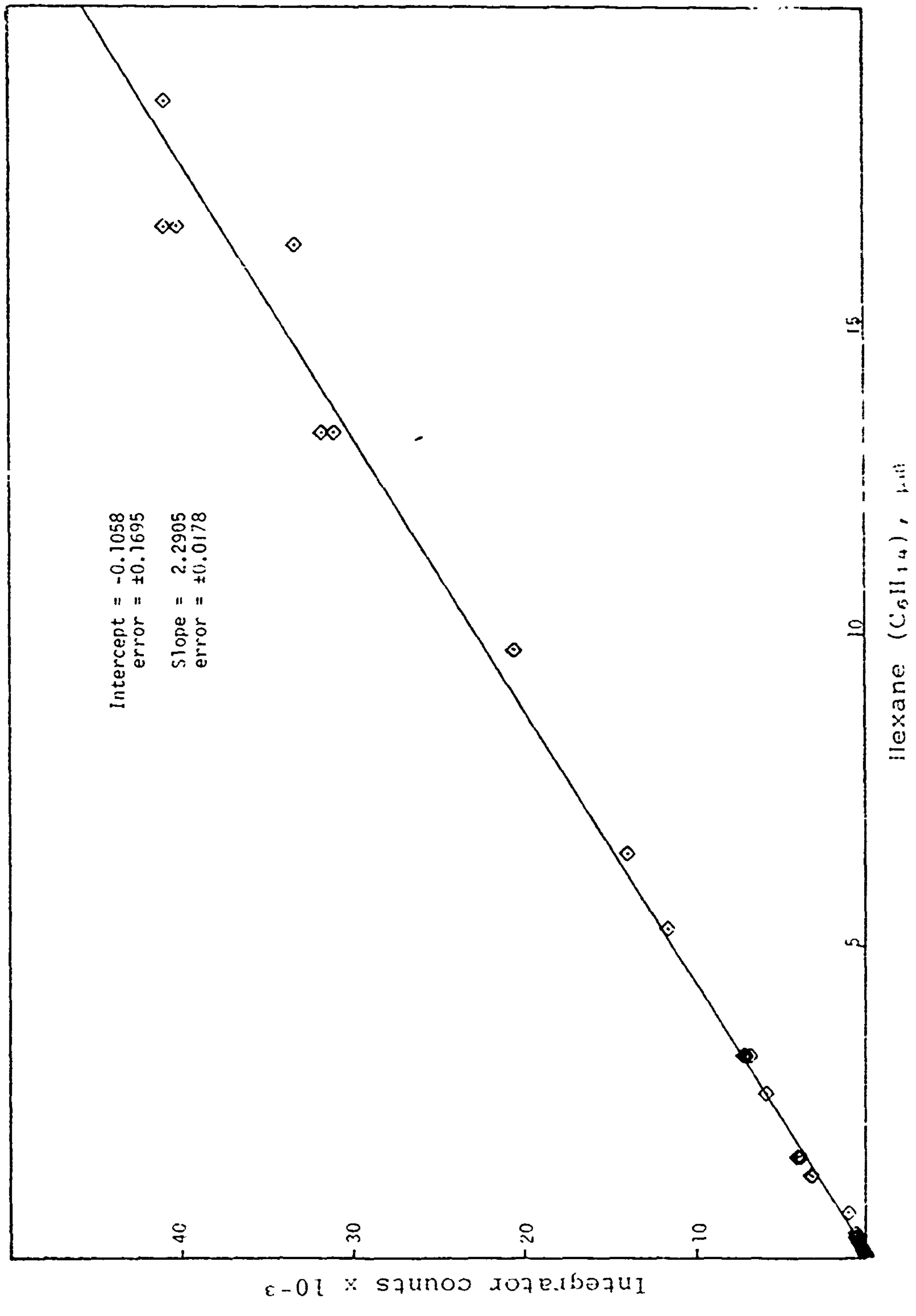

Figure 15. Hexane calibration curve.

divided into two regions (corresponding to the area detected at each FID), and the total area for each region is obtained. Correction is made to the area detected at FID B to account for a rise in baseline and an impurity peak. These "excess areas" are measured using either a manual Ott Compensating Polar Planimeter or a Hewlett-Packard electronic planimeter. An empirically determined conversion factor is used to relate the planimetry values to integrator counts. The corrected integrator counts are converted to an equivalent mass of hexane (μg) by using the calibration curve in Figure 15. The hexane calibration curve was obtained using FID A; consequently, the hexane equivalent at FID B must be corrected to compensate for the difference in response between FID A and FID B. Finally, the hexane mass equivalents are converted into concentrations [ppm (v/v) as hexane] using the ideal gas law and taking into account the total exhaust volume sampled. If it is desirable for comparison purposes to express the values as ppm methane, they are simply multiplied by 6.

e. Tabulated Data

Table 9 is a summary sheet of all samples analyzed in this exhaust analysis program. The analytical results are listed in terms of mass (μg as C_6) and concentration (μg/cm^3). Type I analyses were obtained at FID A without the subtractor in the system (see Figure 4) and Type I(S) were obtained at FID A with the subtractor in the system. Type II analyses were obtained at FID B. Therefore:

Type I = olefins + light oxygenates + paraffins

Type I(S) = paraffins = total unreactive

Type II = oxygenates + aromatics

Type I-Type I(S) = olefins + light oxygenates

[Type I-Type I(S)] + Type II = olefins + oxygenates
+ aromatic = total reactive

Type I + Type II = total hydrocarbons

The various classifications of the hydrocarbon exhaust products were obtained either by direct analysis or by difference and/or summation of the analyses results as indicated above. Not all classifications were equally well determined due to limited samples at some of the test points. In general, when multiple samples were obtained, the precision of the determinations was very good (see Table 9). Certain values were rejected on a statistical basis or because some problem in the analytical procedure caused them to yield erroneous results.

TABLE 9. HYDROCARBON ANALYSES SUMMARY SHEET

Data point	Trap No.	Sample volume	Type I µg as C_6	Type I µg/cm³	Type I(S) µg as C_6	Type I(S) µg/cm³	Type II µg as C_6	Type II µg/cm³	THC µg as C_6	THC µg/cm³	Reactive µg as C_6	Reactive µg/cm³	Unreactive µg as C_6	Unreactive µg/cm³
5BAXX	16	810	0.571	0.0007			1.780	0.0022	2.351	0.0029				
No fuel background	17	775	0.458	0.0006			1.368	0.0018	1.826	0.0024				
Av				0.0007				0.0020		0.0026				
5BBXX	4	290	6.186	0.0213			7.774	0.0268^R	13.960	0.0481^R				
JP-4	3		2.469^R				7.900		10.369					
33 psig	6	290	6.716	0.0232			9.040	0.0312	15.756	0.0543				
	7	305			2.446	0.0080	9.318	0.0306					2.446	0.0080
	5	305	6.013	0.0197			9.401	0.0308	15.414	0.0505				
	2	320	1.701^R				9.839	0.0307						
Av				0.0214		0.0080		0.0308		0.0524		0.0442		0.0080
5BCXX	19	245	4.3/5	0.0178			12.512	0.0511	16.887	0.0689				
JP-4	20	325					12.990	0.0400						
33 psig														
Av				0.0178				0.0456		0.0689				
5BFXX	17	295			0.268	0.0009	2.532	0.0086						
JP-4	23	365			0.480	0.0013	4.770	0.0131						
50 psig	16	375	2.808	0.0075			3.841	0.0102	6.649	0.0177				
	21	370	2.493	0.0067			2.996	0.0081	5.489	0.0148				
Av				0.0071		0.0011				0.0162		0.0160		0.0011
5BIXX	4	160	15.425	0.0964										
JP-4	13	145	14.346	0.0989			20.527	0.1416	34.873	0.2405				
15 psig	14	150	16.225	0.1082			23.579	0.1572	39.804	0.2654				
	12	150			10.550	0.0703	22.970	0.1531					10.550	0.0703
	6	160			10.892	0.0681	24.268	0.1517					10.892	0.0681
Av				0.1012		0.0692		0.1509		0.2530		0.1829		0.0692
5BLXX	10	280	4.704	0.0168			13.420	0.0479	18.124	0.0647				
JP-8	11	305	(Bad analysis)											
33 psig														
Av			0.0168					0.0479		0.0647				
5BMXX	18	380	4.767	0.0125			8.390	0.0221	13.157	0.0346				
DEL-6	7	365	5.376	0.0147			9.987	0.0274	15.363	0.0421				
33 psig	5	275			1.033	0.0038	10.972	0.0399						
Av				0.0136		0.0038		0.0298		0.0384		0.0396		0.0038
5BPXX	2	450	7.984	0.0177			19.531	0.0434	27.515	0.0611				
DEL-5	4	375	6.396	0.0171			12.855	0.0343	19.251	0.0513				
33 psig	9	375			2.525	0.0067	12.038	0.0321						
Av				0.0174		0.0067		0.0366		0.0562		0.0473		0.0067
5BQXX	5	280	2.860	0.0102			7.821	0.0279^R	10.681	0.0381				
Isooctane	18	575	4.679	0.0081			2.783	0.0048	7.462	0.0130				
33 psig	17	380			1.925	0.0051	1.452	0.0038						
	7	580					2.485	0.0043						
Av				0.0091		0.0051		0.0043		0.0130		0.0083		0.0051

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^{R}Rejected statistically or otherwise.

Table 10 lists the average values in terms of ppm C for the various hydrocarbon classifications at the different test points. The percent composition of the exhaust is tabulated in Table 11. A comparison of the THC results obtained in this study with those obtained on-line during sampling at APL is contained in Table 12.

TABLE 10. HYDROCARBON ANALYSES SUMMARY

Fuel	Inlet pressure, psig	ppm Carbon Olefins + light oxygenates	Oxygenates + aromatics	Total reactive	Total unreactive	THC
JP-4	15	54.6	257	312	118	430
JP-4	33	22.8	52.5	75.4	13.6	89.0
JP-4	50	10.2	17.0	27.3	1.88	29.2
JP-5	33	-	77.7	-	-	117
JP-8	33	-	81.7	-	-	110
DEL-5	33	16.7	50.8	67.5	6.48	74.0
DEL-5	33	18.2	62.4	80.6	11.4	92.0
Isooctane	33	6.82	7.33	14.1	8.70	22.8

TABLE 11. HYDROCARBON ANALYSES SUMMARY

Fuel	Inlet pressure, psig	Percent olefins + light oxygenates	Percent oxygenates + aromatics	Percent reacted	Percent unreacted
JP-4	15	12.7 (8.6)[a]	59.8 (40.4)	72.6 (49.1)	27.4 (18.6)
JP-4	33	25.6 (13.8)	59.0 (31.8)	84.7 (45.7)	15.3 (8.2)
JP-4	50	34.9 (17.9)	58.2 (29.8)	93.5 (47.9)	6.4 (3.3)
JP-5	33		66.4 (23.1)		
JP-8	33		74.3 (40.2)		
DEL-5	33	22.6 (14.8)	68.6 (45.0)	91.2 (59.7)	8.8 (5.7)
DEL-5	33	19.8 (11.8)	67.8 (40.5)	87.6 (52.3)	12.4 (7.4)
Isooctane	33	29.9 (21.3)	32.1 (22.9)	61.8 (44.1)	38.2 (27.2)

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[a] Numbers in parentheses represent percentages compared to APL THC results.

TABLE 12. COMPARISON OF ARL AND APL TOTAL HYDROCARBON (THC) RESULTS

Fuel	Inlet pressure, psig	ARL THC, ppm carbon	APL THC, ppm carbon	Percent ARL THC/ APL THC
JP-4	15	430	636	67.6
JP-5	33	117	337	34.9
JP-8	33	110	203	54.3
DEL-5	33	92.0	154	59.7
JP-4	33	89.0	165	53.9
DEL-5	33	74.0	113	65.5
JP-4	50	29.2	57	51
Isooctane	33	22.8	32	71.3

2.2.3 Discussion of Results

There are many methods for analyzing the data obtained in these analyses. Three of the more logical methods of comparing the results and studying trends are described below.

1. Compare the results of different fuels at the same combustion conditions (i.e., same inlet pressure) to assess the fuel dependence of the hydrocarbon exhaust makeup.

2. Compare the results of one fuel at several different combustion conditions to assess the combustion condition dependence of the hydrocarbon exhaust makeup.

3. Compare the results with those from other comparable analyses to assess the consistency and efficiency of the method.

2.2.3.1 Results for JP-4, JP-5, JP-8, DEL-5, and Isooctane at 33 psig

a. THC

Under moderate combustion conditions (33 psig), JP-5 and JP-8 produced the highest THC content in the exhaust (Table 10). JP-4 and the special blend DEL-5 produced a slightly lower THC concentration (74 to 92 ppm), but by far the cleanest burning fuel was the pure isooctane, producing ∿23 ppm THC. The composition of the THC portion of these exhausts will now be discussed in terms of the various classifications described in this report.

b. Total Reactive

For the purposes of this report, "reactive" is defined as that portion of exhaust made up of all nonparaffinic organic compounds. Due to limited numbers of samples, total reactive data were not obtained for JP-5 or JP-8. However, for the other fuels, Tables 10 and 11 show that reactive compounds constituted the major portion of the hydrocarbon exhaust. JP-4 and DEL-5 had roughly comparable concentrations (65 to 80 ppm) of reactive compounds at 33 psig, while in isooctane exhaust the concentration was about five times smaller and constituted the lowest percentage contribution (62%) to the THC value of any fuel sampled. Eighty-five percent to ninety percent of the total mass of hydrocarbon species sampled in the exhaust of JP-4 and DEL-5 was reactive in nature.

c. Total Unreactive

We have defined "unreactive" to mean paraffinic compounds. Isooctane had the highest percentage (38.2%) of unreactive compounds in its exhaust. The concentration range for unreactive species was very narrow (6.5 to 13.6 ppm) for all of the fuels sampled at 33 psig.

d. Oxygenates Plus Aromatics

The major fraction of the reactive portion of all exhaust samples taken at 33 psig was made up of oxygenated and aromatic compounds. In fact, in every case except for isooctane (32%), this fraction constituted >55% of the total mass sampled. JP-4 and DEL-5 exhibited very similar concentrations of oxygenates + aromatics, although the percentage appeared to be slightly higher in the case of DEL-5.

e. Olefins Plus Light Oxygenates

The term "light oxygenates" is used to describe oxygenated compounds (principally acetaldehyde) which have a shorter retention time than propionaldehyde on the TCEP column and thus are eluted along with olefins and paraffins. The $PdSO_4/H_2SO_4$ section of the subtractor removes these compounds so that their contribution is combined with that of the olefins. All fuels sampled had 20% to 30% olefins + light oxygenates in their exhaust at 33 psig.

2.2.3.2 Results for JP-4 at 15, 33, and 50 psig

The results for JP-4 at 15, 33, and 50 psig are contained in Tables 10 and 11 and summarized graphically in Figure 16. The triangular points on the graph represent on-line THC values recorded at the time of sampling.

a. THC

The graph in Figure 16 shows that as the power was increased (i.e., higher inlet pressure), the total hydrocarbon concentration dropped off dramatically. The THC dropped from 430 ppm at a very inefficient combustion condition (15 psig) to 30 ppm at a more moderate condition (50 psig). This was as expected from more efficient combustion.

b. Total Reactive

The total reactive portion is represented in Figure 16 by the dotted area designated "olefins + light oxygenates" and the cross-hatched area designated "oxygenates + aromatics." The trend to lower concentrations at a higher power setting which was observed in the THC results was also observed in the concentrations of reactive compounds. These values decreased from 312 ppm at 15 psig to 27.3 ppm at 50 psig. However, the percentage of the THC concentration represented by reactive species increased as the inlet pressure was increased. This is

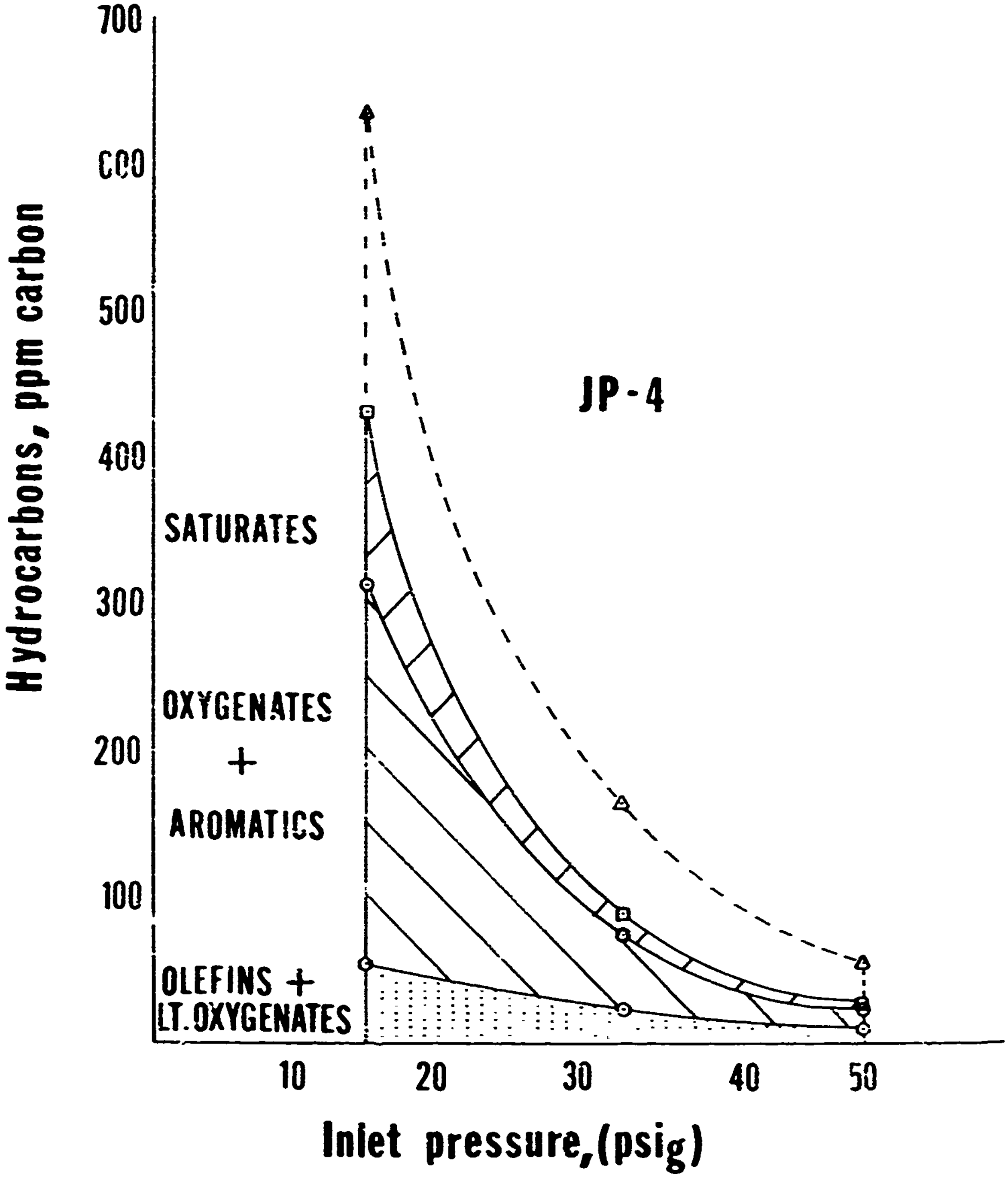

Figure 16. Graphical representation of JP-4 data.

consistent with the reasoning that under more efficient combustion conditions more oxidized and partially oxidized species would be produced.

c. Total Unreactive

The total unreactive results were also lower at higher power settings. The percentage contribution of unreactive species to the THC concentration decreased at higher inlet pressures, consistent with the reasoning described in b above.

d. Oxygenates Plus Aromatics

A surprising result was that the percentage of the THC value represented by oxygenates + aromatics was constant (∿59%) for JP-4 at all conditions sampled. The general trend, as in all cases, was toward lower absolute concentrations at higher power settings.

e. Olefins Plus Light Oxygenates

Since the percentage contribution of oxygenates + aromatics at the different inlet pressures (described in d above) was constant, the higher percentage contribution of total reactive species described in b above was due entirely to an increase in the percentage of olefins + light oxygenates (Table 11). At 15 psig, olefins + light oxygenates constituted only 12.7% of the THC value, while at 50 psig, they constituted 34.9%.

2.2.3.3 Comparison of ARL and APL THC Results

The values recorded on-line by a Beckmann 402 Total Hydrocarbon Analyzer at APL were the only results available for comparison with our results. Table 12 lists these THC values and gives a percent comparison. These are also displayed graphically for JP-4 in Figure 16, with the triangular points representing APL results and the square points representing ARL results. The results in Table 12 are listed in decreasing order according to ARL THC values. Note that with one exception this also represents the decreasing order for the APL results. This exception is eliminated, however, if one considers that the ARL THC values of 92 and 89 ppm C (JP-4 and DEL-5 at 33 psig) are equal within the experimental error of the analyses. Thus the gross order (i.e., highest to lowest) is consistent for the two sets of THC data.

With one exception, ARL THC values are 50% to 70% of the APL THC values. The one exception is JP-5 at 33 psig. Since only one sample was used to obtain this value, the reliability of the result is in question. In an effort to explain the apparent discrepancy between the two sets of THC data, we returned to APL to collect more exhaust samples. This time the sorbent sampling trap was followed by an evacuated sample bulb. The data obtained are of little quantitative value, but there are definite indications that the major portion of the difference between the ARL and APL results was due to sample breakthrough. Characterization of the portion trapped in the sample bulb indicated that, like the sorbent trapped sample, it was primarily reactive in nature. Methane analyses run at MRC showed no methane content in the bulb samples. These results are very preliminary. Another possible source of error was a yellow-orange tarry deposit which was occasionally observed at the outlet of the sample tube when the sample was desorbed. This residue was not characterized.

The values in parentheses in Table 11 represent percentages for the various classifications compared to APL THC results. If one accepts the on-line THC values as being correct, the percentages in parentheses represent minimum values of the various hydrocarbon classifications present in the exhaust.

2.3 CONCLUSIONS

2.3.1 Analysis of Aqueous Nitrates, Nitrites, and Nitrogen Oxide

The procedure described in section 2.1.2.4 for the analysis of aqueous nitrates and nitrites by the conversion to nitrobenzene is very sensitive. A calibration procedure using nitrobenzene in benzene standards which have undergone the same reaction procedure as unknowns was found to be the best. The efficiencies of conversion of nitrate (KNO_3), nitrite (KNO_2), and nitric acid (HNO_3) were 90.3%, 100.4%, and 99.9%, respectively, using this method. The analyses for nitrate in urine and drinking water showed good precision.

We envision several possible advantages accruing from perfection of the method described in section 2.1.2.7 for the conversion of nitrogen dioxide to nitrobenzene. In comparison with the phenodisulfonic acid method, it is faster and potentially applicable over a wider concentration range. In qualitative experiments, it was possible to detect ambient levels of oxides of nitrogen in air samples from a metropolitan area. It could also afford an alternative means of calibration for other instrumentation. The instrumentation is widely available, is not highly specialized, and, consequently, can be used for the analysis of other sample types. Finally, the EC-GC method appears to be highly specific. Even samples as complex as auto exhaust produce chromatograms with no evidence of interfering peaks.

2.3.2 Sampling and Hydrocarbon Classification System

2.3.2.1 Analytical System

The analytical system performed very satisfactorily for its first test with real-world samples. The precision on replicate samples was good. There are, however, several obvious improvements that can be made in the system:

(1) Shorten analysis time - approximately 1 hr is required to analyze the contents of each trap.

(2) Improve reproducibility through automation - the switching valve is now manually actuated at some specified time after sample desorption.

(3) Eliminate the necessity of planimeter corrections - these are necessary because of baseline rise associated with heating the Chromosorb 105 column.

(4) Develop method for including "light" oxygenates with other oxygenates.

(5) Develop analytical capability to obtain concentrations of aromatics and oxygenates separately.

The relatively high concentrations of water in the samples did not prove to be a problem in the analyses. This led to speculation that the function of the Chromosorb 105 column might not be necessary. Elimination of this column would solve problem 3 above. A simple time-programmed automatic backflush of the TCEP column would then shorten total analysis time to less than 10 minutes.

There are several prospective subtractor substances which might serve to preferentially remove either oxygenates or aromatics. Since a second sample is already required to obtain paraffinic and olefinic classifications, a second subtractor could be used at the same time to achieve the aromatic and oxygenate breakdown. The installation of valves to allow these subtractors to be automatically switched into the system would be an added improvement.

2.3.2.2 Sampling System

The sampling system is the weakest link in the overall system developed to conduct the hydrocarbon analyses. The problem with sample breakthrough is major and places serious limitations on the data obtained. A thorough study needs to be conducted on samples of known concentrations under simulated conditions to establish the sampling and desorption efficiencies of the traps and sorbent materials. Perhaps very minor changes such as increasing the trap size or volume will eliminate the problem.

Another possible improvement is gradient cooling rather than isothermal cooling.

2.3.2.3 Exhaust Analyses

Subject to the limitations expressed above, some tentative conclusions can be drawn from the analytical data obtained:

(1) The major portion of the hydrocarbon exhaust from all fuels tested is reactive in nature.

(2) For a given fuel, the percentage composition of reactive compounds increases as the power is increased.

(3) There is a general decrease in absolute concentration of all classifications of compounds as the power is increased.

(4) The distribution of hydrocarbon species into the various classifications does not differ appreciably for JP-4 compared to DEL-5 even though DEL-5 is JP-4 with increased aromatic content.

(5) Greater than 55% of the THC sampled from actual jet fuels was classified as either aromatic or oxygenated.

(6) The pure isooctane showed market reduction in THC compared with actual jet fuels and had the highest percentage contribution from unreactive compounds.

SECTION 3

TASK I - NEW CONCEPTS IN PREDICTING ENGINE WEAR THROUGH OIL ANALYSIS

3.1 INTRODUCTION

The goal of Task I was to assess the role of nonmetallic oil indicators in predicting engine wear. The traditional approach used in SOAP analyses has been to measure the actual wear product (i.e., metal content of the oil). The thrust of Task I was to investigate the possibility of performing "predictive" rather than the conventional "after-the-fact" oil analyses. Stated differently, this task sought to discover if lubricating oil undergoes some detectable change prior to the onset of inordinate engine wear which can be used as an indicator of the impending wear.

Several physical techniques [22] were examined as potential methods for characterizing the oils and studying changes which occur with use. The techniques examined were gel permeation chromatography (GPC), reverse phase liquid chromatography (RPLC), ultraviolet (UV) absorption, infrared (IR) spectrophotometry, and gas chromatography. The most promising methods for evaluating changes which occur in the synthetic ester lubricants of interest were found to be chromatographic. Gas chromatography gave the best resolution of individual lubricant constituents, and GC instrumentation was more readily available for our use than was other chromatographic instrumentation.

Task I research concentrated on the development and evaluation of gas chromatographic methods for the characterization of new and used synthetic lubricants. Significant progress was made in the analyses of these lubricants by GC and the handling and presentation of the data obtained. This resulted in the accumulation of valuable baseline data on the unused lubricants and preliminary success in using GC for detecting changes occurring in the lubricants with use.

Specific progress resulted in three areas: (1) More detailed characterization of a MIL-L-23699 lubricant, (2) Development of a technique for determining the composition of MIL-L-7808 lubricant mixtures, and (3) The evaluation of base stocks.

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[22] Ross, W. D., Brooks, J. J., Duffy, T. G., Wininger, M. T., Rehg, W. R., Buttler, G. W., Black, M. S., Pustinger, J. V., and Snyder, A. D., "Trace Chemical Analysis Methodology," First Annual Report, Contract F33615-75-C-1130, 5 February 1975 - 16 February 1976.

3.2 EXPERIMENTAL

Gas chromatographic analyses of the synthetic lubricants were performed on a Hewlett-Packard Model 5830A chromatograph. Initially the instrument was equipped with an OV-101 SCOT column using the instrumental conditions described in Table 13, column A. Since it was believed that the higher molecular weight compounds in the MIL-L-23699 oil samples were not being eluted under these conditions, successive injections of MIL-L-23699 oil were made to determine if the condition of the column was changing during daily operation. By the successive increase in retention times, the data in Table 14 indicate that the condition of the column was definitely changing throughout the day. The results from April 20 show that the column recovered to the original performance capability after 4 days of inactivity. However, the retention times again increased on successive injections of MIL-L-23699 oil. The analysis of another sample on the following morning showed that the column performance capability could not be recovered by the next day. In addition, there was some loss of peak intensity during this experiment. The results strongly suggest that the higher molecular weight components of the MIL-L-23699 oil were remaining in the column and subsequently functioning as a liquid phase to increase the retention times of the ester components.

TABLE 13. OPERATING CONDITIONS FOR HEWLETT-PACKARD 5830-A GAS CHROMATOGRAPH

Parameter	A	B
Column	OV-101 SCOT, stainless steel, 0.02-in. ID, 0.030-in. OD, 50-ft long	3% Dexsil 400 on 80/100 Chromosorb W, glass, 0.08-in. ID, 0.25-in. OD, 6-ft long
Sample	∿10 vol % oil in methylcyclohexane	6.85 wt % oil in methylcyclohexane
Split ratio	∿10:1	--
Flow rate	∿8 mL/min He	∿25 mL/min He
Inlet temp	250°C	340°C
FID temp	300°C	340°C
Temp program	200-250°C at 2°C/min	180-350°C at 2°C/min
Chart speed	0.2 cm/min	0.5 cm/min

TABLE 14. EFFECT OF REPLICATE INJECTIONS OF MIL-L-23699 LUBRICANT ON THE RETENTION TIMES OBTAINED FROM AN OV-101 SCOT COLUMN

Date	Injection No.	Retention times of three representative peaks, min		
15 April	1	21.21	33.75	66.78
	2	21.27	33.85	66.93
	3	21.32	33.92	67.23
20 April	1	20.86	33.18	65.17
	2	21.01	33.39	65.78
	3	21.13	33.62	66.38
21 April	1	21.67	34.57	69.01

A 6-ft glass column was packed with 3% Dexsil 400 on 80/100 mesh Chromosorb W to attain a higher operating temperature capability. This new column was installed in the Hewlett-Packard chromatograph, and the instrument was then operated using conditions described in Table 13, column B. Figure 17 contrasts the chromatograms obtained from the analyses of MIL-L-23699 oil samples using the OV-101 SCOT column and the Dexsil 400 column. Careful comparison of the two chromatograms shows that the last significant peak in the OV-101 chromatogram (retention time, 67.69 min) corresponds to the peak at 42.67 minutes in the Dexsil 400 chromatogram. The appearance of numerous additional peaks after this peak in the Dexsil 400 chromatogram indicates additional capability for eluting the higher molecular weight esters in the MIL-L-23699 lubricant. Successive runs on the Dexsil 400 column did not significantly change the retention times, and no loss of peak intensity was observed. This column was used for all subsequent analyses of ester-based synthetic lubricants because of its superior analytical capabilities.

3.3 RESULTS AND DISCUSSION

3.3.1 Characterization Studies of a MIL-L-23669 Type Lubricant

3.3.1.1 Statistical Evaluation of Base Stock Constituents

The group of used oil samples from the T-43A navigator trainers at Mather AFB, California was the most controlled set of used lubricant samples available at AFML, since they were all from a single engine type (JT-8D-9A) which used only MIL-L-23699 lubricant from a single source. Some information on the composition of this MIL-L-23699 lubricant is contained in the patent

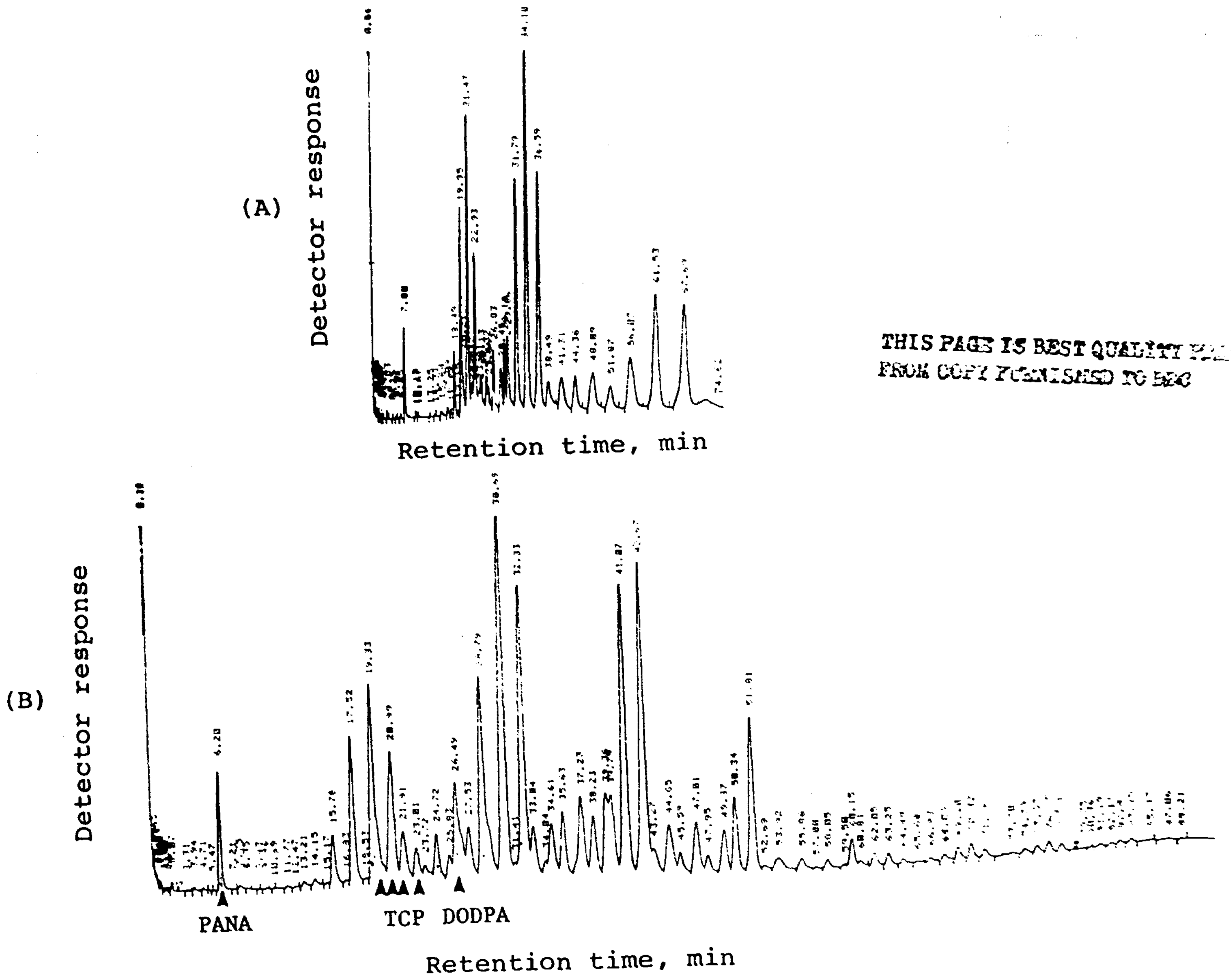


Figure 17. Gas chromatograms of unused MIL-L-23699 oil using (A) an OV-101 SCOT column and (B) a Dexsil 400 packed column.

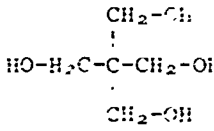
literature [23]. Table 15 contains an example of the lubricant formulation that is the major constituent of this MIL-L-23699 lubricant.

TABLE 15. COMPOSITION OF THE MAJOR CONSTITUENT OF MIL-L-23699 LUBRICANT [23]

Component	Wt %
Ester A (base stock)	94.88
Phenyl-α-naphthylamine (PANA)	1.00
Dioctyldiphenylamine (DODPA)	1.00
Salt A	0.10
Quinizarin (1,4-dihydroxyanthraquinone)	0.02
Tricresyl phosphate (TCP)	3.00
Dimethyl silicone	5[a]

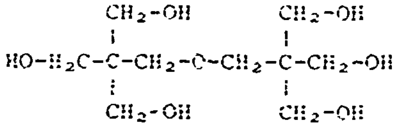
[a] Value in parts per million.

Ester A is formed from the reaction of technical grade pentaerythritol (a mixture of ∿88% monopentaerythritol and ∿12% dipentaerythritol) with a mixture of pelargonic acid, C_9, and commercial isopentanoic acid, C_5 (a mixture of two parts by weight of n-valeric acid and one part by weight of isovaleric acid). Figure 18 shows the chemical structures of monopentaerythritol and dipentaerythritol. Analysis of the product obtained from this reaction gives a balance of 1 molar proportion of pentaerythritol to about 1 molar proportion of C_9 and 3 molar proportions of the commercial C_5. It follows that the molar ratio of the acids in the product is $1:2:1/C_9:C_{5n}:C_{5i}$.



$$\begin{array}{c} CH_2-OH \\ | \\ HO-H_2C-C-CH_2-OH \\ | \\ CH_2-OH \end{array}$$

Pentaerythritol (PE)



$$\begin{array}{c} CH_2-OH \qquad\qquad CH_2-OH \\ | \qquad\qquad\qquad\quad | \\ HO-H_2C-C-CH_2-O-CH_2-C-CH_2-OH \\ | \qquad\qquad\qquad\quad | \\ CH_2-OH \qquad\qquad CH_2-OH \end{array}$$

Dipentaerythritol (DPE)

Figure 18. Polyols used in base stock of MIL-L-23699 lubricant.

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[23] Oberright, E. A., and Hepplewhite, H. L., "High Temperature Jet Lubricant," U.S. Patent No. 3,247,111. April 9, 1966.

With this information it was possible to formulate the major base stock synthesis scheme shown in Figure 19. Since monopentaerythritol (PE) has 4 esterification sites and dipentaerythritol (DPE) has 6, it was possible to obtain 15 unique PE products and 55 unique DPE products from the synthesis reaction. Therefore, there are potentially 70 different esters in the major base stock constituent of the MIL-L-23699 lubricant.

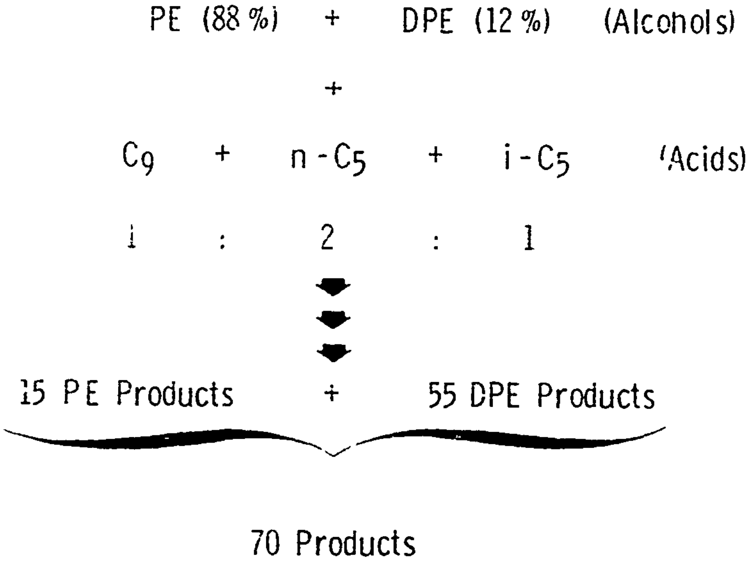


Figure 19. Synthesis of MIL-L-23699 base stock ester.

If one assumes the relative molar concentrations listed in the patent and further assumes that any of the 3 acids is equally capable of reacting at any of the esterification sites, it is possible to statistically predict the relative abundances of the 70 ester products in the base stock. A simple multinomial distribution of the form

$$\frac{n!}{x!y!z!} p_x^x p_y^y p_z^z$$

was used to predict the relative abundance of the PE products since all four esterification sites are equivalent. In this expression, n is the number of esterification sites (i.e., four for PE) in the product, x is the number of C_9 esters, y is the number of C_{5n} esters, and z is the number of C_{5i} esters in the product. P_x, P_y, and P_z are the probabilities (based on abundances of the acids) for forming C_9, C_{5n}, and C_{5i} esters, respectively (i.e., 0.25, 0.50, and 0.25). The case for the DPE product is more complicated since DPE contains two sets of three equivalent esterification sites. The expression for predicting the relative abundances of these products is a joint multinomial distribution of the form

$$\frac{n_\ell!}{x_\ell!\,y_\ell!\,z_\ell!}\,P_x^{x_\ell}P_y^{y_\ell}P_z^{z_\ell}\;\frac{n_r!}{x_r!\,y_r!\,z_r!}\,P_x^{x_r}P_y^{y_r}P_z^{z_r}$$

which is simply the product of the multinomial distribution expressions for the left-hand and right-hand sides of the molecules. The symbols in this expression are the same as those described for the PE case with the addition of the subscripts ℓ and r to designate left and right. A computer program was developed to calculate the relative abundances of the 70 potential products based on the above expressions. Appendix C lists the computer program and Table 16 contains the calculated values. It should be noted that these relative abundances were determined strictly on the basis of statistics and do not take into consideration differing reaction rates and thermodynamic considerations.

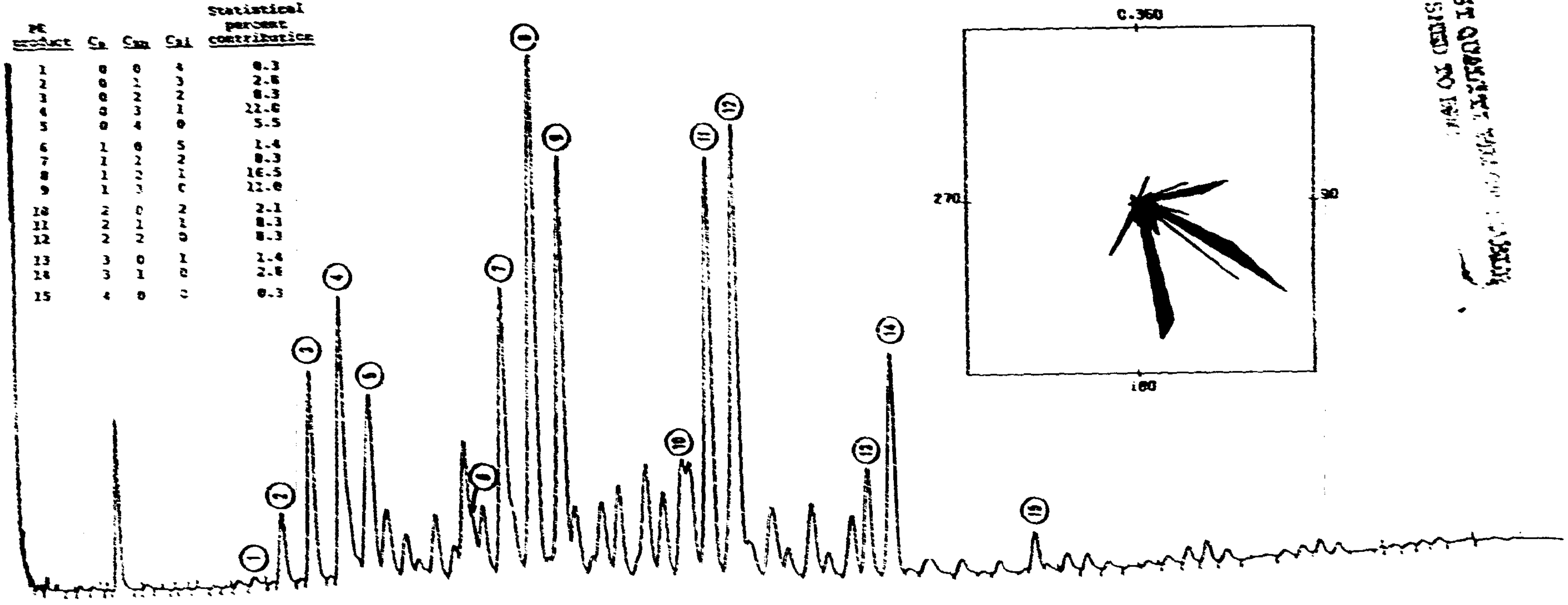
A sample of this MIL-L-23699 oil (Formulation A) was subjected to gas chromatographic analysis using the Dexsil 400 column and the conditions listed in Table 13, Column B. The chromatogram obtained from this analysis is shown in Figure 20.

A second unused sample of the MIL-L-23699 (Formulation B) oil was obtained and subjected to an identical gas chromatographic analysis. Figure 21 is the chromatogram obtained from this analysis. It is immediately obvious that Formulation B (Figure 21) is different from Formulation A (Figure 20). More specifically, Formulation B's larger peaks are reduced in size while its smaller ones are enhanced. The shift in relative peak intensities indicates that more than one base stock formulation is used in preparing this particular MIL-L-23699 lubricant. Since the major base stock constituent is "Ester A" (the complex mixture of esters depicted in Figure 19), by superimposing the chromatograms from the analyses of Formulations A and B (Figures 20 and 21) it is possible to identify which peaks are due to Ester A since they are larger in Figure 20 than in Figure 21. In contrast, the peaks that are due to base stock formulations other than Ester A are smaller in Figure 20 than in Figure 21.

