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TRACE ORGANIC ANALYSIS OF MICROENCAPSULATED MATERIALS

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Detection and identification of trace target species in complex polymeric mixtures requires application of advanced analytical instrumentation and methodology. The major goal of this task is the development of analytical systems and/or methodologies to detect/identify/quantitate trace organic chemical species in complex microencapsulated mixtures. To accomplish this goal, the approach is based on sample processing, concentration, separation, detection/identification, and data manipulation/processing. This task emphasized the application and development of commercially available analytical systems.

Specific objectives were: (1) Develop current awareness of the extensive microencapsulation research and technology base; (2) Provide detection and characterization of microcapsules with their chemical/physical microstructure; (3) Establish detection and identification schemes for signature analysis and classification of core/shell formulated products,

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Fiber optic monitors (FOM)
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Neural network
Pattern recognition
EXMAT
MicroEXMAT

19. Abstract (continued)

including thickeners, additives, and carriers; (4) Determine the quantitative amounts of microcapsule samples (milligrams) at trace parts per million, parts per billion levels; (5) Encode information in an applied artificial intelligence format.

Four analytical instrumental systems were assembled to examine microencapsulated materials: System 1 - Pyrolysis atmospheric pressure chemical ionization (APCI) tandem mass spectrometer; System 2 - Pyrolysis/concentrator interfaced to GC-MS and GC-MS/MS units; System 3 - GC interfaced to Fourier transform infrared (FTIR) spectrometer; System 4 - Supercritical fluid chromatograph for extraction, desorption, reaction and chromatography. These analytical systems integrate automated and spectral detection/identification units.

Exploratory research was conducted for prototyping trace detection/identification instrumentation, which included fiber optic monitors, AI expert systems, and neural networks for in-field threat analysis in diverse environments.

PREFACE

The work described in this report was authorized under Project No. DAAA15-87-D-0007-0001. This work was started in January 1987 and completed in January 1989.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for release to the public.

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We appreciate the background information microencapsulation supplied by Dorothea Paterno, the initial activities in supercritical fluid technology provided by Emory W. Sarver and Leon J. Schiff of CRDEC, and the cooperative research by R. Fifer of the U.S. Army Ballistic Research Laboratories in the fiber optic monitor development. Loan of the Guided Wave unit by Ted Novak and technical assistance by Vikki Henderson of CRDEC are also appreciated in addition to the cooperation provided by Raymond Herd and Phyllis Gray, Analytical Division, CRDEC, and Barbara Ball and Sol Heller, Audio-Visual, CRDEC. The outstanding continued assistance by Linda Jarvis of GEO-Centers, Incorporated, is gratefully acknowledged. In-depth technical review and general project management by Louis Isaacson, Geo-Centers, Incorporated, are sincerely appreciated.

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TRACE ORGANIC ANALYSIS OF MICROENCAPSULATED MATERIALS

1. INTRODUCTION

1.1 Definition of the Problem and Program Goals.

Detection and identification of trace target species in complex polymeric mixtures requires application of advanced analytical instrumentation and methodology. In particular, microencapsulated toxic substances present a demanding challenge for their detection and identification in the environment. The accomplishment of this task requires knowledge of microencapsulation technology including the formulation and processing of complex materials, so that analytical characterization can be designed in a comprehensive and meaningful manner. The initial activity on this task utilizes background information in microencapsulation research and technology that involves the food, agricultural, pharmaceutical, consumer product, and biomedical industries.

The major goal of this task is the development of analytical systems and/or methodologies to detect/identify/quantitate trace organic chemical species in complex microencapsulated mixtures. The analytical chemistry required to characterize formulated materials has been developed over many years in context to polymeric substances, both natural and synthetic origins. The instrumentation and methods developed and applied have focused on analytical pyrolysis interfaced to chromatographic and spectral separation/detection/identification systems (1). Trace organic analysis involves the use of enrichment or concentration units which are manufactured as highly automated systems. This Integrated Intelligent Instrument (I^3) approach, outlined in Figure 1, is based on sample processing, concentration, separation, detection/identification, and applied artificial intelligence.

The approach selected for this task emphasizes selected analytical tools that are commercially available and used for detection and identification of trace amounts of toxic species that are in formulated polymeric forms, such as immobilized carriers or microencapsulated materials. Development of the I^3 approach focused on two major technologies; namely, analytical pyrolysis and supercritical fluids, with advanced data analysis and applied artificial intelligence (AI) methods. Figure 2 outlines how formulated (e.g. microencapsulated) materials are studied within the I^3 approach.

Specific program objectives are outlined in the following five statements:

1. Develop current awareness of the extensive microencapsulation research and technology base.

2. Provide detection and characterization of microcapsules with their chemical/physical microstructure.

3. Establish detection and identification schemes for signature analysis and classification of core/shell formulated products, including thickeners, additives, and carriers.

4. Determine the quantitative amounts of microcapsule samples (milligrams) at trace ppm, ppb levels.

5. Encode information in an applied artificial intelligence format.

The means to accomplish these objectives include (a) assessment of microencapsulated R&D as background for developing analytical schemes; (b) assessment and assembly of selected analytical instrumentation to qualitatively and quantitatively determine component levels in complex mixtures; and (c) document and outline the information with applied AI. Our approach is shown schematically in Figures 3 and 4.

The long-term goal includes extension of laboratory results from these studies to the in-field, battlefield environment. This longer-term goal was considered in the initial design and execution of the task. The role of highly automated, expert-system oriented analytical instrumentation is significant in this regard. Specialty hardware/software designed to accomplish the detection and identification of trace toxic materials in complex matrices can be realistically proposed based on results from this and allied studies. Following the current emphasis on technology assessment and transfer methods for R&D links to commercially significant ends, such specialty tools based on the I^3 approach have significance throughout our industrial processing and environmental fields. This contract research provides the technical basis for the design and manufacture of a prototype highly automated portable, modular threat analyzer to meet Army needs.

1.2 Experimental Design.

Although there are numerous methods available to statisticians in the conduct of experimental design for chemical studies (2-5), the choice of a Box-Behnken design was made for specific reasons important to the interpretation stage. The Box-Behnken is a central composite, blocked design to randomize experimental error. The design provides an excellent multivariate tool for evaluation of experimental parameters. The pure experimental error is determined, in addition to measuring how well the variables account for the system variance (or lack of fit to the model). A typical output is shown in Figure 5. The response surface is determined over the instrumental range under study, so as to detect main variables responsible for the measured response, and importantly, any second order or quadratic interactions. Use of experimental designs are emphasized in current industrial R&D to provide the most information in the shortest possible time, thereby resulting in productive research. Background experience in this area led to the specific choice of the Box-Behnken and also led to extensions of its use for multivariate response data needed in our studies.

1.3 Data Analysis.

The role of chemometrics has increased significantly over the past decade (6-8) to increase the information content from data generated by highly automated instruments. Only such reproducible, accurate data can be handled by chemometric techniques, including factor analysis and pattern recognition software. The mathematical and statistical treatments common in classification or multivariate analysis were further developed in this project to include applied artificial intelligence. Use was made of AI shell software packages, as well as specialty software, to develop a prototype expert system network, EXMAT. The need for combined numeric and symbolic computing was recognized early in our program and ideas were presented at a Workshop held in Seattle, WA in August 1985, sponsored by the American Association for Artificial Intelligence and Boeing Computer Services. Extension of this approach is being made to current developments in neural networks addressing both hardware and software aspects in cooperation with General Research Corporation, McLean, Virginia.

2. MICROENCAPSULATION RESEARCH AND TECHNOLOGY BACKGROUND

2.1 General Considerations.

Microencapsulation technology has developed over the past decade in a rapid and diverse manner throughout the food, chemical (pesticides, consumer products, etc.) agricultural, and pharmaceutical industries (9). Aerosol carriers, agent thickeners, and additives are composed of varied organic substances, many of which are polymeric in nature. Complex mixtures result when such materials (surfactants, surface and viscosity modifiers, emulsifiers, plasticizers, humectants, etc.) are formulated to achieve specific performance and compatibility requirements. Wall materials or specialty membranes and polymers may surround the encapsulated core or serve as transport agents in novel ways (10). These multicomponent products are formulated to provide "tailored" physicochemical behavior over a range of environmental stabilities, controlled release mechanisms, and transfer/distribution means. The advantages of providing reactive or labile species in timed-release/encapsulated formulations are given extensively in the agrochemical, biomedical, and pharmaceutical industries.

Fabrication techniques needed to produce such materials are likewise varied, including microencapsulation processes; e.g.

Wuster coating, centrifugal extrusion, vapor deposition (Parylene), liquid walls, interfacial polymerization, phase separation, complex coacervation (thermal, nonsolvent, interfacial), in-situ and matrix polymerization. Many processes are commercially developed and available for specialty applications (9).

Characterization of microcapsules thus requires detailed, comprehensive analytical methods for microstructure, composition, and physicochemical information. Concerted organic trace analysis conducted in the industrial R&D sector ensures that needed production quality and in-field applications are achieved over the planned range of formulation, processing, and end-use conditions. Furthermore, prediction of physical/mechanical properties for the intended lifetime of the material requires knowledge of degradation mechanisms and associated kinetics. Such controlled release performance critically depends on polymeric microstructure and compositional details of the thickeners, additives, and carriers used in the process. Thus, instrumentation designed for analysis of complex materials are required in our study.

2.2 CRDEC Microencapsulation Workshop, December 3-4, 1986.

Of singular importance to the Army was the Microencapsulation Workshop that was organized and held at CRDEC in December, 1986. Collection of the Workshop presentations has been published as "Macromolecules in Microencapsulation Research and Technology," CRDEC-SP-87022, August 1987.

The purpose of the CRDEC Microencapsulation Workshop was to encourage technology transfer among active industrial R&D, academic and U.S. Government investigators. Emphasis was placed on the physicochemical characterization of natural and synthetic macromolecules used in the microencapsulation field, with the associated synthesis, formulation, and processing aspects. Specialty design of polymeric microstructure and formulation/processing variables required for wide-ranging performance was emphasized with regard to controlled release, transport mechanisms, microporosity, and environment stability.

Over 50 companies, 20 academic/research institutes, and 8 government agencies participated. Nearly 160 persons attended the Workshop. Topics of research presentations included preparation, chemical/physical modification, and characterization of specialty polymers, surfaces, and membranes; design and monitoring of selected diffusion, permeability, adsorption/absorption or stabilization phenomena; and macromolecules and associated materials used as carriers, stabilizers, or thickeners in microemulsions and colloidal systems.

Directly relevant for Army applications is research that involves the production, delivery, and detection of substances encapsulated/immobilized in complex polymeric/inorganic systems.

The analytical capabilities needed for these materials also impact industrial manufacturers in food, chemical, agricultural, pharmaceutical and consumer product fields, as well as forensic sciences. Environmental and legal requirements, as well as quality control/assurance operations require that modern analytical systems be integrated into most corporate R&D programs.

Relevant literature in the microencapsulation field is given in Bibliography 10.1, (page 38), including references in microemulsions, microcapsules, polymeric/liposome delivery systems, physicochemical research, and specialty polymer information.

3. INSTRUMENTATION BACKGROUND

3.1 General Trace Organic Analysis.

The concerted organic analysis approach has been discussed (11) and developed over nearly two decades for applied research and problem-solving in industrial R&D (1). A schematic (Figure 6a) outlines the approach as it was presented in 1971 (12) and updated in Figure 6(b) in 1986. Figure 7(a, b) show the background information for sample processing and on-line analysis. The specific advantage of our study over previous and on-going efforts in polymer characterization is that of developing and/or applying new and automated instrumentation that is now available. Analysis of synthetic and natural polymeric mixtures have benefitted from the advantages of combined dynamic headspace analysis (DHS) with pulse and/or programmed pyrolysis. Careful thermal processing under controlled conditions is accomplished on small (milligrams or micrograms) amounts of sample. For many cases, this thermal method replaces solvent extraction or time-consuming isolation methods. For samples that are thermally labile, nonthermal treatment is used, and supercritical fluid (SF) instrumentation (e.g., extraction) achieves this goal. Our general problem-solving in materials science uses these two major instrumental fields as outlined in Figure 6(b).

3.2 Analytical Pyrolysis Technology.

The pyrolysis instrumentation available for performing this task is the Chemical Data Systems (CDS) Model 123 Pyroprobe, configured with a programmable pyrolyzer interfaced to the Model 320 Sample Concentrator. For samples that may be thermally labile and for ultra-trace analyses, the Model 330 Sample Concentrator is used with cryogenic enrichment and direct transfer of the trapped volatiles (splitless mode) to the separation or identification system (GC, FTIR, MS, etc.). The latter system, the Pyroprobe Model 124, provides one of the most sensitive means for trace organic analysis of complex materials. The acquisition and method development performed as part of this task established the significance of the pyrolysis technology to study the selected microcapsules (see Section 5).

In a Dynamic Headspace (DHS) experiment, a small (mg) sample is placed in the thermal desorber unit of the sample concentrator and heated to the desired temperature which is below the degradation level for the sample. Volatiles (residual monomers, water, additives, solvents, etc.) are released from the matrix and trapped or concentrated by means of the on-line internal trapping system. This enrichment stage uses either solid adsorbents and/or cryogenic means such as liquid N_2. When desired, the trapped volatiles are pulse-heated off/out of the trap and delivered to the analytical system. In some cases, DHS may not be needed and the pyrolyzate (from pulse or programmed treatment) is delivered directly to the GC or analytical unit. Hence, pure materials for reference patterns, as well as those that must be manipulated from complex matrices are examined in an absolutely repeatable, reliable manner in the microprocessor-controlled system under the conditions to obtain the most useful diagnostic information.

Furthermore, in an example of DHS combined with pyrolysis, Figure 8 illustrates results from thermal processing of a high molecular weight polyethylene-vinyl acetate (PE-PVA) copolymer with He and air atmospheres, respectively. The DHS analysis revealed low-level volatiles (ppm amounts) that were removed from the polymer matrix in the low-temperature (120°C for 5 min) mode and the pulse pyrolysis step (750°C) showed the characteristic triplets from PE, as well as the PVA fragments.

Importantly, programmed pyrolysis or "time-resolved" pyrolysis exhibits advantages over pulse methods for detection of microstructural details and mechanistic information (1). In Figure 9, programmed pyrolysis results (1°C/min to 850°C) are compared to pulse data (800°C/20 sec) on an NBS reference polymer, high density PE. A major difference is seen in the fragmentation pattern which has been used for diagnostic purposes. Development of linear, low-density PE (LLDPE) systems provides improved processing and performance behavior by means of incorporating small amounts of comonomers such as butene, pentene, and octene with ethylene. Compounding co- or terpolymers results in "tailor-made" materials for desired ranges of performance which are illustrative of the microencapsulation field.

Common polymers which are employed as wall materials, carriers, thickeners, or stabilizers for microencapsulation applications have been studied with analytical pyrolysis over the past two decades and are discussed in reference 1, (e.g., see Chapter 5 (Synthetics) and Chapter 8 (Biopolymers)). For natural polymers used in the food and pharmaceutical industries, pyrolysis methodology has proved to be important. Figure 10 (a, b) illustrates typical results from a concentrator/ capillary GC study obtained from a DHS analysis of volatiles from two lots of a formulated product. Lot #1 (Figure 10a) shows three major peaks that were reduced significantly in Lot #2 (Figure

10b). Further, quantitative assays may be needed, such as pharmaceutical products that are processed with various solvents that must be removed to very low levels. A DHS experiment provides the needed information on residual solvents in the part-per-million or part-per-trillion range in this automated system (13).

Other naturally occurring materials, such as protein in hair samples or microorganisms are studied in crime laboratories using analytical pyrolysis (1). The need for glass-lined systems is demonstrated in the pyrograms of human hair, raw wool, microorganisms, silk, cellulose, and chitin shown in Figures 11 (a-f). Naturally-occurring materials are often more thermally/catalytically sensitive and require non-reactive surfaces to ensure high reproducibility. It is thus concluded, analytical pyrolysis technology has emerged as a powerful means to study diverse materials over wide concentration and thermal ranges for industrial R&D, and the materials, environmental and forensic sciences.

3.3 Supercritical Fluid Technology.

In addition to using thermal methods (e.g., DHS, pyrolysis) to assist in characterizing complex polymeric materials, nonthermal methods may be necessary for difficult samples, such as microcapsules with thermally sensitive core targets. The supercritical fluid (SF) treatments that can be used involve extraction (SFE), desorption (SFD), reaction (SFR), and on-line SF chromatography (SFC) or capillary GC. Background information in this field is given in Bibliography 10.2 (page 40).

Since supercritical fluid (SF) densities resemble liquid densities, high solvating power can be achieved with SF, yet the diffusivity/viscosity property of the fluids are gas-like for fast mass-transfer behavior. Temperature influences solubilities of solutes in ways that depend on the involved region of the solubility diagram. The general statement may be made that "the dissolving power of the SF is essentially proportional to its density". Therefore, significant changes in solvent properties are brought about by variation in temperature and pressure. Instrumentation with highly controlled temperature and pressure (density) parameters was used in these analytical applications. A beta-site arrangement with Computer Chemical Systems, Avondale, PA, made possible the development of this technology for microcapsule analysis at CRDEC.

For all analyses, the supercritical mobile fluid employed was CO_2 (critical temp = 31°C, critical pressure = 1070 psi), since it has properties that permit safe use at moderate temperatures and pressures (1100 psi to 6000 psi). Therefore, SFE or SFD analyses were conducted with complex materials, including consumer products, microcapsules, charcoals, soils, etc. Samples were placed into the extraction/desorber unit (up to ca. 400 mg of sample) and treated under SF conditions, a typical set of conditions being 3000 psi, 100°C, 15 min with mobile fluid CO_2. The effluent containing the solvated species is transferred automatically to the on-line chromatographic unit for separation in packed or microbore columns. Simultaneously, the SFE effluent is monitored by a flame ionization detector (FID) to establish extraction profiles of the SF process. Detectors other than those used with GC instruments may also be on-line with the SF unit such as HPLC-type detectors, including ultra-violet (UV), visible (VIS), or spectral systems (MS, FTIR, or MS/MS). Exploratory research described in Section 6 (page 32) describes activities in fiber optic monitors (FOM) for the SFE unit throughout various spectral regions. This permits real-time, on-line detection and identification of SFE effluents (14 b, c).

4. EXPERIMENTAL DESIGN AND APPLIED ARTIFICIAL INTELLIGENCE

4.1 Experimental Design and Method Development.

Development of specific analytical methods proceeded on the pyrolysis and SF systems, which in two cases used an experimental design for assistance in method parameter screening, or defining a "response surface". The chosen design for this purpose was a five-factor, three-level Box-Behnken program (15). Extension was made of this well-known approach (which uses a single response) to a multivariate response because of the unique needs of our analytical data. The 46-run design used for analytical pyrolysis and SFE method development is shown in Figures 12 and 13. Patterns from GC, MS, or FTIR data were the needed "responses" upon which our interpretations were based and, therefore, the object of our attention. Method development is *designed* to provide the most information in an efficient manner, so generation of the "most informative" pattern is the goal in this situation. To quantitate these patterns, an extended Box-Behnken design was developed using a multivariate response derived from factor analysis and principle component analysis (16).

4.2 Applied Artificial Intelligence and Expert System Networks.

The concerted analysis of complex organic materials with modern instrumentation involves many judgemental decisions to be made in analytical strategy, instrumental configurations, data analysis and interpretation (Figure 14 (12)). Computer-assisted experimentation with microprocessor-based tools often includes embedded intelligence in the diagnostics, data acquisition, advanced data analysis and failsafe operations. However, need exists for the analyst to approach problem-solving for difficult materials such as microcapsules using the instrumental capabilities combined with some problem-solving expertise in the strategy and interpretive areas. An AI approach was developed that aids in the experimental determination of chemically significant information for these materials. A commercial shell, TIMM, (General Research Corp., McLean, VA) was used to develop the prototype network, EXMAT, a linked network of expert systems for materials analysis (17). The prototype system also included the database management expert system, EXDBM, and the expert system for chemometrics EXMATH. The outline is given in Figure 15 (a-f) (17). AI-based work at CRDEC involved a test series of organic amine salts analyzed with analytical pyrolysis/concentrator/GC-MS instrumentation. Completion of the prototype development was shown by the use of the AI software and by chemometric analysis software to provide classification of the three groups of structurally similar organic amine salts (Figure 15 (e, f)) (18).

The EXMAT prototype network was extended for application to the microencapsulation field. This development included a decision structure outline for microencapsulated materials (MICROCAP) using an analytical strategy based on nine available and functional instrumental capabilities. In addition to the four major systems noted above, other analytical systems include FTIR, high pressure liquid chromatography (HPLC), thermal analysis (DSC, TGA, TMA), microscopy (SEM, TEM), X-ray fluorescence, and microchemical C,H,N,O elemental determinations.

Background in sensors and artificial intelligence topics is given in Bibliography 10.3 (page 41).

4.3 Technical Resources: Materials, Instrumentation, and Software.

4.3.1 Materials.

Necessary reference and control samples were obtained for method development within each instrumental field. Bend Corporation (Bend, OR) made available three different core pesticides with polymer shells/walls, solvent, emulsifier and surfactant. R.T. Dodge Corporation provided additional test samples with gelatin and isocyanurate cores inside variously sized polymer walls. This series is different from the Bend series not only in the type of shell and core material, but in the relative amounts; the former contained large amounts of target core species (50-80% by wt.), whereas the Dodge series had smaller amounts of different targets (2-5% by wt.). Selected test materials were used to establish analytical ranges of detection and sample loadings needed for the different instrumental techniques. The samples are representative of the materials to be analyzed and were available alone and as fully formulated products. Experimental designs require representative materials of varied process, treatment, or compositional parameters and the two sources provided the initial test materials.

<u>Bend Research</u>: Specific Sample Inventory: Microcapsules and Ingredients

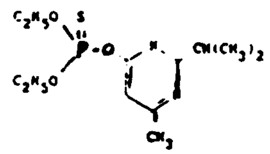
Batch 1 - polycarbonate/Diazinon; Batch 2 - polysulfone/Diazinon; Batch 3 - polyetherimide (Ultem)/Diazinon;

Batch 4 - polysulfone/Cypermethrin; Batch 5 - polycarbonate/Dursban. Thus, the requested three polymer shells and three different pesticide cores were supplied along with the formulation ingredients: emulsifier A = gelatin; emulsifier B = (Pluronic)-polyol surfactant (31R2-BASF); solvent = methylene chloride; and water.

Bend core pesticides are: Diazinon, mol. wt. 304, decomposes above 120°C, Cypermethrin, mol. wt. 416, semisolid mp. 60-80°C, and Dursban mol. wt. 350, granular white solid, mp. 41-42°C. Their structures are shown below:

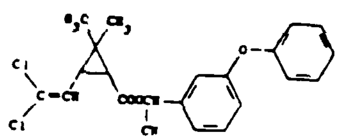
Pesticide Structures:

Diazinon (Merck Index)



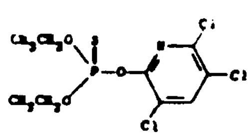
Liquid. Faint ester-like odor. d_4^{20} 1.116-1.118. $bp_{0.002}$ 83-84°. n_D^{20} 1.4978-1.4981. Vapor pressure at 20° = 1.4 × 10^{-4}, at 40° = 1.1 × 10^{-3} (about 5 times vapor pressure of parathion). Volatility at 20° = 2.4 mg/cubic meter; at 40° = 17.6 mg/cubic meter. Decomposes above 120°. Sol in water at 20° = 0.004%. Miscible with alcohol, ether, pet ether, cyclohexane, benzene, and similar hydrocarbons

Cypermethrin



Commercial product is a mixture of eight isomers. Viscous semi-solid, mp 60-80°. Insol in water; sol in methanol, acetone, xylene, methylene dichloride.
USE: Insecticide

Dursban



White granular crystals, mp 41-42°. Vapor press at 25°: 1.87 × 10^{-5} mm Hg. Soly at 25°: water 2 ppm, isooctane

R.T. Dodge, Co.: Specific Sample Inventory: Microcapsules and Ingredients: (20 gm)

18 samples: 2% gelatin/33.3% polyethersulfone (PES)/64.7% polysulfone; 5% gelatin/16.7% PES/78.3% (PS) polysulfone; 3% caffeine HCl/97% PS; 6% caffeine HCl/94% PS; 6% ACl 59 (Potassium Dichloroisocyanurate)/94% PS; 3% ACl 59/97% PS; 3% gelatin/97% PS; 6% gelatin/94% polyurethane (PU) (label); (3% caffeine HCl/97% PU); (3% ACl 59/97% PU); 6% ACl 59/94% PU; Gelatin; Caffeine HCl; ACl 59; PS; PES; PU.

The microcapsules contain core materials (bleach (ACl 59) or caffeine HCl); Wall materials - PS, PES or PU; Core sizes ranged by a factor of 3 to 10 (e.g., 20 microns/200 microns); wall thickness expressed in volume percent, 10 and 20%; isolation method was conducted with and without fumed silica.

In addition to these reference microencapsulated materials, numerous consumer products were available, such as the pesticide in the polymeic "No-Pest Strip", and over-the-counter medications as formulated in final products (Contac, Bufferin, etc.).

4.3.2 Instrumentation.

Four analytical instrumental systems were assembled to examine microencapsulated formulations:

System 1. Pyrolysis Atmospheric Pressure Chemical Ionization (APCI) Tandem Mass Spectrometer (Sciex TAGA 6000 unit).

System 2. Pyrolysis/Concentrator System (Pyroprobe Model 124) interfaced to (a) Hewlett-Packard 5985B GC/MS and to (b) Finnigan TSQ in MS and MS/MS modes. These modules allowed the following variations of operation: dynamic headspace, programmed and pulse pyrolysis, cryogenic and sorbent bed concentration/enrichment.

System 3. Pyrolysis GC with Fourier Transform Infrared Spectrometer (FTIR) (Hewlett-Packard IRD) at BRL.

System 4. Supercritical Fluid Chromatograph (CCS Model 5000) for extraction, desorption, reaction and chromatography.

Detection and identification were conducted using the instrumentation and protocols for development of analytical capability at CRDEC. These analytical systems combine sample processing (thermal and nonthermal) with concentrator and chromatographic units interfaced to spectral detection/identification systems. Also, data needed in the concerted analysis approach, included an elemental analysis capability. Conversion of an existing microchemical reaction unit (Chemical Data Systems Model 820) was completed for on-line C,H,N,O elemental determinations on gas, liquid, or solids at microgram quantities. However, the recent announcement in 1989 by Hewlett-Packard of an atomic emission detector (AED) for GC effluents makes this unit obsolete. It is evident that elemental data are important for overall integration into the concerted analytical approach, whether achieved by a microchemical system or an AED unit.

The general schematic shown in Figure 4 outlines the experimental setup.

4.3.3 Software: Artificial Intelligence and Experimental Design.

Analytical strategy, data analysis, and interpretation were topics included in development of applied artificial intelligence (AI) capabilities at CRDEC (Figure 15a). The expert system network, EXMAT, is outlined in Figure 15 (b). One of the seven outlined knowledge bases was developed (ES#1, Figure 15c) for analytical strategy to include over two hundred rules. The other six were only roughly outlined and remain to be properly developed and/or modified into a functional expert systems network. The prototype development, however, provided invaluable experience in opening up this field to Army applications. These activities are discussed in detail in references 17 and 18. The testing of the database management expert system EXDBM (A.M. Harper, (18)) in the EXMAT network is illustrated (Figure 15 d) with data from the analytical pyrolysis study on a group of twenty samples of three structurally similar groups (discussed in Section 5.2.2). Classification was achieved and extended analysis (factor rotation and plotting of covariance data) are shown in Figure 15 (e, f).

Within the EXMAT network (Figure 16) is a specific expert system, MICROCAP, which includes a prototype decision structure and a few test rules in the knowledge base. The instrumentation needed to determine such complex materials and the accompanying method details are part of the main EXMAT network. The software includes descriptive commentary under "HELP" or "Verbose Version" options for each of the analytical systems developed for the CRDEC facilities, as well as those at Ballistics Research Laboratory (BRL) (pyrolysis/concentrator GC-MS and FTIR units). General information is grouped under "HELP" for analytical pyrolysis/concentrator and chromatographic/spectral units with varying levels of detail. For example, the TAGA 6000 triple quadrupole MS/MS unit includes specific settings for a "typical" run using the Pyroprobe Model 122 sample treatment interfaced to it (Figure 17). The documentation of this applied AI activity for development of CRDEC short- and long-term capability is given in Bibliography 10.3 (page 41), and 10.5.1 (page 44), Presentations.

5. RESULTS OF TRACE ORGANIC ANALYSIS METHOD DEVELOPMENT

5.1 Experimental Design.

Work reported from BRL (15) permitted adaptation of the Box-Behnken experimental design to the microencapsulation task. The Box-Behnken computer program was adapted for the Compaq computer following minor changes in the Pascal code. Use of the design was made in a screening mode as in the pyrolysis runs, rather than a strict statistical manner, because of experimental limitations at that time. Similarly, SFE method development was approached for the first time with this same Box-Behnken experimental design for a complete 46-run series (see Figures 18 and 19).

The 46-runs in this central composite design include six replicates of the centerpoint to evaluate experimental reproducibility. The use of this experimental design for both analytical pyrolysis and SFE method development brought out an important limitation in the approach as noted from the BRL work. The statistical data can be evaluated using only a single response, rather than the resultant GC, MS, or SFC PATTERN response that is informative for the method development. Extended study has pointed out the benefits of extended Box-Behnken designs, if use is made of a multivariate response that represents the pattern generated from the multiparameter study (16). This extended software, now operational on the CRDEC Compaq, is ready for application studies to determine its utility in general method development involving multivariate or pattern response, rather than the single response format.

5.2 Experimental Data and Discussion.

5.2.1 System 1. Py/APCI/MS/MS

The combination of the Pyroprobe Model 122/TAGA 6000 provided analytical pyrolysis (pulse and programmed to 1400^{o}C) and detection/identification with atmospheric pressure chemical ionization MS/MS. Applications include detection and identification of volatiles in solids or semi-solids, volatile liquids and occluded solvents or degradation products from thermal treatments.

The APCI-MS/MS TAGA unit received volatiles from a pyrolyzer unit, Model 122, which provides only thermal processing, but no enrichment/concentration capability. The inert N_2 or air atmospheres were provided by modification of the Pyroprobe coil insert when interfaced to the APCI MS/MS unit, as discussed elsewhere (19), and shown in Figure 20(a).

In context to a general method for determination of polymer microstructure, decomposition products or low-level thermal treatments applied to various materials, the following polymers were studied with pyrolysis APCI MS/MS and examined in the single quadrupole mode: poly(methylmethacrylate) (PMMA), poly(ethyleneimine) copolymer, poly(vinylchloride) (PVC), formulated PVC (Shell No-Pest Strip), polyethylene - high density (HDPE), hydroxy-terminated polybutadiene (R-45M) (HTPB), formulated R-45M (HTPB-1, -2, -3), carbon fibers (pitch, polyacrylonitrile-carbonized PAN), nylon 6/6 poly(hexamethyleneadipamide), nylon 6/9 poly(hexamethylenenonanediamide), nylon 6/10 poly(hexamethylene-adipamide sebacamide), oxidized PE, polypropylene isotactic (iso-PP), glycogen, polyethylene terephthalate (PET), sodium alginate, PE-oxidized 2, Pellethane (Upjohn) polyurethane, Estane 5703 (B.F. Goodrich) polyurethane, ethyl cellulose, polyacrylamide (high carboxyl-modified and low carboxyl-modified), polyethylene oxide (PEO), poly(butyl methacrylate) (PBMA), ethylene-vinyl acetate copolyer (18% VA) (PE-VA), butyl methacrylate-isobutyl methacrylate copolymer (PBMA-IBMA), polyacrylic acid, polyacrylamide.

Pyrograms shown in Figure 20(b) demonstrate the value of comparing inert (N_2) vs. oxidative (air) pyrolyses for a PE; an oxidized PE, and an "in-chain" oxygen polymer PEO $(CH_2CH_2-O)_n$. The APCI MS/MS has excellent sensitivity to oxidative products produced in these studies and is a preferred method for such analyses.

The microcap #1 sample and the three polymer shells A, B, and C from Bend Research were studied with this system under a range of pyrolysis conditions, pulse and programmed, and appropriate reference (blank) conditions (240°C/min to 700°C) under air flow of ca. 150 ml/min with the interface configured as in Figure 20a. Figure 21 (a, b) gives the observed patterns for microcap #1 under (1) 180°C/min to 400°C control run with no heat (shows no molecular ion for diazinon at m/z 304) (2) 180°C/min to 400°C (with heat) for a comparison of volatiles detected under identical conditions of flow, etc. to those with a specific low-level DHS-like treatment (although no enrichment is possible in this configuration). The 18 m/z dalton loss in Figure 21b is likely the H_2O loss from the microencapsulated formulation and could not be obtained in other systems with FID detection (either PGC-FID or SFE-SFC). Other experiments include: (3) pulsing the same sample from (2)-treatment to 400°C/20 sec to give an excellent m/z 304 molecular ion peak for the core Diazinon and an m/z 153 minor peak; a second pulse at 400°C/20 sec on the same sample from (3)-treatment did not give a significant peak at m/z 304, but peaks at m/z 153, 127, and 99. A pulse to 375°C/40 sec on microcap #1 gave an easily distinguished m/z 304 peak, a minor m/z 121, as did pulsing to 400°C/20 sec. A pulse to 700°C/20 sec (Figure 21c) gave no significant m/z 304 ion, but a major fragment was observed at m/z 153 and a minor peak at m/z 137. Programming at 240°C/min to 500°C (Figure 21d) gave a minor m/z 304, strong m/z 153, and minor m/z 127, not unlike the 700°C/20 sec pulse. Programming 300°C/min to 200°C (Figure 21e) (4 min interval) gave a moderate m/z 304, and m/z 288, and major m/z 153, 139 and 111 fragments. This last run compares the fast rate (300°C/min) to get a relatively low (200°C) final temperature to the pulse treatment of 400°C in other runs not shown) which yield a predominant m/z 304 core peak. Several in the series are given in Figures 21 (a-e).

This series of runs would conclude that the pulse at 375°C/20 sec or 400°C/20 sec is most informative as to the detection of the m/z 304 molecular ion for Diazinon and the shell polymer fragments. The polymer shell fragments are seen separately in Figure 22 when the polycarbonate shell was programmed to 400°C at 180°C/min. Hence, both shell and core were detected by their MS fragment patterns when thermally treated. A further comparison is shown in Figure 23 (a, b, c) for microcaps #1, 2, and 3 all with the Diazinon core, pulsed at 400°C/20 sec to give a strong m/z 304 m/z and less intense fragments at m/z 288 and 152/153. Figure 23 (d) presents a microencapsulated protein and its reference run to demonstrate MS pattern comparisons for protein detection in microencapsulation (19b).

5.2.2 System 2. Pyrolysis-Concentrator GC-MS, and -MS/MS

Pyrolysis/Concentrator Pyroprobe 124 with Hewlett-Packard 5985B GC-MS and with Finnigan TSQ in MS and MS/MS modes were used, including DHS, pulse and programmed pyrolysis, cryogenic and/or sorbent bed concentration/enrichment. Sample processing can be conducted under inert or reactive atmospheres, with either a coil or ribbon pyrolyzer sampling system or thermal desorption module for aerosol samples. Not included in this study was the demonstrated use of the purge and trap module for analysis of dissolved targets in water/liquids or from bulky solids placed in glass desorption vessels up to 50 ml size.

