EVALUATION OF METHODS FOR THE ISOLATION OR CONCENTRATION OF ORGANIC SUBSTANCES FROM WATER

by

Edward S.K. Chian, Johannes H. Reuter and Maurizio F. Giabbai
Georgia Institute of Technology
Atlanta, Georgia 30332

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Project Officer

H. Paul Ringhand

Toxicology and Microbiology Division
Health Effects Research Laboratory
Cincinnati, Ohio 45268

HEALTH EFFECTS RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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NOTICE

FOREWORD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our Nation's population.

The complexities of environmental problems originate in the deep interdependent relationships between the various physical and biological segments of man's natural and social world. Solutions to these environmental problems require an integrated program of research and development using input from a number of disciplines. The Health Effects Research Laboratory conducts a coordinated environmental health research program in inhalation toxicology, genetic toxicology, neurotoxicology, developmental and experimental biology, and clinical studies using human volunteer subjects. These studies address problems in air pollution, water pollution, non-ionizing radiation, environmental carcinogenesis and the toxicology of pesticides and other chemical pollutants. The Laboratory participates in and provides data for the development and revision of criteria documents on pollutants for which national ambient air quality and water quality standards exist or are proposed, provides the data for registration of new pesticides or proposed suspension of those already in use, conducts research on hazardous and toxic materials, and is primarily responsible for providing the health basis for non-ionizing radiation standards. Direct support of the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of environmental regulatory decisions involving the protection of the health and welfare of all U.S. inhabitants.

This report presents the results obtained during the development and evaluation of a method for the isolation and concentration of trace organic substances from water. The method should be used for the preparation of concentrates for the estimation by toxicologic studies of the health risk associated with the consumption of waterborne organics.

F. G. Hueter, Ph.D.
Director
Health Effects Research Laboratory

ABSTRACT

This research program was initiated with the overall objective of developing a practical method for the concentration of trace amounts of organic compounds in water for use in biological testing.

The principal behind the isolation-fractionation scheme developed in this program is to separate dissolved organics into fractions by adsorption onto different adsorbants (i.e., XAD-8 resin, AG MP-50 cation exchange resin, and graphitized carbon black) under varying pH conditions. A limited effort was also made to investigate membrane rejection of dissolved organics by two commercially available reverse osmosis membranes.

Twenty-two model organic compounds covering a broad spectrum of chemical classes, functional groups and molecular weights were used to monitor process performance. Lab-scale experiments, using 500 mL of test solutions spiked with the model compounds at μg/L levels, were performed in an effort to determine optimum conditions for the final pilot-scale evaluation of the isolation-fractionation scheme. The amounts of each model compound on each fraction were monitored using GC/MS procedures that were developed specifically for this program. Recoveries ranging from 30 to 90% were obtained for fifteen of the twenty-two compounds.

In addition, the isolation-fractionation scheme was evaluated for the effects that inorganic salts and humic acids had on the recovery of the model compounds. Experimental data indicated that the recovery of the model compounds was essentially unaffected by the presence of humic acid and inorganic salts.

The results of the pilot-scale study utilizing five 100-liter test solutions spiked with model compounds at μg/L concentrations confirmed those of the lab-scale studies. However, reduced flow rates resulting in prolonged sampling times were encountered in the large scale study. The reduced flow rates were attributed to the use of insufficient amounts of resin.

An investigation of the effects of a 2 ppm chlorine residual solution on the isolation-fractionation scheme was also made. No GC detectable artifacts were found.

FIGURES

FIGURES (continued)

TABLES

TABLES (continued)

TABLES (continued)

ACKNOWLEDGEMENTS

In addition to the authors listed on the title page the following were involved in carrying out various tasks of this research project. Dr. M. Ghosal and Dr. L. Roland contributed to the establishment of analytical procedures for the model organic compounds. Mrs. Z. Geskin assisted in the analytical method development and in the assessment of the resin fractionation scheme at the lab-scale and the pilot-scale level; Mr. P. Mayer and Mr. J.S. Kim assisted in the preliminary evaluation of the resin scheme, whereas Mr. S. Ghosh assisted in the carbon and reverse osmosis evaluation, and in the establishment of the process for the production of organic-free water.

SECTION 1

INTRODUCTION

Mutagenesis, carcinogenesis or cocarcinogenesis and teratogenesis are current serious concerns. These biological reactions are monitored to assess the effects of chronic exposure to drinking water organics. The available tools are provided by the epidemiologist and the experimental toxicologist. Although epidemiologic studies have suggested a relationship between the ingestion of waterborne pollutants and cancer and have been influential in drawing attention to this possible health hazard (1, 2), it is very difficult to establish the significance of this relationship merely from statistical population data. Moreover, mutagenic and teratogenic effects resulting from the consumption of drinking water cannot be assessed by the epidemiological approach since the latter lacks the necessary data on the expression of these effects in human population. Therefore, estimates of the health risks associated with the exposure of human population to organic chemicals are presently provided by experimental toxicological tests wherein animals or lower organisms are exposed to the chemicals at levels that insure potential positive responses.

Ultimately a complete characterization of the organic substances present in drinking water would enable a comprehensive assessment of the health risks based on accepted toxicological principles. Analytical methodologies have thus far been successful in the identification of hundreds of organic substances in drinking water, primarily the "volatile" or "gas chromatographable" ones; however, it is widely recognized that they represent only a small part of the entire water organic content. The "nonvolatile" fraction, which is present as a complex mixture of thousands of components in dilute solution, is not as amenable to current analytical procedures. Since the organic material connot be accurately identified, it cannot be purchased or synthesized for use in the biological tests. Therefore, an alternative approach for the health risks assessment based on toxicological studies consists of directly isolating and concentrating the organic constituents from the drinking water itself.

Several isolation and concentration methods have been tested during the past years. Both laboratory-scale units for processing a few liters of water and pilot-scale units for the handling of several hundred liters of water have been devised. A comprehensive literature review on these methods has been recently published by Jolley (3). The realization of the inadequacy of any single method for the concentration of all organic substances in water has led most researchers to combine several methods in a sequential scheme, in an attempt to achieve the highest possible recovery of the organic matter. The most common schemes thus far evaluated make use of techniques such as re-

verse osmosis (RO), macroreticular non-ionic resin, ion-exchange resins, carbonaceous adsorbents and solvent extraction (4-8).

Several critical areas of concern must be considered when attempting to concentrate waterborne organic concentrates for biological testing: i) the aqueous organic concentrate prepared by the selected concentration scheme has to be representative of the original water sample with regard to the relative abundance of the individual components; ii) transformation of organic constituents between preparation of concentrates and biological testing and/or chemical analysis must be avoided; iii) the effect of humic material, which constitutes the bulk of the organic fraction, on the recovery of trace solutes has to be taken into account; iv) introduction of artifacts and constituent alteration by the concentration method must be kept at a minimum; v) co-recovery of toxic inorganic constituents by the concentration scheme must be evaluated; and vi) effect of chlorine residual on the material used in the concentration scheme (i.e., resins, membranes, etc.) must be assessed. Moreover, model organic compounds representative of a wide range of chemical classes, functional group contents and molecular weights, have to be selected for a comparison of different concentration schemes.

These considerations, as well as the necessity for a comprehensive approach toward the isolation, concentration and fractionation of dissolved organic carbon in water, have led to the investigation of a fractionation scheme in which organic compounds with different functionalities and sorption parameters were separated and concentrated. A mixture of twenty-two model compounds proposed by the Health Effects Research Laboratory (HERL) of EPA (Cincinnati, OH) was chosen for process evaluation. The proposed fractionation scheme was first tested on a laboratory scale and then adapted for processing several hundred liters of water.

SECTION 2

CONCLUSIONS

1. A method for the isolation and concentration of a wide spectrum of model organic compounds from water was developed. The process separated the organic colutes into several fractions based on adsorption onto different adsorbents (i.e., Amberlite XAD-8 resin, AG MP-50 cation exchange resin and Carbopack B graphitized carbon black) under varying pH conditions. Fifteen (i.e., stearic acid, trimesic acid, isophorone, biphenyl, 1-chlorododecane, quinoline, 2,4'-dichlorobiphenyl, 2,6-di-tert-butyl-4-methylphenol, 2,2', 5,5'-tetrachlorobiphenyl, phenanthrene, bis(2-ethylhexyl)phthalate, caffeine, glycine, anthraquinone and humic acid) out of the twenty-two model compounds evaluated showed average recoveries between 30% and 90%. A 2,4-Dichlorophenol appeared to be concentrated on the Ag MP-50 cationic ion exchange resin and Carbopack B, while furfural was not retained on any of the adsorbents used in this study. Quinaldic acid, methylisobutylketone and 5-chlorouracil were found only in very low concentration (i.e., <1% recovery) in the respective fractions and chloroform was not detected at all.

2. The presence of inorganic salts (i.e., $NaHCO_3$ 70 ppm, $CaSO_4$ 120 ppm and $CaCl_2 \cdot H_2O$ 47 ppm), which were added to the test solution to simulate natural and drinking water samples, may generate negative effects on the recovery of the model compounds. Preliminary experiments, which consisted of adsorption of solutes onto XAD-8 under alkaline conditions followed by adsorption under acidic conditions, revealed that the presence of inorganic salts could adversely affect the recovery of organic compounds (i.e., quinoline) by formation of heavy parecipitates. Among the alternatives considered to overcome such problems, a reverse of pH of the adsorption sequence onto XAD-8 resin (i.e., acidic followed by alkaline conditions), provided satisfactory results. By employing this experimental procedure, the formation of precipitates was eliminated and the presence of inorganic salts appeared to have no effects on the recovery of the model compounds in the absence of humic acid.

3. Lab-scale experiments revealed that the adsorption of test solutes was unaffected by the presence of humic acid. On the other hand, pilot-scale studies demonstrated that the simultaneous presence of inorganic salts and humic acid under certain circumstances could be troublesome because they caused the formation of non-homogeneous solutions. The formation of precipitates under alkaline conditions was rather severe as it drastically reduced the flow through the second XAD-8 resin column. However, this problem was attributed to a smaller than required (calculated) amount of resins used in order to minimize introduction of resin artifacts. This suggested that great care should be given to the selection of the resin bed size if proper performance of this fractionation scheme is to be assured. The pilot-scale experimentalal re-

sults showed that the Ca humate precipitate affected primarily the recovery of 1-chlorododecane, since higher amounts of it were detected.

4. Satisfactory results were obtained with the GC-MS analysis of less volatile organics (i.e., trimesic acid, quinaldic acid, stearic acid, glycine). The extraction and derivatization methods developed in this study proved to be adequate in providing reproducible results which could be used to effectively monitor these compounds on the fractionation process. The use of surrogates (e.g., undecanoic acid, 3-quinoline carboxylic acid and L-alanine), however, was found necessary in order to monitor the extraction and derivatization procedures. Glucose could not be analyzed by GC-MS since the derivatization step failed to give the required level of reproducibility. The open tubular columns prepared in this study provided the required inertness, temperature stability and resolution for the direct GC-MS analysis of fifteen out of twenty-two model compounds.

5. Contamination introduced during the handling of the sample through the fractionation scheme appeared to be contained within reasonable limits. In the bench-scale experiments only two or three major impurities (i.e., phenol, bromoform, dibromochloromethane) were detected whose abundance was comparable to that of the model compounds spiked (i.e., at the ppb levels). Whereas the rest of the contaminants were less than 10% of the level of model compounds spiked. The final clean-up of XAD-8 with the solvent used in the desorption of the solutes was necessary to assure the "cleanliness" of the isolated fraction. The presence of other artifacts was attributed to chemical transformation of the model compounds. This was the case for 2,6-di-tert-butyl-4-methylphenol, since 2,5-bis-chcylohexadiene, 1,4-dione-2,6-bis-(1,1-dimethylethyl) was tentatively identified in the test solution extract and the "hydrophobic neutral" fraction. The use of a 2 ppm (mg/L) chlorine residual solution through the scheme did not produce any major GC detectable artifacts.

SECTION 3

RECOMMENDATIONS

The integrated adsorption scheme developed and evaluated in this study may be employed in the preparation of concentrates of aqueous organic substances for toxicologic testing. However, it should be emphasized that the isolation/fractionation scheme is effective only for the recovery of certain classes of organic compounds. The process failed to concentrate highly volatile compounds (i.e., chloroform, methylisobutylketone) and highly soluble substances (i.e., furfural, glucose, quinaldic acid and 5-chlorouracil).

The use of an appropriate amount of resin bed volume for the concentration of organics from large quantities of water should be more fully explored.

To demonstrate the applicability of this process to natural and drinking waters would require the addition of "surrogates" or "internal standards" in the form of selected deuterated model compounds to the water samples.

Since this study has not accounted for significant losses of several model compounds, further investigations in this area are warranted.

The analysis of trace amounts of 5-chlorouracil and glucose by GC-MS still requires improvements.

Although an unweighted average recovery of model compounds were at the 60% level, resin adsorption still has decisive advantages over reverse osmosis in concentrating organics from drinking water especially at higher concentration factors. Because, under these conditions, a larger fraction of organics would have been lost even with the use of membranes having local rejection of 90% of the model organic compounds. However, by combining resin adsorption with reverse osmosis membrane processes would seem to be the ultimate solution to the maximum recovery of a broad spectrum of organic compounds from drinking water.

SECTION 4

MATERIALS AND METHODS

Resins, Carbon and Membranes

Amberlite XAD-8 was obtained from Rohm & Haas (Philadelphia, PA) as an industrial grade preparation in 20-40 mesh size beads. The cation-exchange resin AG MP-50, 20-50 mesh size, was supplied by Bio-Rad Laboratories (Richmond, CA). The graphitized carbon black (GCB) Carbopack-B, 100-120 mesh size, was obtained from Supelco (Bellefonte, PA). Details regarding the physical and chemical characteristics of these materials as specified by the manufacturers are reported in Table 1. The reverse osmosis (RO) membranes evaluated in this study included a DuPont Permasep® B-10 hollow fiber permeator (Wilmington, DE) and an UOP TFC 4400-PA spiral wound module (San Diego, CA). Specifications of the RO modules are shown in Tables 2 and 3, respectively.

Reagents

Anthraquinone, methylisobutylketone, isophorone, furfural, bis(2-ethylhexyl)phthalate, quinoline, caffeine, phenanthrene, 2,4-dichlorophenol, 2,6-di-tert-butyl-4-methylphenol, stearic acid, trimesic acid, 3-quinoline carboxylic acid, undecanoic acid, glycine, L-alanine and glucose were obtained from Aldrich Chemicals Company (Milwaukee, WI). Biphenyl, 5-chlorouracil and 1-chlorododecane were obtained from Alfa Products (Danvers, MA). Quinaldic acid was obtained from Fluka Chemical Company (Hauppauge, NY); 2,4'dichlorobiphenyl and 2,2',5,5'-tetrachlorobiphenyl were purchased from Analabs (North Haven, CT). The purity of the model compounds varied from 96% to 99% as reported by the manufacturer. Sodium bicarbonate, anhydrous calcium sulfate, calcium chloride dihydrate and hydrogen peroxide (50% solution) were purchased from Fisher Scientific Company (Fair Lawn, NJ). All organic solvents employed for the resin and analytical operations were Burdick & Jackson "distilled in glass" obtained from Bodman Chemical Company (Atlanta, GA). The humic acid in these experiments was provided by the Health Effects Research Laboratory - EPA (Cincinnati, OH), and had been prepared from a commercial grade humic acid (Fluka Chemical Company). Heptafluorobutyric anhydride and triflouroacetic anhydride were purchased from PCR Research Chemicals (Gainesville, FL); acetylchloride was supplied by Mallinkrodt Inc. (Paris, KY); Diazald by Aldrich Chemicals Company (Milwaukee, WI); N-methyl-bis-(trifluoroacetamide) and N,O-bis-(trimethylsilyl)-trifluoroacetamide by Pierce Chemical Company (Rockford, IL).

Preparation of "Organic Free" Water

The current study demonstrated the effectiveness of the fractionation

TABLE 1. PHYSICO-CHEMICAL CHARACTERISTICS OF RESINS AND CARBON USED IN THIS STUDY

Parameter	XAD-8	AG MP-50	Carbopack-B
Chemical Nature	Acrylic Ester	Styrene-Divinyl Benzene with Sulfonic Acid Exchange Group	Graphatized Carbon Black
Surface Area (m^2/g)	160	35	100
Porosity Volume (%)	52	30-35	Non-porous
Nominal Mesh Size	25-60	20-60	80-120
Exchange Capacity per Unit Volume (meq/ml)		1.7	

scheme from water solutions spiked with the model organic compounds at the parts per billion (ppb) level. The use of water with low total organic carbon (TOC) background was therefore mandatory. Malayindi et al. (9) have successfully demonstrated the production of a low TOC water by exposing a controlled mixture of distilled water and hydrogen peroxide to a source of UV light in a custom made quartz reactor. On this basis, we designed a flow-through system, in which the final stage consisted of a UV unit (Model #50, Ultraviolet Technology, Inc., San Diego, CA). The UV unit for the production of a large quantity of "organic free" water employs a patented transparent teflon® tubing instead of a conventional quartz tubing and is housed in a protective metal cover. In addition to the final stage UV unit, the overall water purification system consists of a Millipore #360 activated carbon cartridge (Continental Water Systems Company, El Paso, TX), a Millipore #300 deionizer cartridge, and a glass column (1" in diameter and 2' long) packed with a 50 g of 16-30 mesh size Filtrasorb F-400 virgin activated carbon (Calgon Company; Pittsburgh, PA). A controlled amount of hydrogen peroxide is added prior to the introduction of water into two modified UV units connected in series. The schematic diagram of the overall assembly is shown in Fig. 1. All of the wetted surfaces are either glass, stainless steel or teflon in order to minimize contamination contributed by organics. The finished water was analyzed for TOC in an ultra-low-level carbon analyzer (Dohrmann DC-54, Envirotech Company, Santa Clara, CA). The detector response was calibrated with eight standard potassium acid phthalate solutions at different concentrations (Table 4) and plotted in Figure 2. A parametric study of the system, particularly of the UV units, was carried out in order to optimize the quality and quantity of the finished water. The effect of UV irradiation intensity, hydrogen peroxide concentration and flow rate are reported in Table 5 through 7. The residual peroxide was monitored by starch-iodometry (10). The efficiency of the overall water treatment in terms of organic removal is reported in Table 8. The following optimum conditions for ultra-low TOC level water were established: i) tap water treated through Continental-Millipore 2500 system and followed by Filtrasorb F-400 activated carbon; ii) hydrogen peroxide volu-

TABLE 2. SPECIFICATIONS OF B-10 PERMASEP RO MODULE

Membrane Type	B-10 aromatic polyamide
Membrane Configuration	Hollow-fiber
Nominal Permeate Flow(1)	1500 gpd
Sodium Chloride Rejection(1)	98.5%
Rated Operating Pressure	800 psig
Maximum Operating Temperature	32°C
pH Range (Continuous Exposure)	5-9
Free Chlorine Tolerance	Nil

(1) Based on operation with a feed of 30 g/L NaCl at 800 psig, 25°C and 30% water recovery.

TABLE 3. SPECIFICATIONS OF TFC-4400 PA RO MODULE

Membrane Type	Poly (ether/amide) (PA-300)
Membrane Configuration	Spiral-Wound
Nominal Permeate Flow(2)	1000 gpd
Sodium Chloride Rejection(2)	97%
Rated Operating Pressure	600 psig
Maximum Operating Temperature	45°C
pH Range (Continuous Exposure)	4-6
Free Chlorine Tolerance	Nil

(2) Based on operation with a feed of 30 g/L NaCl at 800 psig, 25°C and 7% water recovery.

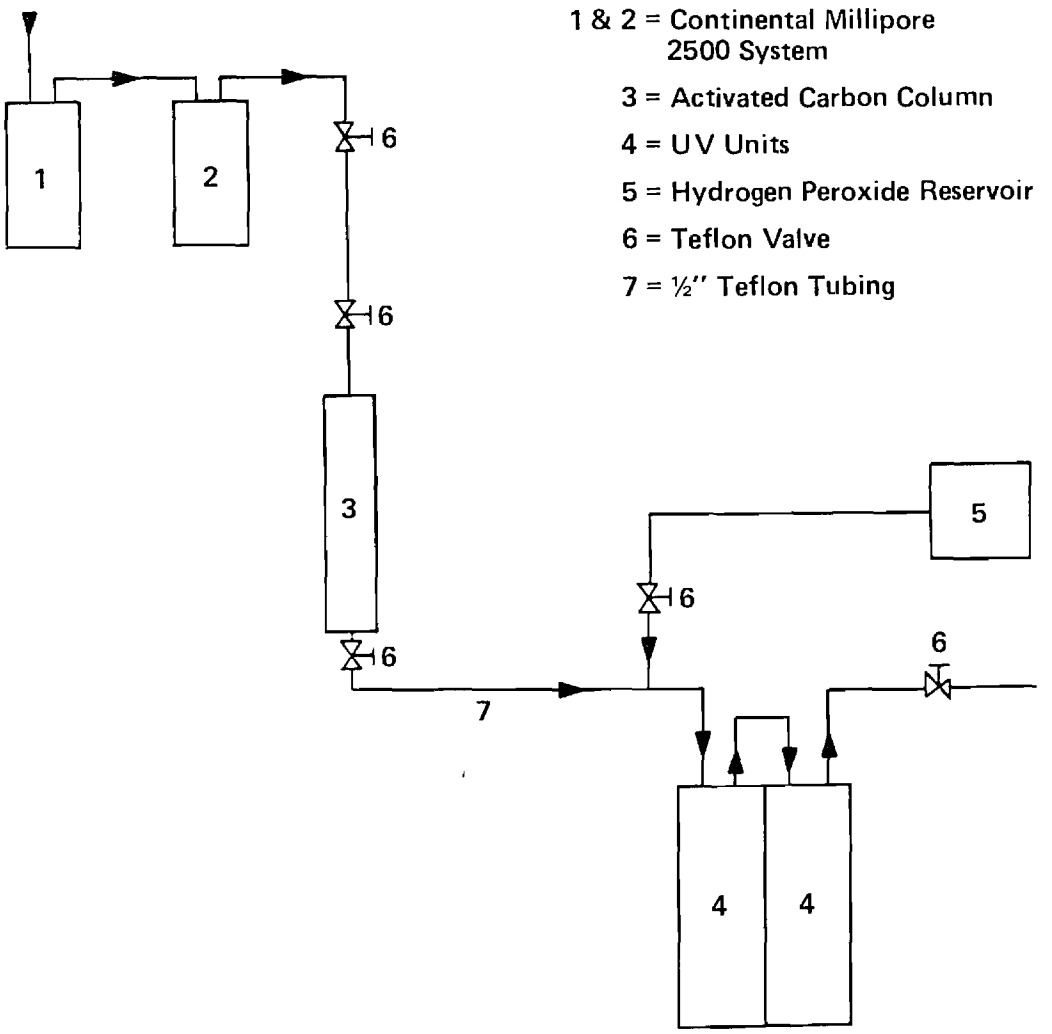


Figure 1. Schematic of System for Production of "OFW"

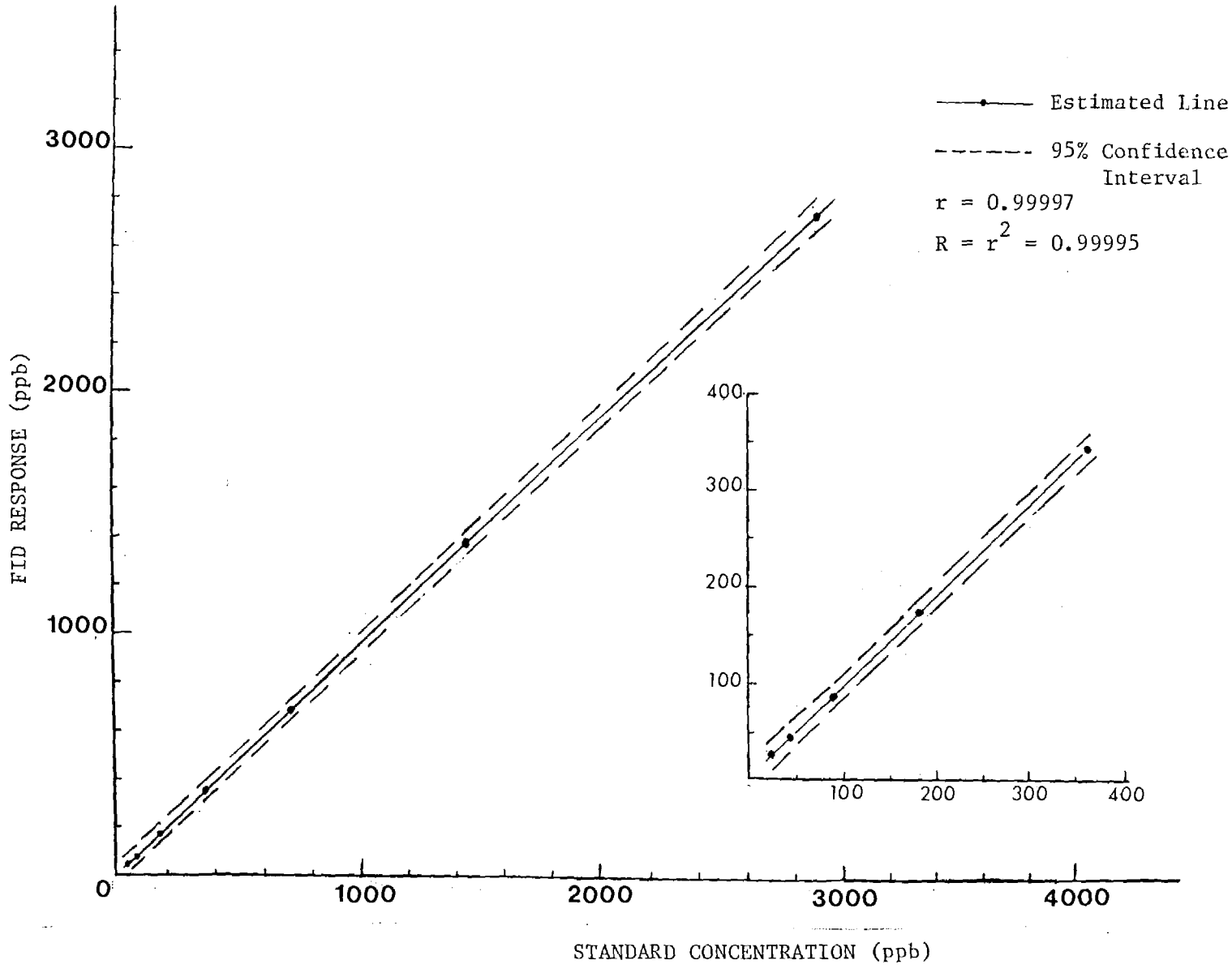


Figure 2. Calibration Curve for Dohrmann DC-54 Carbon Analyzer

TABLE 4. CALIBRATION STUDY OF DOHRMANN DC-54 CARBON ANALYZER

Standard Concentration (ppb) (x)	FID response TOC (ppb) (y)	Mean (ppb) ($\bar{y}$)	Standard Deviation s(ppb)	Coefficient of Variation $cu = \frac{s}{y}$	Estimated FID response by Linear Regression Y (ppb)	95% Confidence Inval (ppb)
27	23 25 24 30	28	4.2	0.150	27.33	±15.87
45	48 44 44 46	45.5	1.9	0.041	44.37	±15.72
90	92 89 89 87	89.2	2.0	0.022	86.99	±15.37
180	176 172 177 174	174.2	2.2	0.012	172.22	±14.78
360	351 345 343 343	345.5	3.7	0.010	342.68	±13.65
720	675 666 663 668	668	5.1	0.007	683.60	±12.75
1440	1370 1379 1363 1375	1371.7	6.9	0.005	1365.40	±16.14
2880	2710 2748 2735 2726	2729.5	15.9	0.005	2729.16	±32.25

TABLE 5. EFFECT OF UV RADIATION INTENSITY ON THE QUALITY OF FINISHED WATER

Sample Point and Description	TOC in Water at Inlet of UV Unit-I	TOC (ppb)	% V/V H_2O_2 Addition	Residual H_2O_2 (ppb)
Finished Water, (Lamps off, and no H_2O_2 addition)	52.1	56.3	0	-
Finished Water, (Lamps off)	52.1	51.0	0	35.0
Finished Water, (Lamps in UV Unit-I on; Residence time in UV Unit-I 20 min)	52.1	45.2	0	11.7
Finished Water, (Lamps on in both the units; Residence time = 61 min)				

TABLE 6. EFFECT OF DIFFERENT % H_2O_2 ADDITIONS ON THE QUALITY OF FINISHED WATER

% v/v H_2O_2 (50%) Addition	Sample Description	TOC in Water at Inlet of UV Unit-I	TOC (ppb)	Residual H_2O_2 (ppm)
0.5	Finished Water	52.1	27.2	N.D*
1.0	Finished Water	52.1	25.7	0.39
2.0	Finished Water	52.1	24.1	2.5

*N.D. - Not Detectable

TABLE 7. EFFECTS OF FLOW RATE CHANGES ON TOC AND RESIDUAL PEROXIDE CONCENTRATION IN FINISHED WATER

Flow Rate (L /min)	Residence Time in UV Unit (min)	TOC in Water at Inlet of UV Unit-II (ppb)	TOC in Finished Water (ppb)	Residual H_2O_2 Concentration in Finished Water (ppb)
50	36.8	55.2	27.2	N.D*
100	18.4	59.4	36.3	2.5
150	12.2	83.7	49.9	3.9

*N.D. - Not Detectable

TABLE 8. ORGANIC CARBON REMOVAL EFFICIENCY OF THE WATER TREATMENT

Sample Point	TOC (PPb)	Remarks
Tap Water	1100.8	
Inlet Carbon Column	135.5	87.7% removal by Continental Millipore System
Inlet UV Unit	52.1	61.5% removal by Activated Carbon
"OFW"	25.7	56.9% removal by UV units

metric concentration: 0.5%; and iii) flow rate: 50 ml/min. Under these conditions it is possible to generate 72 liters per day of "organic free" water (OFW) with an average of 27 $\pm$ 15 ppb TOC and a hydrogen peroxide residue of <100 ppb.

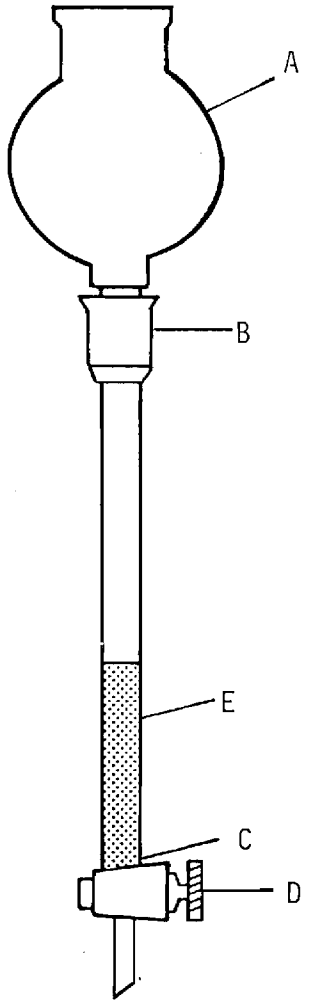
Preparation of Resins, Carbon and Membrane

The XAD-8 resin was air dried and sieved through 20 and 50 mesh size sieves respectively. The 20-50 mesh size fraction was washed with 0.1N NaOH and then stored for 24 hrs in clean 0.1N NaOH. The remaining fines were removed by decanting. The resin was soxhlet extracted for 24 hrs each with acetone, hexane and methylene chloride. The cleaned resin was finally stored in methanol. In the lab-scale experiments, glass columns (200 x 13 mm I.D.) with teflon stopcock were packed with 15 ml bed volume of XAD-8. In order to process 100 liter of water solution, larger glass columns (500 x 34 mm I.D.) with 250-ml bed volumes of XAD-8 were prepared. Immediately before passage of the test solution, the resin bed was rinsed with 1 bed volume of 0.1N NaOH, 1 bed volume of 0.1N HCl and 3 bed volumes of "OFW" in order to eliminate methanol and stabilize the column. The samples were processed at a flow rate of <30 bed volume/hour.

AG MP-50 (20-50 mesh, H^+-form) resin was purified by soxhlet extraction with methanol (24 hrs.) and subsequently stored in fresh solvent. Glass column dimensions were the same as for the XAD-8 resins in both the lab-scale and 100-liter experiments. The resin bed was rinsed with 3N NH_4OH, until breakthrough of ammonia was observed, followed by four bed volumes of 2N HCl, and finally with "OFW" until the effluent was Cl^- free.

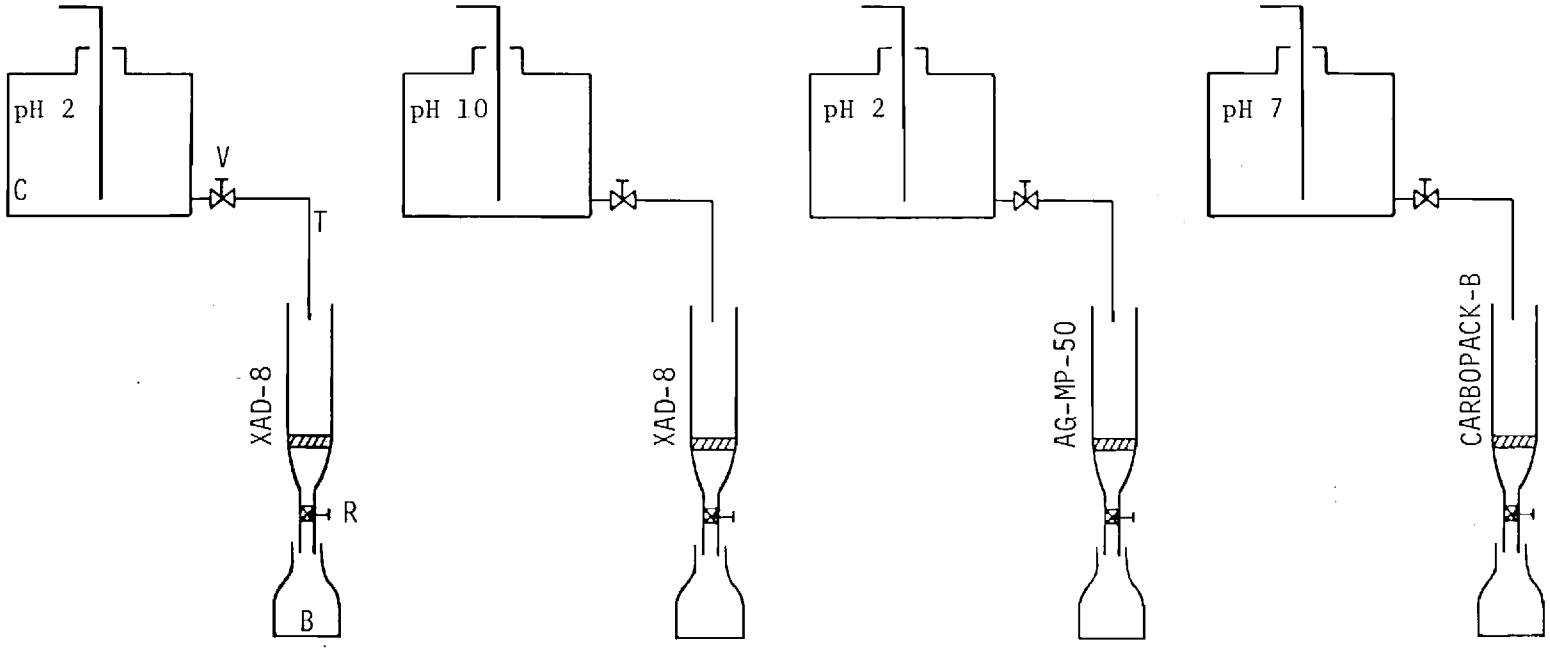
Carbopack B GCB was washed with 20 ml acetone, 20 ml methylene chloride and 50 ml "OFW" prior to column packing. Since this material is fragile, care was taken to avoid any mechanical stress which would cause particle rupture and consequently generate flow rate problems. In the lab-scale experiments 200 mg of Carbopack B were packed in a glass column (200 x 5 mm I.D.) with teflon stopcock, as recommended by Bacaloni et al. (11). In the large-scale experiments, 10 g of GCB were packed in a glass column (300 x 35 mm I.D.) provided with a teflon rotaflo valve.

