



**UNION CARBIDE CORPORATION**  
**CHEMICALS AND PLASTICS**

RIVER ROAD, BOUND BROOK, N. J. 08805 · TELEPHONE (201) 356-8000

July 2, 1974

The Hearing Clerk (3 copies)  
Food and Drug Administration  
Room 6-86  
5600 Fishers Lane  
Rockville, Maryland 20852

Dear Sir:

In accordance with the request of the Commissioner of Food and Drugs published in the Federal Register for April 22, 1974 the attached information relative to the use of polyvinyl chloride resins in contact with foods, drugs and cosmetics and in medical devices is submitted. This information includes data on the vinyl chloride monomer content of vinyl chloride homopolymers and copolymers produced by Union Carbide and provides the analytical procedures used in these determinations.

Union Carbide Corporation manufactures vinyl resins by each of the four generally recognized polymerization processes, (1) solution, (2) dispersion or emulsion, (3) non-solvent or bulk, and (4) suspension. Each process yields resins having characteristic properties of value in specific end-use applications. Both vinyl chloride homopolymers and vinyl chloride-acetate copolymers are produced. Union Carbide solution, dispersion, and non-solvent vinyl resins are used extensively in applications regulated by the Food and drug Administration and information on these types of resins are given.

On the other hand the major applications for Carbide suspension resins are in non-regulated applications such as floor and wall coverings, home and automotive upholstery, etc. and to our knowledge these resins are not used in contact with foods, drugs, or cosmetics or in medical devices. Although Union Carbide filed a food additive petition for vinyl chloride-ethylene copolymers produced by the suspension process which resulted in the issuance of Food Additive Regulation 121.2609 on March 12, 1969, these copolymers are not currently used in food contact applications.

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July 2, 1974

Accordingly, this submission contains no data for suspension vinyl resins.

The residual vinyl chloride monomer content of the various Union Carbide vinyl resins will vary depending upon the polymerization process used. The retained vinyl chloride monomer content of these resins is not and has not been a specification parameter and is not therefore a measured value we can furnish from accumulated historical data.

However within recent months an ongoing surveillance program has been instituted which now has yielded the residual monomer information reported herein. This program at this time has not progressed to the determination of rates and levels of vinyl chloride monomer extraction from fabricated containers or their liners to various foods and cosmetics, although an extraction apparatus and validated analytical procedures have been developed which have this capability and such data are being developed.

No data are available on percutaneous absorption of vinyl chloride from cosmetics and devices in contact with skin or mucous membranes, on migration of vinyl chloride to drug products from medical devices composed of polyvinyl chloride, or on the effect on blood and tissues of vinyl chloride monomer extracted from implanted polyvinyl chloride devices. The accumulation of such information is more properly the responsibility of the manufacturer of the end-use item fabricated from polyvinyl chloride resins than of the supplier of the base resin.

The present submission consists of the following items, copies attached:

Exhibit A - memorandum report entitled "Vinyl Resins for Solution Coatings" dated June 10, 1974. This report describes the Union Carbide solution polymerization process used to prepare the designated solvent vinyl resins intended for interior coatings on metal containers. Residual monomer levels, undetectable by an analytical method sensitive to 1.5 ppm, indicate a maximum migration of monomer to food of 0.001 ppb.

Exhibit B - memorandum report entitled "Vinyl Chloride Based Dispersion Resins" dated June 11, 1974. This report describes the process used to prepare poly (vinyl chloride) dispersion resins intended for use in fused plastisol closure gaskets and organosol coatings on metal containers. Residual monomer levels of indicated resins, not detectable by a method sensitive to 1.5 ppm, indicate maximum monomer migration from a

July 2, 1974

gasket to contained food to be <1 ppb and from a coated metal jar lid to food to be <0.0003 ppb.

Exhibit C - memorandum report entitled, "Non-Solvent Vinyl Resins", dated May 31, 1974. This report describes the non-solvent polymerization process for producing vinyl resins used in the fabrication of medical devices including blood collection units. Residual monomer data indicate levels ranging from about 10 ppm to <1.5 ppm.

Exhibit D - Analytical Procedures for the Determination of Residual Vinyl Chloride Monomer in Vinyl Resins and A Procedure for the Determination of Extractable Monomers from Polyvinyl Chloride Films and Coatings.

We understand this information will be generally available to the public in the Office of the Hearing Clerk.

Very truly yours,



W. B. Ackart  
Manager, FDA Liaison

WBA:deb  
att.

cc: Mr. Gerard L. McCowin (3 copies)  
Division of Food and Color Additives  
Food and Drug Administration  
200 C Street, S. W.  
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VINYL RESINS FOR SOLUTION COATINGS  
GENERAL PROCESS DESCRIPTIONS AND  
USE IN COATINGS FOR FOOD CONTACT APPLICATIONS:  
RESIDUAL VINYL CHLORIDE MONOMER

AUTHORS: J. J. Brezinski

DATE: June 10, 1974

PROJECT NO.: 328K10

SUPERVISOR:

FILE NO.: 19574

A general description of the solution process used to prepare Union Carbide's solvent vinyl resins is presented together with considerations regarding residual vinyl chloride monomer in the powdered resin and in baked coatings used in food contact applications. Arguments are presented to demonstrate that the maximum possible migration of vinyl chloride monomer from the coating to food in typical beverage containers is 0.001 ppb.

This information is intended for submission to the Food and Drug Administration in response to the request of the Commissioner as indicated in the Federal Register, Vol. 39, No. 78, Monday, April 22, 1974.

**INTRODUCTION** Vinyl chloride copolymer coatings have been used in interior coatings of beer and beverage metal containers and in other food contact coatings for more than forty years. In these uses, these coatings provide a tasteless, odorless barrier between the metal surface and the food in the container. The consistent quality performance of these coatings has been recognized around the world.

Solution Polymerized Resins - Process Description

A major class of vinyl chloride copolymer resins used in coatings for food contact applications are produced by Union Carbide Corporation via a unique solution polymerization process.

In a typical case of the preparation of a vinyl chloride-vinyl acetate copolymer, the monomers, solvent and organic peroxide are charged to a stirred autoclave in which the polymerization is conducted under controlled conditions of temperature and pressure. The polymer formed is soluble in the solvent and thus a single homogeneous liquid phase is present throughout the polymerization step. Varnish containing the dissolved

polymer is withdrawn into a separate vessel where residual vinyl chloride monomer is removed (and recovered) by a stripping process.

