STATUS REPORT

# VINYL CHLORIDE

## DETERMINATION OF TRACE IMPURITIES IN MONOMER PRODUCED BY SYNTHESIS FROM ACETYLENE AND HYDROGEN CHLORIDE

**Authors:** J. F. Haskin
V. A. Yarborough*
H. F. White
W. R. Godbey

**Date:** November 25, 1964
**Project No.:** 320G10
**File No.:** 3301

SUMMARY Incremental expansion of the vinyl chloride unit of the South Charleston Plant has revived the question of "heavy end" impurities in vinyl chloride monomer. The proposed expansion makes use of increased catalyst concentration and reactant pressure in the synthesis section. A weathering-off method has been developed that can be applied by the Quality Control Laboratory for routine monitoring of the vinyl chloride product. This method is specific for the determination of higher boiling impurities in the vinyl chloride monomer. However, impurities whose boiling points are between -15°C and 30°C may be overlooked by this procedure, and, because this boiling point range should be included in any impurity study, further work is indicated.

In comparing the modified to unmodified convertor effluent over a period of two months, no difference was found in the quality of monomer produced. However, upon increasing the pressure of reactant in the convertors, a higher concentration of the dimolar addition product (1,1-dichloroethane) has been found in the convertor effluent. After proper purification, this increased impurity concentration should not effect the final product, and, hence, neither increased catalyst concentration nor reactant pressure has had a demonstrated effect on product quality.

INTRODUCTION Incremental expansion of the South Charleston vinyl chloride plant has been undertaken via the expansion of the synthesis unit. This expansion has been necessary to meet the increasing demands for vinyl chloride monomer and to keep the production of hydrogen chloride by the pyrolysis unit more closely in balance with its use in the synthesis unit. The expansion of production in the synthesis unit is being accomplished not by construction of more catalytic convertors, but rather by increasing the concentration of mercuric chloride catalyst on the carbon support (from 10 to 25 per cent $HgCl_2$) and by increasing the flow of acetylene and hydrogen chloride over the catalyst as a result of increasing the reactant gas pressure.

*This project was initiated while Dr. Yarborough was group leader

**Research and Development Department**
**Chemicals Division**
**Union Carbide Corporation**

DISCUSSION Several methods (1,2) have been proposed for the determination of trace quantities of materials in vinyl chloride monomer, but no effort will be made here to evaluate the various procedures. Suffice it to say that for various reasons these methods were deemed not applicable. After discussions with Messrs. W. E. Whitehurst and J. P. Fletcher it was decided that the separation and analysis scheme (3) devised by Mr. J. E. Larkin of the Firestone Plastics Company would be modified for our use.

## Analytical Method

The Firestone procedure was developed for the determination of ethylene dichloride (1,2-dichloroethane) in vinyl chloride monomer. "...a large amount of liquid vinyl chloride monomer is mixed with a small amount of a high boiling solvent. The vinyl chloride is allowed to weather off and the higher boiling ethylene dichloride remains in the solvent. The ethylene dichloride is separated by means of gas chromatography and its concentration in the solvent is determined by proportionation of peak areas. Concentration of ethylene dichloride in vinyl chloride may then b calculated. ..." (3). In a normal analysis, the following peaks will be seen in the order given: air, vinyl chloride (dissolved in the solvent), ethylene dichlorid and solvent.

The exact procedure used will be discussed in the procedure section, but the above outline was followed to yield chromatographic analyses of the "heavy ends" in vinyl chloride. Instead of the one heavy implied in the above outline, as many as fourteen impurity peaks have been found in unrefined vinyl chloride obtained from the bottom of a synthesis unit convertor as shown in Figure 1. As discussed in the next section only the major peaks are identified, and, even though a doublet is observed at about three minutes retention time, only one compound could be identified (1,1-dichloroethane) in this peak. Refined vinyl chloride, on the other hand, may show no or only one (acetone at measured 10 ppm level) impurity peak by this technique.

## Impurity Identification and Concentration

Occurrence of several impurity peaks in the convertor product stream has necessitated their identification. Again in this instance, we profited by the experience of our predecessors in these investigations. The Goodrich method (2) lists some 25 impurities while the Carbide methods (1) suggest some 15 materials that may be present. Impurities whose peak area suggests they are present at 10 parts per million or less were not identified; higher concentration impurities were identified mass spectrometrically after a gas chromatographic isolation. The important heavy impurities found in the unrefined synthesis stream were found to be acetone, 1,1-dichloroethane, and 1,2-dichloroethane. The reader should be reminded that volitle materials such as hydrogen chloride, acetylene, ethane, ethylene, vinyl chloride and the "heavy ends" of a chromatographic separation using a hexadecane column (such as n-butane, vinylidene

chloride and acetaldehyde) were all evaporated in the weathering process. Concentrations (as measured) of the detectable impurities in the two streams monitored over a period of two months are listed in Table I and shown graphically in Figures 2, 3 and 4. Methods and errors in the calculation of these impurity concentrations will be discussed in the next section, but because computational errors are common to both sets of data, comparisons between them may be made. From these data it must be concluded that the two convertors are producing equivalent monomer.

## Methods of Calculating Impurity Concentration and Associated Errors

The concentration of various impurities in the high boiling solvent is a function of their concentration in the vinyl chloride, the amount of vinyl chloride weathered off, the amount of solvent used, the relative volatiles of the individual impurities, and the kettle temperature at which the distillation is terminated. In an effort to keep the variables minimized one set of conditions has been followed (see procedure section).

In addition to minimizing variables, the "standard conditions" procedure also permits the direct comparison of results regardless of errors in the method of treating the data. A gas chromatogram of the contaminated solvent is analyzed by proportionation of peak areas (area per cent). Because it has been found that in the region of 75 per cent styrene and 25 per cent impurities the factor between weight per cent impurity and its chromatographic area per cent is essentially one (ranges between 0.9 and 1.1 were found), the gas chromatographic area per cent is designated weight per cent impurity in solvent.

