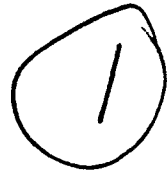


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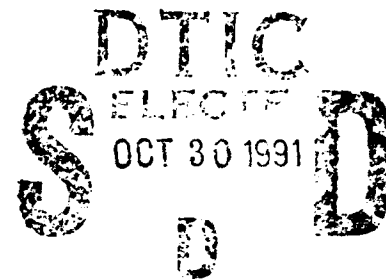
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**VOC EMISSION REDUCTION STUDY AT
THE HILL AIR FORCE BASE BUILDING 515
PAINTING FACILITY**

J. AYER, C. HYDE

**ACUREX CORPORATION
ENVIRONMENTAL SYSTEMS DIVISION
555 CLYDE AVENUE
P. O. BOX 7044
MOUNTAIN VIEW CA 94039**



SEPTEMBER 1990

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19 ABSTRACT (Continue on reverse if necessary and identify by block number) The goal of this project was to develop safe and cost-effective strategies for controlling volatile organic compound (VOC) emissions from Air Force painting facilities. To this end, a series of sampling and analysis tests were conducted to measure hazardous constituent compound concentrations in a typical crossdraft Air Force paint booth during painting; pollutant emission rates were simultaneously measured. Particulate, isocyanate, and VOC emission rates were measured in the booth exhaust; concentration profiles of these constituents within the booth were determined during painting. The results of these tests indicate that significant pollutant stratification occurs in the crossdraft booth during painting. Based on these results, a cost-effective means of controlling VOC emissions was developed in which the exhaust from the zone of the booth having the highest VOC concentrations is passed to an emission control device. The remainder is vented to the outside. This flow reduction/control technology requires the installation of a split-flow ventilation system, which separates the exhaust from the high-concentration zone from the remainder of the exhaust. An alternative cost-effective flow reduction/VOC control technology involving exhaust flow recirculation was proposed. Finally, the possibility of combining these two ventilation systems (split-flow and recirculation) was explored.					
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EXECUTIVE SUMMARY

A. OBJECTIVE

The objective of this project was to develop practical technologies for economically reducing volatile organic compound (VOC) emissions from typical Air Force painting operations. The painting facility selected for study is located in Building 515 at Hill Air Force Base, Utah. Practical and economical emission control technologies that may be used at this and other Air Force facilities were developed based on the results of in-booth and exhaust duct sampling for particulate and hazardous constituent concentrations.

B. BACKGROUND

Under the Clean Air Act and various state and local laws, organic solvents and coating compounds used in routine Air Force maintenance operations are subject to VOC emission regulations. Air Force installations are experiencing increased pressure from regulatory agencies to reduce organic compound emissions from painting and coating operations. The capital and operating costs associated with controlling emissions from such operations are a function of the exhaust gas flow rate passing through the control device. The goal of this program is to develop safe and cost-effective VOC emission control strategies.

C. SCOPE

To characterize the emission rate and distribution of hazardous compounds in the paint booth during painting operations, simultaneous air samples were taken in the exhaust duct and at 22 positions inside the booth. VOC, particulate, and isocyanate air samples were taken during normal operation of the painting facility. A solvent mass balance was performed in which VOC emission rates were compared to paint usage and analysis data to confirm measurement accuracy.

D. METHODOLOGY

Personal sampling pumps were suspended at 22 sampling positions in the paint booth during painting. To determine in-booth particulate concentrations, sample air was drawn through cellulose ester filters connected to the suspended sampling pumps, in accordance with National Institute of Occupational Safety and Health (NIOSH) Method 500. The filters were weighed several times before and after sampling to determine the quantity of particulate collected from the known sample volume. To determine particulate emission rates from the booth, isokinetic particulate samples were drawn from the exhaust duct according to Environmental Protection Agency (EPA) Method 5. For comparison, particulate samples were drawn from the duct using the NIOSH 500 method.

Integrated VOC concentration measurements were taken in the booth and exhaust duct by drawing sample air through NIOSH charcoal tubes, in general accordance with NIOSH

Method 1300. Organic constituents were adsorbed onto the charcoal, which was subsequently extracted with a solvent formulation developed specifically for this test series. The extract was analyzed with a gas chromatograph/flame ionization detector (GC/FID). Continuous (real-time) organic sampling was performed in the exhaust duct to determine VOC emission rates. Two continuous organic sampling methods were used for this test series: Bay Area Air Quality Management District (BAAQMD) Method ST-7 and EPA Method M25A. Method ST-7 specifies that sample air be drawn through a catalytic furnace, in which the organic constituents are oxidized to CO₂. The sample stream is then passed through a nondispersive infrared detector (NDIR), which monitors the CO₂ concentration. Method 25A specifies that the sample stream be passed through an FID, which measures organic concentrations directly.

Isocyanate concentrations in the booth and exhaust duct were measured according to Occupational Safety and Health Administration (OSHA) Method 42, which specifies that sample air be passed through chemically treated glass fiber filters. Isocyanates are collected on the filters, which are subsequently analyzed using high performance liquid chromatography (HPLC).

Airflow rates were measured in the booth using a calibrated hot wire anemometer and in the exhaust duct according to EPA Method 2 procedures. In addition, paint usage rates were determined by posting a crew member in the booth to monitor paint start and stop times and by weighing the paint-dispensing container before and after the painting cycle.

Volatile and semivolatile organic compound concentrations were measured in the water curtain sump water according to EPA Methods 8240 and 8270, respectively. The total organic carbon (TOC) and residue concentrations were monitored twice daily by collecting water samples and analyzing them according to EPA Methods 9060 and 160.3, respectively.

E. TEST DESCRIPTION

Operating parameters (i.e., flow rates and paint usage rates) were evaluated before and after each paint cycle; sampling was performed during painting. Each day, a different sampling protocol was used (i.e., VOC, particulate, and isocyanate sampling were performed on different days). Because there were two painting cycles per day, each sampling effort was performed in duplicate.

F. RESULTS

Except for areas directly in the path of the paint spray gun, the highest concentrations of hazardous constituent compounds were found in the lower strata of the booth, at 4 feet in height. Above 8 feet, nondetectable levels of hazardous compounds were found. Some of the highest VOC concentrations measured were near the painter. Metals, particulate, and isocyanate concentrations were also somewhat high in the vicinity of the painter; however, the highest concentrations were measured at ground level near the booth exhaust face. Occasionally, high concentrations of hazardous compounds were measured in singular isolated areas. It is

suspected that these high concentrations resulted from the painter inadvertently applying paint directly to the sample surface.

G. CONCLUSIONS

The concentration profiles obtained for the hazardous compounds present in the booth indicate that significant stratification occurs during painting. A system for decreasing the flow to a downstream VOC emission control device can be designed that takes advantage of this concentration stratification. Decreasing the flow rate to a VOC emission control device lowers associated control costs. The flow-reduction system proposed on the basis of the test results employs a split-flow exhaust process in which the exhaust stream from the lower zone of the booth (containing the highest concentrations) is vented to a VOC emission control device. The exhaust stream from the upper zone of the booth is vented to the outside. A system such as this can lower the flow rate to an emission control device by 50 percent or more and, at the same time, decrease VOC emissions by 70 percent or more.

Additional conclusions are that hazardous compound concentrations in the vicinity of the painter are higher than in other regions of the booth, and that concentrations of hazardous compounds measured in the exhaust duct are far below the permissible exposure limits (PELs) specified by OSHA. These results indicate that a recirculation system, in which a large portion of the exhaust air is recirculated back into the booth, can be safely adopted as an alternative means of decreasing the exhaust flow rate. In this system, the portion not recirculated is vented to an emission control device.

H. RECOMMENDATIONS

Emission reductions may be achieved through a number of possible system and process alterations. Some emission reductions can be achieved by replacing the two-part green primer currently used by the facility tested with a three-part, water-reducible primer that is in common use at other Air Force painting facilities.

Cost-effective VOC emission control can be realized by reducing the flow rate to an emission control device. This may be done by either employing a split-flow ventilation system as described above, or installing an exhaust air recirculation system. A third option combining these ventilation system modifications is perhaps the most environmentally sound and economical option.

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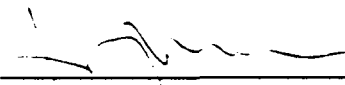
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This report summarizes work done between December 1988 and February 1990, under the direction of Dr. Dean Wolbach, Acurex Corporation. The EPA work assignment officer was Charles H. Darwin, Air and Energy Engineering Research Laboratory, Research Triangle Park, North Carolina. Mr. Surendra B. Joshi and Dr. Joseph D. Wander were the Air Force project officers for this contract.

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This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for public release.



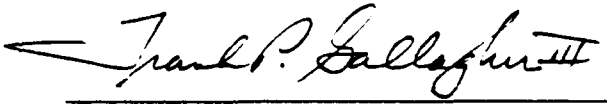
JOSEPH D. WANDER
Project Officer



F. THOMAS LUBOZYNSKI, Lt Col, USAF, BSC
Chief, Environics Division



WAYNE P. CHEPREN, Capt, USAF
Chief, Environmental Compliance
R&D Branch



FRANK P. GALLAGHER III, Col, USAF
Director, Engineering and Services
Laboratory

TABLE OF CONTENTS

SECTION I	INTRODUCTION	1
	A. OBJECTIVE	1
	B. BACKGROUND	1
	C. SCOPE/APPROACH	1
	D. SITE DESCRIPTION	2
SECTION II	SAMPLING LOCATIONS AND PROCEDURES	4
	A. SAMPLING LOCATIONS	4
	B. SAMPLING PROCEDURES	4
	1. Paint Sampling and Usage Rate Determination	4
	2. Integrated Air Sampling Procedures Used in the Booth ...	4
	3. Continuous Air Sampling Procedure Used in the Booth ..	8
	4. Water Curtain Sampling and Airflow Rate Measurements ..	8
	5. Exhaust Duct Sampling and Airflow Rate Measurements ..	9
SECTION III	TEST RESULTS AND DISCUSSION	11
	A. RESULTS OF PAINT ANALYSES AND USAGE MONITORING	11
	B. AIRFLOW RATE MEASUREMENTS	11
	C. AIRBORNE ORGANIC COMPOUND CONCENTRATION MEASUREMENTS	11
	1. In-Booth Measurement Results	11
	2. Exhaust Duct Measurements	28
	D. AIRBORNE PARTICULATE AND METALS CONCENTRATION MEASUREMENTS	39
	1. In-Booth Measurement Results	39
	2. Exhaust Duct Measurement Results	55
	E. AIRBORNE ISOCYANATE CONCENTRATION MEASUREMENTS	55
	1. In-Booth Measurement Results	55
	2. Exhaust Duct Measurement Results	57
	F. WATER ANALYSIS RESULTS	68
	G. MEASUREMENT OF WATER CURTAIN PARTICULATE AND ISOCYANATE REMOVAL EFFICIENCIES.	72
SECTION IV	EMISSION CONTROL CONCEPTS	75
	A. PROCESS AND EQUIPMENT CHANGE	75
	B. PAINT REFORMULATION	76
	C. ADD-ON VOC EMISSION CONTROL DEVICES	76

TABLE OF CONTENTS (Concluded)

	1. Types of Emission Control Devices	76
	2. Flow Reduction for Efficient Control Device Operation	77
SECTION V	ENGINEERING EVALUATION	79
	A. PAINT REFORMULATION	79
	1. Compatibility of Coating with Equipment	79
	2. Requirements for Substituting Low-Solvent Coatings	79
	3. Emissions Reductions Through Coating Substitution	80
	B. FLOW REDUCTION COMBINED WITH A VOC EMISSION CONTROL DEVICE	80
	1. Design Criteria for Building 515 Paint Booth Split-Flow Ventilation System	80
	2. Design Criteria for Building 515 Paint Booth Recirculation System	81
	3. Combined Recirculation/Split-Flow Ventilation System	85
SECTION VI	CONCLUSIONS AND RECOMMENDATIONS	88
	A. CONCLUSIONS	88
	B. RECOMMENDATIONS	88
	REFERENCES	89
APPENDICES		
A	QUALITY ASSURANCE/QUALITY CONTROL EVALUATION REPORT	91
B	SAMPLING METHODS USED IN THE HILL AIR FORCE BASE PAINT SPRAY BOOTH	111
C	OSHA RULING ON PAINT BOOTH EXHAUST GAS RECIRCULATION	161

LIST OF FIGURES

Figure	Title	Page
1	Schematics of Paint Spray Booth Located in Building 515, Hill Air Force Base, Utah	3
2	Sample Locations in the Building 515 Paint Spray Booth, Side View	5
3	Sample Locations in the Building 515 Paint Spray Booth, Plan View	6
4	Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 4 Feet from North Wall	18
5	Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 6 Feet from North Wall	18
6	Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 8 Feet from North Wall	19
7	Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 10 Feet from North Wall	19
8	Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 12 Feet from North Wall	20
9	Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Plan View at a Height of 4 Feet	20
10	Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Plan View at a Height of 9 Feet	21
11	Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 4 Feet from North Wall	24
12	Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 6 Feet from North Wall	24
13	Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 8 Feet from North Wall	25

LIST OF FIGURES (Continued)

Figure	Title	Page
14	Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 10 Feet from North Wall	25
15	Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 12 Feet from North Wall	26
16	Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Plan View at a Height of 4 Feet	26
17	Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Plan View at a Height of 9 Feet	27
18	Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 4 Feet from North Wall	45
19	Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 6 Feet from North Wall	45
20	Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 8 Feet from North Wall	46
21	Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 10 Feet from North Wall	46
22	Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 12 Feet from North Wall	47
23	Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Plan View at a Height of 4 Feet	47
24	Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Plan View at a Height of 9 Feet	48
25	Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 3, Side View, 4 Feet from North Wall	51
26	Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 3, Side View, 6 Feet from North Wall	51
27	Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 3, Side View, 8 Feet from North Wall	52

LIST OF FIGURES (Continued)

Figure	Title	Page
28	Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 3, Side View, 10 Feet from North Wall	52
29	Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 3, Side View, 12 Feet from North Wall	53
30	Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 3, Plan View at a Height of 4 Feet	53
31	Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 3, Plan View at a Height of 9 Feet	54
32	Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 4 Feet from North Wall	59
33	Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 6 Feet from North Wall	59
34	Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 8 Feet from North Wall	60
35	Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 10 Feet from North Wall	60
36	Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 12 Feet from North Wall	61
37	Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Plan View at a Height of 4 Feet	61
38	Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Plan View at a Height of 9 Feet	62
39	Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 4 Feet from North Wall	64
40	Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 6 Feet from North Wall	64
41	Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 8 Feet from North Wall	65
42	Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 10 Feet from North Wall	65
43	Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 12 Feet from North Wall	66

LIST OF FIGURES (Concluded)

Figure	Title	Page
44	Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Plan View at a Height of 4 Feet	66
45	Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Plan View at a Height of 9 Feet	67
46	Schematic of Building 515 Paint Booth Before and After Split-Flow Modification	82
47	Schematic of Building 515 Paint Booth Before and After Recirculation Modification	84
48	Schematic of Building 515 Paint Booth Before and After Combined Split-Flow/Recirculation Modification	87

LIST OF TABLES

Table	Title	Page
1	RESULTS OF PAINT SPECIATION ANALYSES.	12
2	RESULTS OF PAINT DENSITY AND PERCENT VOLATILE ANALYSES.	13
3	RESULTS OF PAINT ISOCYANATE ANALYSES.	13
4	PAINT USAGE RATES OBSERVED THROUGHOUT TEST SERIES.	14
5	RESULTS OF VOLUME FLOW RATE MEASUREMENTS AT WATER CURTAIN.	15
6	RESULTS OF VOLUME FLOW RATE MEASUREMENTS IN EXHAUST DUCT.	15
7	RESULTS OF INTEGRATED ORGANIC CONCENTRATION MEASUREMENTS IN BOOTH—TEST 1.	17
8	RESULTS OF INTEGRATED ORGANIC CONCENTRATION MEASUREMENTS IN BOOTH—TEST 2.	22
9	RESULTS OF INTEGRATED EXHAUST DUCT ORGANIC SPECIATION AND QUANTIFICATION MEASUREMENTS.	29
10	BAAQMD ST-7 CONTINUOUS ORGANIC SAMPLING RESULTS.	31
11	EPA M25A CONTINUOUS ORGANIC SAMPLING RESULTS.	33
12	SOLVENT MASS BALANCE RESULTS.	37
13	RESULTS OF INTEGRATED PARTICULATE CONCENTRATION MEASUREMENTS IN BOOTH—TEST 1.	41
14	RESULTS OF INTEGRATED PARTICULATE CONCENTRATION MEASUREMENTS IN BOOTH—TEST 2.	41
15	RESULTS OF INTEGRATED PARTICULATE CONCENTRATION MEASUREMENTS IN BOOTH—TEST 3.	42
16	RESULTS OF INTEGRATED METAL CONCENTRATION MEASUREMENTS IN BOOTH—TEST 2.	43
17	RESULTS OF INTEGRATED METAL CONCENTRATION MEASUREMENTS IN BOOTH—TEST 3.	49
18	EPA METHOD 5 INTEGRATED PARTICULATE SAMPLING RESULTS.	56
19	EPA METHOD 5 INTEGRATED METALS SAMPLING RESULTS.	56

LIST OF TABLES
(Concluded)

Table	Title	Page
20	RESULTS OF INTEGRATED ISOCYANATE CONCENTRATION MEASUREMENTS IN BOOTH—TEST 1.	58
21	RESULTS OF INTEGRATED ISOCYANATE CONCENTRATION MEASUREMENTS IN BOOTH—TEST 2.	63
22	RESULTS OF SUMP WATER VOLATILE ORGANIC COMPOUND ANALYSES.	69
23	RESULTS OF SUMP WATER SEMIVOLATILE ORGANIC COMPOUND ANALYSES.	70
24	RESULTS OF SUMP WATER TOTAL ORGANIC CARBON (TOC) ANALYSES.	71
25	RESULTS OF SUMP WATER RESIDUE ANALYSES.	71
26	RESULTS OF WATER CURTAIN PARTICULATE REMOVAL EFFICIENCY MEASUREMENTS.	74
27	RESULTS OF WATER CURTAIN ISOCYANATE REMOVAL EFFICIENCY MEASUREMENTS.	74
A-1	DATA QUALITY OBJECTIVES.	93
A-2	MATRIX SPIKE METALS RECOVERY RESULTS FROM FILTER SAMPLE ANALYSES.	96
A-3	RELATIVE PERCENT DIFFERENCE MEASUREMENTS BETWEEN DUPLICATE NIOSH 1300 CHARCOAL TUBE SAMPLES.	98
A-4	NIOSH 1300 CHARCOAL TUBE DESORPTION EFFICIENCY RESULTS.	99
A-5	NIOSH 1300 CHARCOAL TUBE SURROGATE RECOVERY RESULTS.	100
A-6	MATRIX SPIKE VOLATILE ORGANIC COMPOUND RECOVERY RESULTS FROM SUMP WATER ANALYSES.	107
A-7	MATRIX SPIKE SEMIVOLATILE ORGANIC COMPOUND RECOVERY RESULTS FROM SUMP WATER ANALYSES.	107

GLOSSARY OF TERMS

ACFM	Actual cubic feet per minute
ACGIH	American Conference of Governmental Industrial Hygienists
AEERL	Air and Energy Engineering Research Laboratory
AFESC	Air Force Engineering and Services Center
BAAQMD ST-7	Bay Area Air Quality Management District Standard Test 7: A sampling and analysis procedure for continuously monitoring the total unburned hydrocarbon concentration in a gas stream
DQO	Data quality objective
EPA	Environmental Protection Agency
EPA M2	Environmental Protection Agency Method 2: A procedure for measuring flow rates in ducts
EPA M25A	Environmental Protection Agency Method 25A: A sampling and analysis procedure for continuously monitoring the total unburned hydrocarbon concentration in a gas stream
EPA M5	Environmental Protection Agency Method 5: A sampling and analysis procedure for isokinetically measuring particulate concentrations in ducts
FID	Flame ionization detector
GC/MS	Gas chromatograph/mass spectrometer
HDI	Hexamethylene diisocyanate
inHg	Inches of mercury: A unit of pressure measurement
LEL	Lower explosive limit
MEK	Methyl ethyl ketone
MIBK	Methyl isobutyl ketone
MW	Molecular weight
NDIR	Nondispersive infrared detector
NFPA	National Fire Prevention Association
NIOSH 500	National Institute of Occupational Safety and Health Method 500: An integrated air sampling method for determining particulate concentrations
NIOSH 1300	National Institute of Occupational Safety and Health Method 1300: An air sampling method for determining ambient organic concentrations

OSHA 42	Occupational Safety and Health Administration Method 42: An air sampling method for determining ambient isocyanate concentrations
OVA	Organic vapor analyzer
ppm	Parts per million: A measure of concentration by volume
QA/QC	Quality assurance/Quality control
QAPP	Quality Assurance Project Plan
RPD	Relative percent difference
TDI	Toluene diisocyanate
TOC	Total organic carbon
TSS	Total suspended solids
TUHC	Total unburned hydrocarbon
VOA	Volatile organic analysis
VOC	Volatile organic compound

METRIC CONVERSION TABLE.

English	SI	SI Symbol	To Convert from English to SI, Multiply By
Area			
Square inch	Square centimeter	cm ²	6.452
Square foot	Square meter	m ²	0.09290
Length			
Inch	Centimeter	cm	2.54
Foot	Meter	m	0.3048
Volume			
Cubic inch	Cubic centimeter	cm ³	16.387
Cubic foot	Cubic meter	m ³	0.02832
Mass			
Pound mass	Kilogram	kg	0.4536
Work, Energy, Heat			
Btu	Joule	J	1055
Btu	Kilowatt-hour	kWh	0.000293
Kilowatt-hour	Kilojoule	kJ	3600
Power, Heat Rate			
Horsepower	Watt	W	745.7
Btu/hour	Watt	W	0.2931
Temperature			
Fahrenheit	Celsius	°C	(5/9)(°F-32)
Flow Rate			
Cubic foot/minute	Cubic meter/second	m ³ /s	0.0004719

SECTION I

INTRODUCTION

A. OBJECTIVE

The objective of this project was to develop practical strategies for economically decreasing volatile organic compound (VOC) emissions from typical Air Force painting operations. With this objective, the focus of this study was to confirm that recirculating a portion of paint booth exhaust air is a safe and economical means of achieving cost-effective control by lowering the flow rate to a VOC emission control device. In a previous study performed at Travis and McClellan Air Force Bases (Reference 1), recirculation was recommended as the optional method of reducing VOC emissions from Air Force painting operations. However, this recommendation raised several issues and questions pertaining to in-booth concentrations of hazardous compounds resulting from the recirculation modification. This report addresses these issues.

B. BACKGROUND

The U.S. Air Force uses a number of organic solvents and coatings in routine maintenance operations. The Air Force facilities that use these solvents and coatings are sources of VOC emissions regulated under the Clean Air Act and related state and local laws. Because increasing pressure is being exerted by regulatory agencies on Air Force facilities to decrease solvent emissions, the U.S. Air Force Engineering and Services Center (AFESC), in a joint effort with the EPA's Air and Energy Engineering and Research Laboratory (AEERL), is studying ways of achieving cost-effective VOC emission control.

The Air Force is focusing on military painting facilities in which solvent-based epoxy primers and topcoats are used; however, the EPA is interested in all commercial applications of the technologies developed by this project.

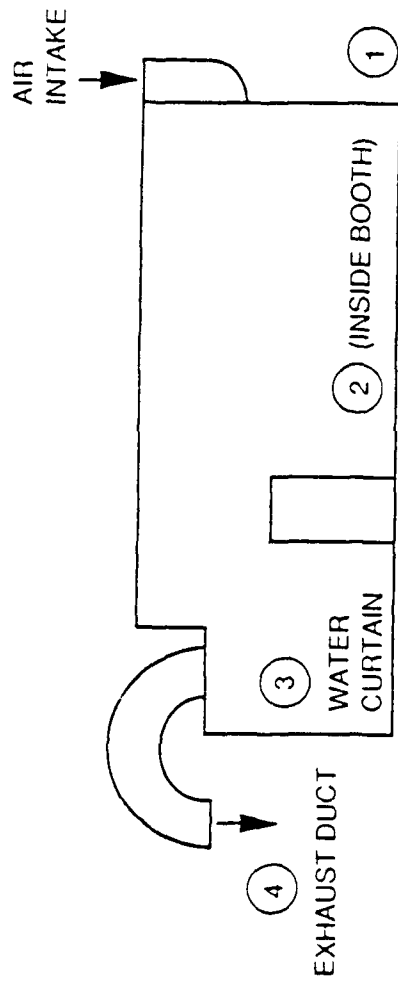
C. SCOPE/APPROACH

The paint booth located in Building 515 at Hill Air Force Base, Utah, was selected for study. At this site, pollutant emission rates were quantified, and pollutant concentration profiles were determined in the booth during painting. In addition, engineering parameters such as temperature, pressure, and airflow rates, were measured.

The hazardous constituent concentrations in the paint booth were determined by simultaneously sampling at 22 locations in the booth during painting. A three-dimensional sampling grid was devised to perform integrated sampling at heights up to 12 feet and across the width and length of the booth. This sampling effort resulted in the quantification of in-booth concentrations of organics, particulate, metals, and isocyanates during painting. Emissions from the booth were quantified by sampling in the booth exhaust duct to determine particulate and organic concentrations.

D. SITE DESCRIPTION

The paint booth selected for study is the contractor-operated facility located in Building 515 at Hill Air Force Base, Utah. This booth, illustrated in Figure 1, is approximately 35 feet long, 16 feet wide, and 16 feet high. It is equipped with a crossdraft ventilation system in which fresh air enters the booth through a filter system at the front and exits through a water curtain emission control system located at the back of the booth. The ventilation air is exhausted outside Building 515 from a curved duct directed toward the ground. The unit is maintained under negative pressure to prevent solvent emissions into the surrounding work areas in Building 515. Before testing, the exhaust duct outside of Building 515 was modified to permit isokinetic sampling.



EXTERNAL SIDE VIEW

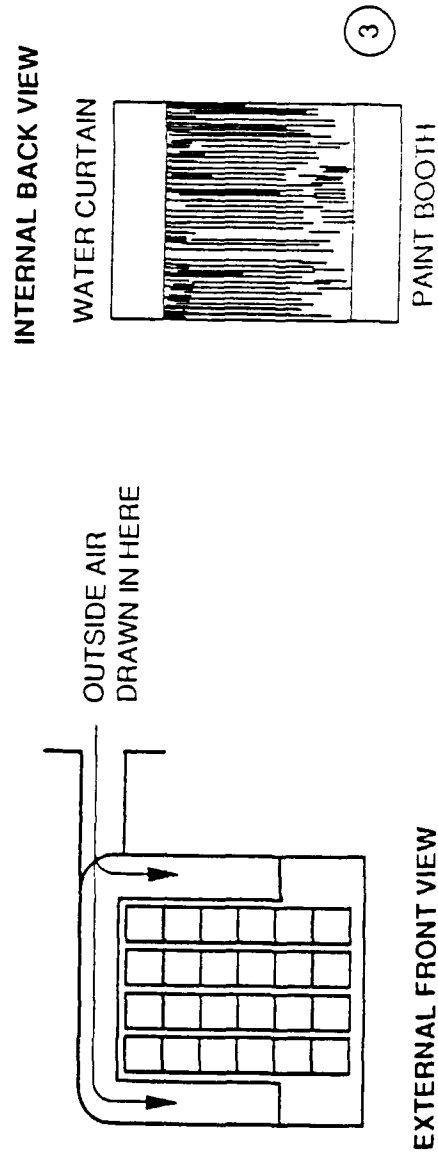


Figure 1. Schematics of Paint Spray Booth Located in Building 515, Hill Air Force Base, Utah

SECTION II

SAMPLING LOCATIONS AND PROCEDURES

A. SAMPLING LOCATIONS

The four sampling locations at the Building 515 facility are indicated and circled in Figure 1. The first sampling location was near the booth, where paint and solvent samples were taken for bulk analysis, and paint and solvent usage was determined by gravimetric analysis. The second sampling location was the interior of the booth, where paint times were recorded, and air samples were taken to determine in-booth concentrations of particulate, metals, volatile organic compounds, and isocyanates. The third sampling location was the water sump, where water and air samples were taken and airflow rates were measured. The final sampling location was in the exhaust duct, where volume flow measurements and air samples were taken to determine compound emission rates. These four sampling locations are discussed more fully in the following section.

B. SAMPLING PROCEDURES

1. Paint Sampling and Usage Rate Determination

Paint samples were drawn for speciation, density, isocyanate, and percent volatile analyses at location 1. Paint samples taken to determine species concentration were collected in 2-mL vials for subsequent analysis using a gas chromatograph/mass spectrometer (GC/MS). Paint samples taken for density, isocyanate, and percent volatile analyses were collected in 40-mL volatile organic analysis (VOA) vials. Paint usage rates were determined gravimetrically by weighing the paint-dispensing containers before and after usage. To monitor painting operations, a field crew member remained in the booth during all painting operations and recorded painting start and stop times with a stopwatch.

2. Integrated Air Sampling Procedures Used in the Booth

At sampling location 2, a three-dimensional sampling grid inside the paint booth was devised and constructed for collecting integrated air samples to determine concentration profiles of particulate, organic compounds, and isocyanates during painting. A side view of the sampling grid is illustrated in Figure 2. The numbered sampling points are arranged in this figure to indicate the vertical distance from the sample point to the ground. Figure 3 illustrates a plan view of the sampling grid in which numbered sampling points are arranged to indicate the horizontal distance from a sample point to the back wall. Sampling pumps suspended in the booth were used to collect the integrated air samples at the positions indicated in Figures 2 and 3.

This grid system was used in seven sampling tests. Three sampling tests were performed using National Institute of Occupational Safety and Health (NIOSH) 500 sampling procedures to determine particulate concentration profiles in the booth; two tests were performed

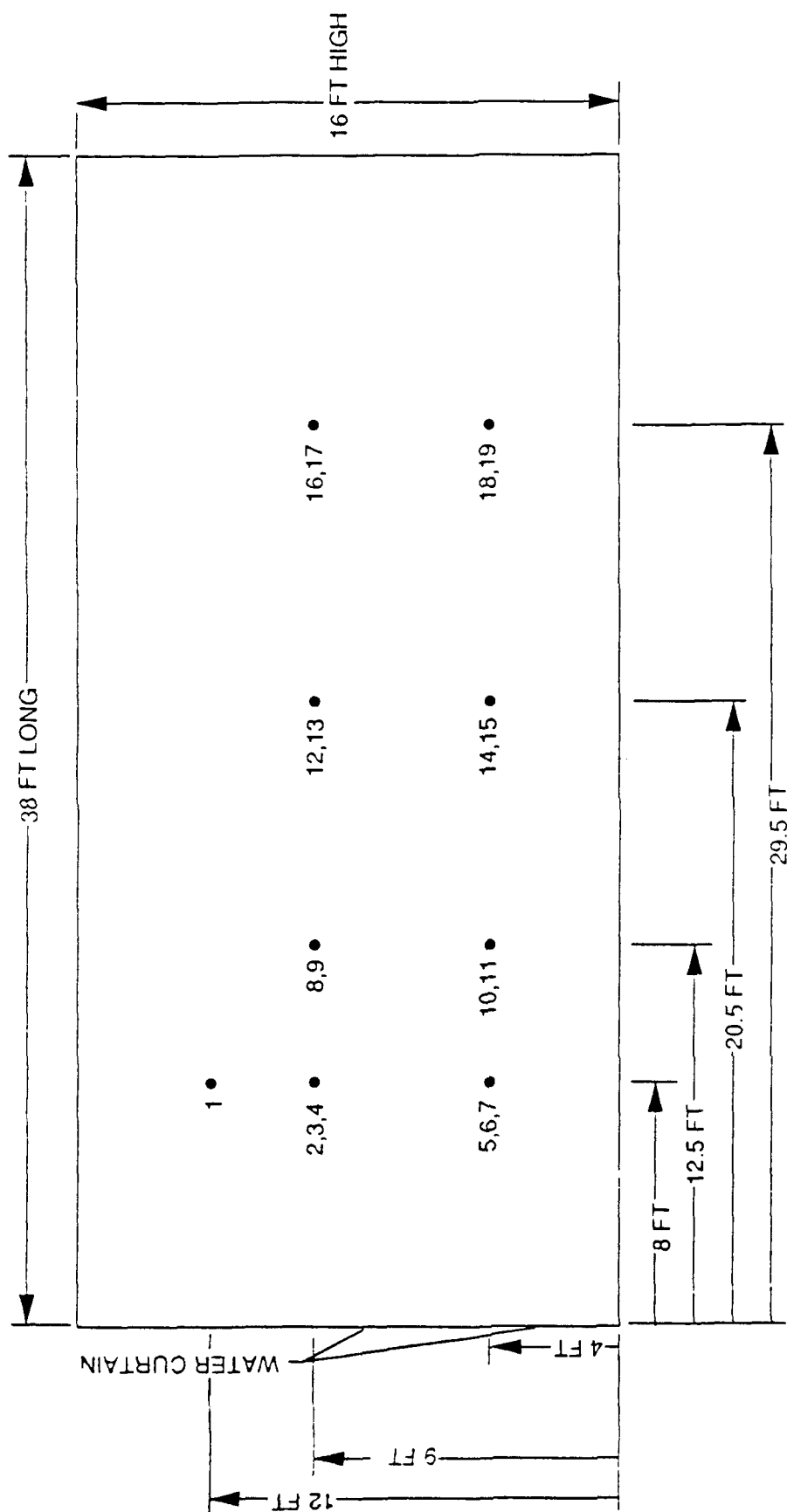


Figure 2. Sample Locations in the Building 515 Paint Spray Booth, Side View

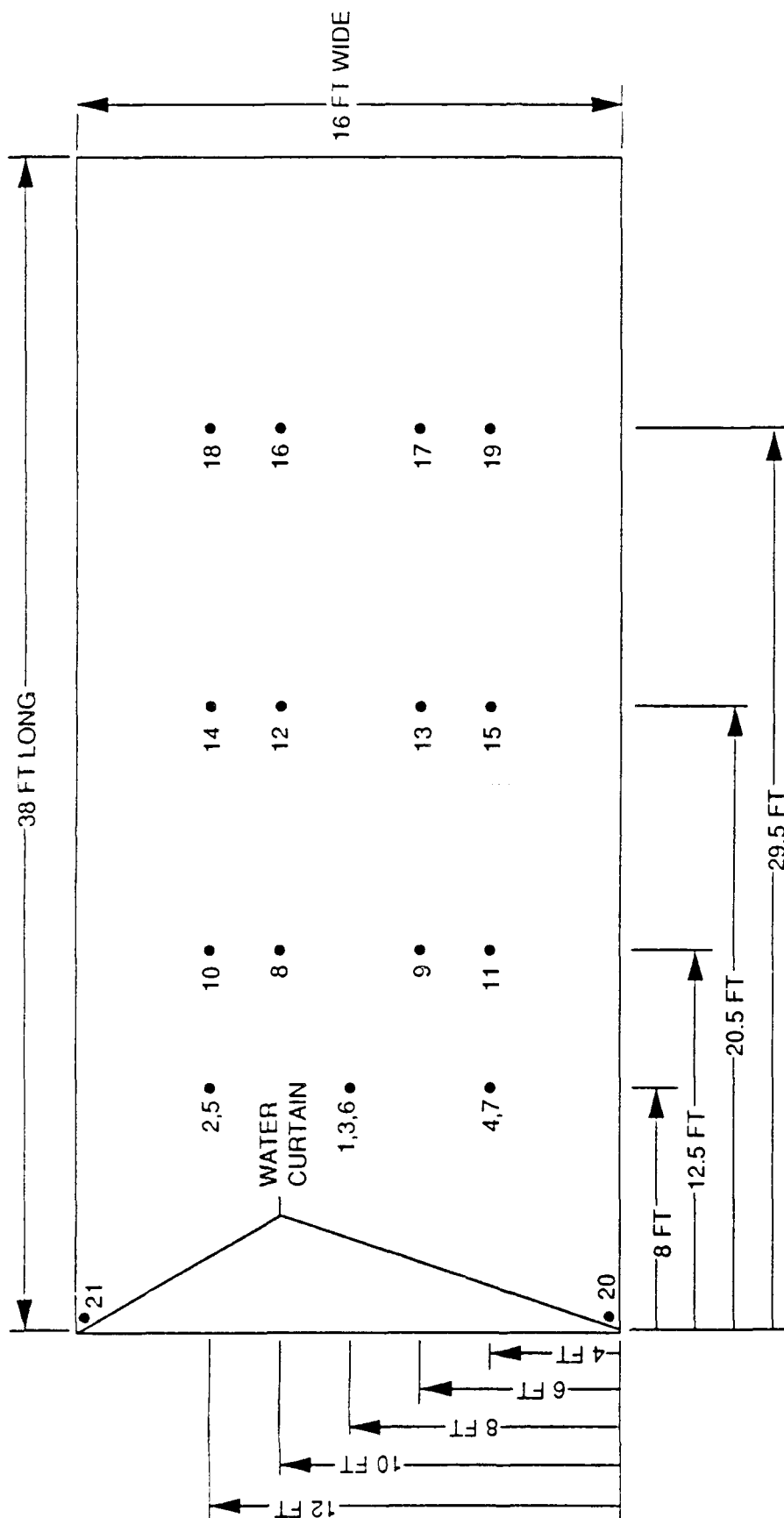


Figure 3. Sample Locations in the Building 515 Paint Spray Booth, Plan View

using NIOSH 1300 sampling procedures to determine organic compound concentration profiles; and two tests were run according to Occupational Safety and Health Administration (OSHA) Method 42 sampling procedures to determine isocyanate concentration profiles. Samples from two of the three particulate tests were analyzed for the presence of metals. These sampling methods are described below. In addition, copies of the methods are provided in Appendix B.

a. NIOSH 500 Air Sampling

NIOSH Method 500 is used to measure ambient particulate concentrations, and is therefore nonisokinetic (Reference 2). Particulate matter from a known volume of gas is collected on an open-faced, preweighed filter. The filter is reweighed after the test to determine the amount of particulate deposition that occurred. For this test series, the filter samples were subsequently analyzed to determine hazardous constituent metal concentrations in the paint particulate. For accurate metal analysis results, cellulose ester filters were used rather than the glass fiber filters recommended in the NIOSH 500 sampling procedure.

b. NIOSH 1300 Air Sampling

Ambient VOC sampling was conducted in the booth in general accordance with NIOSH Method 1300 procedures (Reference 3). This integrated sampling method entails drawing a known volume of sample air through an adsorbing charcoal tube. Volatile organics are removed from the air sample by adsorption onto the charcoal medium. The charcoal tube is then extracted with a specific solvent that is selected based on the species to be recovered. The extract is analyzed using a GC/MS.

c. OSHA 42 Air Sampling

Isocyanate concentrations were measured in the paint booth according to OSHA Method 42 (Reference 4), which is similar to NIOSH Method 500. The only difference is that a specially treated glass fiber filter is used.

OSHA Method 42 may be used to collect both the polymeric and monomeric form of toluene diisocyanate and hexamethylene diisocyanate, the two isocyanate compounds of interest in this test series. This implies that both the volatile and nonvolatile forms of these compounds are sampled by this procedure. The retention efficiency of this method was determined using a vapor spiking technique.

Several methods of determining isocyanate concentrations could have been implemented; however all of them (except OSHA Method 42) require the use of either an impinger system or a spectrophotometer. It was determined that these systems were neither safe nor practical for use within an operating paint booth; therefore, the OSHA Method was selected.

The OSHA 42 sample cassettes were prepared by the Occupational and Environmental Health Laboratory (OEHL) of Brooks Air Force Base. After sampling, the filters

were returned to Brooks Air Force Base, where they were extracted and analyzed by high performance liquid chromatography (HPLC).

3. Continuous Air Sampling Procedure Used in the Booth

In addition to integrated air sampling performed at the designated grid points, continuous monitoring of organic compound concentrations was performed at the back of the booth immediately upstream of the water curtain. An organic vapor analyzer (OVA) was used to monitor temporal variations of organic vapor concentrations. These data were used to supplement the integrated NIOSH 1300 sampling data, which measures spatial variations in organic concentrations. Air samples for this measurement were taken at the back of the paint booth, centered immediately upstream of the water curtain.

4. Water Curtain Sampling and Airflow Rate Measurements

Airflow rate measurements and air samples were taken at the water curtain face. In addition, water samples were drawn from the water curtain sump. Descriptions of these sampling procedures are given in the following sections.

a. Airflow Rate Measurements

Airflow rate measurements were taken daily at the water curtain face. Flow rates were determined using the American Council of Governmental Industrial Hygienists (ACGIH) method for determining open face flows in rooms, hoods, and ventilation systems (Reference 5). This method specifies the use of an anemometer or other low flow rate measuring device. The water curtain was divided into sectors, and the flow rate through each sector was determined by measuring the linear flow rate over each sector area with an anemometer. The linear flow rate measurement was multiplied by the area of the sector to determine the volumetric airflow rate through the sector in actual cubic feet per minute (acfm).

b. Integrated Air Sampling

Particulate and isocyanate removal efficiencies of the water curtain were determined by measuring the concentrations of these parameters at the water curtain face and in the exhaust duct downstream from the water curtain. These measurements were done during actual painting operation. The particulate sampling was done according to the NIOSH 500 method described above using glass fiber filters rather than cellulose ester filters because this test did not require any metals analyses. Isocyanate sampling was performed according to OSHA Method 42, as described above.

c. Water Sampling

Water samples were drawn daily from the sump. The sampling procedure used depended on the type of analysis required. Water samples were collected for total organic carbon (TOC) analyses, volatile and semivolatile organic analyses, and total suspended solids (TSS) measurements.

(1) TOC Sampling. Water samples were collected once or twice daily for TOC analysis. The samples were collected in 40-mL VOA vials and preserved with H_2SO_4 . These samples were taken to monitor the sump water organic carbon content and to demonstrate that the water curtain has no impact on VOC emissions from painting facilities.

(2) Volatile and Semivolatile Organic Sampling. Water samples submitted for volatile organic analysis were collected with no headspace in 40-mL VOA vials. Samples submitted for semivolatile organic analysis were collected in 1-gallon amber glass jars. These samples were taken at the beginning, middle, and end of the test series to speciate and quantify the TOC sample results.

(3) TSS Sampling. Water samples were collected in 1-liter polypropylene containers for the measurement of TSS concentrations. These samples were taken to monitor the sump water suspended solids content.

5. Exhaust Duct Sampling and Airflow Rate Measurements

Continuous and integrated air samples and airflow rate measurements were taken in the paint booth exhaust duct.

a. Airflow Rate Measurements

Volume flow rate measurement procedures specified in EPA Method 2 were used to determine airflow rates in the exhaust duct (Reference 6). This procedure requires the use of a pitot tube in a straight duct at a location eight duct diameters downstream from any flow obstructions or variations.

b. Integrated Air Sampling

Several integrated air sampling methods were used in the exhaust duct of the paint spray booths. Most of these sampling procedures (NIOSH 500, NIOSH 1300, and OSHA 42) are described in an earlier section. In addition to these sampling methods, EPA Method 5 (M5) was used for isokinetically sampling airborne particulate concentrations in the exhaust duct (Reference 7).

c. Continuous Air Sampling

EPA Method M25A and Bay Area Air Quality Management District (BAAQMD) Method ST-7 were used to continuously monitor organic compound emissions from the paint booth exhaust duct. Both of these methods measure the organic carbon concentration, however BAAQMD Method ST-7 also measures carbon monoxide concentrations. Because the carbon monoxide concentration in the booth exhaust stream is the same as ambient levels (i.e., negligible), only organic carbon is assumed to be measured.

(1) BAAQMD Method ST-7. The BAAQMD ST-7 procedure requires that the gas sample be passed through a combustion tube, in which all organic compounds are oxidized to CO_2 and water (Reference 8). The products of combustion are then passed through a

nondispersive infrared analyzer (NDIR), which continuously monitors the CO₂ concentration in the gas stream. The combustion tube is periodically bypassed to determine background CO₂ concentrations, at which time the sample gas passes directly through the NDIR. Total oxidizable carbon is measured as the difference between the CO₂ concentrations measured in the sample and bypass streams.

The BAAQMD ST-7 sampling technique yields a measure of the total amount of organic carbon in the sample stream. To correctly assess the VOC concentration in the sample, the components and the relative concentrations of the components in the sample stream must be known. Thus, the results of the ST-7 measurement must be combined with the exhaust duct NIOSH 1300 speciation results to determine the VOC concentration in the exhaust stream. This will be discussed in more detail in the following section.

(2) EPA Method M25A. EPA Method 25A uses a flame ionization detector (FID) to measure the organic carbon concentration in the sample stream (Reference 9). The FID is sensitive to the total hydrocarbon concentration in the sample stream and does not distinguish between organic species. As with the ST-7 procedure, the results of this measurement are reported in parts per million (ppm) as carbon. Therefore, to correctly assess the VOC concentration in the sample stream, the organic components and their relative concentrations in the sample stream must be determined.

The FID is calibrated with propane, which has a detector response factor that differs significantly from the response factors of the organics measured in this test series. In addition, the presence of oxygenated organic compounds in the FID causes the organic carbon concentration to be underpredicted. Note that, unlike EPA M25A, the BAAQMD ST-7 equipment is calibrated with CO₂, which is also the gas being measured. These factors and operational constraints cause Method M25A to be less quantitative, although more sensitive than the ST-7 Method. Method M25A is therefore used primarily as a check of the ST-7 results.

SECTION III

TEST RESULTS AND DISCUSSION

A. RESULTS OF PAINT ANALYSES AND USAGE MONITORING

The paints used at the Building 515 facility are two-part coatings; the two parts (pigment and catalyst) are mixed in equal volumes. Samples of each pigment and catalyst used in the test series were collected and analyzed for organic speciation, density, percent volatiles, and percent isocyanates. The results were used to perform the solvent mass balance calculations and in the analysis of the water and NIOSH 1300 charcoal tube samples. The results of these analyses are shown in Tables 1, 2, and 3. The paint speciation results were obtained by performing a library search of the NBS/NIH (National Bureau of Standards/National Institute of Health) Mass Spectral Database, which is comprised of more than 42,000 organic compounds. The database search resulted in the identification of most of the organic compounds detected, however some compounds could not be identified. These compounds are listed by scan number in Table 1.