A typical glass column and reservoir used in the lab-scale experiments is represented in Figure 3. The final demonstration of the efficiency of the fractionation scheme required the process of a total volume of 500 liters of test solution. Since the scheme evaluated is based primarily on adsorption-desorption mechanisms, it was agreed to employ modular units whose column dimensions and amount of adsorbents would suffice 100 liters of water solution. The overall scheme of the modular units used in the processing of 500 liters of water is represented in Figure 4. Glass carboys of 45-liter capacity served as feeding reservoirs and glass bottles of 1-gallon capacity were used for column effluent collection and manual transfer of the test solution to the next feeding reservoir. Sample transfer lines, valves and columns were made of glass and teflon in order to minimize loss of solute and introduction of contaminants. The column head required for maintaining the designed flow rates was calculated by using the Carmen-Kozeny (12) equation:



A = 2 liter reservoir
B = 24/40 ₮ - Joint
C = Sintered glass filter
D = PTFE stopcock
E = Adsorbent

Figure 3. Glass Column and Reservoir for Resin and Carbon (Lab-Scale) Study



B = 1 gallon bottle
C = 45 liter glass carboy
V = teflon valve
R = rotaflo valve
T = teflon tubing

Figure 4. Schematic of Modular Units for Pilot-Scale Study

$$\Delta P = u\eta L \frac{5(1-\varepsilon)^2 S_o^2}{\varepsilon^3} = \rho g h$$

$$h = \frac{u\eta L}{\rho g} \frac{5(1-\varepsilon)^2 S_o^2}{\varepsilon^3}$$

u = flow velocity, cm/sec

L = height of bed volume, cm

η = viscosity, 0.01 poise at 20°C

ε = porosity

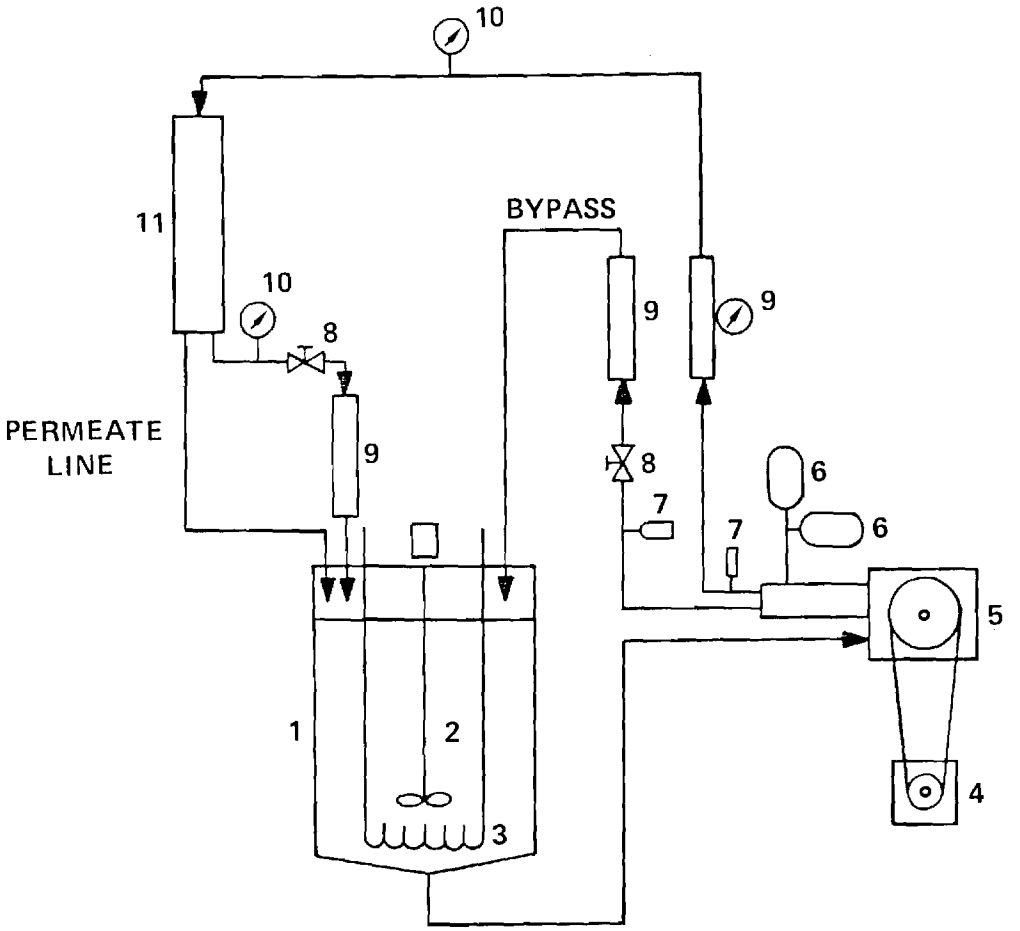
S_o = specific surface area, $cm^{-1} = 6/\phi d$ (see Table 9 for definitions)

The calculated head loss and the dimensions of each column for a given flow rate are given in Table 9.

The RO membranes were evaluated for their rejection of methylisobutylketone (MIBK) and furfural. The DuPont B-10 hollow fiber RO module Permasep permeator (Model 6440-015) consisted of a tightly packed bundle of aromatic polyamide (nylon) hollow fibers, having dimensions of 52 μm I.D. and 85-100 μm O.D., housed in a reinforced fiberglass pressure vessel. The UOP (San Diego, CA) TFC 4400-PA spiral wound module is in a 4"-diameter by 42" long single leaf configuration. The module consists of two membrane sheets (with skin layer oriented outwards) separated by a spacer, which supports the membranes and provides a flow path for the permeate. The set is rolled up around the collector tube, which has an anti-telescopic device at both ends, and the entire assembly is enclosed in a reinforced fiberglass pressure vessel. The RO system was operated in a closed-loop configuration (see schematic in Figure 5) at constant temperature with the aid of a separate cooling unit. A positive displacement piston pump (Cat Model 520, Cat Pumps, Minneapolis, MN) was used to deliver the feed from the storage tank to the module. The feed flow rate and pressure were controlled with the aid of a needle valve in the by-pass line and a pressure regulator in the concentrate line. The cooling unit employed to maintain the feed temperature at 25°C was a Blue M Model PCC-34 C (Blue M Electric Company, Blue Island, IL). Cooling water was stored in a separate holding tank and then pumped through a copper coil submerged in the feed storage tank.

Preparation of Model Compound Test Solution

Five hundred mg/L of quinaldic acid, glycine and glucose stock solutions were prepared directly with "OFW"; 500 mg/L of 5-chlorouracil with a 2N NH_4OH solution; and 500 mg/L of all the other compounds with methanol. The humic acid stock solution was dissolved in 0.02 NaOH. The test solutions containing all model substances were prepared by addition of salts (70 ppm $NaHCO_3$; 120 ppm $CaSO_4$; 47 ppm $CaCl_2 \cdot 2H_2O$) and by diluting the required volumes of stock solutions in "OFW". Phenanthrene, 1-chlorododecane, 2,4'-dichlorobiphenyl and 2,2',5,5'-tetrachlorobiphenyl were spiked by sonicating and blowing dry solutions in hexane and acetone prior to addition of "OFW" (see Appendix B).



1 - Feed Storage Tank
2 - Stirrer
3 - Cooling Coil
4 - Electric Motor
5 - High-Pressure Pump
6 - Hydraulic Accumulator
7 - Pressure Relief Valve
8 - Pressure and Flow Regulator
9 - Flowmeter
10 - Pressure Gauge
11 - RO Module

Figure 5. Schematic of RO System

TABLE 9. CALCULATED HEAD LOSS FOR THE SPECIFIED COLUMN DIMENSION

	XAD-8	AG MP-50	Carbopack B
Column dimension	51 cm x 3.4 cm I.D.	51 cm x 3.4 cm I.D.	30 cm x 3.5 cm I.D.
Particle diameter(d)			
mesh	20/60	20/50	80/120
geometric average	0.045 cm	0.0494 cm	0.0146 cm
Shape factor (ϕ)	1.0	1.0	0.7
Specific surface area (S_o)	131.0	121.5	587.1
Porosity	0.4	0.4	0.5
Flow (liters/hour)	15	15	15
Height (h)	53.5 cm	46 cm	125 cm

Instrumentation

Total organic carbon (TOC) was analyzed by a Dohrmann DC-54 ultra-low level carbon analyzer (Envirotech Company, Santa Clara, CA). A Hewlett-Packard 5830-A gas chromatograph (Avondale, PA) equipped with a capillary injection system and a flame ionization detector was employed for the quantitative analysis of each model compound. Separation of the organic compounds was accomplished on glass capillary columns (0.3 mm I.D. x 30 m) coated with SE-54 silicone gum-phase (Applied Science, State College, PA). Soft glass tubings of 121 x 0.6 cm O.D. x 0.4 cm I.D. (Kimble Div., Toledo, OH) were washed with detergent solution, rinsed with tap water, distilled water and acetone, and finally drawn on a glass drawing machine (Shimadzu GDM-1; Tokyo, Japan) to capillary tubing 100 meters long with 0.3 mm I.D. Each capillary was leached overnight at 150°C with a 20% solution of HCl and dehydrated according to the procedure outlined by Grob (13). Following dehydration, the capillary was deactivated by the persilylation method according to Grob (14) and coated by the static method (15) with a known amount of stationary phase. The GC conditions were generally as follows: injection volume 1 L (splitless injection mode), oven temperature from 40°C up to 290°C (rate 10° or 4°C/min). Hexamethylbenzene was used as internal GC standard for both relative retention time and quantitative data evaluation. 5-Chlorouracil was analyzed on a Perkin-Elmer Series 3 liquid chromatograph (Norwalk, CT) equipped with a Rheodyne (Berkeley, CA) injection system, a LC65-T variable wavelength (UV/Visible) detector, and a Lichrosorb-C18 reverse phase column (Altex, Berkeley, CA). LC conditions were as follows: solvent: H_2O-methanol (90:10) in isocratic conditions: flow rate: 4 ml/min; UV monitored at 254 mm. Analytical confirmation of the model compounds and tentative identification of organic impurities introduced during the handling of the test solution through the fractionation scheme was accomplished by means of a Finnigan 4000 MS-DS (Sunnyvale, CA) interfaced with a Hewlett-Packard 5830-A GC, as described elsewhere (16). The sample transfer line between the capillary column and the MS ionization source consisted of a fused silica tubing (80 x 0.015 cm), which was deactivated with Carbowax 20M. The MS operating conditions were as follows: EI ionization mode, electron multiplier 1500 V, electron energy 70eV, emission current 0.5 mA, mass range 45-450 a.m.u., scan rate 1 scan/sec. The GC conditions were identical to those in the GC analysis. Perfluorotributylamine (FC-43) was used to initially tune the MS and decafluorotriphenylphosphine was used to verify the tune thus obtained, according to Eichelberger *et al*. (17).

SECTION 5

EXPERIMENTAL PROCEDURES

Isolation-Fractionation Scheme

The flow schematic of the isolation-fractionation scheme devised and evaulated in this study is given in Figure 6. The test solution was first acidified to pH 2 and passed through the XAD-8 column by gravity flow at a rate of <30 bed volumes/hour. The final portion of the sample (i.e., test solution) was displaced from the resin by 1 bed volume of 0.01 HCl rinse, which was recombined with the test solution. The "hydrophobic acid" fraction was desorbed with 0.25 bed volume of 0.1N NaOH, followed by 1.5 bed volume of "OFW". The test solution effluent from the XAD-8 (still at pH 2) was adjusted to pH 10 with 1N NaOH and recycled through the XAD-8 column at a flow rate of <30 bed volumes/hours.

In the large-scale experiments two XAD-8 columns were used, one for each pH condition. In this case the test solution effluent from the first XAD-8 column was processed through a second XAD-8 column after pH adjustment. Following the sample, 2.5 bed volumes of "OFW" were used to rinse the XAD-8 column and combined with the test solution effluent. The "hydrophobic base" fraction was eluted with 0.25 bed volume of 0.1N HCl, followed by a 1.5 bed volume of 0.01N HCl. Finally the XAD-8 resin was transferred from the column to a separatory funnel and extracted with three 50 ml aliquots of methylene chloride in order to desorb the "hydrophobic neutral" fraction. The resin used in the large volume experiments was extracted by shaking resin and solvent within the glass column. The test solution,which should contain only hydrophilic substances was readjusted to pH 2 with HCl and then passed through the AG MP-50 cation-exchange column at a flow rate of <30 bed volumes/hour. The "hydrophilic base" fraction was desorbed by elution with approximately 0.8 bed volume of 1N NH_4OH. Finally, the test solution effluent was adjusted to pH 7 and processed through the Carbopack B column at a flow rate that allows a contact time of approximately 0.5 minutes.

Analytical Procedures

The "hydrophobic neutral" fraction, which is desorbed in methylene chloride, was concentrated in a Kuderna-Danish evaporator (Kontes, Vineyard, NY) to the appropriate volume (1 ml for the lab-scale experiments and 50 ml for the pilot-scale study) and after addition of an internal standard analyzed by GC-FID and GC-MS. A known amount of surrogate compounds (undecanoic acid and 3-quinoline carboxylic acid) was added to one or two mL of the hydrophobic acid fraction and the solvent removed by purging with pure nitrogen; the residue was acidified with approximately 0.5 mL of 6N HCl, again dried with pure

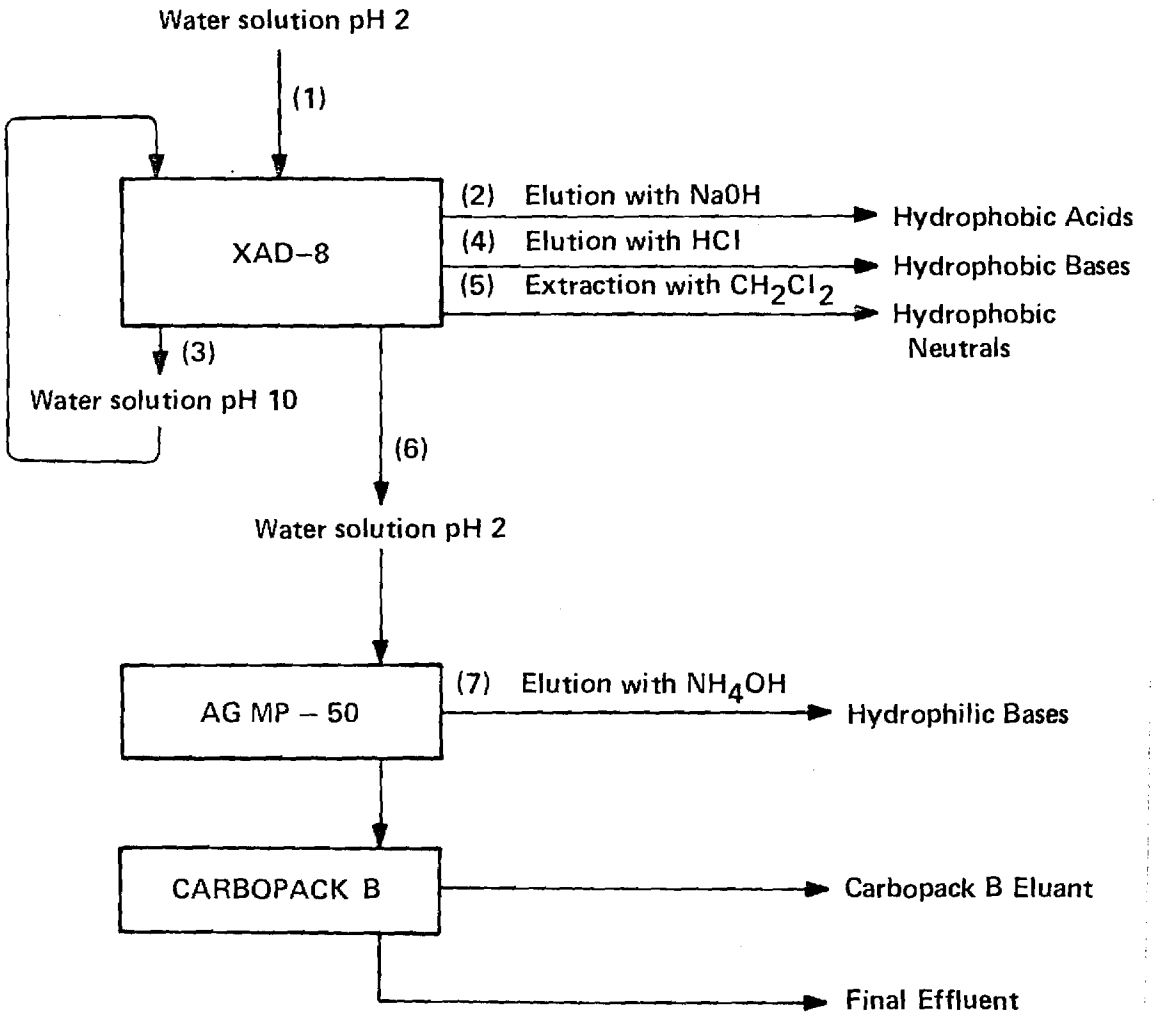


Figure 6. Flow Schematic of Isolation/Fractionation Scheme

nitrogen and finally redissolved in approximately 1 mL of diethyl ether by stirring carefully with a glass rod in order to help dissolve any acids. The solution was subsequently methylated with gaseous diazomethane. The latter was generated by adding 15 drops of aqueous NaOH solution (35%) into a solution of diazald in methanol (0.2 g in 5 liters). Nitrogen gas was blown into the solution and the diazomethane gas was transferred into the ethereal solution containing the acids for approximately 10-20 seconds. Hexamethylbenzene (I.S.) was then added to the solution and analyzed by GC. For every batch of hydrophobic acid samples a standard solution consisting of trimesic, stearic, quinaldic and surrogate acids was prepared by dissolving the appropriate amount in "OFW" (e.g., to prepare a 50 μg/mL solution), with solvent removal and methylation according to the above method. This standard solution served as the basis for the quantitative evaluation of the samples.

The "hydrophobic base" fraction was solvent extracted with methylene chloride after adjusting the pH to 10 with 0.1N NaOH. The organic solvent extract was concentrated in a Kuderna-Danish apparatus and under a stream of nitrogen, and finally analyzed by GC-FID and GC-MS. The aqueous solution (50 μL) was subjected to HPLC in order to test for the presence of 5-chlorouracil. One or two mL of the "hydrophilic base" fraction was dried under a stream of N_2, acidified with HCl and analyzed for glycine after derivation with isoamylalcohol, acetylchloride and heptafluorobutyric anhydride according to the method described by Burleson et al. (18). One or two mL of the same "hydrophilic base" fraction was analyzed for quinaldic acid following the procedure mentioned for the "hydrophobic acid" fraction. The presence of quinaldic acid in this fraction was suggested speculatively. Solvent extraction with three 50-mL aliquote of methylene chloride was performed on the remaining portion of this fraction at pH 10 and the extract analyzed for caffeine. The Carbopack B fraction was obtained by desorption with 50 mL of methylene chloride. After solution concentration to 1 mL, it was directly analyzed by GC-FID and GC-MS. The final effluent was solvent extracted with methylene chloride and analyzed by GC. The humic acid was quantitated in the "hydrophobic acid" fraction by spectrophotometric analysis at 430 nm. Nine solution concentrations, which covered a range between 10 and 400 mg/L, were used for instrument calibration. Standards and samples were analyzed under the same pH conditions.

SECTION 6

RESULTS

The list of organics that were evaluated in this study and the composition of the test solution is reported in Table 10.

Analytical Procedures

A substantial effort was dedicated to the development of analytical procedures for the qualitative and quantitative assessment of the model organics in each separated fraction. An attempt was made to use GC-MS analysis as the ultimate identification method; therefore, emphasis was placed on the selection of the appropriate GC system which would allow direct analysis of the majority of the organic compounds. For those not directly amenable to GC analysis, volatile derivatives were prepared. In some cases, HPLC was employed as an alternate technique.

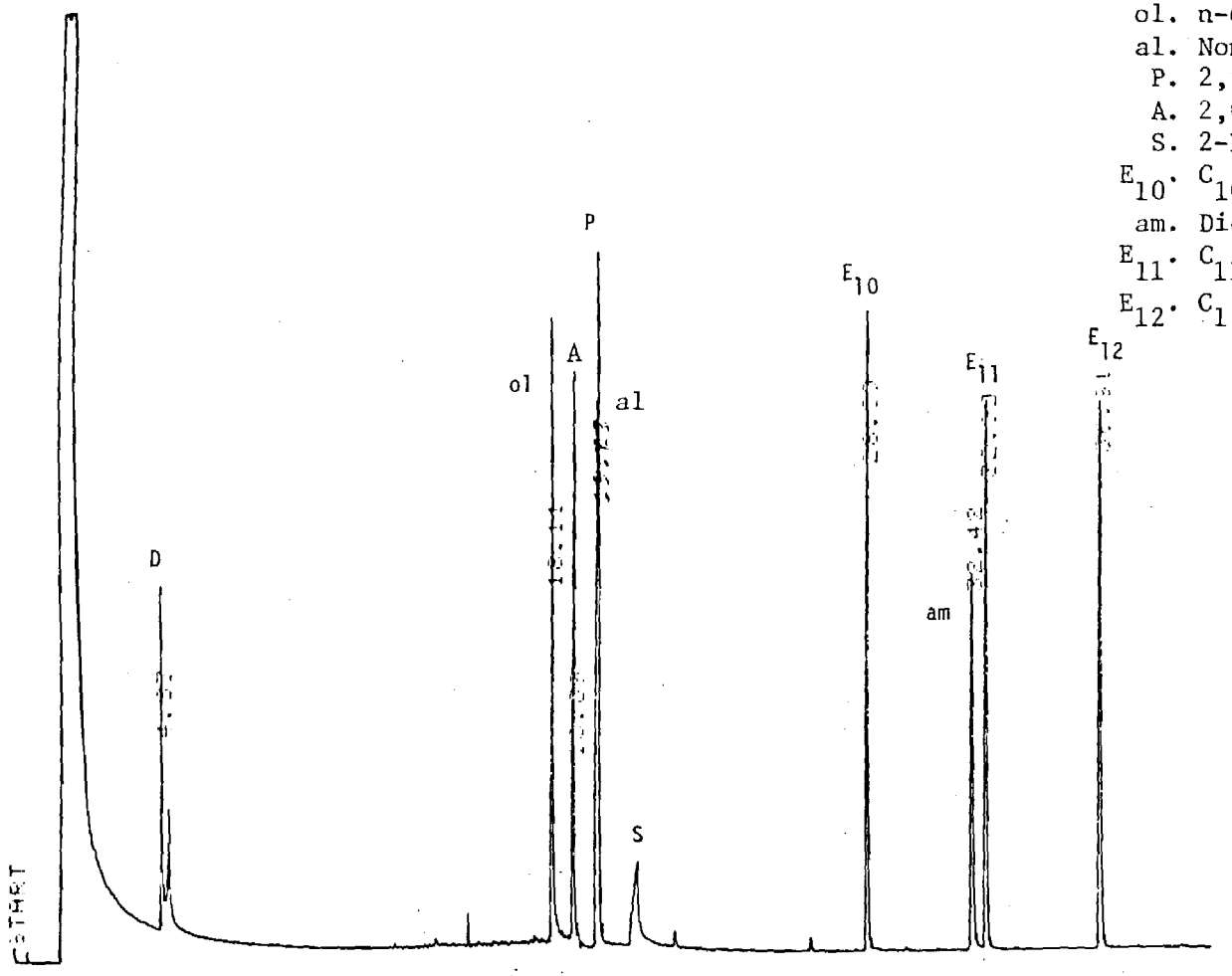
Following recent developments in the preparation of glass capillary columns, efforts were made in this lab to improve column inertness, temperature stability and resolution. These represent the most important parameters for the analysis of organic compounds with a wide range of functionalities, molecular weight and chemical stability. Ultimately the GC columns had to be suitable both for organic compounds that required a preliminary derivatization and those directly amenable to the GC system. Moreover, the column had to be suitable for GC-MS analysis. The combination of effective deactivation by persilylation, as proposed by Grob (14), and the selection of SE-54 or SE-52 silicone gum-phases as stationary phase, led to satisfactory results. A typical chromatogram is given in Figure 7 for the test polarity mixture (19) used for column testing and comparison. All compounds were satisfactorily chromatographed except 2-ethylhexanoic acid which still interacted strongly with the column surface and/or the stationary phase. Fourteen out of the 22 model organics investigated in this study were directly amenable to GC analysis as shown by their FID trace presented in Figure 8. Under these experimental conditions, chloroform coeluted with the solvent front. However, the resolution offered by the same column type for highly volatile and purgeable compounds is still satisfactory, as demonstrated by the reconstructed ion chromatogram (Figure 9) of a standard solution (20 ppb level) of purgeable priority pollutants which includes also chloroform, as analyzed by the purge-and-trap method (20). The reproducibility of the GC analysis in terms of peak area or amount and GC-FID linear response was evaluated for selected model organics (see Tables 11 and 12).

The use of untreated fused silica tubing as sample transfer line between the GC column effluent and the MS ionization source was found satisfactory.

in retaining the inertness and resolution offered by the chromatographic column. A reconstructed ion chromatogram of the model compounds directly amenable to GC is shown in Figure 10. Their mass spectra are reported in Appendix A (see Figures A-1 through A-15).

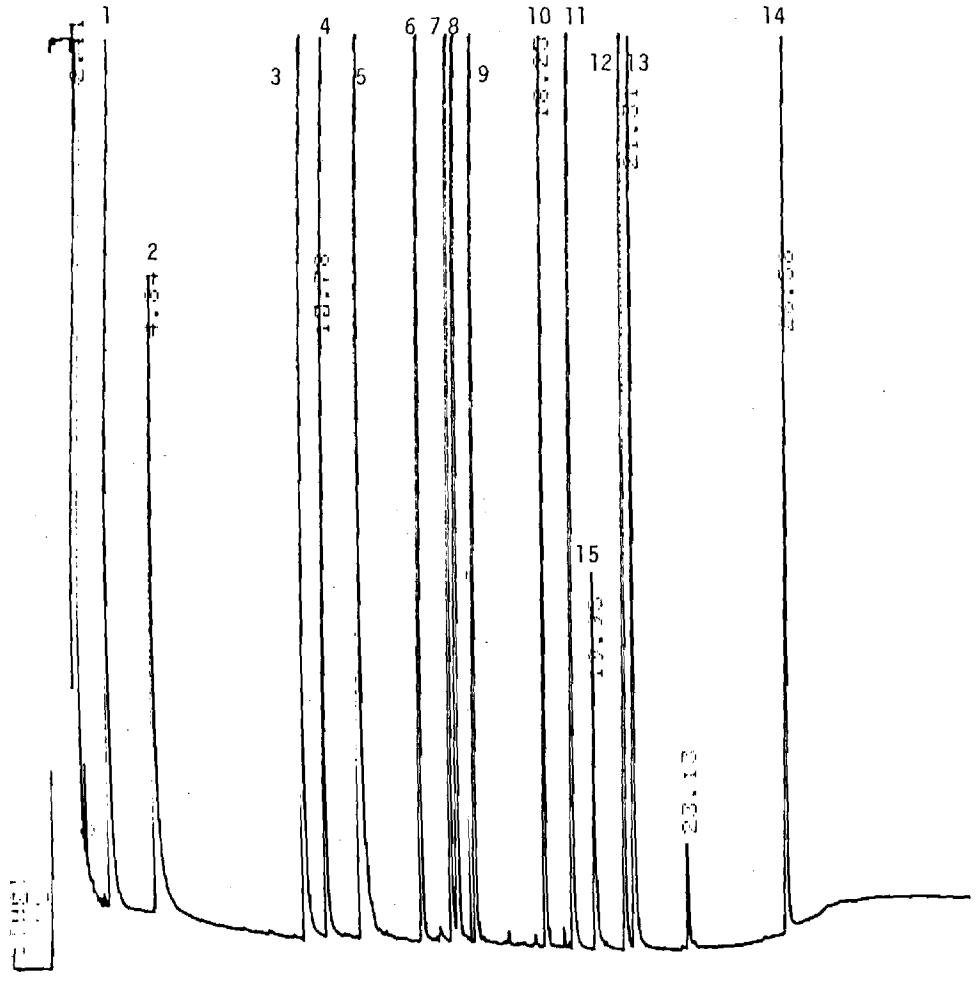
TABLE 10. MODEL COMPOUNDS AND TEST SOLUTION COMPOSITION

Compound	Concentration, μg/L
Trimesic Acid	50
Stearic Acid	50
Quinaldic Acid	50
Humic Acid	2000
Glycine	50
Furfural	50
Quinoline	50
Caffeine	50
5-Chlorouracil	50
Glucose	50
2,4'-Dichlorobiphenyl	50
2,2',5,5'-Tetrachlorobiphenyl	5
bis(2-Ethylhexyl)phthalate	50
1-Chlorododecane	5
Biphenyl	50
Phenanthrene	1
Isophorone	50
Anthraquinone	50
Methylisobutylketone (MIBK)	50
2,4-Dichlorophenol	50
2,6-di-tert-Butyl-4-methylphenol (BHT)	50
Chloroform	50
$NaHCO_3$	70000
$CaSO_4$	210000
$CaCl_2 \cdot 2H_2O$	47000



D. 2,3-Butanediol
ol. n-Octanol
al. Nonylaldehyde
P. 2,6-Dimethylphenol
A. 2,6-Dimethylaniline
S. 2-Ethylhexanoic acid
E_{10}. C_{10}-methyl ester
am. Dicyclohexylamine
E_{11}. C_{11}-methyl ester
E_{12}. C_{12}-methyl ester

Figure 7. GC-FID Trace of Polarity Mixture for Column Testing (Grob). SE-54 Silicone Gum Phase; film thickness ≈ 0.2 μm. Temperature Program 39°C (0.1 min.)-290°C at 3°C/min; Coating Efficiency = 89%; TZ = 36.



1. MIBK
2. Furfural
3. Isophorone
4. 2,4-Dichlorophenol
5. Quinoline
6. Biphenyl
7. Hexamethylbenzene (I.S.)
8. 1-Chlorododecane
9. 2,6-di-tert-Butyl-4-methylphenol
10. 2,4'-Dichlorobiphenyl
11. Phenanthrene
12. 2,2',5,5'-Tetrachlorobiphenyl
13. Anthraquinone
14. bis(2-Ethylhexyl)phthalate
15. Caffeine

Figure 8. GC-FID Trace of Model Compounds

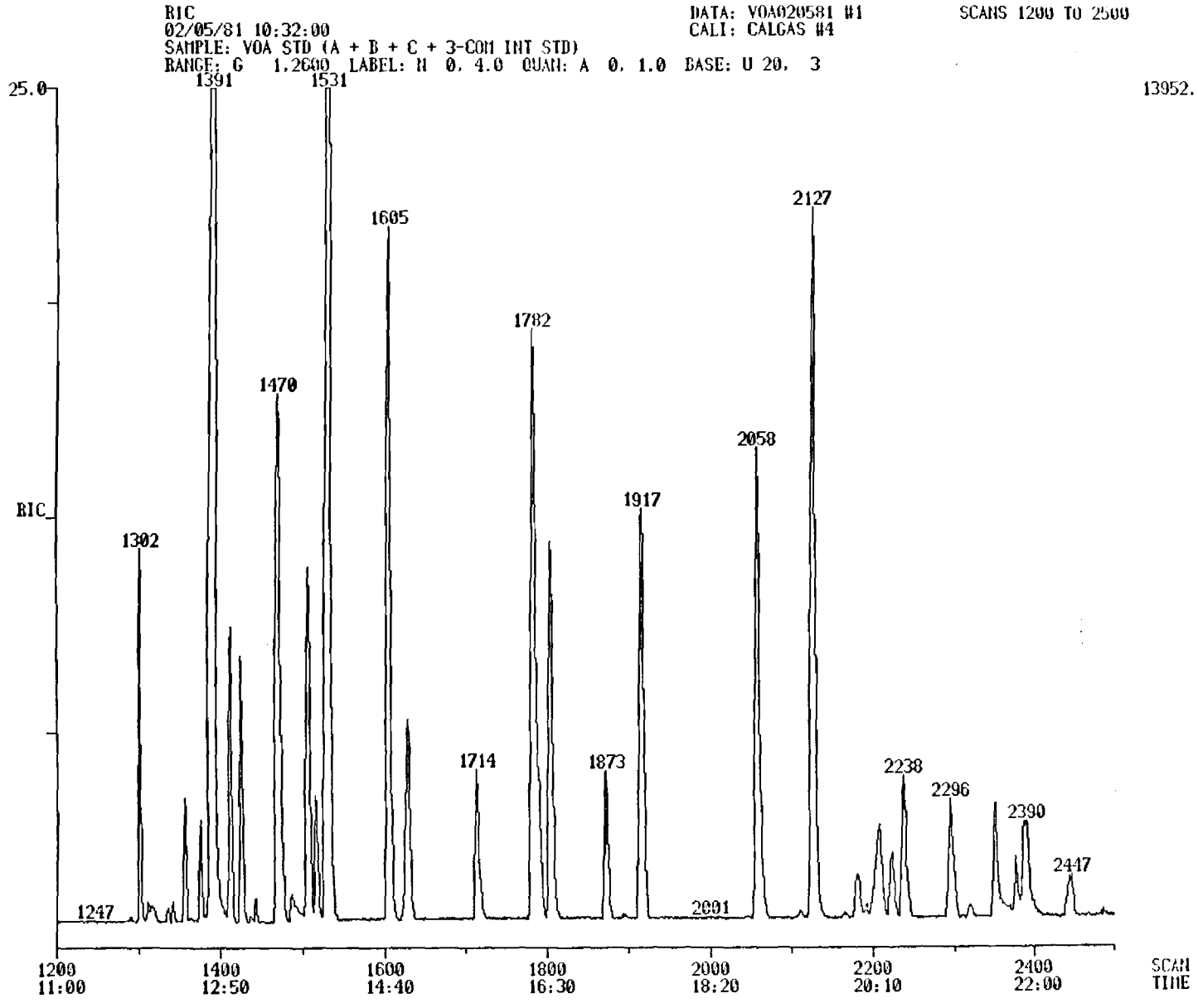


Figure 9. RIC of Purgeable Priority Pollutants (16).