Weight fraction of impurity in the solvent is obtained by multiplying weight per cent impurity by one hundredth the solution density. The density of a solution containing eighty per cent styrene, ten per cent vinyl chloride and ten per cent other impurities would be close to the density of styrene (0.908 at 20°C (4) ). Because the density is close to one and if sample sizes are constant, the weight per cent impurity in the solvent can be assumed to be 100 times its weight in the solvent. But the weight of impurity in solvent is just the weight of impurity in the original volume of vinyl chloride provided none of the impurity is lost by the weathering process.

The weight per cent impurity in vinyl chloride is obtained by dividing the weight of impurity in solvent by the weight of vinyl chloride allowed to evaporate. The specific gravity of vinyl chloride is 0.912 at 20°C (4) which is also close enough to one to again allow rounding without significant loss of accuracy. Appendix A compares the results calculated with and without the rounding assumptions discussed; it can be seen that either method of calculation will produce the same result provided computational consistency is maintained.

An even greater source of error than the simplifications described above is found in the tacit assumption that the impurities will not evaporate, or that the "as measured" concentrations are the actual impurity concentrations in the vinyl chloride monomer. Because of the volatility of the impurities, for comparative analyses it is important to maintain both reproducible sample size (vinyl chloride) and weathering conditions (time and temperature). Heeding these precautions, it is possible to obtain reproducible values on the amount of impurity remaining in the solvent after the weathering process. Table II shows the amounts of the three major impurities recovered when various solutions of the individual impurity in styrene were mixed with two hundred milliliters of liquid vinyl chloride, forming a homogeneous solution, and the vinyl chloride is allowed to evaporate in accordance with the procedure discussed. From this table it can be seen that the recoveries are reproducible, but the recovered amount is less than half the original concentration. Such recovery data again points up the necessity of using "standard conditions" in this determination particularily if comparisons are to be made.

Table II also lists some "analytical factors"; these factors are the multipliers that convert the "as measured" concentrations discussed throughout this report to the actual concentration of impurity in liquid vinyl chloride monomer.

Process Data

Returning now to the purpose of this work, the vinyl chloride monomer produced in the catalyst modified convertor is compared with that produced in the unmodified convertor in Table I and Figures 2, 3 and 4. The table and figures sh w that both convertors are producing equivalent vinyl chloride. The figures do show, however, a great increase in concentration of acetone and 1,1-dichloroethane in the product since the initiation of this study.

The authors have no immediate explanation for the increased concentration of acetone in the product, but they do understand how the concentration of 1,1-dichloroethane could increase. The process under study is the synthesis of vinyl chloride from acetylene and HCl over $HgCl_2$ catalyst. With the increased catalyst concentration and pressure of reactants, it seems logical to expect an increase in the two molar addition product or in the addition of hydrogen chloride to vinyl chloride. Such a higher boiling impurity should be rectified in the purification process and never get into the product. It will, however, put an increased load on the purification stage of this process. It should again be emphasized that the numbers quoted in Table I and Figures 2, 3 and 4 are the "as measured" concentrations; true impurity levels are obtained by using the analytical factors of Table II.

PROCEDURE Two hundred milliliters of liquid vinyl chloride (measured to the nearest milliliter) are mixed with one milliliter of styrene in a two hundred fifty cubic centimeter Erlenmeyer flask (previously chilled to liquid nitrogen temperature). This solution is allowed to stand unstoppered in a fume hood for not longer than three hours or until the bottom of the flask is no longer cold to the touch which ever is sooner (the vinyl chloride is completely weathered off). The cont nts of the flask are transferred to a one-ounce vial and are ready for chromatographic analysis.

Gas chromatographic analysis of the weathering residues is done using a six-foot column of 15 per cent substrate (equal parts of TERGITOL - E68, Apiezon N and Apiezon W) on acid washed Chromosorb W operated isothermally at 100°C. Helium carrier gas flow is adjusted to give a styrene retention time of 32 minutes. Other gas chromatographic parameters for an F & M 500 gas chromatograph are listed in Table IV. Under these conditions the retention times of the various components are as follows:

| Component | Retention Time (minutes) |
|---|---|
| Vinyl Chloride | 1.0 |
| Acetone | 2.0 |
| 1,1-Dichloroethane | 3.0 |
| Unidentified No. 1 | 4.0 |
| Unidentified No. 2 | 4.5 |
| 1,2-Dichloroethane | 6.2 |
| Unidentified No. 3 | 9 |
| Unidentified No. 4 | 11 |
| Unidentified No. 5 | 15 |
| Unidentified No. 6 | 18.5 |
| tert-Butylcatechol | 21 |
| Styrene | 32 |

Figure 1 shows a chromatogram obtained using these conditions. The styrene retention time is only thirty minutes, but such a slight increase in carrier flow does not seriously affect the analysis because the major peaks are well resolved.

Areas of all peaks are measured with attenuation factors being duly applied. The total area under the chromatogram is, then, the sum of the individual peak areas, and the individual peak area percentages are calculated from this total area. As stated in a previous section, factors for the conversion of gas chromatographic area per cent to weight per cent impurity in styrene solution have been found to be essentially unity; therefore, the measured area percentages are defined as the weight percentages of th individual components in the styrene mixture. As shown in Appendix A these area percentages can be assumed to be 100 times the weight fraction of impurity in one milliliter of styrene, or equal to 100f times the weight of impurity in 200 milliliters of vinyl chloride solution (here f is the recovery factor which also need not be known in treating

a consistent set of data). Parts by weight of impurity per million (ppm) parts of vinyl chloride are obtained by dividing the gas chromatographic per cent by the volume (200 ml) of vinyl chloride used in the weathering process (yielding parts per hundred) multiplying the resulting quotient by 10000:

$$\left( \frac{\text{GC area per cent}}{\text{ml vinyl chloride}} \right) \times 10^4 = \text{as measured ppm impurity in vinyl chloride.}$$

While these values have been used throughout this report and can be used whenever comparisons are made, they do not represent the true concentration of the impurity in vinyl chloride. Actual impurity concentrations are obtained by multiplying the "as measured" value by the analytical factor.

