

AIR POLLUTION EMISSION TEST

DENKA CHEMICAL CORPORATION

HOUSTON, TEXAS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Emission Measurement Branch
Research Triangle Park, North Carolina

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Office of Air Quality Planning and Standards

DATE: 8/14/78

Research Triangle Park, North Carolina 27711

SUBJECT: Source Test Report

FROM: J. E. McCarley, Chief, Field Testing Section, *EMME*
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TO: See Below

The enclosed final source test report is submitted for your information. Any questions regarding the test should be directed to the Project Officer (telephone: 8/629-5243). Additional copies of this report are available from the ERC Library, Research Triangle Park, North Carolina 27711.

Industry: Maleic Anhydride Manufacturing

Process: Partial oxidation of benzene

Company: Denka Chemical Corp.

Location: Houston, Texas

Project Report Number: 78-OCM-4

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Enclosure

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APTIC (MD-18)

STATIONARY SOURCE TESTING OF A MALEIC ANHYDRIDE PLANT AT THE
DENKA CHEMICAL CORPORATION, HOUSTON, TEXAS

by

William H. Maxwell
George W. Scheil

FINAL REPORT

EPA Contract No. 68-02-2814, Work Assignment No. 5
EPA Project No. 78-OCM-4
MRI Project No. 4468-L(5)

For

Emission Measurement Branch
Field Testing Section
Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Attn: Mr. J. E. McCarley, Jr.

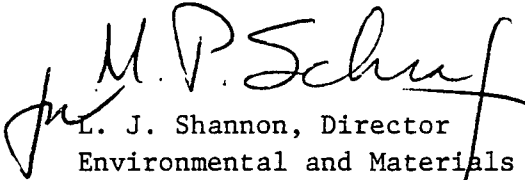
PREFACE

The work reported herein was conducted by Midwest Research Institute under Environmental Protection Agency Contract No. 68-02-2814, Work Assignment No. 5, and Change No. 1.

The project was under the supervision of Mr. Doug Fiscus, Head, Field Programs Section, and Mr. William Maxwell, Program Manager. Mr. Maxwell served as field team leader and was assisted in the field by Messers George Scheil, John LaShelle, Chris Cole, and in the lab by Messers George Cobb and Doug Bischoff.

Approved for:

MIDWEST RESEARCH INSTITUTE


L. J. Shannon, Director
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SECTION 1

INTRODUCTION

This report presents the results of source testing performed during the period March 20 to 24, 1978, by Midwest Research Institute (MRI) on the maleic anhydride plant of the Denka Chemical Corporation, Houston, Texas. The facility is a typical maleic anhydride plant by the partial oxidation of benzene process. The process includes a wet scrubber for product recovery. The effluent gases are then passed through an incinerator for hydrocarbon emission control to the atmosphere via a 15.2 m (50 ft) stack.

Testing was done before and after the incinerator during periods of normal process operation. Inlet testing was done for benzene, total hydrocarbons (THC), carbon dioxide (CO₂), oxygen (O₂), carbon monoxide (CO), methane, ethane, total organic acids (TOA), total aldehydes, formaldehyde, temperature, and duct pressure. Outlet testing was done for benzene, THC, methane, ethane, CO₂, O₂, CO, TOA, total aldehydes, formaldehyde, nitrogen oxides (NO_x), temperature, duct pressure, and duct volumetric flow. Portions of the gas samples were given to Denka personnel following MRI analysis so that they could also perform the analyses. Their results are not included in this report.

The results of these tests are to be used in the establishment of emission standards for this industry.

SECTION 2

SUMMARY AND DISCUSSION OF RESULTS

The results of the analyses for benzene and total hydrocarbons are shown in Table 1. In all test runs, benzene was the primary component found. However, several additional peaks were measured in some of the samples. A list of these peaks is given in Table 2. The compounds listed for peaks 2 through 6 and 8 are possibilities only (peak 7 was benzene). The tentative identifications are based upon retention index data provided by Dr. Joseph E. Knoll, QAB/EMSL, Environmental Protection Agency, Research Triangle Park (EPA/RTP). Many of the peaks are probably present in the ambient air or are outgassing products from the sample bags. Peak 3 was a very broad peak which was not resolved well. The width of this peak indicates a highly polar compound such as maleic acid. Examples of representative gas chromatograph (GC) plots for the samples may be found in Appendix A.

The results of the audit samples may be found in Table 3. The MRI and Research Triangle Institute (RTI) values are presented. The audit report itself is in Appendix B. The MRI values in Table 3 and Appendix B differ because of recalculations based on all of the acquired data being done after return to Kansas City. The calibration curves used in the field assumed that the response outside the calibration range continued curving at the same rate. Tests run after returning indicate that much of the apparent curvature was due to random errors of the calibration gases. The later calculated values assume that points outside the calibration range have the same relative response as the nearest calibration point.

The carbon monoxide analysis results are given in Table 4. The values reported are minimum concentrations. The highest calibration gas mixture available was 500 ppm carbon monoxide and the instrument response is known to be slightly nonlinear at high concentrations.

The TOA results are presented in Table 5. The data are presented both as acetic acid and as maleic acid. The field data may be found in Appendix C.

The total aldehyde and formaldehyde results are given in Table 6, while the NO_x data are presented in Table 7.

Table 8 presents a summary of the duct flow and temperature measurements made during the test series.

TABLE 1. SUMMARY OF RESULTS - BENZENE AND TOTAL HYDROCARBONS

| Date | Site | Run No. | Benzene | | | Total Hydrocarbons | | | | | | Benzene/ THC ratio |
|-------------------|--------|---------|--------------------------------|---------------------|---------------------|--------------------------------|---------------------|---------------------|--------------------------------|---------------------|---------------------|--------------------------|
| | | | Benzene (ppm) ^{a/} | lb/hr ^{b/} | kg/hr ^{c/} | Benzene (ppm) ^{a/} | lb/hr ^{b/} | kg/hr ^{c/} | Propane (ppm) ^{d/} | lb/hr ^{e/} | kg/hr ^{f/} | |
| March 21, 1978 | Inlet | 1 | 780 | 339 | 154 | 830 | 360 | 164 | 1,520 | 373 | 169 | 0.940 |
| | Outlet | 1 | 11.1 | 4.8 | 2.2 | 12.9 | 5.3 | 2.4 | 24.3 | 5.9 | 2.7 | 0.860 |
| March 22, 1978 | Inlet | 2 | 820 | 355 | 161 | 950 | 412 | 187 | 1,880 | 460 | 209 | 0.863 |
| | Outlet | 2 | 11.8 | 5.4 | 2.4 | 12.4 | 5.7 | 2.6 | 23.6 | 6.1 | 2.8 | 0.952 |
| March 23, 1978 | Inlet | 3 | 940 | 407 | 185 | 1,070 | 463 | 210 | 2,090 | 511 | 232 | 0.879 |
| | Outlet | 3 | 14.4 | 6.4 | 2.9 | 14.3 | 6.4 | 2.9 | 26.5 | 6.7 | 3.0 | - |

^{a/} Parts per million (volume/volume) as benzene.

^{b/} Pounds per hour, as benzene.

^{c/} Kilograms per hour, as benzene.

^{d/} Parts per million (volume/volume) as propane.

^{e/} Pounds per hour, as propane.

^{f/} Kilograms per hour, as propane.

TABLE 2. SUMMARY OF RESULTS - MISCELLANEOUS HYDROCARBON DATA

| Peak No. | Compound ^{a/} | Retention index | Run No. 1 | | Run No. 2 | | Run No. 3 | |
|----------|-------------------------------------|-----------------|------------------|------------------|-----------|--------|-----------|--------|
| | | | Inlet | Outlet | Inlet | Outlet | Inlet | Outlet |
| 1 | Methane, ethane, propane | 100-300 | 10 ^{b/} | 3 | 5 | 3 | 4 | 5 |
| 2 | Acetaldehyde | 560 | 3 | ND ^{c/} | 0.2 | ND | 4 | ND |
| 3 | Maleic acid | ~ 600 | NR ^{d/} | NR | NR | ND | NR | ND |
| 4 | Methanol, ethanol | 630 | 0.4 | 2 | Trace | ND | 10 | 7 |
| 5 | Acetone, cyclo-hexane | 660 | 0.4 | ND | 0.4 | ND | 3 | ND |
| 6 | Acetonitrile | 680 | 0.4 | ND | 0.4 | ND | 1 | ND |
| 7 | Benzene ^{e/} | | | | | | | |
| 8 | Isobutanol, thio-phene | 750 | ND | ND | 0.4 | ND | ND | ND |
| 9 | Toluene | 810 | 0.4 | ND | 10 | ND | 2 | ND |

^{a/} Tentative identification based on retention index data only.

^{b/} Parts per million (volume/volume) as propane.

^{c/} ND = Not detectable.

^{d/} NR = Peak present but very broad and not readable.

^{e/} See Table 1.

TABLE 3. SUMMARY OF RESULTS - AUDIT SAMPLES

| Audit Sample No. | RTI results benzene ^{a/} (ppm) | MRI results benzene ^{a/} (ppm) | Audit accuracy (%) ^{b/} |
|------------------|---|---|----------------------------------|
| B-1117 | 101 | 112 | -10.89 |
| B-1529 | 387 | 418 | -8.01 |

^{a/} Parts per million (volume/volume) as benzene.

^{b/} Audit accuracy (%) = $\frac{(\text{RTI value} - \text{MRI value})}{\text{RTI value}} \times 100$

TABLE 4. SUMMARY OF RESULTS - CO DATA

| Data | Site | Run No. | CO | | | |
|-------------------|--------|------------|-------------------|-------------|---------------------|---------------------|
| | | | ppm ^{a/} | % by volume | lb/hr ^{b/} | kg/hr ^{c/} |
| March 21, 1978 | Inlet | 1 | > 2,000 | > 0.2 | 312 | 142 |
| | Outlet | 1 | > 1,060 | > 0.1 | 164 | 74 |
| March 22, 1978 | Inlet | 2 | > 1,070 | > 0.1 | 166 | 75 |
| | Outlet | 2 | > 2,130 | > 0.2 | 350 | 159 |
| March 23, 1978 | Inlet | 3 | > 1,990 | > 0.2 | 309 | 140 |
| | Outlet | 3 | > 950 | > 0.1 | 152 | 69 |

^{a/} Minimum concentrations present, parts per million.

^{b/} Pounds per hour.

^{c/} Kilograms per hour.

TABLE 5. SUMMARY OF RESULTS - TOTAL ORGANIC ACIDS

| Date | Run No. | Site | Concentration, total organic acids | | | | | | | |
|-------------------|---------|--------|------------------------------------|---------------------|-----------------------|---------------------|----------------|-------|---------|-------|
| | | | As acetic acid | | | | As maleic acid | | | |
| | | | gr/dscf ^{a/} | lb/hr ^{b/} | mg/dscm ^{c/} | kg/hr ^{d/} | gr/dscf | lb/hr | mg/dscm | kg/hr |
| March 21, 1978 | 1 | Inlet | 0.034 | 10.4 | 78 | 4.7 | 0.067 | 20.5 | 153 | 9.3 |
| | 1 | Outlet | 0.082 | 24.9 | 188 | 11.3 | 0.158 | 48.1 | 362 | 21.8 |
| March 22, 1978 | 2 | Inlet | 0.047 | 14.4 | 108 | 6.5 | 0.091 | 27.8 | 208 | 12.6 |
| | 2 | Outlet | 0.020 | 6.6 | 46 | 3.0 | 0.039 | 12.7 | 89 | 5.8 |
| March 23, 1978 | 3 | Inlet | 0.064 | 19.5 | 146 | 8.8 | 0.123 | 37.5 | 281 | 17.0 |
| | 3 | Outlet | 0.013 | 4.1 | 30 | 1.9 | 0.025 | 7.9 | 57 | 3.6 |

^{a/} Grains per dry standard cubic foot.

^{b/} Pounds per hour.

^{c/} Milligrams per dry standard cubic meter.

^{d/} Kilograms per hour.

TABLE 6. SUMMARY OF RESULTS - TOTAL ALDEHYDES AND FORMALDEHYDE

| Date | Run No. | Site | Total aldehydes | | | | Formaldehyde | | | |
|-------------------|---------|--------|--|--------------------|-----------------------|---------------------|----------------------------------|-------|---------|-------|
| | | | lb/dscf ^{a/} (x 10 ⁻⁷) | lb/hr ^b | mg/dscm ^{c/} | kg/hr ^{d/} | lb/dscf (x 10 ⁻⁷) | lb/hr | mg/dscm | kg/hr |
| March 21, 1978 | 1 | Inlet | 21.2 | 4.5 | 33.9 | 2.0 | 6.9 | 1.48 | 11.0 | 0.67 |
| | 1 | Outlet | 2.9 | 0.6 | 4.7 | 0.3 | 0.4 | 0.09 | 00.6 | 0.04 |
| March 22, 1978 | 2 | Inlet | 31.0 | 6.6 | 49.7 | 3.0 | 13.6 | 2.91 | 21.8 | 1.32 |
| | 2 | Outlet | 3.8 | 0.9 | 6.2 | 0.4 | 0.0 | 0.00 | 0.0 | 0.00 |
| March 23, 1978 | 3 | Inlet | 56.2 | 12.0 | 90.1 | 5.4 | 29.9 | 6.39 | 47.8 | 2.90 |
| | 3 | Outlet | 2.9 | 0.6 | 4.7 | 0.3 | 0.4 | 0.09 | 0.6 | 0.04 |

^{a/} Pounds (x 10⁻⁷) per dry standard cubic foot.

^{b/} Pounds per hour.

^{c/} Milligrams per dry standard cubic meter.

^{d/} Kilograms per hour.

TABLE 7. SUMMARY OF RESULTS - NO_x DATA

| Date | Site | Run No. | Sample | NO _x | | | |
|-------------------|--------|------------|-------------|---|-----------------|-------------------|-----------------|
| | | | | lb/dscf (x 10 ⁻⁷) <u>a/</u> | lb/hr <u>b/</u> | mg/dscm <u>c/</u> | kg/hr <u>d/</u> |
| March 21, 1978 | Outlet | 1 | 1 | 9.2 | 2.0 | 14.7 | 0.9 |
| | | | 2 | 9.1 | 1.9 | 14.6 | 0.9 |
| | | | 3 | 11.0 | 2.3 | 17.6 | 1.0 |
| | | | Average | 9.8 | 2.1 | 15.7 | 1.0 |
| March 22, 1978 | Outlet | 2 | 1 | 12.1 | 2.7 | 19.5 | 1.2 |
| | | | 2 | 9.9 | 2.2 | 15.9 | 1.0 |
| | | | 3 | 10.5 | 2.4 | 16.8 | 1.1 |
| | | | Average | 10.8 | 2.4 | 17.4 | 1.1 |
| March 23, 1978 | Outlet | 3 | 1 | 8.3 | 1.8 | 13.3 | 0.8 |
| | | | 2 | 9.5 | 2.1 | 15.2 | 1.0 |
| | | | 3 <u>e/</u> | 7.7 <u>e/</u> | 1.7 <u>e/</u> | 12.4 <u>e/</u> | 0.8 <u>e/</u> |
| | | | Average | 8.5 | 1.9 | 13.6 | 0.9 |

a/ Pounds (x 10⁻⁷) per dry standard cubic foot.

b/ Pounds per hour.

c/ Milligrams per dry standard cubic meter.

d/ Kilograms per hour.

e/ Portion of sample spilled during recovery; value may be unreliable.

