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FINAL REPORT on

2, 4, 5-Trichlorophenol

Optimization of the Hydrolysis of 1, 2, 4, 5-Tetrachlorobenzene

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I. INTRODUCTION

The incidence of chloracne has been almost universal among personnel engaged in the manufacture of 2, 4, 5-trichlorophenol (TCP) and 2, 4, 5-trichlorophenoxyacetic acid (2, 4, 5-T). The most severe cases have occurred in individuals involved in the clean up of uncontrolled autoclave batches (hydrolysis of tetrachlorobenzene). However, cases of varying severity have occurred consistently among operators primarily employed around the 2, 4, 5-T work up equipment - filtration, acidification, drying, etc.

In 1960, Dr. Oettel at Badische expressed the opinion that tetrachlorodibenzodioxane (TDD) was the chloracnegenic material. In 1965, Dow presented an analytical method for the determination of TDD to representatives of Monsanto and Hercules Powder and presumably to other interested parties. With the availability of the analytical method Monsanto began to monitor various process streams in the Nitro plant. This program has continued to the present date.

In 1967 our Medical Department stated that the chloracnegen in the 2, 4, 5-T process was indeed TDD. This opinion led directly to the present work whose aim was to minimize the formation of TDD in the hydrolysis of tetrachlorobenzene.

It was felt that the alternate approach of removing the TDD after its formation was less satisfactory since it would present a serious exposure hazard in handling high concentrations of TDD in a still residue or a filter cake.

II. OBJECTIVES

To define and evaluate the important process variables which influence the formation of TDD.

To determine the optimum mode of operation of the autoclave hydrolysis of tetrachlorobenzene (TCB) adaptable to plant operation.

III. SUMMARY

The major process variables influencing the course of the hydrolysis reaction were studied in a statistically designed experiment. The variables studied were the reaction temperature, the rate of TCB addition, the methanol/TCB mole ratio, the NaOH/TCB mole ratio and the H_2O/TCB mole ratio. The effects of iron and dimethyl ether were found to be negligible at the optimum levels of the variables.

The most important variable was found to be the methanol/TCB mole ratio and the least important was the TCB addition time. Each set of conditions corresponds to an optimum hold time and in this sense hold time is an important variable.

The recommended process changes will result in a more dilute batch and a shorter time cycle so that autoclave productivity will remain virtually unchanged. Additional methanol distillation capacity will be necessary to maintain full rate in the autoclaves.

The recommended process gives a TDD content in the TCP of 6 ppm as compared to 35 ppm using the old process conditions. This is expected to result in a consistent level of <2 ppm in the 2, 4, 5-T as compared to previous concentrations of 3-20 ppm. The environmental hazards associated with working in the 2, 4, 5-T department will be significantly reduced.

IV. RECOMMENDED HYDROLYSIS PROCEDURE

The recommended charges are based on the production of 100 pounds of technical TCP in alkaline solution. To a mild steel autoclave are pressure-charged 113 pounds (7.9 gallons) of 72% NaOH and 252 pounds (37.5 gallons) of 96.4% methanol. If the assay of the NaOH or methanol varies from the above values, the charges should be adjusted as necessary to give 81 pounds as 100% NaOH and 243 pounds as 100% methanol. The autoclave contents are heated to 165°C and 109.5 pounds (7.7 gallons) of molten TCB is charged over a two hour period. The temperature of the autoclave contents is allowed to rise to 170°C during the early part of the TCB addition and is held at 170 ± 1°C for the balance of the addition and for a 1.8 hour hold period following the addition. At the end of the hold period the autoclave contents are immediately cooled and the methanol recovery is conducted in the same manner as is presently used.

Technical TCP produced in this manner will contain less than 1% trichloroanisole (TCA) and about 6 ppm TDD. If 85% methanol is used in the reaction the hold period is increased to 2.5 hours and the TDD concentration will be increased to about 7 ppm.

V. REFERENCES

1. Memo, WRU/EFT, September 14, 1965.

2. Memo, WRU/VLR, July 3, 1968.

3. Shein, S. M. and Evstifeev, A. V., Izvestiya Sibirskogo Otdeleniya Akademii Nauk SSSR, Seriya Khimicheskikh Nauk, No. 2, pp. 118-121 (1967).

4. Notebook Pages

   AG 72101, AG 85301, AG 90001, J. L. Sims
   AG 52101, W. R. Udell

VI. EXPERIMENTAL DETAILS

A. Equipment

A 1-l., 316 stainless steel, electrically heated magnedrive packless autoclave, fitted with a bottom sampling valve was used for the reactions. The autoclave head was removed and suspended by a chain hoist to enable charging solid sodium hydroxide. Water and methanol

were charged to the sealed autoclave through a Jerguson gauge, size 17-TL-10. Plant TCB was charged to the autoclave through a calibrated, steam traced Jerguson gauge, size 27-T-20. Nitrogen pressure, usually 500 psig, was used to facilitate the charging of water, methanol and TCB. The rate of TCB addition was controlled manually, using a steam-jacketed needle valve. The equipment is shown schematically in Figure 1.

b. Statistical Experiment

The independent variables chosen for investigation were the reaction temperature, the TCB addition time, the CH_3OH/TCB mole ratio, the NaOH/TCB mole ratio and the H_2O/TCB mole ratio. The H_2O/TCB mole ratio refers only to the H_2O charged to the autoclave and does not include the two moles of H_2O formed in the reaction. These variables were studied in a partial factorial central composite experiment. The ranges over which the variables were studied and their code designations are given in Table 1.

