Monsanto

MIC Applied Sciences
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Final REPORT
(TYPE OF REPORT)

#37,297

AUTHORS: M. W. Dietrich, et al
TITLE: FINAL REPORT ON SPECTROSCOPY METHODS AND SPECIAL STUDIES - 1975

REPT. NO.: 3979
COPY NO.: 1

R-1068(B)
R-1068(A)

REPORT NO.: 3979

JOB/PROJECT NO.: 43-000-760.21-8502009

DATE: April, 1976

TITLE: FINAL REPORT ON SPECTROSCOPY METHODS AND SPECIAL STUDIES - 1975

AUTHORS: M. W. Dietrich, et al

ABSTRACT: This report describes special spectroscopy studies, new techniques investigated and methods developed by the Applied Sciences Spectroscopy Group at St. Louis during 1975. The individual report sections were issued on a continuing basis during the year. These investigations were undertaken utilizing spectroscopy techniques to solve technical problems encountered by business units of Monsanto Industrial Chemicals Company.

Fifty-five special spectroscopy studies were completed and three methods developed during 1975.

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ST. LOUIS TECHNOLOGY DEPARTMENT

St. Louis Research Report No. 3979

FINAL REPORT ON

SPECTROSCOPY METHODS AND SPECIAL STUDIES - 1975

Job No. 43-000-760.21-8502009

Date: April, 1976

Work Done and Reported By:

M. W. Dietrich
L. M. Chapman
D. Guerry
D. B. Hines
B. Katlafsky
O. E. Klnast
G. W. Mappes
E. S. Tucker
H. Yepez

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I. INTRODUCTION

This report describes special spectroscopy studies, new techniques investigated and methods developed by the Applied Sciences Spectroscopy Group at St. Louis during 1975. The individual report sections were issued on a continuing basis during the year. These investigations were undertaken utilizing spectroscopy techniques to solve technical problems encountered by business units of Monsanto Industrial Chemicals Company.

II. GENERAL SUMMARY

Fifty-five special spectroscopy studies were completed and three methods developed during 1975. The studies provided data for MIC projects from the Detergent and Fine Chemicals, Food and Fine Chemicals, Plasticizer, Process Chemicals, Flavor/Essence and Specialty Products business units. Pollution control projects for the Krummrich, Nitro, Queeny and Seattle Plants and special studies involving worker safety for the Corporate Medical Department at twelve Monsanto plants or research facilities were also undertaken.

III. NEW COMPOUNDS FOR SRC

No new compounds were prepared in the course of these investigations.

IV. SPECTROSCOPY METHODS

This work is further summarized under each of the appended specific reports (Methods 75-1 to 75-4).

A. Component Index (1975)

Method No.	Component
75-1	Potassium, AA Determination in Aircraft Hydraulic Fluids
75-2	Potassium, AA Determination in Aircraft Hydraulic Fluids (Revised)
75-3	Not issued
75-4	Lead, AA Determination in U.S.P. Vanillin

IV. SPECTROSCOPY METHODS (Cont'd)

B. Product Index (1975)

Method No.	Product
75-1	Aircraft Hydraulic Fluids, Potassium Content
75-2	Aircraft Hydraulic Fluids, Potassium Content (Revised)
75-3	Not issued
75-4	Vanillin (U.S.P.), Lead Content

V. SPECTROSCOPY SPECIAL STUDIES

This work is further summarized in each of the appended specific reports (Special Studies 75-1 to 75-57).

Report No.	Title
75-1	Determination of Volatiles in Decatur, Alabama Plant Air (II)
75-2	Identification of Different Cresylic Phosphate Esters in Stauffer Fluids
75-3	Air Monitoring for Phenol at Port Plastics Plant, Addyston, Ohio
75-4	Analyses for Organics in the Air at Pensacola
75-5	Identification of Minor Components in Ethyl Benzene and Tetrachlorophthalic Anhydride
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75-7	Radioactivity in Diphenyl Oxide Intermediates, Finished Goods and Environmental Effluent
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75-9	Maleic Anhydride Refining Process Impurity
75-10	Analysis of Benzene in Air at Anniston, Alabama Plant
75-11	Analysis of Volatiles in Decatur, Alabama Plant Air (III)

V. SPECTROSCOPY SPECIAL STUDIES (Cont'd)

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75-17	Chlorodibenzo-p-Dioxins in Pentachlorophenol Treated with Morpholine
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75-19	Determination of Maleic Anhydride and Vinyl Acetate in Air: Port Plastics
75-20	Determination of Chloroprene in Air at Port Plastics Plant, Addyston, Ohio
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V. SPECTROSCOPY SPECIAL STUDIES (Cont'd)

Report No.	Title
75-28	Personnel Monitoring of PCP Unit at Nitro Plant
75-29	Bischloromethyl Ether Content of Dequest Products and Everett Plant Air
75-30	Trace Lithium Analyses - Nitro Plant Effluent (II)
75-31	Analyses of Nitro Plant Waste Waters for Trace Organic Pollutants
75-32	Determination of Volatiles in Decatur, Alabama Plant Air (V)
75-33	Tracer Lithium Analyses - Nitro Plant Effluent (III)
75-34	Determination of Trichloroethylene (TCE) in Air at Delaware River
75-35	Determination of Benzene in Air at Anniston, Alabama Plant (II)
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75-42	Determination of Aroclor 1016 in Air at Electric Utilities Company, LaSalle, Illinois
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75-44	Not Issued
75-45	Determination of Maleic Anhydride and Styrene in Air at Everett, Massachusetts

V. SPECTROSCOPY SPECIAL STUDIES (Cont'd)

Report No.	Title
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75-57	Organic Contaminants in Trenton Phosphate Products

DIRECT DETERMINATION OF POTASSIUM IN AIRCRAFT HYDRAULIC FLUIDS BY ATOMIC ABSORPTION

SCOPE

This method is intended for the direct determination of potassium in aircraft hydraulic fluids at a level of about 18-20 ppm with an estimated precision of ± 6.7% of the amount present for single analyses.

PRINCIPLE

A weighed sample of fluid for analysis is dissolved in a 1:1 (v/v) mixture of glacial acetic acid and methyl isobutyl ketone and diluted to volume with this mixed solvent. The potassium is determined by the method of standard additions in the presence of a high concentration of lithium to suppress potassium ionization in the flame.

REAGENTS

1. Standard reference solution of 1000 µg/ml potassium (Note 1).
2. Methyl isobutyl ketone (Note 2).
3. Glacial acetic acid (Note 3).
4. Solution of 1000 µg/ml lithium in 1:1 (v/v) glacial acetic acid/methyl isobutyl ketone solvent (Note 4).

APPARATUS

1. Volumetric pipets as appropriate.
2. Volumetric flasks as appropriate.
3. Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer equipped with a hollow cathode potassium source and an air/acetylene burner with a 4-inch single slot.
4. Specific instrumental conditions for the Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer:
   a. Hollow cathode lamp: Potassium (Note 5).
   b. Wavelength: 7665A.
   c. Slit: 4 (7A.).
   d. Readout: Digital, concentration mode.
   e. Burner: Titanium, 4-inch single slot (Note 6).
   f. Flame: Air/acetylene; lean, blue oxidizing.

PROCEDURE

1. Weigh accurately about 5 g of sample into a 50 ml volumetric flask (Note 7).

2. Add about 25 ml of mixed solvent, dissolve the fluid sample with agitation and dilute to volume.

3. Prepare a 2 ppm potassium standard in mixed solvent.

4. Set up the atomic absorption instrument as follows:

   a. "Concentration" and "Repeat" mode.

   b. "Onset" at 0.

   c. "Magnitude" at 0.

   d. 10 Average mode.

5. Aspirate mixed solvent into the flame and set the base line to zero with the "Auto Zero" button.

6. Prepare four standard addition (Note 8) solutions from the sample solution as follows:

   a. Aliquot 1 ml of the sample solution into four 10-ml volumetric flasks.

   b. Add 0 ml of 2 ppm potassium standard to the first flask, 1 ml of standard to the second flask, 2 ml of standard to the third flask and 3 ml of standard to the fourth flask.

   c. Add 5 ml of 1000 ppm lithium solution to each 10-ml flask.

   d. Dilute each flask to volume with mixed solvent and mix thoroughly.

   e. The standard addition concentrations are thus 0, 0.2, 0.4 and 0.6 ppm potassium.

7. Briefly aspirate the standard addition solution containing the largest amount of added potassium (0.6 ppm) and set the readout to about 0.250 (Note 9).

8. Depress the "Manual" and "100 Average" buttons.

9. Check the base line and add or subtract a small correction to each solution reading as required.

10. Measure the observed absorbance of each of the four standard addition solutions.

11. Plot the observed absorbance vs. concentration of added potassium in each solution and determine the concentration of potassium in the usual way from the intersection of the straight line with the concentration axis (Note 10).

CALCULATIONS

$$\text{ppm K} = \frac{I \times 500}{W} - C_{Li}$$

where

- I = ppm K determined from the standard addition plot, Step 11.
- W = Sample weight (g)
- C_{Li} = ppm K correction due to potassium presence in the lithium solution added to suppress potassium ionization (Note 11).

NOTES

1. Catalog No. SO-P-351, Fisher Scientific Co., Fair Lawn, N.J. 07410
2. AR grade, Catalog No. 6247, Mallinckrodt, Inc., St. Louis, Mo. 63147
3. AR grade, Catalog No. 2504, Mallinckrodt, Inc., St. Louis, Mo. 63147
4. This solution may be prepared from "potassium-free" Li_2CO_3. Spectroscopic grade Li_2CO_3 from Spex Industries, Inc., 3880 Park Ave., Metuchen, N.J., Cat. No. 1234, purity 5-9s (K content = 2-3 ppm) is satisfactory. Weigh 5.3249 g of Li_2CO_3 into a 400-ml beaker. Add slowly with gentle agitation enough glacial acetic acid to neutralize the carbonate with a small excess of acetic acid. Using 1:1 mixture of glacial acetic acid/methyl isobutyl ketone, quantitatively transfer the solution to a 100-ml volumetric flask and dilute to volume with the mixed solvent and thoroughly mix. Aliquot 10 ml of this solution to a 100-ml volumetric flask and dilute to volume with mixed solvent to obtain the 1000 µg/ml lithium solution for use in the analysis.
5. Catalog No. JA45-36052, Fisher Scientific Co., Fair Lawn, N.J. 07410. Adjust the lamp current to 5-6 MA to avoid severe self-absorption. The current of 12 MA stated on the lamp is much too high.
6. Part No. 303-0418, Perkin-Elmer Corp., Norwalk, Conn.
7. This may be easily done with a 5-ml pipet or syringe which delivers about 4.9 g of fluid.
8. Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corp., Norwalk, Conn. (revised 1968).
9. The results may be conveniently plotted on graph paper having 10 X 10 divisions to the 1/2 inch, 7 1/2 X 10 inches (Keuffel and Esser No. 46-1470) with spectrometer readout values on the ordinate with 5 divisions = 0.010. Do not turn the "Concentration" dial more than about halfway (500-600)' use a lower readout if necessary.

10. To avoid bias, the intercept of the straight line on the concentration axis is best calculated by regression analysis (least squares fit). A Texas Instruments, Model SR-51, Calculator is used for this purpose in this laboratory.

11. The Li_2CO_3 used in the development of this method of analysis was found to contain 2.6 ppm potassium by our analysis. The correction to be subtracted (C_{Li}) from each analytical result may be calculated as follows:

$$C_{Li} = \frac{(\text{ppm K in } Li_2CO_3)}{(\text{Fluid Sample Wt., W})} \times 1.33 \text{ ppm}$$

For 2.6 ppm K in Li_2CO_3 and a fluid sample weight of 5 g the correction to be subtracted would be:

$$C_{Li} = \frac{(2.6)(1.33)}{(5)} = 0.7 \text{ ppm}$$

APPENDIX

A. Precision and Accuracy of Method

A standard was prepared in the laboratory containing 18.5 ppm potassium. Five analyses of this standard by the above procedure were done with the following results:

Trial	PPM K Found
1	18.3
2	18.0
3	18.9
4	18.3
5	19.1

Statistical Data:

a. Standard Deviation = 0.46

b. Average = 18.52 ppm K

c. Standard Deviation of Average = 0.206

d. Confidence Limits for single analysis = $\pm$ 1.28 ppm K

e. Confidence Limits for five analyses = $\pm$ 0.57 ppm K

f. Precision of single analysis = $\pm$ 6.7% of amount present

g. Precision of five analyses = $\pm$ 3.0% of amount present

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Monsanto Industrial Chemicals Co.
Applied Sciences
St. Louis, Mo.

8/75 - D. Guerry, M. W. Dietrich

REVISED METHOD FOR THE DIRECT DETERMINATION OF POTASSIUM IN AIRCRAFT HYDRAULIC FLUIDS BY ATOMIC ABSORPTION

SCOPE

This method is intended for the direct determination of potassium in aircraft hydraulic fluids at a level of about 18-20 ppm with an estimated precision of ± 9.5% of the amount present for single analyses. It should be used in place of S-75-M-1.

PRINCIPLE

A weighed sample of fluid for analysis is dissolved in a 1:1 (v/v) mixture of glacial acetic acid and methyl isobutyl ketone and diluted to volume with this mixed solvent. The potassium is determined by the method of standard additions in the presence of a high concentration of lithium to suppress potassium ionization in the flame.

REAGENTS

1. Standard reference solution of 1000 µg/ml potassium (Note 1).
2. Methyl isobutyl ketone (Note 2).
3. Glacial acetic acid (Note 3).
4. Solution of 2000 µg/ml lithium in 1:1 (v/v) glacial acetic acid/ methyl isobutyl ketone solvent (Note 4).

APPARATUS

1. Volumetric pipets as appropriate.
2. Volumetric flasks as appropriate.
3. Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer equipped with a hollow cathode potassium source and an air/acetylene burner with a 2-inch single slot or a nitrous oxide burner.
4. Specific Instrumental conditions for the Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer:
   a. Hollow cathode lamp: Potassium (Note 5).
   b. Wavelength: 7665A.
   c. Slit: 4 (7A.).
   d. Readout: Digital, concentration mode.
   e. Burner: 2-inch single slot (Note 6), rotated 90° to direction of the lamp beam. The burner is rotated perpendicular to the lamp beam to reduce the effects of potassium contamination from the added lithium and from the solvent system.
   f. Flame: Air/acetylene; lean, blue oxidizing.

PROCEDURE

1. Weigh accurately about 5 g of sample into a 25 ml volumetric flask (Note 7).

2. Add about 15 ml of mixed solvent, dissolve the fluid sample with agitation and dilute to volume. Mix thoroughly.

3. Prepare a 10 ppm potassium standard in mixed solvent.

4. Set up the atomic absoprtion instrument as follows:

   a. "Concentration" and "Repeat" mode.

   b. "Onset" at 0.

   c. "Magnitude" at 0.

   d. 10 Average mode.

5. Aspirate mixed solvent into the flame and set the base line to zero with the "Auto Zero" button.

6. Prepare four standard addition (Note 8) solutions from the sample solution as follows:

   a. Aliquot 2 ml of the sample solution into four 10-ml volumetric flasks.

   b. Add 0 ml of 10 ppm potassium standard to the first flask, 1 ml of standard to the second flask, 2 ml of standard to the third flask and 3 ml of standard to the fourth flask.

   c. Add 5 ml of 2000 ppm lithium solution to each 10-ml flask.

   d. Dilute each flask to volume as required with mixed solvent and mix thoroughly.

   e. The standard addition concentrations are thus 0, 1, 2 and 3 ppm potassium.

7. Briefly aspirate the standard addition solution containing the largest amount of added potassium (3 ppm) and set the readout to about 0.250 (Note 9).

8. Depress the "Manual" and "100 Average" buttons.

9. Check the base line and add or subtract a small correction to each solution reading as required.

10. Measure the observed absorbance of each of the four standard addition solutions.

11. Plot the observed absorbance vs. concentration of added potassium in each solution and determine the concentration of potassium in the usual way from the intersection of the straight line with the concentration axis (Note 10).

CALCULATIONS

$$\text{ppm K} = \frac{I \times 125}{W}$$

where:

I = ppm K determined from the standard addition plot, Stp 11.

W = Sample weight (g).

NOTES

1. Catalog No. SO-P-351, Fisher Scientific Co., Fair Lawn, N.J. 07410.

2. AR grade, Catalog No. 6247, Mallinckrodt, Inc., St. Louis, Mo. 63147.

3. AR grade, Catalog No. 2504, Mallinckrodt, Inc., St. Louis, Mo. 63147.

4. This solution may be prepared from "potassium-free" Li_2CO_3. Spectroscopic grade Li_2CO_3 from Spex Industries, Inc., 3880 Park Ave., Metuchen, N.J., Cat. No. 1234, purity 5-9s (K content = 2-3 ppm) is satisfactory. Weigh 5.3249 g of Li_2CO_3 into a 400-ml beaker. Add slowly, with gentle agitation, enough glacial acetic acid to neutralize the carbonate with a small excess of acetic acid. Using glacial acetic acid, quantitatively transfer the solution to a 100-ml volumetric flask, dilute to volume with glacial acetic acid and thoroughly mix. Aliquot 20 ml of this solution to a 100-ml volumetric flask and dilute to volume with mixed solvent to obtain the 2000 µg/ml lithium solution for use in the analysis.

5. Catalog No. JA45-36052, Fisher Scientific Co., Fair Lawn, N.J. 07410. Adjust the lamp current to 5-6 MA to avoid severe self-absorption. The current of 12 MA stated on the lamp is much too high.

6. Part No. 303-0420 (2-inch single slot) or 303-0419 (nitrous oxide burner), Perkin-Elmer Corp., Norwalk, Conn.

7. This may be easily done with a 5-ml pipet or syringe which delivers about 4.9 g of fluid.

8. Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corp., Norwalk, Conn. (revised 1968).

9. The results may be conveniently plotted on graph paper having 10 X 10 divisions to the 1/2 inch, 7 1/2 X 10 inches (Keuffel and Esser No. 46-1470) with spectrometer readout values on the ordinate with 5 divisions = 0.010. Do not turn the "Concentration" dial more than about halfway (500-600); use a lower readout if necessary.

10. To avoid bias, the intercept of the straight line on the concentration axis is best calculated by regression analysis (least squares fit). A Texas Instruments, Model SR-51, Calculator is used for this purpose in this laboratory.

APPENDIX

Precision and Accuracy of Method

A standard was prepared in the laboratory calculated to contain 21.5 ppm potassium. Five analyses of this standard by the above procedure were done with the following results:

Trial	PPM K Found
1	22.3
2	22.2
3	22.5
4	23.0
5	24.1

Statistical Data:

1. Standard Deviation = 0.78
2. Average = 22.82 ppm K
3. Standard Deviation of Average = 0.348
4. 95% Confidence Limits for single analysis = $\pm$ 2.16 ppm K
5. 95% Confidence Limits for five analyses = $\pm$ 0.97 ppm K
6. Precision of single analysis = $\pm$ 9.5% of amount present
7. Precision of five analyses = $\pm$ 4.3% of amount present

ss

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St. Louis, Mo.

11/75 - D. Guerry, M. W. Dietrich

DETERMINATION OF TRACE LEAD IN U.S.P. VANILLIN BY FLAMELESS ATOMIC ABSORPTION

SCOPE

This method is intended for the determination of lead in U.S.P. vanillin at a level of about 0.1 ppm with an estimated precision of ± 22% (95% confidence limits) of the amount present for single analyses.

PRINCIPLE

A weighed sample for analysis is digested with concentrated nitric acid and 30% hydrogen peroxide, and made up to volume with water. The lead is determined by the method of standard additions using a flameless atomic absorption technique with a graphite furnace atomizer.

REAGENTS

1. Standard reference solution of 1000 µg/µl lead (Note 1).

2. Concentrated nitric acid (Note 2).

3. Hydrogen peroxide, 30% (Note 3).

APPARATUS

1. Hot plate.
2. Volumetric pipets as appropriate.
3. Volumetric flasks as appropriate.
4. Beakers as appropriate.
5. Eppendorf pipette, 25 microliter volume (Note 4).
6. Perkin Elmer Model 303 Atomic Absorption Spectrophotometer equipped with a hollow cathode lead source, a deuterium background corrector and a graphite furnace atomizer for flameless atomic absorption analysis.
7. Specific instrumental conditions for the Perkin Elmer Model 303 Atomic Absorption Spectrophotometer:

    a. Hollow cathode lamp: Lead (Note 5).
    b. Wavelength: 2833 A.
    c. Slit: 4 (7A).
    d. Readout: Recorder (Note 6): Chart speed 0.75 in/min, noise suppression 1, scale expansion X1.
    e. Graphite furnace atomizer: Graphite tube type (Note 7): Drying, 150°C for 30°sec.; Ashing, 700°C for 30 sec.; Atomization, 2500°C for 8 sec. Nitrogen gas purge rate at 30.

PROCEDURE

1. Weigh accurately about 2 g of sample into a 400-ml beaker.

2. Add slowly and continuously 25 ml of concentrated HNO_3 and allow to stand until the initial reaction has moderated.

PROCEDURE (Cont'd)

3. Place on a hot plate, set at "Medium" and boil off HNO_3 down to about 5 ml.

4. Add 5 ml of 30% hydrogen peroxide.

5. Boil off excess liquids down to about 2-3 ml, remove from the hot plate and cool.

6. Quantitatively transfer to a 10-ml volumetric flask and dilute to volume with water.

7. Prepare a 0.4 µg/ml lead standard.

8. Prepare three standard addition (Note 8) solutions from the sample solution as follows.

   a. Aliquot 3 ml of the sample solution into three 10-ml volumetric flasks.
   b. Add 0 ml of 0.4 µg/ml lead standard into the first flask, 1 ml of standard into the second flask and 2 ml of standard into the third flask.
   c. Dilute each flask to volume and mix thoroughly.
   d. The standard addition concentrations are thus 0, 0.04 and 0.08 µg/ml of lead, and 25 microliters (0.025 milliliter) of each of these solutions give 0, 1 and 2 nanograms of lead respectively.

9. Turn on the recorder and press the "High Temperature" button for 2-3 seconds to clean the graphite furnace before introducing samples for analysis. Note any response (peaks) on the recorder, and continue the cleaning intervals until any peak disappears.

10. Using an Eppendorf pipette, introduce a 25 microliter aliquot of each sample solution in turn into the graphite furnace and atomize each according to the temperature program previously set.

11. Run each solution at least twice and average the peak absorbance values.

12. Plot the observed absorbance vs. concentration of added lead in each solution (absorbance vs. nanograms lead/25 microliters solution) and determine the concentration of lead in the usual way from the intersection of the straight line with the concentration axis (Note 9).

CALCULATIONS

$$\text{ppm Pb} = \frac{I \times 1.333}{W}$$

where I = Intersection of the standard addition plot with the concentration axis, Step 12 (nanograms Pb/25 microliters)

W = Sample weight (g)

PRECISION AND ACCURACY OF METHOD

Five standards were prepared in the laboratory by adding 0.5 ppm lead to 2-g samples of U.S.P. vanillin. These five lead-spiked standards along with five 2-g blanks of U.S.P. vanillin treated to remove lead (Note 10) were analyzed according to the above procedure. The following results were obtained:

Trial	Blank (ppm Pb)	Spiked (ppm Pb)
1	0.095	0.622
2	0.012	0.712
3	0.083	0.646
4	0.115	0.754
5	0.198	0.655
Average:	0.1006	0.6778
Stand. deviation:	0.0669	0.0539
Stand. deviation average:	0.0299	0.0241

Difference: Spiked-Blank

(a) Average, difference = 0.5772

(b) Stand. deviation, difference = 0.0859

(c) Stand. deviation, average difference = $0.0859/\sqrt{10} = 0.0272$

For 5 duplicate analyses, average difference: 0.577 ppm Pb $\pm$ 10.9% relative found.

For a single analysis of a spiked standard: 0.678 ppm Pb $\pm$ 22% relative found.

NOTES

1. Catalog No. SO-L-21, Fisher Scientific Co., Fair Lawn, N.J. 07410
2. B&A Electronics Grade, Code 108-2677, Allied Chemical Co., Specialty Chemicals Division, P.O. Box 1087 R, Morristown, N.J. 07960.
3. Catalog No. 5240, Mallinckrodt, Inc., St. Louis, Mo. 63147.
4. Catalog No. 21-370D, Fisher Scientific Co., Fair Lawn, N.J. 07410.
5. Catalog No. JA45-36039, Fisher Scientific Co., Fair Lawn, N.J. 07410.

NOTES (Cont'd)

6. Servo-riter II, Texas Instruments, Inc., Dallas, Texas 75222.

7. Model HGA-2100 Graphite Furnace, The Perkin Elmer Corp, Norwalk, Conn.

8. Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin Elmer Corp., Norwalk, Conn. (revised 1968).

9. To avoid bias, the intercept of the straight line on the concentration axis is best calculated by regression analysis (least squares fit). A Texas Instruments, Model SR-51, calculator is used for this purpose in this laboratory.

10. U.S.P. vanillin was dissolved in 1:1 (v/v) isopropyl alcohol/water solvent and 15% of its weight of Imac TMR thiol resin (Akzo Chemie, Netherlands) was added. The mixture was stirred overnight, the resin filtered off and the vanillin was recrystallized from the solution. Thiol ion-exchange resins are reported to be efficient in removing heavy metals such as lead. No effort was made to determine whether the apparent 0.1 ppm Pb in the treated vanillin was actually Pb or a background effect. Analyses of 10 random lots of U.S.P. vanillin (untreated) showed an average level of 0.12 ppm and a range of 0.05 to 0.24 ppm Pb.

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St. Louis, Mo.

12/75 - D. Guerry, M. W. Dietrich

ANALYSIS OF VOLATILES IN DECATUR, ALABAMA PLANT AIR (II)

INTRODUCTION

This is an investigation to determine concentration levels of vinyl bromide (VBr), vinyl acetate (VA), and acrylonitrile (AN) in air at the North polymer area of the Decatur, Alabama plant. The data obtained will be used to determine exposure levels to the worker in this area.

SUMMARY

Results of the study are found in the attached table. GC retention times for VA and AN were so similar under these conditions that they could not be used to distinguish between them. Only one sample contained either, and this was at a level too low for identification with our existing mass spectrometer. VBr was observed and identified by GC/MS at levels from $\leq$0.03 ppm to 8.15 ppm. Only one sample contained an unknown, at a concentration of $\sim$0.06 ppm as shown in the table. None of the samples contained detectable levels of vinyl chloride or vinylidene chloride.

EXPERIMENTAL

Refer to Spectroscopy Special Study 74-32 for procedure.

A sample calculation is listed below. Values were based on a vinyl bromide standard.

Calculation

Volume sampled = flow rate (ml/min.) x minutes x 10^{-3}

ex: L3

Volume sampled = 44 ml/min. x 60 min. x 10^{-3} = 2.64 L

$$\text{Weight Sample} = \text{sample area (counts)} \times \frac{\text{x std. conc. } (\mu g)}{\text{x std. area (counts)}}$$

ex: L3, VBr

$$122340 \times \frac{2.6}{3342} = 96\ \mu g = \text{wt. sample}$$

Concentration sample $\mu g/L$ = wt. sample/volume sampled

conc. $\mu g/L$ = 96 μg/2.64 L = 36.3 $\mu g/L$

Concentration (ppm) = $\mu g/L$ x .024/MW x 1000

= 36.3 x .024/107 x 1000 = 8.1 ppm

VBr std. 2.6 $\mu g/\mu L$ x 1 μL

Reference: GC/MS File #75-4.

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	Concentration (ppm)			
Sample	VBr	[3]AN	[3]VA	Unknown
L-3	8.1	x ≤0.07	x ≤0.05	
L-4	0.7	x ≤0.07	x ≤0.05	
L-7	≤0.03	x ≤0.07	x ≤0.05	
L-11	≤0.03	0.1	0.07	~0.06 ppm
L-12	≤0.03	x ≤0.07	x ≤0.05	
L-5	blank			

x None detected

[1] L-3 and L-4 used the millipore M-2 pump for sampling with a flow rate of 44 ml/min.

[2] L-7, L-11 and L-12 used the air check SKC 222-451 pump for sampling with a flow rate of 17 ml/min.

[3] Note AN and VA have the same retention time and values are based on individual molecular weight. Since the concentration is so low, mass spectrometric confirmation was not attainable.

Special Study
S-75-SS-2

IDENTIFICATION OF DIFFERENT CRESYLIC PHOSPHATE ESTERS IN STAUFFER FLUIDS

SUMMARY

Three samples of fluids from Stauffer Chemical Company showed significant differences in the type of phosphate ester used. The esters were found to range from a cresyl diphenyl phosphate type to a very highly substituted phosphate ester.

DISCUSSION

NMR shows that the phosphate esters in three Stauffer fluids, 149 ELT, FQ 150, and FQ SCF, are cresyl type esters. That is, any substitution on the basic triphenyl phosphate molecule is mainly methyl substitution on the aromatic portion of the molecule. Some ethyl substitution is also present in these fluids and this is probably the result of ethyl phenols being present in cresols.

The GC traces of these fluids, however, are quite different as shown in the figure. The ester in 149 ELT is basically a cresyl diphenyl phosphate with a significant amount of triphenyl phosphate and dicresyl phenyl phosphate. The phenol analysis on the bomb hydrolized esters is shown in the table. The high percentage of phenol for 149 ELT is consistent with the large amount of triphenyl phosphate and cresyl diphenyl phosphate in this ester.

The ester in FQ 150 is a dicresyl phenyl type with a small amount of triphenyl phosphate. The ester in SCF is even higher boiling and is on the average tricresyl phosphate or xylyl dicresyl phosphate. The low level of phenol in the table and the large amount of xylenols agree with the high boiling characteristics of the ester.

GC/MS analyses of the phenols from bomb hydrolysis is in basic agreement with the identifications done at J. F. Queeny Plant by retention time. Some changes in the identifications were made because of the GC/MS data and these are clearly indicated.

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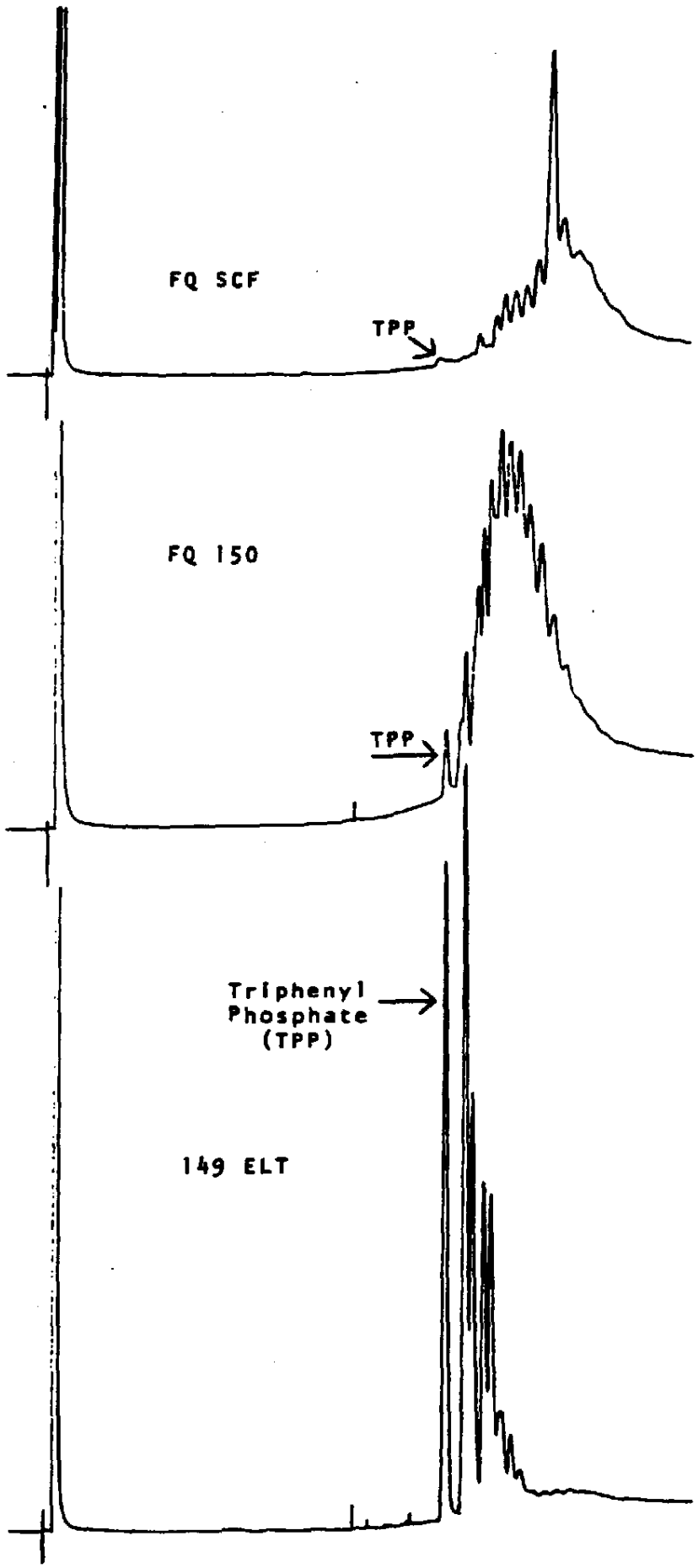
1/75 - G. W. Mappes, M. W. Dietrich



RSV 0010550

TABLE

PHENOL ANALYSIS OF BOMB HYDROLIZED FLUIDS

J. F. QUEENY PLANT

19-DEC-74 TIME: 16:13
COMPETITIVE PHOSPHATE ESTER HYDROLYZATES
FC-149ELT LOT #4022-4-2 MIC-255215

NORMALIZATION COMPUTATIONS

TIME	AREA	FACTOR	PCT	
47				
64	553392	1.0000	50.49	PHENOL
68	8654	1.0000	0.81	O-CRESOL
75	329738	1.1000	33.09	M&P-CRESOL
91	19119	1.0000	1.74	2,6-XYLENOL
100	25565	1.0000	2.33	O-ETHYLPHENOL
107	44688	1.0000	4.08	2,4&2,5-XYLENOLS
120	43437	1.0000	3.96	M&P-ETHYLPHENOL, 3,5-XYLE
132	18718	1.0000	1.71	2,3-XYLENOL
146	17896	1.0000	1.63	3,4-XYLENOL
176	765	1.0000	0.07	TRIALKYLPHENOLS AND
200	829	1.0000	0.08	HIGH BOILERS

19-DEC-74 TIME: 16:12
COMPETITIVE PHOSPHATE ESTER HYDROLYZATES
FC-150 #3503-3-1

NORMALIZATION COMPUTATIONS

TIME	AREA	FACTOR	PCT	
45	54885	1.0000	18.27	PHENOL
66	37282	1.0000	12.41	O-CRESOL
73	100038	1.1000	36.64	M&P-CRESOL
91	2671	1.0000	0.89	2,6-XYLENOL
100	2878	1.0000	0.96	O-ETHYLPHENOL
106	33622	1.0000	11.19	2,4&2,5-XYLENOLS
119	38931	1.0000	12.96	M&P-ETHYLPHENOL, 3,5-XYLE
132	6923	1.0000	2.31	2,3-XYLENOL
145	7153	1.0000	2.38	3,4-XYLENOL
162	1355	1.0000	0.45	
175	1876	1.0000	0.62	TRIALKYLPHENOLS & HI BOIL
199	2728	1.0000	0.91	

19-DEC-74 TIME: 16:15
COMPETITIVE PHOSPHATE ESTER HYDROLZATES
MIC-255258 FYFCUEL SCF #4181-1-1

NORMALIZATION COMPUTATIONS

TIME	AREA	FACTOR	PCT	
46	92260	1.0000	5.89	PHENOL
61	176688	1.0000	11.28	~~UNKNOWN~~ O-CRESOL
67	6915	1.0000	0.44	~~O-CRESOL~~ UNKNOWN
74	153721	1.1000	10.79	M,P-CRESOL
91	6751	1.0000	0.43	2,6-XYLENOL
100	7827	1.0000	0.50	O-ETHYLPHENOL
108	261382	1.0000	16.68	2,4&2,5-XYLENOL
124	390971	1.0000	24.96	M&P-ETHYLPHENOL, 3,5-XYLE
133	91734	1.0000	5.86	2,3-XYLENOL
145	89811	1.0000	5.73	3,4-XYLENOL
161	28454	1.0000	1.82	
173	44711	1.0000	2.85	TRIALKYLPHENOLS AND
194	48802	1.0000	3.12	OTHER HIGH BOILERS
209	27787	1.0000	1.77	
227	7015	1.0000	0.45	
245	116378	1.0000	7.43	TRIALKYLPHENOLS

Special Study
S-75-SS-3

AIR MONITORING FOR PHENOL AT PORT PLASTICS PLANT, ADDYSTON, OHIO

INTRODUCTION

This study was made to determine levels of phenol and alkylbenzenes being evolved in the cooling process of phenol formaldehyde resin at the Port Plastics Plant, Addyston, Ohio.

SUMMARY

The level of phenol in air while the alkylated product was being dropped for cooling was about 23 ppm. A sampling from the second floor gave a level of about 1.4 ppm and a sampling when no product was on the cooling floor gave none detected (<0.8 PPM).

EXPERIMENTAL

A Tenax GC glass insert was used for collection of phenol in air and a Tenax GC served as the analytical column. The Bendix pump Model C115 with a flow rate of 120 ml/min provided the means of sampling the air. See attached table for results. Sampling was made for two minutes.

SAMPLE CALCULATIONS

$$\frac{\text{Concentration of Std}}{\text{Area of Standard}} \times \text{Area of Sample} = \text{Concentration}$$

Example IX $\frac{7.5\ \mu g}{37413} \times 108241 = 21.7\ \mu g$

$$10^{-3} \times \text{Flow Rate} \times \text{Time of Sample} = \text{Volume}$$

Example IX $10^{-3} \times 120\ \text{ml/min} \times 2\ \text{min} = 240\ \text{ml} \times 10^{-3} = .24\ \text{l}$

$$\frac{\text{Conc}}{\text{Volume}} = \mu g/l$$

Example IX $21.7\ \mu g/.240\ l = 90\ \mu g/l$

$$\mu g/l \times 1000 \times \frac{.024}{\text{mol wt}} = \text{ppm}$$

Example IX $90 \times 1000 \times \frac{.024}{94} = 23.1\ \text{ppm}$

REFERENCE: MS File #75-23.

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2/75 - L. M. Chapman, M. W. Dietrich

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TABLE

	Phenol	Alkylbenzenes	Comments
I	ND (<0.8 ppm)	ND (<0.8 ppm)	Blank
II	ND (<0.8 ppm)	ND (<0.8 ppm)	2 Min. Sampling
IX	23 ppm	1.5 ppm	2 Min. Sampling
XI	1.4 ppm	ND (<0.8 ppm)	2 Min. Sampling
XIV	ND (<0.8 ppm)	ND (<0.8 ppm)	Not used
XVI	ND (<0.8 ppm)	ND (<0.8 ppm)	Not used

Special Study
S-75-SS-4

ANALYSES FOR ORGANICS IN AIR AT PENSACOLA

INTRODUCTION

Analyses were performed to identify and determine levels of organics in the air from the nylon molding resin process at Pensacola. Main compounds of interest are caprolactam and Dechlorane 25.

SUMMARY

Caprolactam in levels from 0.08-8.6 ppm and 0.03 ppm of tolualdehyde (1 sample only) was found. Dechlorane 25 could not be detected under the GC conditions used. It is questionable whether the method can be modified to measure Dechlorane 25. No other organics were found with a detection limit of 0.02 ppm.

EXPERIMENTAL

A 0.15 Tenax GC glass insert was used for collection with a SKC model 222-451 pump. Thirty minute samples were taken with a flow rate of 60 mℓ/min. See attached table for results.

CALCULATIONS

A) $\text{Concentration } (\mu g) = \frac{\text{Concentration of Std } (\mu g)}{\text{Area of Std}} \times \text{Area of Sample}$

B) $\text{Volume (Liters)} = \text{Flow Rate } (m\ell/\text{min}) \times \text{Time of Sample (min)} \times 10^{-3}$

C) $\mu g/\ell = \frac{\text{Concentration } (\mu g)}{\text{Volume } (\ell)}$

D) $\text{ppm} = \mu g/\ell \times \frac{24.5}{\text{Molecular Weight}}$

Example

(Die Face) Caprolactum

A) C = 6.15 µg/ 6.10 X .80 = .81 µg

B) V = 10^{-3} X 60 mℓ/min X 30 = 1.8ℓ

C) µg/ℓ = .81/1.8 = .45

D) ppm = .45 X 24.5/113 = 0.10 ppm

Reference: MS File #75-30

db

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TABLE I

	Caprolactam	Tolualdehyde
Extruder Nozzle(V)	8.6 ppm	0.03 ppm
Extruder Hopper(III)	N.D. (<.02 ppm)	
Die Face(VII)	0.10 ppm	
Change Desk(VIII)	0.16 ppm	
Operator(X)	N.D. (<.02 ppm)	
Extruder Nozzle(XII)	0.08 ppm	

No other organics were detected.
Detection limit 0.02 ppm.

Special Study
S-75-SS-5

IDENTIFICATION OF MINOR COMPONENTS IN ETHYL BENZENE AND TETRACHLOROPHTHALIC ANHYDRIDE

INTRODUCTION

This analysis was performed to identify unknown components in ethylbenzene and tetrachlorophthalic anhydride (TCPA) which might inhibit catalyst performance at the Delaware River Plant.

SUMMARY

The results of the analysis are shown in Table I and in attached GC/MS chromatograms.

EXPERIMENTAL

GC conditions are given in Table II. The ethylbenzene was also run on a flame photometric GC in the sulfur detection mode. The latter confirmed that no volatile sulfur compounds were present.

Reference: MS File #75-40.

db

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TABLE I

ETHYLBENZENE

Peak*	Identification
1	Benzene
2	MW 98: possibly dimethyl or methyl pentanone
3	MW 100: possibly methyl isobutyl ketone or hexanone or methyl pentanone
4	Toluene
5	MW 112: possibly dimethyl cyclohexane or trimethyl pentene
6	MW 112: possibly acrolein dimer or dimethyl hexene

*See attached chromatogram for peak number reference

Peak*	TCPA Identification
1	Tetrachlorobenzene
2	Pentachlorobenzene
3	Hexachlorobenzene

TABLE II

A HP 5700 GC and HP 5980 mass spectrometer were used for identification analysis using one micro-liter injection of the neat solution.

Conditions for Ethylbenzene

Column: 3% OV 101 1m with a 1/8" I.D.

Program: 0° - 70°C @ 4°/Min

Mass Gain: 5

Mass Scan: 10-400 amu

Conditions for TCPA

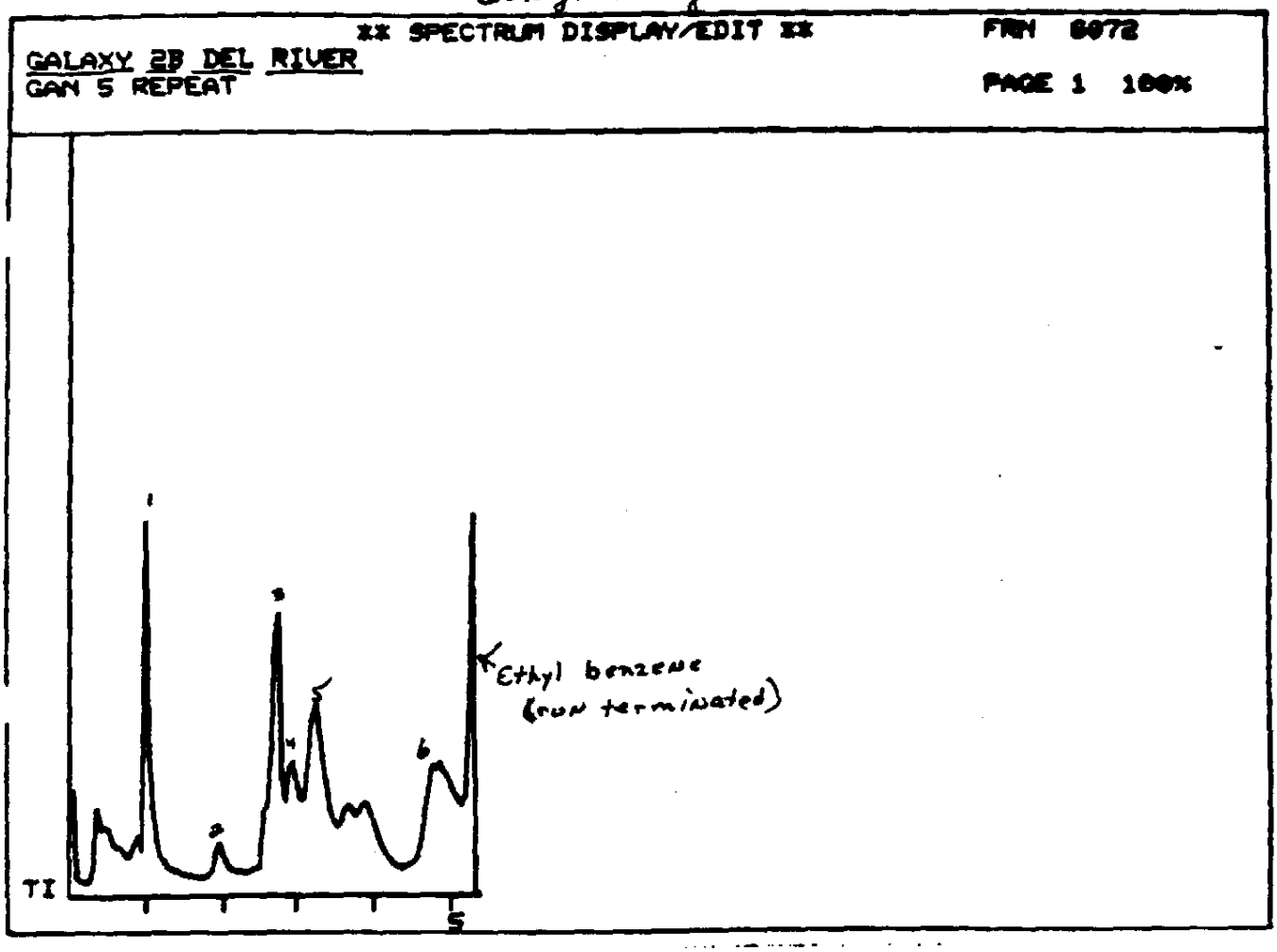
Column: 3% OV 101 1m with 1/8" I.D.

Program: 100-160 @ 8°/Min

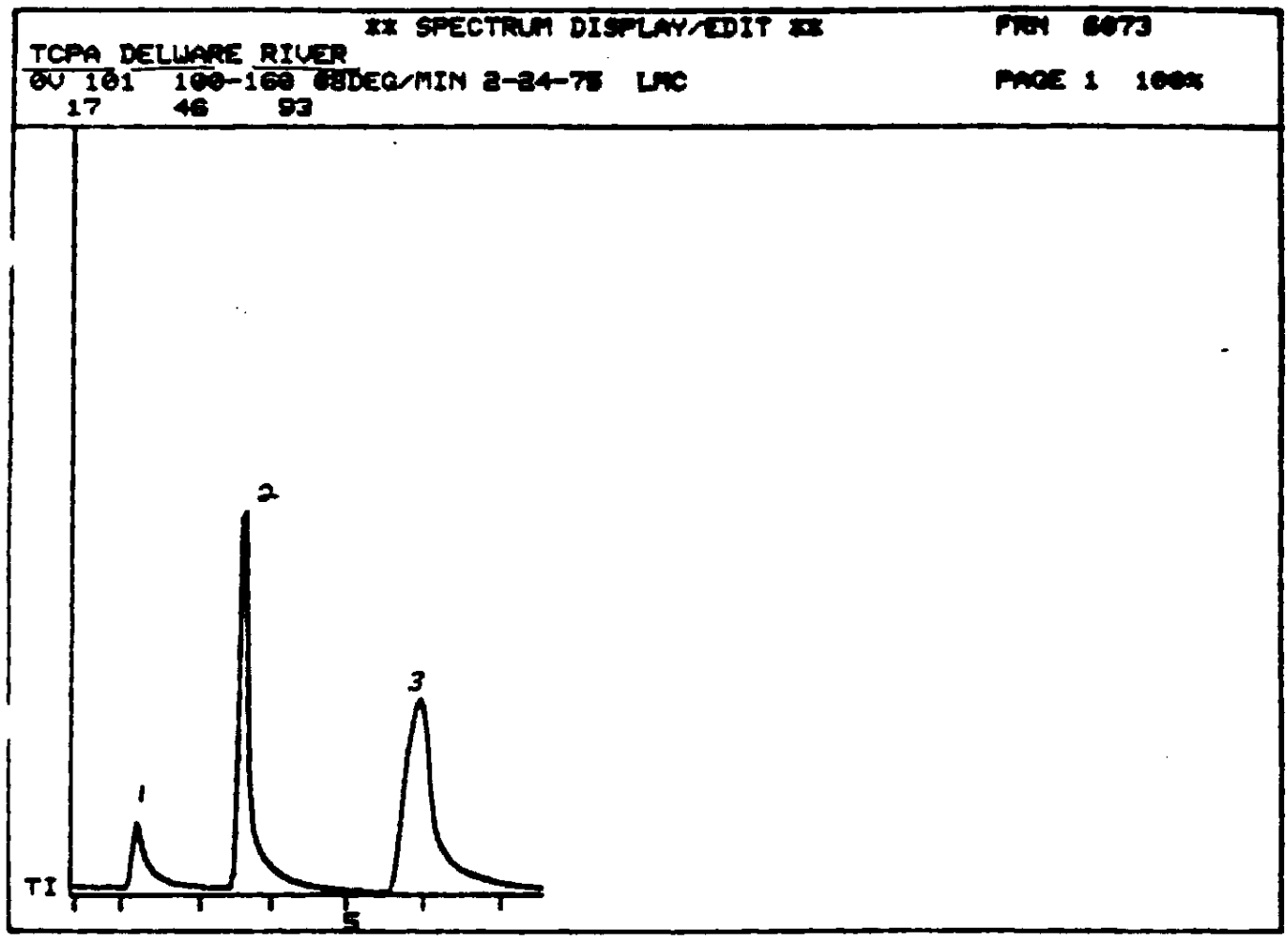
Mass Gain: 4

Mass Scan: 10-400 amu

Ethyl Benzene



TCPA


xx SPECTRUM DISPLAY/EDIT xx
PRN 6073
TCPA DELWARE RIVER
OV 101 100-160 8DEG/MIN 2-24-75 LMC
PAGE 1 100%
17 46 93
1
2
3
TI
5

J. F. QUEENY PLANT STANDARD OIL AND GREASE RESIDUES

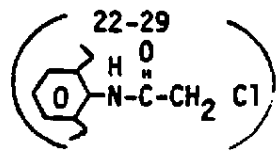
SUMMARY

Residues from the standard "Oil and Grease" test were found by GC/MS to contain 35 to 45% Monsanto products or intermediates. The remaining residue could be "Oil and Grease".

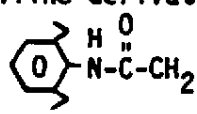
DISCUSSION

Five samples of residue obtained by Standard Method No. 137, American Public Health Association, as applied to the Clean Acid Stream were analyzed by GC/MS. The results are given in the following table.

TABLE
COMPONENTS OF RESIDUES FROM THE STANDARD OIL AND GREASE ON CLEAN ACID STREAM

Sample Identification	Percent Accounted for by GC/MS	Percent Lasso	Percent Butyl Phthalyl Butyl Glycolate	Percent Other Materials
Hexane 8/26-8/30	35-45	-	35-45	-
Freon 8/26-8/30	30-40	3-4	5-7	22-29 
Freon and Hexane Combined 9/20-9/27	35-45	21-27	14-18	
Freon 10/4-10/11	35-45	9-11	16-21	10-13 Not Identified
Freon 10/12-10/16	60-70	24-28	24-28	12-14 Not Identified

The material "not identified" represents 8 to 10 GC peaks of about 1% concentration. The diethyl aniline derivative

 is related to Lasso production.

db

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3/75 - G. W. Mappes, M. W. Dietrich

Special Study
S-75-SS-7

RADIOACTIVITY IN DIPHENYL OXIDE INTERMEDIATES, FINISHED GOODS AND ENVIRONMENTAL EFFLUENT

INTRODUCTION

Manufacturing and Research representatives held a meeting on 2-5-75 in St. Louis to review status of data required for a radioactive materials license application to the state of Texas for the new thoria catalyst diphenyl oxide plant to be built at Chocolate Bayou. The status of this application and additional information required is summarized in D. R. Miller's meeting report of 2-26-75 (Reference 1). This report summarizes results and conclusions of the additional research support requested at that meeting.

SUMMARY

1. Gamma spectrometry was investigated as an alternative/supplementary radiochemical analytical tool to liquid scintillation spectrometry for measuring radioactivity in crude DPO, distillation fractions, refined DPO and miscellaneous samples such as vent traps, filters etc. Sensitivity comparisons between gamma and liquid scintillation spectrometry were made on selected crude DPO distillation fractions including refined DPO.

2. Radioactivity material balance measurements were provided for a pilot plant scale crude DPO distillation. This experiment was carried out under "worst case" plant simulated time table to learn (a) if measurable radioactivity was present in refined DPO, (b) the fate of short half-lived Radon 220 and daughter products in crude DPO distillation, and (c) if significant long-lived radioactivity (Thorium) was present in still bottoms.

3. Before-and-after radioactivity measurements were provided for evaluation of the effectiveness of a 10 micron opening Teflon disk filter for removing radioactivity from crude DPO.

4. Radioactivity measurements were provided to estimate the amount of radioactivity vented to atmosphere from the crude DPO storage tank under plant simulated "worst case" conditions.

5. Analysis for long half-life radioactivity was made on selected distillation residues and crude DPO samples. A similar investigation was also made on Teflon filter disks from crude DPO filtrations.

CONCLUSIONS

1. Gamma spectrometry has been demonstrated to have sensitivity greater than 2 x 10^{-6} uci/ml for thorium in DPO process materials. Data appear in Table 1A and footnotes. Comparison with liquid scintillation spectrometry indicates the gamma method better for dark crude DPO, distillation residues, carbon filters etc. However, liquid scintillation on refined DPO and light colored scintillator-soluble samples is 5-100 times more sensitive than gamma spectrometry (Table 1B).

