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METHYLATION AND GAS CHROMATOGRAPHIC ANALYSIS OF THE DECOMPOSITION PRODUCTS OF TRIBUTYL PHOSPHATE

A. H. Kibbey and W. Davis, Jr.

ABSTRACT

Mixtures of the decomposition products formed from tributyl phosphate (TBP) in 3 and 5 M HNO_3 at 50°C, i.e., ortho-, monobutyl, and dibutyl phosphoric acids (H_3PO_4, H_2MBP, and HDBP), were quantitatively analyzed for components by a modified version of a method developed by C. J. Hardy in 1963. The modified method consisted in freezing (to prevent bumping) and removing water and HNO_3 by sublimation, and then methylating the decomposition product residue with diazomethane prior to gas chromatographic analysis. Standard solutions were prepared to check the accuracy and precision of the method. The calculated uncertainty in determining quantities of HDBP in the range of 6.5 to 32.5 mg was ± 0.95 mg; for 2.2 to 22.3 mg quantities of H_2MBP the uncertainty was ± 1.5 mg; and for H_3PO_4 in the 1- to 10-mg range uncertainty was ± 0.3 mg. Limits of detection for the acids by the techniques described here are, approximately, 0.6 mg, 1 mg, and 0.2 mg for HDBP, H_2MBP, and H_3PO_4, respectively.

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1. INTRODUCTION

When tributyl phosphate (TBP) is decomposed thermally or radiolytically, the products formed are dibutyl phosphoric acid (HDBP), monobutyl phosphoric acid (H_2MBP), and orthophosphoric acid (H_3PO_4). Until recently, the problem of quantitatively analyzing a mixture of these in the presence of TBP was almost insurmountable. In 1963, however, Hardy[1] developed a gas chromatographic method for separation of the components in such mixtures and obtained quite satisfactory quantitative results. The work described in the present paper makes use of later technological advances to extend Hardy's gas chromatographic work. The whole method depends upon the conversion of the relatively nonvolatile acid decomposition products of TBP to their more volatile methyl esters.

2. SAMPLE PREPARATION

Baker Analyzed "Reagent" orthophosphoric acid (H_3PO_4), Aldrich Chemical Company research-grade trimethyl phosphate (TMP), Victor Chemical Works best-grade dibutyl phosphoric acid (HDBP), Victor Chemical commercial-grade monobutyl phosphoric acid (H_2MBP), and Eastman "white label" tributyl phosphate (TBP) were used as the starting materials in these experiments. Prior to use, the TBP was further purified by vacuum distillation in a falling film molecular still at about 45°C and the H_2MBP was fractionated from the crude commercial mixture of H_2MBP-HDBP by a two-phase water extraction. This latter process was carried out by using one liter of the crude H_2MBP and an equal volume of water. Two layers were obtained – an amber upper layer (~ 1500 cc) containing mixed HDBP and H_2MBP, and a colorless bottom layer (~ 500 cc) that was 3.07 M in H_2MBP. A second partitioning of the upper layer was performed after it had been evaporated to about 800 cc (~ 5.25 M H_2MBP); this, in turn, yielded another 575 cc of 3.06 M H_2MBP solution. Essentially no HDBP was found in the H_2MBP bottom phases.

2.1 Methyl Ester Standards

2.1.1 Dimethyl Monobutyl Phosphate (M_2MBP)

A 96.76 mole % sample of dimethyl monobutyl phosphate was prepared for standardization of the gas chromatograph used for analyzing the TBP-decomposition products. Approximately 0.5 mole of purified monobutyl phosphoric acid was methylated with twelve batches of ethereal diazomethane that had been prepared by the Diazald-Carbitol (diethylene glycol monoethyl ether) method.* Methylation was complete when the yellow color persisted and no more N_2 bubbles formed. After the excess methylating agent and ether had been allowed to evaporate in air at room temperature, the dimethyl monobutyl phosphate was fractionated in a molecular still. A preparative gas chromatograph was used to achieve final purification and concentration of the product from the molecular still. Mass spectrographic analysis confirmed that, with the exception of very small amounts of impurities, the material was dimethyl monobutyl phosphate.