The 15 PE products and their statistical percent contributions (relative abundances) are listed in the table inset in Figure 20. The numbers under the column headings C_9, C_{5n}, and C_{5i} indicate how many esters of each type are present in each of the possible PE products. These products can be divided into groups of isomers depending upon the number of C_9 and the number of C_5 esters in the molecule. Products 1 through 5 are isomers (mol wt 472) that contain four C_5 esters and no C_9; products 6 through 9 are isomers (mol wt 528) with three C_5 esters and one C_9 ester each; products 10 through 12 (mol wt 584) have two C_5 and two C_9 esters each; products 13 and 14 (mol wt 640) have one C_5 and three C_9 esters each; and product 15 (mol wt 696) has no C_5 and four C_9 esters. The isomers within these groups have been arranged in the expected order of elution since in general C_{5i} compounds are

TABLE 16. STATISTICALLY DETERMINED RELATIVE ABUNDANCES OF PE AND DPE ESTERS

Product	C_5	C_5n	C_5i	C_5	C_5n	C_5i	Probability	Percent	Relative abundance
							PE Esters		
1	0	0	4				0.003906	0.88	0.003437
2	1	0	3				0.015625	0.88	0.013750
3	2	0	2				0.023438	0.88	0.020625
4	3	0	1				0.015625	0.88	0.013750
5	4	0	0				0.003906	0.88	0.003437
6	0	1	3				0.031250	0.88	0.027500
7	1	1	2				0.093750	0.88	0.082500
8	2	1	1				0.093750	0.88	0.082500
9	3	1	0				0.031250	0.88	0.027500
10	0	2	2				0.093750	0.88	0.082500
11	1	2	1				0.187500	0.88	0.165000
12	2	2	0				0.093750	0.88	0.082500
13	0	3	1				0.125000	0.88	0.110000
14	1	3	0				0.125000	0.88	0.110000
15	0	4	0				0.062500	0.88	0.055000
							DPE Esters		
16	0	0	3	0	0	3	0.000244	0.12	0.000029
17	0	0	3	1	0	2	0.001465	0.12	0.000176
18	0	0	3	2	0	1	0.001465	0.12	0.000176
19	0	0	3	3	0	0	0.000488	0.12	0.000059
20	0	0	3	0	1	2	0.000488	0.12	0.000059
21	0	0	3	1	1	1	0.005859	0.12	0.000703
22	0	0	3	2	1	0	0.002930	0.12	0.000352
23	0	0	3	0	2	1	0.002930	0.12	0.000352
24	0	0	3	1	2	0	0.005859	0.12	0.000703
25	0	0	3	0	3	0	0.005859	0.12	0.000703
26	1	0	2	1	0	2	0.002197	0.12	0.000264
27	1	0	2	2	0	1	0.004395	0.12	0.000527
28	1	0	2	3	0	0	0.001465	0.12	0.000176
29	1	0	2	0	1	2	0.008789	0.12	0.001055
30	1	0	2	1	1	1	0.008789	0.12	0.001055
31	1	0	2	2	1	0	0.008789	0.12	0.001055
32	1	0	2	0	2	1	0.017578	0.12	0.002109
33	1	0	2	1	2	0	0.017578	0.12	0.002109
34	1	0	2	0	3	0	0.011719	0.12	0.001406
35	2	0	1	2	0	1	0.002197	0.12	0.000264
36	2	0	1	3	0	0	0.001465	0.12	0.000176
37	2	0	1	0	1	2	0.008789	0.12	0.001055
38	2	0	1	1	1	1	0.017578	0.12	0.002109
39	2	0	1	2	1	0	0.017578	0.12	0.002109
40	2	0	1	0	2	1	0.017578	0.12	0.002109
41	2	0	1	1	2	0	0.017578	0.12	0.002109
42	2	0	1	0	3	0	0.011719	0.12	0.001406
43	3	0	0	3	0	0	0.000244	0.12	0.000029
44	3	0	0	0	1	2	0.002930	0.12	0.000352
45	3	0	0	1	1	1	0.005859	0.12	0.000703
46	3	0	0	2	1	0	0.002930	0.12	0.000352
47	3	0	0	0	2	1	0.005859	0.12	0.000703
48	3	0	0	1	2	0	0.005859	0.12	0.000703
49	3	0	0	0	3	0	0.003906	0.12	0.000469
50	0	1	2	0	1	2	0.008789	0.12	0.001055
51	0	1	2	1	1	1	0.035156	0.12	0.004219
52	0	1	2	2	1	0	0.017578	0.12	0.002109
53	0	1	2	0	2	1	0.017578	0.12	0.002109
54	0	1	2	1	2	0	0.035156	0.12	0.004219
55	0	1	2	0	3	0	0.035156	0.12	0.004219
56	1	1	1	1	1	1	0.035156	0.12	0.004219
57	1	1	1	2	1	0	0.035156	0.12	0.004219
58	1	1	1	0	2	1	0.070313	0.12	0.008437
59	1	1	1	1	2	0	0.070313	0.12	0.008437
60	1	1	1	0	3	0	0.046875	0.12	0.005625
61	2	1	0	2	1	0	0.008789	0.12	0.001055
62	2	1	0	0	2	1	0.035156	0.12	0.004219
63	2	1	0	1	2	0	0.035156	0.12	0.004219
64	2	1	0	0	3	0	0.023438	0.12	0.002812
65	0	2	1	0	2	1	0.035156	0.12	0.004219
66	0	2	1	1	2	0	0.070313	0.12	0.008437
67	0	2	1	0	3	0	0.070313	0.12	0.008437
68	1	2	0	1	2	0	0.035156	0.12	0.004219
69	1	2	0	0	3	0	0.046875	0.12	0.005625
70	0	3	0	0	3	0	0.015625	0.12	0.001875



PE product	C_5	C_{7n}	C_{9i}	Statistical percent contribution
1	0	0	4	0.3
2	0	1	3	2.6
3	0	2	2	8.3
4	0	3	1	22.6
5	0	4	0	5.5
6	1	0	3	1.4
7	1	1	2	8.3
8	1	2	1	16.5
9	1	3	0	12.0
10	2	0	2	2.1
11	2	1	1	8.3
12	2	2	0	8.3
13	3	0	1	1.4
14	3	1	0	2.6
15	4	0	0	0.3

Figure 20. Gas chromatogram and circular plot of Formulation A of MIL-L-23699 oil.

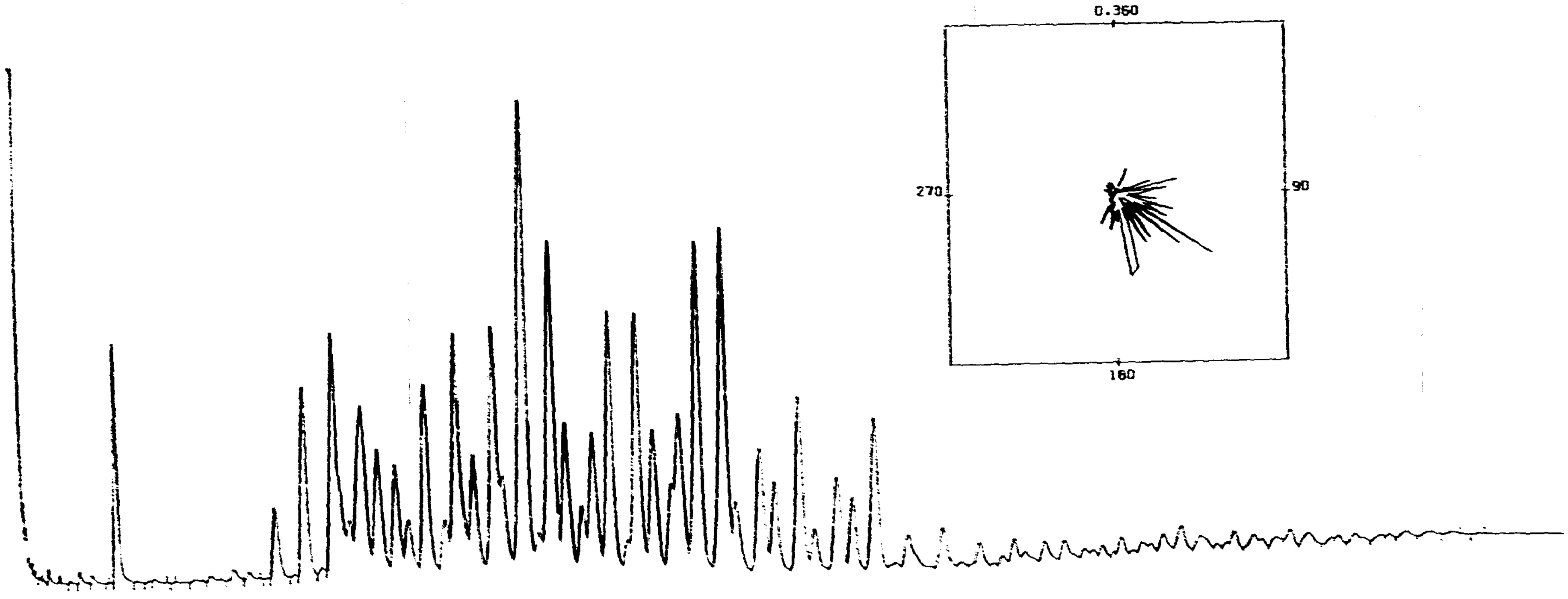


Figure 21. Gas chromatogram and circular plot of Formulation B of MIL-L-23699 oil.

expected to be more volatile (and therefore have shorter retention times) than C_{5n} compounds. Therefore, the order indicated in the table in Figure 20 represents the intuitively derived order of elution for the 15 PE products.

The correctness of this logically derived order is dramatically illustrated by superimposing the chromatograms in Figures 20 and 21. Statistics (Table 6) predict that certain of the PE products will be the most abundant in Ester A. Using this knowledge and the fact that the peaks from Ester A are larger in Figure 20 than in Figure 21, it is possible to readily identify the five sets of PE isomers shown in the table of Figure 20. With careful observation all 15 PE products in Ester A can be identified. These are indicated by the circled numbers in Figure 20. The statistically determined distribution of the PE products follows the trends observed in the actual peak heights. For example, in the first set of isomers (products 1-5) statistics predict that product 1 should be represented by the smallest peak of the group, product 2 should have the next to smallest peak, product 3 should have the next to largest peak, product 4 should have the largest peak, and product 5 should be the middle peak of the group in terms of size. This trend is observed in the actual chromatogram, giving credence both to the presumed order of elution and the statistical prediction of relative product abundances.

There is a reasonably consistent spacing between the peaks in each set of isomers which can be correlated to the increase in retention time when a C_{5n} ester is substituted for a C_{5i} ester in the product (Figure 20). This fact was useful in identifying the location of product 6, which appears as a shoulder (indicated by the arrow) on the side of a larger peak in Figure 20.

The serendipity of obtaining two formulations of the MIL-L-23699 lubricant with different ratios of base stock ester constituents combined with chromatographic intuition and statistical predications has enabled what we feel to be the unambiguous identification of all 15 PE esters from Ester A in the chromatogram without the aid of standards or other confirmatory methods such as mass spectrometry. This represents a significant accomplishment in light of the complexity of the separation problem.

There is potentially much additional information that can be obtained from the chromatographic data in Figure 20. For example, the table in Figure 20 indicates that on the basis of statistics there should be equal abundances of certain of the PE products. However, in actuality, when these products are not in the same group of isomers (e.g., products 1 and 15), the peak corresponding to the product with the longer retention time is larger than that for the product with the shorter retention time. This most likely is due to the increased FID response which would be expected as the result of the combustion of a larger molecule.

Thus, in theory, it should be possible to obtain response factor data from the chromatograms and predict the increase in FID response due to the substitution of a C_9 ester for a C_5 ester.

3.3.1.2 Analysis of Additives

Samples of each of the three major additives in Table 15 were analyzed using the conditions in Table 13, column B. Figure 22 contains separate chromatograms for tricresyl phosphate (TCP), phenyl-α-naphthylamine (PANA), and dioctyldiphenylamine (DODPA). The positions of the major additive peaks are indicated on the chromatograms of the MIL-L-23699 lubricant (Figure 17) on the basis of these retention times. Note that the PANA peak is well resolved and free from any interference from other components, but the TCP and DODPA peaks are obscured by other (ester) components of the lubricant.

In an effort to eliminate these interference problems it was decided to examine the applicability of the Hewlett-Packard nitrogen-phosphorus (N-P) specific detector for the analysis of additives in synthetic lubricants. A sample of the MIL-L-23699 lubricant was submitted to the Hewlett-Packard Applications Laboratory for analysis by this detector. The chromatogram (Figure 13) shows peaks only for PANA, TCP isomers, and DODPA. No response to the esters is seen. The advantage of the N-P specific detector is obvious in this application.

3.3.1.3 Analysis of Used Lubricant Samples

In addition to the GC characterization of unused MIL-L-23699 samples, two used samples were analyzed under identical conditions. These particular samples were chosen because they represented the two extremes of wear metal content and total hours of operation available from the MIL-L-23699 samples. The extreme of wear metal content was represented by a sample with 508 hours of operation and 37 ppm iron (Fe), while the extreme of hours of operation was represented by a sample with 1072 hours (4 ppm Fe). The resulting chromatograms along with that of an unused sample of MIL-L-23699 oil are displayed for comparison in Figure 24. The depletion of the PANA peak is the most obvious change in the chromatograms for the used oils. Another obvious change is observed in the ratio of the two peaks in the doublet at ∿39.8 minutes.

3.3.2 MIL-L-7808 Type Lubricants

The jet lubricants most widely used in the USAF are of the MIL-L-7808 type. The problems associated with the analysis of used MIL-L-7808 oils are complicated by the fact that several different manufacturers currently supply MIL-L-7808 lubricants to the Air Force, and, in general, the compositions vary widely among these

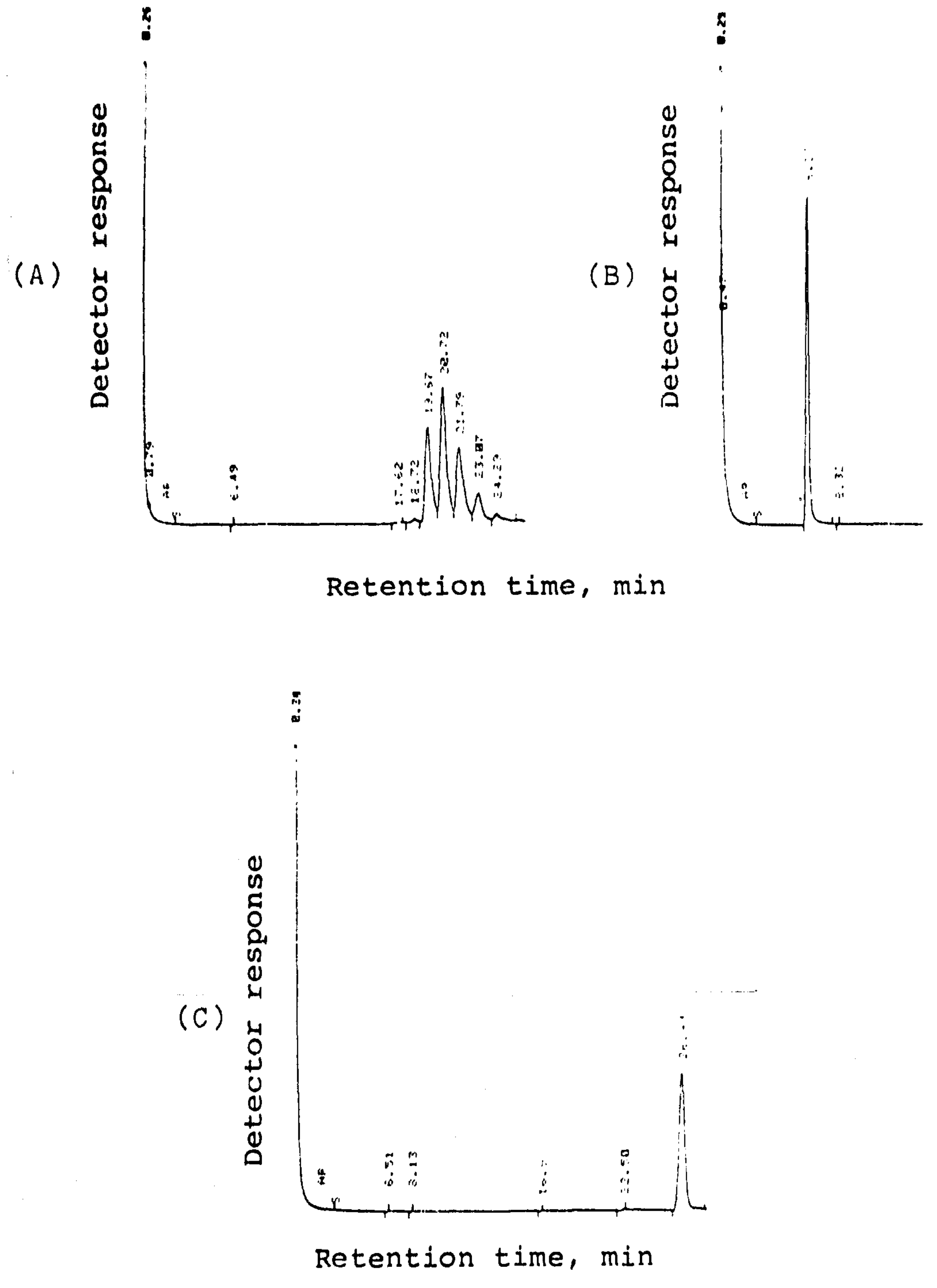


Figure 22. Gas chromatograms of (A) tricresyl phosphate (TCP), (B) phenyl-α-naphthylamine (PANA), and (C) dioctyldiphenylamine (DODPA).

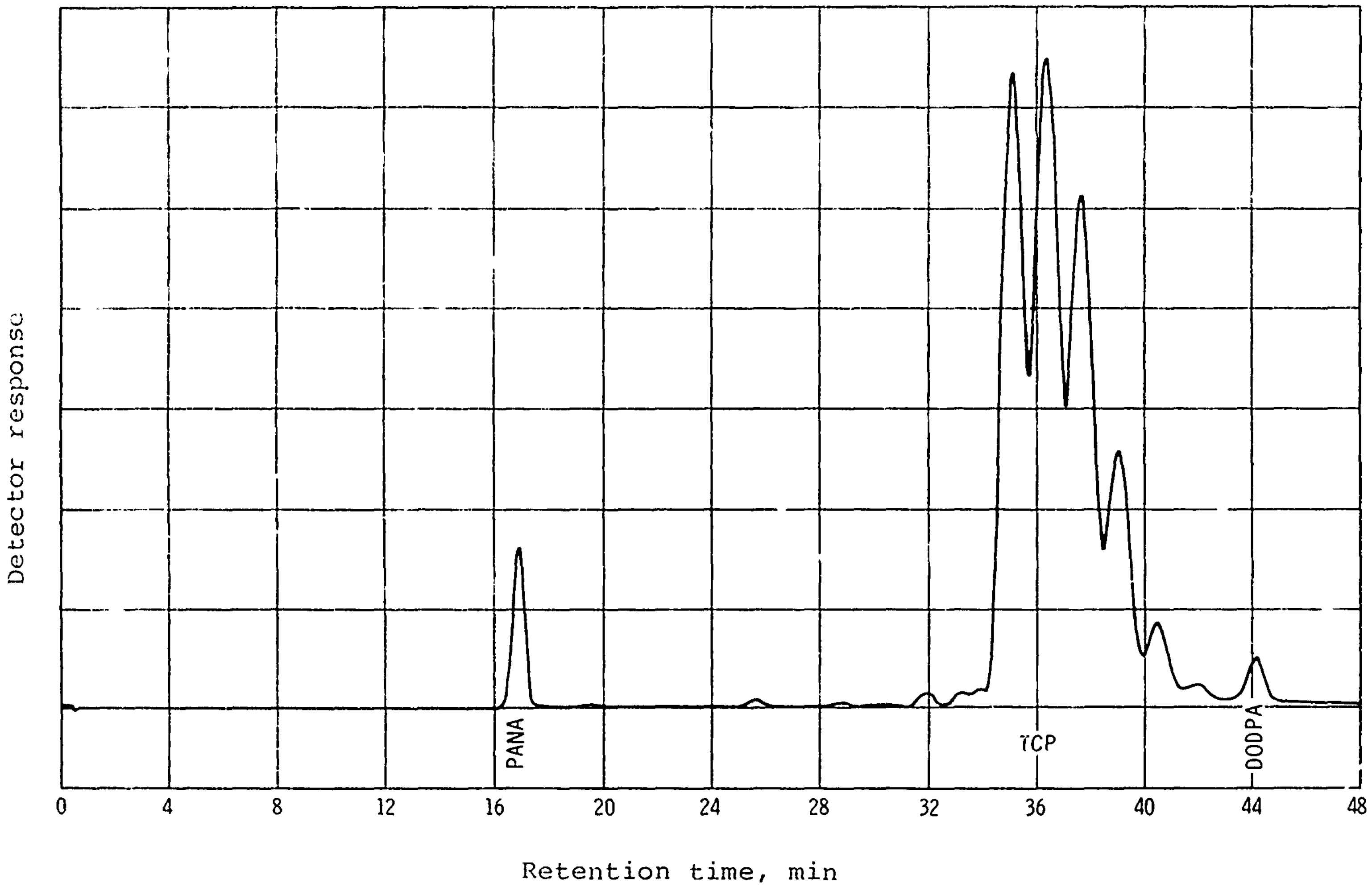


Figure 23. Gas chromatogram from the GC analysis of a MIL-L-23699 type lubricant using a nitrogen-phosphorus FID.

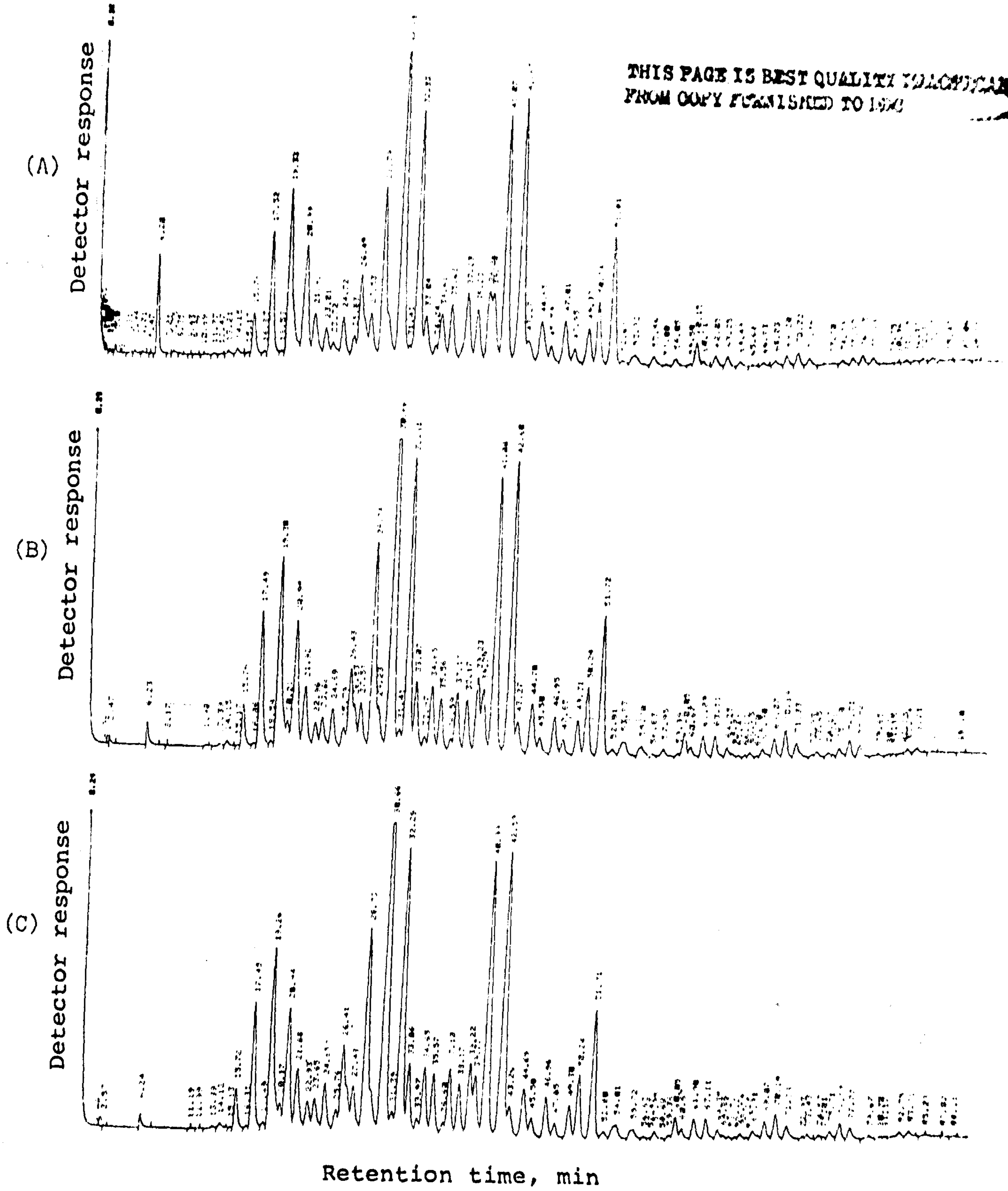


Figure 24. Gas chromatograms of MIL-L-23699 oil samples; (A) unused, (B) after 508 hours operation (37 ppm Fe), and (C) after 1072 hours operation (4 ppm Fe).

manufacturers. Since the various 7808 formulations can be mixed, used MIL-L-7808 oil samples potentially represent complex mixtures of several manufacturers' products. Nonetheless, because of their widespread use, it is necessary to pursue the characterization of MIL-L-7808 type lubricants along with the better defined MIL-L-23699 lubricant in hopes of finding changes in lubricant composition which can be correlated to eventual engine wear.

Samples were obtained of MIL-L-7808 lubricants that are representative of the products from six manufacturers who currently supply the USAF. These unused samples (designated 7808-1 through 7808-6 for identification purposes) were subjected to gas chromatographic analyses using the conditions listed in Table 13, column A. The resulting chromatograms are shown in Figures 25 through 30. A comparison of these chromatograms reveals striking similarities and differences among the oils. For example, 7808-1 and 7808-2 (Figures 25 and 26) are very similar as are 7808-3 and 7808-4 (Figures 27 and 28), but the two groups are vastly different in composition. Samples 7808-5 and 7808-6 (Figures 29 and 30) are representative of oils which have only a few major ester constituents (one and two, respectively).

3.3.2.1 Visual Pattern Recognition

Because of the wide variations in the compositions of some of the 7808 lubricants and close similarities in others, it was desirable to have some method of easily recognizing the various lubricants and assessing their contribution in mixed lubricant samples. We developed a process of pattern recognition based on a unique method of displaying and condensing chromatographic data. The result is a plot which produces a characteristic pattern that is indicative of each of the different 7808 lubricants. This unique method of plotting, concentrates chromatographic data in a manner that facilitates the rapid visual comparison of data contrasted with the usual evaluation of chromatograms.

The plotting technique produces a circular plot by manipulating the chromatographic data in the following manner: the retention times of the various peaks are plotted in terms of degrees by multiplying them by an appropriate factor which is selected to maximize the use of the 360° in the circular plot area. In this report, a factor of 4 was used to maintain a consistent scale (in degrees) for comparison of the various lubricants. The corresponding area percents (from integrator data) are plotted linearly along the radii emanating from the center of the circle at the appropriate number of degrees dictated by the retention times (as described above). To maximize the use of the plot area, the area percent data are normalized to the area percent value of the largest peak in any particular data set, then multiplied by the radius of the plot area. The points determined by

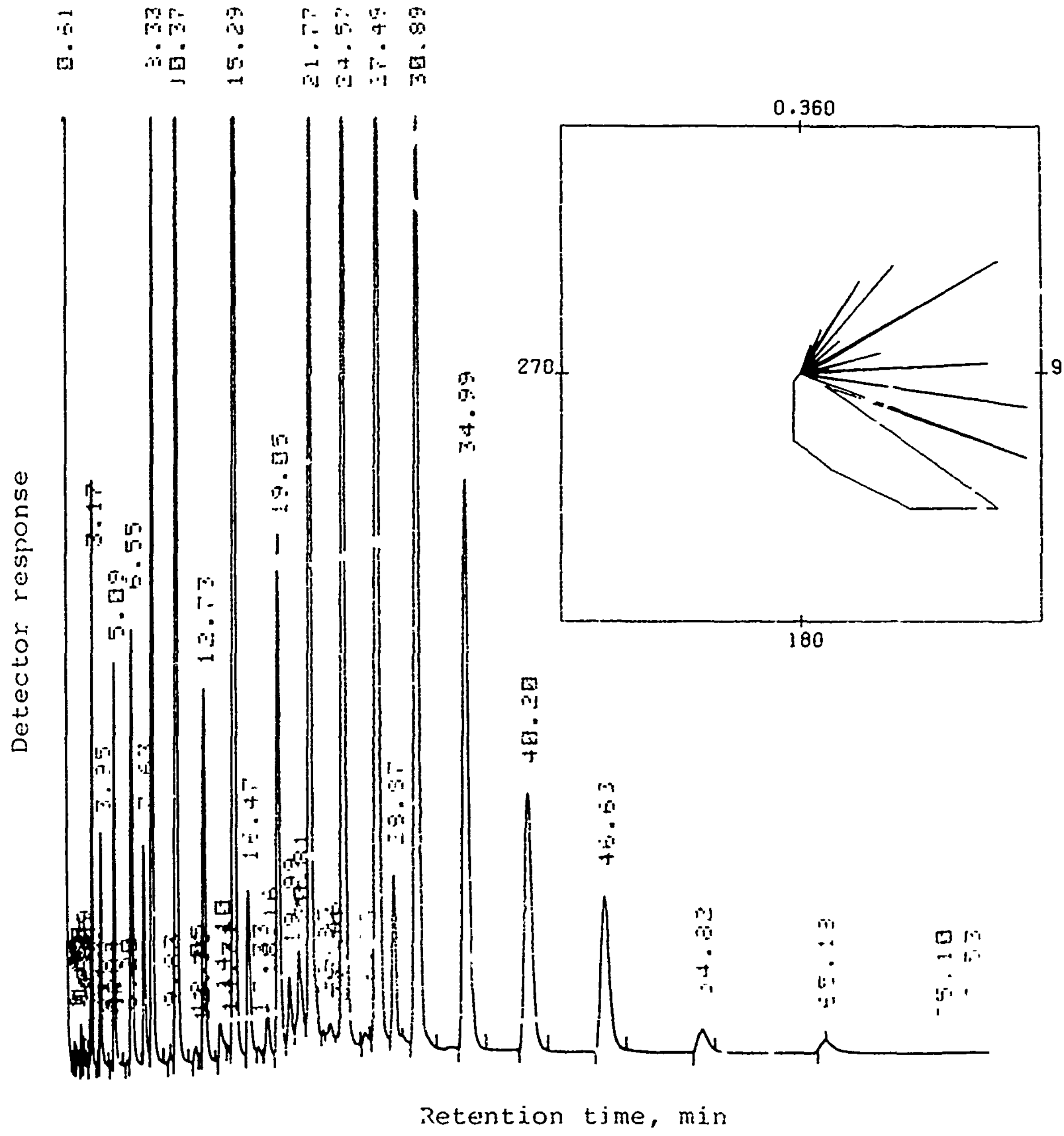


Figure 25. Gas chromatogram and circular plot of 7808-1.

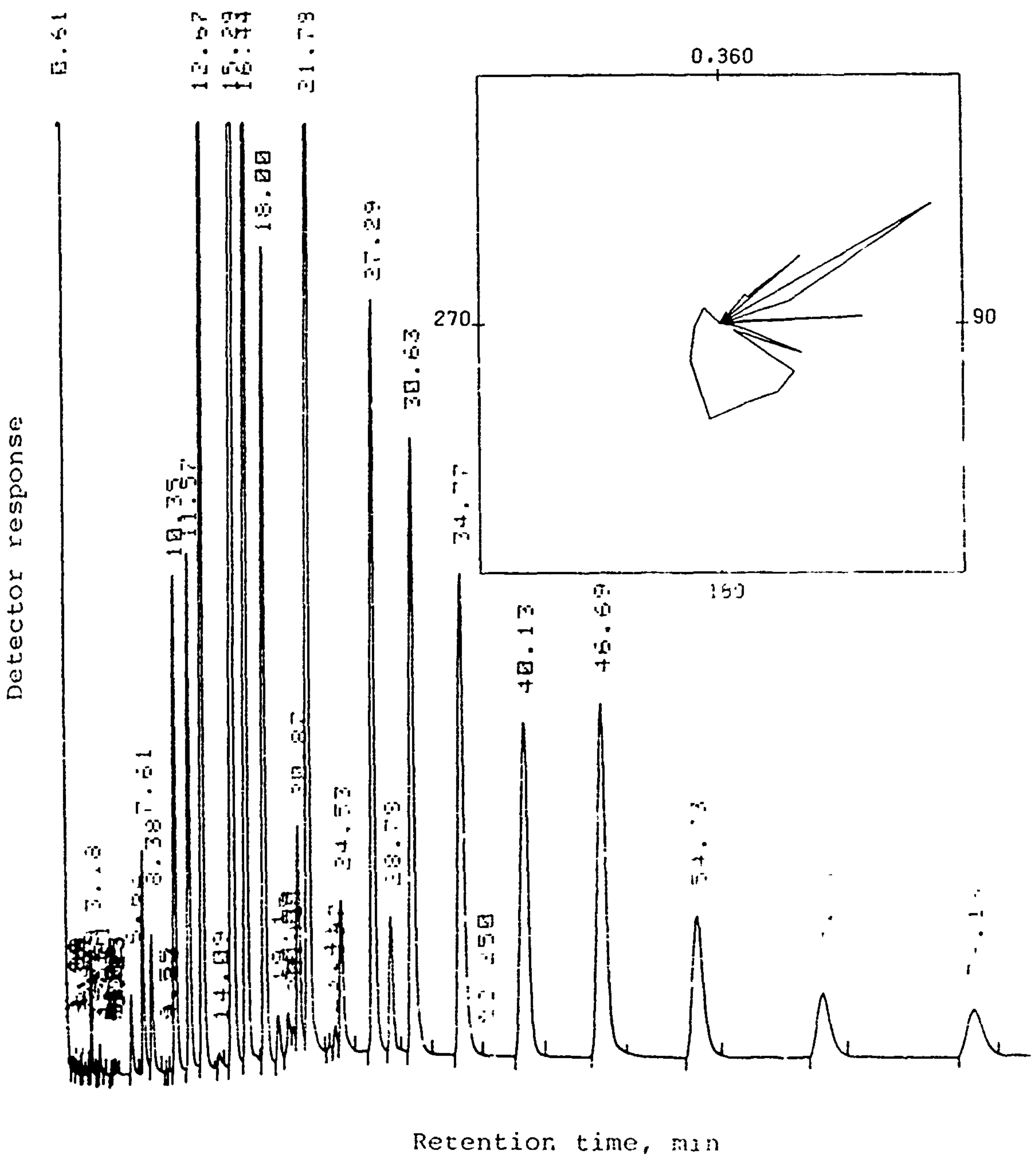


Figure 26. Gas chromatogram and circular plot of 7806-2.

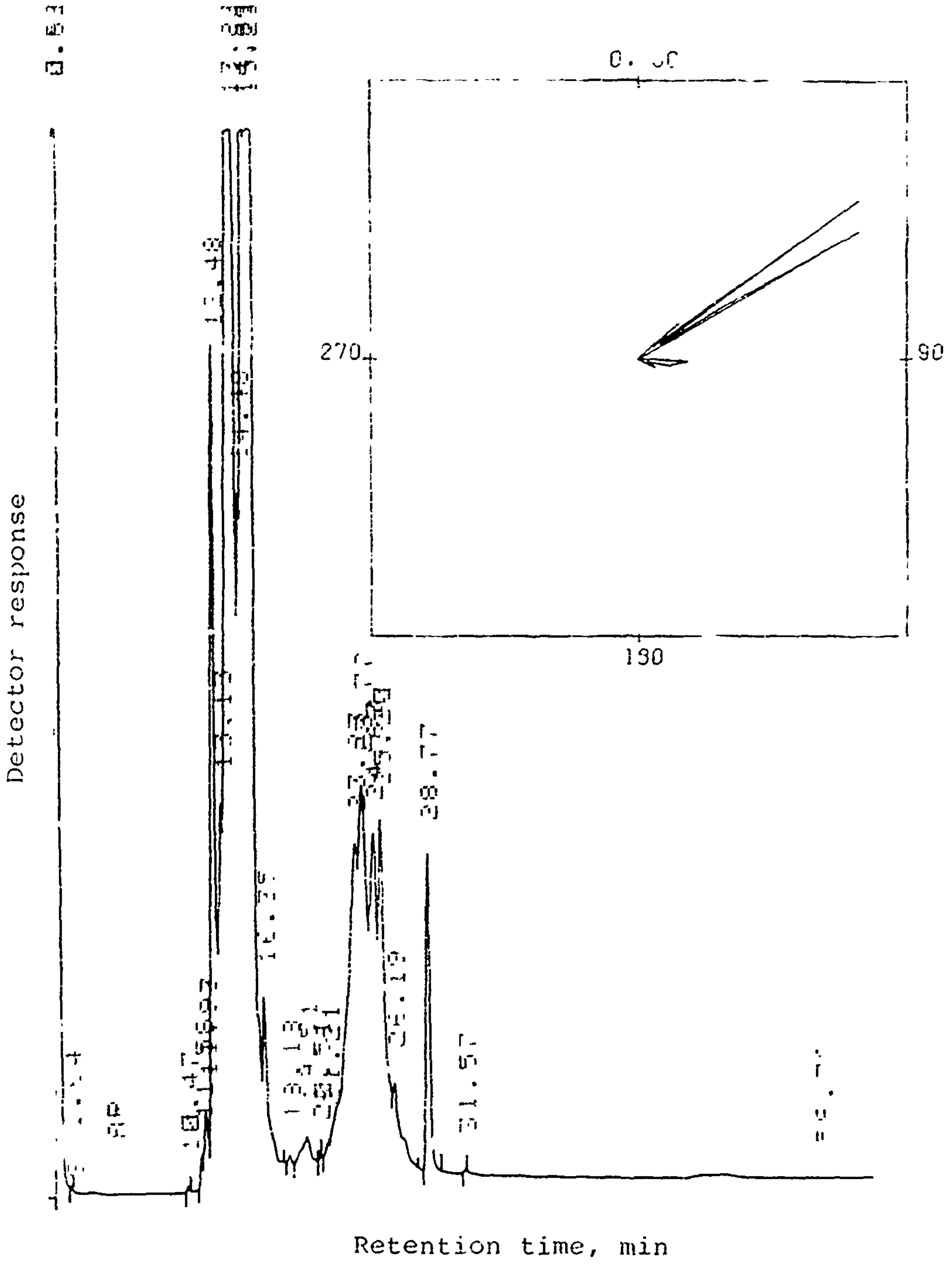


Figure 27. Gas chromatogram and circular plot of 7808-3.

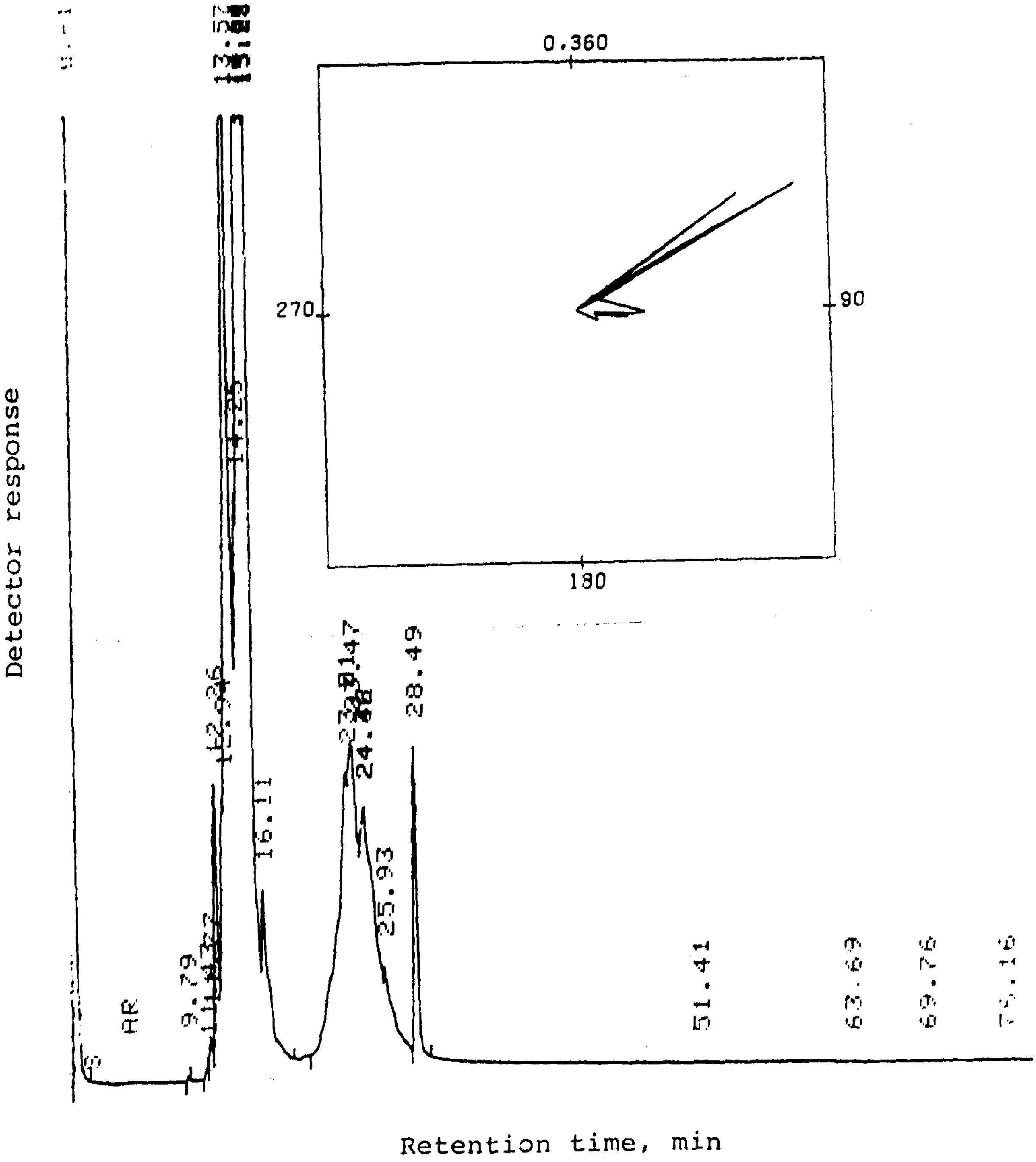


Figure 28. Gas chromatogram and circular plot of 7808-4.

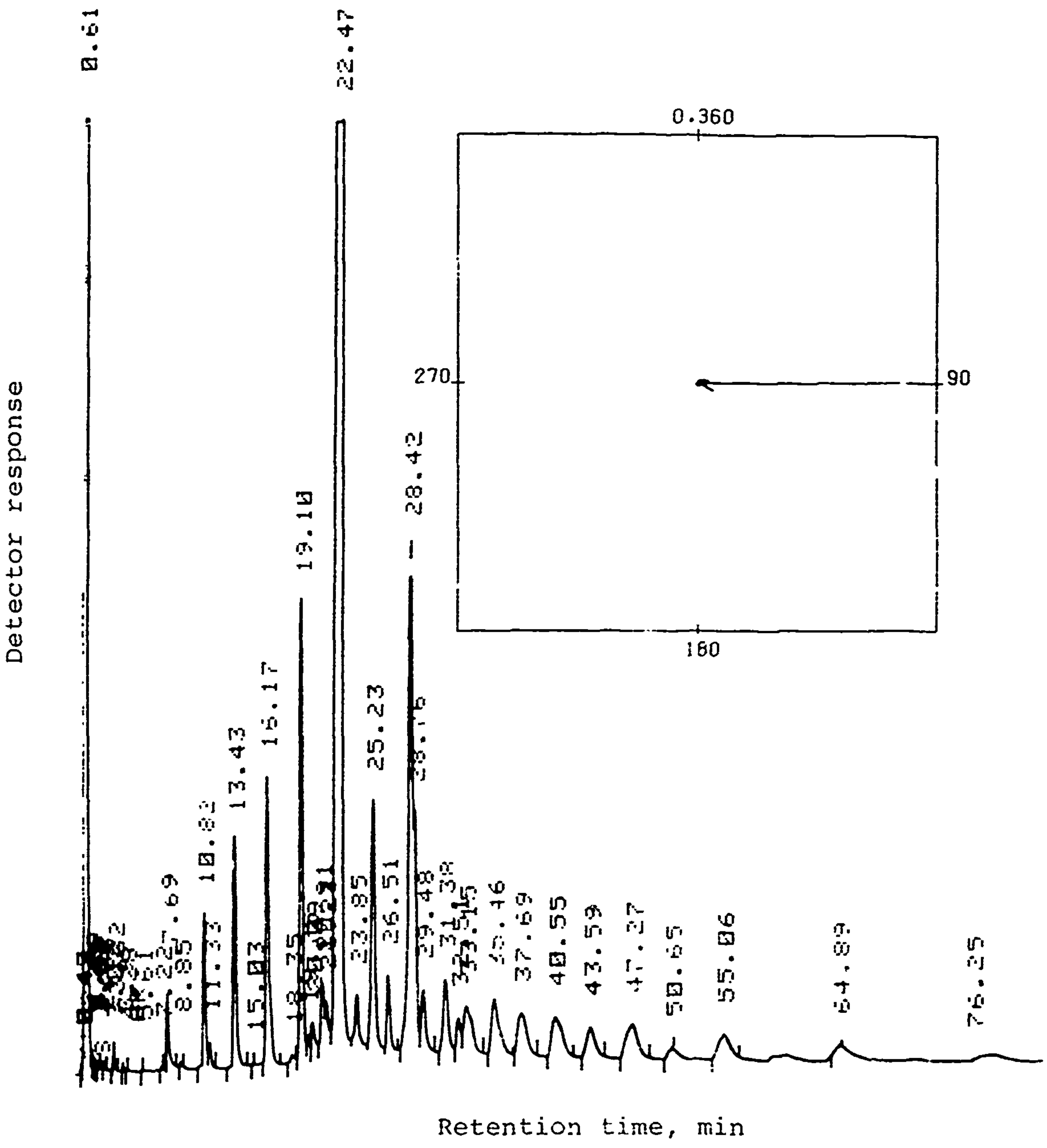


Figure 29. Gas chromatogram and circular plot of 7808-5.

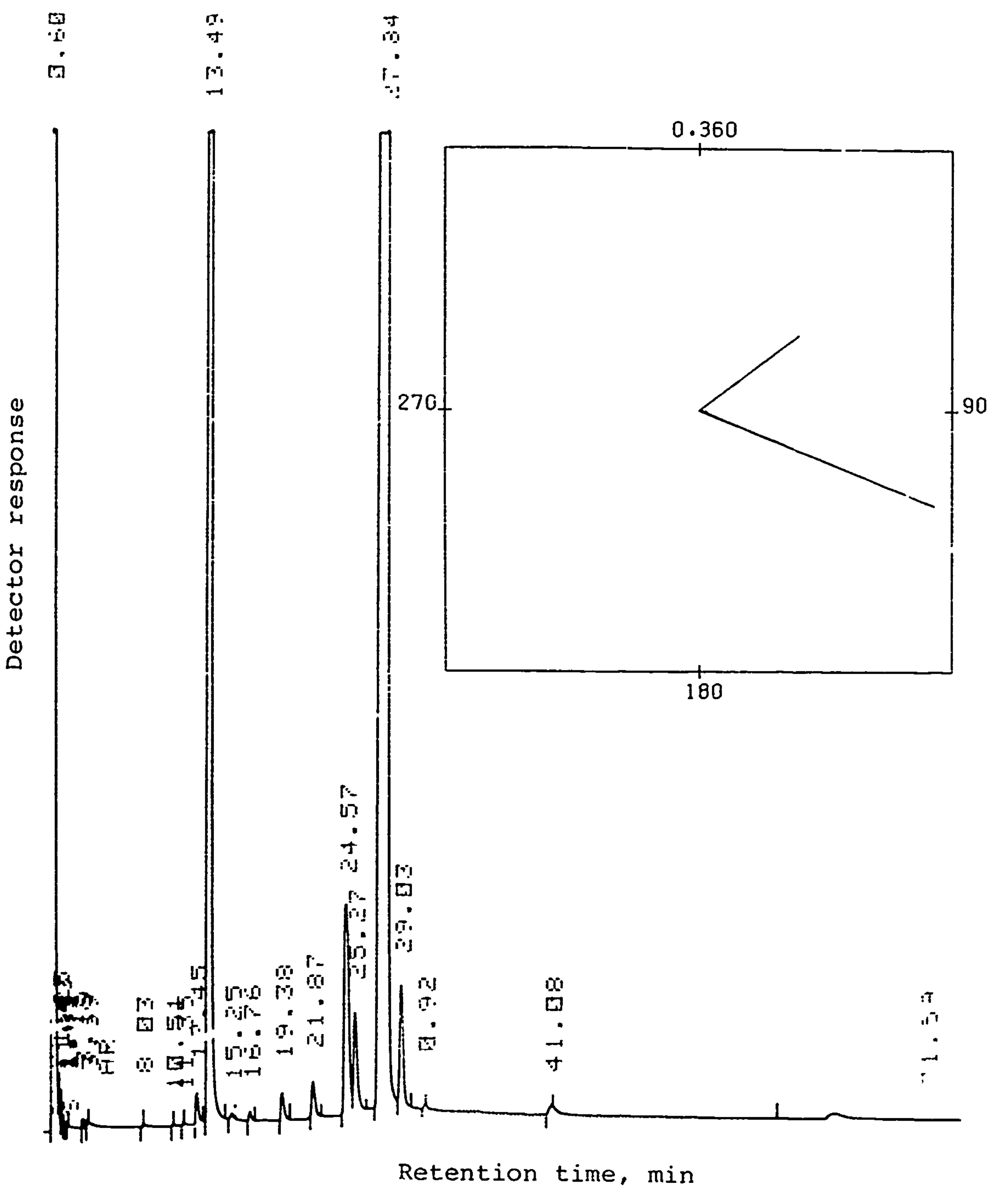


Figure 30. Gas chromatogram and circular plot of 7808-6.

this process are connected by a continuous line to form the pattern. A computer program was written to accomplish the manipulation and plotting of the data. This program is listed in Appendix D. The chromatograms in Figures 20, 21, and 25 through 30 have the computer produced circular plots of the chromatographic data inset in boxes. Each of these plots has been normalized to the largest peak in that particular data set (as described above). The advantages for rapid recognition and comparison are obvious. For closer comparisons, Figure 31 contains the circular plots for the six 7808 oils put on a common scale by normalizing each peak to the largest peak in all of the data sets.