TABLE 8. SUMMARY OF RESULTS - DUCT FLOW AND TEMPERATURE DATA

| Date | Run No. | Site | Barometric pressure | | % Moisture (% by volume) | Stack temperature | | Static pressure | | Stack velocity | | Stack flow rate | |
|-------------------|---------|---------------------|---------------------|----------------------|-----------------------------|-------------------|------------------|-----------------|------------------------------------|-------------------|-------------------|---------------------|---------------------|
| | | | mm Hg ^{a/} | in. Hg ^{b/} | | °C ^{c/} | °F ^{d/} | mm Hg | in. H ₂ O ^{e/} | mps ^{f/} | fpm ^{g/} | dscnm ^{h/} | dscfm ^{i/} |
| March 21, 1978 | 1 | Inlet ^{j/} | 766 | 30.16 | 6.8 | 41 | 105 | 5.6 | 3.00 | 12.88 | 2,535 | 1,011.3 | 35,713 |
| | 1 | Outlet | 766 | 30.16 | 11.7 | 174 | 345 | 0.5 | 0.27 | 12.79 | 2,519 | 1,003.6 | 35,443 |
| March 22, 1978 | 2 | Inlet ^{j/} | 768 | 30.22 | 4.4 | 41 | 105 | 6.0 | 3.20 | 12.50 | 2,460 | 1,009.2 | 35,638 |
| | 2 | Outlet | 768 | 30.22 | 12.2 | 152 | 325 | 0.5 | 0.28 | 13.37 | 2,631 | 1,065.5 | 37,628 |
| March 23, 1978 | 3 | Inlet ^{j/} | 764 | 30.06 | 5.3 | 39 | 102 | 5.8 | 3.10 | 12.61 | 2,482 | 1,008.5 | 35,614 |
| | 3 | Outlet | 764 | 30.06 | 12.3 | 179 | 355 | 0.5 | 0.28 | 13.57 | 2,672 | 1,041.1 | 36,766 |

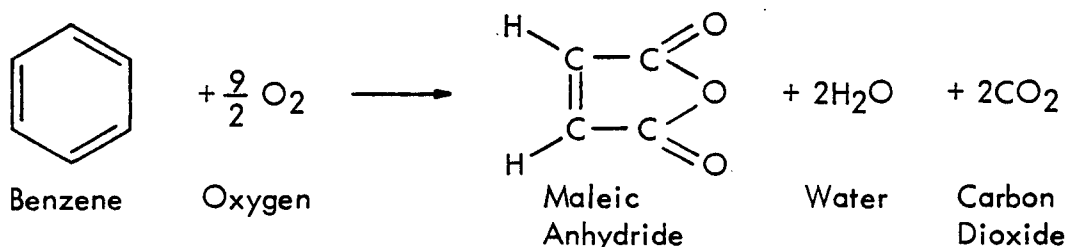
^{a/} Millimeters mercury.^{b/} Inches mercury.^{c/} Degrees Centigrade.^{d/} Degrees Fahrenheit.^{e/} Inches water.^{f/} Meters per second.^{g/} Feet per minute.^{h/} Dry standard cubic meters per minute.^{i/} Dry standard cubic feet per minute.^{j/} Assumes 16 sq ft (1.49 sq in) cross-sectional area.

SECTION 3

PROCESS DESCRIPTION AND OPERATION^{a/}

The Denka maleic anhydride facility has a nameplate capacity of 23,000 Mg per year (50 million pounds per year). The plant was designed by Scientific Design and purchased from Petro-Tex Chemical Corporation on July 1, 1977. The plant was operating at about 70% of capacity when the sampling was conducted; the plant personnel did not think that the lower production rate would seriously affect the validity of the results.

The plant consists of a single train of equipment, with the exception of multiple reactors and condensation equipment. Maleic anhydride is produced by the following vapor-phase chemical reaction:



A mixture of benzene and air enters a tubular reactor where the catalytic oxidation of benzene is carried out. The reactor feed mixture is provided with excess air to keep the benzene concentration below its explosive limit of 1.5 volume percent. The resultant large volume of reactor exhaust directly influences the size of the subsequent product recovery equipment. After reaction, the stream passes through a cooler, partial condenser, and separator in which a portion of the maleic anhydride is condensed and separated as a crude product. The remaining product and other organics enter the product recovery absorber where they are contacted with water or aqueous maleic acid. The liquid effluent from the absorber is about a 40 weight percent aqueous solution of maleic acid. The absorber vent is directed to the incinerator.

^{a/} This section furnished by EPA.

The maleic acid is dehydrated by azeotropic distillation with xylene. Any xylene retained in the crude maleic anhydride is removed in a xylene stripping column, and the crude maleic anhydride from this column is then combined with the crude maleic anhydride from the separator. The crude maleic anhydride is fed to a fractionation column which yields purified molten maleic anhydride as the overhead product. The fractionation column bottoms containing the color-forming impurities are removed as liquid residue waste.

Essentially all process emissions will exit through the product recovery absorber. These emissions will include any unreacted benzene, which can constitute 3 to 7% of the total benzene feed. The only other process emission source is the refining vacuum system vent, which can contain small amounts of maleic anhydride, xylene, and a slight amount of benzene, since benzene could be absorbed in the liquid stream from the product recovery absorber or in the crude maleic anhydride from the separator.

Table 9 summarizes data on the process and incinerator operation during the sampling runs. There were no process upsets during the sampling effort.

The following relation was provided to convert the waste gas flow rate in pounds per hour to SCFH by Denka:^{a/}

$$\begin{aligned}\text{Vol. Flow rate, SCFH} &= \frac{(\text{Mass flow rate, lb/hour})(1.03)(359 \text{ SCF/mole})}{\text{MW of air}} \\ &= \frac{(160,800)(1.03)(359)}{29} \\ &= 2.05 \times 10^6 \text{ SCFH} \\ &= 34,000 \text{ SCFM}\end{aligned}$$

Where 1.03 is a meter factor (standard conditions are 32°F and 30 in. Hg).

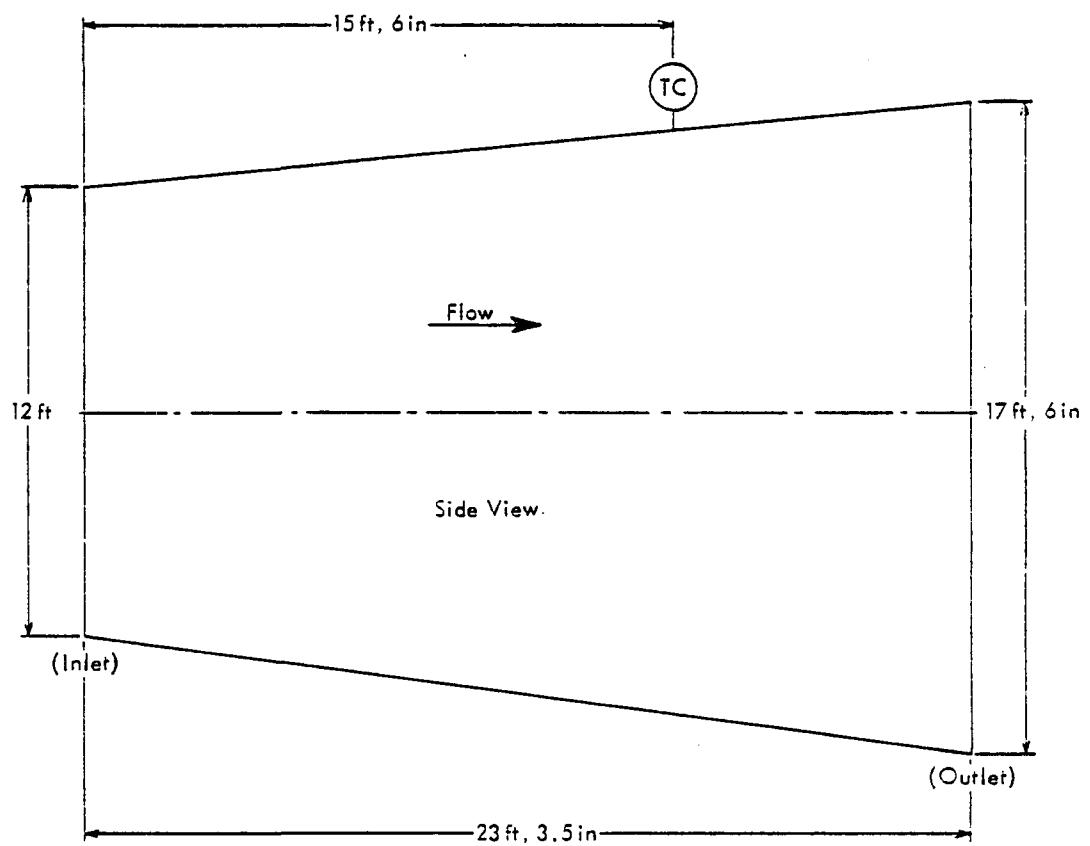
The size of the combustion chamber is 2,195 ft³. There are three thermocouples used to sense the flame temperature, and these are averaged to give the temperature recorded in the control room. A rough sketch of the combustion chamber is provided in Figure 1.

^{a/} MRI used the following, similar equation:

$$\begin{aligned}\text{Vol. flow rate, SCFH} &= \frac{(\text{Mass flow rate, lb/hour})(24 \text{ l/g-mole})(453.4 \frac{\text{g-mole}}{\text{lb-mole}})}{(28.3 \text{ l/SCF})(\text{Dry mol. wt. stack gas, } \frac{\text{lb}}{\text{lb-mole}})} \\ &(\text{std. conditions of } 68^\circ\text{F and } 29.92 \text{ in. Hg}).\end{aligned}$$

TABLE 9. PROCESS AND INCINERATOR OPERATION DATA

| Parameter | Sample No. 1 | Sample No. 2 | Sample No. 3 |
|--|-----------------|-----------------|-----------------|
| Production Rate (lb/hour) | 4,200 | 4,200 | 4,200 |
| Natural Gas Flow Rate (SCFH at 145 psig) | 63,000 | 64,000 | 64,000 |
| Incinerator Temperature (°F) | 1,400 | 1,400 | 1,400 |
| Supplemental Combustion Air Flow Rate (lb/hour at 80°F) | 51,300 | 51,300 | 51,300 |
| Waste Gas Flow Rate to the Incinerator (lb/hour) | 160,800 | 160,800 | 160,800 |
| Rate of Steam Production (lb/hour at 736°F) | 54,000 | 55,000 | 55,000 |



There are three thermocouples spaced evenly across the top of the firebox.

The width of the firebox is 6 ft, 6 in.

Figure 1. Incinerator Combustion Chamber

SECTION 4

LOCATION OF SAMPLE POINTS

Figure 2 presents a schematic of the overall sampling site. The single inlet sampling port was located in an expansion between a 0.91 m (36 in.) diameter duct and the incinerator. No additional ports could be established in any of the inlet ducting. The inlet was sampled using a 1.27 cm (0.5 in.) ID stainless steel tube whose tip was 0.53 m (21 in.) into the duct.

The eight outlet ports were located five to six diameters downstream of any disturbances. For the velocity traverse, 48 points were used. These point locations are presented in Table 10.

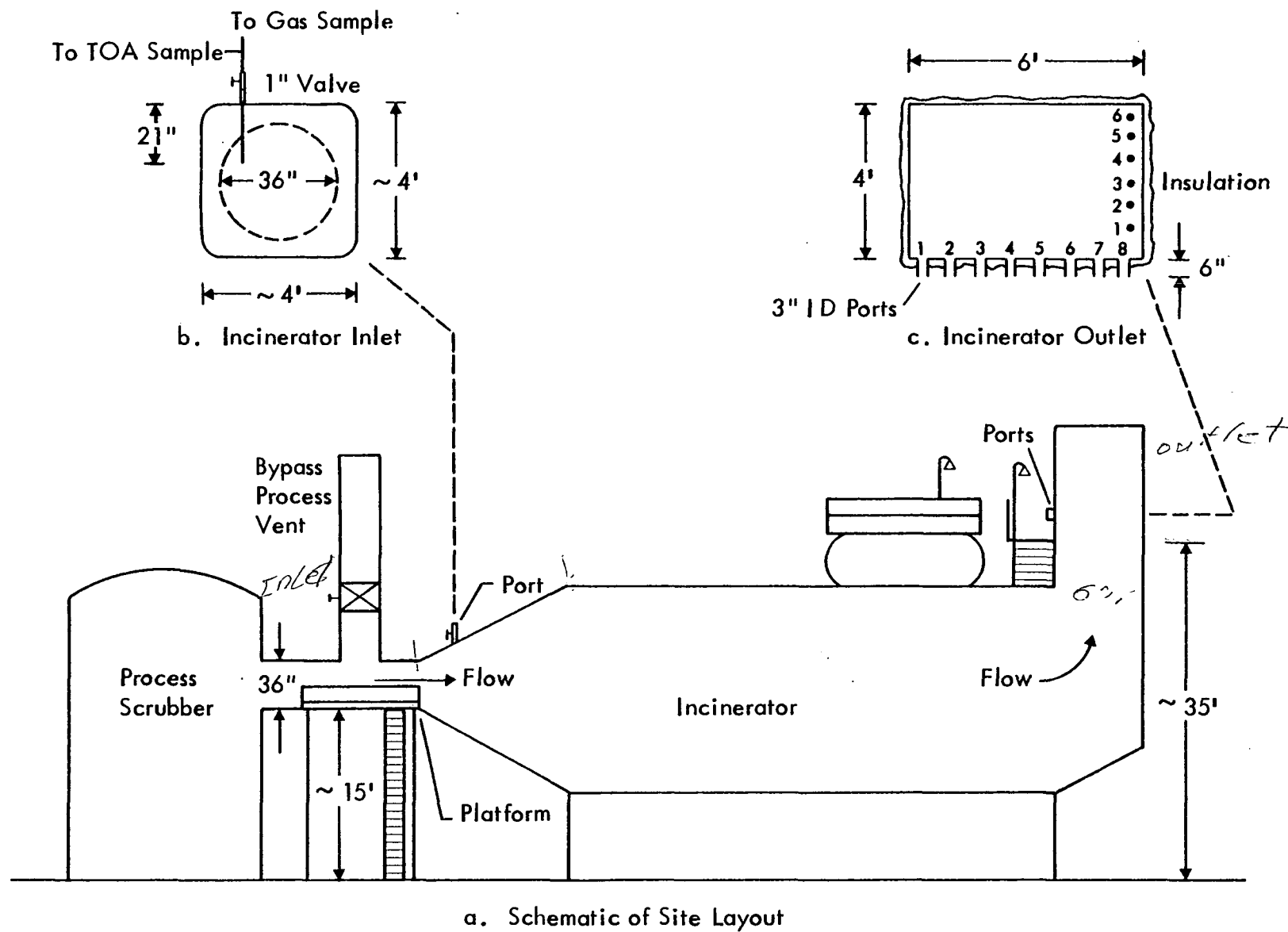


Figure 2. Sampling site - Denka Chemical Corporation, Houston, Texas.

TABLE 10. SAMPLE POINT LOCATION - OUTLET DUCT

Duct size: 1.22 x 1.83 m (4 x 6 ft)

| Traverse point | <u>Distance from inside wall</u> | |
|----------------|----------------------------------|-----|
| | cm | in. |
| 1 | 10.2 | 4 |
| 2 | 30.5 | 12 |
| 3 | 50.8 | 20 |
| 4 | 71.1 | 28 |
| 5 | 91.4 | 36 |
| 6 | 111.8 | 44 |

SECTION 5

SAMPLING AND ANALYTICAL PROCEDURES

THC, BENZENE, METHANE, AND ETHANE

The gas samples were obtained according to the September 27, 1977, EPA draft benzene method (Appendix D). Seventy liter aluminized Mylar bags were used with sample times of 2 to 3 hr. The sample box and bag were heated to approximately 66°C (150°F) using an electric drum heater and insulation. During Run 1-Inlet, the variac used to control the temperature malfunctioned so the box was not heated for this run. A stainless steel probe was inserted into the single port at the inlet and connected to the gas bag through a "tee." The other leg of the "tee" went to the TOA train. A teflon line connected the bag and the "tee." A stainless steel probe was connected directly to the bag at the outlet. The lines were kept as short as possible and not heated. The boxes were transported to the field lab immediately upon completion of sampling. They were heated until the GC analyses were completed.

A Varian model 2440 gas chromatograph with a Carle gas sampling valve equipped with 2 cm³ matched loops was used for the integrated bag analysis. The SP-1200/Bentone 34 column was operated at 80°C. The instrument has a switching circuit which allows a bypass around the column through a capillary tube for THC response. The response curve was measured daily for benzene (5, 10, and 50 ppm standards) with the column and in the bypass (THC) mode. The THC mode was also calibrated daily with propane (20, 100, and 2,000 ppm standards). The calibration plots showed moderate nonlinearity. For sample readings which fell within the range of the calibration standards an interpolated response factor was used from a smooth curve drawn through the calibration points. For samples above or below the standards the response factor of the nearest standard was assumed. THC readings used peak height and column readings used area integration measured with an electronic "disc" integrator.

CO₂, O₂, AND CO

Analysis for these constituents was done on samples drawn from the integrated gas bag used in THC, benzene, methane, and ethane. Carbon monoxide analysis was done following the GC analyses using EPA Reference Method 10

(Federal Register, Vol. 39, No. 47, March 8, 1974). A Beckman Model 215 NDIR analyzer was used. Analyses were done on both the inlet and outlet samples.

Orsat analysis was performed to determine the carbon dioxide and oxygen fractions. Denka has requested that the CO₂ data from the incinerator inlet be termed "confidential." EPA is honoring this request until such time the data are determined to be nonconfidential. The O₂ and CO₂ data are being filed under separate cover.

TOA

The total organic acid samples were obtained according to the Los Angeles Air Pollution Control District (LAAPCD) method (Appendix E). The inlet sample was run from a "tee" on the integrated gas probe while the outlet sample was obtained from port No. 3. Sample times varied from 2 to 3 hr with a flow rate of approximately 14.1 liters/min (0.5 ft³/min).

