2-100

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Organic Chemicals Division
St. Louis Research Department

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FINAL REPORT

ON

ANALYTICAL CHEMISTRY AND SPECTROSCOPY INVESTIGATIONS - 1962

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Part II - Special Studies

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TABLE OF CONTENTS

INTRODUCTION

Special investigations were carried out by the Analytical Chemistry And Spectroscopy Group during 1962 to support Organic Research Department and Manufacturing Department projects. The studies also included certain projects listed in the September 29, 1961 PA ("nclassified Anal. Chem. - 5a).

SUMMARY

Fifteen analytical studies covering Organic Division products were carried out to provide information needed for Research Department and Manufacturing Department projects. Chemical and instrumental techniques were used to:

- show Aroclor 1242 product variations
- characterize the structure of substituted benzimidazolines
- evaluate Biolite under use situations
- show the composition of dibutyl phenyl phosphate reaction products
- identify inhibitors in competitive functional fluids
- measure methyl lactate in process reaction mixtures
- show the crystal form and transition of pentachlorophenol
- identify contaminants in p-phenetidine
- measure reaction rates of resorcinol in sodium sulfite solution
- show the oxidation products formed from tricosane
- show the components in vanadium oxide catalyst mixtures
- evaluate an Infotronics CRS-1 integrator for NMR
- set up an analytical scheme for identification and measurement of plasticizers and other high boiling esters
- demonstrate the potential utility of Infrared Attentuated Total Reflectance as an instream monitoring device for sodium phenate and sodium benzenesulfonate
- demonstrate thin layer chromatography techniques.

SECTION A

AROCLOR 1242 PRODUCT VARIATION - INFRARED AND GAS CHROMATOGRAPHY STUDY

Introduction

Infrared absorption and GLPC (gas liquid partition chromatography) methods were used to study compositional variations between five lots of Aroclor 1242 representing typical production material shipped to General Electric from the Anniston plant over a six month period. The study was initiated to determine if abnormal variations were present and, if so, the cause of the difference. IR and GLPC are complementary techniques for such a study, since IR can detect gross isomeric distribution differences and GLPC can identify and measure the individual isomers.

Summary

An infrared and GLPC (gas-liquid partition chromatography) study of five normal production samples of Aroclor 1242 from Anniston showed that most of the variations in isomer content were small and random. However, one pronounced periodic variation was observed in the infrared spectra in the region of 14.3-14.4 microns which was shown by a combination of infrared and GLPC analysis to be the result of variations in the lower chlorination level isomers, namely the 2-chloro, 2,2'-dichloro and the 2,4'-dichlorobiphenyls.

Analytical Studies

Reserve samples of lots D-122, D-145 and D-185 were obtained from Anniston to represent normal production material. Since no sample of lot D-153,the subject of a recent General Electric complaint, was available,samples of lots D-152 and D-154 were substituted. Infrared spectra were run under conditions such that the gross infrared spectra could be compared rather than under special conditions to study a particular isomer. The GLPC analysis was carried out using a 150' x 0.020" stainless steel capillary column coated with silicone gum rubber and a flame ionization detector.

A critical comparison of the IR spectra showed primarily the minor random variations expected for small differences in isomer distribution. However, in the region of 14.3 to 14.4 microns, two weak absorption bands were observed whose intensities varied periodically with lot number. The attached IR spectrum shows the superimposition of the spectra of the five lots of Aroclor 1242 studied run under conditions to amplify the difference. Examination of the spectra in the region

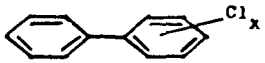
of 14.3-14.4 microns shows that the intensity of the absorption bands at these wavelengths increases sharply from lot D-122 to D-145. The absorption reaches a maximum in lot D-152, then tapers off in lots D-154 and D-185. The maximum variance observed between lots D-122 and D-152 was 30% in terms of optical absorption units.

The GLPC data for the five samples shows the random variations of isomers also detected by IR. No variations in a single component was observed that could explain the difference found in the IR spectra. The GLPC data is tabulated in Table I. Where possible, the GLPC fraction has been identified as a particular isomer on the basis of retention time.

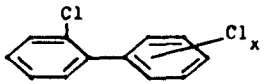
Despite the fact that the positive identification of the components involved in the observed periodic variation in the IR spectra could not be made, structural characteristics of the materials contributing to this variation could be assigned, based on infrared interpretation of aromatic absorption patterns.

The chlorine distribution patterns in Aroclor 1242 fit the following general classes:

Type I



Type II



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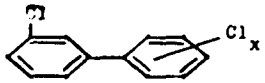

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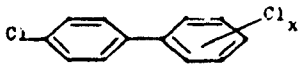


Of these four general classes of chlorine distribution patterns, only Types I and II (the monosubstituted aromatics and the ortho disubstituted aromatics) produce absorption bands in the 14.3-14.4 micron region. Although it is possible to detect and differentiate the Types I and II materials in other regions of the IR spectra, interferences and overlapping of bands prevents this in the bulk sample.

In order to resolve this problem and identify the components causing the observed variance in the IR spectra, lot D-152 was fractionally distilled by Mr. George Ashworth under reduced pressure and four top fractions, representing a total of 8.4% of the charge, were isolated for subsequent analysis. The GLPC analytical data which was confirmed by IR analysis shows that the mono and dichlorobiphenyls having the type I and II structures postulated by IR interpretation of the bulk sample were the major contributors to the variation observed in the IR spectra of the bulk sample. The GLPC data is tabulated in Table II.

A combination of IR and GLPC analysis has demonstrated that the periodic variation observed in Aroclor 1242 lots D-122, D-145, D-152, D-154 and D-185 are the cumulative effects of variations primarily of the 2-chloro, 2,2'-dichloro and the 2,4'-dichlorobiphenyls.

2/62 - R. E. Keller, B. Katlafsky, E. M. Emery

Table I

AROCLOR 1242

Fraction/Component	Lot D-122	Lot D-145	Lot D-152	Lot D-154	Lot D-185
1 Biphenyl	0.04	0.03	0.3	0.2	0.03
2 Ortho	0.8	1.0	1.9	1.8	0.9
3) Meta	0.2	0.3	0.6	0.5	0.2
4) Para					
5 2,2'	4.5	4.9	5.2	4.8	4.6
6 2.5	0.8	0.8	1.0	1.0	0.8
7 (2,4 or 2,3 or 2,3')	1.4	1.8	1.9	1.8	1.6
8 2,4'	9.1	9.6	10.3	9.6	9.5
9 (3,5 or 3,3')	0.7	0.8	0.6	0.7	0.7
10 (3,4 or 2,5,2')	10.2	10.0	9.4	9.5	10.1
11 4-4'	5.3	5.7	5.2	5.3	5.4
12	0.2	0.5	0.3	0.4	0.5
13 2,3,2'	4.8	5.8	5.1	5.2	5.7
14)	1.5	1.8	1.5	1.4	1.6
15)					
16) 2,5,4'	15.3	14.9	13.7	14.1	15.0
17)					
18 3,4,2'	6.7	6.6	6.0	6.1	6.6
19 2,3,4	3.0	3.0	2.7	2.7	3.0
20	0.7	0.7	0.6	0.7	0.7
21	0.2		0.2		0.2
22	3.6	3.4	3.4	3.9	3.5
23	2.7	2.4	2.4	2.6	2.6
24	1.9	1.5	1.7	1.8	1.8
25	3.5	3.3	3.3	3.4	3.3
26 3,4,4'	3.3	3.2	3.1	3.0	3.2
27	3.4	3.2	3.1	3.3	3.4
28	0.6	0.7	0.6	0.6	0.8
29	0.1	0.1	0.1	0.1	0.1
30	0.1	0.05	0.05	0.05	0.1
31)	5.1	4.6	4.9	5.1	4.9
32)					
33	3.9	3.5	3.7	4.0	3.8

Table I (cont'd)

Fraction/Component	Lot D-12[illegible]	Lot D-145	Lot D-152	Lot D-154	Lot D-185
34	0.2	0.1	0.2	0.2	0.2
35	2.7	2.4	2.6	2.6	2.6
36	0.3	0.3	0.3	0.3	0.3
37	0.5	0.5	0.7	0.7	0.5
38	0.2	0.2	0.5	0.3	0.2
39	0.03	0.05	0.1	0.05	0.02
40	0.2	0.2	0.3	0.2	0.2
41	0.4	0.3	0.5	0.4	0.3
42	0.2	0.2	0.3	0.2	0.1
43	0.8	0.8	1.1	0.9	0.7
44	0.1	0.2	0.1	0.2	0.1
48	0.6	0.4	0.3	0.5	0.4
52	0.3	0.4	0.3-	0.3	0.2

Table II

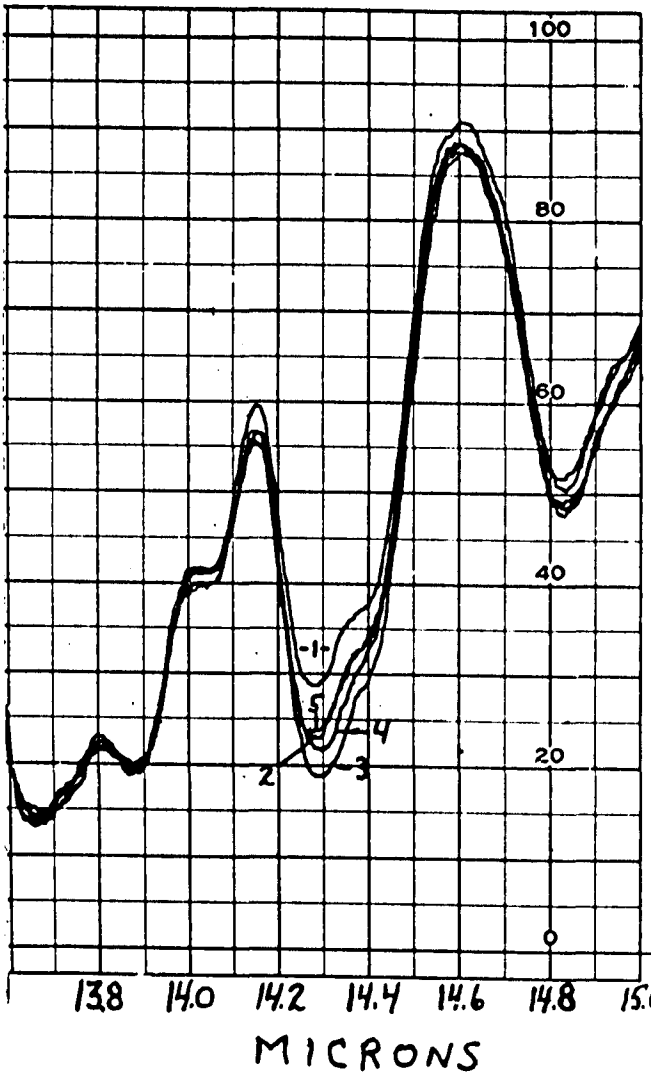
ARCOCLOR 1242 LOT D-152 TOPPING EXPERIMENT

Fraction/Component	Starting Mat'l	F#1 1.9%	F#2 1.7%	F#3 2.3%	F#4 2.5%	Residue 91.6%
1 Biphenyl	0.3%	8.6%	0.8%	trace	trace	0
2 ortho	1.9	29.7	26.0	7.1%	1.3%	0
3) meta	0.6	6.5	7.3	5.9	4.1	trace
4) para						
5 2,2'	5.2	36.8	43.0	41.3	36.0	0.2
6 2,5	1.0	2.8	3.4	5.6	6.6	0.2
7(2,4 or 2,3 or 2,3')	1.9	2.9	4.2	6.9	9.2	0.9
8 2,4'	10.3	11.5	14.1	27.4	35.0	5.7
9 (3,5 or 3,3')	0.6	0.3	0.3	1.1	1.5	0.5
10(3,4 or 2,5,2')	9.4	0.8	1.0	3.5	4.7	9.9
11 4,4'	5.2			0.8	1.2	6.6
12	0.3	0	0	0.1	0.1	0.5
13 2,3,2'	5.1	trace	trace	0.3	0.4	6.1
14)	1.5			0	0	2.1
15)						
16) 2,5,4'	13.7			trace	trace	17.6
17)						
18 3,4,2'	6.0					7.7
19 2,3,4	2.7					2.1
20	0.6					0.7
21)	3.6					4.5
22)						
23	2.4					3.1
24	1.7					2.0
25	3.3					4.1
26 3,4,4'	3.1					3.8
27	3.1					3.8
28	0.6					0.7
29	0.1					0.1
30	0.1					
31)	4.9					6.1
32)						
33	3.7					4.5

Table II (cont'd)

Fraction/Component	Starting Material	F#1	F#2	F#3	F#4	Residue
34	0.2					0.2
35	2.6					3.1
36	0.3					0.2
37	0.7					0.6
38	0.5					0.3
39	0.1					trace
40	0.3					0.3
41	0.5					0.4
42	0.3					0.2
43	1.1					1.0
44	0.1					0.1
48	0.3					0.5
52	0.3					*

* instrument shut down before this peak was eluted from the column.



SPECTRUM NO. _____

SAMPLE AROCLOR 1242

ORIGIN _____

PURITY PRODUCTION SAMPLES

PHASE LIQUID

THICKNESS 0.05 mm.

1 LOT D-122 | 4. LOT D-154

2 LOT D-145 | 5. LOT D-185

3 LOT D-152

DATE 1/15/62

OPERATOR BK

REMARKS 78% TRANS. SCREEN REFERENCE

PRISM NaCl

RESOLUTION 927

RESPONSE _____

GAIN 4.2

SPEED 32

SUPPRESSION 4

SCALE 10 cm./μ

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SECTION B

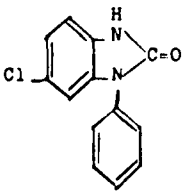
NMR STUDY OF SUBSTITUTED BENZIMIDAZOLINONES

Introduction

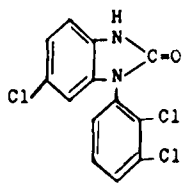
Research to define the scope and limitation of 3,4,4'-trichlorocarbanilide (TCC) as a soap bacteriostat has established that TCC loses its bacteriostatic activity when used in conjunction with hypochlorite bleach. A chemical study of the action of hypochlorite on TCC indicated that this loss of bacteriostatic activity was due to the conversion of TCC to a trichlorinated 1-phenyl-2-benzimidazolinone which is biologically inactive. This NMR study was instigated to provide additional evidence for the proposed ring system, and to determine the location of the 3 chlorine atoms in this system.

Summary

Proton NMR spectra were obtained from the product isolated from the reaction of TCC with bleach, from a related monochloro compound obtained from the reaction of carbanilide with bleach, the monoacetate derivatives of these compounds, and appropriate reference compounds. Analysis of these spectra indicated the structure of the compound formed in the reaction of carbanilide with hypochlorite ion to be -



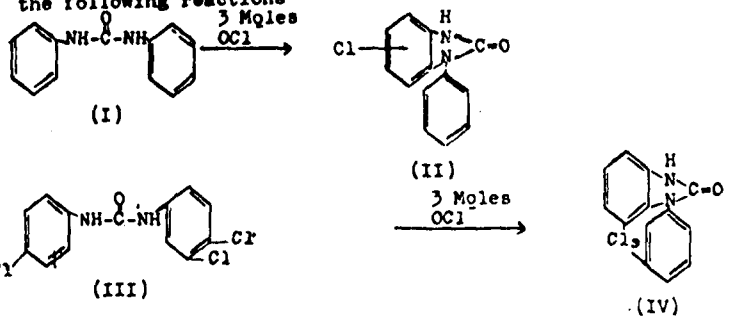
and the compound formed in the reaction of TCC with hypochlorite ion to be -



Analytical Studies

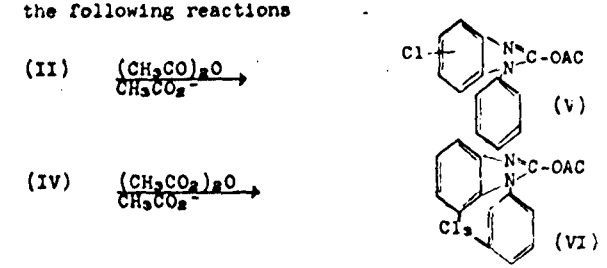
A. Preparation of Benzimidazolinones

The benzimazolinones described above were prepared by the following reactions



*These compounds are shown as o-acetate, but may be N-acetate.

The benzimidazole derivatives* of II and IV were prepared by the following reactions



B. NMR Measurements

All measurements were made on 0.50 M solutions in dimethyl acetamide unless otherwise state. Chemical shifts are reported relative to $(CH_3)_4Si$ (TMS) defined as $\delta = 10^6 \frac{(H_{TMS} - H)}{H_{TMS}}$

i.e. $\delta_{TMS} = 0$. Peak area measurements, not reported, were

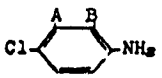
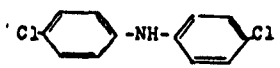
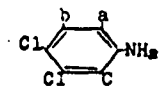
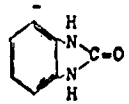
made on all compound and reference peaks with a Varian V-3521 integrator, and are consistent with the proposed structural assignments to ±3% in all cases.

C. Reference Compounds

The NMR parameters of the reference materials examined are given in Table I. As is shown the peaks due to the two rings in the 1-phenyl-2-benzimidazolinone are well separated. Unless complicated by spin-spin interactions, this should also be true for the chlorinated compounds in question. The acetate derivative displays a well separated peak for proton C, that nearest the introduced unsaturation.

TABLE 1

NMR Data from Reference Compounds

Compounds	Chemical Shift (ppm) a	b	c	J (cps)
	7.05	6.57		J_{AB} = 8.7
		7.10*		J_{AB} = 9.0
	6.81	6.58	7.11	J_{AB} = 8.5, J_{AC} = 2.5
		6.80		

*Indicates the average peak displacement; in all cases but peak (A) of the last reference - a single narrow peak is observed.

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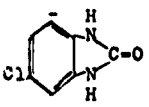
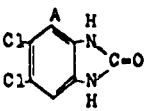
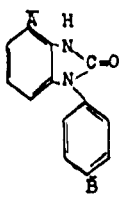
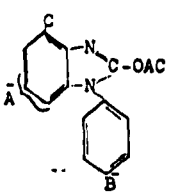
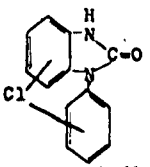
Table 1 (cont'd.)

NMR Data from Reference Compounds

Compounds	Chemical Shift (ppm) a	b	c	J (cps)
	6.81			
	6.81			
	6.82	7.32		
	6.96m	7.46	8.01	

D. Proof of Structure of (II)



Other physical and chemical measurements indicate the structure shown above, with 1 chlorine atom molecule, but the location of the chlorine as to ring and position on ring is uncertain.

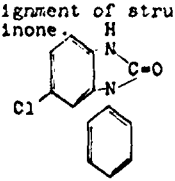
Figure A)I. Aromatic proton spectrum of (II)

Three peaks are seen in this spectrum. Based on their absorption positions the two high field peaks are assigned to the benzimidazolinone ring and the lower field peak is assigned to the phenyl ring. Area measurements of these peaks show 3.0 protons to 5.0 protons. This shows positively that the single chlorine atom is on the benzimazolinone ring. However, because of uncertain spin-spin coupling, no definite assignment as to the ring position can be made.

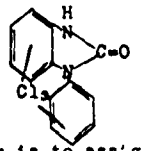
Figure B) Aromatic proton spectrum of (V)

From measurements of peak area and chemical shift, peaks 4,5, and 7 are assigned to protons in the benzimidazole ring; the remaining peak is assigned to phenyl ring protons. The areas of peaks 4,5, and 7 are identical and correspond to 1 proton/peak. The analysis of this first order spectrum for the benzimidazole ring protons leads directly to the indicated assignment. Peak 4 is assigned as indicated because of the large shift to lower field observed when unsaturation is introduced one atom removed from this position.

This then allows an unambiguous assignment of structure (II) as 1-phenyl-6-chloro-2-benzimidazolinone.



E. Proof of Structure of (IV)



As in Structure (11) the problem is to assign the position of the 3 chlorine atoms in the two-ring system. The nature of the reaction is such that there should be 2 chlorine atoms in 1 ring, and 1 chlorine atom in the other ring.

Figure C) Aromatic proton spectrum of (IV)

Four peaks of varying area are seen in this spectra. Based on their absorption positions the high field peak is assigned to the benzimidazolinone ring; the remaining peaks are assigned to the phenyl ring. Area measurements of these peaks indicate one chlorine atom/benzimidazolinone ring and two chlorine atoms/phenyl ring. No detailed analysis as to substitution positions was attempted.

Figure D) Aromatic proton spectrum of (VI)

Seven distinct absorption peaks are seen. No interpretation is attempted but comparison to Figures B and C suggests a monochlorinated benzimidazole ring and a dichlorinated phenyl ring. Area measurements are in agreement with this interpretation.

F. Solvent Effects

Before trying to build a convincing argument for the chlorine ring positioning necessary to explain spectra C and D, an attempt was made to utilize the slight variation in chemical shift of o, m, and p protons to be expected in various solvents. Since a strong interaction between solvent and the N atoms is likely as well as between the aromatic π electrons and solvent, noticable effects can be expected. These effects may remove the overlap of peaks thought to be present in spectra C and D.

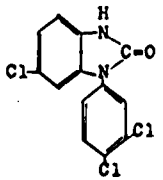
Spectra of IV and VI in several solvents were obtained. Solvent effects on the observed spectra were observed. The spectrum of VI in dioxane gave the best resolved spectrum; this spectrum is shown as Figure E.

Figure E) Aromatic proton spectrum of (VI) in dioxane (~.7 M).

Comparison to spectrum B indicates that peaks 4,5, and 7 are due to the aromatic protons in the benzimidazole ring while the remaining peaks are due to the phenyl ring protons. Determination of protons/peak by integration and observation of repetitive peak separations, indicating spin-spin coupling, shows that each ring exhibits a first order spectrum. The interpretation of this spectrum is indicated.

Calculations using the observed chemical shifts and coupling constants indicates the peak intensities in the phenyl ring spectrum are as predicted.

This allows an unambiguous assignment of Structure IV as 1-(3,4-dichlorophenyl)-6-chloro-2-benzimidazolinone.



6/62 - R. E. Keller, M. W. Dietrich

FIGURE A

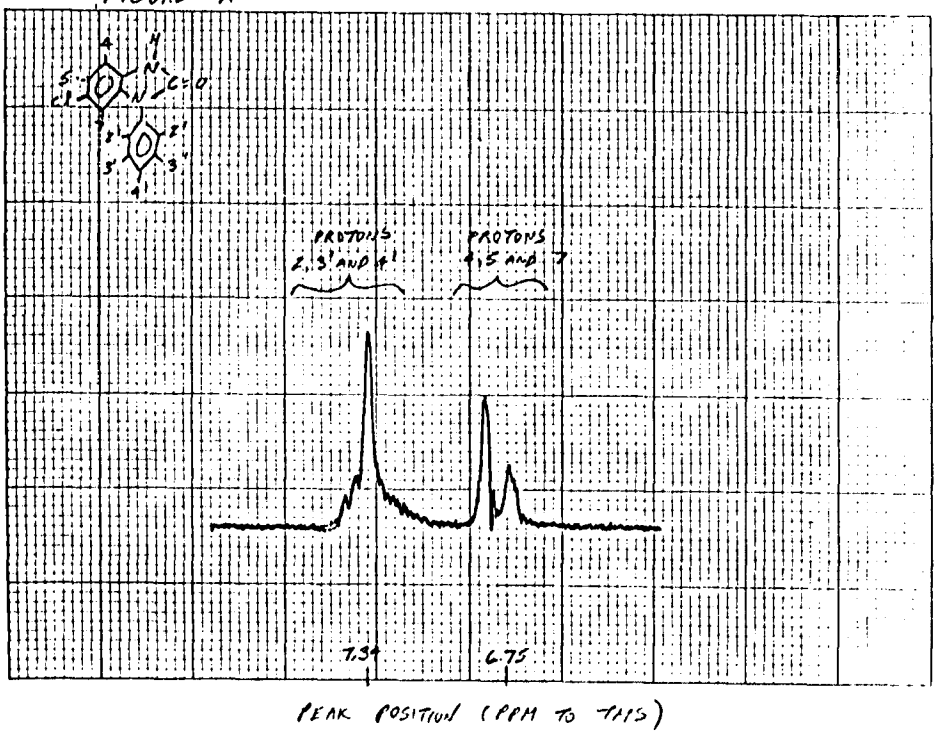


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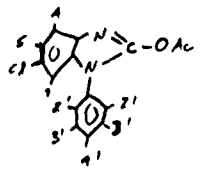
FIGURE 2



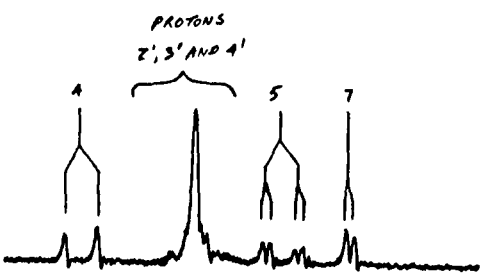


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FIGURE C

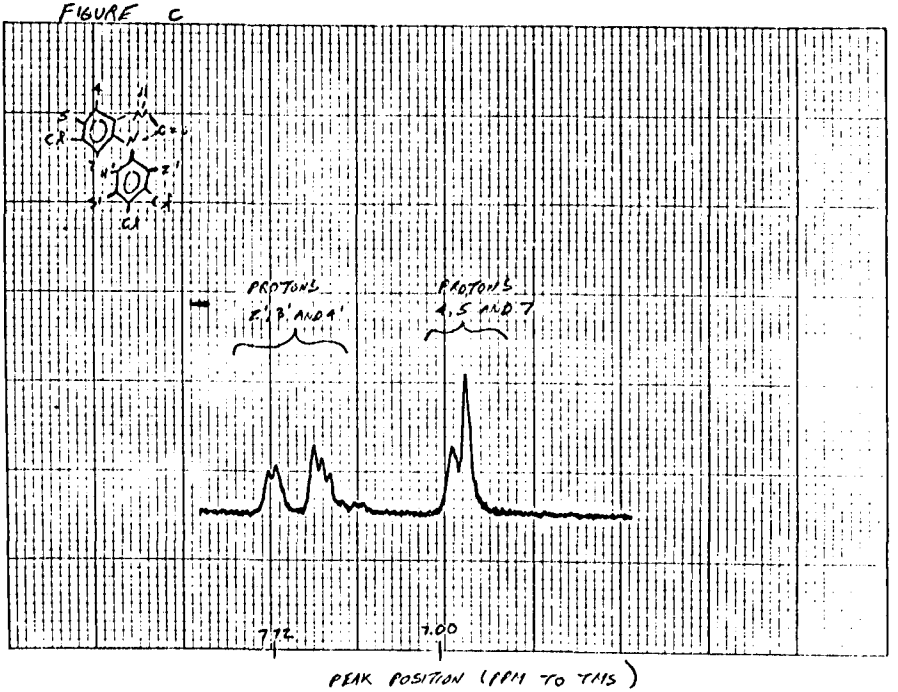

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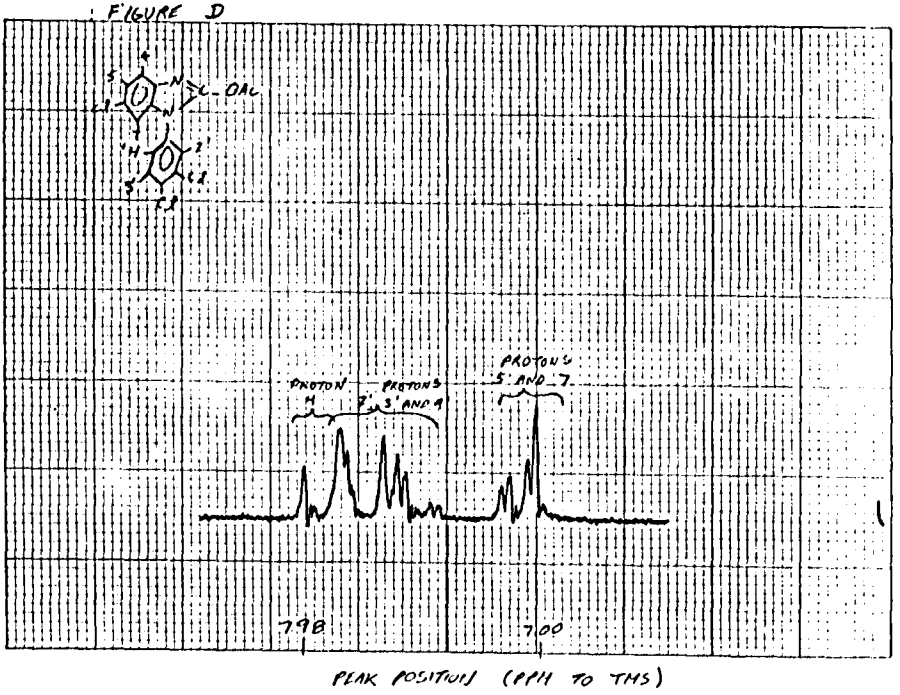
FIGURE D



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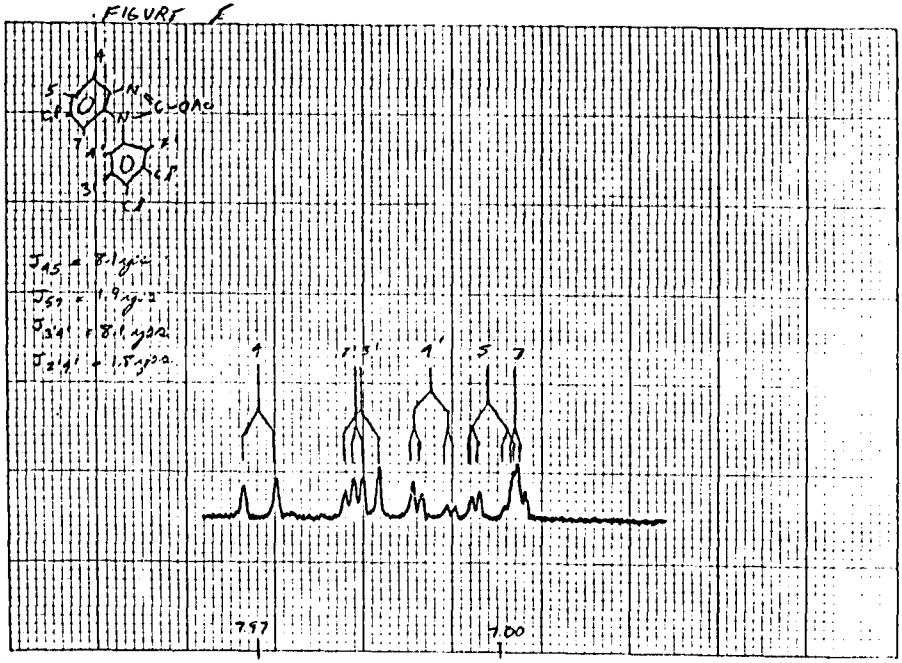
K·E 10 X 10 TO THE INCH KEUFFEL & ESSER CO. MADE IN U.S.A.