TABLE 11. INSTRUMENTAL VARIATION OF GC-FID (Based on 14 Repetitive runs of 20 ng Standard Solution + 20 ng Internal Standard)

Compound	Mean ($\bar{X}$)	Standard Deviation (s)	$\frac{s}{\bar{X}}$ .100%
1. Furfural	18.7	1.63	8.7%
2. Isophorone	19.0	0.8	4.2
3. 2,4-Dichlorophenol	20.6	0.81	3.9
4. Quinoline	21.3	0.91	4.3
5. Biphenyl	20.7	0.34	1.7
6. 1-Chlorododecane	19.8	0.09	0.5
7. 2,6-di-tert-Butyl-4-methylphenol	19.8	0.45	2.3
8. 2,4' -dichlorobiphenyl	19.9	1.29	6.5
9. Caffeine	19.3	0.77	4.0
10. 2,2',5,5'-Tetrachlorobiphenyl	19.3	1.23	6.4
11. Anthraquinone			
12. bis(2-Ethylhexyl)phthalate	17.0	1.09	6.4

TABLE 12. DATA FOR MINIMUM DETECTABLE LIMIT AND LINEAR RESPONSE FOR GC-FID

Compound	Level Injected (ng) 1.0	10.0	20.0	100.0
1. Furfural		16.6	20.8	129.1
2. Isophorone	0.92	13.2	19.0	126.2
3. 2,4-Dichlorophenol		12.9	19.7	140.2
4. Quinoline		12.4	19.4	128.1
5. Biphenyl	1.4	13.7	20.5	126.4
6. 1-Chlorododecane	1.2	13.1	19.9	119.4
7. 2,6-di-tert-Butyl-4-methylphenol	1.2	10.5	19.4	96.7
8. 2,4'-Dichlorobiphenyl	1.0	10.3	18.6	109.9
9. Caffeine	0.4	10.0	18.5	166.9
10. 2,2',5,5'-Tetrachlorobiphenyl	1.1	10.1	18.1	115.8
11. Anthraquinone				
12. bis(2-Ethylhexyl)phthalate	1.3	10.2	17.3	101.0

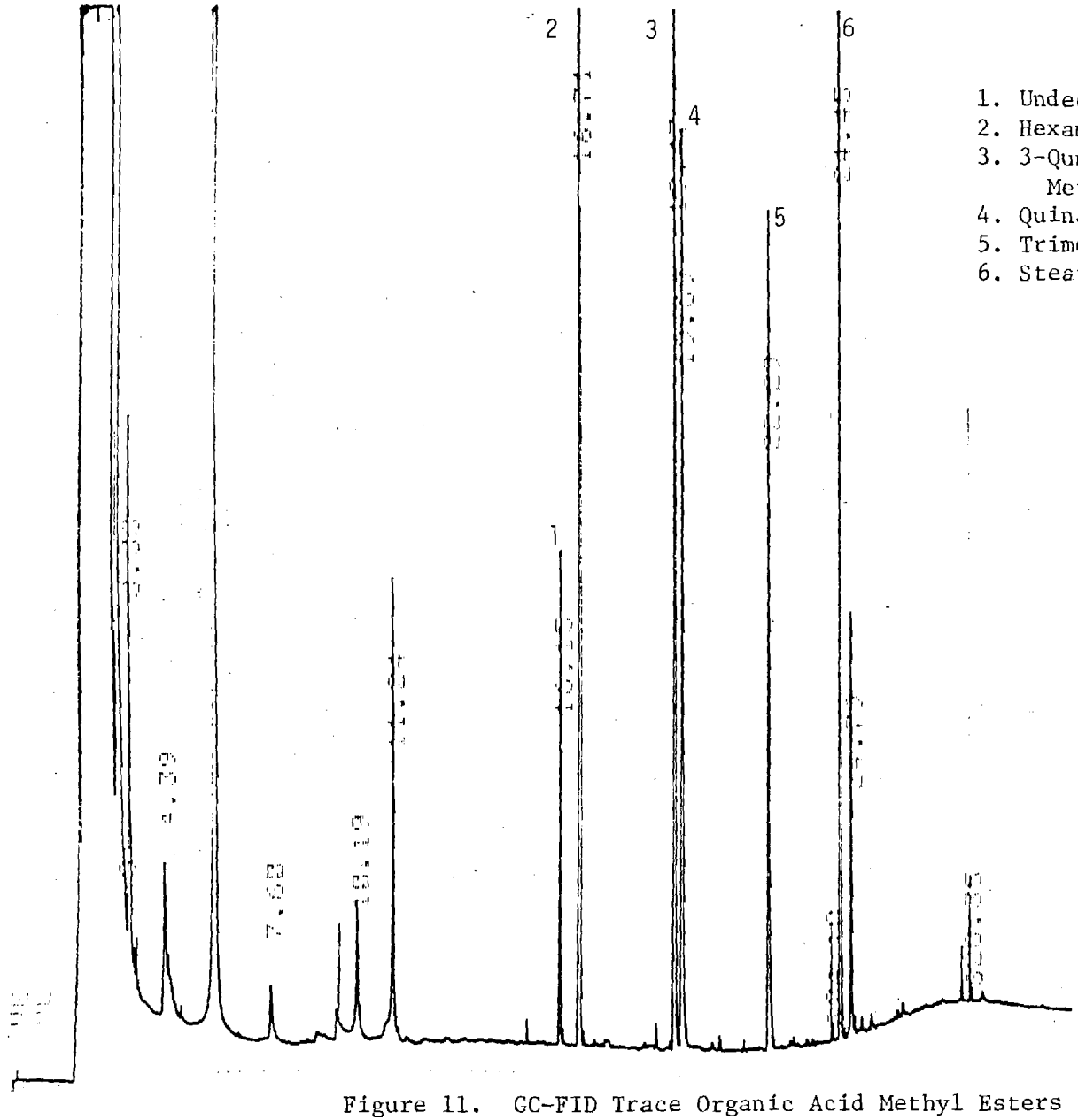
The following 6 model compounds required chemical derivatization before GC analysis: stearic acid, trimesic acid, quinaldic acid, glucose, glycine and 5-chlorouracil. All of these compounds were eluted from the resin by means of aqueous solutions and therefore, before proceeding with chemical derivatization, a solvent exchange from water to an organic solvent was required. The acids were converted to methyl esters by bubbling diazomethane gas through the reactant solution (21). Attempts to isolate the carboxylic acids from aqueous solutions by solvent extraction proved to be unsatisfactory. Stearic acid was quantitatively extracted in ethyl acetate or methylene chloride, whereas trimesic and quinaldic acid, could not be efficiently extracted with any solvent immiscible with water. Therefore, it was decided to dry 1 or 2 mL of aqueous carboxylic acid solutions under a stream of nitrogen at room temperature. The dried sample was redissolved in ether and then derivatized with diazomethane (see Appendix B). This approach was employed to verify the concentrations of acid solution ranging from 10 to 200 μg/mL which was selected by taking into account the final concentration of acids that were expected in the fraction eluted from the resin. This implied that the final volume of the ethereal solution had to be adjusted to 100 μL before GC analysis. Results of the reproducibility and linearity of the sample preparation for the three acids are reported in Table 13. A typical GC-FID trace is shown in Figure 11. Undecanoic acid and 3-quinoline carboxylic acid were used as surrogates at the 50 μg/mL level in order to monitor the behavior of the test compounds during the evaporation and derivatization procedures. A reconstructed ion chromatogram of the carboxylic acid methyl esters is reported in Figure 12. The mass spectra of the carboxylic acid methyl esters are reported in Appendix A (see Figures A-16 through A-20).

Glucose presents a peculiar analytical problem since an equilibrium mixture may contain the α- and β- anomers as well as the ring isomers (pyranose and furanose). Therefore, derivatization and GC of glucose may give as many as 4 peaks in the chromatogram, all of which have to be evaluated for quantitative analysis. Two derivatization methods were pursued during this study. The aqueous solutions were evaporated under a stream of nitrogen, and the dry samples subjected to derivatization by trifluoroacetic anhydride (TFA)(22) and N-methyl-bis-trifluoroacetamide (MBTFA)(23). The initial results however, suffered from poor reproducibility. A GC-ECD trace of a successful glucose derivatization with TFA is presented in Figure 13. The lack of reproducibility, caused by problems in the preparation of glucose derivatives from aqueous solutions, prevented the quantitative assessment of this compound at the required concentration level.

Among the derivatization methods available for the GC analysis of glycine, the preparation of N(O)-heptafluorobutyric isoamyl ester (18) proved to be a reliable method, and thus it was used to assess glycine during the isolation/fractionation scheme study. The reproducibility of the analytical procedure is reported in Table 14. The GC-FID and GC-MS traces are shown in Figures 14 - 15. The mass spectrum is reported in Appendix A (Figure A-21). L-alanine was selected as surrogate to monitor the analytical procedure when analyzing for glycine in the "hydrophilic base" fraction from the isolation/fractionation scheme.

TABLE 13. REPRODUCIBILITY AND LINEARITY RESPONSE FOR STEARIC, TRIMESIC AND QUINALDIC METHYL ESTERS

Trimesic Acid	RT	Area (1)	IS (10 ng) RT	IS (10 ng) Area (2)	Respone = Area (1) / Area (2)	Mean	S
10µg	27.37	1868	20.53	19890	.0939		
	27.36	1851	20.53	21030	.0880	.0920	0.0035
	27.34	1724	20.52	18300	.0942		
50µg	27.33	10730	20.51	17580	.6103		
	27.35	11340	20.53	17660	.6421	.6315	0.0018
	27.34	11500	20.53	17910	.6421		
100µg	27.38	37770	20.53	19240	1.9600		
	27.37	27860	20.53	13390	2.0807	2.0313	0.0632
	27.38	37510	20.53	18270	2.0531		
Stearic Acid	**RT**	**Area (1)**	**RT**	**Area (2)**	**Area (1) / Area (2)**	**Mean**	**S**
10µg	29.99	2664	20.53	14770	.1804		
	29.99	2598	20.54	13660	.1902	.1863	.0052
	29.99	2807	20.54	14910	.1883		
50µg	30.00	18590	20.55	16070	1.1568		
	29.99	17030	20.55	17090	.9965	1.0537	.0895
	30.00	16800	20.54	16670	1.0078		
100µg	30.00	50300	20.53	18140	2.2216		
	30.00	33010	20.53	15560	2.1215	2.1757	.0506
	30.01	33700	20.55	15430	2.1841		
Quinaldic Acid	**RT**	**Area (1)**	**RT**	**Area (2)**	**Area (1) / Area (2)**	**Mean**	**S**
20µg	16.63	825		17890	.046		
	16.64	1029		12790	.080		
	16.62	486		13928	.035	.081	.027
	16.65	1023		9252	.111		
	16.69	932		10728	.087		
50µg	16.66	3871		12990	.298		
200µg	16.66	25815		8212	3.144		



1. Undecanoic Acid Methyl Ester
2. Hexamethylbenzene (I.S.)
3. 3-Qunoline Carboxylic Acid Methyl Ester
4. Quinaldic Acid Methyl Ester
5. Trimesic Acid Methyl Ester
6. Stearic Acid Methyl Ester

Figure 11. GC-FID Trace Organic Acid Methyl Esters

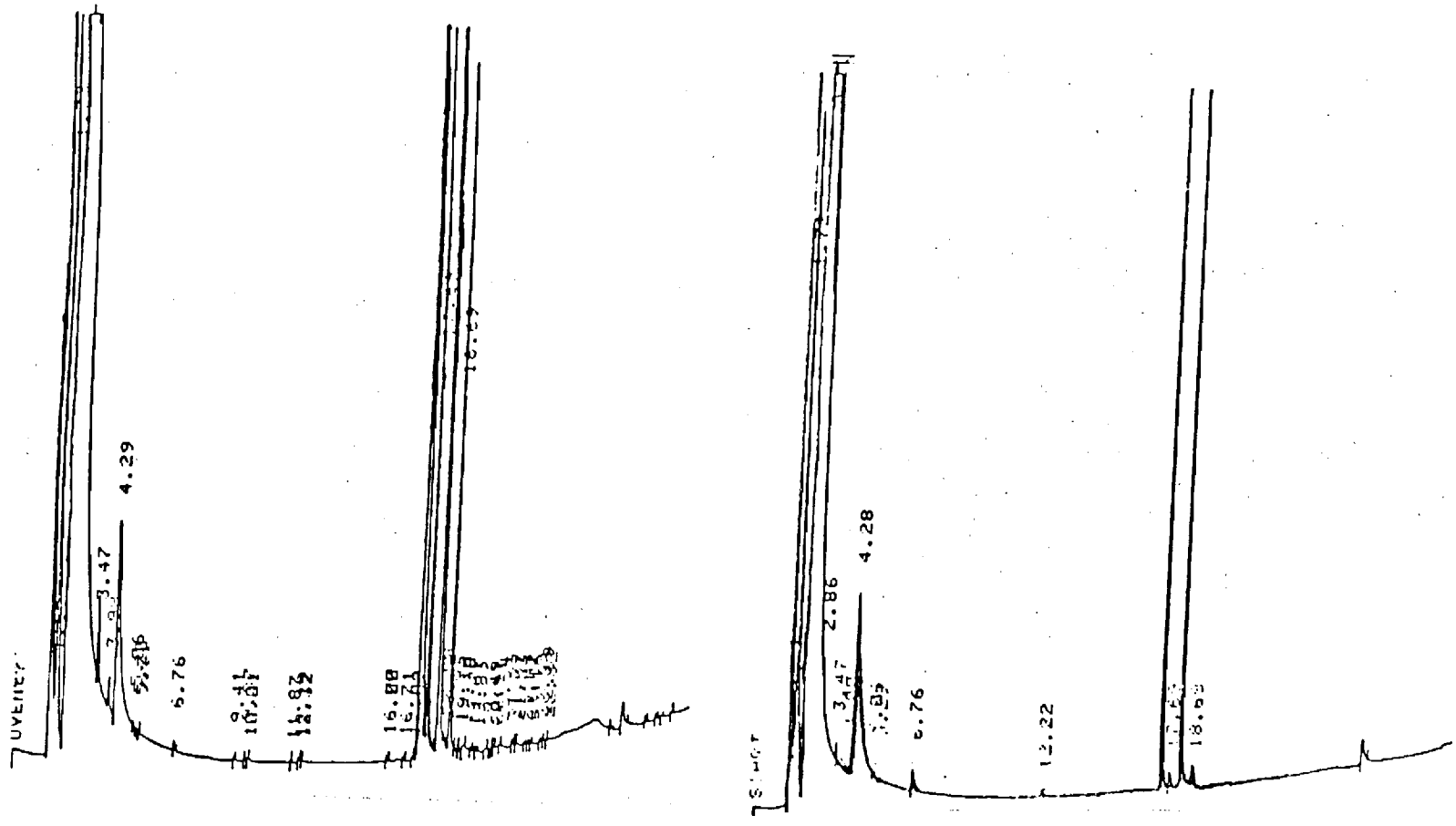
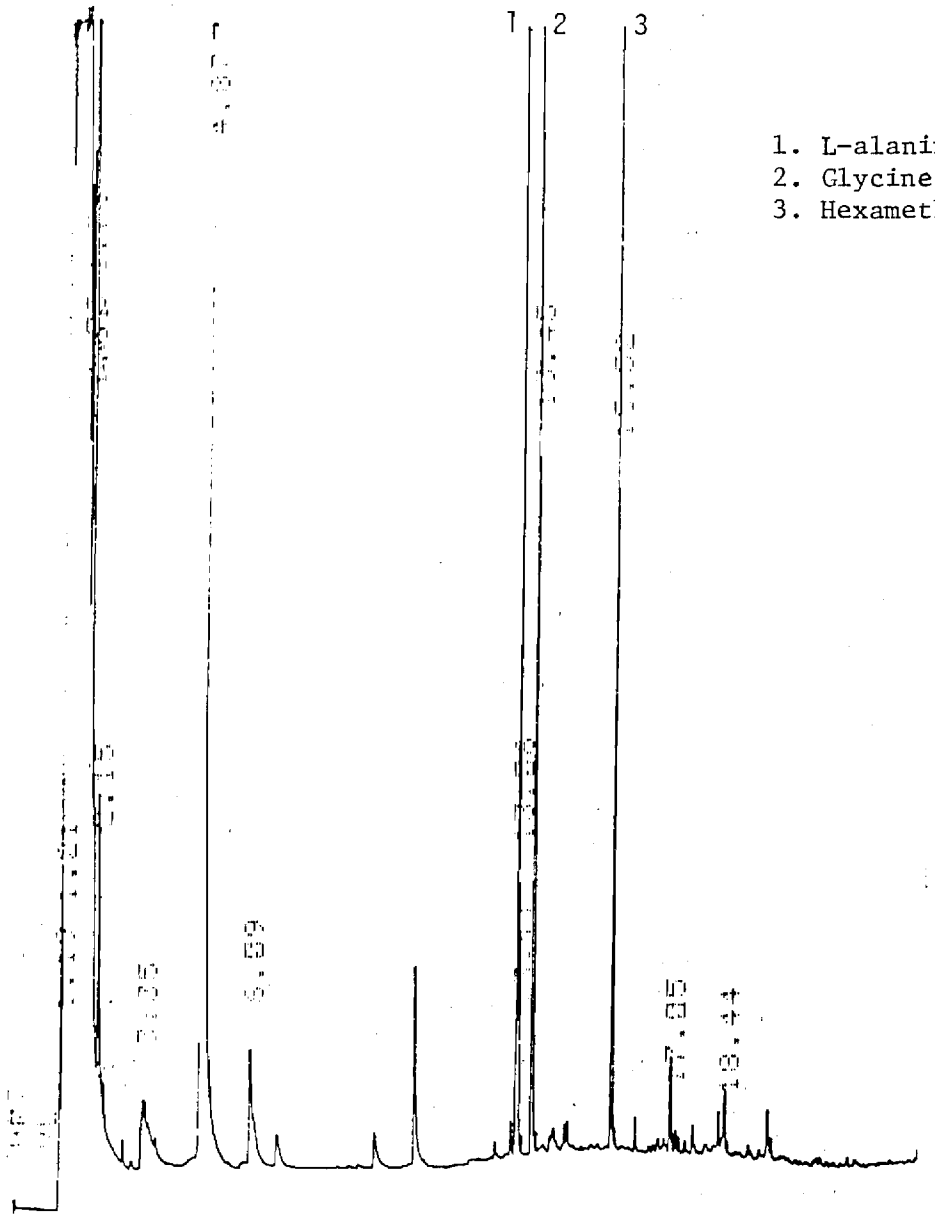


Figure 13. ECD Trace of Penta-(trifluoroacetyl)glucose Split Injection (50:1) 50 ng Left and 5 ng Right

TABLE 14. REPRODUCIBILITY AND LINEARITY OF THE ANALYSIS OF N(O)-HEPTAFLUOROBUTYRYLGLYCINEISOAMYL ESTER

Weight of Glycine (μg)	RT	Area (1)	IS (10ng) RT	IS (10ng) Area (2)	Response = Area (1) / Area (2)	Mean	S
10	10.89	3547	12.09	0868	.5090		
10	10.89	4180	12.03	5833	.7166	.5723	.113
10	10.91	3942	12.11	6532	.5035		
10	10.81	2793	12.09	6070	.4601		
2		106		6112	.0200		
5		554		7126	.0800		
10		1096		5170	.2100		
55		6148		5691	1.0800		



1. L-alanine derivative
2. Glycine derivative
3. Hexamethylbenzene (I.S.)

Figure 14. GC-FID Trace of N-heptafluorobutyric-O-isoamyl Derivatives of L-alanine and Glycine

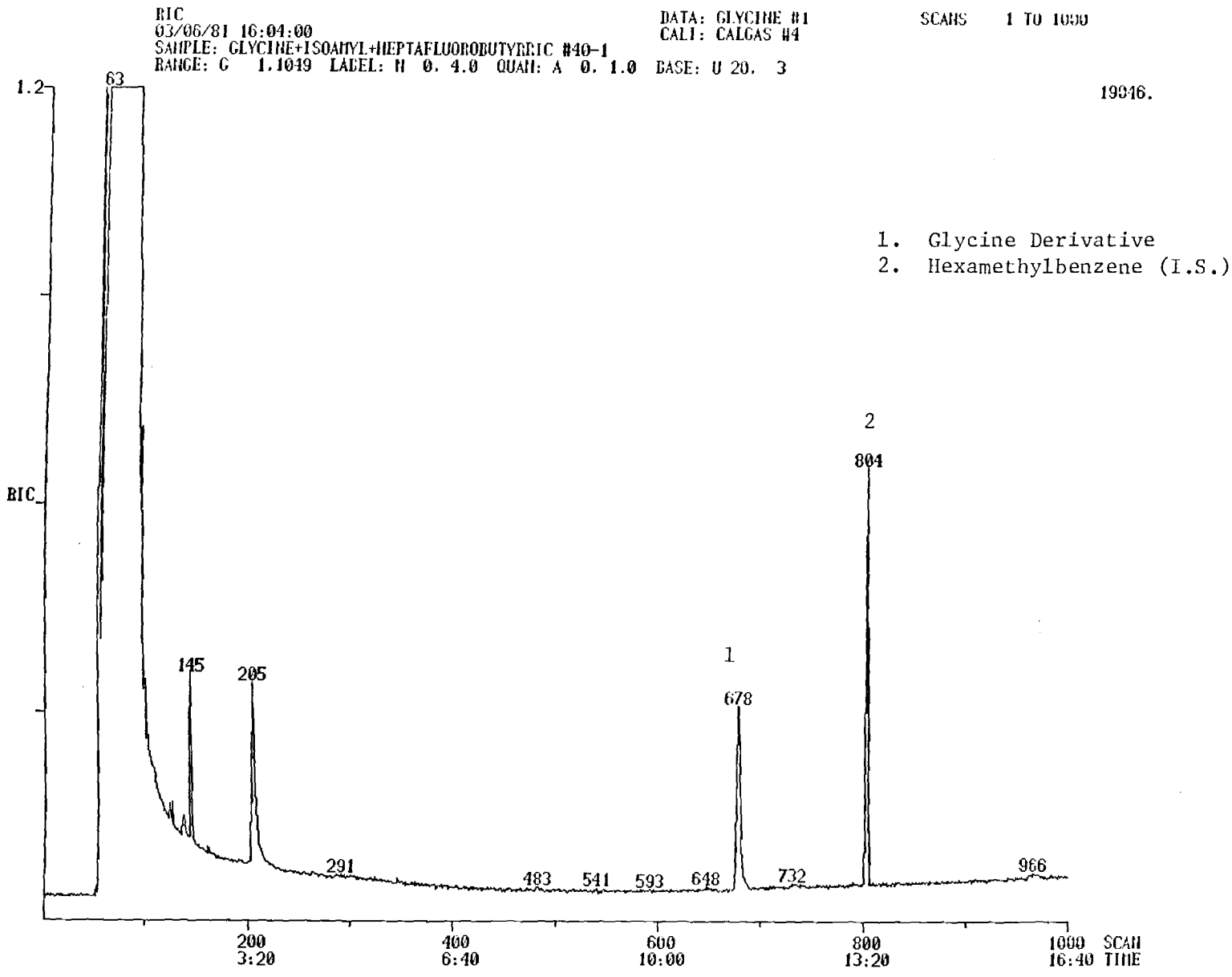


Figure 15. RIC of Glycine Derivative Standard

TABLE 15. REPRODUCIBILITY OF THE ANALYSIS OF QUINOLINE, CAFFEINE, MIBK AND FURFURAL

Compound	% Recovery	Mean % Recovery ($\bar{X}$)	s
MIBK	75.32		
	51.58		
	66.96	71.01	12.25
	79.39		
	81.84		
Furfural	80.73		
	62.83		
	60.5	70.56	8.57
	74.16		
Quinoline	101.4		
	79.6	106.5	20.6
	125.0		
	120.0		
Caffeine	103.4		
	101.2	110.2	9.3
	116.4		
	119.8		

The lack of literature information on the physico-chemical properties of 5-chlorouracil led us to investigate its solubility in several commonly used organic solvents (methanol, acetone, ether, methylene chloride, tetrahydrofuran and acetonitrile). Because of its insolubility in any of the above solvents a decision was made to dissolve it in 2N NH_4OH. As such, it could not be determined whether 5-chlorouracil could be directly chromatographed by GC or whether it required preceding chemical derivatization. The trimethylsilyl derivative was prepared according to Gehrke et al, (24). The FID traces of products from the reaction mixture with and without 5-chlorouracil are shown in Figures 17 and 18 and the mass spectrum of the derivative is presented in Appendix A (Figure A-22). This method proved to be unreliable for trace amounts of 5-chlorouracil since the results lacked accuracy and precision. Therefore, we resorted to HPLC for the analysis of this compound. This approach proved to be satisfactory for the direct analysis of aqueous solutions of 5-chlorouracil. However, the drawback is that this method lacks the confirmation capabilities offered by a GC-MS method.

Some of the model compounds (i.e., quinoline, caffeine, methylisobutylketone, furfural) were assessed in aqueous solutions by solvent extraction with methylene chloride. Results regarding the reporducibility and linearity study are presented in Table 15.

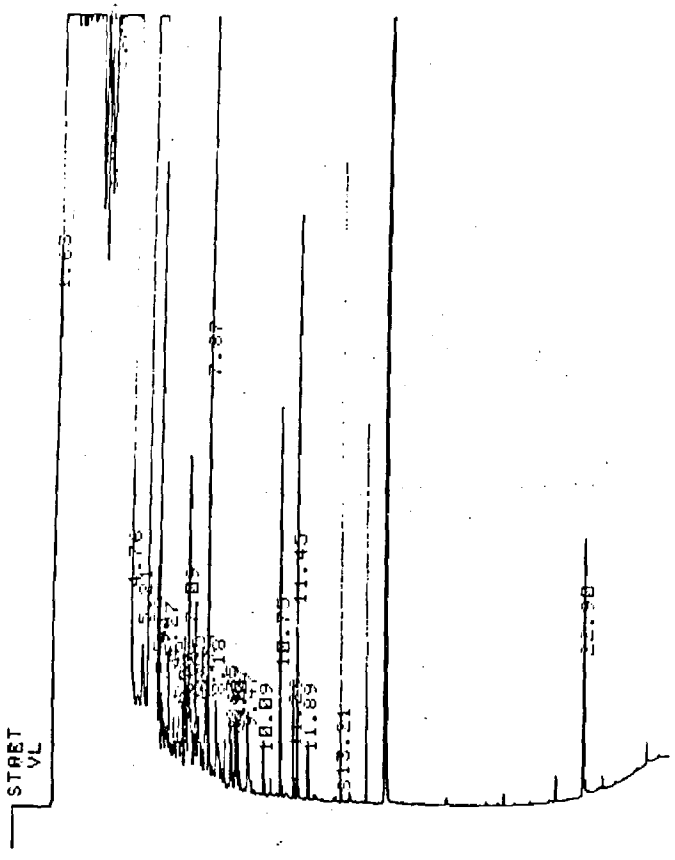
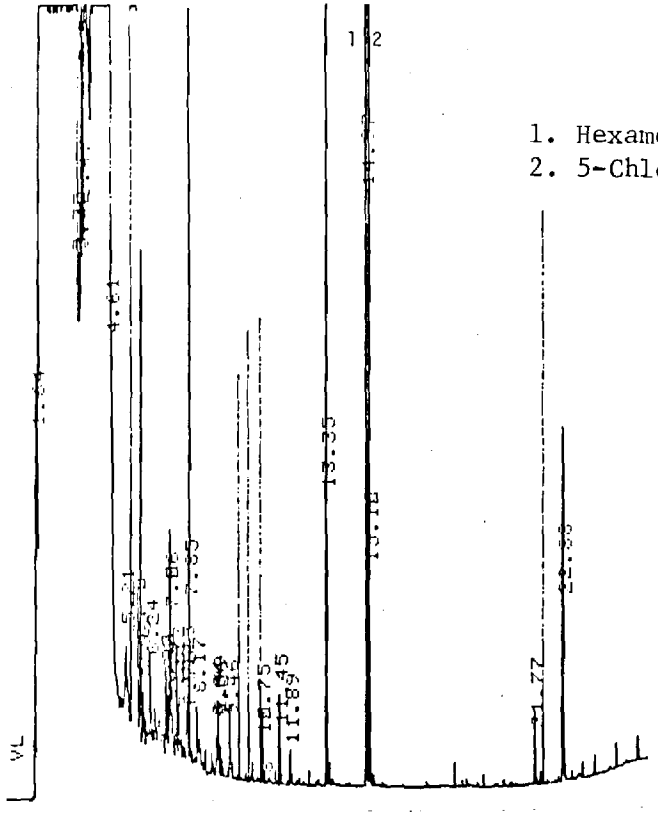


Figure 17. GC-FID Trace of Reaction Mixture Blank



1. Hexamethylbenzene (I.S.)
2. 5-Chlorouracil Derivative

Figure 18. GC-FID Trace of 5-Chlorouracil Trimethylsilyl Derivative

Isolation and Concentration Methods

Although the isolation-fractionation scheme developed in this study was based on adsorption onto resins and carbon, a limited amount of effort was however devoted toward studying the concentration of selected model organic compounds by RO membranes.

The scheme originally proposed included the use of XAD-8 macroreticular adsorbent resin, AG MP-50 cation-exchange resin and Duolite A-7 anion-exchange resin in a sequential order, together with the experimetnal procedures proposed by Leenheer and Huffman (25) and Leenheer (7). Preliminary evaluations of the test solution spiked with all model organics, except humic acid and inorganic salts, revealed complications that ultimately could have affected the recovery of the model compounds.

Precipitates formed when the pH was raised to 10 for the first pass through the XAD-8 resin column. Another serious problem was encountered when a heavy precipitate formed upon addition of NaOH before solvent extraction of quinoline with methylene chloride from the "hydrophobic base" fraction. These problems were apparently caused by the presence of high Ca^{++} concentrations which in alkaline conditions may form insoluble $Ca(OH)_2$.

Several alternatives have been taken to overcome these problems. Desalting of the test solution by reaction with a cation exchange resin (AG 50-X-8, Na^+ form) before processing through the fractionation scheme led to the adsorption of most of the organics, especially biphenyls and 1-chlorododecane which were quantitatively adsorbed (see Table 16). Adjustment of the test solution pH to 7 instead of 10 did not appear to improve the final recovery of quinoline. Addition of NH_4Cl to buffer the solution before adjusting to pH 9 actually increased the ionic concentration without simultaneously increasing the recovery of quinoline. Finally, it was decided to reverse the sequence of adsorption onto XAD-8. The test solution was first adjusted to pH 1.8, to adsorb the "hydrophobic acid" and "hydrophobic neutral" fractions, and then the test solution effluent was adjusted to pH 10 to adsorb the "hydrophobic base" fraction. This approach appeared to eliminate or at least minimize both the turbidity and the precipitate formation and was therefore adopted for our subsequent studies. The original experimental procedures were further modified: soxhlet extraction of the dried resin with methanol for the desorption of the "hydrophobic neutral" fraction was replaced by batch solvent extraction with methylene chloride of the wet XAD-8 resin. A possible increase in organic contaminants extracted from the resin by methylene chloride called for an additional clean-up step of final soxhlet extraction with the same solvent.

The recovery of the model organic compounds with the modified experimental conditions by reversing the sequence of pH of the test solutions is reported in Tables 17 and 18. It is also seen from these tables (Tables 17 and 18) that the presence of inorganic salts has little or no effect on the recovery of the model compounds in the absence of humic acid, except for a marginal effect seen on quinoline. The results obtained in the Duolite anion-exchange fraction (see the "hydrophilic base" fraction in Table 17 and 18) under the conditions investigated in these experiments showed that no model

compounds were recovered in this fraction. It was therefore decided that Duolite be eliminated from the fractionation scheme as originally proposed.

TABLE 16. EFFECT OF INITIAL DESALTING OF TEST SOLUTIONS USING A CATION-EXCHANGE RESIN

Compound	% Passing Resin*
Isophorone	76
2,4-Dichlorophenol	48
Quinoline	14
2,6-di-tert-Butyl-4-methyl phenol	10
Caffeine	96
Anthraquinone	52
bis(2-Ethylhexyl)phthalate	62
Biphenyl	0
1-Chlorododecane	0
2,4'-Dichlorobiphenyl	0
2,2',5,5'-Tetrachlorobiphenyl	0

*Average for two runs

In view of these preliminary data, extensive efforts were then given to investigate the recovery and behavior of the model organic compounds with a further modified scheme employing XAD-8 and AG MP-50 resins (See Figure 19). Six repetitive experiments were then conducted for 500-mL batches of test solution with the following composition: i) 100 ppb each of the organic compounds, except for 2 ppb of phenanthrene; ii) 2 ppm of humic acid; and iii) 70 ppm $NaHCO_3$, 120 ppm $CaSO_4$, 47 ppm $CaCl_2 \cdot 2H_2O$. The solvent extractable compounds (i.e., 2,4-dichlorophenol, isophorone, biphenyl, 1-chlorododecane, 2,6-di-tert-butyl-4-methylphenol, 2,4'-dichlorobiphenyl, 2,2',5,5'-tetrachlorobiphenyl, anthraquinone, phenanthrene, bis-(2-ethylhexyl)phthalate, furfural, quinoline, caffeine and methylisobutylketone) were monitored in every fraction. On the other hand, stearic acid, trimesic acid, quinaldic acid and glycine were monitored only in the expected fractions. The results of the recovery of the model compounds are reported in Tables 19 - 24 and will be discussed later.