The samples were recovered in the field lab, transferred to glass bottles, and trucked to MRI for analysis.

TOTAL ALDEHYDES AND FORMALDEHYDE

These samples were obtained from the integrated bag samples from the THC, benzene, methane, and ethane section. The LAAPCD method was used for each (Appendix F). Two flask samples were obtained from each bag sample. The samples were recovered in the field lab, transferred to glass bottles, and trucked to MRI for analysis. One flask sample per run was used for the aldehyde analysis and one was used for the formaldehyde analysis.

NO_x

NO_x samples were obtained according to EPA Reference Method 7 (Federal Register, Vol. 42, No. 160, August 18, 1977). Three samples per run were obtained from the outlet stack. Samples were taken from ports 2 and 3.

The samples were recovered in the field lab, transferred to shipping bottles, and trucked to MRI for analysis.

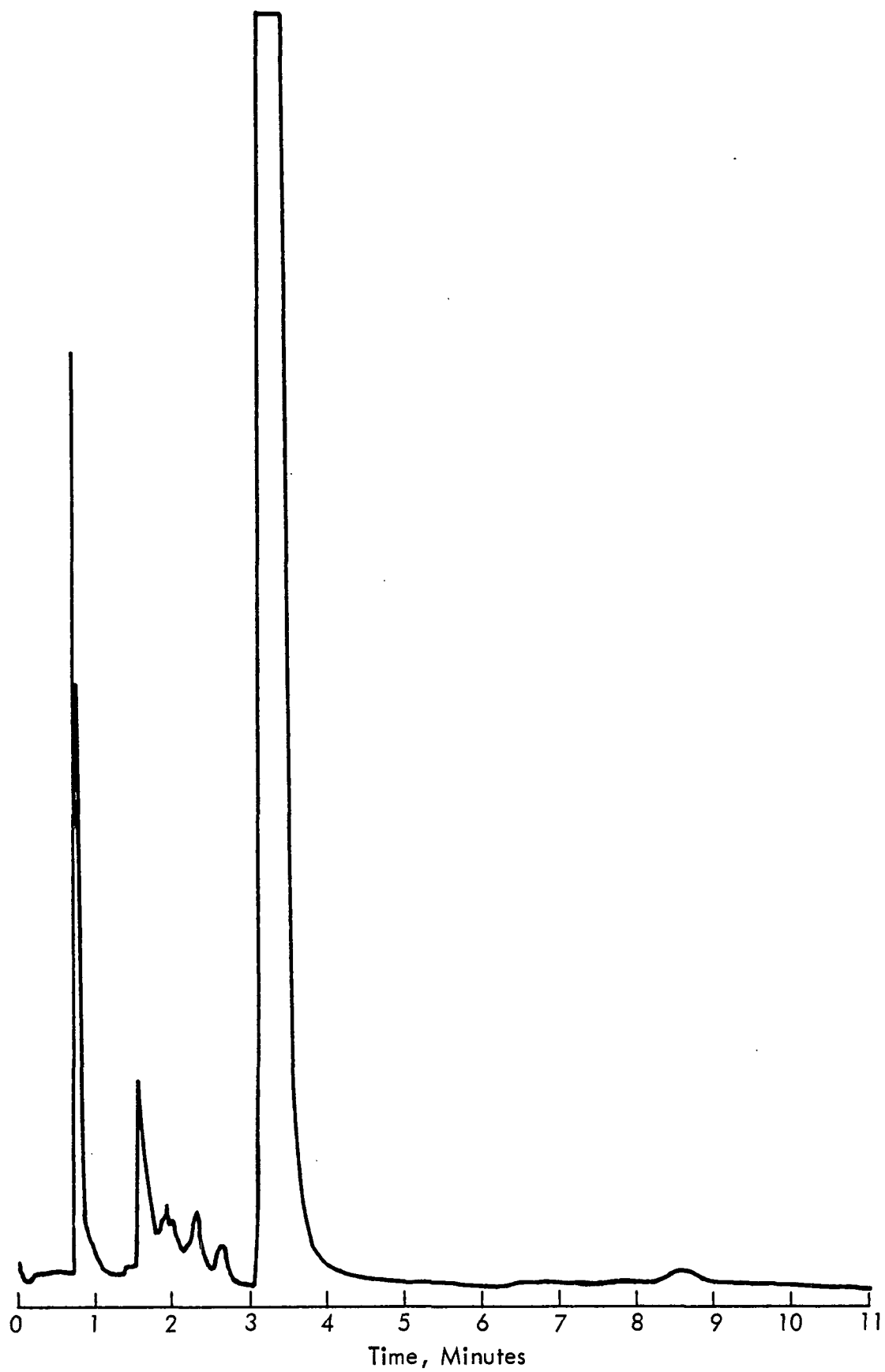
DUCT TEMPERATURE, PRESSURE, AND VELOCITY

Duct temperature and pressure values were obtained from the existing inlet port. A thermocouple was inserted into the gas sample probe for the temperature while a water manometer was used for the pressure readings. These values were obtained at the conclusion of the sampling period.

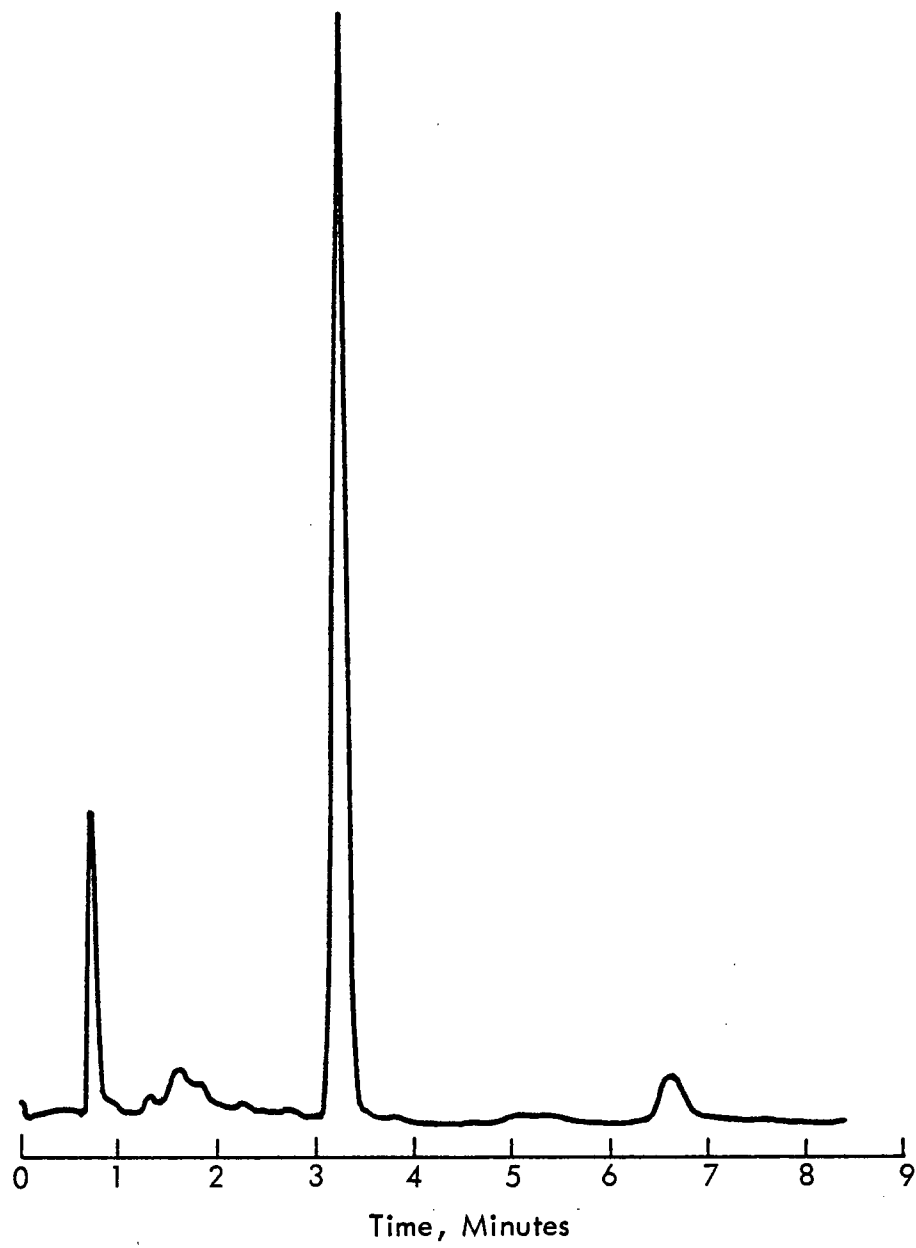
Temperature, pressure, and velocity values were obtained for the outlet stack. Temperature values were obtained by thermocouple during the gas sampling. Pressure and velocity measurements were taken according to EPA Reference Method 2 (Federal Register, Vol. 42, No. 160, August 18, 1977). These values also were obtained at the conclusion of the sampling period.