2.1.2 Methyl Dibutyl Phosphate (MDBP)

The reagent-grade HDBP, as received, was methylated as described in the preceding section. An analysis of the HDBP follows:

Density at 27.4°C	0.9581 g/ml
Meq HDBP/g	4.290
Meq/ml	4.11
Mg/meq HDBP	233.
Theoretical mg/meq HDBP·H_2O	228.2
Theoretical mg/meq HDBP	210.2

*Distillation from Carbitol-KOH pot solution eliminated low-boiling, low-mass contaminants in the methylated phosphate ester product. These contaminants had presented analytical difficulties when the pot solution was ethanol-KOH. Both methods of diazomethane preparation are given in Appendix I.

(These results are indicative of an approximately 50 mole % H_2O-HDBP solution.)

A high yield (97.6%) of pure ester was obtained without difficulty by molecular distillation[2] at 35 to 45°C; consequently, further concentration by the gas chromatographic preparative technique was not necessary. Some of this material was used for measuring vapor pressures at 80, 125, and 145°C; values of 2, 13, and 47 mm, respectively, were obtained. Extrapolation of these data to the temperature range over which our distillation was performed indicate that the pressure was on the order of 100 μ or less.

2.2 Standard Solutions and Mixtures

In order to determine the efficiency of the total handling and methylation procedures, two types of standard solutions were prepared: (1) solutions of MDBP, M_2MBP, and TMP in TBP; (2) nitric acid solutions of HDBP, H_2MBP and H_3PO_4. The former solutions provided information on our accuracy in dispensing 1- to 10-μl quantities of the methyl esters, while the latter solutions provided a check on the entire handling procedure. This procedure involved removal of H_2O and HNO_3 from the solutions by sublimation at low temperature and a few tens of microns pressure, methylation, dilution with TBP, and gas chromatographic analysis. Freezing the solutions by immersion in a dry ice--trichloroethylene bath prior to evacuation of the system prevented bumping and spattering during initial degassing. An estimate of the actual solution temperature can be made from the freezing point diagram for the H_2O-HNO_3 system reported by Chedin,[3] which shows that at 15 mole % HNO_3 the freezing point is -45°C. Our solutions, even after melting, were considerably below 0°C, as evidenced by the collection of frost on the outside of the evaporation vessel during most of the distillation. The amounts of acids used in these standard mixtures and solutions ranged from 0.98 to 9.8 mg of H_3PO_4, from 2.23 to 22.3 mg of H_2MBP, and from 6.5 to 32.5 mg of HDBP. In all cases a 1.0-cc volume of TBP was used for dilution prior to, or after, treatment with diazomethane, as described previously.

3. DATA HANDLING

3.1 Standard Curves

Gas chromatographic analytical results were obtained in mole % of each component sought, that is, TBP, MDBP, M_2MBP, and TMP. A computer program (see Appendix II) was written to convert these raw data to concentrations in milligrams or millimoles of the original acid constituent present per liter of solution.

Standard curves for each component were obtained by using the output from DECOMP as input data for POLFIT II,[4] a program for polynomial least-squares fitting. Straight-line equations and standard errors (σ) for plots of the concentration of each component found (y) vs its known concentration (x) were thus calculated. These are summarized in Table 1.

Table 1. Values of the Slope, Intercept, and Independent Variable for Standard Butyl Phosphoric Acid Curves

$$y = b_1 + b_2x$$

Compound	No. of Points	x (mg)	b_1 (mg)	$\sigma(b_1)$ (mg)	b_2 (mg)	$\sigma(b_2)$ (mg)	σ_{fit} (mg)
HDBP	20	6.5-32.5	0.16	0.45	0.714	0.023	0.95
H_2MBP	18	2.2-22.3	-0.31	0.66	0.751	0.081	1.52
H_3PO_4	16	1.0-9.8	-0.04	0.11	0.391	0.035	0.31

The experimental points for each standard curve and the standard error of each point are shown in Figs. 1, 2, and 3 for HDBP, H_2MBP, and H_3PO_4, respectively.