Impurity concentration = (as measured ppm) $f_i$, where the impurity concentration is now ppm in liquid vinyl chloride and the $f_i$'s are given in Table II.

The attached method, Appendix B, outlines this procedure in the methods manual format.

RECOMMENDED FUTURE STUDIES As indicated in the discussion section, impurities such as n-butane, acetaldehyde and perhaps vinylidene chloride ($CH_2 = C Cl_2$) may evaporate in the weathering process. These impurities and others boil in the -15°C to 40°C range, and surely those materials boiling in the lower 40° of this range are lost by evaporation and entrainment in boiling vinyl chloride. The procedure might be extended to include this range if a lower weathering temperature were maintained (flask in an ice bath) and rectification were attempted via a cold reflux condensor.

The plant expansion, of course, is not complete; a caustic scrubber system will be installed in the product stream somewhere ahead of the refining still. Product quality should be monitored by this and other methods during and after this installation.

In addition to the above additional studies, this report leaves at least two questions unanswered. These questions are as follows:

1. Will the concentration of 1,1-dichloroethane continue to increase with time or will it reach a limiting value?

2. At what concentration level of 1,1-dichloroethane in the crude product will it begin to appear in the refined product under present refining conditions?

These questions may be resolved by further sampling of the convertor effluent, perhaps at less frequent intervals, and by comparing the weathering analysis of the new samples with the analyses in this report. In addition the new samples' analyses should be

compared with a weathering analysis of refined product from the synthesis unit.

The basis of this report and future studies should be not just current plant expansion but in the general knowledgeability of our product. The projected oxychlorination process will produce monomer by a different route; these studies will insure complete knowledge of our monomer and, hence, the maintenance of future product quality.

BIBLIOGRAPHY

(1) Union Carbide Chemicals Company, Laboratory Manual 58C-9C1-V6.1, -V6.2, and V6.3a.

(2) American Society for Testing and Materials, Committee D-20 on Plastics "Proposed Gas Chromatographic method for Vinyl Chloride Monomer" by J. P. Cornwell, B. F. Goodrich Chemical Company, May 22, 1964.

(3) Larkin, J. E., Raw Material Test No. R-001-15, Ethylene Dichloride in Vinyl Chloride Monomer, Resin Plant Laboratory, Chemical Division, Firestone Plastics Company, June 13, 1960.

(4) Tables of Physical Properties, Laboratory Manual Volume 40, Table 40-1-1b Pages 50 and 56.

NOTEBOOK REFERENCE: 4848-32

ATTACHMENTS
3 Tables
4 Figures
2 Appendices
58C-9C1-V6.4

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TABLE I

COMPARISON OF "AS MEASURED" CONCENTRATIONS OF IMPURITIES IN SYNTHESIS PROCESS CONVERTOR EFFLUENT

| Week ending | 8/8 | 9/5 | | 9/12 | | 9/19 | | 9/26 | | 10/10 | | 10/17 | | 10/24 | | 10/31 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C nvertor No. | 3 | 3 | 4 | 3 | 4 | 3 | 4 | 3 | 4 | 3 | 4 | 3 | 4 | 3 | 4 | 3 | 4 |
| Impurity | | | | | | | | | | | | | | | | | |
| Acetone | 77 | 397 | 480 | 397 | 304 | 300 | 448 | 826 | 626 | 720 | 170 | 740 | 384 | 332 | 278 | 306 | 273 |
| 1,1-Dichloroethane | 21 | 58 | 610 | 58 | 76 | 64 | 61 | 36 | 40 | 30 | 350 | 60 | 461 | 166 | 249 | 403 | 358 |
| Unidentified No. 1 | 2 | 45 | -- | -- | 2 | 12 | 9 | 4 | 7 | 13 | 60 | 5 | 2 | 4 | 2 | 2 | 2 |
| No. 2 | 51 | TR | -- | 5 | TR | TR | 4 | 4 | -- | 5 | 5 | 3 | 2 | 4 | 4 | 6 | 4 |
| 1,2-Dichloroethane | 51 | 63 | 120 | 63 | 60 | 138 | 105 | 92 | 79 | 90 | 110 | 100 | 82 | 81 | 75 | 94 | 106 |
| No. 3 | 2 | 1 | TR | 1 | -- | -- | 2 | 16 | 9 | 10 | 5 | 3 | 4 | 4 | 4 | 4 | 4 |
| No. 4 | 2 | TR | TR | TR | 2 | TR | 14 | -- | 3 | -- | 3 | TR | 9 | 2 | 4 | 2 | 2 |
| No. 5 | 6 | 33 | 30 | 33 | 4 | 15 | 2 | -- | 10 | 6 | 3 | 7 | -- | -- | -- | -- | -- |
| No. 6 | 2 | Nil | -- | Nil | -- | -- | 9 | -- | -- | TR | -- | TR | -- | -- | -- | -- | -- |

TABLE II

RECOVERY EXPERIMENTS

1,2-DICHLOROETHANE

| Weight Per Cent in Styrene | | Weight Per Cent Recovered | | | Mean Recovery | Per Cent (1) Recovered | Analyses Factor (2) |
|---|---|---|---|---|---|---|---|
| Added, wt % | Analysis, area % | No. 1 | No. 2 | No. 3 | | | |
| 1.74 | 1.80 | 0.95 | 0.94 | 0.93 | 0.94 | 52.2 | 1.85 |
| 3.53 | 3.78 | 2.07 | 1.86 | 1.92 | 1.95 | 51.6 | |
| 12.84 | 13.00 | 7.76 | 7.77 | 7.23 | 7.59 | 58.4 | |
| | | | ACETONE | | | | |
| 5.17 | 6.07 (3) | 1.95 (1.66) | 1.69 (1.44) | 1.71 (1.46) | 1.78 (1.52) | 29.3 (29.3) | 2.90 |
| | | | 1,1-DICHLOROETHANE | | | | |
| 7.59 | 7.05(4) | 1.96 | 2.06 | 2.08 | 2.03 | 28.8 | 3.74 |

(1) Per cent recovery based upon area per cent (analysis) in styrene.