Figure 24 a is the experimental schematic. Figure 24b and c illustrate the results from conducting a DHS/pyrolysis GC-MS experiment with the Pyroprobe Model 124 interfaced to the Hewlett-Packard GC-MS on a series of twenty organic amine salts from three structurally similar groups and relevant referenced compounds (Figure 25).

The same Pyroprobe 124 system was then interfaced to the Finnigan TSQ GC/MS unit. Microcapsule components were examined for their behavior in the new configuration. Control runs were made on a reference polymer HDPE, as well as oxidized PE and short-branched PE to compare "standard" PGC pyrograms on the capillary DB-5 30 meter x .33mm fused silica column. Figures 26 (a-f) show the excellent triplet pattern and short-branch and oxidation information that can be obtained with the TSQ unit on the reference polymer (20). More detailed pyrograms are illustrated in Figures 26 (b, d, and f) for the region between 650 and 950. Figure 27 records the experimental conditions under which the GC-MS spectra were obtained.

Selected microencapsulated materials from the Bend and Dodge Co. series were examined over a range of pyrolysis conditions. The core ingredient, Diazinon (Bend Corp.), was examined under a 240°C/min to 700°C final temperature with the thermal desorber at 150°C to give the RIC seen in Figure 28(a). EI/MS examination of the reconstructed ion chromatogram (RIC) for scanset 672 is shown in Figure 28(b) and served to identify the pesticide as Diazinon. Its definitive EI-MS pattern consists of the molecular ion at m/z 304 and fragments at 276, 179, 152, 137, etc. Figure 29 (a, b) shows the detection of Diazinon in a shell of polycarbonate (microcap #1) examined under the same conditions as Figure 28. Several combinations of pulsed/programmed pyrolysis were examined for behavior of the core/shell degradation patterns, e.g., compare microcap #1 run at 180°C/min to 600°C in an 8-min interval (Figure 30 a, b) to that obtained at 240°C/min to 700° in a 4 min interval (Figure 30c). Both runs gave easy definition of the pesticide core from the polymer/ingredients fragments in scansets 409, 437, 455, 479, 481, 515, and 581 regions. The intensity of the core (scanset #668) in Figure 30c in the faster 240°C/min to 700°C indicated it to be the preferred programmed pyrolysis condition for maximum Diazinon release with minimum thermal degradation. Separate runs under pulse conditions (500°C/20sec) gave the RIC and MS patterns for Diazinon and the MS/MS run of m/z 304 ion seen in Figure 31 (a, b, c).

Under the pulse mode of 500°C/20 sec, the Bend Microcap #4 (Cypermethrin) gave the patterns in Figure 32 (a, b). The EI/MS pattern from scanset #608 yields fragments at m/z 208, 173, 163, 122, 109, 91, etc. Programmed pyrolysis (240°C/min to 400°C) of the Microcap #4 gave scanset #395 which shows an EI/MS pattern of m/z 208, 184, 173, 163, 127, 109, 91, etc. (Figure 33 a,b). Microcap #5 containing Dursban in a polycarbonate shell gave the RIC shown in Figure 34a. The EI/MS pattern of scanset #831 is shown in Figure 34b. The MS/MS run of the m/z 199 parent MS fragment (Figure 34c) yields a m/z 171 and minor m/z 163, 100 fragments. The Dursban core differs from Diazinon by the polychlorinated pyridine ring linked to the phosphorothioate portion, whereas Diazinon has the alkylated pyrimidyl thiophosphate structure (see page 22).

The gelatin emulsifier (5%) in a polysulfone-polyethersulfone shell (Dodge) gave an RIC with scansets at 168, 202, 320 and others (Figure 35a). Gelatin from different sources gave RIC results seen in Figure 35 (b), (c), and (d) with comparison of the Bend gelatin, P.S. and Dodge (500 micron size range) gelatins. The P.S. gelatin RIC (Figure 35c) gave scansets 196, 206, 258, and 301 when treated at 240°/min to 700°C, 8 min. interval, while the Dodge gelatin (Figure 35d) gave scansets 191, 276, 345, 387. The Dodge gelatin desorbed 5 min at 260°C gave the RIC of Figure 35e. The EI-MS of scanset 206 yields fragments at 207, 191, 133, etc. (Figure 35f).

5.2.3 System 3. Pyrolysis/Concentrator GC-FTIR

System 3 is a Pyroprobe Model 122 coupled to a GC with a Fourier transform infrared spectrometer (FTIR). A representative total response chromatogram (TRC) is shown (Figure 36a) for the Bend microcapsule #1 and the associated FTIR pattern (Figure 36b) (also shown are the library search results). Since Diazinon was not present in the library used in this search (EPA/Sadtler), a direct match was not obtained, nor was a separate reference run conducted to add it to the library. Importantly, however, the major functionality (phosphorothioic acid derivative) was identified. The significance of this complementary data to the MS spectral pattern cannot be overstated. Identification of "true" unknowns requires the combined information from GC-MS/GC-FTIR instrumentation.

5.2.4 System 4. Supercritical Fluid Instrumentation

5.2.4.1 SFE. Supercritical Fluid Extraction

Supercritical Fluid Chromatograph Model 5000 SFC/GC is configured for extraction, desorption, reaction, and/or chromatography. The initial studies with SFE and SFR involved a polymer matrix containing many propellant formulation ingredients and a sensitive component, RDX, as the target species, albeit not in a microencapsulated form. Figure 37 illustrates the resultant SFE profiles of formulated binders 1, 2, 3 with species extracted under non-optimized conditions. Automatic transfer of the extractables into the on-line SFC unit provided the separation of components in a standard microbore chromatographic column. Many feasibility runs on components in polymeric materials (polyurethanes, polyethylenes, etc.) demonstrate the potential for full SFE-SFC analyses for temperature sensitive substances in microcapsule or immobilized form. Figure 38 presents the analogous SFE-SFC analyses for two samples from the same batch of formulated microcap #1.

The Bend Research microcap series of known compositional variations provided the background for parameterization of the SFE method. Within the experimental limits of the instrument, the task was to determine the "optimum" combinations of pressure, temperature, density, flow, time, etc. to yield the most comprehensive information on such complex samples. Hence, the design was used in a non-statistical "response surface" screening mode.

Results from this series are non-statistical because the response of concern is an extraction profile, not a standard chromatographic or spectral pattern. Figure 39 (a-c) gives a range of typical profiles obtained in the Box-Behnken series. The information content resides in the core target extraction "efficiency" and the pesticide core separation, as well as associated formulation ingredients. This screening or experimental response surface showed that the SFE method permits wide ranges of pressure, temperature, flows, and residence times for satisfactory detection/analysis of these representative core targets in the selected polymeric shells.

Since the payload or core of the test microcaps was high ($\sim$ 50-80% by wt) and only a few milligrams of sample were used in each run, it is safe to say that a typical SFE experiment for these types of studies would be conducted with microgram amounts of sample under nominal conditions: i.e., 1200 psi initial CO_2 mobile fluid, 8 min. extraction time at 100^{o}C, and pressure programming at 200 psi/min to 4000 psi (Figure 39b). Presence of emulsifiers/surfactants are not necessarily detected under these conditions, and therefore, varied conditions are needed to ensure a more complete analysis of all the formulation ingredients. Perhaps a two-step pretreat/extraction or reactive extraction may be used for this purpose, not unlike the route taken in analytical pyrolysis method development: i.e., dynamic headspace thermal preprocessing of volatiles, followed by pulse or programmed pyrolysis.

Since SFE is only one step in the detection of a core target in a polymeric or complex matrix, the identification step must involve more than a proper extraction time. The automatic SFE-SFC system provides chromatographic separation and detection systems for more complete characterization.

Figure 39a shows the SFE profiles of microcapsule #1 from three runs in the experimental design. Five samples of microcapsules examined under a single set of "reasonable" (as seen in the Box-Behnken) experimental settings are given in Figure 39b. Microcaps 1,2, and 3 contain Diazinon within three different shells...polycarbonate, polysulfone, and polyetherimide (Ultem), respectively. Microcap 4 contains Cypermethrin inside a polysulfone shell and Microcap 5, Dursban inside a polycarbonate shell. Each of the three pesticides are readily extracted under these conditions, but the profiles differ according to the shell/formulation content (Figures 39c-e). Variability between microcapsule formulation or relative ease of extraction through the different shells cannot be determined from this series. Repeat runs (see Figures 39(d) and (e)) with a different sample from the same batch illustrate this point...in-group variability can be monitored and compared to profiles from different batches or to different shell/core formulations. The data only serve to demonstrate that the target cores and some formulation ingredients are readily analyzed with SFE. Also, the three selected target cores are easily differentiated by their extraction behavior in this trial series.

Furthermore, Figure 40 shows SFE-SFC data for gelatin (emulsifier A) (used in the Bend microcapsule formulation) and a typical polyol emulsifier/surfactant (emulsifier B). The complex profile with several individual peaks seem to indicate solubilization of at least some of the gelatin material. The proteinaceous gelatin serves as a reference for developing the analytical SFE-SFC method.

These microcapsules of known compositional variations thus provide the background for the parameterization of the SFE method. Within the experimental limits of the instrument, the task remains to determine what are the combinations of pressure, temperature, density, flow, time, etc. to provide the most comprehensive and quantitative information on such complex materials that may vary over wide ranges of composition.

5.2.4.2 SFR. Supercritical Fluid Reaction

Extension to SFR was also shown with the RDX formulated system, since research on RDX decomposition mechanisms had resulted in significant new information in an important area of research (19). The exploratory runs with RDX decomposition under CO_2 SF conditions and with superimposed thermal input (up to ca. 250°C) in the extractor gave SFR results shown in Figure 41. These runs demonstrated that monitoring/analyzing decomposition products over a range of extended reaction conditions were possible and enabled comparisons to be made for catalytic vs. noncatalytic decompositions. These RDX mechanism studies demonstrated extended capability for thermally sensitive and reactive targets to be analyzed over a range of conditions, including high pressure regimes not previously available with commercial analytical systems with such automated capabilities. Extension to "reactive extraction" of different biologicals, toxins, etc. is an important direction to follow.

5.2.4.3 SFD. Supercritical Fluid Desorption

A simulant, bis-(ethylhexyl)phosphonate, was examined by (SFE) SFD/SFC in trial runs. Results are shown in Figure 42a indicating successful analysis is possible when the simulant is in a soil matrix at ppm levels. Extrapolation of the data to expected detection levels in a method development mode indicates detection in the nanogram range with many adjustable parameters to extend it even further. Hence, targets such as the simulant phosphonate appears readily extracted/desorbed at trace detection levels. Identification again would require more than the retention time in either SFC or GC on-line analysis. An important illustration of SFD is given in Figure 42(b) showing different charcoal samples analyzed in the system. The on-line capillary GC analyses are preferred for these studies, since the complex hydrocarbon adsorbents are readily separated using typical environmental analysis protocols; i.e., spectral identification by SF interfaced to an FTIR or MS unit. The fiber optic feasibility studies would be particularly useful in this regard...use of a fiber optic monitor (FOM) in the mid-IR region for identification using the IR pattern and/or information on chemical functionality (see Section 6.1)

5.3 Supercritical Fluid Extraction-Chromatography SFE/SFC.

SFE-SFC configurations, as well as SFE-, SFD-, or SFR-capillary GC are important integrated analytical tools for detection and identification. SF extraction with minimal thermal input is needed for the target species that are thermally labile followed by on-line automated separation (SFC or capillary GC). These analytical steps have been demonstrated for microcapsules (Figure 38) in this series. Integration with spectral detection (MS and/or FTIR) and enrichment or concentration stages provide the means for identification of trace targets or classification of unknowns with the aid of chemometric approaches. The newly emerging fields of neural network/applied AI and fiber optic sensors are directly relevant to a capability for in-field, portable analytical monitors of target species in complex environmental scenarios. Results from the microEXMAT development (the expert system network for supercritical fluid technologies) are reported in context to the importance of applied AI to analytical chemical instrumentation with "embedded" intelligence. General conclusions of the SF technology series with microencapsulated pesticides are given in Figure 42(c).

6. EXPLORATORY RESEARCH AND TECHNOLOGY ASSESSMENT

6.1 Fiber Optics.

Exploratory research was conducted with fiber optic monitoring of supercritical fluid extractables in the UV, VIS, NIR, and mid-IR regions using probe/cables with suitable spectrometers. These latter units included (1) Guided Wave's Model 100 spectrometer (CRDEC); (2) Mattson's FTIR spectrometer (R. Fifer, BRL); and (3) Infrared Fiber Systems' potential use of a solid state spectrometer based on an acousto-optic tunable filter (AOTF). The feasibility studies were documented (14b, c) and included special configurations that were tested for the SFE-FOM interface (Figure 43). Feasibility runs on the system for detection of trace aromatics are shown in Figure (44 a, b). Extension to the mid-IR is shown in Figure 45. The summary/conclusions of this fiber optic development are given in Figure 46 (a and b).

6.2 AI and Neural Networks.

Extension of EXMAT to microEXMAT (an expert system for supercritical fluid technologies) was documented (21) and is illustrated in Figure 47. Figure 47 (a) shows the "EXCONFIG" outline and 47 (b) the outline of "EXMETH". These are two of the initial expert systems in the network.

Technology assessment of the AI field indicated that neural networks (noted in the 1987 literature) have realistic potential for applications of particular significance in pattern recognition. The hardware and software were tied into sensor systems and adaptive training algorithms for classification and prediction. Decisions are directly analogous to those developed using the AI software of TIMM. Neural networks, as is TIMM, are used on microcomputers, not just mainframes such as the VAX 8600 or MicroVAX II computers that run the existing TIMM software. This fast-paced development within the AI/computer industry must be followed closely to make use of relevant technology for the CRDEC mission; particularly in the areas of pattern recognition and information fusion from selected chemical sensors (see Bibliography 10.3 on Sensors/AI, (page 41), (see ref. 42).

6.3 Inverse GC and SFC.

Inverse GC has been shown to be a useful tool for the study of surfaces and subsurfaces of polymers (1). The method involves use of GC/SFC instrumentation for close control of time, temperature, flows, and sensitive detection units just as in normal GC, but the nature of the column function is changed. Rather than inject unknown liquids/gases into the separation column so that they elute according to the chromatographic process, injection of known "molecular probes" is made into a chromatographic column containing the substrate film, coated particulates, or other solid materials (fibers, etc.) which are to be studied. Behavior of the selected molecular probes in the mobile phase as they interact with the stationary phase in a classic chromatographic separation experiment provides detailed information on thermodynamics of mixing and interaction; e.g., free energy, enthalpy and entropy of adsorption, partial molar free energy, enthalpy and entropy of mixing, solubility parameters, heats of solution, diffusion coefficients, surface concentration at monolayer coverage, chemical potentials, and other data not easily obtained by other analytical methods for polymeric materials.

Extension to the SF field provides a new opportunity to examine fibers, surfaces, and subsurfaces of materials with the added dimension of high pressure and unique properties of SF mobile phases. One potential application involves SF technology applied to preparation and analysis of specialty treated charcoals. Solubilizing oligomeric/polymer coatings and depositing them upon desired charcoal or solid surfaces presents a new way of preparing coated high surface-area materials. Evaluation of these coated materials then is achieved by challenging the treated samples in-situ with the appropriate vapors and measurement of classic breakthrough/quantitation information. Use of the SFD mode as discussed above for analysis of charcoal traps from air pollution studies involved desorption from charcoal placed in the extractor/desorber accessory module. The inverse GC or SFC mode may or may not use the accessory, but uses the chromatographic portion of the system most appropriate for the nature of the information needed.

7. SUMMARY AND CONCLUSIONS

The intended task to establish at CRDEC the capability to perform trace organic analysis in the field of microencapsulated materials and complex polymeric materials of concern in threat analysis has been outlined and in part completed. The selected instrumental tools and methods emphasizing analytical pyrolysis and supercritical fluid technologies were demonstrated and made operational at CRDEC for a variety of test materials. These concerted analyses on microencapsulated samples successfully showed that trace detection and identification can be carried out for target cores in a range of polymer matrices and for targets that are immobilized in soils, adsorbed on charcoal surfaces or other particulate carriers/solid matrices.

During the initial work, only qualitative and semi-quantitative analyses were conducted. It is necessary to have a full quantitative study on a selected system that would demonstrate the necessary detailed methodology in terms of the reproducibility at the sampling stage, data generation (pyrolysis or extraction), and in data analysis/interpretation. Extension of the applied AI decision structure and initial input to the knowledge base in this specific domain was made in context to the EXMAT network. Extension to initial assessment of neural networks was undertaken in relation to pattern recognition and multi-sensor fusion which have the potential for real-time detection and identification.

8. RECOMMENDATIONS

Existing instrumentation and method development should be used and extended to establish full qualitative and quantitative determination of trace amounts of microencapsulated materials important in threat analysis. This must be combined with appropriate sampling common to multimedia environmental protocols. Pattern recognition algorithms with some AI treatment should be developed from the background in AI and multivariate data analysis that exists from the CRDEC/BRL studies. The prototype EXMAT requires an improved, current decision structure, as well as development of the associated knowledge bases on the microVAXII system. Of the existing seven linked expert systems, only one ("strategy") has a sizeable knowledge base (250 rules). Persons knowledgeable (i.e., experts) in environmental and trace organic analysis could develop the needed decision structure/knowledge bases with reasonable effort (approximately 8-10 months).

Development of microEXMAT illustrated the capability of a PC-level shell for a focused field (supercritical fluid technology). The associated chemometric software developed at CRDEC can thus be used in conjunction with the GRC-AI shell (microTIMM) if purchased for this purpose. In this case, development of the chemometrics/AI expert system would require not only expertise in the analytical chemistry applications, but specific capability for efficient microTIMM (Fortran 77)/chemometric software integration. General Research Corporation has demonstrated such embedded intelligence software for a range of multi-sensor applications (Figure 47c). The down-sizing of computer hardware/software now used for multi-sensor data treatments and pattern recognition/ classification studies fits directly into the threat analysis area in a very realistic manner.

Importantly, extension of these laboratory units/methods to microtechnology in manufacturing would make possible a modular "universal organic threat analyzer" in a highly automated, miniaturized form. Sampling modules for air, liquid, or solids can be integrated into the unit and thermal/nonthermal sample processing would provide "extractables" automatically delivered to the multidetection/identification unit, with or without the immediate concentration or separation. The resultant set of descriptor patterns from the key GC, IR, and MS detection units for the selected target species would be combined with elemental data and provide input to a knowledge base trained for the unit. Expertise in handling a range of experimental and interpretive decision-making stages would be included in the applied AI format, using advantages of neural network advances. This potential system would be designed as an "on-site", in-field portable threat analyzer for screening a selected range of targeted materials, but also providing information on unknowns <u>not</u> in the library "trained" for detection of specific species. Knowledge base extensions would be made accordingly. The key datasets would provide the most efficient, reliable, and versatile screening approach to handle difficult unknowns, including threat agents formulated within microencapsulated materials in multimedia.

Thus, results from microcapsule method development combined with exploratory research efforts in fiber optics, applied AI and neural networks provide information needed to design and fabricate a modular portable threat analyzer for military, forensic, and environmental uses. This combined user-manufacturer development is one of the most productive ways for technology transfer to take place (22).

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Figure 1

INTEGRATED INTELLIGENT INSTRUMENTS (I^3)

AUTOMATED/INTERFACED

- SAMPLE PROCESSING
- MONITORING/SAMPLING
- ACCUMULATOR/PREP SCALE
- SEPARATION
- DETECTION/IDENTIFICATION
- DATA ANALYSIS/CHEMOMETRICS
- APPLIED AI

Figure 2

TRACE ORGANIC ANALYSIS OF ANALYTES IN GAS, LIQUID, SOLID MATRICES

AGENTS, EXPLOSIVES, PROPELLANTS, ADDITIVES, SIMULANTS, TOXINS, PRIORITY POLLUTANTS, BIOPOLYMERS, SYNTHETIC POLYMERS, FORMULATED MATERIALS, DEGRADATION AND REACTION PRODUCTS, FORENSICS

INSTRUMENTATION AND METHODOLOGY

AUTOMATED SAMPLE PROCESSING/CONCENTRATOR TECHNOLOGY

THERMAL TREATMENTS

DYNAMIC HEADSPACE (DHS)
ANALYTICAL PYROLYSIS (PY)
SIMULATED ENVIRONMENT DEGRADATION PROFILES

SUPERCRITICAL FLUID TREATMENT

SUB-, NEAR, SUPERCRITICAL FLUID
EXTRACTION (SFE)
DESORPTION (SFD)
REACTION (SFR)

ON-LINE DETECTION AND IDENTIFICATION

CAPILLARY GC/FID
GC-FTIR
GC-MS/MS
APCI MS/MS
SF CHROMATOGRAPHY (SFC)

INTEGRATED SYSTEMS

DHS/PGC/FID
DHS/PGC/MS/DS
DHS/PGC/FTIR
PY-MS/MS/DS
PY-APCI MS/MS/DS
SFE/SFD/SFR-SFC
SFE/SFD/SFR-CAPILLARY GC/FID

ADVANCED DATA ANALYSIS

EXPERIMENTAL DESIGN
CHEMOMETRICS
APPLIED ARTIFICIAL INTELLIGENCE

Figure 3

MICROENCAPSULATED SYSTEMS AND THE I[3] APPROACH

CHEMICAL SYSTEMS:

COMPONENTS

- o SHELL - NATURAL AND SYNTHETIC POLYMERS
- o CORE - PESTICIDES, TOXINS, SIMULANTS, BIOLOGICALS, VOLATILE/REACTIVE, ENERGETIC CHEMICALS
- o IMMOBILIZED SPECIES - ORGANICS AND INORGANICS IN/ON MATRIX
- o ADDITIVES - BINDERS, SURFACTANTS, EMULSIFIERS, THICKENERS, PROCESSING AIDS, STABILIZERS, SOLVENTS, INORGANICS, CATALYSTS, BUFFERS, SIZINGS/INTERFACE - SURFACE TREATMENT CHEMICALS

CONCENTRATION RANGE

TARGET SPECIES: TRACE (MICROGRAM/NANOGRAM) TO 50-80% BY WT

SAMPLE (TARGET AND MATRIX) AMOUNT AVAILABLE

TRACE (MICROGRAM/NANOGRAM) TO UNLIMITED

SAMPLING PROTOCOLS - ENVIRONMENTAL

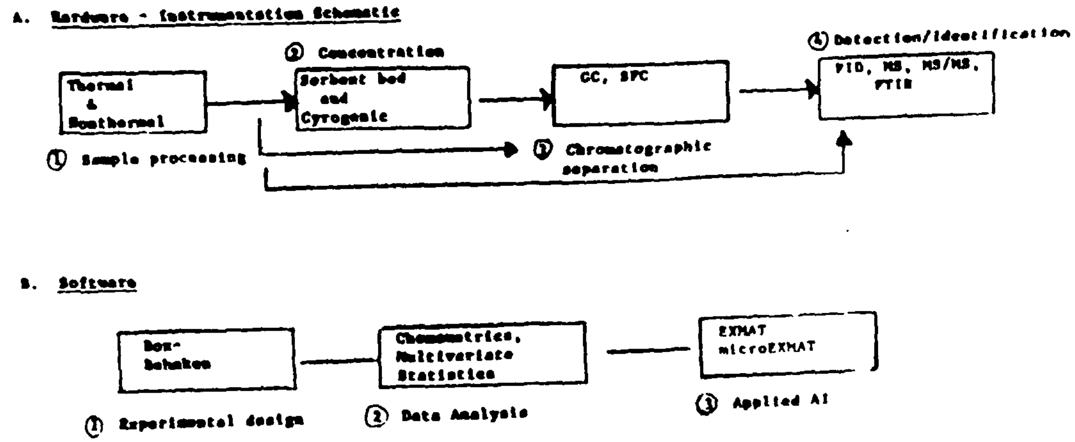
AIR/AEROSOLS, WATER, SOLIDS

INSTRUMENTATION AND METHODS

ENCODE ANALYTICAL STRATEGY AND SPECIFIC CONFIGURATIONS/ METHODS INTO CRDEC AI EXMAT NETWORK

CRDEC Instrumentation Schematic

Figure 4



TYPICAL ANALYSIS OF VARIANCE OUTPUT FROM BOX-BEHNKEN

Figure 5

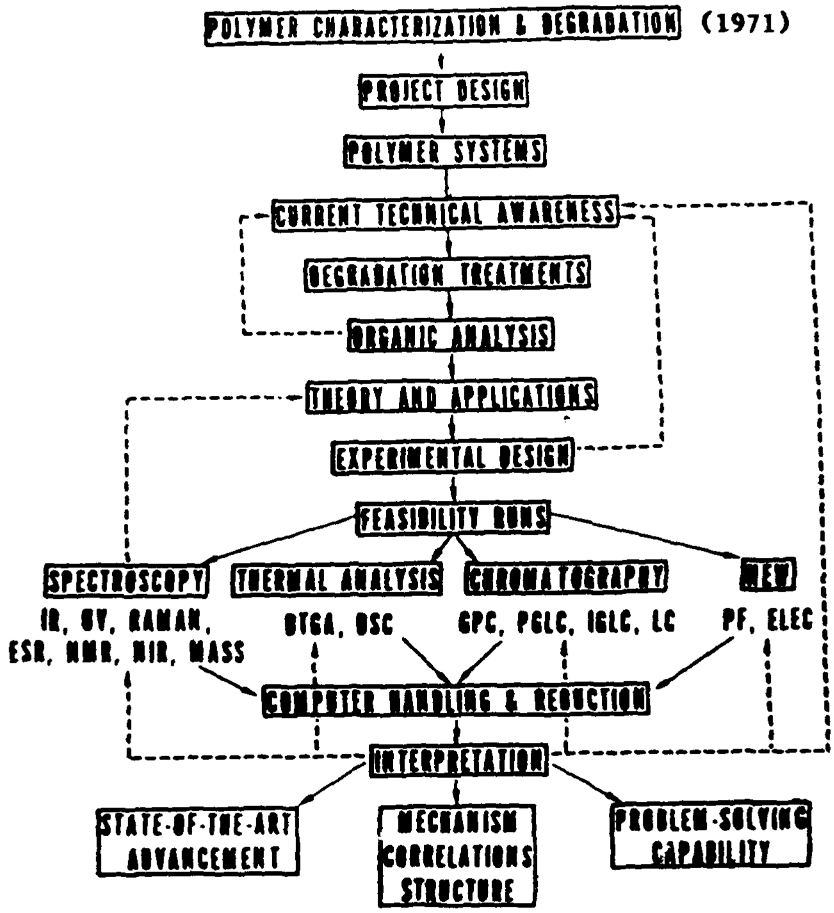
C:\PASCAL>TYPE OUTPUT.DAT

ANALYSIS OF VARIANCE

SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN SQUARE
TOTAL SUM OF SQUARES	2561.0000	46	
DUE TO THE MEAN	2439.6739	1	
DUE TO FIRST ORDER TERMS	7.2500	5	
DUE TO SECOND ORDER TERMS			
INTERACTIONS	16.5000	10	
QUADRATICS	21.6592	5	
LACK OF FIT	67.0836	19	3.5307
ERROR SUM OF SQUARES	8.8333	6	1.4722

POOLED ESTIMATE OF VARIANCE = 3.0367

Figure 6(a)



PROBLEM-SOLVING IN MATERIAL SCIENCE (1986) Figure 6(b)

POLYMER CHARACTERIZATION AND DEGRADATION MECHANISMS

GENERAL PERSPECTIVE

- **MICROPROCESSOR - BASED INSTRUMENTATION AND METHOD DEVELOPMENT**
- **SAMPLE PROCESSING WITH TRACE DETECTION/IDENTIFICATION**
- **CHEMOMETRICS AND APPLIED AI**

SPECIFIC EXPERIMENTATION

- **ANALYTICAL PYROLYSIS/CONCENTRATOR GC, GC-MS, MS/MS AUTOMATED SYSTEMS**
- **INVERSE GC FOR SURFACE, SUBSURFACE ANALYSIS THERMODYNAMIC CONSTANTS, SOLUBILITY PARAMETERS, DIFFUSION CONSTANTS**
- **SUPERCRITICAL FLUID TECHNOLOGY EXTRACTION, DESORPTION, REACTION, CHROMATOGRAPHY**

CURRENT FOCUS

INTEGRATED INTELLIGENT INSTRUMENTS (I^3)

EMBEDDED INTELLIGENCE AND DECISION-SUPPORT/INTERPRETATION

Figure 7(a)

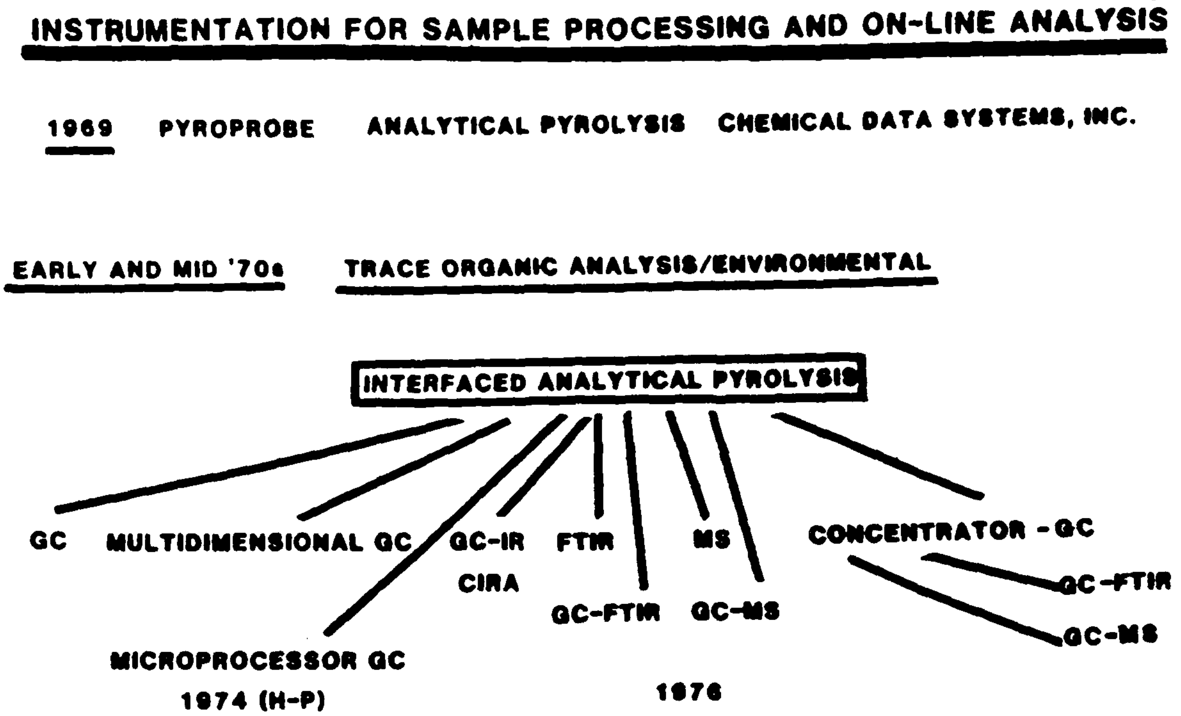


Figure 7(b)

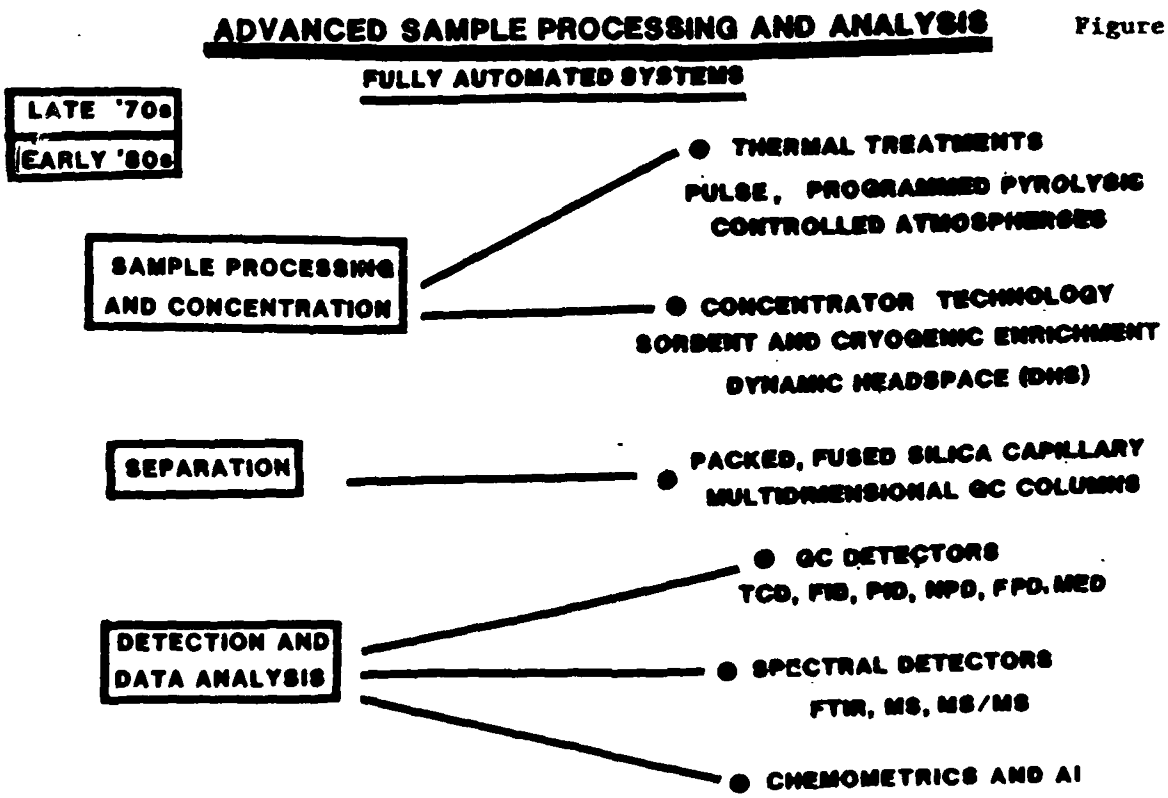
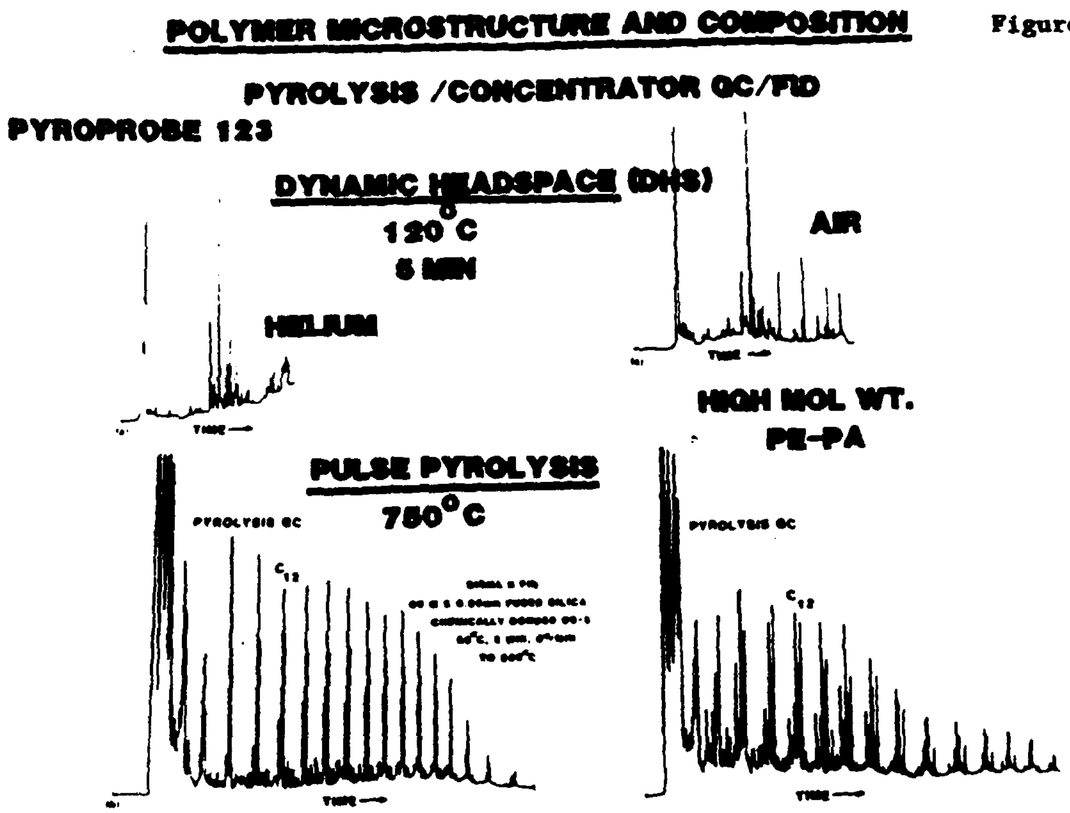


