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DEC 18 1975

December 15, 1975

RESEARCH AND
DEVELOPMENT DEPARTMENT

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Managing Editor
International Scientific Communications, Inc.
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Dear Sir:

I respectfully submit a paper titled "A Sealed System for the Analysis of Vinyl Chloride" for your consideration to publish in the AMERICAN LABORATORY and INTERNATIONAL LABORATORY. This paper is original work and has not been submitted for publication elsewhere but it was presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in March, 1975. The work was performed at the Union Carbide Corporation, Chemicals and Plastics Division, Technical Center, South Charleston, West Virginia. The paper is co-authored by Messrs. A. E. Gabany, Jr. and H. Senman.

Your consideration of this paper for publication is highly appreciated.

Yours very truly,

A. E. Gabany, Jr.
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AEG, jr./dk

Attachment

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A SEALED SYSTEM FOR THE ANALYSIS
OF VINYL CHLORIDE

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SUMMARY

Recent interest by the Food and Drug Administration (FDA) to define the migration of vinyl chloride monomer from food contacting surfaces to food-simulating solvents had lead to the development of a unique sealed system to obtain the analysis. The sealed system consists of a glass jar to contain the polymer sample and extraction media, a special sealing device, and a sample holder. After the system is assembled, it is torqued tight, then incubated at an elevated temperature. Upon cooling to ambient temperature the extraction media is sampled for a gas chromatographic analysis.

Experimental data are presented, verifying that there is no loss of vinyl chloride from the aqueous and organic solvents up to 250°F. Additional analytical data are presented which confirm that vinyl chloride monomer migration into food-simulating solvents at the 50 ppb level is readily obtainable with this system.

INTRODUCTION

Vinyl chloride (bp. - 13.9°C) is widely used in polymerization reactions to make resins, homopolymers and copolymers, which are used in a diverse gamut of end products that have become an integral part of our daily lives. Until recently, it was generally believed that these polymerization reactions were complete and that essentially no residual monomer existed in the resins. However, with the advent of gas chromatography, it has been demonstrated that

detectable levels of residual monomers, eg. vinyl chloride, can exist in the resin after a polymerization reaction. Also the question of what is a detectable level has undergone much scrutiny and in the past year there has been considerable progress in lowering the detectable level.

Residual vinyl chloride monomer (VCM) determinations alone have become an industry-wide challenge, but its migration into food products through contact with the packaging materials has become an even more important subject for the Food and Drug Administration and the food-packaging industry. FDA's three-fold criteria for clean resins to assume "no reasonable expectation of migration into food" are 1) no detectable VCM in a food contact article, 2) no detectable extractions of VCM from the article into food-simulating solvent, and 3) a sound theoretical basis for predicting no migration below the detectable level.

This paper presents a method to define the migration of vinyl chloride monomer from food contacting surfaces to food-simulating solvents using specific extraction conditions defined by the Food and Drug Administration. Included in these conditions are contact periods which are maintained at above ambient temperatures. These conditions are as follows:

1. Extraction of the polymer with water at 250°F for two hours, followed by an additional lower temperature extraction whereby the extraction system is maintained at 120°F and subsequently analyzed for vinyl chloride monomer at 72-, 98-, and 120-hour intervals.

2. Three percent aqueous acetic acid extraction at 212°F for two hours followed by an additional lower temperature extraction as described with the water extraction.
3. Eight percent ethanol in water extraction at 150°F for two hours followed by the previously described lower temperature extraction.
4. Extraction of the polymer with n-heptane at 150°F for two hours followed by an additional lower temperature extraction whereby the extraction system is maintained at 120°F and analyzed for vinyl chloride monomer at 6-, 8-, and 10-hour intervals.

As is indicated, these extraction conditions require an extremely well-sealed system which prevents the escape of vinyl chloride monomer (up to 16 psig at 250°F) for the designated time periods. Also, a suitable system would have to provide proper sampling capability to the analyst.

EXTRACTION SYSTEM AND INSTRUMENTATION

A system meeting these requirements, developed and fabricated by the Measurement and Control Technology Division of Union Carbide Corporation, is exhibited in Figure I.

The system consists of a glass jar to contain the polymer sample and extraction media and a special sealing device and sample holder. The glass jar containing the sample and extraction media is capped with a 0.020" thick Teflon diaphragm: the Teflon provides an inert barrier on which there is no absorption of vinyl chloride monomer.