Because of the predominance of one or two major constituents in 7808-5 and 7808-6 (Figures 29 and 30), information which might be contained in the smaller peaks is greatly reduced in the circular plot. In such instances it may be of value to plot area percent values on a log scale to emphasize the smaller peaks. This capability was added to the computer program (Appendix D) and log plots were obtained for the 7808-5 and 7808-6 oils. These plots are shown in Figure 32. The area percent values were multiplied by the common factor (i.e., decimal point moved) necessary to convert the smallest value into a number which would produce a positive logarithm (i.e., characteristic of at least 0) before the logarithms were computed. The log data were normalized to the largest log value and multiplied by the radius of the plot area to maximize the plot size.

3.3.2.2 Computer-Assisted Pattern Recognitio

Perhaps the most promising application of pattern recognition techniques for this research effort is the elucidation of the composition of lubricant mixtures. Figure 33 contains the chromatograms and circular plots for samples of unused 7808-1 and 7808-3 oils and the plot for a mixture of 28.3 wt % 7808-1 and 71.7 wt % 7808-3. The features from the unused samples are evident in the circular plot of the mixture. One could estimate the contribution of each of the lubricants in the mixture based on a visual comparison of the circular plot for the mixture with those of the pure samples (Figure 33). Such an estimate would at best produce a gross quantitation.

To obtain a better measure of the composition of mixtures, a computer-assisted pattern recognition method was developed. Figures 34, 35, and 36 contain the chromatograms and circular plots for lubricants 7808-1, 7808-3, and the mixture described above, analyzed using the conditions in Table 13, column B. The data from these chromatograms can be used to demonstrate the computer-assisted process by which mixture composition is determined. A data set was prepared consisting of retention times and corresponding peak heights for the mixture. Peaks which exceeded the limit of the chromatogram and those which represented

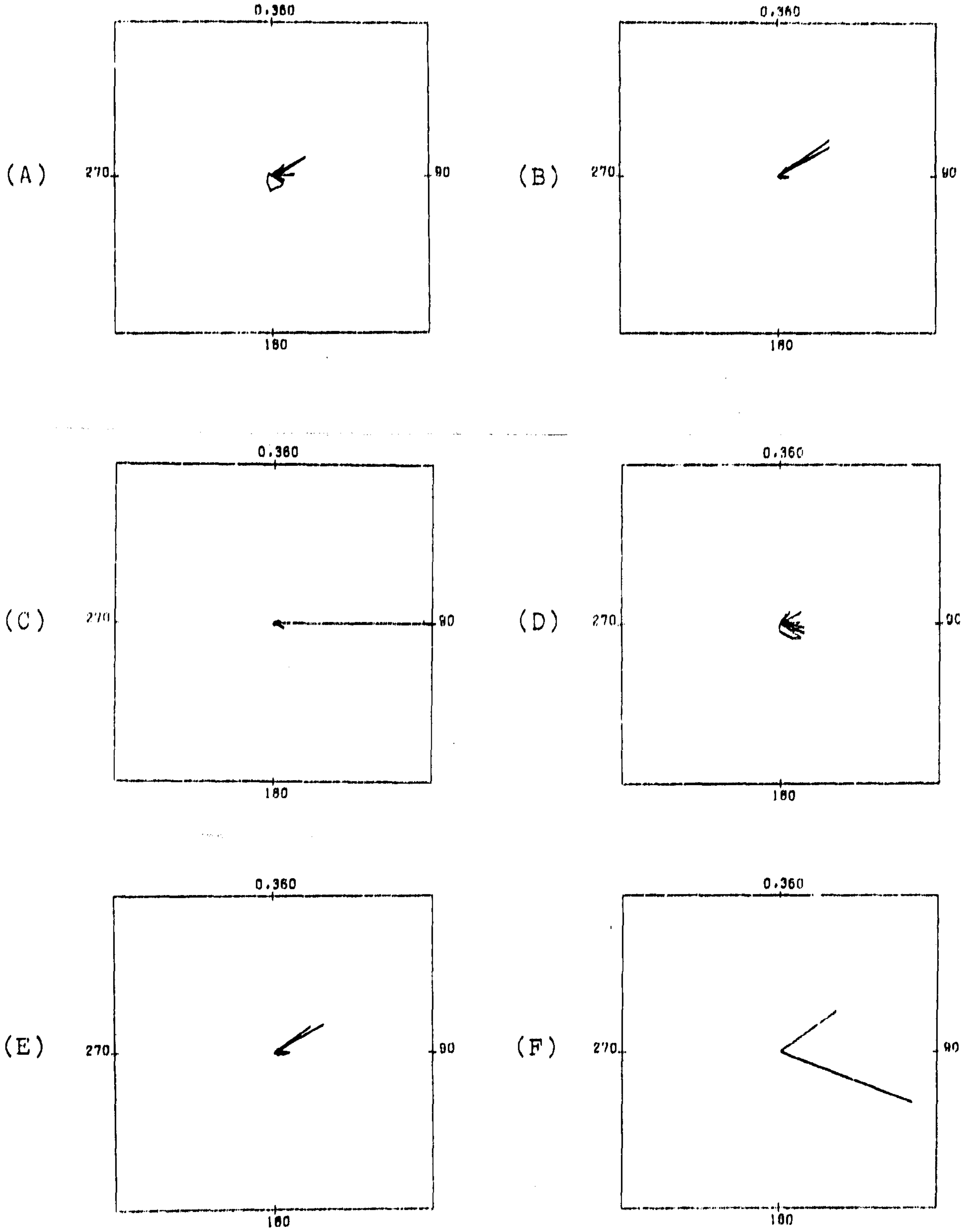


Figure 31. Circular plots of (A) 7808-1, (B) 7808-2, (C) 7808-3, (D) 7808-4, (E) 7808-5, and (F) 7808-6 on a common scale.

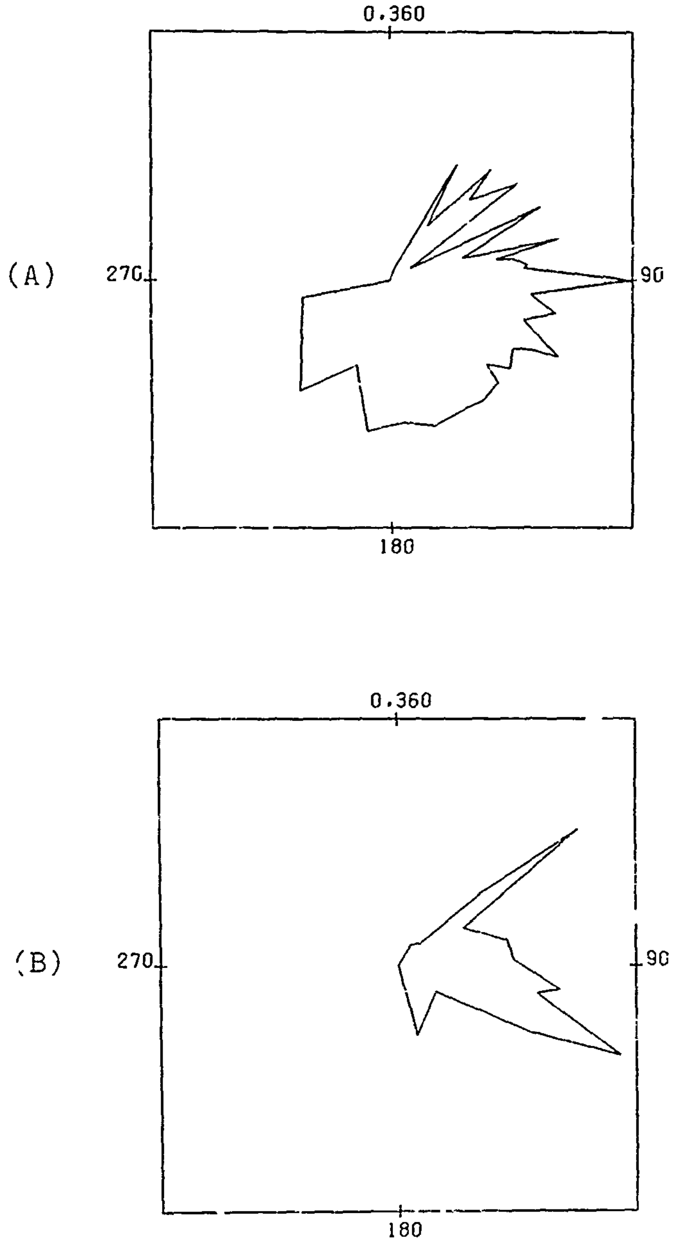


Figure 32. Circular log plots of (A) 7808-5 and (B) 7808-6.

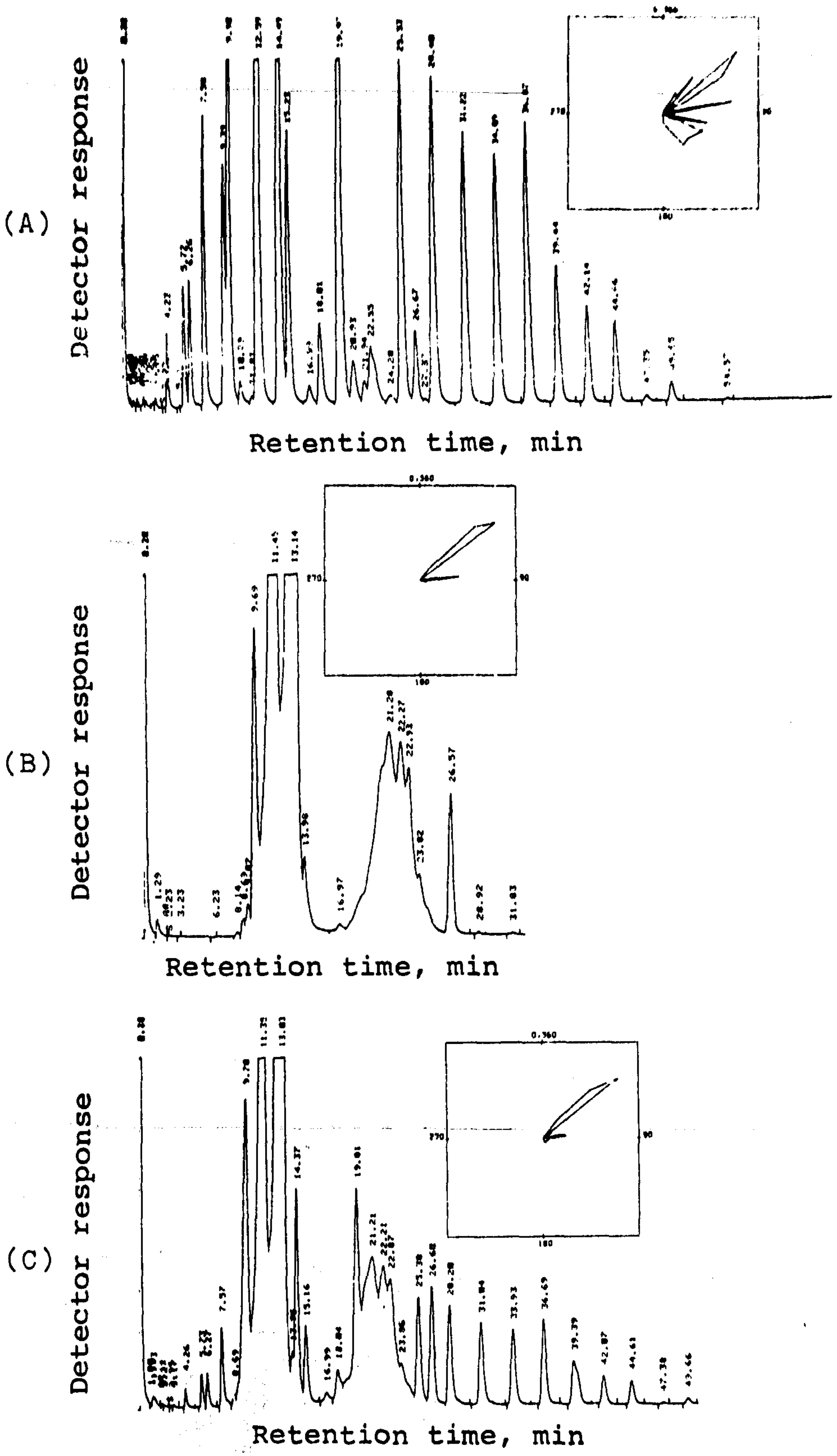


Figure 33. Chromatograms and circular plots of (A) 7808-1, (B) 7808-3, and (C) a mixture of 28.3% 7808-1 and 71.7% 7808-3.

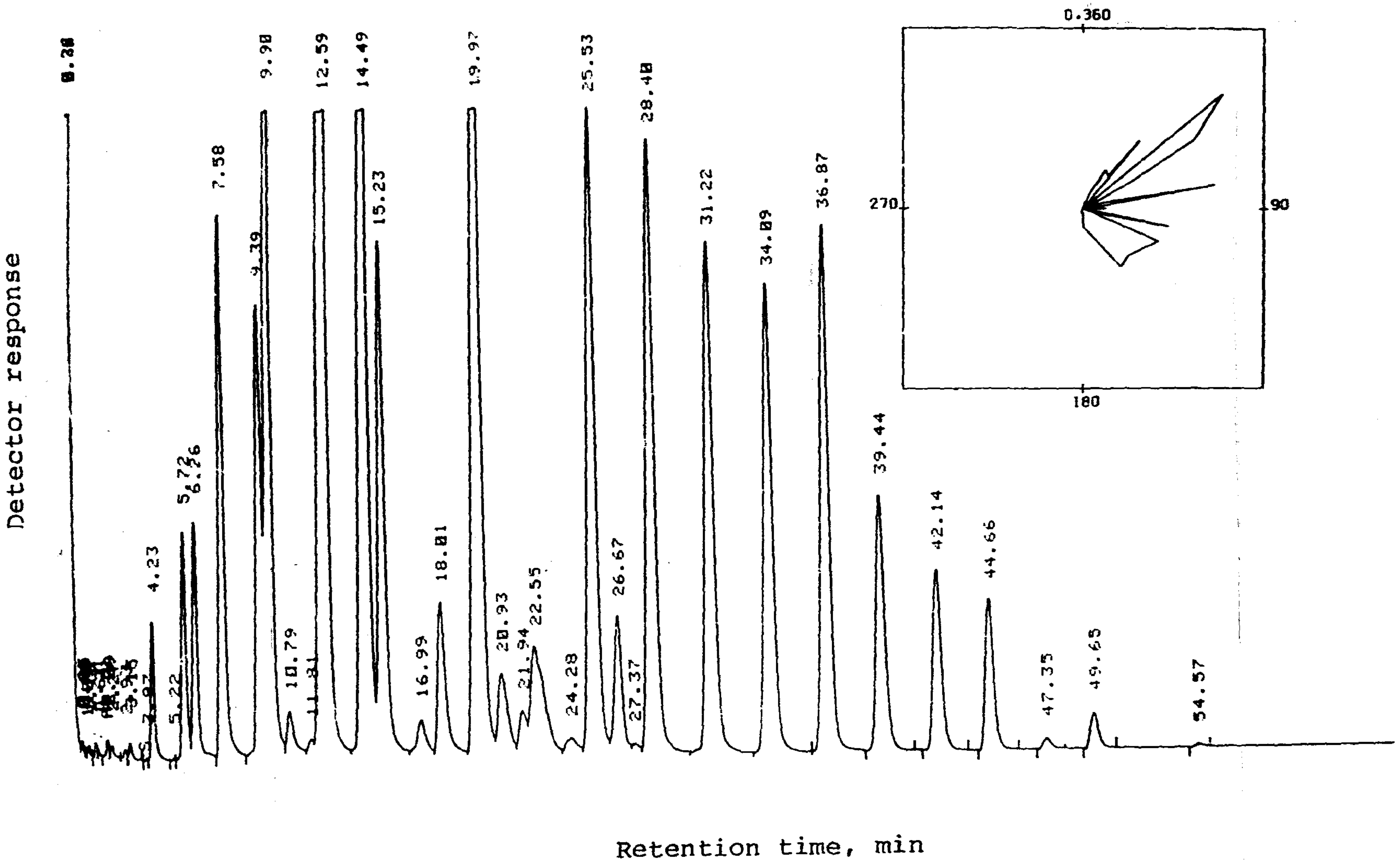


Figure 34. Gas chromatogram and circular plot of 7808-1.

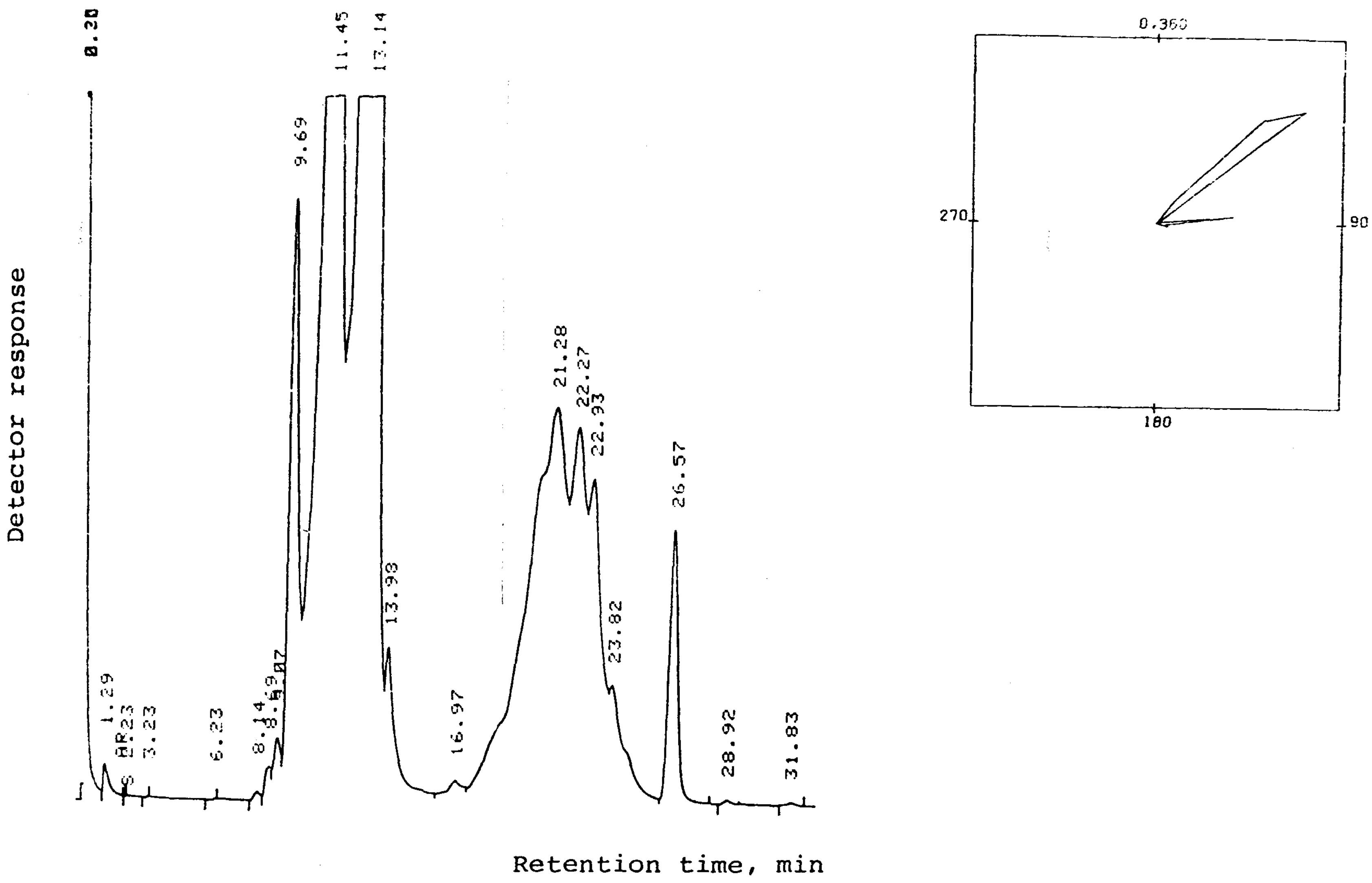


Figure 35. Gas chromatogram and circular plot of 7808-3.

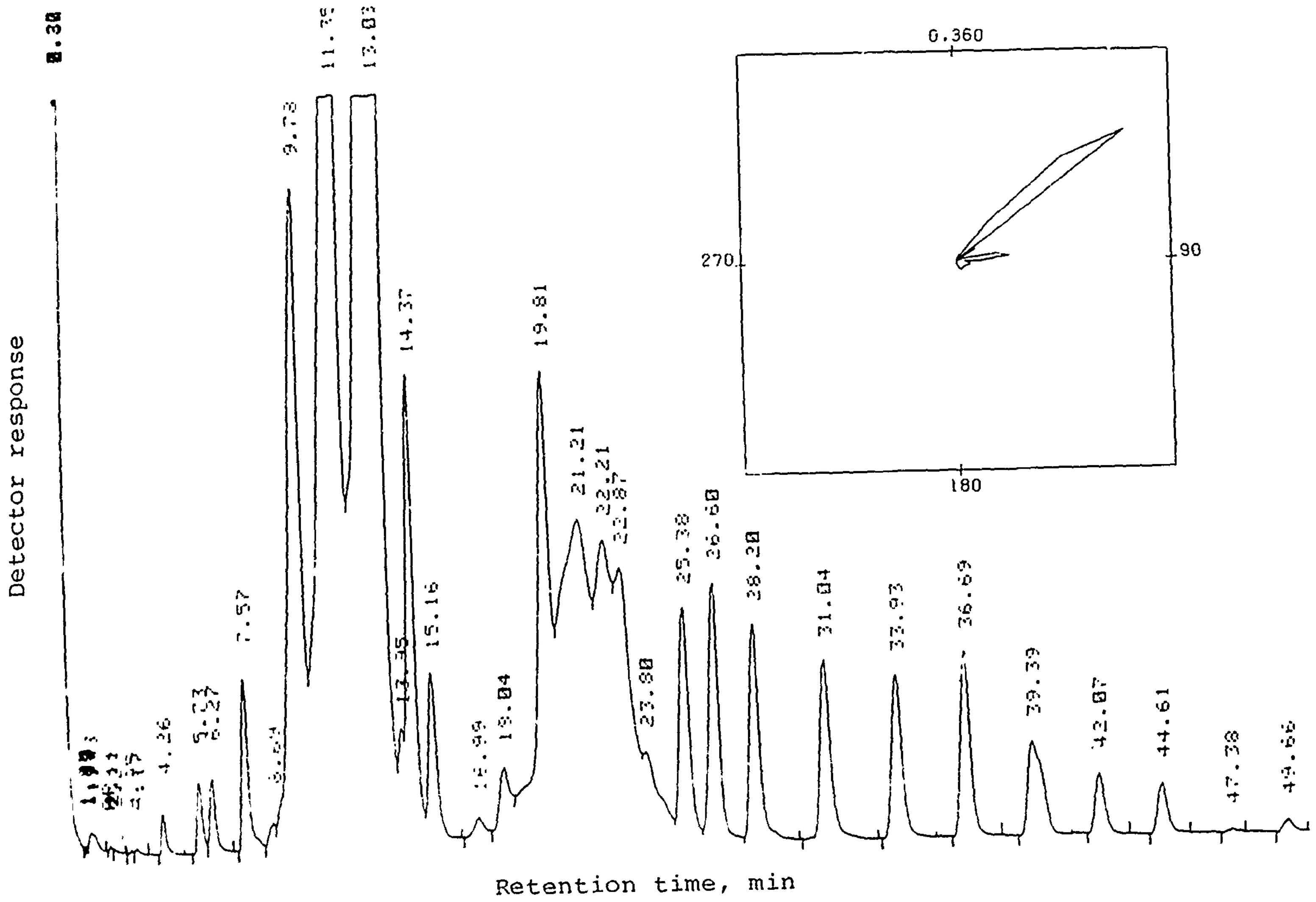


Figure 36. Gas chromatogram and circular plot of a mixture of 28.3% 7808-1 and 71.7% 7808-3.

less than 0.05 area percent were not included in the data set. In the same manner, data sets were generated for each of the five MIL-L-7808 oils designated 7808-1, 7808-3, 7808-4 (Figure 37), 7808-5 (Figure 38), and 7808-6 (Figure 39). The computer compared the data from the mixture with each of the MIL-L-7808 oils in the following manner:

(a) The retention time for each peak in the mixture was compared with retention times of the pure source oils.

(b) A ratio of peak heights (mixture/pure) was calculated when a correspondence to within ± 0.2 minute was found between retention times in the pure oil and the mixture.

The peak height ratios obtained by this method can have many values depending upon peak coincidences and relative abundances of the oils that make up the mixture. There should, however, be a significant number of peaks in the mixture which are solely due to one specific oil, and the ratios obtained for these peaks should be reasonably consistent and represent the weight fraction of that oil in the mixture. These ratios will always be less than one.

Table 17 shows the results obtained from the comparison of the previously described mixture with five pure source oils by this technique. Only two of the pure oils have a significant number of peak height ratios falling in a narrow range (± 5%). The comparison with 7808-3 produces 7 peak height ratios in the range of 0.7184 to 0.7915, while comparison with 7808-1 yields 13 peak height ratios in the range of 0.2480 to 0.3125. A reasonable representation of the mixture composition is obtained from the average (mean) values of these ratios. By this method, the composition of the mixture was calculated to be 75.2% 7808-3 and 28.6% 7808-1 compared to the actual values of 71.7% and 28.3%.

The chromatograms and circular plots of 7808-4, 7808-5, and 7808-6 oils are shown in Figures 37, 38, and 39, respectively, for comparison with the two oils used to make up the mixture (Figures 34 and 35).

Of particular interst is the close similarity of 7808-4 (Figure 37) and 7808-3 (Figure 35). It is significant that the computerized mixture analysis technique showed no significant correlation between the mixture and 7808-4 even though the latter is so closely similar to the 7808-3 oil. This illustrates a high degree of specificity for the technique.

It should be noted that the chromatograms, both linear and circular plots, of 7808-1 (Figure 34), 7808-3 (Figure 35), 7808-4 (Figure 37), 7808-5 (Figure 38), and 7808-6 (Figure 39) were obtained using the instrument conditions listed in column B of

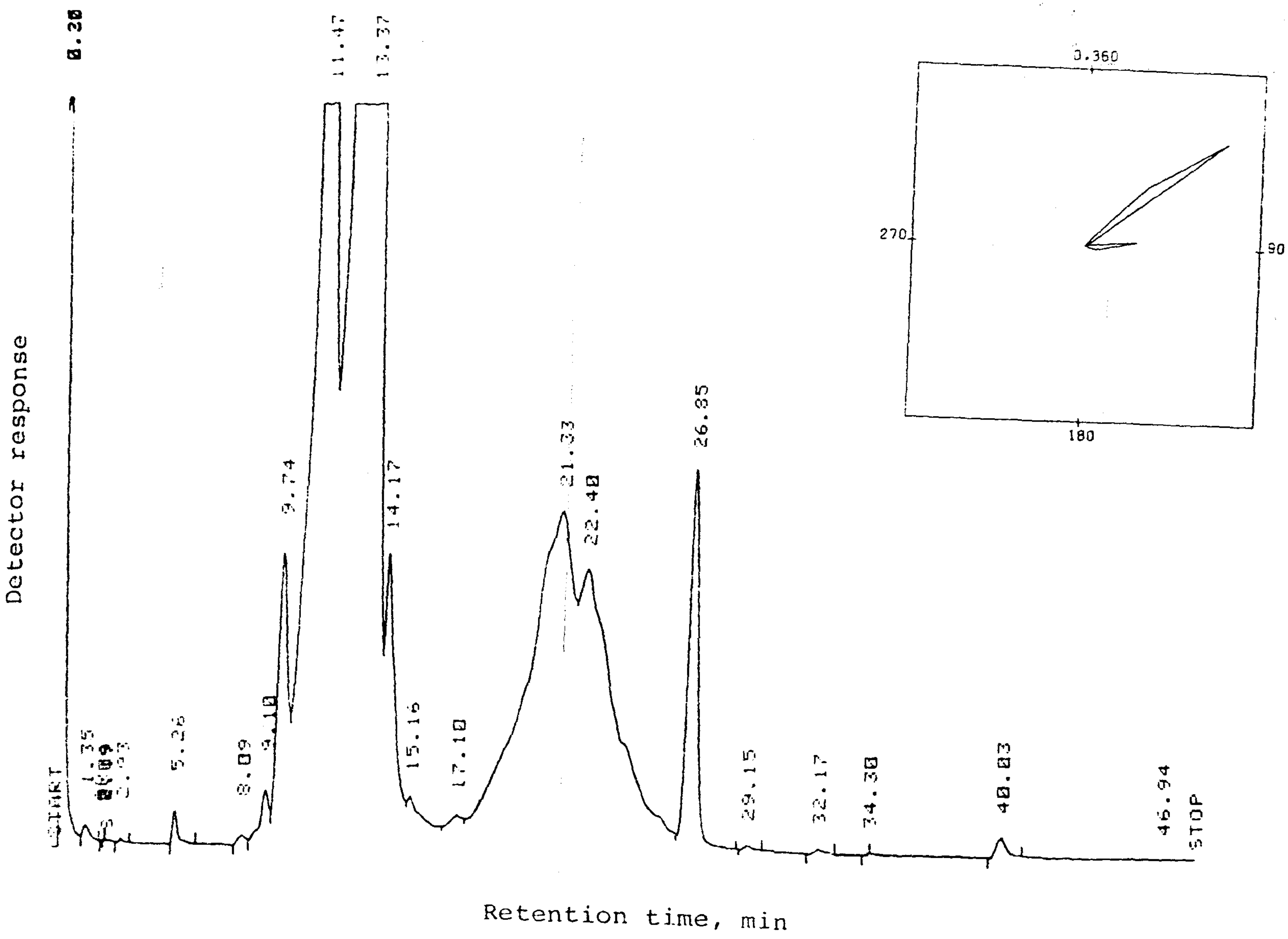


Figure 37. Gas chromatogram and circular plot of 7808-4.

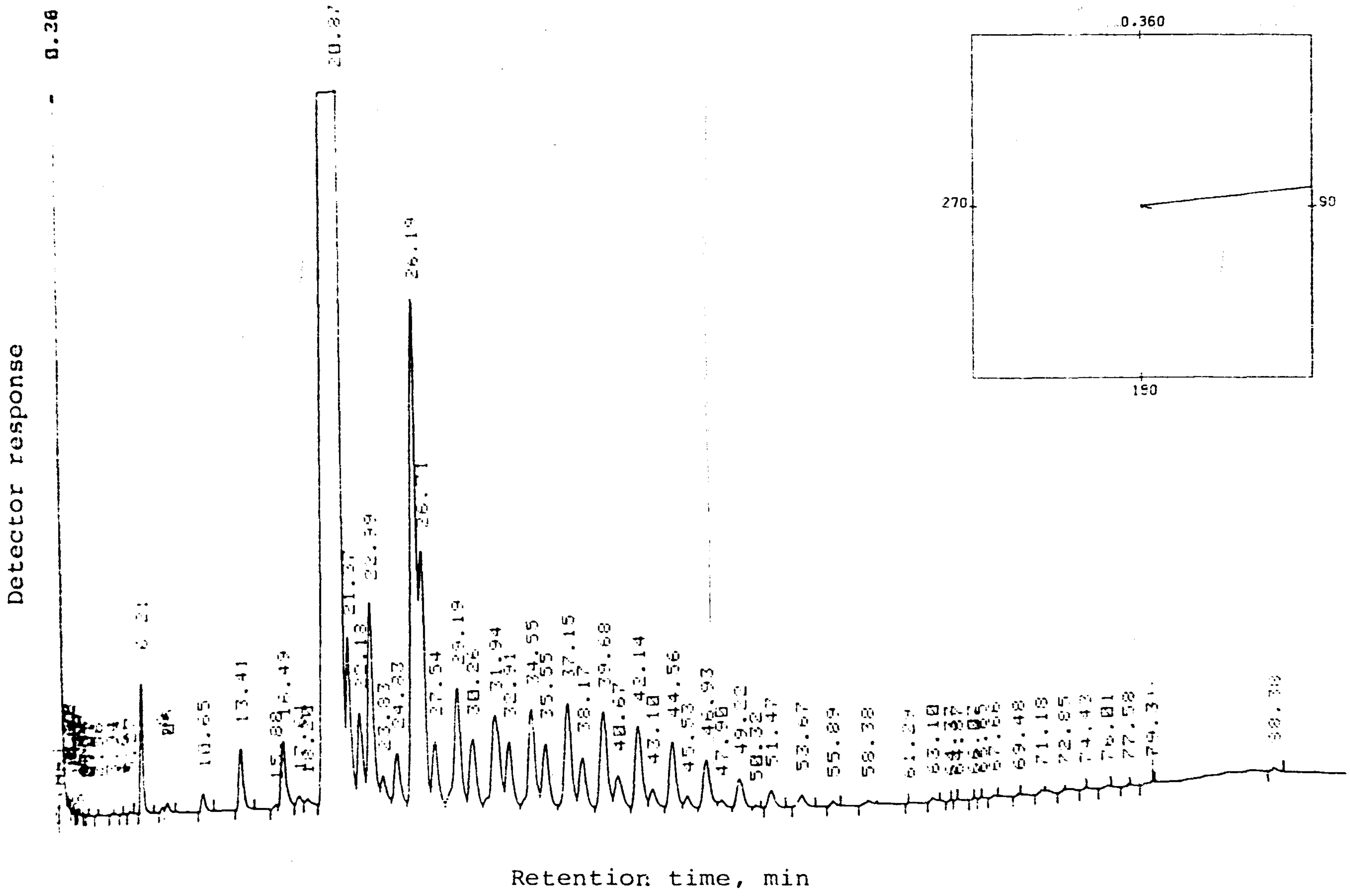


Figure 38. Gas chromatogram and circular plot of 7808-5.

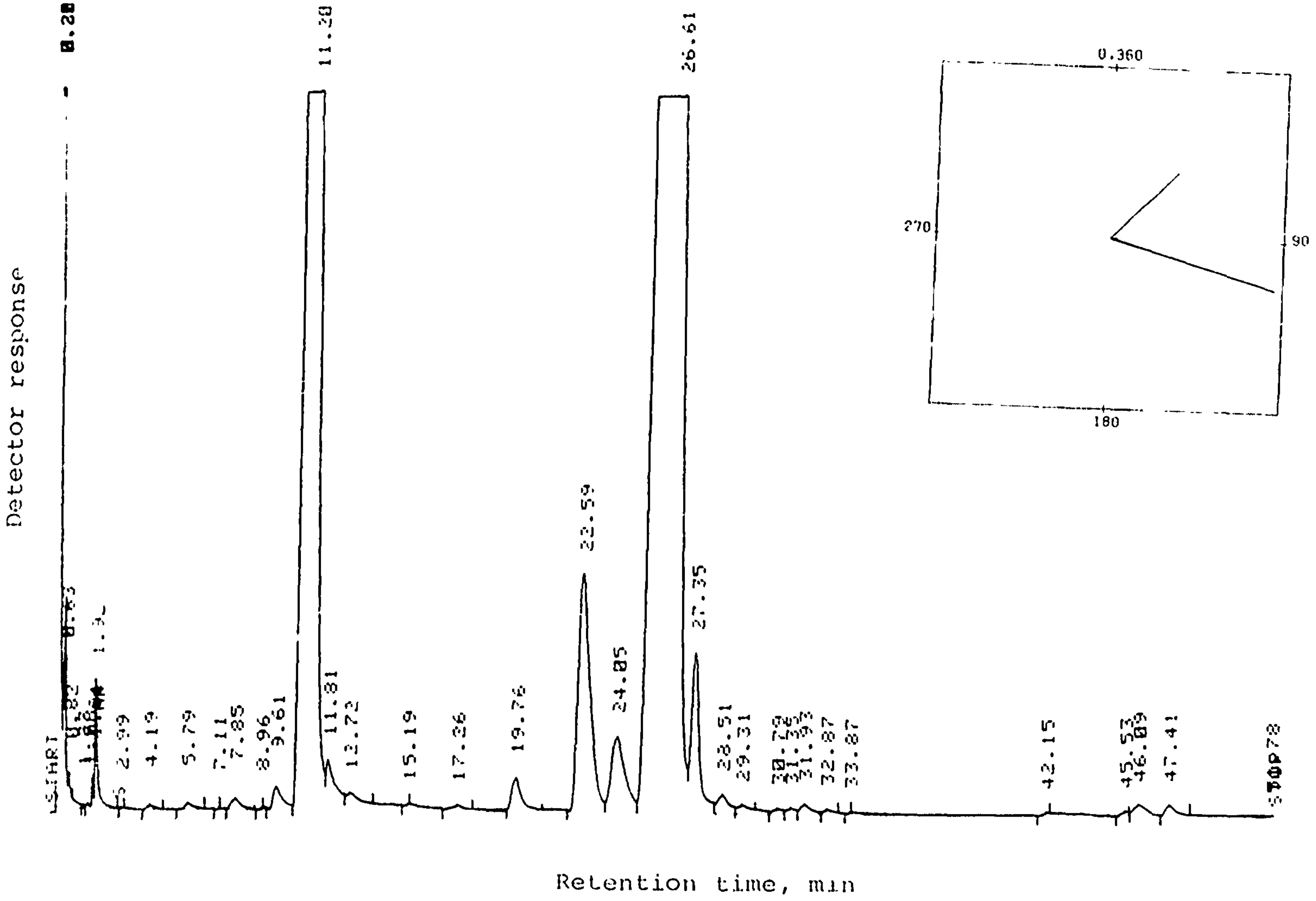


Figure 39. Gas chromatogram and circular plot of 7808-6.

TABLE 17. COMPUTER-ASSISTED MIXTURE ANALYSIS

Mixture retention time, min	Peak weight ratios				
	7808-1	7808-3	7808-4	7808-5	7808-6
4.26	0.248	–[a]	–	–	–
5.73	0.268	–	–	–	–
6.27	0.266	–	–	0.531	–
7.57	0.273	–	–	–	–
8.69	–	0.759	–	–	–
9.78	–	>1.0	>1.0	–	>1.0
13.95	–	0.731	–	–	–
14.37	–	–	–	–	–
15.16	0.292	–	>1.0	–	–
16.99	0.706	>1.0	0.857	–	–
18.04	0.444	–	–	>1.0	–
19.81	–	–	–	–	>1.0
21.21	–	0.763	0.943	>1.0	–
22.21	–	0.751	>1.0	>1.0	–
22.87	–	0.792	–	>1.0	–
23.80	–	0.718	–	>1.0	–
25.38	0.311	–	–	–	–
26.60	>1.0	0.875	–	0.963	–
28.20	–	–	–	–	–
31.04	0.301	–	–	–	–
33.93	0.299	–	–	–	–
36.69	0.300	–	–	–	–
39.39	0.312	–	–	–	–
42.07	0.286	–	–	0.696	–
44.61	0.284	–	–	0.714	–
49.66	0.273	–	–	–	–
Average[b]	28.6%	75.2%			

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[a] Indicates no corresponding peak within ± 0.2 min.

[b] Average of underlined values.

Table 13. The chromatograms for the same lubricants in Figures 25 through 30 were obtained using the instrument conditions in Table 13, column A. Although the linear chromatograms appear quite similar, the circular plots amplify the subtle differences due to different instrument conditions.

A manuscript describing the circular profiling techniques which resulted from this research was published in the October 1977 issue of the Journal of Chromatographic Science under the title "Use of Circular Profiling Techniques in Gas Chromatography." A preprint of this manuscript is included in Appendix E.

3.3.3 Evaluation of Base Stocks

To gain a better understanding of the chromatographic properties of synthetic ester lubricants, samples of commercially available base stocks were obtained from Emery Industries and Hercules Incorporated, two major suppliers of synthetic esters. These samples were analyzed by GC using the conditions in Table 13, column B.

Several of these base stocks are esters of pentaerythritol (PE) and dipentaerythritol (DPE). The chromatogram of one of the PE-based base stocks (with small amounts of DPE) is shown in Figure 40. This particular sample is reported to be made up of the esters of normal C_5, C_6, C_7, C_8, and C_9 acids with PE and DPE. A logical interpretation for the chromatogram follows when one considers the possible products which would be obtained from the esterification of a mixture of C_5, C_6, C_7, C_8, and C_9 acids with PE and DPE. The products for the PE esters are listed in Table 18.

TABLE 18. PRODUCTS FROM THE REACTION OF C_5, C_6, C_7, C_8, AND C_9 ACIDS WITH PENTAERYTHRITOL

Molecular weight	Products[a]	Number of isomers	Peak number[b]
472	5555	1	[illegible]
486	5556	1	[illegible]
500	5557, 5566	2	3
514	5558, 5567, 5666	3	[illegible]
528	5559, 5568, 5577, 5667, 6666	5	[illegible]
542	5569, 5578, 5668, 5677, 6667	5	[illegible]
556	5579, 5588, 5669, 5678, 5777, 6668, 6677	7	[illegible]
570	5589, 5679, 5688, 5779, 6669, 6678, 6777	7	[illegible]
584	5599, 5689, 5779, 5788, 6679, 6688, 6778, 7777	8	[illegible]
598	5699, 5789, 5888, 6689, 6779, 6788, 7778	7	10
612	5799, 5889, 6699, 6789, 6888, 7779, 7788	7	11
626	5899, 6799, 6889, 7789, 7888	5	12
640	5999, 6899, 7799, 7889, 8888	5	13
654	6999, 7899, 8889	3	14
668	7999, 8899	2	15
682	8999	1	16
696	9999	1	17
	Total	70	

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[a] Product designation is accomplished by a series of four numbers which indicate the number of carbon atoms in the acids that react at each of the four esterification sites in pentaerythritol (e.g., the product designated 5567 is formed by the esterification of two C_5, one C_6, and one C_7 acid with a molecule of pentaerythritol).

[b] The peak numbers refer to those in Figure 40.

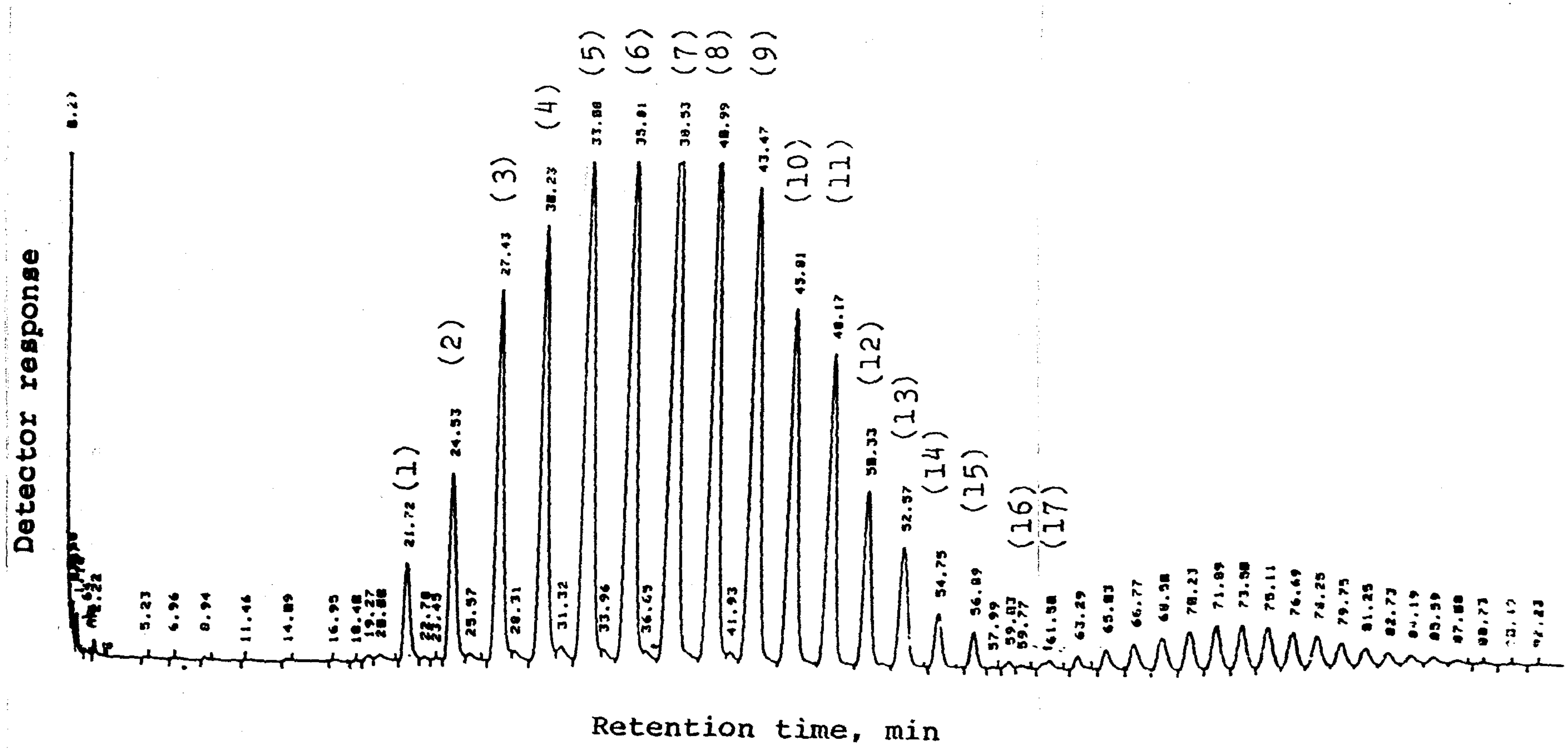

Figure 40. Gas chromatogram of a pentaerythritol-dipentaerythritol ester base stock with C_5, C_6, C_7, C_8, and C_9 acids.

The 70 potential products can be grouped into 17 sets of isomers ranging in molecular weight from 472 to 696. The chromatogram (Figure 40) is rather nicely divided into two parts corresponding to the PE and DPE esters. From the number of peaks in the chromatogram it is obvious that the individual isomers are not resolved; therefore, one would expect 17 peaks for the PE esters, some of which contain as many as 8 isomers (see Table 18).

The key to the assignment of the various groups of PE isomers came from work (described in section 3.3.1.1) on a MIL-L-23699 type lubricant known to contain the esters of PE with iso and normal C_5 and normal C_9 acids. The chromatogram for this lubricant is included as Figure 41 because the esters designated 5555, 5559, 5599, 5999, and 9999 (Table 18) appear in the chromatogram as peaks 5, 9, 12, 15, and 15, respectively. By comparing the retention times for these peaks in Figure 41 with the PE ester peaks in Figure 40, it was possible to make the peak assignments indicated. The validity of these assignments is indicated by the agreement of the retention times with the peak order expected on the basis of molecular weights. For example, peak 5 of Figure 41 has a retention time which agrees with the peak at 21.72 minutes in Figure 40. Since this peak is due to the 5555 ester we assume that the peak at 21.72 minutes in Figure 40 is also the 5555 ester and assign it a peak number of 1, representing the first of 17 expected groups of PE esters (see Table 18). Using this as a reference, we would expect from Table 18 that the 5559, 5599, 5999, and 9999 esters would appear in peaks 5, 9, 13, and 17 respectively in Figure 40. As expected, these peaks correspond in retention times with peaks 9, 12, 14, and 15 of Figure 41.

