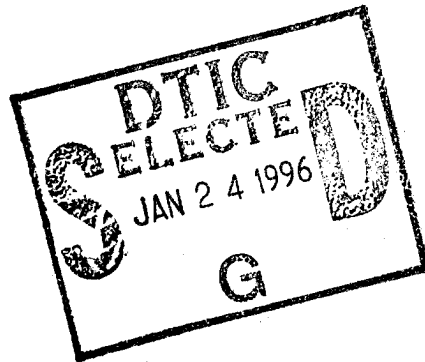


NASA CR-159745
TRW 31782-6082-RU-00

TRW[®]
DEFENSE AND SPACE SYSTEMS GROUP



ANALYSES OF MOISTURE IN POLYMERS AND COMPOSITES

19951226 031

BY
L.E. RYAN
R.W. VAUGHAN

PREPARED FOR NATIONAL AERONAUTICS
AND SPACE ADMINISTRATION
NASA NASA LEWIS RESEARCH CENTER

DTIC QUALITY INSPECTED

CONTRACT NAS 3-20406
RICHARD GLUYAS, PROJECT MANAGER

DEPARTMENT OF DEFENSE
PLASTICS TECHNICAL EVALUATION CENTER
ARRADCOM, DOVER, N. J. 07801

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

PLASTED 34822

NASA CR-159745
TRW 31782-6082-RU-00



ANALYSES OF MOISTURE IN POLYMERS AND COMPOSITES

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

BY
L.E. RYAN
R.W. VAUGHAN

PREPARED FOR NATIONAL AERONAUTICS
AND SPACE ADMINISTRATION
NASA NASA LEWIS RESEARCH CENTER

CONTRACT NAS 3-20406
RICHARD GLUYAS, PROJECT MANAGER

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

1. Report No. NASA CR-159745		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Analyses of Moisture in Polymers and Composites				5. Report Date 11 January 1980	
				6. Performing Organization Code	
7. Author(s) L. E. Ryan R. W. Vaughan				8. Performing Organization Report No. 31782-6028-RU-00	
9. Performing Organization Name and Address				10. Work Unit, No.	
				11. Contract or Grant No. NAS3-20406	
				13. Type of Report and Period Covered Contractor Report	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546				14. Sponsoring Agency Code	
15. Supplementary Notes Project Manager, R. E. Gluyns, Materials and Structures Division, NASA-Lewis Research Center, Cleveland, Ohio, 44135					
16. Abstract A suitable method for the direct measurement of moisture concentrations after humidity/thermal exposure on state of the art epoxy and polyimide resins and their graphite and glass fiber reinforcements was sought through this study. Four methods for the determination of moisture concentration profiles, moisture diffusion modeling and moisture induced chemical changes were investigated. Carefully fabricated, precharacterized epoxy and polyimide neat resins and their AS-graphite and S-glass reinforced composites were exposed to humid conditions using heavy water (D ₂ O), at ambient and elevated temperatures. These specimens were fixtured to theoretically limit the D ₂ O permeation to a unidirectional penetration axis. The analytical techniques evaluated were: (1) laser prolysis gas chromatography mass spectrometry, (2) solids probe mass spectrometry, (3) laser prolysis conventional infrared spectroscopy and (4) infrared imaging thermovision. The most reproducible and sensitive technique was solids probe mass spectrometry. The fabricated exposed specimens were analyzed for D ₂ O profiling after humidity/thermal conditioning at three exposure time durations.					
17. Key Words (Suggested by Author(s)) Graphite Fiber Composites Glass Fiber Composites 3501-5 Epoxy Resin PMR-15 Polimide Resin Moisture Absorption Pyrolysis Gas Chromatography/Mass Spectrometry				18. Distribution Statement Unclassified-unlimited	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 98	22. Price*

* For sale by the National Technical Information Service, Springfield, Virginia 22161

FOREWORD

This document constitutes the final report for the work accomplished between 3 June 1977 and 30 June 1979 by TRW Defense and Space Systems Group for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS 3-20406 on Analyses of Moisture in Polymers and Composites. This work was conducted under the technical direction of Dr. Richard E. Gluyas of the Lewis Research Center, Cleveland, Ohio.

The Chemistry Department of the Chemistry and Chemical Engineering Laboratory of TRW DSSG was responsible for the work performed on this program. Ms. L.E. Ryan was the Program Manager and Dr. R.J. Jones, Assistant Manager, Chemistry Department, provided program administrative guidance. Acknowledgement is made of the technical contributions of Mr. R. W. Vaughan, Dr. R.G. Beimer, Mr. J.F. Clausen, Dr. M.J. Sabety-Dzvonik, and technical assistance of Messrs. K.K. Ueda, J.N. Kennedy and H.D. Lindewall.

Accession For	
NTIS CRA&I	<input type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special

Prepared by  _____
L. E. Ryan

Prepared by  _____
R. W. Vaughan

SUMMARY

The absorption of moisture by high-performance structural composites, particularly at high temperature exposure is known to degrade their mechanical properties. A suitable method for the direct measurement of moisture concentrations after humidity/thermal exposure on state of the art epoxy and polyimide resins and their graphite and glass fiber reinforcements was sought under this contract. Four methods for the determination of moisture concentration profiles, moisture diffusion modeling and moisture induced chemical changes were investigated. Carefully fabricated, precharacterized epoxy and polyimide neat resins and their AS-graphite and S-glass reinforced composites were exposed to humid conditions using heavy water (D_2O), at ambient and elevated temperatures. These specimens were fixtured to theoretically limit the D_2O permeation to a unidirectional penetration axis, and analyzed. The analytical techniques evaluated were: (1) laser prolysis gas chromatography mass spectrometry, (2) solids probe mass spectrometry, (3) laser prolysis conventional infrared spectroscopy and (4) infrared imaging thermovision. The most reproducible and sensitive technique was solids probe mass spectrometry. The fabricated exposed specimens were analyzed for D_2O profiling after humidity/thermal conditioning at three exposure time durations.

CONTENTS

	<u>Page</u>
Foreword	iii
Summary	v
Figures	viii
Tables	viii
1.0 Introduction	1
2.0 Specimen Preparation	5
2.1 Resin and Fiber Selection	5
2.2 Specimen Fabrication.	5
2.2.1 Neat Resin Specimens	5
2.2.2 Composite Specimens.	9
2.3 Quality Assurance Testing	11
2.3.1 Neat Resin Specimens	11
2.3.2 Composite Specimens.	12
2.4 Discussion of Specimen Quality.	13
3.0 Selection of Method for Analysis	21
3.1 Exposure Technique.	21
3.2 Laser Pyrolysis-Gas Chromatography Mass Spectrometry (LP-GC/MS)	24
3.2.1 Korad Ruby Laser System.	25
3.2.2 Maintenance/Analytical Cells	25
3.2.3 Gas Chromatography/Mass Spectrometry System.	26
3.2.4 Feasibility Experiments.	28
3.3 Laser Pyrolysis - Conventional Infrared Spectroscopy.	31
3.3.1 Infrared Spectrophotometer	32
3.3.2 Feasibility Experiments.	33
3.4 Infrared Imaging Technique.	35
3.4.1 Infrared Imaging Camera.	36
3.4.2 Feasibility Experiments.	36
3.5 Solids Probe Mass Spectrometry.	36
3.5.1 Solids Probe Mass Spectrometry Technique	37
3.5.2 Feasibility Experiments.	37
3.6 Method Selection.	46
4.0 Analysis of Specimens and Interpretation of Results.	49

(Continued)

CONTENTS (Continued)

	<u>Page</u>
4.1 Routine Analytical Procedure	49
4.2 Acquired D ₂ O Concentration Data.	49
4.3 Discussion of D ₂ O Data Quality	64
5.0 Conclusions	65
6.0 Recommendations for Future Studies.	66
Appendices:	
Appendix A Composite Characterization	67
Appendix B Computer Prepared Ion Chromatograms for Initial Solids Probe Mass Spectrometry Experiments	71
References	90
Distribution List.	91

TABLES

<u>Number</u>		<u>Page</u>
1	PMR-15 Resin Formulation	7
2	Density of Resin Moldings	11
3	Laminate Physical Properties	12
4	Interlaminar Shear Strengths of Molded Specimens, MPa (KSi)	13
5	Inspection Results TRW-D&SS Group	14
6	Laser Pyrolysis Gas Chromatography Mass Spectrometry Feasibility Experiments	30
7	Mass Ratio Summary from Solids Probe Mass Spectrometry Technique	46
8	D ₂ O Concentration Data on Exposed Specimens	50

FIGURES

1	Compression Mold for Polyimide Powder	8
2	Molded Neat PMR-15 Resin	9
3	Laminate Bleed/Cure Configuration 3501-S/AS-1 Laminates	10
4	C-Scan of Neat Epoxy Specimens	16
5	C-Scan of Epoxy Composite Specimens	17
6	C-Scan of Polyimide Composite Specimens	18
7	Fixtured Specimens	23
8	Maintenance/Analytical Cells	27
9	Maintenance/Analytical Cell Interfaced with the Finnigan Mass Spectrometry	29
10	Infrared Scan of D ₂ O in 10 cm Heated Gas Cell	33
11	D ₂ O Calibration Curve for LP-IR Experiments	34
12	Infrared Imaging Hardware	35
13	MS Scan of Dry Epoxy Specimen	39
14	MS Scan of D ₂ O Exposed Epoxy Specimen	40
15	Illustration of Samples Acquired by Drilling Technique	42
16	Sample Removal Technique Method 2	43
17	Reconstructed Mass Chromatograms for a Subsurface Sample Removed by Method 2	44
18	Calibration Curve for Solids Probe Mass Spectrometric Technique	45

FIGURES (Continued)

<u>Number</u>		<u>Page</u>
19	D ₂ O Concentrations as a Function of Sampling Depth for the Samples at 22% RH, 344°K (71°C), 1440 Exposure Hours	52
20	D ₂ O Concentrations as a Function of Sampling Depth for the Samples at 22% RH, 344°K (71°C), 3670 Exposure Hours	53
21	D ₂ O Concentrations as a Function of Sampling Depth for the Samples at 54% RH, Room Temperature, 1440 Exposure Hours	54
22	D ₂ O Concentrations as a Function of Sampling Depth for the Samples at 54% RH, Room Temperature, 3670 Exposure Hours	55
23	D ₂ O Concentrations as a Function of Sampling Depth for the Samples at 59% RH, Room Temperature, 8850 Exposure Hours	56
24	D ₂ O Concentrations as a Function of Sampling Depth for the Samples at 59% RH, Room Temperature, 10700 Exposure Hours.	57
25	D ₂ O Concentrations as a Function of Sampling Depth for the Samples at 75% RH, 344°K (71°C), 1440 Exposure Hours	58
26	D ₂ O Concentrations as a Function of Sampling Depth for the Samples at 75% RH, 344°K (71°C), 3670 Exposure Hours	59

1. INTRODUCTION

Since the initial discovery of the deleterious effect of moisture on epoxy resins by investigators at General Dynamics Corporation⁽¹⁾, studies have been undertaken to characterize and define the rate and mechanism of the transport of water into polymers and fiber-reinforced composites. One significant study performed by the United States Air Force⁽²⁾ showed that the initial degradation in neat epoxy resin can be predicted using standard diffusion models.

TRW, under this contract (NAS 3-20406) sponsored by the National Aeronautics and Space Administration, Lewis Research Center, investigated analytical methods for the positive quantitation of diffusing moisture in epoxy resins and fiber-reinforced composites. The approach as employed in this research program was selected to investigate analytical methods which could quantitatively establish the moisture concentration profile on unidirectional moisture diffusion for thermally spiked and ambient humidity exposed test specimens. In addition, the analytical techniques investigated were theoretically capable of detecting chemical changes in these complex systems.

The program delineation for "The Analyses of Moisture in Polymers and Composites" is set forth in the following task and subtask program outline.

Task I. Specimen Preparation

Fabrication

- Use of one state of the art epoxy and one addition curing polyimide resin systems (Hercules 3501-5 and PMR -15).
- In-house, carefully controlled, fabrication of cast neat resin samples and their unidirectional AS-1 graphite and S-glass fiber reinforced composites.
- Complete quality control analysis: C-Scan, density (gas comparison pycnometer), fiber volume, void content, volatile content, and shear strength.

Exposure

- Fixturing of specimens to allow unidirectional moisture exposure, parallel and perpendicular to the fiber direction.
- Use of heavy water, D₂O, as the exposure medium to aid in concentration profiling and chemical analysis.
- Constant relative humidity solutions (ASTM E104) at ambient and elevated temperature to provide the moisture and thermal environments.

Task II. Selection of Methods for Analysis

Methods for Feasibility Studies

- Closed system laser pyrolysis-gas chromatography/mass spectrometry (LP/GCMS) for D₂O concentration profiling and chemical effects.
- Closed system laser pyrolysis-infrared spectroscopy (LP/IR) for D₂O concentration profiling.
- Infrared imaging for a physical diagnostic technique to determine moisture depth of penetration and void effects.
- Solids probe mass spectrometry for direct thermal desorption and quantitation of D₂O in specimen segments.

Feasibility Studies

- Technique evaluation using dry, D₂O boiled, and humidity exposed test specimens.
- Technique selection based on: method sensitivity, specificity, reproducibility, consistency and cost compatibility.

Technique Refinement

- Optimization of selected technique.

Task III. Analysis and Interpretation of Results

Analysis

- Determination of D_2O concentrations in the exposed specimens at three time intervals.

Interpretation of Results

- A two-dimensional penetration of D_2O as a function of the distance from the exposed surface, with respect to exposure duration and external moisture (D_2O) concentrations in two thermal environments consisting of $298^{\circ}K$ and $344^{\circ}K$.

2. SPECIMEN PREPARATION

The resin and composite materials analyzed in this program were selected because of their broad acceptance in the aerospace industry. Fabrication processes and quality assurance methods have been relatively well-established for these materials and are presented in the following sections.

2.1 RESIN AND FIBER SELECTION

TRW selected two polymer systems to fabricate test specimens for this program, e.g., one state of the art epoxy resin and one addition-curing polyimide resin. The particular epoxy resin selected by TRW was Hercules 3501-5 because this material currently is one of the most widely used epoxy resins in graphite composites for 450°K service applications. Furthermore, there is a large background of experimental information based on this resin.

Selection of a polyimide resin for this program required an addition-cure polymer that offers processibility acceptable to aerospace industry use. For this purpose, the PMR-15 polyimide resin developed at NASA Lewis Research Center was chosen.

The same reinforcement materials were used in both polymer systems; AS-1 graphite and S-glass fibers.

2.2 SPECIMEN FABRICATION

Test specimens consisting of neat resin moldings, S-glass laminates, and AS-1 graphite fiber laminates were fabricated according to procedures outlined by the developers of the respective matrices. The 3501-5 specimens were prepared using methods developed at Hercules, Inc. and AFML, and PMR-15 specimens were fabricated using procedures developed at NASA Lewis Research Center.

2.2.1 Neat Resin Specimens

Test specimens were cast from 3501-5 epoxy resin using a procedure developed at AFML. The resin used for these specimens was mixed at Hercules Inc. and shipped to TRW DSSG. During storage its temperature was kept below 273°K. The casting mold consisted of two polished, 30 cm x 30 cm x 0.5 cm aluminum alloy plates. These were sealed around three sides

by a neoprene rubber dam. This assembly was clamped using spring clamps while the thickness, 0.8 cm, was maintained with appropriate steel spacers. Once the mold was prepared, the 3501-5 epoxy resin was weighed into a glass beaker and degassed in a vacuum oven at 350°K under sufficient vacuum to remove all entrapped air. After degassing, the resin was poured into a mold preheated to 394°K. The mold was placed in a vacuum oven preheated to 373°K and held under sufficient vacuum to remove air but not to cause resin boiling. After all air had been removed, the resin was cured for a minimum of 30 minutes at 450°K.

PMR-15 neat resin specimens were molded using a process similar to that developed at NASA Lewis Research Center.⁽³⁾ Resin for these specimens was synthesized at TRW DSSG. In order to prepare this resin, it was necessary first to prepare the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) and to recrystallize the 4,4'-methylenedianiline (MDA). The monomethyl ester of 5-norbornene 2,3-dicarboxylic acid (NE) was procured from Burdick and Jackson.

BTDE was prepared by dissolving 3,3',4,4'-benzophenone-tetracarboxylic acid in methyl alcohol. This solution then was refluxed for two hours under a nitrogen purge. Recrystallization of the MDA was performed by dissolving it in isopropyl alcohol and then heating the solution with decolorizing carbon for fifteen minutes. The solution was filtered through a Buchner funnel and cooled in a refrigerator for 16 hours. After breaking up the resultant crystals and filtering, the MDA was dried in a vacuum oven for 16 hours.

PMR-15 solution (see Table 1) then was prepared by first dissolving the recrystallized MDA in methyl alcohol. To this solution was added first, the NE and second, the BTDE. It was then mixed for 15 minutes while cooling.

The resin then was dried and imidized in an air-circulating oven. This was accomplished by evaporating the solvent at 355°K for three days and then grinding the resultant dry cake with a mortar and pestle. The powder then was treated for three hours at 394°K, plus two hours at 477°K, to produce a dry polyimide prepolymer. Additional grinding with a mortar and pestle was required in order to obtain a fine, free-flowing powder.

The polyimide powder was weighed and loaded into the compression mold, (see Figure 1) which was heated to 505°K in an air-circulating oven. After

the polyimide powder and mold had reached 505°K, the mold was placed in an hydraulic press preheated to 615°K. Contact pressure was held until the mold temperature reached 588°K; i.e., for 20 minutes, after which 35.6 kN load was applied. The mold was bumped (pressure removed and reapplied) six times to permit escape of volatile matter prior to increasing the load to 436 kN. An additional two-bump cycle was performed under this load and the press temperature was then reduced to 588°K. These bump cycles were deviations from the referenced process. The resin was cured for one hour at this temperature and the mold was cooled down to 477°K, after which the applied load was reduced to 178 kN. Cooling of the mold was continued down to 372°K, at which time it was removed from the press and the molded PMR-15 specimen was ejected from the mold.

The resultant neat PMR-15 resin specimens appeared to be of high quality and have smooth, glossy surfaces (see Figure 2). Density of the specimens was measured and was determined to be 1.31 grams/cc.

Table 1. PMR-15 Resin Formulation

Constituent	PBW
Benzophenone tetracarboxylic* acid dianhydride (BTDA)	18.6
Methyl alcohol*	26.0
Methylene dianiline (MDA)	16.9
Monomethyl ester of nadic anhydride (NE)	10.8
Methyl alcohol	27.7
	<hr/> 100.0

* Premix to form the dimethylester of BTDA (BTDE)

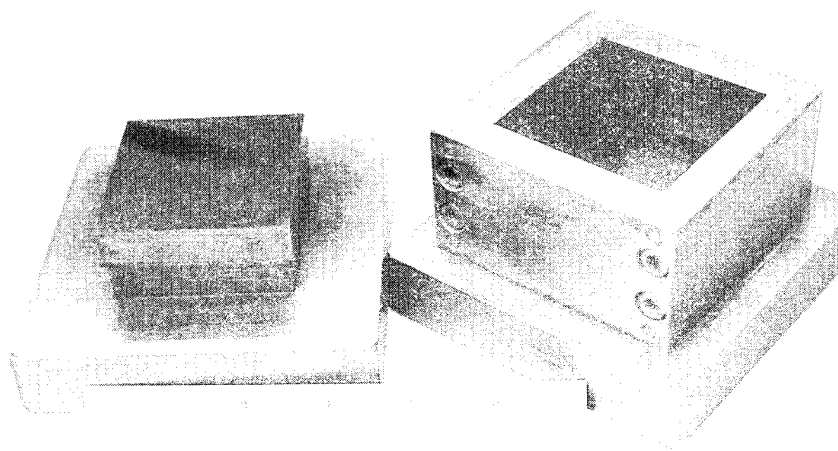


Figure 1. Compression Mold for Polyimide Powder

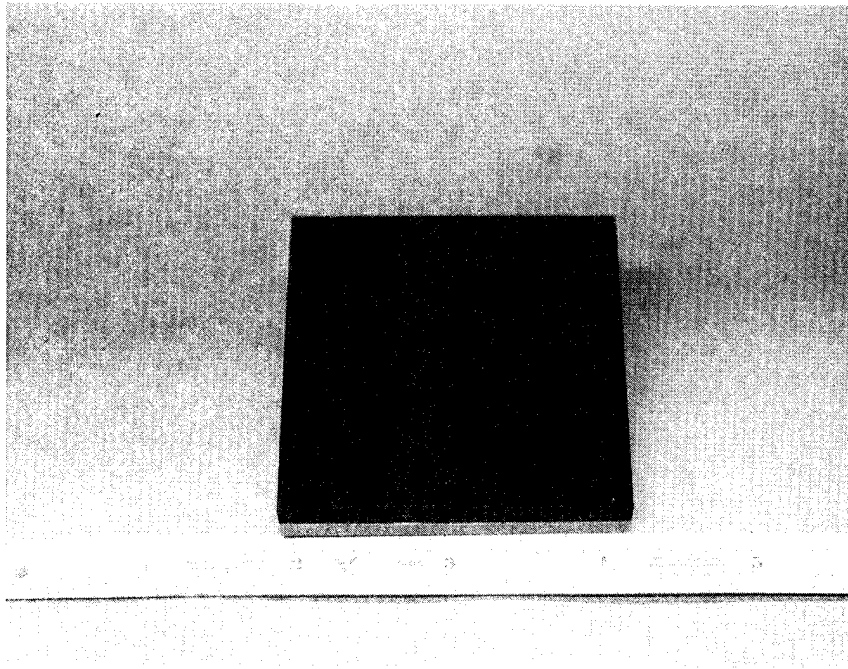


Figure 2. Molded neat PMR 15 Resin

2.2.2 Composite Specimens

S-glass reinforced laminates and AS-1 graphite reinforced laminates were processed using similar procedures. PMR-15 prepreg materials were manufactured by U.S. Polymeric and the 3501-5 materials were prepared by Hercules Inc.

PMR-15 processing utilized cure schedules that have been previously established for this matrix material.⁽³⁾ All laminates were prepared in a matched metal mold using compression molding techniques.

The prepreg tape then was laid up 34 plies thick to form a panel 30 cm x 30 cm x 0.5 cm thick. Because the prepreg tape was 8 cm wide, it was necessary to butt the prepreg tapes together in order to obtain 30 cm width. All joints were staggered throughout the lay-up. This panel was placed in a 30 cm x 35 cm window-frame mold and the mold top was placed on top of the prepreg. The mold then was placed in an air-circulating oven at 477°K for two hours in order to imidize the PMR 15 polyimide resin. After two hours the mold was transferred directly into a preheated platen press at 589°K and held without pressure for ten minutes. A molding pressure of 6.89 MPa (1000 psig) was applied and maintained for one hour.

After curing, the pressure was reduced to 3.45 MPa (500 psig) and the press was cooled to 533°K. These conditions were maintained for one hour in order to permit the laminate to stabilize, after which the press was cooled to 477°K. Pressure was released and the press was cooled to room temperature.

Laminate fabrication using 3501-5/AS-1 prepreg was performed in accordance with the cure cycle recommended by Hercules Inc. in their product data sheet. All composites were prepared by autoclave molding methods using 30 cm-wide prepreg to mold 30 cm x 30 cm x 0.5 cm laminates. The lay-up configuration for these composites is shown in Figure 3. The specific cure cycle used involved applying vacuum pressure at ambient temperature, heating the laminate to 375°K and holding that temperature for 30 minutes. At this point 60 KN augmented pressure was applied, and the laminate temperature was brought to 450°K. The laminate was held at this temperature for one hour and then cooled to ambient temperature while under vacuum bag pressure.

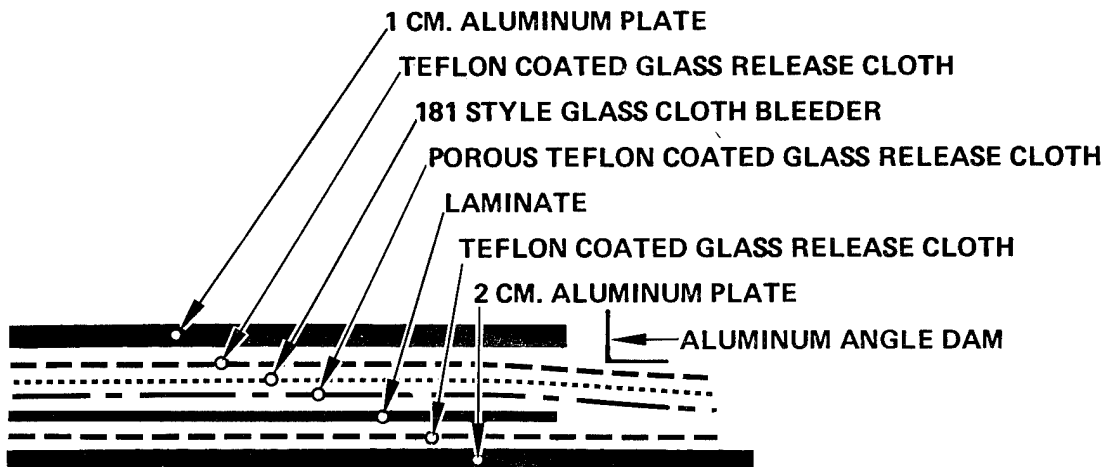


Figure 3. Laminate Bleed/Cure Configuration 3501-5/AS-1 Laminates

2.3 QUALITY ASSURANCE TESTING

In order to assure that the test specimens were of acceptable quality and representative of composite materials currently in use, certain quality assurance tests were performed. These included visual examination, density measurements, void content determinations, shear strength measurements, and ultrasonic C-scans. The results of these determinations on neat resin specimens and on composite specimens are discussed in the following sections.

2.3.1 Neat Resin Specimens

The quality of neat resin moldings was primarily determined by visual inspection for flaws, voids and cracks. In addition, density measurements were made in accordance with the procedure given in Appendix A. These results are shown in Table 2.

Table 2. Density of resin Moldings

	Density g/cm ³
3501-5	1.28
PMR-15	1.31

Moldings of the epoxy resin, 3501-5, were clear, and as such they could be readily examined for flaws. All of these specimens were homogeneous and void-free. PMR-15 moldings were opaque and could not be directly examined for the presence of internal flaws, e.g., voids. To check for porosity, several initial moldings were sectioned and their cross section was examined. Several specimens contained internal, visible voids while the remainder had homogeneous and void-free cross sections. Density of these flaw-free specimens was determined, and was used as a guide to define the quality of the additional molded specimens. Low density specimens were discarded while specimens showing equivalent density to the void-free sectioned moldings were considered of good quality and were used for moisture analysis.

2.3.2 Composite Specimens

The definition of S-glass and graphite composite specimen quality was made using similar methods. The techniques used were based upon accepted methods employed in the fiber reinforced plastics industry. The specific techniques used on the four laminate compositions of this program are given in Appendix A. These encompass laminate physical property determinations of resin content, density, fiber volume, and void content. Interlaminar shear strength, a common laminate mechanical strength property, was used to indicate the integrity of the resin matrix. In addition, ultrasonic C-scans were taken of selected specimens to define void contents, delaminations, resin starved regions or other defects.

Physical properties are very basic parameters to measure the quality of laminates. Correct fiber volumes and low void contents are necessary for reproducible and structurally sound laminates. A summary of the physical properties of the epoxy 3501-5 and PMR-15 laminates is shown in Table 3.

Table 3. Laminate Physical Properties

Laminate	Resin Content (% W/W)	Density (g/cm ³)	Fiber Volume (% V/V)	Void Volume (% V/V)
3501-5/AS Graphite	29.1	1.59	64.1	0
3501-5/S Glass	23.6	1.97	60.4	3
PMR-15/AS Graphite	40.3	1.49	50.5	4
PMR-15/S Glass	25.2	1.99	59.8	2

Interlaminar shear strength is the most widely accepted mechanical property used in the quality assurance of fiber reinforced laminates. Relatively high values usually reflect a resin matrix of low void content and a laminate of proper fiber volume and fiber geometry.⁽⁴⁾ The average

interlaminar shear strengths of specimens taken from each 30-centimeter square panel analyzed in this program are presented in Table 4.

Table 4. Interlaminar Shear Strengths of Molded Specimens, MPa (ksi)

Laminate Matrix/Fiber	1	2	3	4	5	Avg.
3501-5/AS Graphite	70.9 (10.3)	62.6 (9.1)	64.7 (9.4)	71.6 (10.4)	62.7 (9.1)	66.8 (9.7)
3501-5/S Glass	76.4 (11.1)	84.7 (12.3)	89.5 (13.0)	83.3 (12.1)	83.3 (12.1)	83.3 (12.1)
PMR-15/AS Graphite	106.0 (15.4)	99.8 (14.5)	102.6 (14.9)	108.1 (15.7)	108.8 (15.8)	105.3 (15.3)
PMR-15/S Glass	64.7 (9.4)	66.8 (9.7)	75.7 (11.0)	55.1 (8.0)	71.6 (10.4)	66.8 (9.7)

2.4 DISCUSSION OF SPECIMEN QUALITY

The principal method employed to determine the quality of individual specimens used on this program was visual inspection. This was accomplished by first establishing a correlation between quality assurance tests, ultrasonic inspection and visual inspection. Results of the ultrasonic inspections provided the primary guide to the visual inspections as discussed below.

Three randomly selected specimens from each type of material were examined ultrasonically to detect voids and delaminations. This work was performed by the NDE Development Department of TRW Equipment in Cleveland. The method used to inspect the specimens was ultrasonic through transmission which was recorded by C-scan. Specimens were held in a simple rail fixture in batches of three, i.e., in sets of each material type. This method provided a convenient means of inspection sensitivity selection and scanning although it masked an area approximately 5 mm wide around the periphery of each specimen. All specimens were inspected with at least three sensitivity settings using titanium alloy and stainless steel blocks as reference standards (see Table 5).