3.2 Determination of "Unknowns"

Once the standard curves and their standard errors were obtained for HDBP, H_2MBP, and H_3PO_4, it was possible to introduce an option into program DECOMP

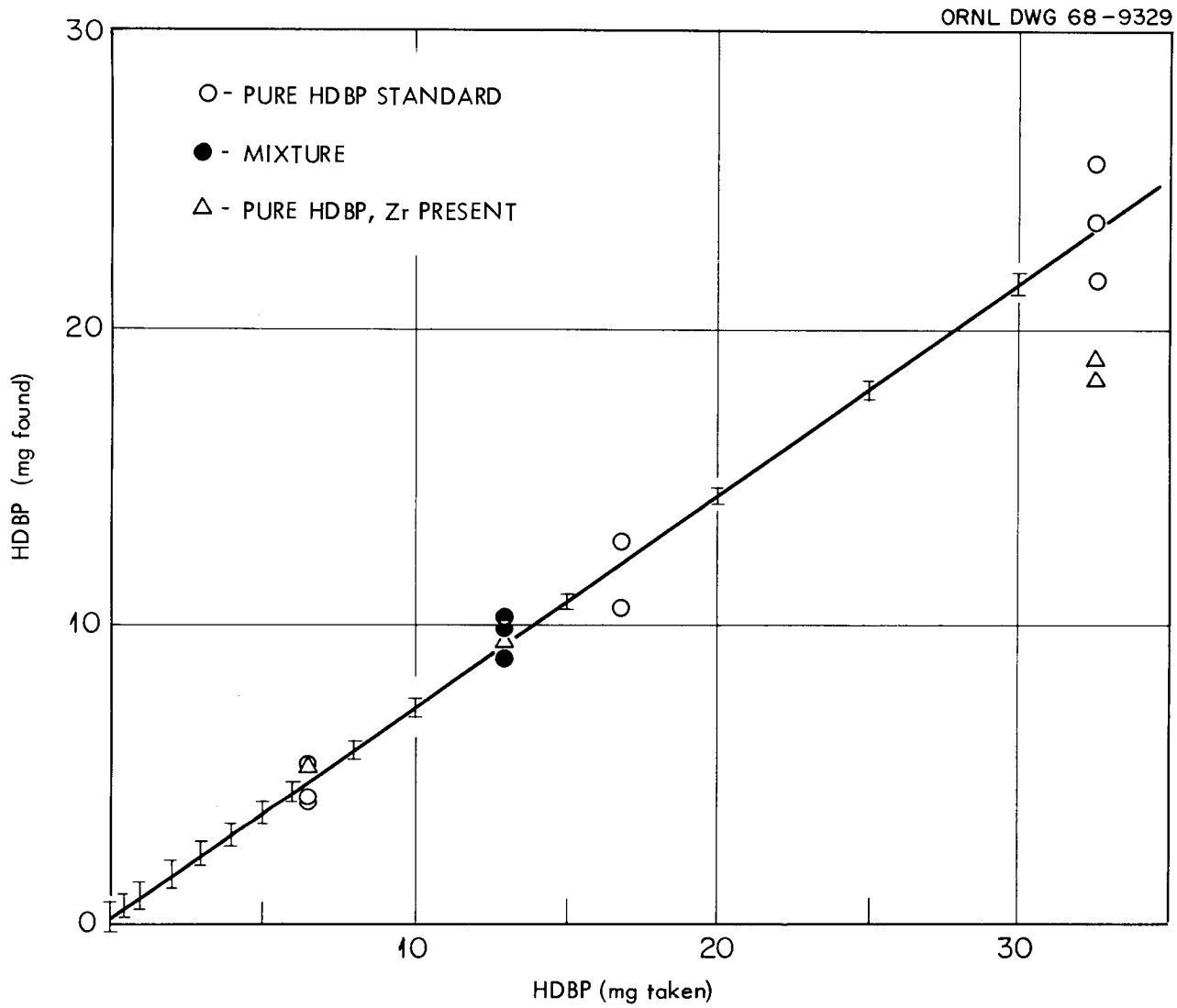

Fig. 1. Calibration Data and Least-Squares Line for Gas Chromatographic Analysis of the Methyl Ester of HDBP.