In a similar manner one can predict that there are 25 sets of isomers for the DPE esters formed with a mixture of C_5, C_6, C_7, C_8, and C_9 acids. There are 22 distinguishable peaks in the DPE portion of the chromatogram in Figure 40. The other three are either lost in overlap with PE ester peaks or too small to be detected at this sensitivity level.

Most of the base stocks analyzed appeared to be variations of similar PE and DPE esters either in quantities or types of acids used. One common variation produced chromatograms which had similar numbers of peaks to that of Figure 40 but different retention times. This created an interleaving of peaks particularly in the lower PE ester region when the chromatograms were superimposed. One such example is shown in Fgiure 42. Another variation (illustrated by Figure 43) had high amounts of DPE esters, while others were based on esters of trimethylol propane (Figure 44).

Perhaps the major benefit gained by the investigation of the base stocks was a better understanding of the MIL-L-23699 type lubricant which we examined rather extensively (section 3.3.1.1).

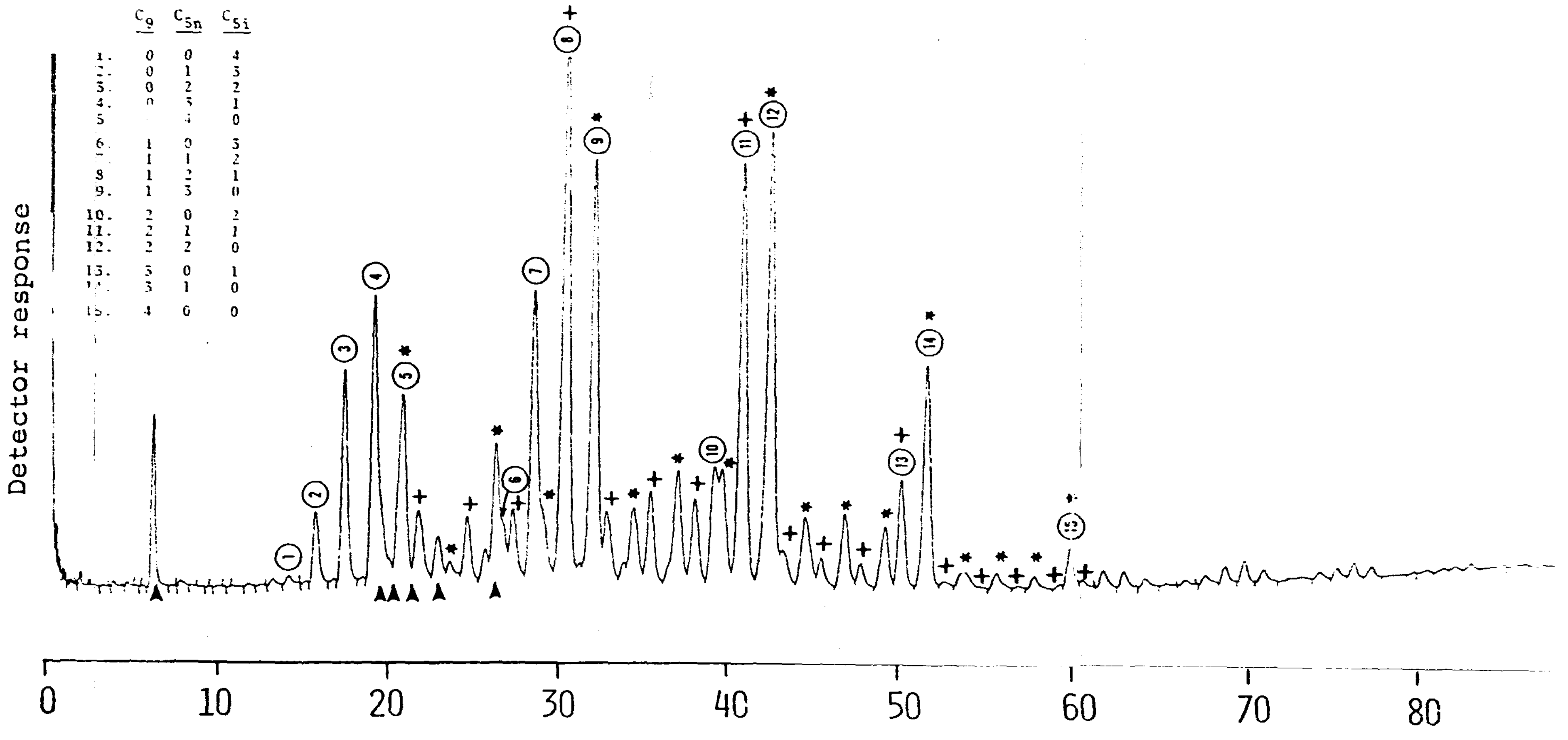

Figure 41. Gas chromatogram of MIL-L-23699 type lubricant.

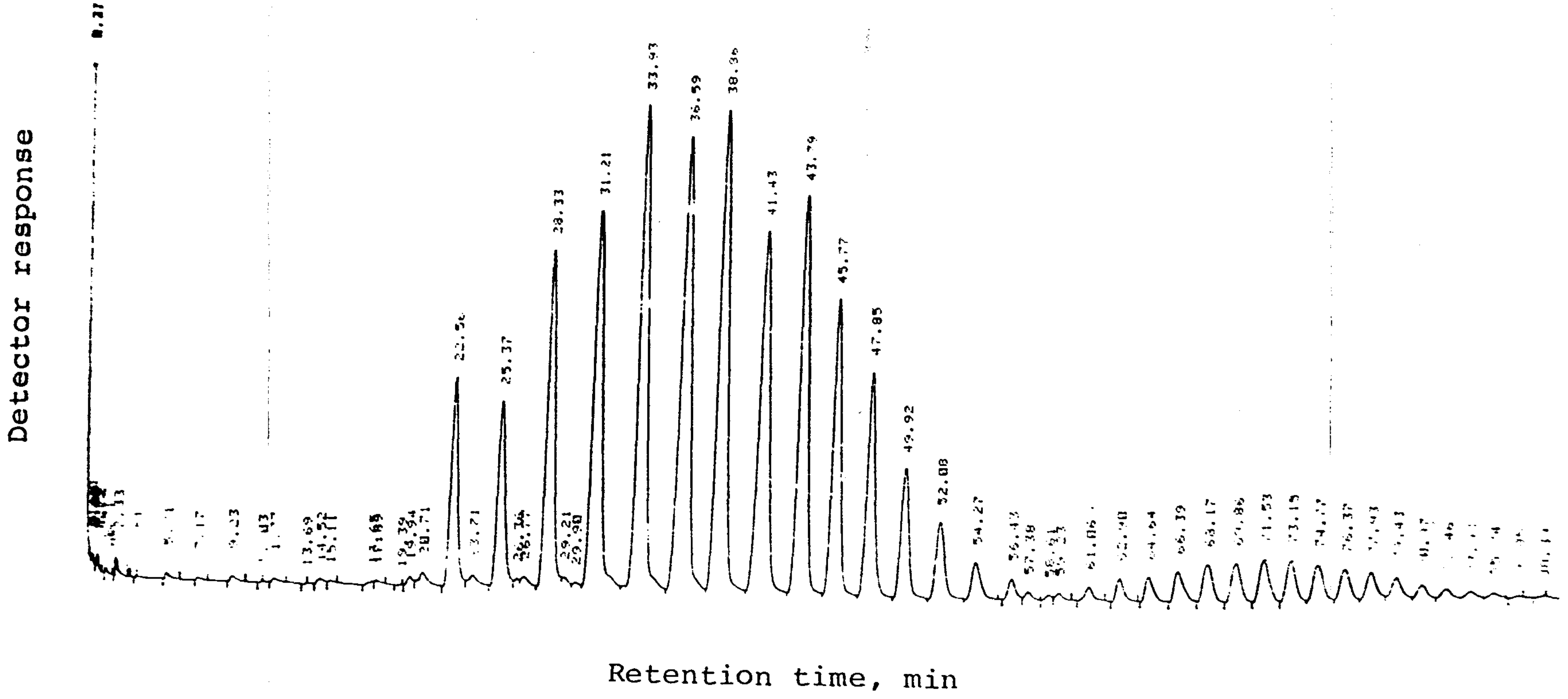

Figure 42. Gas chromatogram of a pentaerythritol-dipentaerythritol ester base stock.

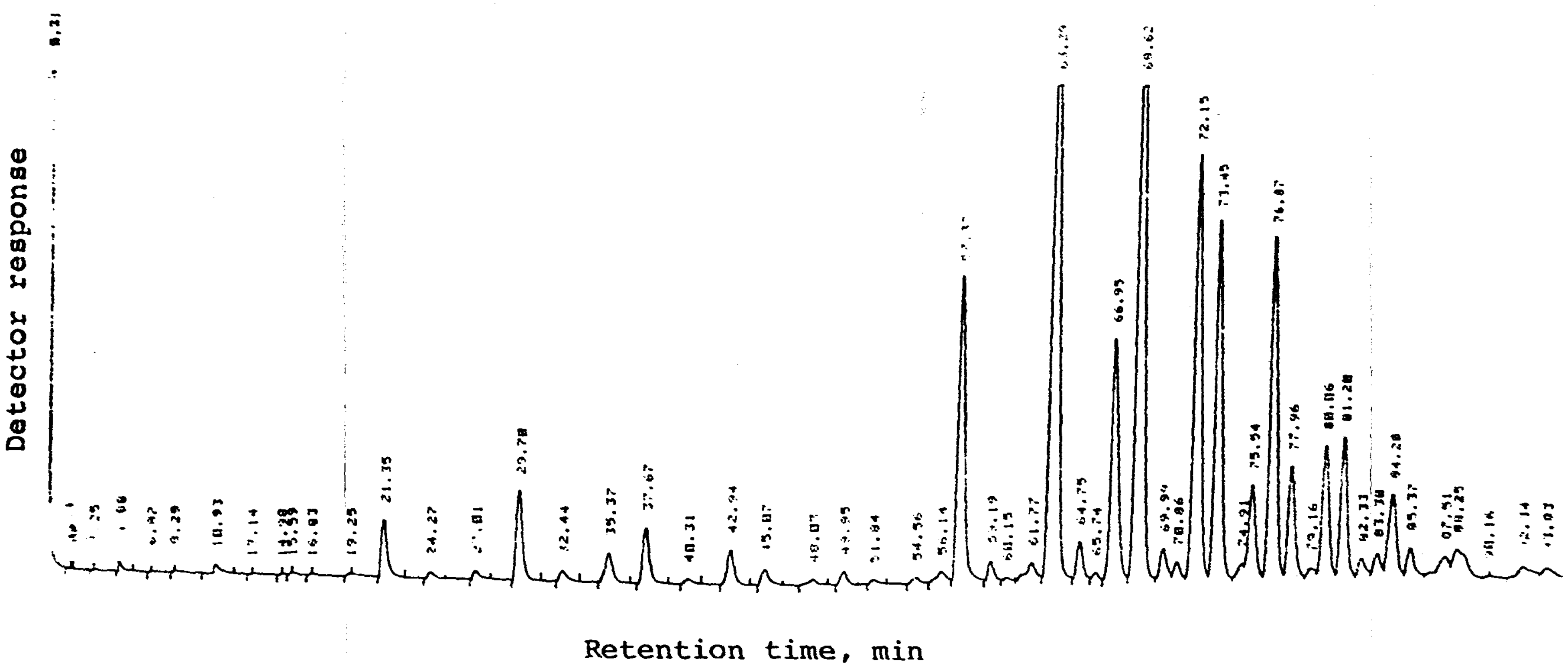

Figure 43. Gas chromatogram of a high dipentaerythritol base stock.

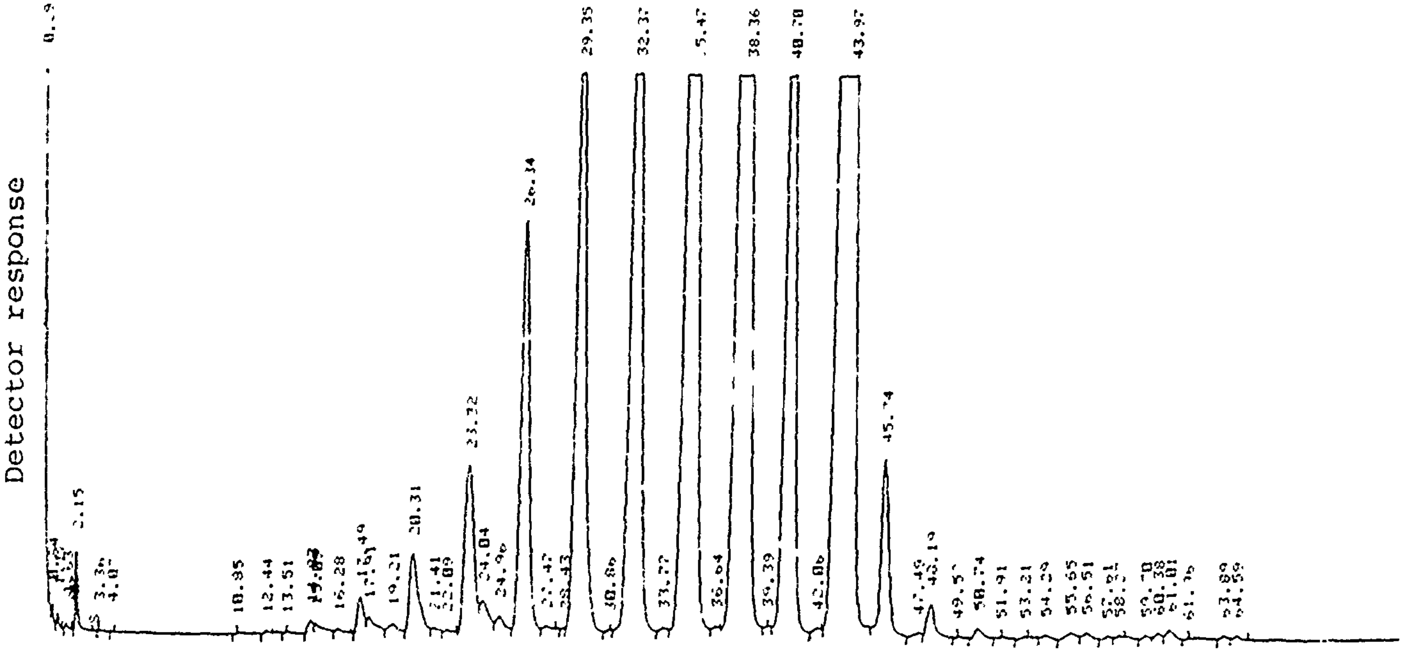

Figure 44. Gas chromatogram of a trimethylol propane base stock.

We originally postulated that the difference between the two formulations which made these assignments possible was a different ratio of PE to DPE used in the formulation of the base stock. The base stock analyses showed that DPE esters cannot overlap with the PE esters to the extent seen in Figure 41, and that a more likely explanation for the additional peaks in the PE ester region of Figure 41 is another series of PE type esters with different acids. In fact, a series of peaks was identified in Figure 41 which closely correspond to the retention times of the PE esters in the base stock of Fgiure 40. These peaks are marked with asterisks (*) in Figure 41. A second series of peaks shows a character similar to the esters in the base stock of Figure 42 in that their retention times are intermediate to those of the first series at the lower molecular weight end of the PE ester region. These peaks are denoted with pluses (+) in Figure 41. Although these base stocks are obviously not the specific ones used in the production of this particular MIL-L-23699 lubricant, they have provided considerable insight into the complexity of the formulation used. We concluded that the base stock used in this MIL-L-23699 contained at least two sets of PE esters in addition to Ester A of Table 15.

3.4 CONCLUSIONS

Gas chromatographic techniques offer the best opportunity for analyzing new and used synthetic lubricants. Significant progress was made in the analyses of these lubricants by GC and in the handling and presentation of the data obtained. All 15 esters from Ester A, the base stock ester of MIL-L-23699 lubricants, were identified by GC without the aid of standards or other confirmatory methods such as mass spectrometry. Due to the complexity of the chromatogram, the additives used in MIL-L-23699 lubricant were only partially identified using a FID detector, but they were easily identified when a N-P detector was used. Several differences were found between the chromatograms of used and unused MIL-L-23699 lubricants, but we were unable to correlate these to either lubricant degradation or engine wear.

The jet engine lubricants most widely used in the USAF are MIL-L-7808 type, produced by several manufacturers. A computer-assisted pattern recognition technique was developed to identify the composition of mixtures of MIL-L-7808 lubricants. This technique was successful in identifying and quantifying each manufacturer's type in a mixture.

To gain a better understanding of the chromatographic properties of synthetic lubricants, samples of commercially available base stocks were obtained from two major suppliers of synthetic esters. Gas chromatographic analyses of these base stocks led to a better understanding of the complex chromatograms obtained from the MIL-L-23699 lubricants.

SECTION 4

TASK II - RAPID TECHNIQUES FOR THE ANALYSIS OF WEAR METAL IN LUBRICATING OILS

4.1 INTRODUCTION

The utimate goal of Task II was to develop a rapid, portable flight-line method for assessing the iron content in lubricating oil. Present procedures call for lubricating oil samples to be sent to a laboratory for detailed SOAP analysis by atomic absorption (AA) and/or emission spectroscopy (ES). These laboratories are in general removed from the flight-line area and in some cases may even be located at sites distant from the operating location. Such a situation can produce considerable lag time between sampling, analysis, and action which might be dictated by the analytical results. This creates the possibility that corrective response time may in some cases be too long to prevent engine failure. A simple, on-the-spot flight-line test for a major wear indicator such as iron would be of value in eliminating this problem.

In formulating a research plan for Task II, the decision was made to initially pursue the development of a colorimetric method for iron. A major problem associated with the development of such a method is the separation of the color of the Fe-indicator chelate from the background oil coloration. Two methods, which we have titled "indicator chelate immobilization" (ICI) and "solvent extraction-chelation" (SEC), were investigated as ways of overcoming this problem. Although these methods are different, there are many common elements in their experimental approaches which made their simultaneous investigation practical.

Indicator chelate immobilization involves the incorporation of a ligand which forms a highly colored complex with iron into the solid support of a chromatographic column. As the used oil passes through the column, the iron is retained through chelation, resulting in a residual coloration of the column which can be correlated to the iron concentration. Preliminary studies into this method involved two indicators: 4,7-diphenyl-1,10-phenanthroline (commonly called bathophenanthroline) and 4,7-diphenyl-1,10-phenanthrolinedisulfonic acid. Two solid supports were considered for use: open-pore polyurethane (OPP) and open-pore urea/formaldehyde (OPUF). However, this approach was abandoned in favor of the SEC method because:

(1) SEC showed more promise as a rapid portable system;

(2) Interference from the oil coloration was encountered with the ICI method; and

(3) Formation of the colored iron-liqand complex was slow with the ICI method.

The concept of analysis by solvent extraction-chelation generally involves four common steps performed in varying order for different methods:

(1) Extraction of all iron into an immiscible layer,
(2) Conversion of iron to an appropriate oxidation state,
(3) Chelation with a colorimetric indicator, and
(4) Determination of color intensity.

We investigated several methods of solvent extraction-chelation and chose the method outlined by M. M. George [24] as the most promising. However, in its referenced form George's method was too involved for the average flight-line attendant to perform, and we modified the procedure to simplify it and adapt it to our particular analytical problem. The modified procedure was packaged into a portable kit that was subjected to an Air Force field test.

4.2 EXPERIMENTAL

The SEC method has been modified and improved many times during the course of this research. The conditions described below are those preferred for this colorimetric method, which can be performed in either four or five steps. Many other conditions were investigated throughout the course of the project, and these are appropriately noted in the Results and Discussion section. Both the five- and four-step methods are described here for clarity. The four-step method is the one used in the flight-line kit.

This colorimetric method requires the following supplies:

<u>Reagents</u>: (1) H_2SO_4 solution - 7.6 mL concd H_2SO_4 + 63.6 mL iron-free deionized H_2O + 28.8 mL ethanol.

(2) Isoamyl alcohol - reagent grade.

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[24] George, M. M., "Iron and Copper Content of Lubricating Oils Colorimetric Method," Australian Defense Scientific Services, Defense standards Laboratories, Maribyrnong, Victoria, Report 452, June 1971.

(3) Buffer solution - 50 g sodium acetate dissolved in iron-free deionized water by diluting to 100 mL.

(4) Reducer solution - 40 g hydroxylamine hydrochloride dissolved in iron-free deionized water by diluting to 100 mL.

(5) Indicator solution (0.019M) - 0.1 g bathophenanthrolinedisulfonic acid in 10 mL iron-free deionized water.

Instrumentation: Chemtrix 20 colorimeter or Hach DR/2 spectrophotometer

Standards: Conostan standards in MIL-L-7808

Used Oil: MIL-L-7808 type

Procedure - Five-Step Method

Step 1. To 1 mL of used oil (or standard) in a 3-dram vial add 1 mL H_2SO_4 solution. Shake for 2 min on a vortex mixer.

Step 2. Add 2 mL of reagent-grade isoamyl alcohol. Shake well for 1 min and allow to separate.

Step 3. Add 1 mL of the buffer/reducer solution (45 g sodium acetate plus 20 g hydroxylamine hydrochloride dissolved in iron-free distilled H_2O by diluting to 100 mL). Shake for 1 min.

Step 4. Add 0.5 mL of 0.019M indicator solution. Shake well for 1 min and allow to separate.

Step 5. Withdraw 1 mL of aqueous phase and place in a test cell. Mix in 5 mL of iron-free deionized water and test on Chemtrix 20 colorimeter at 530 nm.

Procedure - Four-Step Method

Step 1. To 1 mL of 3N H_2SO_4 solution and 2 mL of isoamyl alcohol in a 1-oz French square bottle, add 1 mL of used oil. Shake for 2 min on a vortex mixer.

Step 2. Add 1 mL of the buffer solution (50 g sodium acetate dissolved in iron-free deionized water by diluting to 100 mL) and 0.5 mL of reducer solution (40 g hydroxylamine hydrochloride dissolved in iron-free deionized water by diluting to 100 mL). Shake for 1 min.

Step 3. Add 0.5 mL of 0.019M indicator solution. Shake well for 1 min and allow to separate.

Step 4. Add 20 mL of iron-free deionized water and test on a Hach DR/2 spectrophotometer at 530 nm.

The red coloration of the lower aqueous layer is indicative of the iron concentration. A blank, prepared by substituting 0.5 mL of iron-free distilled water for the indicator solution was simultaneously carried through each procedure. This blank was used to zero the meter of the Chemtrix 20 colorimeter or the Hach DR/2 spectrophotometer.

4.3 RESULTS AND DISCUSSION

4.3.1 Colorimetric Method Development

The five-step procedure outlined above is similar to the first procedure we developed in this research. However, six important changes were made in our first procedure to make it effective for our purposes. Our first procedure required four steps:

(1) To 1 mL of used oil (or standard) in a 3-dram vial, add 1 mL H_2SO_4 solution and shake (by hand or on a wrist-action shaker) for 5 min. (This will extract the iron into the aqueous phase.)

(2) Add 1 mL of the buffer/reducer solution and shake for 1 min. Check the pH to confirm that the solution is near the optimum pH of 4.

(3) Add 1 mL of isoamyl alcohol to break up any emulsion in the aqueous layer. Shake well for 1 min and allow to separate.

(4) Add 0.5 mL of the indicator solution (0.006M bathophenanthrolinedisulfonic acid), shake for 1 min, and allow the solution to separate.

However, six important changes were made in our first procedure to make it effective for the intended application.

4.3.1.1 Improvement of Indicator Performance

The first change was to increase the indicator concentration from 0.006M to 0.019M bathophenanthrolinedisulfonic acid. Stoichiometric calculations indicate that a 0.006M indicator solution should provide an excess of bathophenanthrolinedisulfonic acid at the 50-ppm level. However, Table 19 shows that there is an inadequate amount of indicator present at the 50-ppm level. The data in Table 19 were obtained by carrying a 50-ppm oil calibration standard through the five-step procedure using a 0.006M

TABLE 19. RESULTS OF THE COLORIMETRIC TITRATION OF A 50-PPM OIL CALIBRATION STANDARD USING 0.006M INDICATOR SOLUTION

Indicator added, mL	Absorbance
0.5	0.52
0.6	0.62
0.7	0.66
0.8	0.64
0.9	0.62
1.0	0.60

indicator solution. All of the aqueous phase was drawn off and the indicator solution added in 0.1-mL increments. The absorbance was measured on the Chemtrix 20 colorimeter after each addition. Table 19 data show that maximum absorbance was obtained after 0.7 mL of 0.006M indicator solution was added. Calculations from these data predicted that the indicator concentration should be increased to 0.009M bathophenanthrolinedisulfonic acid so that the convenient volume of 0.5 mL of solution could be maintained.

The USAF oil calibration standards used contained 12 wear metals, including 2 (copper and manganese) that are known to form noninterfering complexes (at 530 nm) with bathophenanthroline. This offers a reasonable explanation for the fact that the stoichiometric calculations did not accurately predict the amount of indicator required to completely complex the iron at the higher ppm levels. As a result of these tests and calculations the concentration of bathophenanthrolinedisulfonic acid was increased to 0.019M in the procedure outlined above, to insure that an excess of indicator was present at all levels likely to be found in the used oil samples containing high levels of wear metals.

Figure 45 contains two calibration curves for the USAF oil calibration standards. The curve designated by the triangular points (0.006M indicator) shows significant deviation from linearity at the 50-ppm level. When the procedure outlined above was followed the curve designated by the circular points was obtained. This curve represents a least squares fit of the data for 0-, 2-, 5-, 10-, 20-, and 50-ppm standards. The correlation coefficient for this curve is 0.9993, with 1.0000 being a perfect fit. Each point on this curve represents the average of five replicates.

4.3.1.2 Improvement of Isoamyl Alcohol Performance

Two changes were made involving the isoamyl alcohol that is used in the procedure to prevent the formation of interfering emulsions or oil droplets in the aqueous phase. Initially 1 mL of the isoamyl alcohol was added after the buffer/reducer solution. Early in the research the colored aqueous phase turned cloudy after each shaking and could not be tested on the colorimeter.

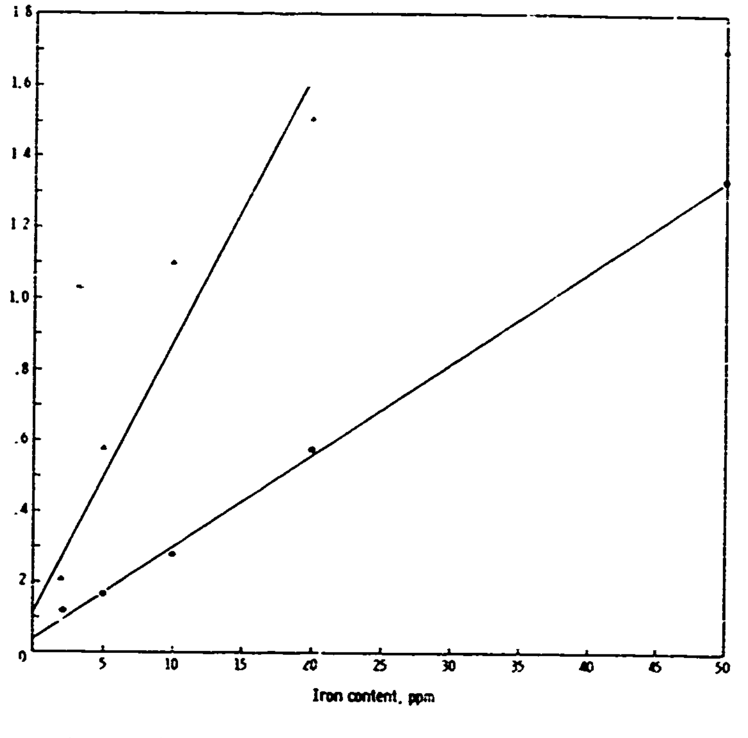

Figure 45. Calibration curves for colorimetric determination of iron using a Chemtrix 20 colorimeter.

The cloudy aqueous phases from several samples were centrifuged, after which the aqueous phase was clear and an oil droplet was found at the top of each aqueous phase. This indicated that an emulsion was forming that was not being brokenup sufficiently by the isoamyl alcohol to allow a complete separation of the two phases in a reasonable amount of time.

After several unsuccessful experiments to find a substitute for the isoamyl alcohol, the problem was solved by (1) increasing the amount of isoamyl alcohol from 1 mL to 2 mL and (2) adding the alcohol prior to addition of the buffer/reducer (B/R) solution instead of after its addition. These two changes were then incorporated into the colorimetric procedure resulting in the five-step method listed in Section 4.2. Thereafter the cloudy aqueous phase problem never reoccurred.

4.3.1.3 Improvement of Sulfuric Acid Performance

The fourth change to the procedure involved the first step, the sulfuric acid extraction. The procedure described above utilized a 1N H_2SO_4 solution. Table 20 displays the results of the analysis of 27 actual used oil samples by atomic absorption and the colorimetric method. While there is good agreement between results from the two methods for most samples, 10 of the samples gave substantially lower colorimetric results, and the colorimetric results were generally lower than the atomic absorption results.

TABLE 20. COMPARATIVE RESULTS FOR IRON ANALYSIS OF USED OIL SAMPLES BY ATOMIC ABSORPTION ANALYSIS AND BY THE FIVE-STEP COLORIMETRIC METHOD

Sample No.	Iron content, ppm Atomic absorption	 Five-step
3	2.2	1.5
15	5.2	4.3
790	10.0	6.7
700	6.0	5.4
710	6.3	6.0
852	11.3	6.3
683	11.9	7.1
259	11.0	11.6
352	13.8	12.2
861	12.9	13.8
354	17.5	17.7
863	31.8	30.4
F-1	0.8	1.2
P-6	4.7	2.5
O-1	5.1	4.0
R-5	9.2	7.7
O-6	6.8	7.9
P-8	8.6	8.0
H-9	18.8	9.5
O-2	13.6	10.2
P-12	17.4	12.5
H-15	15.0	14.5
P-13	20.8	16.5
H-2	17.2	17.6
H-18	24.2	18.1
P-11	60.5	55.1
P-10	68.8	70.4

At this point it was felt that increasing the efficiency of the extraction step would provide the greatest improvement in the colorimetric results. It was further thought that the iron particles present in some of the used oil samples were not being dissolved and extracted efficiently by the 1N H_2SO_4 solution.

Several experiments were conducted to determine if the procedure could be improved by changing the first step. Some of the acid solutions used in the tests described below were made by diluting the acid with distilled water only; these are designated "no ethanol." Four different acids at various concentrations were used to extract a 100-ppm synthetic oil sample, made by dispersing 325-mesh iron powder in unused type MIL-L-7808 oil. The resulting aqueous phases were analyzed for iron content by atomic absorption, and the results are shown in Table 21. Hydrochloric acid and sulfuric acid (no ethanol) did not extract iron as well

TABLE 21. AQUEOUS PHASE IRON CONTENT AFTER EXTRACTION BY VARIOUS ACIDS OF TYPE MIL-L-7808 OIL CONTAINING 100 ppm IRON

Acid	Normality	Aqueous phase iron content, ppm
H_2SO_4	1	21
	2	21
	4	24
	6	21
	8	18
	10	13
	20	5
H_2SO_4	1	20
(no ethanol)	6	8
	10	6
HNO_3	1	49
(no ethanol)	2	50
	3	48
	4	48
	5	51
	6	53
	10	49
HCL	1	16
	6	6
	10	2
Aqua regia	1	27
(no ethanol)	3	40

as the sulfuric acid. The aqua regia performed better than the sulfuric acid, but the nitric acid solutions extracted approximately twice as much iron as the sulfuric acid solutions. However, the nitric acid solutions still extracted only one-half of the iron present in the oil. This is probably because the iron powder used had an average particle size of 44 μm, which is larger than particle sizes found in most used oil samples. The larger particle may not have been extracted, and even if they were, they could not have been detected by atomic absorpiton unless digested by the acid.

Table 21 shows that the 6N HNO_3 extracted the most iron from the oil, but the resulting aqueous phase was a blue-green color, indicating the strong acids may attack the oil. The aqueous phase resulting from the 6N HNO_3 extraction of the 100-ppm oil contained a precipitate when examined the day following the extraction.

This indicated more positively that the strong acids degrade the oil and might hinder the colorimetric procedure.

The data in Table 21 show that the 1N HNO_3 solution extracted the iron nearly as well as the 6N HNO_3. Also, the 1N HNO_3 gave a clear aqueous phase after the extraction procedure while the 6N HNO_3 gave the aforementioned blue-green color. The 1N HNO_3 solution was therefore chosen to be used in a colorimetric analysis of 10 used oil samples. Table 22 compares the data from the five-step colorimetric method using 1N HNO_3 and 1N H_2SO_4 (our standard acid solution). The data for samples extracted with nitric acid were lower in every instance than for those extracted with sulfuric acid. This was exactly opposite what was predicted from the data in Table 21. Therefore, the nitric acid was not incorporated into the solvent extraction-chelation procedure.

TABLE 22. COMPARATIVE RESULTS FOR IRON ANALYSIS OF USED OIL SAMPLES BY THE FIVE-STEP COLORIMETRIC METHOD USING 1N HNO_3 AND 1N H_2SO_4

Sample No.	Iron content, ppm	
	1N HNO_3	1N H_2SO_4
F-1	0.0	1.2
P-6	1.5	2.5
R-5	6.1	7.7
H-9	7.1	9.5
O-2	6.7	10.2
P-12	9.7	12.5
P-13	12.4	16.5
H-2	9.1	17.6
H-18	15.0	18.1
P-11	42.7	55.1

Since these results were inconclusive it was decided to subject the five-step method to a ruggedness test for procedures developed by Youden [25]. This test was designed to determine if an analytical procedure is "rugged" (that is, if the procedure is immune to small changes in the stated procedure). We used this test to determine if changing certain parameters of the five-step method would improve the analytical results. The basic concept of this test is to make several alterations at one time in such a manner that the effects of individual changes can be determined. Table 23 presents the basic matrix used for the ruggedness test. This matrix allows one to determine the individual effects of seven different changes at one time. For our purposes the capital letters A, B, C, D, E, F, and G denoted the conditions normally

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[25] Youden, W. J., "Statistical Techniques for Collaborative Test," The Association of Official Analytical Chemists, Inc., 1969. pp 33-36.

TABLE 23. RUGGEDNESS TEST MATRIX FOR SEVEN FACTORS

Experiment	Factor combinations						
1	A	B	C	D	E	F	G
2	A	B	c	D	e	f	g
3	A	b	C	d	E	f	g
4	A	b	c	d	e	F	G
5	a	B	C	d	e	F	g
6	a	B	c	d	E	f	G
7	a	b	C	D	e	f	G
8	a	b	c	D	E	F	g

used in our five-step procedure. The conditions denoted by the lowercase letters a, b, c, d, e, f, and g were the alternate conditions. Table 23 shows that when the eight determinations are split into two groups of four on the bases of one of the letters (e.g., A and a), all other factors within each group cancel out. The effect of changing A to a (for example) is determined by comparing the average of the results of tests 1, 2, 3, and 4 with the average of the results of tests 5, 6, 7, and 8.

Two ruggedness tests were conducted on the five-step method. The conditions for them are shown in Tables 24 and 25. Used oil sample P-43 was used for the experiment and each test was done in duplicate. Table 26 presents the mean absorbance values obtained from each experiment, and Table 27 is calculated from the appropriate absorbance values of Table 26 as follows:

$$\text{FE (A-a)} = \frac{\text{tests 5, 6, 7, 8}}{4} - \frac{\text{tests 1, 2, 3, 4}}{4}$$

A positive factor effect (FE) indicates that the a factor gave higher absorbance values than did the A factor. The largest factor effects obtained in test 1 were both negative, indicating that factors A and E gave higher absorbance values than did factors a and e. This was expected in both cases because the amount of an aqueous reagent was being increased from the normal 1 mL to 1.5 mL, causing the lowercase factor to have lower absorbance values because of the dilution effect. All the factor effects resulting from test 2 were positive numbers with factor effect A-a being approximately four times the next largest number. In factor effect A-a of test 2 the strength of the H_2SO_4 solution was increased from 1N to 2N. This indicated that increasing the strength of the H_2SO_4 solution may yield increased absorbance values in used oil samples. Additional research was done in this area to determine if increasing the acid strength would benefit our solvent extraction-chelation method.

TABLE 24. RUGGEDNESS TEST CONDITIONS FOR TEST 1

Factor	Description	Factor levels A-G	a-g
A-a	H_2SO_4 solution added, mL	1	1.5
B-b	Shaking time after step 1, min	2	5
C-c	Isoamyl alcohol added, mL	2	3
D-d	Shaking time after step 2, min	1	3
E-e	B/R solution added, mL	1	1.5
F-f	Shaking time after step 3, min	1	3
G-g	Shaking time after step 4, min	1	3

TABLE 25. RUGGEDNESS TEST CONDITIONS FOR TEST 2

Factor	Description	Factor levels A-G	a-g
A-a	Concentration of H_2SO_4 to make solution, mL	3	5
B-b	Shaking time after step 1, min	2	5
C-c	Isoamyl alcohol added, mL	2	3
D-d	Hydroxylamine hydrochloride in B/R solution, g	20	25
E-e	Shaking time after step 3, min	1	2
F-f	Bathophenanthrolinedisulfonic acid in indicator, g	0.1	0.15
G-g	Shaking time after step 4, min	1	2

TABLE 26. RUGGEDNESS TEST RESULTS FOR TESTS 1 AND 2

Experiment	Absorbance Test 1	Test 2
1	0.555	0.510
2	0.497	0.565
3	0.670	0.570
4	0.557	0.605
5	0.447	0.687
6	0.560	0.725
7	0.397	0.715
8	0.525	0.757

TABLE 27. FACTOR EFFECT DATA FOR THE RUGGEDNESS TEST RESULTS FOR TESTS 1 AND 2

Factor	Factor effect Test 1	 Test 2
A-a	-0.087	0.158
B-b	0.022	0.040
C-c	0.017	0.040
D-d	0.065	0.010
E-e	-0.103	0.002
F-f	0.010	0.004
G-g	0.017	0.006

Sulfuric acid diluted to 1N with deionized water and ethanol was used in our method to digest and extract the iron from the oil. Ruggedness test results indicated that increasing the acid strength might increase extraction efficiency. An earlier sulfuric acid strength test [26], which was done using large (44 μm average) iron powder, showed no increase in extraction efficiency for increased acid strengths. However, the iron powder used in this earlier test was not representative of the particle size typically found in used oils. Therefore, more acid extraction studies were conducted to conclusively resolve this question.

Table 28 presents the results of a study in which the effect of using different acids at various strengths for the five-step colorimetric analysis of an actual used oil (F-18) was investigated. The sulfuric acid solutions extracted the iron better than perchloric acid, the mixtures of sulfuric and hydrochloric acids, and mixtures of sulfuric and nitric acids. The 0.5N sulfuric acid did not extract the iron as well as the other sulfuric acid solutions. The 1N, 2N, and 4N sulfuric acids extracted equally well and the 6N and 8N acids gave increased results.

Table 29 presents the results of the colorimetric analysis of a MIL-L-7808 oil doped with <25-μm iron powder. The sulfuric acid solution used was varied from 0.5N to 20N and the sample was analyzed in duplicate at each acid level. Figure 46 shows that the 0.5N and 1N sulfuric acid solutions yielded lower results than the other concentrations. The absorbance remained relatively constant from 2N through 14N but showed a decrease at the 20N level.

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[26] Ross, W. D., Brooks, J. J., Hillan, W. J., "Trace Chemical Analysis Methodology," Third Annual Report, Contract F33617-75-C-1130, 16 February 1977 - 15 February 1978.

TABLE 28. IRON CONTENT OF USED OIL SAMPLE F-18 BY THE FIVE-STEP METHOD USING VARIOUS ACIDS

Acid	Normality	Iron content, ppm
H_2SO_4	0.5	43
	1	56
	2	51
	4	56
	6	66
	8	61
$HClO_4$	1	38
	4	43
H_2SO_4/HCl	1/0.5	41
	2/1	45
H_2SO_4/HNO_3	1/1	39
	2/1.5	39

TABLE 29. EFFECTIVENESS OF 0.5N TO 20N SULFURIC ACID FOR EXTRACTING IRON FROM MIL-L-7808 LUBRICATING OIL USING THE FIVE-STEP METHOD

Acid normality	Absorbance
0.5	0.061
	0.365
1	0.48
	0.57
2	0.77
	0.76
3	0.73
	0.72
4	0.74
	0.76
5	0.84
	0.81
6	0.73
	0.73
8	0.79
	0.78
10	0.74
	0.74
14	0.73
	0.70
20	0.63
	0.65

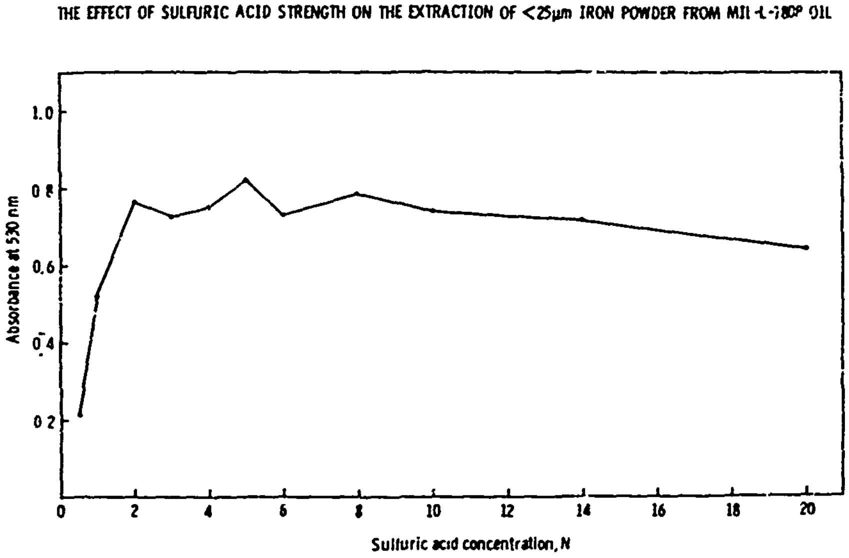

Figure 46. The effect of sulfuric acid strength on the extraction of iron powder from MIL-L-7808 oil.

The above acid studies were inconclusive and sometimes contradictory. Therefore, it was decided to analyze several used oil samples using increasing strengths of sulfuric acid solutions. The colorimetric results presented in Table 30 were obtained by analyzing 17 MIL-L-7808 used oil samples using 1N, 2N, and 3N H_2SO_4 in the five-step method.

Results in Table 30 show that colorimetric analysis using 2N H_2SO_4 gave higher values than those obtained using 1N H_2SO_4 in 15 of the 17 samples analyzed. The other two samples (P-86 and F-38) gave comparable results (6.3 vs. 6.1, and 3.4 vs. 3.4) for the 1N and 2N H_2SO_4. Examination of the data for the 15 samples which yielded increased iron results show that the increase ranged from 1.4 to 10.5 ppm or from 7% to 85%. When the same samples were analyzed using 3N H_2SO_4, 12 of the 16 samples that gave reliable results yielded higher values when compared with the 2N H_2SO_4 data, and 14 of the 16 gave higher values when compared with the 1N H_2SO_4 data. Comparing the 2N and 3N H_2SO_4 data, the increase for the 12 samples showing an increase ranged from 0.5 to 7.5 ppm or from 5% to 22%. This indicates that the 3N acid is more efficient for digesting and extracting iron than the 2N H_2SO_4.

The above experiments resulted in an increase from 1N to 3N in the sulfuric acid concentration used in the colorimetric method. This change necessitated an increase in the buffer strength of

TABLE 30. COMPARATIVE RESULTS FOR IRON ANALYSIS OF USED OIL SAMPLES BY THE FIVE-STEP COLORIMETRIC METHOD USING 1N, 2N, AND 3N H_2SO_4

Sample No.	Iron content, ppm		
	1N H_2SO_4	2N H_2SO_4	3N H_2SO_4
H-63	16.3	22.4	26.6
H-65	13.5	14.9	13.3
P-44	32.3	41.5	43.6
P-62	21.8	26.1	29.4
P-64	22.3	25.0	30.4
P-86	6.3	6.1	6.6
P-87	2.0	3.7	–[a]
P-88	30.1	38.3	40.8
P-90	8.6	10.4	12.2
P-91	13.9	16.9	19.5
F-17	49.0	52.2	58.2
F-18	41.8	47.9	44.5
F-23	37.9	48.4	55.9
F-37	8.6	10.9	9.6
F-38	3.4	3.4	2.1
F-39	14.1	19.6	27.1
R-424	9.5	12.5	14.3

[a] The 3N H_2SO_4 result for this sample was 44 ppm; the wrong sample may have been analyzed.

the buffer/reducer solution. Therefore, the amount of sodium acetate was increased from 30 g to 45 g to maintain the pH of the aqueous phase at approximately 4.

4.3.1.4 Development of a Four-Step Method

The fifth change was to reduce the number of steps in the colorimetric method from five to four. Because of the desire to make the colorimetric method as rapid and as easy to do as possible, methods of shortening the procedure were investigated from the time the first working procedure was established. Finally, the first two steps of the well documented five-step procedure (addition of H_2SO_4 solution and addition of isoamyl alcohol) were combined into one step.

Figure 47 shows calibration curves for the four-step (round data points) and five-step (square data points) procedures covering the range from 0 to 30 ppm iron. The standards used for this test were made with MIL-L-7808 oil. The correlation coefficients

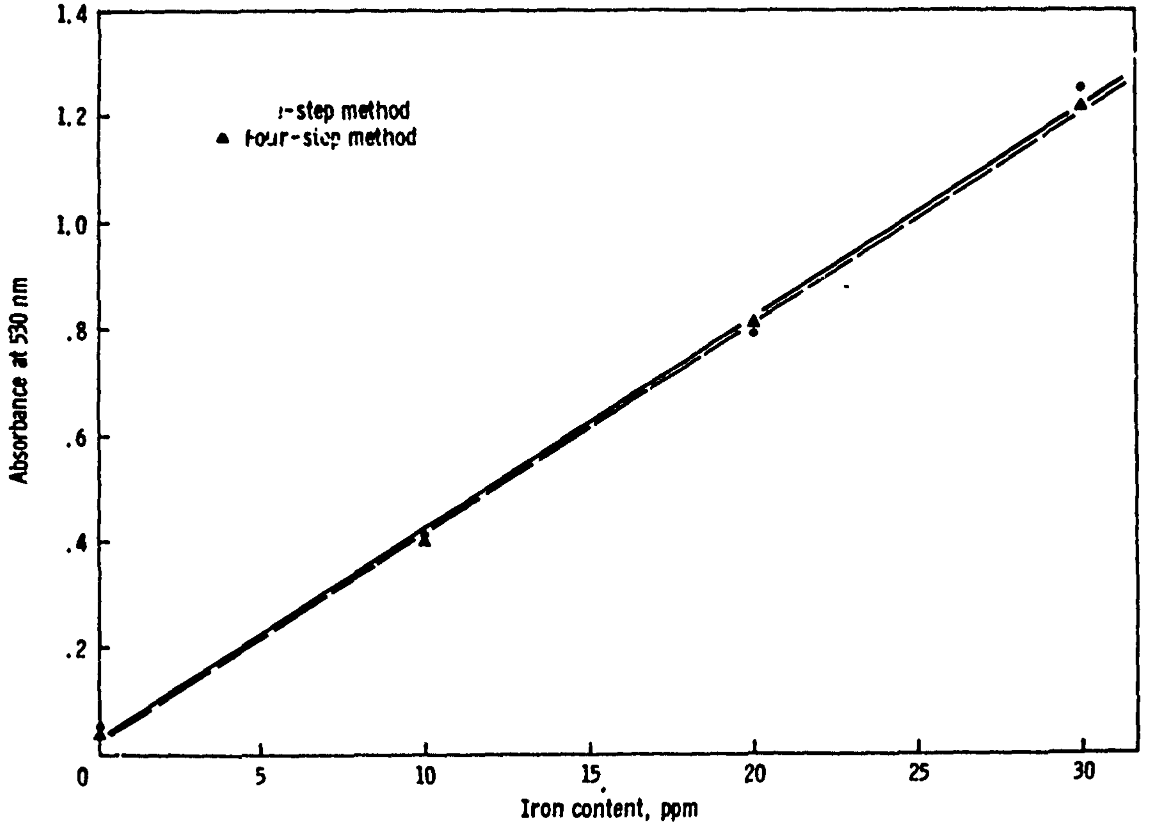

Figure 47. Comparison of calibration curves obtained from the analysis of jet engine oil containing iron by the five-step and four-step colorimetric methods.

for the four-step and five-step curves are 0.9995 and 0.9984, respectively, and the slopes are 0.0395 and 0.0399 for the four-step and five-step data, respectively. The calibration curve for the four-step method compares very favorably with that for the five-step curve.