Figure 8



Pulse and Programmed Pyrolysis of Polyethylene

Figure 9(a)

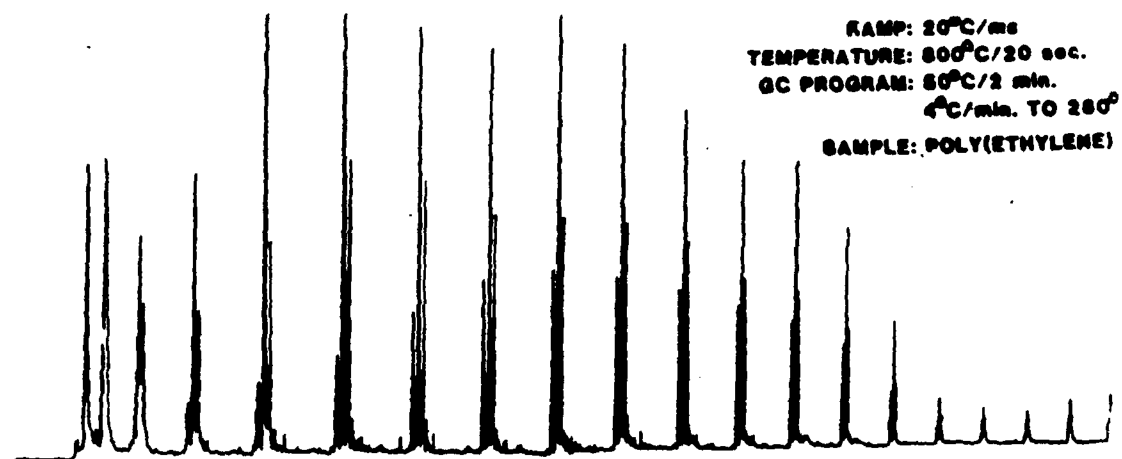
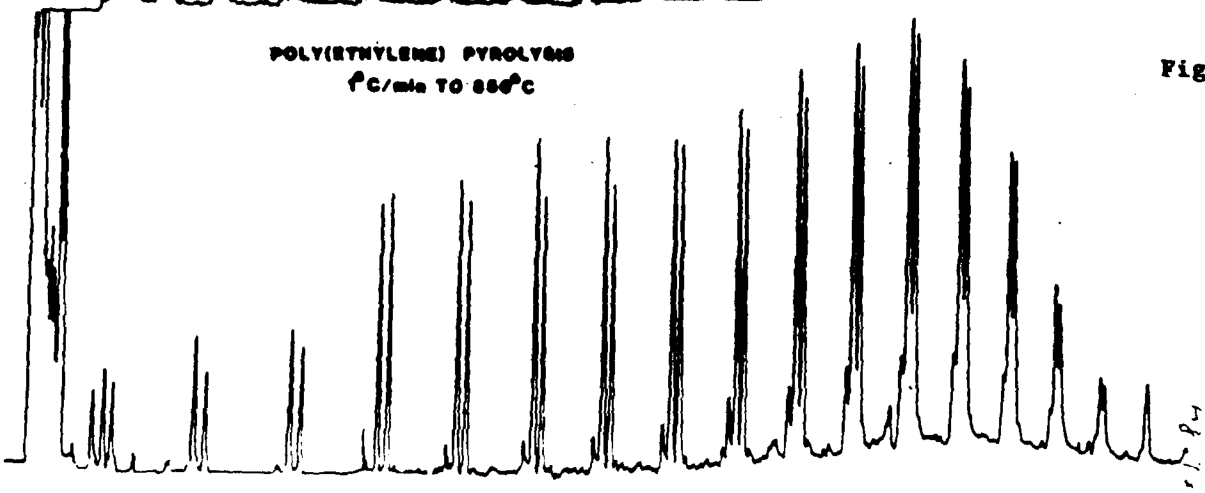
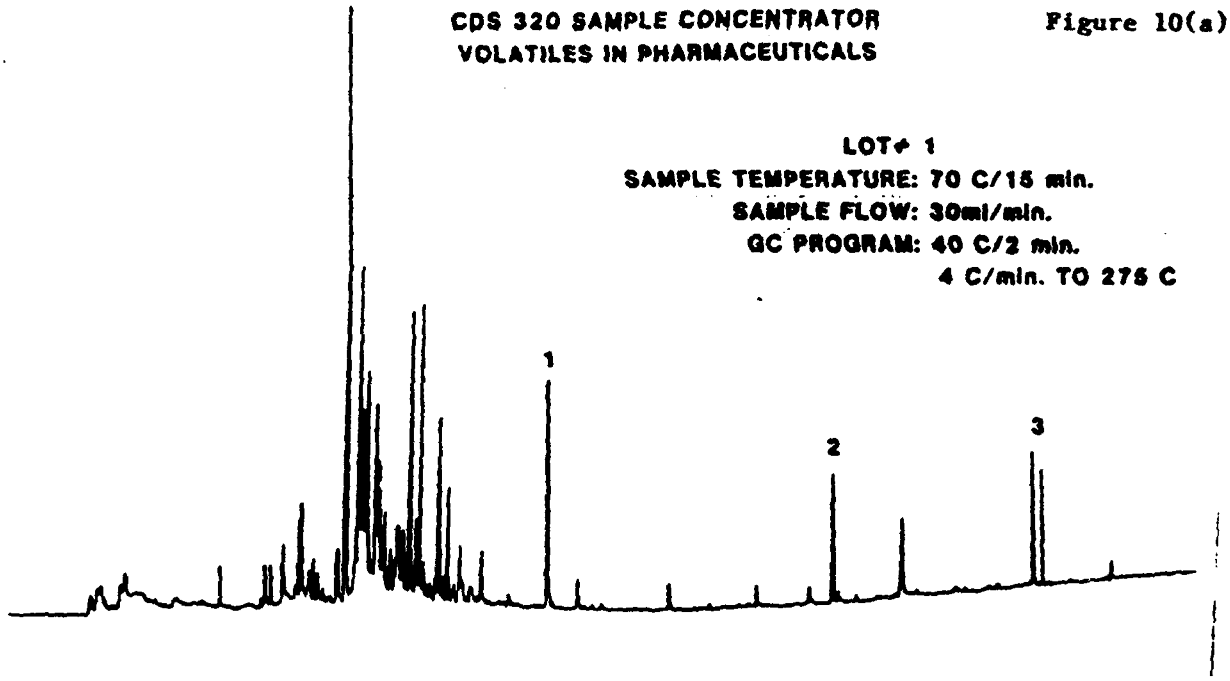


Figure 9(b)



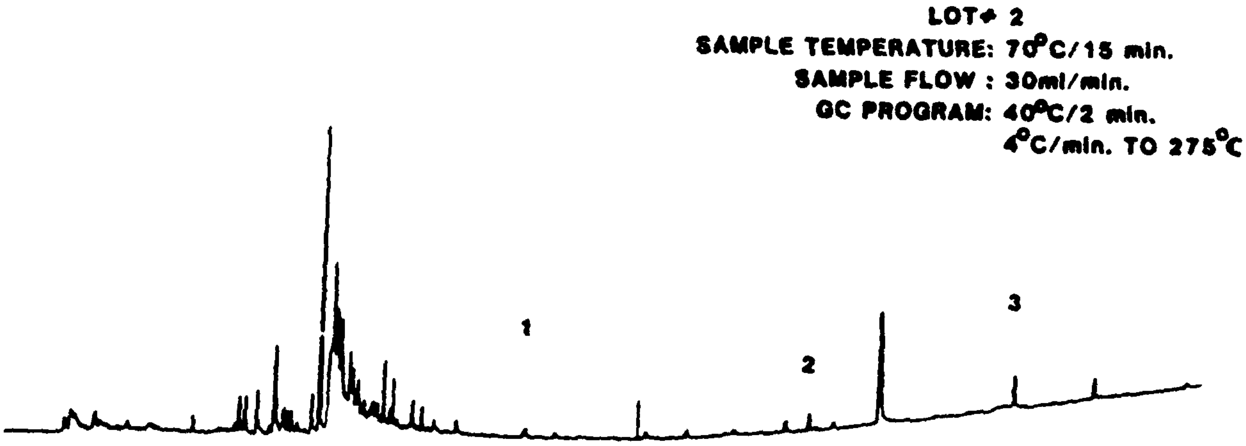
CDS 320 SAMPLE CONCENTRATOR
VOLATILES IN PHARMACEUTICALS

Figure 10(a)



CDS 320 SAMPLE CONCENTRATOR
VOLATILES IN PHARMACEUTICALS

Figure 10(b)



Pyrolysis and Reproducibility of Glass-Lined System CDS Pyroprobe Model 124

(Human Hair)

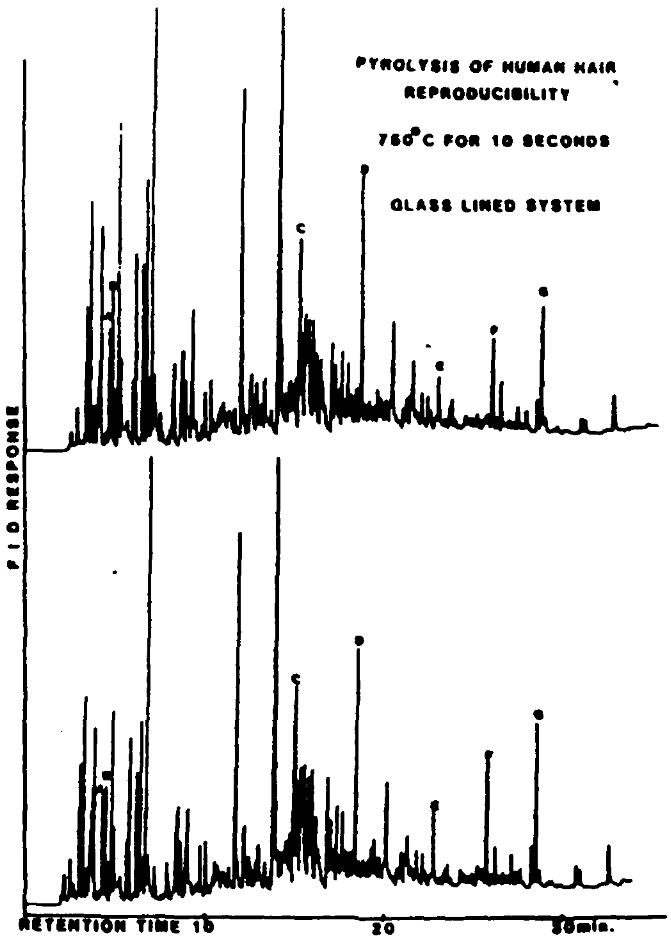


Figure 11(a)

(Raw Wool)

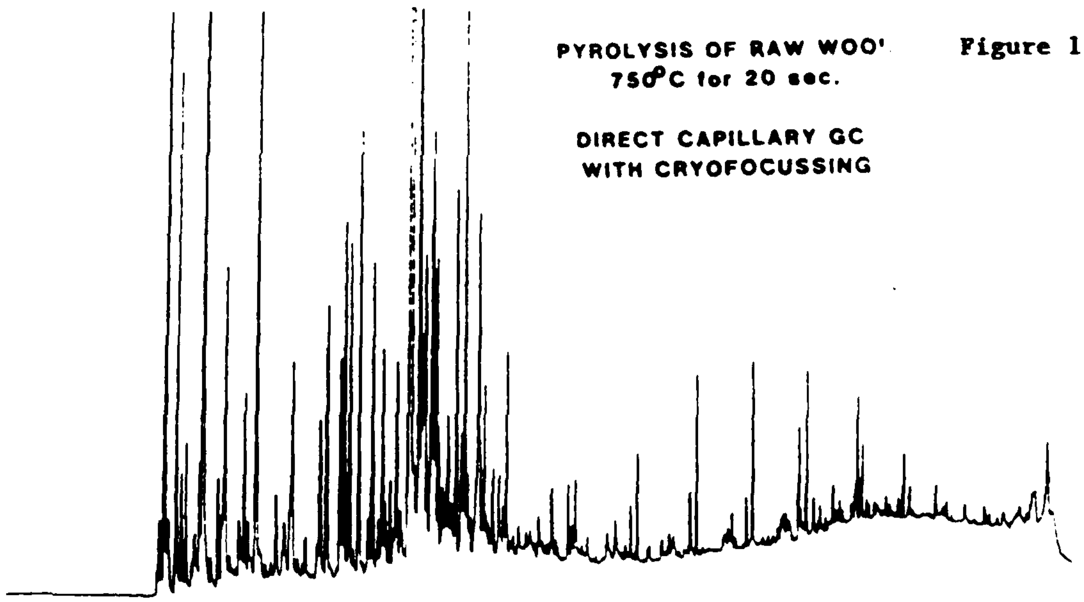
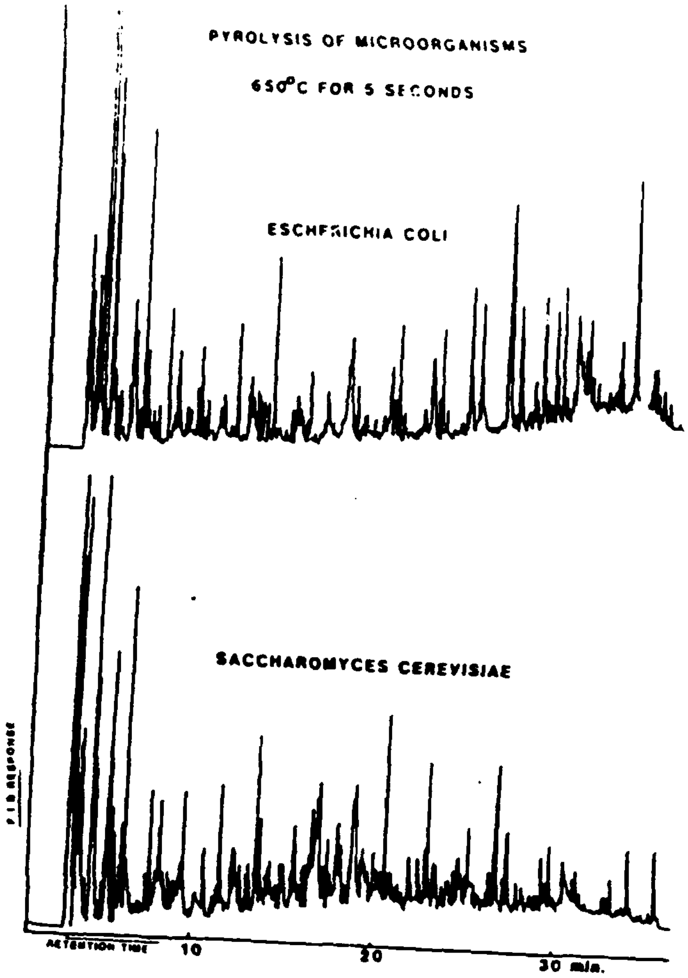


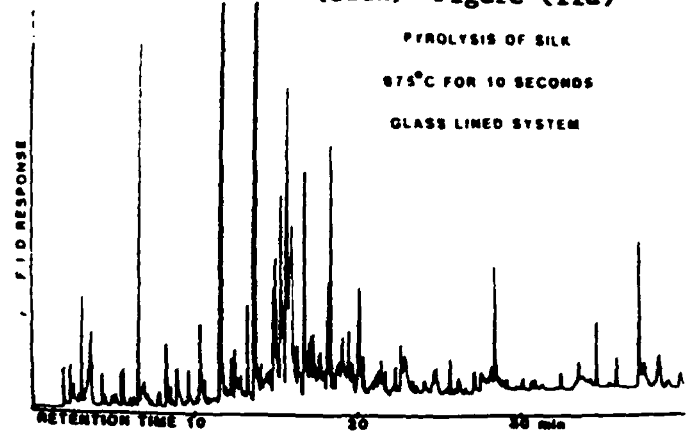
Figure 11(b)

Figure 11(c)

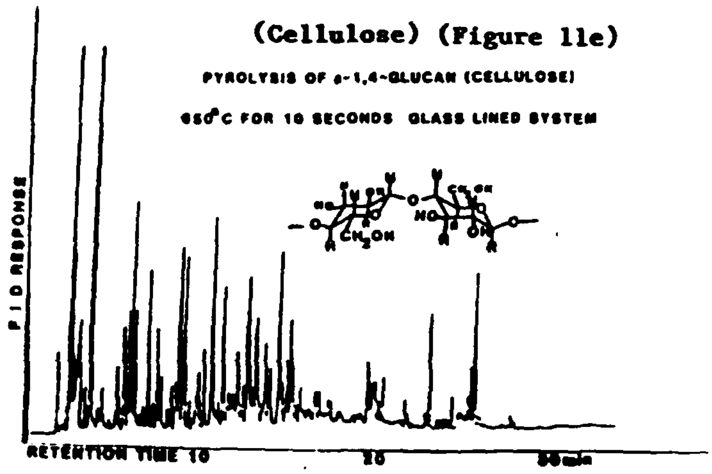
(Microorganisms)



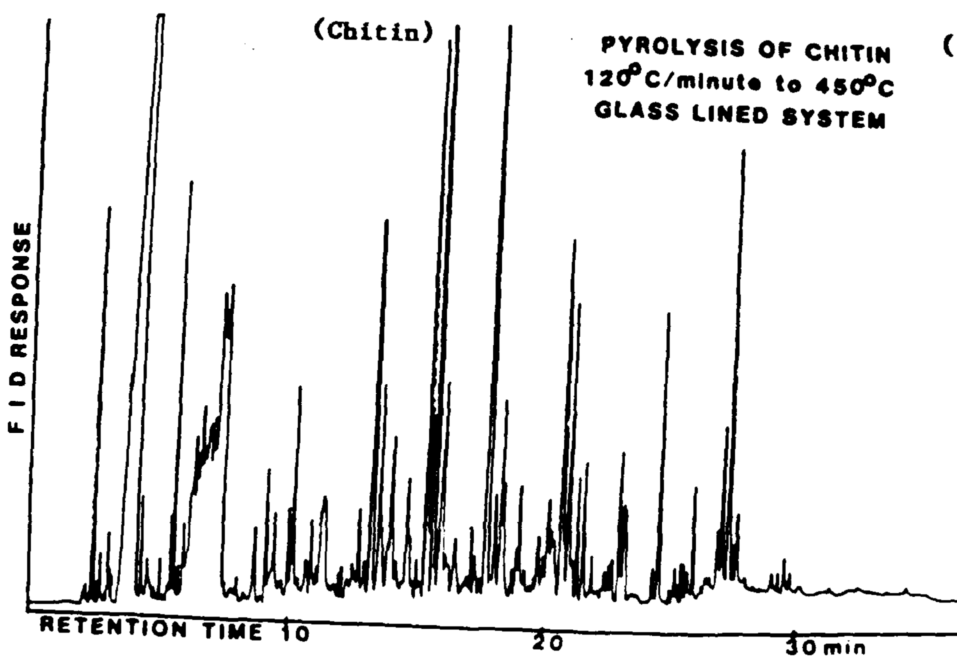
(Silk) Figure (11d)



(Cellulose) (Figure 11e)



(Chitin) (Figure 11f)



BOX-BEHNKEN EXPERIMENTAL DESIGN USED IN ANALYTICAL PYROLYSIS METHOD DEVELOPMENT

Figure 12

- MODIFIED TURBOPASCAL (3^5) PROGRAM FOR MICROCOMPUTERS
- ESTABLISH EXPERIMENTAL ERROR IN MULTIVARIATE PARAMETER STUDY
  - —PYROLYSIS TEMP
  - —PYROLYSIS MODE
  - —PRETREAT TEMP
  - —MATRIX
  - —ANION TYPE

BOX-BEHNKEN EXPERIMFNTAL DESIGN
SFE METHOD DEVELOPMENT
FIVE-FACTOR THREE-LEVEL (3^5) OUTLINE

Figure 13

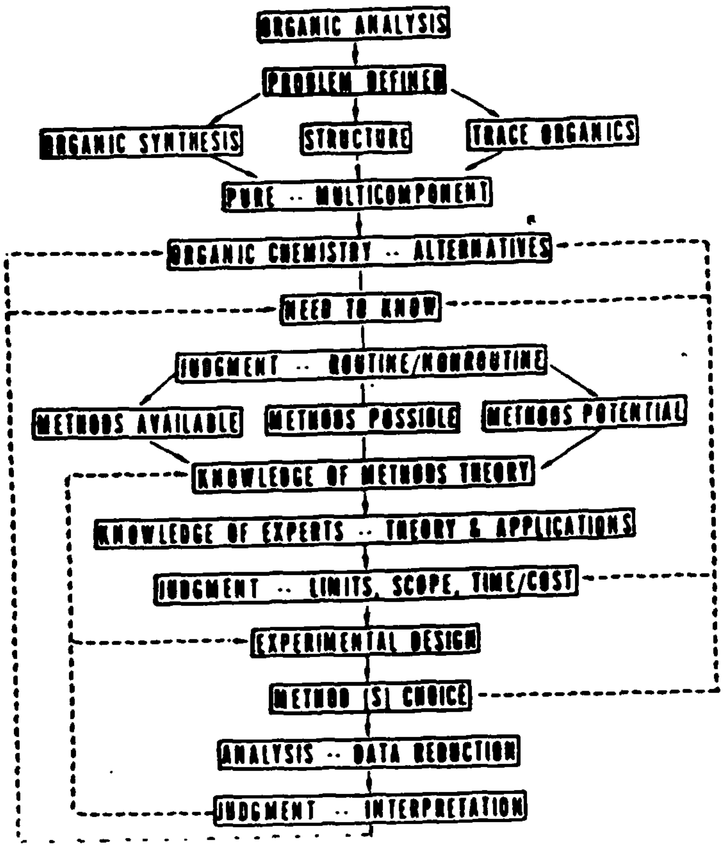
INITIAL PRESSURE (PSI)	TIME (MIN)	TEMP (C)	RATE/FINAL (PSI/MIN)	MicroCAP
1000	10	R.T.	100/3500	1
1200	8	100	200/4000	2
1500	6	120	300/4000	3

EXPERIMENTAL

#1 1200	8	100	200/4000	2
#2 1200	8	100	200/4000	2
⋮				
#16 1500	8	120	200/4000	2
⋮				
#22 1200	8	100	100/3500	3
⋮				
#36 1200	8	120	200/4000	1
⋮				
#46 1200	10	100	100/3500	2

General Processes Involved in Organic Analysis

Figure 14



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MULTILEVEL EXPERT SYSTEMS OUTLINE

Figure 15(a)

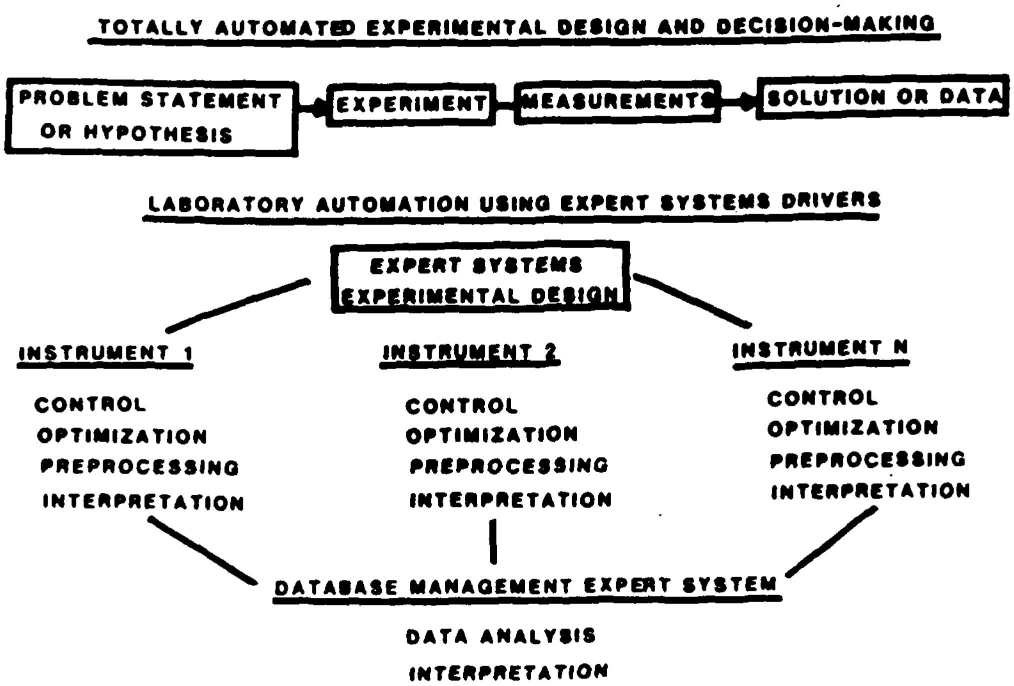


Figure 15(b)

EXMAT

A LINKED NETWORK OF EXPERT SYSTEMS

WITH PATTERN RECOGNITION AND SEARCH PROGRAMS FOR MATERIALS CHARACTERIZATION

COMPONENTS	ATTRIBUTES
1. DATABASE MANAGEMENT	A. STORAGE OF PARAMETERS AND DATA ON SAMPLES FOR SELECTED INSTRUMENTAL TECHNIQUES
	B. RETRIEVAL OF SELECTED SAMPLES FORMING A DATA SET FORMATTED FOR MULTIVARIATE ANALYSIS
	C. CREATE, ADD, DELETE, HELP AND SHOW FUNCTIONS
2. EXPERT SYSTEMS AND EMBEDDING SUBPROGRAMS-TIMM	A. FORTRAN SOURCE CODE
	B. EMBEDDING OF TIMM SYSTEM WITHIN USER PROGRAMS
	C. CAPABLE OF HANDLING METRIC AND NON-METRIC INFORMATION
	D. HEURISTIC DESIGN

Figure 15(b) (continued)

COMPONENT	ATTRIBUTES
3. PATTERN RECOGNITION EXPERT SYSTEM - EXMATH	A. HEURISTIC DESIGN
	B. SUPERVISED AND UNSUPERVISED PATTERN RECOGNITION, FACTOR ANALYSIS, PLOTTING
	C. EXPERTISE INCLUDES DATA PREPROCESSING AND EVALUATION OF RESULTS
	D. USER INTERVENTION FOR DATABASE MODIFICATIONS
	E. IMPLEMENTABLE AS JACKNIFING PROCEDURE
4. SPECTRAL SEARCH AND MATCH ALGORITHIMS PARTIAL INTERPRETATION AIDS	A. PAIRS INFRARED SPECTRA
	B. PBM-MASS SPECTRA

DEVELOPMENT OF EXMAT Figure 15(c)

A LINKED NETWORK OF EXPERT SYSTEMS FOR MATERIAL ANALYSIS

ES #1 ANALYTICAL STRATEGY FOR DEFINED PROBLEM

ES #2 INSTRUMENTAL CONFIGURATION/CONDITIONS

ES #3 DATABASE GENERATION

ES #4 DATA TREATMENT

ES #5 DATA RESULTS

ES #6 DATA INTERPRETATION

ES #7 ANALYTICAL GOAL

Figure 15(d)

PYROLYSIS/CONCENTRATOR WITH CAPILLARY GC-MS/DS

FORMATTED FOR ENTRY INTO DATABASE MANAGEMENT SYSTEM, EXDBM

SAMPLE ID = 0001
SAMPLE NAME = EA4004
SAMPLE REP. NO.=1
SAMPLE EXP. NO.=1
PYROPROBE 124-HP 5985B GC-MS
ANALYSIS TYPE = DHS/PGC-MS
TYPE = CORR. AREA, % OF TOTAL
SAMPLE FILE BASIS = S0087
NO. VARIABLES = 16

20
87/28/7
600C/20 SEC
175C/3 MIN
-50/4 MIN
-50/4 MIN
290C/3 MIN
290C/3 MIN
300/7 MIN
DB-5 (30M .25MM)
10 PSI
50C (3M) TO 300C
30C/MIN
EI (70EV)/300UA
200C
33 TO 500/SEC

PEAK1=6.285
15012
1.781
PEAK2=6.835
11391

Figure 15(e)

FACTOR ANALYSIS

Test Data for Chemometrics

FACTOR 1 VS FACTOR 2

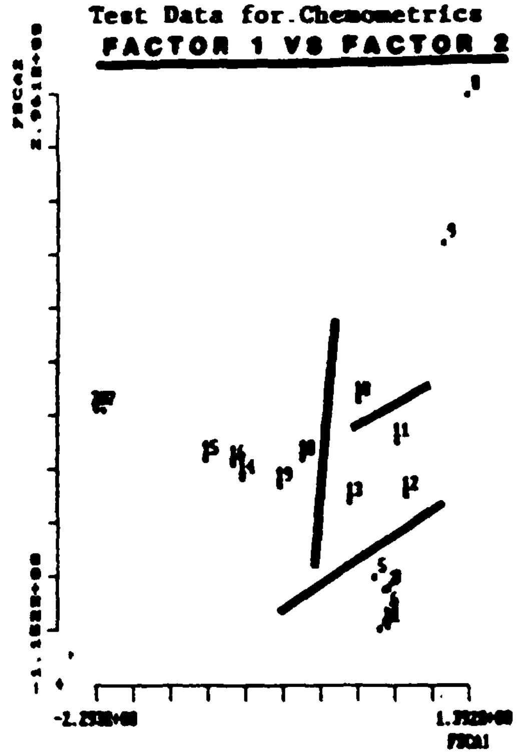
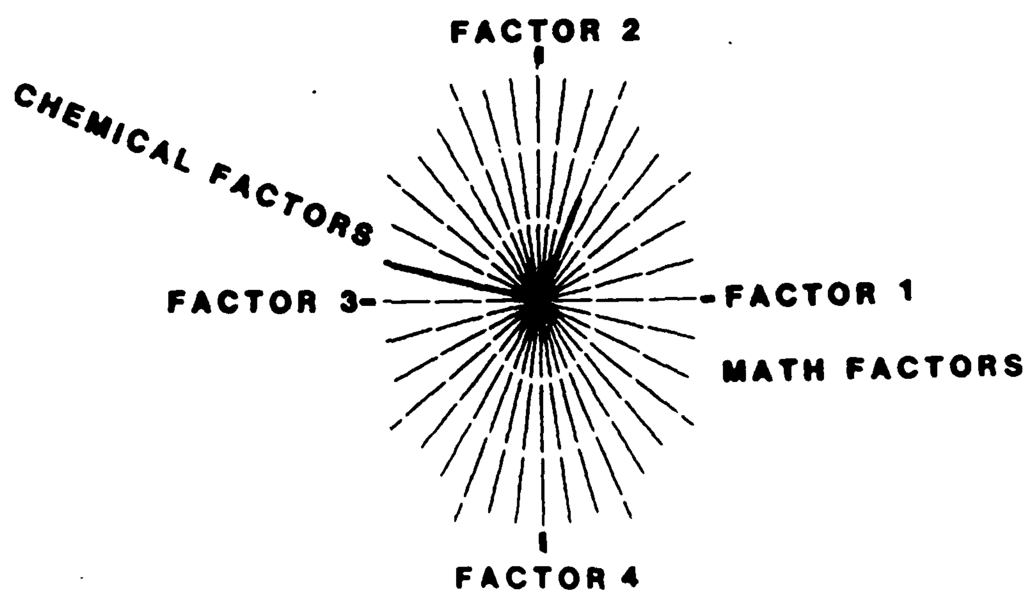


Figure 15(f)

FACTOR ROTATION

Test Data for Chemometrics

PLOT OF COVARIANCE MATRIX



EXMAT Network, MICROCAP Expert System **FIGURE 16**

```
The allowable responses are shown below.

*MAIN MENU*   |  B  Build      T  Train               E  Exercise
Type letter   |  I  Inquire    G  Generalize          C  Compress
+ file name   |  M  Modify     N  Check consistency   P  Check completeness
and return.   |  V  Convert    R  Recover             S  Stop

Selection?  e

First, some preliminaries ...

Do you want to record this in a print file?  n

Tell me the names of all the files containing the expert systems you want
to exercise.  Enter one per line, and enter a "/" as the last line:
    EXCONFIG
    strategy
    config
    datgen1
    datarea
    datarea1
    interpt1
    angoall
    microcap  <----

Shall I pick the test cases for you ( Y or N ) ? n

Shall I narrow down the possible choices as I go ( Y or N ) ? n

Do you want me to use terse (T) or verbose (V) mode?  t

Ok, we're ready to start ...

    SCOPE               IS screen
    SAMPLE AMT          IS mg
    SAMPLE FORM         IS powder
    SAMPLING PROCESS    IS *
    SAMPLE HISTORY      IS *
    INSTR. AVAIL        IS all

    ANALY STRATEGY      IS FTIR/SYS2(80)
                           GC/SYS1(20)
                           (Reliability = 100)
```

EXMAT - HELP "CHOICE SYS 8/CT" **FIGURE 17**

TAGA 6000 Triple Quadrupole MS/MS Interfaced with Pyroprobe Model 122

CHOICE "SYS8/CT"

Operational settings for the Pyroprobe are under condition C; for the triple quadrupole Sciex TAGA 6000, under condition T. When using the CDS Pyroprobe Model 120 or 122, the probe is positioned in the glass tube support about 1.5 cm from the end with the metal outside rods just near the glass. The corona discharge needle in the APCI source should be ca. 2 mm from the inside quartz tube insert of the Pyroprobe which holds the samp. Carrier gas stream or air or N_2 of 80 ml/min sweeps the volatiles into the ionization chamber. Condition T: The TAGA may be operated in the MS-mode or MS/MS-mode, with each parameter set to its optimum in terms of peak resolution, shape, and transmission of the ions thru the mass filters of quad 1-quad 3. Recommended values for the conventional MS quad 1 scan parameters are given in (....) and for the daughter-ion mode (MS/MS) in [....]. MTL (sec) measurement time limit: (0.0100/[0.0300]; STEP (amu) mass increments: (1.00000)/[1.0000]; PE (sec) delay period between scans: (0.00)/[0.00]; C = constant time mode: (10)/[1]; TH (ions/sec) Threshold (10)/[1]; TT (min.) total time: (2.00)/[2.00]; MO (amu) mass offset: (-0.1)/[[-0.1]; DI (uA) discharge current: (2.000)/[2.500]; IN (volt) interface plate voltage: (650)/[650]; L1 (volt) Lens 1: (63)/[70]; CB (volt) Lens 2 (48)/[58]; L3 (volt) Lens 3a and lens 3b: (40)/[50]; L4 (volts) lens 4: (5.)/[40]; L5 (volt) lens 5: (-250)/[-250]; L6 (volt) lens 6: (25)/[25]; R1 (volt) rod offset of quad 1: (38)/[45]; RE1 (volt)
("$" stops output, "#" stops paging ...)
mass resolution of quad 1: (153)/[135]; R2 (volt) rod offset of quad 2: (15)/[0]; CG (volt) collision gas: (off)/[Ar]; L10 (volt) lens 10: (60)/[60]; MU (volt) multiplier voltage: (-3650)/[-4200]; R3 (volt) rod offset of quad 3: (15)/[auto]; RE 3 (volt) mass resolution of quad 3: (120)/[153]. Parameters SY, SE, PE, G1, G2, G3, BAF, DC, MC1, DM1, Q2r, and DM3 are not important in the above compilation.