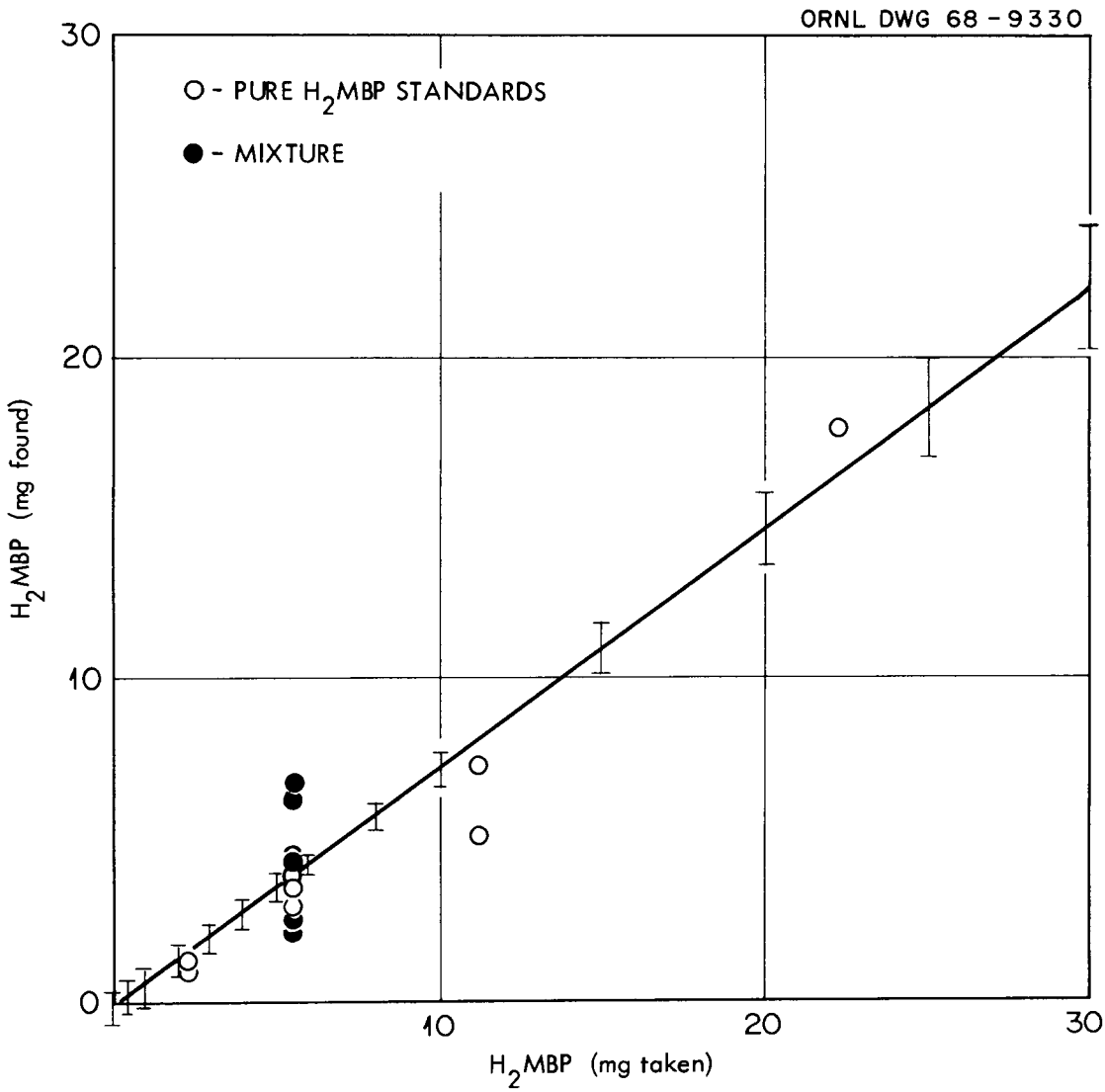

Fig. 2. Calibration Data and Least-Squares Line for Gas Chromatographic Analysis of the Methyl Ester of H_2MBP.

