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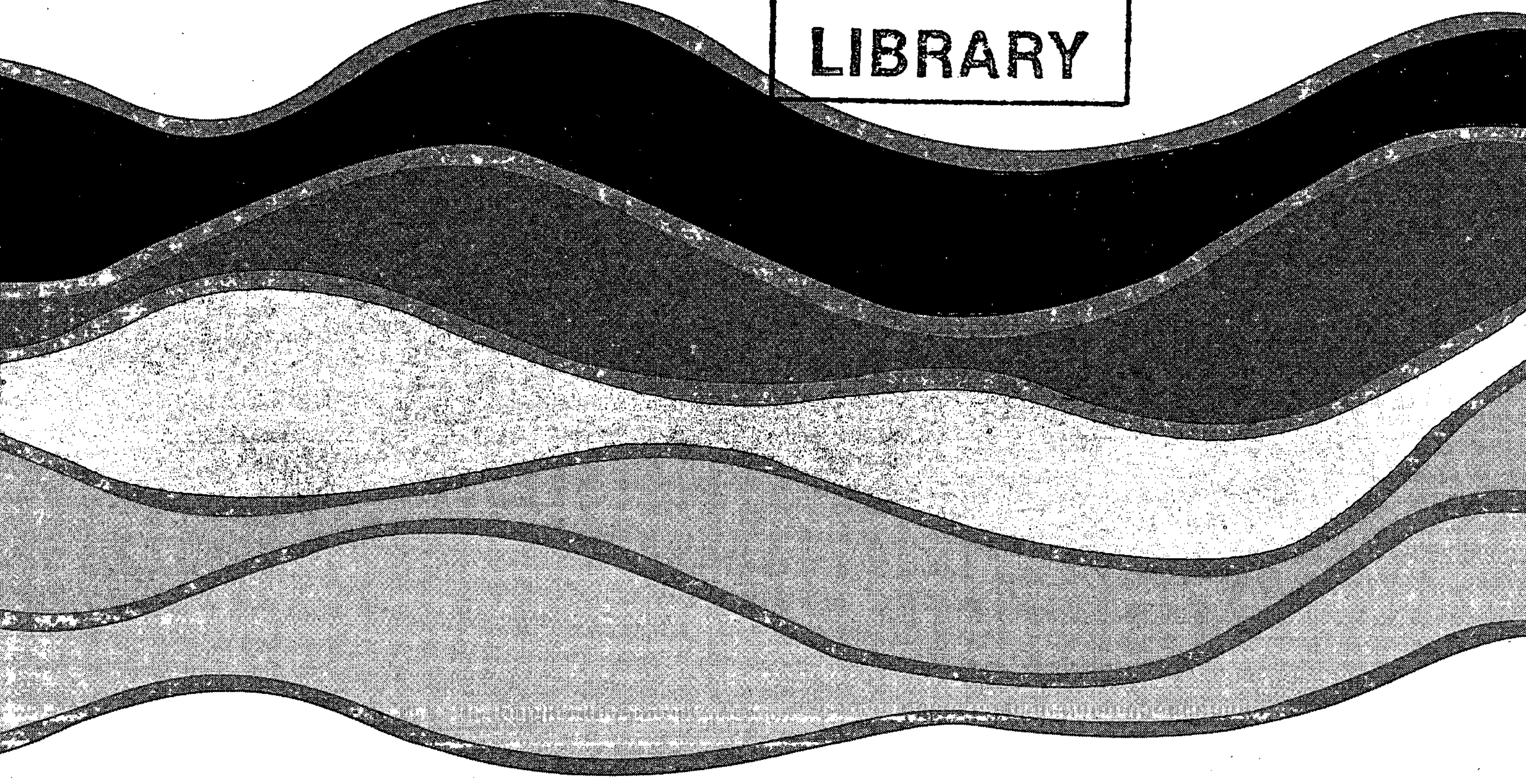

A PRELIMINARY CHEMICAL EXAMINATION OF HYDROPHOBIC TIRE LEACHATE COMPONENTS

PART III

PRELIMINARY CHROMATOGRAPHIC AND FTIR/UV/VIS SPECTROMETRIC EXAMINATION OF MAJOR TIRE LEACHATE COMPONENTS

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NWRI Contribution No. 93-78

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PART III

PRELIMINARY CHROMATOGRAPHIC AND FTIR/UV/VIS SPECTROMETRIC EXAMINATION OF MAJOR TIRE LEACHATE COMPONENTS

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MANAGEMENT PERSPECTIVE

This report describes preliminary results of the application of molecular spectrometric techniques and separational methods to an examination of major organic components in large-sample preconcentrates of tire leachate in order to identify or chemically characterize those demonstrating toxicity in biological tests. A comprehensive approach to the identification/characterization of unknown contaminants in aqueous matrices, using tire leachate components as an example, has been discussed in **Part I** of this series; the preconcentration technique used to isolate hydrophobic tire leachate components has been described in **Part II.**

The results of this preliminary work demonstrate the validity of developing a comprehensive analytical approach to the problem of identifying/characterizing unknown organic contaminants in environmental aqueous systems and provide a basis for further development.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Le présent rapport présente les résultats préliminaires de l'application de techniques spectrométriques moléculaires et de méthodes de séparation à l'examen des principaux constituants organiques de préconcentrés de gros échantillons de lixiviats de pneus afin d'identifier ou de caractériser chimiquement les constituants qui se révèlent toxiques dans les essais biologiques. On a discuté dans la **Partie I** de la présente série d'une approche globale pour l'identification et la caractérisation des contaminants inconnus dans les milieux aqueux, en prenant les constituants des lixiviats de pneus comme exemple; la **Partie II** décrit la technique de préconcentration utilisée pour isoler les constituants des lixiviats hydrophobes de pneus.

Les résultats de ces travaux préliminaires montrent la validité de l'élaboration d'une approche analytique globale au problème d'identification et de caractérisation des contaminants organiques inconnus dans les milieux aqueux et pourront être utilisés pour perfectionner cette approche.

ABSTRACT

Extract concentrates of 100 L samples of water used in studies of tire leachate toxicity to rainbow trout fry were fractionated using thin-layer chromatography (TLC) and liquid chromatography (LC) to isolate major components. Bulk extracts and fractions were then examined using liquid phase (attenuated total reflectance, (ATR)) and vapour phase (GC) Fourier Transform Infrared (FTIR) spectrometry and liquid phase ultraviolet/visible (UV/VIS) spectrometry to identify/characterize these components.

Two major components of the test extracts were "identified" by GC/FTIR and a further six partially characterized by the same technique. TLC showed evidence of several hydrophillic compounds which were not GC-chromatographable but should be amenable to separation and identification/characterization by high performance liquid chromatography (HPLC). UV/VIS absorbence was seen in all fractions. These preliminary results will be integrated with GC/MS and GC/atomic emission detector (AED) data as part of a larger study within the Analytical Chemistry Research Project (ACRP)/RAB to identify and characterize toxic tire leachate components and to develop a comprehensive analytical approach to the identification/characterization of unknown organic contaminants in aqueous systems.

RÉSUMÉ

Des extraits concentrés d'échantillons de 100 L d'eau utilisés dans des études de la toxicité de lixiviats de pneus chez les alevins de truite arc-en-ciel ont été fractionnés à l'aide de la chromatographie en couche mince (CCM) et de la chromatographie liquide (CL) afin d'isoler les principaux constituants. Les extraits totaux et les fractions ont ensuite été examinés par spectrométrie infrarouge en phase liquide (réflexion totale atténuée) et en phase gazeuse (CG) à transformée de Fourier (SITF) et par spectrométrie en phase liquide dans l'ultraviolet ou le visible (UV/VIS) afin d'identifier ou de caractériser ces constituants.

Deux principaux constituants des extraits ont été «identifiés» par CG/SITF et six autres ont été partiellement caractérisés par la même technique. La CCM a révélé plusieurs composés hydrophiles qui ne pouvaient pas être séparés par CG, mais qui pourraient être séparés et identifiés ou caractérisés par chromatographie liquide à haute performance (CLHP). Toutes les fractions absorbaient dans l'UV ou le visible. Ces résultats préliminaires seront intégrés aux données de CG/SM et de CG avec détection par émission atomique dans le cadre d'une étude plus importante du Projet de recherche en chimie analytique de la Direction de la recherche pure et appliquée dans le but d'identifier ou de caractériser les constituants toxiques d'un lixiviat de pneus et de mettre au point une méthode analytique globale pour l'identification et la caractérisation de contaminants organiques inconnus dans des milieux aqueux.

INTRODUCTION

Basic difficulties involved in identifying or chemically characterizing unknown contaminants in environmental aqueous matrices using currently "routine" techniques (GC/MS, GC/ECD) optimized for "target" compound determination have been discussed in **Part I** of this series and a more comprehensive analytical approach suggested (1). This approach, and its integration with biological toxicity testing, is being developed within the ACRP/RAB using tire leachate components as a test matrix. The isolation of sufficient tire leachate component material for these studies has been described in **Part II** of this series (2).

This report describes chromatographic separation and molecular spectrometric examination (UV/VIS, ATR/FTIR, GC/FTIR) of tire leachate components in concentrates of test extracts collected as described in **Part II.**

EXPERIMENTAL

Strategy

Examination of major components of the tire leachate extracts utilized the following analytical separation/detection techniques; TLC, GC/FID, ATR/FTIR, UV/VIS, and GC/FTIR. A flow-diagram of the strategy is shown in **Fig. 1 (Part I)**.

Other than drying, the extracts and concentrates were not subjected to any further cleanup procedures as the object of this work was to identify or characterize all organic components of the matrix, using information gained from determination of major components to suggest suitable analytical cleanup procedures.

The tire extracts and the subsequent concentrates (2) were intensely coloured. TLC, UV/VIS spectrometry and ATR/FTIR spectrometry were applied to collect LC separation characteristics and UV/VIS and ATR/FTIR spectral absorption characteristics of coloured species and possible major UV absorbing species, for use in structure elucidation and for archival purposes. Both the ATR/FTIR and UV/VIS techniques give an overall indication of the "average" functionality of the mixtures which is dominated by principal components of the mixtures. They therefore may show whether toxicity can be attributed to this functionality.

The scrap and new tire concentrates were fractionated on a qualitative silica gel LC column using a range of eluotropic-series solvents and UV/VIS spectra and ATR/FTIR spectra of these fractions were recorded and interpreted. Information obtained from application of the above techniques was used in establishing initial conditions for HPLC separation of extract components using various detection techniques (2).

The concentrates would then have been analysed by GC/FID to visualize major GC "chromatographable" components and estimate their concentration **(Fig.1, Part I).**

This approach is preferred as the FID is a relatively non-selective detector and shows the presence of most carbon-containing species. This exercise would also serve a precautionary function in determining GC/FTIR conditions necessary to elute all GC chromatographable components and to indicate the presence of high-boiling components. This is of importance in GC/FTIR as the light-tube has an upper temperature limit for sensitive operation and considerable time is required to purge the tube of higher-boiling components which may have condensed in it. As a GC/FID was not available for use in this study, GC/AED (Carbon (C)-channel) chromatograms of the extracts were used for the same purpose (3).

Once appropriate GC conditions for the separation had been established, the extract concentrates and concentrate fractions from the LC fractionation (above) were analysed by GC/FTIR to identify or characterize the major components.

Instrumentation and Techniques

Sample treatment

Subsamples (20.0 mL) of each extract **(Part B)** were dried with anhydrous sodium sulphate and used for initial studies. Aliquots (25 mL) of the 100 mL concentrates produced by concentration of the bulk extracts (1) were similarly dried before use. No other cleanup procedures were used. The subsamples and concentrates were further concentrated by evaporation under a stream of dry, ultra high purity nitrogen using a Teflon delivery line.

TLC (Thin-Layer Chromatography)

1-2 μL of test concentrates were spotted on 20 x 100 mm silica gel TLC plates (Baker-Flex Silica Gel IB) and developed with a solution of toluene:acetone (7:3 v/v). Short wave UV illumination was used to visualize non-coloured UV sorptive components.

LC Fractionation

Fractionation of the scrap and new tire extracts was performed on dry-packed silica gel (J.T. Baker 40-140 mesh) column (11x300 mm) having a bed volume of ~20 mL. For the scrap tire extract, the column was eluted sequentially with benzene, ethyl acetate, acetonitrile, 2-propanol and 2-propanol:water (3:1 v/v). Three 10 mL fractions were collected for each eluent. The new tire extract was fractionated sequentially with hexane, benzene, dichloromethane (DCM), acetonitrile, isopropanol and isopropanol/water (4:1 v/v). The variation in procedure was used to remove hydrocarbons (observed in early scrap tire fractions) from the benzene fraction. The extract and fraction concentrates were evaporated to dryness at water bath temperatures (80-90°C) under a stream of dry nitrogen and redissolved in 2.0 mL of DCM. These concentrates were examined directly by UV/VIS spectrometry and by liquid phase FTIR using the ATR "Circle Cell". They were then concentrated further for examination using the ATR "micro Circle Cell" and GC/FTIR and finally were "dried" (evaporation of solvent) on KBr discs for a transmission cell study.

UV/VIS Spectrometry

A Hewlett Packard Model 8451A single beam photodiode array UV/VIS spectrometer was used with standard 1 cm path-length silica cuvettes. Measurements were made without the use of optical filters over the region 180-820 nm with 2 nm resolution. Spectra were recorded in DCM, acetonitrile, cyclohexane and methanol to detect chromophoric shifts, if any.

ATR (Attenuated Total Reflectance)/FTIR Spectrometry

Liquid phase measurements were made using both a standard ATR liquid cell, a low dead volume liquid flowcell ("Circle Cell", and "micro-Circle Cell"; Spectra-Tech Inc.), and a standard KBr disc transmission cell (Perkin Elmer, F-05) in a Nicolet model 730 FTIR spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector (DET 1 mode). The spectrometer was continuously purged with "CO_2-, H_20-free" air (Barnstead, Model 75-45, air dryer-CO_2 remover). Measurements were made over the mid-IR region of 580-4000 cm^{-1} with 4 cm^{-1} resolution and 1 s scans. Scans were co-added as necessary to improve the signal/noise (S/N) ratio of absorption peaks. All measurements were ratioed to air to remove spectral features of residual CO_2 and H_20. Interactive background subtraction, using solvent as background, was used to distinguish absorption bands due to the sample.

GC/FID Measurements

Major gas-chromatographable components were determined by GC/AED, (C-channel) in lieu of determination by GC/FID (p.3). The scrap and new tire extracts were chromatographed on a J&W DB-5 30m column using the following conditions (3):

Injector:	250 °C
Purge:	0.83 min.
Column Temp. Program:	2 min @ 90 6°C, 30 C°/min to 200 °C, 6 C°/min to 255 °C, 10 min hold at 255 °C.

GC/FTIR Identification and Characterization

Measurements were conducted using a Nicolet model 730 FTIR spectrometer/ model 620 workstation interfaced with a Hewlett Packard model 5880A GC equipped with an on-column injector and controlled by a Hewlett Packard model 5880A GC Terminal. FTIR spectra, gas chromatograms (selected wavenumber) and Gram-Schmidt reconstructed chromatograms were plotted on a Hewlett Packard model "ColorPro" plotter. FTIR measurements were made using the more sensitive mercury-cadmium-telluride (MCT) detector (DET 2 mode) operated at liquid nitrogen temperature.

Chromatographic and interface conditions used were as follows:

Column : 15 m, J&W DB-5, .32 mm OD, .25 mm ID, 1 μ film thickness

Injector : HP, Model 1, on-column, air-cooled (passive)

Injection Volume : 1-2 uL

Solvent : dichloromethane

Column Temperature : 38 °C initial (2 min hold), 15 C°/min to Program 250 °C (15 min hold)

Transfer Line Temp : 250 °C

Light Tube Temp : 250 °C

Carrier gas (He) Flow rate : 1.5 mL/min

Make-Up Gas (He) Flow Rate : .3 mL/min

These rather conservative temperature conditions were shown to be sufficient (by pre-analysis using more "severe" GC/AED conditions) for examination of the extracts. Based on manufacturer's specifications and calibration data, the GC/FTIR as configured would provide ≈ 42,000 plates with a capacity for 300-500 ng of sample. The GC/FTIR was operated in the SX mode (10) at 8 cm^{-1} resolution using 1 s scans (data points) for the Gram-Schmidt chromatogram reconstructions. Chromatographic peaks were individually selected and their IR spectra recorded for comparison with spectral library entries (Sigma-Aldrich and EPA Vapor Phase IR Libraries). Where no existing spectra were found or for library "hits" which were of poor quality, conventional IR interpretation was used to characterize the peaks (4-8). These identifications/characterizations will later be integrated with those obtained through application of other techniques (GC/MS, GC/AED, HPLC, etc) (1).

The GC/FTIR technique was used to characterize the chromatographic background so that some insight could be had as to how to remove this feature for subsequent examination of trace and ultratrace components of the extracts.

RESULTS AND DISCUSSION

TLC, UV/VIS and ATR/FTIR Examination

Extracts

Nine distinct coloured spots (between Rf 0.26-0.86 were observed for the new tire extract. A single distinct spot was seen for the scrap tire extract with a tailing band of colour to the origin at which the majority of coloured material remained. After 72-96 hours, a number of the initially visible spots faded and were replaced with a new series of coloured spots. Examples of these TL chromatograms are shown in **Fig.1.** A summary of the TLC examination is given in **Table I.** Illumination by short wave UV did not show additional spots, suggesting that major components were not aromatic. This latter technique, however, serves only to suggest the presence or absence of very concentrated and/or strongly absorbing UV/VIS components. The control extract showed no visible, UV absorbing, iodine visible or fluorescent spots.

UV/VIS spectra of the control and test tire extracts are shown in **Appendix A.** Significant absorbances were as follows:

	< 195 nm	**270-275 nm**	**450-460 nm**
new tire	major	major	minor
scrap tire	major	minor	none
control	major	none	none

These data show that the new tire and scrap tire extracts differ by the presence, in the new tire extract, of a chromophore species absorbing at 450 nm. This chromophore is likely responsible for the marked yellowish colour of the new tire extract.

The absorbances in the 180 to 275 nm region are typically caused by a variety of conjugated and heteroatom absorbances (C=C, ketone, nitrile, sulfone, nitrate, carboxyl and amido functionalities). The lack of a distinctive UV absorbance, with the exception of the broad band at 450 nm, suggests that the UV spectra of the extracts are not dominated by any one component or class. Functionalities such as carbonyl, carboxyl, sulfone, and amido have been ruled out as major species due to the absence of significant and distinctive characteristic IR absorbances for such functional groups in the ATR/FTIR spectra. UV absorptions in the 180-275 nm range are also characteristic of aromatic E (189-220 nm) and B (250-290 nm) bands having substituents incapable of conjugating with the aromatic ring (eg. diphenylamine is a component of both test extracts and the major component of the new tire extract).

Comparison of UV/VIS spectra with liquid-phase FTIR spectra must be done considering that the two techniques are based on different chemical effects (electronic vs vibrational excitation) and the same functional group, therefore, will not necessarily produce comparably intense absorption by both techniques. For example, species with strong UV/VIS absorbances such as C=C, C≡C, and C=N do not show strong IR absorbences while functional groups such as C=O and C≡N and their derivatives can show dominant IR spectral features but weak UV/VIS absorbances.

The liquid ATR cell technique was found to be relatively insensitive for this application. Even the "micro-Circle Cell" requires concentrations of the order of 0.1 % to provide useful spectra. Although the liquid cell technique certainly is an improvement over transmission cell capabilities, substantial modifications to the technique are necessary before it could be used as an LC detector for trace analysis. Without such modification, the technique is useful primarily as a qualitative tool or as a quantitative tool in Principal

Components Analysis (PCA) where the number of components is small and identities of components are known (eg. composition of industrial formulations). With modifications to instrumental conditions and improvements to solvent spectral background subtraction its use as an LC detector may be substantially improved as the LC separation would allow examination of single substances with a pure solvent background which can be removed by spectral subtraction. ATR solid sampling devices (for examination of residue after solvent removal, similar to the transmission technique used in this work) may be more appropriate for the type of examination required in the present work. The ATR technique was useful in showing that the major component of the scrap tire extract dominated the IR spectrum **(Fig.2)**. This compound appears to be an aliphatic nitro species, possibly linked to a 5-membered ether heterocycle. By contrast, the ATR spectrum of the new tire extract did not appear to be dominated by any one compound.

Transmission FTIR spectra, obtained by depositing thin films of DCM concentrates of the control, scrap and new tire extracts onto KBr windows and "completely" evaporating the solvent, were examined in lieu of solid sampling ATR spectra as the appropriate sampling equipment was not available. The control tire concentrate spectrum was not notable. The FTIR transmission spectra of the scrap and new tire concentrates showed similarities in the C-H and C-O stretch regions **(Figs. 3, 4)**. The spectrum of the control extract concentrate is shown in **Fig. 5.**

Scrap Tire Extract LC Fractions

TLC examination of the silica gel column fractions displayed a series of spots consistent with those shown by the scrap tire extract. This suggests the presence of major non-gas-chromatographable components which continuously bleed off the origin of the LC column. Some fractions showed areas of fluorescence under long-wave UV illumination. TL chromatograms of the scrap tire LC column fractions are shown in **Fig 6.**

UV/VIS examination of these column fractions showed several distinct absorption bands corresponding roughly to the coloured bands observed during column elution (**Appendix A**). Major UV/VIS absorption bands (other than the characteristic broad bands observed between 180-275 nm) were obtained in fractions #6 (338 nm), #9 (320 nm) and #12 (316 nm). These bands can be produced by nitrogen containing species such as nitrile but are more likely to be chromophoric shift bands from other substituents. Nitrile C=N absorption, a very characteristic IR absorption, was not noted in the ATR/FTIR examination.

FTIR (transmission cell, residue)) spectra, obtained from fractionation of the scrap extract showed that the bulk of IR absorbing material is concentrated in fractions #3 and #5. The spectra are dominated by the presence of a strong, sharp absorption at 1554 cm^{-1} and related absorptions at 1485, 1387, and 1081 cm^{-1}. The 1554 cm^{-1} absorption is likely the N-O stretch associated with an aliphatic nitro group. The absorptions at 1485 and 1081 cm^{-1} suggest an ether linkage, possibly a 5-membered ring ether. Based on the proportion of material contained in fractions #2-5, this fraction contains about 80% of the IR-absorbing material and about 60% by weight of the total extracted compounds. The IR spectra of these fractions and that of the unfractionated scrap tire extract are very similar, supporting the conclusion that these fractions contain the bulk of the extracted material. Fraction #6 and subsequent fractions did not appear to contain significant amounts of chromatographable material. Fractions #6, 9 and 12, however, did possess distinct UV/VIS absorbing bands in the area of 300 nm, reinforcing the view that chromatographable material contained in these fractions is not aromatic in nature. A summary of the elution procedure and the observed UV/VIS spectral information regarding these fractions is given in **Table II.**

The UV/VIS and transmission/FTIR spectra of scrap tire fractions and of the unfractionated extract (**Appendix A, B**) suggest that the IR-absorbing material is not strongly coloured. The initial coloured material (fraction #2) is largely confined to a single fraction whereas the IR-active material is spread over at least six fractions showing little or no colour. In general, the coloured materials did not exhibit strong IR spectra at the concentration levels used.

New Tire Extract LC Fractions

Chromatographic conditions used in elution of new tire components were similar to those used above with the exception that the elution sequence was begun with hexane to elute aliphatic hydrocarbons prior to the components of greater interest. A total of 15 fractions were prepared. The bulk of coloured material was concentrated in fractions 4-6 (brown colour, benzene fraction) and in fraction 12 (blue colour, isopropanol). The UV/VIS information is summarized **Table II** ; UV/VIS spectra and transmission/FTIR spectra of the fractions and of the unfractionated extract are shown in **Appendices A & B.**

GC/FID Examination

GC/AED (C-channel) was used in lieu of GC/FID for estimation of the number of major organic leachate components. Some similarities between the GC/FTIR chromatograms and the GC/AED chromatograms (3) of the extracts were noted. The latter chromatograms showed that the GC conditions used for GC/FTIR were satisfactory for the number of, and elution characteristics of the gas-chromatographable components. Only the test tire extracts were examined by GC/AED. A re-examination of these and blank extracts by GC/FID is planned.

GC/FTIR Examination - Extracts

Analysis of the concentrated test extracts showed the presence of several gas-chromatographable, IR-sensitive components. It is estimated that up to 40-80% (w/w) of the total non-volatile material in the test extracts is gas-chromatographable. Chromatographic peaks for each of the three extracts and structural comments are given in **Tables III and IV**; GC/FTIR Gram-Schmidt reconstructed chromatograms of the extract components are shown in **Fig.7.** FTIR spectra of the individual peaks are shown in **Appendix C.**

Control Extract

The control extract provided the largest number of distinct peaks (between 10 and 12) although at much lower concentrations. None of these compounds could be identified with certainty. The principle component (> 90%) appears to be an alkoxy ether/alcohol derivative whose IR spectrum is identical to the alkoxy ether/alcohol characterized in the scrap tire extract. This compound may be present as a residue of materials used to clean the leachate aquaria (eg. a nonionic surfactant). Two phthalate esters (Rt 10.7 min/Di-allyl phthalate and Rt 17.45 min/unidentified phthalate) were also observed. Remaining components consisted of a series of alkyl siloxane derivatives (absorbances at 2980 cm^{-1} [C-H stretch], 1090 and 1044 cm^{-1} [C-O stretch] and a moderate absorbance at 804 cm^{-1} [Si-C stretch]). Extraction and transmission/FTIR analysis of the detergent formulation used to clean the aquaria showed the detergent extract spectrum to be very different from that of the major component of the control extract **(Fig. 8).**

Scrap Tire Extract

Morpholinothio-benzothiazole, and bis(2-ethylhexyl)phthalate were tentatively identified in this extract. Other compounds characterized were an olefinic hydrocarbon, an alkoxy ether/alcohol compound (small hydroxyl band at 3725 cm^{-1} coupled with a strong C-O stretching absorption at 1080 cm^{-1}), and a series of nitro-aliphatic ether compounds with very similar IR spectra (no aromatic C-H stretching bands, strong C-NO2 stretching bands at 1556 cm^{-1} [sym] and 1388 cm^{-1} [asy] and C-O absorbances at 1098 and 1030 cm^{-1} characteristic of ethers). The absorbances of this latter series of compounds suggest an aliphatic nitro group attached to an aliphatic 5-membered ether heterocycle. The spectral similarity of the three nitro compounds suggests that they are close structural or geometric isomers.

New Tire Extract

The new tire extract contained 10 major gas-chromatographable peaks; six were of sufficient intensity to yield informative IR spectra. Four principle components (accounting for 98-99% of the total chromatographable material) were identified. The major component at Rt 14.10 min was identified as morpholinothio-benzothiazole on the basis of its distinctive IR spectrum (aromatic C-H at 3074 cm^{-1}, aromatic ring stretch at 1597 and 1446 cm^{-1}). The presence of a very strong C=N stretch is characteristic of 2-substituted benzothiazoles. The fingerprint IR region corresponds exactly with the EPA Vapour Phase spectrum for this compound. The second major compound (Rt 12.10 min) found in the "new" tire extract was identified as diphenylamine (N-H stretch at 3434 cm^{-1}, C=C stretches at 1596 and 1501 cm^{-1}, and C=N stretch at 1302 cm^{-1}). Two smaller absorbances at 746 cm^{-1} (def) and 692 cm^{-1} (bend) are characteristic of monosubstituted aromatics. A third major peak (Rt 9.65 min) shows an IR spectrum characteristic of an amine substituted aromatic (N-H stretch at 3412 cm^{-1} coupled with aromatic C-H stretching absorbances at 3066 and 3030 cm^{-1}). The substitution pattern cannot be readily determined due to the presence of N-H stretch absorption in the fingerprint region.

Other peaks at Rt 9.57, 9.97 and 10.91 min were characterized as possibly amino alcohols/diols (broad absorbances at 3705-3730 and 3627- 3601 cm^{-1}), beta hydroxy ketones (absorbances at 3629, 3050 and 1672 cm^{-1}) and aromatic hydroxy ketones (absorbances at 3650, 3062, 3022 and 1719 cm^{-1}), respectively.

The gas chromatographic background was characterized as resembling that of long-chain aliphatic hydrocarbons.

A summary of GC/FTIR peaks observed for the extracts and general structural comments is given in **Tables III and IV.** Extract GC/FTIR chromatograms are shown in **Fig.7.** FTIR spectra of the individual GC/FTIR peaks are given in **Appendix C.**

LC Fractions

Scrap Tire

The first fraction of the scrap tire extract contains the aliphatic hydrocarbon species (C25 and above) eluting as a series of distinct peaks (Rt 15.52 - 28.8 min) following a broadly eluting hydrocarbon background (between Rt 12-16 min). A single phthalate ester also eluted in this fraction. Fraction #2 contained representative amounts of most compounds seen in the scrap tire extract with the exception of the olefinic hydrocarbon (Rt 10.15 min) seen in the non-fractionated extract. The nitro compounds observed in the extract continue to elute through fractions #3, 4 and 5. Fraction #5 contains one early-eluting nitro compound (Rt 15.12 min) similar to the three nitro compounds found in fractions #2, 3 and 4. This series of compounds lends itself to further examination by GC/MS to obtain the molecular ion for each compound and, possibly, further chemical information which may assist in establishing the identities of the compounds.

The more polar fractions (#6-10) did not show any discernable peaks by GC/FTIR even on concentration by a factor of 20. The last fraction (#12), eluted with isopropanol-water, contained material similar to that observed in fraction #1; primarily C25 and greater aliphatic hydrocarbons with traces of phthalate and adipate esters (commonly used industrially as plasticizers). The cause of this anomalous separatory behaviour is unknown at present but may be related to overloading of the column (the concentrations of components in the extract was unknown at the time of the fractionation thus precluding a determination of capacity factors). A summary of the number of peaks and a brief structural characterization of components is given in **Table V.**

GC/FTIR chromatograms of the scrap tire extract fractions are shown in **Appendix D.**

New Tire

In general, the chromatographic separation was similar to that obtained for the scrap tire extract. The initial hexane fraction (#1) contained small amounts of aliphatic hydrocarbon material eluting between 13 and 17 minutes. No individual peaks could be resolved even on further concentration. On this basis, the scrap tire extract seems to contain a larger proportion of hydrocarbons than the new tire extract. Fraction #3 showed a small amount of diphenylamine (Rt 11.1 min) which continued to elute in fractions #4 and 5 (trace). Fraction #5 contained the bulk of the sample material seen in the extract and showed at least nine distinct peaks of which six yielded useful FTIR spectra. The largest single component of the fraction (≈ 85 % of the chromatographable material) was identified as 2-morpholino-benzothiazole (Rt 13.92 min). Other significant peaks include a hydroxy-alkene at Rt 10.1 min (absorption at 3624 and 1672 cm^{-1}) that was also found in the scrap tire extract, and an aromatic amine at Rt 9.74 min (3409, 1650, 1462, 740 cm^{-1}). Minor components include an aromatic amino alcohol/phenol (Rt 12.16 min), an aromatic phenolic compound (Rt 13.44 min) and an aromatic heterocycle (Rt 15.9 min). Fractions 6,7 and 9 contain small amounts of "nitro compounds" (Rt 16.6 and 17.6 min) identical to those found in the scrap tire extract. Unlike the scrap tire extract, the new tire extract fractions contain relatively small amounts of these materials which are not observed in the crude extract. If these unidentified "nitro compounds" are responsible for the toxicity of the leachates, then the differential amounts may explain the relative toxicities of the two test leachates. Fraction 12 contained a phthalate/phosphate derivative at Rt 13.45 min (absorption at 1746, 1272, 1123, 1073 cm^{-1}) as well as a series of what may be alkyl sulphonates/phosphates (Rt 17.0, 17.5, 18.1 min), although the IR spectra contain only C-H absorbances (peaks at 2932, 2863 cm^{-1}). Fraction 15 showed two GC peaks (Rt 10.72, 11.10 min) whose IR spectra indicated a substituted amine derivative (peaks at 1253 and 1122 cm^{-1}) and an aliphatic acetyl amide compound (peaks at 1682, 1409, 1232, 1129 cm^{-1}). A summary of principal components characterized in the fractions is given in **Table V.** GC/FTIR chromatograms of the new tire extract fractions are shown in **Appendix E.**

General Comments on Quantitation and Identification by FTIR

Quantitation of compounds in IR spectrometry requires calibration with standard solutions of the substance of interest (external calibration), by addition of concentrated standards of the substance of interest to the sample (generalized standard addition method, alias "spiking"), or by comparison with known amounts of a substance with which analytical response can be reliably compared (internal standard method, "surrogate standard" method). These techniques, however, are of little use in the quantitation of unknown compounds (9). A common practice in this case is to form a rough estimate of the concentration of an unknown compound by reporting it as an analytical response related to that of a known compound (ie. an "operational" estimate). An example is the reporting of unknown contaminants in high purity solvents as "equivalent" concentrations of heptachlor epoxide). IR quantitation in this type of approach is further complicated by the existence of several functional group responses for a single compound. As several of the compounds characterized in this study are unidentified, a similar approach was taken to estimate the concentration of major components. The concentration of the major component of the new tire matrix (ie. concentration in the aqueous test matrix) was estimated to be 10-50 ppm. The major component of the scrap tire matrix was estimated as being 1/2 of this concentration and the major component of the control sample as 1/10 of this concentration.

Spectral identification using GC/FTIR library search routines is based on selecting known spectra having minimum differences ("best match") with the spectrum of interest. The matching algorithms chosen for this work were those of absolute differences and absolute derivative differences (10). These matching routines are capable only of "speeding up" the identification/characterization process and are not used in place of visual comparison and classical interpretation of spectra. The "identification" of diphenylamine and morpholinothio-benzothiazole in this work was done using very good library matches (very low number of absolute spectral differences) and visual interpretation. A more rigorous identification requires comparable information from other structure elucidation techniques (**Part I**). Library match spectra, such as those shown in **Appendix C** for other leachate components, were not of good quality and were visually not the compounds suggested by the library match. In these cases, visual interpretation was used to characterize the compounds, the best library matches serving only as functional group confirmation.

The integration of this work with the application of other structure elucidation techniques (eg. GC/MS, GC/AED) for a more rigorous confirmation of the identity or character of "known" and "unknown" extract components, as well as their concentration levels in the leachates, is an area for further study.

CONCLUSIONS

The principle component (> 90%) of the control extract was characterized as an alkoxy/ether alcohol derivative. Components found at lower levels in the control extract appear to be primarily alkyl silicone derivatives. These compounds were found, again at trace levels, in the test extracts. The compounds may originate from materials used to clean the aquaria and tires (11), construct the aquaria, the plastic aquaria covers, from the atmosphere or from the dilution water or components of its distribution system. Diallyl phthalate was tentatively identified in the control extract. The extraction blank showed none of these compounds.

Two compounds have been tentatively identified (best IR "library-hit") in the two test extracts; these are diphenylamine (new tire extract), and morpholino-thio-benzothiazole (new and scrap tire extracts). The latter compound is the major gas-chromatographable component (63%) of the new tire extract. Several other compounds in the test extracts have been characterized; these are an olefinic hydrocarbon, an orthocarbonate, an N-dialkylaniline derivative and two nitro-compounds. One of the nitro-compounds is the major gas-chromatographable component (66%) of the scrap tire extract. The second nitro-compound may be a "daughter" compound of the stronger nitro-species resulting from decomposition of the parent compound or a geometric isomer owing to the almost identical nature of their IR spectra. These may be implied in the observed toxicity to rainbow trout fry as their concentration in the two test leachates parallels the toxicity.

Integration of the GC/FTIR data with that of GC/AED and GC/MS should serve to characterize these compounds more completely, as suggested in **Fig.1 (Part I)**. The results of this identification/characterization scheme should serve as a basis for toxicity assessment of the principal components and a rational fractionation scheme for toxicity assessments and further identification/characterization work at trace and ultratrace levels (12).

The concentrations of materials in the new tire leachate sample (10-50 mg/L) are estimated as being twice those in the scrap tire leachate sample.

The GC background, as visualized by FTIR, appears to be characteristic of a high molecular weight aliphatic hydrocarbon(s). This background was seen to be largely removed in silica gel fractionation of the scrap tire extract. GC/FTIR examination of LC fractions of this extract showed that high molecular weight hydrocarbons (C25 and greater) are removed by the initial elution with benzene. Further characterization of this background would require HPLC or supercritical fluid (SCF) separation as the background characteristics suggest a high molecular weight compound or mixture of similar compounds not amenable to "standard" GC separation.

GC/FTIR analysis of coloured fractions of the scrap tire extract suggest that the coloured compounds are not gas-chromatographable (high molecular weight, high boiling point, low vapour pressure, polar characteristics) and will require LC techniques for separation and characterization. Molecular size exclusion chromatography (gel permeation chromatograph (GPC)) may be required if the compounds, as suggested by this work, are of high molecular weight. Some of the coloured compounds are evidently easily oxidized by ambient oxygen as indicated by colour changes in TLC chromatograms on standing. This suggests that they may contain oxidizable functionalities (eg. aldehydes, quinones and nitrogen-containing heterocycles). This would explain their polarity and consequent non-chromatographable behaviour on a relatively non-polar (DB-5) GC bonded phase column. It should be recalled that in the large-sample preconcentration (2) the new tire extract was much more intensely coloured than the scrap tire extract although the latter test material was more toxic.

It is important to emphasize that this work describes only the identification/ characterization of principal components of the hydrophobic fraction of the tire leachate samples. Similar work at trace and ultratrace levels will require research into analytical cleanup procedures to remove chromatographic background and modifications to the present GC/FTIR set-up. Additionally, removal of GC background material observed in extracts is necessary before trace analysis can be considered.

The results of this work can be integrated with information obtained from fundamentally different analytical techniques, such as GC/AED and GC/MS, to provide a more chemically rigorous identification/characterization of both known and unknown compounds than can be obtained through the application of any single technique. This information, in combination with advanced fractionation/separation/isolation techniques, can be used to identify or characterize toxic components which as yet have remained unidentified and unquantitated. Work is in progress to optimize chromatographic and spectral performance of the GC/FTIR system to increase the detection capability of the system into the trace component range.