Box-Behnken Design for SFE

Block 1

Figure 18

	Initial Pressure (psi)	Time (min)	Temp	Rate/Final	Microcap
	1000	10	R.T.	100/3500	1
	1200	8	100	200/4000	2
	1500	6	120	300/4500	3
1	1200	8	100	200/4000	2
2	1200	8	100	200/4000	2
3	1200	8	100	200/4000	2
4	1500	6	100	200/4000	2
5	1500	10	100	200/4000	2
6	1000	6	100	200/4000	2
7	1000	10	100	200/4000	2
8	1200	8	120	300/4500	2
9	1200	8	120	100/3500	2
10	1200	8	R.T.	300/4500	2
11	1200	8	R.T.	100/3500	2
12	1200	10	100	200/4000	3
13	1200	10	100	200/4000	1
14	1200	6	100	200/4000	3
15	1200	6	100	200/4000	1
16	1500	8	120	200/4000	2
17	1500	8	80 R.T.	200/4000	2
18	1000	8	120	200/4000	2
19	1000	8	80 R.T.	200/4000	2
20	1200	8	100	300/4500	3
21	1200	8	100	300/4500	1
22	1200	8	100	100/3500	3
23	1200	8	100	100/3500	1

Box-Behnken Design for SFE

Block 2

Figure 19

	Initial Pressure (psi)	Time (min)	Temp	Rate/Final	Microcap
24	1200	8	100	200/4000	2
25	1200	8	100	200/4000	2
26	1200	8	100	200/4000	2
27	1200	6	120	200/4000	2
28	1200	6	80 R.T.	200/4000	2
29	1200	10	120	200/4000	2
30	1200	10	80 R.T.	200/4000	2
31	1500	8	100	300/4500	2
32	1500	8	100	100/3500	2
33	1000	8	100	300/4500	2
34	1000	8	100	100/3500	2
35	1200	8	120	200/4000	3
36	1200	8	120	200/4000	1
37	1200	8	80 R.T.	200/4000	3
38	1200	8	80 R.T.	200/4000	1
39	1500	8	100	200/4000	3
40	1500	8	100	200/4000	1
41	1000	8	100	200/4000	3
42	1000	8	100	200/4000	1
43	1200	6	100	300/4500	2
44	1200	6	100	100/3500	2
45	1200	10	100	300/4500	2
46	1200	10	100	100/3500	2

Figure 20(a)

TIME-RESOLVED ANALYTICAL PYROLYSIS APCI MS/MS SCHEMATIC

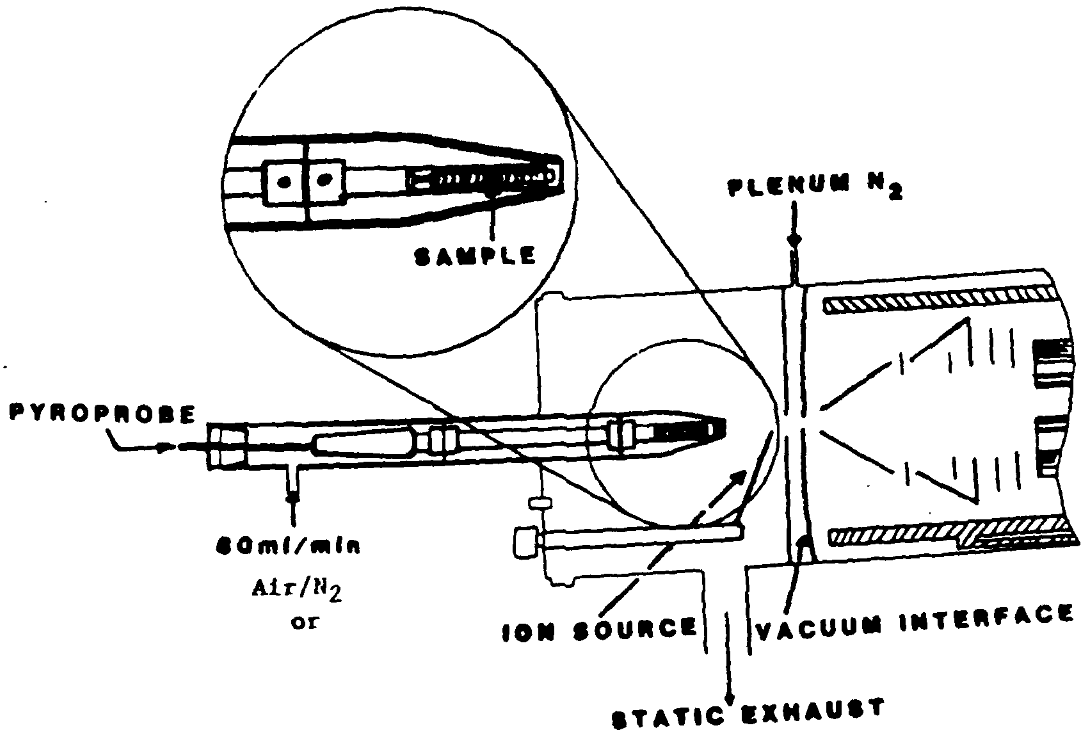


Figure 20(b)

Pyrogram Pulse 700°C/20 sec Polyethylene (Air, N_2), Oxidized PE (Air, N_2) and PEO (Air, N_2)

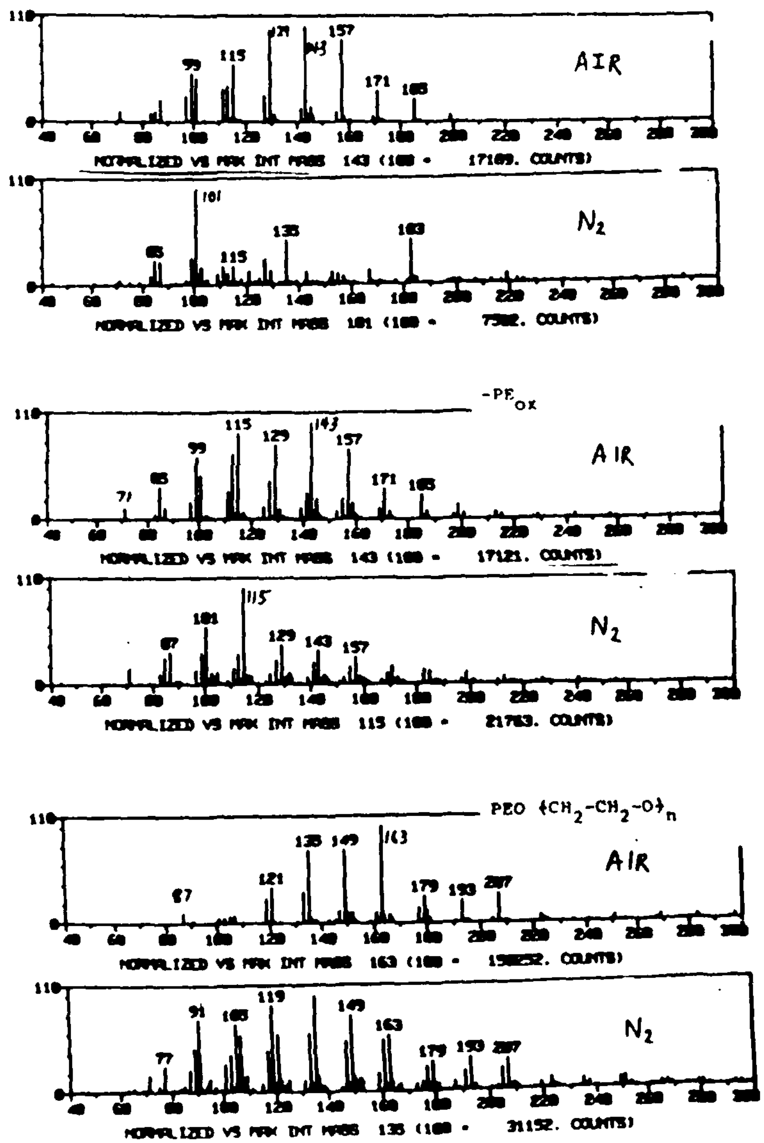


Figure 21(a)

Pyrograms - Microcap #1 (180°/min to 400°C) No Heat

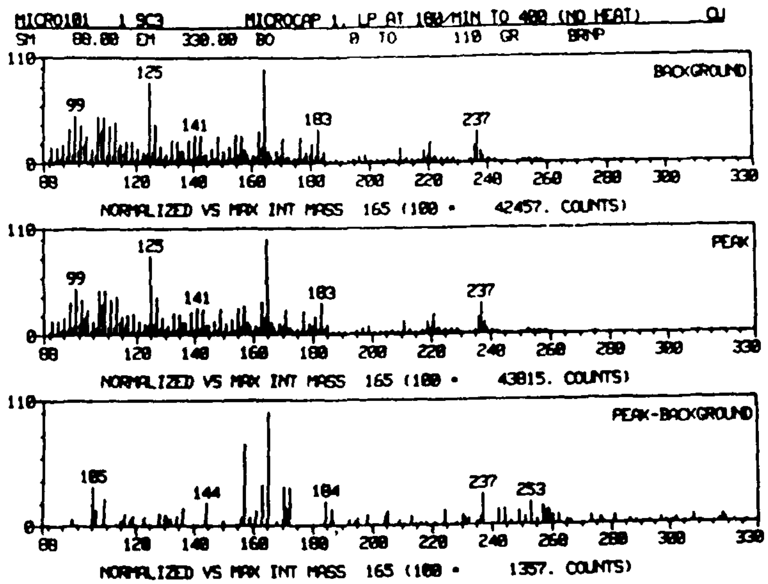


Figure 21(b)

Pyrograms - Microcap #1 (180°/min to 400°C) With Heat

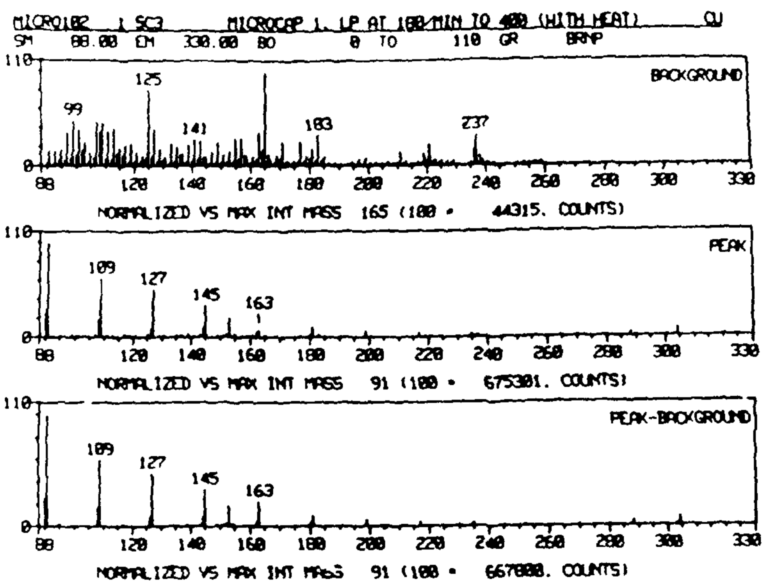


Figure 21(c)

Pyrograms - Microcap #1 (Pulse to 700°C/20 sec)

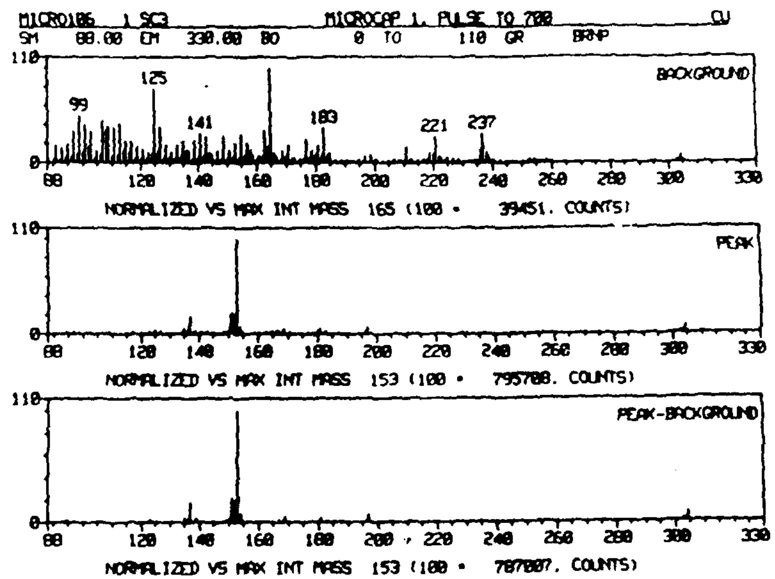


Figure 21(d)

Pyrograms - Microcap #1 (240°C/min to 500°C)

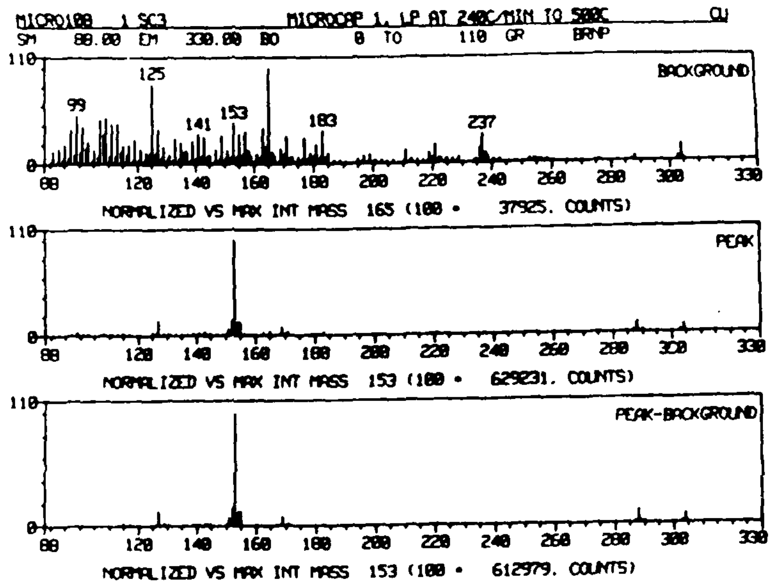


Figure 21(e)

Pyrograms - Microcap #1 (300°C/Min to 200°C), 4 Min Interval

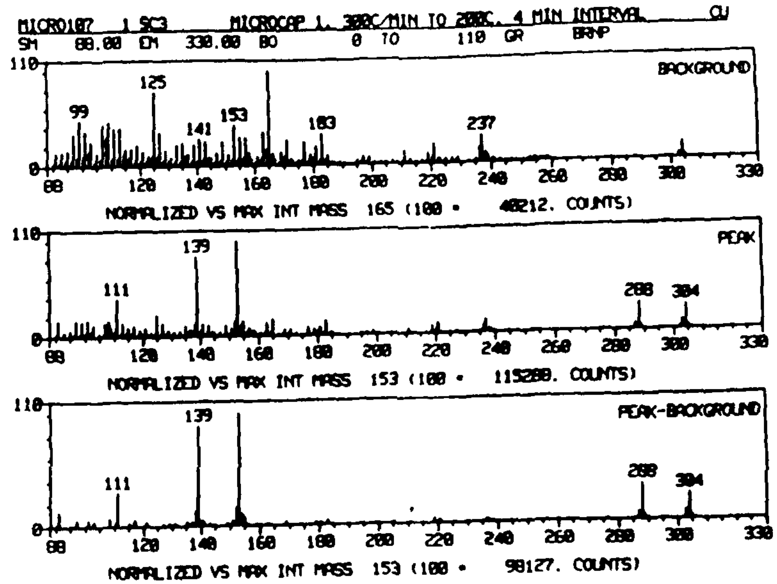


Figure 22

Pyrogram Polymer A 180°/min to 400°

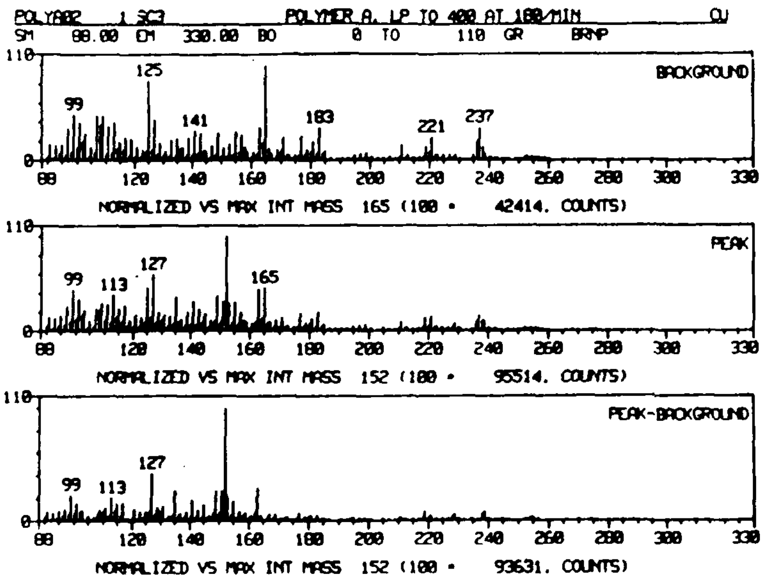


Figure 23(a)

Pyrogram Microcap #1 pulse to 400°C/20 sec

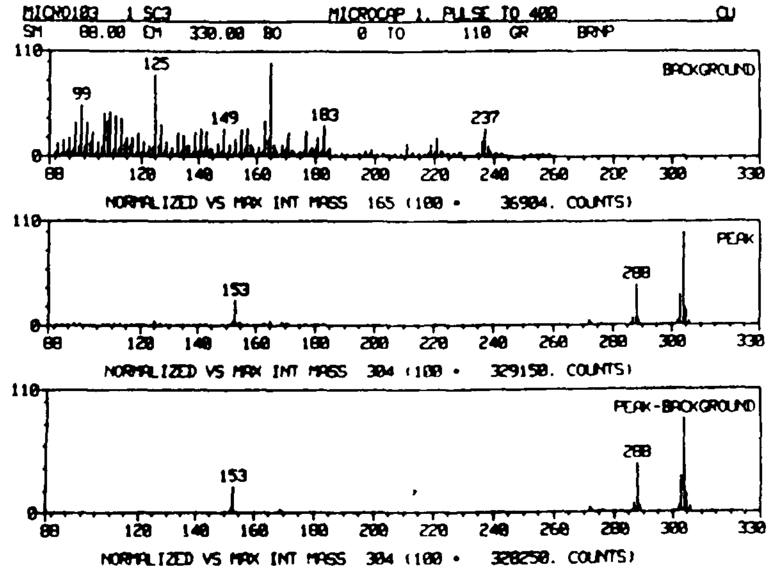


Figure 23(b)

Pyrogram Microcap #2 pulse to 400°C/20 sec

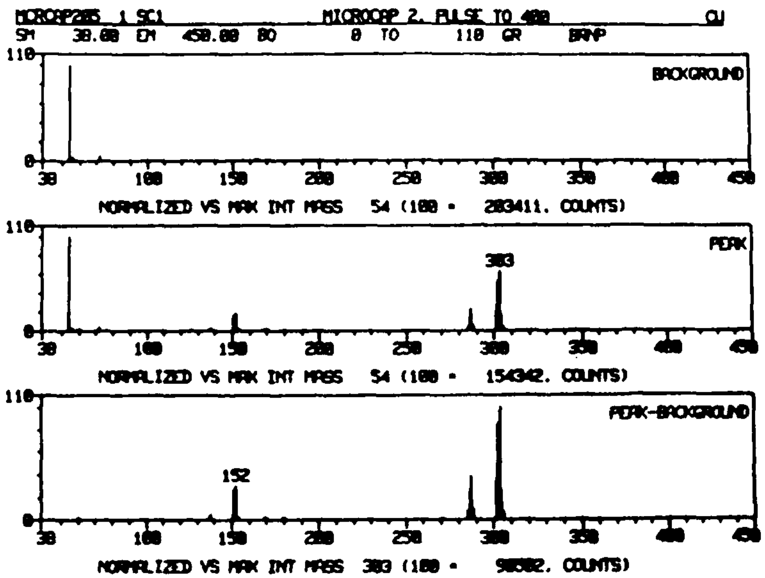


Figure 23(c)

Pyrograms Microcap #3 pulse to 400°C/20 sec

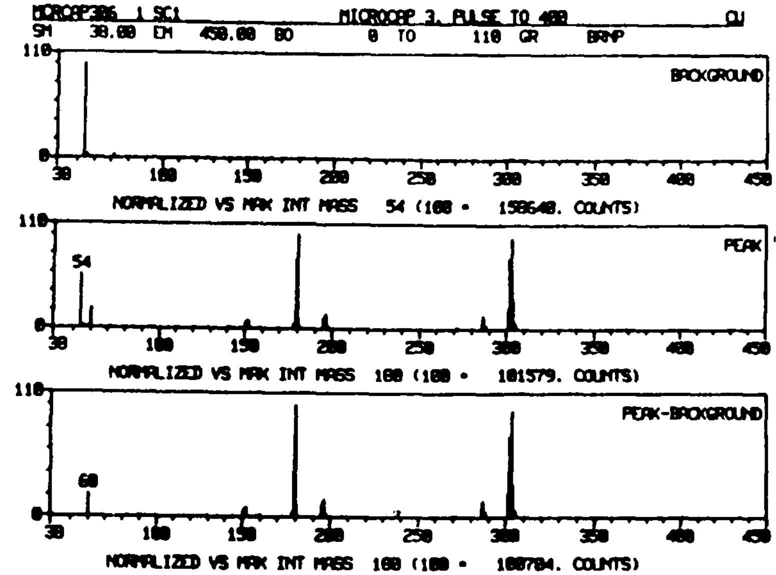


Figure 23(d)

Pyrograms of Microencapsulated Protein, Gelatin Powder and Microencapsulated Gelatin

APCI MS/MS OF MICROENCAPSULATED MATERIALS

METHOD DEVELOPMENT

700 C/20 SEC

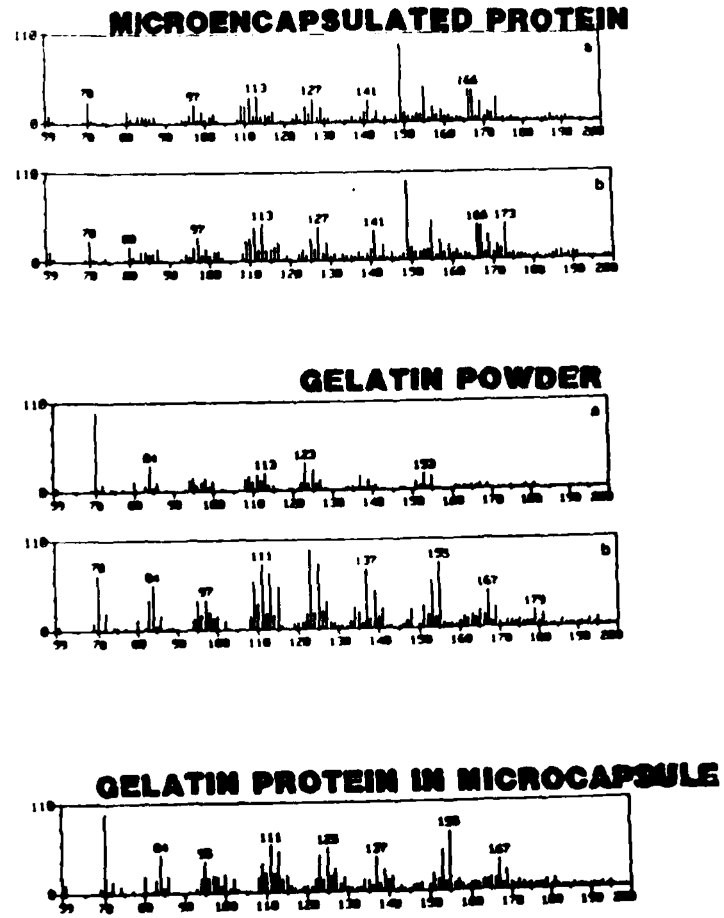


Figure 24(a)

INSTRUMENTATION FOR TRACE ORGANIC ANALYSIS

ANALYTICAL PYROLYSIS/CONCENTRATOR GC-MS/DS

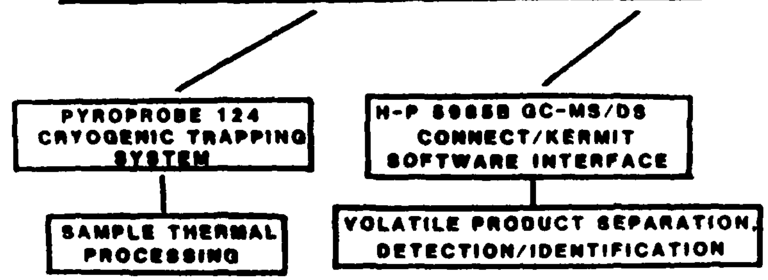


Figure 24(b)

Pyrograms - Concentrator/GC-MS (HP 5985B) Data Generation -

Groups I, II, III Organic Amine Salts

DATA GENERATION

PYROGRAMS (TIC)

GROUP I **GROUP II** **GROUP III**

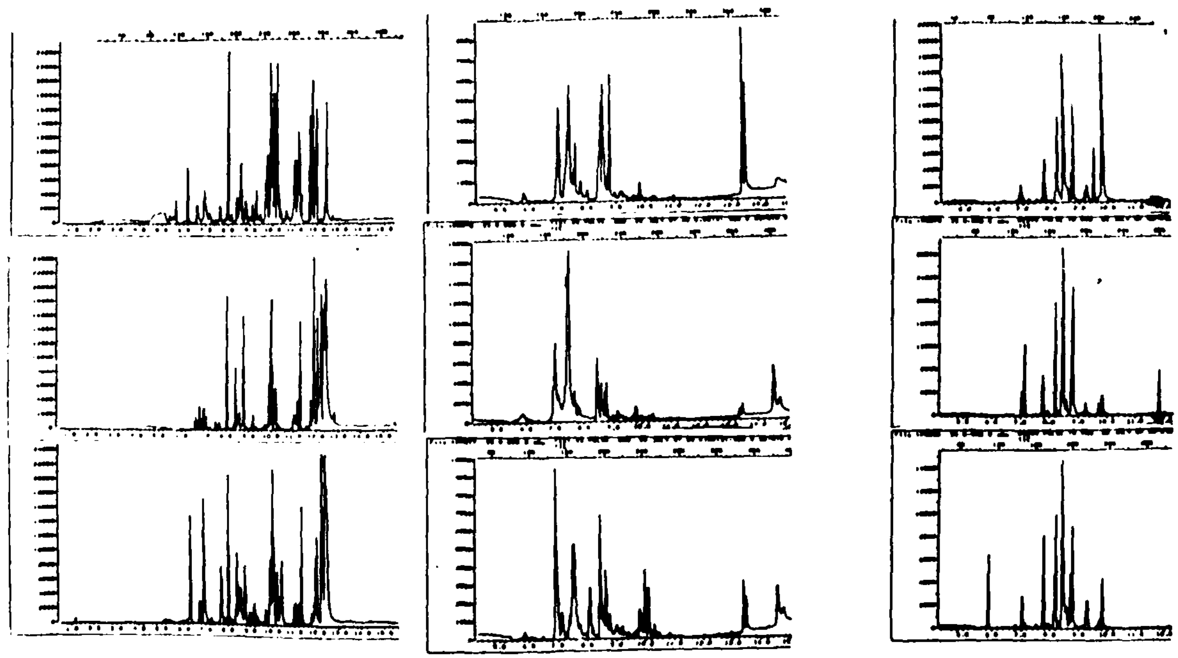


Figure 24(c)

MS Patterns of TIC Peaks from Pyrograms and Library Match

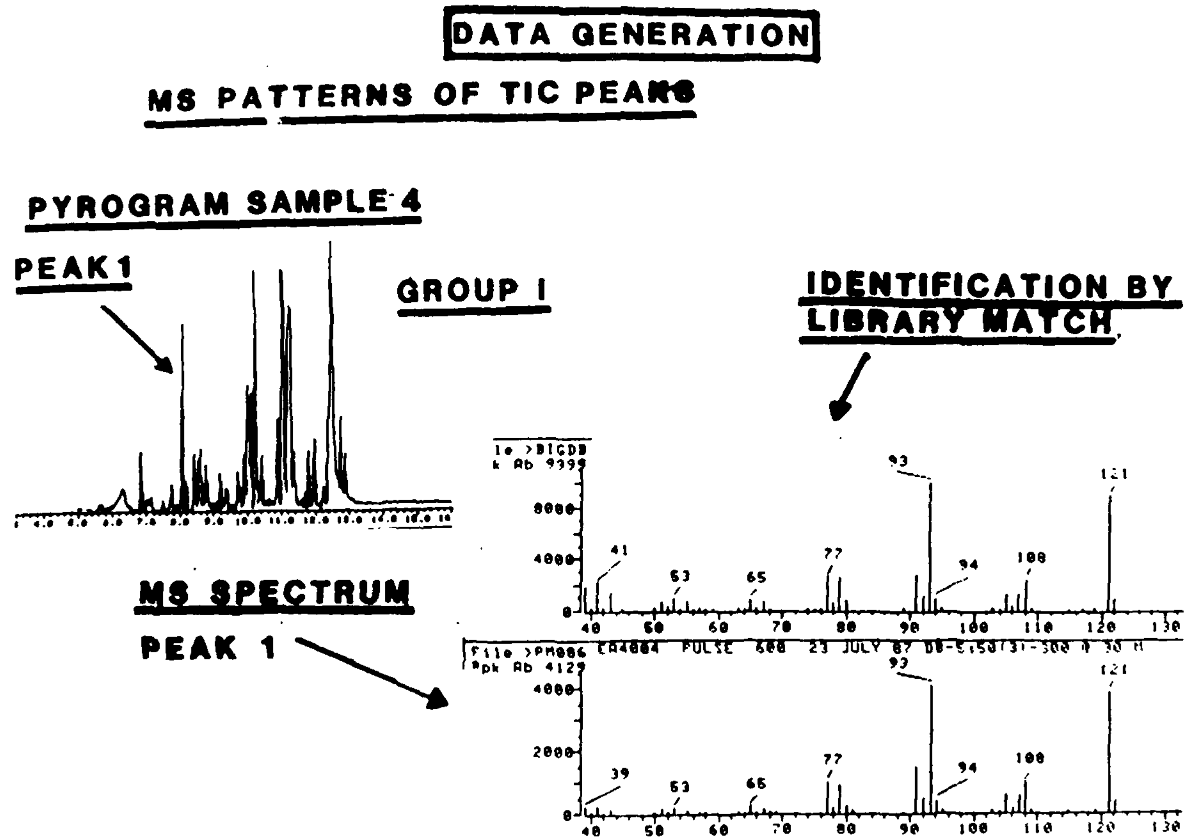
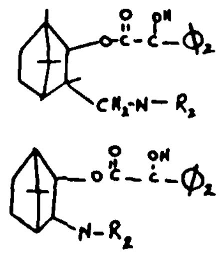


Figure 25

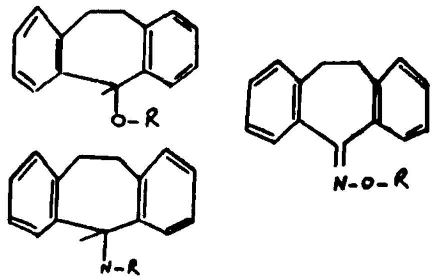
AMINE SALT STRUCTURES FOR TEST METHOD

(EXMAT SERIES)