Table 1

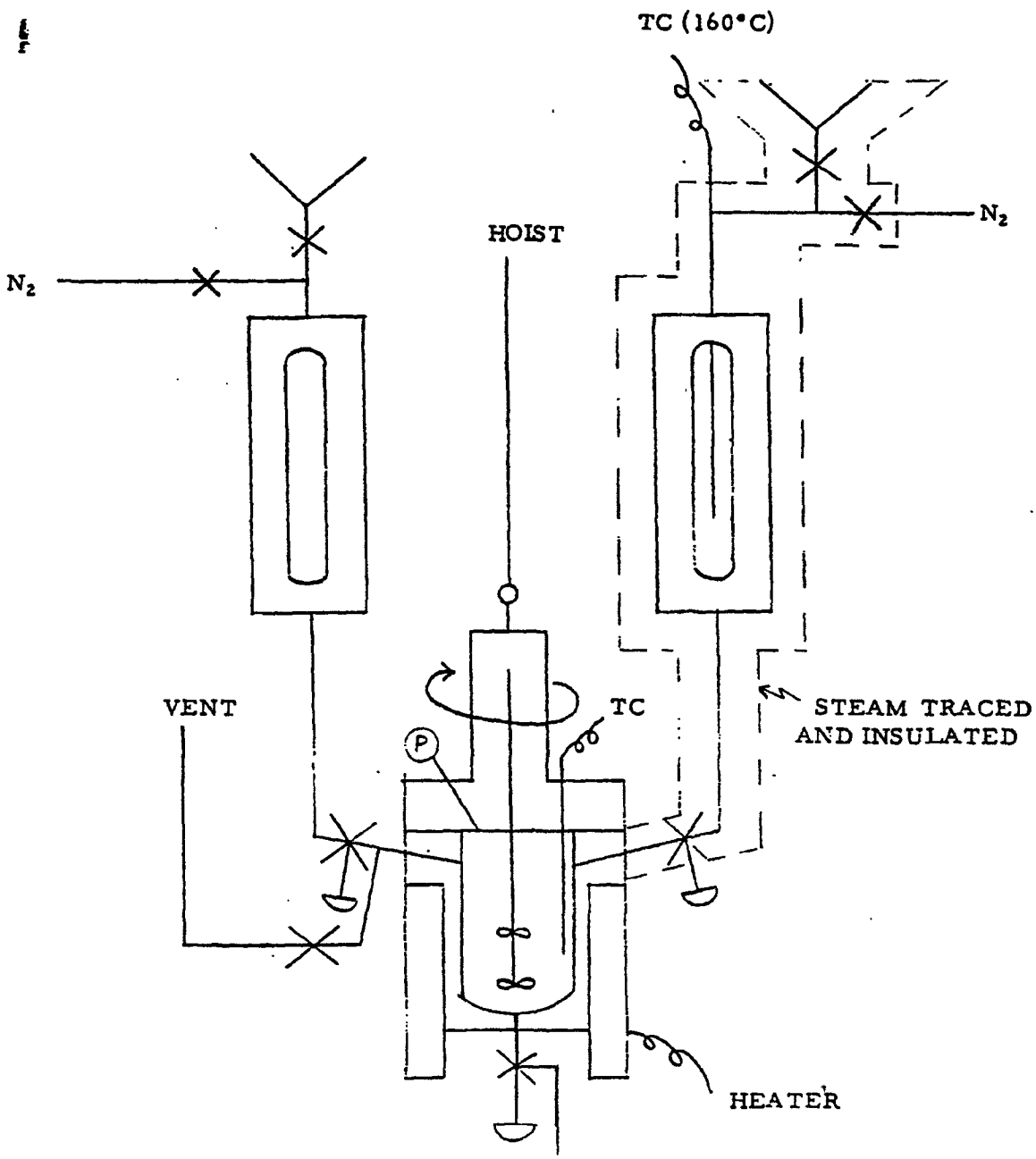
Variable	Designation	Range
Temperature (°C)	X_1	160-180
TCB addition time (hours)	X_2	0.5-3.5
CH_3OH/TCB (mole ratio)	X_3	3-15
NaOH/TCB (mole ratio)	X_4	2-4
H_2O/TCB (mole ratio)	X_5	2.5-10.5

The range of each of the independent variables was divided into five equally spaced levels and these levels were coded for ease of computation. The code is presented in Table 2.

Table 2

Code \ Variable	X_1	X_2	X_3	X_4	X_5
-2	160	0.5	3	2	2.5
-1	165	1.25	6	2.5	4.5
0	170	2.0	9	3	6.5
1	175	2.75	12	3.5	8.5
2	180	3.5	15	4	10.5

FIGURE I



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The independent variables evaluated were Y1, the ppm of TDD based on the weight of total products derived from TCB at the end of the hold period, and Y2, the hours of hold time required for level of TCA to reach 1% of the weight of the total products. The end of the reaction was taken as the time when the TCA content had been diminished to 1%. This was determined by interpolation or extrapolation of the analytical results from periodic samples taken during the hold period. The analytical methods used are described in another section of this report.

Thirty-eight runs were made. The results (Y1, Y2) and the conditions(X1-X5) for these runs are given in Appendix I. The general procedure followed in the individual runs was as follows:

> To the open autoclave is charged a quantity of solid sodium hydroxide corresponding to the desired level of variable X4. The autoclave is sealed and a Jerguson gauge is charged with quantities of methanol and water corresponding to the desired levels of variables X3 and X5. The Jerguson gauge is pressured to 500 psig with nitrogen and the Jerguson gauge contents are admitted to the autoclave through a needle valve. The autoclave agitator is turned on and the speed of agitation is gradually increased to 1000 rpm. The autoclave heater is turned on and the contents are heated to the desired level of variable X1. The calibrated, steam-traced and insulated Jerguson gauge is charged with a quantity of molten TCB in excess of that desired in the autoclave. The Jerguson gauge is pressured to 500 psig with nitrogen and the quantity of TCB corresponding to the desired levels of variables X3, X4 and X5 is charged to the autoclave uniformly over a period of time corresponding to the desired level of variable X2. The TCB is thus charged by differential readings of the Jerguson gauge level. The total charge for each run was scaled to give an approximate volume of 600 ml. The total charge varied from 542 to 671 g. and the TCB charge varied from 0.583 to 1.07 moles.
>
> Periodic samples were taken after the end of the TCB addition (usually four samples). These were analyzed for phenates, TCA, TCB and TDD. The results were plotted to give to values of Y1 and Y2. Plots of two of the runs are shown in Figure 2. These are run 19, which used conditions similar to those presently employed at Nitro, and run 32, which is representative of the conditions recommended in this report.
>
> The data were submitted to multiple linear regression analysis using a slightly modified version of a library program of Com-Share, Inc. The regression analysis was first made after run 27. The results indicated areas of interest and led to 11 additional runs during which several more regression analyses were made in the zeroing in process. This efficient approach was made possible by the ready accessibility of a Com-Share, time-sharing computer terminal. A good fit to the data was obtained by relating the

logarithms of the dependent variables (ln Y1 and ln Y2) to the first and second order terms and first order interactions of the independent variables (X1---X5, $X1^2$---$X5^2$, X1X2----X4X5). The coefficients of the X terms and the equation constants are given in Table 3 for both Y1 and Y2.

Figure 2

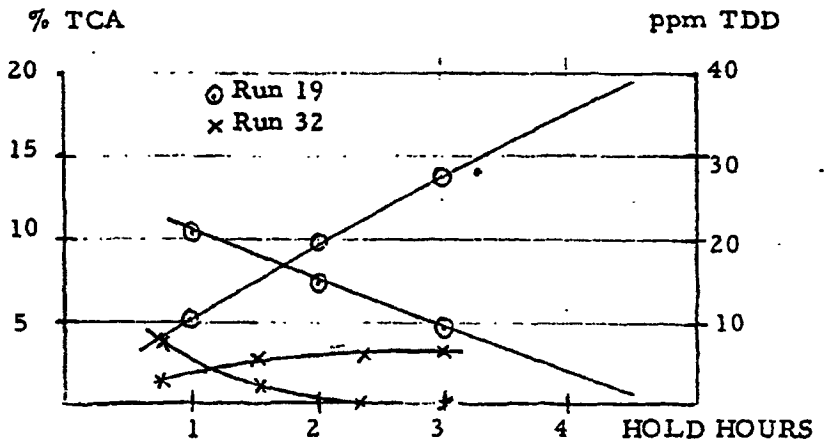


Table 3

	ln Y1	ln Y2
Constant	3.5371	1.6641
X1	0.53147	-0.2769
X2	0.062191	-0.021751
X3	-0.57546	-0.50761
X4	-0.39892	-0.35998
X5	0.17796	0.19933
$X1^2$	0.10629	0.074312
$X2^2$	0.074174	0.033993
$X3^2$	0.081683	0.13785
$X4^2$	0.10876	0.13086
$X5^2$	0.051283	0.0027183
X1X2	0.13675	0.044485
X1X3	-0.053003	0.08469
X1X4	-0.094779	-0.074724
X1X5	-0.050022	0.035781
X2X3	-0.053186	-0.0021128
X2X4	-0.071901	-0.022779
X2X5	-0.15061	0.018533
X3X4	-0.12213	-0.055681
X3X5	0.08317	-0.030519
X4X5	-0.10367	0.0022746

In solving the equations for a specific set of conditions, the values to be used for the X terms are the coded ones as given in Table 2.

A mechanical plotting program is available for use with the GE time-sharing computer. A modified version of this program was used to create the graphs presented in Appendix II. Reference will be made to these graphs in the subsequent discussion of the effects of changes in the individual variables.

VII. DISCUSSION

A. Optimum Conditions

The optimum conditions for the hydrolysis of TCB, based on the statistical experiment are as follows:

Temperature	170°C
TCB addition time	1 to 2 hours
CH_3OH/TCB	15 moles/mole
NaOH/TCB	4 moles/mole
H_2O/TCB	4.5 moles/mole

These conditions lead to a hold time of 1.8 hours to reduce the TCA content to 1%, and result in a TDD concentration of 6 ppm.

B. Correlations with Plant Data

Samples have been taken from the autoclaves at Nitro in three separate programs comprising a total of 13 batches since 1965 (Ref. 1, 2). The final samples of batches which employed the usual 3.5 hour hold time showed TDD concentrations of 27 to 60 ppm. A single batch which was held for 5.5 hours had a TDD concentration of 70 ppm. The TCA concentration in these samples varied from 0.2 to 3.3% based on the total products from TCB. The lab run most closely approximating plant conditions was run 19 (see Fig. 2). In this reaction a hold period of 4.6 hours was required to reach 1% TCA and the TDD concentration was 39 ppm.

The regression equations for plant conditions indicate a hold period of 4.5 hours to give 1% TCA and a TDD concentration of 70 ppm. For a 3.5 hour hold period the TDD would be reduced to about 50 ppm and the TCA content would be about 2%. This is in close agreement with plant experience. The TCA concentration is reduced by about 1% during the methanol recovery operation (codistillation) and this accounts for a typical TCA content of 1% in the NaTCP storage tank.

The concentration of TDD in the 2,4,5-T acid product has usually varied from 5-20 ppm in periodic samples from the past 10 years, although higher concentrations have occasionally been observed. The highest observed

concentration was 55 ppm in a lot made during April of 1965. It seems likely that the autoclave production of TDD is relatively constant at 30-50 ppm. The limited solubility of the material permits much of it to settle out in the NaTCP storage tank during periods when a high storage tank level is being maintained. A recent sample from the top of the storage tank analyzed 15 ppm of TDD. The TDD can then be introduced to the condensation reactors in a sporadic fashion, thus accounting for the varying TDD content in the finished 2, 4, 5-T acid. A significant fraction of the TDD is lost in the aqueous waste streams. A recent analysis of the Eimco filtrate showed an absolute concentration of 0.3 ppm TDD. A higher concentration would be expected in the higher temperature pan filter filtrate.