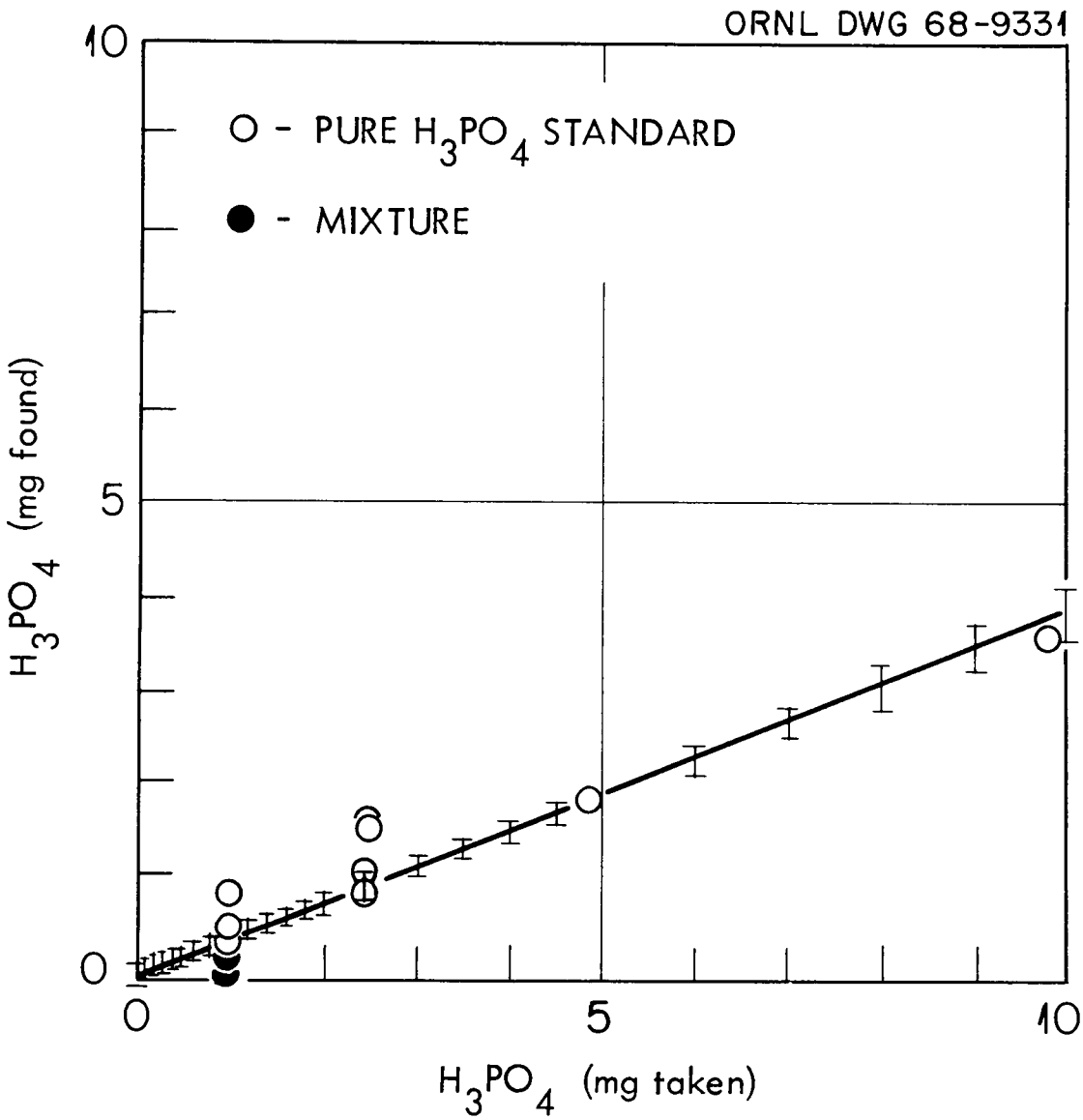

Fig. 3. Calibration Data and Least-Squares Line for Gas Chromatographic Analysis of the Methyl Ester of H_3PO_4.