2. The determination of the fate of radioactivity from crude DPO in a plant simulated distillation showed it to be completely held up in the still pot. No detectable amounts were present in the refined DPO. The pilot plant distillation did not employ filtration or vacuum transfer of crude DPO, but did attempt to simulate plant "worst case" conditions by distillation of the final eight hours of crude DPO production to maximize total radioactivity present. Results appear in Table 2.

3. Filtration of crude DPO through a single 10 micron opening Teflon disk gave no detectable reduction of short-lived radioactivity.

4. Radioactivity vented from the pilot plant storage under plant simulated "worst case" conditions was completely held up in the first of a train-of-three granular active carbon filled absorbers (Nuchar WV-W, 80 x 30 mesh) and was calculated to be equivalent to 9 x 10^{-7} uci/ml (air) of thorium. The "worst case" conditions were the total filling of the DPO storage container over an eight-hour period totally displacing gas space into the train of absorbers.

5. A very small (unquantified) amount of long-lived radioactivity (natural thorium plus daughters) has been found to come forward with crude DPO from the reactor and has been found on filter disks and in distillation residues. Additional work is needed to quantify results since the total amounts of crude DPO used and the quantitativeness of retention/transfer of radioactivity was not sufficiently documented. All samples associated with eight hours or less of crude DPO production show no detectable levels of long half-life radioactivity (less than 2 x 10^{-6} uci/ml thorium) after 120-140 hours monitoring. Data on the individual samples is given in Table 3.

DETAILS

Determination of Radioactivity Vented to Atmosphere from Continuous Pilot Plant Crude DPO Storage

Absorption Apparatus

Radioactivity absorbers were prepared by filling three pyrex glass tubes 25 mm diameter x 60 mm long open at both ends with Nuchar WV-W, 80 x 30 mesh carbon. The carbon was held in the absorber with a small wad of glass wool on each end and a one-hole rubber stopper. The absorbers were close coupled in series with short lengths of glass tubing. The absorber tubes were designed to permit insertion into the count well of the 2 x 2 NaI detector of the RIDL gamma counter after replacement of the end connectors with thin flush-mounted rubber stoppers.

Absorption Experiment

The pilot plant crude DPO effluent tube was connected to an empty 2-liter Erlenmeyer flask through a two-hole stopper. The series train of 3 carbon absorbers was attached to the discharge opening of the collection flask. An electronic timer switch was set to divert the last eight hours of crude DPO production (prior to catalyst bed regeneration) to the special receiver. Sufficient crude DPO was collected to totally fill the receiver and exit line to the absorbers forcing the original 2 liter air volume through the absorber train. Care was then taken that no crude DPO reached the first absorber by holding the absorber train vertically as the line was filled with liquid and diverting flow just before liquid reached the absorber inlet.

Quantification of Radioactivity Found in Carbon Absorbers

Immediate check for radioactivity in all three absorbers showed detectable levels only in absorber No. 1. Further counting of absorber No. 1 with inlet and exit ends of the absorber inserted into the detector well respectively indicated higher activity at the inlet side. A radioactivity standard was prepared by addition to a section of stoppered glass tubing identical to the absorbers, 9 ml deionized water, 0.5 ml concentrated nitric acid and 0.0169 gram Thorium (250 µl of a standard prepared by dissolution of Thorium oxide pellets from the reactor catalyst stock). After mixing the liquid contents the carbon charge (8.4 g.) was added to the tube. An additional 1.5 ml deionized water was added to bring water level to top of carbon. The tube was stoppered, mixed and counted. The radioactivity in absorber No. 1 was measured in the same way. The absorber was opened and and the carbon removed and mixed to better distribute the

radioactivity. The deionized water and nitric acid were added to the empty adsorber tube and the mixed carbon charge was added back. Additional water was added to cover the carbon and the tube was then stoppered, mixed and counted 20 minutes. The same quantity of unexposed carbon, water, and nitric acid was prepared and counted as a background sample. The following count data was obtained. (See Page 4A)

REFERENCES

1. "DPO Radiological Licensing/Safety Research Center Meeting", D. R. Miller, 2-26-75.

2. Notebook Pages MIC 254342-254400, 269401-296406 (D. Hines).

3. Notebook Pages MIC 296001-296063+ (D. Hines).

4. Notebook Pages MIC OR214268 (J. E. Silver).

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4/75 - D. B. Hines, M. W. Dietrich

Sample	Time Clock	Time Elapsed (Hrs.)	Min. Counted	Total Counts	Total cpm	Background	Net cpm	Remarks
Absorber #1	3:08PM	12.7	10.0	7927	792.9	(235)	558	
Carbon Background Standard	2:43PM		10.0	2348	---	234.8	---	
Thorium Standard	2:27PM		10.0	9317	931.7	(217)	715	0.0169 g. Thorium
DPO Crude	10:28AM	8.0	5.0	23211	4642	(217)	4425	Elapsed time = 0
	3:16PM	12.8 hr.	5.0	18672	3734	(217)	3517	Decay correction standard and background
Deionized Water, Background Sample	8:48AM		20.0	4293	---	214.7	217	
	4:20PM		20.0	4378	---	218.9		

The net cpm radioactivity found in the carbon absorber was corrected to zero elapsed time using the crude DPO decay standard. This result was computed as equivalent Thorium using the thorium standard and expressed as equivalent uci thorium/ml using the "empty" volume of the crude storage tank as representing the volume of radioactivity discharged to environmental air.

Calculation:

1. Absorber count data corrected to time zero $558 \times \frac{4425}{3517}$

   = 702 net cpm

2. Thorium equivalence of absorber corrected count data = $\frac{702 \times 0.0169}{715}$ = 0.0166 g Th

   = 1.84×10^{-3} uci Th

3. Radioactivity expressed as thorium equivalent per ml of crude DPO storage tank displaced air =

   $$\frac{1.84 \times 10^{-3} \text{ uci Th}}{2 \times 10^{9} \text{ ml}} = 9 \times 10^{-7} \text{ uci Th/ml}$$

TABLE 1

ANALYTICAL SENSITIVITY OF GAMMA AND LIQUID SCINTILLATION SPECTROMETRY FOR THORIUM

A. GAMMA SPECTROMETRY - AQUEOUS THORIUM STANDARDS

Sample Size (ml)	Count Period (min)	Thorium Present (grams)	Sample Radioactivity net cpm (±2σ)	Sample Radioactivity uci Thorium per ml. (1)	Sensitivity (2) grams/ml.	Sensitivity (2) uci/ml.
5	1	0.3397	20,800 (±288)	2.5×10^{-3}	2.24×10^{-4}	2.49×10^{-5}
20	1-5	0.3397	14,509 (±248)	1.9×10^{-3}	1.38×10^{-4}	0.8×10^{-6}
20	20	6.76×10^{-4}	28.7 (±9.9)	3.75×10^{-6}	1.17×10^{-5}	1.30×10^{-6}
400	10	1.69×10^{-3}	21.6 (±14.5)	4.69×10^{-7}	2.86×10^{-6}	3.2×10^{-7}
400	10	3.38×10^{-3}	50.7 (±10.8)	9.38×10^{-7}	1.80×10^{-6}	2.0×10^{-7}

B. LIQUID SCINTILLATION - CRUDE DPO AND DISTILLATION CUTS

Sample	Sample Size (ml)	Scintillator and Volume	Thorium Added As Int.Std. (grams)	Sample Radioactivity net cpm (±2σ)	Sample Radioactivity uci Thorium per ml. (1)	Sensitivity (2) grams/ml.	Sensitivity (2) uci/ml.
Crude DPO	2.0	Packard Instagel/ 18.0 ml.	0.006758	577±15	0.86×10^{-4}	1.36×10^{-7}	1.51×10^{-8}
Phenol-Water Cut 1 (Top phase)	2.0	Packard Instagel/ 20.0 ml.	"	0±3	--	2.22×10^{-6}	2.47×10^{-7}
Phenol-Water Cut 1 (Bottom Phase)	3.0	" 19.0 ml.	"	0±3	--	1.23×10^{-6}	1.37×10^{-8}
Refined DPO	10.0	" 10.0 ml.	"	0±3	--	6.36×10^{-7}	7.07×10^{-8}

RSV 0010568

Table 1 Footnotes

(1) DPO process gamma radioactivity may arise from both short- and long-lived nuclides. It is not practical to duplicate the many gamma energies in the short-lived radioactivity of DPO samples with calibrated long-lived standards in order to determine precise counting efficiencies and permit expressing the radioactivity levels in the regulatory units of uci/ml for each nuclide. Instead, the catalyst thorium oxide catalyst pellets which contain these short-lived along with longer lived daughters are dissolved and used as the radioactivity standard. The "catalyst thorium" with its mixture of daughter products is taken to be the "natural thorium" given in the AEC regulations (Part 20, Appendix B). The use of this material as a radioactivity standard has the advantage of a regulations defined weight/radioactivity relationship: 9000 Kg thorium natural equals 1 curie. Therefore, all radioactivity in DPO process samples is expressed as that of an equivalent amount of catalyst thorium radioactivity measured under the same conditions.

(2) Method sensitivity is taken as that quantity of thorium catalyst standard giving the net counts per minute equal to twice (2σ) the theoretical or experimental standard deviation of the background determined for the same period of time.

Example: The background of 20 ml of distilled water counted in a gamma count vial for 20 minutes is 4352 counts. The theoretical standard deviation is

$$\sigma = \pm \frac{\sqrt{N}}{20} \text{ cpm} = \pm \frac{\sqrt{4352}}{20} = \pm 3.3 \text{ cpm}$$

where N is the total number of counts taken and 20 is the minutes counted.

The thorium standard used in this study counts 42748 net cpm/gram thorium per 20 ml sample. The sensitivity is then determined as

$$S_{(\text{grams thorium})} = \frac{2(\pm\sqrt{N})}{42748} = \frac{2(\pm 3.3)}{42748} = 1.54 \times 10^{-4}$$

Since 9000 Kg natural thorium = 1 curie
9 grams thorium = 1 uci and

$$S_{\text{uci thorium}} = \frac{1.54 \times 10^{-4}}{9} = 1.72 \times 10^{-5}$$

Since 20 ml samples are used

$$S = \frac{1.72 \times 10^{-5}}{20} = 8.58 \times 10^{-7} \text{ uci thorium/ml.}$$
$$= 0.86 \times 10^{-6} \text{ " " "}$$

TABLE 2

CRUDE DPO DISTILLATION EXPERIMENT
(DISTRIBUTION OF RADIOACTIVITY DETERMINED BY GAMMA COUNTING (6))

Component	Weight (grams)	Thorium		Method Sensitivity (2)
		net cpm per 20 g. ($\pm 2\sigma$)	uci/ml. (1)	(2σ, uci/ml.)
Crude DPO Charge	2006	3487 ± 29 (3) (328984 ± 2748) (Total charge)	4.5×10^{-4}	$(0.86\text{-}1.3) \times 10^{-8}$
Phenol-Water Cut 1	90		ND ≤	
Top phase		0-9.6 ± 9.5	1.3×10^{-6}	"
Bottom phase		0 ± 9.3		"
Phenol Cut	1261	0-8.6 ± 9.3	ND ≤ 1.3×10^{-6}	"
Phenol - DPO Slop Cut	138	0-10.9 ± 9.5	ND ≤ 1.3×10^{-6}	"
Refined DPO Cut	399	11.0 ± 9.5	ND ≤ 1.3×10^{-6}	"
Column Holdup	84	27.0 ± 9.5	3.5×10^{-6}	"
Residue	15	38,448 (4)	5000×10^{-6}	"
Still Pot Rinses	--	290,997 (5)	$37,818 \times 10^{-6}$	"
Cold Traps	3	--	--	--
Unaccounted for	16	--	--	--

Table 2 Footnotes:

(1) See Footnote 1, Table 1.

(2) See Footnote 2, Table 1.

(3) The radioactivity of fresh crude DPO may hold fairly constant or increase slightly for the first few minutes of elapsed time due to the rapid decay of Rn-220 and Po-216 and the buildup of longer lived Pb-212. On older samples the radioactivity holds fairly constant for about the first hour. This value is the average of the first five 5-minute counts of the crude DPO distillation charge.

(4) This level of radioactivity is obtained by applying a linear extrapolative based on the ratio of radioactivity in crude DPO at time 0 and at an elapsed time equal to that of the sample(s). This is not strictly a linear relationship (Fig. 1).

Table 2 Footnotes (continued)

(4) (continued) The actual radioactivity balance in charged DPO crude and still bottom residue at the end of distillation was made at the more linear region of the decay curve at the 500-600 elapsed minutes region.

(5) The major portion of the radioactivity balance was recovered as a series of eight rinses of the still pot in this order: 1 - acetone, 2-acetone, 3-aqueous radiac concentrate, 4-aqueous radiac concentrate, 5-acetone, 6-chloroform, 7-chloroform, 8-10% HF.

(6) The gamma counting was performed on a Radioactive Industry Development Laboratory (RIDL) modular single channel analyzer utilizing a RIDL 2" x 2" NaI (T 1) well crystal detector. Well dimensions are 1 inch diameter x 1-1/2 wide deep. Instrument count parameters were optimized using the thorium catalyst standard. Twenty milliliter samples were counted for periods of 1-30 minutes in the evaluation.

FIGURE 1
DECAY CURVE, CRUDE DIPHENYL OXIDE FROM THORIA CATALYST PROCESS
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TABLE 3

EXAMINATION OF THORIUM CATALYST DPO PILOT PLANT PROCESS SAMPLES FOR LONG-LIVED RADIOACTIVITY

A. SAMPLES FROM CRUDE DPO DISTILLATION (8 HRS. OF PILOT PLANT PRODUCTION, RUN E-327)

Sample	Elapsed Time (hrs.)	Net cpm ($\pm 2\sigma$)	Count Method
1. Still Pot Residue	0	22,049	Gamma Spectrometry
	40	1,866	" "
	73	211 ± 11.5	" "
	139	0 ± 9.2	" "
	161	0.9 ± 6.2	" "
2. Still Pot Rinse 3 (Radiac Concentrate)	0	60,043	" "
	73	520	" "
	140	1.9 ± 7.3	" "
3. Still Pot Rinse 6 (Chloroform)	0	39,912	" "
	120	25.9 ± 7.6	" "
	137	29.3 ± 6.6	" "
	189	24.5 ± 13.2	" "
4. Still Pot Rinse 7 (Chloroform)	0	27,190	" "
	120	33.2 ± 7.7	" "
	138	28.1 ± 6.5	" "

B. CRUDE DPO, RUN E-331 FRACTIONS 0-23 AND 24-57 MINUTES FOLLOWING CATALYST REGENERATION

Elapsed Time (Hrs.)	Fraction Net Cpm ± 2σ		Count Method
	0-23 Min.	23-57 Min.	
0	12,652	6,067	Gamma Spectrometry
4-5	12,485	7,117	" "
70	187.6 ± 9.6	115.7 ± 11.4	" "
100	31.6 ± 6.6	19.5 ± 8.7	" "
125	10.6 ± 5.9	5.2 ± 8.5	" "
145	4.0 ± 13.1	0 ± 8.5	" "

TABLE 3 (Continued)

C. TEFLON FILTER DISK FROM CRUDE DPO FILTRATION

Sample	DPO Crude Batch	Elapsed Time (Hrs.)	Net cpm (±2σ)	Count Method
10 micron opening Teflon Filter Disk, Acetone Rinsed	(1)	0	57,896	Flow Proportional Counting
		4	53,737	
		19	20,333	
		27	14,663	
		48	3,321	
		67	923	
		140	30.4	
		164	24.8 ± 3.6	
		212	24.6 ± 7.5	
		237	27.4 ± 3.9	
		310	20.8 ± 4.9	
		331	25.2 ± 4.1	
		364	21.8 ± 4.6	
10 micron opening Teflon Filter Disk, Acetone Rinsed	E-328 (Last 8 hours Collection)	0	19,912	"
		26	5241 ± 65	
		94	65.6 ± 7.3	
		120	10.3 ± 2.8	
		150	2.1 ± 1.2	
		172	0.0 ± 1.6	

(1) Sample came from a filtration technique evaluation and represent an estimated 4000 ml crude DPO. The container, however, had been used to collect numerous batches.

TABLE 4

CRUDE DPO DISTILLATION FRACTIONS - COUNT DATA UNCORRECTED TO TIME ZERO

Sample	Clock Time (1)	Total Counts	Min. Counted	Total cpm	Remarks
Crude DPO Charged to distillation	8:05AM	18,560	5.0	3712	Average of first 5 counts = 3701 ± 27.6 (2σ)
	8:13AM	18,389	5.0	3678	
	8:19AM	18,587	5.0	3717	
	8:25AM	18,485	5.0	3697	
	8:32AM	18,499	5.0	3697	
	8:55AM	18,184	5.0	3637	
	9:00AM	18,048	5.0	3610	
	11:12AM	16,572	5.0	3314	
	12:30PM	3,087	1.0	3087	
	2:56PM	13,484	5.0	2697	
	4:50PM	12,050	5.0	2410	
	7:05PM	10,701	5.0	2140	
Phenol - Water Cut 1 Top Phase	9:42AM	197	1.0	197	
	9:47AM	2,215	10.0	222	
	11:34AM	4,517	20.0	226	
	12:25PM	4,334	20.0	217	
Bottom Phase	10:01AM	218	1.0	218	
	10:11AM	2,225	10.0	223	
	10:43AM	4,289	20.0	214	
Phenol Cut	2:08PM	4,477	20.0	224	
Refined DPO Cut	1:27PM	4,519	20.0	226	
Phenol - DPO Slop Cut	2:29PM	4,507	20.0	225	
Column Holdup	2:50PM	4,727	20.0	236	

Footnotes -- see following page.

TABLE 4 (continued)

Sample	Clock Time (1)	Total Counts	Min. Counted	Total cpm	Remarks
Residue as received (15 grams)	12:26PM	44,604	1.0	44,604	
Residue diluted to 20 ml. with acetone	6:05PM	111,419	5.0	22,284	
Still Pot Rinse 1 (Acetone, 20 ml.)	1:03PM	4,885	1.0	4,885	
	6:53PM	12,973	5.0	2,595	
Still Pot Rinse 2 (Acetone, 20 ml.)	1:05PM	1,618	1.0	1,618	
	6:35PM	5,227	5.0	1,045	
Still Pot Rinse 3 (Radiac, 20 ml.)	3:53PM	71,680	1.0	71,680	
	6:50PM	301,392	5.0	60,278	
Still Pot Rinse 4 (Radiac, 20 ml.)	4:43PM	12,306	1.0	12,306	
	6:57PM	54,436	5.0	10,887	
Still Pot Rinse 5 (Acetone, 20 ml.)	6:20PM	28,234	5.0	5,646	40 ml. rinse, 20 ml. counted.
Still Pot Rinse 6 Chloroform, 20 ml.	5:03PM	41,670	1.0	41,670	
	6:45PM	200,736	5.0	39,912	
Still Pot Rinse 7 Chloroform, 20 ml.	6:12PM	137,126	5.0	27,190	
Still Pot Rinse 8	5:51	5,969	1.0	5,969	60 ml. rinses combined, 20 ml. aliquot counted
9, 10 (10% HF, 20 ml.)	5:57	29,972	5.0	5,994	
Charcoal Absorber 1	2:58PM	228	1.0	228	Absorbers used between still overhead rec and vacuum pump.
	3:04PM	979	5.0	196	
Charcoal Absorber 2	3:06PM	235	1.0	235	
	3:11PM	1,162	5.0	232	

TABLE 4 (Continued)

Sample	Clock Time (1)	Total Counts	Min. Counted	Total cpm	Remarks
Steel wool from DPO Product line of Distillation Equipment	3:20PM	221	1.0	221	
Deionized Water, 20 ml.	9:50AM	2,140	10.0	214	Sample was used as background sample.
	11:06AM	4,352	20.0	218	
	4:14PM	4,664	20.0	233	
	5:44PM	4,747	20.0	237	
	7:20PM	2,372	10.0	237	

Footnotes:

(1) All measurements for radioactivity material balance made on 3-11-75.

Time "0" taken as 8:19AM since the 2σ confidence limits of the average of the first 5 five minute counts of crude DPO was indistinguishable from the difference of 1st and 5th count.

Special Study
S-75-SS-8

TRACER LITHIUM ANALYSES - NITRO PLANT EFFLUENT

SUMMARY

Lithium is used as a tracer to observe the dilution of the Nitro plant liquid effluent. Thirty-one effluent samples ranging from 0.05 to 0.13 ppm Li were analyzed by atomic absorption.

DETAILS

The samples appeared uniform but cloudy, almost neutral. Cursory analyses showed much sodium, calcium, but less than 1 ppm Li. Both air-acetylene and nitrous oxide-acetylene flames were tried, and the Boling burner. The latter produced acute curvature. The best ratio of response over noise was found with the nitrous oxide burner using air-acetylene as a strongly oxidizing flame. The effects of sodium ion and acid addition were checked. These did not affect the base line run in water. Hydrochloric acid addition had no effect on the sample response. All samples contain sodium which produces enhancement. There is a matrix effect, cause unknown, therefore the method of standard additions for calibration was chosen. Because this method is very time-consuming and because the most dilute sample would have a response of only ten times the noise level, the method was applied to a random selection of five of the samples. All of the samples, including the selected five were run directly, without dilution and without additions. Each sample was agitated, then allowed to stand for one minute before analysis. Each sample was run at least twice, using deionized water as reference. The standard addition zero level was run before and after its set. The five standard addition ppm values were graphically plotted against their direct run absorbance values. The "best line" through this plot was used as the calibration curve from which each sample's absorbance value was read to provide the corresponding ppm as listed in the table.

db

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St. Louis, Mo.

4/75 - O. E. Kinast, M. W. Dietrich

Sample Number	ppm Li	Sample Number	ppm Li
1	0.046	17	0.087
2	.136 (0.134)*	18	.085
3	.129	19	.079
4	.124	20	.076 (0.074)
5	.124	21	.071
6	.122	22	.070
7	.121	23	.068
8	.119 (0.122)	24	.066
9	.115	25	.061
10	.113	26	.059 (0.061)
11	.111	27	.057
12	.108	28	.055
13	.104	29	.052
14	.100 (0.096)	30	.051
15	.098	31	.049
16	.093		

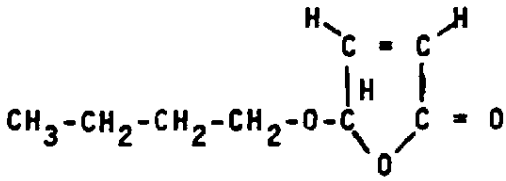
*Values in parentheses were obtained by method of standard additions

Special Study
S-75-SS-9

MALEIC ANHYDRIDE REFINING PROCESS IMPURITY

SUMMARY

An impurity with a boiling point between maleic anhydride and dibutyl maleate was observed in the refining step for new process maleic anhydride. The possibility that this impurity could cause quality problems required that it be identified. NMR, IR, and two types of mass spectroscopy were required to identify the impurity. It was identified as



DISCUSSION

GC analysis of a residue from the maleic refining process showed two unknown impurities which eluted between maleic anhydride and phthalic anhydride. These are designated peaks A and B in the figure. Electron impact GC/MS did not give molecular weight information on either impurity and showed unusual fragment ions for peak A.

The IR spectrum of B trapped from the GC separation showed that it was dibutyl maleate. Although succinic anhydride has the same retention time as dibutyl maleate on the GC column used for this analysis, no succinic anhydride was observed in the IR spectrum with a detection limit of 5 to 10% of the dibutyl maleate concentration.

The IR spectrum of peak A trapped from the GC separation suggested that this material was not one of the expected process impurities and that it had some unique structural features. GC/MS analysis of peak A using chemical ionization mass spectrometry indicated a molecular weight of 156. Hexane extraction of the residue produced a large enough sample of impurity A for NMR analyses. This analytical data indicated impurity A has the structure shown above. Since this impurity was obtained by extraction as well as GC separation, it could not be the result of some sample decomposition during the GC analysis.

db

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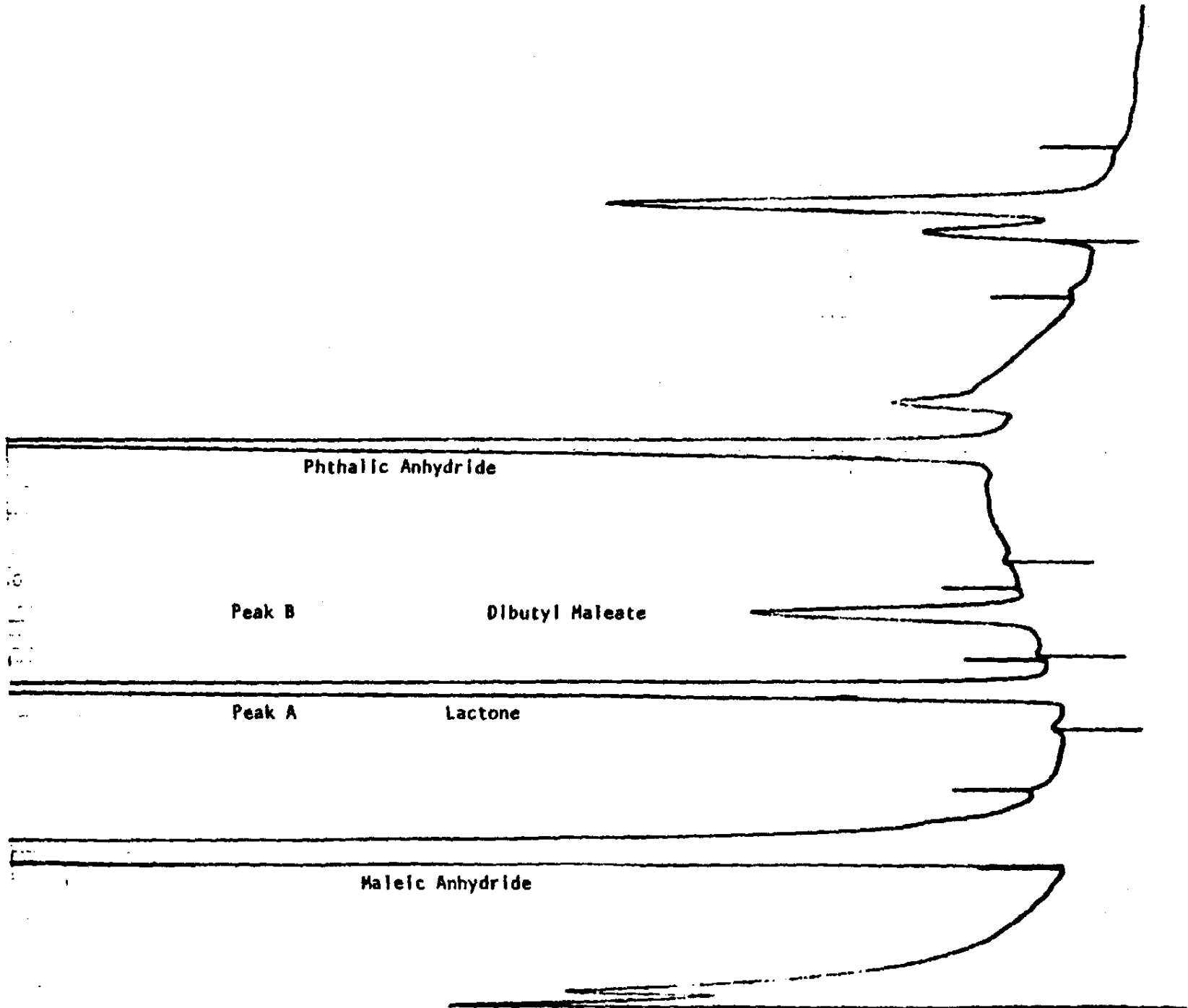

FIGURE

RSV 00105811

93 0.8 µl 291844 Residue Purge on Col A

Special Study
S-75-SS-10

ANALYSIS OF BENZENE IN AIR AT ANNISTON, ALABAMA PLANT

INTRODUCTION

The purpose of this investigation was to determine worker exposure to benzene.

SUMMARY

The first three sets of samples collected over an 8-hour day were all below 5 ppm. One high non-representative sample was found due to direct exposure of the collection tube to a benzene bath. During this study, we found that benzene vapors slowly permeate the teflon tape used for sealing the ends of the collection columns. This gave detectable levels of benzene in tubes used as blanks at Anniston. Tubes kept in St. Louis did not have detectable levels of benzene. The levels given in the tables should be considered maximum exposure values since as much as 3 ppm may be due to this benzene blank.

The fourth set of samples were taken for fifteen minutes in high exposure regions of the benzene process. The results are given in Table IV. As much as 39 ppm benzene was observed.

EXPERIMENTAL

GC/MS was used in the verification of benzene and calculations are based on a benzene standard. An example of the calculations is given below. Results shown for the blanks were calculated on the basis of the same volume of air used for the samples.

Calculations

$$\text{Volume of Air Sampled (liters)} = \text{pump flow rate (ml/min.)} \times \text{sampling time (min.)} \times 10^{-3}$$

$$\text{Wt. of sample } (\mu g) = \text{area sample peak (counts)} \times \frac{\text{conc. std.}(\mu g/\mu l)\,\text{Vol.inj.}(\mu l)}{\text{Area of std. (counts)}}$$

$$\text{Concentration of sample } (\mu g/l) = \frac{\text{Weight of sample } (\mu g)}{\text{Volume of air sampled (liters)}}$$

$$\text{Concentration of sample (ppm)} = \mu g/l \text{ (sample)} \times \frac{24.5}{\text{M.W.}} \text{ (sample)}$$

For Sampling #2 of Set 4

Volume of air sampled (liters) = 817 ml/min. x 15 min. x 10^{-3} = 12.26

Wt. of sample (μg) = $695 \times \frac{17.3}{7.8} \times 1.0 = 1542$

Conc. Benzene (μg/l) = $\frac{1542}{12.26} = 126$

Conc. Benzene (ppm) = $126 \times \frac{24.5}{78} = 39$

Reference: GC/MS File #75-24

Monsanto Industrial Chemicals Company
Applied Sciences Section
St. Louis, Missouri

4/9/75 - L. M. Chapman, M. W. Dietrich

TABLE I

Set I

Pump flow, 20 ml/min. (Model 222-451 SKC pump)

Sample Time, 8 hr.

Tube	ppm of Benzene
# 3	0.2
# 4	0.7
# 5	0.7
# 1 (blank)	lost in analysis

TABLE II

Set II

Pump flow, 20 ml/min. (Model 222-451 SKC pump)

Sample Time, 8 hr.

Tube	ppm of Benzene
#16 (blank)	0.4
# 6 (St. Louis blk.)	0.02
#17	120.0 x not a representative sample because of direct exposure to benzene.
#18	4.2
#19	1.5
#23	0.2

TABLE III

Set III

Pump flow, 20 ml/min. (Model 222-451, SKC pump)

Sample Time, #1 and #2 - 8 hr. and 15 min.
Remaining samples - 8 hr.

Tube	ppm of Benzene
# 1	1.0
# 2	1.0
# 3	1.4
# 4	2.3
# 5 (blank)	1.5
# 6 (St. Louis blk.)	0.02

TABLE IV

Set IV

Pump flow, 817 ml/min. (Model C-115, Bendix pump)

Sample Time, 15 min.

Tube	ppm of Benzene
# 2	39.
# 3	33.
# 4 (blank)	3.0
# 5	High level*
#16	21.
#17 (sealed blk.)	0.7
#23 (St. Louis blk.)	0.3

* shut down instrument

Special Study
S-75-SS-11

ANALYSIS OF VOLATILES IN DECATUR, ALABAMA PLANT AIR (III)

INTRODUCTION

This is a continuation of an investigation to determine concentration levels of vinyl acetate (VA) and acrylonitrile (AN) in air at the north continuous polymer area of the Decatur, Alabama plant. The data obtained will be used to identify areas where worker safety problems may exist.

SUMMARY

Results of the study are found in Table I. GC/MS provided the means of identification of the volatiles. Acrylonitrile had values of from 0.4 to 2.4 ppm while vinyl acetate values ranged from 0.2 to 1.0 ppm.

EXPERIMENTAL

Refer to Spectroscopy Method 74-7 for the analyses procedure used. Ten minutes was allowed for the heating of the external collection column to collect the acrylonitrile before proceeding as in Method 74-7. Adaptions of hardware have been made for our new HP GC/MS. An example of the procedure used to calculate concentration is given in the S-75-SS-1 report. Sample collection was made using a Model 222-451 SKC pump. Calculations were based on known VA and AN standards.

Reference: GC/MS File #75-57.

db

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St. Louis, Mo.

4/75 - L. M. Chapman, M. W. Dietrich

TABLE I

		ppm	
		AN	VA
*M-3	#7 Reactor cleaning-chipping scale and removal by operator	≤2.4	≤1.0
M-4	Reactor overflow sampling and cleaning	0.4	0.9
M-5	Changing filter cloth on B line secondary filter	0.5	0.2

*Values for M-3 are maximums because of possible interference of other components when calculating concentrations.

Special Study
S-75-SS-12

ORGANIC CHEMICALS IN CHOCOLATE BAYOU PLANT WATERS

SUMMARY

Waters from various places in the steam and water systems at the Chocolate Bayou plant were analyzed for organics to determine its suitability for the sorbic acid process. No organics were found in the finished water samples with a detection limit of 0.5 ppm total. Low levels of aliphatic compounds were found in steam condensate samples.

DISCUSSION

Water for plant usage is taken from the Brazos River, filtered, passed through water softening resins, flash evaporated and pumped to various plant uses. Two samples of water from each of four points in the purification were taken for analysis. One sample of each pair was acidified to pH=2 with sulfuric acid. Two additional samples of condensate returned from steam usage were also analyzed. One was from the phenol process, the other was from the ethylene process. The results for these samples are given in the table.

The filtered water is river water which has been filtered only. The polished water has been filtered and softened. The evaporator water has been filtered, softened and flash evaporated to remove dissolved solids. The medium pressure water is polished water and condensate returned from steam usage. All were analyzed by methylene chloride extraction as outlined in Spectroscopy New Technique 70-3. Identification was done by GC/MS and IR. Extractable organics were found in only the steam condensate. GC/MS analysis of these organics showed that they were a series of aliphatic compounds. IR showed definite nitrogen content. This suggests that these compounds are related to the inhibitor used in the steam lines and probably are decomposition products of the inhibitor. The total organic Carbon TOC values for the steam condensates were done using the Envirotech DC-50 Organic Analyzer.

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5/75 - G. W. Mappes, O. E. Kinast, M. W. Dietrich

ORGANICS IN CHOCOLATE BAYOU WATER

	Extractable Organics Total (ppm)	Phenol (ppm)	TOC (ppm)
Filtered Water			
pH 8	<0.5	<0.2	<5*
pH 2	<0.5	<0.2	<5*
Polished Water			
pH 10	<0.5	<0.2	<5*
pH 2	<0.5	<0.2	<5*
Evaporator Water			
pH 8	<0.5	<0.2	<5*
pH 2	<0.5	<0.2	<5*
Med. Press. Water			
pH 10	<0.5	<0.2	<5*
pH 2	<0.5	<0.2	<5*
Steam Condensate Phenol Process	0.5 to 1.0	<0.2	6±2
Steam Condensate Ethylene/Hydrocarbon Process	1.0 to 1.5	<0.2	7±2

*Determined at Chocolate Bayou

Special Study
S-75-SS-13

DETERMINATION OF BENZYL CHLORIDE IN DELAWARE RIVER PLANT AIR

INTRODUCTION

Personnel monitor for benzyl chloride in air to determine worker exposure levels at the Delaware River plant was carried out in the S-160 department.

SUMMARY

See the attached table for results. Levels of benzyl chloride found were ≤ 0.1 µg/ℓ. Other components identified were toluene, xylene, chlorotoluene, chlorobenzene, dichlorobenzene, dichlorotoluene, and naphthalene. Levels of these components can also be found in the table.

EXPERIMENTAL

Tenax GC was used for collection and analysis. GC/MS was used for identification. Calculations are based on a benzyl chloride standard. Air sample sizes were between 7 and 16 liters with flow rates between 35-45 mℓ/min.

Calculations

$$\text{Volume of Air Samples (Liters)} = \text{Pump Flow Rate (mℓ/min)} \times \text{Sampling Time (min)} \times 10^{-3}$$

$$\text{Weight Sample (µg)} = \text{Area Sample Peak (Counts)} \times \frac{\text{Conc. Std. (µg/µL)} \times \text{Vol. Injected (µL)}}{\text{Area of Standard (Counts)}}$$

$$\text{Concentration Sample (µg/L)} = \text{Weight Sample (µg)/Volume of Air Sampled (Liters)}$$

For Sampling OP-1

$$\text{Volume of Air Sampled (L)} = 40.6 \times 293.6 \times 10^{3} = 11.92\text{ℓ}$$

$$\text{Weight Sample (µg)} = 1589474 \times \frac{1.5 \times 1}{2483156} = 1.0\ \mu g$$

$$\text{Concentration (µg/L)} = \frac{1.0}{11.92} = 0.08 \simeq 0.1$$

Reference: GC/MS File #75-89.

Benzyl Chloride Method Validation

A series of experiments were performed to verify this procedure is quantitative for benzyl chloride. The set of GC conditions are given at the end of this report; other experimental conditions are described separately.

Test 1

The analytical column was connnected to the GC and an empty glass insert used. Then 1.5 µℓ of the standard was injected and the program initialized. Peak area of benzyl chloride was observed and recorded.

Test II

This time, when the analytical column was connected, a packed insert was placed in the injection port. Note this was a freshly conditioned insert and no air had been passed through it. Again 1.5 µℓ of the standard was injected, the program initialized, and peak area of benzyl chloride recorded.

Test III

Next, 1.5 µℓ of the standard was injected into a 50 mℓ gas sampling bulb. A diagram of the apparatus is given at the end of the report. A SKC-222-451 pump was used in collecting the sample. A collection with flow 76 mℓ/min for one hour was made and the insert placed in the GC as in Test II and run.

Test IV

The last experiment was the same as Test III except a flow of 25 mℓ/min for 5 hours was made. [A sampling for 4 hours at 4 mℓ/min was also conducted with a C-105 insert and showed 95% recovery.]

RESULTS

From Test I and II, the results showed that the material absorbed on the Tenax insert was desorbed in the analysis. Similarly results from Test III and IV verified that the sample is quantitatively collected from the air by the insert whether it be a fast or slow flow rate. Accurate analyses should be obtained as long as the breakthrough volume for benzyl chloride is not exceeded. See table for percent recovery in the experiments described.

GC Conditions

GC-7620 H.P. Flame

Analytical Column: 2M glass Tenax GC

Collection Column: Glass Tenax Insert

Program: 50 (4 min) → 250 @ 15°/Min.

Attenuation: $4 \times 10^3 \times 1$

Reference: GC File #75-95.

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TABLE

	Concentration (µg/ℓ)									
	Benzyl Chloride	Unknown	Toluene*	Chloro-benzene	Xylene*	Chloro-toluene	Dichloro-benzene	Dichloro-toluene	Naphtha-lene	Comments
OP-1	<0.1	<0.1	0.2	ND**	<0.1	0.1	0.1	<0.1	<0.05	
COP-1	<0.1	<0.05	0.2	ND	<0.05	<0.1	<0.1	<0.05	<0.05	
LT-1	<0.1	<0.05	0.2	<0.05	<0.1	ND	<0.05	<0.05	<0.05	
OP-2	<0.1	<0.05	0.2	<0.05	<0.05	<0.1	<0.1	<0.05	ND	Sample partially lost due to leak in system
COP-2	<0.1	<0.05	0.2	<0.05	<0.05	<0.1	<0.1	<0.05	<0.05	
OP-3	<0.1	<0.1	0.2	ND	<0.1	0.1	0.1	<0.05	ND	
D-1	<0.1	<0.05	0.2	ND	<0.05	<0.1	ND	<0.05	<0.05	
LD-1	0.1	ND	0.2	ND	ND	ND	ND	ND	ND	
OP-4	<0.05	<0.05	0.1	ND	<0.05	ND	<0.05	<0.05	ND	
COP-3	<0.05	<0.05	<0.1	ND	<0.05	<0.05	<0.05	<0.05	ND	

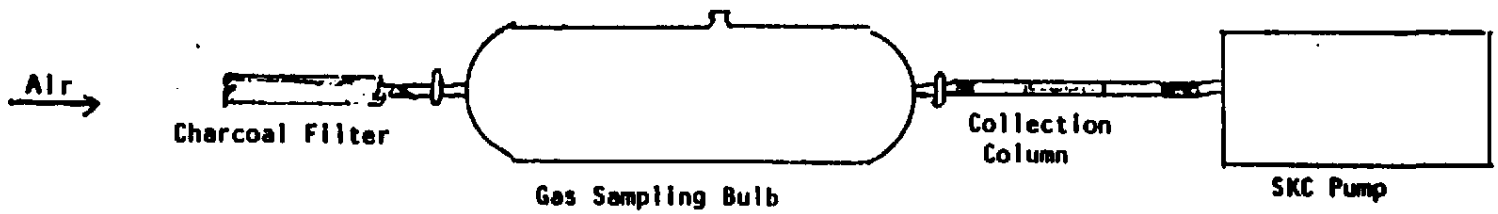
*Toluene and xylene results are probably low because the breakthrough volume of these components was exceeded.

**ND = Detection limit $\leq$0.05

TABLE

		Amount Injected of 1.56 µg/µl Std.	Amount Recovered
Test I:	Direct Injection on Analytical Column	1.5 µl	100%
Test II:	Injection on Collection Column and Analytical Column	1.5 µl	95%
Test III:	Collection @ 76 ml/ min for 1 Hour on Tenax	1.5 µl	83%
Test IV:	Collection @ 25 ml/ min for 5 Hours on Tenax	1.5 µl	98%
	Collection @ 4 ml/ min for 4 min on C-105	1.5 µl	94%

APPARATUS



Special Study
S-75-SS-14

DETERMINATION OF TOLUENE DIISOCYANATE IN AIR (II) IN THE SUPER DOME

INTRODUCTION

This analyses was undertaken to determine concentrations of toluene diisocyanate (TDI) in air during Astroturf installation in the Super Dome at New Orleans.

SUMMARY

Samples from the installation showed no TDI detected with a detection limit of 4 ppb. Methyl Ethyl Ketene (MEK) was observed at a level of $\geq$0.06 ppm. Concentration of other unidentified organics totaled around 0.02 ppm. A description of the samples is given in the attached memo.

Two samples of the adhesive used in planting the Astroturf were also examined. The first, Vorite 677, an adhesive previously used in this application, showed only MEK and TDI in the headspace. The adhesive now used in Astroturf installation, Spencer Kellogg, contained besides MEK and TDI, a considerable amount of toluene and some xylene. Several other trace components not specifically identified appeared to be alkylated benzenes and aliphatic amines. A chromatogram is attached.

In comparing the adhesives with the air samples, toluene does seem to be present in the air samples. The amount would be invalid because breakthrough would have occurred.

Reference: GC/MS File #75-93.

db

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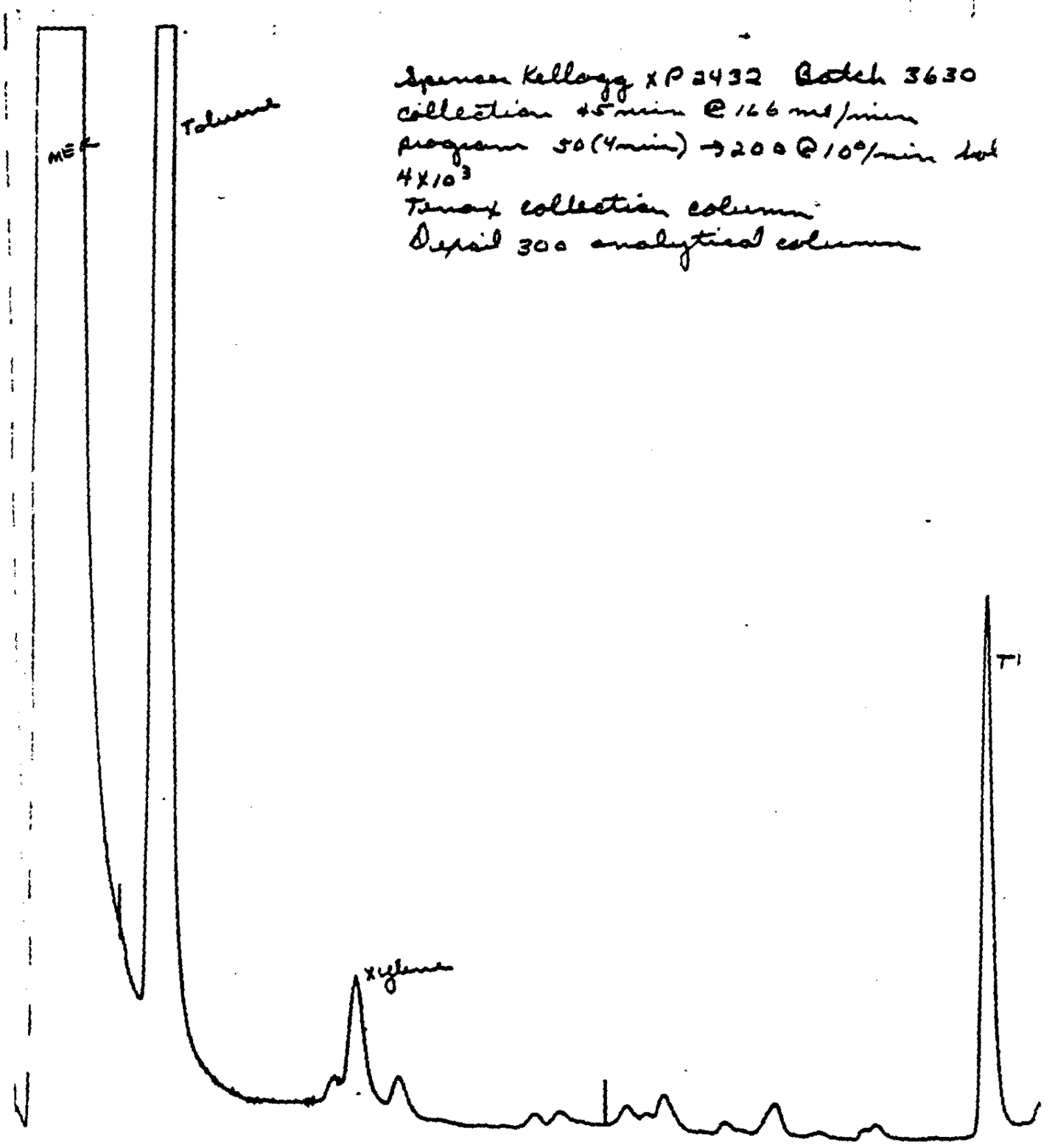

Spencer Kellogg xP 2432 Batch 3630
collection 45 min @ 166 ml/min
program 50 (4 min) → 200 @ 10°/min Vol 4×10^3
Tenax collection column
Dexsil 300 analytical column

RSV 0010596

Monsanto

FROM (NAME & LOCATION): Carl D. Bohl - Medical Dept. - A2SA

DATE: April 7, 1975

cc: J. T. Garrett

SUBJECT:

REFERENCE:

TO : Linda Chapman - T2B

All samples were obtained with a flow rate of 2 lpm indicated on the rotameter. Two pumps were used, and two orifices only. The sample orifice was always used with the same pump. You have one set for calibration. The other set is presently at the Luling, Louisiana Plant and will be given to you for calibration when it is returned.

The samples that were obtained were as follows:

Tube 98 was sampled using Pump #6 with orifice #56 from 8:30 a.m. to 9:12 a.m. during which time glue was being applied to the back of Astroturf with a 2½" paint brush. This was being performed by Mr. Sandy Clark.

Tube #64 was obtained using Pump #6 and orifice #56 from the operator of the grass tractor starting at 10:57 a.m. and ending at 11:19 a.m.

Tube #109 was obtained using Pump #2 and orifice #60. The sample was started at 10:32 and ended at 11:52. It is the ✓ exposure of the glue tractor driver. At 11:15 a.m. trouble developed with the glue pump, and for the last seven minutes the exposure was during repair of the pump.

Tube #57 was obtained using Pump #6 with orifice #56. The sample was started at 3:13 and ended at 3:25, and represented the entire time that seam spraying was performed.

Tube 97 was obtained with the use of Pump #2 and #60 orifice. ✓ It was started at 8:13 a.m. and ended at 10:13 a.m. during the performance of hand seaming.

Tube 33 was used with Pump #6 and orifice #56 by the shield man during the spraying of glue. The sample was started at 12:25 p.m. and ended at 1:27 p.m.

Carl D. Bohl

mlw

MODIFICATION OF A GAS CHROMATOGRAPH FOR EXTERNAL USE OF THE CARRIER GAS

SUMMARY

This report describes the modification of a gas chromatograph which makes the carrier gas conveniently available for use external to the chromatograph. For example, the helium carrier gas may be used to purge the organics from an externally mounted air sampling tube onto the head of an analytical column mounted in the GC oven.

DISCUSSION

Most gas chromatographs have a carrier gas fitting which is connected to the injection port through a flow controller valve and a molecular sieve trap. A three port valve can be placed in the carrier gas line between the molecular sieve trap and the injection port and mounted on the top or the side of the chromatograph (see diagram attached). With a valve of this type installed, the carrier gas can easily be switched to the external line. Since the valve is after the flow controller, one can use the external helium line for chromatographic purposes. We typically connect this external carrier gas line to one end of an air sampling tube. The other end of the tube is connected to the injection port of the chromatograph at the septum nut. Using the three port valve the carrier gas can be switched to the external line and used to flush organics from the heated sampling tube onto the head of the analytical GC column. In this position the three port valve closes the normal carrier gas line to the injection port. This keeps sample and carrier gass from leaving the injection port through the normal carrier gas line.

We have found that a Whitey valve SS-42XF2 works well for this modification. This valve has an intermediate position at which the input port is connected to neither exit port. This position can be used as a convenient shut-off for the carrier gas.

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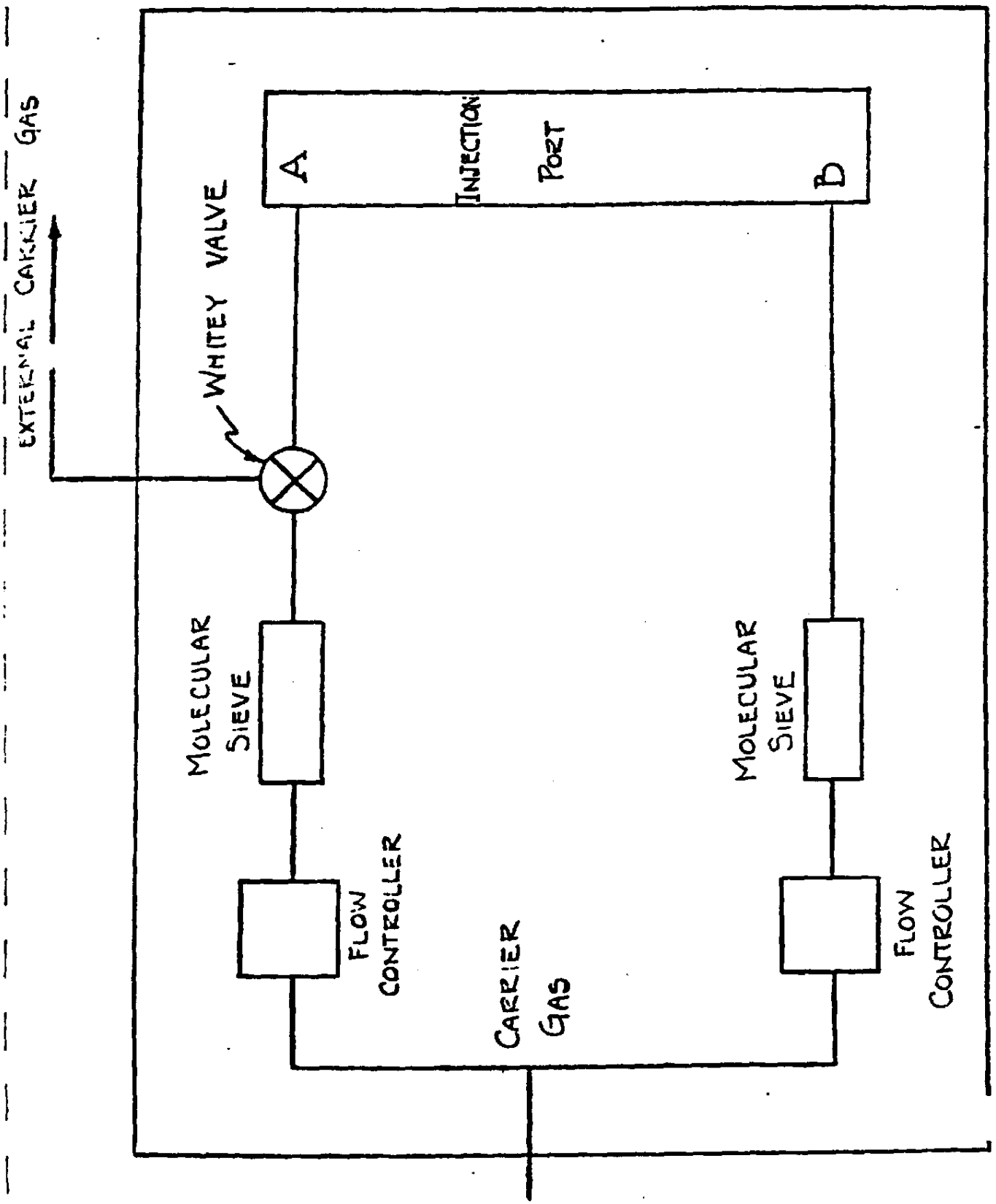
7/75 - G. W. Mappes, L. M. Chapman, M. W. Dietrich

DIAGRAM FOR S-75-SS-15



RSV 0010599

Special Study
S-75-SS-16

NC-220 QUALITY

INTRODUCTION

In a previous study of deposit formation in Pydraul fluids (MICC Applied Sciences Spectroscopy Special Study 74-14), amides were detected in many of the samples analyzed. These amide components could be caused by:

1. Reaction products of the 1-methyl-2-pyrrolidone catalyst used in the manufacture of the Pydraul base stock phosphate ester.

2. Contamination by the customer.

3. Nitrogen fixation of the air trapped in the hydraulic system.

An in-depth study was made of a reserve production sample of NC-220, the Pydraul base stock, by earth filtration, IR (infrared) analysis, NMR (nuclear magnetic resonance) analysis, XRF (X-ray fluorescence), and GPC (gel permeation chromatography) to determine if any of the amide components are inherent in the manufacturing process.