APPENDIX A

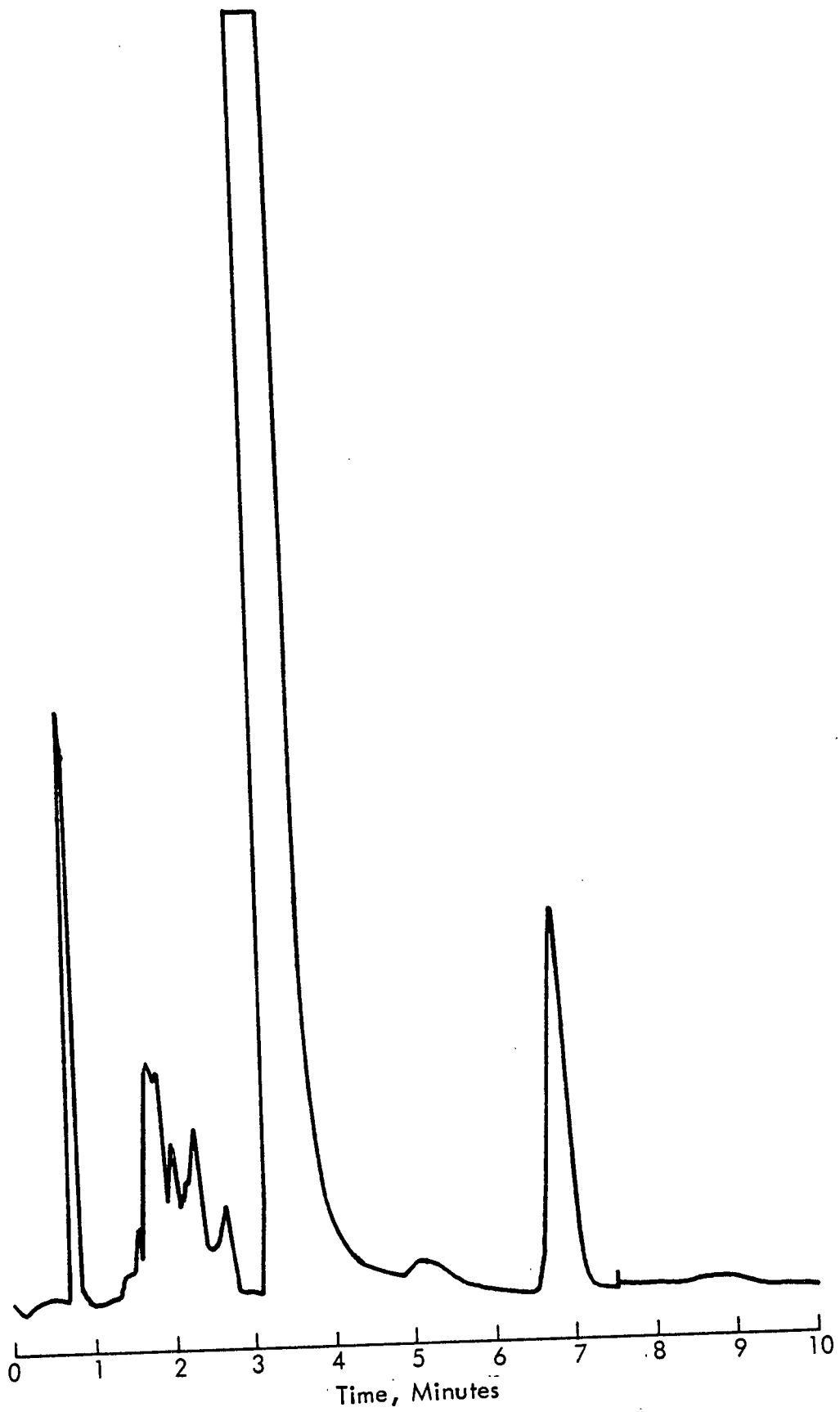
REPRESENTATIVE SAMPLE GC PLOTS



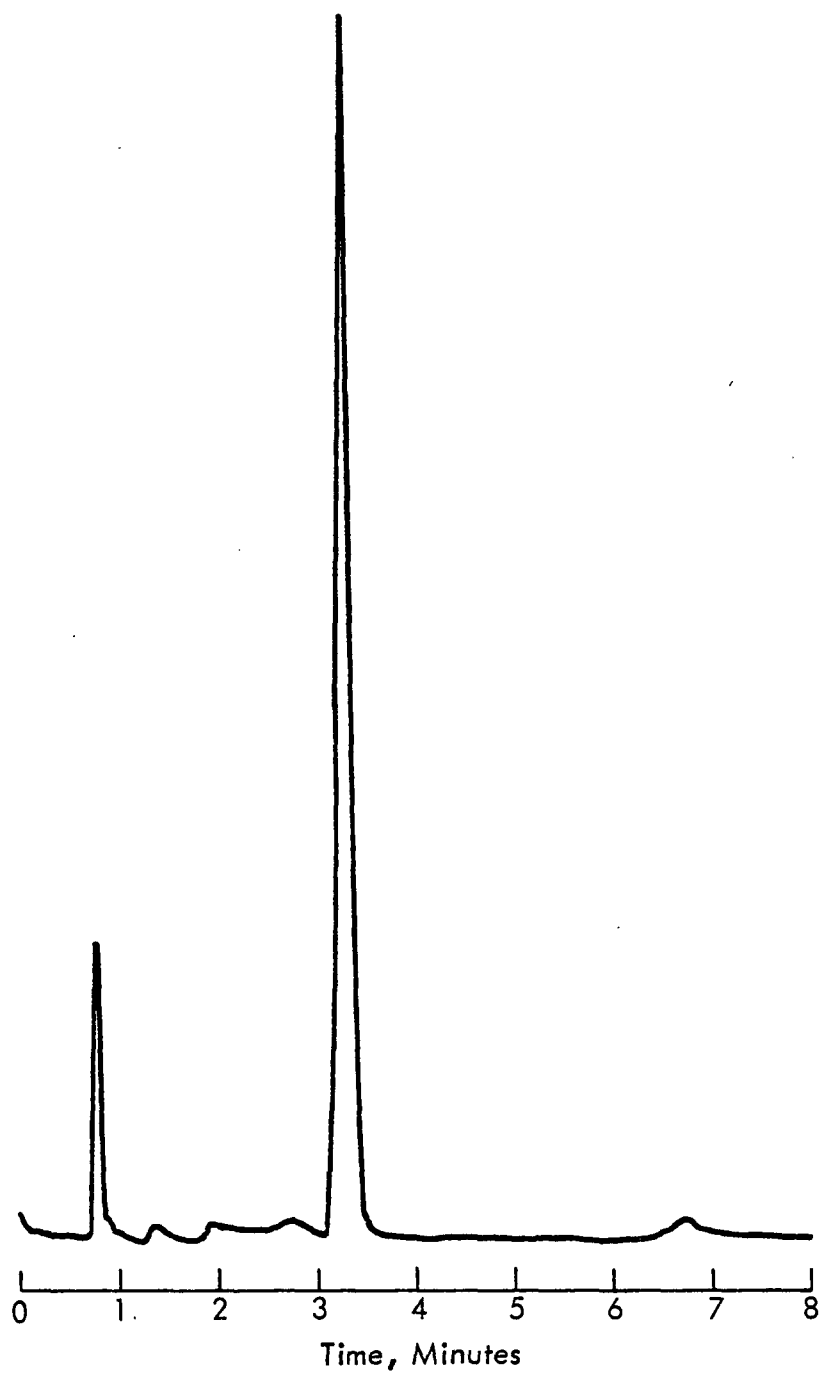
Run 1 - Inlet



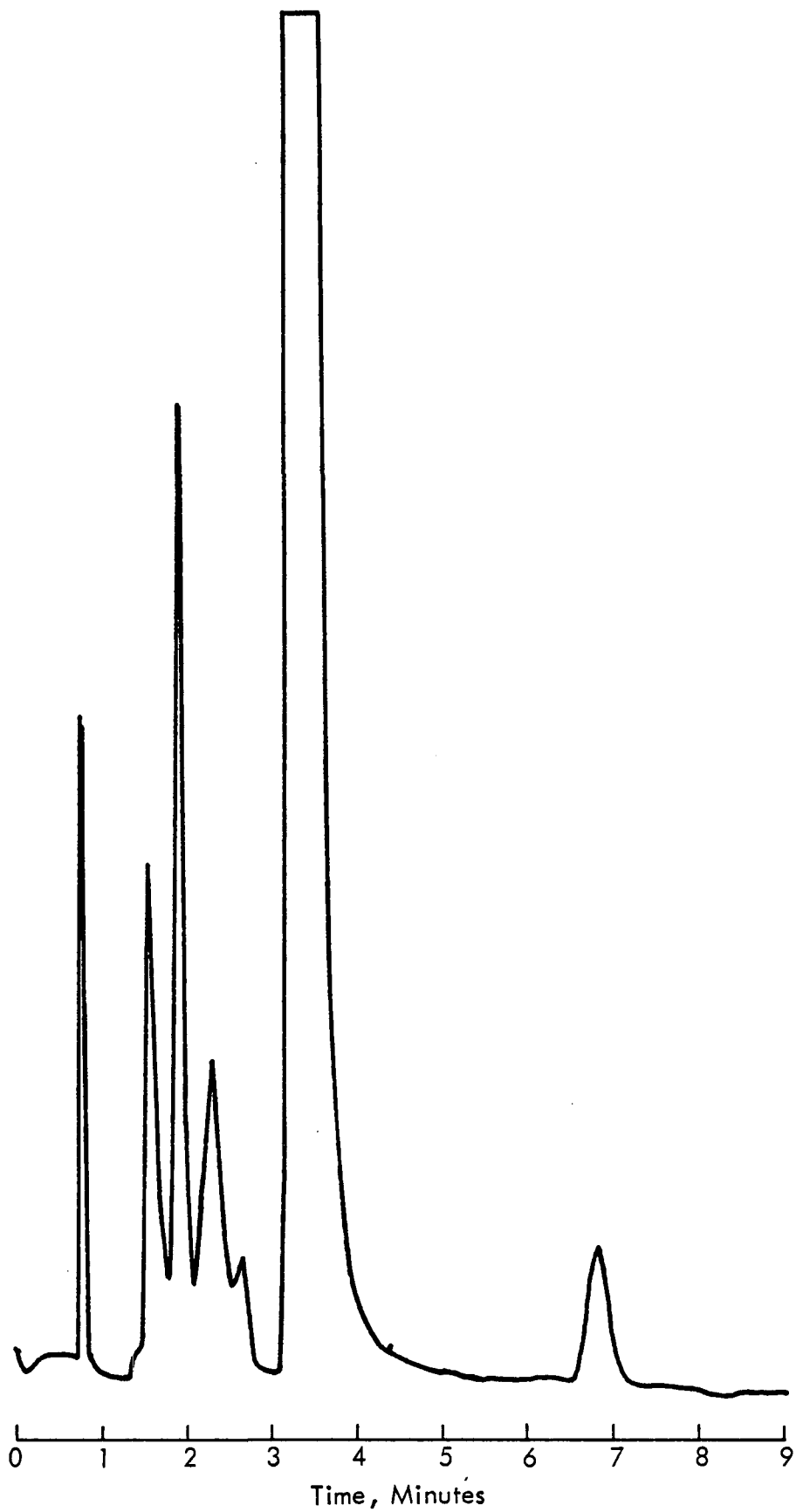
Run 1 - Outlet



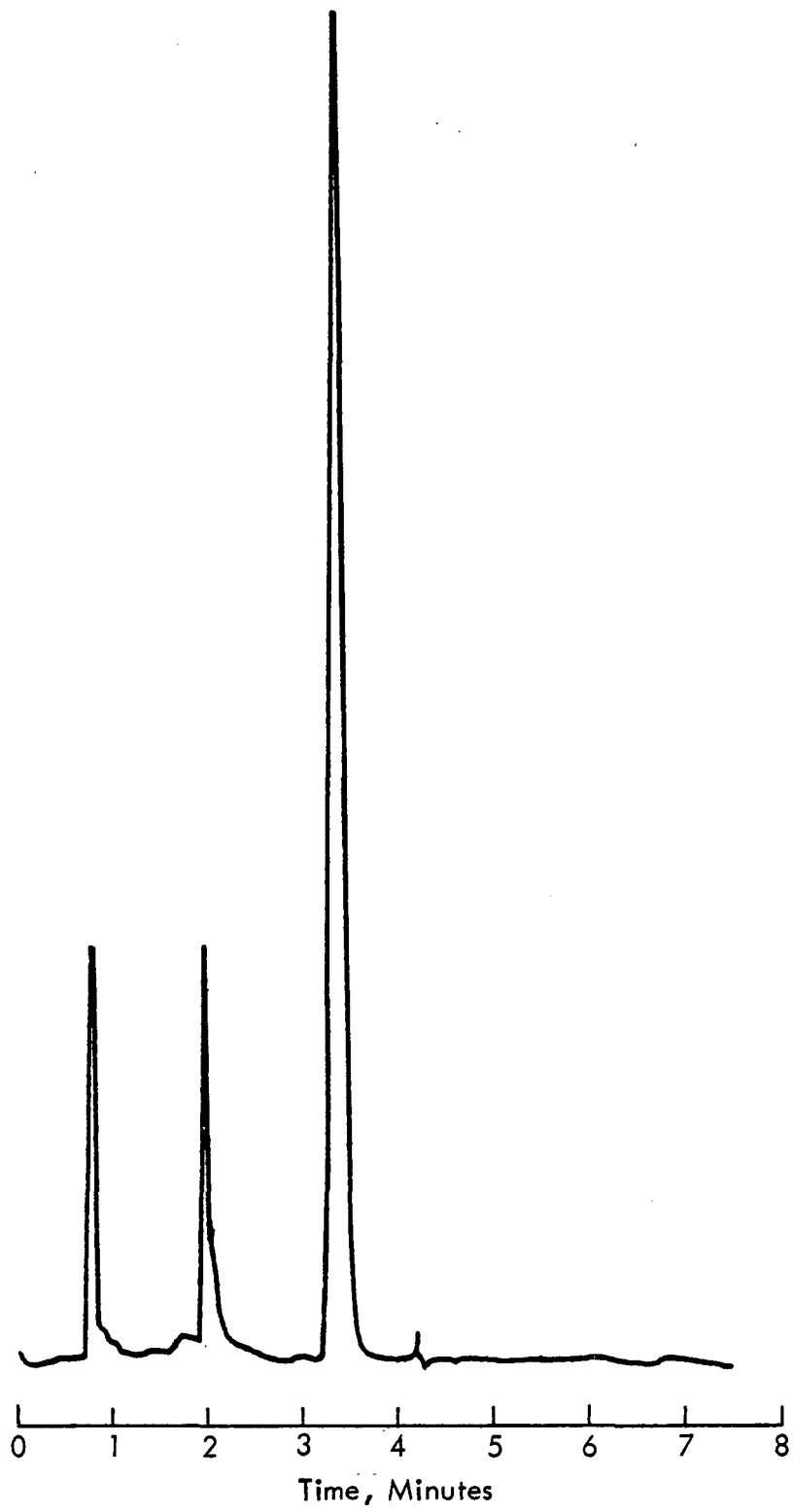
Run 2 - Inlet



Run 2 - Outlet



Run 3 - Inlet



Run 3 - Outlet

APPENDIX B

AUDIT SAMPLE RESULTS

AUDIT REPORT

PART A - (Filled out by RTI)

1. ESED, EMB Project Officer Dennis Holzschuh
2. Location Where Audit Cylinders Shipped Midwest Research Institute
425 Volker Blvd., Kansas City, Missouri 64110
3. Planned Shipping Date for Cylinders March 1, 1978
4. Details on Audit Cylinders

| | <u>Benzene</u> | |
|--------------------------------|-----------------------|------------------------|
| | Low Conc. Cylinder | High Conc. Cylinder |
| A. Cylinder Number | <u>B-1117</u> | <u>B-1529</u> |
| B. Cylinder Pressure, PSI | <u>2000</u> | <u>1900</u> |
| C. Cylinder Concentration, ppm | <u>101</u> | <u>387</u> |
| D. Date of Cylinder Analysis | <u>2/8/78</u> | <u>2/9/78</u> |

PART B - (Filled out by ESED, EMB Project Officer)

5. Type of Organic Manufacturing Process Maleic Anhydride
6. Location of Audit Denka Chemical - Houston, Texas
7. Name of Individual Audited and Organization George Scheil
Midwest Research Institute

AUDIT REPORT (Continued)

8. Audit Results

| | Low Conc. Cylinder | High Conc. Cylinder |
|--|-----------------------|------------------------|
| A. Cylinder Number | <u>B-117</u> | <u>B-1529</u> |
| B. Cylinder Pressure Before Audit, psi | <u>2000</u> | <u>1900</u> |
| C. Cylinder Pressure After Audit, psi | <u>2300</u> | <u>2000</u> |
| D. Audit Date and Measured Concentration, ppm | <u></u> | <u></u> |
| Analysis #1 on <u>3/21/78</u> (date) | <u>114/ppm</u> | <u>443/ppm</u> |
| Analysis #2 on <u>3/21/78</u> (date) | <u>114/ppm</u> | <u>443/ppm</u> |
| Analysis #3 on <u>3/21/78</u> (date) | <u>114/ppm</u> | <u>443/ppm</u> |
| E. RTI Concentration, ppm | <u>101/ppm</u> | <u>387/ppm</u> |
| F. Audit % Accuracy* | <u></u> | <u></u> |
| Analysis #1 | <u>-12.87%</u> | <u>-14.47%</u> |
| Analysis #2 | <u>-12.87%</u> | <u>-14.47%</u> |
| Analysis #3 | <u>-12.87%</u> | <u>-14.47%</u> |

* Calculate % Accuracy = $\frac{\text{Conc. RTI} - \text{Conc. Measured}}{\text{Conc. RTI}} \times 100$

G. Description of Problems Detected _____

APPENDIX C

FIELD DATA

MIDWEST RESEARCH INSTITUTE

RUN 1

MRI Project Number 4468-LS
Field Dates 20-24 MAR 78
Plant Denka, Houston, Tx.
Sampling Location Maleic
Sampling Date 21 MAR 78

FIELD CREW

Crew Chief MAXWELL

Testing Engineer 1 MAXWELL
2 LA SHELLE
3

Engr. Technician 1
2
3

Lab Technician 1 SCHEIL
2 COLE
3

Process Engineer 1 EPA
2

Other 1
2

FIELD DATA

OENKA CHEMICAL CO.
 PLANT _____
 DATE 21 MAR. 78
 SAMPLING LOCATION INLET
 SAMPLE TYPE TOTAL ORGANIC ACID / INTEG. BAG
 RUN NUMBER 1
 OPERATOR LASHELLE
 AMBIENT TEMPERATURE 78
 BAROMETRIC PRESSURE 30.16"
 STATIC PRESSURE (P_s) _____
 FILTER NUMBER (S) _____

TENG
 IMPIN

PROBE LENGTH AND TYPE _____
NOZZLE I.D. _____
ASSUMED MOISTURE, % _____
SAMPLE BOX NUMBER _____
METER BOX NUMBER _____
METER ΔH_c _____
C FACTOR _____
PROBE HEATER SETTING _____
HEATER BOX SETTING _____
REFERENCE ΔH_c _____

INT. BAG.

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY _____ MINUTES

Acid

| TRAVERSE POINT NUMBER | <div>CLOCK TIME <small>(24 hr)</small></div> SAMPLING TIME min | GAS METER READING $V_m \cdot ft^3$ | VELOCITY HEAD $\left(\frac{sp_s}{\rho} \right)_{in. H_2O}$ | ORIFICE PRESSURE DIFFERENTIAL $\Delta P_{orif.}, in. H_2O$ | | STACK TEMPERATURE $T_s, ^\circ F$ | DRY GAS METER TEMPERATURE | | ROTAMETER ROTA | BOX °F Box °F | Time Time |
|-----------------------------|---|---------------------------------------|--|--|--------|---|--------------------------------|----------------------------------|---|-----------------------------|-------------------------|
| | | | | DESIRED | ACTUAL | | INLET $T_{m.in.}, ^\circ F$ | OUTLET $T_{m.out.}, ^\circ F$ | | | |
| — | — | 1437 | 893.32 | .54 | .74 | — | 92 | 90 | 52 | 140 | 1435 |
| | | 1537 | 915.43 | .53 | .79 | — | 90 | 89 | 47 | 125 | 1450 |
| | | 1637 | 942.14 | .50 | .77 | — | 98 | 98 | 47 | 125 * | 1510 |
| | | | | | | | | | 40 | 120 | 1525 |
| | | | | | | | | | 30 | 120 | 1535 |
| | | | | | | | | | 32 | 115 | 1545 |
| | | | | | | | | | 27 | 105 | 1600 |
| | | | | | | | | | 20 | 105 | 1615 |
| | | | | | | | | | 20 | 105 | 1635 |
| | | | | | | | | | * HOATING SYSTEM DISCONTINUED DUE TO BROKEN VARIAC. | | |

Begin

200

* HOATING
SYSTEM
DISCONTINUED
DUE TO
BROKEN
VARIAC

COMMENTS

FIELD DATA

PLANT Danka
DATE 21 May 73
SAMPLING LOCATION OUTLET
SAMPLE TYPE _____
RUN NUMBER 1
OPERATOR MAXWELL
AMBIENT TEMPERATURE 70
BAROMETRIC PRESSURE 30.14
STATIC PRESSURE, (P_s) _____
FILTER NUMBER (s) —

PROBE LENGTH AND TYPE 4'-9/16" / 41-33
NOZZLE I.D. _____
ASSUMED MOISTURE, % _____
SAMPLE BOX NUMBER _____
METER BOX NUMBER _____
METER ΔH @ _____
C FACTOR _____
PROBE HEATER SETTING _____
HEATER BOX SETTING _____
REFERENCE Δp _____

30" Lbs. Lbs. +
70.9
35" Lbs. Lbs. +
80.9

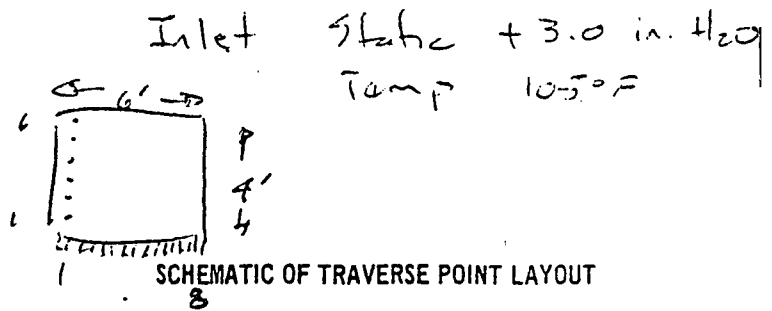
SCHEMATIC OF TRAVERSE POINT LAYOUT
READ AND RECORD ALL DATA EVERY _____ MINUTES

[illegible]

COMMENTS

PRELIMINARY VELOCITY TRAVERSE

PLANT Denka
 DATE 21 Mar-78
 LOCATION Outlet
 STACK I.D. 11 x 6 ft
 BAROMETRIC PRESSURE, in. Hg _____
 STACK GAUGE PRESSURE, in. H₂O +0.27
 OPERATORS MAXWELL, HOLLISCHULT



| TRAVERSE POINT NUMBER | VELOCITY HEAD (Δp_s), in. H ₂ O | STACK TEMPERATURE (T_s), °F |
|-----------------------|--|---------------------------------|
| 1-1 | .13 | |
| 2 | .19 | |
| 3 | .31 | |
| 4 | .47 | |
| 5 | .50 | |
| 6 | .47 | |
| 2-2 | .17 | |
| 2 | .27 | 345 |
| 3 | .42 | |
| 4 | .52 | |
| 5 | .57 | |
| 6 | .56 | |
| 3-1 | .18 | |
| 2 | .28 | |
| 3 | .45 | |
| 4 | .52 | |
| 5 | .62 | |
| 6 | .61 | |
| 4-1 | .13 | |
| 2 | .16 | |
| 3 | .26 | |
| 4 | .31 | |
| 5 | .47 | |
| 6 | .57 | |
| AVERAGE | | |

| TRAVERSE POINT NUMBER | VELOCITY HEAD (Δp_s), in. H ₂ O | STACK TEMPERATURE (T_s), °F |
|-----------------------|--|---------------------------------|
| 5-1 | .14 | |
| 2 | .22 | |
| 3 | .41 | |
| 4 | .50 | |
| 5 | .53 | |
| 6 | .47 | |
| 6-2 | .15 | |
| 2 | .28 | |
| 3 | .39 | |
| 4 | .55 | |
| 5 | .61 | 345 |
| 6 | .59 | |
| 7-1 | .19 | |
| 2 | .28 | |
| 3 | .41 | |
| 4 | .55 | |
| 5 | .55 | |
| 6 | .52 | |
| 8-1 | .14 | |
| 2 | .24 | |
| 3 | .39 | |
| 4 | .51 | |
| 5 | .49 | |
| 6 | .45 | |
| AVERAGE | .39 | 345 |