C. Effect of Temperature

The effects of changing the temperature (X1) while holding the other four variables constant at recommended conditions (App. II-1) and present plant conditions (App. II-2) are shown in the Appendix. It will be noticed that higher temperatures result in higher TDD concentrations but shorter required hold periods. At the recommended conditions, however, the TDD level is relatively insensitive to temperature between 160 and 170°C. The recommended temperature of 170°C results in the shortest hold period consistent with a low TDD concentratinn.

D. Effect of TCB Addition Time

The effects of changing the TCB addition time (X2) while holding the other four variables constant at recommended conditions (App. II-3) and present plant conditions (App. II-4) are shown in the Appendix. The TCB addition time has very little effect on either TDD or hold period. Slightly longer hold periods are required when extremely short addition periods are used. More TDD is produced at the longer addition times under present plant conditions. The slightly lower temperature normally used at the beginning of the addition period in the plant (165°C) has the same effect as a shorter addition time at 170°C. This partially accounts for the higher TDD level observed in the lab data for plant conditions. The balance of the discrepancy is caused by the shorter hold period (higher TCA) used in the plant (see earlier discussion).

The recommended two hour TCB addition is considered conversative. The recommended conditions result in a much faster reaction and even a one hour addition period would be quite safe with respect to any build up of unreacted material.

E. Effect of CH_3OH/TCB Mole Ratio

The effects of changing the CH_3OH/TCB ratio are given in Appendices II-5 and II-6 for recommended and present plant conditions, respectively. Both TDD and required hold period are dramatically reduced by increasing methanol concentration.

On two occasions lab batches made with low CH_3OH/TCB ratios (<6/1) gave noticeable temperature jumps. It is believed that poor control of this variable can and, perhaps, has resulted in runaway batches.

F. Effect of NaOH/TCB Mole Ratio

Both TDD and required hold time are quite sensitive to the NaOH/TCB mole ratio. This is shown in Appendices II-7 and II-8. Both TDD and required hold period are reduced by increasing the NaOH/TCB ratio. The beneficial effect levels off at a ratio of about 4 and, therefore, this is the recommended NaOH/TCB mole ratio.

G. Effect of H_2O/TCB Mole Ratio

The TDD level and the required hold period are both increased slightly with increasing water concentration (Appendices II-9 and II-10). When 72% NaOH is used in the process at a NaOH/TCB ratio of 4, the water introduced with the caustic is 3.5 moles/mole of TCB. The recommended H_2O/TCB ratio of 4.5 would require a combined fresh and recovered methanol charge containing 96.4% methanol (at a CH_3OH/TCB ratio of 15). This is probably not practical with the present plant methanol recovery system. Fortunately, the TDD level and the required hold time are only slightly increased by H_2O/TCB ratios up to about 8.2 (85% methanol - 15% water). Specific gravity of the recovered methanol is an inadequate indicator of the methanol and water content since the recovered methanol normally contains 4 to 6% dimethyl ether. A GLC method for analysis of recovered methanol is included in the analytical section of this report.

H. Miscellaneous Reactions

Run 36 was made under conditions identical to run 32 except that an iron coupon was present in the reaction. There was no significant difference in the TDD or in the required hold time in the presence of iron. The possibility of a catalytic effect of iron has been suggested in the literature (Ref. 3).

In another run, 24 g. of dimethyl ether was added to a reaction mixture otherwise identical to run 32. The CH_3OCH_3 was added with the methanol and water through the Jerguson gauge. Again, no significant change in TDD or hold period was found.

The actual charge for each reaction, along with the temperature, the TCB addition time and the maximum pressure attained (this always occurred near the end of the hold period) are given in Appendix III.

I. Reaction Mechanism

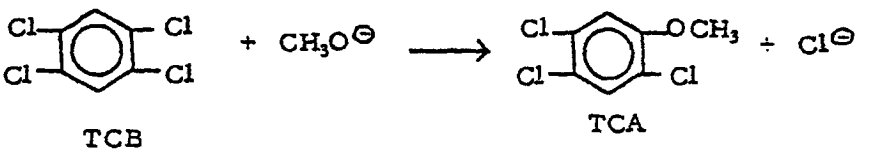
A GLC peak which elutes after TDD was present in all of the runs. This material usually decreased as TDD increased during the hold period. In slow reactions

where a significant TCA concentration was present throughout the hold period. the unknown peak continued to increase until the reaction was terminated. These observations suggest that TCA is a precursor of the unknown material and that the unknown, in turn, is a precursor of TDD. A set of reactions was carried out to test this hypothesis. The reactions were run at 170°C for 8 hours. The charges and analytical results are given in the following table:

Run	A	B	C	D
TCA charge	5 mmoles	5 mmoles	-	2.5 mmoles
TCP charge	-	-	5 mmoles	2.5
CH_3OH charge	100	100	100	100
H_2O charge	22	22	22	22
NaOH charge	-	10	10	5
TDD produced	0 ppm	2.5 ppm	7.5 ppm	30 ppm
UNK produced	0	0	0	8

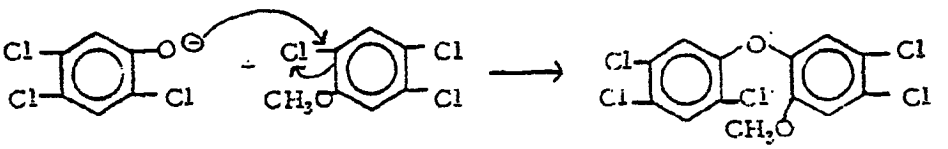
All of the results are consistent with the following reaction scheme:

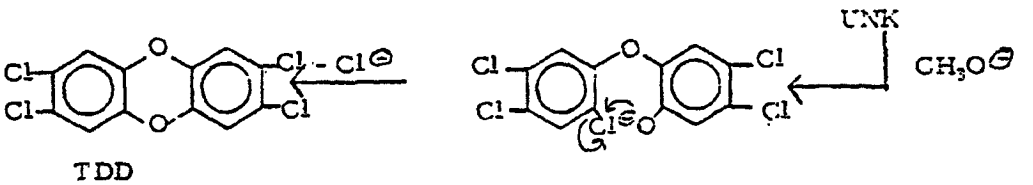
$$CH_3OH + Na^{\oplus} + OH^{\ominus} \rightleftharpoons CH_3O^{\ominus} + Na^{\oplus} + H_2O$$



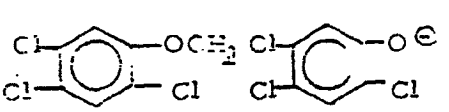
TCB TCA

NaTCP

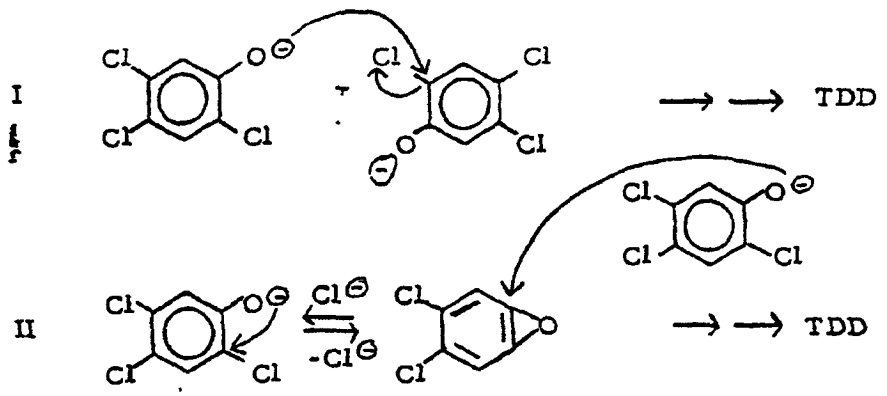




TDD



The fact that a small amount of TDD was produced in reaction C (but no unknown) indicates that a second pathway for the formation of TDD is available. Two possibilities are suggested:



Route II requires the intermediacy of dichloroepoxybenzyne. Although there are no other known reports of epoxybenzynes in the literature it is doubtful that route I, involving the attack of an anion on an anion, would be energetically feasible.

VIII. ANALYTICAL PROCEDURES

A. General

The analytical procedure devised for the study of the hydrolysis of tetrachlorobenzene comprises four methods. Trimethylsilylation is used on the assay for the various phenols (AG. Res. Final Report No. 37) and is a very accurate and reliable method. Unreacted tetrachlorobenzene (TCB) and intermediate trichloroanizole (TCA) are monitored by a second method; the analysis for tetrachlorodibenzo-p-dioxin (TDD) has been revised and the result is a method which gives reliability in low ranges of concentration (<0. 1 ppm), and finally, a GLC method for characterization of the recovered methanol samples.

The silylation procedure affords a method by which the sodium salts of the phenols can be esterified directly on aqueous medium. Esterification is quantitative. p-Chlorophenol is used as the internal standard.

From the benzene extract of the autoclave samples, the disappearance of tetrachlorobenzene and trichloroanisole is monitored, assayed and plotted as a function of time.

In the earlier stages of this work, the TDD analysis on a thermal conductivity detector was sufficient due to the fact that large levels of TDD were analyzed.

Realizing that much lower levels of TDD would have to be encountered, a new analytical method was developed using a flame detection system. The method gives very good sensitivity at low levels with no evidence of deterioration of the compound.

The autoclave samples were diluted and transferred with water to give an approximate weight ratio of 1: 1. To the aqueous sample was then added an aliquot of benzene and the sample placed on a Kahn Shaker for thirty minutes. If the two layers did not separate on standing, the sample was centrifuged. TCA and TCB were then analyzed from the benzene layer as well as the assay for TDD. The phenol analysis was then analyzed from the aqueous layer.

The analytical method devised for methanol analysis in plant distillate and recovered MeOH samples provides a fast, accurate measure of methanol, water and the low boiling impurity, dimethyl ether. The GLC column support is a relatively new porous polymer bead, Porapak. This support is used uncoated and gives good separation for gases and low-boiling organic molecules.

B. 2, 4, 5-TCP Analysis. GLC Standard Preparation

Liquid additions are made with pipettes and bulb or dropwise with droppers. Weights are to ±0. 0001 g. The standard preparation is facilitated by the use of pre-mix solutions of the dichlorophenols and methoxydichlorophenols.

1. Methoxydichlorophenol Pre-mix Preparation

   a. Into a tared 1-ounce round-bottom bottle is weighed 0. 09-0. 11 g. (±0. 0001 g.) of 2, 4-dichloro-5-methoxyphenol and 0. 09 g. -0. 11 g. (±0. 0001 g.) of 4, 5-dichloro-2-methoxyphenol.

   b. To this is added 9. 9-10. 1 g. (±0. 0001 g.) of pyridine. The contents are swirled and phenols allowed to dissolve.

