GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 10/27/80

Project Title: Evaluation of the Methods for the Isolation or Concentration of Organic Substances from Water

Project No: E-20-688 (Subproject is G-35-683/Reuter/GeoPhy Sci)

Project Director: Dr. E.S.K. Chian

Sponsor: Environmental Protection Agency

Agreement Period: From 9/29/80 Until 12/28/82 (Rpts.) 9/28/82 (Perf.)

Type Agreement: Contract No. 68-03-3000

Amount: $189,725 (E-20-688)
$ 21,643 (G-35-683)
$211,368 TOTAL

Reports Required: Milestone Chart; Detailed Statement of Work; Planned Expenditure of Effort Table; Quarterly Progress; Final

Sponsor Contact Person (s):

Technical Matters

Paul Ringhand
Health Effects Research Laboratory
Environmental Protection Agency
Cincinnati, OH 45268
(513) 684-7450

Contractual Matters
(thru OCA)

James M. Bzdusek
Negotiated Contracts Branch
Contracts Management Division
Environmental Protection Agency
Cincinnati, OH 45268
(513) 684-7721

Defense Priority Rating: N/A

Assigned to: Civil Engineering (School/~~Laboratory~~)

COPIES TO:

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date February 2, 1984

Project No. E-20-688 School/~~Lab~~ Civil Engineering

Includes Subproject No.(s) G-35-683

Project Director(s) Dr. E.S.K. Chain GTRI / ~~GIT~~

Sponsor Environmental Protection Agency

Title Evaluation of the Methods for the Isolation or Concentration of Organic Substances from Water

Effective Completion Date: 9/28/82 (Performance) 12/28/82 (Reports)

Grant/Contract Closeout Actions Remaining:

- [ ] None
- [ ] Final Invoice or Final Fiscal Report
- [ ] Closing Documents
- [ ] Final Report of Inventions
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [X] Other Cumulative Claim and Reconciliation (EPA form 1900-10)

Continues Project No. _____ Continued by Project No. _____

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Form OCA 60:1028

E-20-688

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
CIVIL ENGINEERING

October 31, 1980

TELEPHONE:
(404) 894-22

Mr. Paul Ringhand
Project Officer
Health Effects Research Laboratory
Environmental Protection Agency
26 W. St. Clair Street
Cincinnati, OH 45268

Re: EPA Contract No. 68-03-3000

Dear Mr. Ringhand:

I tried to reach you by phone several times, and was unable to get hold of you. Also, I am sorry about being unable to get acquainted with you during your trip with Fred to Georgia Tech.

Enclosed please find a copy of a milestone chart, together with a detailed statement of work and a planned expenditure of effort chart.

If you have any questions regarding these, please feel free to call me at (404) 894-2265.

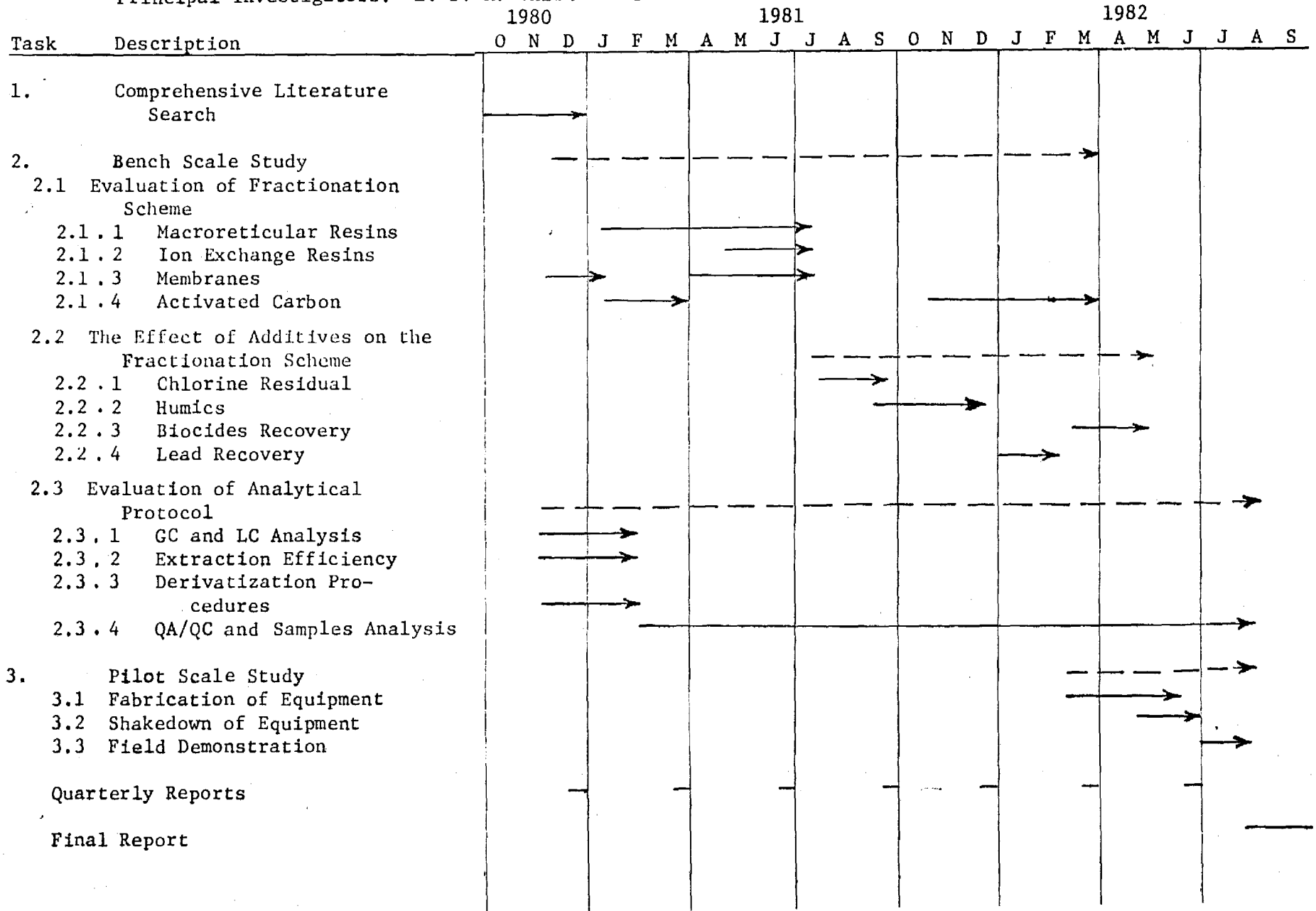
Sincerely,

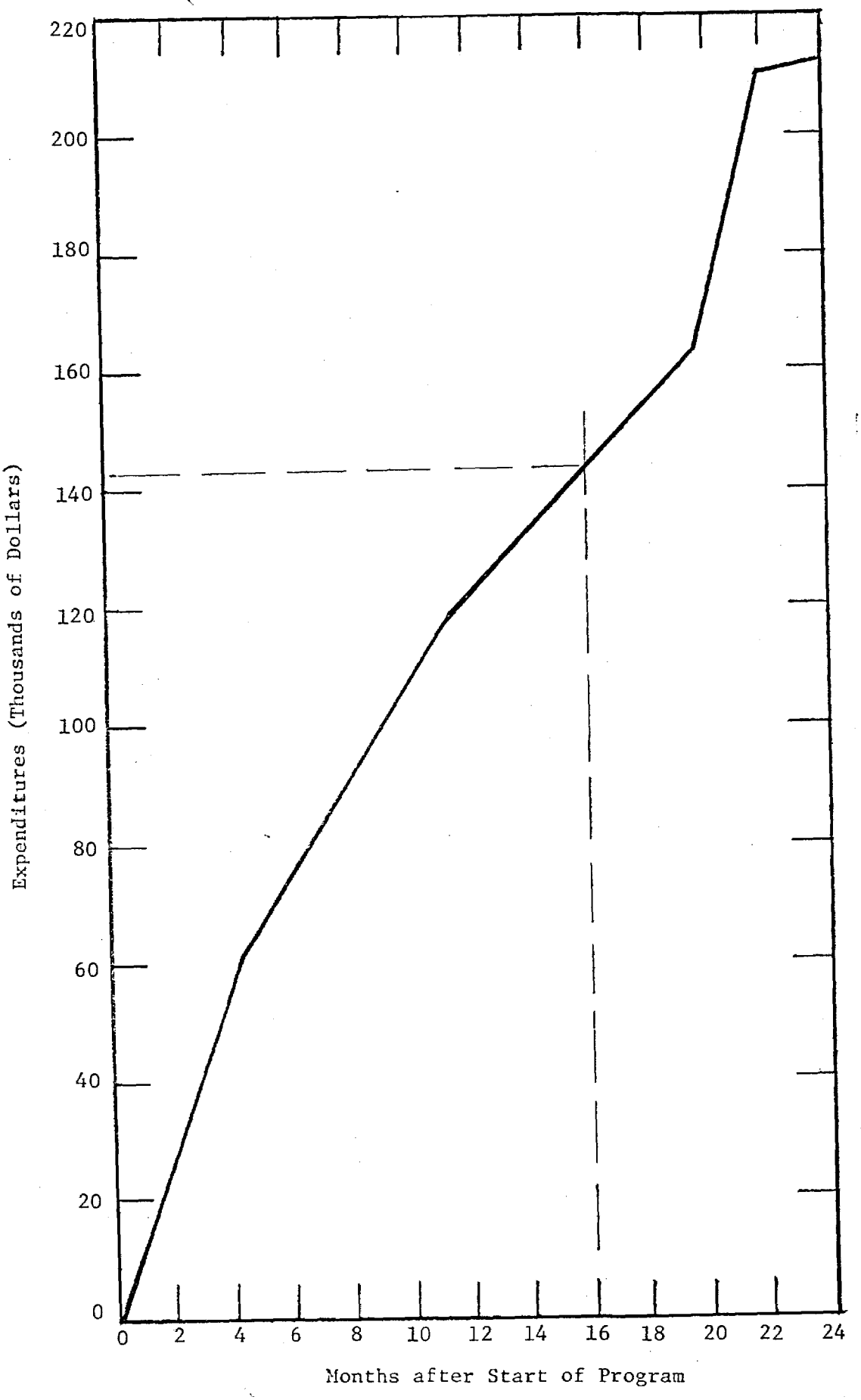
Edward S. K. Chian, Sc.D.
Professor of Environmental Engineering

ESKC:jp
Enclosure
cc: Dr. J. H. Reuter
Dr. M. Ghosal
Carol Cook, OCA Carol please pass this to Faith Ee.
Dr. M. Giabbai

Chart I - Schedule for the Proposed Research Program

Project: Evaluation of Methods for the Isolation or Concentration of Organic Substances from Water
Principal Investigators: E. S. K. Chian and J. H. Reuter

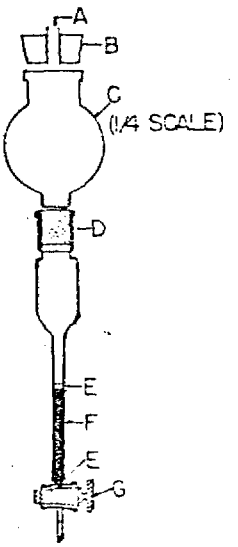




Projected Expenditures for EPA
Contract No. 68-03-3000

ADSORPTION BY RESINS

A comprehensive study on the use of macroeticular resins in the analysis of water for trace organic contaminants has been reported by Junk et al[1]. The XAD-2 resin will be cleaned by Soxhlet solvent extraction, and kept in a wetted condition. The purified XAD resin is added as a methanol slurry to make a 6cm high resin bed in a 10/0.6cm long silanized glass column (Fig. 1). One litre of the organic-free distilled water, spiked with organic compounds (50ppb to 20ppt) and adjusted to the desired pH will be passed through the column. The adsorbed organic compounds will be eluted with 25ml of ether, dried over baked Na_2SO_4, concentrated and analyzed with GC. Immediately after this analysis, a standard solution containing the same organic compounds at



A = Nitrogen inlet
B = Cap
C = 2 litre reservoir
D = 24/40
E = Silarized glass wool plug
F = 0.6cm I.D.
G = PTFE Stopcock

Figure 1

an identical concentration will be analyzed. Further confirmation of chemical identity will be obtained by GC-MS analysis. Recovery data for a cross section of organic compounds indicate that out of the 110 compounds studied, poor recovery was noticed in 3 compounds (35, 40 and 47%), moderate in 6 compounds (less than 80%) and good (greater than 80%) in the rest. The average reproducibility of these values is $\pm$ 12%.

Kunin[2] has stipulated that the nonpolar adsorbents are particularly effective for adsorbing non-polar solutes from polar solvents,while polar adsorbents are more effective for adsorbing polar solutes from nonpolar solvents. Although his paper does not show comparative figures of recovery with solvents of different polarity, it has been claimed that phenols have been successfully removed and regenerated by the use of XAD-4.

Since we have to deal with samples containing humic acid, it is interesting to note the different views on adsorption and desorption of humic acids on macroreticular resins. Cheng[3] proclaimed that XAD-12 was the most effective resin in removing humic acid from a solution, with the optimum effect at pH 5. Malcolm[4] proved that XAD-8 had several advantages over other resins for the purpose of preconcentration of organic matter in natural water. The same authors[5] published a detailed study of evaluation of 5 resins for concentration of low-molecular-weight humic substances from aqueous solution. Elution efficiencies were determined by desorption with 0.1N NaOH. Highest recoveries were obtained with XAD-7 and XAD-8. However, XAD-7 exhibited excessive bleeding and hence was considered inferior to XAD-8. McCarthy[6] applied this technique to show that the humic material was desorbed by a pH gradient solution in two distinct bands. In our effort[7] to recover humic acids from Satilla river water, we determined XAD-7 to be more efficient in adsorbing humics than XAD-8. It appears that the subject of adsorption and desorption of aquatic humic material depends on the particular humics in question, and it has to be individually determined which resin performed the best.

We intend to use XAD-8 and XAD-4 (or XAD-2) in order to follow the scheme of fractionation over these resins (Fig. 2). We shall be cautious about using XAD-2 because it has been reported that certain compounds initially adsorbed on XAD-2 apparently desorb later.[8]

ION EXCHANGE RESINS

Khym has published a review on the use of ion exchange resins for analytical ion exchange procedures. There are crosslinked polyelectrolyte framework which is held together by chemical bonds. The macroporous resins consist of a highly crosslinked styrene-divinylbenzene matrix containing large pores. Their large surface area confers fast kinetics in the separation of both high and low molecular weight solutes. We intend to use Bio-Rad AGMP-1 (anion exchanger; Resin 1), Bio-Rad AGMP-50 (cation exchanger; Resin 2) resins. Their properties are listed below:

No	Resin	Surface Area	Porosity
1	AG MP-1	23 m^2/gm	20%
2	AG MP-50	35 m^2/gm	30-35%

Resin (1) will be used to liberate the free bases (Fraction I and IV, Figure 2) while Resin (2) will be used to liberate the free acids (Fraction III and V, Fig. 2). The fractions referred to in Figure 2 represent the fractionation scheme proposed in this study.

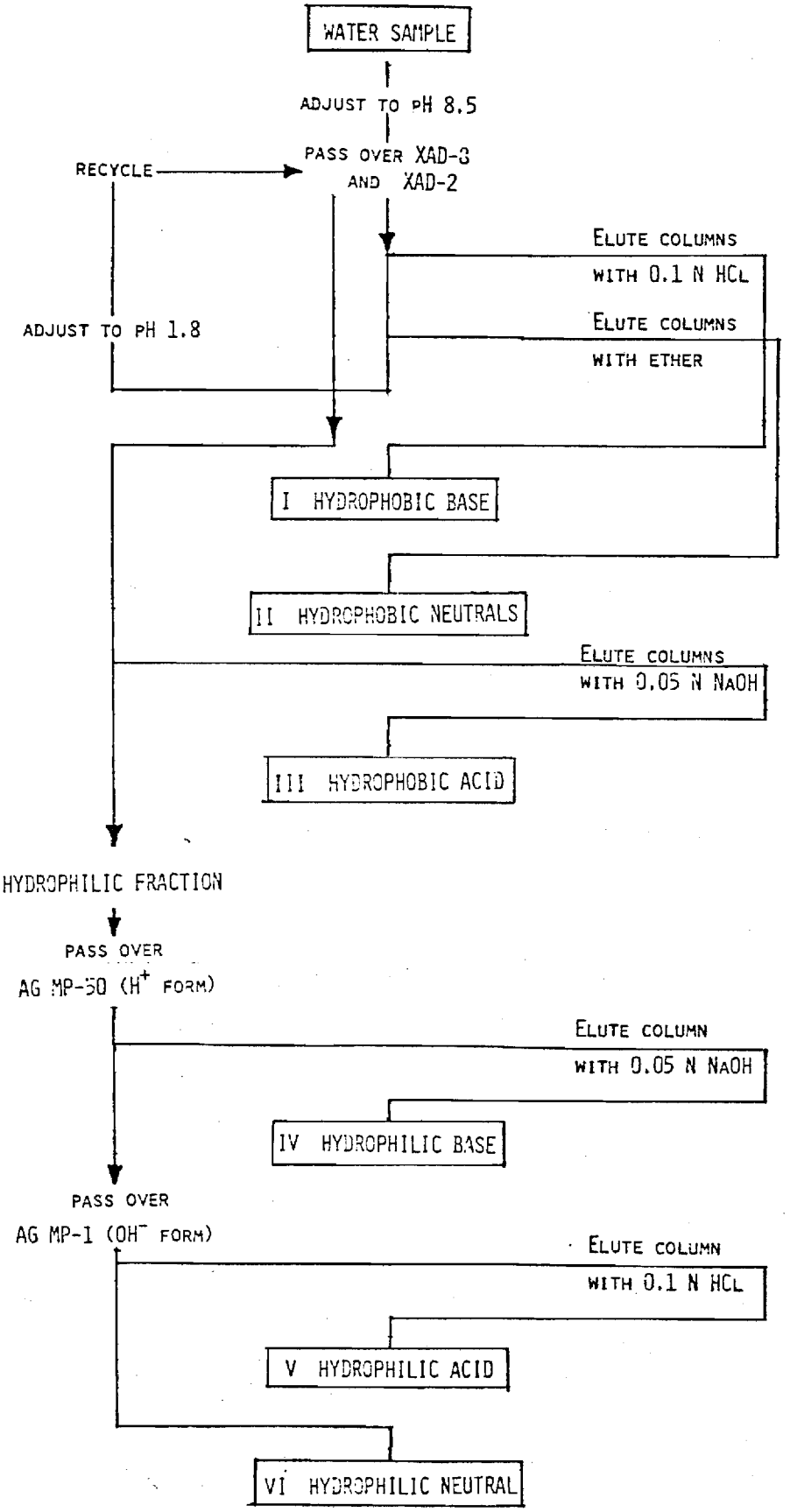

WATER SAMPLE
ADJUST TO pH 8.5
PASS OVER XAD-3
AND XAD-2
RECYCLE
ADJUST TO pH 1.8
ELUTE COLUMNS
WITH 0.1 N HCL
ELUTE COLUMNS
WITH ETHER
I HYDROPHOBIC BASE
II HYDROPHOBIC NEUTRALS
ELUTE COLUMNS
WITH 0.05 N NaOH
III HYDROPHOBIC ACID
HYDROPHILIC FRACTION
PASS OVER
AG MP-50 (H^+ FORM)
ELUTE COLUMN
WITH 0.05 N NaOH
IV HYDROPHILIC BASE
PASS OVER
AG MP-1 (OH^- FORM)
ELUTE COLUMN
WITH 0.1 N HCL
V HYDROPHILIC ACID
VI HYDROPHILIC NEUTRAL

Figure 2

REVERSE OSMOSIS

Quantitative recovery of organic compounds with the membrane process can only be accomplished if the membrane has better than 99% rejection of these compounds. This is especially true at a high degree of concentration factors. Of all the model compounds covered in this study, only a few compounds are rejected effectively with the state-of-the-art membranes. They include tetrachlorobiphenyls, benzo(e)pyrene, bis(2-ethylhexyl) phthalate, glucose and, of course, humic substances. However, the first two compounds, i.e., PCB and PAH, tend to be adsorbed onto the membrane materials according to the work of Chian et al.[9] on the membrane rejection of a wide spectrum of pesticides. This may also be true with the phthalate and humic acids under study. Fortunately, these compounds can be quantitatively recovered by various macroreticular resins which will be employed in our concentration scheme. Since glucose is not adsorbable on these resins, it can be concentrated effectively with the membrane process.

One of the major problems associated with the membrane process is the formation onto the membrane surface of a scale caused by the precipitation of the less soluble inorganic salts, e.g., calcium sulfate, at a high degree of concentration factors. This problem can, however, be circumvented by treating the solution with ion-exchange resins (both cationic and anionic) prior to the membrane process, such as that proposed in our fractionation/concentration scheme.

Several state-of-the-art membranes will be employed in this study to quantitatively recover glucose, along with partial recovery of some of the hydrophilic neutral fraction (such as furfural, croton-aldehyde and chloroform that are either poorly or not absorbed by the preceeding resin extraction processes. Membrane rejections of these poorly adsorbable

compounds will be evaluated with three commercially available membrane materials; namely, cellulose acetate, PA-300 (modified NS-100) and polyamide (nylon) membranes. A 150-ml all stainless high pressure test cell will be used for this study. The pressure will be supplied by nitrogen pressure. The solution will be agitated by means of a Teflon coated magnetic stirring bar housed in the stainless steel test cell.

While a major effort will be directed toward the evaluation of membrane rejection of the hydrophilic neutrals, membrane rejection of other model compounds will also be studied in order to establish data base for the membrane process.

An all stainless reverse osmosis pumping system (6 gpm), along with UOP's cellulose acetate and PA-3000 spiral wound modules and the DuPont's B-10 hollow fiber module, are currently available in our laboratory. Extensive effort will be made to study background contamination introduced by this system as well as methods of eliminating the contamination problem. This is necessary for the concentration of a large volume of spiked water at the end of this project period.

ACTIVATED CARBON

Activated carbon will serve as a universal tool for concentrating/isolating those compounds that are otherwise leaking through the afore-proposed isolating processes. An initial effort will be made to evaluate the background levels of a number of commercially available highly activated granular carbon, e.g., those supplied by Calgon (F-400), Westvaco, Nuchar etc. Soxhlet extraction similar to that proposed for cleaning resin will be used in this study.

Isotherms of the hydrophilic neutrals, such as crotonaldehyde, furfural and chloroform will be studied extensively using the carbons having the least background contamination. Results of this study will be used to compare with data available in the literature. A 16 x 30 mesh granular carbon will be evaluated due to a favorable breakthrough curve obtainable with this size carbon.

Batch studies using gravity flow will be used to concentrate the hydrophilic neutrals in a carbon column. A continuously-operated flow system will be fabricated with all wetted parts made of stainless steel and Teflon. This will be used for the isolation of a larger volume of water toward the end of this project. Background contamination with this pumping system will be evaluated.

Recovery of model compounds (e.g., hydrophilic neutrals) may be accomplished by using a J&W liquid CO_2 (at the critical conditions of CO_2) extractor followed by passing through a cryogenic trap set at a temperature somewhat higher than the sublimation point of dry ice (-78.5°C) say -75°C. This would allow the passage of CO_2 and trapping of other compounds; namely, chloroform

(melting point, -63.5°C), crotonaldehyde (melting point, -69°C) and furfural (melting point, -38.7°C). A sufficient amount of surface area as well as intimate contact will be provided to ensure highly efficient trapping of these compounds. This can be accomplished by using a large number of quartz or stainless steel coils (1/8" diameter). After these compounds are trapped in the cryogenic system, they can be desorbed with the aid of a stream of ultrapure helium (catalytically cleaned at 900°C) at room or elevated temperature. The helium stream will then be sparged through a chilled aqueous solution containing the concentrated model compounds. An alternative of this will be to directly dissolve the liquid CO_2 containing the hydrophilic neutrals into the aqueous solution containing the concentrated model compounds.

ANALYTICAL PROTOCOL

The proposed fractionation scheme will also determine the analytical protocols to be used for the quantitation of the organic compounds under study. In our proposed scheme, the "hydrophobic neutral" group do not need any extraction from aqueous solutions since they can be desorbed quantitatively from the macroreticular resins with one or a combination of two organic solvents. The subsequent analysis of these compounds will be performed directly by instrumentation methods, e.g., GC-FID, GC-MS-DS. A preliminary solvent exchange, e.g., Methanol → CH_2Cl_2, Ether → CH_2Cl_2, however, will have to be carried out in order to meet the solvent requirements in the introduction of these samples into the glass capillary column (splitless or on-column injection).

A particular consideration must also be placed on the broad range in solution concentration of the substances under investigation (50 µg/l to 10 ng/l) with respect to instrument detectability (linear response and lower detectable limit).

The "hydrophobic and hydrophilic acid and base" groups as proposed in our fractionation scheme will require an extraction step. Stir-bar liquid-liquid extraction, continuous liquid-liquid extraction and vapour-phase extraction will be investigated for the concentration of these groups of organic compounds along with the selection of appropriate solvents (e.g., CH_2Cl_2, $CH_3COOC_2H_5$, $CHCl_3$) and pH of the solutions. The "hydrophobic and hydrophilic acid" solutions will eventually be combined, and subjected to extraction, derivatization, and finally to instrumental analysis. Three derivatizing agents (CH_2N_2, BF_3-Methanol, Pentafluorobenxylbromide) will be evaluated for: 1) derivatization efficiency; 2) reproducibility; 3) gas chromatographic interferences; and 4) the ease of operation. The

"hydrophobic and hydrophilic base" fractions will be combined and subjected to extraction followed by analysis with GC-FID, GC-NPD, GC-MS-DS.

The amino acid (glycine), left in the alkaline aqueous solution after extraction, will be derivatized by reaction with heptafluorobutirric anhydride and iso-amylalcohol and then quantitated by GC-ECD and GC-MS-DS.

Glucose, concentrated in the reverse osmosis (RO) fraction, will be analyzed according to the method described by Euklund, et al.[10]

Furfural, crotonaldehyde, chloroform which are poorly recovered by RO will be adsorbed onto activated carbon. Heat desorption and liquid desorption (liquid CO_2, CS_2) will be investigated for the quantitative recovery of these compounds as determined by GC-FID and GC-MS-DS.

The gas chromatography will be performed using the high resolution of glass capillary columns. Several stationary phases will be evaluated in order to optimize the resolution and chromatographic behavior of each organic compound under study.

The mass-spectrometer will be operated in the electron impact (EI) mode under the total and multiple ion (MID) acquisition.

Standard solutions of the 22 organic compounds will be analyzed by GC-MS-DS; their spectra and response factors relative to the internal standards will be stored in a separate library which will be used subsequently as reference in the quantitation program of the Incos data system.

High Performance Liquid Chromatography will also be investigated for the direct analysis of the less or non-volatile organic compounds which require a derivatization step prior to GC analysis.

Quality Assurance and Quality Control (QA/QC)

A QA/QC program will be implemented which will consist of the following elements: contamination control, containment/recovery of samples and instrumental calibration.

Contamination control is addressed by carefully defining materials and cleaning procedures used in the operation of the fractionation scheme, and is monitored by blank determinations. The blank determination consists of exposing the organic-free distilled water to the same glassware and manipulated and handled through the fractionation scheme as proposed for the real samples. Each fraction will be monitored by GC-MS-DS after derivatization, wherever necessary, and each possible contaminant present identified and quantified. The overall contamination contribution of the entire scheme will also be assessed. This study will be particularly helpful when a sample blank in the presence of residual chlorine will be evaluated through the fractionation scheme.

Containment/recovery will be evaluated for each organic compound spiked in organic-free distilled water at the concentration level specified. The influence of humics on the recovery of each compound will be assessed.

The internal standard method will be used for instrumental quantitation. A solution containing the substances under investigation and the internal standard at a known concentration will be used for the calibration of the instrument and up-dating the quantitation library prior to quantitation with the instrumental method. The mass-spectrometer will require a preliminary tune-up with Perfluorotributylamine (FC43) and cross-checking of the tune thus obtained with decafluorotriphenylphosphine (DFTPP).

REFERENCES

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2. Kunin, R., Polymer Eng. Sci., 17, 58 (1977).

3. Cheng, K. L., Mikrochim. Acta, 2, 389 (1977).

4. Malcolm, R. L., Thurman, E. M. and Aiken, G. R., Proceedings of 11th Annual Conference on Trace Substances in Environmental Health, D. D. Hemphill, Ed., Missouri, 1977, pp. 307-14.

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7. Reuter, J. H. and Ghosal, M., Monthly Report dated 8/11/77, EPA Contract No. 68-10-4480.

8. Suffet, I. H., Brenner, L., Coyle, J. T. and Cairo, P. R., Environ. Sci. & Tech., 12, 1315 (1978).

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10. Eklund, G., et al., J. Chromat., 142, 575 (1977).

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

Quarterly Report
December 1980

by

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J. Helmut Reuter
Maurizio Giabbai
Monojit Ghosal
Luther Roland
Zhana Geskin
Sarba Ghosh

Georgia Institute of Technology
Atlanta, Georgia 30332

Supported by

The U.S. Environmental Protection Agency
HERL, Cincinnati, OH 45268
Contract No. 68-03-3000

Project Officer
Mr. Paul Ringhand

This report summarizes the work performed during the first quarter (September 29, 1980 through December 5, 1980) of the EPA research program on "Evaluation of Methods for the Isolation and Concentration of Organic Substances from Water" (Contract No. 68-03-3000). The major efforts have been directed toward update of literature search on the fractionation scheme,estimation of membrane rejection of model compounds, and development of preliminary analytical protocols for the model compounds. The progress of these efforts are depicted in the Grant Chart (Chart 1) for the above contract.

Macroreticular Resin Fractionation

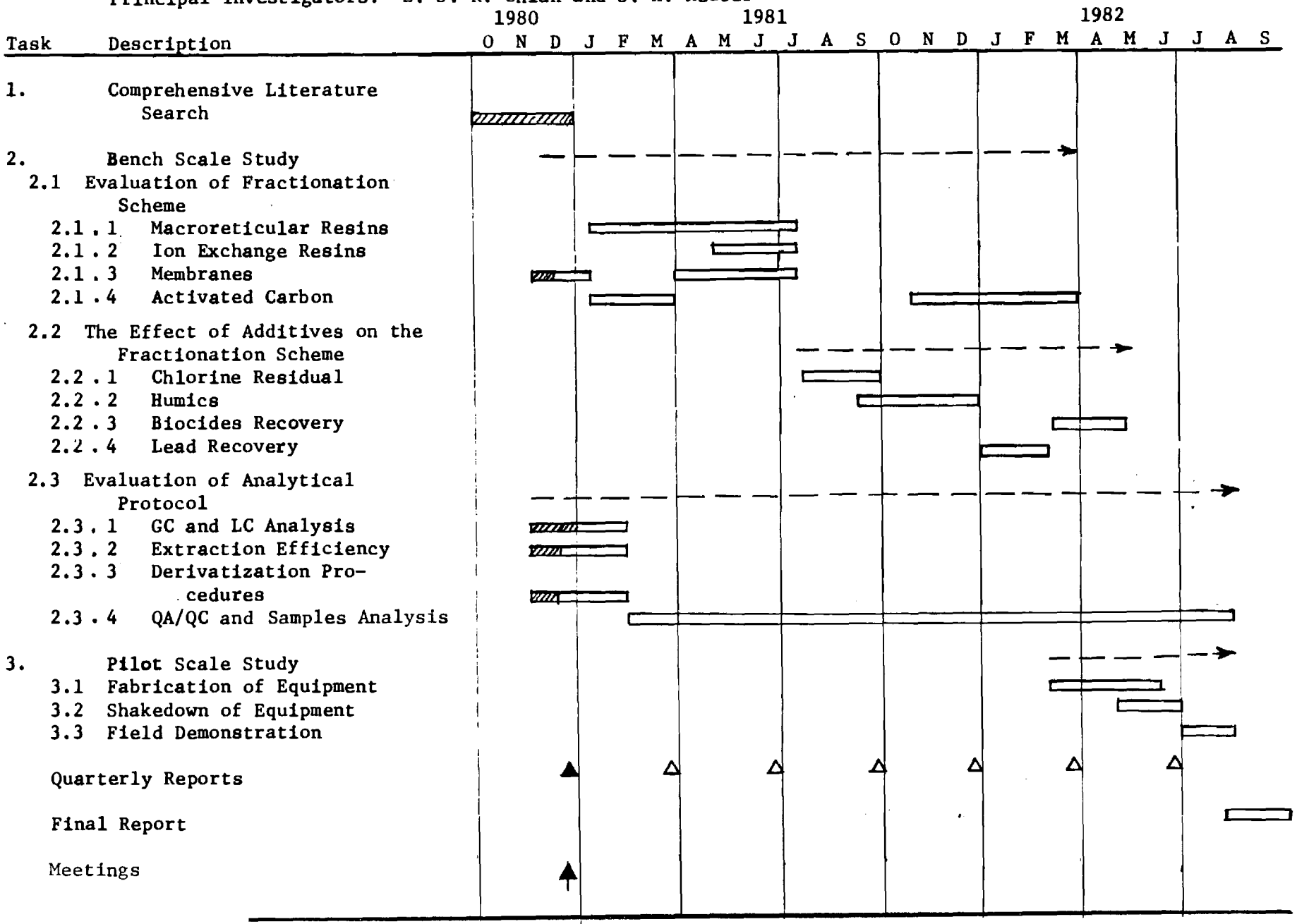
The present project envisages isolation and/or concentration of 23 organic compounds present in water at trace levels. 19 of them are present at 50 ppb level, 2 at 5 ppb and 1 at 10 ppt. In addition, humic acid may be added at a concentration of 2 ppm, and its affect on the recovery of the other 22 organic compounds will be studied.

Porous organic polymers have been used and studied for the extraction of trace organics from water[1-7]. These are solid polymeric macroreticular resin commercially available in a range of polarity, though they are non-ionic. The two important class of structures for these resins are represented by styrene-divinylbenzene copolymer (XAD-2 and 4) which are non-polar and the acrylic ester polymers (XAD-7 and 8) which are polar. A good review of the physical and chemical properties of the resins has been done by Kumin[8]. The surface characteristics of the resin is well defined and a wide range of pore structure can be developed within the framework of the chemical system.

The surface of these adsorbent polymers are inert and they do not react with the adsorbed organic molecules. Adsorption of water on the polymeric resin is minimal, although satisfactory transport of the organic substances towards the polymer surface is made possible by the wetting of the polymer

Chart I - Schedule for the Proposed Research Program

Project: Evaluation of Methods for the Isolation or Concentration of Organic Substances from Water
Principal Investigators: E. S. K. Chian and J. H. Reuter



with water. The organic solutes are adsorbed on the surface of the polymer, and a large volume of water can be processed with a small volume of the polymeric resin[9].

The 5 important resins and their properties are listed below:

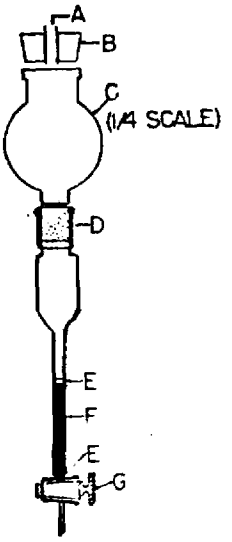
Name	Surface area (m^2/g)	Polarity
XAD-1	100	Non-polar
XAD-2	330	
XAD-3	750	
XAD-7	450	Intermediate polarity
XAD-8	140	

There are several advantages of synthetic resin adsorbents. Firstly, the process of adsorption from within the aqueous environment is a low energy process; and secondly, loss of volatile solutes is prevented in this process[10].

Classification of Organic Solutes. Organic solutes have been broadly classified into hydrophilic and hydrophobic classes. This classification refers to mechanisms by which organic solutes interact with the solvent, with each other and with adsorbents. The concept is defined and described by Simpson[11]. Leenheer defined the hydrophobic solutes as those that are adsorbed on the macroreticular resin surfaces of low and intermediate polarity.[10] The hydrophilic solutes are not adsorbed on these resins[10]. Hydrophobic organic molecules have hydrocarbon moieties which repel water, and are attracted towards hydrocarbon surfaces while hydrophilic molecules have polar moieties (containing O, N, S, etc.) which interact through electrostatic forces (like hydrogen bonding) with water and other polar molecules. Therefore, hydrophobic molecules are attracted by hydrophobic resins and hydrophilic molecules are attracted by hydrophilic surfaces. Weak acids will be adsorbed on Amberlite resins more strongly in the acid form than in the salt form.[12]

Once the hydrophobic molecules are adsorbed on the resins, the acids can be desorbed by bases, the bases by acids, and the neutrals by solvents like ether and methanol.

Fractionation of Organic Solutes. Junk et al.[13] carried out a study of fractionation of recovery of 110 hydrophobic compounds on XAD-2. The resin was cleaned by Soxhlet solvent extraciton, and kept in a wetted condition. The purified XAD resin was added as a methanol slurry to make a 6-cm high resin bed in a 10 x 0.6-cm I.D. silanized glass column (Fig. 1). One liter of pure water, spiked with organic compounds (50 ppm to 20 ppt) adjusted to the desired pH was passed through the column. The adsorbed organic compounds were eluted with 25 ml of ether, dried, concentrated and analyzed by GC. Immediately after this analysis, a standard solution containing the same organic compounds at an identical concentration was analyzed. Further confirmation of chemical identity was obtained by GC-MS analysis. Recovery data for a cross section of organic compounds indicate that out of the 110 compounds studied, poor recovery was noticed in three compounds (35, 40 and 47%), moderate in six compounds (less than 80%) and good (greater than 80%) in the rest. The average reproducibility of these values is $\pm$ 12%.



A = Nitrogen inlet
B = Cap
C = 2 litre reservoir
D = 24/40
E = Silarized glass wool plug
F = 0.6cm I.D.
G = PTFE Stopcock

Figure 1

These compounds include alcohols, aliphatic and aromatic aldehydes, ketones, esters, acids, ethers, polynuclear aromatics, phenols, alkylbenzenes, halogenated aromatic hydrocarbons, pesticides and a few nitrogen containing compounds which include quinoline, N-methylaniline and hexadecylamine.

The other comprehensive study for the preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters has been done by Leenheer[10,14,15]. The scheme is outlined in Fig. 2. It makes use of polymeric resins that are non-polar and of intermediate polarity as well as anion and cation exchange resins to fractionate organic compounds into the following six classes:

I	Hydrophobic Base
II	Hydrophobic Neutral
III	Hydrophobic Acid
IV	Hydrophilic Base
V	Hydrophilic Acid
VI	Hydrophilic Neutral

They studied adsorption and desorption on XAD-8, 1:1 mixed bed of XAD-2 and XAD-4, and stratified column of XAD-8 (5g) over XAD-2 (5g). The use of the stratified column is favored because it can adsorb both the low and high molecular weight hydrophobic organic solutes. High molecular weight solutes like fulvic acid are adsorbed on XAD-8, and it does not come in contact with XAD-2 resin. However, only XAD-8 has been used more recently[15]. Recovery of the compounds were monitored by determination of DOC (dissolved organic carbon in each fraction).

Aiken et al.[16,17] evaluated several resins and found XAD-8 to be most advantageous for the purpose of concentration of organic compounds because they give the best recovery. XAD-7 gives comparable recovery but it exhibited excessive bleeding and hence was considered inferior to XAD-8.

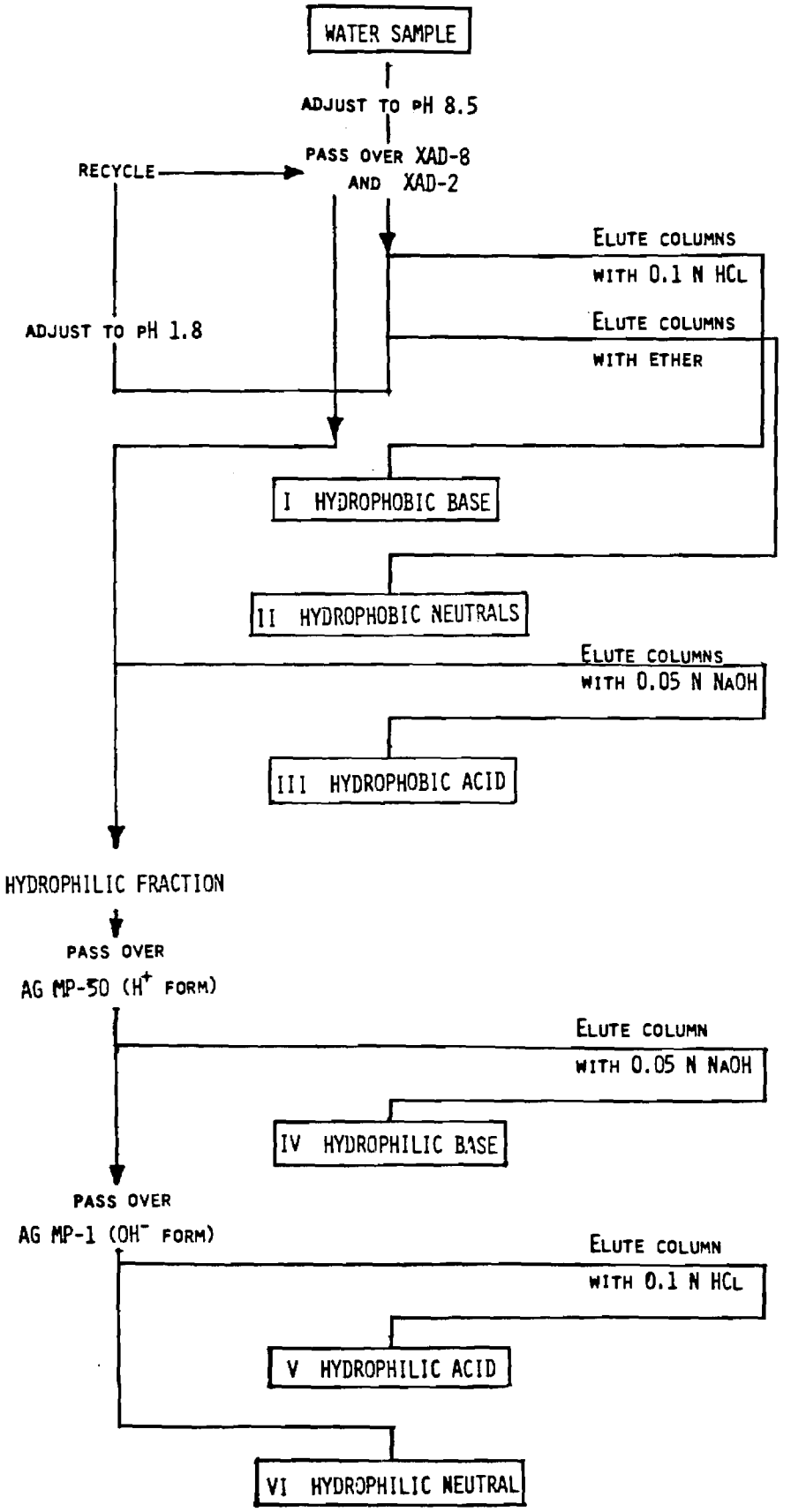

WATER SAMPLE
ADJUST TO pH 8.5
PASS OVER XAD-8 AND XAD-2
RECYCLE
ADJUST TO pH 1.8
ELUTE COLUMNS WITH 0.1 N HCL
ELUTE COLUMNS WITH ETHER
I HYDROPHOBIC BASE
II HYDROPHOBIC NEUTRALS
ELUTE COLUMNS WITH 0.05 N NaOH
III HYDROPHOBIC ACID
HYDROPHILIC FRACTION
PASS OVER AG MP-50 (H^+ FORM)
ELUTE COLUMN WITH 0.05 N NaOH
IV HYDROPHILIC BASE
PASS OVER AG MP-1 (OH^- FORM)
ELUTE COLUMN WITH 0.1 N HCL
V HYDROPHILIC ACID
VI HYDROPHILIC NEUTRAL

Figure 2

Ion-Exchange Resins. The next sequence in the fractionation scheme (Fig. 2) calls for the use of ion-exchange resins to adsorb hydrophilic organic solutes.

The principal cation and anion exchangers contain the styrene-divinyl benzene copolymer. The strongly acidic cation exchanger is produced by sulfonating the copolymer. The strongly basic anion exchanger is produced by chloromethylation followed by conversion to quarternary ammonium salt. Discussions and reviews of the ion exchange process and synthesis of different ion exchangers are found elsewhere[18-21]. An ideal ion exchange resin should combine high capacity, excellent equilibrium properties and rapid kinetics. It should undergo minimum chemical breakdown itself in its applications[22].

The two ion exchange resins used by Leenheer are Bio-rad A G MP-50 for cation exchange and Bio-rad A G MP-1 for anion exchange. Both of them have the same macroreticular structure as XAD-2. The cation exchange group is $-SO_3O^-$ and the anion exchange group is $-N^+$. The cation exchange resin was placed immediately after the XAD resins because the eluent from the XAD resin is acidic (Fig. 2), which protonates the hydrophilic base solutes such that they act as cations and are adsorbed on the cation exchange surface[10].

More recently, Duolite A-7 anion exchange resin has been used.[15] It is a macroporous phenol-formaldehyde resin available from Diamond-Shamrock (Cleveland, OH). Fritz and Richard[23] have used a new anion exhcnage resin prepared from XAD-4 to isolate and concentrate acidic organic material from aqueous solution.

Experimental Cautions

1. The XAD resin and ion-exchange columns must be cleaned by solvent extraction. Junk, et al.[13] recommends sequential soxhlet extraction of the XAD resins with methanol, acetonitrile and diethylether.

Leenheer[15] recommends sequential soxhlet extraction of XAD resins with acetone and hexane for 24 hr, extraction of AG-MP-50 with methanol for 24 hr, and extraction of Duolite A-7 with acetone.

2. All apparatus to be used should be made of glass or teflon. Glass apparatus can be cleaned free from organic material by baking at 450°C for 4 hr.

3. Water, free from organic substances should be available. Distillation of distilled water over permangate[15,24] and sodium hydroxide[25] gives a TOC of less than 0.1mg $C\,l^{-1}$. The commercially available water purifiers do not produce consistently a desirable blank level, while water cleaned by ultraviolet radiation was found to have a TOC (.056mg $C\ l^{-1}$) less than the detection limit.[26]

4. Solvents for elution should be pure.

5. Standard solutions should be prepared from organic solutes that are about 99% pure.

6. XAD resins may be stored in methanol.

7. The quantity of resin required can be calculated. Flow rate should not exceed 30 bed volume/hr except in case of the Duolite A-7 column, where flow rate should not exceed 15 bed volume/hr.

8. The XAD column should be covered with fluid all the time during extraction. The method of extraction has been described previously. An apparatus for continuous extraction of the resin column, after adsorption of trace organics from water, without drying in a modified soxhlet apparatus has been designed.[27] The advantage of the device is claimed to be the use of a small volume of solvent, and the disadvantage is that the solvent must be miscible with water.

Solvent Extraction

The concentrated fractions derived from the resin fractionation will be further concentrated and dissolved in organic solvents in order to be analyzed by GC or GC-MS.

Solvent extraction is one of the processes to achieve the goal. It can be done manually in batches by extraction of the aqueous solution with an organic solvent which has to be chosen carefully, or the extraction may be done continuously in a liquid-liquid extractor. The other two modes of extractions are continuous vapor-phase extraction and batch extraction by vigorous stirring with a magnetic stir bar.[28]

Lyophilization

Hydrophilic organic compounds may not be extracted with organic solvents. The aqueous solution may be freeze-dried (i.e., lyophilized) and only then the organic compound may be dissolved in an organic solvent or derivatized in order to render it soluble in an organic solvent, as the case may be. This process entails loss of the compound.

Solvent Evaporation

Prior to analysis, sizeable quantities of organic solvents have to be removed. Such concentration is commonly done by (1) rotary evaporation, (2) Kuderna-Danish evaporation,and (3) evaporation of solvents by blowing nitrogen gas. A systematic study of these three methods reveal that the best recovery will be obtained by a two-stage concentration. The first stage concentration of 150 ml to 4 ml can be done either by process (1) or (2) giving equal recovery of organic solutes. The second stage concentration with minimum loss of solute is done by process (3).[28]

Member Separation

Although the use of reverse osmosis membrane is intended to recover the non-adsorbable glucose, and possibly some of the aldehydes (i.e., furfural and crotonaldehydes) in the present study, it can also be used to recover other organic compounds that may not be completely recovered by the preceeding resin separation scheme. In practice, it can also be used to recover whatever inorganic compounds that may be present in the natural water. As such, the method available for the prediction of membrane rejection of solutes in aqueous solutions are presented in this report. In essence, if the physical characteristics of the organic solutes of interest are known, together with the characteristics of different membrane materials in rejecting a reference compound, e.g., sodium chloride, membrane rejection of these organic compounds with various membrane materials can be estimated. This would represent a great reduction in experimental efforts whenever a new membrane material is available in the future.

The concept of free energy parameter controlling reverse osmosis separations of ionic solutes in aqueous solution has been studied by Matsuura et al.[29], Dickson et al. [30] These authors used a modified form of the Born expression for free energy of ion-solvent interaction to both the bulk solution phase and the membrane-solution interface where water is preferentially absorbed. The free energy change ($\Delta\Delta G$) involved in the repulsion of the ion at the interface is represented by $(-\Delta\Delta G/RT)_i$ where R is the universal gas constant, T is the absolute temperature, and the subscript i, represents the particular ion under consideration. Matsuura[29] et al., related the solute transport parameter $(D_{AM}/K\delta)$ according to the following equation

$$\ln(D_{AM}/K\delta) = \ln C^* + \Sigma(-\Delta\Delta G/RT)_i \qquad (1)$$

where ln C* is a constant depending only on the chemical nature of the membrane material and the effective average pore size on the membrane surface. For any given film ln C* is usually represented in terms of the $(D_{AM}/K\delta)$ data for any suitable reference solute. If NaCl is considered as a reference solute then

$$\ln (D_{AM}/K\delta) = \ln C^*_{NaCl} + \Sigma(-\Delta\Delta G/RT)_i \qquad (2)$$

where the quantity $\ln C^*_{NaCl}$ is obtained from Equation (2) using the experimental $(D_{AM}/K\delta)$ data for NaCl and known values of $(-\Delta\Delta G/RT)_i$ for the Na^+ and Cl^- ions.[29,30] Matsuura et al.,[31] extended this concept to undissociated polar organic solutes in dilute aqueous system. Matsuura and Sourirajan[32] recommended a method for obtaining data on $(D_{AM}/K\delta)$ for organic solutes. Matsuura et al.,[33] suggested the following general expression for solute transport parameter $(D_{AM}/K\delta)$ for reverse osmosis systems involving preferential sorption of water at the membrane solution interface.

$$\ln (D_{AM}/K\delta) = \ln C^* + \rho^*\Sigma\sigma^* + \delta^*\Sigma E_S + \omega^*\Sigma s^* \qquad (3)$$

where, $\Sigma\sigma^*$ and ΣE_S are the Taft polar and steric parameter, respectively, for the substituent group in the solute molecule,and Σs^* is an applicable non polar parameter for the solute molecule, ρ^*, δ^* and ω^* are the characteristic proportionately constants associated with $\Sigma\sigma^*$, ΣE_S and Σs^*, respectively. The porous structure of the membrane surface, the chemical nature of the membrane material, and the nature of the funcational group in the solute molecule are accounted for in the constant ln C*.

Matsuura and Sourirajan[33] reported for a class of organic solutes the nonpolar effect may be considered negligible if the molecular structure of the solute contains a straight chain involving no more than three carbon

atoms non-associated with a polar functional group. For such solutes the reverse osmosis separations are governed by polar and steric effects only.

$$\ln (D_{AM}/K\delta) = \ln C^* + \rho^*\Sigma\sigma^* + \delta^*\Sigma E_S \quad (4)$$

A general expression for the solute transport parameter has been given by Matsuura et al.[36] using appropriate parameters representing the effect of pore size on the membrane surface, and the polar and steric effects, on solute transport parameter.

$$\ln(D_{AM}/K\delta) = \ln C^*_{NaCl} + \ln \Delta^* + (\frac{-\Delta\Delta G}{RT}) + \delta^*\Sigma_S \quad (5)$$

$\ln \Delta^*$ accounts for the overlap of pore size effect in the combined quantity ($\ln C^*_{NaCl} + \delta^*\Sigma E_S$). The quantity $\ln \Delta^*$ is a function of $\ln C^*_{NaCl}$ only (Matsuura et al,[36]) and, $(\frac{-\Delta\Delta G}{RT})$ represents the polar effect.

From Equation 5, the quantity $\ln \Delta^*$ can be considered to set a scale for $\ln (D_{AM}/K\delta)$ with respect to $\ln C^*_{NaCl}$ when the polar and steric parameters are each set equal to zero. Equation (5) is considered as a general expression for solute transport parameter for nonionized polar aliphatic and alicyclic organic solutes in aqueous solutions; where reverse osmosis separations are controlled by polar and/or steric effects and preferential sorption of water at the membrane-solution interface. In Equation (5) the quantity $\ln C^*_{NaCl}$ for a given film can be obtained from reverse osmosis for the reference feed solution NaCl - H_2O, when $\ln \Delta^*$, $(\frac{-\Delta\Delta G}{RT})$ and $\delta^*\Sigma E_S$ can be calculated. Thus from Equation (5) one can predict $(D_{AM}/K\delta)$ for different organic solutes for a given film, from the experimental data for the system NaCl - H_2O. Matsuura et al.[29] and Dickson et al.[30] defined

$$\Delta\Delta G = \Delta G_I - \Delta G_B \quad (6)$$

where ΔG represents the free energy of solute-solvent interaction and the subscripts I and B represent the membrane solution interface and bulk solution phase, respectively.

Matsuura et al.,[31] investigated the additivity principle for estimating ΔG_B. They assumed that the free energy of hydration ΔG_B for an organic molecule can be considered to be the sum of incremental free energy of hydration for each structural group involved represented by the symbol Y_B (structural group), and a characteristic constant $Y_{B,D}$ applicable to all structural groups

$$\Delta G_B = \Sigma Y_B \text{ (structural group)} + Y_{B,D} \tag{7}$$

the subscript B represents the bulk phase. The results matched well with the theoretical expression for G_B proposed by Butler[35]

$$\Delta G_B = RT \ln \frac{P_o \text{ mm Hg}/1 \text{ mm Hg}}{N_s} \tag{8}$$

where p_o is the vapor pressure, and N_s is the solubility mole fraction. Similarly for ΔG_I

$$\Delta G_I = \Sigma Y_I \text{ (structural group)} + Y_{I,O} \tag{9}$$

where I represents the interfacial region.

Thus the key to the prediction technique is the evaluation of applicable $(D_{AM}/K\delta)$ value for organic solute by Equation (5). $\ln C^*_{NaCl}$ is obtained from Equation (2). $\ln \Delta^*$ is obtained from the correlation between $\ln C^*_{NaCl}$ and $\ln \Delta^*$. $(-\Delta\Delta G/RT)$ is calculated on the basis of molecular structure using the additivity principle, and $\delta^* \Sigma E_s$ is obtained from Taft's data on E_s along with the correlation between δ^* and $\ln C^*_{NaCl}$. Matsuura et al.[31] presented this practical technique for predicting solute transport parameters for organic solutes used in conjunction with membranes of different surface porosities and polymeric materials (e.g., cellulose acetate and polyamide).

Adsorption on Carbon

A comprehensive literature review has been reported by Suidan et al.[36] on the adsorption of chlorinated organic compounds onto activated carbon, and other adsorbents. Recently, Belfort[37] reported the use of the solvophobic interaction theory as basis for correlating the adsorption capacity of different single organic solutes (such as aliphatic alcohols, aldehydes, ketones, organic acids and substituted aromatic compounds) with the physicochemical (such as polar and steric) structural parameters of these compounds. By correlating the molar adsorptivity of organic homologues with the physicochemical parameters of these compounds, as suggested by the solvophobic theory along with certain simplifying assumptions, it is feasible to establish a rationale predictive theory for the adsorption processes in presence of liquid phase. Further theoretical considerations and the solvent effects on adsorption on carbon were discussed recently by the same author.[38,39]

Concern on the equilibrium of isotherm studies was reported by Peel and Benedek.[40] Experimental evidence obtained by these authors demonstrated the need for extended period of contacting during isotherm evaluations to ensure that equilibrium is attained. Van Rossum and Webb[41] reported the use of activated carbon, immediately after macroreticular adsorption, for the removal and subsequent analysis of trace organic contaminants present in the tap water supply of Athens (GA). A better method than soxhlet extraction for producing acceptable backgrounds in the carbon used was obtained by simple in-column wash with several solvents just before passing the water sample through. Graphitized Carbon Black (Carbopack B) has been evaluated recently for the concentration/isolation of organic compounds from water.[42] Preliminary results showed that the adsorbent is effective for the adsorption of chlorinated pesticides, organic acids, PAHs, phenols, ethers, PCBs, ketones, aromatic

hydrocarbons, organophosphorus pesticides. Mediocre results were obtained for benzylaldehyde, and very poor adsorption was experienced with hydrocarbons and esters. Several types of water samples, e.g., distilled, drinking, sea and river water, were used in their study.

Dobbs et al.[43] have studied carbon adsorption isotherms with Filtrasorb 300 GAC for a large number of toxic organics. The criteria for the selection of these compounds were based largely on the annual quantity of these compounds produced, their probability of occurrence in water and wastewater, persistence in the aqueous environment, solubility and their toxic levels. The selection of these compounds was, however, prior to the list of "Priority Pollutants" was assembled by EPA.

Activated carbon will serve as a universal tool for concentrating/isolating those compounds that are otherwise leaking through the afore-proposed isolating processes. An initial effort will be made to evaluate the background levels of a number of commercially available highly activated granular carbon, e.g., those supplied by Calgon (F-400), Westvaco, Nuchar, etc. Soxhlet extraction similar to that proposed for cleaning resin will be used in this study.

Isotherms of the hydrophilic neutrals, such as crotonaldehyde, furfural and chloroform will be studied extensively using the carbons having the least background contamination. Results of this study will be used to compare with data available in the literature. A 16 x 30 mesh granular carbon will be evaluated due to a favorable breakthrough curve obtainable with this size carbon.

Batch studies using gravity flow will be used to concentrate the hydrophilic neutrals in a carbon column. A continuously-operated flow system will be fabricated with all wetted parts made of stainless steel and Teflon.

This will be used for the isolation of a larger volume of water toward the end of this project. Background contamination with this pumping system will be evaluated.

Recovery of model compounds (e.g., hydrophilic neutrals) may be accomplished by using a J&W liquid CO_2 (at the critical conditions of CO_2) extractor followed by passing through a cryogenic trap set at a temperature somewhat higher than the sublimation point of dry ice (-78.5°C) say -75°C. This would allow the passage of CO_2 and trapping of other compounds; namely, chloroform (melting point, -63.5°C), crotonaldehyde (melting point, -69°C) and furfural (melting point, -38.7°C). A sufficient amount of surface area as well as intimate contact will be provided to ensure highly efficient trapping of these compounds. This can be accomplished by using a large number of quartz or stainless steel coils (1/8" diameter). After these compounds are trapped in the cryogenic system, they can be desorbed with the aid of a stream of ultrapure helium (catalytically cleaned at 900°C) at room or elevated temperature. The helium stream will then be sparged through a chilled aqueous solution containing the concentrated model compounds. An alternative of this will be to directly dissolve the liquid CO_2 containing the hydrophilic neutrals into the aqueous solution containing the concentrated model compounds.

Gas-Chromatography

Comprehensive reviews of recent literature on the theory and applications of gas chromatography,[44-46] and, in particular, the identification and quantitation of organic compounds in water are given by a number of authors.[47,48]

Gas Chromatographic System

The most widely used column types are packed, micropacked, support coated open tubular and wall coated open tubular. Generally, gas chromatographic columns are made from glass, stainless steel, teflon, aluminum, copper or nickel. Considerations of inertness, chromatographic working limits and efficiency render the choice of material to glass, especially with respect to capillary columns.

Recent improvements in the quality of solid supports for packed columns include the preparation of "support bonded stationary phases"[49] and "acid washed graphitized carbon blacks."[50] Better temperature stablility and higher inertness are the advantages of these solid supports. Their application proved to be effective in the analysis of several underivatized phenols.

New procedures have been reported for preparing high efficiency packed columns.[51-55] The use of a smaller particle size packing material has drastically increased the efficiency of packed columns, making the analysis time required for a determined separation much shorter.[56,57]

Glass capillary columns are having the major attention because of their potential in better handling very complex mixtures, and are improving very steadily. Better understanding of the properties of the glass surface and its influence on the chromatographic process of a wide variety of classes of organic compounds has permitted the preparation of high quality glass capillary columns.[58-65] Particularly effective was the introduction of a procedure for the preparation of inert, relatively non-polar stationary phase wall coated

columns. The procedure involves: 1) leaching-out the metal ions from the surface of the glass; 2) preparation of the glass surface for the subsequent deactivation process; 3) deactivation of the surface by reaction with hexamethyl disilazane at 400°C; and 4) coating of the stationary phase by the static method. Relatively non-polar wall coated glass capillary columns (SE-30, SE-52, SE-54, OV-1) were prepared by this method and demonstrated to be suitable in the analysis of certain underivatized organic acids and amines, esters, aldehydes, ketones and underivatized diols. Higher temperature stability limit (300°-350°C) and 90-95% coating efficiency was also noted. The introduction of fused silica capillary columns is making the use of this powerful analytical tool even more popular.[66,67] The use of other deactivating agents, as proposed by Grob[69], will eventually make possible to use an even broader range of stationary phases, still maintaining the inertness of the surface and the efficiency obtainable with a given capillary column dimension. All the range between the relatively non-polar and the polar stationary phases will then be available for specific separations. The types of stationary phases used in the analysis of several given classes of organic compounds has been extensively reviewed and reported in a tabulated form.[68]

The advances in capillary column technology has even stimulated a search for improvements of the instrumentation. Particular attention is being devoted toward new solutions for the injection of a sample into a capillary column. The split and splitless mode of injection are by now routinely applied in laboratories working with high resolution gas chromatography. Recently Grob[69] introduced a third approach in which the sample is actually introduced in the liquid form into the capillary instead of being pre-vaporized in a hot injector port. This new solution denominated "on-column injection", presents considerable advantages particularly when analyzing for samples containing a wide range of

molecular weight compounds (decreased discrimination for higher molecular weight compounds), as well as labile and polar compounds.

Some attention has been devoted to the gas chromatograph pneumatics[70,71] and an excellent review about the detectors employed in gas chromatography has been reported.[44]

In accordance to the literature we will investigate the suitability of high resolution chromatography for the quantitative analysis of the model organic compounds under study (Table 1). Relatively non-polar wall coated glass capillary columns will be preferred because of their higher resolution temperature stability and relatively longer life. The recent "on-column injector" introduced by Hewlett-Packard will be adapted on a H-P 5830 gas chromatograph and evaluated with respect to splitless injection mode. The column effluent will be monitored by a flame ionization detector (FID) and mass spectrometer-data system (GC-DS).

High Performance Liquid Chromatography

Undoubtedly the most rapid growing area of interest in chromatography is liquid chromatography, and in particular high performance liquid chromatography (HPLC). There is an ever growing number of published articles on the theory and applications of HPLC. We recognize this analytical tool as complementary and not competitive with gas chromatography. Therefore only recent applications to the analysis of model organic compounds not directly amenable to gas chromatography will be reviewed. A general review appeared in Analytical Chemistry[73] can be consulted for the specific analytical problems resolvable by this technique.

Analysis of free saccharides by HPLC has been reported by several laboratories.[74-76] An amino bonded phase was prepared and used for the separation of fructose, glucose, sucrose, maltose and lactose with acetonitrile-water as solvent system. Optimization of the separation involved the investigation

Table 1

I. Hydrophobic base (2)
   quinoline
   5-chlorouracil

II. Hydrophobic neutrals (10)
   2, 4' - dichlorobiphenyl
   2, 2', 5, 5' - tetrachlorobiphenyl
   bi s (2 ethylhexyl) phthalate
   1- chlorododecane
   biphenyl
   isophorone
   anthraquinone
   methyl isobutyl ketone
   2, 6 - di - tert - butyl - 4 - methylphenol
   benzo (e) pyrene

III. Hydrophobic acids (4)
   Stearic acid
   Humic acid
   Trimesic acid
   2, 4 - dichlorophenol

IV. Hydrophilic base (2)
   caffeine
   glycine

V. Hydrophilic acid (1)
   Quinaldic acid

VI. Hydrophilic neutrals (3)
   glucose
   furfural
   crotonaldehyde
   chloroform

of support loading, factors affecting support loading, slurry packing and analysis time. An amino bonded phase has been used even for the separation within 30 minutes of free amino acids and some vitamins[77] with acetonitrile/ phosphate buffer gradient as eluent. The separation of enantiomeric amino acids was accomplished on octadecyl silica column using aqueous mobile phase containing the chiral reagent L-aspartylcycloexylamide-Cu(II).[79] 2,4 Dinitrophenyl derivatives of amino acids were prepared and separated on a reversed phase (C-18) column within 50 minutes.[78]

Aromatic carboxylic acids, phenols and sulphonic acids have been separated by reverse phase-ion pair liquid chromatography.[80] The influence of ionic compounds added to an aqueous-methanol eluent on the retention behavior of sulphonic, carboxylic acids and phenols is demonstrated. The same principle has been shown[81] to be effective in the separation of 5-fluoro uracil nucleosides and nucleotides by the reversed phase liquid chromatography.[124] An octadecyl silica column with 2×10^{-2}M KH_2PO_4 + 5%(v/v) methanol solution as solvent system is used.

High performance liquid chromatography will eventually be investigated for the analysis of the organic compounds that require derivatization prior to gas chromatography (glucose, glycine, trimesic acid, stearic acid, guinaldic acid and 5-chloro uracil). The two analytical approaches will be compared, but derivatizion and GC will be preferred where possible because of the possible use in combination with the mass spectrometer.

Chemical Derivatization

Chemical derivatization is the transformation of a functional group in an organic compound to another group for the purpose of identification, or quantitation. Classical qualitative analysis of an organic compound depended heavily on matching the physical properties of the parent organic compound as well as the derivative to confirm the identity of the compound. One of the expected underlying property of this operation is that it should be quick, besides being reproducible quantitatively.

In the context of GC analysis, chemical derivatization is utilized to replace an acidic or basic group by some other less polar function in order to make it more volatile, less strongly adsorbed in order to reduce any possibility of irreversible adsorption, and to reduce the tailing of the peak. Lately, several solumns have come to use which are capable of giving a good gas-chromatographic analysis of phenols and amines without derivatization, reducing our list of compounds that need derivatization.

Out of the 22 organic compounds in our list, the following 6 need to be derivatized:

1. Stearic acid
2. Trimesic acid
3. Quinaldinic acid
4. Glucose
5. Glycine
6. 5-Chlorouracil

Derivatization methods and techniques are reviewed in the context of our objective of derivatizing these compounds. The functional groups present in these compounds requiring derivation are -COOH, $-NH_2$ and -OH groups. Compound 1 and 2 contain only -COOH group, Compound 3 has a -COOH and a tertiary amine group, Compound 5 has a -COOH and a $-NH_2$ group, while glucose has several -OH groups. Derivatization of 4 and 5 will be discussed separately, while that of 1, 2 and 3 will be grouped together.

Acids

Acids are derivatized to esters. The reaction replaces the polar O^-H^+ bond by a covalent bond like O-C or O-Si.

Methyl ester is the most common derivative prepared from acids. The following reagents have been used to prepare methyl esters:

(a) Methanol with an appropriate acid catalyst, which may be a strong mineral acid like HCl, H_2SO_4 (Fischer esterification),[82] BF_3[83]

(b) Pyrolysis of quarternary ammonium salts[82,84]

(c) Dimethylsulfate[85,86]

(d) Dimethoxypropane[87]

(e) Diazomethane[88,89]

A number of studies have assessed the relative merits of the different methods. A recent one[90] concluded that diazomethane is the most efficient reagent. This method is fast, simple and the yields are high. Excess reagent is evaporated off signalled by the disappearance of the yellow color of the reagent. This gaseous reagent can be used either in ethereal solution[88] or by bubbling the gas through the reactant solution.[89] It can be used to methylate sterically hindered acid groups where other reagents would fail to methylate. The disadvantages of the reagent are that it is toxic and explosive. It has to be generated in an efficient hood to avoid toxicity, and glass apparatus with smooth ends are to be used to avoid explosion.

The second esterifying reagent that appears to be of interest is pentafluorobenzylbromide.[91,92] This fluorinated ester can be detected by the highly sensitive EC detector, and it is relatively nonvolatile. The disadvantage of the reagent is that it is strongly lachrymatory. Even working in a hood causes irritation. We propose to use it in a glove chamber inside a hood.

The third method of interest for esterification is silylation. A trimethylsilyl group (Me_3S-) replaces a hydrogen from -OH, -COOH, -SH, $-NH_2$ and -NH group by reaction with one of the various reagents,[93] and as such the silylation is a more versatile reaction. The reaction products (besides the silyl ester) and the reagents are generally more volatile than the silyl ester, and no attempt is made to separate them;[94] except in case of mass spectrometry in which case a deposition of silica in the ion source may cause tailing, drifting of baseline and variable sensitivity. The worst disadvantage of the silyl derivatives of carboxylic acids are their sensitivity to moisture. Tertiary-butyl silyl reagents[95] produce derivatives

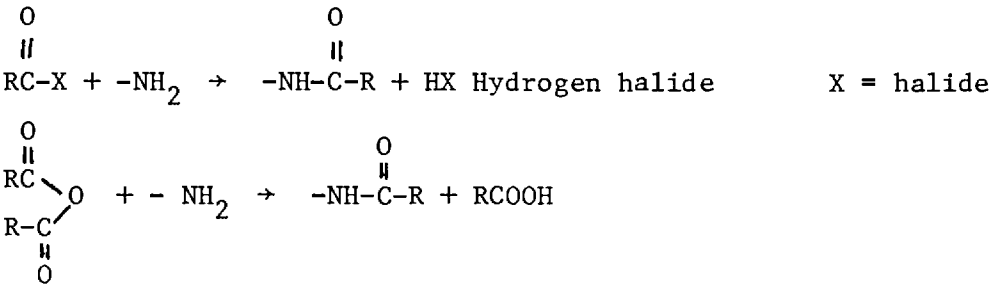
that are comparatively more stable to moisture presumably due to prevention of hydrolysis due to steric hindrance.

Silyl derivative of stearic and quinaldic[96] acids have been used for their GC analysis. None of the analysis was aimed at determination at the low level we intend to probe.

Glycine

This compound has two functional groups. One is the acid (-COOH) whereas the other is basic ($-NH_2$). Derivatization of the -COOH group has been discussed above and it has been stated that a trimethylsilyl derivative can be formed for both the functional groups at the same time and by the same reagent. Attempt to derivatize glycine by sulylating -COOH and $-NH_2$ group resulted in more than one derivative.[97] Our objective is to get a single derivative in reproducible yield so that the quantitation of the derivative will substitute for the quantitation of the parent polar compound.

The other alternative is to make an ester derivative of the acid group and an acyl derivative of the amino group. The later derivatization reaction is accomplished by reacting an amino compound with an acyl halide or acid anhydride:[98]



Reaction with acylhalide eliminates a molecule of hydrogen halide. A basic catalyst drives the reaction forward. The reaction has several disadvantages. Presence of either acid or excess halide salt may cause chromatographic problems. Excess of the highly reactive acylhalide may cause irreversible alteration to the chromatographic column or corrode inside the GC or GC/MS. These

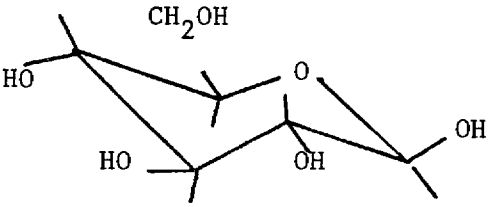
problems can be avoided by using acid anhydrides.

Several double derivatizations of glycine have been reported.[99-103] Heptafluorobutyrylanhydride is the reagent of choice for acylation, because of its capability of rendering the derivative detectable in a much lower limit by the use of EC detector in contrast to nonhalogenated derivatives detectable by FID detectors only.

The acid group may be derivatized to give the (a) propyl ester with propyl alcohol or (b) isoamyl ester with either tri-isomeoxymethane[104] or isoamylalcohol.

Both methods will be tried to assess their comparative merits.

Glucose



β-D-Glucopyranose

Glucose has 5 hydroxyl groups which can be derivatized. One of these is associated with the hemi-acetal group which can open and close easily giving rise to anomers (α and β) and ring isomers (pyranose and furanose). Therefore, a derivative of glucose can give up to 4 peaks in the GC.

There are two ways of circumventing this problem. One is to reduce the hemiacetal group with sodium borohydride and convert all anomers to a single alditol. The reduction product from glucose will be sorbitol, which can be derivatized by treatment with acylating reagent.[105,106] The disadvantage of this method is that it will not distinguish between several pairs of monosac-

charides in natural water. As for example, glucose and sorbose will give the same derivative, and so will glucose and gulose.

The other method is to derivatize the monosaccharides with TFA to achieve very high sensitivity with an electron capture detector[107] and then sum up the peak areas of the anomers to quantitate.[108]

TFA derivatives can be prepared by heating a freeze dried sample containing glucose with TFAA in dichloromethane at 130°C for 2 hr in a sealed reactival, and subsequently replacing the solvent with hexane and at the same time removing excess amount of unreacted reagent.[108]

Different conditions have been recommended for preparing TFA derivatives.[107,109,11] It is important to remove any excess fluorinated reagent, otherwise the detector may be overloaded. HFBA and PFPA derivatives were found unsatisfactory because after some injections, a broad peak appeared which was a result of the remaining acid in the column.[108]

The third type of derivative used to analyze glucose is the trimethylsilyl ether.[111,112] Apparently, fluorinated derivatives are more attractive due to their detection with EC detectors.

Gas Chromatography-Mass Spectrometry - Computer Techniques

The use of this powerful analytical tool is steadily increasing, particularly in the case of highly complex mixtures such as the case of environmental samples. Two comprehensive literature review have been recently reported.[68,113] Particularly active is the application of high resolution gas chromatography in combination with a low resolution mass spectrometer and data system. Glass capillary columns, because of their relatively low flows (1-5 ml/m), can be directly connected to the high vacuum of the ion source. Usually the pump system of a quadrapole mass spectro-

meter is able to handle such volumes of gas without the aid of a separator, like in the case of packed columns.

Decreased separation efficiency of the analytical column up to 20-25% has been experienced by Verzele et al.[114] when capillary columns and mass spectrometer were interfaced. The transfer line plays then a major role on the final result of the analysis and several short communications have appeared recently which are proposing simple and inert transfer lines for GC-MS interface.[115-118] In our experience we found it to be very effective to use a short length ($\sim$ 40 cm) of fused silica tubing (0.1 mm I.D.). Relatively non-polar wall coated capillary columns are preferred when used in combination with mass spectrometry because of their lower bleeding. Among several recent applications appeared in the literature the analysis of derivatized amino acids[119], nitrogen aromatic compounds in complex mixtures[120], low volatile compounds[121], secondary amines[122] and derivatized nucleosides[123] will be addressed.

The elution pattern of components after separation on the capillary column is recorded in the dats system as a relative ion chromatogram. Each peak is designated by scan number and can be searched for its identity against a library of more than 25,000 compounds stored in the data system from the National Bureau of Standard Library. Computer programs are available that can handle the automatic identification search routine.

The quantitation of each compound is based on the comparison of selected ion plot (SIP) with respect to the one of the internal standard. The Finnigan computer program that handles the identification and quantitation routine of the mass spectrometer data and that is currently in use in our lab involves two steps. First, a standard solution, containing known amounts of the compounds under study and internal standard, is analyzed and recorded.

The relative retention times of the compounds are adjusted with respect to the internal standard. For quantitation, the peak area of a single ion, generally the base peak of each spectra, is normalized relative to the base peak of the internal standard spectra, which is supposed to have a response factor of 1. This step constitutes initialization of identification and quantitation parameters for a set of compounds. A library containing each compound mass spectra, name, absolute retention time, relative retention time and response factor is set up once forever and used as reference. Second, the unknown solution with the same amount of internal standard as in the previous step is run, and the compounds quantitated on the basis of single ion peak areas.

It is advisable to run the standard solution every day, after tuning the mass spectrometer with perfluoro tributylamine (FC43) and pentafluoro triphenylphosphine (PFTPP), particularly for quadrapole-type mass spectrometers.

Quality Assurance/Quality Control

The organization and the implementation of a strict quality assurance/quality control program has been recognized as an important issue for any laboratory involved in environmental analysis. EPA's Environmental Monitoring and Support Laboratory Cincinnati has made available a "Handbook for Analytical Quality Control in Water and Wastewater Laboratories."[124] A recent review is also reported on "Master Scheme for the Analysis of Organic Compounds in Water".[68]

A QA/QC program will be implemented which will consist of the following elements: contamination control, containment/recovery of samples, and instrumental calibration.

Contamination control is addressed by carefully defining materials and cleaning procedures used in the operation of the fractionation scheme, and is monitored by blank determinations. The blank determination consists of exposing the organic-free distilled water to the same glassware and manipulated and handled through the fractionation scheme as proposed for the real samples. Each fraction will be monitored by GC and GC-MS-DS, after derivatization wherever necessary, and each possible contaminant present identified and quantified. The overall contamination contribution of the entire scheme will also be assessed. This study will be particularly helpful when a sample blank in the presence of residual chlorine will be evaluated through the fractionation scheme.

Containment/recovery will be evaluated for each organic compound spiked in organic-free distilled water at the concentration level specified. The influence of humics on the recovery of each compound will be assessed. Extraction recovery study, wherever is needed (i.e. acid, bases), and derivatization yield will be statistically evaluated.

The internal standard method will be used for instrumental quantitation as reported in the GC-MS-DS section.

Effects of the Addition of Humic Acids to the Experimental Solution

Two major effects need to be considered:

a) interaction of humic acid with metals through sorption and complex formation, and

b) binding of organic solutes to humic acid

Lead

The most important metal in question is the added lead (II). It should be noted beforehand that the addition of "humic acid" of a poorly characterized quality poses additional problems. Part of this material may be found in true solution, whereas another part may exist in particulate form. Analysis

of the interaction with lead (II) thus has to take into account both sorption and complexation. According to Kerndorff and Schnitzer[125] sorption efficiency onto humic acid of metals in aqueous solution tended to increase with the rise in pH, the decrease in metal concentration and the increase in humic acid concentration. They found an empirical expression to describe the sorption efficiency in the form

$$Y = 100/[1 + e^{-(A + BX)}]$$

where Y = % of metal removed by humic acid; X = mg of humic acid, and A and B are empirical constants. The mechanisms of sorption however, could not be elucidated at this time.

Saar and Weber[126] have discussed lead (II)-fulvic acid complexes in terms of their conditional stability constants, and found that from pH 4.0 to 6.0 the logarithm of 1:1 lead (II)-soil fulvic acid conditional stability constants increased from 4.0 to 6.3. In addition, they have found that lead (II) forms insoluble precipitates at low lead (II)/fulvic acid ratios. Under these conditions, physical association of lead (II) with lead-fulvate solids as well as complexation by sites still available in the precipitates probably causes the increased removal of free lead (II) from solution after precipitation begins.

Organic Model Compounds

The interaction of humic acids with organic solutes such as folic acid, 2,4-D and malathion has been studied by Adhikari et al.[127]. Using electrometric titrations and IR spectroscopy, they considered the bonding sites on humic acid to be carboxyl, phenolic hydroxyl, carbonyl and N-containing groups such as >NH and $-NH_2$. In most cases it appears that H-bonding is mostly responsible for the humic acid-organic solute interaction, although the

authors considered the additional participation of other weak forces such as the intermolecular Van der Waals forces.

In a study of the interaction of N-containing heterocycles and humic acid, Muller-Wegener and Ziechmann[128] discussed the electron-donor-acceptor-complexes. Methanolic extracts of a synthetic humic acid were mixed with different aromatic N-heterocycles. Precipitates were obtained and identified by IR spectroscopy as electron-donor-acceptor-complexes. Since N-heterocycles are known to be n-electron donors, the humic acid has to be interpreted as the π-electron-acceptor part of the molecular complexes.

In the present investigation, humic acid will be in the presence of a multitude of organic solutes. In view of the fact that there are many varied ways of humic-organic interactions possible, we need to monitor very carefully the concentrations of those solutes immediately after addition of the humic acid. For both the humic-metal and the humic-organic solute interactions it will be of tantamount importance to assure that the humic acid is introduced into the experimental mixture in true solution rather than in a particulate suspended form. Therefore the specific procedures for the introduction of humic acid in the solute form by all contractors participating in this research program should be followed in order to eliminate any inconsistency that may exist.

Expenditures

The actual expenditures incurred during the first quarter of this research program are represented by the dashed line in Figure 3. The solid line represents the expected expenditures in the months to come. It is anticipated that initial high level expenditures will be tapered off somewhat during the second quarter.

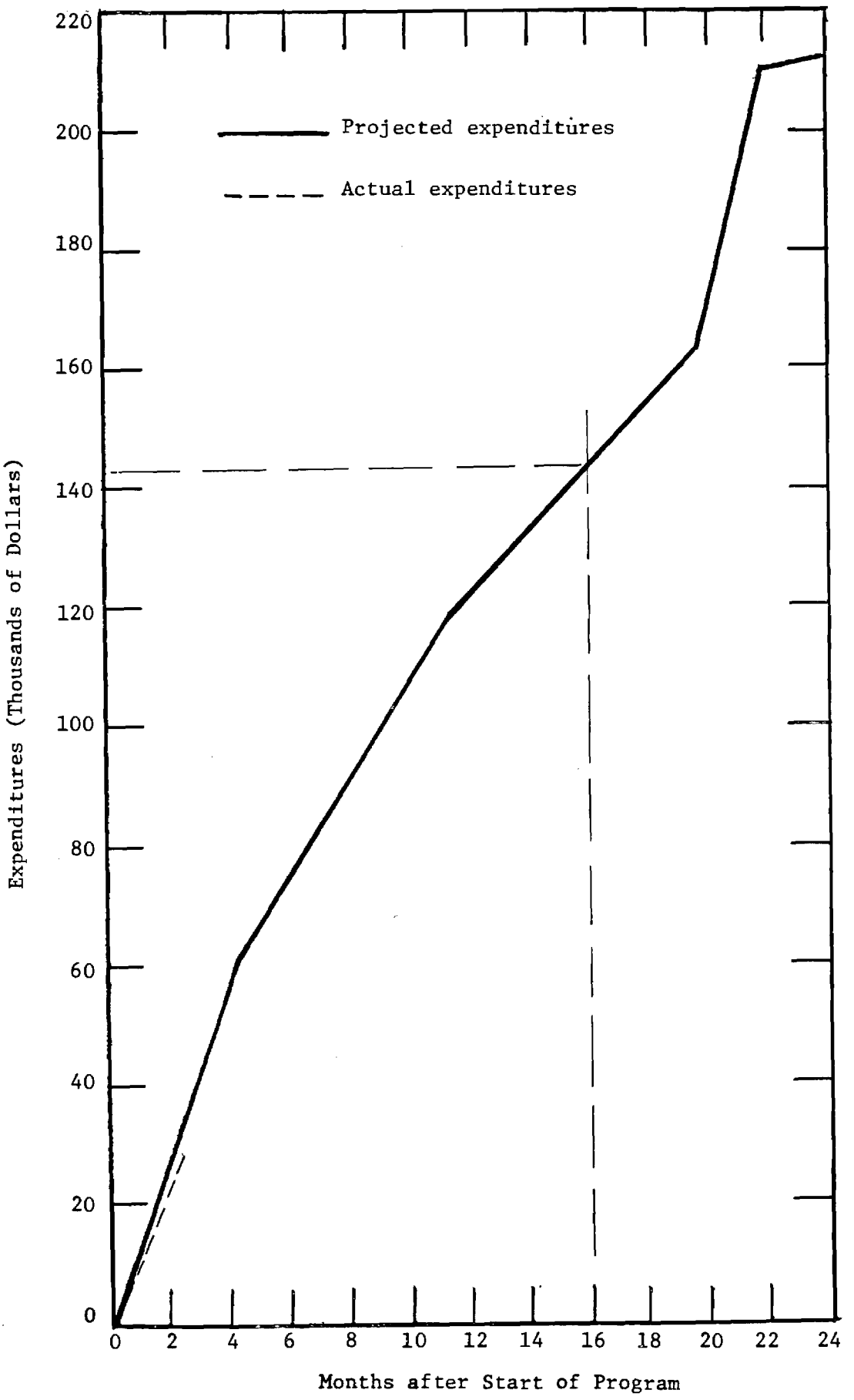


Figure 3. Projected and Actual Expenditures for EPA Contract No. 68-03-3000

If there is any questions regarding this quarterly report, please contact Edward S. K. Chian at (404) 894-2265 or (404) 894-2242.