ACKNOWLEDGEMENTS

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Thin Layer Chromatograms of Tire Extracts
Developed in Toluene: Acetone (8:2)

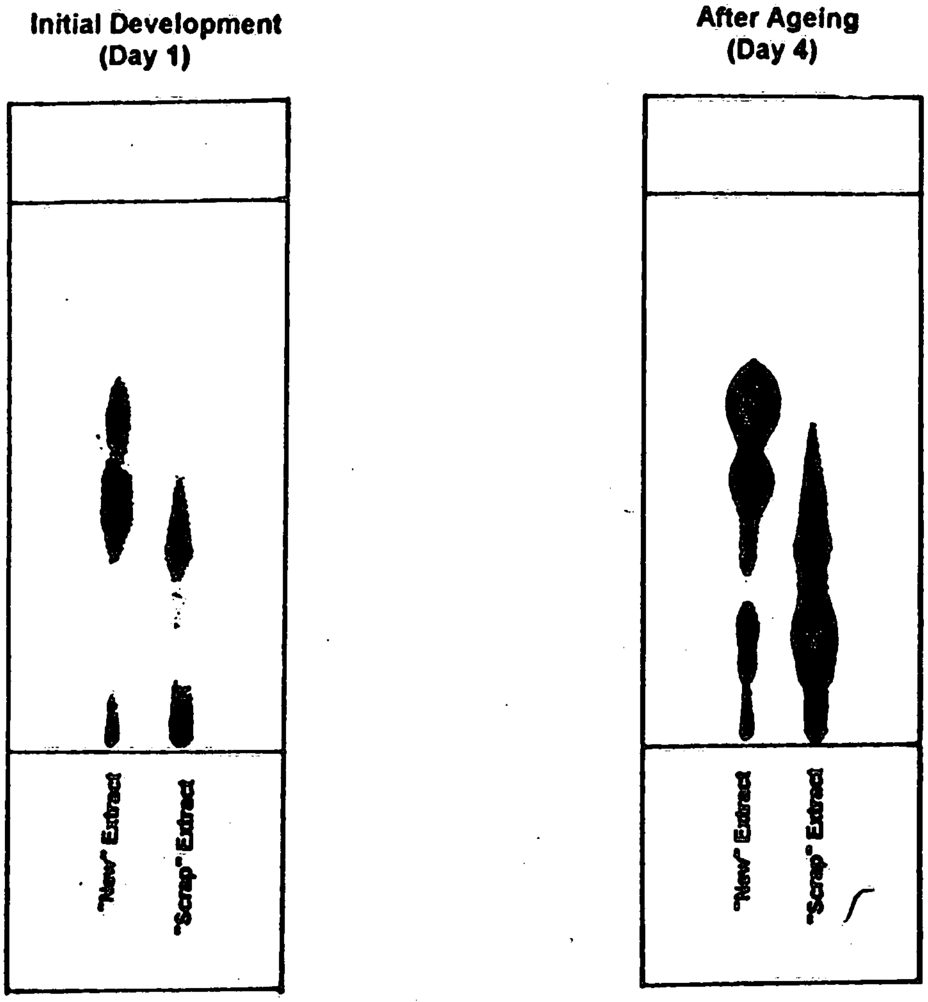
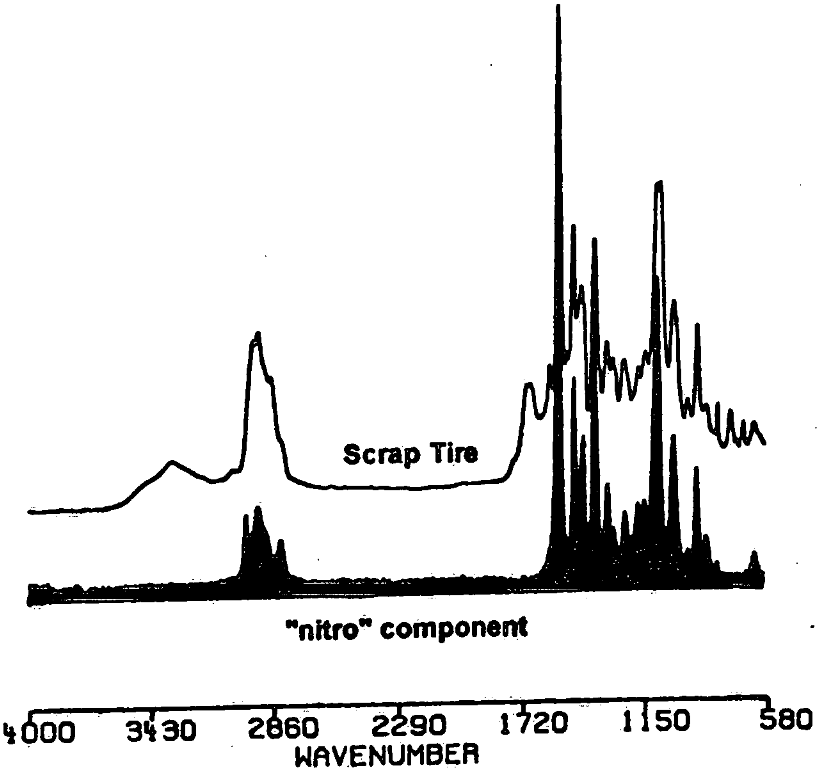


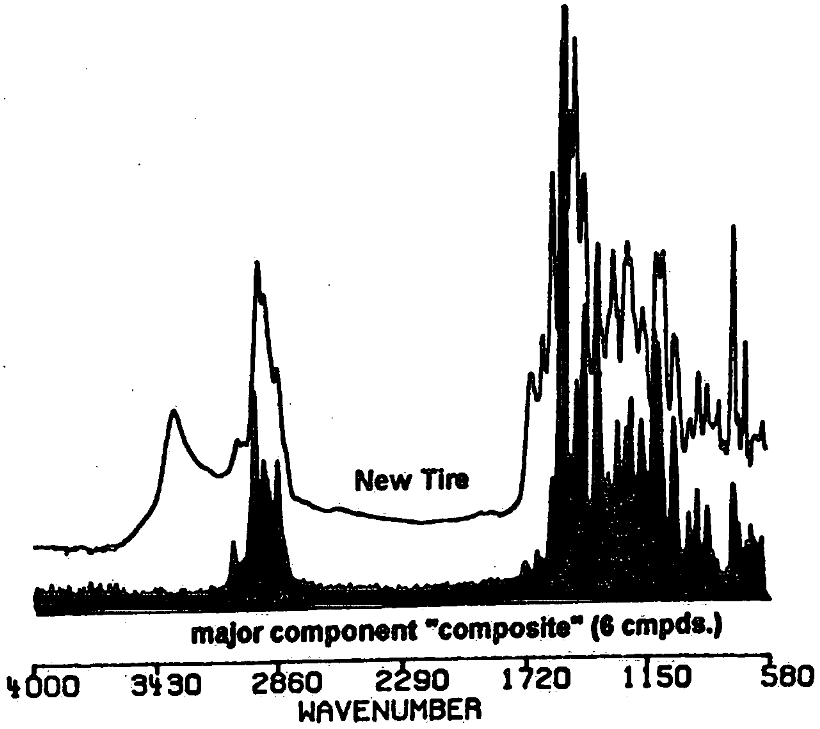
Figure 1

Figure 2 Comparison between GC-IR major component(s) and Total Extract IR

Scrap Tire Extract and unidentified major component



New Tire Extract and major components



FTIR Transmission Spectra of "Scrap" Tire Fractions

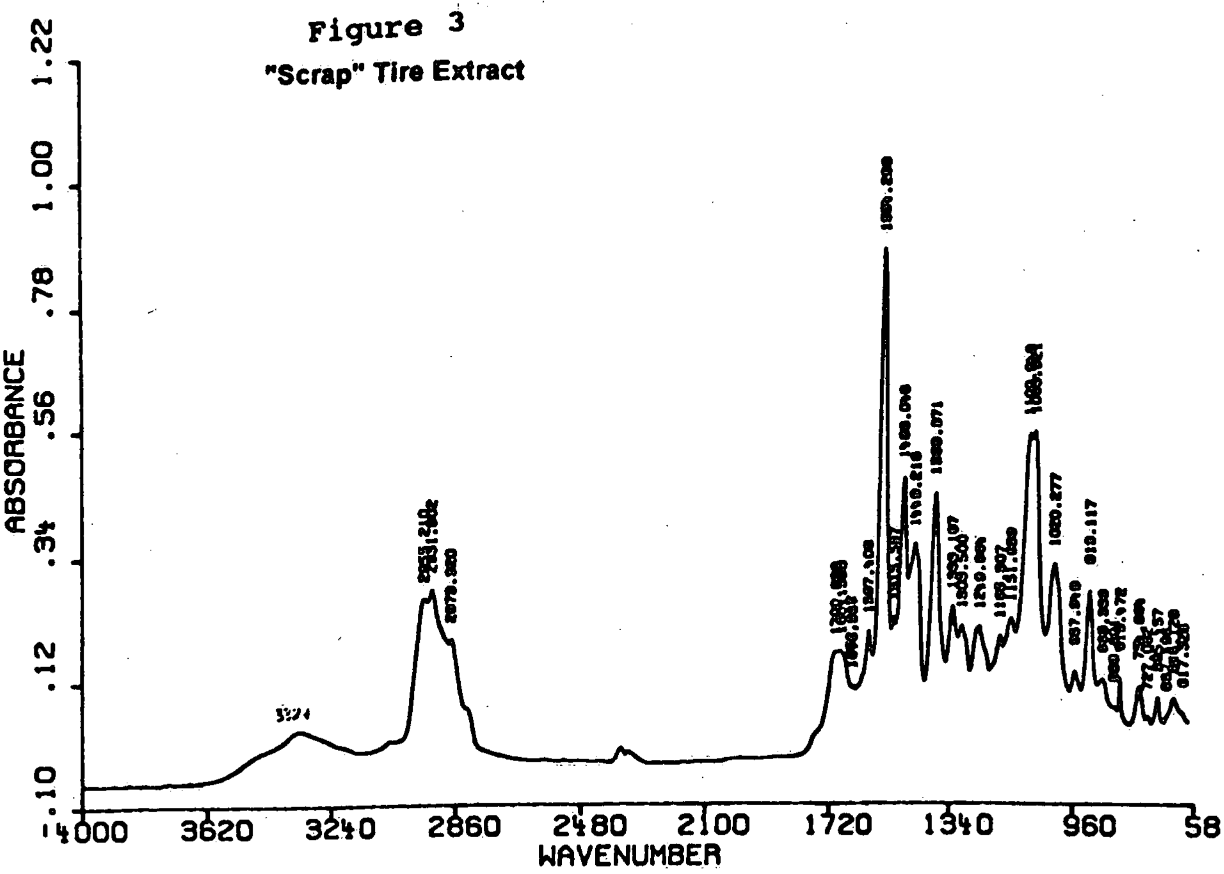


Figure 3
"Scrap" Tire Extract

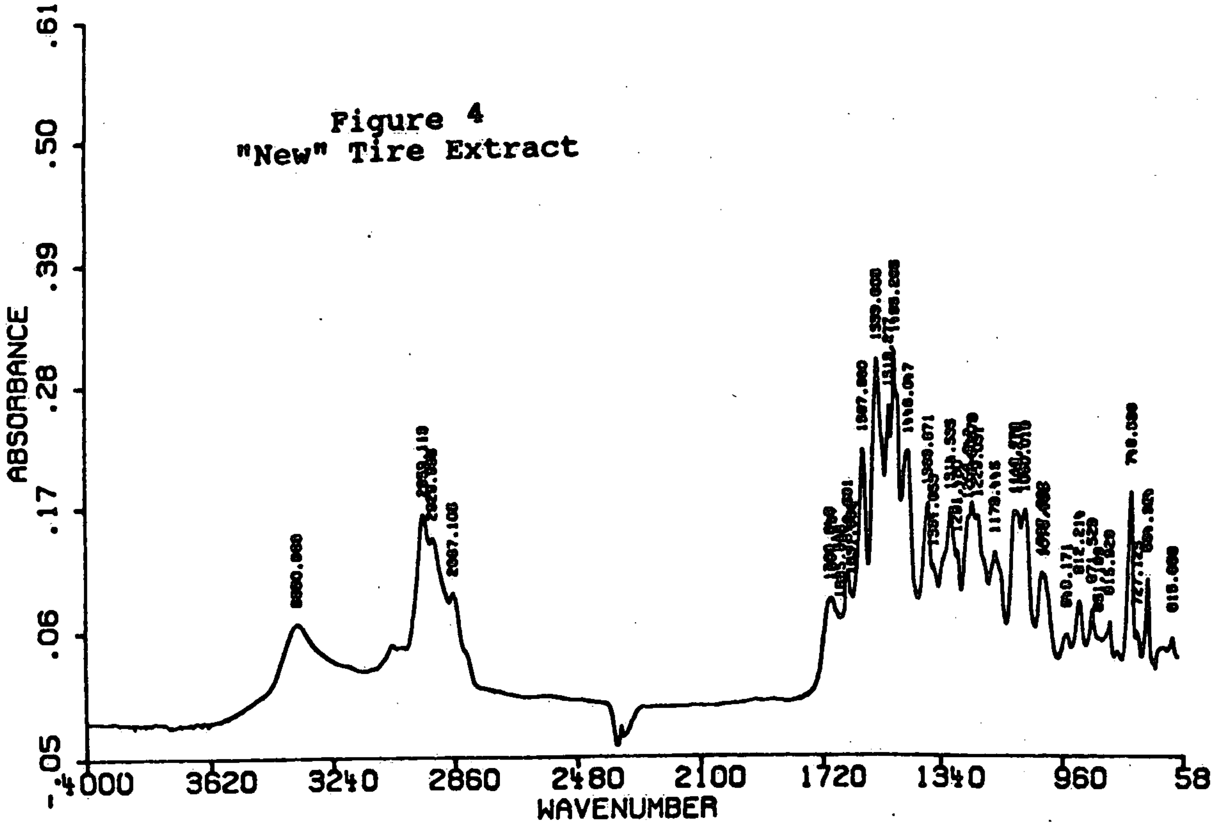
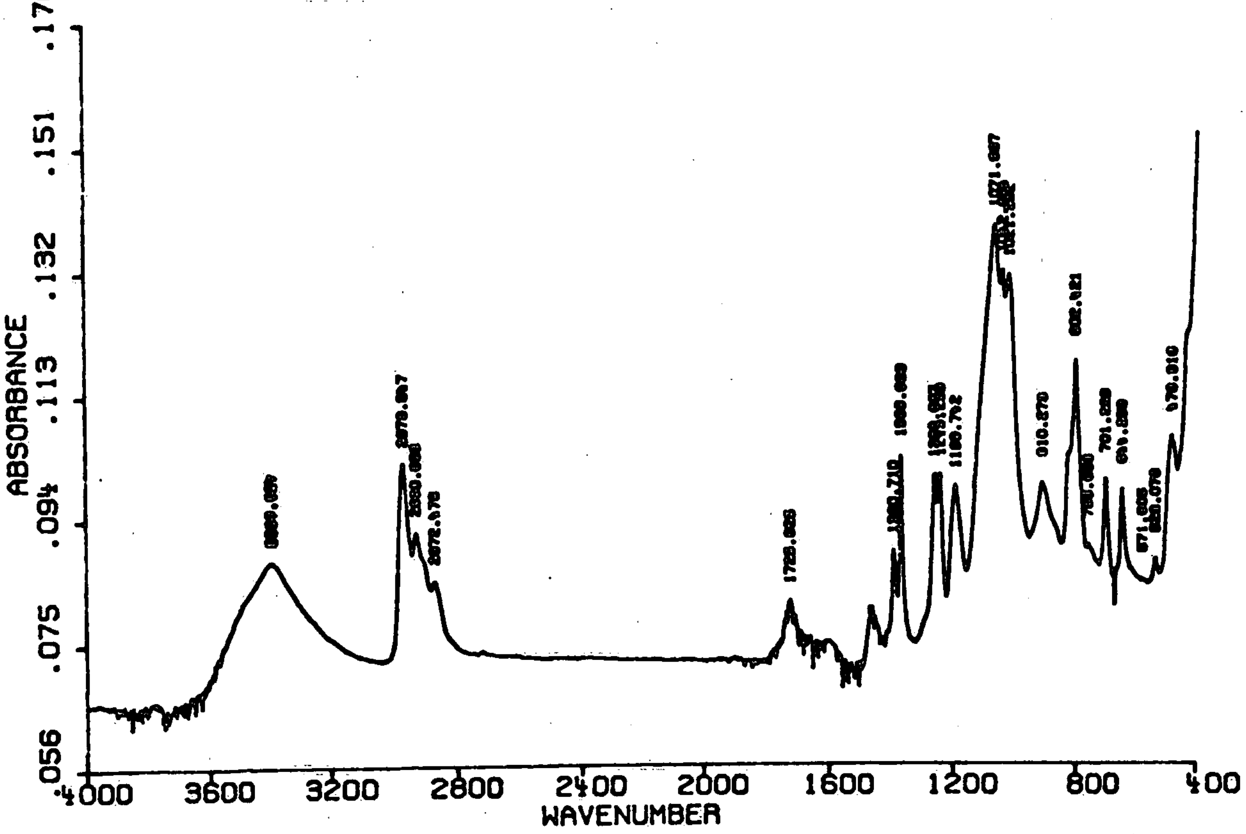


Figure 4
"New" Tire Extract

Figure 5
"Control" Extract



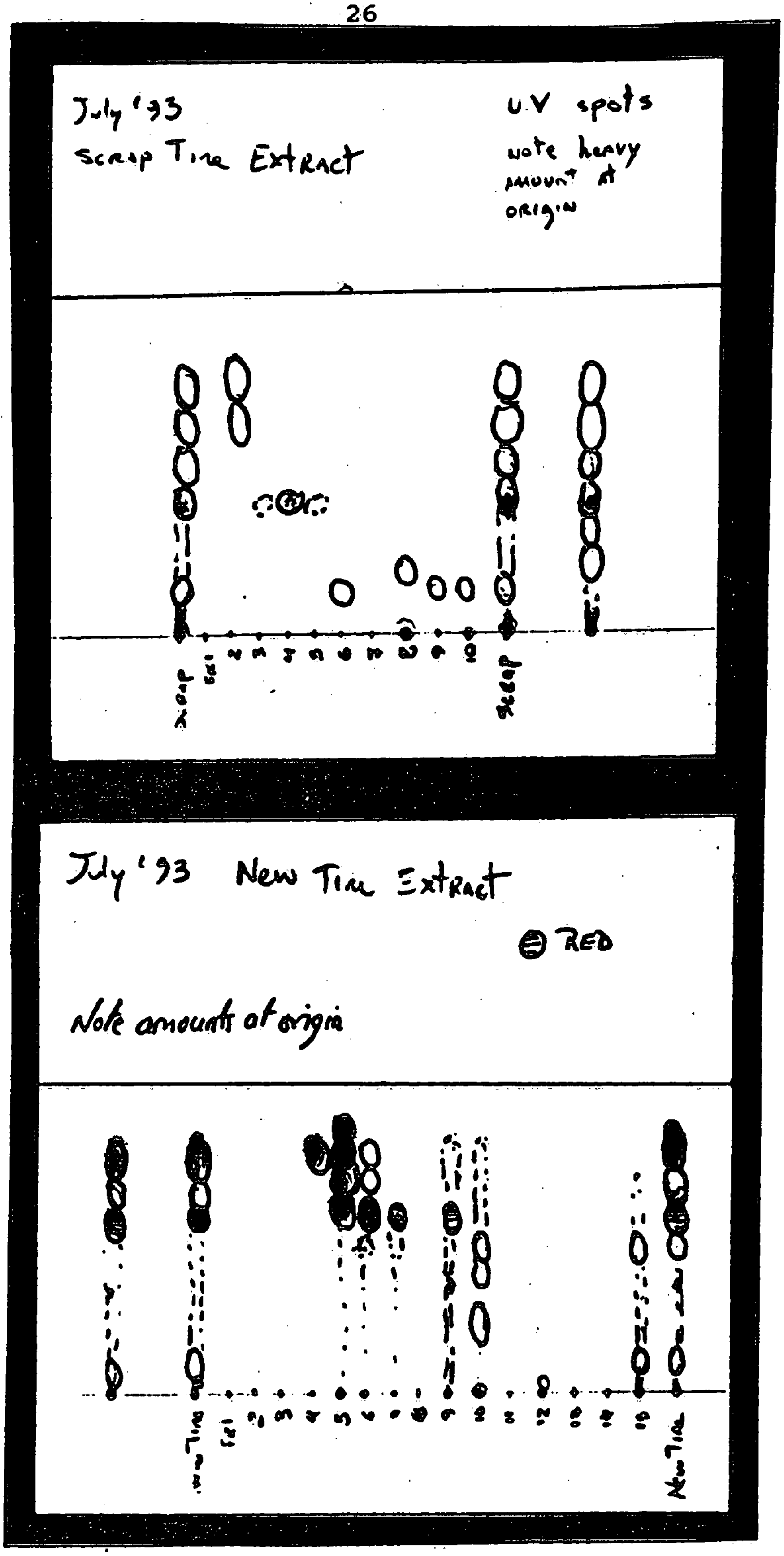


Figure 6 : TL Chromatograms of Leachate Extract Fractions

Figure 7 GC/FT-IR chromatograms of tire extracts and control
Gram-Schmidt Reconstructions (retention times not normalized)

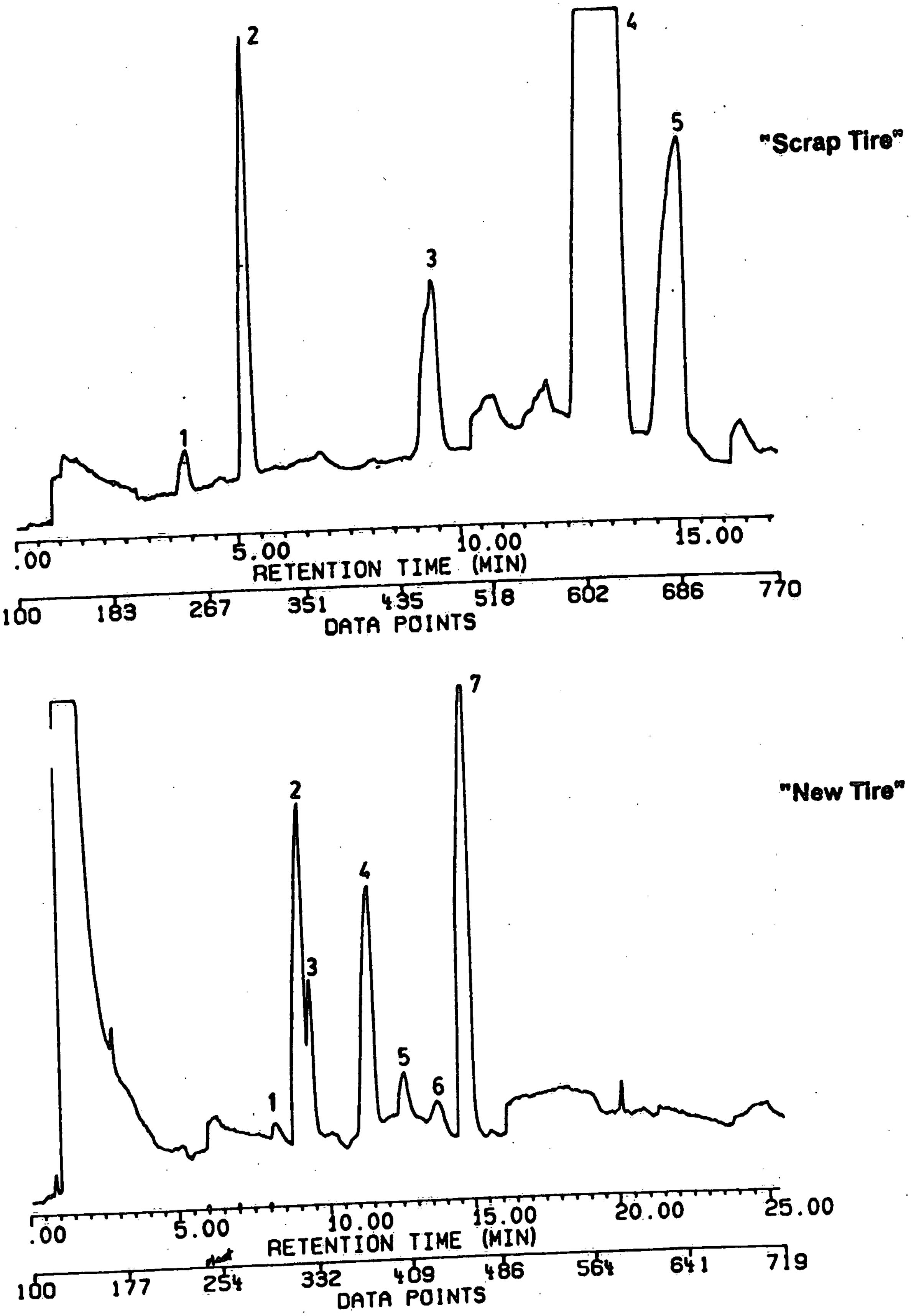


Figure 7

(Continued)

GC/FT-IR chromatograms of tire extracts and control

Gram-Schmidt Reconstructions (retention times not normalized)

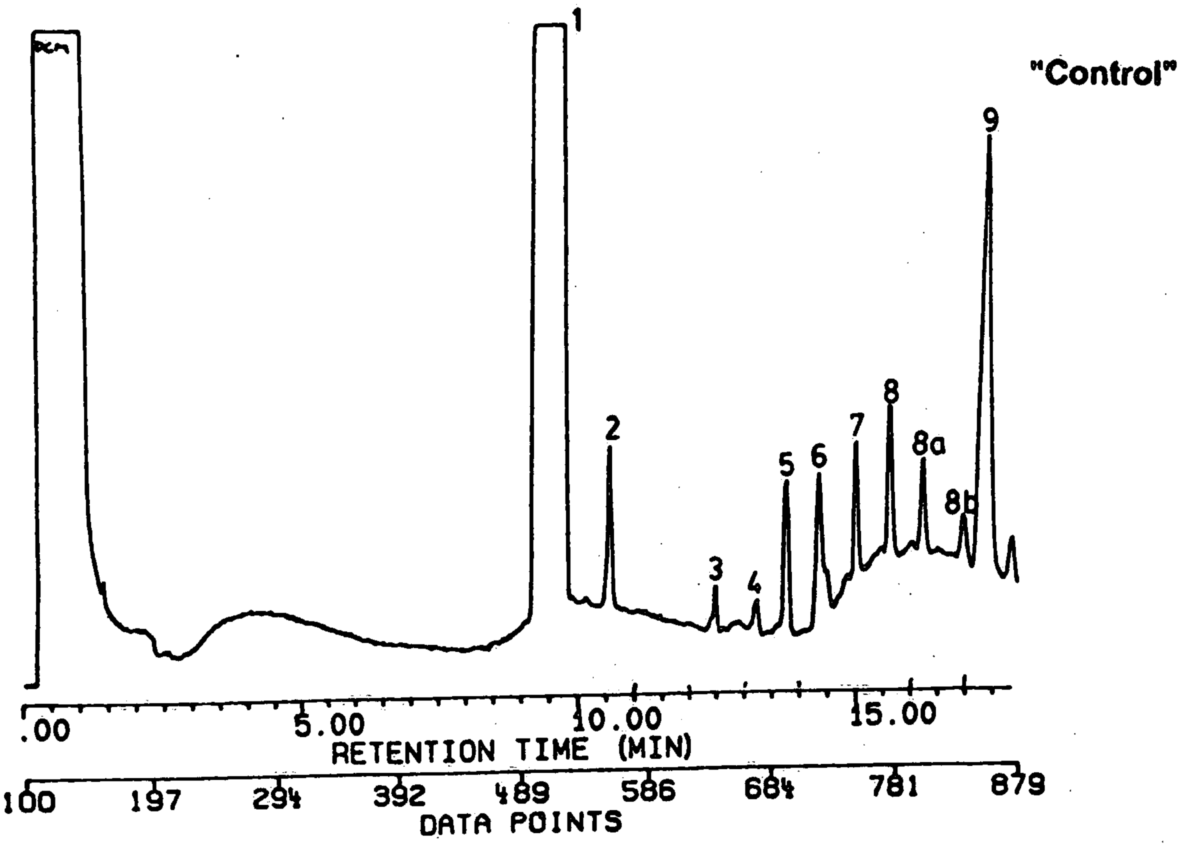
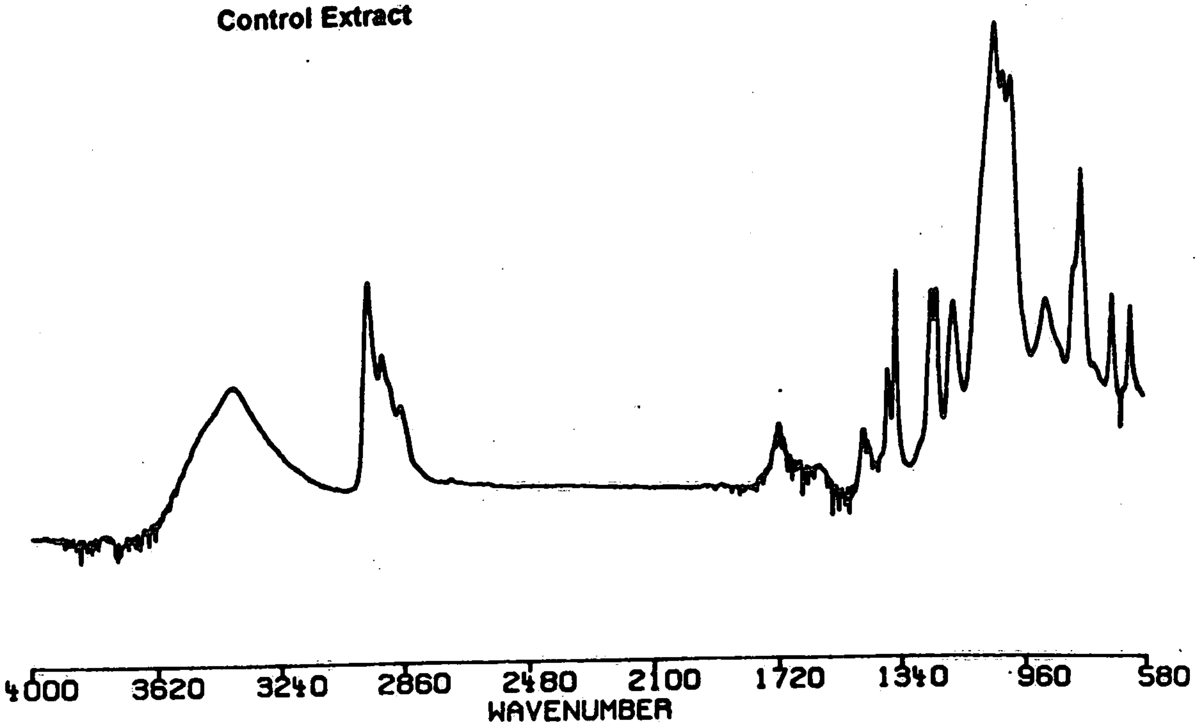


Figure 8 :Thin film Transmission IR spectra of Control Extract and Ivory Extract

Control Extract



Ivory Extract

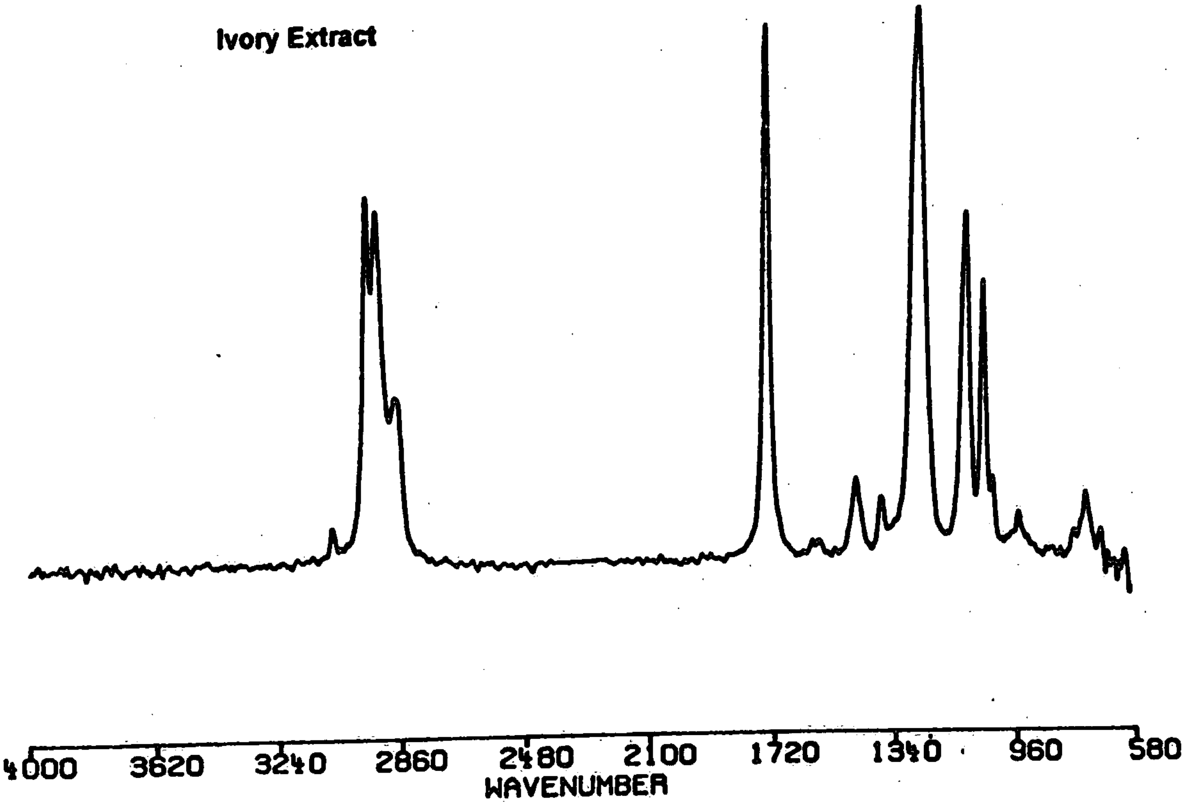


TABLE I : Summary of TLC Examination of Large-Sample Extracts

Fresh		Aged*	
Rf Value	Colour	Rf Value	Colour
<u>"Control"</u>			
No visible spots			
<u>"Scrap" Tire</u>			
-	-	0.20	red-orange
-	-	0.26	brown
-	-	0.58	light brown
-	-	0.68	yellow
0.73	yellow	-	-
<u>"New" Tire</u>			
-	-	0.19	red-orange
0.26	grey-green	-	-
-	-	0.25	brown
0.30	brown	-	-
0.42	blue-grey	-	-
0.45	orange	-	-
0.50	violet	-	-
0.57	orange	-	-
-	-	0.61	brick
0.71	yellow	-	-
0.79	brown	-	-
-	-	0.81	brown
0.86	light brown	-	-

* "Aged" refers to an approximate 72 h exposure to the atmosphere

TABLE II : Tire Fractionation and UV/VIS Information

Fraction #	Eluent	UV/VIS peaks (nm)	Comments
"Scrap" Tire			
1	Benzene	254	colourless
2	Benzene	265 (shoulder)	coloured
3	Ethyl Acetate	286	colourless
4	Ethyl Acetate	295	colourless
5	Ethyl Acetate	296	coloured
6	Acetonitrile	338 (broad)	slightly coloured
7	Acetonitrile	295 (shoulder)	slightly coloured
8	Isopropanol	290-340 (broad)	coloured
9	Isopropanol	320 (broad shoulder)	slightly coloured
10	iPrOH/Water (3:1)	broad shoulder	colourless
11	iPrOH/Water (2:1)	broad shoulder	colourless
12	iPrOH/Water (2:1)	316 (broad)	coloured

continued...

TABLE II : continued

"New" Tire

1	Hexane	254 (small)	
2	Hexane/ Benzene	224, 254	
3	Benzene	254 (trace)	
4	Benzene	284 (large)	Lt. orange
5	Benzene/ DCM	222, 280	Brown
6	DCM	276	Orange
7	DCM	270-275 (shoulder)	
8	DCM/ Acetonitrile	274 (small)	
9	Acetonitrile	288	Yellow-orange
10	Acetonitrile/ iPrOH	212, 285 (shoulder)	
11	Isopropanol	204	
12	Isopropanol	230, 285, 618	Blue
13	iPrOH/Water	620 (small)	Lt. blue
14	iPrOH/Water	220 (broad)	
15	iPrOH/Water	220, 350 (shoulder)	Lt. brown

TABLE III : GC/FTIR Characterization and Identification Summary of Principle Components of Large-Sample Extracts

Retention Time (min)	Estimate of % contribution (w/w) to total GC/FTIR components	Characterization / Identification* Summary
"Control"		
9.4	90	Carboxy compound (orthocarbonate)
10.70	1	**Di-allyl phthalate**
12.45	< 0.5	Methyl siloxane polymer
13.20	< 0.5	Methyl siloxane polymer
13.77	< 0.5	Methyl siloxane Polymer
14.38	1	Carboxy compound (orthocarbonate)
15.00	1	Methyl siloxane polymer
15.65	1	Methyl siloxane polymer
17.45	5	Phthalate compound
"New" Tire		
9.65	20.6	Amine (N-dialkyl analine derivative)
9.97	3.2	Hydrocarbon (olefin/aromatic)
12.10	13.2	**Diphenylamine**
14.10	63.0	**Morpholinothio-benzothiazole**
"Scrap" Tire		
10.15	0.9	Amine (N-dialkyl analine derivative)
11.16	8.5	Carboxy compound (orthocarbonate)
14.25	6.7	**Morpholinothio-benzothiazole**
18.00	66.0	Nitro compound (Nitro-ether derivative
19.20	18.0	Nitro compound (isomer of major peak)

* Compounds highlighted in bold print have been tentatively identified by spectral library search routines.