The polymer is precipitated from the well-stirred varnish by the addition of a mixture of water and alcohol, the resin slurry is centrifuged and well washed with water, after which the resin particles are dried in a flash dryer, screened to remove oversize particles and packaged for shipment.

The resins during normal storage show an equilibrium solids level of 99.7-99.8 percent, the volatiles consisting dominantly of water and trace amounts of alcohol and vinyl acetate monomer. Only a trace quantity of residual organic catalyst is present in the dry powder (<5 ppm calculated as peroxidic oxygen). The catalyst is decomposed to volatile components during the conversion of the product into a coating.

#### Residual Vinyl Chloride Content

The unique solvent polymerization/precipitation recovery process results in the formation of relatively porous particles with high effective surface area, highly favorable to the efficient removal of residual vinyl chloride monomer. On the basis of an ungoing surveillance program, BAKELITE solvent-polymerized resins have been found to contain no detectable vinyl chloride monomer when analyzed by the attached gas chromatographic method sensitive to 1.5 ppm of vinyl chloride.

#### Resins Prepared by Solvent Polymerization Process

The preceding comments about vinyl chloride monomer apply to the following products all prepared via the solvent polymerization process. The resins are listed by trade name with appropriate composition and molecular weight information and are used in food contact applications.

VINYL COPOLYMER RESINS MADE BY SOLVENT PROCESS

(Typical Values)

Resin	(Percent by Weight)			Intrinsic Viscosity dl./gm.	Number Average Molecular Weight
	PVC	PVOAc	Other		
VYNS	89.6	10.4	--	0.75	34,800
VYHH	85.1	14.9	--	0.52	20,400
VYHD	85.4	14.6	--	0.40	15,200
VYLF	89.4	10.6	--	0.28	8,500
VYDS	85.4	14.6	(a)	0.40	15,200

Acid-Modified Resins

VMCH	85.3	13.7	1.0(b)	0.52	21,700
VMCC	82.0	17.0	1.0(b)	0.36	13,900
VMCA	81.9	16.1	2.0(b)	0.30	8,100

Hydroxyl-Modified Resins

VAGH	90.9	3.6	5.5(c)	0.55	24,100
VAGD	91.0	3.5	5.5(c)	0.44	15,300

Glycidyl-Methacrylate-Modified Resin

VERR	80.0	10.0	1.0(d)	0.32	11,000
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(a) Supplied as Solution in MEK-Toluene

(b) Percent as maleic acid

(c) Percent as poly(vinyl alcohol)

(d) Percent as oxirane oxygen (FDA Sanctioned for Fatty Foods)

Maleic Acid-Modified Resins

The process used to prepare the maleic acid-modified resins, VMCH, VMCC and VMCA, is essentially the same as that described for the vinyl chloride-vinyl acetate copolymers except that a low concentration of maleic acid is included with the monomers. The concentration of free maleic acid in the precipitated, water washed polymers is essentially nil.

Vinyl Alcohol Modified Resins

The VAGH and VAGD resins are vinyl chloride-vinyl acetate-vinyl alcohol terpolymers (90:4:6 weight ratio) which are prepared from vinyl chloride-vinyl acetate copolymers (VYHH and VYHD, respectively). In the process, the copolymer resin is dissolved in a low boiling ester solvent containing a volatile primary alcohol. Transesterification is effected in solution in the presence of a catalyst to convert a majority of the acetate groups of the polymer backbone to hydroxyl groups. These acetate groups are combined with the volatile alcohol present to form the corresponding volatile alkyl acetate.

The varnish is withdrawn from the reaction autoclave and a water-alcohol mixture is added to precipitate the resin, the resin slurry is centrifuged and thoroughly washed, after which the resin powder is dried, screened and stored for shipment. During the addition of water to the varnish, the transesterification catalyst is converted to a water-soluble salt and a volatile alcohol which are essentially completely removed during the washing and drying steps. Equilibrium total solids of the polymer is 99.7-99.8%, the volatiles consisting of a trace amount of water, alcohol and volatile acetate ester. No residual vinyl chloride or vinyl acetate monomer is present.

VYDS Resin Solution

The VYDS resin solution is equivalent to a solution of VYHD resin in a mixture of methyl ethyl ketone and toluene. Two versions of this product are available: VYDS Resin Solution and VYDS-66 Resin Solution. In the latter product, the concentration of toluene present is reduced to allow the formulation of coatings systems which comply with the "Rule 66" solvent regulations.

Use in Beverage Containers

These vinyl copolymer resins are currently used in coatings for food contact applications. One of these applications is in the interior coating of metal beverage containers. Typically, the solids in the coating formulation contains the following materials:

VCl-VOAc Copolymer	90
Hydroxyl-Modified VCl-VOAc Copolymer	5
Acid-Modified VCl-VOAc Copolymer	5
Epoxy Stabilizer	0.1

These materials are applied by air-less spray technique as a 22% total solids solution in a mixture of solvents of which the following system is typical:

Solvent Composition

<u>Solvent</u>	<u>Wt. %</u>	<u>B.P.</u>
Xylene	18.5	285°F
Toluene	56.6	230°F
MEK	14.9	80°F
Acetone	10.0	56°F
	100.0	

The formulation is applied to deposit an average coating weight of about 5.5 mg/in<sup>2</sup> of surface; the corresponding thickness of the dry coating is approximately 0.25 mils. Application weight can vary between 4 to 7 mg/in<sup>2</sup>.

Following the spray-application, the coated beverage container is passed through a high velocity air oven (>2000 cfm), maintained at ~320°F to remove the solvents. The normal residence time of the container in the oven is about 6 minutes. It is essential to the end use of the product that essentially no residual solvent remains in the coating, as even low amounts will adversely effect the taste of the packaged products. The thin coating containing approximately 78 weight percent of solvents which boil above 50°F, with the bulk (~75%) boiling above 230°F is so processed to remove virtually all traces of the solvent present.

Probability of VCl Monomer Migration to Food

The removal of the solvent from the can coating is in excess of 99.9+%. Assuming that the vinyl chloride monomer content of the vinyl copolymer resins used in the coating was 1.5 ppm, it is reasonable to expect that 99.9+% of any vinyl chloride monomer present would be volatilized with the solvent. (Vinyl chloride monomer has a very low boiling point [-13.9°C] compared to that of the solvents used to apply the coating.)