FIGURE E



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SECTION C

BIOLITE ANALYTICAL INVESTIGATIONS

Introduction

Basic data were needed to define the scope and limitations of Biolite as a bacteriostat. This study covered the following problems:

1. Development of method for ppm pentachlorophenol and/or Biolite on cloth.

2. Stability studies -

   a. Biolite in detergents.
   b. Coated Biolite in detergents.
   c. Experimental fungistat in detergent.

3. Retention studies -

   a. Biolite on cloth from Terg-O-Tometer washes.
   b. Biolite on cloth from full scale washing machine washes.

4. Miscellaneous studies -

   a. Effect of sterilization of cloth on Biolite analyses.
   b. Stability of Biolite-detergent-water at 140°F.
   c. Determination of Biolite by reduction with sodium biphenyl and measurement of the liberated chloride.

Summary

1. A method has been developed for the determination of pentachlorophenol and/or Biolite (2-chloroethyl pentachlorophenyl carbonate used as a bacteriostat-fungistat) on cloth. The method is based on the hydrolysis of Biolite to pentachlorophenol followed by extraction with chloroform and measurement by ultraviolet absorption in alkaline aqueous solution. The method sensitivity is a few parts per million Biolite and the accuracy is believed to be within ± 10% of the amount present.

2. Stability tests run at 80°F. in the humidity cabinet on 1% Biolite (99% assay and < 100 mesh) in All showed that approximately 50% of the Biolite remained after two months. Approximately 70% remained after two months with 90% assay, 20-100 mesh Biolite in All, Fab and Tide.

Accelerated stability tests (one week at 60°C. which the soap manufacturers claim equivalent to a one-year shelf life) were run on 1% Biolite in Tide. The Biolite was coated with various materials which might prevent decomposition. A 10% coating of polyvinyl alcohol increases the stability of the Biolite in the presence of the detergent from 40% to 80%.

Accelerated stability tests showed approximately the same decomposition for an experimental phenyl pentachlorophenyl carbonate as for Biolite.

3. The Terg-O-Tometer which is used to determine the effectiveness of various detergents in laundering was used to evaluate Biolite in the detergents. Cloth laundered in the Terg-O-Tometer and air dried contained approximately 17 ppm Biolite while the samples washed in an automatic washer and dried in a commercial drier contained 100 to 140 ppm Biolite. Cloth washed in the Terg-O-Tometer where the wash as well as all the rinse solutions are poured (filtered) through the cloth to simulate the full scale washer gave 60 to 160 ppm Biolite on the cloth. These findings indicate that the Terg-O-Tometer is not equivalent to standard washing machines for studies of this type.

The analysis of cloth from ten successive washes showed no build-up of Biolite.

Three full scale washer experiments resulted in the following conclusions:

(1) Less than 8 ppm (calculated as Biolite) is present on cloth as pentachlorophenol after the wash, the first and second rinse and the air drying steps. This represents about 7% of the total Biolite present.

(2) The pentachlorophenol content of the heat dried cloth increased to 20 ppm or about 18% of the total Biolite present.

(3) Upon sterilization, the pentachlorophenol increases in the washed and dried samples to 80 ppm. About 70% of the Biolite is hydrolyzed. This shows that the biological testing was carried out with cloth containing 70% pentachlorophenol and 30% Biolite.

(4) The explanation for twice the Biolite content in heat dried samples in comparison to the air dried samples is not known. Analytical method error and/or difficulties in sampling due to the non-uniform distribution of the Biolite may account for this.

4. Analyses show that sterilization does not change the recovery of known amounts of Biolite added to cloth.

Approximately 5% of the Biolite in detergent in wash solution is decomposed in 10 minutes at 140°F. The state of subdivision of the Biolite affects this decomposition. 16% decomposition occurs in 10 minutes if the Biolite is added as a solution in acetone.

The reduction of Biolite with sodium biphenyl and titration of the resulting chlorides with standard silver nitrate has been used as an independent method to check the validity of the extraction-ultraviolet method. Both methods give essentially the same results for the analysis of cloth from washing tests.

Analytical Studies

1. Development of Method for ppm Pentachlorophenol and/or Biolite on Cloth

Preliminary results were obtained using a method based on extraction of the cloth in a Soxhlet extractor with ethanol. The optical brightener offers serious interference with ultraviolet measurements. Attempts to effect purification by extraction procedures proved unsuccessful due to emulsions.

Extraction of the pentachlorophenol from the cloth with chloroform in the presence of water eliminates most of the above difficulties. Quantitative extraction is slow because of the entrainment of the chloroform by the cloth and because equilibrium in the extraction is established slowly. This requires 5 minutes of vigorous shaking. To accomplish equilibrium on the Wrist Action Shaker, the samples must be shaken at least 1 hour 15 minutes and preferably 2 hours. All the pentachlorophenol is found in the chloroform layer so that if a known amount of chloroform has been added, quantitative analysis can be made on a measured aliquot. Biolite does not interfere if the solution is acid. The chloroform solution is washed with 10 ml. 0.1 N sodium hydroxide and the ultraviolet absorption of the aqueous alkaline phase is measured at 320 mμ.

For the determination of Biolite and pentachlorophenol, the cloth is moistened with 0.1 N 50% methanol-H_2O-sodium hydroxide. After standing a few minutes, the hydrolyzed sample is acidified and the pentachlorophenol extracted in the usual manner. There is very little background interference using this procedure. The reproducibility of the method is believed to be within ± 10%.

The method is as follows:

Determination of Biolite and/or Pentachlorophenol on Cloth
Method # 3

SCOPE

The method is designed to determine the Biolite and/or pentachlorophenol present in cloth at the level of 5 ppm or higher. It is a modified and improved version of Method # 2 developed earlier.

PRINCIPLE

The pentachlorophenol is extracted with chloroform directly from the cloth suspended in water, the chloroform washed with water and finally with a small volume of dilute sodium hydroxide solution. The ultraviolet absorption of this alkaline solution is measured at 320 mμ where sodium pentachlorophenate has maximum absorption. Biolite does not interfere.

The cloth is moistened with alcoholic sodium hydroxide and the Biolite is decomposed instantly to pentachlorophenol. The total pentachlorophenol is determined. The Biolite is the difference between the total pentachlorophenol and the pentachlorophenol found directly.

REAGENTS

Chloroform - A.R.
Sodium Hydroxide - A.R. 50% Sol'n.
Hydrochloric Acid - A.R.
Methyl Orange Indicator
Methyl Alcohol - A.R.

APPARATUS

Burell Wrist Action Shaker
1 - 250 ml. Separatory Funnel
3 - 125 ml. Separatory Funnels
Cary Recording Spectrophotometer with 2.0 cm. Fused Silica Cells
8 oz. Narrow Mouth Bottles with Polyethylene Closures
Usual Laboratory Glassware

STANDARD SOLUTIONS

0.1 N Sodium Hydroxide -

No. 1 - Add 2.6 ml. 50% sodium hydroxide to 500 ml. distilled water and mix thoroughly.

No. 2 - Add 2.6 ml. 50% sodium hydroxide to 250 ml. distilled water and add 250 ml. methyl alcohol.

PROCEDURE

A. Pentachlorophenol

1. Take a 5.0 g. sample of cloth and cut into suitable size pieces or strips and place in a clean dry 8 oz. bottle.

2. Add 150 ml. of distilled water and 6 drops of 1-1 hydrochloric acid.

3. Add, by pipette, 25 ml. of chloroform and shake vigorously for 30 seconds or until cloth is dispersed throughout water and chloroform.

4. Clamp in a horizontal position on the Wrist Action Shaker and shake with maximum shaking action for 1.5 hours (8 samples may be shaken at one time).

5. Remove the cloth from the bottle with the aid of a wire hook. Squeeze the cloth against the neck of the bottle during the withdrawal to minimize the amount of chloroform discarded with the cloth.

6. Transfer the contents of the bottle to a clean dry 250 ml. separatory funnel.

7. Drain the clear chloroform layer into a clean dry 25 ml. graduate and record the volume to the nearest one tenth of a ml.

8. Place 25-30 ml. of distilled water into each of two 125 ml. separatory funnels.

9. Pipette 10 ml. of 0.1 N aqueous sodium hydroxide (sol'n. No. 1) into a third 125 ml. clean dry separatory funnel.

10. Transfer the chloroform from the graduate quantitatively, with the aid of a little chloroform, to the 1st wash water funnel, stopper and shake for 15 seconds.

11. Drain the chloroform into the second wash water funnel.

12. Add approximately 25 ml. of fresh chloroform to the first wash water funnel.

13. Shake both the first and second wash funnel for 15 seconds (these can both be shaken at the same time).

14. Drain the chloroform in the second wash funnel into the third funnel containing the sodium hydroxide (# 9 above).

15. Drain the chloroform from the first wash funnel into the second wash funnel.

16. Shake the second wash funnel and the third funnel containing the sodium hydroxide for 15 seconds (these can be shaken at the same time).

17. Discard the chloroform layer from the alkaline funnel.

18. Transfer the chloroform from the second wash funnel to the third funnel containing the alkali.

19. Shake for 15 seconds, and discard the chloroform.

20. Apply vacuum to the top of the separatory funnel and open the bottom stopcock to allow air to bubble up through the solution for several minutes or until all the chloroform has been removed (odor).

21. Pour the solution into a 2 cm. cell and measure the absorption in the range of 400 to 230 mμ using distilled water in the reference.

22. Draw in the background which is a straight line extension of the curve from 400 to 350 mμ. The absorbance measured at the maximum of 320 mμ is corrected for the background from the curve at this wavelength and the difference used in calculating the results.

B. Biolite and Pentachlorophenol - Total

1. Take approximately a 5 gram sample of cloth, weighed to the nearest 0.1 gram, cut into suitable size pieces or strips and place in a clean dry 8 oz. bottle.

2. Add 10 ml. of 0.1 N sodium hydroxide in 50% methanol-water mixture (sol'n. No. 2). Stir the cloth around with a stainless steel spatula to make certain that the cloth is thoroughly wet with the alcoholic sodium hydroxide solution.

3. Rinse off the spatula with water using a total volume of 150 ml. Add 1 drop methyl orange indicator solution.

4. Add approximately 6-10 drops 1-1 hydrochloric acid solution and shake. The indicator should be red, showing the solution is acid.

5. Proceed with the analysis starting with Procedure A, Pentachlorophenol, # 3.

CALCULATIONS

ppm pentachlorophenol =

$$\frac{(\text{O. D. at } 320 - \text{O.D. at } 320 \text{ of background}) \times \frac{\text{Vol. of Chloroform Sol'n. Extracted}}{25} \times \text{Vol. of 0.1 N NaOH Taken in ml.} \times 10^4}{(\text{Absorption coefficient* of pentachlorophenol at } 320\ m\mu) \times \text{Cell length in cm.} \times \text{Wt. sample in g.}}$$

$$= \frac{\text{Corr. O.D. at } 320 \times 10 \times 10^4 \times \text{fraction chloroform extracted}}{200 \times 2.0 \times 5.0}$$

$$= \text{Corr. O.D. at } 320 \times 50 \times \text{chloroform fraction}$$

$$\text{* Absorption coefficient} = \frac{\text{Optical Density}}{(\text{g./100 ml.})(\text{Cell length, cm.})}$$

PRECISION AND ACCURACY

No data were obtained for statistical calculation of accuracy or precision. The five extracts give better than 90% recovery with known pentachlorophenol from cloth at the 50 ppm level. The reproducibility is within 1 ppm at the 30 ppm level. The accuracy and reproducibility are believed better than with Method # 1 and equivalent to Method # 2.

DISCUSSION

Pentachlorophenol can be quantitatively extracted from water solution by chloroform in one 15 second extraction. However, in the actual extraction of the pentachlorophenol from the cloth, only 60% is extracted in the one minute time. Quantitative extraction is obtained using 30 minute shaking. No intermediate shaking times have been run but a 5 minute shaking would probably give quantitative transfer from the cloth to the chloroform solution.

In shaking the cloth, water and chloroform, with 25 ml. chloroform, about 21 ml. of chloroform is the most that can be drained forward. This means that the practical recovery is only 85% of the amount present. Thus, two additional extractions are needed for quantitative transfer of the pentachlorophenol. An alternative procedure could be used where an aliquot of the chloroform is washed and the pentachlorophenol transferred to the sodium hydroxide solution for UV measurement. This is the basis of the present method.

When extractions are shaken by hand, 5 min. is sufficient for complete extraction whereas 1.5 hrs. is required using the Burell Wrist Action Shaker. The shaking action must disperse the cloth throughout the solutions,otherwise the extraction will be incomplete in 1.5 hrs. The purpose of the 1 minute vigorous shaking initially is to thoroughly disperse the sample before the mechanical shaking is started.

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12/62 - O. W. Ashworth, R. E. Keller

2. Stability Studies

a. Biolite in Detergents

The stability of 1% Biolite in standard All and dry mix All was determined. The samples were prepared in individual 8 oz. bottles by accurately weighing in 0.2 g. Biolite and adding 20.0 g. of the detergent. At the end of the test period, the entire sample was used for analysis. The dry mix All contained no brightener or perfumes. The control sample was kept tightly capped while the sample (cap removed), was placed in the humidity cabinet. The results of the first series are as follows.

The Biolite used was 99% assay and less than 100 mesh.

Percent Biolite in Sample

Time of Test	Standard All		Dry Mix All	
	Control	Humidity	Control	Humidity
Initial	0.97		0.98	
1 day	0.91	0.90	0.89	0.87
2 days	0.88	0.86	0.82	0.85
3 days	0.87	0.82	0.84	0.84
1 week	0.91	0.77	0.74	0.78
2 weeks	0.81	0.67	0.58	0.65
4 weeks	0.81	0.63	0.38	0.61
8 weeks	0.83	0.46	0.31	0.33

The results indicate moisture may be a contributing factor in the decomposition.

A second series of tests were run using 90% Biolite (90% pentachloro - the balance being the tetrachloro analogue of Biolite) with mesh size of 20-100. Several detergents were used in this series. The results are given in the following table.

Analyses of Biolite - Heavy-Duty Detergents Up Through Two Months

(Containing 1% Biolite after 3 days, 1 week, 2 weeks, and 1 month at 80°F. in the humidity cabinet.)

	Percent Biolite				
	3 days	1 wk.	2 wks.	1 mo.	2 mo.
All - 99% Biolite - 20-100 mesh	0.97%	0.93%	0.92%	0.83%	0.69%
All - 90% Biolite - 20-100 mesh	0.92	0.85	0.84	0.77	0.65
Fab - 90% Biolite - 20-100 mesh	0.90	0.91	0.85	0.79	0.70
Tide- 90% Biolite - 20-100 mesh	0.90	0.90	0.88	0.84	0.70
Climalene - 90% Biolite - 20-100 mesh	0.92	0.92	0.90	0.85	0.76
Beads O'Bleach (1) - 90% Biolite - 20-100 mesh	0.90	0.95	0.95	0.90	0.78
Snowy Bleach (2) - 90% Biolite - 20-100 mesh	0.91	1.01	1.00	0.79	0.69

(1) Assay corrected by 0.20% as blank correction.
(2) Assay corrected by 0.25% as blank correction.

The above results do not show as much decomposition as when the fine mesh (< 100) Biolite was used. The results at the two-month period show that the decomposition is approximately 70% for all the detergents. The 46% obtained on the first series is probably due to the fine mesh size of the Biolite.

b. Coated Biolite in Detergents

Dr. J. Baker had 90% Biolite coated with various coating agents at the Wisconsin Alumni Research Foundation. This Biolite was tested by an accelerated test used by the soap manufacturers. The sample is heated at 140°F. (60°C.) for one week. It is claimed that this test is equivalent to a one-year shelf life. The analytical data for this test using the method based on measurement of CO_2 are given in the following table.

Heat Stability Studies

Sample	% Biolite in Detergent Originally	At 60°C. 1 wk.	% of Original Remaining		Remarks
90% Biolite - 20-100 mesh	1.00	0.46	46		
99% Biolite - 20-100 mesh	1.00	0.39	39		
99% Biolite - < 100 mesh	1.00	0.24	24		
Control - Biolite used in subsequent tests	1.00	0.36	36		
5% Carbowax 6000	0.95	0.38	40		
10% Carbowax 6000	0.90	0.46	51		
2.5% Methocel - Ethocel	0.975	0.39	40		
5% Methocel - Ethocel	0.95	0.48	51		
10% Methocel - Ethocel	0.90	0.41	46		
2.5% Carbowax 6000 + Methocel-Ethocel	0.975	0.45	46		
5% Carbowax 6000 + Methocel-Ethocel	0.95	0.46	48		
7.5% Carbowax 6000 + Methocel-Ethocel	0.925	0.45	49		
10% Carbowax 6000 + Methocel-Ethocel	0.90	0.44	49		
2.5% Polyvinyl Alcohol	0.975	0.44	45		
5% Polyvinyl Alcohol	0.95	0.62	65	0.92)	% Biolite in original formulation
7.5% Polyvinyl Alcohol	0.925	0.71	77	0.93)	
10% Polyvinyl Alcohol	0.90	0.76	84	0.91)	
5% Sugar	0.95	0.48	51		
10% Sugar	0.90	0.49	54		
15% Sugar	0.85	0.51	60		
20% Sugar	0.80	0.48	60		
25% Sugar	0.75	0.39	52		Coated Biolite Sticky-necessary to grind before formulating.
5% Dextrin 600	0.95	0.52	55		

One percent formulations in Tide of the 5, 7.5 and 10% polyvinyl alcohol coated Biolite samples were analyzed by the regular procedure. The values obtained - 0.92 in place of 0.95; 0.93 vs. 0.925 and 0.91 in place of 0.90 - are in close agreement with the theoretical values. The other samples were not analyzed. The percentage of the coating was assumed to be correct and this value was used in determining the percentage of the original remaining.

As a check on the uniformity of the coating, three individual samples (0.2 g.) of the 10% coated material were weighed out, dissolved in approximately 25 ml. of alcohol and 10 ml. of 0.1 N sodium hydroxide were added. This hydrolyzed the Biolite to pentachlorophenol which was determined by measurement of its ultraviolet absorption with an appropriate dilution. The assay figures obtained by this method were 87.0, 86.0 and 86.3% Biolite. These are in close agreement as well as with the 90% nominal figure and the 91% obtained by the method involving the measurement of carbon dioxide.

Of the coated materials tested, polyvinyl alcohol appears to be the most promising. There is a trend showing less decomposition as the amount of the polyvinyl alcohol is increased up to the 10% level.

c. Experimental Fungistat in Detergent

The accelerated test - one week at 140°F. - was run on 1% phenyl pentachlorophenyl carbonate in Tide. 33% of the fungistat remained after one week. This is approximately the same as obtained for Biolite.

3. Retention Studies

a. Biolite on Cloth from Terg-O-Tometer Washes

Experimental washings were run in the Terg-O-Tometer to test the effect of particle size of the Biolite. An average value of 17 $\pm$ 2 ppm Biolite was found on the cloth while cloth laundered in an automatic washer contains 50-100 ppm. Thus, the Terg-O-Tometer cannot be used to duplicate the results of a full scale washer.

To check the deposition of Biolite on cloth by filtration, eleven circular swatches of cloth were washed in the Terg-O-Tometer but the samples were arranged on a Buchner funnel after each cycle in the same order and the solution poured through the swatches after the wash as well as after the first and second rinse. Biolite < 100 mesh was used on one test and 20-100 mesh material was used in a second experiment. The results are given in the following table.

Cloth Sample No. From Top to Bottom	ppm Total Biolite	
	<100 Mesh	20-100 Mesh
1	84	166
2	46	131
10	30	61
11	31	60

The range of 60-166 ppm is higher than the 17 ppm obtained when the Terg-O-Tometer is operated in the usual manner. The data indicate that Biolite is retained for the cloth by a filtering action during standard washing machine tests. This work shows that the Terg-O-Tometer tests must be changed in order to simulate the retention of Biolite on cloth laundered in a standard automatic washer.

b. Biolite on Cloth from Full Scale Washing Machine Tests

The analysis of cloth from ten successive washes showed no build-up of Biolite with each successive wash. The average amount found was 8 ppm which is so low that there is a large experimental error in the determinations. Only one-eighth the normal amount of Biolite was used in this series of experiments. (0.5% Biolite in detergent and 0.25% used in the wash.)

The results of three full scale washer experiments carried out to show the retention of Biolite on cloth are summarized in the following table.

Cloth Sample	Washer #1 Penta-chloro-phenol as Biolite (ppm.)	Washer #1 Total as Biolite (ppm.)	Washer #2 Total as Biolite Std. Method (ppm.)	Washer #2 Total as Biolite Av. (ppm.)	Washer #3 Std. Method (ppm.)	Washer #3 Av. (ppm.)	Washer #3 Re-analysis (ppm.)	Na bi-phenyl Method (ppm.)
Wash	8	109	54,142,61	86 ± 38				
1st rinse	8	139	52,75,88	72± 13				
2nd rinse	3	71,86	75,73,51	66 ± 10				
2nd rinse + sterilized			70,97	84 ± 13				
Air dried	7	50,49	70,68,66	68 ± 1	38,38,36(2)	37 ± 1	61,57	86
Air dried + sterilized			82,82,79(1)	81 ± 1				
Air dried + sterilized	82	110	84,66,70(1)	73 ± 7	112,64,73	83 ± 19		
Air dried + sterilized + 65 hrs. at 75°			64,69	67 ± 3				
Heat dried	20	116	136,99,107	114 ± 15	139,137,148(3)	141 ± 4	129	120
Heat dried + sterilized	76	110	123,106,108	112 ± 7	156,166,160	162 ± 3		

(1) Two sets of samples analyzed.
(2) Re-analysis of the samples gave 13,9,7 ppm. total.
(3) Re-analysis of the samples gave 9 ppm. Biolite - essentially all Biolite removed.

Cloth from the first washing experiment was analyzed for both pentachlorophenol and Biolite. Samples taken up through the air dried step contained no more than 8 ppm pentachlorophenol or 7% of the total Biolite. The air dried sterilized sample contained 82 ppm pentachlorophenol or about 70% of the Biolite. The heat dried sample contained 20 ppm Biolite or 18% of the total Biolite. The fungistat activity of all samples were thus determined on cloth containing 70% of the Biolite present as pentachlorophenol as all samples were sterilized before running the biological tests.

In Washer Test # 1 only one sample of each was analyzed. The erratic values make it difficult to draw conclusions. The air dried sample contains about one-half the Biolite found in the sterilized sample and the heat dried and sterilized sample.

Washer Test # 2, involving triplicate samples, was made to determine the reproducibility of the sampling. The large difference between air dried and heat dried samples is again noted and unexplained. There is good agreement between the sterilized and unsterilized air dried samples. The reproducibility of the wash sample before rinsing is poor. This value does not decrease rapidly with two rinses which shows the tenacity with which the Biolite is held by the cloth. This cannot be called adsorption because, if it were, the amount on the cloth would be the same when using the Terg-O-Tometer under similar concentrations.

The results of the third washer experiment show a maximum variation of four-fold between air dried and heat dried sterilized samples. Two additional samples of the air dried were run at a later date and the values of 57 and 61 agree nicely but do not agree with the average of 37 $\pm$ 1 obtained originally. A check of the analytical method disclosed no serious errors in the procedure. A very non-uniform deposition of the Biolite on the cloth might contribute materially to a non-representative sampling error. The analysis of an additional sample of heat dried cloth agreed better with the value obtained previously.

The reduction of Biolite with sodium biphenyl and titration of the liberated chloride with standard silver nitrate was developed and used as an independent method of analysis. Results showing 86 ppm and 120 ppm for air dried and heat dried samples from Run #3 confirm that the difference in Biolite content of air dried and heat dried cloth is real and that the data obtained with the extraction-ultraviolet method are of the correct order of magnitude.

Samples of the air dried and heat dried cloth were re-analyzed and only a small amount of Biolite was found. This shows that all extractable Biolite was removed from the cloth by the analytical method.

4. Miscellaneous Studies

a. Effect of Sterilization of Cloth on Biolite Analyses

To determine the effect of sterilization on the analysis, a series of experiments were run where a known amount of Biolite was added in acetone solution to a swatch of cloth and this, in turn, was analyzed. The swatches used were unwashed, washed with water only and washed with Tide. Residual amounts of detergent or other impurities left on the cloth were considered as possible sources of trouble with the method.

The results given in the following table show that recoveries are generally better than within ± 10% of the amount added with outside variations of ± 20%.

Effect of Sterilization of Cloth on Biolite Analyses

Sample and Treatment	Biolite Added as ppm	Total Pentachlorophenol and Biolite Reported as ppm Biolite
Plain Cloth - Unwashed	0	4
" " - Unwashed - Sterilized	0	5
" " - Unwashed - Acetone	0	4
" " - Unwashed - Acetone - Sterilized	0	5
" " - Unwashed	50	49
" " - Unwashed - Sterilized	50	57
" " - Unwashed	100	94
" " - Unwashed - Sterilized	100	105
" " - Washed with Water	0	0
" " - Washed with Water - Acetone	0	0
" " - Washed with Water	50	66
" " - Washed with Water - Sterilized	50	56
" " - Washed with Water	100	122
" " - Washed with Water - Sterilized	100	107
" " - Washed with Tide + Bleach	0	0
" " - Washed with Tide + Bleach + Acetone	0	0
" " - Washed with Tide + Bleach	50	67
" " - Washed with Tide + Bleach - Sterilized	50	56
" " - Washed with Tide + Bleach	100	116
" " - Washed with Tide + Bleach - Sterilized	100	75

b. Stability of Biolite-Detergent-Water at 140°F.

A study to determine the extent of degradation of Biolite in All during the washing step at 140°F. was carried out. In one experiment, the Biolite was added to the detergent-water solution (1%) at 140°F. as a solid. In the second experiment, the Biolite was added in an acetone solution. This wash solution turned turbid immediately and stayed turbid more than 10 minutes. This probably is caused by excess Biolite precipitated in colloidal form which hydrolyzed faster than Biolite added as a solid. The results in the following table show that less than 5% of the Biolite would be decomposed in the normal 10-minute wash cycle.

Percent Biolite Decomposed to Pentachlorophenol

Time in Minutes	Added as Solid	Added in Acetone Solution
5	2	11
10	5	16
20	10	24
30	15	31
40	22	38
50	29	44
60	32	48
90	46	66
120	57	74

c. Determination of Biolite by Reduction with Sodium Biphenyl and Measurement of the Liberated Chloride

The sodium biphenyl method for the analysis of Biolite on treated cloth consists of the following operations. A 5.0 g. cloth sample (diced) is covered with 30 ml. chlorine-free xylene and stirred for several minutes. A 10 ml. aliquot of sodium biphenyl reagent is added and the sample mixed 5 minutes. The excess sodium is reacted with 1 ml. ethyl alcohol. Five ml. of fresh 3% hydrogen peroxide is added and the sample is boiled 10 minutes. After cooling, 100 ml. acetone and 1 ml. strong sulfuric acid (1 to 1 concentrated sulfuric acid to water by volume) are added. The sample is stirred thoroughly and the solution is decanted off. The cloth is extracted four more times using for each extract 5 ml. of distilled water, 100 ml. acetone and 1 ml. 1 to 1 sulfuric acid. The separate extracts are collected and titrated with 0.0025 N silver nitrate to potentiometric endpoint using glass-silver electrode system and an L & N expanded scale potentiometer.

Analytical data obtained using this procedure are reported in the following table.

Sample	Ml. Sodium Biphenyl	Equivalent Biolite Added (ppm)	Equivalent Biolite Found (ppm)	Remarks
1. Xylene Solution of Pentachlorophenol	5.0	100 100	98 98	Cloth Absent " "
2. Xylene Solution of Pentachlorophenol Plus 5.0 Grams Control Cloth	5.0	100	77	5.0 Gram Cloth Control Present
3. Same as Sample 2	10.0	100	93	5.0 Gram Cloth Control Present
4. Treated Cloth Air Dried, 3rd Washer	10.0	---	86	36,38,57,61 ppm Biolite by UV Method
5. Treated Cloth Heat Dried, 3rd Washer	10.0	---	120	129,137,146 ppm Biolite by UV Method

This work was carried out to provide data for studies under Job No. 4162 - "Soap and Detergent Bacteriostats". Messrs. K. L. Godfrey, D. P. Roman, J. W. Baker, J. P. Speyrer and J. R Wiedemann carried out the Terg-O-Tometer and full scale washing tests, the special sample preparation, including the sterilization studies, and the preparation of coated Biolite which are given in this report.