TABLE IV **Structural Features of Principle Extract Components as Determined by GC/FT-IR**

New Tire peaks	Rt min.	Significant peaks (cm-1)	Correlation
Peak 1	9.57	3730 - 3705	OH stretch
		3627 - 3601	NH / maybe OH
possibly an amino alcohol phenyl compound		3016	CH (C=C type)
		2974 - 2915 - 2861	CH aliphatics
		1471 - 1436	C=C type
		1292 - 1240	C-O ether type
		1125 - 1061	C-N type
		669	C-Cl possibly
Peak 2	9.65	3412	N-H stretch
		3066 - 3030	C-H aromatic
possibly an N-alkyl aniline derivative		2974 - 2932 - 2872	C-H aliphatic
		1650 - 1607	C=C ring
		1463	C=C ring
		1162	C-N type
		741	aromatic ortho or C-Cl
Peak 3	9.97	3626	O-H stretch
		3049	C-H olefinic
olefinic alcohol		2987 - 2881	C-H aliphatics
		1673	C=C olefin type
		1366	C-O alcohol type
Peak 4	12.10	3434	N-H stretch
		3055	C-H aromatic
diphenyl amine		1596 - 1501	C=C aromatic ring
		1302	C-N phenyl amine
		746 - 692	C-H aromatic ring
Peak 5	12.8	3650	O-H stretch
		3062 - 3022	C-H aromatic/olefin
possibly an olefinic ester		2965 - 2930 - 2884	C-H aliphatic
		1720	C=O (weak/conjugated)
		1605	C=C aromatic ring
		1479	C=C aromatic ring
		1363 - 1308 - 1255	C-O ester
		1161	C-O phenolic
		749	C-Cl or ortho aromatic
Peak 6	13.6	3050 (weak)	C-H aromatic
		2974 - 2904 - 2858	C-H aliphatic
olefin		1478	C=C aromatic/olefinic
Peak 7	14.10	3074	C-H aromatic
		2974 - 2920 - 2863	C-H aliphatic
morpholinothio benzothiazole		1597 - 1446	C=C aromatic ring
		1539	C=N

Table IV (continued)

Scrap Tire peaks	Rt min.	Significant peaks (cm-1)	Correlation
Peak 1	10.15	Same as New Tire Peak 3	same
olefinic alcohol			
Peak 2	11.16	3725	O-H stretch
alkoxy alcohol		2980	C-H aliphatic
		1369	O-H (def)
		1236 - 1193	C-C skel. vib.
		1080	C-O ether
Peak 3	14.25	*Same as New Tire Peak 7*	*same*
morpholinothio benzothiazole			
Peak 4	18.0	2994 - 2936 - 2830	C-H aliphatic
		1556	NO2 asy. stretch
nitro ether		1485 - 1442	C-H asy. def
		1388	NO2 sym. stretch
		1098	C-O ether type
Peak 5	19.2	*Same as Scrap Tire Peak 4*	*same*
nitro ether			
Control Extract peaks			
Peak 1	9.4	*Same as Scrap Tire Peak 2*	*same*
Peak 2	10.7	3079	C-H aromatic
Di-allyl phthalate		2957	C-H aliphatic
		1750	C=O ester
		1270	C-O phenyl ester
		1124 - 1066	C-H aromatic bend
Peak 3	12.45	2969	C-H aliphatic
Alkyl tetrasiloxane		1267	Si-CH3
		1089	C-O ether / Si-O-Si
		1032	C-O or Si-O-Si
		810	Si-O siloxane
Peak 4	13.2	*Same as Control Peak 3*	*same*
Peak 5	13.77	*Same as Control Peak 3*	*same*
Peak 6	14.38	2982 - 2941	C-H aliphatic
Alkyl orthocarbonate		1087 - 1045	C-O ether
Peak 7	15.0	*Same as Control Peak 3*	*same*

Table IV (continued)

Control Extract peaks	Rt min.	Significant peaks (cm-1)	Correlation
Peak 8	15.65	2981 - 2860	C-H aliphatic
		1265	Si-CH3
		1090 - 1044	C-O or Si-O-Si
		804	Si-O siloxane
Peak 9	17.45	2976 - 2938 - 2885	C-H aliphatic
		1745	C=O
		1467 - 1390 - 1369	C=C aromatic
		1270	C-O phenyl ester
		1119	C-H aromatic bend
		1078 - 1036	C-O ether/alkoxy

TABLE V : Summary of GC/FTIR analysis of Tire Extract Fractions

Fraction #	Number of major peaks	Comments
"Scrap" tire		
1	11	C25 and greater hydrocarbons
2	5	Bulk of "scrap" tire compounds
3	3	Primarily nitro compounds
4	3	Residual nitro compounds
5	3	Traces of nitro compounds
6-9	No peaks	-
10	2	Unable to characterize
11	No peaks	-
12	10	Hydrocarbons, phthalates
"New" Tire		
1	No peaks	Broad hydrocarbon background
2	No peaks	
3	2	Possibly trace phthalates
4	1	Diphenylamine
5	7	Bulk of "New" tire compounds
6	1	Major nitro compound
7	3	Nitro compounds and unknown aromatic compound
8	No peaks	

(continued)

Table V (continued)

9	4	Nitro compounds
10	2	Traces of nitro compounds
11	No peaks	
12	7	Aliphatic hydrocarbons, phthalates
13	No peaks	
14	No peaks	
15	No peaks	

APPENDIX A

UV/VIS Spectra of Tire Extracts and Fractions

U.V/ Visible Spectroscopy of "Scrap" and "New" Tire Fractions

All measurements performed between 190 and 820 nm with 1 cm. cell in Acetonitrile or Dichloromethane

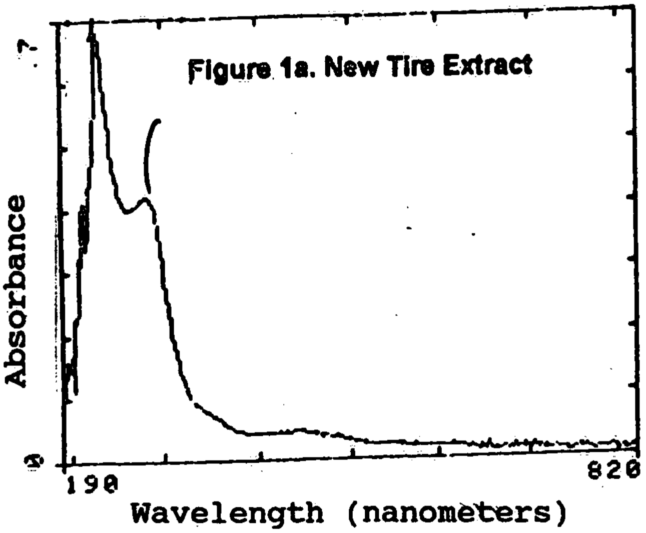


Figure 1a. New Tire Extract

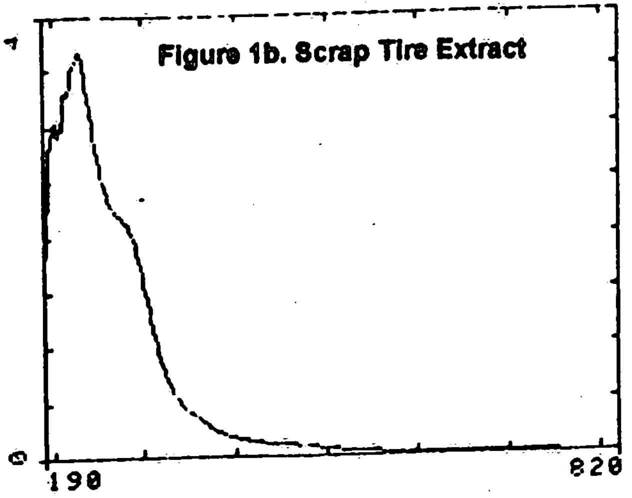


Figure 1b. Scrap Tire Extract

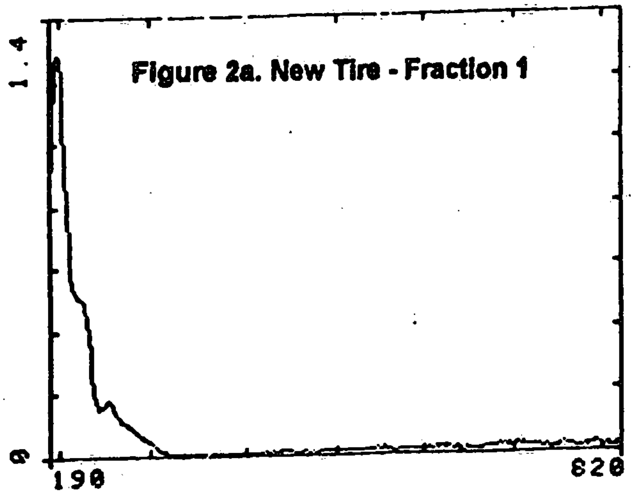


Figure 2a. New Tire - Fraction 1

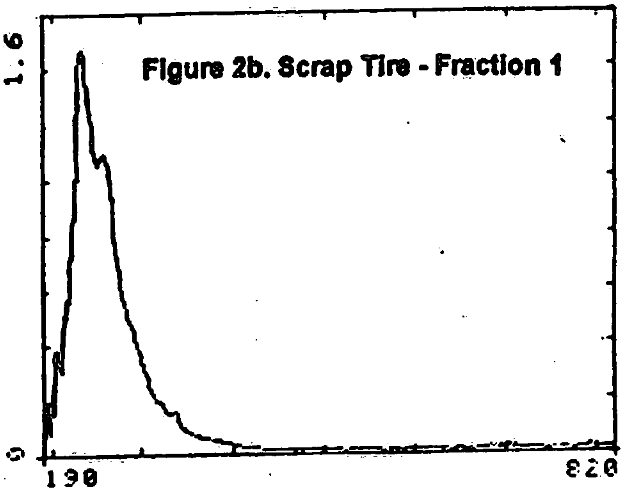


Figure 2b. Scrap Tire - Fraction 1

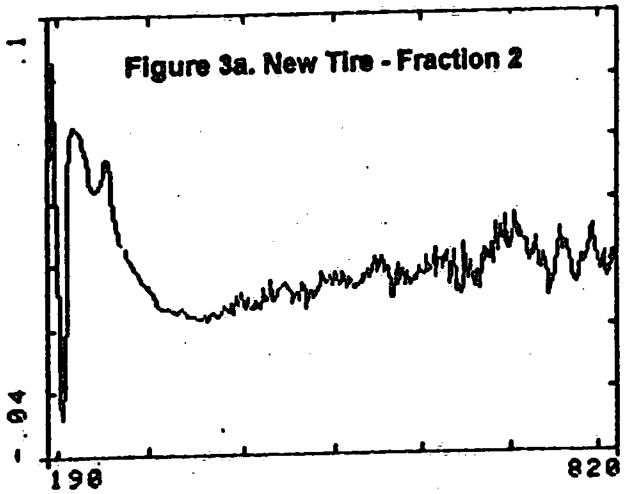


Figure 3a. New Tire - Fraction 2

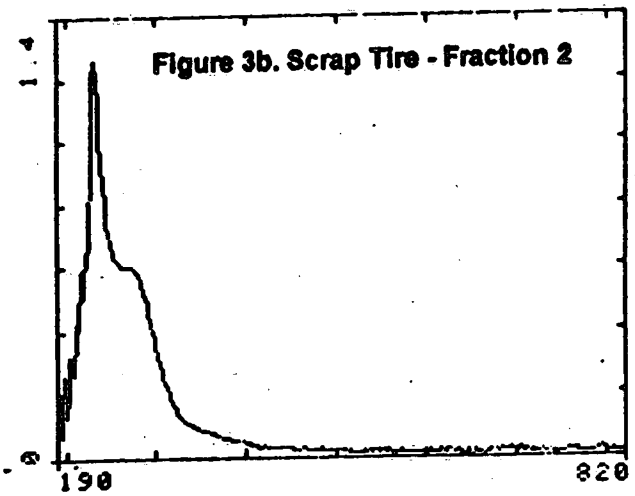


Figure 3b. Scrap Tire - Fraction 2

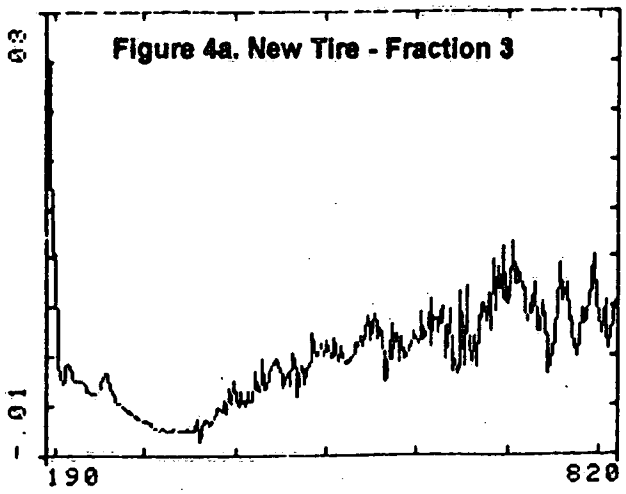


Figure 4a. New Tire - Fraction 3

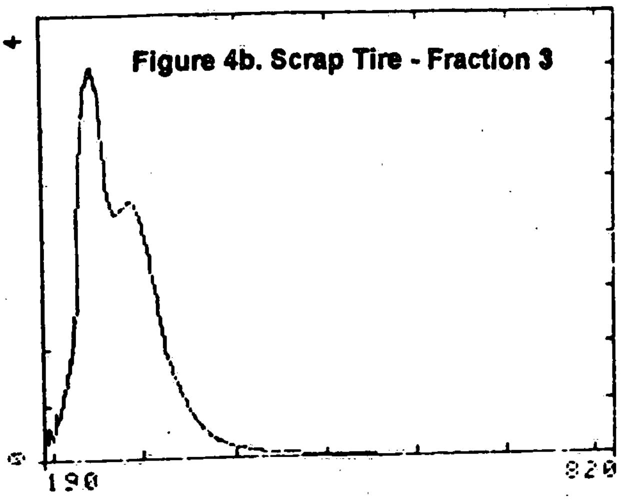


Figure 4b. Scrap Tire - Fraction 3

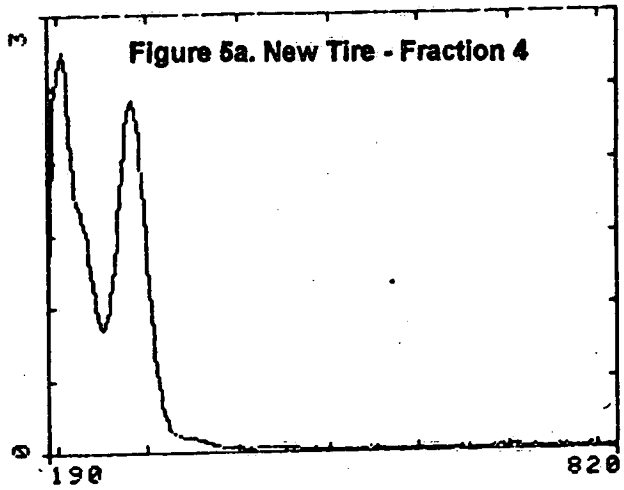


Figure 5a. New Tire - Fraction 4

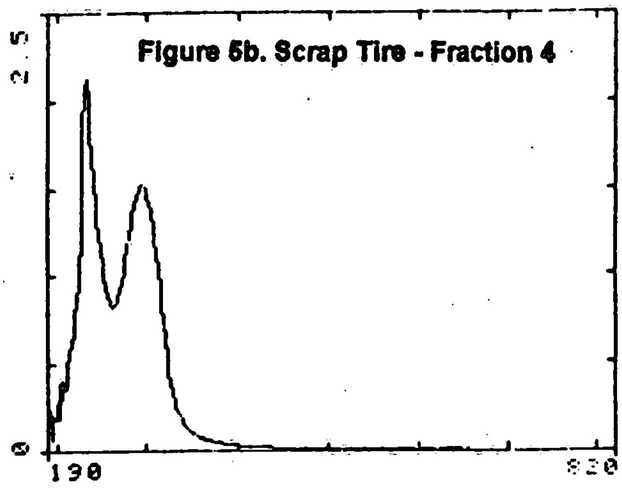


Figure 5b. Scrap Tire - Fraction 4

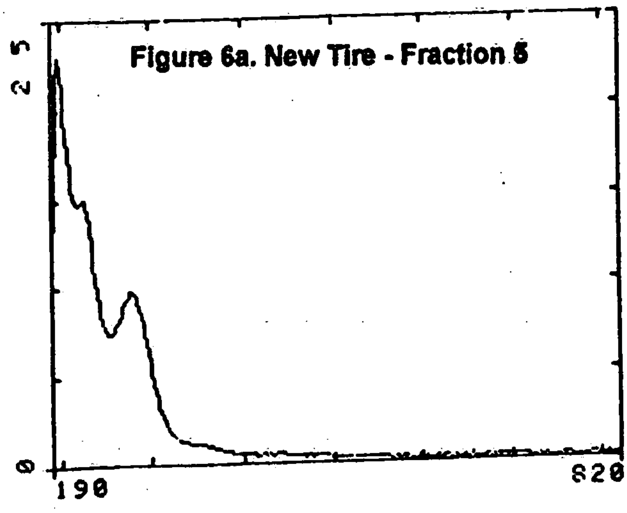


Figure 6a. New Tire - Fraction 5

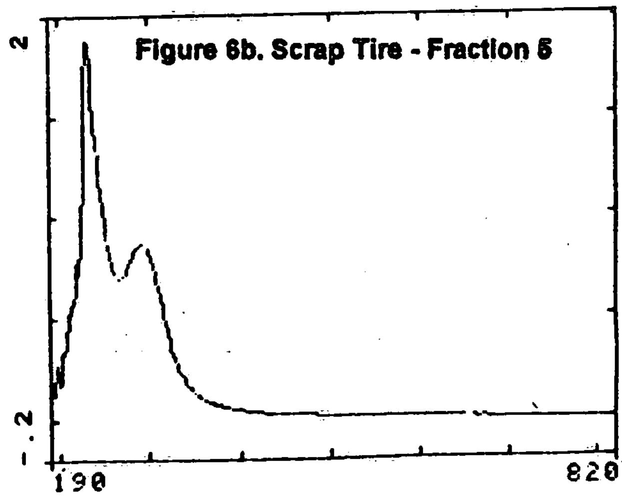


Figure 6b. Scrap Tire - Fraction 5

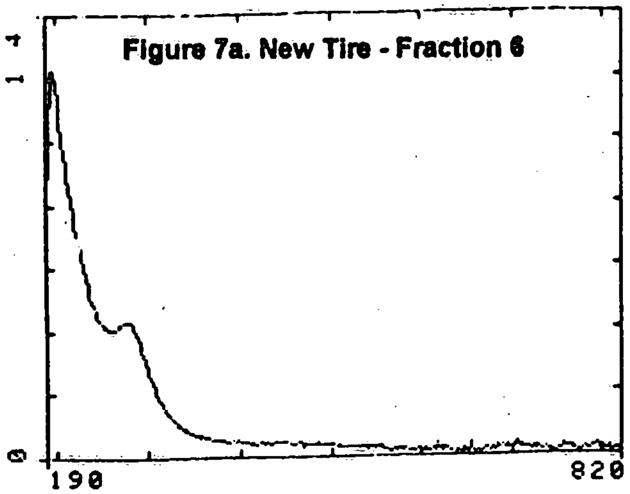


Figure 7a. New Tire - Fraction 6

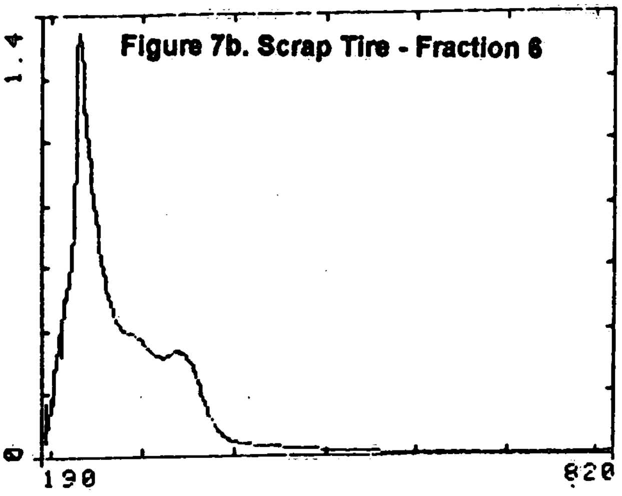


Figure 7b. Scrap Tire - Fraction 6

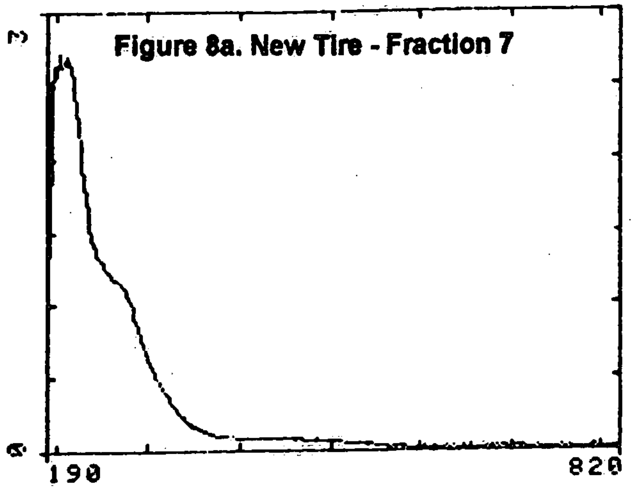


Figure 8a. New Tire - Fraction 7

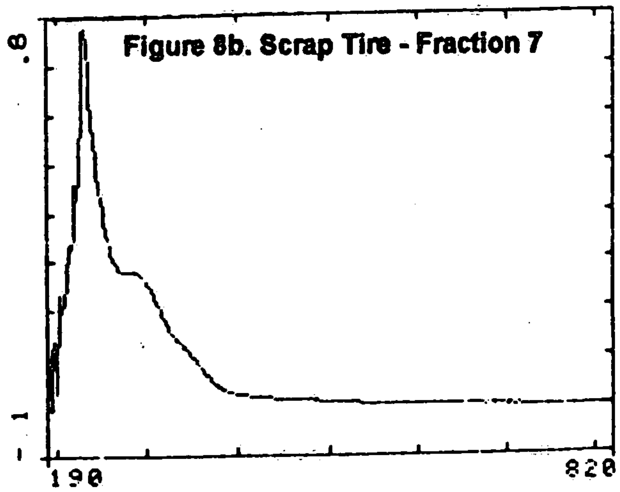


Figure 8b. Scrap Tire - Fraction 7

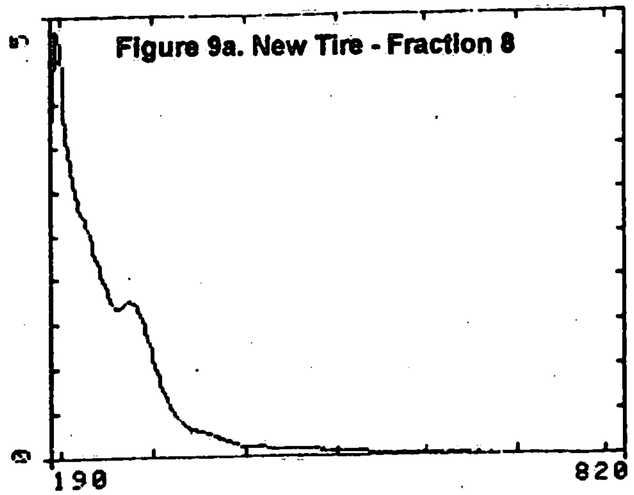


Figure 9a. New Tire - Fraction 8

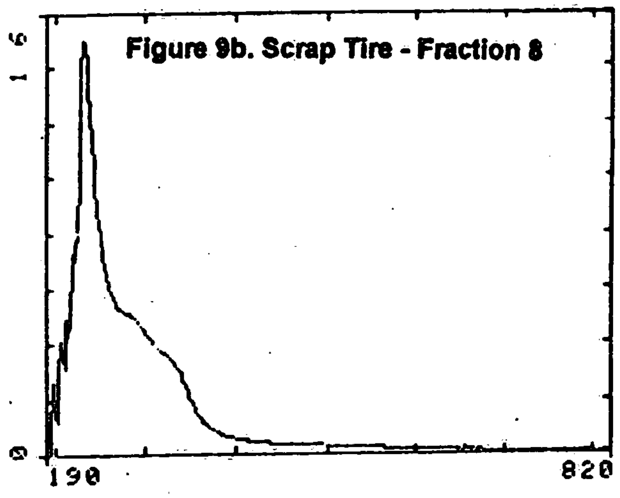


Figure 9b. Scrap Tire - Fraction 8

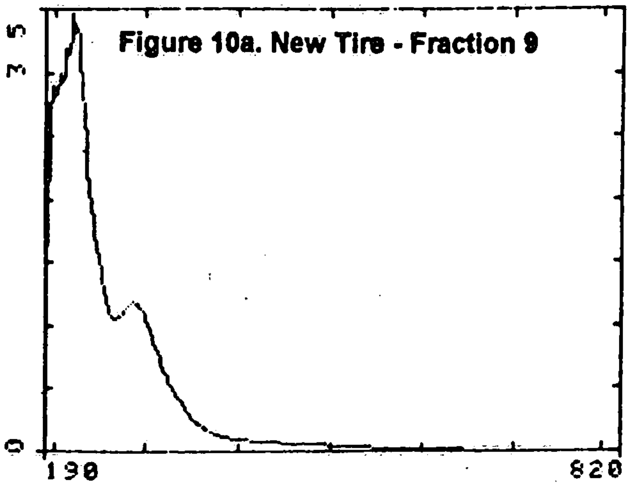


Figure 10a. New Tire - Fraction 9

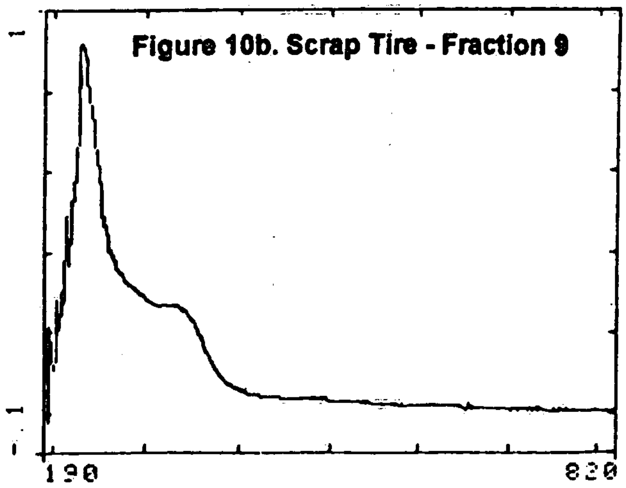


Figure 10b. Scrap Tire - Fraction 9

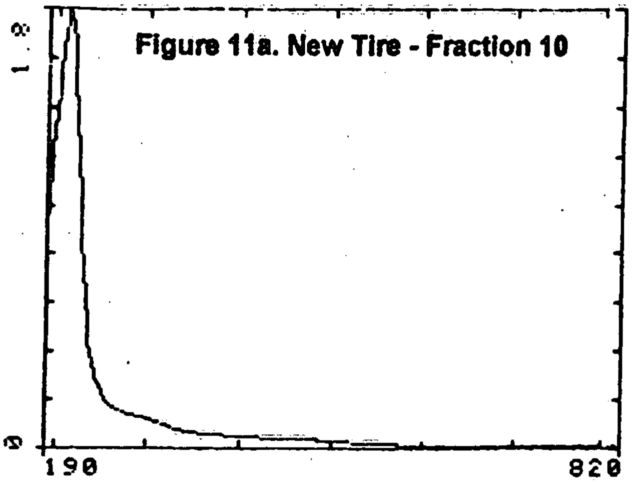


Figure 11a. New Tire - Fraction 10

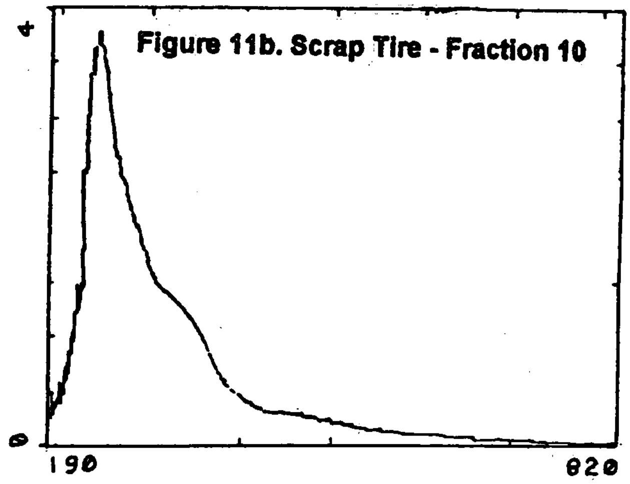


Figure 11b. Scrap Tire - Fraction 10

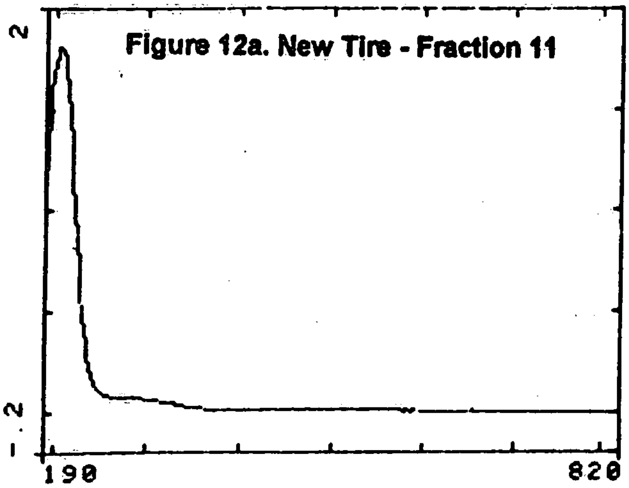


Figure 12a. New Tire - Fraction 11

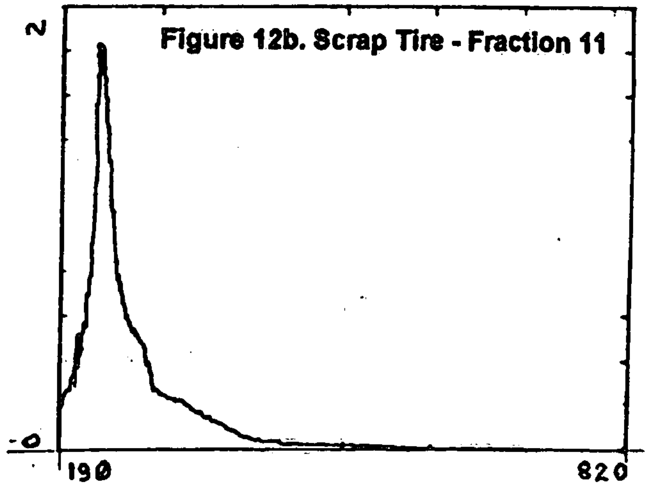


Figure 12b. Scrap Tire - Fraction 11

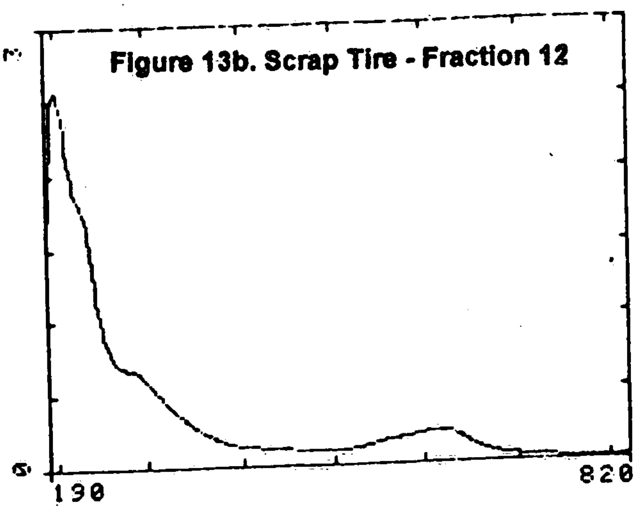


Figure 13b. Scrap Tire - Fraction 12

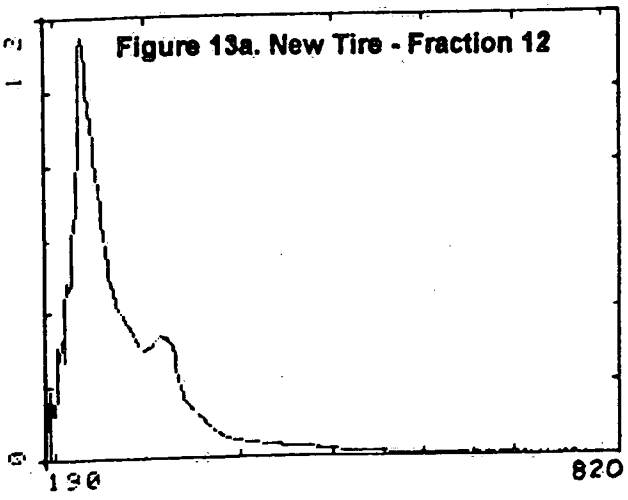
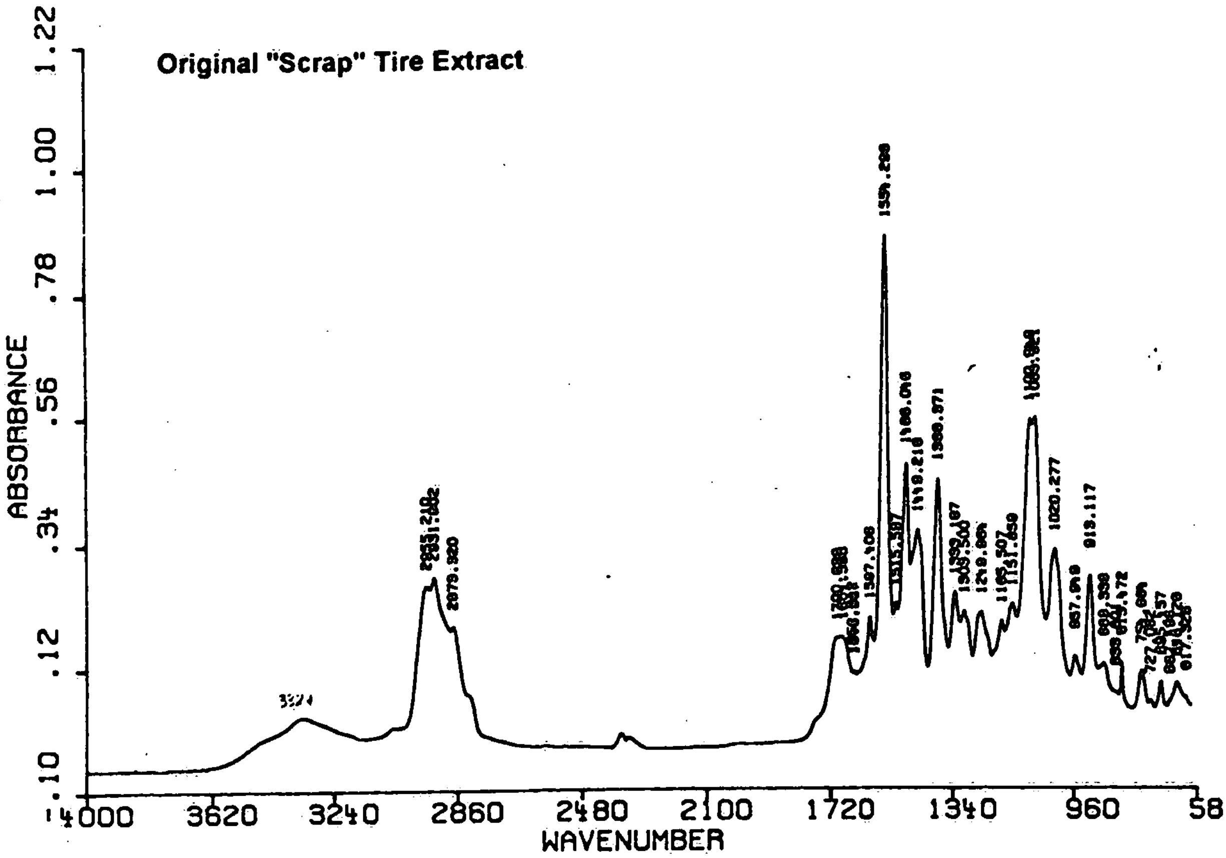