SUMMARY

IR, NMR and XRF analyses of materials isolated from new NC-220 showed:

1. Presence of a reaction product of an amide with the phosphate ester.

2. Pyrophosphate or polyphosphate esters.

3. An amide compound free of phosphorus which is not 1-methyl-2-pyrrolidone or 2-pyrrolidone.

4. No epoxy stabilizer-phosphate ester reaction product (NC-220 should contain no epoxide stabilizer).

5. Presence of metallic entities with calcium as the major and iron, nickel and zinc as the minor elements detected.

Materials isolated from a filter deposit from a Pydraul 50E system at Chevrolet's Messina plant (TSR 74-123) contained mixtures of the epoxy-phosphate ester and amide-phosphate ester reaction products. The probable structure of the epoxide reaction product is indicated in the discussion. The presence of the epoxide reaction product prevented establishing whether the amide reaction product was the same as that found in new NC-220.

Total nitrogen levels in five random reserve samples of NC-220 varied from 0.03 to 0.06%. Filtration through attapulgus earth reduced the nitrogen level in one sample by a factor of three.

RESULTS AND DISCUSSION

A plant batch of NC-220 (MIC 225748-C) was percolated through an "earth" column without dilution. After elution of the fluid, the absorbed materials were recovered by washing the column with acetone and methanol.

A filter deposit from a Pydraul 50E installation at Chevrolet's Messina plant was fractionated by solvent extraction with hexane, chloroform, acetone, methanol and water.

IR analysis of the acetone and methanol fractions from the "earth" filtration after hexane washing to remove residual NC-200 indicated high nitrogen contents, apparently a reaction product of an amide with a partially hydrolyzed phosphate ester. The reaction product contains both

$$-\overset{\overset{O}{\|}}{C}-N-$$

, P-O and P=O bonding.

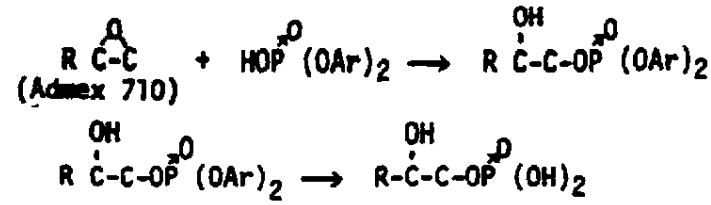
IR analysis of the fractionated filter deposits showed the same types of products found previously in Pydraul 50E deposits namely the reaction product of the epoxy stabilizer with the partially hydrolyzed phosphate ester base stock, and metal salts of these interaction products. The fraction isolated by acetone extraction of the hexane and chloroform insoluble portion of the deposit showed the presence of an interaction product of an amide and the phosphate ester.

The acetone and the methanol eluted fractions from the earth filtration of the new NC-220 (MIC 225748-C) and the isolated hexane and chloroform insoluble/acetone soluble fraction from TSR 74-123 were further separated by molecular size using GPC. The isolated fractions were analyzed by IR and NMR.

The results tabulated in Tables I and II for the acetone and methanol eluted fractions from the earth filtration showed as expected no indications for the presence of the sticky epoxy-phosphate ester reaction product associated with valve, filter or pump problems encountered using Pydraul E series fluids (see MICC Applied Sciences Spectroscopy Special Study 74-14). Two types of amide containing reaction products were observed in the acetone eluted fraction: about a 1:1 and about a 2:1 amide-phosphate ester reaction product. Since the catalyst 1-methyl-2-pyrrolidone is the only nitrogen containing entity used in the phosphate ester process, it must be assumed that the catalyst is the amide portion of the observed reaction products.

The methanol eluted fraction from the earth filtration showed the presence of polyphosphates or pyrophosphates. NMR and IR again indicated the presence of an amide reaction product. The NMR spectra were very similar to that of N-methyl pyrrolidone including the presence of a signal attributed to N-methyl. A low molecular weight amide was also found that may be the active component in the reaction product with the phosphate ester. The quantities isolated were too small for further characterization by other instrumental methods.

The GPC fractionation of the acetone soluble portion of the Chevrolet Messina plant filter deposit (TSR 74-123) showed the presence of mixtures of the epoxy stabilizer-phosphate ester reaction product seen in all the previous problems with Pydraul E series fluids. The NMR spectrum of this adduct looks very much like that of Admex 710 which is further reacted with a molecule containing no ArH and no other RH. A possible mechanism of formation could be reaction of an acid phosphate with Admex 710 followed by hydrolyses of the reaction product.



In addition, an amide-phosphate ester was present. Because of interferences by the epoxy reaction product, it could not be established if the amide reaction product was the same as that found in the new fluid.

Total nitrogen analysis of the new NC-220 used in this study before and after earth filtration and of four reserve samples of NC-220 from June 1974 and October 1974 production were obtained by Kjeldahl digestion and measurements with an ammonium ion specific electrode. The results tabulated in Table IV show an almost constant level of nitrogen containing contaminants. About a 3-fold decrease in nitrogen level is obtained by earth filtration.

XRF (X-ray fluorescence) analysis of GPC F #1 and F #2 of the methanol recovered fraction from the earth filtration indicated partial metal salts were present in addition to esters of the pyro- and/or polyphosphates. The major metallic element present was calcium and the minor elements detected were iron, nickel and zinc.

References: NMR 16-1046, 16-455, 16-1047.
IR 74-396, 74-511, 74-512.

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6/75 - B. Katlafsky, W. J. Litschgi, M. W. Dietrich

TABLE I

GPC SEPARATION OF EARTH COLUMN ACETONE FRACTION

FRACTION NO.	GPC VOLUME CUT	APPARENT MOL. WT.	WEIGHT PERCENT	COMMENTS
1	33.0-40.0	1170-730	17.8	1:1 reaction produce of amide with phosphate ester - ester portion high in cumylphenyl groups
2	40.0-44.3	730-420	16.1	Similar to F #1, amide content higher, contains cumyl and some nonyl contains $N-CH_3$
3	44.3-47.8	420-255	22.4	Residual NC-220 containing about 10% amide reaction product
4	47.8-51.7	255-150	40.8	Similar to F #3, ~20% amide reaction product
5	51.7-53.6	150-118	1.6	~2:1 amide to ester reaction product
6	53.6-60.0	118-70	1.3	Similar to F #5, may involve preferentially the cumylphenyl component

TABLE II

GPC SEPARATION OF EARTH COLUMN METHANOL FRACTION

FRACTION NO.	GPC VOLUME CUT	APPARENT MOL. WT.	WEIGHT PERCENT	COMMENTS
1	31.0-35.1	>3000	41.6	Pyro or polyphosphate ester containing a low level of amides - contains ArH and RH, may contain iron
2	35.1-37.7	>3000-990	22.4	Same as F #1 - XRF analysis of combined F #1 and F #2 indicated the presence of calcium, iron, nickel and zinc
3	37.7-43.9	990-420	10.6	Similar to F #1, amide content much higher
4	43.9-47.3	420-270	5.5	∿2:1 amide to orthophosphate ester reaction product
5	47.3-53.1	270-130	9.0	Same as F #4, contains cumyl unit, NMR similar to N-methyl pyrrolidone, contains N-methyl
6	53.1-58.1	130-66	5.1	Same as F #4
7	58.1-60.0	<66	3.1	No phosphorus present. A primary and/or secondary amide which is not 1-methyl-2-pyrrolidone or 2-pyrrolidone, 110 ArH, NMR similar to N-methyl pyrrolidone, contains N-methyl
8	60.0-65.0	<66	2.7	Same as F #7

TABLE III

GPC SEPARATION OF ACETONE FRACTION FROM PYDRAUL 50E DEPOSIT (TSR 74-123)

FRACTION NO.	GPC VOLUME CUT	APPARENT MOL. WT.	WEIGHT PERCENT	COMMENTS
1	27.0-30.0	>3000	7.7	Epoxy reaction product with phosphate ester - polymer is low in aromatic components. Presence of nitrogen detected qualitatively
2	30.0-35.0	>3000-1500	46.8	Same as F #1, no aromatic H, contains fatty acid and ester, NMR looks very much like Admex 710 which has reacted with a molecule which contains no ArH and possibly no RH
3	35.0-40.0	1500-730	16.8	~2:1 mixture of epoxy-phosphate and amide-phosphate reaction products
4	40.0-43.9	730-430	12.9	~1:1 mixture of epoxy-phosphate and amide-phosphate reaction products
5	43.9-45.3	430-360	5.2	Phosphate ester salts containing low level of amide
6	45.3-47.5	360-270	5.8	Similar to F #5
7	47.5-55.0	270-70	4.8	Similar to F #5

TABLE IV
TOTAL NITROGEN CONTENT OF PRODUCTION NC-220

SAMPLE	% NITROGEN
NC-220 MIC 225748-C Neat	0.04 0.06
NC-220 MIC 225748-C After Earth Filtration	0.01 0.02
NC-220 Lot QD-33 5/29/74	0.03
NC-220 Lot QD-39 6/10/74	0.04 0.04
NC-220 MIC 255274 10/19/74	0.03 0.04
NC-220 MIC 255274 10/21/74	0.04 0.03

Special Study
S-75-SS-17

CHLORODIBENZO-p-DIOXINS IN PENTACHLOROPHENOL TREATED WITH MORPHOLINE

SUMMARY

The Hewlett-Packard GC/MS system was used to identify and measure non-phenolics in five different lots of pentachlorophenol. These samples of penta had been subjected to a morpholine treatment at the W. G. Krummrich plant. They were found to contain levels of pentachloro, hexachloro and heptachloro-dibenzodioxins at least ten times higher than found in pentachlorophenol which has not been treated. This suggests that the morpholine treatment may convert dioxin precursors to dioxins.

DISCUSSION

Solutions of the non-phenolics in benzene were received from Steve Vogel, W. G. Krummrich plant containing the non-phenolics from 0.1 gram of each lot of pentachlorophenol. Phenolics had been removed by NaOH extraction. The measurement procedure is the same as that described in Special Study AC-75-SS-3. The amounts of various dioxins are reported as ppm based on 0.1 gram sample weight and are given below:

Sample Identification	Concentration (ppm)			
	Unknown Chloro Aromatic	Penta CDD	Hexa CDD	Hepta CDD
212180-1	0.2	<0.1	120	2100
212180-7	0.3	<0.1	110	1800
211535	4	0.4	73	1400
KM-261	0.3	0.4	50	1500
256338	2	1.5	180	1600

No dichloro or trichlorodibenzodioxins were observed with a detection limit of 0.1 ppm. The unknown chloro aromatic has a significantly different GC retention time and mass spectrum from 2,3,7,8-tetrachlorodibenzodioxin. However, its spectrum does contain 322 and 259 ions which would be expected of any tetrachlorodibenzodioxin. The full mass spectrum, however, contains ions which should not come from a dioxin. Because this spectrum is very weak, the possibility that this component is a tetrachlorodibenzodioxin (but not the 2,3,7,8 isomer) cannot be ruled out.

db

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6/75 - G. W. Mappes, M. W. Dietrich

Special Study
S-75-SS-18

JUNE 1975 MERCURY INVENTORY, W. G. KRUMMRICH PLANT, CHLOR-ALKALI DEPARTMENT

INTRODUCTION AND SUMMARY

The mercury inventory made at W. G. Krummrich plant has been completed. The sum of the average weights for the 22 cells was 251,135 pounds ±5697 (2 sigma limits). This is 5146 pounds less than the inventory of October 1974.

Cell house mixing was followed on cells 1, 7, 14, 15 and 22; all cells were completely mixed after 24 hours. Inventory by individual cells is tabulated in Table I attached.

The 2 sigma confidence estimate of ±5697 pounds of mercury (2.27% of total inventory) was double that of most previous inventories primarily due to abnormally low sample radioactivity. An investigation showed that the initial radioactivity in the Mercury-203 shipment was about 1/3 that of previous shipments. Also plant delays of about 20 days of targeted spike date further diminished the 46.7 day halflife radioactivity by an additional 25%. Subsequent discussions with plant personnel indicated that they did not feel that to recount the samples at longer count intervals (50 min. per sample vs the normal 20 min.) was justified.

REFERENCES

Research Notebook MIC 264367A-2643832B.

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Applied Sciences
St. Louis, Mo.

6/75 - H. Yepez, D. B. Hines, M. W. Dietrich

TABLE I

MERCURY INVENTORY — MERCURY INVENTORY W.G.K. PLANT JUNE 1975

CELL NO.	AVERAGE MERCURY INVENTORY (LBS)	STANDARD DEVIATION (LBS)	TWO SIGMA (LBS)	TWO SIGMA - PERCENT OF TOTAL
1	10266.35	146.90	293.81	2.862
2	11009.81	146.41	292.82	2.660
3	11889.56	87.44	174.88	1.471
4	11306.52	126.39	252.78	2.236
5	10889.75	117.58	235.15	2.159
6	11259.05	67.12	134.25	1.192
7	12076.07	104.51	209.02	1.731
8	10275.38	99.49	198.98	1.937
9	11578.00	118.01	236.02	2.039
10	11272.66	90.51	181.02	1.606
11	12087.04	161.06	322.13	2.665
12*	9218.55	108.00	216.01	2.343
13	12524.33	215.46	430.91	3.441
14*	11009.25	96.35	192.71	1.750
15	13488.73	218.29	436.58	3.237
16	11309.94	126.39	252.78	2.235
17	11216.91	106.45	212.91	1.898
18	10359.34	58.20	116.41	1.124
19	11988.21	97.76	195.52	1.631
20*	10623.32	145.47	290.95	2.739
21	14134.02	251.97	503.94	3.565
22	11353.46	158.93	317.86	2.800

RSV 0010609

THE SUM OF THE AVERAGE WEIGHTS IS 251135.88 LBS.

THE SUM OF ALL TWO-SIGMA IS 5697.41 LBS.

THE PERCENT THE SUM OF ALL TWO-SIGMAS IS OF THE TOTAL INVENTORY WEIGHT = 2.269 PERCENT

* CELLS 12, 14 and 20 HAD 836 # VIRGIN MERCURY ADDED AFTER CELLS WERE SPIKED. THE INVENTORIES GIVEN ABOVE WERE BASED ON SAMPLES FROM THE 3 CELLS TAKEN BEFORE THE MERCURY WAS ADDED.

Spectroscopy
Special Study 75-19

DETERMINATION OF MALEIC ANHYDRIDE AND VINYL ACETATE IN AIR: PORT PLASTICS

INTRODUCTION

Analyses were performed to determine levels of Maleic Anhydride (MA) and Vinyl Acetate (VA) in air during a maleic anhydride resin process at Port Plastics, Addyston, Ohio. Workers in this area wear inhalation aspirators. The results given are not exposure levels but are the levels workers would be exposed to if they did not have protective equipment.

SUMMARY

Levels of MA and VA found are given in the attached table.

EXPERIMENTAL

A glass Tenax GC insert was used for collection and analyses. Calculations and identifications based on known standards, GC retention time and GC/MS verification.

Calculations

Volume of Air Sampled (Liters) = Supplied by Steve Roberts

$$\text{Weight Sample } (\mu g) = \text{Area Sample Peak (counts)} \times \frac{\text{Conc. Std. } (\mu g/\mu L) \text{ Vol. Injected } (\mu L)}{\text{Area of Standard (counts)}}$$

Concentration Sample (µg/L) = Weight Sample (µg)/Volume of Air Sampled (Liters)

$$\text{Concentration Sample (ppm)} = \mu g/L \text{ (sample)} \times \frac{24.5}{\text{M. W. (sample)}}$$

For Sampling 001

Volume of Air Sampled = 2.3 liters

$$\text{Weight Sample } (\mu g) = 16069 \times \frac{3.2 \times 1.5}{10719} = 7.2 \ \mu g$$

$$\text{Concentration VA } (\mu g/L) = \frac{7.2}{2.3} = 3.1 \ \mu g/L$$

$$\text{Concentration VA (ppm)} = 3.1 \times \frac{24.5}{86} = 0.9 \text{ ppm}$$

Reference GC/MS File #75-112

ss

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St. Louis, Mo.

6/75 - L. M. Chapman, M. W. Dietrich

S-75-SS-19

	CONCENTRATION (PPM)		
Sample	MA	VA	Comments
001	ND (≤ .2 ppm)	0.9 ppm	2.3 l sampled
002	ND (≤6.6 ppm)	1.8 ppm	0.75 l sampled
003	≤0.3 ppm	1.1 ppm	MA wasn't positively identified because of interferences: 2.4 l sampled

DETERMINATION OF CHLOROPRENE IN AIR AT PORT PLASTICS PLANT, ADDYSTON, OHIO

INTRODUCTION

The purpose of this investigation was to determine worker exposure in the handling of chloroprene.

SUMMARY

Two samples were analyzed for chloroprene. One sample taken during a leak in the operation gave a concentration of 1.2 ppm in the air while the other sample had a concentration of 0.8 ppm. Both are well below the TLV.

EXPERIMENTAL

A C-105 insert was used for collection and a 3% OVI glass analytical column was used for the analysis. A description of the calculations is given below. Identification was by GC retention time of known standards.

Calculations

Volume of Air Sampled (Liters) = Supplied by Steve Roberts

Weight Sample (µg) = Area Sample Peak (counts) $\times \frac{\text{Conc. Skd. (µg/µL) Vol. Injected (µL)}}{\text{Area of Standard (counts)}}$

Concentration Sample (µg/L) = Weight Sample (µg)/Volume of Air Sampled (Liters)

Concentration Sample (ppm) = µg/L (sample) $\times \frac{24.5}{\text{M. W. (sample)}}$

For Sampling 75-19

Volume of Air Sampled = 9.3 liters

Weight Sample (µg) = $5292 \times \frac{25 \times 1.5}{4874} = 40.7$ µg

Concentration Chloroprene (µg/L) = $\frac{40.7}{9.3} = 4.4$ µg/L

Concentration Chloroprene (ppm) = $4.4 \times \frac{24.5}{88.5} = 1.2$ ppm

Reference: GC/MS File #75-111

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Applied Sciences
St. Louis, Mo.

6/75 - L. M. Chapman, M. W. Dietrich

DETERMINATION OF VOLATILES IN DECATUR, ALABAMA PLANT AIR (IV)

INTRODUCTION

This is a continuation of an investigation to determine levels of vinyl acetate (VA), acrylonitrile (AN), vinyl bromide (VBr), vinlyidene chloride ($VnCl_2$), DMAC and DMF in air at the north continuous polymer area of the Decatur, Alabama plant. The data obtained will be used to identify areas where worker safety problems may exist.

SUMMARY

Results of two sample sets are found in Table I and Table II. GC retention time provided the means of identification of the volatiles. Acrylonitrile had values of from 0.2 to 2.0 ppm, vinyl acetate values ranged from 0.1 to 11.4 ppm, VBr ranged from 0.1 to 1.6 ppm and vinilidene chloride ranged from 1.2 to 4.0 ppm. Values for DMAC and DMF are uncertain because the columns used for collection have not been fully investigated for these components.

EXPERIMENTAL

Refer to Spectroscopy Method 74-7 for the analyses procedure used. Twelve minutes were allowed for the heating of the external collection column to collect the acrylonitrile before proceeding as in Method 74-7. An example of the procedure used to calculate concentration is given in the S-75-SS-1 report. Sample collection was made using a Model 222-451 SKC pump. Calculations were based on known standards.

Reference: GC/MS File #75-114

ss

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TABLE I
CONCENTRATION (PPM)

	VBr	AN	VA
M-3	1.0 PPM	2.0 PPM	0.4 PPM
M-4	1.6	2.0	0.3
M-5	0.1	1.2	0.2
L-4	0.8	0.1	ND

Samples from 5-19-75

Volume sampled ≈ 2 liters
Flow rate ≈ 17 mℓ/min
Sampling time ≈ 2 hours

TABLE II
CONCENTRATIONS (PPM)

	VBr	$VnCl_2$	VA	AN	DMF**	DMAC**
L-12	0.4	1.6	$\leq$ 0.1*	ND	2.7	ND
L-7	ND	1.2	$\leq$ 0.1*	0.2*	ND	$\leq$ 1.1*
L-11	ND	ND	1.0	ND	2.0	ND
L-10	0.4*	4.0	$\leq$11.4*	ND	ND	$\leq$ 1.7*
L-1	- - - - - - - -	Lost in analysis			- - - - - - - - - -	
L-3	- - - - - - - -	Lost in analysis			- - - - - - - - - -	

* Due to interference from other components these are maximum values.

** Values for DMF and DMAC are questionable because the columns used for the collection have not been fully investigated for these compounds.

Samples from 6-9-75

Volumes sampled $\approx$ 2 liters
Flow rate $\approx$ 16 ml/min
Sampling time $\approx$ 2 hours

DETERMINATION OF CONTAMINANTS IN DIMETHYL SULFIDE

INTRODUCTION

Dimethyl sulfide is a component in an artificial tomato flavor to be sold to General Foods. The purpose of this study was to identify impurities in certain lots of dimethyl sulfide which cause the product to be non-acceptable to General Foods.

SUMMARY

Impurities identified are given in the attached table. The major difference between the acceptable and non-acceptable products was the presence of C_3H_8S and $C_4H_{10}S$ components in the non-acceptable product. These components may explain the differences observed by General Foods.

EXPERIMENTAL

A Chromosorb 105 analytical column was used for the analyses. Calculations are based on a dimethyl sulfide standard. GC/MS provided the identification of components.

Reference: GC/MS file #75-116

ss

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7/75 - L. M. Chapman, M. W. Dietrich

Table for S-75-SS-22

	CONCENTRATION (g/ℓ)						
	DMS	Propene*	C_2H_6S	C_3H_8S	C_3H_8S	$C_4H_{10}S$	Misc**
Phillips (better than acceptable)	997	1.0	2.3	ND	ND	ND	< 0.1
Aldrich #2 (acceptable)	996	1.4	2.8	ND	ND	ND	< 0.1
Penwalt (not acceptable)	975	1.2	2.4	3.1	1.0	16.7	≤ 0.2
Penwalt Ex Drum (not acceptable)	989	1.8	2.5	0.7	0.3	4.8	≤ 0.2

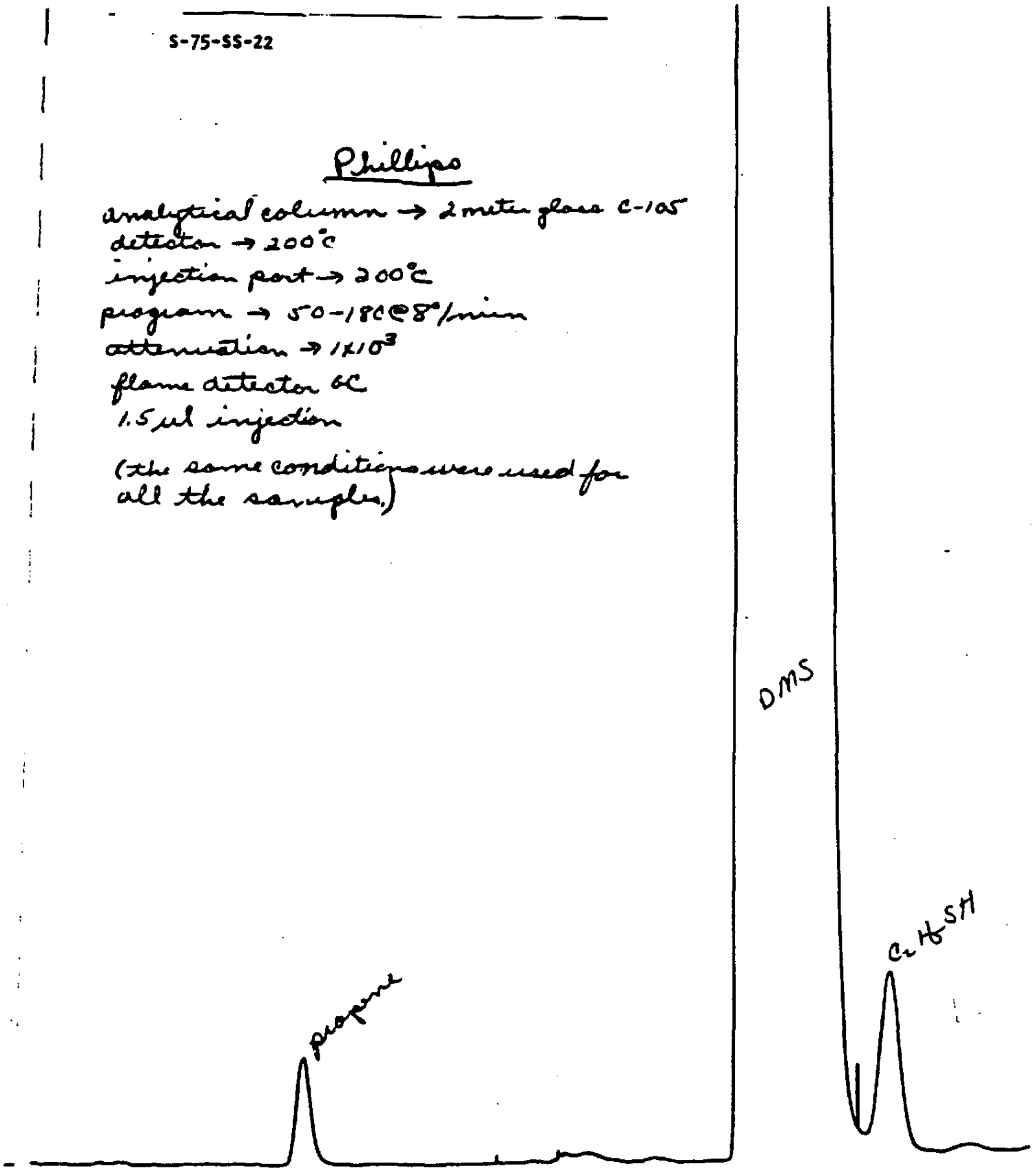
* Tentative identification only
** The sum of other small contaminants not specifically identified

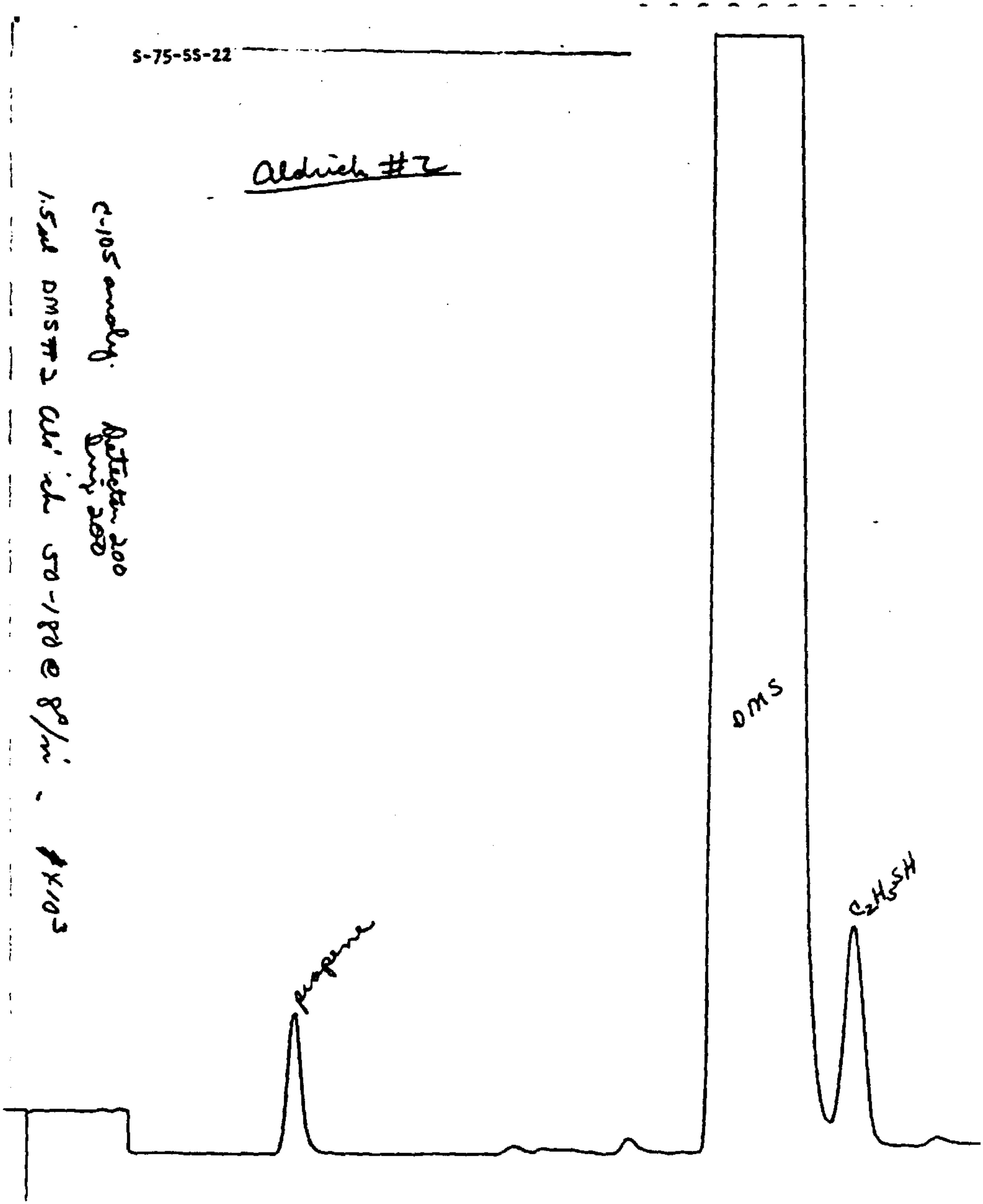
S-75-SS-22

Phillips

analytical column → 2 meter glass C-105
detector → 200°C
injection port → 200°C
program → 50-180@8°/min
attenuation → 1×10^3
flame detector GC
1.5 µl injection

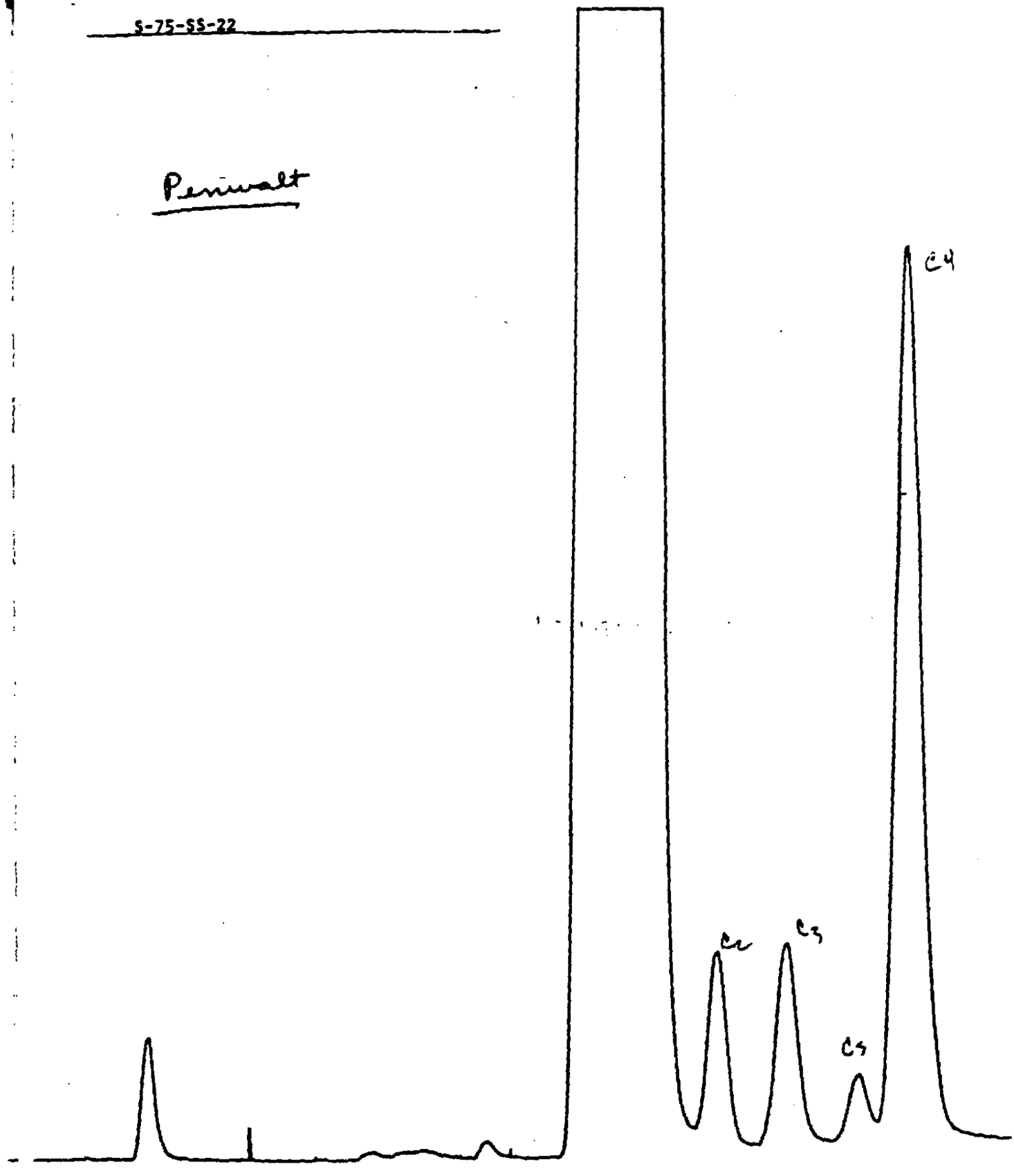
(the same conditions were used for all the samples.)




S-75-55-22
Aldrich #2
C-105 analy.
DMS
C_2H_5SH
propene

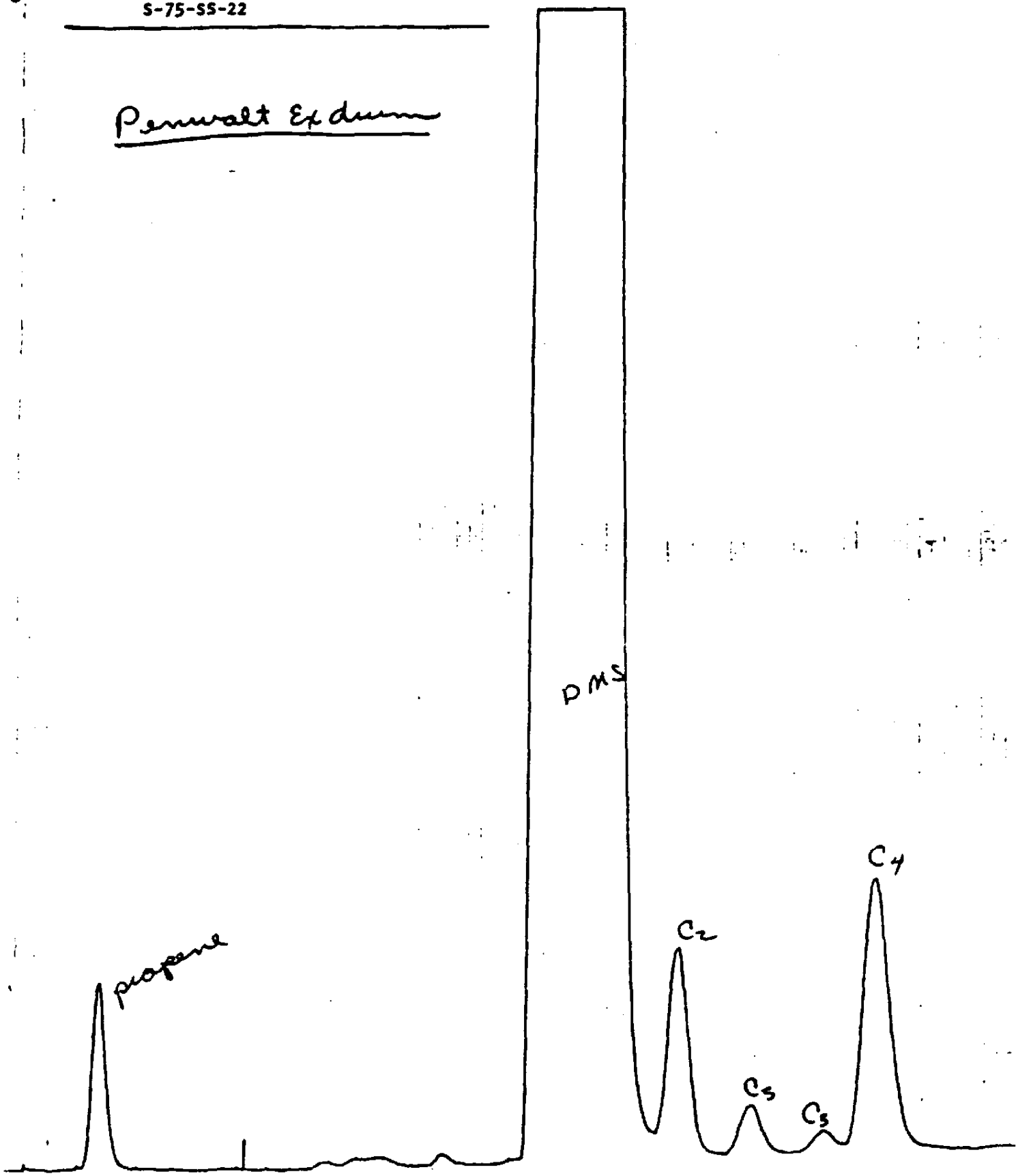
S-75-SS-22

Perivalt



S-75-SS-22

Pennwalt Exhaust



VOLATILE ORGANICS EVOLVED DURING THERMOGRAVIMETRIC ANALYSIS OF FLAME AND SMOKE RETARDING PVC FORMULATIONS

SUMMARY

Volatile organics from PVC decomposition between 250 and 350°C were identified and quantified. Fifteen components were identified. The total organics observed accounted for from 0.5 to 3 percent of the sample weight. Under these conditions, the TGA indicated from 5 to 60 percent weight loss. The material not measured is presumed to be principally HCl and high boiling organics.

DISCUSSION

The twelve PVC sheets submitted for thermogravimetric analysis, Physical Chemistry Special Study 74-48, were decomposed in the TGS-1 thermobalance using sample weights of 10 to 15 milligrams. The temperature program rate was 10°/min. with an air purge gas flowing at 10 mℓ/min.

The air and organics exiting from the TGS-1 were sampled by a loop of 1/8 inch O.D stainless tubing having a volume of 10 mℓ. After sampling, the loop was transferred to a gas chromatograph where the gas sample was trapped on the head of a Tenax GC column at -40°C. The Tenax GC column was temperature programmed from -40 to 250°C. The organics which eluted were identified by a combination of GC/MS and GC retention time.

The data from these analyses are presented in two forms. One is a graph showing both the TGA weight loss and the total organics for each gas sampling as a percent of sample weight. The other is a table for each sample showing component identification and concentration of that component as a percentage of all the organics measured from that sample. The temperatures are not the same for each table because the gas samples were taken at corresponding points of weight loss on the TGA curve rather than at corresponding temperatures.

The sample loops were attached to the TGA apparatus when the apparatus reached the temperature indicated in the table and were left connected during the next 10 degree temperature increase, i.e. for one minute. This means that the concentrations given in the table reflect an average composition over the period of this 10 degree increase.

GC/MS identifications were done on the basis of three sample loops. The peaks in the remaining 69 GC separations were identified by retention time relative to the GC/MS data. This is a good method of identification for all of the components except C_9 olefin, alkyl chloride and C_{10} olefin which are incompletely resolved. If the identity of one of these components becomes critical for a given point on the TGA curve of a particular sample, we will have to check that sample by GC/MS.

Some of the very small peaks are not included in the table so that addition of all the entries in each table will not quite equal 100%.

ss

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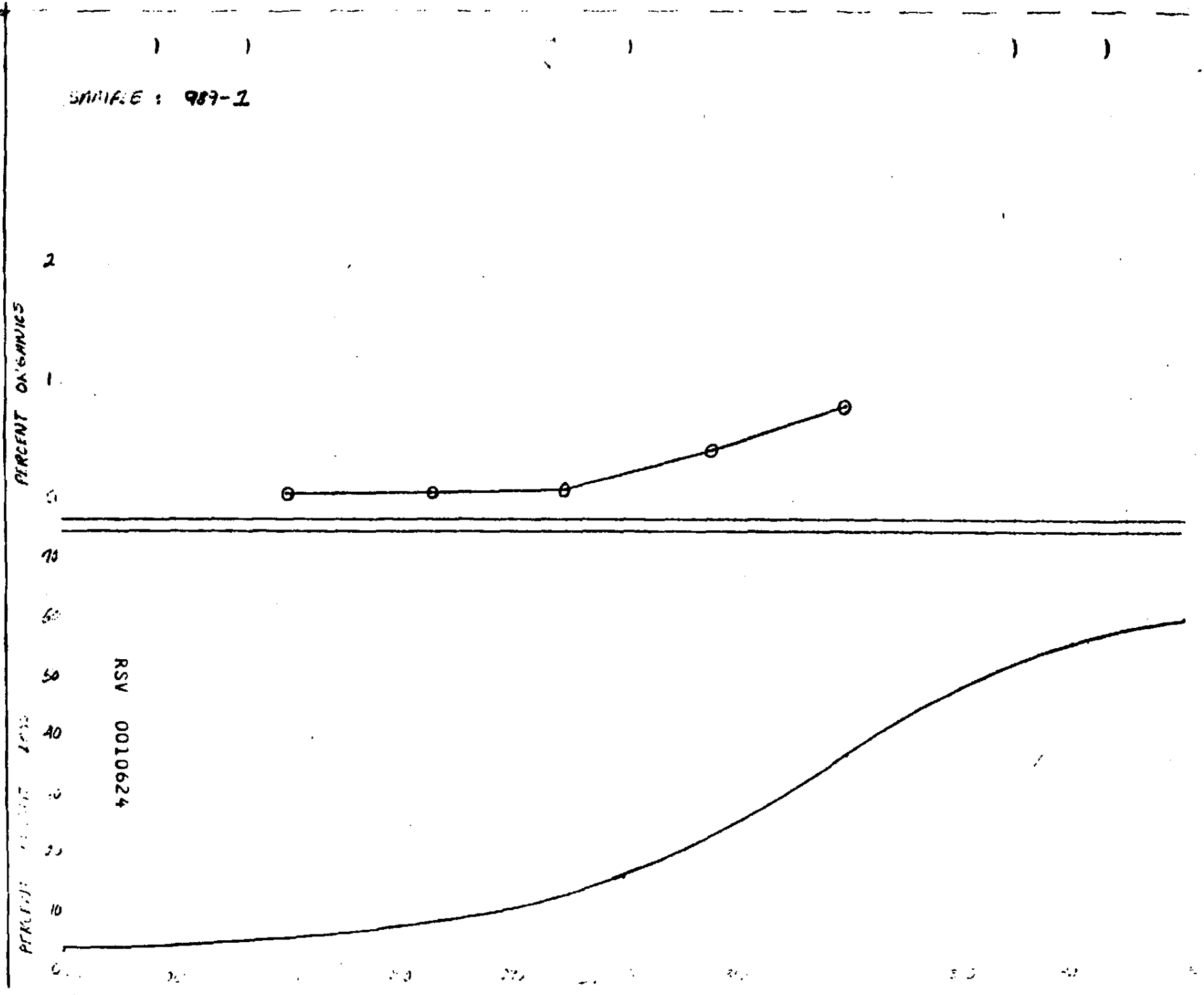
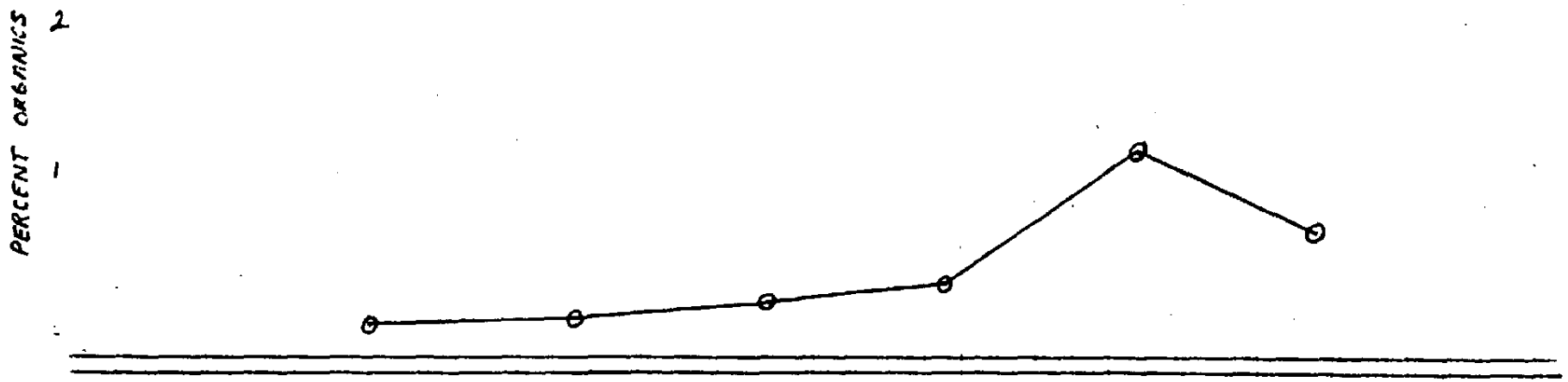
7/75 - G. W. Mappes, C. Calvert, M. W. Dietrich