12/62 - R. E. Keller, D. B. Hines, G. W. Ashworth

0692875

SECTION D

P^{31} NMR Analysis of Process Reaction Products

Introduction

In the development of the new dibutyl phenyl phosphate process, analytical methods were needed to evaluate the two major steps of the process: (1) $POCl_3$ + phenol, and (2) $(\emptyset O)POCl_2$ + butanol. In both cases several by-products are formed along with the major product. A method was needed to characterize the reaction mixtures and to determine the yield of the desired product.

Summary

P^{31} NMR methods were developed to analyze mixtures from both steps in the process. Several by-products were identified. Major and minor components were determined quantitatively. The following components were identified in the reaction mixtures examined: $POCl_3$, $(\emptyset O)POCl_2$, $(\emptyset O)_2POCl$, $(\emptyset O)_3PO$, $(BuO)_3PO$, $(BuO)_2(\emptyset O)PO$, $(BuO)(\emptyset O)_2PO$ and two pyro compounds.

The developed methods will measure 0-100% of a given component, and are considered accurate to about $\pm$ 2% absolute (based on total phosphorus containing compounds). However, it was not found possible to analyze accurately for both $POCl_3$ and $(\emptyset O)POCl_2$ since the P^{31} NMR peaks of these materials overlap. A combined analysis of these materials can be made.

The developed methods provide a fast, comparatively accurate, non-destructive method for quantitative analysis of sample mixtures of phosphorus compounds. The various components are identified by inspection of the spectra. The method is unaffected by components which do not contain phosphorus.

Analytical Studies

The developed methods are based on the difference in chemical shift of the various phosphorus containing components. In a mixture these components were identified using chemical shift data obtained from the pure materials. Quantitative analysis was performed by measurement of the area of each peak, the area being proportional to the concentration of the component.

Samples from the laboratory and pilot plant were examined, covering both steps of the process. The data obtained were used to optimize yields and to determine the nature and quantity of impurities present. Data and additional details can be found on Analytical Data Sheets filed in the Analytical and Spectroscopy Group.

NMR Determination of Reaction Products from the Dibutyl Phenyl Phosphate Process

A. Step I - Reaction of $POCl_3$ with Phenol

SCOPE

This method describes a phosphorus NMR procedure for the determination of the amounts of the various phosphorus components formed in the reaction of $POCl_3$ with phenol. The phosphorus components can be determined to about ± 2 mole % (of the total phosphorus components) in the range 0-100%.

PRINCIPLE

The P^{31} NMR spectrum of a typical reaction mixture (see Figure 1) contains peaks for each of the phosphorus containing components present. These peaks were identified by reference to spectra of the pure materials. The concentration of each component is determined by measuring the area of the peak associated with each component and comparing to the area of all peaks in the spectrum.

APPARATUS AND REAGENTS

High-Resolution NMR Spectrometer capable of measuring P^{31} (a Varian HR-60 was used).

Equipment for measuring area such as a planimeter or electronic integrator.

PROCEDURE

1. Instrument Settings

   Choose optimum settings to give signal display most convenient for the integration method to be used.

2. Calibration

   No calibration is necessary.

3. Sample Analysis

Fill 5 mm. thin walled NMR cells with sample (add CCl_4 to reduce viscosity if necessary). Adjust spectrometer for maximum homogeneity and minimum drift. Introduce sample and record spectrum (and integral). Add H_3PO_4 capillary to sample, rerun and obtain spectrum with scale calibration.

Calibrate spectra and identify components by chemical shift values. Determine area of each component by means chosen. Sum up areas of all peaks in spectrum. Determine the mole % of a given component using the equation:

$$\text{Mole \% X} = \frac{\text{Area X}}{n_X} \cdot \frac{1}{\text{Total Area}} \cdot 100$$

where n = number of phosphorus atoms per molecule

$$\text{Total Area} = \sum_i \frac{\text{Area } i}{n_i}$$

where i = the phosphorus compounds present

If both $POCl_3$ and $(\phi O)POCl_2$ are present, the amounts of these components are reported as a sum of the two concentrations, since the peaks of these species are incompletely resolved.

Area measurements were made by planimeter in the examples reported here.

B. Step II - Reaction of $(\phi O)POCl_2$ with Butanol

SCOPE

This method describes a phosphorus NMR procedure for the determination of the amounts of the various phosphorus components formed in the reaction of $(\phi O)POCl_2$ with butanol. The phosphorus components can be determined to about ± 2 mole % absolute (of the total phosphorus components) in the range 0-100%.

PRINCIPLE

See Section A. A NMR spectrum obtained from a typical sample is shown in Figure II.

APPARATUS AND REAGENTS

See Section A.

PROCEDURE

1. Instrument Settings

   See Section A.

2. Calibration

   No calibration is necessary.

3. Sample Analysis

   See Section A.

Monsanto Chemical Company
Organic Chemicals Division
St. Louis Research Department
12/62 - M. W. Dietrich, R. E. Keller

FIGURE I

REACTION MIXTURE $POCl_3$ + PHENOL

PEAK	SEPTH TO CAL. H_3PO_4	COMPOUND	AREA	MOLE %
1	-1.5	$POCl_3$	0.263	62
2	+1.0	$(\phi O)POCl_2$		
3	+6.4	$(\phi O)_2POCl$	0.036	9
4	+11.8	PARA HYDROXY TRIS	0.036	4
5	+17.9	$(\phi O)_3PO$	0.076	18
6	+25.6	PARA HYDROXY TRIS	0.020	7

* CALIBRATION SPIKE ADD

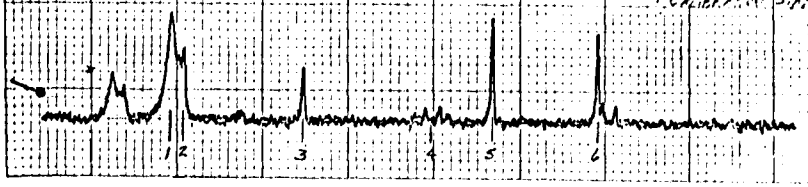

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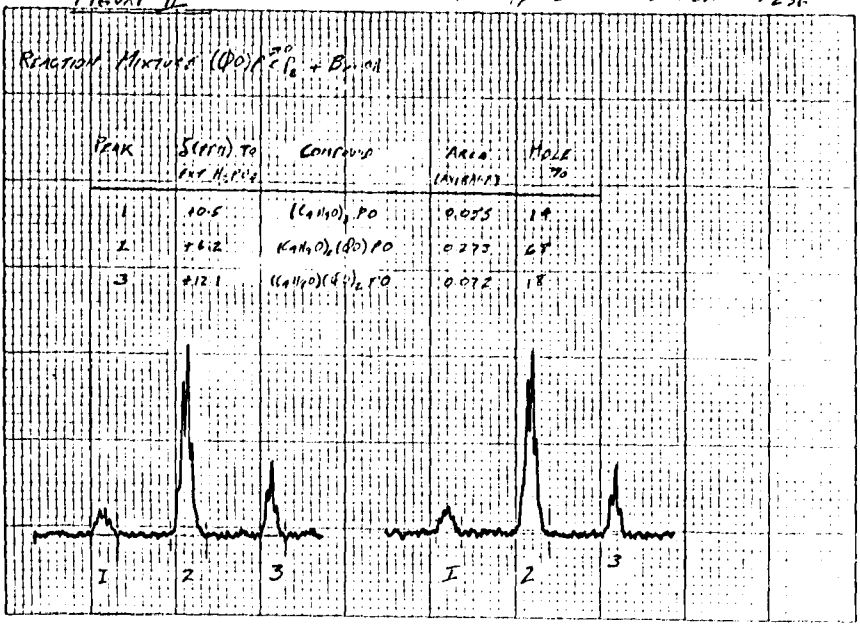
FIGURE II



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0692881

SECTION E

Identification of Inhibitors in Competitive Hydrocarbon Ester Fluids

Introduction

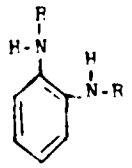
This study was undertaken to characterize the oxidation inhibitors present in competitive turbofan fluids. The information was needed to better select an inhibitor for a Monsanto C_{40} alkane product.

The techniques applied in the identification were column chromatography, ultraviolet absorption spectroscopy, infrared spectroscopy and nuclear magnetic resonance spectroscopy

Summary

Esso, Texaco and Socony turboban fluids were found to contain one or more components with an aromatic secondary amine structure.

The findings suggest components of the type -



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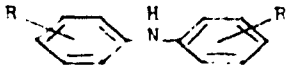
and



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Analytical Studies

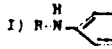
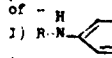
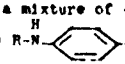
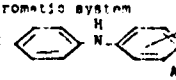
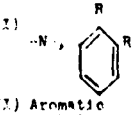
Following is a chart of the work carried out.

Also attached are the ultraviolet spectra of the three turbofan fluids examined and the typical ultraviolet spectra of the suggested components.

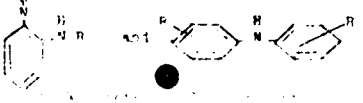
0692882

Experimental Competitive Turbofan Fluids

Structure Data for Inhibitor

	L-742 Esso	L-757 Texaco	L-793 Socony
Column Chromatography	Two aromatic inhibitors	------	------
Ultraviolet Material "Per Se"	Spectra characteristic of -  I) R-N(H)-C6H4-N(H)-R II) Aromatic system (aliphatic aromatic tertiary amine)	Spectra characteristic of -  I) R-N(H)-C6H4-N(H)-R (Disubstituted aromatic secondary amine "ortho" position - phenylene diamine type)	Spectra characteristic of a mixture of -  I) R-N(H)-C6H4-N(H)-R II) Aromatic system III) 
Infrared Chromatographic Fractions	I)  II) Aromatic Possibles a) Multi-system with para and tri-substitution. b) Multi-system - all tri-substitution c) Heterocyclic nitrogen system. No pri. or sec. amine -carbonyl or ether oxygen.	------	------
NMR Chromatographic Fractions and Material "Per Se"	Two aromatic proton signals, I and II. II, ratio aromatic hydrogen to aliphatic hydrogen, at least 3/1.	One aromatic proton signal, I. Signal strength indicates 1/3 amount present in L-793 and L-742	One aromatic proton signal, but different from I and II.

Conclusion: The fluids contain one or more components as inhibitors with an aromatic secondary amine structure. The findings suggest components of the type -



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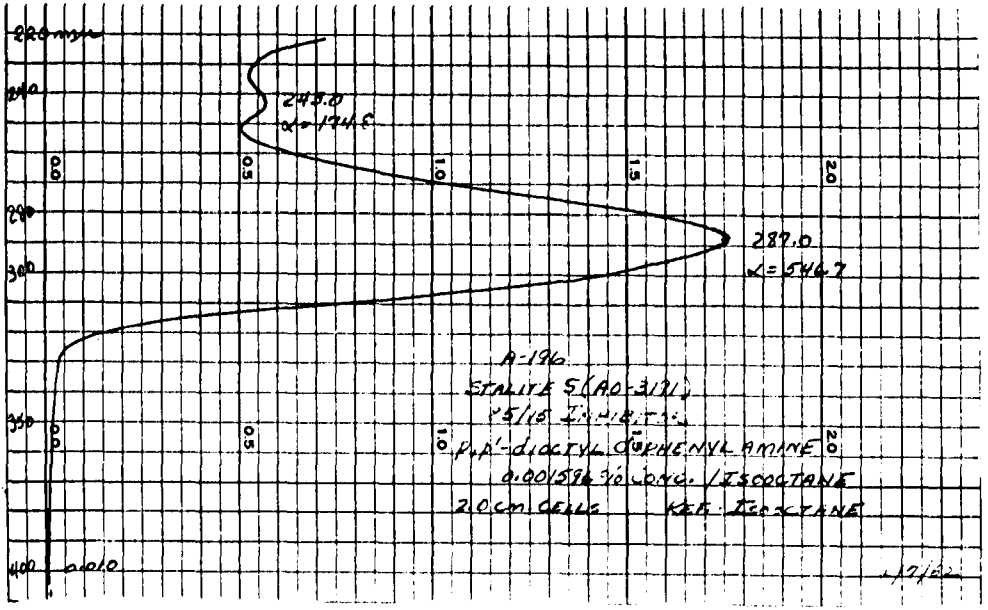

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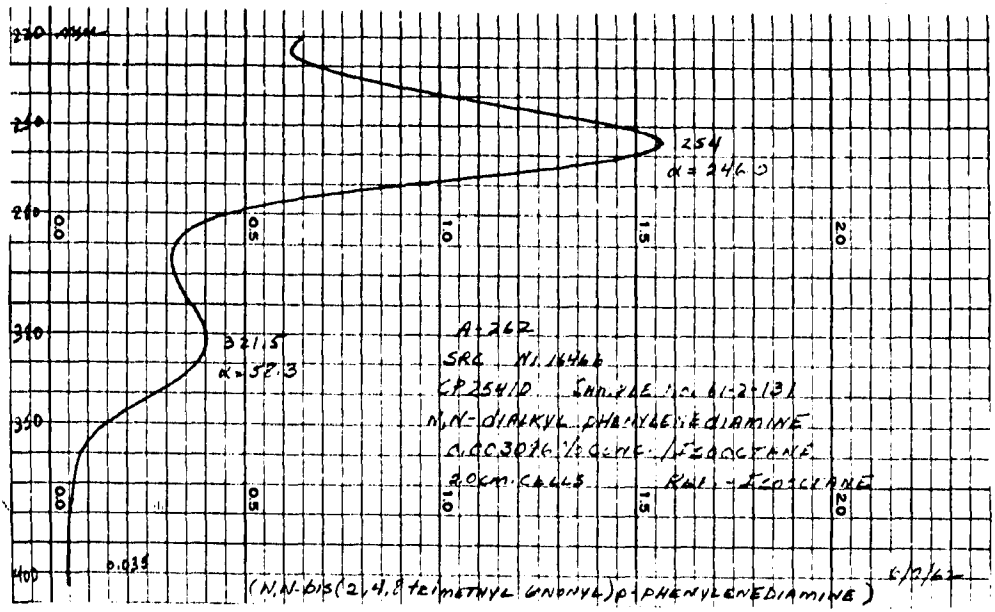

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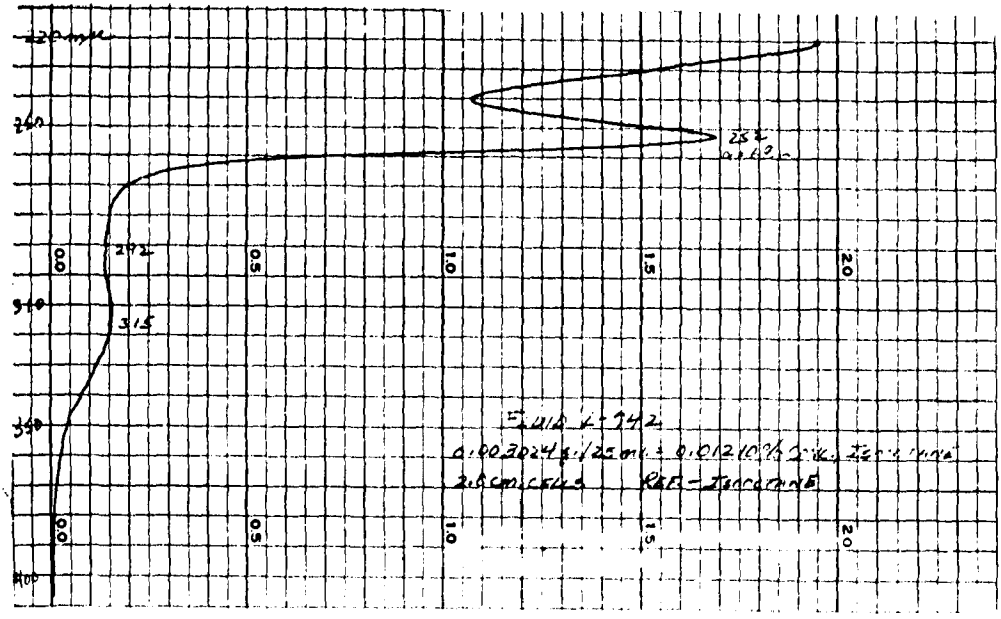

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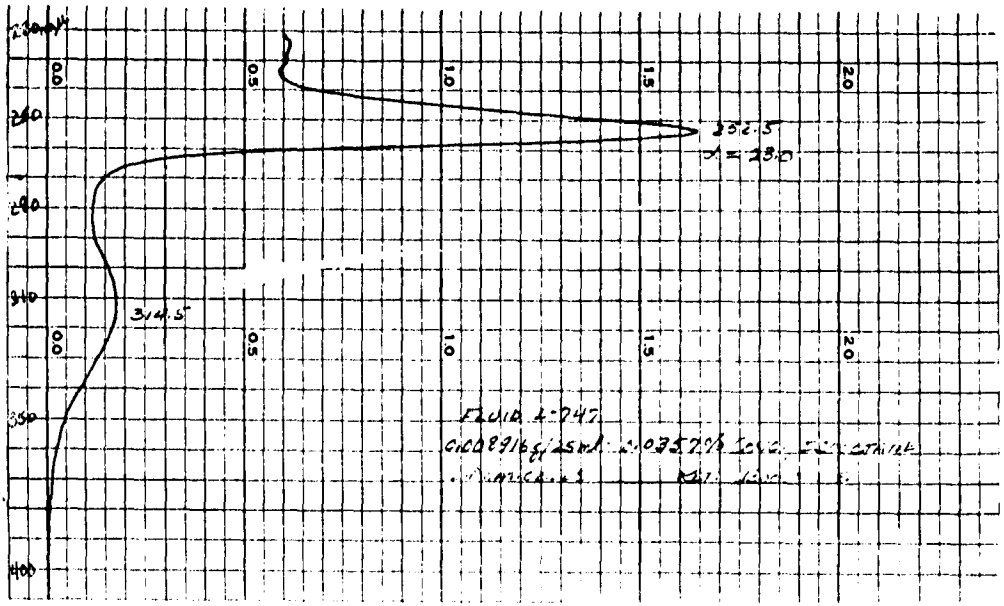

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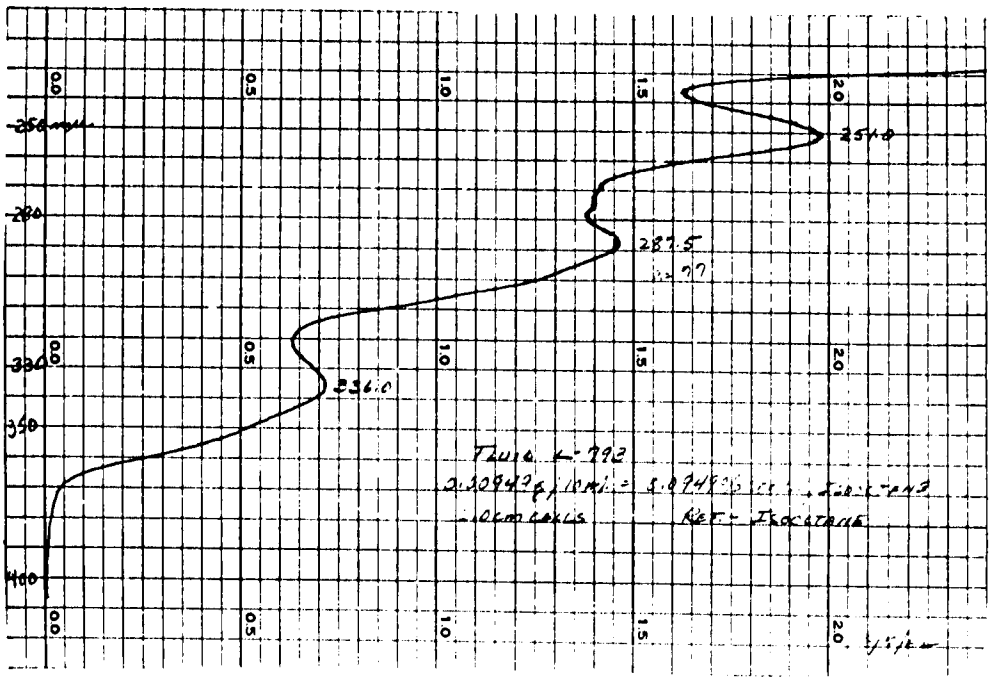

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SECTION F

Evaluation of Infotronics CRS-1 Integrator for NMR Signals

Introduction

The Infotronics CRS-1 Digital Chromatograph Readout System is designed for integration of signals obtained from a gas chromatograph. It has been found to be very satisfactory in this use. Since it possesses potential advantages of speed and accuracy over other methods presently available for integration of NMR signals, it has been evaluated for this use.

Summary

The Infotronics Corporation Model CRS-1 Digital Chromatograph Readout System has been evaluated as a method of integrating NMR signals. This instrument was evaluated with and without signal preamplification using both the signal taken directly from the Varian HR-60 NMR spectrometer and the base line stabilized signal obtained from the Varian Model V-3521 integrator. Two major limitations in usefulness of this instrument were found. Difficulty in zeroing the integrator before integration was observed when using the signal obtained directly from the NMR spectrometer as well as a tendency of the zero position to drift. These difficulties were minimized by using the base line stabilized signal from the Varian integrator. The second limitation observed was a tendency to discriminate against peaks with a low signal to noise ratio. In a sample containing both a strong and a weak peak, the weaker peak may either be omitted, or an improperly low integral value recorded. With sufficiently concentrated samples of high signal to noise ratio, this instrument was found to perform well, being both accurate and rapid.

Analytical Studies

A. Description of the Infotronics Integrator

The Infotronics Model CRS-1 integrator is designed specifically as an adjunct to laboratory gas chromatographs. The instrument is intended to produce a printed record of the areas of the chromatographic peaks, with the time of emergence of each peak shown opposite the recorded area. Input to the integrator is an electrical voltage of 50 millivolts nominal maximum (100 millivolts is permissible); the time integral of the input voltage is produced, the recorded value being 100 times the value of the integral in millivolt-seconds. Positive input voltages only are integrated.

Structurally, the integrator includes two components, the integrator proper and the printer which produces a printed tape listing the integrals of successive peaks. Functionally, the integrator component in turn contains two principal elements, an integrating unit and a peak-sensing unit. The integrating unit comprises a voltage-to-frequency converter and a counter; the peak detector is essentially a differentiating element which detects changes of slope indicative of the start, top and end of a peak. The sequence of operations of the integrator and printer is as follows:

Input	Operation
Start of peak (positive slope exceeding selected level).	Start counting.
Top of peak (zero slope).	Transfer time reading to printer.
End of peak (negative slope less than selected level).	Transfer accumulated count to printer, print count and time.

Controls for operating the integrator manually are also provided, and the printer includes a control for manual printing of total counts for a series of peaks.

B. Connection of the Integrator to the NMR Spectrometer

The radio frequency unit of the NMR spectrometer provides outputs for both oscilloscope and recorder. The arrangement of these (when using phase detection of the radio frequency signal) is shown in Figure 1.

The total resistance in series with the spectrometer output is less at the oscilloscope terminal than at the recorder terminal, so the CRS-1 integrator was first connected directly to the oscilloscope terminal. Initial trials, with the voltage-frequency converter and slope detector inputs of the integrator connected together, showed an apparent large zero offset. This was found to be caused by an alternating voltage present in the slope detector input. (The slope detector includes a magnetic amplifier energized at the line frequency.) Connection of a capacitor across the slope detector input served to bypass the alternating voltage present here, but to avoid excessive damping of the oscilloscope it was necessary to add a resistance in series, as shown in Figure 2(a). Because the input resistance of the voltage-frequency converter is 100 kilohms and the input resistance of the slope detector is 2 to 50 kilohms, depending upon the sensitivity setting, the result of using this circuit was a decrease of integrator sensitivity combined with an apparent decrease of recorder and oscilloscope sensitivity. A similar result was obtained by connecting the integrator directly to the recorder terminal of the spectrometer; the shunt capacitance at that terminal (see Figure 1) provided the required a.c. bypass.

A possible means of avoiding a.c. feedback from the slope detector and simultaneously reducing loading of the spectrometer output circuit was to place an isolating amplifier between the voltage-frequency converter and the slope detector. A transistor emitter follower was tried, as shown in Figure 2(b); it was effective for isolating the slope detector from the integrator input circuit, but the transistor base current was sufficient to produce an objectionable offset of the zero of the voltage-frequency converter.

A more elaborate isolating amplifier was tried in the form of a Leeds and Northrup No. 9834-2 electronic D-C null detector. It was connected as shown in Figure 2(c). The 1 megohm resistor in series with the input to the null detector served to reduce the sensitivity of this unit to the required level. It also slowed the response of the null detector; a voltage divider might have been preferable for reducing the input voltage. In general, however, performance of the apparatus assembled as in Figure 2(c) was satisfactory. Because the null detector had been borrowed from the manufacturer and had to be returned after a short time, some alternative amplifier was sought.

The alternative chosen was the use of a Leeds and Northrup No. 7401 pH meter as a preamplifier. The connections were as shown in Figure 3. The good linearity and low output resistance of the pH meter permitted it to be used to drive both the voltage-frequency converter and the slope detector. As set up, the range of the pH meter was ± 50 millivolts. A range perhaps twice this wide would have been better to prevent the meter being driven off-scale on large peaks. In other respects, performance of the pH meter as a preamplifier was satisfactory.

With all of the circuits tried, it was difficult to obtain a suitable compromise between sensitivity to small peaks and sensitivity to noise. The effect of large amounts of damping was not tried in the present work, but presumably the discrimination between noise and spectral peaks could be improved by use of greater damping with correspondingly slower sweep rates. A filtered output is available from the spectrometer at the recorder terminal, as indicated in Figure 1. To make the best use of this output, it would be necessary to apply a preamplifier because of the high internal resistance of the spectrometer and the low resistance of the integrator.

C. Evaluation

1. General Comments

All measurements were made with the zero of Infotronics integrator adjusted so as to give a counting rate of < 10 counts/sec. (manufacturer's recommendation). The effect of higher zero settings is discussed later.

By recording the CH_2 quartet in CH_3CH_2OH at various sweep rates, the resolution of the integrator was determined to be better than one peak every 2.0 seconds. The manufacturer reports one peak every 1.5 seconds and that resolution can be improved considerably if data is recorded on magnetic tape. Accurate phase settings appear unnecessary, see Figure 4.

2. Operation without Preamplification

With the Infotronics integrator connected to the recorder output of the HR-60 spectrometer a sample was examined which contained two peaks in the area ratio 6.0/1.0. Signal intensity was varied by adjusting RF. The results obtained are given in Table I; increasing total count indicates increasing signal.

Table I

Effect of Signal Intensity on Accuracy

Total Counts on Integrator	Observed Area Ratio* Infotronics Integrator	Planimeter
15,000 ± 600	∞	5.90
36,000 ± 1,500	5.41 ± 0.45	6.08
53,000 ± 2,000	5.83 ± 0.20	----
162,000 ± 10,000	5.55 ± 0.30	----

* Actual area ratio = 6.00

When the base line statilized signal obtained from the Varian V-3521 integrator (spectrum position) was used as in input signal for the Infotronics integrator, the same biasing against weak peaks was observed.

0692892

3. Operation with Preamplification

a. pH Meter

At low counting rates (weak signals) the same bias against weak peaks was observed. At high counting rates a bias against strong peaks was observed apparently due to overloading of the pH meter. For these reasons, no detailed study was made.

b. D. C. Null Meter

A synthetic mixture was prepared containing components of 61.1, 30.0 and 8.9 mole percent phosphorus. Signal intensity was varied by adjusting H_1, signal to noise ratio was varied by adjusting the frequency response. Representative spectra are found in Figures 5-8; the data obtained are summarized in Table II (attached). The results obtained are considerably better than those obtained with no preamplification, but the bias against weak signals remains.

To determine the effect of background level on accuracy, the relative areas of several of the multiplet components in the P^{31} spectrum were obtained at various background readings. As the background was increased, the area ratio decreased approaching the correct area ratio (with and without background subtraction). However, at the high background level needed to obtain the correct area ratio, the background was a major part of the total count. Since peaks with different line widths would have different backgrounds, no simple method is available to accurately subtract the contribution of the background from the observed count.

D. Suggested Operating Procedure

a. Connect recorder output of HR-60 to input of a preamplifier.

b. Connect output of preamplifier to input of Infotronics integrator.

c. After warm-up of equipment, adjust zero setting of Infotronics integrator to give a counting rate of less than ten counts/second (adjusting the red probe paddles if necessary).

d. Switch function control switch of Infotronics integrator to automatic (integration).

e. Record spectrum and integral.

f. Press total button on calculator. (If spurious peaks are recorded, adjust the sensitivity control of the Infotronics integrator to give decreasing sensitivity and repeat steps c-f.)

E. Feasibility and Recommendations

Under the operating conditions investigated, the Infotronics CRS-1 integrator is not satisfactory as an instrument for general use in integrating NMR signals. In certain cases of samples with strong signals, its operating speed may prove useful in obtaining area measurements from a large set of similar samples (where its accuracy on one of the samples can be independently determined).