A Silastic septum provides a seal of the system during and after sample withdrawal. The 0.125 inch thick Silastic septum is placed on the outer Teflon surface and a 0.25 inch thick aluminum plate containing two sampling ports is then placed on the Silastic septum. These sampling ports, located near the periphery of the thicker center section, permit the withdrawal of a sample with a microsyringe. A depression located in the center of the top of the aluminum plate serves as a guide for the acceptance of a tightening screw for the assembly.

A specially designed aluminum screw-type cap installed on the glass jar serves to hold the assembly together prior to being placed in the holder. The aluminum plate is situated above the threads in the cap and thus is not tightened firmly against the Silastic septum when the cap is screwed on the jar.

A special holder is used to seal the system. After the sample assembly is placed in the holder, the screw at the top center is tightened into the center depression of the aluminum plate to seal the unit. A bottom pad of 0.125 inch thick Silastic, on which the glass jar sets gives enough flexibility to allow the application of 50 inch-pounds torque through the screw onto the aluminum plate.

The assembled sealed system is torqued tight prior to incubation at elevated temperature. For safety reasons, the entire system is placed in a canvas bag prior to applying the 50 inch-pound torque, after which the bagged system is placed in a suitable wire-formed cage container. The wire cage container containing the assembly is then heated in an air-circulating oven maintained at $\pm 1^{\circ}\text{F}$ of the desired temperature.

As stated previously, vinyl chloride has a sub-ambient boiling point of -13.9°F . It is also a hydrophobic compound; therefore, the sampling of the aqueous media for analysis required some modification of the system. The procedure used was the addition of 150 ml of aqueous extraction solvent and 15-ml of n-heptane to the system prior to sealing and subjection to the designated heat treatment. Upon cooling to ambient temperature the system was shaken vigorously thereby extracting the migrated and/or spiked vinyl chloride into the heptane layer which was sampled for analysis.

Any vinyl chloride present is distributed in the aqueous, organic and gas phases of the system with a constant distribution coefficient. The distribution ratios obtained for vinyl chloride on test samples of the various aqueous solvent extractants which had been spiked with 0.5 ppm vinyl chloride are listed in Table I. In all cases, the highest concentration of vinyl chloride is in the heptane layer, however the increased solubility effect from the aqueous organic coextractant is also evident.

The heptane layer was sampled for analysis from the glass jar by injection of a microsyringe through the septum port. A hypodermic needle of a 10 or 50 - μl syringe is long enough to penetrate through the Silastic septum and Teflon barrier into the heptane layer. After the microsyringe is filled with sample and is withdrawn, the system is self resealing due to the Silastic septum. The recovered sample is injected into a gas chromatograph for its subsequent analysis.

The gas chromatographic analyses were performed on a Hewlett-Packard (F and M) Model 5750 gas chromatograph equipped with a hydrogen flame ionization detector. The analytical column was a 6-ft. x 1/8-in. O.D. S.S. Tubing packed with Chromosorb 102, 60/80 mesh, which was operated isothermally at 100°F; however, approximately three minutes after a 10- μ l sample was injected, the temperature was manually increased to 250°F to elute the n-heptan solvent. The injection port was held at 100°F (maximum) and helium, the gas carrier, was regulated at 30 cc/minute. Using these parameters, vinyl chloride elutes at approximately 2.4 minutes.

DISCUSSION AND EXPERIMENTAL RESULTS

The system was checked to determine if it would indeed hold the vinyl chloride monomer (VCM) at the elevated temperatures. An experiment was performed which involved filling five (5) systems with 150 ml of distilled water and 15 ml of n-heptane. A stock solution of 100 ppm vinyl chloride in heptane was used to spike each container as shown in Table 2. The standard samples included no vinyl chloride, 0.5 ppm, 1.0 ppm, and two 2.0-ppm samples, one of which was a control maintained at room temperature. The other standards were heated at 250°F for two hours, and then allowed to cool to ambient temperature. Ten μ l of the heptane layer from each sample was obtained as described previously and injected into the gas chromatograph for analysis. In the last column are listed the peak heights obtained for the vinyl chloride peak for each sample.

Partial chromatograms showing the vinyl chloride peak for the five samples obtained on a Chromosorb 102 column operated at 100°C are shown in Figure 2. The peak on the left represents the vinyl chloride obtained on the ambient control sample, the next is the zero ppm heated standard, then the 0.5 ppm, the 1 ppm and to the last which was the 2.0 ppm heated standard. These data in graphic form (Figure 3) demonstrate that the detector response versus the concentration of vinyl chloride in the calibration standards is a linear relationship. More importantly, from the data, the system was judged acceptable to perform the required analysis.