As discussed previously, paint usage was monitored by a field crew member who recorded the type of paint being used, and the weight of the paint in the spray system before and after use. The quantity of paint used and the recorded time intervals observed during the test series are summarized in Table 4.

B. AIRFLOW RATE MEASUREMENTS

Results of airflow rate measurements taken at the water curtain and in the exhaust duct are presented in Tables 5 and 6, respectively. Comparing the results of these two measurements reveals that the flow rates measured at the water curtain with the anemometer are consistently 25 percent lower than the flow rates measured in the exhaust duct following EPA Method 2 procedures. This constant discrepancy indicates that there is probably in-leakage occurring somewhere between the water curtain and the exhaust duct. This discrepancy does not affect the results reported in this section because appropriate flow rate data were collected when emission concentrations were measured.

C. AIRBORNE ORGANIC COMPOUND CONCENTRATION MEASUREMENTS

1. In-Booth Measurement Results

a. Integrated Sampling

Two VOC concentration measurements were taken on 7 December 1988, using NIOSH charcoal tubes positioned at the three-dimensional sampling grid points discussed in Section II. The NIOSH 1300 method is an integrated sampling technique that yields an average, speciated organic concentration over the entire sampling period. The results of these tests, or

TABLE 1. RESULTS OF PAINT SPECIATION ANALYSES.

Compound	Compound Concentration (g/L)								
	Green Primer		Green Paint		Yellow Paint		Orange Paint		Lacquer Thinner
	Pigment	Catalyst	Pigment	Catalyst	Pigment	Catalyst	Pigment	Catalyst	
1,1'-oxybis[2-methoxyethane]	38.5	<0.025	<0.050	<0.020	<0.050	<0.025	33.5	<0.025	31.0
2-Butanone (MEK)	3.49	119	121	386	272	472	180	383	222
2-Ethoxyethyl acetate	<0.05	<0.025	162	60.0	4.45	75.0	150	70.0	22.0
2-Propanol	36.0	55.0	<0.050	<0.20	<0.050	<0.025	<0.05	<0.025	<0.050
2-(2-Methoxyethoxy)ethanol	8.00	<0.025	<0.050	<0.20	270	<0.025	4.30	<0.025	<0.050
4-Methyl-2-pentanone (MIBK)	1.00	0.08	<0.050	106	<0.050	1.98	<0.05	31.3	<0.050
Acetone	18.1	0.13	10.3	<1.0	4.50	2.35	15.0	7.03	<0.0250
Chloromethane	0.55	<0.025	<0.050	<0.20	<0.050	<0.025	0.35	<0.025	<0.050
Ethyl acetate	<0.05	<0.025	112	<0.20	<0.050	<0.025	10.0	0.90	<0.050
Ethylbenzene	0.80	0.28	0.10	6.50	0.75	9.13	0.15	9.00	0.05
Methylcyclohexane	<0.05	<0.025	<0.050	<0.20	<0.050	<0.025	<0.05	<0.025	17.0
Methylene chloride	0.30	<0.025	<0.050	<0.20	<0.050	<0.025	0.30	0.03	<0.050
m & p-Xylene	<0.05	<0.025	<0.050	<0.20	1.46	24.6	<0.05	20.4	0.90
n-Butyl acetate	<0.05	<0.025	50.0	105	48.5	48.0	<0.05	60.0	50.0
o-Xylene	0.70	0.15	0.20	9.00	0.70	13.0	0.20	9.50	<0.050
Styrene	<0.05	<0.025	<0.050	<0.20	0.30	<0.025	<0.05	<0.025	<0.050
Toluene	84.0	86.3	6.00	26.2	9.20	0.90	3.00	4.65	81.3
Unknown (scan #252)	<0.05	<0.025	<0.050	<0.20	<0.050	<0.025	<0.05	<0.025	80.0
Unknown (scan #263)	<0.05	90.0	<0.050	<0.20	<0.050	<0.025	<0.05	<0.025	<0.050
Unknown (scan #311)	<0.05	<0.025	5.20	<0.20	<0.050	<0.025	<0.05	<0.025	<0.050
Unknown (scan #319)	110	<0.025	<0.050	<0.20	5.00	<0.025	<0.05	<0.025	<0.050
Unknown (scan #330)	<0.05	<0.025	<0.050	<0.20	<0.050	<0.025	2.25	<0.025	<0.050
Unknown (scan #414)	<0.05	<0.025	<0.050	<0.20	<0.050	<0.025	<0.05	<0.025	150
Unknown (scan #558)	38.5	<0.025	<0.050	<0.20	<0.050	1.75	33.5	1.50	<0.050
Unknown (scan #562)	<0.05	<0.025	<0.050	<0.20	<0.050	<0.025	<0.05	<0.025	13.0
Unknown (scan #589)	12.0	<0.025	<0.050	<0.20	9.00	<0.025	6.50	<0.025	<0.050
Unknown (scan #606)	11.5	<0.025	<0.050	<0.20	<0.050	<0.025	12.5	<0.025	<0.050
Unknown (scan #691)	29.5	<0.025	<0.050	<0.20	<0.050	<0.025	<0.05	<0.025	<0.050
Unknown (scan #737)	<0.05	<0.025	50.0	<0.20	<0.050	<0.025	<0.05	<0.025	<0.050

TABLE 2. RESULTS OF PAINT DENSITY AND PERCENT VOLATILE ANALYSES.

Paint Type	Percent Volatile Measurement			Density Measurement			
	Initial Weight (g)	Final Weight (g)	Percent Volatile	Measured Density		Published Density	
				Pigment (kg/L)	Catalyst (kg/L)	Pigment (kg/L)	Catalyst (kg/L)
Forest Green	0.99	0.60	39.4	1.25	0.86	1.24	0.90
Yellow	1.01	0.69	31.7	1.34	0.925	1.25	0.93
Green Primer	1.18	0.71	40.0	1.27	0.864	1.27	0.82
International Orange	1.37	0.94	31.4	1.27	0.921	1.33	0.93
Gun Cleaning Fluid	0.74	0.04	94.6	0.842	NA ^a	NI ^b	NA
Method Blank	1.10	0.00	NA	1.00	NA	1.00	NA

^a NA Not applicable

^b NI No information

TABLE 3. RESULTS OF PAINT ISOCYANATE ANALYSES.

Sample Type	Percent by Mass Isocyanate Group	
	Measured Value	Published Value ^a
Forest Green Pigment	<.2	0.0
Forest Green Catalyst	6.60	7.1
Green Primer Pigment	<.2	0.0
Green Primer Catalyst	NA ^b	0.0 ^c
Yellow Pigment	<.2	0.0
Yellow Catalyst	6.62	7.1
International Orange Pigment	<.2	0.0
International Orange Catalyst	5.72	7.1
Gun Cleaning Fluid	<.2	0.0

^a These values were obtained from the Material Safety Data Sheets (MSDS) on file for each paint sampled. The reported values include the monomeric form (at a maximum of .5%) and the polymeric form of the isocyanate group. According to manufacturer data and MSDSs for the paints sampled, the polymeric form is attached to a biuret resin, which is present in the catalyst at approximately 30 percent. The biuret resin is composed of approximately 23.5 percent polymeric isocyanate, thus the total isocyanate group concentration is approximately 7.1 percent.

^b NA No Analysis. The total isocyanate group concentration could not be determined using the colorimetric method selected (ASTM 2572-80) because of interference by the catalyst coloring.

^c No MSDSs examined indicate that isocyanates are present in the green primer catalyst. However, the information obtained may be incomplete, thus isocyanates may be present.

TABLE 4. PAINT USAGE RATES OBSERVED THROUGHOUT TEST SERIES.

Date	Test	Time	Paint Type	Quantity (kg)	Comments
6 Dec	Particulate 1 Approximately 1130-1300	1127.22 - 1135.03	Forest Green	3.3	Air-atomized gun
		1136.01 - 1142.04	Forest Green		
		1143.43 - 1153.10	Forest Green		
		1156.20 - 1202.59	Forest Green		
		1203.20 - 1204.59	Forest Green		
		1205.55 - 1212.57	Forest Green		
	Particulate 2 Approximately 1400-1530	1405.45 - 1409.50	Green Primer	1.3	Air-atomized gun
		1410.49 - 1412.24	Green Primer		
		1413.00 - 1414.00	Paint Thinner	< 0.5	Cleaning out gun
		1431.58 - 1433.40	Yellow	4.0	Air-assisted airless gun
		1434.15 - 1436.55	Yellow		
		1440.42 - 1447.12	Yellow		
		1448.30 - 1450.25	Yellow		
		1500.53 - 1507.13	Yellow		
		1508.01 - 1508.26	Yellow		Switched to air-atomized gun
7 Dec	VOC 1 Approximately 0945-1030	0954.17 - 0955.30	Forest Green	6.6	Air-assisted airless gun
		0956.50 - 1009.50	Forest Green		
		1012.06 - 1023.56	Forest Green		
		1025.40 - 1029.35	Forest Green		
		1104.43 - 1108.50	Green Primer	2.0	Air-atomized gun
		1109.30 - 1110.20	Green Primer		
		1110.55 - 1113.30	Green Primer		
		1114.15 - 1119.08	Green Primer		
					Blowing out solvent 10 sec.
	VOC 2 Approximately 1305-1350	1325.02 - 1331.40	Green Primer	2.0	Air-assisted airless gun
		1332.34 - 1337.58	Green Primer		
		1338.27 - 1340.56	Green Primer		
		1408.35 - 1431.12	Forest Green	4.6	
		1431.55 - 1432.58	Forest Green		
8 Dec	Isocyanates 1 Approximately 0850-1015	0856.53 - 0908.43	Green Primer	1.8	Air-atomized gun (?)
		0909.27 - 0916.17	Green Primer		
		0919.22 - 0932.54	Int'l Orange	6.0	
		0937.42 - 0949.50	Int'l Orange		
	Isocyanates 2 Approximately 1230-1350	1246.31 - 1252.04	Int'l Orange	9.2	Air-assisted airless gun
		1253.12 - 1259.35	Int'l Orange		
		1303.41 - 1311.15	Int'l Orange		
		1312.17 - 1318.30	Int'l Orange		
		1320.08 - 1330.40	Int'l Orange		
		1331.25 - 1335.03	Int'l Orange		
9 Dec	Particulate 3 Approximately 0810-0940	0819.30 - 0834.29	Green Primer	2.1	Gun unknown
		0835.41 - 0848.06	Green Primer		
		0849.33 - 0849.42	Paint Thinner	0.8	Assumed 1 liter used (Painter's estimate)
		0850.36 - 0850.46	Paint Thinner		
		0853.06 - 0854.56	Forest Green	7.0	
		0855.06 - 0918.46	Forest Green		

TABLE 5. RESULTS OF VOLUME FLOW RATE MEASUREMENTS AT WATER CURTAIN.

Date	Time	Actual		Standardized ^a	
		(m ³ /min)	(ft ³ /min)	(m ³ /min)	(ft ³ /min)
7 Dec	1842	230	8132	233	8217
8 Dec	1115	240	8485	246	8682
9 Dec	am	239	8430	242	8545
9 Dec	1315	240	8485	235	8284

^a These data are standardized at a barometric pressure of 29.92 in Hg and temperature of 60 °F.

TABLE 6. RESULTS OF VOLUME FLOW RATE MEASUREMENTS IN EXHAUST DUCT.

Date	Actual		Standardized ^a	
	(m ³ /min)	(ft ³ /min)	(m ³ /min)	(ft ³ /min)
6 Dec	307	10845	311	10972
7 Dec	311	10986	312	11030
7 Dec	307	10827	313	11059
8 Dec	317	11206	325	11484
9 Dec	301	10629	311	10995

^a These data are standardized to a barometric pressure of 29.92 in Hg and temperature of 60 °F.

indeed of any integrated sampling procedure, cannot be used to draw conclusions regarding instantaneous concentrations.

The results of the first VOC sampling efforts inside the booth (Test 1) are presented in Table 7 and are plotted in Figures 4 through 10. Figures 4 through 8 present side view concentration profiles at several distances from the north wall of the booth. Figures 9 and 10 present plan view concentration profiles measured at two different heights.

As indicated in Figures 4 through 10, organic compound concentrations measured in the booth are highest at the 4-foot level. In addition, the concentrations increase significantly as a function of proximity to the water curtain. The highest concentrations measured were near the water curtain. The second highest concentrations measured were in the vicinity of the painter. These results indicate significant pollutant stratification in the booth during painting. They also indicate that, although generally located upwind of the object being painted, the painter is exposed to relatively high solvent concentrations.

The Test 2 results of the in-booth VOC sampling efforts are presented in Table 8 and plotted in Figures 11 through 17. Figures 11 through 15 present side view concentration profiles at several distances from the north wall of the booth. Figures 16 and 17 present plan view concentration variations measured at two different heights. Again, significant pollutant stratification occurs.

In comparing the data presented in Table 7 with those presented in Table 8, it appears that both the number of solvent species and the total solvent concentrations measured in Test 2 are much higher than those measured in Test 1. However, as indicated in Table 4, significantly more paint was applied during Test 1 than Test 2. This apparent discrepancy is due to the fact that the extraction solvent used on the charcoal tubes generated in Test 1 is different from the solvent used to extract the charcoal tubes from Test 2. When the Test 1 extracts were analyzed, it was found that the extraction solvent used did not have as high a recovery efficiency as expected. Thus, a different solvent having a higher recovery efficiency was used to extract the charcoal tubes from Test 2. The result of this change was that more sample compounds were successfully extracted from the Test 2 tubes. It cannot be inferred, therefore, that the solvent concentration in the booth was higher during Test 2 than during Test 1.

Because an improved extraction solvent was used on the Test 2 charcoal tubes, the results reported for Test 2 are considered more reliable than those reported for Test 1.

b. Continuous Sampling

As discussed in Section II, continuous organic concentration measurements were taken in the booth with an OVA, which is equipped with an FID. The instrument measures instantaneous concentrations of organic carbon present in the sample stream and plots the result on a logarithmic strip chart recorder. The OVA was located in the middle of the booth at

TABLE 7. RESULTS OF INTEGRATED ORGANIC CONCENTRATION MEASUREMENTS IN BOOTH—TEST 1.

Grid Number	Volume Sampled (L ^a)	2-Butanone		Ethoxyethanol		MIBK		bis(2-Methoxy-ethyl) Ether		Total Solvent
		(μg/tube)	(mg/m ³)	(μg/tube)	(mg/m ³)	(μg/tube)	(mg/m ³)	(μg/tube)	(mg/m ³)	(mg/m ³)
1	55.8	288	5.2	53.5	0.96	108	1.93	<2.0	<0.04	8.0
2	49.4 ^b	430	8.7	126	2.55	96.6	1.96	<2.0	<0.04	13
3	57.0	691	12.1	66.4	1.17	180	3.15	<2.0	<0.04	16
4	48.1	466	9.69	32.2	0.67	123	2.56	<2.0	<0.04	13
5	39.8	6085	153	919	23.1	1326	33.3	<2.0	<0.05	209
6	51.2	8953	175	2748	53.7	2431	47.5	<2.0	<0.04	276
7	55.2	114	2.07	10.2	0.18	< 2.0	<0.04	<2.0	<0.04	2.3
8	57.0	802	14.1	50.3	0.88	193	3.38	<2.0	<0.04	18
9	52.6	1551	29.5	96.8	1.84	309	5.88	<2.0	<0.04	37
10	61.9	5761	93.0	1230	19.9	1464	23.6	<2.0	<0.03	137
11	50.8	64	1.25	9.9	0.19	< 2.0	<0.04	<2.0	<0.04	1.4
12	55.5	308	5.54	27.7	0.50	104	1.87	<2.0	<0.04	7.9
13	54.5	236	4.33	27.4	0.50	84.7	1.55	<2.0	<0.04	6.4
14	51.9	912	17.5	289	5.56	288	5.54	<2.0	<0.04	29
15	50.2	539	10.7	54.0	1.08	141	2.81	<2.0	<0.04	15
16	49.0	242	4.94	167	3.41	85.0	1.73	<2.0	<0.04	10
17	44.1	193	4.37	16.0	0.36	96.3	2.18	<2.0	<0.05	6.9
18	44.3	1153	26.0	360.1	8.13	348	7.86	<2.0	<0.05	42
19	50.8	237	4.67	68.3	1.34	49.9	0.98	<2.0	<0.04	7.0
Painter	17.2 ^c	888	51.8	45.0	2.62	142	8.28	<2.0	<0.11	63
20	59.5	14209	239	2774	46.7	3734	62.8	17.0	0.29	349
21	59.5	7685	129	1739	29.2	2045	34.4	5.6	0.09	193
Blank	NA ^d	<2.0	NA	<2.0	NA	<2.0	NA	<2.0	NA	NA
Blank	NA	<2.0	NA	<2.0	NA	<2.0	NA	<2.0	NA	NA

^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 °F

^b Estimated time of pump operation

^c Pump failed after 24 minutes

^d Not applicable because no sample air was drawn through the blank sample tubes

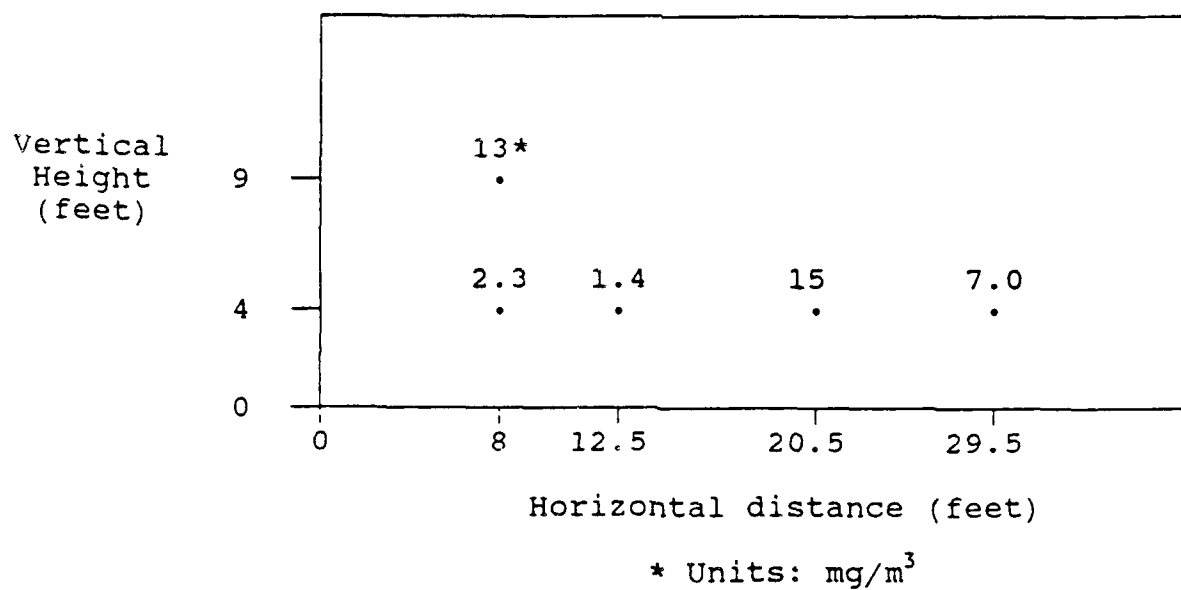


Figure 4. Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 4 Feet from North Wall

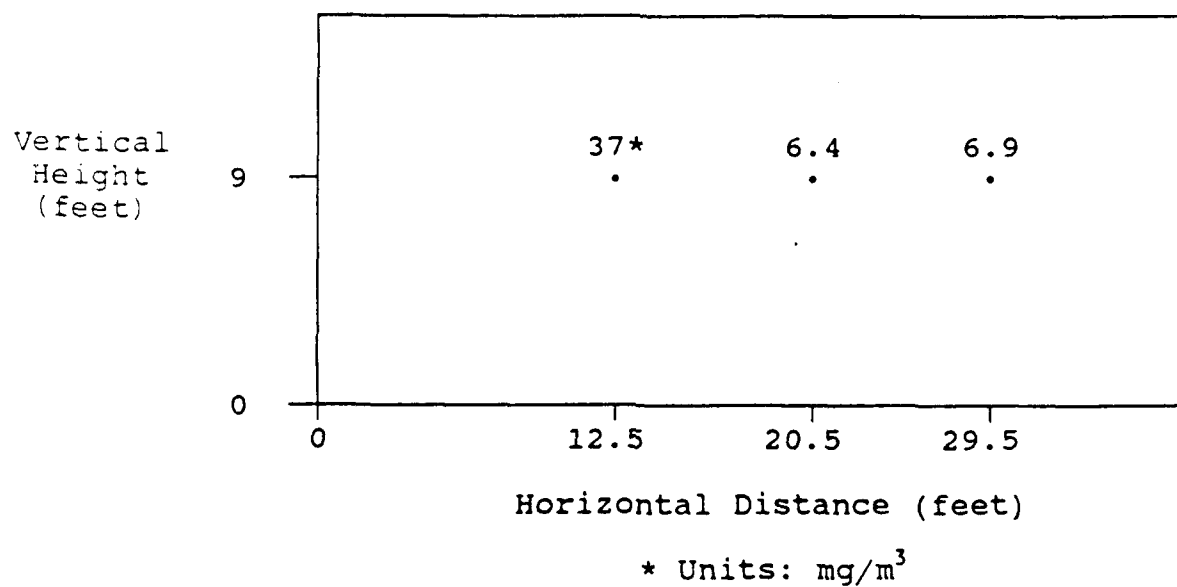


Figure 5. Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 6 Feet from North Wall

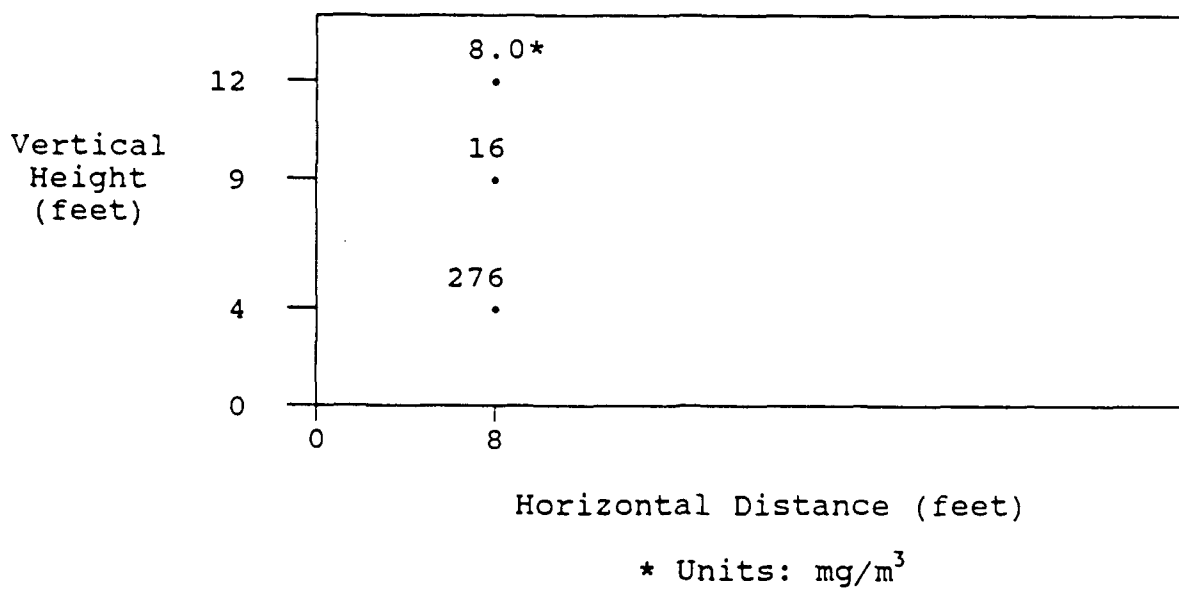


Figure 6. Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 8 Feet from North Wall

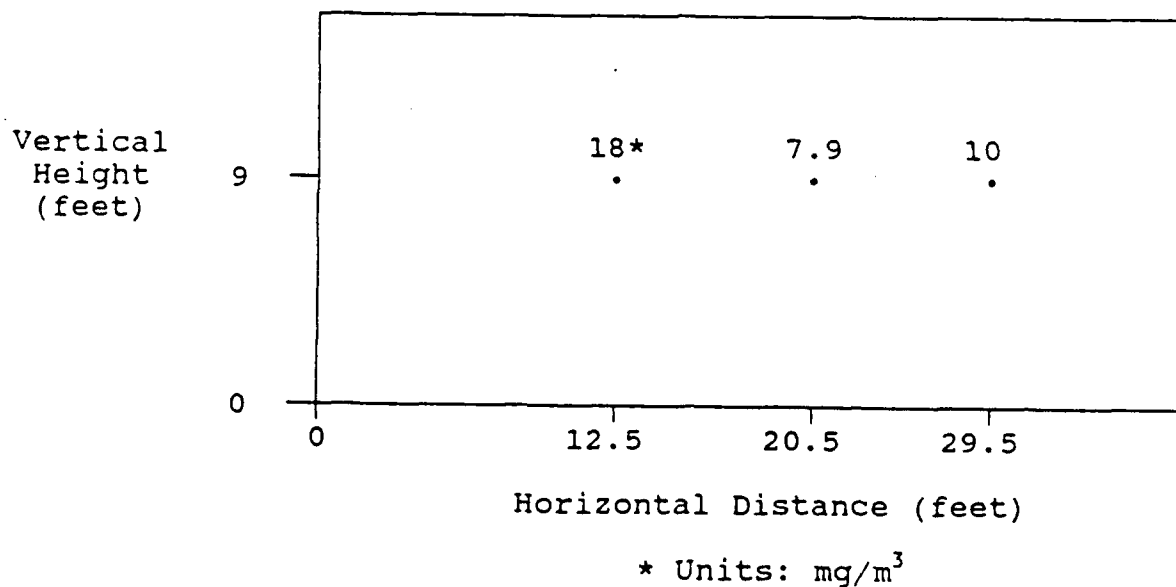


Figure 7. Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 10 Feet from North Wall

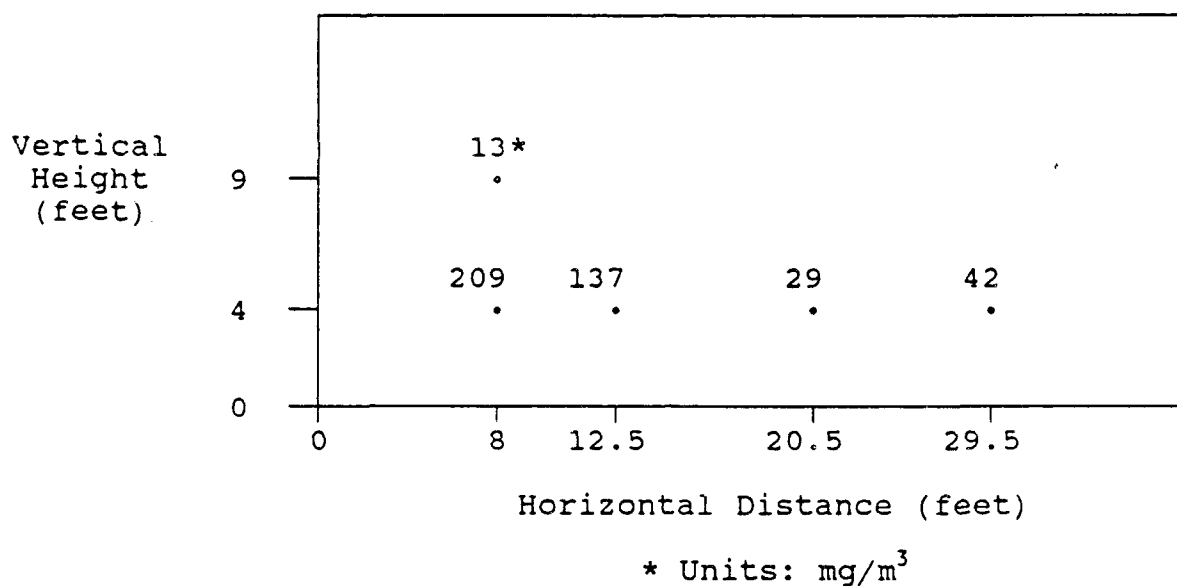


Figure 8 Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 12 Feet from North Wall

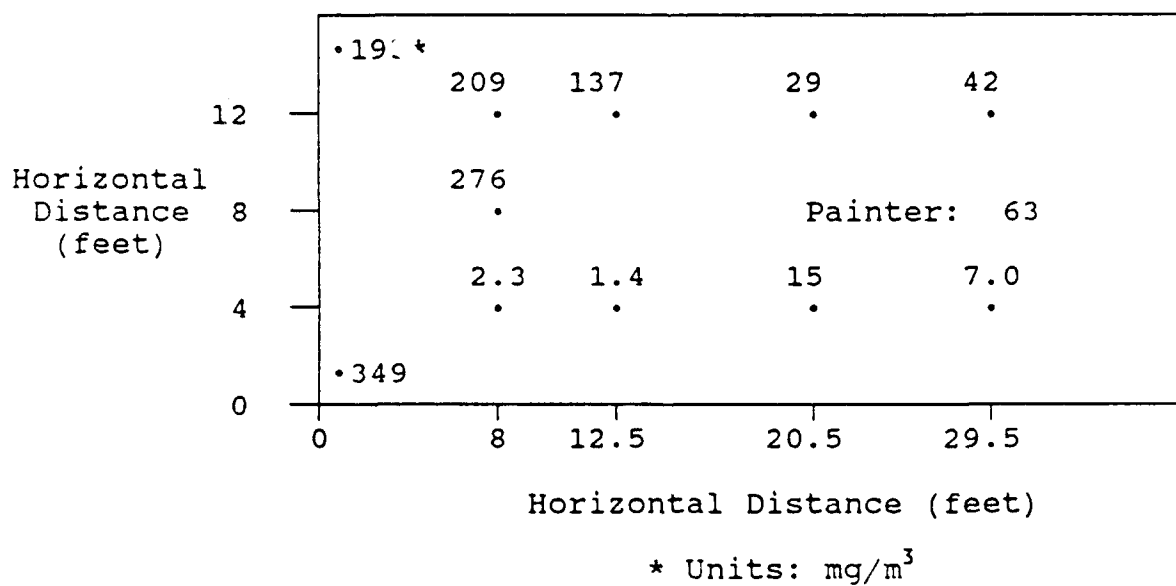


Figure 9. Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Plan View at a Height of 4 Feet

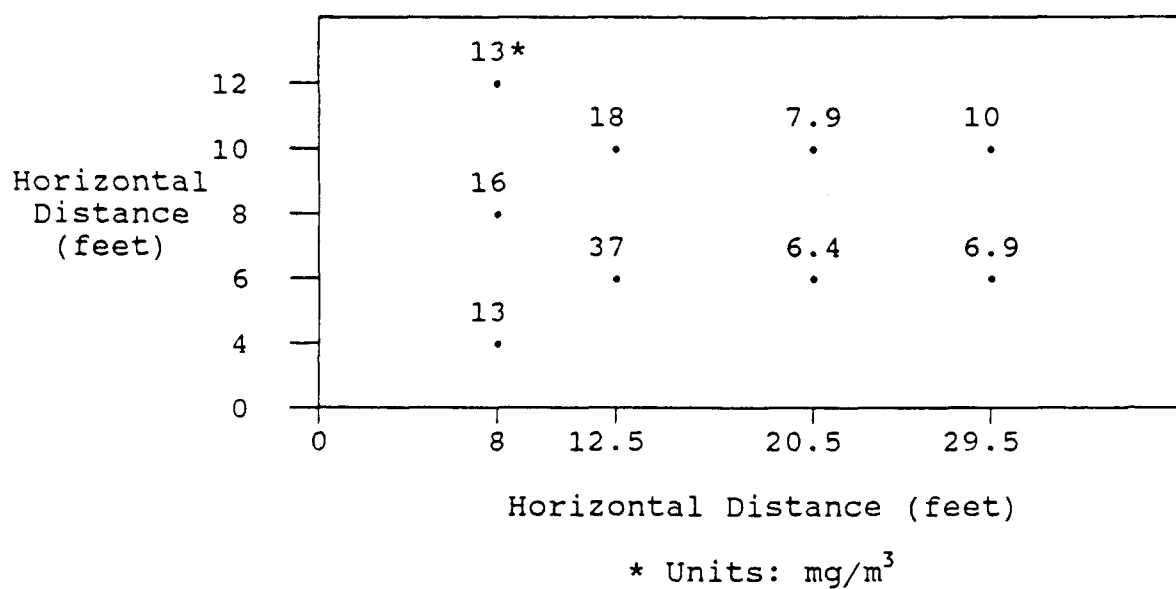


Figure 10. Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Plan View at a Height of 9 Feet

TABLE 8. RESULTS OF INTEGRATED ORGANIC CONCENTRATION MEASUREMENTS
IN BOOTH—TEST 2.

Grid Number	Volume Sampled (L) ^a	2-Butanone		Toluene		Butyl Acetate		Ethylbenzene		Total Xylenes		Ethyl Acetate	
		($\mu\text{g}/\text{tube}$)	(mg/m^3)	($\mu\text{g}/\text{tube}$)	(mg/m^3)	($\mu\text{g}/\text{tube}$)	(mg/m^3)	($\mu\text{g}/\text{tube}$)	(mg/m^3)	($\mu\text{g}/\text{tube}$)	(mg/m^3)	($\mu\text{g}/\text{tube}$)	(mg/m^3)
1	48.7	169	3.46	583	12.0	70.9	1.45	9.5	0.19	34.2	0.70	175	3.59
2	41.4 ^b	350	8.44	700	16.9	238	5.74	8.5	0.21	32.6	0.79	363	8.77
3	45.7	278	6.09	770	16.9	168	3.67	11.6	0.25	41.7	0.91	289	6.33
4	41.5	249	6.01	642	15.5	125	3.01	9.8	0.24	35.7	0.86	259	6.24
5	39.7	887	22.4	1122	28.3	687	17.3	11.7	0.29	38.6	0.97	921	23.2
6	38.7	868	22.4	1018	26.3	620	16.0	11.1	0.29	37.1	0.96	901	23.3
7	44.3	< 10	< 0.20	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05
8	45.8	8	0.18	< 2.0	< 0.04	< 2.0	< 0.04	< 2.0	< 0.04	< 2.0	< 0.04	8.6	0.19
9	41.0	276	6.72	600	14.6	124	3.03	9.4	0.23	33.3	0.81	286	6.98
10	47.7	< 10	< 0.20	< 2.0	< 0.04	< 2.0	< 0.04	< 2.0	< 0.04	< 2.0	< 0.04	< 2.0	< 0.04
11	36.5	< 10	< 0.30	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05
12	0.0 ^c												
13	41.0	172	4.18	646	15.7	72	1.76	9.9	0.24	35.8	0.87	178	4.34
14	35.2	471	13.4	730	20.7	242	6.88	7.7	0.22	29.8	0.85	490	13.9
14	20.9	320	15.3	274	13.1	173	8.26	3.6	0.17	12.5	0.60	333	15.9
15	37.9	254	6.71	578	15.3	98.6	2.60	9.2	0.24	32.8	0.87	264	6.97
16	43.9	114	2.59	572	13.0	26.2	0.60	11.0	0.25	38.6	0.88	118	2.69
17	44.3	96	2.17	647	14.6	24.4	0.55	10.8	0.24	39.8	0.90	6	0.13
18	40.4	356	8.80	687	17.0	154	3.80	8.5	0.21	30.8	0.76	369	9.14
19	44.6	191	4.28	615	13.8	41.7	0.94	10.7	0.24	38.8	0.87	198	4.45
Painter	32.6 ^d	485	14.8	526	16.1	189	5.80	7.1	0.22	28.1	0.86	503	15.4
20	36.8	1669	45.3	1657	45.0	1317	35.8	14.4	0.39	64.9	1.76	733	19.9
21	37.8	1389	36.7	15	0.40	1010	26.7	12.2	0.32	39.3	1.04	1440	38.2
Blank	NA ^e	< 10	NA	< 2.0	NA	< 2.0	NA	< 2.0	NA	< 2.0	NA	< 2.0	NA
Blank	NA	< 10	NA	< 2.0	NA	< 2.0	NA	< 2.0	NA	< 2.0	NA	< 2.0	NA

- ^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 °F
^b Estimated operating time of 47 minutes
^c One end of charcoal tube remained sealed; no air sample was taken
^d Pump failed after 42 minutes
^e Not applicable because no sample air was drawn through the blank sample tubes.

TABLE 8. RESULTS OF INTEGRATED ORGANIC CONCENTRATION MEASUREMENTS IN BOOTH—TEST 2 (CONCLUDED).

Grid Number	Volume Sampled (L ^a)	Methoxyacetone		Ethoxyethanol		MIBK		2-Ethoxyethyl Acetate		bis(2-Methoxyethyl) Ether		Total Solvent (mg/m ³)
		(μg/tube)	(mg/m ³)	(μg/tube)	(mg/m ³)	(μg/tube)	(mg/m ³)	(μg/tube)	(mg/m ³)	(μg/tube)	(mg/m ³)	
1	48.7	33.1	0.68	< 2.0	< 0.04	30.3	0.62	33.5	0.69	< 2.0	< 0.04	21.9
2	41.4 ^b	73.6	1.78	< 2.0	< 0.05	35.4	0.86	35.0	0.85	< 2.0	< 0.05	38.6
3	45.7	< 2.0	< 0.05	38.9	0.85	42.0	0.92	< 2.0	< 0.05	< 2.0	< 0.05	32.2
4	41.5	52.6	1.27	< 2.0	< 0.05	32.3	0.78	34.6	0.83	< 2.0	< 0.05	31.7
5	39.7	195	4.93	< 2.0	< 0.05	50.0	1.26	61.0	1.5	< 2.0	< 0.05	82.9
6	38.7	196	5.07	< 2.0	< 0.05	48.4	1.25	59.6	1.5	< 2.0	< 0.05	81.1
7	44.3	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05	< 0.70
8	45.8	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05	0.37
9	41.0	53.4	1.30	< 2.0	< 0.05	31.5	0.77	35.8	0.87	< 2.0	< 0.05	32.3
10	47.7	< 2.0	< 0.04	< 2.0	< 0.04	< 2.0	< 0.04	< 2.0	< 0.04	< 2.0	< 0.04	< 0.60
11	36.5	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05	< 2.0	< 0.05	< 0.80
12	0.0 ^c											
13	41.0	36.2	0.88	< 2.0	< 0.05	32.9	0.80	37.6	0.92	< 2.0	< 0.05	28.0
14	35.2	93.6	2.66	< 2.0	< 0.05	26.1	0.74	53.0	1.5	< 2.0	< 0.05	54.0
14	20.9	68.4	3.27	< 2.0	< 0.09	17.2	0.82	23.8	1.1	< 2.0	< 0.09	50.3
15	37.9	48.0	1.27	< 2.0	< 0.05	32.4	0.86	58.0	1.5	< 2.0	< 0.05	33.7
16	43.9	30.8	0.70	< 2.0	< 0.05	30.7	0.70	37.4	0.85	8.2	0.19	21.9
17	44.3	23.0	0.52	< 2.0	< 0.05	31.3	0.71	37.4	0.84	< 2.0	< 0.05	20.1
18	40.4	68.3	1.69	< 2.0	< 0.05	31.5	0.78	62.8	1.6	< 2.0	< 0.05	39.9
19	44.6	33.8	0.76	< 2.0	< 0.05	31.8	0.71	61.8	1.4	7.1	0.16	26.7
Painter	32.6 ^d	87.3	2.67	< 2.0	< 0.06	24.7	0.76	40.6	1.2	< 2.0	< 0.06	52.1
20	36.8	394	10.7	< 2.0	< 0.05	69.8	1.9	62.2	1.7	< 2.0	< 0.05	127
21	37.8	327	8.64	< 2.0	< 0.05	54.4	1.4	70.7	1.9	< 2.0	< 0.05	88.6
Blank	NA ^e	< 2.0	NA	< 2.0	NA	< 2.0	NA	< 2.0	NA	< 2.0	NA	NA
Blank	NA	< 2.0	NA	< 2.0	NA	< 2.0	NA	< 2.0	NA	< 2.0	NA	NA

^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 °F

^b Estimated operating time of 47 minutes

^c One end of charcoal tube remained sealed; no air sample was taken

^d Pump failed after 42 minutes

^e Not applicable because no sample air was drawn through the blank sample tubes.