2. Dichlorophenol Pre-mix Preparation

   a. Into a 2-ounce round-bottom bottle is weighed 0. 40-0. 60 g. (±0. 0001 g.) of 2, 5-dichlorophenol, 0. 20-0. 40 g. (±0. 0001 g.) of 2, 4-dichlorophenol and 0. 10-0. 30 g. (±0. 0001 g.) of 3, 4-dichlorophenol.

   b. To this is added 45. 0-47. 0 g. (±0. 0001 g.) of pyridine and contents thoroughly mixed

3. 2, 4, 5-TCP Standard Preparations

a. Into a 4-dram vial fitted with a polyethylene-lined cap are weighed 0. 0900-0. 1100 g. samples (±0. 0001 g.) of pure p-chlorophenol (PCP) and 2, 4, 5-trichlorophenol.

b. To this is added 0. 1000-0. 2000 g. samples (±0. 0001 g.) of the methoxydichlorophenol and dichlorophenol pre-mix solutions. Phenol content of the pre-mix solutions is calculated from the original preparation.

c. A 2. 0 ml. portion of pyridine is added to the vial and the contents are mixed thoroughly.

d. Chlorotrimethylsilane (0. 5 ml.) is then added slowly to the solution. Heat will evolve along with some fuming as a white solid precipitates. Carefully swirl the mixture and allow to cool.

e. Add 7. 0 ml. of hexomethyldisilazane (HMDS) carefully with mixing, whereupon a vigorous exothermic reaction will occur with ammonia evolution. This vigorous reaction will be more predominant in the silylation of the process samples due to the presence of water. When this initial reaction has subsided, the vial with loosened cap, is placed on a steam bath or heated block for 30-45 minutes. During the heat period, the contents of the vial are thoroughly mixed by tightening the cap and shaking vigorously. The solids can be washed down by tilting the vial on an inclined position.

f. After the heat period or upon the end of ammonia evolution, the vial is removed from heat source, allowed to cool slightly and again shaken with tight cap and solids washed down from walls.

g. After the solids have settled, withdraw 50 µl. samples of supernatant liquid for GLC runs. Prior to area correction factor runs, the column should be conditioned by 2-3 injections of 50 µl. samples of standard in rapid succession followed by a normal program sequence. Following this conditioning treatment, standard samples should be run daily to check the various ACF's (area correction factors).

h. Area correction factors for the various phenols with respect to PCP are determined in the usual manner; employing standard base-line corrections to each peak as needed, or by the method used in this report, an automatic integrator. If manual calculations are used the equation for an area correction factor is:

$$ACF_x = \left(\frac{\text{Area PCP}}{\text{Area X}}\right)\left(\frac{\text{Wt. X}}{\text{Wt. PCP}}\right)$$

where x = phenol constitutent

It is to be noted that although peaks are for the trimethylsilyl derivatives, the weight percent and area correction factor calculations are based on the free trichlorophenol and p-chlorophenol on the standards and are therefore expressed as phenol. (See Fig. 4) Conversion to other component forms are obtained by employing molecular weight ratio conversion factors, i. e. phenol x 1. 112 gives Na-TCP weight percent.

4. 2, 4, 5-TCP Analytical Sample Preparations

a. Into a 4-dram vial is weighed 0. 0900-0. 110 g. of p-chlorophenol (±0. 0001 g.).

b. A 0. 2000-0. 3000 g. sample of the aqueous Na-TCP autoclave solution is weighed into the vial (±0. 0001 g.). This weight is based on a 40-50% wt. ratio of sample and water on the aqueous sample of NaTCP. From this prior weight ratio calculation, the actual weight of sample can be calculated and should be in the range of 0. 0900-0. 1500 g.

c. A 2. 0 ml. aliquot of pyridine is then added to the vial and the contents mixed.

d. 0. 5 ml. of chlorotrimethylsilane is then introduced slowly. Heat will evolve, fuming will occur and white solids will precipitate. Mix the contents gently.

e. A 7. 0 ml. portion of HMDS is then introduced carefully. A vigorous reaction will set in with ammonia evolution. Tighten the cap and shake the contetns several times, venting the ammonia each time. Wash down the walls and heat the sample with cap loosened for 30-45 minutes or until ammonia evolution ceases.

f. After the heating period, tighten the cap and shake vigorously, vent and wash the particles from the walls.

g. When solids have settled and sample is cool, withdraw 50 µl. of supernatant liquid for GLC analysis. It should be noted at this point that in this silylation procedure, NaTCP is being reacted upon in the presence of water; therefore, excess HMDS must be used not only to react with the water that is

present to form the volatile hexamethyldisiloxane but to protect the silyl ethers from subsequent hydrolysis. If a sample is less than the 40-50% concentration figure, more HMDS will have to be used in the sample. (1 gram of water requires 9 grams of hexamethyldisilazane for effective control.)

g. If the weight percents of the components are manually calculated, the equation is:

$$\text{Wt. \% X} = \frac{Y\,(\text{Area X})(\text{ACF X})(\text{Wt. PCP})(100)}{(\text{Area PCP})\,(\text{Sample Wt.})}$$

where X is component
Y = 1.000

A typical chromatogram is illustrated by Figure 1.

5. GLC Instrument and Conditions

Instrument - F-M Model 720 with dual thermal conductivity detectors.

Columns - 10' x 1/4" S.S. packed with 5% DCQF-1 (Fluorosilicone oil) on 60-80 mesh Chromasorb W (HMDS). Thermal openings are plugged lightly with silanized glass wool.

Operating Temperatures -

Column oven - Programmed temperature from 100-250°C at a rate of 10°C/min.
Injector - 250°C
Detector - 265°C. WX Filaments,

Carrier Gas - Helium, inlet pressure - 40 psig., 100 ml./min. at column exit.

Sample Size - 50 µl.

Chart Speed - 30 in./hour.

6. Automatic Integrator System

The instrument used for the phenol analysis was hooked to an automatic integrator system which accepted the signal directly, converted it to a digital number and this number fed to a teletypewriter-printer which displayed the data andprovided a punched tape output. The punch tape is the fed to the computer through a time-shared terminal and data obtained.