Thus, the maximum amount of vinyl chloride monomer in the coating which would be expected to remain after the baking cycle would be:

$$0.1/100 \times 1.5 = 0.0015 \text{ ppm}$$



- 6 -

If all the 0.0015 ppm of monomer assumed to be present in the coating migrates from the coating into the 12 ounces of beverage (assumed to weigh 400 g.), the amount of monomer that could possibly migrate into the beverage is calculated by the following:

$$5.5 \text{ mg/in}^2 \times 50 \text{ in}^2 \times \frac{0.0015}{10^6} \times \frac{1}{400 \text{ g.}} \times \frac{1 \text{ g.}}{1000 \text{ mg.}} =$$

$$\frac{5.5 \times .5 \times 10^2 \times 1.5 \times 10^{-3}}{4.0 \times 10^2 \times 10^9} = \underline{0.001 \text{ ppb}}$$

On the basis of these assumptions, which are considered conservative, the maximum migration of vinyl chloride monomer to the beverage would be 0.001 ppb.

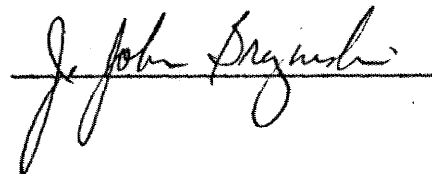
These calculations support the conviction that with the use of the vinyl copolymer resins shown to contain <1.5 ppm of residual vinyl chloride monomer and in consideration of the essential features of the solution coating process and baking conditions employed to insure removal of essentially all solvent from the coatings, the probability of experiencing any vinyl chloride monomer migration from the baked coating to the food in the container is essentially nil.

Similar arguments can be advanced for vinyl coatings applied from solution to metal used in fabrication of jar lids for food containers and for the coating of aluminum foil used for food contact applications in which the vinyl formulations are applied as thin coatings and are subjected to a baking cycle to remove essentially all the solvent.

Manuscript Date: June 6, 1974

Date Typed: June 7, 1974

JJB:pw



VINYL CHLORIDE BASED DISPERSION RESINS  
GENERAL PROCESS DESCRIPTION AND USE IN  
GASKETS AND COATINGS FOR FOOD CONTACT APPLICATIONS:  
RESIDUAL VINYL CHLORIDE MONOMER

AUTHORS: J. J. Brezinski  
K. D. Cavender

DATE: June 11, 1974

PROJECT NO.: 328K10

SUPERVISOR:

FILE NO.: 19575

A general description is presented of the process used by Union Carbide Corporation to prepare poly(vinyl chloride) dispersion resins recommended for use in food contact applications together with a discussion relating to residual vinyl chloride monomer in the powdered resin and that predicted to be present in fused plastisol gaskets and organosol coatings. Data is shown indicating maximum monomer migration from a plastisol gasket to food in a typical glass beverage container to be <1 ppb; monomer migration from an organosol-coated metal jar lid to food in a 1-pt. glass container is estimated at <0.0003 ppb.

The information is intended for submission to the Food and Drug Administration in response to the request of the Commissioner as requested in the Federal Register, Vol. 39, No. 78, April 22, 1974.

**INTRODUCTION** Union Carbide Corporation currently produces and markets poly(vinyl chloride) dispersion resins recommended for use in food contact applications. This memorandum documents the products involved, and discusses the residual vinyl chloride monomer present in the powdered resin and in typical fabricated food contact products such as gaskets and coatings.

Production Process

In the production of the BAKELITE Vinyl Dispersion Resins, the vinyl chloride monomer, water, oil-soluble catalyst and emulsifying agent are emulsified in a sealed, stirred autoclave and the temperature adjusted to initiate polymerization. The polymer is produced in the form of a fine dispersion of small solid particles in water; the particle size of the particles in the latex varies between 0.01 to 1.0 microns.

- 2 -

After the polymerization is complete, the bulk of the residual vinyl chloride monomer is removed (and recovered) by a stripping process. The polymer latex, which contains approximately 35 percent solids, is then spray-dried through a hot column in the presence of a large volume of heated air. During the drying process, the primary latex particles of polymer within each sprayed droplet agglomerate to form larger particles with a medium diameter of about 25 $\mu$ ; the dry powder is subjected to grinding to reduce the average size to about 1 - 4 microns. The fine powder is packaged in multi-wall kraft paper bags.

#### Residual Vinyl Chloride Monomer

As a result of the production process employed, the BAKELITE vinyl dispersion resins are recovered in an extremely fine form (median particle size of 1-4 microns) characterized by a high surface to volume ratio, very favorable to the efficient removal of residual vinyl chloride monomer. Based on the results of an ongoing surveillance program, the BAKELITE vinyl dispersion resins contain no detectable vinyl chloride monomer when analyzed by a gas chromatographic method sensitive to 1.5 ppm.

#### Products

The specific products recommended for use in food contact applications are listed in the following table by trade name, composition and inherent viscosity. The products are all high in molecular weight (>50,000).

The resins are prior sanctioned by the Food and Drug Administration for use in food contact applications.

<u>Resin</u>	<u>Type</u>	<u>Inherent Viscosity (Typical Values)</u>
QYKV	PVC Homopolymer	1.20
QYJV	PVC Homopolymer	0.9
QYOH	PVC Homopolymer	1.25
VLFV	VCl-VOAc Copolymer (95:5 ratio)	1.0

#### Use in Food Contact Applications

BAKELITE vinyl dispersion resins are used in a variety of food contact applications. Among the larger volume uses are in the production of plastisol gaskets for glass beverage and food containers as well as in coatings for metal which is subsequently post-formed into covers or lids for glass food containers.