Table 5. Inspection Results TRW-D&SS Group

Scan No.	Specimen No.	Sensitivity % (1)	Ref. Std. % (2)
1		75	1/8-inch
2	A, B & C	50	Ti. Block
3		25	45%
4		75	
5	D, E & F	50	
6		25	
7		75	1-inch
8	G, H & I	50	S/S Block
9		25	25%
10	G	25	1" SS, 40%
11		75	1/8-inch
12	1, 2 & 3	50	Ti Block
13		25	35%
14		75	1/8-inch
15		50	Ti Block
16		25	60%
17	4, 5 & 6	75	1-inch
18		50	S/S Block
19		25	80%
20		75	1/8-inch
21		50	Ti Block
22		25	80%
23	7, 8 & 9	75	1-inch
24		50	S/S Block
25		25	50%

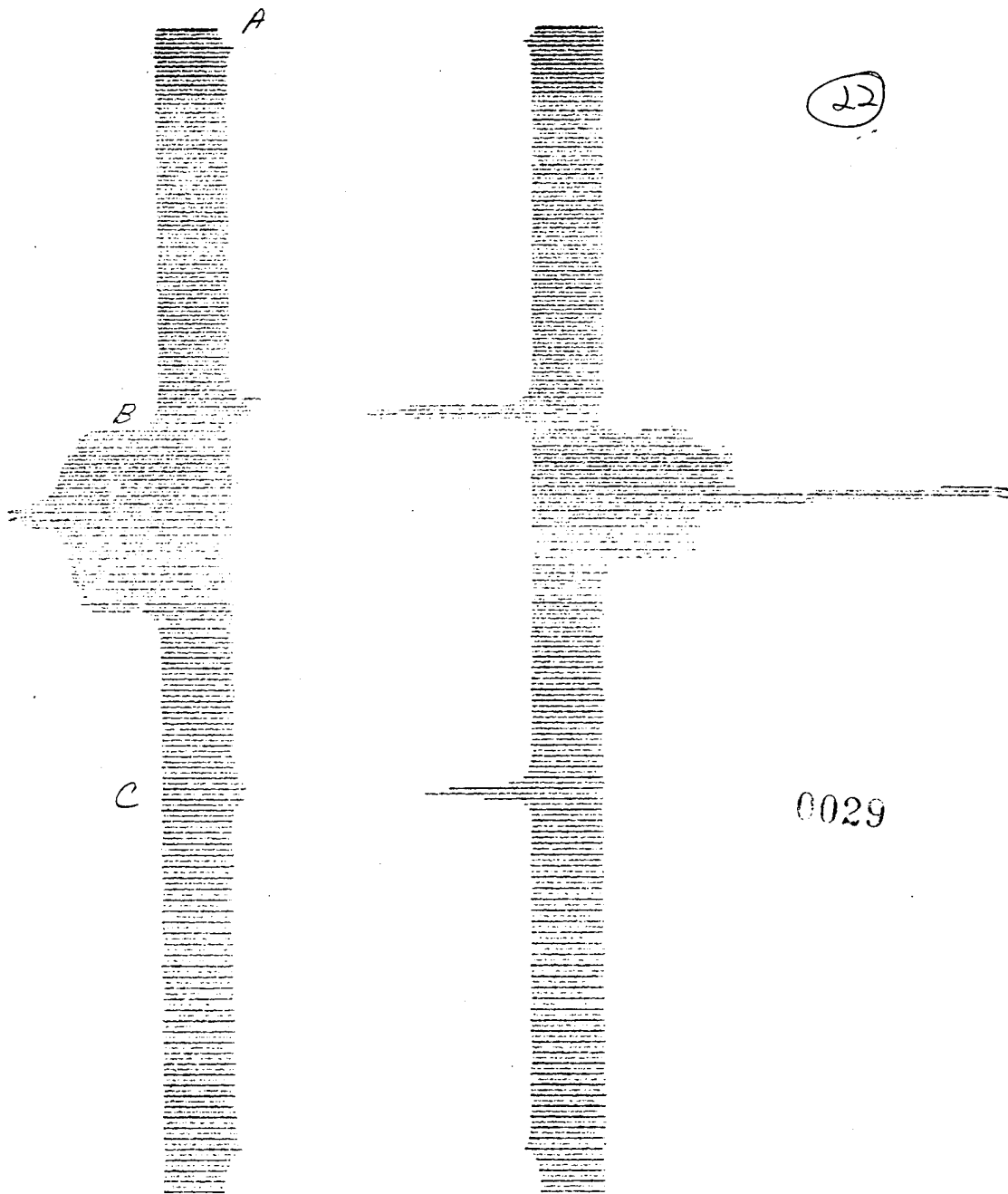
NOTES: (1) Sensitivity setting is in CRT screen height indication.
(2) Sensitivity setting is obtained on Reference Standard arbitrarily selected.

The method employed was such that when the internal losses of the sound propagating through the material exceeded a predetermined level, the recorder began making its marks (dark lines on the C-scan). Actual sensitivity settings were tailored to specimen acoustic alternatives.

It was difficult to cross-correlate the results within the samples because of the large spread in acoustic properties. The NDE Development department recommended an approach to take measurements (velocity and attenuation coefficient) of acoustic properties although this was not performed because it was decided it would be beyond the scope of this program. Consequently, each specimen was inspected at three sensitivity settings (see Table 5) and then the resultant C-scan recordings were interpreted to select the most appropriate setting for that material.

Based on these interpretations it was concluded that the 50 percent sensitivity setting for the neat epoxy resin castings clearly showed that all three of the epoxy resin specimens inspected were high quality (see Figure 4). This observation correlates with the measurements of the laminate physical properties (see Table 5) where the calculated void volume was zero. Similarly, the same sensitivity setting showed some defects in the graphite fiber/epoxy resin composite specimens (Figure 5) which also correlates with the calculated void volume (3 percent V/V). Inspection of the S-glass fiber/polyimide resin (Figure 6) specimens showed one specimen to be extremely poor quality, one specimen appeared to be excellent quality and the other specimen showed a large defect area. Thorough visual examination of these three specimens confirmed that one of the specimens contained delaminations and consequently was discarded. The other two specimens appeared to be of high quality and no defects could be found in the area identified by ultrasonic inspection.

Interpretation of the S-glass reinforced epoxy resin specimens provided similar conclusions to those for the polyimide specimens i.e., one specimen was excellent, one was acceptable and the other had delaminations. NDE inspection of the polyimide graphite fiber specimens indicated that one specimen was of questionable quality although this was not confirmed by visual inspection.

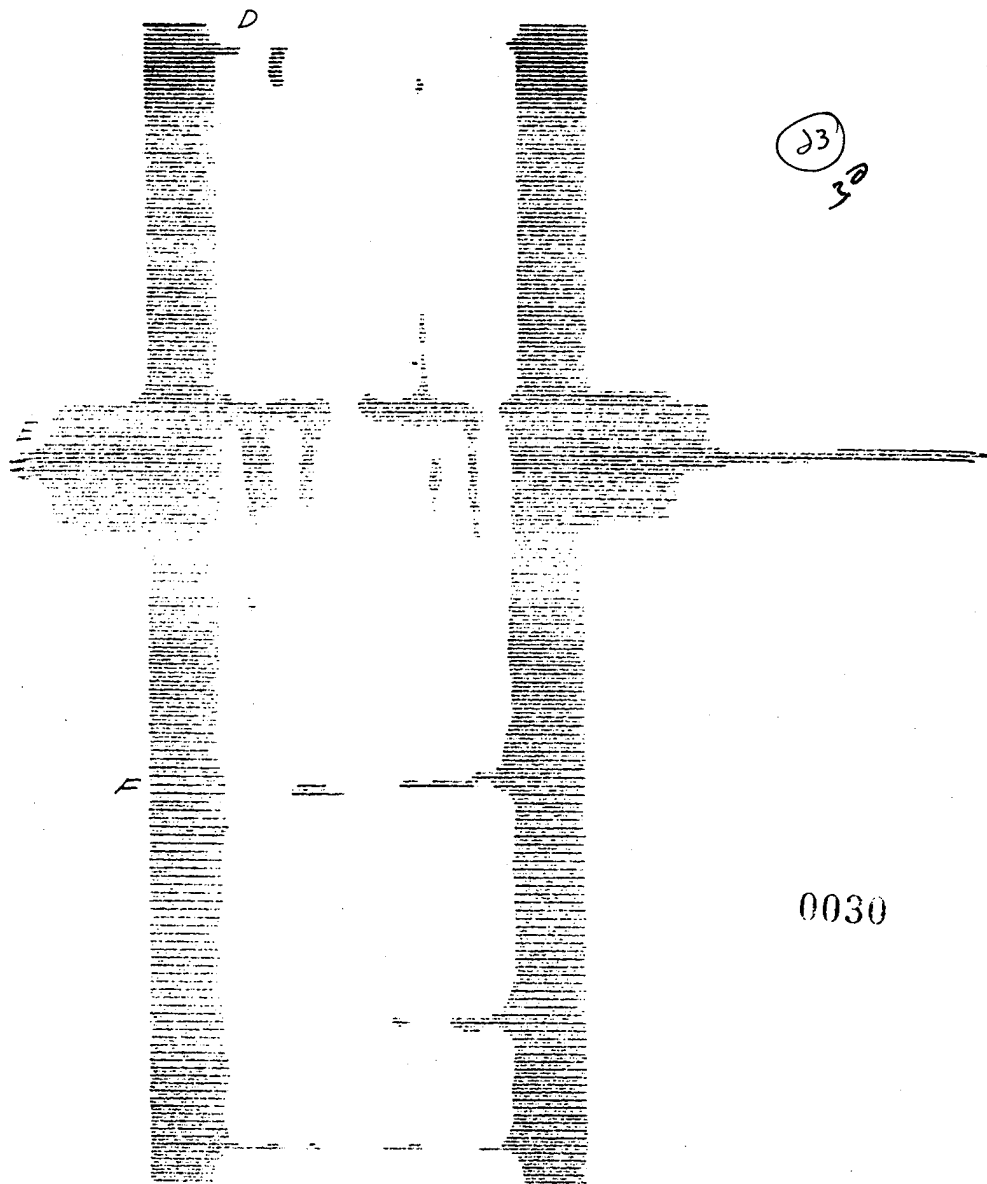


2

TRW EQUIPMENT MAT. DEV. D. P.	
SPECIMEN No.	A, B, C STD T ₁ 1/8" 45°
SCAN No	2 50%
OPERATOR:	JT DATE: 5/8/76
TEST METHOD:	TRW
FREQ:	10.10 MHz SCALE: 1:1

Figure 4. C-Scan of Neat Epoxy Specimens

00023

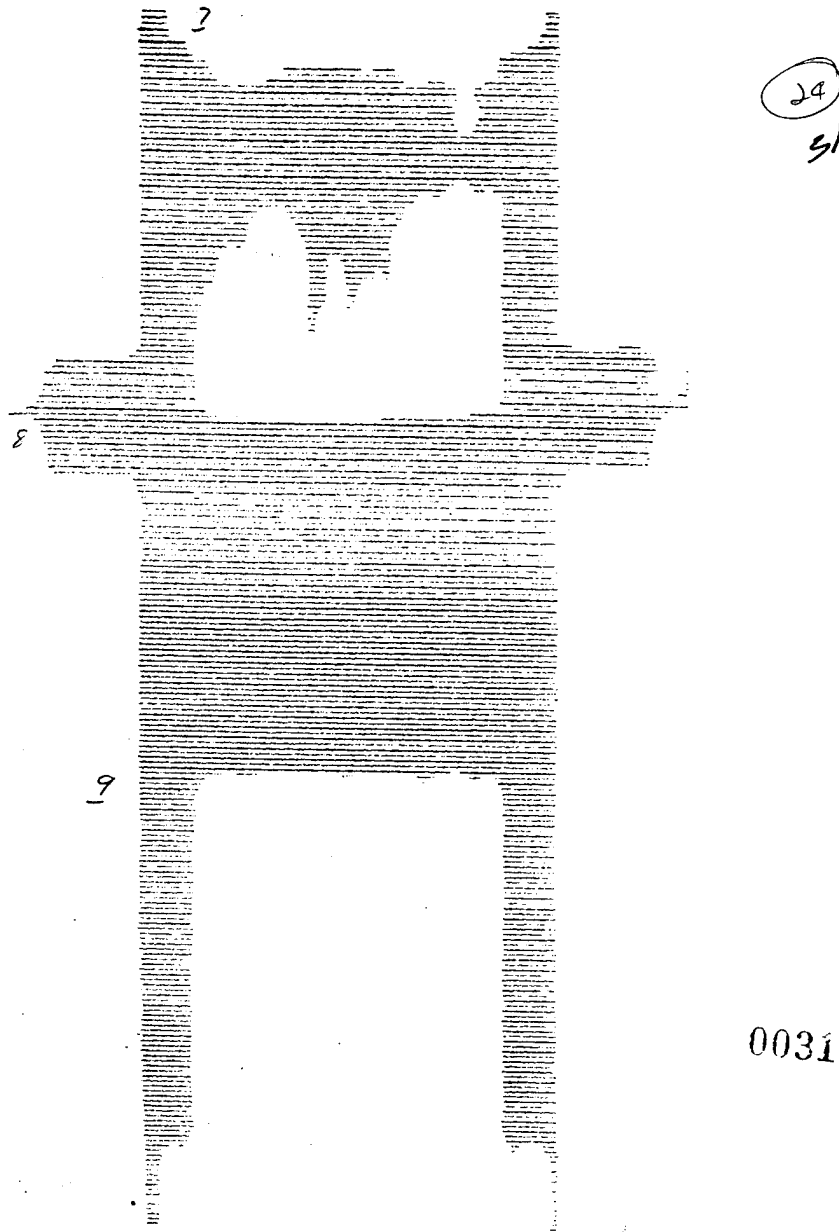


TRW EQUIPMENT MAT. DEV. DEPT.	
SPECIMEN No.	D, E, F STD T. 1/8 45%
SCAN No.	42 509
OPERATOR:	DATE: 5/8/76
TEST METHOD:	TDR
FREQ: 10.0 MHz	SCALE: 1/1

(5)

00025

Figure 5. C-Scan of Epoxy Composite Specimens



TRW EQUIPMENT MAT. DEV. DEPT.	
SPECIMEN: 7, 8, 9	STD 551" 50%
SCANNING: 4-5 50%	
OPERATOR: JT	DATE: 5/11/78
TEST METHOD: TRW	
FREQ: 10 MHz	SCALE:

(24)

00027

Figure 6. C-Scan of Polyimide Composite Specimens

It was concluded from these inspections that each specimen used on the program should be thoroughly examined visually to detect major defects such as delaminations. This was deemed necessary because the ultrasonic inspections indicated a variation in quality of the moldings. However, it should be noted that because the selection of specimens for ultrasonic inspection was made from the first batches of specimens fabricated, it was anticipated that specimen quality improved as the molding experience increased. For the same reasons, the shear strength values reported in Table 4 cannot be assumed typical for all specimens, particularly since all specimens for each material type were taken from the same molding.

Therefore, to summarize the results of the quality assurance tests, it was concluded that the quality of the specimens most probably varied. Because visual inspection of the neat epoxy resin specimens clearly defined defects, the variability between these specimens was probably low. Neat polyimide resin specimens were probably of similar quality to the epoxy resin specimens, although clear definition by visual examination was not possible because they were opaque. The quality of all composite specimens selected for use on the program was high with any defects confined to micro-voids. Major defects such as delaminations were easily detected by visual examinations as confirmed by ultrasonic inspection and suspect specimens were eliminated from further work.

3. SELECTION OF METHOD FOR ANALYSIS

Method selection activities investigated the feasibility of each experimental method designed for the analysis of moisture distribution in resin and composite specimens. At the completion of this task the most effective method for the analysis of moisture, the solids probe mass spectrometry technique, was chosen for use in Task III. The analytical techniques evaluated were: (1) laser pyrolysis gas chromatography mass spectrometry, (2) laser pyrolysis conventional infrared spectroscopy, (3) infrared imaging thermovision and (4) solids probe mass spectrometry.

The following sections report the details of each method's principle of operation, instrumental set-up, implementation, evaluation, information derived and limitations. The D₂O specimen exposure technique is also described.

3.1 EXPOSURE TECHNIQUE

From the program start, it was planned that when a technique for moisture concentration profiling was established, an evaluation of moisture permeation with respect to fiber orientation would be made. Therefore, a fixturing device was designed to allow only unidirectional moisture migration.

This designed fixture consisted of stainless steel clamps with butyl rubber gasket sheets. Between the stainless steel and each specimen, a butyl rubber sheet was placed, then pressure was applied evenly on the four corners of each specimen group. Figure 7 shows a group of fixtured specimens. The groupings chosen consisted of a neat resin system and its two fiber composites in their two fiber orientations. This was determined to be the best organization of the samples in terms of subsequent analytical work. Only the specimens' smallest surface area was available for moisture absorption and transfer. If the fixturing were successful, based on past studies, after 5000 hours of exposure at 75 percent R. H and 344°K, ⁽²⁾ > 2 percent of D₂O would be detected on the exposed surface, approximately 1 percent – 0.5 percent D₂O at 0.64 cm (0.25") from the exposure and < 0.5 percent D₂O at 1.27 cm (0.5") from the exposure.

Constant relative humidity solutions (ASTM E104) were prepared according to the specifications given in reference 5. The solutions use the sulfuric acid formulation given in the reference with the refractive index checked for each D₂O concentration prepared. Heavy water was the fluid used in each case. Desiccators were found adequate as exposure chambers. These were tested prior to having the samples installed for fluid retention during a 48-hour temperature exposure at 344°K. Changes in fluid levels were monitored and none were noted during this time interval.

During the period of performance of the program the desiccator fluid levels were monitored on a bimonthly basis. There was a notable decrease in fluid levels in the 344°K chambers. Late in the program, during one check of the elevated temperature specimens, it was noted that, unfortunately, an oven thermal runaway had occurred and all the elevated temperature specimens were pyrolyzed. New elevated temperature specimens were initiated at that time (January 30, 1979). The loss of these specimens and delays during method development resulted in a more limited specimen availability when analytical efforts were begun (Section 4.0).

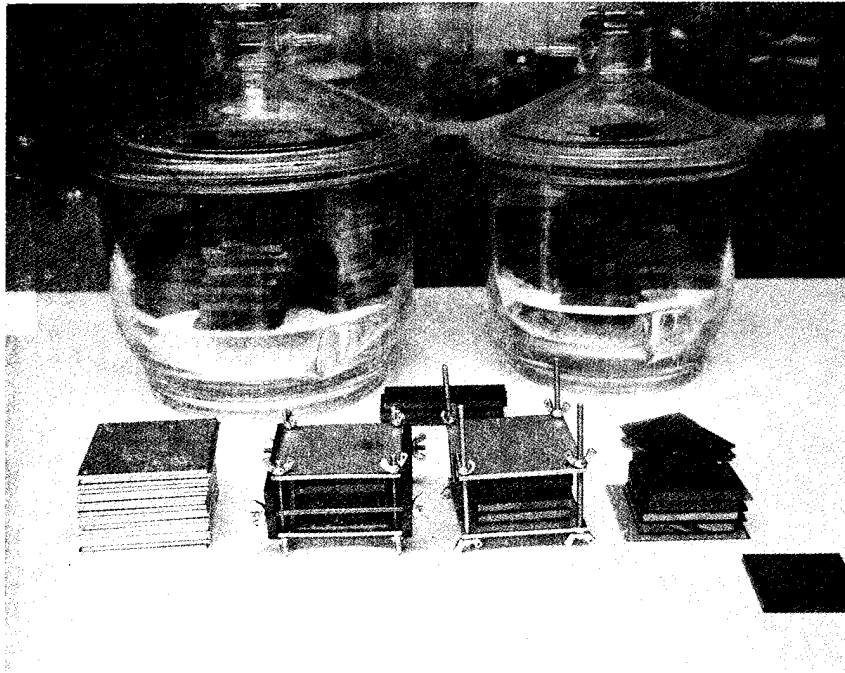


Figure 7. Fixtured Specimens

As a quality control check on the humidity levels in the test chambers, a hygrometer (Airguide, accuracy ± 5.0 percent, precision ± 0.5 percent RH), was used to verify RH conditions and these changed markedly during the program duration. During the final analytical effort when D₂O concentration data were gathered on all available exposed specimens (Section 4.3), the exposure conditions and duration were:

- ● Desiccated at Room Temperature
1440, 3670, 8850, 10700 and 13010 hours
- ● 22 Percent RH (hygrometer reading) at 344°K,
1440 and 3670 hours
- ● 54 Percent RH* (hygrometer reading) at Room Temperature,
1440 and 3670 hours
- ● 59 Percent RH* (hygrometer reading) at Room Temperature,
8850 and 10700 hours

* Therefore, for the 54-59 percent RH at room temperature exposure four time sets are available: 1440,3670,8850 and 10700 hours.

- 75 Percent RH (hygrometer reading) at 344°K, 1440 and 3670 hours

The specimens used for method feasibility studies were: (1) dried (constant weight obtained and desiccator stored over program length), (2) D₂O saturated (boiled in D₂O for 2-4 hours, and stored under D₂O with surface wiped dried and desiccated for 12 hours prior to analytical run) and (3) D₂O conditioned (stored unfixtured in the room temperature, 59 percent RH chamber). This group was found to represent the best range of D₂O concentrations for method evaluation. Fixtured exposure specimens were originally scheduled for the method feasibility. However, only a limited number of these were used because the dry and D₂O saturated samples provided better samples.

3.2 LASER PYROLYSIS-GAS CHROMATOGRAPHY/MASS SPECTROMETRY (LP-GC/MS)

Laser Pyrolysis-Gas Chromatography/Mass Spectrometry was thought to be the most promising technique for D₂O concentration mapping and the identification of D₂O induced chemical effect without requiring specimen preparation. The components of this instrumental system are a Korad, K-1 model ruby laser system, a hermetic sample cell, and a Finnigan 4000 GC/MS system.

In laser pyrolysis gas chromatography mass spectrometry (GC/MS) the laser is used as a high-intensity heat source producing localized (0.03 cm²) thermal degradation of the test specimen. The resultant gaseous products are either pumped into the mass spectrometer through its vacuum system by way of a variable leak valve or purged into the mass spectrometer using an inert carrier gas and the separating capability of a gas chromatograph.

In GC/MS the gas chromatograph is used to separate the volatile materials under analysis and reduce the complexity and number of ion fragments recorded by the mass spectrometer. Early in this method development effort, the gas chromatograph was eliminated as the inletting method for

the MS. The pyrolysis products were not found to be of a complexity which warranted isolation by GC before MS analysis. A variable leak method of inletting the gaseous products followed by mass spectroscopy was used.

Normal mass spectrometry is accomplished by bombarding the sample under vacuum with 70 eV electrons. The ionization process produces a spectrum which contains characteristic fragment ions from the molecules under study. In most cases an ion representative of the compound's molecular weight is produced e.g., mass 20 for D_2O and identification is routine.

3.2.1 Korad Ruby Laser System

The laser employed was a commercially available ruby laser (Korad) which operates in the non Q-switched mode. A pulse energy of 10 Joules at a wavelength of 6943\AA is nominally available which has a duration of 800 microseconds. The unfocussed laser beam has a cross-sectional area of 0.13 cm^2 . In order to reduce the beam diameter, a quartz lens (f/2) was used to focus the beam to an area of 0.03 cm^2 .

Because of the focussing of the lens, the peak power density near the substrate material was approximately 0.4 megawatt/cm^2 (energy density $\approx 0.3\text{kJoule/cm}^2$), high enough to damage the cell window (Section 3.2.2). As a result of initial focussing experiments, a 1-cm spacer was inserted between the window and the sample substrate. Although initial experiments were performed using sapphire windows, it was found that fused quartz (or high quality pyrex) could be used for future experiments. The absorption loss in quartz at 6943\AA was minimal and polymer damage was not affected.

The specimens were found to be efficiently pyrolyzed from one pulse to a depth of approximately 25 microns.

This commercial laser system, once adapted for the localized pyrolysis required for program use was integrated with the maintenance/analytical cells described in Section 3.2.2. These cells were precision mounted to the laser optical bench and translated by a micrometer screw for mechanical sample advancement along the analytical axis.

3.2.2 Maintenance/Analytical Cells

Three cells were designed and built for program use. They provide an enclosure for samples undergoing analyses which is protected from ambient

and, therefore, D₂O concentration profiling is capable of being accomplished with minimal sampling handling. The main features of these cells (Figure 8) were:

- Small internal volume, approximately 15 cm³.
- Dual valves for purging with carrier gas and providing direct inlet to the L/GCMS and L/IR diagnostic techniques.
- Offset 5.1-cm-diameter sapphire windows — leading edge of specimen is 0.3 cm from window edge. The specimen's depth axis is parallel with the window. This exposes adequate depth for moisture analysis determination with analysis being conducted across the window's horizontal diameter (4.3 cm of specimen depth available for analyses).
- Sapphire windows also provide transmission for the infrared imaging and the laser pulse.
- Isolation of only one specimen at a time for analysis.
- Flange configuration provides for seal integrity.
- Viton O-ring seals have been designed to be isolated from the cell interior.
- Mounting bracket for alignment with Korad laser.
- Easily interfaced with mass spectrometric system through heatable or ambient gas transfer lines.

The simplicity of design of these cells provides ease of cleaning between use and less anticipated problems with sample condensation as a high volume purge can be used during laser operation.

3.2.3 Gas Chromatography/Mass Spectrometry System

The gas chromatography mass spectrometry (GC/MS) system employed for pyrolysis product identification and D₂O quantitation was a state of the art Finnigan 4000 GC/MS. This instrument is constructed with a microprocessor-controlled gas chromatograph, with an MS capable of a one-second scan time, high sensitivity, high resolution, switchable dual CI/EI source and capillary GC capability.

This GC/MS system is interfaced to an INCOS 2000 data system. The data acquisition system consists of a Nova III computer, high-density dual disk storage, a Versetec printer/plotter and a CRT terminal. The data system features a foreground/background processing capability which allows for simultaneous data acquisition and processing of mass spectrograms.

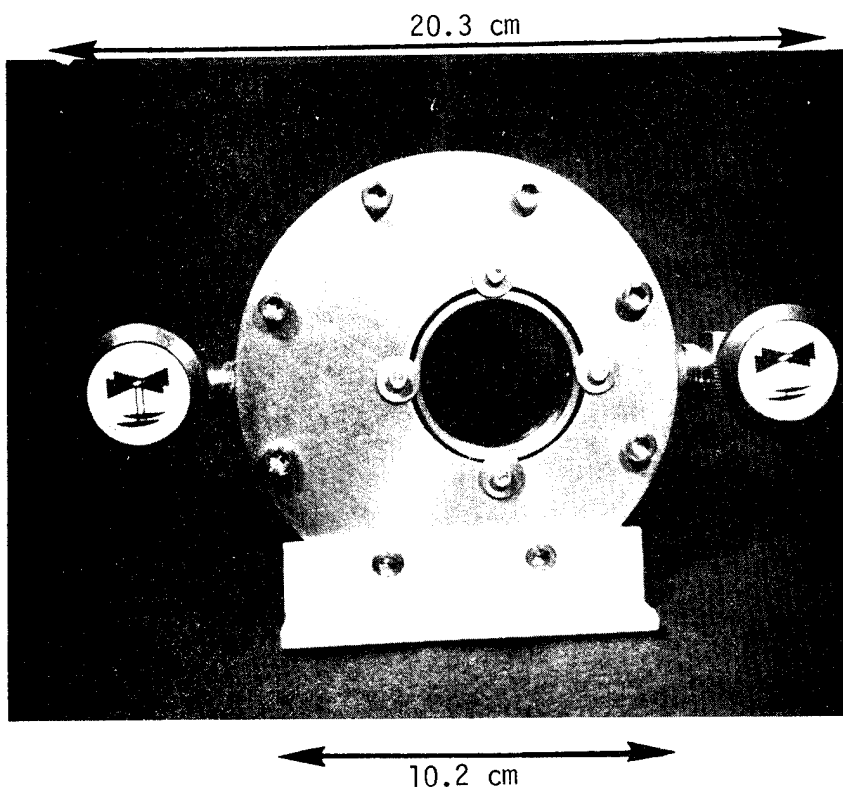
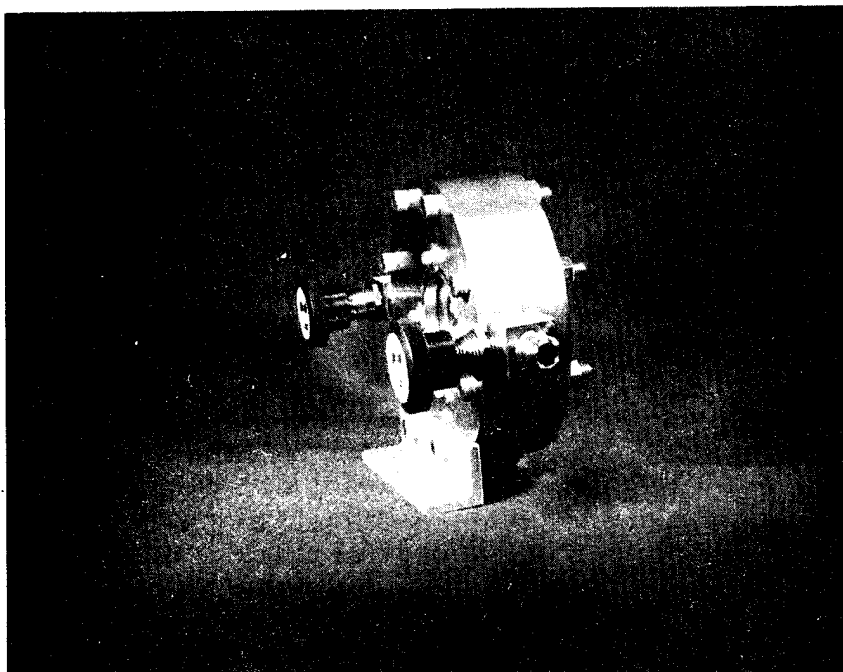


Figure 8. Maintenance Analytical Cells for Laser Pyrolysis Experiments

Spectra may be displayed from previously recorded files or from the file actually being acquired. This feature reduces instrument and operator time. External data files may be accessed with ease via a direct modem link. Software is resident in the data system for direct computer access of Cyphernetics and Cornell library search services. For this program the data system was used to perform basic calculations and concentration.