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E-20-688

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

QUARTERLY REPORT
March 1981

by

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TABLE OF CONTENTS

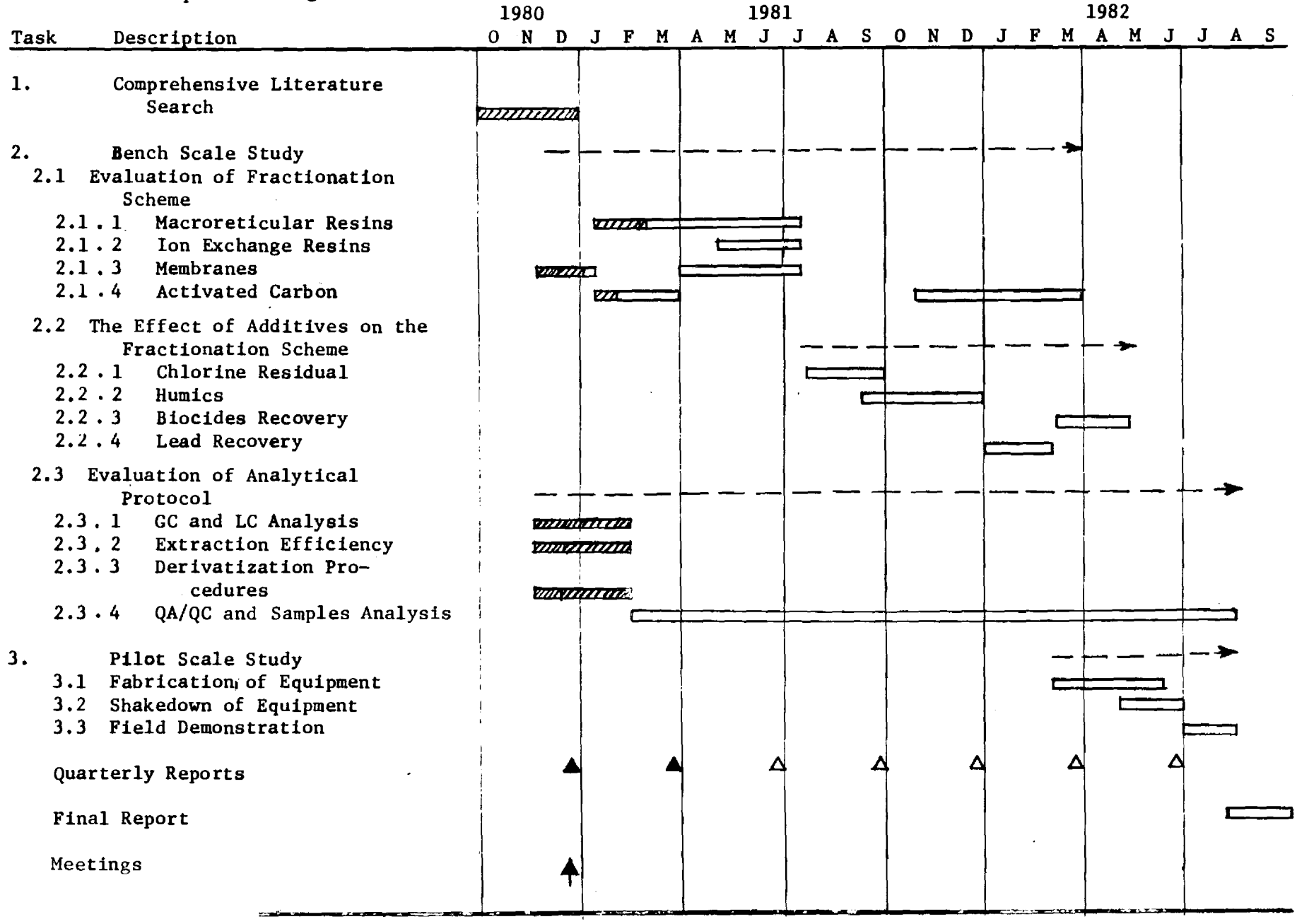
I. INTRODUCTION

This report summarizes the work performed during the period from December 1, 1980 through February 28, 1981 on the EPA research program on "Evaluation of Methods for the Insolation or Concentration of Organic Substances from Water" (Contract No. 68-03-3000). The major efforts have been directed toward evaluation of the resin separation scheme, development of methodologies for the analysis of the model compounds under study by GC/MS, preparation of organic-free water for purposes of both analytical, and process evaluation and calibration of the low level TOC Analyzer. The progress of these efforts are depicted in the Gannt Chart (Chart 1) for the above contract, and are presented in details in the following sections:

Chart I - Schedule for the Proposed Research Program

Project: Evaluation of Methods for the Isolation or Concentration of Organic Substances from Water

Principal Investigators: E. S. K. Chian and J. H. Reuter



II. PRELIMINARY EVALUATION OF MACRORETICULAR AND ION EXCHANGE RESIN FRACTIONATION

A test solution of pure water containing 100 mg/1 each of the organic compounds listed in Table 1 was used to qualitatively evaluate the proposed fractionation scheme. The procedure was adopted from that proposed by Leenher and Huffman (1976) and Leenher (1980).

The resins used were Amberlite XAD-8, a macroporous methylmethacrylate copolymer for adsorption of the hydrophobic bases, acids and neutrals; Bio-Rad AG-MP-50 strongly acidic macroporous cation-exchange resin for adsorption of hydrophilic bases; and Duolite A-7 weak base anion-exchange resin for adsorption of hydrophilic acids. The resins were cleaned and the columns packed and prepared according to the procedure described by Leenher (1980). In each case the columns (200 x 13 mm) were packed to 120 mm with resin.

The test solution, with no pH adjustment, was first passed through the XAD-8 column. The adsorbed hydrophobic bases were eluted with 0.1 and 0.01 N HCl. The test solution effluent from the initial pass through the column was acidified with HCl to pH 2 and was recycled through the same XAD-8 resin. The hydrophobic acids adsorbed during this pass were desorbed with 0.1 N NaOH. The hydrophobic neutral fraction,which remained adsorbed on the XAD-8 resin after these acid and base elutions,was desorbed with methanol. For this purpose the resin was first air-dried and then extracted for 2 hours with MeOH in a soxhlet extractor.

The test solution with the remaining hydrophilic fractions was passed through the AG-MP-50 cation exchange resin (in H^+ form). The

TABLE 1.

Test Organic Compounds

Trimesic Acid	1-Chlorododecane
Stearic Acid	Biphenyl
Glycine	Isophorone
Quinoline	Anthraquinone
Caffeine	Methyl Isobutyl Ketone
5-Chlorouracil	2,4'-Dichlorobiphenyl
Glucose	2,2',5,5'-Tetrachlorobiphenyl
Furfural	Bis (2-ethylhexyl) phthalate
Crotonaldehyde	2,4-Dichlorophenol
Benzo(e)pyrene	2,6-Di-tert-butyl-4-methylphenol

adsorbed organics (hydrophilic bases) were desorbed with 1.0 N NH_4OH. The test solution effluent from this column (containing the hydrophilic acids) was then passed through the anion-exchange resin, Duolite A-7 (in OH^- form). The adsorbed hydrophilic acids were desorbed with 3 N NH_4OH. The hydrophilic neutral fraction remains in the test solution effluent of the Duolite A-7 column.

The following extraction, concentration and derivatization steps were completed prior to GC analysis of the fractions:

Hydrophobic and Hydrophilic Bases: After adjustment to pH 10 with NaOH, each fraction was extracted with CH_2Cl_2 in a separatory funnel. The solvent portion was subsequently dried with Na_2SO_4 and concentrated on a Kuderna-Danish (K-D) apparatus to about 3ml followed by further concentration to 1ml under a nitrogen stream.

Hydrophobic Acid: After adjustment to pH 2 with HCl, the fraction was extracted with ethyl acetate in a separatory funnel. After drying with Na_2SO_4, the solvent fraction was evaporated to dryness on a rotary evaporator. The dry sample was dissolved in 5 ml of ethyl acetate and concentrated down to about 0.5 ml in a K-D vial with mini-condensor. The sample volume was adjusted to 1.0 ml with CH_2Cl_2. Finally the acids were methylated with diazomethane.

Hydrophobic Neutral: The fraction (in methanol) was concentrated to about 2 ml in a K-D apparatus with vacuum attachment and further concentrated to 0.5 ml under a nitrogen stream. The sample volume was adjusted to 1 ml with chloroform.

Hydrophilic Acids: The fraction (in 3 N NH_4OH) was evaporated on a rotary evaporator until crystals started to form (at a concentration of about 5 N NH_4OH). This concentrate was acidified with HCl to pH 1 and passed through XAD-8 resin (1 ml for each 10 ml resin) followed by 0.1 N HCl (1.5 ml for each 10 ml resin) and distilled water. The hydrophilic acids are adsorbed on the resin and subsequently eluted with 0.1 N NaOH. This effluent is concentrated to dryness and the acids are methylated with diazomethane in CH_2Cl_2.

Hydrophilic Neutrals: Concentration and derivatization procedures for the hydrophilic neutrals is still being studied.

Table 2 summarizes the result of the fractionation process as analyzed by GC. The following compounds, although present initially in the test solution, could not be detected in any of the fractions:

methyl isobutyl ketone
2,6-di-tert-butyl-4-methylphenol
Glycine
Trimesic acid
2,4 - Dichlorophenol
* glucose
* furfural
* crotonaldehyde

Glycine and glucose were not found because suitable derivatization techniques had still to be worked out. Trimesic acid was apparently not extracted by ethyl acetate. MIBK was probably lost in the solvent concentration step by K.D. 5-chlorouracil, furfural and crotonaldehyde were not detected at this time because suitable GC techniques had to be developed. The reason for the loss of the phenols was not clear. It is noted that bis (2-ethylhexyl) phtahalate was found in several fractions, probably due to contamination.

* Proposed to be present in the hydrophilic neutral fraction which was not analyzed because concentration and derivatization procedures are still being developed.

After completion of the initial qualitative experiment, a second test solution was prepared with the same concentrations of organics as in the first experiment. In addition, the effect of inorganic compounds on the fractionation scheme was investigated by adding to the test solution 70 ppm of $NaHCO_3$, 47 ppm of $CaCl_2$ $2H_2O$ and 136 ppm of $CaSO_4$. A second solution containing only the inorganic compounds was carried through the fractionation, concentration and analytical scheme as a procedural blank.

For this experiment we adjusted the pH of both solutions to 9 prior to the first pass through the XAD-8 column.

The same procedures for extraction and concentration of the fractions were followed with the exception of the hydrophobic acid fraction. In order to avoid the problem of extracting the trimesic acid from the aqueous solution, a 1-ml aliquot of the fraction was carried to dryness under an air stream at 50°C in a 3-ml Reacti-vial. The dry sample was taken up in 1 ml CH_2Cl_2 and methylated with diazomethane.

Table 3 summarizes the result of the fractionation process as analyzed by GC. Trimesic acid occurs in the hydrophobic acid fraction and 2,6-di-tert-butyl-4-methylphenol in the hydrophobic neutral fraction. Compared with the first experiment, caffeine moved from the hydrophilic base to the hydrophobic neutral fraction, as a result of the initial pH adjustment. Phthalate was found only in the hydrophobic neutral fraction. The absence of the other compounds is attributed to either imcomplete derivatization and/or lack of proper chromatographic conditions. Both problems are presently being investigated. Figure 1 gives the reconstructed ion chromatogram (R.I.C.) of the hydrophobic neutral fraction.

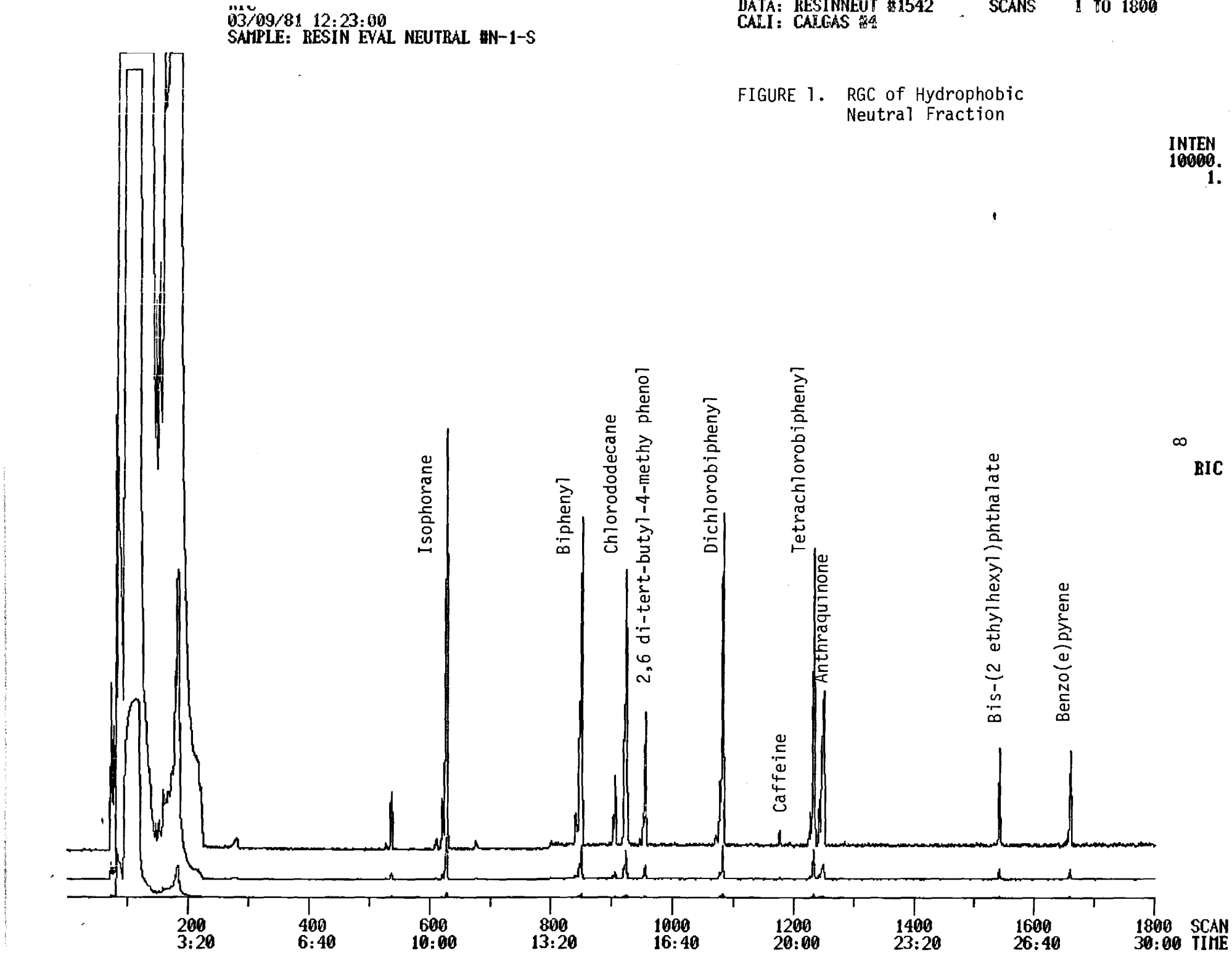


FIGURE 1. RGC of Hydrophobic Neutral Fraction

TABLE 2.

Results of Initial Resin Fractionation Experiment

I. Hydrophobic Bases

Quinoline
Bis (2-Ethylhexyl) Phthalate

II. Hydrophobic Acids

Stearic Acid

III. Hydrophobic Neutrals

Isophorone
Biphenyl
1-Chlorododecane
2,4'-Dichlorobiphenyl
2,2',5,5'-Tetrachlorobiphenyl

IV. Hydrophilic Base

Caffeine
Bis (2-Ethylhexyl) Phthalate

V. Hydrophilic Acid

None

VI. Hydrophilic Neutrals

Not Analyzed

TABLE 3.

Results of Second Resin Fractionation Experiment
(Standard Organics with Inorganics)

I. Hydrophobic Bases

Quinoline

II. Hydrophobic Acids

Stearic Acid
Trimesic Acid
2,4-dichlorophenol

III. Hydrophobic Neutrals

Isophorone
Biphenyl
1-Chlorododecane
2,4'-Dichlorobiphenyl
2,2',5,5'-Tetrachlorobiphenyl
Anthraquinone
Bis (2-Ethylhexyl) Phthalate
Benzo(e)pyrene
2,6-di-tert-butyl-4-methylphenol
Caffeine

IV. Hydrophilic Base

None

V. Hydrophilic Acid

None

VI. Hydrophilic Neutrals

Not analyzed

The blank solution contained no organic compounds with gas chromatographic retention times of the test compounds.

These preliminary experiments indicate that, qualitatively, the resins provide a means for the fractionation of trace organics. The fraction samples were retained so that additional analyses can be obtained as soon as all derivatization and GC procedures are optimized.

The next set of experiments, which are now underway, is designed to yield a quantitative evaluation of our fractionation procedure.

III. ANALYTICAL METHODOLOGIES

A. Preparation of Organic-Free Water

For a small quantity of organic-free water, it has been prepared by slow distillation of deionized water over potassium permanganate, after adjusting the pH to 10 with NaOH. The total organic carbon of the distillate has been monitored on a regular basis. Samples of distillate showing a level of TOC higher than 0.3 mg C/l would be rejected. So far, the TOC measurement of distillate has not exceeded this limit. The observed range of TOC was 0.08 to 0.25 mg C/l.

For a larger quantity of organic-free water, the following procedures will be employed. Deionized water will be prepared by passing the City of Atlanta tap water (TDS = 40 ppm) through a DuPont B-10 reserve osmosis module operated at 600 psig. The permeate (TDS = 1 ppm) will then be put through a Corning disposable 3508-ORC "organic-free" and/or 3508-B high capacity deminearalizer cartridges, Reagent grade, stabilized hydrogen peroxide (50%), will be added to the deionized water at a level of 1-2% by volume. Irradiation will be carried out in a modified ultraviolet disinfection unit (Model H-50) manufactured by Ultraviolet Technology, Inc. The H_2O_2/UV treatment was reported to yield 95% or better reduction of TOC (Malaiyandi et al., 1980)

B. Ultra Low-Level Total Organic Carbon Analysis

The total Organic Carbon analysis was performed on a Dohrmann DC-54, ultra low total organic carbon analyzer system. It has a forward sweep purge method for purgeable organics followed by a UV promoted wet chemical oxidation method for non-purgeable organics, which in turn is combined with subsequent reductive pyrolysis and flame ionization detection to determine

the organic carbon content of the water sample to be analyzed.

The carbon standard sample was an aqueous solution of potassium hydrogen phthalate (KHP; $C_8H_5O_4K$). A standard carbon sample was discarded as soon as fibrous or flaky matter was visible in the solution upon shaking. The concentration of carbon standard solution was 180,000 ppb as carbon.

The sample reagent was prepared by adding 5.0 gram of reagent grade potassium persulfate ($K_2S_2O_8$) and 3.0 ml of concentrated (85%) reagent grade phosphoric acid (H_3PO_4) to 100 ml of organic free water. One ml of this reagent was added per 50 ml of sample to be analyzed.

This method requires a Purgeable Organic Carbon (POC) system blank <10 ppb C and a non-Purgeable Carbon (NPOC) system blank <50 ppb C. To obtain the aforementioned values for system blanks, the water sample analyzed was transferred back to the POC sparger at the end of the cycle and was again subjected to the entire cycle. This procedure was followed till the recommended system blanks were obtained. The DC-54 system was calibrated by adding various volumes of 180,000 ppb carbon standard to 10 ml of sample to be analyzed. The span on the F.I.D. was adjusted for 135 ppb carbon. The final TOC value was the final NPOC value minus the system blank. Results of calibration of the DC-54 system are given in Table 4 and illustrated in Figure 2. It can be seen from Figure 2 that an excellent linearity is obtained with the instrument.

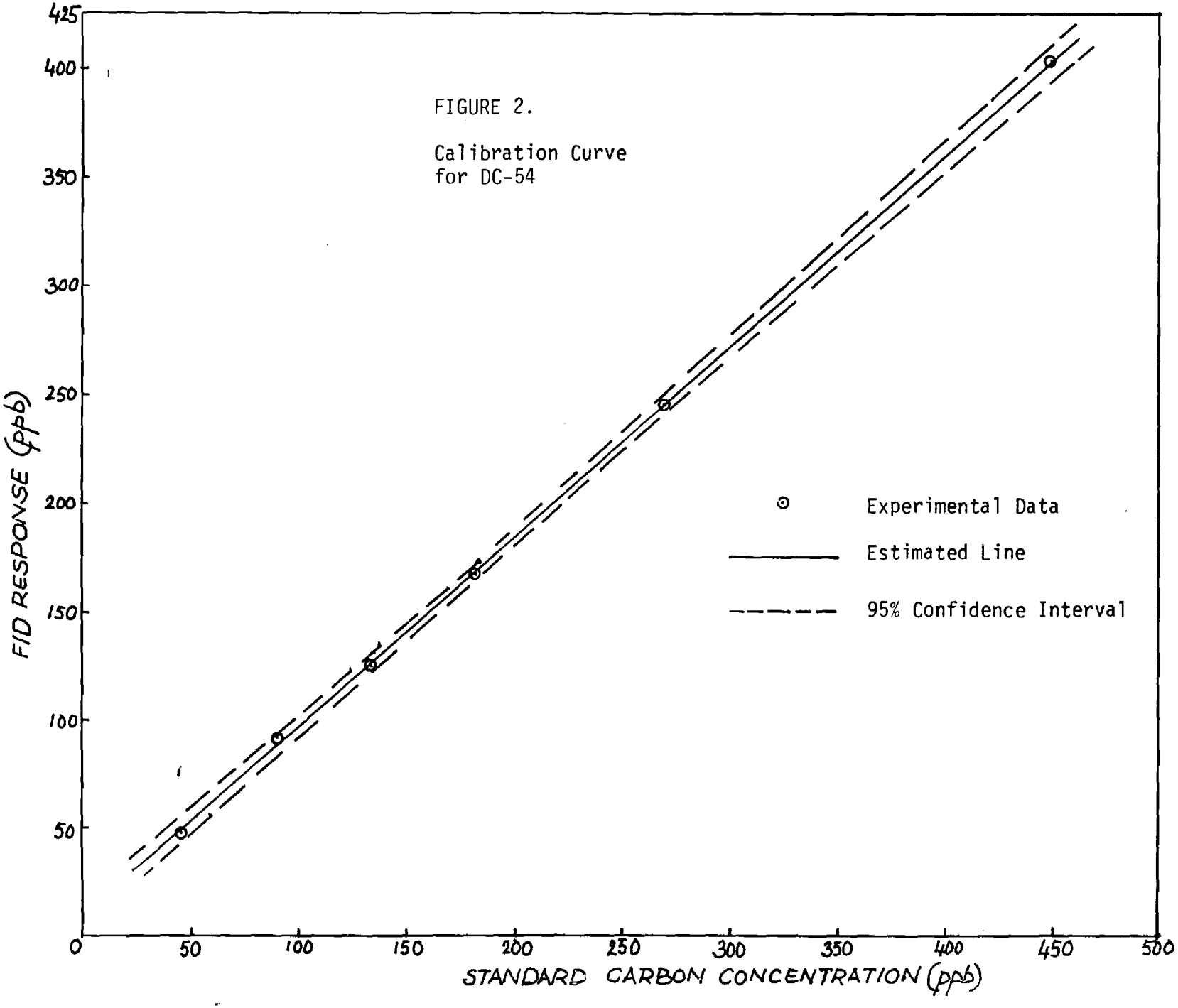


FIGURE 2.
Calibration Curve
for DC-54
FID RESPONSE (ppb)
425
400
350
300
250
200
150
100
50
0
50
100
150
200
250
300
350
400
450
500
STANDARD CARBON CONCENTRATION (ppb)
Experimental Data
Estimated Line
95% Confidence Interval

TABLE 4.

Calibration of the DC-54 System

Standard Concentration (ppb) (x)	FID Response TOC (ppb) (y)	Mean (ppb) ($\bar{y}$)	Standard Deviation σ (ppb)	Coefficient of Variation $C_v = \frac{\sigma}{\bar{y}}$	Estimated FID Response; by linear Regression Y (ppb)	95% Confide Interva (ppb)
45	50 44 51 43 47	47	3.53	0.075	50.98	± 5.58
90	92 95 92 91 92	92.4	1.52	0.016	90.17	± 4.73
135	129 131 138 137 137	134.4	4.09	0.030	129.37	± 4.08
180	159 167 168 171 169	166.8	4.60	0.027	168.56	± 3.751
270	241 242 248 245 250	245.2	3.83	0.016	246.95	± 4.27
450	397 397 401 414 411	404	8.0	0.02	403.73	± 8.00

Regression results:

Estimated model	Coefficient of Correlation (r)	Coefficient of Determination (R^2)	F_o
Y = 0.871x+11.785	0.9997	0.9991	4474.82

C. Extraction, Lyophilization and Derivatization

1. Blanks and Controls

All solvents used have been concentrated 100 fold and analyzed by GC to ascertain their purity. The water distillate was extracted with CH_2Cl_2, the solvent was then concentrated and analyzed by GC to assure the absence of impurities. Controls have been run with the reagents and solvents, without the primary reactant for derivatization, to confirm that impurities are not introduced.

2. Derivatization

The following 6 compounds require chemical derivatization before they can be analyzed on GC:

Stearic acid

Trimesic acid

Quinaldic acid

Glucose

Glycine

5-Chlorouracil

All of the above compounds will end up in aqueous solutions after elution from the resin sorbent columns. Therefore, investigations have been directed towards finding the best method for: (1) extracting these compounds from the aqueous solution; and then (2) derivatizing them to obtain quantitative results with analysis. To achieve these purposes, the above 6 compounds have been subdivided into 4 classes according to their chemical natures:

Carboxylic acids -stearic, trimesic and quinaldic acids. They will be encountered in the hydrophobic and hydrophilic acid fractions.

Glucose - It will be eluted in the hydrophilic neutral fraction.

Glycine - The amino acid is expected to come out with the hydrophilic base fraction.

5-Chlorouracil

The above four classes of compounds are discussed in detail in the following:

(1) Carboxylic Acids

The investigation was limited to only trimesic acid and stearic acid. Quinaldic acid has not yet been received from the vendors at the time of this report.

A stock solution containing 500 ppm of trimesic acid and stearic acid was prepared in methanol. 20,100 and 200 μℓ of these solutions were spiked into 1 mℓ of $CH_2C\ell_2$, derivatized with diazomethane and analyzed by GC.

Diazomethane was generated by adding 15 drops of aqueous NaOH solution (35%) into a solution of Diazald (Aldrich Chemical, 0.2g) in methanol (5ℓ). N_2 gas was blown into the solution and the diazomethane gas was trained into the acid solution for 10 seconds. It was observed that the conventional procedure for treating an acid solution with an excess amount of diazomethane to let the solution become deep yellow was not only redundant, but harmful because it introduced a lot of contamination. Three experiments were conducted by bubbling diazomethane for 10, 20, and 30 seconds respectively into a solution containing identical amounts of stearic and trimesic acid. The reaction products with the longest reaction time showed the most contamination, while that with the shortest reaction time the cleanest as evidenced by the GC traces. The peak areas were within the range of variability,

indicating that by varying the time of reaction it had no effect on the completion of the reaction.

Results of this study on reproductibility and linearity of GC response are presented in Table 5.

The other objective of this study was to extract these acids from water with an organic solvent followed by evaporating the solvents, derivatizing the acids and analyzing them on GC. While stearic acid was quantitatively extracted from an aqueous solution with ethyl acetate or methylene chloride, trimesic acid, however, can not be extracted efficiently with any solvent immisable with water.

In light of this observation, it was decided to evaporate 1 mℓ of water containing 2 μg (= 4 μℓ of our 500 ppm stock solution) of the two acids by heating them to 100°C and blowing with N_2. The dried sample was covered with ether, derivatized as described, and analyzed by GC-FID. The reproducibility of the analysis is presented in Table 5. The choice of spiking low concentration of acid was aimed at simulating evaluation of resins with 1 liter of spiked water distillate. The eluent from the XAD column, which may be typically 25 mℓ, containing 50 μg of the acids. (2) Glucose was derivatized to its penta-(trifluroacetate) derivatives by heating the dry sample with trifluoroaceticanhydride (TFAA) in a sealed reactivial at 130°C for 2 hr. A stock solution of glucose (500 ppm) was prepared and 4 mℓ of this solution was dried by heating (60°C) and blowing with nitrogen in a reactivial. 100 μℓ of TFAA and 100 μℓ of $CH_2Cℓ_2$ were added, and the vial was closed and heated at 130°C for 2 hr. After cooling, the reaction mixture was evaporated under dry N_2 followed by addition of 100 μℓ of dry n-hexane containing 1% TFAA and drying again. Finally another batch of 100 μℓ of n-hexane-TFAA mixture was added and the solution was analyzed by GC-EC.

Table 5.

Reproducibility and Linearity of GC-detector response for stearic acid and trimesic acid after being derivatized into their methyl esters

Trimesic Acid

Wt. of Acid Derivatized	IS (10 ng) RT	Area (1)	RT	Area (2)	Response = Area (1) / Area (2)	Mean	σ
10ng	27.37	1868	20.53	19890	.0939		
	27.36	1851	20.53	21030	.0880	.0920	3.496×10^{-3}
	27.34	1724	20.52	18300	.0942		
50ng	27.33	10730	20.51	17580	.6103		
	27.35	11340	20.53	17660	.6421	.6315	1.836×10^{-2}
	27.34	11500	20.53	17910	.6421		
100ng	27.38	377.0	20.53	19240	1.9600		
	27.37	27860	20.53	13390	2.0807	2.0313	6.324×10^{-2}
	27.38	37510	20.53	18270	2.0531		

Stearic Acid

X Wt. of Acid derivatized	RT	Area (1)	RT	Area (2)	Y Response = Area (1) / Area (2)	Mean	σ
10μg	29.99	2664	20.53	14770	.1804		
	29.99	2598	20.54	13660	.1902	.1863	
	29.99	2807	20.54	14910	.1883		.00520
50μg	30.00	18590	20.55	16070	1.1568		
	29.99	17030	20.55	17090	.9965	1.0537	
	30.00	16800	20.54	16670	1.0078		.0895
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		

Ratio of Wts. of Acid (X)	Ratio of response for Trimesic acid (Y_1)	Stearic acid (Y_2)
10	10	10
50	68	57
100	221	117

[NB: As we did not start with pure esters, the true response factor of the ester was not complete.]

To simulate analysis of real samples, 4 μℓ of the stock solution spiked into 1 mℓ of pure water, which was dried by heating (100°) and blowing with N_2. The rest of the procedure is the same as described above. Unfortunately, it has not been successful in achieving reproducibility in making this derivative in our lab. One set of results shows four peaks for the derivative for 4 anomers, and the area of these peaks have been summed up to give the following results:

Wt	Area	Ratio
10 ng	496,117	10
25	507,314	10
50	5,051,180	101.8

The retention time of the four peaks are 17.34, 17.69, 18.17 and 18.69 minutes. We are actively engaged in resolving this problem.

(3) A stock solution of 500 ppm glycine was prepared in water. 20 μℓ of this solution was transferred to a reactivial with a drop of HCℓ added, and the aqueous solution was dried by simultaneous heating (~100°C) and nitrogen blowing. A solution of 100 μℓ of acetylchloride in 1.1 mℓ of iso-amylalcohol was added to the residue and heated at 110°C for 2 hr. The sample was cooled, and dried only by blowing with nitrogen. To this, 100 μℓ of acetonitrile were added followed by 20 μℓ heptafluoro butyricanhydride, and the reaction mixture was heated at 150°C for 10 min. The product was dried by blowing with nitrogen. After the addition of 50 μℓ of ether, the vial was sealed. The final product is N(O)-heptafluorobutyrylisoamyl ester of glycine.

To simulate an analysis of real samples, 20 μℓ of a 500 ppm glycine solution was spiked into 1 mℓ of water followed by a drop of HCℓ, and the solution was evaporated by heating to 100°C and blowing with nitrogen. The residue was converted to the N(O) heptafluorobutyrylisoamyl ester as described

earlier. Results of reproducibility and linearity of response are presented in Table 6 and Table 8, respectively.

The bases, quinoline and caffeine, would end up in aqueous solution and hence an extraction of composite and GC response have been examined for reproducibility and linerity. Results are presented in Table 7 and Table 8.

A list of abbreviations and notations used in Table 5 through 8 is given in Table 9.

TABLE 6

REPRODECIBILITY OF THE ANALYSIS OF

N(O)-HEPTAFLUOROBUTYRYLGLYCINEISOAMYL ESTER

Sample	IS			Glycine					
No	WT	RT	Area	WT	RT	Area	Response	Mean	σ
40-2	10ng	12.09	6968	10ng	10.89	3547	.5090		
40-3	10ng	12.09	5833	10ng	10.89	4180	.7166	.5723	.113
40-4	10ng	12.11	6532	10ng	10.91	3942	.5035		
40-5	10ng	12.09	6070	10ng	10.81	2793	.4601		

IS = Hexamethylbenzene

95% CI for response for 10ng is

$$.5723 \pm t_{.025} \cdot \frac{S}{n}, \quad DF = 3$$

where $t_{.025} = 3.182$, $n - 4$, $S - .113$

$= .3925$ to $.7521$

[NB. As the pure derivative was not used as standard, the response factor is not known.

TABLE 7

REPRODUCIBILITY OF THE COMBINED OPERATIONS OF EXTRACTION AND GC-ANALYSIS OF QUINOLINE AND CAFFIENE

Sample	Quinoline (50ng)				IS(10ng)		Caffeine (50ng)			
No.	RT	Area	RF	Wt	RT	Area	RT	Area	RF	WT
16-5*	9.98	3551	.1088	20ng	12.9	16820	15.41	1447	.0430	20ng
16-1	9.97	11390		50.7	12.10	20640	15.43	4592		51.7
16-2	9.99	8712		39.8	12.10	20100	15.43	4370		50.6
16-3	9.99	13150		62.5	12.11	19320	15.43	4831		58.2
16-4	9.99	15500		60.0	12.11	24160	1544	6222		59.9

* This sample gives the results of GC analysis of 20ng of the bases in 1µℓ og $CH_2C\ell_2$. No extraction was involved.

It gives the RF's.

Summary

	Mean Weight	S	Mean recovery %	95% CI
Quinoline	53.25ng	10.3	106.5	53.25±16.39
Caffeine	55.1ng	4.6	110.2	55.1±7.32

$$95\%\ CI = \text{Mean weight} \pm t_{.025} \cdot \frac{S}{n}, \quad DF = 3$$

where $t_{.025} = 3.182$, $n = 4$

TABLE 8

REGRESSION RESULTS OF LINEARITY STUDY

Name	Wt	Response	Slope	Intercept	R	σ	CV
Steric acid	10ng	10	1.19	-2.10	.99998	0.45	0.7%
	50	57					
	100	117					
Trimesic acid	10	10	2.37	-26.93	.98196	29.15	29.3
	50	68					
	100	221					
Quinoline	10	10	0.59	7.41	.99792	6.52	8.4
	100	71.5					
	250	152.5					
Caffeine	10	9.3	0.41	10.48	.98917	10.56	17.5
	100	60.5					
	250	111					
Glycine	2	2	1.4	-4.4	0.98813	7.3	25.7

All regressions were run with SOSS package program.

TABLE 9

LIST OF ABBREVIATIONS AND NOTATIONS

IS = Internal Standard

RF = Response Factor

σ = Sample Standard Deviation

RT = Retention Time

WT = Weight

t = Value of student's t disbribution that will be exceeded with specified probabilities and degrees of freedom.

DF = Degrees of Freedom

n = Number of Observations

R = Correlation Coefficient

R^2 = Coefficient of Determination

CI = Confidence Interval

CV = Coeffieient of Variability

D. Gas Chromatographic Analysis

Recent developments in the preparation of glass capillary columns have permitted the preparation of high quality columns. In particular, the persilylation method proposed by Grob (1979) and the alkylpolysiloxane degradation method proposed by Schomburg (1979) to prepare inert, relatively non-polar stationary phase wall coated columns were investigated.

Soft glass tubing was used exclusively in this work. The tubing was washed with detergent and rinsed with tap water, distilled water and acetone. Capillary tubing was drawn from 121-cm lengths of soft glass tubing (6 mm o.d. x 2.5 mm i.d.) using a Shimadzu glass drawing machine. Capillary tubing 15 to 50 meters long with 0.3 mm to 0.4 mm i.d. was used.

Each capillary tubing was filled (95%) with a 20% solution of HCl and leached overnight at 140°C. After leaching, the capillary tubing was flushed with a 0.5 N HCl solution and dehydrated according to the procedure outlined by Grob (1979).

The capillary columns were deactivated differently depending on the phase used to coat the surface. For the apolar phases (SE-54, SE-52, SE-30, OV-1, OV-101), either persilylation according to Grob (1979) or alkyl-polysiloxane degradation according to Schomburg (1979) was used. In the case of polar stationary phases, deactivation by decomposition of various polyethylenglycols according to Cronin (1974) was used. The apolar phases were preferred becasue of their higher temperature stability and efficiency.

Specific columns were prepared by considering the types of samples to be analyzed during this study. Columns were evaluated before use by injecting a standard test mixture. This test mixture consisted of the following compounds: nonanal (to determine catalytic activity); 1-octanol and 2,3-butanediol (to determine adsorption of polar functional groups, i.e., hydrogen bonding); 2,6-dimethylphenol and 2-ethyl-hexanoic acid (to determine

-basic sites); and C_{10}, C_{11} and C_{12}-acid methyl ester (to determine separation number and film thickness). Test conditions were those as described by Grob (1978).

The chromatogram of the standard test mixture for one of the columns used during this study is shown in Figure 3. The test indicates some catalytic activity (adsorption of nonanal) and to some degree adsorption of the hydroxyl group (i.e., octanol). Butanediol is typically not eluted well from silicone type phases (Grob, 1978) as is the case here. Ethylhexanoic acid is typically neither eluted 100% nor as a symmetric peak from silicone type phases.

The gas chromatographic analysis was carried out on a Hewlett Packard Model 5830 gas chromatograph equipped with glass capillary column, flame ionization detector (FID) and/or electron capture detector (ECD). Approximately 1 μℓ of the standard solution was injected using the splitless injection technique. The chromatographic conditions were as follows:

Column: glass capillary 30m x 0.3 mm i.d.;
SE-54 (0.25 μm film thickness);
TZ (separation number) = 30

Temperatures: Oven temp. program
45°C (5 min)
6°C/min
290°C (10 min)
Injector - 250°C
Detector - 300°C

Gases: Carrier - Helium (≈ 4 mℓ/min)
Auxilary - Helium

Detector: FID

A typical FID trace of a standard mixture containing all the gas chromatographable compounds is shown in Figure 4. Identification was

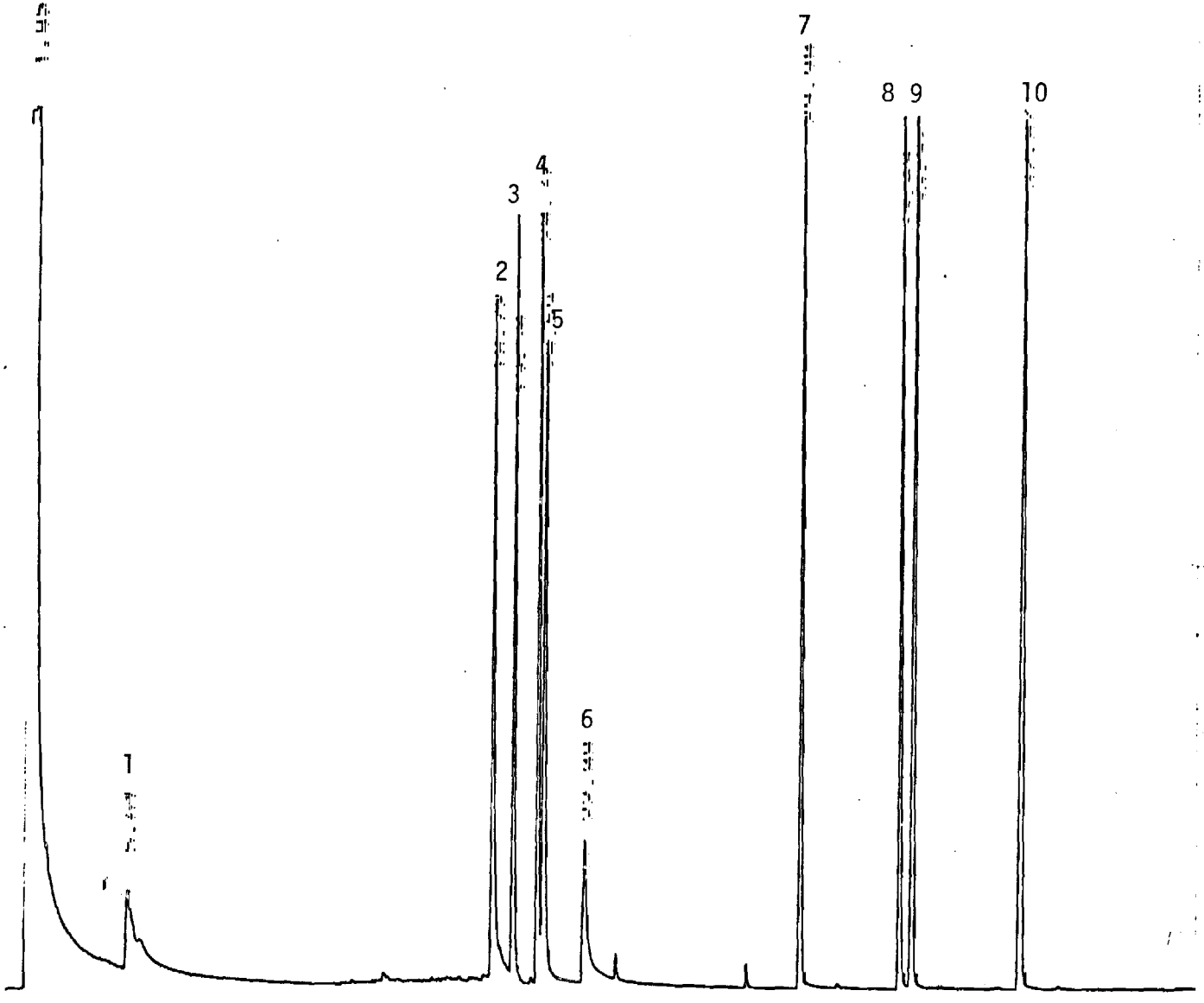


FIGURE 3 - Polarity mixture used to evaluate columns.
For identification of peaks, see Table 10.
See text for chromatographic conditions.

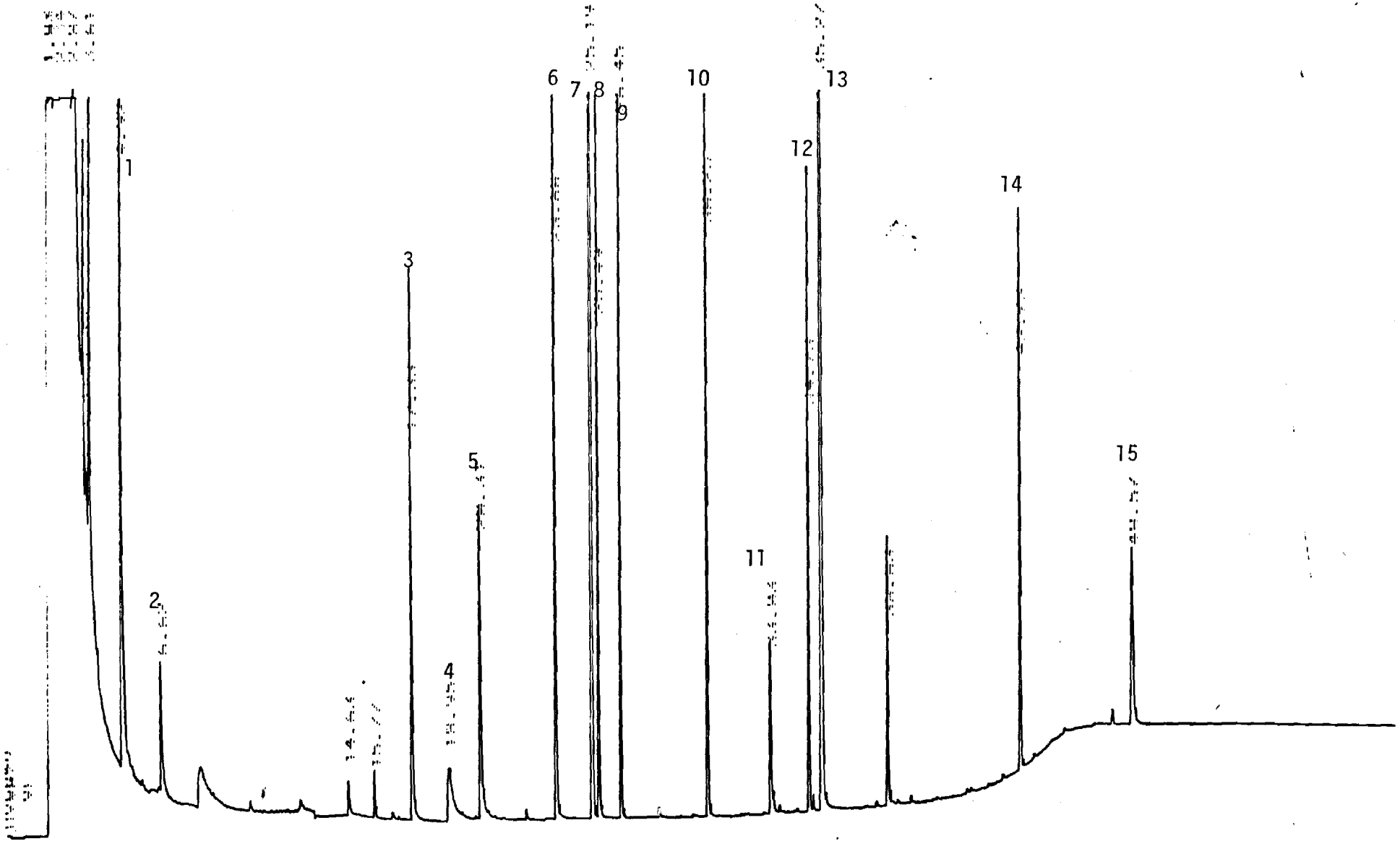


FIGURE 4 - Chromatogram of model compounds used during this study.
For identification of compounds, see Table 11.
See text for chromatographic conditions.

TABLE 10

ASSIGNMENT OF COMPONENTS OF
POLARITY MIXTURE FOR FIGURE 1

2,3-Butanediol	1
n-octanol	2
2,6-dimethylaniline	3
2,6-dimethylphenol	4
nonanal	5
2-ethylhexanoic acid	6
$C_{10,11,12}$ - esters	7,9,10
dicyclohexylamine	8

TABLE 11

COMPOSITION OF STANDARD MIXTURE
CONTAINING COMPOUNDS USED FOR STUDY

Methyl isobutyl ketone	1
Crotonaldehyde	2
Isophorone	3
2,4-dichlorophenol	4
Quinoline	5
Biphenyl	6
Hexylmethyl benzene (I.S.)	7
1-Chlorodecane	8
2,6-ditertiarybutyl-4-methylphenol	9
2,4'-dichlorobiphenyl	10
Caffeine	11
2,2',5,5'-tetrachlorobiphenyl	12
Anathraquinone	13
Bis(2-ethylhexyl)phthalate	14
Benzo(e)pyrene	15

confirmed by mass spectrometry. Baseline separation is achieved for 2,2', 5,5'- tetrachlorobiphenyl from anthraquinone as well as elution in a reasonable analytical time for benzo (e) pyrene. A similar run done on a Carbowax 20M column (upper limit 220°C) is shown in Figure 5. An additional 15 min analysis time per run is required if this polar phase is used instead of the relatively non-polar phase. Temperature stability is one reason prompted us to use relatively non-polar phases. Figure 4 also indicates adsorption of 2,4-dichlorophenol (i.e., small tailing peak). Analytically, this could pose a serious problem (irreversible adsorption of small quantities of compounds); however, the 2,4-dichlorophenol is derivatized in the hydropholic acid fraction and is chromatographed without problems (see Figure 6). We have also prepared columns to analyze for the phenolics (including 2,4-dichlorophenol) without derivatization; therefore, this is also a viable alternative.

Furfural and crotonaldehyde have been somewhat difficult to chromatograph also. These aldehydes co-elute with the solvent peak (note that they are missing from the previous chromatograms). We have had limited success in using a different stationary phase (see Figure 7) but thus far we have been unable to obtain reproducible results. The use of other stationary phases and different film thickness is being investigated now.

Preliminary results using the "on-column injection" technique indicated this to be a viable alternative worth pursuing. Figure 8 is a chromatogram of an on-column injection of the standard solution. Note the increased response for all compounds (compare with Figure 4 in which all parameters are the same), especially 2,4-dichlorophenol, bis (2-ethylhexyl) phthalate and benzo (e) pyrene. There is less of a discrimination between high and low boiling compounds, one of the major advantages of on-column injection. Also note the better resolution of the early eluting compounds (i.e., aldehydes)

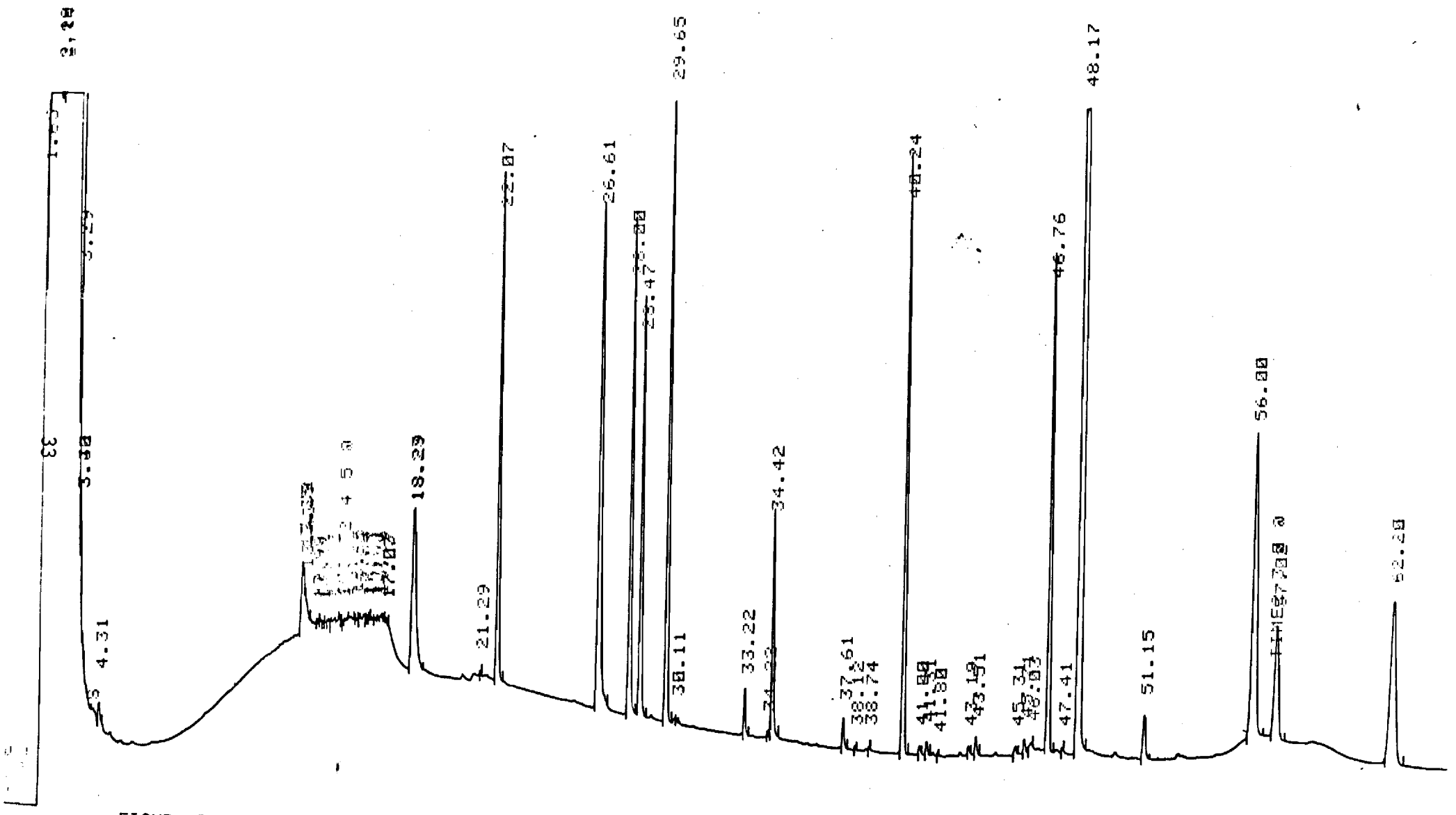


FIGURE 5 - Model compounds evaluated on a polar column (i.e. CW20M) GC conditions as follows: Temp. programming 45°C(5 min) to 220°C (45 min) @ 6°C/min. All others same as in text.

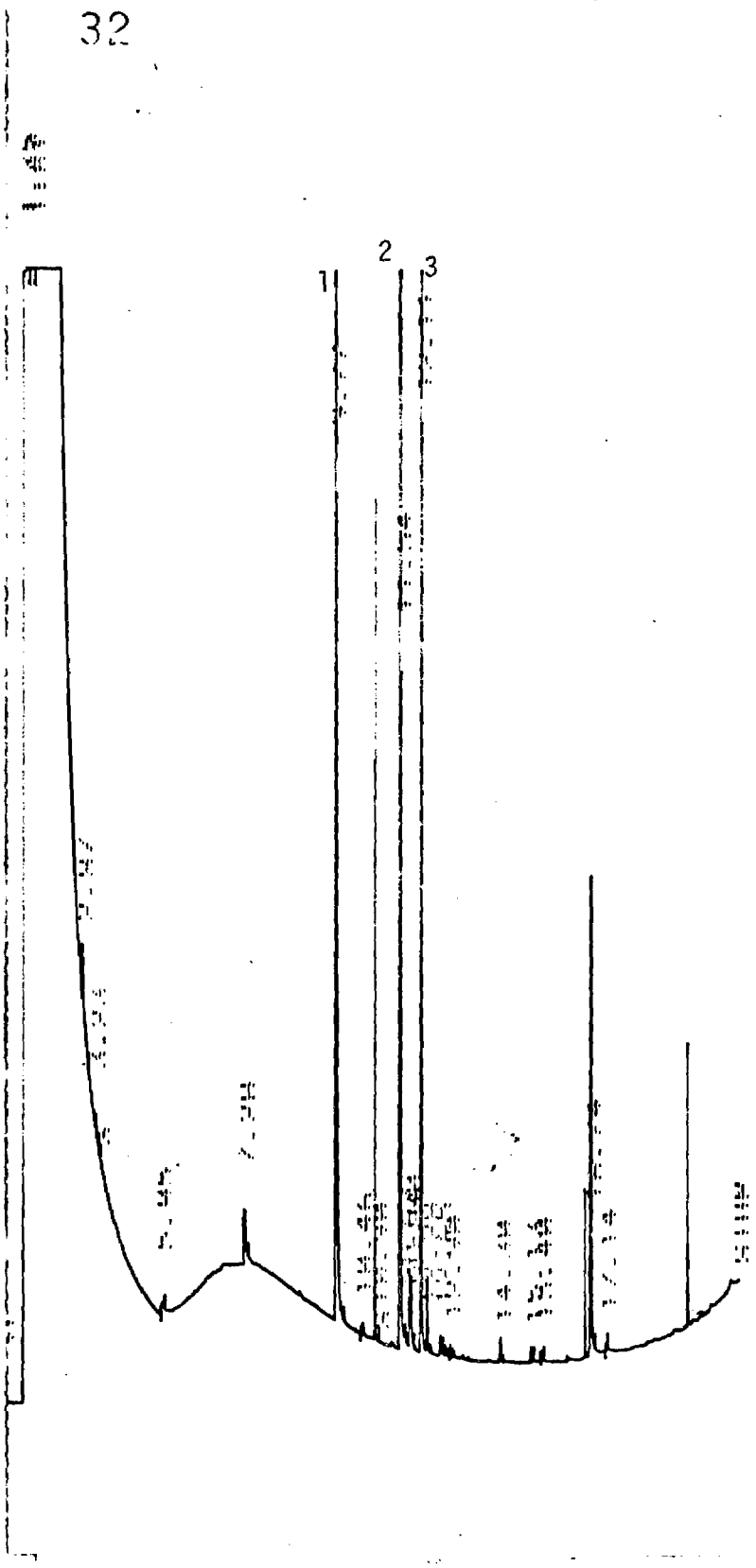


FIGURE 6 - Derivatized 2,4-dichlorophenol
(1) 2,4-dichlorophenol methyl ether;
(2) internal standard;
(3) 2,6-ditertiarybutyl-4-methylphenol. GC Conditions: 45°C(5 min) 280°C (10 min) @ 15°C/min.

FIGURE 7 - Aldehydes evaluated on SE-52 column.
Peak @ 14.90 is Quinoline.
GC conditions same as in text.

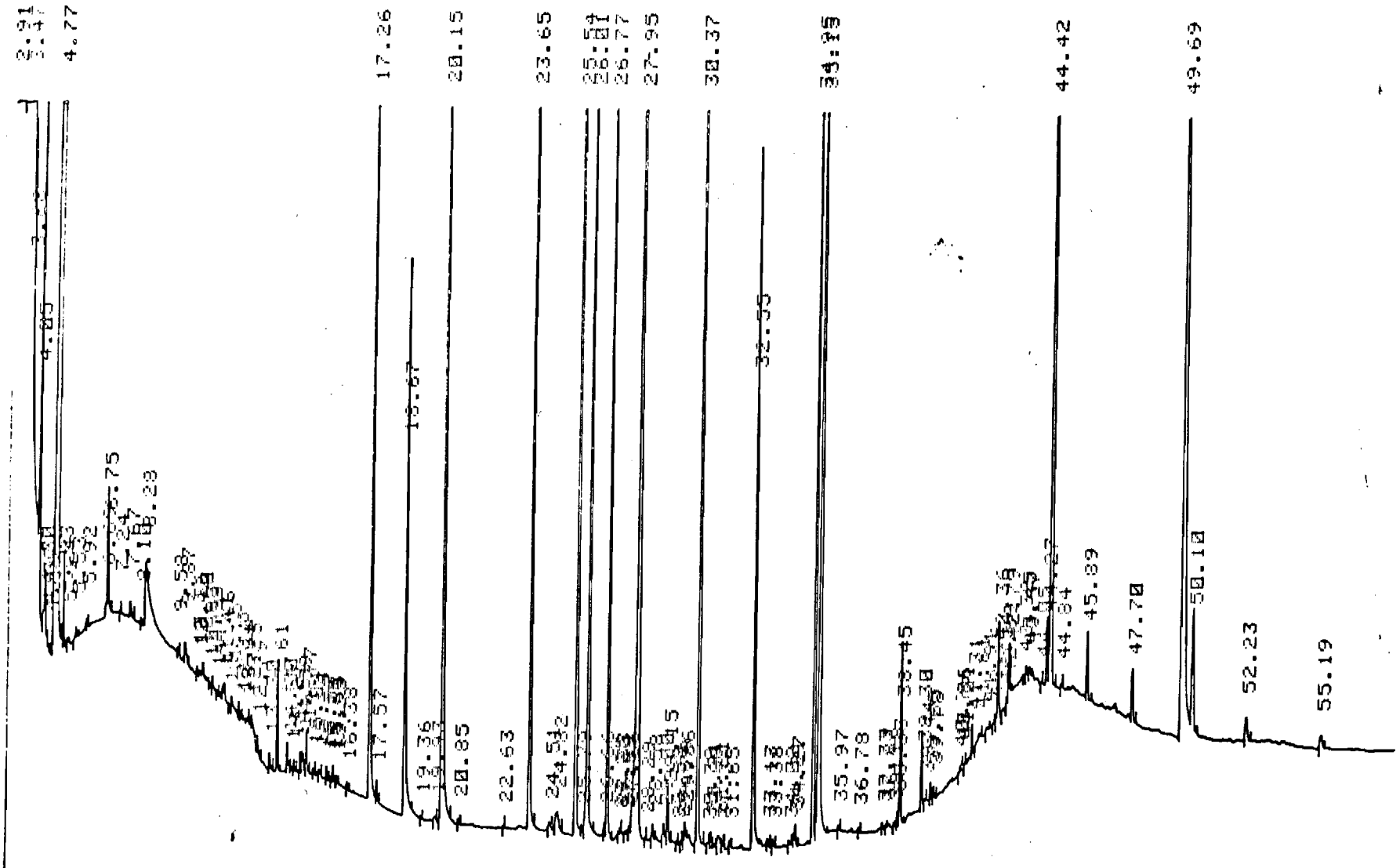


FIGURE 8 - On column injection of model compounds. GC conditions:
Injector temperature 250°C, termperature programing 30°C (5 min) to 290°C (10 min) @ 6°C/min.

from the solvent. Figure 9 shows similar results with "on-column injection" for the Carbowax 20M column (compare with Figure 5 which is twice the concentration as in Figure 9).

To determine the reproducibility, linearity and minimum detectable limit (MDL) of the gas chromatographic system, a study of the model compounds at different concentration levels and many repetitive runs of the same standard solution was conducted. Arithmetic mean values and the standard deviation of the GC response determined from fourteen injections using a 7672A H-P liquid automatic sampler, are given in Table 12. As shown in the table, the mean varies from 17.0 for benzo (e) pyrene to 21.3 for quinoline. In all cases, the relative standard deviation is less than 8.7%. No data for antraquinone is given. The reason for this is that at the time of the evaluation the porblem of resolving antraquinone from 2,2', 5,5'-tetrachlorobiphenyl had not been solved (see Figure 10 and compare with Figure 4).

The evaluation to determine the minimum detectable limit and concentration-response linearity for the model compounds is shown in Table 13. As shown in the table, many of the compounds can be detected at the 1 ng level, with all of them being detectable at 10 ng. Glycine, Trimesic and Stearic acid, after a preliminary derivatization as described in the previous section, were analyzed on the same gas chromatographic system Figure (11) and (12) represent their FID trace. Glucose, as trifluoro acetic derivative, was evaluated by GC-ECD and a typical trace is reported in Figure 13. The GC conditions were as follow:

GC Column: SE-30 17m 0.25 mm I.D.
Temperature program: 45^{o}(5 min) 280^{o}C 6^{o}C/m
Carrier gas: He
Make-up gas: Ar/Me (95%+5%)

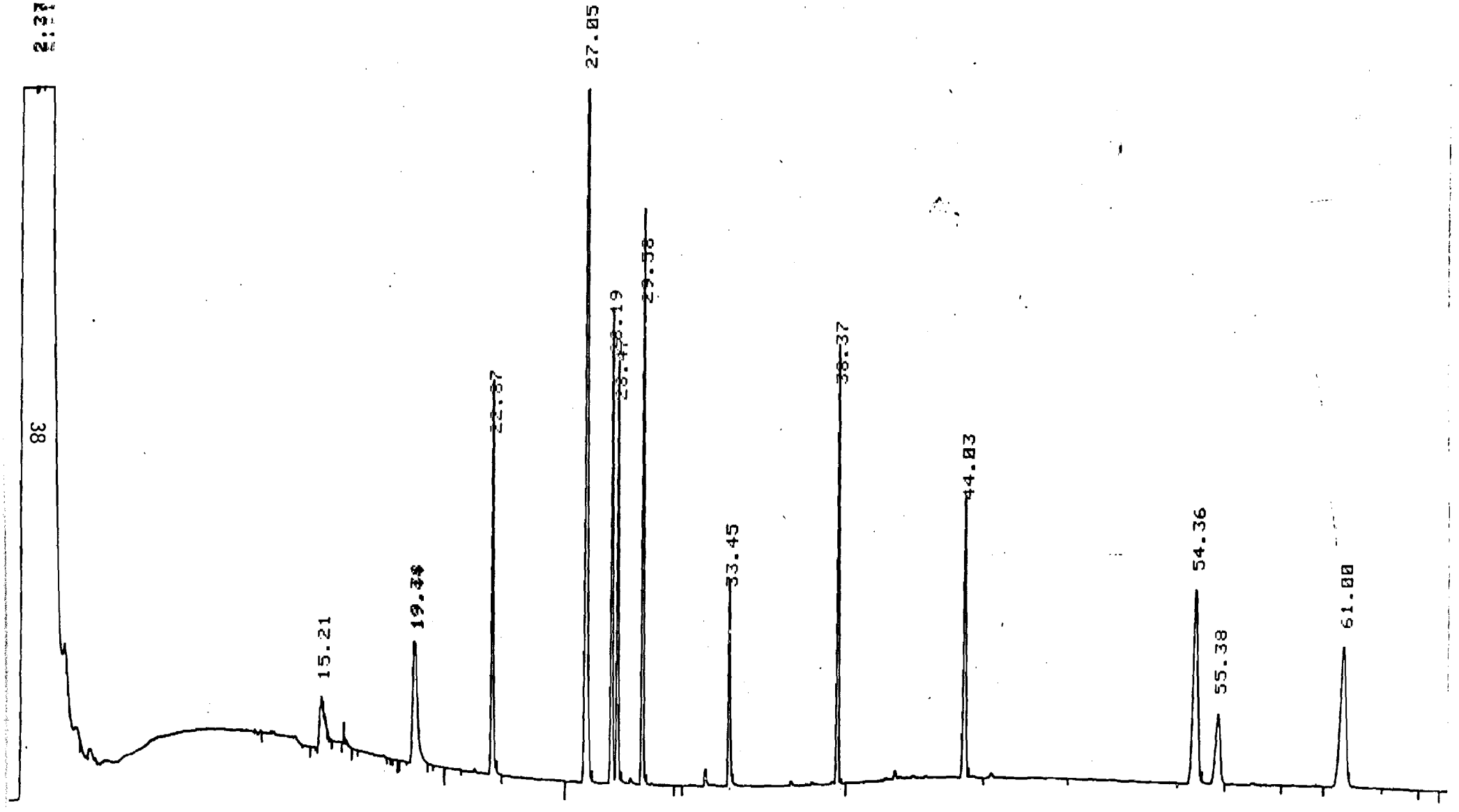


FIGURE 9 - On column injection of model compounds on CW 20M column. GC conditions: Injector temperature 250°C, temperature programming 30°C (5 min) to, 220°C (45 min) @ 6°C/min.

TABLE 12

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

Compound	Mean ($\bar{X}$)	Standard Deviation (σ)	$\frac{\sigma}{\bar{X}}$ .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-ditertiarybutyl-4-methylephenol	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
13. Benzo(e)pyrene	17.0	1.21	7.1

TABLE 13

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-ditertiarybutyl-4-methylephenol	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)phthalat-	1.3	10.2	17.3	101.0
13. Benzo(e)pyrene		8.8	17.3	101.2

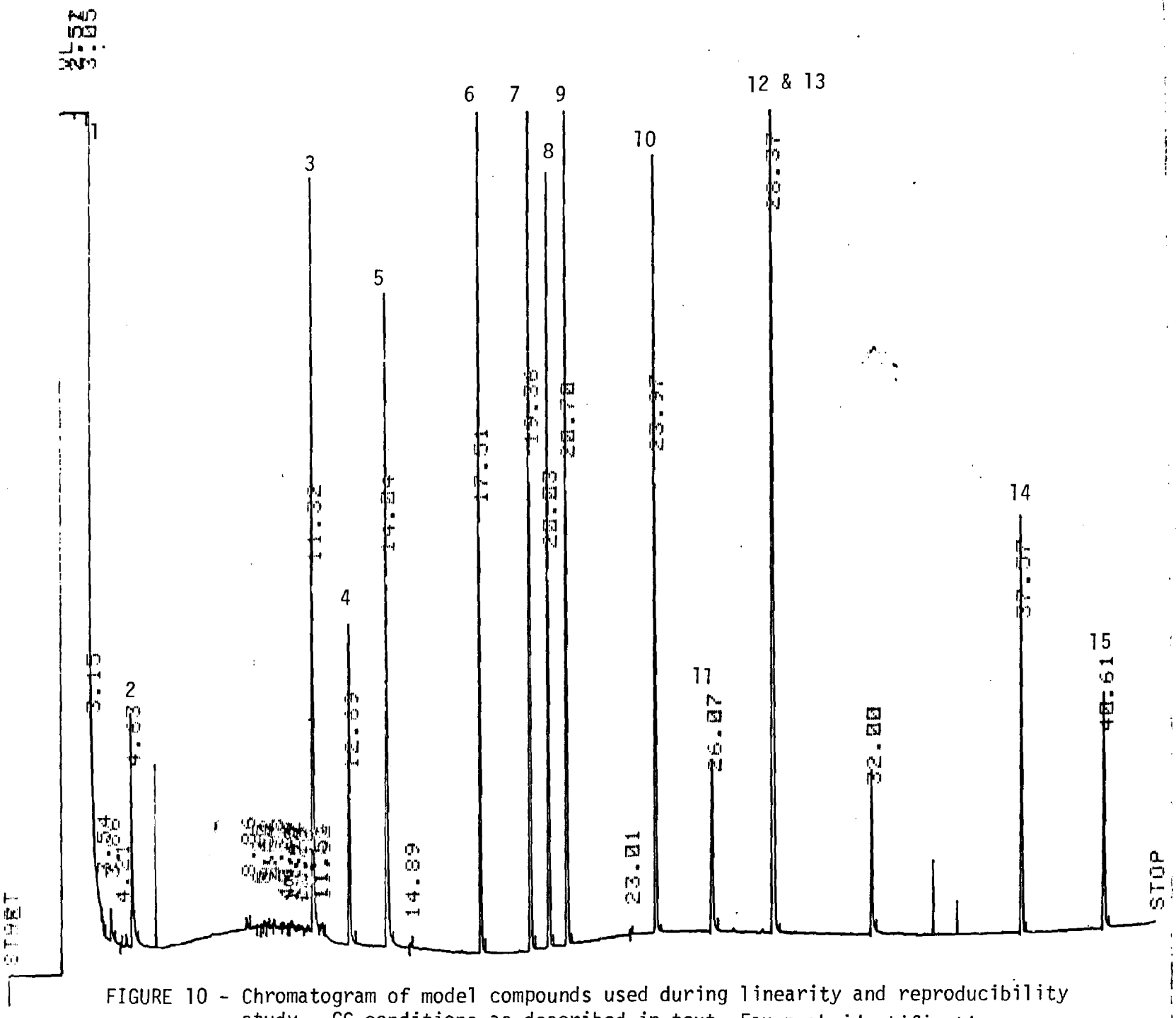


FIGURE 10 - Chromatogram of model compounds used during linearity and reproducibility study. GC conditions as described in text. For peak identification, see Table 11.

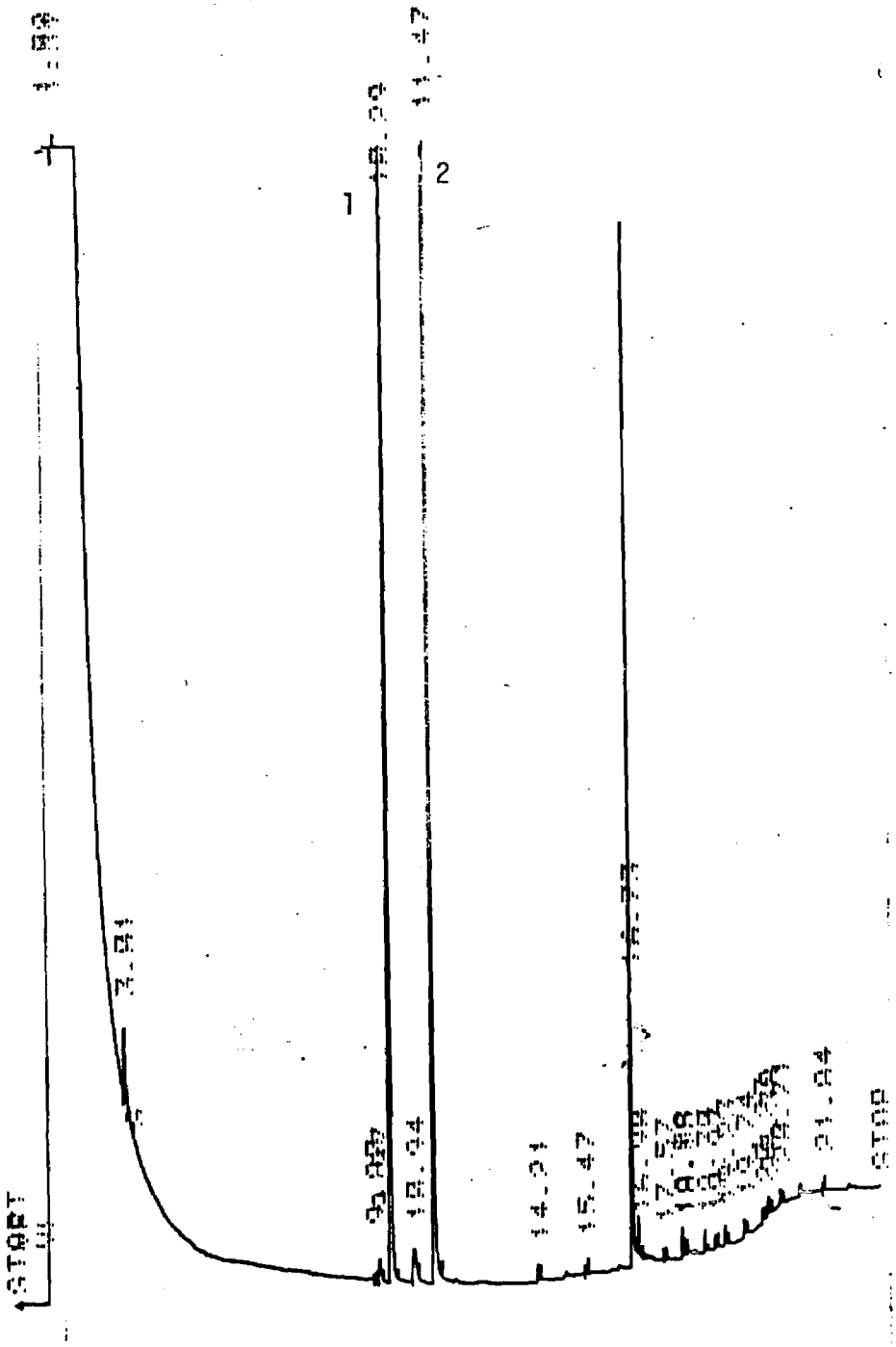


FIGURE 11 - Derivatized glycine.
(1) N(O)-Heptafluorbutsyro-isoamyl ester of glycine
(2) Internal Standard.
GC conditions: 45°C (5 min) to 280°C (10 min) at 15°C/min.

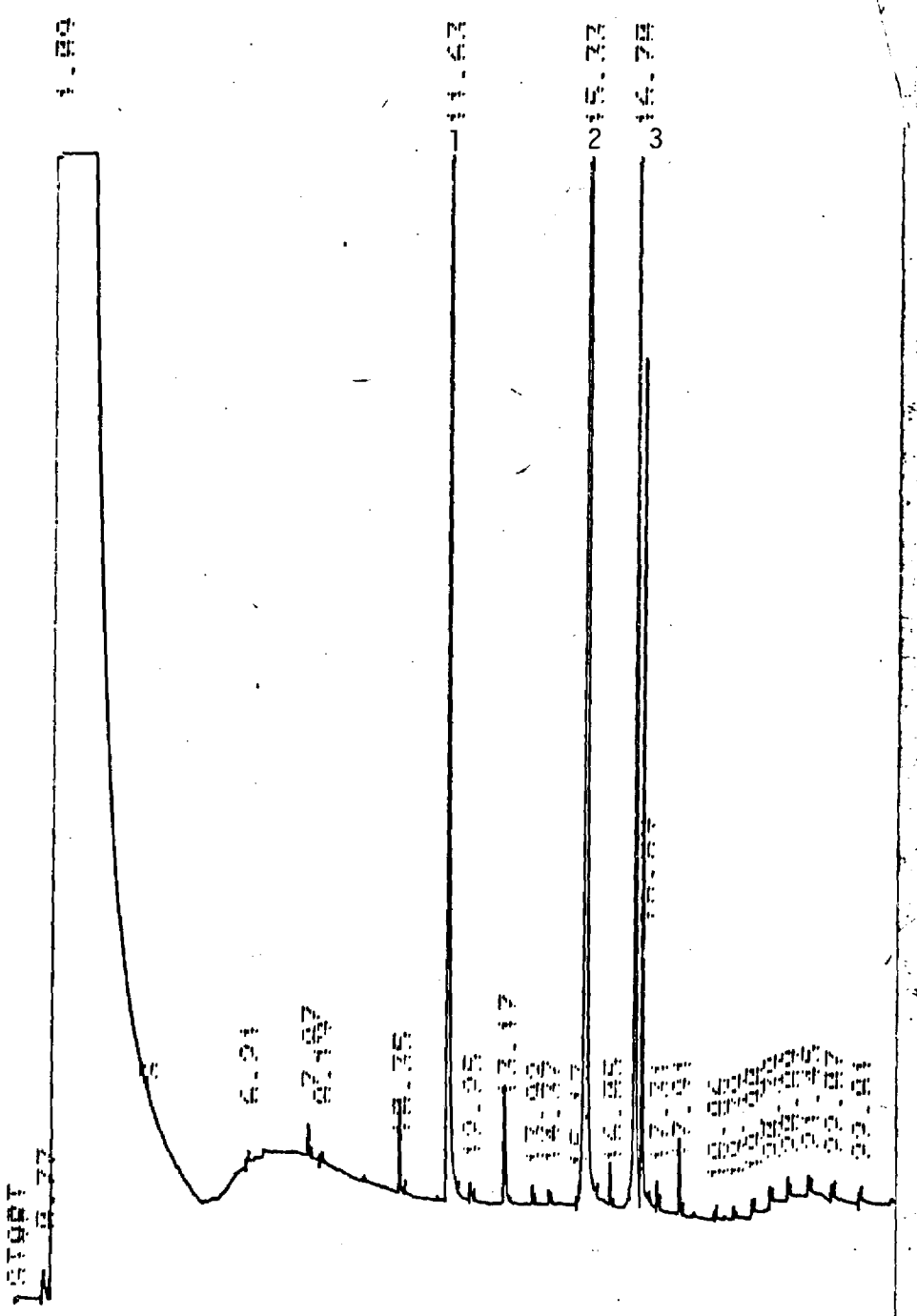


FIGURE 12 - Derivatized stearic and trimesic acid. (1) Internal Standard: (2) 1,3,5-Benzene-tricarboxylic acid trimethylester; (3) Methylstearate. GC conditions: 45°C (5 min) to 280°C (10 min) at 15°C/min.

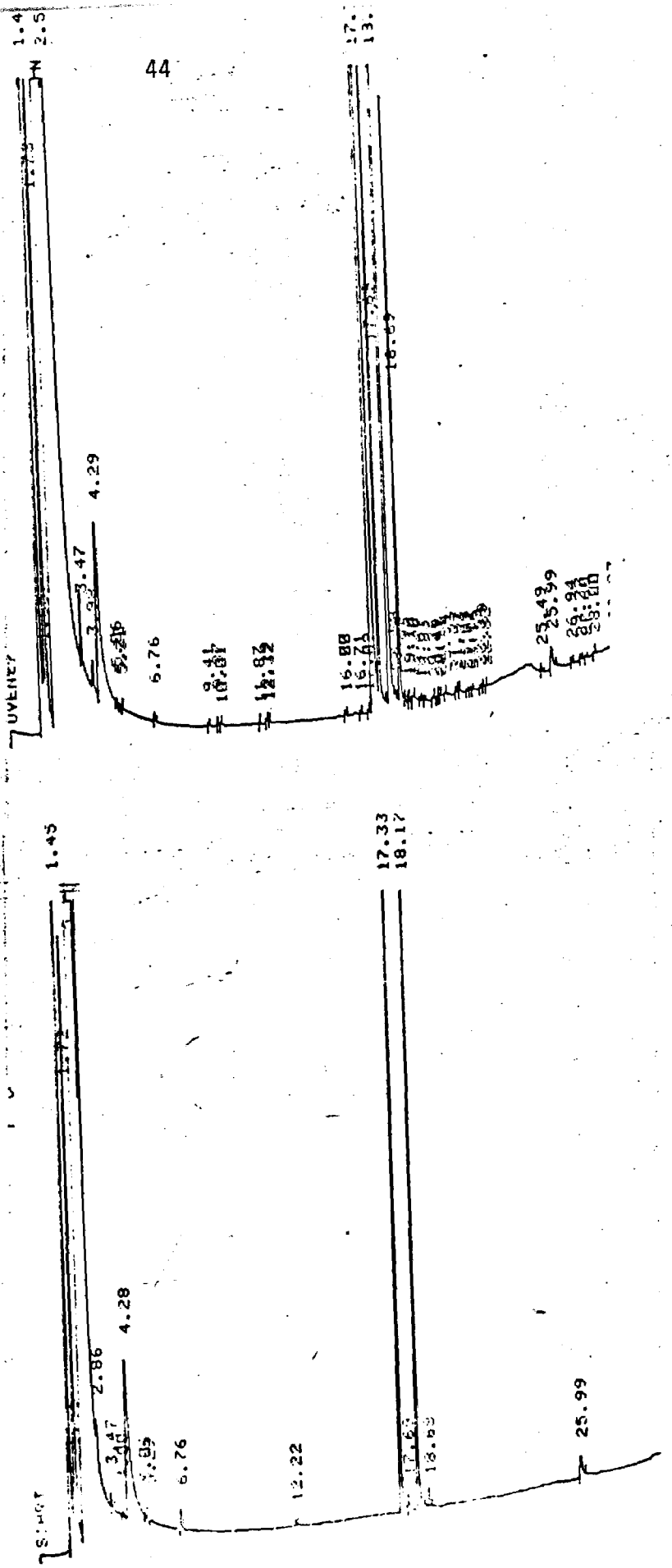


FIGURE 13 - ECD trace of derivatized glucose [Penta - (trifluoroacetyl) glucose. GC condition: 45°C (5 min) to 270°C (10 min) at 6°C/min; SE-30, split injection (50:1) 50 ng injection top chromatogram, 5ng bottom

E. Gas Chromatography - Mass Spectrometry - Data System

A FINNIGAN 4023 GC-MS equipped with Incos data system has been employed in the mass spectrum determination of the organic compounds under investigation.