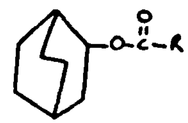
GROUP I



GROUP II

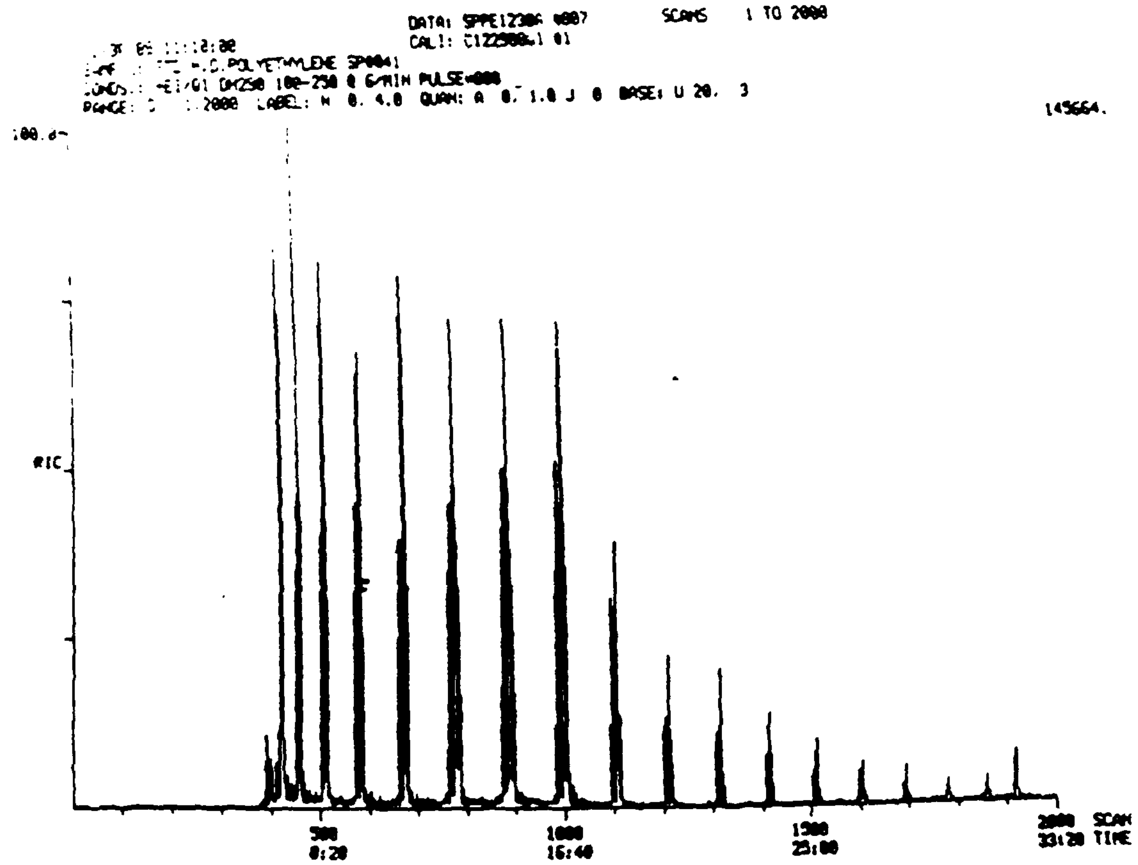


GROUP III

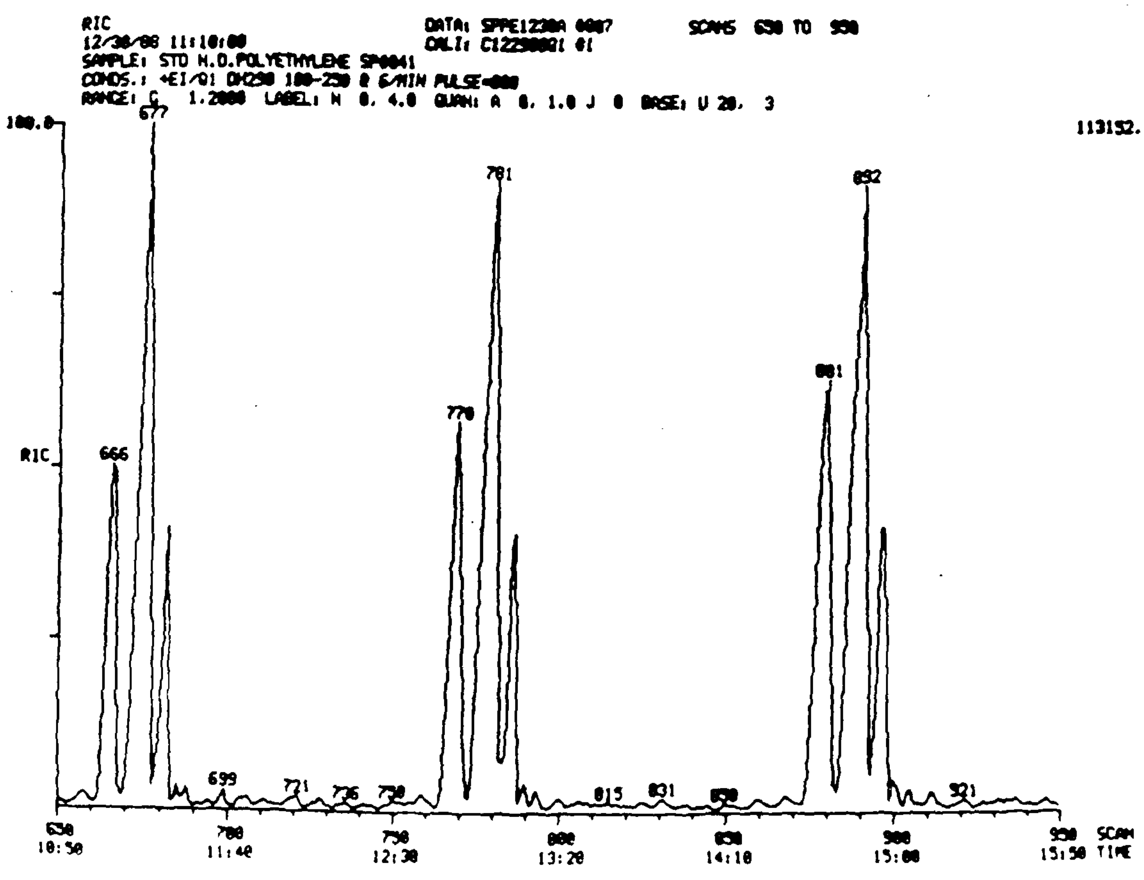


- o HCl
- o FUMARATE
- o MALEATE

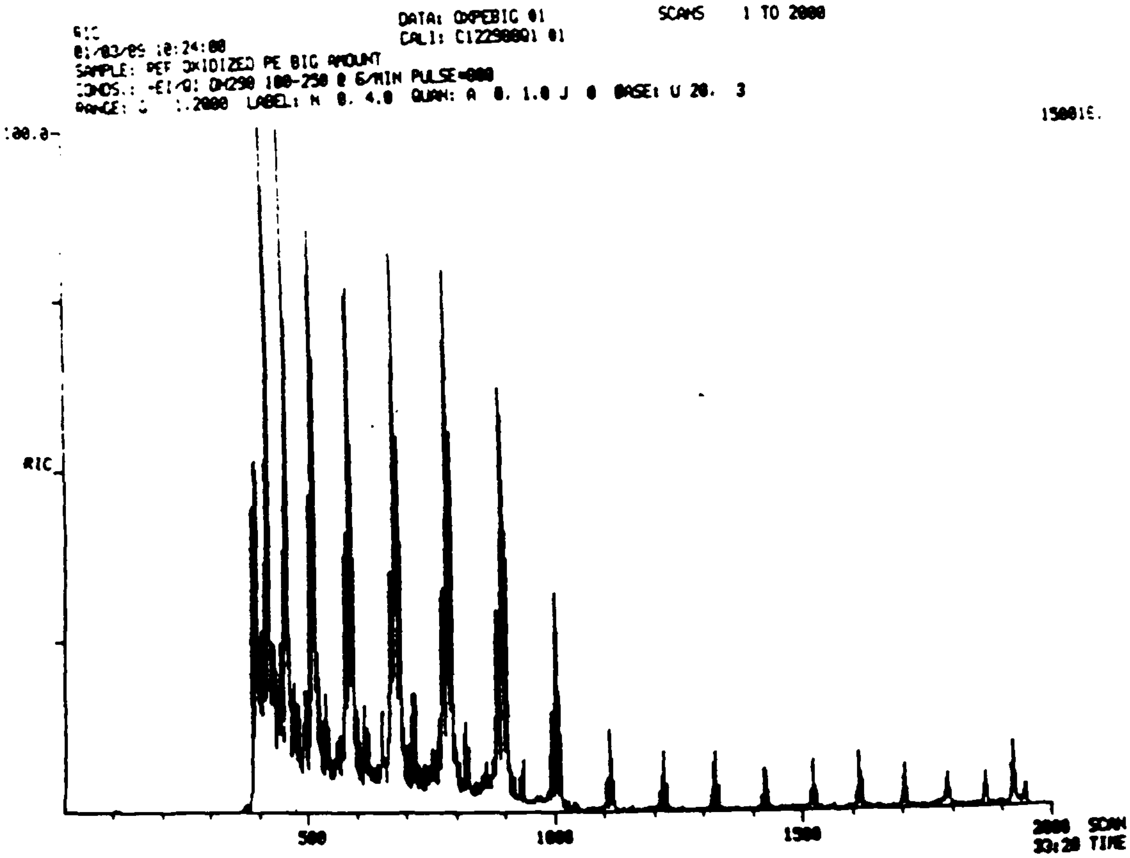
High Density PE, 800°C/20 sec Pyrogram - RIC   Figure 26(a)



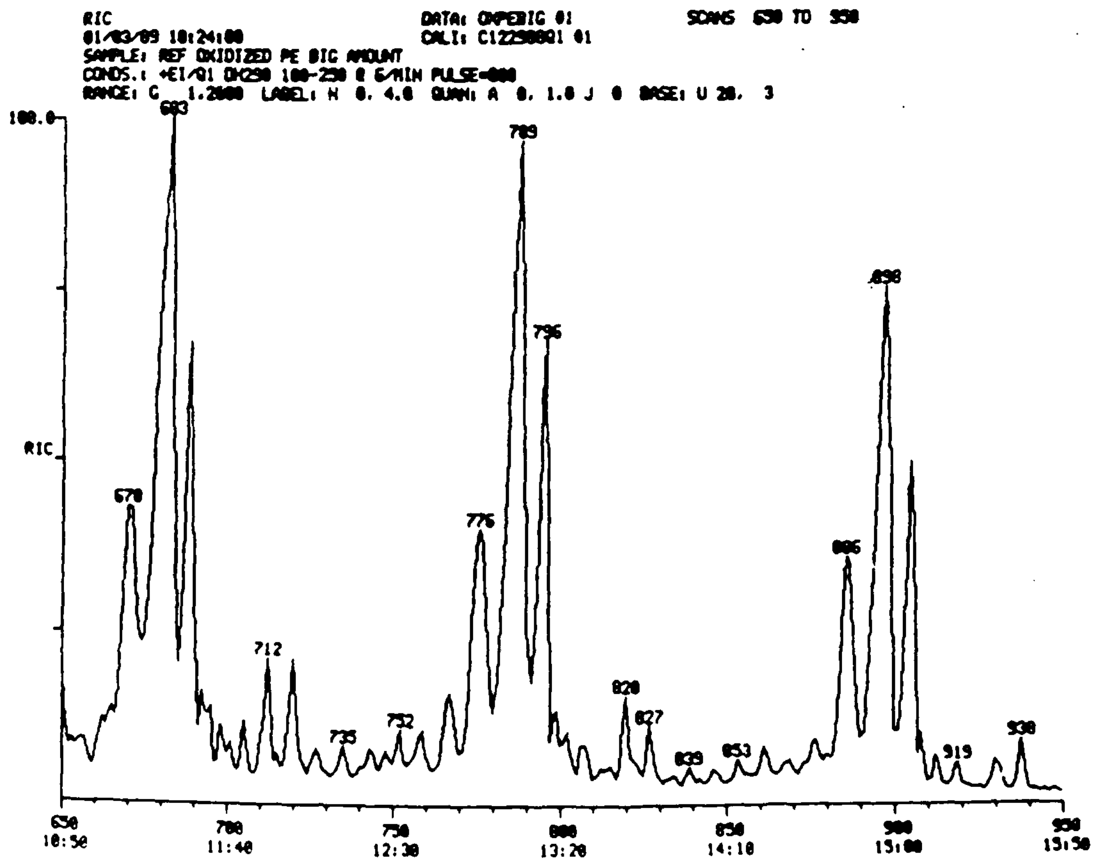
Scansets 650-950, Carbon Triplets ~ C_{13}-C_{15} of 26(a)   Figure 26(b)



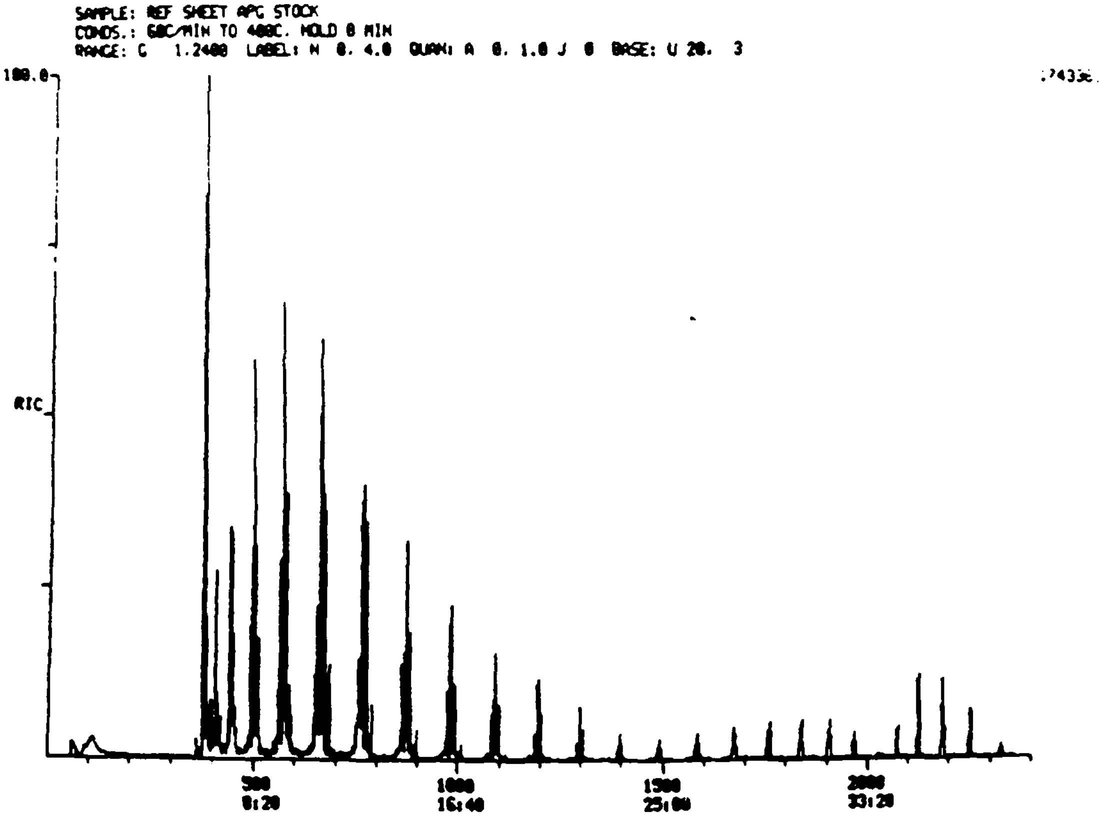
Oxidized PE, 800°C/20 sec Pyrogram - RIC **Figure 26(c)**



Scansets 650-950, ~C_{13}-C_{15} of 26(c) **Figure 26(d)**



Polymer Bulk Ref. 60°/min to 400°C Figure 26(e)



Scansets 650-950, ~ C_{13}-C_{15} of 26(e) Figure 26(f)

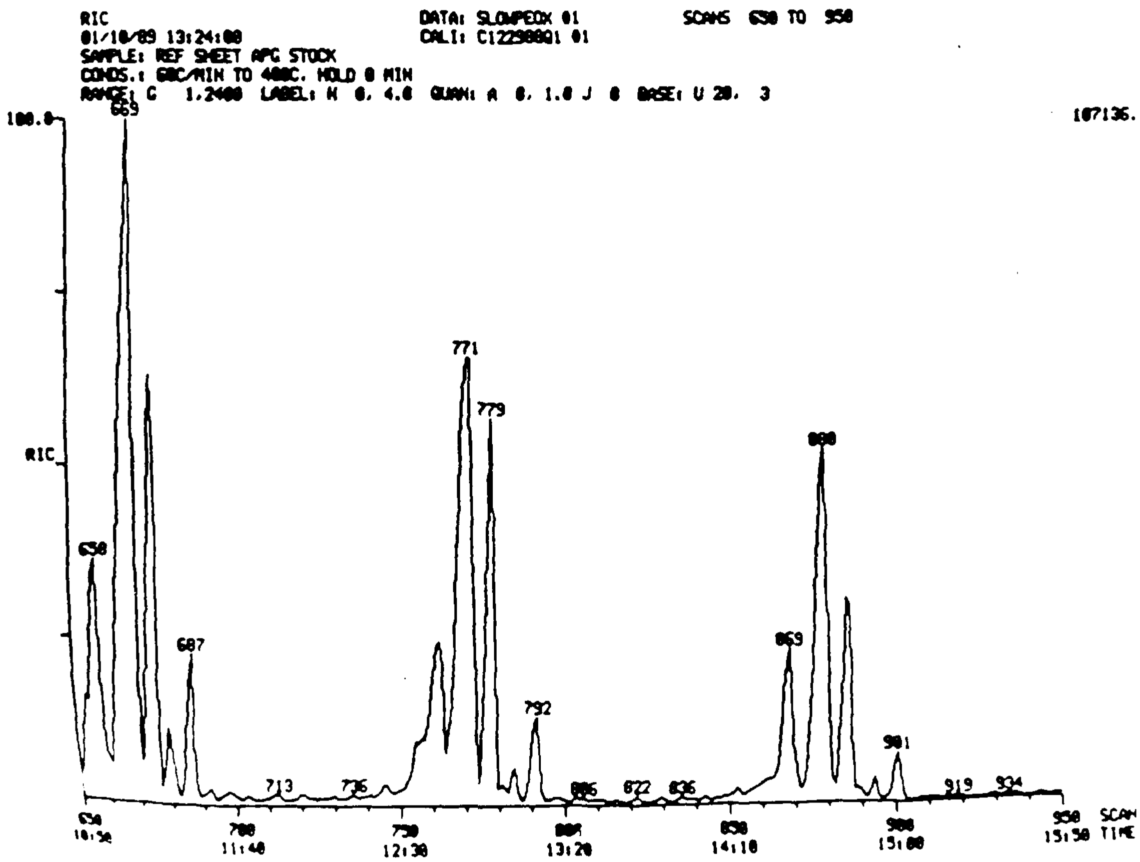
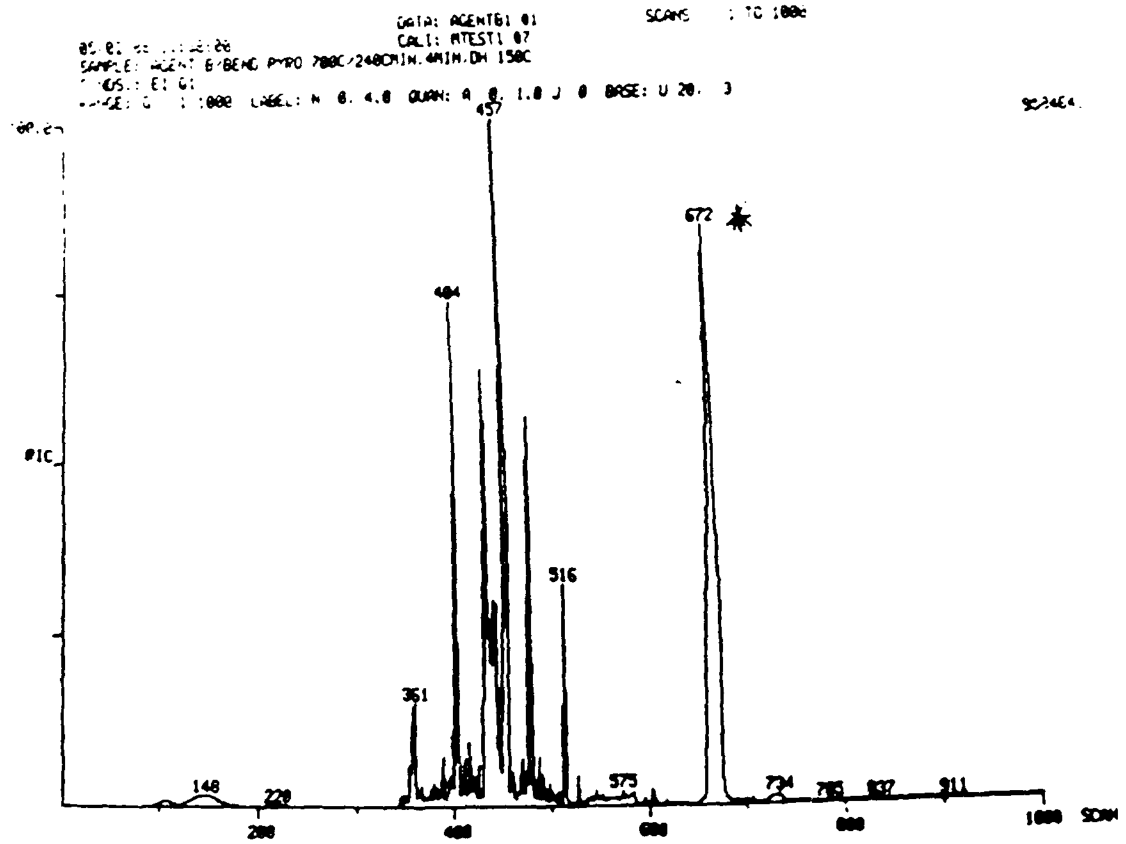


Figure 27

GC-MS Experimental Conditions (Finnigan TSQ GC/MS)

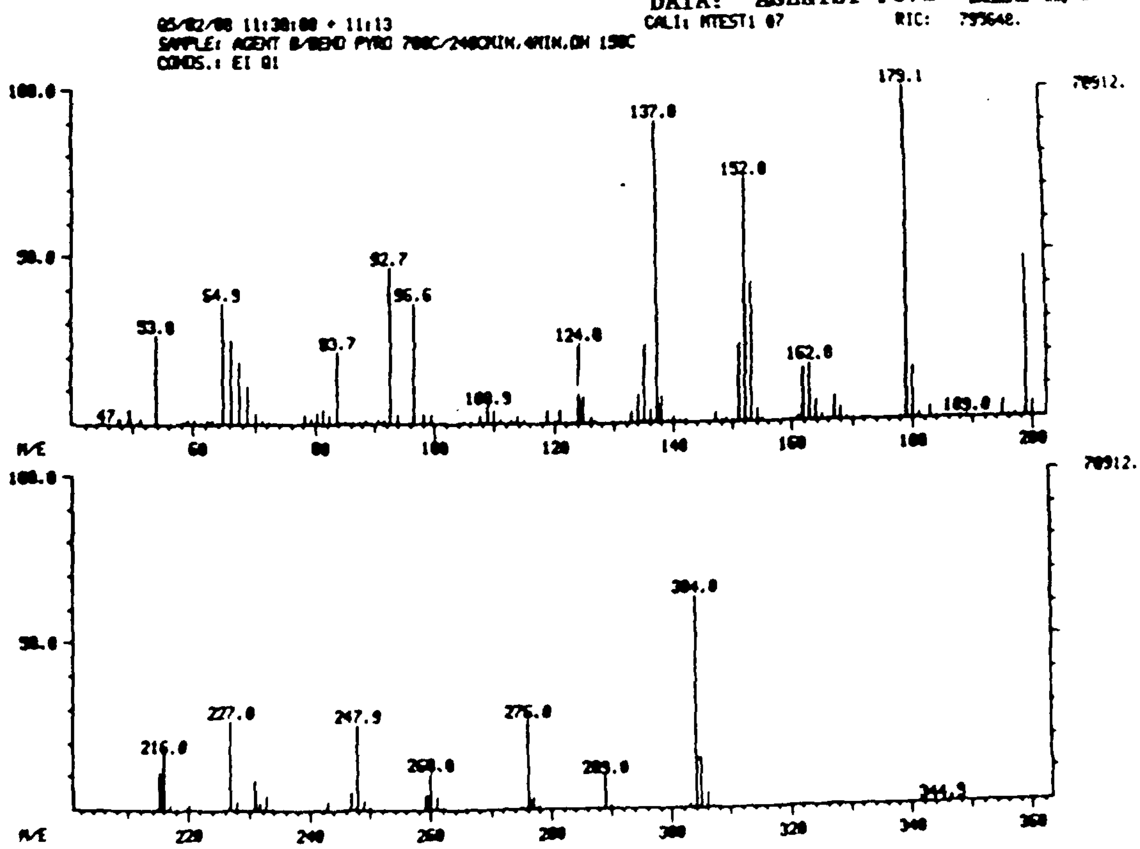
```
12/30/88     11 :: 2.              SCAN 1 OF 2000
     ACQUISITION STARTED

ACQUIRE                             RUN 0 SPPE1230A          ACQUIRING
12/30/88 11 10 00 -  0 03           FREE SECTORS 20966       SCAN  3 OF 2000
SAMPLE  STD H D POLYETHYLENE SP8041
CONDS    +EI/Q1 DH290 100-250 @ 6/MIN PULSE=800
FORMULA  -                          INSTRUMENT  Q1           WEIGHT     0 000
SUBMITTED BY  MW                    ANALYST  MW              ACCT  NO   M687

**********************       GC PARAMETERS       **********************
LOADED  GC DESC PE   CURRENT GC OVEN TMP  100 DEGC    INJECTOR : 280 DEGC
CURRENT GC DESC PE   GC ELAPSE TIME           0  7 MIN  INT OVEN : 280 DEGC
SEQ #  TEMP(C)  RATE(C/M)  TIME(MIN)  TOTAL TIME(MIN)        OPEN  CLOSE
 1   100 - 100     -          5 0            5 0   SWEEP/SPLIT  1.0   0.0
 2   100 - 250    6 0        25 0           30 0   DIVERT      17.0   0.0
 3   250 - 300   25 0         2 0           32 0

**********************       SCAN PARAMETERS     **********************

LOW MASS      45                 UP   0 95 L*                 TOP:  0.00
HIGH MASS    650               DOWN   0.00 L               BOTTOM:  0.05

CENT S/P  10  ACTUAL   10      SAMP INT (MS)  0 150     PEAK WIDTH: 1000.
FRAG S/P  10  ACTUAL   10      SAMP INT (MS)  0 150     INTEN/ION:  2

MIN PEAK WIDTH    3            MIN FRAG WIDTH %:  80    MIN AREA:  20
A/D THRESHOLD     1            BASELINE   0

*****   MODE:  CENTROID

     INTERFACE NUMBER               0
     SUB-INTERFACE NUMBER           0
     # OF ACQU BUFFERS             16
     INSTRUMENT TYPE                Q
     FULL SCALE MASS             1009  AMU
     ZERO SCALE MASS                1  AMU
     INTENSITY/ION                  2
     PEAK WIDTH                 1000.  MMU
     OFFSET AT LOW MASS             0  MMU
     OFFSET AT HIGH MASS            0  MMU
     VOLTAGE SETTLING TIME(MS)      4

12/30/88     12 06 47
     ACQUISITION COMPLETED
     SCANS      1 TO 2000 CENTROID

MODE        SCANS    SECS   OUT OF       %     PEAKS PER SCAN   PER SEC
CENTROID    2000    658 0   2000 0     32 9    51365      26.       26.




PARAMETERS                          DATA  SPPE1230A TI (SPPE1230A MI)
12/30/88 11 10 00 + 33 20           CALI  C12298801            SCANS    1 TO 2000
SAMPLE  STD H D POLYETHYLENE SP8041
CONDS    +EI/Q1 DH290 100-250 @ 6/MIN PULSE=800
FORMULA  -                          INSTRUMENT  Q1             WEIGHT     0 000
SUBMITTED BY  MW                    ANALYST  MW                ACCT  NO   M687

ACC  VOL       8000                 THRESHOLD          1       INTEN/ION          2
A/D S I       0 025                 CENT S I       0 150       FRAG S I       0 150
PEAK WIDTH     1000                 CENT SAMP/PK      10       FRAG SAMP/PK      10
MIN  WIDTH        3                 MIN  FRAG  WIDTH (%)  80   MIN AREA          20

2000 SCANS (453 SECTORS) OF LINEAR UP CENTROID DATA

LOW MASS      45  SCAN TIMES (SECS ) UP   0 95      TOP    0 00
HIGH MASS    650                   DOWN   0 00   BOTTOM    0 05
```

Diazinon-Pyrogram, 240°/min to 700°C, 4 min (Scanset #672) Figure 28(a)

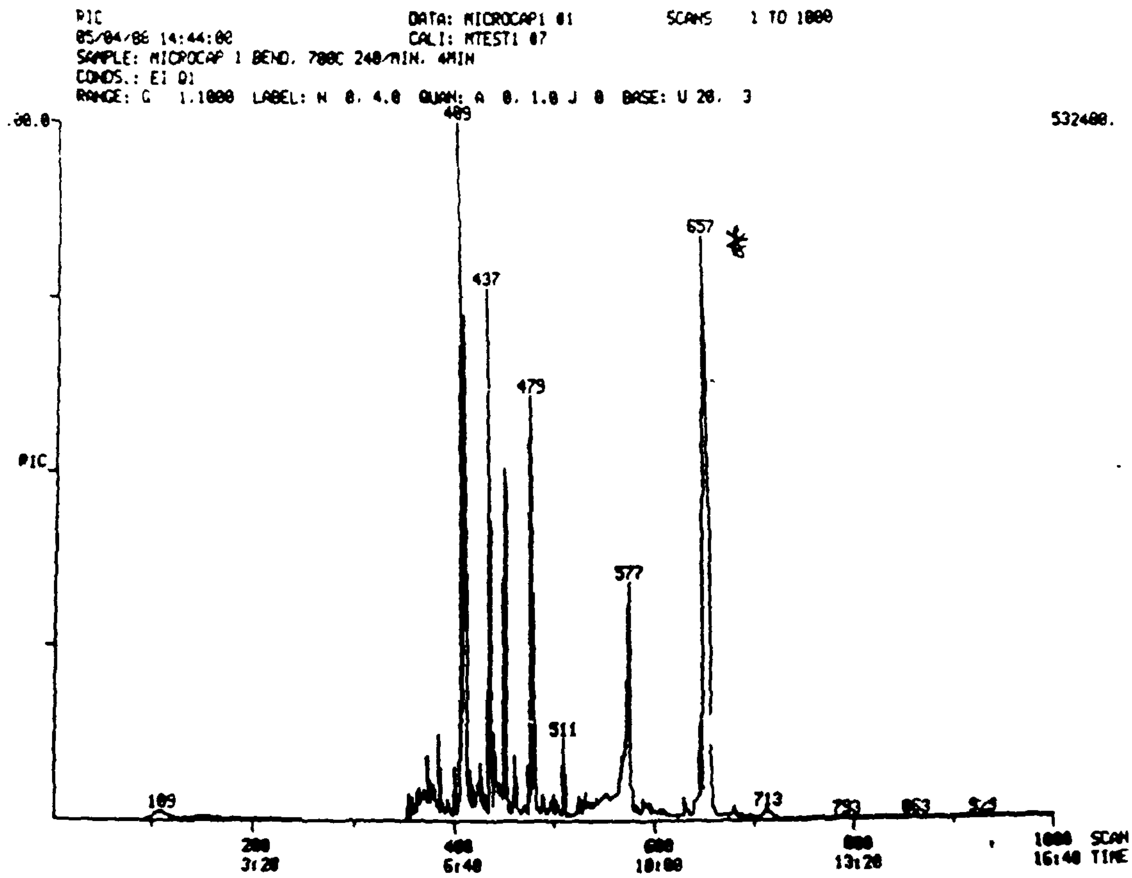


EI-MS of Scanset #672 - Diazinon Figure 28(b)

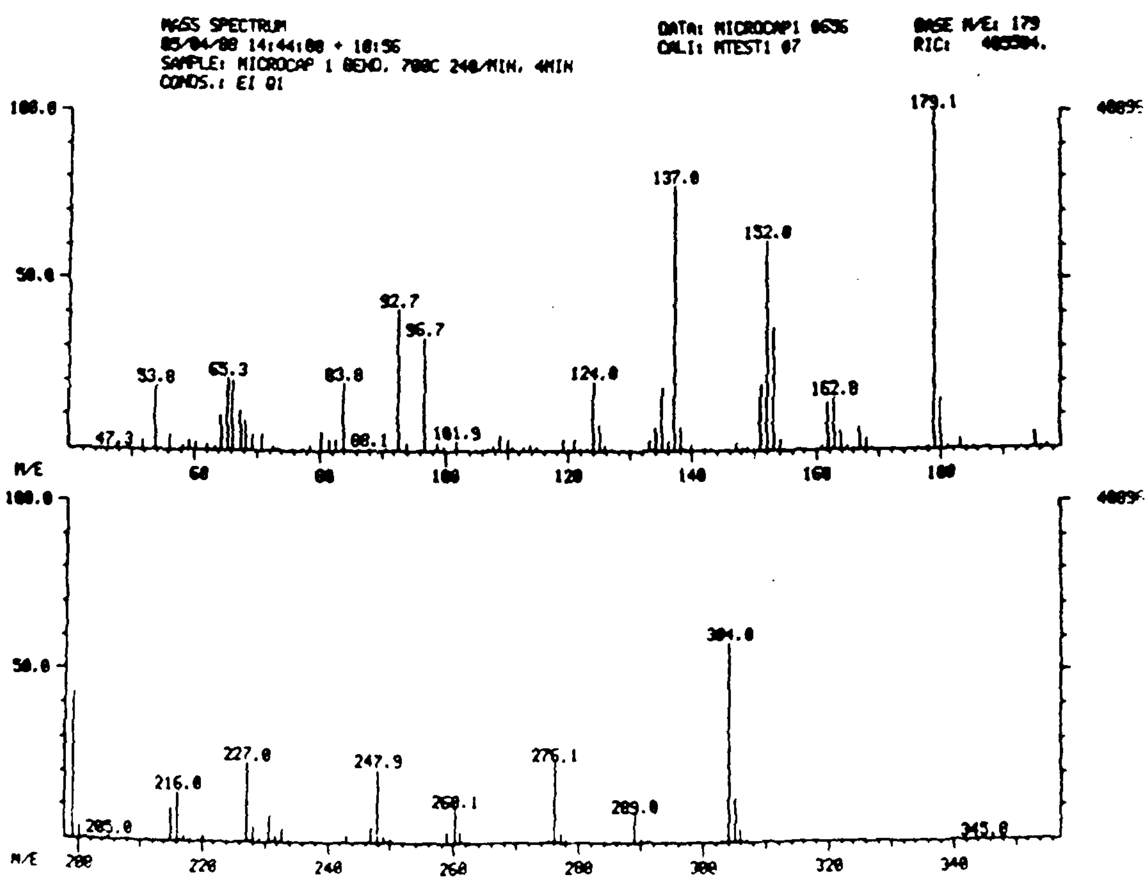
DATA: AGENTB1 #672 BASE M/E: 179



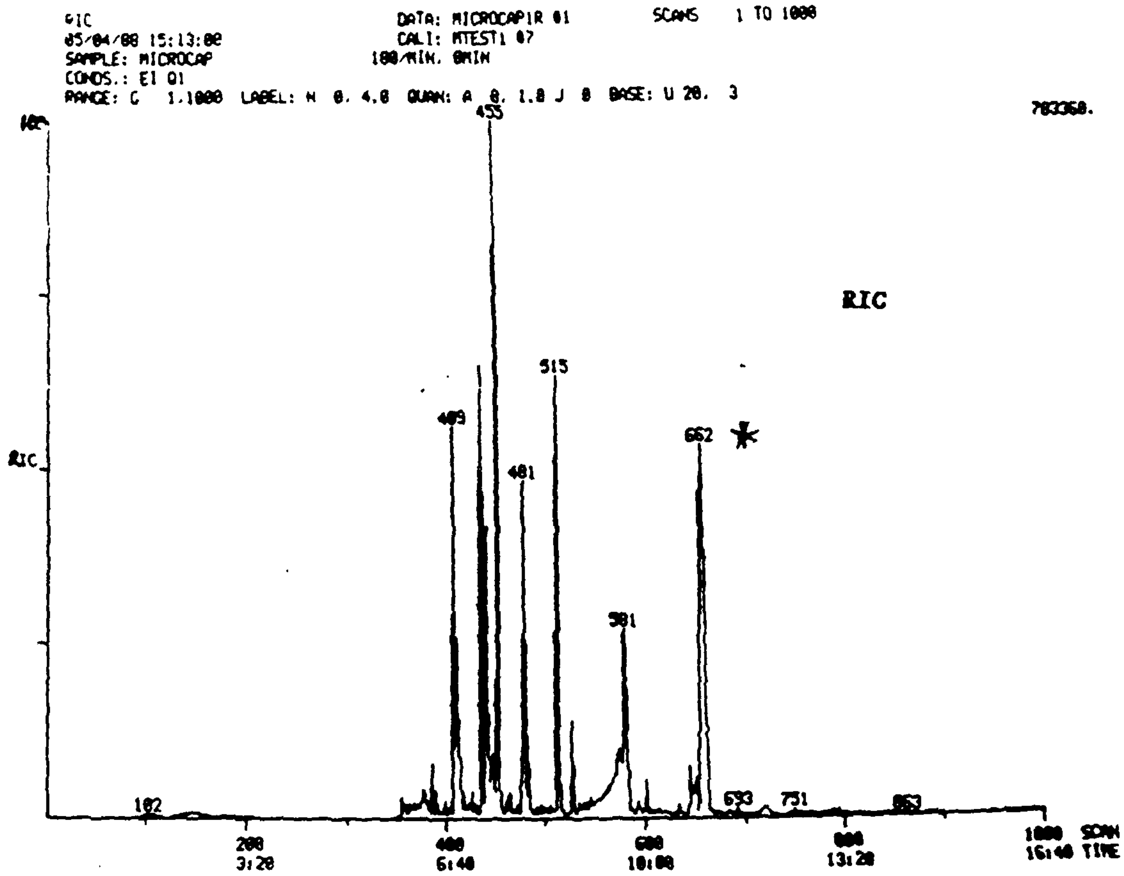
Microcap #1, 240°/min to 700°C, 4 min (Scanset #657) **Figure 29(a)**