Two methods for inletting the laser pyrolysis products into the GC/MS were initially investigated: (1) through the gas chromatograph and (2) directly into the MS source through a Granville-Phillips variable leak valve.

A Porapak P column was used for the gas chromatographic inletting approach. It was operated at 423°K and proved to be acceptable for eluting water and D₂O standards to the MS. Standards were initially prepared in carbon tetrachloride in order to prevent proton/deuteron exchange within the solvent. The column did not separate D₂O from H₂O but did allow these two species to elute completely separated from CCl₄ or other organic species. The data system allowed for specific detection of D₂O as M/e 20.

The Finnigan variable leak assembly was an acceptable means of interfacing the maintenance/analytical cells with the source of the mass spectrometer. Gases generated from pyrolysis were conveyed directly into the source at the point where the batch or solids probe inlet tube normally is placed. The Granville-Phillips variable leak valve was opened to permit introduction of pyrolysis products as fast as possible and consistent with maintaining proper source pressure. Figure 9 shows the constructed maintenance/analytical cell interfaced through the Granville-Phillips variable leak to the Finnigan mass spectrometer.

3.2.4 Feasibility Experiments

In evaluating the analysis of laser pyrolysis products through gas chromatograph mass spectrometric and mass spectrometric techniques, a number of method modifications were attempted to improve the reliability of D₂O detection. These modifications, and their effect on the data are presented in Table 6.

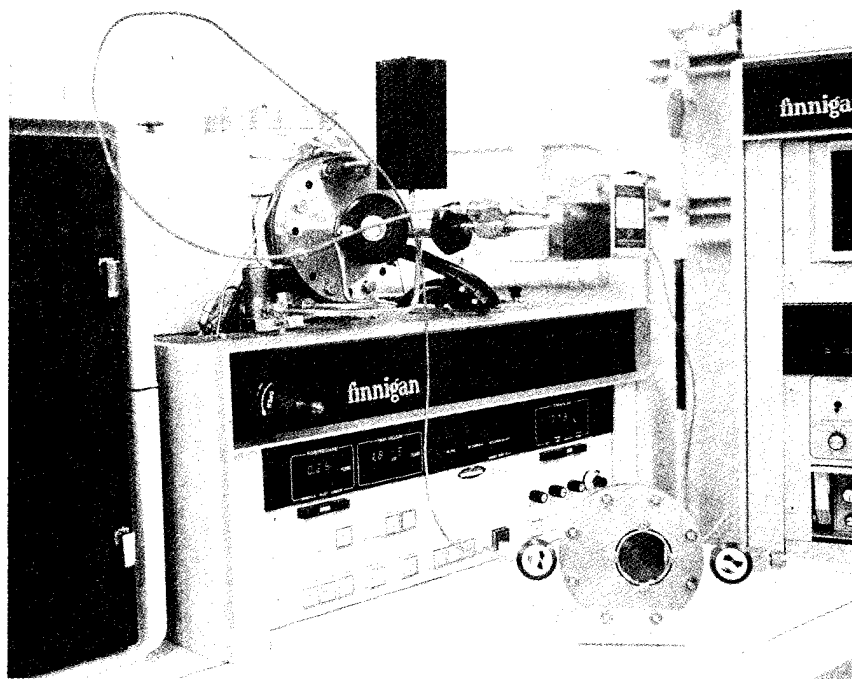


Figure 9. Maintenance/Analytical Cell Interfaced With Finnigan Mass Spectrometer

Table 6. Laser Pyrolysis Gas Chromatography Mass Spectrometry Feasibility Experiments

Instrumental Operating Mode	Samples Analyzed	Results Obtained	Conclusions
GC inletting with a porapak P column (92cm x 2mm ID at 423K, 150°C)	<ul style="list-style-type: none"> D₂O in CCl₄ Pyrolysis products of D₂O saturated neat epoxy 	<ul style="list-style-type: none"> 100 nanograms of D₂O detectable H₂O exchanging and interfering with D₂O 	<ul style="list-style-type: none"> GC inletting not required - H₂O eluting with D₂O GC inletting may enhance D₂O/H₂O exchange because of residence time
Cell interfaced with Granville-Phillips variable leak valve (0.05mm OD copper line with Cajon VCR vacuum coupline). Pyrolysis products pumped into instrument by MS vacuum system.	<ul style="list-style-type: none"> Cell background Cell background with dry epoxy and polyimide Cell with D₂O injected Pyrolysis products of D₂O saturated neat epoxy Pyrolysis products of dry neat epoxy 	<ul style="list-style-type: none"> extensive D₂O/H₂O exchange, M/e 19 > M/e 20. Cell background and dry polymer pyrolysis products background acceptable 	<ul style="list-style-type: none"> Convert instrument H₂O background to D₂O by flooding with D₂O for several hours prior to test Heat all cell lines to reduce H₂O background Purge sample into MS to reduce wall contact time
Cell interfaced with Granville-Phillips variable leak valve as above with all lines heated to 323K (50°C)	<ul style="list-style-type: none"> Cell background Cell with D₂O injected 	<ul style="list-style-type: none"> Indeterminant D₂O/H₂O exchange still occurring 	<ul style="list-style-type: none"> Convert to dry gas purge of sample into MS to reduce residence time
Cell interfaced with Granville-Phillips variable leak valve with heated lines. Pyrolysis products swept into instrument by dry N ₂ purge	<ul style="list-style-type: none"> Cell background Cell background with dry and D₂O saturated neat epoxy specimens Pyrolysis products from a segmented specimen with sharp D₂O/H₂O boundaries D₂O saturated nitrogen 0.01cc/ATM and 0.02cc/ATM 	<ul style="list-style-type: none"> On analysis of saturated sample the D₂O and H₂O background remains constant and reduces instrument sensitivity In segmented specimen D₂O background interferes through test. However, D₂O boundary is easily detected. Repetitive analysis of nitrogen standards gave large variations in response 	<ul style="list-style-type: none"> Less total sample can be inletted under this mode because of increase in instrument pressure due to purge gas. Therefore, the D₂O detection limit is reduced. No improvement over above mode.
Cell interfaced with Granville-Phillips variable leak valve, all lines heated to 323K (50°C), vacuum inletting, MS conditioned with D ₂ O (saturated nitrogen for 12 hours).	<ul style="list-style-type: none"> D₂O saturated nitrogen, 0.01cc/ATM and 0.02cc/ATM Variation in rates of cell pump out Analysis of pyrolysis products from 200 hour, 344K (71°C), 75% RH polyimide specimens. D₂O peak at M/e 20 + H₂O peak at M/e 19 rationed to H₂O peak at M/e 18 	<ul style="list-style-type: none"> Variations in D₂O response Evacuation rate of cell effects D₂O response Data on specimens shows high scatter when duplicated 	<ul style="list-style-type: none"> A reliable calibration cannot be achieved Wall conditioning in the cell lines and MS has large and indeterminant effect on D₂O measurement.
Direct injection of D ₂ O saturated nitrogen into Granville-Phillips variable leak valve	<ul style="list-style-type: none"> D₂O saturated nitrogen 0.01cc/ATM and 0.02cc/ATM 	<ul style="list-style-type: none"> Variations in D₂O response 	<ul style="list-style-type: none"> D₂O/H₂O exchange is not limited to cell and external hardware. A reliable calibration cannot be achieved standard deviation ± 40%

The general conclusions from these feasibility studies were:

- Reasonably accurate determinations of D₂O concentrations in laser pyrolyzed products through a mass spectrometry and combined gas chromatography/mass spectrometry is not feasible because of the indeterminate rate of D₂O/H₂O exchange. However, positive identification of D₂O can be accomplished. Therefore, the extent of D₂O migration into the specimen can be made.
- A technique for direct sample insertion into the MS source may provide a reasonable alternative (solids probe mass spectrometry). Time and available surface for D₂O/H₂O exchange would be reduced to a minimum.
- The laser operation was routine. However, the size of the test burns (quantity of pyrolysis products produced) varied dependent on polymer and fiber type. Therefore, the method of determining the sample quantity inletted for analysis was labor intensive and approximate. A microscopic inspection of each burn had to be made, the approximate volume recorded and the quantity calculated from the specimen's density.
- The pyrolysis products from the D₂O exposed epoxy specimens contained: H₂O, DHO, D₂O, O₂, N₂, Ar, CO₂, CO, acetylene (C₂H₂), butadiene (diacetylene, C₄H₂) and benzene. Although only a limited number of specimens were analyzed, D₂O exchange with polymer ion fragments was not noted.

3.3 LASER PYROLYSIS-CONVENTIONAL INFRARED SPECTROSCOPY (LP-IR)

This analytical approach utilizes the laser for localized pyrolysis of the polymers and composites and infrared spectroscopy for D₂O quantitation in the gaseous pyrolyzate. The laser has been described in Section 3.2.1 and the maintenance/analytical cell used to stage the samples in Section 3.2.2.

Conventional infrared spectroscopy measures the infrared absorption spectrum of a material from 4000 - 200 cm⁻¹ (2-15 microns). In this wavelength region, energy is absorbed by atom-to-atom bonds in a molecule. The wavelength and intensity of each absorption is, therefore, unique and identification of compounds is made by correlation of absorption wavelength with compound functionality e.g., C-O, C-H, C=O, etc., bands. Quantitative data can be established by measurement of absorption peak intensity and calibration (an application of Beer's Law).

The application of conventional infrared spectroscopy to quantitate D₂O in laser pyrolysis products was theoretically feasible. The documented pyrolysis products of polymers⁽⁵⁾ and those found in initial GC/MS analyses on this program did not contain species expected to interfere with the D₂O absorption peak at 2500 cm⁻¹ (4.0 μ). The evaluation undertaken for this program was, therefore, to establish the D₂O detection limit and determine if it could fulfill program requirements.

Fourier Transformed Infrared Spectroscopy (FTIR) was not available at TRW during the methods development portion of this program. When evaluation experiments determined that conventional infrared spectroscopy required a factor of 100 more sensitivity, program work in this area was terminated.

3.3.1 Infrared Spectrophotometer

The feasibility experiments conducted utilized a Perkin-Elmer 521 and 283 grating dispersion infrared spectrophotometers. Both instruments were wavelength calibrated using a standard polystyrene film and acceptably resolved standard spectra were obtained. Scan times for 4000 – 200 cm⁻¹ (2.5 – 15 micron) were 10 minutes and scale expansion were 1X-50X in transmittance mode.

3.3.2 Feasibility Experiments

A preliminary experiment using the Perkin-Elmer 521 and a 10-cm hermetic heated gas cell gave an excellent spectra at normal resolution for 0.5g of D₂O with a small quantity of H₂O present (Figure 10). Possible analytical wavelengths for D₂O were determined to be at 2500 cm⁻¹ (4.0 μ) where CO, and CO₂ in the pyrolyzate were not anticipated to interfere and at 1200 cm⁻¹ (8.34 μ) where some low molecular epoxy fragments could produce some possible absorption. Two μg of D₂O was easily detected in this cell during preliminary experimentations.

A calibration curve was generated (Figure 11) for the 2500 cm⁻¹ (4.0 μ) absorption wavelength which was linear and reproducible in the 0-10 μg D₂O range. It was calculated that at a 2.0 percent absorption of D₂O by the sample, approximately 1 x 10⁻⁴ μg of D₂O (0.005 μg of material pyrolyzed x 0.02 = 1.0 x 10⁻⁴ μg) would be liberated by a saturated specimen from

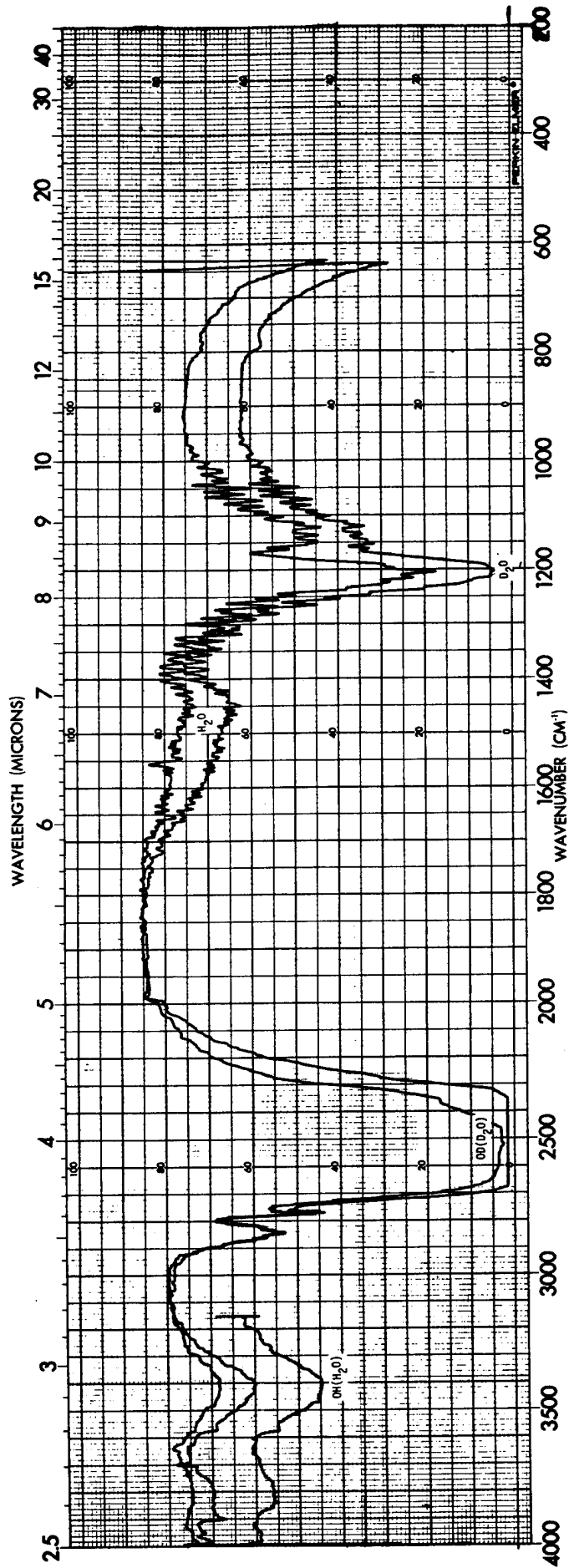


Figure 10. Infrared Scan of D₂O in 10 cm Heated Gas Cell

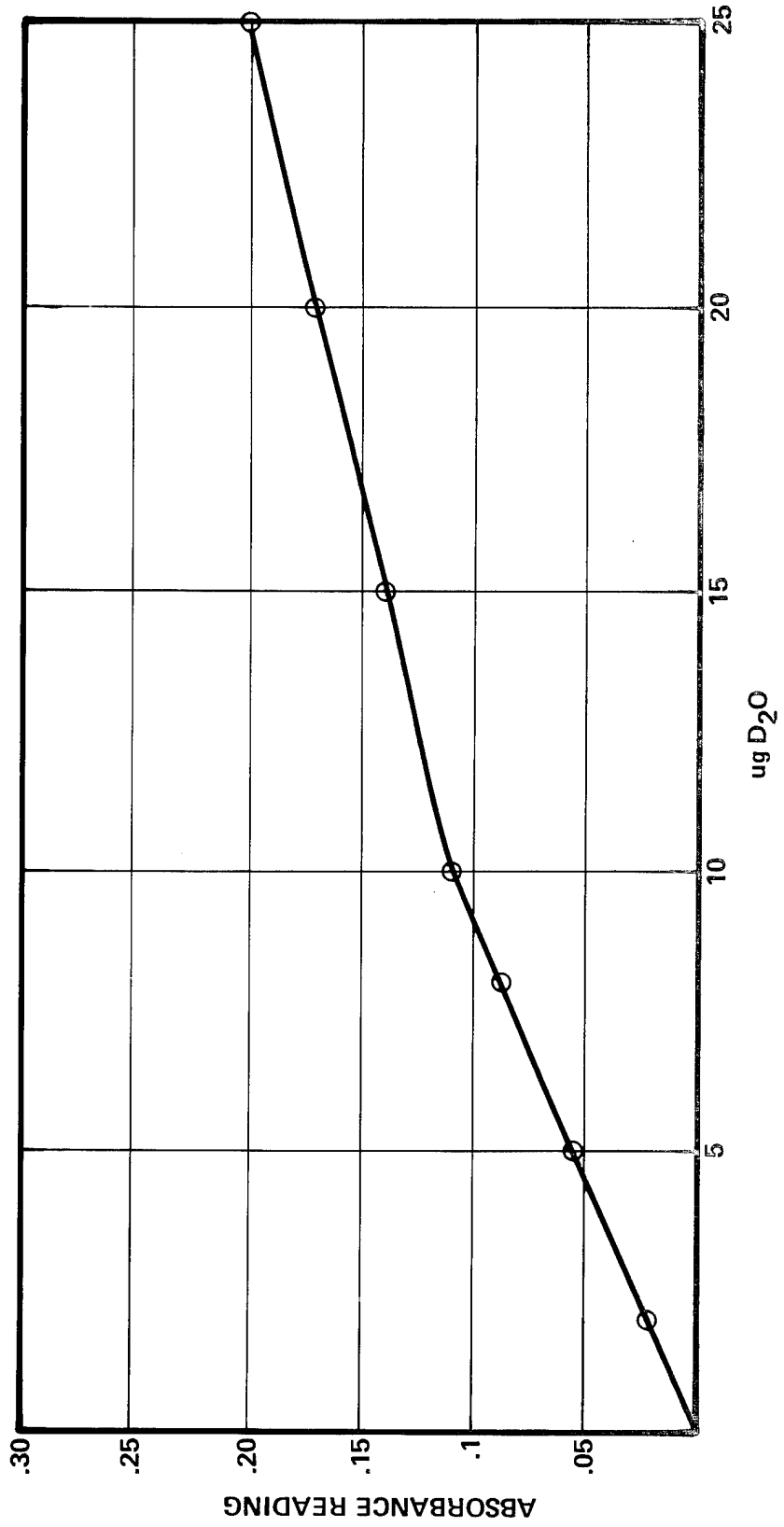


Figure 11. D₂O Calibration Curve 10 cm Heated Cell (86°C)

one laser pulse. Through detection limit extrapolation, the liberated D₂O would not be detectable by this technique. However, multiple laser pulses on D₂O saturated specimens were used to evaluate this technique. Neat epoxy and neat polyimide specimens were boiled for two hours in D₂O and the laser was operated in a pulse mode for five successive laser pulses at the identical distance from the exposed surface. The IR spectra obtained produced no observable D₂O nor HDO absorption bands. Feasibility experiments were terminated at this point because detection sensitivity of conventional infrared spectroscopy was lacking and efforts were diverted to additional mass spectrometric experiments.

3.4 INFRARED IMAGING TECHNIQUE

Infrared imaging is an analytical method based on the infrared transmission properties of the resins and composites. It had been proposed to study the effects of moisture-induced voids or other defects. Epoxy and polyimides are known to transmit in the infrared region of 2500 - 1800 cm⁻¹ (4.0-5.5 μ) where D₂O is an absorber. Therefore, good contrast between moisture voids and matrix materials could, in principle, be achieved by using an IR-imaging camera. In essence, this device incorporates a viewing optical system which provides two-dimensional scanning of an object and a sensitive IR detector, which registers intensity of IR-radiation transmitted (or, in some cases, emitted) by the scanned parts of an object. Obtained in this manner, intensity distribution is electronically processed and displayed on a TV-like screen. The TV-like scanning system essentially sees the heat patterns as thermograms.

On application of this technique to monitoring D₂O migration in these specimens, it was planned that the specimens would appear transparent to the TRW device because of their inability to absorb in the operational wavelength region of the IR camera and that voids filled with D₂O as well as migrated D₂O would absorb and be imaged. However, during the feasibility studies the specimens were found to be too thick and thus they produced an opaque image which masked any D₂O present.

3.4.1 Infrared Imaging Camera

The infrared imaging (IR-imaging) camera used in the feasibility experiments was a Dynard, Type 602, IR-imaging camera. It is sensitive from 2.0 to 5.5 microns, and provides a 10° by 10° field of view. The infrared scan is displayed on a TV screen. This equipment was extensively modified from the as-purchased condition for this and other project uses. Figure 12 shows the infrared emission imaging hardware. Once the IR imaging camera was functioning properly, an absorption infrared image of Teflon which has a weak absorption at 2400 cm^{-1} ($4.3\ \mu$) was produced without difficulty and Teflon at ambient was used for equipment checkout during the method evaluation.

3.4.2 Feasibility Experiments

Dry and D₂O saturated neat epoxy and polyimide specimens were imaged in both transmission and emission modes. In every configuration, an acceptable imaging of the specimens could not be obtained. To determine if this problem was due to specimen thickness a high temperature heat source (600°C) was imaged by the camera and then the polymer specimens inserted between the heat source and detector. The heat source image was lost. The specimens were, therefore, determined to be of a thickness which is not suitable for this experimental technique.

3.5 SOLIDS PROBE MASS SPECTROMETRY

The laser pyrolysis gas chromatography mass spectroscopy studies proved that D₂O can be positively detected by the mass spectrometer (MS) but that quantitation was impossible because of the indeterminate factors affecting D₂O/H₂O exchange. Although one of the program objectives was to analyze specimens without preparation e.g., sectioning, a direct insertion of sample segments (approximately 0.001 g) was investigated to determine if D₂O/H₂O exchange could be reduced to a minimum if the samples were introduced directly into the MS source.

The solids probe inletting system of the Finnigan 4000 GC/MS, described in Section 3.2.3, was used in these studies. The results obtained from experiments described in Section 3.5.2 demonstrated the feasibility of this approach and it was the technique chosen for specimen analysis.

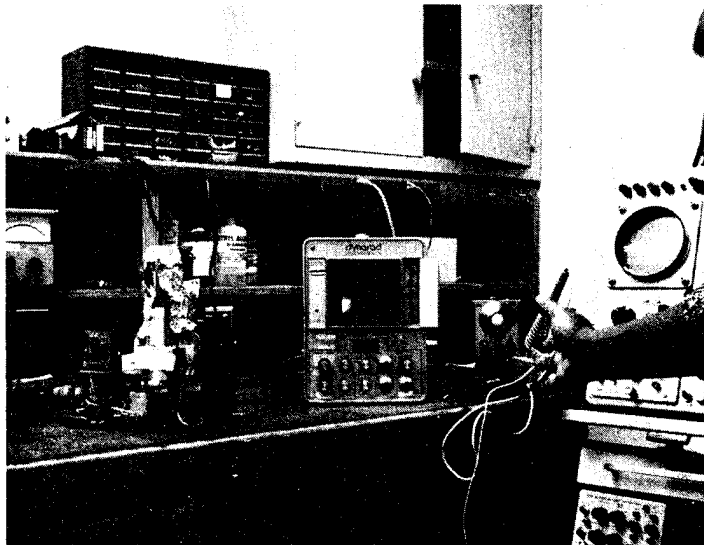


Figure 12. Infrared Imaging Hardware.

3.5.1 Solids Probe Mass Spectrometry Technique

The Finnigan solids inletting probe is mounted directly in front of the MS chamber. Specimens undergoing analysis are placed into glass sample holders which are, in turn, placed in the end of the solids probe. This probe can be temperature programmed or run isothermally. This is a conventional MS technique.

3.5.2 Feasibility Experiments

Initial experiments used D₂O soaked, small cast epoxy fragments estimated to weigh between 1/3 to 1/2 mg. A similar lot of chips was placed in an empty bottle for non-D₂O control samples. For analysis, each epoxy segment was mounted in a glass solids probe sample holder which, in turn, was placed in the end of the solids probe. The D₂O soaked chips were blotted dry and left to air dry for 1 hour prior to loading. The following sequence was carried out:

- 1) The solid sample probe was inserted into the outer chamber of the mass spectrometer inlet.
- 2) The acquisition was started. Ten scans of instrument background and approximately 30 scans of instrument background were taken at sensitivities of 10^{-17} amps/volt and 10^{-6} amps/volt respectively.

- 3) With the filament on and in rapid sequence, the inlet was evacuated, the inlet valve opened and the solids probe inserted all the way into the ionizer block. Step 3 took 30 - 40 seconds to perform.
- 4) Data acquisition was continued until 500 scans were obtained. The important operating parameters for the Mass Spectrometer/Data System (MS/DS) were as follows:
 - MS was scanned from M/e 10 to M/e 225 every second in a continuous cyclic recording.
 - The solids probe was not heated by its own circuitry but was instead warmed by the ionizer block which is at approximately 475°K
 - Mass spectral data was collected at a preamplifier setting of 10^{-6} amps/volt except for the first 10 scans of background at 10^{-7} amps/

Examination of the total ion chromatograms (TIC) (comparable to gas chromatograms) did not provide any clear differentiation between dry and exposed chips. The mass spectra in the region of the large peaks in the TIC's showed the presence of air, which is unavoidably inhaled when the solid probe is fully inserted, with the bulk of the signal caused by H₂O.

The single mass chromatograms for mass 19 and 20 showed significant differences between the dry and exposed samples. The M/e 20 mass chromatogram for the exposed sample showed an increasing level of M/e 20 up to about scan 275 and then slowly decreased. The M/e 19 and 20 mass chromatograms for the dry specimen showed asymptotically decreasing levels.

The mass spectra shown in Figures 13 and 14 clearly detect the presence of M/e 19 and 20 in the exposed sample with little or no M/e 19 and 20 seen in the non-D₂O exposed sample. The detection of D₂O is clearly established using this sample inletting technique.

The presence of adsorbed DHO, and D₂O on surfaces remained a slight problem. However, it is much diminished from the previous experiments using the laser. This behavior results in spectra containing M/e 19 and 20 for some period after the analysis of an exposed specimen. It was determined that most of the adsorbed D₂O and DHO was on the surface of the probe. Much of this background was removed by simply removing the probe.

MASS SPECTRUM
07/24/78 2:26:00 + 8:20
SAMPLE: EPOXY NON D20 EXPOSED

DATA: DRYEPOX2 #500
CALL: C8724 #1

BASE M/E: 18
R/C: 3744.

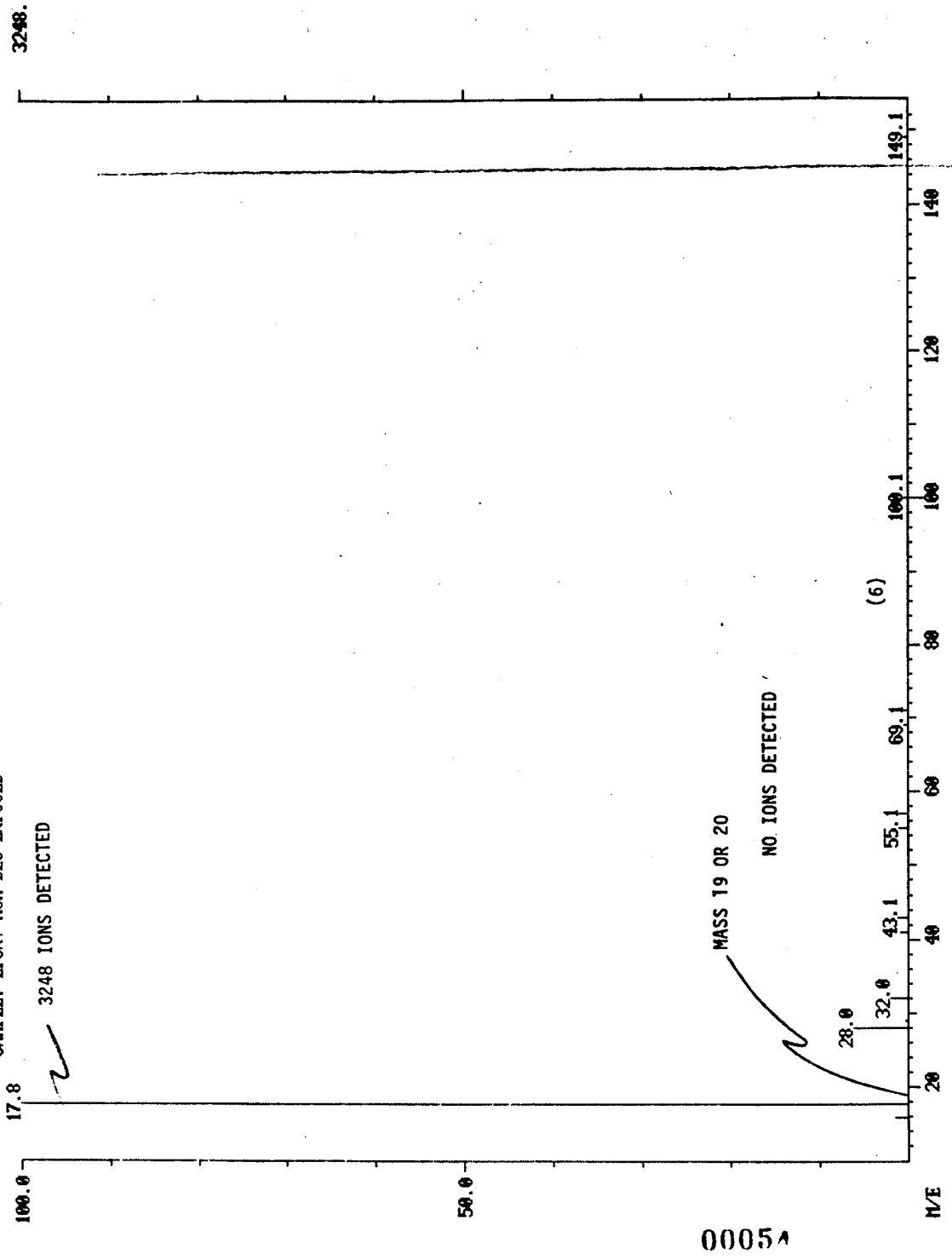


Figure 13. MS Scan of Dry Epoxy Specimen

MASS SPECTRUM
07/24/78 4:05:00 + 8:20
SAMPLE: D20 EXPOSED

DATA: EXPOXYS #500
CALL: 09/24 #1

BASE M/E: 18
R/C: 3756.