Table 31 displays comparative results for 25 used oil samples analyzed by atomic absorption and the five- and four-step colorimetric methods. Comparison of the four-step colorimetric and atomic absorption data show the following:

(1) The colorimetric data were higher (<1 ppm higher for five samples.

(2) The colorimetric and atomic absorption data were equal (<1 ppm difference) for 10 samples.

(3) The colorimetric data were lower (<1 ppm lower) for 10 samples.

Data for 5 of the 10 samples that gave lower colorimetric results were within 2 ppm of the atomic absorption data. Agreement between the four-step colorimetric method and atomic absorption data was generally good.

Figure 48 shows the results of a shelf-life/compatibility study done to determine if any problems resulted from storage of the isoamyl alcohol and acid solution in contact with each other. The test was conducted by loading 1-oz French square bottles with 1 mL of 3N H_2SO_4 solution and 2 mL of isoamyl alcohol. A stock oil containing $\sim$10 ppm iron was analyzed in triplicate using the previously loaded bottles. The other reagents were made up fresh for each test. Test results indicated that the acid solution and isoamyl alcohol did not degrade after 15 weeks and can be stored together. A long-term, more complete shelf-life study, conducted later, is discussed in Section 4.3.1.5.

Therefore, the four-step method was chosen for use in the field test. This method provides several advantages over the five-step method:

(1) It cuts the analysis time by $\sim$2 minutes.

(2) It allows for easier packaging.

(3) It makes the analysis procedure less complicated.

(4) It eliminates the transfer of the isoamyl alcohol.

TABLE 31. COMPARATIVE RESULTS FOR IRON ANALYSIS OF USED OIL SAMPLES BY ATOMIC ABSORPTION ANALYSIS AND BY THE FIVE-STEP AND FOUR-STEP COLORIMETRIC METHODS

Sample	Iron content, ppm		
number	Atomic absorption	Five-step	Four-step
P-27	8.3	-	11.9
P-62	26.3	29.4	24.4
P-65	15.0	15.3	15.1
P-86	7.1	6.6	6.5
P-87	2.9	3.7	4.1
P-90	12.4	12.2	9.7
P-91	11.0	19.5	15.6
P-95	3.8	-	3.9
P-98	2.0	-	2.6
P-100	0.9	-	1.5
P-101	14.0	11.3	10.4
P-103	10.0	7.8	6.9
P-104	7.0	-	5.4
P-105	7.0	-	5.7
P-106	26.0	22.9	21.5
P-107	0.9	-	0.7
P-108	8.3	-	7.1
P-109	4.4	-	4.4
P-110	6.5	-	5.5
H-63	20.7	26.6	24.2
H-64	7.6	8.2	6.7
H-65	12.3	13.3	14.8
H-69	14.2	-	10.9
H-70	11.2	-	9.3
R-443	7.0	6.5	7.8

4.3.1.5 Improvement of Long-Term Stability of Buffer/Reducer Solution

The sixth change, involving the buffer/reducer (B/R) solution, was made due to a degradation problem encountered during packaging of the method into a portable kit. Preparations were being made for a long-term shelf-life study when it was found that the colorimetric procedure was not working. A series of tests was therefore run to locate the problem. It was found that every time the stored B/R solution was used, the pH was approximately 1 and essentially no color developed. However, when fresh B/R solution was used in conjunction with any combination of the other reagents, the pH was approximately 4 and the color developed as expected.

It was concluded from these tests that the B/R solution was the cause of the problem, and more tests were run to determine why it became ineffective. These further tests indicated that there

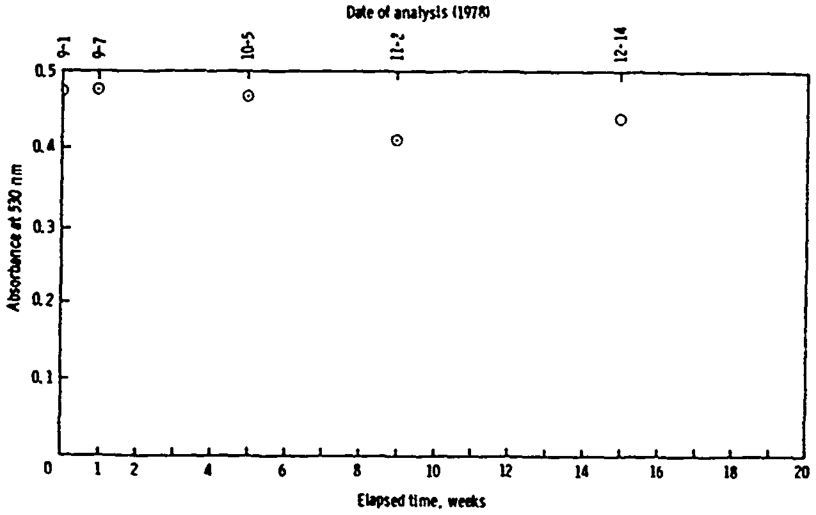

Figure 48. Shelf-life/compatability study of H_2SO_4 solution and isoamyl alcohol stored in a 1-oz French square bottle at room temperature.

was more than just a pH problem. That is, a test was run using fresh reagents except for the buffer/reducer solution, which was taken from storage. The pH was adjusted to ∿4 by adding fresh buffer solution. However, the color that developed was still pale and measured well below the expected value, indicating that there was insufficient reducing agent present to convert all of the iron present to the ferrous state as required by the indicator.

At this point attempts were made to perform infrared analysis on the B/R solution. Initial attempts were unsuccessful, and a dried sample of the stored solution was obtained for analysis by infrared spectroscopy. Figures 49, 50, and 51 show the spectra obtained by infrared analysis of sodium acetate, hydroxylamine hydrochloride, and B/R solution [as potassium bromide (KBr) pellets]. The buffer/reducer spectrum (Figure 51) shows evidence of very little if any hydroxylamine hydrochloride, as indicated by the disappearance of the strong doublet at 1200 and 1160 cm^{-1} as well as those bands at 1880, 1590, 1480, 1000, and 600 cm^{-1} (when compared with Figure 50). The presence of some sodium acetate is indicated by the bands at 1590, 1410, and 640 cm^{-1}. However, the buffer/reducer spectrum (Figure 51) shows the appearance of a very strong band at 1660 cm^{-1} and lesser ones at 1515 and 1410 cm^{-1}. These new peaks match up very well with the infrared spectrum of acetohydroxamic acid found in the Sadtler

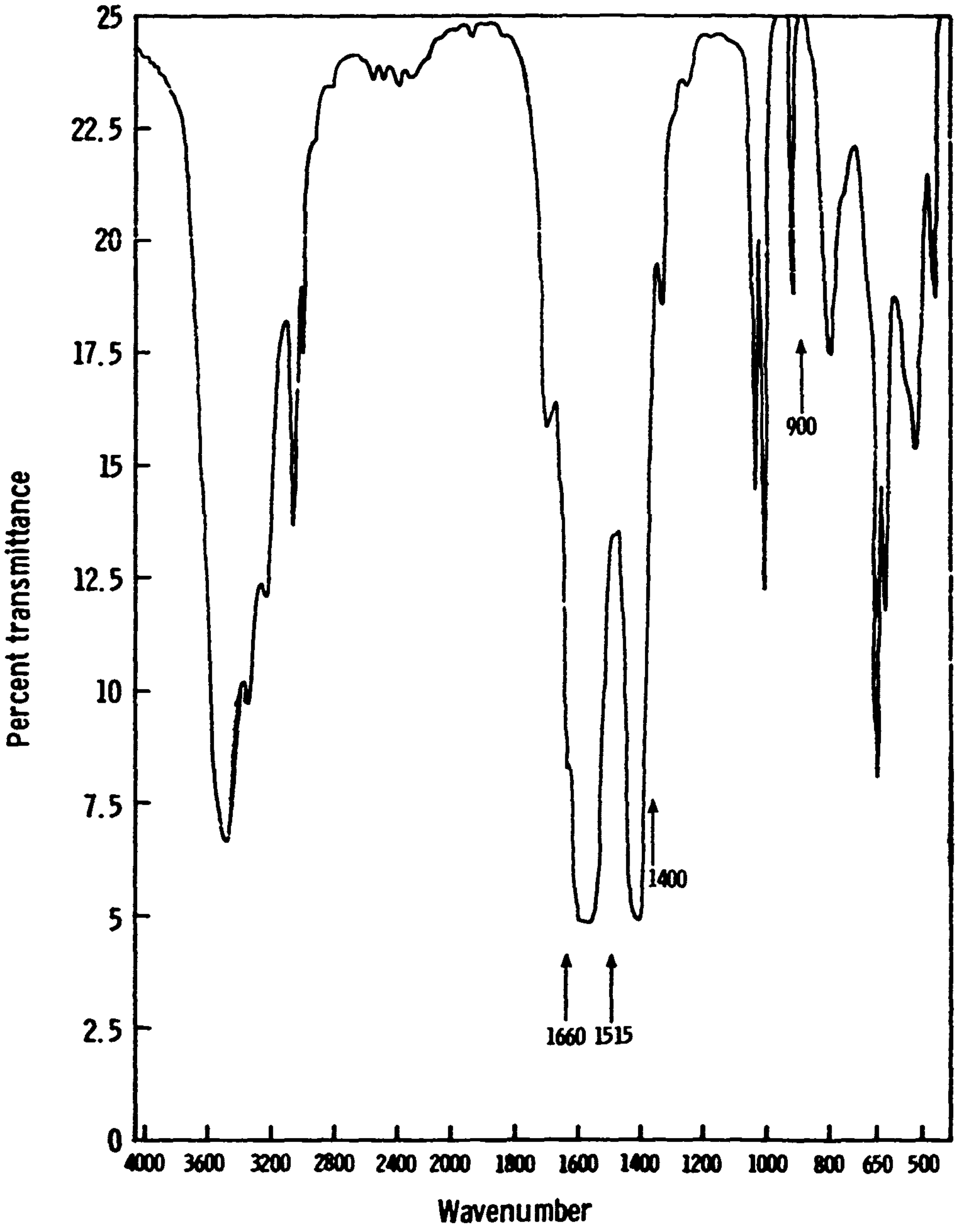

Figure 49. Infrared spectrum of sodium acetate (KBr pellet).

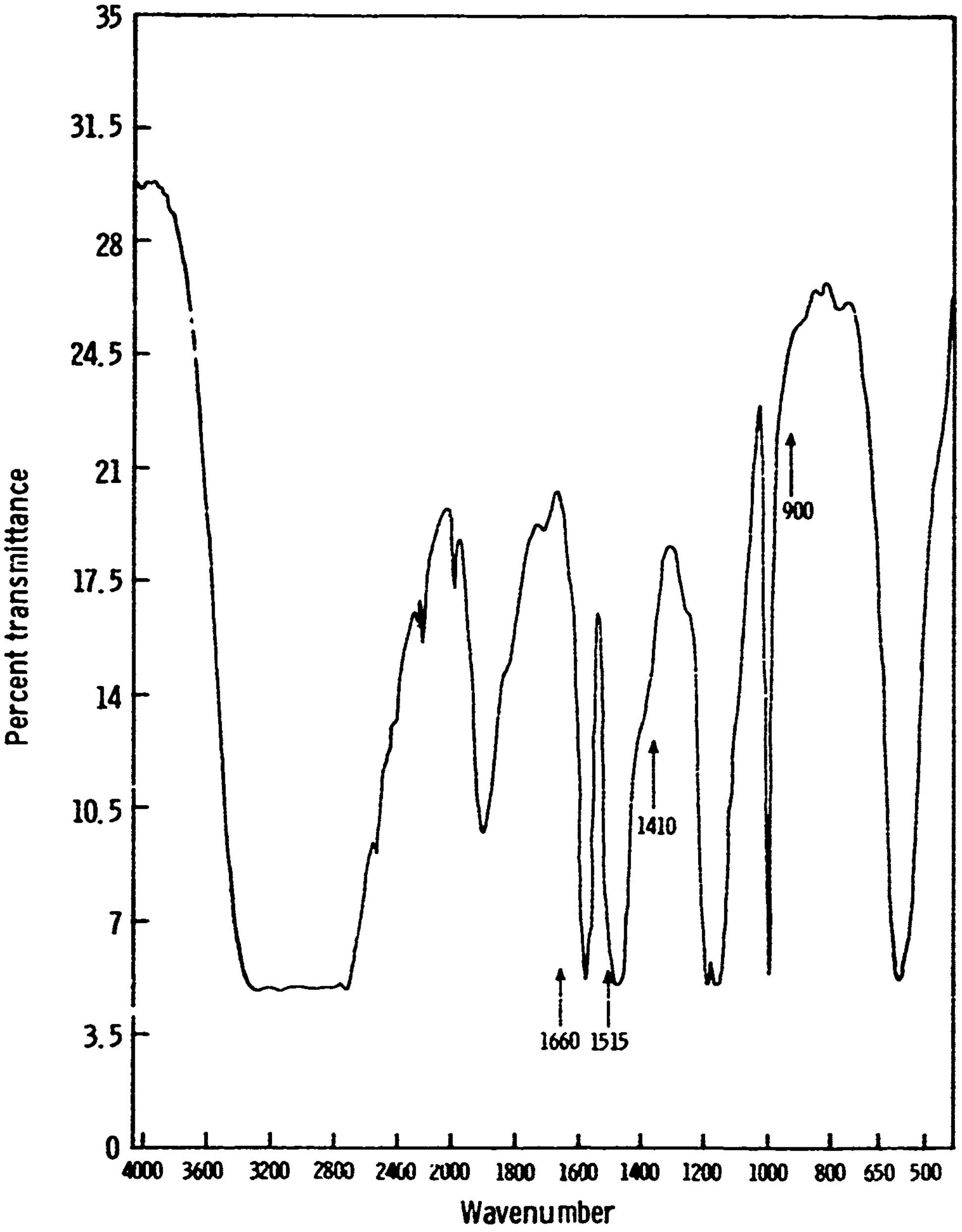

Figure 50. Infrared spectrum of hydroxylamine hydrochloride (KBr pellet).

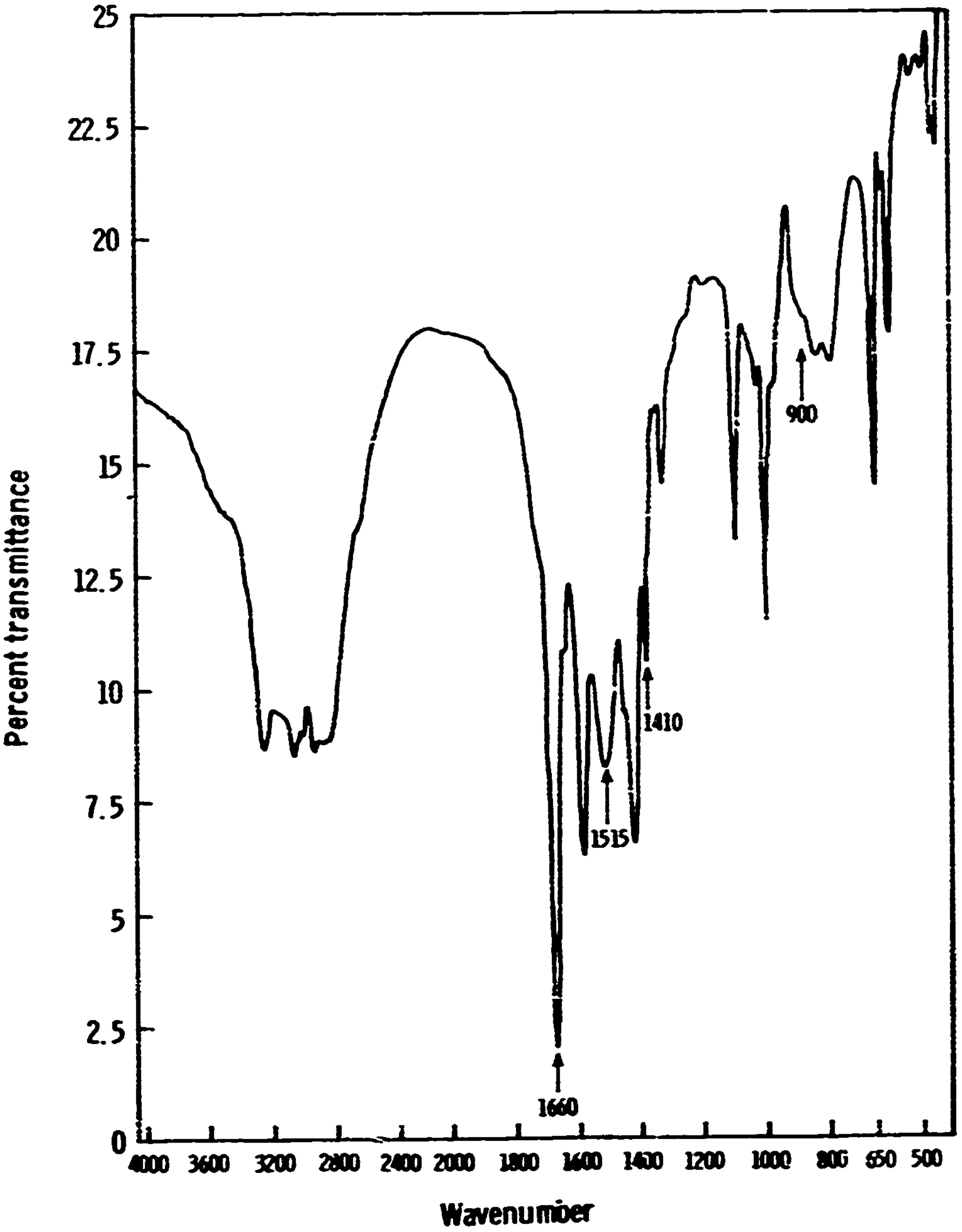

Figure 51. Infrared spectrum of stored buffer/reducer solution (KBr pellet).

reference spectrum. The acetohydroxamic acid could be formed by the reaction of sodium acetate and hydroxylamine hydrochloride.

It is known from the literature [27] that the ferric salt of acetohydroxamic acid gives a cherry red color. When 0.02 g of ferric chloride was added to 5 mL of fresh B/R solution, the solution turned amber in color. But when the same amount of ferric chloride was added to 5 mL of stored B/R solution, the solution turned cherry red in color.

While these tests did not positively confirm the presence of acetohydroxamic acid, they did show the following:

(1) The stored B/R solution contained very little, if any, hydroxylamine hydrochloride.

(2) There was less sodium acetate in stored B/R solution than in fresh solution.

(3) The stored B/R solution contained a compound not present in fresh solution.

Therefore, it was concluded that the degradation of B/R solution was due to a reaction between the sodium acetate and hydroxylamine hydrochloride, which was accelerated when the sodium acetate concentration was increased from 2.8M to 5.5M.

Consequently, it was decided to split the buffer/reducer solution into two solutions (a buffer solution and a reducer solution) to solve the degradation problem that occurs when the combined solution is stored for extended periods of time. Table 32 shows the colorimetric results for 15 used oil samples analyzed using the split buffer and reducer solutions and also using the premixed buffer/reducer solution. The concentration of the sodium acetate in the buffer solution was increased from 5.5M to 6.1M. This was done to increase the pH of the aqueous phase to ∿4.3 from ∿3.8 when using the 3N H_2SO_4 solution. The concentration of hydroxylamine hydrochloride in the reducer solution was doubled so that 0.5 mL of reducer solution could be used instead of 1 mL. This increase the total volume of the aqueous phase resulting from the colorimetric procedure by only 0.5 mL instead of 1 mL.

The resulting four-step procedure used for the portable kit is as follows:

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[27] Sidgwick, N. V. "The Organic Chemistry of Nitrogen," Oxford University Press, 1937, p 198.

TABLE 32. THE EFFECT OF SPLITTING THE BUFFER/REDUCER SOLUTION ON COLORIMETRIC DATA FROM USED OILS

Sample number	Iron content, ppm Split buffer/reducer solutions	Iron content, ppm Combined buffer/reducer solution
P-62	24.5	23.5
P-64	24.5	23.5
P-65	12.6	13.1
P-86	6.6	6.0
P-87	3.4	3.0
P-88	34.0	35.0
P-90	11.2	10.2
P-91	15.0	14.8
H-58	1.9	1.7
H-64	7.0	6.6
H-65	13.5	13.5
H-68	7.0	6.7
R-424	10.5	10.3
R-429	5.8	5.6
R-437	1.8	2.0

Step 1. To a 1-oz French square bottle containing 1 mL of H_2SO_4 solution and 2 mL of isoamyl alcohol, add 1 mL of oil sample. Shake in a vortex mixer for 2 minutes.

Step 2. Add 1 mL of buffer solution and 0.5 mL of reducer solution. Shake on the vortex mixer for 1 minute.

Step 3. Add 0.5 mL of indicator solution and shake on the vortex mixer for 1 minute.

Step 4. Add 21 mL of deionized water. Invert the bottle three times and take a reading on the direct-reading spectrophotometer.

4.3.2 Colorimetric Method Capabilities

4.3.2.1 Used Oil Analysis

The experiments described in section 4.3.1.3 resulted in a decision to increase the sulfuric acid concentration used in the colorimetric method. Atomic absorption, colorimetric, and particle independent data for 29 used oil samples are compared in Table 33, which includes the type of engine the oil sample was removed from, the hours since overhaul, and the hours since oil change. The colorimetric data were obtained by the five-step method using 3N sulfuric acid. The particle size independent method was developed

TABLE 33. COMPARATIVE RESULTS FOR IRON ANALYSIS OF USED OIL SAMPLES BY ATOMIC ABSORPTION, COLORIMETRIC, AND PARTICLE SIZE INDEPENDENT METHODS

	Iron content, ppm					
Sample number	Atomic absorption	Colorimetric (3N acid)	Particle size independent	Engine type	Time since overhaul, hr	Time since oil change, hr
P-44	35.1	43.6	-	J-79	55	0
P-62	26.3	29.4	28	T-56	2027	728
P-64	26.0	30.4	27	T-56	2058	759
P-65	15.0	15.3	16	J-56	3173	657
P-78	11.8	9.8	16	J-85	2202	165
P-81	6.5	3.7	-	J-79	486	9
P-86	7.1	6.6	10	J-79	566	550
P-87	2.9	3.7	-	F-100	271	202
P-88	33.9	40.9	42	TF-33	6080	462
P-90	12.4	12.2	13	J-85	452	0
P-91	11.0	19.5	19	J-85	680	0
R-424	12.7	14.3	13	T-56	3798	2034
R-429	6.5	5.9	-	J-85	1773	150
R-437	2.0	1.3	-	J-57	1511	817
R-443	7.0	6.5	-	J-85	1815	172
R-452	3.1	2.8	-	J-85	1540	-
H-51	16.8	18.7	-	T-56	1616	80
H-58	2.0	1.4	3	F-100	3025	869
H-63	20.7	26.6	25	J-85	2092	110
H-64	7.6	8.2	10	J-85	430	2
H-65	12.3	13.3	18	T-56	2031	568
H-68	7.7	7.2	9	T-56	4537	833
F-17	30.9	58.2	49	J-85	1982	3
F-18	60.5	44.5	115	T-56	1633	527
F-23	16.1	55.9	64	T-56	1123	400
F-34	6.2	5.7	7	T-56	284	284
F-37	3.3	9.6	13	TF-39	1863	617
F-38	3.2	2.1	5	TF-56	1850	765
F-39	22.0	27.1	33	TF-56	1720	130

at the Air Force Materials Laboratory to minimize the effect of large metal particles on the analysis of used jet engine oils for wear metal content.

Comparison of the atomic absorption and colorimetric data in Table 33 shows the following:

(1) The colorimetric data were >1 ppm higher for 13 samples.

(2) The colorimetric and atomic absorption data were equal (<1 ppm difference) for 13 samples.

(3) The colorimetric data were >1 ppm lower for three samples.

Since the Air Force field test for the colorimetric method was done on aircraft engines which have threshold limits of 8 ppm iron, particular attention was paid to used oil samples containing <15 ppm iron. The calibration curve developed for the range from 0 to 15 ppm iron is shown in Figure 52. This curve has a correlation coefficient of 0.9963, an intercept of 0.053, and a slope of 0.0337.

Table 34 displays the comparative result for 19 used oil samples analyzed by atomic absorption, particle size independent, and the five-step colorimetric method using 3N H_2SO_4. Comparison of the colorimetric and atomic absorption data show the following:

(1) The colorimetric data were higher (>1 ppm higher) for four samples.

(2) The colorimetric and atomic absorption data were equal (<1 ppm difference) for 12 samples.

(3) The colorimetric data were lower (>1 ppm lower) for three samples.

This shows that the colorimetric and atomic absorption data agree very well for oil samples containing less than 15 ppm iron. This was expected, since these samples probably contain very few large particles.

In summary, it can be said that the 3N colorimetric method did better than atomic absorption (AA) analysis in 48% of the samples analyzed, and as well as or better than AA in 90% of the samples analyzed.

4.3.2.2 Effect of pH on Color Formation

Another important parameter that was defined by research performed on this contract is the effect of the aqueous phase pH on the color formation by the bathophenanthrolinedisulfonic acid

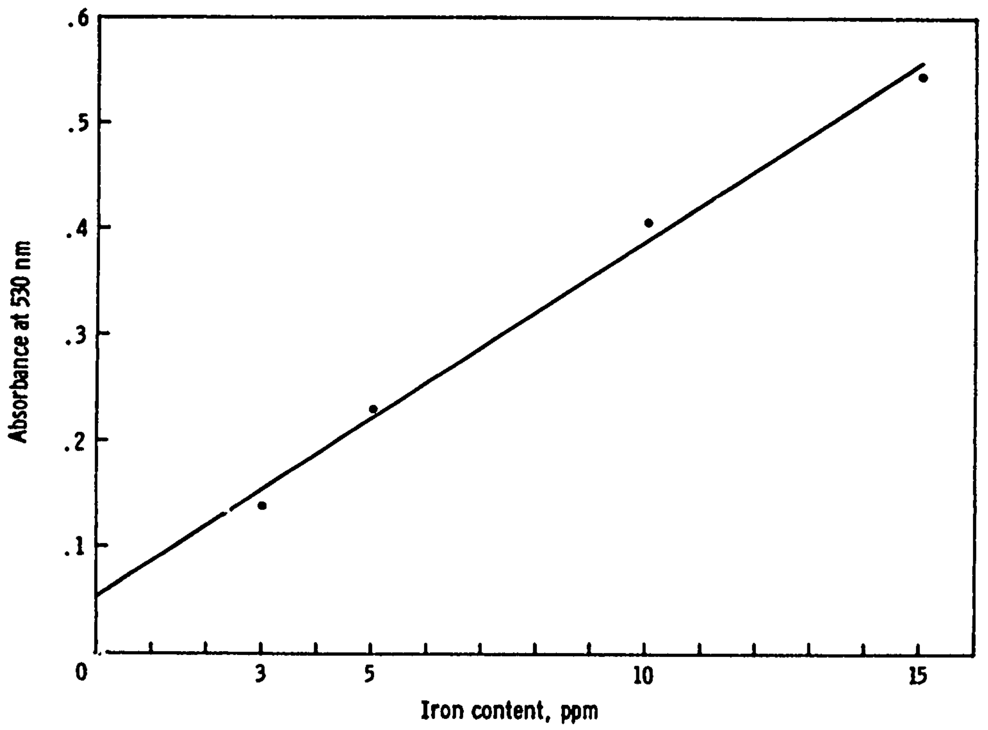


Figure 52. Calibration curve for the colorimetric determination of iron in jet engine lubricating oil in the 0- to 15-ppm range.

TABLE 34. COMPARATIVE RESULTS FOR IRON ANALYSIS OF USED OIL SAMPLES CONTAINING <15 ppm IRON BY ATOMIC ABSORPTION, COLORIMETRIC, AND PARTICLE SIZE INDEPENDENT METHODS

Sample number	Iron content, ppm		
	Atomic absorption	Colorimetric ($3N$ acid)	Particle size independent
P-65[a]	15.0	15.3	16
P-78	11.8	9.8	16
P-81	6.5	3.7	-
P-86	7.1	6.6	10
P-87	2.9	3.7	-
P-90	12.4	12.2	13
P-91	11.0	19.5	19
R-424	12.7	14.3	13
R-429[a]	6.5	5.9	-
R-437[a]	2.0	1.3	-
R-443[a]	7.0	6.5	-
R-452[a]	3.1	2.8	-
H-58[a]	2.0	1.4	3
H-64[a]	7.6	8.2	10
H-65	12.3	13.3	18
H-68[a]	7.7	7.2	9
F-34[a]	6.2	5.7	7
F-37	3.3	9.6	13
F-38	3.2	2.1	5

[a] Colorimetric data for these samples were taken from the 0- to 15-ppm calibration curve.

indicator. Table 35 shows the results of a test conducted to determine the pH range over which the bathophenanthrolinedisulfonic acid indicator was effective. These results are graphically displayed in Figure 53, which shows the effective pH range to be between 1 and 7. The aqueous phase of the solvent extraction chelation procedure is buffered to a pH of approximately 4, which falls in the middle of the pH range over which the indicator is effective. These data show that small deviations from pH 4 will not interfere with the indicator color formation. Color formation was essentially instantaneous in all cases except for the pH 0.61 test.

4.3.2.3 Upper Level Detection Limits of the Indicator

Tests were conducted to determine the upper level detection limit of the 0.019M indicator solution used in our method. These tests

TABLE 35. THE EFFECT OF pH OF THE AQUEOUS PHASE ON THE COLOR FORMATION OF THE IRON BATHOPHENANTHROLINEDISULFONIC ACID COMPLEX

Aqueous phase pH	Absorbance
0.61	0.012
1.02	0.365
1.91	0.365
3.50	0.350
4.04	0.355
5.04	0.355
6.60	0.350
8.04	0.340
9.57	0.295
13.05	0.225

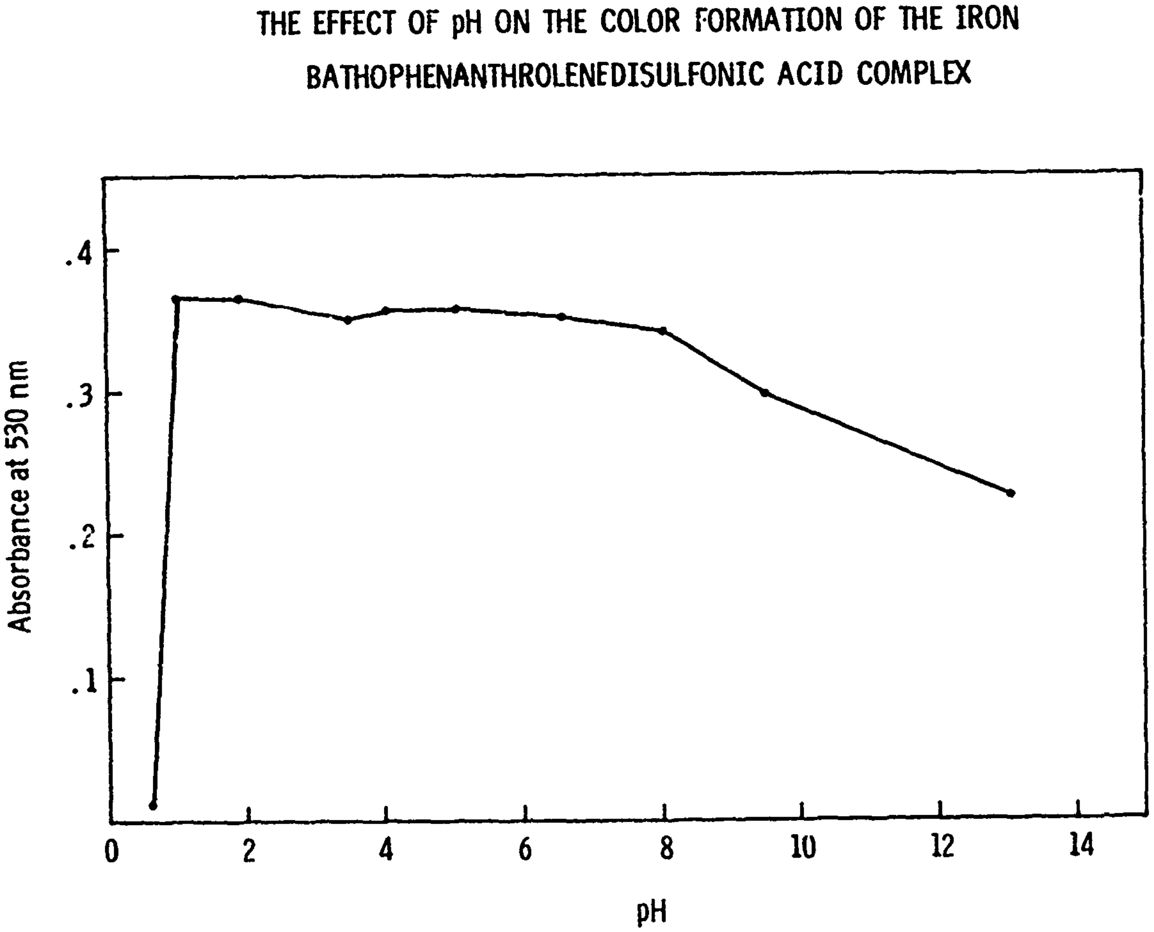


Figure 53. The effect of pH on the color formation of the iron bathophenanthrolinedisulfonic acid complex.

were designed to determine the upper detection limit under the following two conditions: (1) when iron only was present in the oil, and (2) when iron and 11 other metals were present at equal concentration levels in the oil. The calibration curve presented in Figure 54 is for condition 1. The straight line calibration curve shown represents the best straight line fit of the 0- to 120-ppm data. The correlation coefficient (r) for the 0- to 120-ppm data is 0.9997, while that for the 0- to 110-ppm data is 0.9998, indicating that the 0- to 120-ppm line could be used with confidence. The 140-ppm data point shows a significant deviation from linearity, and the resulting lower correlation coefficient (0.9975) reinforces this observation.

The calibration curve shown in Figure 55 is for condition 2. (The 11 other metals are aluminum, chromium, copper, lead, magnesium, nickel, silicon, silver, molybdenum, tin, and titanium.) It was expected that this curve would deviate from linearity at a lower ppm level than the curve for condition 1 because copper and magnesium form colorless complexes with the indicator. The straight line calibration curve shown in Figure 55 represents the best straight line fit of the 0- to 85-ppm data and shows that the data start to deviate from linearity in the 85- to 90-ppm region. The correlation coefficients for the 0- to 85-ppm and 0-to 90-ppm data are 0.9996 and 0.9995, respectively, while the correlation coefficient for the 0- to 100-ppm data is 0.9990. Even though the data start to deviate from linearity in the 85-to 90-ppm region, the calibration curve could be used from 0-to 90 ppm.

Figure 56 shows a calibration curve for 0 to 500 ppm iron in oil when using the five-step method. The only changes from the five-step method outlined earlier were that the strength of the indicator solution was increased and the aqueous phase (step 5) was further diluted so that the absorbance could be measured on the Chemtrix 20. The correlation coefficient for these data is 0.9994. This was done to demonstrate the feasibility of analyzing oils with very high iron content.

4.3.2.4 Precision of the Colorimetric Method

The precision of the colorimetric method was tested by performing repetitive analysis of oil samples containing various amounts of iron. The colorimetric results presented in Table 36 were obtained by analyzing six oil samples by the five-step method. Tests 1 and 2 were done 10 days apart, and ten determinations were made on each sample for each test. The data for samples 107, P-17, P-10, and D12-30 were generated using 1N H_2SO_4. Samples 107, P-17, and P-10 were used MIL-L-7808 oils that were available in sufficient quantity for the test. Sample 107 was one of the used oil samples from the SOAP lab round-robin testing. The D12-30 sample was from the old batch of spectrometric oil calibration standards which had traditionally yielded low

COLORIMETRIC DATA FOR SYNTHETIC OILS CONTAINING IRON ONLY

USING 0.019M INDICATOR SOLUTION

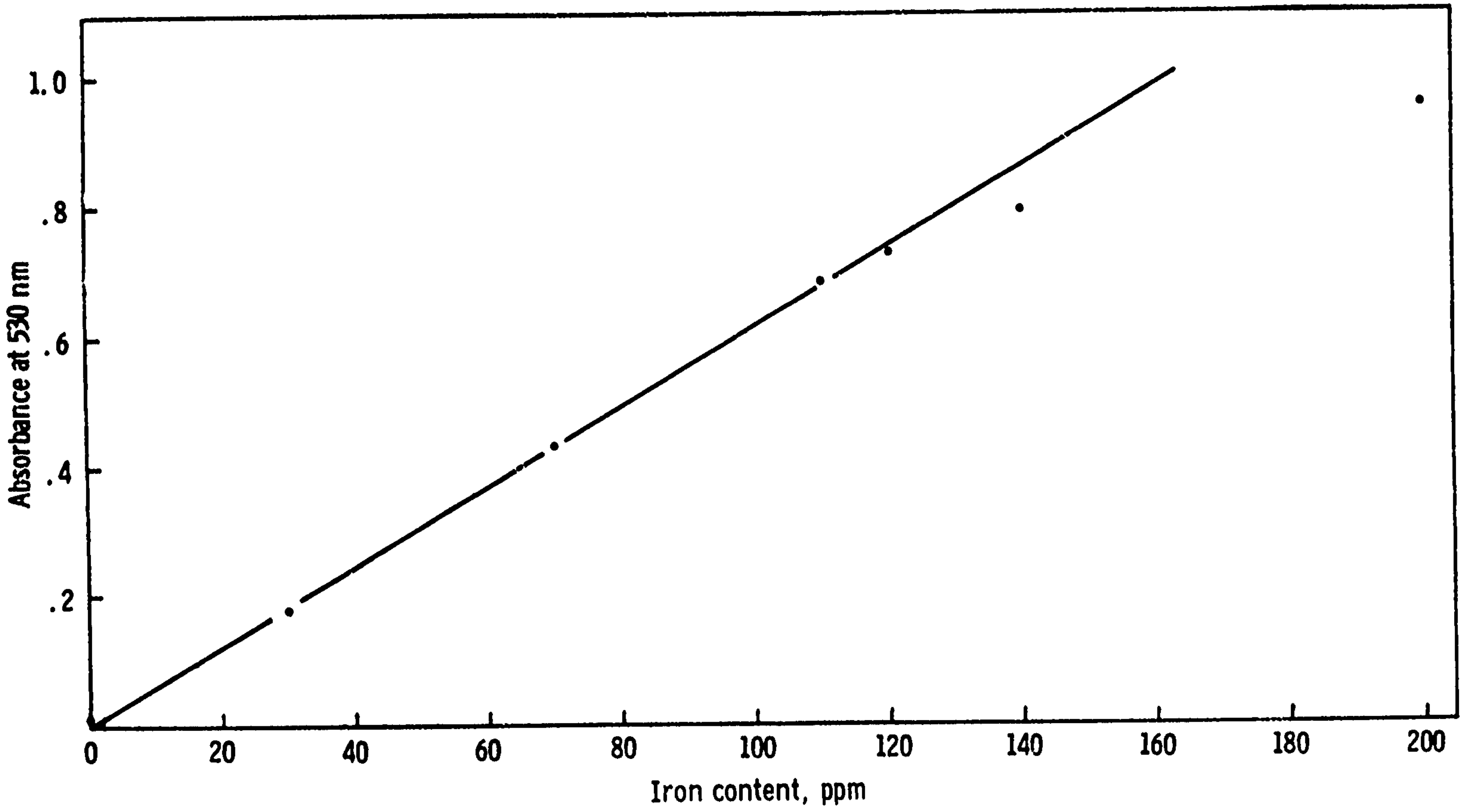


Figure 54. Calibration curve using 0.019M indicator solution for the analysis of oil containing iron only.

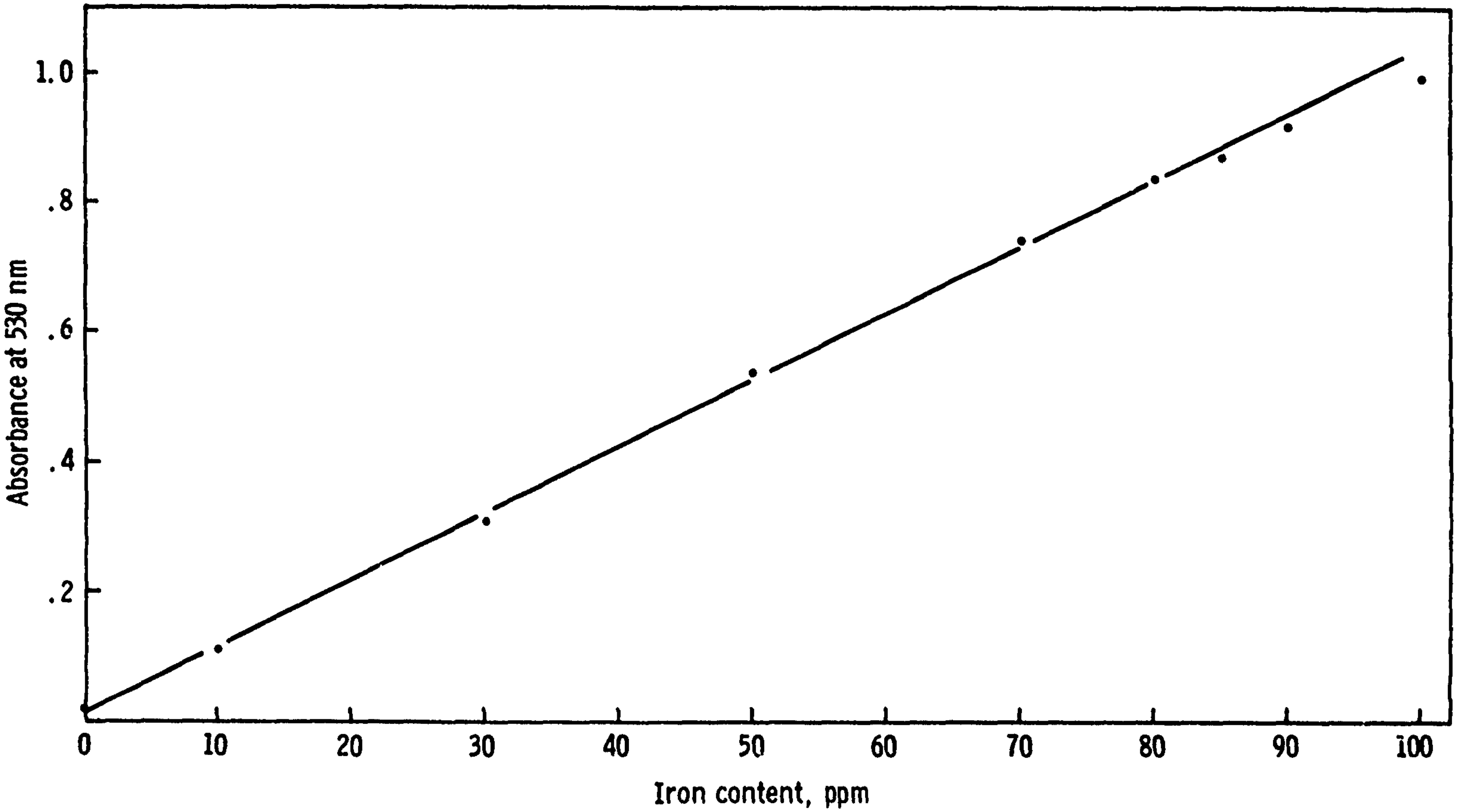


Figure 55. Calibration curve using 0.019M indicator solution for the analysis of oil containing iron plus 11 other elements.

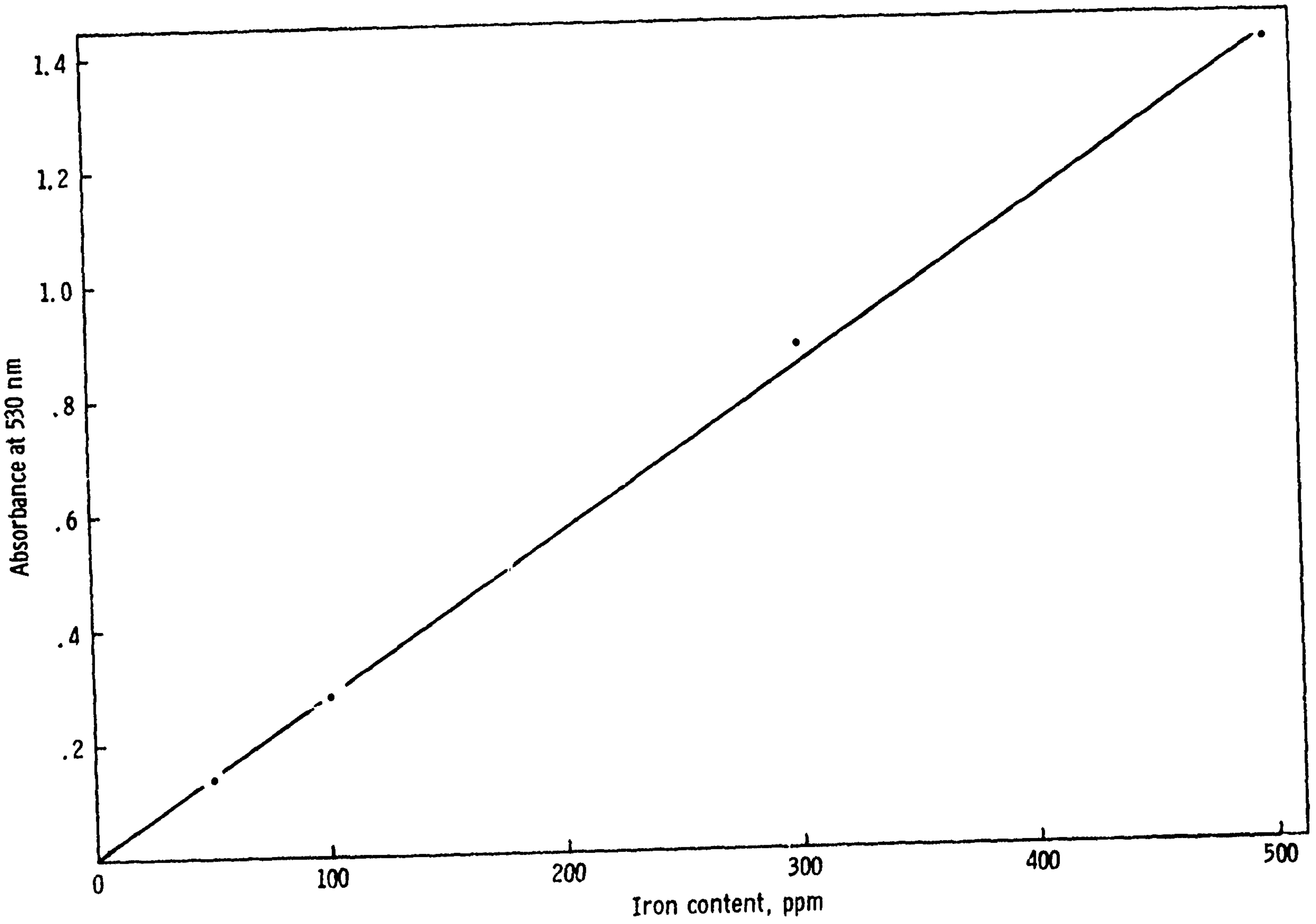


Figure 56. Calibration curve for synthetic luricants containing up to 500 ppm iron.