The chromatography was carried out on the same wall coated glass capillary columns evaluated previously in the GC determination. Splitless injection mode was used for the introduction of samples into the GC column. The broad range in molecular weights of the organic compounds usually required GC temperature programs from $40^{o}C$ up to 290^{o}-$300^{o}C$. The sample transfer line between the chromatographic column and the mass spectrometer ion source consisted of a fused silica tubing with an internal diameter of 0.1 mm and circa 40 cm long. The transfer line oven temperature was maintained at $290^{o}C$ and the mass spectrometer was operated under the following conditions:

Ionization Mode	=	Electron Impact
Electron Energy	=	70V
Emission Current	=	0.5 mAmp
Sensitivity	=	10^{-7} Amp/V
Electron Multiplier	=	1600 V
Mass range	=	41-300 or 41-450 a.m.u.
Scan time	=	1 sec per scan

Instrumental calibration was performed on daily basis before any sample was investigated. Perfluorotributylamine (FC 43) was used to initially tune the mass spectrometer; decafluorotriphenylphosphine (DFTPP) was subsequently introduced through the GC and checked the acceptability of the tune thus obtianed. Figure 14 represents a typical acceptable mass spectrum of DFTPP.

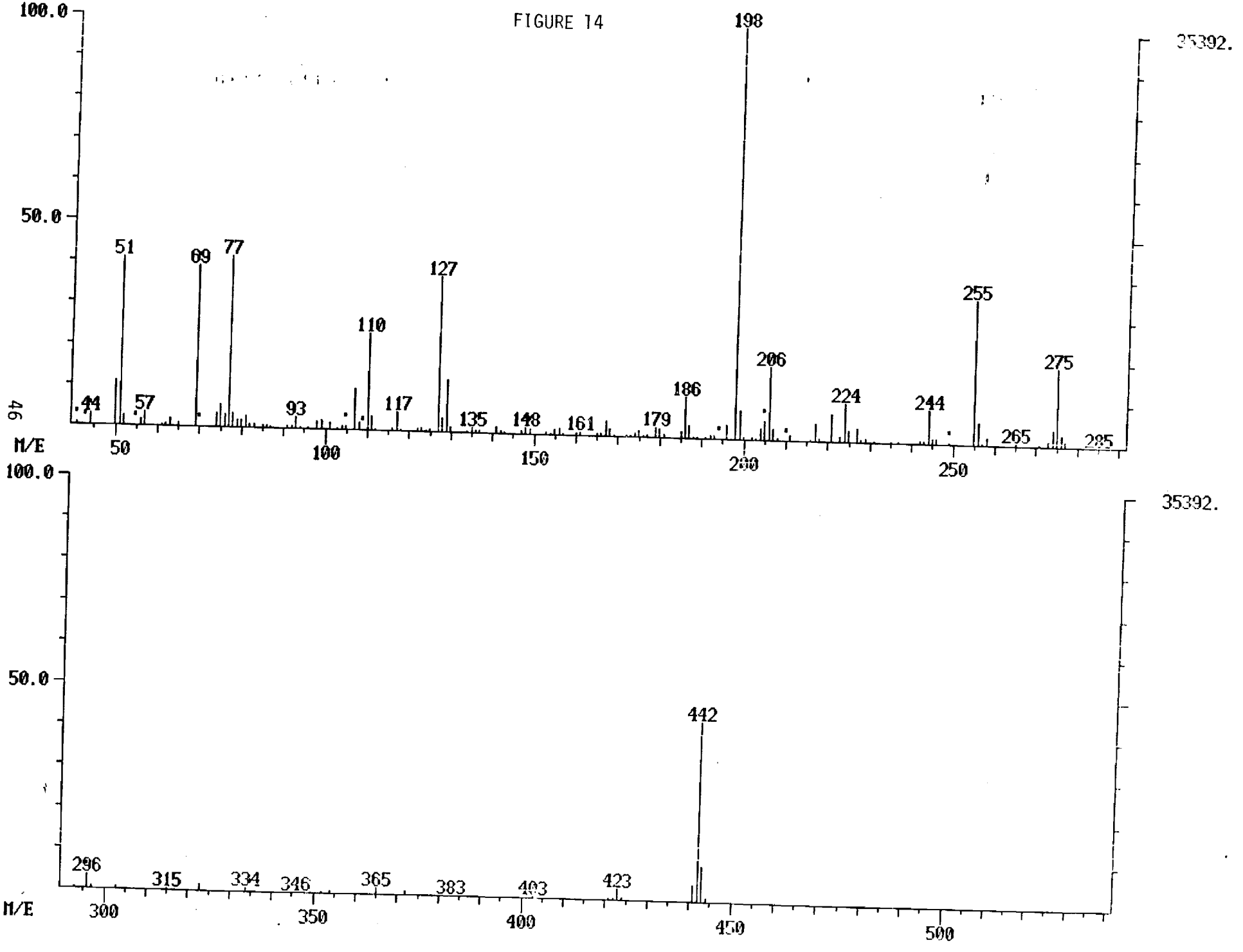
The suitability of the GC-MS system for the analysis of the organic compounds under investigation was evaluated, particularly in regard to

03/09/81 9:51:00 + 10:36

DATA: DFTPP030981 #636
CALI: CALGAS #4

BASE M/E: 198
RIC: 233984.

FIGURE 14



sample losses in the transfer line due to adsorption or catalytic degradation.

Figure 15-17 represent the reconstructed ion chromatogram (R.I.C.) and relative mass spectrum for methylisobutylketone and furfural. Figure 18 represents the mass spectrum of furfural obtained with a mass range starting from 27 a.m.u. in order to confirm the presence of m/e 29, characteristic of the aldehyde group (CHO).

The GC conditions were as follows:

W.C.O.T. column SE-54 30 m 0.3 mm I.D.;
Temperature program 40^{o}(5 min) - 200^{o}C 10^{o}C/m;
Injection volume 1 µℓ; amount 20 ng/µℓ

The R.I.C. and the relative mass spectrum for isophorone, 2,4-dichlorophenol, quinoline, biphenyl, hexamethylbenzene (I.S.), 1-chlorododecane, 2,6-di-ter-butyl-4-methylphenol, 2,4-dichlorobiphenyl, caffeine, 2,2', 5,5'-tetrachlorobiphenyl, anthraquinone, bis-(2-ethylhexyl) phtalate and benzo (e) pyrene are reported in Figure 19-31, respectively.

The GC conditions were as follows:

W.C.O.T. column SE-54 30m 0.3 mm I.D.;
Temperature program 40^{o}(2 min) - 290^{o}C at 10^{o}C/m;
Injection volume 1µℓ ; amount 20 ng/µℓ

Glycine, Trimesic and Stearic acid, after derivatization as described in the previous section, were analyzed under the following GC conditions.

W.C.O.T. column SE-54 30m 0.3 mm I.D.
Temperature program 40^{o}(2 min) - 280^{o}C 10^{o}C/m
Injection volume 1µℓ; amount 20 ng/µℓ

Figure 32-36 represent the R.I.C. and relative mass spectrum.

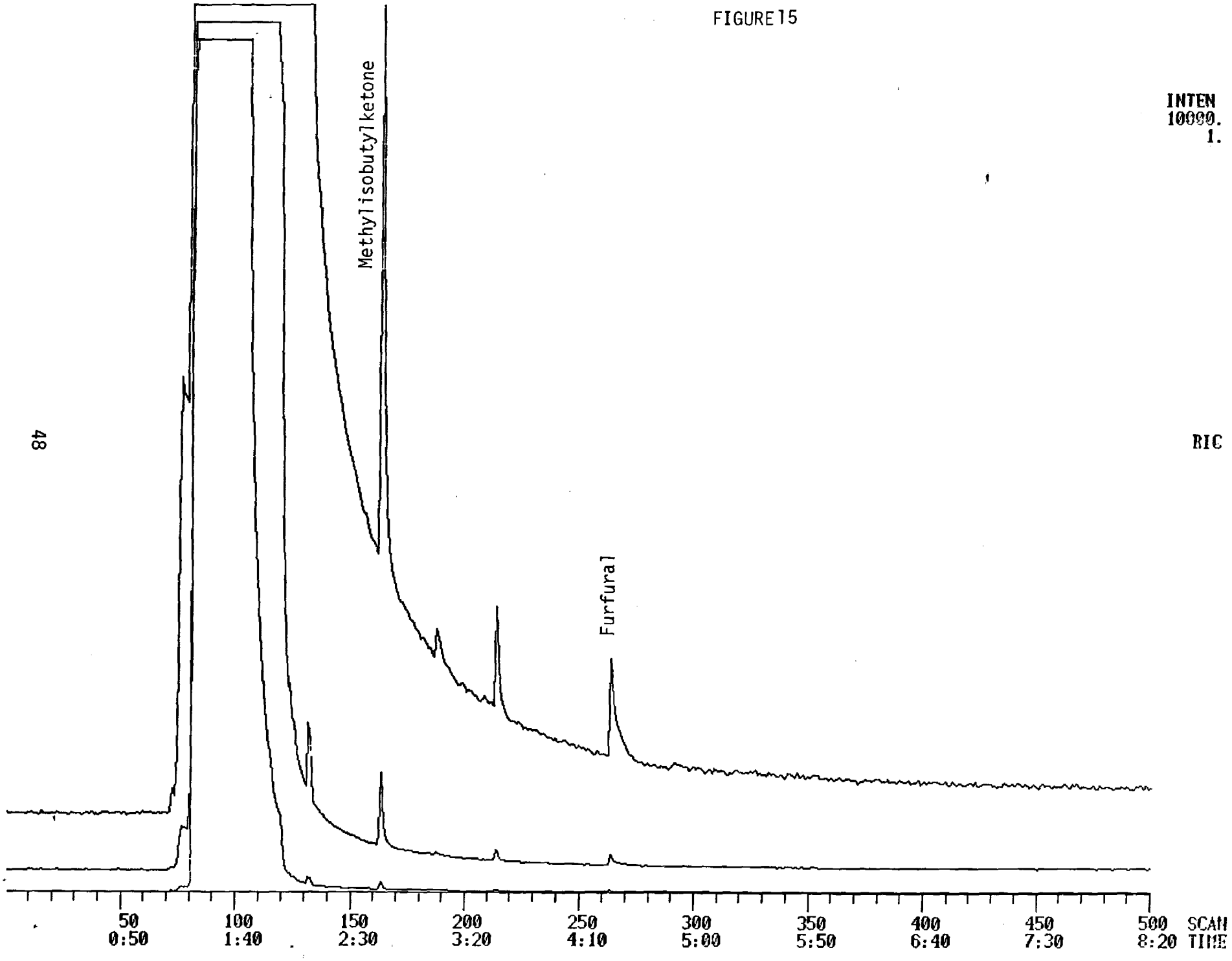
Chloroform, which has a relatively higher volatility among all the organics under this investigation, was analyzed by the pruge and trap method. In this regard a Hewlett-Packard 5830 GC equipped with a 7675A H-P Purge and Trap unit, was interfaced with the FINNIGAN 4000 MS. The utilization

03/09/81 10:45:00
SAMPLE: FURFURAL.CROTONALDEHYDE.MIK

DATA: STDT #132
CALI: CALGAS #4

SCANS 1 TO 500

FIGURE 15

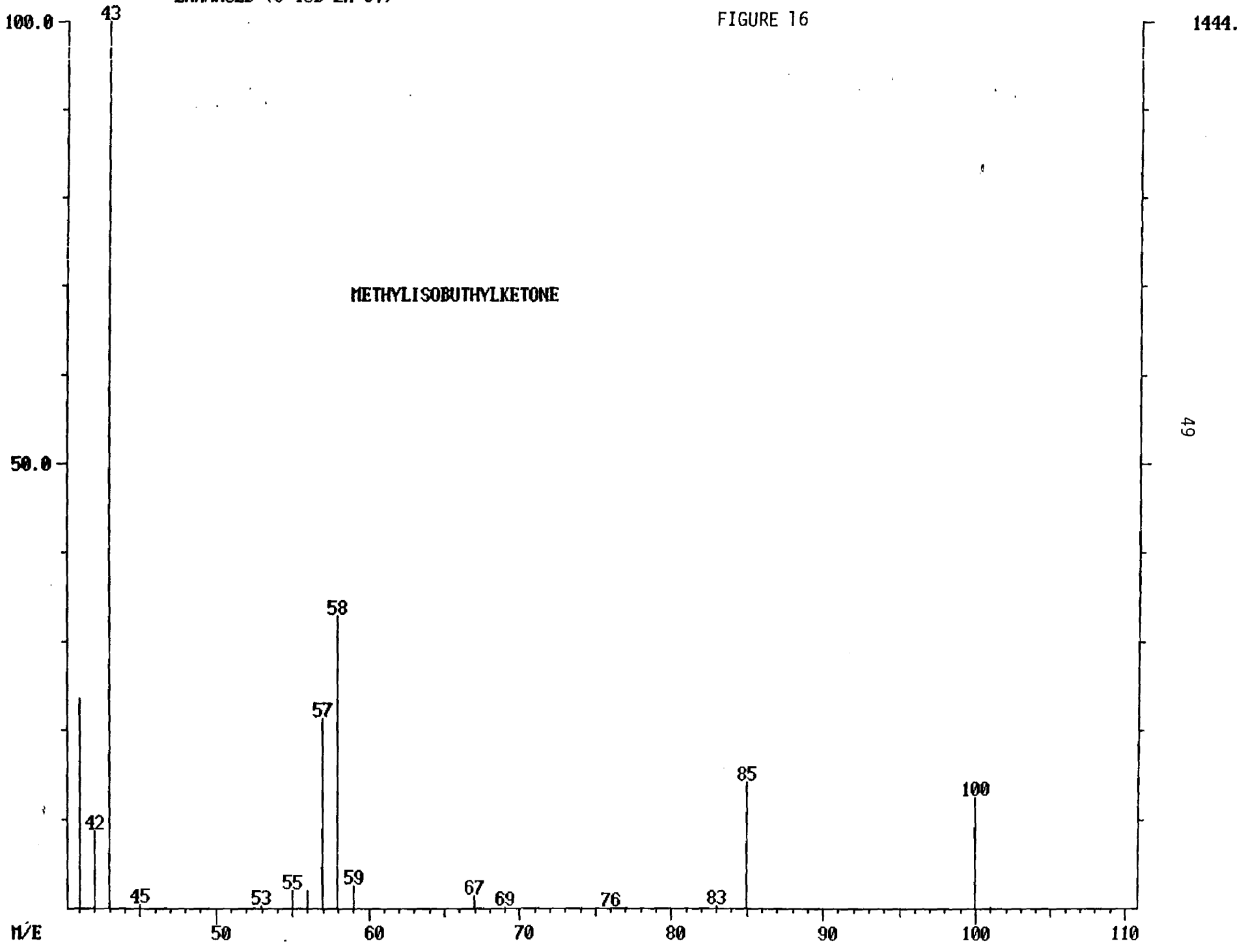


03/09/81 10:45:00 + 2:43
SAMPLE: FURFURAL.CROTONALDEHYDE.MIK
ENHANCED (S 15B 2N 0T)

DATA: STDT #163
CALI: CALGAS #4

BASE M/E: 43
RIC: 3220.

FIGURE 16

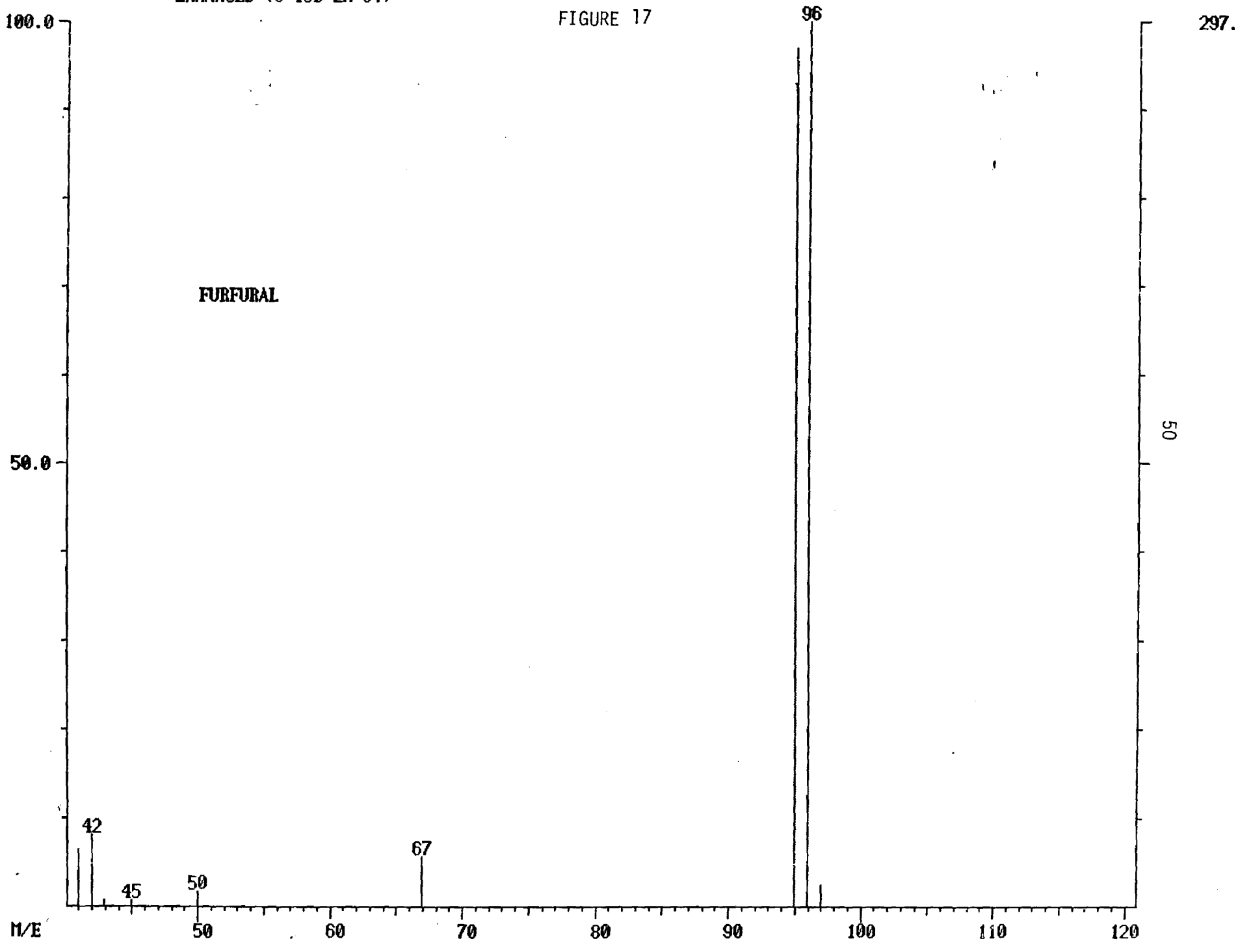


03/09/81 10:45:00 + 4:24
SAMPLE: FURFURAL,CROTONALDEHYDE,MIK
ENHANCED (S 15B 2N 0T)

DATA: STD1 #264
CALI: CALGAS #4

BASE M/E: 96
RIC: 663.

FIGURE 17

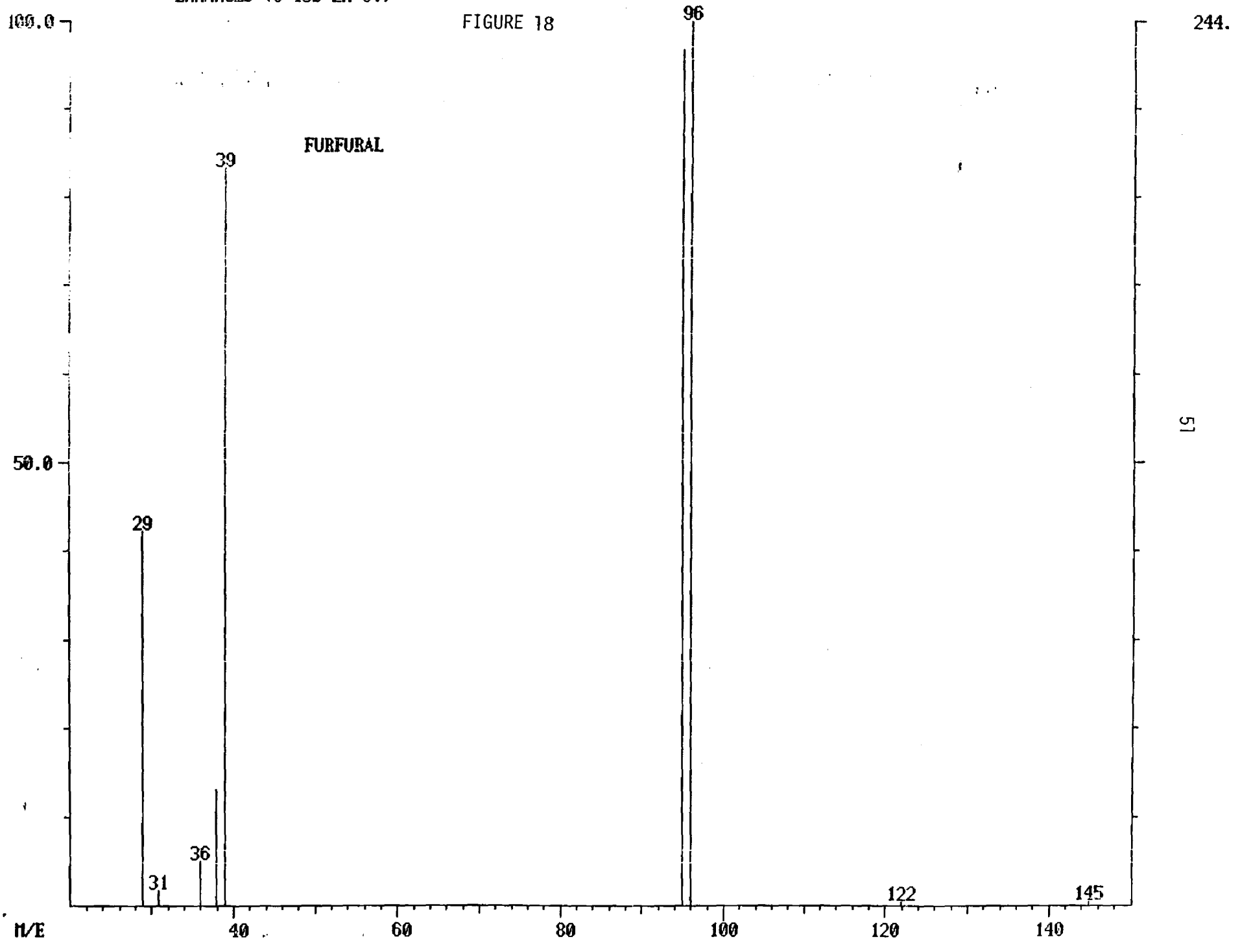


03/09/81 11:39:00 + 4:22
SAMPLE: FURFURAL,CROTONOALDEHYDE
ENHANCED (S 15B 2N 0T)

DATA: STD2 #262
CALI: CALGAS #4

BASE M/E: 96
RIC: 836.

FIGURE 18

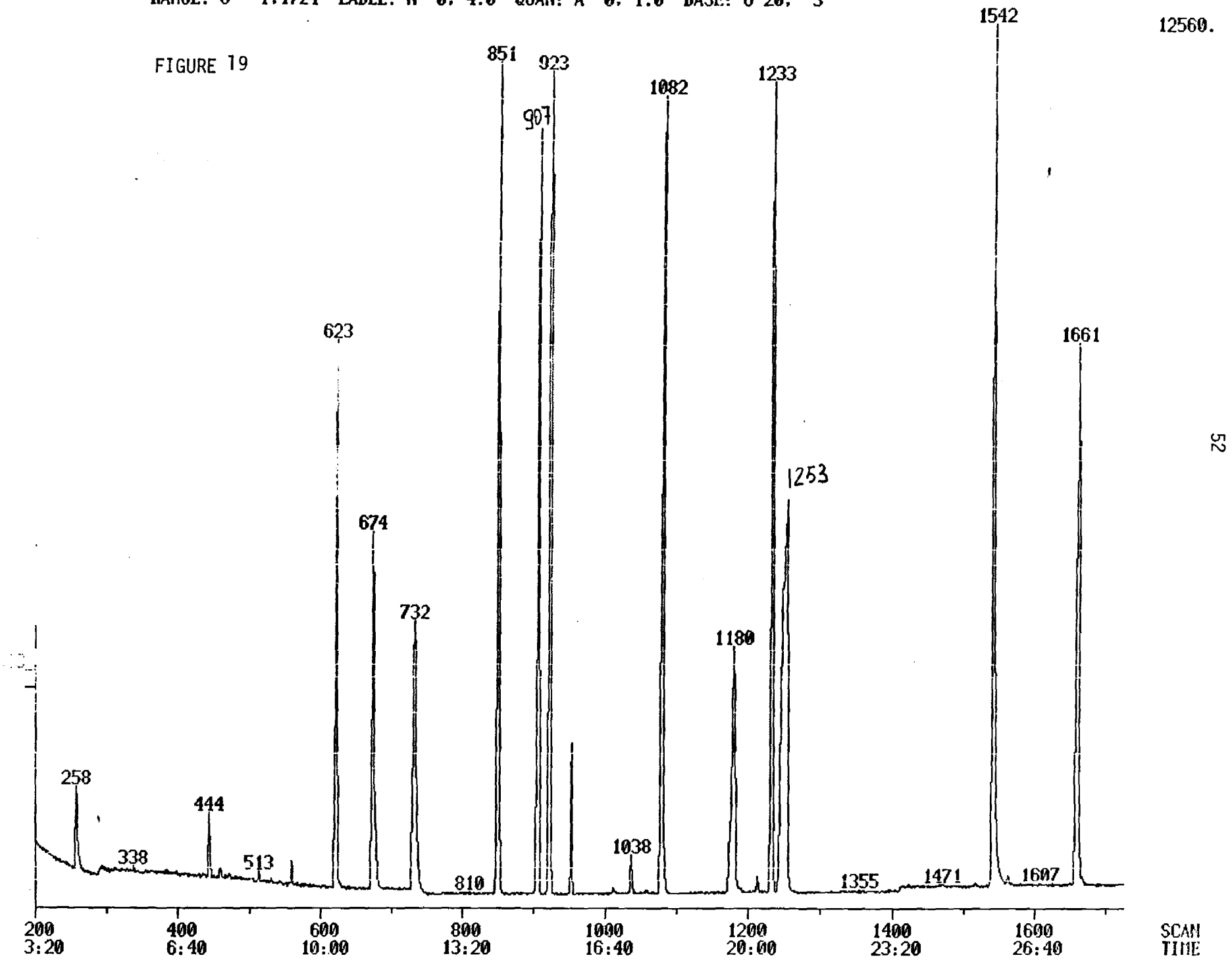


03/08/81 18:59:00
SAMPLE: ORGANIC STD
RANGE: G 1.1724 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: STD #1
CALI: CALGAS #4

SCANS 200 TO 1724

FIGURE 19

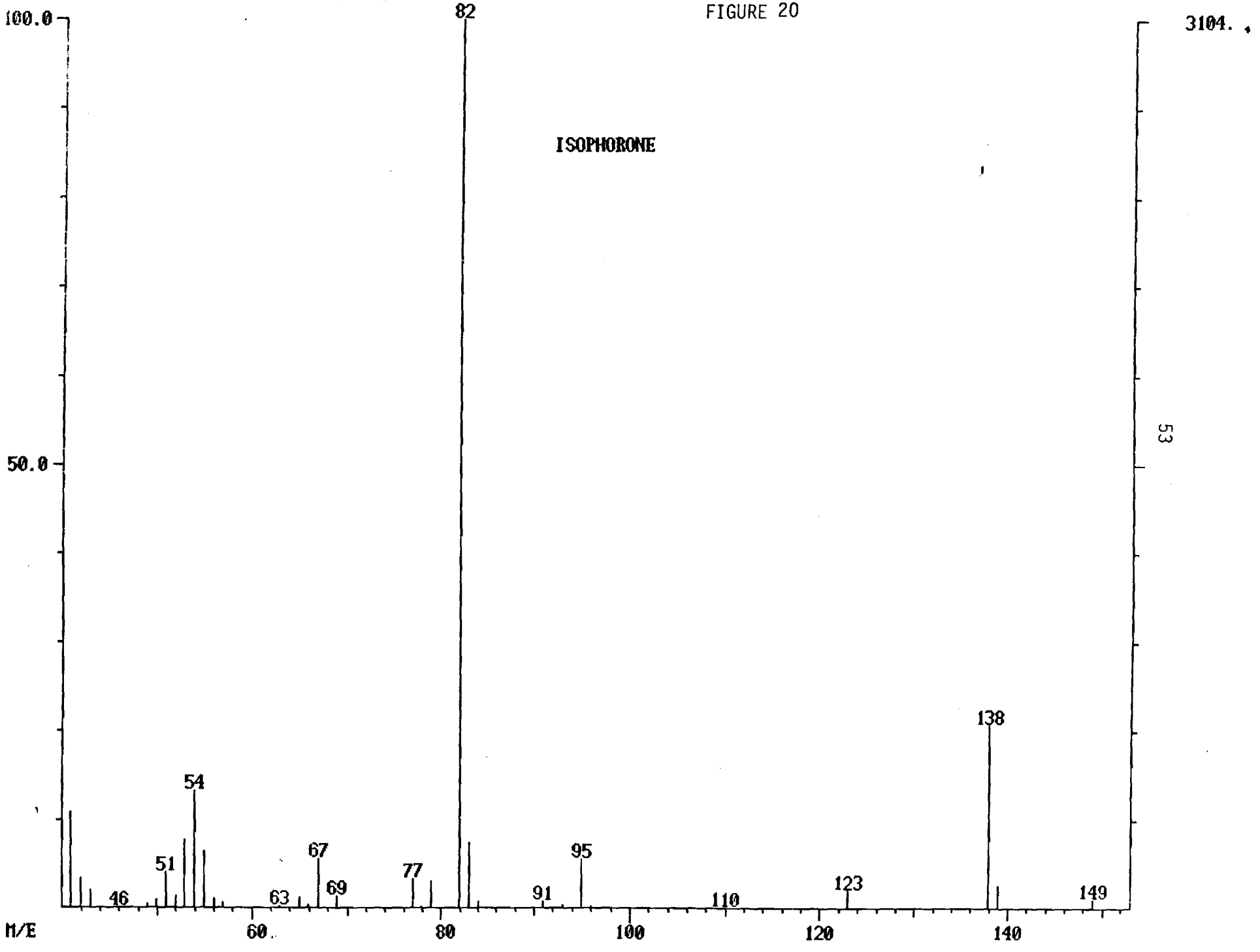


03/08/81 18:59:00 + 10:23
SAMPLE: ORGANIC STD
ENHANCED (S 15B 2N 0T)

DATA: STD #023
CALI: CALGAS #4

BASE M/E: 82
RIC: 6456.

FIGURE 20

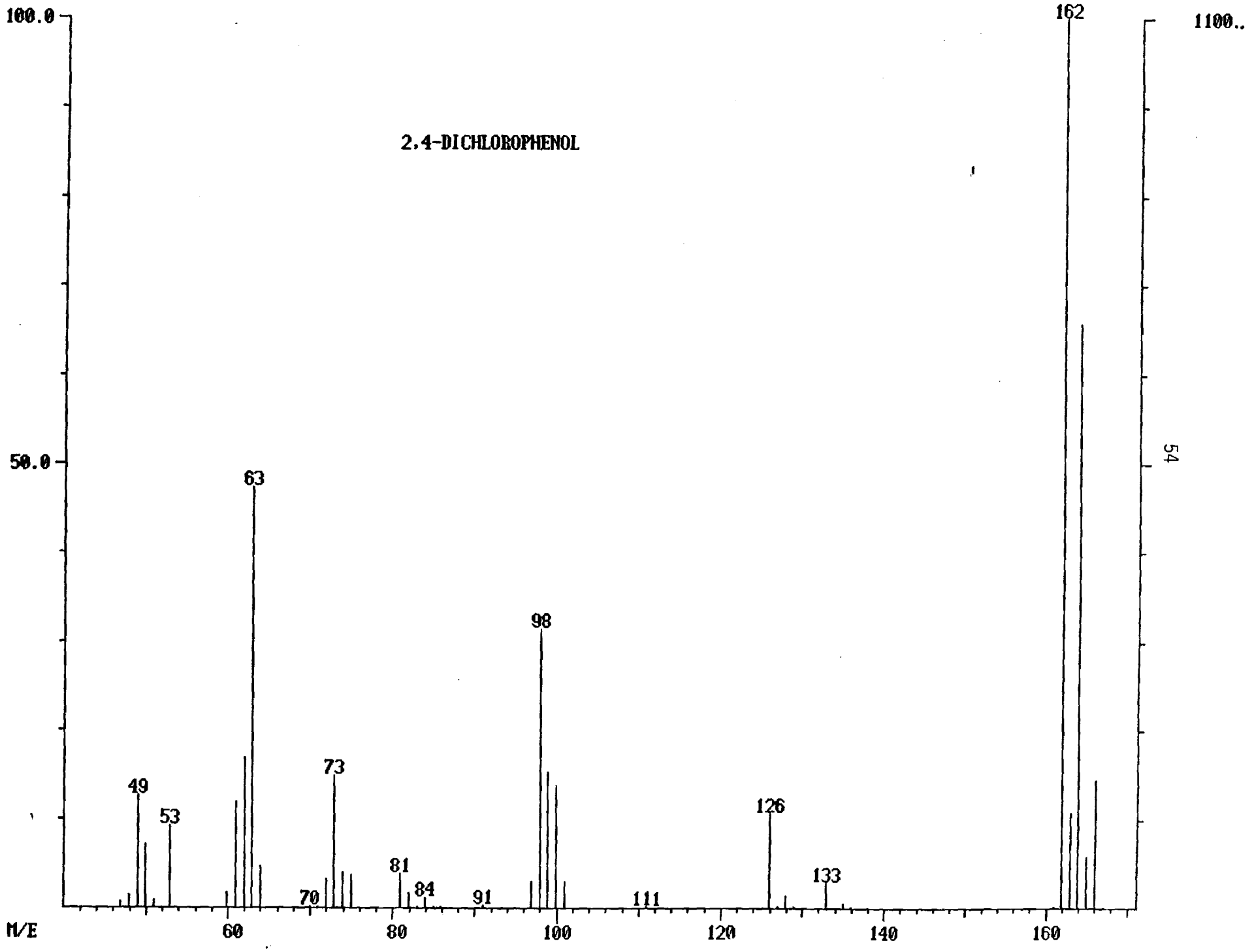


05/06/01 18:59:00 * 11:14
SAMPLE: ORGANIC STD
ENHANCED (S 15B 2N 0T)

FIGURE 21

DATA: STD #074
CALI: CALGAS #4

BASE M/E: 162
RIC: 4712.

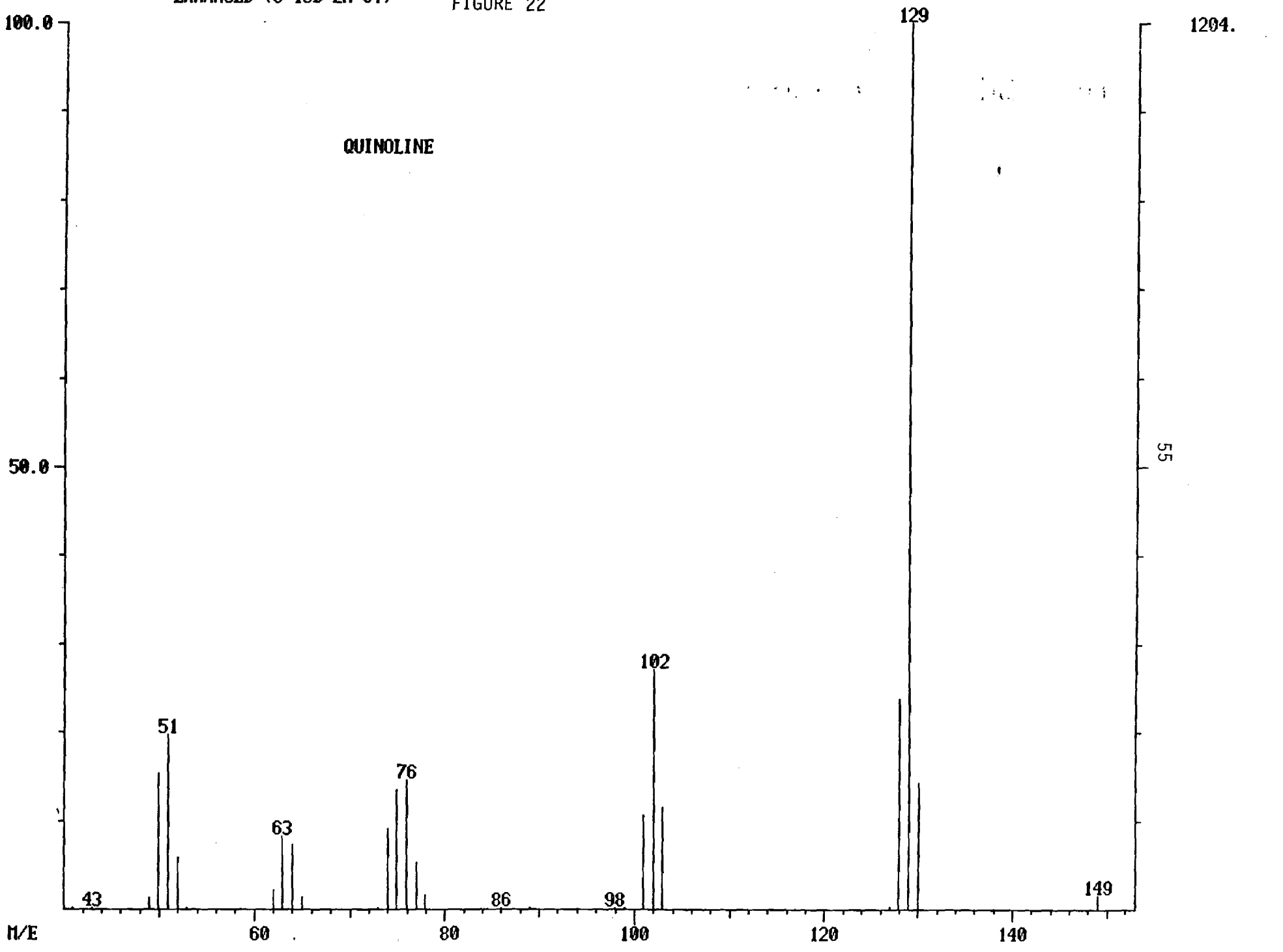


03/08/81 18:59:00 + 12:12
SAMPLE: ORGANIC STD
ENHANCED (S 15B 2N 0T)

DATA: STD #732
CALI: CALGAS #4

BASE M/E: 129
RIC: 3564.

FIGURE 22

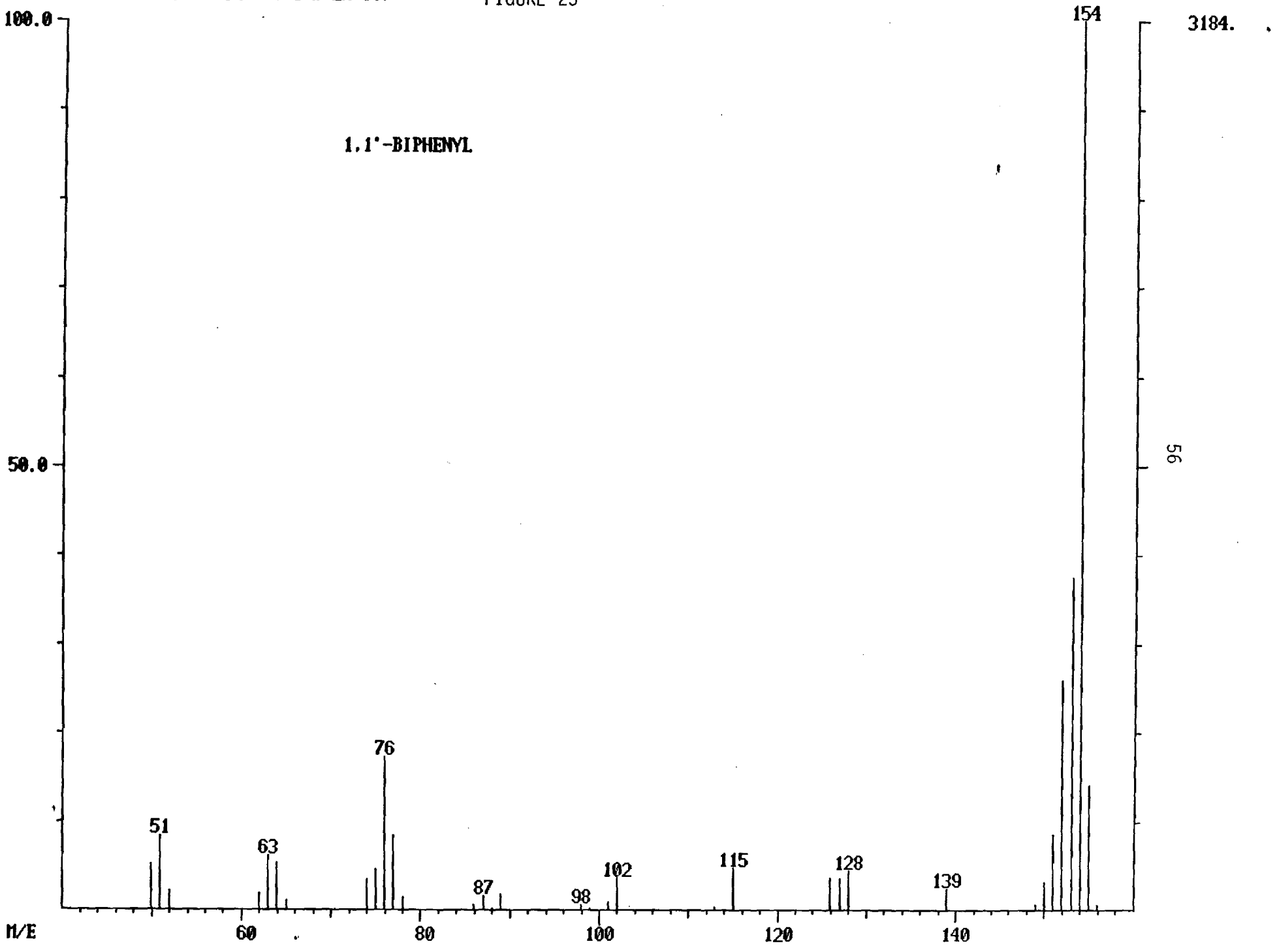


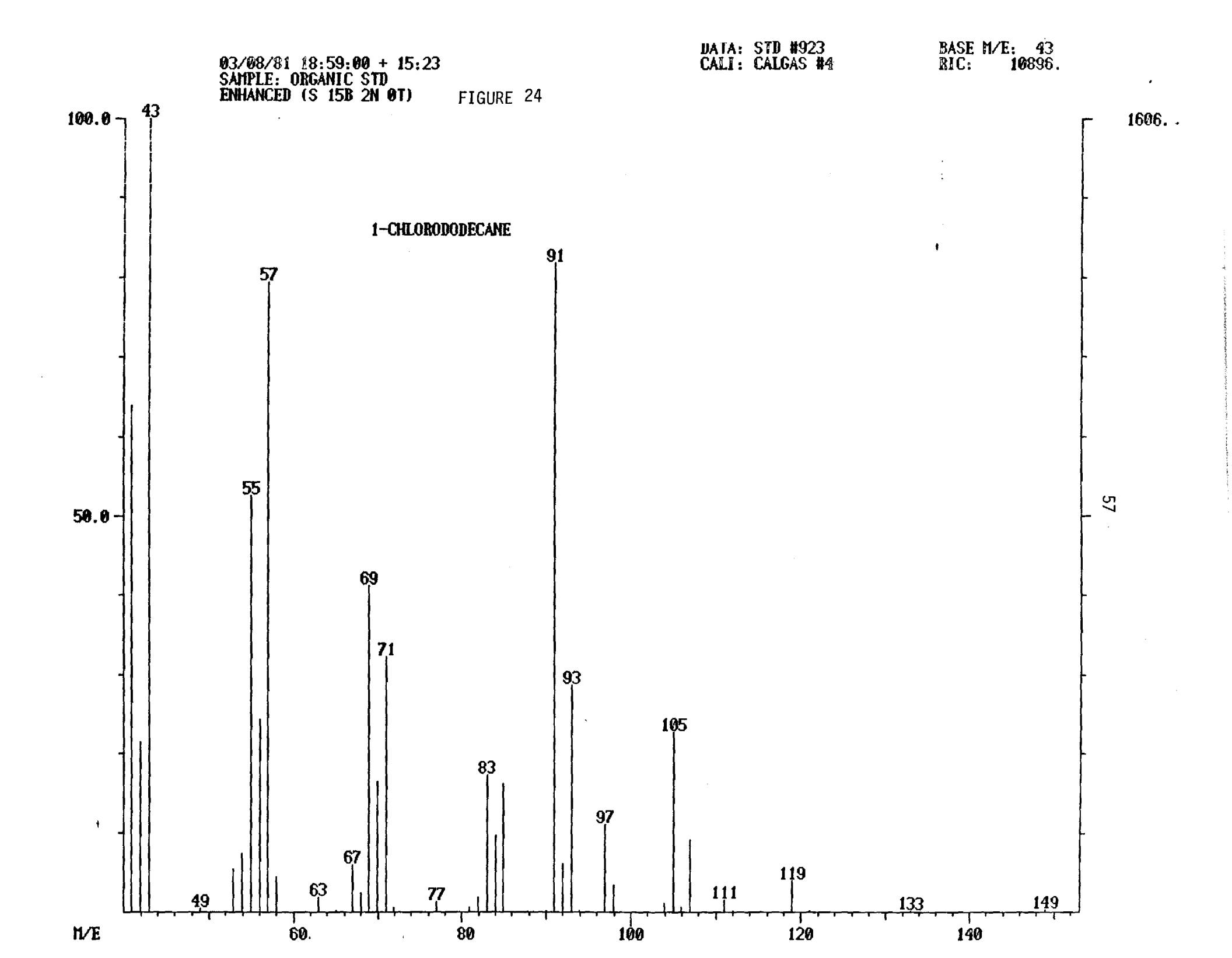
03/08/81 18:59:00 + 14:11
SAMPLE: ORGANIC STD
ENHANCED (S 15B 2N 0T)

DATA: STD #851
CALI: CALGAS #4

BASE M/E: 154
RIC: 9040.

FIGURE 23



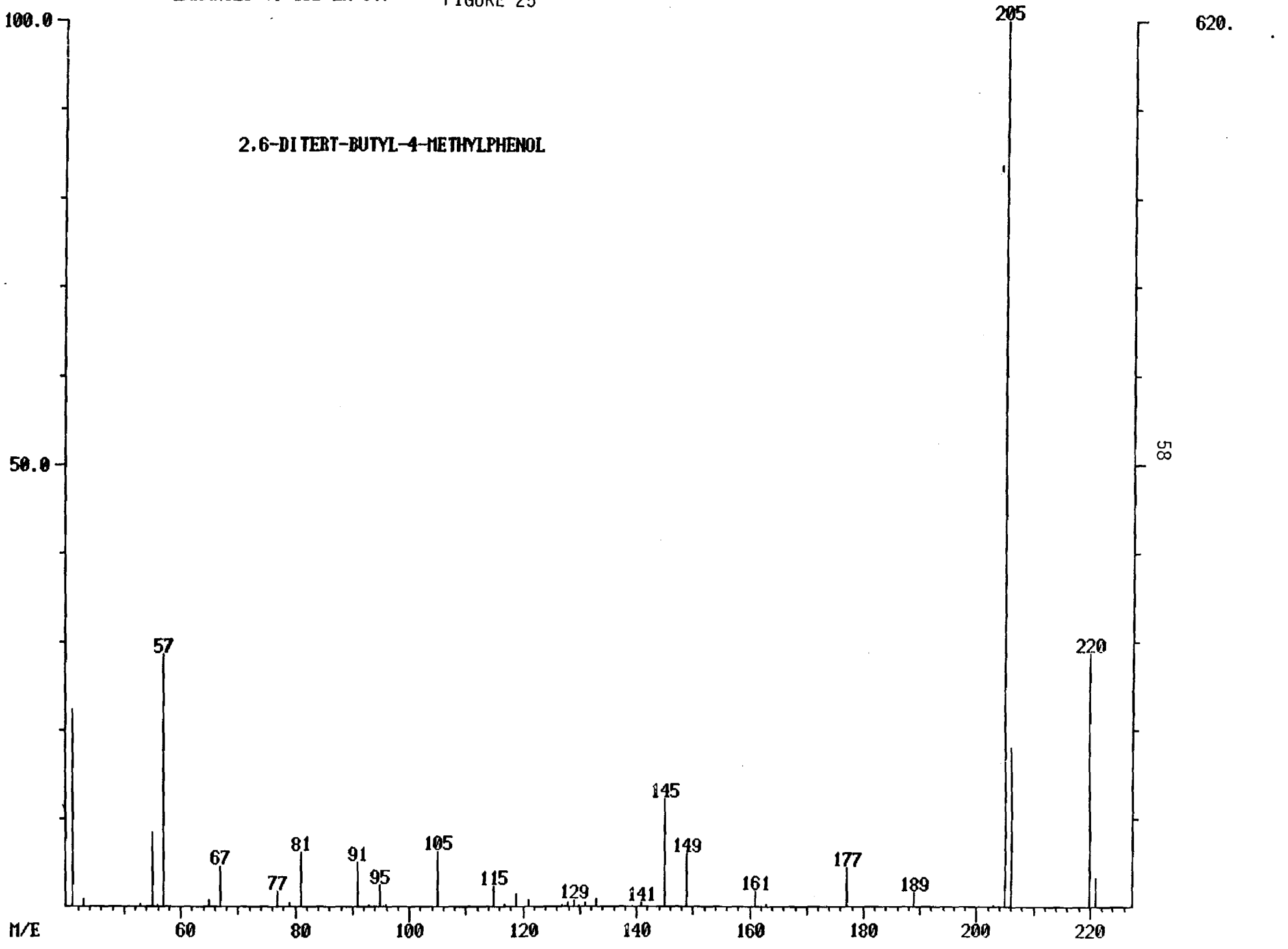

03/08/81 18:59:00 + 15:23
SAMPLE: ORGANIC STD
ENHANCED (S 15B 2N 0T)
DATA: STD #923
CALI: CALGAS #4
BASE M/E: 43
RIC: 10896.
FIGURE 24
100.0
50.0
1606..
57
1-CHLORODODECANE
43
57
91
55
69
71
93
105
83
97
67
63
77
119
111
49
133
149
M/E
60.
80
100
120
140

03/08/81 18:59:00 + 15:54
SAMPLE: ORGANIC STD
ENHANCED (S 15B 2N 0T)

DATA: STD #952
CALI: CALGAS #4

BASE M/E: 205
RIC: 1690.

FIGURE 25



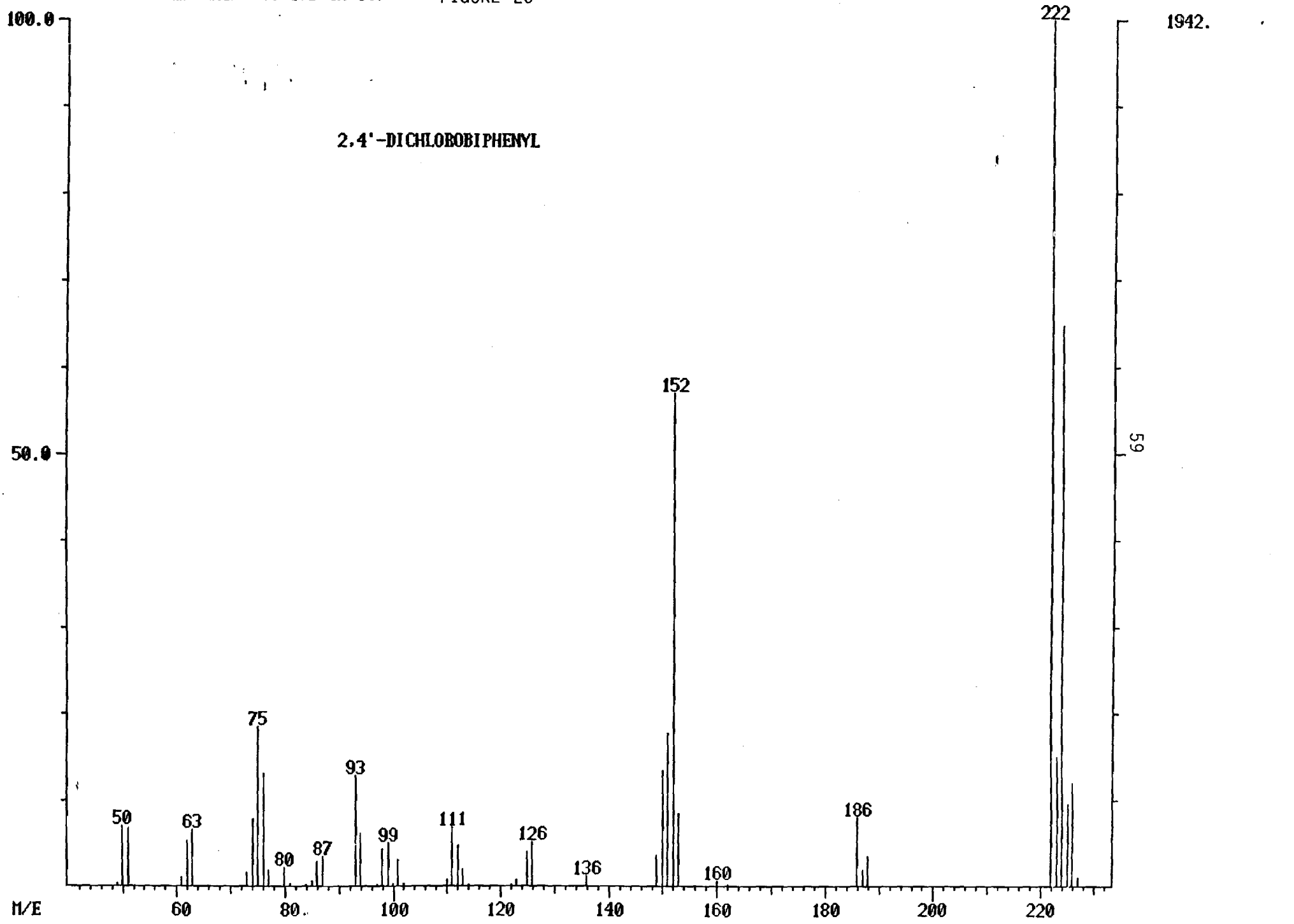
2,6-DITERT-BUTYL-4-METHYLPHENOL

03/08/81 18:59:00 + 18:02
SAMPLE: ORGANIC STD
ENHANCED (S 15B 2N 0T)

DATA: STD #1082
CALI: CALGAS #4

BASE M/E: 222
RIC: 8800.

FIGURE 26

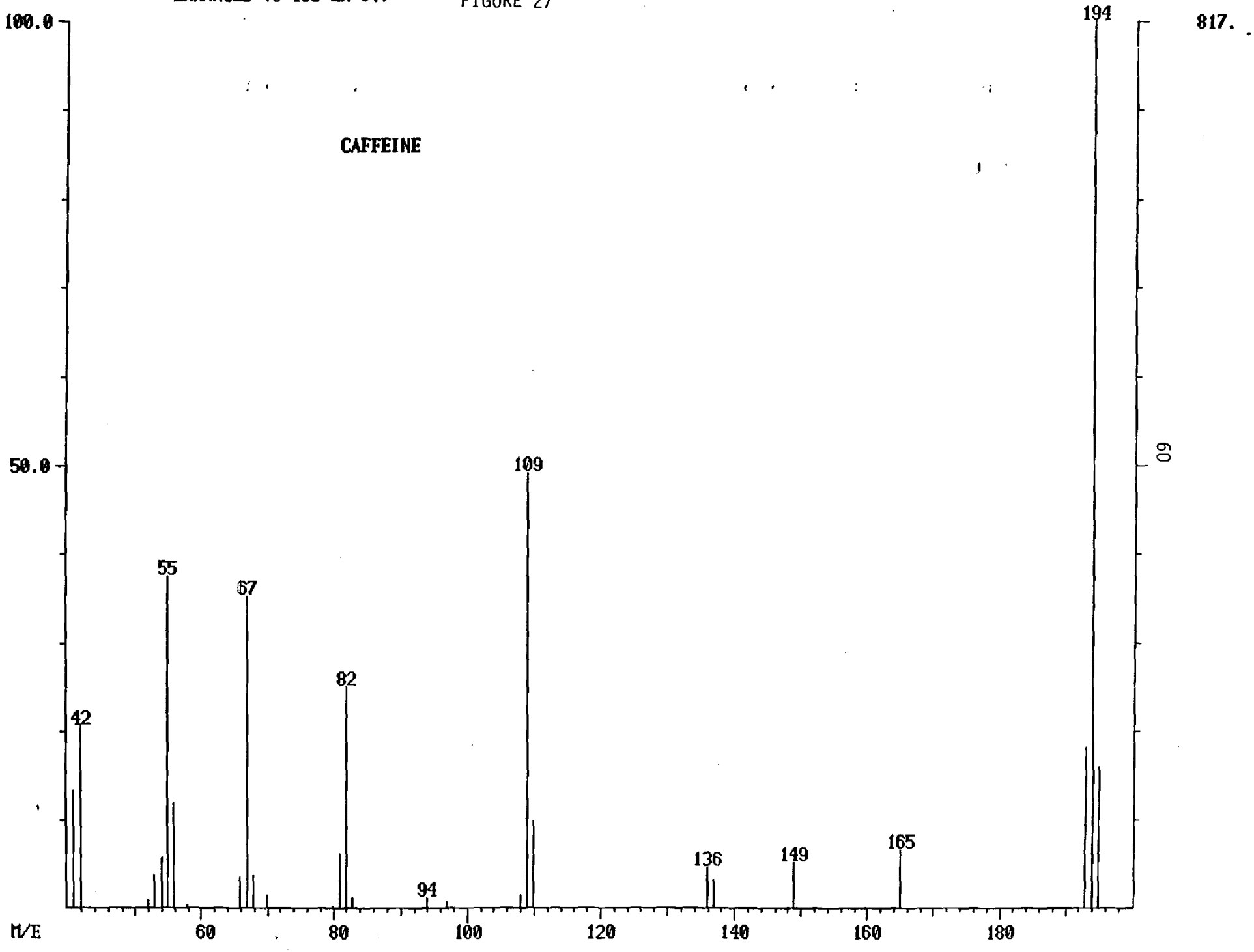


03/08/81 18:59:00 + 19:40
SAMPLE: ORGANIC STD
ENHANCED (S 15B 2N 0T)

DATA: STD #1180
CALI: CALGAS #4

BASE M/E: 194
RIC: 3156.

FIGURE 27

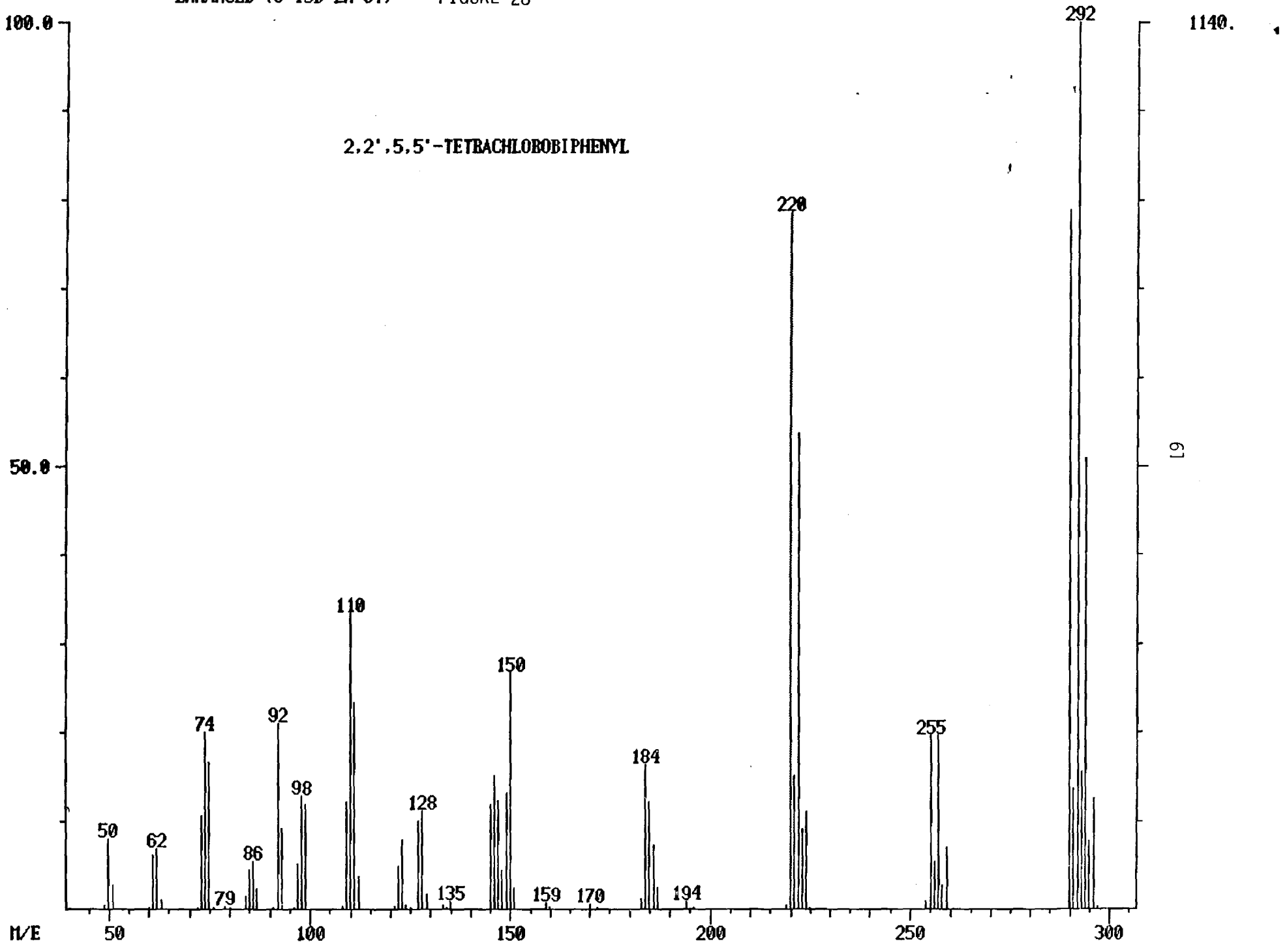


03/08/81 18:59:00 + 20:33
SAMPLE: ORGANIC STD
ENHANCED (S 15B 2N 0T)

DATA: STD #1233
CALI: CALGAS #4

BASE M/E: 292
RIC: 10128.

FIGURE 28

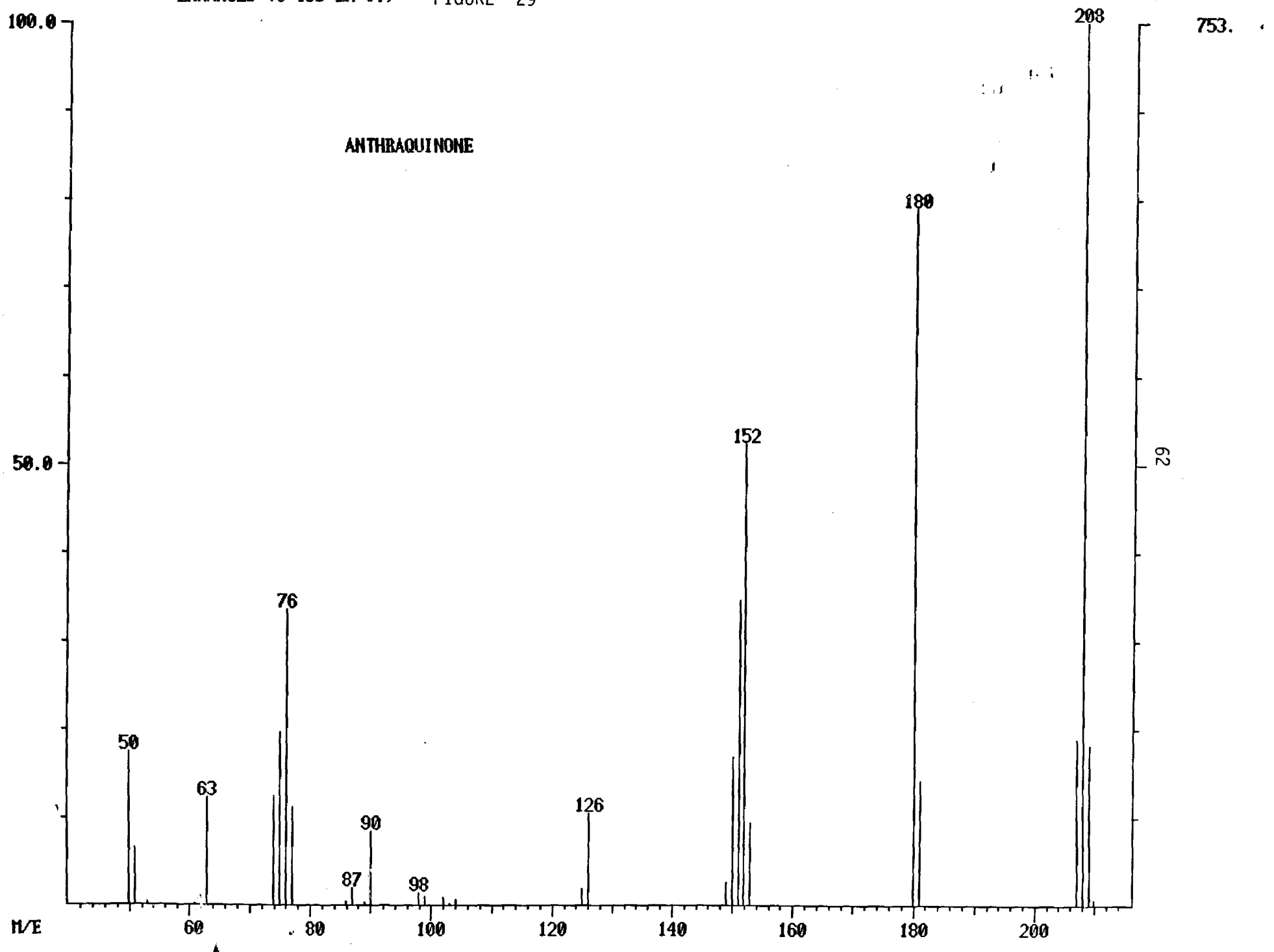


03/08/81 18:59:00 + 20:53
SAMPLE: ORGANIC STD
ENHANCED (S 15B 2N 0T)

FIGURE 29

DATA: STD #1253
CALI: CALGAS #4

BASE M/E: 208
RIC: 3684.

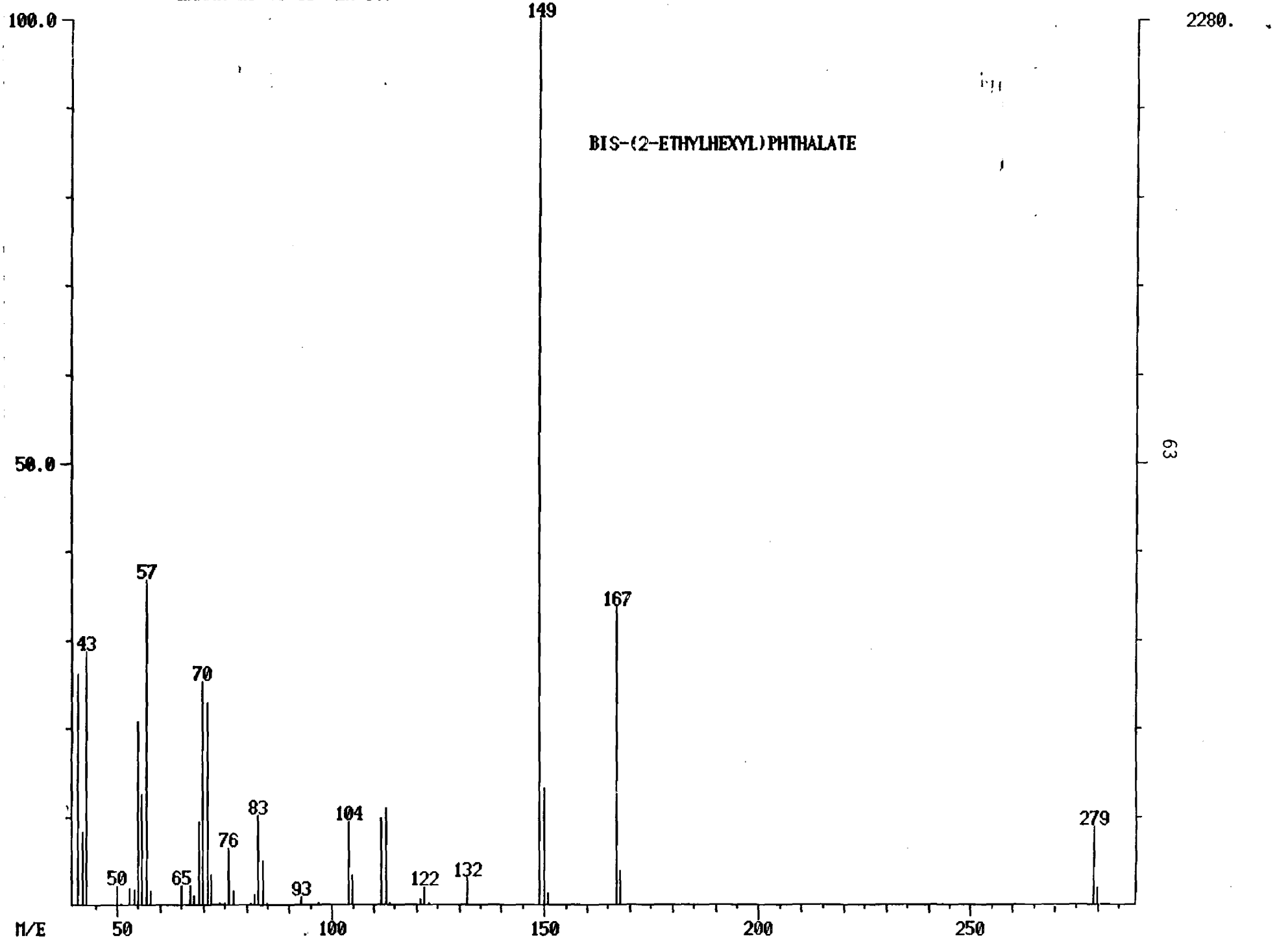


03/08/81 18:59:00 + 25:42
SAMPLE: ORGANIC STD
ENHANCED (S 15B 2N 0T)

FIGURE 30

DATA: STD #1542
CALI: CALGAS #4

BASE M/E: 149
RIC: 9920.

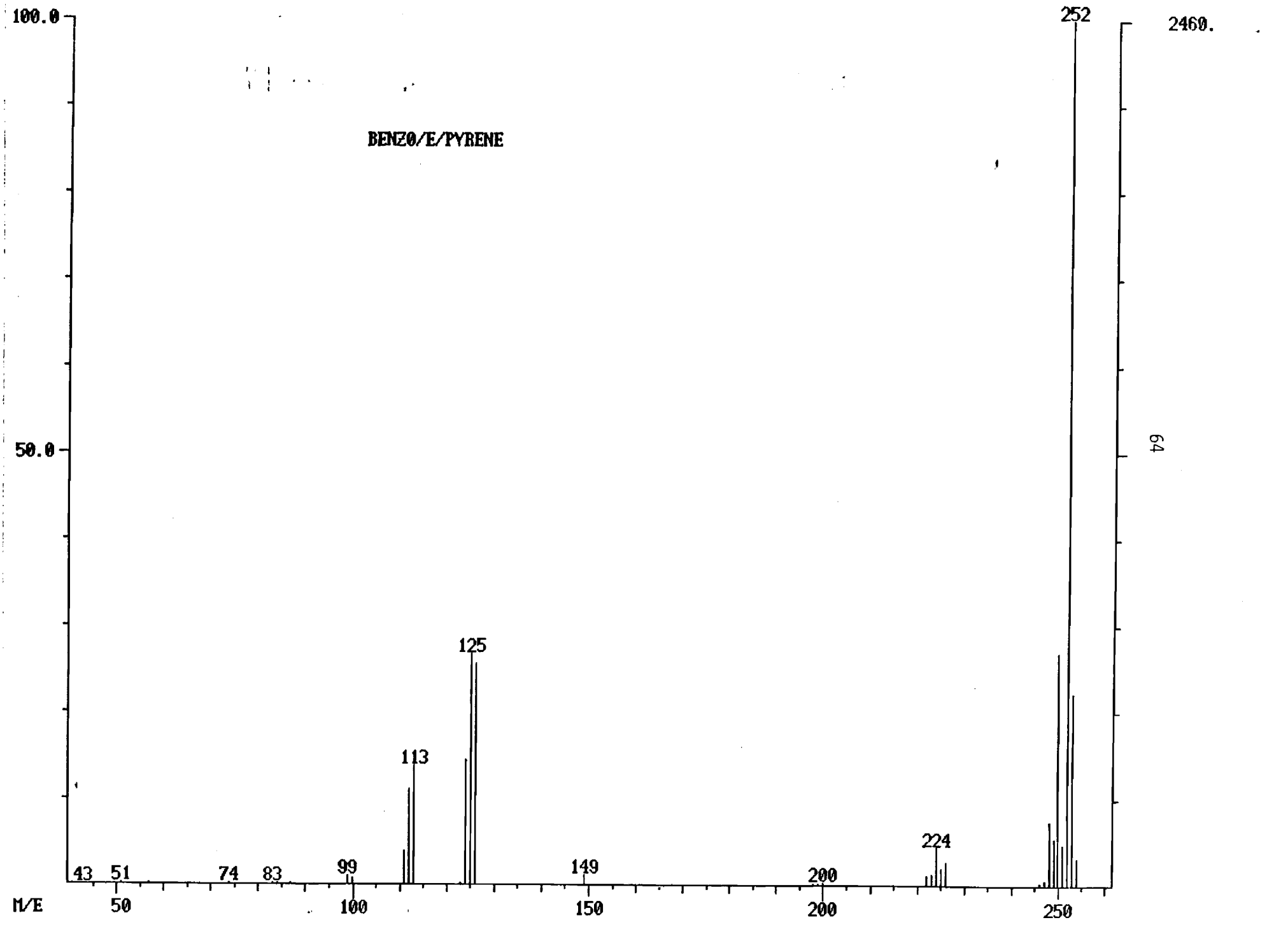


03/08/81 18:59:00 + 27:41
SAMPLE: ORGANIC STD
ENHANCED (S 15B 2N 0T)

DATA: STD #1661
CALI: CALGAS #4

BASE M/E: 252
RIC: 6944.

FIGURE 31



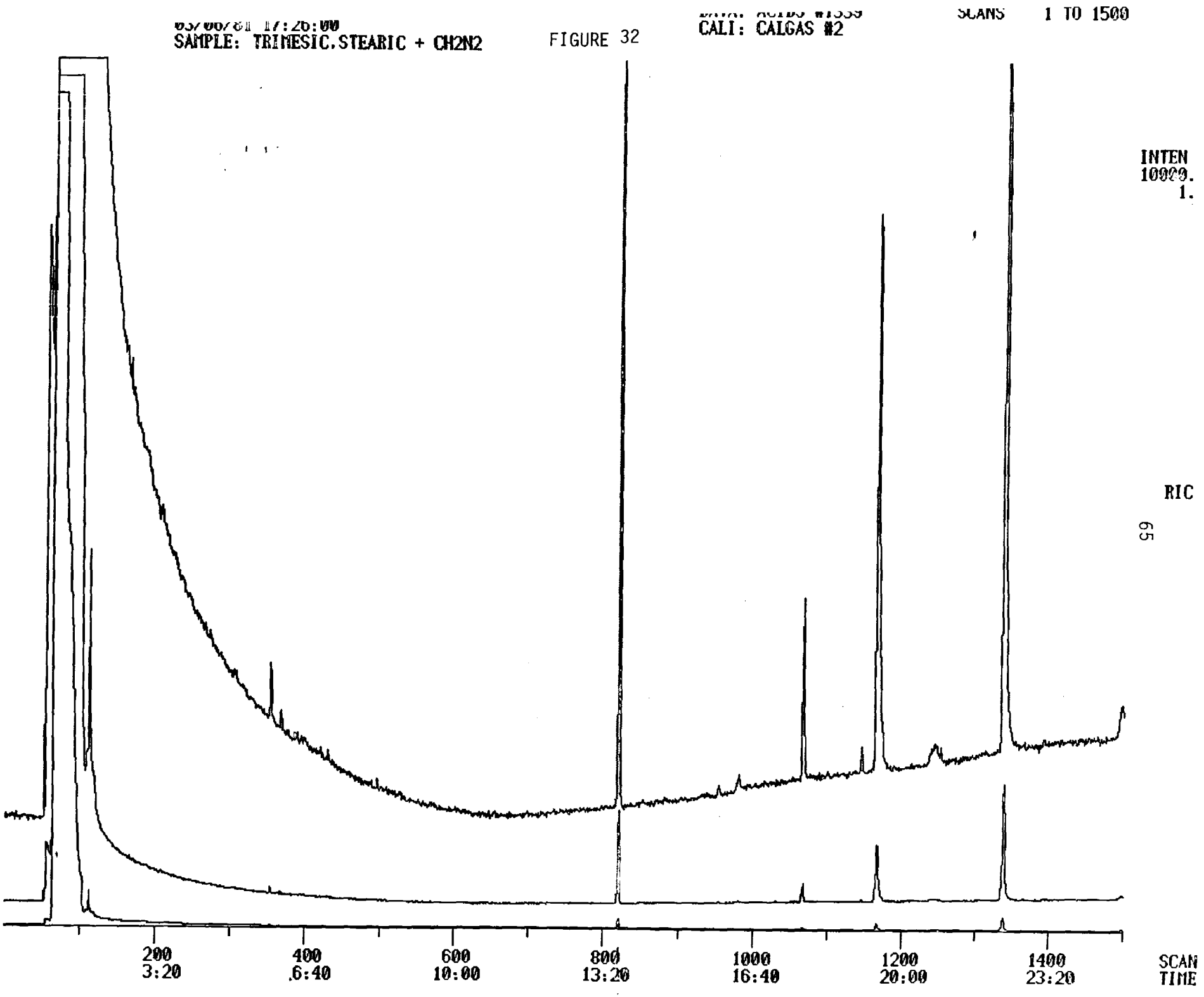
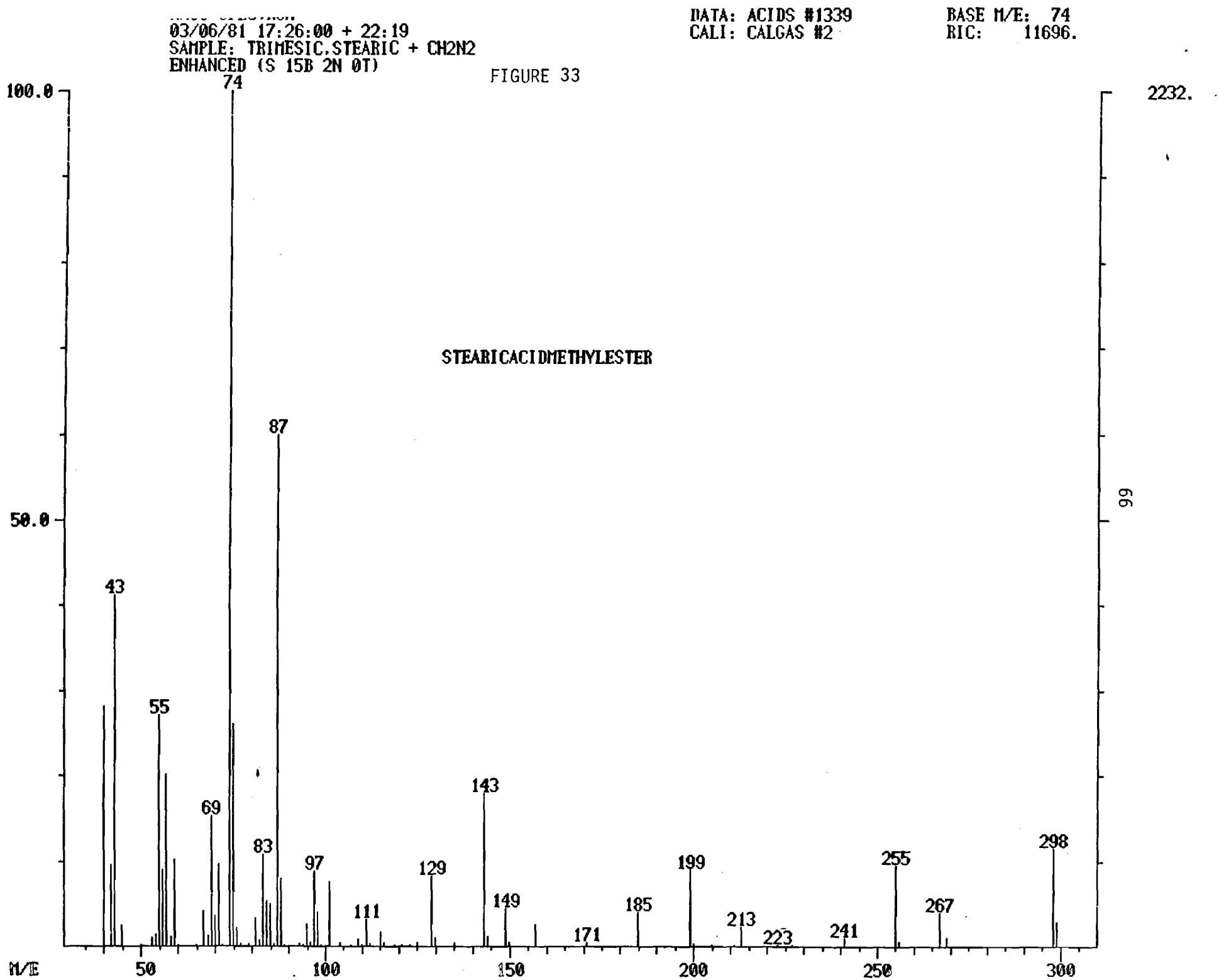

SAMPLE: TRIMESIC.STEARIC + CH2N2
CALI: CALGAS #2
SCANS 1 TO 1500
INTEN
10000.
1.
RIC
65
200
3:20
400
6:40
600
10:00
800
13:20
1000
16:40
1200
20:00
1400
23:20
SCAN
TIME

FIGURE 32

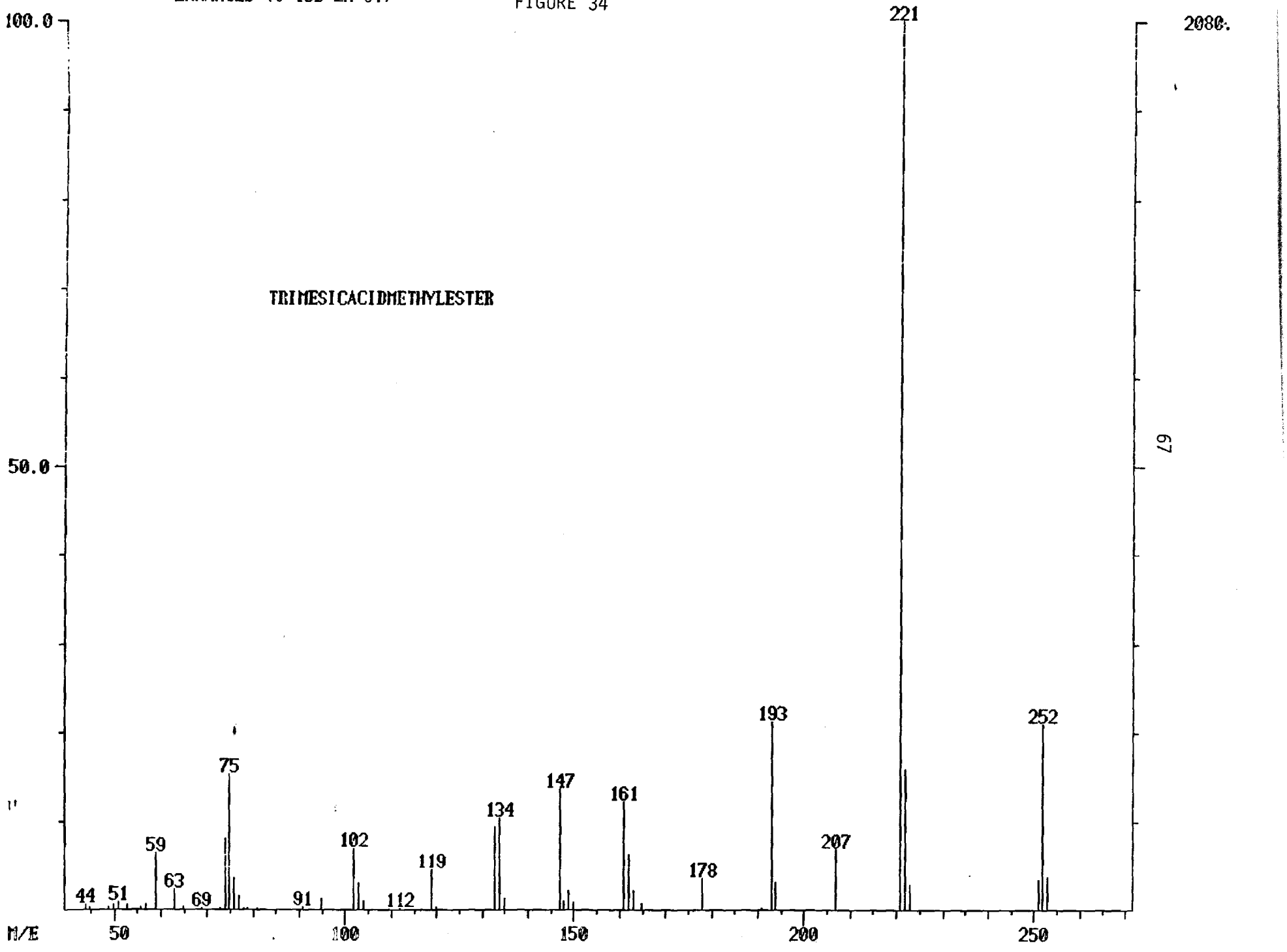

03/06/81 17:26:00 + 22:19
SAMPLE: TRIMESIC,STEARIC + CH2N2
ENHANCED (S 15B 2N 0T)
DATA: ACIDS #1339
CALI: CALGAS #2
BASE M/E: 74
RIC: 11696.
FIGURE 33
STEARICACIDMETHYLESTER
100.0
50.0
2232.
99
M/E
50
100
150
200
250
300
74
87
43
55
69
83
97
111
129
143
149
171
185
199
213
223
241
255
267
298

03/06/81 17:26:00 + 19:27
SAMPLE: TRIMESIC,STEARIC + CH2N2
ENHANCED (S 15B 2N 0T)

DATA: ACIDS #1167
CALI: CALGAS #2

BASE M/E: 221
RIC: 6344.