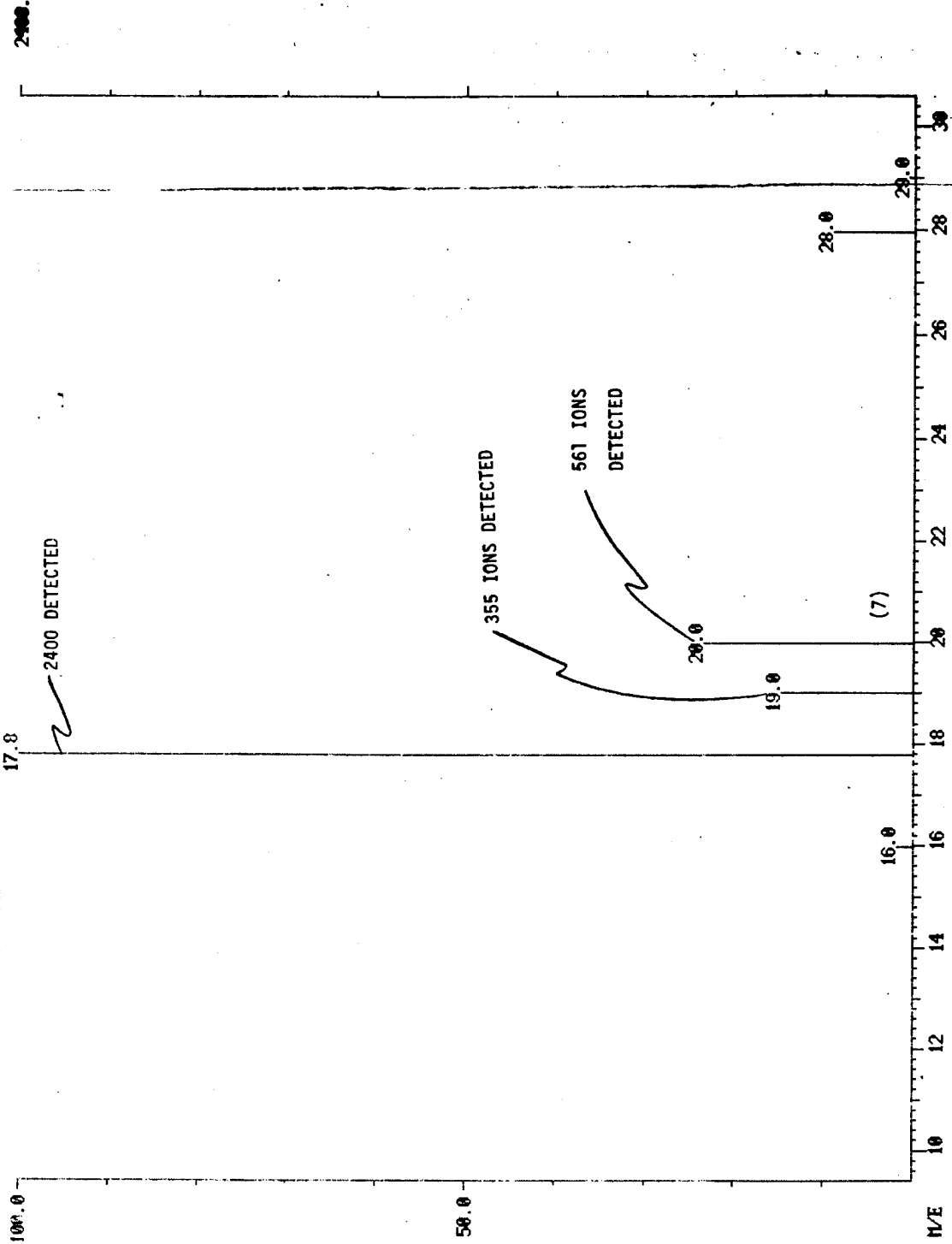


Figure 14. MS Scan of D₂O Exposed Epoxy Specimen

00055

An additional set of confirmatory experiments were initiated for procedure verification. Experiments were conducted on five D₂O soaked (30 days) cast epoxy fragments and a dry control group which were estimated to weigh between 1/3 to 1/2 mg.

Appendix B contains the computer prepared ion chromatograms for these experiments. These chromatograms were included to clearly demonstrate the technique's D₂O detection consistency. The sample designation can be found in the heading at the top of each figure next to "Data:". Results on the analysis of epoxy chips which were exposed to D₂O in a 75 percent relative humidity chamber at 344°K for 18 days gave positive results. These exposed chips were also alternated with dry non-D₂O exposed epoxy chips to verify analytical specificity in D₂O detection. These D₂O exposed samples are designated "Test Sample XX" and the non-exposed samples are designated "Control XX".

After this set of experiments it was established that a method for reliable detection of D₂O in small cast epoxy polymer specimens had been clearly demonstrated.

This use of solids probe mass spectroscopy necessitated the development of a suitable sample removal technique from the fixtured exposed specimens. The first approach investigated was a low-speed, motorized, hand-drilling technique. An epoxy cast specimen which had been immersed overnight in D₂O, wiped dry, and stored overnight in a desiccator was analyzed. Samples of 0.13 mg in weight were taken from the surface to the interior as illustrated in Figure 15. A total of five probes were made yielding 25 samples for D₂O determination. Known dry and D₂O wet samples were intermixed with these test runs. As was expected, only the first surface drilling showed positive D₂O detection. The underlayers were D₂O dry and uncontaminated by the sampling technique. Samples which remained at ambient in excess of 24 hours did not lose D₂O.

This sampling methodology was then applied to both a fixtured cast epoxy and a fixtured cast polyimide specimen. These were taken at 5000 hours from the room temperature, 59 percent RH exposure. A positive D₂O control:

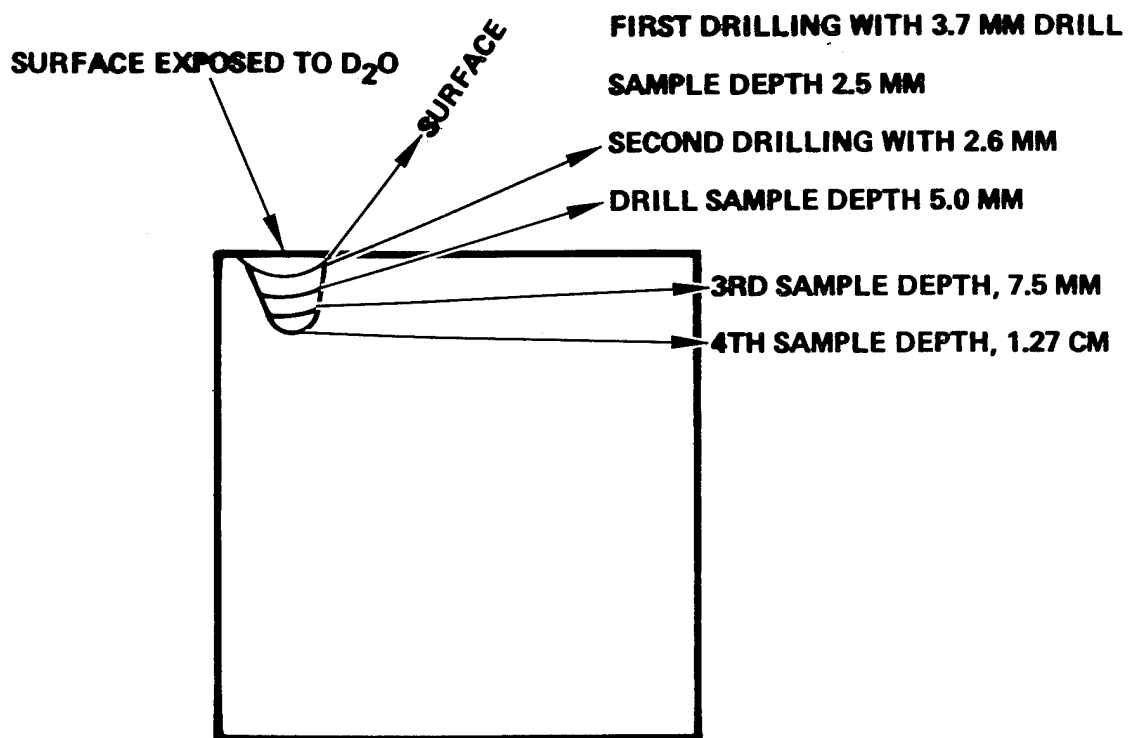


Figure 15. Illustration of Samples Acquired by Drilling Technique

of an unfixtured cast epoxy specimen and a dry specimen were included with the set of samples. Surface to interior drillings were made as indicated in Figure 15. Each drilling produced three samples: a surface scraping, one from the surface to a depth of approximately 2.5 mm (0.1"), the other from 2.5 mm (0.1") to approximately 5.0 mm (0.2"). The second technique removed samples as illustrated in Figure 16. Sample Nos. 1, 5, 1A, and 5A were along the fixtured face where the butyl rubber gasket had been in contact with the specimens. These were assessed to evaluate capillary action along the interface. Sample Nos. 6 and 7 were from the exposed 0.50 cm edged without contributions from the surface in contact with the butyl rubber. Figure 17 illustrated positive detection of D₂O in Sample No. 6B, the subsurface, 2.5 mm (0.1"), sample.

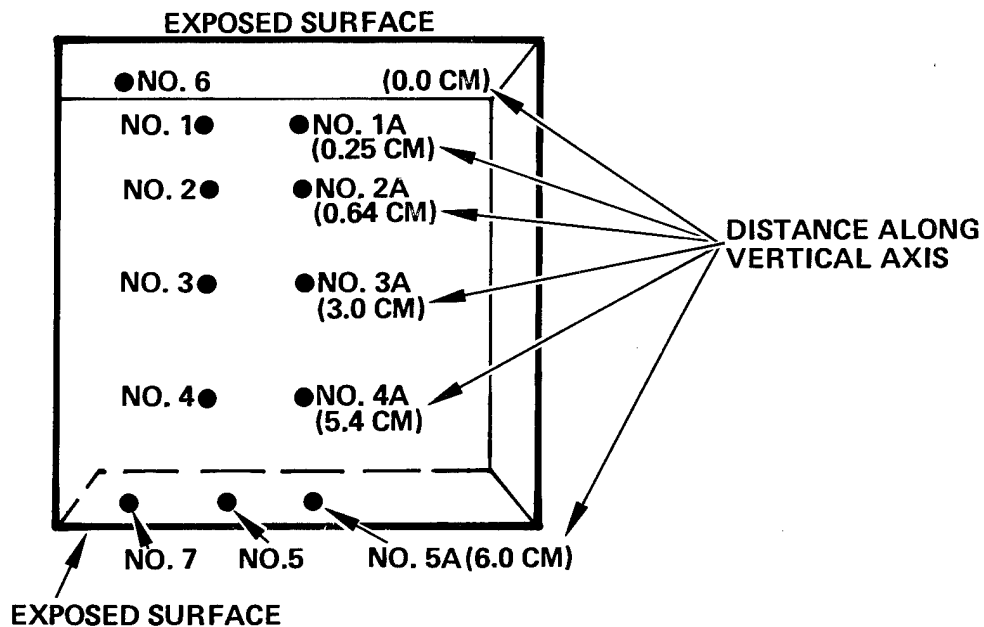


Figure 16. Sample Removal Technique, Method 2

All the samples taken from this cast epoxy specimen showed positive for D_2O . Although semi-quantitation was not yet possible in these samples, the D_2O was easily detected.

The sampling technique was adequate from the standpoint of D_2O retention with handling time. The establishment of sampling depth (micrometer measurement) was crude and limited the D_2O profiling to a coarser measure than was originally considered for this project.

The data gathered from the 5000-hour humidity-exposed specimen strongly indicated that D_2O had migrated along the butyl rubber/epoxy interface. Samples directly in contact with the gasket were not used in later quantitation experiments.

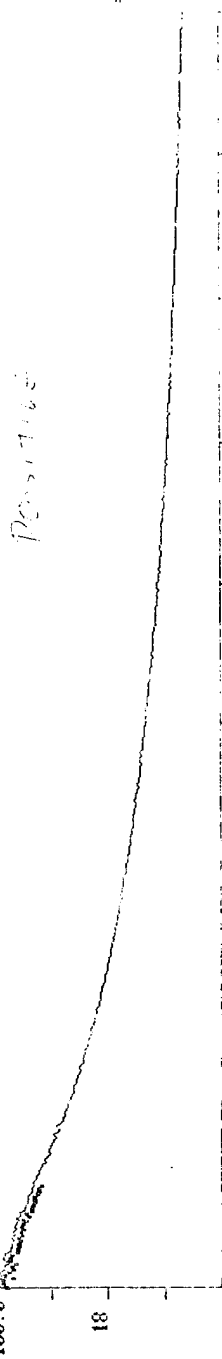
Instrument calibration for D_2O quantitation was accomplished using ground polymer wet with weighable quantities of D_2O and analyzed by the

RIC + MASS CHROMATOGRAMS
 10/18/78 14:49:00
 SAMPLE: DRILLINGS FROM DEFIXTURED SLAB-10/16/78
 RANGE: G 1.500 LABEL: H 0.4.0 QUAN: A 0.1.0 EASE: U 20. 3

DATA: VETTEST6B4 #1
 CALI: C1016 #3

SCANS 51 TO 500

581632.



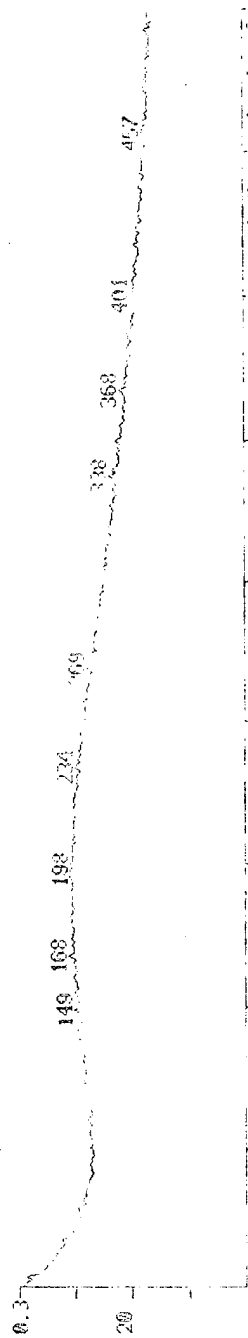
18.005
± 0.500

5344.



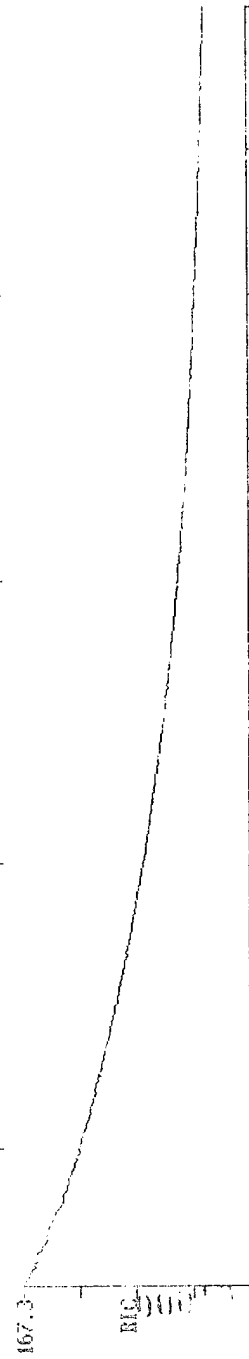
19.005
± 0.500

1840.



20.006
± 0.500

972800.



500 SCAN
16:40 TIME



Figure 17. Reconstructed Mass Chromatograms for a Subsurface Sample Removed by Method 2

developed solids probe mass spectrometric technique. A slight modification to the stepwise sample inletting method was made at this point to improve detection sensitivity. The resultant operating procedure was modified as follows:

- 1) The solid sample probe is inserted into the outer chamber of the mass spec inlet.
- 2) The acquisition is started. At least ten scans of instrument background are taken at sensitivities of 10^{-7} amps/volt and approximately 30 scans of instrument background at 10^{-6} amps/volt. The preamplifier is left at 10^{-6} amps/volt.
- 3) With the filament on and in rapid sequence, the inlet is evacuated, and the source is vented. The inlet valve is opened and the solids probe inserted all the way into the ionizer block. This step takes 30 - 40 seconds to perform.
- 4) Data acquisition is continued until 500 scans are obtained. The important operating parameters for the MS/DS are as follows:
 - MS was scanned from M/e 10 to M/e 225 every two seconds in a continuous cyclic recording.
 - The solids probe was not heated by its own circuitry but was instead warmed by the ionizer block which is at approximately 473°K. The probe warmed to between 413° - 423°K over the duration of the 500 scan run (ca. 17 minutes).
 - Mass spectral data was collected at a preamplifier setting of 10^{-6} amps/volt except for the first 10 scans of background at 10^{-7} amps/volt.

The addition of source venting was found to lower the pressure, thereby reducing the possibility of mass misassignments or data system signal saturation. The above sequence was followed in analyzing the Task III specimens.

Cast polymer was ground to a powder and D₂O was quantitatively added. Standards of dry, 0.1 percent, 0.05 percent, and 1.0 percent were allowed to equilibrate for 48 hours and were subjected to frequent agitation. Analyses were conducted in triplicate on the wet samples and in sextuplicate on the dry. These runs were performed to generate a baseline calibration curve. More data points were acquired for the full calibration necessary to quantitate the D₂O in analyzed specimens.

Table 7 lists the weight percent D₂O in each standard and the respective $\left(\frac{M/e\ 20}{M/e\ 19}\right)$ ratios. Figure 18 is the resultant calibration curve.

Table 7. Mass Ratio Summary

% D ₂ O	Ratio $\frac{M/e\ 20}{M/e\ 19}$
0	0.194 ± 0.01
0.12	0.141 ± 0.001
0.59	0.106 ± 0.009
1.18	0.053 ± 0.003

In subsequent calibration runs, data points were acquired between 0.2 percent to 0.6 percent and 0.6 percent to 1.18 percent.

This completed the method development phase for the Solids Probe Mass Spectrometric technique.

3.6 METHOD SELECTION

The Solids Probe Mass Spectrometry technique was the only evaluated method which met the program's analytical objectives:

- Method Sensitivity — 0.1 percent D₂O on ground polymer can be consistently detected and twice the instrumental noise level produces a lower detection limit of 0.01 percent D₂O.
- Method Specificity — The mass peaks used, M/e 20 (D₂O) and M/e 19 (HDO) are specific for D₂O. D₂O is naturally abundant in H₂O only at 0.015 percent and interferences are therefore, minimal.
- Method Reproducibility — Calibration checks (4 data points) are necessary at the start of each analytical run because of shifts in instrumental sensitivity. However, standards run in replicate agree within ± 10 percent.
- Methods Consistency — It is difficult to correlate the data generated from this direct D₂O profiling with past data and thus prove this technique's acceptability. However, boiled and surface samples from the humidity exposure consistently give D₂O concentrations between 1.5-2.5 percent and this is consistent with past experiments and accepted theory.
- Method Cost — By limiting the number of data points to three per specimen, a reasonable cost, and one consistent with project funds, was achieved.

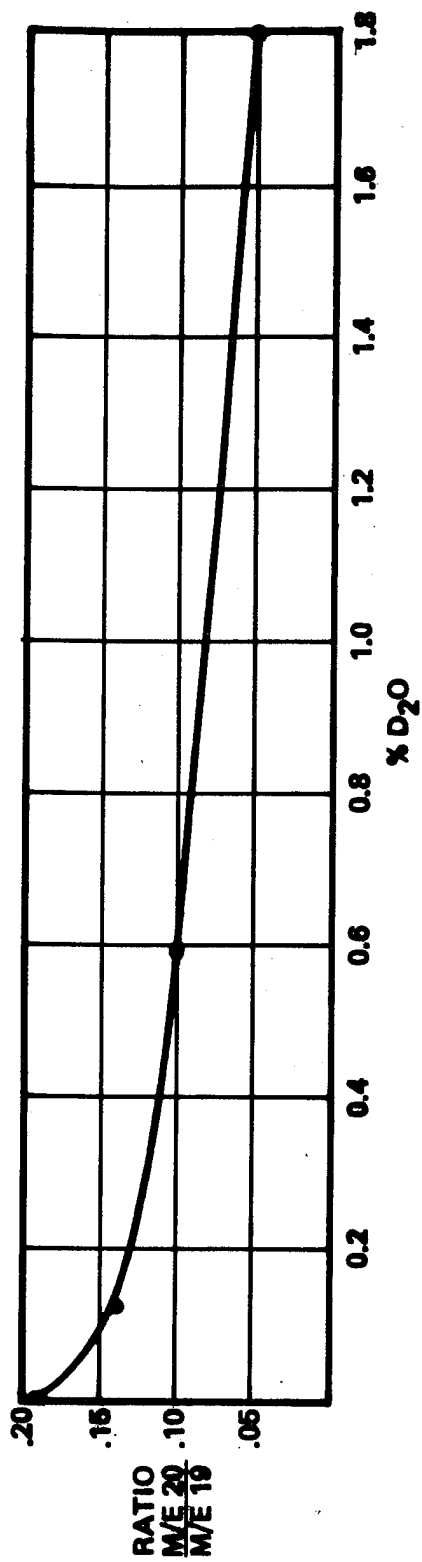


Figure 18. Calibration Curve for Solids Probe
Mass Spectrometric Technique - Run No. 1

The Solids Probe Mass Spectrometry technique does require sample segment removal and therefore, uncertainties regarding sample quality cannot be resolved. Sample handling and exposure to ambient was minimized as much as possible.

4. ANALYSIS OF SPECIMENS AND INTERPRETATION OF RESULTS

Analyses were conducted routinely, by the Solids Probe and Mass spectrometry technique on the exposed fixtured epoxy specimens. The results of this analysis task are presented in this section.

4.1 ROUTINE ANALYTICAL PROCEDURE

The Mass Spectrometry/Data System operating parameters given on page 43 were used throughout this data gathering task. The MS data system was used to calculate the M/e 20 to M/e 19 ratios with the total ion counts at these mass units ratioed at the maximum for M/e 20.

The sampling procedure shown in Figure 16 on page 41 was employed. The specimens initially analyzed had samples removed at the surface, and 0.64 cm (0.25") and 3.81 cm (0.5") from the exposed surface. After these data were reduced, closer increments were run on the next set. These increments were: at surface, 2.5 mm (0.1"), 5.0 mm (0.2"), 7.5 mm (0.3") and 1.27 cm (0.5").

The majority of the exposed specimens analyzed had samples removed: at the surface, 0.64 cm (0.25") and 1.27 cm (0.5").

4.2 ACQUIRED D₂O CONCENTRATION DATA

Table 8 presents the D₂O concentrations determined on the exposed epoxy specimens.

A series of graphs presents the determined D₂O concentration with respect to sampling distances.

Table 8. Determined D₂O Concentrations in Fixtured Exposed Epoxy Specimens

Exposure Conditions	Sample Type	Time (Hours)	% D ₂ O Surface	% D ₂ O	% D ₂ O	% D ₂ O	% D ₂ O	% D ₂ O	% D ₂ O
				2.5mm (0.1")	5.0mm (0.2")	7.5mm (0.3")	0.64cm (0.25")	1.27cm (0.50")	3.81cm (1.50")
Desiccated at RT	Neat Epoxy	all exposure times	0	0	0	0	0	0	0
	Graphite Fiber/ Parallel	all exposure times	0	0	0	0	0	0	0
	Graphite Fiber/ Perpendicular	all exposure times	0	0	0	0	0	0	0
	Glass Fiber/ Parallel	all exposure times	0	0	0	0	0	0	0
	Glass Fiber/ Perpendicular	all exposure times	0	0	0	0	0	0	0
22% RH, 344K(71°C)	Neat Epoxy	1440	2.4	N.D.	N.D.	N.D.	0.2	0	N.D.
	Graphite Fiber/ Parallel	1440	0.04	N.D.	N.D.	N.D.	0.02	0.01	N.D.
	Graphite Fiber/ Perpendicular	1440	0.07	N.D.	N.D.	N.D.	0.29	0.08	N.D.
	Graphite Fiber/ Perpendicular	1440	0.08	N.D.	N.D.	N.D.	0.29	0.08	N.D.
	Glass Fiber/ Parallel	1440	0.10	N.D.	N.D.	N.D.	N.D.	0.06	0.05
	Glass Fiber/ Perpendicular	1440	0.66	N.D.	N.D.	N.D.	N.D.	0.02	0.04
22% RH, 344K(71°C)	Neat Epoxy	3670	1.20	N.D.	N.D.	N.D.	0.75	2.35	N.D.
	Graphite Fiber/ Parallel	3670	0.38	N.D.	N.D.	N.D.	0	0	N.D.
	Graphite Fiber/ Perpendicular	3670	0.53	N.D.	N.D.	N.D.	1.18	1.04	N.D.
	Glass Fiber/ Parallel	3670	1.59	N.D.	N.D.	N.D.	0.35	0	N.D.
	Glass Fiber/ Perpendicular	3670	2.50	N.D.	N.D.	N.D.	0.22	0.47	N.D.
54% RH, RT	Neat Epoxy	1440	1.69	0.50	1.10	0.20	N.D.	1.0	N.D.
	Neat Epoxy	1440	0.57	0.43	0.25	1.15	N.D.	N.D.	N.D.
	Neat Epoxy	1440	0.20	1.20	1.15	0.27	N.D.	0.99	N.D.
	Graphite Fiber/ Parallel	1440	0.74	0.39	0.76	0.46	N.D.	0.24	N.D.
	Graphite Fiber/ Perpendicular	1440	N.D.	1.21	0.25	0.01	N.D.	0.51	N.D.
	Glass Fiber/ Parallel	1440	0.49	1.21	0.78	0	N.D.	0.86	N.D.
	Glass Fiber/ Perpendicular	1440	0.90	1.28	0.43	0.16	N.D.	0.51	N.D.

N.D. Is Not Determined

Table 8. Determined D₂O Concentrations in Fixtured Exposed Epoxy Specimens (Continued)

Exposure Conditions	Sample Type	Time (Hours)	% D ₂ O Surface	% D ₂ O	% D ₂ O	% D ₂ O	% D ₂ O	% D ₂ O	% D ₂ O
				2.5mm (0.1")	5.0mm (0.2")	7.5mm (0.3")	0.64cm (0.25")	1.27cm (0.50")	3.81cm (1.50")
54% RH, RT	Neat Epoxy	3670	2.3	N.D.	N.D.	N.D.	0	0	N.D.
	Graphite Fiber/ Parallel	3670	0.1	N.D.	N.D.	N.D.	1.5	0	N.D.
	Graphite Fiber/ Perpendicular	3670	0	N.D.	N.D.	N.D.	0	0	N.D.
	Glass Fiber/ Parallel	3670	0.7	N.D.	N.D.	N.D.	0.35	0.75	N.D.
	Glass Fiber/ Perpendicular	3670	0.32	N.D.	N.D.	N.D.	>2.5	0.10	N.D.
59% RH, RT	Neat Epoxy	8850	0.75	0.71	1.52	0.07	N.D.	0	N.D.
	Graphite Fiber/ Parallel	8850	0.05	N.D.	N.D.	N.D.	N.D.	0	0.01
	Graphite Fiber/ Perpendicular	8850	0.04	N.D.	N.D.	N.D.	N.D.	0.02	0
	Glass Fiber/ Parallel	8850	0.15	N.D.	N.D.	N.D.	N.D.	0	0
	Glass Fiber/ Perpendicular	8850	1.5	N.D.	N.D.	N.D.	N.D.	0.35	0.2
59% RH, RT	Neat Epoxy	10700	>2.5	N.D.	N.D.	N.D.	0	0.2	N.D.
	Graphite Fiber/ Parallel	10700	0.73	N.D.	N.D.	N.D.	0.1	0	N.D.
	Graphite Fiber/ Perpendicular	10700	1.0	N.D.	N.D.	N.D.	0.5	0	N.D.
	Glass Fiber/ Parallel	10700	0	N.D.	N.D.	N.D.	0	1.1	N.D.
	Glass Fiber/ Perpendicular	10700	2.38	N.D.	N.D.	N.D.	1.38	1.02	N.D.
75% RH, 344K(71°C)	Neat Epoxy	1440	2.2	N.D.	N.D.	N.D.	0.51	0.30	N.D.
	Graphite Fiber/ Parallel	1440	>2.5	N.D.	N.D.	N.D.	0.57	0.73	N.D.
	Graphite Fiber/ Perpendicular	1440	>2.5	N.D.	N.D.	N.D.	1.03	0.88	N.D.
	Glass Fiber/ Parallel	1440	>2.5	N.D.	N.D.	N.D.	0.38	0.96	N.D.
	Glass Fiber/ Perpendicular	1440	>2.5	N.D.	N.D.	N.D.	0.17	0.56	N.D.
75% RH, 344K(71°C)	Neat Epoxy	3670	0	N.D.	N.D.	N.D.	1.0	>2.5	N.D.
	Graphite Fiber/ Parallel	3670	1.37	N.D.	N.D.	N.D.	0	0	N.D.
	Graphite Fiber/ Perpendicular	3670	1.65	N.D.	N.D.	N.D.	0	0	N.D.
	Glass Fiber/ Parallel	3670	2.5	N.D.	N.D.	N.D.	0.95	2.4	N.D.
	Glass Fiber/ Perpendicular	3670	0.92	N.D.	N.D.	N.D.	1.38	1.38	N.D.