TABLE 17. PERCENT RECOVERY OF ORGANIC COMPOUNDS
TEST SOLUTION WITHOUT INORGANIC SALTS

	OA	OB	ON	IB	IA	IN	Total
Stearic acid	20					46	66
Trimesic acid	6					6.4	12.4
2,4-Dichlorophenol	NF	-	-			-	NF
Quinaldic acid					NF	-	NF
Isophorone	-	-	66.5			-	66.5
Biphenyl	-	-	84.8			-	84.8
1-Chlorododecane	-	-	33.8			-	33.8
2,6-ditert-Butyl-4-methyl phenol	-	-	45.4			-	45.4
2,4'-Dichlorobiphenyl	-	-	55.4			-	55.4
Phenanthrene	-	NQ	56.8			-	56.8
Anthraquinone	-	-	49.4			-	49.4
bis(2-Ethylhexyl)phthalate	-	-	13.6			26.1	39.7
Glucose							
Furfural						NF	NF
Quinoline		11.0					11.0
5-Chlorouracil		NF					NF
Caffeine				2.9			2.9
Glycine				55.7			55.7

NF: Not found in the expected fraction
NQ: Not quantified
- : Check but not found

OA: Hydrophobic acid fraction
OB: Hydrophobic base fraction
ON: Hydrophobic neutral fraction
IA: Hydrophilic acid fraction
IB: Hydrophilic base fraction
IN: Hydrophilic neutral fraction

TABLE 18. PERCENT RECOVERY OF ORGANIC COMPOUNDS: TEST SOLUTION WITH ORGANIC SALTS

	OA	OB	ON	IB	IA	IN	Total
Stearic acid	40.5					-	40.5
Trimesic acid	27.6					-	27.6
2,4-Dichlorophenol	NF		-			-	NF
Quinaldic acid					NF	-	NF
Isophorone	-	-	60.5			-	60.5
Biphenyl	-	-	88.7			-	88.7
1-Chlolododecane	-	-	33.7			-	33.7
2,6-di-tert-Butyl-4-methyl phenol	-	-	33.7			-	33.7
2,4'-Dichlorobiphenyl	-	-	47.0			-	47.0
Phenanthrene	10.7	-	50.0			1.8	62.5
Anthraquinone	-	-	40.4			-	40.4
bis(2-Ethylhexyl)phthalate	21.9	-	12.7			13.9	48.5
Glucose							
Furfural						NF	NF
Quinoline		NQ					NQ
5-Chlorouracil		NF					NF
Caffeine				5.0			5.0
Glycine				68.6			68.6

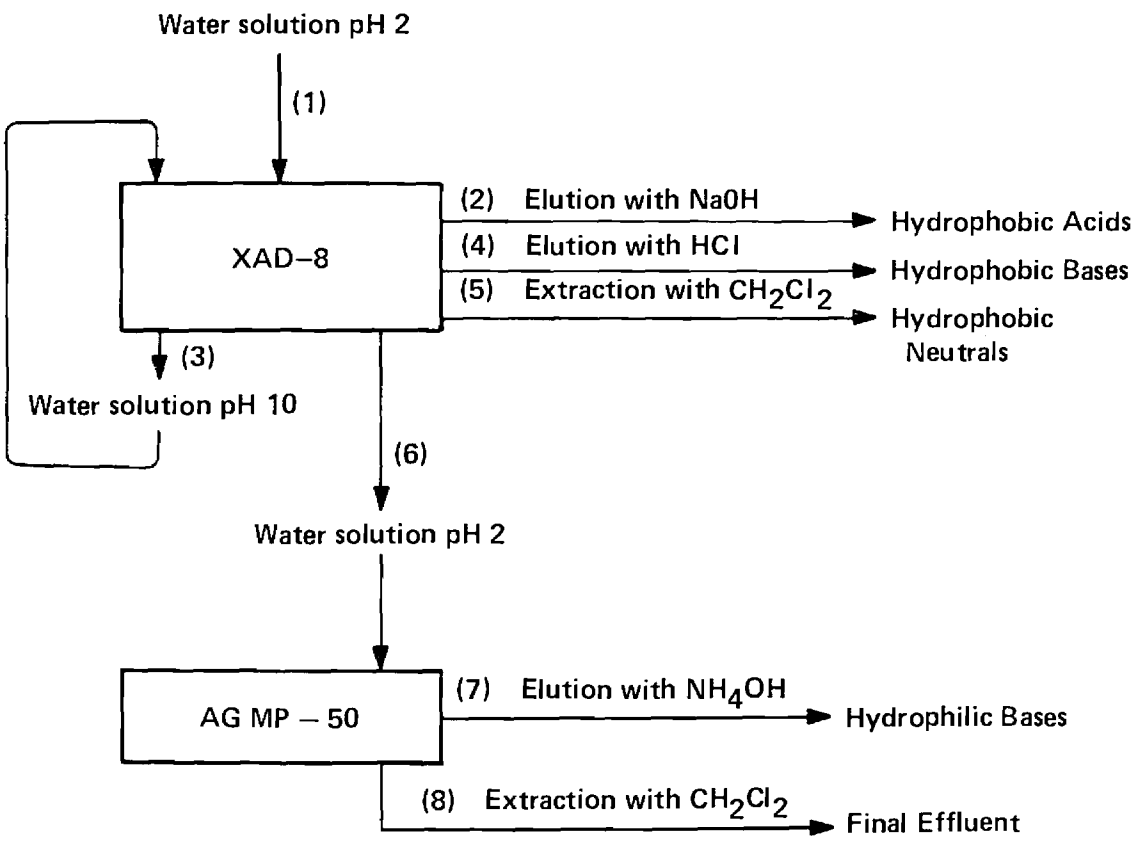


Figure 19. Flow Schematic of Resin Fractionation Scheme at Lab-Scale

TABLE 19. RECOVERY OF ORGANIC COMPOUNDS WITH INORGANIC SALTS AND HUMIC ACIDS ON XAD-8 AND AG MP-50 (Test Solution #1)

	% Recovery					
	OA	OB	ON	IB	EF	Total
Stearic acid	49.1					49.1
Trimesic acid	32.5					32.5
2,4-Dichlorophenol	NF		NQ	NF	29.9	29.9
Quinaldic acid	NF			NQ		NQ
Isophorone		NF	88.2	NF	11.9	100.1
Biphenyl		NF	80.5	NF	NF	80.5
1-Chlorododecane		NF	33.3	NF	0.7	34.0
2,6-ditert-Butyl-4-methyl-phenol		NF	58.5	NF	NF	58.5
2-4'-Dichlorobiophenyl		NF	70.6	NF	NF	70.6
2,2',5,5'-Tetrachloro-biphenyl		NF	30.7	NF	0.4	31.1
Anthraquinone		NF	62.4	NF	0.4	62.8
Phenanthrene		NF	57.5	NF	-	57.5
Bis(2-Ethylhexyl)phthalate		0.5	27.5	2.1	8.1	38.2
Glucose						
Furfural		NF	NF	NF	88.5	88.5
Quinoline		22.6	5.4	NF	NF	28.0
5-Chlorouracil						
Caffeine		NQ	10.4	NQ	29.9	40.3
Glycine				76.3		76.3
Humic acids	88.7					88.7
Chloroform	NS					
MIBK	NS					

NF = Not found
NQ = Found but not quantified
NS = Not spiked

OA = Hydrophobic acid
OB = Hydrophobic base
ON = Hydrophobic neutral
IF = Hydrophilic base
IB = Hydrophilic base
EF = Final effluent (Solvent Extraction)

TABLE 20. RECOVERY OF ORGANIC COMPOUNDS WITH INORGANIC SALTS AND HUMIC ACIDS ON XAD-8 AND AG MP-50 (Test Solution #2)

	% Recovery					
	OA	OB	ON	IB	EF	TOTAL
Stearic acid	32.2					32.2
Trimesic acid	NQ					NQ
2,4-Dichlorophenol	NF		NF	NQ	43.8	43.8
Quinaldic acid	NF			NQ		NQ
Isophorone		NQ	92.9	NF	12.0	104.9
Biphenyl		NF	84.6	NF	NF	84.6
1-Chlorododecane		NF	40.0	NF	0.5	40.5
2,6-ditert-Butyl-4-methyl-phenol		NF	59.6	NF	NF	59.6
2,4'-Dichlorobiphenyl		NF	72.3	NF	NF	72.3
2,2',5,5'-Tetrachloro-biphenyl		NF	32.9	NF	NF	32.9
Anthraquinone		NF	81.8	NF	NF	81.8
Phenanthrene		NF	45.0	NF	NF	45.0
bis(2-Ethylhexyl)phthalate		0.6	48.6	1.3	3.8	54.3
Glucose						
Furfural		NF	NQ	NF	91.1	91.1
Quinoline		22.7	8.1	NQ	NF	30.8
5-Chlorouracil						
Caffeine		NQ	13.1	NQ	32.4	46.1
Glycine				62.5		62.5
Humic acids	73.1					73.1
Chloroform	NS					
MIBK	NS					

TABLE 21. RECOVERY OF ORGANIC COMPOUNDS WITH INORGANIC SALTS AND HUMIC ACIDS ON XAD-8 AND AG MP-50 (Test Solution #3)

	% Recovery					
	OA	OB	ON	IB	EF	Total
Stearic acid						
Trimesic acid						
2,4-Dichlorophenol		NF	1.2	12.4	30.0	43.6
Quinaldic acid						
Isophorone		NF	92.0	NF	9.2	101.2
Biphenyl		NF	93.0	NF	0.4	93.4
1-Chlorododecane		NF	31.1	NF	0.9	32.0
2,6-ditert-Butyl-4-methyl-phenol		NF	45.6	NF	NF	45.6
2-4'-Dichlorobiphenyl		NF	81.1	NF	NF	81.1
2,2',5,5'-Tetrachloro-biphenyl		NF	28.6	NF	NF	28.6
Anthraquinone		NF	47.4	NF	0.5	47.9
Phenanthrene		NF	119.6	NF	NF	119.6
bis(2-Ethylhexyl)phthalate		NQ	32.7	1.2	13.3	47.2
Glucose						
Furfural		NF	NF	NF	86.7	86.7
Quinoline		18.1	2.5	NF	NF	20.6
5-Chlorouracil		20.0				20.0
Caffeine		NQ	26.1	2.2	27.0	55.3
Glycine						
Humic acids	82.2					82.2
Chloroform		NS				
MIBK		NS				

TABLE 22. RECOVERY OF ORGANIC COMPOUNDS WITH INORGANIC SALTS AND HUMIC ACIDS ON XAD-8 AG MP-50 (Test Solution #4)

	% Recovery					
	OA	OB	ON	IB	EF	Total
Stearic acid						
Trimesic acid						
2,4-Dichlorophenol		NF	NQ	30.0	27.3	57.3
Quinaldic acid						
Isophorone		NQ	96.5	NF	1.1	97.6
Biphenyl		NF	76.3	NF	NQ	76.3
1-Chlorododecane		NF	21.7	NF	NF	21.7
2,6-ditert-Butyl-4-methyl-phenol		NF	36.5	NF	NF	36.5
2-4'-Dichlorobiphenyl		NF	66.7	NF	NF	66.7
2,2',5,5'- Tetrachloro-biphenyl		NF	28.6	NF	NF	28.6
Anthraquinone		NF	45.0	NF	NF	45.0
Phenanthrene		NF	101.2	NF	NF	101.2
bis (2-Ethylhexyl)phthlate		NQ	32.7	4.7	11.5	48.9
Glucose						
Furfural		NF	NF	NF	63.1	63.1
Quinoline		23.1	4.5	NF	NF	27.6
5-Chlorouracil		10.0				10.0
Caffeine		NQ	17.8	5.3	26.9	50.0
Glycine				NQ		
Humic acids	89.6					89.6
Chloroform						
MIBK						

TABLE 23. RECOVERY OF ORGANIC COMPOUNDS WITH INORGANIC SALTS AND HUMIC ACIDS ON XAD-8 AG MP-50 (Test Solution #5)

	% Recovery					
	OA	OB	ON	IB	EF	Total
Stearic acid	15.8					15.8
Trimesic acid	15.1					15.1
2,4-Dichlorophenol		NF	NF	6.6	22.8	29.4
Quinaldic acid						
Isophorone		NQ	56.5	NF	22.9	79.4
Biphenyl		NF	79.4	NF	NF	79.4
1-Chlorododecane		NF	37.6	NF	NF	37.6
2,6-ditert-Butyl-4-methyl phenol		NF	48.7	NF	NF	48.7
2-4'-Dichlorobiphenyl		NF	77.7	NF	NF	77.7
2,2',5,5'-Tetrachloro-biphenyl		NF	69.9	NF	NF	69.9
Anthraquinone		NF	55.1	NF	NF	55.1
Phenanthrene		NF	70.7	NF	NF	70.7
bis (2-Ethylhexyl)phthalate		3.5	40.9	NF	NQ	44.4
Glucose						
Furfural		NF		NF	6.8	6.8
Quinoline		37.9	6.6	NF	NF	44.5
5-Chlorouracil		NQ				
Caffeine		NF	16.6	NQ	18.6	35.2
Glycine				57.6		57.6
Humic acids	88.2					88.2
Chloroform	NS					
MIBK		NF	NF	NF	NF	

TABLE 24. RECOVERY OF ORGANIC COMPOUNDS WITH INORGANIC SALTS AND HUMIC ACIDS ON XAD-8 AG MP-50 (Test Solution #6)

	% Recovery					
	OA	OB	ON	IB	EF	Total
Stearic acid						
Trimesic acid						
2,4-Dichlorophenol		NF	NF	6.2	26.8	33.0
Quinaldic acid						
Isophorone		NQ	57.5	NF	25.1	82.6
Biphenyl		NF	82.5	NF	NF	82.5
1-Chlorododecane		NF	39.0	NF	NF	39.0
2,6-di-tert-Butyl-4-methyl phenol		NF	52.5	NF	NF	52.5
2,4'-Dichlorobiphenyl		NF	76.9	NF	NF	76.9
2,2',5,5'-Tetrachloro-biphenyl		NF	75.7	NF	NF	75.7
Anthraquinone		NF	56.1	NF	NF	56.1
Phenanthrene		NF	73.0	NF	NF	73.0
bis(2-Ethylhexyl)phthalate		2.7	43.3	NF	NQ	46.0
Glucose						
Furfural		NF	NF	NF	10.2	10.2
Quinoline		8.6	4.3	NF	NF	12.9
5-Chlorouracil		NQ				
Caffeine		NF	14.2	NF	16.8	31.0
Glycine				29.6		29.6
Humic acids	89.0					89.0
Chloroform	NS					
MIBK		NF	NF	NF	NF	

Based on adsorption studies on Carbopack B (11) experiments were conducted to investigate the effectiveness of this material in recovering model compounds (i.e., 2,4,-dichlorophenol, isophorone, bis(2-ehtylhexyl)phthalate, caffeine) that showed partial or no adsorption onto the XAD-8 and AG MP-50. Two 500-mL batches of test solution containing selected model organics at 100 μg/L level and pH 7 were evaluated with the use of Carbopack B in the absence of humic acid and inorganic salts. The behavior and recoveries of these model organics are reported in Table 25. These data demonstrated the adsorptive effectiveness of this material toward adsorbing several model compounds, and prompted us to include a Carbopack B column into the isolation/fractionation scheme used for the evaluation of 500 liters of test solutions (see Figure 6).

TABLE 25. RECOVERY OF MODEL COMPOUNDS ON CARBOPACK B

Compound	Desorbed From GCB	Extracted from water after GCB
2,4-Dichlorophenol	115.2	NF
Quinoline	97.5	NF
Isophorone	16.3	92.4
1-Chlorododecane	51.2	NF
2,4'-Dichlorobiphenyl	48.6	0.9
2,2',5,5'-Tetrachlorobiphenyl	54.1	3.7
Anthraquinone	92.1	NF
bis-(2-Ethylhexyl)phthalate	51.1	64.3
Phenanthrene	114.0	NF
Caffeine	92.1	NF
Furfural	NF	26.0
MIBK	6.7	65.5

NF = Not found

The effects of an aqueous chlorine residual on the materials used in the fractionation scheme (i.e., XAD-8, AG MP-50) were evaluated by processing a 2 ppm aqueous chlorine solution under experimental conditions identical to the fractionation runs. The following experiments were conducted: i) "OFW" and glassware blank; ii) "OFW" and resin blank; iii) 2 ppm chlorine solution

and glassware; iv) 2 ppm chlorine solution at pH 2 and resins; and v) 2 ppm chlorine solution at pH 10 and resins. The experimental sequence and the fractions monitored are schematically represented in Figure 20. No GC-FID detectable artifacts were produced under any of the above experimental conditions.

In order to estimate the amount of adsorbent required to process 500 liters of water, two 2 liter test solutions were evaluated under each pH adsorption condition. In the first experiment, 2 liters of test solution were adjsuted to pH 2 and passed through a XAD-8 column (resin bed volume 9 ml) at a flow rate of 166 mL/hr. The composition was as follows:

Stearic acid	50 ppb
Trimesic acid	50 ppb
Isophorone	50 ppb
Biphenyl	50 ppb
2,6-di-tert-Butyl-4-methyl-phenol	50 ppb
2,4'-Dichlorobiphenyl	50 ppb
Anthraquinone	50 ppb
bis-(2-Ethylhexyl)phthalate	50 ppb
Chloroform	50 ppb
MIBK	50 ppb
1-Chlorododecane	5 ppb
2,2',5,5'-Tetrachlorobiphenyl	5 ppb
Phenanthrene	0.5 ppb
Humic acid	2000 ppb

Twenty-mL fractions were collected and their absorbance measured at 254 nm. The results shown in Figure 21 appeared to indicate that an initial breakthrough occurs after approximately 40-50 bed volumes. After that a continuous raising in the absorbance values is observed which suggest a continuing elution of model organics with strong absorbance capacity at 254 nm. In an attempt to confirm these findings and to single out the breakthrough characteristic of the individual model organics, 20-ml fractions were combined in sequential order into 5 major aliquots as follows: 1) first 30-bed volume aliquot; 2) second 30-bed volume aliquot; 3) and 4) third and fourth 50-bed volume aliquots; and 5) remaining effluent. Each aliquot was extracted with methylene chloride, followed by GC-FID analysis. The acids (i.e., trimesic and stearic acid) were assessed by solvent exchange to ether, derivatization by diazomethane and GC-FID analysis (see Appendix B). The results of this evaluation, reported in Table 26, confirmed that bis-(2-ethylhexyl)phthalate was found in the second 30-bed volume aliquot and continued to be detected in the following aliquots. Furthermore, isophorone appeared in the third 50-bed volume aliquot and trimesic acid was found in the fourth 50-bed volume aliquot.

In the second breakthrough experiment, 2 liters of test solution were adjusted to pH 10 and processed through a XAD-8 column (resin bed volume 10.5 ml) at a flow rate of 166 mL/hr. The composition was as follows:

Isophorone	50 ppb
Biphenyl	50 ppb

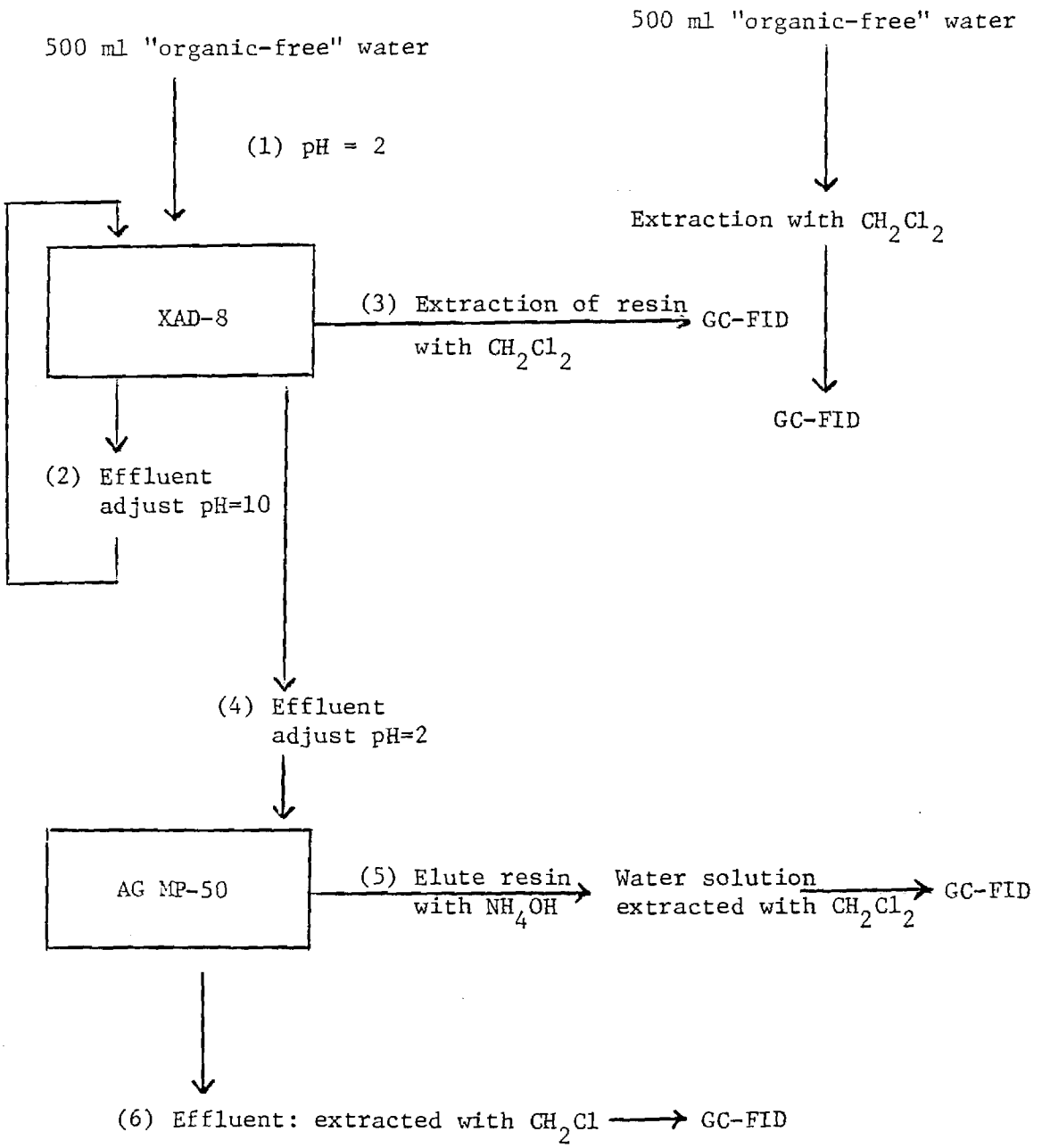


Figure 20. Experimental sequence for the chlorine residual study.

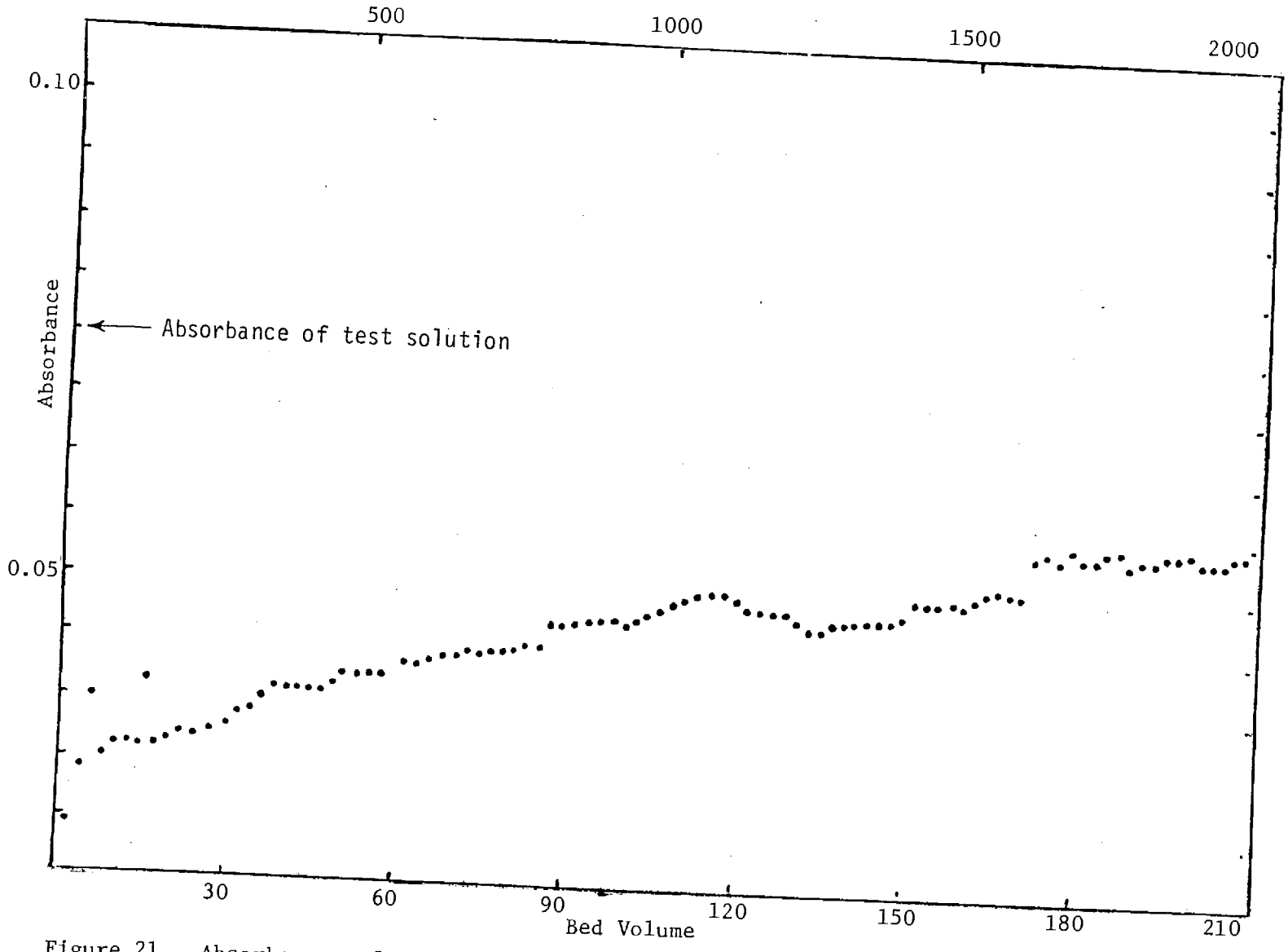


Figure 21. Absorbsance of each 20-mL fraction (Test Solution pH 2).

TABLE 26. BREAKTHROUGH OF EACH ORGANIC COMPOUND (Test Solution pH 2)

Compounds	Total Amount of Components (μg/2L)	Found in each fraction (μg)					
		30 bed vol. (0-290 mL)	30 bed vol. (290-580 mL)	50 bed vol. (580-1060 mL)	50 bed vol. (1060-1540 mL)	Final Vol. (1540-2000 mL)	Total Found (μg)
Isophorone	100	-	-	23.28	47.81	78.14	149.23
Biphenyl	100	-	-	-	-	0.72	0.72
1-Chlorododecane	10	-	-	-	-	0.10	0.19
2,6-di-tert-Butyl-methyl-phenol			-				
2,4'-Dichlorobiphenyl	100	-	-	-	-	-	-
Phenanthrene	1	-	-	-	-	-	-
2,2'-5,5'-Tetrachlorobiophenol	10	-	-	-	-	-	-
Anthraquinone	100	-	-	-	-	0.12	0.12
bis(2-Ethylhexyl)phthalate	100	-	3.28	7.60	7.20	9.57	27.65
Trimesic acid	100	-	-	-	3.97	33.07	37.04
Steric acid	100	-	-	-	-	22.51	22.51

2,6-di-tert-Butyl-4-methyl-phenol	50 ppb
2,4'-Dichlorobiphenyl	50 ppb
Anthraquinone	50 ppb
Quinoline	50 ppb
Caffeine	50 ppb
5-Chlorouracil	5 ppb
2,2',5,5'-Tetrachlorobiphenyl	5 ppb
Phenanthrene	0.5 ppb

The same monitoring program, as used in the first breakthrough experiment, was carried out for this test solution. The results of this evaluation, presented in Figure 22 and Table 27, indicated that an early breakthrough occurred and caffeine was specifically identified as the model compound which was not efficiently retained. Breakthrough of isophorone and quinoline were found in the third 50-bed volume aliquot.

A third experiment was performed for the breakthrough evaluation of AG MP-50 with a 2-liter test solution having the following composition:

Caffeine	50 ppb
Glycine	50 ppb
Quinaldic acid	50 ppb
$NaHCO_3$	70 ppm
$CaSO_4$	120 ppm
$CaCl_2 \cdot 2H_2O$	47 ppm

The test solution was acidified to pH 2 and passed through an AG MP-50 column (resin bed volume 11 ml) at a flow rate of 166 mL/hr. Since the absorbance at 254 nm of these compounds was too low, no spectrophotometric monitoring was possible. The effluent was divided into 5 fractions, according to the previous experiments, and analyzed for each specific compound. Caffeine was solvent extracted with methylene chloride and analyzed by GC-FID. Glycine and quinaldic acid were analyzed according to the procedures described in the experimental protocol (see Appendix B). The results, reported in Table 28 confirmed the early breakthrough of caffeine. This was followed by quinaldic acid which was found in the third 50-bed volume aliquot. The overall breakthrough study was then utilized to estimate the volume of resins needed to process 500 liters of test solution. The resin bed volumes were calculated from the breakthrough volumes of bis-(2-ethylhexyl)phthalate and quinaldic acid respectively, for XAD-8 and AG MP-50. It was found that 10 liters of each resin type were needed.

The investigation of the membrane rejection of MIBK and furfural was carried out with two RO modules using approximately forty liters of aqueous solution. A "system blank" was also performed with both modules by analyzing the permeate collected after thirty minutes of operation. No interferences or the presence of major artifacts were noted as evidenced by their FID traces. The feed solutions (500 ppb) of the model compounds was prepared by diluting an appropriate amount of methanol stock solution (500 ppm) into water. Since the water held up in the RO system would have an effect on diluting the feed solution, the system was operated for twenty minutes

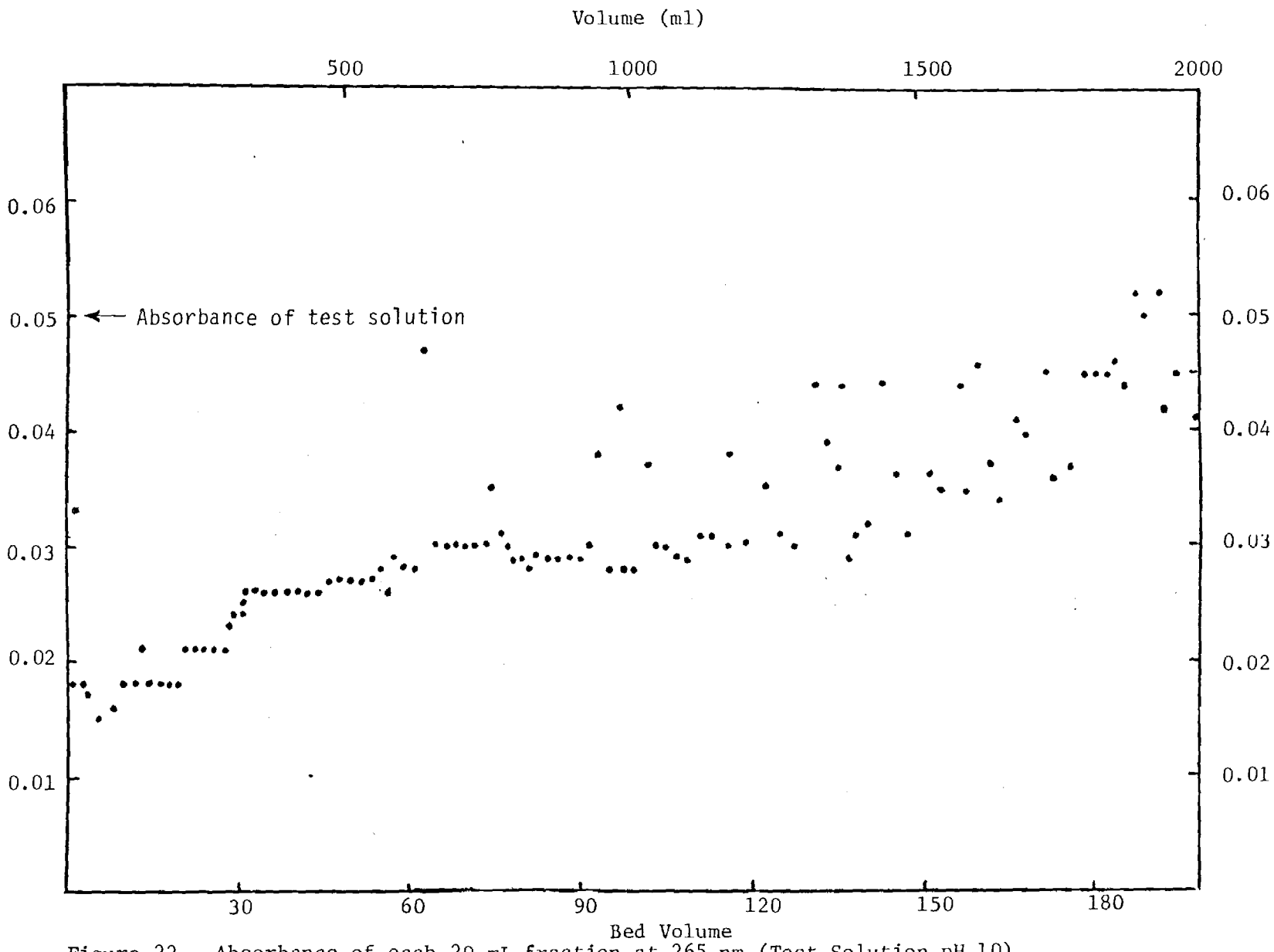


Figure 22. Absorbance of each 20-mL fraction at 265 nm (Test Solution pH 10).