MIDWEST RESEARCH INSTITUTE

Run Number 1Date 21 Mar 78NO_x SAMPLINGPROBE

| <u>Unit No.</u> | <u>Length =</u> | <u>Lining Material</u> | <u>Pre-Filter</u> | <u>Heated</u> | <u>Pitot Tube</u> |
|-----------------|-----------------|--|--|--|--|
| | <u>5</u> ft | <input type="checkbox"/> S. Steel <input checked="" type="checkbox"/> Pyrex | <input checked="" type="checkbox"/> Glass Wool <input type="checkbox"/> _____ | <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No | No. _____ Coefficient: <input type="checkbox"/> .85 <input type="checkbox"/> _____ |

SAMPLING DATA

| | | | | |
|------------------------------|---------------|--------------|--------------|--|
| Flask No. | <u>N2</u> | <u>N7</u> | <u>N23</u> | |
| Volume of Flask | <u>2052</u> | <u>2095</u> | <u>2062</u> | |
| Less Absorb. Soln. | <u>-25</u> | <u>-25</u> | <u>-25</u> | |
| | <u>2027</u> | <u>2070</u> | <u>2037</u> | |
| Initial Conditions: | | | | |
| Barometric Pressure (in. Hg) | <u>30.12</u> | <u>30.12</u> | <u>30.12</u> | |
| Flask Temperature (°F) | <u>72</u> | <u>72</u> | <u>72</u> | |
| Flask Vacuum (in. Hg): | | | | |
| Top | _____ | _____ | _____ | |
| Bottom | _____ | _____ | _____ | |
| Difference | <u>27.6</u> | <u>27.6</u> | <u>27.6</u> | |
| Leak Check | <u>OK</u> | <u>OK</u> | <u>OK</u> | |
| Sampling Location: | | | | |
| Port | <u>2</u> | <u>2</u> | <u>2</u> | |
| Point or Distance from | | | | |
| Inside of Port | <u>5</u> | <u>5</u> | <u>5</u> | |
| Clock Time | <u>1611</u> | <u>1623</u> | <u>1705</u> | |
| Performed by | <u>W.H.N.</u> | | | |
| Comments: | | | | |

MIDWEST RESEARCH INSTITUTE

RUN 2

MRI Project Number 4408-LS
 Field Dates 20-24 MAR 78
 Plant Danka
 Sampling Location Maleic
 Sampling Date 22 MAR 78

FIELD CREW

Crew Chief MAXWELL

Testing Engineer 1 MAXWELL
 2 LASHELLE
 3

Engr. Technician 1
 2
 3

Lab Technician 1 SCHILL
 2 COLE
 3

Process Engineer 1 EPA
 2

Other 1
 2

FIELD DATA

PLANT OPENKA CHEMICAL
DATE 22 MAR. 78
SAMPLING LOCATION 1460
SAMPLE TYPE INTEG. BAG- / TOMR organic ACID
RUN NUMBER 2
OPERATOR LASHELLE
AMBIENT TEMPERATURE 76°F
BAROMETRIC PRESSURE 30.22
STATIC PRESSURE (PSI) + 3.2 in H₂O
FILTER NUMBER (SI) —

IMP.
TEMP.

PROBE LENGTH AND TYPE _____
NOZZLE I.D. _____
ASSUMED MOISTURE, % _____
SAMPLE BOX NUMBER _____
METER BOX NUMBER _____
METER ΔH_c _____
C FACTOR _____
PROBE HEATER SETTING _____
HEATER BOX SETTING _____
REFERENCE Δp _____

TOTAL
ORGANIC
ACID -

Imp.
Temp.

INTEG.
BAG.

SCHEMATIC OF TRAVERSE POINT LAYOUT
READ AND RECORD ALL DATA EVERY _____ MINUTES

[illegible]

COMMENTS

FIELD DATA

PLANT Danka
DATE 22 MAR. 78
SAMPLING LOCATION OUTLET
SAMPLE TYPE _____
RUN NUMBER 2
OPERATOR MAXWELL
AMBIENT TEMPERATURE 75
BAROMETRIC PRESSURE ~~30.06~~ 30.22
STATIC TEMPERATURE (°F) +20.20
FILTER NUMBER (S) _____

PROBE LENGTH AND TYPE _____
NOZZLE I.D. _____
ASSUMED MOISTURE, % _____
SAMPLE BOX NUMBER _____
METER BOX NUMBER _____
METER ΔH _____
C FACTOR _____
PROBE HEATER SETTING _____
HEATER BOX SETTING _____
REFERENCE Δp _____

TOA

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY _____ MINUTES

CO₂ ROTAMETER

INTEGRATED
GAS

| TRAVERSE POINT NUMBER | CLOCK TIME (24 hr CLOCK) | GAS METER READING (V_m) ft ³ | VELOCITY HEAD (ΔP_s) in. H ₂ O | ORIFICE PRESSURE DIFFERENTIAL (ΔH) in. H ₂ O | | STACK TEMPERATURE (T_s) °F | DRY GAS METER TEMPERATURE | | PUMP VACUUM (in. Hg) | SAMPLER BOX TEMPERATURE °F | WATER TEMPERATURE °F Port |
|-----------------------------|--------------------------------|--|---|---|--------|--------------------------------------|-----------------------------------|-------------------------------------|----------------------------|----------------------------------|--|
| | | | | DESIRED | ACTUAL | | INLET ($T_{m\text{ in}}$) °F | OUTLET ($T_{m\text{ out}}$) °F | | | |
| 3-5 | 1131 | 942.12 | | .70 | | 300.2 | 79 | 79 | 94 | | 6-5 |
| | 1200 | 952.97 | | .70 | | 85 | 88 | 82 | 94 | 135 | |
| | 1231 | 968.91 | | .70 | | 84 | 90 | 86 | 96 | 150 | |
| | 1250 | 977.74 | | .70 | | 90 | 92 | 89 | 94 | 150 | |
| | 1310 | 986.74 | | .70 | | 90 | 91 | 88 | 98 | 160 | |
| | 1331 | 999.24 | | .70 | | 350.9 | 92 | 88 | 98 | 135 | |
| | 1431 | 1027.79 | | | | | | | 97 | 140 | |

Time

1120

1143

1203

1250

1250

310

1331

1420

COMMENTS

PRELIMINARY VELOCITY TRAVERSE

PLANT Danka
 DATE 22 Mar 78
 LOCATION Outlet
 STACK I.D. 4' x 6'
 BAROMETRIC PRESSURE, in. Hg ~~30.26~~ 30.22
 STACK GAUGE PRESSURE, in. H₂O + 0.28
 OPERATORS Maxwell

SCHEMATIC OF TRAVERSE POINT LAYOUT

| TRAVERSE POINT NUMBER | VELOCITY HEAD (Δp_s), in. H ₂ O | STACK TEMPERATURE (T _s), °F |
|-----------------------|--|---|
| 8-1 | .15 | |
| 2 | .32 | |
| 3 | .47 | |
| 4 | .55 | |
| 5 | .54 | |
| 6 | .51 | |
| 7-1 | .24 | |
| 2 | .38 | |
| 3 | .49 | |
| 4 | .64 | |
| 5 | .62 | |
| 6 | .56 | |
| 6-1 | .15 | |
| 2 | .28 | |
| 3 | .44 | |
| 4 | .63 | |
| 5 | .67 | |
| 6 | .67 | |
| 5-1 | .17 | |
| 2 | .24 | |
| 3 | .43 | |
| 4 | .58 | |
| 5 | .56 | |
| 6 | .49 | |
| AVERAGE | | |

| TRAVERSE POINT NUMBER | VELOCITY HEAD (Δp_s), in. H ₂ O | STACK TEMPERATURE (T _s), °F |
|-----------------------|--|---|
| 4-1 | .13 | |
| 2 | .20 | |
| 3 | .31 | |
| 4 | .39 | |
| 5 | .58 | |
| 6 | .66 | |
| 3-1 | .19 | |
| 2 | .32 | |
| 3 | .50 | |
| 4 | .59 | |
| 5 | .68 | |
| 6 | .67 | |
| 2-1 | .18 | |
| 2 | .31 | |
| 3 | .47 | |
| 4 | .56 | |
| 5 | .61 | |
| 6 | .61 | |
| 1-1 | .14 | |
| 2 | .21 | |
| 3 | .34 | |
| 4 | .46 | |
| 5 | .50 | |
| 6 | .49 | |
| AVERAGE | | |

MIDWEST RESEARCH INSTITUTE

Run Number 2Date 22 Nov 78NO_x SAMPLINGPROBE

| <u>Unit No.</u> | <u>Length =</u> | <u>Lining Material</u> | <u>Pre-Filter</u> | <u>Heated</u> | <u>Pitot Tube</u> |
|-----------------|-----------------|---|--|--|--|
| | <u>5</u> ft | <input type="checkbox"/> S. Steel | <input checked="" type="checkbox"/> Glass Wool | <input type="checkbox"/> Yes | No. <u> </u> |
| | | <input checked="" type="checkbox"/> Pyrex | <input type="checkbox"/> <u> </u> | <input checked="" type="checkbox"/> No | Coefficient: <input type="checkbox"/> .85 <input type="checkbox"/> <u> </u> |

SAMPLING DATA

| | | | | |
|--|-----------------|-----------------|-----------------|--|
| Flask No. | <u>N/2</u> | <u>N/7</u> | <u>N/23</u> | |
| Volume of Flask Less Absorb. Soln. | <u>2027</u> | <u>2070</u> | <u>2037</u> | |
| Initial Conditions: | | | | |
| Barometric Pressure (in. Hg) | <u>30.22</u> | <u>30.22</u> | <u>30.22</u> | |
| Flask Temperature (°F) | <u>71°F</u> | <u>71°</u> | <u>71°</u> | |
| Flask Vacuum (in. Hg): | | | | |
| Top | <u> </u> | <u> </u> | <u> </u> | |
| Bottom | <u> </u> | <u> </u> | <u> </u> | |
| Difference | <u>27.6"</u> | <u>27.6"</u> | <u>27.6"</u> | |
| Leak Check | <u>O.K.</u> | <u>O.K.</u> | <u>O.K.</u> | |
| Sampling Location: | | | | |
| Port | <u>2</u> | <u>3</u> | <u>3</u> | |
| Point or Distance from Inside of Port | <u>5</u> | <u>5</u> | <u>5</u> | |
| Clock Time | <u>1320</u> | <u>1455</u> | <u>1500</u> | |
| | | <u>1555</u> | <u>1600</u> | |
| Performed by | <u>WHM</u> | <u>WHM</u> | <u>WHM</u> | |

Comments:

Final Conditions:

Bp inches Hg

Flask Temp. °F

Flask Vacuum (in Hg)

30.0830.0830.0867°67°F67°F1.4"1.1"1.5"

MIDWEST RESEARCH INSTITUTE

RUN 3

MRI Project Number 4468-LS
Field Dates 20-24 MAR 78
Plant Den Ka
Sampling Location Maleic
Sampling Date 23 MAR 78

FIELD CREW

Crew Chief MAXWELL

Testing Engineer 1 MAXWELL
2 LASHELLE
3

Engr. Technician 1
2
3

Lab Technician 1 SCHILL
2 COLO
3

Process Engineer 1 EPA
2

Other 1
2

2

PROBE LENGTH AND TYPE _____
NOZZLE I.D. _____
ASSUMED MOISTURE, % _____
SAMPLE BOX NUMBER _____
METER BOX NUMBER _____
METER ΔH_d _____
C FACTOR _____
PROBE HEATER SETTING _____
HEATER BOX SETTING _____
REFERENCE Δp _____

Imp. Temp.

TOTAL ORGANIC ACID

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY _____ MINUTES

INTEG. BAG

ROTA BOX

[illegible]

COMMENTS

FIELD DATA

PLANT Danka
DATE 23 Mar 78
SAMPLING LOCATION Outlet
SAMPLE TYPE _____
RUN NUMBER 3
OPERATOR Maxwell
AMBIENT TEMPERATURE 70
BAROMETRIC PRESSURE 30.06
STATIC PRESSURE (P_s) +0.28
FILTER NUMBER (S) _____

PROBE LENGTH AND TYPE _____
NOZZLE I.D. _____
ASSUMED MOISTURE, % _____
SAMPLE BOX NUMBER _____
METER BOX NUMBER _____
METER ΔH_g _____
C FACTOR _____
PROBE HEATER SETTING _____
HEATER BOX SETTING _____
REFERENCE Δp _____

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY _____ MINUTES

| TRAVERSE POINT NUMBER | CLOCK TIME 124 hr CLOCK | GAS METER READING (V _m × 11) ³ | VELOCITY HEAD (ΔP _s × 11 / 12.2) in. H ₂ O | ORIFICE PRESSURE DIFFERENTIAL (ΔH) in. H ₂ O | | STACK TEMPERATURE (T _s) °F | DRY GAS METER TEMPERATURE | | PUMP VACUUM (in. Hg) P _{ts} meter | SAMPLE BOX TEMPERATURE °F | THERMISTOR TEMPERATURE °F T _{inc} |
|-----------------------------|-------------------------------|---|--|---|--------|--|----------------------------------|------------------------------------|---|---------------------------------|---|
| | | | | DESIRED | ACTUAL | | INLET (T _{m in}) °F | OUTLET (T _{m out}) °F | | | |
| G-5 | 0945 | 028.37 | 74°F | .7 | | 358 | 68 | 68 | 94 | | 0934 |
| | 1024 | 47.00 | | .7 | | | 86 | 78 | 94 | 140 | 1024 |
| | 1045 | 057.10 | 72 | .7 | | | 88 | 82 | 93 | 140 | 1045 |
| | 1120 | 072.81 | | .7 | | 352 | 90 | 84 | 94 | 140 | 1120 |
| | 1210 | 97.70 | 67 | .7 | | | 90 | 85 | | 140 | 1210 |
| | 1245 | 115.11 | | .7 | | 355 | | | | 140 | 1234 |

COMMENTS

PRELIMINARY VELOCITY TRAVERSE

PLANT Denka
 DATE 23 Mar 78
 LOCATION Outlet
 STACK I.D. 4' x 6'
 BAROMETRIC PRESSURE, in. Hg _____
 STACK GAUGE PRESSURE, in. H₂O + 0.28 in. H₂O
 OPERATORS MANUEL LASHLEY

SCHEMATIC OF TRAVERSE POINT LAYOUT

| TRAVERSE POINT NUMBER | VELOCITY HEAD (Δp_s), in. H ₂ O | STACK TEMPERATURE (T _s), °F |
|-----------------------|--|---|
| 8-1 | .15 | |
| 2 | .29 | |
| 3 | .45 | |
| 4 | .54 | |
| 5 | .53 | |
| 6 | .49 | |
| 7-1 | .25 | |
| 2 | .37 | |
| 3 | .49 | |
| 4 | .60 | |
| 5 | .60 | |
| 6 | .57 | |
| 6-1 | .20 | |
| 2 | .31 | |
| 3 | .45 | |
| 4 | .59 | |
| 5 | .65 | |
| 6 | .64 | |
| 5-1 | .17 | |
| 2 | .26 | |
| 3 | .43 | |
| 4 | .56 | |
| 5 | .50 | |
| 6 | .47 | |
| AVERAGE | | |

| TRAVERSE POINT NUMBER | VELOCITY HEAD (Δp_s), in. H ₂ O | STACK TEMPERATURE (T _s), °F |
|-----------------------|--|---|
| 4-1 | .15 | |
| 2 | .20 | |
| 3 | .32 | |
| 4 | .37 | |
| 5 | .59 | |
| 6 | .66 | |
| 3-1 | .19 | |
| 2 | .35 | |
| 3 | .49 | |
| 4 | .59 | |
| 5 | .63 | |
| 6 | .66 | |
| 2-1 | .19 | |
| 2 | .32 | |
| 3 | .46 | |
| 4 | .57 | |
| 5 | .61 | |
| 6 | .62 | |
| 1-1 | .14 | |
| 2 | .21 | |
| 3 | .33 | |
| 4 | .43 | |
| 5 | .50 | |
| 6 | .48 | |
| AVERAGE | | |