N.D. Is Not Determined

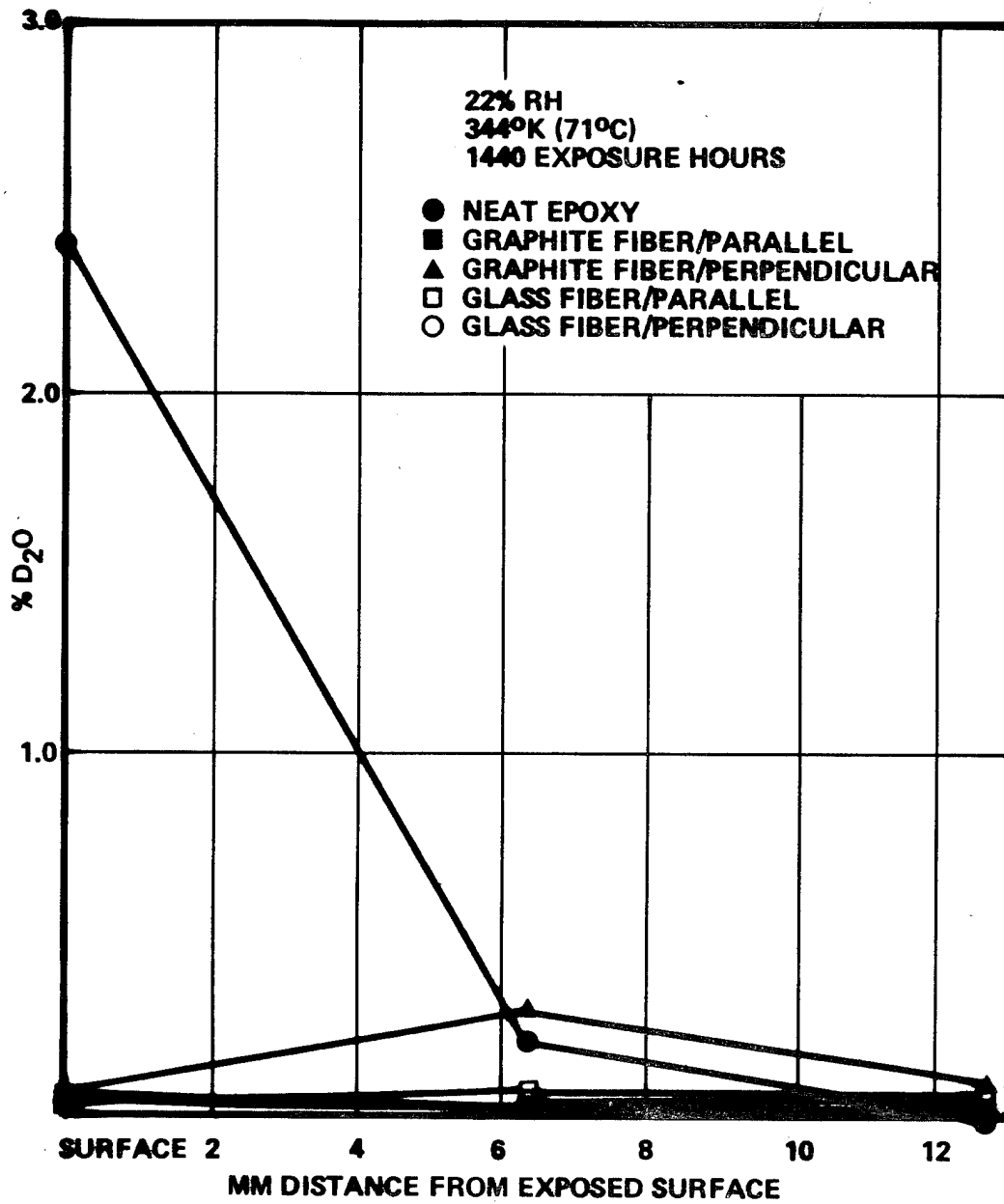


Figure 19. D₂O Concentrations as a Function of Sampling Depth for the Samples at 22% RH, 344°K (71°C), 1440 Exposure Hours

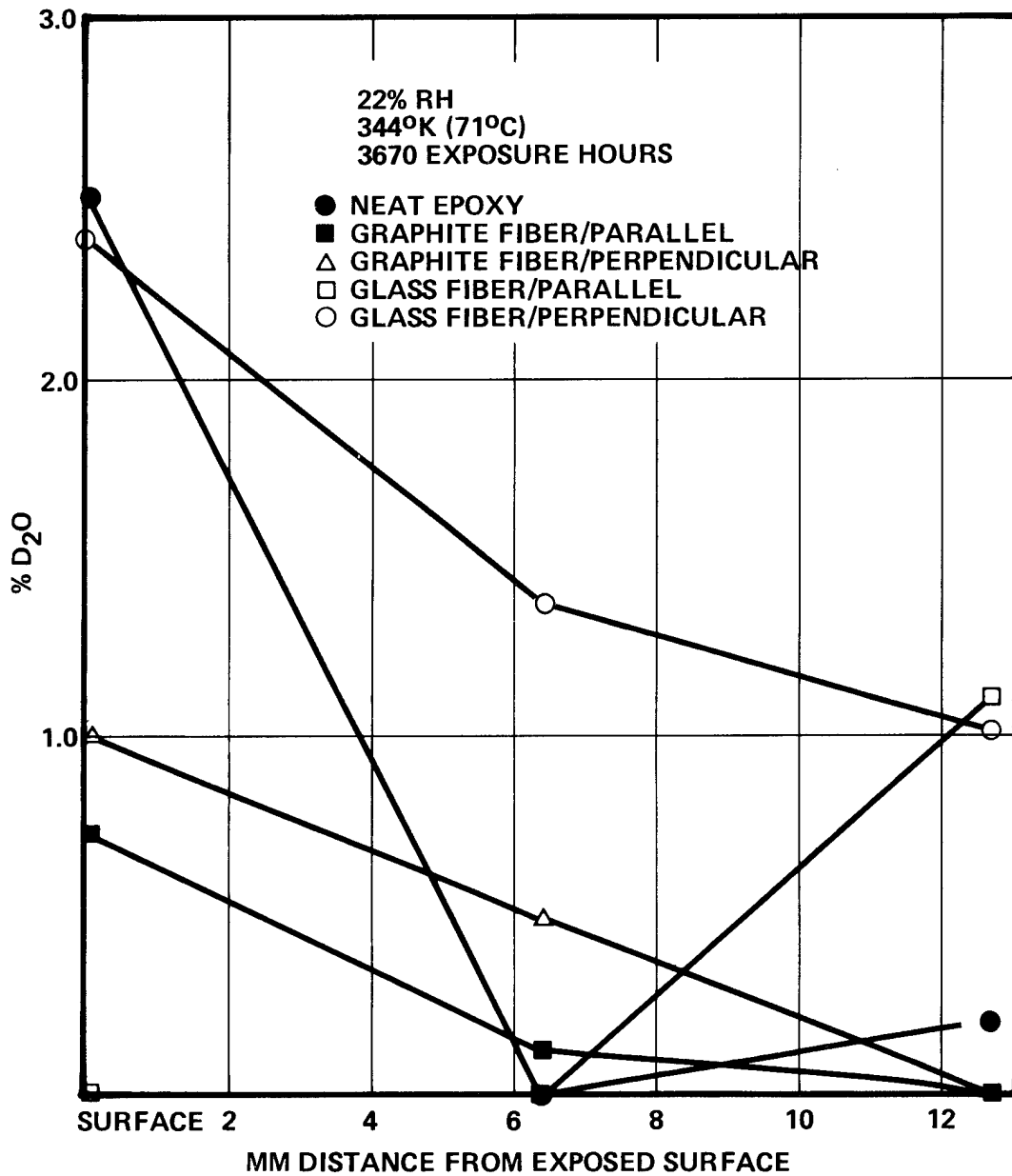


Figure 20. D₂O Concentrations as a Function of Sampling Depth for the Samples at 22% RH, 344°K (71°C), 3670 Exposure Hours

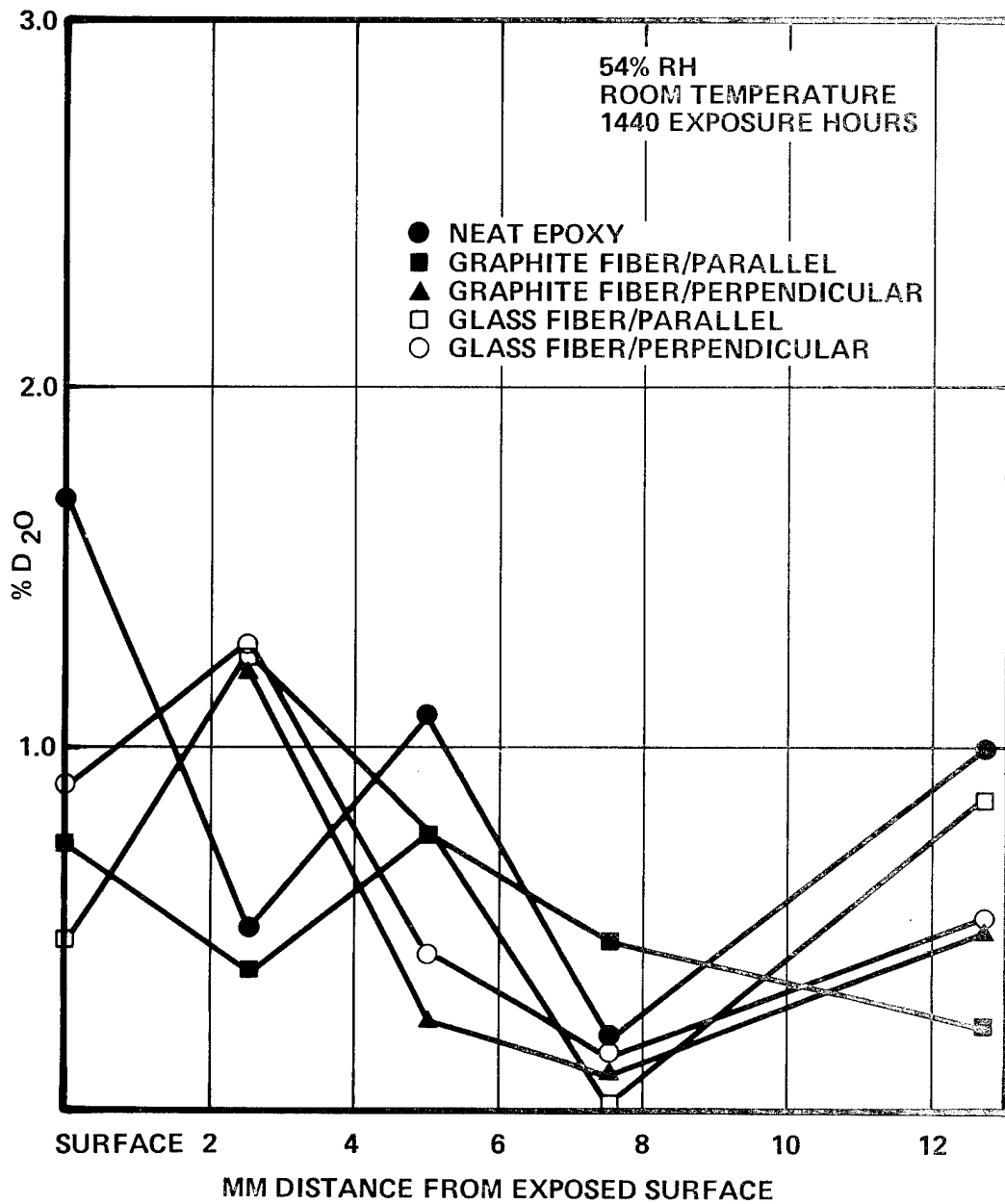


Figure 21. D₂O Concentrations as a Function of Sampling Depth for the Samples at 54% RH, Room Temperature, 1440 Exposure Hours

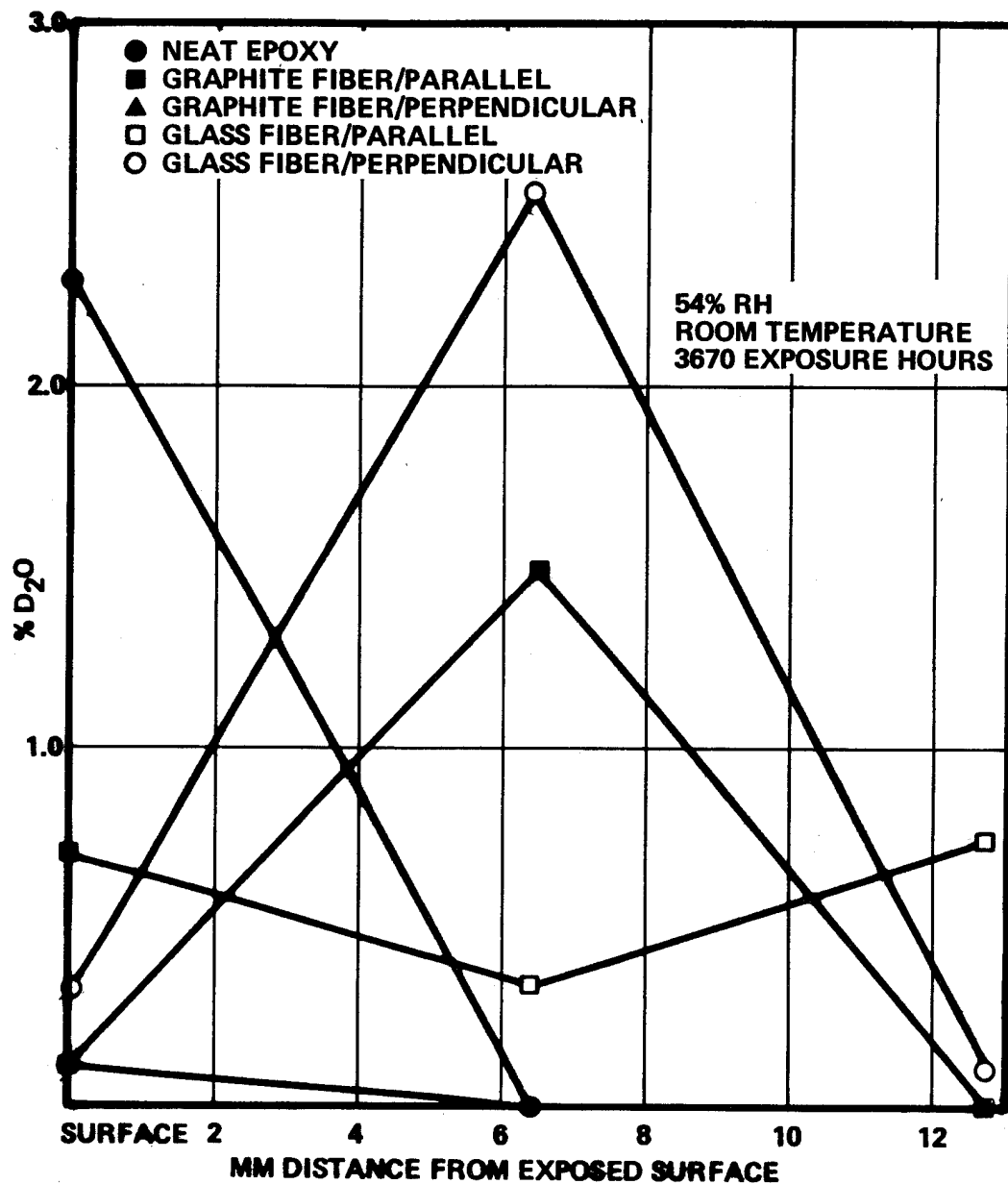


Figure 22. D₂O Concentrations as a Function of Sampling Depth for the Samples at 54%, Room Temperature, 3670 Exposure Hours

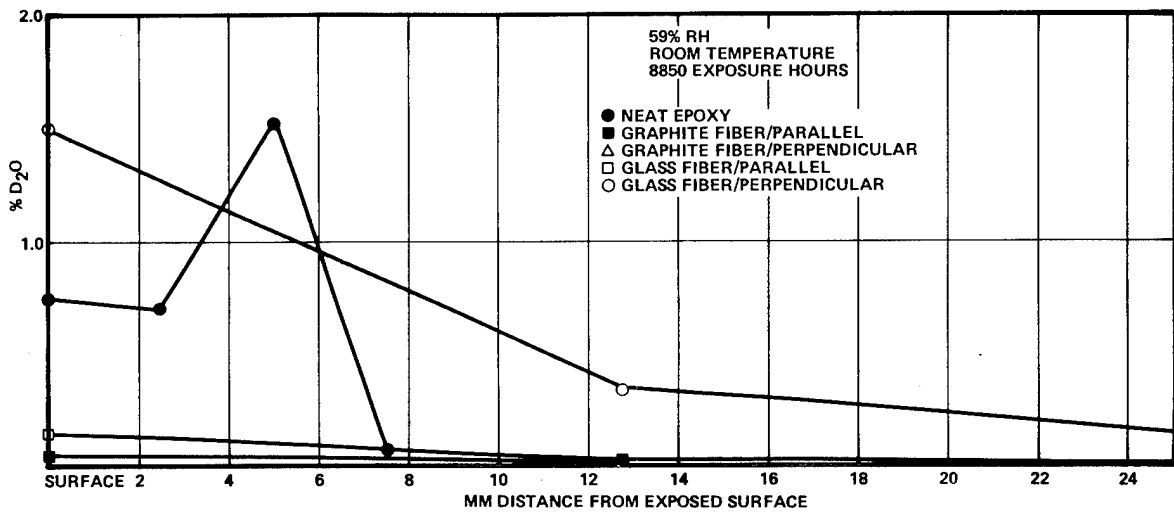


Figure 23. D₂O Concentrations as a Function of Sampling Depth for the Sample at 59% RH, Room Temperature, 8850 Exposure Hours

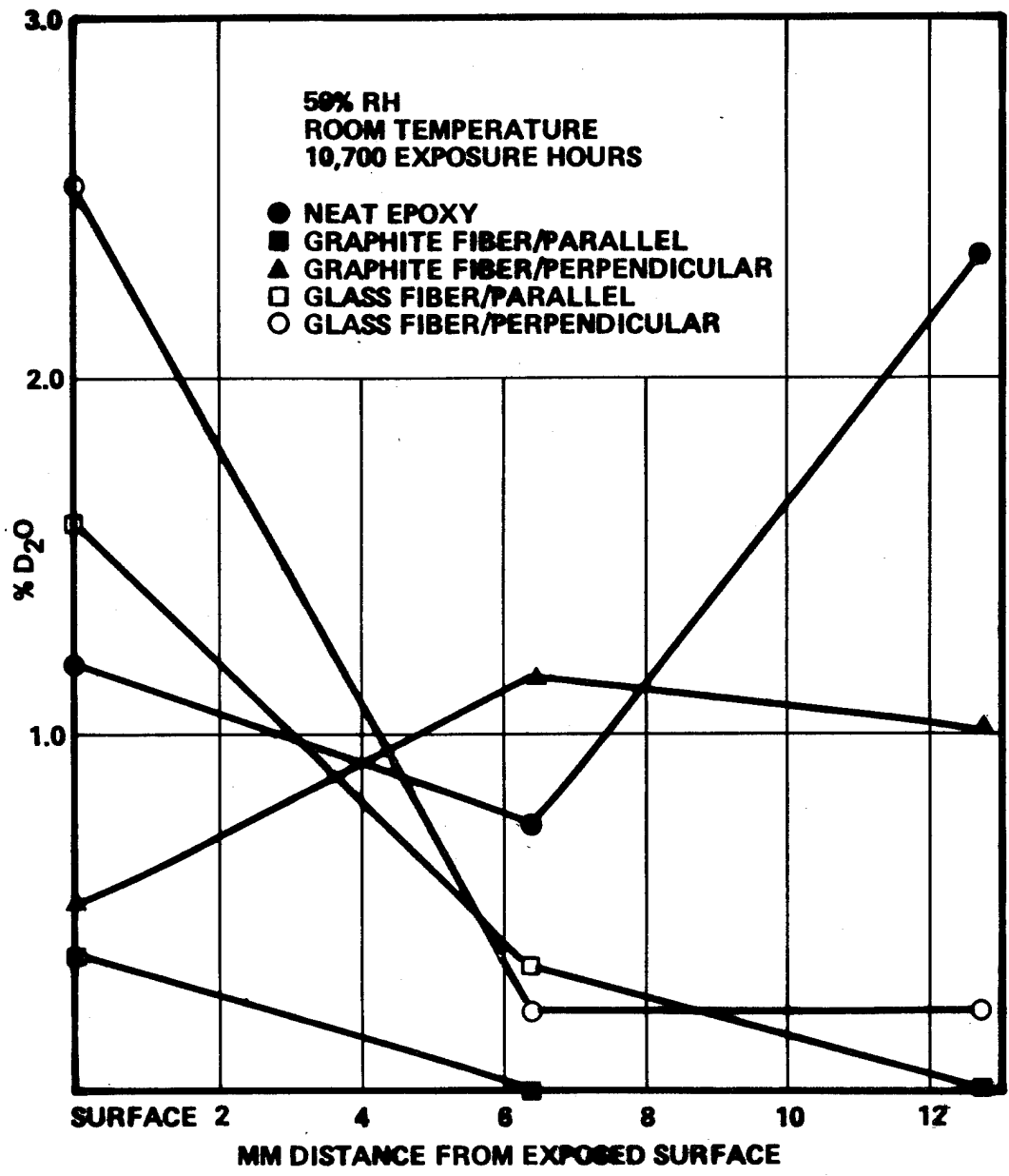


Figure 24. D₂O Concentrations as a Function of Sampling Depth for the Samples at 59% RH, Room Temperature, 10700 Exposure Hours

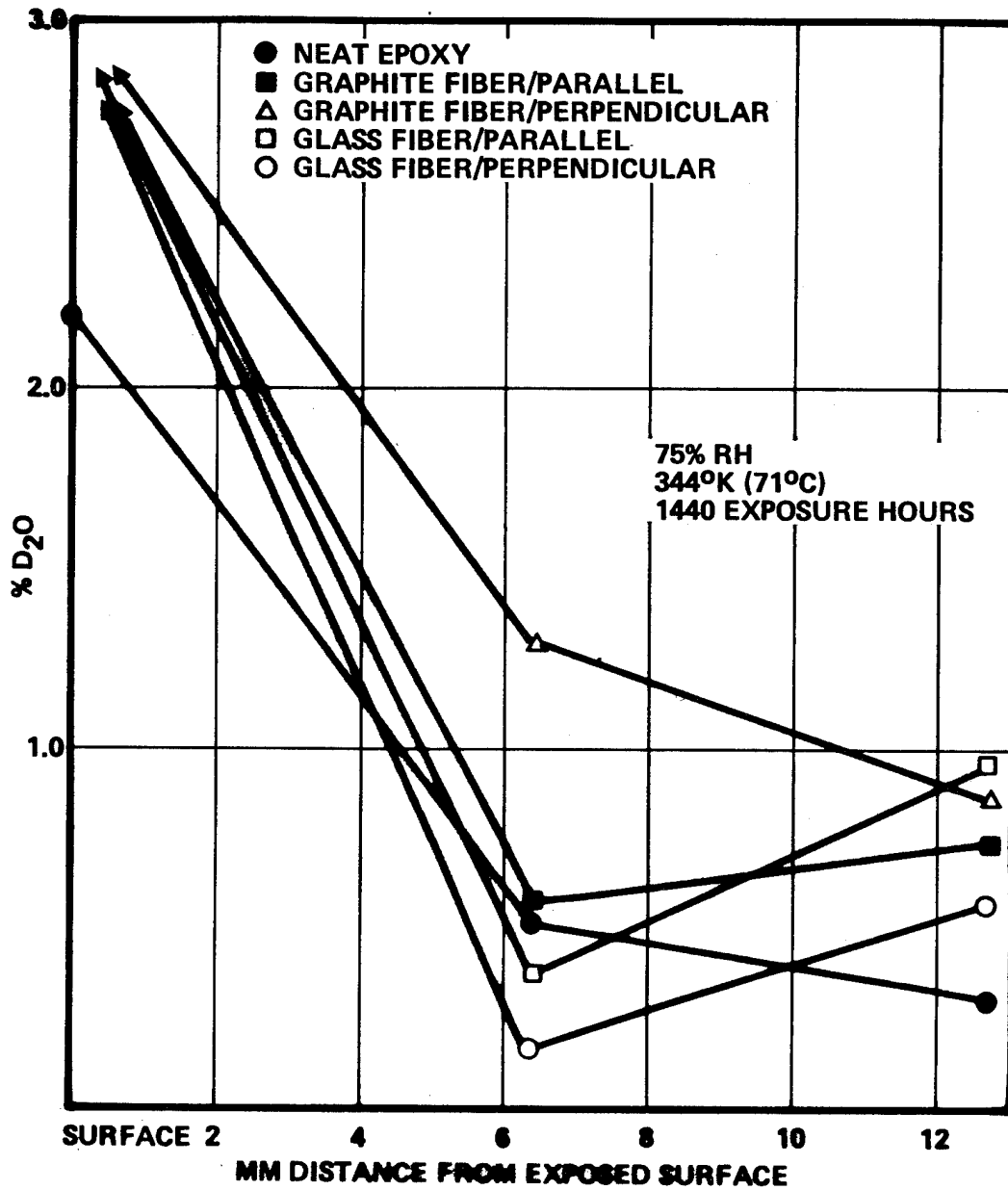


Figure 25. D₂O Concentrations as a Function of Sampling Depth for the Samples at 75% RH, 344°K (71°C), 1440 Exposure Hours

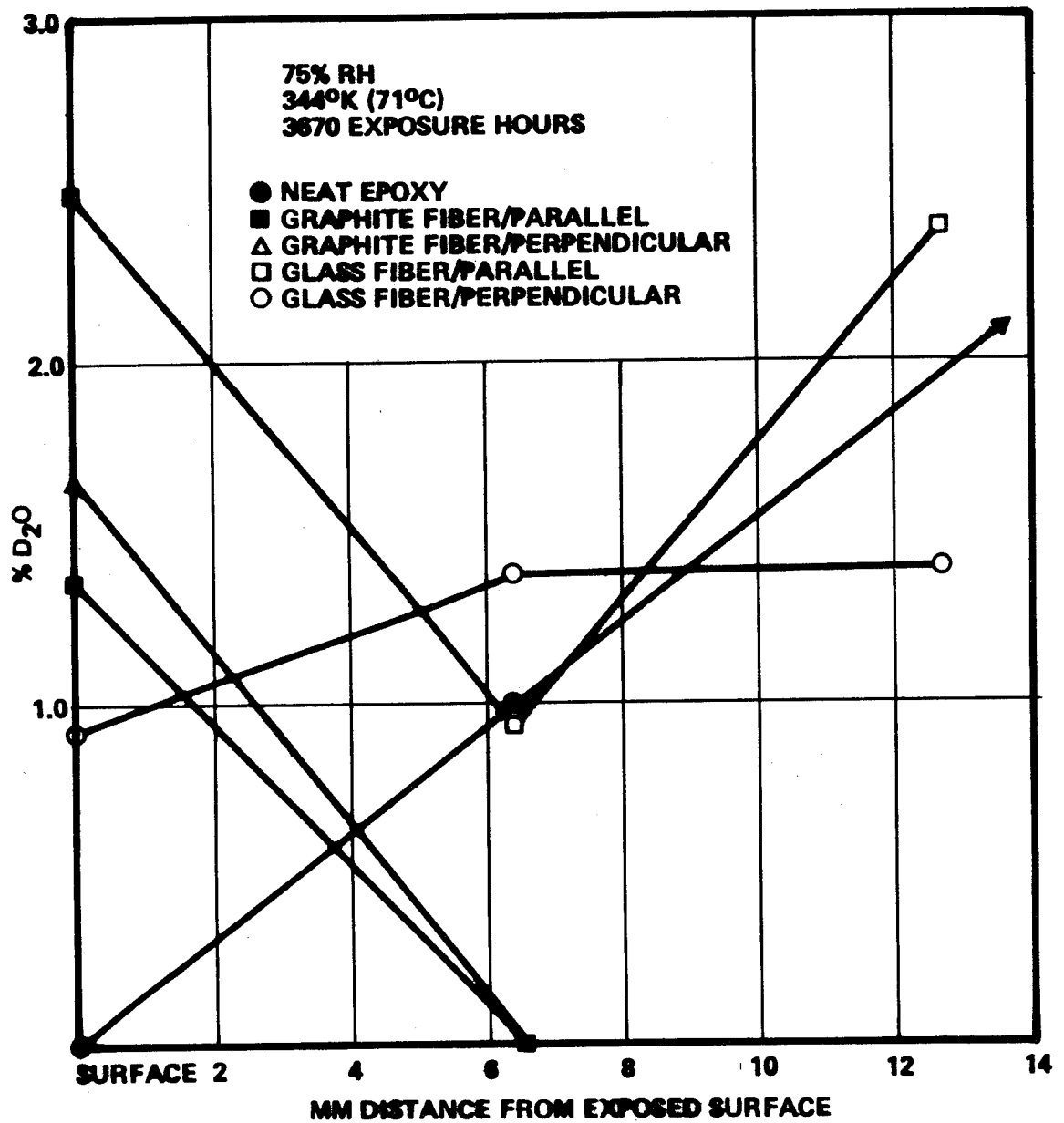


Figure 26. D₂O Concentrations as a Function of Sampling Depth for the Samples at 75% RH, 344°K (71°C), 3670 Exposure Hours

4.3 DISCUSSION OF D₂O DATA QUALITY

There are many uncertainties associated with this data set:

- The exposure technique did not maintain the desired humidity environment. Humidity conditions at the program start were different than those existing during the analytical phase.
- The fixturing technique appeared to be adequate. However, some D₂O did migrate along the fixtured interface. This adds to data uncertainty especially when D₂O concentrations determined at interior sample locations are higher than exposed surface concentrations.
- Sample segmentation can have a highly indeterminate effect on D₂O concentrations. The technique exposes a large surface area of the removed material to ambient conditions. The analyzed samples are not uniform in resin/fiber content. This nonuniformity may explain some of the observed data scatter.
- The solids probe mass spectrometric technique relies on the thermal desorption of D₂O. Chemically bound D₂O may not be released.
- The solids probe mass spectrometric technique uses a very small sample aliquot. If the D₂O migration is random along the migration axis e.g., penetrating at different distances, then the technique cannot efficiently map the D₂O front.
- The calibration standards and standards used to check the instrument during run time are prepared by wetting ground epoxy with D₂O. A method to prepare standards and then segment them was not achievable. Therefore, the standards used are not identical to the sample matrix.