TABLE 27. BREAKTHROUGH OF EACH ORGANIC COMPOUND (Test SOlution pH 10)

Compounds	Total Amount of Components (μg/2L)	Found in each fraction (μg)					
		30 bed vol. (0-290 mL)	30 bed vol. (290-580 mL)	50 bed vol. (580-1060 mL)	50 bed vol. (1060-1540 mL)	Final Vol. (1540-2000 mL)	Total Found (μg)
Isophorone	100	-	-	35.19	37.63	42.37	115.19
Quinoline	100	-	-	0.52	14.47	23.23	38.22
Biphenyl	100	-	-	-	-	-	-
1-Chlorododecane	10	-	-	-	-	-	-
2,6-di-tert-Butyl-4-methyl-phenol							-
2,4'-Dichlorobiphenyl	100	-	-	-	-	-	-
Phenanthrene	1	-	-	-	-	-	-
Caffeine	100	6.24	14.14	18.36	20.56	17.27	76.57
2,2',5,5'-Tetrachlorobi-phenyl	10	-		-	-	0.08	0.08
bis(2-Ethylhexyl)phthalate							-
Anthraquinone	100	0	-	-	-	-	-

TABLE 28. BREAKTHROUGH OF SELECTED ORGANIC COMPOUNDS ON AG MP-50 (Test Solution pH 2)

Compounds	Total Amount of Components (μg/2L)	Found in each fraction (μg)					
		30 bed vol. (1-290 mL)	30 bed vol. (290-580 mL)	50 bed vol. (580-1060 mL)	50 bed vol. (1060-1540 mL)	Final Vol. (1540-2000 mL)	Total Found (μg)
Caffeine	100	7.68	8.92	12.93	14.26	9.46	53.25
Glycine	100	-	-	-	-	-	-
Quinaldic acid	100	-	-	3.83	16.21	-	20.04

(pressure 600 psig, flow rate 250 gph) prior to taking an aliquot of the feed solution (250 mL) for the determination of the concentration of the model compounds. The RO experiment was conducted for thirty more minutes before a permeate aliquot (250 mL) was collected for analysis. The results of membrane rejection with the two RO modules are reported in Tables 29 and 30. The percent rejection (R) were calculated using the following equation.

$$R(\%) = (1 - \frac{C_P}{C_B}) \times 100$$

R = rejection %

C_P = concentration of model compound in permeate

C_B = concentration of model compound in feed.

TABLE 29. PERFORMANCE OF B-10 RO MODULE

Compound	Feed Concentration (ppb)	Permeate Concentration (ppb)	Rejection %
MIBK	195.68	4.04	97.9
Furfural	231.16	36.28	84.3

TABLE 30. PERFORMANCE OF TFC-4400 PA MODULE

Compound	Feed Concentration (ppb)	Permeate Concentration (ppb)	Rejection %
MIBK	162.88	85.64	48.7
Furfural	832.27	454.6	45.4

Pilot-Scale Study

A total volume of 500 liters of test solution, which contained all model organic compounds and inorganic salts, was employed for the final evaluation of the isolation-fractionation scheme. The overall process was carried out in five equal volumes of test solutions (5 X 100 liters) so that a statistically meaningful data base could be established for the calculation of recovery of the model compounds. The difficulties encountered during the bench-scale experiments owing to the presence of inorganic salts (i.e., $NaHCO_3$, $CaSO_4$, $CaCl_2 \cdot 2H_2O$) was confirmed. A highly turbid solution was formed upon the addition of the salts to the 40 liters of "OFW" at pH 7. Moreover, some undissolved salts settled out at the bottom of the feeding reservoir. Only after a pH adjustment with HCl to 2, the turbidity disappeared, and some of the undissolved salts went back into solution. Therefore, the 40-liter test solutions were prepared by first acidifying the "OFW", then adding the inorganic salts and finally the model organic compounds. Humic acid was the last component to be added. This approach provided a clear and apparently homogeneous test solution, and eliminated the subsequent pH adjustment required for the first process of passing the solution through the XAD-8 resin column. The adverse effects of adding inorganic salts and humic acid on solution homogeneity, however, appeared again during the second step of the fractionation scheme, while adjusting the pH of the first column effluent to 10. The addition of NaOH produced a "cloudy" solution, which became more evident as the amount of humic acid that broke through the first XAD-8 column increased. Although the small amount of humic acid added to the solution should be soluble in aqueous solutions under alkaline condition, the presence of an inorganic solid phase in suspension may serve as nuclei to induce precipitation of this substance. The most obvious effect of precipitation of humics involved a decrease of the solution flow rate through the second XAD-8 resin column and an accumulation of a brown precipitate throughout the top 1/2 cm of the resin bed. Attempts were made to restore the original flow rate conditions by stirring the solution immediately above the resin bed to break up the precipitate. This, however, only decreased the flow since once the precipitate was dispersed it traveled down the column and deposited on the glass frit at the bottom of the column. The best alternative found was to leave the resin bed undistrubed while processing the entire 100 liters of test solution. The decreased flow rate that was experienced using this approach was as much as one half of the original. The AG MP-50 and the Carbopack B columns did not present any operational difficulties.

A mass balance of the solvent extractable compounds was made by analyzing all of the isolated fractions. The results of the percent recovery of the organics on the pilot-scale study are reported in Tables 31-35 and will be discussed later.

Artifacts and Contaminants

An examination of the FID traces of the isolated fractions revealed the presence of organics other than the model compounds added to the test solutions. The "hydrophobic neutral" fractions presented a relatively higher level of contamination. In order to confirm the origin of these contaminants

TABLE 31. PILOT-SCALE STUDY (FIRST 100 L Batch)

	% Recovery				
	OA	OB	ON	IB	GCB
Stearic acid	2.7				
Trimesic acid	75.8				
2,4-dichlorophenol	24.3	-	-	-	-
Quinaldic acid				NQ	
Isophorone	-	-	34.4	-	5.5
Biphenyl	-	-	45.8	-	-
1-Chlorododecane	-	-	98.4	-	-
2,6-di-tert-Butyl-4-methylphenol	-	-	1.2	-	-
2,4'-Dichlorobiphenyl	-	-	58.3	-	-
2,2',5,5'-Tetrachlorobiphenyl	-	-	39.7	-	-
Anthraquinone	-	-	45.2	-	0.2
Phenanthrene	-	-	30.0	-	-
bis(2-Ethylhexyl)phthalate	1.1	-	52.2	-	0.4
Glucose					
Furfural	-	-	-	-	-
Quinoline	-	30.4	-	-	-
5-Chlorouracil				17.0	
Caffeine	-	-	-	-	4,2
Clycine				7.4	
Humic acids	41.3				
Chloroform					
MIBK	-	-	-	-	-

NQ = Found but not quantitated
- = Checked but not found
OA = Hydrophobic Acid (XAD-8)
OB = Hydrophobic Base (XAD-8)
ON = Hydrophobic Neutral (XAD-8)
IB = Hydrophilic Base (AG MP-50)
GCB= Carbopack B

TABLE 32. PILOT-SCALE STUDY (SECOND 100 L BATCH)

	% Recovery				
	OA	OB	ON	IB	GCB
Stearic acid	23.8				
Trimesic acid	23.2				
2,4-Dichlorophenol	-	-	15.8	-	5.9
Quinaldic acid				NQ	
Isophorone	-	-	36.8	-	4.4
Biphenyl	-	-	38.2	-	-
1-Chlorododecane	-	-	97.8	-	-
2,6-di-tert-Butyl-4-methylphenol	-	-	2.1	-	-
2,4'-Dichlorobiphenyl	-	-	74.8	-	-
2,2',5,5'-Tetrachlorobiphenyl	-	-	67.1	-	-
Anthraquinone	-	-	42.5	-	0.7
Phenanthrene	-	-	47.5	-	-
bis(2-Ethylhexyl)phthalate	-	0.4	71.9	0.2	1.5
Glucose					
Furfural	-	-	-	-	-
Quinoline	-	93.2	-	-	-
5-Chlorouracil				32.1	
Caffeine	-	-	-	-	71.5
Glycine				5.6	
Humic acids	29.8				
Chloroform					
MIBK	-	-	-	-	-

TABLE 33. PILOT-SCALE STUDY (THIRD 100 L BATCH)

	OA	OB	ON	IB	GCB
Stearic acid	5.3				
Trimesic acid	57.0				
2,4-Dichlorophenol	-	-	1.1	-	
Quinaldic acid					
Isophorone	-	-	42.9	-	4.0
Biphenyl	-	-	60.5	-	-
1-Chlorododecane	-	-	95.0	-	-
2,6-di-tert-Butyl-4-methylphenol	-	-	27.4	-	-
2,4'-Dichlorobiphenyl	-	-	77.3	-	-
2,2',5,5'-Tetrachlorobiphenyl	-	-	74.2	-	-
Anthraquinone	-	-	70.2	-	-
Phenanthrene	-	-	34.4		
bis(2-Ethylhexyl)phthalate	4.2		84.9	0.4	1.1
Glucose					
Furfural	-	-	-	-	-
Quinoline	-	42.7	-	-	-
5-Chlorouracil				44.4	
Caffeine	0.2	0.1	11.2	0.4	53.3
Glycine				4.0	
Humic acids	32.8				
Chloroform					
MIBK	-		2.0	-	NQ

TABLE 34. PILOT-SCALE STUDY (FOURTH 100 L BATCH)

	% Recovery				
	OA	OB	ON	IB	GCB
Stearic acid	5.8				
Trimesic acid	42.4				
2,4-Dichlorophenol	0.1	-	-	-	9.0
Quinaldic acid	NQ			NQ	
Isophorone	-	0.1	35.1	<0.1	5.8
Biphenyl	-	-	68.4	-	-
1-Chlorododecane	-	-	90.8	-	-
2,6-di-tert-Butyl 4-methylphenol	=	=	3.1	-	-
2,4' -Dichlorobiphenyl	-	-		-	-
2,2',5,5'-Tetrachloro-biphenyl	-	-	66.5	-	-
Anthraquinone	-	-	65.9	-	-
Phenanthrene	-	-	43.0	-	-
bis(2-Ethylhexyl)phthalate	-	0.1	57.1	0.2	0.6
Glucose					
Furfural	-	-	-	-	-
Quinoline	-	79.1	-	-	-
5-Chlorouracil				22.8	
Caffeine	-	0.3	5.1	0.2	43.9
Glycine				5.0	
Humic acids	30.7				
Chloroform					
MIBK	-	-	7.2	-	-

TABLE 35. PILOT-SCALE STUDY (FIFTH 100 L BATCH)

	% Recovery				
	OA	OB	ON	IB	GCB
Stearic acid	1.6				
Trimesic acid	39.5				
2,4-Dichlorophenol	0.2	-	-	-	-
Quinaldic acid				NQ	
Isophorone	-	-	38.1	0.1	-
Biphenyl	-	-	71.5	0.4	-
1-Chlorododecane	-	-	91.5	2.6	-
2,6-di-tert-Butyl-4-methylphenol	-	-		-	-
2-4'-Dichlorobiphenyl	-	-		2.7	-
2,2',5,5'-Tetrachloro-biphenyl	-	-	76.5	0.7	-
Anthraquinone	-	-	73.7	1.2	-
Phenanthrene	-	-	38.5	-	-
bis(2-Ethylhexyl)phthalate	0.7	0.1	38.7	0.7	-
Glucose					
Furfural	-	-	-	-	-
Quinoline	-	62.7	-	0.1	-
5-Chlorouracil				22.8	
Caffeine	-	-	6.0		-
Glycine				2.2	
Humic acids	35.4				
Chloroform	-	-	-	-	
MIBK	-	-	7.3	-	

(e.g., resins, stock solution spiking, glassware, reagents, etc.) a "blank run" was performed by processing a sample of "OFW" at the bench-scale level. Moreover, 1 liter of test solution containing all the organic and inorganic constituents was divided into two equal portions. One of them was processed through the isolation-fractionation scheme and the other was solvent extracted. A GC-MS analysis was pursued for the tentative elucidation of the nature of these contaminants. The reconstructed ion chromatograms of the solvent extracted sample and the "hydrophobic neutral" fraction of the same test solution are presented in Figures 22 and 23, respectively. Except for two or three major impurities, whose abundance was comparable to that of the model compounds, the bulk of the impurities appeared to be relatively small (i.e., <1 ng/μL). Some of them (e.g., phenol, bromoform, dibromochloromethane) were detected in several samples and sometimes in relatively large concentrations (between 5-50 μg/mL). The high volatility of the majority of these impurities prompted us to speculate the presence of these compounds in the contaminated air of the lab environment. A list of tentatively identified impurities, based on computer matching of Library Mass Spectra, is presented in Table 36. The extent of contamination introduced during the processing of 100-liter test solutions was also investigated. GC-MS analysis of the solvent extracted sample and the "hydrophobic neutral" fraction of the same test solution was carried out to elucidate the origin of the impurities. The reconstructed ion chromatograms are shown in Figures 25 and 26, respectively, and a list of the tentatively identified contaminants is reported in Table 37. Also in this case the major part of identified contaminants appeared to be related to atmospheric contamination from the lab environment. However, the presence of 2,5-cyclohexadiene, 1,4-dione-bis-(1,1-dimethylethyl) was attributed to the oxidative reaction of 2,6-di-tert-butyl-4-methyl-phenol.

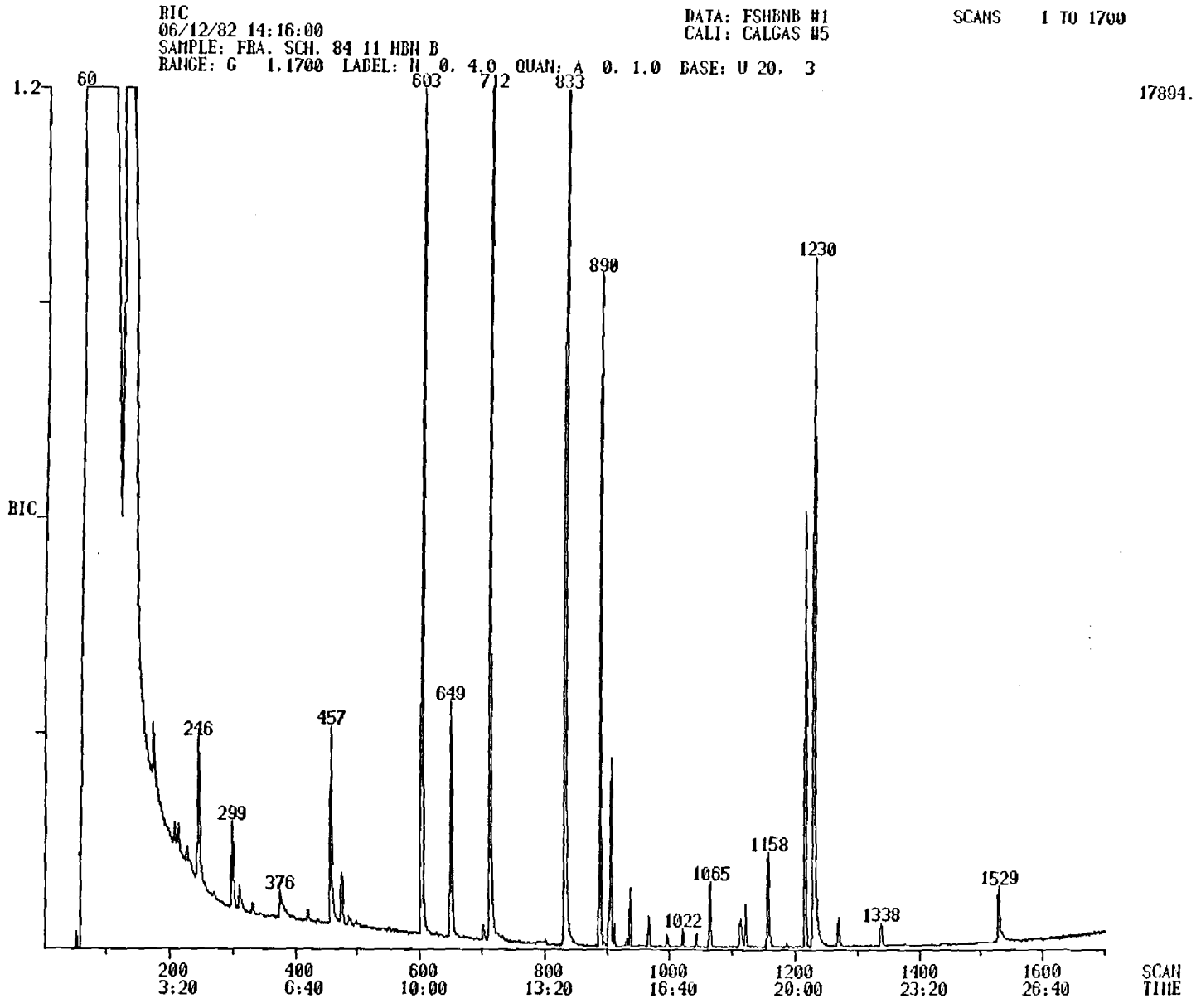


Figure 24. RIC of "Hydrophobic Neutral" Fraction

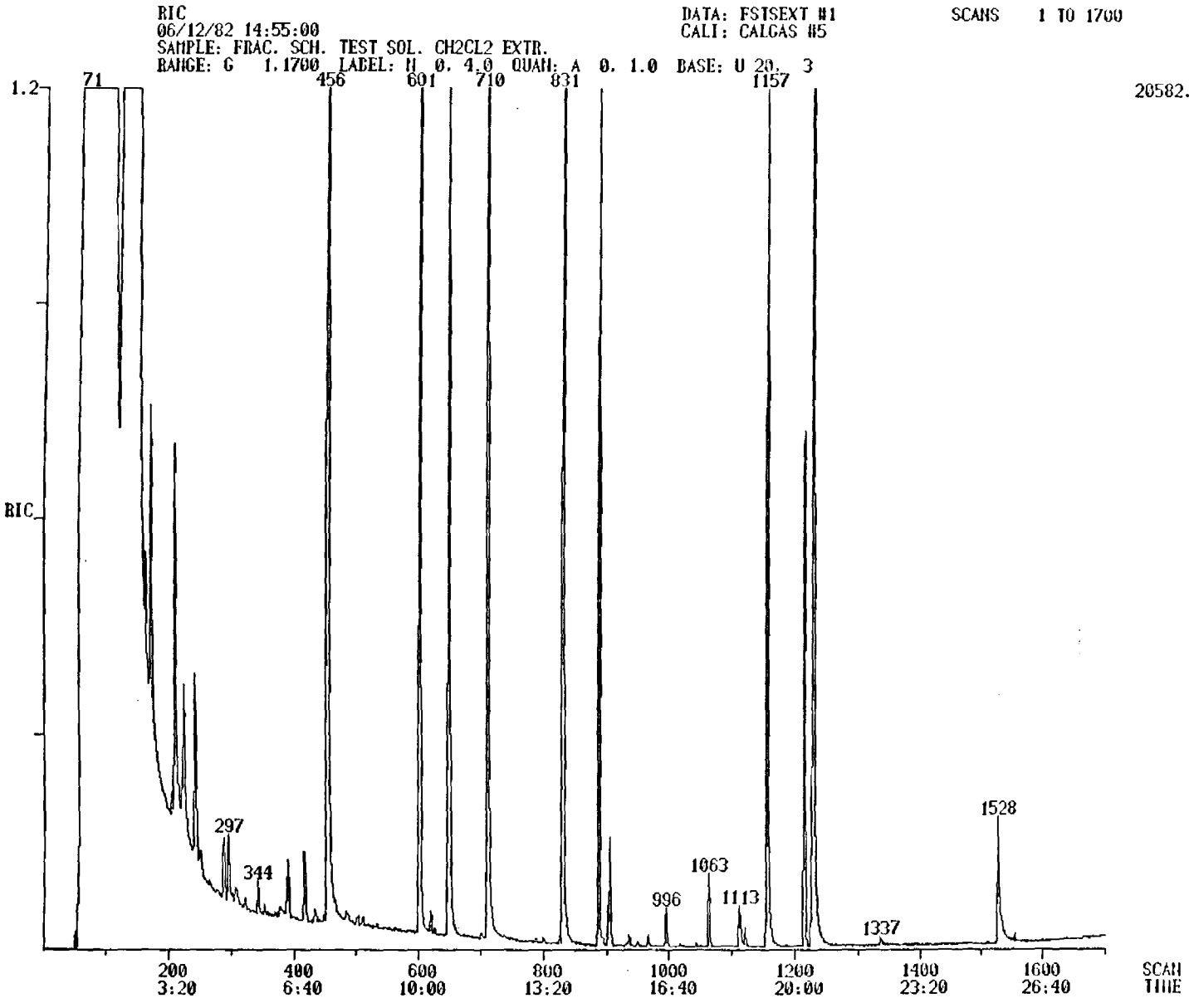


Figure 23. RIC of Test Solution Extract

TABLE 36. ARTIFACT CONTAMINANTS FROM LAB-SCALE FRACTIONATION SCHEME

ON	OB	IN
Cyclohexene, 3-chloro	Cyclohexanol, 4-chloro	Ethanone,1-(4-hydroxy phenyl)
Phenol	Benzene sulfonamide,N,4-dimethyl	Cyclohexane, 1,4-dichloro
2,4 (1H,3H)-Pyrimidinedione, 5-amino	Phthalate	Cyclohexanol, 2-chloro
Benzenesulfonamide, N,4-dimethyl	Phthalate	Phenol
Phthalate		Cyclohexene, 3-chloro
Phthalate		Ethane, Tetrachloro
Bromoform		Bromoform
Xylene		Ethylbenzene
Ethylbenzene		Benzene, chloro
Chlorobenzene		Pentanone, 3-methylene
3-Penten-2-one,4-methyl		Methane, dibromochloro
Methane, dibromochloro		

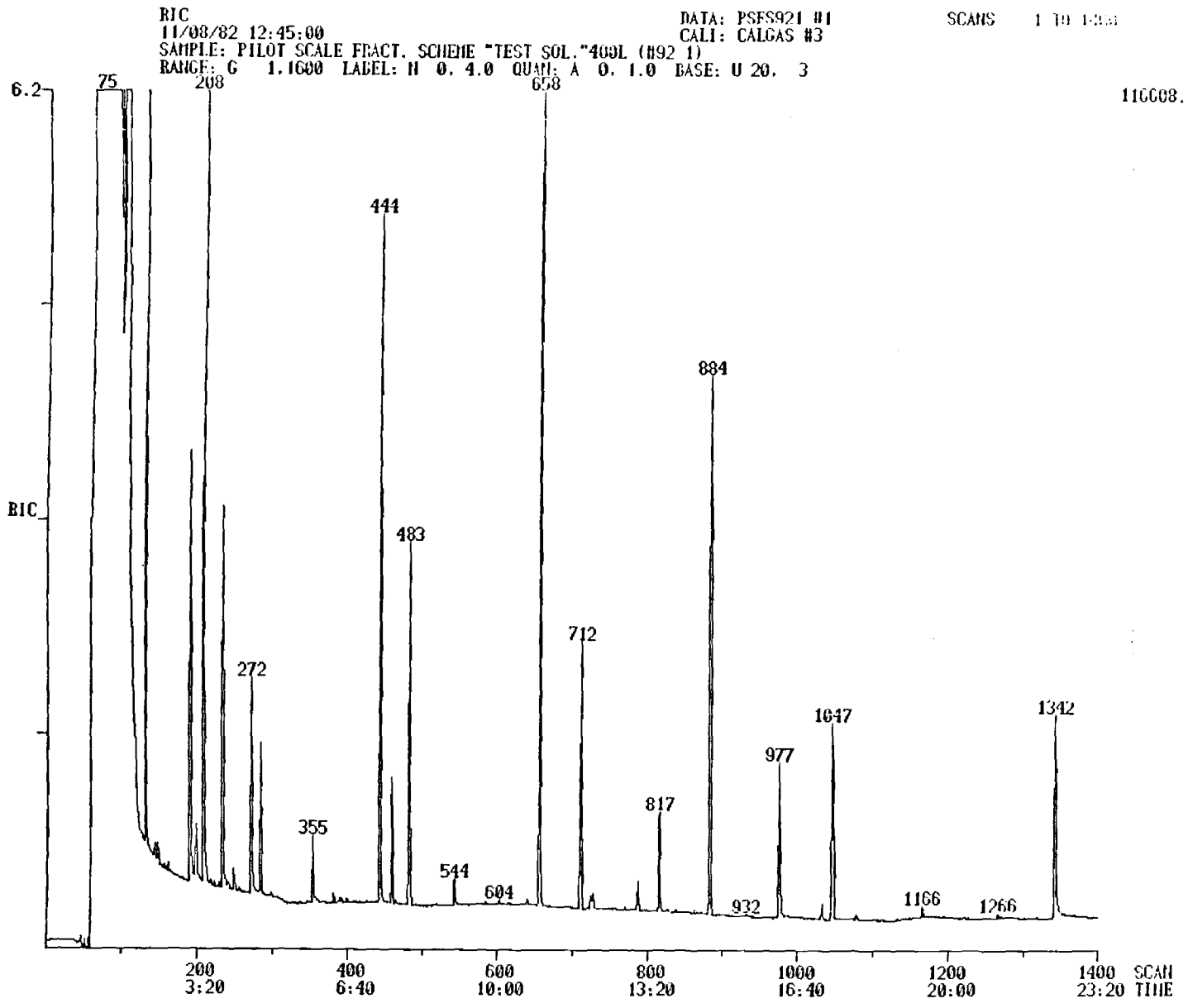


Figure 25. RIC of Test Solution Extract for Pilot-Scale Study

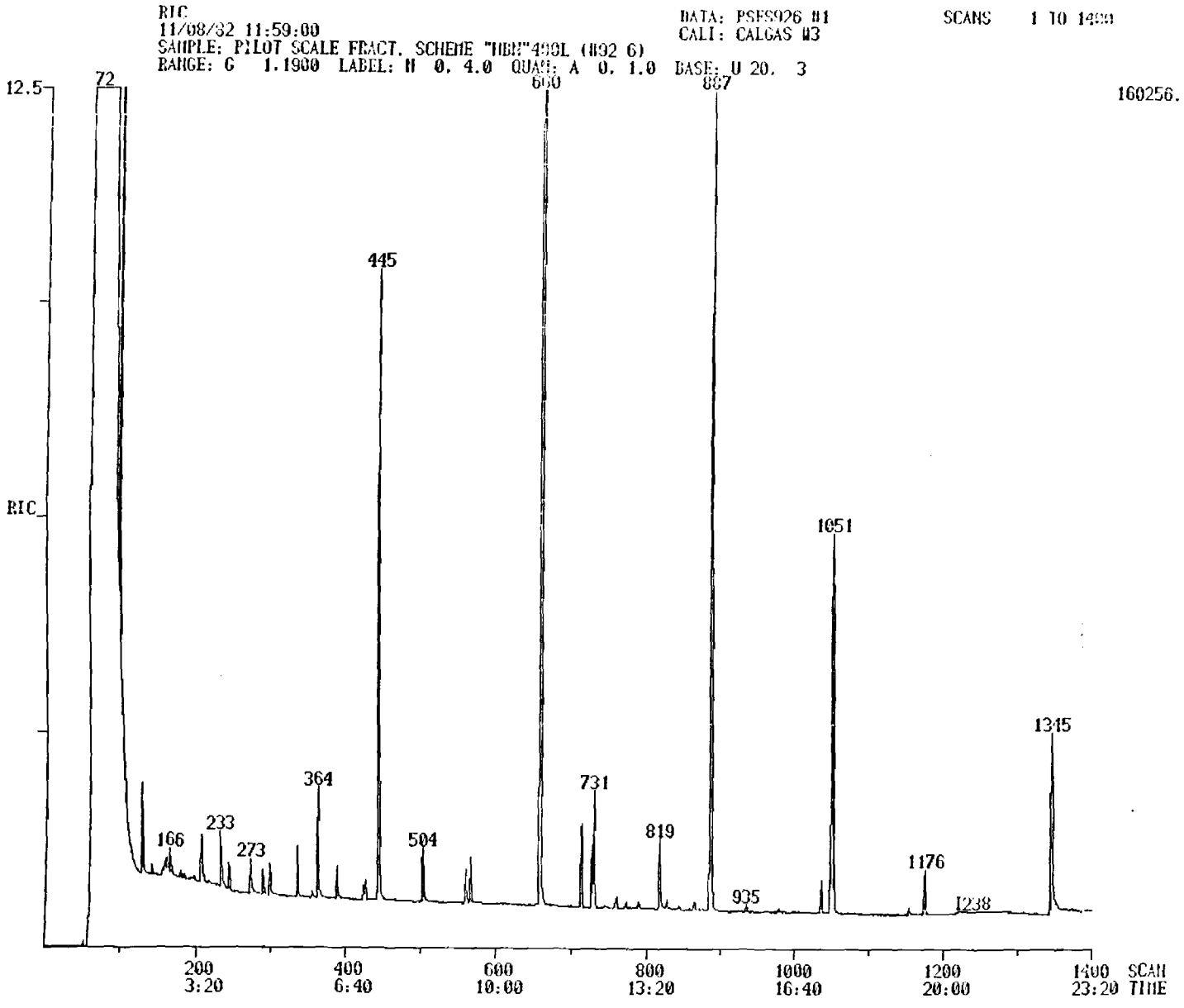


Figure 26. RIC of "Hydrophobic Neutral" Fraction from Pilot-Scale Study

TABLE 37. ARTIFACT CONTAMINANTS FROM PILOT-SCALE FRACTIONATION SCHEME

Fraction from XAD-8 (ON)	Solvent extracted test solution (pH 2 and pH 10)
Methylbenzene	Chlorobenzene
3-Hexanone	1-Cyclohexene-1-01
1-Cyclohexene-1-01	2-Cyclohexene-1-one
Nonane	Trichloropropene
2-Cyclohexene-1-one	Chlorocyclohexanol
Decane	2,4-Cyclohexadiene, 1,4-dione-bis-(1,1-dimethylethyl)
1-Hexanol, 2-ethyl	Diethylphthalate
Undecane	Pyridine
Ethanone, 1-(hydroxyphenyl)	Methylbenzene
2,4-Cyclohexadiene, 1,4-dione-bis-(1,1-dimethylethyl)	Trichloroethane
Diethylphthalate	Ethylbenzene
	Xylene
	Tribromomethane

SECTION 7

DISCUSSION

Current concerns over the health risks associated with the consumption of waterborne organics has spurred the establishment of experimental toxicologic tests which could provide on a short-term basis estimates of the extent of this hazard. The low concentration of the organic constituents in natural and drinking water, however, requires that isolation-concentration methods be developed which could satisfy the detection limits of the current toxicologic tests. Furthermore, because the organic compounds in natural and drinking water are generally present as complex mixtures, the integration in the sample preparation method of a fractionation scheme, which could allow the separation of the organic substances in groups of similar physico-chemical properties, would be regarded as a noteworthy advantage. In light of the key role it might play in the overall health assessment study, it is imperative that these isolation/concentration/fractionation schemes be thoroughly evaluated and compared with each other. The basis of evaluation and comparison should be on a broad spectrum of organic compounds from a variety of chemical classes, functional groups and molecular weights, which implies that chemical analytical techniques be available or developed to monitor each specific model constituent.

Although several other analytical techniques, such as HPLC-MS, supercritical fluid GC-MS, GC- and HPLC-FT/IR and MS-MS are being investigated, GC-MS is presently still the most reliable for the ultimate identification and quantitation of trace organic compounds in complex mixtures. In this study, GC-MS was used for the qualitative and quantitative analysis of the model organics. Emphasis was therefore placed on the quality of the GC column and on suitable derivatization methods for the non-volatile model organics (i.e., glycine, trimesic acid, stearic acid, quinaldic acid, 5-chlorouracil and glucose). Moreover, since some of these model organics occurred in aqueous solution, extraction and isolation methods had to be developed. Open tubular glass columns have meanwhile achieved a degree of inertness and temperature stability which enabled us to analyze fifteen out of twenty-two model compounds directly by GC. Some compounds (e.g., furfural) still gave analytical problems, such as slight peak tailing, caused by residual non-linear interaction with the glass surface and/or stationary phase. The analysis of organics in concentrated aqueous solutions may benefit from improvements in "bonded phase" capillary columns, since direct injection of aqueous phases may become possible. This would of course eliminate the cumbersome exchange into an organic phase.

Glucose was the only model compound not analyzed in this study. All derivatization methods investigated in this study failed to give reproducible results. Presently, continuing efforts in this area indicate that the preparation of alditol derivatives (25) is a promising approach. Since 5-chlorouracil presented difficulties in the GC analysis, we resorted to HPLC with UV

TABLE 38. AVERAGE RECOVERY OF MODEL COMPOUNDS FROM LAB-SCALE STUDY

	% Recovery ± s				
	OA	OB	ON	IB	EF
Stearic acid	32.4*±16.5				
Trimesic acid	41.8**±13.1				
2,4-Dichlorophenol				13.8±11.1	23.6± 3.9
Quinaldic acid					
Isophorone			80.6±18.5		13.7± 8.9
Biphenyl			82.7± 5.8		
1-Chlorododecane			33.8± 6.8		
2,6-di-tert-Butyl 4-methylphenol			50.2± 8.6		
2,4'-Dichlorobiphenyl			74.2± 5.3		
2,2',5,5'-Tetrachloro-biphenyl			44.4±22.1		
Anthraquinone			58.0±13.3		
Phenanthrene			77.8±27.8		
bis(2-Ethylhexyl)-phthlate	1.8***±1.5		37.6± 7.9	2.3***±1.6	9.2± 4.2
Glucose					
Furfural					38.3±38.1
Quinoline		22.1±10.6	5.2± 1.9		
5-Chlorouracil					
Caffeine			16.4± 5.4	3.7**±2.2	25.2±6.2
Glycine				56.5***±19.6	
Humic acids	85.1± 6.5				
Chloroform					
MIBK					

OA = Hydrophobic Acid (XAD-8)
OB = Hydrophobic Base (XAD-8)
ON = Hydrophobic Neutral (XAD-8)
IB = Hydrophilic Base (AG-MP-50)
EF = Final Effluent (solvent extraction)

* 3 values
** 2 values
*** 4 values

detection. No confirmation by MS was then performed. The preparation of derivatives for glycine and the three carboxylic acids was satisfactory as demonstrated by the analytical reproducibility reported in Tables 13 and 14. However, surrogates (e.g., L-alanine, undecanoic acid and 3-quinoline carboxylic acid) were needed in the analysis of the aqueous solutions in order to detect problems associated with the derivatization procedure.

The preparation of a homogeneous test solution was considered a prerequisite for the evaluation of the isolation-fractionation scheme. Therefore, great care was taken to completely dissolve the inorganic and organic species in the aqueous phase. Most of the model compounds were spiked from stock solutions which were prepared in either methanol or "OFW". The dissolution of the highly hydrophobic compounds (i.e., phenanthrene, 2,2',5,5-tetrachlorobiphenyl, 2,4'-dichlorobiphenyl and 1-chlorododecane) required a procedure in which they were gradually exposed to an increasingly more polar solvent (see Appendix B). Inorganic salts were particularly troublesome since they often caused turbid solutions and precipitates under alkaline or even neutral conditions. In the presence of humic acid, formation of Ca-humate flocs invariably occurred which were particularly heavy under alkaline conditions. The choice of a humic acid as a representative of aqueous humic substances thus proved to be a rather unfortunate one. Under both neutral and alkaline conditions the test solutions became non-homogeneous because of the formation of a solid humate phase. In the particular case of the pilot study where 100 L of solution were processed at a time, settling of the solids on the walls of the glass vessels became a cumbersome problem. Of course natural waters, and especially drinking water, may not contain such high-molecular-weight model humus employed in this study. They were actually isolated from water by the very processes that were used in the preparation of the test solution.