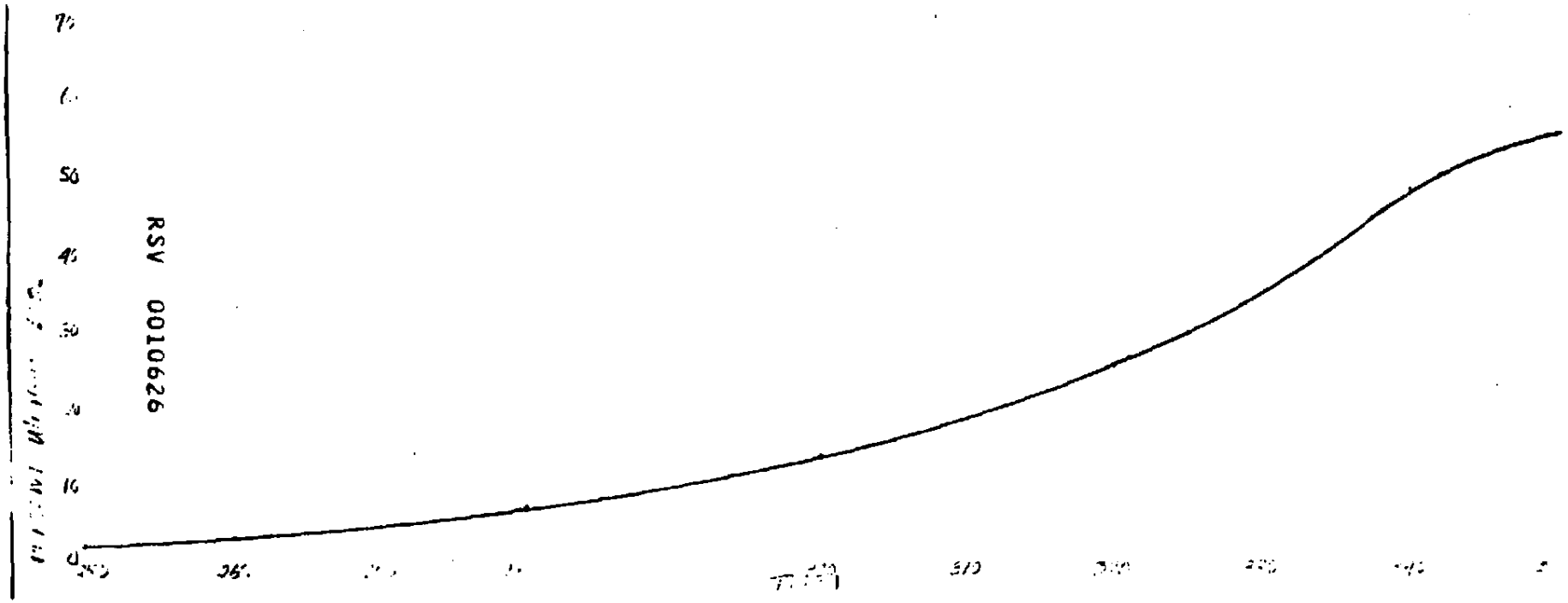
SAMPLE : 987-1


PERCENT OXIDANTS
2
1
0
PERCENT
70
60
50
40
30
20
10
0
RSV 0010624

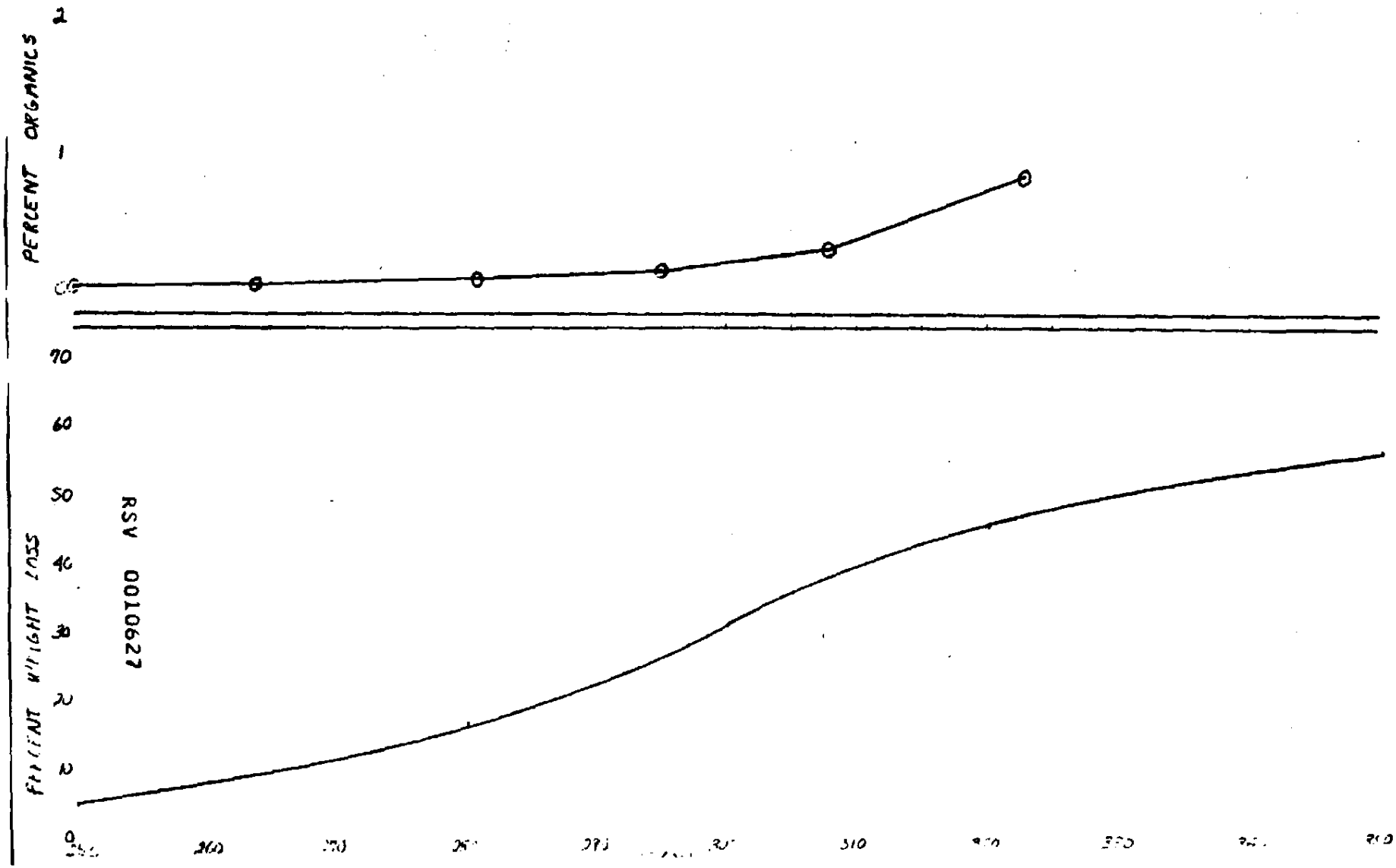
PERCENT ORGANICS
RSV 0010625

SAMPLE : 787-3



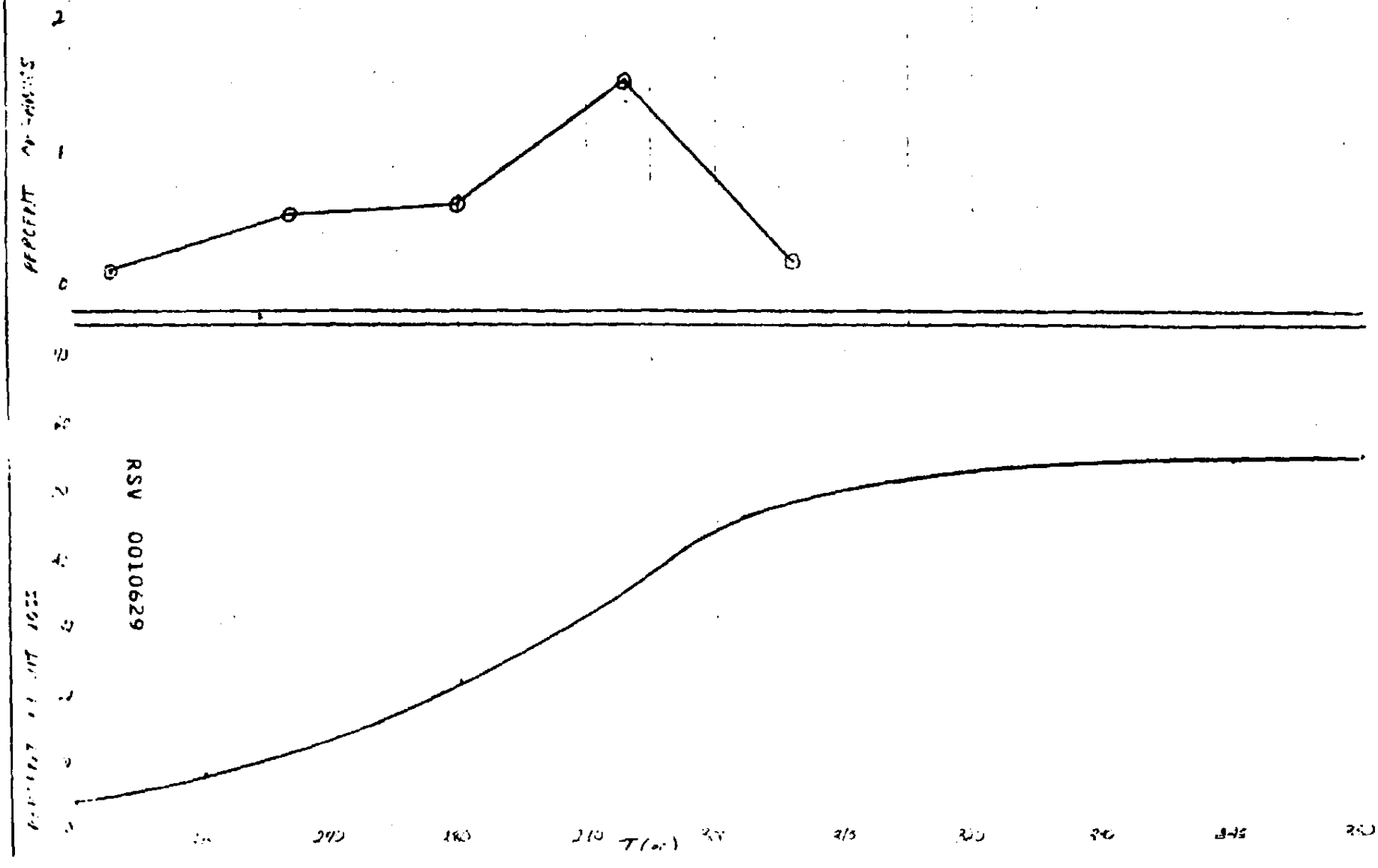


SAMPLE : 989-4

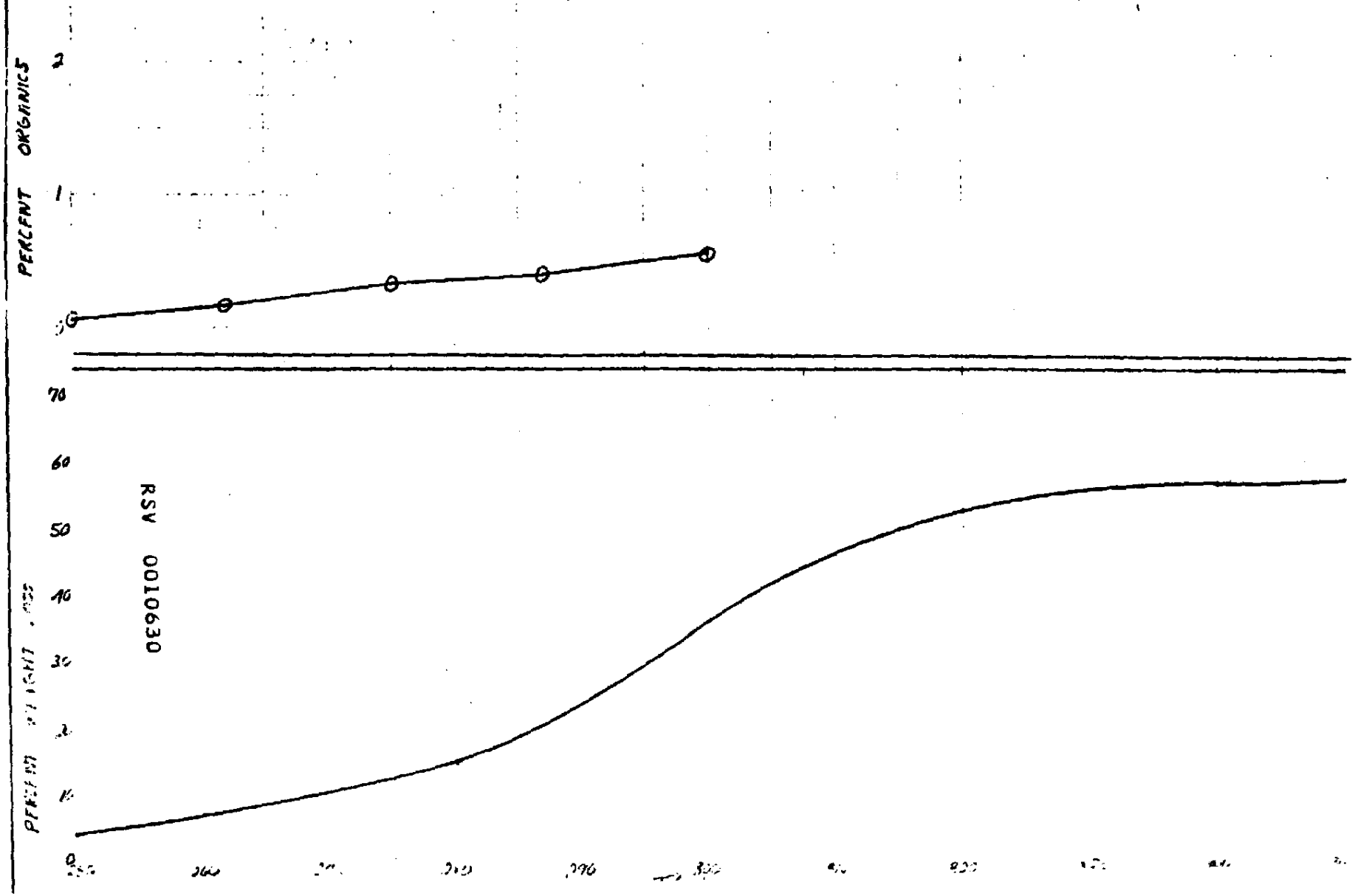


SAMPLE : 99-5
PERCENT OPENINGS
PERCENT WEIGHT LOSS
RSV 0010628

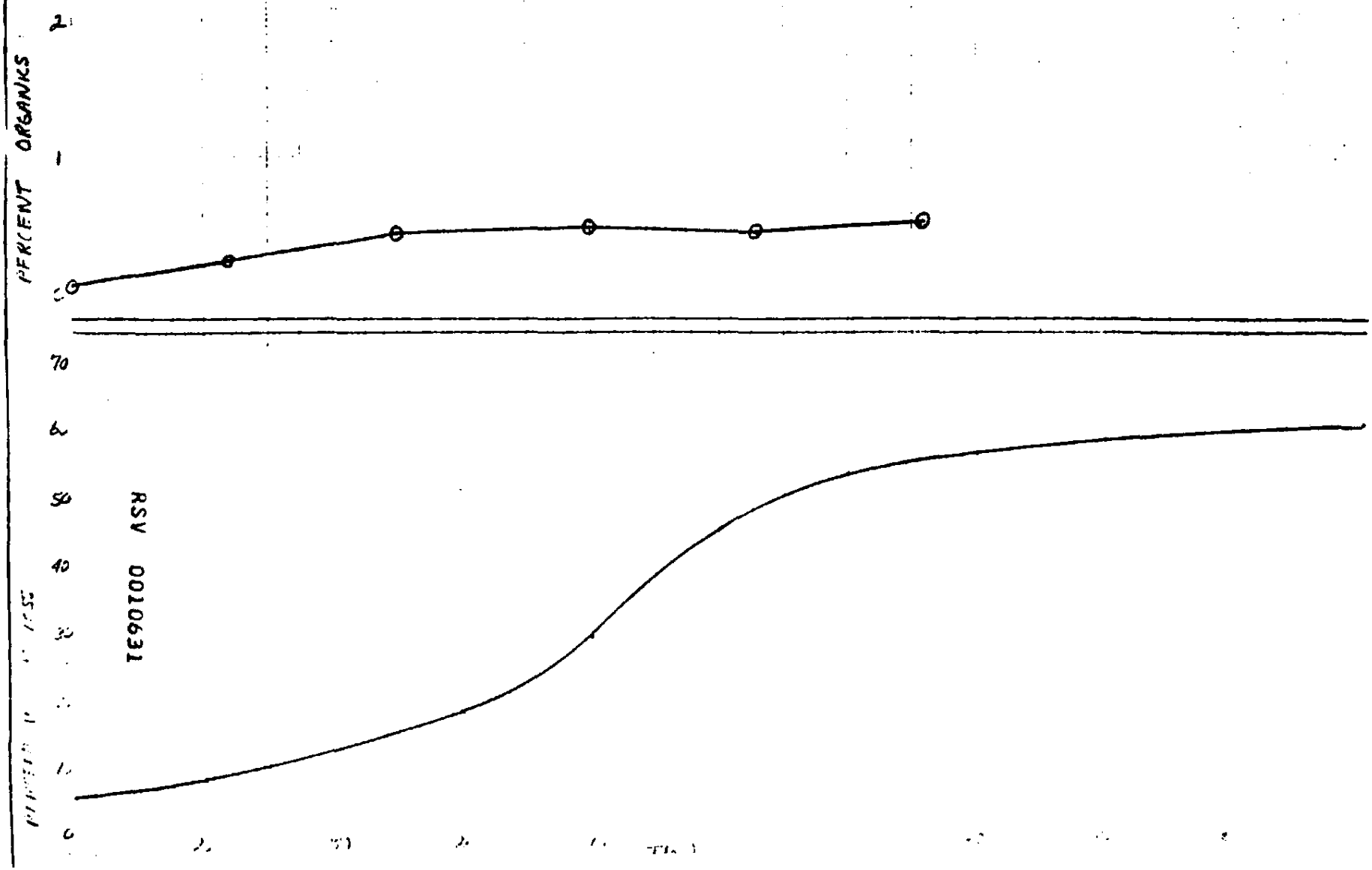
SAMPLE: 989-6

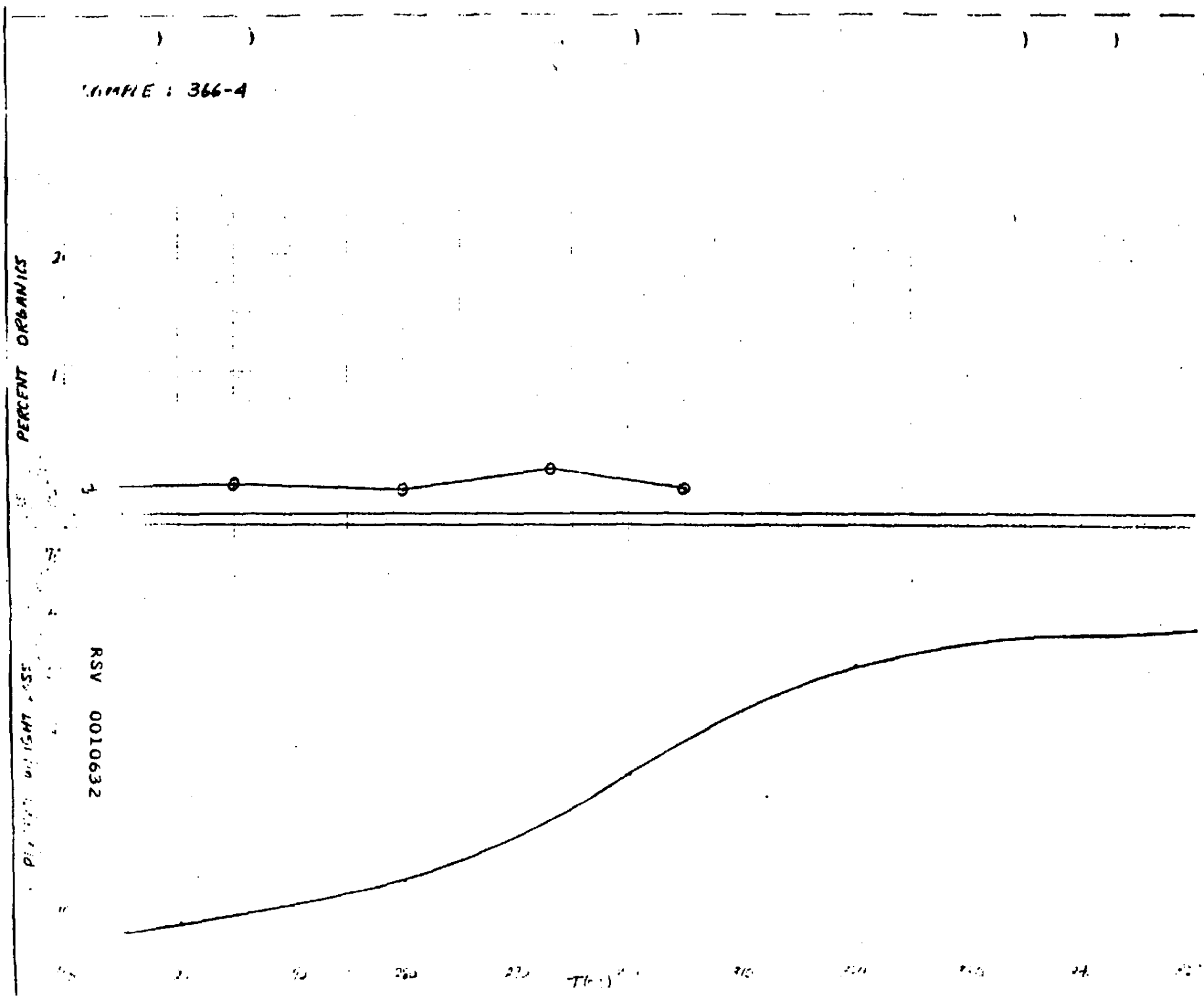


SAMPLE : 366-6

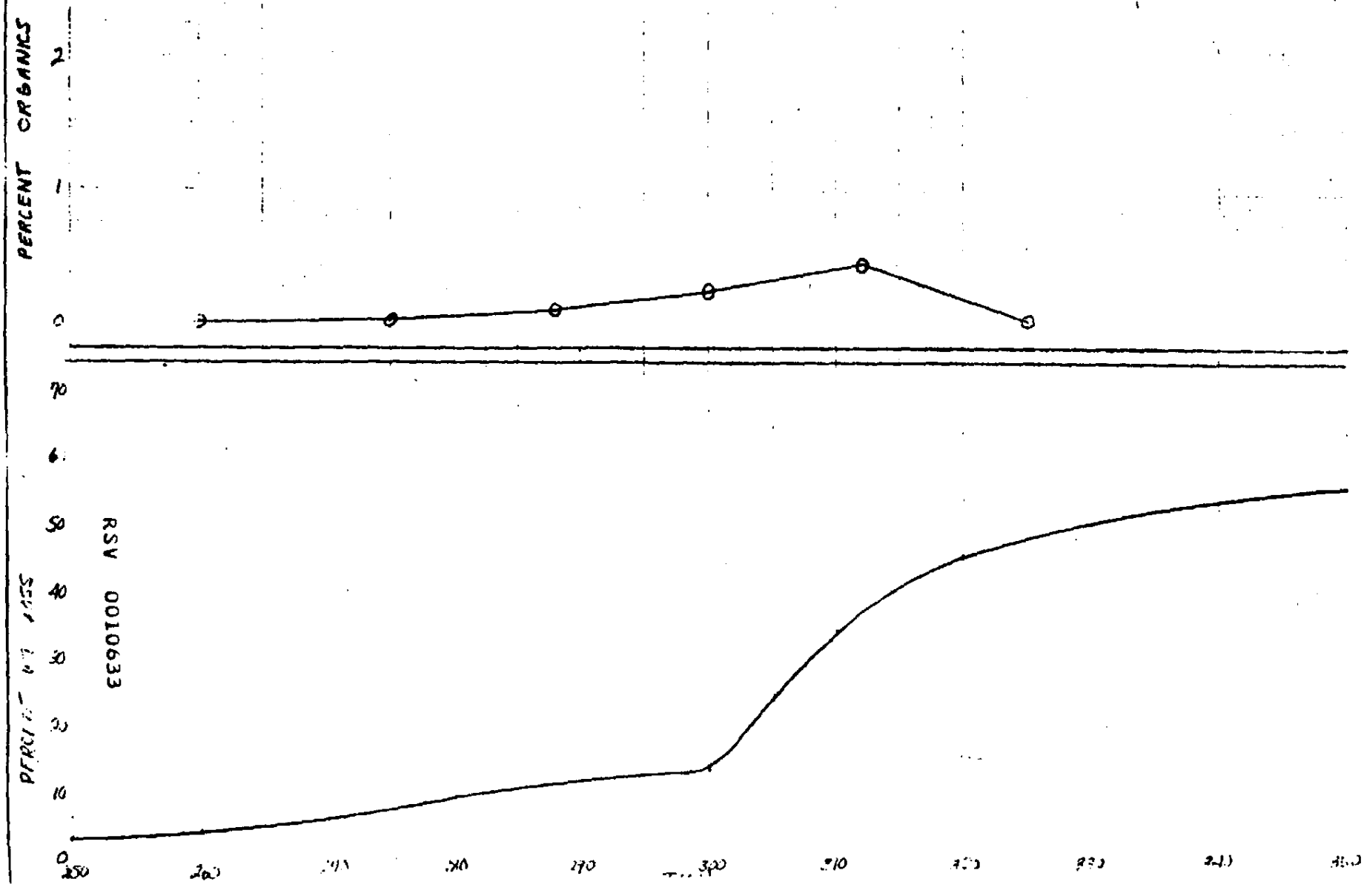


SAMPLE 366-5

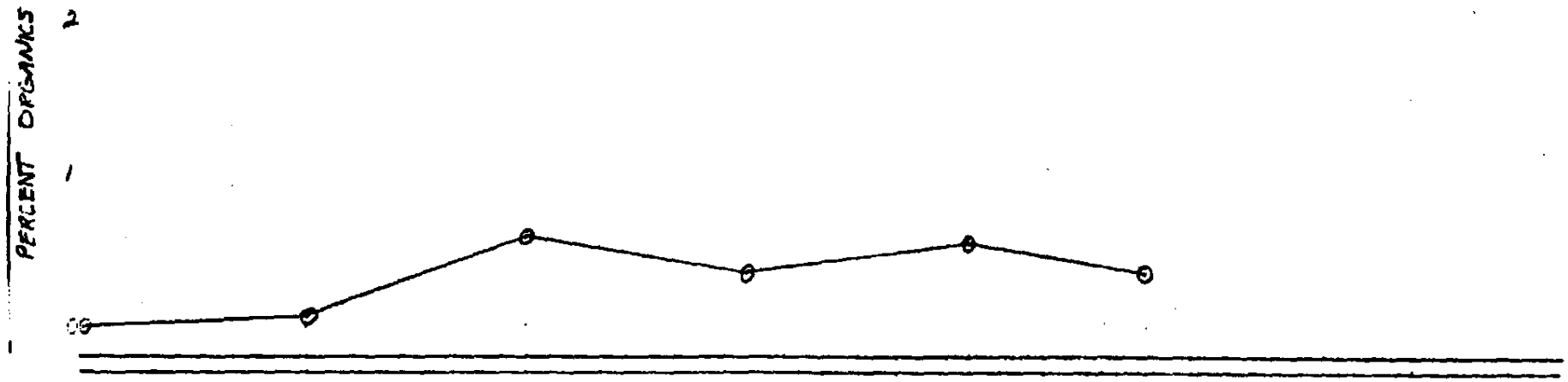


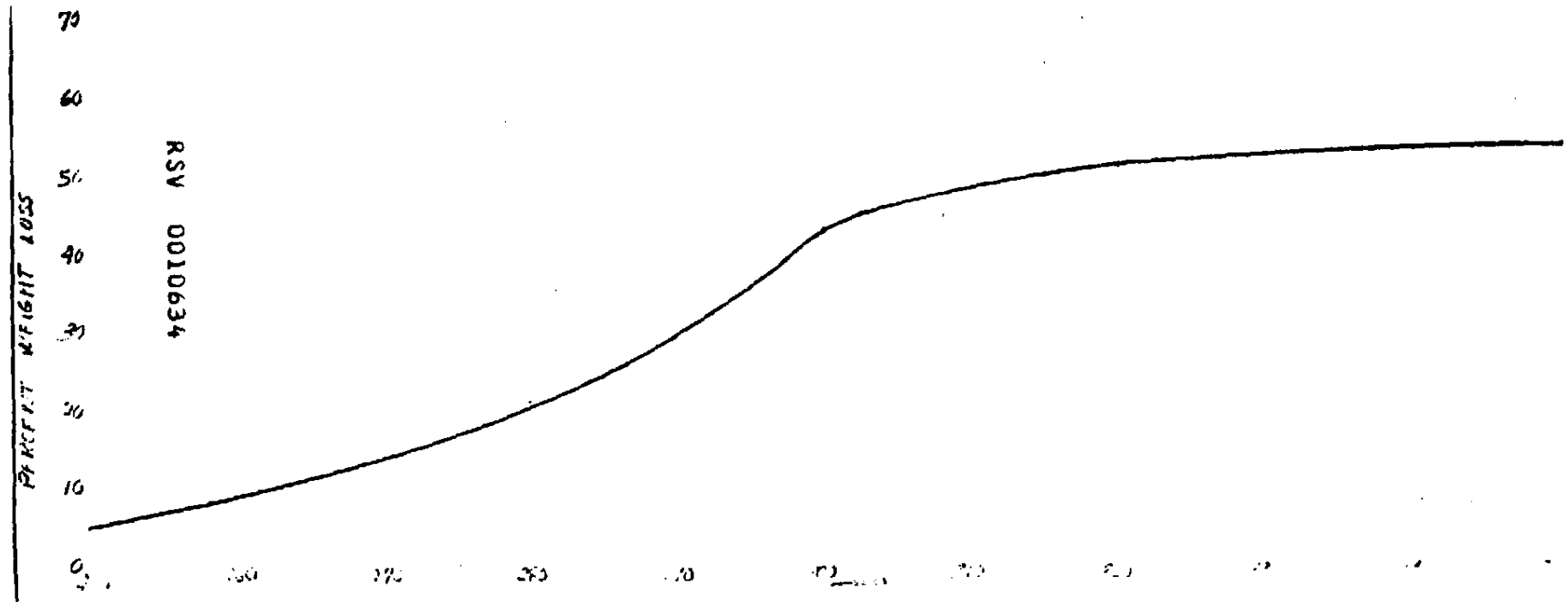

SAMPLE : 366-4
PERCENT ORGANICS
RSV 0010632

SAMPLE : 366-3

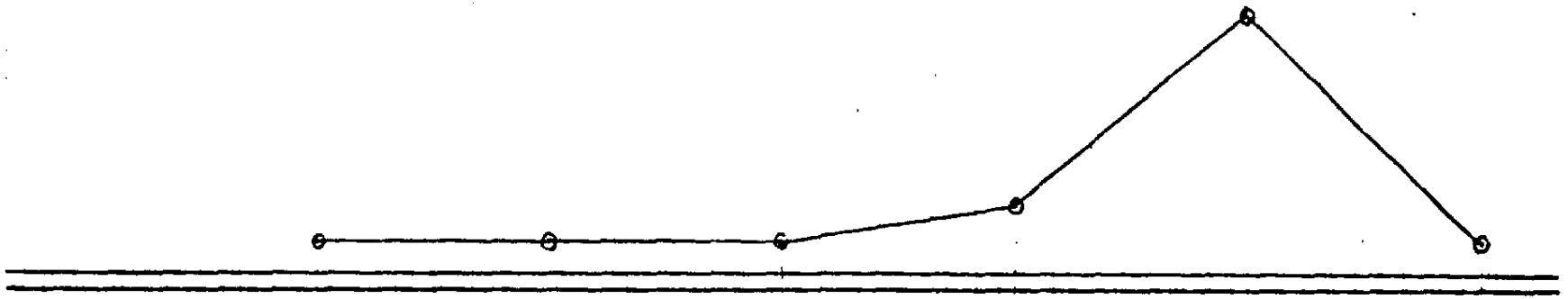


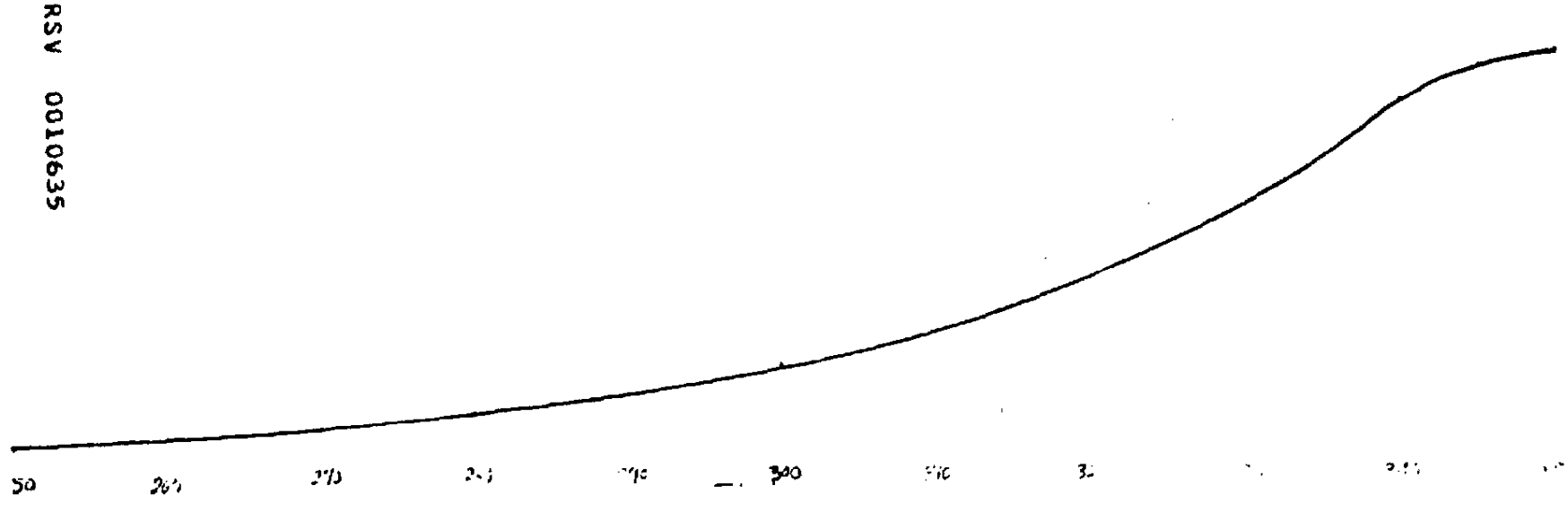
SAMPLE: 366-2


PERCENT ORGANICS
2
1
0


PERCENT WEIGHT LOSS
70
60
50
40
30
20
10
0
RSV 001063A

SAMPLE 366-1





S-75-SS-23

Sample 366-1 Percent of Volatile Organics Detected

Temperature	Propene	Methyl chloride	Propane	Butene	Pentene	Pentane	Benzene
270	.06	--	.09	--	.11	.20	--
285	.08	.009	--	.12	--	.04	.63
300	.44	.16	.44	.23	--	.61	6.88
315	.89	.47	.20	.74	--	.32	21.69
330	.67	.29	.73	.56	.12	.69	47.10
345	2.25	.25	.17	1.75	--	NI	.06

Temperature	C_7 olefin	Toluene	C_9 olefin	An alkyl chloride	C_{10} olefin	Total organics measured at each temperature
270	.53	--	.06	--	.26	1.31
285	.42	.006	.16	--	--	1.465
300	1.71	.097	.50	--	--	11.067
315	--	.26	.81	--	--	25.38
330	1.42	1.04	1.72	1.19	.24	55.77
345	--	--	.17	--	--	4.65

S-75-SS-23

Sample 366-2 Percent of Volatile Organics Detected

Temperature	Propene	Methyl chloride	pw pase	Butene	Pentene	Pentane	Benzene
250	--	.32	--	--	--	.13	1.18
265	--	.15	.13	.09	--	.31	4.71
280	.03	.09	.06	--	--	.44	6.13
295	.14	.18	.02	.09	--	.07	5.29
310	.06	.07	.09	.08	--	.17	15.71
322	.08	.06	.05	.06	--	.05	16.13

Temperature	C_7 olefin	Toluene	C_9 olefin	An alkyl chloride	C_{10} olefin	Total organics measured at each temperatur
250	.17	.83	.19	--	--	2.82
265	--	6.33	--	--	--	11.72
280	--	9.53	12.92	--	--	29.20
295	--	1.49	1.94	--	--	9.22
310	.35	1.70	6.12	--	--	24.35
322	--	1.55	3.11	--	--	21.09

S-75-SS-23

Sample 366-3 Percent of Volatile Organics Detected

Temperature	Propene	Methyl chloride	Propane	Butene	Pentene	Pentane	Benzene
260	--	.21	--	--	.08	.06	.20
275	.18	.21	--	--	.90	.65	6.74
288	.78	.29	.61	.83	.75	1.52	23.26
300	.15	.05	.08	.08	--	.16	7.32
312	.33	.10	.19	.14	.06	.29	12.28
325	1.47	.38	.82	.70	--	.09	.60

Temperature	C_7 olefin	Toluene	C_9 olefin	An alkyl chloride	C_{10} olefin	Total organics measured at each temperatur
260	--	--	.07	--	--	.62
275	.94	.05	1.84	.28	--	11.79
288	12.19	.81	1.91	--	--	42.95
300	5.17	.02	.02	--	--	13.05
312	9.52	.17	3.01	.44	--	26.53
325	--	--	--	0	--	4.06

S-75-SS-23

Sample 366-4 Percent of Volatile Organics Detected

Temperature	Propene	Methyl chloride	Propane	Butene	Pentene	Pentane	Benzene
252	--	.46	.10	--	.02	.05	.58
265	--	.15	.15	--	.08	.07	1.16
280	--	.47	.28	--	.45	.45	6.60
293	.11	.03	--	--	--	--	--
305	.14	.08	.18	.22	.15	.38	10.33
316	.06	.02	--	.22	--	--	--

Temperature	C_7 olefin	Toluene	C_9 olefin	An alkyl chloride	C_{10} olefin	Total organics measured at each temperatur
252	NI	.76	1.22	.28	--	3.47
265	.48	1.73	3.41	2.26	.26	9.75
280	2.12	8.93	14.94	6.51	1.45	42.20
293	--	--	NI	--	--	.14
305	3.91	6.14	11.36	8.47	1.40	42.76
316	--	--	--	--		.30

S-75-SS-23

Sample 366-5 Percent of Volatile Organics Detected

Temperature	Propane	Methyl chloride	Propene	Butene	Pentene	Pentane	Benzene
250	--	.31	--	--	--	.12	.57
262	--	.03	--	.04	--	.08	2.20
275	.02	.04	--	.11	.10	.36	4.08
290	.02	.02	.001	.02	--	.14	2.00
302	.04	.05	.06	.06	.04	.07	9.22
306	.06	.09	.05	.06	--	.09	14.00

Temperature	C_7 olefin	Toluene	C_9 olefin	An alkyl chloride	C_{10} olefin	Total organic measured at each temperat
250	.24	.91	1.95	1.17	1.35	6.62
262	.35	2.04	8.81	--	4.99	18.54
275	--	4.40	11.52	--	1.02	21.65
290	.55	1.86	2.30	3.71	3.02	13.641
302	1.23	.67	4.38	--	2.21	18.03
306	--	.12	.10	--	6.15	20.72

S-75-SS-23

Sample 366-6 Percent of Volatile Organics Detected

Temperature	Propane	Methyl chloride	Propene	Butene	Pentene	Pentane	Benzene
250	--	.14	--	--	--	8.18	2.05
262	.03	.13	--	--	--	12.60	5.20
275	.02	.08	--	--	--	11.77	5.39
287	.05	.08	--	--	--	7.82	8.27
300	.09	.06	--	--	--	3.84	13.11

Temperature	C_7 olefin	Toluene	C_9 olefin	An alkyl chloride	C_{10} olefin	Total organics measured at each temperatu
250	.07	.004	.05	.04	.65	11.184
262	.37	.04	--	.005	.21	18.585
275	.59	.21	--	.16	.87	19.09
287	.71	.17	.10	.19	.04	17.43
300	.83	.21	.15	--	--	18.29

S-75-SS-23

Sample 989-1 Percent of Volatile Organics Detected

Temperature	Propene	Methyl chloride	Propane	Butene	Pentene	Pentane	Benzene
270	.05	.27	.13	.17	--	.80	.66
283	.29	.40	.55	.82	.16	1.62	8.12
295	.21	--	.10	.19	--	.86	13.30
308	.22	.07	.47	.20	--	.97	21.42
320	.37	.37	.20	.16	.14	.86	25.95

Temperature	C_7 olefin	Toluene	C_9 olefin	An alkyl chloride	C_{10} olefin	Total organic measured at each temperat
270	.86	.06	.76	.56	.42	4.74
283	2.75	--	2.88	1.44	--	19.03
295	--	.17	1.20	.06	--	16.09
308	--	.19	1.75	1.36	.98	27.63
320	.67	.34	1.02	.91	.14	31.13

S-75-SS-23

Sample 989-2 Percent of Volatile Organics Detected

Temperature	Propene	Methyl chloride	Propane	Butene	Pentene	Pentane	Benzene
260	--	1.22	.17	--	--	--	--
274	--	--	.29	--	.18	.52	7.69
287	--	--	.57	--	--	.56	16.22
300	.42	.12	.50	.12	--	.82	18.84
313	.45	.07	.10	.29	--	.31	18.76
325	.95	.09	.25	.54	.09	.79	17.98

Temperature	C_7 olefin	Toluene	C_9 olefin	An alkyl chloride	C_{10} olefin	Total organics measured at each temperatu
260	.70	--	NI	.13	.15	2.37
274	1.89	--	1.21	1.04	--	12.82
287	.20	--	--	--	--	17.55
300	--	--	1.10	.15	--	22.07
313	--	.13	.69	.17	--	20.97
325	--	.16	.51	.03	--	21.39

S-75-SS-23

Sample 989-3 Percent of Volatile Organics Detected

Temperature	Propene	Methyl chloride	Propane	Butene	Pentene	Pentane	Benzene
270	--	2.34	1.05	--	NI	1.27	4.02
284	.21	.72	1.40	.08	.20	1.75	8.31
297	.24	.34	1.12	.48	.16	1.71	10.61
309	.50	.14	.93	.51	.18	.66	15.49
322	.71	.14	1.16	.52	.13	.95	8.58
334	1.29	.11	.62	.68	--	.92	11.10

Temperature	C_7 olefin	Toluene	C_9 olefin	An alkyl chloride	C_{10} olefin	Total organics measured at each temperatu
270	2.48	--	--	--	--	11.16
284	--	NI	1.56	.10	--	14.33
297	1.63	.27	.73	.11	--	17.40
309	--	--	--	--	--	18.41
322	2.11	.29	2.56	--	--	17.15
334	2.16	--	--	.009	--	16.889

S-75-SS-23

Sample 989-4 Percent of Volatile Organics Detected

Temperature	Propene	Methyl chloride	Propane	Butene	Pentene	Pentane	Benzene
250	--	2.13	.52	--	--	.69	3.45
264	--	.38	.53	--	.18	--	13.91
281	--	--	.50	--	.21	.50	18.58
295	--	.04	.10	--	.07	.13	10.45
308	--	--	.08	--	--	--	23.13
323	.04	--	--	--	--	--	21.88

Temperature	C_7 olefin	Toluene	C_9 olefin	An alkyl chloride	C_{10} olefin	Total organics measured at each temperatur
250	--	--	--	--	--	6.79
264	--	--	--	--	--	15.00
281	--	--	--	--	--	19.79
295	--	--	--	--	--	10.79
308	--	--	--	--	--	23.21
323	--	.54	--	--	1.45	22.46

S-75-SS-23

Sample 989-5 Percent of Volatile Organics Detected

Temperature	Propene	Methyl chloride	Propane	Butene	Pentene	Pentane	Benzene
280	--	.37	.39	.11	.48	.40	9.62
294	--	.18	.20	.32	.28	.18	14.95
306	.10	.16	.14	.31	.12	.21	13.52
318	.19	.14	.10	.49	.12	.11	14.71
330	.25	.16	.23	.38	.06	.13	15.40
344	.29	.12	--	.20	--	.04	15.69

Temperature	C_7 olefin	Toluene	C_9 olefin	An alkyl chloride	C_{10} olefin	Total organics measured at each temperatu
280	--	1.87	--	--	.15	13.39
294	--	1.09	--	--	--	17.20
306	--	1.91	--	--	--	16.47
318	--	.93	--	--	--	16.79
330	--	.74	--	--	--	17.35
344	--	--	--	--	--	16.34

S-75-SS-23

Sample 986-6 Percent of Volatile Organics Detected

Temperature	Propene	Methyl chloride	Propane	Butene	Pentene	Pentane	Benzene
253	--	.07	--	.52	--	8.99	2.19
267	.02	.07	.03	1.37	--	15.12	3.74
280	.07	.09	.05	3.49	--	13.22	4.59
293	.07	.10	.03	1.96	--	10.02	5.53
306	.21	.10	--	4.16	--	.55	6.92

Temperature	C_7 olefin	Toluene	C_9 olefin	An alkyl chloride	C_{10} olefin	Total organics measured at each temperature
253	.06	--	--	--	--	11.83
267	.90	.03	.04	.55	.05	21.92
280	1.00	.01	--	--	--	22.52
293	1.21	.12	.58	3.22	--	22.84
306	1.03	--	--	.10	--	13.07

VOLATILES FROM ABS AND STYRENE POLYMERS AT PROCESSING TEMPERATURES

SUMMARY

Two samples of acrylontrile/butadiene/styrene polymer (ABS) and one sample of high impact polystyrene were heated in air at 200°C and 260°C to simulate processing conditions. Volatiles given off by these polymers ranged in concentration from ten to several hundred ppm of the sample weight and were identified by GC/MS.

DISCUSSION

A ten to twenty milligram piece of each polymer was placed in a small porcelain boat and heated to the desired temperature. This was done in a quartz tube connected to the injection port of the Hewlett Packard GC/MS system. Air flowing at 15 mℓ/min. passed over the boat and carried volatile materials onto the head of the GC/column (2.5% OV 17) which was held at -40°C. After heating for the desired time, the sample was removed from the quartz tube and hellum carrier gas was used to sweep any volatiles remaining in the tube onto the head of the GC column. The GC column was then temperature programmed from -40°C to 250°C and the eluting components analyzed by mass spectrometry.

Each sample was heated for one minute and for 15 minutes at each temperature, 200°C and 260°C. In order to keep the sampling times the same for all samples, the 15 minute heating was done in a forced air oven. The sample was then transferred rapidly to the quartz tube where it was heated for one minute at the same temperature and sampled for volatiles. The one minute samples were heated for one minute at the desired temperature and sampled for volatiles during the heating period.

The attached table shows the volatiles found from each sample at each of the four experimental conditions. Component G may be a substituted indene; component A probably has a molecular weight of 73 but could not be identified by its mass spectrum. The components in the table account for 90% or more of the components observed by GC/MS (except for the samples heated to 260°C for one minute and the LNIFC 500 15 min. @ 260 sample). These samples have components with molecular weights higher than 200 that amount to 10-30% of the components measured by GC/MS for each of these samples. They could not be identified by their mass spectra. However, the data indicate that some are probably styrene dimers.

The amount of volatiles measured in this type of experiment may depend on the surface area exposed to the heated air. All of the samples analyzed had approximately the same surface area since they were the same size and shape. A very finely divided sample may give higher values than those reported here.

Acidic components such as HCN, HCl and HBr would not have been measured by this method.

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TABLE FOR S-75-SS-24

VOLATILES FROM ABS AND HIPS POLYMERS

PPM BASED ON WEIGHT OF SAMPLE ANALYZED

SAMPLE								
LNIFC 500	Acrylonitrile	Ethylbenzene	Styrene	C_3alkylbenzene	Terpinolene	Dibutyl cresol		
1 min @ 200°C	74	80	210	43	97	50		
15 min @ 200°C	8	11	72	5	25	40		
1 min @ 260°C	160	160	230	52	120	120		
15 min @ 260°C	12	19	84	10	50	130		
LNI 440	Acrylonitrile	Ethylbenzene	Styrene	C_3alkylbenzene	Terpinolene	Dibutyl cresol	G	
1 min @ 200°C	230	130	230	38	100	110	15	
15 min @ 200°C	20	13	63	6	23	22	3	
1 min @ 260°C	260	170	140	41	89	130	92	
15 min @ 260°C	11	23	76	10	50	88	26	
LUSTREX 6400	A	Ethylbenzene	Styrene	C_3alkylbenzene	Terpinolene	Dibutyl cresol	Styrene dimers	Tinuvin-P
1 min @ 200°C	16	210	150	35	<10	55	54	46
15 min @ 200°C	5	15	49	4	<10	15	9	5
1 min @ 260°C	34	320	400	57	100	100	120	76
15 min @ 260°C	18	10	33	2	11	18	7	9

DETERMINATION OF BIS (2-CHLOROETHYL) ETHER IN PHOSGARDS

INTRODUCTION

The presence of bis (2-chloroethyl) ether (BCEE) may pose a threat to the product acceptability of our Phosgards. Both EPA and NIOSH (administrators of OSHA) have expressed concern over the toxicity and possibly carcinogenicity of BCEE. This study was undertaken to determine if any of our Phosgard products contain BCEE and if so to determine the levels.

SUMMARY

A headspace GC method has been developed for determining BCEE in Phosgards and in ethylene dichloride. Data from several product and process samples are given in the attached Table I. As is indicated, BCEE was found in several samples. Values of $\leq$.005% are questionable because of possible equipment contamination. The significance of these levels of BCEE in our products is unknown.

DETAILS

A. Identification of BCEE

The presence of BCEE was confirmed by GC/MS techniques using headspace samplings from several products. These identifications were carried out under modified GC conditions to minimize chances of thermal decomposition of other components in the products. The headspace sample was collected from Phosgards at room temperature (this will leave behind high boiling materials). The collected sample was placed in a warm only (100°C) injection port. GC analyses conditions were chosen so that BCEE eluted below 110 C°(see Figure 1). Under these conditions, it is very unlikely that interfering components which liberate BCEE could be present. The mass spectra, from GC/MS, and the GC retention time obtained in this way were identical to known BCEE.

B. Alternative Analyses Procedure

Liquid Chromatography (LC) and direct GC analyses were also studied. LC appeared promising but did not have sufficient sensitivity. Detection limits using the refractive index dectector were only ca 0.1%. BCEE does not have sufficient UV response to allow the use of this detector. Direct GC analyses was found to give erroneously high results on some samples. This is presumed to be due to a Phosgard component decomposing on the hot injection port of the GC and forming BCEE. Table II compares data obtained by Headspace GC to that obtained by LC and GC.

C. Sample Collection

The sample collection apparatus consists of a 125 mℓ suction flask fitted with a dip tube, stopper, and a two-inch Teflon covered magnetic stir bar. The stopper is a #12 cork bored to snugly fit a 5 mm o.d. tube and with the surfaces exposed to the sample covered with Teflon

C. Sample Collection (cont'd)

tape. A 130 mm length of 5 mm o.d. glass tube was inserted through the Teflon tape until it would clear the flask bottom by ca 20 mm, thus exposing ca 20 mm above the cork. The flask side arm carried a short tube charged with activated charcoal granules. A 15 psi house N_2 line was led to the charcoal trap, passed over the stirred sample, through the dip tube and via a short Teflon connection into a collection tube. An ideal refrigeration valve after the regulator throttled the N_2 flow. N_2 flow was measured by a Buble-O-Miter as it left the collector and was adjusted for 100 mℓ/25 seconds.

The collection tube is a six-inch length of 1/4-inch standard stainless steel tubing fitted with two Swazelok nuts back-to-back on one end, the long part measured to fit as an insert into the injection port. It is charged with 150 mg Tenax 60/80 retained centrally by plugs of silanized glass wool. The inserts are conditional at 200°C and cooled before use.

D. Calibration

A standard was prepared that contained 80.5 micrograms of bis-chloroethyl ether per microliter of methylene chloride. A one microliter injection of this standard, with needle correction provided 90.1 micrograms of BCEE. To calibrate the vapor collection, an equilibrium process, a degassed Phosgard 1227 was used. Degassing was done by passing air at room temperature over a shallow stirred pool of Phosgard for three weeks.* Ten mℓ of this BCEE-free Phosgard 1227 was charged into the flask and a collection made to establish the "zero" level. Then ten microliters of the standard and later an additional 90 microliters to give collections representing 10 and 100 microliters or 80 and 800 ppm in the liquid. The GC results, versus the injected standard, indicated 0.98 and 6.9 micrograms in air respectively. A calibration curve of micrograms in air versus ppm in liquid from these data was used to determine the ppm of BCEE in the Phosgards analyzed. As a first approximation, BCEE-free Phosgard 1227 was used to calibrate for all the Phosgards analyzed.

An all-glass 10 mℓ syringe equipped with a 3 mm i.d. by 5-inch length of Teflon tube is used to transfer 10 mℓ of the Phosgard sample to the flask. Without the collection tube the dip tube/cork assembly is set in place and with moderate stirring the sample is equilibrated with N_2 flow for ten minutes. Then the collection tube is attached for about eight minutes to collect the components swept out of the flask by two liters of N_2 flow.

*GC analyses indicated this Phosgard was essentially free of BCEE and other low-boiling impurities.

E. Analyses

A Hewlett Packard 7620A gas chromatograph capable of sub-ambient operation via liquid nitrogen cooling was used. The analytical column used is a 1/8-inch by 2 meter 10% S-409 on 60/100 Chrom WHP. With the helium flow off and the injection port at 200°C, the collection tube is first attached to the head of the analytical column. The collection tube is then inserted into injection port, secured, and the liquid nitrogen cooling turned on the achieve -30°C. The Autolab is set at peak width five, slope sensitivity 30 and attenuation one. When ready the helium flow, Autolab and program are initiated. The temperature program used was -30°C to 150°C at 20°C per minute, followed by a purge at 180°C for five to ten minutes. GC attenuation is typically 1 X 1000. Quantitative data were obtained using an Autolab System IV and standatd GC techniques. A typical chromatogram is attached as Figure 2.

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St. Louis, Mo.

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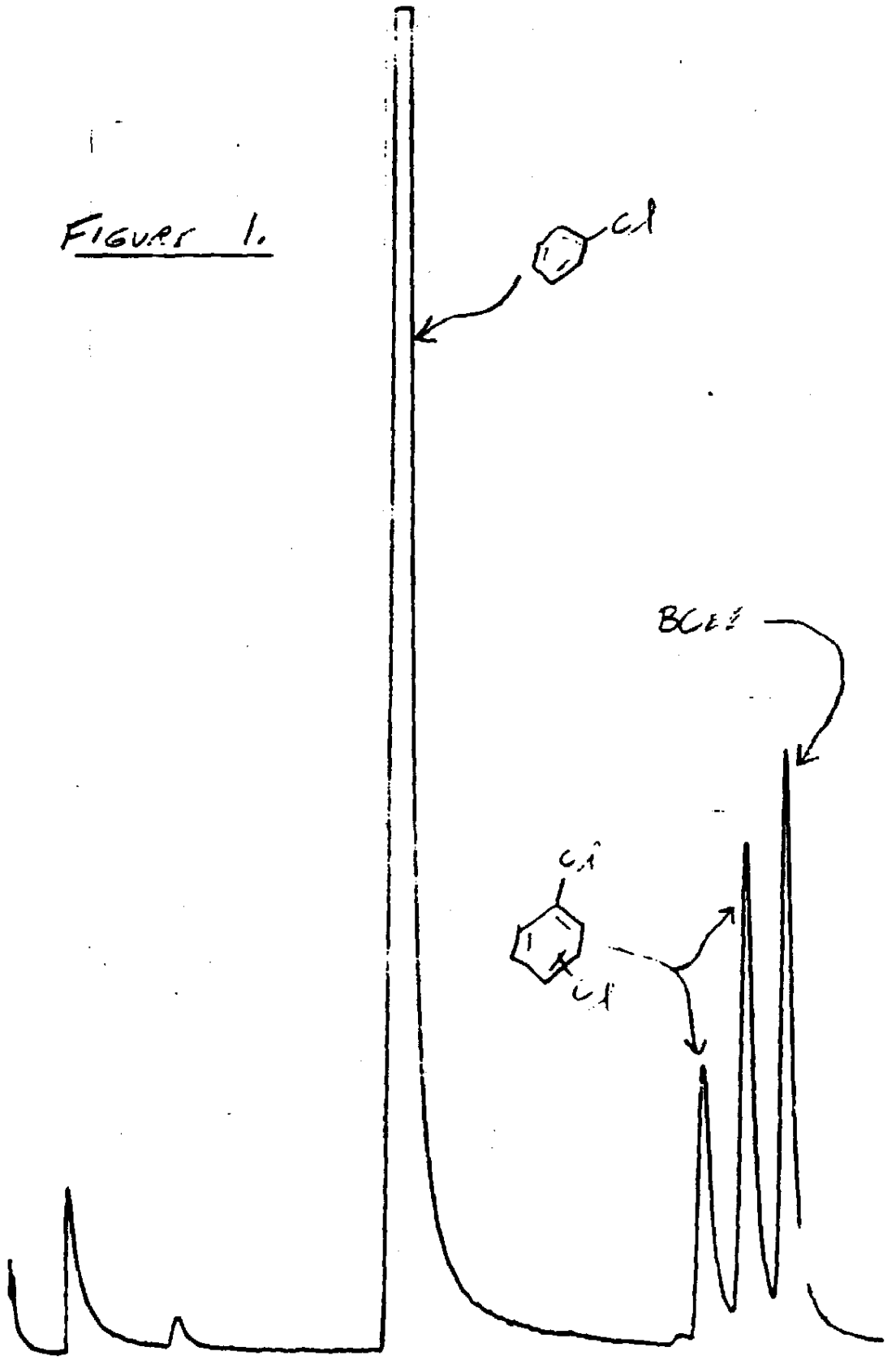
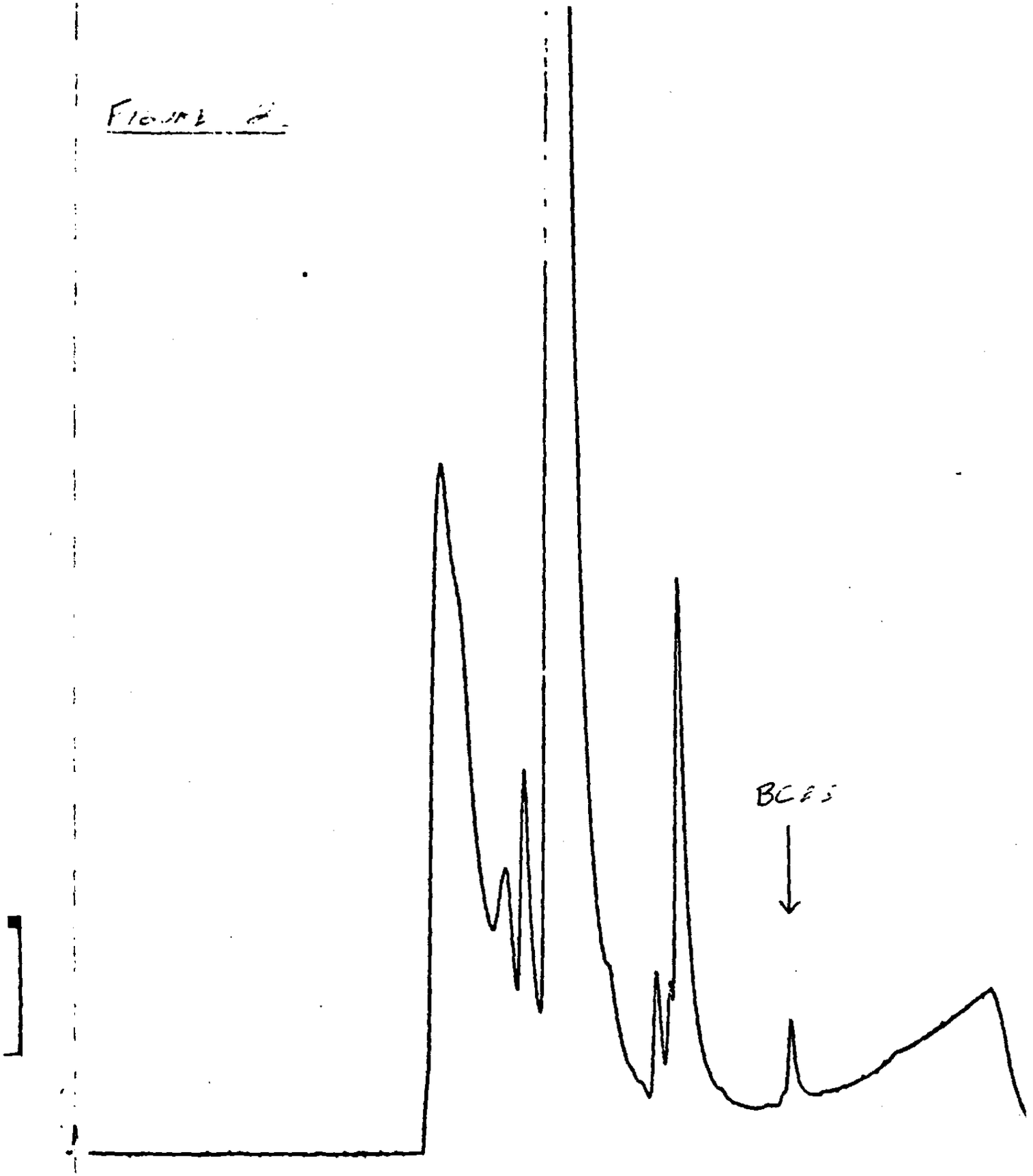
FIGURE 1.