TABLE 36. REPETITIVE ANALYSIS RESULTS FOR SIX OIL SAMPLES BY THE FIVE-STEP COLORIMETRIC METHOD

Sample number	Mean iron content, ppm		Standard deviation, ppm		Range[a], ppm	
	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
P-81	3.7	-	0.18	-	0.5	-
107	10.5	10.4	0.25	0.37	0.8	1.3
P-17	10.8	11.0	0.33	0.45	0.8	1.2
H-51	18.7	-	0.57	-	1.2	-
D12-30	24.0	23.0	0.54	0.34	1.8	1.1
P-10	45.4	49.7	2.44	0.97	6.8	2.6

[a] Difference between the high and low values.

readings with the colorimetric test. A calibration curve from 0 to 50 ppm iron using the D12 spectrometric oil calibration standards was generated for each test. Samples P-81 and H-51 were analyzed using 3N instead of 1N H_2SO_4, and a 3N H_2SO_4 calibration curve was used to convert absorbance values to parts per million. Samples P-81 and H-51 were analyzed in 1-oz French square bottles and tested on the Hach DR/2 spectrophotometer, both of which are being used in the flight-line kit developed for the Air Force field test program. Samples P-81 and H-51 were analyzed approximately 4 months after the other four samples.

Table 36 displays the data from the repetitive analysis of the sox samples described above. The data for samples 107, P-17, D12-30, and P-10 show very good agreement between the test 1 and test 2 mean iron content values. Also, the standard deviation and range values agree very well for all samples except P-10. Standard deviation and range values for sample P-10 are very good for test 2, but the standard deviation is much higher (2.44 vs. 0.97) and the difference between the high and low values (range) is much broader (6.8 vs. 2.6) in test 1. The test 2 results for P-10 are what one would expect based on the results from the other three samples. None of the data points for P-10 test 1 could be statistically eliminated, but there was a decreasing trend from the 1st to the 10th replicate. This might have been caused by a problem in pipetting the oil or a settling of metal particles in the oil due to inadequate mixing of the sample.

Table 37 shows the mean iron content, standard deviation, and range values for the 20 determinations made on each sample in tests 1 and 2. The standard deviation and range (2.8 and 8.5, respectively) for P-10 are greatly affected by the test 1 results.

Analysis of the data for samples P-81 and H-51 (Table 36) shows that the standard deviations and the ranges are what would be predicted from the four samples previously analyzed. This indicated that both the square bottles and the Hach DR/2

TABLE 37. COMPOSITE RESULTS FOR TESTS 1 AND 2 OF THE REPETITIVE ANALYSIS STUDY OF FOUR OIL SAMPLES

Sample number	Mean iron content, ppm	Standard deviation, ppm	Range[a], ppm
107	10.4	0.31	1.3
P-17	10.9	0.39	1.5
D12-30	23.6	0.74	2.3
P-10	47.6	2.8	8.5

[a] Difference between the high and low values.

spectrophotometer would work well with our procedure. These results also increased our confidence in the ability of the method to reproducibly analyze used oils containing small amounts of iron (<10 ppm) and in the effectiveness of the 3N H_2SO_4.

Table 38 compares the standard deviations obtained for six samples by the five-step method with those obtained by George [24] with his method. The data indicate that our precision is at least as good as his. This means that our procedure, even though it is easier and faster than the George procedure, still gives precise results.

TABLE 38. COMPARISON OF STANDARD DEVIATIONS FROM THE ANALYSIS OF LUBRICANTS BY THE FIVE-STEP AND GEORGE [24] METHODS

Sample number	Iron content, ppm, by the five-step method		Sample number	Iron content, ppm, by the George method	
	Mean	Standard deviation		Mean	Standard deviation
P-81	3.7	0.18	1	4.8	0.35
107	10.4	0.31	2	6.3	0.36
P-17	10.9	0.39	3	11.3	0.53
H-51	18.7	0.57	4	17.8	0.34
D12-30	23.6	0.74	5	20.3	0.61
P-10	47.6	2.8	6	30.4	1.3

4.3.2.5 Reagent Shelf-Life Studies

Shelf-life studies were conducted between 23 May and 26 September 1978 to determine the effective life of the reagents. The 1N sulfuric acid, buffer/reducer, and indicator solutions were prepared on 23 May and stored along with the isoamyl alcohol in aliquots in plastic syringes at room temperature. A D-12 spectrometric oil calibration standard was analyzed in triplicate using both fresh and stored reagents according to the schedule shown in Table 39. Fresh reagents were prepared on each test date. This was done to insure that any scatter in the data would not be erroneously attributed to degradation of the stored reagents.

TABLE 39. SCHEDULED DATES FOR SHELF-LIFE STUDY TESTS

Elapsed time, wk	Date (1978)	Elapsed time, wk	Date (1978)
1	31 May	10	1 August
2	6 June	13	23 August
4	20 June	15	5 September
6	5 July	18	26 September
8	18 July		

Figure 57 displays the study results. The stored reagents consistently gave higher absorbance values than did the fresh reagents. This was probably due to the difference in the delivery of the reagents; that is, the stored reagents were pipetted into the syringes and delivered from the syringes, but the fresh reagents were delivered from a Centaur pipette. If the stored reagents were degrading, one would expect that the absorbance values would begin to decrease for the stored reagents while the absorbance values for the fresh reagents would remain constant. However, both the fresh and stored reagent data points generally followed the same pattern, and it can be said that the stored reagents did not degrade after 18 weeks of storage at room temperature.

The shelf-life study described above was initiated approximately 3 months before the decision was made to replace the 1N sulfuric acid solution with the 3N solution. This change also required an increase in the concentration of buffer in the buffer/reducer solution to adjust the pH of the aqueous phase to ∿4. No problems were encountered until the reagents had been stored for approximately 13 weeks.

While setting up a long-term shelf-life study on the reagents packaged for the field test kits, it was found that the colorimetric procedure was not working. This led to the discovery of the degradation of the buffer/reducer solution (discussed in section 4.3.1.5). Once this problem was corrected (by separating the buffer/reducer solution into two solutions), a shelf-life study using the 3N H_2SO_4 solution system and the four-step colorimetric method (used in the field test kits) was started.

One hundred analysis packets prepared for the Air Force field test were returned to us for use in a shelf-life study. This study tested the packaging components and the reagents used in the colorimetric iron kit. Table 40 shows the dates each reagent was prepared and packaged.

An oil standard containing 9.8 ppm iron in MIL-L-7808 oil was prepared fresh on each test date. The oil standard was analyzed in triplicate using both the stored reagents and fresh reagents prepared at the time of test. The colorimetric procedure used was the four-step method used in the colorimetric iron kit and

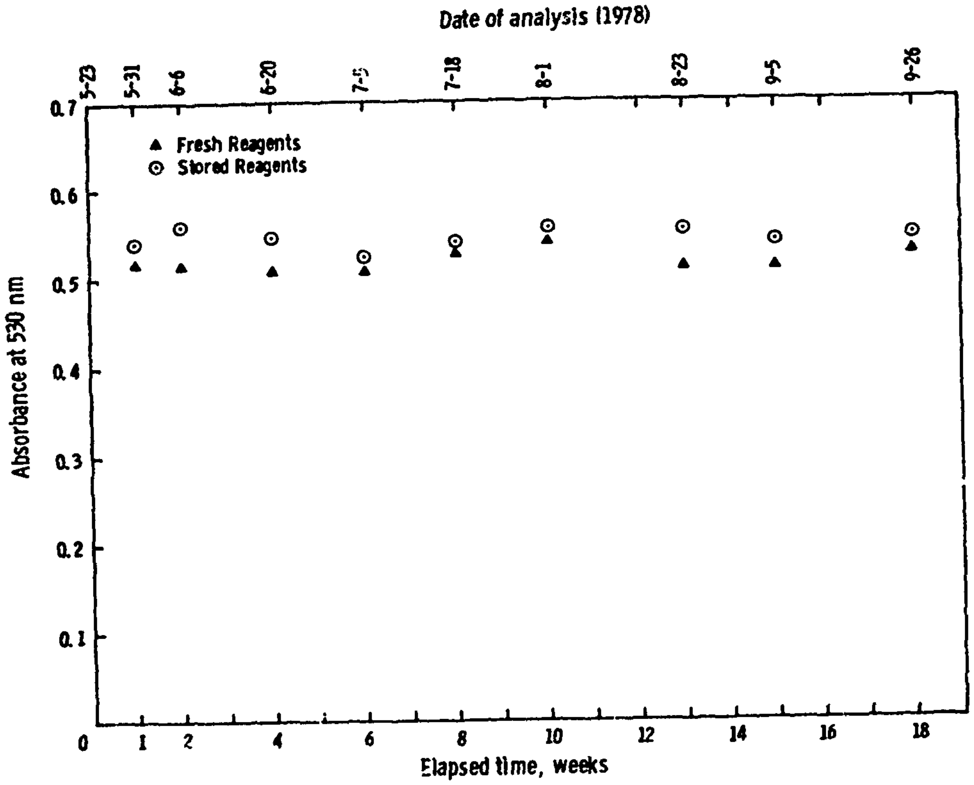


Figure 57. Effect of room temperature storage on the colorimetric reagents.

TABLE 40. PREPARATION AND PACKAGING DATES FOR REAGENTS USED IN THE SHELF-LIFE STUDY

Reagent	Date prepared	Date packaged
H_2SO_4 soln	27 Oct 78	28 & 30 Oct 78
Buffer soln	13 Feb 79	15 Feb 79
Reducer soln	13 Feb 79	15 Feb 79
Indicator soln	13 & 21 Sep 79	4 Oct 78
Water	-	3 Oct 78

described in section 4.3.1.5 of this report. Table 41 presents the scheduled dates for the shelf-life study.

TABLE 41. SCHEDULE OF 1979 TEST DATES FOR THE SHELF-LIFE STUDY

Date
13 April
14 May
13 June
13 July
13 August
13 September
12 October
13 November
13 December

Figure 58 displays the results of the shelf-life tests. There is no data point for the stored reagents in the May test because the reagents were contaminated during testing, resulting in unreliable data. No degradation of the reagents or packaging components was found through nine shelf-life tests. Figure 58 also displays the age of each reagent (in weeks) across the top of the figure. The indicator solution was stable after 65 weeks, the buffer solution and reducer solution were stable after 43 weeks, and the 3N H_2SO_4 solution was stable after 59 weeks of storage at room temperature.

4.3.2.6 Colorimetric Analysis of Particulate Iron in Oil

Work was begun during the late stages of the research period to determine the ability of the colorimetric method to analyze particulate iron in synthetic jet engine oil. The initial work was done using iron powder suspended in MIL-L-7808 oil. Ten-ppm iron samples containing iron particles of <1-μm, 1- to 3-μm, and 10- to 12-μm sizes were analyzed by the particle size independent method and in triplicate by the colorimetric method. Table 42 shows that the colorimetric method gave slightly higher results for the <1-μm sample than did the particle size independent method. However, the colorimetric method gave decidedly lower results (1.9 and 1.7) for the 1- to 3-μm and 10- to 12-μm samples than did the particle size independent method (10.3 and 10.7). The

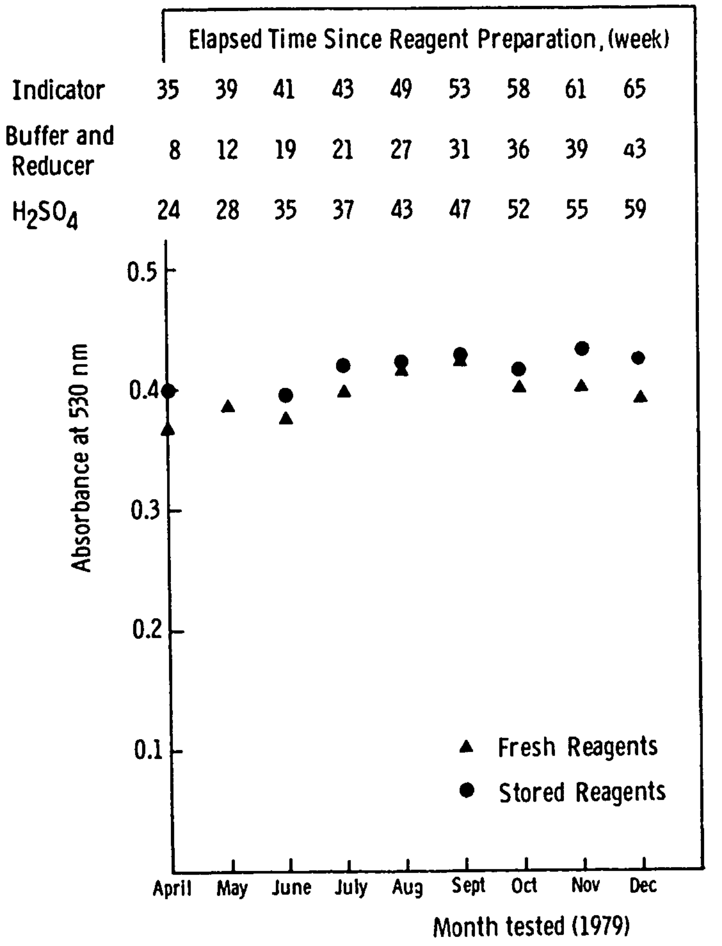


Figure 58. Long-term shelf-life compatibility study of the colorimetric reagents stored at room temperature.

TABLE 42. COMPARISON OF COLORIMETRIC AND PARTICLE SIZE INDEPENDENT ANALYSIS OF MIL-L-7808 OIL CONTAINING PARTICULATE IRON

Particle size, µm	Iron content, ppm	
	Colorimetric	Particle size independent
<1	6.5	5.3
1-3	1.9	10.3
10-12	1.7	10.7

The particle size independent result indicates that the <1-µm sample may not have contained 10 ppm iron.

A well characterized oil sample containing iron particles (Atlantic Equipment Engineers) in MIL-L-7808 oil was obtained from Dr. W. Rhine of the University of Dayton Research Institute (UDRI). The concentration of this sample (hereafter called UDRI-1) was 100 ppm iron and all the powder used had passed through a 20-µm filter. Aliquots of the sample were filtered through 12-, 10-, 8-, 5-, 3-, and 1-µm filters and then analyzed by the particle size independent method. Table 43 shows the results obtained by UDRI using this procedure.

TABLE 43. RESULTS FOR THE PARTICLE SIZE INDEPENDENT ANALYSIS OF SAMPLE UDRI-1 AND ITS FRACTIONS

Filter size, µm	Iron content, ppm
20	100 ± 1
12	79 ± 3
10	71 ± 3
8	63 ± 3
5	42 ± 3
3	25 ± 1
1	3 ± 1

A portion of sample UDRI-1 was diluted with MIL-L-7808 oil to contain 10 ppm iron. The average of 10 replicate analyses of this sample by the colorimetric method was 0.58 ppm. This sample was then analyzed by modifying the first step of the four-step colorimetric procedure as follows:

Step 1. To 1 mL H_2SO_4 solution and 2 mL isoamyl alcohol add 1 mL oil; mix on vortex mixer for ~15 s; place in 70°C water bath for 1 min; remove and vortex for 2 min.

This modified four-step method gave results of 5.9 and 6.1 ppm for duplicate analysis. The same sample was analyzed in triplicate 1 day later and gave results of 8.5, 8.5, and 8.2 ppm. A 10-ppm iron standard (containing only dissolved iron) was analyzed in triplicate by the four-step and the modified four-step methods and gave 9.7 and 9.9 ppm iron, respectively. Table 44 shows the results of the analysis of three used oil samples by the four-step and modified four-step methods. All three samples gave higher results with the modified method.

This modified four-step method appears to be a promising alternative when the analysis of particulate iron is a consideration.

TABLE 44. COMPARATIVE RESULTS FOR IRON ANALYSIS OF USED OILS BY THE FOUR-STEP AND MODIFIED FOUR-STEP COLORIMETRIC METHODS

Sample number	Iron content, ppm	
	Four-step	Modified four-step
P-78	8.0	11.2
P-90	10.2	14.0
F-18	45	50

4.3.3 Development of a Flight-Line Kit

When the Air Force decided to conduct a field test on the colorimetric method it became imperative to develop an easy-to-use, portable, safe kit for the method. The first prototype kit described below had already been built and served as a starting point for the design of the second-generation kits. MRC was required to design and build six flight-line kits capable of performing a total of 1500 analyses.

4.3.3.1 First Prototype Kit

The first prototype kit for the determination of iron in lubricating oils is shown assembled in its carrying case in Figure 59. The kit, designed for carrying out the 5-step method, contains enough of the expendable items to analyze 10 samples. The contents of the kit are as follows:

Chemtrix 20 colorimeter
colorimeter test cells (4)
3-dram vials with caps (10)
1-mL aliquots H_2SO_4 solution (10)
2-mL aliquots isoamyl alcohol (10)
1-mL aliquots buffer/reducing solution (10)
0.5-mL aliquots indicator solution (10)
5-mL aliquots distilled H_2O (10)
1-mL Centaur pipette
pipette tips (30)
0-, 10-, 30- and 50-ppm Fe aqueous phase standards
0-, 3-, 10-, 30- and 50-ppm Fe D12 spectrometric oil calibration standards

The reagents are sealed in prescored glass breaktop ampules. The Styrofoam® holder has been raised in Figure 60 to show that the ampules are numbered and arranged in order of addition as described by the simplified instructions on the lid of the carrying case. Figure 60 also gives a good view of the Chemtrix 20 colorimeter. Shown in Figure 61 are the reagents and equipment required to analyze one oil sample. The reaction is carried out in the 3-dram vial shown at the left of the reagents in Figure 61. The resulting red-colored aqueous phase can then be tested in the

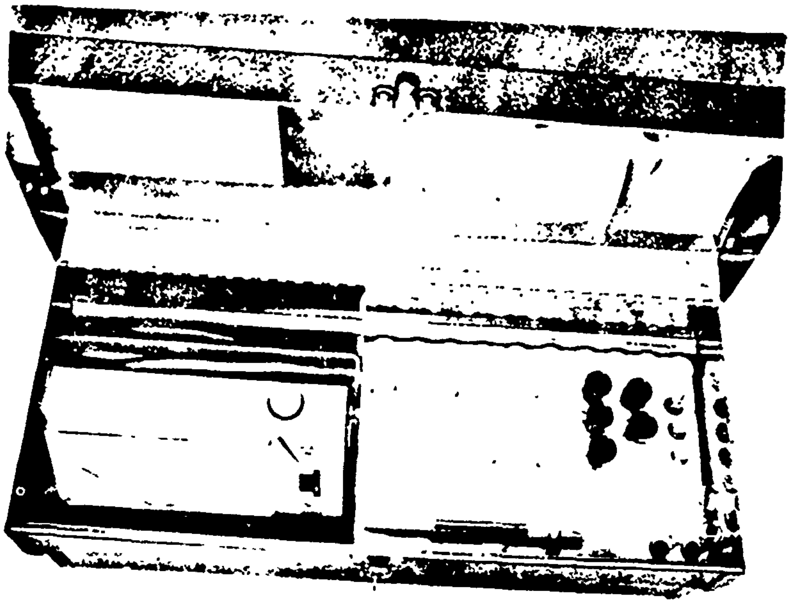


Figure 59. Assembled kit for the determination of iron content in synthetic lubricating oils.

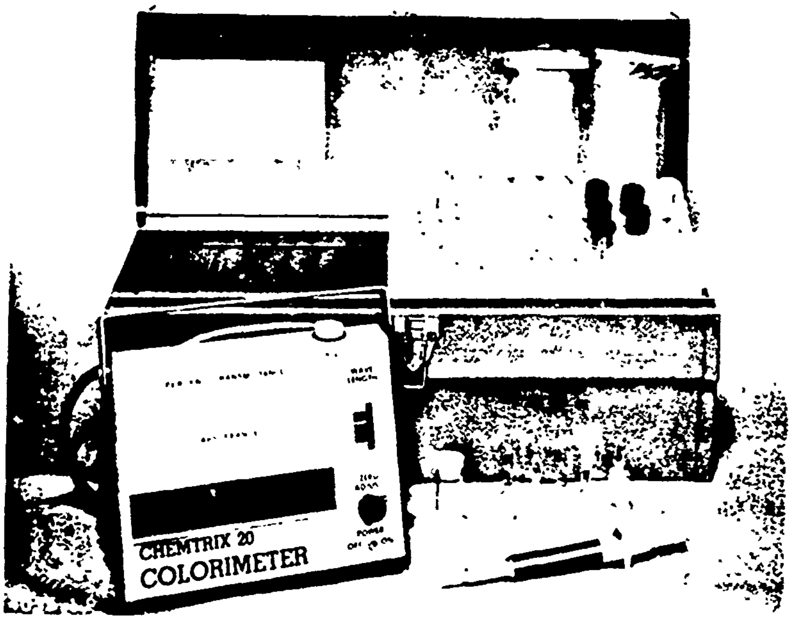


Figure 60. Iron determination kit with Chemtrix 20 colorimeter displayed.

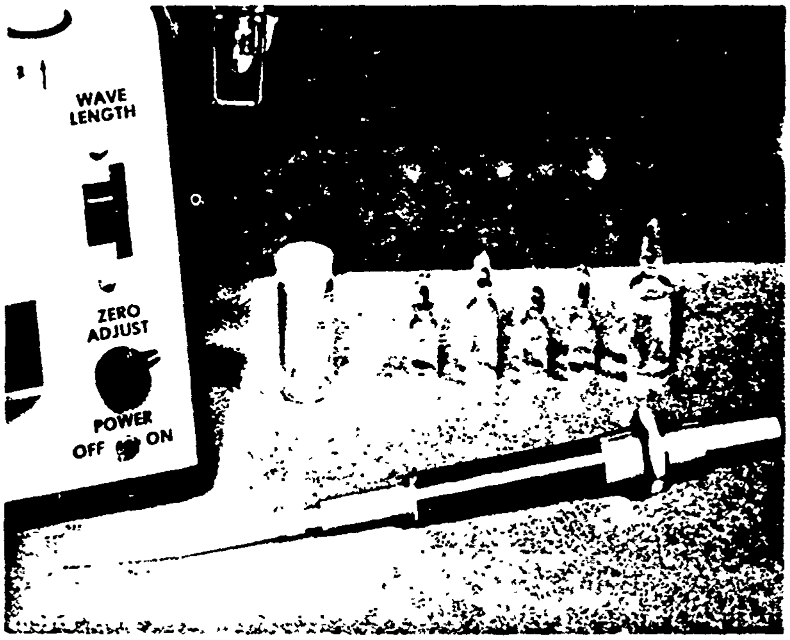


Figure 61. Reagents and equipment required for the iron determination of one oil sample.

Chemtrix 20 using the test cells shown in the lower right corner of the Styrofoam block in Figures 59 and 60. This Chemtrix 20 was used for much of the development on this task and functioned very well.

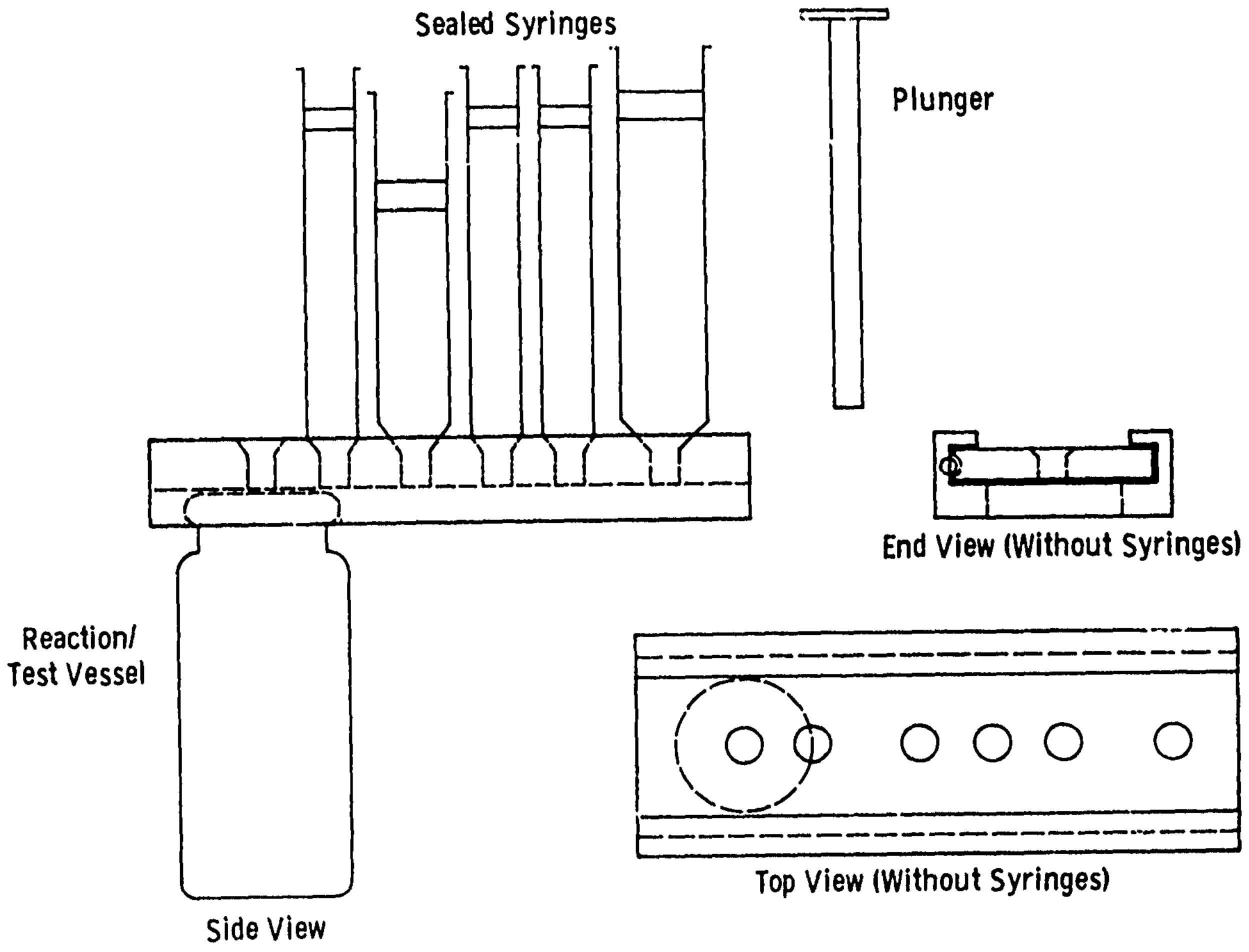
The inexpensive Chemtrix 20 colorimeter ($139) included in the prototype kit requires a 110-volt power supply. After the kit was assembled, a relatively low-cost ($185) battery-powered colorimeter was specially designed and manufactured for this project by Chemtrix, Inc. The instrument, designated Chemtrix 22, can be fitted into the Chemtrix 20 instrument case shown in Figure 60. Battery power makes the instrument highly portable, and the batteries can be recharged by a calculator type charger. The Chemtrix 22 may be operated using the batteries only or with the charger plugged into an a.c. outlet. The Chemtrix 22 differs from the Chemtrix 20 in that it is a single-wavelength (530 nm) instrument and has a push button instead of a toggle switch to actuate the light source. The latter feature was included to prevent rapid draining of the batteries, because the battery charge with continuous operation is approximately 2 hours. However, the Chemtrix 22 was found to be unstable and was never put into routine use.

The reagent packaging system employed in the first flight-line kit was quickly found to be cumbersome and unacceptable. However, this prototype demonstrated the basic simiplicity that was the goal of this task.

4.3.3.2 Packaging of the Reagents

Several methods of packaging the reagents for the field test kit were considered, and two systems were chosen for further development. The first was designated as the linear advance reagent storage (LARS) system.

As shown in Figure 62, the LARS system consists of a square glass or plastic vial, a two-piece plastic (e.g., Teflon®) bar, and five disposable syringes. The vial serves as the reaction vessel and test cell. The lower section of the plastic bar snaps onto the square vial, and the upper section, which holds the syringes, slides into the lower section. The lower section has one port located over the mouth of the vial, and the upper section has six ports which are brought into position above the single port of the lower section in sequence. The first port of the upper section is used to introduce the oil sample into the vial, and ports two through six hold the syringes. The syringes contain the required amount of each reagent and are loaded into the sliding block in the proper order to carry out the five-step procedure. A positive stop is incorporated so each port easily lines up directly over the vial. The syringes are sealed with a silicone sealant that is pushed out by the syringe plunger. The syringes are locked firmly into the sliding bar with Luer-Lok® fittings.



DESIGN CONCEPT OF LINEAR ADVANCE REAGENT STORAGE SYSTEM

Figure 62. Design concept of the linear advance reagent storage (LARS) system.

A prototype of this design was built and tested. The basic concept of the design worked well, but the following problems were encountered during testing:

(1) The material used to plug the tubes was difficult to lossen and caused the reagents to spray about when being dispensed.

(2) The linear advance system caused the vortex mixer to "walk" during agitation.

(3) The reagent/oil solution splashed up on the LARS during agitation, causing some of the aqueous phase to be lost.

A second prototype of the LARS system, shown in Figure 63, was built in an attempt to correct the above problems. To solve problem 1, ployethylene tubes were substituted for the syringes, and a knife edge was incorporated in the crossmember just below the sliding bar and ahead of the reaction test vessel. The knife edge sliced the tips off of the polyethylene tubes. However, when the polyethylene tubes were dragged across the knife edge during the cutting operation, reagents were deposited on it. The knife edge used in the prototype was not stainless steel and the indicator deposited on it turned brilliant red. This contaminated the test solution, causing poor results.

Problem 2 was corrected by mounting the whole LARS system, including the vortex mixer, on a base. The vortex mixer was isolated from the base by rubber mountings and from the crossmember by a flexible tube fitted to the cap of the reaction/test vessel. The flexible tube also prevented the reagent/oil solution from splashing up on the LARS, solving problem 3.

The LARS system offers the potential for performing multiple analyses simultaneously. But due to the problems encountered and the time frame within which a working system had to be developed, further development of the LARS was abandoned.

Figure 64 is a drawing of the second packaging system developed, the one selected for use in the colorimetric kit. Called the manual system, it was chosen for the following reasons:

(1) The components were inexpensive.
(2) The components were readily available.
(3) The system can be used by inexperienced personnel.
(4) The system is safe.
(5) The colorimetric method works when packaged in this system.

Figure 63. Second prototype of the linear advance reagent storage (LARS) system.

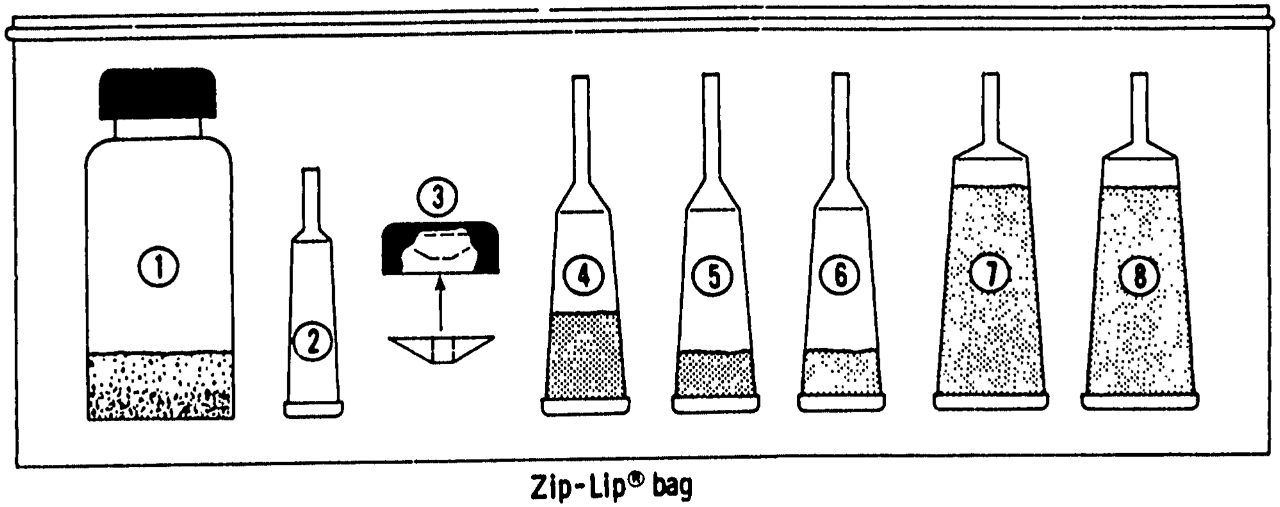


Figure 64. Reagent packaging system for the four-step colorimetric method.

All of the other systems investigated did not meet one or more of the above criteria. The system shown in Figure 64 is packaged in a 5-in. by 5-in. Zip-Lip® polyethylene bag. All one-time-use items are contained in this bag and can be returned to the bag after use for disposal. The reagents are sealed . polyethylene tubes. These tubes were purchased from and filled by Paket Corporation of Chicago. The bag contains the following items, numbered to correspond to the numbers in Figure 64:

(1) One 1-oz French square bottle containing 1 mL H_2SO_4 solution and 2 mL isoamyl alcohol.

(2) Pipette tip for the oil pipette.

(3) Plastic cap (with hole in top) and cap liner (with hole to fit reagent tubes).

(4) Tube containing 1 mL of buffer solution.

(5) Tube containing 0.5 mL of reducer solution.

(6) Tube containing 0.5 mL of indicator solution.

(7) and (8) Two tubes, each containing 10.5 mL of deionized water.

The 1-oz French square bottle was chosen to serve as both the reaction vessel and test cell because it was inexpensive, and it fit the specimen chamber of the Hach DR/2 spectrophotometer used for the field test kits. These bottles were tested to determine their performance as the reaction/test vessel.

Table 45 gives the absorbance values obtained on 12 different 1-oz French square bottles chosen at random. Two stock aqueous solutions were used and six bottles were tested with each solution. These results indicate that these inexpensive ($0.12 ea., including cap) bottles would be adequate replacements for the expensive ($7.75 ea.) cells provided with the instrument. These bottles are thick walled, making them very difficult to break, and they were readily available.

TABLE 45. ABSORBANCE VALUES FOR TWELVE 1-OUNCE FRENCH SQUARE BOTTLES

Stock solution #1		Stock solution #2	
Bottle No.	Absorbance	Bottle No.	Absorbance
1	0.550	7	0.164
2	0.545	8	0.156
3	0.555	9	0.150
4	0.555	10	0.156
5	0.525	11	0.156
6	0.535	12	0.152

The D-12 spectrometric oil calibration standards form droplets on the walls of the bottles which cause interferences in the light path of the spectrophotometer. However, the MIL-L-7808 oils do not adhere to the walls of the bottles and therefore do not interfere with use of a bottle as the test cell. Many used oils analyzed by the colorimetric method were reacted and tested in these square bottles. Figure 47 (section 4.3.1.4) shows two calibration curves obtained by analyzing MIL-L-7808 oil standards by the four- and five-step methods using the 1-oz French square bottles. The correlation coefficients for the four- and five-step data are 0.9995 and 0.9984, and the slopes are 0.0395 and 0.0399, respectively.

4.3.3.3 Modification of the DR/2 Spectrophotometer and Its Carrying Case

The instrument used in the kit is a Hach DR/2 spectrophotometer. This instrument was chosen because it fit our needs better than other commercially available instruments. That is, it was relatively low in cost ($525), and it has its own large carrying case and can operate on either 115-V alternating current or on battery power (self-contained). The square specimen chamber that allowed us to use the 1-oz French square bottles is also an important feature.

The following modifications were made to all six of the instruments provided for the field test:

(1) The variable wavelength disc was fixed at 530 nm.

(2) The zero adjust and light adjust knobs were replaced by locking screwdriver adjust knobs (see Figure 65).

(3) The removable scale card was replaced by a permanent card that reads directly in parts per million (ppm) iron (see Figure 65).

(4) A plastic cover was placed over the wavelength thumbwheel to protect the interference filter from spills.

In addition, a timer which controls the vortex mixer was hard wired into the spectrophotometer, and the vortex mixer was pluged into the timer. Therefore, only one power supply cord is required to operate the spectrophotomer, timer, and mixer. A holder for the screwdriver and stainless steel scissors was fitted into the large compartment on the spectrophotomer face. The screwdriver is used to adjust the zero adjust and light adjust knobs, and the stainless steel scissors are used to cut the tips off of the reagent tubes.

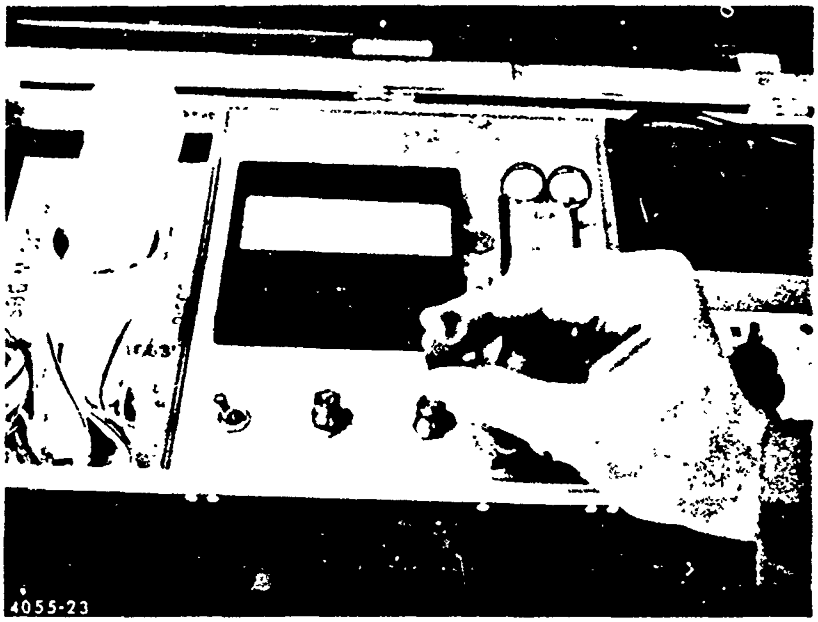


Figure 65. Modified DR/2 spectrophotometer face.

Several modifications and additions were made to the spectrophotometer carrying case. Figure 66 shows the kit with all modifications and additions. The timer is fastened to the right-hand compartment of the carrying case, and the vortex mixer, power supply cord, and safety goggles are stored there also. The left-hand compartment is reserved for the 12 analysis packets and microwipe tissues supplied with the kit. The lid was modified to accommodate the laminated step-by-step instruction sheet (see Figure 67) in the left-hand side. Also included in the lid are the oil pipette and the color comparison chart. The color comparison chart is intended for emergency use only (that is, in the event the spectrophotometer becomes inoperable).

A detailed operating manual was prepared and a copy was included with each kit. The pages of the manuals were laminated for protection from spills and other possible flight-line hazards. Appendix F is a copy of this manual.

4.3.4 Air Force Field Test Program

Six colorimetric kits and 1491 analysis packets were delivered to the Air Force for use in field tests designed and administered by the Materials Laboratory. The tests were successfully performed at Myrtle Beach and Luke Air Force Bases on A-10 and F-15 aircraft. Detailed results are presented in a technical report (AFWAL-TR-80-4022) prepared by the Materials Laboratory.

4.4 CONCLUSIONS

The solvent extraction-chelation method developed in this program is a simple, on-the-spot test for iron, a major wear metal in jet engine lubricating oil. The four-step method has been packaged into a portable, safe, and easy-to-use kit which can be used by nontechnical personnel. Some of the major characteristics of the portable kit are:

1. Rapid - single analyses requires $\sim$8 minutes; two analyses require $\sim$12 minutes.
2. Accurate - results comparable to atomic absorption data.
3. Precise - repetitive analysis of used oil showed good precision.
4. Portable - packaged in a 23.5- by 10- by 8.5 inch carrying case weighing 25 pounds.
5. Inexpensive - each kit would cost less than $1,000 when mass produced, and the cost of reagents and disposable items is approximately $1.50.

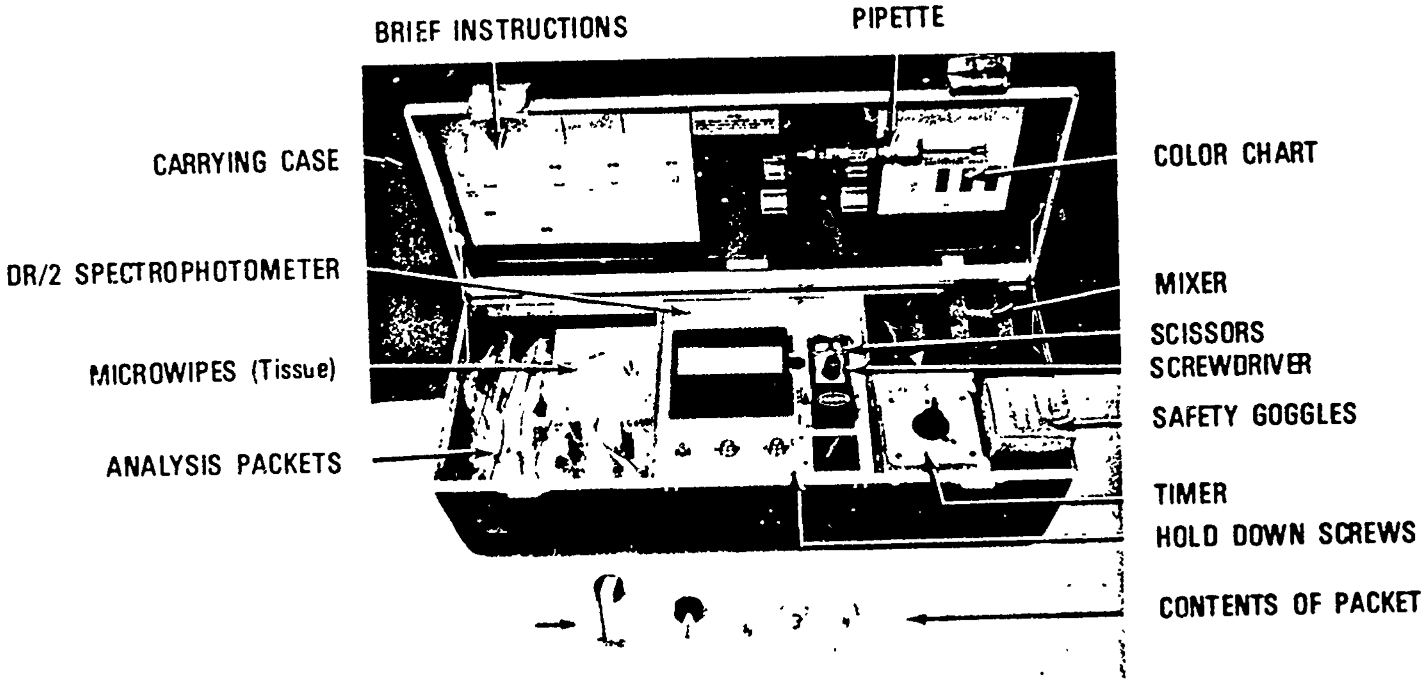
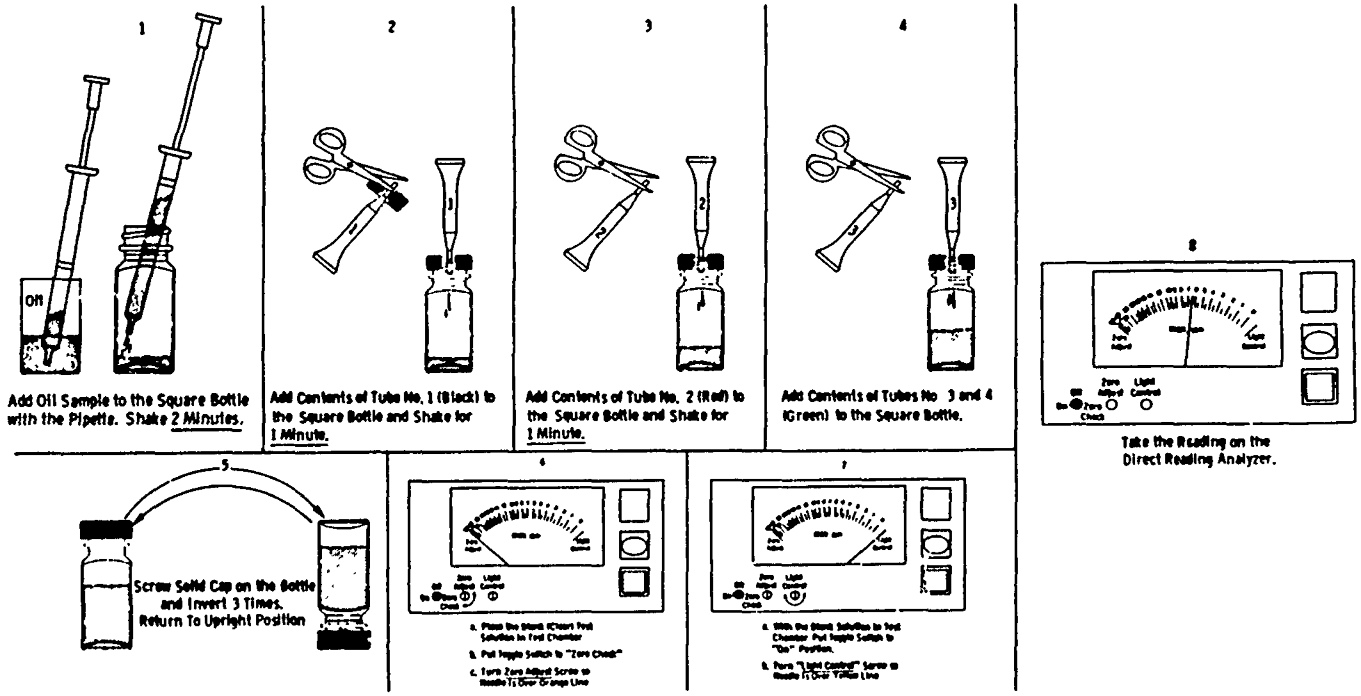


Figure 66. Colorimetric oil analysis field test kit.



Add Oil Sample to the Square Bottle with the Pipette. Shake 2 Minutes.

Add Contents of Tube No. 1 (Black) to the Square Bottle and Shake for 1 Minute.

Add Contents of Tube No. 2 (Red) to the Square Bottle and Shake for 1 Minute.

Add Contents of Tubes No. 3 and 4 (Green) to the Square Bottle.