MIDWEST RESEARCH INSTITUTE

Run Number 3
Date 3/23/78NO_x SAMPLINGPROBE

| <u>Unit No.</u> | <u>Length =</u> | <u>Lining Material</u> | <u>Pre-Filter</u> | <u>Heated</u> | <u>Pitot Tube</u> |
|-----------------|-----------------|---|--|--|--|
| | <u>5</u> ft | <input type="checkbox"/> S. Steel | <input checked="" type="checkbox"/> Glass Wool | <input type="checkbox"/> Yes | No. <u> </u> |
| | | <input checked="" type="checkbox"/> Pyrex | <input type="checkbox"/> <u> </u> | <input checked="" type="checkbox"/> No | Coefficient: <input type="checkbox"/> .85 <input type="checkbox"/> <u> </u> |

SAMPLING DATA

| <u>Flask No.</u> | <u>N7</u> | <u>N23</u> | <u>N2</u> | <u> </u> |
|--|------------------|------------------|------------------|---------------|
| Volume of Flask Less Absorb. Soln. | <u>2070</u> | <u>2037</u> | <u>2027</u> | <u> </u> |
| Initial Conditions: | | | | |
| Barometric Pressure (in. Hg) | <u>30.06"</u> | <u>30.06"</u> | <u>30.06</u> | <u> </u> |
| Flask Temperature (°F) | <u>68°</u> | <u>68°</u> | <u>68°</u> | <u> </u> |
| Flask Vacuum (in. Hg): | | | | |
| Top | <u>14.5"</u> | <u>14.5"</u> | <u>14.5"</u> | <u> </u> |
| Bottom | <u>13"</u> | <u>13"</u> | <u>13"</u> | <u> </u> |
| Difference <u>Sum</u> | <u>27.5"</u> | <u>27.5"</u> | <u>27.5"</u> | <u> </u> |
| Leak Check | <u>20.1"/min</u> | <u>20.1"/min</u> | <u>20.1"/min</u> | <u> </u> |
| Sampling Location: | | | | |
| Port | <u>2</u> | <u>2</u> | <u>2</u> | <u> </u> |
| Point or Distance from Inside of Port | <u>5</u> | <u>5</u> | <u>5</u> | <u> </u> |
| Clock Time | <u>1200</u> | <u>1105</u> | <u>1142</u> | <u> </u> |
| Performed by | <u>W.H.M.</u> | <u>W.H.M.</u> | <u>W.H.M.</u> | <u> </u> |

Comments:

Final Conditions

Bp. 30.10

Flask Temp. 62°

Flask Vacuum 2.1"

| | | |
|--------------|--------------|--------------|
| <u>30.10</u> | <u>30.10</u> | <u>30.10</u> |
| <u>62°</u> | <u>61°</u> | <u>62°</u> |
| <u>2.1"</u> | <u>1.2"</u> | <u>1.2"</u> |

APPENDIX D

DRAFT EPA BENZENE METHOD

METHOD . DETERMINATION OF BENZENE
FROM STATIONARY SOURCES

INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to benzene, a carcinogen.

1. Principle and Applicability

1.1 Principle. An integrated bag sample of stack gas containing benzene and other organics is subjected to gas chromatographic (GC) analysis, using a flame ionization detector (FID).

1.2 Applicability. The method is applicable to the measurement of benzene in stack gases only from specified processes. It is not applicable where the benzene is contained in particulate matter.

2. Range and Sensitivity

The procedure described herein is applicable to the measurement of benzene in the 0.1 to 70 ppm range. The upper limit may be extended by extending the calibration range or by dilution of the sample.

3. Interferences

The chromatograph columns and the corresponding operating parameters herein described have been represented as being useful for producing an adequate resolution of benzene. However, resolution interferences may be encountered on some sources. Also, the chromatograph operator may know of a column that will produce a superior

resolution of benzene without reducing the response to benzene as specified in Section 4.3.1.

In any event, the chromatograph operator shall select a column which is best suited to his particular analysis problem, subject to the approval of the Administrator. Such approval shall be considered automatic provided that confirming data produced through a demonstrably adequate supplemental analytical technique, such as analysis with a different column or g.c./mass spectroscopy, is available for review by the Administrator.

4. Apparatus

4.1 Sampling (see Figure 1).

4.1.1 Probe. Stainless steel, Pyrex¹ glass, or Teflon tubing according to stack temperature, each equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample Line. Teflon, 6.4 mm outside diameter, of sufficient length to connect probe to bag. A new unused piece is employed for each series of bag samples that constitutes an emission test.

4.1.3 Male (2) and female (2) stainless steel quick connects, with ball checks (one pair without) located as shown in Figure 1.

4.1.4 Tedlar or aluminized Mylar bags, 100 liter capacity. To contain sample.

4.1.5 Rigid leakproof containers for 4.1.4, with covering to protect contents from sunlight.

¹Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

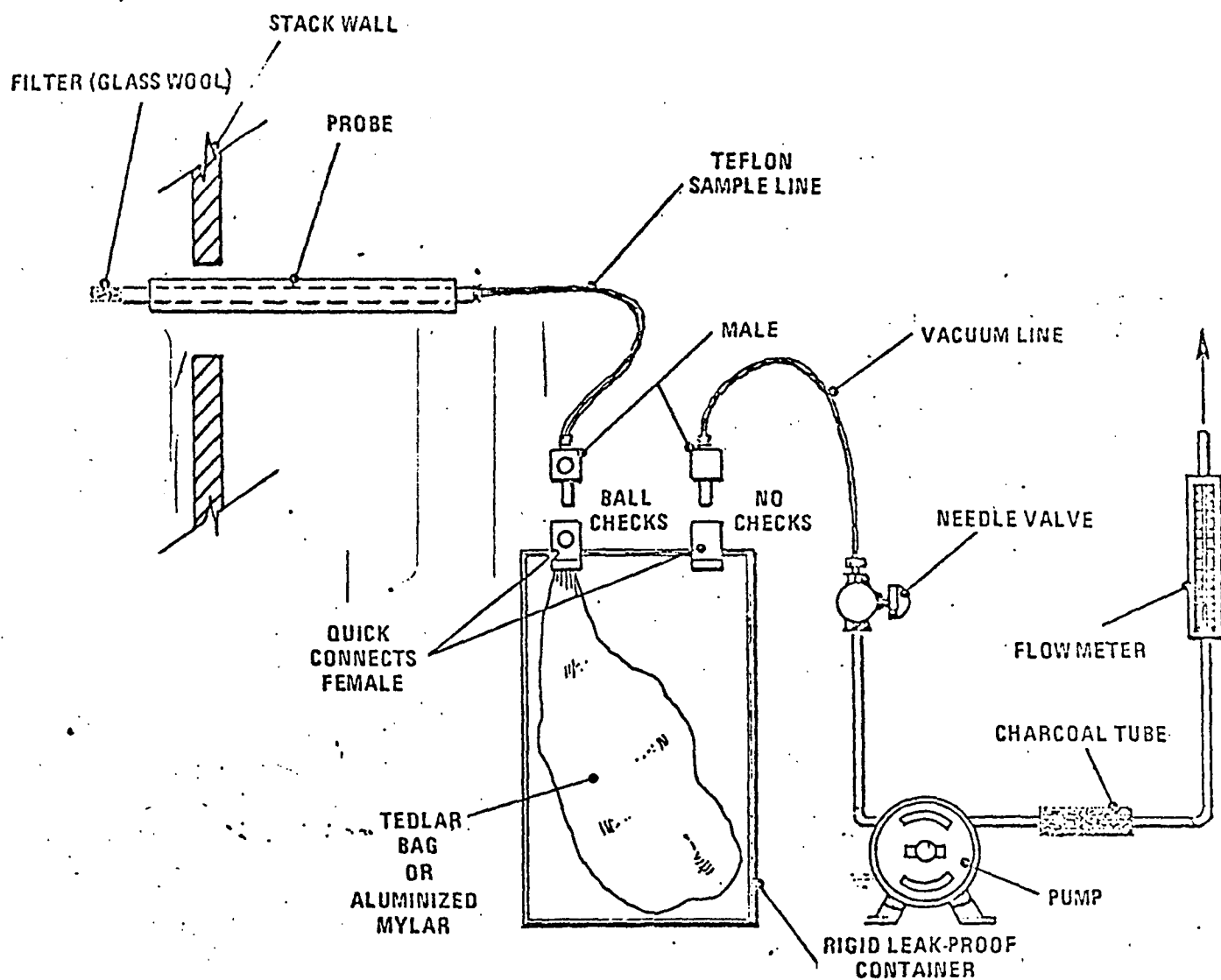


Figure 1. Integrated-bag sampling train. (Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.)

4.1.6 Needle Valve. To adjust sample flow rate.

4.1.7 Pump--Leak-free. Minimum capacity 2 liters per minute.

4.1.8 Charcoal Tube. To prevent admission of benzene and other organics to the atmosphere in the vicinity of samplers.

4.1.9 Flow Meter. For observing sample flow rate; capable of measuring a flow range from 0.10 to 1.00 liters per minute.

4.1.10 Connecting Tubing. Teflon, 6.4 mm outside diameter, to assemble sample train (Figure 1).

4.2 Sample Recovery.

4.2.1 Tubing. Teflon, 6.4 mm outside diameter, to connect bag to gas chromatograph sample loop. A new unused piece is employed for each series of bag samples that constitutes an emission test, and is to be discarded upon conclusion of analysis of those bags.

4.3 Analysis.

4.3.1 Gas Chromatograph. With FID, potentiometric strip chart recorder and 1.0 to 2.0 ml heated sampling loop in automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1 ppm benzene that is at least as great as the average noise level. (Response is measured from the average value of the baseline to the maximum of the waveform, while standard operating conditions are in use.)

4.3.2 Chromatographic Column.

4.3.2.1 Benzene in the Presence of Aliphatics. Stainless Steel, 2.44 m x 3.2 mm, containing 10 percent TECP on 80/100 Chromosorb P AW.

4.3.2.2 Benzene With Separation of the Isomers of Xylene. Stainless steel, 1.83 m x 3.2 mm, containing 5 percent SP-1200/1.75 percent Bentone 34 on 100/120 Supelcoport.

4.3.3 Flow Meters (2). Rotameter type, 0 to 100 ml/min capacity.

4.3.4 Gas Regulators. For required gas cylinders.

4.3.5 Thermometer. Accurate to one degree centigrade, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump--Leak-free. Minimum capacity 100 ml/min.

4.3.8 Recorder. Strip chart type, optionally equipped with disc integrator or electronic integrator.

4.3.9 Planimeter. Optional, in place of disc or electronic integrator, for 4.3.8 to measure chromatograph peak areas.

4.4 Calibration. 4.4.2 through 4.4.6 are for section 7.1 which is optional.

4.4.1 Tubing. Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar or Aluminized Mylar Bags. 50-liter capacity, with valve; separate bag marked for each calibration concentration.

4.4.3 Syringe. 1.0 μ l, gas tight, individually calibrated, to dispense liquid benzene.

4.4.4 Syringe. 10 μ l, gas tight, individually calibrated, to dispense liquid benzene.

4.4.5 Dry Gas Meter, With Temperature and Pressure Gauges. Accurate to ± 2 percent, to meter nitrogen in preparation of standard gas mixtures.

4.4.6 Midget Impinger/Hot Plate Assembly. To vaporize benzene.

5. Reagents

It is necessary that all reagents be of chromatographic grade.

5.1 Analysis.

5.1.1 Helium Gas or Nitrogen Gas. Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen Gas. Zero grade.

5.1.3 Oxygen Gas or Air as Required by the Detector. Zero grade.

5.2 Calibration. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Benzene, 99 Mol percent pure benzene certified by the manufacturer to contain a minimum of 99 Mol percent benzene; for use in the preparation of standard gas mixtures as described in Section 7.1.

5.2.2 Nitrogen Gas. Zero grade, for preparation of standard gas mixtures as described in Section 7.1.

5.2.3 Cylinder Standards (3). Gas mixture standards (50, 10, and 5 ppm benzene in nitrogen cylinders) for which the gas composition has been certified with an accuracy of ± 3 percent or better by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change greater than ± 5 percent from the certified value. The date of gas cylinder preparation, certified benzene concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards may be directly used to prepare a chromatograph calibration curve as described in Section 7.3.

5.2.3.1 Cylinder Standards Certification. The concentration of benzene in nitrogen in each cylinder must have been certified by the manufacturer by a direct analysis of each cylinder using an analytical procedure that the manufacturer had calibrated on the day of cylinder analysis. The calibration of the analytical procedure shall, as a minimum, have utilized a three-point calibration curve. It is recommended that the manufacturer maintain two calibration standards and use these standards in the following way: (1) a high concentration standard (between 50 and 100 ppm) for preparation of a calibration curve by an appropriate dilution technique; (2) a low concentration standard (between 5 and 10 ppm) for verification of the dilution technique used.

5.2.3.2 Establishment and Verification of Calibration Standards. The concentration of each calibration standard must have been established by the manufacturer using reliable procedures. Additionally, each calibration standard must have been verified by the manufacturer by one of the following procedures, and the agreement between the initially determined concentration value and the verification concentration value must be within ± 5 percent: (1) verification value determined by comparison with a gas mixture prepared in accordance with the procedure described in section 7.1 and using 99 Mol percent benzene, or (2) verification value obtained by having the calibration standard analyzed by the National Bureau of Standards. All calibration standards must be renewed on a time interval consistent with the shelf life of the cylinder standards sold.

6. Procedure

6.1 Sampling. Assemble the sample train as in Figure 1. Perform a bag leak check according to section 7.4. Determine that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow of 0.5 lpm. After a period of time sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate constant. Direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

6.2 Sample Storage. Sample bags must be kept out of direct sunlight. Analysis must be performed within 24 hours of sample collection.

6.3 Sample Recovery. With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to withdraw gas from the bag through the sample loop. Plumb the equipment so the sample gas passes from the sample valve to the leak-free pump, and then to a charcoal tube, followed by a 0-100 ml/min rotameter with flow control valve.

6.4 Analysis. Set the column temperature to 80°C for column A or 75°C for column B, the detector temperature to 225°C, and the sample loop temperature to 70°C. When optimum hydrogen and oxygen flow rates have

been determined, verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 20 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. Record the laboratory pressure. From the chart, note the peak having the retention time corresponding to benzene, as determined in section 7.2. Measure the benzene peak area, A_m , by use of a disc integrator or a planimeter. Record A_m and the retention time. Repeat the injection at least two times or until two consecutive values for the total area of the benzene peak do not vary more than 5 percent. The average value for these two total areas will be used to compute the bag concentration.

6.5 Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag. (Assume the relative humidity to be 100 percent unless a lesser value is known.)

7. Calibration and Standards

7.1 Preparation of Benzene Standard Gas Mixtures. (Optional-- delete if cylinder standards are used.) Assemble the apparatus shown

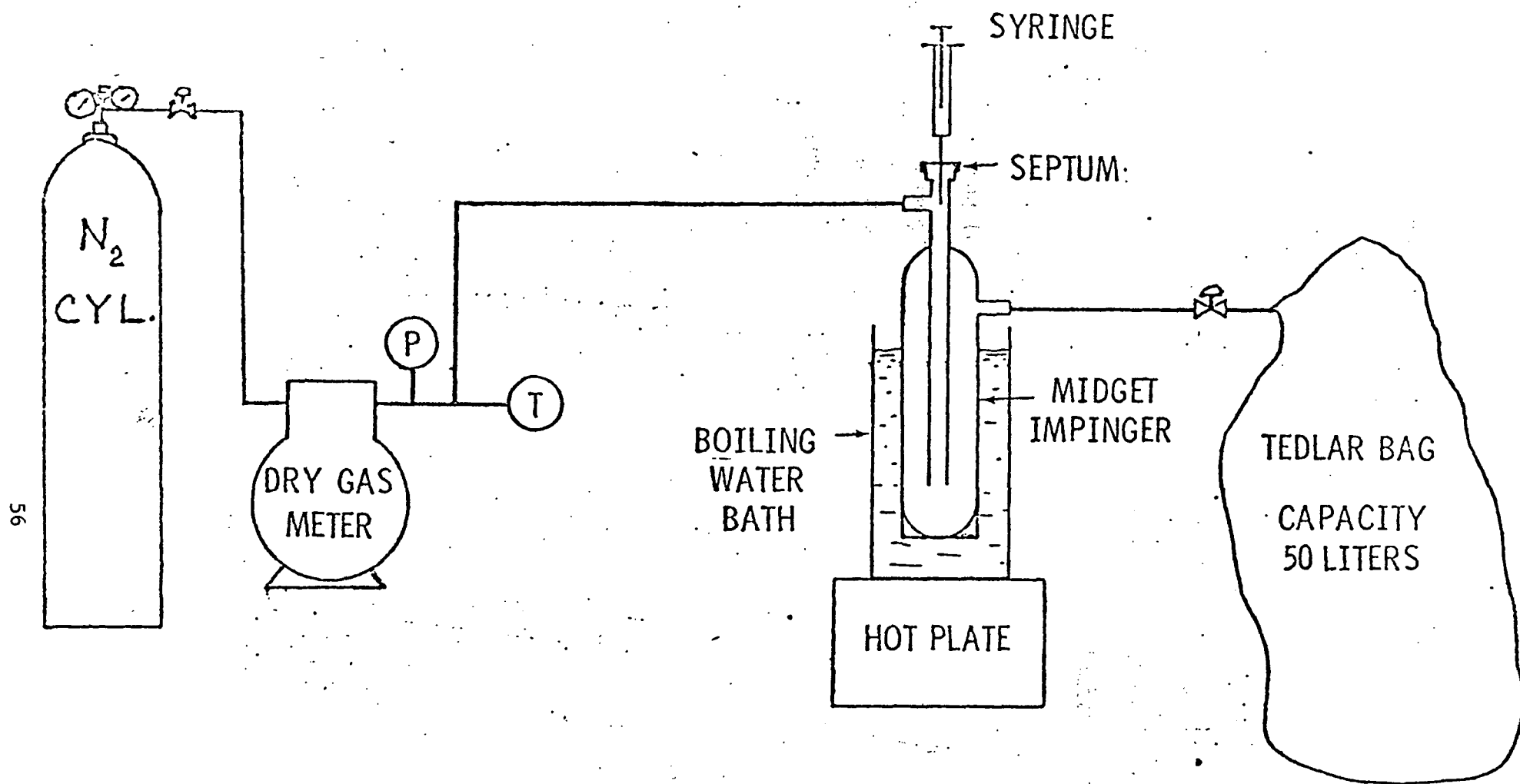


FIGURE 2. PREPARATION OF BENZENE STANDARDS
(optional)

Record the injection time. Select the peak that corresponds to benzene. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity, divided by the chart speed, is defined as the benzene peak retention time. Since it is quite likely that there will be other organics present in the sample, it is very important that positive identification of the benzene peak be made.