RSV 0010654

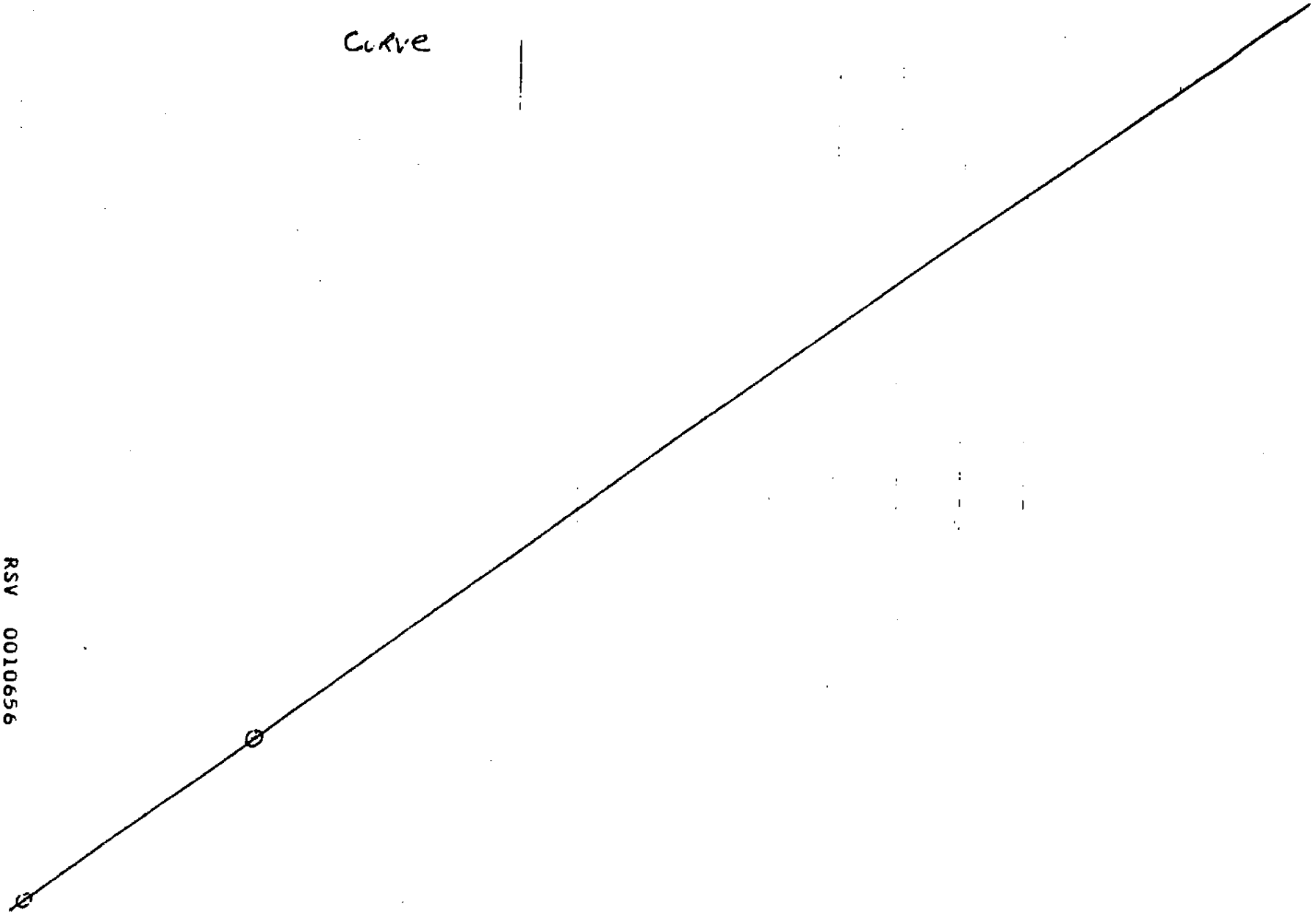
FIGURE 4



RSV 0010655

CALIBRATION

CURVE



S-75-SS-25

TABLE 1

SAMPLE	% BCEE (HEADSPACE GC)
P 1227 Lot 1053	0.2
P 1227 Lot 1050	ND ≤0.3*,**
P 1227 Lot 1054	0.2*
P C22R, QD 7256	≤.005*
DOW EDC	≤.001
EDC: Neutralized Ba 7323, P C22R Byproduct	0.03*
EDC: Un-neutralized, Ba 7446	0.3*
P 1227 Run 3, Cut 1	.0005
P 1227 Run 6, Cut 1	.001

*Identification confirmed by GC/MS.

**Very high level residual chlorobenzenes.

RSV 0010657

TABLE II

SAMPLE	% BCEE		
	HEADSPACE GC	LC	GC
P 1227 Lot 1053	0.2	0.1	1.1
P 1227 Lot 1050	ND ≤0.3*,**	<0.1	-
P 1227 Lot 1054	0.2*	0.15	-
P C22R, QD 7256	≤.005*	ND	.005
DOW EDC	≤.001	ND	-
EDC: Neutralized Ba 7323, P C22R Byproduct	0.03*	<0.1	0.43
EDC: Un-neutralized, BA 7446	0.3*	0.15	-
P 1227 Run 3, Cut 1	.0005	-	-
P 1227 Run 6, Cut 1	.001	-	-

*Identification confirmed by GC/MS.

**Very high level residual chlorobenzenes.

S-75-SS-25

RSV 0010658

Special Study
S-75-SS-26

HYDROLYTIC STABILITY OF PYDRAULS AND COMPETITIVE PRODUCTS

SUMMARY-

UV fluorescence analysis for phenolics in Monsanto and competitive hydraulic fluids using a General Motors stability test and analytical method showed:

1. Pydraul 50 E (QC-12820) with Admix 710 indicates less stability compared to HS-1120 after seven days in a series run for a General Motors project. The inhibitive effect of the HS-1120 decays rapidly and after fourteen days the phenolic levels in both fluids are comparable.

2. Similar stability was observed with 1974 production Pydraul 50 E, Pydraul 30 E and laboratory preparations containing production NC-220 ester (12/2/74) stabilized with Unox 289 (7-day stabilities) as compared to Pydraul 50 E (QC-12820) used in G. M. Study (1.).

3. Seven-day and fourteen-day stabilities of production NC-220 ester containing MCS 1562 epoxide were better than the HS-1120 used in the G.M. test.

4. Cartridge clay treatment of the production NC-220 ester with either Unox 289 or MCS 1562 showed significant improvement over untreated ester. The MCS 1562 stabilized system was far superior to HS-1120 used in the G.M. series in both seven-day and fourteen-day phenolic levels.

5. Pydraul 179 B from Europe has a seven-day stability equal to HS-1120 used in the G.M. series and contains 50% less phenolics after fourteen days.

6. The competitive product FQ 220 CF shows a seven-day stability equal to that of the clay-treated production NC-220 ester with MCS 1562. The fourteen-day phenolic level is the best of all samples analyzed, about 2/3 that of the clay-treated NC 220/MCS 1562 sample or the Pydraul 179 B from Europe.

7. Wide variations were observed in competitive samples having the same designation suggesting changes in formulation. HS-1120 #C2281 shows poor stability compared to HS 1120 used in the G.M. series. FQ 220 #3733-5-7 shows poor stability compared to FQ 220 CF. Phenolic levels after seven and fourteen days are equal to those of the production Pydraul 50 E and Pydraul 30 E samples.

8. At the completion of the tests, fourteen days, all of the Pydraul fluids except Pydraul 179 B, all of the untreated production NC-220 samples containing either Unox 289 or MCS 1562 and all of the laboratory samples of NP cresylic and NP phenol showed black precipitates. No precipitates were observed in the clay-treated NC-220 ester samples or in the competitive products.

Jrpic Ab

INTRODUCTION

A large sales potential for Pydraul fluids exists with General Motors if the hydrolytic stability of Monsanto's products can be shown to be equal to or better than competitive products.

A joint project was initiated with Chevrolet's Central Laboratory to measure phenolics generated using their stability test and their UV fluorescence analytical method. General Motors had reported high values, for example 1,200 ppm at 0 hrs. for a Pydraul 50 E sample (lot unknown) which appeared questionable.

The program was extended to obtain internal data on the stability of new phosphate esters, production samples of Monsanto Pydraul series fluids, competitive products and the effects of new epoxide acid scavengers to improve the stability of Monsanto products.

EXPERIMENTAL

100g test fluid and 1g water were vigorously shaken for one minute and transferred to a mini o/c tube (1" diameter X 10") equipped with a condenser. The test mixture was held in a mini o/c bath at 250°F for seven days. One mℓ aliquots were removed periodically for analysis of generated phenolics. The test was extended to fourteen days to overcome an initial induction period or inhibitive action observed with some samples.

Analytical data for phenolics were obtained in duplicate. 0.200 to 0.250g of the aliquot was weighed to the nearest mg and sufficient water adjusted to pH 4 with H_3PO_4 added (200 to 250 mℓ) to give a 1,000:1 mixture of water to sample. The 1,000:1 mixture was vigorously stirred for 30 minutes at room temperature with a magnetic bar, allowed to settle for 15 minutes and filtered through 12.5 cm Whatman #42 paper. The first 25 to 30 mℓ of filtrate were discarded and the next 100 mℓ collected for analysis. Samples of new fluids were equilibrated in a similar manner to obtain 0 hour data on phenolic levels.

Ultraviolet fluorescence analysis was carried out using an Aminco-Bowman SPF using 1 cm^2 cells and a 1.0 µg/mℓ quinine sulfate solution in 0.1 N H_2SO_4 as reference. The quinine sulfate was excited at 350 mm and the emission detected at 450 mm.

The UV fluorescence method was calibrated using J. T. Baker's phenol (cat. no. 2858) as the standard. The substitution of phenol for p-cresol, the standard specified by the G.M. method, was mutually agreed on by G.M. and Monsanto because of the long-term storage instability of the dilute p-cresol solution used to check the spectrofluorometer. A series of standard solutions containing 0.15 to 3.0 µg phenol/mℓ water were prepared and fluorescence measurements made using 273 mm excitation and 302 mm emission. A

few drops of 0.1 N NaOH were added and the fluorescence measured again. The difference between the acid and base values was the fluorescence due to phenol. A plot of relative fluorescence calculated by:

$$\text{rel. fluor.} = \frac{(\%T \times \text{sensitivity})_{acid} - (\%T \times \text{sensitivity})_{base}}{(\%T \times \text{sensitivity})_{QS\ std.}}$$

versus phenol concentration showed a linear relationship in the range of 0.15 to 2.50 µg/mℓ.

Linear regression analysis gave the straight line equation relating phenol concentration to relative fluorescence as:

$$\mu g\ \text{phenol} = \frac{\text{rel. fluor.} + 0.0012}{0.1320}$$

and ppm phenolics measured as phenol as:

$$\text{ppm} = 1000 \times \mu g = \frac{(\text{rel. fluor.} + 0.0012)\ (\text{Vol.})}{(0.1320)\ (\text{wt. of spl.})}$$

SYSTEMS STUDIED

A. General Motors Series

1. Pydraul 50 E Lot QC 12820 MIC 255266
2. HS-1120 obtained from Chevrolet Central Laboratory O% ring isoprophyl

B. NC-220 Ester (12/2/74) - New Epoxides

1. 0.5% Unox 289 MIC 285108
2. 1.0% Unox 289 MIC 285108
3. 1.0% MCS 1562 MIC 285108
4. 1.5% MCS 1562 MIC 285108

C. Cartridge Clay-Treated NC-220 Ester

1. MCS 1742 - 1.0% Unox 289 MIC 285101
2. MCS 1743 - 1.5% MCS 1562 MIC 285101

D. NP Esters with 1.5% Admix 710 epoxide + 30 ppm DCF

1. MCS 1769 NP cresylic 220 MIC 285112
2. MCS 1770 NP cresylic 150 MIC 285115
3. MCS 1776 NP phenol 220 MIC 285128
4. MCS 1779 NP phenol 150 MIC 285129

E. Monsanto Products

1. Pydraul 179 B Europe 9/12/72 MIC 285135
2. Pydraul 30 E Lot QD 33701 MCS 1772
3. Pydraul 50 E Lot QD 34520 MCS 1771

SYSTEMS STUDIED (CONT'D)

F. Competitive Products

1.	FQ 220 CF 6/22/73	MIC 285135	0% ring isopropyl
2.	FQ 220 3733-5-7	MIC 285135	24% ring isopropyl
3.	HS-1120 C-2281	MIC 285135	96% ring isopropyl

DISCUSSION

The experimental data are tabulated in Tables I to VI and shown graphically in Figures 1 to 7.

A. General Motors Series

At the end of seven days (the conditions of the Chevrolet Central Lab. test) HS-1120 was considerably better than Pydraul 50 E (6,300 ppm phenolics vs. 31,000). The shape of the HS-1120 curve (cf. Figure 1) shows that up to five days there was an inhibitive effect on phenolic generation. After this induction period, phenolic generation was rapid. On extension of the test to fourteen days, this validity of this premise was demonstrated. Phenolic levels in the HS-1120 system comparable to those in the Pydraul 50 E system were obtained.

B. NC-220 Ester - New Epoxides

1. Unox 289

At the 0.5% level, this epoxide shows some inhibition to phenolic formation, but between four and seven days this effect is removed and phenolic levels equal to that of the Admix 710 system are obtained. At the 1.0% level of Unox 289, the system shows a pattern similar to HS-1120 with early inhibition.

2. MCS 1562

At both the 1.0 and 1.5% levels, better inhibition to formation of phenolics is found than in the G.M. HS-1120 series after seven days. After fourteen days, this inhibitive effect is still operating with phenolic levels 1/2 to 2/3 those observed in the HS-1120 system.

C. Cartridge Clay-Treated NC-220 Ester

Vast improvements in phenolic levels were observed using either 1.0% Unox 289 or 1.5% MCS 1562 in clay-treated NC-220 Ester. Both systems are better than HS-1120 after both seven days (5,300 and 1,000 ppm vs. 6,300 ppm) and fourteen days (21,000 and 15,000 ppm vs. 28,000 ppm).

D. NP Series Esters with Admix 710

The NP Cresylic 220, the NP Phenol 220 and NP Phenol 150 esters containing 1.5% Admix 710 show less inhibition to phenolic generation. NP Cresylic 150 containing 1.5% Admix 710 is somewhat better but much higher after seven days than the HS-1120 in the General Motors Series (20,000 ppm phenolics vs. 6,300).

E. Monsanto Production Samples

Pydraul 179 B (Europe 9/12/72) gives phenolic levels after fourteen days comparable to clay-treated NC-220 ester containing 1.5% MCS 1562. Inhibition time is shorter for Pydraul 179 B. Phenolic levels after fourteen days are lower than HS-1120 and equal to those obtained with clay-treated NC-220 stabilized with MCS 1562.

Pydraul 30 E (QD 33701) and Pydraul 50 E (QD 34520) gave almost identical results to those obtained for Pydraul 50 E (QC 12820) used in the General Motors series. There is minimal inhibition to phenolic generation.

F. Competitive Products

FQ 220 CF outperforms all the fluids tested at fourteen days. Seven-day phenolic levels are comparable to HS-1120 (4,200 ppm vs. 6,300 ppm), but higher than clay-treated NC-220 with MCS 1562 (1,000 ppm).

FQ 220 #3733-5-7 and HS-1120 #C-2281 tend to be unstable under these conditions. Both systems show some inhibition to phenolic generation for two to three days. Phenolic levels increase rapidly to those found in Pydraul 50 E and Pydraul 30 E after seven and fourteen days.

G. Fluid Appearance After Fourteen Days

1. Precipitates

Black precipitates were observed in all the production Pydraul samples except Pydraul 179 B, all samples prepared with NC-220 (12/2/74) and the laboratory batches of NP cresylic and NP phenol.

Pydraul 50 E (QC 12820) G.M. Test	- medium to heavy
Pydraul 50 E (QD 34520) MCS 1771	- medium to heavy
Pydraul 30 E (QD 33701) MCS 1772	- medium to heavy
NC-220 ester - 0.5% Unox 289	- medium
NC-220 ester - 1.0% Unox 289	- light to medium
NC-220 ester - 1.0% MCS 1562	- heavy
NC-220 ester - 1.5% MCS 1562	- heavy
NP cresylic 220 MCS 1769	- heavy
NP cresylic 150 MCS 1770	- heavy
NP phenol 220 MCS 1776	- medium to heavy
NP phenol 150 MCS 1779	- medium to heavy

No precipitates were observed in the laboratory clay-treated NC-220 samples, the Pydraul 179 B sample from Europe or in any of the competitive samples.

G. Fluid Appearance After Fourteen Days (Cont'd)

2. Color

Orange

Pydraul 179 B Europe 9/12/72
FQ 220 CF

Slight Darkening

HS-1120 G.M.series
Clay-treated NC-220 - 1.0% Unox 289 MCS 1742
Clay-treated NC-220 - 1.5% MCS 1562 MCS 173

Dark

NP phenol 220 MCS 1776
FQ 220 #3733-5-7
HS-1120 G.M. test
HS-1120 CF 6/22/73

Very Dark

Pydraul 50 E (QC 12820) G.M. test
Pydraul 50 E (QD 34520) MCS 1771
Pydraul 30 E (QD 33701) MCS 1772
NC-220 0.5% Unox 289
NC-220 1.0% Unox 289
NC-220 1.0% MCS 1562
NC-220 1.5% MCS 1562
NP cresylic 220 MCS 1769
NP cresylic 150 MCS 1770
NP phenol 150 MCS 1779

H. Maximum Phenolic Values

A theoretical calculation was made to determine the maximum level of phenolics that could be generated under the General Motors test conditions.

Water	18 g/mole	1 g = 0.0556 moles
cumylphenol	212 g/mole	
monylphenol	220 g/mole	

0.0556 moles X 212 g/mole = 11.8g cumylphenol
= 118,000 ppm cumylphenol
0.0556 moles X 220 g/mole = 12.2g monylphenol
= 122,000 ppm monylphenol

If no water is lost during the test, the phenolic levels of 35,000 to 40,000 ppm observed probably represent an equilibrium condition of:

$$(ArO)_3\ P(=O) + H_2O \longrightarrow ArOH + (ArO)_2\ P(=O)\ OH$$

$$ArOH + (ArO)_2\ P(=O)\ OH \longrightarrow (ArO)_3\ P(=O) + H_2O$$

References: MIC 255266
MIC 255267
MIC 285101
MIC 285108
MIC 285112
MIC 285115
MIC 285128
MIC 285129
MIC 285135
MIC 285149

ss

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TABLE I

HYDROLYTIC STABILITY OF GENERAL MOTORS SERIES
ppm PHENOLICS CALUCLATED AS PHENOL

Hours	Pydraul 50 E QC 12820 MIC 255266	HS 1120 Chevrolet Central Lab. Spl. MIC 255266
0	450 450	600 600
48	3,800 3,750	840 820
96	26,900 27,000	
120	27,300 25,800	1,100 1,050
144	30,400 31,500	
168	30,300 32,800	6,250 6,300
240	35,900 36,800	
336	38,500 38,000	28,000 27,800

Appearance after 336 hours

Fluid	Very dark	Dark-clear
Tube	Med-heavy black ppt. - dark streaks on upper walls	Clean

TABLE II

HYDROLYTIC STABILITY OF NC-220 ESTER SERIES
ppm PHENOLICS CALCUALTED AS PHENOL

Hours	0.5% Unox 289 MIC 285108	1.0% UNOX 289 MIC 285108	1.0% MCS 1562 MIC 285108	1.5% MCS 1562 MIC 285108
0	285 282	295 295	278 278	274 274
48		1,340 1,330		
72	1,130 1,220		1,290 1,270	1,830 1,760
96	5,200 5,270	2,160 2,730	1,560 1,540	2,030 2,100
144		4,180 4,260		
168	34,000 33,700	9,600 9,700	4,140 3,950	3,280 3,300
240		33,400 33,200		
336		38,500 38,200	15,700 15,900	18,100 17,900
Appearance after 336 hours				
Fluid	Very dark	Very dark	Very dark	Very dark
Tube	Heavy black ppt. black spots on upper walls	Light to medium black ppt.-black streaks on upper walls	Heavy black ppt. black spots on upper walls	Heavy black ppt. black spots on upper walls

TABLE III

HYDROLYTIC STABILITY OF CARTRIDGE CLAY-TREATED NC-220
ppm PHENOLICS CALCULATED AS PHENOL

Hours	MCS 1742 1.0% Unox 289 MIC 285101	MCS 1743 1.5% MCS 1562 MIC 285101
0	445 449	267 267
72	543 600	456 426
96	895 925	524 566
168	5,440 5,160	1,040 980
336	20,900 20,700	14,800 14,900
Appearance after 336 hours		
Fluid	Some darkening	Some darkening
Tube	Clean	Clean

TABLE IV

HYDROLYTIC STABILITY OF NP ESTERS WITH 1.5% ADMIX 710
ppm PHENOLICS CALCULATED AS PHENOL

Hours	MCS 1769 NP Cresylic 220 MIC 285112	MCS 1770 NP Cresylic 150 MIC 285115	MCS 1776 NP Phenol 220 MIC 285128	MCS 1779 NP Phenol 150 MIC 285129
0	532 536	422 430	683 695	452 433
48			1,720 1,750	2,280 2,270
72	4,070 4,260	2,050 2,030		
96	16,100 15,900	5,800 5,730	18,400 19,100	18,300 18,100
168	34,300 34,300	20,500 20,300	42,500 41,900	34,000 34,900
Appearance after 366 hours				
Fluid	Very dark	Very dark	Dark	Very dark
Tube	Heavy black ppt. a few black spots on upper walls	Heavy black ppt. a few black spots on upper walls	Medium to heavy black ppt.	Medium to heavy black ppt.

TABLE V

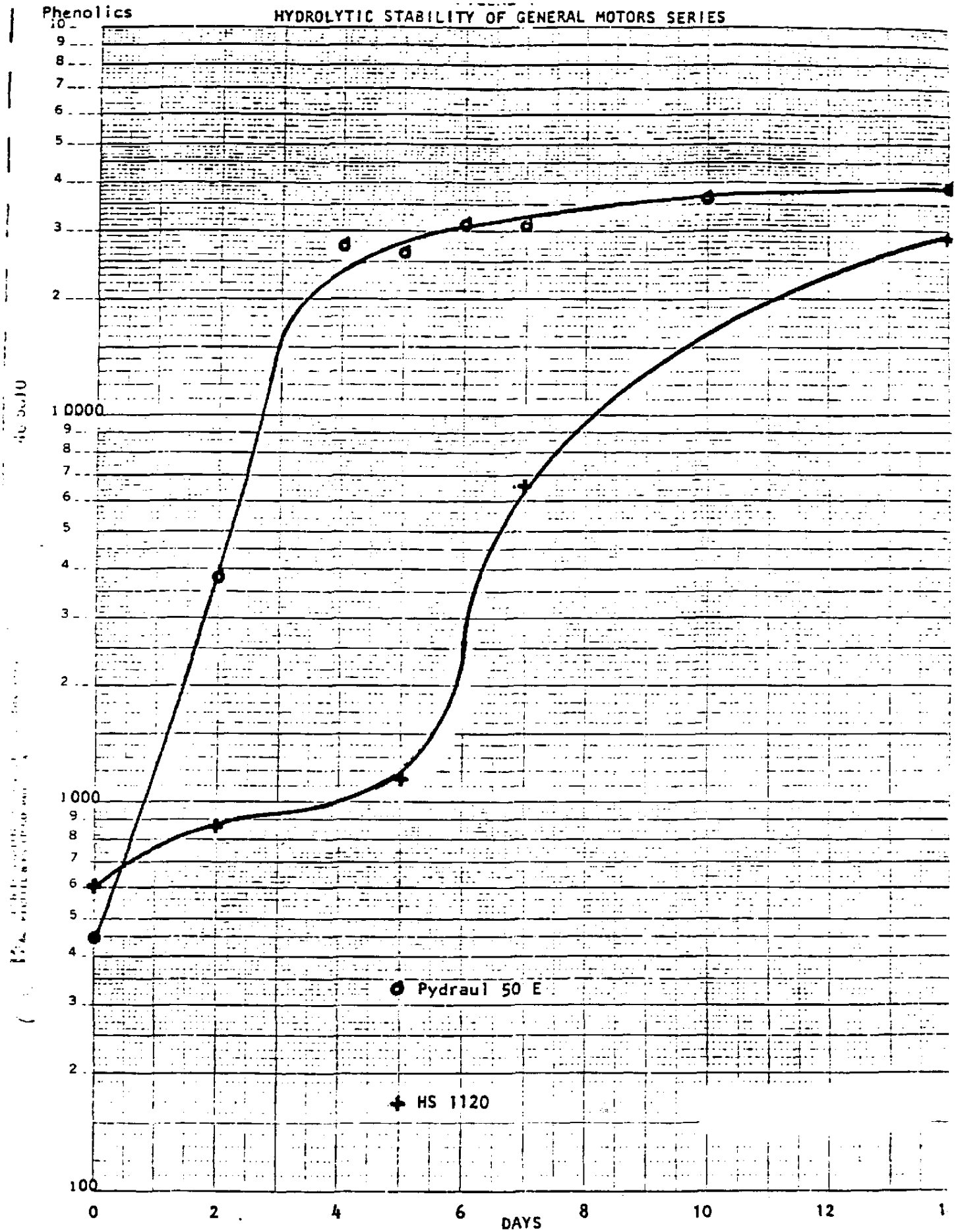
HYDROLYTIC STABILITY OF MONSANTO PRODUCTS
ppm PHENOLICS CALCULATED AS PHENOL

Hours	Pydraul 179 B Europe 9/12/72 MIC 285135	Pydraul 30 E QD-33701 MCS 1772	Pydraul 50 E QD-34520 MCS 1771
0	153 149	289 282	361 373
48	543 532		
96	1,810 1,850	18,100 18,000	25,400 26,600
144		30,800 28,900	27,800 27,600
168	7,590 7,670		
240		39,500 38,300	31,800 32,700
336	14,600 14,300	41,700 41,600	35,300 34,400
Appearance after 336 hours			
Fluid	Orange	Very dark	Very dark
Tube	Clean	Medium to heavy black ppt. - dark granular spots on upper walls	Medium to heavy black ppt. - dark granular spots on upper walls

TABLE VI

HYDROLYTIC STABILITY OF COMPETITIVE PRODUCTS
ppm PHENOLICS CALCULATED AS PHENOL

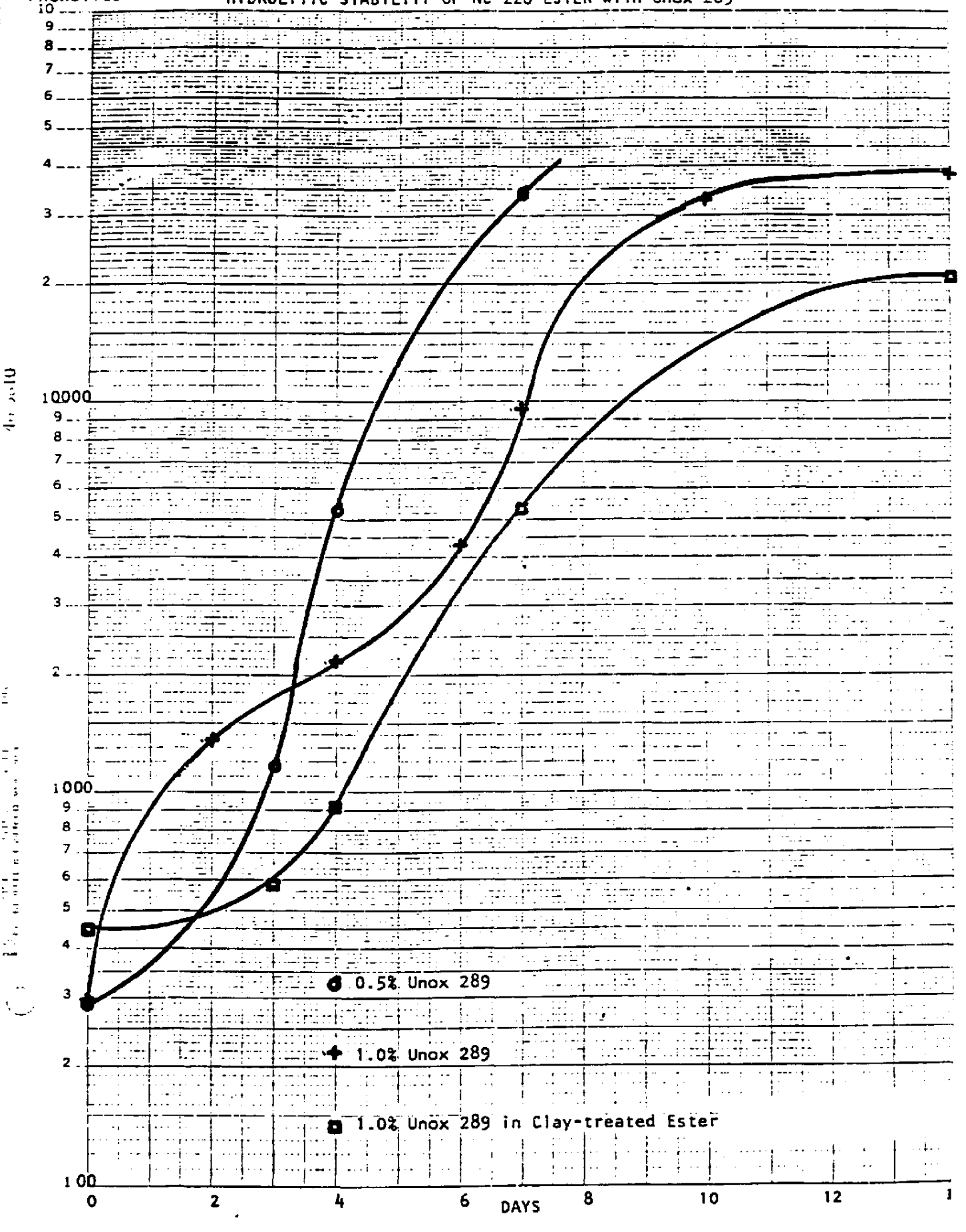
Hours	FQ 220 CF 6/22/73 MIC 285135	FQ 220 3733-5-7 MIC 285135	HS 1120 C-2281 MIC 285135
0	551	1,370	358
	558	1,400	350
48	710	1,980	1,360
	668	1,940	1,350
96	1,000	6,370	8,360
	960	6,480	8,360
168	4,250	26,400	22,300
	4,120	27,000	22,800
336	10,400	30,700	28,800
	10,900	31,300	28,700
Appearance after 336 hours			
Fluid	Orange	Dark	Dark orange
Tube	Clean	Clean	Clean


Phenolics
HYDROLYTIC STABILITY OF GENERAL MOTORS SERIES
10
9
8
7
6
5
4
3
2
1 0000
9
8
7
6
5
4
3
2
1 000
9
8
7
6
5
4
3
2
100
0
2
4
6
8
10
12
DAYS
Pydraul 50 E
HS 1120

RSV 0010672

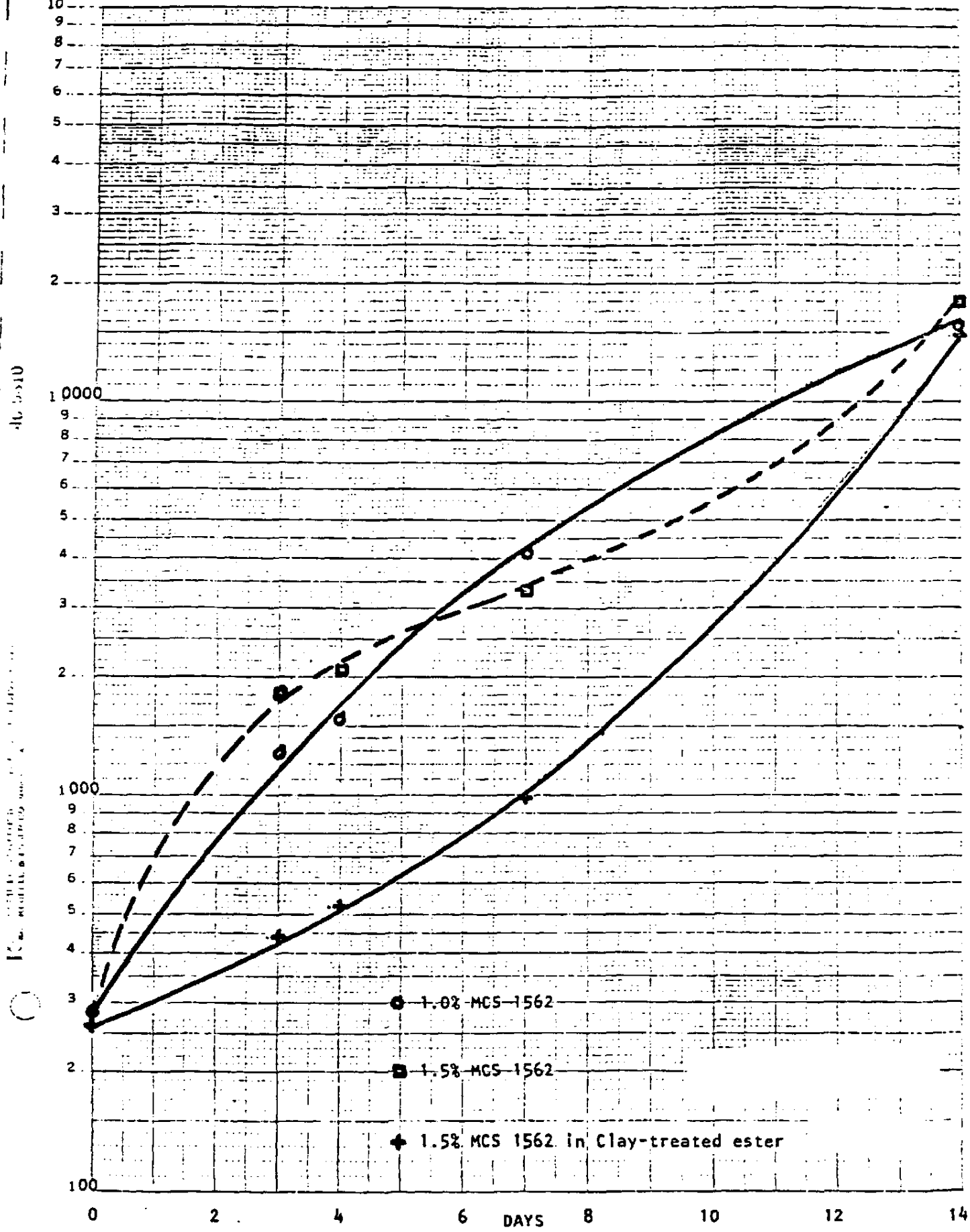
FIGURE 2

HYDROLYTIC STABILITY OF NC-220 ESTER WITH Unox 289



RSV 0010673

FIGURE 3
HYDROLYTIC STABILITY OF NC-220 ESTER WITH MCS 1562

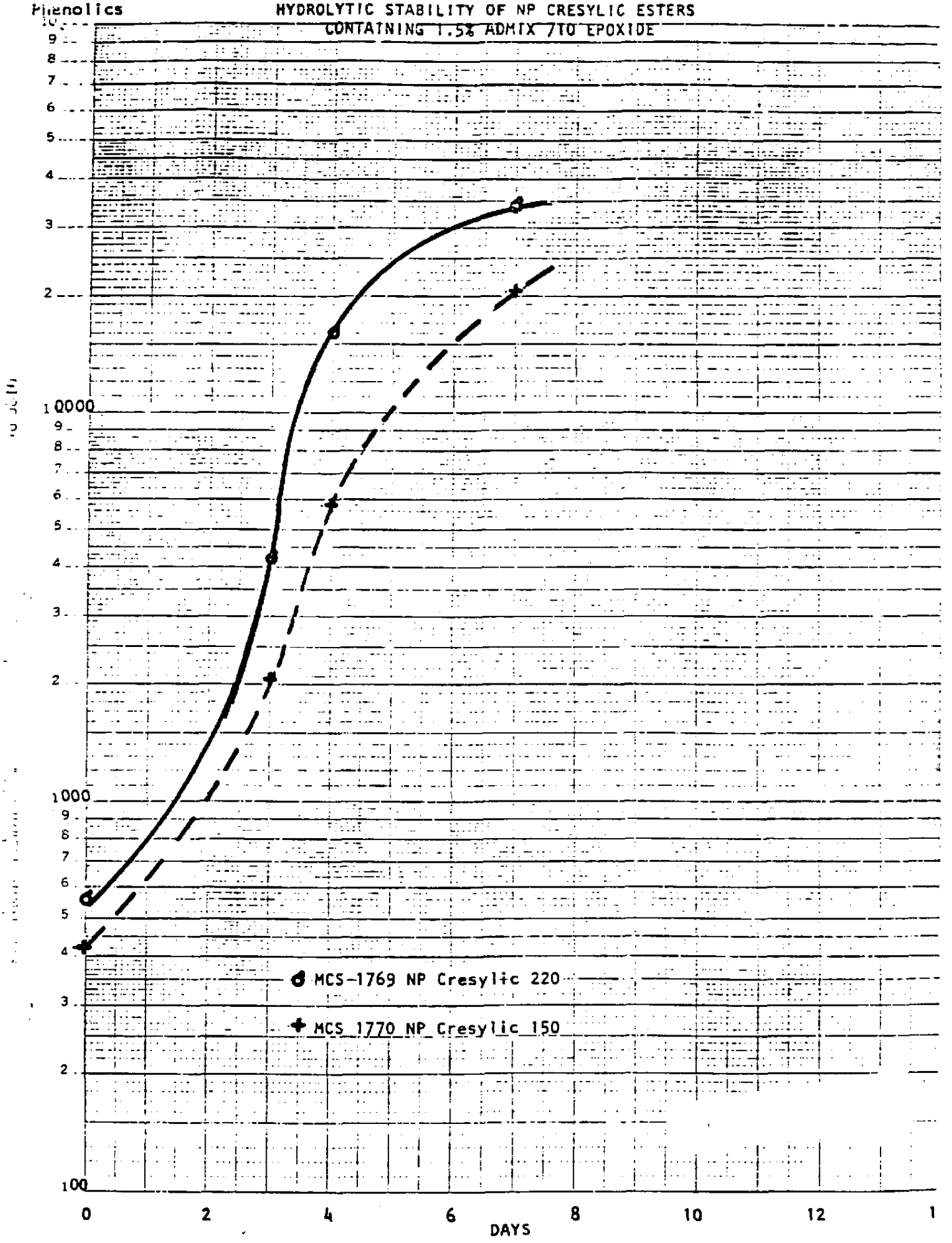


RSV 0010674

Phenolics

HYDROLYTIC STABILITY OF NP CRESYLIC ESTERS

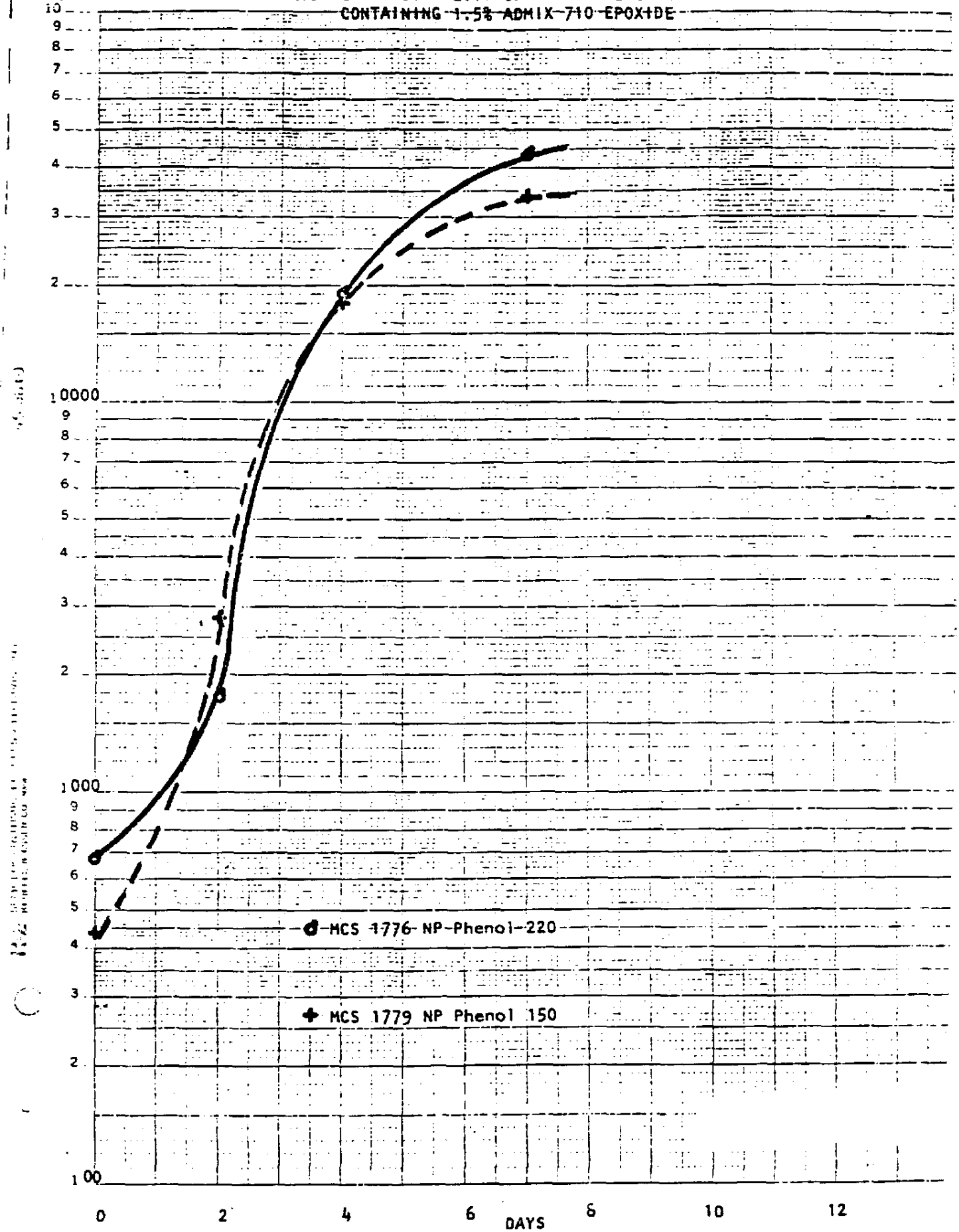
CONTAINING 1.5% ADMIX 7TO EPOXIDE



RSV 0010675

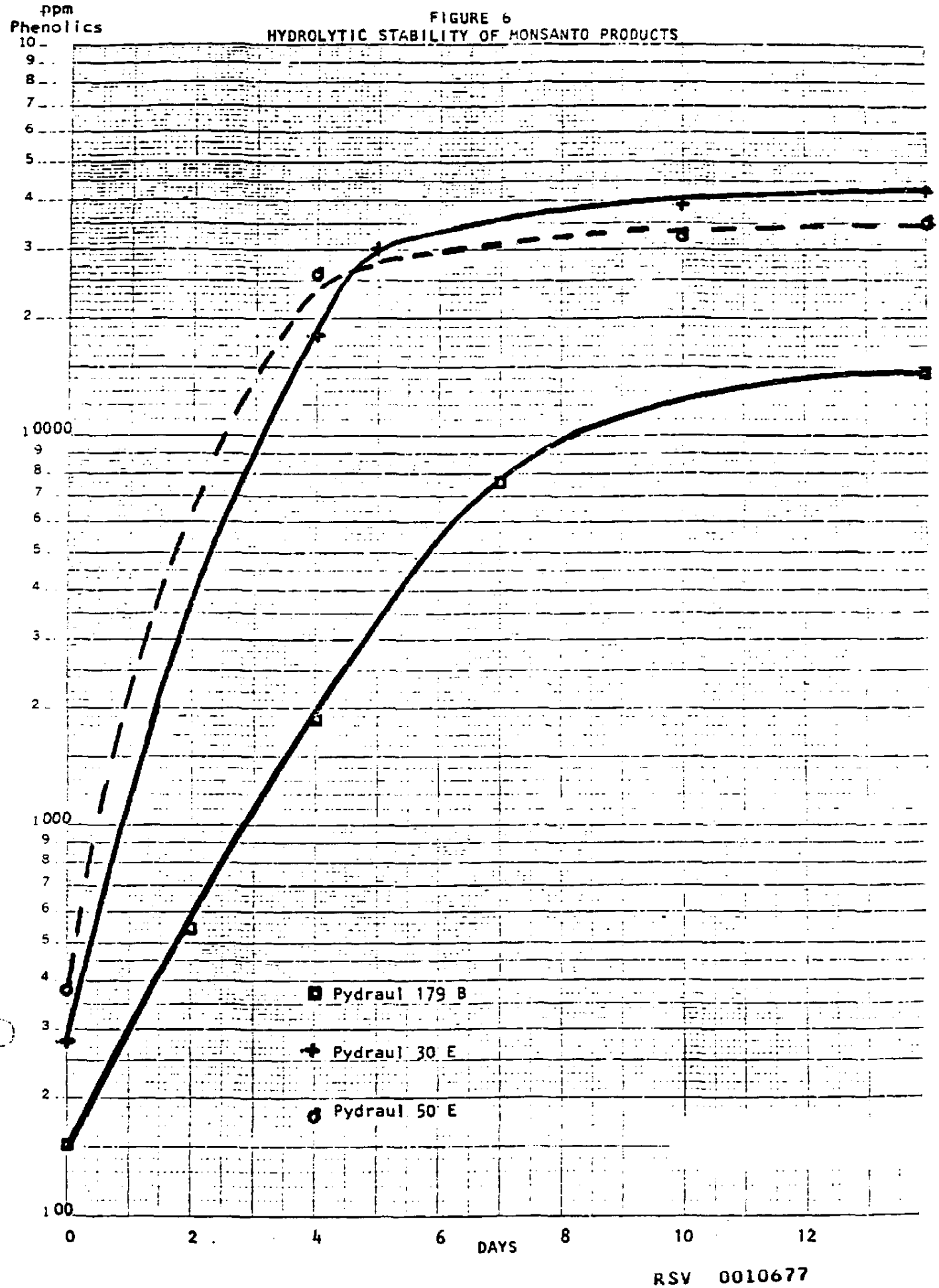
FIGURE 5

HYDROLYTIC STABILITY OF NP PHENYL ESTERS
CONTAINING 1.5% ADMIX 710 EPOXIDE



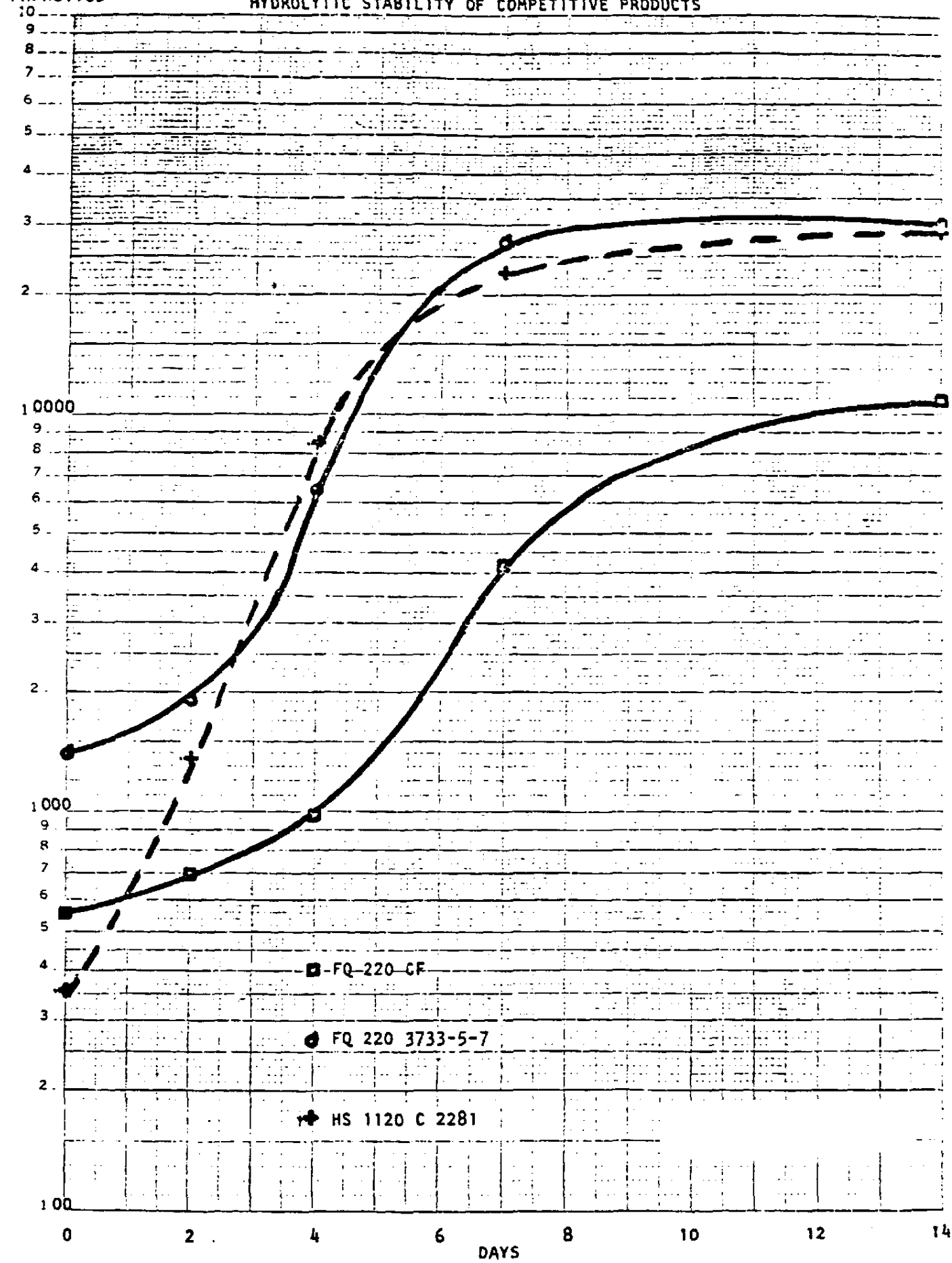
RSV 0010676

FIGURE 6
HYDROLYTIC STABILITY OF MONSANTO PRODUCTS



RSV 0010677

FIGURE 7
HYDROLYTIC STABILITY OF COMPETITIVE PRODUCTS



RSV 0010678

DETERMINATION OF VINYL CHLORIDE, TRICHLOROETHYLENE AND EPICHLOROHYDRIN IN AIR AT BAXLEY, GEORGIA PLANT

INTRODUCTION

This study determined levels of vinyl chloride (VCl), trichlorethylene (TCE), and epichloropydrin (ECH) in the air at this location.

SUMMARY

Results are given in the attached table. The values reported in this table may be high due to the presence of interfering components. They should be considered as upper limits. Concentration for TCE ranged from 2.8 to 0.3 ppm, while ECH was detected in amounts of 8.3 to 0.3 ppm. Vinyl chloride was not detected with a detection limit of 0.3 ppm.

EXPERIMENTAL

Samples were collected on a C-105 1 meter column and analyzed on a tenax column. Two-hour samples were taken with a flow of about 10 mℓ/min. Spectroscopy Method 74-7 and Special Study 74-34 give details of the method and procedure of analysis and calculations. GC retention times were used for identification.

Reference: GC/MS file #75-124

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Jaffich

S-75-SS-27

SET I*

	ECH (ppm)	*TCE (ppm)
M-4 8:00-10:00 a.m.	N.D. $\leq$.3	0.4
M-2 10:00-12:00 p.m.	N.D. $\leq$.3	1.3
M-3 2:00-4:00 p.m.	lost in analysis	
M-5 4:00-6:00 p.m.	0.4	0.3

SET II*

	ECH (ppm)	TCE (ppm)
L-4 12:00-2:00 p.m.	8.3	2.8
L-6 2:00-4:00 p.m.	0.3	N.D. $\leq$.3
M-1 4:00-6:00 p.m.	3.0	0.6

*The values reported in this table may be high due to the presence of interfering components. They should be considered upper limits.

PERSONNEL MONITORING OF PCP UNIT AT NITRO PLANT

INTRODUCTION

This study was conducted to determine personnel exposure to polychlorinated propenes and propanes.

SUMMARY

Results are given in the attached table. In sample # P-4003 taken during the process, several chlorinated propanes and propenes were detected. The attached spectrum illustrates how selected ion detection (at mass 75) in conjunction with a total ion scan (TI) on our new HP MS obtained a good identification and separation of the following components: dichloropropene, trans-trichloropropene, cis-trichloropropene, tetrachloropropane, and tetrachloropropene. Levels of these materials ranged from 0.4 to about 3.0 ppm. Background samples showed more than thirty organics ranging from 10 to 43 ppm present. This high background may be due to a rubber cap used in shipping the sampling tubes to St. Louis.

EXPERIMENTAL

For basic procedure, refer to Spectroscopy Method 74-7. An OV-1 one-meter glass column was used for the analyses and a tenax GC for collection. From 3 to 8 liters of air were taken with an SKC personnel pump. Calculations are based on known standards and identification was made by GC/MS in the selected ion mode.