12/62 - M. W. Dietrich, W. M. Trump, R. E. Keller

Table II

Data Obtained Using D. C. Null Meter

HR-60 Instrument Setting	Sample Composition								
	Actual			By Infotronics Integrator			By Planimeter		
	A	B	C	A	B	C	A	B	C
55 db in., HR = 4	61.1	30.0	8.9	62.2 ± 1.3	29.7 ± 0.7	8.1 ± 0.8	64.9	25.1	10.0
70 db in., HR = 4				63.4 ± 0.6	30.2 ± 0.8	6.4 ± 0.5	60.7	30.8	8.4
55 db in., HR = 1				62.8 ± 1.2	30.4 ± 0.8	6.8 ± 0.6	60.0	29.7	10.3
70 db in., HR = 1				67.1 ± 0.4	29.7 ± 0.4	3.3 ± 0.2	63.7	26.6	9.7

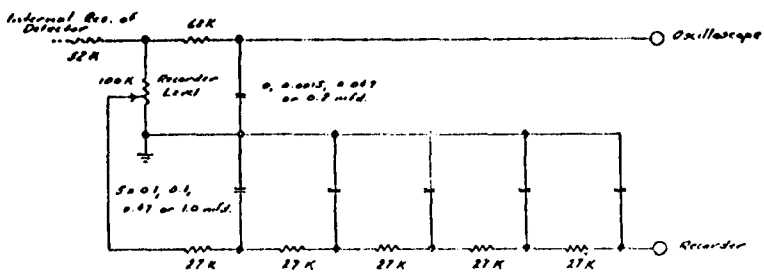

Fig. 1. Output Circuit of Vh311 Radio Frequency Unit (HR Phase Detector).

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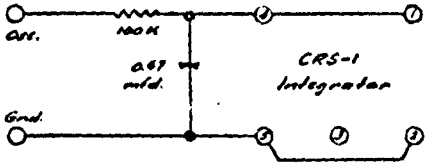
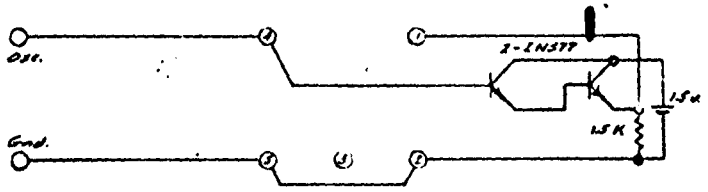
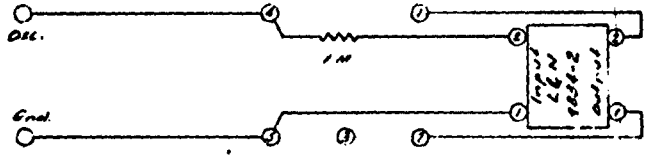


(a) Bypass for a.c. from slope detector.



(b) Transistor driver for slope detector.



(c) LEN Null Detector as driver.

Fig. 2. Circuits for avoiding feedback of a.c. from slope detector into integrator.

0692897

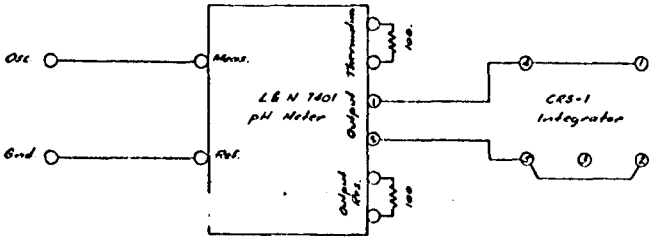
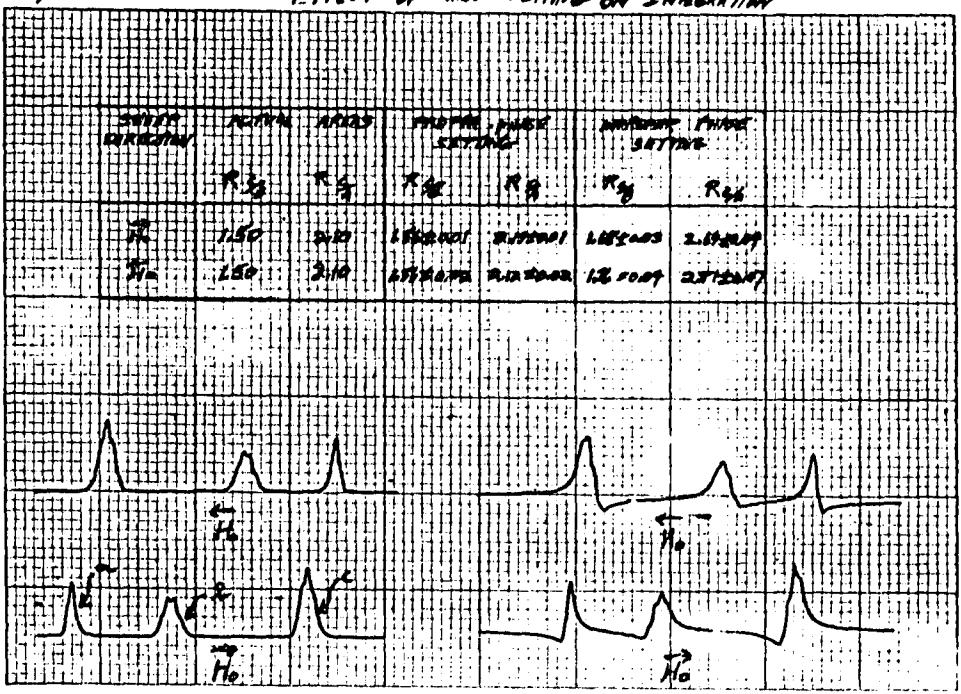


Fig. 3. Connection of pH meter as preamplifier.

0692898

FIG. 4

EFFECT OF PHASE SETTING ON INTEGRATION



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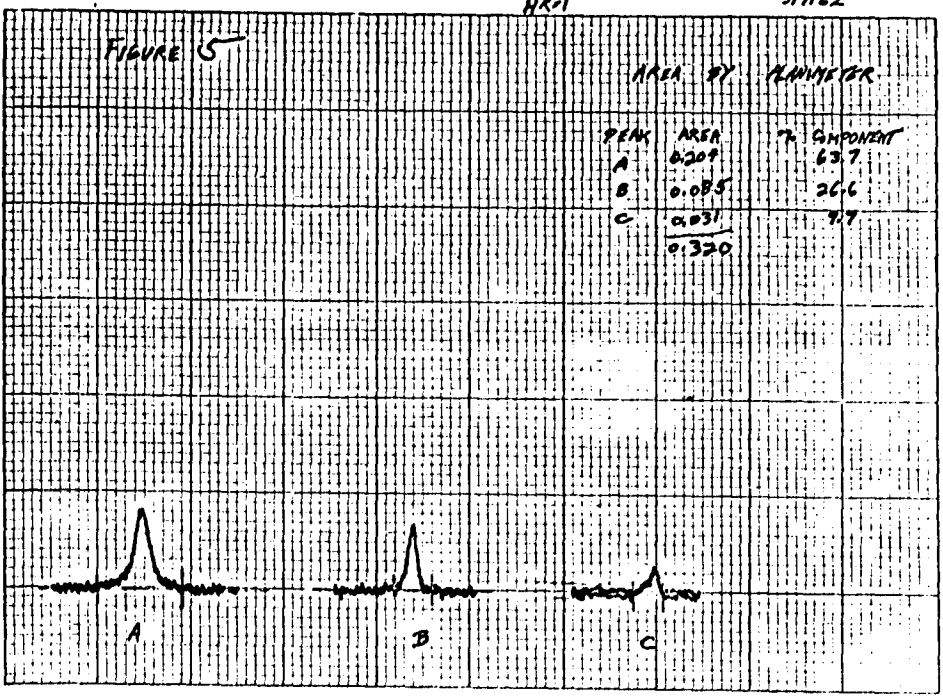
SR=10x50
Rodbin
x=100, y=.5
HR=1

3/11/62

FIGURE 5

AREA BY PLANIMETER

PEAK	AREA	% COMPONENT
A	0.209	63.7
B	0.085	26.6
C	0.031	9.7
	0.320	



53.

0692900

K+E 10 X 10 TO THE INCH 359T-5G

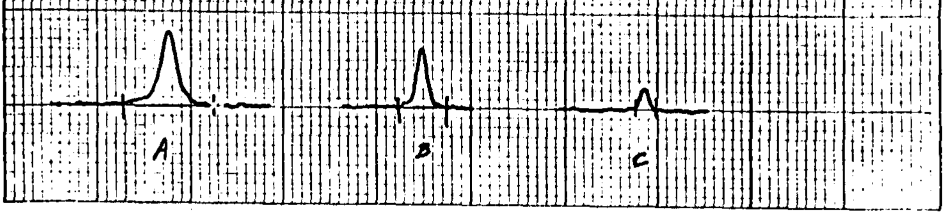
R=10X50
10 dk IN
X=100, Y=.5
NR=9

S(21)6

FIGURE 6

AREA BY PLANIMETER

PEAK	AREA	MOLE %
A	0.187	60.7 %
B	0.095	30.8
C	0.026	8.4
	.308	



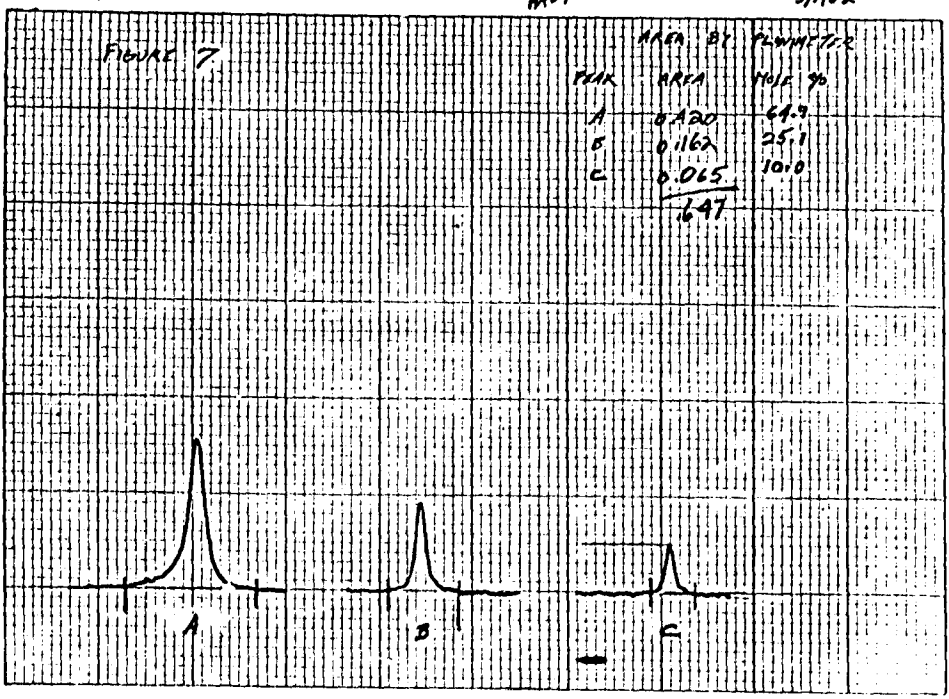
54.

0692901

K-E 10 X 10 TO THE INCH 359T 50

SR=10X50
ESA=W
R=1M, y=0.5
HA=9

3/1162



0692902

SECTION G

NMR Determination of Methyl Lactate in First Step Reaction Mixtures

Introduction

In the development of a synthetic lactic acid process, it was found that an analytical method was needed to determine the methyl lactate (ML) in first step reaction mixtures. NMR spectra of the pure materials, as well as typical reaction mixtures, were obtained and analyzed. It was found that an NMR peak specific for the methyl of the ester in the presence of methyl alcohol and residual lactonitrile could be used for analytical purposes.

Summary

A method was developed based on the measurement of the area of the methyl peak of the ester in ML. The weight percent ML is determined from a calibration curve obtained from area measurements of standard mixtures of ML and methyl alcohol. With this method it is possible to determine the weight % ML covering the range 0-100% with an accuracy of about $\pm$ 1% absolute. Other methyl esters are the only components expected to interfere with this method.

The method developed is preferred to a gas chromatography procedure when precise data are required. The NMR method is less rapid than the gas chromatography procedure and it will probably not be the method of choice where many samples and the need for less precise results are involved.

Analytical Studies

No analytical studies were carried out. The VPC method developed was chosen for routine analysis for the reasons given above. The NMR method will be used to provide more accurate data when needed, such as confirmation of doubtful VPC results.

NMR Determination of Methyl Lactate in First Step Reaction Mixtures

SCOPE

This method describes a proton NMR procedure for the determination of the concentration of methyl lactate in reaction mixtures containing methyl lactate, methanol, and impurities at relatively low concentration levels. The methyl lactate can be determined to about ± 1% absolute in the range 0-100%.

PRINCIPLE

The proton NMR spectrum of methyl lactate (see Figure I) contains peaks for the OH, H and two types of CH_3 present in methyl lactate. The same spectrum (OH peak shifted) is observed for reaction mixtures containing methanol and impurities (see Figure II). This analysis is based on the peak area of the methyl group of the ester. The other peaks in the methyl lactate spectrum cannot be used since impurities expected to be present would interfere in these measurements (other methyl esters would interfere with the measurement described).

APPARATUS AND REAGENTS

High-Resolution NMR Spectrometer (a Varian HR-60 was used).

Methyl Lactate - Reference of at least 98% purity.

Methanol - reagent grade.

Synthetic mixtures covering the concentration range of interest. The mixtures used were:

Weight, %	
Methyl Lactate	Methanol
35.0	65.0
40.2	59.8
43.9	56.1
47.9	52.1
51.7	48.3
54.9	45.1

PROCEDURE

A. Instrument Settings

The settings given are for a Varian HR-60 Spectrometer equipped with V-3521 integrator and a Mosely Autograph X-Y Recorder.

V-4311 RF Unit:	80 db In Recorder Level: Maximum Receiver Gain: 3 Frequency Response: WLØ Detector
V-3521 Integrator:	Input Level: 650 Output: Coarse X.1 Fine X.1 Frequency Response: 20 cps
Autograph XY Recorder:	X: 100 sec. full scale Y: 500 mVo - full scale
Slow Sweep Unit:	Increase 1 x 100
Sample:	5 mm., spinning

B. Calibration

Fill precision NMR cells (Varian or equivalent) with the prepared synthetic mixtures. Adjust the spectrometer carefully for maximum homogeneity and minimum drift. Using the reference mixture with highest concentration methyl lactate, record the integral curve. Make any adjustments necessary so that this integral is near recorder full scale. Also, make any adjustments necessary to optimize the appearance of the integral curve. In sequence, run the set of standard mixtures making spectrometer adjustments when necessary. Obtain as many integral traces for each sample as needed to give the desired measure of precision.

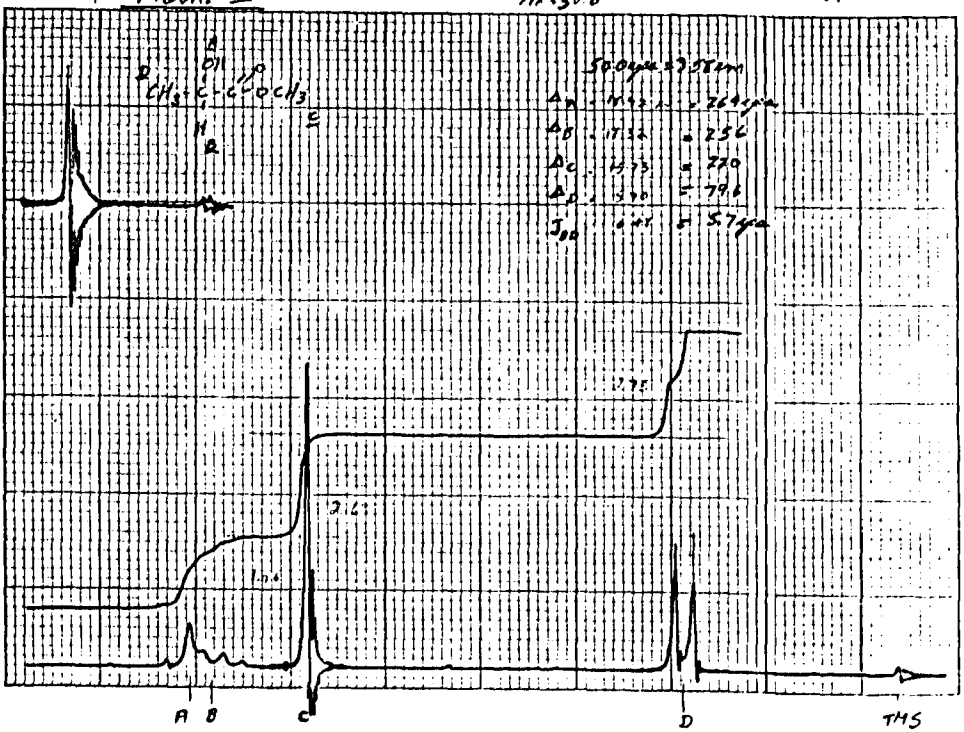
On each integral trace, draw parallel lines through the baseline before and after integration of the ester methyl peak in methyl lactate. Measure the distance between these baselines for each trace with an accurate ruler. Calculate the standard deviation (if desired) for each standard mixture.

On coordinate paper, plot the areas of each sample against the percent, by weight, methyl lactate. Draw the best smooth curve through these points. The working calibration curve set up for the method is shown in Figure III.

C. Sample Analysis

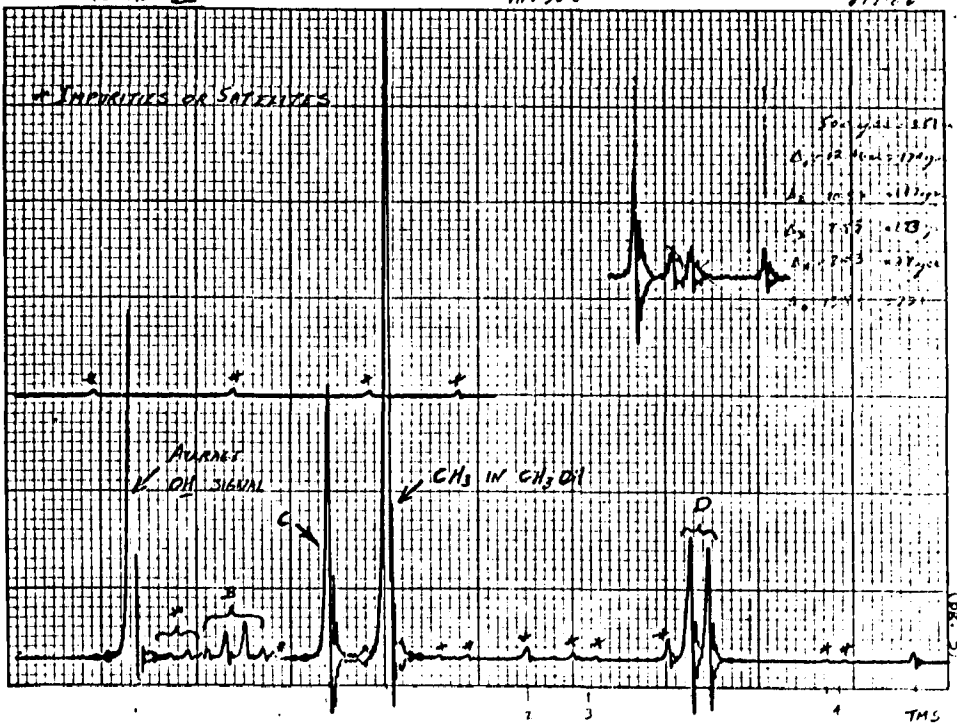
Prepare samples, obtain and analyze spectra by the procedure described for the synthetic mixtures. (If the samples and standards are run on different days, one or more of the standard mixtures should be re-run and the results compared to those obtained previously. If necessary, appropriate corrections in the areas obtained for the samples should be made.) Compute the peak area for each sample and equate this to the weight percent methyl lactate using the calibration curve.

Monsanto Chemical Co.
Organic Research Department
St. Louis, Missouri
8/62 - M. Dietrich, R. E. Keller



K&E 10 X 10 TO THE INCH 359T 50
KEUFFEL & ESSER CO.
ALBANY, N.Y.

FIGURE II



METHOD NO. 62-22
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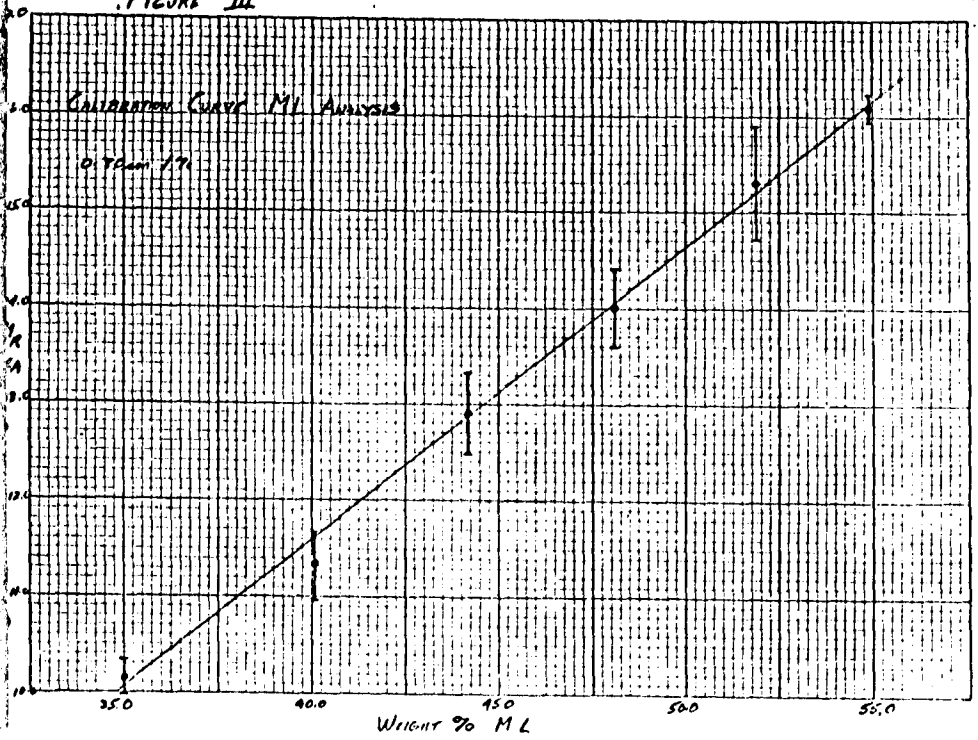
K&E 10 X 10 TO THE INCH 359T DG

FIGURE III



METHOD NO. 62-22

F.S.D.

0692909

SECTION H

X-Ray Diffraction Studies of Pentachlorophenol

Introduction

Caking and sublimation problems with plant pentachlorophenol were thought to be caused by crystalline form transitions. X-ray diffraction studies with a Norelco X-ray Diffractometer were carried out to provide basic data about the crystal forms and their transformation. Special sample preparation techniques were developed to overcome particle size and preferred orientation problems. A heated sample holder operating in the range of 25-100°C. was constructed to permit direct measurement of crystal transitions too rapid to be followed by intermittant sampling.

Summary

Results show that different diffraction patterns are given by pentachlorophenol when held above or below the transition temperature of approximately 60°C. The transition is reversible. The more complex diffraction pattern of technical pentachlorophenol indicates the presence of one or more crystalline impurities.

Quantitative measurements in the 2θ range of 32.0° to 34.5° were used to evaluate effects on the transition rate by chemical impurity, storage form, storage temperature, and crystal seeding. These studies indicate that the crystal change in itself is not the cause of caking of technical "Penta" in storage. Details of this work not reported here appear in Research Progress Report 4304, No. 1, entitled, "Pentachlorophenol" by M. E. Gibbs, R. W. Bucknell and D. B. Hines.

Analytical Studies

A. Development of Techniques

1. X-ray diffraction studies by pressed disk techniques

Problem of sample preparation were encountered in initial X-ray powder diffraction experiments with pentachlorophenol. The crystals are soft and it is difficult to grind them to the fine powder (200 mesh or smaller) required for powder diffraction work. The crystals are also highly susceptible to alignment along crystal planes (preferred orientation). Accurate determination of relative intensity of the various diffraction peaks necessary for quantitative analysis depends on uniformly small particles with completely random orientation.

It was found that 150 mesh "Penta" powder could be pressed into smooth, dense disks at pressures as high as 16,000 pounds per square inch, the maximum pressure developed by the laboratory Carver Press. Three grams of powder pressed in a 1 3/8" diameter, non-evacuable die gave a disk approximately 2 mm. thick. This disk can be substituted for the specimen holder in the Norelco Diffractometer and its pattern readily measured.

This technique, however, produced diffraction patterns exhibiting extreme preferred orientation with all peaks highly suppressed except for the one at 12.2° 2θ. Putting this technique on a quantitative basis appeared rather difficult, and alternative solutions were explored. However, the pressed disks look promising for future applications as a means of increasing sensitivity for a minor component or perhaps in the suppression of the diffraction pattern of an interferring component.

2. X-ray diffraction studies with nujol mulls of pentachlorophenol

The problems of particle size reduction and preferred orientation in "Penta" diffraction samples were largely

overcome by preparation of a mull of Penta and Nujol. The mull is prepared by weighing 0.2 grams Nujol into a 2 ml. stainless steel WIG-L-BUG grinding vial. Penta is added equivalent to exactly 3.5 times the weight of Nujol. Prilled Penta may be used directly in preparing the mull but flaked Penta was pre-ground on a Wiley intermediate mill to 40 mesh. After the grinding vial is charged, two 1/4" stainless steel balls are added. The vial is capped and the contents ground for 3 minutes in a model 3110B WIG-L-BUG. The contents of the vial after grinding are transferred to a Norelco standard aluminum powder diffraction specimen holder and a plane sample surface is prepared by pressing with a microscope slide or other smooth flat-surfaced object. The diffraction pattern is recorded using the following instrument settings on the Norelco Diffractometer and Electronic Panel: 35 kilovolts, 25 milliamperes, medium millispere range control, 2 ratemeter scale factor, 0.8 multiplier, 4 time constant, proportional counter, 1675 counter voltage. If the total diffraction pattern is of interest the sample is scanned over a 2θ angle range of 10-50° at a rate of 1° per minute. For measurement of the ratio of the two crystalline forms present, the 2θ regions of 32.0 to 34.5 are recorded at a scan rate of 1/4° per minute. The peak height ratio of the intensity peak at 32.7° 2θ to the peak at 33.0° 2θ was used as an empirical representation of the amount of the higher temperature crystal form present.

The work necessary to put the method on an absolute basis was considered impractical because of the difficulty of preparation of standards with known ratios of crystalline forms.

3. X-ray diffraction studies at variable temperature conditions

In the exploration of means to accelerate the crystal form transition, a study was made of the transition rate at temperatures just below the transition temperature. A heated specimen holder, Fig. 1, was constructed to permit measurement of the change in diffraction pattern with time as the temperature was varied. The special

holder was milled from a solid 5/8" x 1 5/8" type 2024-T4 rectangular aluminum alloy bar. The holder is heated with a Watlow GLE2A Cartridge Heater, 100 watt, 115 volt, available from the Watlow Electric Mfg. Co., St. Louis, Mo. The raised "island" in the sample cavity prevents fissuring of molten samples upon solidification and also houses a No. 30 teflon-insulated, iron-constantine thermocouple probe. The temperature is registered on an Leeds and Northrup Speed-O-Max Model H recorder equipped with a 0-200°C. iron-constantine scale. Electrical connection of heater and thermocouple were made through a hole drilled in the diffractometer x-ray scatter shield, Fig. 2.

B. Experimental Findings

1. Confirmation of crystalline form transition

Preliminary experiments carried out with pure pentachlorophenol and with Monsanto and Reichhold technical "Penta" confirmed that exposure of Penta to a temperature of 75°C. for several hours or melting it gives a product with a changed diffraction pattern. Examination of samples undergoing transition shows several intensity peaks characteristic of both crystal forms and their ratio changes with time. The two regions in the pattern where this change is most evident is the 2θ range of 11.5 to 13.0° and 32.0 to 34.5°. The 11.5° to 13.0° region had limited use in quantitative measurement because intensities here seemed more affected by sample surface reproducibility. However, this region was favorable for study of samples showing marked preferred orientation such as pressed disks or solidified melts because of the greater sensitivity.

2. Effects of purity on transition rate

Study of transitions at room temperature of solidified melts of pure pentachlorophenol and technical "Penta" from Reichhold and Monsanto exhibited sharp rate differences. Pure pentachlorophenol underwent essentially complete transition in about 4 hours whereas Monsanto and Reichhold Penta still showed substantial amounts of the high temperature form after 14 and 20 days respectively.

3. Effects of storage form on transition rate

Monsanto Penta stored as flakes at room temperature showed essentially no transition from the high temperature form in a five day period following flaking. But a portion of the same sample ground to a 40 mesh powder immediately after flaking underwent nearly complete transition at room temperature in the same five day period.

Monsanto flaked Penta stored for 9 months contained small amounts of the high temperature form.

Nujol mulls on pure pentachlorophenol in the high temperature form showed nearly complete transition within the forty five minute period required to prepare the mull and obtain its diffraction pattern. Transition of a solidified melt of this same material took four hours.

4. Exploration of practical methods to accelerate crystal form transition

The study of the transition rate of pure pentachlorophenol in the high temperature form showed essentially no change in 3 hours time while maintained at 55°C. which is just below the transition temperature. This same sample underwent nearly complete transition at room temperature in about four hours.

5. Transition of Monsanto Prilled "Penta"

Freshly prilled Monsanto "Penta" showed only slight transition from the high temperature form over a 30 hour test period signifying that this physical form does not appreciably accelerate the crystal form transition.