7.3 Preparation of Chromatograph Calibration Curve. Make a gas chromatographic measurement of each standard gas mixture (described in section 5.2.3 or 7.1) using conditions identical with those listed in sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with one of the standard gas mixtures and activate the sample valve. Record C_c , the concentration of benzene injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_c , the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two values vs C_c . When the other standard gas mixtures have been similarly analyzed and plotted, draw a smooth curve through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

7.4 Bag Leak Checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows: to leak check, connect a water manometer and pressurize the

in Figure 2. Evacuate a 50-liter Tedlar or aluminized Mylar bag that has passed a leak check (described in Section 7.4) and meter in about 50 liters of nitrogen. Measure the barometric pressure, the relative pressure at the dry gas meter, and the temperature at the dry gas meter. While the bag is filling use the 10 μ l syringe to inject 10 μ l of 99 + percent benzene through the septum on top of the impinger. This gives a concentration of approximately 50 ppm of benzene. In a like manner, use the other syringe to prepare dilutions having approximately 10 and 5 ppm benzene concentrations. To calculate the specific concentrations, refer to section 8.1. These gas mixture standards may be used for four days from the date of preparation, after which time preparation of new gas mixtures is required. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

7.2 Determination of Benzene Retention Time. This section can be performed simultaneously with section 7.3. Establish chromatograph conditions identical with those in section 6.3, above. Determine proper attenuator position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of benzene. Maintain conditions, with the equipment plumbing arranged identically to section 6.3, and flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the benzene calibration mixtures and activate the sample valve.

bag to 5-10 cm H₂O (2-4 in. H₂O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: an alternative leak check method is to pressurize the bag to 5-10 cm H₂O or 2-4 in. H₂O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. Calculations

8.1 Optional Benzene Standards Concentrations. Calculate each benzene standard concentration prepared in accordance with section 7.1 as follows:

$$C_c = \frac{X(.8787 \text{ mg}) \frac{10^3 \mu\text{g}}{\text{mg}} \frac{\mu\text{g} \cdot \text{mole}}{78.11 \mu\text{g}} \frac{24.055 \mu\text{l}}{\mu\text{g} \cdot \text{mole}} 10^6}{Y \frac{10^6 \mu\text{l}}{1} \frac{293}{T_m} \frac{P_m}{760}}$$

$$= \frac{X (270.6)}{Y \frac{293}{T_m} \frac{P_m}{760}} \quad \text{Equation 1}$$

where:

- C_c = The benzene standard concentration.
- X = The number of μl of benzene injected.
- Y = The dry gas meter reading in liters.
- P_m = The absolute pressure of the dry gas meter, mm Hg.
- T_m = The absolute temperature of the dry gas meter, °A.
- .8787 = The density of benzene at 293°A.

78.11 = The molecular weight of benzene.

24.055 = Ideal gas at 293°A, 760 mm Hg.

10^6 = Conversion factor, ppm.

8.2 Benzene Sample Concentrations. From the calibration curve described in section 7.3, above, select the value of C_c that corresponds to A_c . Calculate C_s as follows:

$$C_s = \frac{C_c P_r T_i}{P_i T_r (1 - B_{wb})} \quad \text{Equation 2}$$

where:

B_{wb} = The water vapor content of the bag sample, as analyzed.

C_s = The concentration of benzene in the sample in ppm.

C_c = The concentration of benzene indicated by the gas chromatograph, in ppm.

P_r = The reference pressure, the laboratory pressure recorded during calibration, mm Hg.

T_i = The sample loop temperature on the absolute scale at the time of analysis, °A.

P_i = The laboratory pressure at time of analysis, mm Hg.

T_r = The reference temperature, the sample loop temperature recorded during calibration, °A.

APPENDIX E

LAAPCD TOTAL ORGANIC ACIDS METHOD

5.4.2 ORGANIC ACIDS

5.4.2.1 METHOD SUMMARY

The only collection method used by the APCD for organic acids is continuous sampling with an impinger absorption train. The procedure entails the collection of the sample by bubbling the gases through dilute caustic followed by acidification and ether extraction of the free organic acids. A liquid-liquid extractor is used to provide multiple contact of ether and aqueous media. The organic acids in ether are subsequently titrated with a standard base and reported as acetic acid. The lower limit of the method is about 0.2 ppm in a 60 cubic foot sample.

Aliquot portions of the impinger solution can also be analyzed for total oxides of sulfur (see Sect.5.4.7).

5.4.2.2 PREPARATION FOR SAMPLING

The collection train is assembled as shown in Figure 5.1. The first two impingers each contain exactly 100 ml of 5% sodium hydroxide solution, while the third is operated dry to catch any carry-over spray and to protect the gas meter. An ice bath is used to cool the impingers. Glass, quartz-composition, or stainless steel sampling probes of any convenient size may be used. All equipment is tested for proper operation and freedom from leaks.

5.4.2.3 SAMPLING

Any convenient sampling rate, not to exceed 1 cfm, may be used. *Proportional sampling*, as described in Section 5.2.1, may be necessary when there are wide fluctuations in both gas flow rate and composition.

The data recorded during sampling should include:

- a) Time (clock) of test and data recordings
- b) Gas meter reading (initial), cubic feet
- c) Gas meter vacuum, inches of mercury below atmospheric
- d) Gas meter temperature, degrees Fahrenheit
- e) Temperature of gas at exit of third impinger, degrees Fahrenheit.

Readings may be taken at five- or ten-minute intervals during a one-hour test, and the data are recorded as indicated on the upper tabular portion of Figure 4.9. Sampling for particulate matter usually accompanies this procedure; if this is not the case, *reference point velocity* head and temperature readings should be made, as described in Section 3.3.2.

At the completion of sampling, the pump is shut off and the train allowed to come to atmospheric pressure before disconnecting the vacuum line. The final gas meter reading is

recorded. The impingers and associated tubing are suitably sealed for transfer to the laboratory for processing. Condensate, if any, in the probe and inlet tubing is allowed to flow into the first impinger.

5.4.2.4 SAMPLE PROCESSING

The total volume of liquid contained in the impingers is carefully measured. The difference from the initial volume is recorded as the condensate volume.

The impingers and associated tubing are carefully rinsed with small portions of distilled water, the liquid and washings being kept in a beaker or flask. If aliquots are to be taken for analysis, the combined liquid and washings are made up to an exact volume. Aliquots can be taken if the organic acids exceed 50 ppm by volume.

5.4.2.5 ANALYTICAL PROCEDURE

The reagents needed for the analysis are concentrated sulfuric acid, reagent-grade ethyl ether, and 0.1 N sodium hydroxide solution. The 0.1 N sodium hydroxide solution should be prepared and stored in a manner to avoid contamination by atmospheric carbon dioxide. The solution is standardized by titration using potassium biphthalate (primary-standard grade) and phenolphthalein indicator.

The liquid-liquid extractor (Item No. 92232, Corning Glass Works, Corning, New York, or equivalent) and water heating bath are shown disassembled in Figure 5.5. The procedure for each sample is as follows:

An 80-100 ml aliquot of the solution is transferred to a 500-ml three-neck glass flask equipped with a reflux condenser, separatory funnel, and gas inlet tube. The latter should project below the level of the liquid in the flask. Four drops of methyl red indicator are added and the sample is acidified by addition

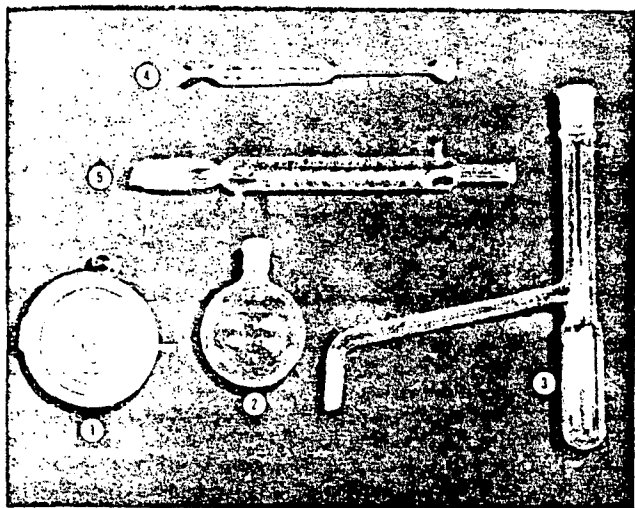


FIGURE 5.5. Equipment used for extraction of organic acids. Equipment shown is (1) steam bath; (2) round bottom flask; (3) extractor; (4) inner collector tube; (5) condenser.

of concentrated sulfuric acid from the separatory funnel. During acidification, the sample is agitated by intermittent bubbling of nitrogen into the flask. After acidification, nitrogen is bubbled through the sample until sulfur dioxide ceases to evolve from the condenser (determined by holding wet litmus test paper strips at the top of the condenser). The sample is now heated just to the boiling point to ensure complete removal of SO_2 . The sample is allowed to cool and the condenser is rinsed with water into the flask. The sample is transferred to a volumetric flask and diluted to a suitable exact volume. Fifty ml aliquots are transferred to 150-ml beakers and adjusted to pH 2 (pH paper) with 30% sodium hydroxide solution. A blank containing the same amount of original sodium hydroxide as the aliquots is adjusted to pH 2 with concentrated sulfuric acid and is analyzed with the aliquot samples.

Transfer the sample and blank mixtures to separate 500-ml liquid-liquid extractors. A long-stemmed funnel is useful for making the transfers. The final aqueous levels should be 3 or 4 inches below the side arms. Carefully insert the inner collector tubes, and attach

the condensers and 500-ml round bottom flasks. Slowly add ether through the condensers, allowing it to rise in the extractors. Continue adding ether until about 200 ml has overflowed into the flasks. Heat the flasks to steady boiling on water baths or with Glass-Col heating mantles, and allow the extractions to proceed for 8 hours.

After the flasks have cooled, tilt the extractors to allow as much as possible of the ether to decant over into the flasks without removing any aqueous material. Transfer the ether extracts to separatory funnels and remove any traces of aqueous material that may be present. Add about 40 ml of water and 3 drops of phenolphthalein indicator to each of the ether solutions in the separatory funnels. Titrate the mixtures in the funnels with standard 0.1 N sodium hydroxide to the phenolphthalein end point. As the end point is approached, stopper the separatory funnels and shake with each small titration increment until a pink color persists.

5.4.2.6 CALCULATIONS

The sequence of calculations, using the data obtained during sampling, processing, and analysis, is as follows:

- a) Volume of stack gas sampled
- b) Organic acid concentration
- c) Emission rate of organic acids
- d) Water vapor content of stack gas

The APCD forms shown in Figures 4.9 and 4.13 are convenient for many of the calculations to be described.

5.4.2.6.1 Sample Volume

The volume of stack gas sampled is calculated in the same manner as described for ammonia (Sect. 5.4.1.6.1). It may be noted that a slight error occurs in the sample volume calculation when stack gases containing moderate amounts of carbon dioxide are sampled with absorption trains containing sodium hydroxide

solution. The alkali will react with the carbon dioxide, forming water, sodium carbonate, and possibly some bicarbonate. The pH of the resulting solution is still high enough, however, for efficient absorption of oxides of sulfur, organic acids, or fluorides. As a result of this reaction, the measured condensate volume will be high due to production of water, and the metered gas volume will be low due to loss of a small volume of carbon dioxide from the gas sample. These two small errors will tend to cancel each other for calculation of total sample volume.

5.4.2.6.2. Concentration

The weight of organic acids (expressed as acetic acid) collected by the sampling train is given by

$$W_{OA} = 0.0601fn(v_s - v_b) \quad (5.7)$$

where,

W_{OA} = weight of organic acids, grams

f = aliquot factor: the ratio of total solution volume to aliquot volume

n = exact normality of 0.1 N sodium hydroxide

v_s = volume of 0.1 N sodium hydroxide used for the sample titration, milliliters

v_b = volume of 0.1 N sodium hydroxide used for the blank titration, milliliters

The concentration of organic acids in the gas sample is given by the two relations,

$$C_{OA} = 15.53 \frac{W_{OA}}{V_T} \quad (5.8)$$

$$c_{OA} = 13,900 \frac{W_{OA}}{V_T} \quad (5.9)$$

where,

C_{OA} = concentration of organic acids (as acetic acid), grains per standard foot

c_{OA} = concentration of organic acids, parts per million by volume

V_T = volume of stack gas sampled, from Equation 4.9, standard cubic feet

Although weight-volume concentrations (Eq. 5.8) require that some particular acid such as acetic be used as a basis, volume-volume concen-

trations (Eq. 5.9) will be the same for any monocarboxylic acid.

5.4.2.6.3 Emission Rate

The emission rate of organic acids at the sampling station location is given by either of the two relations,

$$M_{OA} = 0.00857 C_{OA} Q \quad (5.10)$$

or

$$M_{OA} = 9.52 \times 10^{-6} c_{OA} Q \quad (5.11)$$

where,

M_{OA} = emission rate of organic acids, pounds per hour

C_{OA} = concentration, from Equation 5.8, grains per standard cubic foot

c_{OA} = concentration, from Equation 5.9, parts per million by volume

Q = stack gas flow rate, from Equation 3.12, standard cubic feet per minute

5.4.2.6.4 Moisture Content

The water vapor content of the stack gases is calculated by the procedure described in Section 4.4.1.8.3. The calculation is made only for comparison with the results from the particulate train processing. The difference is due to errors in condensate volume and water vapor volume calculations, caused by chemical reactions during absorption and the lowered vapor pressure (relative to pure water) of the absorbent solution. Both effects mentioned will produce small positive errors in calculation of water vapor content.

APPENDIX F

LAAPCD ALDEHYDES AND FORMALDEHYDE METHODS

5.4.3 ALDEHYDES

5.4.3.1 METHOD SUMMARY

In practically all tests, samples for aldehyde analysis are collected in evacuated flasks, using grab sampling techniques (Sect. 5.3.2). In rare instances, impinger absorption trains have been used, but this collection method is more applicable to the low aldehyde

concentrations experienced in atmospheric monitoring.

In either case, aldehydes in the sample react with a solution of sodium bisulfite to form addition compounds. The excess bisulfite ion is destroyed with iodine solution. By adjusting the pH of the solution, the addition compounds are decomposed, freeing bisulfite ion equivalent to the aldehydes present in the sample. The liberated bisulfite ion is then titrated with standard iodine. Methyl ketones, if present in the sample, will be included in the results. The lower limit of the method, using 2-liter gas samples, is about 1 ppm.

Since the collection methods are identical, aliquot portions of the solutions can be analyzed for formaldehyde alone (Sect. 5.4.4).

5.4.3.2 PREPARATION FOR SAMPLING

Two-liter round bottom flasks, as shown in Figure 5.2, are used for grab sampling. Ten ml of 1% sodium bisulfite solution (1g per 100 ml solution) are added to each flask. The flask is then evacuated to the vapor pressure of the solution, the screw clamp closed, and the solid glass plug inserted into the open end of the tubing until ready for sampling.