Screw Solid Cap on the Bottle and Invert 3 Times. Return To Upright Position

a. Place the Blank (Clear) Test Solution in Test Chamber
b. Put Toggle Switch to "Zero Check"
c. Turn Zero Adjust Screw so Needle Is Over Orange Line

a. With the Blank Solution in Test Chamber Put Toggle Switch to "On" Position.
b. Turn "Light Control" Screw so Needle Is Over Yellow Line

Take the Reading on the Direct Reading Analyzer.

Figure 67. Pictorial step-by-step instruction sheet for the four-step colorimetric method.

The colorimetric iron kit provides a viable aid to the SOAP program. The kit is capable of providing rapid analyses in situations where sending a sample to a SOAP laboratory is impractical or would cause delays in aircraft mission performance.

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APPENDIX A

BIBLIOGRAPHY

The list that begins on the next page is a bibliography of SOAP related material collected during the course of our study. These publications are on file at the Air Force Materials Laboratory, Wright-Patterson Air Force Base. The file code designation (e.g., A.5.) is used to locate the article in the file. The abbreviations used in the bibliography are explained below.

ASLE - American Society of Lubricating Engineers.

AFAPL - Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

ASD - Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio 45433.

AFML - Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

ARL - Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio. This organization was abolished on 1 July 1975.

ASTM - American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

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APPENDIX B

SAMPLE HYDROCARBON DATA REDUCTION

To illustrate the manner in which concentration values are obtained from the raw data, the data reduction sequence is detailed for the chromatogram shown in Figure 14 (JP-4 at 15 psig).

The output from the Autolab System IV integrator is contained in Table B1.

First the area values are converted to a common attenuation ($10^3 \times 8$) which is the attenuation of the hexane calibration curve (Figure 15). Previous experience has shown that the attenuation correction is linear within the limits of injection precision for the H-P Model 5750B used in the analyses. Attenuation corrected data are listed in Table B2.

Next the area values are divided into two sets (indicated by the line in Table B2) corresponding to the two portions of the chromatogram on either side of the column switch. The FID designation in Table B2 indicates the flame ionization detector at which each peak is detected (see Figure 4). The total area in each of these sets is obtained by summing the individual peak areas. The values obtained are:

$$\sum \text{Area at FID A} = 24165 \text{ counts}$$

$$\sum \text{Area at FID B} = 52746 \text{ counts}$$

The area detected at FID B must be corrected for baseline rise and the impurity peak associated with the heating of the Chromosorb 105 column (see Figure 14). The excess area associated with this correction is measured by planimetry. The value obtained for the excess area associated with the baseline rise and the impurity peak in Figure 14 is 8.313 square inches (at 10 x 64 attenuation). Converting to $10^3 \times 8$ attenuation gives:

$$\text{Planimeter Attenuation Correction} = 8.313 \left(\frac{640}{8000}\right) = 0.665 \text{ sq in.}$$

This value must be converted to integrator counts. The empirically determined conversion factor is 21983 counts/sq. in. Therefore:

$$\text{Planimeter Correction} = (0.665 \text{ sq. in.})(21983 \text{ counts/sq. in.}) = 14619 \text{ counts}$$

This value is subtracted from the area detected at FID B to yield:

$$\text{Corrected} \sum \text{Area at FID B} = 52746 - 14619 = 38127 \text{ counts}$$

TABLE B1. RAW INTEGRATOR DATA

Sample 12 3-4-75

Time, sec.	Area, counts	Attenuation
29	20288	10^3 x 8
60	3204	"
71	673	"
419	936	10 x 64
832	11436	"
860	1073	"
928	25280	"
1012	21208	"
1104	32482	"
1208	47708	"
1372	115585	"
1528	118486	"
1748	277546	"
2132	7581	"

TABLE B2. INTEGRATOR DATA CORRECTED TO 10^3 x 8 ATTENUATION

Time, sec.	Area, counts	FID
29	20288	A
60	3204	A
71	673	A
419	75	B
832	915	B
860	86	B
928	2022	B
1012	1697	B
1104	2598	B
1208	3817	B
1372	9247	B
1528	9479	B
1748	22204	B
2132	606	B

Next the integrator area counts are related to an equivalent mass of hexane (in μg) by using the calibration curve (Figure 15). This yields:

Hexane Equivalent at FID A = 10.55 μg

Hexane Equivalent at FID B = 16.65 μg

The data must be corrected to account for differences in the responses of FID A and FID B. Since the calibration curve was obtained on FID A, the FID B data must be corrected by the conversion factor:

Response FID A = (1.38) Response FID B

Therefore:

Corrected Hexane Equivalent at FID B = (16.65 μg)(1.38) = 22.97 μg

These values are converted to concentrations in ppm (v/v) by applying the ideal gas law:

V_S = Total Volume Sampled = 0.150 ℓ
P = 1 atm
T = 298°K
R = 0.082 ℓ•atm/mole °K
V_H = volume hexane equivalent
$n = \dfrac{\text{g hexane equivalent}}{\text{mol weight hexane}}$

$$C_H = \text{Concentration (ppm as hexane)} = \frac{V_H}{V_S} \times 10^6$$

$$V_H = \frac{nRT}{P}$$

At FID A

$$V_H = \frac{[(10.55 \times 10^{-6}\text{g})/(86 \text{ g/mole})](0.082\ \ell\cdot\text{atm/mole °K})(298\text{°K})}{1 \text{ atm}}$$

$$= 3.0 \times 10^{-6}\ \ell$$

$$C_H = \frac{2.0 \times 10^{-6}\ \ell}{0.150\ \ell} \times 10^6 = 20.0 \text{ ppm} \quad \text{(paraffins)}$$

At FID B

$$V_H = \frac{[(22.97 \times 10^{-6} g)/86\ g/mole)](0.082\ \ell \cdot atm/mole\ ^\circ K)(298^\circ K)}{1\ atm}$$

$$= 6.53 \times 10^{-6}\ \ell$$

$$C_H = \frac{6.53 \times 10^{-6}\ \ell}{0.150\ \ell} \times 10^6 = 43.6 \text{ ppm (oxygenated + aromatics)}$$

When it is desirable to express these as ppm methane, the values are multiplied by 6, giving:

Paraffins (unreactive) = 120 ppm as C

Oxygenates + aromatics = 262 ppm as C

APPENDIX C

MULTINOMIAL DISTRIBUTION PROGRAM FOR STATISTICALLY PREDICTING THE ABUNDANCES OF BASE STOCK ESTERS IN MIL-L-23699 LUBRICANT

```
C
C         MULTINOMIAL PROBABILITY PROBLEM
C         PROGRAMMER              MS. KATHY FLAYLER
C         REQUESTOR               MR. JOE BROOKS
C         PROJECT NUMBER          200.3060
C         DATE                    FEB 76
C
C
      INTEGER A,B,C,D,E,F
      DIMENSION NA(100),NB(100),NC(100)
      CALL FREMAT
      LCR=1
      LPR=5
      SUM=0.
      K=1
      WRITE(LPR,510)
      DO 10 L=1,2
      J=1
C
C         READS % CONTRIBUTION,DEPENDENCE,NUMBER OF BONDS PER MOLECULE
C
    2 READ(LCR,500) N,PERCNT,NDEP
      NN=N+1
C
C         PICKS OUT ONLY UNIQUE OCCURRENCES
C
      DO 3 NB1=1,NN
      DO 1 NA1=1,NN
      NB(J)=NB1-1
      NA(J)=NA1-1
      NC(J)=N-(NA(J) + NB(J))
      IF (NC(J) .LT. 0) GO TO 1
      J=J+1
    1 CONTINUE
    3 CONTINUE
      NJ=J-1
      IF (NDEP .EQ. 1) GO TO 15
C
C         MULTINOMIAL PROBABILITY EQUATIONS
C
      DO 10 J=1,NJ
      VAL=(FLOAT(IPERM(N))/(FLOAT(IPERM(NA(J)))*
     1FLOAT(IPERM(NB(J)))*FLOAT(IPERM(NC(J)))))*
     2(.25**NA(J)*.5**NB(J)*.25**NC(J))
      VALP=VAL*PERCNT
      WRITE(LPR,520) K,NA(J),NB(J),NC(J),VAL,PERCNT,VALP
      K=K+1
      SUM=SUM+VALP
   10 CONTINUE
   15 NN=1
      DO 100 I=NN,NJ
      A=NA(I)
      B=NB(I)
      C=NC(I)
      DO 1000 II=NN,NJ
      D=NA(II)
      E=NB(II)
      F=NC(II)
      VALR=(FLOAT(IPERM(N))/(FLOAT(IPERM(A))*FLOAT(IPERM(B))*
     1FLOAT(IPERM(C))))*(.25**A*.5**B*.25**C)
```

```
      VALL=(FLOAT(IPERM(N))/(FLOAT(IPERM(D))*FLOAT(IPERM(E))*
     1FLOAT(IPERM(F))))*(.25**D*.5**E*.25**F)
      IF (A.EQ.D.AND.B.EQ.E.AND.C.EQ.F) VAL=VALL*VALR
C
C        MULTIPLIES BY 2 ONLY IF LEFT SIDE NOT = RIGHT SIDE BECAUSE OF THE
C        MIRROR IMAGE EFFECT
C
      IF (A.NE.D) VAL=VALL*VALR*2.
      VALP=VAL*PERCNT
      WRITE(LPR,530) K,A,B,C,D,E,F,VAL,PERCNT,VALP
      K=K+1
      SUM=SUM+VALP
 1000 CONTINUE
      NN=NN+1
  100 CONTINUE
      WRITE(LPR,500)  SUM
      STOP
  500 FORMAT(V)
  510 FORMAT('1','COMB',T10,'A',T15,'B',T20,'C',T40,'PROBABILITY',T55,
     1'%',T65,'% CONT'//)
  520 FORMAT(1X,I2,T10,I1,T15,I1,T20,I1,T40,F8.6,T55,F4.2,T65,
     1F8.6)
  530 FORMAT(1X,I2,T10,I1,T15,I1,T20,I1,T25,I1,T30,I1,T35,I1,T40,F8.6,
     1T55,F4.2,T65,F8.6)
      END
C
C        FACTORIAL COMPUTATION SUBROUTINE
C
      FUNCTION IPERM(N)
      IPERM=1
      DO 1 I=1,N
      IPERM=I*IPERM
    1 CONTINUE
      RETURN
      END
```

APPENDIX D

CIRCULAR PLOT PROGRAM FOR PATTERN RECOGNITION STUDIES

```
C
C         PROJECT NAME - PATTERN RECOGNITION
C         PROGRAMMER     MS. KATHY FLAYLER
C         REQUESTORS     MR. JOE BROOKS AND MR. BILL ROSS
C         PROJECT NO.    13-022-760,13-200,3060
C         DATE WRITTEN   MAY  1976
C
      INTEGER OIL(30),QUART1(3),QUART2,QUART3(2),QUART4(2)
      DIMENSION X(100),Y(100),X1(100),Y1(100),NOPT(100)
      DATA QUART1 /'0,','36','0 '/
      DATA QUART2 /'90'/
      DATA QUART3 /'18','0 '/
      DATA QUART4 /'27','0 '/
      LIN=1
      LOUT=5
      LPLOT=12
      IV=MSCFA(LPLOT,'PL')
      CALL PLOTS(NDUM,NDUM,LPLOT)
C
C         NSET = NUMBER OF OILS PER GRAPH
C         NOPT(J) = 0  AREA %
C         NOPT(J) = 1  LOG AREA %
C
      READ(LIN,990) NGRP
      DO 2 K=1,NGRP
      READ(LIN,900) NSETS
      READ(LIN,950) (NOPT(I),I=1,NSETS)
C
C         DRAWS AXES TIC MARKS AND BOX BORDER
C
      CALL PLOT(0.,0.,3)
      CALL PLOT (-4.,-4.,3)
      CALL PLOT(-4.,4.,2)
      CALL PLOT(4.,4.,2)
      CALL PLOT(4.,-4.,2)
      CALL PLOT(-4.,-4.,2)
      CALL PLOT(0.,0.,3)
      CALL SYMBOL(4.2,0.,.21,QUART2,0.,2)
      CALL SYMBOL(-.4,4.2,.21,QUART1,0.,6)
      CALL SYMBOL(-4.7,0.,.21,QUART4,0.,4)
      CALL SYMBOL(-.2,-4.4,.21,QUART3,0.,4)
      CALL PLOT(3.9,0.,3)
      CALL PLOT(4.1,0.,2)
      CALL PLOT(0.,3.9,3)
      CALL PLOT(0.,4.1,2)
      CALL PLOT(-3.9,0.,3)
      CALL PLOT(-4.1,0.,2)
      CALL PLOT(0.,-3.9,3)
      CALL PLOT(0.,-4.1,2)
      CALL PLOT(0.,0.,3)
C
C         READ OIL DESCRIPTION AND SCALE FACTOR
C
      READ (LIN,1000) OIL,NO,SCALES,FACT
      CALL SYMBOL(-4.0,4.8,.21,OIL,0.,60)
      CALL PLOT(0.,0.,3)
      CALL FACTOR (FACT)
C
C         READ POLAR COORDINATES
C
```

```
      DO 1 J=1,NSETS
      YMAX=0.
      DO 5 I=1,NO
      READ(LIN,1005) X(I),Y(I)
      IF (I .EQ. NO) GO TO 5
      X(I)=X(I)*SCALES
      IF (NOPT(J) .EQ. 1) Y(I)=Y(I)*1000.
      IF (NOPT(J) .EQ. 1) Y(I)=ALOG(Y(I))
      IF (Y(I) .GT. YMAX) YMAX=Y(I)
    5 CONTINUE
C
C          CONVERT TO RECTANGULAR COORDINATES
C
      DO 10 I=1,NO
      IF (I .EQ. NO) X1(I)=0.
      IF (I .EQ. NO) Y1(I)=0.
      IF (I .EQ. NO) GO TO 9
      R=X(I)*(3.14159/180.)
      X1(I)=((Y(I)/YMAX)*COS(R))
      Y1(I)=((Y(I)/YMAX)*SIN(R))
    9 CALL PLOT(Y1(I):X1(I),2)
   10 CONTINUE
C
C          LIST INPUT
C
      WRITE(LOUT,1025) OIL
      WRITE(LOUT,1015)
      DO 15 I=1,NO
      WRITE(LOUT,1010) I,X(I),Y(I)
   15 CONTINUE
C
C          LIST OUTPUT
C
      WRITE(LOUT,1020)
      DO 20 I=1,NO
      WRITE(LOUT,1030) I,X1(I),Y1(I)
   20 CONTINUE
      CALL PLOT(0.,0.,2)
      CALL PLOT(0.,0.,2)
    1 CONTINUE
      CALL FACTOR (1.0)
      CALL PLOT(10.,0.,-3)
    2 CONTINUE
      STOP
  900 FORMAT(I2)
  950 FORMAT(I1)
  990 FORMAT(I2)
 1000 FORMAT(30A2,5X,I3,1X,F4.0,1X,F5.2)
 1005 FORMAT(F4.2,5X,F5.3)
 1010 FORMAT(5X,I3,5X,F6.2,10X,F7.3)
 1015 FORMAT(5X,'POLAR COORDINATE PAIRS'//)
 1020 FORMAT(///'RECTANGULAR COORDINATE PAIRS'//)
 1025 FORMAT('1',30A2//)
 1030 FORMAT(5X,I3,5X,F9.4,5X,F9.4)
      END
```

APPENDIX E

USE OF CIRCULAR PROFILING TECHNIQUES IN GAS CHROMATOGRAPHY

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Introduction

Just as "a picture is worth a thousand words," a good graphic presentation can serve to display clearly and effectively a pattern or event embedded in quantities of data. When properly displayed, complex data can be reduced to graphic forms which are much more easily discerned by the human mind. Where very similar and complex sets of data are to be compared and subtle differences noted, the correct plotting technique can readily amplify these differences. This paper describes the application of a circular profiling technique to complex sets of chromatographic data. In one application, visual patterns are created by applying a novel circular plotting technique to the data. A further extension of the technique demonstrates the use of computer-assisted pattern analysis to identify and quantify constituents in a complex mixture. Data obtained from gas chromatographic analyses of synthetic ester-based lubricants are used to illustrate the techniques.

Experimental

The gas chromatographic analyses of the synthetic ester-based lubricants were performed on a Hewlett-Packard Model 5830A chromatograph equipped with a dual flame ionization detector. The following analytical conditions were used:

Column: 3% Dexsil 400 on 80/100 mesh Chromosorb W, glass, 2 mm ID, 6.4 mm OD, 1.8 m long

Sample: 1 μl of ~ 6.85 wt % synthetic lubricant in methylcyclohexane

Flow Rate: ~25 ml/min helium

Inlet Temperature: 340° C

FID Temperature: 340° C

Temperature Program: 180 to 350° C @ 2° C/min

Chart Speed: 0.5 cm/min

Data were manipulated and graphically presented using a General Automation SPC 16/65 computer equipped with a Calcomp 1627 plotter.

Results and Discussion

Because of the wide variations in the compositions of various synthetic ester-based lubricants and close similarities in others, we have found it desirable to have some method of easily recognizing the various lubricants to note subtle changes in the same lubricants as a function of operation time and assess their contributions in mixed lubricant samples. As a result, we have examined various plotting techniques as potential aids in analyzing the chromatographic data obtained from these lubricants. We have developed a circular profiling technique based on a unique method of displaying and condensing chromatographic data. The result is a plot which produces a characteristic pattern that is indicative of each of the several different synthetic lubricants. This unique method of plotting spatially concentrates chromatographic data in a manner that facilitates the rapid visual comparison of data contrasted with the usual method of evaluating chromatograms. A similar approach was described recently for converting histograms into polar graphic displays.(1)

The recognition device is developed by a technique which produces a circular plot by manipulating the chromatographic data in the following manner: the retention times (R.T.) of the various peaks are plotted circularly by relating them to degrees through an appropriate scale factor (S.F.) selected to maximize the use of the

360 degrees in the circular plot area. For our purposes, since none of the retention times exceeded 90 minutes, a factor of 4 was used to maintain a consistent scale for comparison of the various lubricants. The corresponding peak area percent values are plotted linearly along the radii emanating from the center of the circle at the appropriate number of degrees dictated by the retention times. To maximize the use of the plot area, the area percent data are normalized to the area percent value of the largest peak in any particular data set, then multiplied by the radius of the plot area. The distinctive pattern is produced by a line originating at the origin, sequentially passing through each of the data points, and finally returning to the origin. Figure 1 is a schematic representation of the plotting technique.

A computer program was written to manipulate the data. Figures 2-6 show both the computer-produced circular plots and the conventional strip chart displays for chromatographic data from a selection of five synthetic lubricants that conform to a particular lubricant specification. The circular plots are calibrated in 30-degree increments and labeled with the appropriate retention times. It is immediately obvious that, although each of these lubricants qualifies under the same lubricant specification, their detailed chemical compositions vary greatly. Lubricant I (Figure 2) is a mixture of numerous esters. Lubricants II and III (Figures 3 and 4) are generically similar with fewer major constituents, while IV and V (Figures 5 and 6) are predominantly composed of one and two major constituents, respectively. These characteristics are emphasized in the circular plots, and the unique patterns provide an easy method of distinguishing between the various lubricants.

The ability to easily identify a particular lubricant is not, however, the most useful application of this plotting technique, since, in general, differentiation could be made on the basis of conventional chromatograms. A more valuable benefit is obtained when this technique is applied to compare very similar chromatographic data sets. In many instances very subtle differences can be greatly accentuated. An example of such a case is given in Figures 7 and 8. The chromatogram in Figure 8 differs from that in Figure 7 by not having the very small peak at the position indicated by the arrow. To note this very subtle difference would ordinarily require close scrutiny by a trained eye. However, the difference is so greatly enhanced by the circular plotting technique that its advantage, in this instance, is immediately obvious.

In data sets like those for lubricants IV and V (Figures 5 and 6) where one or two major constituents predominate, information which might be contained in the smaller peaks is essentially lost in the normalization step of the circular plotting technique. In such instances it may be of value to plot area percent values on a log scale to emphasize the smaller peaks. This capability was added to the computer program. Figure 9 shows the log plots for the lubricants in Figures 5 and 6. To obtain these plots, the area percent values were first multiplied by the appropriate power of 10 to convert the smallest value into a number which would produce a positive logarithm. As in the case of the linear plots, the log data were normalized to the largest value and multiplied by the radius of the plot area to maximize the plot size. With these plots subtle changes in small peaks can be more easily detected due to the improved resolution of small peak features.

One of our reasons for examining circular profiling techniques for chromatographic data was to aid in determining the composition of lubricants that were mixtures of several manufacturers' products. Figure 10 shows the conventional chromatogram and circular plot for a mixture consisting of 28.3 wt % lubricant I (Figure 2) and 71.7 wt % lubricant II (Figure 3). The features of the circular plots for both of these lubricants are evident in the circular plot for the mixture. A visual estimate of the percent contribution for each of the lubricants in the mixture could be made, but at best this technique would produce only semi-quantitative results.

In order to achieve a more quantitative assessment of mixture compositions, a computer-assisted circular profiling method was developed. The computer recognition device is based on the comparison of chromatographic data from a mixture with a data base consisting of the chromatographic data sets for each of the five reference lubricants (I-V). The mixture data are compared with the reference data on the basis of retention times and peak heights in the following manner:

(a) Peaks exceeding the limit of the chromatogram and those representing less than 0.05 area percent are not included in the data sets.

(b) The retention time for each peak in the mixture is compared with those of the reference lubricants data.

(c) A ratio of peak heights (mixture/reference) is calculated when a correspondence to within ±0.2 minute is found between retention times in the reference and mixture data sets.

The peak height ratios obtained by this method can have many values depending upon peak coincidences and relative abundances of the oils that make up the mixture. There should, however, be a significant number of peaks in the mixture that are solely due to one specific oil, and the ratios obtained for these peaks should be reasonably consistent and represent the weight fraction of that oil in the mixture. These ratios will always be less than one.

Table I shows the results obtained from the comparison of the previously described mixture (Figure 10) with the five pure reference oils by this technique. Only two of the pure oils have a significant number of peak height ratios falling in a narrow range (±5%). The comparison with lubricant II produces seven peak height ratios in the range of 0.718 to 0.792, while comparison with lubricant I yields thirteen peak height ratios in the range of 0.248 to 0.312. A reasonable respresentation of the mixture composition is obtained from the mean values of these ratios. By this method, the composition of the mixture was calculated to be 75.2% lubricant II and 28.6% lubricant I compared to the actual values of 71.7% and 28.3%. No consistent correlation was found between the mixture data and the other three reference data sets. Of particular interest is the lack of significant correlation with reference lubricant III (Figure 4) even though it is closely similar to lubricant II, the major constituent of the mixture. This illustrates a high degree of specificity for the technique.

Conclusions

We have found circular profiling techniques to be of value in both visual and computer-assisted comparisons of chromatographic data from the analysis of synthetic lubricants. Some attractive features of these techniques include:

1. (1) Spatial concentration of data for ease in making comparisons and hard copy storage.
2. (2) Optional logarithmic display of data to emphasize smaller features.
3. (3) Elucidation of the composition of complex mixtures.

There are numerous other possible applications for these techniques including any complex data set (chromatographic or otherwise) for which comparisons with standards or other data sets are required. The mass of data produced in the analysis of environmental samples, fuels, and other multi-constituent samples by capillary column technology is ideally suited for this type of treatment. The circular plotting technique may be especially useful for visual presentation of such data to the uninitiated observer, since, in general, the method of spatially concentrating data facilitates the recognition of subtle differences for the untrained eye.

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Reference

1. Anonymous, Aminco Laboratory News 31, (2), 8-11 (1975).

Table I

Computer-Assisted Mixture Analysis

Mixture	Peak Height Ratios				
R.T.(min)	Lube I	Lube II	Lube III	Lube IV	Lube V
4.26	0.248	-[a]	-	-	-
5.73	0.268	-	-	-	-
6.27	0.266	-	-	0.531	-
7.57	0.273	-	-	-	-
8.69	-	0.759	-	-	-
9.78	-	> 1.0	> 1.0	-	> 1.0
13.95	-	0.731	-	-	-
14.37	-	-	-	-	-
15.16	0.292	-	> 1.0	-	-
16.99	0.706	> 1.0	0.857	-	-
18.04	0.444	-	-	> 1.0	-
19.81	-	-	-	-	> 1.0
21.21	-	0.763	0.943	> 1.0	-
22.21	-	0.751	> 1.0	> 1.0	-
22.87	-	0.792	-	> 1.0	-
23.80	-	0.718	-	> 1.0	-
25.38	0.311	-	-	-	-
26.60	> 1.0	0.875	-	0.963	-
28.20	-	-	-	-	-
31.04	0.301	-	-	-	-
33.93	0.299	-	-	-	-
36.69	0.300	-	-	-	-
39.39	0.312	-	-	-	-
42.07	0.286	-	-	0.696	-
44.61	0.284	-	-	0.714	-
49.66	0.273	-	-	-	-
AVG.[b]	28.6%	75.2%			

[a] - indicates no corresponding peak within ± 0.2 minutes

[b] - average of underlined values

Figure Captions

Figure 1. Schematic of Circular Plotting Technique.

Figure 2. Conventional gas chromatogram and circular plot of lubricant I.

Figure 3. Conventional gas chromatogram and circular plot of lubricant II.

Figure 4. Conventional gas chromatogram and circular plot of lubricant III.

Figure 5. Conventional gas chromatogram and circular plot of lubricant IV.

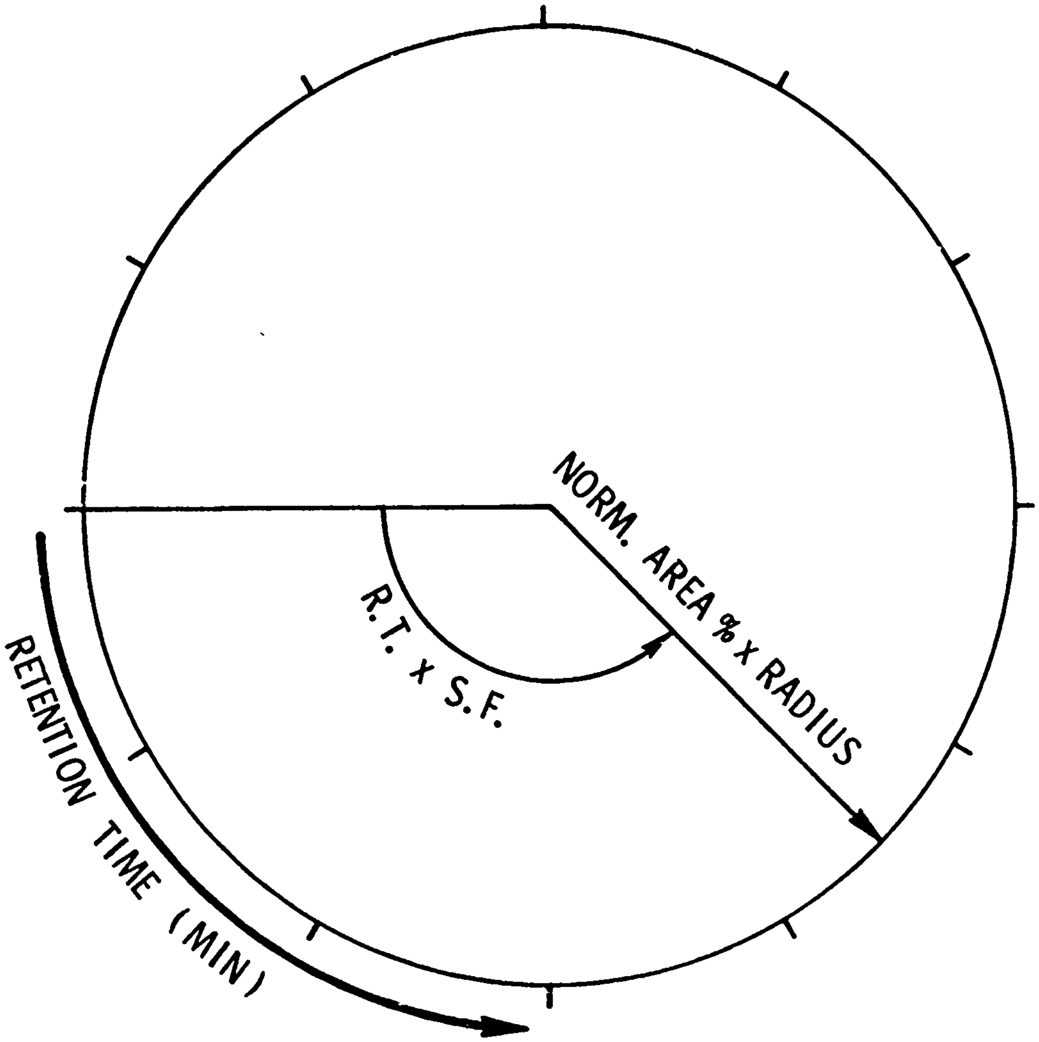
Figure 6. Conventional gas chromatogram and circular plot of lubricant V.

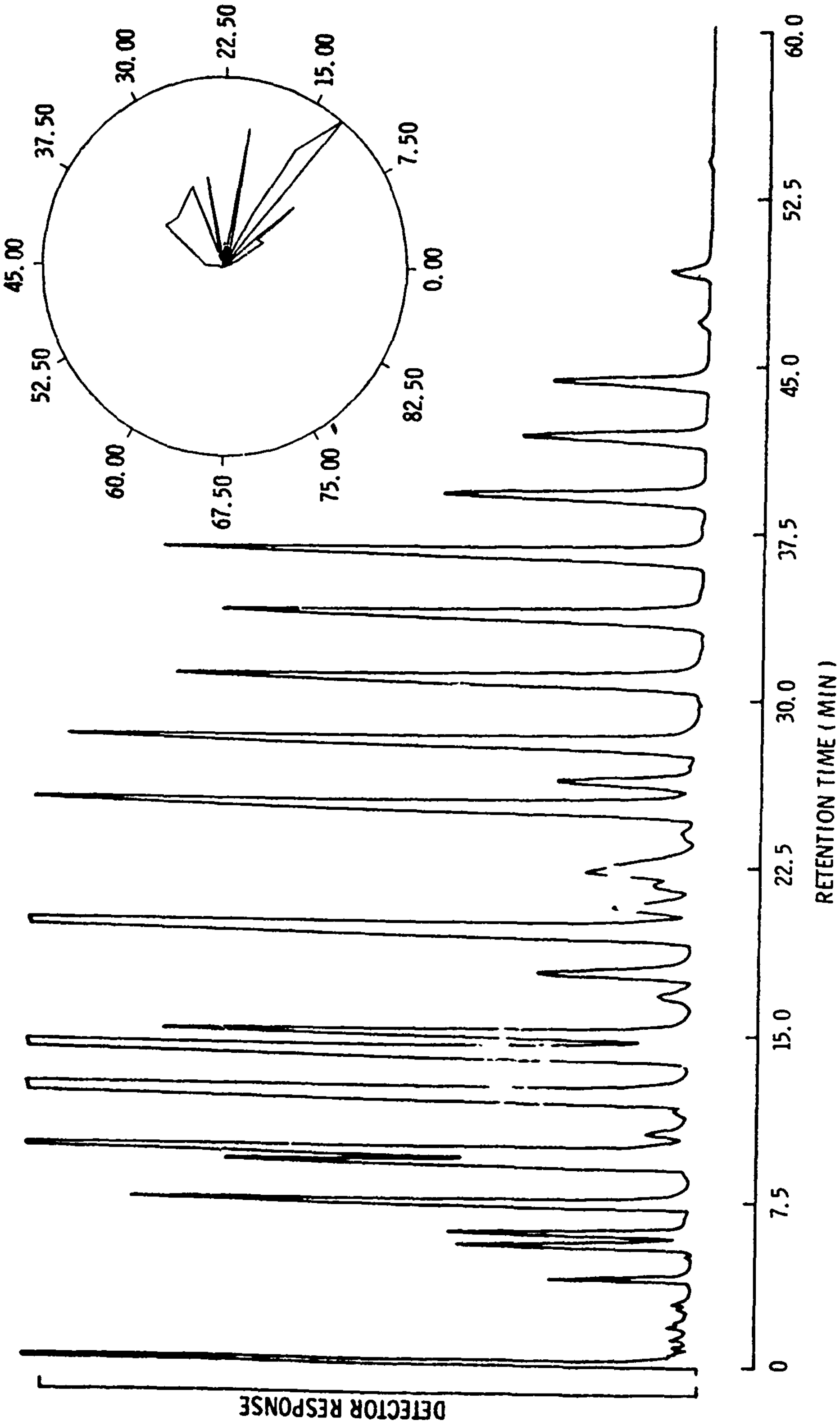
Figure 7. Conventional gas chromatogram and circular plot of synthetic lubricant with minor constituent indicated by an arrow (for comparison with Figure 8).

Figure 8. Conventional gas chromatogram and circular plot of synthetic lubricant without minor constituent at the arrow position (for comparison with Figure 7).

Figure 9. Log plots of data for lubricants IV (Top) and V (Bottom).

Figure 10. Conventional gas chromatogram and circular plot of mixture of 28.3% lubricant I and 71.7% lubricant II.


NORM. AREA % x RADIUS
R.T. x S.F.
RETENTION TIME (MIN)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DETECTOR RESPONSE
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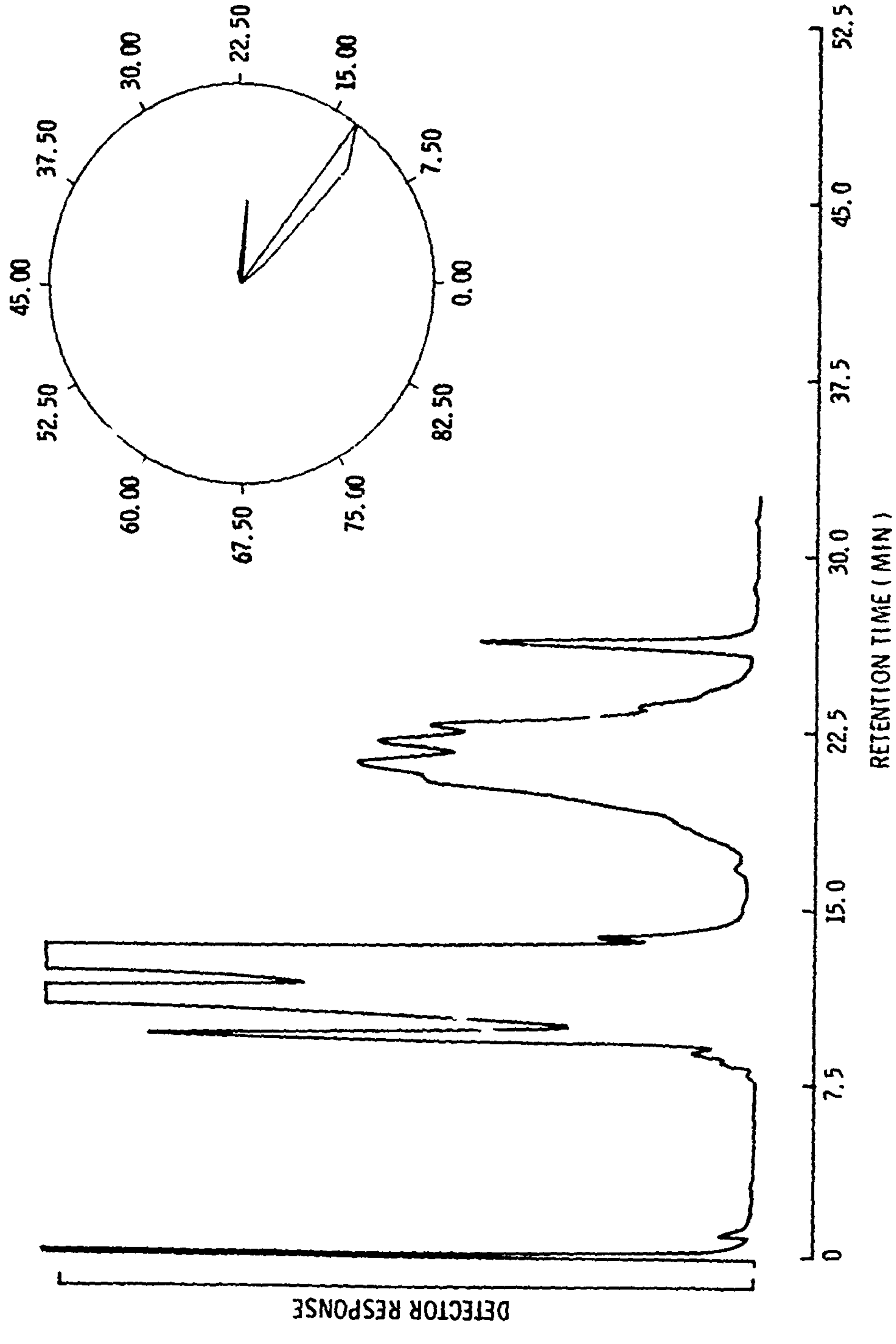
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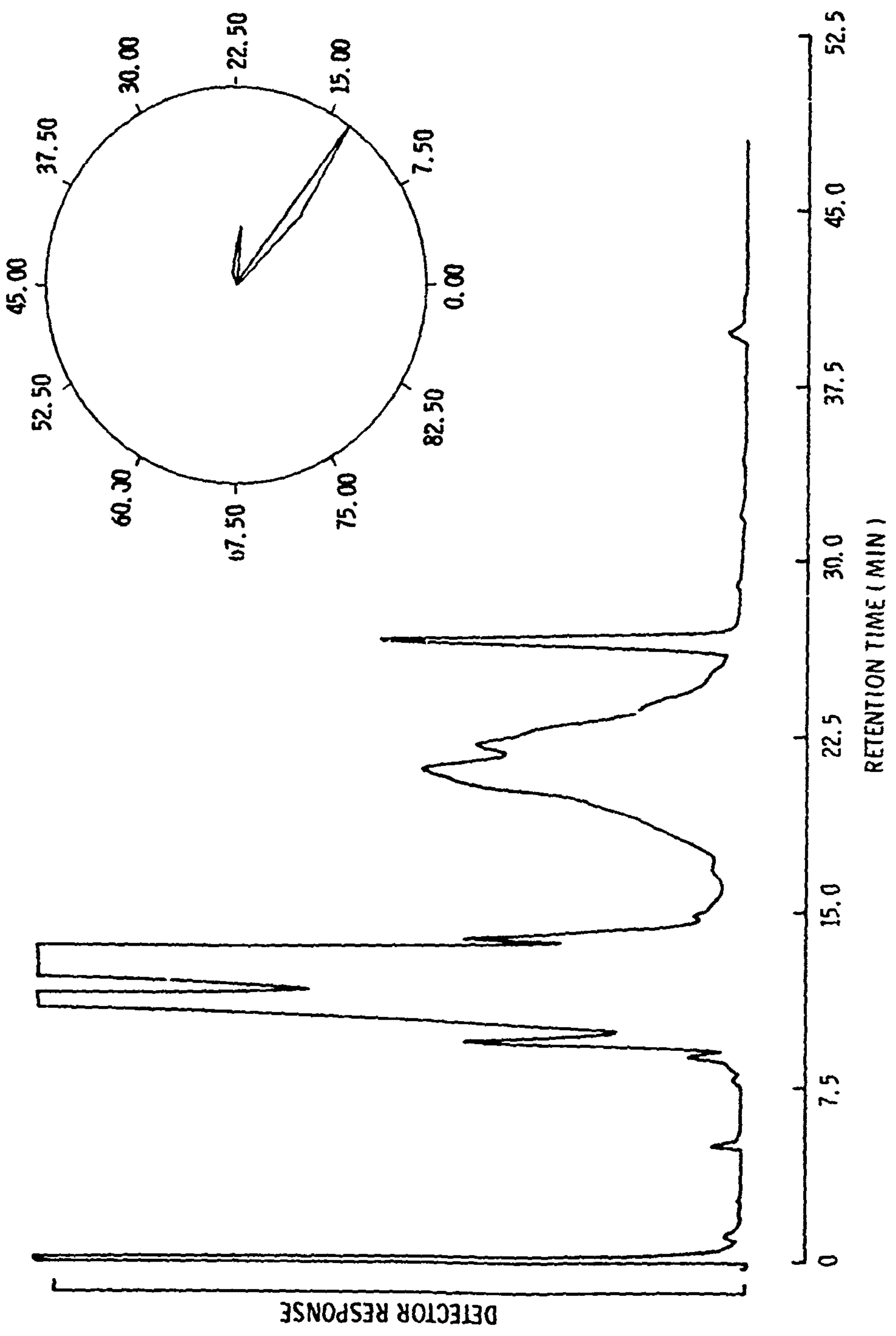
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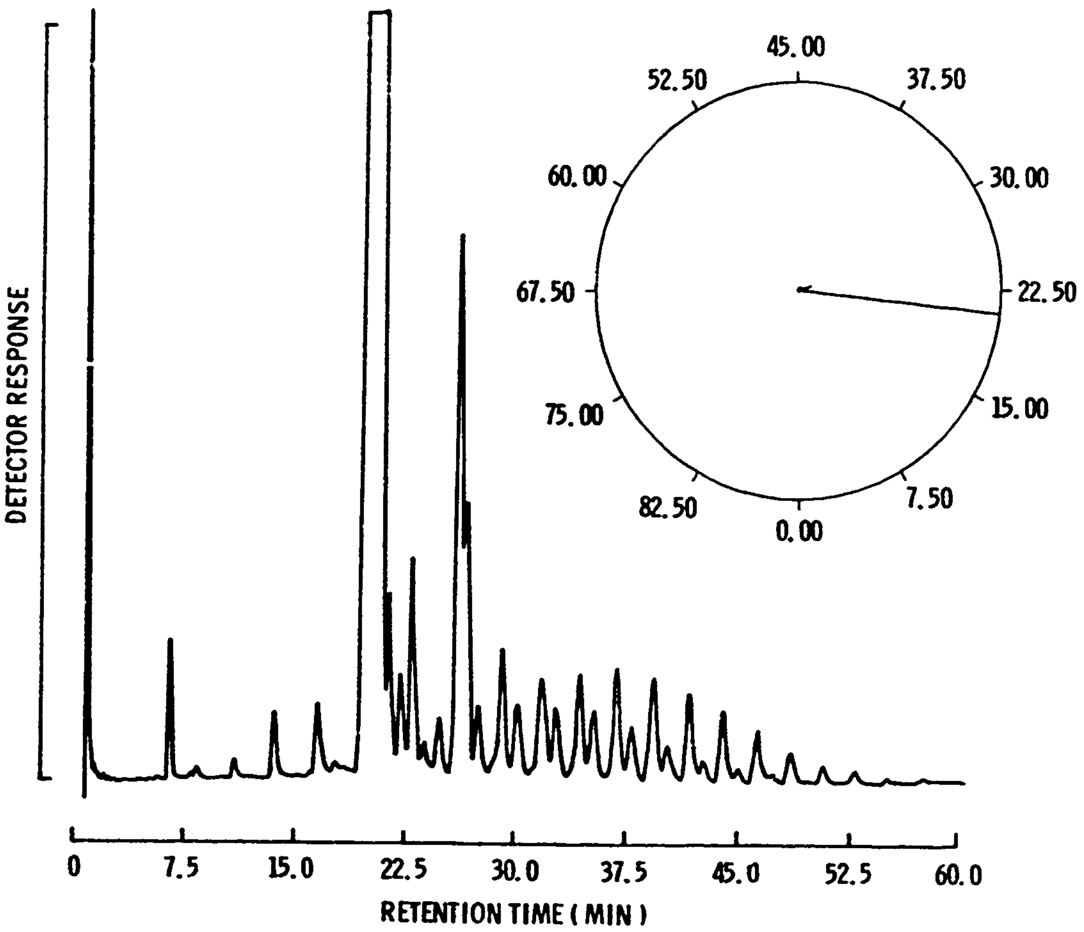