(2) Analysis factor is multiplier that converts area per cent recovered to weight per cent added.

(3) Acetone area per cent to weight per cent factor is 0.852

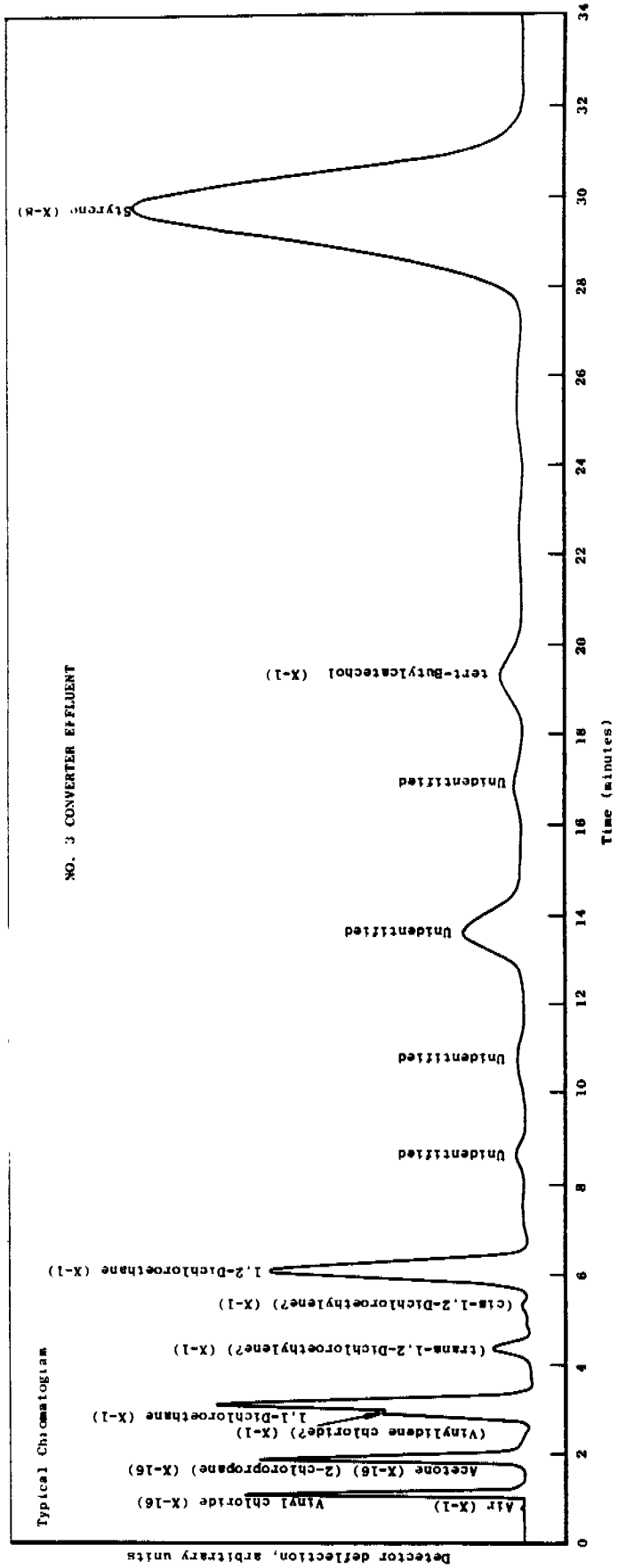
(4) 1,1-Dichloroethane area per cent to weight per cent factor is 1.077.

TABLE III

PARAMETERS FOR AN F & M 500 GAS CHROMATOGRAPH FOR VINYL CHLORIDE RESIDUE ANALYSIS

| | |
|---|---|
| Column | 6 feet of 1/4-inch tubing containing 15 per cent substrate (equal parts of TERGITOL E68, Apiezon N and Apiezon W) on acid washed chromosorb W. |
| Column Temperature | Isothermal at 100°C |
| Flow Rate | Adjusted to give styrene a retention time of 32 minutes |
| Detector current | 200 milliamperes |
| Sample volume | 1 microliter |
| Detector Temperature | 300°C |
| Injection Port Temperature | 250°C |