For continuous sampling by impingers, the collection train is prepared as described for ammonia or organic acids, adding exactly 100 ml of 1% sodium bisulfite solution to each of the first two impingers.

5.4.3.3 SAMPLING

The inlet tube of the 2-liter flask is connected to one leg of a glass tee or three-way stopcock attached to the sampling line. An aspirator bulb, connected to the other leg of the tee, is used for flushing the sample probe and tubing with stack gas just prior to sampling, as illustrated in Figure 5.6. The



FIGURE 5.6. Grab sampling of a gas stream.

screw clamp is opened to admit gas to the evacuated flask. When the flow of gas has ceased, the screw clamp is closed and the glass plug reinserted into the short rubber tube to the flask. The flow of gas may continue for many minutes when the gases are almost 100 per cent steam, thus requiring the flask to be cooled during this process. Such a situation may be encountered, for example, when testing rendering cookers. The procedure in Section 5.5.3 should then be followed for calculations. In order to obtain an average value, four grab samples are usually taken during an hour test.

When absorption impinger trains are used, the sampling procedure is the same as described for organic acids. The sampling rate should not exceed 0.3 cfm.

5.4.3.4 SAMPLE PROCESSING

The sealed collection flasks are shaken for 15 minutes on a mechanical shaker, with frequent rotation to provide a thorough scrubbing action. The temperature and absolute gas pressure in each flask are recorded after the gases have reached ambient temperature. The contents of each sample flask are then rinsed

into conical flasks. A blank is prepared, using the same amount of 1% sodium bisulfite solution used for each sampling flask.

The impinger train collection is processed in a manner analogous to that described for organic acids in Section 5.4.2.4. Unless the aldehyde concentration is very low (below 0.1 ppm), aliquots may be taken for analysis.

5.4.3.5 ANALYTICAL PROCEDURE

The analytical procedure is identical for samples collected either by grab or absorption train sampling.

The reagents needed for the analysis are 0.05 N sodium thiosulfate solution, 0.005 N iodine solution, approximately 0.1 N iodine solution (made by dissolving 12.7 g of iodine in a solution of 25 g of potassium iodide in 50 ml of water, and diluting to one liter with water), and a special buffer solution. The sodium thiosulfate solution is standardized with potassium dichromate (primary-standard grade) according to standard iodometric procedure. The 0.005 N iodine solution, prepared by dilution from the 0.1 N solution, is standardized by titration with the sodium thiosulfate solution using starch indicator. The buffer solution is prepared by dissolving 80 g of anhydrous sodium carbonate in 500 ml of water, slowly adding 20 ml of glacial acetic acid, followed by dilution to 1 l. The pH of the solution is adjusted to 9.6 ± 0.1 with sodium carbonate or acetic acid, as required, using a pH meter.

Two ml of 1% starch indicator solution are added to each sample, and 0.1 N iodine is added dropwise until a dark blue color is produced. Care should be taken to ensure that all of the sulfur dioxide resulting from the decomposition of bisulfite is removed since it may cause the end point to fade. This can be con-

veniently accomplished by blowing a small jet of air into the flask while swirling the contents vigorously for several minutes. Each solution is decolorized by dropwise addition of 0.05 N sodium thiosulfate. The 0.005 N iodine solution is added, to a faint blue end point. The solutions are cooled thoroughly in an ice bath, and 50 ml of chilled buffer are added to each flask. The flasks are kept in the ice bath for 10 to 15 minutes after the buffer addition. The liberated bisulfite is titrated with 0.005 N iodine solution to the same faint blue end point present before addition of the buffer. The sample must remain chilled in order to avoid a fading end point.

5.4.3.6 CALCULATIONS: IMPINGER TRAIN SAMPLES

The sequence of calculations for aldehyde samples collected by impinger trains is as follows:

- a) Volume of stack gas sampled
- b) Aldehyde concentration
- c) Emission rate of aldehydes

5.4.3.6.1 Sample Volume

The calculations for the volume of stack gas sampled are made in the same manner as described previously, in Section 5.4.1.6, for ammonia.

5.4.3.6.2 Concentration

The weight of aldehydes, expressed as formaldehyde, collected by the impinger train is given by the expression

$$W_{\text{ALD}} = 0.015fn(v_s - v_b) \quad , \quad (5.12)$$

where,

- W_{ALD} = weight of aldehydes collected, grams
 f = aliquot factor: ratio of total solution volume to aliquot volume
 n = exact normality of the 0.005 N iodine solution

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v_s = volume of 0.005 N iodine solution used for sample titration following the addition of the buffer solution, milliliters

v_b = volume of 0.005 N iodine solution used for blank titration, milliliters

The concentration of aldehydes in the gas sample is given by the two relations,

$$C_{ALD} = 15.43 \frac{W_{ALD}}{V_T} \quad (5.13)$$

and

$$C_{ALD} = 27,800 \frac{W_{ALD}}{V_T} \quad (5.14)$$

where,

C_{ALD} = concentration of aldehydes (as formaldehyde), grains per standard cubic foot

C_{ALD} = concentration of aldehydes, parts per million by volume

V_T = total sampled volume, from Equation 4.9, standard cubic feet

Unlike weight-volume concentration, volume-volume concentrations will be the same for any aldehyde or methyl ketone having one carbonyl group per molecule.

5.4.3.6.3 Emission Rate

The emission rate, or mass flow rate, of aldehydes at the sampling station location is given by either of the two relations,

$$M_{ALD} = 0.00857 C_{ALD} Q \quad (5.15)$$

or

$$M_{ALD} = 4.75 \times 10^{-6} C_{ALD} Q \quad (5.16)$$

where,

M_{ALD} = emission rate of aldehydes, pounds per hour

C_{ALD} = concentration, from Equation 5.13, grains per standard cubic foot

C_{ALD} = concentration, from Equation 5.14, parts per million by volume

Q = stack gas flow rate, from Equation 3.12, standard cubic feet per minute

5.4.3.7 CALCULATIONS: GRAB SAMPLES

The sequence of calculations for aldehyde samples collected with evacuated flasks is as follows:

- a) Volume of stack gas sampled, dry basis
- b) Aldehyde concentration, dry basis
- c) Aldehyde concentration, stack conditions
- d) Emission rate of aldehydes

5.4.3.7.1 Sample Volume

The dry volume of stack gas sampled is calculated as follows:

$$V_{dg} = \frac{V_f(P_f - P_{H_2O})520}{760 T_f} = 0.685 \frac{V_f(P_f - P_{H_2O})}{T_f} \quad (5.17)$$

where,

V_{dg} = volume of dry stack gas sampled, liters at standard conditions (60 F, 14.7 psia)

V_f = volume of sampling flask, less volume of absorbent solution, liters

P_f = absolute pressure in flask, millimeters of mercury

P_{H_2O} = vapor pressure of water at temperature T_f , millimeters of mercury

T_f = temperature in flask, degrees Rankine

Volumes of the grab samples are not converted to the stack basis (i.e., actual volume of stack gas sampled) because moisture content data for each grab sample of stack gas are not usually available. As a matter of fact, the

excess moisture in the stack gases, precipitated upon cooling in the flask, is usually negligible in comparison with the absorbent solution. Thus, moisture calculations from measurements of the condensate, as done for impinger trains, are not made. An exception does, however, occur when sampling steam (see Sect. 5.5.3).

5.4.3.7.2 Concentration

The aldehyde concentrations are calculated and reported in two ways: (1) on a dry basis; and (2) on a *wet* basis, or under actual stack water vapor conditions.

The calculation of aldehyde concentration on a dry basis uses the relation,

$$(c_{\text{ALD}})_d = \frac{11.85 \times 10^3 n(v_s - v_b)}{V_{dg}}, \quad (5.18)$$

where,

$(c_{\text{ALD}})_d$ = concentration of aldehydes, dry basis, parts per million by volume

n = exact normality of the 0.005 N iodine solution

v_s = volume of 0.005 N iodine solution used for the sample titration following the addition of the buffer solution, milliliters

v_b = volume of 0.005 N iodine solution used for the blank titration, milliliters

V_{dg} = dry volume of gas sample, from Equation 5.17, standard liters

In order to convert concentrations from the dry basis to stack water vapor conditions (sometimes called the *wet* basis), the following relation is used:

$$c_{\text{ALD}} = (c_{\text{ALD}})_d \frac{(100 - \text{W.V.})}{100}, \quad (5.19)$$

where,

c_{ALD} = concentration of aldehydes, at stack conditions, parts per million by volume

$(c_{\text{ALD}})_d$ = concentration of aldehydes, dry basis from Equation 5.18, parts per million by volume

W.V. = water vapor content of stack gas, per cent by volume

It may be noted that this is identical to the concentration defined by Equation 5.14.

The water vapor content of the stack gas is usually determined from the data obtained when sampling and processing the collection train or trains for particulate matter. In other instances, it may be determined with a condensate sampling train, or by dry-wet bulb thermometry, as described in Section 5.5.

The concentrations may be converted from volume-volume to weight-volume units using the conversion

$$C_{\text{ALD}} = 0.000554 c_{\text{ALD}}, \quad (5.20)$$

where,

C_{ALD} = concentration of aldehydes, expressed as formaldehyde, grains per standard cubic foot

5.4.3.7.3 Emission Rate

The emission rate, or mass flow rate, of aldehydes at the sampling station location is given by either of the two relations,

$$M_{\text{ALD}} = 0.00857 C_{\text{ALD}} Q, \quad (5.21)$$

or

$$M_{\text{ALD}} = 4.75 \times 10^{-6} c_{\text{ALD}} Q, \quad (5.22)$$

where,

M_{ALD} = emission rate of aldehydes, as formaldehyde, pounds per hour

C_{ALD} = concentration, from Equation 5.20, grains per standard cubic foot

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C_{ALD} = concentration, from Equation 5.19,
parts per million by volume

Q = stack gas flow rate, from Equation
3.12, standard cubic feet per minute

5.4.4 FORMALDEHYDE

5.4.4.1 METHOD SUMMARY

The methods of sample collection and processing prior to analysis are identical to those described for aldehydes. The samples are collected in a dilute solution of sodium bisulfite. Any aldehydes present form the bisulfite addition compounds. An aliquot of the resultant solution is then treated with chromotropic acid in strong sulfuric acid. Formaldehyde forms a unique colored compound, the exact nature of which is unknown but which appears to be of a quinoidal type. The intensity of the colored compound is then determined in a colorimeter and the corresponding concentration of formaldehyde read from a calibration curve. The lower limit of the method, using 2-liter gas samples, is about 1 ppm.

Two-liter round bottom flasks, prepared in the same manner as described for aldehydes, are used for sampling. Sampling and processing of the flasks and collected samples also are the same as described for aldehydes, except that the solutions from each flask are measured to an exact volume, which should be as small as possible.

5.4.4.2 PREPARATION OF REAGENTS

The special reagents needed for the analysis are 0.05 N sodium thiosulfate solution, approximately 0.1 N iodine solution, 0.005 N iodine solution, buffer solution, standard formaldehyde solution, 76% sulfuric acid solution, and chromotropic acid reagent.

The sodium thiosulfate, iodine, and buffer solutions are prepared and standardized as

described for aldehydes; the other solutions are prepared and standardized as follows:

Standard formaldehyde solution: Dilute 3 ml of formalin (approximately 37%) to 1 l in a volumetric flask. To standardize, pipet 1 ml of the solution into a 250-ml Erlenmeyer flask, and 1 ml of water into another flask as a blank. Add 30 ml of 1% sodium bisulfite and 2 ml of 1% starch to each flask. Add 0.1 N iodine dropwise to each flask until a dark blue color results. Decolorize each flask with 0.05 N sodium thiosulfate and then return to a faint blue with 0.005 N iodine. Chill each flask in an ice bath and add 50 ml of chilled buffer. After addition of the buffer, allow to stand in the ice bath for 10 to 15 minutes, then titrate the liberated bisulfite in each flask to the same faint blue end point with 0.005 N iodine. Subtract the volume of 0.005 N iodine used for the blank determination from the volume used for the sample determination. The strength of the standard in micrograms per milliliter is $1.5 \times 10^4 vn$, where v is the volume, in milliliters, of 0.005 N iodine used for titration following the addition of buffer, less blank; and n is the exact normality of the 0.005 N iodine.

Dilute 1 ml of this standard formaldehyde solution to 1 l. The diluted solution contains approximately $1.2 \mu\text{g}$ of formaldehyde per ml.

76% sulfuric acid: Slowly add 725 ml of concentrated sulfuric acid to 350 ml of water. It is advisable to place the container in which the dilution is to be made in a water bath to absorb some of the heat generated.

Chromotropic acid reagent: Weigh 0.875 g of 4,5-dihydroxy-2,7-naphthalenedisulfonic acid, disodium salt (Eastman No. P230 or equivalent) into a 100-ml beaker and add 4.25 ml of water. Rapidly add 45.75 ml of 76% sulfuric acid and stir to dissolve. Prepare fresh for

each day's analyses because this reagent decomposes on standing. The final mixture contains approximately 71% sulfuric acid by weight.

Prepare a calibration curve for each new bottle of chromotropic acid as follows: Transfer 50 ml of 76% sulfuric acid, by means of a graduate, to each of a series of six 150-ml beakers. Warm the solutions in a water bath to 60 ± 2 C. Add 2 ml of chromotropic acid reagent to each beaker. Pipet 1 ml of the 1.2 μg per ml standard formaldehyde solution and 4 ml of water into the first beaker, 2 ml of the 1.2 μg per ml standard and 3 ml of water into the second, 3 ml of the 1.2 μg per ml standard and 2 ml of water into the third, 4 ml of the 1.2 μg per ml standard and 1 ml of water into the fourth, 5 ml of the 1.2 μg per ml standard into the fifth. The beakers will then contain approximately 1.2, 2.4, 3.6, 4.8, and 6.0 μg of formaldehyde per 5-ml aliquot, respectively. Run a blank by adding 5 ml of water to the sixth beaker containing chromotropic acid. Stir the solutions frequently and maintain at the specified temperature for 20 minutes. The color reaction is, in part, dependent upon the time in the bath and, to a lesser extent, upon the time required before making the colorimeter reading. Hence, the sequence of events is critical. Likewise the solution temperature must be closely controlled. At the end of 20 minutes in the water bath, immerse the beakers in ice water. This procedure impedes the color development somewhat. Rapidly transfer to the colorimeter cell for reading. Measure the light absorption of the solutions in the photoelectric colorimeter (a Klett-Summerson industrial colorimeter, No. 54, or equivalent) with a 500- to 560-m μ green filter and a 20 mm light path. Use the blank solution for zeroing the colorimeter. Prepare a calibration curve by plotting the colorimeter readings against micro-

grams of formaldehyde contained in each solution.

5.4.4.3 ANALYTICAL PROCEDURES

Pour 50 ml of 76% sulfuric acid into each of two 150-ml beakers. Warm the solutions in a water bath to 60 ± 2 C. Add 2 ml of chromotropic acid reagent to each. Transfer a 5-ml aliquot of the sample by pipet to one beaker and 5 ml of water to the other for a blank determination. Stir the solutions frequently and maintain at the specified temperature for 20 minutes. At the end of 20 minutes, remove the beakers from the water bath and immerse them in ice water. Rapidly transfer to the colorimeter cells for reading. Measure the light absorption of the solutions in the photoelectric colorimeter with a 500- to 560-m μ green filter and a 20-mm light path. Use the blank for zeroing the colorimeter. Read the weight of formaldehyde in micrograms from the previously prepared calibration curve.

5.4.4.4 CALCULATIONS

The sequence of calculations for formaldehyde samples collected with evacuated flasks is as follows:

- a) Volume of stack gas sampled, dry basis
- b) Formaldehyde concentration, dry basis
- c) Formaldehyde concentration, stack conditions
- d) Emission rate of formaldehyde

The dry volume of stack gas sampled is calculated using Equation 5.17.

The formaldehyde concentration is calculated on a dry basis by the relationship,

$$(c_{FA})_d = 0.790 \frac{W_{FAf}}{V_{dg}}, \quad (5.23)$$

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where,

$(c_{FA})_d$ = formaldehyde concentration, dry basis, parts per million by volume

w_{FA} = weight of formaldehyde found in 5-ml aliquot of collection solution, micrograms

f = aliquot factor: ratio of total collection solution volume to 5-ml aliquot

V_{dg} = dry volume of gas sample, from Equation 5.17, standard liters

The conversion of formaldehyde concentration to stack moisture conditions is made using Equation 5.19 and 5.20, previously given for aldehydes. The conversion factors are identical, since total aldehydes are expressed as formaldehyde.

The emission rate of formaldehyde, as for aldehydes, is calculated by either Equation 5.21 or 5.22.