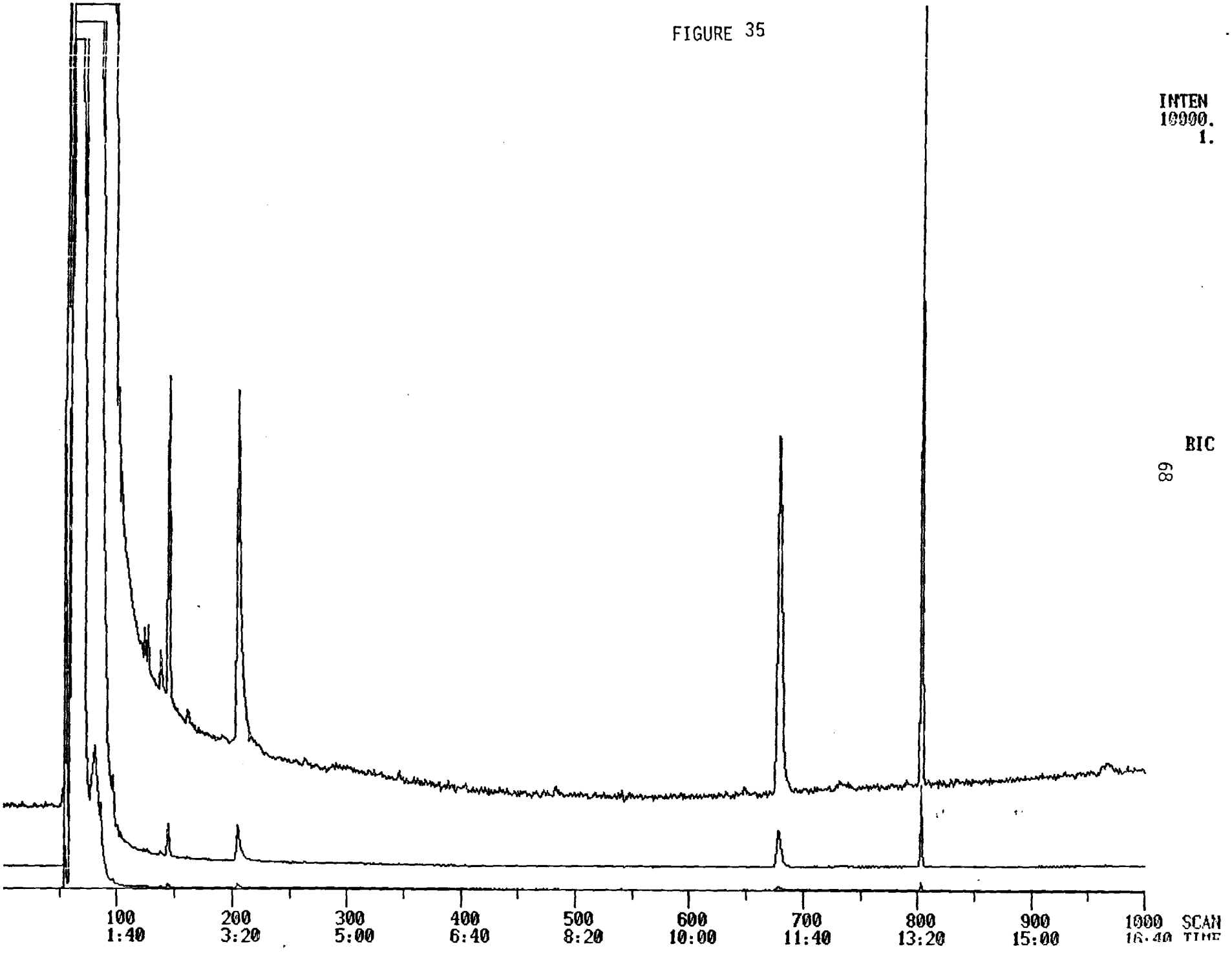
FIGURE 34



03/06/81 16:04:00
SAMPLE: GLYCINE+ISOAMYL+HEPTAFLUOROBUTYRRIC #40-1

DATA: GLYCINE #678 SCANS 1 TO 1000
CALI: CALGAS #2

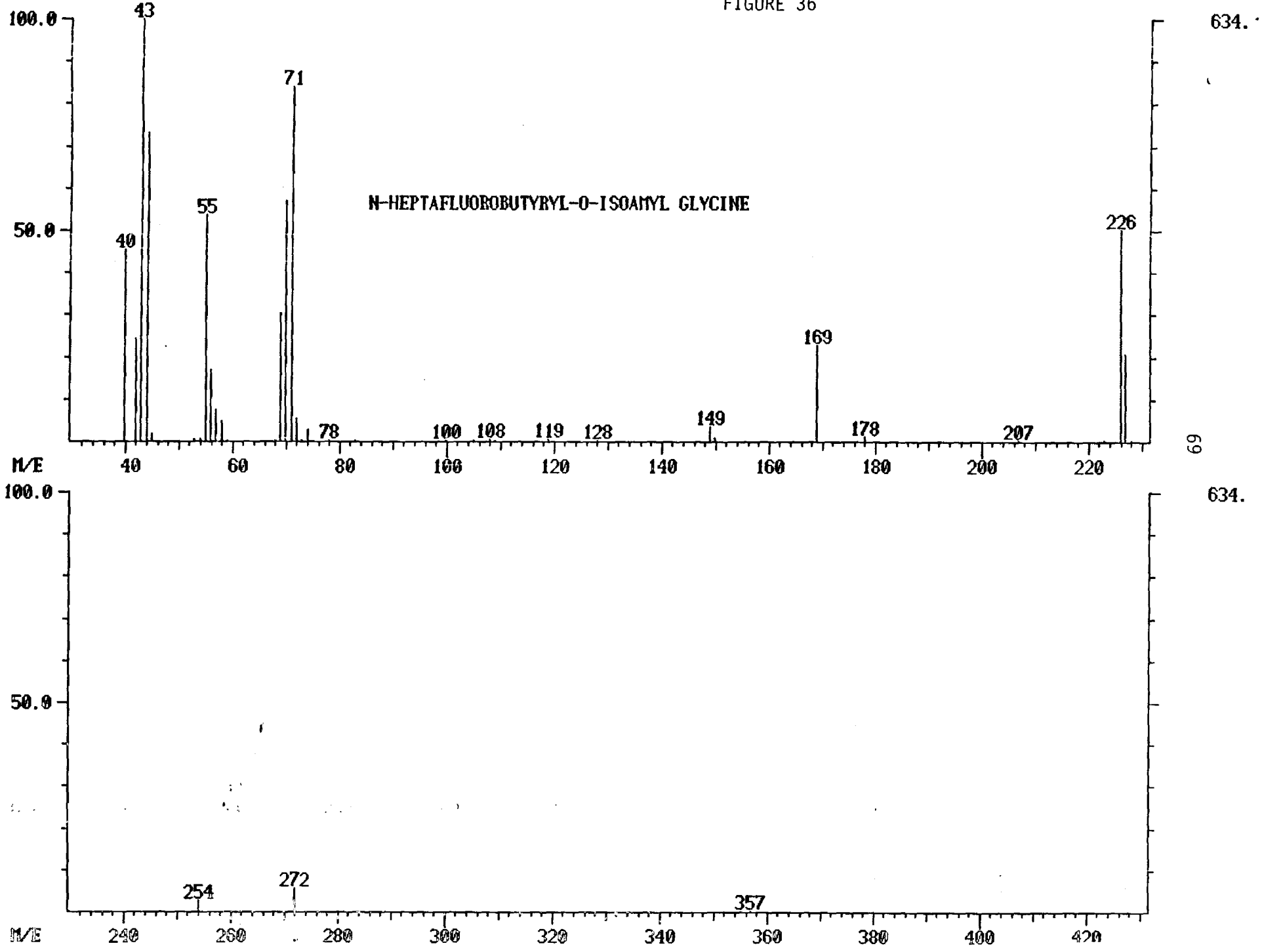
FIGURE 35



03/06/81 16:04:00 + 11:18
SAMPLE: GLYCINE+ISOAMYL+HEPTAFLUOROBUTYRRIC #40-1
ENHANCED (S 15B 2N 0T)

DATA: GLYCINE #678 BASE M/E: 43
CALI: CALGAS #2 RIC: 3972.

FIGURE 36



of wall coated open tubular columns as separation media required the use of on-column cryogenic trapping. The organic compounds were initially purged from the water sample, adsorbed onto the Tenax-GC trap, and subsequently heat desorbed into the GC column equipped with a cryogenic trap at the inlet. Finally, the chromatography was started by further heat desorbing the cryogenic section of the column.

All the operations of the purge and trap unit are controlled by a microprocessor while the on-column cryogenic trapping and heating was operated manually. Figure 37 represents a typical R.I.C. of the priority pollutant purgeable organics and the relative mass spectrum of Chloroform is shown in Figure 38. The sample was analyzed under the following conditions:

W.C.O.T. column SE-54 30m 0.3 mm
Temperature program 30^{o}(2 min)-280^{o}C at 4^{o}C/m
Sample volume 10 mℓ
Spiking level 20 ppb
Purge time 15 minutes
Purge flow 20 mℓ/m

Each spectrum was verified for its identity against the National Bureau of Standards Library (containing more than 25,000 organic compound spectra) stored in the data system memory.

The reproducibility and the concentration-response linearity of the instrument was performed for a limited number of the compounds. Tables 14 and 15 report the results obtained for 5 repetitive runs of the same standard solution and the single runs of standard solutions with different concentrations, respectively.

Hexamethylbenzene was chosen as internal standard (I.S.) for the quantitative evaluation by the "internal standard method". A quantitation library, containing mass spectra, retention time, relative retention time

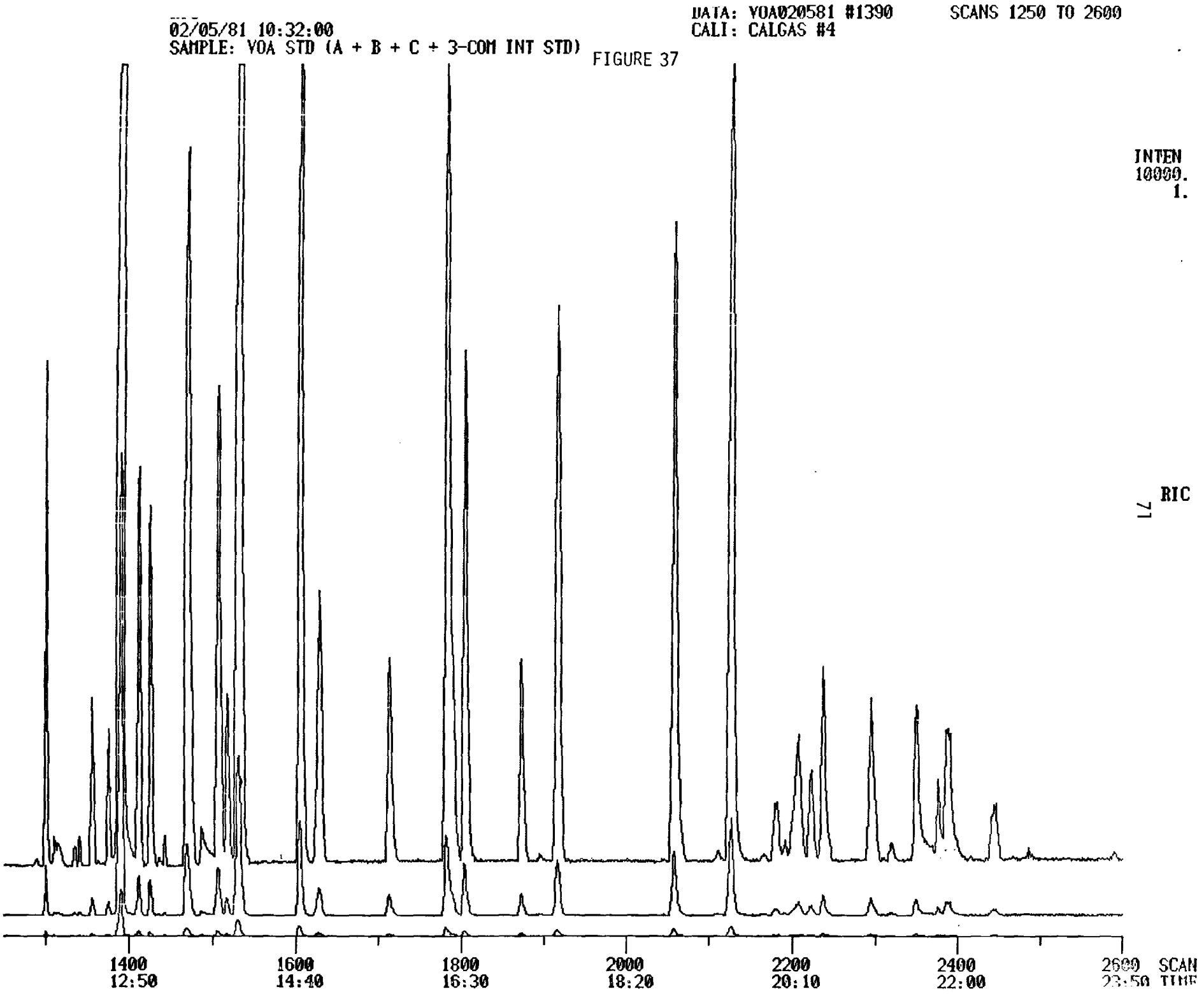

02/05/81 10:32:00
SAMPLE: VOA STD (A + B + C + 3-COM INT STD)
DATA: VOA020581 #1390
CALI: CALGAS #4
SCANS 1250 TO 2600
INTEN
10000.
1.
RIC
71
1400
12:50
1600
14:40
1800
16:30
2000
18:20
2200
20:10
2400
22:00
2600
23:50
SCAN
TIME

FIGURE 37

02/05/81 10:32:00 + 13:28
SAMPLE: VOA STD (A + B + C + 3-COM INT STD)
ENHANCED (S 15B 2N 0T)

DATA: VOA020581 #1470
CALI: CALGAS #4

BASE M/E: 83
RIC: 8192.

FIGURE 38

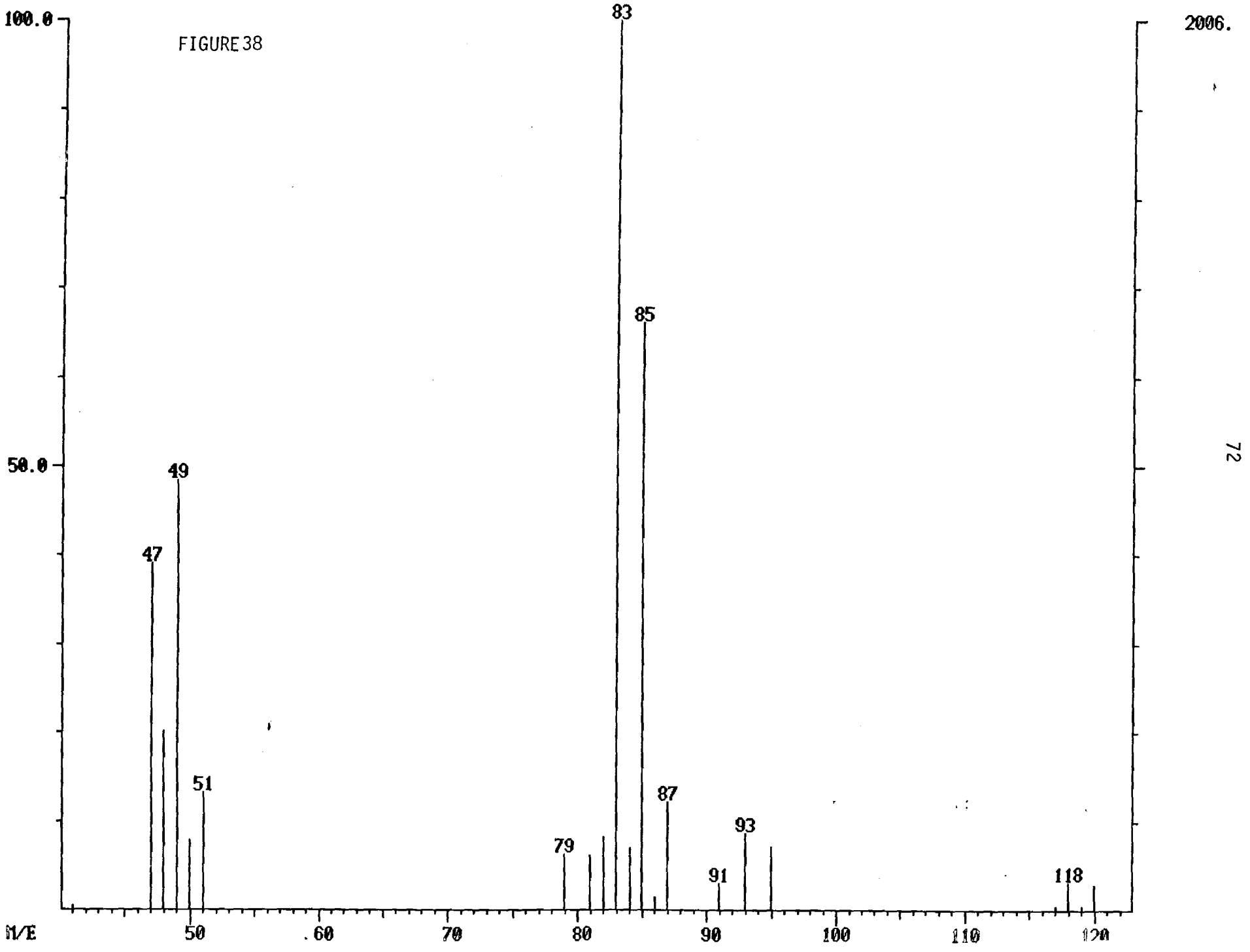


TABLE 14

Instrumental Variation 1μℓ splitless; 20 ng/μℓ

Compound	Mean (μ) MS	Standard Deviation MS	Coefficient Variation MS
Isophorone	20.6 ng	0.50	2.4
2,4-Dichlorophenol	21.1	0.59	2.7
Quinoline	19.9	0.35	1.7
Biphenyl	20.4	0.18	0.8
1-Chlor	20.4	0.07	0.3
2,6-Di-tertiarybutyl 4-methylphenol	19.6	0.17	0.8
2,4-Dichlorobiphenyl	20.4	0.65	3.1
Caffeine	20.2	2.20	10.8
2,2',5,5'-Tetra-chlorobiphenyl	20.5	1.41	6.8
Anathraquinone	20.1	2.19	10.8

$$C_V = \frac{\sigma}{\mu} 100$$

TABLE 15

CONCENTRATION - RESPONSE LINEARITY GC-MS-DS

Compound	(ng)				
	0.1	1.0	10.0	20.0	100
Isophorone		1.3	11.2	20.5	102.7
2,4-Dichlorophenol			10.9	20.4	111.7
Quinoline			8.0	20.3	105.0
Biphenyl		1.3	10.4	19.7	102.2
1-Chlorodecane		1.4	10.8	20.7	111.0
2,6-Di-tertiarybutyl 4-methylphenol			10.3	19.9	109.3
2,4-Dichlorobiphenyl			8.2	19.9	114.2
Caffeine			4.1	19.7	123.3
2,2', 5,5'-Tetrachlordiphenyl			6.5	19.6	109.6
Anathraquinone			4.4	19.4	120.4

and selected quantitation ion for each individual organic compound under study, was incorporated in the data system and used as reference. The quantitation is then based on the comparison of selected ion plot (S.I.P.) of each compound with respect to the one of the I.S. A FINNIGAN computer program handles the identification and quantitation routine of the MS data and it involves two steps. First, a standard solution, containing known amounts of the compounds and I.S., is analyzed and recorded. The relative retention times and the peak areas of the selected quantitation ion are normalized with respect to retention time and peak area of selected ion of I.S. by a program called SININ. Second, the unknown solution, containing the same amount of I.S., is analyzed, recorded and processed by a program called SINUNK. Table 16 represents the selected ion for each compound studied and Figure 39 shows a typical quantitation and identification report obtained through the data system.

TABLE 16

SELECTED IONS FOR EACH INDIVIDUAL COMPOUND

		M+
1.	Quinoline	129
2.	Caffeine	194
3.	Isophorone	82
4.	Anthraquinone	180
5.	2,4-Dichlorobiphenyl	152
6.	2,2',5,5'-Tetrachlorobiphenyl	292
7.	Bis-(2-ethylhexyl)phthalate	149
8.	Biphenyl	154
9.	Biphenyl	154
10.	2,4-Dichlorophenol	162
11.	2,6-Ditertiarybutyl-4-methylphenol	205
12.	Benzo(e)pyrene	252
13.	Chloroform	83

FIGURE 39

```
OLD INITIALIZATION COMPLETE ON:  1/07/81 16:01:03
QUANTITATION REPORT          FILE: STD6

DATA: STD6.TI
01/07/81 11:18:00
SAMPLE: STD SOLN (SAME AS STD5 INCREASED INJ T ... TO 260)
CONDS.: SE30 18M,50(2)280 10/11
FORMULA: INJ TEMP 260        INSTRUMENT: FINN              AMOUNT:     0.000
SUBMITTED BY: EPA            ANALYST: MG,PG,LR             AUT. NO.: -

AMOUNT=AREA * REF.AMNT/(REF.AREA* RESP.FACT)

 NO  NAME
  1  HEXAMETHYLBENZENE
  2  ISOPHORONE
  3  2,4-DICHLOROPHENOL
  4  QUINOLINE
  5  BIPHENYL
  6  1-CHLORODECANE
  7  2,6-DITERTIARYBUTYL-4-METHYLPHENOL
  8  2,4-DICHLOROBIPHENYL
  9  CAFFIENE
 10  2,2',5,5'-TETRACHLOROBIPHENYL
 11  ANTHRAQUINONE

 NO  M/E  SCAN   TIME  REF   RRT  METH      AREA      AMOUNT      %TOT
  1  147   852  14:12   1  1.000  A BB     27396.  20.000 NG      7.88
  2   82   562   9:22   1  0.660  A BB     22362.  20.541 NG      8.10
  3  162   609  10:09   1  0.715  A BB      7633.  20.358 NG      8.02
  4  129   663  11:03   1  0.778  A BB     16534.  20.275 NG      7.99
  5  154   786  13:06   1  0.923  A BB     24729.  19.703 NG      7.77
  6   43   868  14:28   1  1.019  A BB     12381.  20.685 NG      8.15
  7  205   893  14:53   1  1.048  A BB     13440.  19.889 NG      7.84
  8  222  1013  16:53   1  1.189  A BB     10529.  19.949 NG      7.86
  9  194  1085  18:05   1  1.273  A BB     10658.  19.654 NG      7.75
 10  292  1166  19:26   1  1.369  A BB      6692.  19.596 NG      7.72
 11  180  1172  19:32   1  1.376  A BB      7499.  19.445 NG      7.66


UNKNOWN SAMPLE QUANTITATION    REVERSE SEARCH STATUS REPORT
      EXPECTED  BEST                                          # PEAKS   # PEAKS
      SCAN      SCAN      FIT    PURITY    LIBRARY    ENTRY   FOUND     QUANT

        852       852     994       862       OC        1       1         1
        563       562     998       887       OC        2       1         1
        610       609     990       813       OC        3       1         1
        664       663     994       899       OC        4       1         1
        787       786     995       908       OC        5       1         1
        869       868     998       867       OC        6       2         1
        894       893     993       666       OC        7       1         1
       1014      1013     995       890       OC        8       1         1
       1086      1085     989       894       OC        9       1         1
       1166      1166     993       800       OC       10       1         1
       1173      1172     998       929       OC       11       1         1

DATA PROCESSING OF STD6 COMPLETED ON  1/07/81 16:20:25
```

IV. FUTURE WORK

A. Analytical Methodologies

The analytical methodologies developed thus far have shown to be suitable for the evaluation of 18 out of the 22 model organic compounds under this study. Analysis of the remaining four compounds (i. e., 5-chlorouracil, crotonoaldehyde, quinaldic acid and glucose) will be continued into the following quarter until the statistical meaningful methods for quantitation are obtained. Of the four compounds, quinaldic acid was not readily available from the suppliers (Aldrich Chemical, Tridom Fluka), until recently. We have just received it now, and little problems are anticipated in the derivatization of this compound as trimesic and stearic acids have been successfully derivatized.

The preparation of the trifluoroacetyl derivative of glucose by means of trifluoroaceticanhydride (TFAA) is at the present time giving poor reproducible results. Modifications of the derivatization procedure for glucose according to the work of Pritchard et al. (1978) and Sullivan et al.(1978) are currently being investigated.

The preparation of glass capillary columns suitable for the analysis of crotonoaldehyde is under going (e.g., the use of a thicker film for the stationary phase and better deactivation of the glass surface etc.). This column will probably be suitable even for the chromatography of underivatized 5-Chlorouracil, as demonstrated by Sandra et al. (1980) with an analogous class of compounds such as barbiturates. However, a derivatization method proposed by Garzo et al. (1980) is under investigation.

B. Fractionation Scheme

Preliminary results obtained with the resin fractionation scheme followed by membrane concentration and carbon adsorption of hydrophilic neutrals indicated that these processes can best be evaluated when all of the analytical protocals are available. These represent efforts to be devoted in the coming quarter.

V. EXPENDITURES

The actual expenditures incurred during the second quarter of this research program are represented by the dashed line in Figure 40 (between months 3-6). The solid line represents the expected expenditures in the months to come. It is anticipated that the initial high level of expenditures will be tapered off as the development work for analytical methodologies is completed. We have currently been devoting our entire analytical team on the research program in order to get the fractionation work moving smoothly in the coming months.

If there are any questions regarding this quarterly report, please contact either Edward Chian or Maurizio Giabbai at (404)894-2265.

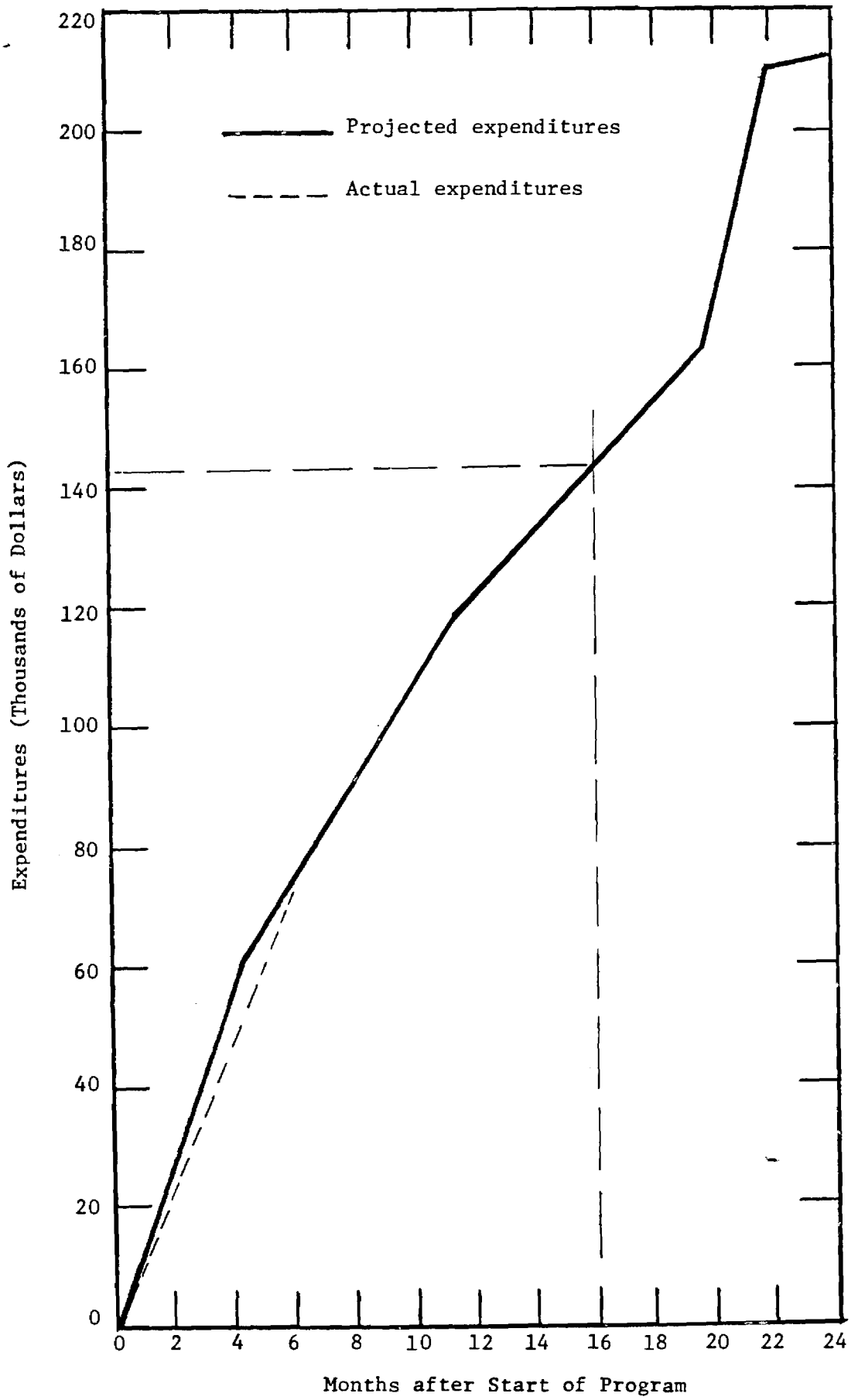


Figure 40. Projected and Actual Expenditures for EPA Contract No. 68-03-3000

VI. REFERENCES

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E-20-688

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

QUARTERLY REPORT

June 1981

by

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The U. S. Environmental Protection Agency
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Contract No. 68-03-3000

Project Officer
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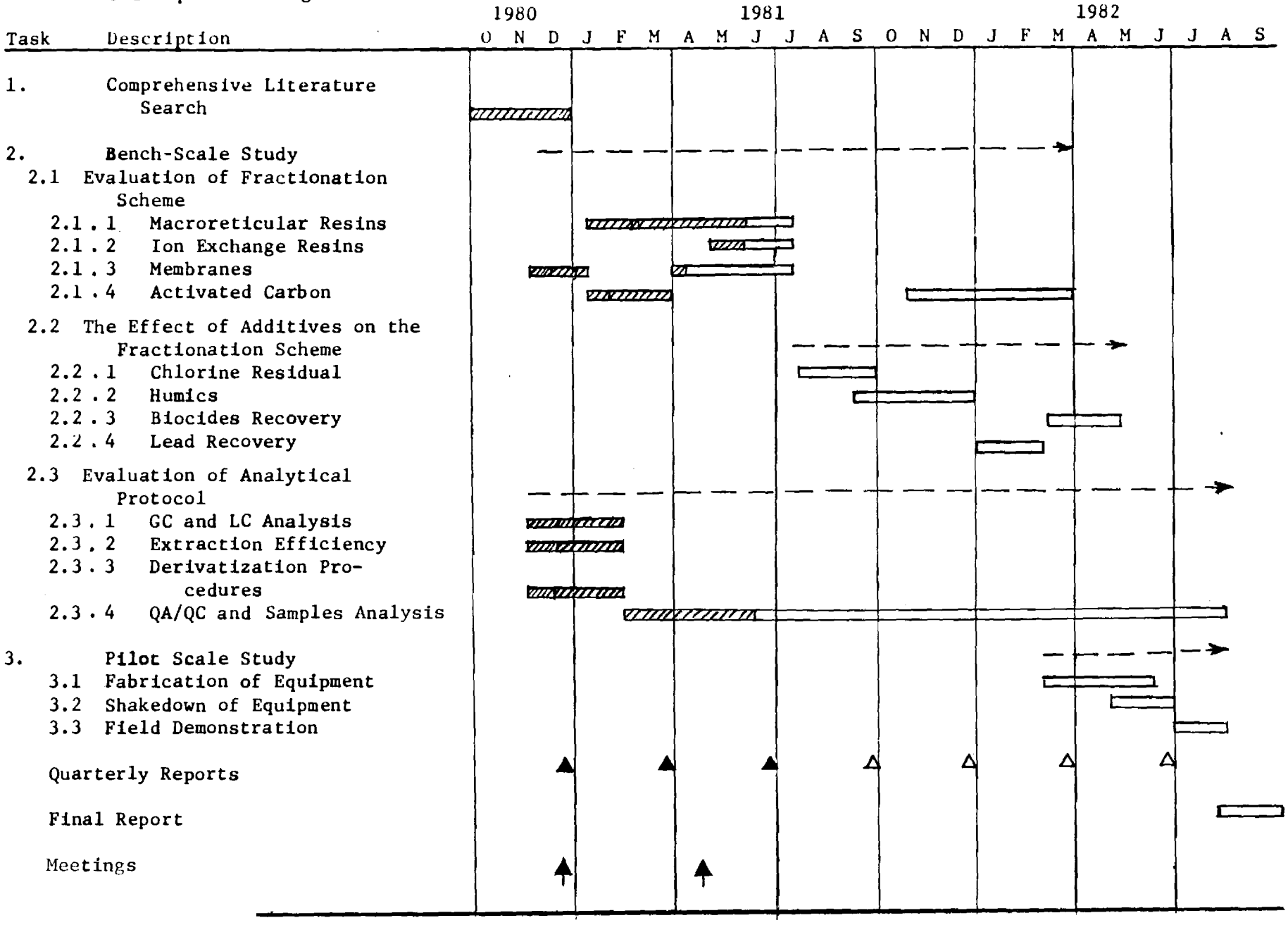
TABLE OF CONTENTS

I. INTRODUCTION

This report summarizes the work performed during the period from March 1, 1981 through May 31, 1981 on the EPA research program on "Evaluation of Methods for the Isolation or Concentration of Organic Substances from Water" (Contract No. 68-03-3000). The major efforts have been directed toward evaluation of the resin separation scheme in the presence of salts, completion of development of methodologies for the analysis of the model compounds under study by GC/MS, design of lab-scale organic-free water for purposes of both analytical and process evaluation and process evaluations with activated carbon and reverse osmosis. The progress of these efforts are depicted in the Gannt Chart (Chart 1) for the above contract, and are presented in detail in the following sections.

Chart I - Schedule for the Proposed Research Program

Project: Evaluation of Methods for the Isolation or Concentration of Organic Substances from Water
Principal Investigators: E. S. K. Chian and J. H. Reuter



II. RESIN FRACTIONATION SCHEME

The earlier qualitative work with the resin fractionation scheme showed that separation of the test compounds into the various fractions was as predicted at least with regard to the separation of bases, acids and neutrals. Work with the resins continued in order to determine the percentage of each compound that can be retained and subsequently eluted from the resin and to delineate problems resulting from the extraction, concentration and GC analyses of the fractions. A number of runs were completed using a test solution containing the following compounds:

Quinoline	Bis(2-ethyl) phthalate
caffeine	Benzo(e) pyrene
glycine	Stearic acid
biphenyl	Trimesic acid
2,3 dichlorobiphenyl	Quinaldic acid
2,2', 5,5' Tetrachlorobiphenyl	Furfural
Anthraquinone	Crotonaldehyde
1-chlorododecane	Methyl Isobutyl Ketone
2,4 dichlorophenol	Glucose
2,6 di-tert-butyl-methyl phenol	Isophorone

at concentrations of 50 µg/500 ml. (Note: due to shortage of organic free water, only 500 ml of the test solution was used in each run -- The quantity of organics applied to the resin was kept equivalent to the 50 µg/1 liter recommended).

In addition to the organic compounds, the following concentrations of inorganic salts were added to the test solution:

$CaSO_4$, 120 mg/liter

$NaHCO_3$, 70 mg/liter

$CaCl_2 \cdot 2H_2O$, 47 mg/liter

Following several partial test runs, it was apparent that the presence of the inorganic salt would introduce problems. The primary problems occurred at two steps in the procedure. When the test solution was adjusted to pH 9-10 before passage through the XAD-8 resin for adsorption of the hydrophobic base fraction, a precipitate formed. A precipitate also forms when the collected base fraction (after elution with acid) is adjusted to pH 10 before extraction and concentration in CH_2Cl_2.

To determine the effect of the precipitate formation on quinoline (a hydrophobic base), a standard concentration of this compound in solution with a small amount of $CaSO_4$ was adjusted to pH 9-10 with NaOH. The resulting $Ca(OH)_2$-precipitate was removed by centrifuging and the supernatant extracted with CH_2Cl_2. The precipitate was sonically redispersed in CH_2Cl_2 and again centrifuged. The supernatant CH_2Cl_2 solution was added to the initial extract. GC analysis showed that about 65% of the quinoline was lost during this procedure. We suspect that some of this is trapped and removed with the $Ca(OH)_2$ precipitate.

The addition of NH_4Cl was found to prevent the formation of a precipitate when the pH was raised to 9. Under these conditions only about 20% of the quinoline was lost. This procedure was therefore adopted before the extraction and concentration of the hydrophobic base fraction with CH_2Cl_2.

It is clear that additional work is needed to determine optimum pH ranges and means to control formation of inorganic precipitates.

Another problem which became apparent in earlier runs was the inability to retain the more volatile compounds MIBK, furfural and crotonaldehyde in the hydrophobic neutral fraction. This loss most probably occurs partially when the resin is dried before Soxhlet extraction with methanol and partially while the methanol solution is further concentrated in the KD apparatus to obtain a chloroform solution of the neutral compounds for GC analysis. In order to determine if the volatiles are being recovered from the resin, the columns were directly eluted with CH_2Cl_2 under N_2 pressure. After separation of the CH_2Cl_2 from a small amount of aqueous phase which was co-eluted, the CH_2Cl_2 solution was analyzed by GC. The resin itself was then dried and Soxhlet extracted with methanol to find out to what extent the compounds had been removed by the CH_2Cl_2 extraction.

A series of six runs were made: A-1, A-2, B-1, B-2, C-1, C-2. The general procedure is as follows:

i. Test solution, adjusted to pH 10 with NaOH is passed over XAD-8

1. Hydrophobic base eluted with HCl

ii. Test solution, adjusted to pH 2 with HCl is passed over XAD-8

2. Hydrophobic acid eluted with NaOH

3. Hydrophobic neutrals eluted with CH_2Cl_2 (directly from the column)

iii. Test solution is passed over MGP-50

4. Hydrophilic base is eluted with NH_4OH

iv. Test solution is passed over Duolite A-7

5. Hydrophilic acid + inorganic salts are eluted with NH_4OH

v. Test solution retained for Hydrophilic neutrals

Modifications of the general procedure:

Samples: B-1, B-2: In step i, the pH was readjusted to 7.5 in order to dissolve the $Ca(OH)_2$ precipitate.

Samples: C-1, C-2: To determine if Soxhlet extraction of the dried resin is more effective than direct elution from the column, the XAD-8 for these runs was dried and Soxhlet extracted with CH_2Cl_2.

The following extraction and concentration procedures were adopted:

1. Hydrophobic base: the aqueous fraction was adjusted to pH 9 with NaOH after NH_4^+ addition. The fraction was then extracted with three successive aliquots of CH_2Cl_2 in a separatory funnel. The CH_2Cl_2 fraction was then dried with Na_2SO_4 and concentrated to 1 ml in the KD apparatus and under N_2 stream at later stages.

Table 1

Average Percentage Recovery ($\bar{X}$) of Model Compounds from Resin

Fraction/Compound	Sample A-1	A-2	B-1	B-2	C-1	C-2	$\bar{X}$	S**
Hydrophobic base								
Quinoline	NQ+	NQ	19%	14%	NQ	NQ		
Hydrophobic acid								
No compounds quantified								
Hydrophobic neutrals								
Isophorone	37%	62%	33%	50%	19%	27%	58	15
Biphenyl	102	140	41	36	56	62	49	12
1-chlorododecane	35	46	25	37	38	36	36	7
2,6 di-tert-butyl-4methyl phenol	41	54	13	20	19	12	26	17
2,4 dichlorobiphenyl	54	60	32	47	65	77	56	15
Anthraquinone	31	38	43	--	37	37	37	9
2,2',5,5' tetrachloro-biphenyl	64	68	39	52	68	79	62	19
Bis (2-ethyl)phthalate	262*	56	NQ	NQ	51	39	49	9
Hydrophilic bases								
No compounds quantified								
Hydrophilic acids								
No compounds quantified								
Hydrophilic neutrals								
Not analyzed, pending analytical procedure for glucose derivatization								

+ not quantified

* contamination

** percent standard deviation of the recovery process

The compounds caffeine, 2,4 dichlorophenol, benzo(e)pyrene, stearic acid, trimesic acid, quinaldic acid, furfural, crotonaldehyde and methyl isobutyl ketone were not quantified in any of the fractions. The volatile compounds furfural, crotonaldehyde and MIBK were not found in the neutral column extract. These compounds will need concentration and analysis by VOA techniques. Work is underway to evaluate such a procedure. The acids stearic, trimesic, quinaldic and 2,4 dichlorophenol were not detected. We have to investigate the possibility that the acids form Ca-salts or Ca-complexes at higher pH and as such may be adsorbed on the XAD resin together with the neutral and basic compounds. Caffeine and benzo(e)pyrene were found in trace amounts too small for GC quantification. Glycine and glucose were not quantified pending finalization of the derivatization procedure.

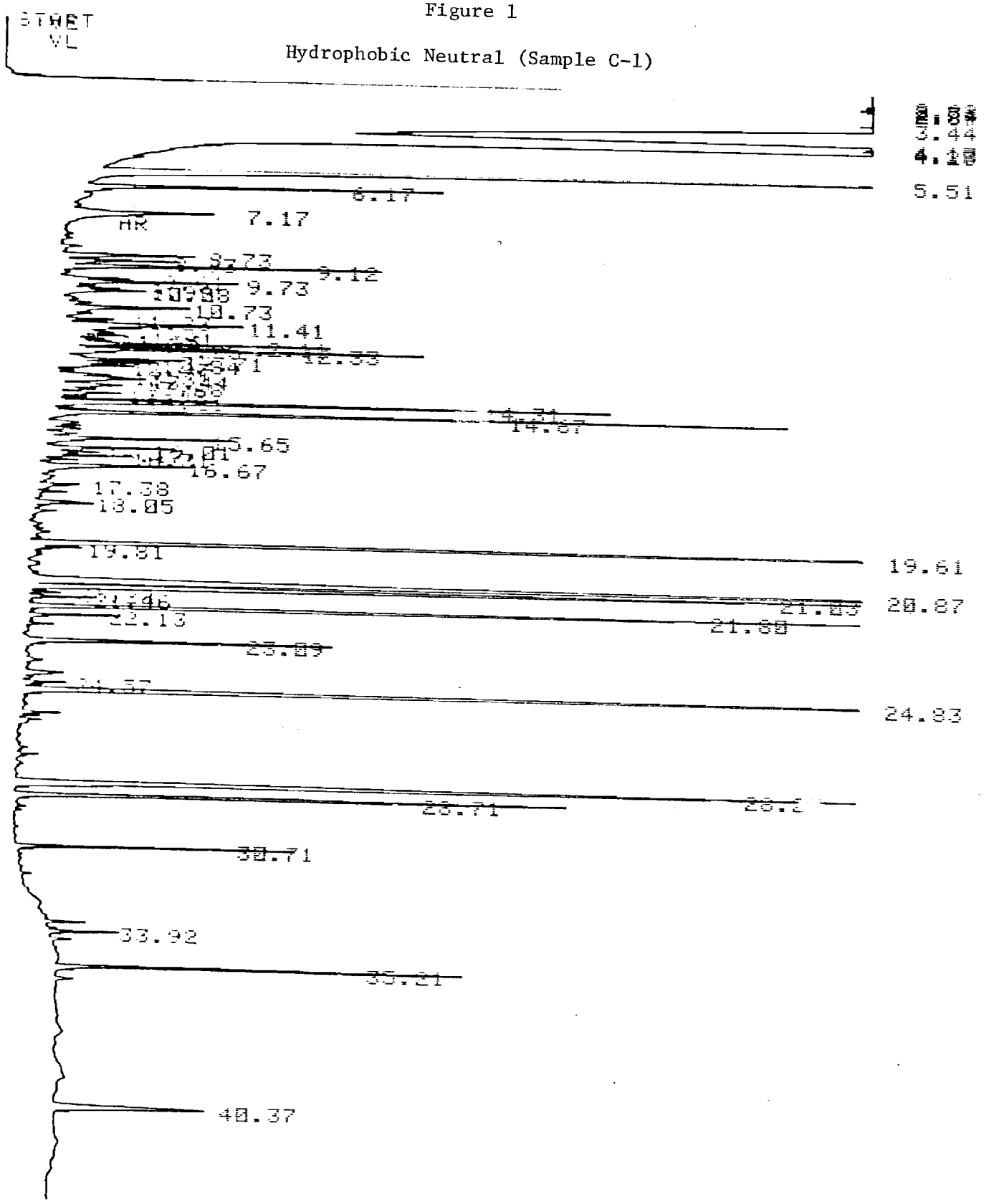
When the resin was dried (in air, 15 hrs.) and Soxhlet extracted with CH_2Cl_2 (samples C-1, C-2), the chromatogram (Figure 1) showed numerous extraneous peaks especially at lower retention times. This was not seen in the earlier qualitative runs when the resin was dried and Soxhlet extracted with methanol. This yielded very "clean" chromatograms. The CH_2Cl_2 is apparently leaching extraneous compounds from the dried resin.

The Soxhlet extraction with CH_2Cl_2 showed no appreciable improvement on the recovery of the test compounds as compared to the elution with CH_2Cl_2 directly from the column. Since the more volatile compounds were not recoverable by elution from the column directly, it is believed that based on the earlier work, Soxhlet extraction with methanol should be the preferred method for elution of the hydrophobic neutrals.

READY

Figure 1

Hydrophobic Neutral (Sample C-1)



Future Work

1. Inorganic precipitates form at the higher pH which is required for fractionation and extraction of hydrophobic bases. We need to determine the optimum pH and evaluate ways to avoid or deal with precipitates.
2. Hydrophobic and hydrophilic acids were not quantified. Problems of complex or salt formation with Ca^{2+} need to be recognized and overcome.
3. Furfural, Crotonaldehyde and MIBK are not recovered by the resin fractionation procedures. We need to determine if they can be handled by VOA procedures.

III. ANALYTICAL METHODOLOGIES

A. Derivatization and Gas Chromatography

A statistical evaluation for the quantitation of glucose after derivatization with N-methylbistrifluoroacetamide has been completed. and the results are presented in the following section, together with glycine and quinaldic acid data. The only compound that needs further study is 5-chlorouracil. The glass capillary columns developed in this work which were expected to be able to handle the underivatized compounds did not give the results as anticipated. Further experiments will be conducted together with a derivatization procedure as reported previously in the second quarterly report.

Glucose

Our major effort in this area was in searching for a good method for derivatizing glucose. The method described in our previous report failed to give reproducible results in our own hands. One of the operational difficulties in this procedure was the escape of all organic reagents and products at 130°C (2-hour reaction time) from the sealed reactivials in spite of taking all reasonable precautions. So, the method developed previously was abandoned in favor of a milder reaction condition.

Literature search revealed that N-methylbistrifluoroacetamide (MBTFA) has been used to derivatize methylglycosides at room temperature and also to derivatize mono- through tetrasccharides (like glucose). The last method was adopted for derivatizing glucose and the procedure we followed is described below.

A measured volume of a standard glucose solution (500 ppm) was taken in a reactivial and dried by blowing nitrogen. Pyridine (40 μℓ) and MBTFA (40 μℓ) were added to the vial which was then heated for one hour at 75°C in a sand bath, and the temperature of the bath was determined accurately with a digital thermometer. All operations were carried out in a nitrogen filled glove chamber. Results of reproducibility are presented in Table 2. A computer printout of the scattergram and regression statistics is presented in Figure 2 showing the linearity of GC-detector response with weight of glucose used to start with.

Glycine

Different weights of glycine, varying between 2 to 50 ng were derivatized to the N(O)-heptafluorobutyrylglycineisoamylester and analyzed by GC. The linear dependence of GC-response on the weight of glycine was determined by regression. The scattergram and regression statistics are presented in Figure 3. The data is also presented in Table 3.

Quinaldic Acid

This acid was derivatized to its methyl ester with diazomethane by the procedure described earlier.[4] The only modification was to add a drop of hydrochloric acid to make sure that the carboxyl group is not in the carboxylate anion form, the possibility of which is due to the presence of a proximal tertiary nitrogen with a lone pair of electrons.

Results of the study of reproducibility and linearity are presented in Figure 4 as well as Table 4.

Table 2

Reproducibility and Linearity of GC-Detector Response for Glucose.

Sample No.	Wt. of glucose Derivatized	Area (1)	IS Area (2)	Response $\frac{\text{Area(1)}}{\text{Area(2)}}$	Mean	σ
56-1	20ng	1479	7048	.21		
56-2		1294	4702	.28	.247	.035
56-3		1209	4791	.25		
56-4	50ng	3087	4466	.69		
56-5	200ng	6700	4118	1.63		

IS = Hexamethylbenzene

95% CI for response for 20ng is

$$.247 \pm t.025\frac{\sigma}{\sqrt{n}} \quad , DF = 2$$

$$= .247 \pm (3.82)(.035)/\sqrt{2}$$

$$= .1683 \text{ to } .3258$$

Retention times and peak areas of glucose anomers (A, B, C, D):

	A		B		C		D		Total
Sample No.	RT	Area	RT	Area	RT	Area	RT	Area	Area
56-1	9.69	595	9.87	327	10.15	239	10.32	318	1479
56-2	9.70	429	9.88	191	10.12	525	10.33	149	1294
56-3	9.51	377	9.88	209	10.15	287	10.21	336	1209
56-4	9.50	1888	-	NQ	-	NQ	10.12	1199	3087
56-5	9.46	3917	-	NQ	9.88	101	10.17	2682	4118

NQ = Not Quantiated

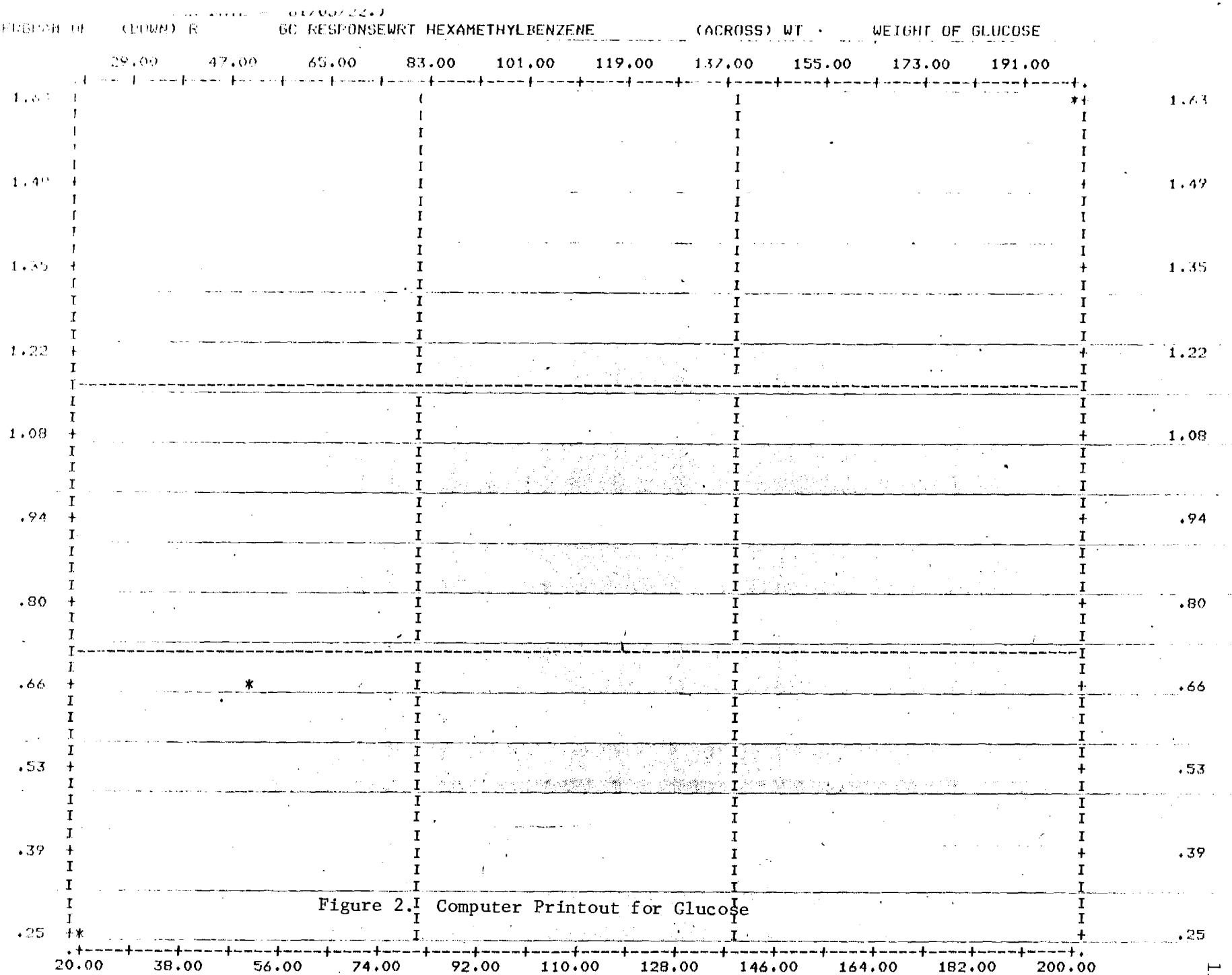


Figure 2. Computer Printout for Glucose

13FD OR REPORT 81/05/22. 10.23.22. PAGE 3

OSTATISTICS..

O CORRELATION (R)-	.98703	R SQUARED -	.97424	SIGNIFICANCE R -	.05131
O STD ERR OF EST -	.16002	INTERCEPT (A) -	.20731	STD ERROR OF A	

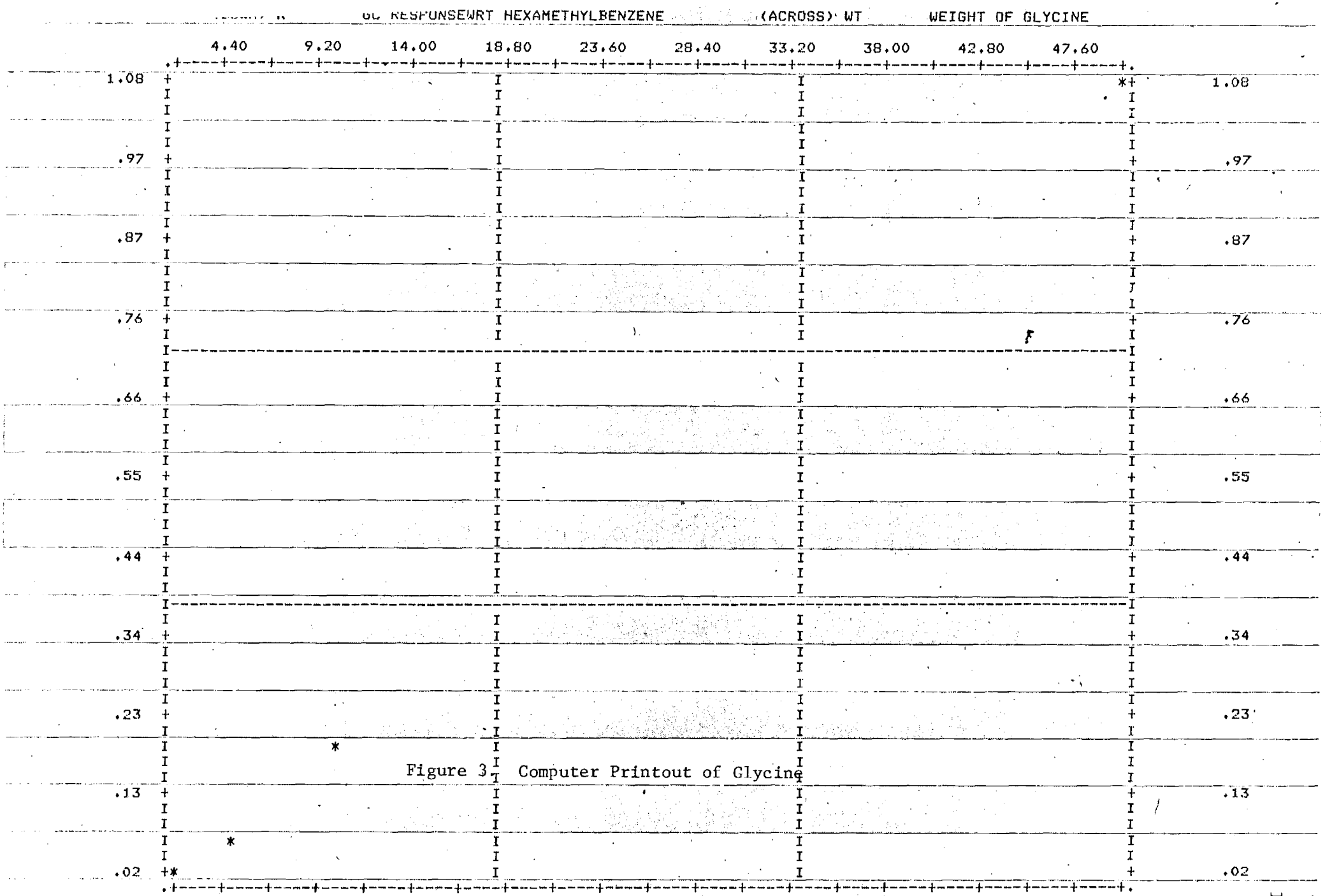


Figure 3. Computer Printout of Glycine

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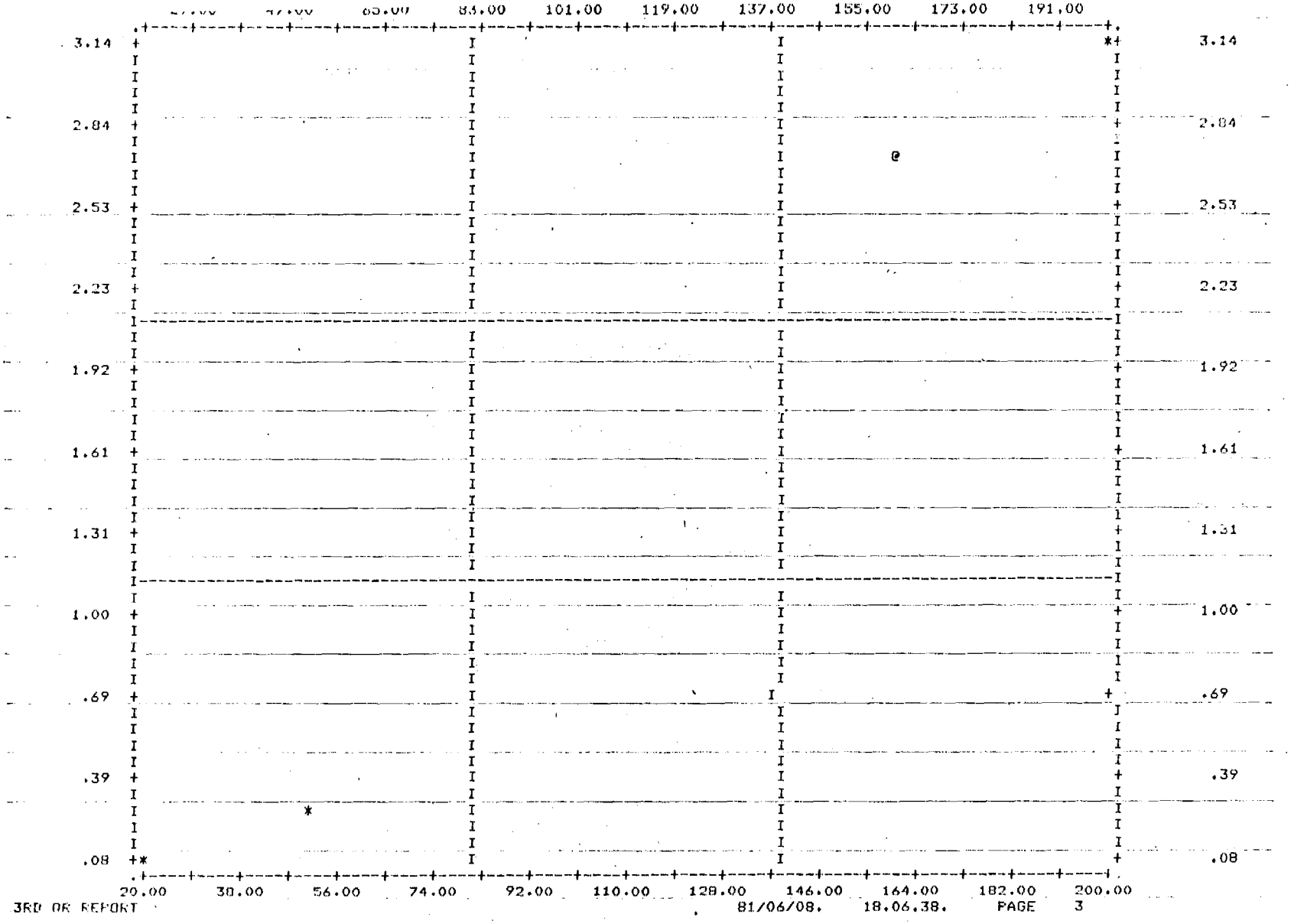
OSTATISTICS..

O CORRELATION (R)-	.99986	R SQUARED -	.99972	SIGNIFICANCE R -	.00007
O STD ERR OF EST -	.01010	INTERCEPT (A) -	-.02221	STD ERROR OF A -	.00667

TABLE 3

Linearity of GC-detector Response for Glycine

Sample No.	Wt. of glycine derivatized	Area (1)	IS Area (2)	Response = $\frac{\text{Area}(1)}{\text{Area}(2)}$	RT
58-15	2 ng	106	6112	.02	15.27 min
58-16	5 ng	554	7126	.08	15.22
58-14	10 ng	1096	5170	.21	15.23
58-17	50 ng	6148	5691	1.08	15:20



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STATISTICS..

CORRELATION (R)-	.99571	R SQUARED -	.99144	SIGNIFICANCE R -	.02949
STD ERR OF EST -	.22365	INTERCEPT (A) -	-.41397	STD ERROR OF A -	.19610
SIGNIFICANCE A -	.14082	SLOPE (B) -	.01765	STD ERROR OF B -	.00164
SIGNIFICANCE B -	.02949				

Figure 4.

Table 4

Reproducibility and Linearity of GE-Dectector Response for Quinaldic Acid

Sample No.	RT	Wt. of Acid Derivatized	Area(1)	IS Area(2)	Response $\frac{\text{Area(1)}}{\text{Area(2)}}$	Mean	σ
46-4	16.63	20 ng	825	17890	.046		
45-2	16.64		1029	12790	.080		
45-3	16.62		486	13928		.081	.027
45-4	16.65		1023	9252	.111		
45-5	16.69		932	10728	.087		
46-2	16.66	50 ng	3871	12990	.298		
46-3	16.66	200 ng	25818	8212	3.144		

A summary of regression results for glucose, glycine and quinaldic acid is presented in Table 5. All regressions were done by SPSS programs.

B. Organic-Free Water

The importance of "organic free" water has assumed gigantic proportions, with the onset of isolation and evalution of organics present in water at parts per billion level. Water with a low background in terms of Total Organic Carbon (TOC) is mandatory for research involving trace organics. Malaiyandi et al.[5] have reported the successful production of water with very low TOC values by exposing a controlled mixture of distilled water and H_2O_2 to a source of U-V light in a custom-made quartz reactor. As the quantity of organic-free water is of a great significance to this project, an attempt has been made to assemble a continuous flow-through system. This system, whose purpose is to process tap water, consists of three main units; namely, a reverse osmosis system (employing DuPont B-9 membrane), a demineralizer and organic removal assembly, and a flow-through U-V unit (Model #-50, manufactured by Ultraviolet Technology, Inc., San Diego, California). The demineralizer has a high capacity cartridge, Corning 3508-B and an organic removal cartridge, Corning 3508-ORC. The U-V unit consists of a Teflon tubing 8 ft. long and 1 in. in diameter exposed to an external U-V source. This entire assembly is housed in a protective cover. H_2O_2 is introduced to the system prior to its entry into the U-V unit.

The overall assembly is shown in Figure 5. The system operates as follows: Tap water is fed continuously to the reverse osmosis unit. The permeate from the reverse osmosis unit was stored in a reservoir made

Table 5

Regression Results of Linearity Study for
Glucose, Glycine and Quinaldic Acid

Name	Wt.	Response	Slope	Intercept	R	σ
Glucose	20 ng	.25	.00722	.20731	.98703	.160
	50 ng	.69				
	200 ng	1.63				
Glycine	2 ng	.02	.02207	-.02221	.99986	.0101
	5 ng	.08				
	10 ng	.21				
	50	1.08				
Quinaldic Acid	20 ng	.081	.01765	-.41397	.99571	.224
	50 ng	.298				
	200 ng	3.144				

R = correlation coefficient

σ = standard error of estimation

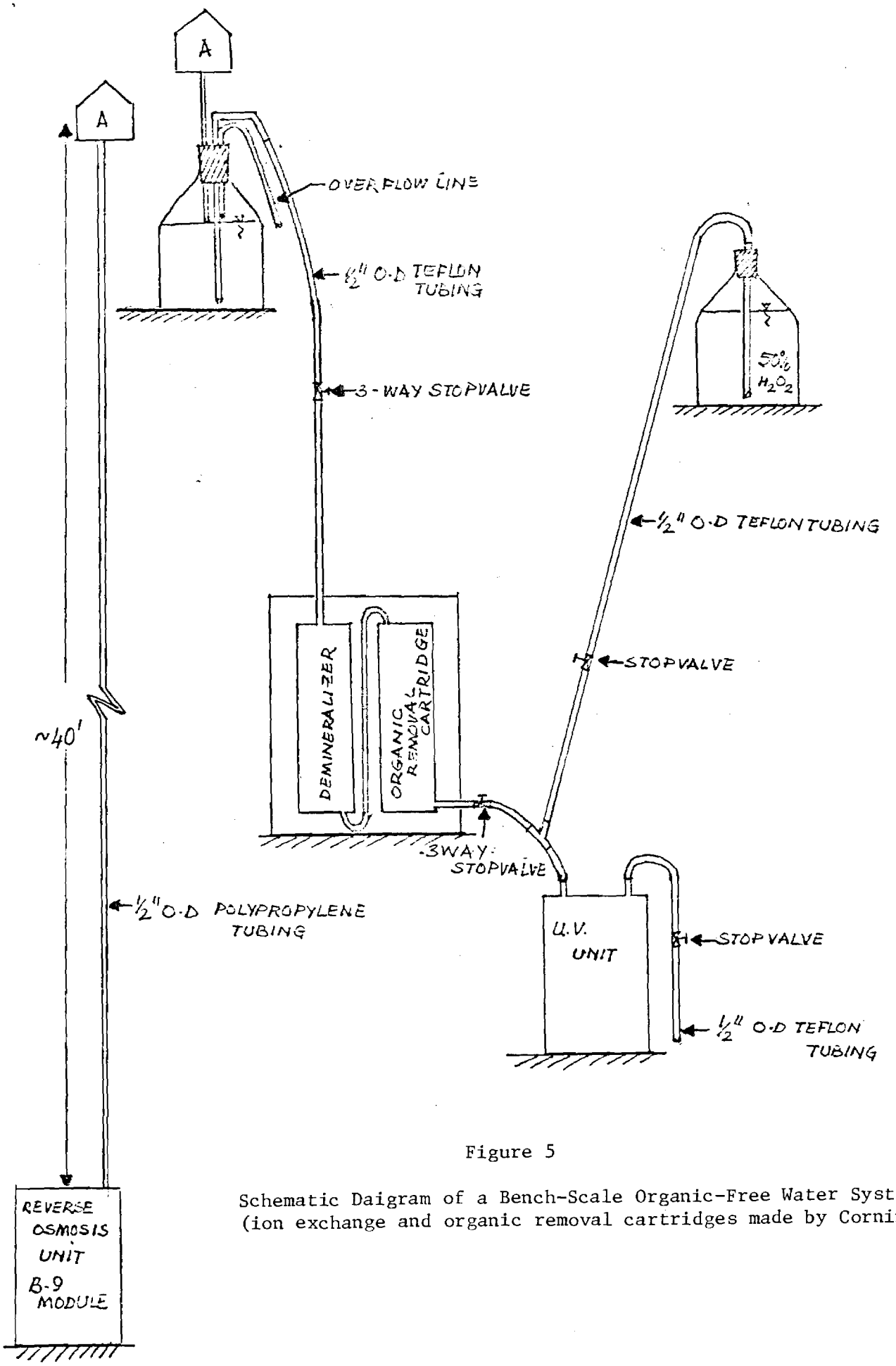

Figure 5

Schematic Daigram of a Bench-Scale Organic-Free Water System (ion exchange and organic removal cartridges made by Corning)

of Pyrex glass. Polypropylene tubing is used to connect the reverse osmosis unit and the reservoir. From this point onwards, all connections are made of Teflon tubing and fittings. From the glass reservoir, the water flows into the demineralize/organic removal assembly under gravity. To the effluent of this assembly, hydrogen peroxide (H_2O_2, 50%) is added prior to its introduction into the U-V unit. Finished water flowed out from the outlet of the U-V unit. The residence time of the water in the U-V unit can be varied from 20 minutes to one hour and 30 minutes.

The hydraulics of the U-V system was established by using sodium chloride as a tracer and the conductivity of the finished water was monitored. The dissolved solids level of the permeate from reverse osmosis unit was 1.5 ppm. A 5000 ppm $NaCl-H_2O$ solution was used as a substitute for H_2O_2. The concentration of the $NaCl-H_2O_2$ solution was established by conductivity measurement.

In order to monitor the contribution of TOC by each component of the system, TOC determination was made with water samples obtained at different points of the system; namely, a) permeate from the reverse osmosis unit, b) effluent from glass reservoir, c) effluent from the demineralizer/organic removal cartridges and d) effluent from the U-V unit. Furthermore, the effect of H_2O_2 on the level of TOC in the effluent from the U-V unit was also evaluated. The results are given in Table 6. As can be seem from this table, the permeate from the RO module is 6.3 ppm. There is a 50% reduction in TOC in the effluent of the demineralizer and organic removal cartridges. The TOC of the H_2O_2/U-V treated water is approximately 1 ppm with a residence time

Table 6

T.O.C. Values (ppm) of Water Samples at Various Points of the System

Sample Source			
Outlet of R.O. permeate	6.31		
Outlet of the glass reservoir	6.45		
Outlet of demineralizer/organic removal cartridges	3.05		
Outlet of the U.V. unit	1.95 (without H_2O_2)	1.14 (with H_2O_2)	5.89 (U.V. light off)

of 1.185 hours in the U-V unit and an addition of 2.78% (V/V) of a 50% H_2O_2 solution. Upon operation of the system without the U-V lights on, the TOC value of the finished water escalated to an alarming value of 5.89 ppm. This indicates that the U-V unit is contributing to the TOC value of the water. This is due to the use of PVC pipe for inlets and outlet, and a plastic holder for the Teflon tubes inside the U-V unit. Based on these results, modifications have been proposed for future experimentation:

i) Obtain a U-V unit with complete Teflon fittings;

ii) The necessity of the demineralizer/organic removal assembly will be evaluated; and

iii) Optimization of operating conditions in terms of residence time inside the U-V unit and % V/V addition of H_2O_2 will be performed.

IV. PROCESS EVALUATIONS

A. Carbon Adsorption

Preparation of Activated Carbon

The activated carbon used in this study was Filtrasorb F400 (Calgon Corp., Pittsburgh, Pennsylvania) supplied in 12 x 40 mesh. The stock carbon was then ground and sieved to 16 x 30 mesh. The carbon (16 x 30 mesh) was then Soxhlet extracted for 12 hours with methylene chloride. The next step in the procedure was the washing of the carbon with "organic-free" water in a previously baked beaker (400 ml). The "organic-free" water was replaced by acetone by decanting and filling the beaker four times; this was helpful as it removed most of the sorbed gases. The carbon was then washed with methylene chloride, acetone and methanol in the order mentioned. The carbon was finally washed with "organic-free" water and was then dried in an oven at 110°C for seven days. The carbon was stored in a desicator in a flash, covered by a previously baked aluminum foil.

Equilibrium Studies

Isotherm studies were carried out in 125 ml French square bottles (previously baked at 400°C overnight) with Teflon coated screw caps. The adsorbent was weighted in the dry state (0.05 gm ± 0.001 gm) and added to it 20 ml of "organic-free water." The adsorbates were added to the sample on volume-per-volume basis and the bottles were quickly sealed so as to prevent any loss of the solute. Samples were run in duplicate. Apart from samples, a set of four bottles were run as blanks (organic-free water) and another set of four bottles had organic-free water

with the aforementioned amount of activated carbon. The reason for using a carbon + water blank was to estimate the TOC contribution of the activated carbon to the "organic-free water" during the equilibrium period. The bottles were then placed in a rotary skaker and were tumbled for a period of six days at 20°C. After six days the bottles were taken out and were monitored for the residual TOC content.

Results and Discussion

The results of isotherm studies for furfural, crotonaldehyde and methylisobutylketone (MIBK) are plotted in Figure 6. The results of the preliminary isotherm study for chloroform reflected a need for change in the method of conducting the isotherm study. This will be discussed later. Figure 6 reflects the attainment of equilibrium. For crotonaldehyde and methylisobutylketone the equilibrium period of six days is sufficient whereas for furfural a longer equilibrium period is needed. Attainment of equilibrium is important as measurements prior to attainment of equilibrium reflects a decrease in capacity with an increase in particle size.

The capacities of the 16 x 30 mesh F400 carbon for the compounds studied were determined using the Freundlich's Isotherm

$$q_e = KC_e^{1/n}$$

q_e = amount (mg) of compound adsorbed per gm of activated carbon

K and n = Freundlich parameters

C_e = concentration (mg/L) of compound left in solution at equilibrium

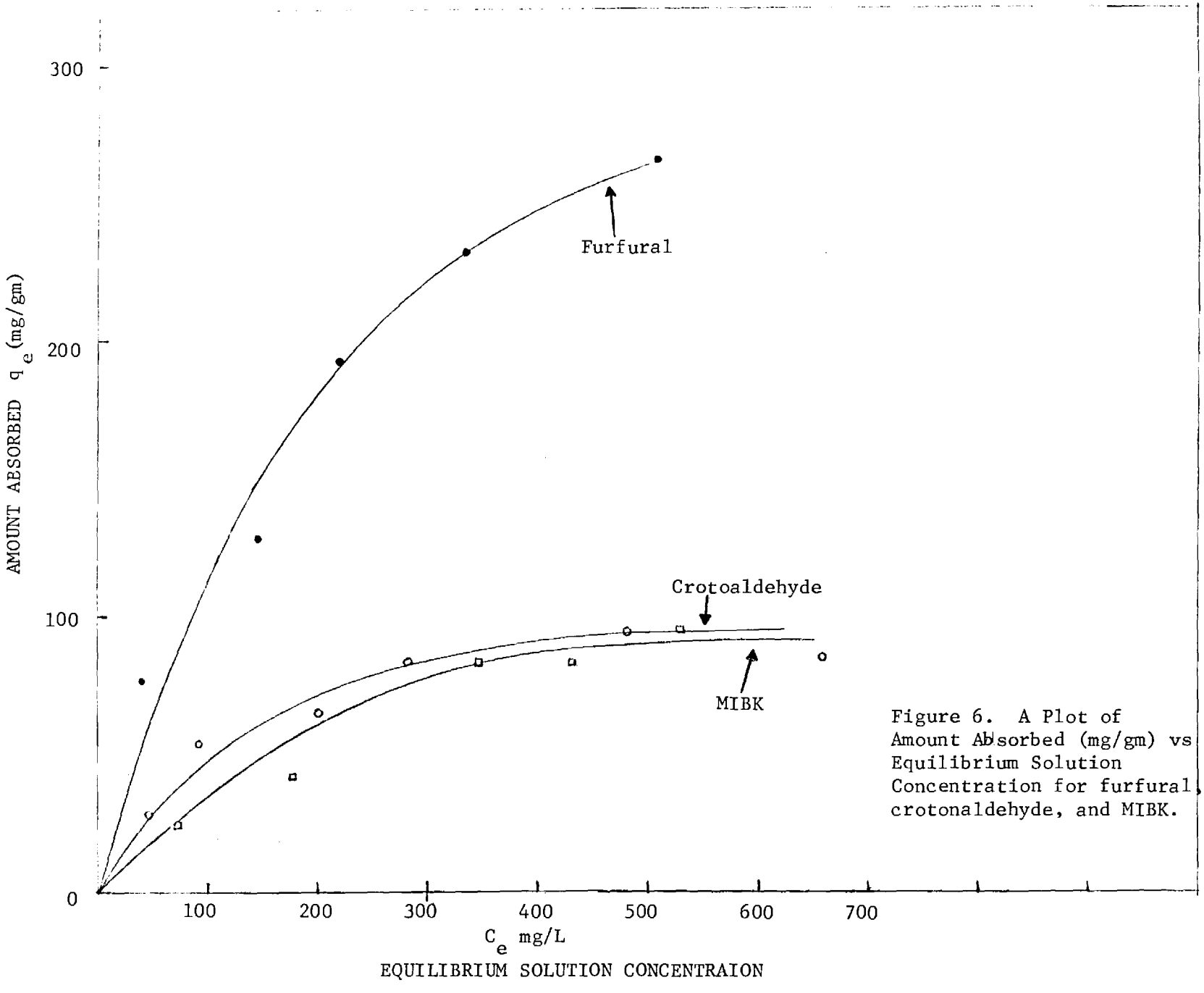

Figure 6. A Plot of Amount Absorbed (mg/gm) vs Equilibrium Solution Concentration for furfural, crotonaldehyde, and MIBK.

Figures 7 and 8 show the plots of Freundlich isotherm for crotonaldehyde methylisobutylketone and furfural. The ultimate capacities for crotonaldehyde, methylisobutylketone and furfural are 120, 170, and 390 mg/g, respectively. Table 7 presents the results of the experimental work for the aforementioned compounds. The values of ultimate (gm of activated carbon) capacity for crotonaldehyde and methylisobutykletone are in close agreement with the values reported for these compounds by Guisti et al.[7] The trend of increase in the ultimate capacity of crotonaldehyde to methylisobutylketone also compares well with that observed by Giusti et al.

Future Work

Based on the results of the preliminary isotherm studies on chloroform the following modifications are proposed for further isotherm studies on chloroform.

i) The studies will be conducted in 125 ml French square bottles, without having any headspace in the bottle. These bottles will be capped with a Teflon coated screw cap.

ii) In addition to the organic-free water blank and the organic-free water plus the adsorbent blank, a control blank on chloroform will be run so as to obtain an estimate of the loss of chloroform due to volatilization.

iii) The time for attainment of equilibrium will be increased to ten days to facilitate the occurrence of proper equilibrium of the compounds studied.