Integrator - Infotronics CRS-12 Digital Integrator

Digital Filtering - 20	Slope Sensitivity - 3
Attenuator - Log, minimum - 10	Threshold Sensing - 50 μv.
Time Constant - 1 sec.	Baseline Tracking - 60 μv/min.
Input Noise - 2.0	Peak Rate - 3 sec.

Teletypewriter - Teletype Model 35

Computer - General Electric 235 Computer
Linked to GE Time-Share Terminal

C. Tetrachlorobenzene and Trichloroanisole Analysis

1. GLC Standard Preparation

This analytical method does not utilize internal standardization due to the wide range of concentration encountered. The following normalization procedure was followed.

a. Into a 2-ounce round-bottom bottle is weighed 2.5-3.0 g. (±0.0001 g.) of tetrachlorobenzene (TCB).

b. To this is added 100 ml. of benzene and contents thoroughly mixed.

c. Prepare 2-3 more standards in this manner varying concentration from 1.0-4.0 g. of TCB. This range will cover from 10-40 mg/ml. concentration.

d. Repeat the procedure with trichloroanisole (TCA).

e. Inject 3 μl. of each solution into the chromatograph and measure the peak height of the components in millimeters. The relative response will be linear and can be plotted. Average the peak heights daily and relate them to a constant attenuation figure. For the 30 mg/ml. standard, an attenuation of X16 is needed for this concentration. See Figure 5 for standard chromatogram.

2. TCA-TCB Analytical Runs

As mentioned previously in this report, the autoclave sample is diluted and extracted with benzene. It has been found in this work that 1 ml. of benzene for 5 grams of sample is very sufficient to extract the TCA, TCB and TDD that is present.

a. From this benzene layer is withdrawn a 3 μl. sample and injected into the instrument. Attenuation is adjusted and duplicate injections for each sample are made.

b. The peak heights for TCB and TCA are measured and averaged. Calculation for weight percent is as follows:

$$\text{Wt. \% X} = \frac{(\text{Peak Height X})(\text{Standard Conc. g/ml})(\text{Total Extract Volume})\ 100}{(\text{Peak Height Normalization Std})(\text{Sample Weight})}$$

where X is TCA or TCB

An example of the analysis is shown on Figure 2.

3. GLC Instrument and Conditions

Instrument - F-M Model 720 with dual thermal conductivity detectors.

Column - 2' x 1/4" S.S. packed with 10% DCSO 710 (Silicone oil) on 60-8- mesh Chromasorb W (HMDS treated).

Operating Temperatures

Column - 170°C Isothermal
Injector - 300°C.
Detector - 260°C.

Carrier Gas - Helium, inlet pressure - 30 psig., 110 ml/min. exit flow.

Sample Size - 3 λ (3μl.)

D. Tetrachlorodibenzo-p-dioxin (TDD) Analysis

1. GLC Standard Preparation

This analytical procedure was developed due to the need of sensitivity in low ranges of concentration. The original analysis was performed on a thermal conductivity detector, but as lower concentrations of TDD would be expected, this procedure proved to give accurate and quantitative measurements at low levels.

This analysis is also based on a normalization procedure. Internal standardization can be incorporated, if needed.

a. Into a 1-liter volumetric flask is weighed 0.0900-0.1000 g. of 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TDD). Care should be taken in this procedure so as not to allow any TDD to contact the skin or eyes.

b. Bring the volume to 1-liter with benzene.

c. From this stock solution, several standards can be prepared. Concentration of this solution will be in the range of .10 mg/ml. or 100 ppm. It is suggested that a range of normalization standards be prepared and used to obtain a normalization curve.

d. A 0.5 µl. aliquot is used for the analysis and gives full-scale deflection at a moderate attenuation level.

Keep the container exposure to air to a very minimum to avoid evaporation. Standards prepared in this lab 7-8 months ago still give no evidence of change in response levels. (See Figure 6 for TDD standard chromatogram)

2. TDD Analytical Runs

a. From the initial benzene layer, a 0.5 µl. sample is withdrawn an injected into the instrument. Attenuations are adjusted and duplicate runs are made. The peak heights of the TDD peaks are calculated and averaged.

b. The concentration of TDD on ppm is then calculated from the following expression:

$$TDD_{(ppm)} = \frac{(\text{Peak Height TDD})(\text{Conc. Std mg. /ml.})(\text{Total Volume Extract})}{(\text{Peak Height Normalization Std.})(\text{Sample Wt.})(\text{mg.})}$$

where: attenuation adjustments are equal for standard and sample.

(See Figure 3 for an actual process sample.)

3. GLC Instrument and Conditions

Instrument - P-E Model 880 with dual flame detectors.

Columns - 6' x 1/8" S.S. packed with 5% DCQF-1 (Fluorosilicone oil) on 60-80 mesh Chromasorb W (HMDS treated).

Operating Temperatures

Column oven - 215°C Isothermal
Injector - 325°C.
Detector - 265°C.

Carrier Gas (N_2) - 40 psig. inlet pressure, 30 ml/min exit flow.

H_2 (Prepurified) - 50 psig. inlet, Reference flame - 15 psig.
Sample flame - 15 psig.

Air (Breathing) - 5- psig. inlet, ≈ 500 ml./min. flow.

Sample Size - 0.5% (0.5 µl.)