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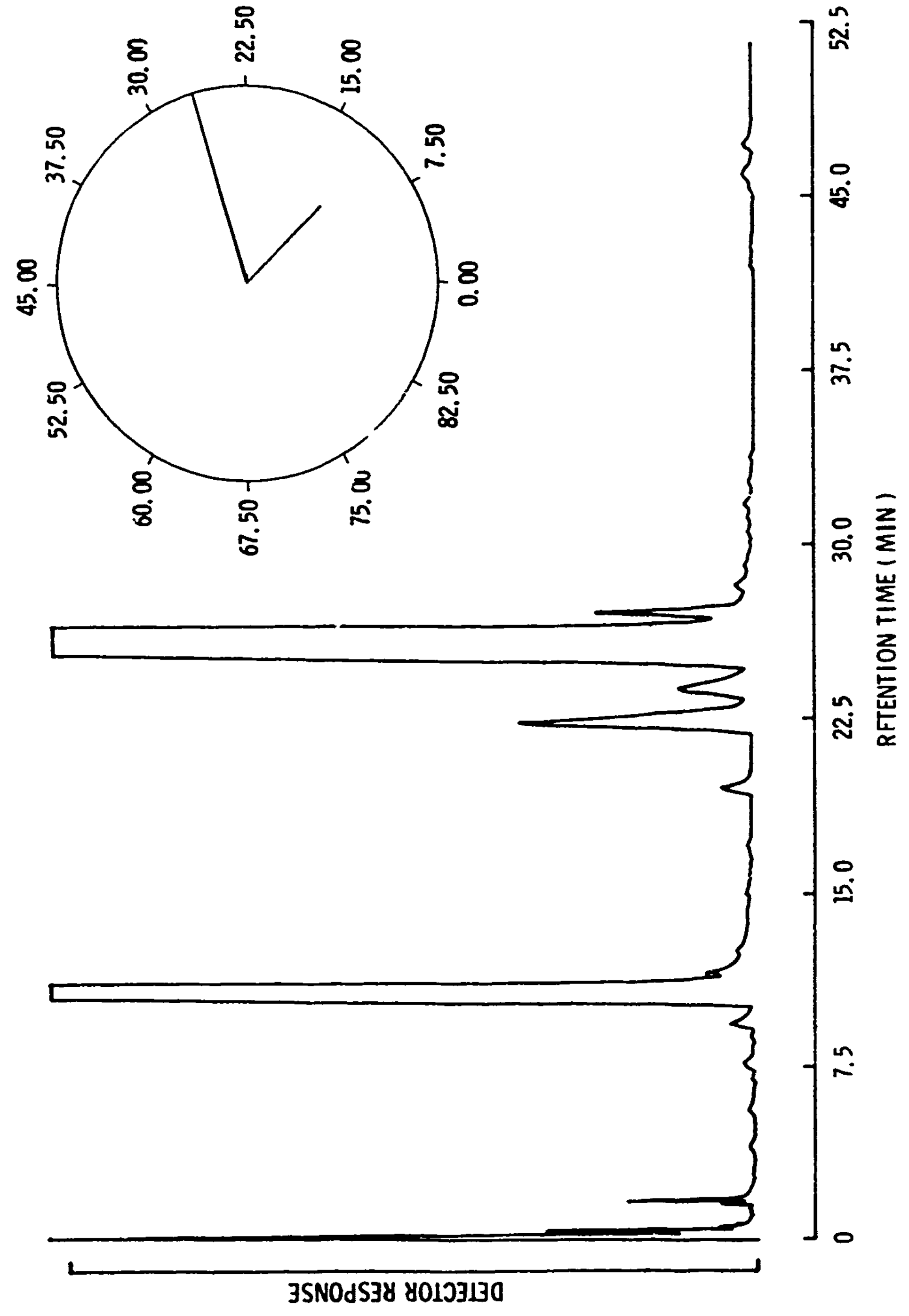
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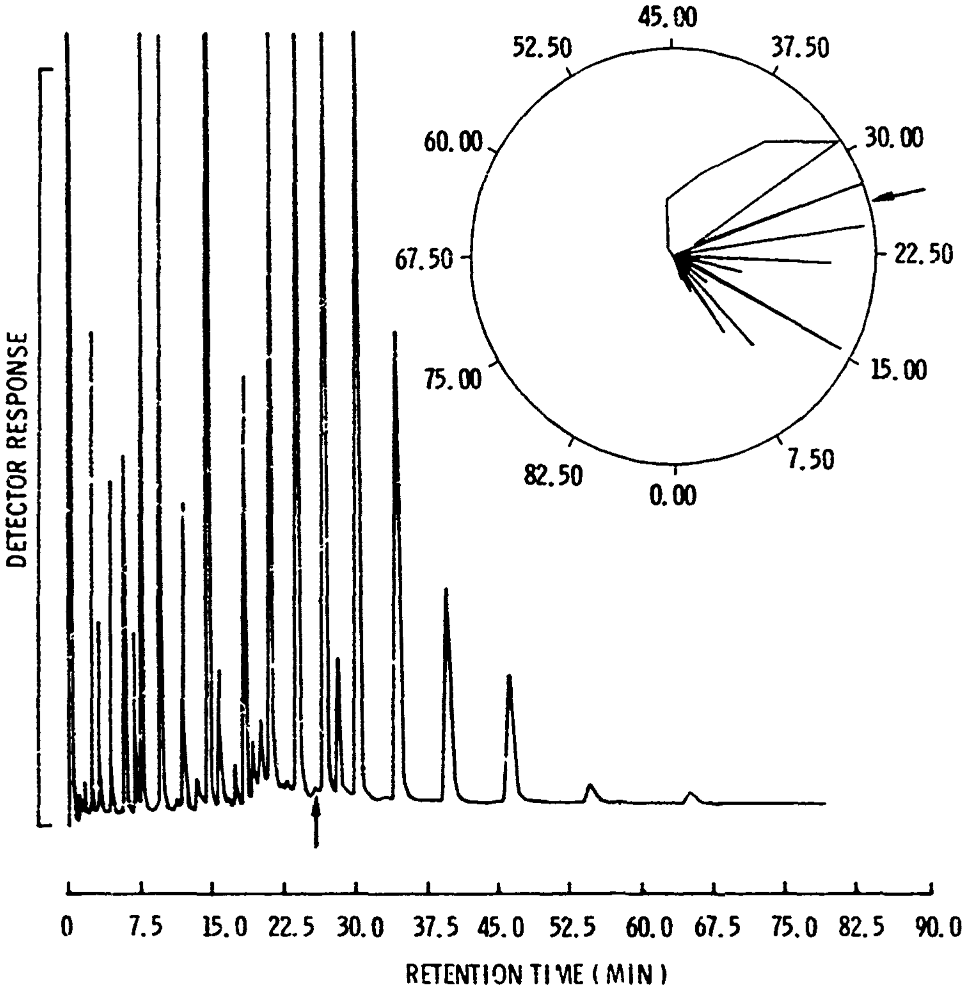
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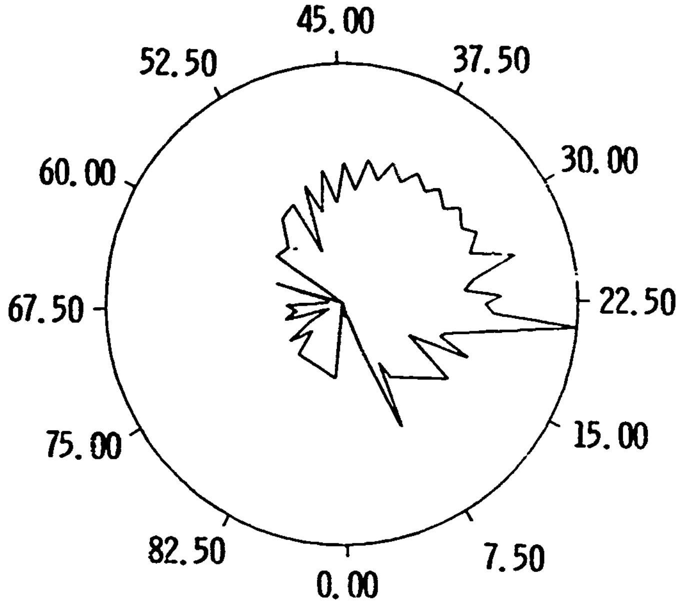
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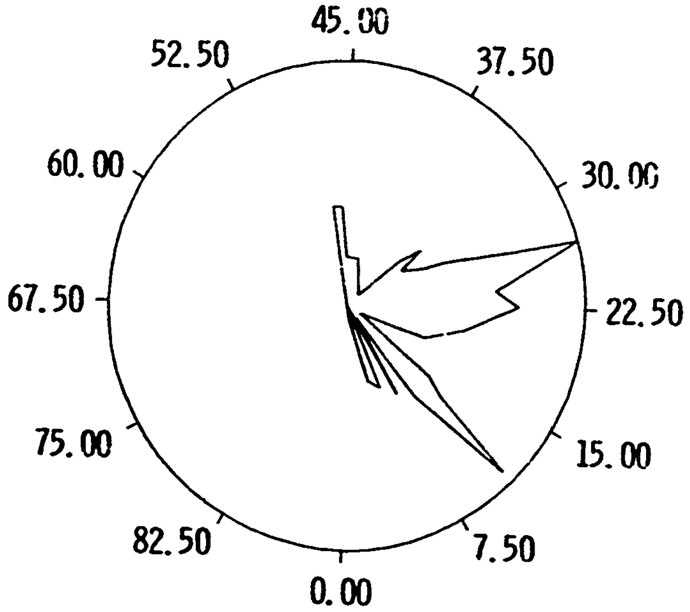
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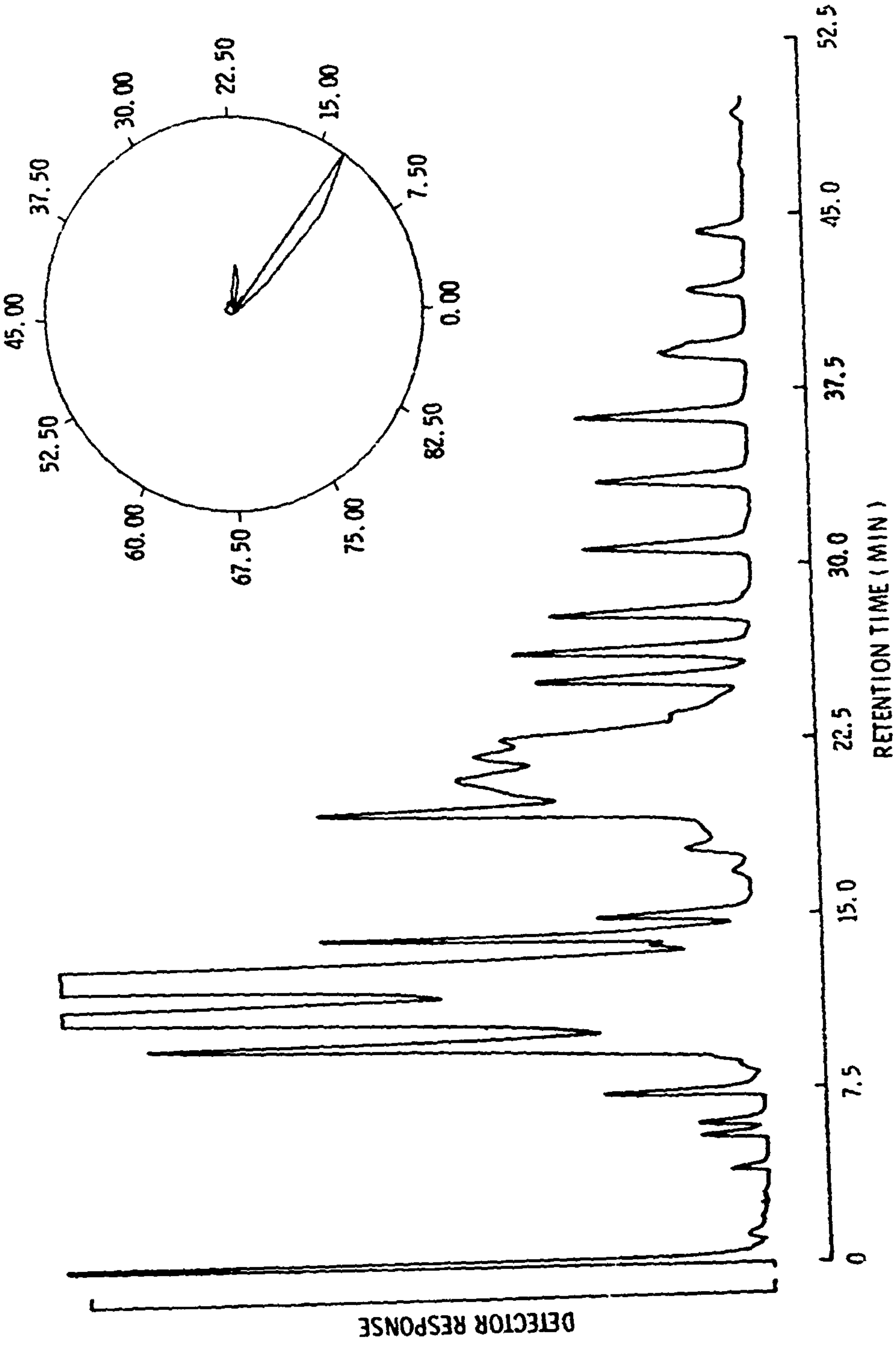
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DETECTOR RESPONSE
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RETENTION TIME (MIN)

APPENDIX F

OPERATION MANUAL FOR COLORIMETRIC IRON KIT

Prepared for
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Air Force Materials Laboratory
Wright Patterson Air Force Base, Ohio 45433
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1. INTRODUCTION

1.1 PURPOSE AND SCOPE

The Colorimetric Iron Test Kit is designed to measure the amount of iron in lubricating oils. It is specifically designed for use on the flight line by technicians without scientific training. This manual describes the principles of operation, pre-operational procedures, use of the kit for iron analysis, maintenance, and trouble-shooting.

1.2 CAUTIONS

Personnel using the kit must wear safety goggles during pre-operational set-up and during operation. One set of goggles is supplied with the kit. Additional goggles can be obtained through normal supply channels.

Some of the reagents used in the analysis may be corrosive. Any spills must be cleaned up immediately. Skin exposed to any spills should be washed immediately with large amounts of water.

1.3 TOOLS REQUIRED

The kit is completely self-contained. No special tools are required for normal operation or for maintenance procedures described in this manual.

2. EQUIPMENT DESCRIPTION

The iron analysis test kit (Figure 1) is based on measurement of the color of a solution formed by reaction of metallic iron in a lubricant with a chemical reagent. The color is measured by a spectrophotometer (Hach Model DR/2) after the necessary reaction has been conducted by adding the reagents in sequence. The reagents are contained, in the proper quantities, in plastic tubes.

The spectrophotometer has been modified to meet the specific requirements of the analysis for iron in jet engine lubricating oils. The instrument is "locked-in" to the required wavelength (530 nm) and the meter scale reads directly in parts-per-million (ppm) iron. Figure 1 shows the kit with the contents labeled. The carrying case provides storage space for 12 iron analysis packets, safety goggles, the mixer and its timer. Stored in the lid of the carrying case are the pipette for the oil, brief instructions, and a color chart for visual comparison. The color chart is to be used only on an emergency basis, in the event of DR/2 spectrophotometer and back-up unit malfunction. Also provided, but not shown, are the BLANK and 10ppm standards for instrument calibration.

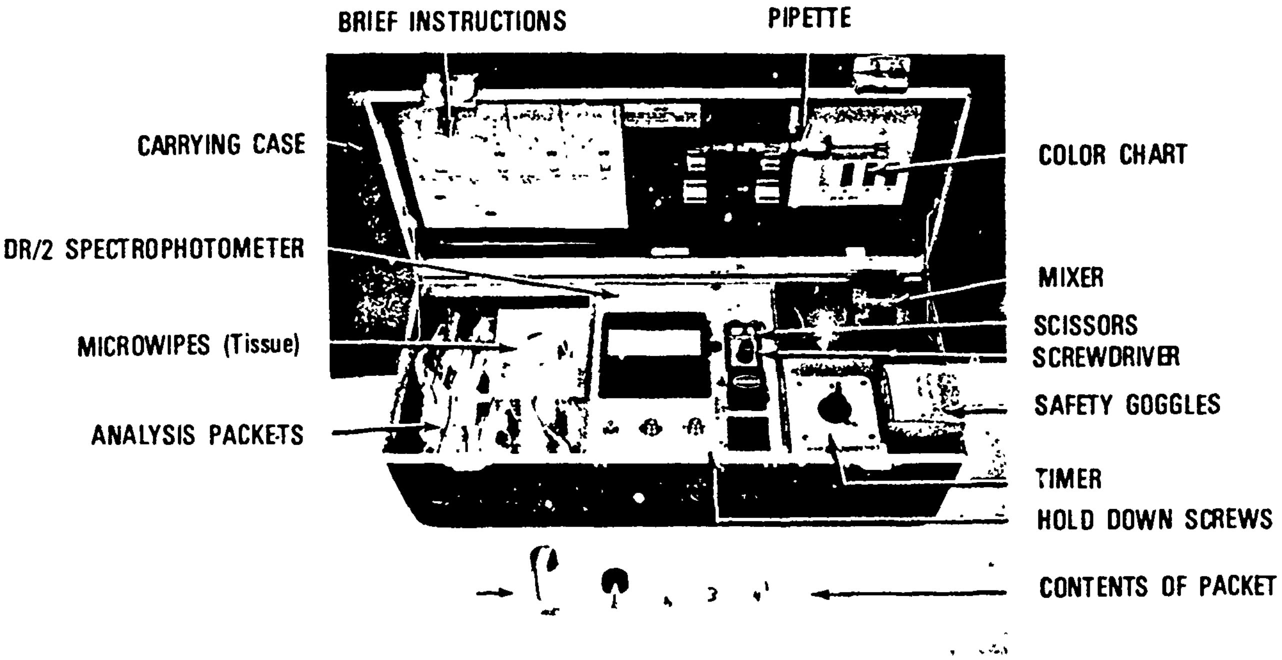


Figure 1. Colorimetric iron kit.

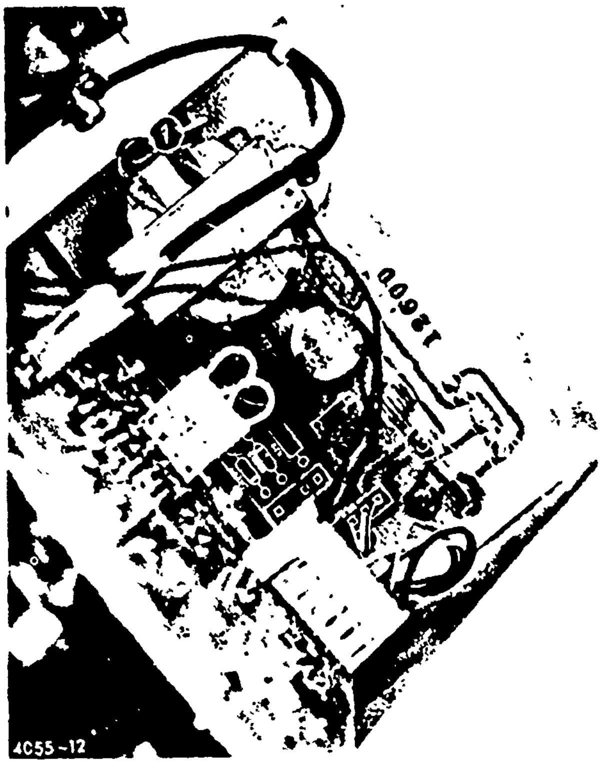
There are three controls on the spectrophotometer.

The OFF-ON-ZERO SWITCH applies electrical power to the instrument when set to the ON position. In the ZERO CHECK position, the lamp is off, allowing the instrument to be electronically zeroed.

The ZERO ADJUST is used to zero the meter when the ON-OFF-ZERO SWITCH is held in the ZERO CHECK position. This adjustment should be made at the beginning of each series of tests and checked periodically thereafter. The light shield over the test chamber must be closed to eliminate stray light.

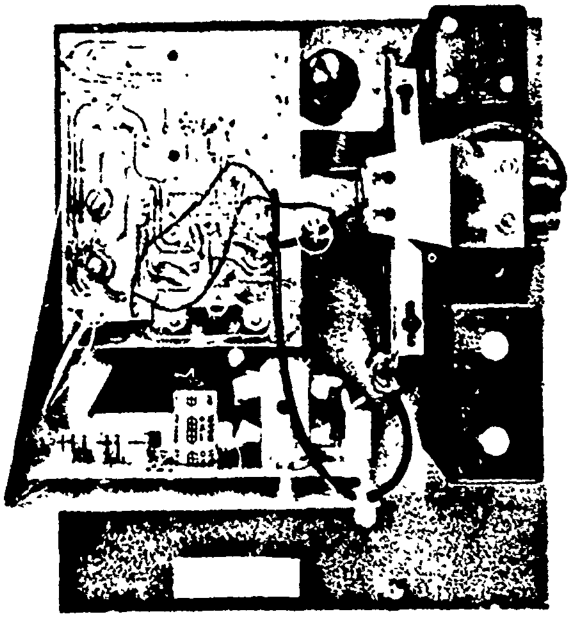
The LIGHT CONTROL varies the lamp brightness. It is used to standardize the instrument with the blank in the test chamber and the OFF-ON-ZERO SWITCH set to the ON position. This adjustment should be made before each series of tests.

Figures 2 and 3 show the interior wiring of the spectrophotometer.



1. Line voltage plug
2. Power supply circuit board
3. Fuse
4. Power supply circuit board connection BC-1

Figure 2. Power conversion.



1. Lamp cable
2. Amplifier board connection BC-4
3. Amplifer circuit board

Figure 3. Spectrophotometer panel, rear view.

3. OPERATION

3.1 PRE-OPERATIONAL SET-UP

3.1.1 Power

The instrument is ready for use with 115-volt AC power supplies, but it can be converted for operation on 220-volt AC power by installing the appropriate 220-volt line voltage plug. This plug is located in a plastic bag taped to the bottom of the case in the instrument compartment. The plugs are stamped 115V and 220V, and can also be identified by the number of jumpers: two on the 115-volt plug and one on the 220-volt plug.

If 220-volt power is to be used, install the 220-volt plug as follows:

(1) Disconnect power to the instrument by pulling the plug from the outlet.
(2) Unscrew the two hold down screws (see Figure 1) on the spectrophotometer face. Carefully remove the spectrophotometer and disconnect the AC power cable from the power supply circuit board connection, BC1.
(3) Install the 220-volt line voltage plug (1, Figure 2).
(4) Reinstall the spectrophotometer by reversing steps 1 and 2.

It is also recommended that the instrument be left ON continuously between readings.

The spectrophotometer should be fully warmed-up before use in analysis.

3.1.2 Mixer and Timer

The mixer is turned on and off by the timer. The timer is hard-wired into the spectrophotmeter and the mixer is plugged into the timer box. The mixer should be left plugged in at all times.

The timer is set to the proper time by lifting the metal tab and setting it to the desired time. To start the timer and mixer, turn the black knob on the timer. The mixer will be turned off when the black knob returns to the zero position. Only two time periods, 1 and 2 minutes, are used in the iron analysis.

3.1.3 Zero Adjustments and Standardization

Before running the first test, zero and standardize the instrument as follows:

(1) Place the BLANK sample bottle in the test chamber and close the lid.

(2) Zero the instrument by holding the ON-OFF-ZERO SWITCH in the ZERO CHECK position while using the ZERO ADJUST control to obtain a zero transmittance reading (needle aligned with the orange mark at extreme left of the meter scale).

(3) Standardize the instrument by setting the light switch to ON and adjusting the LIGHT CONTROL so the needle is aligned with the yellow mark at the extreme right of the meter scale. The instrument is now ready to measure samples. Be sure the light shield is closed before each measurement.

NOTE: The zero adjustment and standardization should be checked before every test during the first 30 minutes of operation.

3.2 ANALYSIS PROCEDURE

Read this section carefully before beginning any tests. The procedure is simple, but the directions must be followed exactly. You must wear safety goggles provided in the kit. If you spill any reagent on your skin, immediately wash the affected area with water.

Figure 1 shows the items necessary to perform the iron analysis. The following describes the procedure in detail:

Before Beginning the Test

- Put on Safety Goggles
- Remove vortex mixer from the case.
- Plug in and turn on the spectrophotometer.
- Do not perform the test over the spectrophotometer or its case.

1. Prepare Sample and Pipette (Figure 4)
   - Shake oil sample vigorously.
   - Remove contents from zip-lock bag.
   - Press new pipette tip firmly onto pipette (make sure it is flush against lip of the pipette).

Figure 4. Installing new pipette tip.

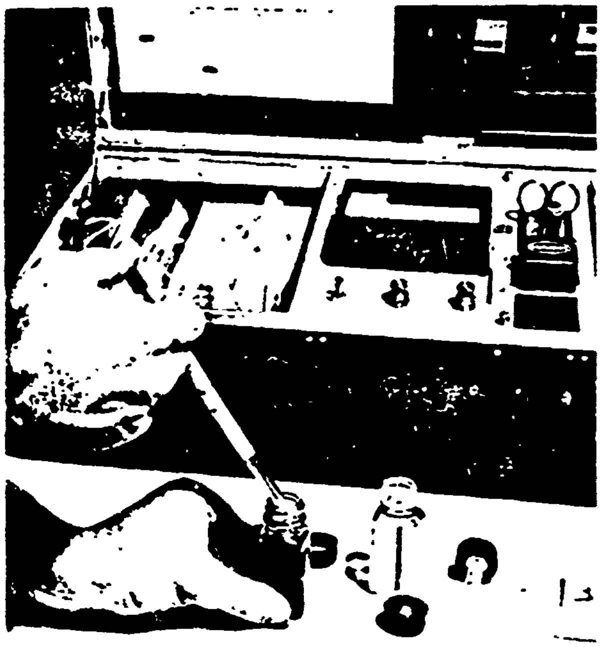


Figure 5. Pipetting oil sample.

2. Pipetting Oil Samples (Figure 5)

- Depress pipette plunger.
- Place tip of the pipette (narrow section only) in the oil and release plunger.
- Depress pipette plunger again (expelling all of the oil).
- Release plunger, allowing tip to fill completely.
- Withdraw pipette from oil.
- Gently draw tip of pipette across lip of oil bottle (to remove excess oil from the outside of pipette tip).

Figure 6. Adding oil to square bottle.

3. Add Oil to Square Bottle (Figure 6)

- Completely depress plunger.
- Touch tip off to side of square bottle.
- Screw the solid cap on the bottle.

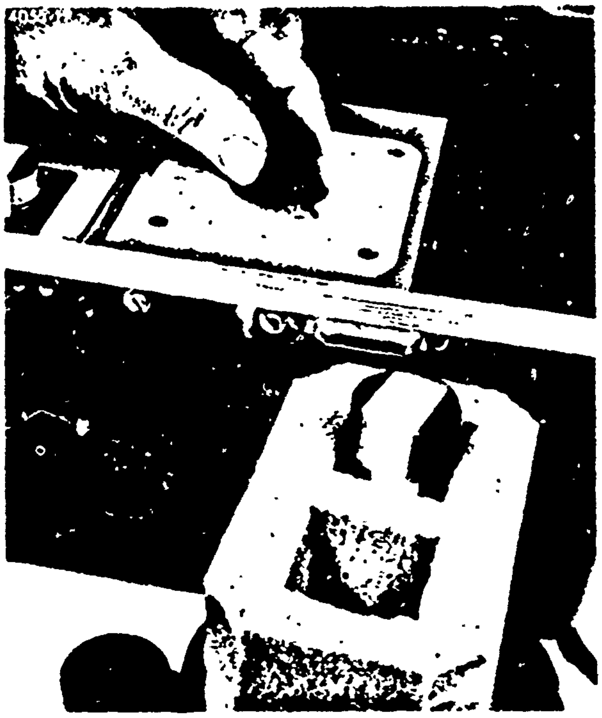


Figure 7. Shaking the square bottle.

4. Shake Square Bottle on Mixer (Figure 7)

- Place square bottle in foam holder.
- Start mixer by turning time to 2 minutes.

Figure 8. Ejecting pipette tip.

5. Eject Pipette Tip (Figure 8).

- Press hard on plunger until tip pops off.
- Gently pull tip from Teflon plunger.
- Wipe off Teflon plunger with tissue.

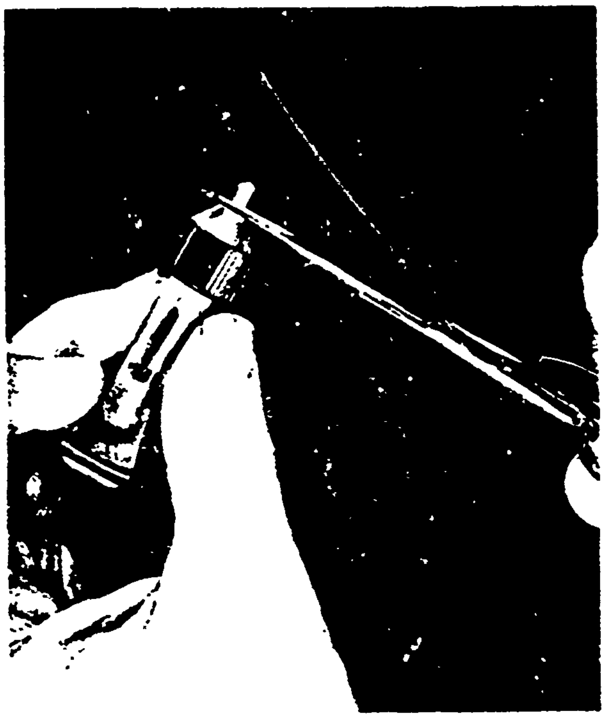


Figure 9. Cutting Tube 1 tip.

6. Cut Tube 1 Tip (Figure 9)

- Remove cap from square bottle.
- Cut off Tube 1 tip at cap liner.

CAUTION: Use ONLY the stainless steel scissors provided with the kit. When cutting tubes, hold them upright and point away from your face.

Figure 10. Square bottle with tube 1 on mixer.

7. Add Contents of Tube 1 and 1A (Figure 10)

- Being careful not to squeeze the tube, screw the elastic cap containing Tube 1 onto the square bottle.
- Squeeze the tube one time.
- Remove Tube 1. (Squeeze tube firmly and pull).
- Cut off Tube 1A tip and insert in cap liner (push down firmly so tube snaps into position).
- Squeeze the tube one time.
- Start the mixer by turning the timer to 1 minute.

Figure 11. Cutting Tube 2 tip.

8. Cut Tube 2 Tip (Figure 11)

- Leave square bottle on mixer.
- Remove Tube 1A from the bottle. (Squeeze tube firmly and pull.)
- Cut off Tube 2 tip just behind white plug.

CAUTION: Leave as much of the tip on the tube as possible.

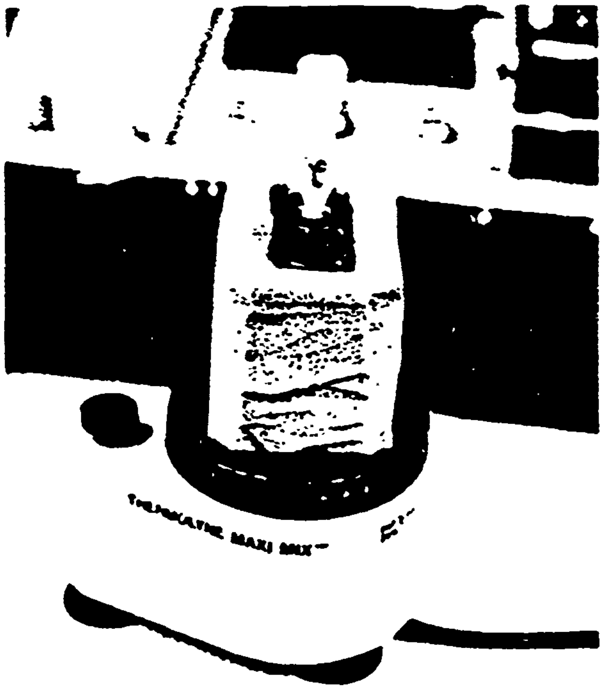


Figure 12. Square bottle with Tube 2 on mixer.

9. Adding Contents of Tube 2 (Figure 12)

- Insert Tube 2 into cap liner. (Push down firmly so tube snaps into position).
- Squeeze tube one time. (Start mixer by turning timer to 1 minute).

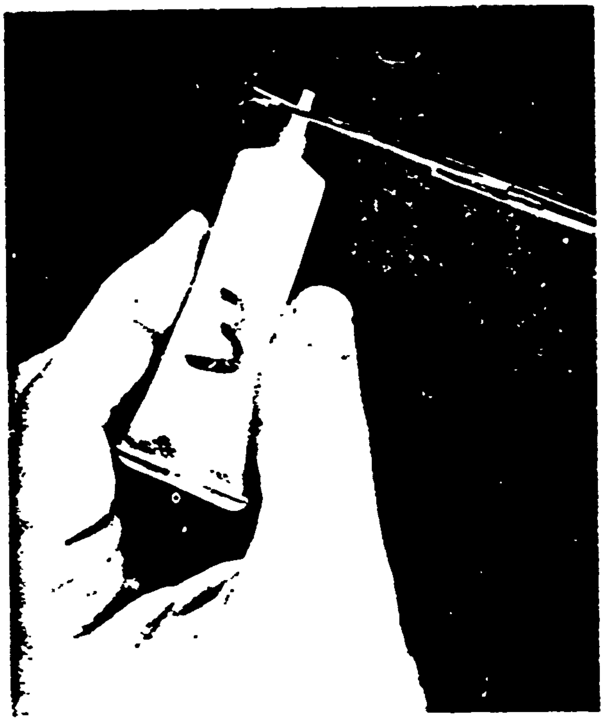


Figure 13. Cutting Tube 3 tip.

10. Cut Tube 3 Tip (Figure 13)

- Remove square bottle from mixer.
- Remove Tube 2 (squeeze tube firmly and pull).
- Cut off one-half of Tube 3 tip.

CAUTION: Leave as much tip as possible on the tube so it will fit into the cap liner.

Figure 14. Inserting Tube 3 into cap liner.

11. Insert Tube 3 Into Cap Liner (Figure 14)

- Tip bottle and Tube 3 slightly.
- Insert Tube 3 firmly into cap liner.

Figure 15. Adding contents of Tube 3.

12. <u>Add Contents of Tube 3 (Figure 15)</u>

- Squeeze tube two times (allow tube to expand between squeezes).

CAUTION: For accurate results, the entire contents of Tubes 3 and 4 must be added to the square bottle.

Figure 16. Cutting Tube 4 tip.

13. <u>Add Contents of Tube 4 (Figure 16)</u>

- Follow steps 10, 11 and 12 using Tube 4.

NOTE: The contents of Tubes 3 and 4 are identical.

Figure 17. Mixing final solution.

14. Mix Final Solution (Figure 17)

- Remove cap, cap liner and tube. (Leave Tube 4 inserted in cap liner for easy removal).
- Screw solid cap onto square bottle.
- Slowly invert bottle three times.
- Return to upright position.
- Allow the bottle to stand undisturbed while doing steps 15 and 16. (Approximately 2 minutes).

CAUTION: Do not shake the square bottle after adding Tubes 3 and 4.

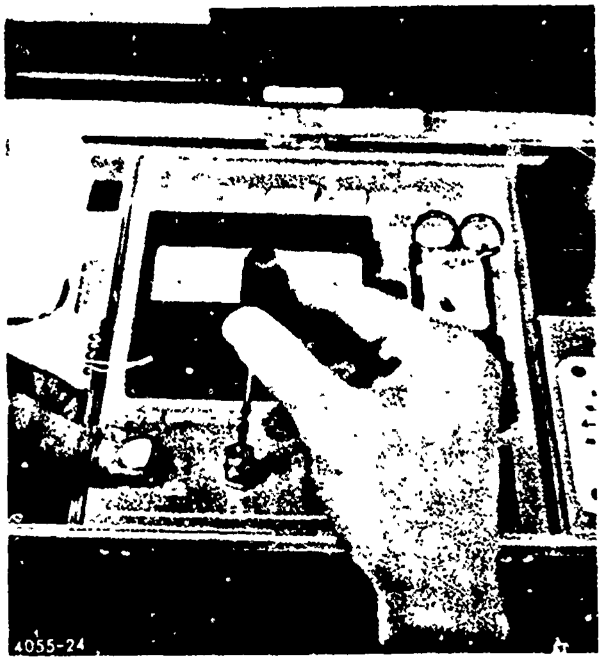


Figure 18. Zeroing the instrument.

15. Zero the Instrument (Figure 18)

- Place bottle marked BLANK in test chamber (arrow on cap pointing toward arrow on instrument).
- Close test chamber lid.
- Hold toggle switch to ZERO CHECK position while turning the ZERO ADJUST control so needle comes to rest over the orange mark at left end of meter scale.

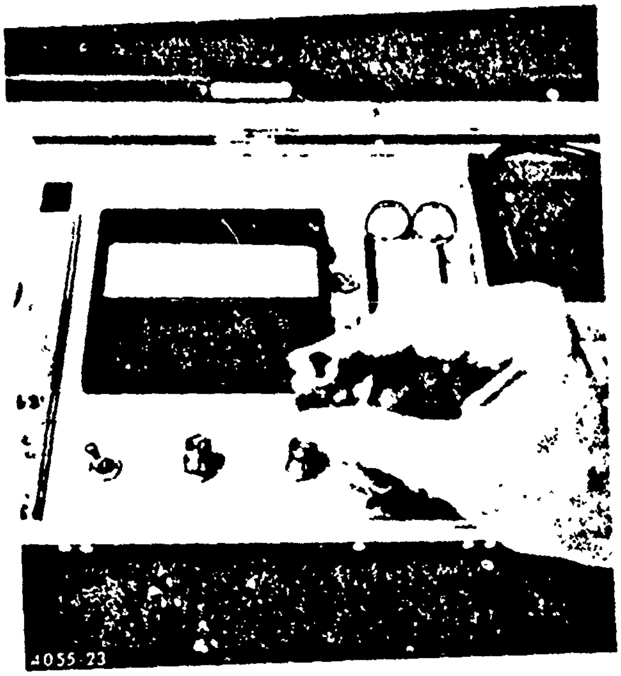


Figure 19. Standardizing the instrument

16. Standardize the Instrument (Figure 19)

- With BLANK in test cell, turn toggle switch to ON.
- Adjust LIGHT CONTROL so needle comes to rest over yellow mark at right end of meter scale.
- Place 10 ppm standard in test cell and note reading. The meter should read 10 ± 1.

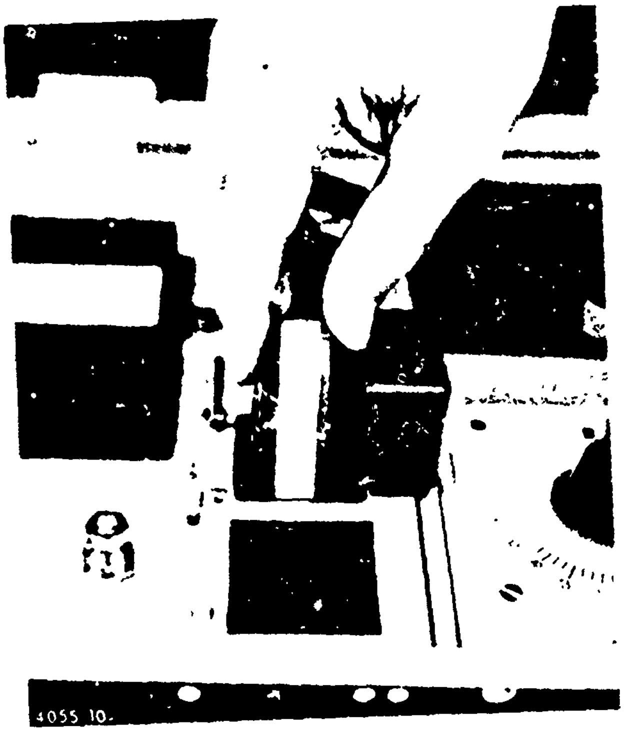


Figure 20. Testing a sample in the spectrophotometer.

17. Testing Sample (Figure 20)

- Place sample to be tested in test chamber (arrow on cap pointing toward arrow on instrument).

CAUTION: Wipe bottle with tissue if outside walls are dirty.

- Close test chamber lid.
- Allow 15 seconds for meter needle to come to rest.
- Take reading and record on data sheet.
- Return tubes, pipette tip, square bottle and used tissue to zip-lock bag for disposal.

3.3 TROUBLE SHOOTING

The following is a list of possible problems and the cause/cure:

Problem	Cause/Cure
Cloudy red layer	Bottle inverted too vigorously after addition of tube 4. Allow to stand undisturbed until clear, or rerun the test.
No red color	Tube 1 or 2 not added or oil contains no iron. Rerun the test.
Less than normal amount of red layer.	Contents of one of the tubes not completely delivered. Rerun the test.
Tubes 1 or 2 fall from cap during shaking.	a) Tip cut off too short (Tube 2). b) Tube not fully inserted into cap liner. Reinsert tube.
Mixer not shaking.	a) Timer not set. Set timer to 1 or 2. b) Mixer not turned on. Depress button on mixer.

4. MAINTENANCE

4.1 CLEANING

The spectrophotometer, mixer, sample cells, and instrument case must be kept clean at all times. Spills should be wiped up promptly. The photocell window, located in the right-hand side of the cell holder should be wiped with lens tissue or the microwipes (tissues) included in the kit.

4.2 LAMP REPLACEMENT

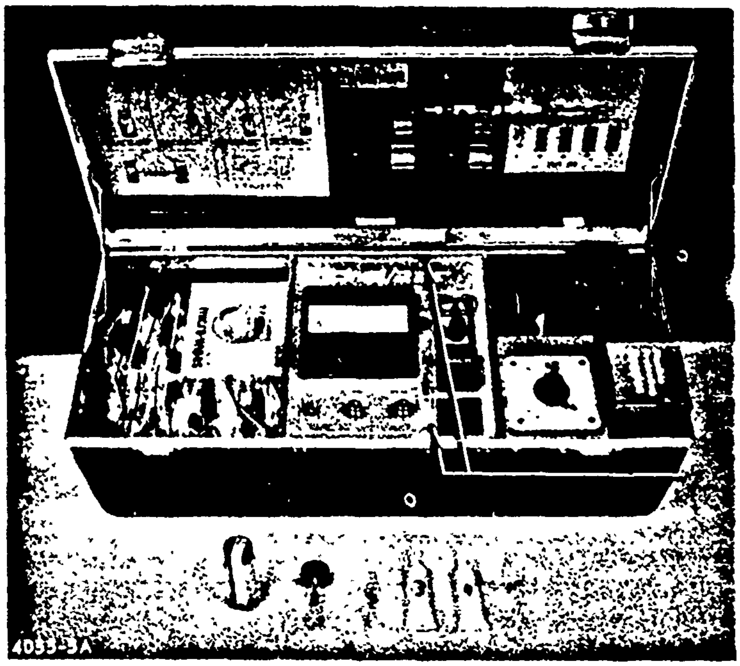
When the spectrophotometer lamp needs to be replaced, the entire lamp assembly, which includes the bulb, lead wires and plug, should be replaced as follows:

(1) Disconnect power to the instrument by pulling the plug from the outlet.

(2) Unscrew the two hold down screws (see Fig. 21) by pulling the plug from the outlet on the spectrophotometer face. Carefully remove the spectrophotometer and disconnect the AC power cable from the power supply circuit board connection BC1. (4, Figure 22)

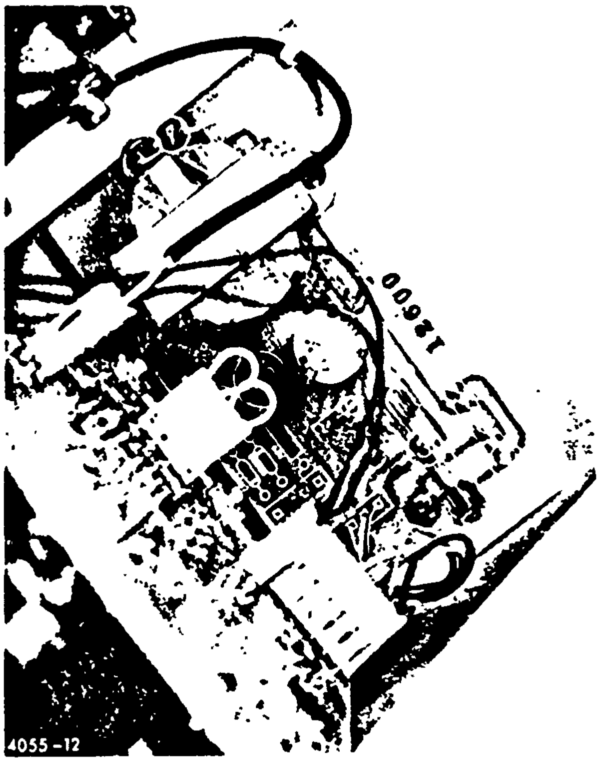
(3) Remove the spectrophotometer panel and lay it face down on a protective mat. Disconnect the lamp cable (1, Figure 23) from the amplifier board connection BC4. (2, Figure 23)

(4) Loosen the setscrew in the lamp holder and extract the lamp.



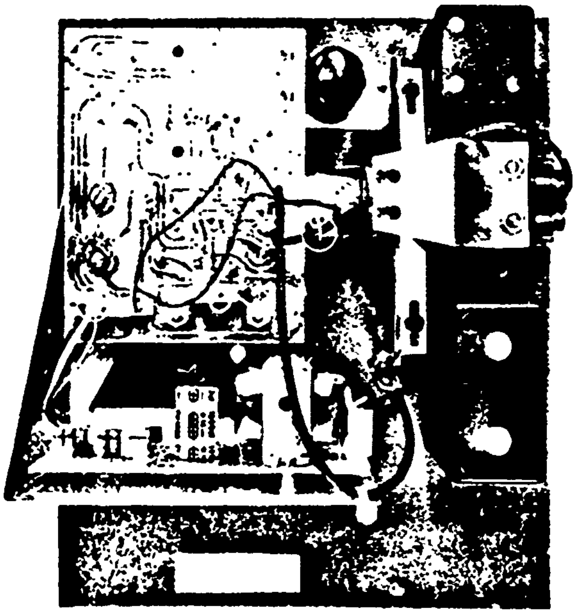
HOLD DOWN SCREWS

Figure 21. Colorimetric iron kit.



1. Line voltage plug
2. Power supply circuit board
3. Fuse
4. Power supply circuit board connection BC-1

Figure 22. Power conversion.



1. Lamp cable
2. Amplifier board connection BC-4
3. Amplifer circuit board

Figure 23. Spectrophotometer panel, rear view.

(5) Install the replacement lamp assembly in reverse order of removal. The lamp must be aligned with the lamp filament positioned vertically, and placed as far in the lamp holder as possible. Check the alignment of the lamp after the instrument is reassembled as follows:

   (a) Place a piece of white paper in the cell holder.

   (b) With the light switch ON, bring the bulb filament image into focus on the paper. Proper alignment gives a green vertical filament image.

   (c) Position the filament image by rotating the bulb within the lamp holder. Avoid overtightening the bulb setscrew. Bulb damage could result.

4.3 FUSE REPLACEMENT

Replace the fuse as follows:

(1) Disconnect power to the instrument by removing the plug from the outlet.

(2) Unscrew the two hold-down screws (see Figure 21) on the spectrophotometer face.

(3) Carefully remove the spectrophotometer and disconnect the AC power cable from the power supply circuit board connection BC1. (4, Fig. 22).

(4) Remove the spectrophotometer panel and lay it face down on a protective mat.

(5) Remove the old fuse and insert a new 3AG, 1/4A, 115V fuse.

NOTE: One extra fuse is located in the plastic bag taped to the bottom of the case in the instrument compartment.

ADDENDUM

During the latter stages of this contract, further research was conducted on Task II to improve the ability of the colorimetric method to analyze particulate iron. This addendum summarizes the results of this work.

The use of aqua regia as a possible alternative to sulfuric acid was investigated after the suggestion of Dr. Costy Saba. 3N aqua regia was prepared as follows:

Concentrated aqua regia - 82 mL HCl + 18 mL HNO_3
Allow to stand at least 48 hours.

3N aqua regia - 25 mL concentrated aqua regia + 80 mL distilled H_2O

The procedure used in this work was the 4 step method described previously. Actual used oils and a suspension of iron powder in MIL-L-7808 oil were analyzed using the aqua regia. The first and second columns of the table below display comparative results for 12 used oil samples analyzed by the colorimetric method using 3N H_2SO_4 and 3N aqua regia. The aqua regia data were significantly higher than the H_2SO data for six of the samples. A 20 ppm iron powder suspension of UDRI-1 in MIL-L-7808 oil was analyzed 12 times using 3N aqua regia. The average of the 12 results was 17.0 ppm, the standard deviation was 1.89 ppm, and the range was 5.8 ppm. The standard deviation and range values were much higher than expected based on our previous work.

In the course of this study it was determined that the isoamyl alcohol used for the comparison of sulfuric acid and aqua regia was discolored. When the discolored isoamyl alcohol was used in the analysis of the iron suspension, higher results were obtained than with normal (colorless) isoamyl (17 vs 7 ppm). The same sample when analyzed using 3N H_2SO_4 and the discolored isoamyl alcohol gave 18.5 ppm but gave only 0.4 ppm when normal isoamyl alcohol was used. Gas chromatography/mass spectrometry (GC/MS) was performed on the discolored isoamyl alcohol to determine impurities. The following impurities were detected in the discolored isoamyl alcohol but not in the normal alcohol: methyl propanol (7000 µg/mL), butanol (6500 ug/mL), butyl formate (5900 µg/mL), normal-amyl ether (2500 µg/mL), isoamyl acetate (900 µg/mL) and methyl pyrazine (350 µg/mL).

The third column of the table displays the colorimetric results obtained by substituting methyl isobutyl ketone (MIBK) for isoamyl alcohol when using 3N aqua regia in the colorimetric method. Six samples gave lower results when compared with the aqua regia/isoamyl alcohol data and five of the six were the same samples that gave higher results for the aqua regia compared to

Sample number	Fe content, ppm			
	H_2SO_4/ isoamyl	Aqua regia/ isoamyl	Aqua regia/ MIBK	Particle Independent
P-81	4.6	5.2	4.6	6
P-86	7.0	6.8	6.4	10
P-88	31.0	37.0	32.0	42
P-91	14.2	13.0	16.2	19
H-58	3.0	3.5	4.2	3
H-63	23.5	23.5	14.5	25
H-65	14.2	23.5	12.8	18
F-18	31.0	135	45.6	132
F-23	60.0	67.0	45.0	64
F-37	5.0	5.1	5.1	13
F-39	18.5	31.0	30.0	33
GE	14.0	63.0	51.6	-

the H_2SO_4 data. The 20 ppm iron powder suspension of VDRI-1 in MIL-L-7808 oil was analyzed ten times using 3N aqua regia and MIBK. The average of the ten results was 12.7 ppm, the standard deviation was 2.74 ppm and the range was 8.1 ppm. The MIBK prevented emulsion formation as well as the isoamyl alcohol.

The data reported in this section is preliminary in nature and should be treated as such. The 3N aqua regia gave higher results for the iron powder suspension and for 6 of the 12 used oils analyzed than did the 3N H_2SO_4. However the standard deviation resulting from the repetitive analysis of the iron powder suspension was poor. The substitution of MIBK for isoamyl alcohol would have to be studied further before conclusions could be drawn.

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