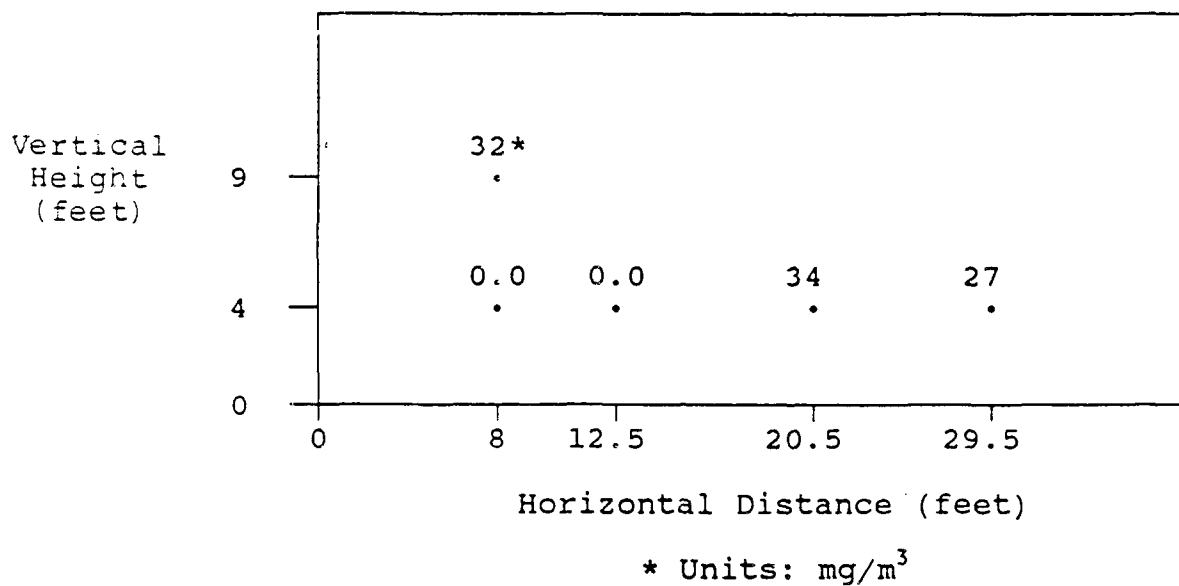


Figure 11. Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 4 Feet from North Wall

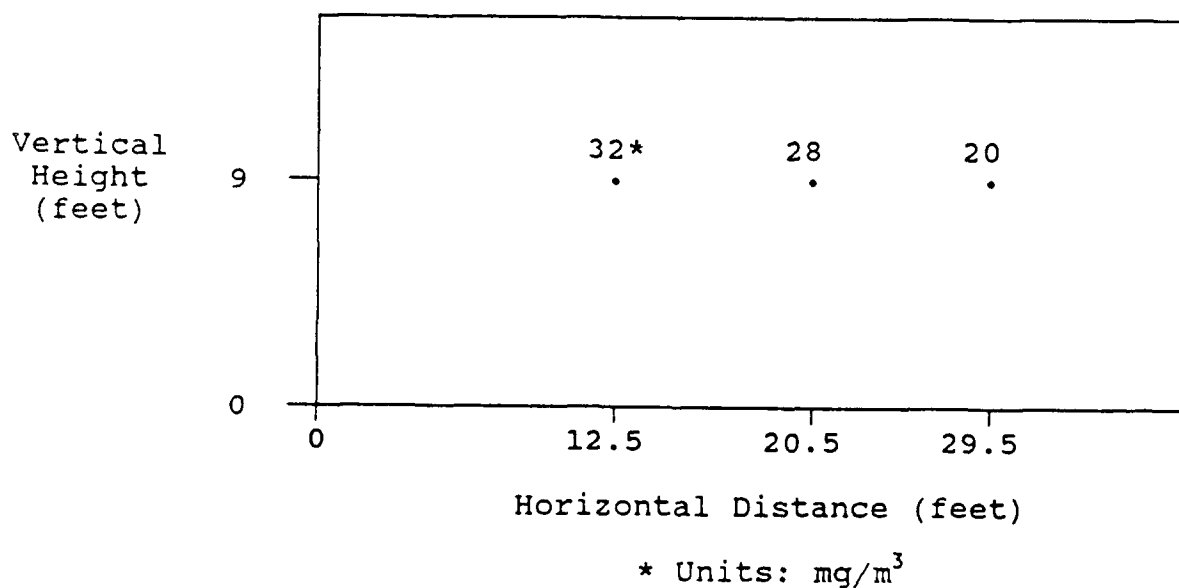


Figure 12. Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 8 Feet from North Wall

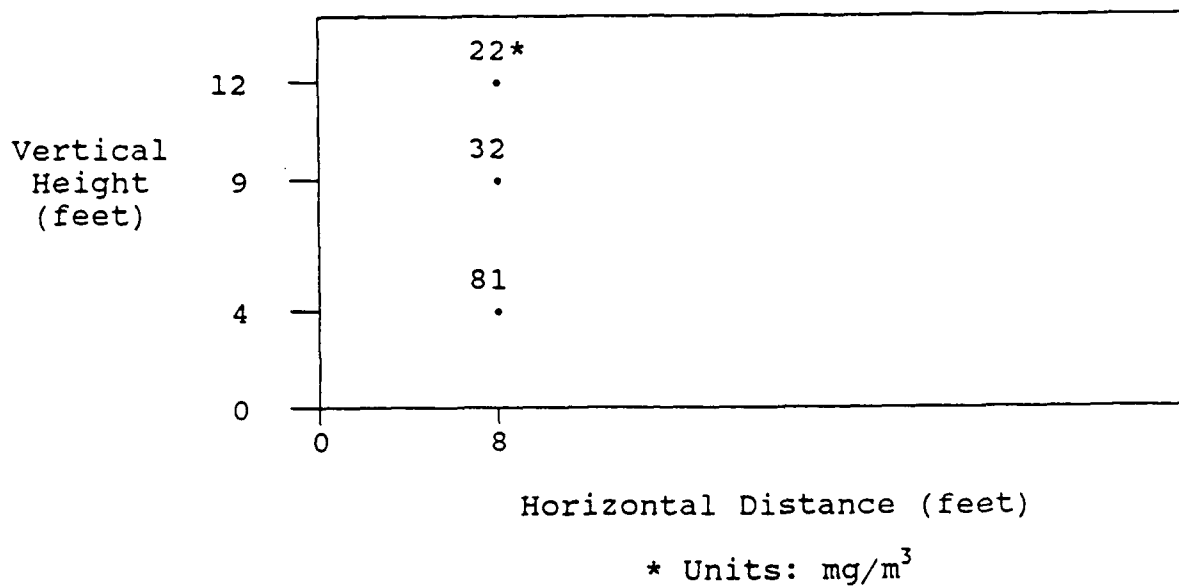


Figure 13. Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 8 Feet from North Wall

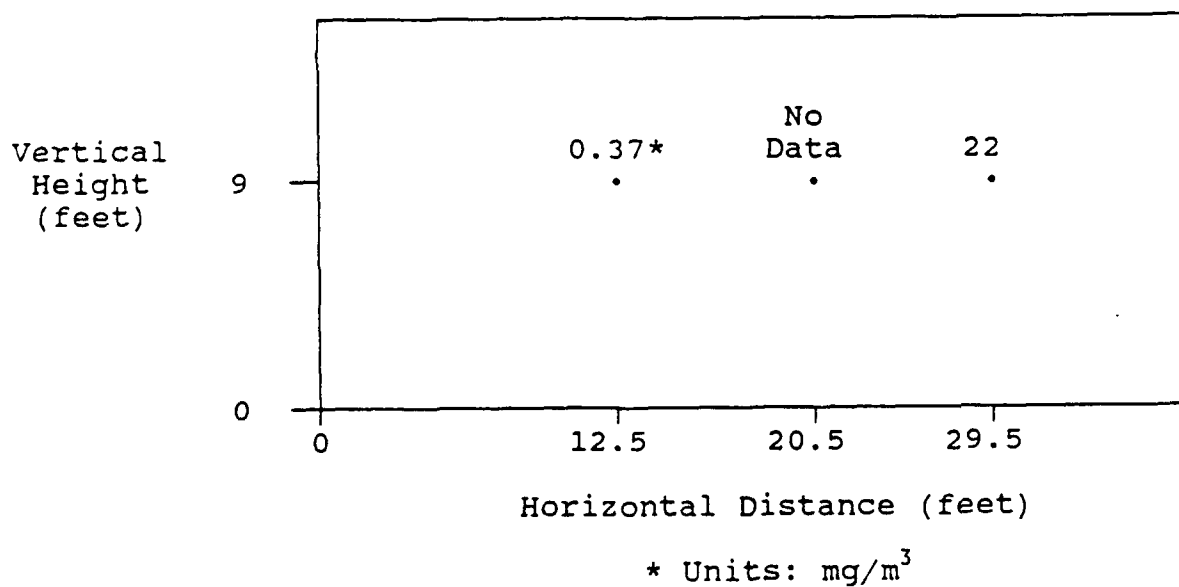


Figure 14. Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 10 Feet from North Wall

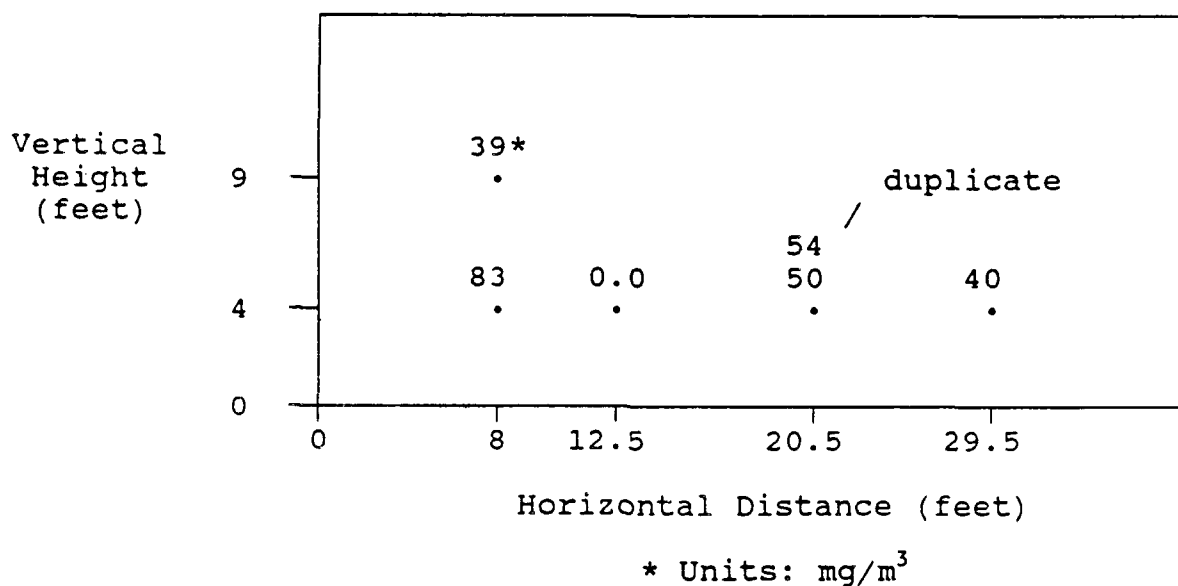


Figure 15. Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 12 Feet from North Wall

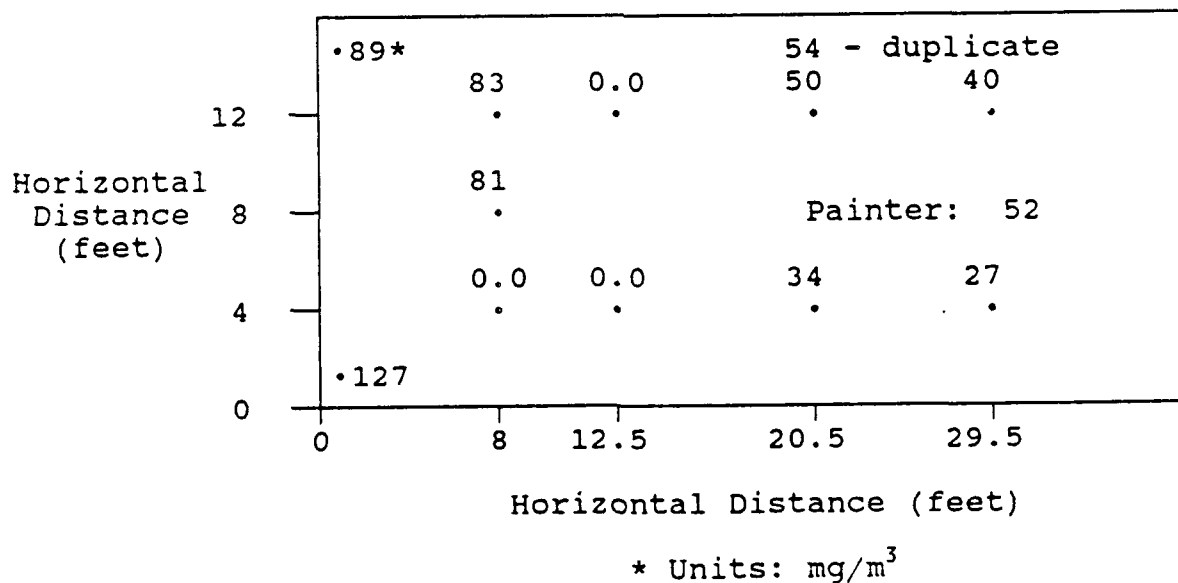


Figure 16. Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Plan View at a Height of 4 Feet

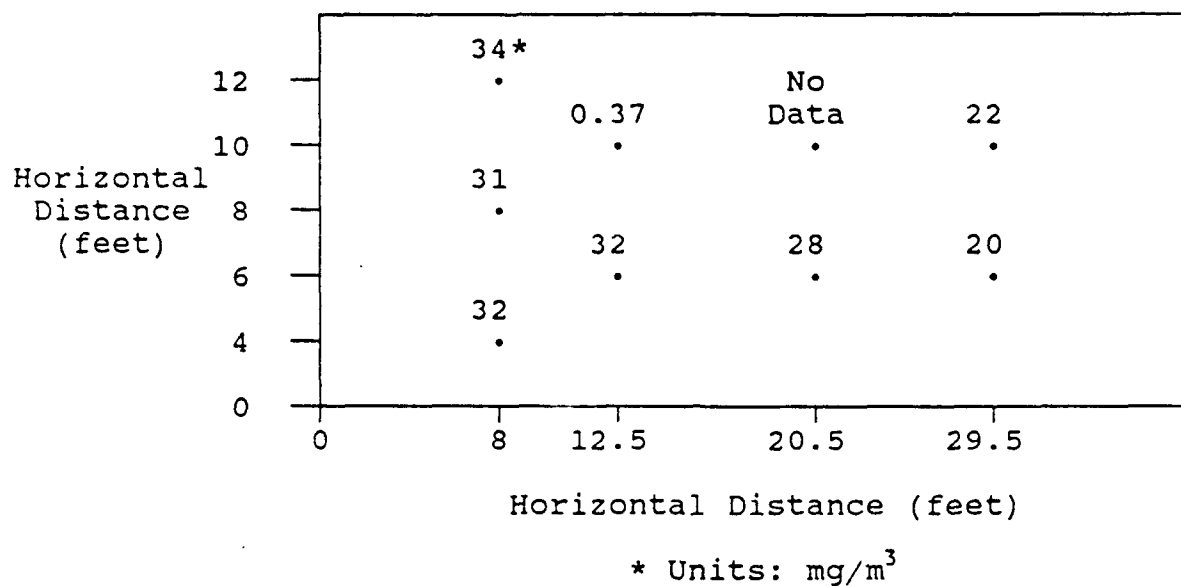


Figure 17. Volatile Organic Compound Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Plan View at a Height of 9 Feet

an approximate height of 4 feet, thus it was at a position exposed to extremely high solvent concentrations.

The results of the OVA sampling efforts were intended for use in establishing how rapidly the solvent concentration varies in time during painting. Thus, the OVA sample line was placed in a region of high solvent concentrations. It was found that the organic carbon concentration in the booth at a given location could vary by 1,000 ppm in less than 20 seconds. The organic carbon concentration measured ranged from 0 to over 1,500 ppm. During painting, the average concentration was approximately 80 ppm organic carbon; however the concentration dropped rapidly to almost zero when painting was stopped.

The instantaneous concentration measurements obtained from the OVA sampling efforts cannot be correlated to the results obtained from the integrated NIOSH 1300 charcoal tube samples for a variety of reasons. The primary reason is that the concentration in the booth varies significantly as a function of location, thus the OVA results obtained at the water curtain cannot be correlated to NIOSH 1300 results obtained anywhere else in the booth. Another reason is that the NIOSH 1300 procedure quantifies average concentrations, while the OVA results give an indication of instantaneous solvent concentrations.

2. Exhaust Duct Measurements

a. Integrated Sampling

The sample intervals and volumes used in the NIOSH 1300 tests performed in the exhaust duct are presented with the results of speciation analyses performed on each charcoal tube in Table 9.

b. Continuous Emissions Monitoring Results

Results obtained from BAAQMD Method ST-7 and EPA Method 25A sampling in the exhaust duct are presented in Tables 10 and 11, respectively. For reasons described previously, the M25A results are used only as a check on the ST-7 data, which are considered more reliable.

As discussed in Section II, the ST-7 results are presented as ppm CO₂, which is easily converted to ppm carbon. The NIOSH 1300 charcoal tube data taken in the exhaust duct (presented in Table 9) can be used to convert the ST-7 results from ppm carbon to ppm solvent. This is done in the following manner:

- (1) Determine Relative Percentage of Each Organic Compound Present.

$$X_i = \frac{\text{Mass of Solvent}_i (\mu\text{g/L})}{\text{Total Mass of Solvent Measured } (\mu\text{g/L})}$$

To check the calculations: $\sum X_i = 1$

TABLE 9. RESULTS OF INTEGRATED EXHAUST DUCT ORGANIC SPECIATION AND QUANTIFICATION MEASUREMENTS.

Date	Time	Volume Sampled (L) ^a	2-Butanone (μg/tube) (mg/m ³)	Toluene (μg/tube) (mg/m ³)	Butyl Acetate (μg/tube) (mg/m ³)	Ethylbenzene (μg/tube) (mg/m ³)	Total Xylenes (μg/tube) (mg/m ³)	Ethyl Acetate (μg/tube) (mg/m ³)	Methoxyacetone (μg/tube) (mg/m ³)							
6 Dec	1126-1226	61.3	176	2.87	<2.0	<0.03	<2.0	<0.03	<2.0	<0.03						
7 Dec	0940-1040	45.8	1830	39.9	597	13.0	450	9.83	65.0	1.4	316	6.91	1293	28.2	24.5	0.5
7 Dec	1042-1122	36.0	311	8.64	330	9.17	497	13.8	<2.0	<0.06	7.8	0.22	<2.0	<0.06	184	5.10
7 Dec	1320-1403	37.3	271	7.27	983	26.4	511	13.7	8.80	0.2	<2.0	<0.05	284	7.62	194	5.21
7 Dec	1404-1450	41.1	1970	47.9	903	22.0	439	10.7	58.4	1.4	273	6.63	1128	27.4	924	22.5
8 Dec	0940-1020	40.2	1760	43.8	104	2.58	190	4.72	27.3	0.7	111	2.77	1828	45.5	<2.0	<0.05
8 Dec	1237-1317	41.4	2800	67.5	229	5.52	455	11.0	66.4	1.6	251	6.05	174	4.19	36.0	0.87
8 Dec	1338-1418	41.4	<10	<0.24	387	9.33	<2.0	<0.05	<2.0	<0.05	<2.0	<0.05	<2.0	<0.05	<2.0	<0.05
8 Dec	1338-1418	43.1	618	14.3	372	8.64	47.9	1.11	5.30	0.1	18.9	0.44	641	14.9	67.2	1.56
8 Dec	Blank	NA ^b	<10	NA	<2.0	NA	<2.0	NA	<2.0	NA	<2.0	NA	<2.0	NA	<2.0	NA
9 Dec	0818-0900	60.1	<10	<0.17	<2.0	<0.03	<2.0	<0.03	<2.0	<0.03	<2.0	<0.03	<2.0	<0.03	125	2.07
9 Dec	0900-0940	57.6	2060	35.9	486	8.43	462	8.03	59.6	1.0	312	5.42	1156	20.1	12.4	0.22
9 Dec	Blank	NA	<10	NA	<2.0	NA	<2.0	NA	<2.0	NA	<2.0	NA	<2.0	NA	<2.0	NA

^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 °F

^b NA Not applicable because no sample air was drawn through the blank tubes.

TABLE 9. RESULTS OF EXHAUST DUCT INTEGRATED ORGANIC SPECIATION AND QUANTIFICATION MEASUREMENTS (CONCLUDED).

Date	Time	Volume Sampled (L) ^a	Ethoxyethanol (µg/tube) (mg/m ³)	MIBK (µg/tube) (mg/m ³)	2-Ethoxyethyl Acetate (µg/tube) (mg/m ³)	2-Butoxyethanol (µg/tube) (mg/m ³)	bis(2-Methoxy ethyl) Ether (µg/tube) (mg/m ³)	2-(2-Methoxy-ethoxy)ethanol (µg/tube) (mg/m ³)	Total VOC Concentration (mg/m ³)
6 Dec	1126-1226	61.3	<2.0 <0.03	<2.0 <0.03	<2.0 <0.03	33.2 0.54	<2.0 <0.03	<2.0 <0.03	3.42
7 Dec	0940-1040	45.8	108 2.36	685 15.0	1331 29.1	<2.0 <0.04	<2.0 <0.04	<2.0 <0.04	146
7 Dec	1042-1122	36.0	<2.0 <0.06	66.1 1.83	78.7 2.18	<2.0 <0.06	<2.0 <0.06	<2.0 <0.06	40.9
7 Dec	1320-1403	37.3	20.2 0.54	28.7 0.77	57.4 1.54	<2.0 <0.05	<2.0 <0.05	<2.0 <0.05	63.3
7 Dec	1404-1450	41.1	122 2.97	597 14.5	1198 29.1	<2.0 <0.05	<2.0 <0.05	<2.0 <0.05	185
8 Dec	0940-1020	40.2	38.4 0.95	<2.0 <0.05	904 22.5	<2.0 <0.05	<2.0 <0.05	63.6 1.58	125
8 Dec	1237-1317	41.4	100 2.41	<2.0 <0.05	1563 37.7	6.5 0.16	9.5 0.23	12.6 0.30	138
8 Dec	1338-1418	41.4	<2.0 <0.05	<2.0 <0.05	<2.0 <0.05	<2.0 <0.05	<2.0 <0.05	<2.0 <0.05	9.33
8 Dec	1338-1418	43.1	32.1 0.74	<2.0 <0.05	297 6.89	39.6 0.92	11.1 0.26	<2.0 <0.05	49.9
8 Dec	Blank	NA ^b	<2.0 NA	<2.0 NA	<2.0 NA	<2.0 NA	<2.0 NA	<2.0 NA	NA
9 Dec	0818-0900	60.1	<2.0 <0.03	<2.0 <0.03	<2.0 <0.03	<2.0 <0.03	<2.0 <0.03	<2.0 <0.03	2.07
9 Dec	0900-0940	57.6	96.8 1.68	730 12.7	1563 27.1	26.2 0.46	<2.0 <0.03	49.0 0.85	122
9 Dec	Blank	NA	<2.0 NA	<2.0 NA	<2.0 NA	<2.0 NA	<2.0 NA	<2.0 NA	NA

^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 °F

^b NA Not applicable because no sample air was drawn through the blank tubes.

TABLE 10. BAAQMD ST-7 CONTINUOUS ORGANIC SAMPLING RESULTS.

Date	Painting Interval	Test	Time Interval	Sample Time (min)	Paint Time (min)	Background CO ₂ (ppm)	Average CO ₂ Concentration (ppm)	Total Unburned Hydrocarbon Concentration (ppm as carbon)
6 Dec	1	Particulate 1	1122-1137	15	14	503	643	140
			1137-1152	15	15		660	157
			1152-1207	15	15		685	182
		Approximately 1130-1300	1207-1222	15	2	528	645	142
			1222-1237	15	0		609	106
			1237-1252	15	0		641	113
			1252-1307	15	0		587	59
			1307-1322	0 ^a	0		ND ^b	ND
			1322-1337	15	0		647	119
			1337-1357	20	0		654	126
	2	Particulate 2	1357-1407	10	2		645	117
			1407-1409	0	2		ND	ND
			1409-1411	2	2		1117	589
		Approximately 1400-1530	1411-1431	20	0		643	115
			1431-1449	18	18		752	224
			1449-1459	10	0		833	305
			1459-1506	7	7		675	147
			1506-1521	15	0		792	264
			1521-1536	15	0		634	106
			1536-1548	12	0		665	137
7 Dec	1	VOC 1	0930-0953	23	4	503	558	55
			0953-1008	15	15		921	418
		Approximately 0945-1030	1008-1029	21	18	503	871	368
			1029-1040	11	0		522	19
			1040-1057	0	0		ND	ND
			1057-1106	9	0		539	36
			1106-1121	15	14		821	318
			1121-1129	8	0		694	191
			1129-1146	0	0		ND	ND
			1146-1201	15	0		677	174
			1201-1216	15	0		572	69
			1216-1231	15	0		581	78
			1231-1246	15	0		598	95
			1246-1300	14	0		634	131
			1300-1315	0	0		ND	ND

^a System calibration^b No data due to system calibration

TABLE 10. BAAQMD ST-7 CONTINUOUS ORGANIC SAMPLING RESULTS (CONCLUDED).

Date	Painting Interval	Test	Time Interval	Sample Time (min)	Paint Time (min)	Background CO ₂ (ppm)	Average CO ₂ Concentration (ppm)	Total Unburned Hydrocarbon Concentration (ppm as carbon)
7 Dec	2	VOC 2 Approximately 1305-1350	1331-1347	16	16	450	734	284
			1347-1402	15	0		749	299
			1402-1414	12	0		649	199
			1414-1429	15	15		877	427
			1429-1439	10	10		846	396
			1439-1454	15	0		638	188
			1454-1509	15	0		466	16
			1509-1525	16	0		449	0
8 Dec	1	Isocyanates 1 Approximately 0850-1015	0854-0913	19	19	478	647	169
			0913-0930	17	14		749	271
			0930-0947	17	17		695	217
			0947-1002	15	0		566	88
			1002-1014	12	0		551	73
	2	Isocyanates 2 Approximately 1230-1350	1243-1301	18	18	452	766	314
			1301-1319	18	18		766	314
			1319-1332	13	13		1046	594
			1332-1347	15	0		836	384
			1347-1401	14	0		600	148
			1401-1418	17	0		653	201
9 Dec	1	Particulate 3 Approximately 0810-0940	0816-0831	15	15	503	589	86
			0831-0848	17	17		627	124
			0848-0902	14	0		860	357
			0902-0917	15	0		972	469
			0917-0934	17	0		635	132
			0934-0942	8	0		770	267

^a System calibration

^b No data due to system calibration

TABLE 11. EPA M25A CONTINUOUS ORGANIC SAMPLING RESULTS.

Date	Painting Interval	Test	Time Interval	Sample Time (min)	Paint Time (min)	Range	Average Hydrocarbon Concentration (ppm as carbon)
6 Dec	1	Particulate 1	1125-1140	15	14	0-100	8.7
			1140-1155	15	15		21.5
		Approximately 1130-1300	1155-1210	15	15		17.3
			1210-1225	15	2		12.3
			1225-1240	15	0		11.8
			1240-1255	15	0		6.4
			1255-1310	15	0		12.1
			1310-1325	15	0		7.9
			1325-1340	15	0		6.2
			1340-1400	20	0		10.5
		Unit out of service for the rest of the day					
7 Dec	1	VOC 1	0945-0956	11	4	0-100	5.9
			0956-1011	15	15	0-1000	113
		Approximately 0945-1030	1011-1032	21	17	0-100	124
			1032-1109	0 ^a	4		ND
			1109-1124	15	10		91.4
			1124-1149	0	0		ND
			1149-1204	15	0		21.5
			1204-1219	15	0		9.31
			1219-1234	15	0		10.7
			1234-1252	18	0		14.0
	2	VOC 2	1334-1350	0	16	0-100	ND
			1350-1405	0	0		ND
		Approximately 1305-1350	1405-1417	12	0		28.7
			1417-1432	15	15		152
			1432-1442	10	10		130
			1442-1451	0	0		ND
			1451-1457	6	0		23.3
			1457-1512	15	0		11.1
			1512-1528	16	0		5.32
			8 Dec	1	Isocyanates 1		0857-0916
0916-0933	17	14				57.8	
0933-0950	17	17				52.3	
Approximately 0850-1015	0950-1005	15			0	12.4	
	1005-1017	12			0	7.73	
2	Isocyanates 2	1246-1304		18	18	0-100	60.0
		1304-1312		8	8	0-1000	111
		1312-1322		0	10	ND	
	Approximately 1230-1350	1322-1335		13	13	0-1000	120
		1335-1350		15	0	66.9	
		1350-1404		14	0	43.5	
		1404-1421		17	0	0-100	30.6
		1421-1426		0	0	ND	
		1426-1445		19	0	19.1	
9 Dec	1	Particulate 3	0819-0834	15	15	0-100	18.8
			0834-0851	17	17	21.7	
			0851-0905	0	0	ND	
		Approximately 0810-0940	0905-0920	15	0	0-1000	61.8
			0920-0937	17	0	44.1	
			0937-0945	8	0	0-100	10.5

^a Difficulties encountered in keeping the TUHC meter on scale

(2) Determine Molecular Weight (MW) of Solvent. The average is weighted according to the relative percentage of each compound present.

$$MW_{avg} = \sum (MW_i \times X_i)$$

(3) Determine Number of Moles of Carbon Present per Mole of Solvent. The average is weighted as a function of the relative percent of each solvent present.

$$\#C_{avg} = \sum (\#C_i \times X_i)$$

(4) Determine Solvent Concentration. The ST-7 results (average ppm as CO₂) are multiplied by the average molecular weight and divided by the number of carbons per molecule of solvent and the conversion factor of 22.4 liters/mole to obtain the solvent concentration in grams per million liters of air.

$$\text{Solvent Concentration} = \frac{\text{ppm}_{CO_2} \times MW_{avg} \times 1 \text{ mole}_{carbon}/\text{mole}_{CO_2}}{(\#C_{avg} \times 22.4 \text{ L}_{CO_2}/\text{mole}_{CO_2})}$$

A sample calculation is provided here for the sampling interval between 0930 and 0953 on 7 December (Note: All dates are 1989). The NIOSH 1300 sampling results for that period indicate that 2-butanone, toluene, butyl acetate, ethylbenzene, xylene, ethyl acetate, 2-methoxyethanol, 2-ethoxyethanol, MIBK, and 2-ethoxyethyl acetate were present in the exhaust duct. The molecular weight of each of these compounds is 72.2, 92.2, 116, 106, 106, 88.1, 76.1, 90.1, 100, and 132, respectively. The number of carbon atoms contained in each of these compounds is 4, 7, 6, 8, 8, 4, 3, 4, 6, and 6, respectively. The ST-7 results indicate that the average carbon concentration for this period was 55 ppm. The sample calculation is as follows:

(1) Determine Relative Percentage of Each Organic Compound Present.

$$\text{2-Butanone: } \frac{39.9 \mu\text{g/L}}{146 \mu\text{g/L}} = 0.27$$

Toluene	0.089
Butyl acetate	0.067
Ethylbenzene	0.010
Xylenes	0.047
Ethyl acetate	0.193
Methoxyethanol	0.003
2-Ethoxyethanol	0.016
MIBK	0.103
2-Ethoxyethyl acetate	0.199

(2) Determine Molecular Weight of Solvent. The average is weighted according to the relative percentage of each compound present.

$$\begin{aligned}
 MW_{avg} &= \sum (MW_i \times X_i) \\
 &= [(72 \times 0.27) + (92 \times 0.089) + (116 \times 0.067) + (106 \times 0.010) + \\
 &\quad (106 \times 0.047) + (88 \times 0.193) + (76 \times 0.003) + (90 \times 0.016) + \\
 &\quad (100 \times 0.103) + (132 \times 0.199)] \\
 &= 106 \text{ grams/mole}_{\text{solvent}}
 \end{aligned}$$

(3) Determine Number of Moles of Carbon Present per Mole of Solvent. The average is weighted as a function of the relative percent of each solvent present.

$$\begin{aligned}
 \#C_{avg} &= \sum (\#C_i \times X_i) \\
 &= [(4 \times 0.27) + (7 \times 0.089) + (6 \times 0.067) + (8 \times 0.010) + \\
 &\quad (8 \times 0.047) + (4 \times 0.193) + (3 \times 0.003) + (4 \times 0.016) + \\
 &\quad (6 \times 0.103) + (6 \times 0.199)] \\
 &= 5.9 \text{ moles}_{\text{carbon}}/\text{mole}_{\text{solvent}}
 \end{aligned}$$

(4) Determine Solvent Concentration. The ST-7 results (ppm as carbon) are multiplied by the average molecular weight and divided by the number of carbons per molecule of solvent and the conversion factor of 22.4 liters/mole to obtain the solvent concentration in grams per million liters of air.

$$\begin{aligned}
 \text{Solvent Concentration} &= \frac{\text{ppm}_{\text{CO}_2} \times MW_{avg} \times 1 \text{ mole}_{\text{carbon}}/\text{mole}_{\text{CO}_2}}{(\#C_{avg} \times 22.4 \text{ L}_{\text{CO}_2}/\text{mole}_{\text{CO}_2})} \\
 &= \frac{55 \text{ ppm}_{\text{CO}_2} \times 106 \text{ gr/mole}_{\text{solvent}} \times 1 \text{ mole}_{\text{carbon}}/\text{mole}_{\text{CO}_2}}{(5.9 \text{ mole}_{\text{carbon}}/\text{mole}_{\text{solvent}} \times 22.4 \text{ L}_{\text{CO}_2}/\text{mole}_{\text{CO}_2})} \\
 &= 44 \text{ grams of solvent}/10^6 \text{ L air} \\
 &= 0.044 \text{ mg/L}
 \end{aligned}$$

c. Mass Balance Results

The paint usage rate information was combined with the ST-7 and the paint samples analysis results to perform a paint solvent mass balance on the Building 515 painting facility. The ST-7 data yield a continuous measurement of the total quantity of organic carbon present in the exhaust duct. The paint usage rate information was combined with the results

of the paint density and percent volatile analyses to determine the quantity of paint solvent emitted into the booth during paint application. Results from the paint speciation analyses were used to determine the quantity of organic carbon released into the booth in the form of paint solvents. The mass balance is the percent agreement between the calculated quantity of organic carbon released into the booth and the quantity measured in the exhaust duct. The mass balance results are presented in Table 12.

A mass balance calculation was performed for every sampling event. Thus, two mass balance results were obtained for each full day of testing (6, 7, and 8 December), and one mass balance was performed for the half day of testing conducted 9 December.

The results of the mass balance efforts are quite good. For the first day of tests (6 December) all of the solvent released into the booth was accounted for in the mass balance. For the first and second sampling events of that day, 108 and 107 percent of the solvent vapor released into the booth was measured in the exhaust duct, respectively. For both the first and second sampling events of 7 December, 134 percent of the solvent released into the booth was measured in the exhaust duct. For the first and second sampling events of 8 December, 98 and 167 percent, respectively, of the solvent released into the booth was measured in the exhaust duct. The mass balance results for the final sampling event (9 December) indicate that 103 percent of the solvent released into the booth was measured in the exhaust duct.

For the first 1-1/2 days of testing, a significant background solvent concentration was present in the paint booth exhaust because the paint booth operators added an unknown quantity of pine-oil-based detergent to the sump immediately prior to testing. This background solvent concentration was quantified for each sampling event by identifying the steady-state solvent concentration measured in the duct at a time when no paint was applied. This steady-state level was assumed to be the background concentration and was not included in the calculation. When painting in the booth stopped, the data collected after the background concentration level was achieved were not included in the mass balance calculation.

The solvent emission rates measured in the exhaust duct are consistently higher than the quantity of solvent released into the booth during painting. The most likely reason for this apparent discrepancy is that the paint booth operators often left open containers of paint and solvent in the booth before, during, and after painting. On occasion, as many as three open paint and solvent containers were left in the booth. The solvent vapors emitted as a result of this practice were measured in the exhaust duct, yet their contribution to the quantity of solvent released in the booth is not included in the paint usage data collected. To quantify contributions from the open containers would require that they be weighed before and after each test to determine the weight loss due to solvent volatilization. During the test series, it was not believed

TABLE 12. SOLVENT MASS BALANCE RESULTS.

Date	Painting Interval	Test	Time Interval	Mass of Carbon Measured in Stack [ST-7 data] (g)	Mass of Carbon Released into Booth [paint usage data] (g)	Percent of Solvents Released in booth that are accounted for (percent)
6 Dec	1	Particulate 1	1122-1137	226	337	
			1137-1152	269	362	
			1152-1207	332	362	
		Approximately 1130-1300	1207-1222	232	48	
			1222-1237	141	0	
			Total:	1200	1109	
	2	Particulate 2	1357-1407	154	148	
			1407-1409	0	148	
			1409-1411	188	148	
		Approximately 1400-1530	1411-1431	304	0	
			1431-1449	599	1331	
			1449-1459	468	0	
			1459-1506	143	518	
			1506-1521	598	0	
			Total:	2454	2293	
						107
7 Dec	1	VOC 1	0930-0953	211	242	
			0953-1008	1050	906	
			1008-1029	1293	1088	
		Approximately 0945-1030	1029-1040	36	0	
			1040-1057	0	0	
			1057-1106	54	0	
			1106-1121	799	846	
			1121-1129	256	0	
			1129-1146	0	0	
			1146-1201	436	0	
			Total:	4135	3082	
						134

TABLE 12. SOLVENT MASS BALANCE RESULTS (CONCLUDED).

Date	Painting Interval	Test	Time Interval	Mass of Carbon Measured in Stack [ST-7 data] (g)	Mass of Carbon Released into Booth [paint usage data] (g)	Percent of Solvents Released in booth that are accounted for (percent)
7 Dec	2	VOC	1331-1347	763	1006	
		2	1347-1402	752	0	
			1402-1414	1074	0	
		Approximately	1414-1429	400	943	
		1305-1350	1429-1439	0	629	
			1439-1454	474	0	
		Total:	3463	2578	134	
8 Dec	1	Isocyanates	0854-0913	559	921	
		1	0913-0930	803	679	
		Approximately	0930-0947	642	824	
		0850-1015	0947-1002	230	0	
			1002-1014	151	0	
		Total:	2385	2424	98	
	2	Isocyanates	1243-1301	903	885	
		2	1301-1319	903	885	
			1319-1332	1286	639	
		Approximately	1332-1347	937	0	
		1230-1350				
		Total:	4029	2409	167	
9 Dec	1	Particulate	0816-0831	216	831	
		3	0831-0848	352	941	
			0848-0902	833	775	
		Approximately	0902-0917	1175	665	
		0810-0940	0917-0934	373	0	
			0934-0942	356	0	
		Total:	3305	3212	103	

that the solvent emissions from these containers were significant. It was not until after the test series was concluded, and the mass balance calculations were completed, that their impact on the results was realized.

As indicated in Table 12, four of the closure results were very close to 100 percent. The remaining three measurements were consistently higher. The more precise closure results were obtained for painting cycles in which an air-atomized spray gun was used, while the results with lower closure agreements were obtained from painting cycles in which an air-assisted airless spray system was used. The quantity of paint and cleaning solvent dispensed by the air-assisted airless spray system is difficult to determine accurately, because a large volume of solvent is stored in the 20+ foot feeder lines that connect the gun to the paint vat. If the quantity of solvent contained in these lines is not accurately estimated, the closure results will be skewed. Thus, the poor closure results obtained for three of the mass balance calculations are due to low paint throughput estimates for the air-assisted airless spray system, combined with the presence of (unaccounted for) open paint cans in the booth.

D. AIRBORNE PARTICULATE AND METALS CONCENTRATION MEASUREMENTS

1. In-Booth Measurement Results

Particulate and metal concentrations in the booth were measured according to NIOSH 500 sampling procedures using the three-dimensional sampling grid discussed in Section II. Two sampling tests were conducted on 6 December, and a third test was performed on 9 December. The mass of particulate collected on each filter was determined for all three tests; however, metals analyses were performed on only the second and third sets of filters.

As discussed previously, the filters used for the NIOSH 500 test series were composed of cellulose ester, rather than the standard glass fiber, because cellulose ester filters give much better metals analysis results than glass fiber. Unfortunately, cellulose ester is hygroscopic, thus the filters tended to absorb moisture during weighing. This tendency made it very difficult to weigh the filters accurately. As a result, a true filter "dry weight" could not be established, and the measured weights themselves are suspect to some degree.

An additional problem that was encountered in using the cellulose ester filters was that some of the filters became fused to the plastic cassettes in which they were loaded and transported after initial weighing was completed. When this happened, the outside of the filter, which was in direct contact with the cassette holder, remained fused to the plastic and could not be completely removed. This affected the particulate measurement results; however, it had no impact on the metals analysis results.

The problems associated with the hygroscopic nature of the cellulose ester filter and the fusion problem contributed to uncertainties in the filter weight results. However, based on the results obtained from the filter blanks, the filter weights reported are believed reliable to within

± 0.1 mg. Obviously, if the associated problems had been known beforehand, a different filter medium would have been used.

The results of the particulate sampling tests in the booth are presented in Tables 13, 14, and 15. The results from these tests indicate that the particulate concentrations measured at the 4-foot level are much higher than at the 9- and 12-foot levels.

The particulate filter samples from Tests 2 and 3 were analyzed for the presence of 14 metals: antimony, barium, cadmium, chromium, cobalt, copper, lead, molybdenum, nickel, silver, thallium, titanium, vanadium, and zinc. The weighing problem associated with the cellulose ester filters did not affect the metals analysis results because the filter weights are not necessary to determine metal concentrations. Furthermore, the problem associated with the filters fusing to the holder cartridge did not affect the metals analysis results because the areas of the filter fused to the cartridge did not contain any sample (and therefore did not contain any metals), thus the loss of those areas is unimportant. For these reasons, the metals analysis results are considered quite valid and a better indication of the particulate distribution in the booth than the results obtained by gravimetric analysis.

The results of the first in-booth metals concentration profile measurement are presented in Table 16 and Figures 18 through 24. In these figures, the total metals concentration was determined by summing the concentrations of all the metals analyzed. Figures 18 through 22 present side view concentration profiles at several distances from the north wall of the booth. Figures 23 and 24 present plan view concentration variations measured at two different heights. These results (which are not blank corrected) indicate that metal concentrations are nearly an order of magnitude higher at the 4-foot level than at the 9- and 12-foot levels. In addition, the metals concentration in the vicinity of the painter was extremely high; higher concentrations were measured in only two locations. At one of these locations (where 1.38 mg/m^3 were measured), it is likely that the paint spray gun was directed toward the filter sample during this test. These results prove that significant pollutant stratification occurs in the booth during painting far more conclusively than the particulate concentration results obtained via gravimetric analysis.

The results of the second metals concentration profile measurements are presented in Table 17 and Figures 25 through 31. Figures 25 through 29 illustrate side view concentration profiles at several distances from the north wall of the booth. Figures 30 and 31 illustrate plan view concentration profiles at heights of 4 and 9 feet. As with the previous test, these results (which are not blank corrected) indicate that concentrations at the 4-foot level are nearly an order of magnitude higher than at the 9-foot level. At some locations, it appears that the paint spray gun was pointed directly at a particular filter because the measured concentrations are quite high. High concentrations were generally found at the northwest and southeast corners

TABLE 13. RESULTS OF INTEGRATED PARTICULATE CONCENTRATION MEASUREMENTS IN BOOTH—TEST 1.

Position	Volume Sampled (L) ^a	Initial Weight (g)	Final Weight (g)	Weight Change (g)	Particulate Concentration (mg/m ³)	Comments
1	91.7	0.0332	0.0330	-0.0002	NA ^b	Filter fused to cartridge
2	83.3	0.0340	0.0343	0.0003	3.72	
3	86.5	0.0338	0.0342	0.0004	4.74	Sample pump failure
4	0.00	0.0336	0.0338	0.0002	ND ^c	
5	94.7	0.0342	0.0344	0.0002	1.90	
6	88.5	0.0361	0.0361	-0.0001	NA	Filter fused to cartridge
7	84.6	0.0356	0.0361	0.0004	4.96	
8	97.1	0.0345	0.0349	0.0003	3.50	Filter fused to cartridge
9	76.4	0.0338	0.0338	0.0001	1.05	
10	94.9	0.0335	0.0338	0.0003	2.95	
11	85.7	0.0341	0.0340	-0.0001	NA	Filter fused to cartridge
12	98.2	0.0348	0.0349	0.0002	1.53	
13	76.6	0.0333	0.0335	0.0002	2.35	Filter fused to cartridge
14	96.0	0.0350	0.0349	-0.0001	NA	
15	85.2	0.0365	0.0356	-0.0009	NA	Filter fused to cartridge
16	103	0.0343	0.0346	0.0002	2.32	
17	80.9	0.0345	0.0348	0.0003	3.21	Filter fused to cartridge
18	101	0.0345	0.0346	0.0001	1.48	
19	0.00	0.0364	0.0363	-0.0001	NA	
20	76.6	0.0373	0.0380	0.0008	9.79	Filter fused to cartridge
21	76.2	0.0354	0.0356	0.0001	1.44	
Painter	65.6	0.0366	0.0370	0.0005	7.02	Sampling Error
Duct	61.2	0.0000	0.0000	0.0000	ND	

^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 °F

^bNA Not applicable due to negative weight gain of filter

^cND No data available due to sampling error

TABLE 14. RESULTS OF INTEGRATED PARTICULATE CONCENTRATION MEASUREMENTS IN BOOTH—TEST 2.

Position	Volume Sampled (L) ^a	Initial Weight (g)	Final Weight (g)	Weight Change (g)	Particulate Concentration (mg/m ³)	Comments
1	<50	0.0341	0.0343	0.0002	ND ^b	Sample pump failure
2	<50	0.0369	0.0371	0.0003	ND	
3	112	0.0385	0.0385	0.0000	0.00	Sample pump failure
4	107	0.0358	0.0360	0.0002	1.69	
5	99.1	0.0341	0.0355	0.0014	14.1	
6	100	0.0344	0.0347	0.0003	3.29	Filter fused to cartridge
7	99.4	0.0350	0.0356	0.0006	5.83	
8	110	0.0363	0.0365	0.0002	1.82	
9	105	0.0362	0.0364	0.0002	2.20	Filter fused to cartridge
10	104	0.0335	0.0340	0.0006	5.31	
11	108	0.0341	0.0344	0.0003	3.06	
12	127	0.0352	0.0351	-0.0001	0.00	Filter fused to cartridge
13	131	0.0351	0.0349	-0.0002	NA ^c	
14	109	0.0371	0.0374	0.0003	3.03	
14	110	0.0366	0.0371	0.0005	4.45	Sampling error
15	113	0.0363	0.0375	0.0012	10.7	
16	133	0.0342	ND	ND	ND	
17	127	0.0345	0.0348	0.0003	2.04	Filter fused to cartridge
18	129	0.0364	0.0365	0.0000	0.31	
19	123	0.0357	0.0362	0.0004	3.50	
20	91.7	0.0340	0.0345	0.0005	5.78	Filter fused to cartridge
21	89.9	0.0343	0.0346	0.0003	2.89	
Duct	95.1	0.0363	0.0363	0.0000	0.00	Sampling Error
Painter	75.1	0.0370	0.0372	0.0003	3.60	

^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 °F

^bND No data available due to sampling error

^cNA Not applicable due to negative weight gain of filter

TABLE 15. RESULTS OF INTEGRATED PARTICULATE CONCENTRATION MEASUREMENTS IN BOOTH—TEST 3.

Position	Volume Sampled (L ^a)	Initial Weight (g)	Final Weight (g)	Weight Change (g)	Particulate Concentration (mg/m ³)	Comments
1	160	0.0373	0.0373	0.0000	0.00	
2	121	0.0367	0.0368	0.0002	1.40	Sampling time was estimated
3	158	0.0372	0.0374	0.0002	1.33	
4	135	0.0369	0.0372	0.0003	1.92	
5	129	0.0362	0.0371	0.0009	7.26	
6	133	0.0364	0.0375	0.0011	8.10	
7	131	0.0371	0.0373	0.0002	1.67	
8	134	0.0375	0.0376	0.0001	1.05	
9	118	0.0356	0.0357	0.0001	0.93	
10	143	0.0368	0.0391	0.0023	16.1	
11	115	0.0349	0.0353	0.0004	3.38	
12	140	0.0354	0.0351	-0.0003	NA ^b	Filter fused to cartridge
13	125	0.0370	0.0372	0.0002	1.44	
14	134	0.0376	0.0379	0.0003	2.47	
15	123	0.0357	0.0363	0.0006	5.03	
16	131	0.0360	0.0363	0.0003	1.98	
17	120	0.0450	0.0449	-0.0001	0.00	
18	125	0.0372	0.0376	0.0004	3.52	
19	117	0.0367	0.0377	0.0011	9.20	
20	109	0.0372	0.0396	0.0024	21.6	Pump failed after 24 min
Painter	104	0.0371	0.0383	0.0012	11.5	

^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 °F

^b NA Not applicable due to negative weight gain of filter

TABLE 16. RESULTS OF INTEGRATED METAL CONCENTRATION MEASUREMENTS IN BOOTH TEST 2.

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TABLE 16. RESULTS OF INTEGRATED METAL CONCENTRATION MEASUREMENTS IN BOOTH—TEST 2.

Position	Volume Sampled (L)	Barium	Chromium	Copper	Lead	Molybdenum	Nickel	Titanium	Zinc	Total Metals
		(μg)	(mg/m^3)	(μg)	(mg/m^3)	(μg)	(mg/m^3)	(μg)	(mg/m^3)	(mg/m^3)
1	0.00	< 0.30	0.39	0.39	0.50	0.32	0.80	< 0.30	2.60	MA
2	0.00	< 0.30	0.42	0.41	< 0.03	0.32	< 0.30	< 0.30	1.40	MA
3	112	0.45	0.65	0.53	0.92	0.40	0.52	< 0.30	3.90	0.066
4	107	0.55	0.71	0.37	0.35	0.32	0.33	< 0.30	3.50	0.057
5	99.1	0.82	10.4	0.62	0.105	0.40	< 0.30	0.50	5.40	0.263
6	100	0.93	12.6	0.67	0.079	0.40	< 0.30	0.63	3.70	0.486
7	92.4	0.71	9.30	0.52	0.304	< 0.30	< 0.30	1.30	4.70	0.426
8	110	0.60	0.91	0.45	0.246	0.47	0.89	0.0077	4.10	0.066
9	105	0.46	0.65	0.47	0.032	< 0.30	0.85	< 0.30	2.10	0.041
10	104	0.65	8.30	0.49	0.059	< 0.30	< 0.30	< 0.30	3.50	0.326
11	108	1.70	9.00	0.47	0.195	0.32	< 0.30	0.32	3.60	0.342
12	127	0.71	0.68	0.47	0.200	< 0.30	< 0.30	0.48	2.70	0.047
13	131	0.53	0.58	0.45	1.10	0.32	< 0.30	< 0.30	2.90	0.043
14	109	0.63	5.60	0.37	0.76	0.32	< 0.30	0.30	3.60	0.236
15	110	1.20	14.6	0.50	14.7	0.47	< 0.30	0.56	5.40	0.490
16	113	1.80	35.2	0.41	31.2	0.40	< 0.30	1.30	8.00	1.36
17	127	0.74	0.55	0.84	0.971	< 0.30	< 0.30	0.48	12.8	0.126
18	129	0.61	2.50	0.44	0.32	0.32	< 0.30	< 0.30	6.80	0.106
19	123	0.65	5.20	0.47	0.0255	< 0.30	< 0.30	< 0.30	17.5	0.329
20	91.7	0.96	17.0	0.50	16.3	< 0.30	< 0.30	0.30	3.00	0.345
21	89.9	0.58	4.30	0.42	0.092	0.40	< 0.30	0.78	2.80	0.177
Duct	95.1	0.49	4.60	0.43	0.0768	0.32	0.56	< 0.30	3.20	0.243
Painter	75.1	0.63	6.80	0.39	14.4	< 0.35	< 0.35	< 0.35	3.20	0.434
Blank	MA	< 0.30	0.45	0.41	20.5	0.32	0.47	0.30	1.50	MA

^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 °F.