CALCULATIONS

Liters of air (l) = supplied by Bruce Eley

$$\text{Weight of sample } (\mu g) = \text{area of sample} \times \frac{\text{conc. std. } (\mu g/l) \times \text{vol. inj. } (\mu l)}{\text{area of std.}}$$

$$\text{Concentration } (\mu g/l) = \frac{\text{weight of sample}}{\text{liters of air}}$$

Example #P-4003 trans-trichloropropene

Liters of air = 6.3

$$\text{Weight of sample} = 992758 \times \frac{7.27 \times 1}{1339381} = 5.4$$

Concentration = 5.4/6.3 = 0.9 µg/l

Referenca: GC/MS file #75-62

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TABLE (µg/l)

	Dichloro propene	Trans-trichloro propene	Cis-trichloro propene	Tetrachloro propane	Tetrachloro propene	Total Other Organics
St. Louis Blk	ND	ND	ND	ND	ND	3
PB-1001*	ND	ND	ND	ND	ND	42
PB-2001*	ND	ND	ND	ND	ND	18
PB-3001*	ND	ND	ND	ND	ND	32
P-4001	2.9	ND	ND	0.6	ND	25
P-4002	2.3	ND	ND	0.4	ND	16
P-4003	1.0**	0.9	0.6	0.5	0.5	10

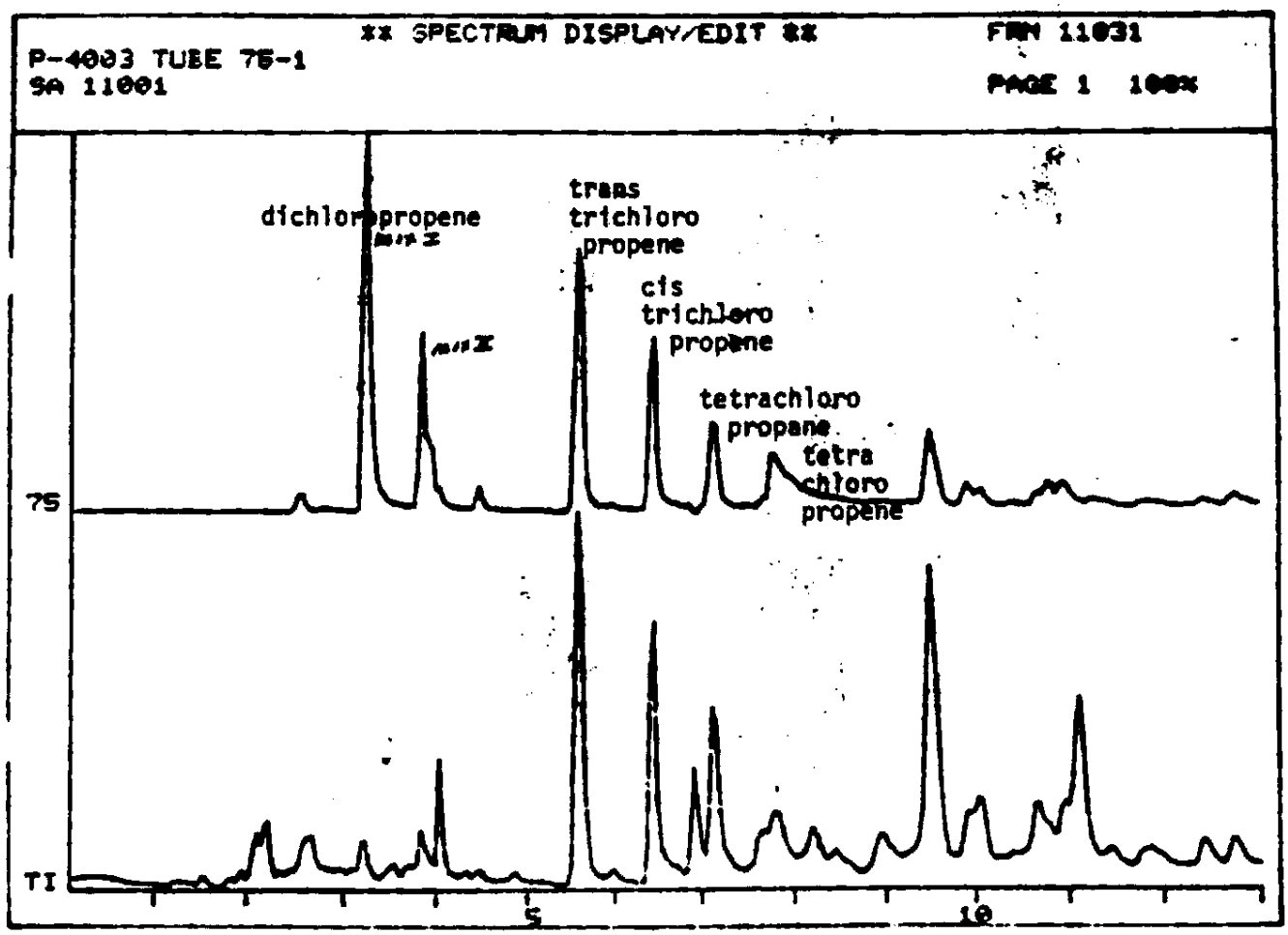
* These samples were taken of the plant air before the process began.

** This value is the combined concentration of isomers of dichloropropenes in Mix I and Mix II (see attached chromatogram). Mix I also has an unresolved component other than dichloropropene which appears to be trichloroethene. Similarly, Mix II also has another component with MW 108. Therefore, the result is a maximum value.

S-75-SS-28

NITRO PLANT

PENTACHLOROPROPANE PROCESS



Spectroscopy
S-75-SS-29

BISCHLOROMETHYL ETHER CONTENT OF DEQUEST PRODUCTS AND EVERETT PLANT AIR

INTRODUCTION

This study was undertaken because of concern that some Dequest products may contain harmful levels of bischloromethyl ether (BCME). BCME is listed by OSHA as a human carcinogen. Both final product and air in various production locations were analyzed to insure no safety problems exist for our workers or customers.

SUMMARY

A method was developed for determining the BCME content in Dequest products via a headspace analyses, i.e. the BCME content of the air above the product was determined rather than the product analyzed directly (see discussion). Results by this method were shown to be consistent with those obtained by a more direct analyses procedure. Our standard methodology for air monitoring was used for determining the BCME content of air in the Everett Plant Dequest department.

Low levels of BCME were found in certain Dequest products and in air taken from a synthesis carried out in a lab reactor. Values found are given in the attached tables. No BCME was found in air taken from a filled Dequest 2041 fiber pack or in air taken in the Dequest department of the Everett Plant.

The Monsanto Medical Department has taken the position that they see no reason that the levels of BCME found would constitute a problem.

DISCUSSION

A headspace GC procedure was chosen for this analysis for two principal reasons. First, it provides a highly sensitive approach free of the matrix effects which might be expected if Dequest products are injected directly into a GC. Interferences have been observed when a similar analysis for BCEE in Phosgards was attempted by direct GC analyses. Extraction of the product followed by GC analyses appears a satisfactory alternative but has poor sensitivity as indicated in Table I. The second reason is more fundamental. Since BCME is formed if both HCl and formaldehyde are present, it is possible that BCME could form in the headspace above Dequest even though there is no BCME in the product. A headspace procedure covers both possibilities since, if BCME were in the product, a significant percentage would also be in the headspace.

I. BCME in Products

A. Sample Collection

Headspace over liquid Dequest samples was taken by charging 5 ml of sample via syringe into a 125 ml suction flask containing a Teflon stir bar and fitted with a 5 X 130 mm glass dip tube set in a Teflon covered cork. The dip tube came within 20 mm of the bottom. The side arm carried a short tube charged with activated charcoal and a T through which excess N_2 flowed. Aspiration was applied through the dip tube for 2.5 min. while stirring for equilibration, flow

I. BCME In Products (Cont'd)

A. Sample Collection (Cont'd)

rate adjusted to 40 ml/min. Then a sampling tube was mounted on the dip tube using a short length of Teflon tubing and aspiration continued for usually 7.5 min. Sampling tubes were 1/4" X 6" glass charged with 150 mg Tenax GC and conditioned at 250°C.

Ether extraction of liquid samples was carried out on 50 ml portions transferred via syringe to a stemless short form 60 ml separatory funnel. A small amount of diethylether was added and after agitation separation was hastened by centrifuging at low speed in a bucket type centrifuge. An estimated 1.5 ml of the ether dissolves and at least 0.5 ml remains in emulsion. The clear ether extract was used for direct GC injection.

B. Analyses

With the helium flow off and the vacuum pump to the mass spectrometer off, a 1/4" X 6" Tenax sampling tube is placed in the heater and externally connected to the injection port of the GC. At this time, the analytical column is cooled to -50°C with liquid nitrogen. Now, the helium flow is diverted to flow through the precolumn. Quickly, check for leaks in the system, turn on vacuum pump to mass spectrometer, turn on heater and start GC program and clock to mass spectrometer. Heat is supplied by a heater consisting of 86 turns of 24 gauge asbestos covered Chromel "A" wire (75 ft.) coiled to fit into a 120 mm X 10.1 mm i.d. Pyrex tube. The coil is lined with two turns of 2.5 mil aluminum foil allowing a slide fit for the sampling tubes. Twenty volts brings the sampling tube to 200°C in about 2.5 minutes. After four minutes, turn off heater and after 7 1/2 minutes open the valve to the mass spectrometer and start scan at 7 minutes 50 seconds.

The following lists the GC/MS parameters:

GC - helium flow about 30 ml/min
auxiliary temp - 250°C
injection port temp - 250°C
analytical column - 10% S-409, 2 meter X 1/8"
on 80/100 Chrom W H.P.
program - -50°C for 4 min then up to 180°C
at 32°/min

MS - internal source heater 166°C
column A, B. valves 290°C
dodecapole 100°C
program SIM
masses scanned-79, 81, 49, 51
dwell time - 250 each
offset - 0
run time - 15 minutes
gain - 7

I. BCME in Products (Cont'd)

B. Analyses (Cont'd)

After the samples were analyzed, a standard of 0.006 µg/µl of BCME was injected into the GC and run under similar conditions. Comparison with the standard by intensity of the characteristic ions and GC retention time provided the means of identification. Attached is the selected ion chromatogram for BCME. Selected ion detection provides very high sensitivity by collecting data only from selected fragment ions of the component of interest rather than the total spectrum. In this case, fragment ions 79, 81, 49 and 51 are characteristic ions of BCME. Calculations were based on the mass 49 ion, since some interferences were observed at the other ions.

The bischloromethyl ether (BCME) used for the standard was provided by Myron J. Holm (lab prep. NBP 222 474 6/73) as a solution ca. 5% in hexane. The standardization was done indirectly on the assumption that the flame ionization detector should have a reasonably equivalent response for BCME and 1, 2-dichloroethane. A standard was prepared of close to 1 g. of 1, 2-dichloroethane in 10 ml of hexane solution and was twice diluted 1 to 10 to provide a 1000 µg/µl standard. By trial a comparable dilution for the BCME was found. Two microliters of these were run alternately on the GC under the analytical conditions to give three sets of area printouts on the Autolab. These were averaged and compared to give the value 0.61 µg/µl for the BCME standard. A thousand-fold dilution provided the working standard labeled #14-D, 0.00061 µg/µl.

II. Dequest 2041 Fiber Pack

A. Sample Collection

Headspace over finished goods was sampled using the same type sampling tube. No vacuum line was available at the site, therefore a one liter suction flask was equipped with a vacuum gauge and an ideal refrigerator valve. With the flask evacuated, a program of valve setting versus gauge reading was determined to maintain approximately 40 ml/min. flow. A one-half and a one liter sample were collected.

B. Analyses

The procedure described in Section I was used.

III. Laboratory Reactor

A. Sample Collection

Reactor headspace "grab" samples were obtained by means of 40 mm diameter cylindrical bulbs, approximately 230 ml volume with Teflon corks at each end. The bulbs were first evacuated via the far end. Then the cork was closed and the near end opened to take up headspace through a short connection. The resultant sample contained approximately 2 ml aqueous HCl condensate.

The sample bulb was supported vertically, a glass/Tenax sample tube attached at the upper end using a short piece of Teflon tubing. The upper 2/3 of the Tenax packing was equipped with a room temperature water jacket. The upper cork was opened, then gentle aspiration was applied to the sample tube while the lower cork was "cracked" to allow a slow bubbling. Nitrogen overflow was supplied to the inlet. A heat gun was employed during the 15 min. transfer period keeping the lower portions of the bulb hottest, the upper portion definitely warm and the upper cork and tubing up to the Tenax packing just warm enough to avoid condensation. Collections from the reactor at 60 min. and 120 min. were taken.

B. Analyses

The procedure described in Section I was used.

IV. Everett Plant Air

A. Sample Collection

Air samples were obtained by drawing air through a Tenax GC pre-column attached to a personnel monitoring pump with rubber tubing. Sample sizes ranged from 4 to 9 liters at the various locations in the plant. See Table IIC for results.

B. Analyses

The procedure described in Section I was used.

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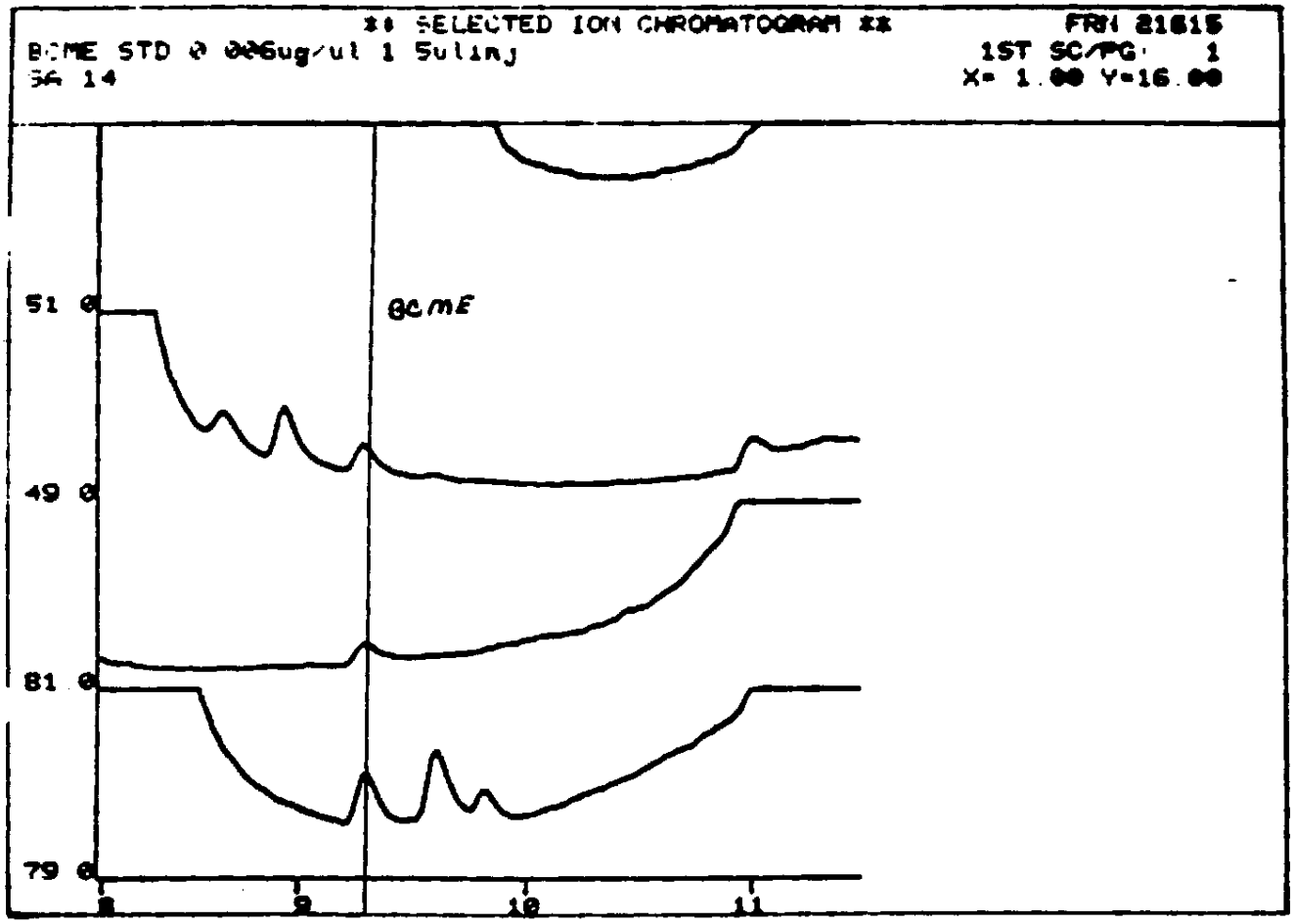
** SELECTED ION CHROMATOGRAM **
FRI 21615
1ST SC/PG: 1
X= 1.00 Y=16.00
51 0
49 0
81 0
79 0
8
9
10
11

S-75-SS-29

TABLE I

BCME IN DEQUESTS

A. HEADSPACE

Sample	Concentration BCME
Dequest 2060, Final Hexagon, Unstripped	1. PPB in Air
Above After Sitting 24 Hours	ca .5 PPB in Air
Dequest 2060, Hexagon, Stripped	N.D. $\leq$.5 PPB in Air
Dequest 2000, Unstripped, 255663 #3	N.D. $\leq$.5 PPB in Air
Dequest 2000, EB1118, Stripped	N.D. $\leq$.5 PPB in Air
Dequest 2054, Lot EC 339-2	N.D. $\leq$.5 PPB in Air
Dequest 2006, Unstripped, #255663 #4 (2 Phase)	N.D. $\leq$5. PPB ? in Air
Unfiltered Lonza By-product (Dequest 2000 Type)	0.4 PPB in Headspace
Filtered Lonza By-product (Dequest 2000 Type)	1.4 PPB in Headspace

B. EXTRACTION (DIETHYL ETHER)

Dequest 2060, Hexagon, Unstripped	N.D.* $\leq$20 PPB in Liquid
Dequest 2006, Unstripped	N.D.* $\leq$100 PPB in Liquid

*Assuming 10% efficiency of solvent extraction

TABLE II

OTHER BCME ANALYSES

A. DEQUEST 2041 FIBER PACK

Sample	Concentration BCME
Dequest 2041 Lot 176-18-8B	N.D. <.5 PPB in Air

B. LABORATORY REACTOR

Sample	Concentration BCME
60 minutes after start of reaction	4. PPB in Air
120 minutes after start of reaction	12. PPB in Air

C. EVERETT PLANT AIR

Sample	Concentration BCME
#77, 6/4/75 Dequest 2000 drum filling	N.D. <0.5 PPB
#18, 6/18/75 Airspace above scrub water	N.D. <0.5 PPB
#68, 6/24/75 Airspace Dequest 2000 drum storage	N.D. <0.5 PPB
#50, 6/27/75 Airspace above scrub water tank	N.D. <0.5 PPB
#34, 6/30/75 Airspace near HCl and formaldehyde storage tanks	N.D. <0.5 PPB

TRACER LITHIUM ANALYSES - NITRO PLANT EFFLUENT-II

SUMMARY

Lithium is used as a tracer to observe the dilution of the Nitro plant liquid effluent. Fifty-four effluent samples ranging from 0.05 to 0.2 ppm Li were analyzed by atomic absorption.

DETAILS

All samples are cloudy and contain some solids. Preliminary survey analyses show they contain considerable sodium and calcium and roughly 0.02 to 0.4 ppm Li. Instrument changes since the previous set were analyzed required a revision of the method used. Sodium ion enhances the lithium response, but enough is present so that all samples are equally enhanced. Addition of sodium ion or hydrochloric acid, agitation or filtration was found to have negligable effect. The lower lithium values are within ten times the system's noise level. Most burner and flame combinations produce an upward curvature in the absorbence versus ppm plot. The nitrous oxide burner using a small and very oxidizing flame was found to provide the flattest response when used at 6 mm below the grazing position. There is a matrix effect, i.e. a given amount of Li in the sample does not produce the same response as a pure water solution. Therefore the samples were taken in two groups and four from each group were analyzed by the method of standard additions. The values obtained for the selected four were used to peg the response for the group. This enabled the quick method of direct analysis to be used for the bulk of each group, without addition or separations, as in the previous work. The ppm Li are listed in the table.

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Applied Sciences
St. Louis, Mo.

7/75 - O. E. Kinast, M. W. Dietrich

S-75-SS-30

SAMPLE NUMBER	ppm Li		SAMPLE NUMBER	ppm Li		SAMPLE NUMBER	ppm Li	
101	0.048		118	0.081		200	0.050	
102	.048		119	.081		201	.054	
103	.047	(0.047)*	120	.080		202	.054	
104	.045		121	.080	(0.080)	203	.049	(0.050)
105	.045		122	.077		204	.095	
106	.049		123	.075		205	.204	
107	.062		124	.074		206	.166	(0.165)
108	.077		125	.074		207	.147	
109	.090		126	.071		208	.110	
110	.101		127	.067		209	.110	
111	.106		128	.066		210	.093	(0.095)
112	.104	(0.103)	129	.059		211	.082	
113	.095		130	.060	(0.060)	212	.074	
114	.090		131	.057		213	.072	
115	.088		132	.056		214	.067	
116	.086		133	.055		215	.059	
117	.085					216	.057	
						217	.055	(0.053)
						218	.052	
						219	.053	
						220	.050	

* Values in parenthesis were those obtained by standard addition.

ANALYSIS OF NITRO PLANT WASTE WATERS FOR TRACE ORGANIC POLLUTANTS

INTRODUCTION

Plant waste water samples equivalent to those collected by EPA representatives were analyzed for trace organic pollutants. The information obtained from these samples will be used to plan possible reaction to EPA results. Analyses of all samples were carried out in accordance with Spectroscopy New Technique 70-3. The analytical techniques used were the same as those it was anticipated the EPA might use.

SUMMARY

Samples obtained from the river water intake, tall oil pond, and treatment plant were analyzed. A total of 16 components were observed in the treatment plant samples and 32 in the tall oil samples. No organic components, <100 ppb, were observed in the river water intake samples. In general the components identified were associated with plant processes and ranged in concentration from 100 ppb to 9 ppm.

RESULTS

The components identified and their approximate levels are shown in Table I. Five of the twelve components observed in the treatment plant samples were identified while only two of the thirty-two components detected in the tall oil samples were identified. The components not identified in the tall oil samples appear to be a complex mixture of phenolic and hydrocarbon type constituents. In Table II the GC retention time and concentration of the individual components formed in a set of tall oil pond samples are shown. Only ten of the thirty peaks detected but not identified were at levels greater than 1 ppm.

Two differences were noted upon comparison of the peaks found in the extracts of the acidified and non-acidified samples. First, the acidified samples contained a larger number of components and secondly, compounds found in both were generally at higher levels in the acidified samples. These differences could be attributed to either microbial degradation or the fact that all samples were extracted as received without any pH adjustment. If the non-acidified samples had been acidified higher recoveries of the acidic components might have occurred.

In order to insure that any basic organics were being extracted, the acidified samples were made basic and re-extracted. No addition compounds were detected in the basic extracts.

No detectable (<.1 ppm) organics were found in the T-56 (River) 69 and 6/11 samples, both as is and acidified.

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8/75 - E. S. Tucker, O. E. Kinast, M. W. Dietrich

TABLE I

Components	PPM* Found			
	MH #3 6-9 & 10 Acid	MH #3 6-9 & 10 N.A.	MH #3 6-11 Acid	MH #3 6-11 N.A.
Benzothiazole	0.2	ND	0.6	ND
2-Methylbenzothiazole	0.5	0.8	0.7	ND
2, 2, 4 - Trimethyl-6-ethoxy-quinoline	1.7	2.1	1.3	ND
2-Hydroxybenzothiazole	6.7	0.2	5.8	ND
2-Mercaptobenzothiazole	1.3	ND	0.7	ND
ppm Not Identified	5.9 (6)**	4.3 (7)**	8.4 (5)**	ND
ppm Total Organics	16.3	7.4	17.5	ND
Components	Tall Oil 6-9 Acid	Tall Oil 6-9 N.A.	Tall Oil 6-11 Acid	Tall Oil 6-11 N.A.
Guaiacol (o-methoxyphenol)	5.2	0.2	ND	ND
1, 2 - di-methoxybenzene	0.8	ND	0.4	ND
ppm Not Identified	31.4 (30)**	32.9 (29)**	21.4 (29)**	26.4 (28)**
ppm Total Organics	37.4	33.1	21.8	26.4

* Calculated using benzothiazole as an internal standard

** Number of components

ND-None detected, <0.1 ppm

TABLE II

Retention Time (Sec)	PPM Tall Oil 6-9 Acid	PPM Tall Oil 6-9 N.A.
37	ND	0.2
62	<0.1	ND
70	0.1	0.3
76	0.1	ND
100	0.2	0.2
117	2.1	1.3
131	ND	0.5
136	5.2	0.2
149	1.8	ND
161	5.3	5.9
173	0.8	<0.1
183	0.8	ND
192	0.8	0.3
200	0.6	0.2
209	0.4	ND
222	1.9	ND
236	2.1	0.8
246	1.0	0.5
263	1.0	<0.1
286	2.7	0.3
299	0.2	ND
313	0.7	ND
324	0.9	ND
348	ND	<0.1
357	ND	<0.1
374	0.3	0.2
393	0.1	ND
405	<0.1	<0.1
421	2.4	3.4
437	0.3	0.5
446	ND	<0.1
445	0.5	0.8
472	1.3	1.8
482	ND	0.9
492	2.1	2.8
499	1.5	2.2
519	0.2	2.1
550	ND	0.5
583	<0.1	0.6
603	<0.1	0.4

ND = None detected, <0.1 ppm

DETERMINATION OF VOLATILES IN DECATUR, ALABAMA PLANT AIR (V)

INTRODUCTION

This is a continuation of an investigation to determine levels of vinyl acetate (VA), acrylonitrile (AN), vinyl bromide (VBr), vinylidene chloride ($VnCl_2$), in air at the south continuous polymer area of the Decatur, Alabama plant. The data obtained will be used to identify areas where worker safety problems may exist.

SUMMARY

Results are found in Table I. GC retention time provided the means of identification of the volatiles. Acrylonitrile had values from 0.4 to 1.6 ppm, vinyl acetate values ranged from 0.2 to 0.9 ppm, VBr ranged from 0.1 to 1.3 ppm and vinylidene chloride ranged from 0.4 to 3.0 ppm.

EXPERIMENTAL

Refer to Spectroscopy Method 74-7 for the analyses procedure used. Fifteen minutes were allowed for the heating of the external collection column to collect the acrylonitrile before proceeding as in Method 74-7. An example of the procedure used to calculate concentration is given in the S-75-SS-1 report. Sample collection was made using a Model 222-451 SKC pump. Calculations were based on known standards.

Reference: GC/MS File #75-150

ss

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8/75 - L. M. Chapman, M. W. Dietrich

TABLE I

CONCENTRATION PPM

	VBr	$VnCl_2$	AN*	VA*
M-4	Blank			
L-12	Blank			
M-2	None Detected			
M-3	0.8	ND	1.1	0.2
L-9	1.3	3.0	1.1	0.4
L-2	0.8	2.1	1.6	0.9
L-1	0.3	0.4	0.6	0.6
L-5	0.1	0.8	0.4	0.3

* AN and VA are maximum values because of interference of other components when calculating concentrations.

Volume sample ≈1-2 liters
Flow rate ≈19 ml/min
Sampling time ≈1-2 hours

TRACER LITHIUM ANALYSES - NITRO PLANT EFFLUENT-III

SUMMARY

Lithium is used as a tracer to observe the dilution of the Nitro plant liquid effluent. Fifty-one effluent samples ranging from 0.05 to 0.26 ppm Li were analyzed by atomic absorption.

DETAILS

This set of fifty-one samples was analyzed in the same manner as the previous (7/75) set. Forty-seven were found to be within a narrow range, the other four are considerably outside this range. The four and a selected spread of seven out of the group were analyzed by the method of standard additions. The values obtained for the selected seven were used to establish the ppm level for the group, all of which were analyzed by direct aspiration.

The ppm values in the table are reported as three significant figures because this reflects a real trend in relative values between adjacent samples. However, only two-figure accuracy should be taken for the actual level.

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8/75 - O. E. Kinast, M. W. Dietrich

AA 813

LITHIUM TRACER IN NITRO EFFLUENT

Sa of 7/23	ppm Direct	Std Addition ppm	Sa of 7/24	ppm Direct	Std Addition ppm	Sa of:	ppm Direct	Std Addition ppm
1	--	.052	1	.161		7/25	.133	.132
2	--	.256	2	.161				
3	.187		3	.158	.158	7/26	.120	
4	--	.228	4	.157				
5	.206		5	.159		7/27	--	.107
6	.177		6	.155				
7	.191	.191	7	.152				
8	.183		8	.153				
9	.187		9	.152				
10	.179		10	.149	.149			
11	.173		11	.149				
12	.176		12	.149				
13	.164		13	.149				
14	.165		14	.144				
15	.167	.170	15	.145				
16	.164		16	.143				
17	.166		17	.143				
18	.166		18	.143				
19	.168		19	.139				
20	.162		20	.140	.136			
21	.165		21	.138				
22	.165		22	.141				
23	.161		23	.143				
24	.160	.162	24	.140				

DETERMINATION OF TRICHLOROETHYLENE (TCE) IN AIR AT DELAWARE RIVER

INTRODUCTION

Air in the Phosphate Ester Department of the Delaware River Plant was sampled while Santicizer 148 was being made. The results obtained indicate worker exposure levels.

SUMMARY

TCE was detected in the samples from levels of 0.3 to 3.0 ppm, well below the TLV.

EXPERIMENTAL

A Chromosorb 105 pre-column was used for sample collection. A Tenax GC analytical solumn was used for analysis.

Refer to Spectroscopy Method 74-7 and Spectroscopy Special Study 73-11 for analysis procedures used. Calculations were based on a known standard. Identification was made by GC retention.

Calculations

$$\text{Volume of Air Sampled (Liters)} = \text{Pump Flow Rate (ml/min.)} \times \text{Sampling Time (min.)} \times 10^{-3}$$

$$\text{Weight Sample (µg)} = \text{Area Sample Peak (counts)} \times \frac{\text{Conc. Std. (µg/µL) Vol. Injected (µL)}}{\text{Area of Standard (counts)}}$$

$$\text{Concentration Sample (µg/L)} = \text{Weight Sample (µg)/Volume of Air Sampled (Liters)}$$

$$\text{Concentration Sample (ppm)} = \text{µg/L (sample)} \times \frac{24.5}{\text{M.W. (sample)}}$$

For Sampling 75-33

$$\text{Volume of Air Sampled} = 32.5 \times 120 \times 10^{-3} = 3.896\text{L}$$

$$\text{Weight Sample (µg)} = 17005 \times \frac{24.2 \times 1.}{10712} = 38.4\ \mu\text{g}$$

Concentration TCE (µg/L) $= \frac{38.4}{3.896} = 9.86$ µg/L

Concentration TCE (ppm) $= 9.86 \times \frac{24.5}{130} = 1.85$ ppm

Reference: GC file #75-151

ss

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St. Louis, Missouri

8/75 - L. M. Chapman, M. W. Dietrich

TABLE

Sample Tube	TCE (ppm)*
75-33	1.9
75-48	0.4
75-28	3.1
75-45	0.3

* Pump flow ≈ 32 ml/min

Sample volume ≈ 3.9 liters

Sample time ≈ 2 hours

DETERMINATION OF BENZENE IN AIR AT ANNISTON, ALABAMA PLANT II

INTRODUCTION

The purpose of this investigation was to determine worker exposure to benzene.

SUMMARY

Benzene ranging from 0.1 to 1.0 ppm was detected. Two samples were obtained for an 8-hour day and two were short-term samplings where high levels of benzene were expected. The results are given in the table.

EXPERIMENTAL

GC/MS was used in the verification of benzene and calculations are based on a benzene standard. An example of the calculations is given below. Results shown for the blanks were calculated on the basis of the same volume of air used for the samples.

Calculations

$$\text{Volume of Air Sampled (liters)} = \text{pump flow rate (ml/min.)} \times \text{sampling time (min.)} \times 10^{-3}$$

$$\text{Wt. of sample (µg)} = \text{area sample peak (counts)} \times \frac{\text{conc. std. (µg/µl) Vol. Inj. (µl)}}{\text{Area of std. (counts)}}$$

$$\text{Concentration of sample (µg/l)} = \frac{\text{Weight of sample (µg)}}{\text{Volume of air sampled (liters)}}$$

$$\text{Concentration of sample (ppm)} = \text{µg/l (sample)} \times \frac{24.5}{\text{M.W.}} \text{ (sample)}$$

For Sample 75-34 Benzene unloading dock

$$\text{Volume of air sampled (liters)} = 400 \text{ ml/min.} \times 15 \text{ min.} \times 10^{-3} = 6 \text{ liters}$$

$$\text{Wt. of sample (µg)} = 25.9 \times \frac{5.9}{16.6} \times 2.0 = 18.4 \text{ µg}$$

$$\text{Conc. Benzene (µg/l)} = \frac{18.4}{6} = 3.1 \text{ µg/l}$$

$$\text{Conc. Benzene (ppm)} = 3.1 \times \frac{24.5}{78} = 0.96 \approx 1.0 \text{ ppm}$$

Reference: GC/MS File #75-144

ss

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St. Louis, Mo.

8/75 - L. M. Chapman, M. W. Dietrich, C. Hoffman

TABLE

*Draining Benzene Feed Tank	≥0.6 ppm***
*Benzene Unloading Dock	1.0 ppm
**Biph Dept 7-8-75	0.2 ppm
**Biph Dept 7-9-75	0.1 ppm
Blank	0.1 ppm

* flow ≈ 400 ml/min
sampling time ≈ 15 min
volume ≈ 6 liters
pump - Bendix

** flow - 25 ml/min
sampling time - 8 hours
volume - 12 liters
pump - SKC

*** Incorrect instrument attenuation used.

PYDRAUL 29ELT / PYDRAUL 50E GEL COMPLAINT FROM REPUBLIC STEEL

SUMMARY

IR (infrared) analysis of fractions isolated by both solvent extraction and GPC (gel permeation chromatography) of the gel formed in a storage tank of a mixture of Pydraul 29ELT and Pydraul 50E at R public Steel showed the gel was composed of:

1. Residual phosphate ester.
2. Styrenated rubber.
3. Polyglycol.
4. Reation procuct of the epoxy stabilizer with the phosphate ester half acid.
5. Metal organopyrophosphate.
6. Inorganic phosphates containing high levels of iron.

The IR spectrum, the GPC retention time and the molecular weight by GPC of the polyglycol indicates this is Ucon's polyoxyalkylene glycol 75-H-350,000. This material is foreign to either Pydraul 29ELT or Pydraul 50E formulations which use Jeffox OL-2700. The IR and GPC also ruled out Ucon concentrate 700 used in other Pydraul formulations as the glycol source.

SEPARATION

The mixture of phosphate ester fluid and gel were poured into a 25 X 80 mm cellulose extraction thimble and the bulk of the fluid separated by gravity filtration. The concentrated gel was fractionated by the sequentional solvent extraction scheme shown in Figure 1.

The hexane insoluble acetone and chloroform soluble fraction, FII, was further fractionated by GPC column with a linear MW range of 80 to 3000. Because of the unknown quantity or residual fluid held up in the gel, no attempt was made to quantitate the solvent extraction. FII was the largest non-fluid fraction isolated.

DISCUSSION

Infrared analysis of the solvent extracted and GPC fractions showed the gel contained the following:

FI (hexane solubles): residual phosphate ester

FII (hexane insoluble-acetone soluble-chloroform soluble)

GPC #1: $\overline{MW}$ > 3000 - mixture of a polyglycol and a styrenated rubber.

GPC #2: $\overline{MW}$ 3000 - 1550 - reaction product of the epoxy component (Admix 710) with the phosphate ester half acid.

GPC #3: $\overline{MW}$ 1550 - 730 - similar to GPC #2. The -OH stretch absorbance about 1/3 of GPC #2.

GPC #4: $\overline{MW}$ 730 - 470 - similar to GPC #3

DISCUSSION

FII (Cont'd)

GPC #5: $\overline{MW}$ 470 - 350 - similar to GPC #3

GPC #6: $\overline{MW}$ 350 - 270 - phosphate ester containing alcohol and possibly ether components. The very low carboxylate ester content indicates low concentration of the epoxy-phosphate ester reaction product. This fraction is either a physical mixture of the base phosphate esters with a low molecular weight polyglycol, or an interaction product of the phosphate ester half acid with the glycol.

GPC #7: $\overline{MW}$ 270 - 145 - similar to GPC #6. The organo portion in this fraction is associated with phenyl or cresyl groups, whereas GPC #6 was associated with nonylphenyl or cumylphenyl groups.

GPC #8: $\overline{MW}$ 145 - <50 - a metal organopyrophate containing either phenyl or cresyl groups.

FIII (hexane insoluble, acetone soluble - chloroform insoluble):

A metal organopyrophosphate similar to GPC #8, differing in that the organo groups are nonylphenyl or cumylphenyl.

FIV (hexane, acetone, chloroform and methanol insolubles):

Inorganics that are high in phosphorus and iron. Probably a mixture of an iron phosphate and iron oxides.

Extraction of the recovered GPC #1 fraction with acetone separated the styrenated rubber from the glycol. The IR spectrum of the glycol showed that it was Ucon's polyoxyalkylene glycol 75-H-350,000, a material foreign to Pydraul formulations. The IR spectrum of the isolated polyglycol ruled out the presence as the main component being Jeffox OL-2700, the glycol used in Pydraul 29ELT, or Ucon Concentrate 700, a glycol used in other Pydraul formulations.

GPC analysis using a column for high molecular weight separations showed the Republic Steel gel contained components with apparent molecular weights of 20,000 and 7900 (relative to polypropylene glycol calibration standards). New Pydraul 29ELT contains apparent $\overline{MW}$ components of 21,000 and 4300. New Pydraul 50E contains no high molecular entities. GPC analysis of known components confirmed the 20,000 $\overline{MW}$ peak is a styrene-polyisobutylene copolymer and the 7900 $\overline{MW}$ peak is Ucon's 75-H-350,000. Table I lists the observed high molecular weight components in the Republic Steel gel and in all the known materials.

References: IR spectra 75-202 A to E, 75-213 to 219, 75-229 to 235, 75-249 to 258.

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12/75 - B. Katlafsky, W. J. Litschgi, M. W. Dietrich

FIGURE 1

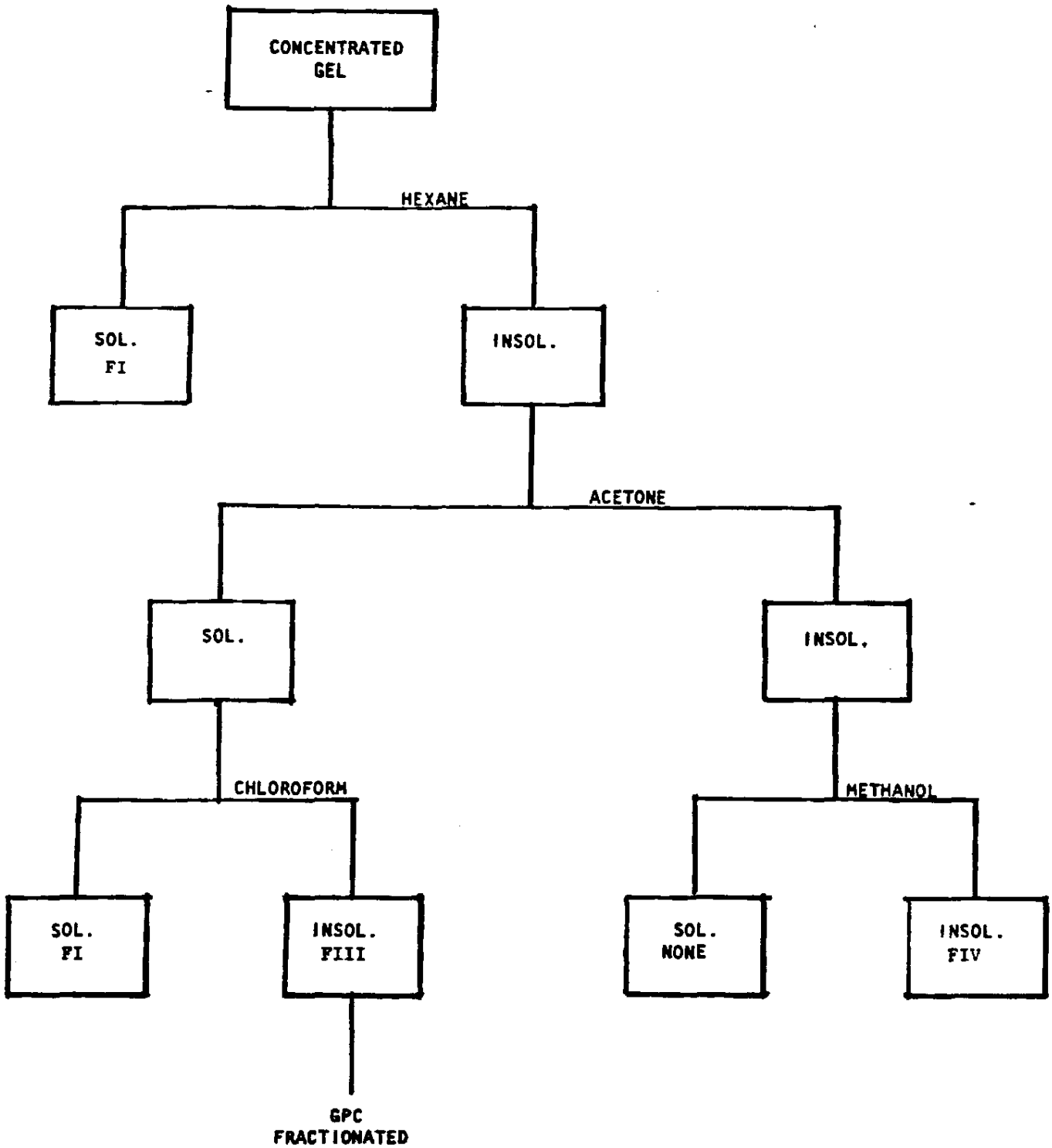

CONCENTRATED GEL
HEXANE
SOL. FI
INSOL.
ACETONE
SOL.
INSOL.
CHLOROFORM
METHANOL
SOL. FI
INSOL. FIII
SOL. NONE
INSOL. FIV
GPC FRACTIONATED

TABLE I

GPC OF HIGH MOLECULAR WEIGHT COMPONENTS

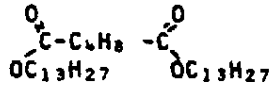
Sample	Apparent Molecular Weight			
Republic Steel Gel	20,000	-	7900	-
New Pydraul 29ELT	21,000	-	-	4300
New Pydraul 50E	-	-	-	-
Jeffox OL-2700	-	-	-	4000
Ucon 75-H-350,000	-	-	7900	-
Ucon Concentrate 700	-	11,600	-	-
Styrene-Polyisobutylene copolymer	19,500	-	-	-

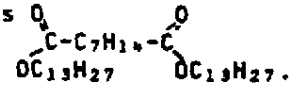
CHEMICAL IONIZATION OF ESTERS AND ALCOHOLS

INTRODUCTION

The reason for this study was to identify a competitor's compressor fluid.

SUMMARY

Sample 1000632-1 seems to be 

and sample 1000632-2 from our analysis is  .

DISCUSSION

The original analysis by NMR revealed the two products to be esters very closely related to diisodecyl adipate. Due to the high boiling point of these products, GC/MS analysis was impractical. Therefore, the lower boiling methyl esters were formed by hydrolizing the fluids. With the aid of chemical ionization (CI) mass spectrometry, we were able to obtain the identification of the fluids given in the summary. CI mass spectrometry of the esters and alcohols worked well. Some of the CI spectra of these fluids and C_7, C_9 alcohol standards are attached.

Reference: GC/MS File #75-158
NMR File #16-1059
Analytical Chemistry, Vol. 47, No. 9, Aug. 1975, pg. 1708
Accounts of Chemical Research, Vol. 1, Aug 1967, pg. 48

ss
Attachments (5)

Monsanto Industrial Chemicals Co.
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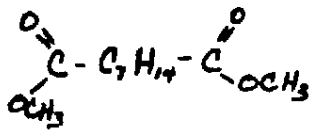
St. Louis, Mo.

10/75 - L. M. Chapman, G. W. Mappes, M. W. Dietrich

S-75-SS-37

DIMETHYL AZELATE



FRN 21821 SPECTRUM 214 RET. TIME • 11 4

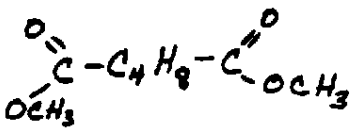
MASS	ABUND
53	2
55	2 6
57	5 1
58	6
59	2 2
60	3 0
61	6
67	.3
68	.1
69	2 1
71	4 8
74	11 6
75	1 1
79	.2
81	6
83	2 3
84	.6
85	4 4
87	1 0
88	.2
89	2
93	3
95	.7
97	2 5
100	3
101	6
102	3
103	.1
107	3
109	8
111	2 9
113	1 8
115	1 4
117	1
121	2
123	.7
124	3
125	3 4
127	1 4
135	6
137	6
139	5
140	.1
141	.7
143	6 2
149	.2
151	3 9
152	1 8
155	.9
156	2
157	1 8
158	2
163	.1
165	.2
167	2
169	.1
171	1 3
183	2 7
185	100 0
186	11 2
187	1 2
199	2
203	1 1
215	3
216 → MW	
217	5 4
218	.7
231	2
245	2 5 – +29
246	.3
257	.5 – +41

>PAUSE

RSV 0010710

S-75-SS-37

DIMETHYL ADIPATE



FRN 21824 SPECTRUM 49 RET TIME • 4 3

MASS	ABUND
55	4
56	1
57	6
59	4
60	5
69	2
71	2
74	7.1
75	2
83	2
85	4
87	1
97	5
101	7
102	1
111	7.2
112	4
113	4
115	2 3
116	1
129	6
143	100 0
144	7 0
145	8

173	174 ⟶ 4 mw
175	6 5
203	4.3 - +29
204	.4
215	2.5 - +41

>PAUSE

RSV 0010711

S-75-SS-37

C_{13} ALCOHOL

$C_{13}H_{27}OH$

FRN 21822 SPECTRUM 81 RET TIME • 5 6

MASS	ABUND		
55	10 9	123	1 0
57	84 3	125	10 3
58	5 4	127	13 5
59	9 4	129	6 7
60	22 9		
61	1 6	139	2.3
		140	1.4
69	17 6	143	58 0
71	100 0	144	1 1
72	7.3		
74	69.3	153	1.4
75	2.5	157	20 7
81	2.1	165	1 0
83	27 5	167	2.2
85	94 1	169	6.5
86	6.4	170	.8
87	2.7	171	3.5
88	.4		
		183	.7
95	1 8	185	8.7
97	34.5		
100	5.3	189	1.5
101	3 2	199	1.0
		200 → mw	
109	2 4	>PAUSE	
111	28 9		
113	38 2		
114	6 0		
115	5 4		

RSV 0010712

S-75-SS-37

C_7 ALCOHOL

$C_7H_{15}OH$

FRN 21811 SPECTRUM 259 RET TIME = 16.4

MASS	X10 ABUND
49	2.1
70	14.1
71	13.3
73	2.9
83	23.2
85	5.2
97	100.0
99	94.2
101	2.7
115	8.8 (m-1)

>PAUSE

5-75-55-37

C_9 ALCOHOL

$C_9H_{11}OH$

FRN 21811 SPECTRUM 309 RET TIME = 18.7

MASS	X10 ABUND	
42	3	
55	8.7	
57	56.5	
59	3.0	
67	.9	
71	100.0	
73	.8	
81	.8	
85	71.1	
86	4.8	
97	5.7	
99	.7	
111	1.4	
125	7.3	
143	3.9	(m-1)

>PAUSE

DETERMINATION OF TRICHLOROETHYLENE (TCE) IN AIR AT ST. PETERS

INTRODUCTION

Air at St. Peters in the De-Composer Units was sampled for TCE. The results obtained indicate worker exposure levels.

SUMMARY

TCE was detected in levels of 0.04 to 3.1 ppm. Inadvertently, the first five samples in the table sat for two months before sampling, which may have affected the accuracy of the analytical data.

EXPERIMENTAL

A Chromosorb 105 column was used for collection. A 2 m Tenax column programmed from 0-200°C at 16°/min was used for analyses. Multiple ion detection at masses 95, 130, 132 and 134 was employed for samples 1, 2, and 7. Total ion detection with two selected ions (95 and 130) for samples 3, 4, and 5 provided the means of identification and quantitation as compared to a known standard.

Calculations

$$\text{Volume of Air Sampled (Liters)} = \text{Pump Flow Rate (ml/min.)} \times \text{Sampling Time (min.)} \times 10^{-3}$$

$$\text{Weight Sample (µg)} = \text{Area Sample Peak (counts)} \times \frac{\text{Conc. Std. (µg/µL)} \times \text{Vol. Injected (µL)}}{\text{Area of Standard (counts)}}$$

$$\text{Concentration Sample (µg/L)} = \text{Weight Sample (µg)/Volume of Air Sampled (Liters)}$$

$$\text{Concentration Sample (ppm)} = \text{µg/L (sample)} \times \frac{24.45}{\text{M.W. (sample)}}$$

For Sampling #1 Spin Mount Polishing

$$\text{Volume of Air Sampled} = 53 \times 1 \times 60 \times 10^{-3} = 3.18 \text{ L}$$

$$\text{Weight Sample (µg)} = 217761 \times \frac{11.07 \times 2.2}{209657} = 25.3$$

$$\text{Concentration TCE (µg/L)} = \frac{25.3}{3.18} = 8.0 \text{ µg/L}$$

$$\text{Concentration TCE (ppm)} = 8.0 \times \frac{24.45}{130} = 1.5 \text{ ppm}$$

References: GC/MS File #75-172

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10/75 - L. M. Chapman, M. W. Dietrich

S-75-SS-38

TABLE

SAMPLE	TCE (ppm)
#1 Polishing-Spin Mount 8-28-75	1.5
#2 Polishing-Spin Mount 9-4-75	2.1
#3 Poly De-Composer 9-4-75	1.2
#4 Poly De-Composer (east) 9-11-75	0.2
#5 West Poly De-Composer - clean up 9-15-75	0.04
#7 Worn by John Wagner 9-18-75	3.1

Pump flow - 53 mls/min

Sample volume ≈ 3.18 liters

Sample time ≈ 1 hour

DETERMINATION OF CONTAMINANT IN OXO ALCOHOL

INTRODUCTION

The reason for this analysis was to check possible contamination in oxo alcohol sent to a customer in Taiwan.

SUMMARY

We found 0.03% dioctylphthalate (DOP) and 0.7% C_{10} hydrocarbon which were not present in a control lot of oxo alcohol.

EXPERIMENTAL

Several different GC columns were investigated in order to separate the 0.7 unknown component from the major alcohols present. A 3 m OV 17 glass GC column gave the best separation. From the mass spectra, the molecular weight of this component was 142. MS fragmentation indicated it was either a C_{10} hydrocarbon, a C_9 ketone or a C_9 aldehyde. A reaction with nitrophenylhydrazine was carried out to determine if this component was a ketone or aldehyde. No derivative formed under conditions in which a C_5 ketone gave a derivative indicating this impurity is a C_{10} hydrocarbon.

Programming used in the analyses was 50-200° @ 8°/min.

References: GC/MS File #75-168
NMR File #16-1078
"The Systematic Identification of Organic Compounds"
by Shiner, Fusan, Curtin, 4th Ed., pg. 219.

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Topic A2

Spectroscopy
Special Study S-75-SS-40

SYNTHETIC FATTY ACID CONTINUOUS PILOT PLANT RADIOTRACER CATALYST STUDY WITH IRIDIUM-192 -- FEASIBILITY INVESTIGATIONS

INTRODUCTION

During 1974-75, the Detergent and Phosphate Division expended considerable research effort toward the development of a continuous synthetic fatty acid plant process. A key factor to the success of the project was satisfactory demonstration of good performance and manageability of the iridium catalyst system in a continuous plant. The catalyst chemistry is complex and its behavior in the process has been, on occasion, baffling. Iridium analytical chemistry has also proved quite difficult contributing to the overall problem of quantifying catalyst characteristics. The possibility of making a better evaluation of the catalyst performance using the gamma emitting radiolabeled iridium-192 was recognized and discussed in early 1975. The main advantages foreseen were the possibilities of:

1. A simpler more reliable analytical method for determination of catalyst concentration by continuous, insitu external gamma radioactivity monitoring;

2. Much greater convenience in determining whether observed loss of catalyst activity was due to loss of catalyst per se or to other phenomena (poisoning, etc.);

3. The elucidation (when, where, how much, etc.) of the apparent catalyst losses in the process.

SUMMARY

Experimental design estimates were made that indicated useful catalyst analytical sensitivities could be probably obtained in the pilot plant using regulatory exempt (10 microcuries) level of radiolabeled iridium-192 (Table IV). Five millicuries of iridium-192 were obtained from New England Nuclear in April and a series of exploratory evaluations were undertaken to assess technical and safety problems involved in the proposed tracer study. Highlights of the feasibility study include:

- Gamma spectral properties of iridium-192 were checked (photopeak energies and intensities).
- Analytical sensitivities were established for continuous gamma monitoring at two pilot plant stages at several iridium concentrations and in different flow cell designs. (Tables I, V)
- Analytical sensitivities were determined for intermittant catalyst monitoring of grab samples for radioactivity using either the gamma or beta radioactivity of iridium-192 (Tables II, VI).
- A suitable explosion proofing cover for the electrical leads of the continuous gamma detector was developed (Figures 2, 3).
- Shielding requirement for minimizing radiation background for continuous gamma detectors was explored and two prototype shield designs were fabricated (Figures 2,3).

SUMMARY (Cont'd)

- Measures were explored for protecting the gamma detector from heatup from hot flow lines during continuous monitoring (Figures 2, 3).
- A technique was devised for volume calibration of short straight tubular flow cells.
- A spiral flow cell for enhanced sensitivity at exempt iridium-192 concentrations was designed, fabricated and evaluated for sensitivity enhancement at simulated reactor concentration of catalyst (Figure 3, Table V).
- Assessment of gamma radiation dosages to personnel from pilot-plant iridium-192 concentrations ranging from 10-100 microcuries were made (Table III). Other radiochemical safety measures for contamination protection of personnel and facility were devised.

During the summer and fall of 1975, formidible process problems continued to plague pilot plant studies to the extent that no radiotracer experimentation was undertaken. At the end of the year a decision was made to switch from continuous to batch operations. It has not yet been determined whether radioisotope applications will be of continued interest under this modified concept. This report of the experimental design application problems and results obtained in the feasibility study under simulated conditions is believed to have considerable value of a general nature in the application of radioisotopes to pilot plant scale process studies especially in the high pressure laboratory.

CONCLUSIONS

1. Two stages of the pilot plant appeared to be adaptable to continuous gamma monitoring - the reactor and the catalyst return line (Figure 1).
2. The reactor stage requires either greater than exempt quantities of iridium-192 and/or use of a larger volume flow cell for insitu continuous monitoring. Limitation of tracer to an exempt quantity (10 microcuries) and use of a short section of 1/4" reactor outlet tubing as flow cell does not permit adequate sensitivity (Table V).
3. The reactor stage can be intermittantly monitored insitu at exempt iridium-192 concentrations with sensitivities of ∿1% iridium by use of a larger volume flow cell and scaler counting for at least 10 minutes (Table V) or by taking grab samples of 1-2 ml and counting for 50-100 minutes in a 3" X 3" NaI gamma well detector (Table VI).
4. The catalyst return line with ∿10,000 ppm catalyst appears feasible for insitu continuous monitoring but requires either higher iridium tracer concentration or a larger volume flow cell (Tables I, V). The monitor region proposed is very crowded and adequate detector shielding against background will be a problem requiring possible redesign.
5. The catalyst return line, as with the reactor stage, can be intermittantly monitored insitu by scaler counting or by grab sampling/gamma well counting (Tables V, VI).

CONCLUSIONS (Cont'd)

6. A larger volume flow cell that appears practical in concept for the reactor stage and possibly for the catalyst return line was obtained by construction of a stainless steel tubing spiral that encircles the gamma detector (Figure 3, Table V).

7. Iridium-192 counting efficiency is significantly improved in grab sampling over insitu continuous monitoring (Tables I, II, V, VI). Gamma counting in the larger NaI well detector is believed more useful than liquid scintillation because of the nearly constant count efficiency as a function of sample volume and its greater freedom from interferences by sample composition, color, etc. (Tables II, VI).

8. Gamma radiation hazard to pilot plant research workers was estimated to be well below safe recommended levels up to 100 microcuries of iridium-192 (Table III).