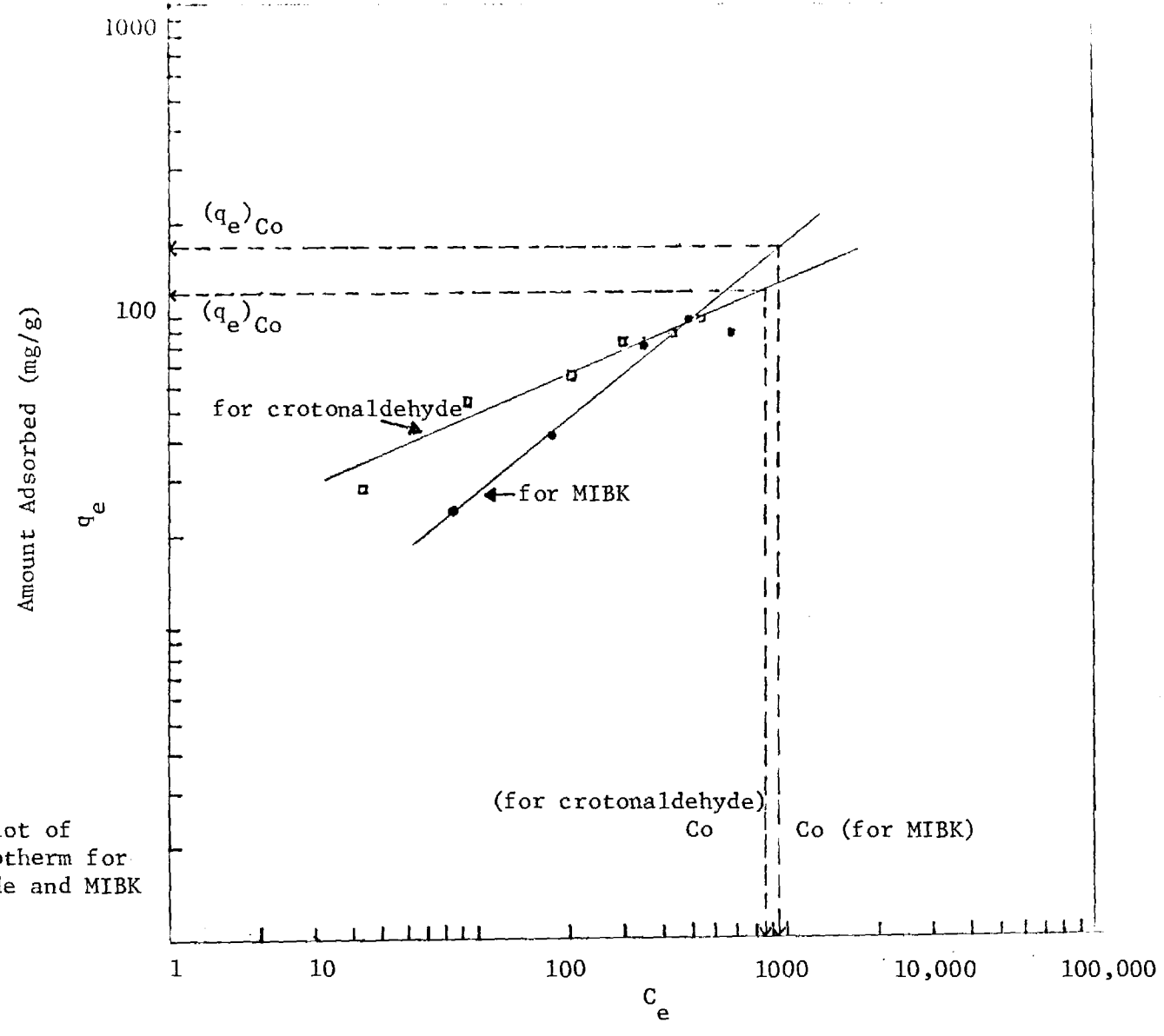

Figure 7. Plot of Freudlich Isotherm for Crotonaldehyde and MIBK

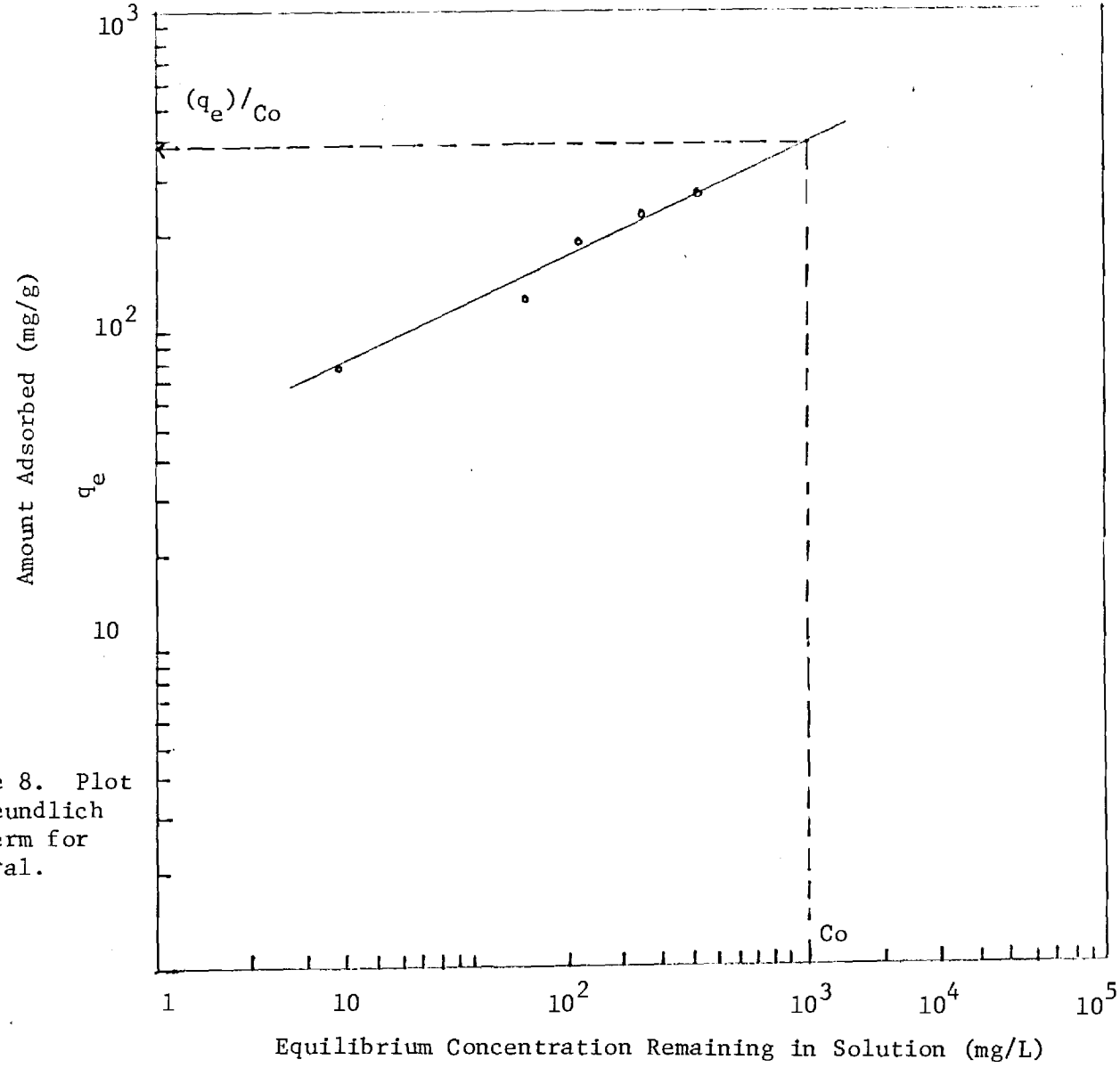

Figure 8. Plot of Freundlich Isotherm for Furfural.

Table 7. Results of Activated Carbon Experiments

Compound	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Volume of Sample (L)	q_e amt. adsorbed / gm of activated carbon (mg/gm)	Freundlich K	Parameters n
Furfural	234.34	38.49	0.02	78.22	12.61	2.04
	468.66	148.36	0.02	128.2		
	703.03	220.99	0.02	192.8		
	937.37	355.54	0.02	232.6		
	1171.71	508.81	0.02	265.2		

Compound	Initial Concentration Co (gm/L)	Equilibrium Concentration Ce (mg/L)	Volume of Sample (L)	q_e amt. adsorbed / gm of activated carbon (mg/gm)	Freundlich K	Parameters n
Crotonaldehyde	145.84	43.17	0.02	28.14	6.127	2.263
	291.68	91.46	0.02	54.88		
	457.36	200.09	0.02	65.08		
	583.36	279.66	0.02	83.24		
	729.20	428.43	0.02	82.46		
	875.06	527.18	0.02	95.36		

Compound	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Volume of Sample (l)	q_e amt. adsorbed / gm of activated carbon (mg/gm)	Freundlich K	Parameters n
Methyliso-butyl ketone	159.2	73.36	0.02	24.7	1.626	1.567
	318.4	178.68	0.02	40.22		
	636.8	363.03	0.02	84.62		
	796.0	481.47	0.02	90.5		
	955.2	660.2	0.02	84.9		

B. Reverse Osmosis

The concept of free energy controlling reverse osmosis separations of undissociated polar organic solutes in diluted aqueous system, has been reported in literature by Matsuura, et al.[8] These authors suggested the following general expression for solute transport parameter ($D_{AM}/K\delta$) for reverse osmosis systems involving preferential sorption of water at the membrane solution interface.

$$\ell n\ (D_{AM}/K\delta) = \ell n\ C^* + \rho^* \Sigma\sigma^* + \delta^* \Sigma E_s + \omega^* \Sigma s^*$$

where, $\Sigma\sigma^*$ and ΣE_s are the Taft polar and steric parameter, respectively for the substituent groups in the solute molecule, and Σs^* is an applicable non-polar parameter for the solute molecule, ρ^*, δ^* and ω^* are the characteristic proportionality constants associated with $\Sigma\sigma^*$, ΣE_s and Σs^*, respectively. ℓnC^* accounts for the chemical nature of the membrane, and the effective average pore size on the membrane surface. For a class of solutes having three or less carbons in the backbone of the molecular, Matsuura and Sourirajan[10] reported that reverse osmosis separations are governed by polar and steric effects only. For these compounds the solute transport parameter is expressed as

$$\ell n\ (DAM/K\delta) = \ell nC^* + \rho^* \Sigma\sigma^* + \sigma^* \Sigma E_s$$

A general expression for the solute transport parameter has been reported by Matsuura, et al.[8] using appropriate parameters representing the effect of pore size on the membrane surface and the polar and steric

effects on the solute beansport parameter

$$\ell n\ (D_{AM}/K\delta) = \ell nC^*_{NaCl} + \ell n\Delta^* + \left(\frac{-\Delta\Delta G}{RT}\right) + \delta^*\Sigma E_s$$

where, ℓnC^*_{NaCl} represents the effect of pore size on the membrane surface for the reference solute which happens to be NaCl in this study. $\left(\frac{-\Delta\Delta G}{RT}\right)$ is analogous to the quantity $\rho^*\Sigma\sigma^*$ as shown by Matsurra et al.[8] $\ell n\Delta^*$ accounts for the overlap of the pore size effect in the combined quantity $(\ell nC^*_{NaCl} + \delta^*\Sigma E_s)$. $\delta^*\Sigma E_s$ can be expressed as a function of ℓnC^*_{NaCl} as for various values of ℓnC^*_{NaCl}. The quantity $(\delta^*\Sigma E_s)/(\delta^*\Sigma E_s)_{lim}$ for cellulose acetate membranes can be obtained from literature[8] and $(\delta^*\Sigma E_s)_{lim}$ can be expressed as an additive property.

$$(\delta^*\Sigma E_s)_{lim} = \Sigma\phi(\text{structural unit}) + \phi_o$$

The values of ϕ (structural unit) for some structural groups (for cellulose acetate membranes) has been reported by Matsuura et al.[8]

The rejection (f) is expressed as

$$f = \left[1 + (D_{AM}/K\delta)\ \frac{\exp(V_s/r)}{v_s}\right]^{-1}$$

where, $v_s = \frac{PR}{3600Sd}$

v_s = permeation velocity of product solution cm/sec

PR = product rate gm/hr

S = effective surface area cm^2

d = density of the solution gm /cm^3

and, k = mass transfer coefficient cm/sec.

The aforementioned method was used to predict the rejections of hydrophilic neutrals. (crotonaldehyde, furfural, chloroform and glocuse) and methylisobutylketone. For cellulose acetate membranes (CA1020), using the mass transfer coefficient, k, from Fang and Chain,[11] the mass transfer coefficient for the organic solubles was determined using the following relationship developed by Matsuura, et al.[8]

$$k = k_{ref} \left[\frac{D_{AB}}{(D_{AB})_{ref}} \right]^{2/3}$$

where k_{ref} is the mass transfer coefficient on the high pressure side of the membrane for the reference solution system NaCl-H_2O. $(D_{AB})_{ref}$ and D_{AB} refer to the diffusibility of NaCl and the organic solute in question in water.

D_{AB} for the organic solute in water was estimated with the help of Wilke and Chang's formula.

$$D_{AB} = \frac{7.4 \times 10^{-8} (XM)^{\frac{1}{2}} T}{\mu V 10.6}$$

where, v_1 = molal volume of solute at normal boiling point cm^3/gm-mole

X = "Association" parameter for solvent = 2.6 for water

T = temp °K

M = molecular weight of solvent = 18.02 gm/mole for water

μ = viscosity, centipoise

Based on this methodology the predictions of the membrane rejections (f) for the various hydrophilic neutrals and methylisobutyl ketone using cellulose acetate membranes are presented in Table 10. From Table 10, it can be seen that under the present operating conditions and using cellulose acetate membranes (Millipore, Bedford, Massachusetts), glucose is rejected 99.5% followed by methylisobutyl ketone which has a rejection of 47.2%. The other three compounds do not have any rejection. This is primarily due to a large solute transport parameter for crotonaldehyde furfural and chloroform. This huge difference in solute transport parameter $\frac{D_{AM}}{K\delta}$ is caused primarily by the vast differences in the polar parameter $\frac{-\Delta\Delta G}{RT}$ which these compounds have for cellulose acetate membranes and a general lack of thermodynamic data on the chlorinated compounds from the literature. Very low rejection of chloroform with cellulose acetate membrane has also been confirmed by the manufacturers of membrane equipment. However, Chian has experienced a 35% rejection of chloroform with DuPont's B-10 module.

Future Work

Future effort will be made to determine experimentally rejection of these compounds by the DuPonts B-10 Permasep and UOP's PA-300 spiral wound modules which are known to have far better rejection of low MW polar organics than the cellulose acetate membrane. Rejection of these compounds will be monitored based on results obtained with the specific analyses for organics developed under this contract.

Table 10

Some Model Compounds with a Cellulose Acetate Membrane

Compound	(D_{AM}/K)	k(cms/s)	f	Calculated
NaCl	4.212×10^{-5}	60.2×10^{-4}	0.9689 (expt.)	0.9636
crotonal-dehyde	1.65×10^{13}	50.89×10^{-6}	No rejection	
furfural	6.652×10^{29}	50.16×10^{-6}	No rejection	
chloroform	1.256×10^{20}	52.2×10^{-6}	No rejection	
MIBK	1.125×10^{-3}	42.44×10^{-6}	0.472	
glucose	4.9×10^{-6}	38.7×10^{-4}	0.9949	

V. FUTURE WORK

Attempt has been made in this report to include future work of this research program at the end of each section.

VI. EXPENDITURES

The actual expenditures incurred during the third quarter of this research program are presented by the dashed line in Figure 9 (between months of 6-9). The solid line represents the expected expenditures in the months to come. So far the actual expenditures run closely to the anticipated one.

If there is any questions regarding this quarterly report, please contact either Edward Chian or Maurizio Giabbai at (404) 894-2265. The co-principal Helmut Reuter is intended to discuss over the phone with the project officer on the future work of himic addtion.

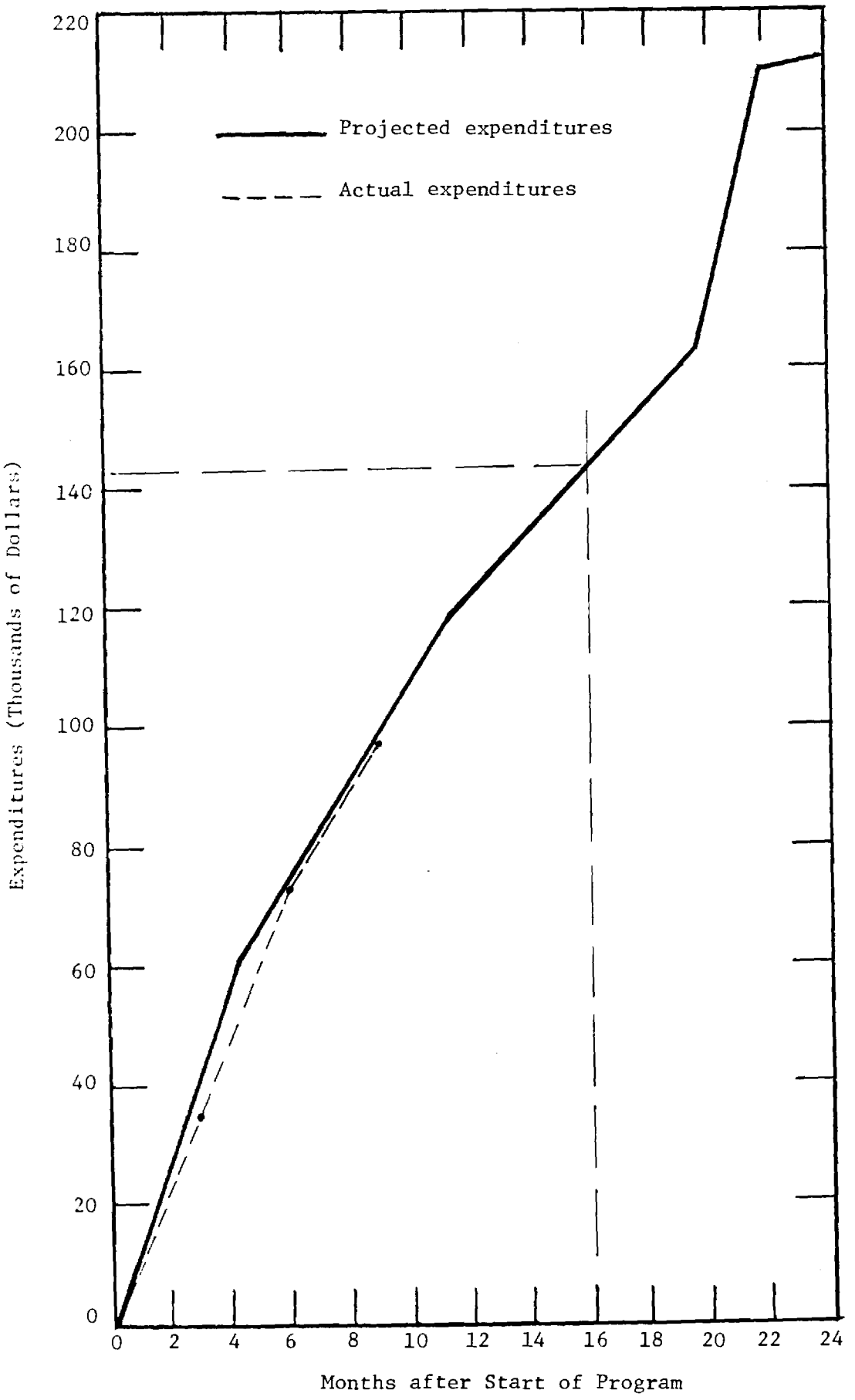

Figure 9. Projected and Actual Expenditures for EPA Contract No. 68-03-3000

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

Quarterly Report
September 1981

by

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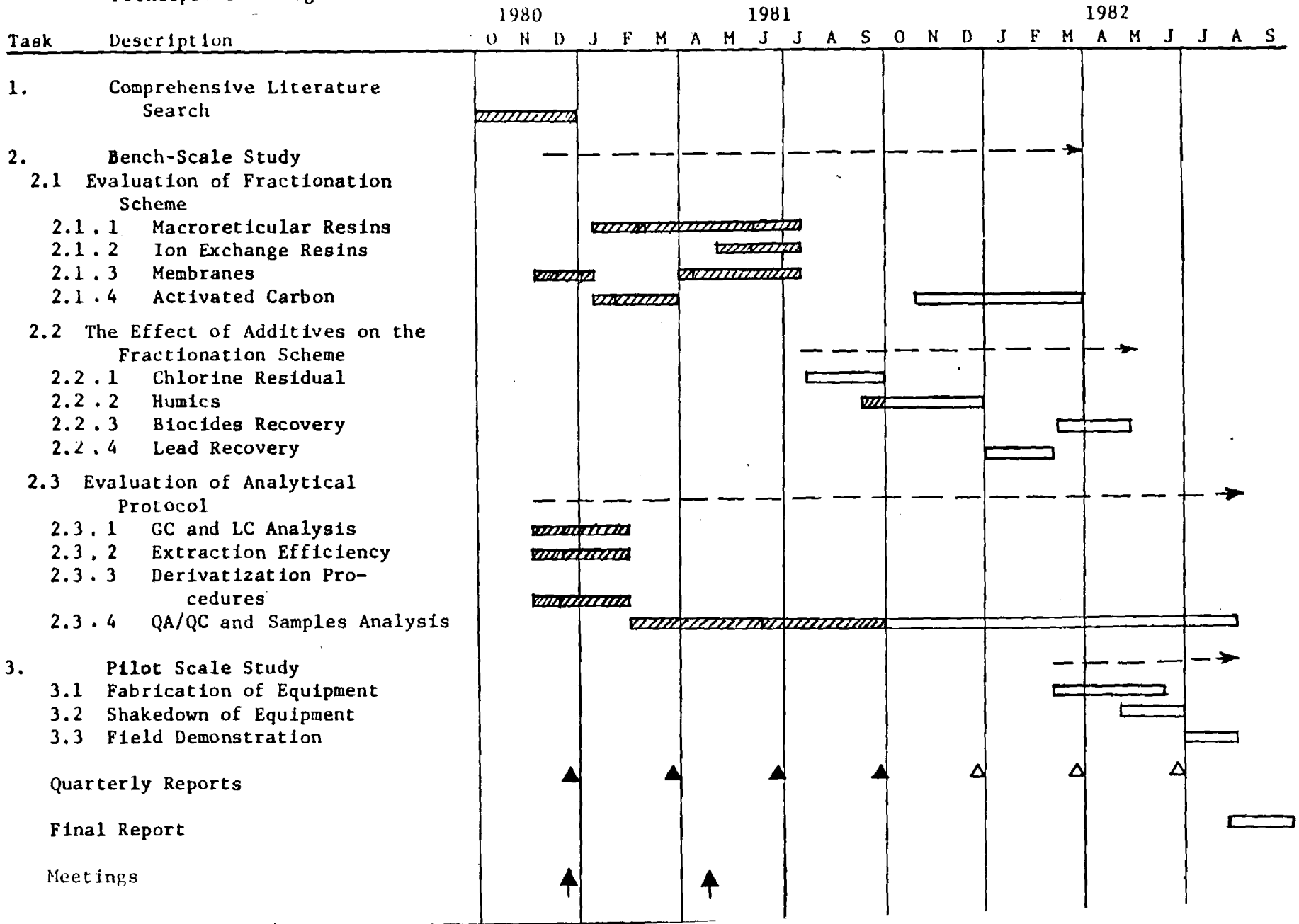
I. INTRODUCTION

This report summarizes the work performed during the period June 1, 1981 through August 31, 1981 on the EPA research program on "Evaluation of Methods for the Isolation or Concentration of Organic Substances from Water" (Contract No. 68-03-3000). The major efforts have been directed toward evaluation of the resin fractionation scheme in the presence of salts, completion of development of methodologies for the analysis of the model compounds under study by GC-MS, improvements of lab-scale "organic free" water for purposes of both analytical and process evaluation and process evaluation with reverse osmosis for specific model compounds. The progress of this efforts are depicted in the Gantt Chart (Chart 1) for the above contract, and are presented in detail in the following sections.

Chart 1 - Schedule for the Proposed Research Program

Project: Evaluation of Methods for the Isolation or Concentration of Organic Substances from Water
Principal Investigators: E. S. K. Chian and J. H. Reuter



II. RESIN FRACTIONATION SCHEME

In the evaluation of the resin fractionation scheme two general problems continued to be prevalent; the relatively low recoveries of test compounds from the resins and the interferences caused by the inorganic salts. In order to minimize these problems several different approaches were investigated.

Recovery

As previously reported, three methods had been utilized for the elution of the hydrophobic neutrals from the XAD-8 resin: 1) soxhlet extraction of the air-dried resin with methanol; 2) soxhlet extraction with CH_2Cl_2; and 3) elution with CH_2Cl_2 directly from the column. It was concluded that soxhlet extraction with methanol was the preferred method. The recoveries of the neutral compounds from the resin, however, were relatively low with an average recovery of only 43% for seven hydrophobic neutral compounds. In an attempt to improve the recovery, an additional elution method was tested. It consisted of a batch elution with CH_2Cl_2 without air-drying the resin. The XAD-8 resin (with the hydrophobic neutral compounds) is transferred to a beaker as a slurry in organic free water. The resin is rinsed several times with water and after each rinse the water is decanted. The resin is then transferred to a separatory funnel with CH_2Cl_2. The organic compounds are extracted by shaking with several volumes of CH_2Cl_2. The collected CH_2Cl_2 is dried with Na_2SO_4 and concentrated to one ml in a KD apparatus.

This procedure was initially tried on run D-2 (see Table 1). For

Table 1

Percentage Recovery ($\overline{X}$) of Model Compounds from Resin

Fraction/Compound	Sample D-1	D-2	E-1	E-2
Hydrophobic bases				
Quinoline	34	26	9	27
5-chlorouracil (not quantified)				
Hydrophobic acids				
Stearic acid	5	10	5	3
Trimesic acid and 2,4 Dichlorophenol (not quantified)				
Hydrophobic neutrals				
Isophorone	33	87	26	28
Biphenyl	27	85	48	44
1-chlorododecane	4	71	29	26
2,6 di-tert-butyl-4 methyl phenol	15	71	51	52
2,4 dichlorobiphenyl	33	112	58	54
Anthraquinone	22	107	43	23
2,2',6,6' tetrachloro-biphenyl	12	49	33	27
Bis (2-ethyl) phthalate	10	225	NQ	194
Benzo (e) pyrene	7	28	NQ	NQ
* 2,4 dichlorophenol	-	34	-	41
Hydrophilic bases				
Caffeine (not quantified)				
Glycine (not quantified)				
Hydrophilic acids				
Quinaldic Acid (not quantified)				
Hydrophilic neutrals				
Glucose (not quantified)				

* pH of test solution at first pass through XAD-8 resin was neutral for runs D-2, E-2.

comparison, the hydrophobic neutrals on run D-1 were eluted by the methanol soxhlet extraction. The test solutions in these runs were 500 ml of organic free water containing 50 µg/liter of the 20 organic compounds plus 120 mg/liter $CaSO_4$; 70 mg/liter $NaHCO_3$; and 47 mg/liter of $CaCl_2 \cdot 2H_2O$. As is clearly shown, the CH_2Cl_2 elution of the neutral compounds resulted in much higher recoveries than the soxhlet with methanol. For the seven compounds previously discussed the average recovery with CH_2Cl_2 was 83%, as compared to a 21% recovery in run D-1. The 83% is also about twice the average recovery of the previous six runs.

The chromatogram of the CH_2Cl_2 extract shared numerous extraneous peaks; however, the response for the test compounds is extremely good. It is believed that the contaminants can be eliminated by including an additional resin clean-up step with CH_2Cl_2 prior to its use for fractionation.

The batch elution method has the potential to allow for relatively high recoveries of the test compounds. The method, however, is apparently very sensitive to technique. As seen on Table 1, two additional runs E-1, E-2 utilizing this method for the elution of hydrophobic neutrals did not result in the high recoveries found in run D-2. It is clear that, when dealing with low concentrations of test compounds, small changes in elution and concentration procedures can produce substantial variances in recovery percentages.

Based on the above data, however, it is apparent that drying the XAD-8 prior to elution of the hydrophobic neutral compounds is not necessary and may be detrimental to their efficient recovery. Batch

elution of the undried resin with CH_2Cl_2 will be evaluated in subsequent runs.

Inorganics

The presence of the inorganic ions, especially Ca^{++} has a profound effect on the fractionation scheme. As previously reported, the formation of a precipitate severely interferes with the recovery of quinoline from the hydrophobic base fraction. In addition to the formation of the $Ca(OH)_2$ precipitate, it is apparent that Ca^{++} affects the acid/base characteristics of the test compounds. Stearic and trimesic acids, for example, have not been quantified in the hydrophobic acid fraction. It is likely that Ca^{++}, the equivalent concentration of which dominates that of the acids by 3 orders of magnitude, may form complexes such as $RCOOCa^+$ and RCOOCaOH. The range of pH at which this occurs is quite large. At an initial test solution pH 7, these neutral complexes may be trapped during the initial pass over the XAD-8 resin. When the hydrophobic bases are eluted with 0.1N HCl the complexes could be reionized to $RCOOCa^+$ and eluted with the base fraction. If not removed with the base fraction, the complexes could be reionized when the test solution at pH 2 is passed through the resin. If charged (ionized) a second time, they would not be adsorbed onto XAD-8.

It is clear that the formation of Ca^{++} complexes has an impact on the fractionation scheme both for the acid and base compounds. In an attempt to eliminate this problem, we tried to desalt the test solution (containing 12 of the test compounds plus the inorganic salts) by passing it through a column containing a cation exchange resin (AG

50 X-8, Na^+ form). It was found that this initial desalting (Ca^{++} removal) step was not feasible because a high percentage of many of the organic compounds was adsorbed on the ion-exchange resin (Table 2). Especially affected were the three biphenyls and 1-chlorododecane, which were quantitatively adsorbed.

Table 2

Effect of Initial Desalting on Test Compounds

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-ethyl)phthalate	62
Benzo(e)pyrene	29
Biphenyl	0
1-Chlorododecane	0
2,4 dichlorobiphenyl	0
2,2',5,5' tetrachlorobiphenyl	0

*Average for two runs

Without the initial Ca^{++} removal, the resin fractionation scheme as presently described may not be effective in separating the acid and base fractions. Additional work is necessary to determine the extent of the Ca^{++} complexing problem and how it affects the ability of the test compounds to be separated into the hydrophobic and hydrophilic acid and base fractions.

SUMMARY OF FRACTIONATION SCHEME

1. Hydrophobic Base Fraction:

Quinoline

5-Chlorouracil

As previously reported, Quinoline is apparently trapped by the $Ca(OH)_2$ precipitate which forms when the base fraction is adjusted to pH 10 prior to the extraction of Quinoline by CH_2Cl_2. Three procedures were tried to overcome this problem. First, a desalting step using an ion-exchange resin (BioRad AG 50 X-8 Na^+ form) was tried on this fraction at neutral pH. It had been shown earlier that 86% of the quinoline was trapped by this resin when a solution of 12 compounds was applied (Table 2). When the base fraction, containing quinoline and possibly 5-chlorouracil, was passed through the resin, however, again a high proportion of the quinoline (75%) was adsorbed. An initial ion-exchange for this fraction is not considered practical because only 25% of Quinoline is recovered. A second method was to perform the CH_2Cl_2 extraction at the highest pH that would not result in precipitate formation. At this pH (8.2), however, it was found that no quinoline was extracted from the base fraction by CH_2Cl_2. Finally we tried to minimize the trapping of organic molecules by the aging and recrystallizing of the $Ca(OH)_2$. We raised the pH of the fraction to 10 and immediately extracted the solution with CH_2Cl_2 before the precipitate was fully developed. This resulted in quinoline recoveries as high as 30% in run D-1, much higher than obtained in previous runs. This procedure is currently the preferred method for quinoline

extraction.

5-Chlorouracil has not been quantified in any of the hydrophobic base fractions. Splits from the other fractions will be derivitized to determine its location in the fractionation scheme.

2. Hydrophobic Acid Fraction:

Stearic acid

Trimesic acid

2,4 dichlorophenol

Until now only stearic acid has been quantified in the hydrophobic acid fraction and this with very small recoveries (<10%). The problem, as discussed above, is most probably caused by the formation of complexes with Ca^{++}. Future work will determine if these acids are being eluted in one of the other fractions.

It should be noted that, although 2,4 dichlorophenol has not been quantified in the hydrophobic acid fraction, it has been recovered in the hydrophobic neutral fraction at recovery percentages of 30-40%. This is found when the test solution is passed through the XAD-8 resin at an initial pH of 7 rather than 10. Runs D-2 and E-2 were initiated with the test solution at neutral pH to prevent precipitate formation. See Table 1 for 2,4 dichlorophenol recoveries in these runs.

3. Hydrophobic Neutrals:

Isophorone	Anthraquinone
Biphenyl	Bis(2-ethyl)phthalate
1-chlorododecane	Benzo(e)pyrene
2,4 dichlorophenol	2,6-di-tert-butyl-4
2,2',5,5' tetrachlorobiphenyl	methyl phenol

The above discussed batch extraction with CH_2Cl_2 increases the recovery of these compounds in the hydrophobic base fraction substantially.

It was suspected that the previous low recovery of benzo(e)pyrene was caused by incomplete dissolution of this compound in the aqueous phase. We therefore prepared a new test solution of benzo(e)pyrene by dissolving the compounds by a method communicated by Horzempa[1] for dissolving PCB's. The compound is added to a large beaker with several milliliters of hexane. The solution is then allowed to evaporate. A few milliliters of acetone is then added and allowed to evaporate. The compound is finally dissolved by filling the beaker with organic free water. Sonification was used after the addition of hexane, acetone and water. Comparison of this solution with a previous standard revealed that the amounts 2,2',5,5' tetrachlorobiphenyl and benzo(e)pyrene in solution increased by factors of 2 and 4 respectively. This procedure was used in all runs reported here.

Bis(2-ethyl) phthalate is an ever present contaminant that probably causes the unusually high reported recoveries.

4. Hydrophilic Base Fraction:

caffeine

glycine

Only trace amounts of caffeine have been found in this fraction so far. Glycine has not been quantitized. Since the GC response for caffeine is relatively low and our recovery percentages are low, caffeine may have escaped detection. Glycine, on the other hand, may be

coming out in another fraction due to effect of Ca^{++} complexing. Other fractions have not yet been checked for the presence of glycine.

5. Hydrophilic Acid Fraction

Quinaldic acid

This compound has not been quantitized in the hydrophilic acid fraction. It appears that we experience the same problems with this acid as with the hydrophobic acids. We have to re-evaluate our procedures in light of the above discussion regarding Ca^{++} complexation.

6. Hydrophilic Neutrals:

Glucose

Glucose has not been quantitized due to derivitization problems.

Future Work

1. Derivatize splits from all fractions to determine if the acids and glycine are being eluted in a different fraction due to Ca^{++} complexing.
2. Determine if graphitized carbon black is effective for the adsorption of the acids.
3. Investigate other methods for the elimination of Ca^{++} complexing problems, e.g. desalting with Chelex-100 resin.
4. Make additional fractionation runs to determine consistency of recovery percentages.
5. Invert the initial sequence of adsorption onto XAD-8: instead of beginning with the hydrophobic bases, acidify the test solution initially to pH 1.8 to first adsorb the hydrophobic acids.

III. ANALYTICAL METHODOLOGY

A. Derivatization, Gas Chromatography

A derivatization method by means of N,O-bis-(Trimethylsilyl)trifluoroacetamide (BSTFA) proved to be successful for the assessment of 5-chlorouracil by GC. Furfural and methylisobutylketone have been quantitatively evaluated by means of liquid-liquid extraction and GC analysis. The experimental details and the statistical evaluation of the quantitative data are reported in the following sections.

The use of surrogates in order to monitor the analytical methodology for the assessment of the model compounds (such as liquid-liquid extraction, derivatization, lyophilization, etc.) has been considered and four compounds have been temporarily selected: L-alanine, undecanoic acid, 3-quinolinecarboxylic acid and 2-methylquinoline. Other surrogates will be added to the list. The statistical evaluation of the quantitative data relative to all surrogates selected will be reported in the next quarterly report.

5-Chlorouracil

Literature search revealed that BSTFA has been used to derivatize pyrimidine and purine bases. According to Gehrke *et al.*[2] (1971) the best reaction conditions for micro amounts of bases were the use of 50 µl BSTFA, 25 µl acetonitrile and 25 µl dichloroethane heated in a closed micro reacti-vial at 150°C for 30 minutes. We followed this experimental conditions and found the method successful for the preparation of trimethylsilyl derivative of 5-chlorouracil. The gas chromatograms relative to the reaction mixture with and without presence of 5-chlorouracil are presented in Fig. 1a and 1b, respectively, and the mass spectra obtained by GC-MS analysis is reported in Fig. 2. Results of the reproducibility study for the derivatization method are reported in Table 3. Figure 3 presents the computer

MASS SPECTRUM
07/23/31 16:47:00 + 17:05
SAMPLE: DERIVATIVE 5-CHLOROURACIL + IS SAMPLE 65-4
ENHANCED (S 15B 2N 0T)

DATA: URACIL #1025
CALI: CALGAS #20

BASE M/E: 275
RIC: 237568.

Figure 2

5-Chlorouraciltrimetylsilyl derivative

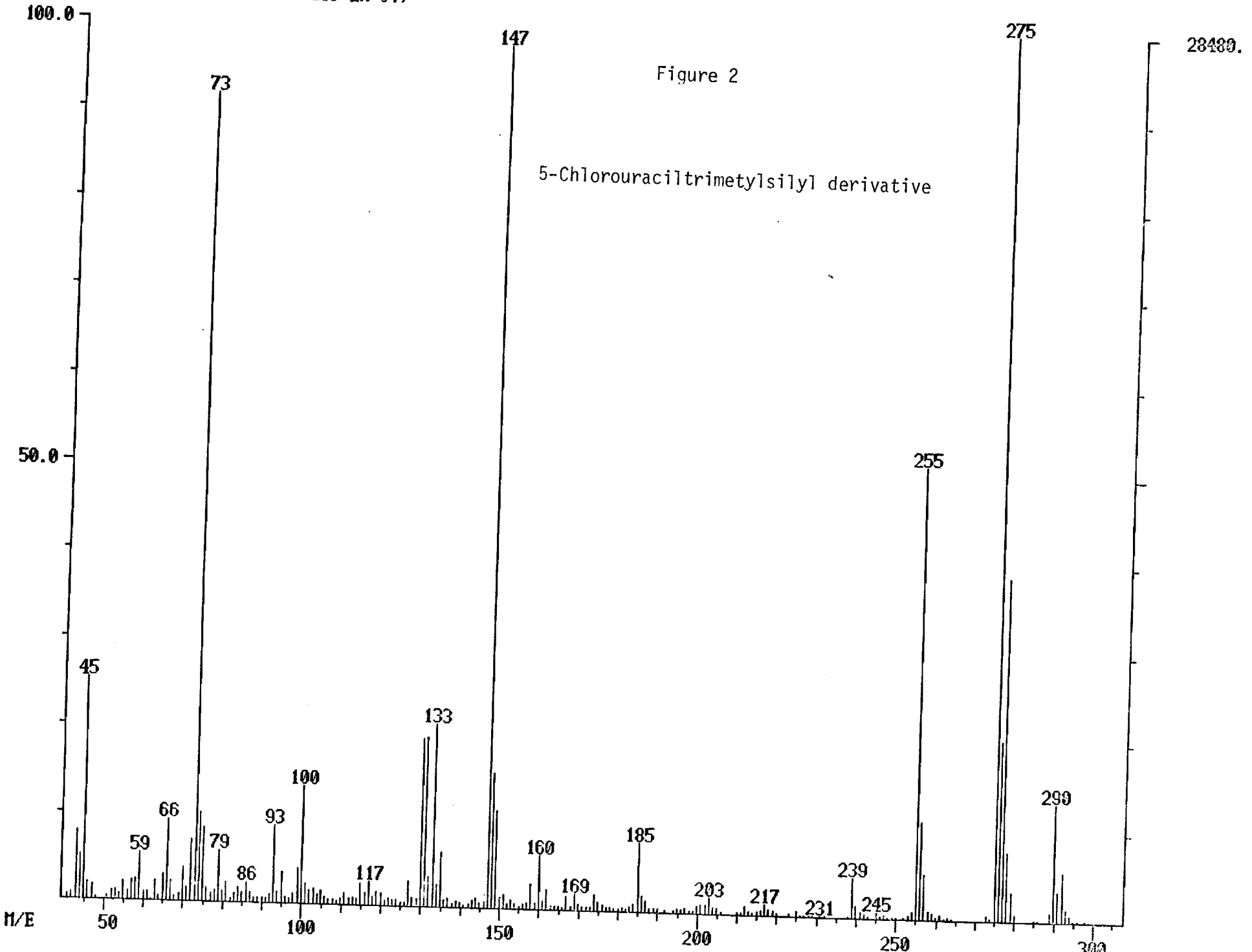


TABLE 3. Reproducibility and Linearity of GC-Detector Response for 5-chlorouracil

Sample No.	Wt. of 5-chlorouracil derivatized	Area (1)	Area (I.S.)	Mean	σ
65-2	10	401	3604		
65-3	50	2101	3765		
65-4	100	3416	2542		
65-5	20	575	2806	17.375	1.463
65-6	20	579	2798		
65-7	20	499	2946		
65-8	20	509	2602		

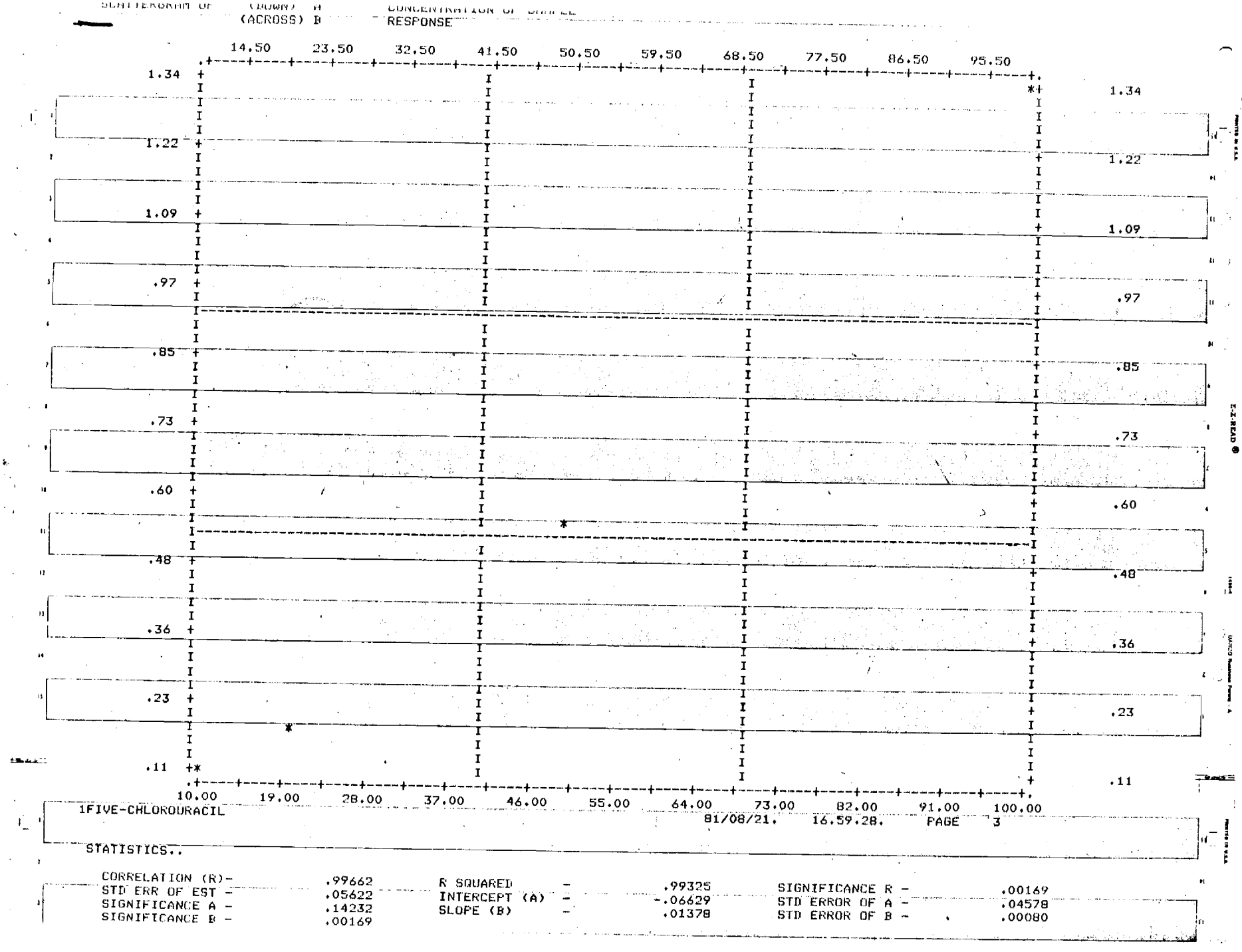

SCATTERGRAM OF (DOWN) A (ACROSS) B
CONCENTRATION OF STD'S
RESPONSE
14.50 23.50 32.50 41.50 50.50 59.50 68.50 77.50 86.50 95.50
1.34
1.22
1.09
.97
.85
.73
.60
.48
.36
.23
.11
10.00 19.00 28.00 37.00 46.00 55.00 64.00 73.00 82.00 91.00 100.00
1FIVE-CHLORODURACIL
81/08/21. 16.59.28. PAGE 3
STATISTICS..
CORRELATION (R)- .99662
STD ERR OF EST - .05622
SIGNIFICANCE A - .14232
SIGNIFICANCE B - .00169
R SQUARED - .99325
INTERCEPT (A) - -.06629
SLOPE (B) - .01378
SIGNIFICANCE R - .00169
STD ERROR OF A - .04578
STD ERROR OF B - .00080

Figure 3

printout of the scattergram and regression statistics for the linearity of GC-FID response with different weight of 5-chlorouracil derivatized.

Furfural, Methylisobutylketone

Liquid-liquid solvent extraction was evaluated for the isolation of furfural and methylisobutyketone from water solutions. 250 ml of "organic-free" distilled water were fortified with the two model compounds at 200ppb level and extracted in a separatory funnel with three aliquots of methylene chloride (50:25:25). The organic solution was then concentrated to 1 ml by K-D and nitrogen blowing. The two compounds were previously analyzed by GC-FID and assessed for reproducibility, linearity and lower detection limit. The reproducibility study was performed by injecting 1 µl of a 50ppm standard solution and the results for 5 readings are reported in Table 4. The linearity study was performed on 10, 20, 50 and 100ppm standard solutions and the results obtained are reported on Table 5. From this evaluation it was possible to establish for furfural a lower detection limit of 20ppm (20 ng/µl), while for MIBK was 10ppm (10 ng/µl). All the quantitations were obtained by the internal standard method using hexamethylbenzene as internal standard. The liquid-liquid extraction evaluation was performed on 5 different water solutions fortified at 200ppb. The results obtained are reported in terms of % recovery, mean % recovery ($\bar{x}$) and standard deviation (σ) in Table 6.

TABLE 4. Reproducibility of GC-FIC response for 50ppm (50 ng/μl), Solutions

Compound	1	2	3	4	5	$\bar{x}$	σ
MIBK	50.0	53.34	50.05	54.03	46.98	50.88	2.85
Furfural	50.0	45.97	55.18	47.00	51.19	49.86	3.5

TABLE 5. Linearity of GC-FID response for 10, 20, 50, 100ppm Solutions

Compound	10ppm	20ppm	50ppm	100ppm	r
MIBK	7.5	18.6	51.4	94.3	0.9979
Furfural	ND	13.6	49.8	130.3	0.9974

TABLE 6. Recovery Study of Liquid-Liquid Extraction of 250 ml Water Solution Spiked at 200ppb Level.

Compound	% Recovery	Mean % Recovery ($\bar{x}$)	σ (%)	Mean Recovery Factor (c)
MIBK	75.32 51.58 66.96 79.39 81.84	71.01	12.25	1.41
Furfural	80.73 62.83 60.5 74.16 74.59	70.56	8.57	1.42

B. "Organic-free" water

The proposed modifications reported in the previous quarterly report have been incorporated: i) the PVC headers of the U.V. unit were removed and substituted with teflon tubing in order to decrease the TOC contribution experienced with the original design; and ii) after discussion with the project officer, the demineralizer and organic removal assembly was replaced by a column (1" in diameter, 2 feet long, PYREX) packed with 50 gr. of Filtrasorb F-400 (16-30 mesh) vergin activated carbon (Calgon Corp., Pittsburgh, PA). Baked glass wool was used to retain the carbon bed into the column. The schematic of the new system is shown in Fig. 4.

A higher flow rate resulted from the replacement of the demineralizer and organic removal assembly. The system was operated at a flow rate of 1.5 l/h and the TOC of the processing water was evaluated at the following points: i) inlet of carbon column; ii) outlet of carbon column; and iii) outlet of U.V. unit. Two water samples at the outlet of the U.V. unit were collected with the U-V lamps "off" and "on" respectively, in order to estimate the contribution of the U.V. unit to the TOC. Samples of finished water with and without H_2O_2 were also analyzed for its TOC content. The results regarding these evaluations are reported in Table 7.

The finished water from this system was also subjected to liquid-liquid extractions in order to verify the level of impurities and possible interferences with model compounds. 250 ml of water was extracted with 100 ml of methylene chloride (50:25:25). The extractions were performed at pH<2 and pH>11. The two extracts were subsequently concentrated to 1 ml using Kuderna-Danish apparatus. D-6 Phenol and Quinoline were used as surrogates.

The results of the study presented in Table 7 imply a definite improvement obtained with the performed modifications. As compared to a two-fold TOC reduction by the demineralizer-organic removal cartridge, the carbon column

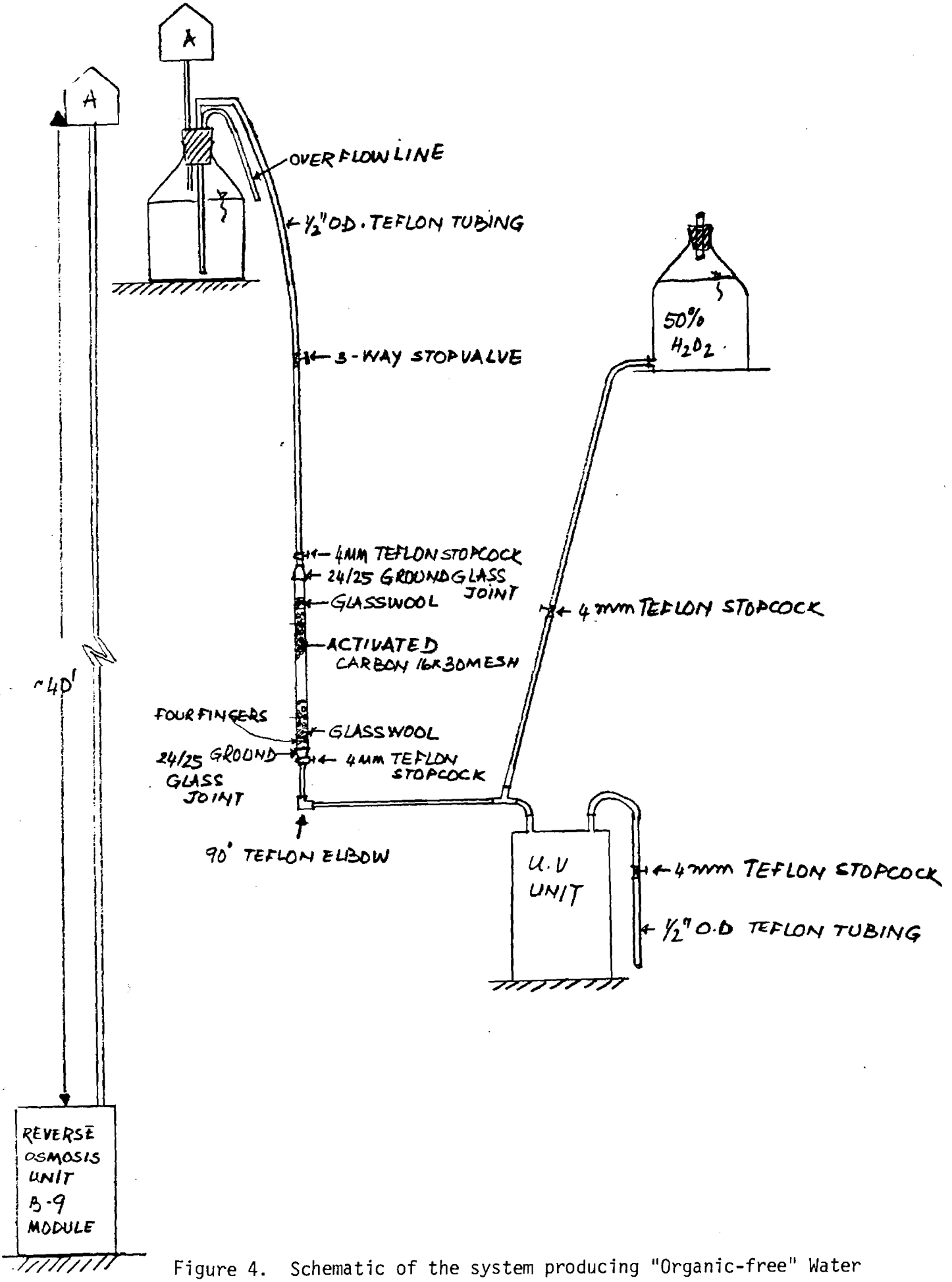


Figure 4. Schematic of the system producing "Organic-free" Water

Table 7. TOC Values (ppm) of Water Samples at Various Stages of the System.

Sample Source	TOC (ppm)		95% CI
Inlet of the carbon column	4.090	±	0.800
Outlet of the carbon column	0.392	±	0.008
Outlet of the U.V. unit			
i) with U.V. lamps "off"	0.478	±	0.008
ii) with U.V. lamps "on"			
a) without H_2O_2 addition	0.329	±	0.007
b) with H_2O_2 addition (3.3% v/v)	0.234	±	0.005

functions much better. It attains a near ten-fold reduction in the TOC values thereby reducing the load on the U.V. unit. A TOC value of 0.478ppm for the finished water with the U.V. lamps "off" imply that the U.V. unit is now contributing less than 0.1ppm TOC. With peroxide addition the finished water has a TOC value of 0.234ppm ± 0.005ppm. This indicates that the U.V. unit is now accomplishing a reduction of 49%.

Figures 5 and 6 present the gas chromatograms of the water extracted at pH<2 and pH>11, respectively. From these figures the absence of major impurities, which eventually may interfere with the model compounds, is ascertained.

A water with even lower TOC background is desirable and to obtain this a new U.V. unit has now been installed. In this U.V. unit the water flows through a teflon tube of 1/2 inch O.D. and 7/16 inch I.D. which is exposed to the irradiation of three U.V. lamps (G.E. Germicidal Lamps 25 watts), instead of two as in the previous unit. The smaller I.D. Teflon tube would facilitate a higher flow rate through the unit and would also allow a better "penetration" of U.V. irradiation. This will probably lead to a more efficient formation of peroxide free radicals, with higher oxidation efficiency and subsequently lower TOC value.

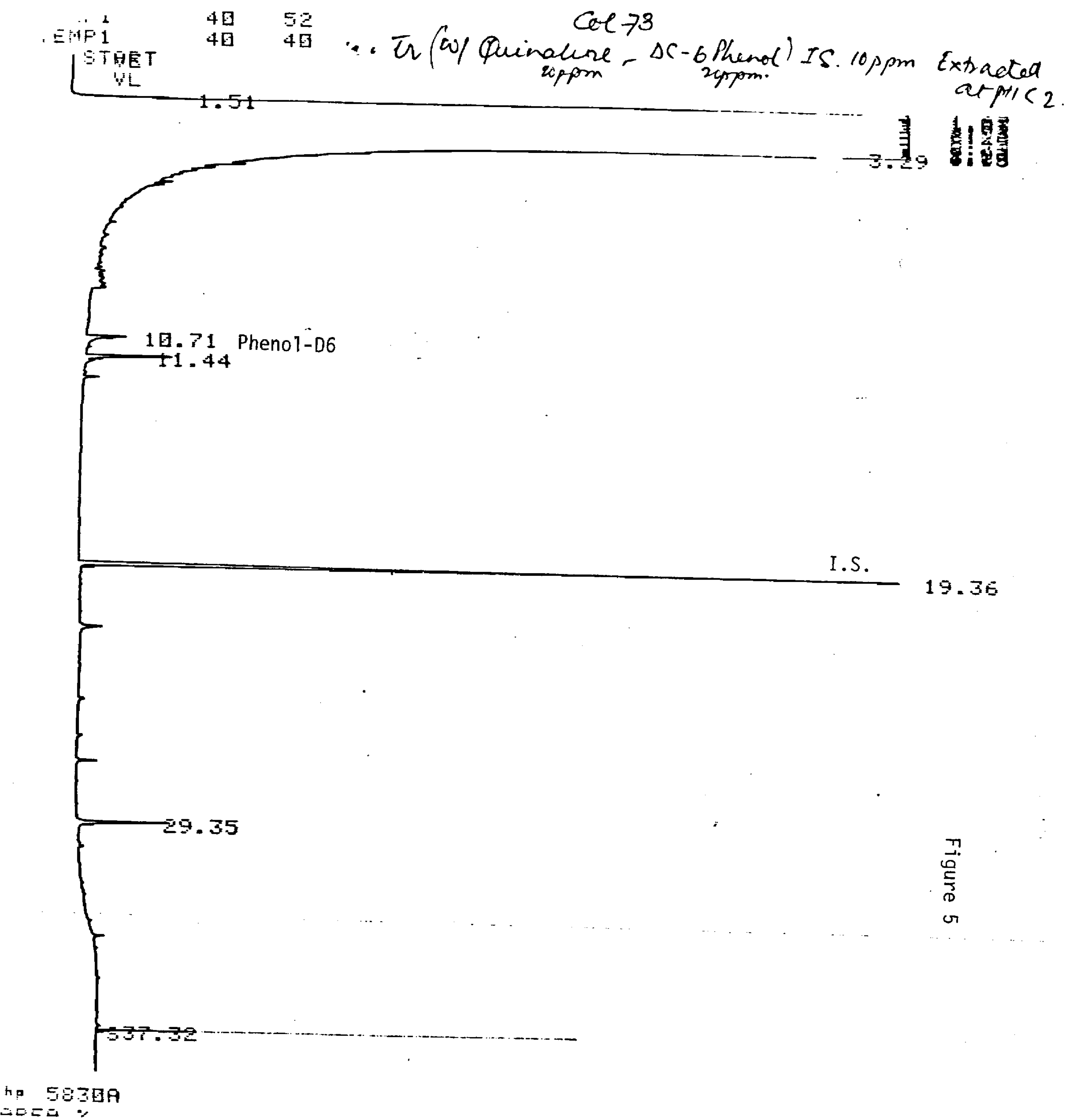

EMP1 40 40
40 52 40
START
VL
Col 73
Tr (w/ Quinaline - DC-6 Phenol) IS. 10ppm Extracted at pH < 2.
20ppm 20ppm
1.51
3.29
10.71 Phenol-D6
11.44
I.S.
19.36
29.35
37.32
hp 5830A

Figure 5

Figure 6

IV. PROCESS EVALUATION

Reverse Osmosis

The study related to this area undertaken during this quarter was the evaluation of the performance of B-10 Hollow fiber polyamide Permasep permeator (DuPont) and TFC 4400-PA spiral wound RO modules (UOP) in rejecting glucose, methylisobutyl ketone (MIBK), crotonaldehyde and furfural.

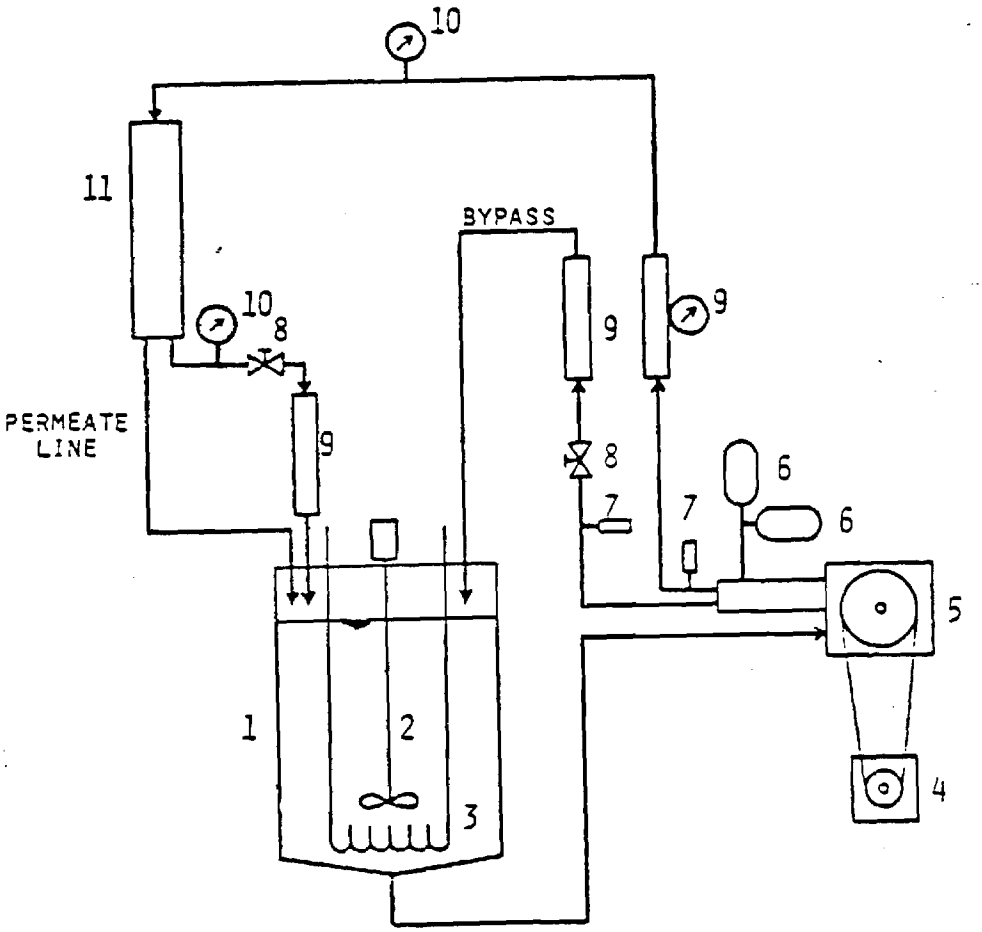
The RO system used in this study was operated in a closed loop configuration (See schematic in Figure 7) at constant temperatures with the aid of a separate cooling unit. A positive displacement piston pump (Cat model 520, Cat Pumps, Minneapolis, Minnesota) was used to deliver the feed from the storage tank to the module. The feed flow rate and pressure were controlled with the aid of a pressure regulator in the concentrate line and a needle valve in the by-pass line. The cooling unit employed to maintain the feed temperature was a Blue M Model PCC-34 C (Blue M Elec. Co., Blue Islands, IL). Water was cooled in a separate holding tank. This water was then pumped through a copper coil submerged in the feed of the storage tank.

B-10 Hollow Fiber Module

The hollow fiber RO module employed in this study was a 5-in diameter DuPont B-10 PERMASEP permeator model 6440-015. Tightly packed bundles of aromatic polyamide (nylon) hollow fibers having dimensions of 52 μm I.D. and 85 to 100 μm O.D. are housed in a reinforced fiberglass pressure vessel. Specifications of this module are presented in Table 8.

TFC 4400-PA Spiral Wound Module

The TFC 4400-PA spiral wound module used in this study was a 4-in diameter, single leaf configuration. The module consists of two membrane sheets (with skin layer oriented outwards) separated by a spacer. This spacer supports the membranes and provides a flow path for the permeate. The set is rolled up



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 - R.O. MODULE

Figure 7. Schematic of the RO System

around the collector tube, which has anti-telescopic device at both ends. The entire assembly is enclosed in a reinforced fiberglass pressure vessel. Specifications of this module are presented in Table 9.

Membrane Rejection of Model Compounds

The feed for these experiments was prepared with the "organic-free" water produced by the system described in the previous section. Forty liters of water was used in each study. Prior to the addition of the model compounds, the water was passed through the RO system for thirty minutes in order to establish a water system blank. Apart from glucose, which was added in powder form, other compounds were added in solution form. Solutions of MIBK, Crotonaldehyde and Furfural in methanol (500 ppm) were used as stock solutions. The feed concentration of glucose was 50 ppm. The feed concentration of MIBK, Crotonaldehyde and Furfural was approximately 500 ppb. In order to take into consideration the residual water present in the system, the system was operated for twenty minutes at 600 psig and 250 gph prior to the experiment. The system was then stopped and a sample was taken from the water in the feed tank and analyzed in order to evaluate the actual starting concentration of the model compounds. The system was then operated at 600 psig, 250 gph and 25°C±1°C for thirty minutes. Permeate samples were then collected from the permeate line.

These samples (250 ml) were analyzed according to the analytical methodology developed and described in the previous sections.

The results of these experiments are presented in Tables 10 and 11. Owing to difficulties in the analytical methodology for glucose and Crotonaldehyde, rejection of these compounds are not reported. The percentage rejections, (r), were calculated using the following equation.

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

TABLE 8. Specifications of B-10 DERMASEP 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	35°C
pH Range (Continuous Exposure)	5-9
Free Chlorine Tolerance	Nil

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

TABLE 9. 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 (Conginuous Exposure	4-6
Free Chlorine Tolerance	Nil

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

TABLE 10. Membrane performance of B-10 RO module.

Compound	Mean Recovery Factor $C^{(1)}$	Feed Concentration		Permeate Concentration		Rejection %
		Raw (ppb)	Corrected (ppb)	Raw (ppb)	Corrected (ppb)	
MIBK	1.41	195.68	275.91	4.04	5.69	97.9
Furfural	1.42	231.16	328.25	36.28	51.52	84.3

TABLE 11. Membrane performance of TFC-4400 PA module.

Compound	Mean Recovery Factor $C^{(1)}$	Feed Concentration		Permeate Concentration		Rejection
		Raw (ppb)	Corrected (ppb)	Raw (ppb)	Corrected (ppb)	%
MIBK	1.41	162.88	229.66	85.64	117.93	48.7
Furfural	1.42	832.27	1181.82	454.6	645.53	45.4

(1) Mean recovery factor = $(\text{Extraction Efficiency})^{-1}$

where:

r = rejection %

C_P = Concentration of compound in permeate

C_B = Concentration of compound in Bulk (feed)

It is seen in Table 10 that a very good rejection (97.9%) of MIBK is accomplished by the B-10 RO module. Furfural was rejected at 84.3%. These rejection values are promising as compared to that obtained with the cellulose acetate membranes. In comparison to the B-10 module, the TFC-4400 PA spiral wound module performed poorly. It gave rejection values of 48.65% and 45.37% for MIBK and Furfural, respectively. The gas chromatograms of water system blank presented in Figure 8 indicate the absence of interference with the compounds studied.

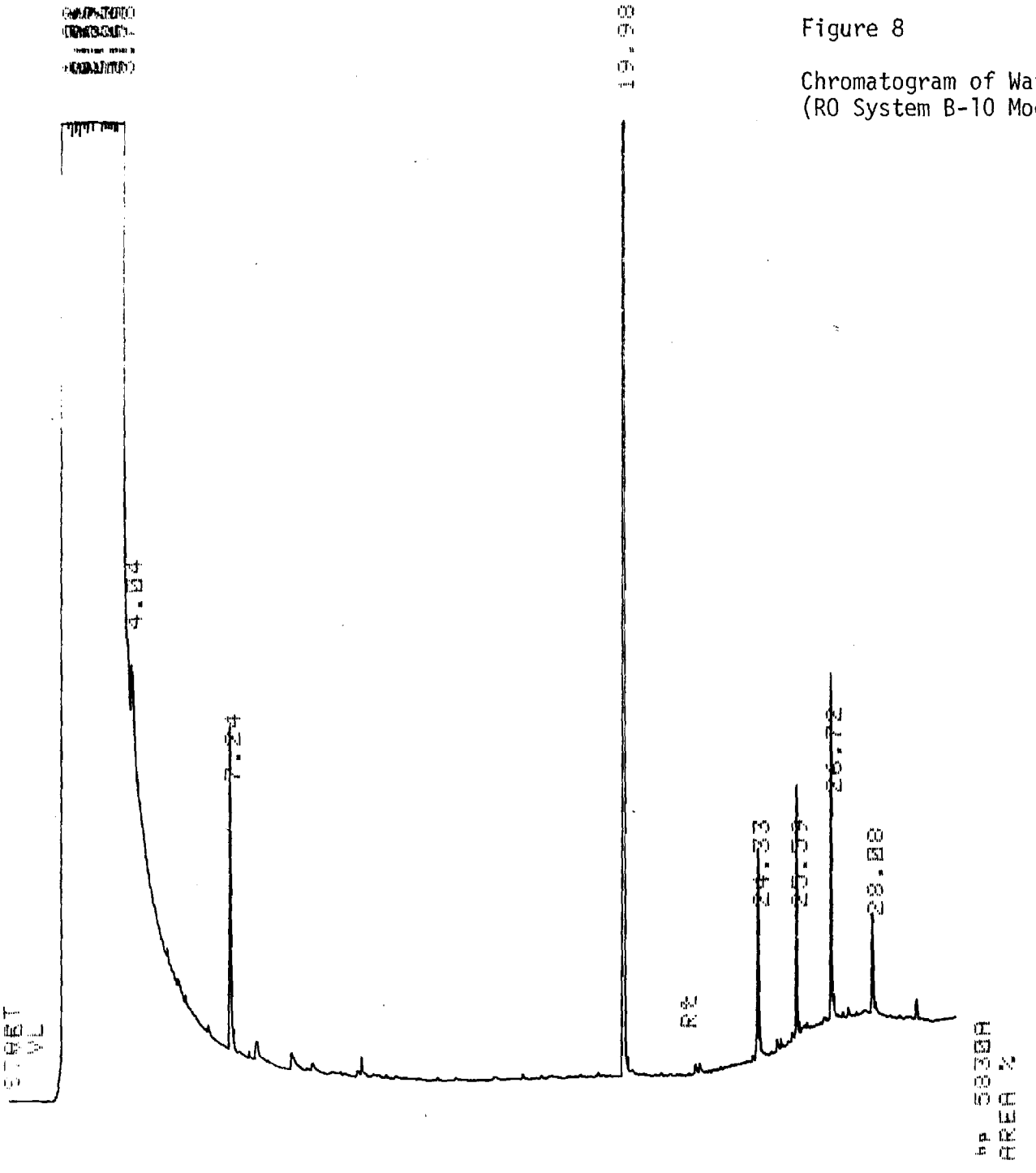


Figure 8

Chromatogram of Water Blank
(RO System B-10 Module)

V. FUTURE WORK

Attempt has been made in this report to include future work of this research program at the end of each section.

VI. EXPENDITURES

The actual expenditures incurred during the fourth quarter of this research program are presented by the dashed line in Figure (between months of 9-12). The solid line represents the expected espenditures in the months to come. So far the actual expenditures run closely to the anticipated ones.

If there is any question regarding this quarterly report, please contact either Edward Chian or Maurizio Giabbai at (404) 894-2265.

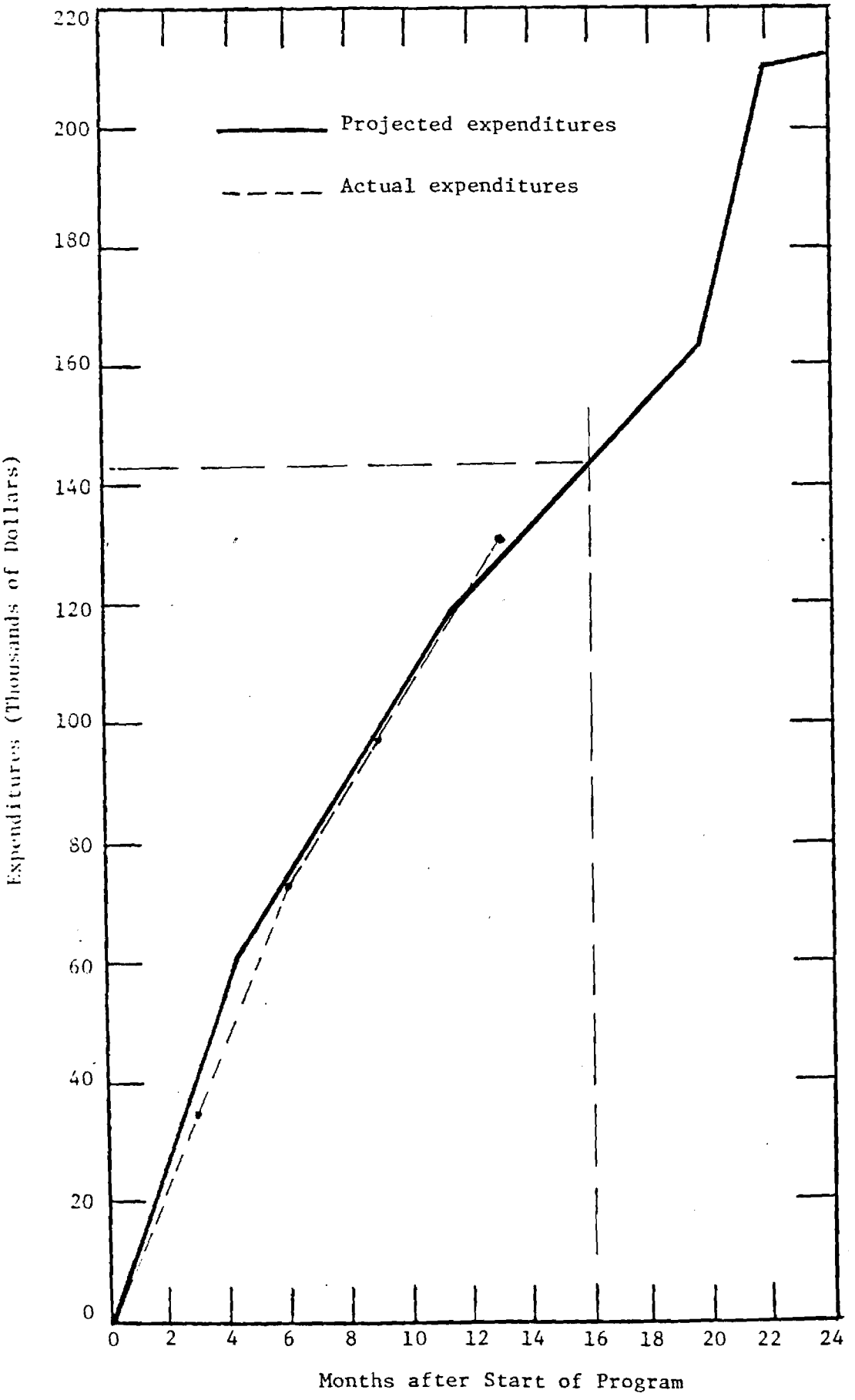


Figure 9. Projected and Actual Expenditures for EPA Contract No. 68-03-3000

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

QUARTERLY REPORT

December 1981

by

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HERL, Cincinnati, OH 45268
Contract No. 68-03-3000

Project Officer
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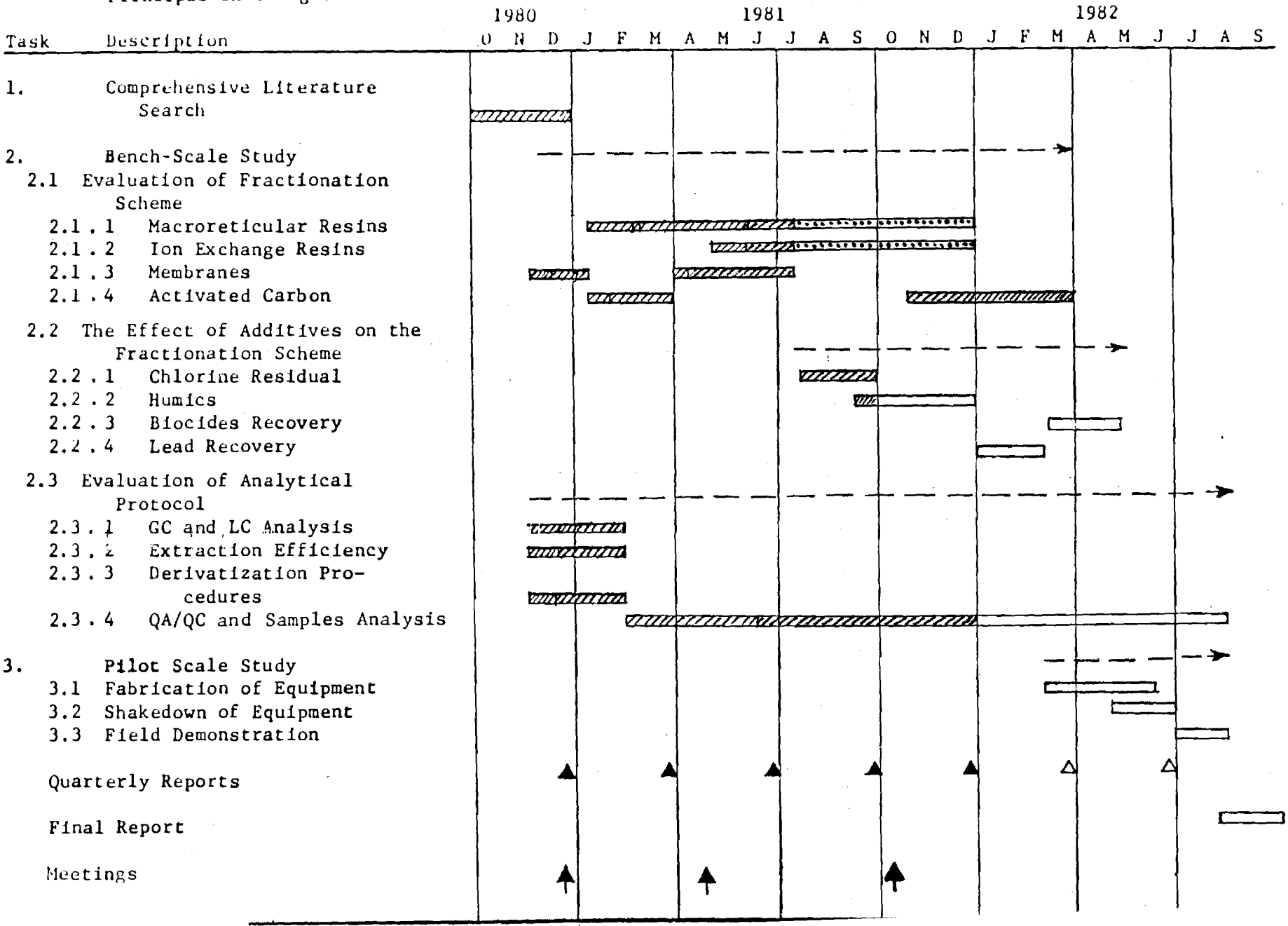
TABLE OF CONTENTS

I. INTRODUCTION

This report summarizes the work performed during the period September 1, 1981 through November 31, 1981 on the EPA research program on "Evaluation of Methods for the Isolation or Concentration of Organic Substances from Water" (Contract No. 68-03-3000). The progress of these efforts are depicted in the Gantt Chart (Chart 1) for the above contract, and are presented in detail in the following sections.

Chart 1 - Schedule for the Proposed Research Program

Project: Evaluation of Methods for the Isolation or Concentration of Organic Substances from Water
Principal Investigators: E. S. K. Chian and J. H. Reuter



II. RESIN FRACTIONATION SCHEME

A. Fractionation and concentration on XAD-8 and AGMP-50

In comparison to our last report we have changed our resin fractionation scheme in the following fashion: we now acidify our test solution to pH 2 (using HCl) before first passage over XAD-8 resin, thus accomplishing the adsorption of hydrophobic acids and hydrophobic neutrals on this first pass. This change in our procedure has eliminated the difficulties we experienced previously with the formation of precipitates upon making the test solution alkaline. However, we are still experiencing difficulties with several compounds: 2,4-dichlorophenol, quinaldic acid, furfural and 5-chlorouracil.

In our previous report (Sept. 81) we noted that 2,4-dichlorophenol could be recovered in the hydrophobic neutral fraction with about 30-40% efficiency if the test solution is passed through the XAD resin at pH 7 (at its first pass). Apparently, the change to pH 2 has a negative effect on the recovery of 2,4-dichlorophenol. More work is needed here.

Since the recovery problems with quinaldic acid from XAD-8 continue to plague us, we have initiated a promising concentration method for the hydrophilic acid fraction on graphitized carbon black (GCB). For details see below.

Table 1 and Table 2 summarize the recovery efficiencies we experience with our revised adsorption scheme. The hydrophobic acids

are recovered first in the same fashion as described previously. The hydrophobic neutrals are extracted from the XAD-resin with methylene chloride. Previously observed contamination of this fraction from the resin was eliminated by the addition of a CH_2Cl_2 clean-up step for the XAD-8. The hydrophobic bases are adsorbed onto XAD-8 at pH 10, and recovered as previously described. The persistently low recovery of quinoline is still troubling.

Comparison of Table 1 and Table 2 shows that with the revised order of adsorption onto XAD-8, the previously reported troublesome salt effects are not experienced, and stearic and trimesic acids are now recovered with comparatively reasonable efficiencies (see Table 2).

During this period we have made an effort to obtain a mass balance for the hydrophobic neutral compounds, indicated in Table 2 by (-). With the exception of phenanthrene and the dialkylphthalate we were unable to detect hydrophobic neutrals in either the hydrophobic acid or the hydrophobic base fraction. They were not detected either in the test solution after the second passage over XAD-8, which should contain the hydrophilic neutral compounds.

Thus, we are forced to conclude that the low recoveries are mainly caused by irreversible adsorption on surfaces of glassware and resins. In view of the low initial concentration of the compounds under investigation, surface adsorption losses appear to be a reasonable explanation, especially since we are making determined

Table 1. Recovery of Organic Compounds;
Test Solution without Inorganic Salts

	% Recovery						
	HBA	HBB	HBN	HLB	HLA	HLN	Total
Acids							
Stearic acid	20					46	66
Trimesic acid	6					6.4	12.4
Quinaldic acid					NF	-	NF
2,4-dichlorophenol	NF	-	-			-	NF
Neutrals							
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
Bases							
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 fractions
NQ: Not quantified
- : Checked but not found

Fraction notations are as follows:

HBA: Hydrophobic acid fraction
HBB: Hydrophobic base fraction
HBN: Hydrophobic neutral fraction
HLA: Hydrophilic acid fraction
HLB: Hydrophilic base fraction
HLN: Hydrophilic neutral fraction

Table 2. Recovery of Organic Compounds;
Test Solution with Inorganic Salts

	% Recovery						
	HBA	HBB	HBN	HLB	HLA	HLN	Total
Acids							
Stearic acid	40.5					-	40.5
Trimesic acid	27.6					-	27.6
2,4-dichlorophenol	NF		-			-	NF
Quinaldic acid					NF	-	NF
Neutrals							
Isophorone	-	-	60.5			-	60.5
Biphenyl	-	-	88.7			-	88.7
1-chlorododecane	-	-	33.7			-	33.7
2,6-ditertbutyl-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
Bases							
Quinoline		NQ					NQ
5-chlorouracil		NF					NF
Caffeine				5.0			5.0
Glycine				68.6			68.6

efforts prior to the experiments to remove organic compounds from these surfaces.

B. Chlorine residual effect study

The effects of a 2 ppm chlorine residual solution on the materials used in the fractionation scheme (i.e., XAD-8, AG MP-50) have been investigated by processing the water solutions under the same experimental conditions used when evaluating the recoveries of the model compounds. "Organic-free" water and the resins were prepared according to the methods reported in previous quarterly reports. The 2 ppm chlorine residual was prepared by diluting a solution of HOCl and verifying it by the DPD Ferrous titrimetric method (1). The following solutions have been processed: 1) water and glassware blank, 2) water and resins blank, 3) 2-ppm chlorine solution and glassware, 4) 2-ppm chlorine solution and resins, 5) 2-ppm chlorine solution at pH 10 and resin. The experimental sequences and the fractions monitored are explained on Figure 1 . All of the experiments were carried out on single runs except for the solution #4 which was run in duplicate. By comparing the GC traces it was possible to verify that no artifacts were introduced in the presence of 2-ppm chlorine residual solutions through the macroreticular and ion-exchange resins.