Polymer samples simulating can coatings were analyzed using seventeen 2-inch diameter aluminum disks which had been coated on both sides with the test vinyl polymer. This arrangement provided a polymer surface area of 106 square inches per 165 ml of liquid or a surface-to-volume ratio of 0.7 square inch to one milliliter. Since the usual food container has a ratio of approximately one square inch to ten ml, this apparatus provides approximately a seven fold exaggeration of the usual surface-to-volume ratio.

Experimental data given in Table 3 indicate that the migration of vinyl chloride from the test polymer is less than 50 ppb to the simulated food solvents. Notice that generally all of the peak heights obtained on the extracted polymer are less than 1 mm with the exception of the acetic acid where there is a 5 and a 2-mm reading. These latter measurements actually may not represent vinyl chloride at all because of the sensitivity level at which they were

measured. The flame ionization detector electrometer was set at almost its maximum sensitivity which greatly amplifies even the slightest noise. Additionally, with the samples tested, acetic acid attack on the uncoated aluminum surface presents an unresolved difficulty.

Table 4 depicts the calculations used to establish the apparent ppb vinyl chloride migration from the gas chromatographic data. The flow scheme on the left depicts the aqueous extraction which was spiked with 0.5 ppm vinyl chloride. The vinyl chloride peak height response was 177 mm as compared to the 1 mm peak height observed from the sample on the right. From these data a factor was determined equating the vinyl chloride concentration in units of detector response. Hence, in our example the factor calculated to be 2.8 ppm/mm. This factor when multiplied by the peak height obtained for the sample under investigation determines the concentration of vinyl chloride in the system.

CONCLUSIONS

To summarize then, we have shown that a sealed system for the analysis of vinyl chloride has been developed and fabricated which is capable of sealing vinyl chloride monomer up to 16 psig at 250°F. Additionally, this system has been successfully employed for the analysis of vinyl chloride monomer migration from PVC coatings into food simulation solvents using gas chromatography as the means of detection. Vinyl chloride migration into food simulating solvents at less than 50 ppm level is readily obtainable with this system.

TABLE I

DISTRIBUTION COEFFICIENT OF
VINYL CHLORIDE MONOMER IN THE SYSTEM (AT 25°C)

	<u>WATER</u>	<u>3% ACETIC ACID</u>	<u>8% ETHANOL</u>
Head Space (Gas)	0.05	0.03	0.03
n-Heptane Phase	7.7	5.2	4.0
Aqueous Phase (as reference)	1.0	1.0	1.0

TABLE 2

LABORATORY PREPARED SYNTHETIC SAMPLES OF
VINYL CHLORIDE IN WATER AND N-HEPTANE

<u>DESCRIPTION OF THE SAMPLE</u>	<u>ML OF N-HEPTANE</u>	<u>ML OF 100 PPM VCL</u>	<u>PEAK HEIGHT OF VCL (CM)</u>
1. Blank at 250°F, 2 hours	15.0	--	N.D.
2. 0.5 ppm VCL at 250°F, 2 hours	14.2	0.8	2.8
3. 1 ppm VCL at 250°F, 2 hours	13.4	1.6	5.6
4. 2 ppm VCL at 250°F, 2 hours	11.8	3.2	11.2
5. 2 ppm Ambient Control	11.8	3.2	11.0

TABLE 3

MIGRATION OF VINYL CHLORIDE MONOMER (VCM) INTO
SIMULATED FOOD EXTRACTS

<u>DESCRIPTION OF EXTRACT</u>	<u>VCM (PEAK HEIGHT, MM)</u>	<u>MIGRATION OF VCM*, PPM</u>
A. <u>WATER:</u>		
at 250°F for 2 hours		
followed by 120°F for:		
72 hours	1.5	<0.05
96 hours	<1.0	<0.05
120 hours	<1.0	<0.05
Control (0.5 ppm VCM)	177	
B. <u>3% ACETIC ACID IN WATER:</u>		
at 212°F for 2 hours		
followed by 120°F for:		
72 hours	5	<0.05
96 hours	<1	<0.05
120 hours	2	<0.05
Control (0.5 ppm VCM)	140	
C. <u>8% ETHANOL IN WATER:</u>		
at 150°F for 2 hours		
followed by 120°F for:		
72 hours	<1	<0.05
96 hours	<1	<0.05
120 hours	<1	<0.05
Control (0.5 ppm VCM)	116	