^b MA Not applicable because no sample air was drawn through filter.

^c NI No information.

Note: These results have not been blank corrected.

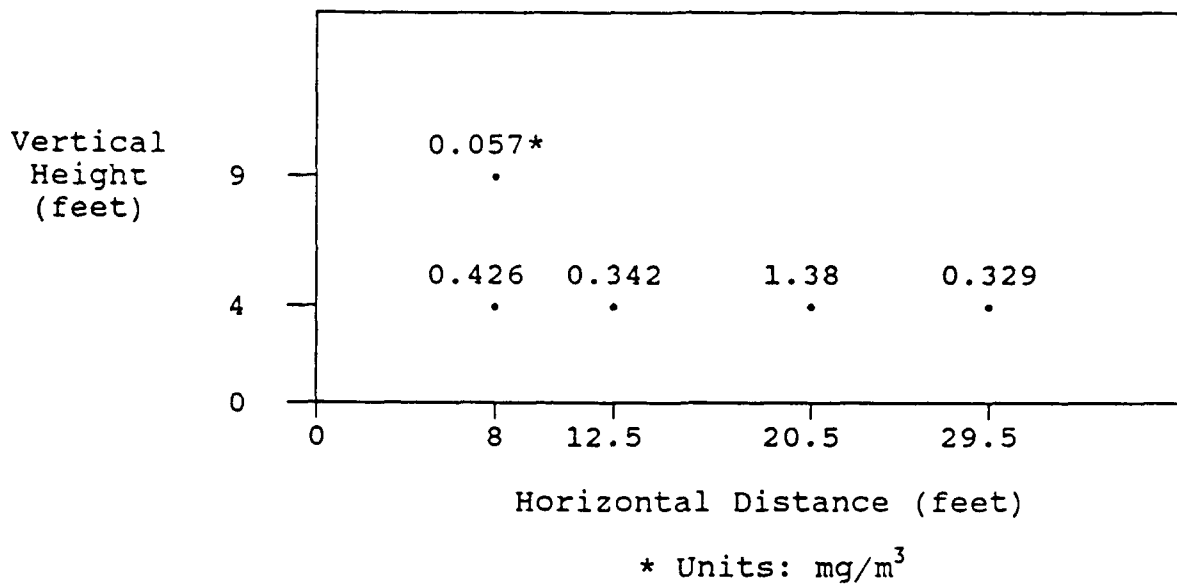


Figure 18. Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 4 Feet from North Wall

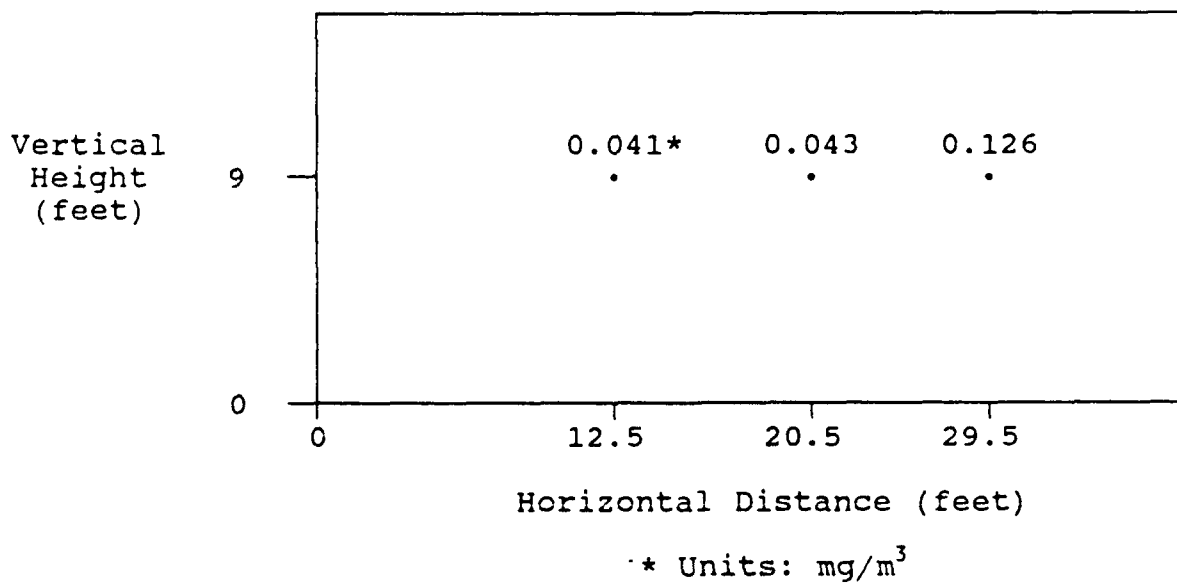


Figure 19. Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 6 Feet from North Wall

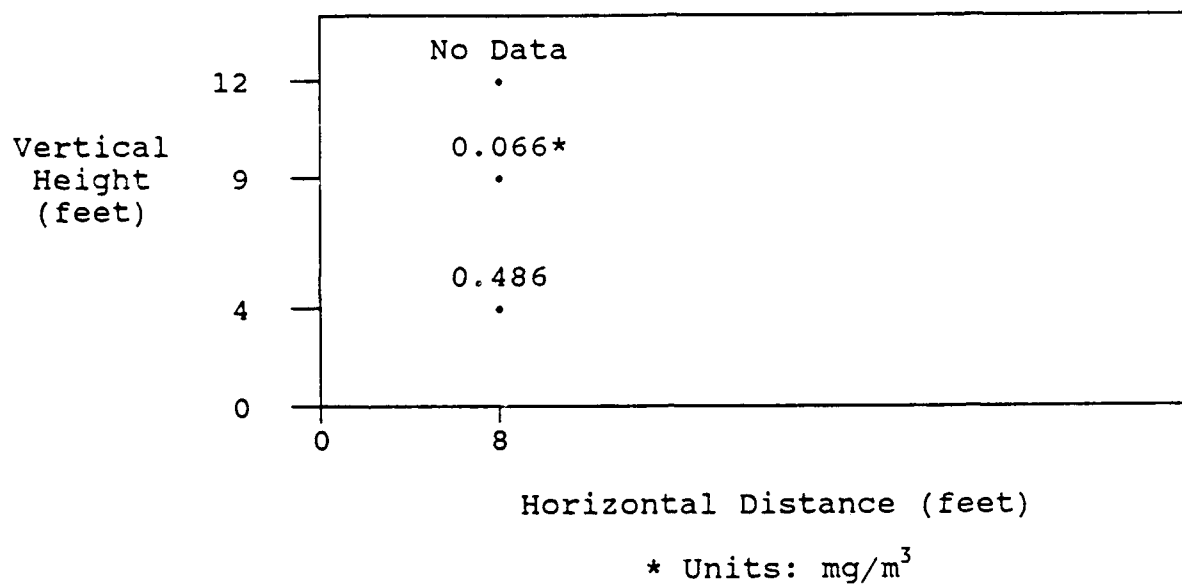


Figure 20. Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 8 Feet from North Wall

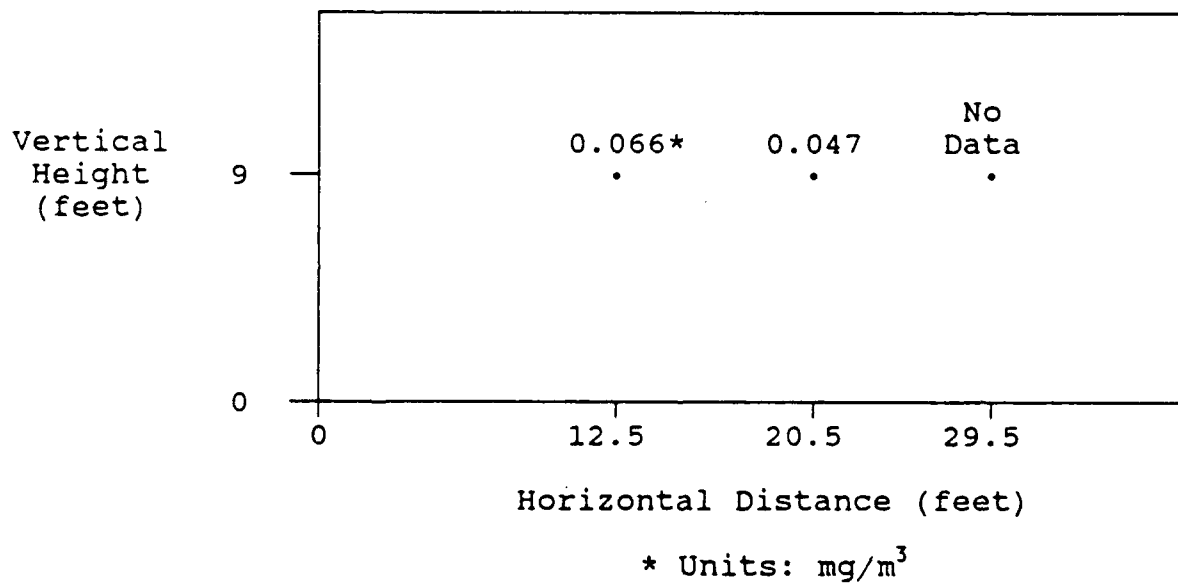


Figure 21. Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 10 Feet from North Wall

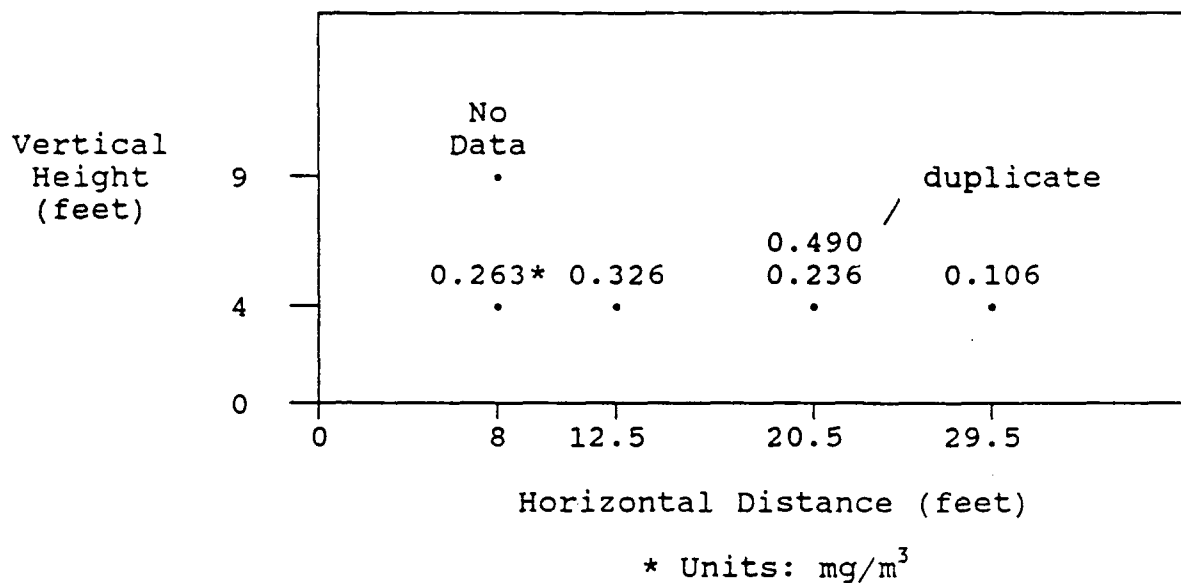


Figure 22. Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 12 Feet from North Wall

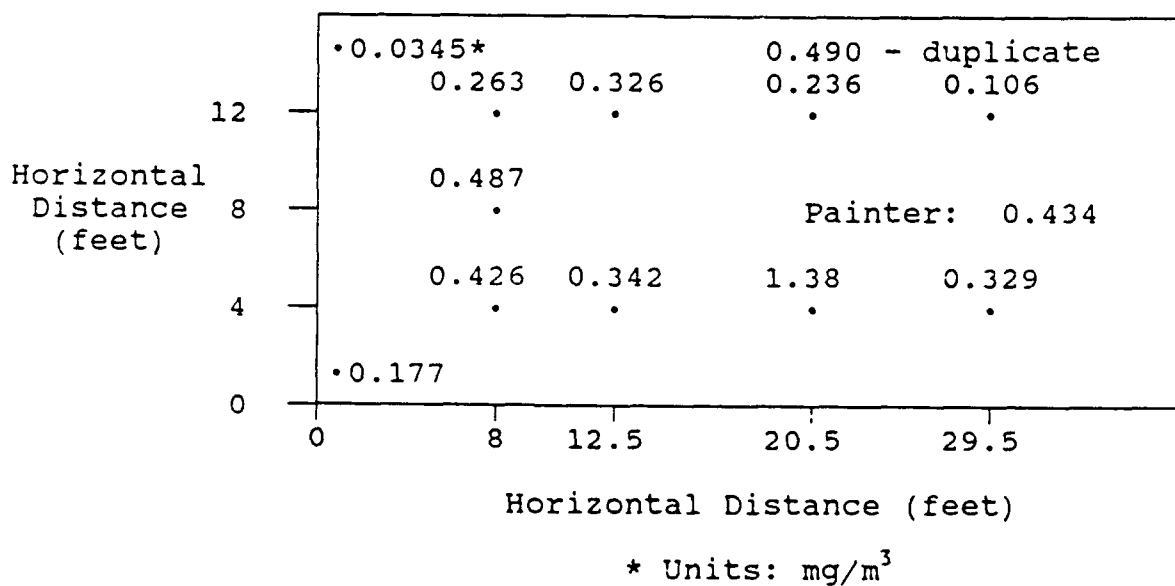


Figure 23. Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Plan View at a Height of 4 Feet

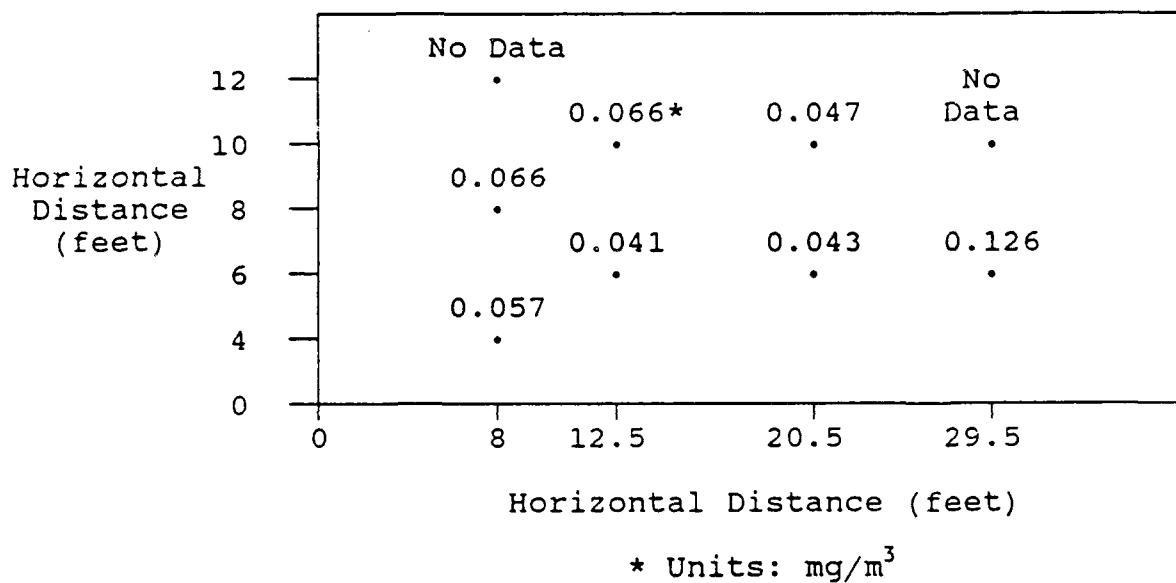


Figure 24. Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Plan View at a Height of 9 Feet

TABLE 17. RESULTS OF INTEGRATED METAL
CONCENTRATION MEASUREMENTS IN
BOOTH - TEST 3.

Position	Volume Sampled (L)	Barium (μg)	Chromium (μg)	Copper (μg)	Lead (μg)	Molybdenum (μg)	Nickel (μg)	Zinc (μg)	Total Metals (mg/m^3)
1	160	1.60	0.0100	0.80	0.0050	0.32	0.0020	< 0.30	0.008
2	121	4.40	0.0362	0.34	0.0009	< 0.30	< 0.0025	11.4	0.071
3	158	5.30	0.0309	0.60	0.0051	0.32	0.0020	1.90	0.016
4	135	8.80	0.0651	0.30	0.0027	< 0.30	< 0.0027	5.80	0.037
5	129	16.2	0.141	0.36	0.0026	0.47	0.0036	8.10	0.060
6	133	29.7	0.223	0.42	0.0031	< 0.30	< 0.0022	3.30	0.025
7	131	3.20	0.024	0.37	0.0028	< 0.30	< 0.0022	2.50	0.019
8	136	2.10	0.0157	0.36	0.0027	< 0.30	< 0.0022	1.70	0.013
9	118	5.50	0.0627	0.45	0.0038	< 0.30	< 0.0025	3.60	0.025
10	163	82.8	0.285	0.46	0.0032	5.40	0.0191	2.20	0.015
11	115	1.10	0.0025	0.45	0.0039	0.32	0.0028	1.90	0.016
12	140	2.09	0.0307	0.71	0.0051	< 0.30	< 0.0021	4.20	0.030
13	125	2.40	0.0192	0.44	0.0033	0.40	0.0032	1.40	0.011
14	134	5.70	0.0427	0.37	0.0028	< 0.30	< 0.0022	2.20	0.016
15	123	13.2	0.1072	0.75	0.0059	0.47	0.0038	5.50	0.045
16	131	6.40	0.0668	0.52	0.0034	0.32	0.0024	1.70	0.013
17	120	2.30	0.0192	0.39	0.0033	< 0.30	< 0.0025	2.10	0.018
18	125	18.5	0.148	0.44	0.0035	< 0.30	< 0.0024	1.70	0.014
19	117	17.1	0.148	0.76	0.0065	0.47	0.0040	9.80	0.083
20	109	97.7	0.899	1.40	0.0129	0.32	0.0029	5.40	0.050
Painter	104	26.0	0.250	0.49	0.0047	< 0.30	< 0.0029	2.40	0.023
Blank	NA ^a	< 0.30	NA	0.41	NA	0.32	NA	1.50	NA

^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 °F.

NA Not applicable because no sample air was drawn through filter.

Note: These results have not been blank corrected.

TABLE 17. RESULTS OF INTEGRATED METAL
CONCENTRATION MEASUREMENTS IN
BOOTH—TEST 3.

Position	Volume Sampled (L ^a)	Barium		Chromium		Copper		Lead		Molybdenum		Nickel		Zinc		Total Metals (mg/m ³)
		(μg)	(mg/m ³)	(μg)	(mg/m ³)	(μg)	(mg/m ³)	(μg)	(mg/m ³)	(μg)	(mg/m ³)	(μg)	(mg/m ³)	(μg)	(mg/m ³)	
1	160	1.60	0.0100	1.40	0.0087	0.80	0.0050	0.24	0.0015	0.32	0.0020	< 0.30	< 0.0019	11.4	0.071	0.098
2	121	4.40	0.0362	4.30	0.0354	0.34	0.0028	0.11	0.0009	< 0.30	< 0.0025	< 0.30	< 0.0025	1.90	0.016	0.091
3	158	3.30	0.0209	2.30	0.0146	0.80	0.0051	0.24	0.0015	0.32	0.0020	0.47	0.0030	5.80	0.037	3.084
4	135	8.80	0.0651	7.00	0.0518	0.36	0.0027	0.33	0.0024	< 0.30	< 0.0022	< 0.33	< 0.0024	8.10	0.060	0.182
5	129	18.2	0.141	28.0	0.216	0.36	0.0028	7.50	0.0579	0.47	0.0036	0.42	0.0032	3.30	0.025	0.450
6	133	29.7	0.223	48.0	0.360	0.42	0.0031	0.29	0.0022	< 0.30	< 0.0022	< 0.30	< 0.0022	2.50	0.019	0.607
7	131	3.20	0.0244	2.50	0.0190	0.37	0.0028	0.06	0.0005	< 0.30	< 0.0023	< 0.30	< 0.0023	1.40	0.011	0.057
8	134	2.10	0.0157	2.20	0.0165	0.36	0.0027	0.30	0.0022	< 0.30	< 0.0022	< 0.30	< 0.0022	1.70	0.013	0.050
9	118	5.50	0.0467	6.40	0.0543	0.45	0.0038	0.19	0.0016	< 0.30	< 0.0025	< 0.30	< 0.0025	3.00	0.025	0.132
10	143	82.8	0.5785	52.4	0.366	0.46	0.0032	120	0.838	5.60	0.0391	< 0.35	< 0.0024	2.20	0.015	1.84
11	115	1.10	0.0095	1.00	0.0087	0.45	0.0039	0.10	0.0008	0.32	0.0028	0.33	0.0029	1.90	0.016	0.045
12	140	2.90	0.0207	2.40	0.0172	0.71	0.0051	0.34	0.0024	< 0.30	< 0.0021	< 0.30	< 0.0021	4.20	0.030	0.075
13	125	2.40	0.0192	2.80	0.0223	0.44	0.0035	0.16	0.0013	0.40	0.0032	< 0.30	< 0.0024	1.40	0.011	0.061
14	134	5.70	0.0427	7.80	0.0584	0.37	0.0028	0.13	0.0010	< 0.30	< 0.0022	0.52	0.0039	2.20	0.016	0.125
15	123	13.2	0.1072	26.7	0.217	0.73	0.0059	0.45	0.0037	0.47	0.0038	0.71	0.0058	5.50	0.045	0.388
16	131	6.40	0.0488	2.50	0.0191	0.32	0.0024	0.12	0.0009	0.32	0.0024	< 0.30	< 0.0023	1.70	0.013	0.087
17	120	2.30	0.0192	2.20	0.0183	0.39	0.0033	0.14	0.0012	< 0.30	< 0.0025	< 0.30	< 0.0025	2.10	0.018	0.059
18	125	18.5	0.148	7.90	0.0632	0.44	0.0035	0.29	0.0023	< 0.30	< 0.0024	< 0.30	< 0.0024	1.70	0.014	0.231
19	117	17.1	0.146	36.9	0.314	0.76	0.0065	0.33	0.0028	0.47	0.0040	0.33	0.0028	9.80	0.083	0.559
20	109	97.7	0.899	85.6	0.788	1.40	0.0129	0.23	0.0021	0.32	0.0029	< 0.30	< 0.0028	5.40	0.050	1.76
Painter	104 ^b	26.0	0.250	46.8	0.449	0.49	0.0047	1.20	0.0115	< 0.30	< 0.0029	< 0.30	< 0.0029	2.40	0.023	0.738
Blank	NA	< 0.30	NA	0.45	NA	0.41	NA	0.17	NA	0.32	NA	< 0.30	NA	1.50	NA	NA

^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 F

^b NA Not applicable because no sample air was drawn through filter

Note: These results have not been blank corrected.

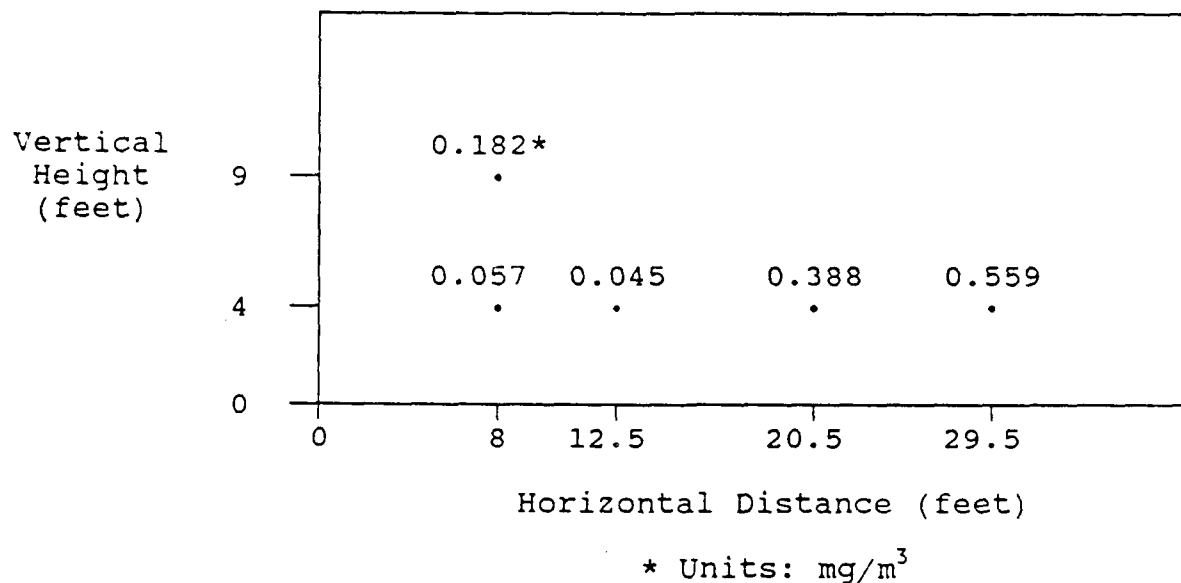


Figure 25. Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 3, Side View, 4 Feet from North Wall

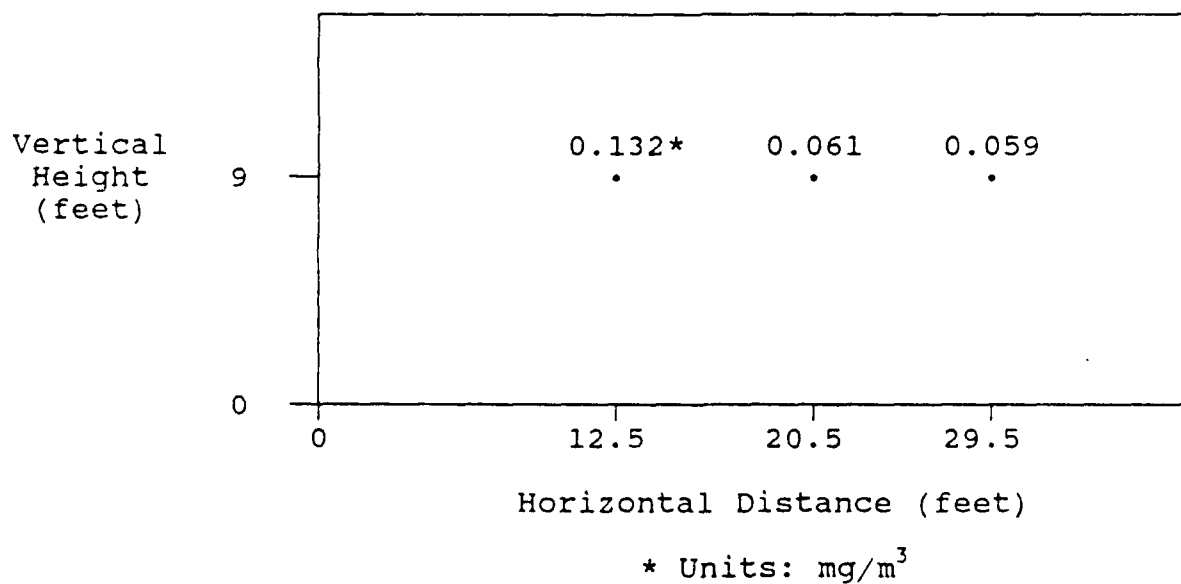


Figure 26. Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 3, Side View, 6 Feet from North Wall

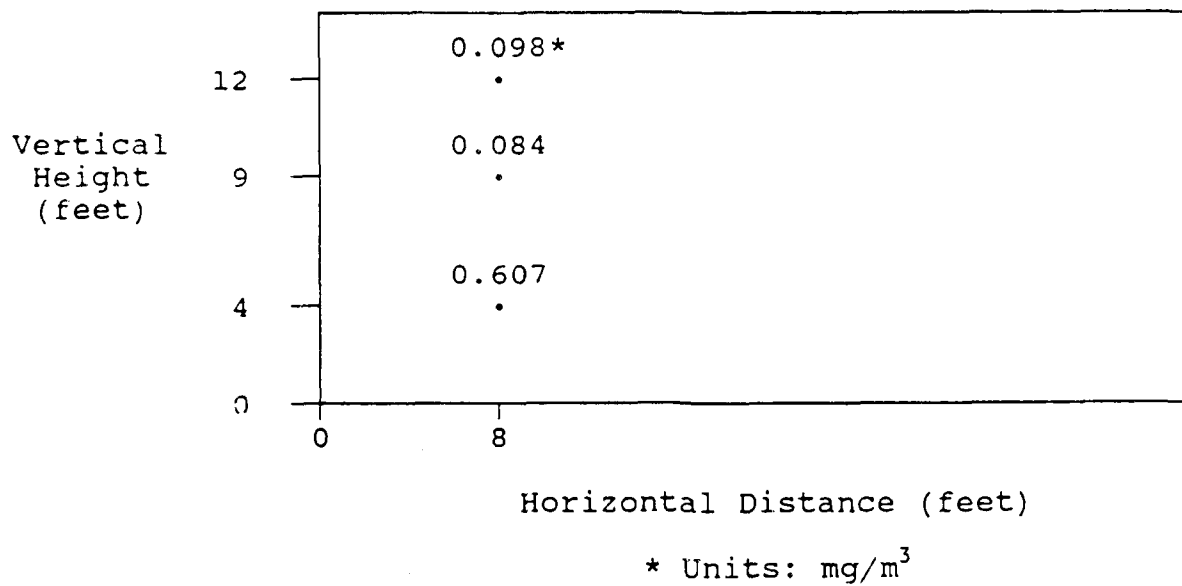


Figure 27. Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 3, Side View, 8 Feet from North Wall

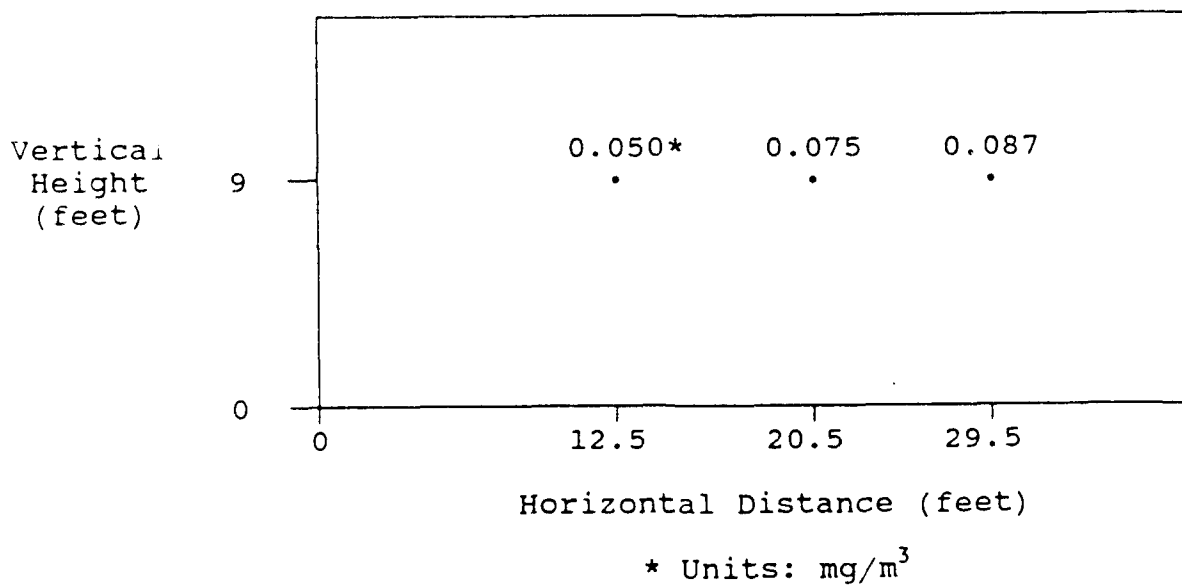


Figure 28. Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 3, Side View, 10 Feet from North Wall

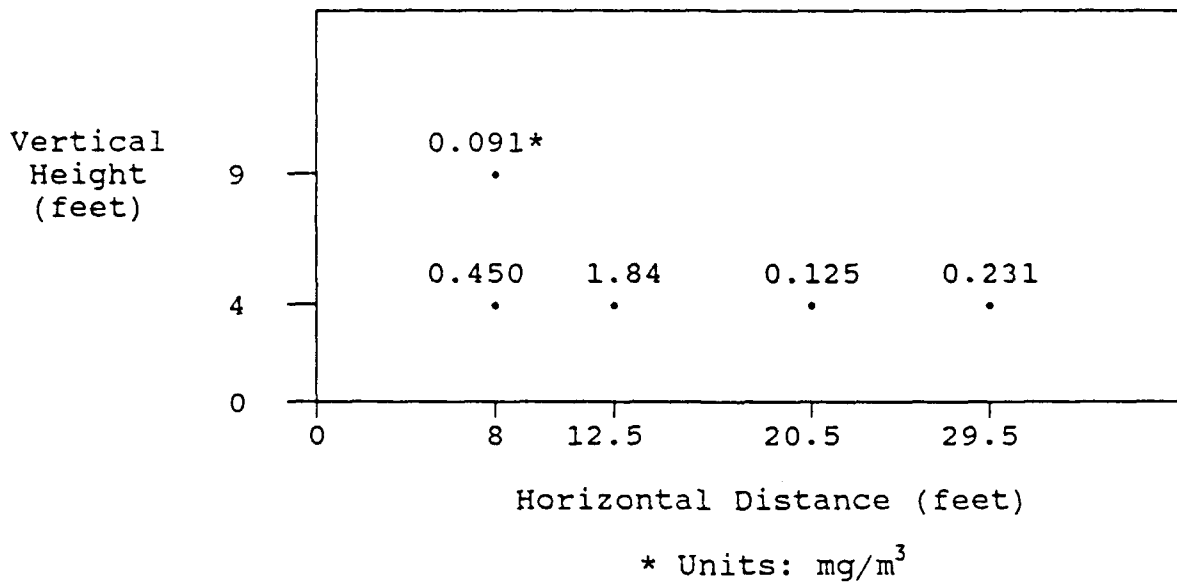


Figure 29. Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 3, Side View, 12 Feet from North Wall

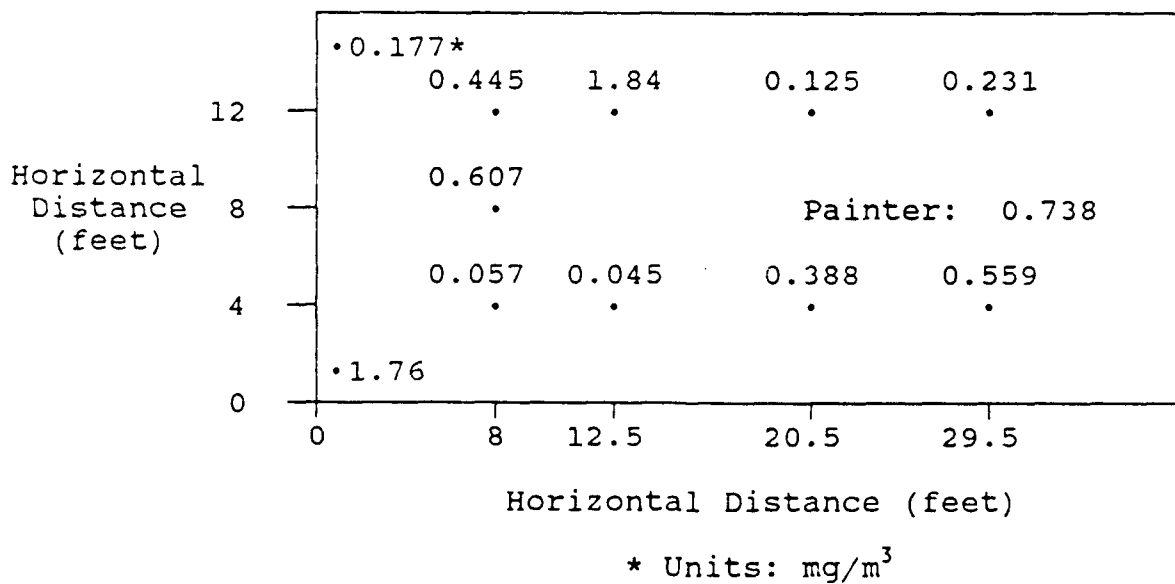


Figure 30. Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 3, Plan View at a Height of 4 Feet

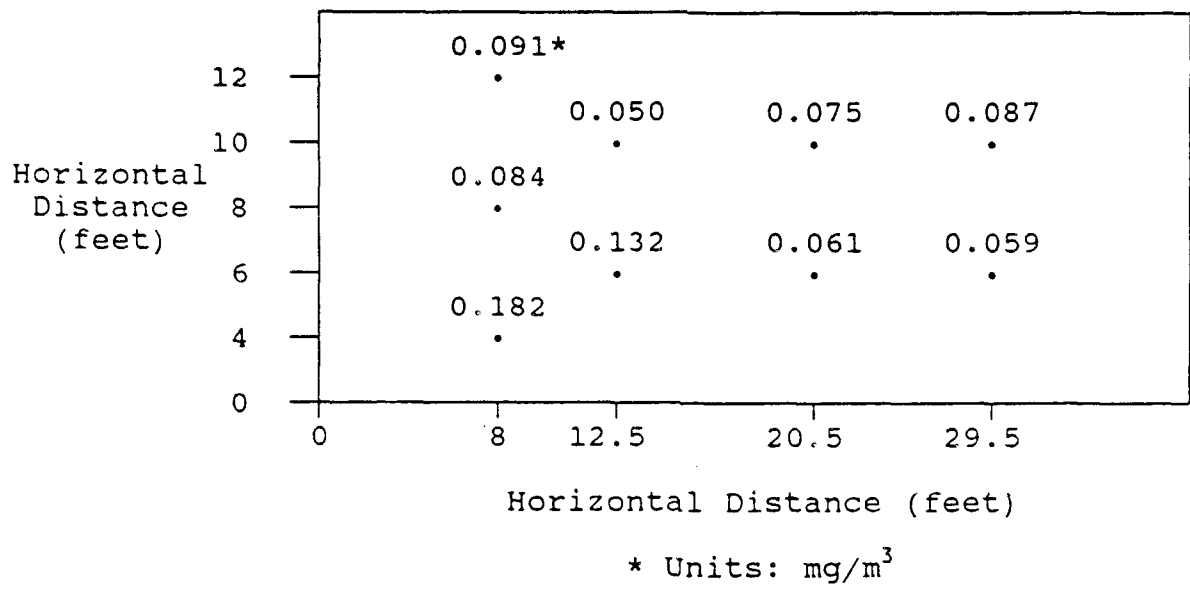


Figure 31. Metal Concentrations Measured at Various Positions in the Paint Spray Booth; Test 3, Plan View at a Height of 9 Feet

of the booth. The metals concentration measured in the vicinity of the painter was among the highest measured in the booth.

2. Exhaust Duct Measurement Results

As discussed in Section II, two test methods were used to measure particulate and metal concentrations in the exhaust duct: NIOSH 500 and EPA Method 5. The original test plan required that the NIOSH 500 and EPA M5 tests be run simultaneously. Due to a scheduling difficulty with the paint booth operators, only one test could be performed in which simultaneous EPA M5/NIOSH 500 particulate concentrations measurements were taken. However, the sampling pump malfunctioned during this test, making the results incomplete.

a. EPA Method 5 Sampling Results

EPA Method 5 tests were performed on the mornings of 6 December and 9 December. The filters submitted for analysis were clean, indicating that very little particulate was collected. The problems encountered in weighing the cellulose ester NIOSH 500 filters were also encountered in weighing the M5 filters, although to a lesser degree. In addition, during shipment the filter samples became damp (they were shipped in ice-chests containing ice); however they were dried thoroughly before weighing. For these reasons the accuracy range for the scale used in these measurements is ± 1.0 mg. The EPA M5 particulate concentration measurement results are presented in Table 18.

The M5 filters were also submitted for metals analysis. The results of these analyses are presented in Table 19.

b. NIOSH 500 Sampling Results

Two NIOSH 500 sampling tests using cellulose ester filters were performed in the exhaust duct on the afternoon of 6 December and the morning of 9 December. The 6 December sampling results are presented in Table 14. A sampling pump system failure invalidated the 9 December test results. The NIOSH 500 results concur with the M5 tests results obtained in the morning; no particulate was measured in the exhaust duct. The NIOSH 500 sample was also analyzed for the presence of metals; the results of this analysis are presented in Table 16.

E. AIRBORNE ISOCYANATE CONCENTRATION MEASUREMENTS

On 8 December, two isocyanate tests were conducted in which integrated air samples were collected both in the paint booth and in the exhaust duct. Only hexamethylene diisocyanate (HMDI) was detected. No toluene diisocyanate was measured in any integrated air samples taken.

1. In-Booth Measurement Results

Isocyanate concentrations in the booth were measured according to OSHA Method 42 sampling procedures, using the three-dimensional sampling grid described in Section II. The

TABLE 18. EPA METHOD 5 INTEGRATED PARTICULATE SAMPLING RESULTS.

Date	Sample Set Number	Volume Collected (L ^a)	Initial Weight (g)	Final Weight (g)	Mass of Particulate (g)
6 Dec	Filter-1	865	1.387	1.386	-0.001
	Probe Wash-1		45.76	45.78	0.023
9 Dec	Filter-2	1,224	1.370	1.365	-0.005
	Probe Wash-2		49.23	49.304	0.036
Blank	Filter-3	NA ^b	1.390	1.387	-0.002

^a Standardized to a pressure of 29.92 in Hg, and a temperature of 60 °F

^b NA Not Applicable

TABLE 19. EPA METHOD 5 INTEGRATED METALS SAMPLING RESULTS.

Metal	6 Dec		9 Dec	
	Filter (μg)	Probe Wash (μg)	Filter (μg)	Probe Wash (μg)
Barium	50	5.4	4.6	6.5
Chromium	7.9	220	31	39
Copper	5.5	17	1.1	24
Lead	5.2	19	12	65
Nickel	1.2	1,600	1.8	92
Titanium	0.6	1.9	< 0.5	600
Zinc	72	210	18	600

sample intervals, volumes, and isocyanate concentrations measured in the paint booth during the first isocyanate test are presented in Table 20 and plotted in Figures 32 through 38. Side view concentration profiles in the booth are plotted in Figures 32 through 36 at various distances from the north wall, and plan view concentration profiles are plotted at heights of 4 and 9 feet in Figures 37 and 38, respectively.

During Test 1, very low isocyanate concentrations were measured throughout most of the booth. The exception is a high concentration measured in the northwest corner of the booth at the 4-foot level ($50.6 \mu\text{g}/\text{m}^3$). In this case, it is likely that the spray gun was temporarily pointed directly at the filter, because analytical results of other filters located nearby indicate isocyanate concentrations below detection limits.

In Test 1, no isocyanates were detected at the 12- and 9-foot levels downwind of painting. However, positions at the 4-foot level and on ground level downwind of the painting showed detectable concentrations of HMDI. The 4-foot level concentrations ranged from 5.5 to $9.5 \mu\text{g}/\text{m}^3$, and the ground-level concentrations at the water curtain were 12.6 and $19.8 \mu\text{g}/\text{m}^3$. The painting occurred in the middle of the booth around the 4-foot level. The low overall isocyanate concentrations measured in the booth suggest that the concentrations in the vicinity of the painter would also be low. In fact, concentrations measured in the vicinity of the painter were below detection limits.

The results of Test 2 isocyanate sampling are presented in Table 21 and plotted in Figures 39 through 45. Side view concentration profiles at several distances from the north wall are provided in Figures 39 through 43, and plan view concentration profiles at heights of 4 and 9 feet are given in Figures 44 and 45, respectively. For Test 2, painting occurred in the middle of the booth around the 4-foot level. An analysis of Figures 44 and 45 indicate that low to nondetectable isocyanate concentrations were found at the 9-foot level, however high isocyanate concentrations were detected at the 4-foot level, except upwind of where painting occurred. These results indicate that significant pollutant stratification occurs in the booth during painting. At most of the 4-foot sampling locations, the isocyanate concentrations measured were lower than the concentrations measured in the vicinity of the painter ($36.4 \mu\text{g}/\text{m}^3$).

2. Exhaust Duct Measurement Results

Isocyanate concentrations were measured in the exhaust duct at the same time as in the booth. During Test 1, the isocyanate concentration in the duct was below detection limits. During Test 2, the isocyanate concentration in the duct was measured at $3.39 \mu\text{g}/\text{m}^3$. This result indicates that the water curtain is successful in removing isocyanate particulate. The concentration immediately upstream of the water curtain was greater than $30 \mu\text{g}/\text{m}^3$; downstream, the concentration measured was an order of magnitude less. However, as noted previously, it cannot be assumed that the high concentrations detected in two locations

TABLE 20. RESULTS OF INTEGRATED ISOCYANATE CONCENTRATION MEASUREMENTS IN BOOTH—TEST 1.