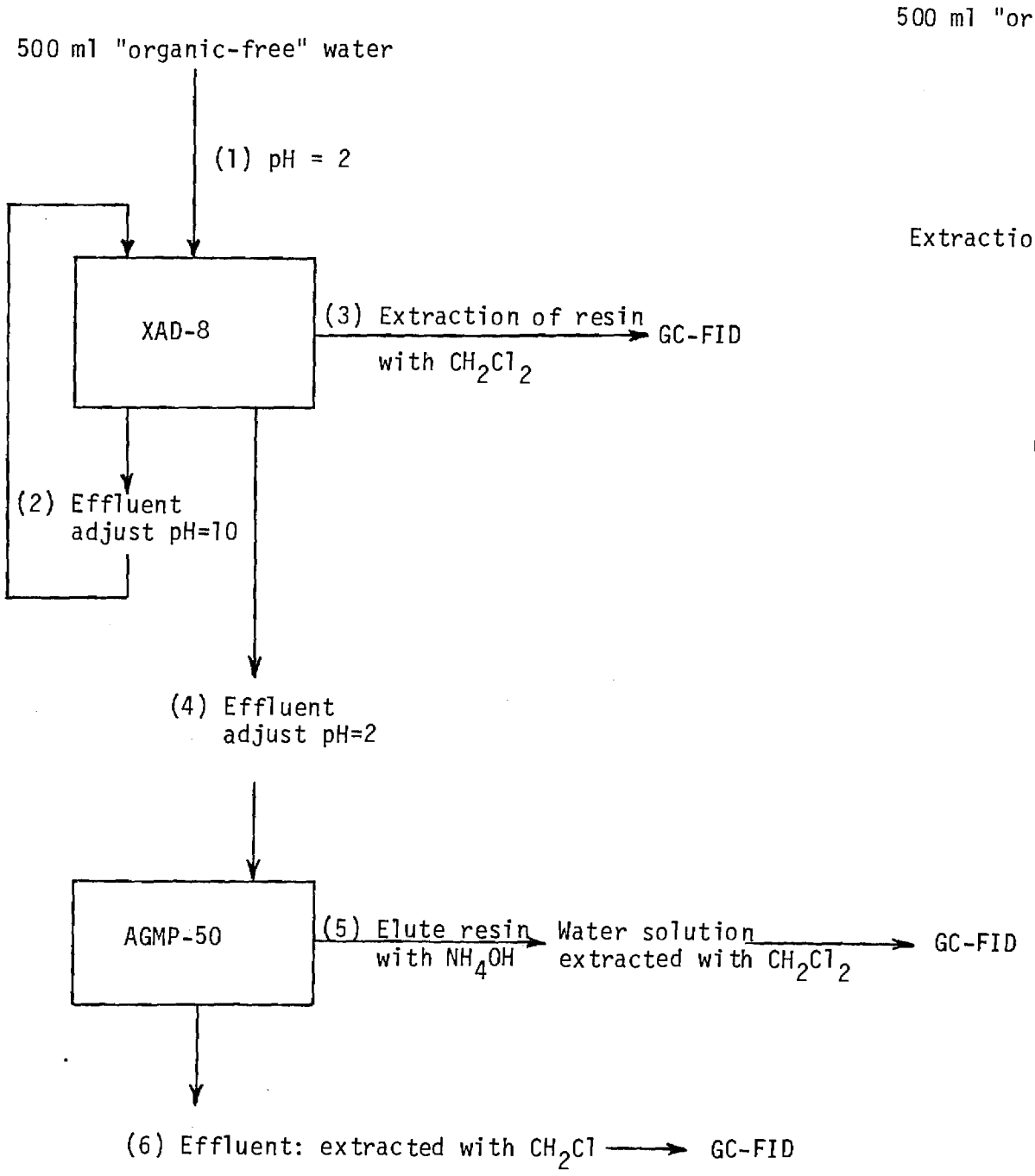


Figure 1. Experimental sequence for the chlorine residual study.

III. Carbon Adsorption Studies

The isolation and recovery of trimesic, stearic and quinaldic acid was evaluated using one type of graphitized carbon black (GCB) and one type of activated carbon (AC).

The GCB employed is denominated Carbopack B (purchased from Supelco, Inc., Bellefonte, PA) which is characterized by a non-porus surface and a specific surface area of approximately 100 m^2/gr. A particle size range of 80-100 mesh was utilized and since the surface is highly homogenous (2), i.e., very low chemical heterogeneities, no pre-washing of the material was necessary. The AC employed is denominated Filtrasorb 400 (purchased from Calgon, Inc., Pittsburg, PA) which is characterized by a highly porous surface and a specific surface area of approximately 1000 m^2/gr. The AC was crushed and sieved to the desired particle size range of 80-100 mesh and then was cleaned according to the method reported by Rossum and Webb (methanol and methylene chloride were used instead of acetone and chloroform, respectively). 200 mg of each adsorbent were packed in a 0.5 cm I.D. glass column which formed a carbon bed height of approximately 4 cm for both materials. The isolation and recovery of the aforementioned compounds was tested at two concentration levels in 500 ml of "organic free" water: 100 and 1000 ppb. The water solution, prior to elution through the adsorbent bed, was acidified to pH 2 with concentrated HCl. The flow rate of the water solution through the carbon bed was maintained at 100 ml/h (~1.66 ml/m) with the help of a water pump, which corresponds to a contact time of approximately 0.47 minutes. Approximately 50 ml of methanol were used to elute the organic compounds from the carbon and at the same flow rate of ~1.66 ml/min. The methanol solution was concentrated to 1 ml by K.D. and after addition of a known amount of surrogates (undecanoic and 3-quinoline carboxylic acid) was solvent exchanged with diethylether. The ether solution was then subjected to derivatization by diazomethane, and after volume adjustment to 1 ml was analyzed by HRCG-FID as described in previous

quarterly reports. A standard solution of the acids and of the surrogates was derivatized right before any batch of samples and analyzed under the same conditions in order to update the GC relative retention times and the relative response factors of each individual compound. The results expressed as % recovery are presented in Table 3 and 4 . It is evident from the comparison of the data that under the afore mentioned experimental conditions, i.e., contact time of approximately 0.47 min., Carbopack B is very effective in retaining the acids, except trimesic acid, however, Filtrasorb 400 instead showed a very low recovery for stearic acid while trimesic and quinaldic acid could not be detected. The generally good recoveries for the surrogates insured that the analytical methodology (i.e., solvent exchange, derivatization) was carried out properly.

No attempt was made to analyze for the acids in the water solution eluted through the carbon column. Therefore it is not possible at this moment to draw exact conclusions regarding the adsorption-desorption process, in particular for AC. However, in the case of GCB we can confidently consider it suitable for the recovery of stearic and quinaldic acid. Assuming that trimesic acid was not efficiently adsorbed, it may be possible to improve its recovery by allowing for longer contact times.

TABLE 3 . Recoveries from Graphitized Carbon Black (GCB)

MODEL COMPOUNDS	% RECOVERY WATER SPIKED AT 100 ppb LEVEL		WATER SPIKED AT 1000 ppb LEVEL
	RUN 1	RUN 2	
Quinaldic Acid	150	126	95
Trimesic Acid	4	8	7
Stearic Acid	48	64	61
Undecanoic Acid(surrogate)	91	102	110
3-Quinoline Carboxylic Acid (surrogate)	121	84	181

TABLE 4 . Recoveries from Activated Carbon

MODEL COMPOUNDS	% RECOVERY WATER SPIKED AT 100 ppb LEVEL	WATER SPIKED AT 1000 ppb LEVEL
Quinaldic Acid	N.F.	N.F.
Trimesic Acid	N.F.	N.F.
Stearic Acid	2	8
Undecanoic Acid (surrogate)	68	6
3-Quinoline Carboxylic Acid (surrogate)	113	96

IV. ANALYTICAL METHODOLOGY

Further improvements and modifications have been undertaken on the system for the preparation of "organic free" water. A better control of the hydrogen peroxide addition and the utilization of a second all-teflon U.V. unit, in series to the first one, enabled us to produce a finished water with a TOC residue of approximately 50 ppb. Details of the modifications and experimental conditions are reported in the following section.

A. "Organic free" water

Two modifications were incorporated and evaluated with respect to the system reported in the last quarterly report: i) another all-teflon U.V. unit was connected in series to the existing one; and ii) the stopcock valve controlling the addition of hydrogen peroxide (H_2O_2) was replaced by a teflon needle valve capable of delivering flow rates up to 4 ml/min.

The addition of another U.V. unit has the scope to increase the total volume of the U.V. system from 1240 ml to 1850 ml and to increase the amount of U.V. irradiation by utilizing five 25-watt germicidal lamps instead of three. This should lead to an increased amount of $HO^{\bullet}$ radicals, generated by U.V. decomposition of the H_2O_2, available to oxidize the organic matter present in the water. The teflon needle valve was necessary in order to exercise a better control of the H_2O_2 addition. Residual amounts of undesirable peroxide residual have been detected in the finished water and attempt has been made with these two modifications to eliminate or at least minimize it.

By maintaining the peroxide addition constant at 1% (V/V) level, different flow rates and consequently different residence times have been achieved for the investigation of their effect on the quality of the finished water. The residence time was varied from 9.2 min (flow rate ≃ 200 ml/min) up to 37.1 min

(flow rate ≃ 49.8 ml/min) with two intermediate ones at 13.8 and 23.1 min. The peroxide residue in water was evaluated by iodometry (3), while the TOC measurements were performed on a Dohrman DC-54 ultra-low total organic carbon analyzer according to the previously reported conditions (4).

The results are reported in Table 5 . While a minimal decrease in the TOC level is obtained, the amount of peroxide is drastically decreased down to undetectable levels (the iodometry has a lower detection limit for peroxide of approximately 1 ppm). Therefore, maintaining the flow rate conditions of 50 ml/min and peroxide addition of 1% (V/V), it is possible to produce approximately 72 liters per day of water with a TOC level of approximately 50 ppb.

It will be the scope of future work to evaluate the effects on the water quality produced by decreasing the amount of peroxide addition and operating at higher flow rates in order to obtain an increase in volume of water per day.

TABLE 5. Performance evaluation of the "organic free" water system.

Sample	Flow Rate ml/min	Retention Time mins	Residual TOC $\bar{x}$ (ppb)	Residual peroxide ppm
Water coming out of the carbon column			217.25±6.07	-
Finished water (1% V/V H_2O_2 added)	200	9.2	69.5±6.9	127.3
	133	13.8	65 ±3.1	47.9
	80	23.1	62.2±5.3	3.9
	49.8	37.1	50.5±4.2	Not detectable

V. Future Work

Considering all the experimental evidences gathered during the first year study, it is evident that the objectives of this research program could be met by the use of the following proposed fractionation scheme. Six out of twenty-two model organic compounds (5-chlorouracil, methylisobutylketone, furfural, crotonoaldehyde, glucose and chloroform) have never been quantitated in the previously proposed fractions. Two bases, quinoline and caffeine, appear to be not efficiently recovered by the macroreticular resin (XAD-8) and ion-exchange AG MP-50, respectively. All the other fourteen compounds have been detected and quantitated in the expected fractions with % recoveries ranging from 20% to as high as 90%.

Crotonoaldehyde appears to be an unstable compound, confirming results obtained from the other groups participating in this research effort. Therefore, it was agreed in a recent meeting with the project officer to eliminate crotonoaldehyde from the list of the model organic compounds. Also, benzo(e)pyrene has been proposed to be replaced by phananthrene and the concentration level increased up to 1 ppb. Chloroform, being a very volatile substance, has been isolated and quantitated by the purge and trap method in combination with GC-MS (4). Methylisobutylketone and furfural have been assessed by liquid-liquid extraction with methylene chloride followed by GC (5). Until now, no attempt has been made to search for 5-chlorouracil in other fractions nor to isolate it by any other method. Glucose was not assessed in hydrophilic neutral fraction because of either analytical difficulties (i.e., isolation from water and derivatization prior to GC) or loss of it through biodegradation during the processing of the sample. The carbon adsorption studies showed that it is feasible to use Carbopack B to efficiently isolate quinaldic and stearic acids.

Consequently with the experimental results obtained thus far, it was decided to pursue a more thorough study in the coming quarter on the revised fractionation scheme as shown in Figure 2. At least three repetitive runs of water solutions spiked at the proposed concentration levels will be processed through the entire shceme in order to gather sufficient data to express the recoveries of each individual compound as mean values and standard deviations. A mass balance for each compound in all the fractions along with the break-through studies will be completed in the coming quarter in order to estimate the amount of resin and carbon required to process 500 liters of water solution. Further, the influence on the recovery of themodel compounds in the presence of humic acids in the water solution will be investigated.

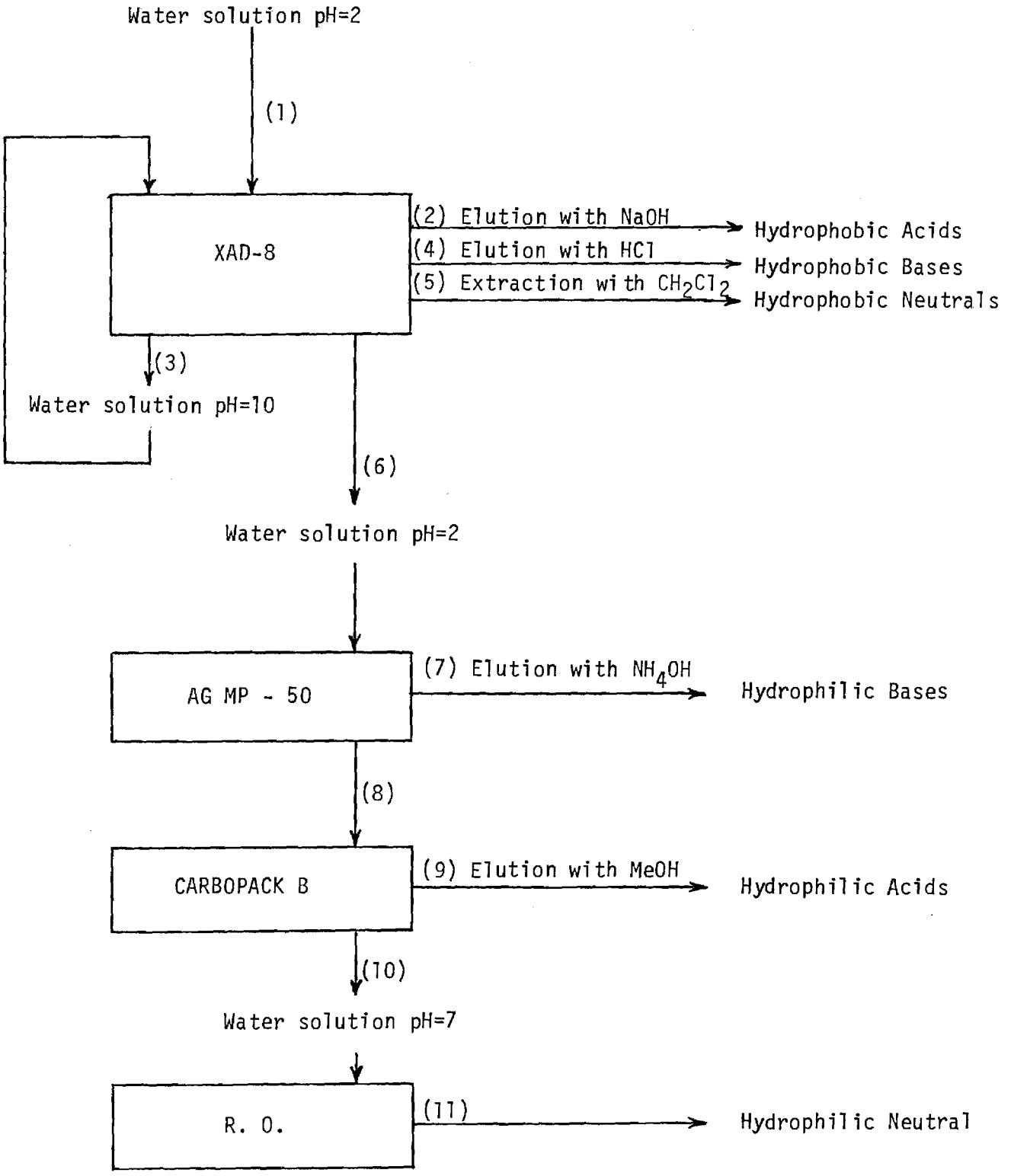


Figure 2. Revised fractionation scheme.

VI. EXPENDITURES

The actual expenditures incurred up to the end of the fifth quarter of this research program are presented by the dashed line in Figure 3 (between months 12-15).

If there is any question regarding this quarterly report, please contact either Edward Chian or Maurizio Giabbai at (404)894-2265.

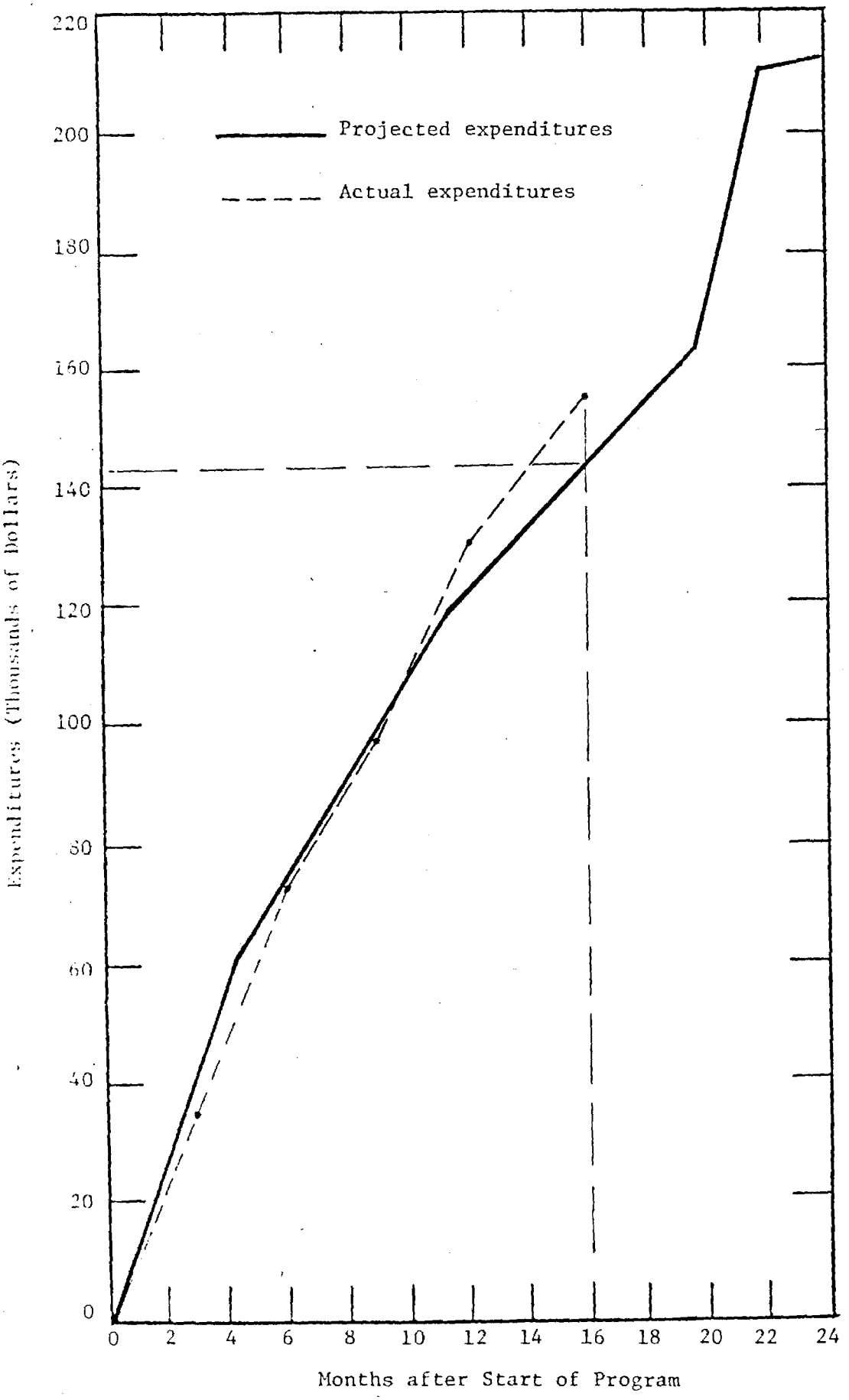


Figure 3. Projected and Actual Expenditures for EPA Contract No. 68-03-3000

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E-20 68

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QUARTERLY REPORT

March 1982

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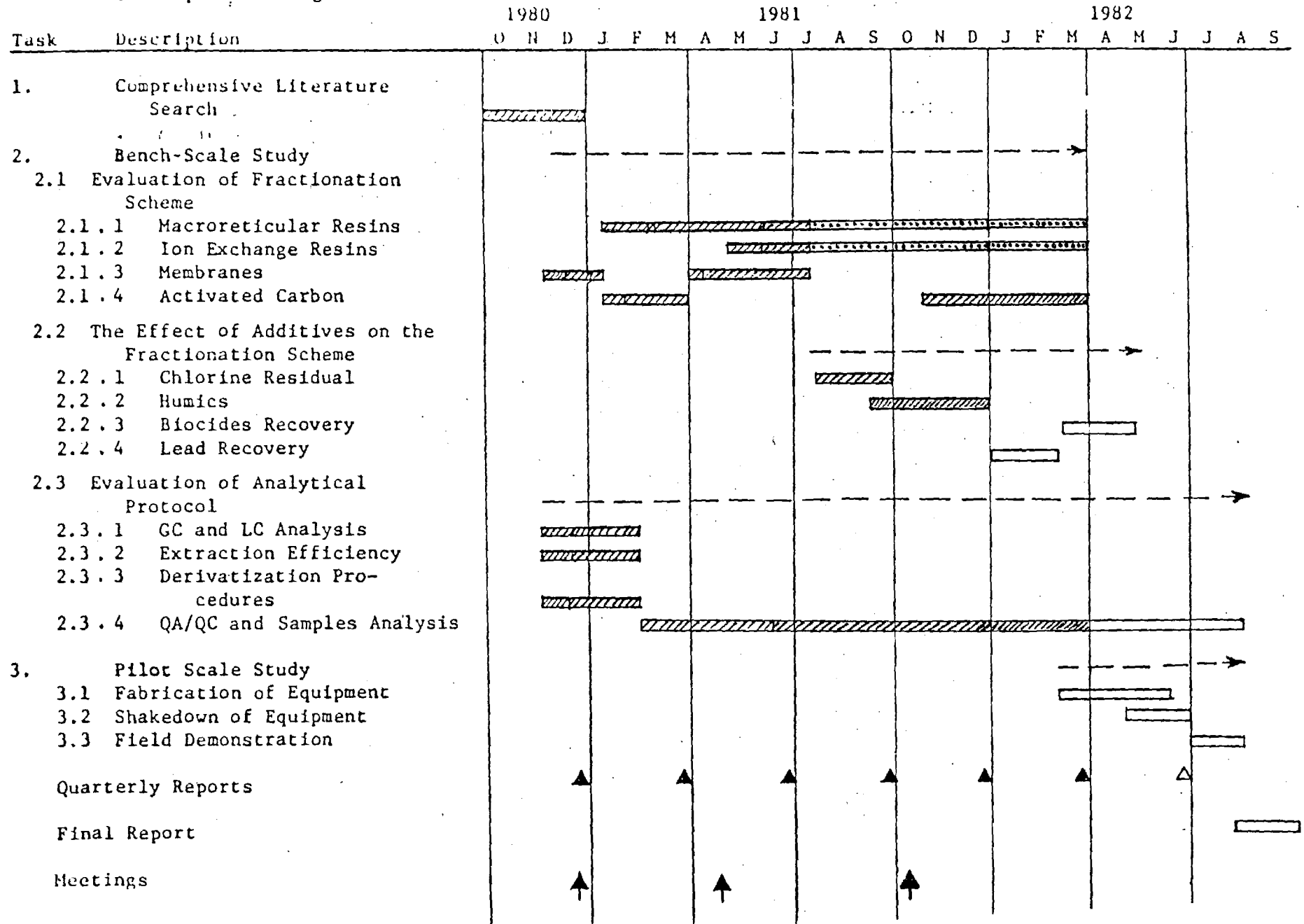
Principal Investigators: E. S. K. Chian and J. H. Reuter



II. Resin Fractionation Scheme

A. Fractionation and concentration of test solutions containing humic acid

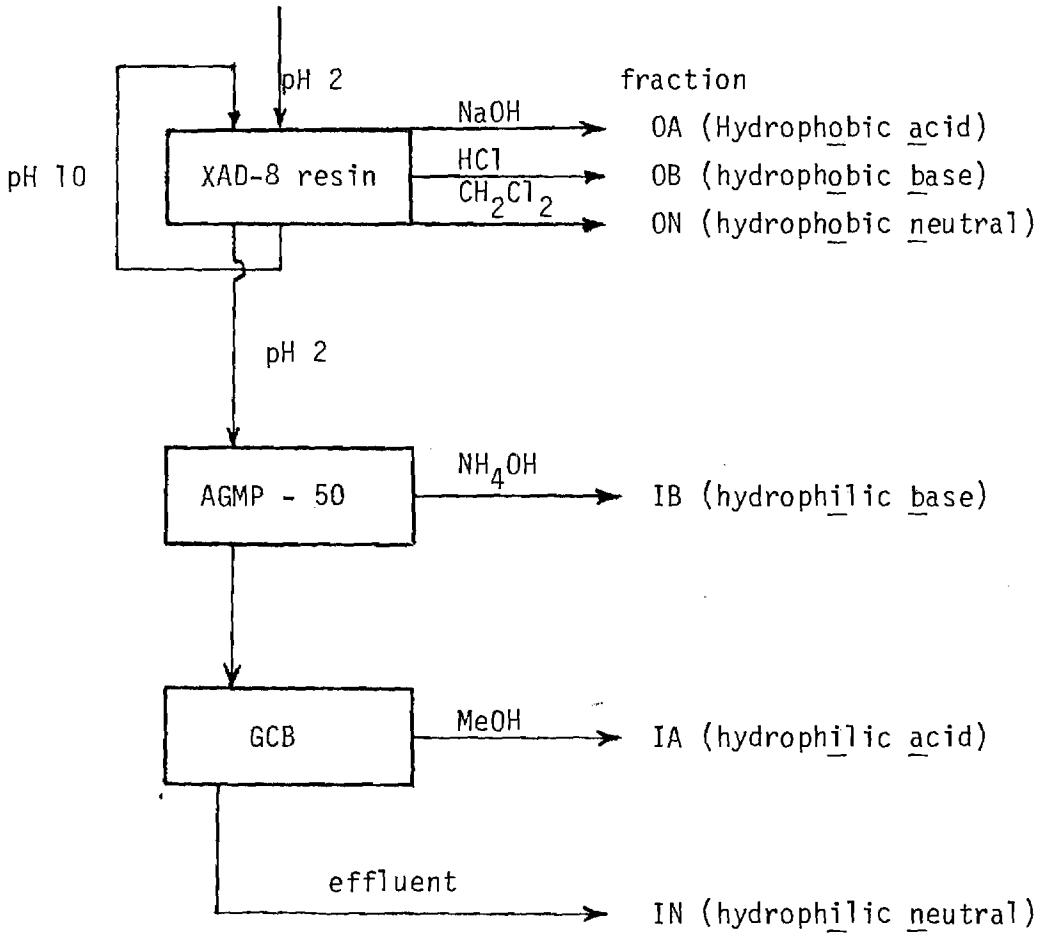
Two 500 ml batches of test solution of the following composition were prepared:

1. 100 ppb of each of the organic compounds, except for 2 ppb of phenanthrene.
2. 2 ppm of "Cincinnati" humic acid.
3. Inorganic salts (70 ppm $NaHCO_3$, 120 mg $CaSO_4$ and 36 ppm of $CaCl_2 \cdot 2H_2O$).

Since the humic acid did not, as suggested by EPA, dissolve in water at pH 7, we dissolved it first in a few ml of water to which we had added 1 ml of 0.1 N NaOH, and added this solution to the test solution. The addition of 2.3 mg Na^+ was considered negligible.

Shortly after addition of the humic acid, the test solution turned cloudy. Apparently, the humic acid, in the presence of the excess Ca^{2+}, forms a precipitate. This means that the system becomes inhomogeneous, with a solid phase present, which could separate by settling. Solid-solute interactions could take place if the solution were allowed to age for some time.

Upon acidification of the solution to pH 2, the floc dissolves, i.e., the solution becomes clear again. After acidification we proceeded with our fractionation on XAD-8 as previously established. (see the following schematic flow diagram)



The recoveries are listed in Tables 1A and 1B. Several compounds that had eluded us so far were now detected. Quinaldic acid behaves like a base under our conditions and appears in the hydrophilic base fraction (IB, i.e., eluted with NH_4OH from the cation exchange column). 2,4-dichlorophenol apperas in the hydrophilic neutral fraction (IN). This means that it is not adsorbed on any of the adsorbent phases in the hydrophobic neutral fraction (ON), whereas the larger part is found in the hydrophilic neutral effluent. None of the test compounds behaves like a hydrophilic acid. Thus, there would be no need for the graphitized carbon black column. However, we will leave it in the fractionation scheme as an adsorbent for a more general test solution that may contain hydrophilic acids (we used to think of quinaldic acid as such a compound, but it is so amphoteric that it can appear as acid or base, depending on the pH of the solution).

TABLE 1-A. Recovery of organic compounds with inorganic salts and humic acid.

	% Recovery						
	OA	OB	ON	IA	IB	IN	Total
Acid							
Stearic acid	NQ						NQ
Trimesic acid							
2,4-dichlorophenol	-					43.8	43.8
Quinaldic acid	-			-	NQ		NQ
Neutrals							
Isophorone		-	92.7		-	12.0	104.9
Biphenyl		-	84.6		-	-	84.6
1-Chlorododecane		-	40.0		-	0.5	40.5
2,6-ditert-butyl-4-methylphenol		-	59.6		-	-	59.6
2,4'-dichlorobiphenyl		-	72.3		-	-	72.3
2,2',5,5 -tetrachloro-biphenyl		-	32.9		-	-	32.9
Anthraquinone		-	81.8		-	-	81.8
Phenanthrene		-	45.0		-	-	45.0
Bis(2-ethylhexyl)phthalate		0.6	48.6		1.3	3.8	54.3
Glucose							
Furfural						91.1	91.1
Bases							
Quinoline		22.7	8.1		NQ		30.8
5-Chlorouracil							
Caffeine			13.7			32.4	46.1
Glycine					62.5		62.5

NF: Not found in the expected fractions
NQ: Not quantified
- : Checked but not found

TABLE 1-B.

	% Recovery						
	OA	OB	ON	IA	IB	IN	Total
Acid							
Stearic acid							
Trimesic acid							
2,4-dichlorophenol	NF					29.9	29.9
Quinaldic acid	-			-	NQ		NQ
Neutrals							
Isophorone		-	88.2		-	11.9	100.1
Biphenyl		-	80.5		-	-	80.5
1-Chlorododecane		-	33.3		-	0.7	34.0
2,6-ditert-butyl-4-methylphenol		-	58.5		-	-	58.5
2,4'-dichlorobiphenyl		-	70.6		-	-	70.6
2,2',5,5 -tetrachloro-biphenyl		-	30.7		-	0.4	31.1
Anthraquinone		-	62.4		-	0.4	62.8
Phenanthrene		-	57.5		-	-	57.5
Bis(2-ethylhexyl)phthalat		0.5	27.5		2.1	8.1	38.2
Glucose							
Furfural						88.5	88.5
Bases							
Quinoline		22.6	5.4				28.0
5-Chlorouracil							
Caffeine			10.4		NQ	29.9	40.3
Glycine					76.3		76.3

B. Breakthrough Study

In order to estimate the amount of adsorbent required to process 500 liters of water, we ran test solutions for each adsorption condition.

Run #1: 2 Liter test solution containing

50 ppb each of
stearic acid
trimesic acid
isophorone
biphenyl
2,6-di-tert-butyl-4-methylphenol
2,4'-dichlorobiphenyl
anthraquinone
bis(2-ethylhexyl)phthalate
chloroform
MIBK

5 ppb each of
1-chlorododecane
2,2',5,5'-tetrachlorobiphenyl

0.5 ppb of
phenanthrene

2 ppm of
humic acid

The solution was acidified to pH 2 and passed through an XAD-8 column (13 mm I.D., resin bed 9 ml) at a flow rate of ~ 166 ml/hr. Fraction of 20 ml were collected. The absorbance at 254 nm was measured for each fraction on a Gilford spectrophotometer (1-cm path) equipped with automatic sampler. The results are shown in Fig. 1. To identify the compound(s) that were breaking through, we combined the 20 ml fractions to 5 larger ones representing, first: 30 bed volumes, second: 30 bed volumes, third: 50 bed volumes, fourth: 50 bed volumes, fifth: remaining effluent. Each of the 5 fractions was analyzed for each of the organic compounds (see Table 2) except chloroform and MIBK. Table 2 shows that bis (2-ethylhexyl) phthalate begins to appear at ~ 40 bed volumes and isophorone at ~ 70 bed volumes.

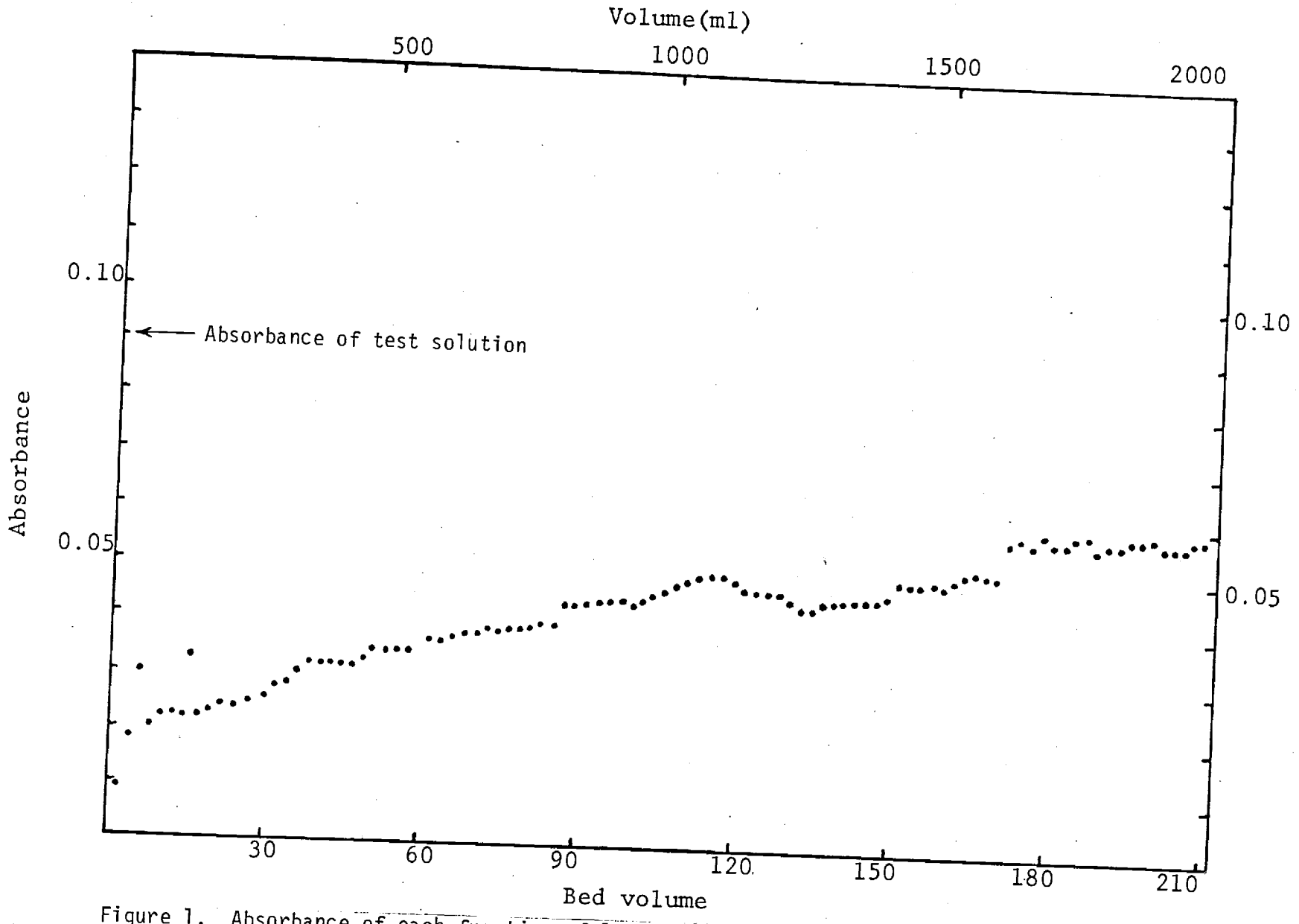


Figure 1. Absorbance of each fraction of 1st run at 254 nm. The test solution which contains 13 organic compounds and humic acid was acidified and passed through XAD-8 resin (see text for more detail).

TABLE 2. Breakthrough of each organic compound (1st run). Test solution which contain humic acids was acidified and passed through XAD-8 resin.

Compounds	Spiked Level (mg/L)	Total Amount of compounds (mg/2L)	Found in each fraction (µg)					
			30 bed vol. (290ml)	30 bed vol. (290ml)	50 bed vol. (480ml)	50 bed vol. (480ml)	Remaining (460ml)	Total Found (µg)
Isophorone	50	100	-	-	23.28	47.81	78.14	149.23
Biphenyl	50	100	-	-	-	-	0.72	0.72
1-Chorododecane	5	10	-	-	-	-	0.10	0.19
2,6-ditert-butyl-4- methylphenol	50	100	-	-	-	-	-	-
24'-dichlorobiphenyl	50	100	-	-	-	-	-	-
Phenanthrene	0.5	1	-	-	-	-	-	-
2,2'-5,5'-tetrachloro biphenyl	5	10	-	-	-	-	-	-
Anthraquinone	50	100	-	-	-	-	0.12	0.12
Bis(2-ethylhexyl)-phthalate	50	100	-	3.28	7.60	7.20	9.57	27.65
Trimesic acid	50	100	-	-	-	3.97	33.07	37.04
Steric acid	50	100	-	-	-	-	22.51	22.51

Run #2: 2 Liters test solution containing

50 ppb each of
isophorone
biphenyl
2,6-di-tert-butyl-4-methylphenol
2,4'-dichlorobiphenyl
anthraquinone
bis(2-ethylhexyl)phthalate
quinoline
caffeine
5-chlorouracil

5 ppb each of
1-chlorododecane
2,2', 5,5'-tetrachlorobiphenyl

0.5 ppb of
phenanthrene

The pH of the solution was adjusted to 10 with NaOH and then passed over XAD-8 (resin bed 10.5 ml) at a flow rate of ~ 166 ml/hr. Fraction collection (20 ml each), spectrophotometry (at 254 nm, 1 cm path), combination of fractions and compound analyses were the same as in the first run. Fig. 2 and Table 3 show the results: caffeine and bis(2-ethylhexyl) phthalate begin to break through within the first 30 bed volumes. Quinoline apperas in the effluent after ~ 100 bed volumes and isophorone after 60 bed volumes. The absorbance data after 90 bed volumes are so strongly scattered that no break through points can be located.

Run #3: 2 Liters test solution containing

50 ppb each of		
caffeine	$NaHCO_3$	70 ppm
glycine	$CaSO_4$	120 ppm
quinaldic acid	$CaCl_2 \cdot 2H_2O$	36 ppm

The solution was acidified to pH 2 and passed through a column (13 mm I.D.) containing 11 ml of AG MP-50 cation exchange resin in the H^+-form, at a flow rate of 166 ml/hr since the absorbance of 255 nm was too low, no spectrophotometric monitoring was possible. We divided the effluent into 5 fractions, comparable

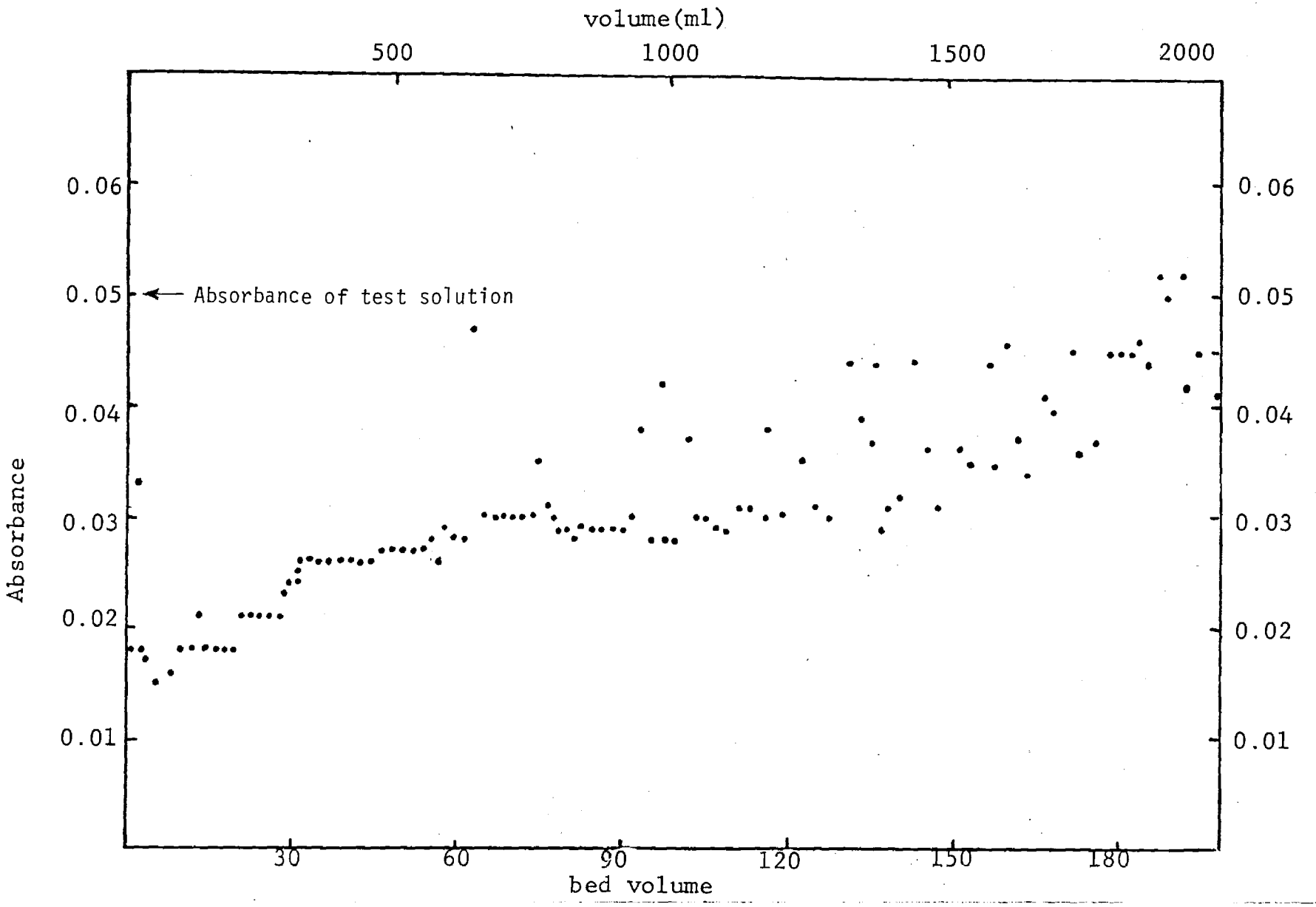


Figure 2. Absorbance of each fraction of 2nd run at 254 nm. The test solution which contains 15 organic compounds and inorganic salts was adjusted to pH 10 and passed through XAD-8 resin (see text for more detail).

TABLE 3. Breakthrough of each organic compound (2nd run). Test solution was adjusted to pH 10 and passed through XAD-8 resin.

Compounds	Spiked Level (mg/L)	Total Amount of compounds (mg/2L)	Found in each fraction (µg)					
			30 bed vol. (290ml)	30 bed vol. (290ml)	50 bed vol. (480ml)	50 bed vol. (480ml)	Remaining (460ml)	Total Found (µg)
Isophorone	50	100	-	-	35.19	37.63	42.37	115.19
Quinoline	50	100	-	-	0.52	14.47	23.23	38.22
Biphenyl	50	100	-	-	-	-	-	-
1-Chlorododecane	5	10	-	-	-	-	-	-
2,6-ditert-butyl-4-methylphenol								-
2,4'-dichlorobiphenyl	50	100	-	-	-	-	-	-
Phenanthrene	0.5	1	-	-	-	-	-	-
Chaffeine	50	100	6.24	14.14	18.36	20.56	17.27	76.57
2,2',5,5' tetrachloro-biphenyl	5	10	-		-	-	0.08	0.08
Bis(2-ethylhexyl) phthalate								-
Anthraquinone	50	100	-	-	-	-	-	-

to the two previous runs, and analyzed for the test compounds. The results are given in Table 4. Caffeine became visible within the first 30 bed volumes of effluent. Quinaldic acid started to break through after more than 60 bed volumes.

Conclusion from breakthrough studies: the final bed volume of the XAD-8 resin has to be at least 10 liters if 500 liters of sample are to be used. The bed volume of cation exchange material would have to be comparable in order to concentrate quinaldic acid. The cost for the latter resin, however, would be non-commensurate.

TABLE 4. Breakthrough of each organic compound (3rd run). Test solution which contains salts was acidified and passed through AG MP-50 resin.

Compounds	Spiked Level (mg/L)	Total Amount of compounds (mg/2L)	Found in each fraction (µg)					
			30 bed vol. (290ml)	30 bed vol. (290ml)	50 bed vol. (480ml)	50 bed vol. (480ml)	Remaining (460ml)	Total Found (µg)
Caffeine	50	100	7.68	8.92	12.93	14.26	9.46	53.25
Glycine	50	100	-	-	-	-	-	-
Quinaldic acid	50	100	-	-	3.83	16.21	-	0.04*

III. ANALYTICAL METHODOLOGY

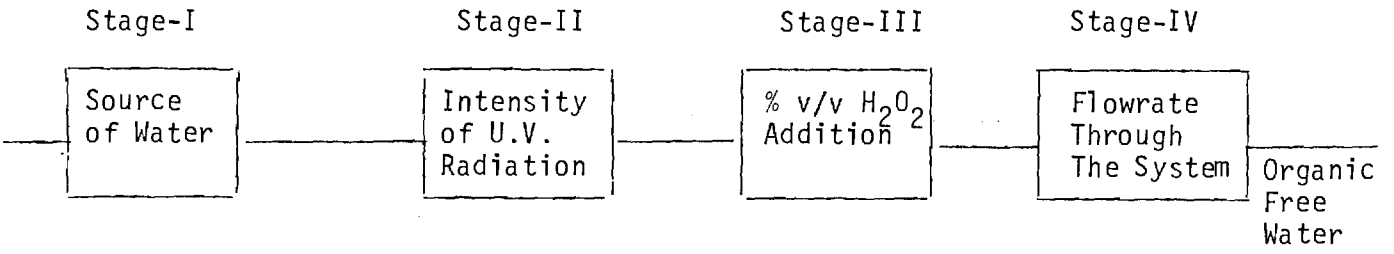
A. Extraction, HPLC

An attempt has been made to assess 5-chlorouracil in water by liquid-liquid solvent extraction and HPLC determination. The physical and chemical properties are not available on the common comprehensive literature (Merck Index, CRC Handbook of Chemistry and Physics) but information could be found for a closely related compound , uracil. Further information relative to 5-chlorouracil were sought through the technical staff of the manufacturing company (Alfa Products) but with limited success. In our lab we could confirm that 5-chlorouracil is not soluble in any of the commonly used organic solvents (methanol, ether, acetone, methylene chloride, tetrahydrofuran, acetonitrile) and could be readily solubilized in ammonium hydroxide solution. A 500 ppm stock solution was prepared by dissolving 50 mg of 5-chlorouracil in 100 ml of 2N ammonium hydroxide. Three 10 ppm solutions were prepared by spiking the proper amount of stock solution in 250 ml of "organic-free" water. One solution was pH adjusted to 2, another to 10 and the third to 7 and each solution was solvent extracted with three aliquots of methylene chloride (50:25:25). A Perkin-Elmer LC-65T with"Series 3"pump system was employed in isocratic conditions, with a Lichrosorb-C_{18} 250x4.6 mm dp=5μm column, solvent system methanol-water (10:90), flow rate 0.6 ml/min and U.V. detection at 254 nm. It was chosen a starting solution concentration of 10 ppm in order to monitor the aqueous phase by direct injection. The organic solvent phase was instead concentrated to 1 ml before instrumental analysis. The same results could be otained from the extractions at three different pH: 5-chlorouracil was not detected in the methylene chloride phase but was quantitatively found in the aqueous phase.

B. "Organic Free" Water

The system assembled for the production of "organic free" water was described in previous quarterly reports. Since this water is being used for all the analytical work and will be used for the production of the 500 liters needed in the last phase of the project, a parametric study of the system was conducted. The objectives of this study were to optimize the quality and quantity of the finished water in terms of TOC content, H_2O_2 residue and maximum output. In this respect water source, intensity of U.V. radiation, % volume by volume (v/v) addition of H_2O_2 and flow rate through the system were the selected variables to be investigated.

The study was conducted in four stages. Each stage was investigated and optimized in sequences as shown in the following block diagram.



The TOC analysis was carried out on a DC-54 Ultra low level carbon analyzer (Dohrmann DW, Envirotech). Potassium hydrogen phthalate was used as calibration standard. Different microliter amounts of a 180 ppm carbon standard solution were directly added to the sample into the sample sparger by means of a syringe. Sample reagent containing potassium persulfate and phosphoric acid (85%) were added as per manual instruction. The calibration curve and the calibration data are reported in Fig.3 and Table 5, respectively. The H_2O_2additions were introduced from a 50% reagent grade H_2O_2 solution (Fisher Scientific). The residual peroxide concentration was monitored by starch idometry ( ).

CALIBRATION CURVE FOR DC-54 SYSTEM

Fig. 3

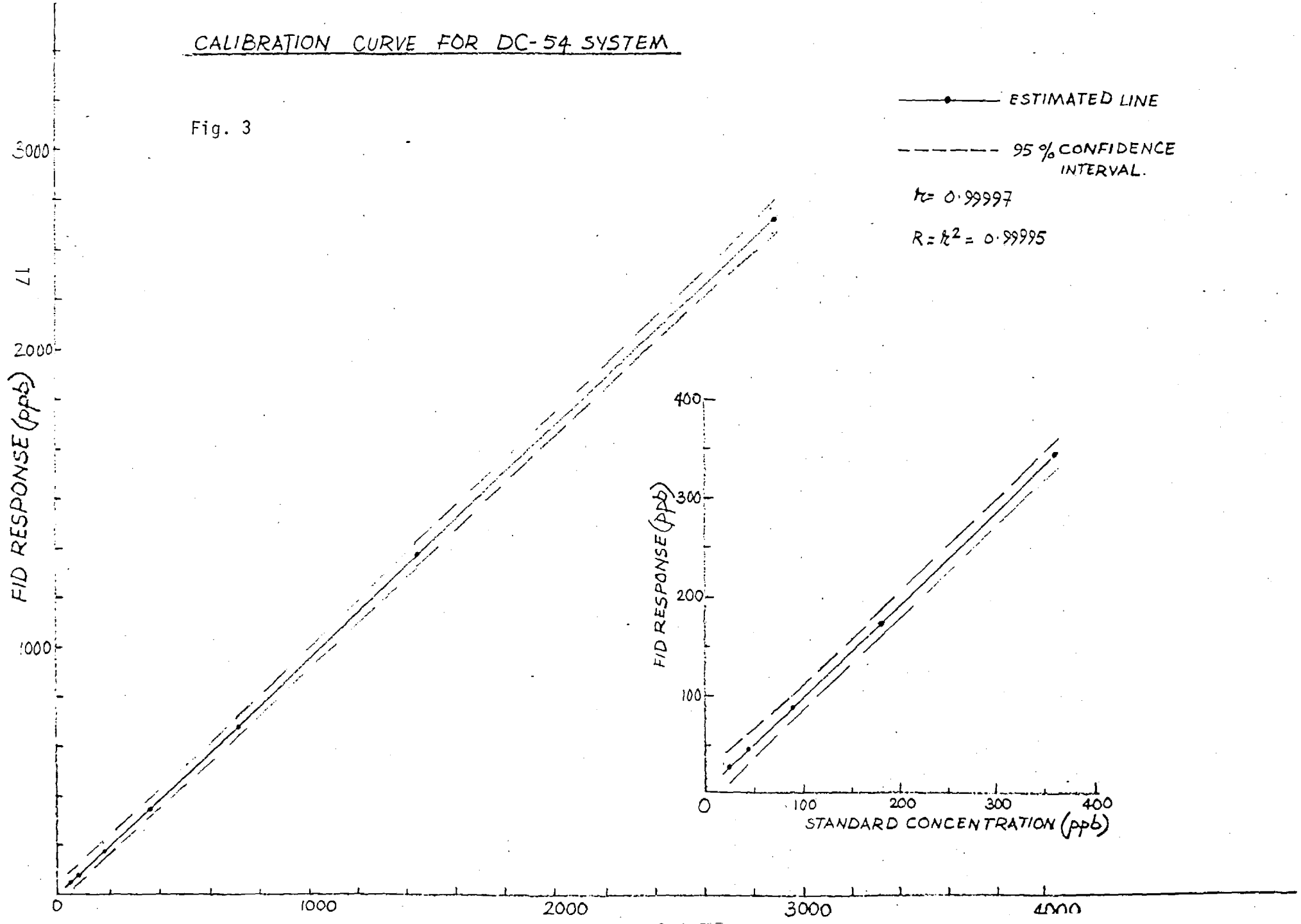
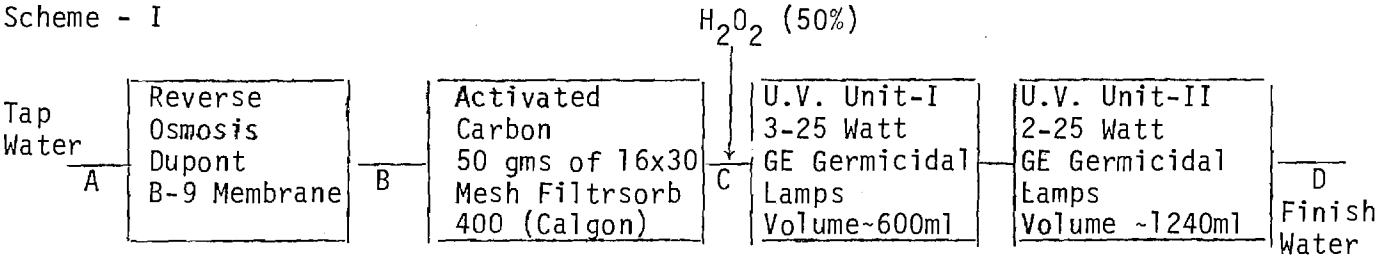


TABLE 5: Calibration of the DC-54 System

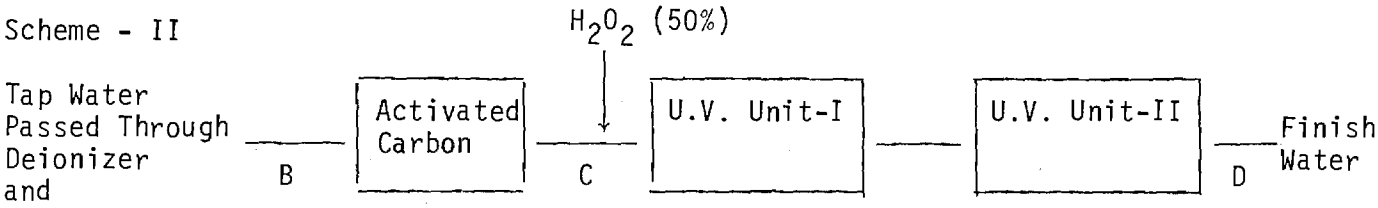
Standard Concentration (ppb) (x)	FID response TOC (ppb) (y)	Mean (ppb) ($\bar{y}$)	Standard Deviation σ(ppb)	Coefficient of Variation $cu = \frac{\sigma}{y}$	Estimated FID response by Linear Regression Y(ppb)	95% Confidence Interval (ppb)
27	33 25 24 30	28	4.2	0.15	27.33	±15.87
45	48 44 44 46	45.5	1.9	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	683.6	±12.75
1440	1370 1379 1363 1375	1371.7	6.9	0.005	1365.4	±16.14
2880	2710 2748 2735 2726	2729.5	15.9	0.005	2729.16	±32.25

Stage-I of this study was performed to identify the best water source. The following schemes were investigated:

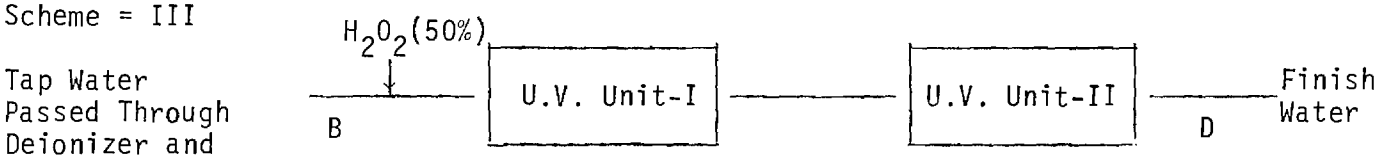
Scheme - I



Scheme - II



Scheme = III



*Deionizer and activated carbon cartridges are currently in use in the laboratory. They are supplied by Continental-Millipore 2500 series.

A, B, C, and D were the locations from where samples were withdrawn for analysis The system was operated at full intensity (all lamps on), 1% v/v H_2O_2 addition and a flowrate of 30 ml/min, (Residence time in U.V units = 61.33 min). These variables were kept constant through Stage-I. The results for the Stage-I of the study are presented in Table-6.

Scheme - II yielded finished water with relatively lower TOC content. Hence this scheme was choosen for further investigations in Stages II, III and IV. Residual peroxide concentration was not monitored as the primary objective of this stage was to obtain water with minimum TOC content.

TABLE 6: TOC of Water at Various Sample Points in Schemes I, II and III

Scheme	Sample Point and Description	TOC (ppb)	Remarks
I	Tap Water, A	1100.8	
	Water at inlet of carbon column, B	301.2	72.6% reduction in TOC after passing tap water through the R.O. module.
	Water at inlet of the U.V unit -I, C	70.5	76.5% reduction in TOC, in the Carbon Column.
	Finished Water, D	48.2	31.6% reduction in TOC, in the U.V units.
II	Water at inlet of the carbon column, B	135.5	
	Water at inlet of the U.V unit - I, C	52.1	61.5% reduction in TOC, in the carbon column.
	Finished water, D	25.7	56.9% reduction in TOC, in the U.V units.
III	Water at inetl of the U.V unit - I, C	135.5	
	Finished Water, D	58.4	56.9% reduction in TOC, in the U.V units.

In Stage-II of the study the effect of U.V radiation intensity was evaluated. The flowrate and H_2O_2 addition were kept constant at 30 ml/min and 1% (v/v), respectively. TOC and residual peroxide concentration were monitored. The results from Stage-II are presented in Table 7.

TABLE 7. Effect of U.V. radiation intensity on the quality of finished water.

Sample Point and Description	TOC in Water at Inlet of U.V. Unit-I	TOC (ppb)	Residual H_2O_2 (ppb)
Finished Water, D (Lamps off, and no H_2O_2 addition)	52.09	56.32	-
Finished Water, D (Lamps off)	52.09	51.04	35.0
Finished Water, D (Lamps in U.V unit-I on; Residence time in U.V unit-I-20mins)	52.09	45.22	11.7
Finished water, D (Lamps on in both the units; Residence time = 61 min)	52.09	25.7	0.3

The results indicate that: 1) there is no significant TOC contribution from the all-teflon U.V. units and 2) in order to achieve a finished water with the lower TOC content and H_2O_2 residue the full intensity of both U.V. units must be employed.

Stage-III of the study was designed to evaluate the effect of different % (v/v) additions of H_2O_2 to the water. The experimental conditions resembled the ones of Stage-II with same water source, both U.V. units operating and a flow rate maintained at 30 ml/min. The results for three levels of H_2O_2 addition are reported in Table 8.

TABLE 8: Effect of Different % H_2O_2 Additions on the Quality of Finished Water

% v/v H_2O_2 Addition	Sample Description	TOC in Water at Inlet of U.V 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

It is evident from these results that an increase in H_2O_2 addition leads to an increase in the H_2O_2 residue and at the same time does not give a corresponding decrease in the TOC content of the finished water. 0.5% addition was then the selected level for production operations.

Finally the flow rate through the system was investigated in order to optimize the maximum amount of finished water per unit time that is possible to produce. Three different flow rates were selected while the water source, U.V. intensity and H_2O_2 addition were maintained constant. The results of Stage-IV are reported in Table 9.

TABLE 9: Effects of Flow Rate Changes on TOC and Residual Peroxide Concentration in Finished Water

Flow Rate (ml/min)	Residence Time in U.V. Unit (min)	TOC in Water at Inlet of U.V. 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

The reduction in TOC content achieved in the U.V. units with the three flow rates; 50, 100 and 150 ml/min are respectively 50.7, 38.9 and 40.3%. It is evident that the residual H_2O_2 concentration increases accordingly to the flow rate (see Table 5) which also dictates the quality of the finished water. Therefore 50 ml/min is the maximum possible output for this system configuration Based on the results obtained from this study it is possible to formulate the following optimum conditions: i) tap water passed through Continental- Millipore series 2500 system; ii) full intensity in the U.V. units; iii) 0.5% H_2O_2 addition; and iv) flow rate of 50 ml/min through the system. Under these conditions it will be possible to produce 72 liters per day of "organic free" water with a 27 ppb TOC content and a residual H_2O_2 concentration lower than 50-100 ppb.

IV. FUTURE WORK

During the next quarter the efforts will be directed toward designing and fabricating the proper equipment for the final phase of the project. At the same time all the results obtained thus far will be completed and eventually confirmed where necessary with the processing of other solutions. The recovery of lead will be assessed during these final experiments and information regarding possible contaminants introduced from the material used in this project will also be addressed.

V. EXPENDITURES

The actual expenditures incurred up to the end of the sixth quarter of this research program are presented by the dashed line in Figure 4 (between months 15-18).

If there is any question regarding this quarterly report, please contact either Edward Chian or Maurizio Giabbai at (404)894-2265.

VI. REFERENCE

1. Shumb, W. C., "Hydrogen Peroxide", ACS Monograph, Series No. 128 (1955)

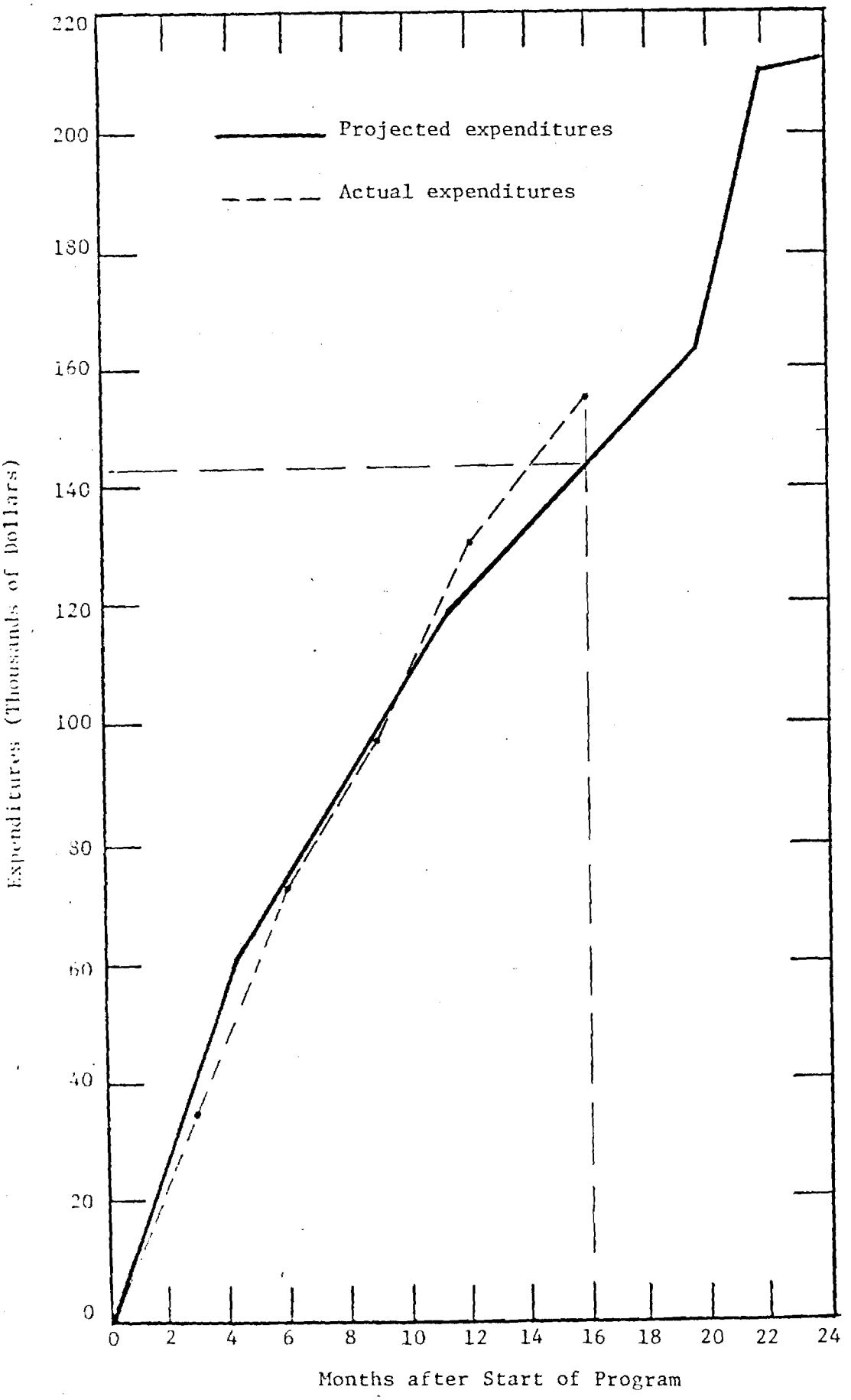


Figure 3. Projected and Actual Expenditures for EPA Contract No. 68-03-3000

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

QUARTERLY REPORT

JUNE 1982

by

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Supported by

The U. S. Environmental Protection Agency
HERL, Cincinnati, OH 45268
Contract No. 68-03-3000

Project Officer
Dr. Paul Ringhand

TABLE OF CONTENTS

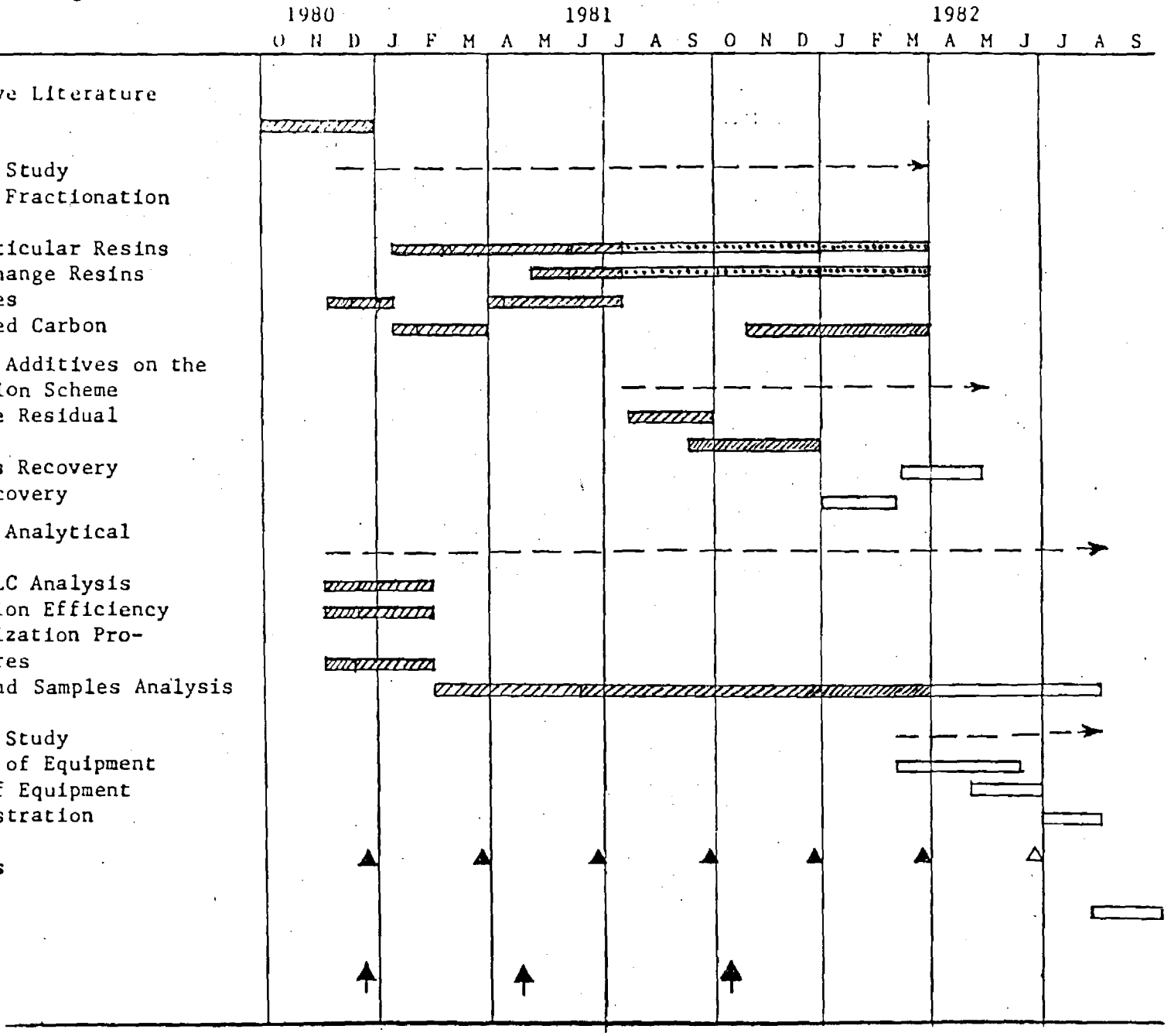
I. Introduction

This report summarizes the work performed during the period March 1, 1982 through June 10, 1982 on the EPA research program on "Evaluation of Methods for the Isolation or Concentration of Organic Substances from Water" (Contract No. 68-03-3000). The major efforts have been directed toward the completion of the study of the proposed fractionation scheme with mass balance determination of the model organic compounds and the fabrication of the equipment for the processing of 500 liters of water solution. The progress of these efforts are depicted in the Gannt Chart (Chart 1) for the above contract and are presented in detail in the following sections.

Chart 1 - Schedule for the Proposed Research Program

Project: Evaluation of Methods for the Isolation or Concentration of Organic Substances from Water

Principal Investigators: E. S. K. Chian and J. H. Reuter



II. FRACTIONATION SCHEME

The study of the recovery of the model compounds on the proposed fractionation scheme was continued. Carbopack B graphitized carbon black (GCB) adsorbent was studied regarding its retention of those model compounds that appear to be only partially retained on the resins,(i.e., 2,4-dichlorophenol, caffeine, bis(2-ethylhexyl)phthalate, isophorone, etc.). 500 ml batches of the following composition were prepared:

1. 100 ppb of each of the organic compounds, except for 2 ppb of phenanthrene.
2. 2 ppm of "Cincinnati" humic acid.
3. Inorganic salts (70 ppm $HaHCO_3$, 120 ppm $CaSO_4$ and 36 ppm $CaCl_2 \cdot 2H_2O$).

The recoveries are presented in Tables 1-6. The quantitative results were obtained by GC-FID and the identity of each compound was confirmed by GC-MS. Humic acids were quantitated by spectrophotometry at 430 nm. Calibration curve was obtained using nine standard solutions of different concentration. Care was taken to assure identical pH values for samples and standard. The analysis of model compounds amenable to solvent extraction revealed that some of them are practically adsorbed under varying experimental conditions. Thus they occur in several fractions. In particular, we observed this behaviour for 2,4-dichlorophenol, caffeine, bis-(2-ehtylhexyl)phthalate and isophorone, which are found in the "hydrophobic base and neutral" fractions and in the "hydrophilic base and neutral" fractions. The macroreticular adsorbent resin XAD-8 plays the major role in isolating the model compounds, while the cation-exchange resin AG MP-50 appears to effect the adsorption of glycine and quinaldic acid. In an effort to improve the recoveries of the substances that are not retained efficiently on these resins, Carbopack B GCB was evaluated by processing 500 ml test solution containing some of the model compounds at the specified concentration. Column size and flow rates were similar to the one previously reported for the evaluation of trimesic, stearic and quinaldic acid. Methylene chloride instead of methanol was used to elute the adsorbed compounds. The recoveries are reported in Table 7.

TABLE 1. Recovery of organic compounds with inorganic salts and humic acids

	% Recovery					
	OA	OB	ON	IB	IN	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-methylphenol		NF	58.5	NF	NF	58.5
2-4'-dichlorobiphenyl		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 quantitated
NS = Not spiked

OA = Hydrophobic acid
OB = Hydrophobic base
ON = Hydrophobic meutral
IB = Hydrophilic base
IN = Hydrophilic neutral

TABLE 2.

	% Recovery					
	OA	OB	ON	IB	IN	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	40.0
2,6-ditert-butyl 4-methylphenol		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					

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

TABLE 3.

	% Recovery				
	OA	OB	ON	IB	IN	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-methylphenol		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				

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

*Analyzed by HPLC

TABLE 4.

	% Recovery					
	OA	OB	ON	IB	IN	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-methylphenol		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)phthalate		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	NS	NF	NF	NF	12.0	12.0
MIBK						

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

*Analyzed by HPLC

TABLE 5.

	% Recovery					
	OA	OB	ON	IB	IN	TOTAL
Stearic acid	15.8					15.8
Trimesic acid	51.1					51.1
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-methylphenol		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	

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

*Analyzed by HPLC

TABLE 6.

	% Recovery					
	OA	OB	ON	IB	IN	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-ditert-butyl 4-methylphenol		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	

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

*Analyzed by HPLC

TABLE 7. Recovery of organic compounds on GCB

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

Examination of the GC chromatograms revealed the presence of peaks which apparently were produced by contaminants introduced during handling of the samples during the fractionation and the subsequent analytical procedures. 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 (their peak size was approximately <10% that of the model organic compounds). Investigation by GC-MS into the nature of these contaminants revealed that several of the impurities, are characteristics of those derived from macroreticular resins (1,2). The "hydrophobic neutral" fraction, "hydrophobic base" fraction and the solvent extract of the aqueous solution which had passed through the entire fractionation procedure generally contained contaminants. A list of tentatively identified compounds is presented in Table 8. Some of them (e.g., phenol, bromoform and dibromochloromethane) were detected in several samples and sometimes in relatively large concentrations (between 5-50 ng/µl). These presumably do not originate from the resins but may have been introduced from other sources (stock solution spiking, reagents, etc.). 2,4(1H,3H)-Pyrimidine-dione, 5-amino has a strong similarity with 5-chlorouracil and it might suggest that the model compound has undergone chemical modification. A system blank would provide the necessary information and be run immediately.

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1. H. A. James et al., J. Chromatogr. 208, 89 (1981).

2. P. Ringhand, personal communication.

TABLE 8. Artifact contaminants from fractionation scheme

ON	OB	IN
Cyclohexene, 3-chloro	Cyclohexanol,4-chloro	Ethanone,1-(4-hyolroxy 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		

III. PILOT SCALE STUDY

The last phase of the project calls for demonstration of the method's efficiency for isolating or concentrating the model organic substances, at the specified concentrations, from 500 liters of water. Since the isolation/fractionation scheme evaluated in this laboratory uses primarily adsorption-desorption columns, we propose to employ modular units for handling larger quantities of water. For this purpose we calculated column dimensions and amount of adsorbents to suffice 100 liters of water solution per modular unit. Five identical modular units would then be necessary for 500 liters of test solution. A scheme for the proposed modular unit is shown in Fig. 1 . Glass carboys of 45L capacity serve as solution feeding reservoirs and glass bottles of 19L capacity are used for column effluent collection, and manual transfer of the test solution to the next feeding reservoir. Sample transfer lines, valves and columns are made of glass and teflon in order to minimize solute losses and introduction of contaminants. According to the breakthrough study the required bed volumes for XAD-8 and AG MP-50 resins are 1L each and for Carbopack B graphitized carbon black 100 ml per modular unit. Flow rates of 15L/hour are needed. The corresponding column head loss required for such flow rates were calculated by the Carmen-Kozeny equation:

$$\Delta P = \mu\eta L \frac{5(1-\varepsilon)^2 So^2}{\varepsilon^3} = pgh$$

$$h = \frac{\mu\eta L}{pg} \frac{5(1-\varepsilon)^2 So^2}{\varepsilon^3}$$

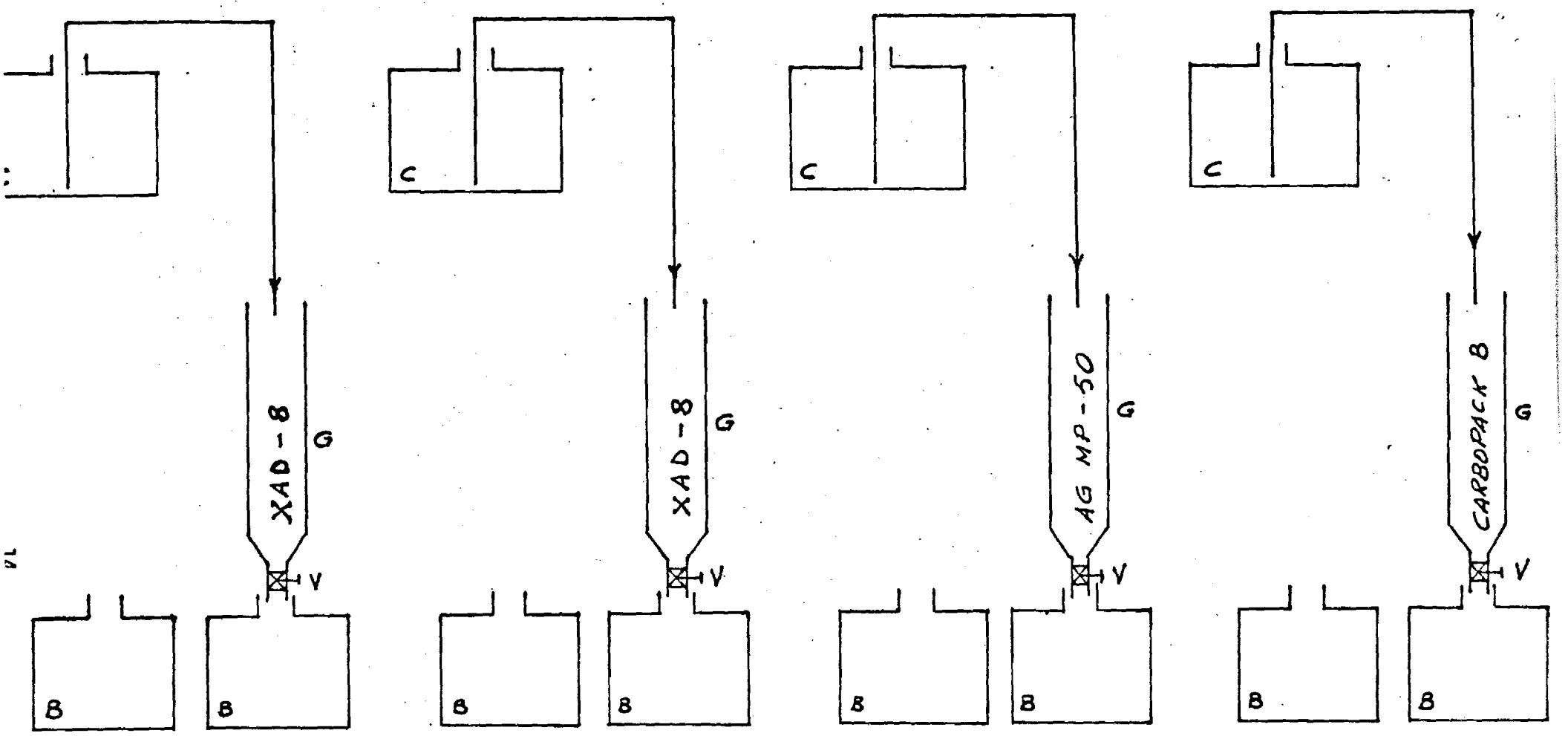
μ = flow velocity

L = height of bed volume

η = 0.01 poise

ε = porosity

So = specific surface area



B = 19 LITERS GLASS BOTTLES

C = 45 LITERS CARBOYS

V = TEFLON VALVE

G = GLASS COLUMN

Fig. 1.

The calculated column head loss and the dimensions of each column are given in Table 9. Should the proposed pilot scale unit be approved by EPA, it is the opinion of this research group that it would be satisfactory to demonstrate the method's efficiency in isolating the model organic substances using one modular unit of 100L, since the handling of additional volumes of test solution only required additional modular units.

	XAD-8	AG MP-50	Carbopack B
Column dimension	51 cm x 5 cm I.D.	51 cm x 5 cm I.D.	9.2 cm x 3.7 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	15 liters/hour	15	15
h	53.5 cm	46 cm	125 cm

TABLE 9. Calculated head loss for the specified column dimension

IV. FUTURE WORK

The next and final quarter will be devoted to the demonstration of the method's efficiency for the proposed fractionation scheme. Mass balance determination will be performed for each analyzed compound and possible contamination introduced during sample processing will also be tentatively identified and quantitated.

V. EXPENDITURES

The actual expenditures incurred up to the end of the seventh quarter of this research program are presented by the dashed line in Figure 2 (between months 19-22). If there is any question regarding this quarterly report, please contact either Edward Chian or Maurizio Giabbai at (404)894-2265.

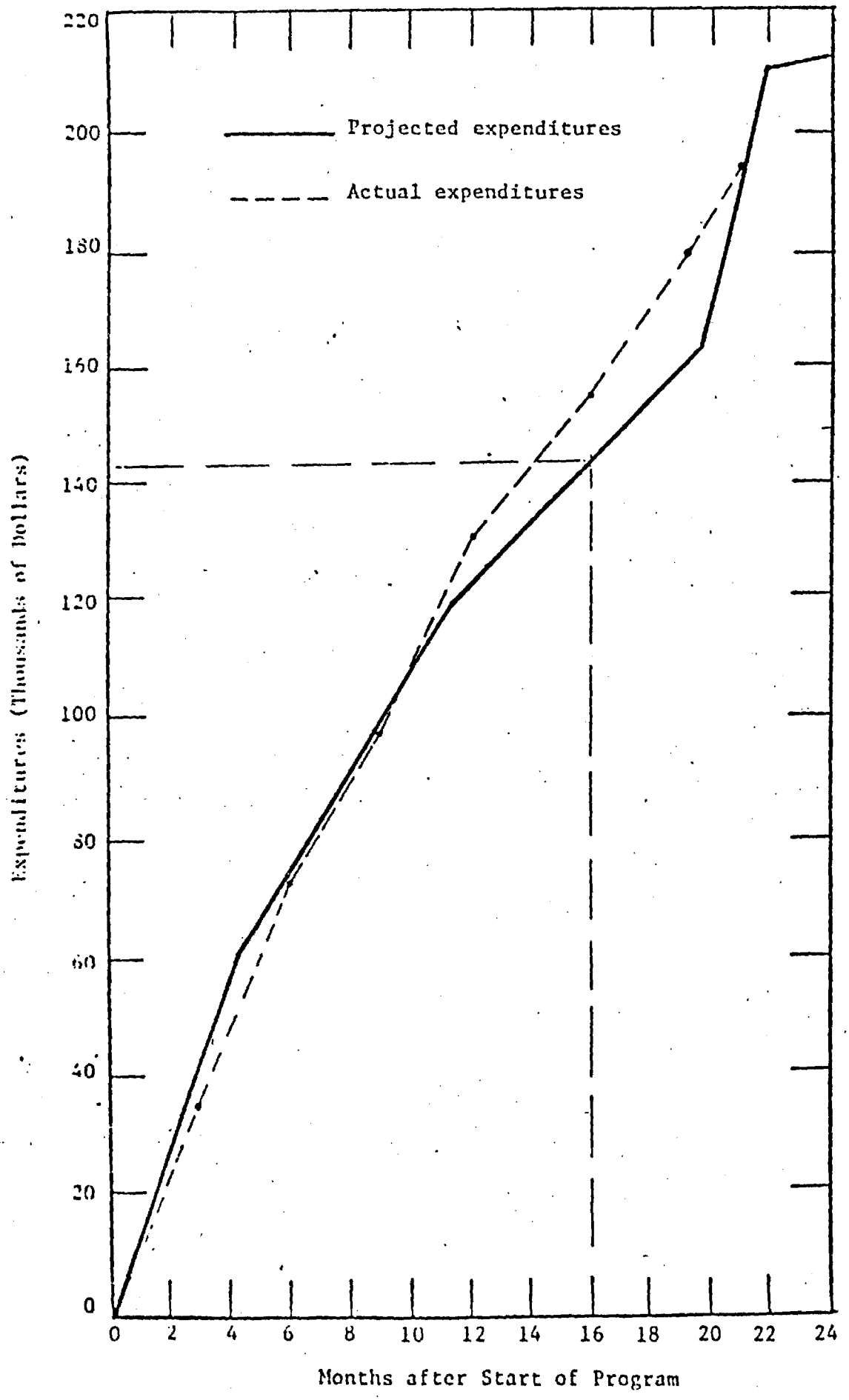


Figure 2. Projected and Actual Expenditures for EPA Contract No. 68-03-3000

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

by

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NOTICE

This report has been subjected to the Agency's peer and administrative review policy and approved. Approval signifies that the contents reflect the views and policies of the U. S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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.