Gaskets for Beverage Containers

The plastisol gasket in the cap or closure used on glass beverage containers is prepared by the extrusion of a small amount of the vinyl plastisol into the cap and then heating the cap and plastisol to about 350°F for 2-3 minutes to fuse the plastisol and thus form the gasket. A typical vinyl plastisol for this use will contain the following ingredients:

<u>Ingredient</u>	<u>Parts</u>
PVC Homopolymer Dispersion Resin	100
"Food Grade" Plasticizer	65
Ca-Zn Stabilizer	1
Epoxidized Soy-Bean Oil	3

In a typical beverage cap gasket, which weighs 0.30 grams, the vinyl dispersion resin will account for approximately 60 percent of the total weight or 0.178 grams. Assuming that the contents of a 12 oz. beverage container weigh 400 grams, that the residual monomer in the dispersion resin used in the plastisol is 1.5 ppm, that all this vinyl chloride monomer remains in the gasket during the high temperature fusion cycle and that all the monomer migrates to food, the maximum amount of vinyl monomer migration to food from the gasket would be calculated as follows:

$$0.178 \text{ g.} \times \frac{1.5}{10^6} \times \frac{1}{400 \text{ g.}} = 0.66 \text{ ppb}$$

The assumptions made would, however, not be realized in practice. If vinyl chloride monomer were present in the dispersion resin, some of it would be removed during the plastisol preparation, some during the vacuum deaeration of the plastisols (a process employed to remove entrained air bubbles) and a considerable portion of remaining monomer would be volatilized during the fusion of the gasket for 2-3 minutes at 350°F. It is conservatively estimated that if 1.5 ppm of vinyl chloride monomer were present in the initial dispersion resin, <0.1 ppb would be expected to be left in the gasket for potential migration to the beverage.

Use in Coatings

BAKELITE vinyl dispersion resins are also used in coatings for metal closures as well as in the interior of metal food containers. In such applications, the dispersion resin is applied to the metal substrate as a low viscosity organosol - which is essentially a dispersion of the vinyl dispersion resin in a combination of volatile solvents. Typically, vinyl

organosols used in such applications are applied at about 40 percent solids to yield a dry coating thickness of approximately 0.5 mil or a coating weight of about 12 mg/in<sup>2</sup>.

The organosol coating is normally baked at an elevated temperature, 350-390°F, for 6-10 minutes in an air-circulating oven (~2000 cfm) to insure that virtually all the solvent present is removed from the coating. It is essential to the end use of the product that 99.9+ of the solvent present is removed from the coating.

A typical one-pint metal jar lid is 3 inches in diameter and thus presents a food contact surface of 7.2 in<sup>2</sup>. The contents of a one-pint jar, assuming a density of 1 will weigh approximately 470 grams.

Assuming that the coating consists only of the dispersion resin, that the resin contains 1.5 ppm of vinyl chloride monomer, that 99.9 percent of the monomer is volatilized during the high temperature baking cycle and that any remaining monomer migrates to food, then the maximum amount of monomer which can migrate to the food in the one-pint jar is calculated as follows:

$$7.2 \text{ in}^2 \times 12 \text{ mg/in}^2 \times \frac{1.5}{10^6} \times 1.0 \times 10^{-3} \times \frac{1}{470 \text{ g.}} \times \frac{1 \text{ g.}}{1000 \text{ mg}} =$$

$$\frac{7.2 \times 12 \times 1.5 \times 10^{-3}}{470 \times 10^9} = \frac{0.00028}{10^9} = 0.00028 \text{ ppb}$$

Thus, under the assumed conditions, the maximum amount of vinyl chloride monomer which would be expected to migrate to food is <0.0003 ppb or essentially nil.

**CONCLUSION** This discussion of the BAKELITE vinyl dispersion resins supports the belief that with the use of these products in food contact applications, the probability of experiencing any significant migration of vinyl chloride monomer from the fused gasket or closure or coating containing these products to food is essentially nil.

Manuscript Date: June 7, 1974  
Date Typed: June 10, 1974  
JJB:KDC:pw

*J. John Brynich*

NON-SOLVENT VINYL RESINS  
GENERAL PROCESS DESCRIPTION AND  
RESIDUAL VINYL CHLORIDE MONOMER CONTENT

AUTHORS: M. E. Eisenhour

DATE: May 31, 1974

PROJECT NO.:

SUPERVISOR:

FILE NO.:

SUMMARY

A general description of the non-solvent polymerization process as practiced by Union Carbide Corporation is presented. Non-solvent resins used in the fabrication of medical devices are identified and residual vinyl chloride monomer data are given.

DISCUSSION

Non-Solvent PVC Resin Process

Union Carbide's Non-Solvent process for manufacturing PVC resins is in fact a bulk process, but unique in the fact that it is a continuous polymerization as opposed to the suspension and dispersion batch polymerization cycle. Polymerization is carried out in an agitated pressure vessel (autoclave). Fresh monomer is fed continuously to the autoclave and a mixture of resin and unreacted monomer is continuously withdrawn. Other than catalyst and its nonane carrier, no other materials are added to the reaction step, accounting for the extreme purity of the non-solvent resins.

The monomer/resin slurry from the autoclave is discharged into a tank of extremely pure hot water where the monomer is boiled off leaving the resin suspended in water. The unreacted monomer is recovered and reused in the process. The resin/water slurry is continuously discharged to a centrifuge and a standard two stage flash drier. Before packaging the resin is classified and screened to remove large particles or dense particles that might be considered contaminants.

Research and Development Department  
Chemicals and Plastics  
Union Carbide Corporation  
Bound Brook, New Jersey

The uniformity of non-solvent resin as expressed by molecular weight is due to the continuous polymerization aspect and the purity, as pointed out before, is due to the lack of contaminants such as suspending agents, soaps, and other additives used in the suspension and dispersion processes.

Non-Solvent Resin Products

Specific products are identified in the following table. QYNA and QYNJ are homopolymers of VCM with the QYNA being the higher in molecular weight. VYNW is a copolymer containing about 2.0% vinyl acetate. Major end uses for QYNA and VYNW are for the medical blood-bag and tubing industry and have been so used since 1957. QYNJ is used in powder coating operations not usually associated with food or drug applications.