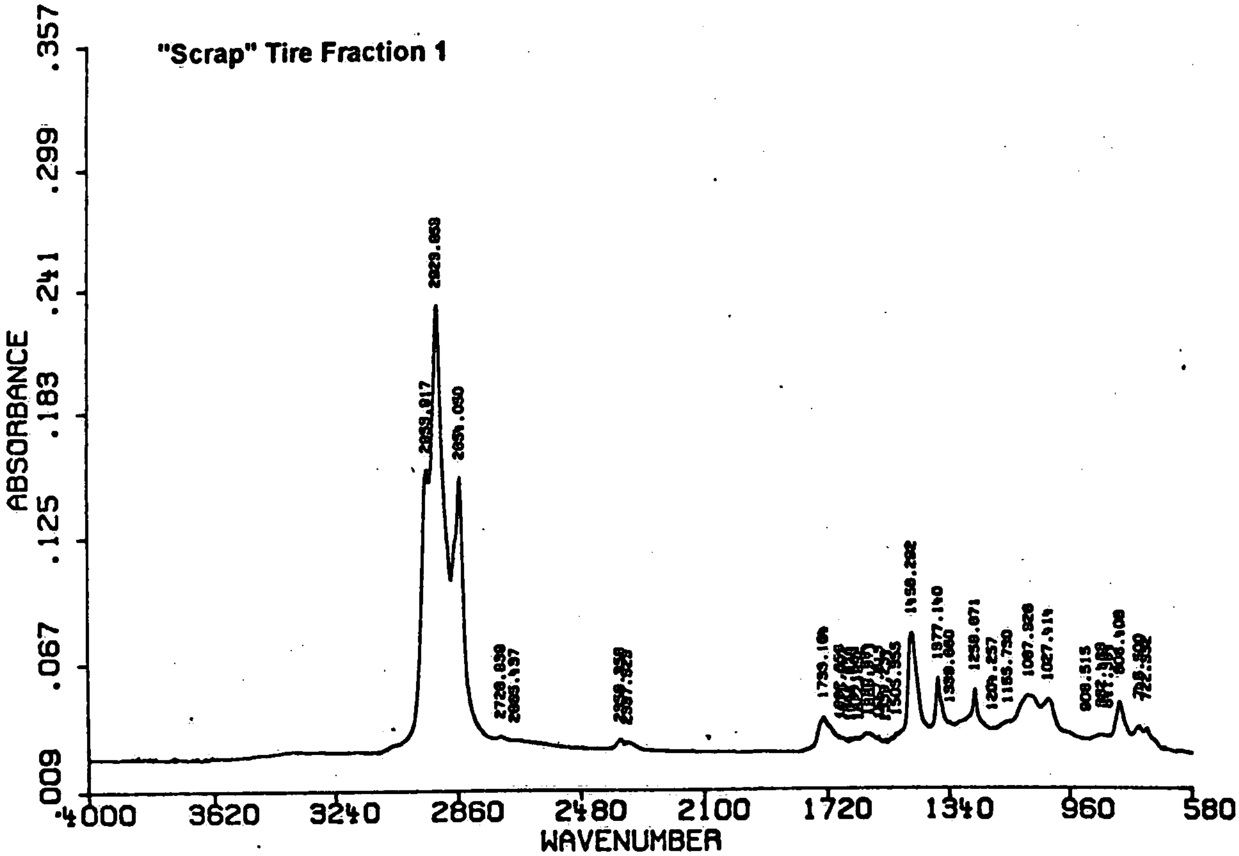
Figure 13a. New Tire - Fraction 12

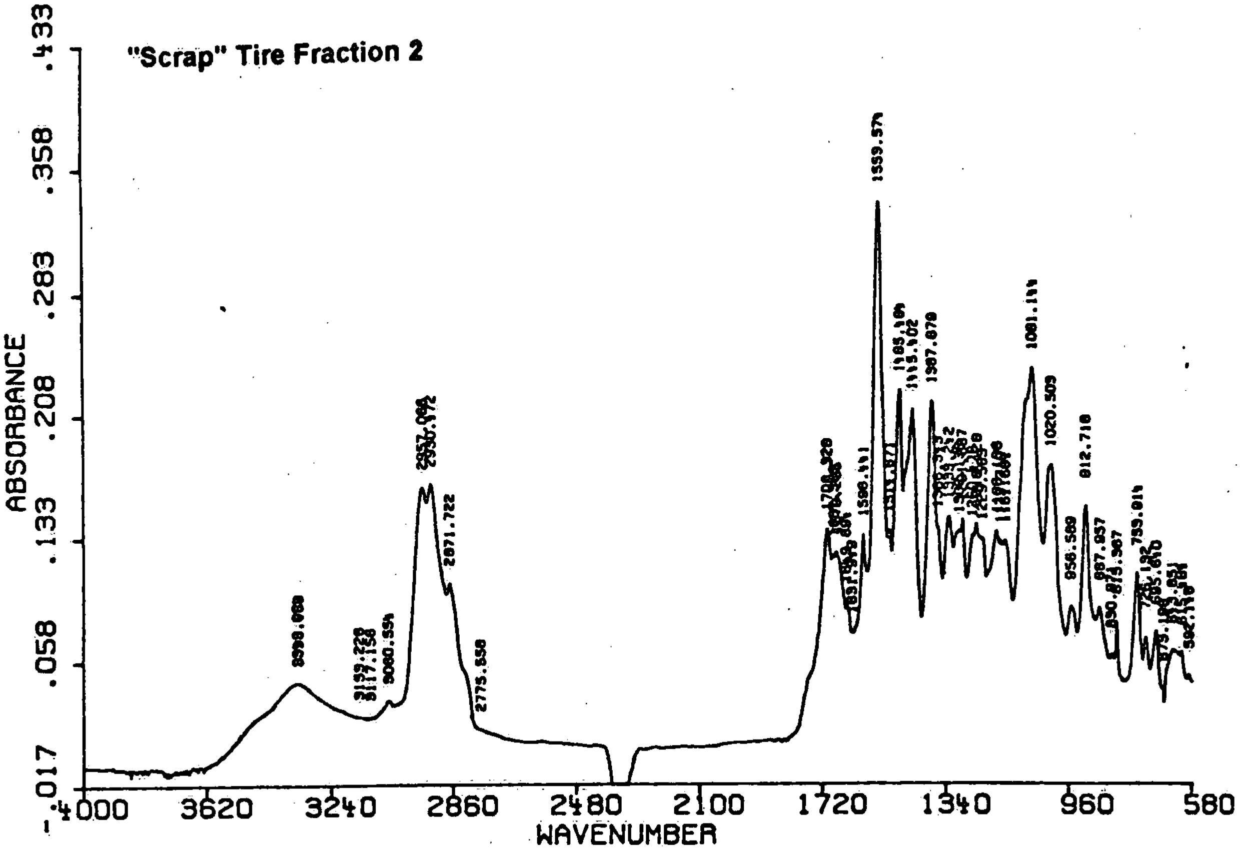
APPENDIX B

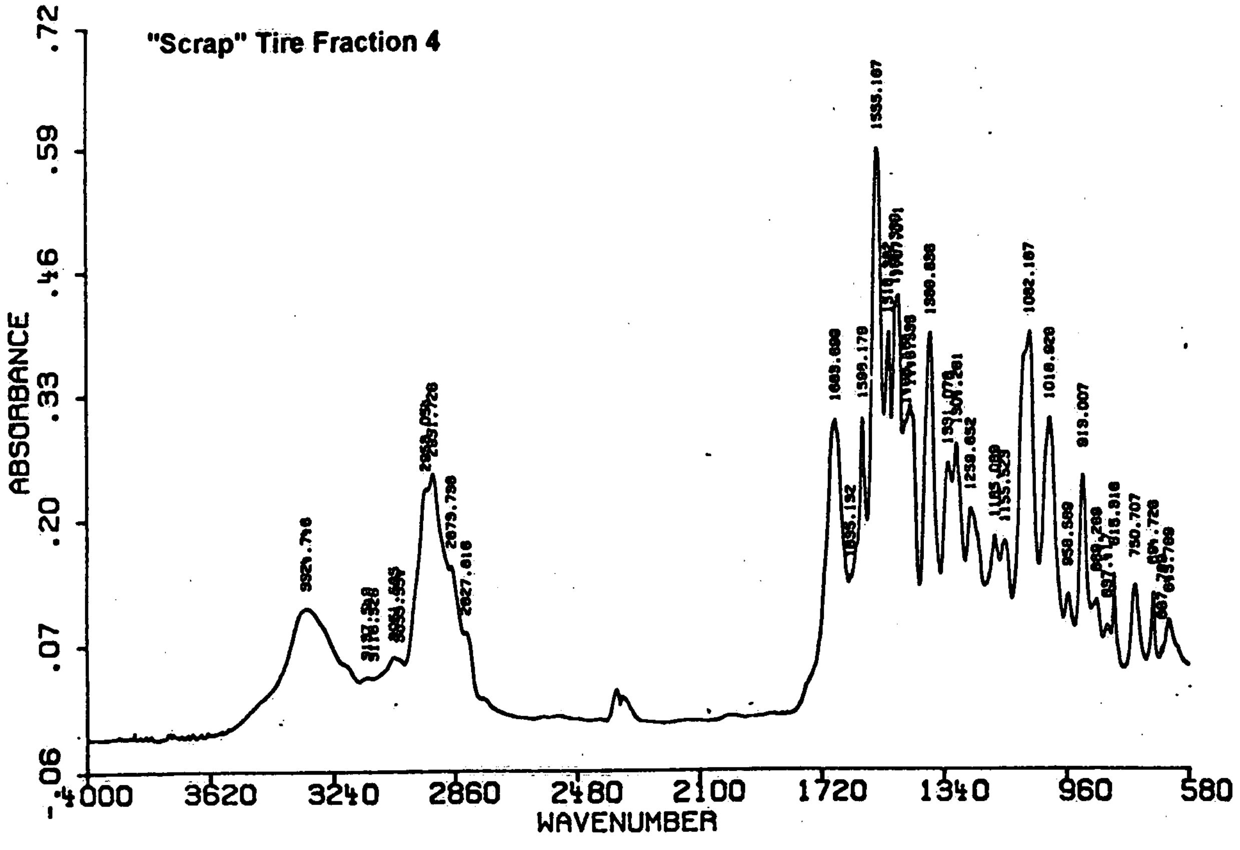
FTIR Spectra of Tire Extracts and Fractions

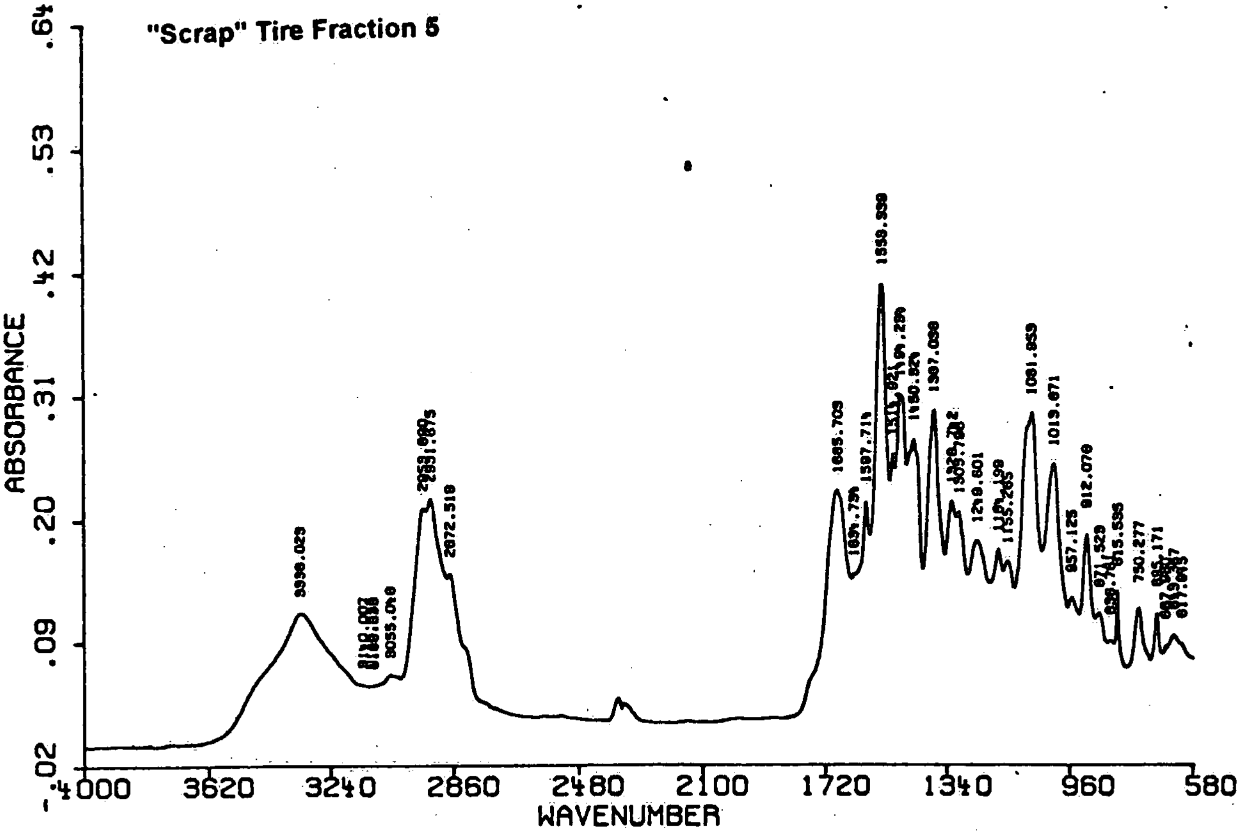
FTIR Transmission Spectra of "Scrap" Tire Fractions

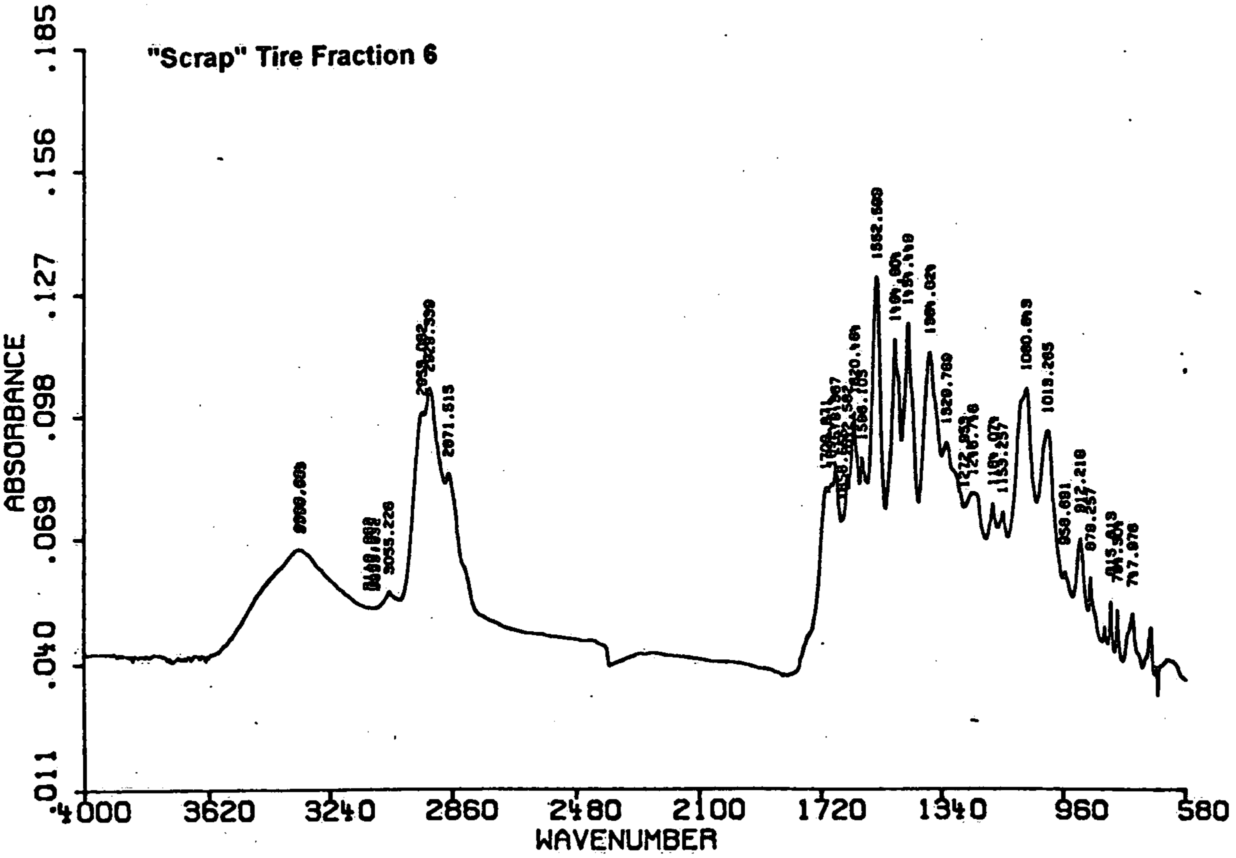


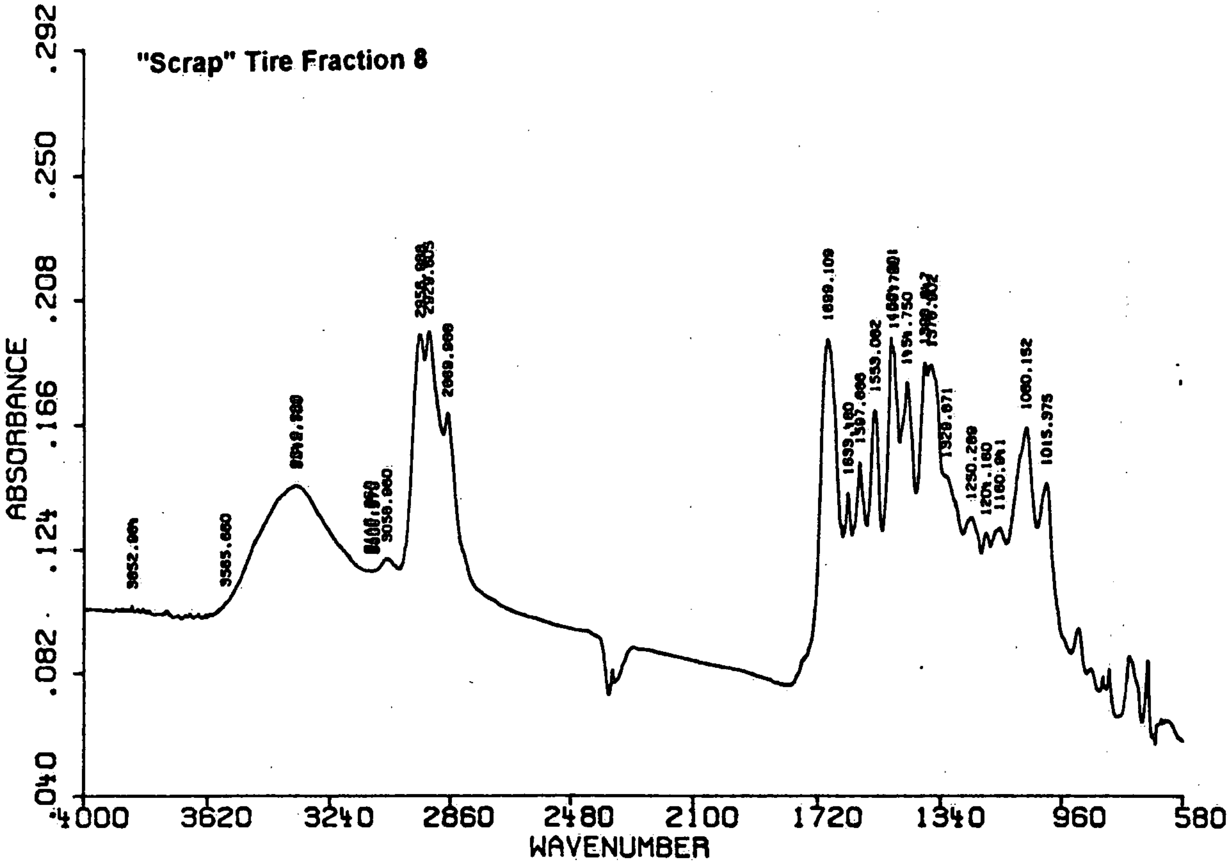


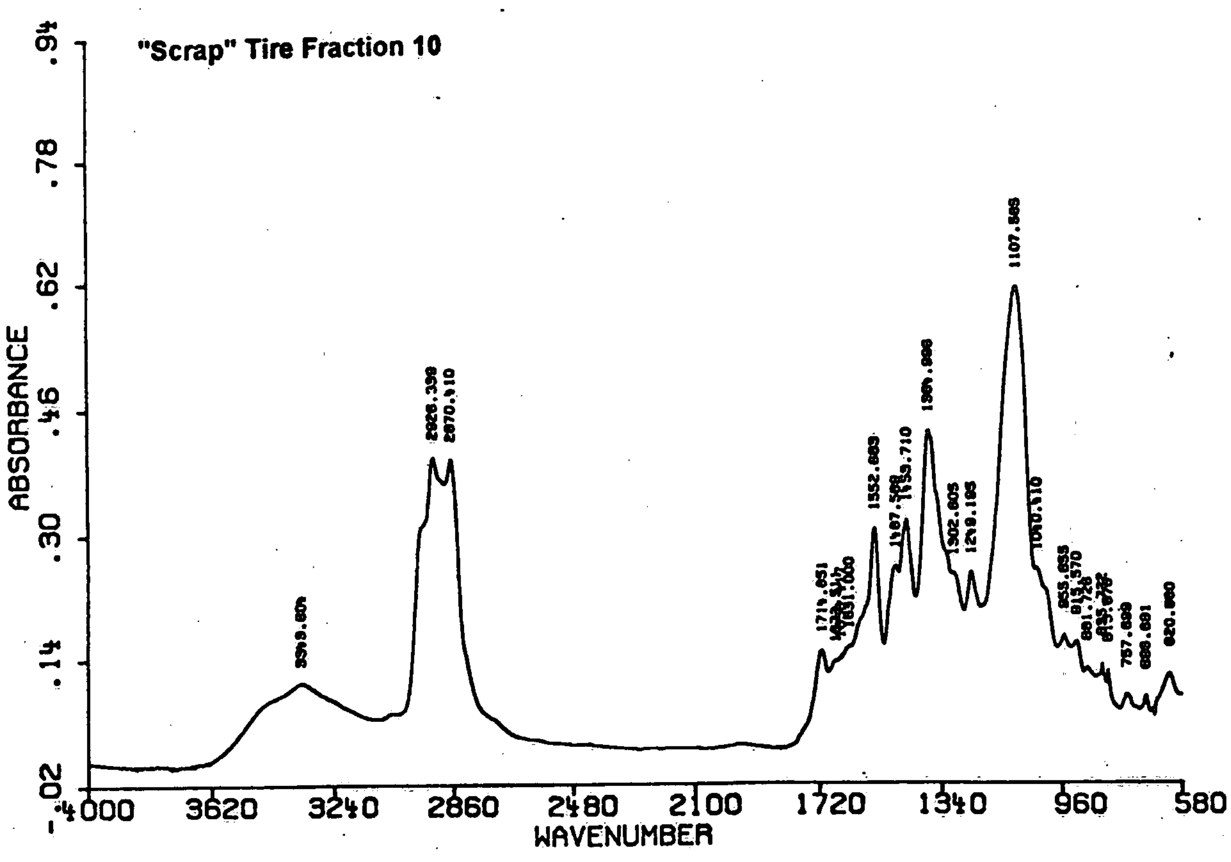

"Scrap" Tire Fraction 2
ABSORBANCE
.433
.358
.283
.208
.133
.058
-.017
4000
3620
3240
2860
2480
2100
1720
1340
960
580
WAVENUMBER
3398.068
3117.158
3060.554
2871.722
2775.558
1599.111
1559.576
1307.878
1081.118
1020.505
912.718
958.589
887.957
759.011

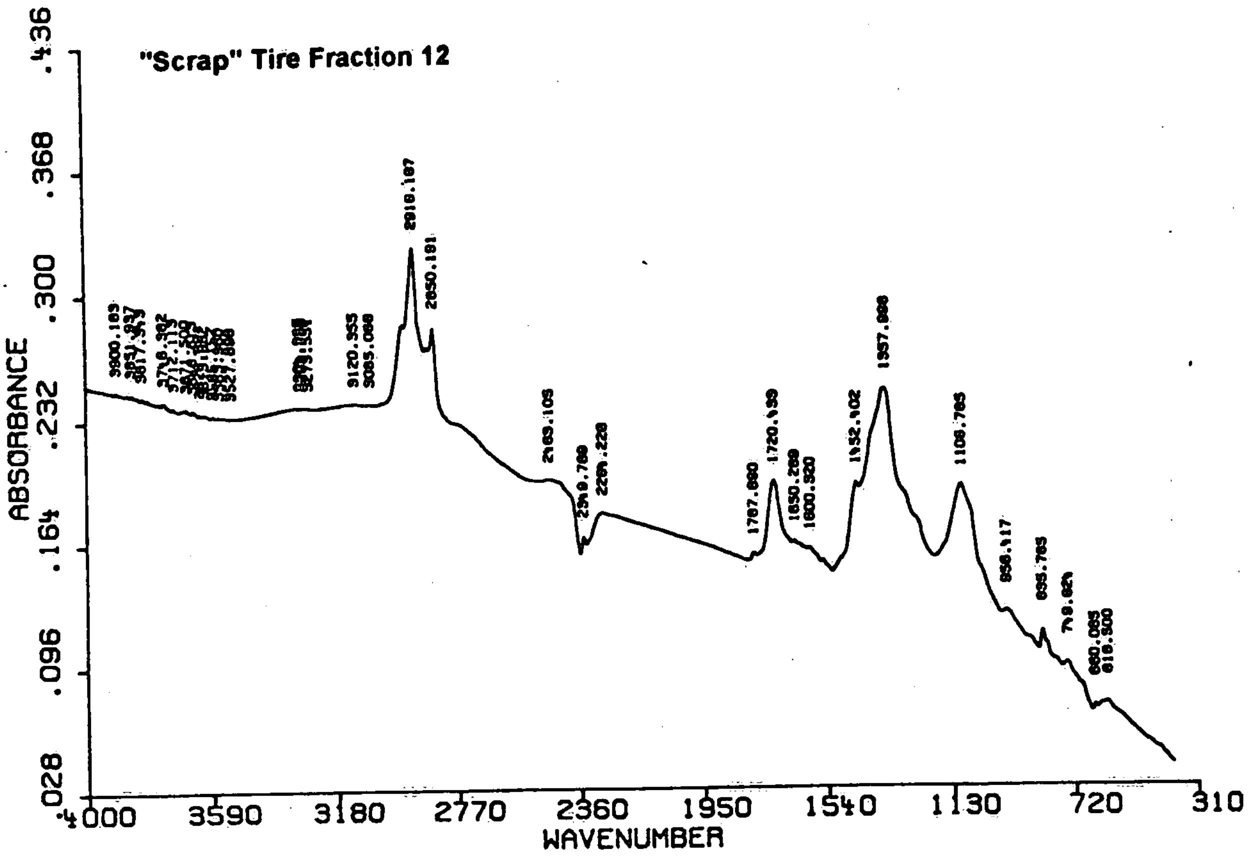

"Scrap" Tire Fraction 4
ABSORBANCE
.72
.59
.46
.33
.20
.07
-.06
4000
3620
3240
2860
2480
2100
1720
1340
960
580
WAVENUMBER
3324.716
2879.798
2827.618
1689.899
1599.178
1555.167
1309.898
1259.652
1082.167
1018.929
919.007
958.589
815.916
750.707


"Scrap" Tire Fraction 5
ABSORBANCE
.64
.53
.42
.31
.20
.09
-.02
4000
3620
3240
2860
2480
2100
1720
1340
960
580
WAVENUMBER
3055.018
2872.518
1685.703
1597.719
1559.939
1450.820
1387.098
1210.601
1155.265
1081.859
1019.671
957.125
912.078
815.535
750.277
695.171


"Scrap" Tire Fraction 6
ABSORBANCE
.185
.156
.127
.098
.069
.040
.011
4000
3620
3240
2860
2480
2100
1720
1340
960
580
WAVENUMBER
3055.226
2871.515
1586.103
1552.580
1320.760
1155.257
1080.849
1019.265
958.081
912.218
878.257
757.976


"Scrap" Tire Fraction 8

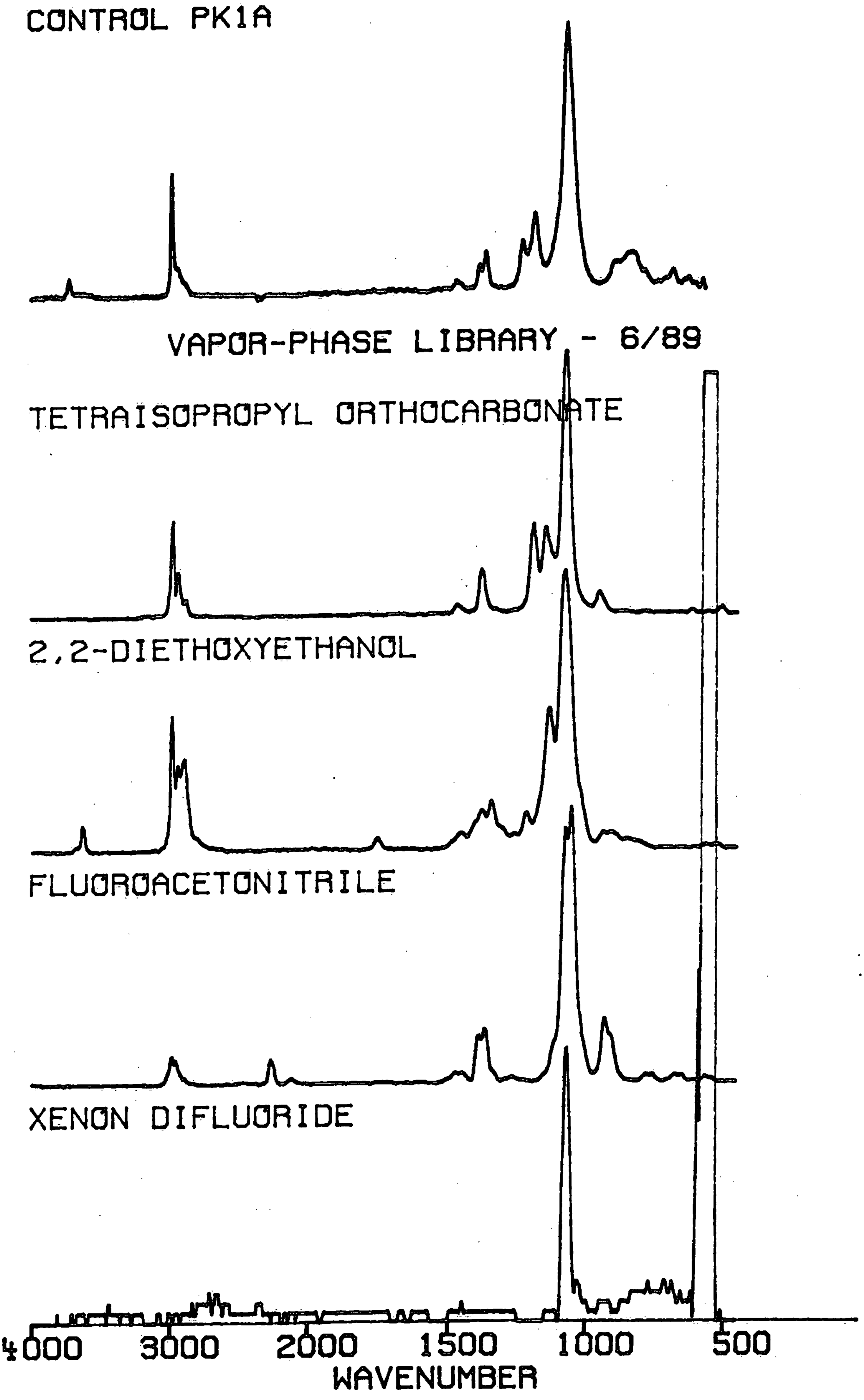

"Scrap" Tire Fraction 10

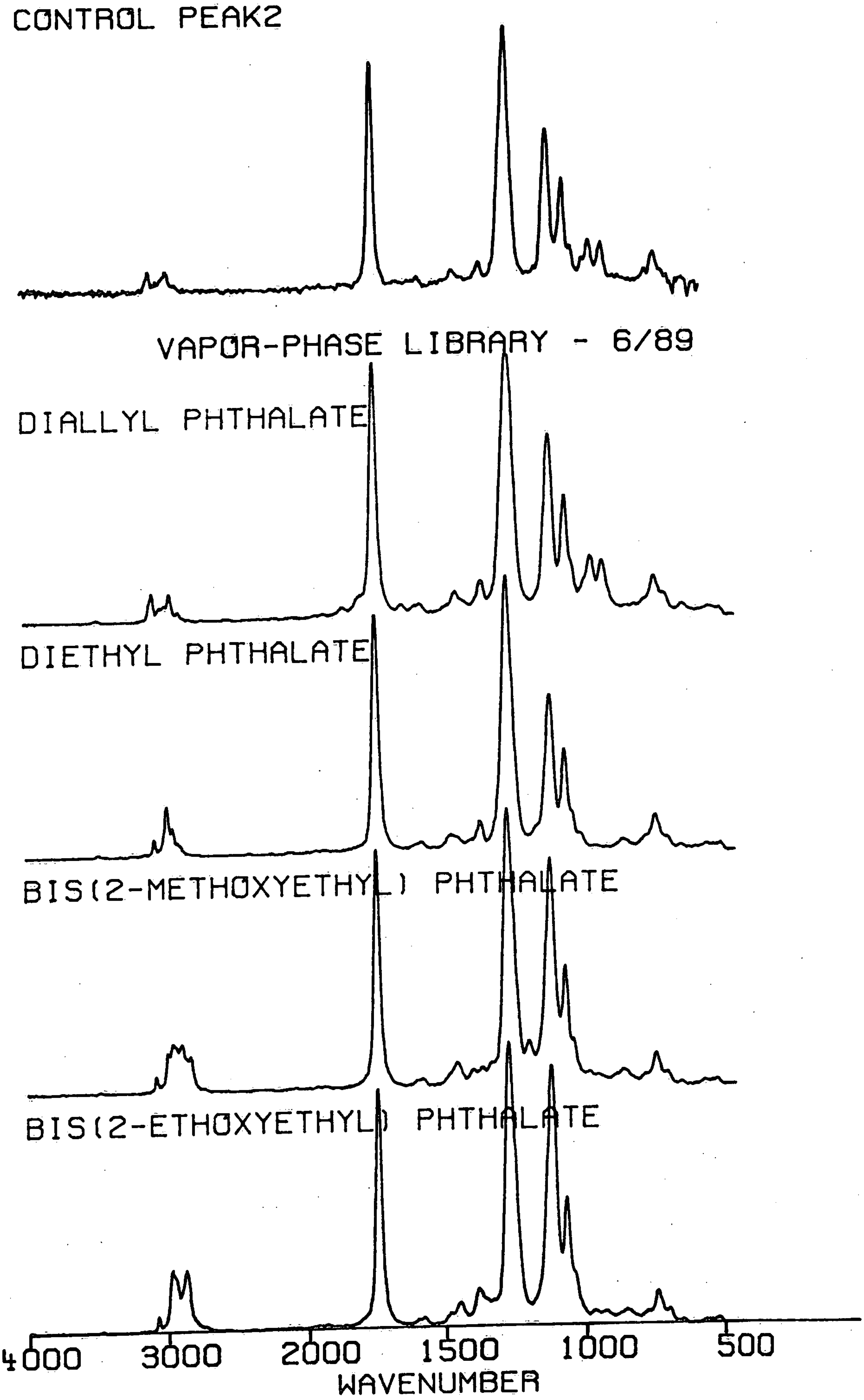

"Scrap" Tire Fraction 12
ABSORBANCE
.436
.368
.300
.232
.164
.096
.028
WAVENUMBER
4000
3590
3180
2770
2360
1950
1540
1130
720
310
3900.169
3120.955
3085.068
2918.167
2850.181
2163.105
1767.880
1720.439
1650.288
1600.320
1452.402
1357.886
1106.765
958.417
835.765
680.085
616.500