In the evaluation of the resin scheme on a lab-scale (see Figure 19), six repetitive experiments were made (see Tables 19-24). The mean recovery and standard deviation(s) of each model compound are reported in Table 38. Fourteen out of twenty-two model organic compounds appeared to be effectively recovered (i.e., stearic acid, trimesic acid, isophorone, biphenyl, 1-chlorododecane, 2,6-di-tert-butyl-4-methylphenol, 2,4'-dichlorobiphenyl, 2,2',5,5'-tetrachlorobiphenyl, anthraquinone, phenanthrene, bis-(2-ehtylhexyl)phthalate, quinoline, humic acid and glycine). MIBK was detected in the "hydrophobic neutral" fraction, whereas 5-chlorouracil and quinaldic acid were found in very low concentration in the "hydrophobic base" fraction. The presence of quinaldic acid in the hydrophobic base fraction confirmed the findings of Leenheer and Huffman (26) for solution concentration at the mg/L level. This suggested the amphoteric behavior of quinaldic acid. Although the latter three compounds were detected however, they showed a poor recovery of <1% Chloroform was expected to be in the "hydrophobic neutral" fraction. However, no trace of it could be detected. This was attributed to the fact that chloroform could be lost through volatilization during solution processing and analytical sample preparation, (e.g., KD solvent evaporation). Several model compounds were found in more than one fracton. For example, in the case of bis-(2-ethylhexyl)-phthalate it was detected essentially in every fraction monitored. This suggested a non-specific adsorption by both macroreticular and ion-exchange resins which was later substantiated by breakthrough studies (see Table 26). Quinoline was partitioned between the "hydrophobic base" and

the "hydrophobic neutral" fractions implying that the volume or the strength of the acid solution used to elute the "hydrophobic base" fraction might not be sufficient to quantitavely desorb this compound. 2,4-Dichlorophenol was partially recovered in the "hydrophobic base" fractions, presumably because of an adsorption affinity to the styrene-divinyl/benzene lattice of the cation-exchange resin. However, the major portion of it was found in the final aqueous effluent of the resin scheme. Caffeine appeared to be recovered in small amounts in the "hydrophobic neutral" and "hydrophilic base" fractions. As can be seen in the breakthrough study (see Tables 27 and 28), this compound was neither retained by the XAD-8 nor by the AG MP-50 resins.

Malcolm et al. (27) and Thurman et al. (28) noticed that the adsorption of solutes onto XAD-8 macroreticular resin could be predicted by means of a linear correlation between the log capacity factor and the inverse of log water solubility of each compound. Their investigation was however limited to approximately twenty selected organics in individual aqueous solutions. Upon examination of the results shown in Table 38, it is possible to state that similar behaviors could be expected with the model compounds used in our study. Therefore, the predictive model could also be utilized as a first estimate of the adsorption on XAD-8 of multi-solute solutions at trace levels. The relatively poor recovery of 1-chlorododecane and 2,2',5,5'-tetrachlorobiphenyl in the "hydrophobic neutral" fraction (see Table 38) may be attributed to difficulties encountered in solubilizing them in water with subsequent losses by adsorption onto the walls of glass reservoir and teflon tubing, although precautions had been taken during the preparation of the test solution (see Appendix B). No attempt was made however, to verify this by desorbing the model compounds from these surfaces.

The presence of appreciable amounts of several model compounds in the final resin effluent has led to the consideration of using a carbonaceous adsorbent as a last step in the fractionation scheme in an attmept to recover those organic compounds which were retained only partially or incompletely by the resins. Granular activated carbon process has been extensively used for several decades (29, 30), however, it is widely recognized that the recovery from the carbon surface of the adsorbed organics is not complete. On the other hand, Carbopack B was recently proposed as an alternative carbonaceous adsorbent for trace organic compounds, because of its effectiveness in the recovery of chlorinated pesticides from water (11). This material has been evaluated with selected model organic compounds and the results are reported in Table 25. It is seen from Table 25 that phenanthrene, quinoline, caffeine and 2,4-dichlorophenol are recovered almost quantitatively. However, furfural, MIBK and isophorone are not effectively retained by Carbopack B, whereas bis-(2-ethylhexyl)phthalate is equally distributed between the aqueous phase and the carbon. The relatively poor recovery of 1-chlorododecane, 2,4'-dichlorobiphenyl and 2,2,'5,5'-tetrachlorobiphenyl confirms the difficulty of solubilizing these compounds in water.

Based on the results obtained from the lab-scale experiments it was decided to select an isolation-fractionation scheme which included XAD-8 macroreticular resin, AG MP-50 cation exchange resin and Carbopack B GCB in an attempt to explore the potential of such schemes for the concentration of organics from a large quantity of water. The flow diagram and the sequence of

operations of the large-scale scheme are reported in Figure 6, which is different from that of the lab-scale study in that it uses two XAD-8 columns in sequence for each pH of the test solutions. Therefore, the "hydrophobic acid" fraction was eluted from the first XAD-8 column with a dilute base, whereas, the "hydrophobic base" fraction from the second resin colunm with a dilute acid. The "hydrophobic neutral" fraction was obtained by solvent desorption with methylene chloride of the XAD-8 resin collected from both columns. The final evaluation of the isolation-concentration scheme with the large-scale units (see Figure 4) was carried out using five repetitive experiments each with 100-liter test solution (see Table 31-35). The mean recovery and standard deviation of each model organic compound is reported in Table 39. By comparing the results of lab-scale and large-scale experiments (Table 38 and 39), a decrease in the recovery of several model compounds (i.e., stearic acid, isophorone, biphenyl, 2,6-di-tert-butyl-4-methylphenol, phenanthrene, glycine and humic acid) is seen for the large-scale unit. A poor recovery of many of these organics was indeed anticipated, since the resin bed volume was purposely kept smaller than that needed to process 100 liters of test solution in order to minimize introduction of contaminants and artifacts from the resin. The bed volume used in the large-scale experiments was only 1/8 (i.e., 250 ml) of the resin bed volume calculated from breakthrough studies (see Tables 26-28). Poorer recovery of 2,6-di-tert-butyl-4-methylphenol was however observed in considerably higher degree than the rest of the model organics. Partial oxidative degradation of this compound was later shown to be the major cause of this drastic decrease in recovery, because 2,5-cyclohexadiene, 1,4-dione-bis (1,1-dimethylethyl) was tentatively identified by computer matching of Library Mass Spectra in the "hydrophobic neutral" fraction.

A major problem encountered with the use of an insufficient amount of resin was the saturation of the first XAD-8 column with humic acid during the first passage of the test solution at pH 2. The humic acid that escaped adsorption by the first column produced a heavy floc upon pH adjustment to 10. This caused a reduction in the test solution flow rate through the second XAD-8 column. The accumulation of solid Ca humate, among other things, may have altered the sorptive characteristics of the resin bed, which explains some of the discrepancies observed in the recovery of several model organics between the lab-scale and the large-scale units. 1-Chlorododecane appeared to be affected markedly with more than 50% increase in recovery as compared to that obtained in the lab-scale study. Quinoline and bis-(2-ethylhexyl)phthalate were also showing higher recoveries but to a less extent.

The use of 1/8 (i.e., 250 ml) of the resin bed volume calculated for AG MP-50 from breakthrough studies affected considerably the recovery of glycine. The presence of large amounts of inorganic cations (i.e., Ca^{++} ions) might have exceeded the exchange capacity volume of the AG MP-50 resin therefore competing successfully with the protonated form of glycine for the available ion exchange sites of the resin. Quinaldic acid, although poorly recovered in the lab-scale experiments, was not even detected in the large-scale experiments. This seems to support the hypothesis of saturation of ion-exchange capacity by cations having stronger ion interaction (i.e., Ca^{++} ions). 5-Chloruracil was found in larger amount than that expected from the lab-scale experiments (see Table 38). However its identity could not be confirmed by GC-MS analysis.

TABLE 39. AVERAGE RECOVERY OF MODEL COMPOUNDS FROM PILOT-SCALE STUDY

	% Recovery ± s				
	OA	OB	ON	IB	GCB
Stearic acid	7.8± 9.1				
Trimesic acid	47.6±19.8				
2,4-Dichlorophenol					
Quinaldic acid					
Isophorone			37.4± 3.4		
Biphenyl			56.8±14.4		
1-Chlorododecane			94.7± 3.5		
2,6-di-tert-Butyl 4-methylphenol			8.4±12.6		
2,4'-Dichlorobiphenyl			70.1±10.3		
2,2',5,5'-Tetrachloro-biphenyl			65.8±14.7		
Anthraquinone			69.5±14.6		
Phenanthrene			38.6± 6.9		
bis(2-Ethylhexyl) phthalate	2.0± 1.9		60.9±17.8		
Glucose					
Furfural					
Quinoline		61.6±25.6			
5-Chlorouracil				27.8±10.7	
Caffeine					43.2±28.4
Glycine				4.8± 1.9	
Humic acids	34.0± 4.6				
Chloroform					
MIBK					

OA = Hydrophobic Acid (XAD-8)
OB = Hydrophobic Base (XAD-8)
ON = Hydrophobic Neutral (XAD-8)
IB = Hydrophobic Base
GCB = Carbopack B

Finally, the high affinity of caffeine for Carbopack B was demonstrated also in the large-scale experiments (see Table 39), although the amount of carbon used (i.e., approximately 10 g) was smaller than the actual amount calculated for the test solution concentration. 2,4-Dichlorophenol, which was expected to be in the Carbopack B fraction was not detected at all in the fractions from the large-scale unit. Analysis of the "hydrophilic base" fractions, as suggested by the lab-scale experiments (see Table 38), did not give any positive results and thus led to a tentative belief that the Ca humate precipitate may have drastically affected its adsorption behavior. Attempts to detect 2,4-dichlorophenol in the "hydrophobic acid, base and neutral" fractions, however, did not provide any confirmatory clues.

In view of the results obtained from this study, it is possible to conclude that the objectives proposed in the initiation of this research project appear to be satisfied, at least partially, by the developed isolation/fractionation scheme. The evaluation carried out at the lab-scale demonstrated the feasibility of the use of XAD-8, AG MP-50 and Carbopack B for the effective isolation and concentration of fifteen model organic compounds. The quantitative evaluation pointed out that the recovery efficiency varies from one model compound to the other within the 30-90% range. A limit of 30% recovery was established as the minimum level required to fulfill the proposed quantitative goal of at least 50-fold solute concentration. In the case of the "hydrophobic neutral" and "GCB" fractions, however, the recovery could be even <30% since the solutes are eluted in a highly volatile organic solvent (i.e., methylene chloride) which simplifies the operations of solution concentration. The use of a volatile organic solvent would also facilitate solvent exchange (e.g., methylene chloride → ethanol) for subsequent preparation of concentrated water solutions which should be used for animal feeding during toxicologic studies. The results concerning the recovery of the model compounds with the large-scale units (see Table 39) should be evaluated taking into account the fact that 1/8 of the required resin bed volume and 1/2 of carbon bed volume were used. These measures were taken in an attempt to minimize introduction of contaminants and artifacts from the resins and to prevent the use of large pressure drops in order to achieve a reasonable flow rate through the small carbon particle bed. In view of these operational modifications it is not surprising to find lower recoveries for the majority of the model compounds (see Table 39). However, it is reasonable to conclude that the isolation/fractionation scheme can also be used for the preparation of concentrates of selected classes of organic compounds from large quantities of water solutions. Since the contaminants were confined within acceptable limits (i.e., the bulk of gas chromatographable impurities was in magnitude <1/10 of the model compounds) and the origin of the majority of them were speculatively related to the "contaminated air" of the lab environment, in our opinion further evaluation of this scheme toward the optimization of the resin and carbon bed volumes is mandatory. The complete adsorption of humic acid substances during the first passage through the first XAD-8 resin, column, in particular, must be carefully addressed.

Investigation on the causes of the lower than usual recovery of 2,6-di-tert-butyl-4-methylphenol indicated that this compound underwent oxidative degradation during the manipulation of the test solution through the scheme, since 2,5-dicyclohexadiene-1,4-dione,2,6-bis(1,1-dimethylethyl) was tentative-

ly identified by computer matching of Library Mass Spectra in the same "hydrophobic neutral" fraction. Particularly severe were the losses incurred in the large-scale experiments. Hydrogen peroxide which was used in small amounts in the final stage of the preparation of "organic free" water may have been present in the test solution as a trace residue and may be indicated as one of the possible causes of the oxidative degradation problem.

Examination of the results obtained by processing through the resin scheme water solutions containing 2 ppm chlorine residue indicated that no gas chromatographable artifacts were detected. This led us to conclude that free chlorine residue (i.e., ClO^-, HClO, Cl_2, Cl^-), which is generally present in drinking water samples, did not have any effects on the materials used in this scheme (i.e., XAD-8, AG MP-50).

In spite of the successful concentration of fifteen model compounds, including four non-volatile ones, it is evident that several classes of organic compounds connot be effectively recovered with the isolation/fractionation scheme developed in this research project. Therefore, if it should be used for a comprehensive study of the organics in water, the investigation of other supplemental isolation and/or concentration methods is warranted in the future work. Reverse osmosis may be used as an integral part of the proposed scheme to concentrate the highly polar compounds (e.g., glucose, quinaldic acid, furfural) present in the effluent from the Carbopack B column. In this respect, preliminary results obtained during this research project indicated that the use of a B-10 RO module could be effective for the concentration of furfural (see Table 29). The highly volatile purgeable organic compounds (i.e., chloroform, MIBK), on the other hand, may first be identified and quantified by means of well established purge-and-trap analytical techniques and then spiked in the aqueous concentrated at a level corresponding to the concentration factors suitable for the toxicologic studies.