that would allow back-calculation of the concentrations of the TBP-decomposition products in solutions of unknown composition by using the mole % data obtained from gas chromatographic analysis of the methyl ester specimen.

This technique, when applied to samples that were withdrawn in actual TBP-decomposition experiments in 3 and 5 M HNO_3 at 50°C, gave good reproducibility for HDBP and H_2MBP; however, the agreement between H_3PO_4 results was less satisfactory.

Zirconium is known to form stable dibutyl phosphate having very low solubilities in 1 to 3 M HNO_3 solutions.[5] The effect of zirconium on the methylation-gas chromatographic analysis for HDBP was studied in one test involving four solutions in which the HDBP/Zr mole ratio was fixed at 2/1; the total quantity of HDBP in the solutions ranged from 6.5 to 32.5 mg. As may be seen from the four points in Fig. 1, the presence of zirconium did not lead to an error in the estimated quantity of HDBP that was greater than the overall uncertainty of the method.

4. DISCUSSION AND CONCLUSIONS

Methylation followed by gas chromatographic analysis is a good method for determining TBP-decomposition products in acid process solutions. The calculated uncertainty in determining quantities of HDBP in the range of 6.5 to 32.5 mg was 0.95 mg (see Fig. 1); for 2.2- to 22.3-mg quantities of H_2MBP the uncertainty was 1.5 mg (see Fig. 2); and for H_3PO_4 in the 1- to 10-mg range uncertainty was 0.3 mg (see Fig. 3). Limits of detection for the acids by the technique described here are, approximately, 0.6 mg, 1 mg, and 0.2 mg for HDBP, H_2MBP, and H_3PO_4, respectively. The presence of zirconium in HNO_3-HDBP solutions in the mole ratio of HDBP/Zr = 2/1 has no observable effect on the accuracy of the method in analyzing for HDBP in the range mentioned above.

5. ACKNOWLEDGMENTS

The help of several people was required for completion of this work. The H_2MBP was prepared by H. F. Soard of the ORNL Chemical Technology Division. The following Analytical Chemistry Division personnel also contributed to this study: A. D. Horton, who made the gas chromatographic analyses; W. T. Rainey, Jr., who made the mass spectrographic analyses; and H. L. Holsopple, who measured the vapor pressures. We express our thanks for their help.

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7. V. F. Raaen, ORNL Chemistry Division, personal communication.

APPENDIX I

Preparation of Diazomethane

Diazomethane[6] is a highly toxic and potentially explosive compound; therefore, CAUTION should be exercised during its preparation and in subsequent handling. No long-term storage should be employed since the formation of an insoluble white polymer, accompanied by release of N_2 gas, occurs at temperatures as low as 35°F. In a tightly capped bottle, this could cause an explosion.[7] Short-term storage (i.e., a matter of a few weeks) has been found to be safe, provided the storage temperature is kept below 0°F and the container is vented frequently.