Position	Volume Sampled (L ^a)	HDI ^b (μg/sample)	HDI ³ (mg/m ³)	Comments
1	71.4	< 0.10	< 0.0014	
2	74.4	< 0.10	< 0.0013	
3	66.6	< 0.10	< 0.0015	
4	66.0	< 0.10	< 0.0015	
5	71.4	0.68	0.0095	
6	64.9	0.36	0.0055	
7	67.0	0.58	0.0087	
8	67.7	< 0.10	< 0.0015	
9	65.3	< 0.10	< 0.0015	
10	62.4	0.59	0.0095	
11	0.0	< 0.10	NI ^c	Sample pump failure
12	60.0	< 0.10	< 0.0017	
13	62.1	< 0.10	< 0.0016	
14	50.9	< 0.10	< 0.0020	
14	55.3	< 0.10	< 0.0018	Duplicate sample
15	61.5	< 0.10	< 0.0016	
16	56.1	< 0.10	< 0.0018	
17	57.6	< 0.10	< 0.0017	
18	57.8	< 0.10	< 0.0017	
19	62.1	3.14	0.0506	
20	61.6	1.22	0.0198	
21	55.6	0.70	0.0126	
Painter	51.4	< 0.10	< 0.0019	
Duct	69.5	< 0.10	< 0.0014	
Blank	NA	< 0.10	NA ^d	

^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 °F

^b Hexamethylene diisocyanate only -- no toluene diisocyanate was detected in any of the samples collected

^c NI No information due to sampling error

^d NA Not applicable because sample air was not drawn through filter

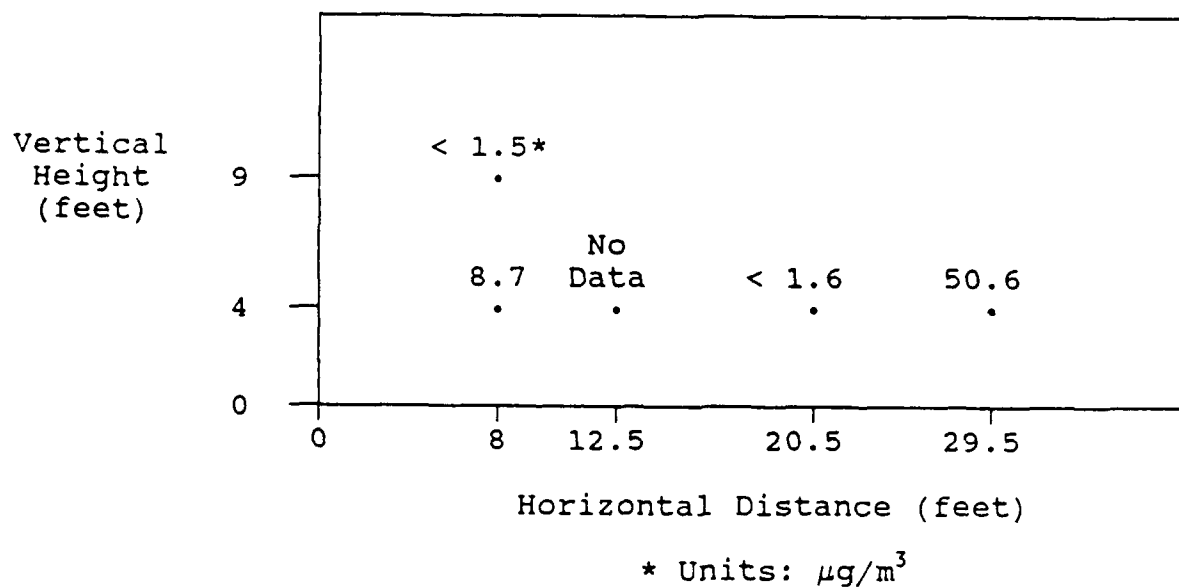


Figure 32. Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 4 Feet from North Wall

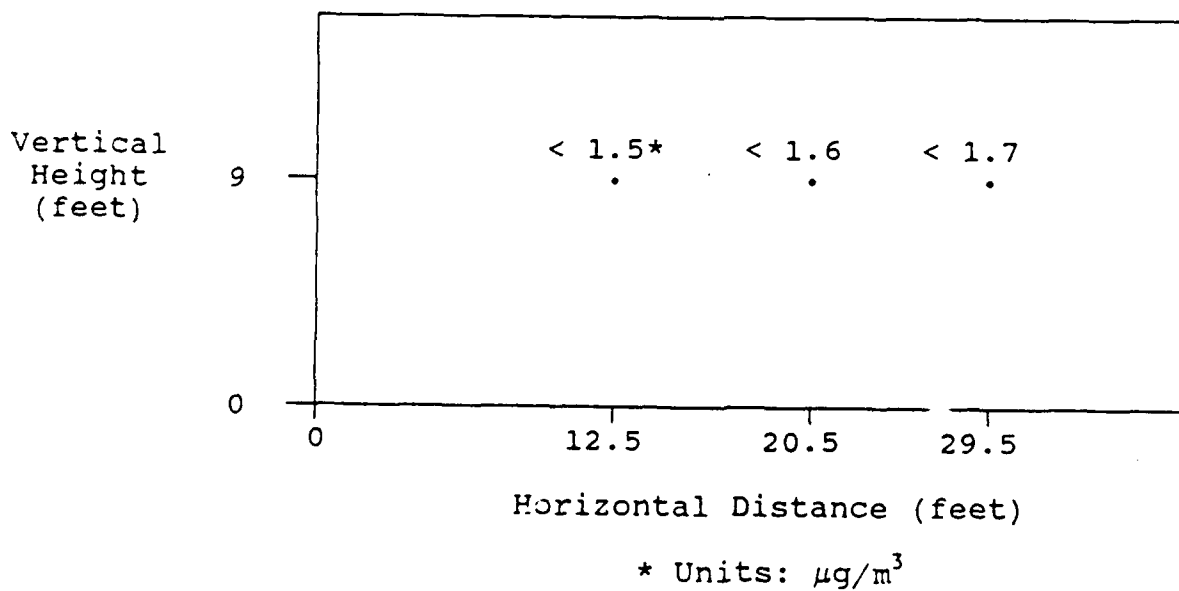


Figure 33. Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 6 Feet from North Wall

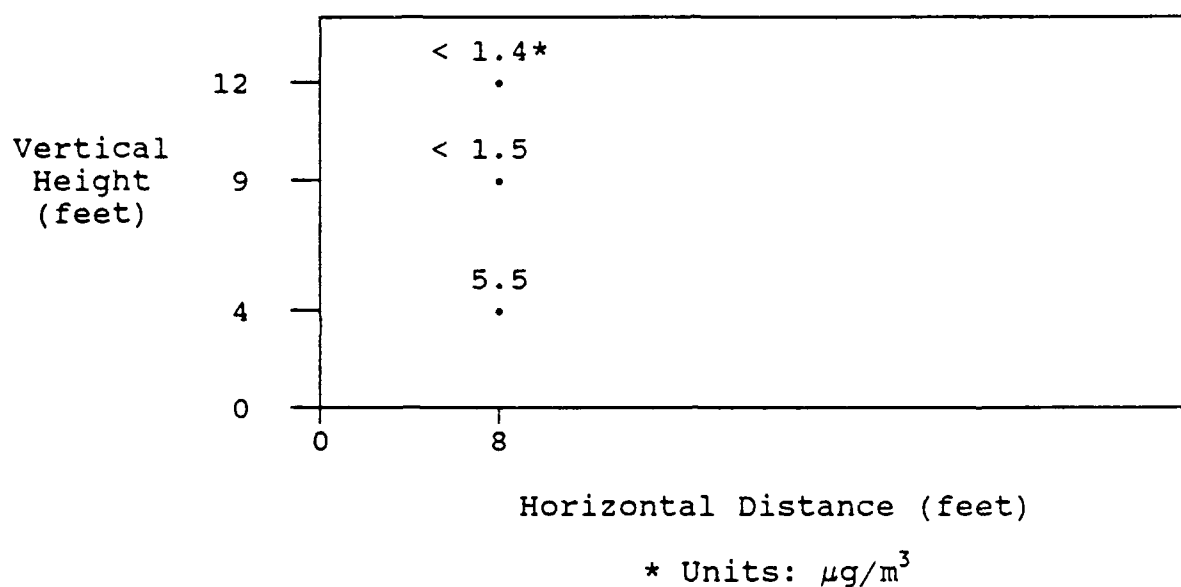


Figure 34. Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 8 Feet from North Wall

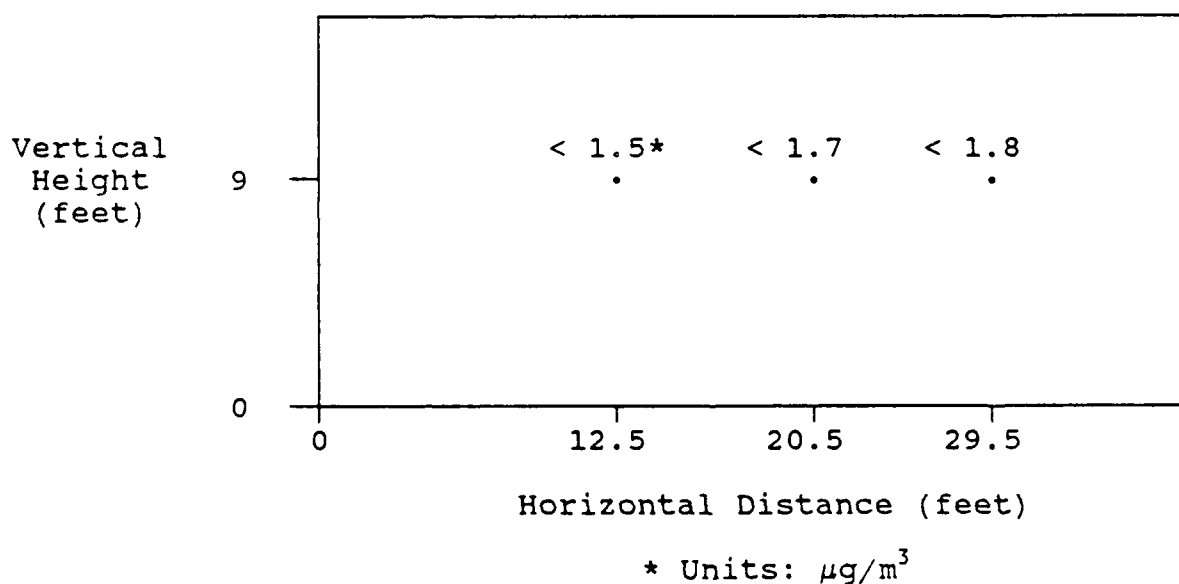


Figure 35. Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 10 Feet from North Wall

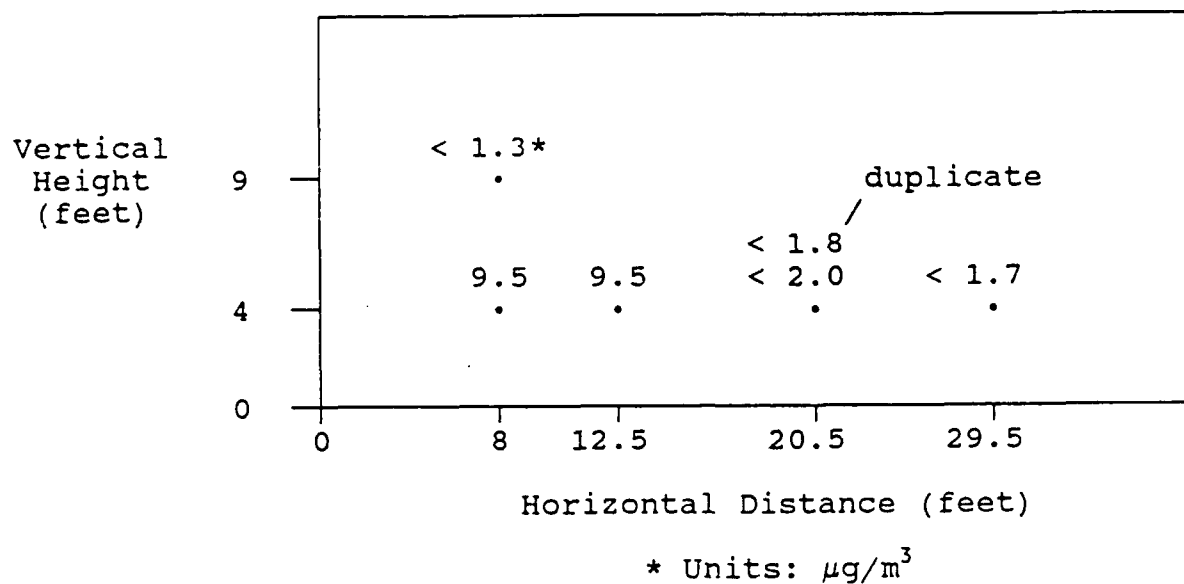


Figure 36. Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Side View, 12 Feet from North Wall

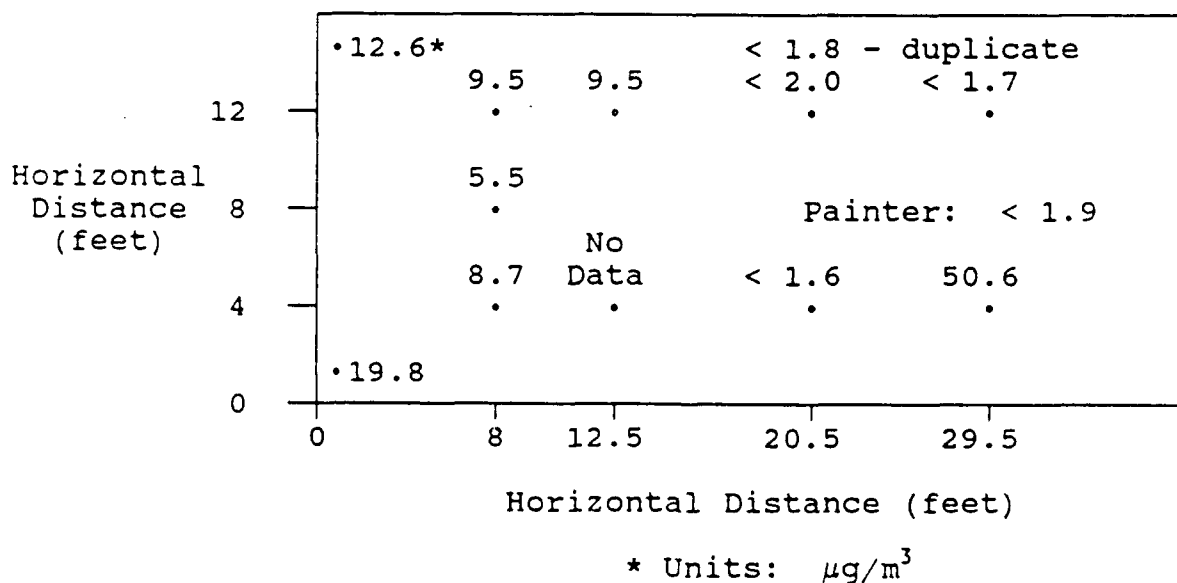


Figure 37. Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Plan View at a Height of 4 Feet

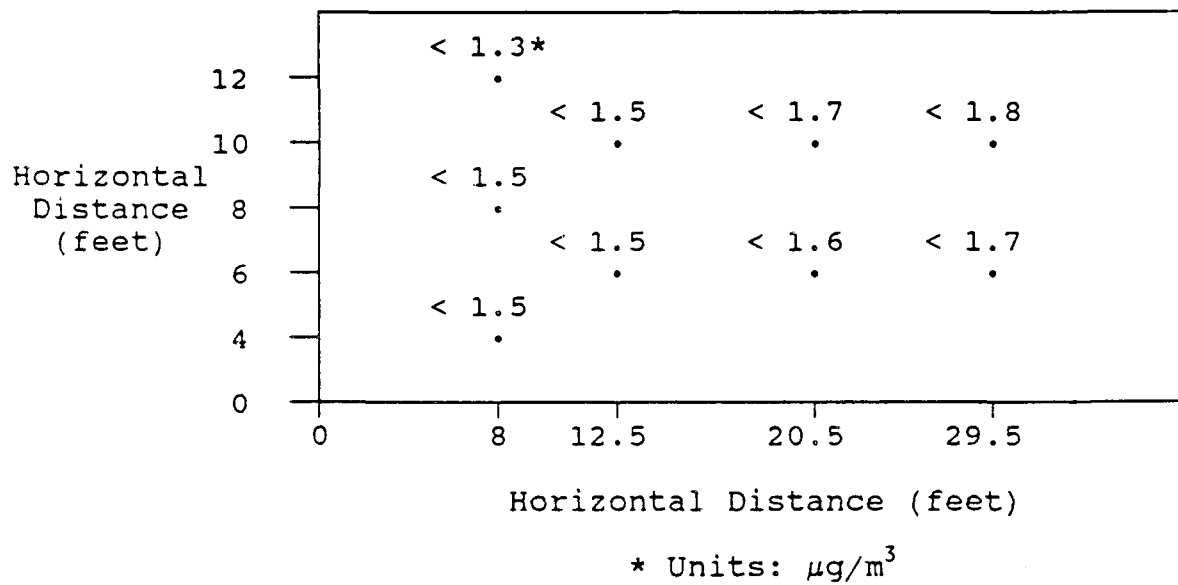


Figure 38. Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 1, Plan View at a Height of 9 Feet

TABLE 21. RESULTS OF INTEGRATED ISOCYANATE
CONCENTRATION MEASUREMENTS IN
BOOTH—TEST 2.

Position	Volume Sampled (L ^a)	HDI ^b (μg/sample)	HDI ^b (mg/m ³)	Comments
1	70.6	< 0.10	< 0.0014	
2	69.4	< 0.10	< 0.0014	
3	72.6	< 0.10	< 0.0014	
4	70.2	< 0.10	< 0.0014	
5	74.9	1.66	0.0222	
6	70.4	2.40	0.0341	
7	69.5	1.05	0.0151	
8	60.0	< 0.10	< 0.0017	
9	69.8	< 0.10	< 0.0014	
10	58.3	1.90	0.0326	
11	66.2	1.04	0.0157	
12	61.7	0.05	0.0008	
13	67.4	< 0.10	< 0.0015	
14	57.1	2.30	0.0403	
14	62.0	6.01	0.0970	Duplicate
15	65.0	2.97	0.0457	
16	66.2	< 0.10	< 0.0015	
17	65.7	< 0.10	< 0.0015	
18	68.1	< 0.10	< 0.0015	
19	69.8	< 0.10	< 0.0014	
20	63.5	1.94	0.0306	
21	63.0	3.70	0.0587	
Painter	49.8	1.81	0.0364	
Duct	70.8	0.24	0.0034	
Blank	NA	< 0.10	NA ^c	

^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 °F

^b Hexamethylene diisocyanate only -- no toluene diisocyanate was detected in any of the samples collected

^c NA Not applicable because sample air was not drawn through filter sample

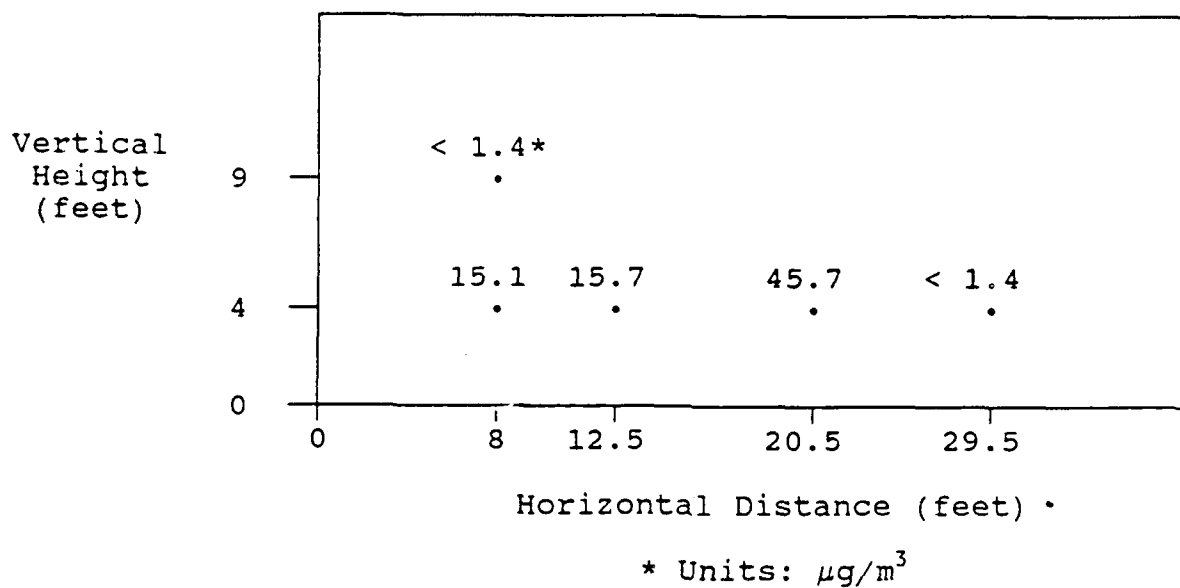


Figure 39. Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 4 Feet from North Wall

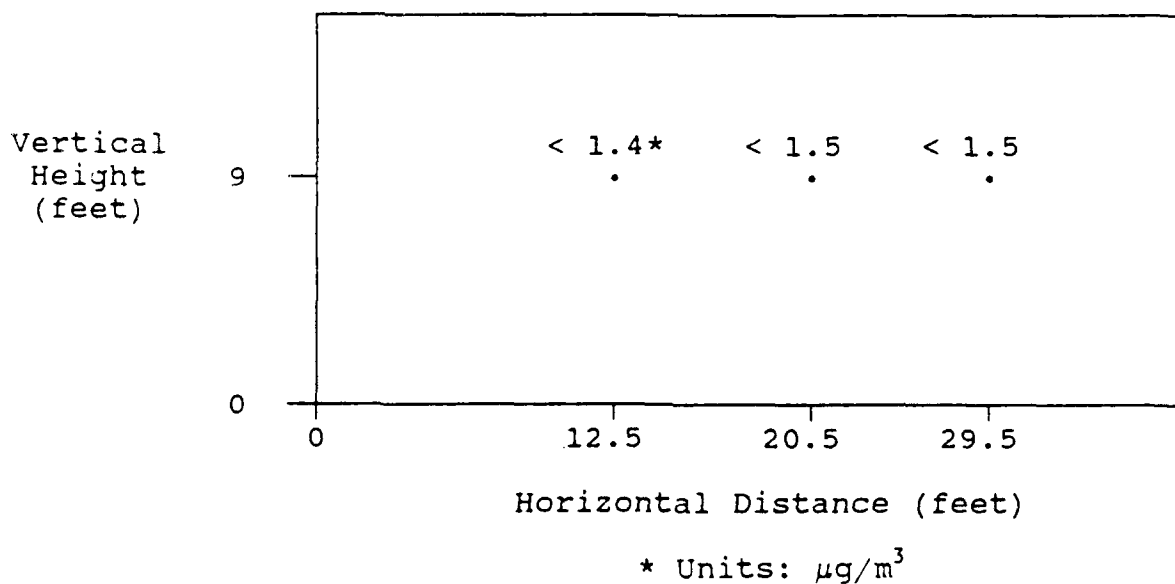


Figure 40. Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 6 Feet from North Wall

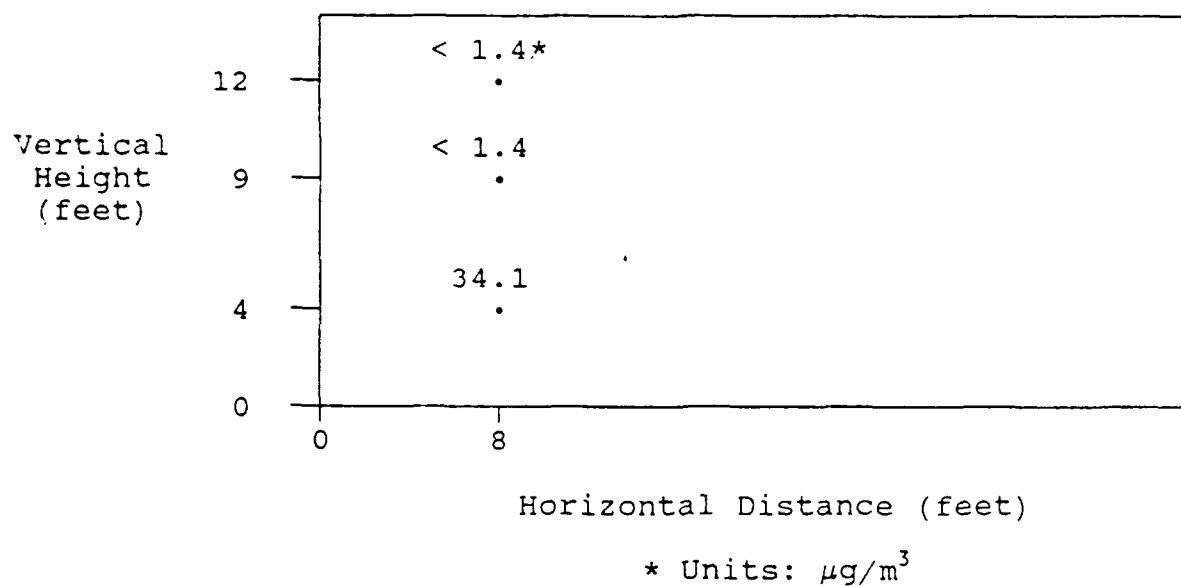


Figure 41. Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 8 Feet from North Wall

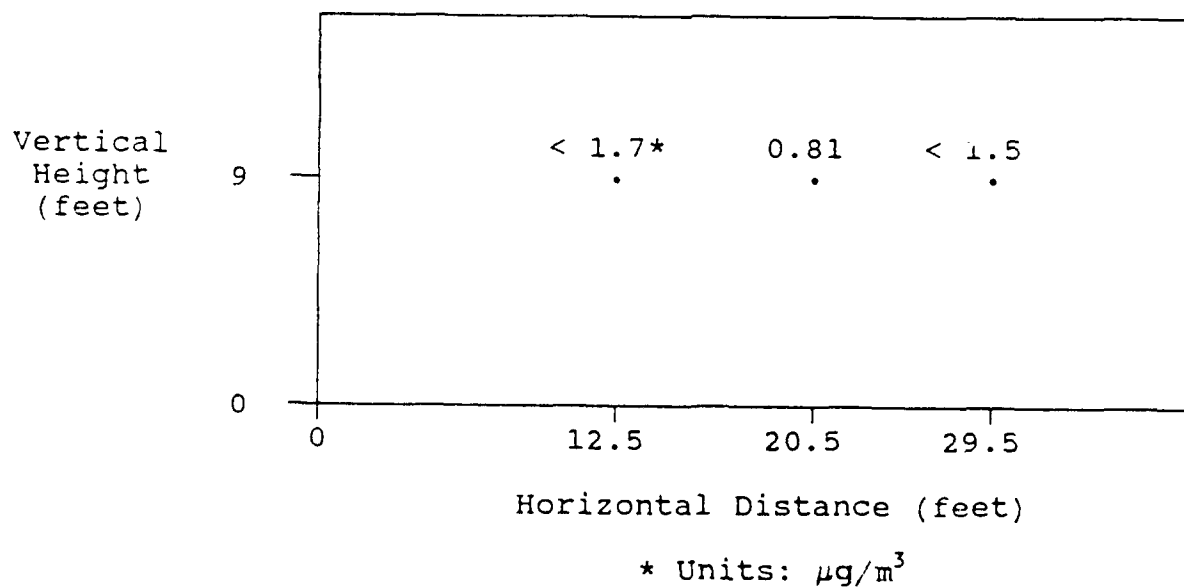


Figure 42. Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 10 Feet from North Wall

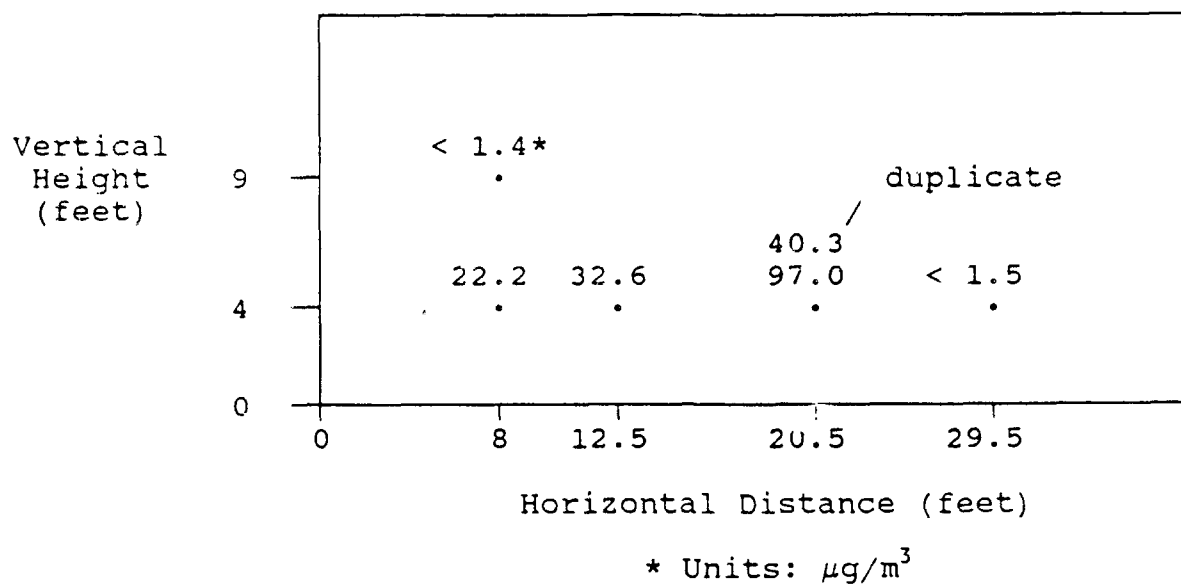


Figure 43. Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Side View, 12 Feet from North Wall

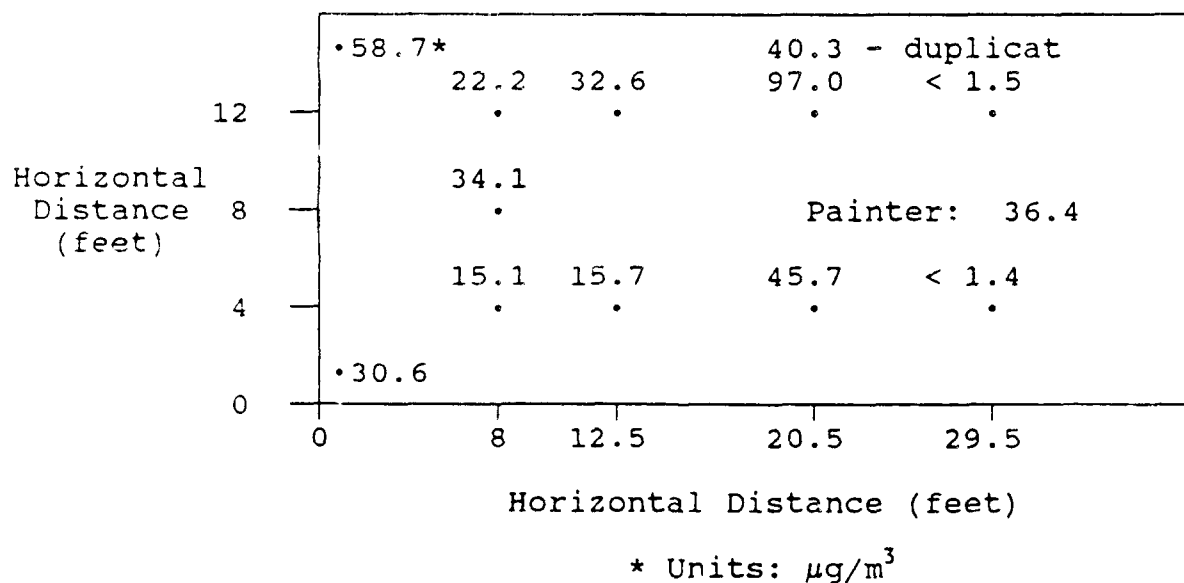


Figure 44. Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Plan View at a Height of 4 Feet

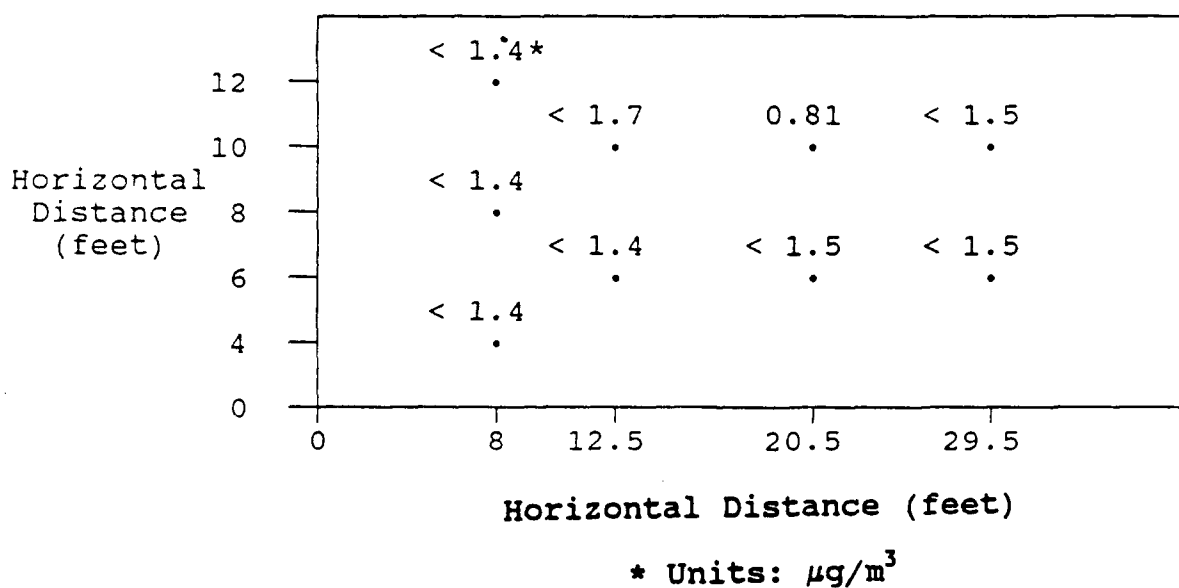


Figure 45. Isocyanate Concentrations Measured at Various Positions in the Paint Spray Booth; Test 2, Plan View at a Height of 9 Feet

immediately upstream of the water curtain are representative of the actual isocyanate concentration in the booth exhaust air influent to the water curtain.

F. WATER ANALYSIS RESULTS

The primary reason for collecting and analyzing sump water samples was to demonstrate that the water curtain particulate emission control device has no impact on VOC emissions. To monitor daily variations in the sump water organic compound concentration, total organic carbon (TOC) samples were collected twice daily. Volatile and semivolatile organic compounds were analyzed in water samples that were taken at the beginning, middle, and end of the test series to speciate the TOC results. A secondary objective of the water sampling efforts was to track the particulate concentration in the sump water, thus frequent residue samples were taken. The sump water residue concentration was expected to increase as a function of time as more paint overspray particulate was collected. The results of the sump water analyses are presented in Tables 22, 23, 24, and 25.

From the 6 December results of the volatile and semivolatile organic compound concentration analyses, it is apparent that substantial quantities of organics were present in the sump water before the test series was initiated. As indicated in the original test plan, the water sump was to be emptied prior to testing, and nothing out of the ordinary was to be done to the sump prior to and during testing. However, in an effort to mask and reduce the solvent smell that generally emanates from the sump, the Building 515 personnel deviated from normal operating procedure by adding an unknown (but fairly large) quantity of general purpose disinfecting detergent into the sump. This detergent is composed of 80 percent pine oil, 13 percent soap, and 7 percent water.

It was not known until after the test series was concluded that adding detergent to the sump prior to painting is not normal operating procedure. The addition of detergent introduced unknown organics into the sump water. The detergent compounds were identified by comparing the results of paint speciation data to the volatile and semivolatile water analysis results; these compounds are indicated in Tables 22 and 23. The sampling crew members observed that, although the detergent smell was quite strong on the first day of testing, it was virtually eliminated by the end of the second day of testing. A comparison of analytical results from 6 and 7 December indicates that all of the volatile and most of the semivolatile organic compounds present in the sump water due to the addition of the detergent were removed (by volatilization) early in the test series. This fact is indicative of the inability of a water curtain particulate emission control system to control VOC emissions.

The concentration of volatile organic compounds (presented in Table 22) varied during the week, depending on the type of paint used. Irregular variations in the types and amounts of volatiles present indicate that the sump does not remove significant amounts of VOCs from the

TABLE 22. RESULTS OF SUMP WATER VOLATILE ORGANIC COMPOUND ANALYSES.

Compound ^a	6 Dec Morning		7 Dec Midday			8 Dec Evening	
	Sample (µg/L)	Duplicate (µg/L)	Sample (µg/L)	Duplicate (µg/L)	Blank (µg/L)	Blank (µg/L)	Evening (µg/L)
2-Butanone (MEK)	ND ^b	ND	33000	76000	13	49	3400
2-Propylfuran	ND	ND	430	440	ND	ND	ND
4-Methyl-2-pentanone	ND	ND	2000	4400	ND	ND	ND
Acetone	ND	ND	16000	54000	ND	ND	1700
Acid Ester	ND	ND	73	89	ND	ND	ND
Butyl Acetate	ND	ND	760	760	ND	ND	29
Chlorobenzene	<5.0	<5.0	<5.0	<5.0	<5.0	7	<5.0
Chloroform	<5.0	<5.0	<5.0	<5.0	42	28	<5.0
Ethylbenzene	<5.0	<5.0	<5.0	10	<5.0	<5.0	<5.0
Methyl Acetate	ND	ND	1300	1200	ND	ND	900
Toluene	17	18	17	20	ND	ND	ND
Total Xylenes	ND	ND	17	14	ND	ND	ND
Subst. aromatic; scan 900 * ^c	410	430	ND	ND	ND	ND	ND
Unknown; Scan 291	ND	ND	ND	ND	ND	ND	470
Unknown; Scan 879 *	1700	1700	ND	ND	ND	ND	ND
Unknown; Scan 909 *	790	790	ND	ND	ND	ND	ND
Unknown; Scan 689	ND	ND	34	5	ND	ND	ND
Unknown; Scan 364	ND	ND	270	240	ND	ND	ND
Unknown; Scan 342	ND	ND	ND	ND	ND	ND	36
Unknown	ND	ND	ND	ND	ND	ND	250
Unknown; Scan 827 *	100	120	ND	ND	ND	ND	ND
Unknown	ND	ND	ND	ND	ND	ND	530
Alkane; Scan 410	ND	ND	710	720	ND	ND	ND
Unk. Acetate; Scan 731	ND	ND	ND	ND	ND	ND	250
Unk. Acetate; Scan 250	ND	ND	ND	ND	ND	ND	450
Cyc. hydrocarbon; Scan 717 *	750	790	ND	ND	ND	ND	ND
Cyc. hydrocarbon; Scan 747 *	410	450	ND	ND	ND	ND	ND
Cycloalkene; Scan 894 *	2400	2400	ND	ND	ND	ND	ND
Cycloalkene; Scan 855 *	640	650	ND	ND	ND	ND	ND
Cycloalkene; Scan 995 *	3000	2800	ND	ND	ND	ND	ND
Cycloalkene; Scan 942 *	400	400	ND	ND	ND	ND	ND

^a The following compounds were analyzed for in the samples collected, but were not found in concentrations in excess of 5 µg/L:

Chloromethane	trans-1,3-Dichloropropene
Bromomethane	1,1,1-Trichloroethane
Vinyl Chloride	Benzene
Chloroethane	Dibromochloromethane
Methylene chloride	1,1,2-Trichloroethane
Trichlorofluoromethane	cis-1,3-Dichloropropene
1,1-Dichloroethene	2-Chloroethyl vinyl ether
1,1-Dichloroethane	Bromoform
Carbon Tetrachloride	1,1,2,2-Tetrachloroethane
Bromodichloromethane	Tetrachloroethene
1,2-Dichloropropane	1,2-Dichloroethane
1,1,2-Trichloroethane	

^b ND Not Detected

^c Compounds identified as being present due to addition of detergent to sump water are indicated with an asterisk (*)

TABLE 23. RESULTS OF SUMP WATER SEMIVOLATILE ORGANIC COMPOUND ANALYSES.

Compound ^a	Scan Number	6 Dec Morning (µg/L)	7 Dec Midday			8 Dec Evening	
			Sample (µg/L)	Duplicate (µg/L)	Blank (µg/L)	Evening (µg/L)	Blank (µg/L)
2-Butoxyethanol	414	ND ^b	ND	ND	ND	1600	ND
Cyclic alcohol * ^c	565	500	590	570	ND	16	ND
Cyclic alcohol	604	14000	30000	27000	ND	ND	ND
Cyclic alcohol	571	ND	790	760	ND	23	ND
Cyclic alcohol *	575	430	240	ND	ND	ND	ND
Cyclic alcohol *	555	1400	200	250	ND	ND	ND
Cyclic alcohol	593	1100	1300	1300	ND	ND	ND
Cyclic alcohol *	588	2100	1600	1500	ND	23	ND
Cyclic alcohol	583	ND	ND	ND	ND	33	ND
Cycloalkene *	537	800	ND	ND	ND	ND	ND
Cycloalkene *	498	840	ND	ND	ND	ND	ND
Hydrocarbon *	992	320	ND	ND	ND	ND	ND
Phthalate	1309	ND	ND	ND	20	ND	ND
Phthalate	1458	ND	ND	ND	10	ND	ND
Substituted alcohol	431	ND	ND	ND	ND	92	ND
Substituted alcohol	498	ND	ND	ND	ND	25	ND
Substituted alcohol	527	ND	ND	ND	ND	11	ND
Substituted alcohol	601	ND	ND	ND	ND	2100	ND
Substituted aromatic *	631	700	ND	ND	ND	ND	ND
Substituted aromatic *	648	660	ND	ND	ND	ND	ND
Substituted carboxylic acid	551	ND	ND	ND	ND	13	ND
Substituted ketone	710	ND	ND	ND	ND	11	ND
Substituted ketone	635	ND	ND	ND	ND	18	ND
Unknown *	659	350	210	200	ND	69	ND
Unknown	373	ND	ND	ND	ND	31	ND
Unknown	643	ND	ND	ND	ND	10	ND
Unknown	541	ND	ND	ND	ND	69	ND
Unknown	423	ND	ND	ND	ND	52	ND
Unknown	488	580	ND	ND	ND	ND	ND
Unknown	649	ND	ND	ND	ND	17	ND
Cycloalkene	428	91	ND	ND	ND	ND	ND

^a The following compounds were analyzed for, but were not found in the samples collected:

Phenol	Acenaphthylene	3,3'-Dichlorobenzidine
Bis(2-chloroethyl) ether	2,4-Dinitrophenol	Benzo(a)anthracene
2-Chlorophenol	4-Nitrophenol	Bis(2-ethylhexyl) phthalate
1,3-Dichlorobenzene	2,4-Dinitrotoluene	Chrysene
1,4-Dichlorobenzene	2,6-Dinitrotoluene	Di-n-octyl phthalate
1,2-Dichlorobenzene	Diethyl phthalate	Benzo(b&k)fluoranthene
Bis(2-chloroisopropyl) ether	4-Chlorophenyl phenyl ether	Benzo(a)pyrene
N-Nitroso-di-n-propylamine	Fluorene	Indeno(1,2,3-cd)pyrene
Hexachloroethane	4,6-Dinitro-2-methylphenol	Dibenzo(a,h)anthracene
Nitrobenzene	N-Nitrosodiphenylamine	Benzo(g,h,i)perylene
Isophorone	4-Bromophenyl phenyl ether	alpha,beta,gamma&delta-BHC
2-Nitrophenol	Hexachlorobenzene	Heptachlor
2,4-Dimethylphenol	Pentachlorophenol	Aldrin
1,2,4-Trichlorobenzene	Phenanthrene	Heptachlor epoxide
Naphthalene	Anthracene	Endosulfan I & II
Hexachlorobutadiene	Di-n-Butyl phthalate	Dieldrin
4-Chloro-3-methylphenol	Fluoranthene	4,4'-DDE, DDD, & DDT
2-Chloronaphthalene	Pyrene	Endrin
Dimethyl phthalate	Butyl benzyl phthalate	Endrin aldenvde
Endosulfan sulfate	PCBs	Acenaphthene

^b ND Not Detected

^c Compounds identified as being present due to addition of detergent to water sump are identified with an asterisk

TABLE 24. RESULTS OF SUMP WATER TOTAL ORGANIC CARBON (TOC) ANALYSES.

<u>Date</u>	<u>Time</u>	<u>Sample Status</u>	<u>TOC Concentration (mg/L)</u>
6 Dec	Morning	Sample	155
		Duplicate	155
	Evening	Sample	244
		Duplicate	244
7 Dec	Midday	Sample	246
		Duplicate	256
	Evening	Sample	170
8 Dec	Midday	Sample	162
	Evening	Blank	8
		Sample	154
		Duplicate	192

TABLE 25. RESULTS OF SUMP WATER RESIDUE ANALYSES.

<u>Date</u>	<u>Time</u>	<u>Sample Status</u>	<u>Residue (mg/L)</u>
6 Dec	Morning	Sample	341
7 Dec	Midday	Sample	276
		Duplicate	356
	Evening	Sample	394
8 Dec	Midday	Sample	367
	Evening	Sample	397
		Duplicate	337
		Blank	4

airstream. The data provided in Table 23 indicate that the semivolatile concentrations also varied throughout the week. Excluding compounds present due to the addition of detergent (indicated with asterisks in Table 23), it appears that the water curtain may collect some water-soluble semivolatile compounds (such as 2-butoxyethanol). However even water-soluble compounds can be removed only until the solubility limit of the sump water is reached. The compounds that were not detected in previous samples, but were detected in the water sample collected on the last day, may be attributed to the preceding painting operation.