C. Future Applications of X-ray Diffraction Techniques

This investigation illustrates several X-ray diffraction techniques that can be used to investigate crystal structure problems of the type described in this report.

1. The powder diffraction pattern is characteristic of a pure crystalline material and is useful in a) making identification, b) determination of purity, c) examination for crystalline changes brought about by decomposition or reaction to form different crystalline products, d) following appearance or disappearance of a crystalline phase, e) measuring transformation of a given substance to a different crystalline form, f) formation of solid solutions or amorphous phases, etc.

2. Measurement of selected diffraction pattern intensities often permits quantitative measurement of one or more crystalline components, the extent of a crystal form transition, rates of changes of crystalline phases and transition temperatures.

3. The special techniques of sample preparation devised should be useful in future studies of organic crystalline matter.

4. The production of diffraction patterns under variable temperature conditions should have future utility.

D. Acknowledgements

Acknowledgement is gratefully given to the following persons for helpful suggestions and support in this problem:

1. W. M. Trump for recommendation of heating and temperature measurement components.

2. To A. J. Bindbeutel for construction of the heated sample holder.

3. V. W. Saeger for suggestions pertaining to preparation of pressed disks of pentachlorophenol.

4. E. D. Pierron and R H. Munch for suggestions on sample preparation by the Nujol Mull Technique.

12/62 - D. B. Hines, R. E. Keller

FIG 1: X-RAY DIFFRACTION HEATED SAMPLE HOLDER

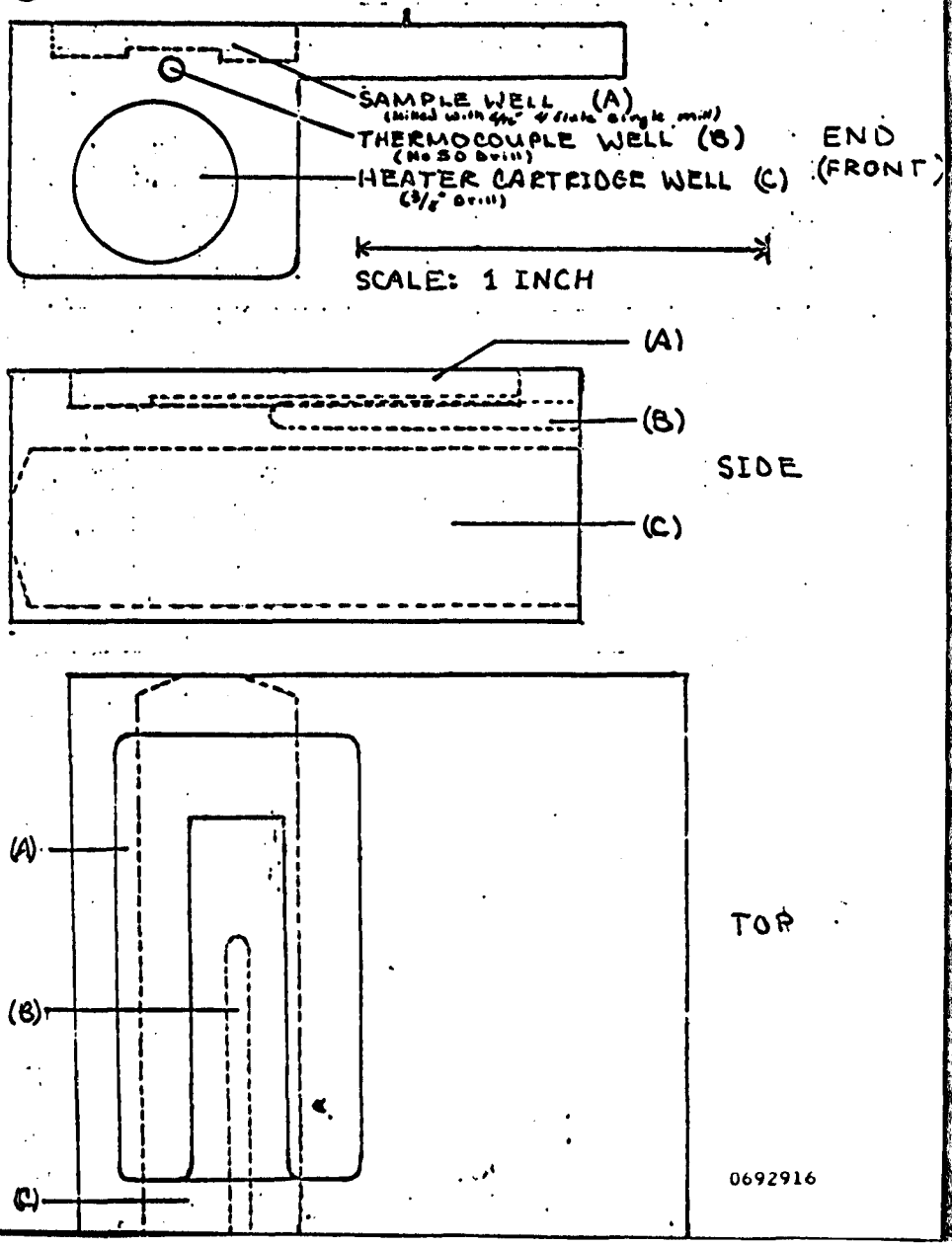
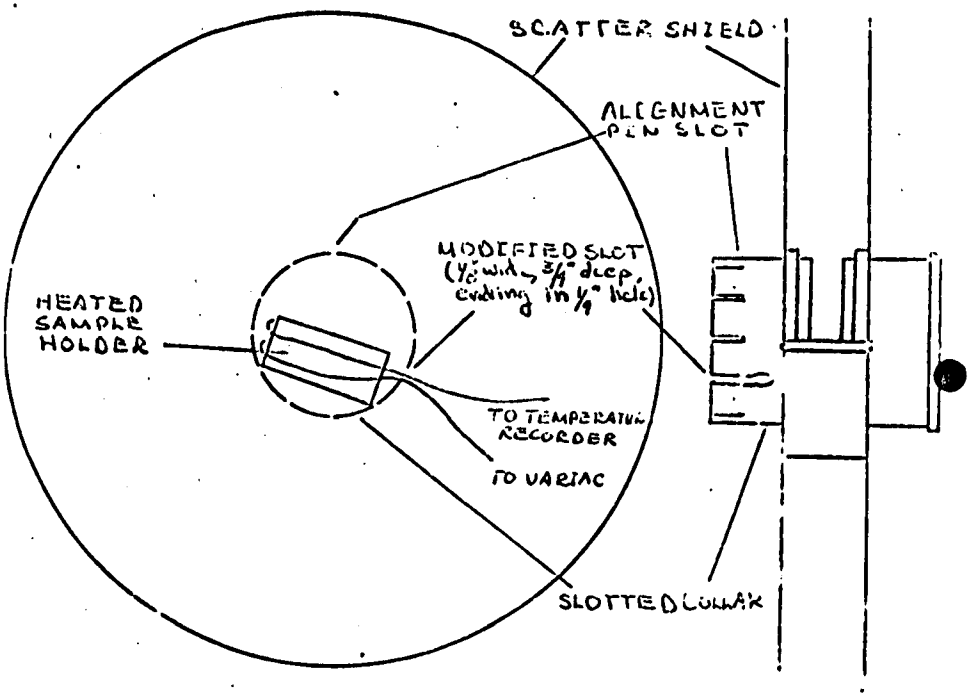


FIG 2: X-RAY SCATTER SHIELD MODIFICATION



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SECTION 1

Identification of Contaminants in para-Phenetidine

Introduction

In the continuous hydrogenation of p-phenetidine, a precipitate was formed that caused a quality problem in the W.G.K. p-phenetidine.

Analytical attempts to identify the organic structures of the contaminants in the p-phenetidine were made by application of infrared spectroscopy. These identifications were attempted using a sample of polymer extracted from p-phenetidine that had been returned from Nitro.

Summary

Solid state infrared spectra (as KBr discs) showed the following structural characteristics of contaminants in p-phenetidine:

1. Secondary amine
2. Aromatic nucleus
3. Aliphatic hydrogen
4. Ethoxy group
5. para-substituted aromatic

and the possible additional structures:

1. nitro group
2. 1,2,4-trisubstituted aromatic ring.

Other techniques - NMR, thin layer chromatography - were unsuccessful.

Analytical Studies

para-Phenetidine Contaminant

Sample - Polymer from para-Phenetidine, 5/24/62, R. Schubert (from material returned from Nitro).

Solubility - Estimated less than 1% soluble in water, benzene, chloroform, acetone, acetone + HCl, dioxane, benzene, DMF and tetrahydrofuran.

Molecular Weight - Average molecular weight range is 475 to 600 using Menzies apparatus and boiling toluene.

Number of Components - At least 3 or 4 as determined by solubility and thin layer chromatography.

Structures Found - Determined by infrared using KBr pressed discs of the samples. No satisfactory solvent was found for a nuclear magnetic resonance study.

(1) -N-, secondary amine

(2)  , aromatic nucleus

(3) -C-H, aliphatic hydrogen

(4) $-O-C_2H_5$, ethoxy group

(5)  R, para-substituted aromatic

Possible Additional Structures

(6) $-NO_2$, nitro group

(7)  , 1,2,4 trisubstituted aromatic ring

12/62 - R. E. Keller, B. Katlafsky

0692919

SECTION J

Identification of Plasticizers and Other High Boiling Esters

Introduction

A meeting of Research Supporting Technical Services personnel was held to discuss our current ability to analyze mixtures of plasticizers. The conclusions drawn also apply to other high boiling esters such as functional fluid base stocks. The three techniques having wide applicability are infrared absorption spectroscopy, nuclear magnetic resonance spectroscopy, and gas chromatography.

The purpose of this discussion was to make certain that the Organic Research Department personnel were well oriented with respect to the advantages and limitations of each technique. Because it was felt that the information presented at the meeting would be of interest to others, this report was drafted for distribution to staff members, group leaders and individual chemists in the plasticizer, resin materials and functional fluids application and process groups.

Summary

Infrared absorption spectroscopy, gas-liquid partition chromatography (GLPC) and nuclear magnetic resonance (NMR) are powerful tools for detecting, identifying, characterizing, and measuring plasticizers. Each method has its advantages and limitations. This report is offered as a guide to those working the plasticizer field in selecting the best physical analytical method of analysis to fit a particular problem.

Analytical Studies

The plasticizers in common use at present can be divided into the following classes:

1. Phthalate Esters
2. Isophthalate Esters
3. Terephthalate Esters
4. Phthalyl Glycolate Esters
5. Benzoate Esters
6. Maleate Esters
7. Fumarate Esters
8. Adipate Esters
9. Azelate Esters
10. Sebacate Esters
11. Citrate Esters
12. Acetyl Citrate Esters
13. Phosphate Esters
14. Sulfonamides
15. Chlorinated Hydrocarbons (Aroclors)
16. Hydrocarbons
17. Polyesters
18. Epoxy Compounds

Table I lists the common members of each class showing those of Monsanto origin, those of competitive origin, and the number of competitive producers of each (data taken from the Encyclopedia of Modern Plastics, Vol. 39, No. 1-a, 1962).

TABLE I

COMMON PLASTICIZERS

Type	Monsanto Origin	Competitive Origin	No. of Competitors
Phthlates	di-methyl		10
	di-ethyl		11
	di-butyl		28
	di-2-ethylhexyl (DOP)		25
	di-isooctyl (DIOP)		21
	di-isodecyl (DIDP)		22
	di-phenyl		none
	di-cyclohexyl		6
	di-tridecyl		7
	butylbenzyl (S-160)		4
	butyloctyl (S-165)		2
	isohexylbenzyl (S-260)		---
	isooctylbenzyl (S-261)		---
	isodecylbenzyl (S-262)		---

Table I (cont'd)

Type	Monsanto Origin	Competitive Origin	No. of Competitors
	(methylcarbityl) benzyl(S-263)		
		dicapryl	6
		butylcyclohexyl	2
		butylphenoxyethyl	---
		ethyleneglycol bis-(butyl)	---
Isophthalates			
	none	di-2-ethylhexyl	1
Terephthalates			
	none	di-2-ethylhexyl	---
Phthalyl glycolates			
	E-15(ethyl-phthalyl ethyl glycolate)		--- ---
	B-16(butylphthalyl butyl glycolate)		--- ---
	M-17(methylphthalyl ethyl glycolate)		--- ---
Benzoates			
	none	dietnyleneglycol dibenzoate	1
		dipropyleneglycol dibenzoate	3
		ethyleneglycol dibenzoate	1

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Table I (cont'd)

Type	Monsanto Origin	Competive Origin	No. of Competitors
Adipates			
	di-2-ethylhexyl (DOA)		23
	di-isodecyl (DIDA)		17
	di-n-octyl-n-decyl		14
	di-isobutyl		8
Maleates			
	dibutyl		5
		dioctyl	1
Fumarates			
	dibutyl		3
		dioctyl	3
Azelates			
	none	di-2-ethylhexyl	10
		di-isooctyl	7
		di-isobutyl	2
Sebacates			
	none	dibutyl	14
		dioctyl	14
		di-isooctyl	10

Table I (cont'd)

Type	Monsanto Origin	Competitive Origin	No. of Competitors
Citrates			
	none	triethyl	2
		tri-n-butyl	3
Acetyl Citrates			
	none	acetyl triethyl	1
		acetyl tri-n-butyl	1
		acetyl tri-(2-ethylhexyl)	1
Phosphates			
	triphenyl		8
	tricresyl		12
	S-140(cresyldiphenyl)		7
	S-141(2-ethylhexyldiphenyl)		---
	S-144(isoctyl diphenyl)		---
Sulfonamides			
	S-1-H(N-cyclohexyl-p-toluene sulfonamide)		none
	S-3(N-ethyl-p-toluene sulfonamide)		none
	S-8(N-ethyl-o,p-toluene sulfonamide)		none
	S-9(o,p-toluene sulfonamide)		none
		N-butyl benzene-sulfonamide	1

0692924

Table I (cont'd)

Type	Monsanto Origin	Competitive Origin	No. of Competitors
Chlorinated Hydrocarbons			
	Aroclor 1221		none
	Aroclor 1232		none
	Aroclor 1242		none
	Aroclor 1248		none
	Aroclor 1254		none
	Aroclor 1260		none
	Aroclor 1262		none
	Aroclor 1268		none
	Aroclor 4469		none
	Aroclor 5442		none
	Aroclor 5460		none
	Aroclor 2565		none
Hydrocarbons			
	HB-20		none
	HB-40		1
	dodecylbenzene		
		misc.	9

0692925

Table I (cont'd)

Type	Monsanto Origin	Competitive Origin	No. of Competitors
Polyesters			
	S-405)1,3-butanediol S-409)adipic acid S-411)polyesters		
		misc.	20
Epoxy Compounds			
		epoxidized soy bean oil	4
		epoxy tallates*	2
		epoxy tetrahydrophthalates	
		epoxy stearates	3
		misc	11

A. Infrared Absorption Spectroscopy

In general, infrared absorption spectra offer a rapid method of determining the class type of an unknown plasticizer (parent acid of the esters type, sulfonamides, phosphates, etc.). The absorption patterns are very consistent for a given class and serve as proof for identification purposes. Identification of a particular compound within a class requires a critical comparison of the spectrum of an unknown material with that of a reference spectrum. Often the positive identification of a given compound in a class is not possible because unless the IR spectrum is obtained under special conditions, the small differences that exist are not easily discernible. For example, the spectra of diisooctyl and diisodecyl phthalate are practically identical.

For mixtures, each case must be considered almost individually. However, the following general rules will apply:

1. For mixtures of two or more compounds in a class (i.e., butylbenzyl, dibutyl and dibenzyl phthalates) infrared will not detect or differentiate the components, only indicate that a phthalate is present.

2. In mixtures of plasticizers of different classes (i.e., fumarates and maleates) infrared spectra will often, but not in every case, be useful in detecting the presence of each of the several classes of plasticizers present.

3. Hydrocarbons in the presence of the other classes of plasticizers cannot be detected directly. Quantitative analysis of such a mixture will give a differential measurement of the hydrocarbon.

A qualitative infrared absorption scheme is attached which can be used to identify the majority of the plasticizer classes on the basis of the presence or absence of key absorption bands in the spectrum. A bar graph is attached showing the characteristic absorption patterns for each plasticizer class. The wave length in microns for these characteristic bands are:

1. Phthalates

5.8
7.9
8.8-8.9
9.3-9.4
9.6-9.7
13.4-13.5
14.2-14.3

2. Isophthalates

5.8-5.9
7.7-7.9 (usually a doublet)
8.1
8.6
8.8
9.1
9.3
13.7-13.8
14.1

3. Terephthalates

5.8-5.9
7.9-8.0 (doublet)
8.9-9.1 (doublet)
9.8
13.7

0692928

4. Phthalyl Glycolates

5.7-5.8
7.8-7.9
8.3-8.4
8.9
9.3
9.6-9.7
13.5
14.3

5. Benzoates

5.8-5.9
7.6
7.8-7.9
8.5
9.0
9.3
9.7
14.0-14.1

6. Maleates

5.75-5.85
6.1
Broad band with four distinct peaks at:
7.7 -7.8
8.0 -8.1
8.25-8.35
8.6 -8.7

7. Fumarates

5.75-5.85
6.1
Broad band with two peaks at:
7.7-7.8
7.9-8.0
8.2
Broad band with two peaks at:
8.5-8.6
8.7
10.2

8. Adipates

5.75-5.85
8.0 -8.1
8.5 -8.6 (usually most intense)
8.8

0692929

9. Azelates

5.75-5.85
8.0
8.5 -8.6
8.8
9.1

10. Sebacates

5.75-5.85
8.0 -8.1
8.5 -8.6
8.85-8.95

11. Citrates

2.9 -3.0
5.75-5.85
8.4 -8.5
8.9 -9.0

12. Acetyl Citrates

2.9 -3.0 (weak)
5.75-5.85
7.75-7.85
8.15-8.25
8.45-8.55
8.75-8.85

13. Phosphates

No band in 5.7-6.0 region.
7.7- 7.8
10.3-10.6

14. Sulfonamides

3.0
No band in 5.7-6.0 region.
7.6
8.7

15. & 16. Hydrocarbons and Chlorinated Hydrocarbons

No absorption in 5.7-6.0 region.
No strong absorption in 7.5-9.0 region.

0692930

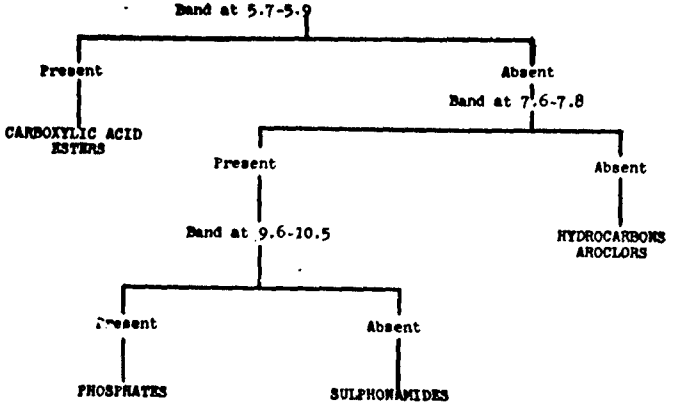
17. Polyesters

Spectra of polyesters resemble those of the parent acid derivatives (i.e., adipic acid polyesters spectra will resemble those of the simpler adipates).

18. Epoxy Compounds

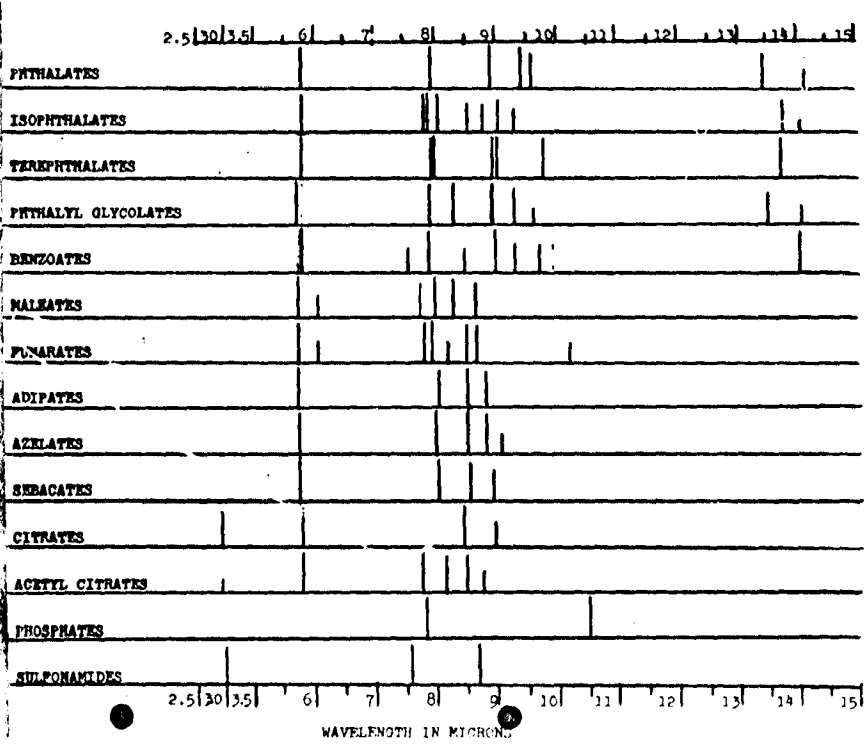
Insufficient data available to characterize this class.

QUALITATIVE INFRARED SCHEME FOR PLASTICIZERS



Wavelength in microns - bands are usually the strongest in the spectrum.

CHARACTERISTIC INFRARED ABSORPTION BANDS OF PLASTICIZERS



B. Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance is a useful analytical tool for determining the structure of unknown compounds and for determining concentrations of components present in a mixture. A particular NMR measurement is sensitive to only one nuclear species; at present, the Organic Research Department is equipped to perform analysis of proton, phosphorus, and fluorine containing compounds. In structural determination, use is made of the position (chemical shift) and the multiplicity of an absorption. The absorption position is characteristic of the molecular environment of particular nuclei; the peak multiplicity gives information concerning the presence or absence of nearby magnetic nuclei. NMR is useful as a quantitative tool since the area observed for an NMR absorption is directly proportional to the number of nuclei giving rise to the absorption.

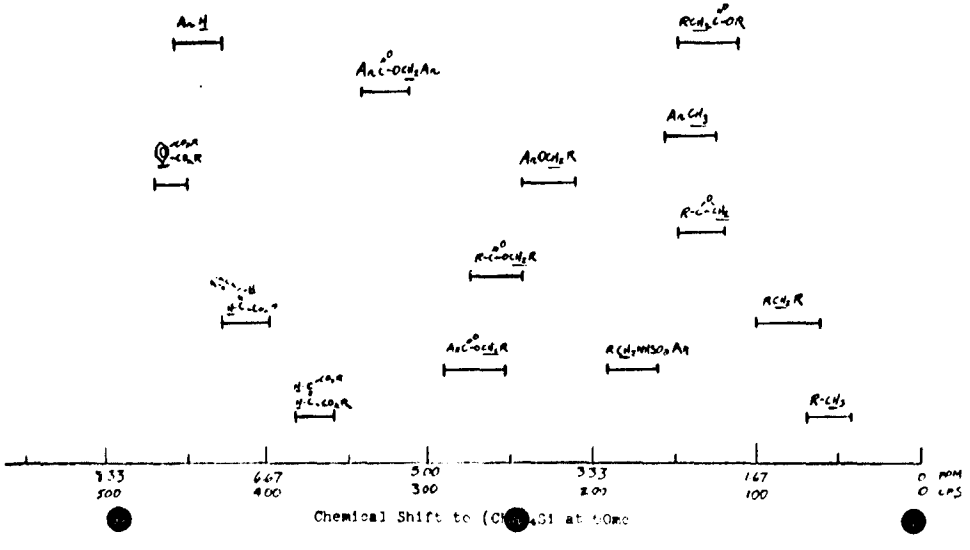
In using NMR for structure elucidation of plasticizers, a given plasticizer class cannot be assigned a characteristic absorption pattern which is unique to that class, as is possible with infrared spectroscopy. Instead, the chemical shifts of the peaks observed in the NMR spectrum are used to identify the structural groups present. Using this information, together with peak multiplicity and relative peak areas, a definite structural assignment can often be made.

The approximate absorption intervals of the structural groups commonly found in commercial plasticizers are indicated in the attached figure. If more than one proton type is present, the indicated absorption is due to the underlined proton type. The second attached figure is a graphical representation of the NMR spectra of a series of phthalate esters showing their characteristic chemical shifts and peak multiplicity; no attempt was made to represent relative peak areas quantitatively in this figure. The compounds listed are DMP, dimethyl phthalate; DEP, diethyl phthalate; DBP, dibutyl phthalate; DIOP, diisooctyl phthalate; DPP, diphenyl phthalate; and S-160, butyl benzyl phthalate.

There are several limitations to the information obtainable by NMR. In mixtures, or very complex molecules, because of the finite line width of the observed NMR signals, it is not always possible to distinguish between structural groups having similar chemical shifts. Also, in general, it is not possible to distinguish between a pure compound and a mixture of compounds containining the same structural groups.

PROTON CHEMICAL SHIFTS OF GROUPS FOUND

IN COMMON PLASTICIZERS



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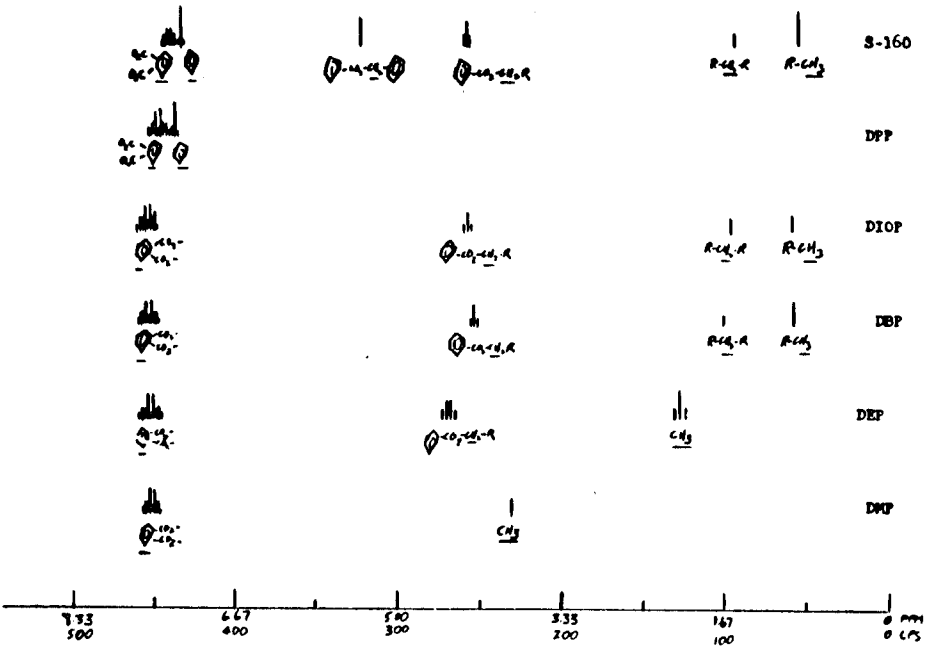
PROTON NMR SPECTRA OF SOME PHTHALATE ESTERS



Chemical Shift to $(CH_3)_4Si$ at 60mc

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C. Gas Chromatography

The following table summarizes our present capability in gas chromatography with respect to plasticizers. This represents the scope of our present experience and not necessarily the limits of capability of gas chromatography. Further experimentation and development of this technique may likely broaden its applications to plasticizers.

3/63 - B. Katlafsky, M. Dietrich, E. Emery, W. E. Koerner, R. E. Keller

0692937

Gas Chromatography Capability in Plasticizers

Plasticizer Systems	Advantages	Limitations	Estimated Time Required per Sample: Elapsed on Instrument (min.)	Man-min.
Dialkyl Phthalates	1. Resolution of mixed esters from the corresponding symmetrical esters (e.g., iso-octylbenzyl and butyl-2-ethylhexyl). 2. General resolution of a mixture of DOP, DIOP, DIDP, S-160, TCP, dibutyl-, dibenzyl- and ditridecylphthalates.		30	30
Dialkyl Fumarates and Maleates	1. Detn. of unreacted esters in bisfumarates. 2. Detn. of unreacted alcohol and other impurities. 3. Resolution of mixed esters from the corresponding symmetrical esters.	Do not resolve the higher maleates from the corresponding fumarates. (We can resolve the dibutyl and diethyl, but not the di-2-ethylhexyl and diisohexyl).	30	30
Alkyl Phosphates	Resolution of most mixed phosphates, such as the methyl-phenyl and butyl-phenyl series.	Cannot as yet resolve the 2-ethylhexyl-phenyl series (S-141).	30	30
Dialkyl Succinates, Adipates, Sebacates, etc.	The same capability should apply in general as with the dialkyl phthalates.			

SECTION K

Infrared Study of the Reaction Rate of Resorcinol in Sodium Sulfite Solution

Introduction

The literature reports that resorcinol in the presence of sodium bisulfite is sulfonated in several intermediate steps to yield sodium 1,3-dihydroxy-1,3,5-cyclohexanetrisulfonate and m-phenol sodium sulfonate as stable end products. Confirmation of this side reaction and reaction rate data were needed to optimize process conditions and minimize resorcinol losses in the acidification and quenched liquor storage steps of the resorcinol process.