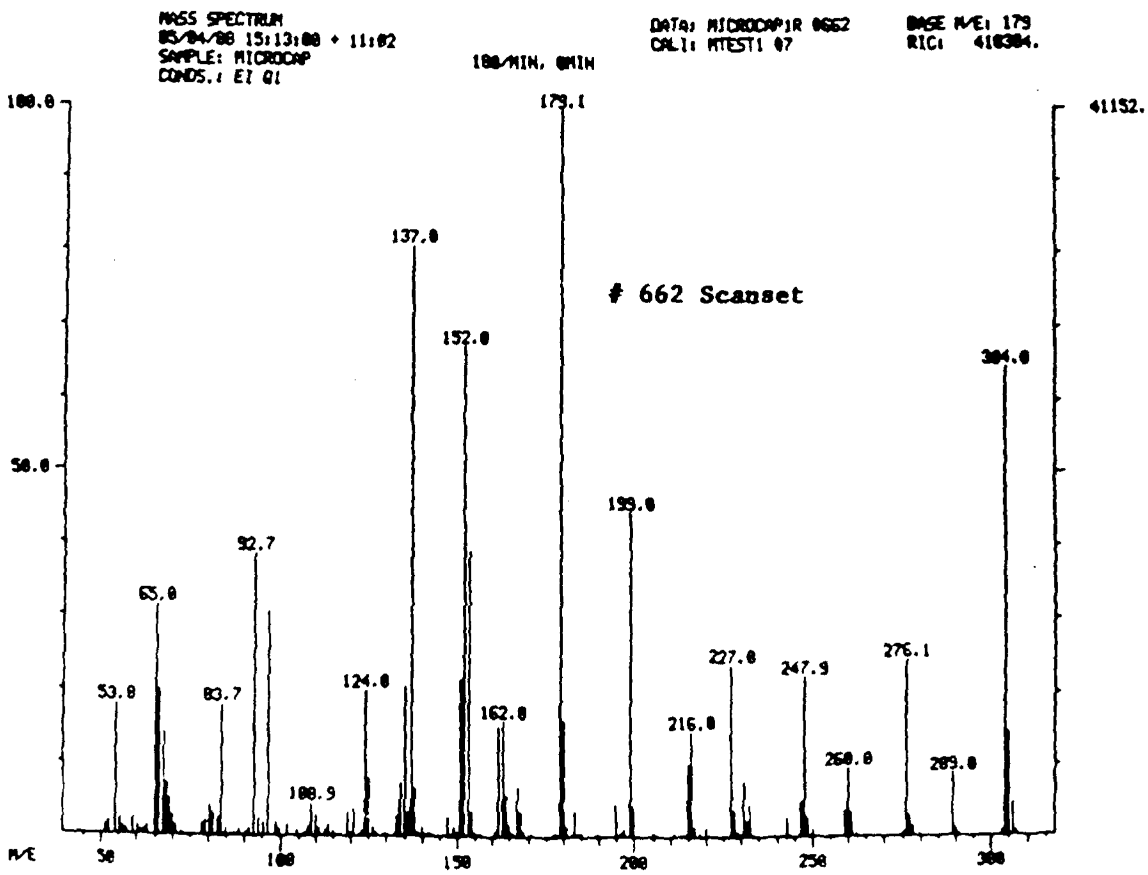
EI-MS of Scanset #656 - Diazinon core **Figure 29(b)**



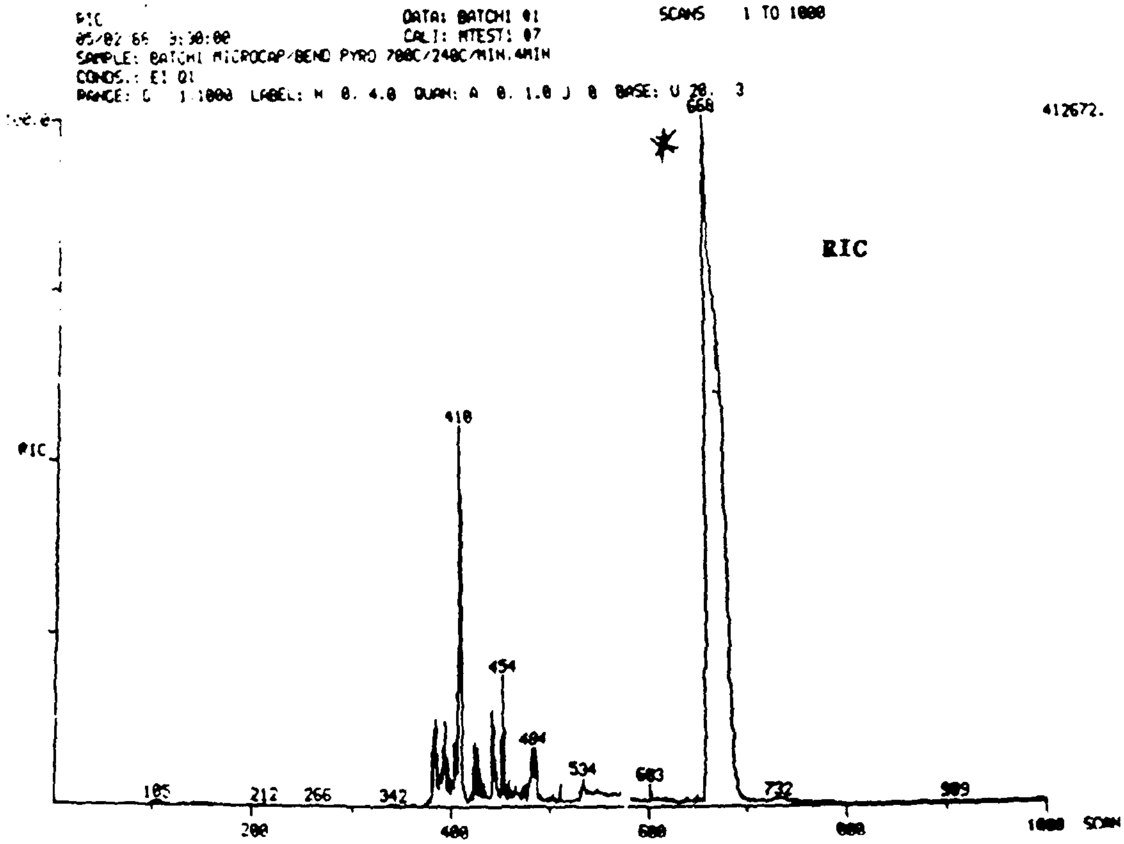
Microcap #1 RIC 180°C/min to 600°C (Scanset #662) **Figure 30(a)**



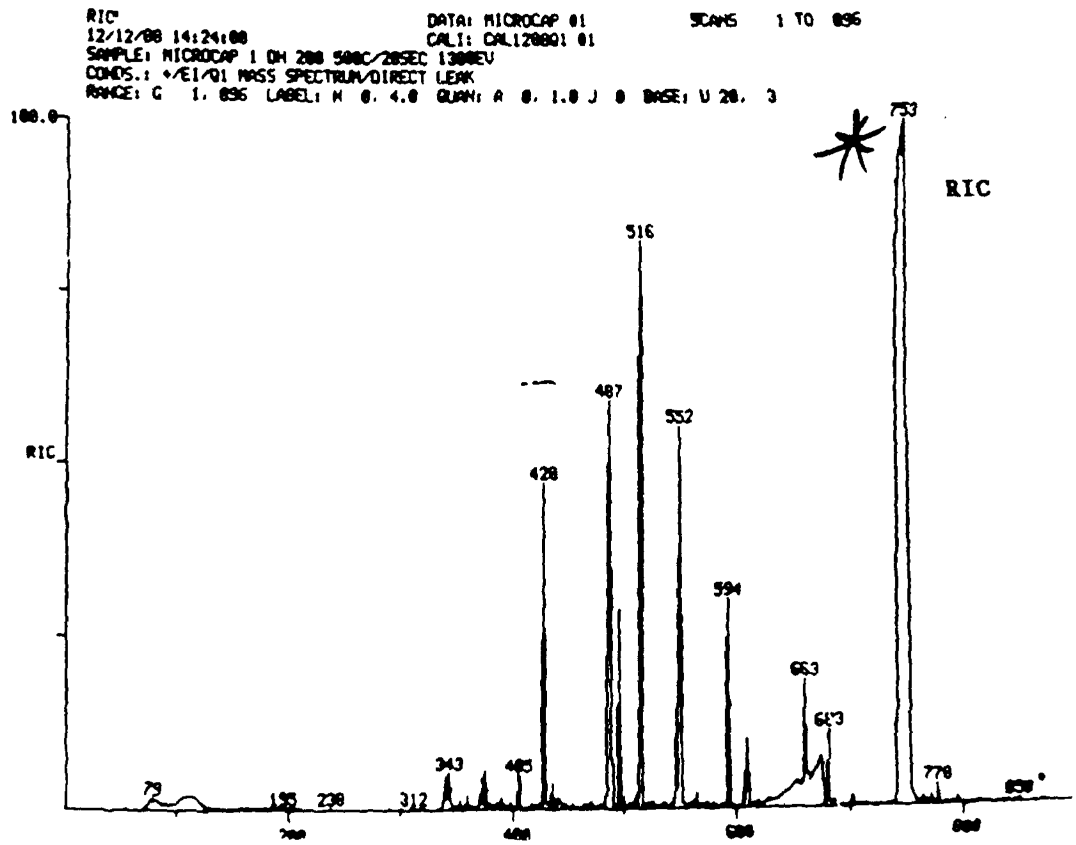
EI-MS of Scanset #662 - Diazinon core **Figure 30(b)**



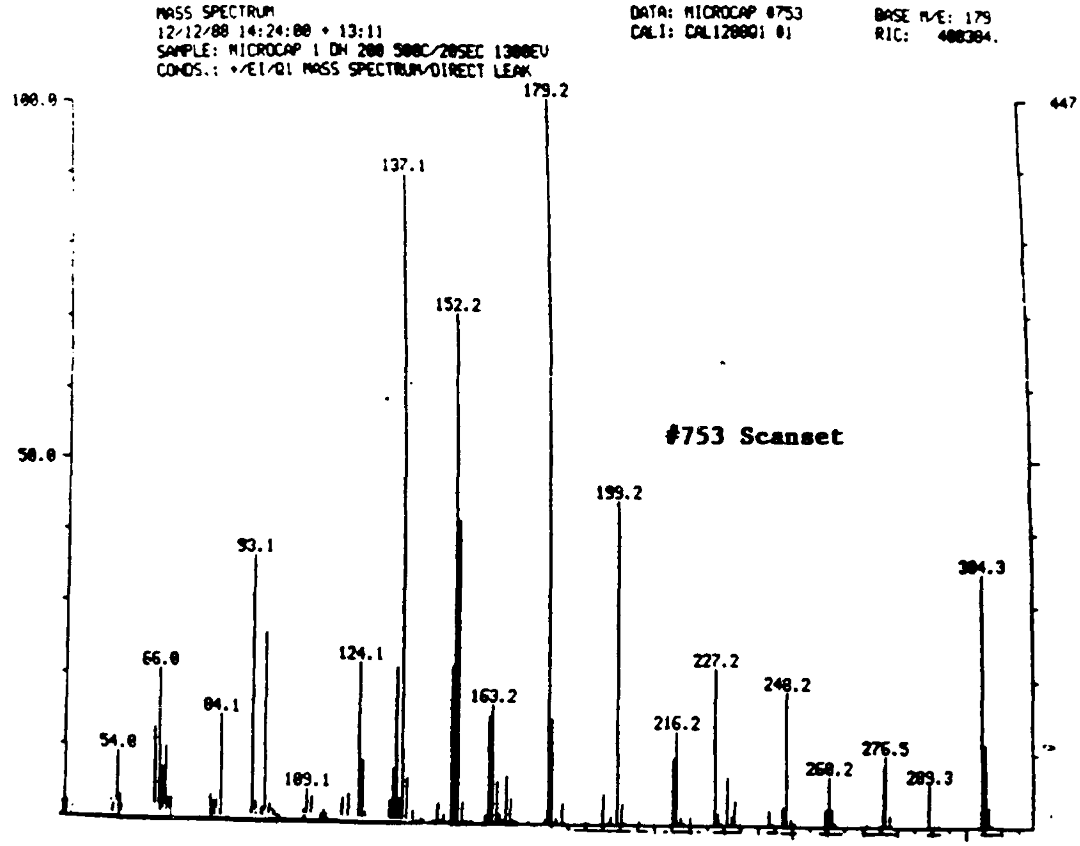
Microcap #1 RIC 240°/min to 700°C (Scanset #668) **Figure 30(c)**



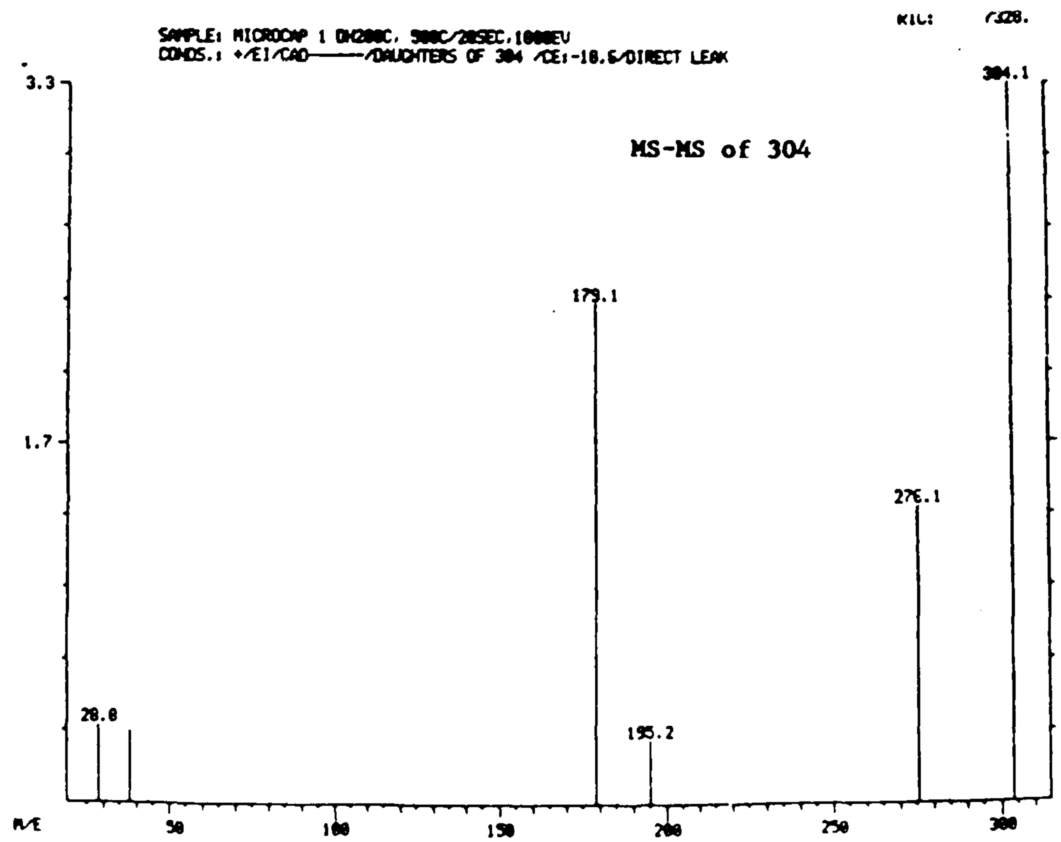
Microcap #1 RIC Pulse 500°/20 sec (Scanset #753) **Figure 31(a)**



EI-MS of Scanset #753 - Diazinon Core **Figure 31(b)**

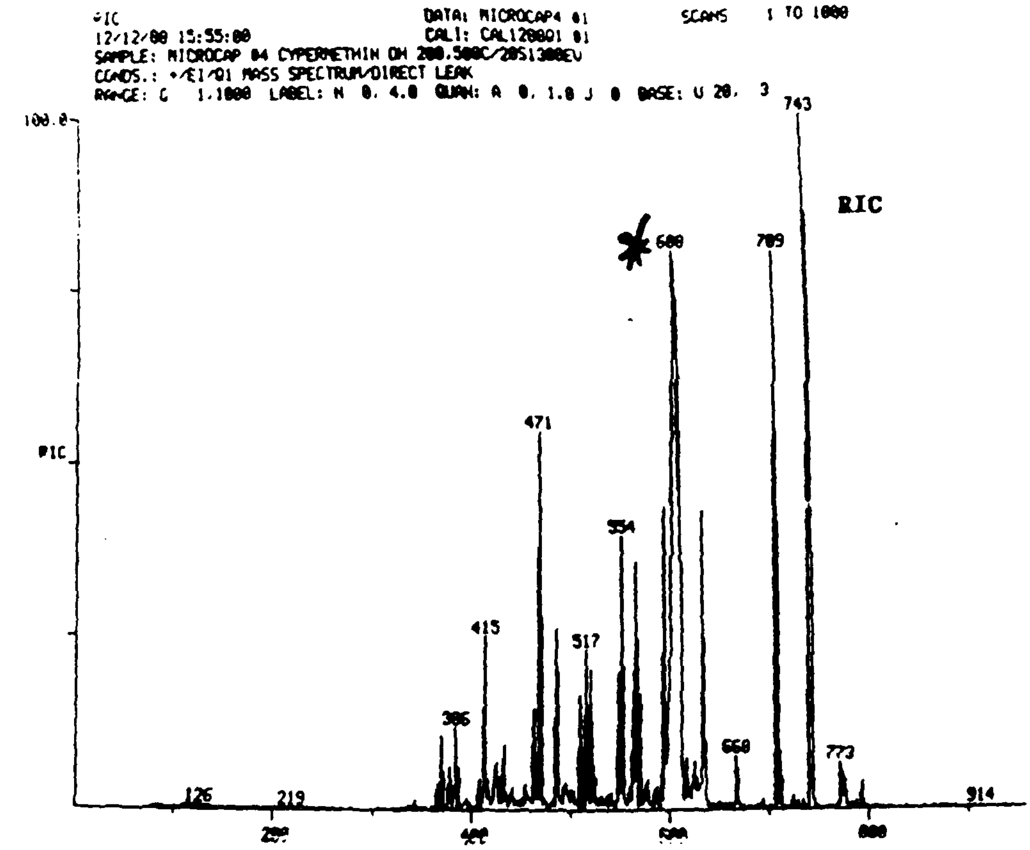


MS-MS Daughter Ions from Parent Ion of Microcap #1 Sample **Figure 31(c)**

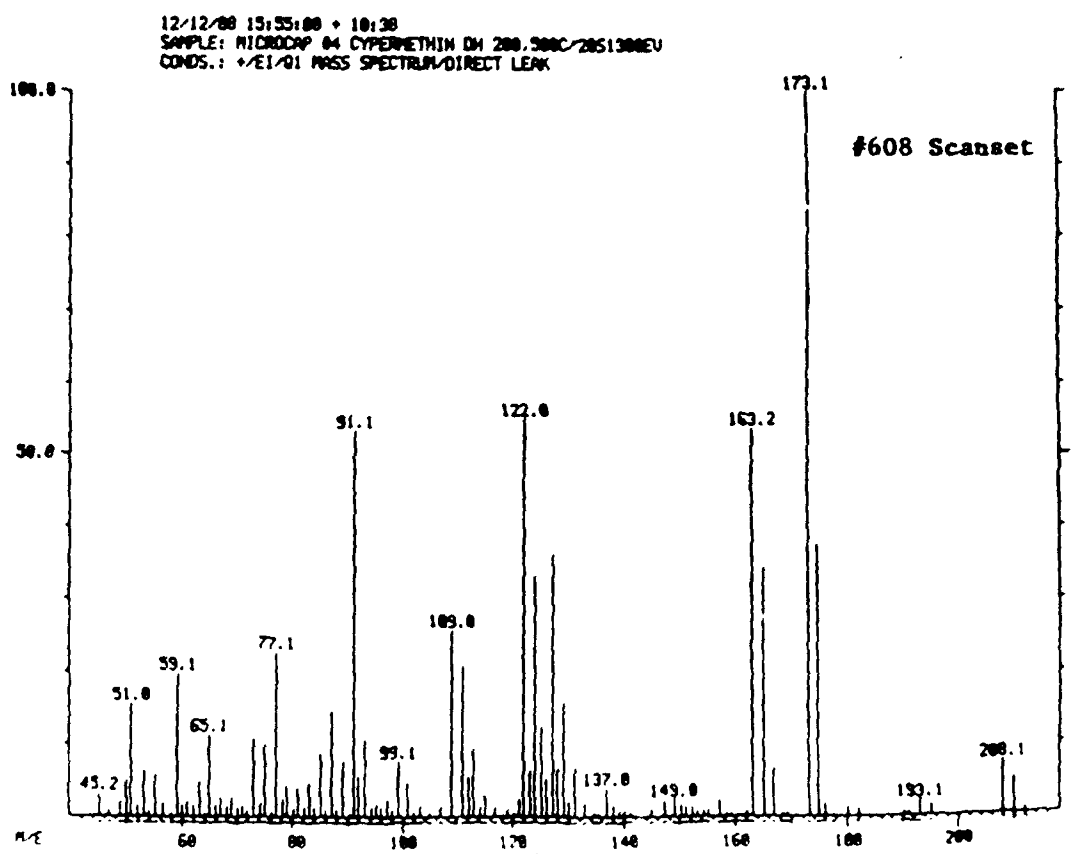


Microcap #4 - Cypermethrin Core Figure 32(a)

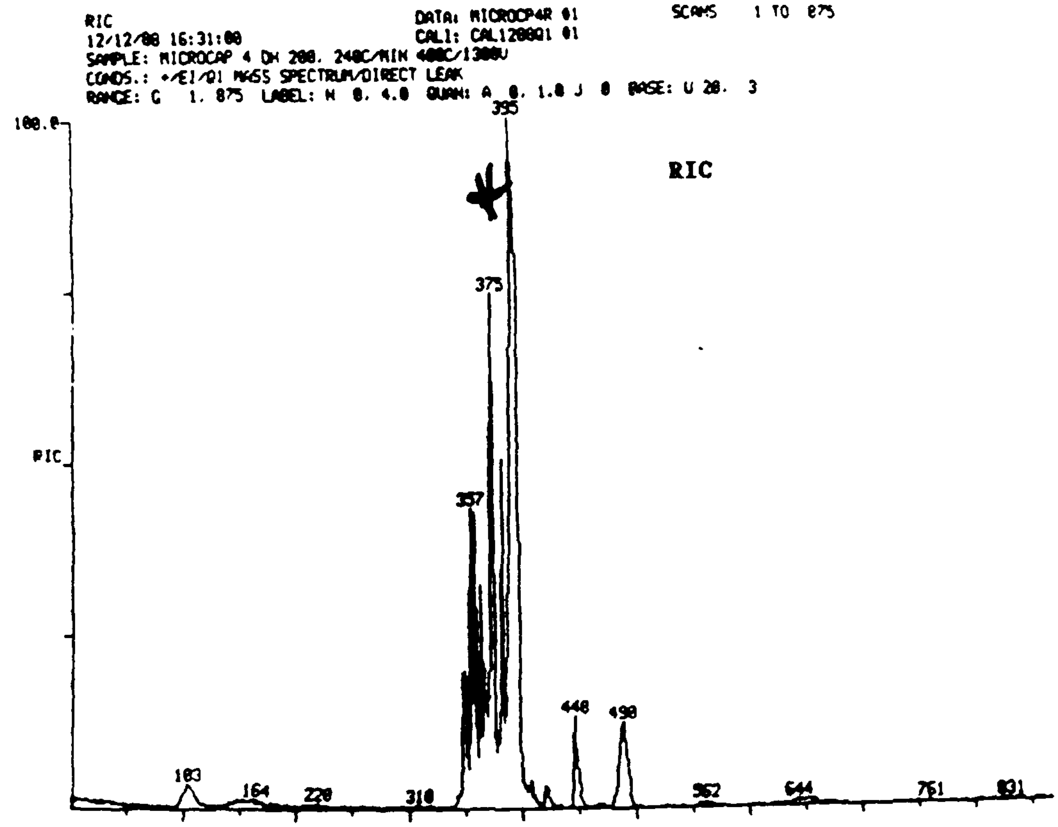
Pulse 500°/20 sec (Scanset #608)



EI-MS of Scanset #608 - Cypermethrin Core Figure 32(b)

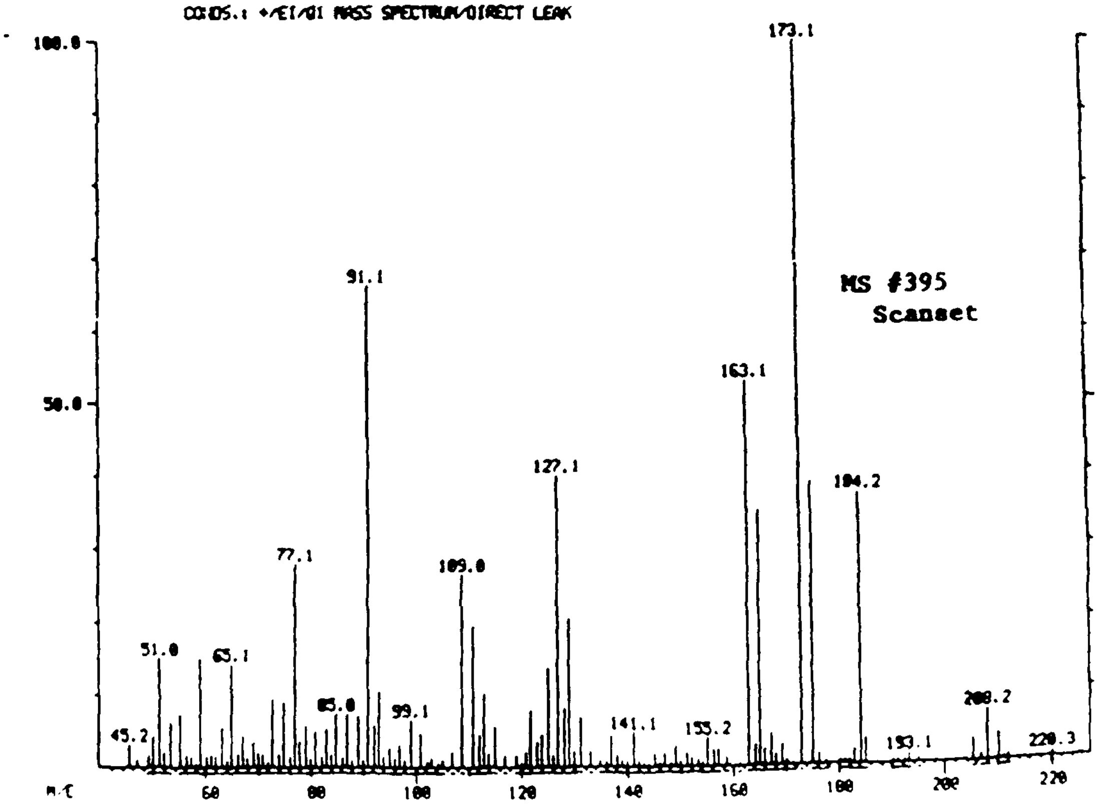


Microcap #4 (RIC) Cypermethrin Core (Scanset #395) Figure 33(a)

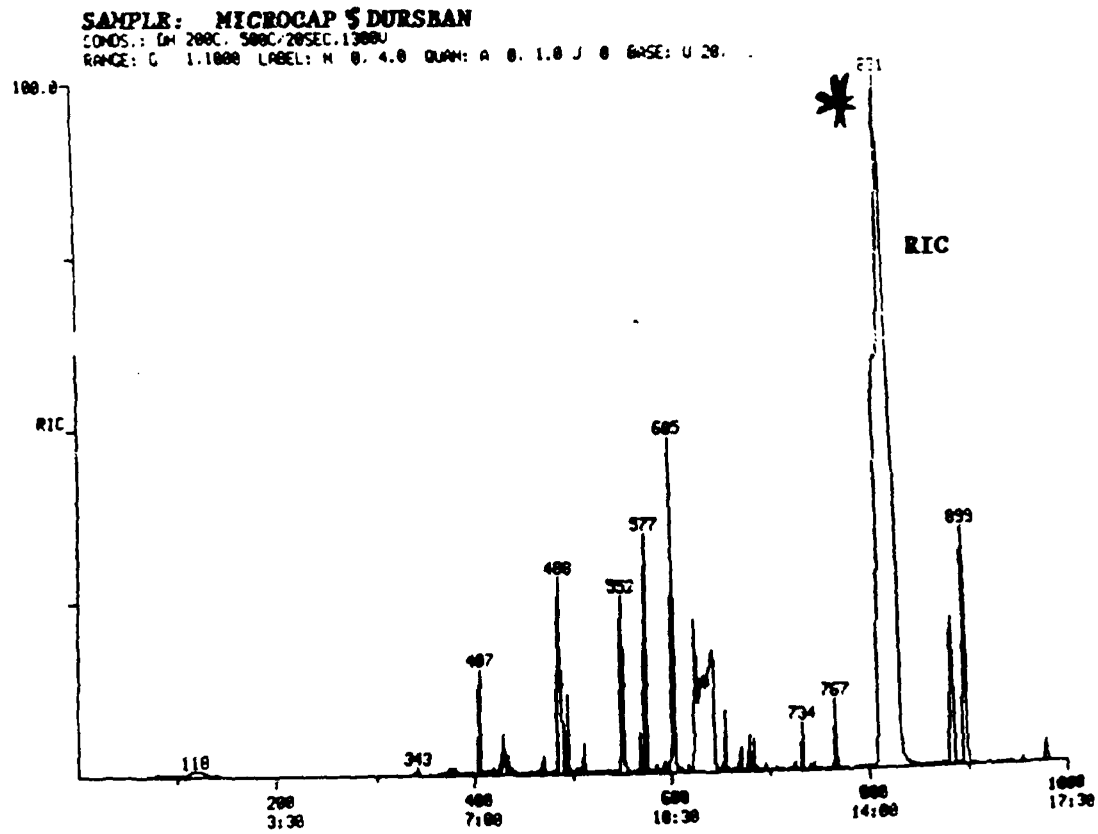


EI-MS of Scanset #395 from Microcap #4 RIC Figure 33(b)

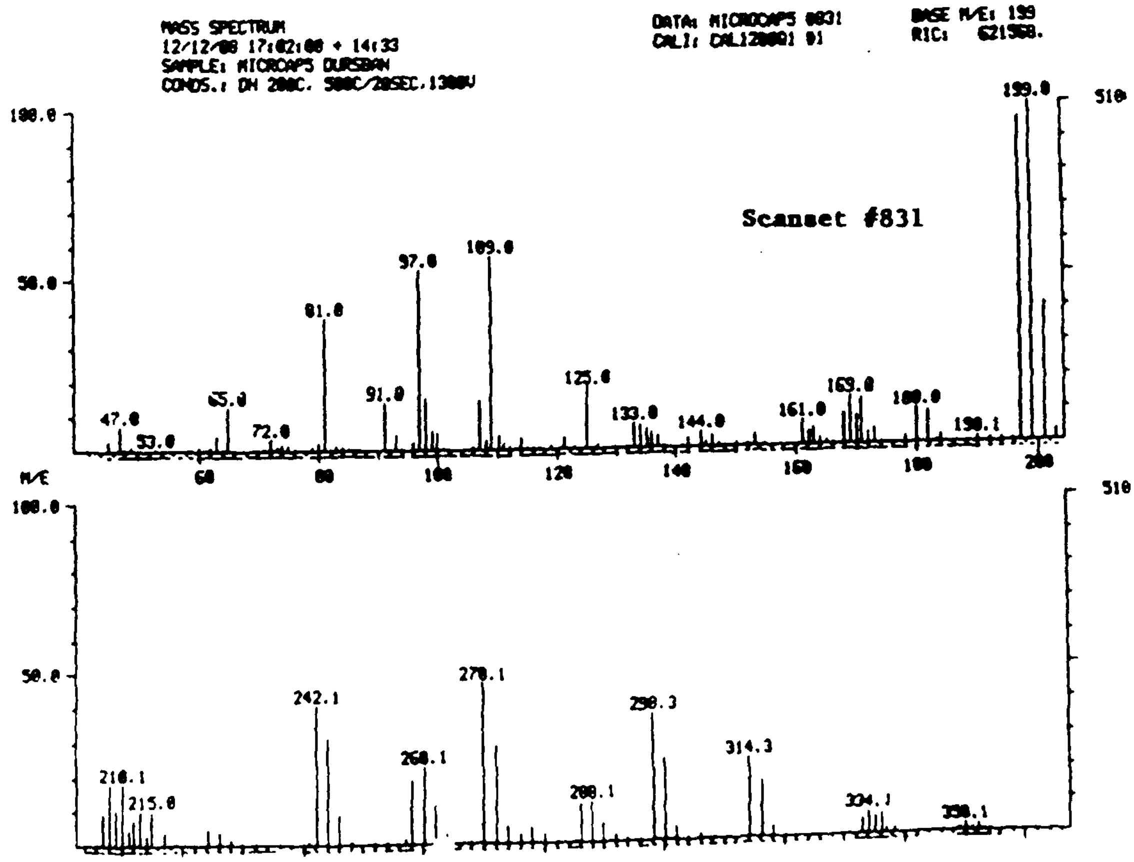
Microcap 4 DH 200, 240C/min 400C/1300U



Microcap #5 (RIC) Dursban Core (Scanset #831) Figure 34(a)