<u>RESIN</u>	<u>TYPE</u>	<u>INHERENT VISCOSITY</u>
QYNA	PVC Homopolymer	1.00 to 1.05
QYNJ	PVC Homopolymer	0.75 to 0.85
VYNW	VCl-V0Ac Copolymer (98:2 ratio)	1.05 to 1.10

Residual Vinyl Chloride Monomer Contents

Residual vinyl chloride monomer contents of the indicated resin blends as determined by a gas chromatographic method of analysis sensitive to 1.5 ppm were as follows:

<u>Resin Type</u>	<u>Blend Number</u>	<u>Date</u>	<u>Vinyl Chloride, ppm</u>
VYNW	B-3787	March 1974	25
	B-3797	April 1974	10
	B-3799		5
	B-3801		5
	B-3802		6
	B-3803		12
	B-3784	May 1974	2
QYNA	B-1394	May 1974	< 1.5
	B-1410		< 1.5
	B-1413		< 1.5
	B-1414		< 1.5
	B-1415		4.0
	B-1416		< 1.5
	B-1417		< 1.5
	B-1418		< 1.5
	B-1420		< 1.5

DETERMINATION OF RESIDUAL VINYL CHLORIDE  
MONOMER IN VINYL RESINS

1 PURPOSE

A procedure for determining the amount of residual vinyl chloride present in vinyl resins is described. The resin is dissolved in a solvent and the vinyl chloride analyzed using a gas chromatographic technique. The method is applicable for use with poly (vinyl chloride), vinyl chloride-vinyl acetate copolymers and other vinyl resins in which there are no volatiles which interfere in the determination.

2 EQUIPMENT AND REAGENTS

Gas Chromatograph, Hewlett-Packard (F and M) Model 5750 or equivalent, equipped with a hydrogen flame ionization detector.

Tetrahydrofuran, reagent grade.

Balance with accuracy to 0.10 gram.

3 SAMPLE PREPARATION

Prepare the sample for chromatograph injection by dissolving the test resin in tetrahydrofuran (THF). Weigh 9 grams of THF into a suitable vial. Add 1 gram of the resin to be tested to the THF. Resin addition should be made as quickly as possible. Cap the bottle and place it on a can-roller to attain complete solution. When complete solution has occurred, the sample is ready for injection into the chromatograph.

4 INSTRUMENT PARAMETERS

Instrument	Hewlett-Packard (F and M) Model 5750 (or equivalent)
Detector	Hydrogen flame ionization
Recorder	0-1 mv
Column	8 ft x 1/8 in, packed with Porapak Q
Oven Temperature	150° for 3 minutes, followed by programming to 240° C at 15°/minute
Carrier Gas	Helium
Flow	3 psi
Sample size	1 microliter
Recorder Speed	5 divisions/minute

Elution Times

Vinyl Chloride	2.1 minutes
Tetrahydrofuran	6.8 minutes



5. CALIBRATION

Prepare solution mixtures of varying amounts of vinyl chloride in tetrahydrofuran to cover the expected range of concentration. Obtain from the chromatograph scan the area per cent of vinyl chloride for each sample of known monomer content. Prepare a chart plotting the area per cent vinyl chloride versus the known weight per cent vinyl chloride to establish the relative detector response of the vinyl chloride with respect to tetrahydrofuran.

6. CALCULATION

Determine the area per cent vinyl chloride from the chromatograph scan for the resin solution to be characterized. Multiply this figure by 10, which converts the data to area per cent vinyl chloride based on resin weight. Using the chart developed with the calibration samples, read off the corresponding weight per cent of vinyl chloride.

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Mr. R. A. Bleidt  
Dr. J. J. Brezinski

June, 1974

FIGURE 1

SYNTHETIC SAMPLE OF 1 PPM VINYL CHLORIDE IN THE SOLVENT  
(Sample Volume = 2 Microliters)