Summary

An extraction procedure and infrared absorption method were developed for the measurement of resorcinol in saturated sodium sulfite solutions which provided analytical data to calculate rate constants. In the temperature range of 50 to 103°C. and the pH range of 6 to 12 the data indicated that at constant pH the reaction rate increased with temperature, and at constant temperature, the rate increased with acidity. Under the tentative operating conditions of pH 7.0 and 50°C., resorcinol is sulfonated in a saturated sodium sulfite solution at a rate of 1.0% per hour. NMR analysis of samples of resorcinol in a saturated sodium sulfite solution refluxed at pH 7.0 showed that sodium 1,3-dihydroxy-1,3,5-cyclohexanetrisulfonate and sodium m-phenol sulfonate were the sulfonation products formed.

Analytical Studies

A. Infrared Spectroscopy

Infrared absorption methods were used to study the disappearance of resorcinol in aqueous solutions saturated with sodium sulfite. This study was requested to provide reaction rate data as a function of pH and temperature to assist in optimizing process conditions and to minimize losses of resorcinol in the acidification and quenched liquor storage stages of the resorcinol process.

The literature [V. N. Ufimtseb, Zhur. Priktad. Khim., 20, 1199 (1947)] reports that resorcinol, in the presence of sodium bisulfite, is sulfonated. The sulfonation proceeds through several steps and 1,5-dihydroxy-5-(1,3-cyclohexadiene sodium sulfonate) and 2,5-dihydroxy-2,5-(cyclohexene disodium sulfonate) have been identified as intermediate products. The stable end products of the reaction are 1,3-dihydroxy-1,3,5-cyclohexanetrisulfonate and m-phenol sodium sulfonate.

Infrared methods were investigated to measure the resorcinol directly in aqueous solution. Attenuated Total Reflectance techniques proved unsatisfactory due to the poor long term stability of the optical bench settings which resulted in poor reproducibility. Direct transmission measurements of the solutions using thin cells with Irtran-2 windows were ruled out because measurements of either the 6.7 micron C=C ring stretching band or the 7.8 micron O-H deformation band showed interference from intermediate products. An extraction method using isopropyl ether was used to isolate the resorcinol from the reaction mixture. The resulting ether solution was analyzed directly using conventional infrared transmission techniques to determine the resorcinol concentration.

In the procedure used to isolate the resorcinol from the reaction mixture, a 20.0 $\pm$ 0.02 gram aliquot of the reaction mixture was cooled to room temperature in a water bath and the pH adjusted to 6.0 by bubbling in sulfur dioxide (SO_2) and using a pH meter. (In this study the reaction mixtures contained approximately 4% resorcinol and were saturated with sodium sulfite.) The solution was transferred to a 75 ml. separatory funnel, the beaker was rinsed with 10 ml. of isopropyl ether and the ether was transferred to the funnel. The system was shaken for 30 seconds, the phases permitted to separate and then shaken for an additional 30 second period. The ether layer was filtered through a cotton plug containing a layer of anhydrous sodium sulfate into a 25 ml. volumetric flask. The water layer was extracted in turn with a second 10 ml. portion of isopropyl ether and finally with a 5 ml. portion of solvent. The funnel was rinsed with a small portion of isopropyl ether and the rinsings were added to the filter. The isopropyl ether volume in the flask was adjusted by adding additional ether dropwise to the filter. Anhydrous sodium sulfate was added to the flask and the mixture shaken. A portion of this isopropyl ether solution was transferred to a 2 dram vial containing a fresh portion of anhydrous sodium sulfate and shaken. This solution was decanted and equilibrated with finely ground sodium chloride in another 2 dram vial. Resorcinol recoveries of 92-93% were obtained by this extraction and drying procedure.

The dried isopropyl ether solution was transferred to a 0.082 mm. rock salt infrared cell and the infrared spectrum was obtained using a 0.076 mm. solvent compensating cell through the region of 10.1-10.7 microns. Measurements were made at 10.38 microns and a background correction measured at 10.25 microns to determine the resorcinol concentration. The instrument conditions used were:

Instrument:	Perkin-Elmer Model 221 Double Beam Infrared Spectrophotometer
Optics:	NaCl prism
Slit Program:	990
Attenuator Speed:	4 seconds full scale deflection
Scanning Speed:	4 minutes/micron
Gain:	4
Suppression:	0
Chart Scale:	10 cm./micron
Sample Cell:	0.082 mm.
Reference Cell:	0.076 mm.
Solvent:	Isopropyl Ether

The resorcinol-sodium sulfite reaction was run under the following conditions:

pH	Temperature
4	70°
6	50
7	50, 70 and 90
8	50, 70
9	90, 103.5 (Reflux)
10	103.5
12.5	103.5

The large excess of sodium sulfite present in the reaction mixture does not buffer the solution. As the reaction of resorcinol proceeds, the pH rises approximately 0.3 to 0.5 pH units when about 25% of the resorcinol has reacted.

A plot of the analytical data, in the form of the logarithm of the resorcinol concentration as a function of time for pH ranges of 6-12.5 and temperatures of 50-103.5°C., shows that the reaction is first order with respect to resorcinol. These plots are shown in Figures 1-4. Plots of the resorcinol loss as a function of time under the conditions indicated above are shown in Figures 5-8.

The rate constants calculated for each pH and temperature condition studied by:

pH	Temperature	Rate Constant[A]	Rate Percent[B]
6	50°C.	0.0180/hour	1.80/hour
7	50°C.	0.0101 "	1.01 "
8	50°C.	0.0044 "	0.44 "
7	70°C.	0.0304 "	3.04 "
8	70°C.	0.0114 "	1.14 "
7	90°C.	0.118 "	11.8 "
9	90°C.	0.0443	4.43 "
9	103.5°C.(Reflux)	0.141 "	14.1 "
10	103.5°C. "	0.0900 "	9.00 "
12.5	103.5°C. "	0.0017 "	0.17 "

(A) Rate Constant = $k = \frac{2.303}{t_2 - t_1} \log \frac{C_1}{C_2}$

where C_1 = concentration at time t_1
and C_2 = concentration at time t_2

(B) Rate Percent = 100 k = percent resorcinol reacting per hour.

A graphical plot of the rate constant vs. pH is shown in Figure 9. The data obtained at 103.5°C. are curvilinear and suggest the data for the lower temperatures are also actually curvilinear with an extrapolation to a common zero point.

The data obtained under acid conditions of pH 4 at 70°C. are somewhat confusing. After one hour under these conditions, the resorcinol concentration is reduced about 1%. During the next three hours the resorcinol is regenerated so that at the end of four hours the resorcinol concentration is the same as the zero time sample. If bisulfite is the active reactant species in this reaction, then at pH 4, where the equilibrium should be shifted entirely to the sulfite ion form, some other complexing mechanism must be operating. Since resorcinol is regenerated under these conditions, the resorcinol complex must be loosely coupled.

B. NMR Spectroscopy

Analysis of NMR spectra obtained from samples of resorcinol in saturated aqueous Na_2SO_3 solution indicate the following transformation:

Resorcinol (A) $\xrightarrow{HSO_3^-}$ (B) $\xrightarrow{HSO_3^-}$ (C)

The rates of these reactions increase with increased temperature. Three samples taken from a solution under reflux conditions at pH 7 indicate the following approximate compositions:

3 hr. reflux	~50% A, 50% B
24 hr. reflux	~90% B, 10% ?
72 hr. reflux	~70% B, 30% C

Analysis of the NMR spectra and related reference materials indicate that (B) is sodium 1,3-dihydroxy 1,3,5-cyclohexanetrisulfonate or some closely related material, and (C) is sodium m-phenol sulfonate. Intermediate compounds between resorcinol and (B) and between (B) and (C) may exist.

12/62 - B. Katlafsky, M. Dietrich, R. E. Keller

FIGURE 1

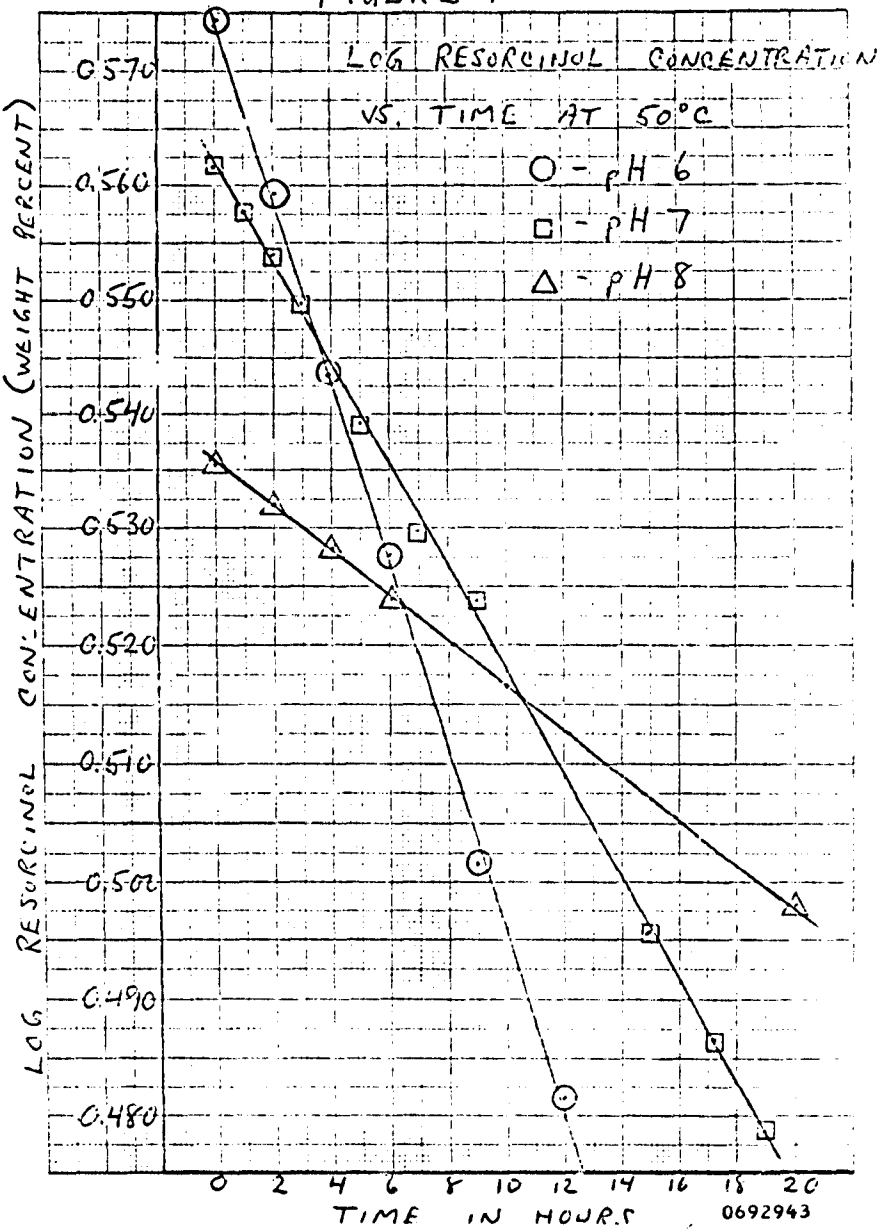


FIGURE 2

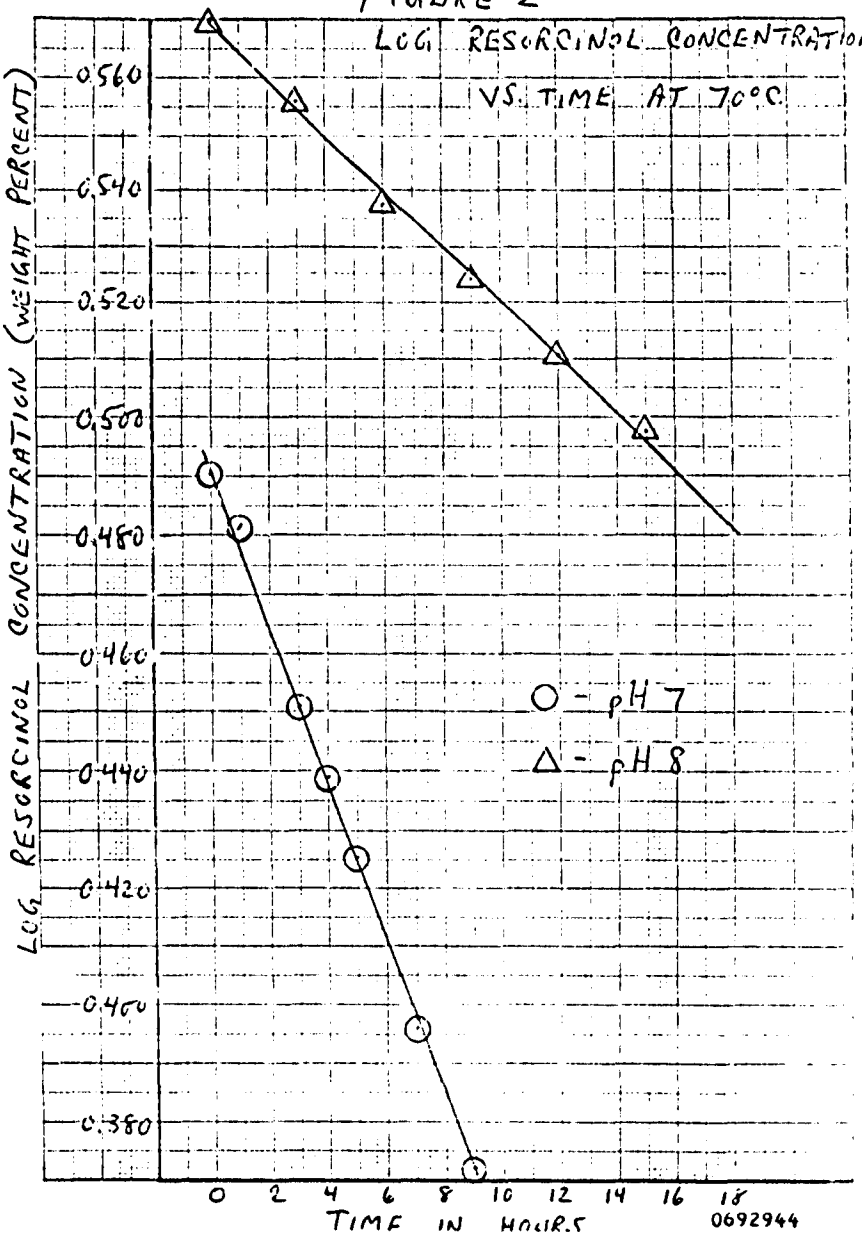


FIGURE 3

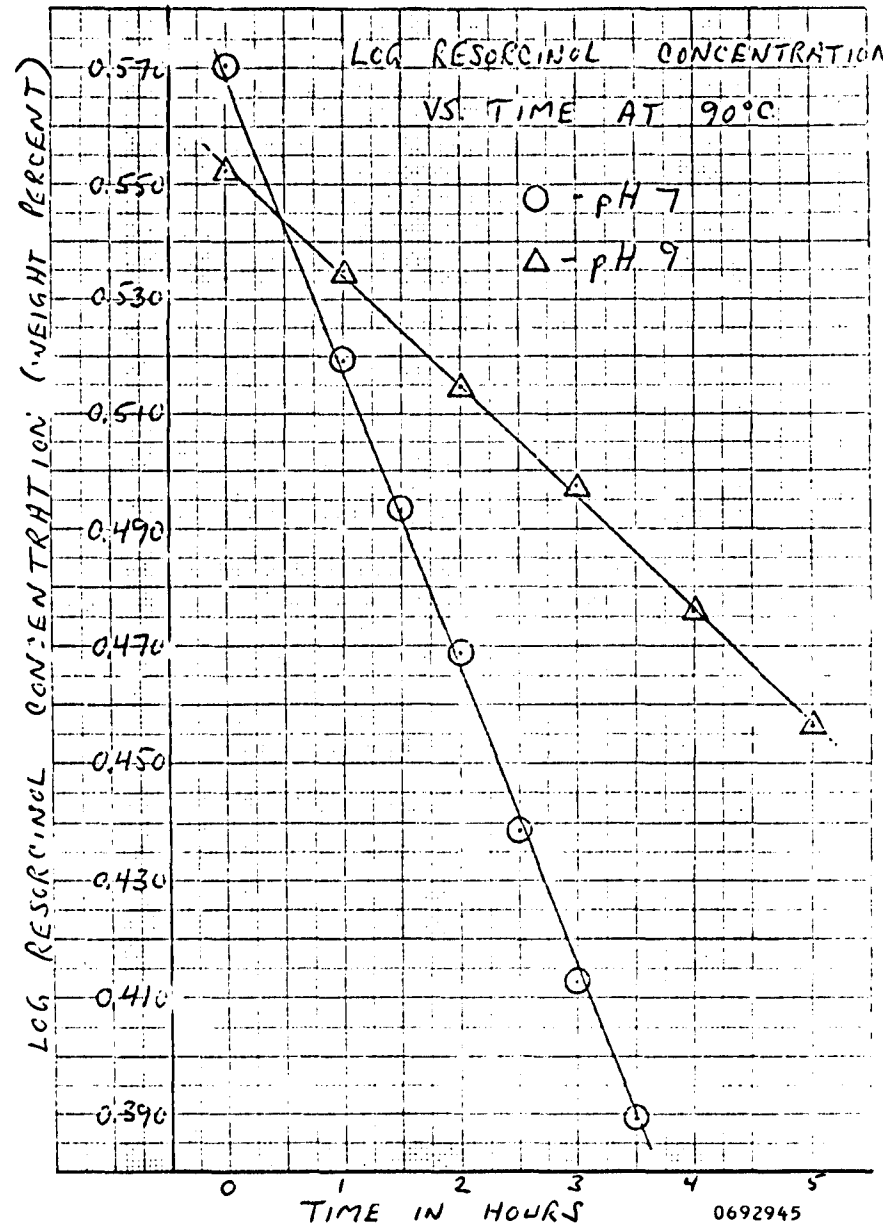
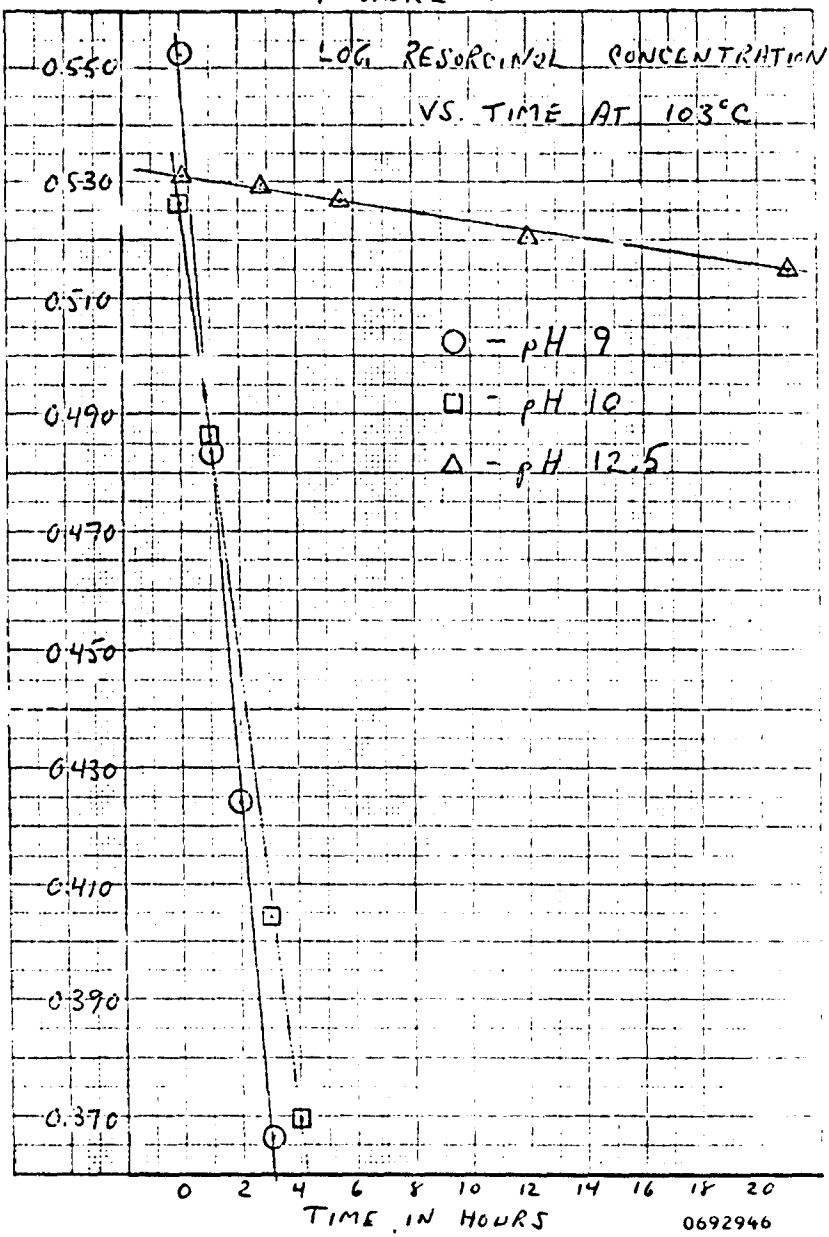


FIGURE 4



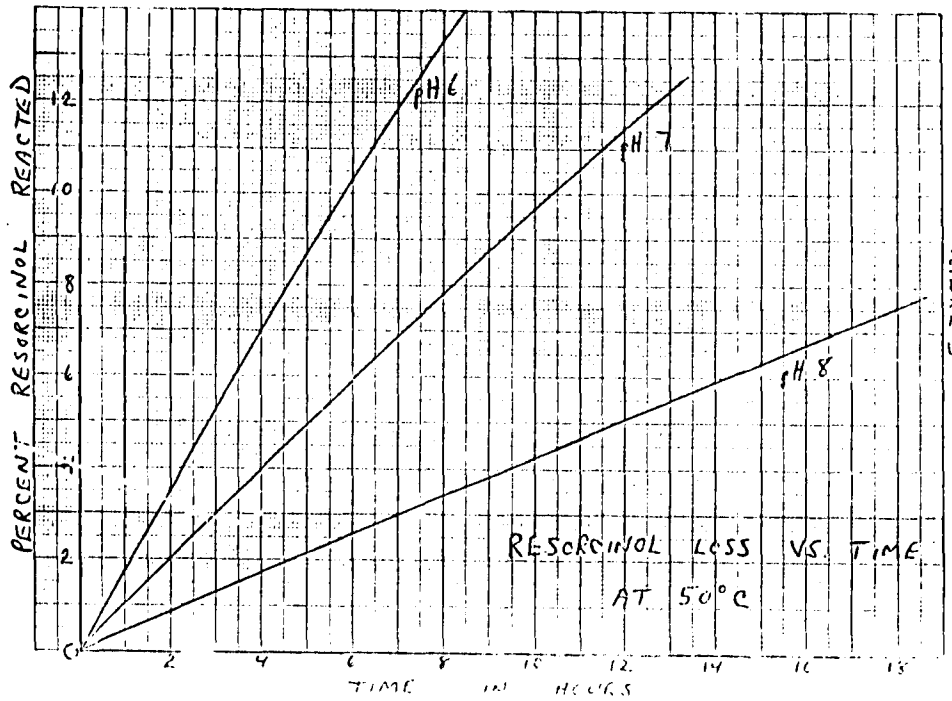


FIGURE 5

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FIGURE 6

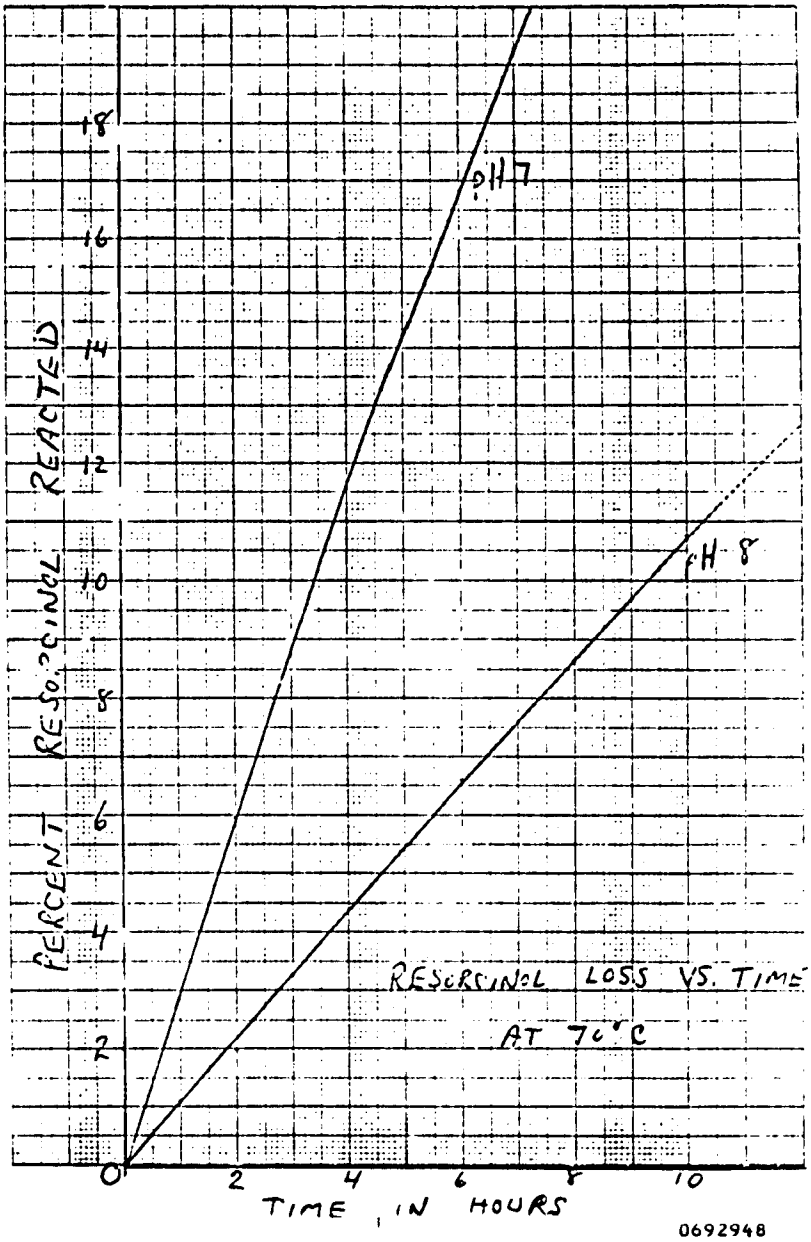

FIGURE 7

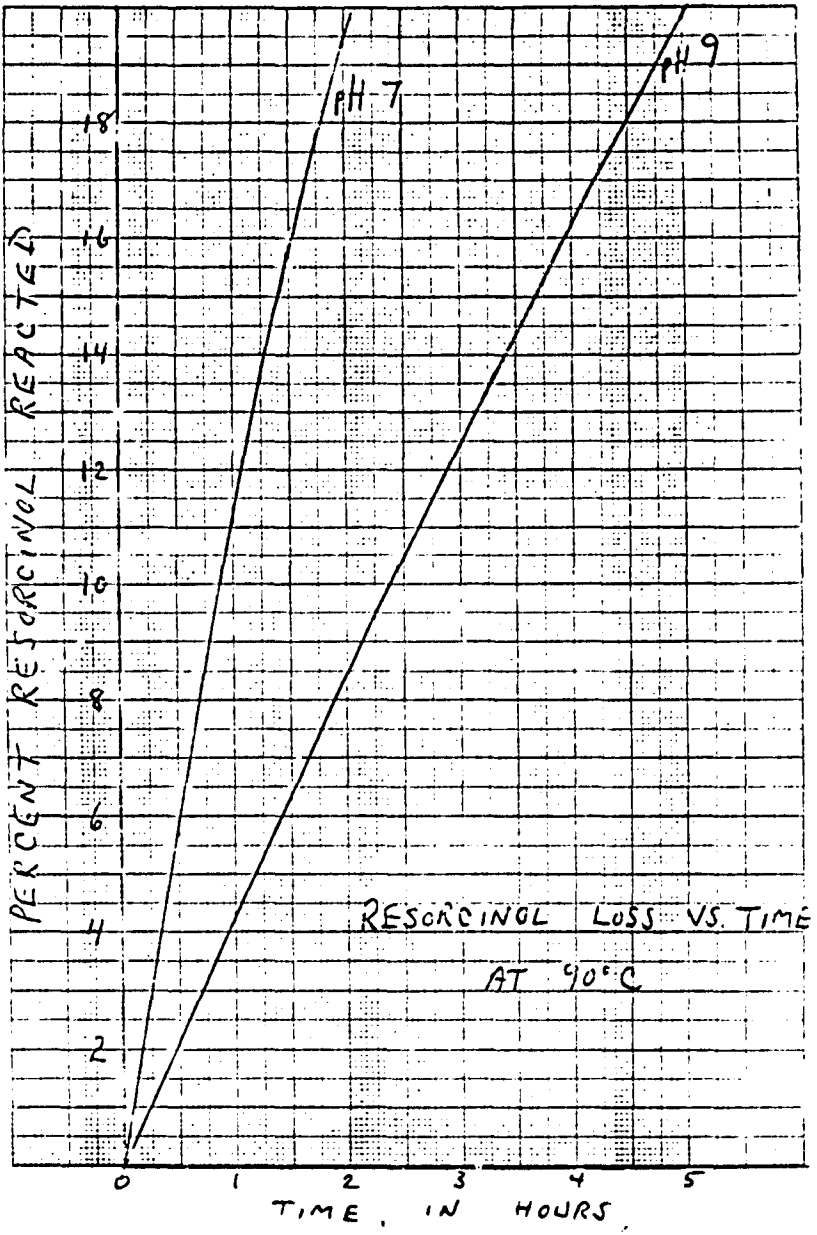

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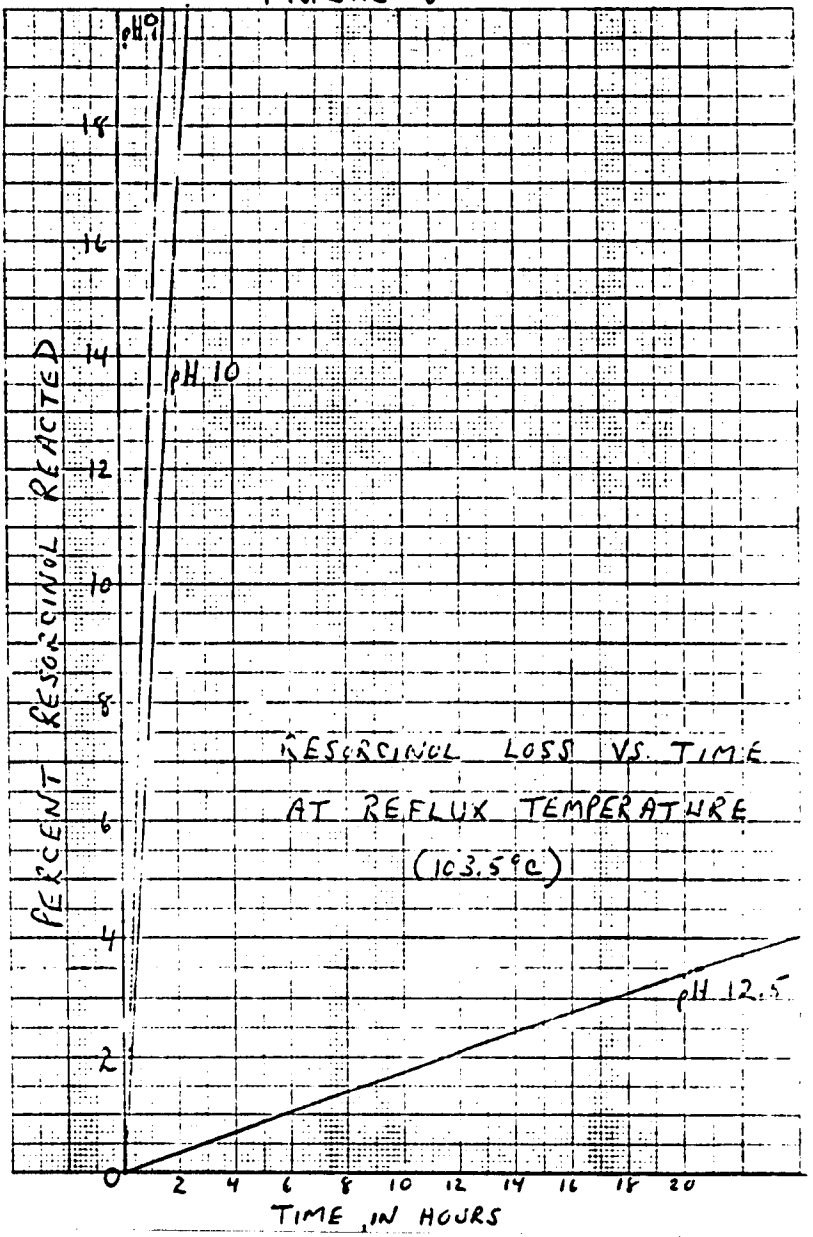
FIGURE 8