TABLE 3 (CONTINUED)

D. n-HEPTANE:

at 150°F for 2 hours

followed by 120°F for:

6 hours	<1	<0.05
8 hours	<1	<0.05
10 hours	<1	<0.05
Control (0.5 ppm VCM)	41.5	

*Apparent migration of VCM from test coating calculated using
volume of extraction solvent and total surface area of coating

TABLE 4

CALCULATIONS FOR VINYL CHLORIDE
IN N-HEPTANE LAYER OF AQUEOUS EXTRACT

POLYMER +
0.5 PPM VCL

POLYMER

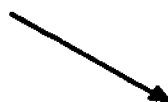
150 ML WATER (0.5 MG VCL IN SOLUTION)

150 ML WATER



15 ML HEPTANE

15 ML HEPTANE



GAS CHROMATOGRAPHIC
ANALYSIS

177 MM VCL

1 MM VCL

$$\text{FACTOR} = \frac{\Delta \text{ VINYL CHLORIDE, PPM}}{\Delta \text{ PEAK HEIGHT}}$$

$$= \frac{0.5 \text{ PPM}}{176 \text{ MM}} = 2.8 \times 10^{-3} \text{ PPM/MM}$$

$$\text{PEAK HEIGHT X FACTOR} = \text{PPM VCL IN POLYMER}$$

$$1 \text{ MM X } 2.8 \text{ PPB/MM} = 2.8 \text{ PPB}$$

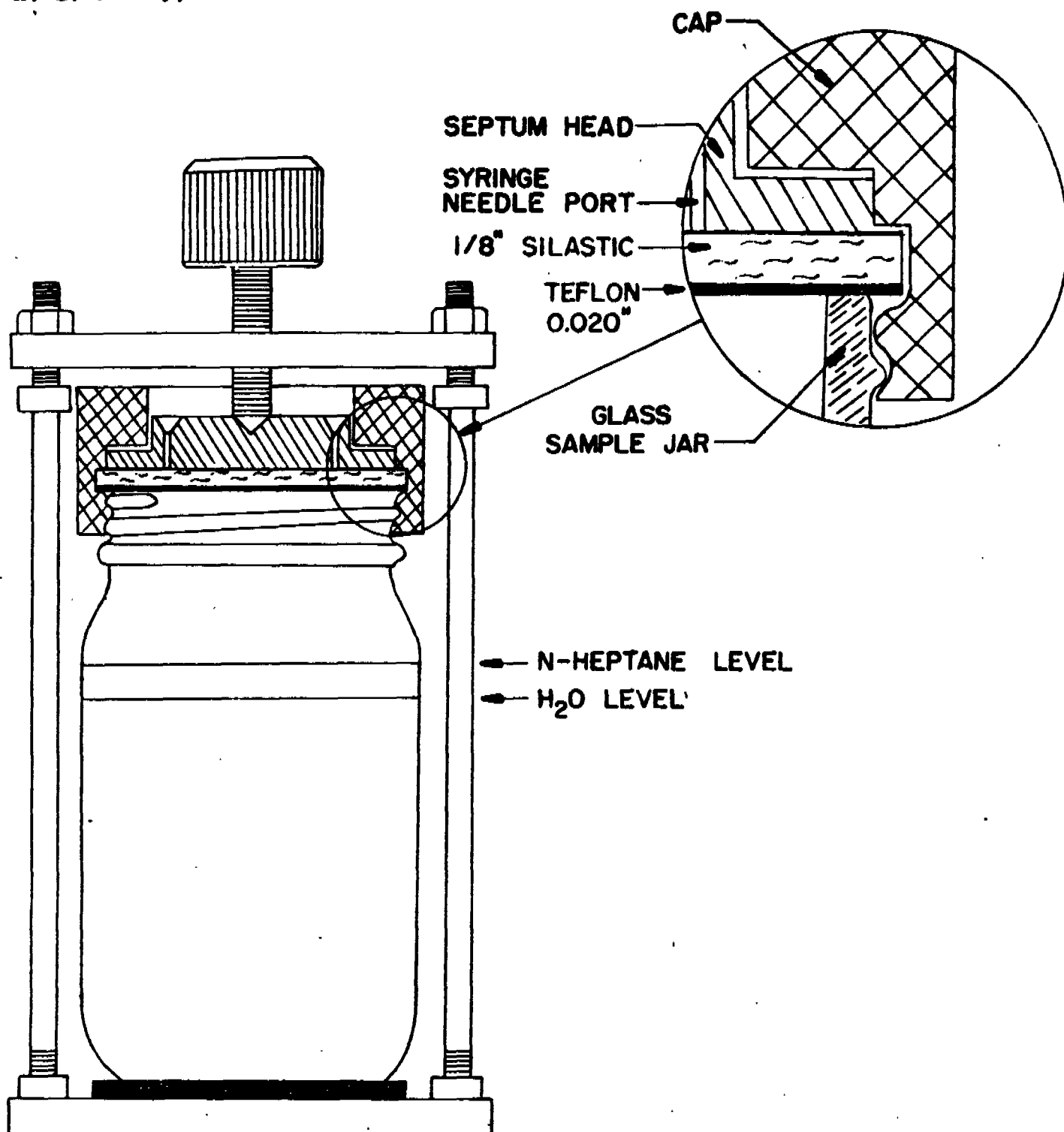


FIGURE 1'