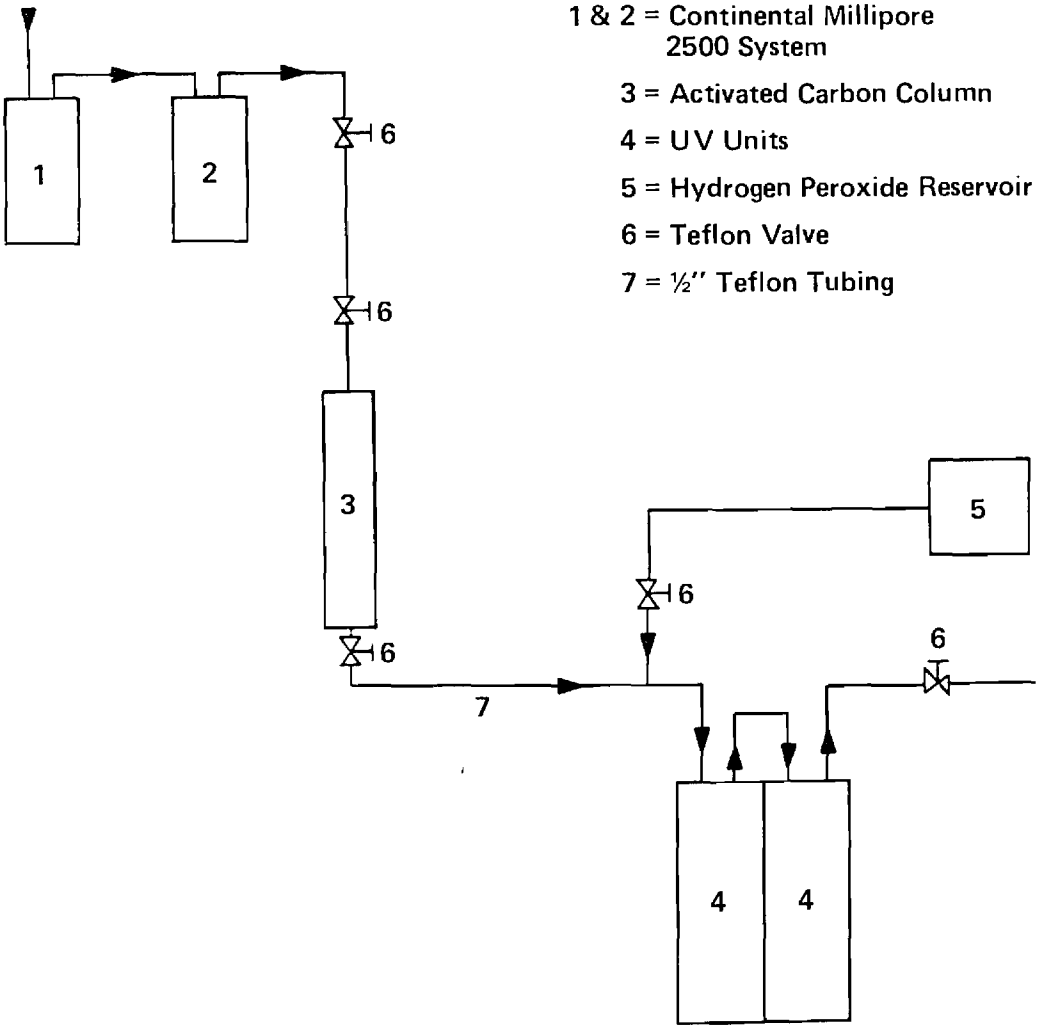


Figure 1. Schematic of System for Production of "OFW"

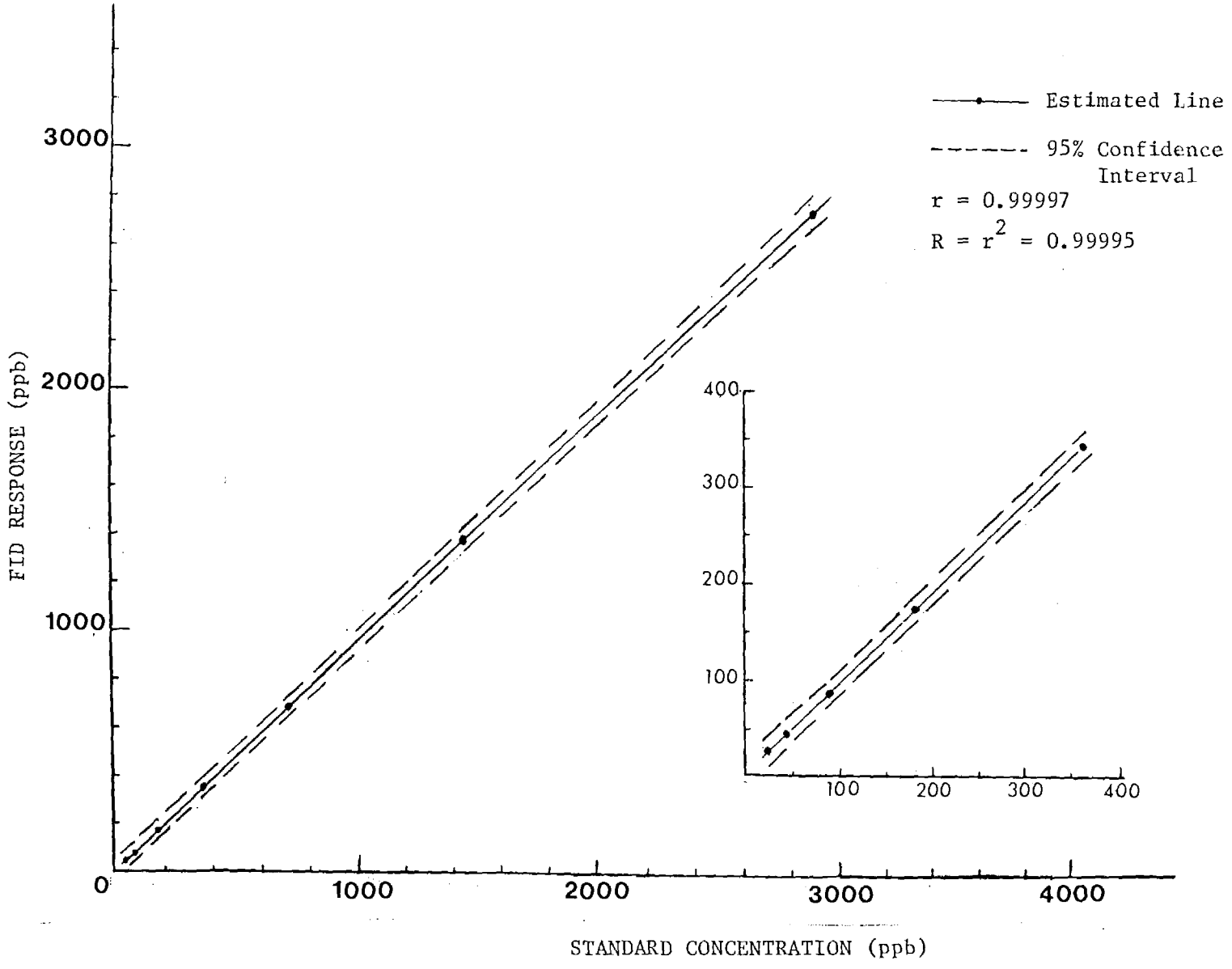


Figure 2. Calibration Curve for Dohrmann DC-54 Carbon Analyzer

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.

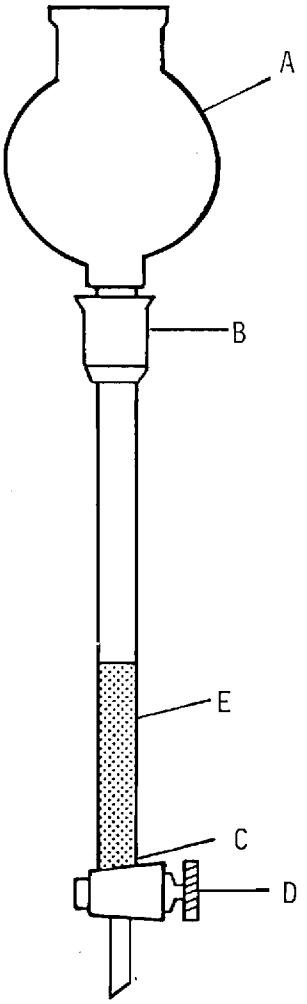
Preparation of Resins, Carbon and Membrane

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.

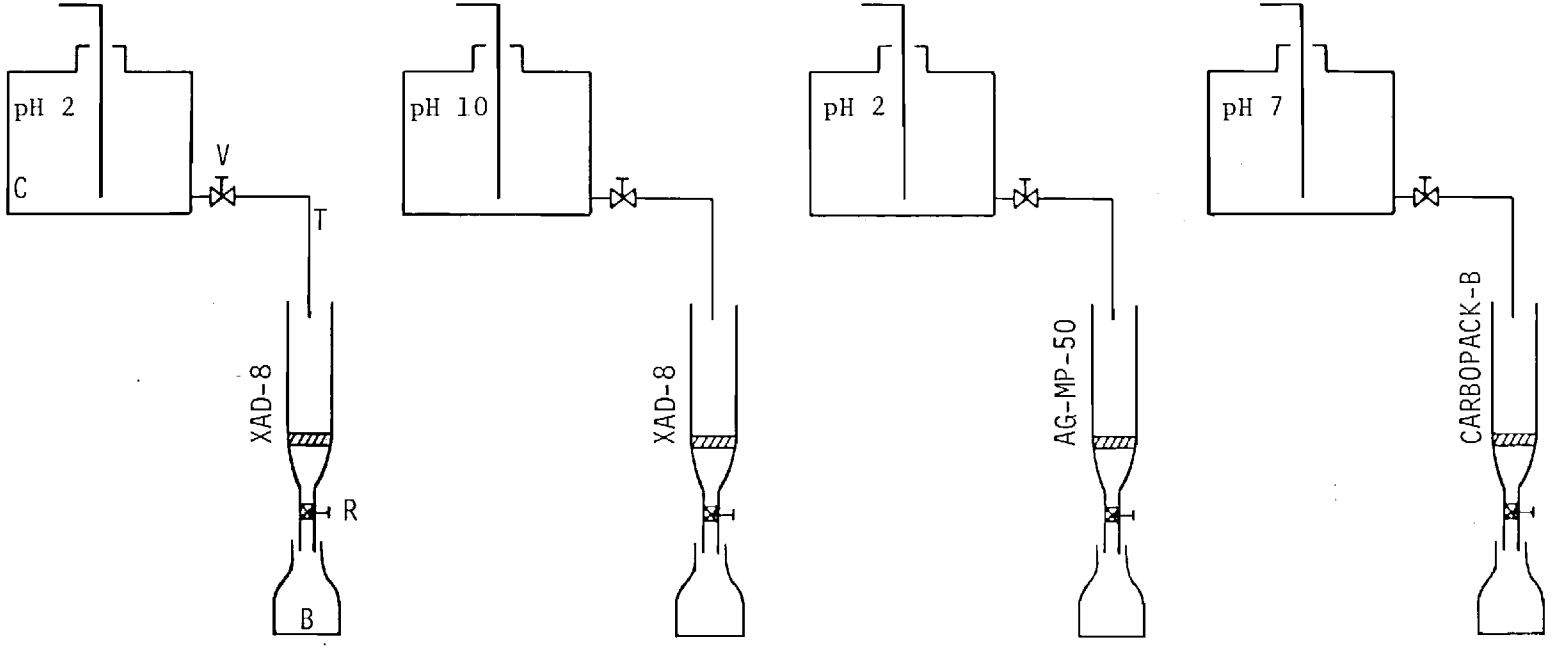
Carbopack B GCB was washed with 20 ml acetone, 20 ml methylene chloride and 50 ml "OFW" prior to column packing. Since this material is fragile, care was taken to avoid any mechanical stress which would cause particle rupture and consequently generate flow rate problems. In the lab-scale experiments 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

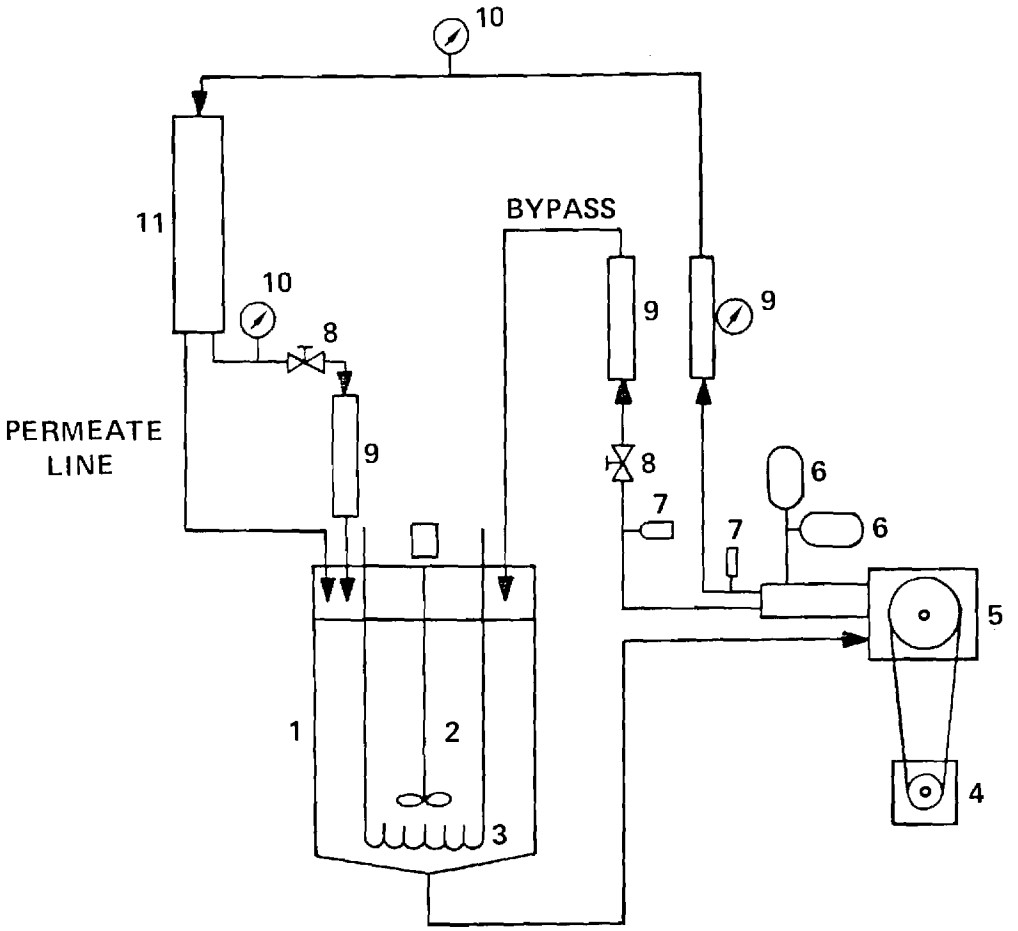
S_o = specific surface area, cm^{-1} = $6/\phi d$ (see Table 9 for definitions)

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

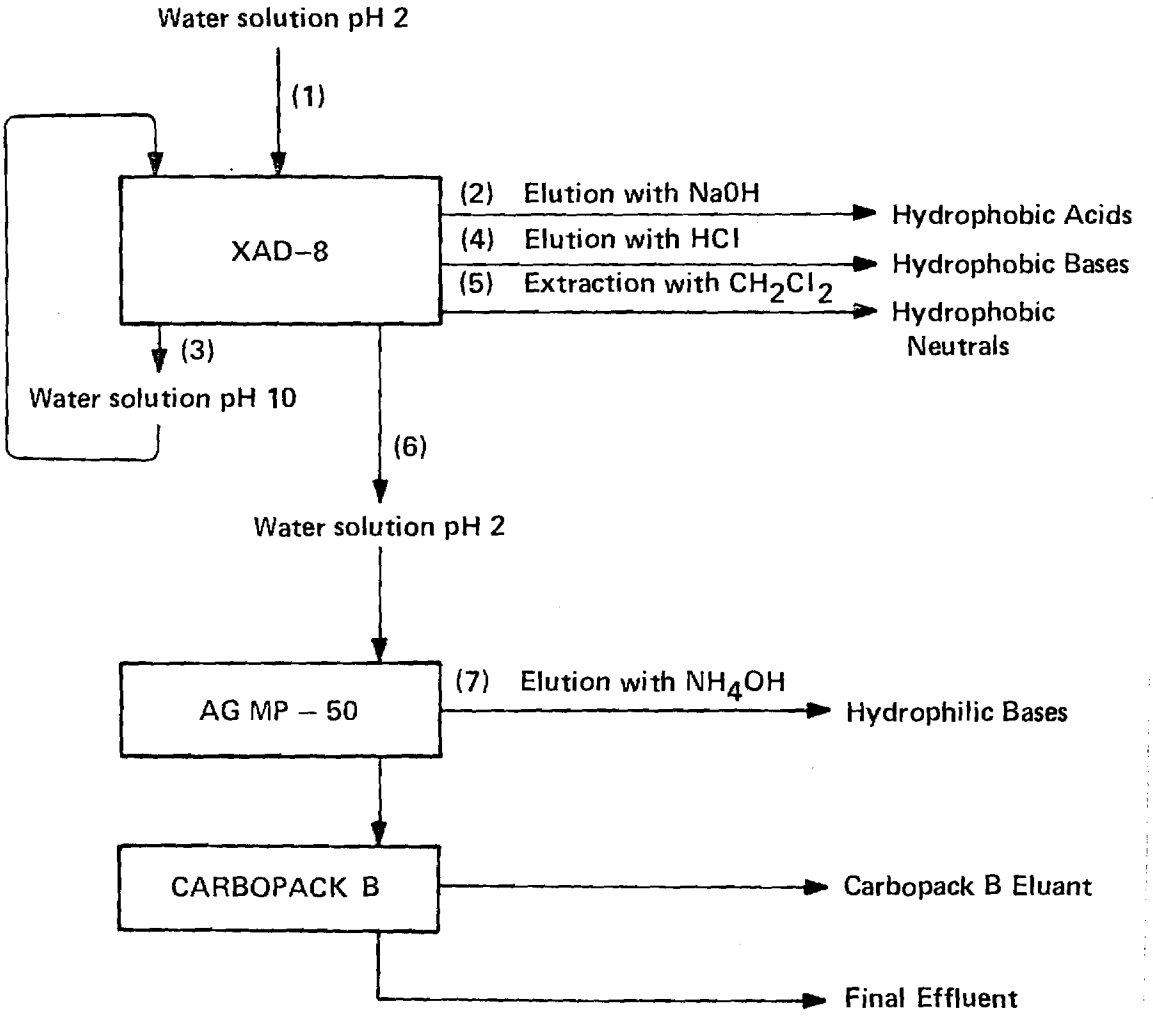


Figure 6. Flow Schematic of Isolation/Fractionation Scheme

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

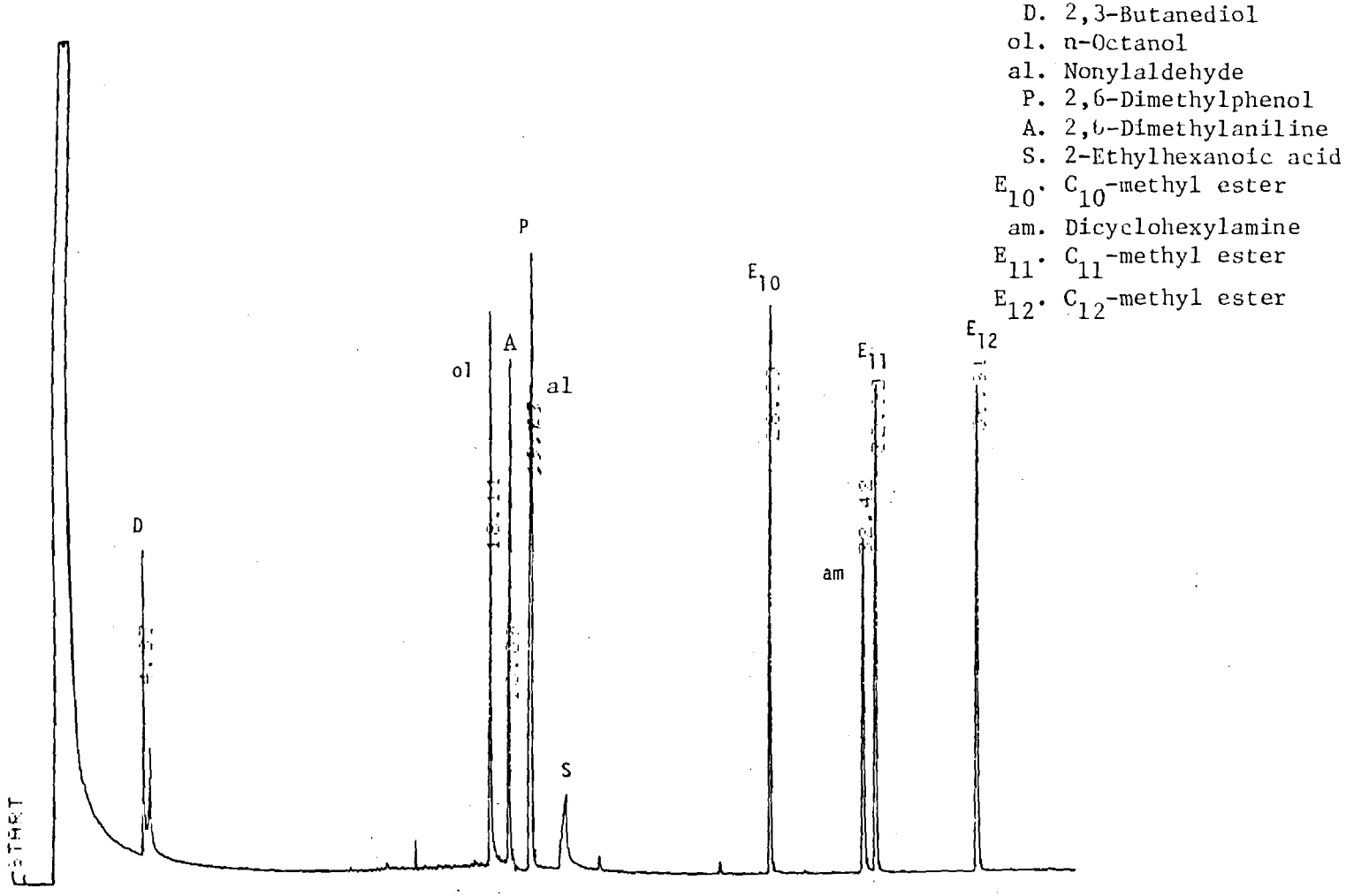
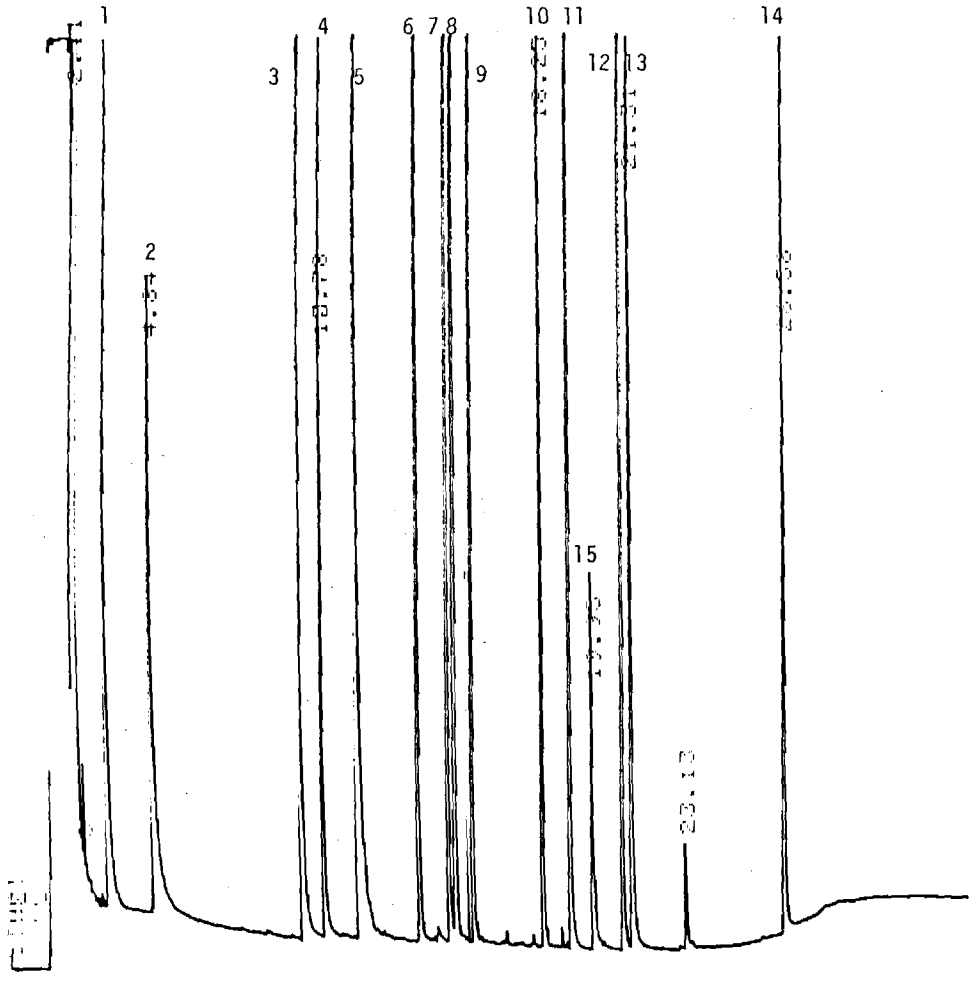


Figure 7. GC-FID Trace of Polarity Mixture for Column Testing (Grob). SE-54 Silicone Gum Phase; film thickness ≈ 0.2 µm. Temperature Program 39°C (0.1 min.)-290°C at 3°C/min; Coating Efficiency = 89%; TZ = 36.



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

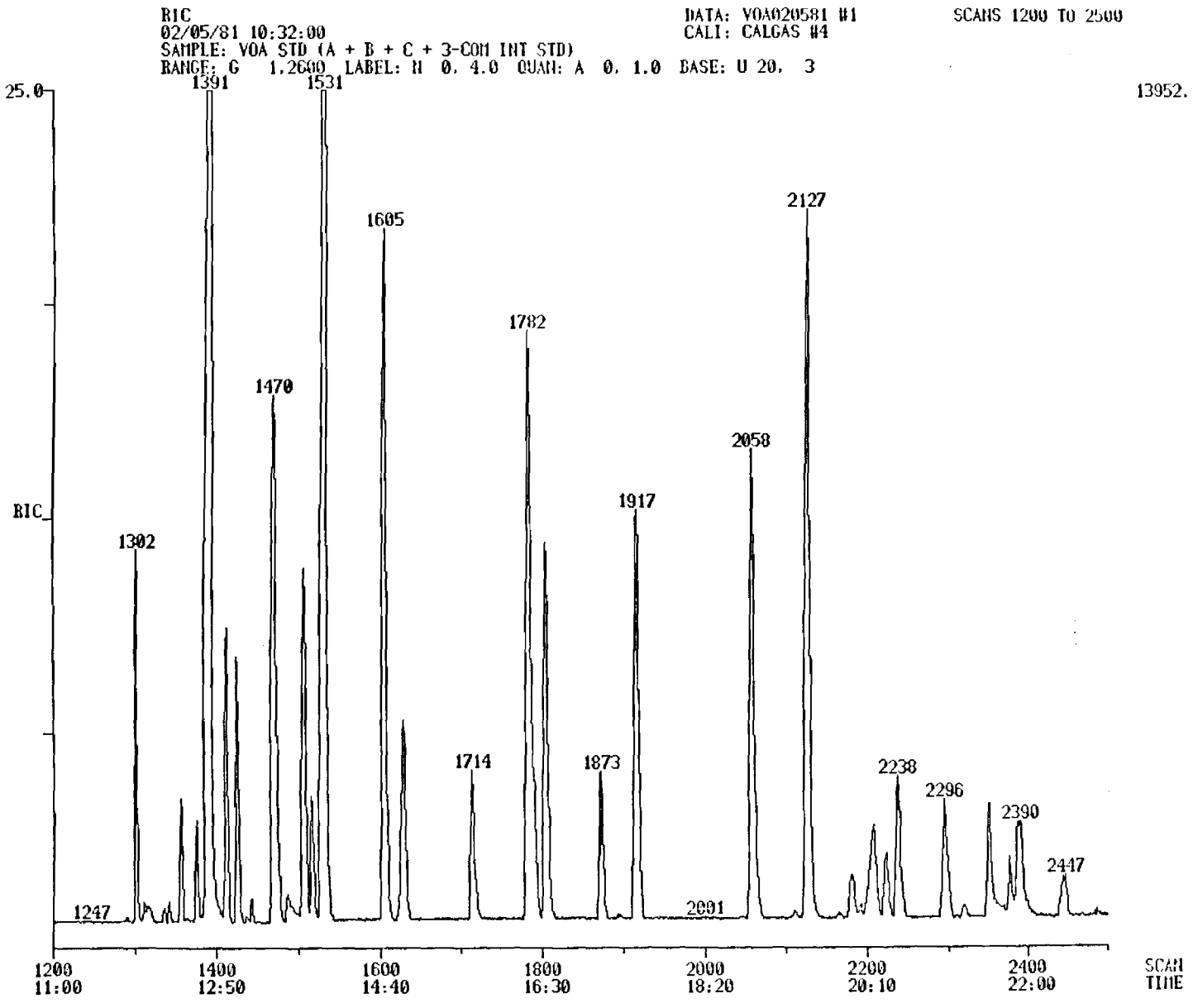


Figure 9. RIC of Purgeable Priority Pollutants (16).

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.

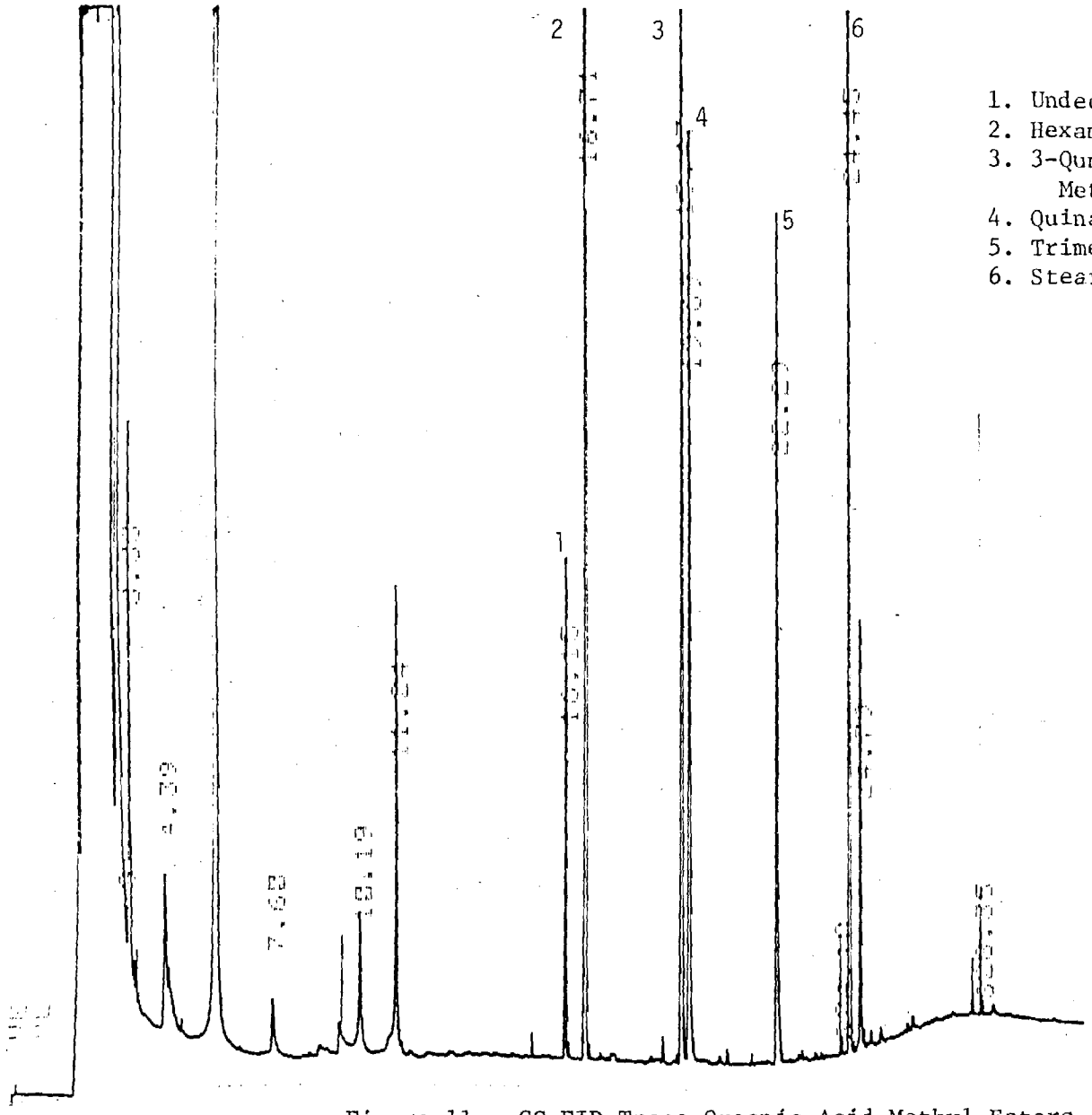
Among the derivatization methods available for the GC analysis of glycine, the preparation of N(0)-heptafluorobutyric isoamyl ester (18) proved to be a reliable method, and thus it was used to assess glycine during the isolation/fractionation scheme study. The reproducibility of the analytical procedure 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

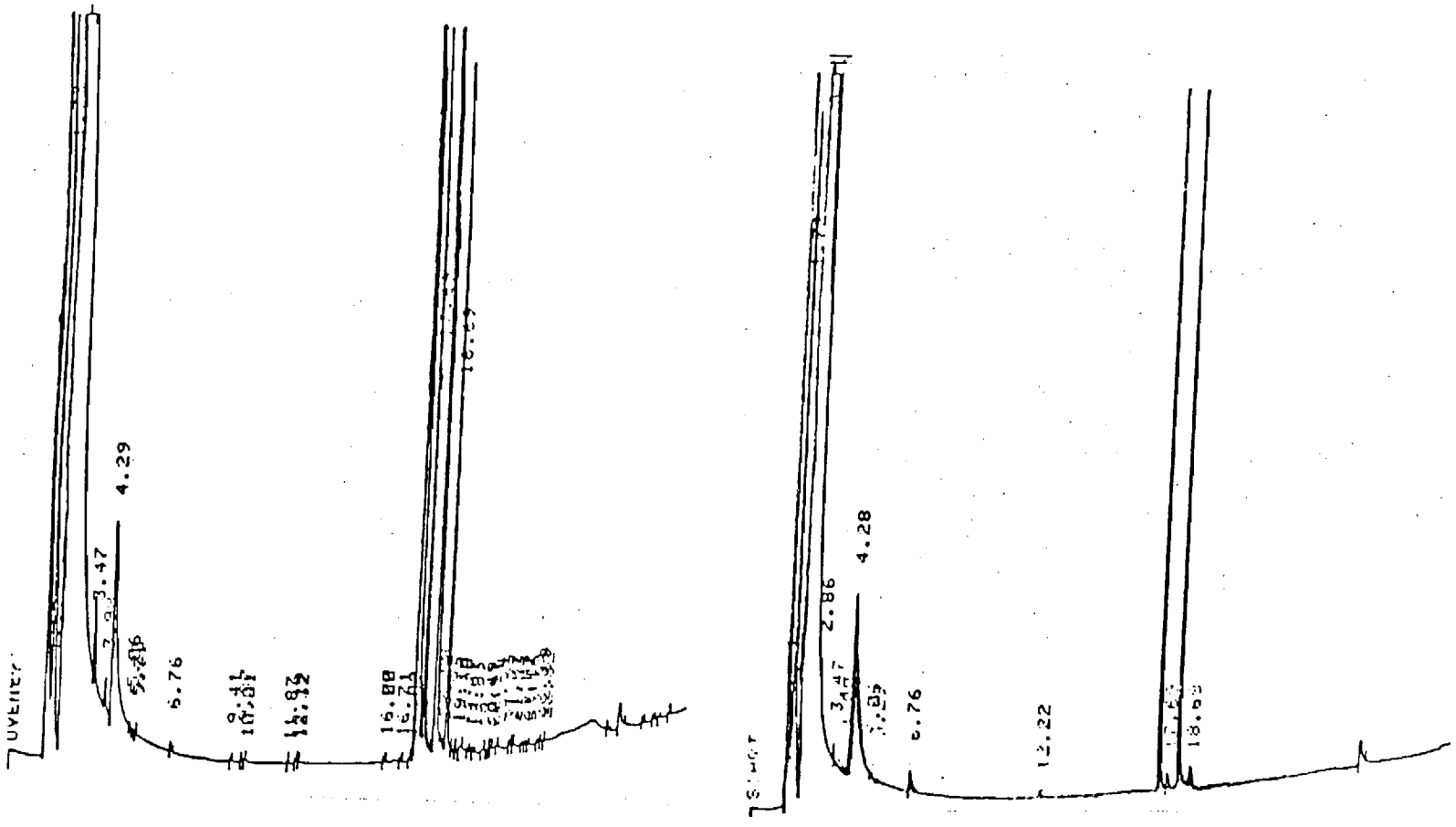
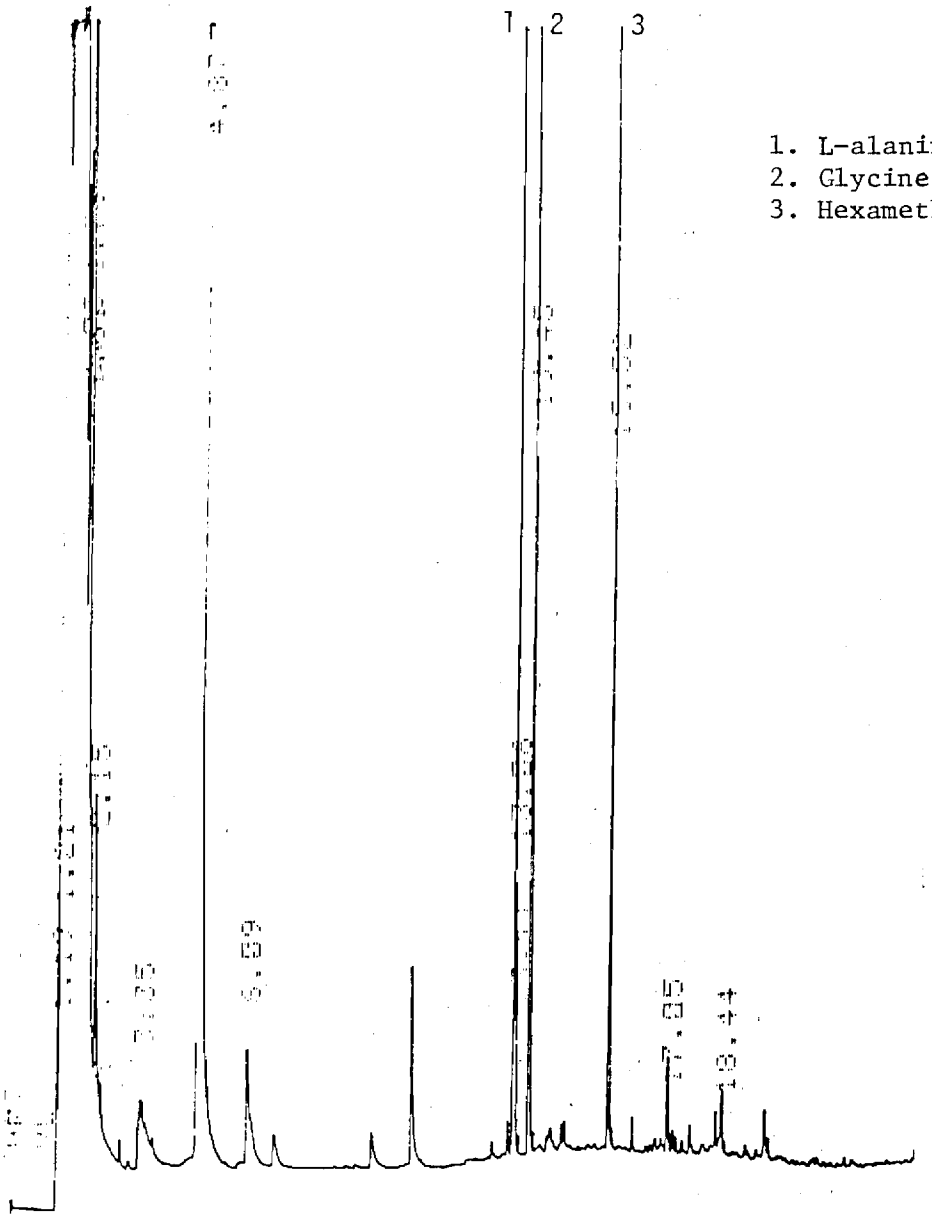


Figure 13. ECD Trace of Penta-(trifluoroacetyl)glucose Split Injection (50:1) 50 ng Left and 5 ng Right

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

Weight of Glycine (μg)	RT	IS (10ng) Area (1)	RT	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

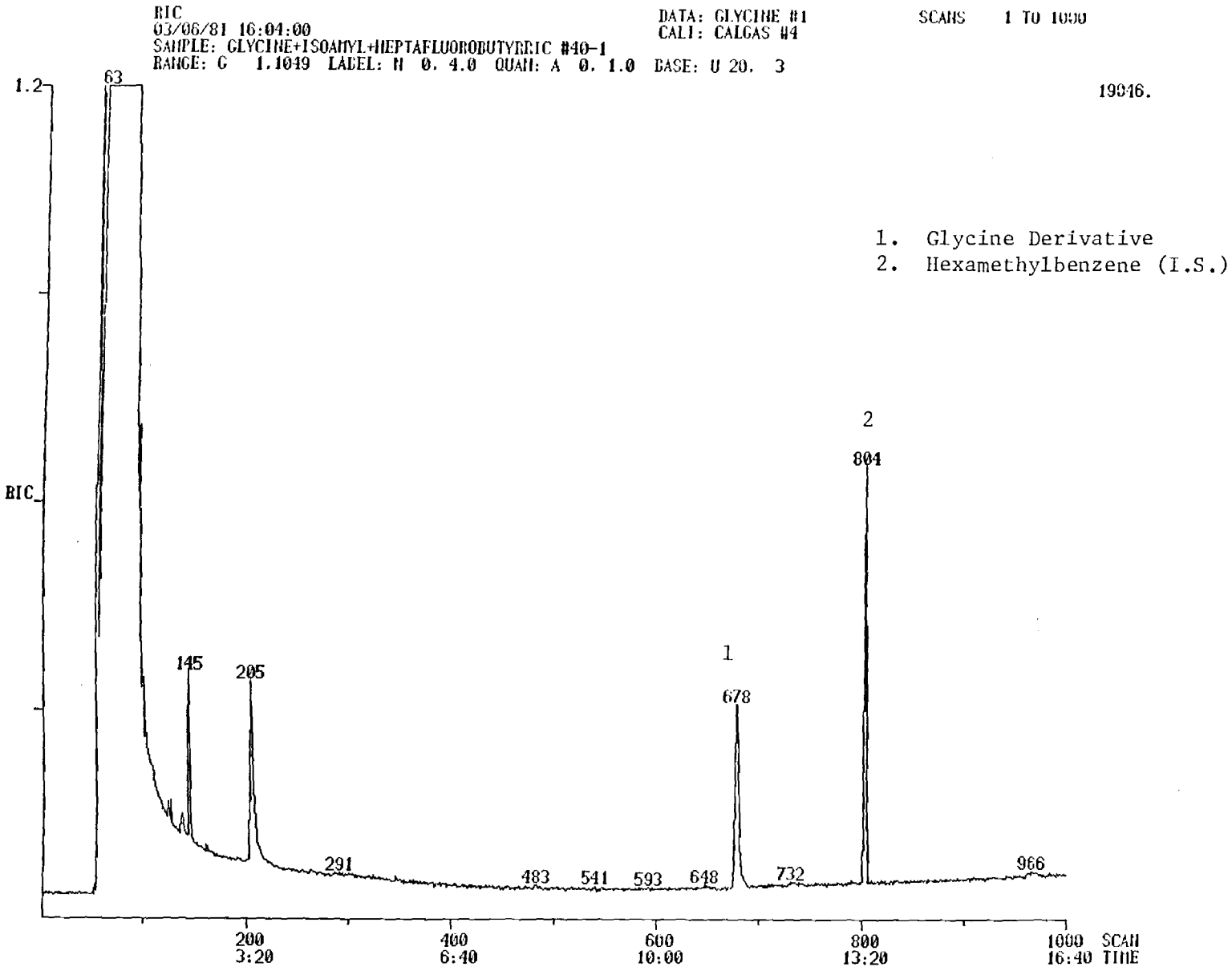


Figure 15. RIC of Glycine Derivative Standard

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.

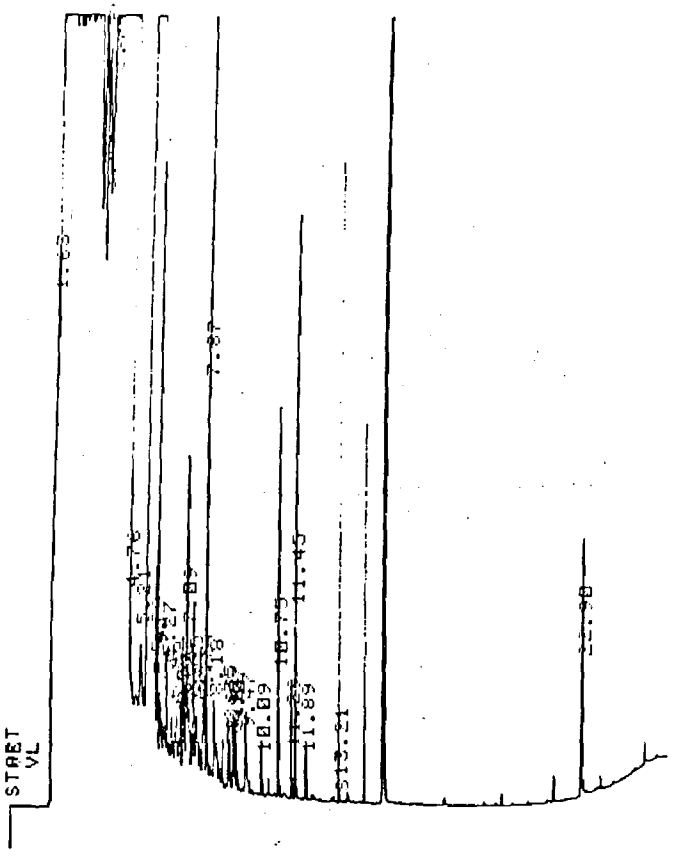
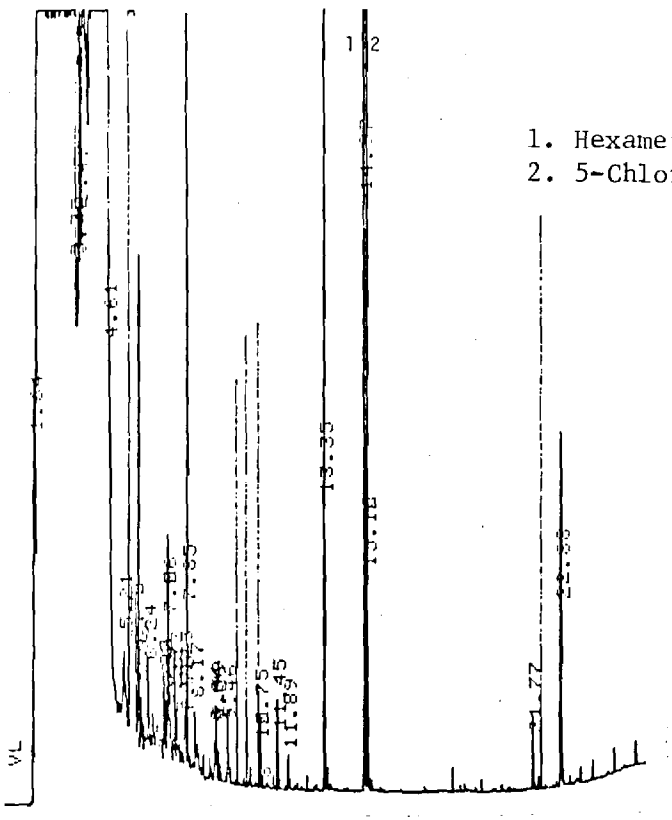


Figure 17. GC-FID Trace of Reaction Mixture Blank



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

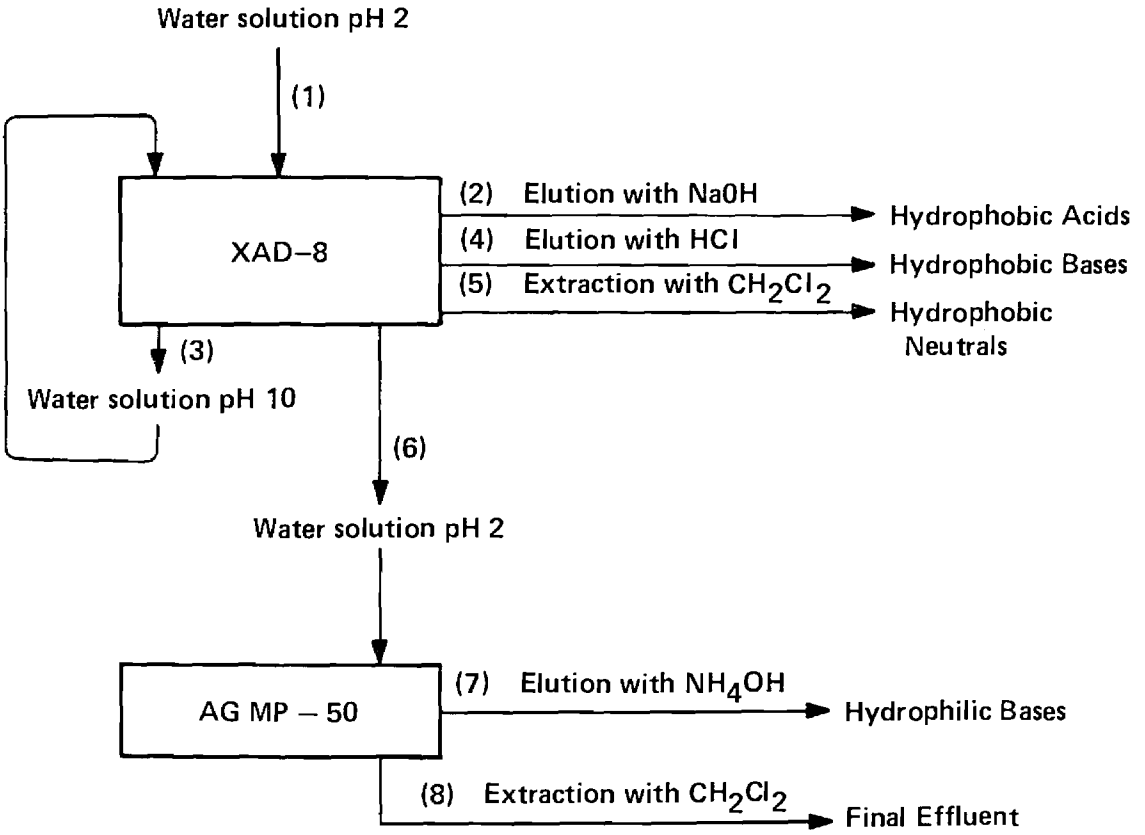


Figure 19. Flow Schematic of Resin Fractionation Scheme at Lab-Scale

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

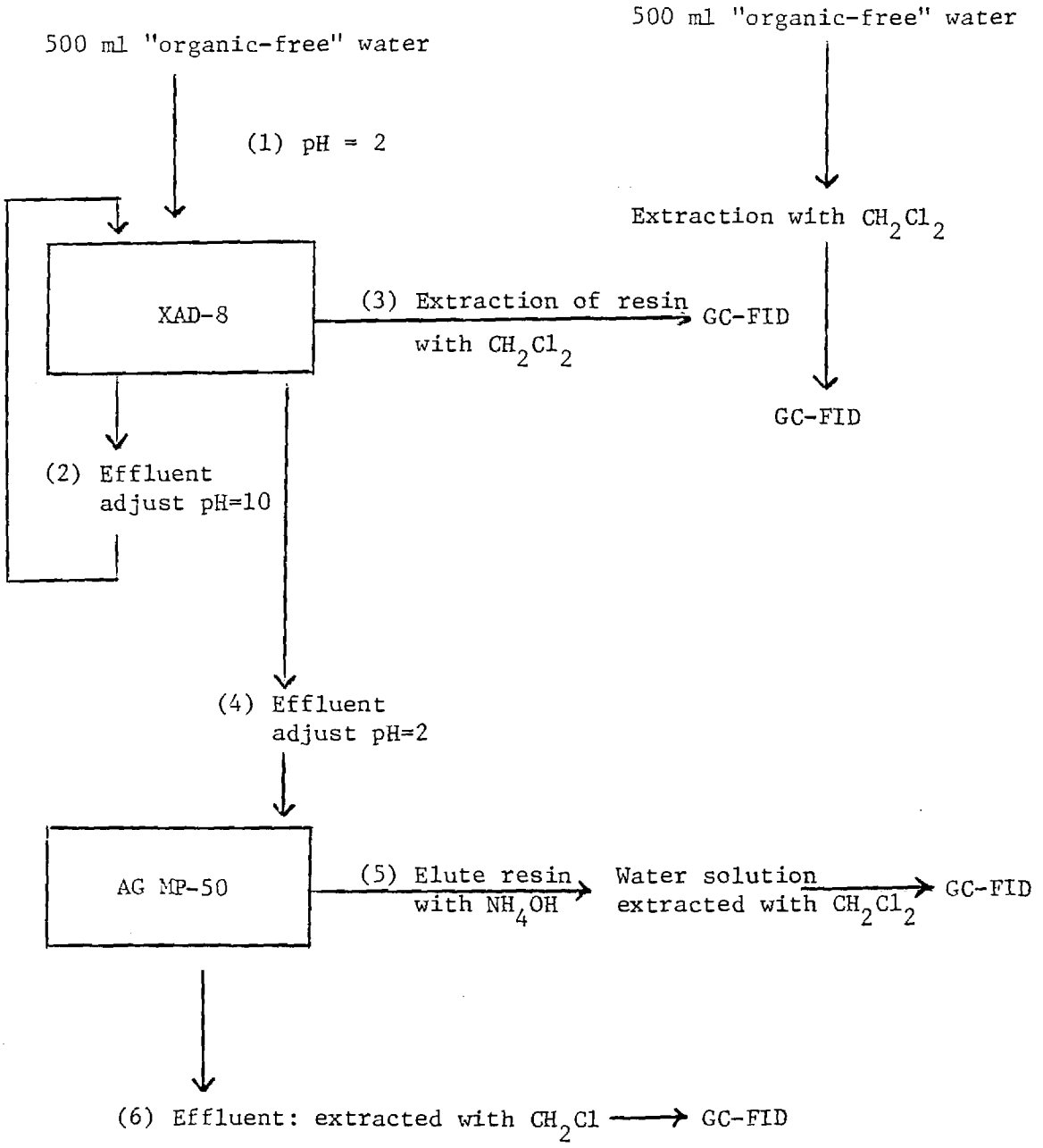


Figure 20. Experimental sequence for the chlorine residual study.

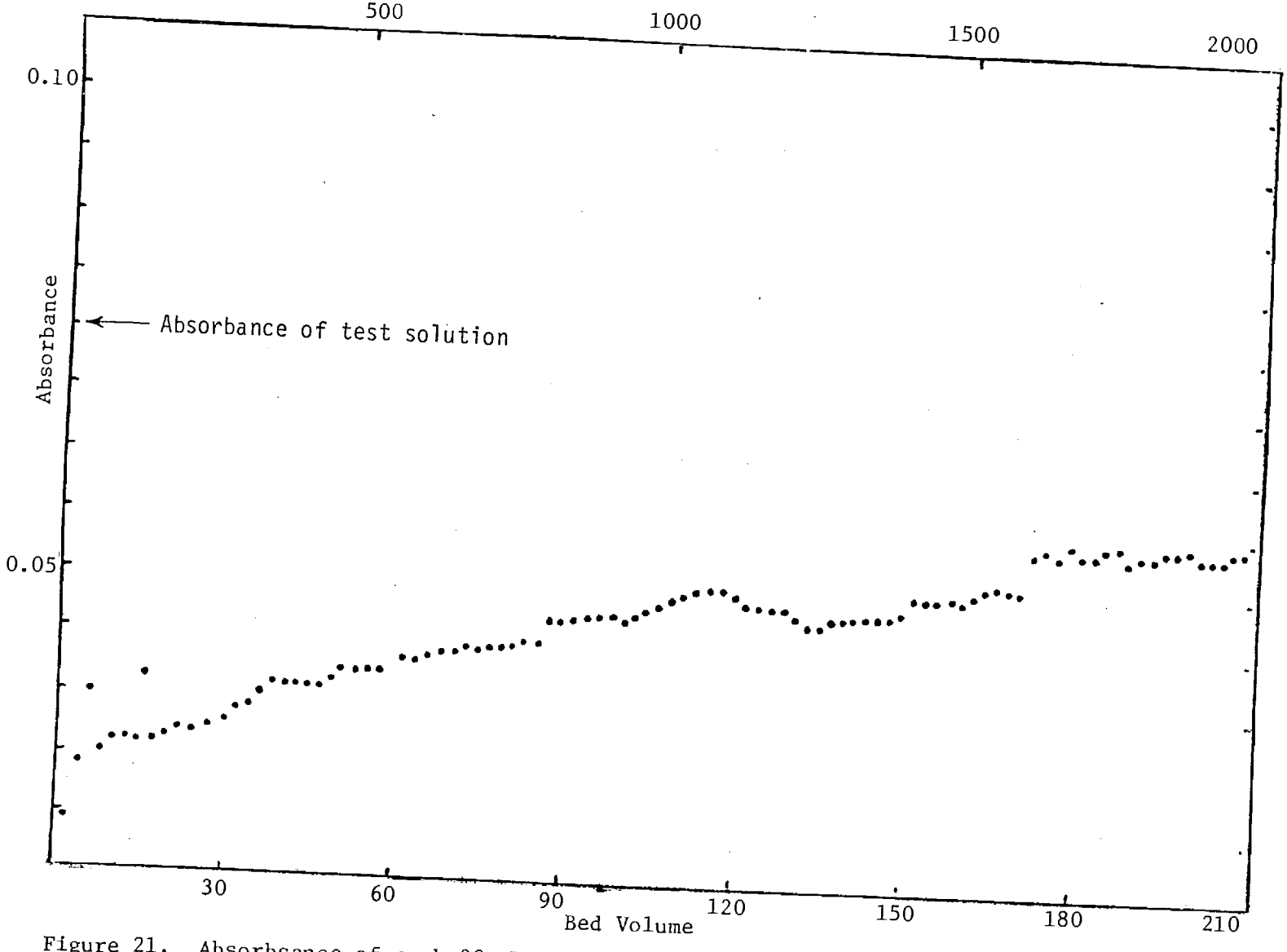


Figure 21. Absorbsance of each 20-mL fraction (Test Solution pH 2).

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'-Tetrachlorobio-phenol	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

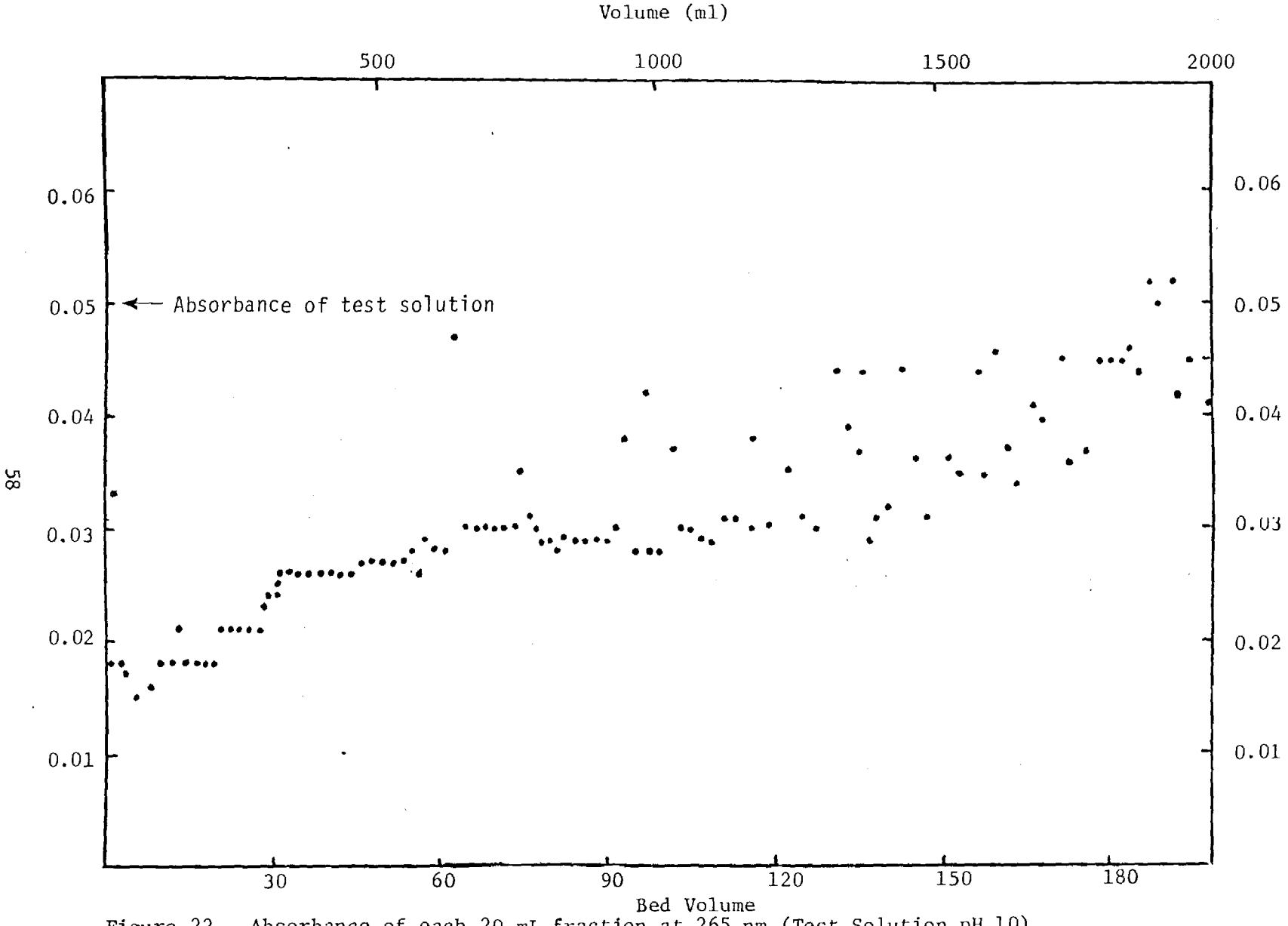


Figure 22. Absorbance of each 20-mL fraction at 265 nm (Test Solution pH 10).

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'-Tetrachloro-biphenyl	-	-	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'-Tetrachloro-biphenyl	-	-	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'-Tetrachloro-biphenyl	-	-	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.

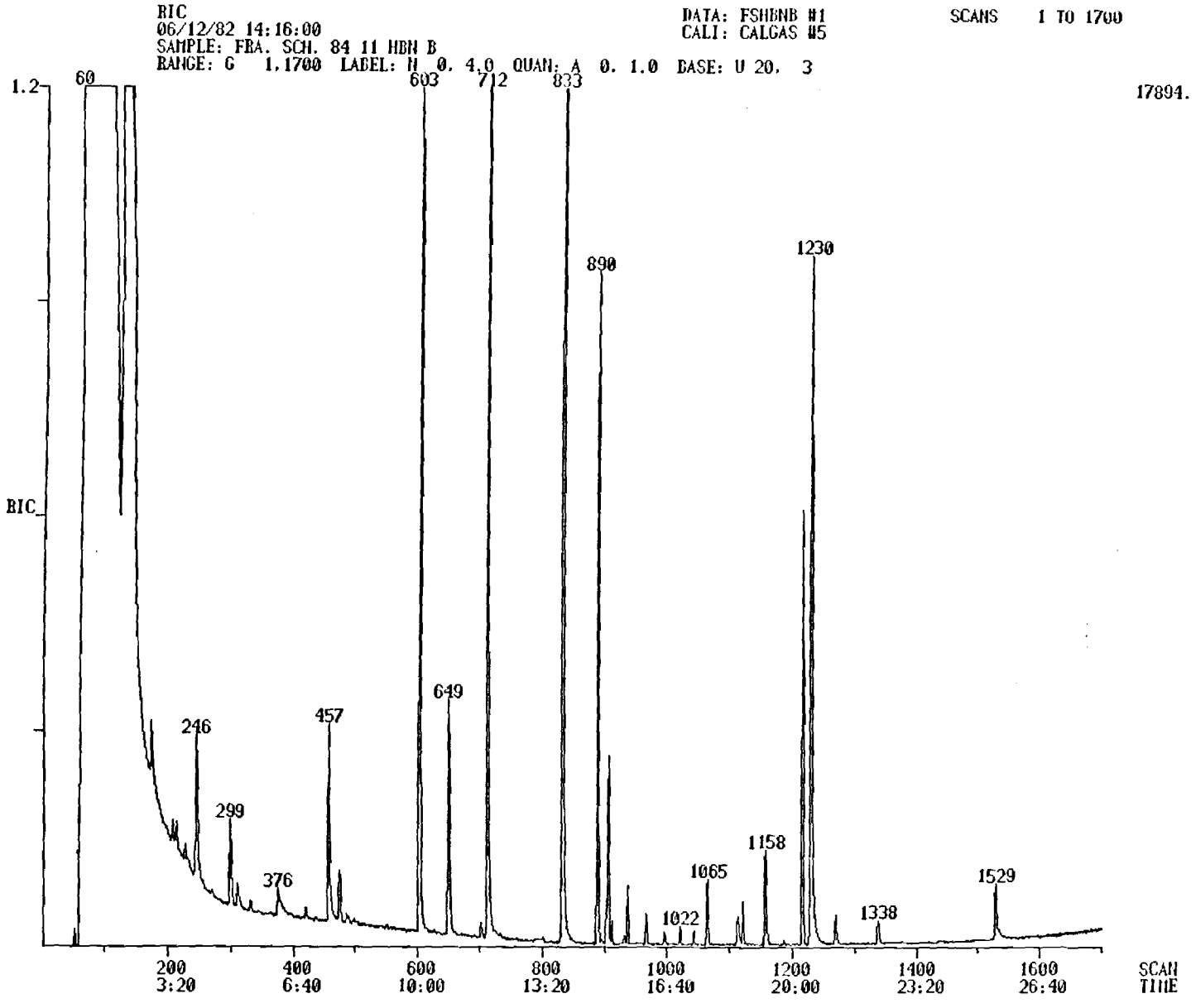


Figure 24. RIC of "Hydrophobic Neutral" Fraction

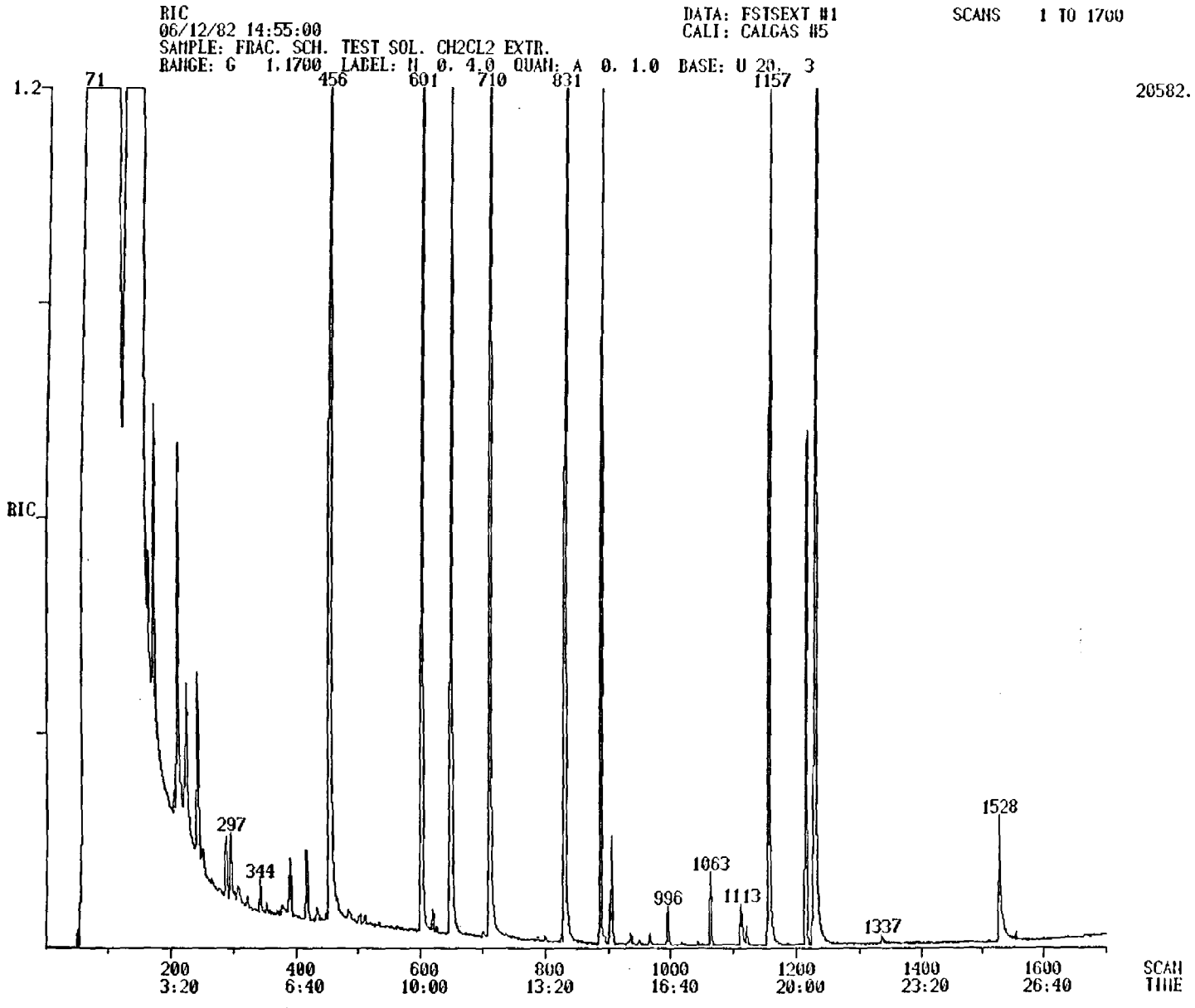


Figure 23. RIC of Test Solution Extract

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		

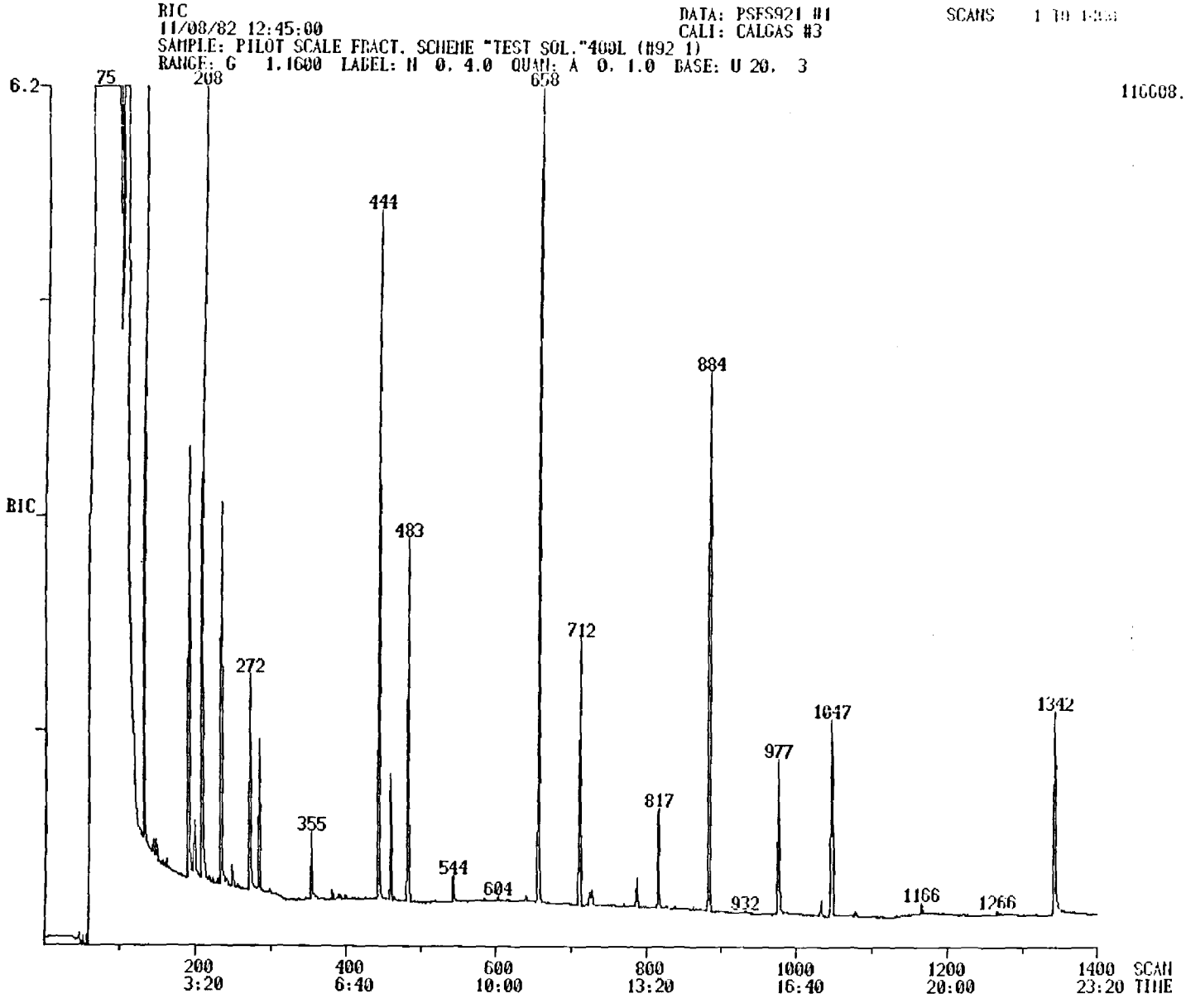


Figure 25. RIC of Test Solution Extract for Pilot-Scale Study

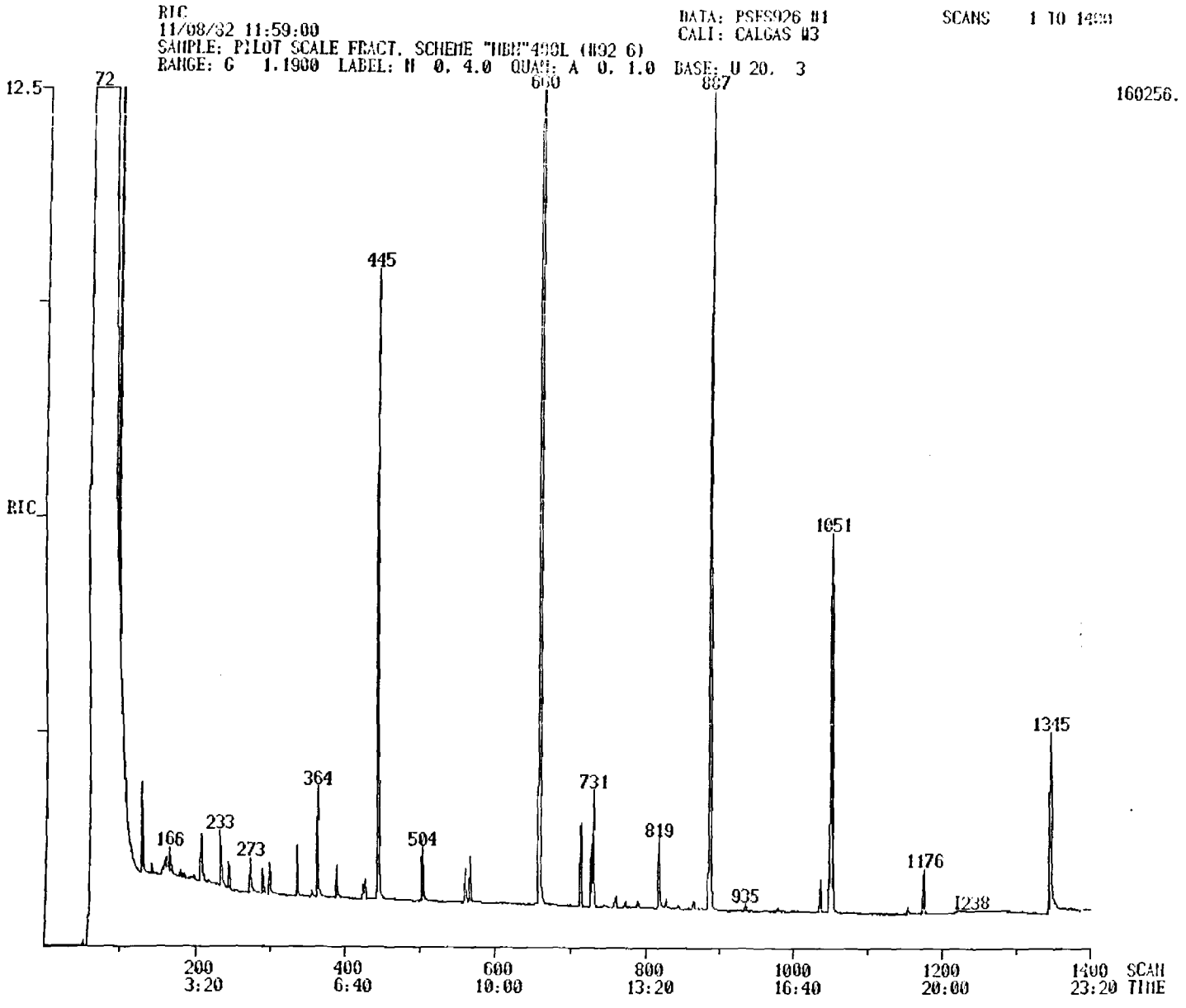


Figure 26. RIC of "Hydrophobic Neutral" Fraction from Pilot-Scale Study

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 column 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