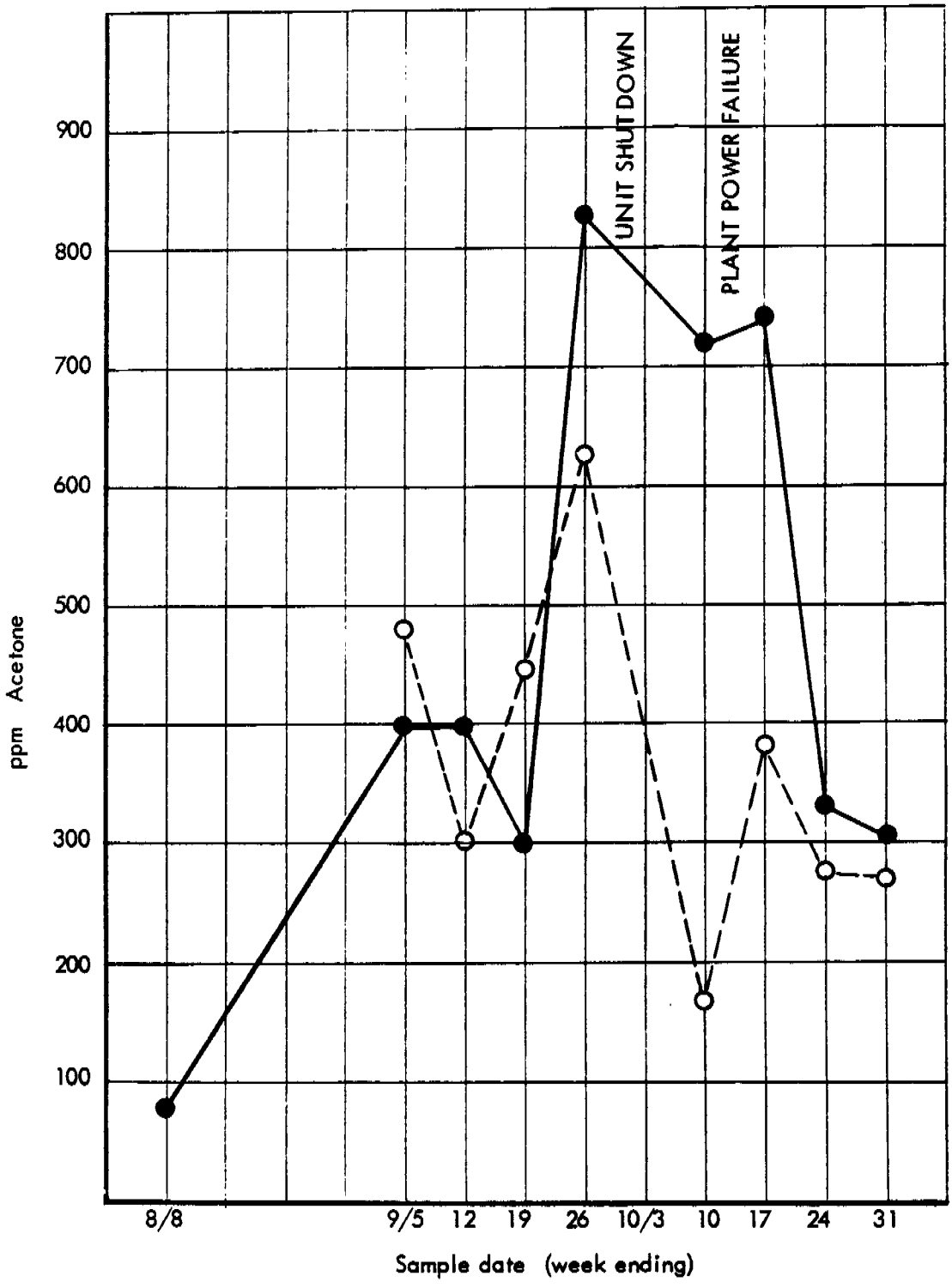
FIGURE 1



ACETONE IN CONVERTOR PRODUCT

Solid Convertor No. 3 (Normal)

Broken No. 4 (Modified)