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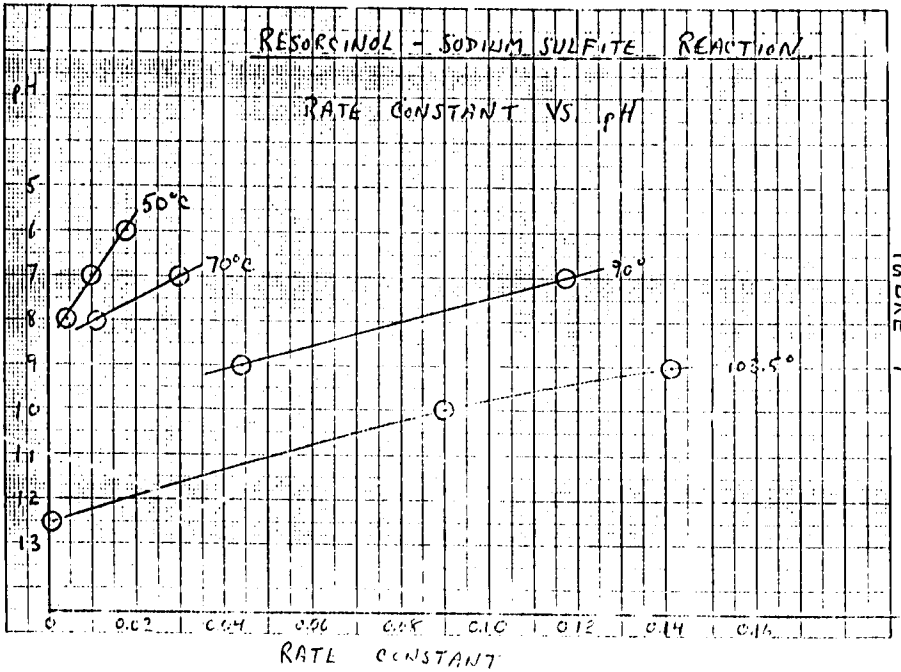

FIGURE 9

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SECTION L

Attenuated Total Reflectance Infrared Study of Sodium Phenate and Sodium Benzenesulfonate

Introduction

Conventional infrared analytical methods for laboratory and plant process aqueous streams have been limited by the intense water absorption which makes it necessary to use extremely thin cells. Problems in plugging or deposits of foreign material in cells of this type in process stream applications result in serious analytical errors. A new infrared technique, known as Attenuated Total Reflectance (ATR), is based on infrared spectra obtained by surface absorption and is independent of sample thickness. The latter feature permits design of sampling cells of sufficient thickness to overcome the sampling problems associated with the normal transmittance techniques. Sodium benzenesulfonate (NaBS) and sodium phenate solutions were investigated to demonstrate the analytical feasibility of this technique, since better control methods for these materials in phenol process streams could result in improved phenol yields.

Summary

ATR infrared studies of aqueous solutions of sodium phenate and sodium benzenesulfonate (NaBS) have demonstrated this technique would be a specific and practical method for monitoring certain phenol process streams. Sodium phenate and NaBS in the concentration range of 10-35% can be measured to within ± 0.5% absolute. In NaBS streams, the components Na_2SO_4, Na_2SO_3, NaOH, Na_2CO_3 and sodium phenate would introduce only negligible errors in measuring NaBS. In sodium phenate streams, small corrections could be made for the contribution of NaOH and Na_2SO_3 to the sodium phenate measurement. The Connecticut Instrument Corporation ATR equipment used in this work should be replaced by a structurally more stable unit for use as a plant stream analyzer.

Analytical Studies

Attenuated Total Reflectance (ATR) infrared methods were investigated to determine the feasibility of this technique for monitoring aqueous NaBS (sodium benzenesulfonate) and sodium phenate process streams in the phenol process. Excellent results obtained with laboratory scale equipment warrants a recommendation to Dr. Fowler's Instrumentation Group to consider construction of an instrument using the ATR principle as a process stream analyzer.

ATR spectra were obtained using a Connecticut Instrument Corporation Model ATR-1 attachment on a Perkin-Elmer Model 221 Infrared Spectrophotometer. Silver chloride, silicon and Irtran-2 (Eastman Kodak) prisms were investigated.

A silver chloride prism was used first, since this was available as a component of the basic ATR-1 kit. NaBS gave no difficulty, but sodium phenate reacted with the silver chloride, leaving a deposit on the back face of the prism. A hemi-cylinder made from zone refined silicon in which the diametrical face acts as the reflecting surface was obtained by Dr. Fowler from the Inorganic Division. Surface oxidation on the exposed faces of the silicon resulted in intense absorption bands in the regions of interest for NaBS and sodium phenate making this optical material unusable for this application. Eastman Kodak's Irtran-2 optical material is infrared transparent in the regions of interest and is relatively unaffected by caustic materials. Two Irtran-2 prisms were obtained from the Connecticut Instrument Corporation and have been used without any adverse effects in this study.

The angle of incidence relative to the reflecting face of the prism was found to have a large effect on the intensity of the absorption bands observed. The bands became more intense as the angle of incidence became smaller and an angle of 45°, the minimum angle that can be set up with the ATR-1 unit, was used.

The phenol process streams of interest have the following typical compositions:

	Process Stream		
	44% NaBS	54% NaBS	Pherate Slurry
Temperature	95°	100°	120°
Component	%	%	%
Water	49.78	44.52	26.30
NaBS	44.68	51.50	0.23
Sodium phenate	0.06	-----	29.90
Sodium sulfite	0.41	0.55	34.82
Sodium sulfate	4.51	2.65	2.76
Sodium chloride	0.05	0.07	1.54
Sodium hydroxide	0.15	0.23	3.80
Sodium carbonate	0.06	0.08	0.41
Diphenyl sulfone	0.25	0.34	-----
Na dibenzenesulfonate	0.06	0.08	-----
Na dihydroxybenzene	-----	-----	0.05
Na o-phenylphenol	-----	-----	0.03
Tars	-----	-----	0.16

Since no provision is made for thermostating the ATR-1 unit or the liquid ATR cells, the laboratory studies were made at room temperature. Solubility limitations at room temperature lowered the concentration ranges in which NaBS and sodium sulfite could be studied. Water solutions in the following concentration ranges were prepared for the principle components in these streams:

NaBS	10-35%
Sodium phenate	10-35%
Sodium sulfite	10-20%
Sodium sulfate	1-5%
Sodium hydroxide	1-8%
Sodium carbonate	0.2-1%

Two ATR units were set up to permit running the spectra of the solutions against water in the reference unit to compensate the water absorption. The ATR spectrum of water is shown in Figure 1 of Progress Report 2-02-760.01-4285, No. 16. The following ATR and infrared spectrophotometer parameters were used in this study:

ATR prism	Irtran-2
Angle of incidence	40°
Solvent	Water
Compensator	Water
Slit program	980
Scanning speed	1 minute/micron
Chart scale	10 cm./micron
IR instrument	Perkin-Elmer Model 221

Spectral Results

a. Sodium Phenate

ATR absorption bands are found at 6.77 microns for the phenyl ring and at 7.90 microns for the Ar-O stretching absorption. Either band is suitable for analytical purposes. However, serious errors due to the presence of sodium sulfite would be introduced to measurements made at 6.77 microns while at 7.90 these effects would be small. Figure 1 shows the superimposed spectra of a series of aqueous solutions of sodium phenate. Figure 2 is a plot of the optical density at 7.90 microns for these solutions versus the sodium phenate concentration (all measurements are made relative to the water blank at this wave). A linear function is obtained showing that Beer's Law is obeyed at this wavelength.

2. NaBS

ATR absorption bands are found at 8.52 microns for the sulfonate group and at 8.90 microns for what is probably due to a vibration of the aromatic ring. Either band could be used to set up an analytical method, but in this system the presence of sodium sulfate would produce serious errors in measurements made at 8.9 microns. The interference due to the sulfate would be small for the 8.52 micron band. Figure 3 shows the superimposed spectra of a series of aqueous solutions of NaBS. Figure 4 is a plot of the optical density of the 8.52 micron band versus the concentration of NaBS (all measurements are relative to the water blank at this wavelength). A linear function is obtained showing that Beer's Law is obeyed at this wavelength.

3. Sodium Sulfate and Sodium Sulfite

Figures 5 and 6 show the superimposed spectra of a series of aqueous solutions containing 1-5% sodium sulfate and 10-20% sodium sulfite. At the analytical wavelengths (7.90 and 8.52 microns), it can be seen that interference errors would be small.

4. Sodium Hydroxide and Sodium Carbonate

Figure 7 shows the spectra of 7.8% sodium hydroxide and 1% sodium carbonate in the spectral region of interest. Sodium hydroxide produces no finite absorption band but merely depresses the background. Its presence would have about equal effect at 7.90 or 8.52 microns. Sodium carbonate produces an absorption band peaking at 7.25 microns which tapers off to a point where its presence would introduce only a slight error in measurements at the two analytical wavelengths.

From the ATR spectra of sodium phenate and NaBS obtained under laboratory conditions, it can be seen that both materials could be easily measured to ± 0.5% absolute. Calculations were made to determine the approximate error that would be introduced by the presence of sodium sulfate, sodium sulfite, sodium hydroxide and sodium carbonate at the concentration levels present in a typical stream in the measurement of sodium phenate and NaBS. The results are:

NaBS Measured at 8.52 μ

44% NaBS Stream

0.4% sodium sulfite	is equivalent to	0.006% NaBS
0.2% sodium hydroxide	is equivalent to	0.06% NaBS
0.06% sodium carbonate	is equivalent to	0.02% NaBS
0.06% sodium phenate	is equivalent to	0.01% NaBS

0692955

5% NaBS Stream

0.6% sodium sulfite is equivalent to 0.01% NaBS
0.2% sodium hydroxide is equivalent to 0.06% NaBS
0.08% sodium carbonate is equivalent to 0.03% NaBS
2.7% sodium sulfate - negligible contribution

Sodium Phenate Measured at 7.90 Microns

Phenate Slurry

34.8% sodium sulfite is equivalent to 0.5% phenate
3.8% sodium hydroxide is equivalent to 1.0% phenate
0.4% sodium carbonate is equivalent to 0.1% phenate
2.8% sodium sulfate - negligible contribution
0.2% NaBS - negligible contribution

These calculations, even if the approximations were in error by a factor of 2, show that a NaBS stream analysis by an ATR method would not be affected by the presence of the other components in the system. Corrections would be necessary in a phenate slurry stream to correct for errors introduced by the presence of sodium hydroxide and sodium sulfite.

The results obtained in this investigation indicate that ATR infrared methods are feasible for the analysis of NaBS and sodium phenate streams in the phenol process. Presently available commercial equipment, however, would not be practical for long term use unless frequent calibration checks were made. The optical bench and the optical mounts of the ATR-1 unit from Connecticut Instrument Corporation are not sturdy enough for long term stability. The design and construction of a more rugged ATR unit should be investigated for application as a plant stream analyzer.

8/62 - B. Katlafsky, R. E. Keller

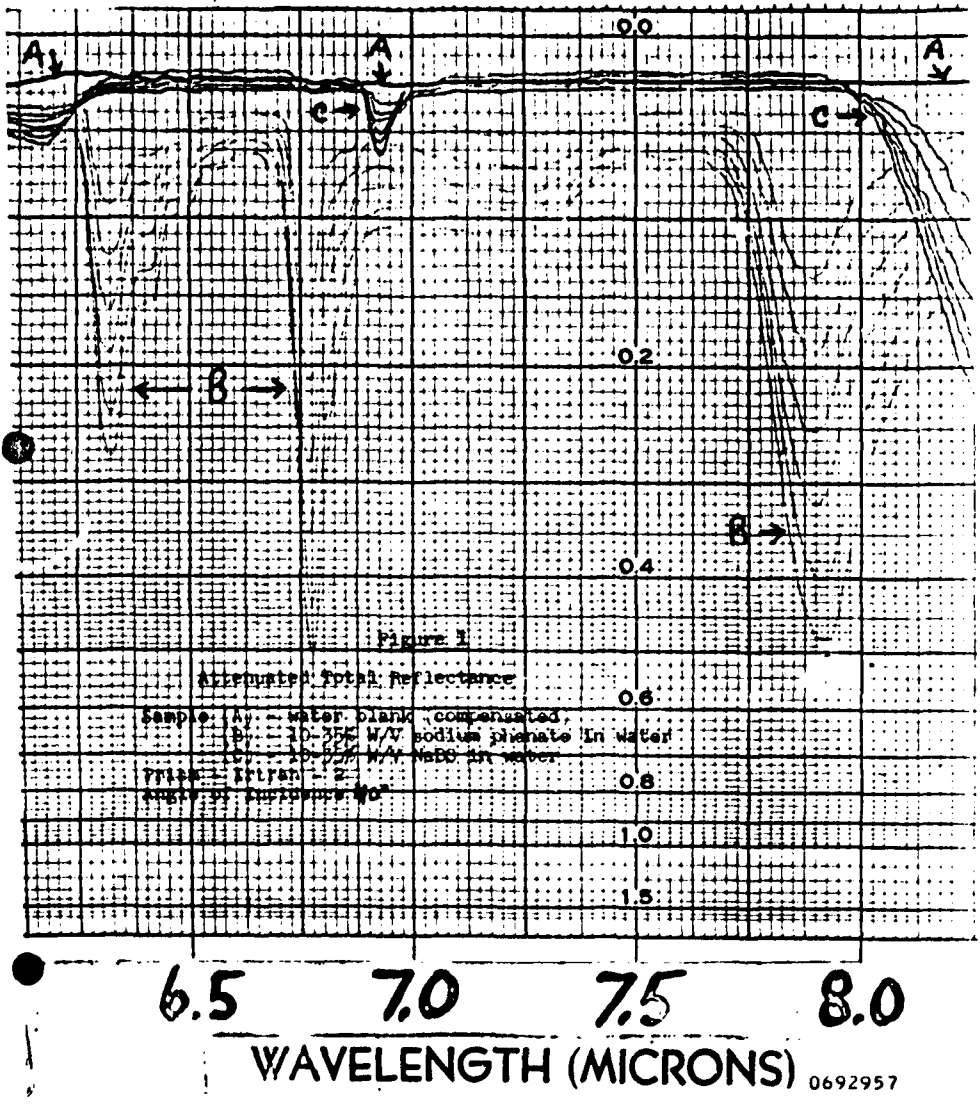


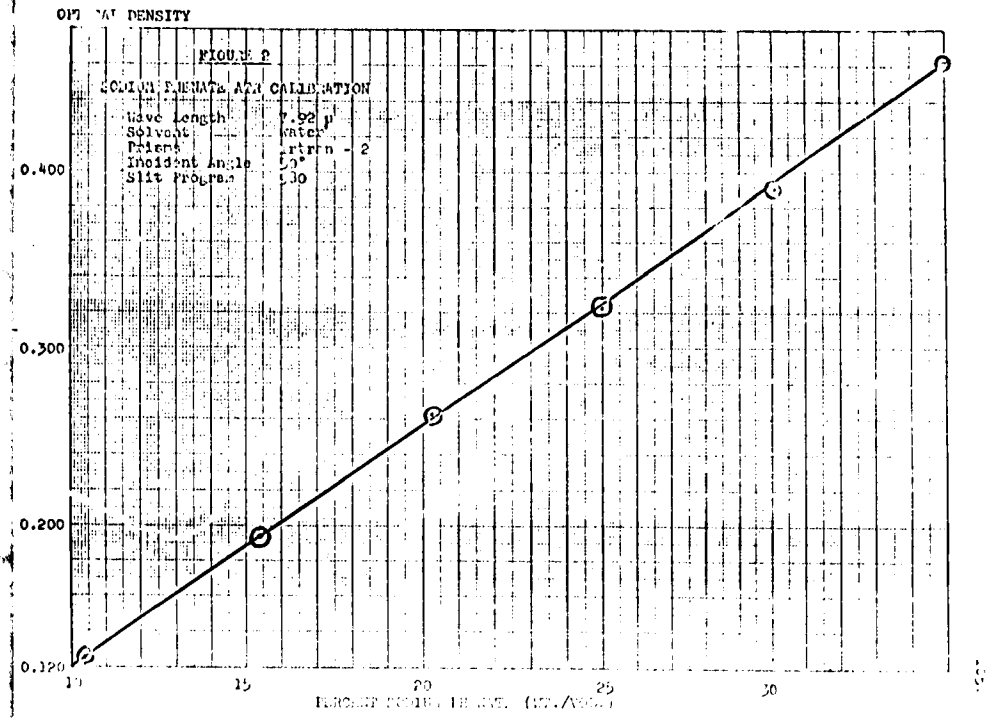
Figure 1

Attenuated Total Reflectance

Sample: A_v – water blank, compensated.
B_v – 10-35% W/V sodium phenate in water
C_v – 10-35% W/V NaOH in water

Prism – Irtran – 2

Angle of Incidence 60°



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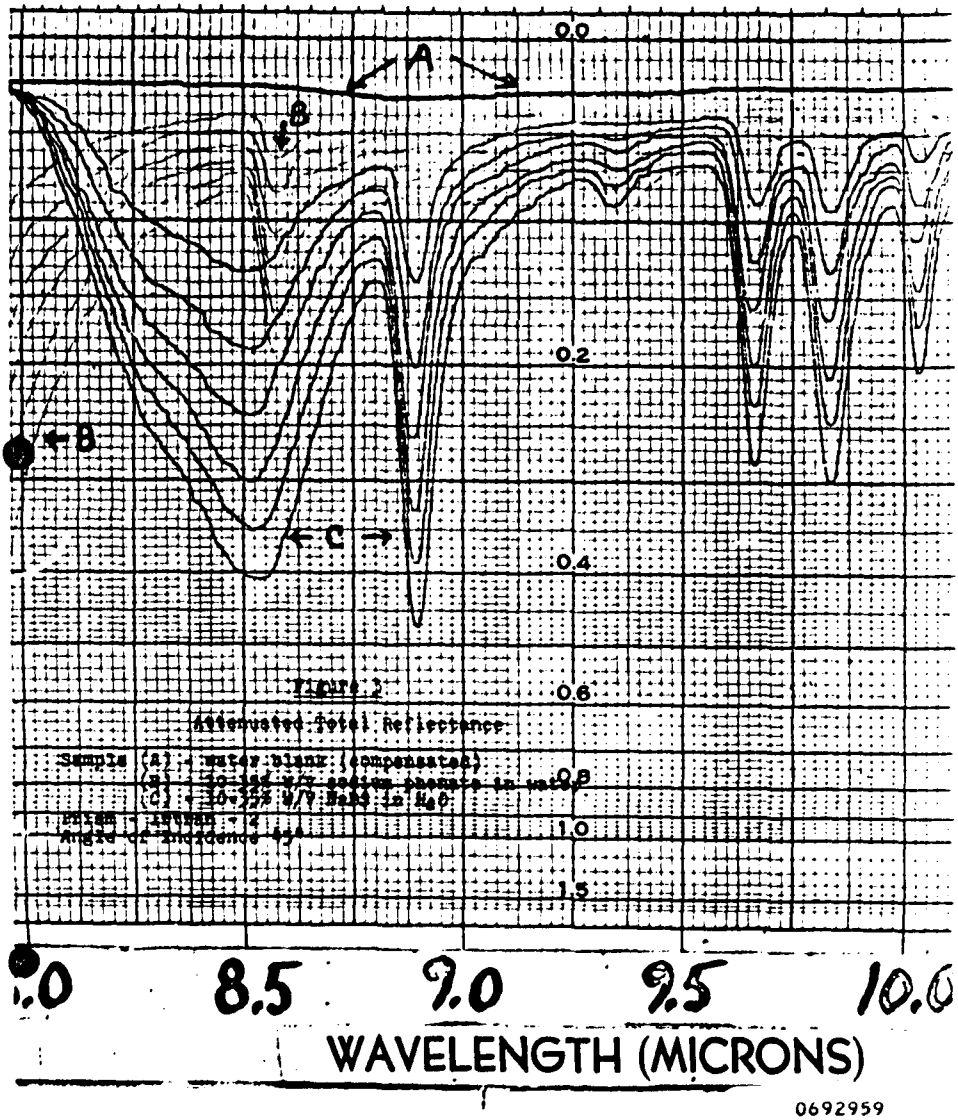

Figure 2

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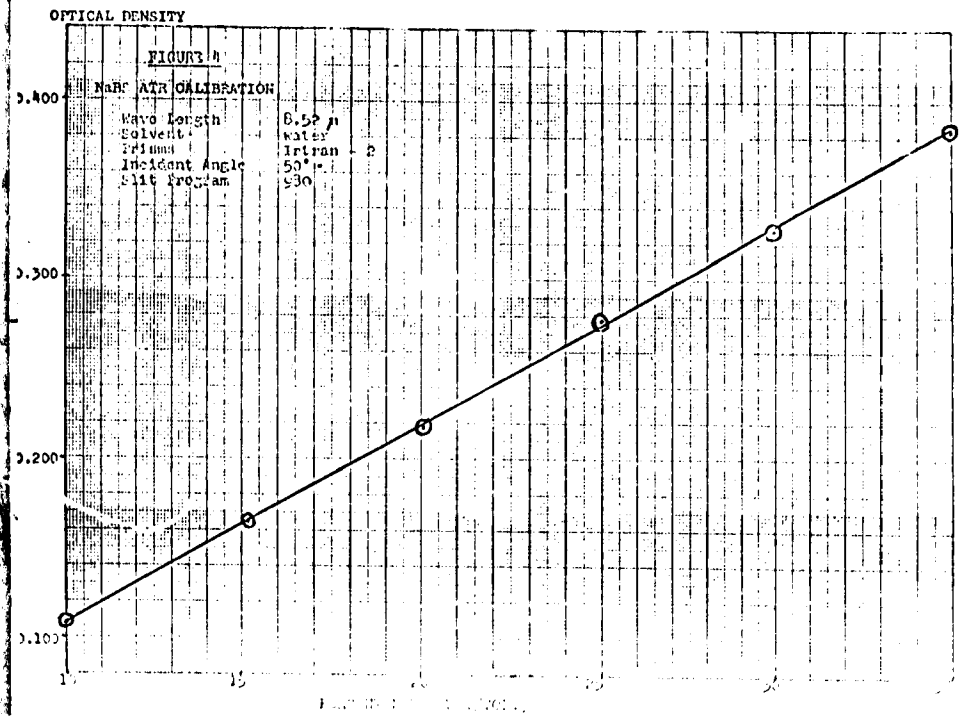

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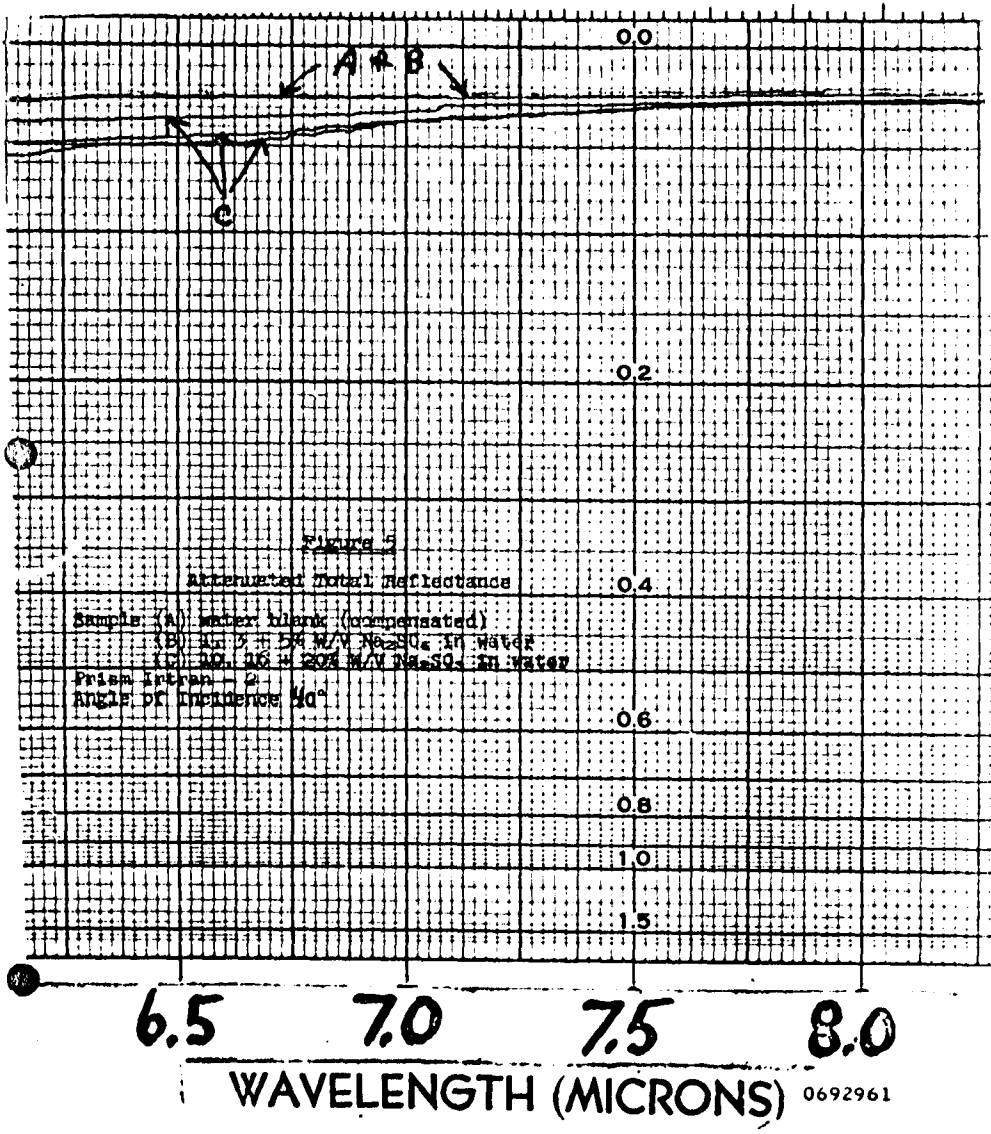


Figure 5

Attenuated Total Reflectance

Sample (A) water blank (compensated)
(B) Un 2 + 5% M/V Na_2SO_4 in water
(C) No. 16 + 20% M/V Na_2SO_4 in water
Prism Intran - 2
Angle of Incidence 45°

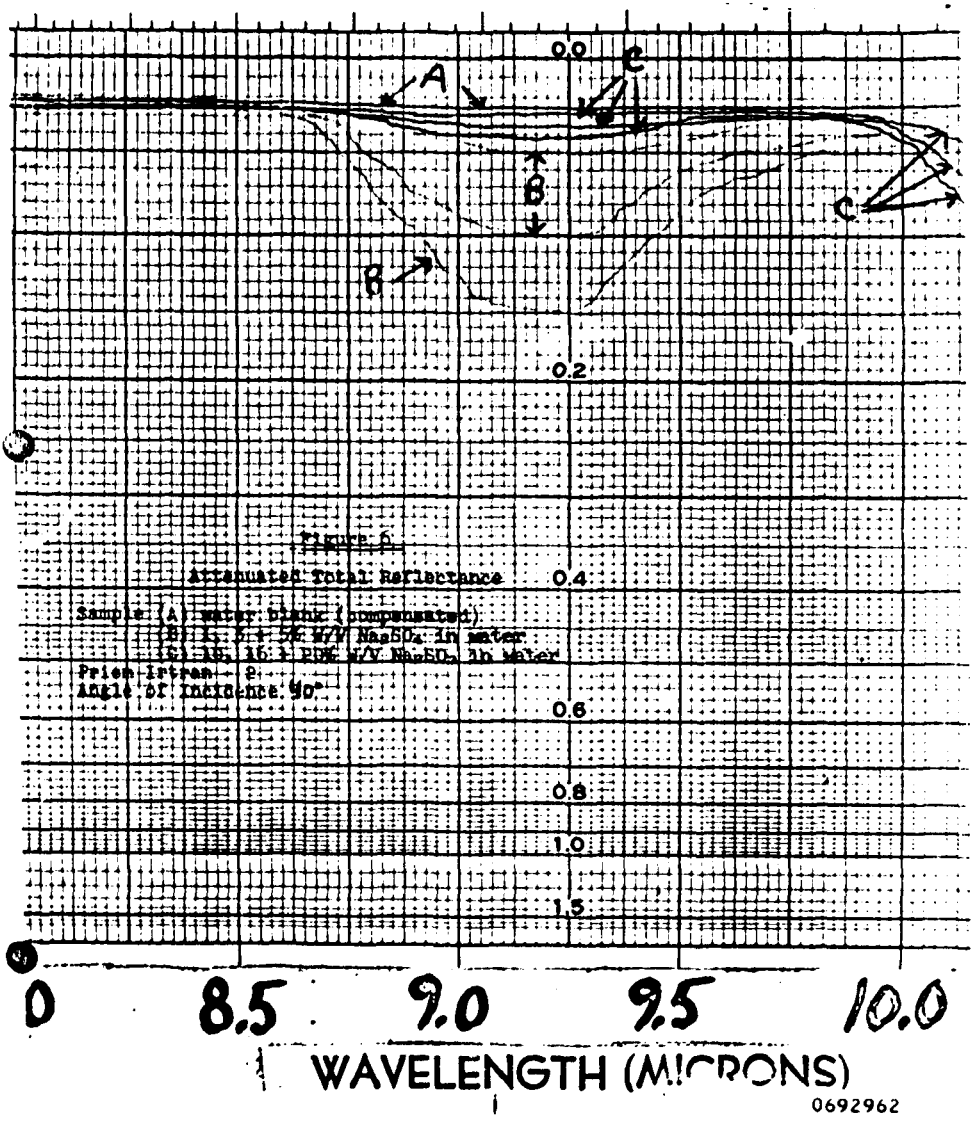


Figure 6.