DETAILS

The considerable quantity of details is reported only in outline form with page references to the project research notebook.

Topic	Notebook Page
• Synthetic Fatty Acid Continuous Pilot Plant Schematics and Specifications	MIC 309101A - 309102B 309156
• Project Justification/Radiochemical Safety Evaluation/Experimental Design	309102B - 309107B 309181-86
• Iridium-192 Radioisotope Shipment Data	309108
• Preparation of Experimental Solutions of Iridium 192	309112, 309120 309131, 309135 309145, 309147 309152
• Determination of Iridium-192 gamma spectrum	309115 - 309119B 309131, 309165 309161B, 309186B-87
• Feasibility studies on insitu continuous gamma monitoring at exempt Iridium-192 levels -- simulated catalyst return line of SFA	309121-2, 309125 309126, 309128 309131-2, 309134 309187B-94A
• Feasibility studies on alternative counting equipment for analysis of Ir-192 radioactivity at exempt level in simulated SFA pilot plant grab samples	309123-5, 309127 309129-34 309161-63 309194B-96B

DETAILS (Cont'd)

Topic	Notebook Page
• Feasibility studies on insitu continuous gamma monitoring of Iridium-192 at higher than exempt quantities	MIC 309135-6, 309141 309196C-97A
• Calibration of Victorine 440 and Eberline PRM 4-3 portable radiation detectors for Iridium-192 dosimetry measurement	309137-40
• Investigation of gamma radiation hazard to personnel from Iridium-192 at levels up to 10 times exempt	309137-40 309197A-98A
• Design of shield setup for SFA pilot plant catalyst return line	309144
• Determination of lead half thickness values for Iridium-192	309149-51B
• Determination of "actual" monitor volume of short 3/8" stainless steel tubular flow cells	309147-8
• Safety assessment of proposed tracer study by Corporate Safety Department	309169-75
• Feasibility studies on simulated continuous monitoring of SFA pilot plant reactor stage using exempt Iridium-192 levels as maximum	309154-5 309157-59 309164-68 3091988-200D
• Design and evaluation of spiral flow cell and lead shielding for continuous monitoring of SFA pilot plant reactor stage	309152-3 309166
• Project Report - Comprehensive Experimental Details	309181A-200D

ACKNOWLEDGMENTS

Assistance of Applied Sciences Instrumentation Group and Research Center Shop for fabrication of lead shielding, flow cells, gamma detector explosion-proof adaptor and other miscellaneous hardware is pridefully acknowledged.

References: Research Notebook Pages 309101A-309200D

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Attachments(9)

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12/75 - Charles Eggert, D. B. Hines, M. W. Dietrich

TABLE I. SIMULATED GAMMA MONITORING OF SFA CONTINUOUS PILOT PLANT CATALYST RETURN LINE - 2.5" X 3/8" OD TUBULAR FLOW CELL AND SOLID 2" X 2" NAI DETECTOR

Flow Cell-Detector Separation Distance (CM)	Flow Cell Signal - (Net CPM)	Back-Ground (CPM)	Ir-192 Count. Eff. (CPM/DPM)	Sample-to-Background Ratio	Sensitivity (As % of Iridium Concentration) Rate - Meter Recording (10 sec Integ)	Scalar Counting (Minutes) 1	10	60
A - 9.24 µcl Ir-192/4 liters (exempt concentration)								
0	1873	428	0.132	4.38	13.7	5.6	1.8	0.7
1.4	1276	428	0.090	2.98	17.8	7.3	2.3	0.9
2.9	848	428	0.060	1.98	23.7	9.7	3.1	1.3
~1.3[1]	1331	428	0.094	3.1	17.0	7.0	2.2	0.9
0[2]	394	19	0.028	21.1	26.5	10.7	3.4	1.4
B - 48 µcl Ir-192/4 liters								
0	9602	437	0.132	21.9	5.2	2.1	0.7	0.3
1.4	6127	437	0.084	14.0	6.7	2.6	0.9	0.4
2.9	4319	437	0.059	9.9	8.1	3.3	1.1	0.4
C - 101 µcl Ir-192/4 liters								
0	19055	547	0.125	34.8	3.6	1.5	0.5	---
1.4	11537	547	0.076	21.1	4.8	1.9	0.6	---
2.9	8804	547	0.058	16.1	5.5	2.3	0.7	---

(1) Flow cell was wrapped in asbestos insulation at thickness similar to that used in SFA Pilot Plant.

(2) A narrow window count of the major Ir-192 photopeak was made for comparison.

TABLE II. ANALYTICAL SENSITIVITY PROVIDED BY VARIOUS COUNT OPTIONS ON GRAB SAMPLES AT THE EXEMPT LEVEL OF IRIDIUM-192

Count Technique	Sample Size (ml)	Sample Net CPM	Background CPM	Count Efficiency (CPM/DPM)	Sample-to-Background Ratio	Sensitivity (As % of Iridium concentration) Count Time, Min		
						1	10	---
RIDL Single Channel Analyzer, Manual Sample Changer, 2" X 2" Well NAI Detector in 2" Lead Shield	0.5	636	137	0.249	4.6	9.5	3.0	1.2[1]
	1.0	1366	137	0.266	10.	6.0	1.9	0.8[1]
	2.0	2855	137	0.277	21.	3.9	1.2	0.5[1]
	5.0	7318	137	0.286	53.	2.4	0.8	0.3[1]
	10.0	14567	137	0.284	106.	1.7	0.5	0.2[1]
Packard Liquid Scintillation Spectrometer Model 3365, Automatic Sample Changer, Low Potassium Glass Count Vial, Packard Instagel Count Cocktail	0.5	1145	21	0.447	54.	6.0	1.9	0.6[2]
	1.0	2381	21	0.464	112.	4.1	1.3	0.4[2]
	5.0	11536	21	0.451	543.	1.9	0.6	0.2[3]
	10.0	21303	21	0.415	1003.	1.4	0.4	0.2[4]

(1) 60 minute counting

(2) 100 minute counting

(3) Counting ~78 min (900,000 count limit)

(4) Counting ~42 min (900,000 count limit)

S-75-SS-40

RSV 0010723

TABLE III. GAMMA RADIATION DOSAGES FROM A SIMULATED SFA PILOT PLANT STAGE CONTAINING HIGHER THAN EXEMPT LEVELS OF IRIDIUM-192

Ir-192 Dosage, 4 Liter Surface Container (mr/hr)			Allowed Gamma Dosage, NRC Regulations Title 10, Part 20, Par 20.101 (calculated mr/hr)		
Contained Ir-192					
10 µci	48 µci	101 µci	Whole Body Head and Trunk Active Blood Forming Organs Lens of Eye Gonads	Hands and Forearms	Skin of Whole Body
Less than 0.1	0.25	~0.45	2.4	36.1	14.4

TABLE IV. SYNTHETIC FATTY ACID PILOT PLANT SPECIFICATIONS PERTINENT TO CATALYST TRACER STUDY

Process Stage	Stage Fluid Capacity		Iridium Catalyst Distribution		Iridium-192 Distribution (10 µci total)		Est. Transit Time (Hours)
	Ml	Grams	Grams	ppm	µci	dpm/ml	
Reactor	4285	3000	6.00	~2000	1.42	736	~1.25
Distillation/ Catalyst Recov.	2344	1875	3.75	~2000	0.89	843	~0.75
Catalyst Return System	3785	3243	32.43	~10000	7.69	4510	~7.33
Totals	10414		42.18	---	10.00	---	9.33

TABLE V. SIMULATED GAMMA MONITORING (WITH VARIOUS FLOW CELL OPTIONS) OF SFA CONTINUOUS PILOT PLANT REACTOR AND CATALYST RETURN LINE AT EQUILIBRATION OF 10 MICROCURIES OF IR-192

Pilot Plant Stage	Type Flow Cell	Flow Cell Volume (ml)	DPM Ir-192 in Flow Cell (DPM/ml)	Flow Cell Signal[1] (Net CPM)	Back-Ground (CPM)	Ir-192 Count. Eff. (CPM/DPM)	Sample-to-Background Ratio	Sensitivity (As % of Iridium Concentration)			
								Rate-Meter Record 10 Sec Integ	Scaler Count 1 Min	10 Min	60 Min
Reactor	1/4" OD/SS	0.93	668 (718)	148	91[2]	0.222	1.63	61.1	24.5	7.8	3.2
	3/8" OD/SS	2.56	1839 (718)	288	91	0.157	3.16	37.3	15.1	4.8	1.9
	1/4" Spiral SS	27.0	19404 (718)	2487	172[3]	0.128	14.5	10.5	4.3	1.4	0.6
Catalyst Return Line	3/8" OD/SS	2.51	11479 (4573)	1413	91	0.123	15.5	14.0	5.7	1.8	0.7

(1) Separation distance of flow cell from solid 2" X 2" NaI Detector essentially zero.
(2) A narrower count window was used than for measurements reported in Table I.
(3) An improved shield was constructed by stacking of lead cribs around spiral cell enclosing the detector.

TABLE VI. ANALYTICAL GRAB SAMPLE SENSITIVITY PROVIDED BY PACKARD AUTO GAMMA (TANDEM MODEL 3365)[1]

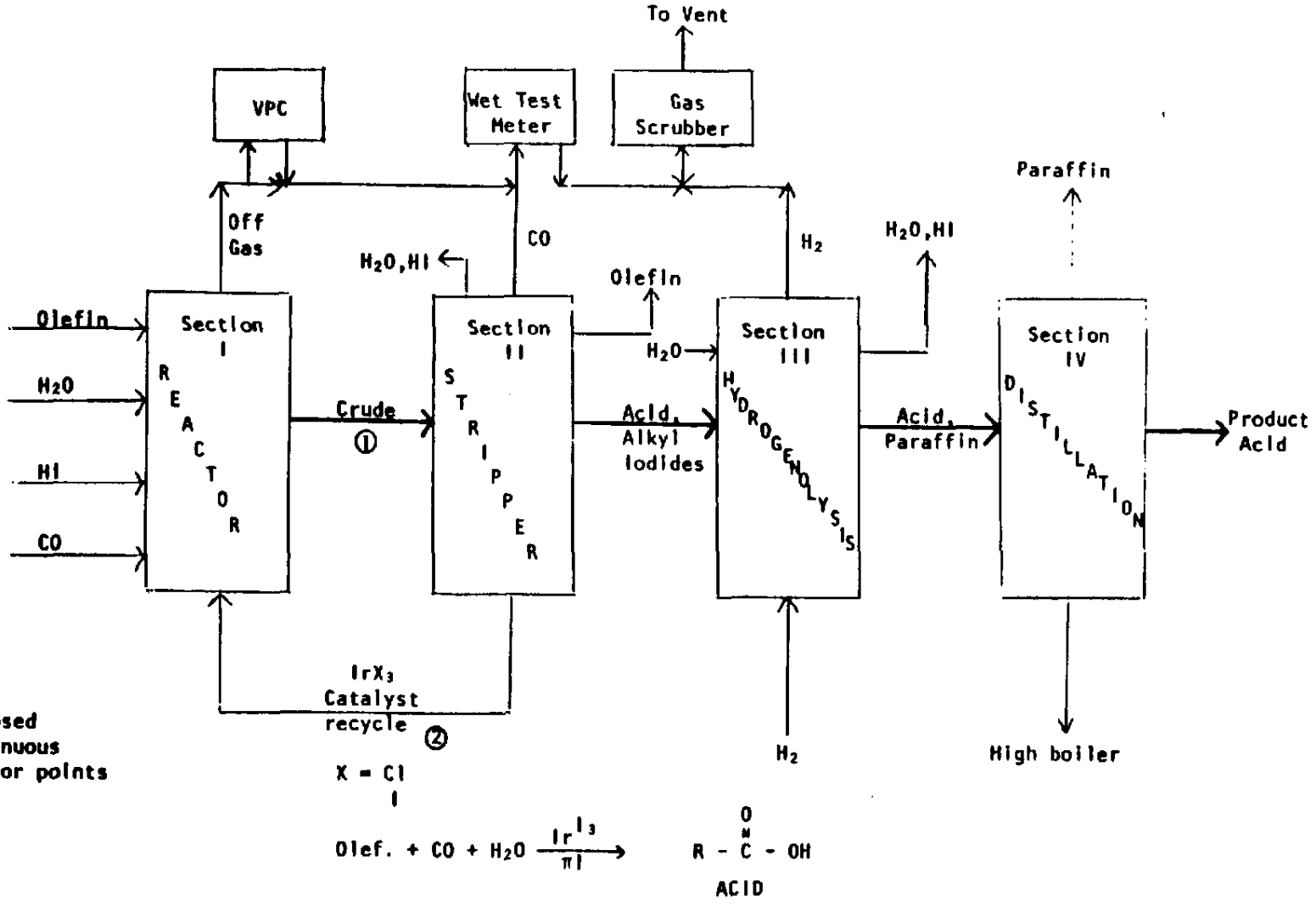
Pilot Plant Stage	Sample Size (ml)	Sample Net CPM	Back-Ground CPM	Count Efficiency (cpm/dpm)	Sample-to-Background Ratio	Sensitivity (As % of Iridium Concentration) Count Time, Min.			
						1	10	50	100
Reactor	1	372	180	0.518	2.1	14.6	4.6	2.1	1.5
	2	752	180	0.528	4.2	8.9	2.8	1.3	0.9
	3	1083	180	0.503	6.0	7.0	2.2	0.9	0.7
	5	1826	180	0.509	10.1	5.2	1.6	0.7	0.5
Catalyst Return Line	1	2364	180	0.517	13.1	4.4	1.4	0.6	---
	2	4677	180	0.511	26.0	3.0	1.0	---	---
	3	6889	180	0.502	38.3	2.5	0.8	---	---
	5	11107	180	0.486	61.7	1.9	0.6	---	---

(1) Catalyst in simulated reactor and catalyst return samples at equilibrium distribution of 10 µCi Ir-192.

S-75-55-40

RSV 0010727

FIGURE I. SYNTHETIC FATTY ACID CONTINUOUS PILOT PLANT SCHEMATIC (PR 7024-K2)

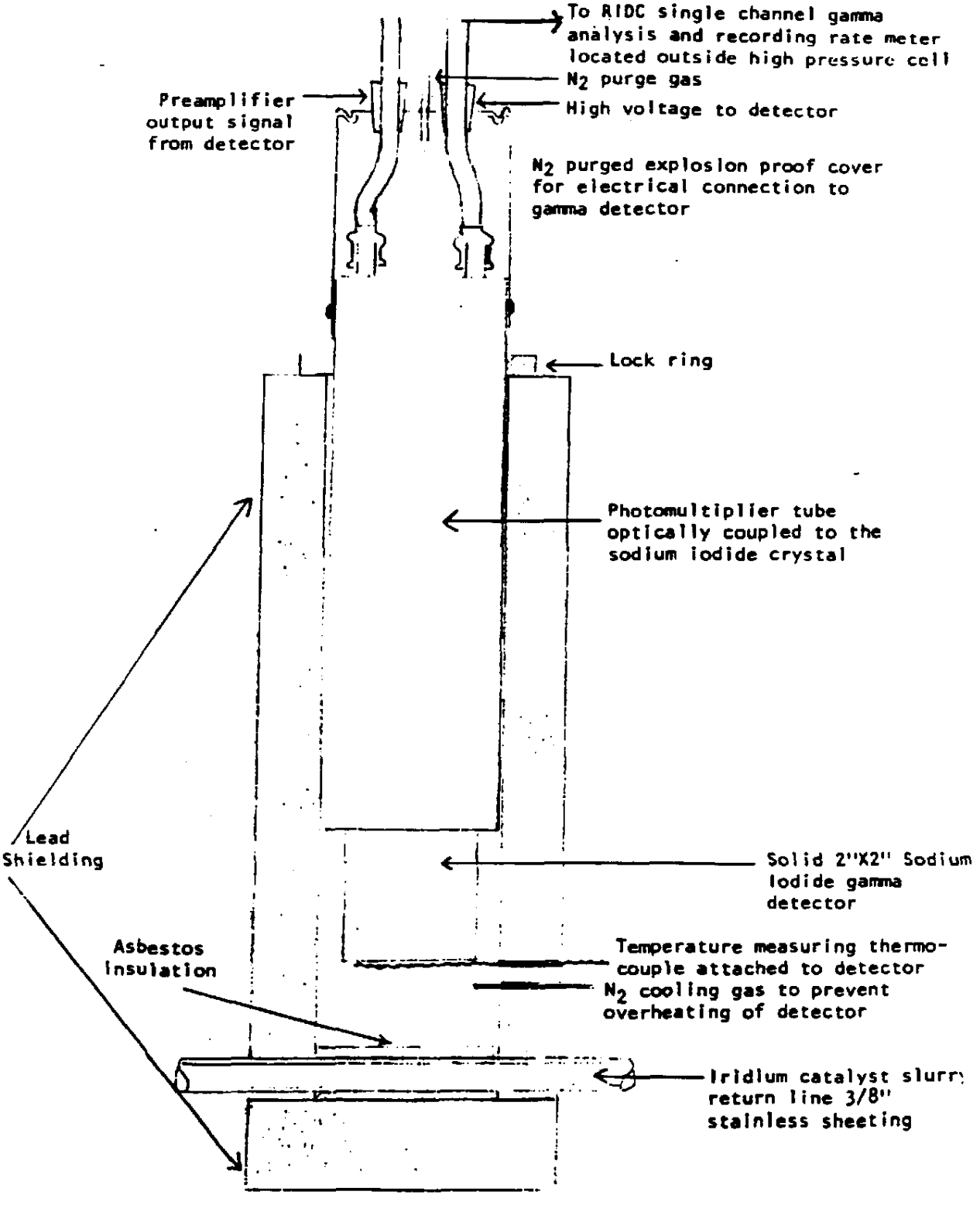


S-75-SS-40

RSV 0010728

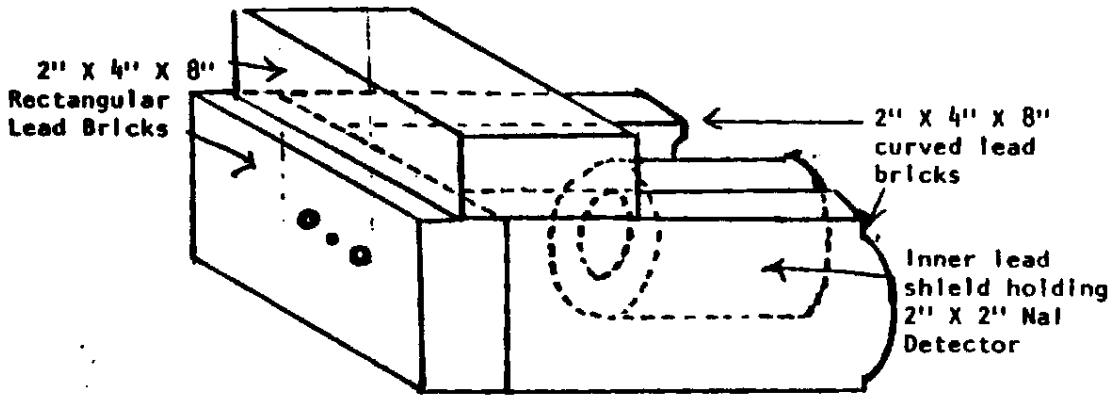
S-75-SS-40

FIGURE 2.
LEAD SHIELDED GAMMA DETECTOR PROPOSED FOR CONTINUOUS MONITORING
OF RADIOACTIVE IRIDIUM CATALYST RETURN LINE

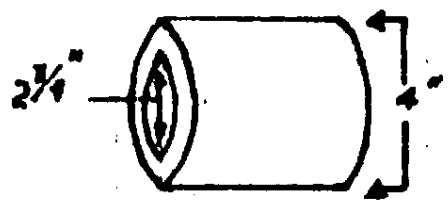


RSV 0010729

FIGURE 3. SHIELD SCHEMATIC FOR SPIRAL FLOW CELL CONTINUOUS MONITORING OF SFA CONTINUOUS PILOT PLANT REACTOR
(Scale, 1 div = 1")

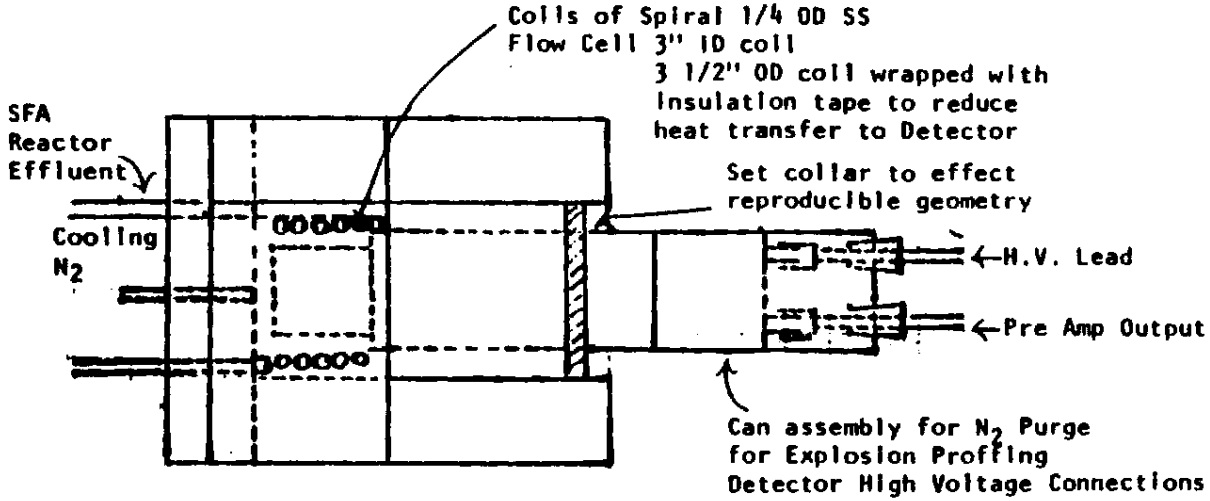


A. Shield Assembly



B.
Inner shield
machined to
hold the Detector
at reproducible
geometry

S-75-SS-40



C. Schematic of
Shield with Detector
in monitoring position
of Spiral Flow Cell

Note 2 essentially identical shield assemblies required:
(1) Houses Spiral Flow Cell from SFA Reactor
(2) Side-by-side of first shield to measure an Ir-192 std. in an identical spiral cell, measure BKE and checking of electronics lab of detector

RSV 0010730

SYNTHESIS, ANALYTICAL CHARACTERIZATION AND PREPARATION OF FDA TEST COATINGS OF MODAFLOW^{14}C

INTRODUCTION

Monsanto Modaflow is an ethyl acrylate-2 ethylhexyl acrylate copolymer of ~10,000 Mol. Wt. that is added to various resin systems such as acrylic and epoxy to produce better quality coatings. One potential application is the inside coating of metal containers targeted for the soft drink and alcoholic beverage industry. Acceptability for this application normally requires either demonstration of low extractability of product into the appropriate solvent system(s) using standard FDA extraction procedure or a feeding study in case of excessive extractability. Previous extractability testing of coatings containing Modaflow gave questionable results because of interference in the infrared spectroscopic measurement of Modaflow. This work was carried out using resins containing Carbon-14 labeled Modaflow to provide the necessary improvement in sensitivity and specificity.

SUMMARY

Approximately 190 grams of low specific activity Modaflow^{14}C was prepared from ethyl acrylate^{14}C raw material. This material was analyzed by a series of tests (Table I) and shown to have physical properties typical of plant material and to have adequate radioactivity concentration to provide the needed analytical sensitivity. The labeled Modaflow was incorporated into acrylic and epoxy resin formulations and used to prepare radioactive coatings onto special release paper. Solution/slurry coating techniques were used for radiochemical safety reasons instead of the normal dry powder electrostatic spray method. FDA extractions on the coated sheets were subsequently carried out as described in Special Study AC-75-SS-13 (Reference 1).

EXPERIMENTAL

Design of Experiment

Calculations showed that a labeled product with a relatively low specific activity (3-4 microcuries/gram) provided Modaflow detectability below 1 ppm with normal sample sizes, counting efficiencies and sample analysis times. This specific activity level appeared readily obtainable with ~1 millicurie of radioactive raw material.

Raw Material/Solvents

Modaflow is prepared by reacting ethyl acrylate and ethylhexyl acrylate (30/70 weight ratio) in a kerosene solvent. The extent of polymerization is controlled by sequential addition of benzoyl peroxide catalyst. Progress is followed by refractive index measurement. Modaflow is isolated after stripping off kerosene solvent by vacuum distillation. Ethyl acrylate^{14}C was purchased from American Radiochemical Corporation, Sanford, Florida. Due to its extreme susceptability to polymerization the ethyl acrylate^{14}C was synthesized immediately before our use. The supplier prepared the material, stabilized it with 1000 ppm hydroquinone (the standard agent and level used in plant raw material) and shipped it to Monsanto frozen in dry ice for next-day use.

EXPERIMENTAL

Raw Material/Solvents (Cont'd)

All the non-labeled raw materials and Penneco kerosene solvent were current Nitro, W. Va. plant stocks.

Synthesis

After the demonstration practice run the solvent stripping procedure following the reaction was modified by (1) the addition of a short, heated column replacing the gooseneck take-over joint and (2) use of a dry ice bath on the receiver. The labeled synthesis produced 187 g product corresponding to a yield of 96% relative to ethyl acrylate. Of this 187 grams, 83% was recovered as neat Modaflow^{14}C and 13% recovered as a solution in kerosene.

Analytical Characterization

The labeled Modaflow was characterized by refractive index, viscosity, molecular weight by GPC and specific activity determination.

Refractive Index

Two refractive index criteria were met:

1. Modaflow polymerization range was controlled by refractive index (RI) measurements on the crude reaction mass. The synthesis procedure allowed a RI range of 1.4460-1.4480 at 25°C. These values were reported to be the uncorrected range normally found relative to the Nitro Plant Bausch and Lomb refractometer. We obtained a comparable instrument and constant temperature bath on site and calibrated it over the desired RI range relative to Cargille RI standards. The corrected refractive index of the labeled crude obtained at reaction endpoint was 1.448 $\pm$ 0.0002 at 25°C.

2. The second refractive index specification was 1.4130-1.4190 at 25°C for a 40% solution of Modaflow^{14}C in 2,2,4-trimethyl pentane (isoctane). The corrected value obtained on labeled Modaflow was 1.416 $\pm$ 0.0002.

Viscosity

The Modaflow viscosity range in Saybolt Furol Seconds (SFS) is specified to be 650-1650 at 210°F. The viscosity of labeled Modaflow and a Nitro plant production lot were determined by Ostwald Kinematic Method at 100 and 125°C and calculated as SFS at ∿210°F according to ASTM Method D-2161-63T. The SFS values found were 965 and 885 respectively for the two products, placing them well within specifications.

Molecular Weight Measurement by GPC

Gel permeation chromatography was used to determine the peak molecular weight of Modaflow. The instrument used was a Waters Associates ALC-100 equipped with μ Styragel columns (Waters Associates) and an R-400 differential refractometer (Waters Associates). The battery of columns used consisted of 10^2Å, 5 X 10^2Å, 10^3Å, 10^4Å, 10^5Å and 10^6Å. UV grade tetrahydrofuran (THF) was

EXPERIMENTAL

Molecular Weight Measurement by GPC (Cont'd)

chosen as the eluting solvent at a flow rate of 1 ml per minute. The sample concentration was approximately 2 parts THF and 1 part Modaflow. A 20 µl portion of this sample was then chromatographed. The peak molecular weight versus polypropylene glycol standards was 9600.

Specific Activity Determination

The experimental design provided for a minimum specific activity of 3.6 microcuries per gram based on the use of one millicurie raw material to produce a 278 gram batch. Actual synthesis scale proved to be 195 g (theory) and American's radioisotope shipment specified 1.25 millicuries. A specific activity, therefore, of ~6.7 microcuries per gram was expected. Specific activity determination was carried out on a xylene stock solution of labeled Modaflow diluted 100 to 1 with cold Modaflow to reduce glass surface adsorptive effects. Radioactivity was measured by liquid scintillation counting using internal standardization. An experimental value of 4.53 microcuries per gram was obtained. The discrepancy between theory and experimental specific activities has been attributed to the delivery of less than the specified amount of labeled raw material.

Preparation of Modaflow ^{14}C/Resin Coatings for FDA Extraction Studies

The conventional electrostatic spraying method used to produce coatings containing Modaflow presented a substantial problem for radiochemical safety. This conventional method consists of several steps likely to produce airborne radioactive powders.

An alternative procedure to produce coatings using safer solution/slurry techniques was developed by the Plasticizer application group (Reference 3). Twenty-four sheets of acrylic and epoxy type coatings were prepared on release paper. In spite of considerable care, occasional small "holes" in the coatings were observed where film had not covered the paper. These holes were patched by addition of a drop of slurry to the area before curing.

References:

1. Analytical Chemistry Group Special Study AC-75-SS-13, "FDA Extractions of Resin Coatings Containing C-14 Radiolabeled Modaflow."

2. R. G. Kaley's memo of 7-22-75 to D. Hines and R. Radue, "Status of C^{14}-labeled Modaflow for FDA Extractions."

3. S. F. Joyce's memo of 9-2-75 to P. R. Graham, "Modaflow-FDA Panels."

4. Research Notebook pages MIC 1,001,101-1,001,173.

ss
Attachment

Monsanto Industrial Chemicals Co.
Applied Sciences
St. Louis, Mo.

12/75 - D. B. Hines, A. R. Atkinson, J. W. Hirzy, W. J. Litschgi, H. W. Luebke, H. Yepez, S. Joyce, M. W. Dietrich

TABLE I

SPECIFICATION VERSUS MEASURED PROPERTIES OF PLANT AND RADIOACTIVE MODAFLOW

Test	Specification	Lot 817-78, QC-343 NB-08-007	Modaflow ^{14}C
Refractive Index @25°C of Reaction Mass Crude	1.4460 - 1.4880	---	1.488 ± 0.0002
Refractive Index @25°C of 40% Modaflow in 2,2,4-trimethyl pentane	1.4130 - 1.4190	1.4170 (Plant Analysis)	1.416 ± 0.0002
Viscosity, SFS at 210°F	650 - 1650	885	964
Peak Molecular Weight by GPC	---	9600	9600
Specific Activity microcuries/gram	---	---	4.53

Spectroscopy
S-75-SS-42

DETERMINATION OF AROCLOR 1016 IN AIR AT ELECTRIC UTILITIES COMPANY, LASALLE, ILLINOIS

INTRODUCTION

The objective of this analysis was to determine levels of polychloro biphenyls (PCBs) in the plant air of Electric Utilities Company.

SUMMARY

The results are attached. The values detected ranged from 0.2 to 2.3 µg/l.

EXPERIMENTAL

Tenax was used for collection of the PCBs and a glass OV 17 was used for the analyses. Identification and quantitation was made with known standards. The calculations are shown below.

Calculations

$$\text{Volume of Air Sampled (Liters)} = \text{Pump Flow Rate (ml/min.)} \times \text{Sampling Time (min.)} \times 10^{-3}$$

$$\text{Weight Sample (µg)} = \text{Area Sample Peak (counts)} \times \frac{\text{Conc. Std. (µg/ L) X Vol. Injected (µL)}}{\text{Area of Standard (counts)}}$$

$$\text{Concentration Sample (µg/L)} = \text{Weight Sample (µg/L)/Volume of Air Sampled (Liters)}$$

For Sampling #1 Plugging Area

$$\text{Volume of Air Sampled (Liters)} = 88 \times 115 \text{ min.} \times 10^{-3} = 10.12 \text{ liters}$$

$$\text{Weight Sample (µg)} = 30584 \times \frac{2.47 \times 3.7}{16419} = 17.02 \text{ µg}$$

$$\text{Concentration (µg/L)} = \frac{17.02}{10.12} = 1.68 \text{ µg/l} \approx 1.7 \text{ µg/l}$$

References GC/MS File #75-202

ss

Monsanto Industrial Chemicals Co.
Applied Sciences
St. Louis, Missouri

11/75 - L. M. Chapman, M. W. Dietrich

TABLE

Location	Aroclor 1016
Plugging Area #1	1.7 µg/l
Plugging Area #2	2.3 µg/l
Press Department #3	0.4 µg/l
Assembly Department #4	0.5 µg/l
Impregnation Department #5	0.7 µg/l
Winding Room #6	0.2 µg/l
Plant Manager's Office #7	ND $\leq$ 0.1
Standard #8	ND $\leq$ 0.1

Pump flow - 88 ml/min.

Sampling time - 1-5 hrs.

Sample volume - 5-30 liters

Spectroscopy
S-75-SS-43

DETERMINATION OF THE LEVELS OF TRIETHYLAMINE AND BUTANOL IN AIR AT THE DELAWARE RIVER PLANT

INTRODUCTION

This investigation was undertaken to determine worker exposure levels to triethylamine (TEA) and butanol. Samples were taken in and around the Santicizer 160 manufacturing structure.

SUMMARY

Results are attached. Triethylamine was detected in levels ranging from 0.4 to 44.8 ppm. The levels of butanol detected were 0.1 to 2.8 ppm. Some values of the triethylamine analyses may be high due to interference by other components.

EXPERIMENTAL

The analytical column used was a 2 meter glass Tenax and collection columns were packed with Chromosorb 103. In identifying and quantitating the samples, knowns were used. Ions 74, 59, 86 and 101 were scanned with the total ion scan in order to get better resolution and identification of butanol and TEA.

Calculations

$$\text{Volume of Air Sampled (Liters)} = \text{Pump Flow Rate (ml/min.)} \times \text{Sampling Time (min.)} \times 10^{-3}$$

$$\text{Weight Sample (µg)} = \text{Area Sample Peak (counts)} \times \frac{\text{Conc. Std. (µg/µL)} \times \text{Vol. Injected (µL)}}{\text{Area of Standard (counts)}}$$

$$\text{Concentration Sample (µg/L)} = \text{Weight Sample (µg/L)} / \text{Volume of Air Sampled (Liters)}$$

For Sampling 75-1 Triethylamine

$$\text{Volume of Air Sampled (Liters)} = 36.8 \times 11 \times 10^{-3} = 0.4048 \text{ liters}$$

$$\text{Weight Sample (µg)} = 4226202 \times \frac{6.76 \times 3.2}{1220429} = 74.9 \text{ µg}$$

$$\text{Concentration (µg/L)} = \frac{74.9}{0.4048} = 185.1 \text{ µg/l}$$

$$\text{Concentration (ppm)} = 185.1 \times \frac{24.45}{101} = 44.8 \text{ ppm}$$

References: GC/MS File #75-200

ss

Monsanto Industrial Chemicals Co.
Applied Sciences
St. Louis, Missouri

11/75 - L. M. Chapman, M. W. Dietrich

Jackie AN

TABLE

SAMPLE	BUTANOL (ppm)	TRIETHYLAMINE (ppm)
75-11	2.8	0.4
75-10	0.3	none detected
75-4	0.5	0.9
75-5	0.5	0.7
75-1	2.5	44.8
75-12	1.2	4.0
75-3	0.8	2.6
75-8	1.8	1.2
75-7	0.1	1.5
75-6	lost in analysis	

These values may be high due to other component interference.

Pump used ⟶ SKC 222-451

Volume sampled ⟶ 0.5-2 liters

Flow rate ⟶ 28-37 ml/min

Sampling time ⟶ 10-60 minutes

Spectroscopy
S-75-SS-45

DETERMINATION OF MALEIC ANHYDRIDE AND STYRENE IN AIR AT EVERETT, MASSACHUSETTS

INTRODUCTION

This study was undertaken to measure worker exposure levels to maleic anhydride and styrene in air.

SUMMARY

Two samples contained 0.2 ppm maleic anhydride and 0.1 ppm styrene. One sample overloaded the system and is probably well over the TLV for both materials. Further details are given in the table.

EXPERIMENTAL

GC separation was made on a S-409 analytical column with identification by GC/MS. Besides scanning the total ions, ions 26, 54, 104 and 103 were also monitored selectively to verify the presence of these components.

Calculations

$$\text{Volume of Air Sampled (Liters)} = \text{Pump Flow Rate (ml/min.)} \times \text{Sampling Time (min.)} \times 10^{-3}$$

$$\text{Weight Sample (µg)} = \text{Area Sample Peak (counts)} \times \frac{\text{Conc. Std. (µg/µL)} \times \text{Vol. Injected (µL)}}{\text{Area of Standard (counts)}}$$

$$\text{Concentration Sample (µg/L)} = \text{Weight Sample (µg/L)/Volume of Air Sampled (Liters)}$$

$$\text{Concentration (ppm)} = \text{µg/L (sample)} \times \frac{24.45}{\text{M.W. (sample)}}$$

For Sampling Maleic Anhydride 75-60

$$\text{Volume of Air Sampled} = 46 \text{ ml/min.} \times 110 \text{ min.} \times 10^{-3} = 5.06$$

$$\text{Weight Sample (µg)} = 1{,}327{,}680 \times \frac{0.519 \times 3}{523{,}287} = 3.95$$

$$\text{Concentration (µg/L)} = \frac{3.95}{5.06} = 0.78$$

$$\text{Concentration (ppm)} = 0.78 \times \frac{24.45}{98} = 0.195 \approx 0.2 \text{ ppm}$$

ss

References: GC/MS file #75-221

Monsanto Industrial Chemicals Co.
Applied Sciences
St. Louis, Mo.

12/75 - L. M. Chapman, M. W. Dietrich

TABLE

Sample	Maleic Anhydride (ppm)	Styrene (ppm)
75-60 North side of #5 Press	0.2	0.1
75-31 Bag filling Operation	0.2	0.1
* 75-35 Between #5 and #6 Press	>10	>20
75-25 South side #6 Press	lost in analyses	

* These values are estimates because this sample overloaded the system.

SYNTHESIS, CHARACTERIZATION AND PURIFICATION OF S-334FM^{14}C

INTRODUCTION

Interest has continued within Monsanto for the development of a polymeric polyester plasticizer to replace DOP in the blood storage bag industry. Continued use of DOP has been questioned by certain medical research workers for several years because of its known extractability into blood during storage and its suspected adverse effects upon transfusion recipients. Monsanto's initial efforts produced Santicizer 334F, a polymer of about 2000 molecular weight, the reaction product of adipic acid and 1,3-butylene glycol. Human blood extractability of the S-334F was determined in 1972-3 by Monsanto research workers using a carbon-14 labeled form of the product synthesized within Monsanto for this work (References 1, 2). The Monsanto study showed that the extractability reduction differential of S-334F over DOP was not as great as had been anticipated. Research continued toward S-334F modificaton to further reduce extractability. By late 1973, S-334FM had been produced by acetylation of the S-334F hydroxyl end groups. The modified product exhibited significantly reduced water extractability compared to S-334F. One of Monsanto's customers, Baxter Travenol Laboratories, requested a radioisotopically labeled form of the modified product for research purposes. This request initiated this project for synthesis and analytical characterization of S-334FM^{14}C (Reference 3).

SUMMARY

- Monsanto agreed to provide Baxter Travenol Laboratories (BTL) with S-334FM^{14}C in which the adipic acid part of the molecule was labeled.
- S-334FM^{14}C was prepared by acetylating the residual stock of S-334F ^{14}C.
- S-334FM^{14}C was analytically characterized by radiochemical assay, radiochemical purity, molecular weight distribution by gel permeation chromatography and product identity confirmation by IR.
- Part of the S-334FM^{14}C was purified by preparative scale gel permeation chromatography to remove a low molecular weight radioactive impurity discovered in the GPC radiochemical purity analysis.
- Baxter Travenol Laboratories were supplied with 0.75 millicuries of GPC purified S-334FM^{14}C as requested.

DETAILS

1. Acetylation of the entire existing stock of S-334F ^{14}C produced an estimated 2.3 gram of S-334FM^{14}C having a specific activity of 4.97 millicuries per gram.
2. The analytical properties of the S-334FM^{14}C were considered acceptable with the exception of low molecular weight radiochemical impurity as determined by gel permeation chromatography (GPC). This impurity, estimated at ~0.4%, if totally extracted into blood from S-334FM plasticized polyvinyl chloride film, represents 1/3 of the total radioactivity previously extracted from the original S-334F^{14}C plasticized PVC film in 30 days at 5°C.

DETAILS (Cont'd)

3. Waters GPC unit, model 301 equipped with μ styragel column proved adaptable without modification for making preparative scale purification of up to 0.3 gram samples of the S-334FM^{14}C.

4. The low molecular weight radiocative impurity was shown to be absent in GPC purified S-334FM^{14}C.

EXPERIMENTAL DETAILS

The details of the synthesis, characterization and purification of S-334FM^{14}C are found in MIC Research Notebook pages 296101-296161 (Reference 4). An outline of this work with notebook page references follows:

Topic	MIC Notebook Page No.
• Miscellaneous Background outlining the origin and early planning of project	296101-5
• Synthesis Practice Runs	296106A-7B
• Labeled Synthesis, Decolorization, Solvent Dilution	296108A-9
• Analytical Characterization	296109A-31A
••Radiochemical Assay	296111A-12A
••Mol Wt by GPC (Kenyon)	296113A-14B
••Mol Wt by GPC (Litschgi)	296115A-24
••Radiochemical Purity (by GPC)	296125A-29B 296132A-B
••IR - sample isolation	296130A
••Summary Table	296131A
• Inventory Information	296133
• GPC Purification of S-334FM^{14}C destined for Baxter Travenol Laboratories	296134-41B
• Quotation on 1,3 butylene glycol^{14}C raw material for alternative labeled S-334FM synthesis	296142A-3
• Technical Information on S-334F/S-334FM for trip to Baxter Travenol Laboratories	296144A-49B
• GPC Preparative Scale Purification of additional stock of S-334FM^{14}C	296150A-60

References

1. Spectroscopy Special Study 74-36 "Synthesis and Characterization of Santicizer 334F^{14}C".

2. Spectroscopy Special Study 74-37 "Human Blood Extraction Studies of PVC Films Containing Labeled Santicizer 334F".

References (Cont'd)

3. P. R. Graham's Commercial Development Call Report No. 74-7, Baxter Travenol Laboratories, 2-14-74.

4. MIC Research Notebook pages 296101-60.

ss
Attachment

Monsanto Industrial Chemicals Co.
Applied Sciences
St. Louis, Mo.

12/75 - D. B. Hines, J. W. Hirzy, W. J. Litschgi, H. Yepez, M. W. Dietrich

TABLE I

ANALYTICAL CHARACTERIZATION OF S-334FM^{14}C

Property	S-334FM^{14}C	Plant S-334FM dtd 1-9-74
Specific Activity	4.97 mci/gm	----
Peak Mol Wt (GPC)	2700	3000
Radioactive Impurities (Mol Wt less than 300)	~ 0.4%	----
IR	Yes[1]	Yes

[1] IR trace agreed acceptably with plant sample except labeled material still contained a small amount of solvent benzene.

SYNTHESIS OF FIVE RADIOLABELED (P-32) FOOD PHOSPHATE SALTS

INTRODUCTION

Synthetic linear and cyclic polymeric phosphate salts are commonly employed as food additives because of the desirable qualities they can impart to foods. These food additives, as well as many others, are currently on the Food and Drug Administration's (FDA) "generally regarded as safe" list. The FDA is now soliciting and reviewing all old and new scientific data that will help reestablish the safety of these food additives.

In order to provide up-to-date definitive data on the metabolic fate and behavior of this class of compounds, when orally ingested, a rat metabolism study is being conducted on contract at the University of Tennessee. Radiolabeled P-32 food phosphate salts were prepared, by Monsanto Applied Sciences, so that the rat study could be performed.

SUMMARY

Radiolabeled monosodium (P-32) phosphate (ortho) was purchased and used to successfully prepare five representative food phosphate salts. The salts prepared were the tripoly, trimeta, tetrameta, hexameta and insoluble meta. After preparation each salt was radiochemically characterized, properly packaged and shipped to the University of Tennessee for use in the contracted rat metabolism study.

DETAILS

A preliminary rat metabolism study was carried out with the ortho, tripoly and trimeta phosphate salts. This study involved dosing (stomach tube) two rats per salt, which had been fed diets containing the respective cold phosphate salts at the 0.1% level for 14 days, with 1.0 milliliter of the P-32 labeled salts containing 25 mg of phosphorus per milliliter with a specific activity in the range of 100-200 µCi/ml. The rats were placed in metabolism cages and fed the same diets and water ad libitum. Periodic fecal and urine collections were made and at the end of 72 hours the rats were sacrificed and liver, kidney, fat (mesenteric) and bone (tibia) samples taken. All samples were analyzed for total activity and the fecal and urine samples characterized chromatographically. A second in depth study was then performed with all six food phosphate salts using ten animals per salt. The ortho, tripoly and trimeta salts were therefore prepared twice and the tetrameta, hexameta and insoluble meat salts once. The details and results of these rat metabolism studies will be published elsewhere.

Ortho: Carrier free monosodium phosphate: $NaH_2\ ^{32}PO_4$ in water, 10 mCi/ml, specific activity 500 mCi/mm, radionuclidic purity >99%, was purchased in 5 mCi packages from New England Nuclear (Catalog No. NEX-063). The ortho salt solution was prepared by syringe addition of an appropriate volume of the P-32 salt to a cold monosodium phosphate solution. After mixing 1.25 ml aliquots were transferred to septum vials and the vials sealed.

Trimeta: The appropriate volumes of the P-32 salt and cold monosodium salt solutions were combined in a platinum crucible. After careful mixing the solution was taken to dryness by placing the crucible in a 110°C oven overnight.

DETAILS

Trimeta: (Cont'd)

The monosodium salt was then converted to trimeta by calcining it for two hours in a muffle furnace at 550°C. The trimeta salt was then removed from the furnace, allowed to cool to room temperature and redissolved in a measured volume of distilled water. Aliquots of this solution (1.25 ml) were then transferred to septum vials and the vials sealed.

Tripoly: The tripoly salt is made from a 2:1 aqueous solution of di- and monosodium phosphate, which must be flask dried to prevent selective crystal growth, prior to calcining.

In order to do this safely and quantitatively the apparatus shown in Figure 1 was used. The appropriate volumes of the radioactive and cold salt solutions were combined in the feed reservoir and mixed by swirling. The apparatus was then attached to the scrubber train and the nitrogen purge started. The stopcock was then opened to allow the feed solution to slowly drip into the drying vessel. After washing the feed reservoir twice with distilled water, the apparatus was removed from the oil bath, wiped clean and placed in a 450°C muffle furnace for two hours.

Once it had cooled to room temperature, the tripoly salt was dissolved in a measured volume of distilled water and transferred to a beaker. Solids which were present were removed by placing a Millipore Millex filter unit between the syringe and needle used to transfer the 1.25 ml aliquots to the septum vials.

Tetrameta: The tetrameta salt was prepared by combining appropriate volumes of the P-32 salt solution and a solution containing equal molar amounts of cold monosodium phosphate and phosphoric acid in a pyrex beaker followed by evaporation to dryness overnight in a 110°C oven. The dried salt was then calcined in a muffle furnace at 325°C for 24 hours, removed from the oven and a few seed crystals of cold tetrameta stirred in with a glass rod. The salt was then replaced in the furnace at 325°C for another 24 hours. When cool, the tetrameta salt was redissolved in a measured volume of distilled water and 1.25 ml aliquots transferred into septum vials using a Millipore Millex filter and syringe to remove solids.

Hexameta:

The appropriate amounts of the P-32 salt solution and a 9/1 cold monosodium disodium phosphate salt solution were combined and mixed in a platinum crucible and the water evaporated by placing it in a 110°C oven overnight. The salt was then calcined in a muffle furnace at 750°C for 20 minutes, removed from the muffle and quickly cooled to room temperature by placing the crucible on a cold ceramic plate. The hexameta salt was then dissolved in a measured volume of distilled water and 1.25 ml aliquots transferred to septum vials using a disposable syringe and Millipore Millex filter to remove solids.

Insoluble Meta: The appropriate amounts of the cold and radiolabeled monosodium phosphate solutions were combined, mixed in a porcelain mortar and the water evaporated by placing it in a 110°C oven overnight. The salt was then calcined in a muffle furnace at 350°C for 2 hours, removed from the

DETAILS

Insoluble Meta: (Cont'd)

furnace and allowed to cool to room temperature. The mortar was placed in a plastic glove bag, the salt ground with a pestle and 0.08 gram portions of the powdered salt loaded into #5 gelatin capsules. Each capsule was then placed in a 2 dram screw cap vial prior to removal from the glove bag.

RADIOCHEMICAL ASSAY AND PURITY

The specific activity and purity of each salt was determined via liquid scintillation spectrometry.

Assay

Each salt solution was diluted gravimetrically with distilled water such that a five ml aliquot of the final dilution had a count rate in the range of 15,000-25,000 CPM. Four 5 ml aliquots of each diluted salt solution were transferred to tarred glass liquid scintillation counting vials. The vials were then reweighed and the sample weights recorded. Two of each set of four vials contained a weighed amount of a certified aqueous P-32 standard (New England Nuclear, NEX0175). Fifteen ml of Insta-Gel LSC coctail (Packard Instrument Co., cat. #6002177) were added to each vial and the vials were equilibrated in the counter at 10°C prior to counting.

The samples were counted with a Mark III Liquid Scintillation Spectrometer (Searle Analytic, Inc. Model 6880) using the preset isotope quench corrected program 4 (P-32) mode. Counting efficiencies were in all cases found to be in the range of 97-99% as determined via the internal standardization method.

The insoluble meta phosphate salt had to be initially solubilized by heating with phosphoric acid. Once solubilized it was assayed in the same manner as the soluble salts.

Radiochemical Purity

License free amounts of each salt were submitted to Industrial Testing Laboratories for separation by paper chromatography. Each sample was spotted in duplicate developed and one-half visualized to aid location of the unvisualized components. The radioactive spots on unvisualized paper chromatograms were then cut out and extracted with 10 ml of distilled water. Five ml aliquots of these extracts were then analyzed in the same manner as the soluble salts. The radiochemical purity of the insoluble meta salt was not determined.

DATA

The analytical data for the phosphate salts are shown in Tables I-III.

RADIATION SAFETY SUMMARY

All labeled syntheses were proceeded by successful completion of an equivalent synthesis with unlabeled starting materials and a complete review by the Radiation Safety Committee. The syntheses were performed in the hood in the hot laboratory and were continuously monitored with a Victorean Model 440

RADIATION SAFETY SUMMARY (Cont'd)

Survey Meter and an Eberline Model DRM-4 Rate Pulse Meter. All personnel were equipped with film badges and protective clothing. Laboratory air and hood air were also sampled and checked for radiation.

In no case were any personnel exposed to radiation levels that exceeded NRC regulations.

ss
Attachments (4)

Monsanto Industrial Chemicals Co.
Applied Sciences
St. Louis, Mo.

12/75 - E. S. Tucker, M. W. Dietrich

TABLE I

SPECIFIC ACTIVITY AND PURITY OF P-32 PHOSPHATE SALTS

1st Preparation

Salt Analyzed	Specific Activity[1] µCi/ml	Salt	Species Distribution[2]	Activity Distribution[3]
Ortho (MSP)	152	ortho	>98.6%	99.8%
Tripoly (STP)	150	ortho	2.1%	0.2%
		pyro	12.7	12.3
		tripoly	82.6	85.7
		trimeta	1.7	1.1
		long chain	0.9	0.7
Trimeta (STMP)	169	ortho	1.5%	0.1%
		pyro	0.5	0.4
		tripoly	2.5	2.0
		trimeta	95.0	97.5
		long chain	0.4	0.1

[1] As of 11-3-75, 10:30 AM CST.

[2] Paper chromatography -

[3] Paper chromatography - Liquid Scintillation Counting.

TABLE II

SPECIFIC ACTIVITY AND PURITY OF P-32 PHOSPHATE SALTS

2nd Preparation

Salt Analyzed	Specific Activity[1] uCi/ml	Salt	Species Distribution[2]	Activity Distribution[3]
Ortho	152	ortho	>99.5%	99.9%
Tripoly	150	ortho	0.3	0.2
		pyro	12.0	9.9
		tripoly	86.5	88.6
		trimeta	0.2	0.3
		long chain	1.0	0.9
Trimeta	169	ortho	0.1	---
		pyro	0.1	0.1
		tripoly	0.8	0.6
		trimeta	99.0	99.2
		long chain	---	0.1

[1] As of 12-3-75, 8:30 AM CST.

[2] Paper chromatography - colorimetrically.

[3] Paper chromatography - Liquid Scintillation Counting.

TABLE III

SPECIFIC ACTIVITY AND PURITY OF P-32 PHOSPHATE SALTS

1st Preparation

Salt Analyzed	Specific Activity[1]	Salt	Species Distribution[2]	Activity Distribution[3]
Tetrameta	193 µCi/ml	ortho	16.5	16.7
		pyro	14.4	15.0
		tripoly	18.4	18.0
		tetrapoly	9.4	9.1
		trimeta	10.9	9.9
		tetrameta	30.1	31.3
		long chain	0.3	0.2
Hexameta	65 µCi/ml	ortho	---[5]	0.2
		pyro	---	0.1
		tripoly	---	0.3
		tetrapoly	---	0.4
		trimeta	---	2.9
		tetrameta	---	1.8
		high meta	---	1.8
		high poly	---	90.9
	Hexameta	long chain	---	1.7
Insoluble Meta[4]	2456 µCi/g	(197 µCi/capsule)		

[1] As of 12-23-75, 10:00 AM CST.
[2] Paper chromatography - colorimetrically.
[3] Paper chromatography - Liquid Scintillation Counting.
[4] Not analyzed for impurities.
[5] Not analyzed colorimetrically.