VINYL CHLORIDE EXTRACTION SYSTEM

FIGURE 2
Gas Chromatograms of Aqueous VCI Standards

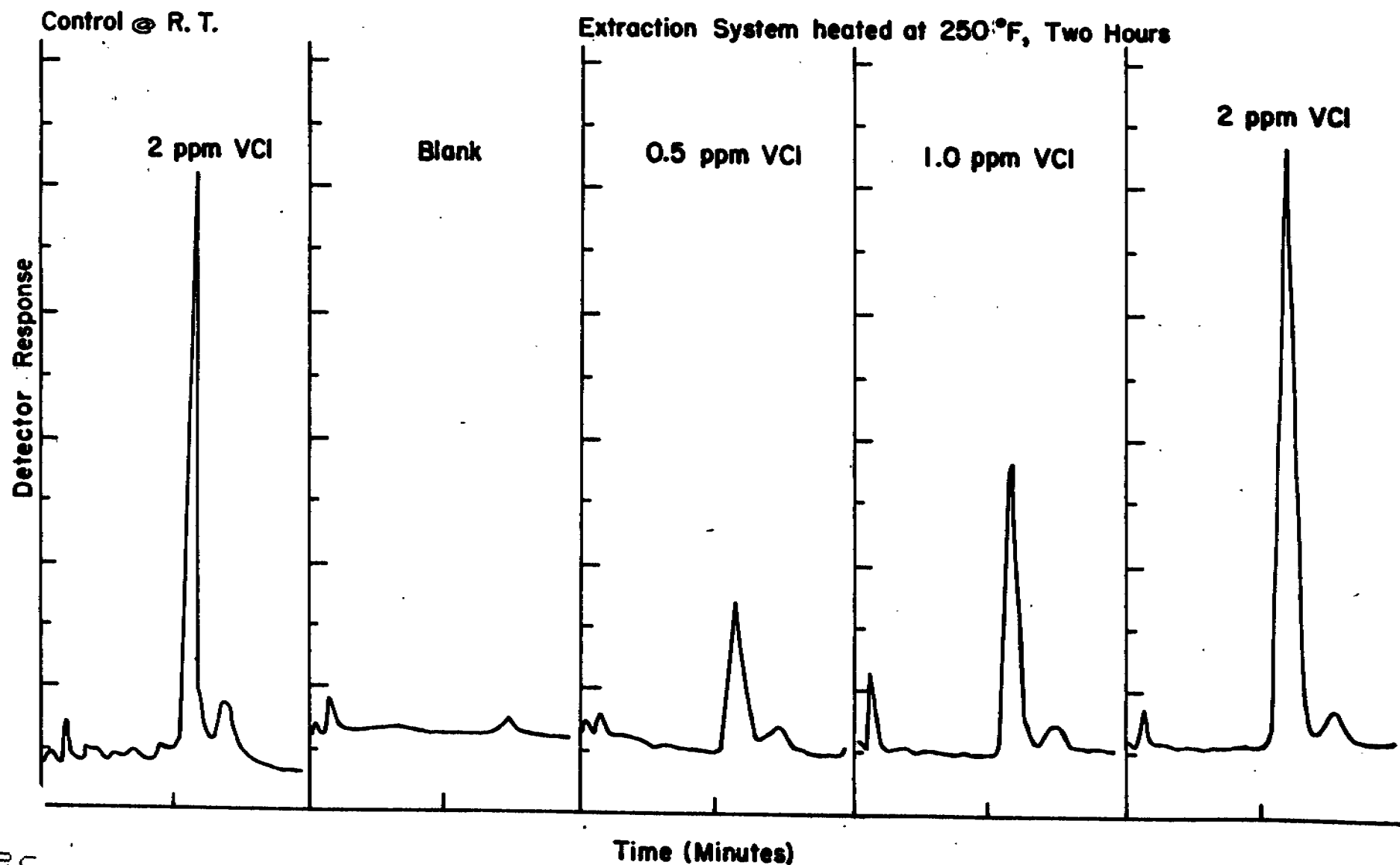
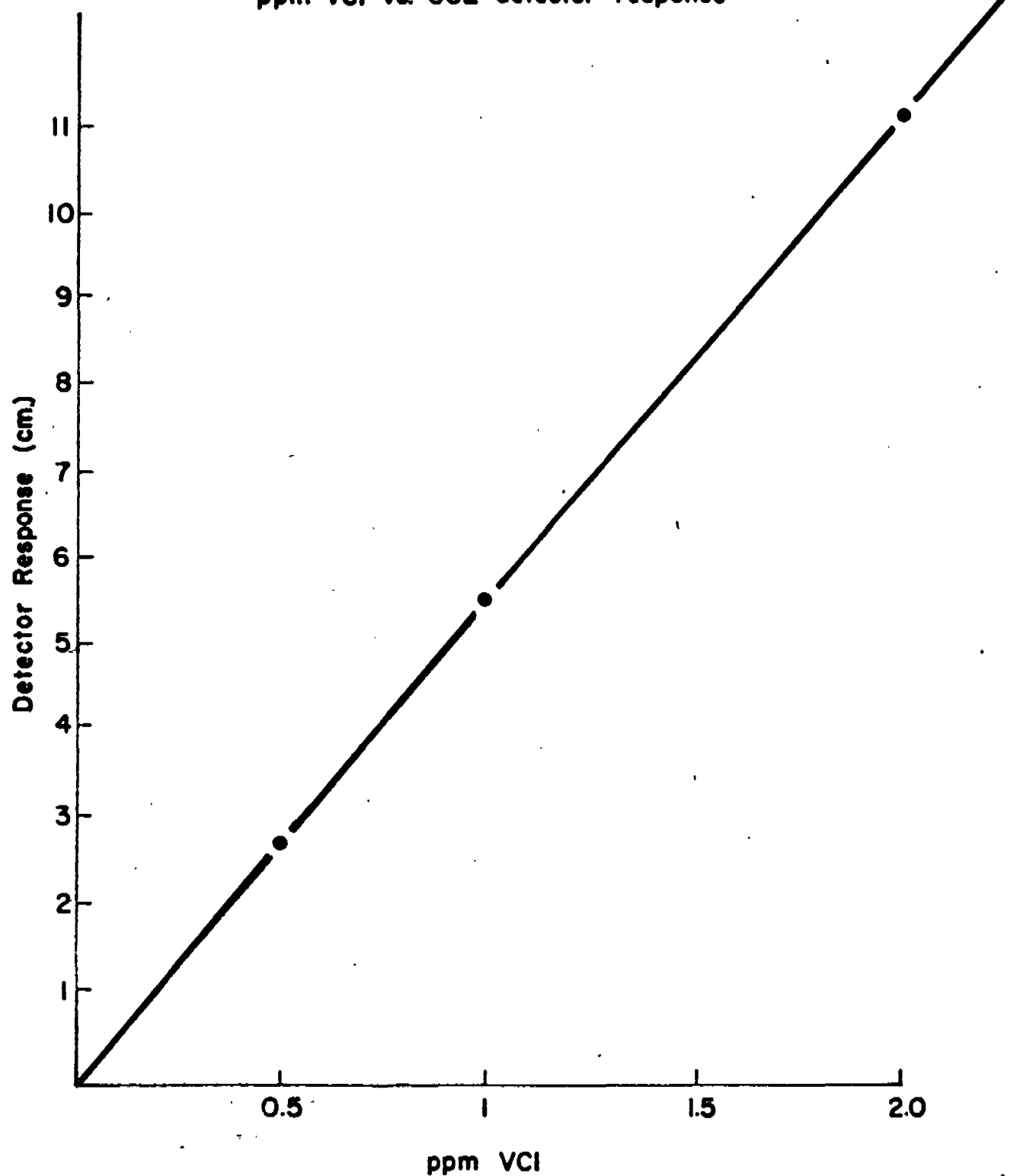


FIGURE 3

Calibration curve for
ppm VCI vs. GCL detector response



Managing Editor

December 15, 1975

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