The analytical results presented in Table 24 indicate that, although TOC concentrations fluctuated during the week, the final TOC concentration was not significantly different from the initial concentration. The TOC concentration in the sump was 155 mg/L before the test series was initiated, increased to a maximum of 246 mg/L half way through the test series, and decreased to 173 mg/L on the evening of 9 December. This result supports the contention that a water curtain does not control organic compound emissions from paint spray booths.

Total residue was also measured in sump water samples collected daily. These results are presented in Table 25. The particulate concentration in the water increased from 341 mg/L on the morning of 6 December to 397 mg/L on the evening of 8 December. Although the general trend in the data is that of increasing particulate concentrations, deviations from the trend occur, possible due to nonrepresentative samples. For these sampling conditions, sample representativeness is difficult to achieve because the particulate in the sump water has a tendency to settle. If not well mixed, the sampling medium becomes stratified. To minimize the possibility of stratification, the pumps were operated to mix the sump water for at least one-half hour before sampling. However, this process does not necessarily guarantee sample homogeneity. Nonetheless, the data indicate that particulate concentrations in the sump water did increase over the test period.

G. MEASUREMENT OF WATER CURTAIN PARTICULATE AND ISOCYANATE REMOVAL EFFICIENCIES.

At the end of the test series, an additional measurement was performed to determine how efficiently the water curtain removes particulate and isocyanates from the paint booth exhaust before it is vented to the outside. An additional objective of the test was to measure particulate and isocyanate concentration gradients along the front of the water curtain. This test was not planned in advance and is therefore not discussed in the original test plan.

Glass fiber NIOSH 50Q filters and isocyanate filters were placed in the booth in several locations across the front face of the water curtain (glass fiber filters were used for the particulate sampling because metal analyses were not required). Two particulate and two isocyanate filters were also placed inside the exhaust duct.

Particulate concentrations measured at the water curtain face, which are summarized in Table 26, range from 2.23 to 13.25 mg/m³, with the average being 9.41 mg/m³. Particulate concentrations measured in the exhaust duct were 3.19 and 3.10 mg/m³.

Isocyanate concentrations measured at the water curtain face, which are summarized in Table 27, range from less than 0.97 to 49.8 µg/m³, the average being 19.3 µg/m³. Isocyanate concentrations measured in the exhaust duct were 6.8 and 4.7 µg/m³.

TABLE 26. RESULTS OF WATER CURTAIN PARTICULATE REMOVAL EFFICIENCY MEASUREMENTS.

Horizontal Distance From North Wall (Feet)	Volume Sampled (L ^a)	Particulate Detected (g)	Particulate Concentration (mg/m ³)
2.7	111	0.0015	13.2
6.3	105	0.0014	12.9
8.0	101	0.0006	6.02
9.8	108	0.0002	2.23
12.3	100	0.0011	10.5
14.3	95.4	0.0011	11.6
Duct	84.6	0.0003	3.19
Duct	80.7	0.0003	3.10
Blank	NA ^b	0.0001	NA

^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 °F

^b NA Not applicable because sample air was not drawn through filter

TABLE 27. RESULTS OF WATER CURTAIN ISOCYANATE REMOVAL EFFICIENCY MEASUREMENTS.

Horizontal Distance From North Wall (feet)	Volume Sampled (L ^a)	HDI Detected (µg/sample)	HDI Concentration (mg/m ³)	Comments
0.8	111	1.90	0.017	
7.1	108	5.38	0.050	
4.3	110	3.34	0.030	
9.8	112	3.49	0.031	Estimated operating time
10.8	94.0	3.52	0.037	
12.8	103	< 0.10	< 0.001	
4.2	91.0	2.42	0.027	
Indoor Blank	NA ^b	< 0.10	NA	
Duct	100	0.68	0.007	
Duct	91.9	0.43	0.005	
Outdoor Blank	NA	< 0.10	NA	

^a Standardized to a pressure of 29.92 in Hg and a temperature of 60 °F

^b NA Not applicable because sample air was not drawn through filter

SECTION IV

EMISSION CONTROL CONCEPTS

The three general approaches to controlling VOC emissions from painting facilities are

- Process and equipment change
- Paint reformulation
- Add-on VOC emission control devices

The first two approaches fall under the general category of source reduction technologies. Such technologies focus on reducing the quantity of solvent generated at a point source and typically require some modifications to paint booth equipment and/or processes. Implementation of source reduction technologies is generally cost effective because it promotes resource conservation and reduces emission control costs. The third approach falls under the general category of emission control. Each of these approaches will be discussed in detail in the following sections.

A. PROCESS AND EQUIPMENT CHANGE

This method entails altering the paint application process. The principal factor used to compare paint application technologies is the transfer efficiency of the painting equipment. Transfer efficiency is defined as the ratio of the quantity of paint deposited on the surface being coated to the quantity of paint exiting the gun. A high transfer efficiency reduces both the quantity of paint lost as overspray and the quantity of solvent vapor emitted from the booth.

The transfer efficiency is a function of the paint application system, type of paint applied, geometry of the target, ambient conditions, and painter's ability. Transfer efficiency tests to evaluate the performance of a variety of application processes indicate that, given identical operating conditions, electrostatic spray systems consistently have the highest transfer efficiency, ranging from 60 to 90 percent. Air-assisted airless systems have slightly higher transfer efficiencies (ranging from 12 to 72 percent) than air-atomized systems (ranging from 12 to 68 percent)(Reference 10). Both air-atomized and air-assisted airless paint spray guns are used at the Hill Air Force Base Building 515 paint booth.

The electrostatic spray application system operates in the following manner. Paint particles are charged to a high potential as they pass through an electrode. The surface to be coated is grounded so that it is at a lower potential than the paint particles. Attraction between the electrically charged paint particles and the grounded surface draws the paint to the surface, thus reducing overspray. A primary limitation of the electrostatic spray coating method is that paints with a high conductivity cannot be applied, because the paint particles do not become highly charged. In addition, if an electrostatic spray system is installed, certain precautions must be

taken to preclude an explosion hazard. For these reasons, the installation of electrostatic spray systems is not considered feasible for some military painting facilities.

B. PAINT REFORMULATION

Paint reformulation entails changing the paints and solvents that are used in the paint booth. In general, either low-solvent coatings having a high solids content or water-borne coatings are substituted for high-solvent coatings. The Department of Defense has performed extensive evaluations of alternate coatings to determine their applicability and has approved several for use in Air Force painting applications.

C. ADD-ON VOC EMISSION CONTROL DEVICES

1. Types of Emission Control Devices

VOC emission control devices fall into two general categories: destruction systems and collection systems.

a. Destruction Systems

The most common solvent vapor destruction method is thermal incineration. Other methods include catalytic incineration and ultraviolet (UV) destruction.

(1) Thermal incineration requires that the process air be heated to at least 1,400°F to achieve 90-percent destruction. Due to the high process temperatures required, the associated operating costs are relatively high.

(2) Catalytic incineration requires that the process air flow through a catalyst matrix maintained at 700 to 1,000°F (depending on the solvents present) to ensure 90-percent destruction. Compared to thermal incineration systems, catalytic systems generally have higher associated installation costs; however, utility operating costs are lower, due to the lower operating temperature.

(3) UV destruction involves exposing the solvent-laden air to UV light for a specified period of time. The high-energy light breaks down the organic molecules of the solvent to CO₂ and water. Although this technology is relatively new, it has proven efficient in some applications.

b. Collection Devices

Collection devices are generally more cost effective than destruction devices if the market value of the recovered solvents is sufficiently high to offset solvent separation (i.e., distillation) costs. The solvents used in most Air Force painting operations have low market value, thus collection devices are generally not recommended for installation. The two types of collection techniques in common use are carbon adsorption and condensation.

(1) Carbon adsorption is a process in which the solvent-laden air passes through an activated carbon filter, in which the solvents are collected by adsorption onto the

carbon. The solvents are retrieved by heating the filter cartridge (usually with superheated steam) to vaporize the solvents, which are then condensed and collected with the steam.

(2) Condensation is a process in which the solvent-laden air is cooled directly, and the solvents are condensed out of the air. A recent advancement of this technology is the development of a turbine expansion process that efficiently cools the solvent/air mixture.

2. Flow Reduction for Efficient Control Device Operation

Installation of a VOC emission control device on the paint booth exhaust duct is an effective method of achieving a high degree of emission control. However, the associated capital, installation, and operating costs are exceedingly high, because the control device must be large enough to process high airflow rates containing low solvent concentrations. Recent innovations in the field of ventilation techniques will significantly decrease the exhaust flow rate from paint spray booths to downstream emission control devices. Two flow-reduction techniques that may be adopted are split-flow exhaust ventilation and recirculation.

a. Split-Flow Ventilation

The results of the test series indicate that significant pollutant stratification occurs in the booth during the paint application process. A flow-reducing ventilation system that takes advantage of this operating characteristic can be designed in which the plenum chamber located behind the exhaust face of the booth is modified to accommodate two exhaust ducts. One duct draws exhaust air from the upper zone of the booth, which contains little or no hazardous constituents. The exhaust from this duct is vented directly to the outside. The second duct draws exhaust air from the lower zone of the booth, in which test results indicate the highest concentrations of hazardous constituents exist. The exhaust flow from the second duct is vented to a VOC emission control device.

The advantage of this system is that the flow rate to a VOC emission control device can be safely and economically reduced, which results in decreased installation and operating costs. The reduction in flow rate achieved is dependent on the height of the zone containing the highest concentrations of hazardous constituents. The smaller the zone, the higher the flow reduction achieved, and therefore the smaller the required emission control device. This ventilation system is applicable only for crossflow booths and cannot be used to control emissions from downdraft booths in which ventilation air flows vertically through the booth. In addition, if the booth is equipped with a water curtain particulate emission control system (such as the one in the Building 515 paint booth), it must be replaced with a dry filter system to accommodate split-flow ventilation.

b. Recirculation

Another method of reducing flow to an emission control device is to install a return airflow system, which recirculates filtered exhaust air into the booth. To control the

accumulation of VOCs in the booth, a bleed-off duct leading to a VOC emission control device is installed at the exhaust plenum. The size of the control device is therefore determined by the bleed-off flow rate. Fresh makeup air, drawn from the outside to replace the bleed-off air, is mixed in an intake plenum chamber before entering the booth. The recirculated process air is filtered twice before it passes back into the booth. The advantage of the recirculation ventilation system is that it reduces the flow to a VOC emission control device up to 90 percent, and therefore significantly reduces the associated control costs (Reference 1).

Unlike the split-flow ventilation system, recirculation requires no modification of the particulate emission control device. In addition, it can achieve a much higher degree of VOC emission control, and it may be installed on either crossdraft or downdraft painting facilities. However, installation costs for recirculation systems are higher than for split-flow systems, because various monitoring and automatic control equipment must be installed to maintain solvent concentrations in the booth at a safe level.

Until recently, OSHA was reluctant to allow recirculation as a means of reducing VOC emission control costs associated with paint spray booths. However, in December of 1989, OSHA ruled that a recirculation ventilation system may be installed on paint booths. A copy of the letter affirming this allowance is provided in Appendix C.

SECTION V

ENGINEERING EVALUATION

Based on the data collected in this test series, the most effective means of reducing VOC emissions from the Building 515 paint booth is through source reduction via paint reformulation and flow reduction combined with thermal incineration.

A. PAINT REFORMULATION

The coatings used at the Hill AFB painting facility located in Building 515 are two-component, solvent-based paints. Paint residue analysis results reported in Table 2 indicate that the paints are 30 to 40 percent volatile by mass. Combining these data with the density measurement yields a coating solvent content of 425, 415, 360, and 340 g/L for the green primer, forest green paint, yellow gloss topcoat, and orange gloss topcoat, respectively.

A number of site-specific issues must be addressed in determining whether or not paint reformulation is feasible for a given facility. Of primary concern is compatibility between the coating compound and the equipment painted. In addition, the ease with which paint reformulation may be adopted at a given facility must be addressed. Finally, the impact that coating substitution will have on solvent emission rates must be considered.

1. Compatibility of Coating with Equipment

The workpieces painted during the test series were all ground equipment such as hydraulic lifts, ladders, equipment stands, stepladders, and fork lifts. Further information was collected concerning the other equipment typically handled by Building 515 personnel. It was found that ground equipment is painted almost exclusively, therefore low-solvent content or water-reducible coatings could be substituted for the specially developed aerospace topcoats currently used.

A survey of the types of low-solvent paints and water-reducible coatings that have been approved for use on rugged ground equipment at DOD facilities revealed that the Air Force has successfully substituted water-reducible primers and low-solvent topcoats for use on ground equipment such as "six-pack" field shelters and hydraulic lifts. All the substitute coatings have been approved for use by DOD installations, except an interior aircraft compartment epoxy topcoat. It is anticipated that the MIL-SPEC for this interior coating will be assigned in the near future.

2. Requirements for Substituting Low-Solvent Coatings

Painting operations at Hill Air Force Base are controlled by specific technical orders, which identify the coating that may be used, as well as the equipment on which it may be used. In conversations with personnel at McClellan Air Force Base, where the standing orders were changed to allow coating substitution, it was learned that the procedure involved was

straightforward and did not involve significant delay. In short, the benefits accrued by coating substitution are worth the paper work involved.

3. Emissions Reductions Through Coating Substitution

The solvent content of the coatings used during the Hill Air Force Base test are listed in Section II. Data on the substituted coatings used at McClellan Air Force Base indicate that the water-reducible primer (MIL-P-85582) used on ground equipment contains a maximum of 350 g/L of VOC, the camouflage coatings (MIL-C-46168 D) contain a maximum of 420 g/L of VOC, and the gloss topcoats (MIL-C-85285) contain a maximum of 340 g/L of VOC.

Substituting the above coatings can result in an 18-percent and 6-percent decrease in VOC content for the green primer and the yellow gloss topcoat, respectively. The paint usage data collected (Table 4) indicate that the primer and yellow gloss paint comprise 18 and 8 percent by mass of the total quantity of coating used, respectively. However, according to Hill Air Force Base personnel, the quantity of green primer generally used in the Building 515 paint booth may be higher than 30 percent. Thus, by substituting the water-reducible primer for the primer currently used, VOC emissions may be decreased 5 to 10 percent.

B. FLOW REDUCTION COMBINED WITH A VOC EMISSION CONTROL DEVICE

As described previously, a typical paint booth VOC emission control device is capable of achieving 95-percent removal efficiency. However, the costs associated with installing and operating a system capable of processing the high-volume flow rates typical of paint booth operations are quite high. The exhaust flow rate from the Building 515 paint booth is 11,000 scfm. The installation of a thermal incineration device equipped with a primary heat recovery unit capable of processing 11,000 scfm costs more than \$250,000 (Reference 11), and daily operating costs exceed \$200.

The high cost of controlling VOC emissions from paint booths can be significantly lowered by decreasing the flow rate that requires treatment. A significant reduction would be achieved by installing one of the flow-reducing ventilation systems described in Section IV. For both the split-flow and recirculation systems, design criteria and calculations specific to the Building 515 painting facility are discussed below.

1. Design Criteria for Building 515 Paint Booth Split-Flow Ventilation System

The exhaust face of the Building 515 paint booth is 16 feet high and 16 feet wide, and is equipped with a water curtain particulate emission control device. To install a split-flow ventilation system, the water curtain will require replacement with a dry filter system to facilitate separation of the two exhaust streams. Converting the particulate emission control system from wet to dry operation is a simple and straightforward task; however, providing conversion details is beyond the scope of this report.

Following conversion of the water curtain device, the split-flow ventilation system is installed. The critical aspect of designing a split-flow system is determining where flow separation should occur. This parameter is most sensitive to the dimensions of the exhaust face and the objects painted; as described previously, the workpieces normally painted in the Building 515 paint booth are small. The flow separation height for the Building 515 painting facility was selected based on test results, which indicate that more than 80 percent of the VOCs, metals, and isocyanates measured in the booth were at or below the 5 foot level. Therefore, the optimal zone separation height for the booth tested is 5 feet. A diagram of the proposed split-flow ventilation system is provided in Figure 46.

Placing the zone separation at 5 feet will result in a flow reduction of approximately 7,500 scfm (or 70 percent) to the VOC emission control device. The test data indicate that approximately 70 percent of the VOCs released into the booth will be concentrated in the 3,500 scfm passing to the control device. If the average control efficiency achieved by the emission control device is 95 percent, the combined split-flow/emission control system will reduce VOC emissions by approximately 65 percent. The cost reductions that will be realized by installing the split-flow system are significant. For a 3,500-scfm thermal incineration system, installation and daily operating costs are approximately \$200,000 and \$80, respectively. This represents 20-percent and 60-percent savings in installation and operating costs, respectively. The cost of converting the water curtain and installing the split-flow system should be included here; however, these costs could not be accurately calculated because insufficient data are available concerning operation and design of the water curtain system currently in place. Conservative estimates for converting the water curtain device and installing the split-flow ventilation system are \$4,000 and \$15,000, respectively.

Additional benefits that may be accrued by installing the split-flow ventilation system include elimination of wastewater treatment and hazardous waste disposal costs incurred due to operation of the water curtain, and electrical operating cost reductions that will be achieved through elimination of the water curtain sump pump.

2. Design Criteria for Building 515 Paint Booth Recirculation System

As discussed briefly in Section IV, recirculation is a technique for concentrating the VOCs, thereby reducing the volume flow rate to a VOC emission control device. The level of VOC control achieved is the same as if an emission control device were used without any flow reduction technique. The extent to which the VOCs may be concentrated is limited by safety considerations. Applicable safety standards are put forth by the National Fire Protection Association (NFPA) and OSHA. To eliminate the possibility of fire and explosive in paint booths, NFPA regulations suggest, and OSHA requires, that sufficient ventilation air be present to dilute the airborne solvents to a concentration below 25 percent of the lower explosion limit (LEL).

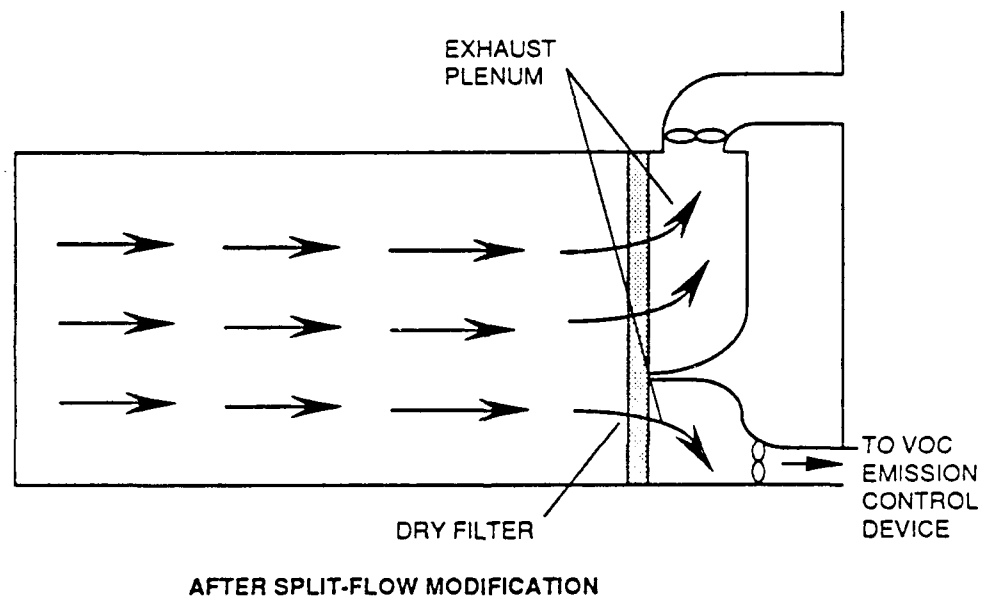
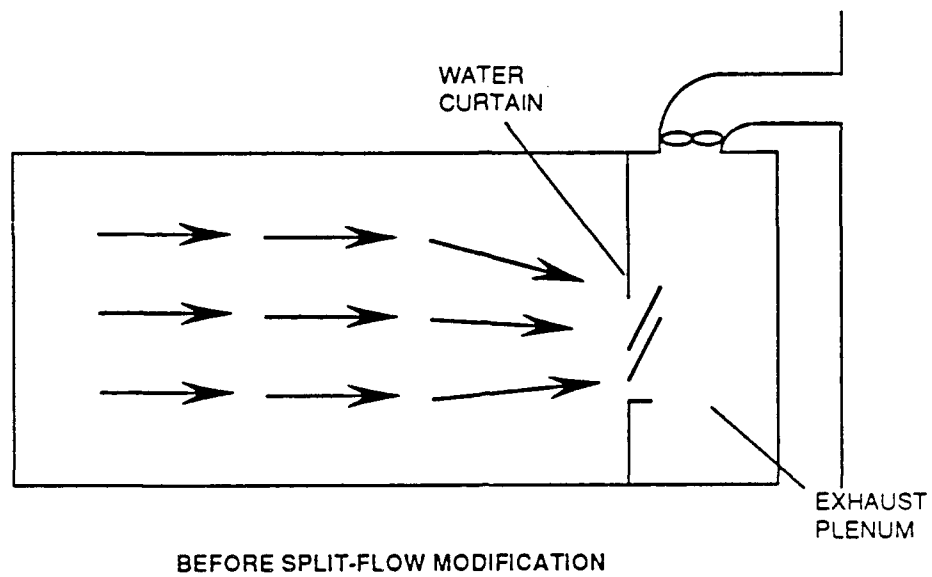


Figure 46. Schematic of Building 515 Paint Booth Before and After Split-Flow Modification

To prevent exposure to dangerously high concentrations of solvent vapors, OSHA requires that workers not be exposed to solvent concentrations in excess of threshold limit values (TLV). In general, TLVs are much lower than 25 percent of the LEL. In the interest of worker health and safety, the TLV will be used for determining the recirculation rate. The lowest TLV of the principal paint solvents measured is 540 mg/m³. Additional parameters that must be thoroughly evaluated before a safe and efficient recirculation system can be designed include paint usage rates, flow rates, booth volumes, and duty cycles.

The spray booth located in Building 515 has a very simple ventilation system and can therefore be modified easily to accommodate recirculation. A schematic of the proposed recirculation system for the Building 515 painting facility is provided in Figure 47. For the sake of comparison, a schematic of the booth as it now stands is also provided. In this design, the exhaust duct is rerouted so that it passes from the existing plenum chamber (located at the back of the booth) over the roof to the front of the spray booth. The recirculated air is drawn with an intake fan placed downstream of a plenum chamber on the roof and passes into the booth through the swing-out doors located at the front. To allow the doors to open easily, flexible ductwork will be installed to connect the front plenum chamber to the door intakes.

To control VOC concentrations in the booth, a portion of the exhaust air is vented to a VOC emission control device through a bleed-off duct connected to the existing plenum chamber located at the back of the booth. The bleed-off air is replaced with fresh makeup air, which is introduced into the front plenum chamber described above.

To ensure that the VOC concentration in the booth remains below a safe level, an LEL monitor is placed in the recirculation duct near the existing plenum chamber located at the back of the booth. The LEL monitor is attached to an automatic control system that switches the booth to single pass operation if the VOC concentration in the booth exceeds a safe level.

The key to designing a safe and efficient recirculation system is selecting the proper bleed-off flow rate. The three site-specific operating parameters that determine the bleed-off flow rate are the paint usage rate, booth size, and maximum allowable solvent concentration. The mathematical derivation of the minimum required bleed-off flow rate is presented in detail in Reference 1. The results of the derivation will be summarized here and adapted to the Building 515 facility.

The bleed-off flow rate is determined iteratively from the following equation:

$$M(t) = \dot{M}_p \frac{V_{\text{booth}}}{\dot{V}_{\text{out}}} \left[1 - e^{-\left(\frac{\dot{V}_{\text{out}}}{V_{\text{booth}}} t \right)} \right]$$

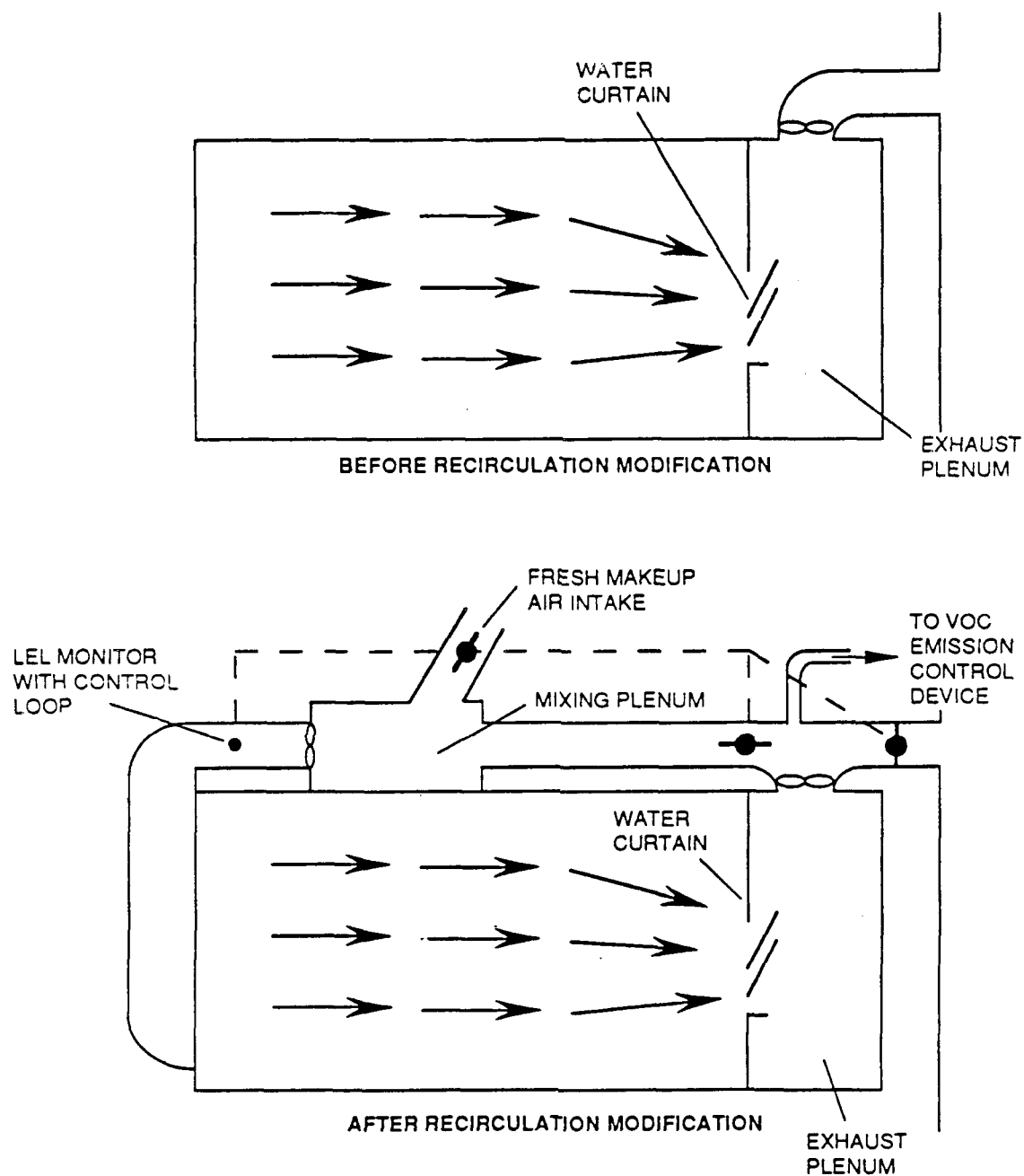


Figure 47. Schematic of Building 515 Paint Booth Before and After Recirculation Modification

Where:

- $M(t)$ = The total mass of solvent in the booth
 $\dot{M}_p$ = Rate at which the solvent is released into the booth
 V_{booth} = Booth volume
 $\dot{V}_{\text{out}}$ = Bleed-off volume flow rate
 t = Time

To calculate the bleed-off flow rate ($\dot{V}_{\text{out}}$), the duration of a typical painting cycle is substituted for t , the maximum allowable solvent concentration (according to OSHA TLV standards) is substituted for $M(t)$, the maximum solvent release rate over the painting cycle is substituted for $\dot{M}_p$, and the volume of the booth (length x width x height) is substituted for V_{booth} . $\dot{V}_{\text{out}}$ is then determined iteratively.

The equation parameters that are specific to the Building 515 booth are derived as follows. V_{booth} is 254 m³ (8,960 ft³). The highest paint consumption rate during the test series was recorded on 9 December, when, in a 25-minute period, 7.0 kg (15.4 lb) of forest green topcoat was used (Table 4). This corresponds to a total of 2.8 kg (6.3 lb) of solvent released in the booth over the 25-minute period (see Table 2). Thus, the maximum solvent release rate ($\dot{M}_p$) recorded at this facility is 6.72 kg/hr (14.8 lb/hr). During the test series, it was observed that a typical painting cycle lasts for an hour. However, to ensure conservative results, a 2-hour painting cycle will be used, throughout which the maximum solvent release rate will be applied. The parameter t in the above equation will be set equal to 2 hours. As indicated previously, the maximum allowable solvent concentration in the booth will be 540 mg/m³. This maximum concentration corresponds to a maximum allowable solvent concentration [$M(t=2 \text{ hr})$] of 0.14 kg (0.31 lb).

Inserting these parameters into the above equation yields a bleed-off flow rate of 5,600 scfm. The installation and daily operating costs associated with a thermal incinerator/heat recovery unit capable of processing 5,600 scfm with a 95-percent removal efficiency, are approximately \$225,000 and \$130, respectively. The economic advantages of operating a recirculation system in conjunction with a VOC emission control device are obvious; the same level of VOC emission control is achieved, yet the control equipment installation costs are nearly 15 percent lower, and operating costs are decreased by more than 35 percent. A conservative cost estimate for installing the recirculation system is \$25,000, which does not include the LEL monitor and the automatic control system. (Note: all costs reported here are in 1989 dollars.)

3. Combined Recirculation/Split-Flow Ventilation System

The optimal flow-reduction system for the Building 515 painting facility is a combination of the recirculation and split-flow strategies. In the combined system, the maximum VOC reduction is achieved (rather than the 70 percent achievable by split-flow), and the bleed-off flow

rate may be lower than if recirculation or split-flow were used alone. Schematic diagrams of the Building 515 paint booth before and after this proposed modification are provided in Figure 48.

To confirm that the combined split-flow/recirculation system will maintain solvent concentrations in the booth below the 540 mg/m^3 limit specified previously, the calculation provided in subsection 2 must be used. The solvent release rate ($\dot{M}_p$) is the amount of the total solvent released into the booth that is recirculated (and not vented directly to the VOC emission control device through the split-flow system). The maximum solvent release rate (calculated previously) is 6.72 kg/hr . A conservative estimate of the quantity of solvent not vented to the control device through the split-flow duct is 50 percent (test results indicate that this parameter may be as low as 30 percent however 50 percent is assumed to ensure conservative results). These assumptions imply that 50 percent (or 3.36 kg/hr) of the solvent released into the booth is recirculated, the remainder passes directly to the VOC emission control device. The value for the actual solvent release rate ($\dot{M}_p$) is therefore 3.36 kg/hr . Inserting this value into the above equation, and assuming 2 hours of operation and a bleed-off flowrate of $3,500 \text{ cfm}$ (calculated previously for the split-flow system), yields a maximum solvent level of 0.097 kg . This quantity is well below the maximum allowable level (0.14 kg) specified previously. Thus, a combination of the split-flow and recirculation strategies results in the most cost-effective means of achieving the highest possible degree of VOC emission control. This calculation also illustrates the possibility of decreasing the bleed-off flow rate even further.

The cost associated with installing a combined split-flow/recirculation system on the Building 515 painting facility is approximately \$35,000. The installation and operating costs associated with the VOC emission control device are the same as those reported previously in subsection 1.

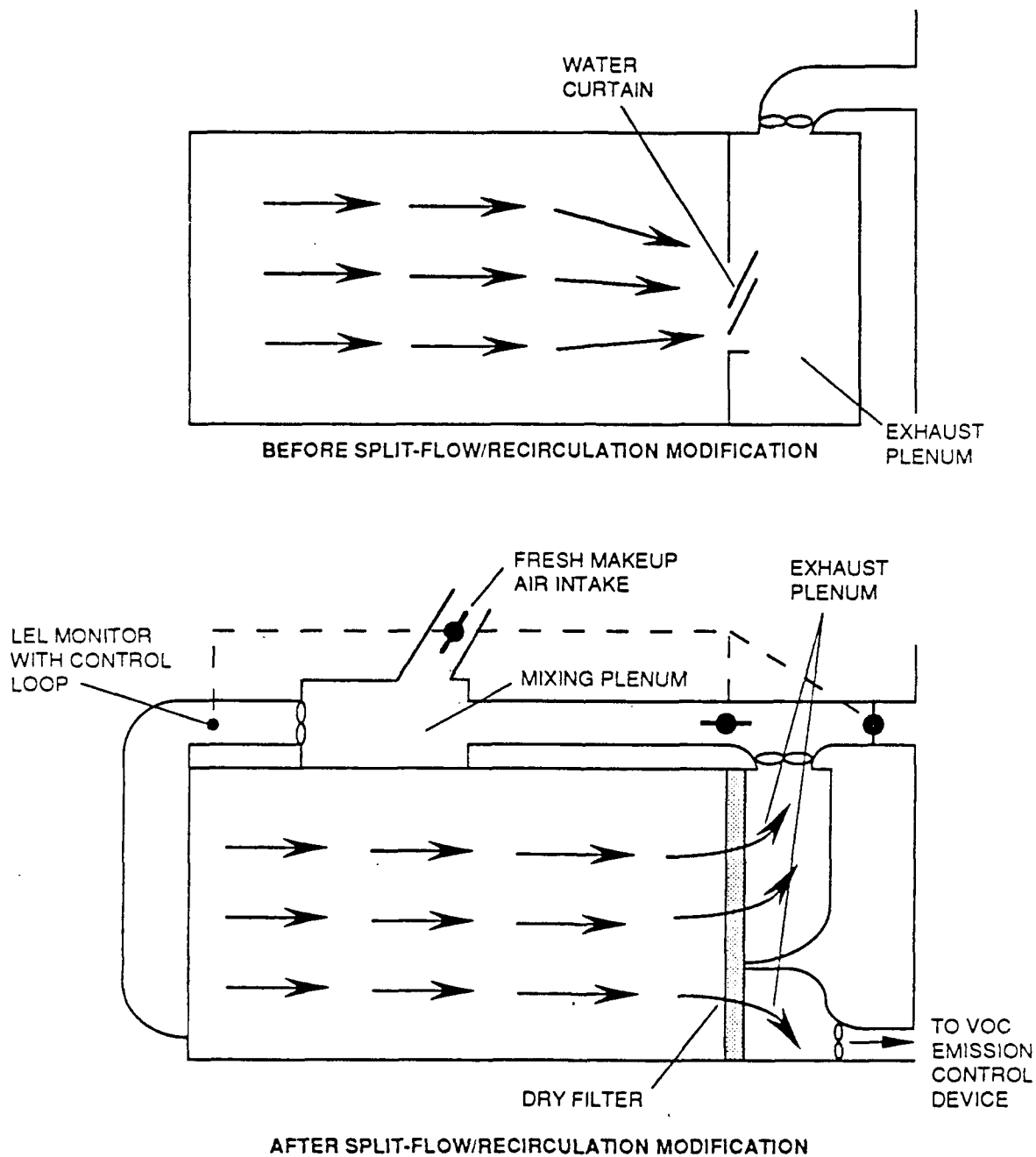


Figure 48. Schematic of Building 515 Paint Booth Before and After Combined Split-Flow/Recirculation Modification

SECTION VI

CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The data collected in the test efforts (presented in Section III) and the subsequent engineering evaluation lead to the following conclusions:

- Hazardous constituent concentrations in the paint booth (such as metals, organics, and isocyanates) during painting operations are highest at or below the 4-foot level.
- Concentrations of hazardous constituents in the vicinity of the painter are among the highest in the booth.
- The water curtain particulate emission control system does not have any impact on the solvent emissions from the paint spray booth.
- The coatings used in Building 515 have a fairly low solvent content, with the exception of the green primer coating.
- A 5- to 10-percent reduction in solvent emissions from the paint booth may be realized by substituting a water-reducible primer coating for the primer currently used.
- Cost-effective elimination of VOC emissions may be achieved with the use of a VOC emission control device operated in conjunction with a process flow reduction system, such as split-flow, recirculation, or a combination of both.

B. RECOMMENDATIONS

The two primary recommendations are:

- Replace the green primer currently used in painting operations in Building 515 with a water-reducible primer. This will involve changing Hill Air Force Base technical orders.
- Consider the implementation of a VOC emission control device operated in conjunction with either a split-flow or recirculation ventilation system, or a combination of both.

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APPENDIX A
QUALITY ASSURANCE/QUALITY CONTROL
EVALUATION REPORT

A number of quality assurance/quality control (QA/QC) procedures were followed to assess the quality of the data reported herein. The data quality objectives (DQOs) as outline in the Quality Assurance Project Plan (QAPP) for this project are given in Table A-1. The results of QA/QC efforts are presented in this section and are organized according to specific types of measurements and analyses performed, such as air samples and flow rate measurements, organic compound concentrations in paint samples, etc. A discussion of the external audit results and variations of methods proposed in the QAPP that were required to obtain accurate sampling and analysis results is included at the end of this appendix.

A. ASSESSMENT OF OVERALL DATA QUALITY

Nearly all the data quality objectives for the 38 QA/QC measurements taken in this test series were achieved. Some objectives were not met for side-by-side duplicate samples taken at specific sampling locations. The variability detected from side-by-side duplicate analyses is doubtlessly due to sample orientation. Great effort was expended to ensure that the duplicate VOC, particulate, and isocyanate sample systems had identical orientations, however, samples were often jostled during painting.

To insure accurate in-booth pollutant concentration measurement results, two sampling events were conducted for each of the pollutant of interest (organics, metals, and isocyanates). For each sampling event and duplicate sampling event, the fundamental results (and therefore conclusions drawn from these results) are the same; namely that significant pollutant stratification occurs in the booth during painting, and that pollutant concentrations in the vicinity of the painter are among the highest in the booth. Although results obtained from side-by-side duplicate analyses are disappointing, precision results obtained for duplicate sampling events are not. Thus, the impact of the side-by-side duplicate analyses on the results and conclusions drawn in this report are small.

B. ASSESSMENT OF AIR SAMPLING AND ANALYSIS AND FLOW RATE MEASUREMENT DATA QUALITY

1. Airflow Measurements in the Duct and at the Water Sump Face

Airflow measurements were performed in the paint booth exhaust duct according to EPA Method 2 procedures. One measurement was taken per day, and a duplicate measurement was taken on 7 December. Precision was assessed at 0.26 percent by calculating the relative percent difference (RPD) between actual and duplicate measurements. The precision DQO of ± 20 percent for the EPA Method 2 measurements was easily met.

The airflow measurements at the water sump face were taken daily using an anemometer, and one duplicate sample was taken. The precision DQO for this measurement was ± 20 percent. Precision was assessed by calculating the RPD between the actual and duplicate measurements, which was 3.1 percent.

TABLE A-1. DATA QUALITY OBJECTIVES.

Measurement Parameter	Measurement/ Analytical Method	Reference	Precision Relative Percent Difference	Accuracy (percent recovery)	Completeness
Volume flow at sump	ACGIH; Anemometer	ACGIH ^a	±20		90
Volume flow in duct	EPA Method 2; Pitot tube	40 CFR 60	±20	±40	90
Particulate concentration in exhaust duct	EPA Method 5; Isokinetic sampling	40 CFR 60	N/A	±40	90
	NIOSH 500; Gravimetric	NIOSH ^b 84-100	±35		90
Metal concentration in airborne paint particulate	EPA methods 3010 and 6010; filter digestion, ICAP analysis	SW-846 ^c	±35	70 to 130	90
Isocyanate concentrations in air	OSHA Method 42; HPLC	Not yet a published method	±35	70 to 130	90
Organic compound concentrations in air	NIOSH 1300; Carbon adsorption, Extraction, GC/FID	NIOSH 84-100 ^b	±35	70 to 120	90
Percent volatiles in paint	Percent weight loss on drying	ASTM 3960 ^d	±20	±40	90
Percent isocyanates in paint	ASTM Method D2572; Reaction with di-n-butylamine	ASTM 2572-80 ^d	±30	70 to 130	90
Speciation of organic compounds in paint	GC/MS analysis	Not a published method	±40	70 to 130	90
Semivolatile organic compounds in water	EPA Method 8270; MeCl ₂ extraction, GC/MS	SW-846 ^c	±30	50 to 140	90
Volatile organic compounds in water	EPA Method 8240; Capillary purge and trap, GC/MS	SW-846 ^c	±30	50 to 140	90
Total organic carbon concentrations in water	EPA 415.1; purge, convert to CO ₂	EMSL ^e	±20	80 to 120	90
Total suspended solids in water	Percent weight loss on drying	EMSL ^e	±20	N/A	90
TUHC	EPA M25A; Continuous FID, BAAQMD ST-7; NDIR	40 CFR 60 BAAQMD Manual ^f	±20	±20	90

^aIndustrial Ventilation — A Manual of Recommended Practices, 14th Ed., American Council of Governmental Industrial Hygienists, Committee on Industrial Ventilation.

^bNIOSH Manual of Analytical Methods, Department of Health Services.

^cProposed Sampling and Analytical Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods (SW-836, 3rd Edition); USEPA [NTIS PB88-239223], September 1986.

^dAmerican Society for Testing and Materials; Annual book of ASTM Standards, Part 28.

^eMethods for Chemical Analysis of Water and Wastes, Environmental Monitoring and Support Laboratory, EPA-600-4-79-020 (Third Edition [NTIS PB84-128677]), March 1983.

^fBay Area Air Quality Management District (BAAQMD) Procedures Manual, Source Test Procedure 7, 1986.

Accuracy for the airflow measurements in the duct was assessed by comparing the EPA Method 2 measurements taken in the duct with the anemometer measurements taken at the water sump face. Because these measurements were taken daily, the accuracy of the airflow measurements could be assessed daily. The accuracy DQO for this measurement was ± 40 percent, and the daily comparison showed agreement within 36, 34, and 32 percent. Thus, the data quality objective for this measurement was achieved.

The completeness DQO for both the EPA Method 2 and the anemometer airflow measurements is 90 percent. The test plan required that these measurements be taken for each of the three test series, and because the test series extended over 3 days, these measurements were taken daily (extra tests were performed during an additional day of testing; airflow measurement were taken on the fourth day as well). All of the airflow measurements in the test plan were taken, thus the DQO of 90 percent for these measurements was achieved.

2. Particulate Concentrations in the Paint Booth and Exhaust Duct

Particulate concentration measurements were performed in the paint booth according to NIOSH 500 sampling procedures and in the exhaust duct according to EPA Method 5 (EPA M5) and NIOSH 500 sampling procedures. Duplicate measurements for the EPA M5 testing were not possible, thus a precision DQO for the EPA M5 tests was not stipulated in the QAPP. However, a precision DQO of 40 percent was stipulated for the NIOSH 500 tests. The precision of this measurement was determined through the use of a duplicate sample taken during one of the NIOSH 500 sampling efforts in the paint booth. A comparison of the sample and duplicate data resulted in a RPD of 38 percent.

Accuracy was assessed by comparing the NIOSH 500 particulate sampling results to the EPA M5 particulate results. The accuracy DQO stipulated in the QAPP for this measurement was ± 35 percent. The NIOSH 500 and M5 results agreed in that no particulate was collected in either samples, however actual accuracy could not be assessed because no material was collected on the filters.

The completeness DQO for both the EPA M5 and NIOSH 500 particulate sampling efforts is 90 percent. The test plan required two of each measurement be taken; these samples were obtained, thus the DQO of 90 percent was met.

3. Metal Concentrations in Airborne Paint Booth Particulate

Metal concentrations in airborne paint booth particulate were determined in general accordance with NIOSH 500 sampling and analysis procedures. Two sets of measurements were performed. To assess precision, a duplicate sample was taken during one of the tests. The term duplicate can be only loosely applied in this case; due to the extremely dynamic nature of the test, and the impossibility of placing the duplicate in the same location and orientation as the sample, a true duplicate measurement was not possible. In particulate sampling, the

orientation of the filter has a significant impact on the mass of particulate collected. Great effort was expended during the test series to ensure that particulate filters faced into the flow of air passing through the booth. However, the filters could be shifted and jostled during the painting process, which would change the filter orientation.

On the duplicate filter, the same metals were present as were found on the sample filter, however the concentrations of each metal on the duplicate filter were approximately one half of the concentrations detected on the sample filter. The precision of this measurement was assessed by the RPD of the metals concentrations found on the duplicate and sample filters. The RPD for barium, chromium, lead, titanium and zinc was 62, 89, 72, 60 and 40 percent, respectively. This indicates that the variability of this measurement may be as high as 89 percent. The factor with the greatest potential impact on measurement variability is the sample orientation, because matrix spike duplicate analyses (see below) indicated far less variability.

Despite a high variability measured for side-by-side duplicate results, the two metal sampling events confirmed that pollutant stratification occurs during painting, and that concentrations in the vicinity of the painter are quite high. These fundamental results (and the conclusions drawn in this report based on those results) are not affected by the high variability indicated from the side-by-side duplicate analyses.

Matrix spike recovery analyses were performed to evaluate the accuracy of the analytical results. The percent recovery results for the metals analyzed are presented in Table A-2. Titanium was not spiked. The accuracy (recovery) DQO for this measurement was 70 to 130; all but one of the percent recovery results were well within this range.