5. CONCLUSIONS

The solids probe mass spectrometry technique for moisture, D_2O , concentration profiling in polymers and composites is a feasible method. The implementation of this technique in the routine evaluation of structural components is possible. A structural component can be exposed to the expected service moisture environment and sample plugs removed from non-critical areas, analyzed, and the structural's component susceptibility to moisture evaluated.

6. RECOMMENDATIONS FOR FUTURE STUDIES

The shortcomings identified to exist with the solids probe mass spectrometer technique as discussed in Section 4 can be eliminated or minimized in future efforts. The key areas requiring technique optimization are as follows:

- More suitable, hermetic enclosures should be employed for humidity chambers.
- Exposure of thick specimens without fixturing should be performed.
- Calibration standards should be made of sample cubes D_2O exposed and gravimetrically certified before analysis.

In addition, experimental investigation of the Fourier Transform Infrared (FTIR) technique on D_2O exposed specimens is deemed worthy of future work.

APPENDIX A

COMPOSITE CHARACTERIZATION

A.1 Graphite Composite Resin Content

The resin was digested from the cured sampled by pouring acid (concentrated H_2SO_4) onto the sample in a glass beaker and then heating the acid until it turned black. At this point, 30% hydrogen peroxide solution was added dropwise to the acid until it turned clear again. The acid was reheated for a minimum of one hour. During this period, further drops of hydrogen peroxide solution were added to clear the acid whenever the acid turned black. Upon completion of this cycle, the acid was cooled to room temperature and an additional 2 ml of hydrogen peroxide solution was added. The solution was heated again until white fumes appeared after which it was cooled to room temperature. The acid was decanted from the filaments using a fritted glass filter, washed first in distilled water and then in acetone, after which the filaments were dried for 15 minutes in a 450°K (350°F) air circulating oven. Resin solids contents were calculated:

$$W_r = \frac{(W_1 - W_2)}{W_1} \times 100$$

Where:

W_r = Weight Content of Resin Solids, % w/w

W_1 = Weight of Cured Composite Sample

W_2 = Weigh of Filaments after Acid Digestion of the Resin Matrix

A.2 S-Glass Composite Resin Content

Resin was ignited from the cured sample by heating it in a crucible at 800°K for 16 hours. Resin solids contents were calculated:

$$W_r = \frac{(W_1 - W_2)}{W_1} \times 100$$

Where:

W_r = Weight content of Resin solids, % w/w

W_1 = Weight of cured composite sample

W_2 = Weight of Filaments after Ignition

A.3 Density of Composites

Specific gravity of composites was determined by weighing specimen in air and in water. Specific gravity was calculated by the formula:

$$\text{Specific Gravity} = \frac{W_A}{W_A - W_W} \times 100$$

Where:

W_A = Weight Sample in Air

W_W = Weight Sample in Water

A.4 Composite Fiber Volume

Fiber volume percent of the composites was calculated by the formula:

$$V_f = 100 (1-K) \frac{D_c}{D_f}$$

Where:

V_f = Volume Percent Fiber, %

D_C = Measured Density of Composite, g/cm³

D_f = Density of Fiber, g/cm³ (S glass = 2.49, AS graphite = 1.76)

K = Weight Fraction, Resin

A.5 Composite Void Content

Void contents of the composites were calculated using the formula:

$$V_v = 100 - D_C \left[\frac{W_r}{D_r} + \frac{W_f}{D_f} \right]$$

Where:

V_v = Volume of Voids, % v/v

D_C = Measured Density of Composite, g/cm³

D_r = Density of Resin, g/cm³ (3501-5 = 1.28, PMR 15 = 1.31)

D_f = Density of Fiber, g/cm³

W_r = Weight Content of Resin, %

W_f = Weight Content of Fiber, %

A.6 Shear Strength of Composites

The cured composites were machined into short beam shear specimens 0.63 cm wide x 6 times the specimen depth in length and tested in flexure loading point using a 4:1 span to depth ratio. Loading rate was 1.3 mm/minute.

Shear strengths were calculated using the simple formula:

$$S_u = \frac{0.75V}{tb}$$

Where:

S_u = Ultimate Shear Strength, MN/m²

V = Load at Failure, N

t = Specimen Thickness, mm

b = Specimen Width, mm

APPENDIX B
COMPUTER PREPARED ION CHROMATOGRAMS
FOR INITIAL SOLIDS PROBE MASS
SPECTROMETRY EXPERIMENTS

RIC + MASS CHROMATOGRAMS
09/14/78 11:02:00
SAMPLE: DRY POLYMER
RANGE: G 1.500 LABEL: N 0.4.0 QUAN: A 0.1.0 BASE: U 20. 3

DATA: DRYSAMPLE3 #1
CALL: C0914A #3

SCANS 1 TO 500

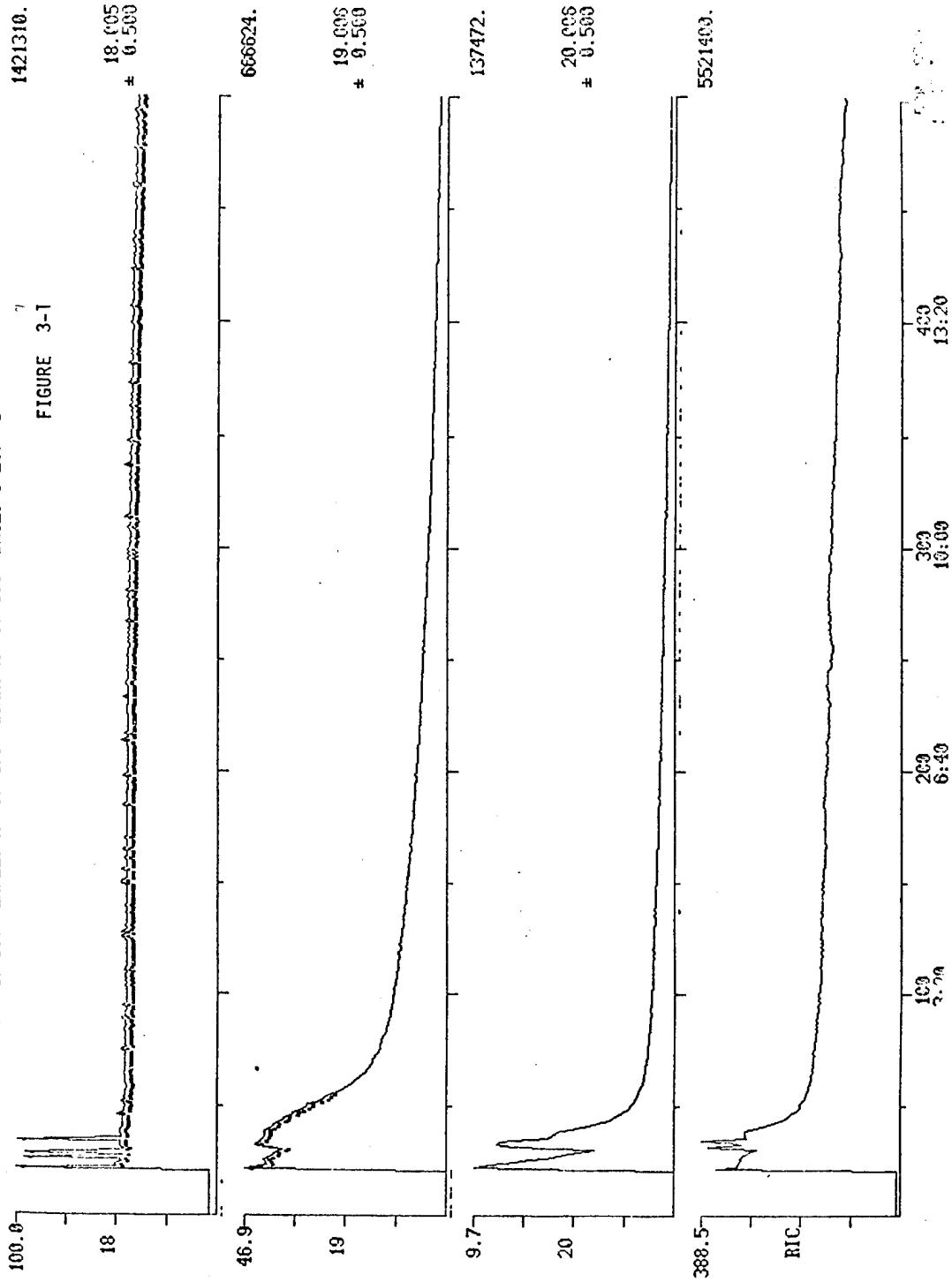
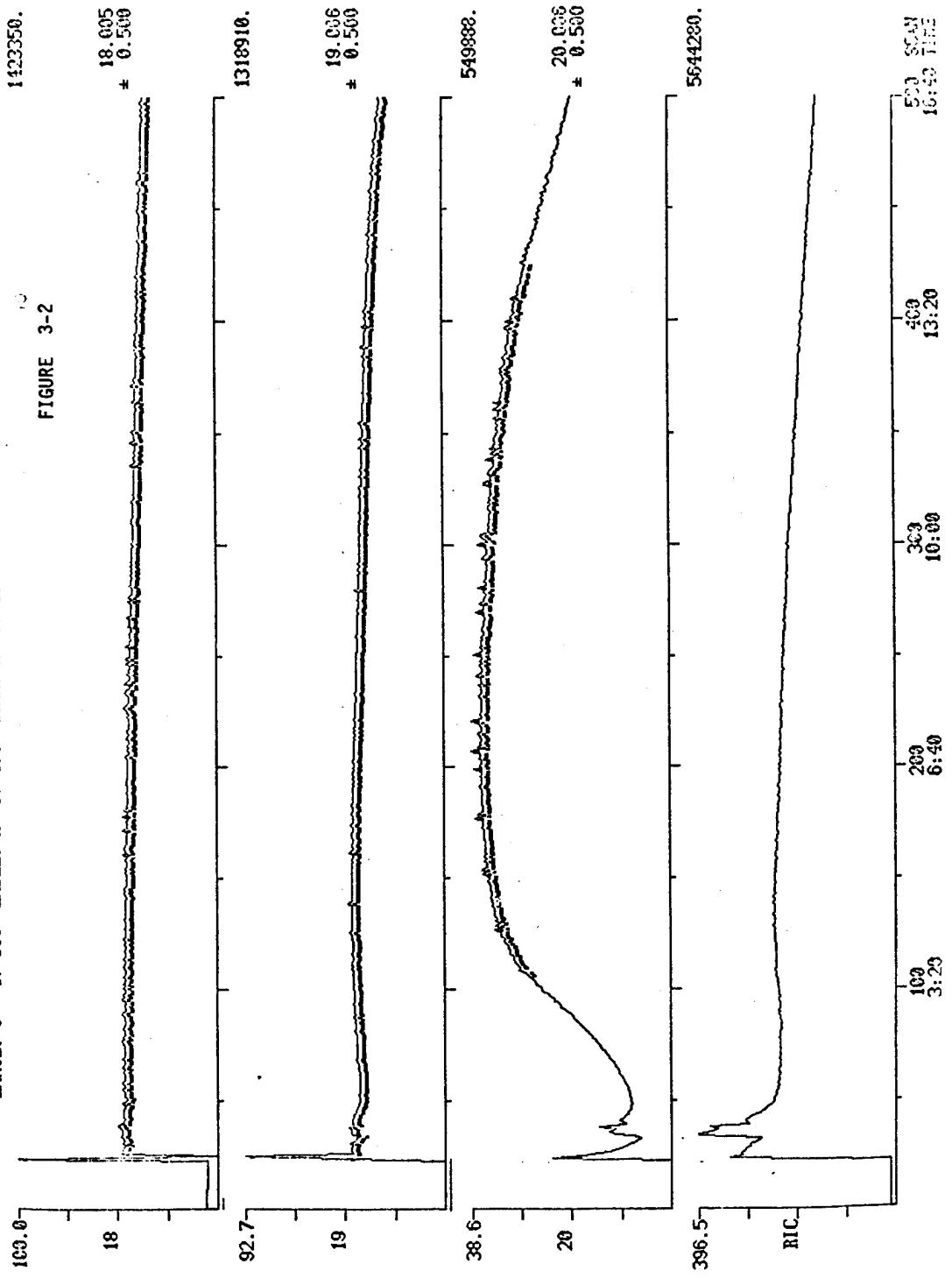


FIGURE 3-1

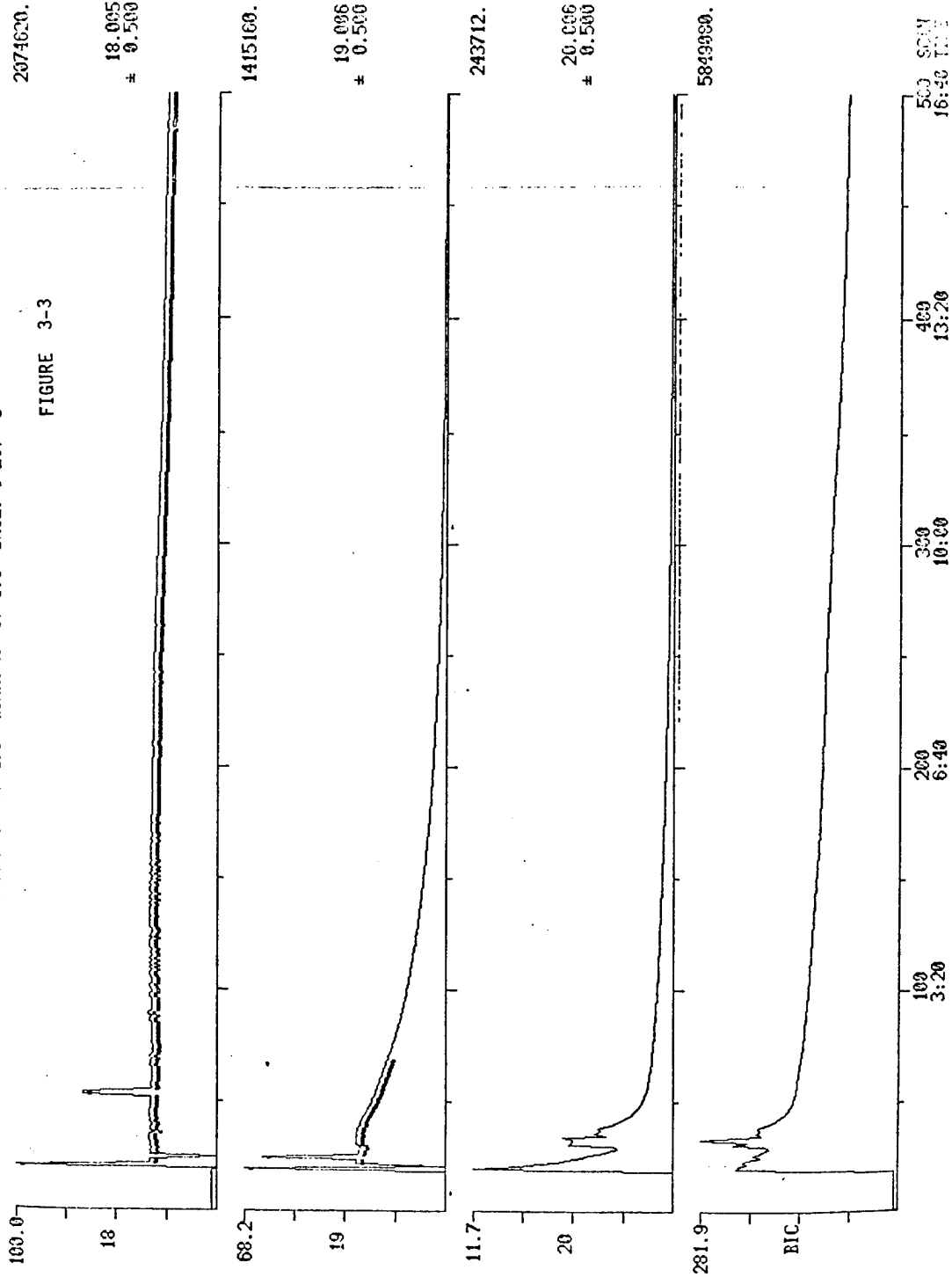
RIC + MASS CHROMATOGRAMS
 09/14/78 11:39:00
 SAMPLE: SOAKED IN D2O
 RANGE: G 1. 500 LABEL: N 0. 4. 0 QUAN: A 0. 1. 0 BASE: U 20. 3
 DATA: UETSAMPLE3 #1
 CALL: C0914A #3
 SCANS 1 TO 500
 1423350.



RIC + MASS CHROMATOGRAMS
09/14/78 13:23:00
SAMPLE: DRY POLYMER
RANGE: C 1.500 LABEL: N 0.4.0 QUAN: A 0.1.0 BASE: U 20. 3

DATA: DRYSAMPLE4 #1
CALL: C0914A 33

SCANS 1 TO 500

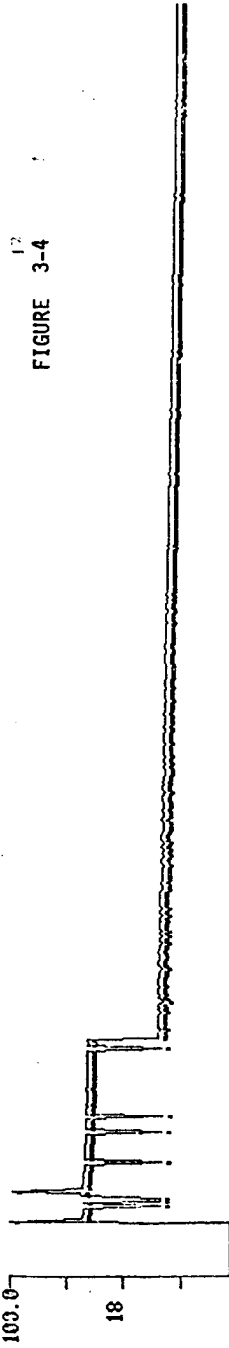


RIC + MASS CHROMATOGRAMS
09/14/78 14:01:03
SAMPLE: SOAKED IN D2O
RANGE: C 1. 500 LABEL: N 0. 4. 0 QUAN: A 0. 1. 0 BASE: U 20. 3

DATA: UETSAMPLE4 #1
CALI: C0914A #3

SCANS 1 TO 500

2109430.



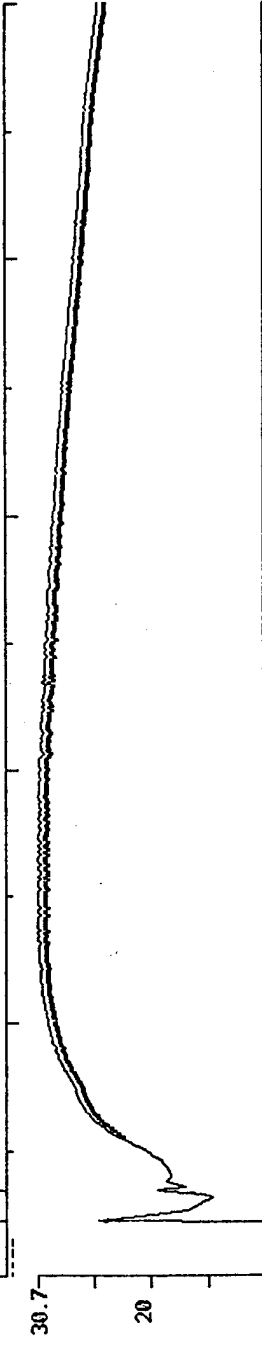
18.005
± 0.500

657408.



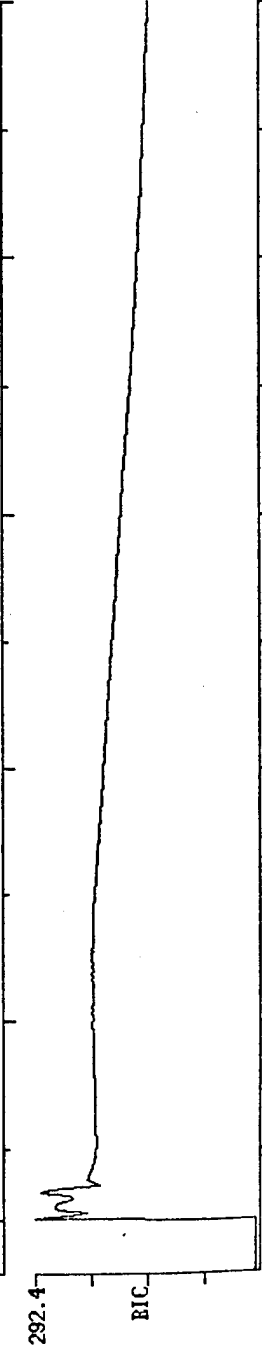
19.006
± 0.500

648192.



20.006
± 0.500

6168570.



100 3:20
200 6:40
300 10:00
400 13:20
500 16:40

RIC + MASS CHROMATOGRAMS
09/14/78 14:33:00
SAMPLE: DRY POLYMER
BARGE: C 1.500 LABEL: N 0.4.0 QUAN: A 0.1.0 BASE: U 20. 3

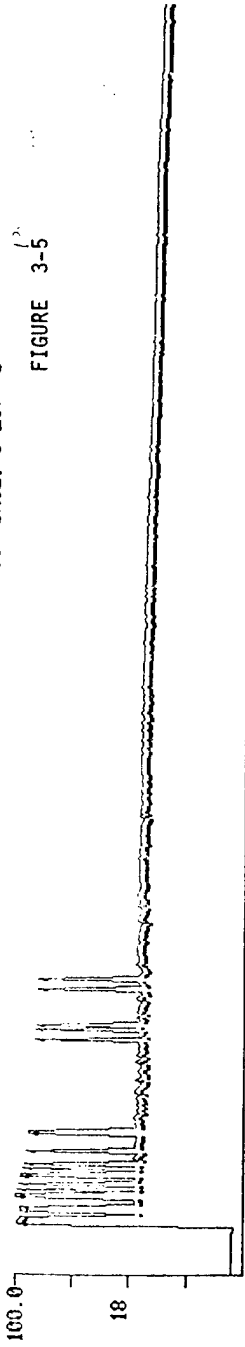
SCANS 1 TO 500

DATA: DRYSAMPLE5 #1
CALI: C6914A #3

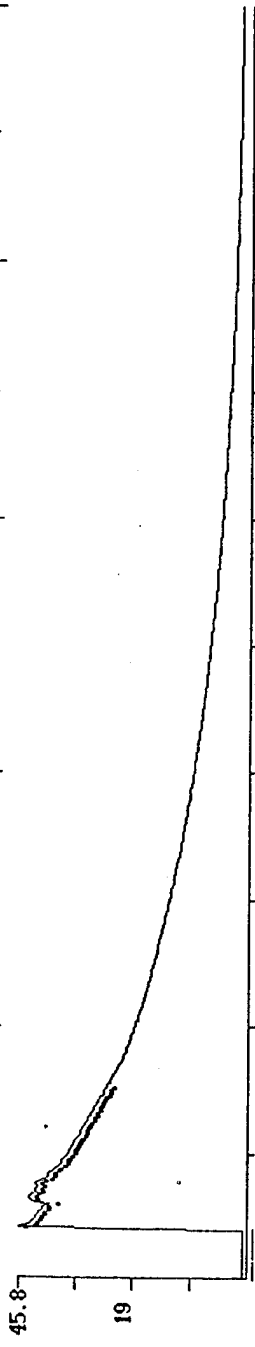
1464310.

FIGURE 3-5

18.005
± 0.500

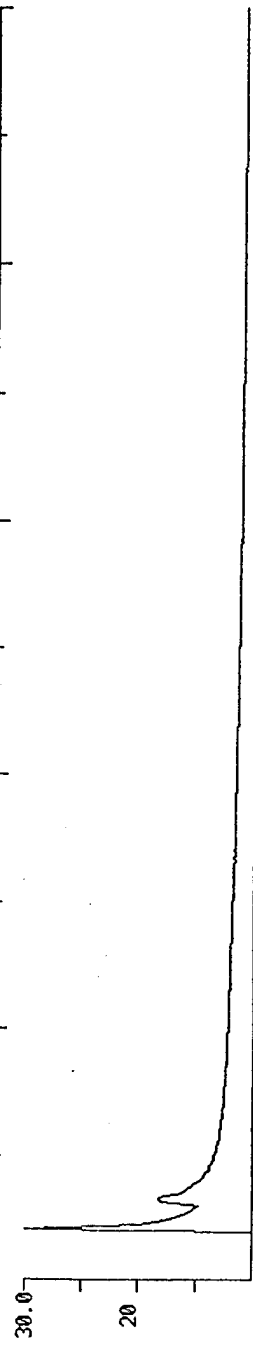


670720.



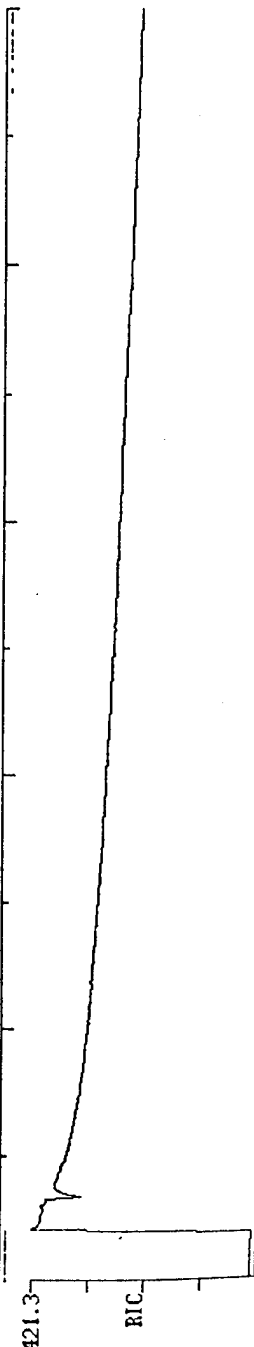
19.036
± 0.500

439296.



20.006
± 0.500

6168570.



500 SCAN
16:49 TIME

400
13:20

300
10:00

200
6:40

100
3:20

RIC + MASS CHROMATOGRAMS
 09/14/78 15:10:00
 SAMPLE: SOAKED IN D2O
 RANGE: G 1. 500 LABEL: N 0. 4.0 QUAN: A 0. 1.C. BASE: U 20. 3

SCANS 1 TO 500

DATA: UETSAMPLES #1

CALI: C0914A #3

1478650.

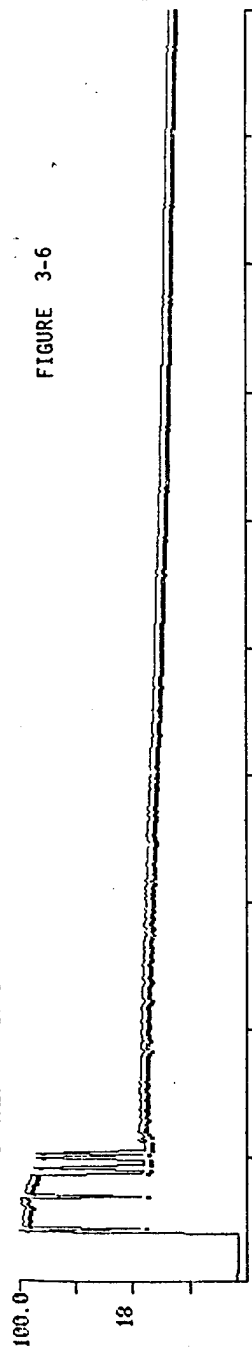
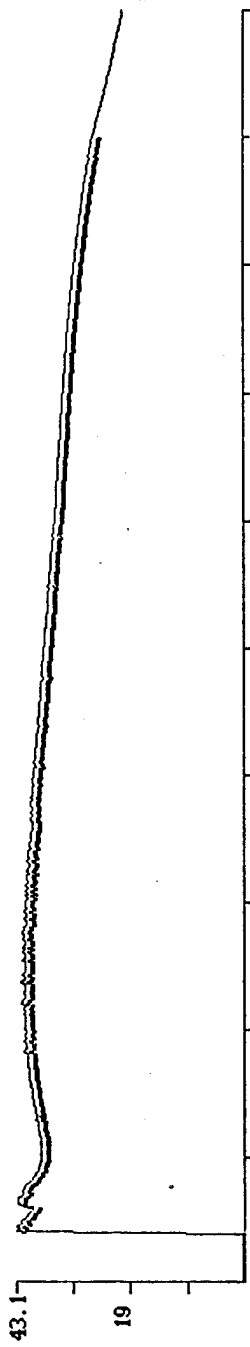
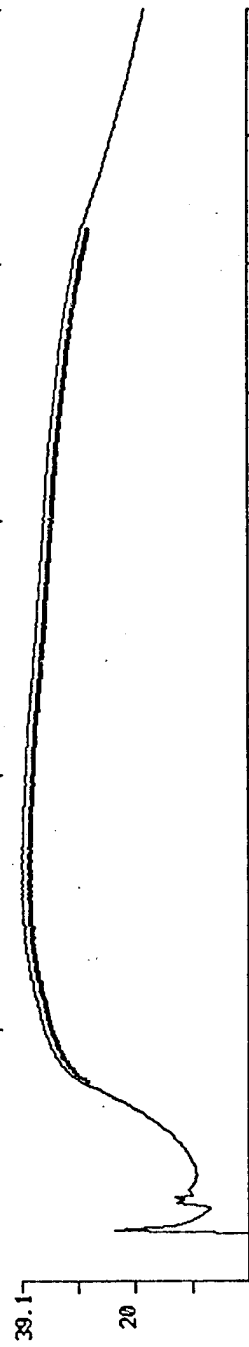


FIGURE 3-6

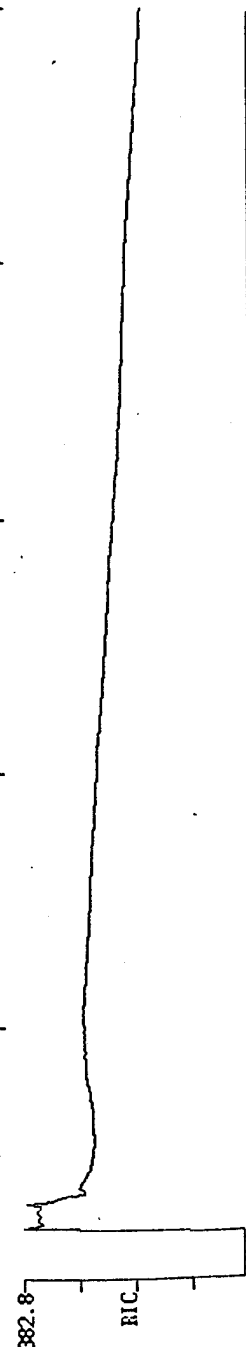
636928.