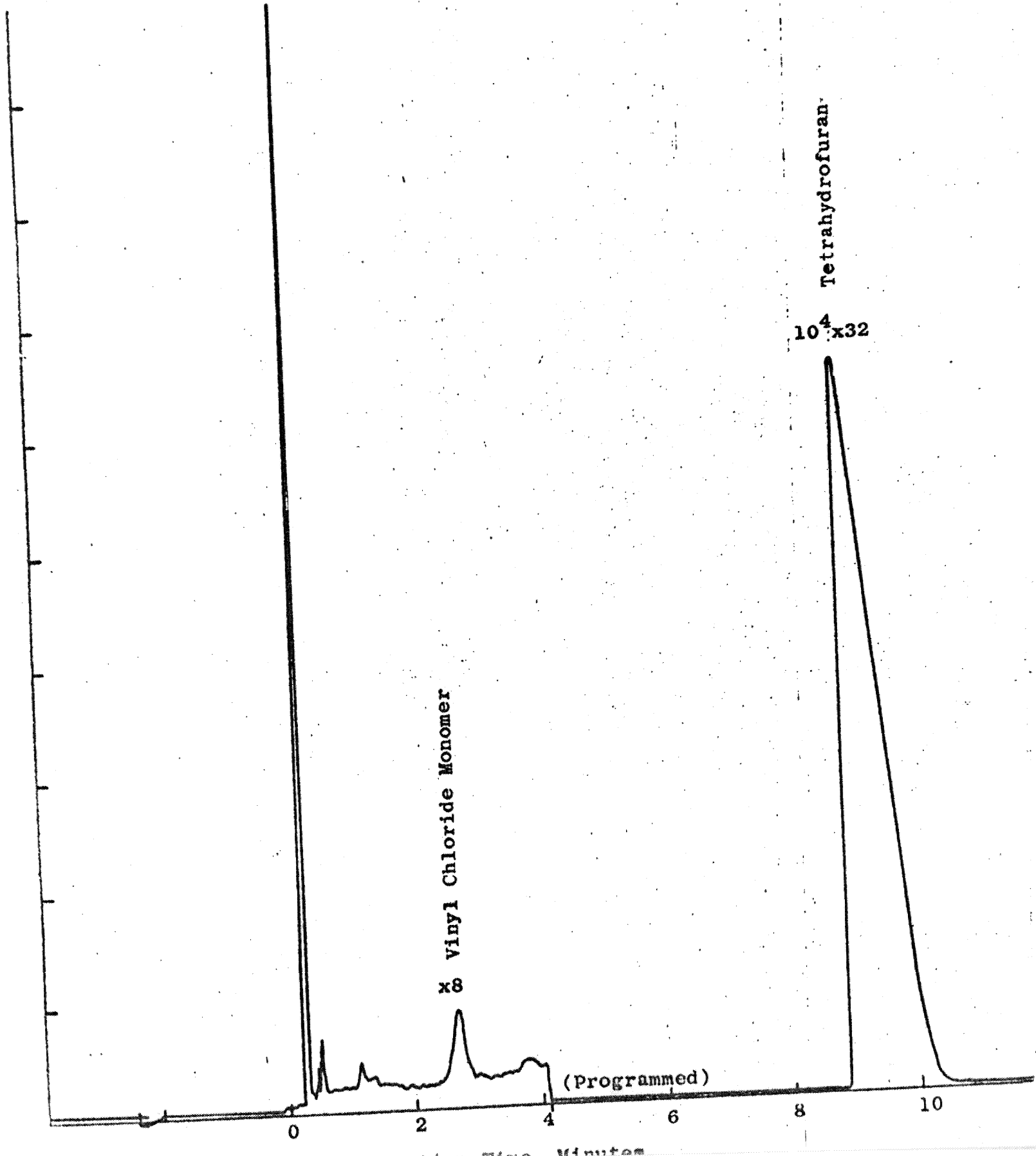
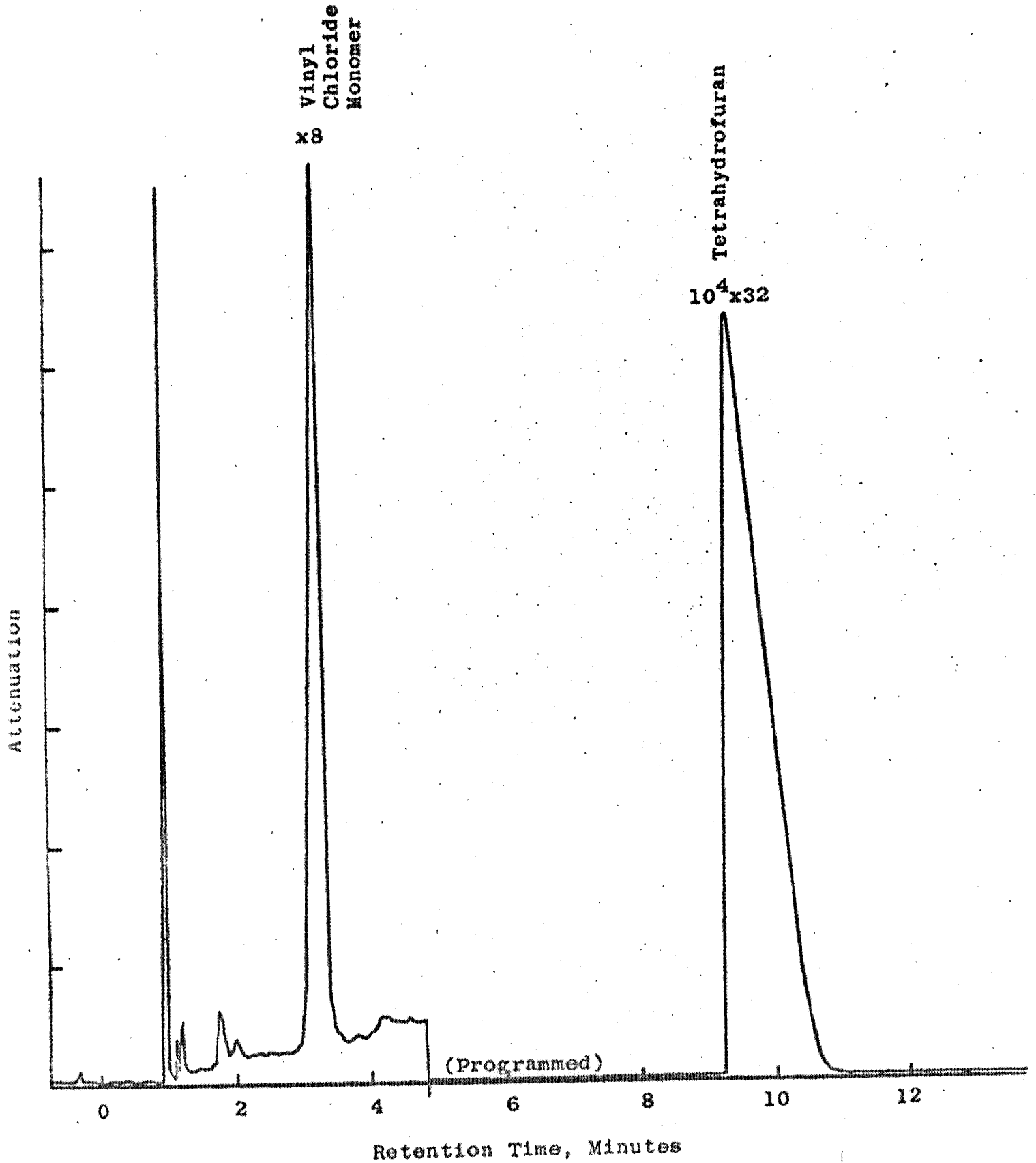