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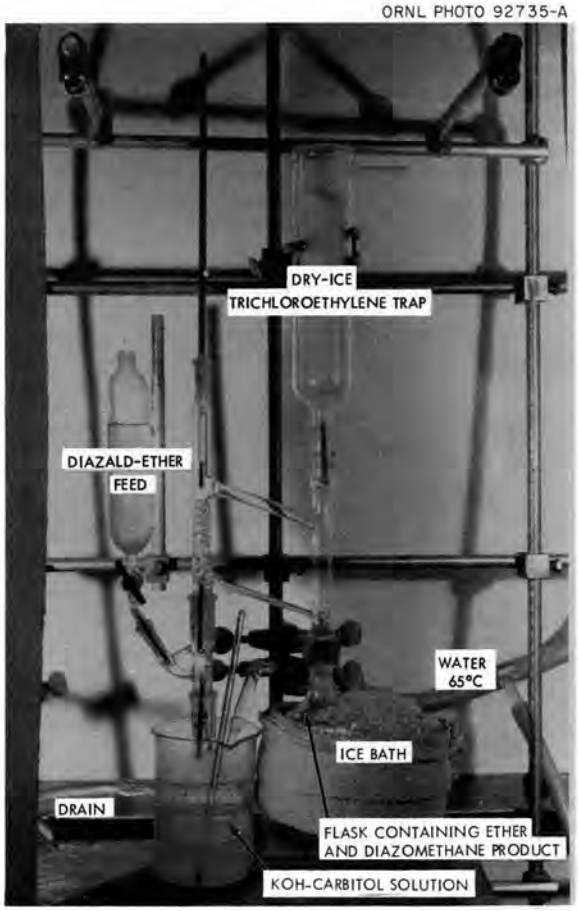

Fig. 4. Photograph of the Apparatus Used in Preparing Diazomethane.

(Note: Spray all ground-glass surfaces with Teflon coating.)

Methods of Preparation

1. Ethereal-alcoholic solutions of diazomethane:

a.	25 ml 95% ethanol 5 g KOH 8 ml H_2O	Combine in 100-ml distillation flask
b.	30 ml ether	Place in product catch vessel
c.	21.5 g Diazald 130 cc ether	Combine for feed solution

Add Diazald solution dropwise to the distillation flask containing the ethanol-KOH maintained at 65°C. The entire addition should require 30 to 40 min so that the rate of addition equals the rate of distillation. Flush the system with an additional 20 to 30 cc of pure ether and distill until distillate is colorless. The product contains approximately 3 g of diazomethane in 160 to 170 cc of ether.

2. Alcohol-free ethereal solutions of diazomethane:

a.	35 ml Carbitol** 6 g KOH 10 ml H_2O	Combine in 100-ml distillation flask
b.	30 ml ether	
c.	21.5 g Diazald 130 cc ether	

The procedure is identical to that just described for the preparation of ethereal-alcoholic solutions of diazomethane.

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* Diazald is N-methyl-N-nitroso-p-toluenesulfonamide supplied by the Aldrich Chemical Co.