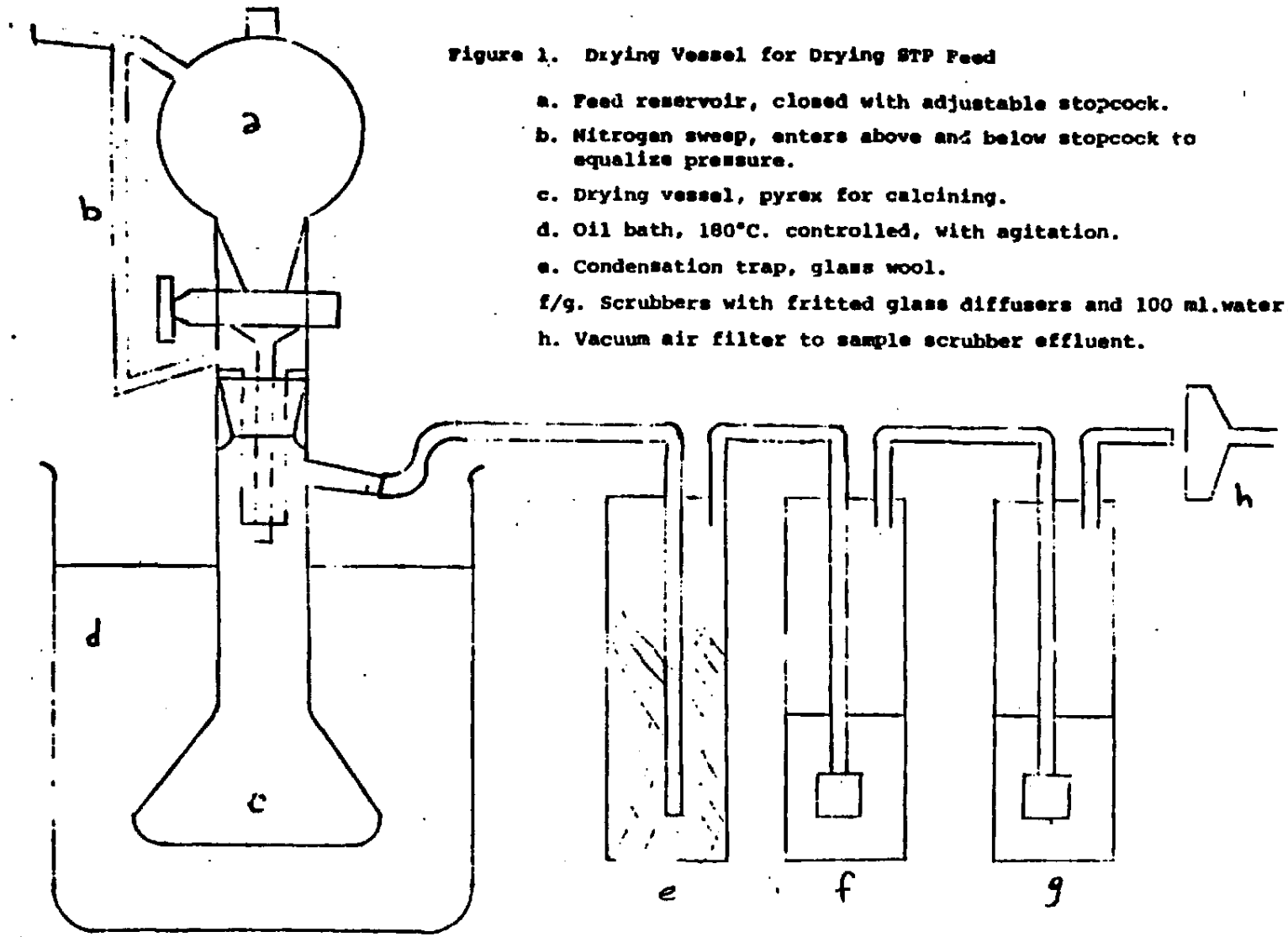


Figure 1. Drying Vessel for Drying STP Feed

a. Feed reservoir, closed with adjustable stopcock.

b. Nitrogen sweep, enters above and below stopcock to equalize pressure.

c. Drying vessel, pyrex for calcining.

d. Oil bath, 180°C. controlled, with agitation.

e. Condensation trap, glass wool.

f/g. Scrubbers with fritted glass diffusers and 100 ml.water.

h. Vacuum air filter to sample scrubber effluent.

Spectroscopy
Special Study S-75-SS-49

DETERMINATION OF BENZENE IN AIR IN THE ST. LOUIS RESEARCH CENTER

INTRODUCTION

The purpose of this investigation is to determine worker exposure to benzene in Q building labs Q309 and Q311.

SUMMARY

Benzene levels ranging from 0.3 to 2.5 ppm were detected. The results are given in the table.

EXPERIMENTAL

GC retention time was used in the verification of benzene and calculations are based on a benzene standard. An example of the calculations is given below.

Calculations

Volume of Air Sampled (Liters) = Pump Flow Rate (ml/min) $\times$ Sampling Time (min) $\times 10^{-3}$

Weight Sample (µg) = Area Sample Peak (counts) $\times \frac{\text{Conc. Std. (µg/µL) X Vol. Injected (µL)}}{\text{Area of Standard (counts)}}$

Concentration Sample (µg/L) = Weight Sample (µg/L)/Volume of Air Sampled (Liters)

Concentration Sample (ppm) = µg/L (sample) $\times \frac{24.45}{\text{M.W. (sample)}}$

For Sampling 75-41

Volume of Air Sampled = 23.6 ml/min X 240 min X 10^{-3} = 5.7 L

Weight Sample (µg) = $37764 \times \frac{5.29 \times 2.9}{12798} = 45.27$

Concentration (µg/L) = $\frac{45.27}{5.66} = 8.00$

Concentration (ppm) = $8.00 \times \frac{24.45}{78} = 2.5$ ppm

Reference: GC/MS File #75-220

ss
Attachment

Monsanto Industrial Chemicals Co.
Applied Sciences
St. Louis, Mo.

12/75 - L. M. Chapman, C. E. Hoffmann, M. W. Dietrich

JHC AR

TABLE

Insert #	Flow Rate	Sampling Time	Benzene Concentration in Air
75-41	23.6 ml/min	4 hrs.	2.5 ppm
75-54	24 ml/min	6 hr 20 min	0.7 ppm
75-35	23.6 ml/min	7 hr 52 min	0.3 ppm
75-45	24 ml/min	3 hr 41 min	2.2 ppm

PREPARATION AND CONDITIONING OF COLLECTION COLUMNS

INTRODUCTION

This report will explain the procedure for preparing and conditioning collection columns used for analyses of organic chemicals in air. Two types of columns are used most frequently: Tenax GC, used mainly for higher boiling materials and Porapak N, used mainly for low boiling compounds. The preparation of columns with these packings is the same but conditioning processes, described below, are quite different.

PREPARING COLLECTION COLUMNS

Materials needed:

1/4" O.D. X 1/8" I.D. X 6" Pyrex glass tubing with dimple 1 1/2" from one end
Silanated glass wool
Tenax-GC 60/80 mesh column packing or
Porapak Type N 50/80 mesh
Supeltex M-2 1/4" vesbel ferro #02-2320
Glass marking pen
Conditioning oven (a GC oven or a column conditioning oven may be used)

Procedure:

1. Being sure the glass tubing is clean, take a pinch of glass wool, push it to the dimple, and snuggly pack it down.

2. Fill the tube with 0.18 grams of packing, if Tenax-GC is used, or 0.31 grams of packing, if Porapak N is used. If the packing for one column is weighed, the rest may be measured by the first.

3. Tap one end of the column on the table so that the packing is firmly packed. This will reduce the chance of having gaps after conditioning.

4. Place another piece of glass wool on top of the packing and mark the tube with an identifying number. It is now ready for conditioning. Attached is a diagram of a collection column.

TENAX-GC COLUMN CONDITIONING PROCEDURE

1. Purge each tube with nitrogen for five minutes and put in a covered container also purged with nitrogen. Place the container in a 275°C oven for 24 hours.

2. After the columns have been removed and cooled, condition them overnight in a 250°C GC oven with helium or nitrogen carrier flow of about 30 mls/min, when connecting the column, gas flow should be through the column toward the end with the dimple. Several columns can be attached in series depending on the capacity of the GC. We recommend vesbel ferros for metal to glass connections because they withstand decomposition at high temperatures and are reusable.

Supelco

TENAX GC COLUMN CONDITIONING PROCEDURE (Cont'd)

3. Remove and cool. The columns are now ready for use. Before a sampling, the columns should be reconditioned at 275°C for 15 to 20 minutes with carrier flow of about 30 ml/min.

PORAPAK N COLUMN CONDITIONING PROCEDURE

1. Attach the column to the GC oven and set a carrier flow of about 30 ml/min. When connecting the column, gas flow should be through the column toward the end with the dimple. Several columns can be attached in series depending on the capacity of the GC available.

2. Slowly program the oven temperature to 180°C and hold overnight or to 190°C and hold for 2 hours.

3. Remove and cool. The columns are now prepared and conditioned for use. Before a sampling, the columns should be reconditioned at 190°C for 15 to 20 minutes with carrier flow of about 30 ml/min.

ss
Attachment

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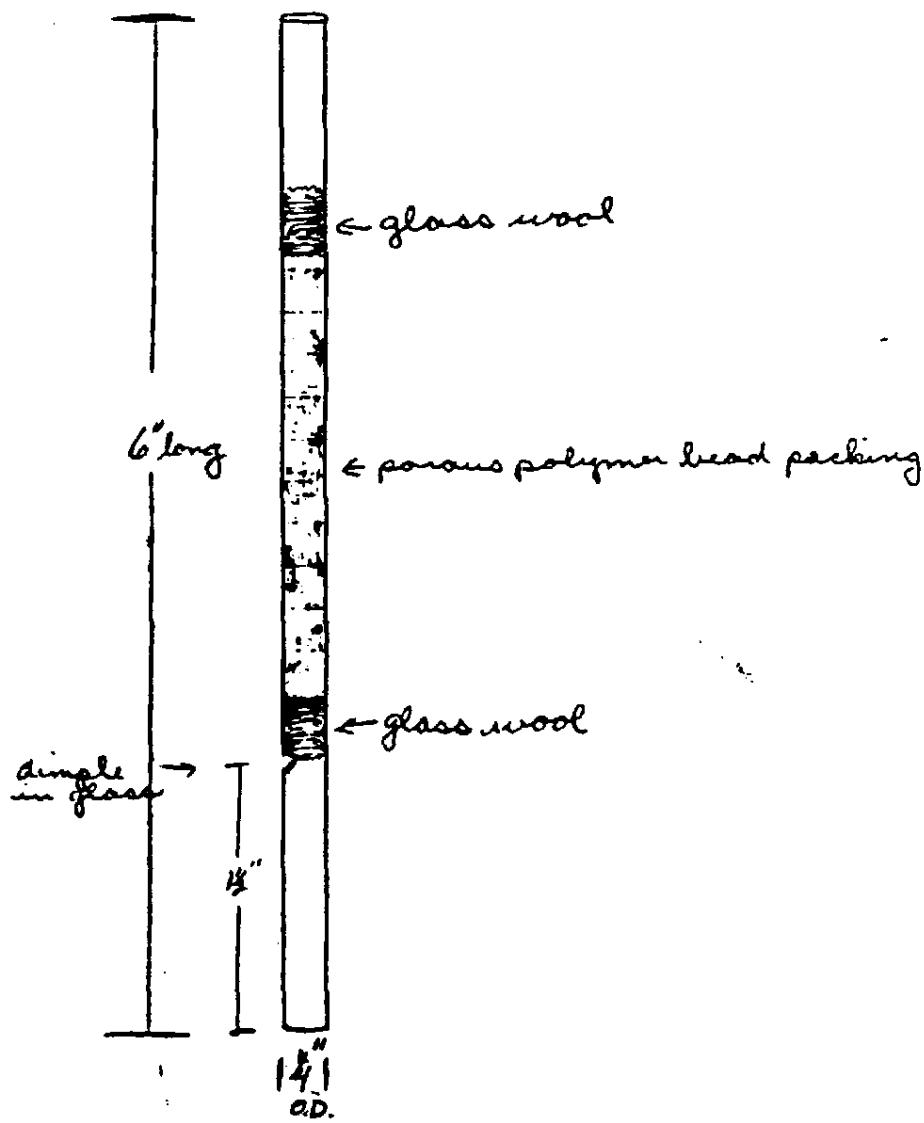
5-75-55-50

Collection Column



GC MODIFICATION FOR MEASUREMENTS OF ORGANIC CHEMICALS IN AIR BY THERMAL DESORPTION

INTRODUCTION

Determination of organic chemicals in air, using the procedure described in Spectroscopy Method 76-1, requires some modifications of a laboratory gas chromatograph. A means must be provided to heat the collection column external to the GC. The heater we use is described in this report. It is also necessary to divert the carrier gas flow to an external line. Finally, the injection port septum nut must be modified so that the collection column can be attached to the GC. These modifications are described in this report for a HP-5710 gas chromatograph. Most other laboratory gas chromatographs can be modified in the same manner.

DETAILS

A. Construction of External Heater

Below is a description of how to prepare a heater for desorbtion of collection columns.

Heater for 1/4" Glass 6" Vapor Sampling Tubes

Materials:

Approximately 8 ft. 24-gauge B&S Chromel "A" yellow asbestos covered Fisher Catalog #15-539C for 100 foot spool
6" length 1/4" S.S. tube
5" X 13/16" paper .003 to .004"
Pyrex tube 10.1 mm i.d. X 4 3/4", notched both ends for wire
5" of narrow (2 mm) glass braid
2 ft. #30 B&S Chromel "A" base Hoskins Resistance wire
1 5/8" X 4 11/16" of .0025" annealed Al foil
8" X 8" - 1/4" polyurethane pad

Straighten yellow heater wire to remove kinks - large bends are O.K. Place 1/4" S.S. tube lengthwise along edge of Al foil on foam pad; press down hard and roll. Al will roll up on tube to form a loose-fitting tube. Dampen paper; make one wrap around S.S. tube lengthwise as with foil; dry. Slip S.S. tube and paper shim into the Al tube. Place on smooth, hard surface; press hard and roll in direction of original roll-up. This will make foil into a snug fit of two turns. Tape one end of heater wire onto the assembly and tightly wind on, keeping it close spaced. Slip assembly into glass tube. Cut braid in half and thread onto end of heater wire to form one final turn in end of glass jacket; bend through notch and enough to wrap on with the #30 wire. Take a few turns of wire around braid; wind remainder around jacket snugly and secure. Check resistance (aim for 12.8 to 12.9) before securing second end. Estimate 86 turns with ~7.5 ft. wire overall for 4 3/4". Finally, flare ends of Al sleeve to keep it from sliding out.

With He flow at ~30 ml/min., empty sampling tube and thermocouple in place situated at median area for the Tenax, a temperature of ~200°C is achieved in 2 1/2 min. and held with Variac set at ~20 V. This calibration should be checked with each Variac used

JAB:cHT

B. GC Modification for External Carrier Gas Flow

Most gas chromatographs have a carrier gas fitting which is connected to the injection port through a flow controller valve and a molecular sieve trap. A three port valve can be placed in the carrier gas line between the molecular sieve trap and the injection port and mounted on the top or the side of the chromatograph (see diagram attached). With a valve of this type installed, the carrier gas can easily be switched to the external helium line for chromatographic purposes. We typically connect this external carrier gas line to one end of an air sampling tube. The other end of the tube is connected to the injection port of the chromatograph at the septum nut. Using the three port valve the carrier gas can be switched to the external line and used to flush organics from the heated sampling tube onto the head of the analytical GC column. In this position the three port valve closes the normal carrier gas line to the injection port. This keeps sample and carrier gas from leaving the injection port through the normal carrier gas line.

We have found that a Whitey valve SS-42XF2 works well for this modification. This valve has an intermediate position at which the input port is connected to neither exit port. This position can be used as a convenient shut-off for the carrier gas.

The diagram is a schematic of how the collection column is attached to the GC. What is not shown is the heater, but the collection column actually fits down into the heater and is attached to the injection port and the external helium flow with 1/4" Swagelok fittings.

C. Modification of Septum Nut

A Swagelok SS-400-R-2 fitting is silver soldered to the septum nut as shown in the second figure. The hole in the septum nut must be enlarged to receive the fitting. A septum is still required to prevent leakage.

*ss
Attachments(2)

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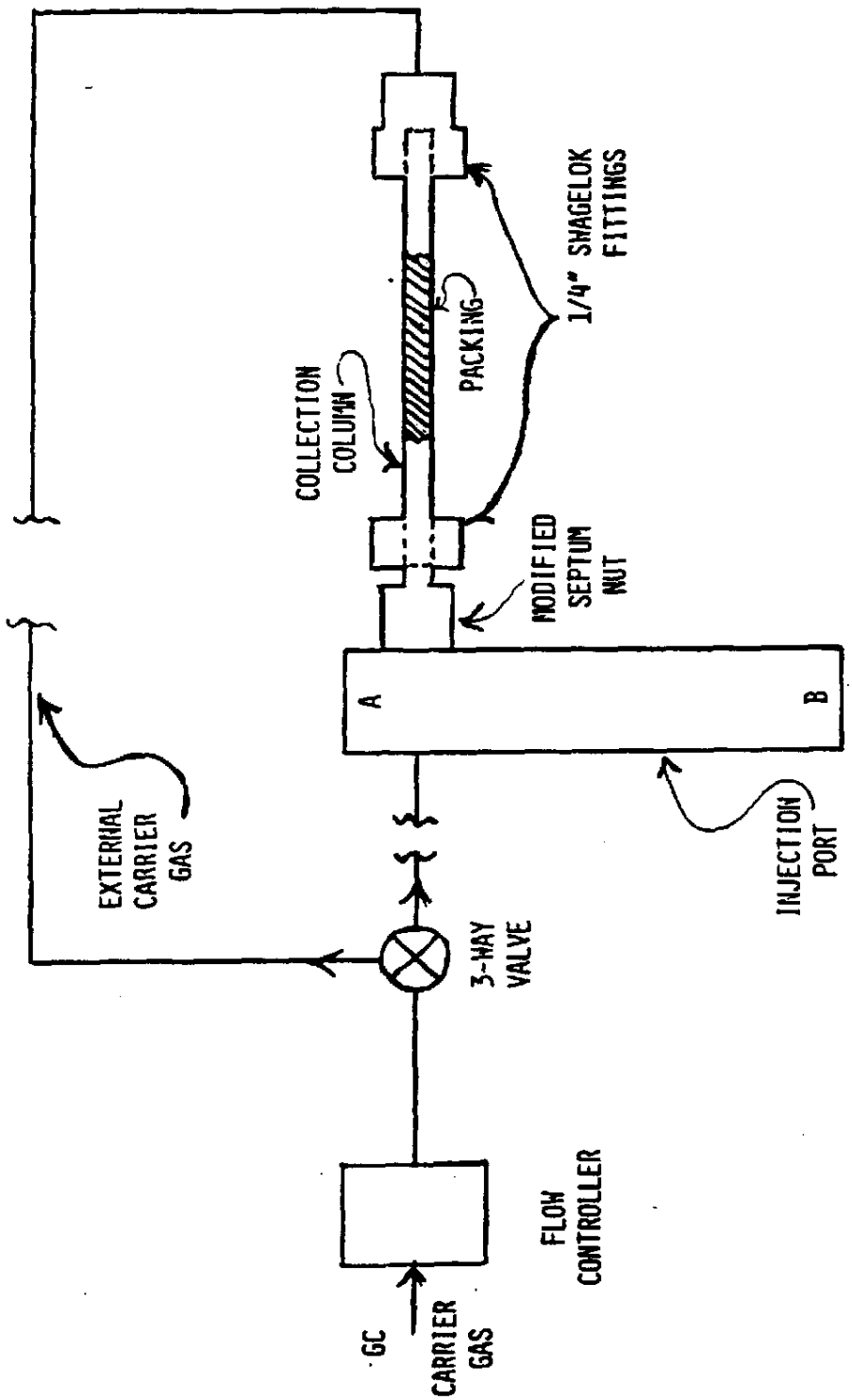
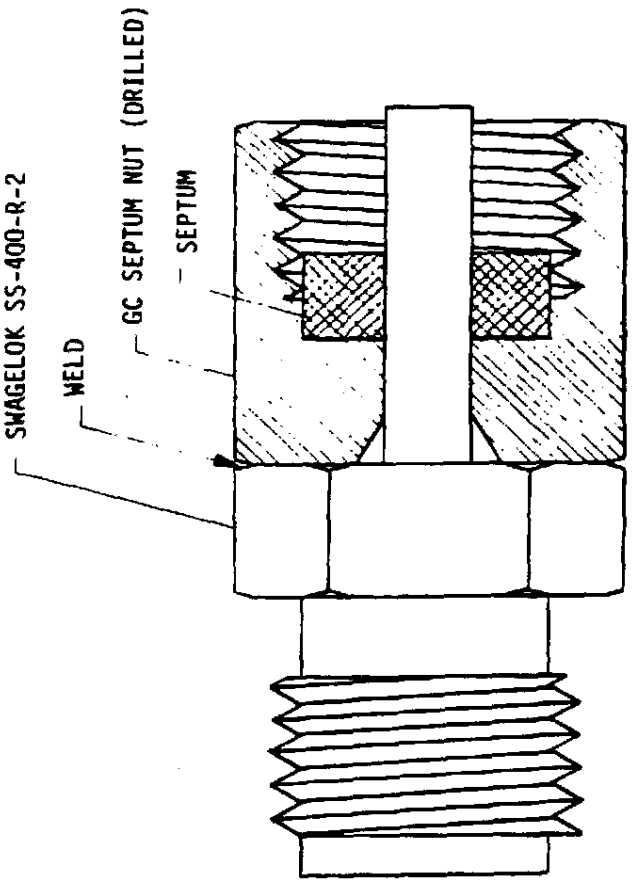

1/4" SWAGELOK FITTINGS
PACKING
COLLECTION COLUMN
MODIFIED SEPTUM NUT
A
B
EXTERNAL CARRIER GAS
INJECTION PORT
3-WAY VALVE
FLOW CONTROLLER
GC
CARRIER GAS


SWAGELOK SS-400-R-2
WELD
GC SEPTUM NUT (DRILLED)
SEPTUM

Spectroscopy
S-75-SS-52

DECEMBER 1975 MERCURY INVENTORY, W. G. KRUMMRICH PLANT, CHLOR-ALKALI DEPARTMENT

INTRODUCTION & SUMMARY

The mercury inventory made at the W. G. Krummrich plant on December 2, 1975 has been completed. The sum of the average weights for the 22 cells is 255,294 pounds, ± 2919.9 (2 sigma limits). This inventory is comparable to that taken in June 1975. Inventory by individual cells is tabulated in Table I attached.

A specific activity of 1.96×10^{-4} microcuries per gram was produced on the spiking date December 2, 1975.

The cell house was mixed for 60 hours except for cells 2, 10 and 19 which were mixed 36, 10 and 20 hours, respectively. Mixing was followed on 7 cells namely 1, 2, 5, 7, 10 and 21. This mixing study indicated complete mixing after 12 hours. On this basis, it was concluded that the three cells mixed less than 60 hours represent an accurate inventory.

ss
Attachments(10)

Reference: Research Notebook MIC 264383-264398

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MERCURY INVENTORY MERCURY INVENTORY AGK DECEMBER 1975

CELL NO.	AVERAGE MERCURY INVENTORY (LBS)	STANDARD DEVIATION (LBS)	TWO SIGMA (LBS)	TWO SIGMA - PERCENT OF TOTAL
1	11916.68	42.13	84.26	0.707
2	10826.75	71.97	143.94	1.329
3	10952.58	72.03	144.06	1.315
4	12201.25	53.55	107.09	0.878
5	10980.16	48.18	95.35	0.868
6	10150.59	50.43	100.86	0.991
7	11620.21	56.04	112.08	0.964
8	10726.66	77.95	155.69	1.452
9	11960.76	67.12	134.25	1.122
10	11656.34	62.92	125.85	1.080
11	11464.16	88.22	176.44	1.539
12	11298.82	45.25	90.51	0.801
13	12695.38	64.00	128.00	1.008
14	12146.14	43.72	87.44	0.720
15	13204.14	64.80	129.60	0.969
16	10671.91	84.76	169.53	1.589
17	12695.06	80.95	161.91	1.275
18	10419.09	37.07	74.13	0.712
19	11387.38	65.06	130.12	1.143
20	10891.55	82.26	164.52	1.512
21	13340.72	142.63	285.26	2.139
22	11963.93	60.72	121.43	1.015

THE SUM OF THE AVERAGE WEIGHTS IS 255294.88 LBS.

THE SUM OF ALL TWO-SIGMA IS 2921.91 LBS.

THE PERCENT THE SUM OF ALL TWO-SIGMAS IS OF THE TOTAL INVENTORY WEIGHT = 1.145 PERCENT

S-75-55-52

RSV 0010763

Spectroscopy
S-75-SS-53

DETERMINATION OF BENZYL CHLORIDE AND TOLUENE IN AIR AT THE DELAWARE RIVER PLANT

INTRODUCTION

The purpose of this study was to determine worker exposure to benzyl chloride and toluene.

SUMMARY

The results are attached. Levels of benzyl chloride ranged from 0.3 to 4.7 ppm. Toluene was detected in levels from 1.4 to 16.1 ppm.

EXPERIMENTAL

An OV 17 column was used for the analysis and Tenax tubes for sample collection.

Calculations are based on benzyl chloride standard. Identification is based on GC retention times. Ortho, meta and para chloro toluene are resolved from benzyl chloride on this column.

Calculations

$$\text{Volume of Air Sampled (Liters)} = \text{Pump Flow Rate (ml/min.)} \times \text{Sampling Time} \times 10^{-3}$$

$$\text{Weight Sample (µg)} = \text{Area Sample Peak (counts)} \quad \frac{\text{Conc. Std. (µg/µL)} \times \text{Vol. Injected (µL)}}{\text{Area of Standard (counts)}}$$

$$\text{Concentration Sample (µg/L)} = \text{Weight Sample (µg/L)/Volume of Air Sampled (Liters)}$$

$$\text{Concentration Sample (ppm)} = \text{µg/L (sample)} \times \frac{24.45}{\text{M.W. (sample)}}$$

For Sampling 75-41 Benzyl Chloride

$$\text{Volume of Air Sampled (Liters)} = 36.2 \times 7 \times 10^{-3} = .253$$

$$\text{Weight Sample (µg)} = 1304 \times \frac{0.147 \times 1.9}{1033} = 0.35$$

$$\text{Concentration (µg/L)} = \frac{0.35}{0.253} = 1.39$$

$$\text{Concentration (ppm)} = 1.39 \times \frac{24.45}{126} = 0.3 \text{ ppm}$$

ss
Attachment
Reference: GC File #75-213

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TABLE

	Toluene (ppm)	Benzyl Chloride (ppm)
+ #75-46 Sampling BzCl Refining Columns Toluene Dryer	7.0	0.8
* #75-57 Changing Filter Screen on Refining Column Feed	3.7	4.7
+ #75-41 Benzyl Chloride to Storage	16.1	0.3
+ #75-37 Benzyl Chloride Operator Rocky	1.4	0.3
* #75-61 Operator while Taking Benzyl Chloride Samples	2.0	1.2

* Sampling time ≈ 7-12 min
  Flow rate = 216 ml/min

+ Sampling time ≈ 4-8 min
  Flow rate = 36.2 ml/min

DETERMINATION OF ACETAMIDE (AC), N-METHYL ACETAMIDE (MMAC) AND DIMETHYLACETAMIDE (DMAC) IN URINE

INTRODUCTION

Samples were analyzed to determine levels of acetamide in the urine of workers at the Decatur, Alabama Plant. Control samples of non-exposed subjects were also analyzed for AC, MMAC and DMAC.

SUMMARY

The results are attached. Acetamide in the first set was detected at about 10 ppm (see Table I). A portion of the material detected was found to come from the resin used in the extraction before analysis. A blank should be run with each batch of samples to correct for this interference. Identification of acetamide was by GC/MS.

The second table shows GC analyses results for acetamide, MMAC and DMAC.

EXPERIMENTAL

Refer to Standard Test Method STM-00498, Textiles Division for procedure. Identification by GC/MS was made by scanning the selected ions of acetamide 41, 59, 44 and 40. Comparison of GC retention time was also used in identification.

References: GC/MS File #75-198
Standard Test Method STM-00498, Textiles Division, January 21, 1975

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Attachments (2)

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TABLE (Set I)

Sample	Acetamide (ppm)
James Aldrich	8.9
Kenneth R. Lambert	11.2
#25 (control)	11.3
#26 (control)	2.7
blank	1.2

TABLE (Set 2)

Sample Number	CONCENTRATION IN PPM DMAC	MMAC	AC	Other Compounds
1	ND	ND	11	
2	ND	ND	15	
3	?	?	4	
4	ND	ND	3	
5	ND	ND	13	
6	ND	ND	20	
7	ND	ND	15	
8	ND	ND	15	ca 5
9	ND	ND	11	
10	ND	5?	25	
11	ND	ND	13	
12	ND	5?	3	
13	ND	ND	7	
14	ND	ND	15	
15	?	5?	15	
16	ND	ND	ND	
17	ND	ND	13	
18	ND	ND	7	15
19	>500?	ND	ND	
20	ND	ND	7	
21	ND	20?	13	
22	ND	ND	5	
23	ND	ND	ND	
24	ND	ND	11	
25	ND	5?	ND	
26	ND	ND	ND	

DMAC ND $\leq$ 5

MMAC ND $\leq$ 3

AC ND $\leq$ 3

Accuracy 0-20 ppm $\pm$ 2 ppm

500 ppm $\pm$ 100 ppm

CHLORINATED DIBENZOFURANS IN CRUDE MONOCHLOROBENZENE FROM THE OXYCHLORINATION PROCESS

SUMMARY

After Process Chemicals research (Dennis Kalota) confirmed the presence of octachlorodibenzofuran on the oxychlorination catalyst, other chlorinated isomers of dibenzofuran were suspected of being produced in the process. GC/MS analysis of crude monochlorobenzene (MCB) and pot residues showed the presence of chlorinated dibenzofurans (dichlorodibenzofuran through octachlorodibenzofuran) at levels in the range of one ppm for the crude MCB and several hundred ppm for the pot residue.

DISCUSSION

The selected ion monitoring (SIM) mode of operation provided the data used to measure the various chlorinated dibenzofurans. The SIM technique and possible interferences are described in detail at the end of this report. Table I shows the results for a pot residue and a crude MCB from laboratory oxychlorination. All isomers with the same number of chlorines are summed to give one value in the table. Diphenyl ethers with two more chlorines than the corresponding dibenzofuran are also included in these values since they have fragment ions which interfere with the dibenzofuran measurements.

A sample of Hooker Crude MCB was analyzed for tetrachloro through octachlorodibenzofuran; the results are shown in Table II.

The initial analyses (Table I) had to be performed on a crude MCB and a pot residue from different laboratory oxychlorinations. Another oxychlorination provided material from each step which was analyzed for two chlorinated dibenzofurans. The refined MCB (1008348) and the recovered benzene (1008348) contained no tetrachlorodibenzofuran with a detection limit of 0.2 ppm and no octachlorodibenzofuran with a detection limit of 0.6 ppm. The base scrubbed crude and the unscrubbed crude contained the same level of octachloro- and tetrachlorodibenzofuran. These data along with the corresponding pot residue are shown in Table III.

Crude MCB from oxychlorination was also analyzed for chlorodioxins using the SIM technique. No dioxins were found and the detection limits are given in Table IV.

EXPERIMENTAL

In the selected ion monitoring (SIM) mode of operation, the mass spectrometer is set to continuously monitor one or several ions characteristic of the compound being measured. SIM is one hundred to one thousand times more sensitive than the standard scanning mode of GC/MS analysis. For this study, electron impact ionization was used to form ions in the mass spectrometer since dibenzofurans and dibenzodioxins give good parent ions and their electron impact fragmentation is documented. The GC conditions used for the analysis are given below.

Column: 1M, 3% OV 1, 3 mm I.D.

Carrier Gas: He, 30 ml/min

Temperature: 110 to 270°C @16°/min

EXPERIMENTAL (Cont'd)

The SIM measurements for chlorinated dibenzofurans and chlorinated dioxins were made by monitoring the parent ion for each compound and matching retention times with known standards. Confirming ions, parent ion less 63 amu, were monitored for tri-, tetra- and octachlorodibenzofuran. The full spectrum of octachlorodibenzofuran was obtained by a solids probe analysis of the material isolated from the oxychlorination catalyst using the Hewlett-Packard 5982 GC/MS system.

Quantitation for both dibenzofurans and dibenzodioxins was done by comparing the response of standards with the response of the corresponding compound in the MCB sample. Because of the low levels being measured the values in the table could vary by ± 20% of the value.

The detection limits for the chlorinated dibenzodioxins vary because the sensitivity of the mass spectrometer changes as the number of chlorine atoms on the molecule changes. The detection limits for tetra-, hexa-, hepta- and octachlorodibenzodioxins were determined by running standards. The detection limit for pentachlorodibenzodioxin was taken as the average of the detection limits of tetra- and hexachlorodibenzodioxin. The detection limits for mono-, di- and trichlorodibenzodioxin were assumed to be the same as that for tetrachlorodibenzodioxin. This is a good assumption for calculating limits of detection since the mass spectrometer sensitivity for the dibenzofurans and dibenzodioxins actually increases with a decrease in the number of chlorine atoms.

The SIM technique is subject to interferences from compounds having ions at the same mass value as those used to detect the target compounds, e.g. dibenzofurans. Normally, these interfering compounds do not have the same GC retention time as the target compounds and can be distinguished on this basis. The loss of specificity is the price paid for the large increase in sensitivity which makes the SIM technique so useful. The chlorinated dibenzofurans are subject to an unusually severe interference from chlorinated diphenyl ethers. The mass spectrum of chlorinated diphenyl ethers all have a very strong fragment ion corresponding to the loss of Cl_2 from the original molecule. This means that the mass spectrum of decachlorodiphenyl ether has a strong ion at 510 (molecular wt.) less 70, or 440. This is exactly the molecular weight of octachlorodibenzofuran and the 440 ion from the ether also has the same chlorine isotope pattern as octachlorodibenzofuran.

Other fragment ions from decachlorodiphenyl ether interfere with possible confirming ions for octachlorodibenzofuran. This type of interference by diphenyl ethers with two more chlorines than the corresponding dibenzofuran holds true for all of the various chlorinated dibenzofurans. The GC retention times of the chlorinated dibenzofurans and the corresponding interfering ethers are close. The analysis of the ethers and dibenzofurans as separate entities at low levels would be very difficult. The business group has agreed that the measurement of the sum of these two types of compounds will be a useful tool for current process studies.

There are definitely chlorinated dibenzofurans in crude MCB which are not obscured by corresponding ethers. Table V gives an estimate of diphenyl ether interference for one sample of pot residue assuming the same sensitivity for both types of compound.

EXPERIMENTAL (Cont'd)

Table VI is a survey of likely interferences for tetrachlorodibenzofuran. Only the major probable interfering ions are listed for each compound. Some of the compounds do not interfere, some interfere with a few ions of tetrachlorodibenzofuran, and hexachlorodiphenyl ether interferes severely. This table illustrates the type of background information which is needed to do careful SIM analysis.

ss
Attachments (6)

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TABLE I

DIBENZOFURANS AND DIPHENYL ETHERS IN PPM*

	Pot Residue 1008339-4	Crude 1008339-8
Octachlorodibenzofuran (and decachlorodiphenyl ether)	440	1.2
Heptachlorodibenzofuran (and nonachlorodiphenyl ether)	230	0.9
Hexachlorodibenzofuran (and octachlorodiphenyl ether)	590	1.1
Pentachlorodibenzofuran (and heptachlorodiphenyl ether)	6.5	0.5
Tetrachlorodibenzofuran (and hexachlorodiphenyl ether)	460	0.4
Trichlorodibenzofuran (and pentachlorodiphenyl ether)	200	0.2
Dechlorodibenzofuran (and tetrachlorodiphenyl ether)	31	0.05
Monochlorodibenzofuran (and trichlorodiphenyl ether)	< 10	< .2

* SIM GC/MS analyses cannot accurately distinguish between these classes of compounds. Both are probably present in most samples (see Table V).

TABLE II

DIBENZOFURANS AND DIPHENYL ETHERS IN PPM
HOOKER CRUDE MCB MIC 1008339-9

Octachlorodibenzofuran (and decachlorodiphenyl ether)	13
Heptachlorodibenzofuran (and nonachlorodiphenyl ether)	9.4
Hexachlorodibenzofuran (and octachlorodiphenyl ether)	6.4
Pentachlorodibenzofuran (and heptachlorodiphenyl ether)	4.2
Tetrachlorodibenzofuran (and hexachlorodiphenyl ether)	1.6

TABLE III

DIBENZOFURANS AND DIPHENYL ETHERS IN PPM

	Crude MCB 1008348-1,2,3	Pot Residue 1008348
Octachlorodibenzofuran (and decachlorodiphenyl ehter)	1.7	110
Tetrachlorodibenzofuran (and hexachlorodiphenyl ether)	.20	17

TABLE IV

DETECTION LIMITS IN PPM
CRUDE MCB 1008339-8

Monochlorodibenzodioxin	ND < 0.1
Dichlorodibenzodioxin	ND < 0.1
Trichlorodibenzodioxin	ND < 0.1
Tetrachlorodibenzodioxin	ND < 0.1
Pentachlorodibenzodioxin	ND < 0.2
Hexachlorodibenzodioxin	ND < 0.3
Heptachlorodibenzodioxin	ND < 0.4
Octachlorodibenzodioxin	ND < 0.4

TABLE V

ESTIMATED DIPHENYL ETHER INTERFERENCE
FOR POT RESIDUE 294141

Dibenzofuran	Concentration	Percent contribution from diphenyl ether
Octachlorodibenzofuran	25 ppm	5-10%
Heptachlorodibenzofuran	23 ppm	10-30%
Pentachlorodibenzofuran	11 ppm	50-80%
Tetrachlorodibenzofuran	39 ppm	50-80%
Dichlorodibenzofuran	0.6 ppm	5-10%

TABLE VI

SURVEY OF POSSIBLE INTERFERENCES DURING SIM ANALYSIS OF TETRACHLORODIBENZOFURAN

Tetrachloro DBF	Pentachloro Naphthalene	Hexachloro Benzene	Pentachloro Phenol	Tetrachloro Biphenyl	Tetrachloro Diphenyl Ether	Hexachloro Diphenyl Ether	Tetrachloromethyl Diphenyl Ether	Tetrachloromethyl Biphenyl	Tetrachloro Dibenzodioxin	Tetrachloro Diphenyl Ethanes
	↑down		↑down	↑down				234 (100)		
	236		237	226				236 (65)		
241 (100)				-Cl		241 (100)		238 (10)		
243 (97)					243 (100)	243 (97)				
245 (31)	-Cl		-Cl		245 (97)	245 (31)				
		247		255	247 (31)					
		↓up		↓up				256 (100)	257 (100)	
	263	-Cl	264 (62)			-COCl		258 (97)	259 (97)	
-COCl	↓up	282 (51)	266 (100)	-Cl	-COCl			260 (31)	261 (31)	
	-Cl	284 (100)	268 (65)	290 (77)				-Cl		
		286 (81)	270 (31)	292 (100)			-2Cl	289 (77)		
		288 (35)	272 (3)	294 (49)				291 (100)		
	298 (62)	290 (8)		296 (10)				293 (49)		
	300 (100)							295 (10)		
	302 (65)							-CN	-COCl	
304 (77)	304 (31)					304 (77)		304 (77)		
306 (100)	306 (3)				306 (77)	306 (100)		306 (100)		
308 (45)					308 (100)	308 (49)		308 (49)		
310 (10)					310 (45)	310 (10)		310 (10)		
					312 (10)					
							320 (77)		320 (77)	
						-2Cl	322 (100)		322 (100)	
							324 (49)		324 (49)	
							326 (10)		326 (10)	
						374 (51)				
						376 (100)				
						378 (81)				
						380 (35)				
						382 (8)				

THE PREPARATION AND CHARACTERIZATION OF CARBON-14 LABELED TETRADECANOL ETHOXYLATES

BACKGROUND/SCOPE

In recent years, the increased emphasis placed on determining the environmental impact of our products has led to sophisticated investigations of their biological fate. The use of radio-tagged materials has gained wide acceptance as a means of following their biodegradation and biomagnification in organic systems. Carbon-14 labeled sodium alkylbenzene sulfonates (LAS) have been prepared and their biomagnification studied in aquatic organisms. To place the results of the above study in the proper perspective, the decision was made to prepare carbon-14 labeled nonionic surfactants and to evaluate their, as well as other tagged surfactants', biological fates.

This report covers the preparation and characterization of carbon-14 labeled nonionics (tetradecanol ethoxylates) incorporating the following objectives:

1. Adapt existing standard bench ethoxylation procedures and equipment to guarantee personnel safety and commercial quality.

2. Prepare 25 gram quantities of the following ethoxylates:

   a. 1-tetradecanol-^{14}C + 7EO; 400 µci/gm.

   b. 1-tetradecanol + 7EO - ^{14}C; 340 µci/gm.

   c. 1-tetradecanol + 14EO - ^{14}C; 60 µci/gm.

3. Prepare 400 grams and 100 grams of cold 7 mole and 14 mole ethoxylated 1-tetradecanol to serve as diluent for labeled products.

SUMMARY AND CONCLUSIONS

A. Existing small-scale ethoxylation procedures and equipment were modified and refined until a high degree of confidence was achieved in providing for personnel safety and high product quality. A final practice ethoxylation was successfully performed in T-305 under actual conditions planned for the tagged syntheses.

B. The labeled syntheses carried out to prepare 1-tetradecanol-^{14}C + 7EO and 1-tetradecanol + 14EO - ^{14}C achieved targeted quality and specific activity. However, a significant labeled ethylene oxide loss (3 grams, 20%) which occured during the preparation of the 1-tetradecanol + 7EO - ^{14}C ethoxylate resulted in a product containing less than desired ethylene oxide content (actual = 5.6 EO) and specific activity (290 µci/gm. vs 340 µci/gm). This material has been judged acceptable and a second synthesis was not necessary. Diluent ethoxylates were prepared as targeted.

C. Radiochemical safety objectives were satisfactorily met. The labeled ethylene oxide leakage did not contaminate either attendant personnel or facilities, but escaped to the atmosphere via the synthesis hood.

SUMMARY AND CONCLUSIONS (Cont'd)

D. A new technique for determining the ethylene oxide adduct distribution of single homolog alcohol based ethoxylates by high pressure liquid chromatography was developed jointly by the MIC Physical Sciences Group and the authors. This method was useful in confirming product quality of both labeled and diluent ethoxylates and is currently being refined for use in tracing intact or partially degraded ethoxylates in biological systems.

E. Aliquots of the labeled and cold ethoxylates were delivered to R. D. Swisher. Unused portions of the labeled ethoxylates are stored in T-305 for future applications.

Reference (Complete Report):

1. Special Report "The Preparation and Characterization of Carbon-14 Labeled Tetradecanol Ethoxylates" by J. B. Hillard and D. B. Hines, Job. No. 74041-10, Report No. 8347.

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Monsanto Industrial Chemicals Co.
Applied Sciences
St. Louis, Mo.

12/75 - J. B. Hillard, D. B. Hines, W. J. Litschgi, M. W. Dietrich

ORGANIC CONTAMINANTS IN TRENTON PHOSPHATE PRODUCTS

INTRODUCTION

The Trenton phosphate plant experienced a problem of contaminants in food grade pohsphates that appeared to be related to the soda ash obtained from Wyandotte BASF. The problem was felt to be due to organic contamination since no quality problems were encountered with the high temperature polyphosphate and IMP products. A study was initiated to identify the organic contaminants so that either new test procedures or new specifications could be formulated to prevent future quality problems.

SUMMARY

The contamination problem was identified in the failure of some phosphate products to pass the food grade patch test. For this test the product is dissolved in water and the solution is filtered. When this test was carried out on "Bad" sodium acid pyrophosphate (SAPP) a dark oily stain was left on the filter pad.

During the period of contamination a balck scale was found in the east MSP hold tank. This contained significant amounts of organic material (~30%) composed mainly of long chain hydrocarbon oil with small amounts of carboxylic acids. This scale is probably not directly responsible for the failure of SAPP to pass the test; however, the scale does represent a likely collection point for any organics getting into the process. Wyandotte essentially agrees with the analyses of the black scale.

Analyses of organics removed from good and bad soda ash and from good and bad SAPP did not give a conclusive reason for the failure of SAPP to pass the test. Small amounts of hydrocarbon oil were found in the bad soda ash but not in the bad SAPP.

Hydrocarbon oil was not found in good soda ash or good SAPP.

Hydrocarbon oil entering the plant through the soda ash raw material and collecting in various parts of the process is the most likely cause of the patch test failure.

RESULTS

Infrared, proton nuclear magnetic resonance and gel permeation chromatography of the organic components isolated by either Soxhlet extractions or surface washings of "good" and "bad" SAPP (sodium acid pyrophosphate), "good" and "bad" soda ash from Wyandotte BASF and a black oily scale from the Trenton plant east MSP hold tank showed:

A. The black scale is a matrix of an acid phosphate coated with a mixture of a long chain hydrocarbon oil and polymeric carboxylic acids.

B. The chloroform surface washings of "good" and "bad" soda ash showed the "bad" ash contained a low level of a hydrocarbon oil. The "good" soda ash wash was a phthalate ester.

C. IR analysis of the chloroform surface washes of "good" and "bad" SAPP indicated both were phthalate esters.

RESULTS (Cont'd)

D. IR comparison of the IR spectra of "good" and "bad" soda ash showed a two-fold increase in the level of THF extractables for the "bad" ash. The THF extractables from the "bad" ash are approximately a 50/50 mixture of a hydroxy carboxylate ester and a phosphate ester. The phosphate ester was not detected in the "good" ash.

E. The THF extractables from "good" and "bad" SAPP showed a seven-fold increase in level of extractables and a difference in chemical identity. The "good" SAPP sample was identified by IR as a carboxylic acid. The "bad" SAPP extract contained the same type of impurities found in the "bad" ash.

F. NMR analysis of the THF extractables from "good" and "bad" soda ash and "good" and "bad" SAPP indicated that the organics isolated from the "good" and "bad" soda ash and the "Bad" SAPP may be principally THF decomposition products. There may be a synergistic effect of a metal impurity triggering the decomposition of the THF. Several possible mechanisms can be proposed for the decomposition of a THF peroxide or hydroperoxide to yield alcohols and carbonyl compounds.

G. IR analysis of the acetone washing of chloroform washed "bad" soda ash and "bad" SAPP showed that the "bad" ash contained a primary amide as its principal component. This amide is absent in the "bad" SAPP and in the acetone blank.

Optical microscopy of the filter patches obtained from "good" and "bad" soda ash and "good" and "bad" SAPP showed all the samples contained particulates. The "bad" ash and "bad" SAPP patches contained in addition an oil coating on the filter fibers.

These results are summarized in Tables I and II.

EXPERIMENTAL

A. Black Scale from East MSP Hold Tank

An 8.000-g sample of the oily black scale from the east MSP hold tank at the Trenton, Michigan phosphate plant was weighed into a cellulose thimble and successively extracted with 50 ml of increasing polarity solvents using a Soxhlet extraction apparatus. The extraction was continued with each solvent (hexane, chloroform, methanol and tetrahydrofuran) until no color was observed in the liquid in the extractor tube. The isolated fraction was quantitatively transferred to a 100-ml beaker and evaporated to about 5 ml on a hot plate under a stream of nitrogen. The reduced volume sample was filtered through a 0.2-μ cellulose filter and the filtrate and filter washings collected in a 3-dram tared vial. The remaining solvent was stripped under a stream of nitrogen on a hot plate. The isolated fractions were placed in a bell jar and pumped to 0.5 to 1 torr to remove any remaining solvent and then weighed.

EXPERIMENTAL (Cont'd)

B. Soda Ash and SAPP (Sodium Acid Pyrophate)

1. Forty to fifty g of "good" and "bad" samples were weighed into a 25 mm X 250 mm chromatography column plugges with glass wool and equipped with a Teflon stopcock. The samples were tightly packed using a mechanical vibrator. Fifty ml of chloroform on the column, the stopcock opened and the solvent allowed to percolate by gravity through the packed sample until the solvent just covered the top of the solids. The eluent from the column was collected in a 25-ml graduated cylinder. The column hold-up, about 30 ml, was determined by subtracting the volume of eluent collected from the 50 ml charged. The collected column eluent was quantitatively transferred from the graduated cylinder to a 250-ml beaker. One hundred ml of fresh chloroform added to the column and the eluent combined with the initial volume collected. When the level of solvent reached the top of the solids, a volume of inhibitor-free tetrahydrofuran (Burdick and Jackson Laboratories, Inc.) equal to the column hold-up was added to the column. This volume of solvent was allowed to flow through the packed solids until the liquid level reached the top of the solids. The eluent was combined with the other chloroform washes. By this means the chloroform was completed, eluted from the column and the packed sample had been washed with about five column volumes of chloroform. One hundred fifty ml of fresh tetrahydrofuran was allowed to percolate through the sample and collected in a clean 250-ml beaker.

   Both the chloroform and tetrahydrofuran eluents were filtered through a 0.2-μ filter to remove any sample fines that might have washed through the glass wool plug. The solvents were stripped to about a 5-ml volume under a stream of nitrogen on a hot plate. The concentrated solution was incrementally transferred to a tared 1-dram vial and evaporated to near dryness under a stream of nitrogen on a hot plate. The beakers were washed with several small volumes of presh solvent, the washings transferred to the tared vials and the solvent completely stripped under a nitrogen stream on a hot plate. The vials containing the solvent extracted fractions were placed in a drying oven at 110°C for about 10 minutes, placed in a bell jar and pumped at 0.5 to 1 torr, cooled in a desicator and weighed.

2. The same procedure was used on "bad" soda ash and "bad" SAPP substituting acetone for tetrahydrofuran.

3. Equipment and solvent blanks were carried using the same glassware used for the samples.

REFERENCES

IR spectra 75-368 to 75-385; NMR 16-1101

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Attachments(2)

Monsanto Industrial Chemicals Co.
Applied Sciences
St. Louis, Mo.

1/76 - B. Katlafsky, M. W. Dietrich, D. B. Hines, O. E. Kinast,
W. J. Litschgi, G. W. Mappes, C. Deatherage

TABLE I

BLACK SCALE FROM EAST MSP HOLD TANK

EXTRACTION SOLVENT	PERCENT EXTRACTED	IDENTIFICATION
Hexane	19.8	Long chain hydrocarbon oil Molecular weight 650 [IR, NMR, GPC (gel permeation chromatography)]
Chloroform (5.9) Methanol (2.4) THF (0.2)	8.5	Carboxylic acid plus alcohol or ether Molecular weight 400 to 2000 [IR, NMR, GPC]
Left after extraction (Includes H_2O)	71.7	(By difference)

TABLE II

ANALYSES OF SAPP AND WYANDOTTE SODA ASH

	GOOD SODA ASH 7-14 to 9-1	GOOD SAPP Lot 456	BLANK
Microscopy of plant filter pads	Particulates	Particulates	
$CHCl_3$ Extract	Phthalate Ester 15 ppm	Phthalate Ester 2 ppm	Phthalate Ester 2 ppm
THF Extract (after $CHCl_3$)	Hydroxy ester* 48 ppm	Carboxylic Acid 34 ppm	Ester 2 ppm
	BAD SODA ASH	**BAD SAPP 1740 W**	
Microscopy of plant filter pads	Particulates + oil coating on fibers	Particulates + oil coatings on fibers	
$CHCl_3$ Extract	Hydrocarbon oil < 2 ppm	Phthalate Ester 41 ppm	Phthalate Ester 2 ppm
THF Extract (after $CHCl_3$)	Hydroxy Ester + Polyphosphate Ester*,** 78 ppm	Ester + Polyphosphate Ester* 229 ppm	Ester 2 ppm
Acetone Extract (after $CHCl_3$)	4 ppm	4 ppm	5 ppm

All extracts are highly colored.

* Material found may be principally THF decomposition products.

** We cannot completely rule out inorganic phosphate and organic ester as separate components

NIOSH PRIORITY LIST FOR CRITERIA

FOR TOXIC SUBSTANCES AND HARMFUL PHYSICAL AGENTS, 1972

Criteria Developed:

- Carbon Monoxide
- Noise
- Heat Stress
- Beryllium
- Asbestos
- Coal Dust[1]

In Progress:

- Arsenic
- Benzene
- Cadmium and Compounds
- Chromic Acid Mist
- Cotton Dust
- Fibrous Glass
- Lead
- Mercury
- Parathion
- Silica
- Trichloroethylene
- Ultraviolet

Priorities:

- Bis(Chloromethyl)Ether
- Coal Tar Pitch Volatiles
1. 2-Naphthylamine
- Toluene Diisocyanate
- Radioactive Products of Uranium Mining (Gaseous and Particulate)

- Benzidine and Its Salts
- Carbon Tetrachloride

[1]According to NIOSH, this criterion was developed in conjunction with the Bureau of Mines, Department of the Interior, in implementing the Federal Coal Mine Health and Safety Act of 1969.

2. Ozone
   Sulfur Dioxide
   Tin and Compounds

   Chromium Compounds
   Dichlorobenzidine
3. Oxides of Nitrogen
   Sodium Hydroxide
   Sulfuric Acid

   Carbaryl
   Chloroform
4. 4-Dimethylaminoazobenzene
   Nitric Acid
   Toluene

   Ammonia
   beta-Propiolactone
5. Epoxy Resins
   Methylene Chloride
   4-Nitrodiphenyl

   Asphalt Fumes
   Ethylene Dichloride
6. Fluoride and Hydrogen Fluoride
   Ploychlorinated Biphenyls
   Tetrachloreethylene

   2-Acetylaminofluorene
   Chlorobenzene
7. Methylene Bisphenyl Isocyanate (MDI)
   Phosgene
   Trichloroethane

   Acetone
   4-Aminodiphenyl
8. Dieldrin
   Malathion
   N-Nitrosodimethylamine

   Aniline
   Copper and Compounds
9. Cyanides
   Styrene
   Zinc and Compounds

Chlorine
Formaldehyde
10. Manganese and Compounds
Phenol
Platinum and Compounds

Acrolein
Aluminum and Compounds
11. Carbon Disulfide
Methyl Ethyl Ketone
Vinyl Chloride

Creosote
Methyl Chloride
12. Nickel and Compounds
Phosphorus and Compounds
Tetrachloroethane

Acrylonitrile
2, 4-Dinitrophenol
13. Magnesium and Compounds
Methyl Alcohol
Paraffin

Ammonium Nitrate
Cold Stress
14. Dioxane
Fluorine
Microwaves

Hydrogen Chloride
Ethyl Benzene
15. Nitroglycerin
Vibration
Xylene

Methyl Butyl Ketone
Mineral Spirits
16. Oil Mists
Selenium and Compounds
Turpentine

APPENDIX I

Arsine
Gasoline
17. Kerosene
Iron and Compounds
Petroleum Naptha

Barotrauma
Cresol
18. Paraquat
Portland Cement
Talc

Carbon Black
Coherent Energy (Laser Radiation)
19. Ethylene Oxide
Impact Noise
Proteolytic Enzymes

Source: NIOSH.