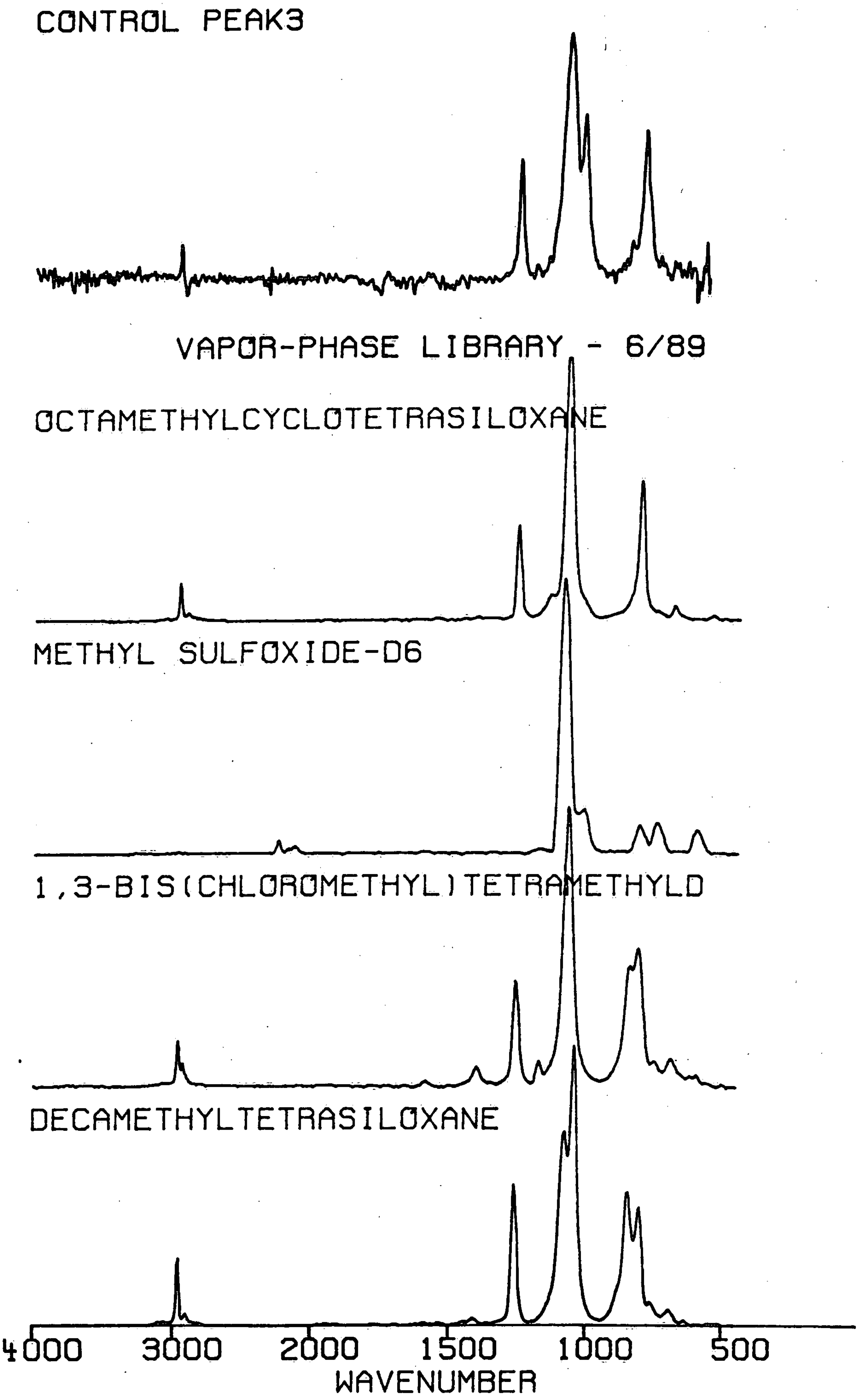
APPENDIX C

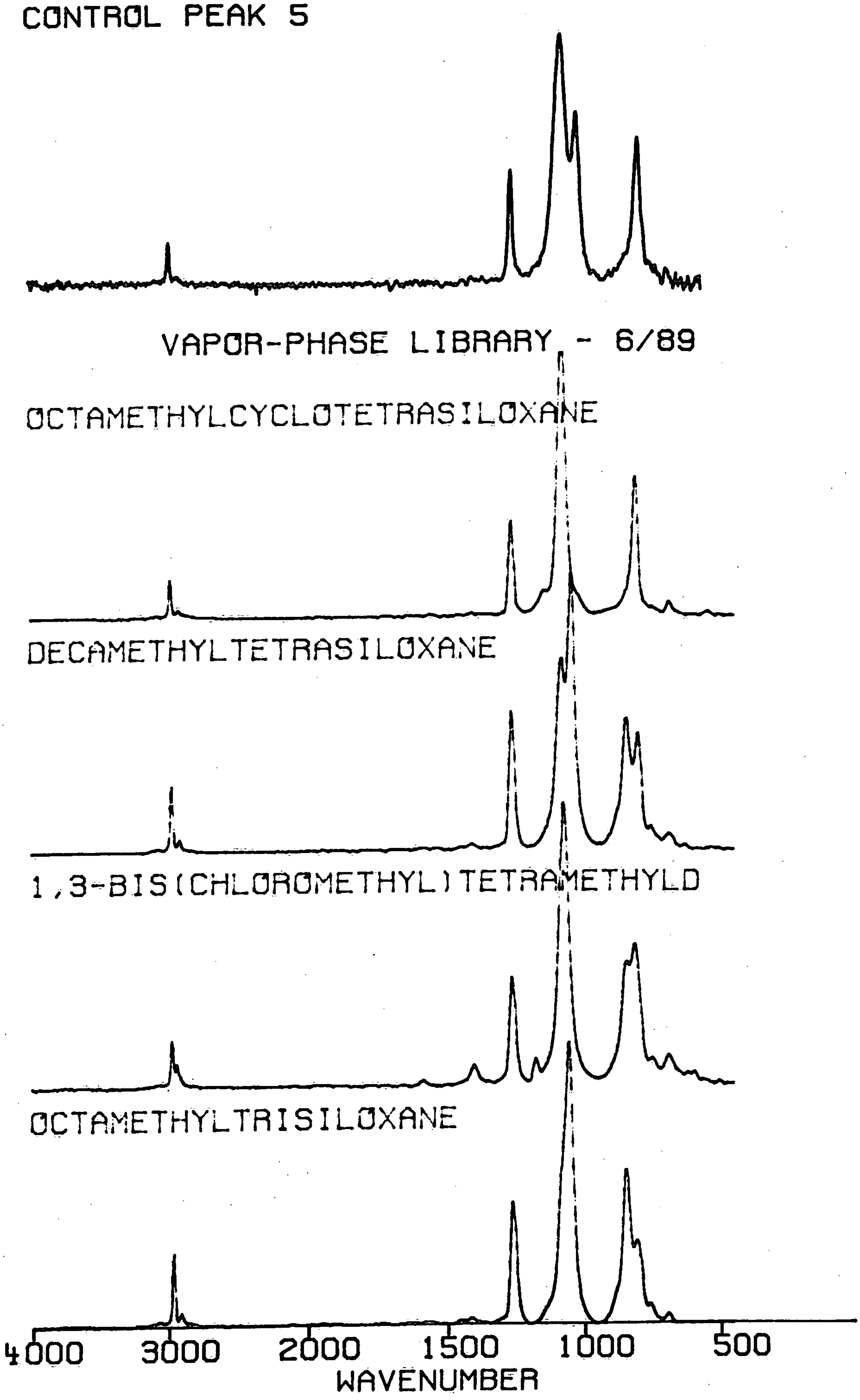
GC/FTIR Spectra of Extract Components

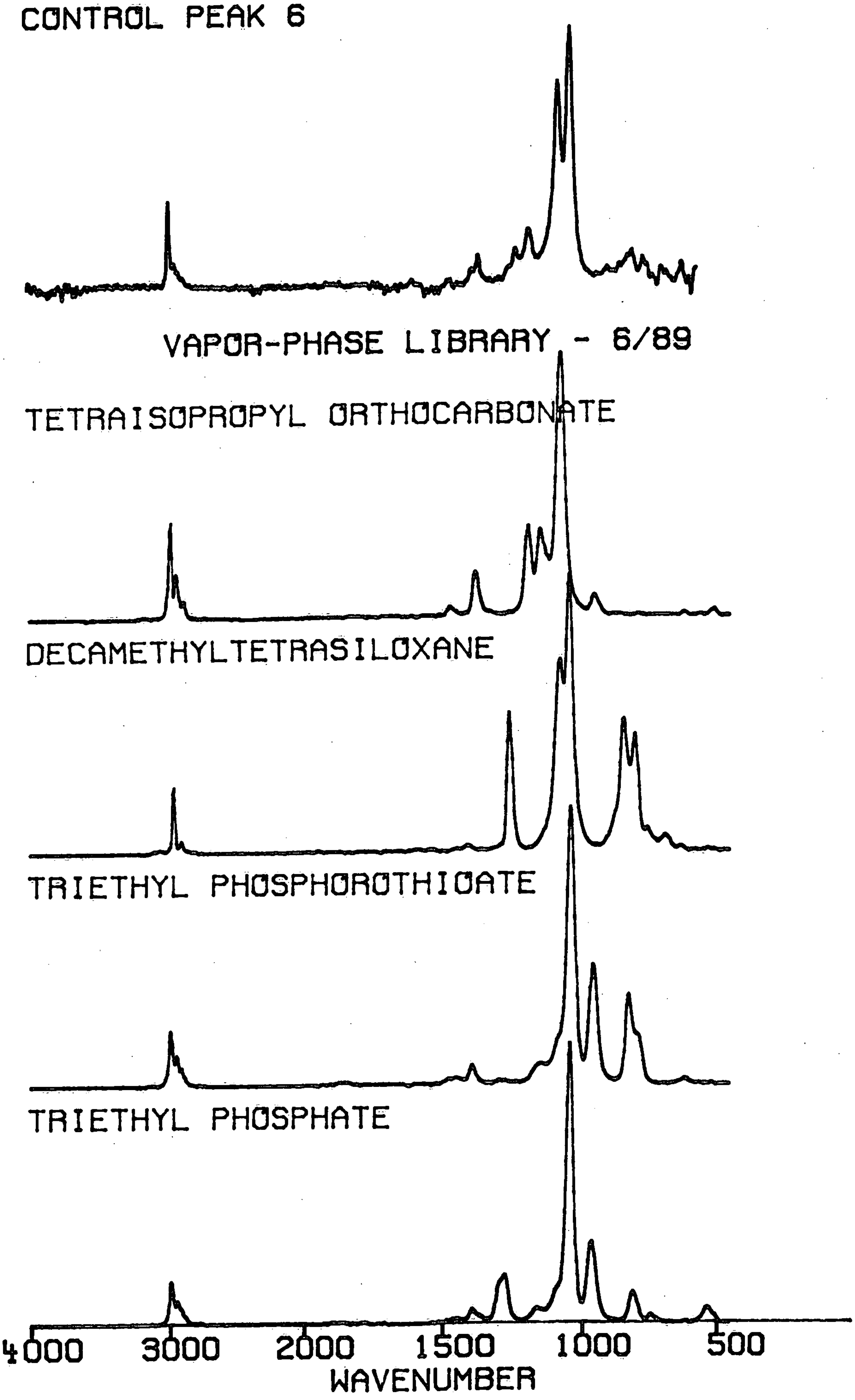
(Refer to **Table IV** for peak retention times and spectral characterizations)


CONTROL PK1A
VAPOR-PHASE LIBRARY - 6/89
TETRAISOPROPYL ORTHOCARBONATE
2,2-DIETHOXYETHANOL
FLUOROACETONITRILE
XENON DIFLUORIDE
4000
3000
2000
1500
1000
500
WAVENUMBER


CONTROL PEAK2
VAPOR-PHASE LIBRARY - 6/89
DIALLYL PHTHALATE
DIETHYL PHTHALATE
BIS(2-METHOXYETHYL) PHTHALATE
BIS(2-ETHOXYETHYL) PHTHALATE
4000
3000
2000
1500
1000
500
WAVENUMBER


CONTROL PEAK3
VAPOR-PHASE LIBRARY - 6/89
OCTAMETHYLCYCLOTETRASILOXANE
METHYL SULFOXIDE-D6
1,3-BIS(CHLOROMETHYL)TETRAMETHYLD
DECAMETHYLTETRASILOXANE
4000
3000
2000
1500
1000
500
WAVENUMBER


CONTROL PEAK 5
VAPOR-PHASE LIBRARY - 6/89
OCTAMETHYLCYCLOTETRASILOXANE
DECAMETHYLTETRASILOXANE
1,3-BIS(CHLOROMETHYL)TETRAMETHYLD
OCTAMETHYLTRISILOXANE
4000
3000
2000
1500
1000
500
WAVENUMBER



CONTROL PEAK 6

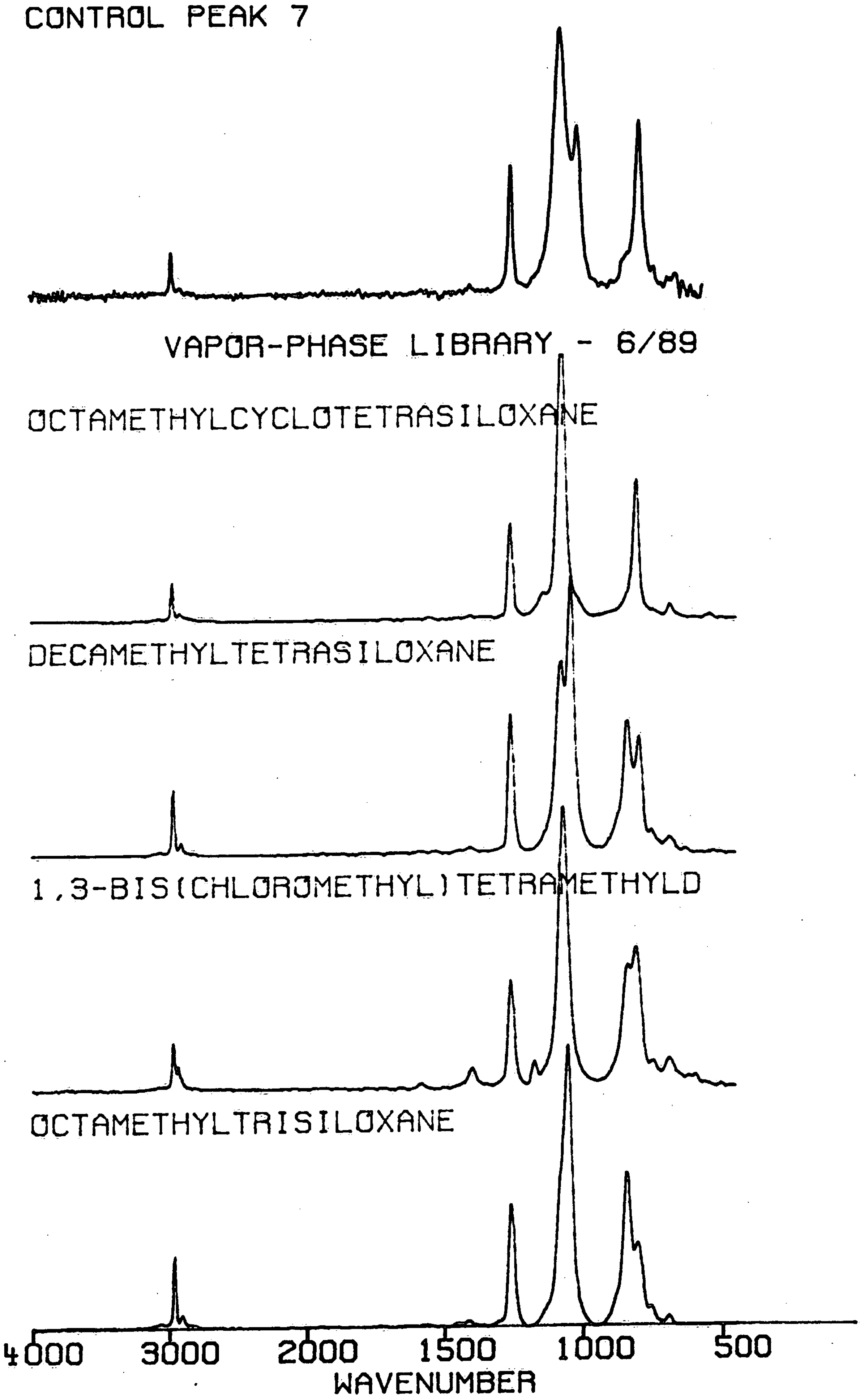
VAPOR-PHASE LIBRARY - 6/89

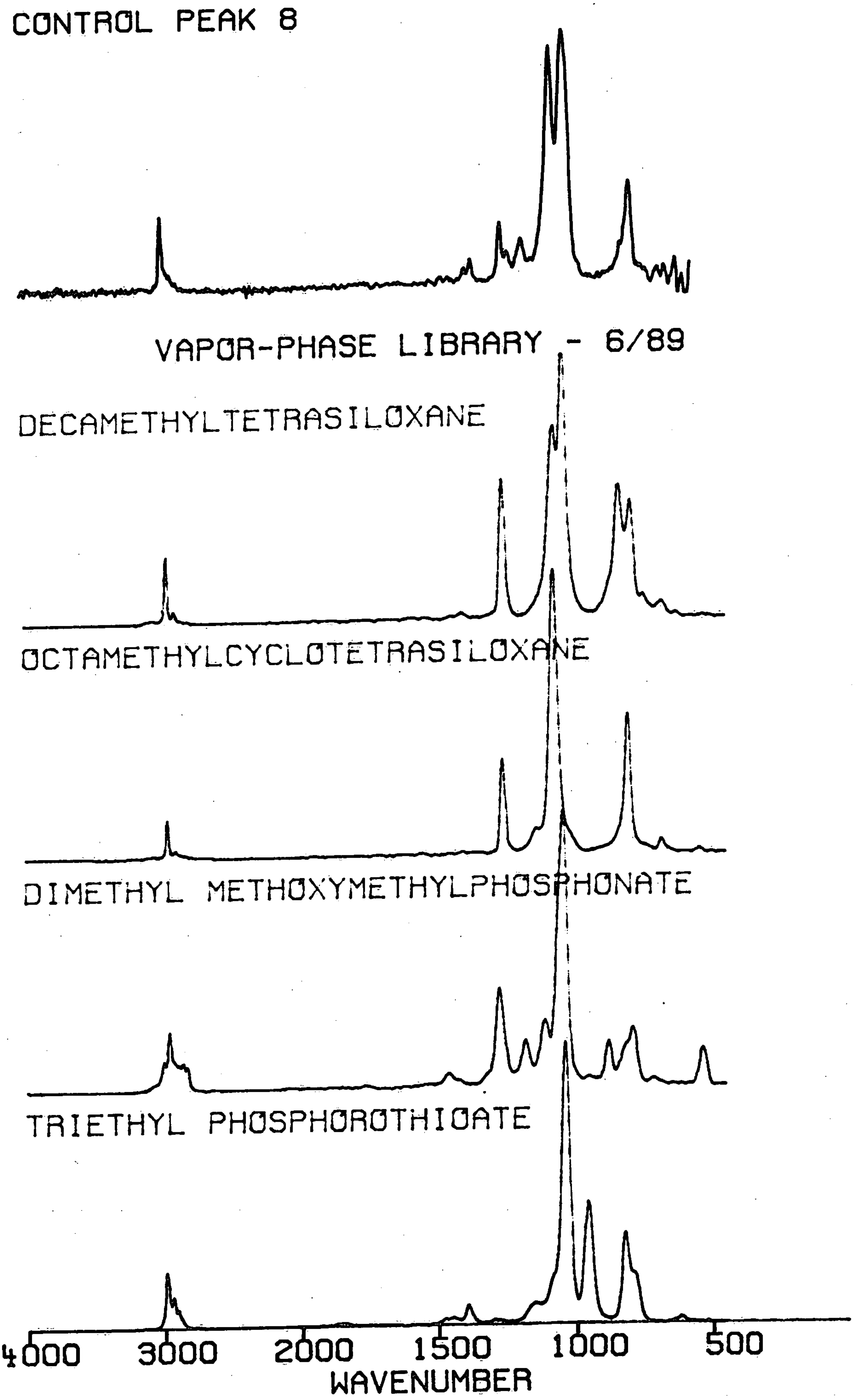
TETRAISOPROPYL ORTHOCARBONATE

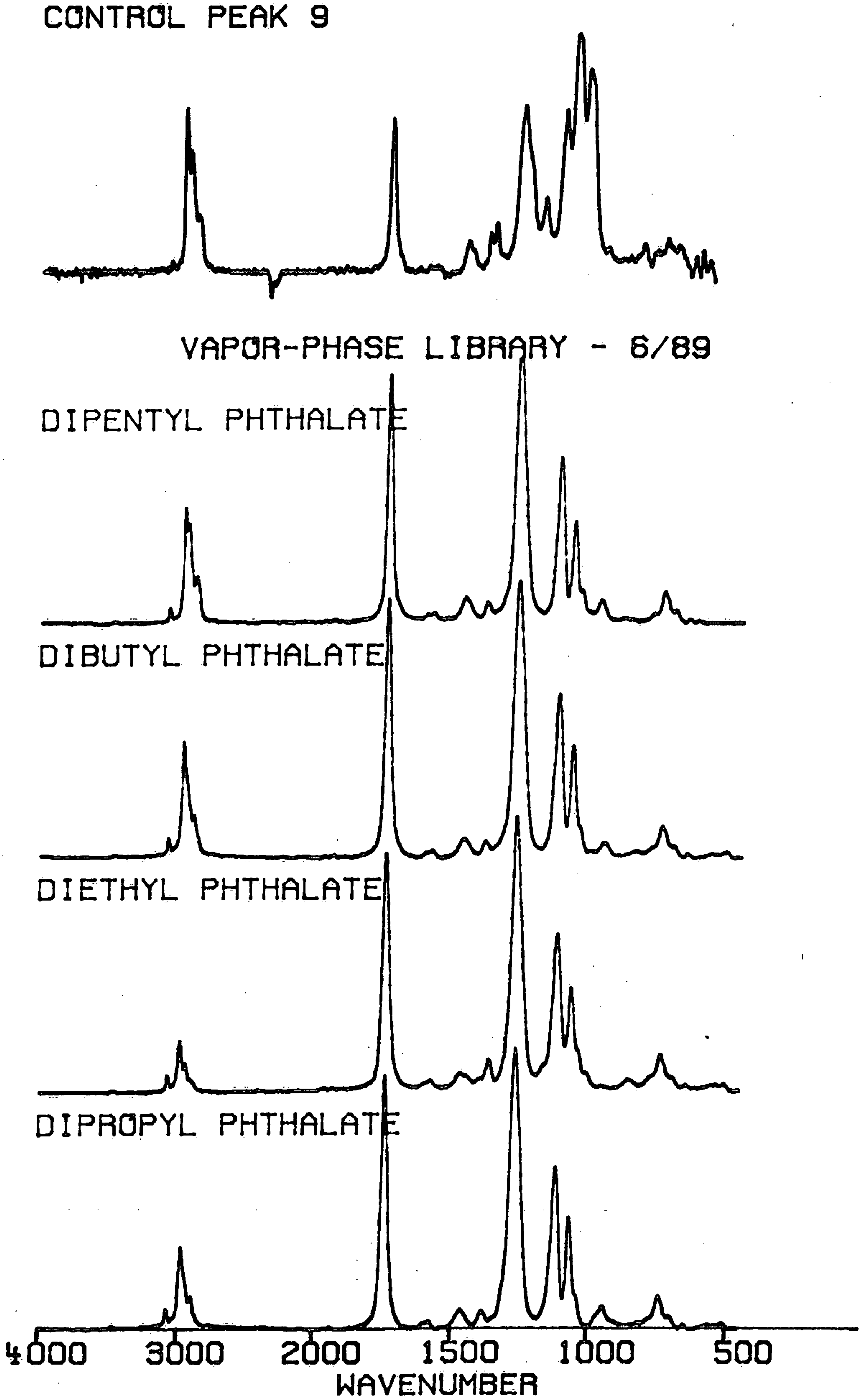
DECAMETHYLTETRASILOXANE

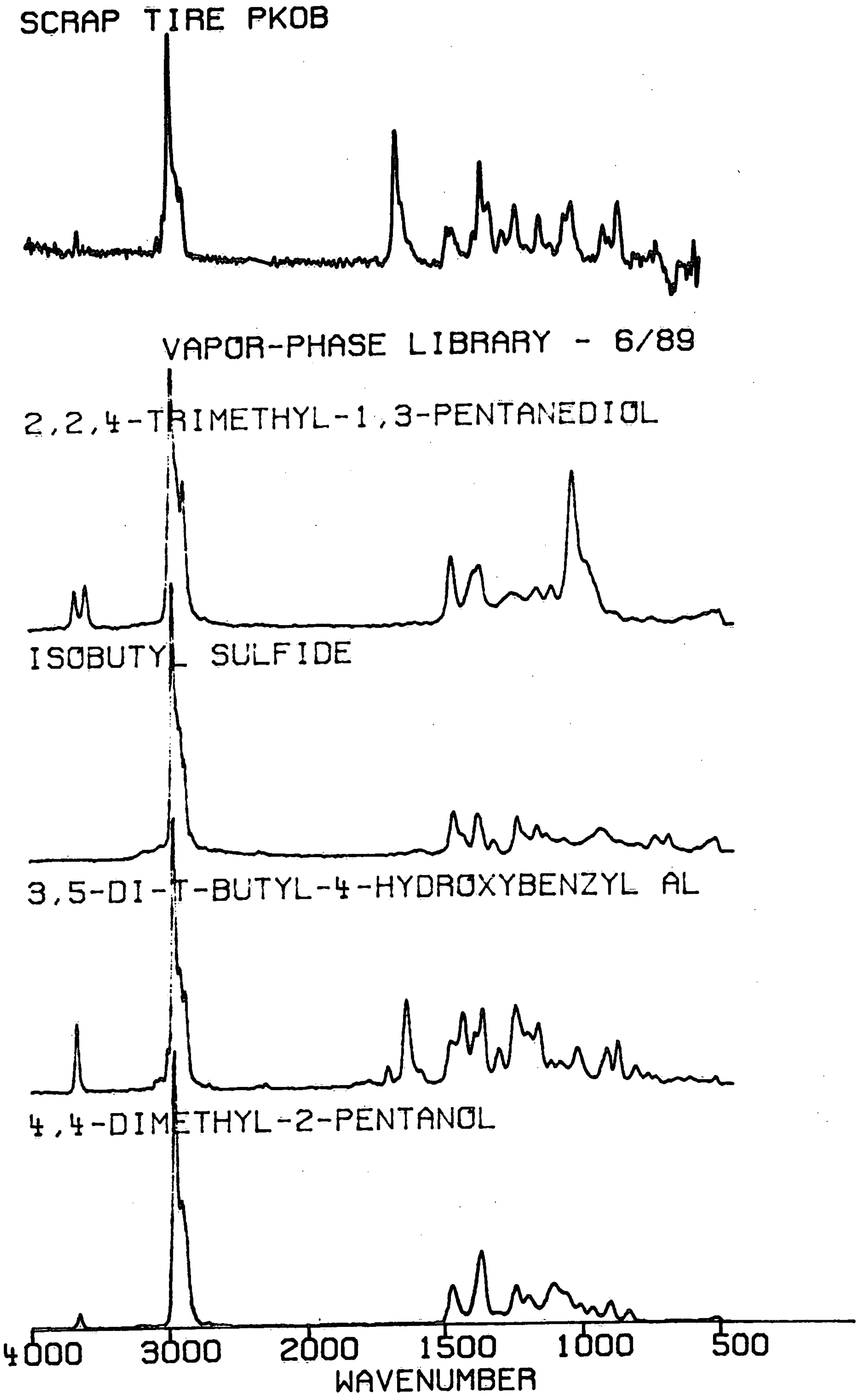
TRIETHYL PHOSPHOROTHIOATE

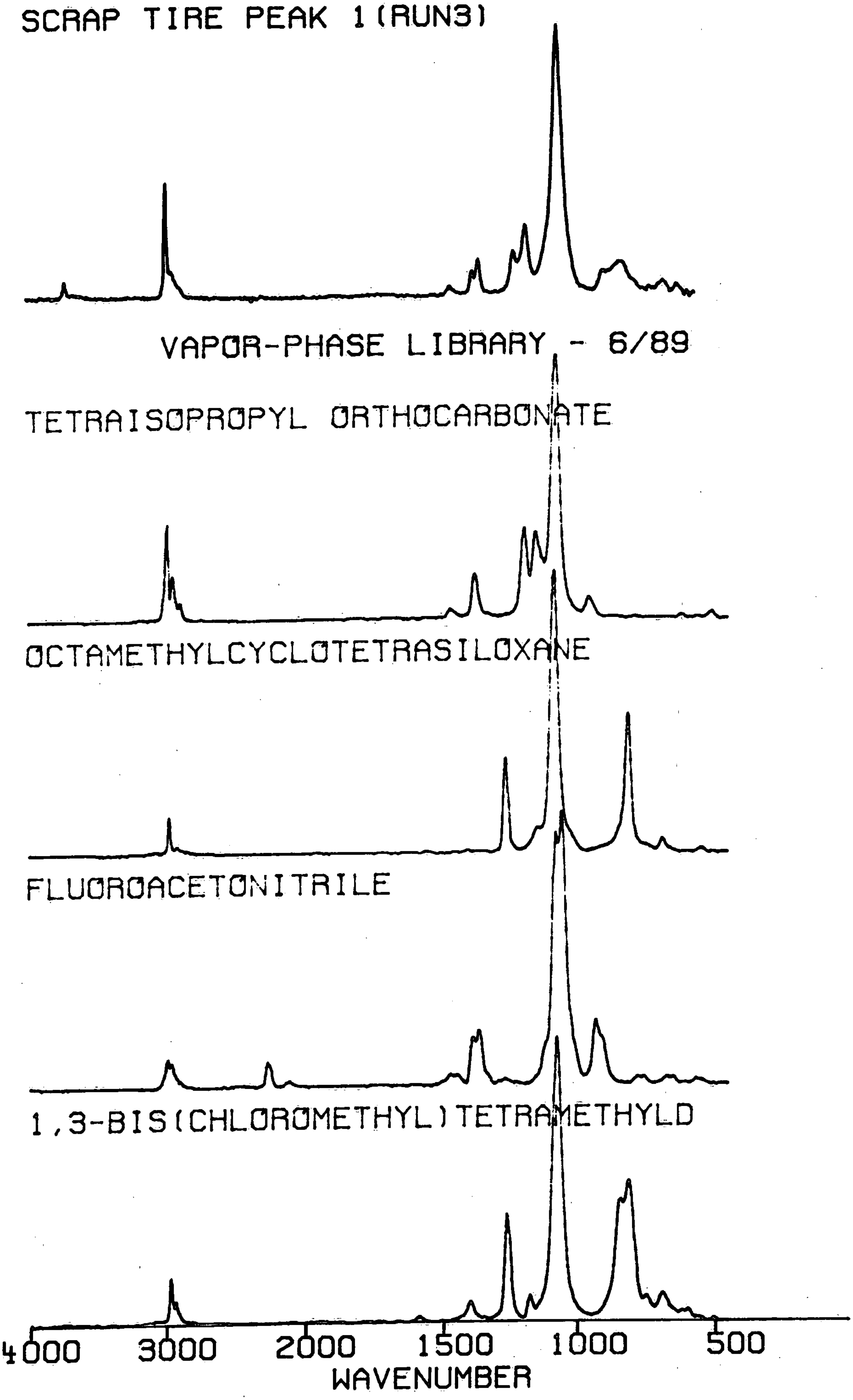
TRIETHYL PHOSPHATE


CONTROL PEAK 7
VAPOR-PHASE LIBRARY - 6/89
OCTAMETHYLCYCLOTETRASILOXANE
DECAMETHYLTETRASILOXANE
1,3-BIS(CHLOROMETHYL)TETRAMETHYLD
OCTAMETHYLTRISILOXANE
4000
3000
2000
1500
1000
500
WAVENUMBER

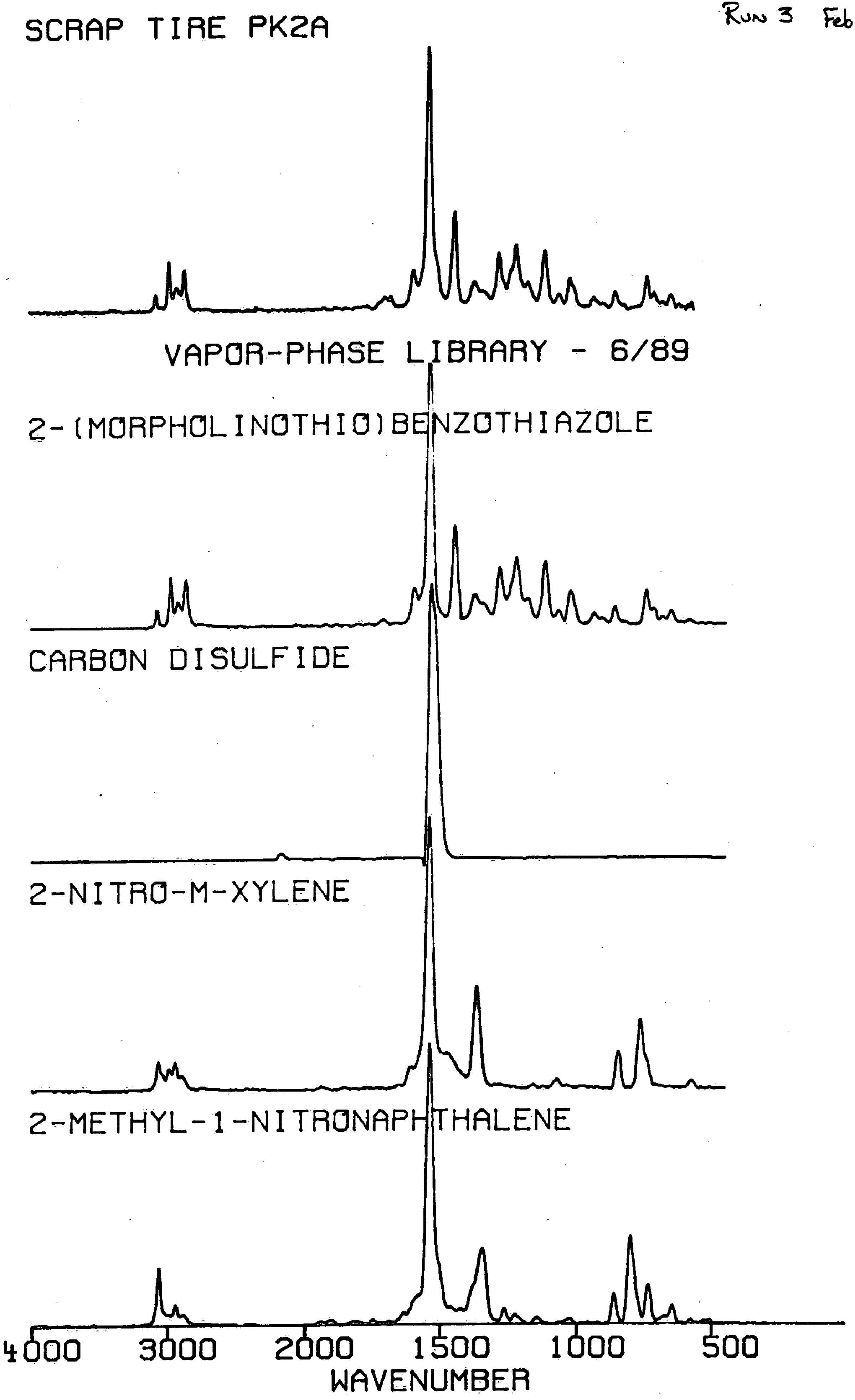

CONTROL PEAK 8
VAPOR-PHASE LIBRARY - 6/89
DECAMETHYLTETRASILOXANE
OCTAMETHYLCYCLOTETRASILOXANE
DIMETHYL METHOXYMETHYLPHOSPHONATE
TRIETHYL PHOSPHOROTHIOATE
4000
3000
2000
1500
1000
500
WAVENUMBER

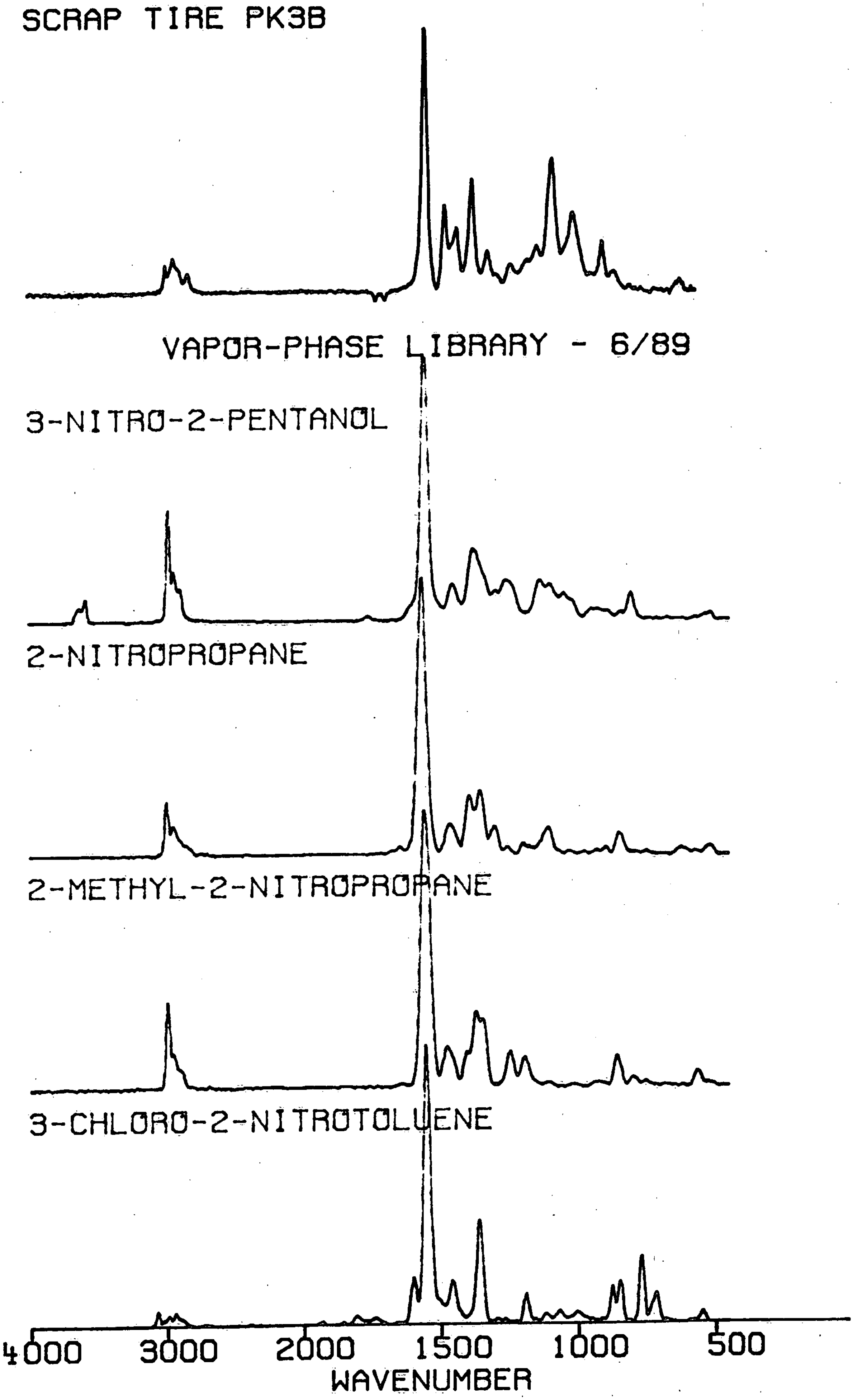

CONTROL PEAK 9
VAPOR-PHASE LIBRARY - 6/89
DIPENTYL PHTHALATE
DIBUTYL PHTHALATE
DIETHYL PHTHALATE
DIPROPYL PHTHALATE
4000
3000
2000
1500
1000
500
WAVENUMBER


SCRAP TIRE PKOB
VAPOR-PHASE LIBRARY - 6/89
2,2,4-TRIMETHYL-1,3-PENTANEDIOL
ISOBUTYL SULFIDE
3,5-DI-T-BUTYL-4-HYDROXYBENZYL AL
4,4-DIMETHYL-2-PENTANOL
4000
3000
2000
1500
1000
500
WAVENUMBER