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APPENDIX A

MASS SPECTRA OF SELECTED MODEL COMPOUNDS

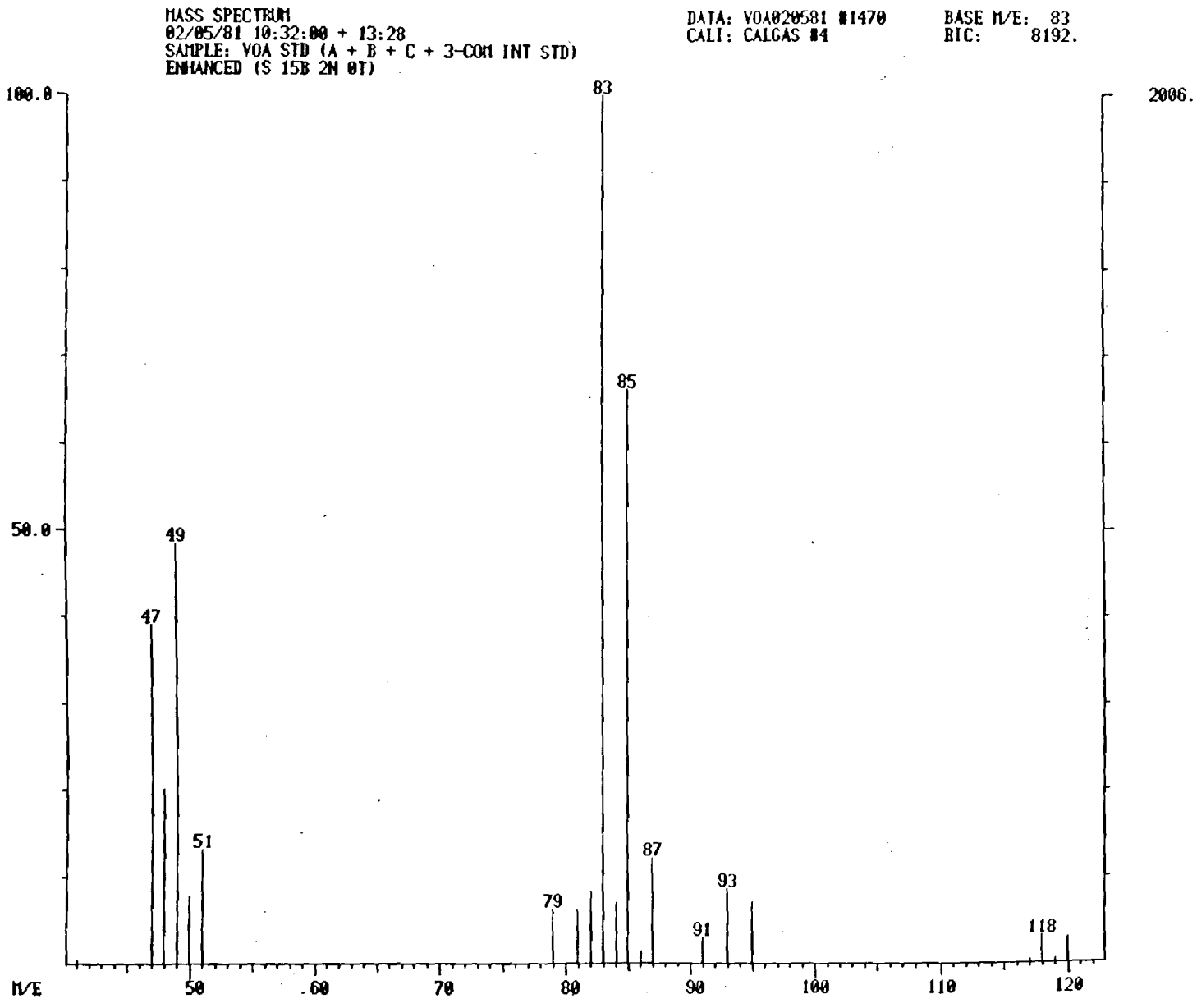

Figure A-1. Mass Spectrum of Chloroform

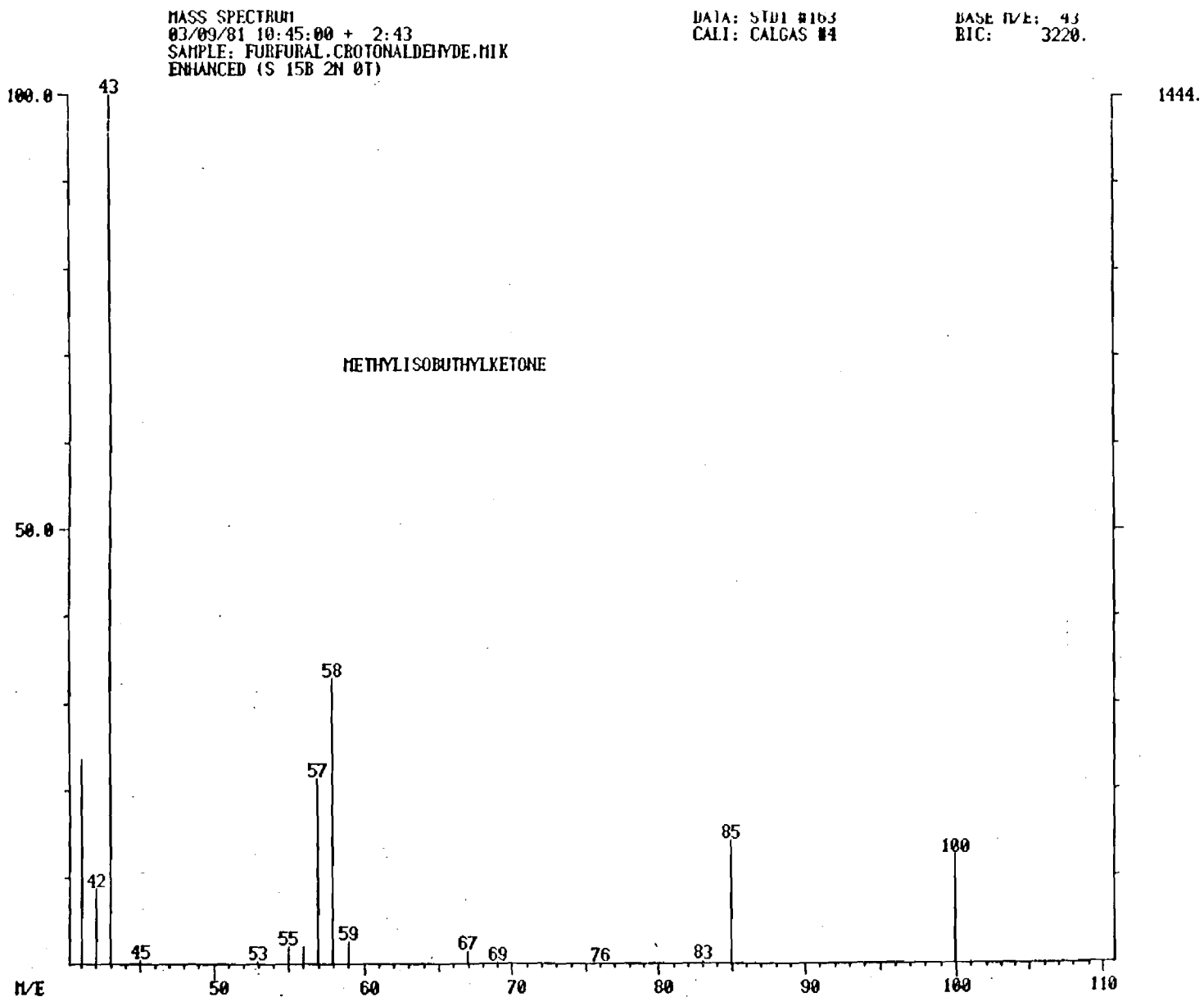

Figure A-2. Mass Spectrum of Methylisobutylketone

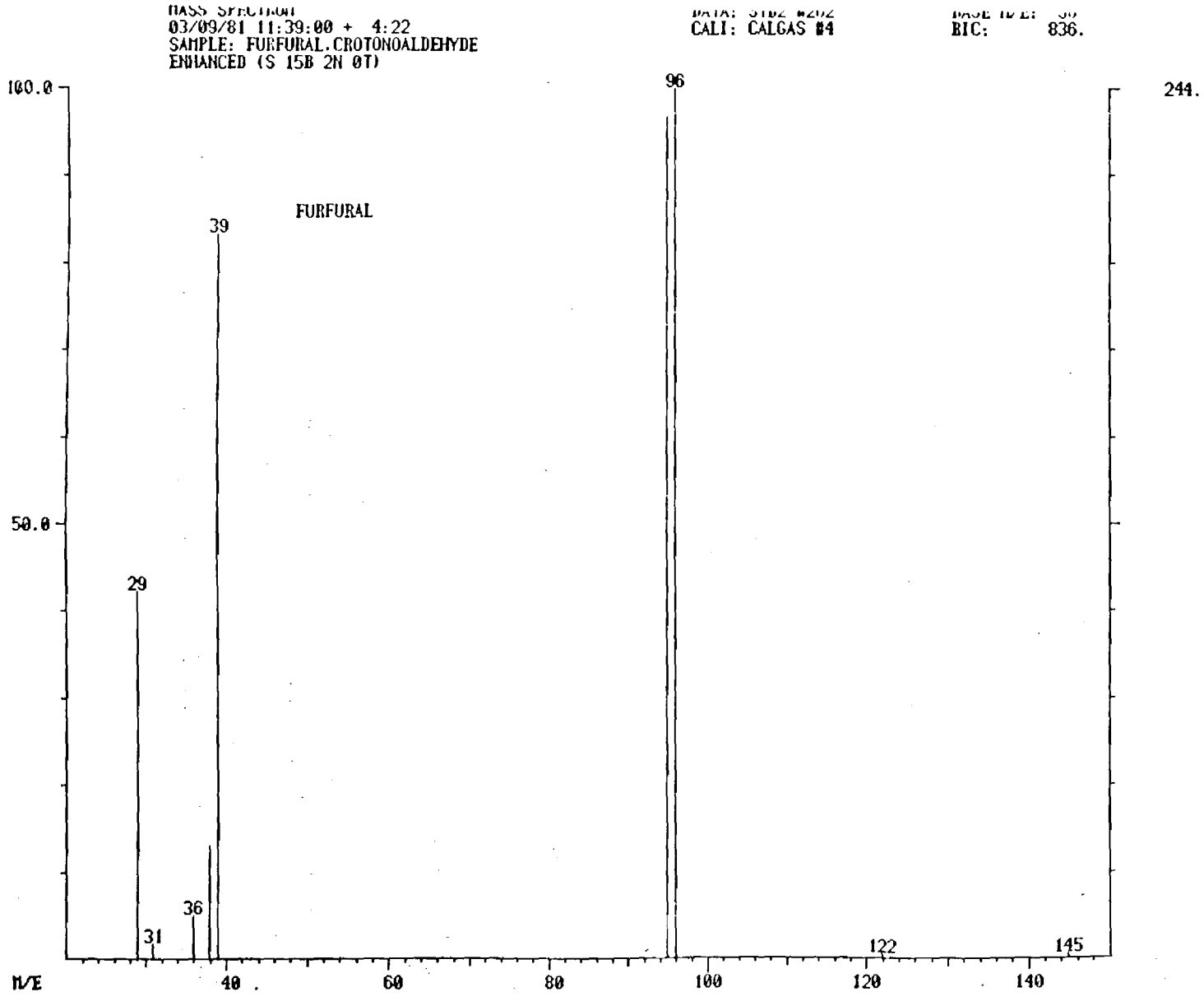

Figure A-3. Mass Spectrum of Furfural

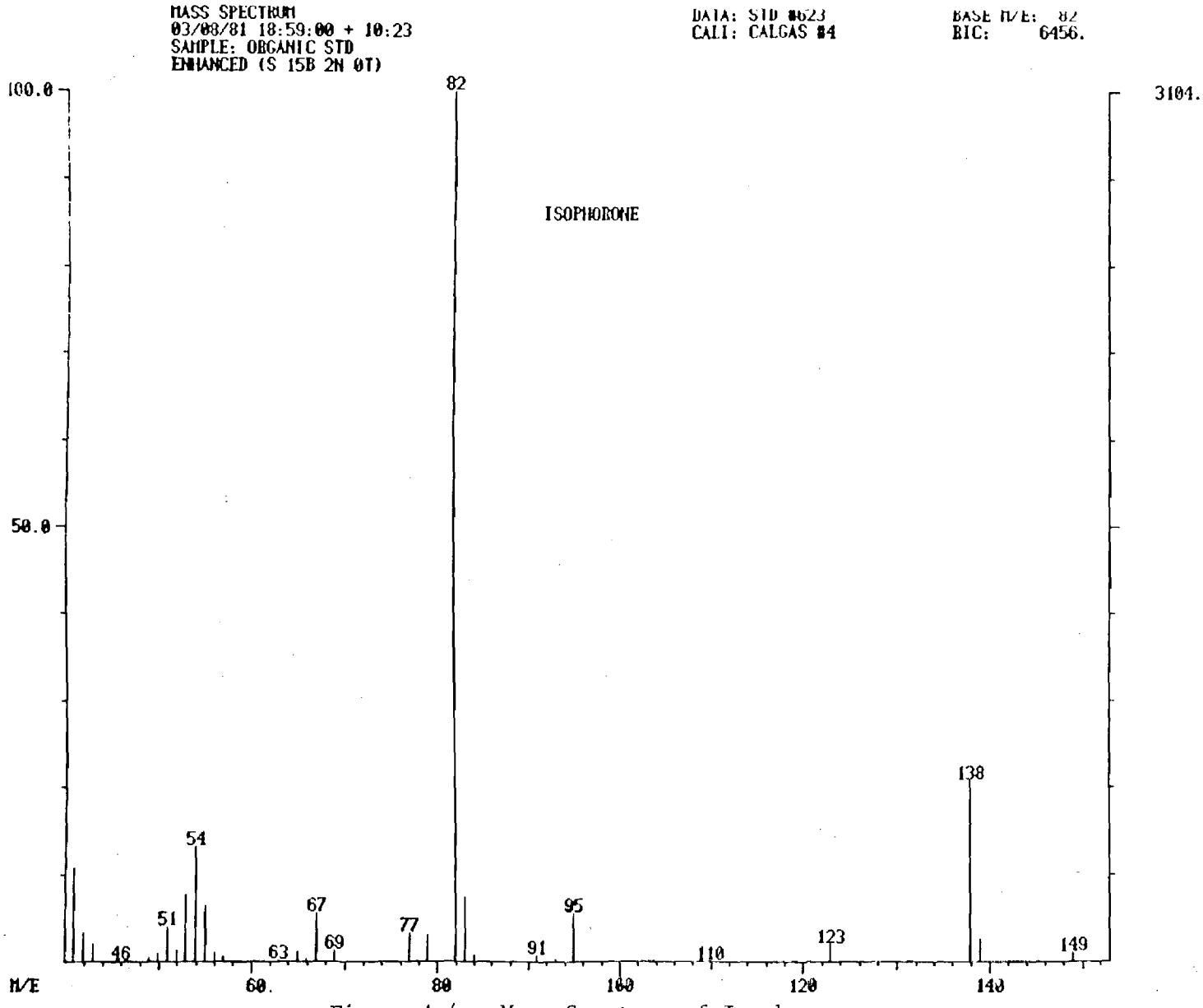

Figure A-4. Mass Spectrum of Isophorone

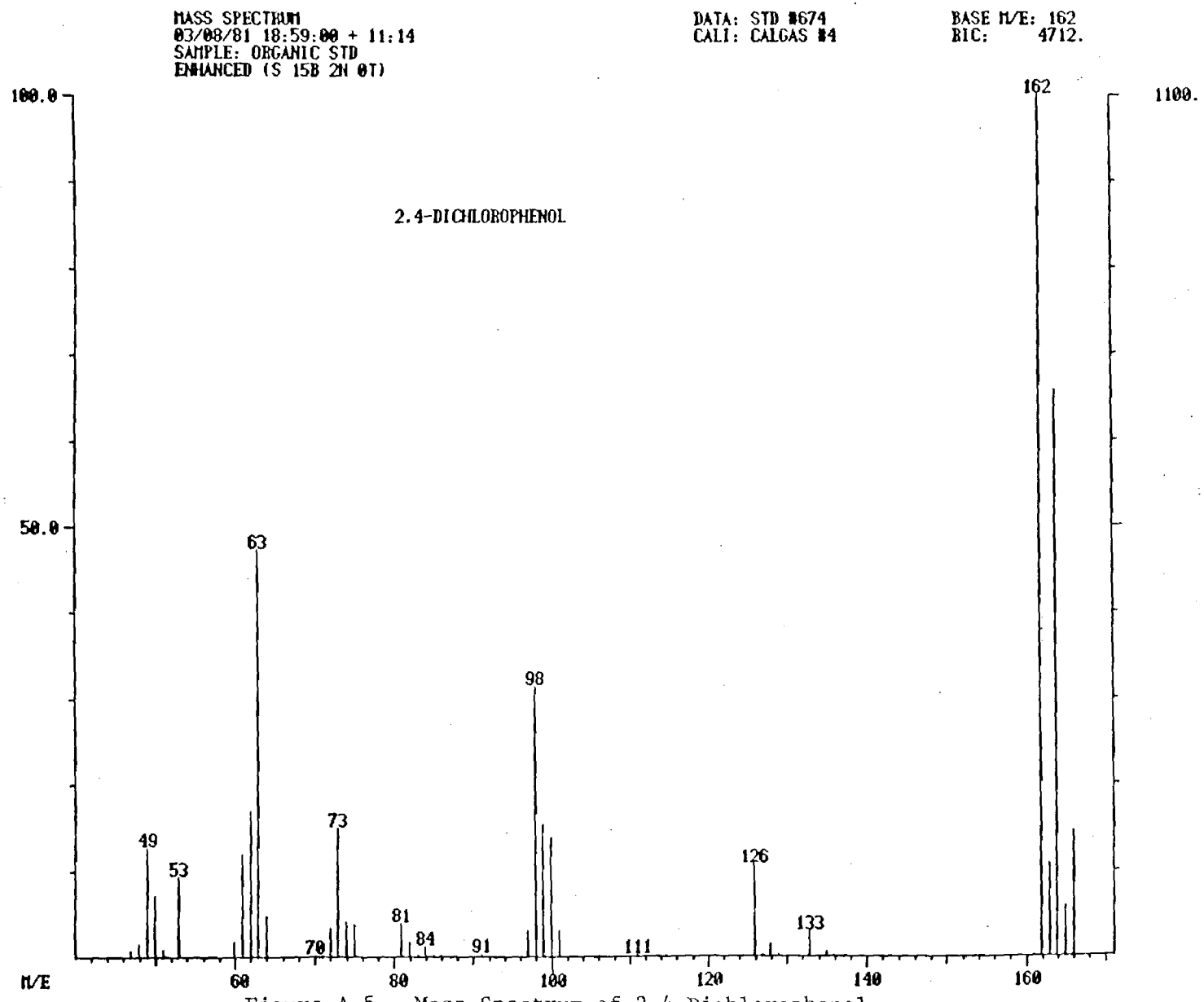

Figure A-5. Mass Spectrum of 2,4-Dichlorophenol

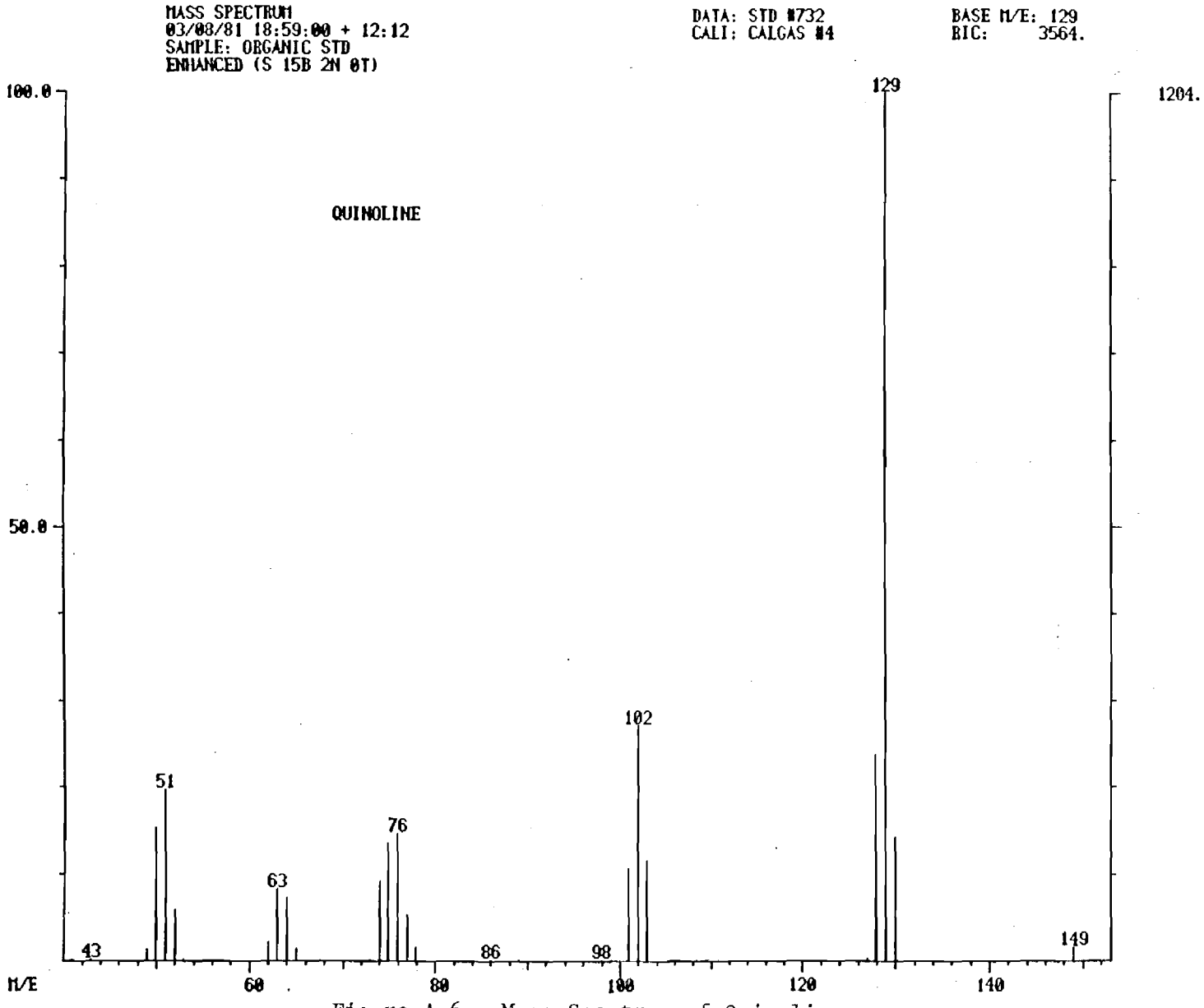

Figure A-6. Mass Spectrum of Quinoline

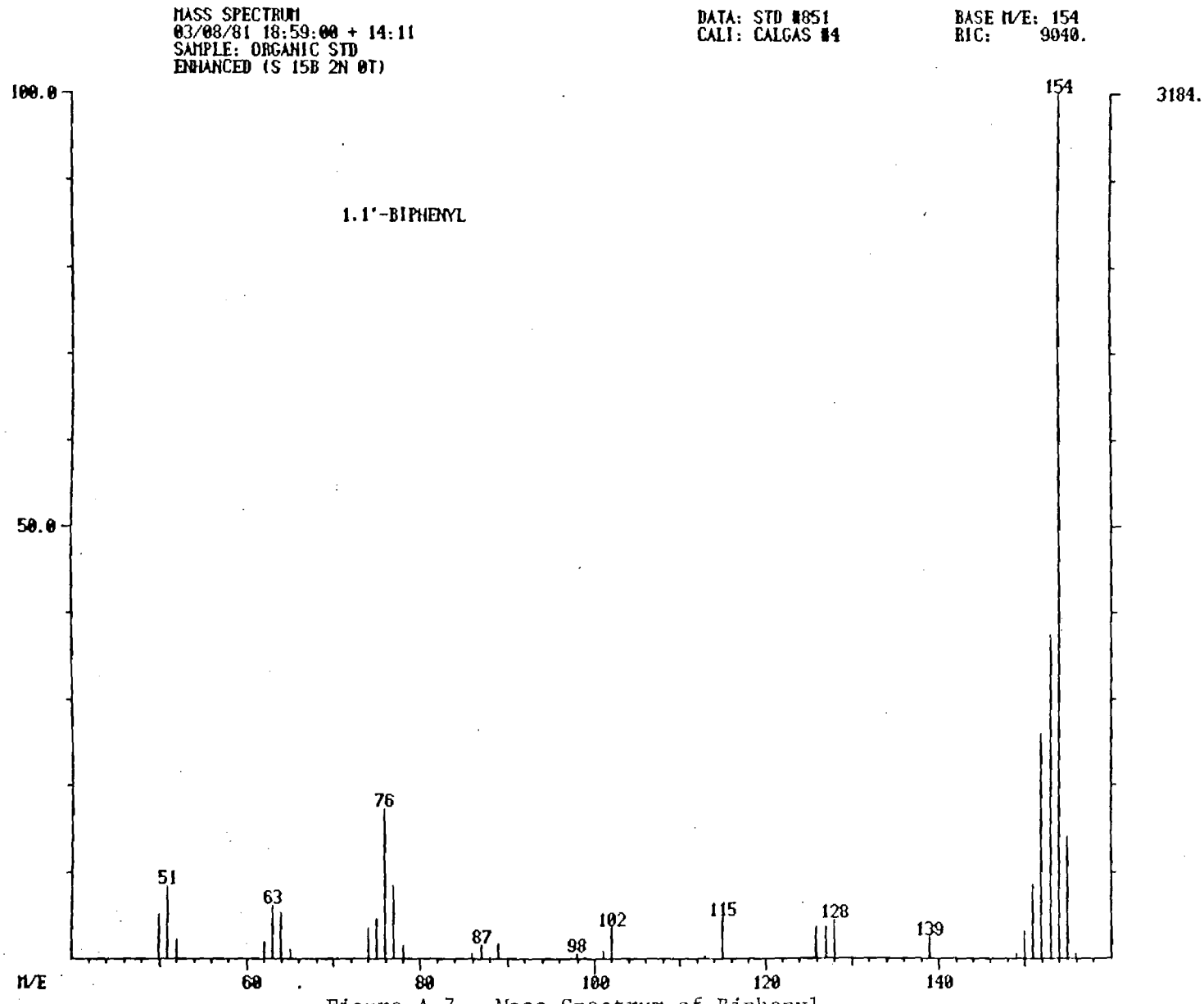

Figure A-7. Mass Spectrum of Biphenyl

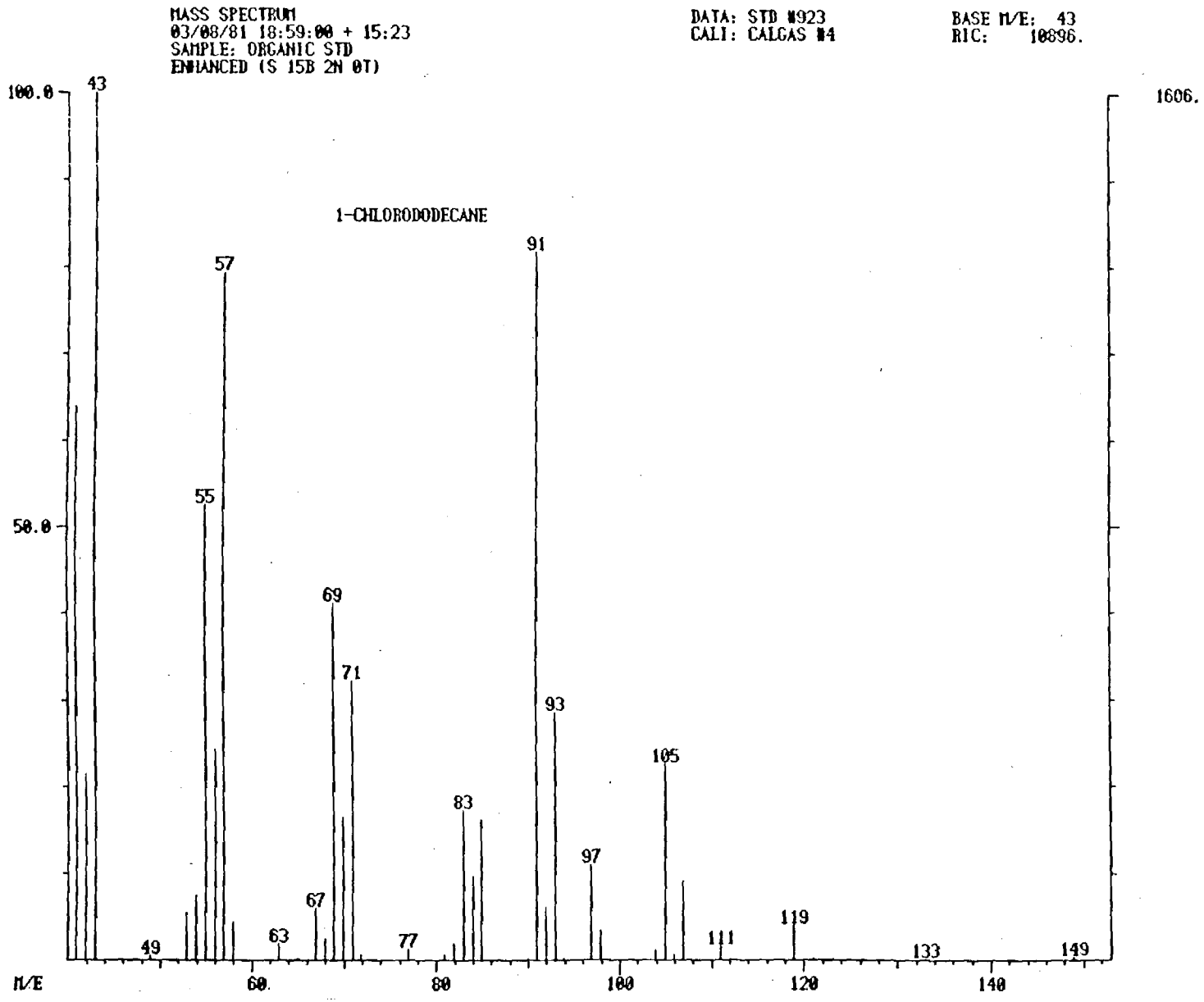

Figure A-8. Mass Spectrum of 1-Chlorododecane

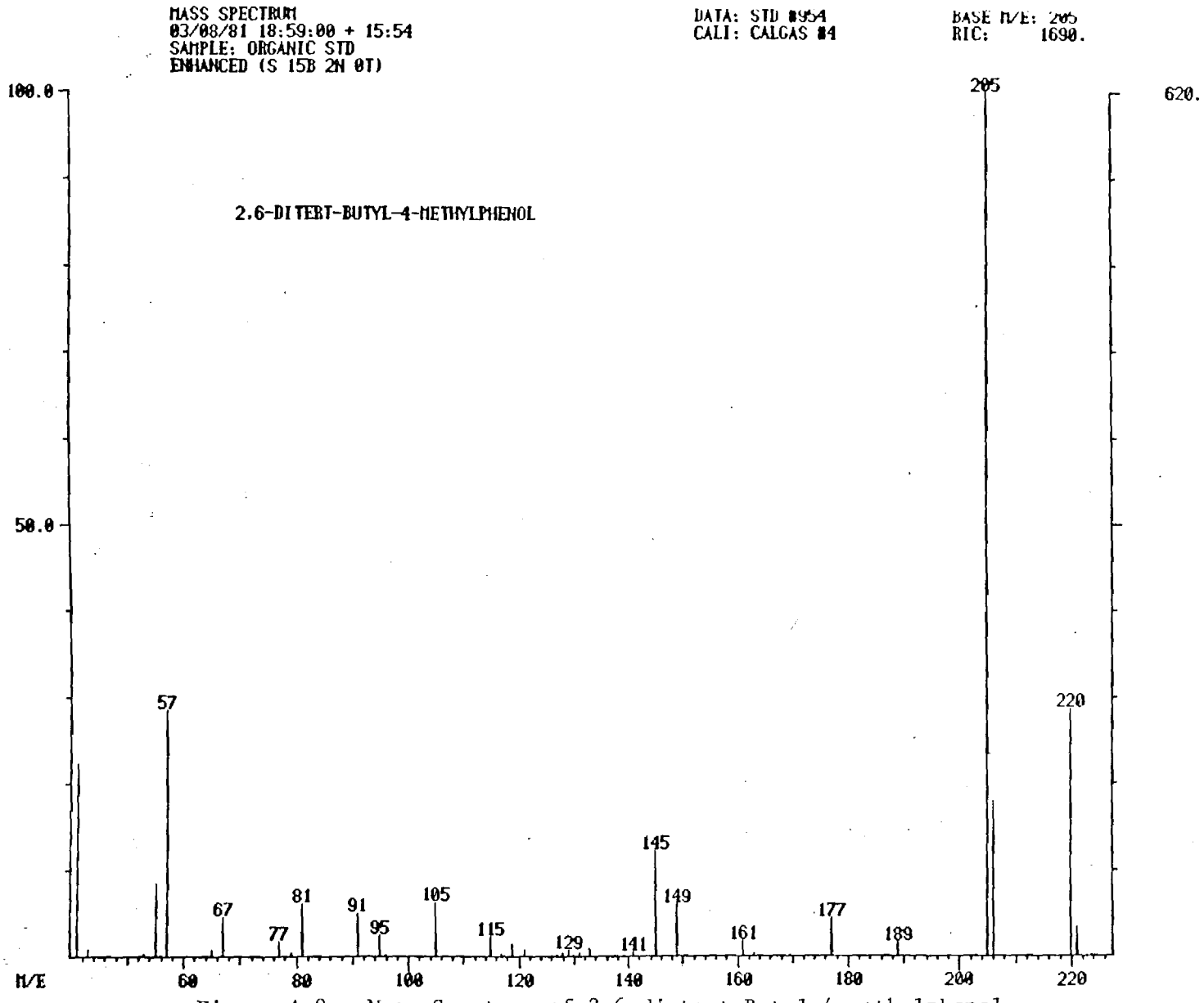

Figure A-9. Mass Spectrum of 2,6-di-tert-Butyl-4-methylphenol

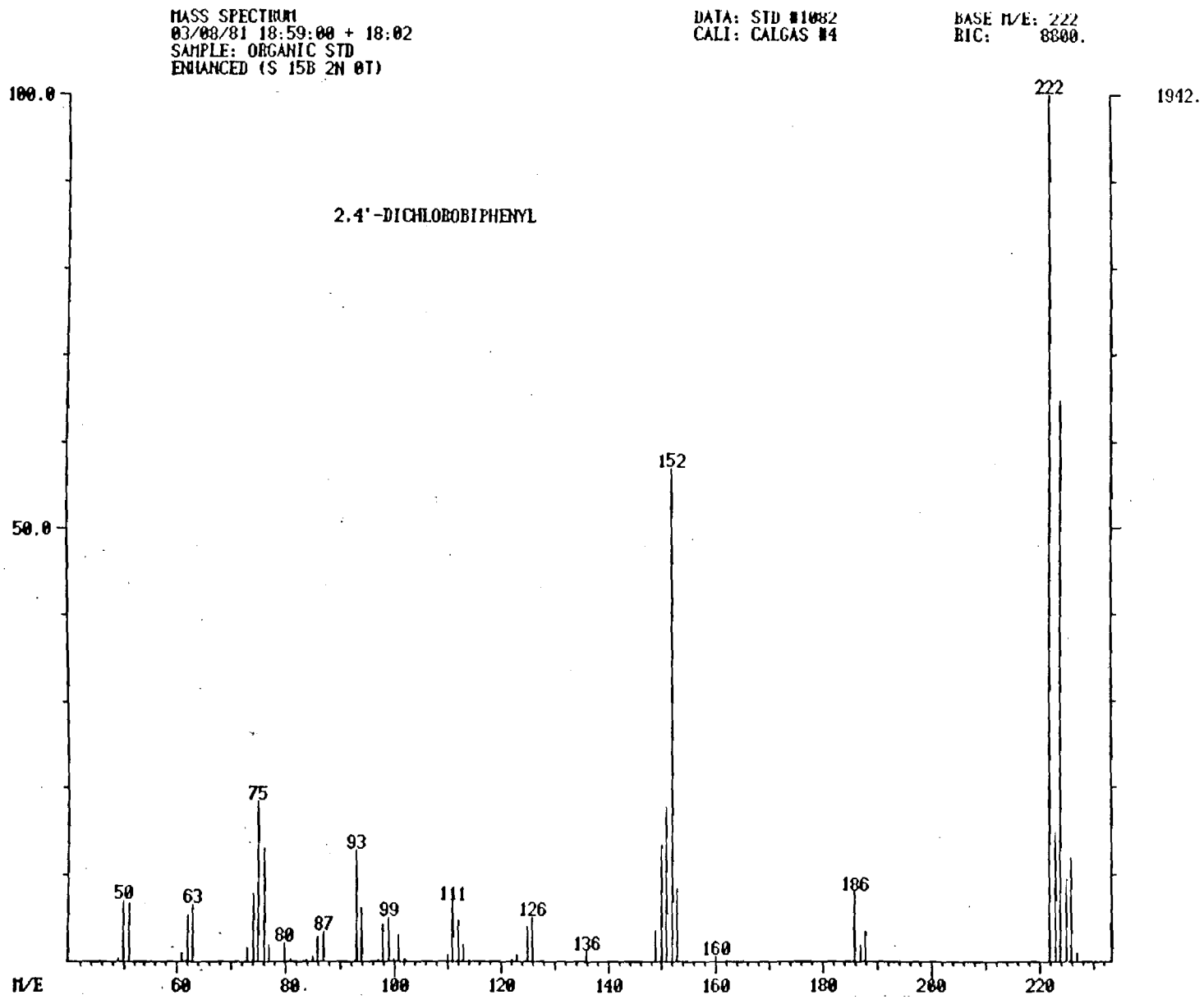

Figure A-10. Mass Spectrum of 2,4'-Dichlorobiphenyl

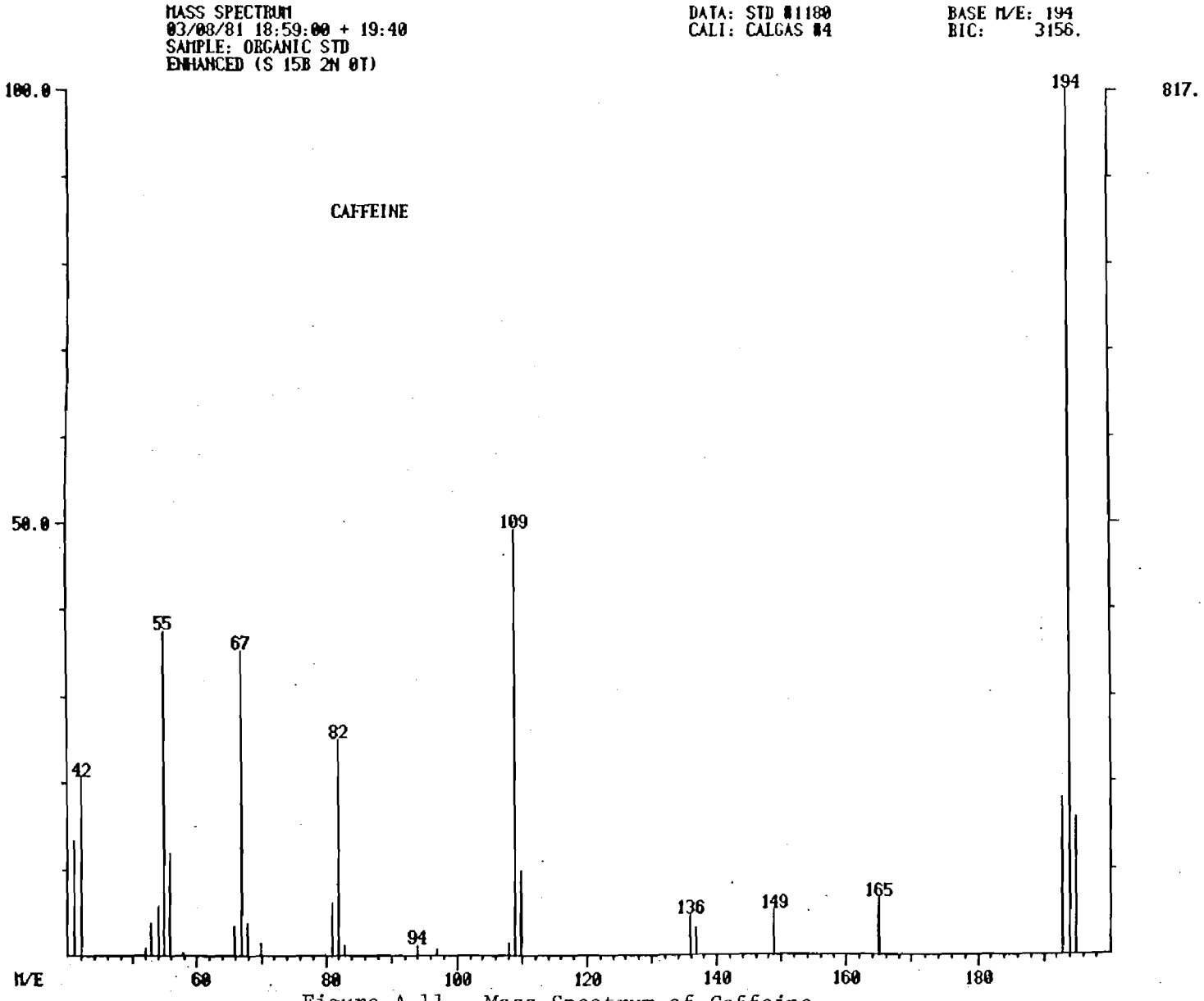

Figure A-11. Mass Spectrum of Caffeine

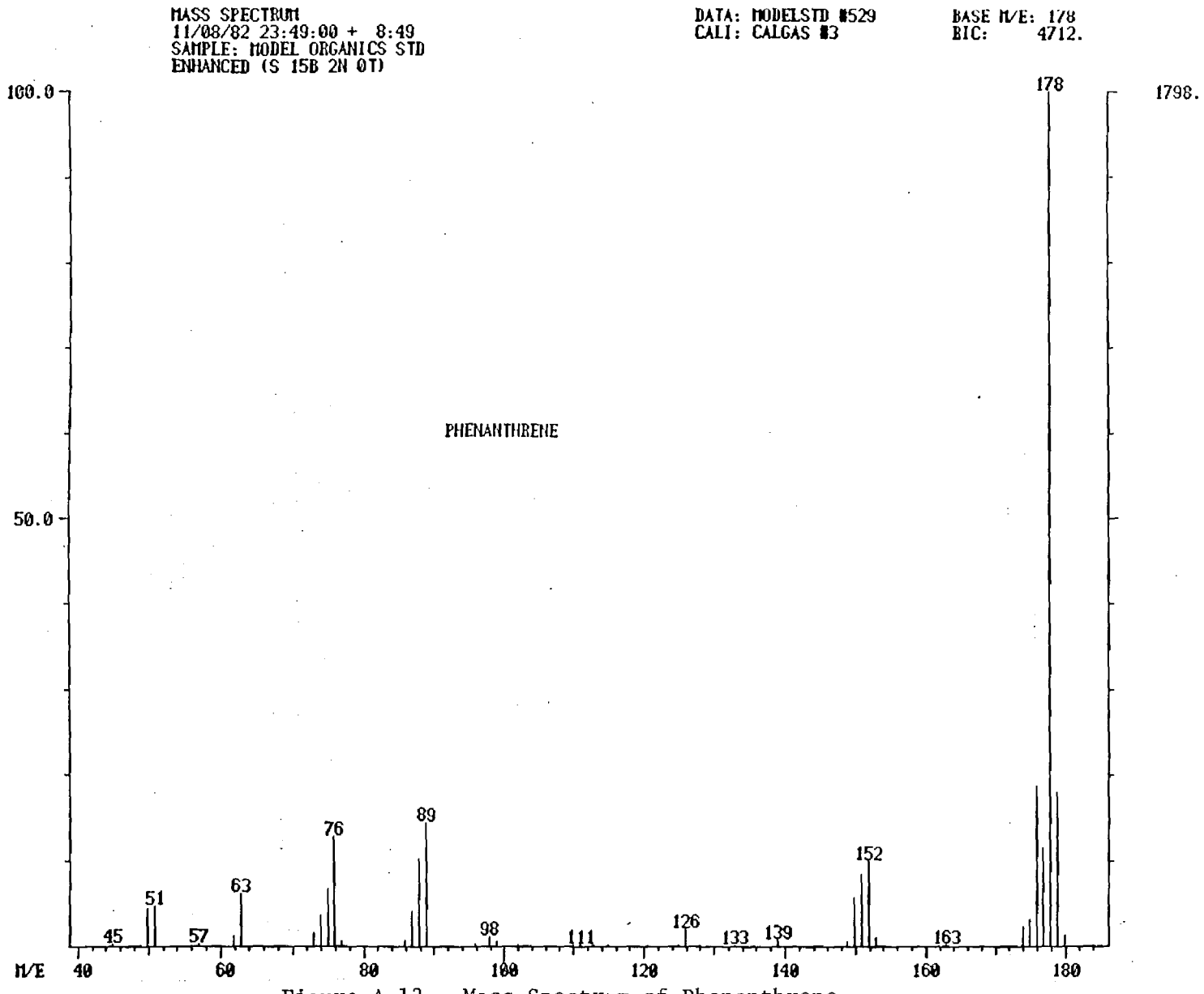

Figure A-12. Mass Spectrum of Phenanthrene

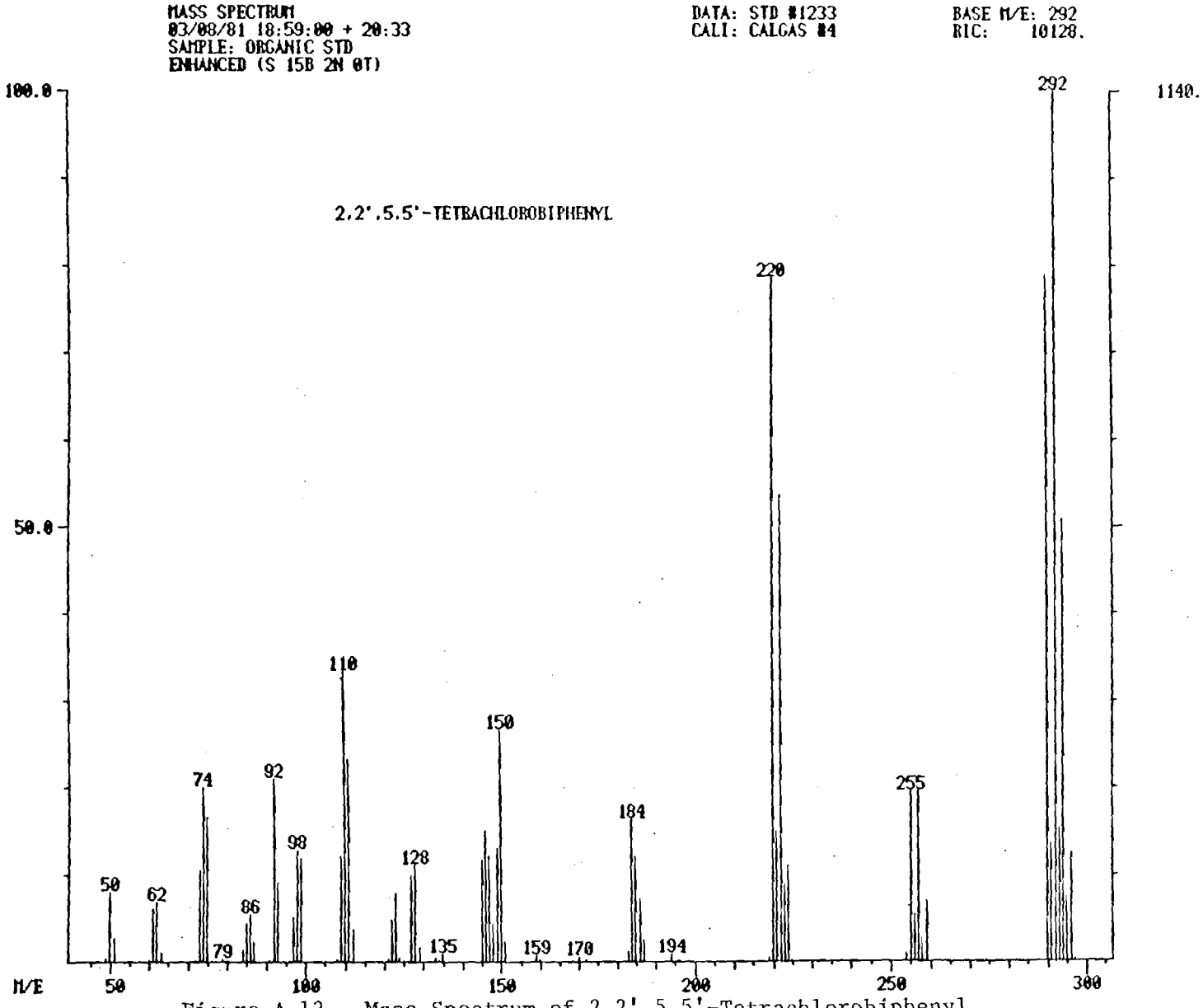

Figure A-13. Mass Spectrum of 2,2',5,5'-Tetrachlorobiphenyl

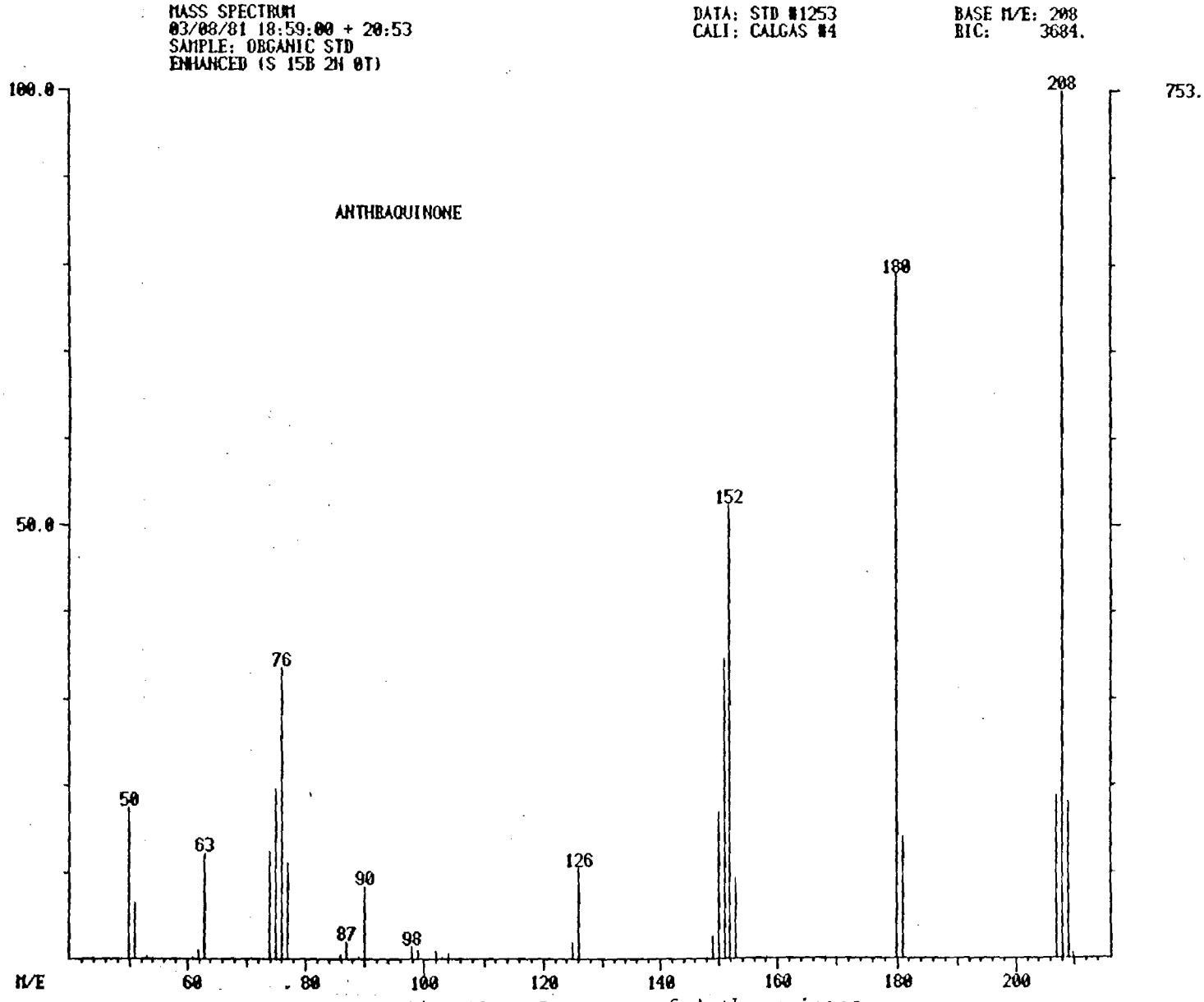

Figure A-14. Mass Spectrum of Anthraquinone

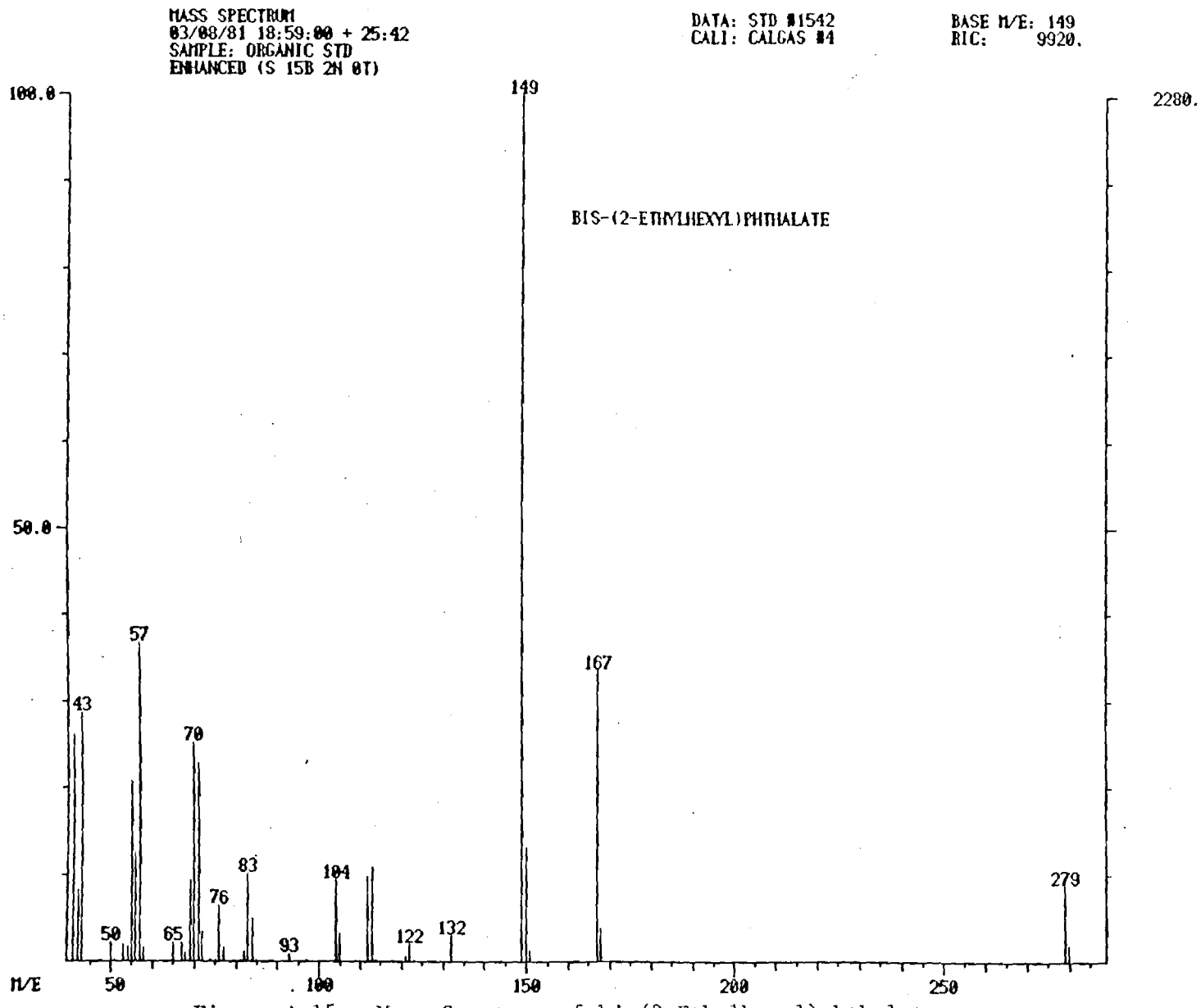

Figure A-15. Mass Spectrum of bis(2-Ethylhexyl)phthalate

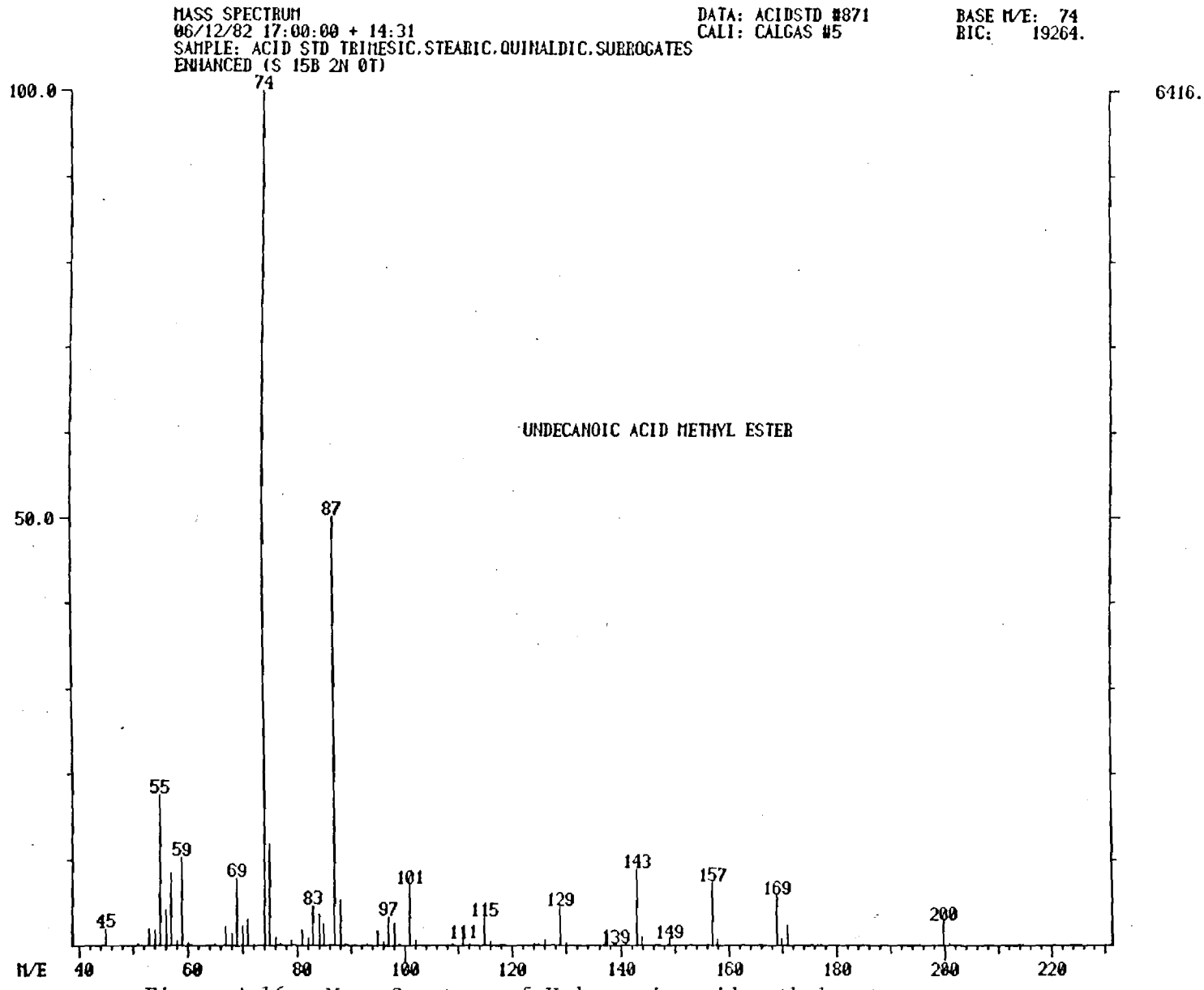

Figure A-16. Mass Spectrum of Undecanoic acid methyl ester

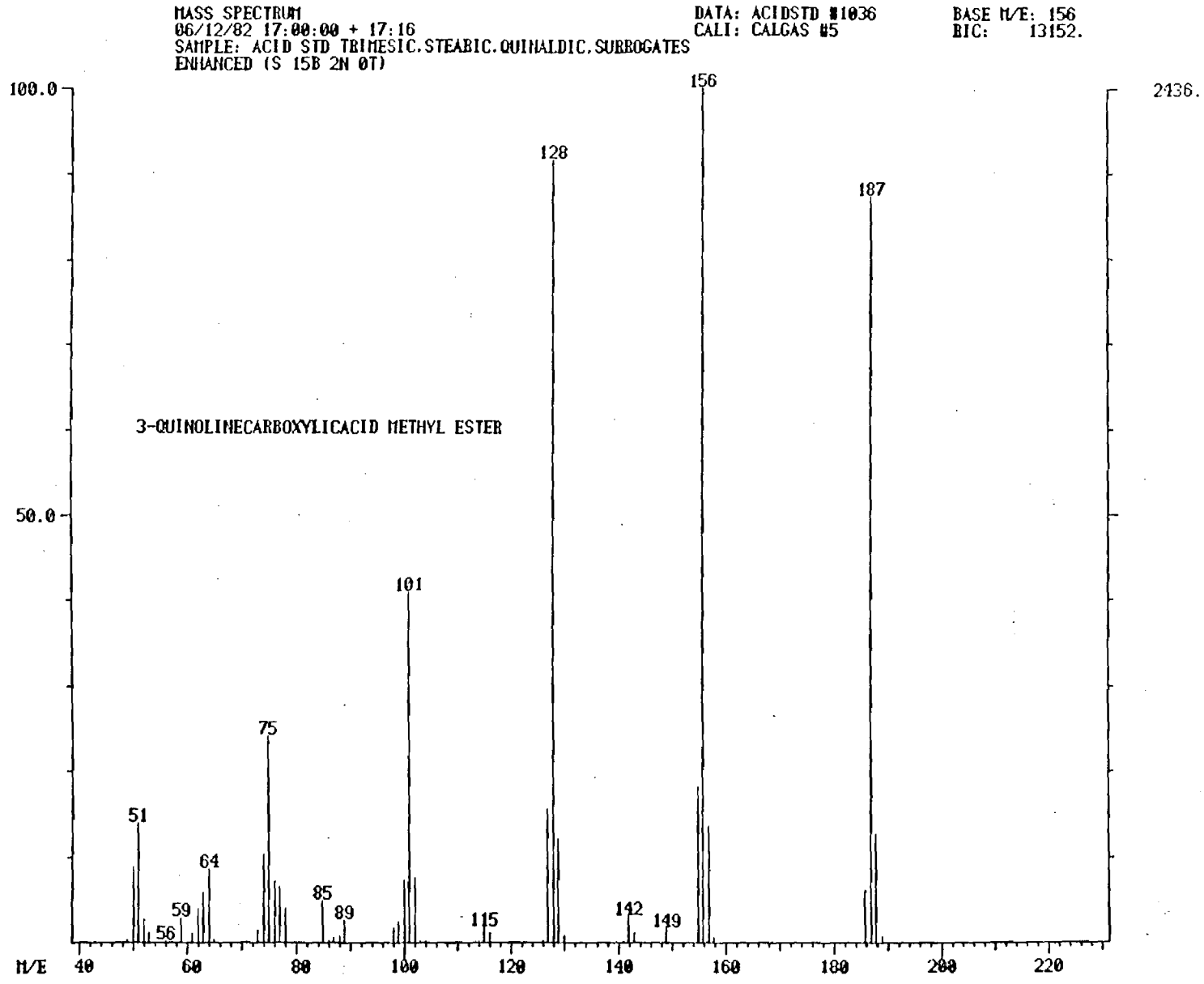

Figure A-17. Mass Spectrum of 3-Quinoline carboxyl acid methyl ester

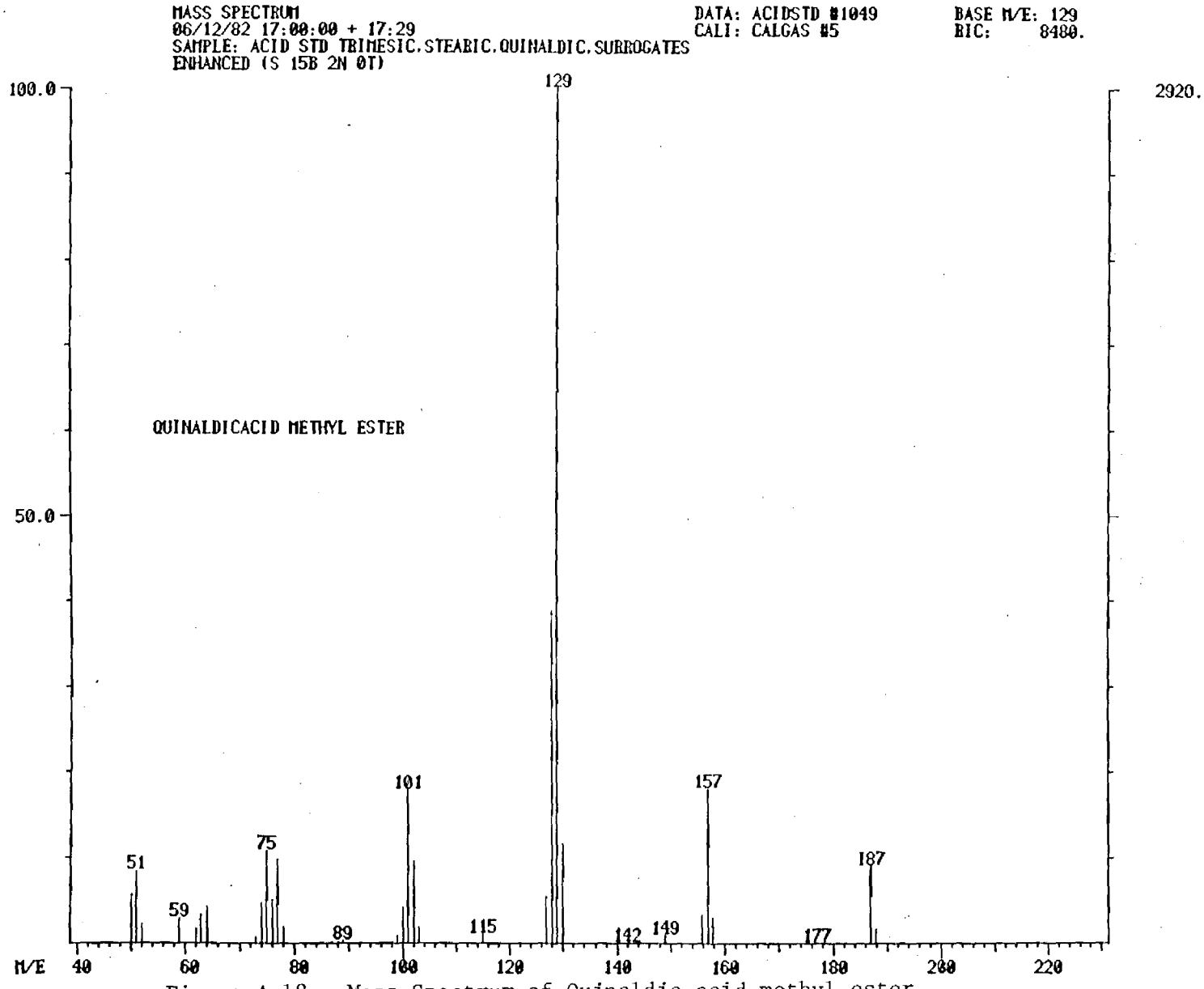

Figure A-18. Mass Spectrum of Quinaldic acid methyl ester

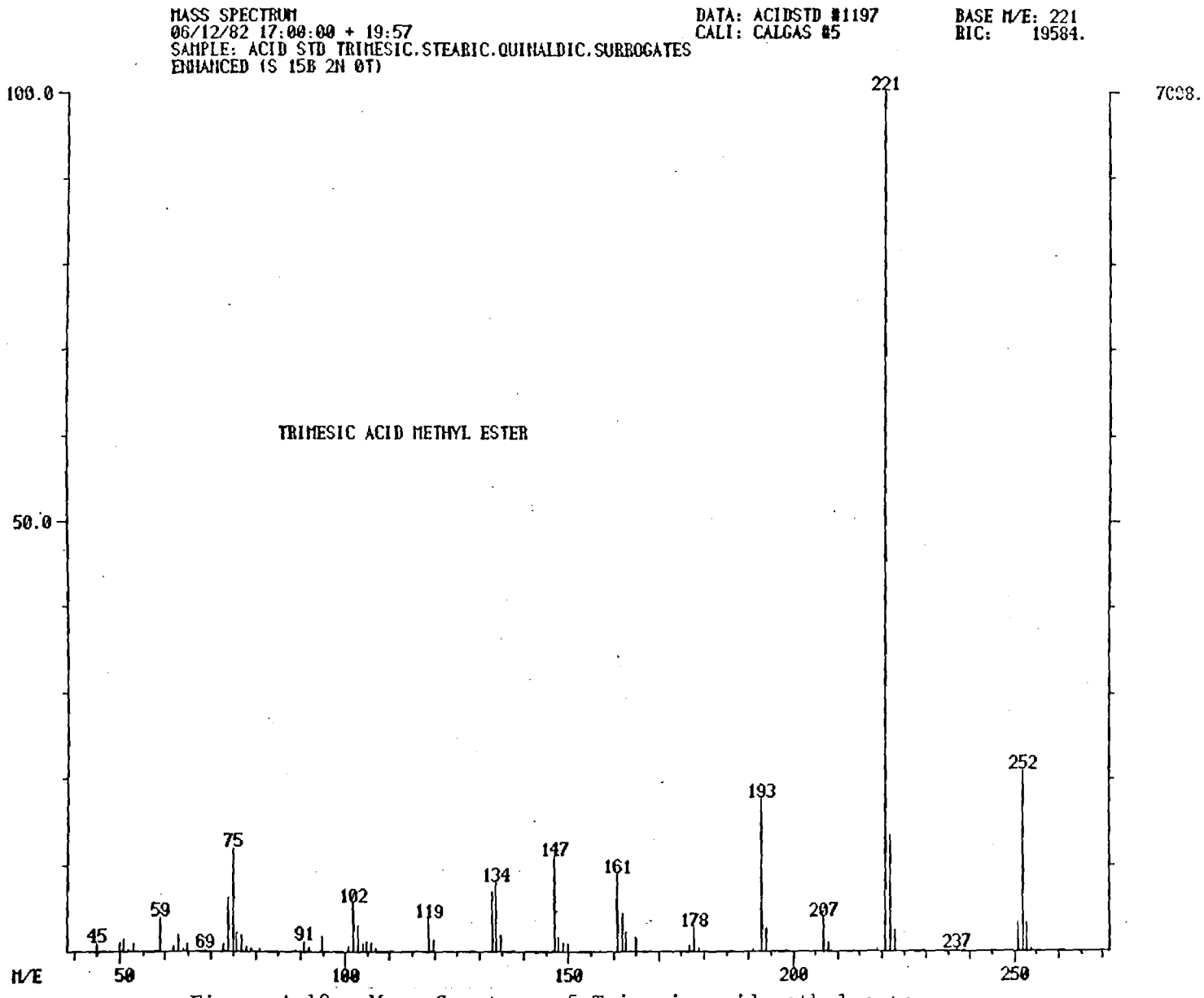

Figure A-19. Mass Spectrum of Trimesic acid methyl ester

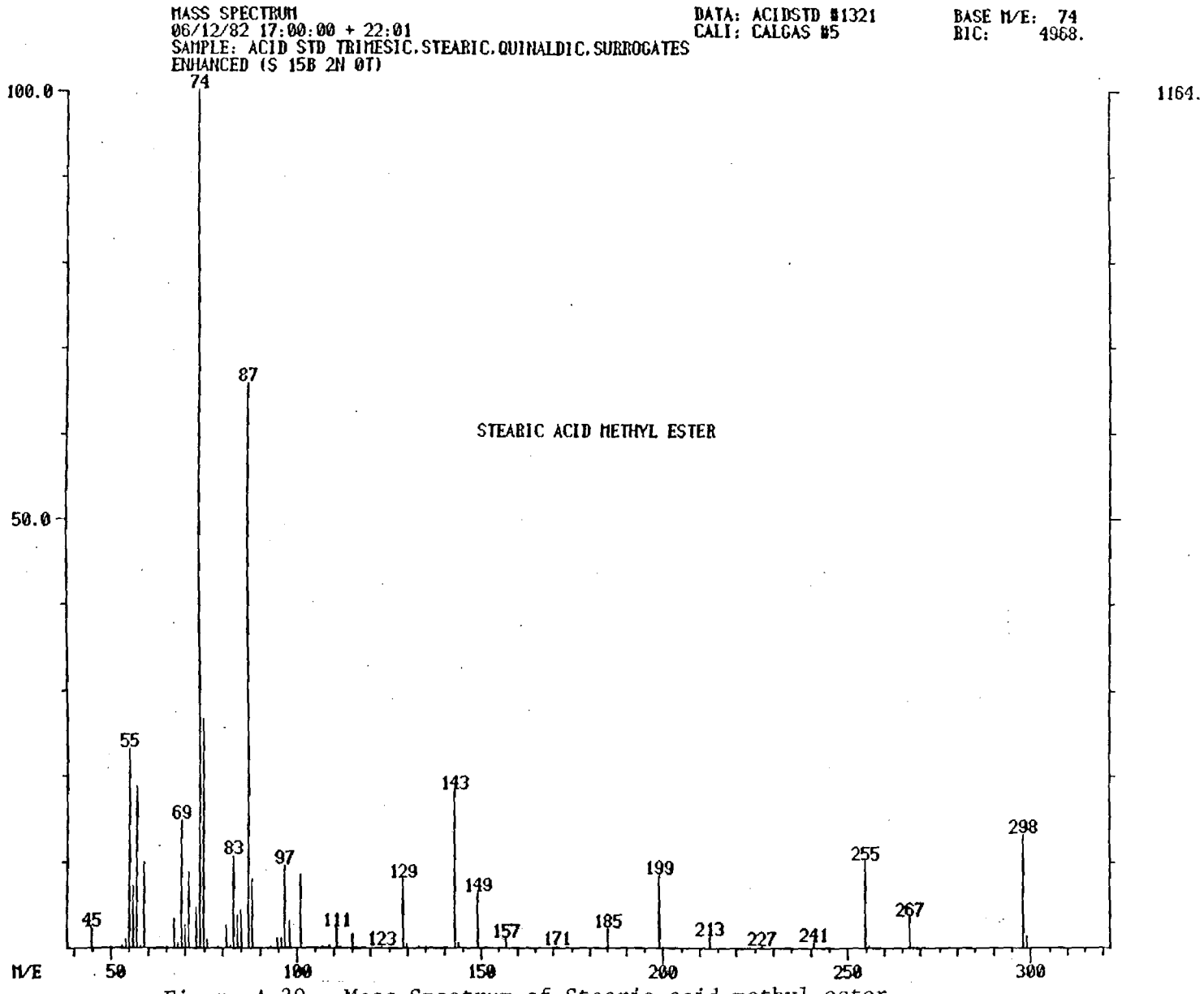

Figure A-20. Mass Spectrum of Stearic acid methyl ester

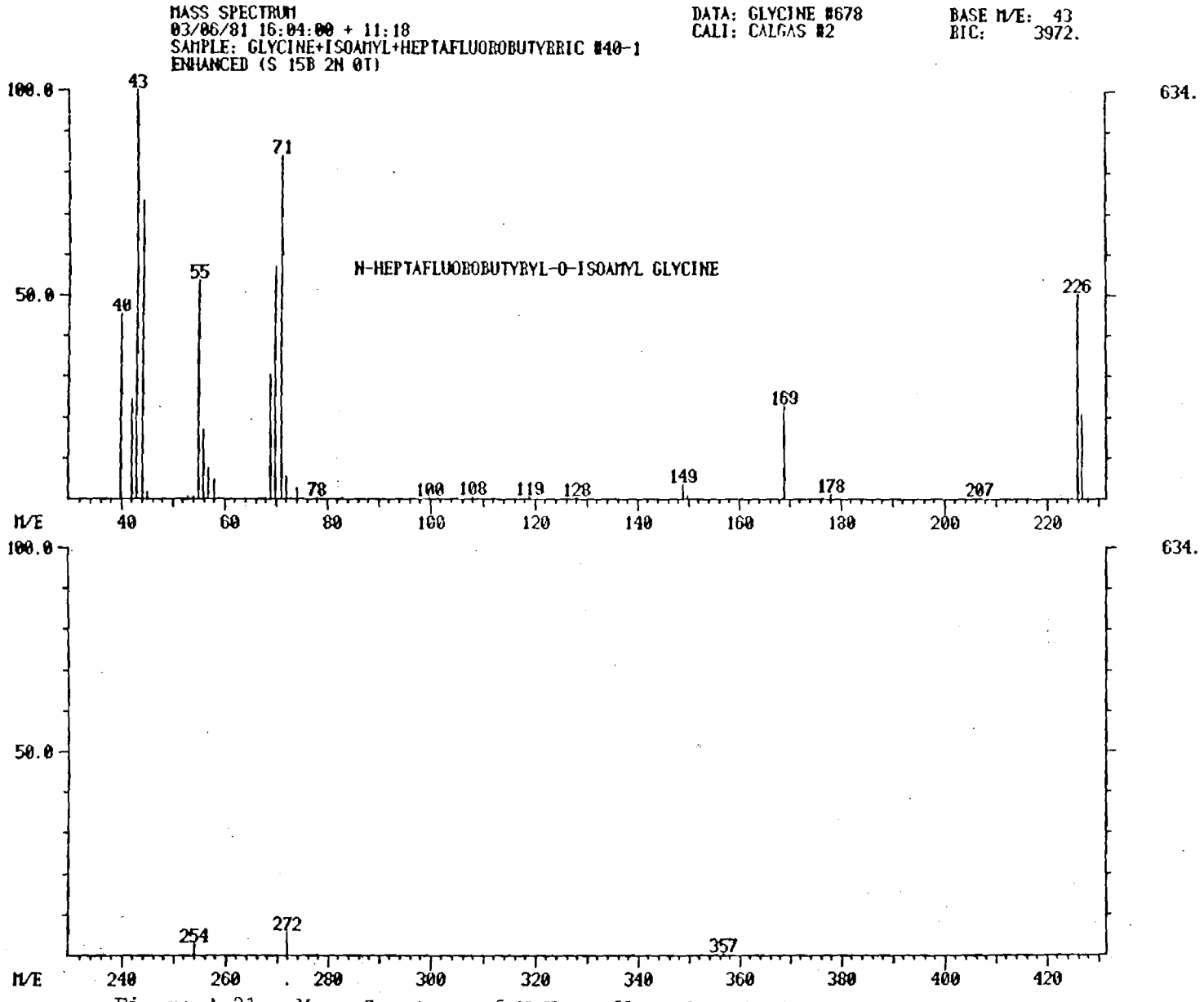

Figure A-21. Mass Spectrum of N-Heptafluorobutylril-O-isoamyl glycine

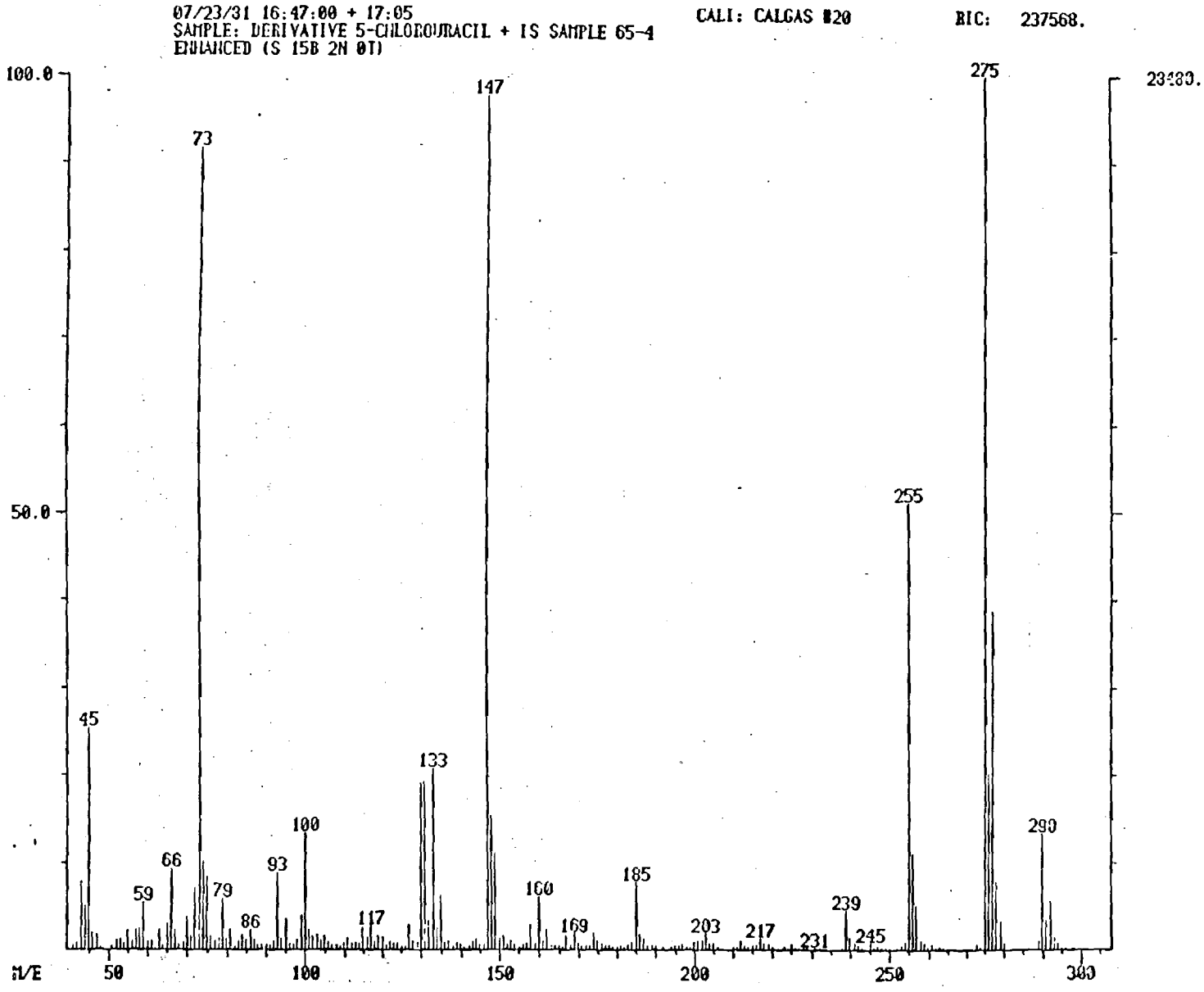

Figure A-22. Mass Spectrum of 5-Chlorouracil trimethylsilyl derivative

APPENDIX B

ANALYTICAL PROCEDURES

B1. Chemical Derivatization of Carboxylic Acids to Methyl Esters

B1.1 Apparatus and Reagents

a. Reacti-vial (5 ml capacity)
b. Normal grade nitrogen gas
c. Molecular sieve and temax-GC trap for nitrogen gas
d. Glassware apparatus for diazomethane generation (see Figure B-1)
e. Diazald (N-methyl-N-nitroso-p-toluene sulfonamide)
f. Methanol "distilled in glass" grade