**Diethylene glycol monoethyl ether; product of the Union Carbide Chemicals Co.

APPENDIX II

```
      PROGRAM DECOMP
      DIMENSION SAMPLE (50),NAME(50)
    1 FORMAT(6F10.5)
    2 FORMAT(60H  H3PO4      H3PO4      H2MBP      H2MBP      HDBP       HDB
     1P    )
    3 FORMAT(60H  FOUND    RECOVERED   FOUND    RECOVERED   FOUND    RECOVE
     1RED )
    4 FORMAT(60H    (MG)    (PERCENT)    (MG)    (PERCENT)    (MG)    (PERCE
     1NT) /)
    7 FORMAT(9A8)
   14 FORMAT(F9.5,F11.5,F9.5,F11.5,F9.5,F11.5)
   18 FORMAT(//)
   19 FORMAT(//////)
  601 FORMAT(10A8)
  501 FORMAT(83H0        H3PO4                  H2MBP                  HDBP
     1       SAMPLE          HOURS   )
  502 FORMAT(84H     MG/L    MMOLES/L      MG/L    MMOLES/L      MG/L    MMOLE
     1S/L     CODE          ELAPSED   //)
  503 FORMAT(F8.2,2X,F8.4,2X,F9.2,1X,F8.4,2X,F9.2,1X,F8.4,2X,A8,A5,F9.2)
      DATA(CX=359.0),(CY=564.5),(CZ=770.1)
C     REFERENCE SOLUTION IS TBP. DENSITY=0.9756 G/CC, GMW=266.32, SO
C                                  1 CC =0.003663 MOLES (THE AMOUNT USED).
C     CX=GMW H3PO4*0.003663*1000 = 97.995 * 3.663 =359.0
C     CY=GMW H2MBP*0.003663*1000 =154.104 * 3.663 =564.5
C     CZ=GMW HDBP *0.003663*1000 =210.212 * 3.663 =770.1
C         (THE 1000 FACTOR CONVERTS GM TO MG BASIS).
C     X= MG H3PO4 BASED ON MOLE ( TMP (TRIMETHYL PHOSPHATE) ANALYZED
C     Y= MG H2MBP BASED ON MOLE (MMBP (DIMETHYL-BUTYL PHOSPHATE)ANALYZED
C     Z= MG HDBP  BASED ON MOLE (MDBP (METHYL-DIBUTYL PHOSPHATE)ANALYZED
C     R= ( RECOVERY OF EACH COMPONENT.
      J=1
      READ 601,(NAME(I),I=1,10)
    6 READ 7,(SAMPLE(I),I=1,9)
      READ 1, XTMP,XMMBP,XMDBP,XTBP,VOS,HOUR
C     THE ABOVE ARE MOLE ( VALUES FOUND BY GAS CHROMATOGRAPHIC ANALYSIS
C         OF THE METHYL ESTERS IN TBP (ANALYTICAL WORK BY A.D.HORTON).
      READ 1, H3PO4,H2MBP,HDBP
C     THE ABOVE ARE THE MG VALUES OF THE ACID COMPONENTS WHICH WERE SUB-
C         SEQUENTLY METHYLATED WITH DIAZOMETHANE PRIOR TO ANALYSIS.
      X=XTMP*CX/XTBP
      IF(H3PO4) 108,8,9
    9 RX=X*100./H3PO4
      GO TO 15
    8 RX=0.0
      GO TO 15
  108 XC=(X+0.04)/0.391
      XC=1000.*XC/VOS
C     THE ABOVE STATEMENT GIVES H3PO4 CONCENTRATION IN MG/L.
      XCC=XC/97.995
C     XCC IS H3PO4 CONCENTRATION IN MMOLES/L.
   15 Y=XMMBP*CY/XTBP
      IF(H2MBP) 109,10,11
   11 RY=Y*100./H2MBP
      GO TO 16
   10 RY=0.0
      GO TO 16
```

```
  109 YC=(Y+0.31)/0.751
      YC=1000.*YC/VOS
C     THE ABOVE STATEMENT GIVES H2MBP CONCENTRATION IN MG/L.
      YCC=YC/154.1037
C     YCC IS H2MBP CONCENTRATION IN MMOLES/L.
   16 Z=XMDBP*CZ/XTBP
      IF(HDBP) 110,12,13
   13 RZ=Z*100./HDBP
      GO TO 17
   12 RZ=0.0
      GO TO 17
  110 ZC=(Z-0.16)/0.714
      ZC=1000.*ZC/VOS
C     THE ABOVE STATEMENT GIVES HDBP CONCENTRATION IN MG/L.
      ZCC=ZC/210.212
C     ZCC IS HDBP CONCENTRATION IN MMOLES/L.
      IF(H3PO4) 200,17,17
   17 PRINT 7,(SAMPLE(I),I=1,9)
      PRINT 1, XTMP,XMMBP,XMDBP,XT3P,VOS,HOUR
      PRINT 1, H3PO4,H2MBP,HDBP
      PRINT 18
      PRINT 2
      PRINT 3
      PRINT 4
      PRINT 14,X,RX,Y,RY,Z,RZ
      PRINT 19
      GO TO 6
  200 IF(J-1) 201,201,211
  201 PRINT 601,(NAME(I),I=1,10)
      PRINT 501
      PRINT 502
  211 PRINT 503,XC,XCC,YC,YCC,ZC,ZCC,SAMPLE(1),SAMPLE(2),HOUR
      J=J+1
      GO TO 6
      END
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