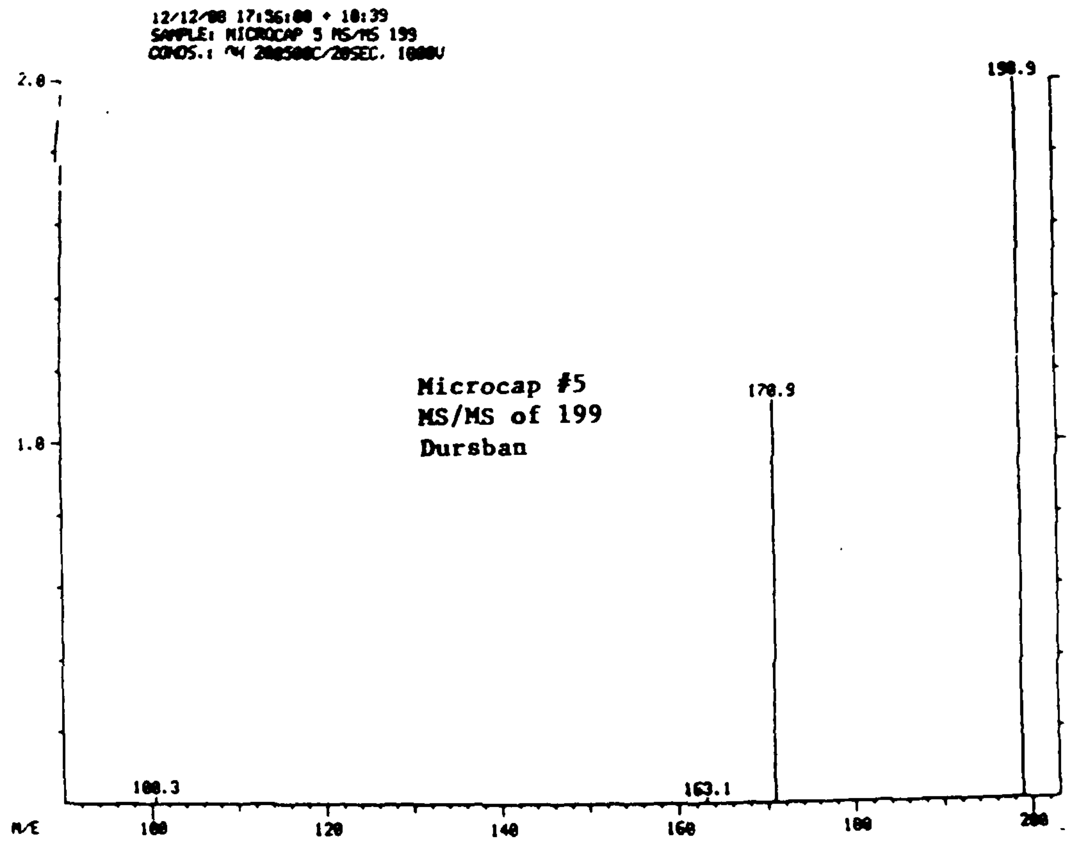


EI-MS of Scanset #831 Dursban Core Figure 34(b)

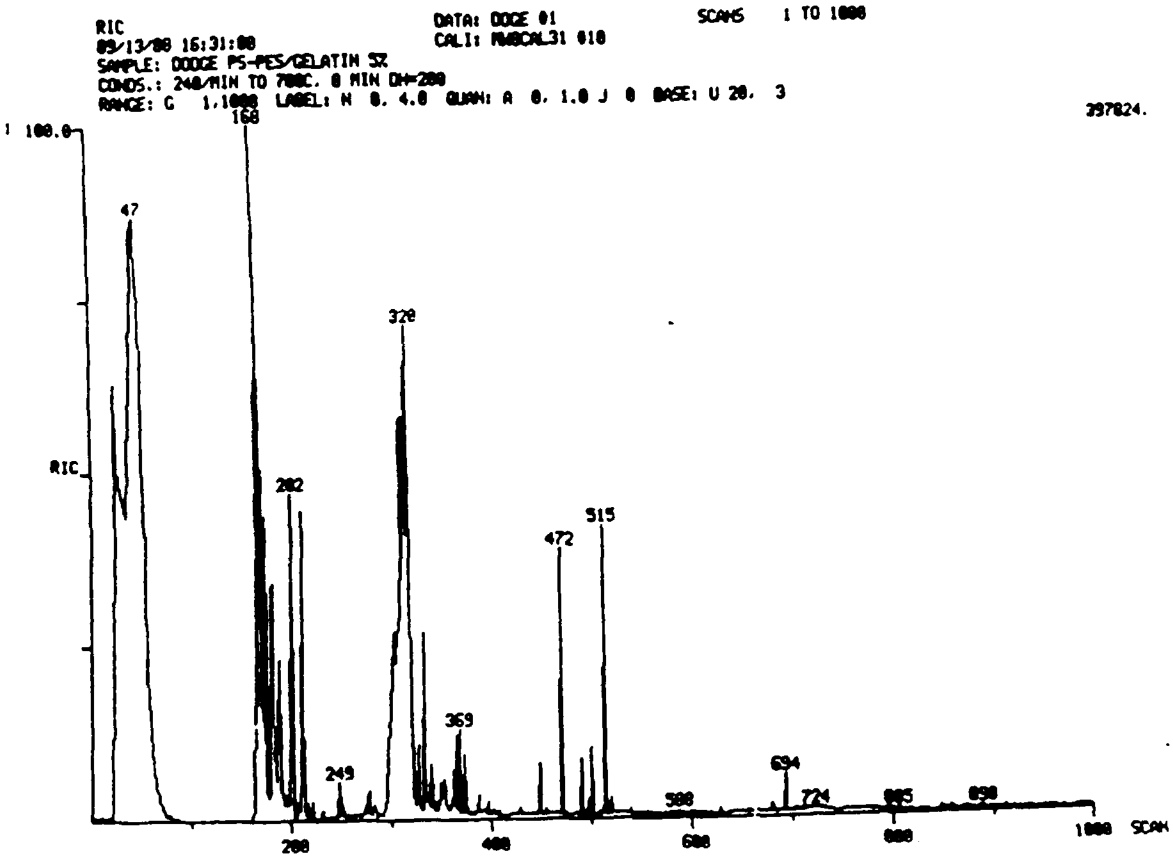


MS-MS Daughter Ions from Parent 199 *Ion*
of Microcap #5 Sample

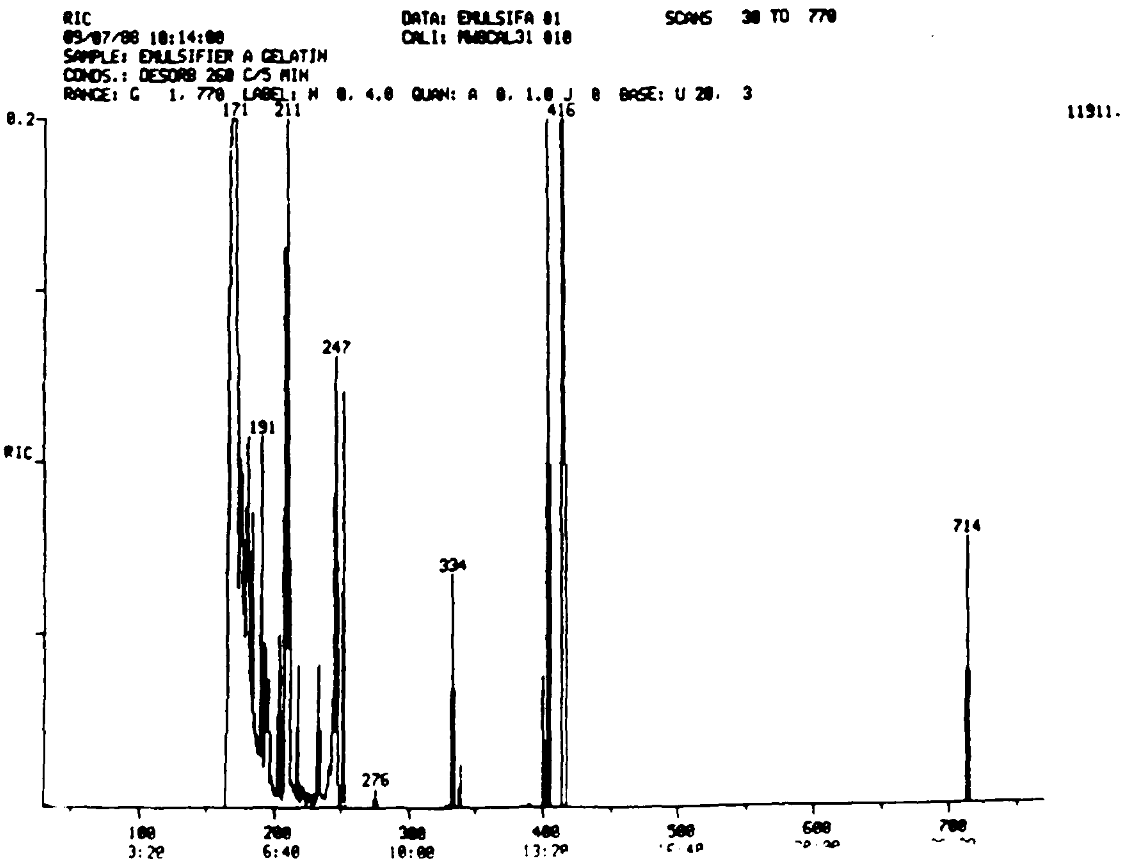
Figure 34(c)



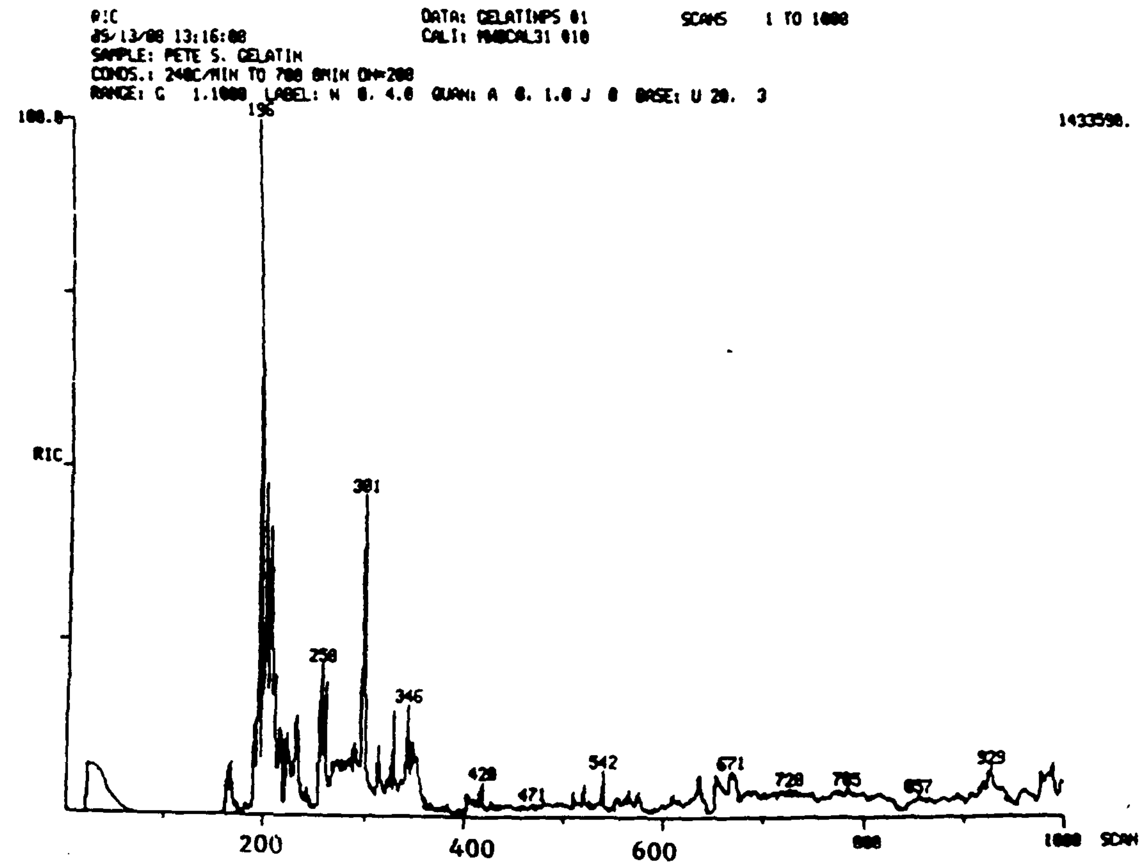
Pyrogram - RIC of Dodge Gelatin in PS-PES Shell **Figure 35(a)**



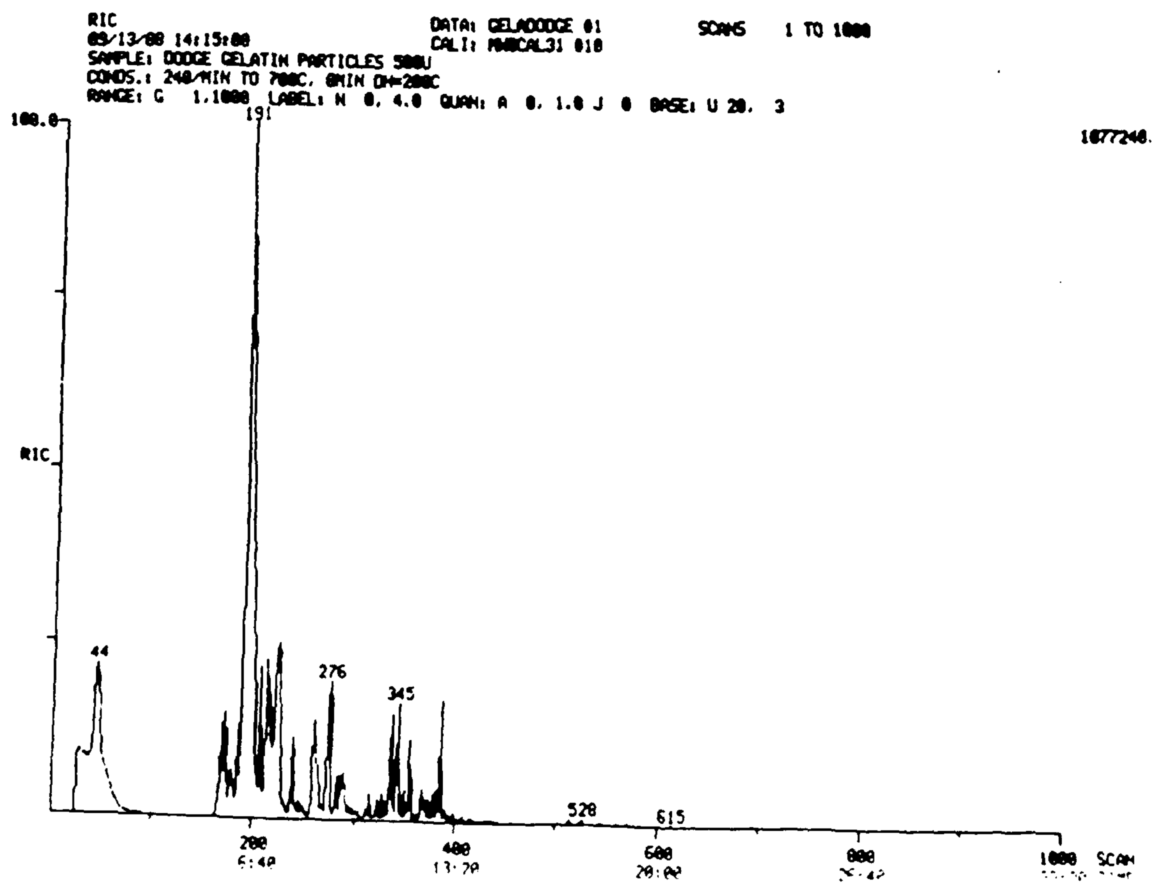
Pyrogram - RIC of Emulsifier Gelatin (Bend) **Figure 35(b)**



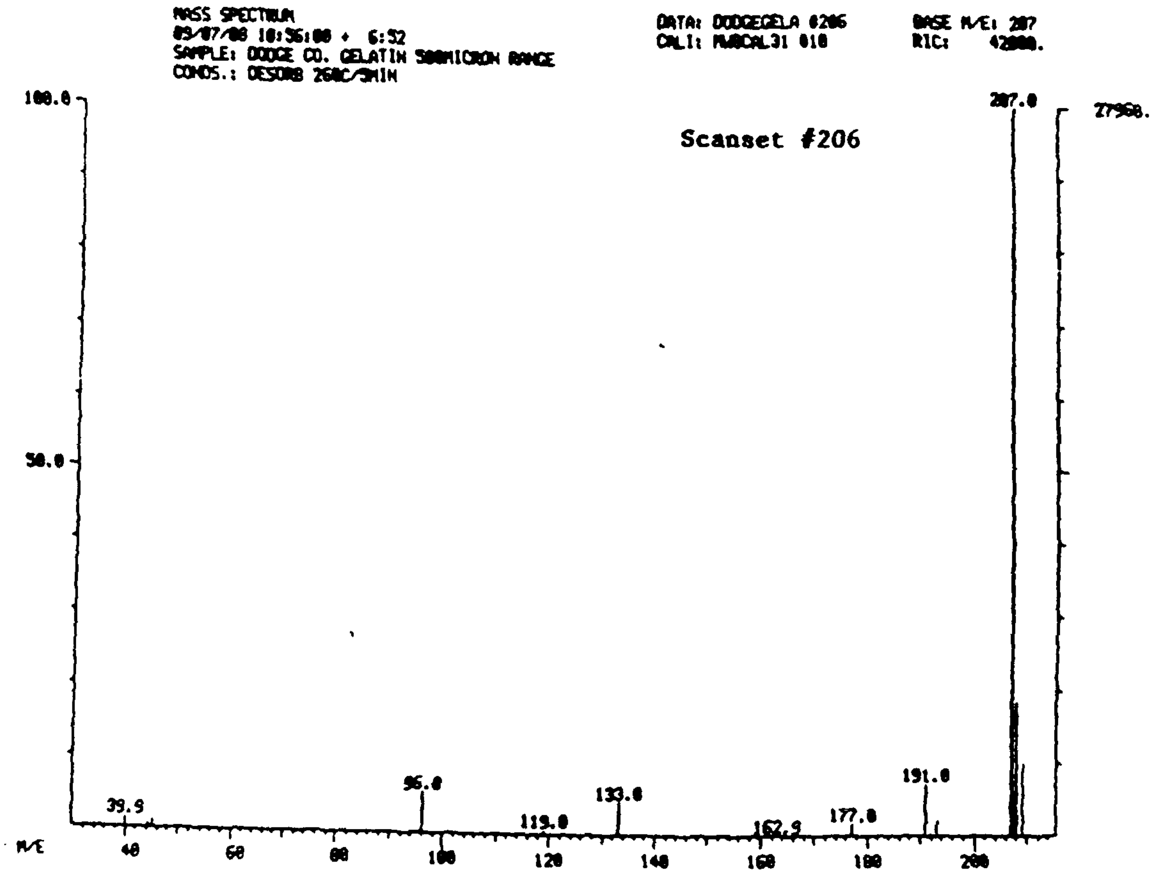
Pyrogram - RIC of Gelatin (P. Snyder) Figure 35(c)



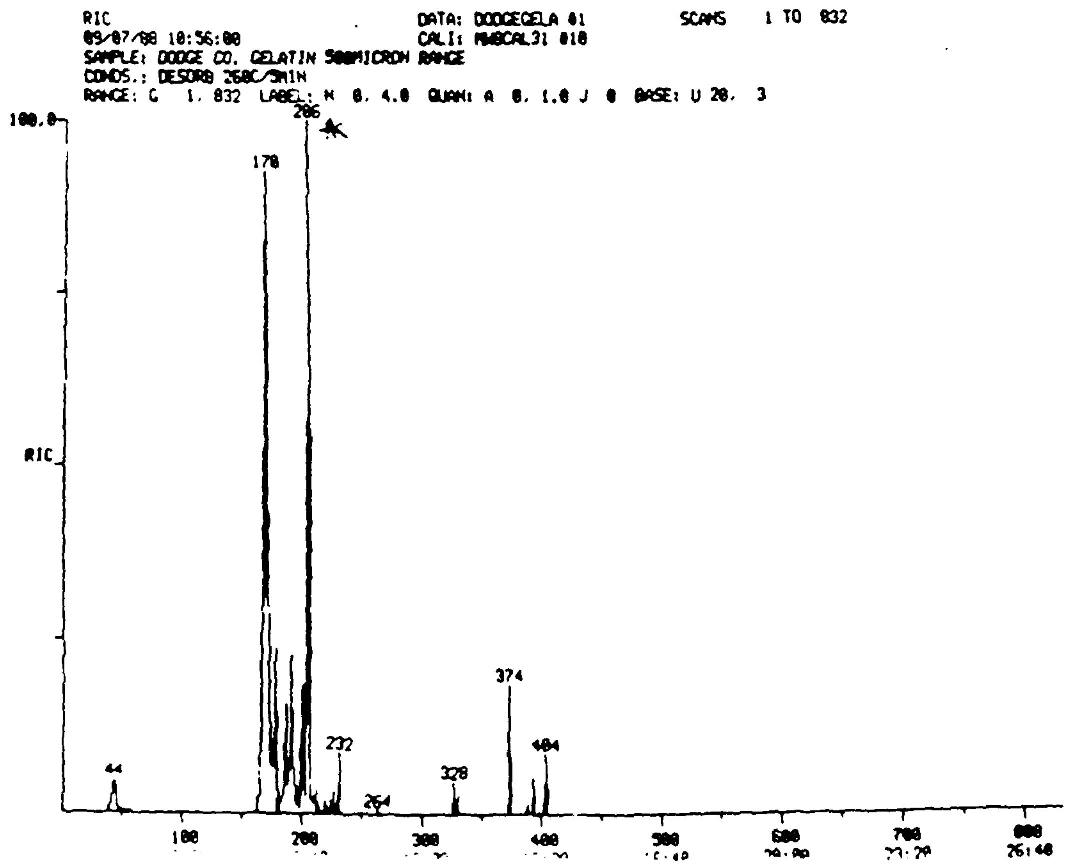
Pyrogram - RIC of Gelatin (~500 µ Particles - Dodge) Figure 35(d)



Pyrogram - RIC of Gelatin (~500 μ Particles - Dodge) Figure 35(e)
Desorb 260°C/5 min (Scanset #206)



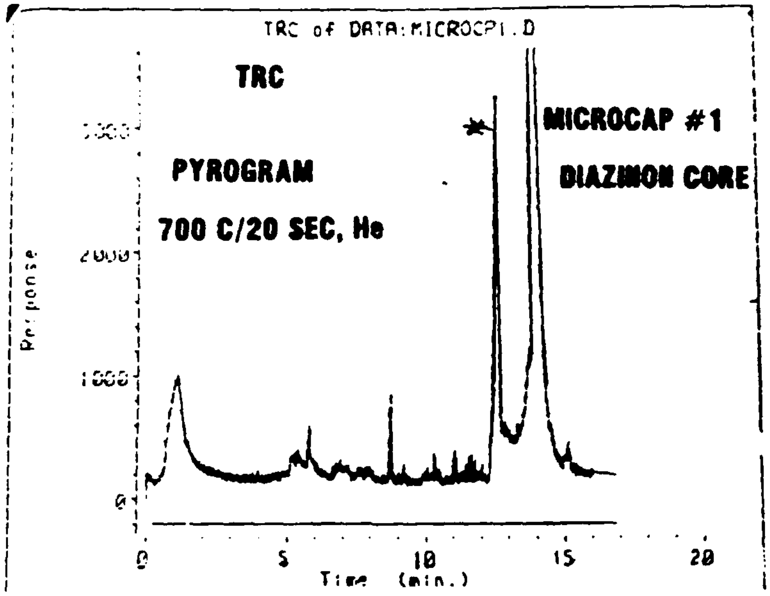
EI-MS of Scanset #206 - Gelatin Particles Figure 35(f)



PYROLYSIS GC-FTIR

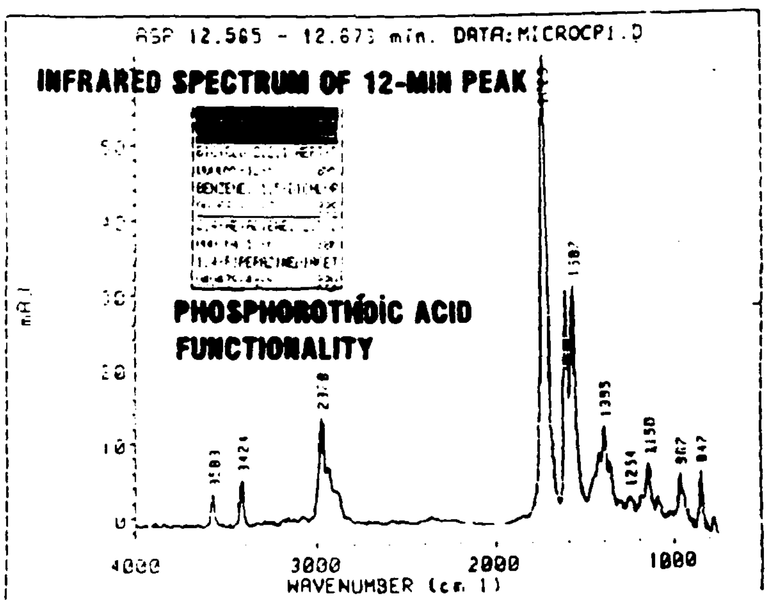
Total Response Chromatogram (TRC)
Microcap #1 (Diazinon Core)

Figure 36(a)



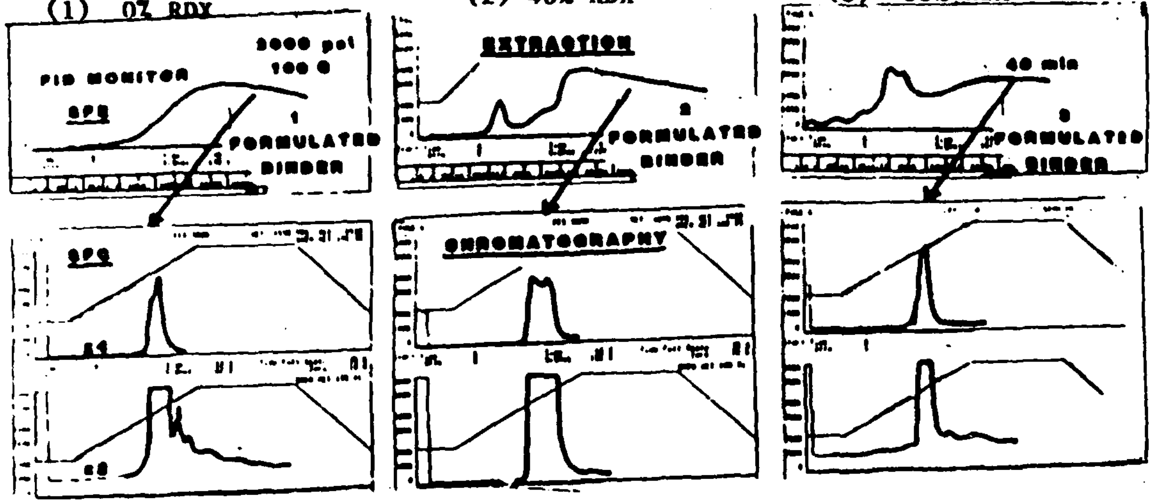
FTIR of ~ 12.5 min Peak with Library Match to Phosphorothioic Derivatives

Figure 36(b)



SFE-SFC of Propellant Formulations   Figure 37

(1) 0% RDX   (2) 40% RDX   (3) 80% RDX



SFE-SFC of Microcap #1, SFE-SFC Two Samples from Same Batch
Figure 38

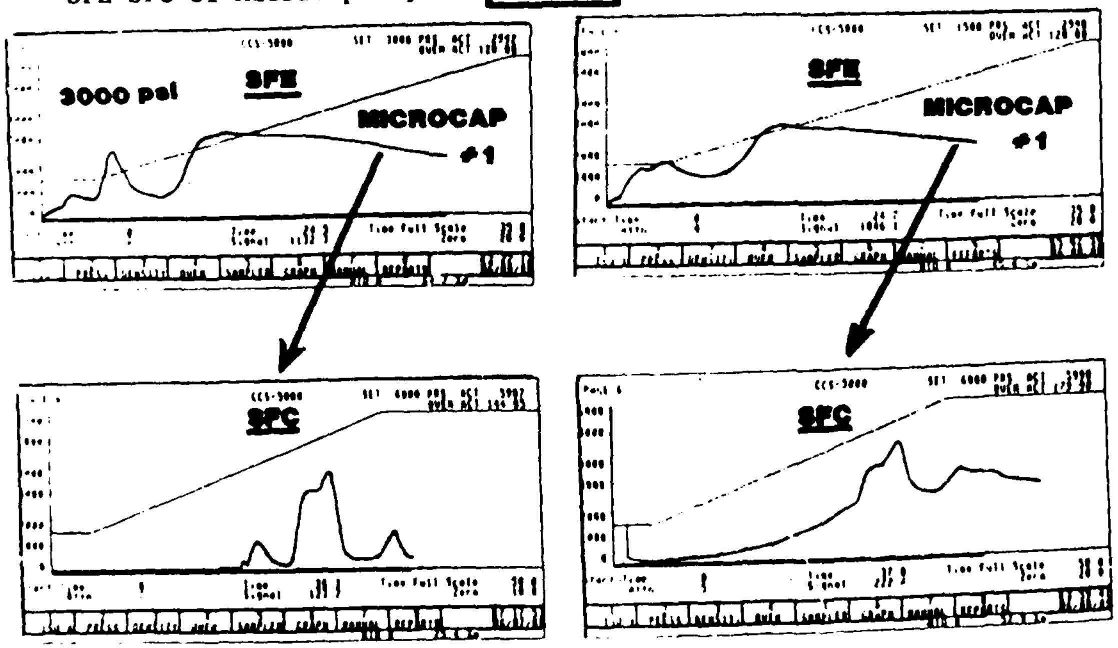


Figure 39(a)
SFE METHOD DEVELOPMENT
BOX-BENHKEN EXPERIMENTAL DESIGN

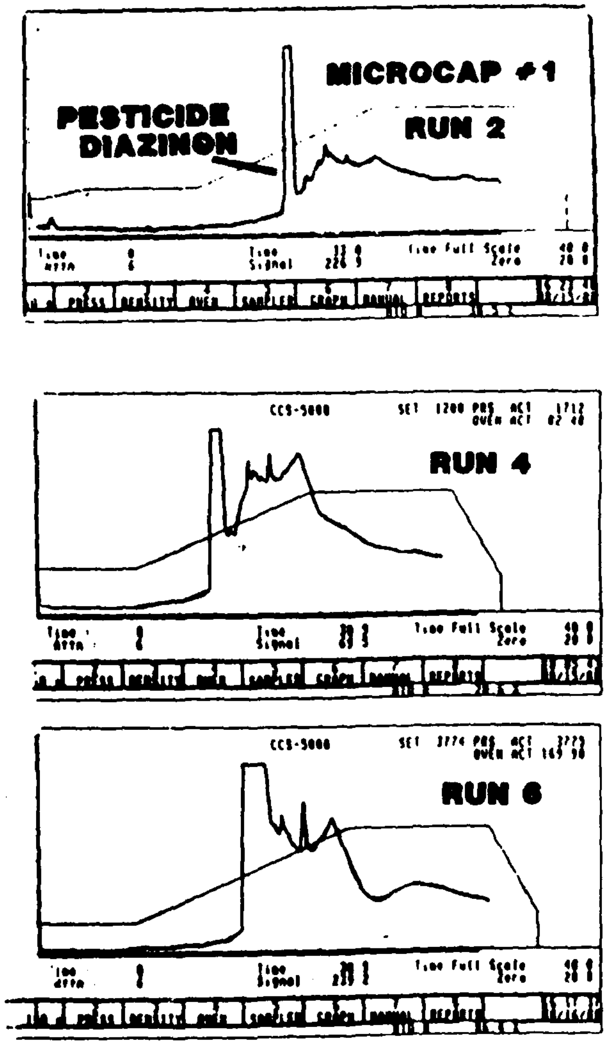


Figure 39(b)

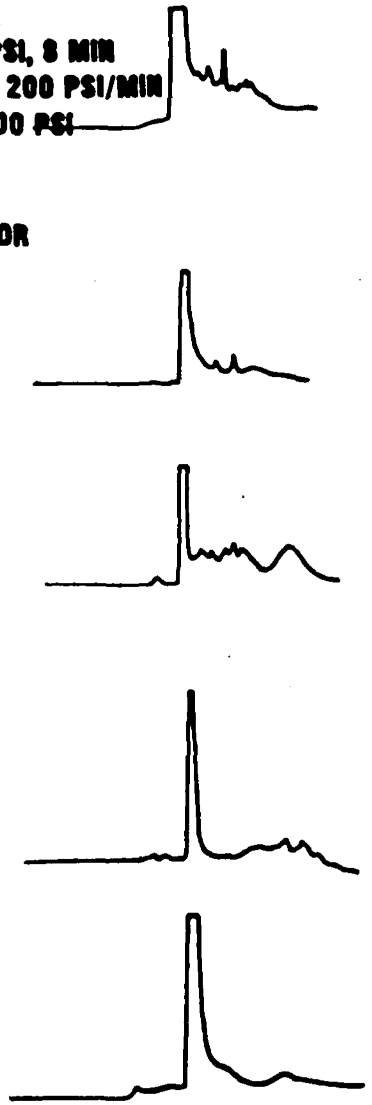
SFE PROFILES FOR MICROENCAPSULATED PESTICIDES

BEND RESEARCH, INC.
BEND, OREGON

SFE

1200 PSI, 8 MIN
100°C, 200 PSI/MIN
TO 4000 PSI

FID
MONITOR



(1) POLYMER SHELL A
DIAZINON CORE

(2) POLYMER SHELL B
DIAZINON CORE

(3) POLYMER SHELL C
DIAZINON CORE

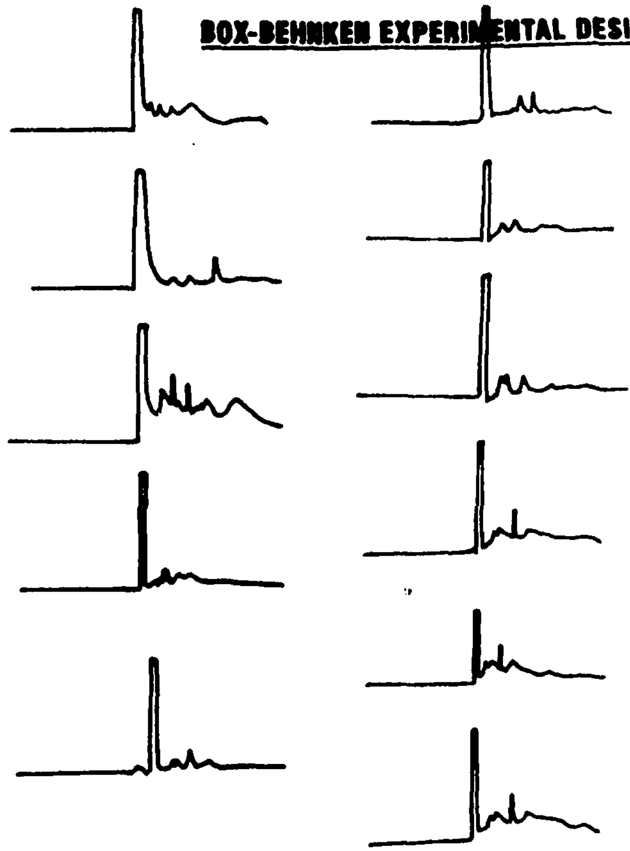
(4) POLYMER SHELL B
CYPERMETHRIN

(5) POLYMER SHELL A
DURSBAN

Figure 39(c)

SFE PROFILES FOR MICROCAP #1

BOX-BEHNKEN EXPERIMENTAL DESIGN



FID
MONITOR

Figure 39(d)