In the original QAPP, 52 field samples were to be collected for this sampling effort. There were 45 valid results obtained, thus a completeness measurement of 87 percent was achieved. The DQO for this measurement was 90 percent; however, the lack of results from one sample will not significantly impact the results of this study.

A field blank filter was also analyzed for the metals listed above. Low concentrations of chromium, copper, lead, molybdenum, and zinc were measured on the blank filter. Results of this analysis are presented in Table 16 and 17.

4. Isocyanate Concentrations in the Paint Booth

Isocyanate concentrations in the paint booth during painting operations were determined in general accordance with OSHA Method 42 sampling and analysis procedures. Two sets of measurements were performed. To assess precision, duplicate analyses were taken during tests. As with the results presented in subsection A-3 of this Appendix, the term duplicate can only be loosely applied.

**TABLE A-2. MATRIX SPIKE METALS RECOVERY
RESULTS FROM FILTER SAMPLE
ANALYSES.**

Metal	Recovery Results (percent)
Antimony	100
Barium	89
Cadmium	90
Chromium	95
Cobalt	94
Copper	90
Lead	96
Molybdenum	101
Nickel	97
Silver	64
Thallium	79
Vanadium	91
Zinc	97

The total isocyanate concentration on the duplicate filter was approximately 40 percent of the concentration detected on the sample filter. The RPD of this measurement is therefore 89 percent. As with the metals results presented in subsection A-3 of this Appendix, the difference between the duplicate and sample results is likely due to filter orientation. This indicates that the variability of this measurement may be as high as 89 percent. The factor having the greatest impact on measurement variability is the sample orientation.

Matrix spike recovery analyses were performed to evaluate the accuracy of the analytical results. The only isocyanate compound detected in these tests series was hexamethylene diisocyanate, thus blank filter samples were spiked with hexamethylene diisocyanate, and 98 percent recovery was achieved. The accuracy DQO for this measurement is 70 to 130; the percent recovery result is well within this range.

A completeness DQO of 90 percent was stipulated in the QAPP. Analytical results from 58 samples were required for an adequate engineering evaluation, however 59 samples were collected, and 59 valid results were obtained. This resulted in a completeness measurement of 101 percent.

Two field blank filters were analyzed for background isocyanate contaminations. No isocyanates were detected on the blank filters in concentrations above method detection limits (0.1 µg per filter).

5. Organic Compound Concentrations in the Paint Booth and the Exhaust Duct

Organic compound concentrations in the paint booth and duct during and after painting operations were determined in general accordance with NIOSH Method 1300 sampling and analysis procedures. Two sets of measurements were performed in the booth, and several

samples were taken in the exhaust duct. The samples taken in the exhaust duct were used to determine the organic compound removal efficiency of the water curtain and to perform a mass balance.

To assess precision, two sets of duplicate samples were taken. The first duplicate set of charcoal tubes was taken in the paint booth during painting. The analytical results indicate that the same organic compounds detected on the duplicate tube were found on the sample tube, however the concentrations of each compound were different. The precision of this measurement was assessed by the RPD of the organic compound concentrations found on the duplicate and sample tubes. The RPDs are presented in Table A-3. These results indicate that measurement variability is on the order of 50 percent. As discussed previously, the high variability is most likely due to the orientation of the sampling system. The variability was not detected until after the analytical results were obtained, at which point it was too late to take any corrective action regarding sample collection.

The most important results obtained from the in-booth sampling and analysis efforts are that pollutant stratification occurs during painting, and that pollutant concentrations in the vicinity of the painter are among the highest in the booth. These results were obtained from 2 integrated VOC sampling events (in which more than 30 samples each were collected) occurring on 9 December. These trends were evident, despite the potential occurrence of variable concentrations at any one sampling position. Thus, VOC sampling variability at any given location will have little or no impact on fundamental results and conclusions.

The second set of duplicate charcoal tube samples was taken in the exhaust duct on 8 December. Nearly identical toluene concentrations were measured in both samples, however no other compounds were detected in the duplicate sample. These results could not be explained. The analytical data were checked thoroughly when this anomaly was detected, however no errors in analysis were found.

The first set of charcoal tubes submitted to the laboratory for analysis were extracted with methanol. It was found that the organic concentrations measured in the extract were not as high as had been anticipated, thus the extraction solvent was changed. The second set of charcoal tubes submitted for analysis was extracted with acetone, the result being that recoveries were much improved. Matrix spike recovery analyses were performed for the analytes detected on the charcoal tubes for each of the extraction solvents used. Desorption efficiencies of the spiked analytes were determined at three spiking levels within the calibration range. The results of these tests are presented in Table A-4. Surrogate spike recoveries were also measured for both types of extraction solvents used; these results are presented in Table A-5.

The test plan stipulated that a total of 62 field samples and six QA/QC samples were to be collected for the organic compound sampling effort. This number was determined by

**TABLE A-3. RELATIVE PERCENT DIFFERENCE
MEASUREMENTS BETWEEN DUPLICATE
NIOSH 1300 CHARCOAL TUBE SAMPLES.**

<u>Compound</u>	<u>Relative Percent Difference</u>
2-Butanone	38
Toluene	90
Butyl acetate	33
Ethylbenzene	73
p-Xylene	81
o-xylene	77
Ethyl Acetate	38
Methoxyacetone	30
4-Methyl-2-pentanone	41
2-Ethoxyethyl acetate	74

assuming that breakthrough would occur in at least 10 percent of the samples, which in turn would require that backup charcoal tubes be analyzed. As breakthrough did not occur in any samples, only 54 field samples and six QA/QC field samples are required for an adequate engineering evaluation. The 57 valid results obtained results in a completeness measurement of 95 percent, which exceeds the completeness DQO of 90 percent, as stipulated in the QAPP.

Analysis of one field blank charcoal tube sample indicated that low concentrations of 2-butanone and ethyl acetate were present. A second blank sample contained no contaminants in concentrations exceeding method detection limits.

6. Total Unburned Hydrocarbon Measurements in the Exhaust Duct

Continuous total unburned hydrocarbon (TUHC) concentration measurements were taken daily in the paint booth exhaust duct according to EPA Method 25A and BAAQMD ST-7 procedures. The precision of these sampling methods was assessed by measuring the RPD between successive calibration measurements. The precision DQO stipulated in the QAPP is ± 20 percent. The successive RPDs calculated for the ST-7 procedure are 0, 17, 0.3, 0.4, 1, 1, 2.2, and 3.2 percent. The RPDs are well within the DQO range.

The midrange calibration gases that were to be used to assess measurement accuracy did not arrive at the test site, thus no calibration gases were used. The M25A results and the ST-7 results were compared and found to be in reasonable agreement. This may be taken as evidence that the continuous organic concentration measurements are valid, despite the absence of the midrange calibration procedure.

TABLE A-4. NIOSH 1300 CHARCOAL TUBE DESORPTION EFFICIENCY RESULTS.

Tubes Extracted With Acetone

CHEMICAL NAME	Average	DE1	DE1	DE2	DE2	DE3	DE3
Compounds, Group 1	Rfactor	Area	%Rec	Area	%Rec	Area	%Rec
2-Butanone	0.112	174202	94	311637	60	419292	58
p-Difluorobenzene (SU1)	0.099	151607	67	166231	62	131956	49
Toluene	0.075	102680	32	223123	34	382810	37
2-Bromo-1-chloropropane (SU2)	0.235	385240	91	385062	90	377367	88
Butyl acetate	0.140	151479	87	294113	83	419818	75
Ethylbenzene	0.074	148976	46	302730	45	488462	47
p-Xylene	0.060	92163	23	197717	24	338113	26
o-Xylene	0.071	56330	16	109080	16	181205	17

Compounds, Group 2

Ethyl acetate	0.158	108682	81	194224	53	395004	80
p-Difluorobenzene	0.086	130766	43	166863	60	164201	56
Methoxyacetone	0.193	77001	52	156092	62	232260	65
Ethoxyethanol	0.194	99872	73	181496	73	279160	74
4-Methyl-2-pentanone (MIBK)	0.112	190333	78	351661	82	483677	75
2-Bromo-1-chloropropane (SU2)	0.244	383605	97	369614	89	363372	86
2-Ethoxyethyl acetate	0.187	110156	77	207667	80	290372	74
2-Butoxyethanol	0.151	121336	68	249477	78	355830	73
bis(2-Methoxyethyl) ether	0.221	70800	59	155966	71	223120	67
2-(2-Methoxyethoxy) ethanol	0.381	NR	NR	81883	65	138629	64
Ethoxyethoxyethanol	0.355	NR	NR	77650	60	134743	59

NR - Not Recovered

Spiking Level (ppm)

Desorption Efficiency 1: 25
Desorption Efficiency 2: 50
Desorption Efficiency 3: 100

Tubes Extracted With Methanol

CHEMICAL NAME	Average	DE1	DE1	DE2	DE2	DE3	DE3
	Rfactor	Area	%Rec	Area	%Rec	Area	%Rec
2-Butanone	1.137	161554	58	NR	NR	233130	42
p-Difluorobenzene (SU)	1.242	157142	78	143539	71	170700	84
2-Ethoxyethanol	4.542	23755	43	61239	56	93003	56
4-Methyl-2-pentanone	1.398	81829	46	155962	44	229034	43
bis(2-Methoxyethyl) ether	2.942	NR	NR	58664	35	726600	28

NR - Not Recovered

SU - Surrogate

Spiking Levels (ppm), based upon 400 mg charcoal front section.

Desorption Efficiency 1: 250
Desorption Efficiency 2: 500
Desorption Efficiency 3: 1000

TABLE A-5. NIOSH 1300 CHARCOAL TUBE SURROGATE RECOVERY RESULTS.

Sample ID	Surrogate Percent Recovery With Acetone Extraction			
	p-Difluorobenzene		1-Bromo-1-chloropropane	
	Front half	Back half	Front half	Back half
905580	81	43	60	88
905576	73	49	358	92
905577	82	44	304	92
905574	85	37	486	91
905586	67	53	83	158
012318	67	48	15	76
012339	60	40	90	90
905581	68	44	216	92
905563	54	45	89	92
905568	62	42	118	91
012322	65	29	164	90
012317	60	27	278	90
000583	52	30	90	91
000588	60	29	92	186
012321	60	30	186	93
905583	61	26	178	91
905571	61	32	22	88
000591	60	35	206	93
000653	57	34	195	91
000655	58	31	158	91
000582	49	35	59	69
012341	89	89	167	90
000640	56	33	147	90
000642	59	32	163	86
000644	58	33	155	90
905565	59	29	156	89
012315	58	32	242	92
905588	99	54	95	47
905530	96	37	180	87
905532	77	40	88	74
905534	91	41	349	89
904347	80	37	87	100
905551	84	37	254	88
904357	76	47	85	88
905612	74	76	93	91
Blank	86	NI	92	NI
Blank	28	NI	98	NI
Blank	83	35	90	92

NI No information

**TABLE A-5. NIOSH 1300 CHARCOAL TUBE
SURROGATE RECOVERY
RESULTS (CONCLUDED).**

Surrogate Percent Recovery
With Methanol Extraction

Sample ID	<u>p-Difluorobenzene</u>	
	Front half	Back half
012297	65	NI
012308	68	45
000649	85	62
000629	106	151
000620	89	85
000625	86	123
012324	118	56
012330	96	50
012332	85	49
012335	88	128
000639	111	116
012329	98	21
000623	82	50
000647	101	66
000637	92	53
000627	90	38
012337	109	66
000596	98	59
000594	94	20
000604	89	48
000635	73	52
000618	110	98
000598	111	60
000601	122	71
Blank	75	32
Blank	64	38

NI No Information

The test plan stipulated that continuous TUHC measurements were to be taken daily during and after all painting operations. Both M25A and ST-7 results were obtained during the three test days, and in addition, results were also obtained for the extra day of testing. Thus the completeness measurement of this test was greater than 100 percent.

C. ASSESSMENT OF PAINT SAMPLING AND ANALYSIS DATA QUALITY

1. Isocyanate Concentrations in Paint

Paint samples were collected to determine the isocyanate concentrations present. The measurement precision was determined through the analysis of one set of duplicate samples. The RPD between the sample result and the duplicate result was less than 1 percent. The DQO of ± 30 stipulated in the QAPP was attained.

Method accuracy was determined by analyzing a matrix spike sample. One paint sample was spiked with toluene diisocyanate, and the percent recovery was 104 percent. The DQO for this measurement stipulated in the QAPP is 80 to 120 percent, and the spike recovery result is well within this range. As an additional measurement of accuracy, the results of the isocyanate analysis for all the paint samples were compared against paint manufacturer data. The manufacturer data furnished were in the form of Material Safety Data Sheets (MSDSs) supplied in Air Force computer format.

Isocyanates are present only in the catalyst components of the paints in the form of isocyanate polymer and prepolymer groups attached to a biuret resin compound. Isocyanate concentrations are not reported in the MSDSs explicitly, rather the concentrations of biuret resin are reported. In all cases, the biuret resin concentrations are present at 30 to 35 percent. Phone conversations with technical representatives of the paint manufacturer (DEFT) indicate that isocyanate groups constitute 23.5 percent of the biuret resin. Thus, the isocyanate concentration in the catalyst component is approximately 7.1 percent. The analytical results obtained were all within 20 percent of the reported value of 7.1 percent, thus the accuracy DQO of 70 to 130 percent was achieved.

The test plan required that 10 paint samples and one duplicate QA/QC sample be collected for isocyanate analysis. In actuality, the number of paint samples required for analysis was a function of the number of different paints that were used during the test series. During the test, only paint thinner and four types of two-part paints were used. The test objective was to obtain 10 paint samples (nine field samples and one QA/QC sample). A total of nine field samples and one duplicate QA/QC sample were collected and analyzed. However, one of the analyses did not yield a valid result, due to colorimetric interference by the paint pigment. Nine valid results were obtained, thus the required completeness measurement of 90 percent was achieved.

2. Percent Volatile Concentration in Paint

Paint samples were collected to determine the percent by weight of volatiles present in the paint. The measurement precision was determined through the analysis of one set of duplicate samples. The RPD between the sample result and the duplicate result was 6.8 percent. The DQO of ± 20 stipulated in the QAPP was attained. Although a DQO was specified in the QAPP for measurement accuracy, it is not possible to perform such a measurement, and inclusion of this DQO was in error.

The test plan required that 10 field samples and one duplicate QA/QC sample be collected. As discussed in Section B-1 of this Appendix, the number of paint samples required for analysis was a function of the number of different paints that were used during the test series. Thus, a total of 10 paint samples (nine field samples and one duplicate QA/QC sample) are required to fulfill the test objectives. A total of nine field samples and one duplicate QA/QC sample were collected and analyzed, thus a completeness measurement of 100 percent was achieved.

3. Density Measurements of Paint

Paint samples were collected to determine density. The measurement precision was determined through the analysis of two sets of duplicate samples. The RPDs between the duplicate samples were 1.3 and 1.4 percent. The accuracy of this measurement was determined by comparing the measured density results with the density values obtained from the paint can labels. The measured results were all within 6 percent of the published results. As with the completeness measurement for the other paint sample analyses, the DQO of 90 percent was attained for the density measurements.

4. Speciation and Quantitation of Organic Compounds in Paint

Paint samples were analyzed by gas chromatography/mass spectrometry (GC/MS) to determine the types and concentrations of organic compounds present in the paints. Initial speciation was achieved by comparing the GC/MS results against the NBS/NIH Mass Spectra Data Base, containing of over 42,000 compounds. Quantification was accomplished by compiling a list of VOC target compounds and generating a calibration standard using compounds on this list. The result of the GC/MS analyses were compared against this calibration curve to determine organic compound concentrations.

Measurement precision was determined through the analysis of two sets of duplicate samples. For the first set of duplicate samples, the RPD between the sample results and the duplicate results ranged from 0 to 11.3 percent. For the second set of duplicate samples, the RPD between the sample results and the duplicate results ranged from 0 to 20 percent. For this set of samples, 86 percent of the RPD results were less than 9 percent. For all results, the DQO of ± 40 percent was achieved.

The high solvent content of the paint precluded matrix spike and matrix spike duplicate analyses to determine measurement accuracy. Preliminary identification of the compounds was performed by comparing results against a standard library of compounds. Accurate quantitation was determined by analyzing calibration standards containing the compounds that comprised the bulk of the solvent present in the paint samples (acetone, methyl ethyl ketone, chloromethane, xylenes, toluene, ethylbenzene, ethyl acetate, and methylene chloride). These calibration standards were analyzed along with a method blank prior to sample analysis. The results of these analyses were used to quantify the compounds detected in the paint.

The test plan required that 10 field samples and one duplicate QA sample be collected. As discussed in Section B-1 above, the number of paint samples required for analysis was a function of the number of different paints that were used during the test series. Thus, a total of 10 paint samples (nine field samples and one QA/QC sample) are required to fulfill the test objectives. A total of nine field samples and two duplicate QA/QC samples were collected and analyzed, therefore a completeness measurement of 110 percent was achieved.

To determine the level of contamination that may have occurred during sample collection and shipment, one deionized field blank sample was collected and analyzed. No contaminants were present in concentrations above method detection limits.

5. Deviations from Proposed Paint Sampling Method

The QAPP for this project indicated that paint samples be collected according to ASTM Method D3925, which specifies that a weight per gallon test (D 1475) be conducted on-site to ensure sample homogeneity. When sampling commenced, the project engineer realized that the quantity of paint and lengthy time required to perform this analysis caused a significant upset in painting operations, especially because two samples were required per painting cycle (note that two parts paint were used). The weight per gallon test could therefore not be conducted on-site, rather samples were shipped to the laboratory for subsequent density analysis. To ensure sample homogeneity insofar as possible, the paint components were well agitated (for more than 10 minutes) prior to mixing.

The method used to determine paint densities is very similar to Method 1475, however a sealed 40 ml VOA vial was used rather than pycnometer. The use of sealed VOA vials ensured no loss of solvent vapor. The density measurement results obtained from this method agree with the published density values for each of the paint components tested to within the 0.5 percent specified in Method 3925 (actually all of the results, except one, agree to within 0.05 percent). Thus, the substitution of an alternate method for determining paint density did not affect either sample homogeneity, or analytical results. As such, this method substitution did not affect the results and conclusions presented in this report.

ASTM Method 3925 also specifies that paint samples be drawn at a random one percent of each lot. However, it is standard operating procedure for the painters to select and mix the paints to be used. The objective of this effort was to characterize standard operations occurring at the painting facility, thus bulk paint samples collected for subsequent analysis had to be drawn from the cans selected by the painters, rather than from a random selection process.

D. ASSESSMENT OF WATER SAMPLING AND ANALYSIS DATA QUALITY

1. Volatile Organic Compounds in Sump Water

The sump water was sampled and analyzed for volatile organic compounds according to EPA Method 8240 protocol. In addition, an identification of major peaks that are not included in the 8240 target compound list was also done. The measurement precision was determined through the analysis of two sets of duplicate samples. For the first set of duplicate samples, the RPD between the sample results and the duplicate results ranged from 0 to 18 percent, thus the DQO of ± 30 was attained for all compounds detected. For the second set of duplicate samples, the RPD between the sample results and the duplicate results ranged from 0 to 148 percent. For this set of samples, 75 percent of the RPD results were within the DQO range of ± 30 percent.

Method accuracy was determined by analyzing matrix spike and matrix spike duplicate samples. Five compounds that simulate the behavior of the compounds of interest were spiked: 1,1-dichloroethene, trichloroethene, benzene, toluene, and chlorobenzene. The results of the spike analyses are presented in Table A-6. The DQO for this measurement stipulated in the QAPP is 50 to 140 percent. All of the matrix spike and matrix spike duplicate recovery results are within this range.

The test plan required that three field samples and three QA/QC samples be collected. A total of three field samples and four QA/QC samples were collected and analyzed, thus the DQO of 90 percent was achieved.

To determine the level of contamination that may have occurred during sample collection and shipment, two field blank samples were collected and analyzed. In one sample, low concentrations of chloroform and 2-butanone were found. In the second blank sample, a low concentration of chlorobenzene was found in addition to these compounds.

On one occasion, the VOA vials containing water samples were not refrigerated immediately after sampling, because ice was not readily available. However, the samples were placed on ice within a few hours. Because the samples were collected with no headspace, and because the temporary storage area used in those few hours was relatively cool (less than 65°F), it is felt that the lack of immediate refrigeration did not affect the results of the Method 8240 analysis.

2. Semivolatile Organic Compounds in Sump Water

The sump water was sampled and analyzed for semivolatile organic compounds according to EPA Method 8270 protocol. In addition, major peaks not included in the 8270 list of target compounds were identified. The measurement precision was determined through the analysis of one set of duplicate samples. For this set of duplicate samples, the RPD between the sample results and the duplicate results ranged from 0 to 22 percent, thus the DQO of ± 30 was attained for all compounds detected.

Method accuracy was determined by analyzing matrix spike and matrix spike duplicate samples. Twelve compounds were spiked that simulate the behavior of the compounds of interest: phenol, 2-chlorophenol, 1,4-dichlorobenzene, N-nitroso-di-n-propylamine, 1,2,4-trichlorobenzene, 4-chloro-3-methylphenol, acenaphthene, 4-nitrophenol, 2,4-dinitrotoluene, pentachlorophenol, di-n-butyl phthalate, and pyrene. The results of these analyses are presented in Table A-7. The DQO for this measurement stipulated in the QAPP is 50 to 140 percent. All but three of the matrix spike and matrix spike duplicate results (or 96 percent) were well within this range.

The test plan required that three field samples and three QA/QC samples be collected. A total of six samples were collected and analyzed, thus a completeness measurement of 100 percent was achieved.

To determine the level of contamination that may have occurred during sample collection and shipment, two field blank samples were collected and analyzed. In one sample, no contaminants were detected. In the second sample, low phthalate concentrations were detected (phthalates are common laboratory contaminants).

On one occasion the Method 8270 samples were not refrigerated immediately after sampling, however they were placed on ice within a few hours. It is not felt that the results were affected by the temporary lack of refrigeration because, in the mean time, the samples were stored in a cool room (less than 65°F). Furthermore, the semivolatile organic composition of the large sample volume collected should not have changed over a 3-hour time span.

3. Total Organic Carbon Concentrations in Sump Water

The sump water was sampled and analyzed for total organic carbon (TOC) according to EPA Method 415 protocol. The measurement precision was determined through the analysis of four sets of duplicate and blind duplicate samples. For each set of duplicate samples, the RPD between the sample results and the duplicate results was 0.0, 0.0, 3.9 and 20 percent. The DQO of ± 20 stipulated in the QAPP was attained.

Method accuracy was determined by analyzing a matrix spike sample. The DQO for this measurement stipulated in the QAPP is 80 to 120 percent. The matrix spike result was 80 percent.

TABLE A-6. MATRIX SPIKE VOLATILE ORGANIC COMPOUND RECOVERY RESULTS FROM SUMP WATER ANALYSES.

Compound	Spike Recovery (percent)		Duplicate Spike Recovery (percent)	
	Set 1	Set 2	Set 1	Set 2
1,1-Dichloroethene	114	110	104	102
Trichloroethene	102	96	100	78
Benzene	118	106	126	84
Toluene	106	112	106	116
Chlorobenzene	110	112	106	110

TABLE A-7. MATRIX SPIKE SEMIVOLATILE ORGANIC COMPOUND RECOVERY RESULTS FROM SUMP WATER ANALYSES.

Compound	Spike Recovery (percent)		Duplicate Spike Recovery (percent)	
Phenol	72		76	
2-Chlorophenol	71		78	
1,4-Dichlorobenzene	57		63	
N-Nitroso-di-n-propylamine	88		96	
1,2,4-Trichlorobenzene	33		37	
4-Chloro-3-methylphenol	54		48	
Acenaphthene	83		91	
4-Nitrophenol	108		100	
2,4-Dinitrotoluene	91		94	
Pentachlorophenol	88		90	
Di-n-butyl phthalate	81		98	
Pyrene	83		90	

The test plan required that five field samples and five QA/QC samples be collected. A total of 11 samples were collected and analyzed, thus a completeness DQO of 90 percent was attained.

To determine the level of contamination that may have occurred during sample collection and shipment, one field blank sample was collected and analyzed. In this sample, a low concentration (8 mg/L) of organic carbon was detected.

4. Total Suspended Solids in Sump Water

The sump water was sampled and analyzed for total suspended solids (TSS) according to EPA Method 160 protocol. The measurement precision was determined by analysis of two sets of blind duplicate samples. For each set of duplicate samples, the RPD between the sample results and the duplicate results was 16 and 25 percent. This result indicates that the variability in this measurement is on the order of 25 percent. The DQO of ± 20 stipulated in the QAPP was attained for one duplicate sample only.

For EPA Method 160 samples, a spike recovery analysis cannot be used to assess measurement accuracy. For this reason, an accuracy DQO was not stipulated in the QAPP.

The test plan required that five field samples be collected. Valid results from five field samples were obtained, thus the completeness DQO of 90 percent was achieved.

To determine the level of contamination that may have occurred during sample collection and shipment, one field blank sample was collected and analyzed. In this sample, no solids were measured above the method detection limit of 4 mg/L.

During sampling, it was noted that some particulate accumulated in a foam at the surface of the sump. It was not possible to mix the accumulated surface particulate in the sump water. Thus, sample representativeness may have been affected slightly. This may also explain to some extent the 25 percent sampling variability. However, the quantity of particulate floating in small clumps on the surface was small compared to the total quantity of particulate accumulated in the entire sump volume, thus it is assumed that the presence of a floating residue did not affect the results obtained from this measurement.

E. EXTERNAL AUDIT RESULTS

The sampling phase of this project entailed an external audit by Research Triangle Institute (RTI). The following items were noted during the audit. Each of these items have been addressed in this Appendix.

- Some water samples taken from the sump were left unrefrigerated for several hours before being placed in an ice chest prior to shipping.
- Paint samples were not drawn at a random one percent of each lot; only one can per lot was sampled.

- The weight per gallon measurement stipulated in the approved ASTM sampling method was not conducted onsite. Furthermore, the density measurement procedure that was used differed from the one proposed in the QAPP.
- The impact that the particulate clumps on the surface of the sump had on the TSS measurement results should be discussed.

APPENDIX B
SAMPLING METHODS USED IN THE HILL AIR FORCE BASE PAINT SPRAY BOOTH

[Unedited reproductions of NIOSH Methods 500 and 1300, and of OSHA Method 42.]

NIOSH METHOD 500

DEFINITION: Total aerosol mass

NUISANCE DUST, TOTAL

METHOD: 0500

ISSUED: 2/15/84

OSHA: 15 mg/m³

NIOSH: no standard

ACGIH: 10 mg/m³, total dust less than
1% quartz

PROPERTIES: quartz less than 1% [1]

SYNONYMS: boron oxide (CAS #1303-86-2) and nuisance dusts [1] including alumina
(CAS #1344-28-1), calcium carbonate (CAS #1317-65-3), cellulose (paper fiber;
CAS #9004-34-6), glycerin mist (CAS #56-81-5), limestone (CAS #1317-65-3), etc.

SAMPLING

MEASUREMENT

SAMPLER: FILTER

(tared 37-mm, 5-µm PVC filter)

FLOW RATE: 1.5 to 2 L/min

VOL-MIN: 25 L @ 15 mg/m³

-MAX: 133 L @ 15 mg/m³

SHIPMENT: routine

SAMPLE STABILITY: indefinitely

BLANKS: 2 field blanks per 10 samples

BULK SAMPLE: none required

!

!TECHNIQUE: GRAVIMETRIC (FILTER WEIGHT)

!

!ANALYTE: airborne particulate material

!

!BALANCE: 0.01 mg sensitivity or better; use same
balance before and after sample
collection

!

!CALIBRATION: National Bureau of Standards
Class M weights

!

!RANGE: 0.3 to 2 mg per sample

!

!ESTIMATED LOD: 0.2 mg per sample

!

!PRECISION: 0.08 mg per sample [3]

!

ACCURACY

RANGE STUDIED: 8 to 28 mg/m³

BIAS: not significant

OVERALL PRECISION (s_p): 0.056 [2]

APPLICABILITY: The working range is 3 to 20 mg/m³ for a 100-L air sample. This method is nonspecific and determines the total dust concentration to which a worker is exposed. It may be applied, e.g., to gravimetric determination of fibrous glass [4] in addition to the other ACGIH nuisance dusts [1].

INTERFERENCES: Organic and volatile particulate matter may be removed by dry ashing [4].

OTHER METHODS: This method is similar to the criteria document method for fibrous glass [4] and Method 5000 for carbon black. This method replaces Method S349 [5]. Impingers and direct-reading instruments may be used to collect total dust samples, but these have limitations for personal sampling.

2/15/84

EQUIPMENT:

1. Environmental chamber at constant temperature and humidity (e.g., $20\text{ }^{\circ}\text{C} \pm 0.3\text{ }^{\circ}\text{C}$ and $50\% \pm 5\% \text{ RH}$).
2. Sampler: 37-mm PVC, 2- to 5- μm pore size membrane or equivalent hydrophobic filter and cellulose supporting pad in 37-mm cassette filter holder.
3. Personal sampling pump, 1.5 to 2 L/min, with flexible connecting tubing.
4. Microbalance, capable of weighing to 0.01 mg.
5. Vacuum desiccator.
6. Static neutralizer: e.g., Po-210; replace nine months after the production date.

SPECIAL PRECAUTIONS: None.

PREPARATION OF FILTERS BEFORE SAMPLING:

1. Dry filters and backup pads under vacuum in the vacuum desiccator for at least 15 min.
2. Release the vacuum, remove the desiccator cover and equilibrate the filters in the environmental chamber for at least 1 hr.
3. Number the backup pads with a ballpoint pen and place them, numbered side down, in filter cassette bottom sections.
4. Weigh the filters in the environmental chamber. Record the filter tare weight, W_1 (mg).
 - a. Zero the balance before each weighing.
 - b. Handle the filter with forceps (nylon forceps if further analyses will be done).
 - c. Pass the filter over an antistatic radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
5. Place the weighed filters on top of the backup pads in the filter cassette bottom sections and allow to stand an additional 8 to 16 hrs in the environmental chamber.
6. Reweigh the filters. If this tare weight differs by more than 0.01 mg from the first tare weight obtained in step 4 above, discard the filter.

NOTE: Insert a rod through the outlet hole of the filter cassette bottom section to raise the backup pad and filter so that the filter can be grasped with forceps.
7. Assemble the filter in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette. Place a cellulose shrink band around the filter cassette, allow to dry and mark with the same number as the backup pad.

SAMPLING:

8. Calibrate each personal sampling pump with a representative sampler in line.
9. Sample at 1.5 to 2 L/min. Do not exceed a total filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

10. Wipe dust from the external surface of the filter cassette with a moist paper towel to minimize contamination. Discard the paper towel.
11. Remove the top and bottom plugs from the filter cassette. Place the filter cassettes in a vacuum desiccator under vacuum for at least 15 min, followed by equilibration for at least 1 hr in the environmental chamber.
12. Remove the cassette band, pry open the cassette and remove the filter. Handle the filters very gently by the edge to avoid loss of dust.

2/15/84

NOTE: If the filter sticks to the underside of the cassette top, very gently lift away by using the dull side of a scalpel blade. This must be done carefully or the filter will tear.

CALIBRATION AND QUALITY CONTROL:

13. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Maintain and calibrate the balance with National Bureau of Standards Class M weights.
14. Take two to four replicate samples for every batch of field samples for quality assurance on the sampling procedures. The set of replicate samples should be exposed to the same dust environment, either in a laboratory dust chamber [6] or in the field. The quality control samples must be taken with the same equipment, procedures and personnel used in the routine field samples. The relative standard deviation calculated from these replicates should be recorded on control charts and action taken when the precision is out of control.

MEASUREMENT:

15. Weigh each filter, including field blanks. Record this post-sampling weight, W_2 (mg), beside its corresponding tare weight. Record anything remarkable about a filter (e.g., overload, leakage, wet, torn, etc.).

CALCULATIONS:

16. Calculate the concentration of total nuisance dust, C (mg/m³), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) + B}{V} \cdot 10^3, \text{ mg/m}^3$$

where: W_1 = tare weight of filter before sampling (mg)

W_2 = post-sampling weight of sample-containing filter (mg)

B = mean change in field blank filter weights between tare and post-sampling (mg)
(+ or -).

EVALUATION OF METHOD:

Lab testing with blank filters and generated atmospheres of carbon black was done at 8 to 28 mg/m³ [2,6]. Precision and accuracy data are given on page 0500-1.

REFERENCES:

- [1] TLVs - Threshold Limit Values for 1983-84, Appendix D, ACGIH, Cincinnati, OH (1983).
- [2] This Manual, Method 5000.
- [3] Unpublished data from Non-textile Cotton Study, NIOSH/DRDS/EIB.
- [4] NIOSH Criteria for a Recommended Standard ... Occupational Exposure to Fibrous Glass, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-152, 119-142 (1977).
- [5] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S349, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
- [6] Documentation of the NIOSH Validation Tests, S262 and S349, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD WRITTEN BY: Kathy Morring, Jerry Clere, and Frank Hearl, P.E., NIOSH/DRDS.

NIOSH METHOD 1300

FORMULA: Table 1

KETONES I

M.W.: Table 1

METHOD: 1300
ISSUED: 2/15/84

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS:	acetone	methyl isobutyl ketone	2-hexanone
(Synonyms	cyclohexanone	2-pentanone	diisobutyl ketone
in			
Table 1)			

SAMPLING		MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)		! TECHNIQUE: GAS CHROMATOGRAPHY, FID
FLOW RATE: 0.01 to 0.2 L/min		! ANALYTE: compounds above
		! DESORPTION: 1 mL CS ₂ , stand 30 min
		! INJECTION VOLUME: 5 µL
		! COLUMN: glass (12 ft x 1/4 inch); 10% SP-2100
		! 0.1% Carbowax 1500 on Supelcoport
		! 100/120
		! TEMPERATURE-INJECTOR: 250 °C
		! -DETECTOR: 300 °C
		! -COLUMN: 50 °C to 170 °C @ 10°/min
		! CARRIER GAS: N ₂ or He, 30 mL/min
		! CALIBRATION: standard solutions of analyte in
		! CS ₂
		! RANGE: see EVALUATION OF METHOD
		! ESTIMATED LOD: 0.02 mg per sample
		! PRECISION (s _p): see EVALUATION OF METHOD
ACCURACY		
RANGE STUDIED, BIAS and		
OVERALL PRECISION (s _p): see EVALUATION OF		
METHOD		

APPLICABILITY: This method is intended as a general method for the ketones listed above. If only certain compounds are of interest, the instrumental conditions can be changed to maximize instrument response for these compounds.

INTERFERENCES: None reported. Alternate columns, e.g., 10% SP-2100 or DB-1 fused silica capillary, can be used.

OTHER METHODS: This method combines and replaces Methods S1, S18, S19 and S20 [1] and S178 and S358 [2].

2/15/84

REAGENTS:

1. Carbon disulfide (GC grade).*
2. Analytes, reagent grade.
3. Nitrogen, prepurified.
4. Hydrogen, dry.
5. Air, filtered, dry.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph equipped with FID, integrator and column (page 1300-1).
4. Vials, 2-mL, glass, PTFE-lined crimp caps.
5. Syringe, 10- μ L, readable to 0.1 μ L.
6. Pipets, various sizes for preparing standards, with pipet bulb.
7. Volumetric flasks, 5- and 10-mL, for standards.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.5 to 3 L for acetone or 1 to 25 L for the other analytes.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS₂ to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.02 to 10 mg analyte per sample.
 - a. Add known amounts of analyte to CS₂ in 10-mL volumetric flasks and dilute to the mark.
 - b. Analyze together with samples and blanks (steps 11 and 12).
 - c. Prepare calibration graph (peak area vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
 - a. Remove and discard back sorbent section of a media blank sampler.
 - b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.

- c. Cap the tube. Allow to stand overnight.
 - d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
 - e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1300-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
- NOTE: If peak area is above the linear range of the working standards, dilute with CS₂, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
- NOTE: If W_b > W_f/10, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The methods were validated under NIOSH Contract CDC-99-74-45 [3]. Desorption efficiency was checked by spiking known amounts of the compounds (either neat or in solutions with CS₂) on coconut shell charcoal. Samples were generated for acetone, cyclohexanone, 2-pentanone, and methyl isobutyl ketone by heating a quantity of the liquid to just below its boiling point in a 3-necked, 500-mL round bottom flask. The compound was carried through a fixed-temperature condenser to the concentrations. Samples were generated for diisobutyl ketone and 2-hexanone using a syringe pump which delivered the compounds to a heated glass-lined inlet which was swept with nitrogen, carrying the vapor to the mixing chamber. Results were as follows:

Compound	Method [1,2]	Overall			Measurement		
		Range (mg/m ³)	Breakthrough ¹ (L)	s _r	Range (mg per sample)	DE ²	s _r
Acetone	S1 [1,3]	1200 to 4500	4.3	0.082	2.4 to 14.2	0.86	0.024
Cyclohexanone	S19 [1,3]	98 to 392	65	0.062	3.8 to 18.0	0.82	0.025
Hexanone	S18 [1,3]	208 to 836	17	0.064	2.1 to 8.3	0.91	0.008
2-Pentanone	S20 [1,3]	395 to 1570	19	0.063	3.5 to 14.0	0.90	0.011
2-Hexanone	S178 [2,3]	188 to 790	>45	0.053	1.5 to 8.1	0.81	0.018
Diisobutyl ketone	S358 [2,3]	145 to 582	44	0.070	1.8 to 7.0	0.97	0.032

¹5% breakthrough, 0.2 L/min at high end of concentration range in dry air.

²Averaged over mass range shown.

REFERENCES:

- [1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S1, S18, S19 and S20, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
- [2] Ibid, V. 3, S178 and S358, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
- [3] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD REVISED BY: Edward J. Slick, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

Table 1. General information.

Compound (Synonyms)	Formula (M.W.)	Exposure Limits, ppm				mg/m ³ /ppm @ NTP	Properties*
		OSHA	NIOSH	ACGIH TLV	STEL		
Acetone (2-Propanone, CAS #67-64-1)	CH ₃ COCH ₃ ; C ₃ H ₆ O (58.08)	1000	250	750	1000	2.37	liquid; BP 56 °C; d 0.791 g/mL; VP 35.5 kPa (266 mm Hg)
Cyclohexanone (CAS #108-94-1)	 C ₆ H ₁₀ O (98.15)	50	25	25	100	4.01	liquid; BP 155 °C; d 0.947 g/mL; VP 0.3 kPa (2 mm Hg)
Methyl isobutyl ketone (MIBK; hexone; 4-methyl-2-pentanone; CAS #108-10-1)	(CH ₃) ₂ CHCH ₂ COCH ₃ ; C ₆ H ₁₂ O (100.16)	100	50	50	75 (skin)	4.09	liquid; BP 117 °C; d 0.800 g/mL; VP 2.0 kPa (15 mm Hg)
2-Pentanone (methyl propyl ketone; CAS #107-87-9)	CH ₃ CH ₂ CH ₂ COCH ₃ ; C ₅ H ₁₀ O (86.13)	200	150	200	250	3.52	liquid; BP 100 °C; d 0.812 g/mL; VP 3.6 kPa (27 mm Hg)
2-Hexanone (methyl n-butyl ketone; MBK; CAS #591-78-6)	CH ₃ (CH ₂) ₃ COCH ₃ ; C ₆ H ₁₂ O (100.16)	100	1	5	--	4.09	liquid; BP 127 °C; d 0.812 g/mL; VP 0.4 kPa (3 mm Hg)
Diisobutyl ketone (2,6-dimethyl-4-heptanone; CAS #108-83-8)	((CH ₃) ₂ CHCH ₂) ₂ CO; C ₉ H ₁₈ O (142.24)	50	25	25	--	5.82	liquid; BP 169 °C; d 0.847 g/mL; VP 0.23 kPa (1.7 mm Hg)

*Density @ 25 °C; VP @ 20 °C.

OSHA METHOD 42

DIISOCYANATES

TOLUENE-2,6-DIISOCYANATE (2,6-TDI)
1,6-HEXAMETHYLENE DIISOCYANATE (HDI)
TOLUENE-2,4-DIISOCYANATE (2,4-TDI)

Method no.: 42

Matrix: Air

Procedure: Samples are collected by drawing a known volume of air through glass fiber filters coated with 0.1 mg of 1-(2-pyridyl)piperazine (1-2PP) which are contained in open-face cassettes. Samples are extracted with 90/10 (v/v) acetonitrile/dimethyl sulfoxide (ACN/DMSO) and analyzed by high performance liquid chromatography (HPLC) using an ultraviolet or fluorescence detector. (The coated filters used in Method 47 for MDI are also acceptable for this procedure. Those filters are coated with 1 mg instead of 0.1 mg of 1-2PP.)

Recommended air volume
and sampling rate: 15 L at a flow of 1 L/min

Special requirements: It is recommended that coated glass fiber filters be stored at reduced temperature until used for sampling.

Status of method: A sampling and analytical method that has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: February, 1983

Chemist: Donald Burright

Carcinogen and Pesticide Branch
OSHA Analytical Laboratory
Salt Lake City, Utah

(Title page continued)

	2,6-TDI	HDI	2,4-TDI
Target concentration			(OSHA PEL)
$\mu\text{g}/\text{m}^3$	140	140	140
ppb	20	20	20
Detection limit of the overall procedure:			
$\mu\text{g}/\text{m}^3$	1.6	2.3	1.3
ppb	0.23	0.32	0.17
Reliable quantitation limit:			
$\mu\text{g}/\text{m}^3$	2.3	2.9	2.5
ppb	0.32	0.43	0.36
Standard error of estimate at target concentration, % (Section 4.9.)	7.63	7.79	6.89
(Air concentrations are based on 15-L air sample volume)			
(ppb = part per billion)			

1. General discussion

1.1. Background

1.1.1. History of procedure

Some of the earliest procedures to determine atmospheric diisocyanate concentrations were developed by Ranta and Marcali (Ref. 5.1.). Both of these procedures are inconvenient as they use a bubbler for sampling and their colorimetric analyses are non-specific. A later sampling procedure uses p-nitrobenzyl-N-n-propylamine (nitro reagent) in toluene bubblers (Ref. 5.2.). While this method is specific for diisocyanates, it still retains the use of the bubbler and nitro reagent which is unstable when stored for long periods of time, even if it is kept at reduced temperature. The past couple of years have seen several new derivatizing reagents being used, N-methyl-1-naphthalenemethylamine (Ref. 5.3.), 9-(n-methylaminomethyl)-anthracene (Ref. 5.4.) and 1-2PP (Ref. 5.5.-5.7.). The collection procedure of these new studies all involve the use of toluene bubblers. The purpose of this study was to find a collection system that does not use a bubbler, yet retains the sensitivity, precision and accuracy of the nitro reagent method.

1-2PP is a suitable derivatizing reagent, when coated on a glass fiber filter, for several reasons:

- 1) The high boiling liquid is retained on a glass fiber filter and stability is not a problem.
- 2) The rapid and exothermic reaction with both aromatic and aliphatic diisocyanates results in derivatization on the filter (Ref. 5.7.).
- 3) The derivatives have higher molar absorptivities in the UV region than those formed with nitro reagent which allows the extraction volume to be larger without loss of sensitivity (Ref. 5.5.).

This procedure compares favorable when tested side-by-side with the nitro reagent method by Cummins (Ref. 5.10.) for 2,4-TDI. (Section 4.10.). Additional work is being done to study 4,4'-methylenediphenylisocyanate (MDI) and isophorone diisocyanate (IPDI) using 1-2PP as the derivatizing reagent.

- 1.1.2. Toxic effects (This section is for information only and should not be taken as a basis for OSHA policy.)

Continued inhalation of diisocyanate vapors or mists can cause nausea, headache, coughing, irritation of the nose and throat, shortness of breath and chest discomfort. Massive exposure can cause severe coughing spasms, bronchitis and chemical pneumonitis. Some people can become sensitized to isocyanates and may suffer asthmatic attacks and respiratory distress when subsequently exposed to very low concentrations (Ref. 5.9.). Recent studies have produced conflicting results about the mutagenicity of TDI (Ref. 5.1. and 5.9.). No data has been found to indicate that diisocyanates are carcinogenic or teratogenic (Ref. 5.1. and 5.9.).

- 1.1.3. Operations where exposure may occur

The manufacture of polyurethane foams, coatings, and elastomers potentially exposes a minimum of 100,000 workers to diisocyanates (Ref. 5.2.). Diisocyanates can be found in paints, insulation, adhesives, automobile bumpers, shoe soles, and hundreds of other applications (Ref. 5.2. and 5.8.). Over 700 million pounds of diisocyanates were produced in 1975 (Ref. 5.2.).

- 1.1.4. Physical properties

	2,6-TDI	HDI	2,4-TDI
CAS number	91-08-7	822-06-0	584-84-9
MW	174.16	168.20	174.16
BP, °C @ mm Hg	96 @ 1.5	213 @ 760	251 @ 760
MP, °C	8	-55	22
Specific gravity @ 75°C	N/A	1.05	1.22
Vapor pressure, mm Hg	N/A	0.05	0.025
Color	All colorless to pale yellow		
Odor	All sharp pungent		
Flash point (closed cup), °C	N/A	140	127

(N/A = Not Available)

Synonyms and structures - See Figure 1.1.4.

- 1.2. Limit defining parameters (The analyte air concentrations listed through this method are based on an air volume of 15 L and an extraction volume of 2 mL.)

1.2.1. Detection limit of the analytical procedure

The detection limit of the analytical procedure is the mass of analyte per injection which will result in a peak whose height is about five times the amplitude of the baseline noise. (Section 4.1.)

The Detection Limit of the Analytical Procedure
ng/injection

2,6-TDI	HDI	2,4-TDI
0.18	0.18	0.18

1.2.2. Detection limit of the overall procedure

The detection limit of the overall procedure is the amount of analyte spiked on the sampling device which allows recovery of an amount of analyte equivalent to the detection limit of the analytical procedure. (Section 4.2.)