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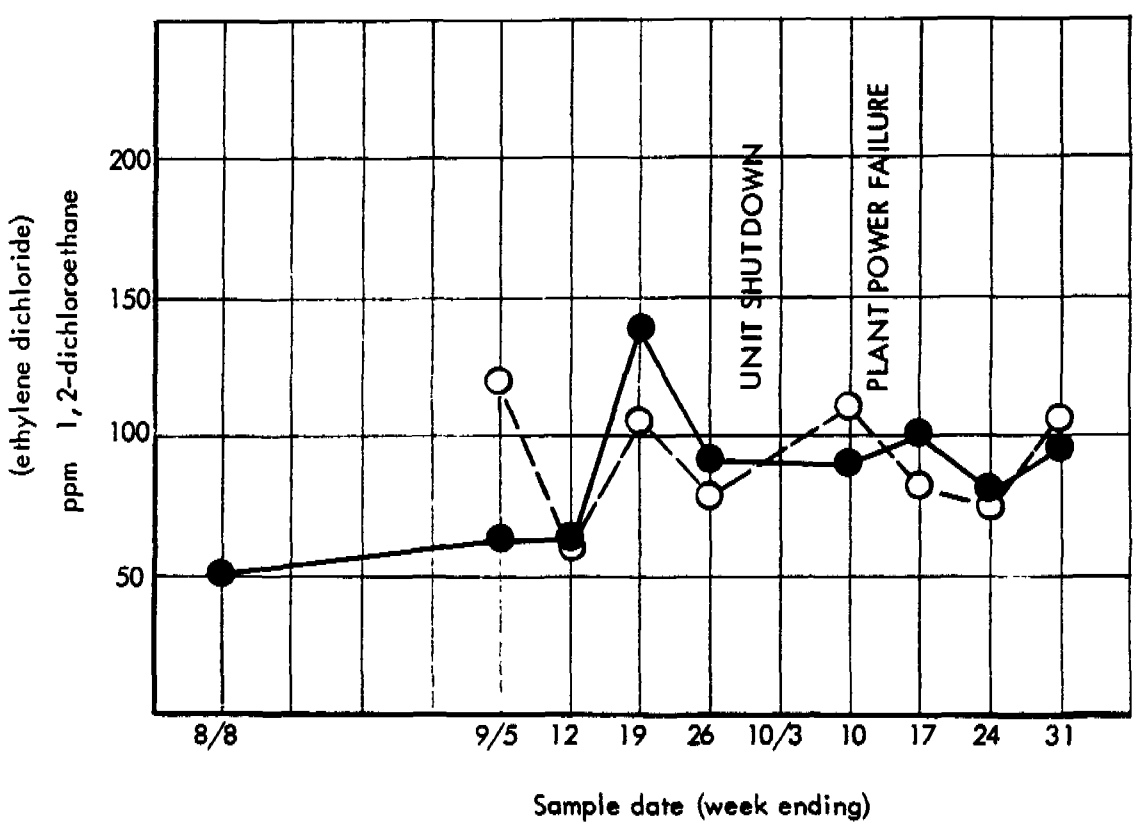
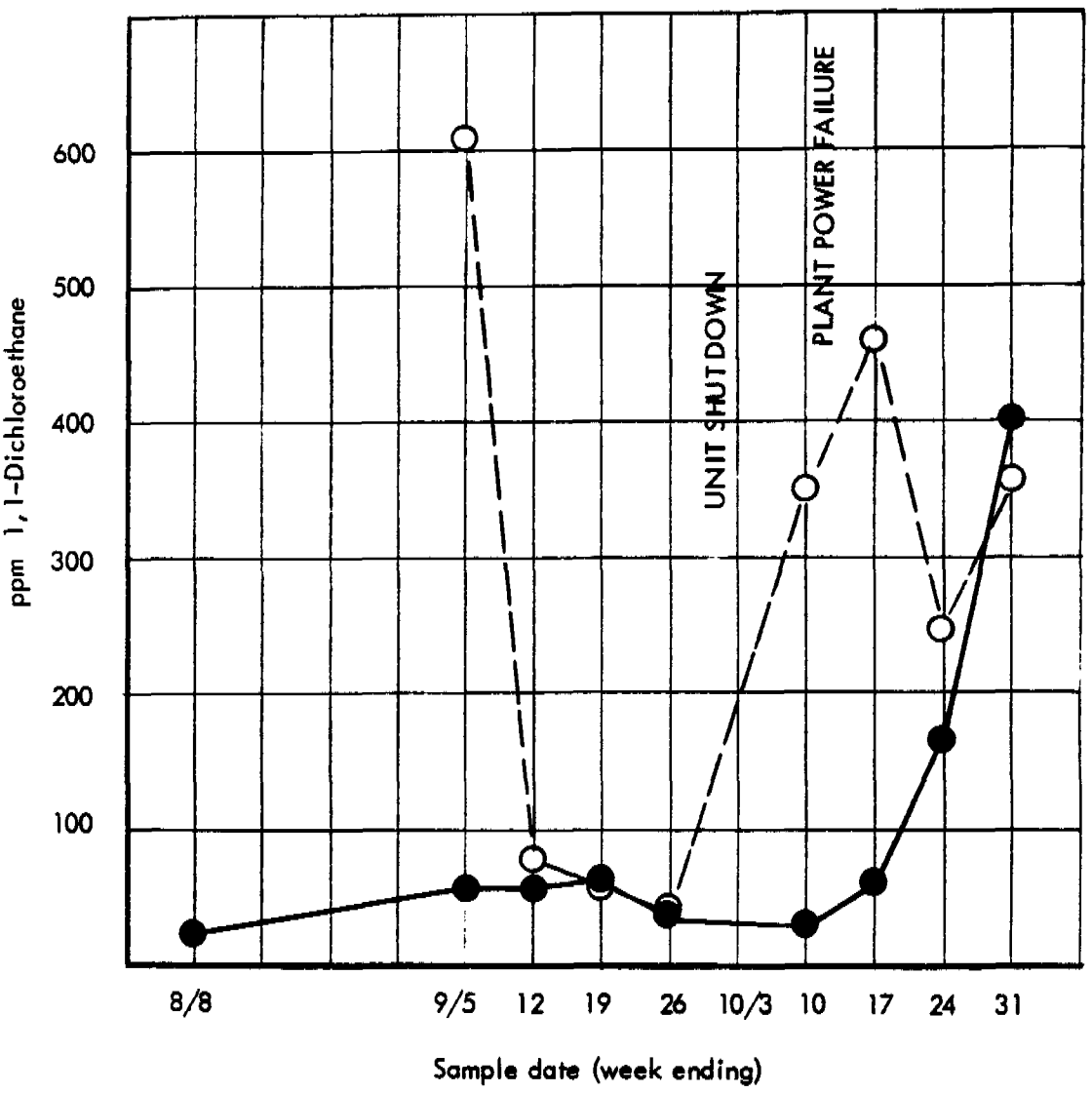
1,2-DICHLOROETHANE IN CONVERTOR PRODUCT

Solid No. 3 (Normal)
Broken No. 4 (Modified)



1,1-DICHLOROETHANE IN CONVERTOR PRODUCT

Solid No. 3 (Normal)
Broken No. 4 (Modified)



## APPENDIX A

## COMPARISON OF CALCULATIVE METHODS IN ANALYSIS OF MEASURED AMOUNTS OF IMPURITIES

At least two assumptions are made in the calculation of impurity concentrations in this procedure. The purpose of this appendix is to show that the effects of these assumptions are both small and in opposite directions so as to be cancelling assumptions.

The first assumption is that the specific gravity of the impurity containing solvent solution is 1.00 instead of the specific gravity of the solvent (styrene, 0.908 20/20 (4) ). Table A-1 presents the area per cent of each component as obtained from the chromatogram and the resulting weight of component for each component in the sample. It can be seen that at the concentrations listed the two weights are the same to within 10 per cent of the contained amount.