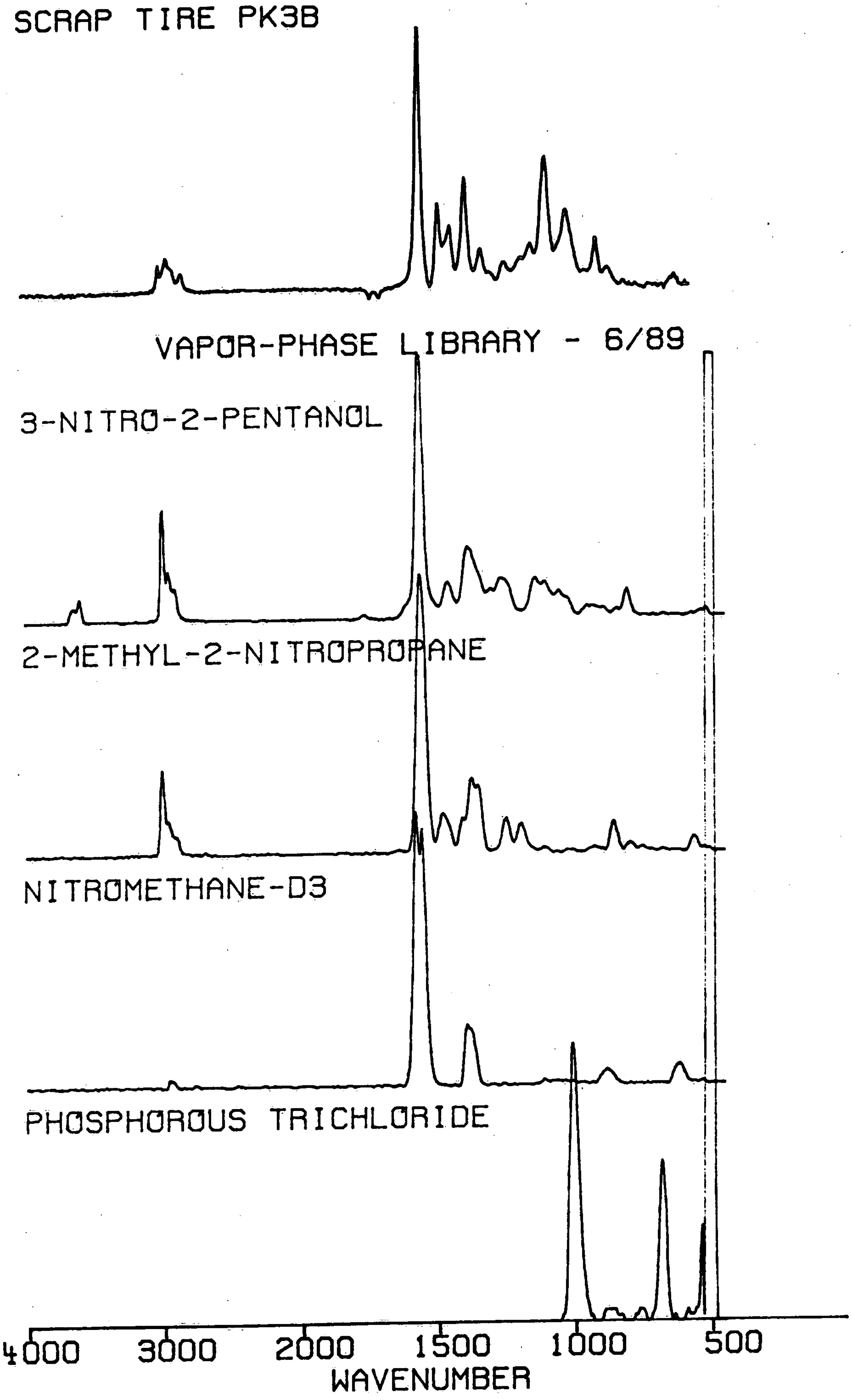

SCRAP TIRE PEAK 1(RUN3)
VAPOR-PHASE LIBRARY - 6/89
TETRAISOPROPYL ORTHOCARBONATE
OCTAMETHYLCYCLOTETRASILOXANE
FLUOROACETONITRILE
1,3-BIS(CHLOROMETHYL)TETRAMETHYLD
4000
3000
2000
1500
1000
500
WAVENUMBER

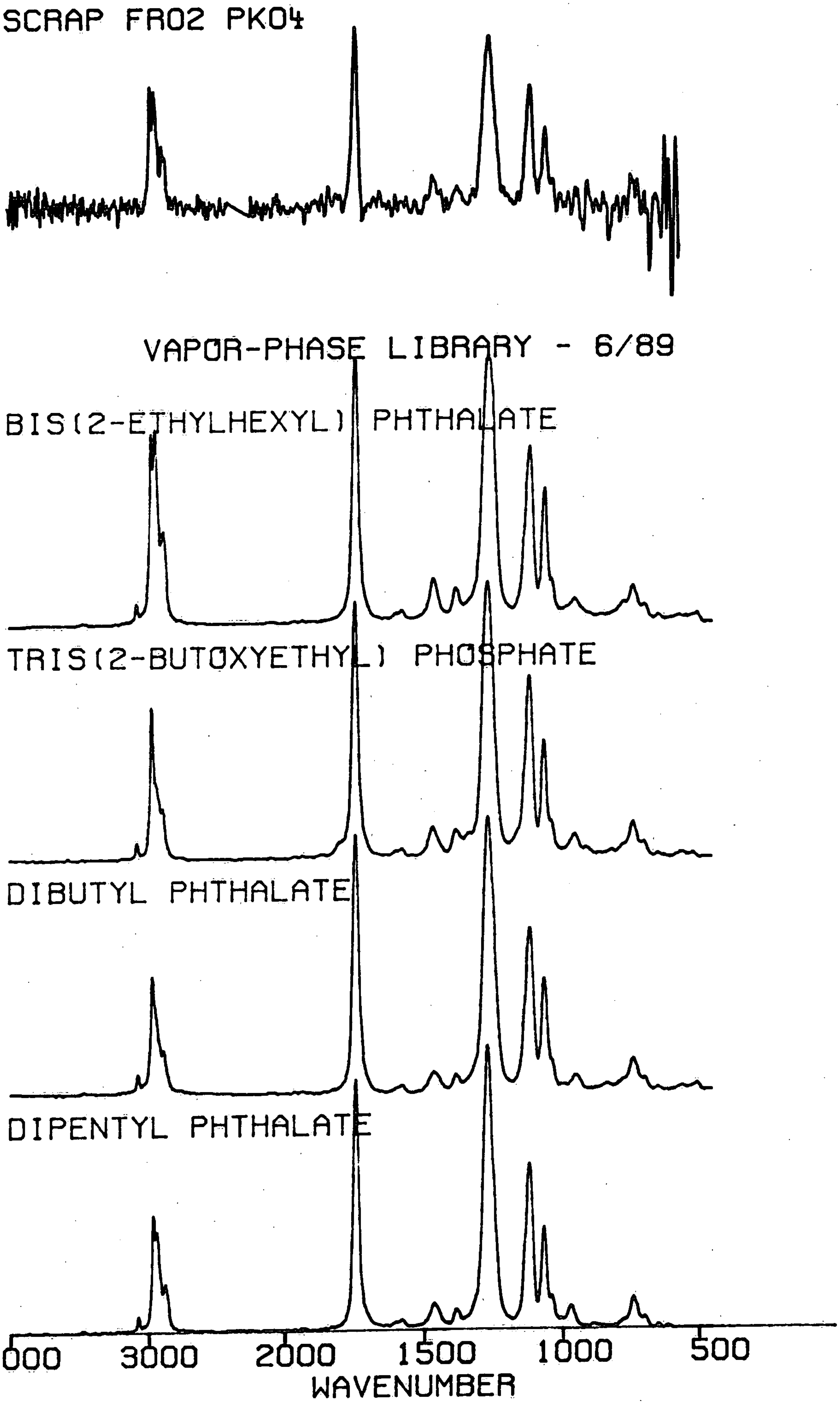
Scrap Tire Ext
Run 3 Feb. 12th

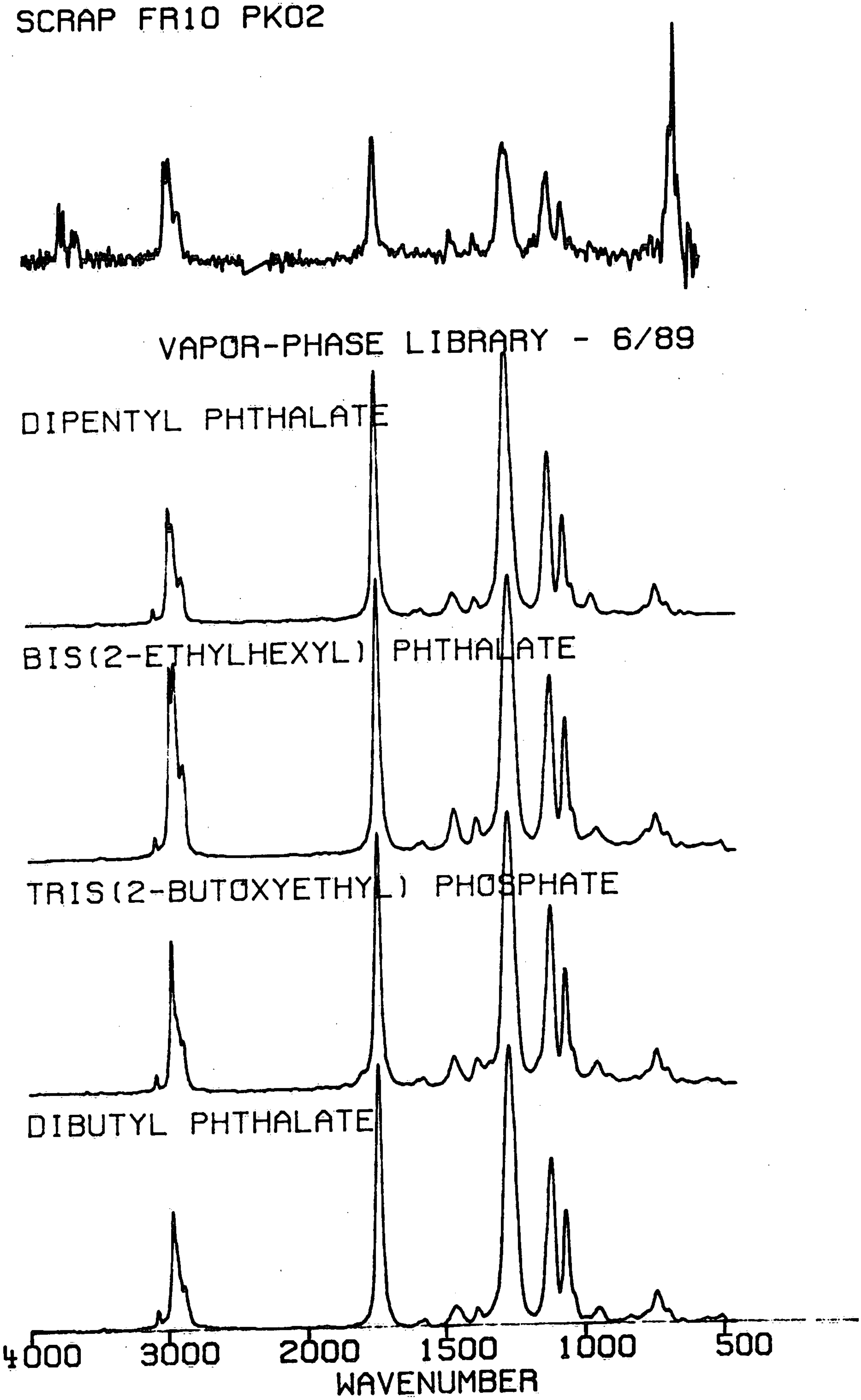


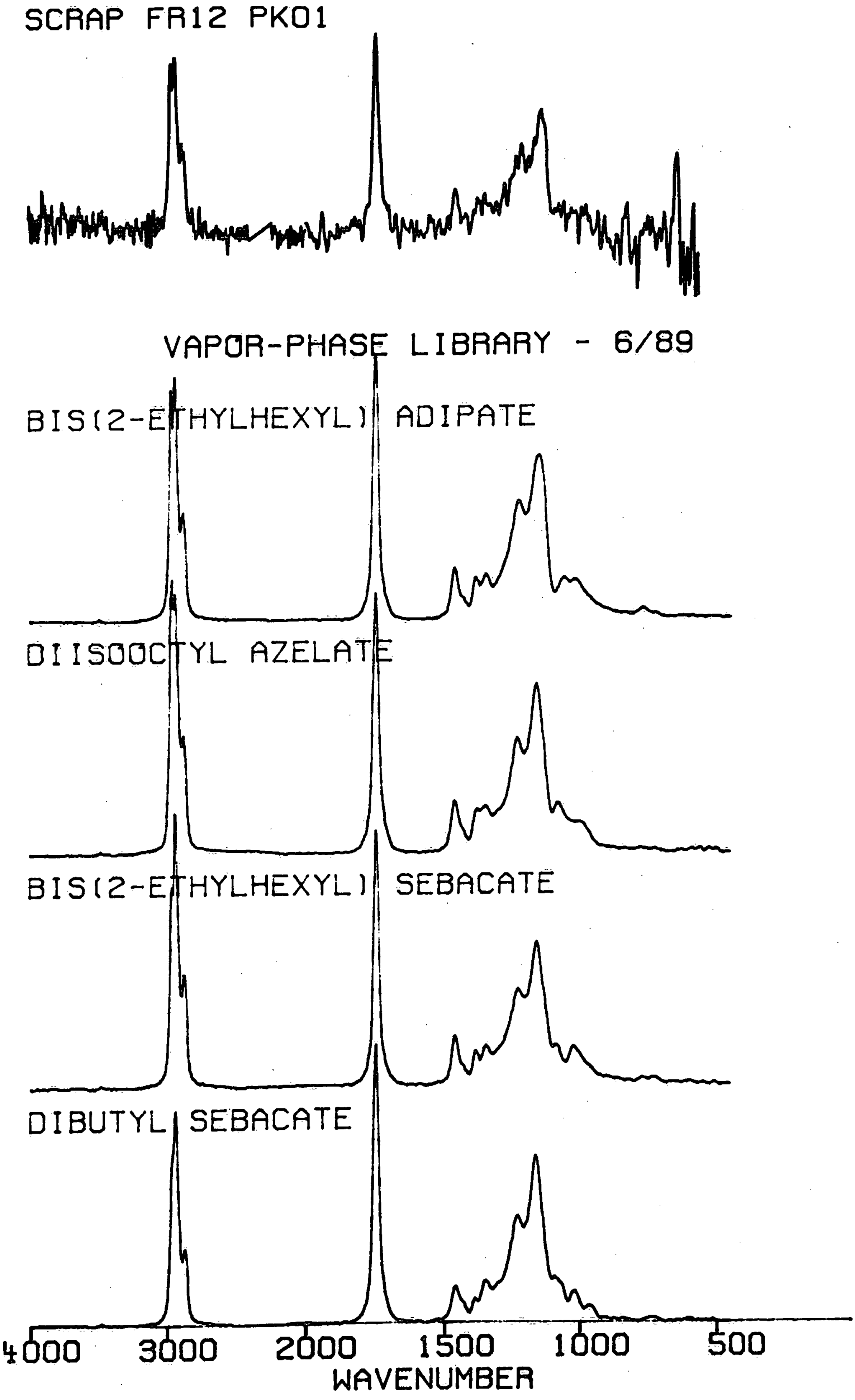

SCRAP TIRE PK3B
VAPOR-PHASE LIBRARY - 6/89
3-NITRO-2-PENTANOL
2-NITROPROPANE
2-METHYL-2-NITROPROPANE
3-CHLORO-2-NITROTOLUENE
4000
3000
2000
1500
1000
500
WAVENUMBER

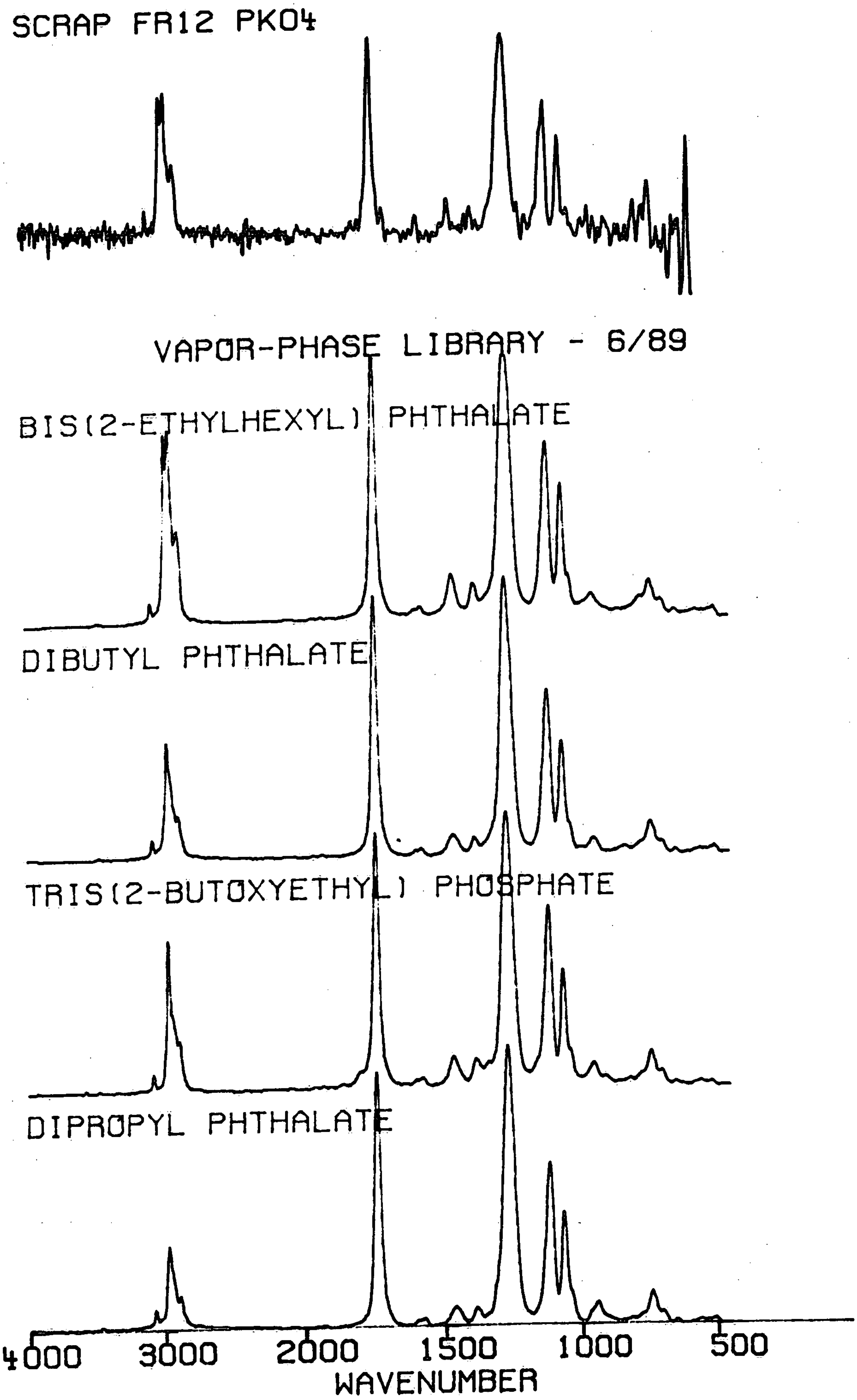
Scrap Tire E
Run 3 Feb 12

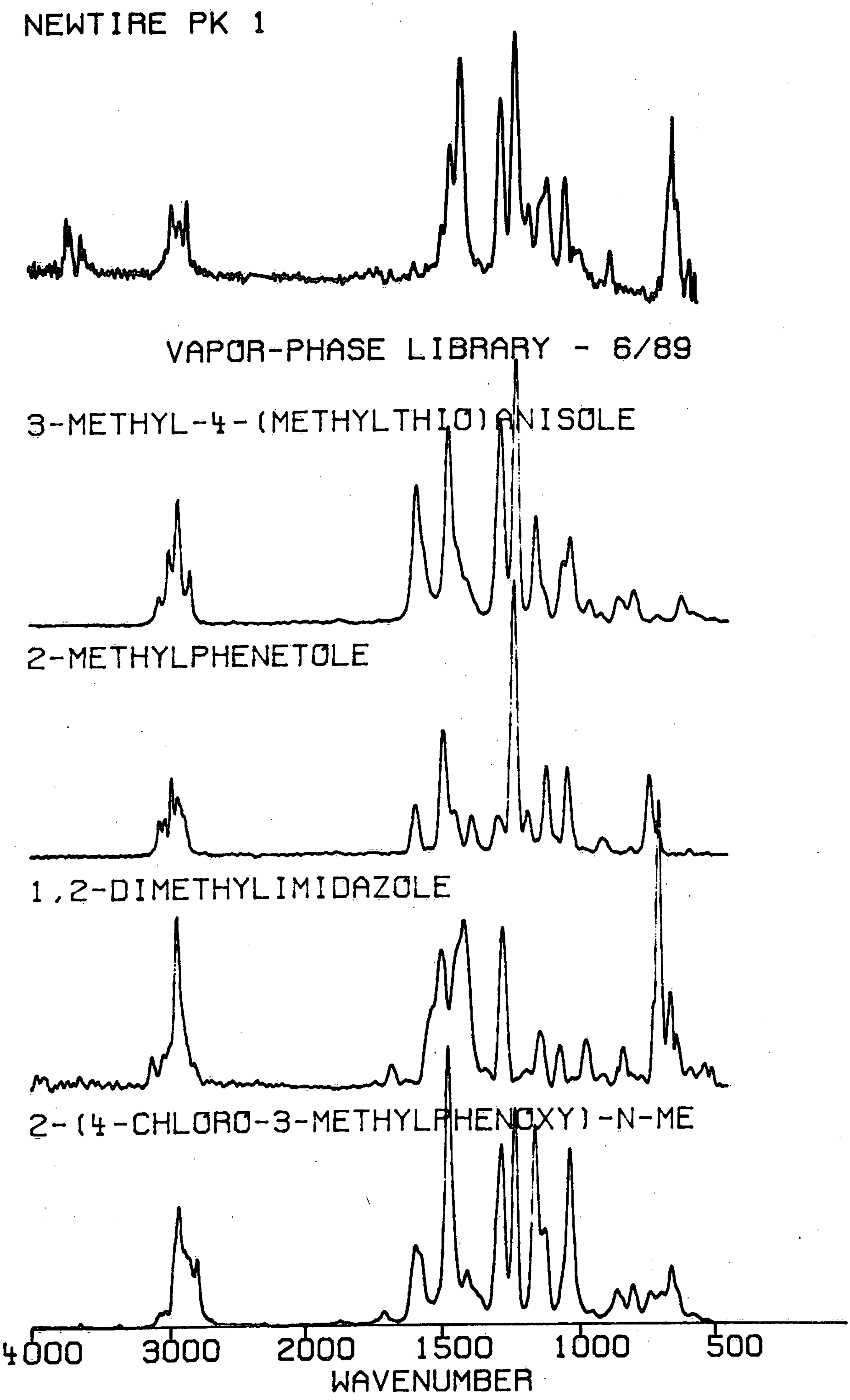



SCRAP FR02 PK04
VAPOR-PHASE LIBRARY - 6/89
BIS(2-ETHYLHEXYL) PHTHALATE
TRIS(2-BUTOXYETHYL) PHOSPHATE
DIBUTYL PHTHALATE
DIPENTYL PHTHALATE
4000
3000
2000
1500
1000
500
WAVENUMBER


SCRAP FR10 PK02
VAPOR-PHASE LIBRARY - 6/89
DIPENTYL PHTHALATE
BIS(2-ETHYLHEXYL) PHTHALATE
TRIS(2-BUTOXYETHYL) PHOSPHATE
DIBUTYL PHTHALATE
4000
3000
2000
1500
1000
500
WAVENUMBER


SCRAP FR12 PK01
VAPOR-PHASE LIBRARY - 6/89
BIS(2-ETHYLHEXYL) ADIPATE
DIISOOCTYL AZELATE
BIS(2-ETHYLHEXYL) SEBACATE
DIBUTYL SEBACATE
4000
3000
2000
1500
1000
500
WAVENUMBER


SCRAP FR12 PK04
VAPOR-PHASE LIBRARY - 6/89
BIS(2-ETHYLHEXYL) PHTHALATE
DIBUTYL PHTHALATE
TRIS(2-BUTOXYETHYL) PHOSPHATE
DIPROPYL PHTHALATE
4000
3000
2000
1500
1000
500
WAVENUMBER