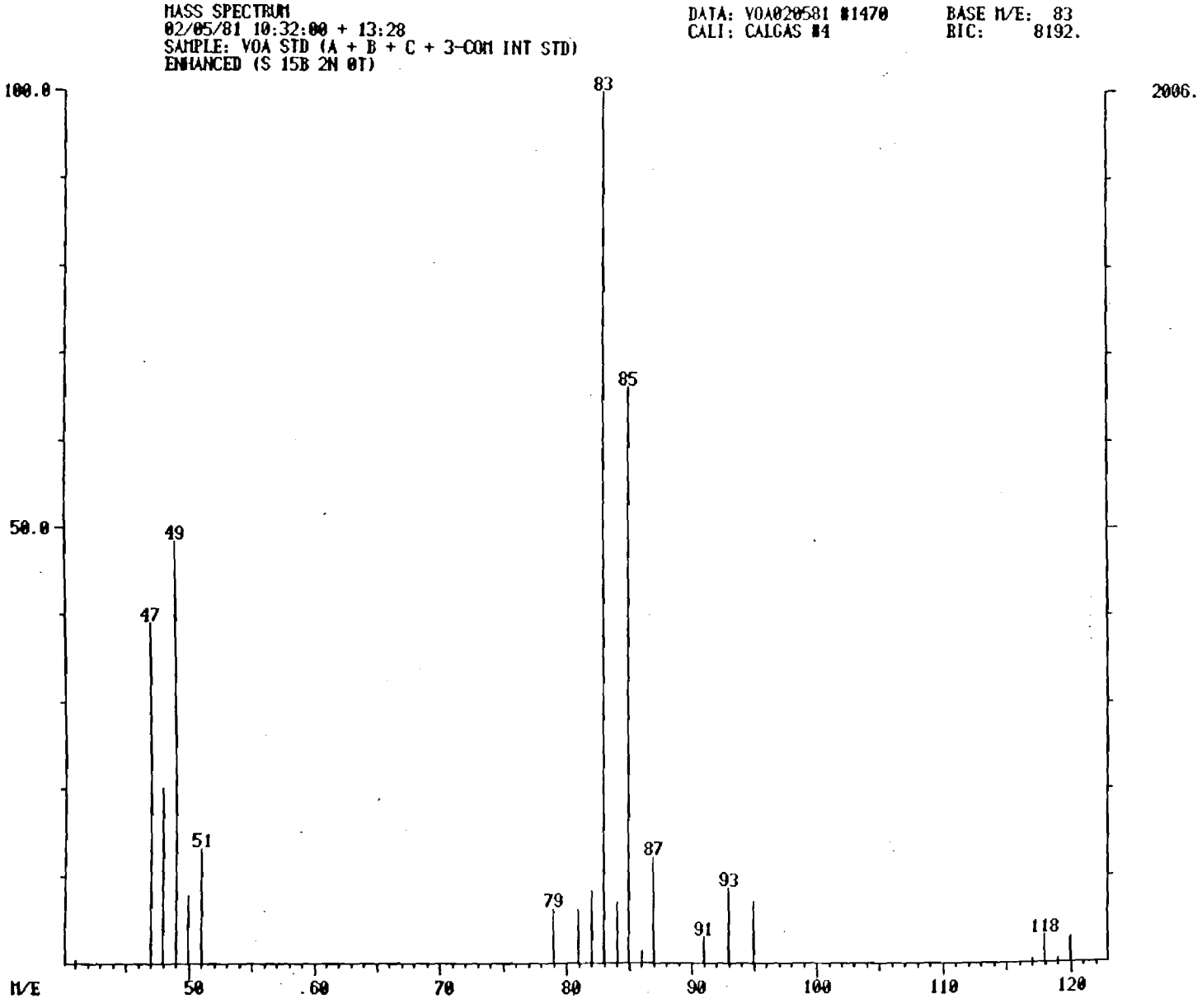

Figure A-1. Mass Spectrum of Chloroform

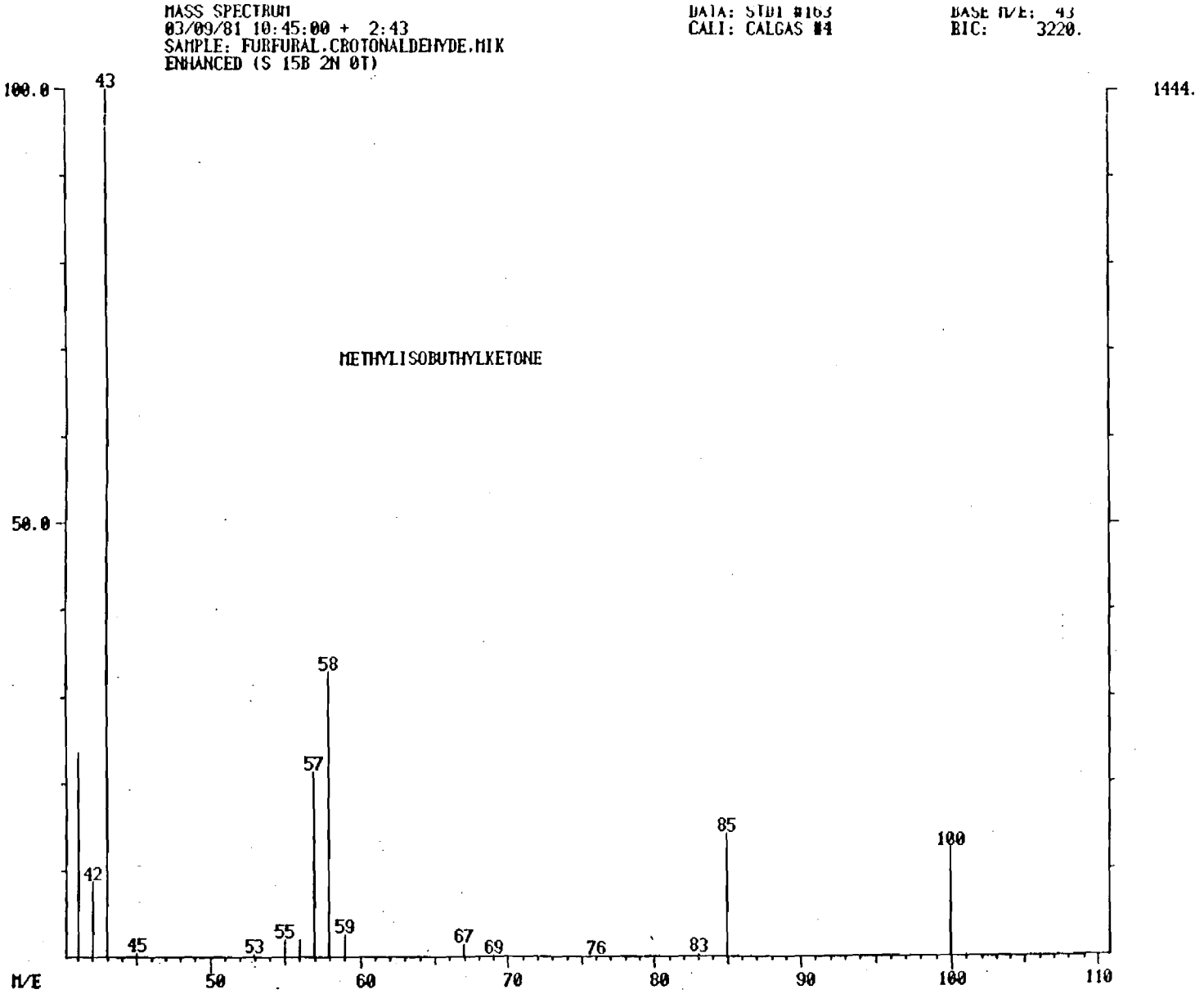

Figure A-2. Mass Spectrum of Methylisobutylketone

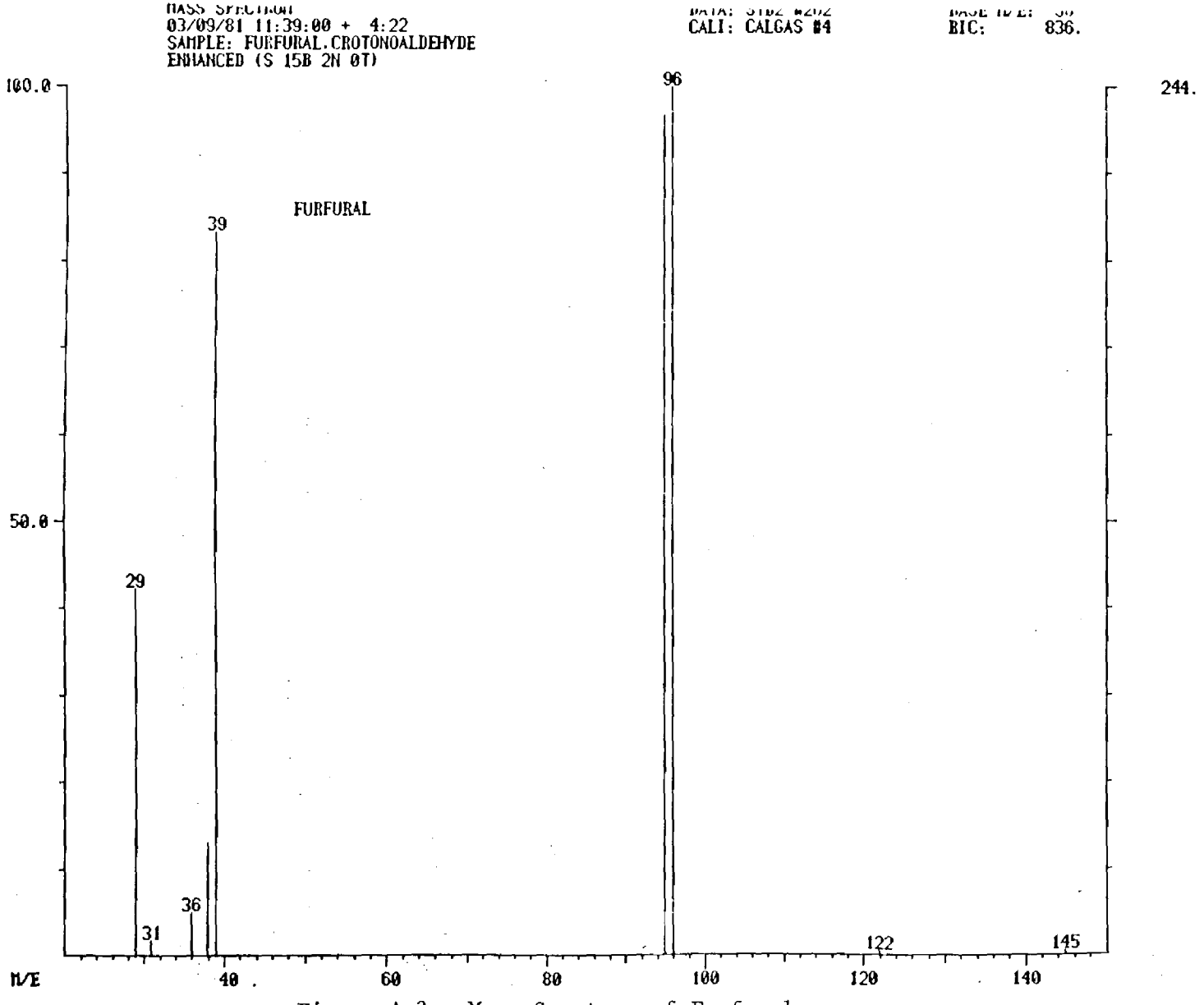

Figure A-3. Mass Spectrum of Furfural

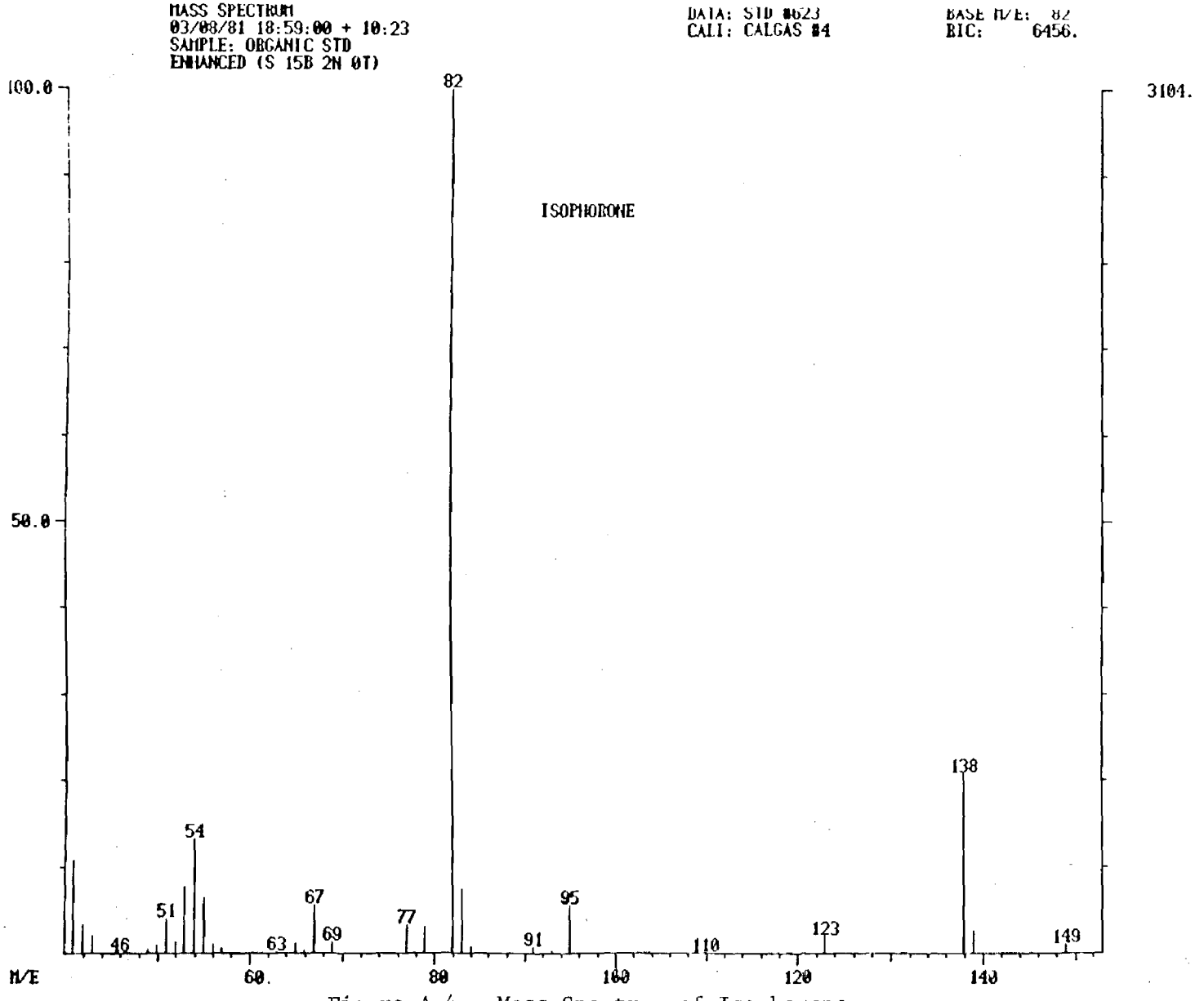

Figure A-4. Mass Spectrum of Isophorone

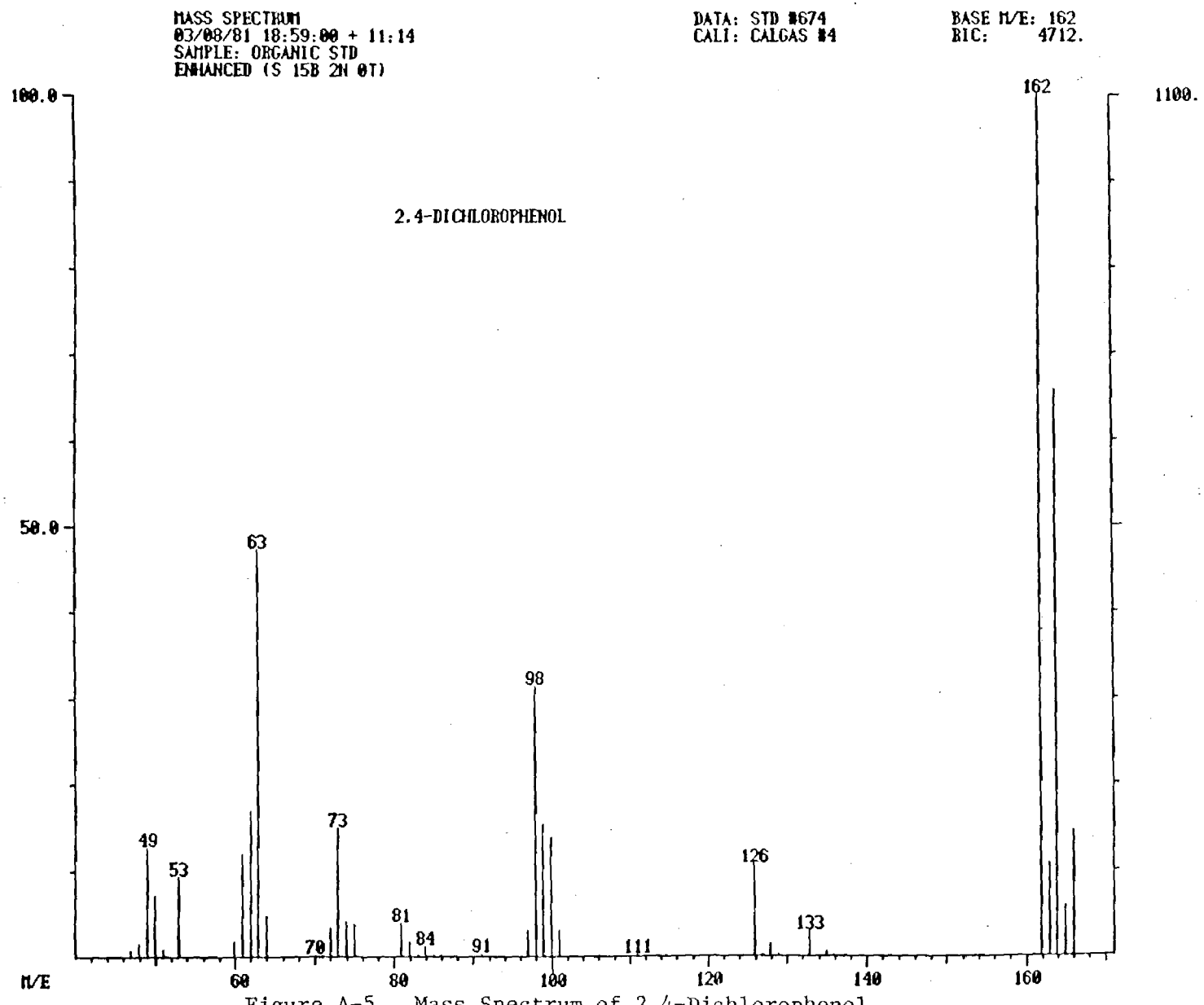

Figure A-5. Mass Spectrum of 2,4-Dichlorophenol

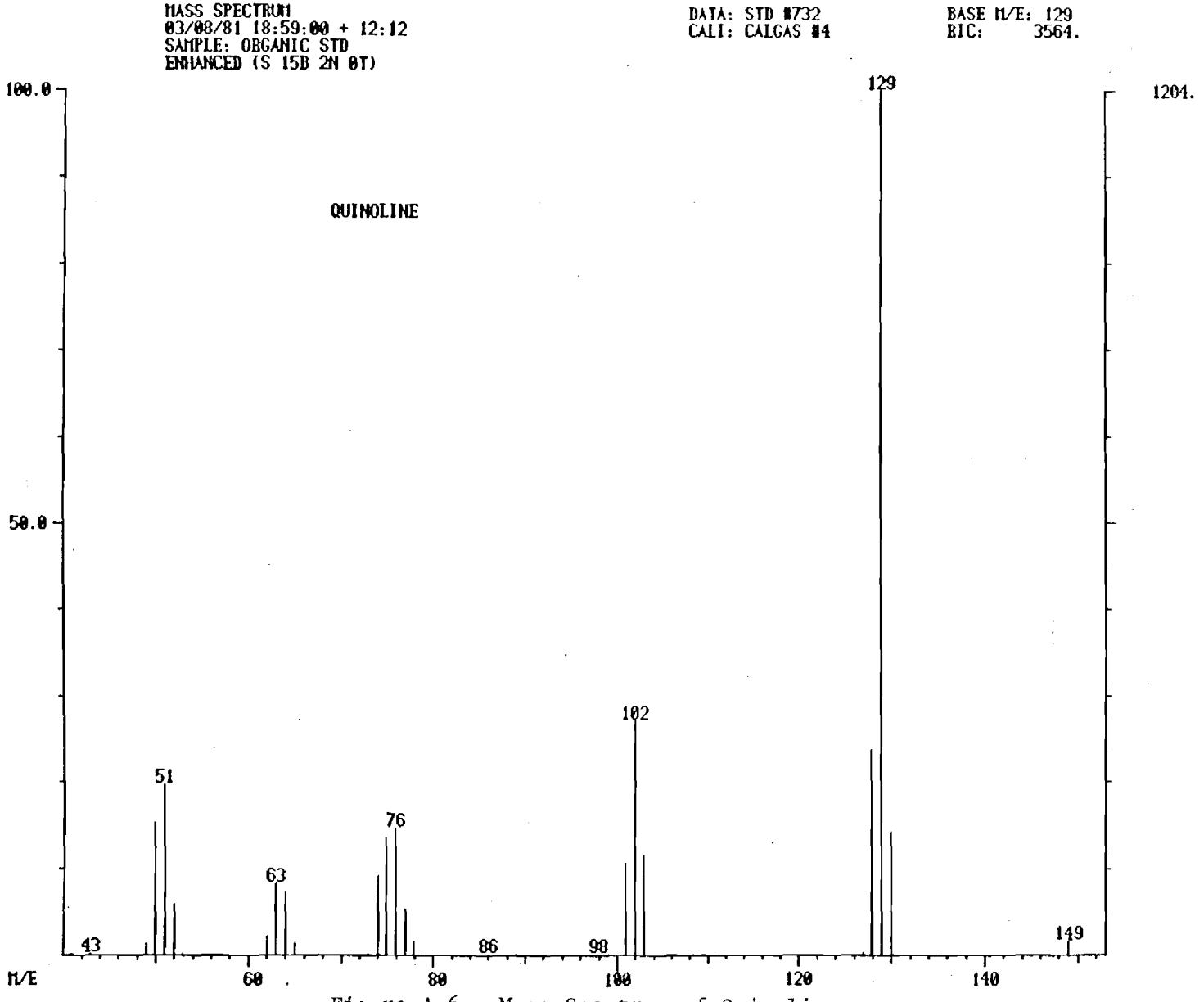

Figure A-6. Mass Spectrum of Quinoline

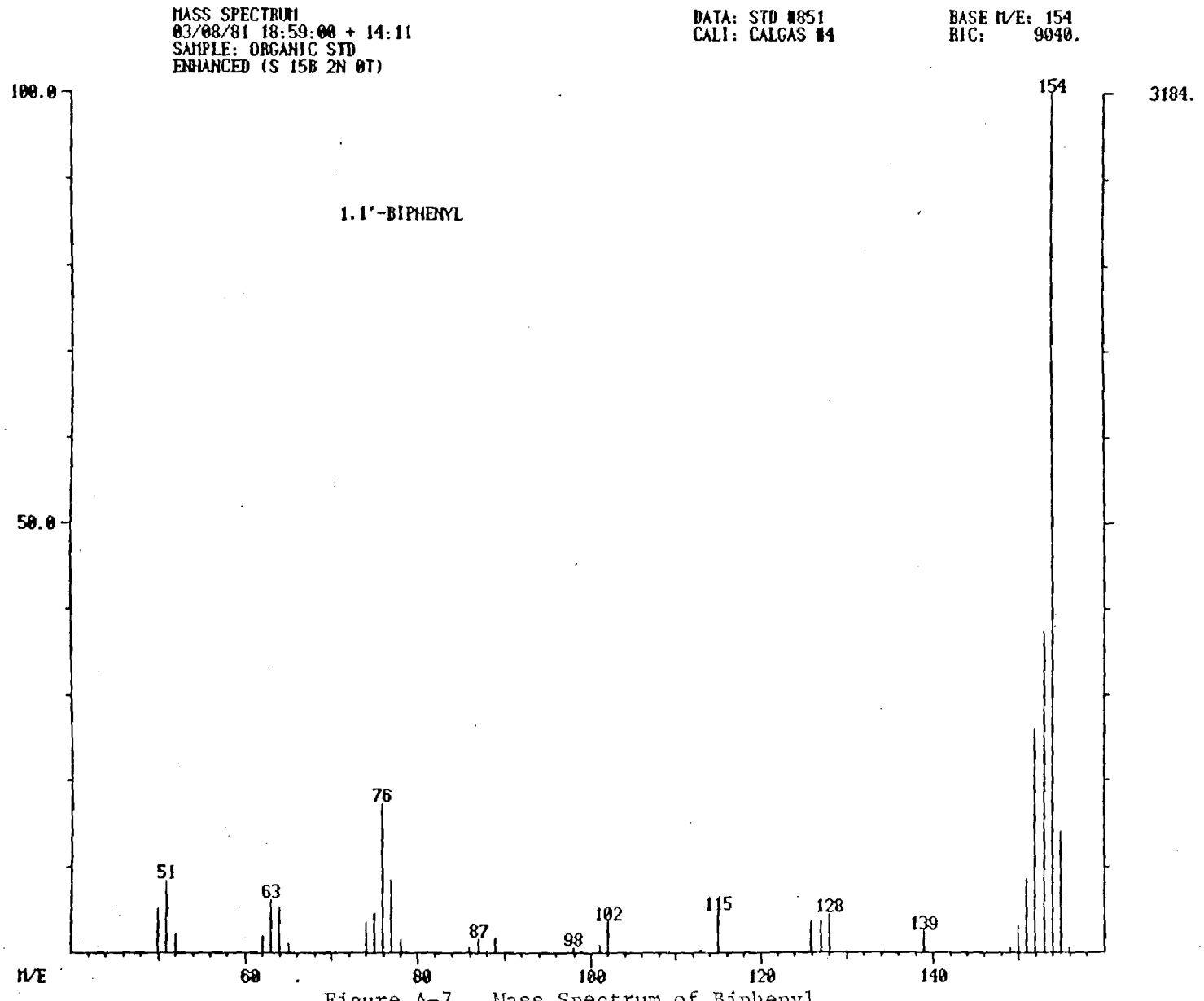

Figure A-7. Mass Spectrum of Biphenyl

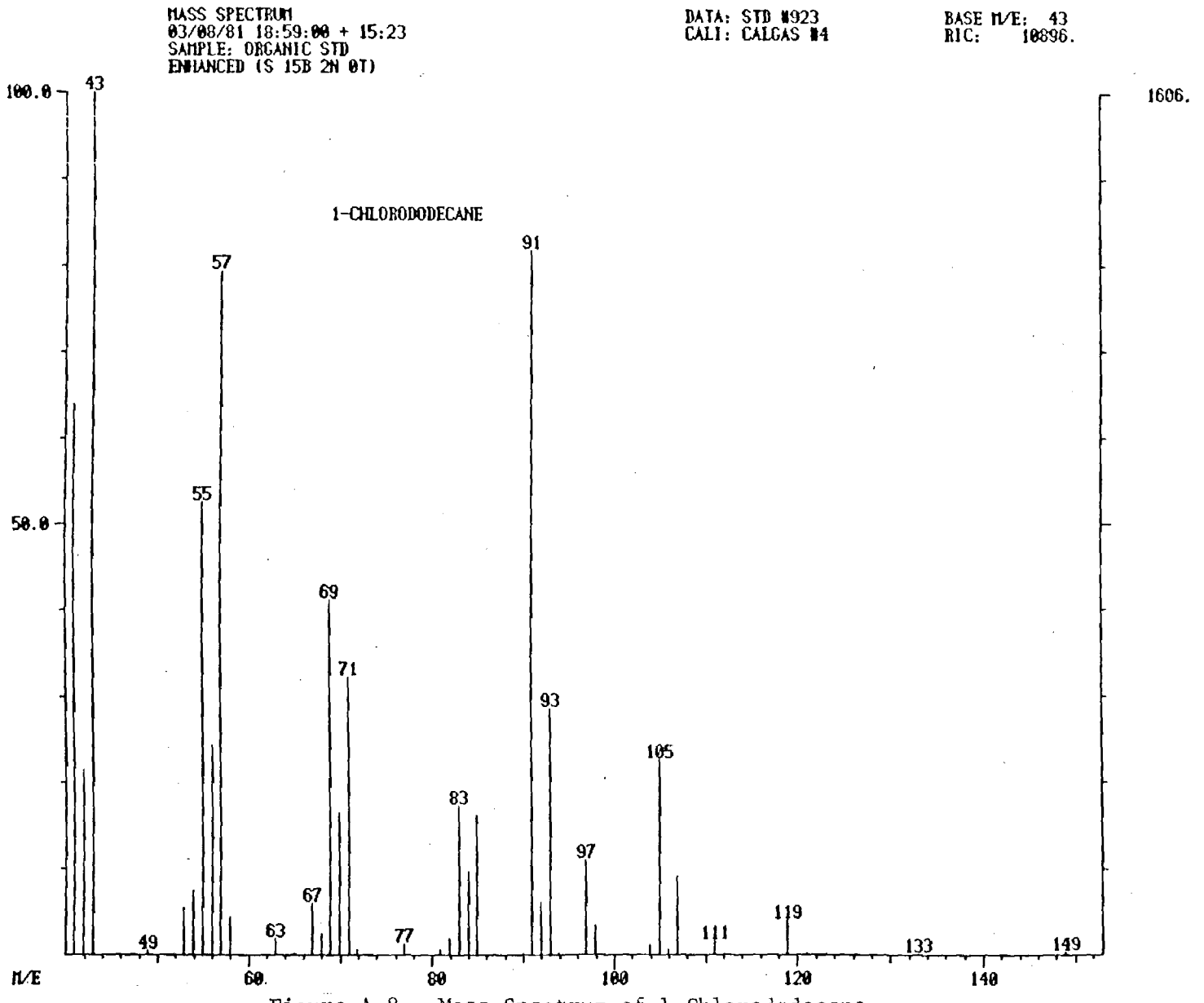

Figure A-8. Mass Spectrum of 1-Chlorododecane

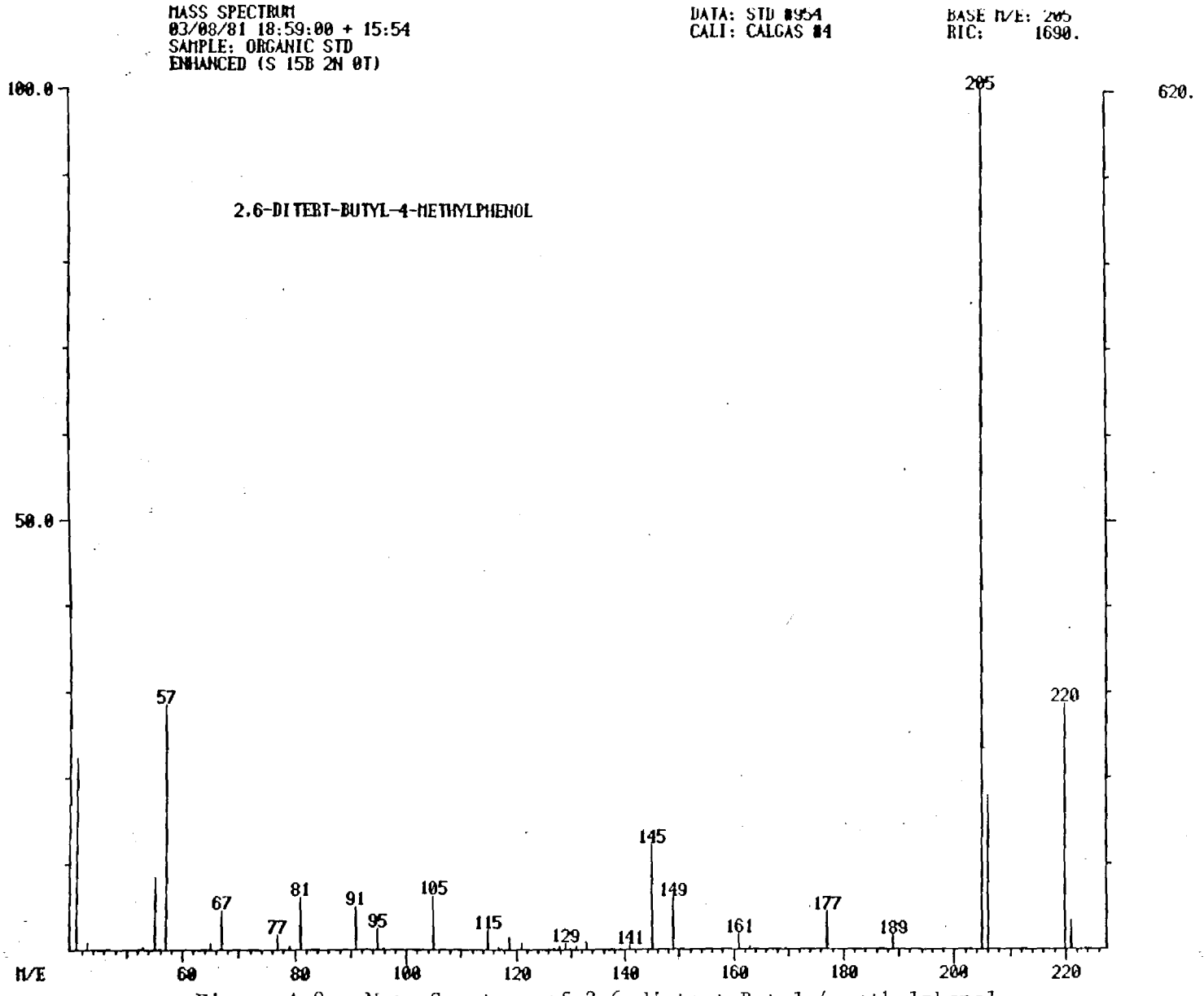

Figure A-9. Mass Spectrum of 2,6-di-tert-Butyl-4-methylphenol

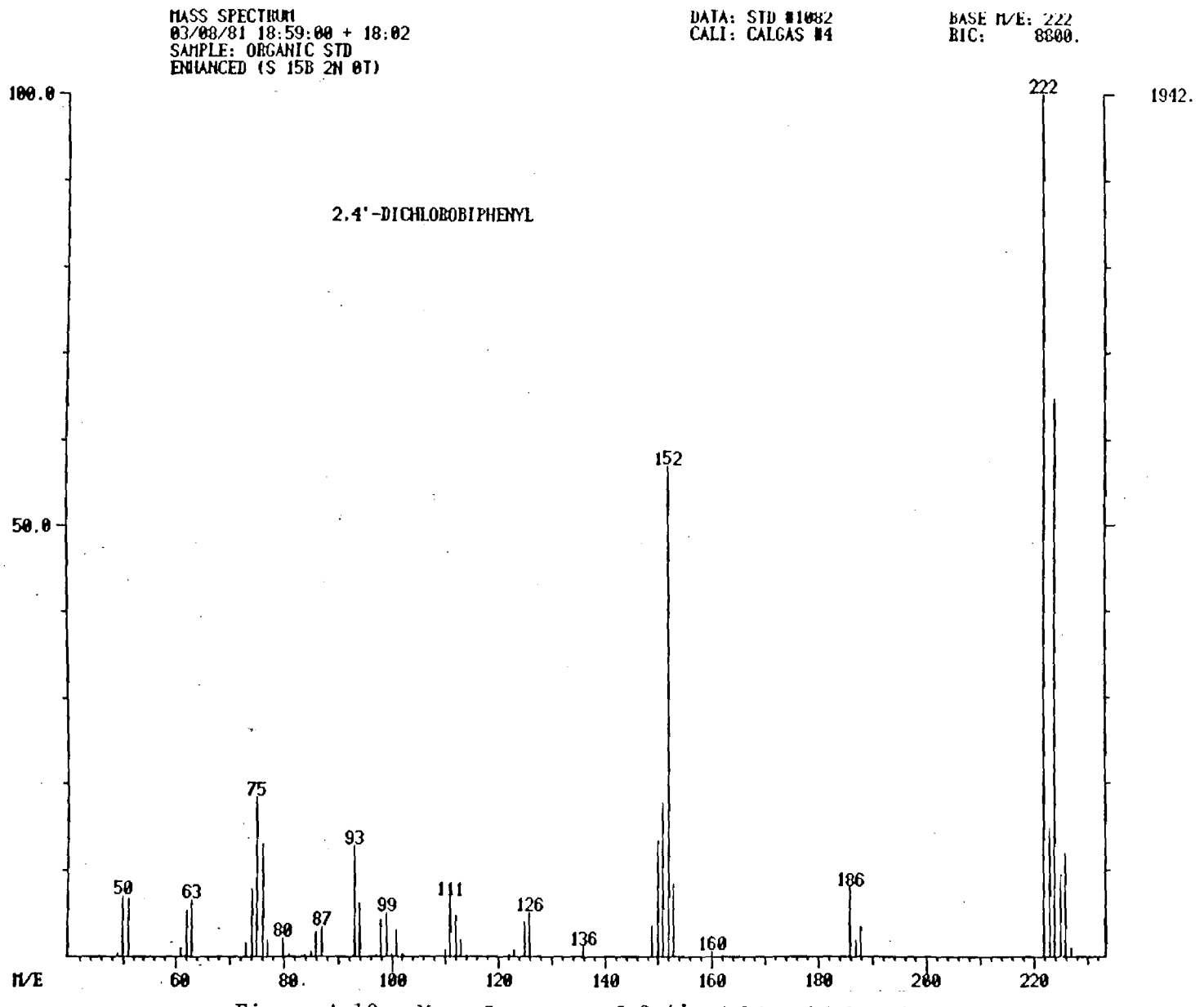

Figure A-10. Mass Spectrum of 2,4'-Dichlorobiphenyl

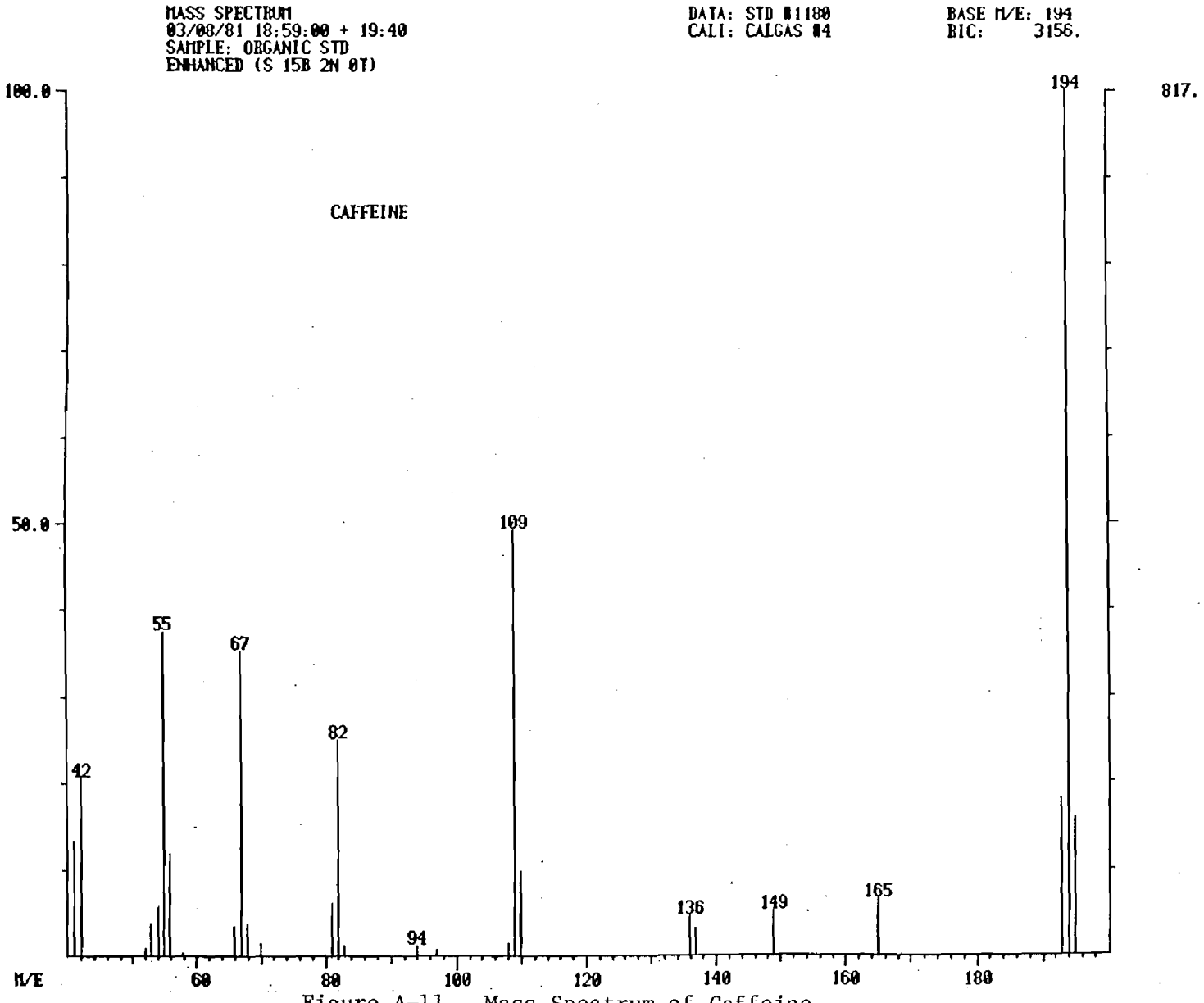

Figure A-11. Mass Spectrum of Caffeine

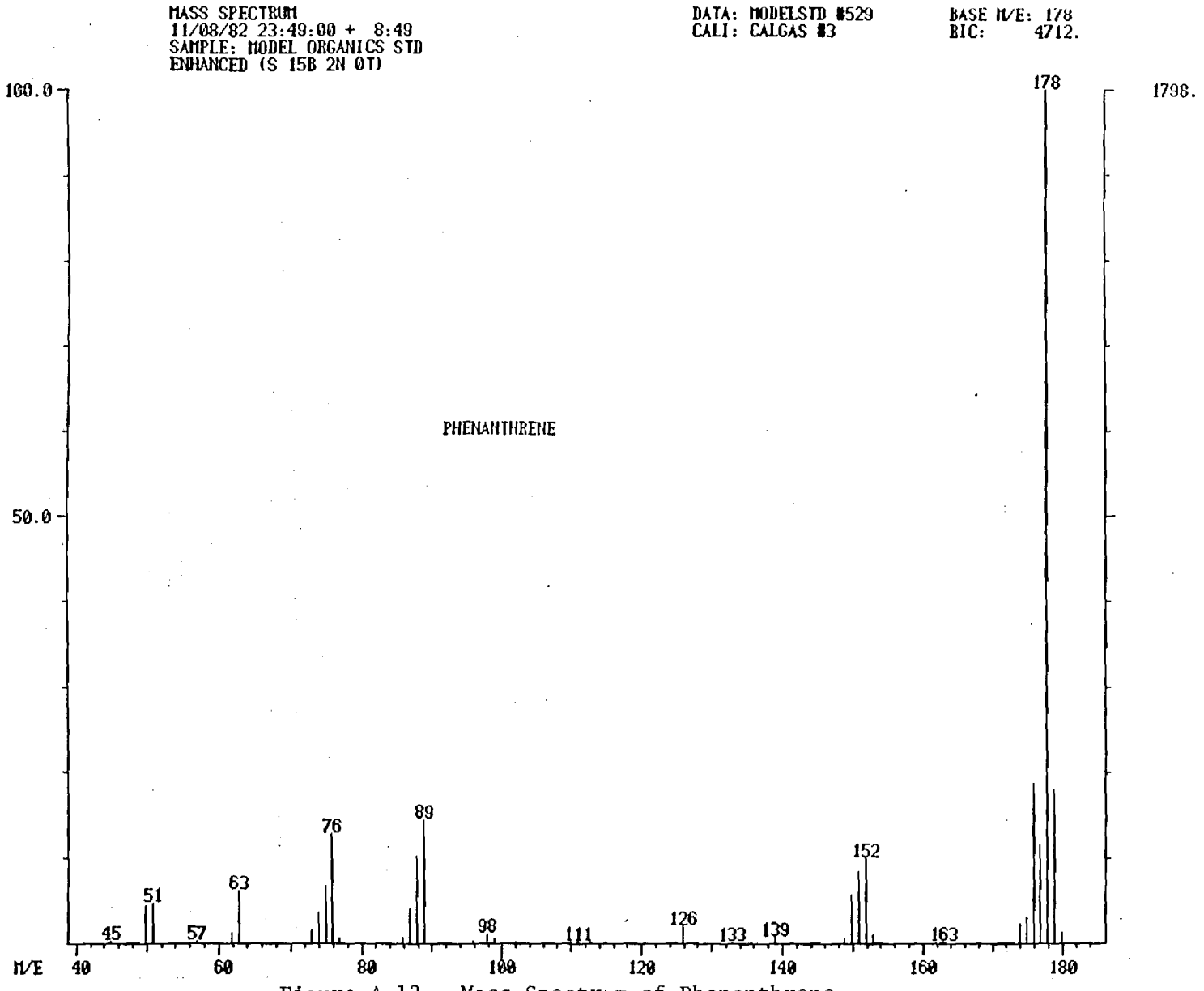

Figure A-12. Mass Spectrum of Phenanthrene

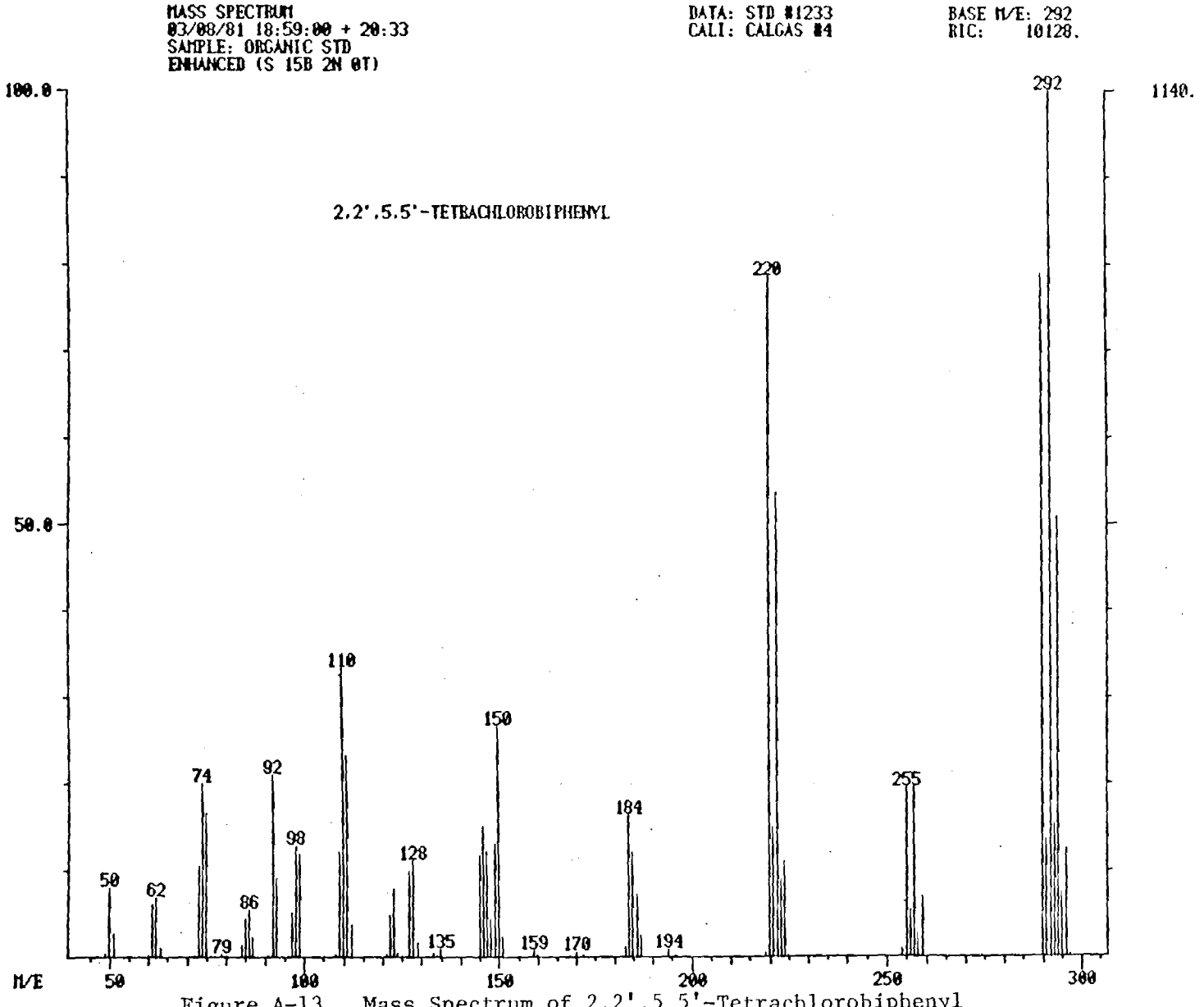

Figure A-13. Mass Spectrum of 2,2',5,5'-Tetrachlorobiphenyl

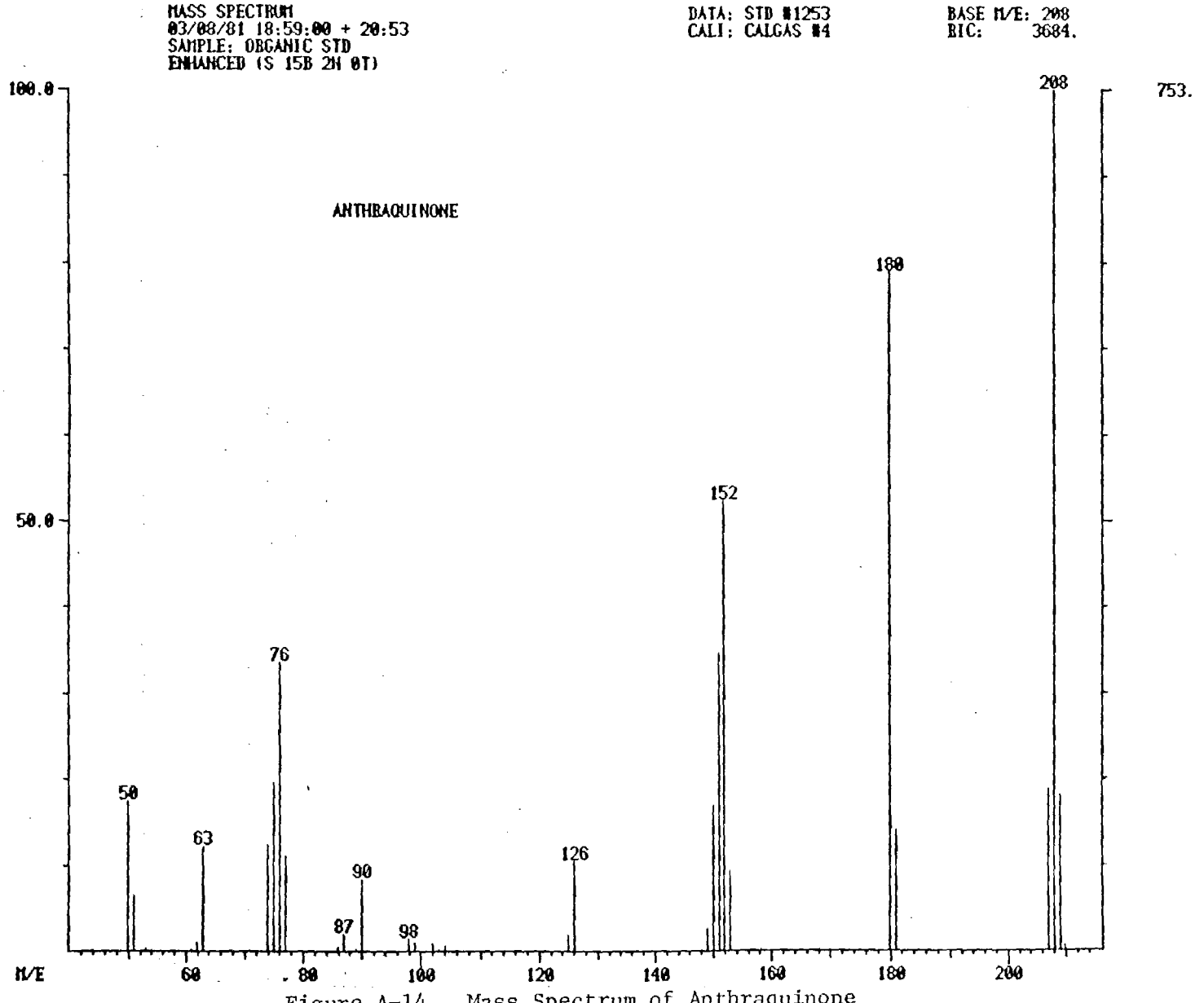

Figure A-14. Mass Spectrum of Anthraquinone

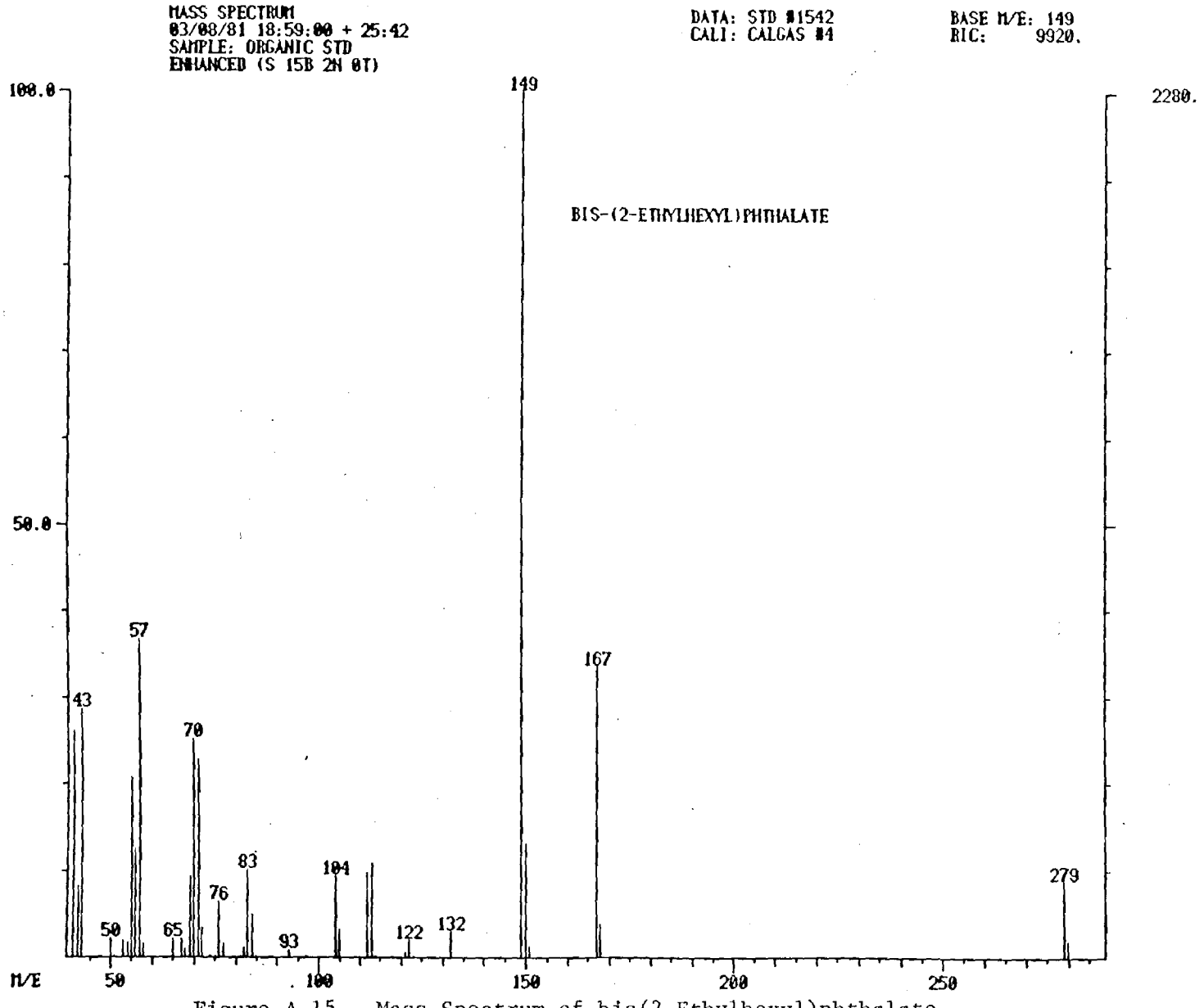

Figure A-15. Mass Spectrum of bis(2-Ethylhexyl)phthalate

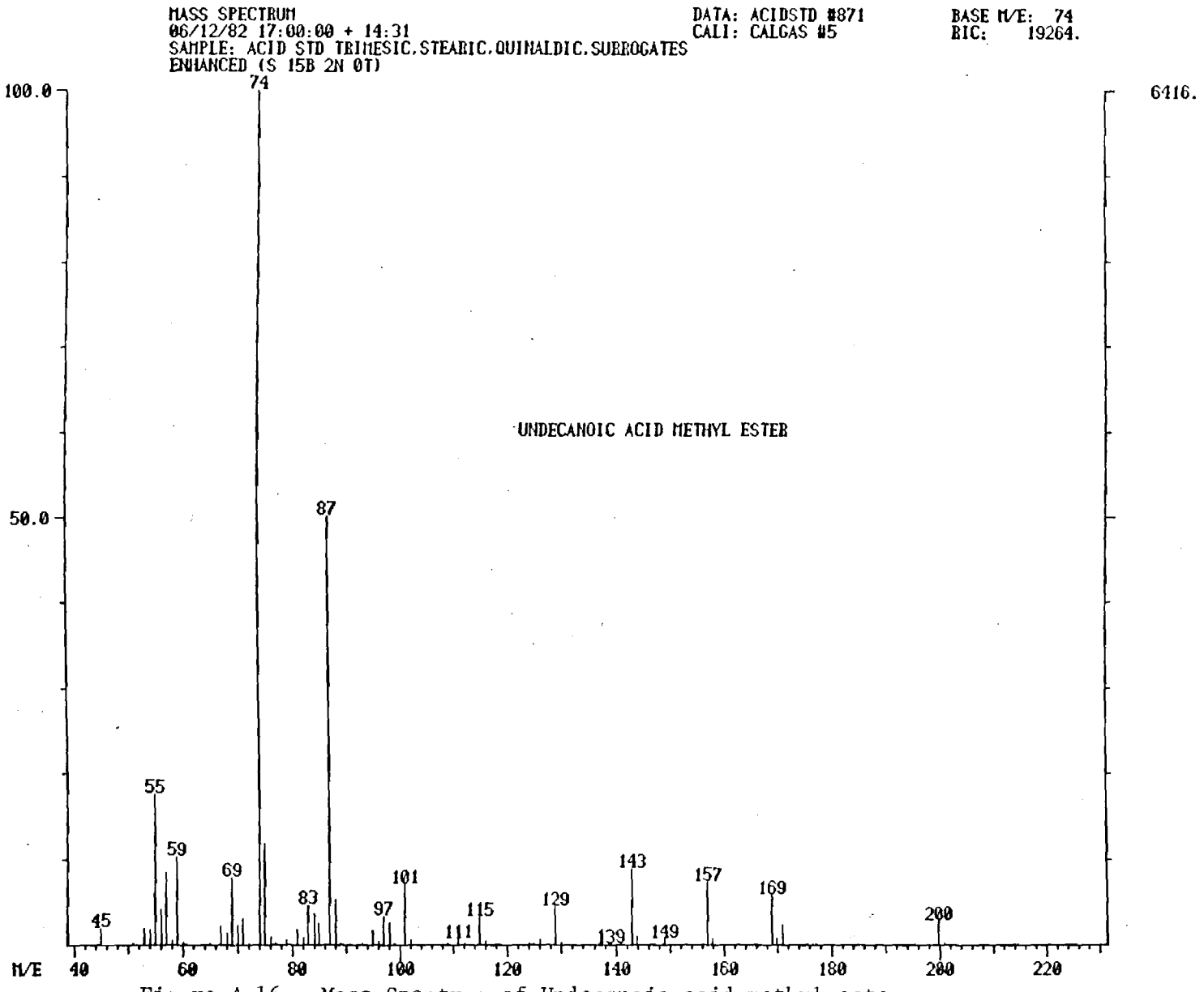

Figure A-16. Mass Spectrum of Undecanoic acid methyl ester

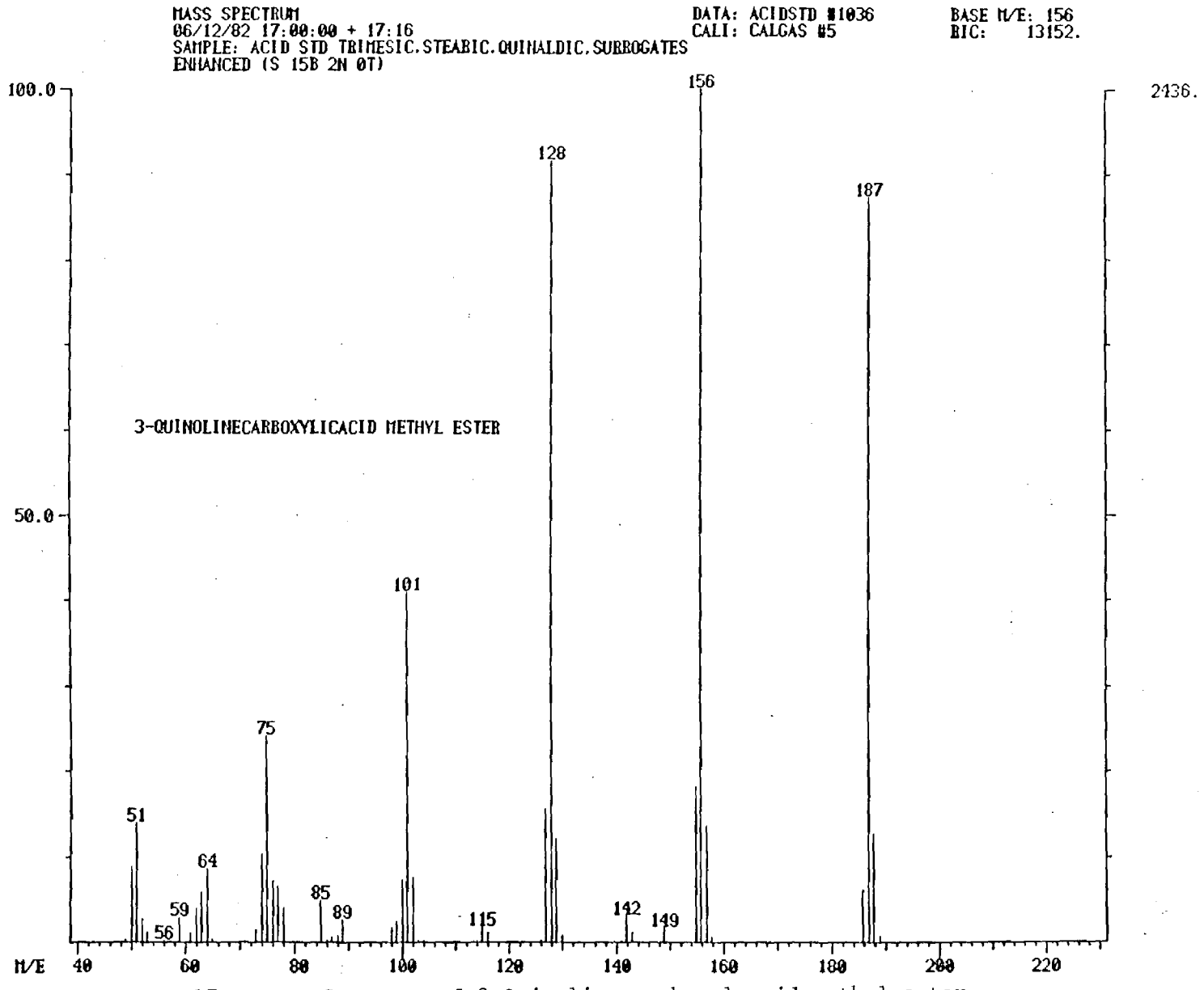

Figure A-17. Mass Spectrum of 3-Quinoline carboxyl acid methyl ester

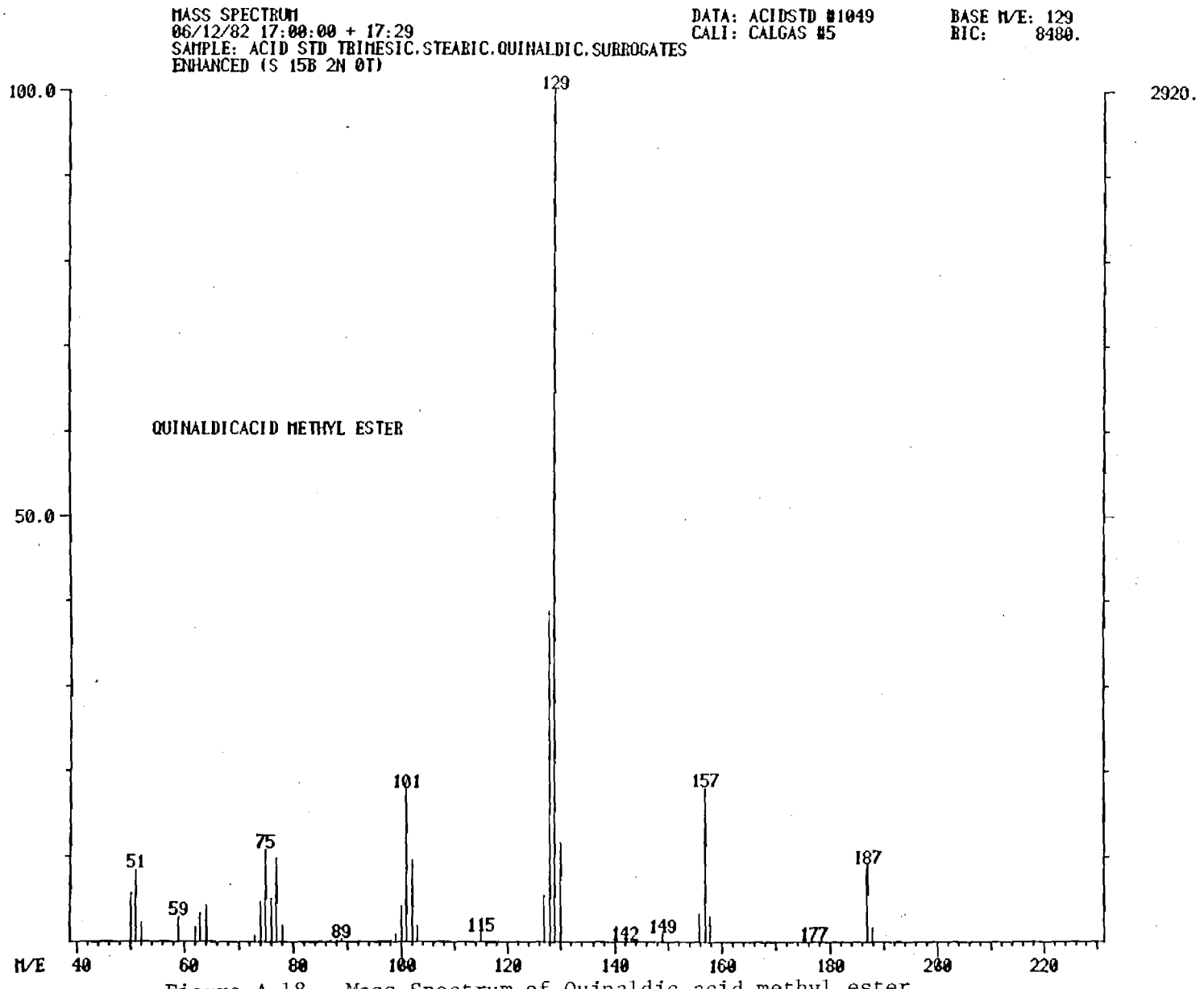

Figure A-18. Mass Spectrum of Quinaldic acid methyl ester

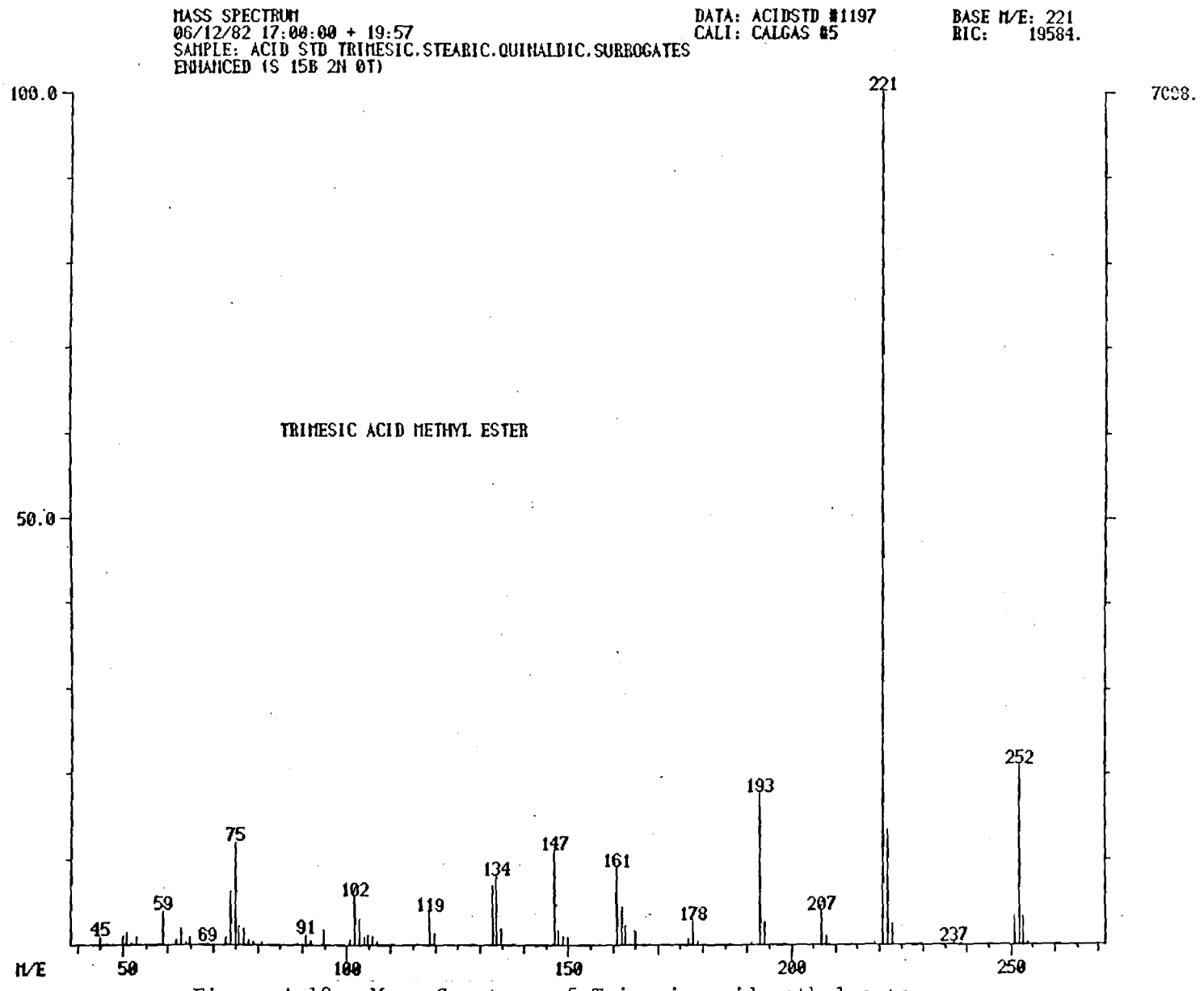

Figure A-19. Mass Spectrum of Trimesic acid methyl ester

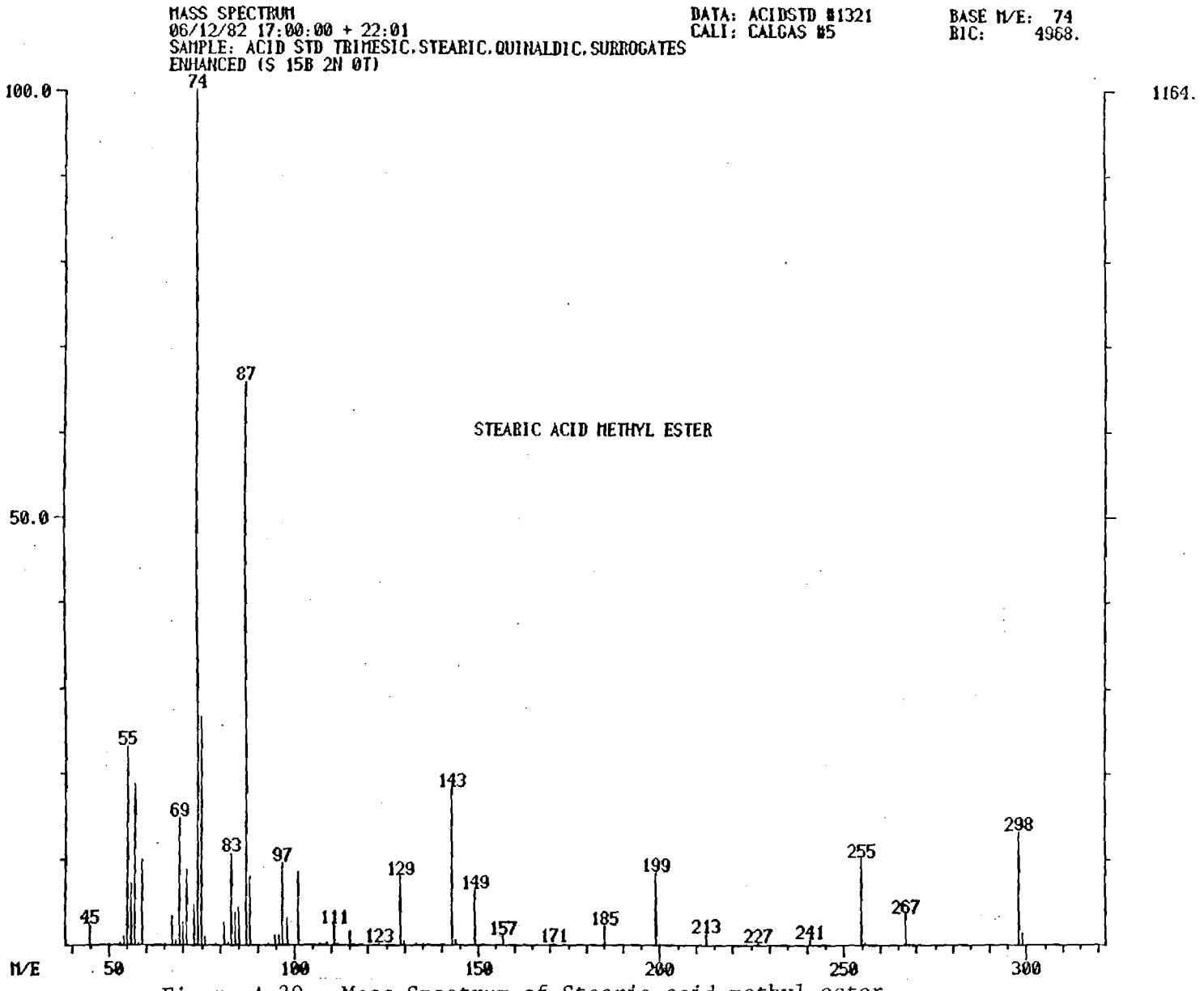

Figure A-20. Mass Spectrum of Stearic acid methyl ester

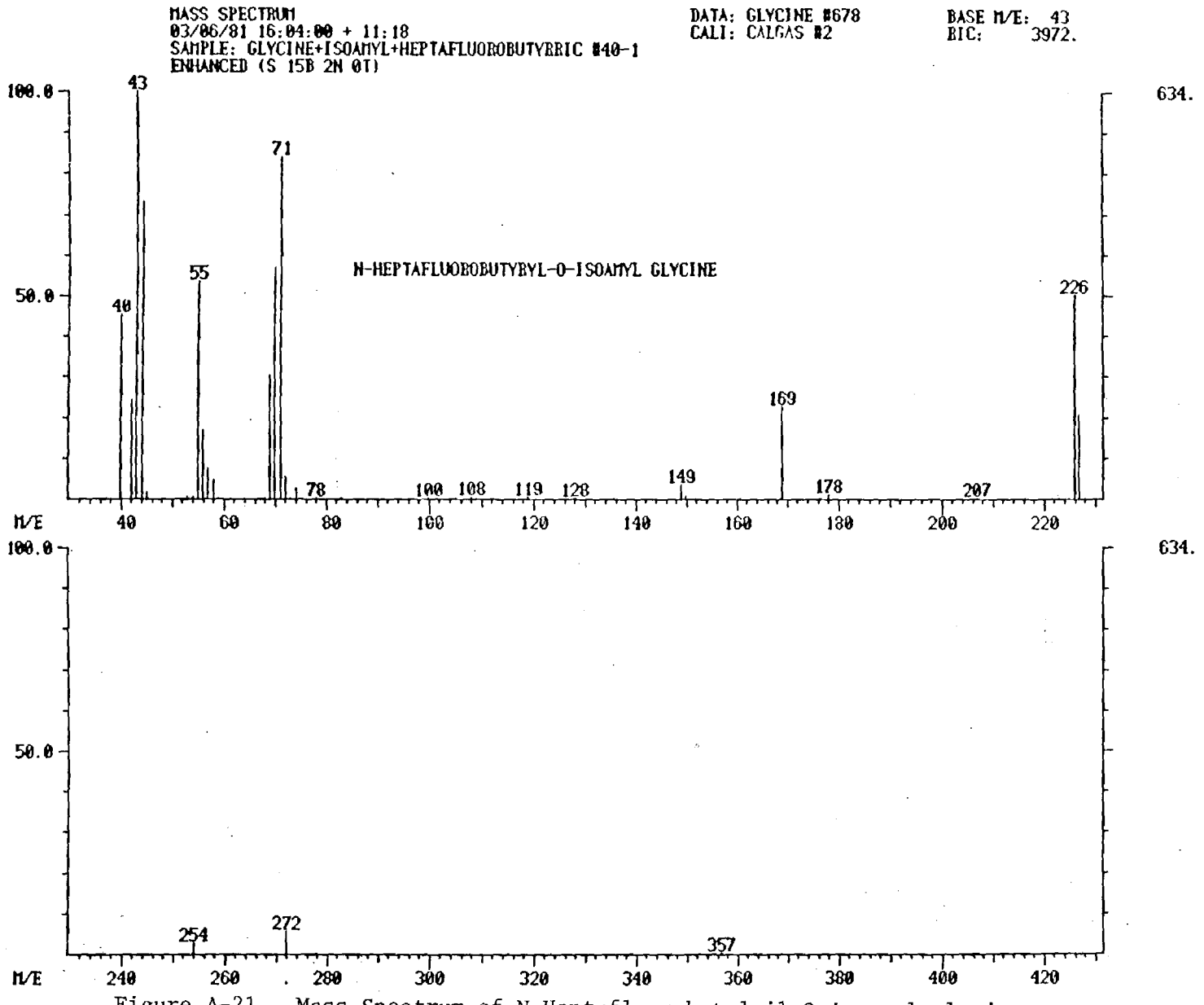

Figure A-21. Mass Spectrum of N-Heptafluorobutylril-O-isoamyl glycine

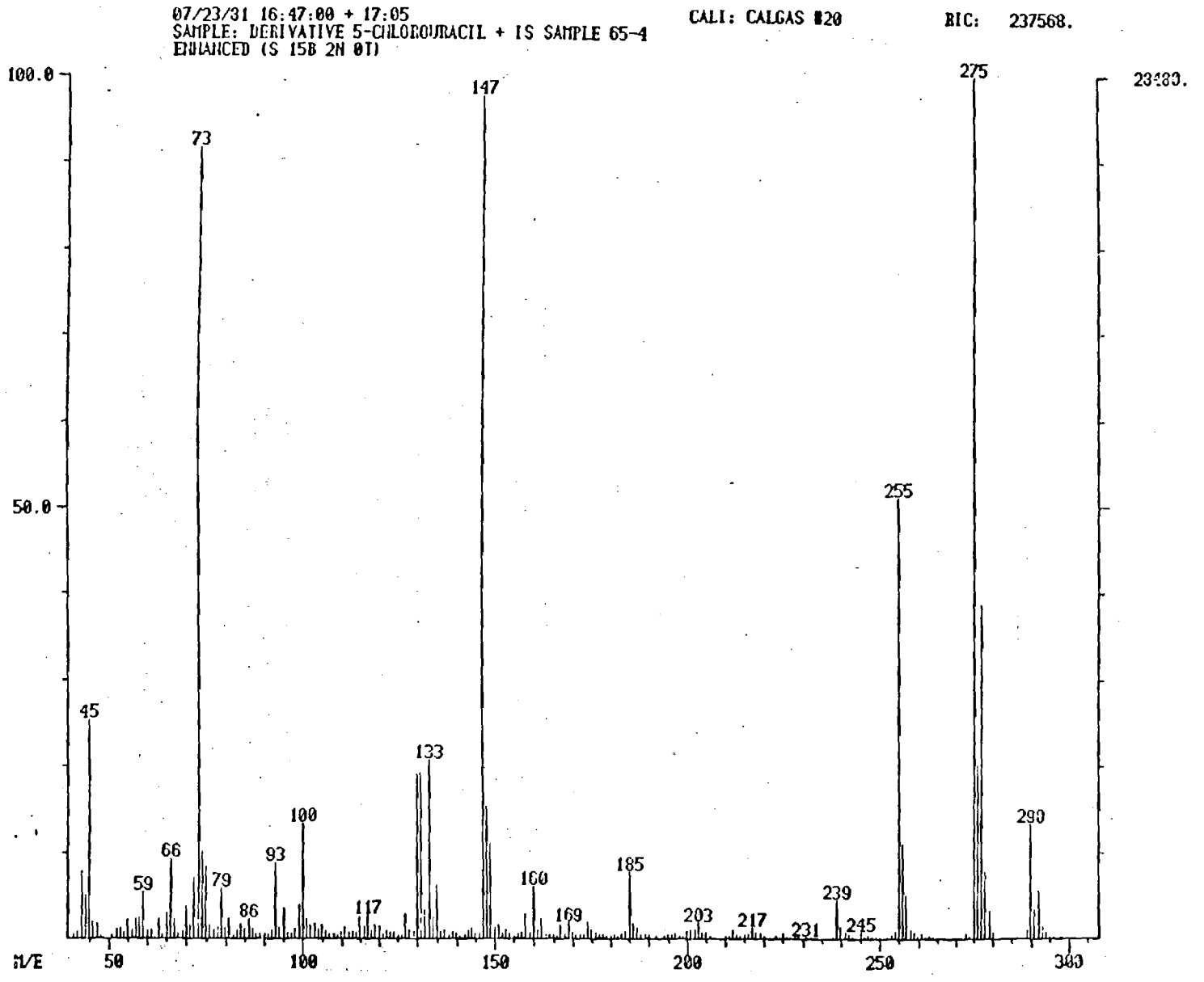

Figure A-22. Mass Spectrum of 5-Chlorouracil trimethylsilyl derivative

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.

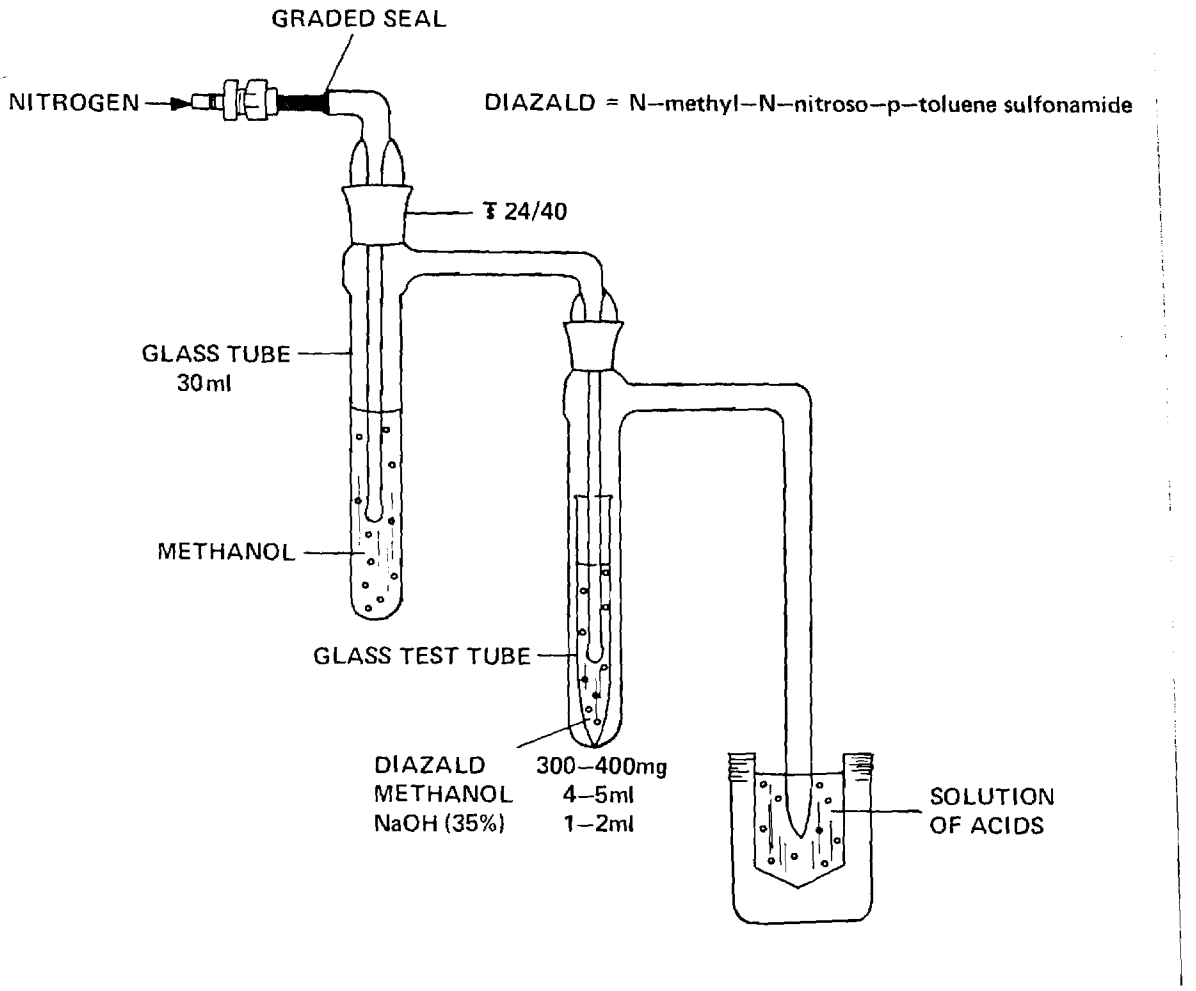

Figure B-1. Apparatus for Diazomethane Derivatization

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.