577536.



5660670.



100 3:20
 200 6:40
 300 10:00
 400 13:20
 500 16:40

RIC + MASS CHROMATOGRAMS
09/14/78 15:58:00
SAMPLE: DRY POLYMER
RANGE: C 1.500 LABEL: N 0.4.0 QUAN: A 0.1.0 BASE: U 20. 3

DATA: DRYSAMPLE6 #1
CALI: C0914A #3

SCANS 1 TO 500

1427450.

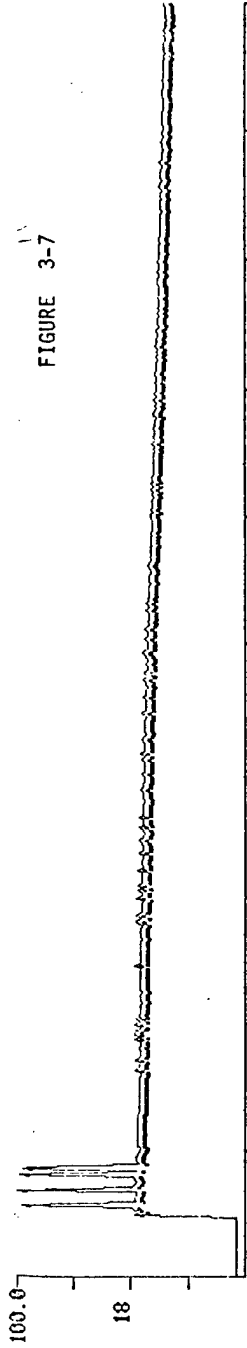
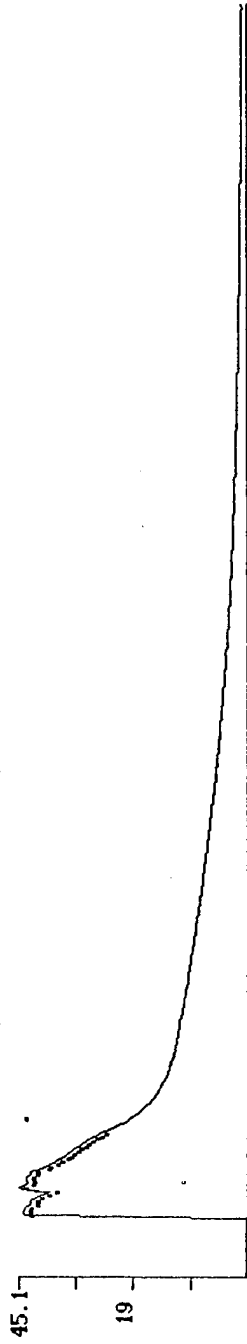
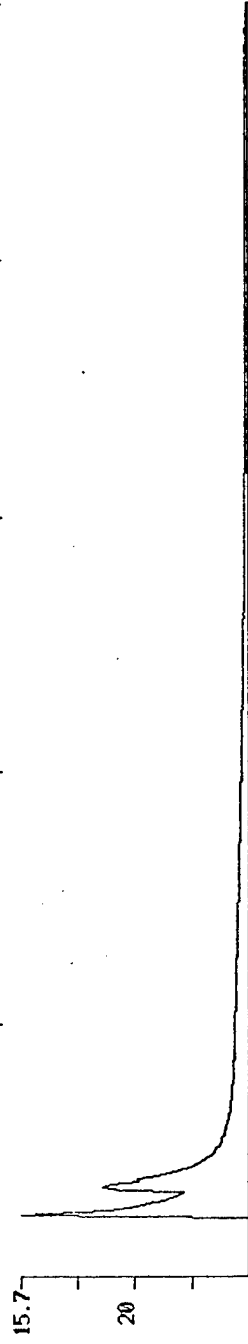


FIGURE 3-7

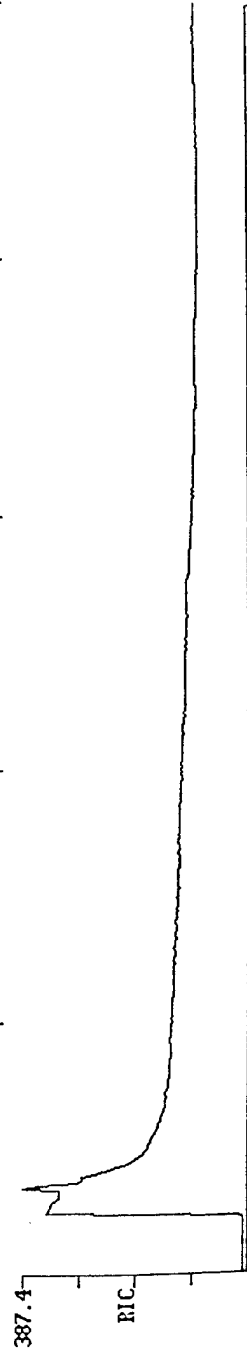
644096.



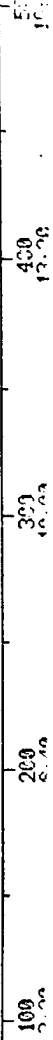
224003.



5529590.



553.000
± 0.500



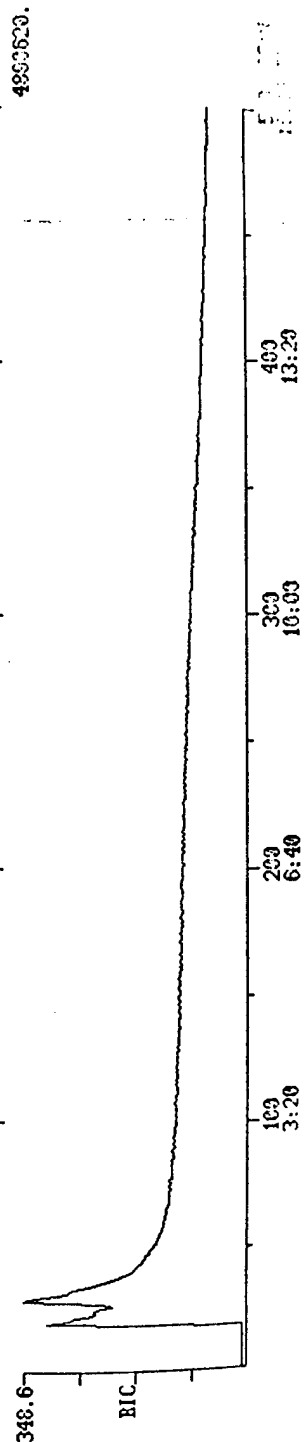
RIC + MASS CHROMATOGRAMS
09/15/78 9:08:00
SAMPLE: DRY POLYMER
RANGE: C 1.500

DATA: BRYSAMPLEIA #1
CALL: C0915 #3
QUAN: A 0.1.0 BASE: U 20. 3

SCANS 1 TO 500



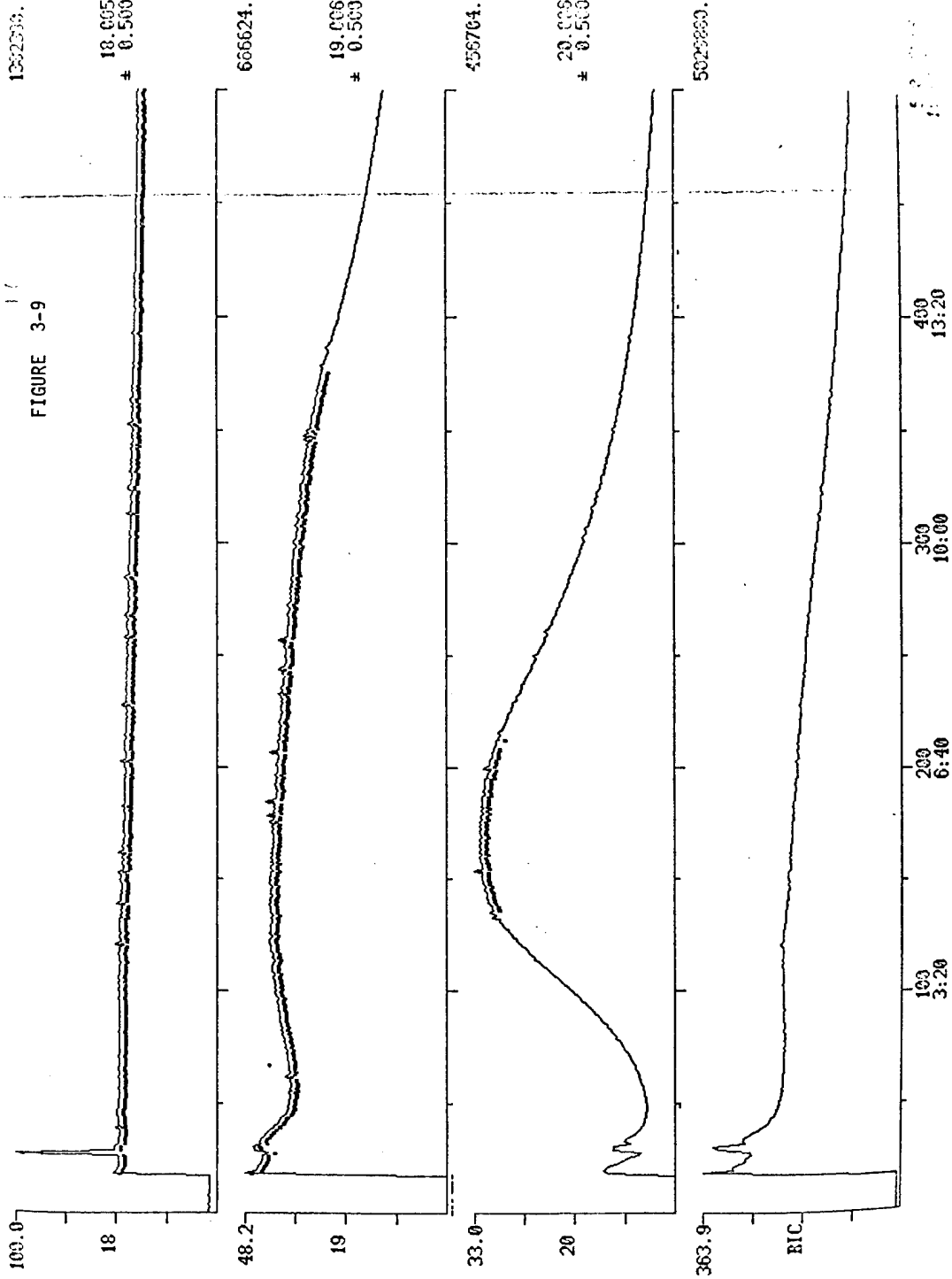
FIGURE 3-8



RIC + MASS CHROMATOGRAMS
09/15/78 9:47:00
SAMPLE: SOAKED IN D2O OVER NIGHT
RANGE: G 1.500 LABEL: N 0.4.0 QUAN: A 0.1.0 BASE: U 20. 3

DATA: UETSAMPLE1A #1
CALL: C0915 #3

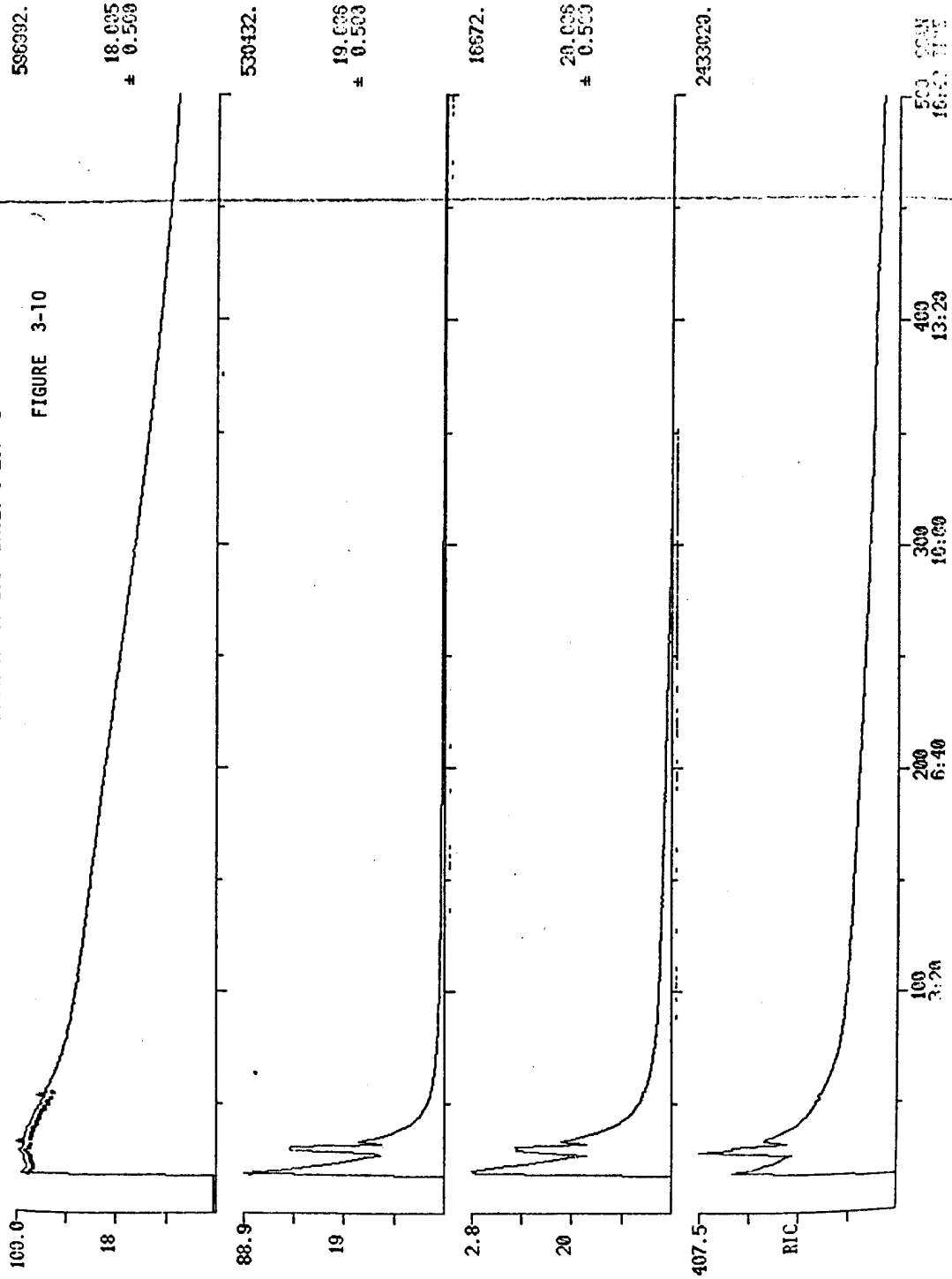
SCANS 1 TO 500



RIC + MASS CHROMATOGRAMS
09/15/78 10:24:00
SAMPLE: DRY POLYMER
EARGE: C 1. 500 LABEL: N 0. 4. 0 QUAN: A 0. 1. 0 BASE: U 20. 3

DATA: DRYSAMPLEZA #1
CALL: C0915 #3

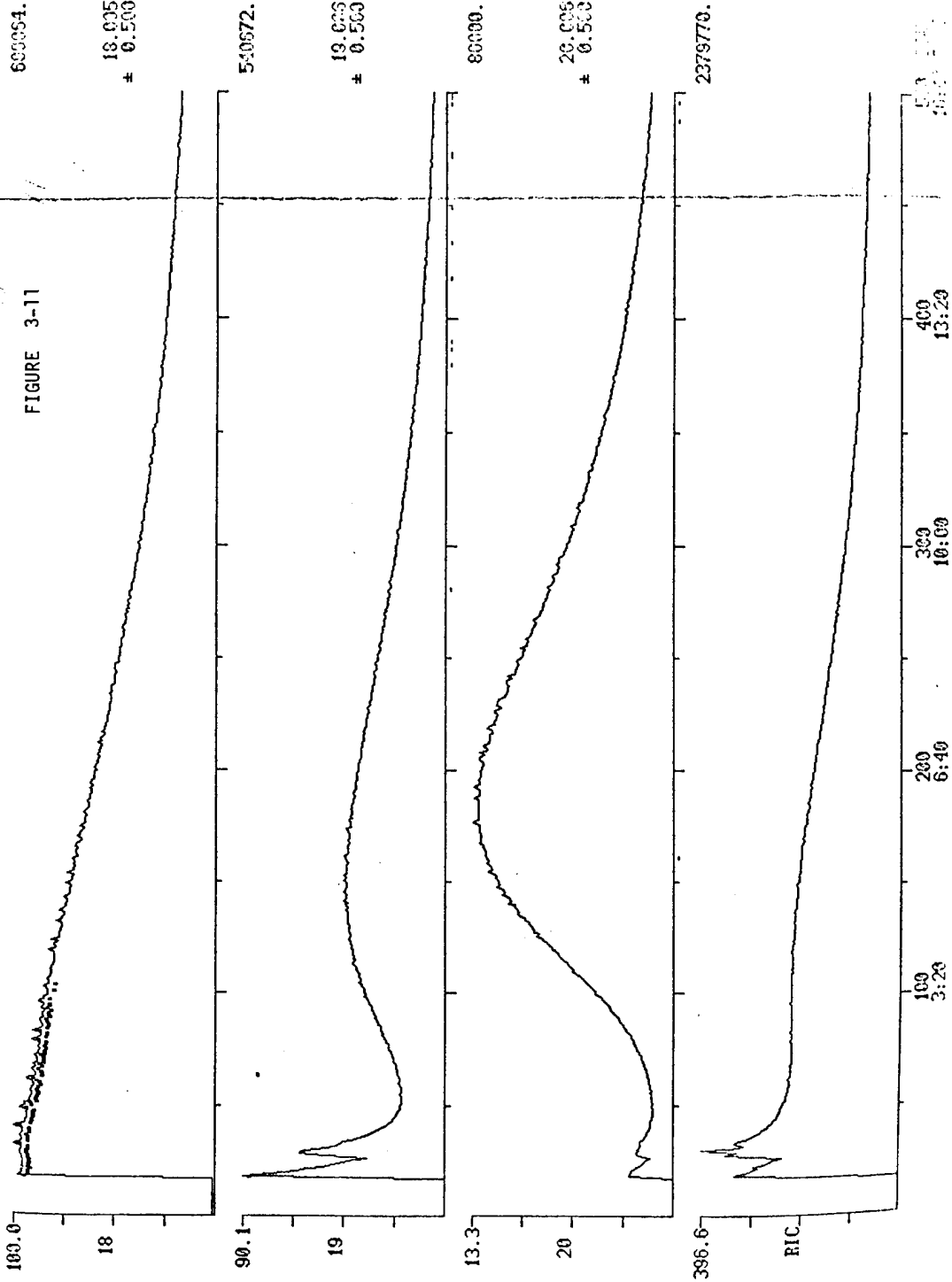
SCANS 1 TO 500



RIC + MASS CHROMATOGRAMS
03/15/78 11:11:00
SAMPLE: SOAKED IN D2O OVER NIGHT
RANGE: C 1.500 LABEL: N 0.4.0 QUAN: A 0.1.0 BASE: U 20. 3

DATA: WETSAMPLE2A #1
CALI: C0915 #3

SCANS 1 TO 500

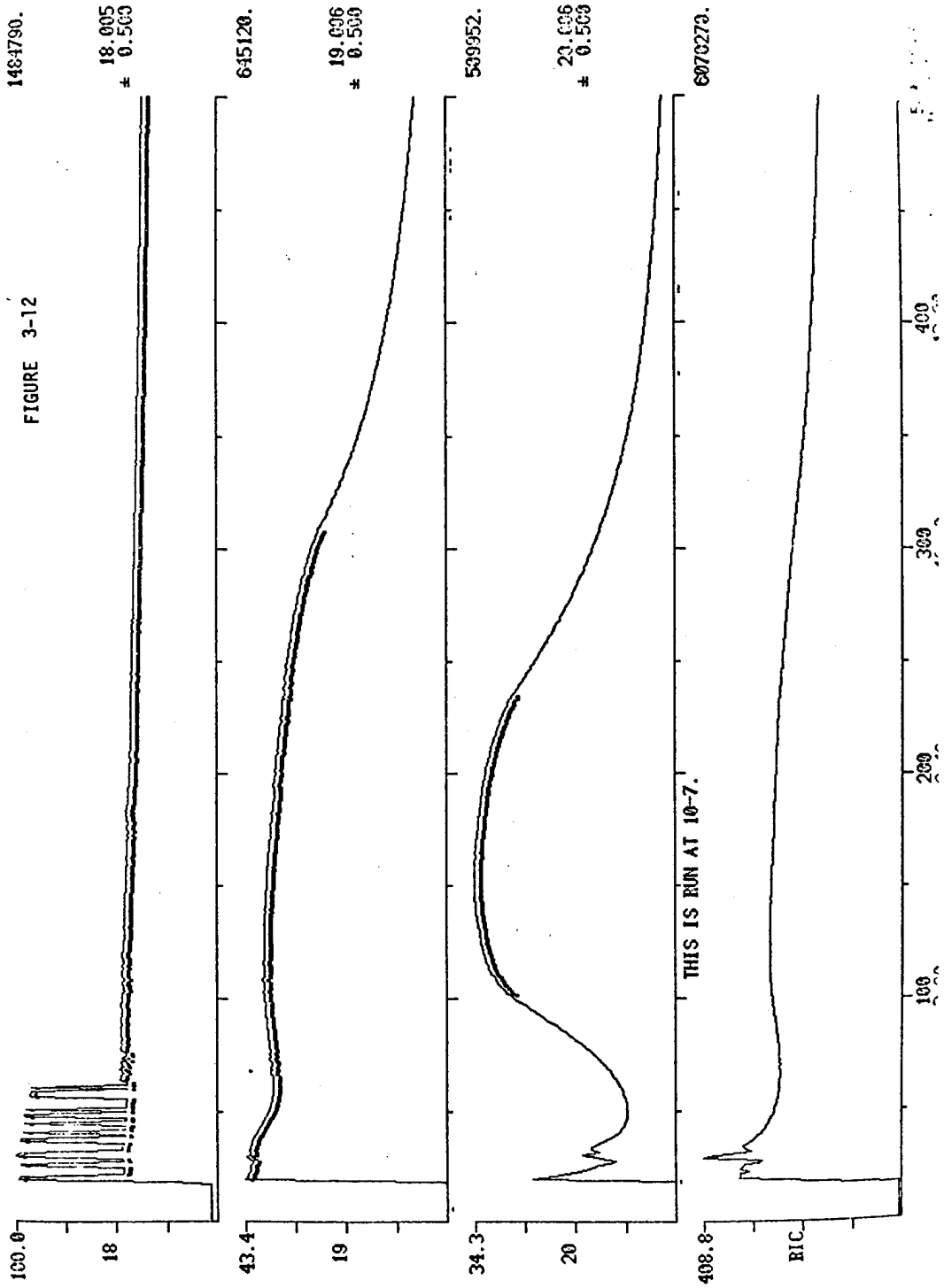


RIC + MASS CHROMATOGRAMS
09/15/78 13:53:00
SAMPLE: TREATED POLYMER
RANGE: G 1.500 LABEL: N 0.4.0 QUAN: A 0.1.0 BASE: U 20. 3

DATA: TESTSAMPLE1 #1
CALL: C0915 #3
SCANS 1 TO 503

1484790.

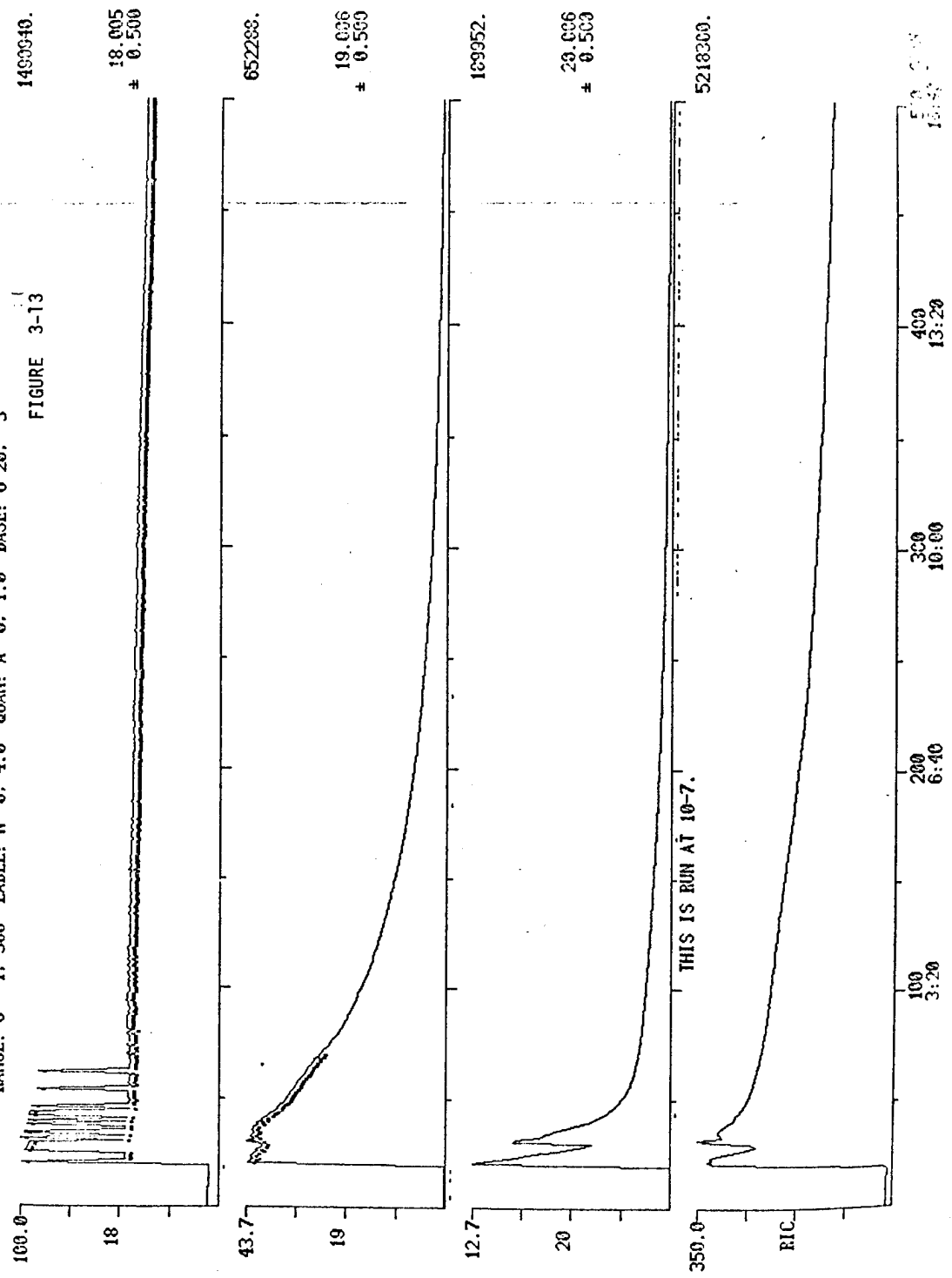
FIGURE 3-12



RIC + MASS CHROMATOGRAMS
 09/15/78 14:24:03
 SAMPLE: DRY POLYMER
 RANGE: G 1, 500 LABEL: N 0, 4.0 QUAN: A 0, 1.0 BASE: U 20, 3

DATA: CONTROL #1
 CALI: C0915 #3

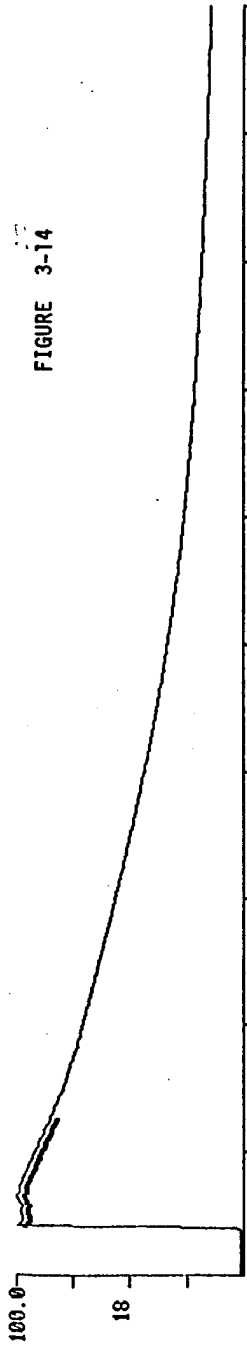
SCANS 1 TO 500



RIC + MASS CHROMATOGRAMS
 09/15/78 14:53:00
 SAMPLE: TREATED POLYMER
 RANGE: C 1.500 LABEL: N 0.4.0 QUAN: A 0.1.0 BASE: U 20. 3

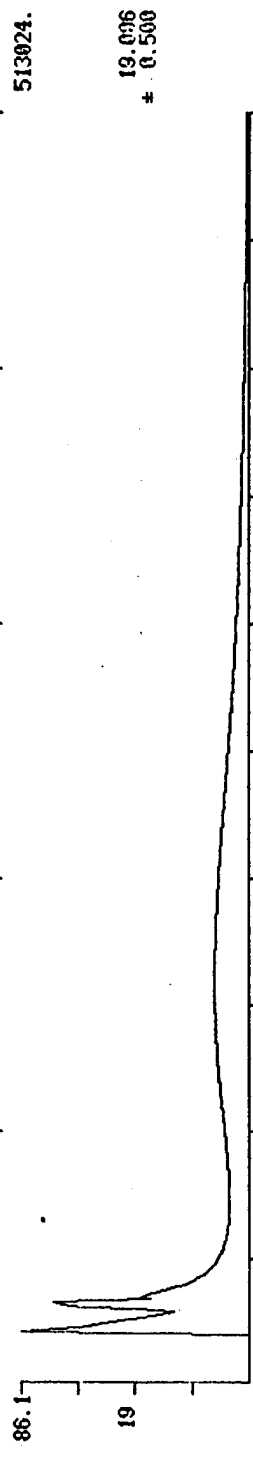
DATA: TESTSAMPLE2 #199
 CALL: C0915 #3
 SCANS 1 TO 500

595968.