NEWTIRE PK 1

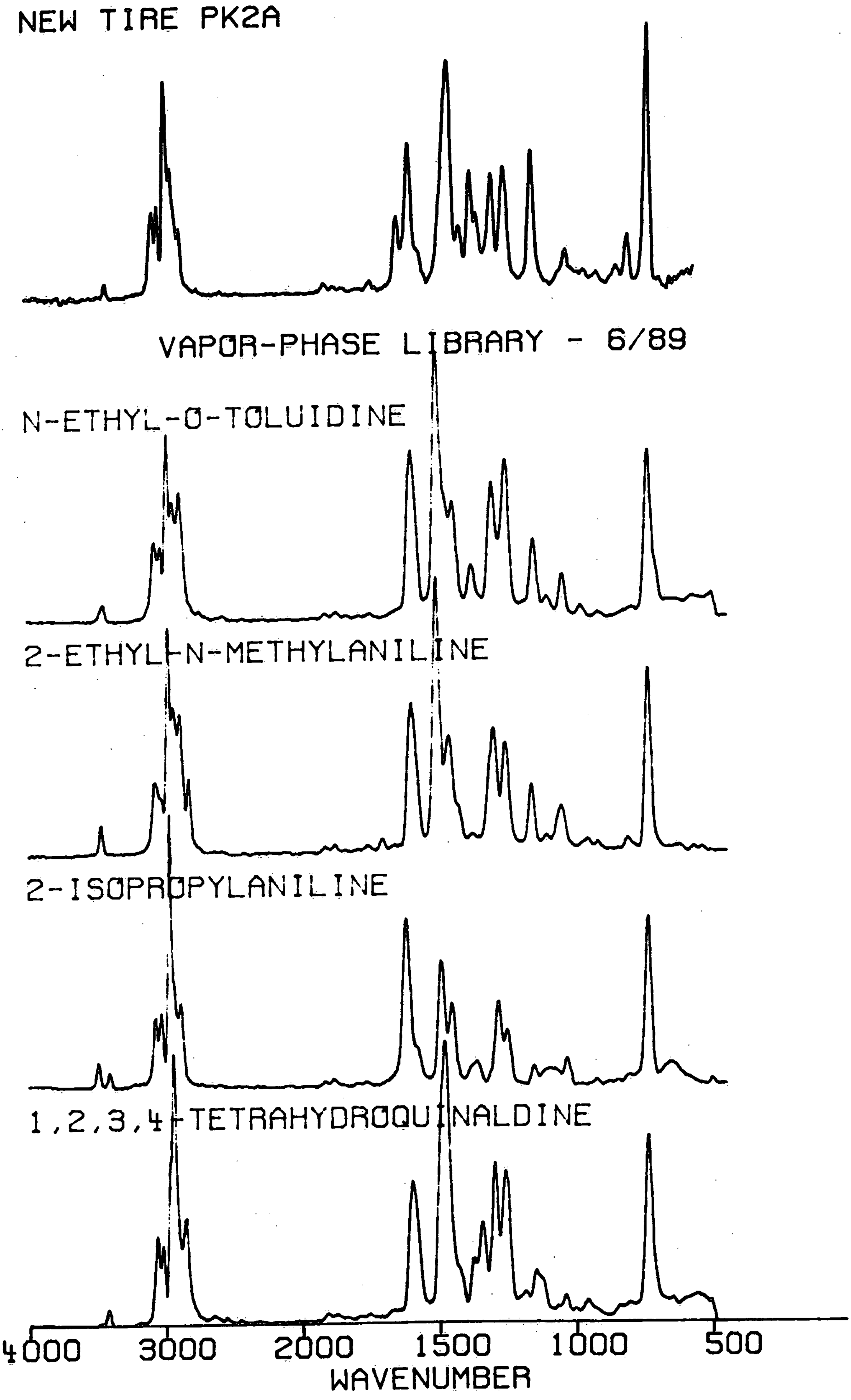
VAPOR-PHASE LIBRARY - 6/89

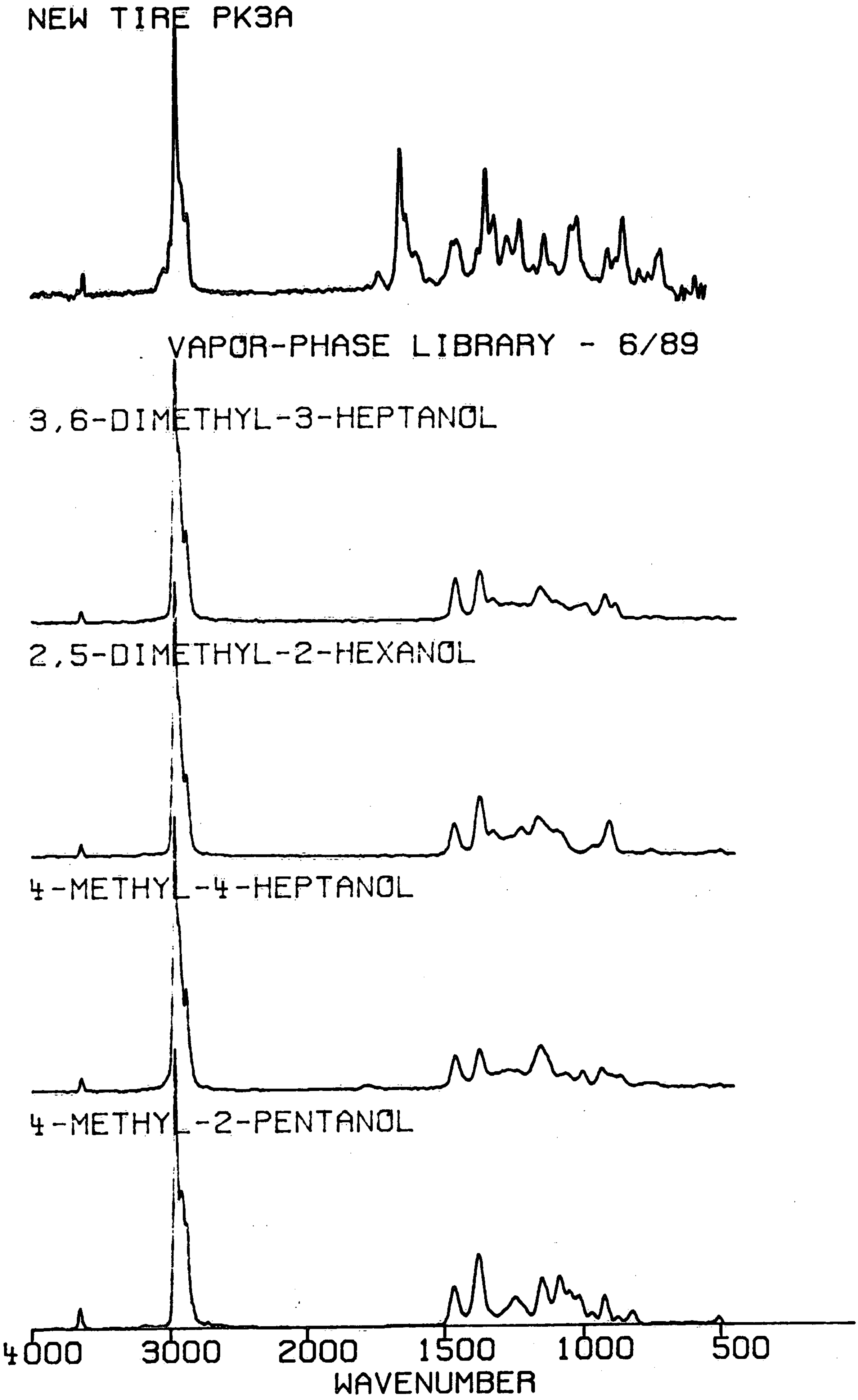
3-METHYL-4-(METHYLTHIO)ANISOLE

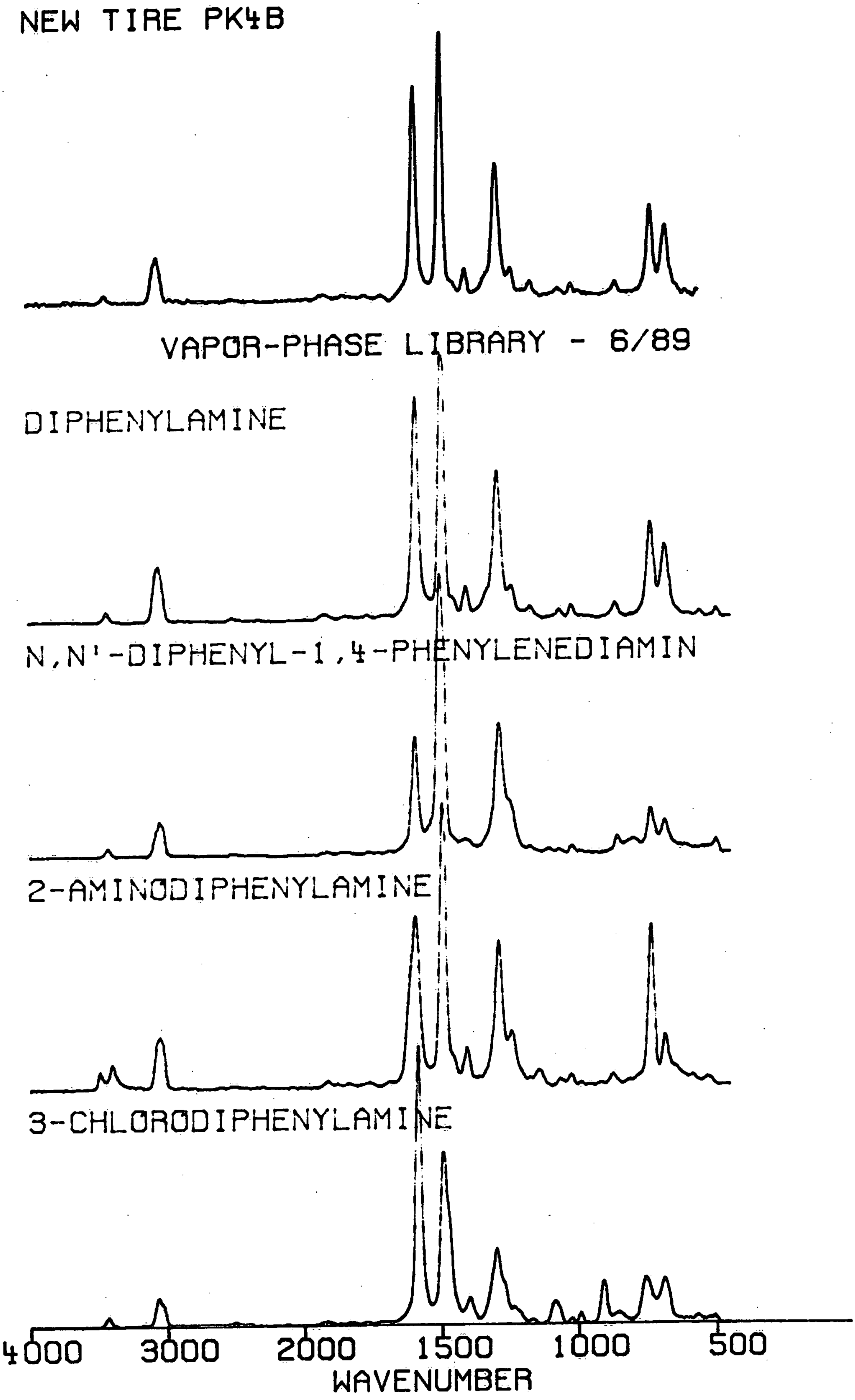
2-METHYLPHENETOLE

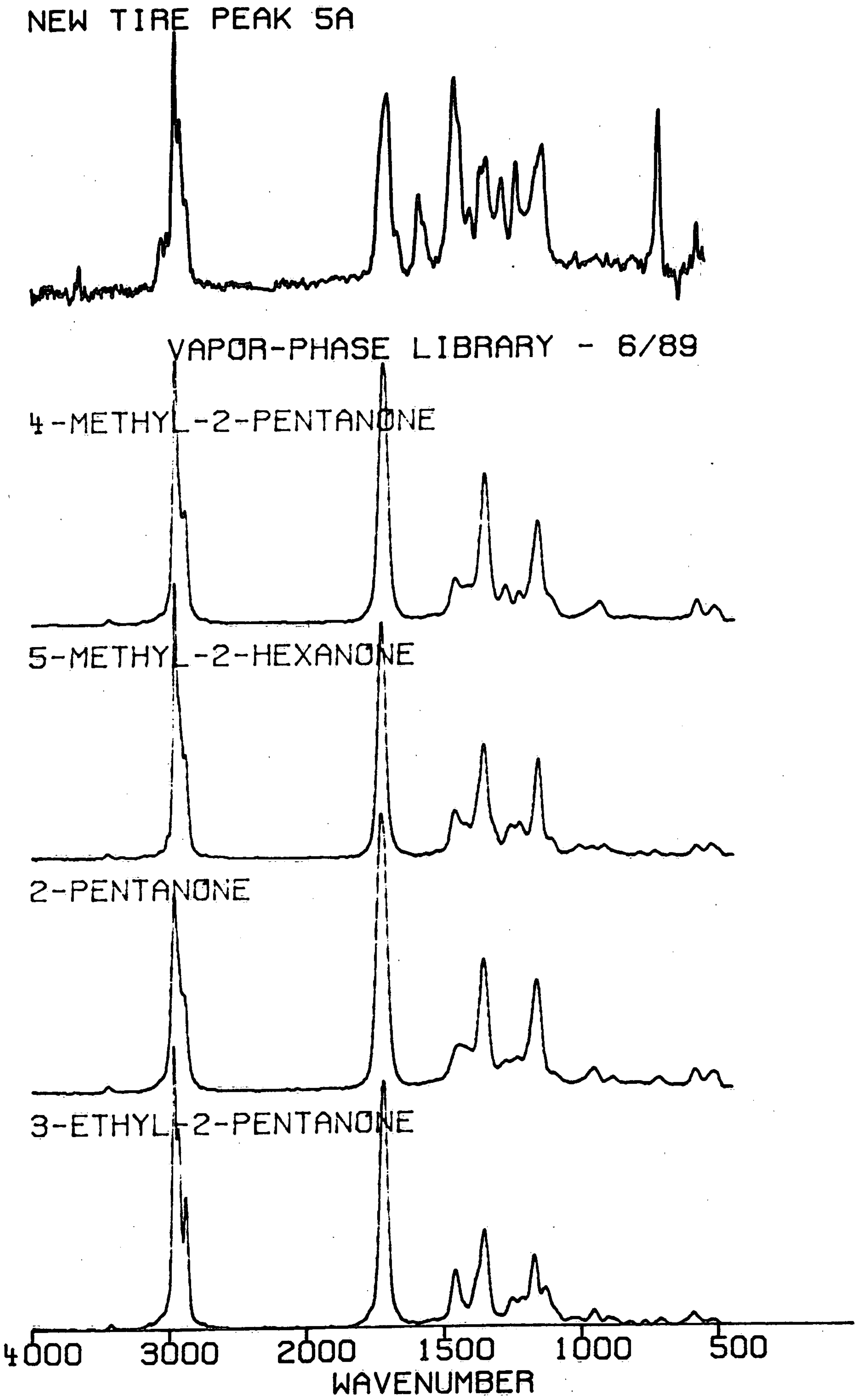
1,2-DIMETHYLIMIDAZOLE

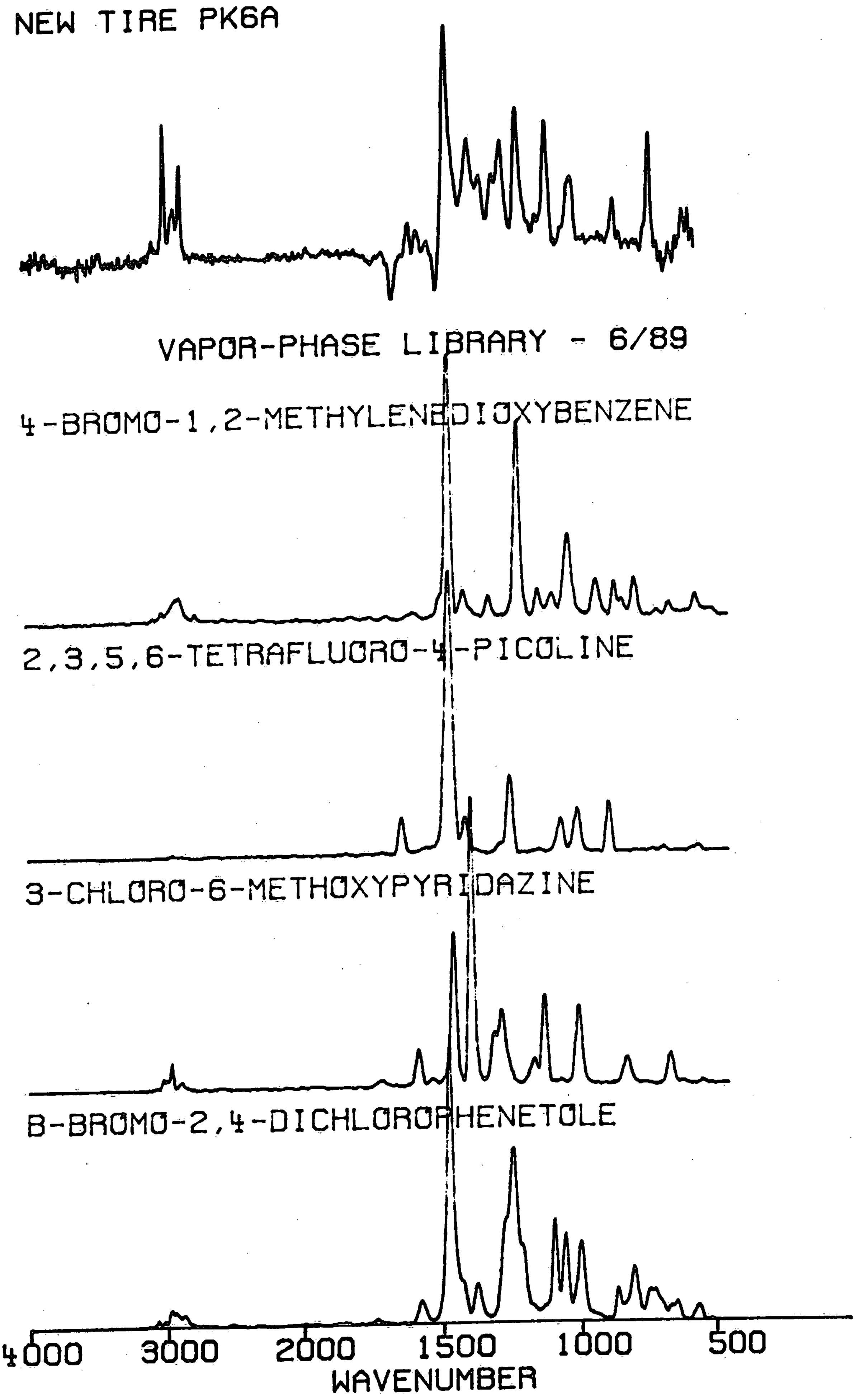
2-(4-CHLORO-3-METHYLPHENOXY)-N-ME

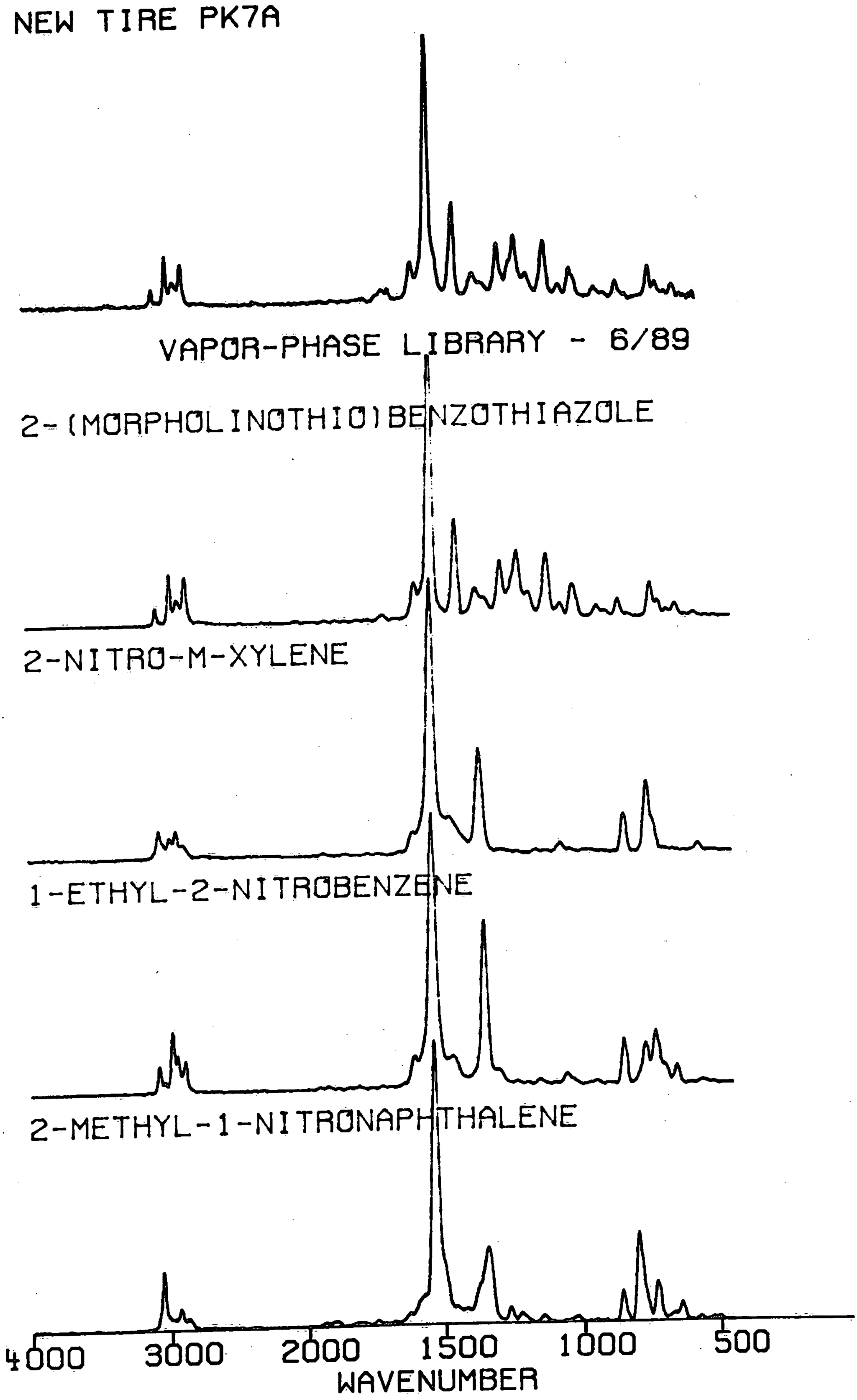

NEW TIRE PK2A
VAPOR-PHASE LIBRARY - 6/89
N-ETHYL-O-TOLUIDINE
2-ETHYL-N-METHYLANILINE
2-ISOPROPYLANILINE
1,2,3,4-TETRAHYDROQUINALDINE
4000
3000
2000
1500
1000
500
WAVENUMBER


NEW TIRE PK3A
VAPOR-PHASE LIBRARY - 6/89
3,6-DIMETHYL-3-HEPTANOL
2,5-DIMETHYL-2-HEXANOL
4-METHYL-4-HEPTANOL
4-METHYL-2-PENTANOL
4000
3000
2000
1500
1000
500
WAVENUMBER


NEW TIRE PK4B
VAPOR-PHASE LIBRARY - 6/89
DIPHENYLAMINE
N,N'-DIPHENYL-1,4-PHENYLENEDIAMIN
2-AMINODIPHENYLAMINE
3-CHLORODIPHENYLAMINE
4000
3000
2000
1500
1000
500
WAVENUMBER


NEW TIRE PEAK 5A
VAPOR-PHASE LIBRARY - 6/89
4-METHYL-2-PENTANONE
5-METHYL-2-HEXANONE
2-PENTANONE
3-ETHYL-2-PENTANONE
4000
3000
2000
1500
1000
500
WAVENUMBER


NEW TIRE PK6A
VAPOR-PHASE LIBRARY - 6/89
4-BROMO-1,2-METHYLENEDIOXYBENZENE
2,3,5,6-TETRAFLUORO-4-PICOLINE
3-CHLORO-6-METHOXYPYRIDAZINE
B-BROMO-2,4-DICHLOROPHENETOLE
4000
3000
2000
1500
1000
500
WAVENUMBER

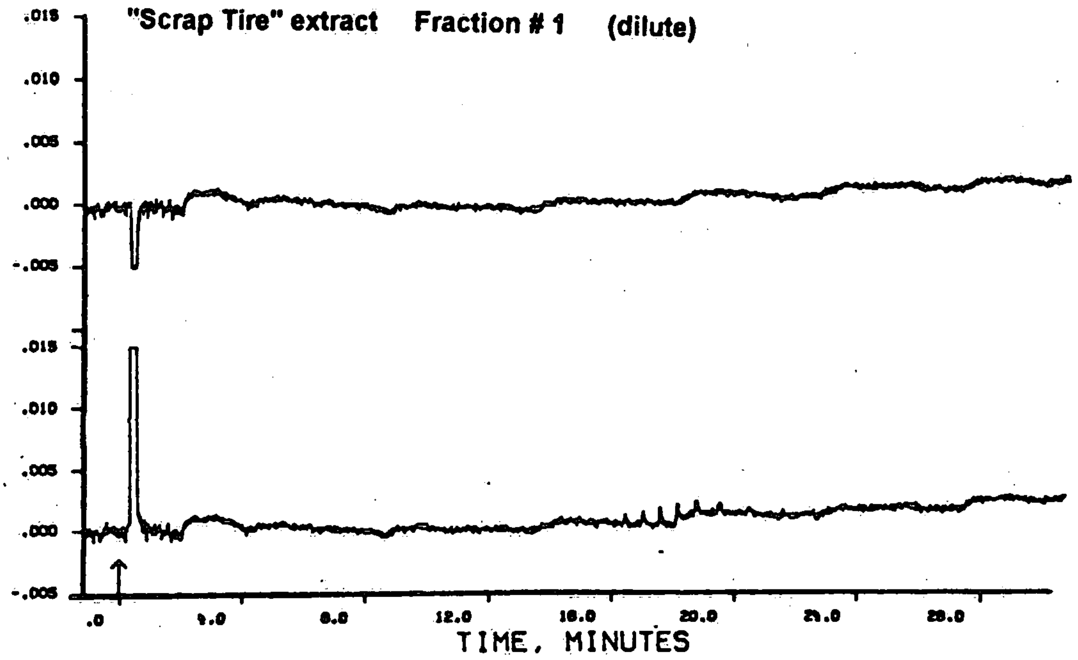

NEW TIRE PK7A
VAPOR-PHASE LIBRARY - 6/89
2-(MORPHOLINOTHIO)BENZOTHIAZOLE
2-NITRO-M-XYLENE
1-ETHYL-2-NITROBENZENE
2-METHYL-1-NITRONAPHTHALENE
4000
3000
2000
1500
1000
500
WAVENUMBER

APPENDIX D

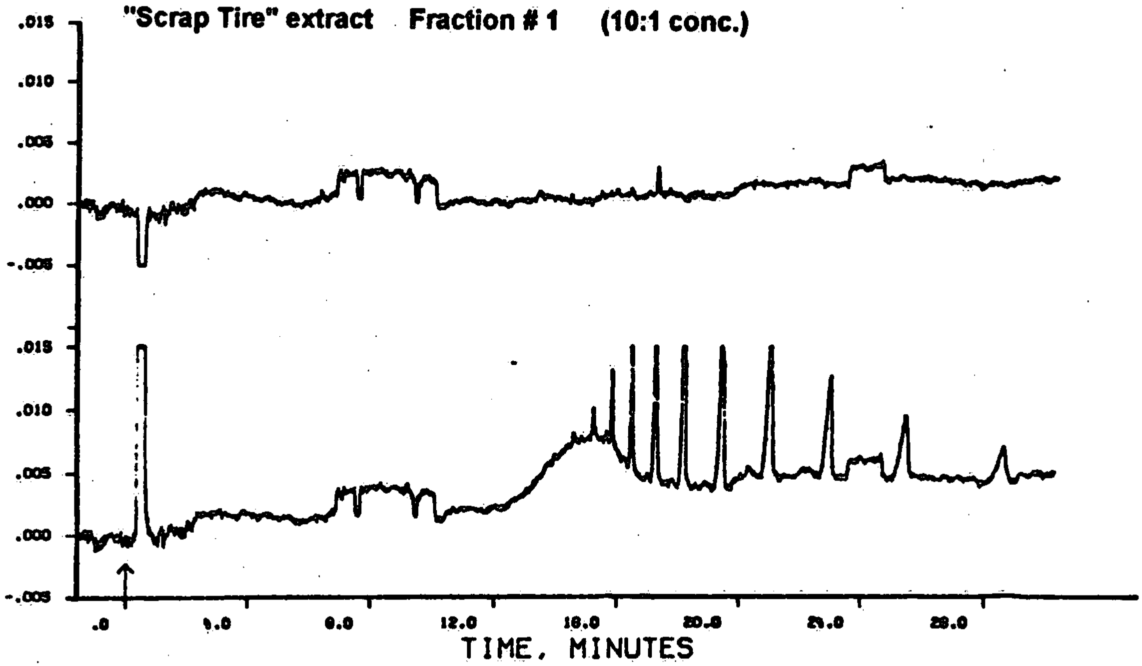
GC/FTIR Chromatograms of "Scrap" Tire Fractions

"Scrap Tire" Extracts* GC/FT-IR chromatograms

2980 - 2910 cm^{-1} (bottom window) and 1170 - 1150 cm^{-1} (top window)

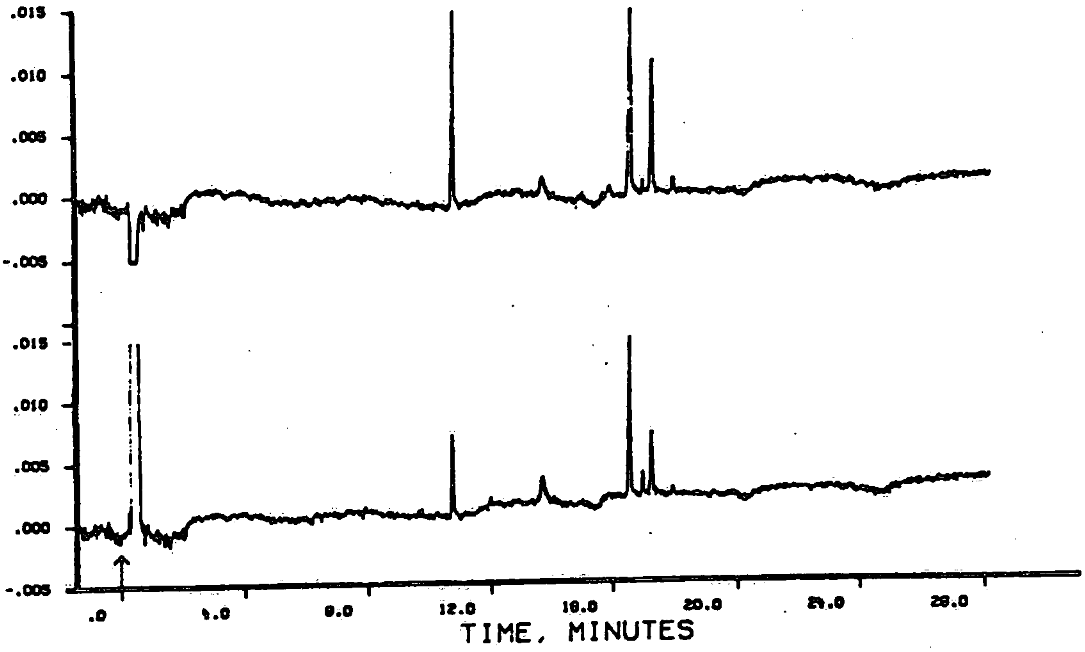


"Scrap Tire" extract Fraction # 1 (dilute)

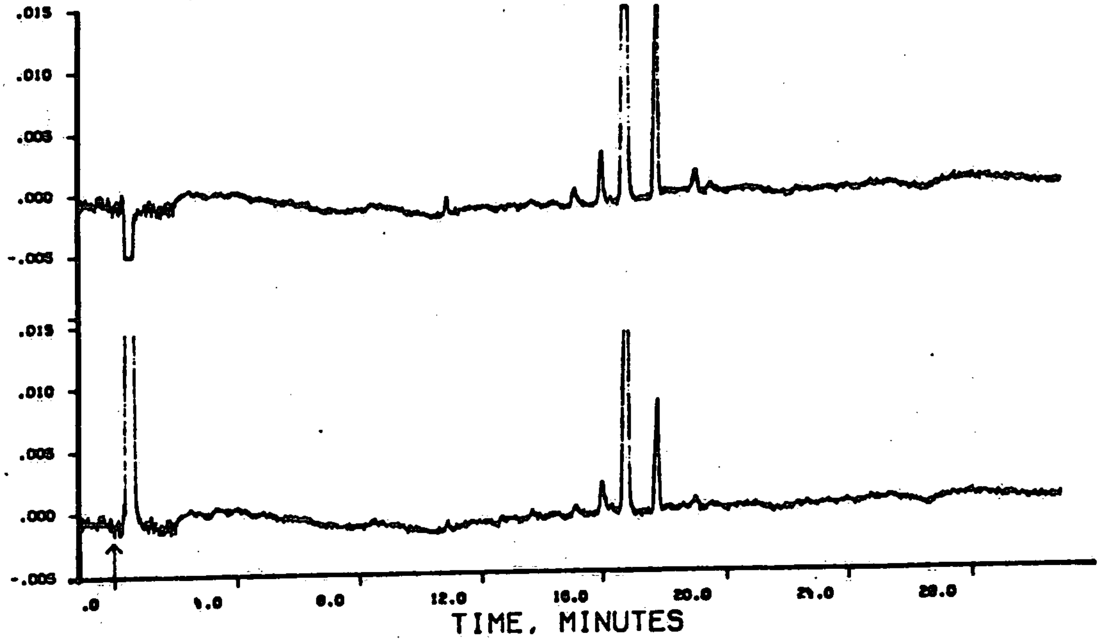


"Scrap Tire" extract Fraction # 1 (10:1 conc.)

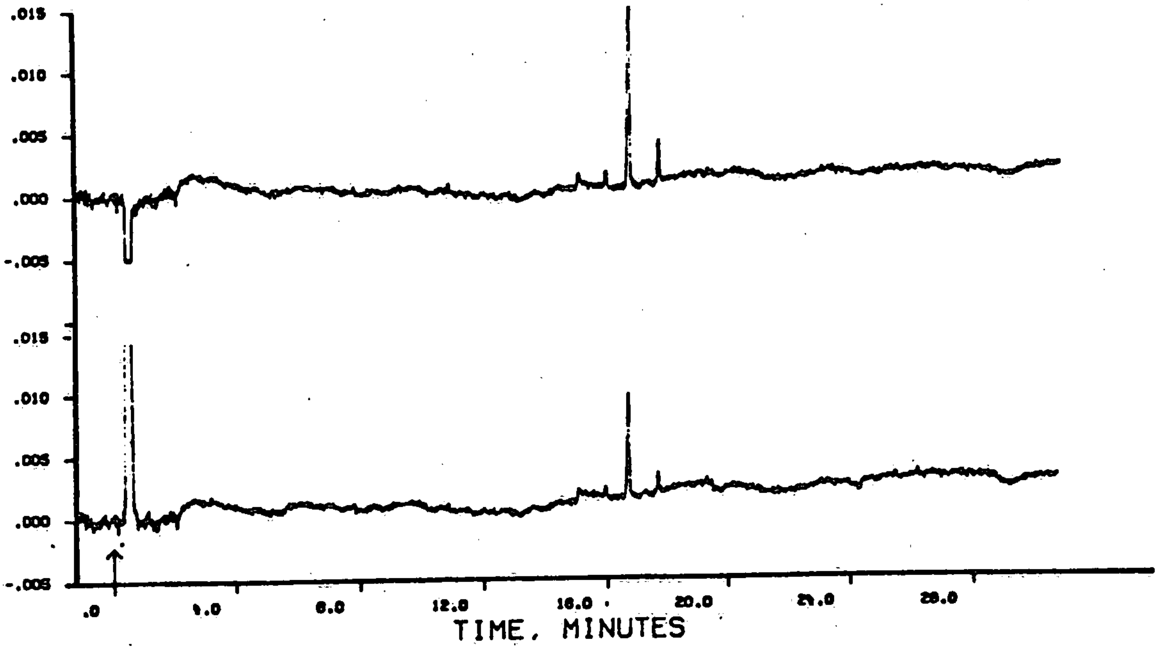
"Scrap Tire" extract Fraction # 2 (dilute)



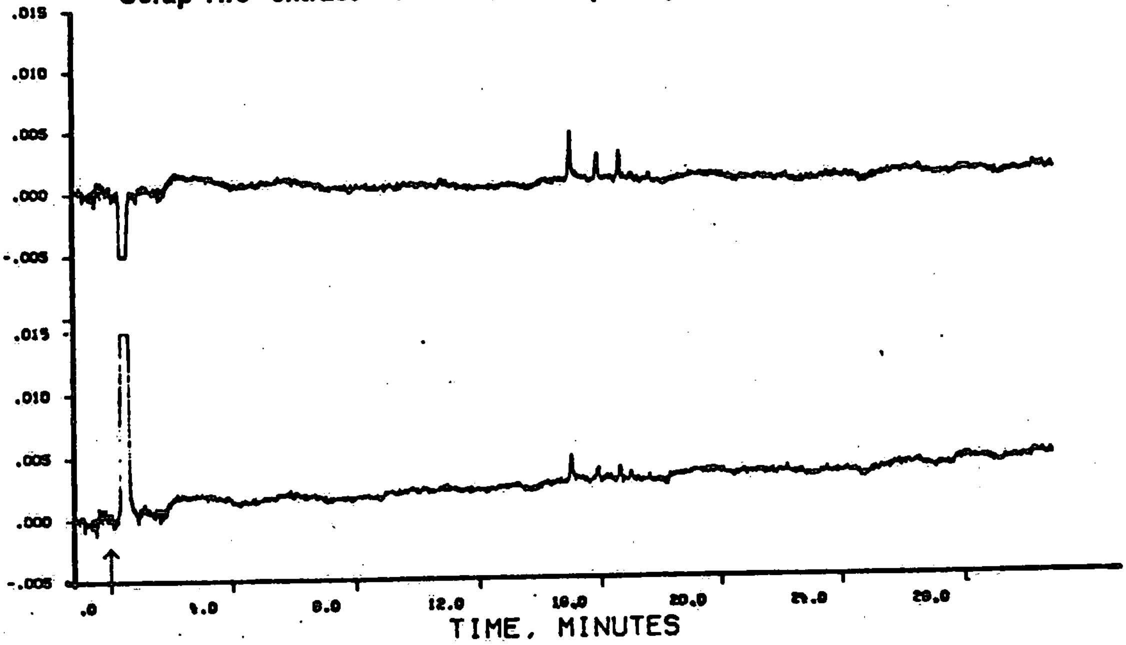
"Scrap Tire" extract Fraction # 3 (dilute)



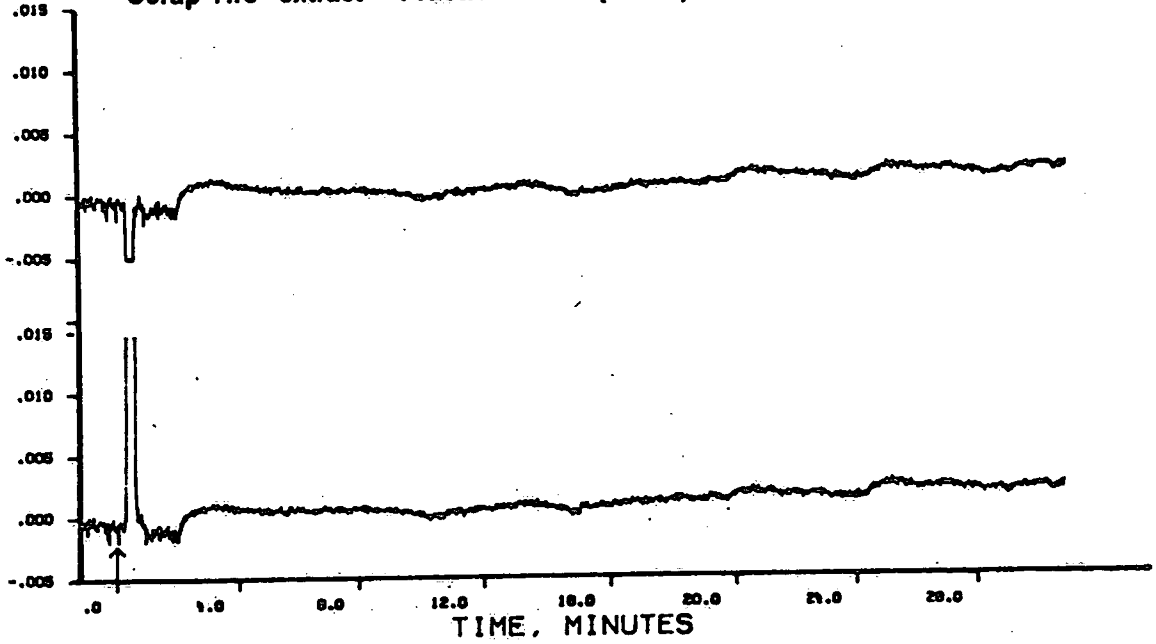
"Scrap Tire" extract Fraction # 4 (dilute)



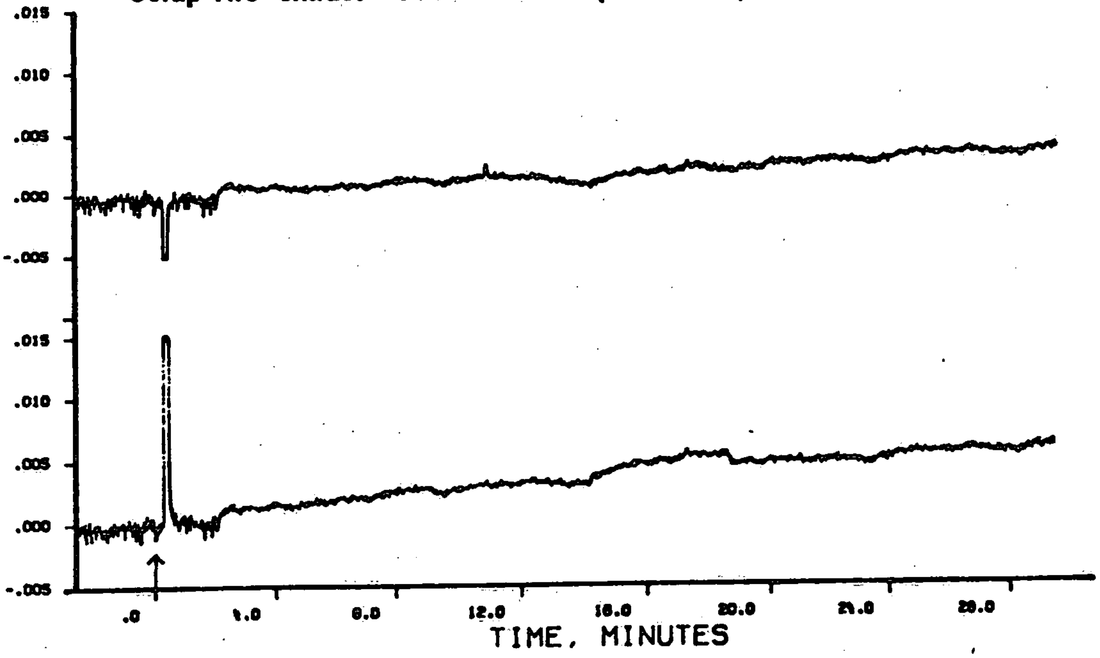
"Scrap Tire" extract Fraction # 5 (dilute)

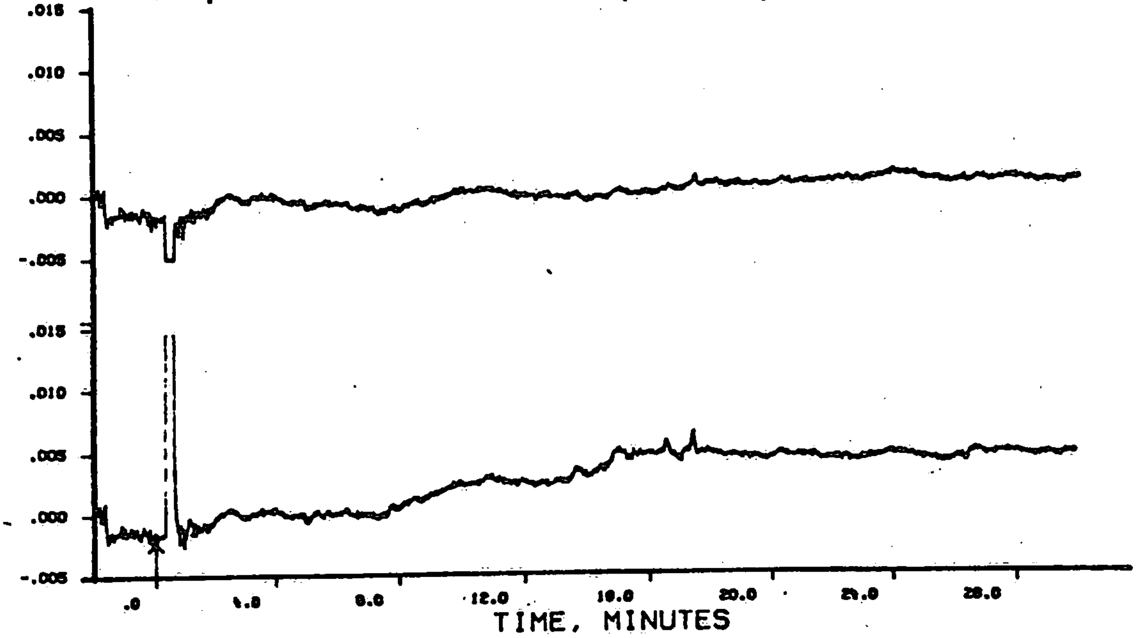


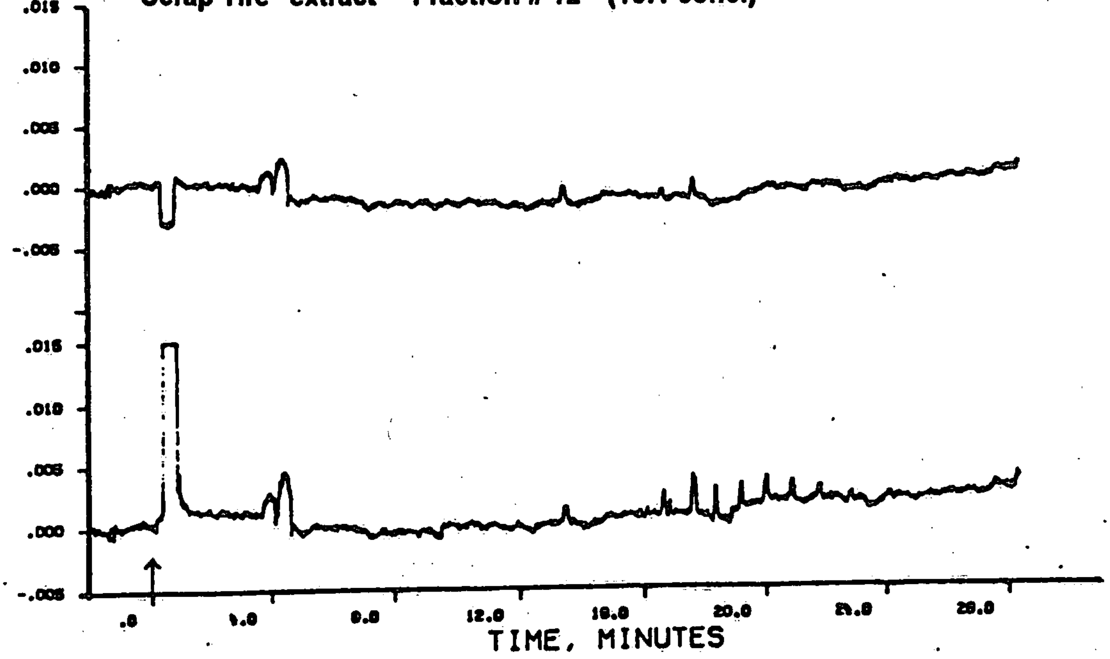
"Scrap Tire" extract Fraction # 6 (dilute)



"Scrap Tire" extract Fraction # 8 (10:1 conc.)




"Scrap Tire" extract Fraction # 10 (10:1 conc.)

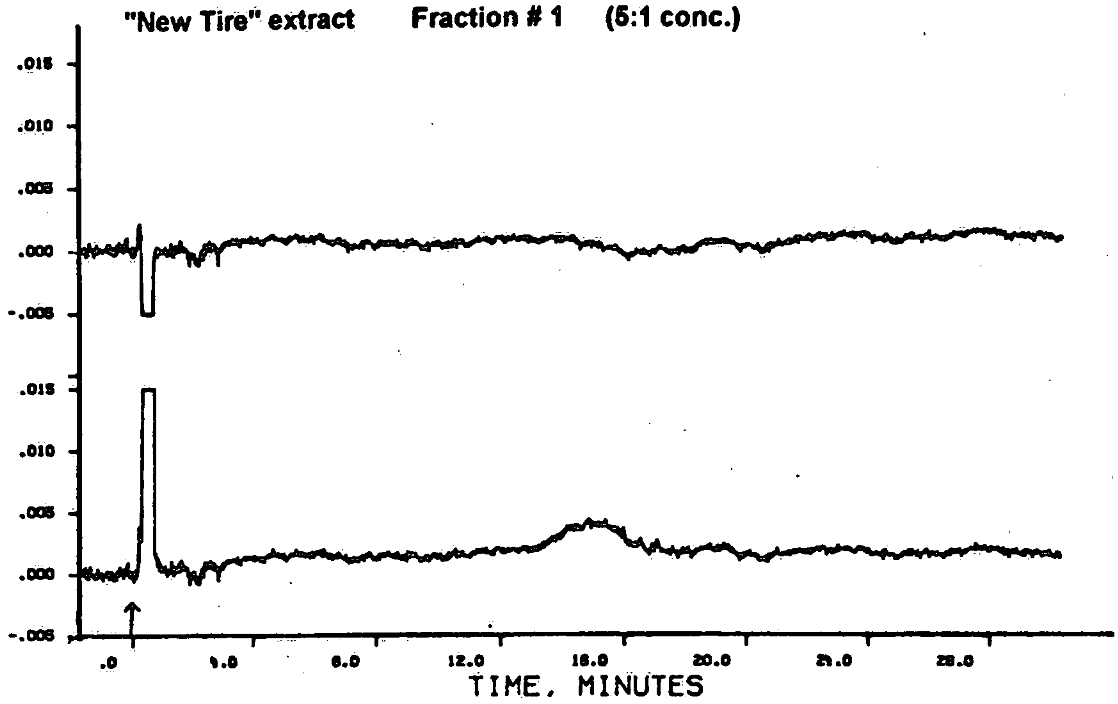

"Scrap Tire" extract Fraction # 12 (10:1 conc.)