Attenuated Total Reflectance

Sample (A) water blank (compensated)
(B) 1, 5 + 5% W/V Na_2SO_4 in water
(C) 10, 15 + 20% W/V Na_2SO_4 in water

Prism-Irtran - 2
Angle of incidence 45°

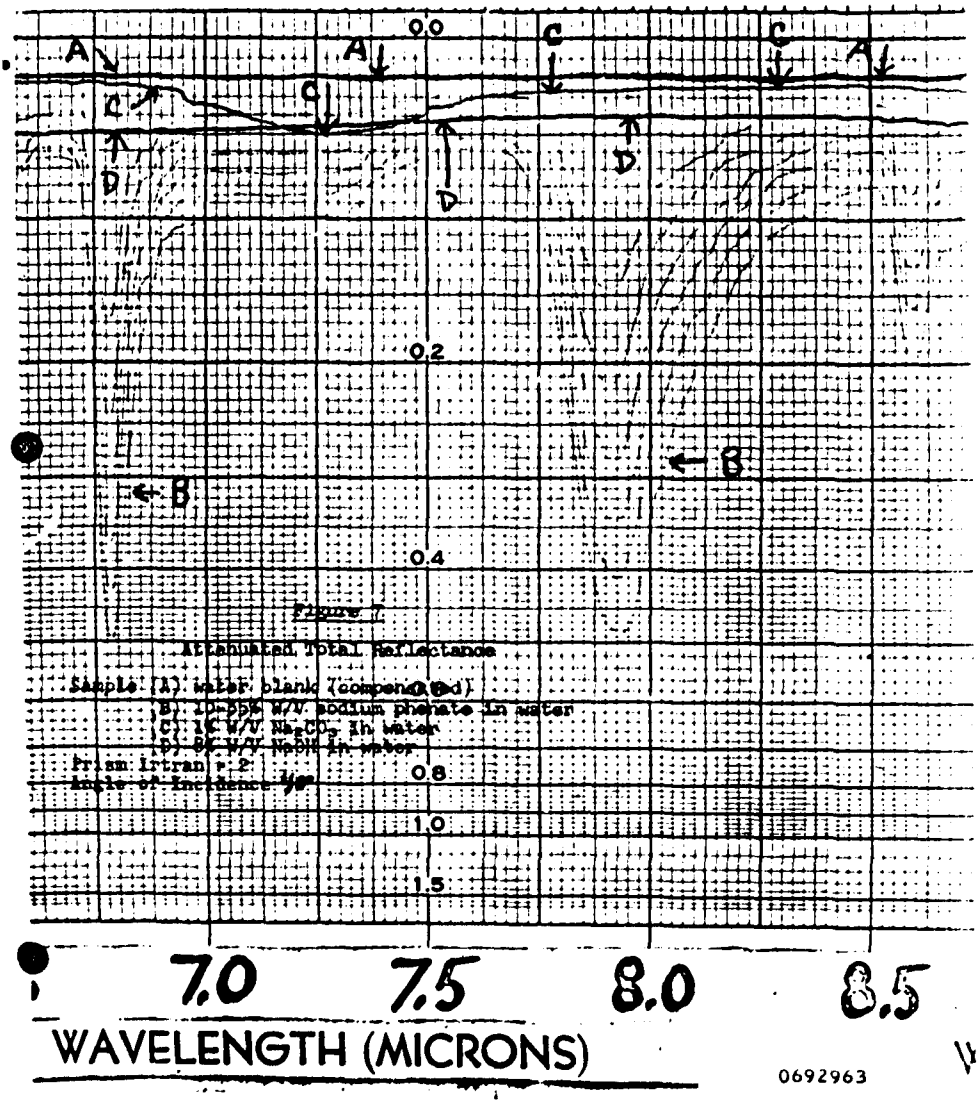


Figure 7.

Attenuated Total Reflectance

Sample (A) water blank (compensated)
(B) 10-25% W/V sodium phenate in water
(C) 1% W/V Na_2CO_3 in water
(D) 8% W/V NaOH in water

Prism Irtran - 2
Angle of Incidence 45°

SECTION M

Thin Layer Chromatography - Evaluation

Introduction and Summary

Thin layer chromatography (TLC) involving the use of an adsorbent spread in a thin layer on a glass plate has been given a preliminary evaluation. Results obtained with silicic acid as the adsorbent show that mixtures of resorcinol, pyrocatechol, phenol, hydroquinone and phloroglucinol can be separated into components and identified within 45 minutes using 10% n-butanol in benzene as the eluant. Semi-quantitative estimations can be made by visual inspection. The prime advantages over paper chromatography appear to be speed and increased resolution. Water content of the adsorbent is a significant variable that must be controlled. As with paper chromatography, accurate quantitative measurements may prove to be difficult.

Analytical Studies

The thin films on glass plates used for TLC may be prepared with a number of supports including silica gel G, aluminum oxide, Kieselguhr G and cellulose powder. The films for this work were prepared with the "Desaga" apparatus designed by Stahl. The samples are applied to the film with a Hamilton microliter syringe with sample volume ranging from 1 to 20 microliters.

The chromatographic separation is dependent upon the amount of moisture in the film and upon the mobile solvent used. In the work with resorcinol, dry plates produced poor separation and tailing. The freshly prepared wet plates were put in a desiccator containing a dish of water to control the moisture. This technique will keep the film sufficiently wet for a few days. As in paper chromatography, the selection of a suitable solvent is based on knowledge of solubilities, partition coefficients and finally by trial and error. In the case of resorcinol, 5% n-butanol in benzene (vol./vol.)was used for our paper chromatography work. The amount of n-butanol was varied and it was found that 10% n-butanol in benzene gave the best separations using the silica gel TLC scheme.

The separated components were detected by color development with a coupling agent (p-nitrobenzene diazonium fluoroborate) followed by alcoholic potassium hydroxide.

The TLC chromatograms are difficult to keep and are somewhat fragile. A solution to this problem is the transferral of the chromatogram to paper with a Xerox 914 copier. Figure I shows a Xerox copy of a chromatogram of individual components and an equal mixture of the resorcinol and related components.

The TLC procedure requires about 45 minutes total elapsed time per chromatogram as compared with 3-4 hours per paper chromatogram. The sensitivity appears greater than that obtainable using paper.

Preliminary work on quantitative measurements shows that the problems common to paper chromatograms also exist with TLC schemes. Removal of the spot can be accomplished easily with a razor blade. Elution of the component can be made with a suitable solvent for subsequent ultraviolet analysis or similar measurement. However, the microgram quantities normally separated make it necessary to use very sensitive methods for measurement. Work at higher concentration levels showed that bands instead of spots could be separated with the purpose of producing larger concentrations of separated components. Area measurements for quantitative determinations apparently can be carried out with about the same accuracy obtainable with paper chromatography. No specific area measurements were carried out as a part of this study.

Work is underway on determining the feasibility of infrared attenuated total reflectance as a means of identifying separated components directly on the silica gel.

12/62 - O. Hicks, R. E. Keller

Figure 1

TLC Chromatogram for Resorcinol and Related Components

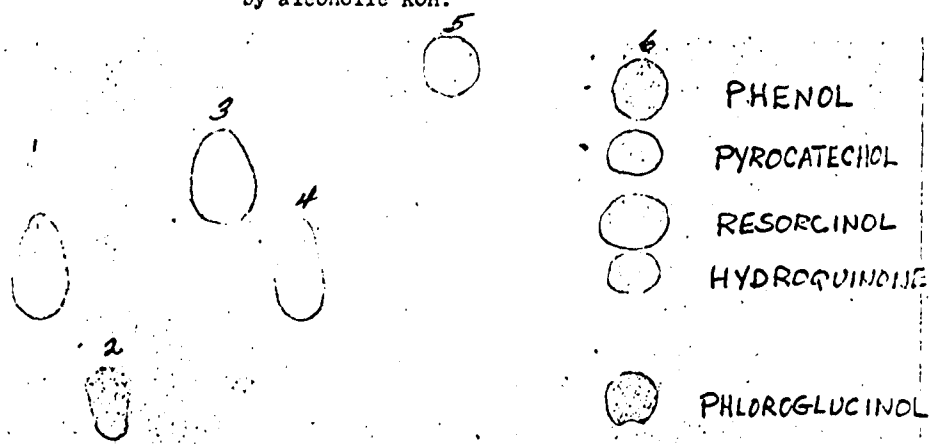
(copied with Zerox 914 copier)

SOLVENT - 10% Butyl Alcohol in Benzene

CARRIER - Silica Gel G
Preparation - 1 part silica gel/2 parts water, film prepared and held 1 hour at room temperature conditions.

DEVELOPMENT TIME - 30 Minutes

SPOT DEVELOPMENT - p-Nitrobenzene diazonium fluoroborate followed by alcoholic KOH.



COMPONENTS

1. Resorcinol, 500 γ in 10 microliters acetone.
2. Phloroglucinol, 500 γ in 10 microliters acetone.
3. Pyrocatechol, " " " " "
4. Hydroquinone, " " " " "
5. Phenol, " " " " "
6. Equal mixture of 1, 2, 3, 4 and 5, " total

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SECTION N

Evaluation of Tricosane Oxidation Study by Infrared Analysis

Introduction

Basic structure data were needed to assist in the selection of an oxidation inhibitor for Tricosane. Arrangements were made to examine a C_{40} alkane that had been analyzed in the laboratory using the Dornte apparatus by a differential infrared absorption procedure.

Summary

Infrared data were collected from five Dornte oxidation runs. The samples were analyzed as capillary films in 0.2 mm. cells using the starting material for compensation. Samples were taken periodically during the laboratory run until the infrared absorption went off-scale. Optical densities were plotted graphically for five wavelength positions representative of the functional groups formed during the oxidation. The family of curves show that the various functions form at somewhat independent rates. Saturated ketones increase at a fairly steady rate. Alcohols rise rapidly initially. Type III olefins rapidly reach a maximum and eventually attenuate to a small fraction of the peak value.

Analytical Studies

Ketone, alcohol and the olefin, $RRC{=}CH_2$, form immediately and become the dominant structures early in the oxidation. Near the peak of olefin production a wide variety of oxidized products appear and esters become significant. There is no evidence for conjugated ketones or aldehydes. Infrared does not provide good evidence for peroxides. None are evident. Eventually a wide variety of carbonyls appear. Unsaturation occurs almost entirely in the Type III form, plus a minor amount of trans olefin.

One gas sample from the laboratory oxidation run was analyzed. The carbon monoxide content of the gas collected from the apparatus was six times as great as the carbon dioxide content. Methane, ethylene and propylene each amounted to about one tenth the carbon dioxide content. An unknown alcohol of more than three carbons appeared in trace quantity.

Table of Wavelengths Studied

Function	Wavelength	Structure
-O-H	2.93 microns	Alcohol hydroxyl
-C=O	5.82	Saturate ketone and ester carbonyl
-C-O	8.62	Ester C-O
-C-O	9.50	Alcohol and ether C-O
=C-H	11.30	Type III olefin

12/62 - O. Kinast, R. E. Keller

SECTION O

Vanadium Oxide Components in Catalyst Mixtures

Introduction

Vanadium can form in addition to V_2O_3, V_2O_4 and V_2O_5 other lesser known oxides with empirical formulas that are intermediate between V_2O_3 and V_2O_4 and V_2O_4 and V_2O_5. X-ray diffraction data indicate the possibility of six oxides between V_2O_3 and V_2O_4 and one between V_2O_4 and V_2O_5. Since these intermediate oxide compounds could be present in conventional vanadium oxide catalyst mixtures, methods for detecting and identifying these species would be helpful. In addition, characterization and correlation of composition with activity would be useful in the design of better catalysts. An infrared study was initiated to elucidate the chemical bonding in a series of intermediate oxides.

Summary

Infrared solid state spectra were obtained for V_2O_3, V_2O_4 and V_2O_5 dispersed in KBr in the 2-35 micron region. Subsequent studies show that radical spectral differences exist for prepared intermolecular complexes including $V_2O_{3.3}$, $V_2O_{3.33}$, $V_2O_{3.4}$, $V_2O_{3.6}$, $V_2O_{3.8}$ and $V_2O_{4.33}$. This work corroborated X-ray diffraction data and indicates new chemical compounds are produced in the systems V_2O_3-V_2O_4 and V_2O_4-V_2O_5 after heating.

Analytical Studies

Vanadium is known to form, in addition to the common oxides V_2O_3, V_2O_4 and V_2O_5, a series of intermediate or suboxides on heating the systems:

$$n\ V_2O_3 + m\ V_2O_4$$

or $$n\ V_2C_4 + m\ V_2O_5$$

where n and m are intergers. Since these suboxides have catalytical application potentials, an infrared study was initiated to detect and characterizes these oxides.

The oxide systems studied were prepared by Dr. R. H. Munch and included:

V_2O_3
$V_2O_{4.5}$ ($V_2O_4 + V_2O_5 = V_4O_9$)
$V_2O_{4.33}$ ($2V_2O_4 + V_2O_5 = V_6O_{13}$)
$V_2O_{4.3}$ ($7V_2O_4 + 3V_2O_5 = V_{20}O_{43}$)
$V_2O_{4.2}$ ($4V_2O_4 + V_2O_5 = V_{10}O_{21}$)
$V_2O_{4.1}$ ($9V_2O_4 + V_2O_5 = V_{20}O_{41}$)
V_2O_4

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$V_2O_{5.0}$ ($V_2O_5 + 9V_2O_4 = V_{20}O_{50}$)
$V_2O_{5.8}$ ($V_2O_5 + 4V_2O_4 = V_{10}O_{18}$)
$V_2O_{5.7}$ ($3V_2O_5 + 7V_2O_4 = V_{20}O_{37}$)
$V_2O_{5.67}$ ($V_2O_5 + 2V_2O_4 = V_6O_{11}$)
$V_2O_{5.6}$ ($2V_2O_5 + 3V_2O_4 = V_{10}O_{16}$)
$V_2O_{5.5}$ ($V_2O_5 + V_2O_4 = V_4O_7$)
$V_2O_{5.4}$ ($3V_2O_5 + 2V_2O_4 = V_{10}O_{17}$)
$V_2O_{5.33}$ ($2V_2O_5 + V_2O_4 = V_6O_{10}$)
$V_2O_{5.3}$ ($7V_2O_5 + 3V_2O_4 = V_{20}O_{33}$)
$V_2O_{5.2}$ ($4V_2O_5 + V_2O_4 = V_{10}O_{18}$)
$V_2O_{5.1}$ ($9V_2O_5 + V_2O_4 = V_{20}O_{31}$)
V_2O_5

The infrared spectra were obtained in the 2-35 micron region for the oxides dispersed in KBr (potassium bromide) and pressed into thin discs. The most significant data were obtained in the rock salt region (2-15 microns). The infrared absorption data observed in this region for the vanadium oxide systems are represented in bar graph form in Figures I and II.

A. V_2O_4-V_2O_5 System (Figure I)

Vanadium pentoxide (V_2O_5) has a very intense, clearly defined absorption spectrum with absorption bands at 9.80 and 12.30 microns. The tetroxide (V_2O_4) shows a very weak, broad band at about 9.6 microns and a slightly stronger band at about 15 microns. The infrared spectra of the oxides obtained having the empirical formulae $V_2O_{4.5}$, $V_2O_{4.3}$, $V_2O_{4.2}$ and $V_2O_{4.1}$ indicate that these materials are mixtures of V_2O_4 and V_2O_5. The spectrum obtained for the material having the empirical formula $V_2O_{4.33}$ shows radical changes compared to those of V_2O_4 and V_2O_5. Two weak bands of approximately the same intensity appear at 8.65 and 8.90 microns and a stronger band at 11.24 with a shoulder at 11.70 microns are observed. No absorption is found at 9.80 or 12.30 microns, indicating that no V_2O_5 is present. This spectral evidence supports X-ray diffraction data that the vanadium oxide having the empirical formula $V_2O_{4.33}$ is a new chemical entity.

B. V_2O_3-V_2O_4 System (Figure II)

Vanadium trioxide (V_2O_3) is practically opaque throughout the spectral region studied and shows only an extremely weak absorption band at about 10 microns. The tetroxide (V_2O_4), as noted before, has a weak band at about 15 microns and a very weak, broad band peaking at about 9.6 microns. The molecular complexes corresponding to the empirical formulae of $V_2O_{3.8}$, $V_2O_{3.7}$, $V_2O_{3.67}$, $V_2O_{3.5}$, $V_2O_{3.2}$ and $V_2O_{3.1}$ produce infrared spectra that are devoid of character, indicating that these are merely mixtures of the V_2O_3 and V_2O_4 entities. The species $V_2O_{3.6}$, $V_2O_{3.4}$ and $V_2O_{3.3}$ have a medium intensity

band at 10.05 microns and $V_2O_{5.5}$ has a strong band at 14.0 microns. Absorption at these wavelengths is absent in both V_2O_5 and V_2O_4 indicating that these four entities are new chemical compounds. This data supports the conclusion drawn from X-ray defraction data for these materials. The species corresponding to the empirical formula $V_2O_{5.33}$ has infrared absorption bands at both 10.05 and 14.0 microns. Although the spectral data can be interpreted either as indicating a new chemical entity or to indicate a mixture of the $V_2O_{5.5}$ and $V_2O_{5.4}$ species, X-ray diffraction data clearly indicate that $V_2O_{5.33}$ is a new chemical compound.

The appearance of an absorption band in the 10 micron region in the $V_2O_{5.8}$, $V_2O_{5.6}$, $V_2O_{5.4}$ and $V_2O_{5.33}$ species is interpreted as indicating that these suboxides have some V=O bonding. This conclusion is based on data compiled in the reference text:

G. Herzberg, "Spectra of Diatomic Molecules", 2nd edition, pp. 501-581 (Van Nostrand, New York, 1950)

In this compilation, spectral data observed for the electronic states of diatomic molecules are used to calculate the vibrational constants for the system. These constants can be used in turn to calculate the vibrational frequency (infrared absorption) of the system. This frequency is conventionally reported in terms of reciprocal centimeters, $cm.^{-1}$ ($cm.^{-1} = 10^4$ x the reciprocal of the wavelength in microns). The vibrational frequency calculated for the M=O entity of vanadium and its neighbors in the first row of transition elements in the periodic table are:

M (=O)	Frequency in $cm.^{-1}$
Se	964
Ti	1004
V	1003
Cr	866
Mn	831
Fe	870
Co	No data
Ni	No data

The observed infrared data for V_2O_5 and the suboxides $V_2O_{4.33}$, $V_2O_{5.33}$, $V_2O_{5.4}$, $V_2O_{5.6}$ and $V_2O_{5.8}$ are:

Oxide	Frequency in $cm.^{-1}$
V_2O_5	1021
$V_2O_{4.33}$	1123, 1156
$V_2O_{5.33}$	995
$V_2O_{5.4}$	995
$V_2O_{5.6}$	995
$V_2O_{5.8}$	995

The close agreement between the observed infrared absorption frequency and the calculated frequency for the V=O vibration is interpreted to indicate that the suboxides $V_2O_{4.33}$, $V_2O_{3.33}$, $V_2O_{3.4}$, $V_2O_{3.6}$ and $V_2O_{3.8}$ contain some V=O bonds.

This infrared study has confirmed X-ray diffraction data that a minimum of five suboxides can be obtained by heating stoichiometric quantities of V_2O_3 and V_2O_4 and one between V_2O_4 and V_2O_5. The observed infrared data have been interpreted to indicate the presence of V=O bonding in five of these suboxides. Further work would be required with known oxide systems to fully characterize the oxygen bridge bond in the vanadium oxides.

12/62 - B. Katlafsky, R. E. Keller

FIGURE I

INFRARED SPECTRA OF VANADIUM OXIDES

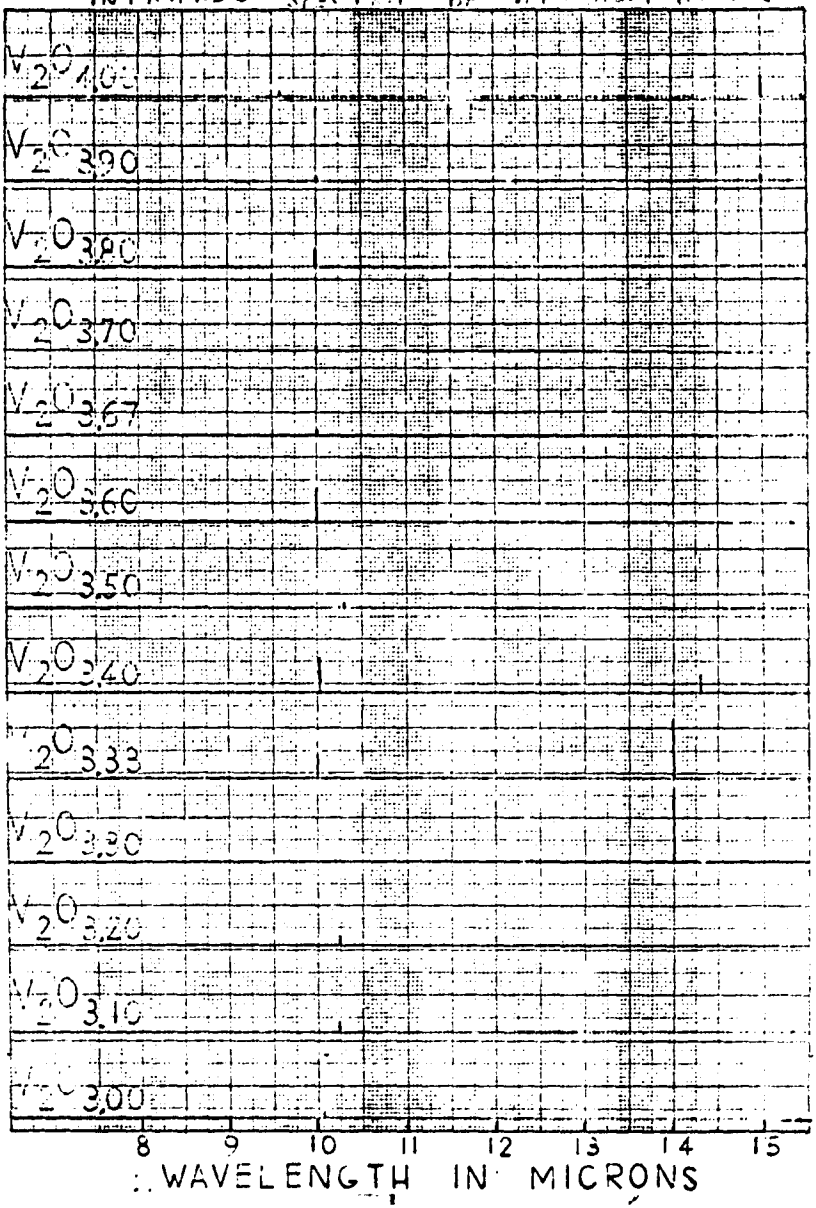
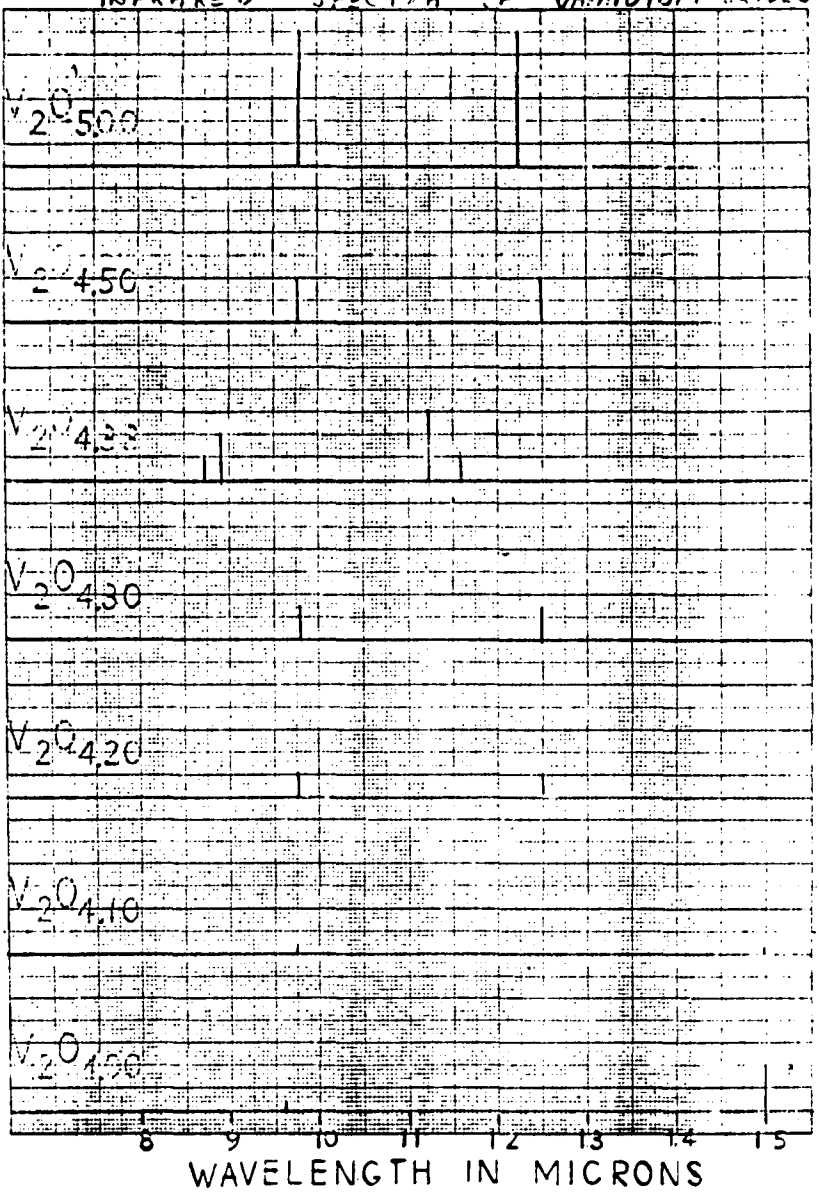


FIGURE II

INFRARED SPECTRA OF VANADIUM OXIDES



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