SFE PROFILES MICROCAP #2

BOX-BEHNKEN EXPERIMENTAL DESIGN

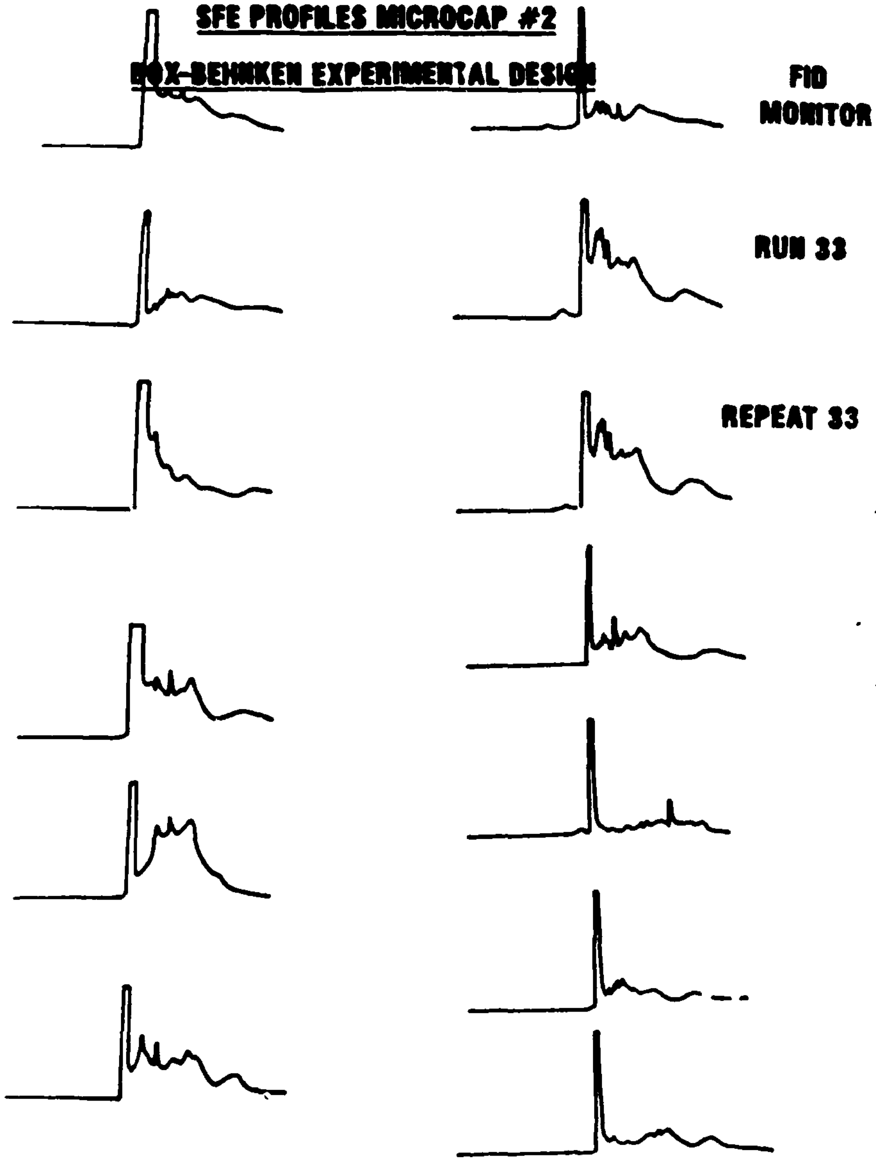
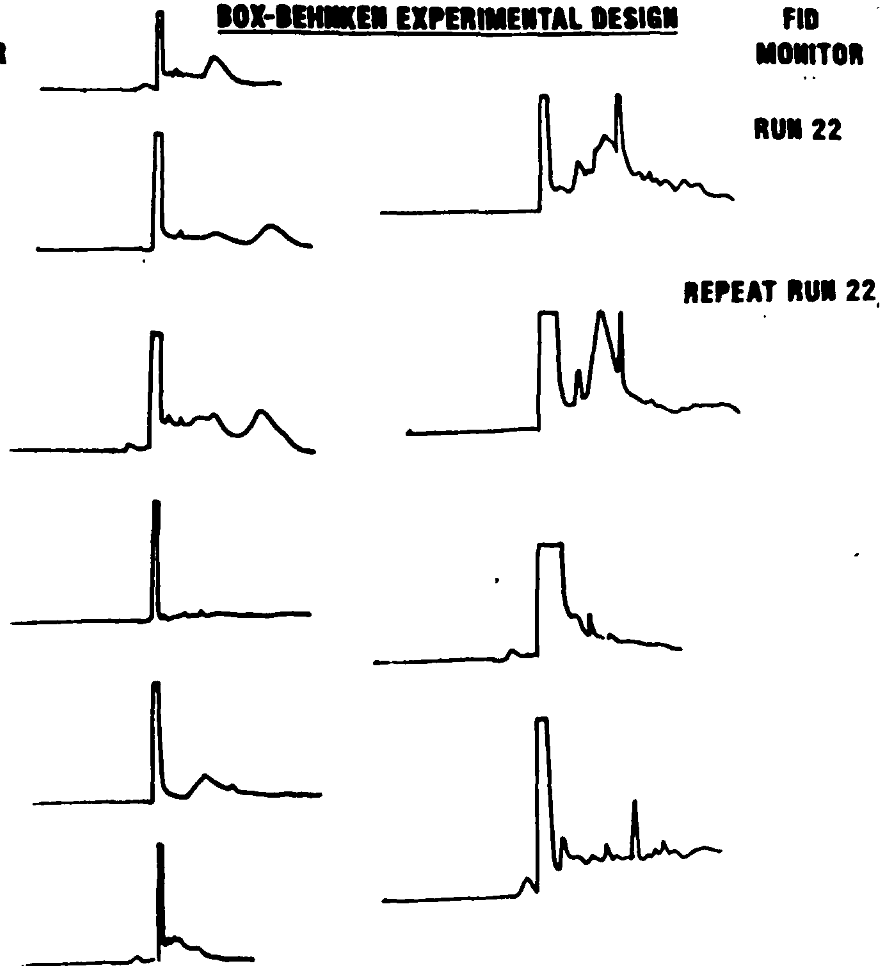


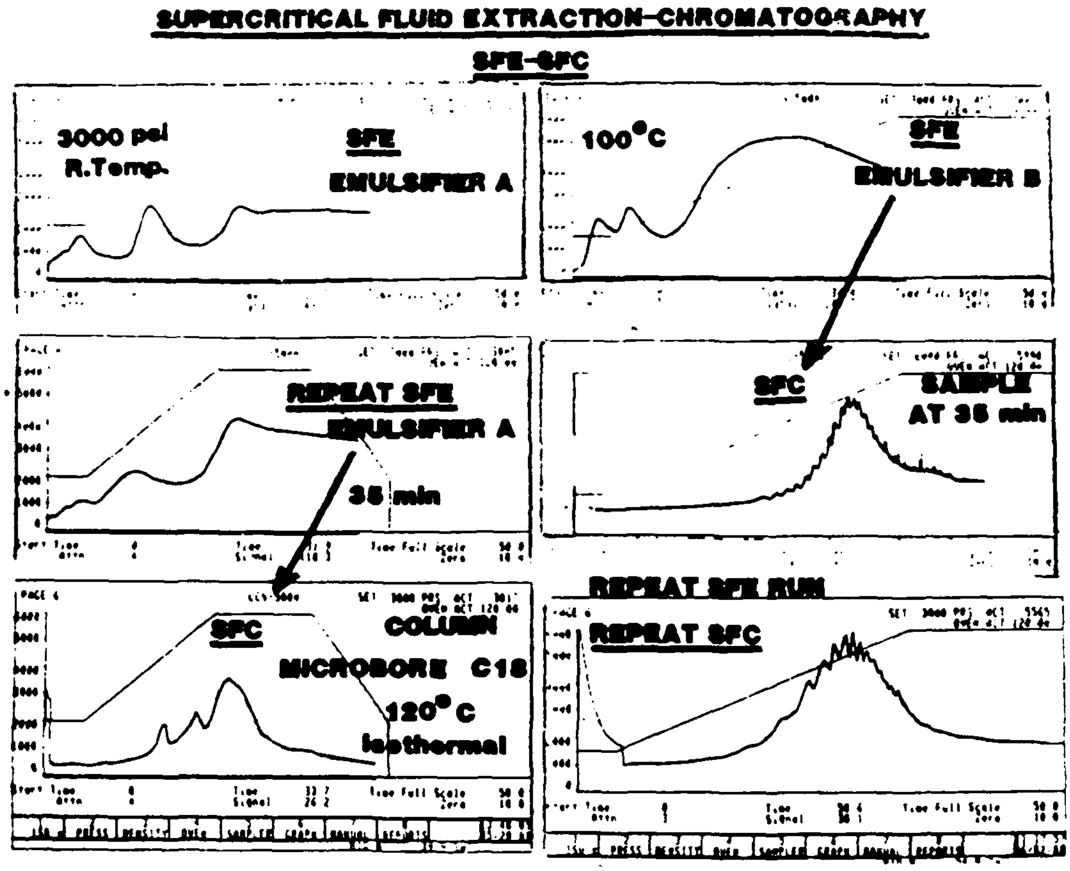
Figure 39(e)

SFE PROFILES FOR MICROCAP #3

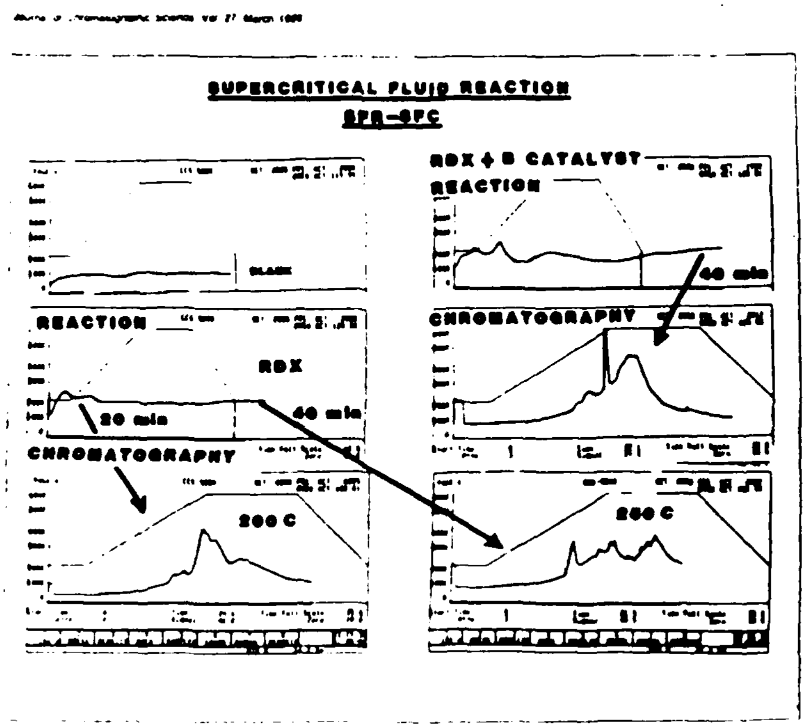
BOX-BEHNKEN EXPERIMENTAL DESIGN



SFE-SFC of Emulsifiers A and B Figure 40

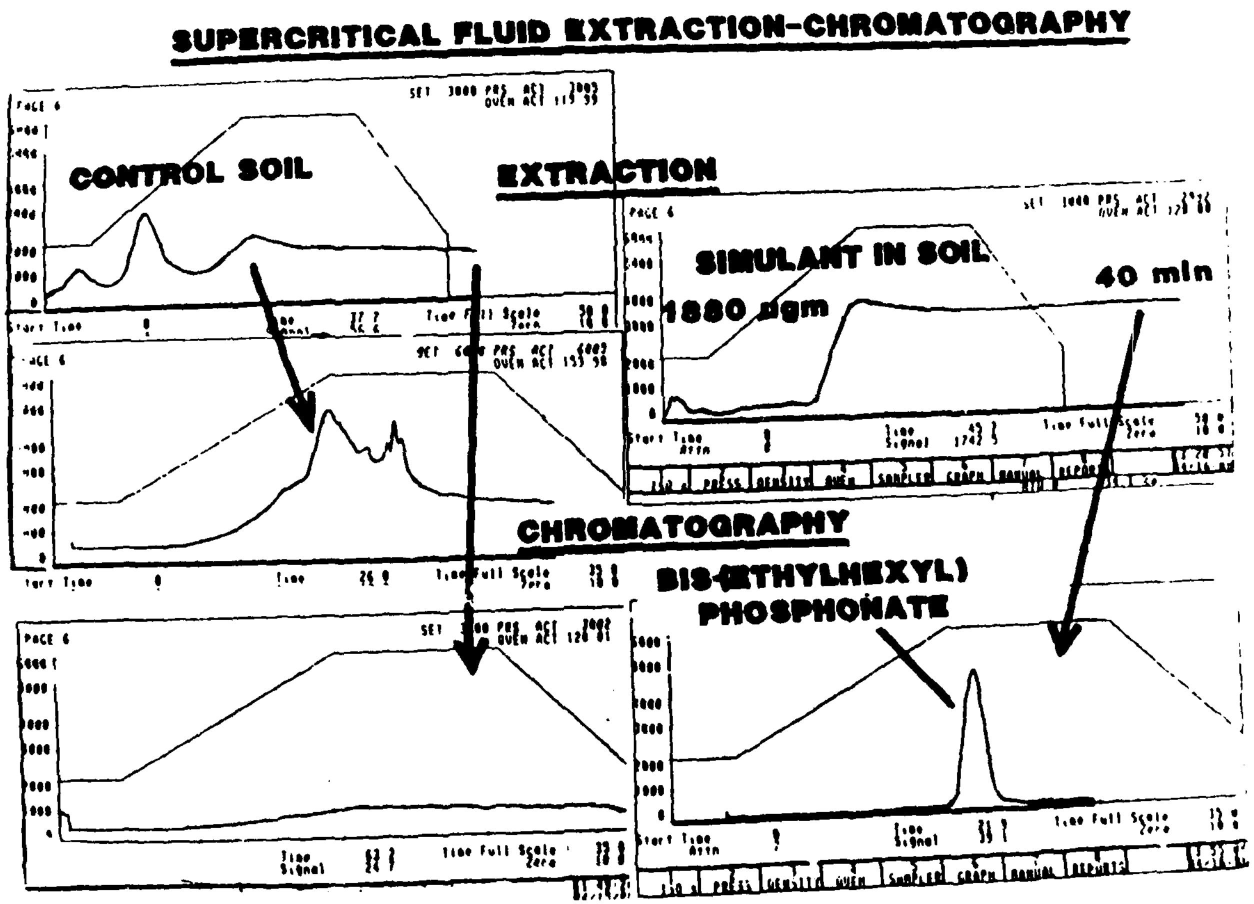


SFR-SFC of RDX and RDX and Catalyst Figure 41

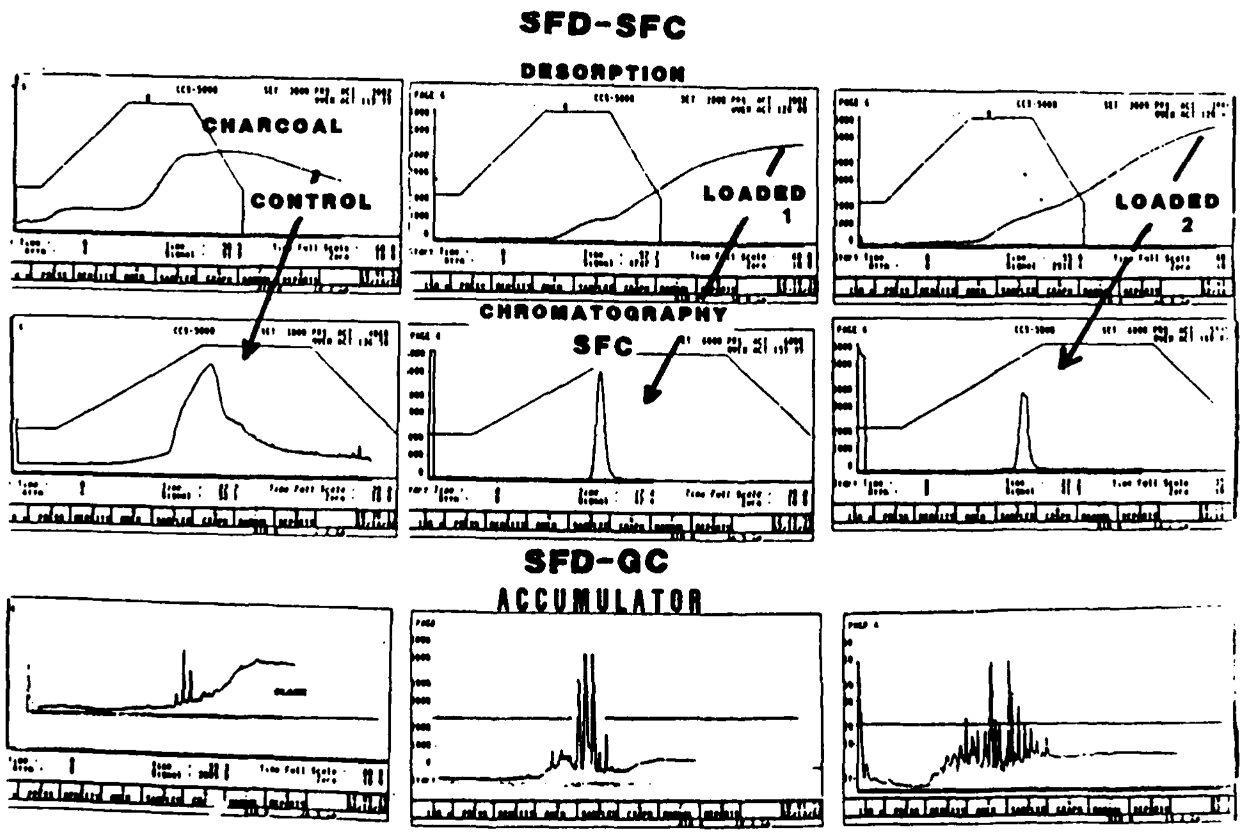


SFD (SFE) - SFC of Simulant in Soil

Figure 42(a)



SFD-SFC and Capillary GC of Charcoals from Air Sampling Figure 42(b)



Conclusions of SF Technology Study for Microencapsulated Materials — Figure 42(c)

CONCLUSIONS

- PESTICIDE CORES (DIAZINON, CYPERMETHRIN, DURSBAN) ARE READILY EXTRACTED FROM FORMULATED MICROCAPSULES HAVING THREE DIFFERENT POLYMER SHELLS OVER A SELECTED SFE RANGE OF PRESSURE (DENSITY), TEMPERATURE, AND TIME.

- SURFACTANT/EMULSIFIER ADDITIVES ARE MORE SENSITIVE TO SFE CONDITIONS. QUALITATIVE AND QUANTITATIVE ANALYSES FOR FULLY FORMULATED PRODUCTS (SHELL, CORE, ADDITIVES) REQUIRE FURTHER METHOD DEVELOPMENT USING SFE/ACCUMULATOR-SFC AND CAPILLARY GC AUTOMATED/INTERFACED INSTRUMENTATION.

- BOX-BEHNKEN EXPERIMENTAL DESIGN HAS BEEN EXTENDED TO INCLUDE A MULTIVARIATE RESPONSE (FACTOR ANALYSIS) FOR COMPLEX CHROMATOGRAPHIC/SPECTRAL PATTERN EVALUATIONS.

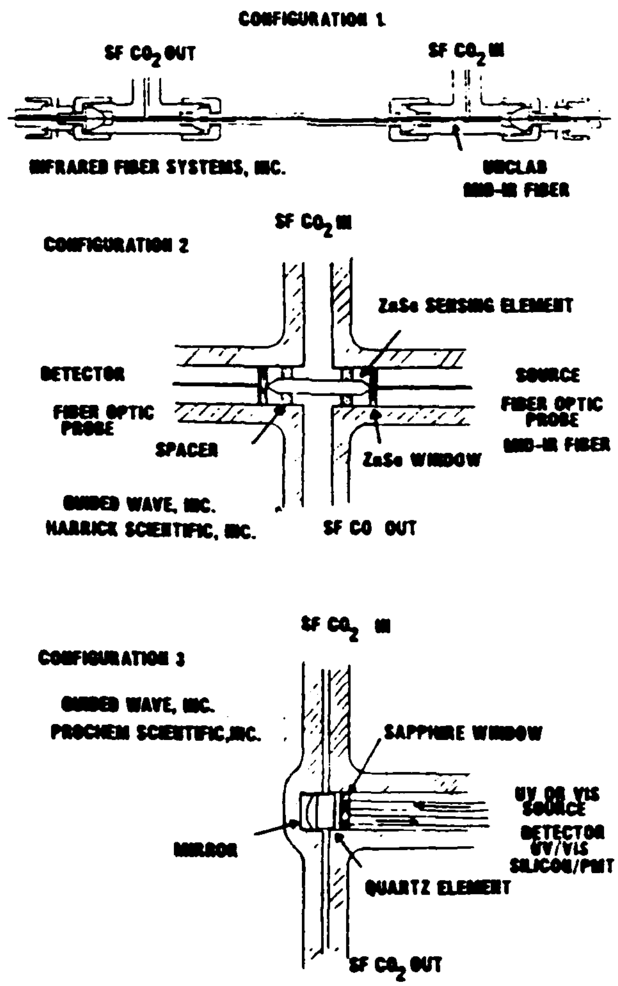
- SFE PROFILES PROVIDE IMPORTANT COMPOSITIONAL INFORMATION FOR PROCESS AND QC/QA OPERATIONS USED IN THE AGRICULTURAL, FOOD, BIOMEDICAL, AND CONSUMER PRODUCT INDUSTRIES IN DEVELOPMENT OF CONTROLLED-RELEASE MATERIALS.

REMOTE SPECTROSCOPY Figure 43

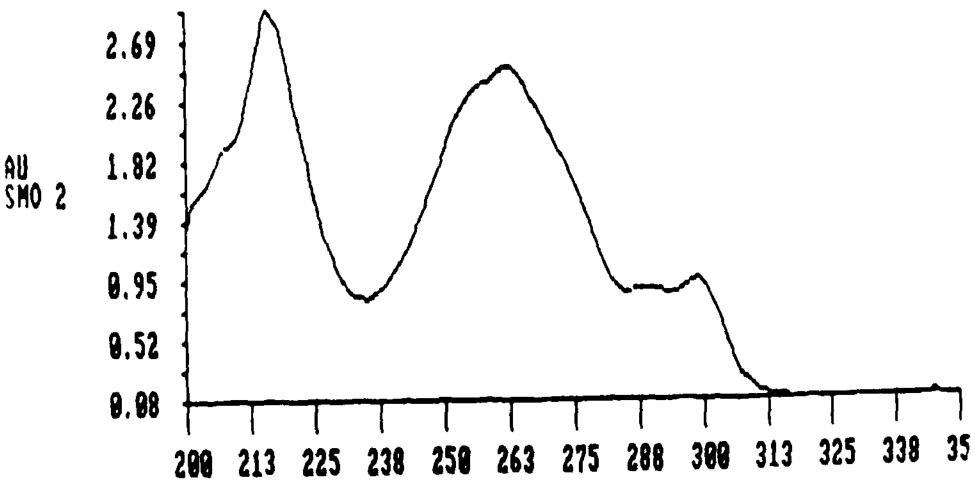
FIBER OPTIC MONITOR (FOM) PROTOTYPES

FOR CCS MODEL 5000 SFC/GC

SUPERCRITICAL FLUID EXTRACTOR/ACCUMULATOR MODULE

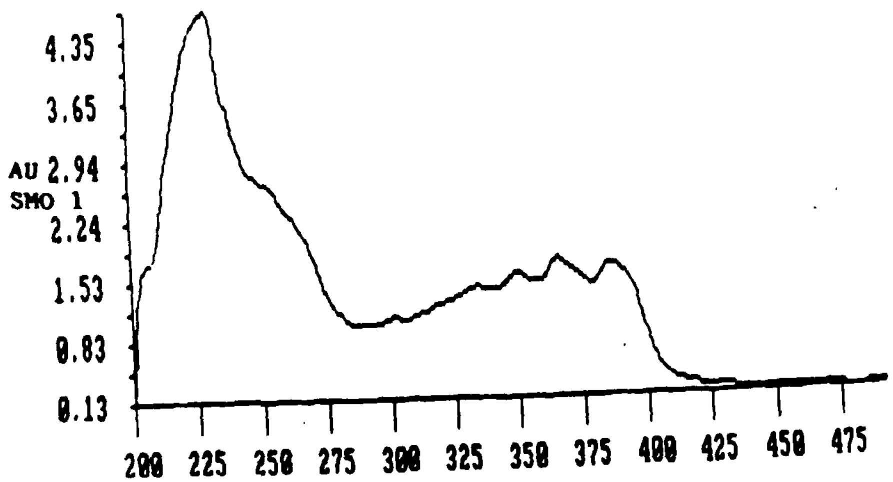


TRACE AROMATICS - CONFIGURATION 2 Figure 44(a)



TRACE TOLUENE, METHYL NAPHTHALENE.
ADDED FLUORENE, (QUARTZ/CROSS UNION)

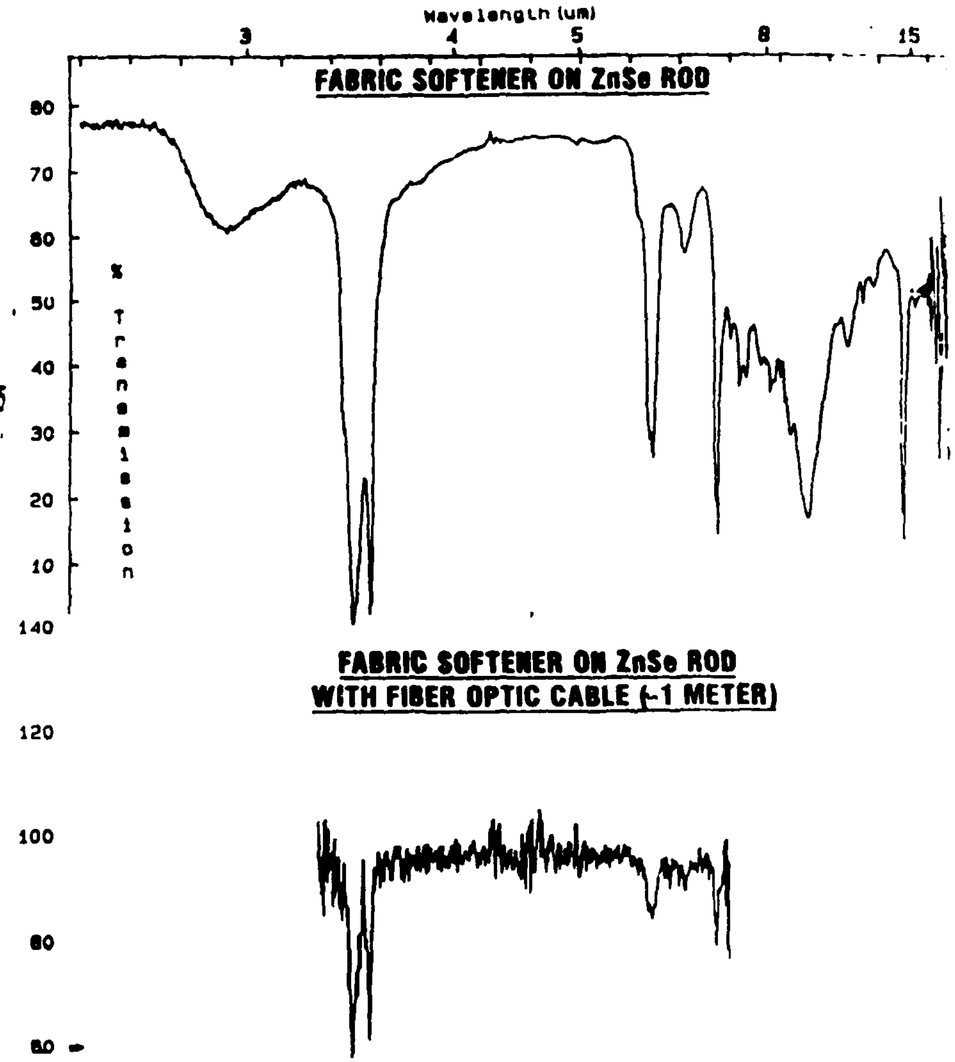
TRACE AROMATICS - CONFIGURATION 2 Figure 44(b)



RE-LIM:1 MENU:2 SMOOTH:3 POINTS:4 COMMENT:5
SHIFT:6 ?

TRACE TOLUENE, FLUORENE, ANTHRACENE ADDED

Mid-Infrared FOM Prototype in Configuration 2
(Modified) for Fabric Softener on ZnSe Rod
and Fiber Optic Cable Figure 45



SUMMARY

Figure 46

Remote Spectroscopy and FOM Applications

- o ADVANTAGES OF REMOTE SPECTROSCOPY ARE EXTENDED TO SUPERCRITICAL FLUID EXTRACTION WITH THREE FOM PROTOTYPES IN UV-VIS-NIR AND MID-IR REGIONS
- o VIS-FOM DEMONSTRATED WITH CCS MODEL 5000 SFC/GC WITH SFE MODULE FOR ELUENTS AT HIGH CONCENTRATIONS
- o UV-FOM DEMONSTRATED WITH SFE/ACCUMULATOR MODULE FOR AROMATICS AT LOW CONCENTRATIONS WITH QUARTZ ELEMENTS
- o MID-IR FORM PROTOTYPES DEMONSTRATED WITH SFE/ACCUMULATOR MODULE FOR POLYOL SURFACTANTS WITH ZnSe ELEMENTS AND CHALCOGENIDE FIBERS/CABLES/PROBES

CONCLUSIONS

- o FOM APPLICATIONS TO SFE TECHNOLOGY PERMIT ON-LINE NON-DESTRUCTIVE ANALYSES TO SUPPLEMENT FID PROFILES WITH SELECTIVE DETECTION/IDENTIFICATION UNITS IN AUTOMATED SUPERCRITICAL FLUID INSTRUMENTATION
- o INTEGRATED SFE/ACCUMULATOR-FOM ELEMENTS WITH SOLID STATE SPECTRAL SYSTEMS WILL PROVIDE TRACE ON-LINE REAL-TIME ANALYSES FOR PROCESS R&D, QC/QA, AND ENVIRONMENTAL APPLICATIONS. POTENTIAL APPLICATION ACOUSTO-OPTIC TUNABLE FILTER (AOTF) SOLID STATE SPECTROMETER WITH FOM UNITS IN UV TO MID-IR RANGE

Applied AI - MicroEXMAT

Decision Structure for Expert System - Configuration "EXCONFIG"

Figure 47(a)

MicroEXMAT

ES #2
"EXCONFIG"

CHOICES -

DIRECT INJECTION CONFIG A
DHS/PYROLYSIS GC
EXTRACTION C
DESORPTION D
REACTION E
HIGH TEMP/PRESSURE HYPERGC F
SF FLOW UNIT G
SF ACCUMULATOR H

FACTOR =

1 SAMPLE PROCESSING

DIRECT INJECTION
FOM/MIDHS/PYROLYSIS
EXTRACTION
DESORPTION
REACTION
HIGH TEMP/HIGH PRESSURE

2 ACCUMULATOR

MACRO - PREP TRAP
MACRO - QUANTITATION
MICRO - TRACE

3 MOBILE FLUID

CO_2
MODIFIED CO_2
$He/N_2/AIR$

4 CHROMATOGRAPHY

GC (PACKED, CAPILLARY)
SFC (PACKED, MICROBORE, CAPILLARY)
HYPERGC (PACKED, MICROBORE, CAPILLARY)

5 DETECTION

FID, NPD, PID
UV, FTIR, MS, MS/MS
FOM (UV, VIS, NIR, IR)
MI^2D (SF-FOM-GC)
(SF-FOM-GC/MS)
(SF-FOM-FTIR)

Partial Decision Structure for Expert System - Method Development "EXMETH"

Figure 47(b)

Journal of Chromatographic Science, Vol. 27, March 1989

A. DECISION STRUCTURE

DECISION

METHOD INFO
CHOICES

SFE/SFD/SFR
SFC/HYPERGC/GC
SF THEORY
REVERSE MICELLE/MICROEMUL
POLAR/IONIC COMPOUNDS
OLIGOMERS, POLYMERS
SAMPLE PROCESSING
EXPERIMENTAL DESIGN

FACTORS:

(1) EXPERIMENTAL CONFIG

DIRECT INJECT	A
DHS/PYROLYSIS	B
EXTRACTION	C
DESORPTION	D
REACTION	E
HIGH TEMP/PRESSURE HYPERGC	F
SF FLOW UNIT	G
SF/ACCUMULATOR	H

(2) SAMPLE TYPE
TYPE OF VALUES UNORDERED DESCRIPTIVE PHRASES
VALUES
CHEM GROUP 1
CHEM GROUP 2
CHEM GROUP 3
CHEM GROUP 4

(3) SF MOBILE PHASE
TYPE OF VALUES UNORDERED DESCRIPTIVE PHRASES
VALUES
CO_2
HEXANE
PROPYLENE
PROPANE
SF_6
N_2O
NH_3
SO_2
REVERSE MICELLE

(4) MODIFIER/COSOLVENT
TYPE OF VALUES UNORDERED DESCRIPTIVE PHRASES
VALUES
WATER
MeOH
ACETONE
N-OCTANE
SO_2

(5) COLUMN
TYPE OF VALUES UNORDERED DESCRIPTIVE PHRASES
VALUES
PACKED
CAPILLARY
MICROBORE

(6) PROCEDURE
TYPE OF VALUES UNORDERED DESCRIPTIVE PHRASES
VALUES
#1
#2
#3
#4

(7) SOURCE REF
TYPE OF VALUES UNORDERED DESCRIPTIVE PHRASES
VALUES
R.W. GALE, J.L. FULTON, R.D. SMITH
ANAL. CHEM., 59 1977 (1987)
REVERSE MICELLE SFC
J.M. DOBBS, J.M. WONG, R.H. LAHIERE, K.P. JOHNSTON
IND. ENG. CHEM. RES. 26, 56 (1987)
MOD. SF PHASE BEHAVIOR USING POLAR COSOLVENTS

VERBOSE VERSIONS

FACTOR "SAMPLE"
Chem type 1 refers to surfactants. Chem type 2 refers to phenols, polar organics. Chem type 3=propellants, Chem Type 4=food, pharmaceuticals, biochemicals, etc.

FACTOR "PROCEDURE"
Procedure 1 refers to injection volume 0.01 µL, expanded gas flow of 22 mL/min at 1800 psi to 50 mL/min at 6000 psi, column oven 70°C, FID at 380°C, water-saturated precolumn (100×5 mm ID) in 6-port switching valve configuration

B. KNOWLEDGE BASE

RULE 9

IF

SAMPLE	IS CHEM TYPE 2
SYSTEM	IS SF FLOW UNIT
MOBILE PHASE	IS CO_2
MODIFIER/COSOLVENT	IS MeOH
PROCEDURE	IS #2
SOURCE REF	IS J.M. DOBBS, J.M. WONG, R.J. LAHIERE, K.P. JOHNSTON

THEN

METHOD INFO	IS SF THEORY (100)

RULE 10

IF

SAMPLE	IS CHEM TYPE 2
SYSTEM	IS SF FLOW UNIT
MOBILE PHASE	IS CO_2
MODIFIER/COSOLVENT	IS ACETONE
PROCEDURE	IS #2
SOURCE REF	IS IND. ENG. CHEM. RES. 26, 56 (1987)

THEN

METHOD INFO	IS SF THEORY (100)

RULE 11

IF

SAMPLE	IS CHEM TYPE 1
SYSTEM	IS SFC CONFIG U
MOBILE PHASE	IS HEXANE/AOT/WATER
PROCEDURE	IS #3
SOURCE REF	ANAL. CHEM., 59, 1977 (1987)

THEN

METHOD INFO	IS REVERSE MICELLE/MICROEMUL (100)

Figure 47(c)

EMBEDDED INTELLIGENCE AND APPLIED AI NETWORKS

GRC