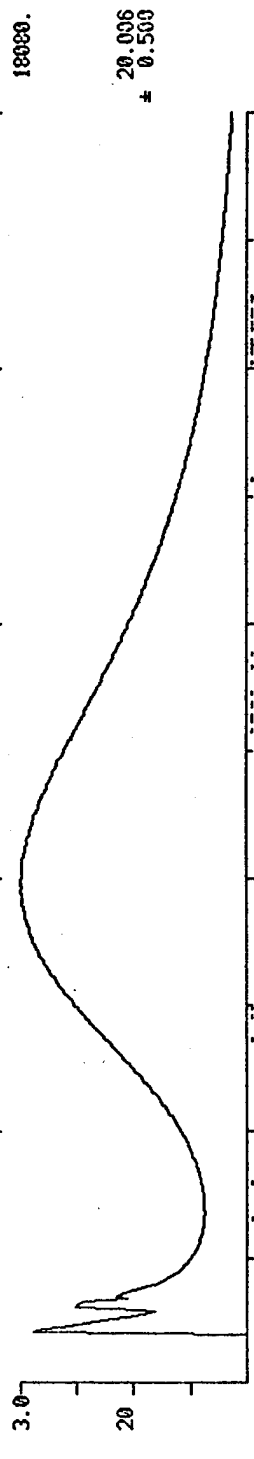
18.005
± 0.500

FIGURE 3-14



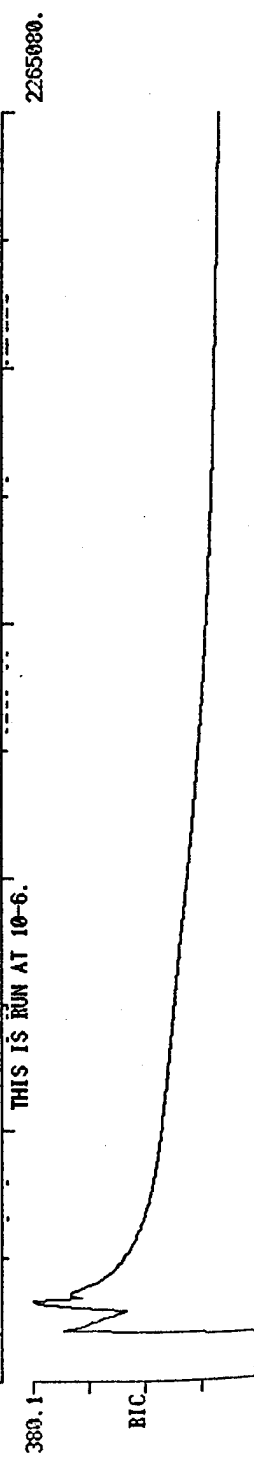
513024.

19.036
± 0.500



180000.

20.006
± 0.500



2265000.

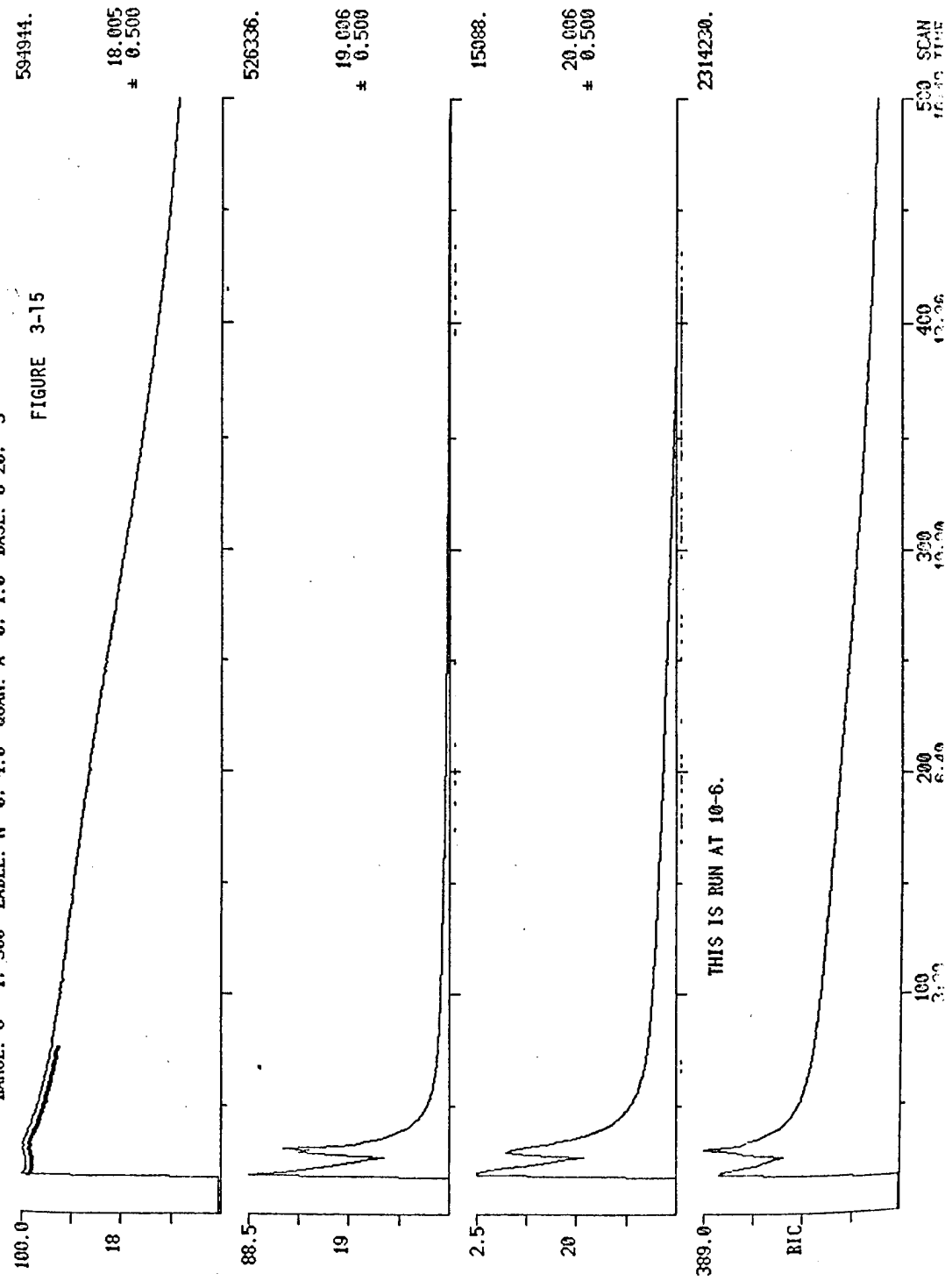
THIS IS RUN AT 10-6.

100 3:20
 200 6:40
 300 10:00
 400 13:20
 500 SCAN 16:40 TIME

FIC + MASS CHROMATOGRAMS
09/15/78 15:21:00
SAMPLE: DRY POLYMER
RANGE: C 1.500 LABEL: N 0.4.0 QUAN: A 0.1.0 BASE: U 20. 3

DATA: CONTROL2 #1
CALI: C0915 #3

SCANS 1 TO 500



RIC + MASS CHROMATOGRAMS
 09/15/78 15:52:00
 SAMPLE: TREATED POLYMER
 RANGE: C 1, 500 LABEL: N 0, 4.0 QUAN: A 0, 1.0 BASE: U 20, 3

DATA: TESTSAMPLE3 #1
 CALI: C0915 #3

SCANS 1 TO 500

603256.

18.005
± 0.500

564224.

19.006
± 0.500

14400.

20.006
± 0.500

2555900.

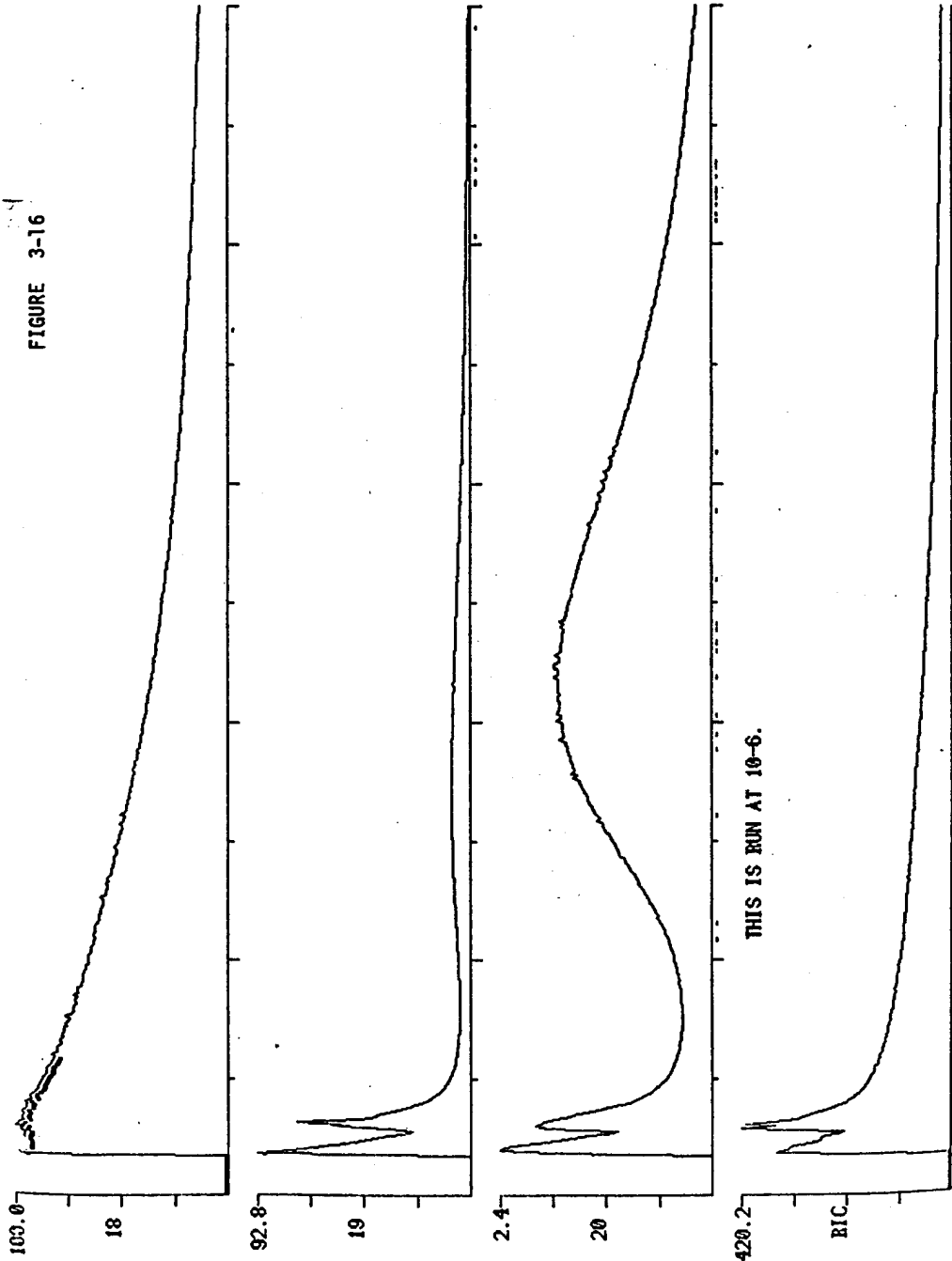


FIGURE 3-16

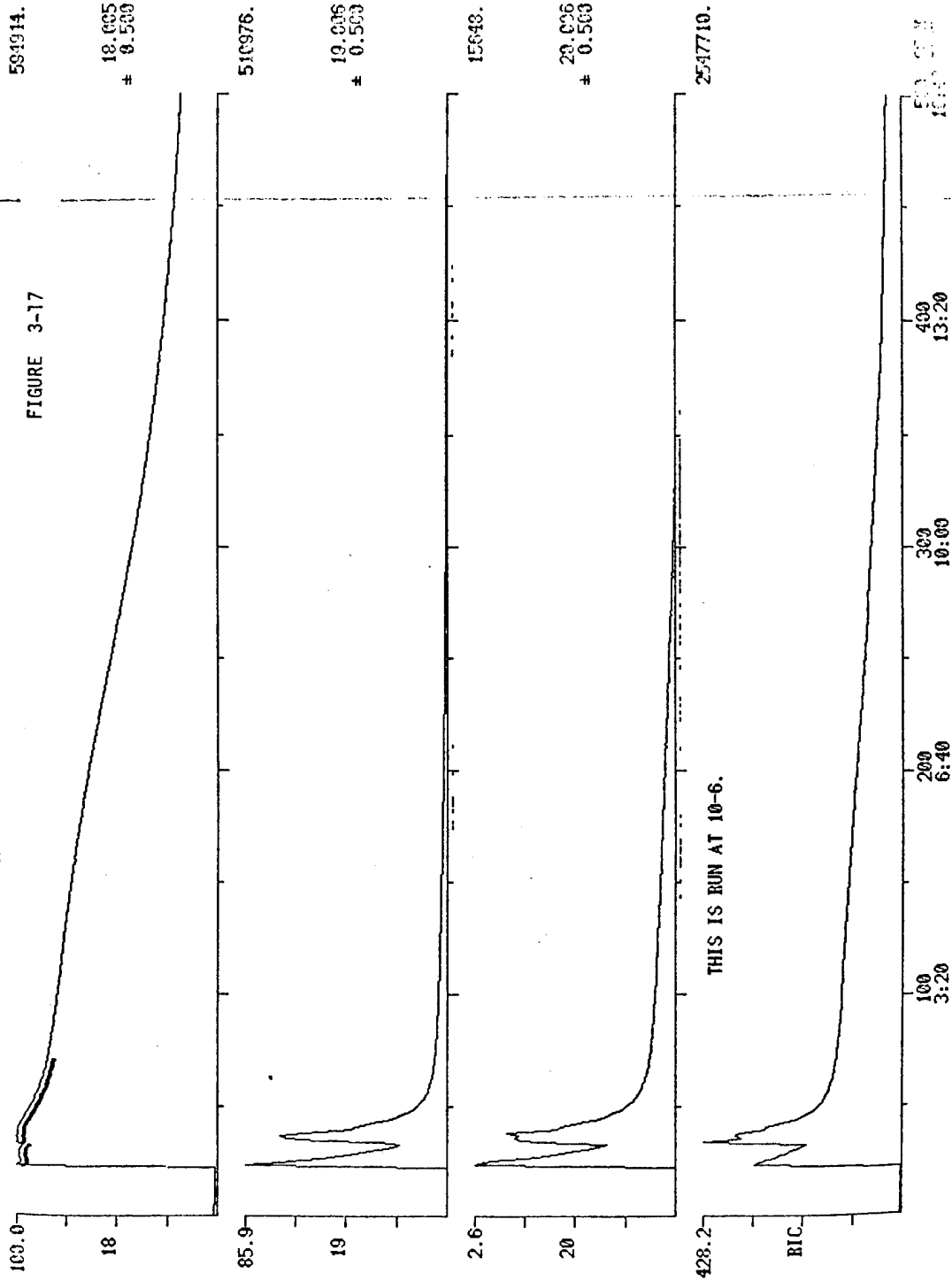
THIS IS RUN AT 10-6.

100 3:20
 200 6:40
 300 10:00
 400 13:20
 500 16:40
 TIME

RIC + MASS CHROMATOGRAMS
09/15/78 16:19:09
SAMPLE: DRY POLYMER
RANGE: G 1.500

DATA: CONTROL3 #1
CALL: C0915 #3
QUANT: A 0.1.0
BASE: U 20. 3

SCANS 1 TO 500

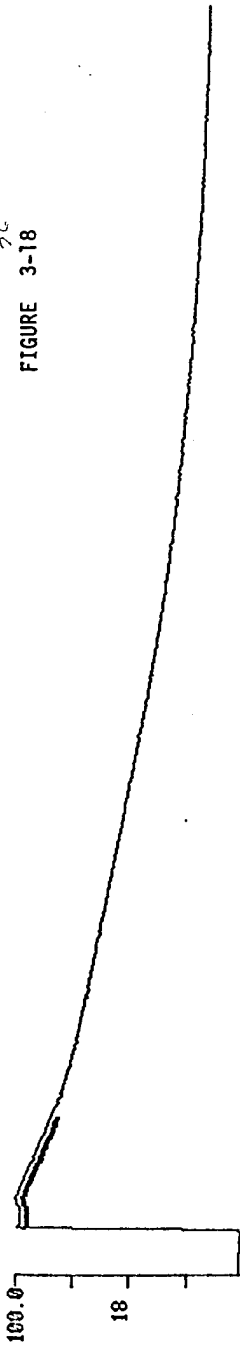


RIC + MASS CHROMATOGRAMS
69/15/78 16:46:00
SAMPLE: TREATED POLYMER
RANGE: G 1.500 LABEL: N 0.4.0 QUAN: A 0.1.0 EASE: U 20. 3

DATA: TESTSAMPLE4 #218 SCANS 1 TO 503
CALI: C0915 #3

593016.

76
FIGURE 3-18



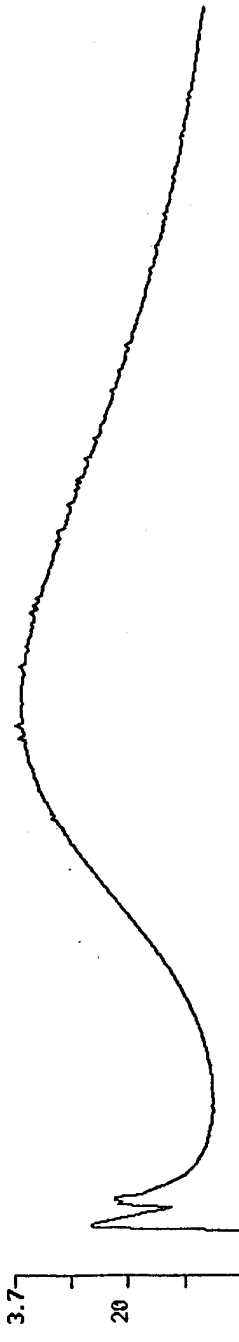
18.005
± 0.500

525312.



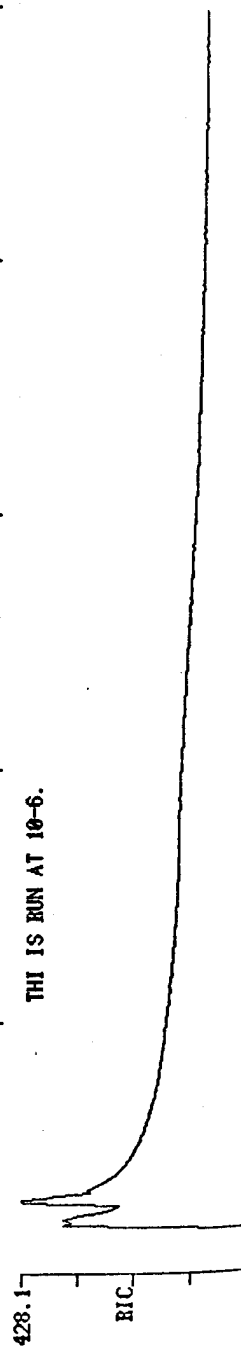
19.006
± 0.500

22336.



20.006
± 0.500

2559990.



100 3:20
200 6:40
300 10:00
400 13:20
500 16:40

REFERENCES

1. Hertz, J. Investigation Into the High Temperature Degradation of Fiber-Reinforced Resin Composite During Ambient Aging. GDCA-DBG73-005, Contract NAS8-27435, June 1973.
2. Browning, C.E. The Mechanisms of Elevated Temperature Property Loss in High Performance Structural Epoxy Resin Matrix Materials After Exposure to High Humidity Environments. AFML TR-79-153, March 1977.
3. Cavano, P.J., and Winters, W.E. PMR Polyimide/Graphite Fiber Composite Fan Blades. NASA CR-135113, December 15, 1976.
4. Chamis, C.C., Hanson, M.P., and Serafini, T.T. Criteria for Selecting Resin Matrices for Improved Composite Strength. Proceedings 28th Annual Technical Conference, Society of the Plastics Industry, Sect. 12-C. 1973.
5. Merrit, C., Sches, R.E., and Peterson, B.A.. Laser Pyrolysis in Gas Chromatographic-Mass Spectrometric Analysis of Polymeric Materials. JOP Chromatography, 99, p. 301-308. 1974.

Distribution List

Copies

NASA-Lewis Research Center
21000 Brookpark Road
Cleveland, OH 44135

Attn: Contracting Officer, J. E. Bolander, M.S. 500-312 1
Technical Report Control Office, M.S. 5-5 1
Technology Utilization Office, M.S. 3-16 1
AFSC Liaison Office, M.S. 4-1 2
Library, M.S. 60-3 2
Office of Reliability & Quality Assurance, M.S. 500-211 1
N. T. Musial, M.S. 500-318 1
T. T. Serafirii, M.S. 49-1 Balance

NASA Headquarters
Washington, DC 20546

Attn: Code RTM-6 1

NASA Scientific & Technical Information Facility
Attn: Acquisitions Branch
P.O. Box 8757
Baltimore/Washington International Airport, MD 21240 20

NASA Ames Research Center
Moffett Field, CA 94035

Attn: John Parker, M.S. 223-6 1

NASA Flight Research Center
P.O. Box 273
Edwards, VA 93523

Attn: Library 1

NASA Goddard Space Flight Center
Greenbelt, MD 20771

Attn: Library 1

NASA John F. Kennedy Space Center
Kennedy Space Center, FL 32899

Attn: Library 1

Distribution List (Cont'd)

Copies

NASA Langley Research Center
Hampton, VA 23665

Attn: V. L. Bell, M.S. 226
N. Johnson, M.S. 226

1
1

NASA Manned Spacecraft Center
Houston, TX 77001

Attn: Library
Code ER

1
1

NASA George C. Marshall Space Flight Center
Huntsville, AL 35812

Attn: J. Curry, EH31
J. Stuckey, EH33

1
1

Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, CA 91103

Attn: Library

1

Office of the Director of Defense
Research and Engineering
Washington, DC 20301

Attn: Dr. H. W. Schulz, Office of Assistant Director
(Chem. Technology)

1

Defense Documentation Center
Cameron Station
Alexandria, VA 22314

1

Research and Technology Division
Bolling Air Force Base
Washington, DC 20332

Attn: Code RTNP

1

Bureau of Naval Weapons
Department of the Navy
Washington, DC 20360

Attn: Code DLI-3

1

Distribution List (Cont'd)

Copies

Director (Code 6180)
U.S. Naval Research Laboratory
Washington, DC 20390

Attn: H. W. Carhart

1

SARPA-FR-MD
Plastics Technical Evaluation Center
Picatinny Arsenal
Dover, NJ 07801

Attn: A. M. Anzalone, Bldg. 176

1

Aeronautics Division of Philco Corporation
Ford Road
Newport Beach, CA 92600

Attn: Dr. L. H. Linder, Manager
Technical Information Department

1

Aerospace Corporation
P.O. Box 95085
Los Angeles, CA 90045

Attn: Library Documents

1

Aerotherm Corporation
800 Welch Road
Palo Alto, CA 94304

Attn: Mr. R. Rindal

1

Air Force Materials Laboratory
Wright-Patterson Air Force Base, OH 45433

Attn: AFML/MBC, T. J. Reinhart, Jr.

1

Office of Aerospace Research (RROSP)
1400 Wilson Boulevard
Arlington, VA 22209

Attn: Major Thomas Tomaskovic

1

Composites Horizons
2303 W. Valley Boulevard
Pomona, CA 91768

Attn: Ira Petker

1

Distribution List (Cont'd)

Copies

Air Force Office of Scientific Research
Washington, DC 20333

Attn: SREP, Dr. J. F. Masi

1

American Cyanamid Company
1937 West Main Street
Stanford, CT 06902

Attn: Security Officer

1

AVCO Corporation
Space Systems Division
Lowell Industrial Park
Lowell, MA 01851

Attn: Library

1

Battelle Memorial Institute
505 King Avenue
Columbus, OH 43201

Attn: Report Library, Room 6A

1

Bell Aerosystems, Inc.
P.O. Box 1
Buffalo, NY 14205

Attn: T. Reinhardt

1

The Boeing Company
Aerospace Division
P.O. Box 3999
Seattle, WA 98124

Attn: J. T. Hoggatt

1

Celanese Research Company
Morris Court
Summit, NJ

Attn: Dr. J. R. Leal

University of Denver
Denver Research Institute
P.O. Box 10127
Denver, CO 80210

Attn: Security Office

1

Distribution List (Cont'd)

Copies

Dow Chemical Company
Security Section
P.O. Box 31
Midland, MI 48641

Attn: Dr. R. S. Karpiuk, Building 1710

1

E. I. duPont de Nemours & Co.
Research & Development Division
Wilmington, DE 19898

Attn: Dr. H. H. Gibbs

1

Ultrasystems, Inc.
2400 Michelson Drive
Irvine, CA 02664

Attn: Dr. R. Kratzer

1

General Dynamics/Convair
Dept. 643-10
Kerry Mesa Plant
San Diego, CA 92112

Attn: J. Hertz

1

Ferro Corporation
3512-20 Helms Avenue
Culver City, CA 90230

Attn: J. Hartman

1

General Electric Company
Technical Information Center
N-32, Building 700
Cincinnati, OH 45215

Attn: M. Grandey

1

Fiberite Corporation
501-559, West 3rd Street
Winona, MN 55987

Attn: J. Allen

1

Distribution List (Cont'd)

Copies

Grumman Aerospace Corporation
Advanced Materials & Processes
Bethpage, NY 11714

Attn: A. London

1

Hexcel
11711 Dublin blvd.
Dublin, VA 94566

Attn: John D. Neuner

1

Hughes Aircraft Company
Culver City, CA 90230

Attn: N. Bilow

1

IIT Research Institute
Technology Center
Chicago, IL 60616

Attn: C. K. Hersh, Chemistry Division

1

Lockheed Missiles & Space Company
Propulsion Engineering Division (D.55-11)
111 Lockheed Way
Sunnyvale, CA 94087

1

McDonnell Douglas Corporation
Douglas Aircraft Company
3855 Lakewood Blvd.
Long Beach, CA 90846

Attn: N. Byrd

1

Monsanto Research Corporation
Dayton Laboratory
Station B, Box 8
Dayton, OH 45407

Attn: Library

1

North American Rockwell Corporation
Space & Information Systems Division
12214 Lakewood Blvd.
Downey, CA 90242

Attn: Technical Information Center, D/096-722 (AJ01)

1

Distribution List (Cont'd)

Copies

Northrop Corporate Laboratories
Hawthorne, CA 90250

1

Attn: Library

Stanford Research Institute
Menlo Park, CA 94025

1

Attn: M. Maximovich

Union Carbide Corporation
12900 Snow Road
Parma, OH 44130

1

Attn: Library

United Technologies Corporation
United Technologies Research Center
400 Main Street
East Hartford, CT 06108

1

Attn: D. A. Scola

United Technologies Corporation
United Technology Cente
P.O. Box 358
Sunnyvale, CA 94088

1

Attn: Library

Westinghouse Electric Corporation
Westinghouse R&D Center
1310 Beulah Road
Pittsburgh, PA 15235

1

Attn: Dr. J. H. Freeman

General Dynamics
Convair Aerospace Division
P.O. Box 748
Fort Worth, TX 76101

1

Attn: Technical Library, 6212

Distribution List (Cont'd)

Copies

Material Science Corporation
1777 Walton Road
Blue Bell, PA 19422

Attn: Ms. N. Sabia

1

U.S. Polymeric
700 E. Dyer Blvd.
Santa Ana, CA 92707

Attn: D. Beckley

1

U.S. Army Air Mobility R&D Lab
Fort Eustis, VA 23604

Attn: Mr. H. L. Morrow, SAVDL-EU-TAP

1

U.S. Army Aviation Systems Command
P.O. Box 209, Main Office
St. Louis, MO 63166

Attn: Mr. Ronald Evers

1

Air Force Materials Laboratory
Wright-Patterson Air Force Base, OH 45433

Attn: Mr. Paul Pirrung, AFML/LTN

1

TRW Equipment
23555 Euclid Avenue
Cleveland, OH 44117

Attn: P. Cavano

1