The weights shown in Table A-1 represent the weight of impurity in the 200 milliliters of vinyl chloride. This volume of vinyl chloride weighs either 200 or 182 grams depending upon the specific gravity used (1.00 assumed or 0.912 20/20 (4) ). The concentrations of the impurities in parts per million are obtained by multiplying the weights listed in Table A-1 by 1000/200 or 1000/182, depending upon the vinyl chloride gravity used; these concentrati ns are listed in Table A-2. The center two columns of this table indicate that either consistent set of assumptions (styrene gravity = 0.908 and vinyl chloride gravity = 0.912 or both gravities = 1.00) yields the same vinyl chloride analysis.

Table A-1

Calculation of Weight of Impurity in One Milliliter Styrene

| Impurity | Gas Chromatographic Area Per Cent (1) | Weight in Solution | |
|---|---|---|---|
| | | Solution Gravity 1.00 | Styrene Gravity 0.908 |
| Vinyl Chloride | 0.16 | 0.0016 | 0.0015 |
| Acetone | 1.54 | 0.0154 | 0.0140 |
| 1,1-Dichloroethane | 0.42 | 0.0042 | 0.0038 |
| Unidentified No. 1 | 0.04 | 0.0004 | 0.0004 |
| No. 2 | 0.04 | 0.0004 | 0.0004 |
| 1,2-Dichloroethane | 1.02 | 0.0102 | 0.0093 |
| Unidentified No. 3 | 0.04 | 0.0004 | 0.0004 |
| No. 4 | 0.04 | 0.0004 | 0.0004 |
| No. 5 | 0.12 | 0.0012 | 0.0011 |
| No. 6 | 0.04 | 0.0004 | 0.0004 |
| Tertiary butylcatechol | 0.43 | | |
| Styrene | 95.09 | | |

(1) Area per cent to weight per cent factor is 1.0 to within ten per cent

Table A-2

Concentration of Impurities in Vinyl Chloride Monomer

| Impurity | Parts Per Million by Weight of Impurity | | | |
|---|---|---|---|---|
| | Vinyl Chloride Gravity = 1.00 | | Vinyl Chloride Gravity = 0.912 | |
| | Solution Gravity | | Solution Gravity | |
| | 0.908 | 1.00 | 0.908 | 1.00 |
| Acetone | 85 | 77 | 77 | 70 |
| 1,1-Dichloroethane | 23 | 21 | 21 | 19 |
| Unidentified No. 1 | 2 | 2 | 2 | 2 |
| No. 2 | 2 | 2 | 2 | 2 |
| 1,2-Dichloroethane | 56 | 51 | 51 | 46 |
| Unidentified No. 3 | 2 | 2 | 2 | 2 |
| No. 4 | 2 | 2 | 2 | 2 |
| No. 5 | 7 | 6 | 6 | 6 |
| No. 6 | 2 | 2 | 2 | 2 |

5 SAMPLE HANDLING Place one ml of styrene in the stoppered Erlenmeyer flask and chill for 15 minutes or until the styrene is frozen (approximately 15 minutes for deep freeze). Into a chilled graduated cylinder measure 100 ml of liquid vinyl chloride and transfer to the flask containing styrene; swirl to insure complete solution of the styrene in the liquid vinyl chloride. Add a second 100 ml of liquid vinyl chloride and again swirl into solution. Allow this solution to stand unstoppered in a fume hood for not longer than three hours or until the bottom of the flask is no longer cold to the touch, whichever is sooner, (the vinyl chloride is completely off). Transfer the contents of the flask to a one-ounce vial and analyze chromatographically.

6 CALCULATION Measure the total area under the chromatogram and calculate the individual peak area percentages.

$$\frac{A}{\text{total area}} \times 100 = \text{area per cent of individual peak}$$

A = area of individual peak

$$\left(\frac{\text{area per cent}}{200}\right) F_i \times 10^4 = \text{ppm impurity in vinyl chloride}$$

$F_i$ = recovery factor of individual component (peak)

It has been demonstrated that the ppm impurity in vinyl chloride calculated by this method is ppm by weight. The density of the styrene solution is nearly equal to the density of liquid vinyl chloride; therefore, these factors cancel. The individual recovery factors, $F_i$, include an area to weight per cent correction.

7 COMPONENT CONSTANTS

| Component | Approximate retention time, min (a) | Recovery factor |
|---|---|---|
| Vinyl chloride | 1.0 | |
| Acetone | 2.0 | 2.90 |
| 1,1-Dichloroethane | 3.0 | 3.74 |
| Unidentified No. 1 | 4.0 | |
| Unidentified No. 2 | 4.5 | |
| 1,2-Dichloroethane | 6.2 | 1.85 |
| Unidentified No. 3 | 9 | |
| Unidentified No. 4 | 11 | |
| Unidentified No. 5 | 15 | |
| Unidentified No. 6 | 18.5 | |
| tert-Butylcatechol | 21 | styrene inhibitor |
| Styrene | 32 | |

a) Retention time measured from point of sample injection to the peak maximum of the component in question.

8 TYPICAL CHROMATOGRAM A typical chromatogram is shown on page 2.

9 RECOVERY FACTORS Determine recovery factors on a particular chromatograph in a given location by preparing solutions of the various components in styrene, mixing with 200 ml of refined vinyl chloride and weathering. Divide the weight per cent of impurity in styrene before weathering by its area per cent after weathering to obtain the recovery factor. Typical recovery data are included

| Weight % added | Component | Mean recovery | Recovery factor |
|---|---|---|---|
| 1.74 | 1, 2-Dichloroethane | 0.94 ± 0.01 | 1.85 |
| 7.59 | 1, 1-Dichloroethane | 2.03 ± 0.08 | 3.74 |
| 5.17 | Acetone | 1.78 ± 0.17 | 2.90 |