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E. Recovered Methanol GLC Procedure

1. GLC Standard Preparation

The procedure for this analysis employs absolute ethanol as an internal standard. Due to the volatility of the components, a special vial is used, namely, a septum vial. After the components are added, the vial is not opened. Sampling is permitted through a teflon-coated septum.

a. Into a 2-dram (7.0 ml.) vial is weighed 1.80-2.00 g. (±0.0001 g.) distilled water.

b. To this is added 0.90-1.10 g. (±0.0001 g.) methanol.

c. Absolute ethanol is then added to the contents with dropper, 1.10-1.30 g. (±0.0001 g.).

d. Finally, 0.09-0.11 g. (±0.0001 g.) of dimethyl ether is added. Dimethyl ether from a lecture bottle was used. The cylinder was inverted and liquid $(CH_3)_2O$ charged in this manner.

e. It is recommended that several standards are prepared with the concentrations of the components being varied to cover a wide range.

f. A 0.5 µl. portion is injected into the GC and temperature programmer activated. Areas for the components are calculated, with corrections, and the area correction factors are ascertained. It is advisable to run daily standards for this analysis also. ACF is calculated from the following equation:

$$ACF_x = \frac{(\text{Area EtOH})\ (\text{Wt. X})}{(\text{Area X})\ \ (\text{Wt. EtOH})}$$

where x = component

A sample chromatogram is attached (Figure 8).

Standard deviations for the components of this analysis are from ±2.0% for dimethyl ether to ±1.0% for methanol.

2. Recovered Methanol Analytical Samples

a. Into a septum-vial is weighed 2.80-3.00 g. (±0.0001 g.) of recovered methanol.

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b. To this is added 2.80-3.00 g. (±.0001 g.) of ethanol. (These weights are designed to leave very little vapor space in the vial.)

c. A 0.5 µl. sample is then withdrawn and injected into the chromatograph. Attenuations are adjusted and areas calculated therefrom by the equation:

$$\text{Wt. \% X} = \frac{(\text{Area X})(\text{ACF X})(\text{Wt. EtOH})(100)}{(\text{Area EtOH})(\text{Sample Wt.})}$$

or by the electronic integrator system that was used in this lab and illustrated in Figures 8 and 9.

3. GLC Instrument and Conditions

Instrument: F-M 720 with dual thermal conductivity detector (WX-Filaments)

Column: 6' x 1/4" S.S. packed with Porapak T (80-100 mesh)

Injector - 250°C

Detector - 265°C

Column Oven - Programmed from 120-180°C. at 10°/min.

Carrier Gas - Helium, 40 psig inlet, 100 ml/min. exit flow.

Sample Size - 0.5 µl.

4. Integrator System

Integrator - Infotronics Model CRS 104

60 µv./min. Basline tracking
4 KC/MV, 50 µv. threshold level

Input noise - 2

3 sec. peak, Sensitivity - 3

F. GLC Results

Excellent precision and accuracy for the 2, 4, 5-trichlorophenol analysis has been evidenced over the entire 1-year period. Table I summarizes area correction factor data obtained over a six month period. The 2, 4, 5-TCP ACF gives a standard deviation of ≤1.0% relative.

The uniqueness of the analytical procedures described in this report lies in simplicity of obtaining all the desired data from one aqueous sample. The TCA and TCB along with the TDD analyses are obtained directly from the organic phase while the aqueous phase renders the chlorophenol values.

The silylation procedure continues to give excellent derivitization of phenols. The ability to convert the phenol to its volatile silyl ether in the presence of water provides a simple, one-step procedure. Several new silylating reagents are available now and could be utilized in place of the combination of HMDS and CTMS, if desired.

The recovered methanol analysis is designed to provide an accurate and reliable GLC analysis. The analysis time required is about 9 minutes.

Comparison of the GLC analysis for methanol with a specific gravity analysis consistently showed a higher analysis of methanol by the gravity method (3-10%).

It is recommended that the GLC method be implemented into the total analytical scheme for the process.

G. Materials and Equipment

Materials used in this report are as follows:

Hexamethyldisilazane, A 3402 (HMDS)	Peninsular Chemresearch
Chlorotrimethylsilane, CX 1495 (CTMS) (This material must be distilled for use, b. p. - 56. 5-57/760 mm.)	Matheson, Coleman and Bell
Pyridine, Anal. Reagent 7180	Mallinckrodt
p-Chlorophenol, 366 m. p. 42-44°	Eastman Organic
2. 4, 5-Trichlorophenol, zone-refined	Hooker Chem.
2, 5-Dichlorophenol, 3523	Eastman Organic
2. 4-Dichlorophenol, 1953	Eastman Organic
3, 4-Dichlorophenol	K and K Labs.
3. 4-Dichloro-5-Methoxyphenol	Ag. Research
4. 5-Dichloro-2-Methoxyphenol	Ag. Research

2, 4, 5-Tetrachlorobenzene, S-63-2258	Hooker Chem.
Trichloroanisole	Ag. Research
2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin	Dow Chem.
Porapak T	Waters Assoc. Framingham, Mass
Dimethyl Ether	Matheson, Coleman and Bell

IX. TOXICITY AND HAZARDS

Hexamethyldisilazane and chlorotrimethylsilane toxicity is not known. Since they are both potent silylating reagents, care should be taken to avoid contact with the skin, eyes, etc. Preparation of all samples in this laboratory was performed in a hood, especially the silylation procedure which evolves considerable ammonia.

Normal precautions should be exercised for all of the analytical procedures in this report.

The acute toxicity of tetrachlorodibenzo-p-dioxin (TDD) cannot be overly emphasized. It is recommended that safety glasses, gloves, safety shoes and face shield constitute the very minimum safety requirement. Care should also be taken to avoid back-flashing from a poor septum in the GLC instrument.

X. APPENDIX

Figures

1. 2, 4, 5-TCP Autoclave Sample Chromatogram
2. TCB-TCA Autoclave Sample Chromatogram
   TDD Autoclave Sample Chromatogram
4. 2, 4, 5-TCP Standard Chromatogram
5. TCB-TCA Standard Chromatogram
6. TDD Standard Chromatogram
7. Current Nitro Storage Tank Chromatogram
8. Methanol Standard
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Tables

I. Materials and Conditions for GC Runs
II. Plots of Y1 and Y2 vs. Individual Variables

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II. Data for 36 Runs

III. ACF for 2, 4, 5-TCP and Chlorophenols