g. Diethyl ether "distilled in glass" grade
h. 35% NaOH solution
i. Conc. HCl solution

B1.2 Chemical Derivatization Procedure

a. All glassware used in this protocol should be prepared according to the requirements set for trace organic analysis. All operations should be carried out under a well ventilated hood.
b. One ml of the aqueous solution (pH=10) of the acids is placed in a 5 ml reacti-vial and blown dry with nitrogen at room temperature.
c. Approximately 200 µl of conc. HCl is added by carefully rinsing the wall of the vial and then dried again with nitrogen.
d. One ml of diethyl ether is added to the dried sample in the attempt to bring the acids at least in partial solution and to form an ethereal diazomethane solution which would react facilely with the solid or dissolved acids. A thin glass stick is used to crash any salty deposits and to remove it from the wall of the vial.
e. Set up the apparatus for the generation of gaseous diazomethane. Regulate the nitrogen flow at ≈50-60 ml/min through the first purging tube filled with methanol. Meanwhile, 300-400 mg of Diazald are placed at the bottom of a 10 ml glass test tube which is then inserted into the second purging tube of the apparatus. Five ml of methanol followed by 1-2 ml of 35% NaOH are then added to the Diazald and the purging tube is immediately connected to the first purging tube.

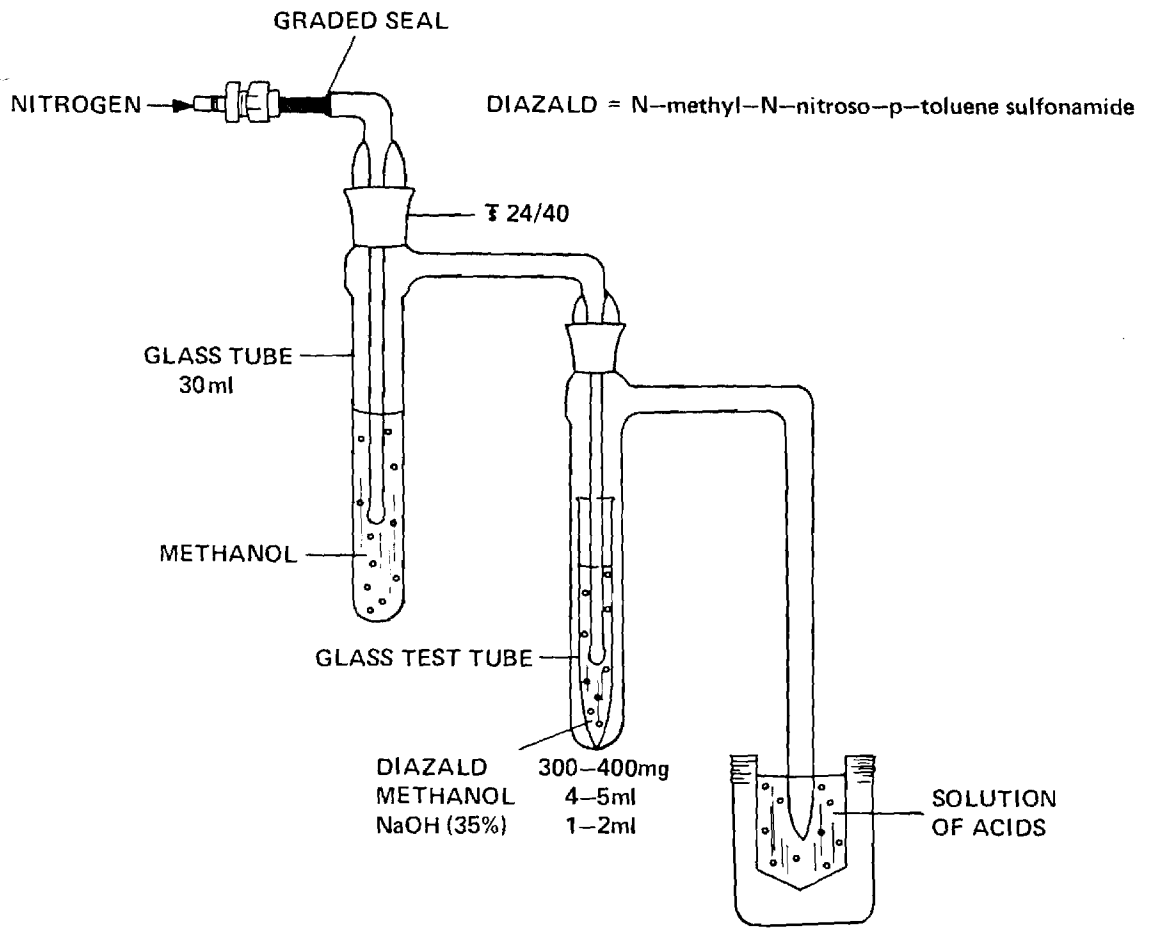

Figure B-1. Apparatus for Diazomethane Derivatization

f. Let the nitrogen + diazomethane bubble in the solution of acids for approximately 10-20 seconds.

g. The methylated acid solution is left open to the atmosphere inside the hood for 10 minutes, N_2 is blown to drive away excess diazomethane and then the volume of the solution is adjusted to 100 µl, and submitted to GC analysis.

B2. Preparation of Test Solution for 2,4'-Dichlorobiphenyl, 2,2',5,5'-Tetrachlorobiphenyl, 1-Chlorododecane and Phenanthrene

B2.1 Apparatus and Reagents

a. Hexane "distilled in glass" grade
b. Acetone "distilled in glass" grade
c. "OFW"
d. Beaker 250 ml
e. Sonicator

B2.2 Procedure

a. The calculated amount of the compounds stock solution is diluted in 10 ml of hexane.
b. The solution is sonicated and then blown dry with nitrogen.
c. Five ml of acetone are added and sonication is applied for 10 minutes to enhance the solubilization of the compounds.
d. Nitrogen is used to blow away the acetone. However, the solution is not dried completely.
e. One hundred ml of "OFW" is added and the solution sonicated for 15 minutes.
f. Finally, the 100 ml solution and the water rinsing of the beaker are added to the test solution.