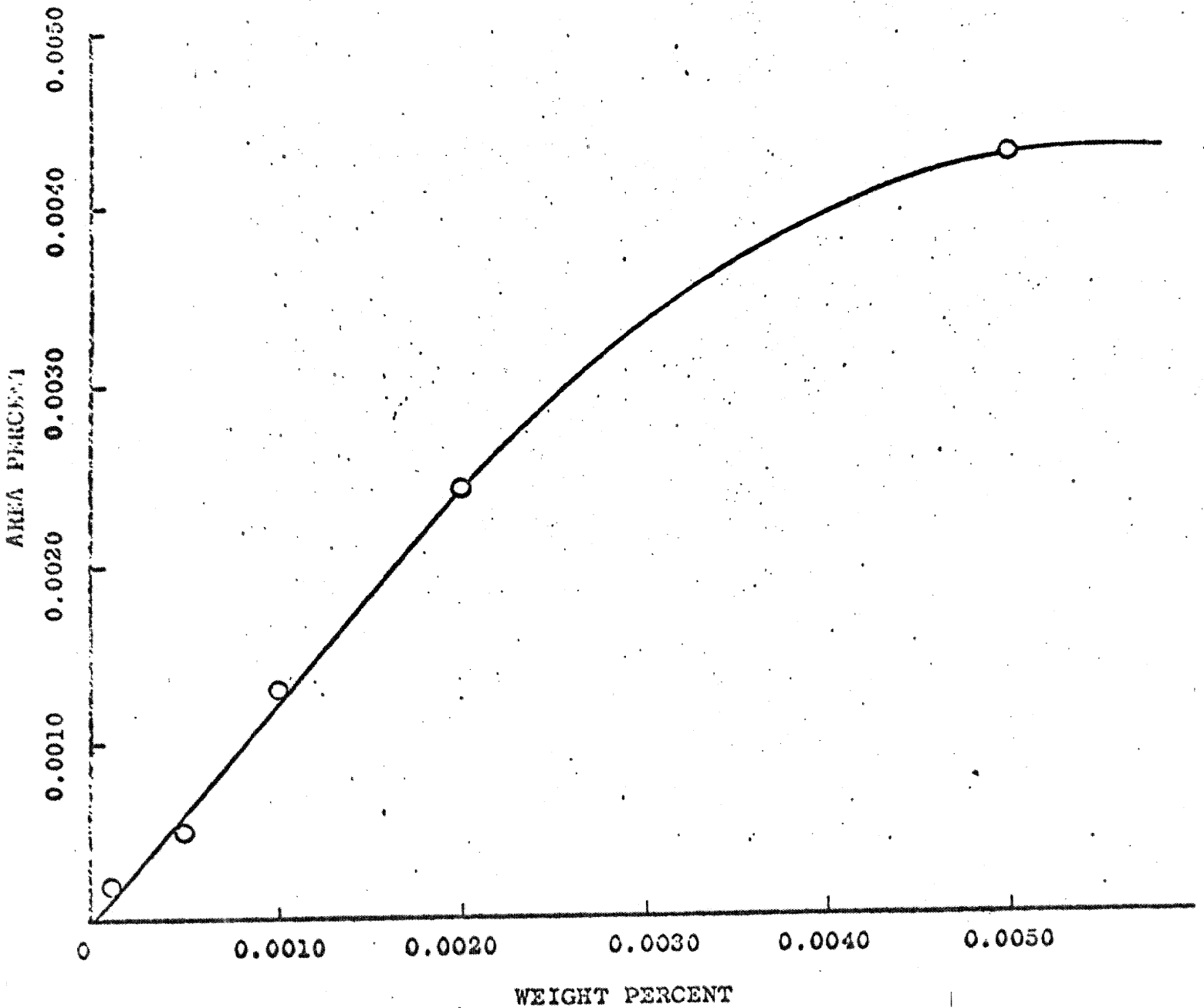
FIGURE 2

SYNTHETIC SAMPLE OF 10 PPM VINYL CHLORIDE IN THE SOLVENT  
(Sample Volume - 2 Microliters)



TYPICAL CALIBRATION CURVE

Residual Vinyl Chloride Monomer in Vinyl Resin  
Area Percent Conversion to Weight Percent



A Procedure for the Determination of Extractable Monomers from polyvinyl chloride films or coatings

The extraction apparatus, drawing attached, consists of a glass vessel with a screw-type closure and a teflon-silastic gasket. Sampling ports by a clamp capable of applying 50 inch-lb. torque to obtain effective seal. The apparatus permits sample exposure at temperatures up to 250°F without loss of monomer.

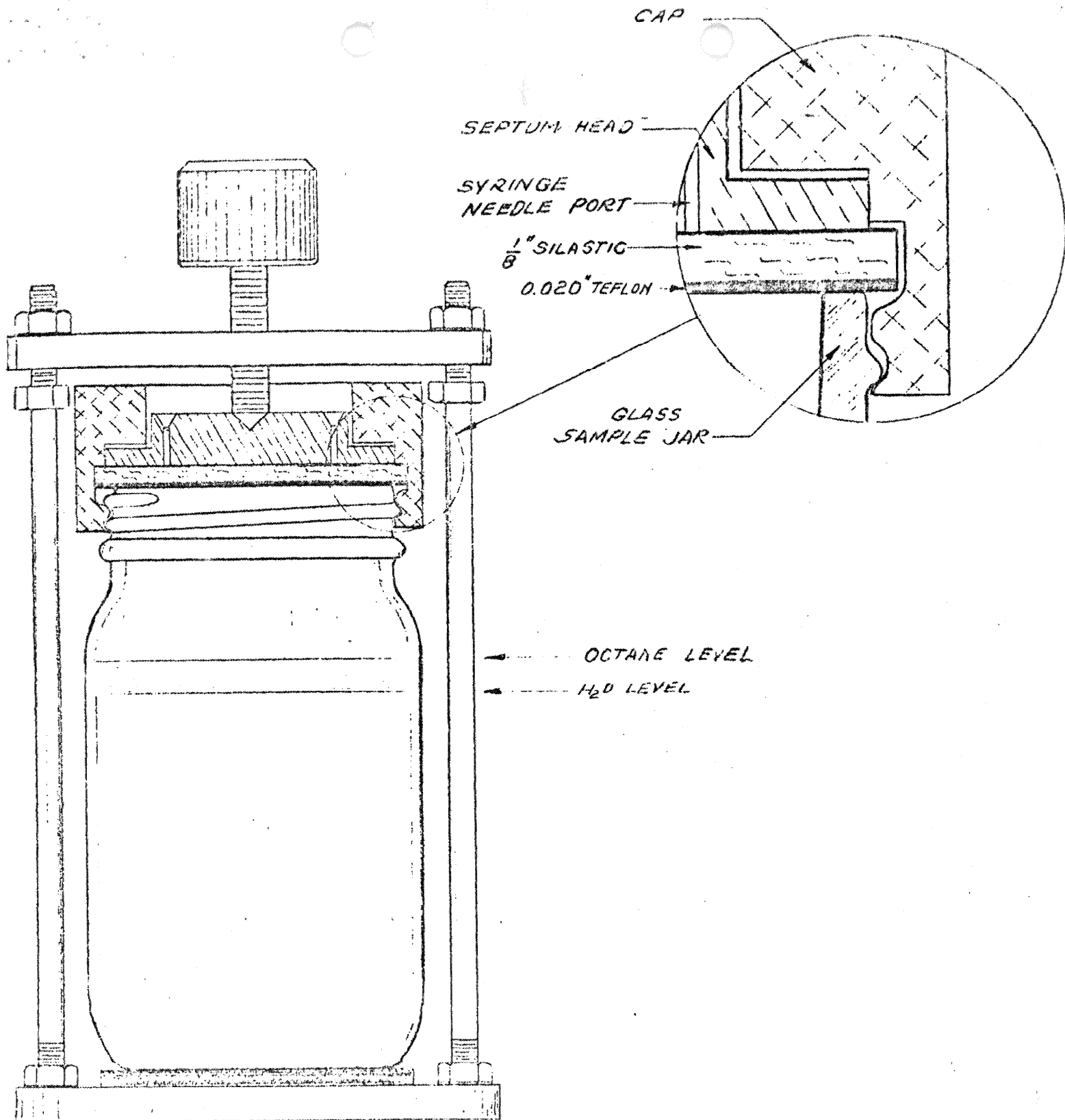
A one hundred fifty milliliter portion of water or other simulated food solvent is placed in the vessel. Following sample exposure 15 ml of n-heptane(a) is injected via a sampling port, the vessel is shaken vigorously, and monomer is recovered from the octane layer.