10 REFERENCE 2-RSC-54

RESEARCH AND DEVELOPMENT DEPARTMENT
TECHNICAL CENTER
South Charleston, West Virginia

ldl/JFH

# VINYL CHLORIDE
# DETERMINATION OF ACETONE, DICHLOROETHANES, AND HIGHER BOILING IMPURITIES

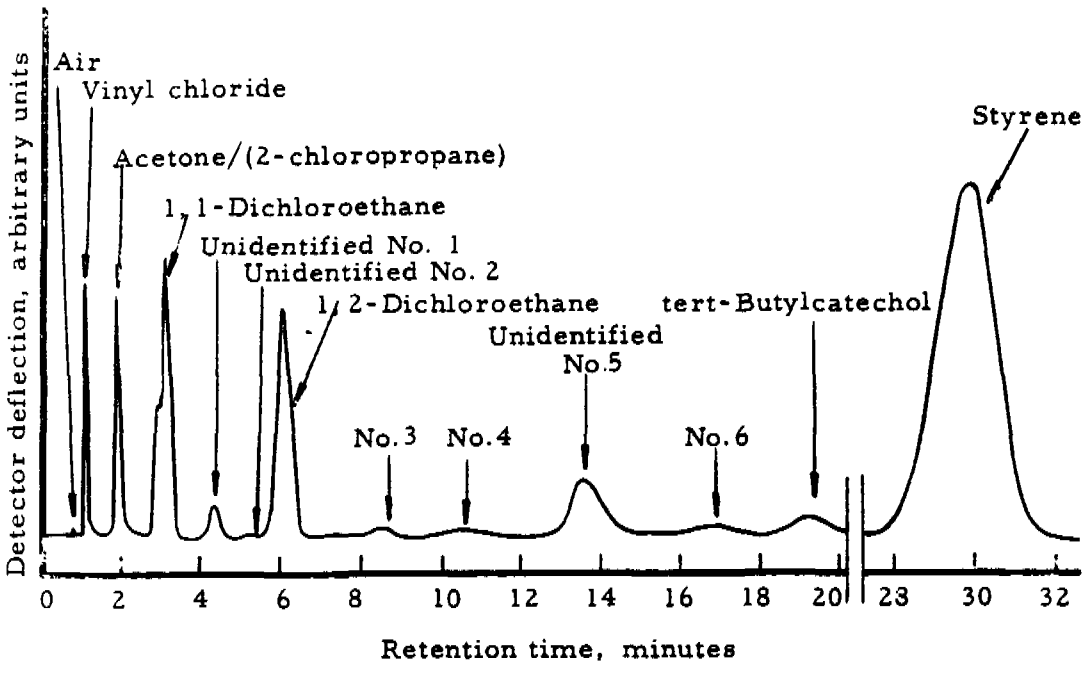
1 PURPOSE AND LIMITATIONS This method was developed for the analysis of crude vinyl chloride and is applicable to the determination of acetone, 1,1-dichloroethane, 1,2-dichloroethane, and higher boiling impurities in the sample. The method is also applicable to refined vinyl chloride; however, the refined material should not give a positive test. Impurities whose boiling points lie between -15°C and about 30°C may not be detected by this method, and those impurities boiling lower than vinyl chloride (-15°C) can be determined by method 58C-9C1-V6.3.

2 PRINCIPLE A large amount of vinyl chloride is mixed with a small amount of a pure, high boiling solvent. The vinyl chloride is allowed to weather off, and the higher boiling impurities remain in the solvent. The impurities are separated by gas chromatography, and their concentrations in the solvent are determined by area per cent. Concentration of the individual impurities in the vinyl chloride may then be calculated by previously determined recovery factors.

3 APPARATUS

a) Deep freeze controlled at -20°C or a one gallon Dewar flask containing about 1 quart of liquid nitrogen.
b) Graduated cylinder, 100 ml, with stopper.
c) Erlenmeyer flask, 250 ml, with stopper.
d) Pipet, 1.0 ml
e) Face shield
f) Leather gloves
g) Microsyringe, 0-10 microliters
h) Vial, one-ounce
i) Planimeter

TYPICAL CHROMATOGRAM




4 INSTRUMENT PARAMETERS

| | |
|---|---|
| Instrument | F&M Model 500 Gas Chromatograph or equivalent |
| Column | 6 feet x 0.25 inch O.D. tubing packed with 15 per cent substrate (equal parts of TERGITOL-E68, APIEZON N and APIEZON W) on acid washed Chromosorb W |
| Column temperature | Isothermal at 100°C |
| Flow rate | Adjusted to give styrene a retention time of 32 minutes |
| Detector current | 200 milliamperes |
| Sample volume | 1 microliter |
| Detector temperature | 300°C |
| Injection port temperature | 250°C |
| Total elution time | 38 minutes |

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Mr. R. E. George, 514
Mr. G. J. Hanks, Jr., 514
Mr. R. J. Hanna, 511
Mr. J. R. Hazle, 514
Mr. J. B. Johnson, 511
Dr. R. L. Meeker, 511
Mr. A. E. Montagna, 511
Mr. L. E. Nugent, 514
Mr. H. E. Persinger, 511
Mr. Q. Quick, 511
Mr. M. E. Sutherland, 511
Mr. W. H. Swango, 514
Mr. R. N. Wheeler, 514
Mr. W. E. Whitehurst, 511
Dr. C. W. Wilson, III, 511
Information Retrieval

Mr. H. F. White

December 11, 1964

TECHNICAL CENTER

Dr. F. E. Bailey, Jr.
Mr. F. D. Dexter
Mr. A. E. Montagna

Vinyl Chloride
Determination of Trace Impurities
in Monomer Produced by Synthesis
File Number 3301

Dear Mr. White:

This work will be very helpful in evaluating vinyl chloride monomer and in process trouble-shooting.

On the negative side, I think the report would not have suffered if the first paragraph of the introduction had been deleted. In today's competitive business, publishing process data unnecessarily often leads to leaks and aid and comfort to our competitors.

Very truly yours,

R. N. Wheeler

RNW/ra