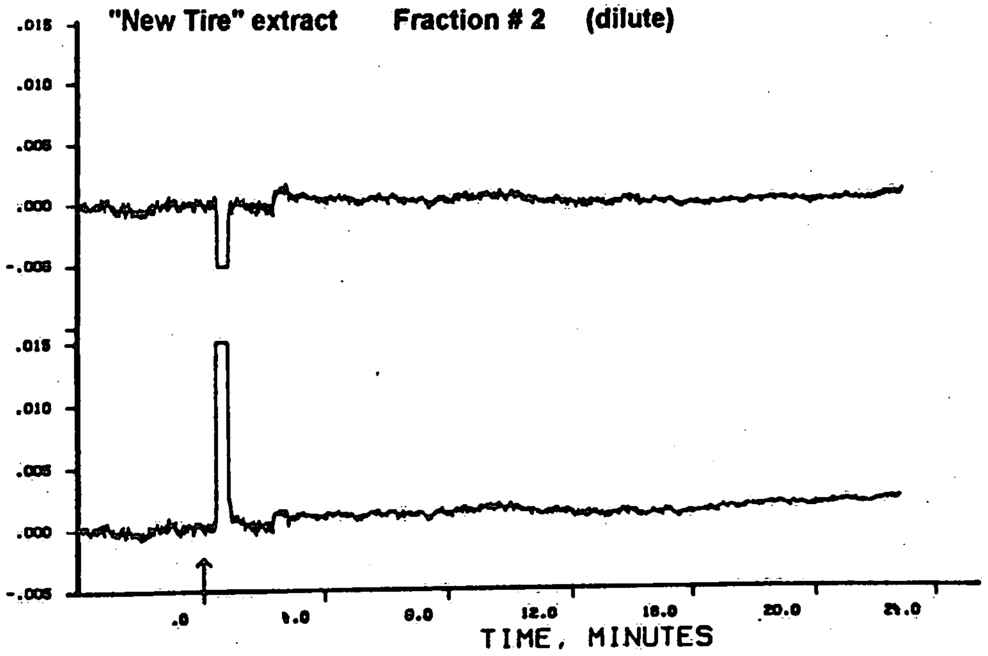
APPENDIX E

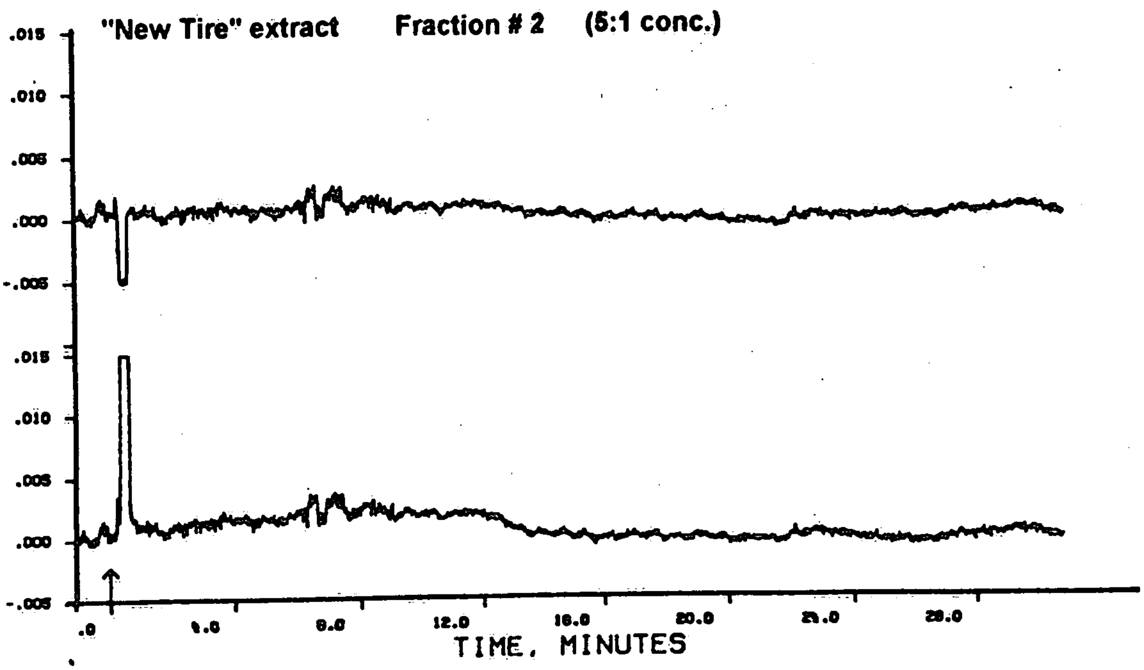
GC/FTIR Chromatograms of "New" Tire Fractions

"New Tire" Extracts GC/FT-IR chromatograms

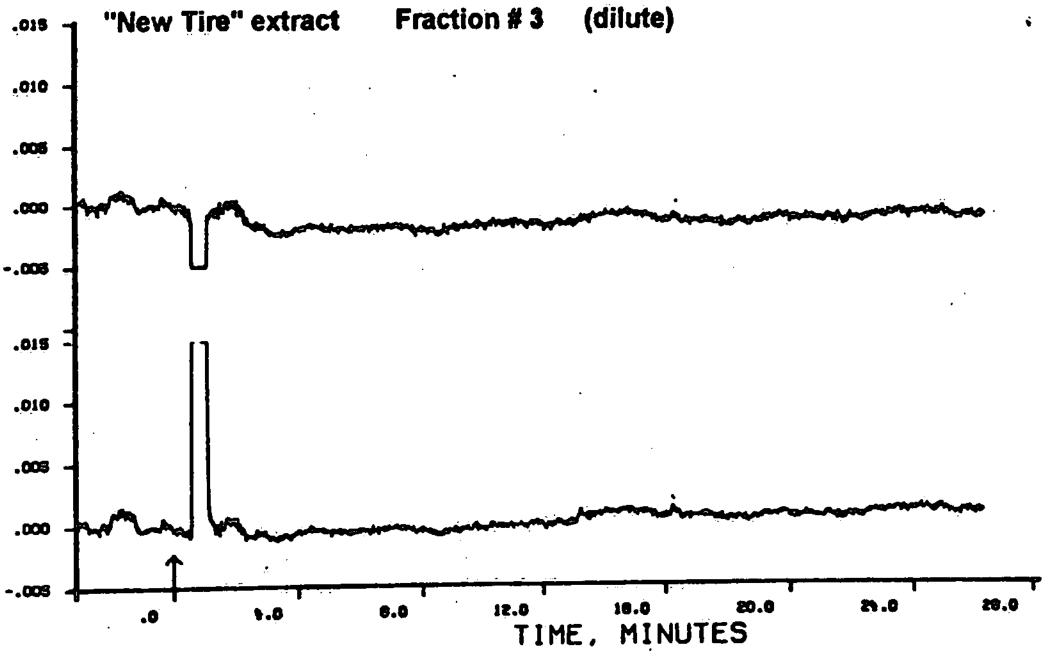
2980 - 2910 cm^{-1} (bottom window) and 1170 - 1150 cm^{-1} (top window)


"New Tire" extract Fraction # 1 (5:1 conc.)


"New Tire" extract Fraction # 2 (dilute)

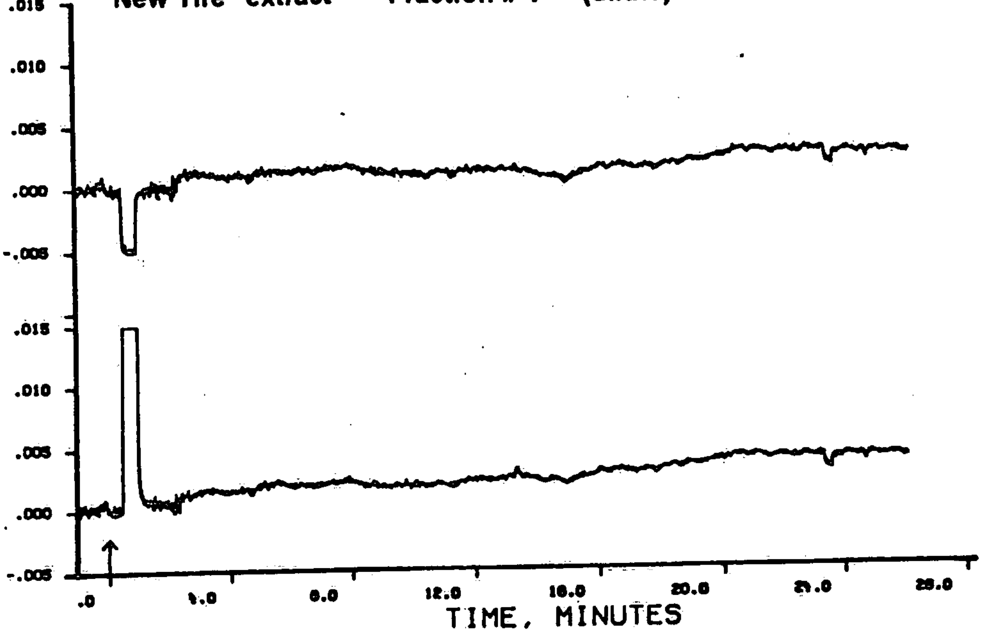


"New Tire" extract Fraction # 2 (5:1 conc.)

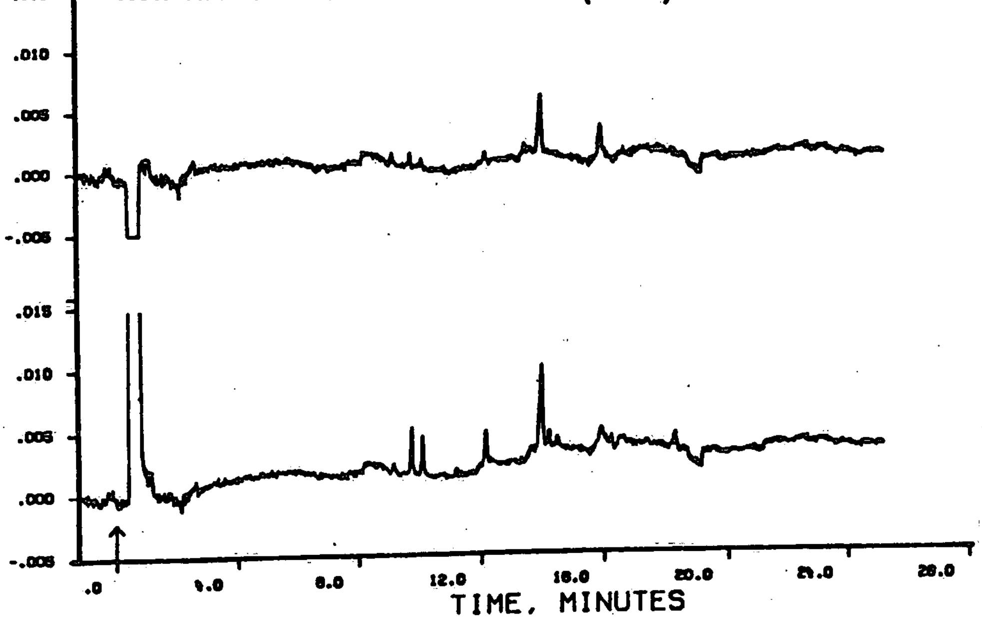


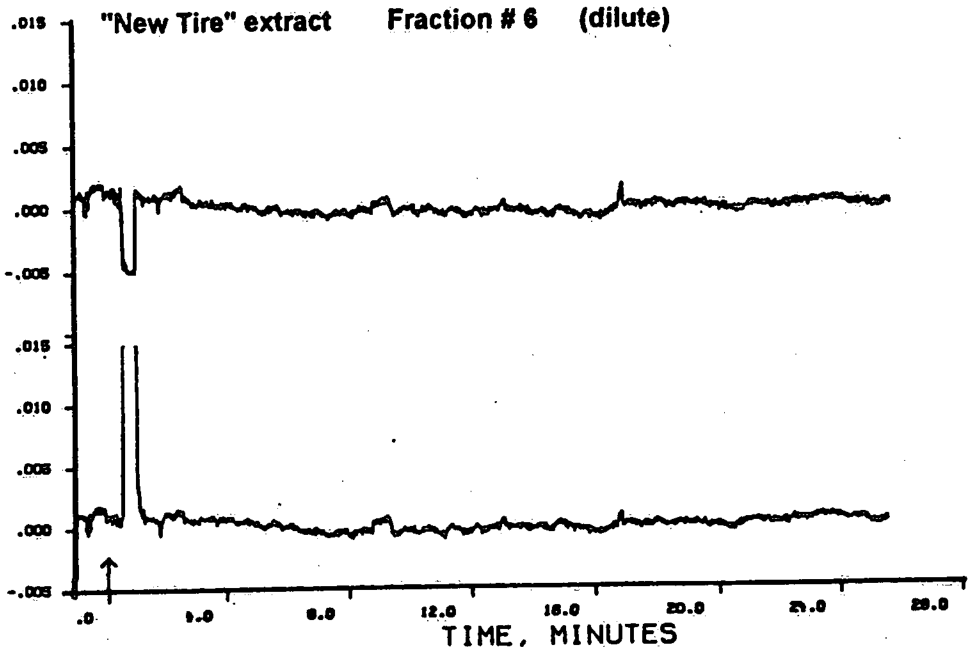
"New Tire" extract Fraction # 3 (dilute)

"New Tire" extract Fraction # 4 (dilute)

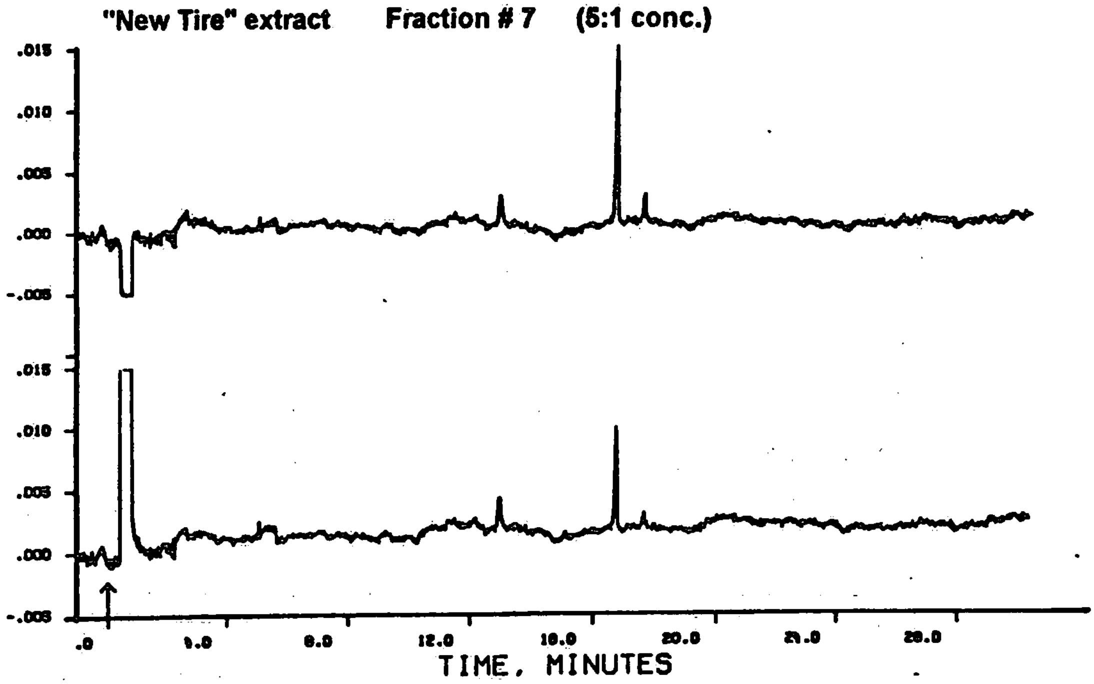


"New Tire" extract Fraction # 5 (dilute)

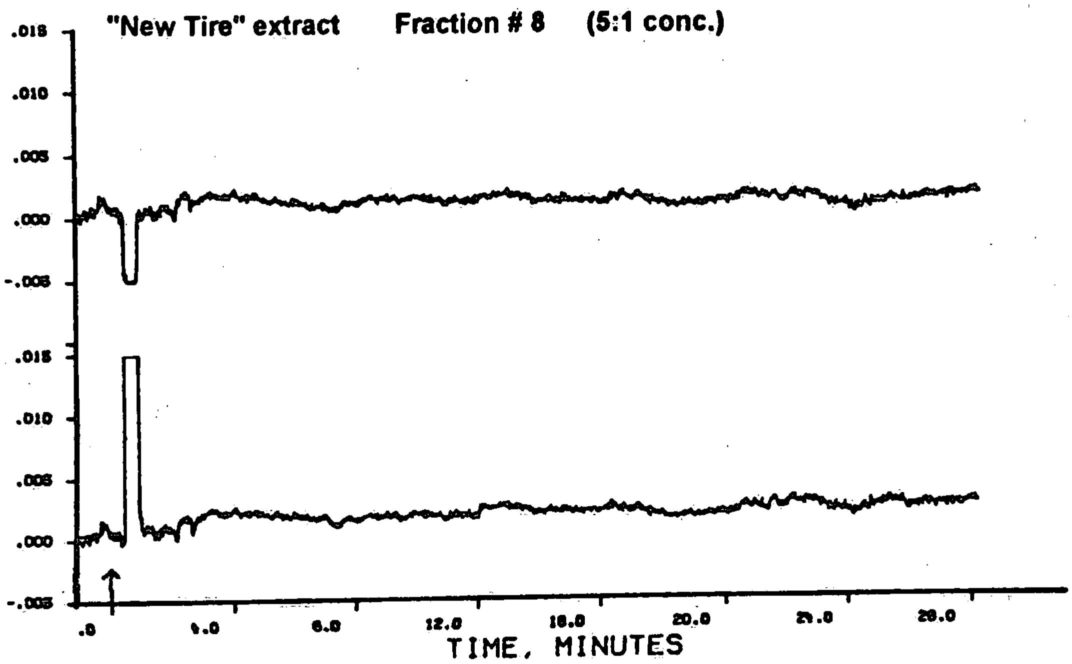


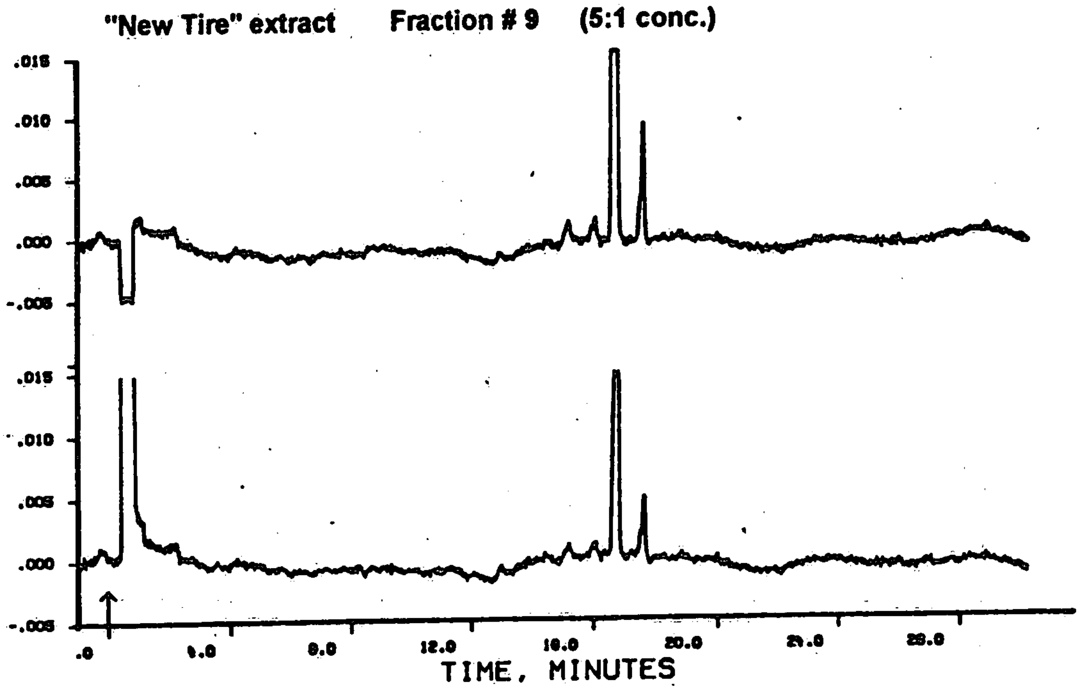


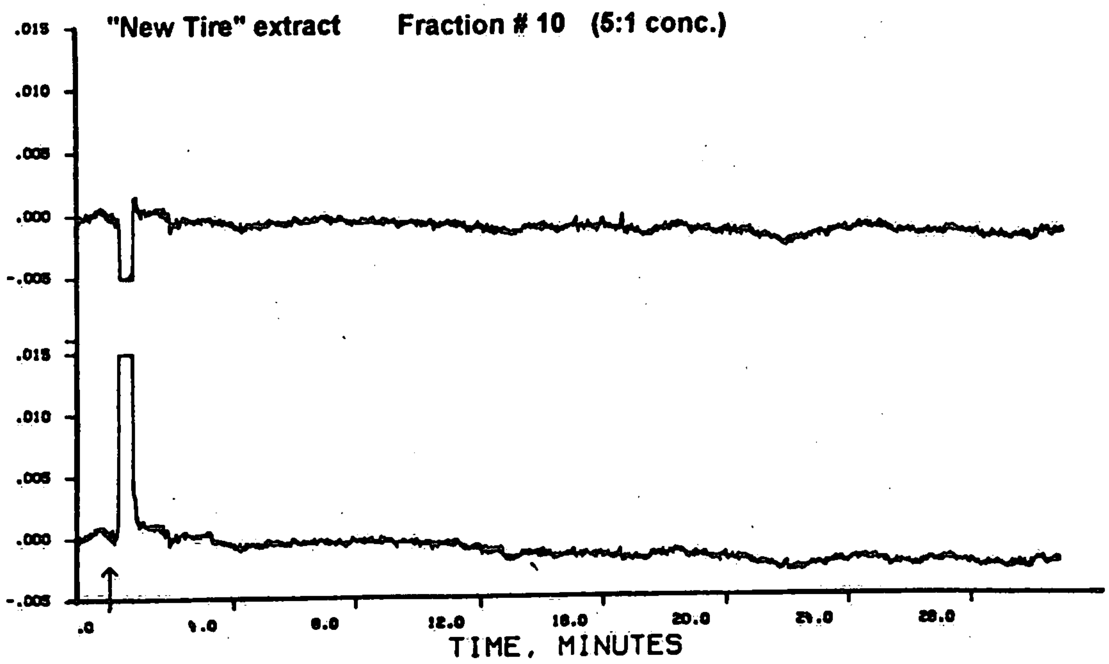
"New Tire" extract Fraction # 6 (dilute)

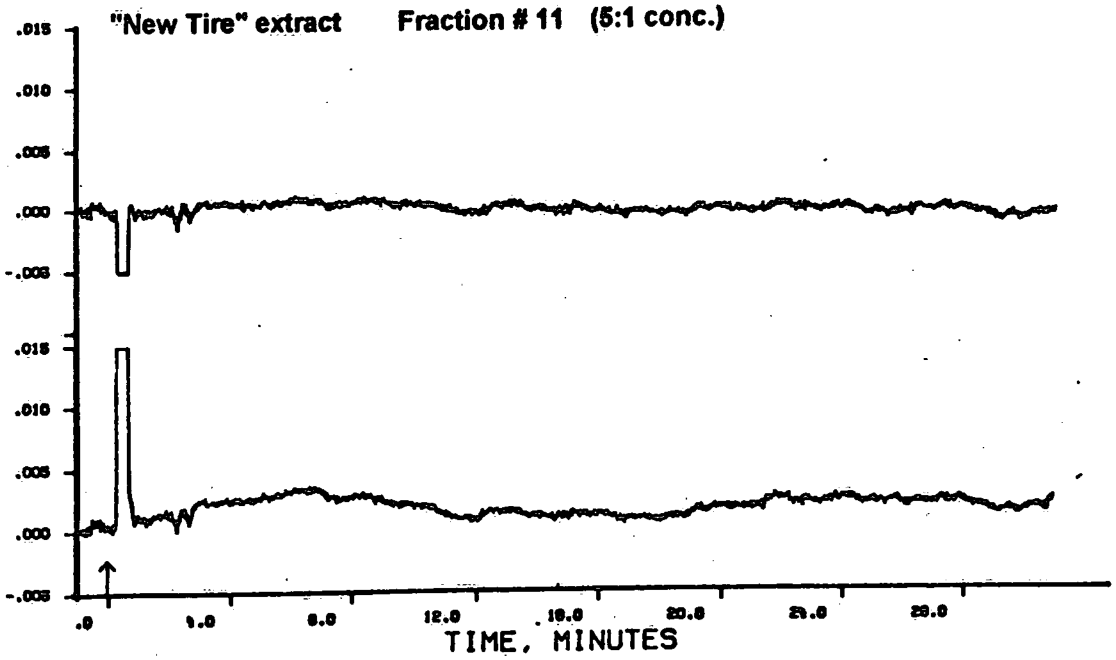


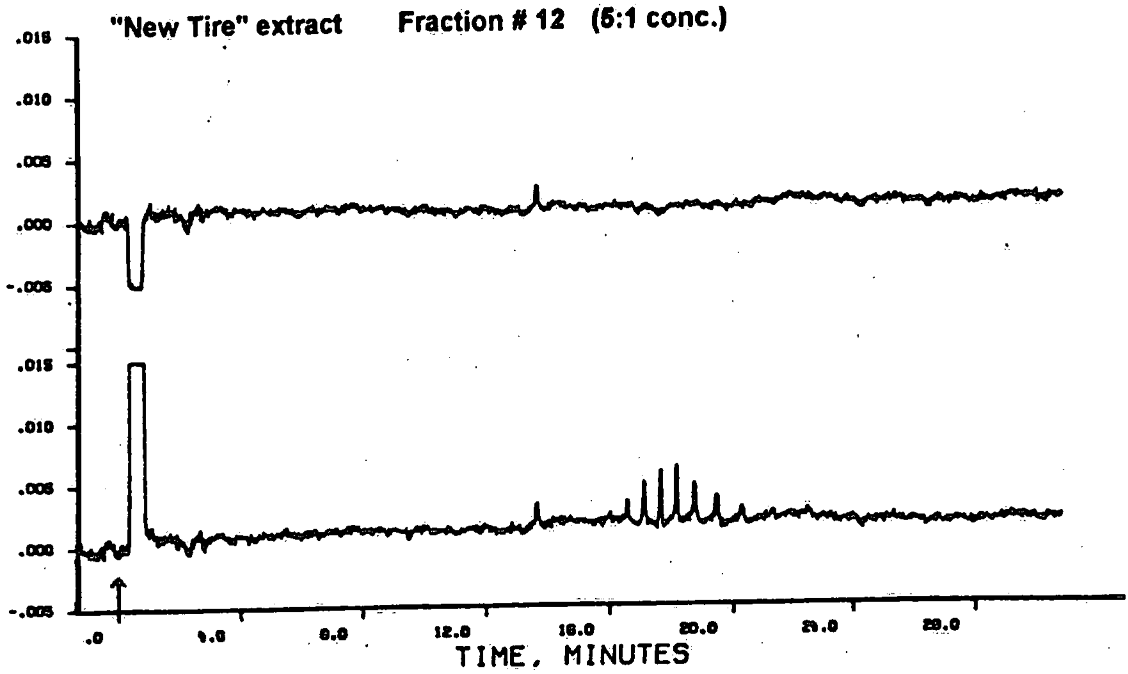
"New Tire" extract Fraction # 7 (5:1 conc.)

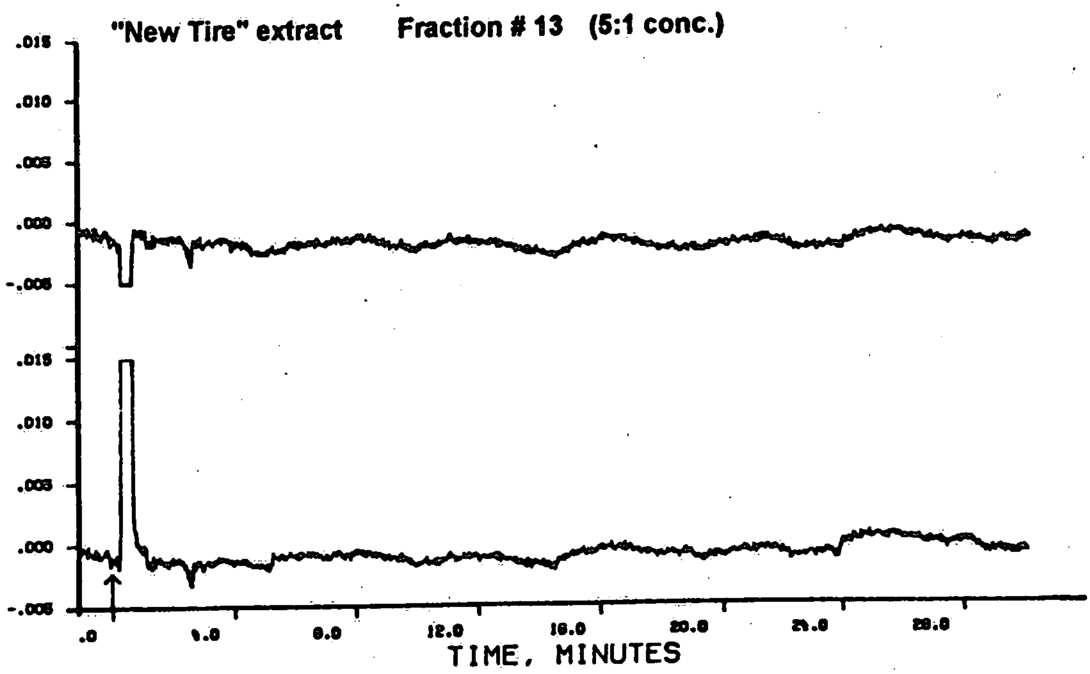

"New Tire" extract Fraction # 8 (5:1 conc.)

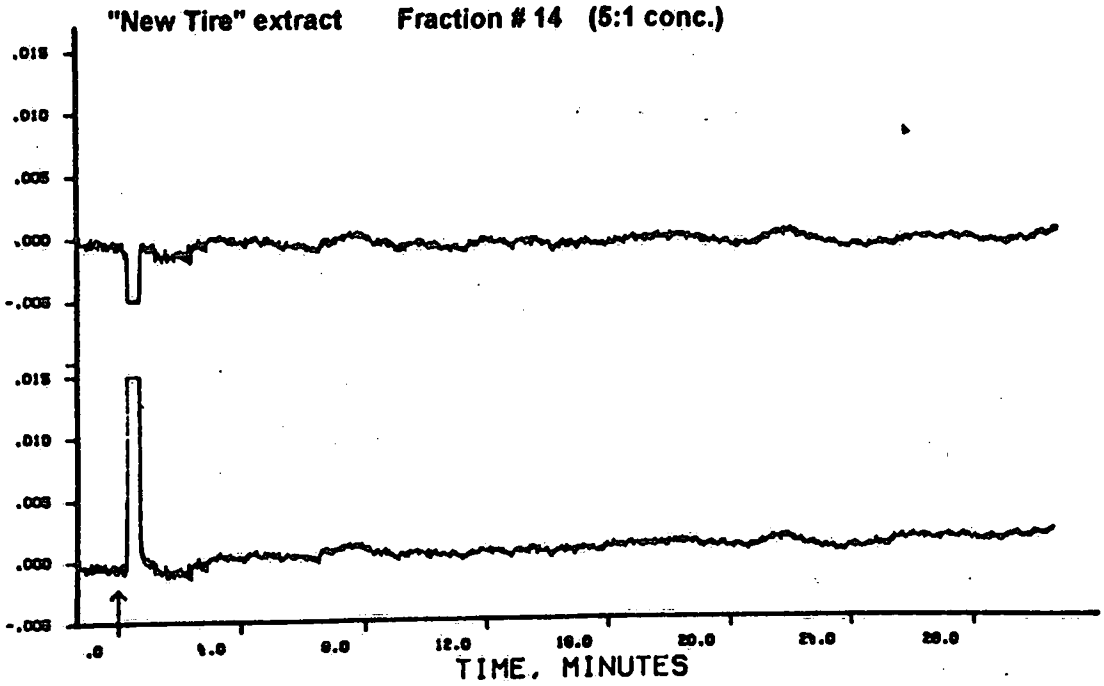

"New Tire" extract Fraction # 9 (5:1 conc.)

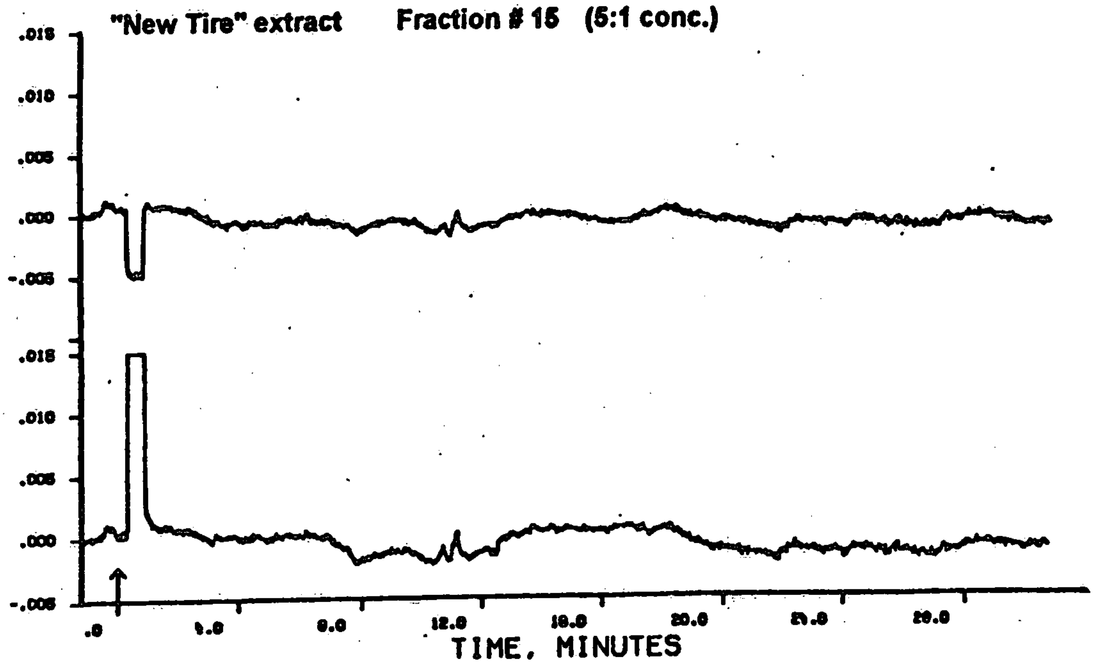

"New Tire" extract
Fraction # 10 (5:1 conc.)
.015
.010
.005
.000
-.005
.015
.010
.005
.000
-.005
.0
4.0
8.0
12.0
16.0
20.0
24.0
28.0
TIME, MINUTES

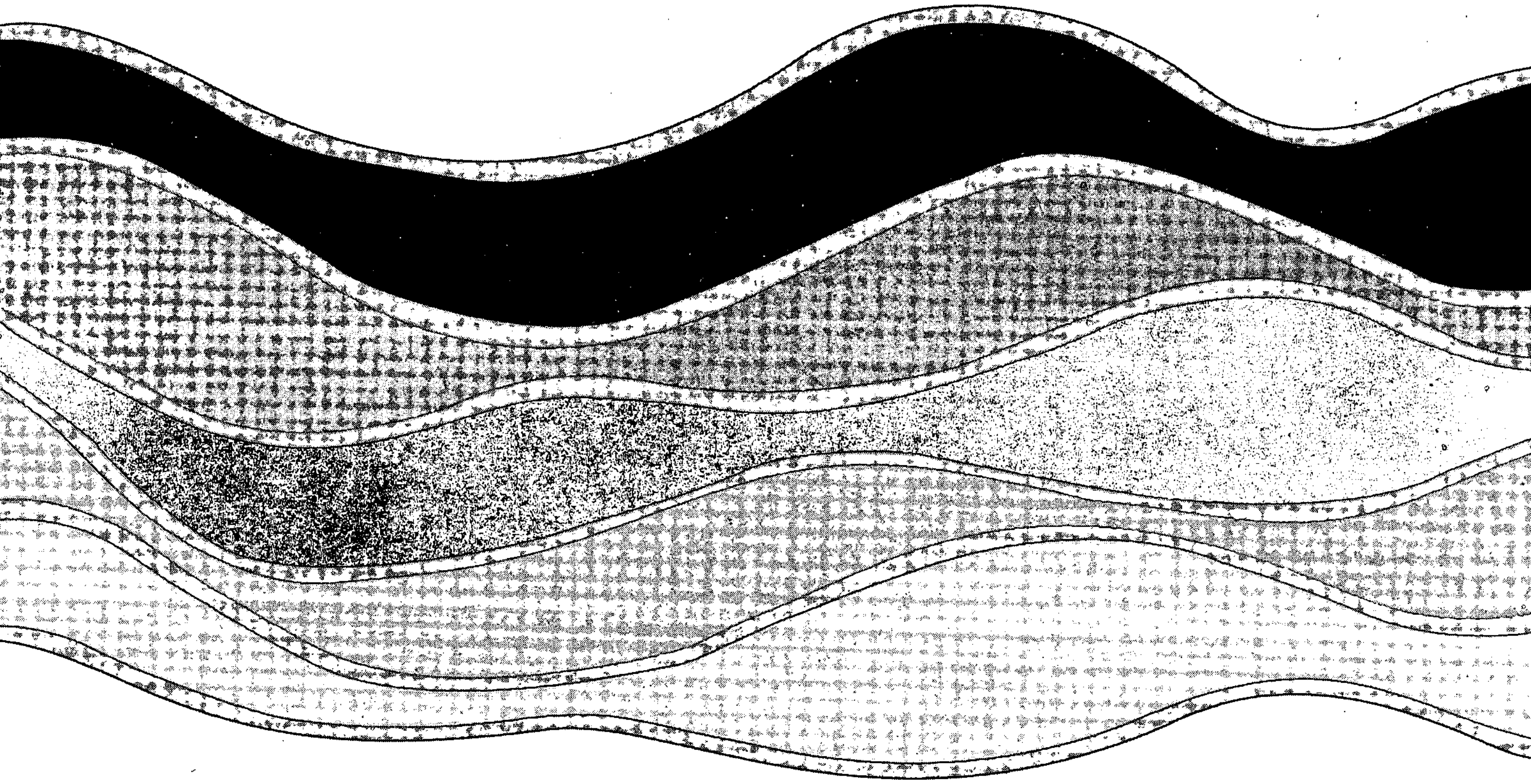

"New Tire" extract
Fraction # 11 (5:1 conc.)
.015
.010
.005
.000
-.005
.015
.010
.005
.000
-.005
.0
4.0
8.0
12.0
16.0
20.0
24.0
28.0
TIME, MINUTES


"New Tire" extract Fraction # 12 (5:1 conc.)


"New Tire" extract Fraction # 13 (5:1 conc.)


"New Tire" extract Fraction # 14 (5:1 conc.)


"New Tire" extract Fraction # 15 (5:1 conc.)



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