Known solutions of vinyl chloride monomer in water at 0.5, 1.0, and 2 ppm. were sealed in the extraction vessel and held at 250°F for 2 hours. After cooling to room temperature, 1/10 volumes of n-heptane were added, the vessels shaken, and the heptane layers sampled and analyzed for vinyl chloride monomer as described previously. Unheated controls and solvent blanks were included. The attached chromatograms show quantitative recovery of the vinyl chloride monomer.

This apparatus allows the extraction of 2 inch diameter discs cut from films on coatings and positioned horizontally in the vessel separated by appropriate spacers such as stainless steel mesh. Twenty four such discs, coated on two sides, provide a surface area of approximately 150 square inches and a surface to volume ratio of one square inch to one ml. Since the usual food container has a ratio of approximately one square inch to ten ml, this apparatus permits the assumption that undetectable levels of vinyl chloride in extract indicate less than 50 ppb in food.

(a) n-heptane, redistilled from reagent grade.

W. B. Ackart  
H. Senman  
dated: June, 1974



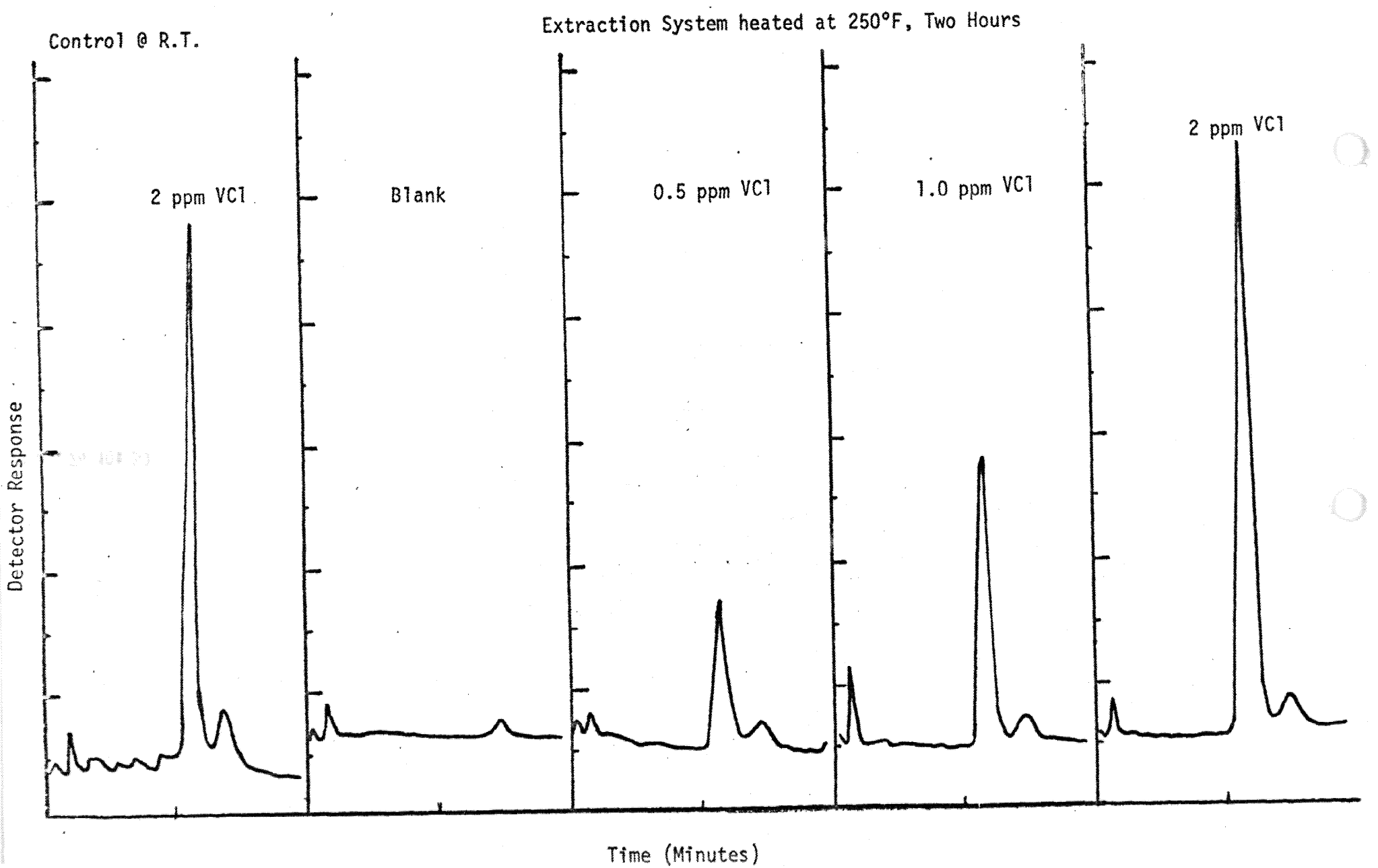
ENGINEERING DEPARTMENT  
 UNION CARBIDE CORPORATION  
 SOUTH CHARLESTON, W. VA.

SEALED SYSTEM FOR 0-250°F

DRAWN BY S.T. MARTIN DATE 6-11-74	6A-3-74 93802-06-1703
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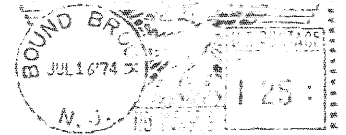
FIGURE 1

Gas Chromatograms of Aqueous VC1 Standards





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*[Handwritten signature]*  
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VIA AIR MAIL

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Food and Drug Administration  
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HFG-20