The Detection Limits of the Overall Procedure

	2,6-TDI	HDI	2,4-TDI
ng/sample	24	33	19
µg/m ³	1.6	2.3	1.3
ppb	0.23	0.32	0.17

1.2.3. Reliable quantitation limits

The reliable quantitation limit is the smallest amount of analyte which can be quantitated within the requirements of at least 75% recovery and a precision (1.96 SD) of $\pm 25\%$ or better. The reliable quantitation limits are higher than the detection limits of the overall procedure to satisfy the precision requirement. (Section 4.3.)

The Reliable Quantitation Limits

	2,6-TDI	HDI	2,4-TDI
ng/sample	34	44	39
µg/m ³	2.3	2.9	2.5
ppb	0.32	0.43	0.36

The reliable quantitation limits and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of an analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters.

1.2.4. Sensitivity

The sensitivity of the analytical procedure is determined by the slope of the calibration curve over a concentration range 0.5 to 2 times the target concentration. The sensitivity will vary somewhat with the particular instrument used in the analysis. (Section 4.5.)

The Sensitivity of the Analytical Procedure

	2,6-TDI	HDI	2,4-TDI
Area units per $\mu\text{g/mL}$	85600	84300	159000

1.2.5. Recovery

The recoveries of the analytes from samples used in the 18-day storage tests remained above the values presented below. These values are determined from the calculated regression lines of the storage graphs. (Section 4.9.)

Recovery, %

T °C	2,6-TDI	HDI	2,4-TDI
-25	86.3	81.1	81.3
22	86.4	83.0	80.3

The recovery of analyte from the collection medium during storage must be 75% or greater.

1.2.6. Precision (Analytical method only)

The pooled coefficients of variation obtained from replicate determinations of analytical standards at 0.5, 1 and 2 times the target concentration are presented below. (Section 4.4.)

The Pooled Coefficients of Variation

2,6-TDI	HDI	2,4-TDI
0.009	0.013	0.009

1.2.7. Precision (Overall procedure)

The overall procedure must provide results at the target concentrations that are $\pm 25\%$ or better at the 95% confidence level. The precisions at the 95% confidence level for the 18-day storage test are presented below. (Section 4.9.) The reported values each include an additional $\pm 5\%$ for sampling error.

Precision at the 95% Confidence Level, %

2,6-TDI	HDI	2,4-TDI
14.9	15.2	13.5

1.2.8. Reproducibility

Five samples, prepared by vapor spiking, and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The samples were analyzed after 6 days of storage at -25°C . The data listed below are corrected for extraction efficiency (Section 4.8.).

Recovery %

	2,6-TDI	HDI	2,4-TDI
$\bar{X}$	101.5	100.4	105.4
SD	1.6	2.0	2.4

1.3. Advantages

- 1.3.1. The sampling and analytical procedures are specific and sensitive for several diisocyanates employed in industry (Ref. 5.7.).
- 1.3.2. The collection system is less cumbersome than the use of a bubbler.
- 1.3.3. 1-2PP is more stable and less expensive than p-nitrobenzyl-N-n-propylamine, (nitro reagent).

1.4. Disadvantages

The use of peak ratios to confirm low concentrations of diisocyanates is impractical due to the small response at 313 nm.

2. Sampling procedure

2.1. Apparatus

- 2.1.1. Samples are collected by use of a personal sampling pump that can be calibrated to within $\pm 5\%$ at the recommended flow rate with the sampling device in line.
- 2.1.2. A three-piece styrene cassette containing a glass fiber filter coated with 0.1 mg of 1-2PP and a backup pad. (See Fig. 4.13.1.)
- 2.1.3. Coated filters are prepared by applying 0.5 mL of a solution of 0.2 mg/mL 1-2PP in methylene chloride to each glass fiber filter. The wet filters are allowed to air dry before placing in a jar. Vacuum is applied to the jar to remove residual methylene chloride. (The coated filters used in Method 47 for MDI are also acceptable for this procedure. These filters are coated with 1 mg of 1-2PP and are prepared as above except a 20 mg/mL solution of 1-2PP in methylene chloride is used.)
- 2.1.4. Coated filters should be stored at reduced temperature as a precaution.

2.2. Reagents

None are required.

2.3. Sampling technique

- 2.3.1. Remove the inlet cover from the three-piece cassette. Save cover for installation after sampling.
- 2.3.2. Attach the cassette in the breathing zone of the employee to be monitored.
- 2.3.3. The recommended flow rate is 1 L/min with a recommended total air volume of 15 L.
- 2.3.4. After sampling for the appropriate time, remove the sampling device and reinstall the small plug and inlet cover.
- 2.3.5. Wrap each sample end-to-end with an OSHA Form 21 seal.

2.3.6. With each set of samples, submit at least one blank sample. The blank should be subjected to the same handling as the samples except that no air is drawn through it.

2.3.7. Bulk samples submitted for analysis must be shipped in sealed vials and in a separate container.

2.4. Retention efficiency

2.4.1. Experimental design

Due to present laboratory limitations, controlled test atmospheres of diisocyanates cannot effectively be generated. However, the following procedure using a vapor spiking technique was used as an alternative to study analyte retention. This was done to approximate the recommended open-face collection of diisocyanates.

A glass syringe barrel equipped with a Luer taper tip was silanized and silanized glass wool was placed into the syringe. The Luer tip was inserted into the inlet part of a cassette so that the tip was flush with the inside surface of the cassette. The other end of the syringe was attached to a sampling port. The outlet of the cassette was attached to a vacuum pump. A critical orifice between the cassette and the pump maintained a constant 1 L/min flow rate.

Dry air samples were prepared by attaching a dry air source to a manifold inlet. Humid air samples were generated by passing air through water in a controlled temperature water bath. The humidity was monitored in the sampling manifold via a humidity probe. The glass wool was spiked with diisocyanate in methylene chloride. The desired quantity of air was then drawn through the glass wool, at a flow rate of 1 L/min, and onto the coated filter, which was analyzed to determine analyte loss.

2.4.2. Retention results

Humidity has an effect on the ability of a glass fiber filter to retain derivatized diisocyanates. When a sample of ten times the target concentration is vapor generated and 200 L of dry air (12% humidity) is drawn through the filter, an average of 95.4% of the diisocyanates is found on the coated filter. Only 1.2% is found on the backup pad.

When higher relative humidity (R.H.) is added to the sampling system, a different result is obtained. Samples,

vapor spiked with 20 L of dry air at the target concentration and with humid air (78% R.H.) pulled through the cassettes at several known air volumes, show a loss of diisocyanate derivative. Based on an extrapolation of these results, the recommended maximum air volume should be 80 L. Exceeding this amount could result in less than 75% recovery of the diisocyanate entering the cassette. (Section 4.6.)

2.5. Extraction efficiency

The average extraction efficiency for each of the analytes spiked at the target concentration on a coated glass fiber filter is presented below. (Section 4.7.)

Average Extraction Efficiencies, %

2,6-TDI	HDI	2,4-TDI
91.2	93.3	90.8

2.6. Recommended air volume and sampling rate

2.6.1. The recommended air volume is 15 L.

2.6.2. The recommended air sampling rate is 1 L/min.

2.7. Interferences

Any compound, that could be collected on the glass fiber filter that could react with the 1-2PP or compete with it in the reaction to derivatize the diisocyanate, should be considered as an interference. Potential interferences include anhydrides, amines, alcohols and carboxylic acids.

2.8. Safety precautions

The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

3. Analytical Procedure

3.1. Apparatus

3.1.1. High performance liquid chromatograph equipped with UV detector, manual or automatic sample injector, and chart recorder.

3.1.2. HPLC stainless steel column capable of separating diisocyanate derivatives. The column employed in this

study was a 25 cm x 4.6 mm ID stainless steel column packed by Alltech with 10 micron C₈.

- 3.1.3. An electronic integrator, or some other suitable method of determining peak areas.
- 3.1.4. Vials, 4-mL with Teflon-lined caps.
- 3.1.5. Syringes, of convenient sizes for sample and standard preparations and injections.
- 3.1.6. Volumetric pipettes and flasks for preparation of standards.
- 3.1.7. Suitable glassware for preparation of diisocyanate urea derivatives.
- 3.1.8. Micro-analytical balance used to weigh standard preparations.

3.2. Reagents

- 3.2.1. HPLC grade methylene chloride, hexane, acetonitrile, and dimethyl sulfoxide.
- 3.2.2. HPLC grade water. Our laboratory employs a commercially available water filtration system for the preparation of HPLC grade water.
- 3.2.3. 1-(2-Pyridyl)piperazine, Aldrich, Milwaukee, WI.
- 3.2.4. 2,6-TDI, Carbolabs, Inc., New Haven, CT.
- 3.2.5. HDI, Aldrich, Milwaukee, WI.
- 3.2.6. 2,4-TDI, Eastman Chemicals, Rochester, NY.
- 3.2.7. HPLC grade ammonium acetate.
- 3.2.8. Glacial acetic acid.

3.3. Standard preparation

- 3.3.1. A solution containing 3.5 g of 2,4-TDI in 25 mL of methylene chloride is slowly added to a stirred solution of 7.25 g of 1-2PP in 100 mL of methylene chloride. The solution is then heated to 35°C for 10 minutes. The product is precipitated with hexane, (precipitation may start without adding hexane), filtered, redissolved in a minimal volume of methylene chloride and reprecipitated. The precipitate is filtered and washed with hexane

(approximate yield is 9 g of the derivative after being dried by vacuum). This preparation is a modification of the procedure reported by Goldberg et al (Ref. 5.7.). Derivatives of the two other diisocyanates are prepared by a similar procedure.

3.3.2. Preparation of working range standards

A stock standard solution is prepared by dissolving the diisocyanate derivatives into DMSO. To express the derivative as free diisocyanate, the amount of 2,4-TDI and 2,6-TDI ureas weighed is multiplied by the conversion factor 0.3479

$$\frac{\text{MW TDI}}{\text{MW urea}} = \frac{174.16}{500.61} = 0.3479$$

Similarly, the conversion factor for HDI urea is 0.3400

$$\frac{\text{MW HDI}}{\text{MW urea}} = \frac{168.20}{494.64} = 0.3400$$

All dilutions of the stock solutions are made with acetonitrile to arrive at the working range.

3.4. Sample preparation

- 3.4.1. The styrene cassette is opened and the glass fiber filter is placed into a 4-mL vial so that the filter is flat against the inside surface of the vial, not folded or crumpled.
- 3.4.2. Two mL of the extracting solution, 90/10 (v/v) ACN/DMSO, are added.
- 3.4.3. A cap equipped with a Teflon liner is installed.
- 3.4.4. The vial is shaken to remove large air bubbles from between the filter and the glass. Let the vial set for one hour.

3.5. Analysis

3.5.1. Reverse phase HPLC conditions

Column: 25 cm x 4.7 mm ID stainless steel column packed with 10 micron Alltech C₈ or suitable equivalent.
Mobile phase: 0.01 M ammonium acetate in 37.5/62.5 ACN/water (v/v) adjusted to pH 6.2 with acetic acid
Flow Rate: 1 mL/min
UV Detector: 254 and 313 nm
Fluorescence Detector: 240 nm excitation
370 nm emission
Injection size: 10-25 µL

3.5.2. Chromatograms (Section 4.11.)

3.5.3. An external standard procedure is used to prepare a calibration curve using at least 2 stock solutions from which dilutions are made. The calibration curve is prepared daily. The samples are bracketed with analytical standards.

3.6. Interferences

- 3.6.1. Any compound having the same retention time as the analyte is a possible interference. Benzaldehyde is an interference for 2,4-TDI urea using the aforementioned analytical conditions but is not normally expected to be found. Generally, chromatographic conditions can be altered to separate an interference.
- 3.6.2. Compounds that can react with a diisocyanate represent a potential interference. These include molecules containing the following functional groups: amines, alcohols, phenols, and carboxylic acids. Compounds, such as anhydrides, that will react with 1-2PP should be considered as potential interferences also.
- 3.6.3. Retention time on a single column is not proof of chemical identity. Analysis by an alternate column system, ratioing of wavelength response, and mass spectrometry are additional means of identity. (See UV spectra for diisocyanate derivatives, Figures 4.12.1.-4.12.3.)

3.7. Calculations

The concentration in $\mu\text{g/mL}$ of diisocyanate present in a sample is determined from the area response of the analytes as measured by an electronic integrator or peak heights. Comparison of sample response with a least squares curve fit for standards allows the analyst to determine the concentration of diisocyanate in $\mu\text{g/mL}$ for the sample. Since the sample volume is 2 mL, the results in $\mu\text{g/m}^3$ of air are expressed by the following equation:

$$\mu\text{g/m}^3 = (\mu\text{g/mL})(2 \text{ mL})/(\text{m}^3 \text{ of air sampled})(\text{Extraction Eff.})$$

3.8. Safety precautions

3.8.1. Avoid skin contact with all solvents.

3.8.2. Wear safety glasses at all times.

3.8.3. Avoid exposure to the diisocyanates standards.

4. Backup data section

4.1. Detection limit of the analytical procedure

The detection limit of the analytical procedure was 0.18 ng for all three analytes. This amount produced a peak whose height was about 5 times the height of the baseline noise. The injection size recommended in the analytical procedure (10 μL) was used in the determination of the detection limit for the analytical procedure. (Figure 4.1.).

4.2. Detection limit of the overall procedure

4.2.1. The following data were obtained by vapor spiking increasing amounts of the analytes onto sampling devices. The injection size recommended in the analytical procedure (25 μL) was used to determine the detection limit of the overall procedure.

Table 4.2.1.

2,6-TDI recoveries near the detection limit

ng spiked	ng recovered
16.9	3.5
25.4	14.0
33.8	27.8
42.2	33.9
67.6	54.2
84.5	61.9
101.4	85.8

Table 4.2.2.

HDI recoveries near the detection limit

ng spiked	ng recovered
33.9	3.9
44.2	44.9
66.2	61.0
88.2	82.6
132.4	133.7

Table 4.2.3.

2,4-TDI recoveries near the detection limit

ng spiked	ng recovered
19.3	12.6
29.0	21.1
38.6	39.0
57.9	61.8
77.2	68.7
96.6	93.8
115.8	120.8

4.2.2. The graphical results of the above data are presented in Figures 4.2.1.-4.2.3., respectively.

Table 4.2.4.

Overall Detection Limit (ng/sample)

2,6-TDI	HDI	2,4-TDI
24.4	33.4	19.2

4.3. Reliable quantitation limit

The following data were obtained by vapor spiking the analytes onto sampling devices. The injection size recommended in the analytical procedure (25 μ L) was used to determine the reliable quantitation limit.

Table 4.3.1.

Extraction Efficiency at the Reliable Quantitation Limit

	2,6-TDI	HDI	2,4-TDI
spike (ng)	33.8	44.2	38.6
% recovery	117.4	124.8	82.9
	103.6	114.7	74.6
	103.6	96.8	70.8
	103.6	114.7	82.9
	103.6	114.7	74.6
	103.6	114.7	70.8
	103.6	96.8	82.9
	103.6	96.8	74.6
$\bar{X}$	105.3	109.3	76.8
SD	4.9	10.9	5.3
1.96 SD	9.6	21.4	10.4

4.4. Sensitivity and precision (analytical method only)

The following data were obtained from multiple injections of analytical standards.

Table 4.4.1.

0.5 X Target Concentration.

	2,6-TDI	HDI	2,4-TDI
$\mu\text{g/mL}$	0.700	0.722	0.704
Area	69054	70015	127935
	69310	70643	127591
	69380	70996	127408
	68824	70340	125457
	68117	68751	124953
	67271	68445	124032
	68701	69385	126054
	68643	69036	125588
	67196	68454	124185
$\bar{X}$	68499.6	69562.8	125911.4
SD	811	967	1454
CV	0.0118	0.0139	0.0115

Table 4.4.2.

1.0 X Target Concentration

	2,6-TDI	HDI	2,4-TDI
$\mu\text{g/mL}$	1.400	1.443	1.407
Area	127643	129539	236004
	126872	130474	235664
	126332	128313	233651
	127445	128379	234337
	126896	129521	234274
	126037	128186	231355
	127077	129882	234258
	126384	125878	229449
	127033	128370	234524
$\bar{X}$	126857.7	128726.9	233723.7
SD	526	1346	2076
CV	0.0041	0.0105	0.0089

Table 4.4.3.

2.0 X Target Concentration

	2,6-TDI	HDI	2,4-TDI
$\mu\text{g/mL}$	2.800	2.886	2.814
Area	249771	252219	459331
	244922	249296	457553
	248641	259363	458572
	246677	252678	461448
	246986	252581	461119
	245615	250940	457897
	252601	247011	463557
	248169	249906	460536
	248014	251679	459259
$\bar{X}$	247932.9	251741.4	459919.1
SD	2309	3396	1925
CV	0.0093	0.0135	0.0042

Table 4.4.4.

The Pooled Coefficients of Variation

2,6-TDI	HDI	2,4-TDI
0.0090	0.0127	0.0087

4.5. Sensitivity

The data in Tables 4.4.1.-4.4.3. are presented graphically in Figures 4.4.1.-4.4.3.

4.6. Retention efficiency

4.6.1. Two retention studies were conducted, the first at 12% relative humidity and the second at 78% relative humidity. The samples were vapor spiked and removed from the sample generator after a known volume of air had passed through the cassette.

Table 4.6.1.

10.0 X Target Concentration at 12%
R.H., 200 L Air Volume
% Recovery

	2,6-TDI	HDI	2,4-TDI
ug spiked	27.92	36.44	31.84
filter	96.9	97.2	94.4
backup	1.0	2.0	0.8
filter	95.6	95.6	92.9
backup	0.9	1.8	0.6

Table 4.6.2.

1.0 X Target Concentration at 78% R.H.
% Recovery

Air Volume, L	2,6-TDI	HDI	2,4-TDI
5.25	90.8	91.5	85.1
5.25	90.3	88.4	84.0
10.5	91.2	89.8	84.5
15.75	89.7	92.0	82.6
15.75	89.7	86.7	78.9
21.0	89.8	90.0	82.3
21.0	85.1	88.4	77.4
26.25	88.8	93.8	81.7
26.25	84.0	92.4	78.2
31.5	84.5	87.5	77.1
36.75	84.7	89.1	80.0
42.0	86.8	90.3	80.1
42.0	85.9	90.0	79.7
47.25	84.9	84.7	79.2
47.25	84.0	84.4	75.7
52.5	87.4	90.9	80.8
52.5	86.4	87.2	79.4

4.6.2. The following data are presented to show that the diisocyanate derivatives, liquid spiked, are retained on the coated glass fiber filter at the recommended air volume:

Table 4.6.3.

Recoveries after 20 liters at 80% R.H.

	2,6-TDI	HDI	2,4-TDI
ug spiked	2.792	3.644	3.184
% Recovery	83.7	79.6	76.0
	93.1	81.4	88.5
	90.1	81.1	86.3
	95.8	81.7	91.4
	89.4	80.8	86.5
	83.6	78.9	78.9
	78.9	75.0	73.0
	88.6	82.3	82.7
$\bar{X}$	87.9	80.1	82.4
SD	5.5	2.3	6.4

4.6.3. Ten liters of 80% R.H. air were drawn through a filter to moisten it and then it was vapor spiked with 20 liters of dry air to observe the retention of the derivative on the wet filter.

Table 4.6.4.

Recoveries from a wet filter

	2,6-TDI	HDI	2,4-TDI
ug spiked	2.792	3.644	3.184
% Recovery	100.5	91.6	84.4
	99.6	90.6	79.4
	97.8	88.8	77.8
	104.2	95.9	84.4
	97.8	89.7	81.7
$\bar{X}$	100.0	91.4	81.5
SD	2.6	2.8	3.0

4.7. Extraction efficiency

The following data represent the analysis of coated glass fiber filters vapor spiked with the analytes at 0.05 X and 1 X the target concentrations:

Table 4.7.1.

Extraction Efficiency at 0.05 X Target Concentration

	2,6-TDI	HDI	2,4-TDI
$\mu\text{g/sample}$	0.1396	0.1822	0.1592
% Recovery	86.0	93.9	98.6
	92.8	90.0	102.1
	80.2	91.7	98.5
	84.2	92.2	100.9
	69.3	91.3	100.1
	89.4	104.9	111.3
	91.7	96.1	96.1
	95.1	91.7	95.6
	77.4	85.6	87.7
	91.7	96.6	101.6
	103.2	107.6	108.2
	94.6	99.6	100.0
$\bar{X}$	88.0	95.1	100.1

Table 4.7.2.

Extraction Efficiency at 1 X Target Concentration

	2,6-TDI	HDI	2,4-TDI
$\mu\text{g/sample}$	2.792	3.644	3.184
% Recovery	92.0	92.2	93.0
	95.6	98.9	98.1
	92.6	94.1	92.9
	92.4	92.9	94.4
	91.8	92.9	92.0
	93.7	94.9	93.9
	88.3	94.5	85.8
	89.6	92.8	85.5
	90.2	94.3	88.6
	90.8	91.5	90.5
	87.7	88.6	87.5
	89.9	92.3	87.6
$\bar{X}$	91.2	93.3	90.8

4.8. Reproducibility data

The data in Table 4.8.1. represent the results of an unassociated chemist analyzing samples that have been stored 6 days at -25°C. The results are corrected for extraction efficiencies.

Table 4.8.1.

Reproducibility Results, % Recovery

	2,6-TDI	HDI	2,4-TDI
	102.5	101.3	106.2
	98.8	97.0	103.4
	102.7	102.0	108.6
	102.5	101.3	106.2
	101.2	100.6	102.6
$\bar{X}$	101.5	100.4	105.4
SD	1.6	2.0	2.4

4.9. Storage data

The data in Tables 4.9.2. and 4.9.3. represent the effects of storage at ambient (22°C) and reduced (-20°C) temperatures on vapor spiked cassettes, which were generated with 20 L of dry air followed by 3 L humid air to moisten the system. The results are not corrected for extraction efficiency. The data are also presented graphically in Figures 4.9.1.-4.9.6.

Table 4.9.1.

Amount Vapor Spiked, µg/Cassette

2,6-TDI	HDI	2,4-TDI
2.792	3.644	3.184

Table 4.9.2.

Ambient Temperature Storage, % Recovery

Day	Sample	2,6-TDI	HDI	2,4-TDI
0	1	77.8	75.9	74.6
	2	85.5	82.3	78.6
	3	90.9	89.7	84.7
	4	89.5	91.2	87.7
	5	84.2	81.9	81.3
	6	87.8	83.8	82.9
4	1	89.8	84.4	83.6
	2	89.0	83.9	82.7
	3	91.0	81.1	81.7
7	1	94.6	82.1	80.4
	2	86.5	75.1	72.9
	3	90.5	81.9	78.6
11	1	95.1	82.2	81.4
	2	97.1	82.5	79.8
	3	87.3	77.7	72.1
14	1	103.7	85.9	84.2
	2	99.4	82.8	78.4
	3	103.9	88.4	82.3
18	1	95.3	81.8	79.8
	2	95.5	84.4	82.0
	3	102.0	85.0	82.9

Table 4.9.3.

Reduced Temperature Storage, % Recovery

Day	Sample	2,6-TDI	HDI	2,4-TDI
0	1	77.8	75.9	74.6
	2	83.5	82.3	78.6
	3	90.9	89.7	84.7
	4	89.5	91.2	87.7
	5	84.2	81.9	81.3
	6	87.8	83.8	82.9
4	1	84.5	79.6	80.5
	2	88.3	80.8	87.8
	3	83.5	79.3	79.5
7	1	91.0	86.9	83.3
	2	92.4	86.2	84.0
	3	99.0	95.4	89.3
11	1	80.9	76.4	75.1
	2	85.7	80.0	80.9
	3	81.4	75.4	76.4
14	1	89.6	87.5	83.9
	2	83.7	81.7	78.4
	3	94.6	91.2	88.4
18	1	75.7	71.4	73.8
	2	85.2	81.1	82.6
	3	89.7	83.0	86.2

4.10. Side-by-side sampling

A simple experiment was designed which allowed a bubbler containing nitro reagent and a glass fiber filter coated with 1-2PP to be simultaneous vapor spiked from the same 2,4-TDI atmosphere. This was accomplished by leaching a known amount of 2,4-TDI off a glass wool plug contained in a glass tube with dilution air which is then passed through a "Y" to each sampler. The air flow was controlled by calibrated orifices of similar flow rate down stream from the samplers.

Each sample was analyzed twice and its average was plotted in Figure 4.10. The differences between the bubbler samples and the filter samples appear to be random with no discernible bias between them. The amount of scatter observed in both collection systems was not expected and probably can be attributed to the

experimental design. The average line plotted in Figure 4.10. represents the average of all the collected samples and the data is presented in Table 4.10.

Table 4.10.

Analysis of Side-By-Side Samples, $\mu\text{g}/\text{m}^3$

Spike	Collection		Collection	
	Average	System	Average	System
1	192	F	207	F
2	197.5	F	209.5	F
3	164.5	B	162.5	B
4	172.5	B	179	B
5	208.5	F	224.5	B
6	231	F	181	B
7	230	F	244.5	B
8	222.5	F	223	B
9	233.5	F	216	B
10	226	F	250.5	B
11	221.5	F	146.5	B
12	226.5	F	199.5	B
13	212	F	240.5	B
14	21	F	218.5	B
15	223.5	F	245	B
16	225	F	296.5	B
17	202.5	B	230	B
18	219.5	B	176.5	B
19	174	F	248	F
20	331.5	F	269	F

F = Glass Fiber Filter with 1-2PP

B = Toluene Bubbler with nitro reagent

4.11. Chromatograms

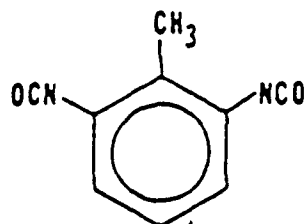
Figure 4.11. is a computer representation of a chromatogram of derivatives of diisocyanate standards.

4.12. UV Spectra

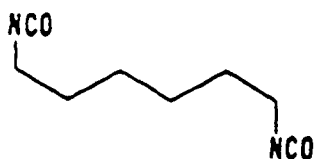
Figures 4.12.1. - 4.12.3. are the UV spectra of the 1-2PP derivatives of the diisocyanates used in this study. The three compounds are named below:

CAS number	Name
	2,6-Bis(4-(2-pyridyl)-1-piperazinylcarbonyl) toluene
72375-27-0	1,6-Bis(4-(2-pyridyl)-1-piperazinylcarbonyl) hexane
72375-21-4	2,4-Bis(4-(2-pyridyl)-1-piperazinylcarbonyl) toluene

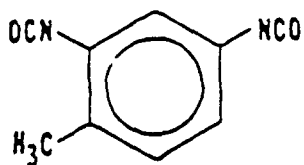
Figure 1.1.4. Synonyms and structures



toluene-2,6-diisocyanate;
2,6-toluene diisocyanate;
2,6-diisocyanato-1-methyl benzene;
isocyanic acid, 2-methyl-1,3-phenylene ester;
2,6-TDI



1,6-hexamethylene diisocyanate;
HDI



toluene-2,4-diisocyanate;
2,4-toluene diisocyanate;
2,4-diisocyanato-1-methyl benzene;
isocyanic acid, 4-methyl-1,3-phenylene ester;
2,4-TDI

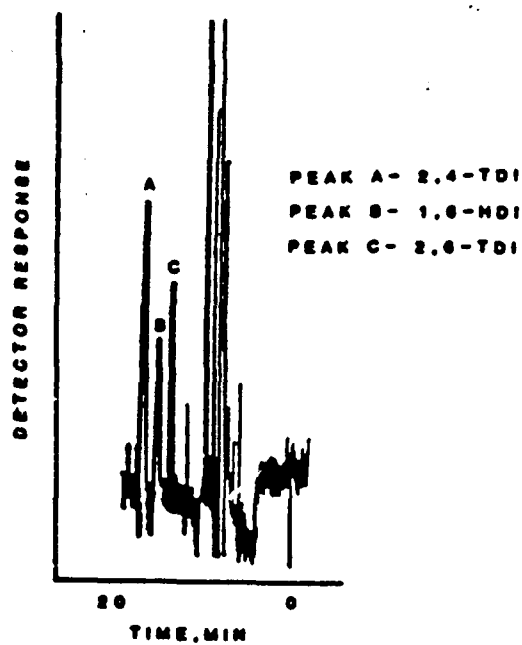


FIGURE 4.1. DETECTION
LIMIT OF THE ANALYTICAL
PROCEDURE.

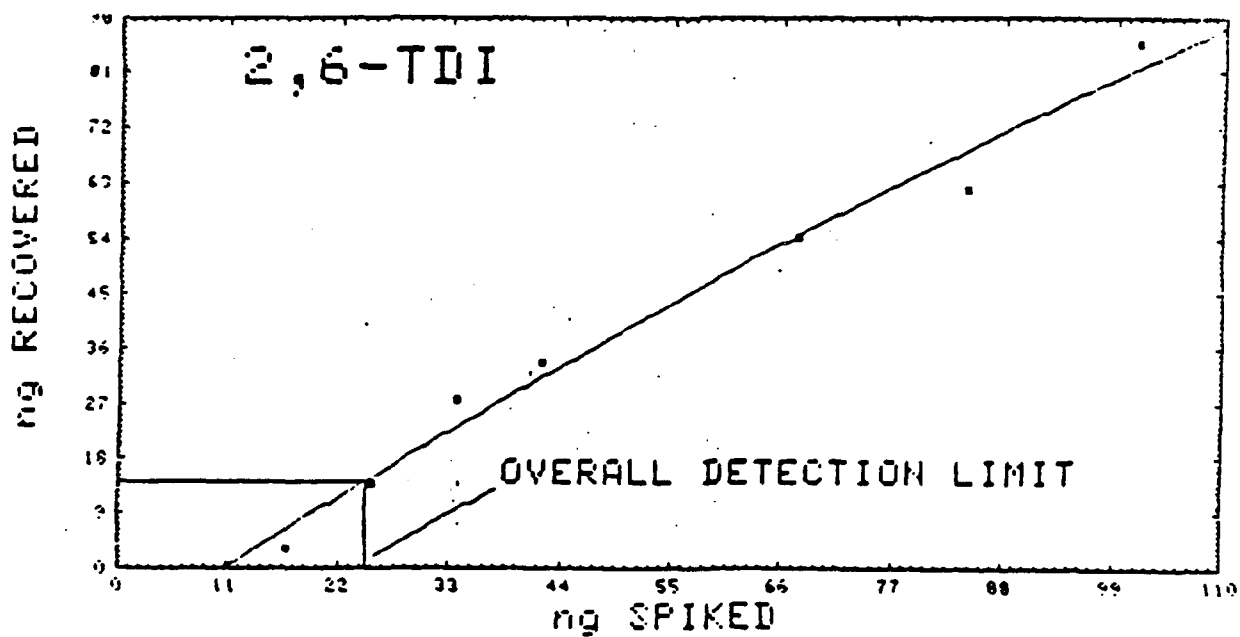


FIGURE 4.2.1.

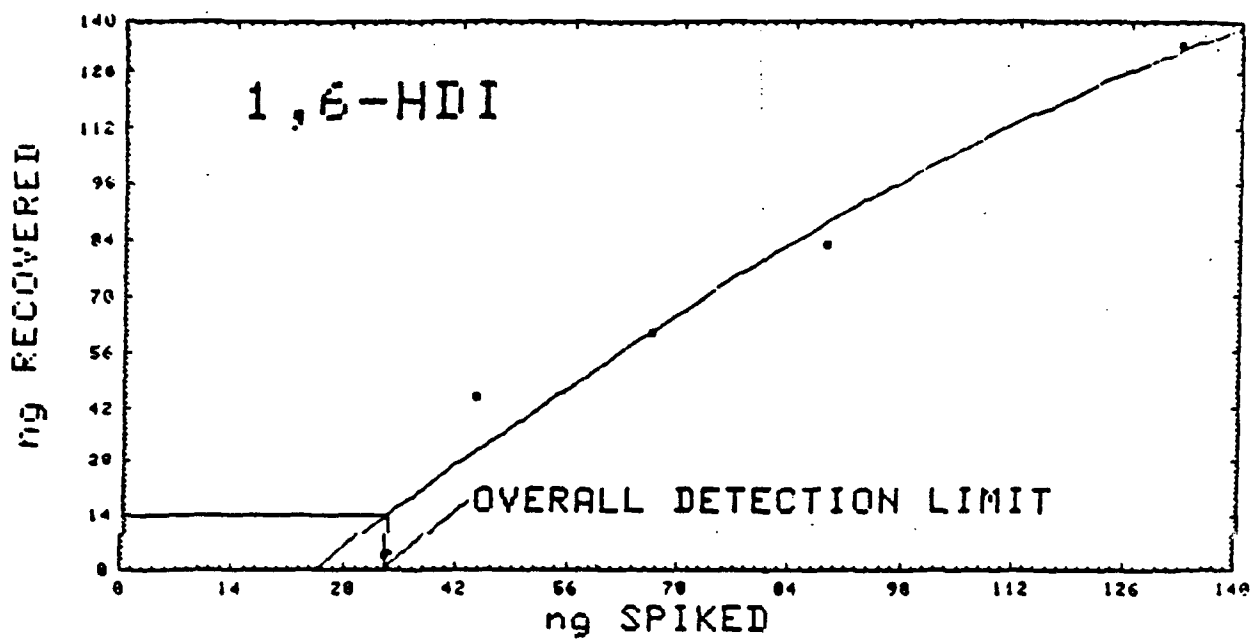


FIGURE 4.2.2

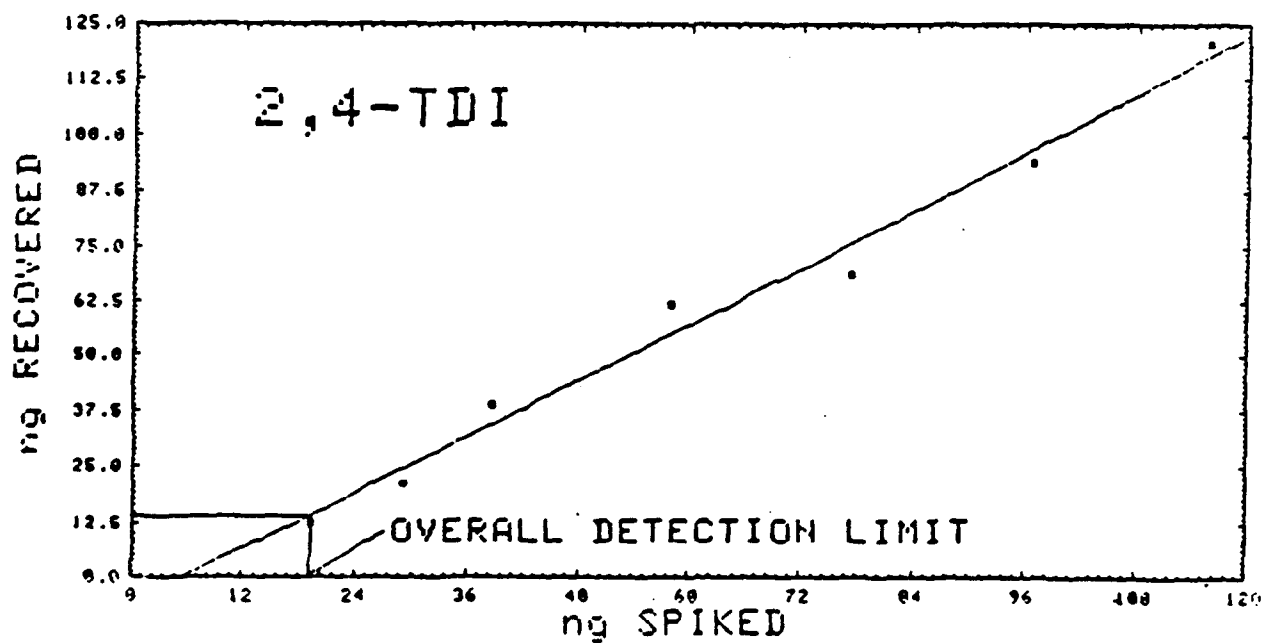


FIGURE 4.2.3.

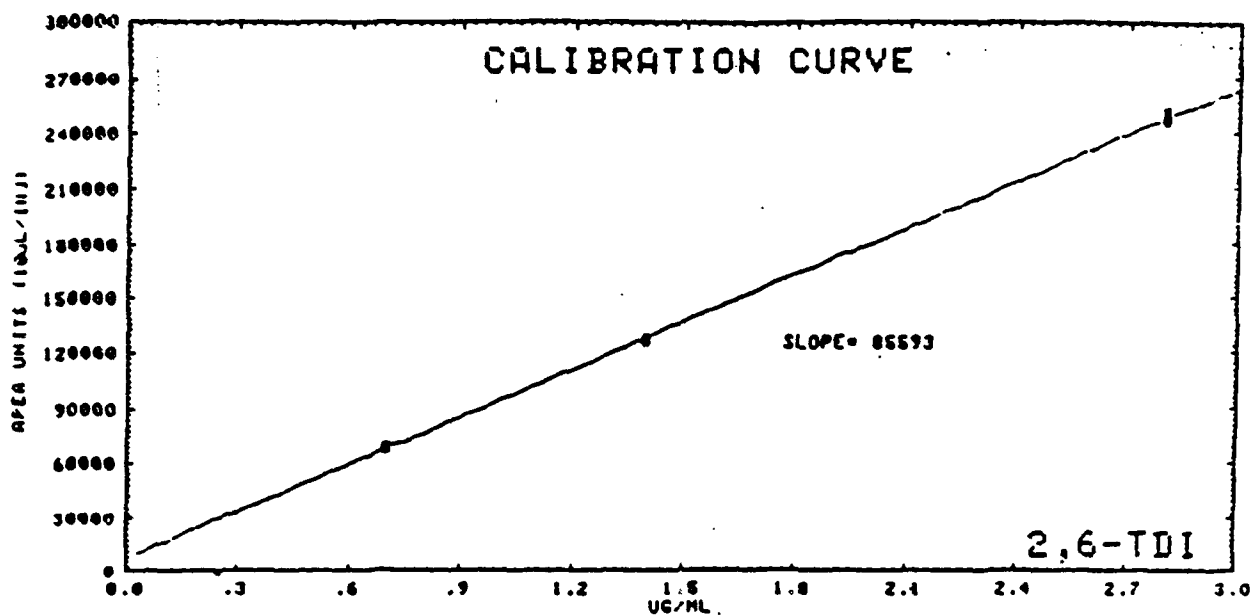


FIGURE 4.4.1.

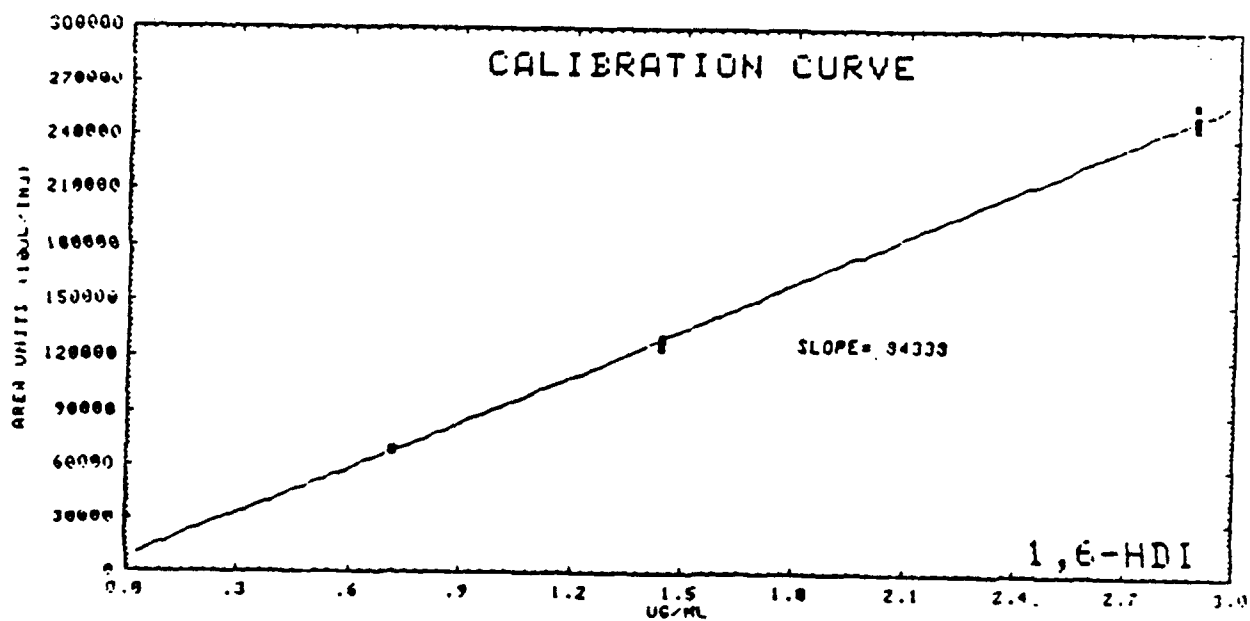


FIGURE 4.4.2.

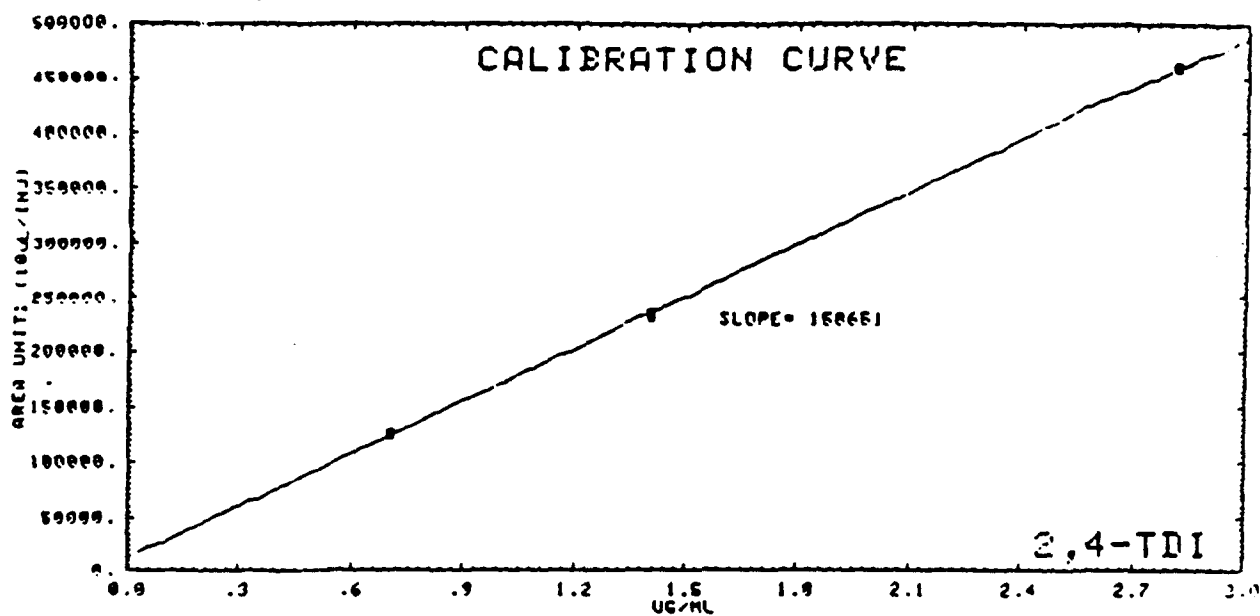


FIGURE 4.4.3.

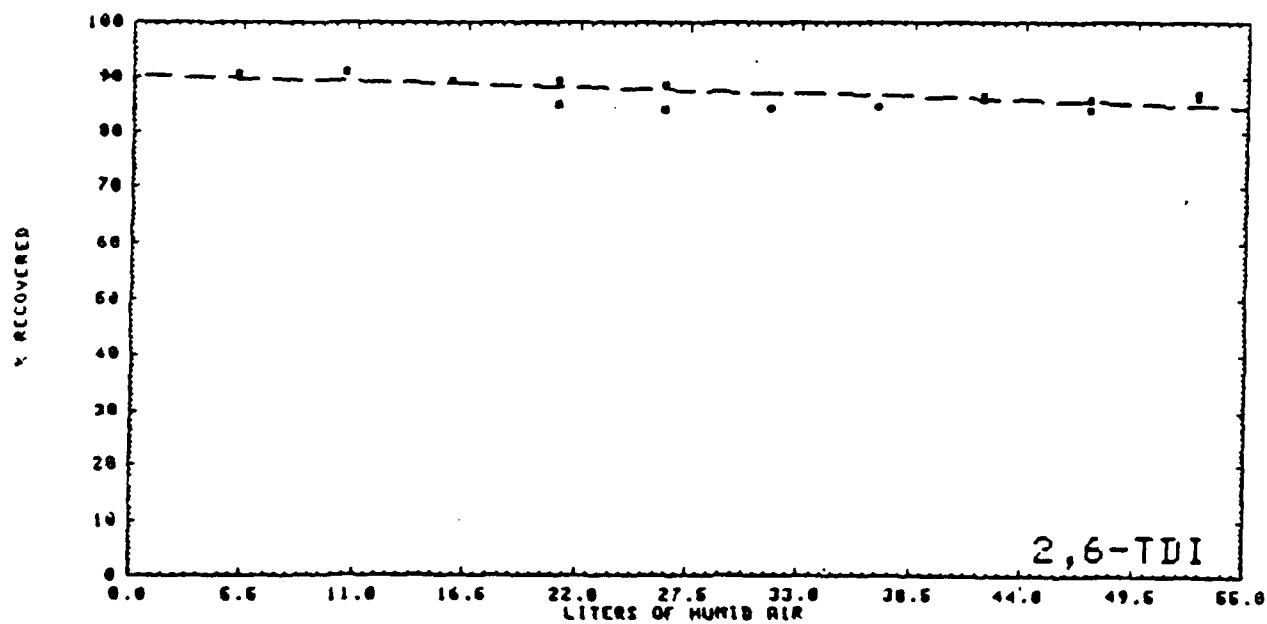


FIGURE 4.6.1. DETERMINATION OF MAXIMUM AIR VOLUME.

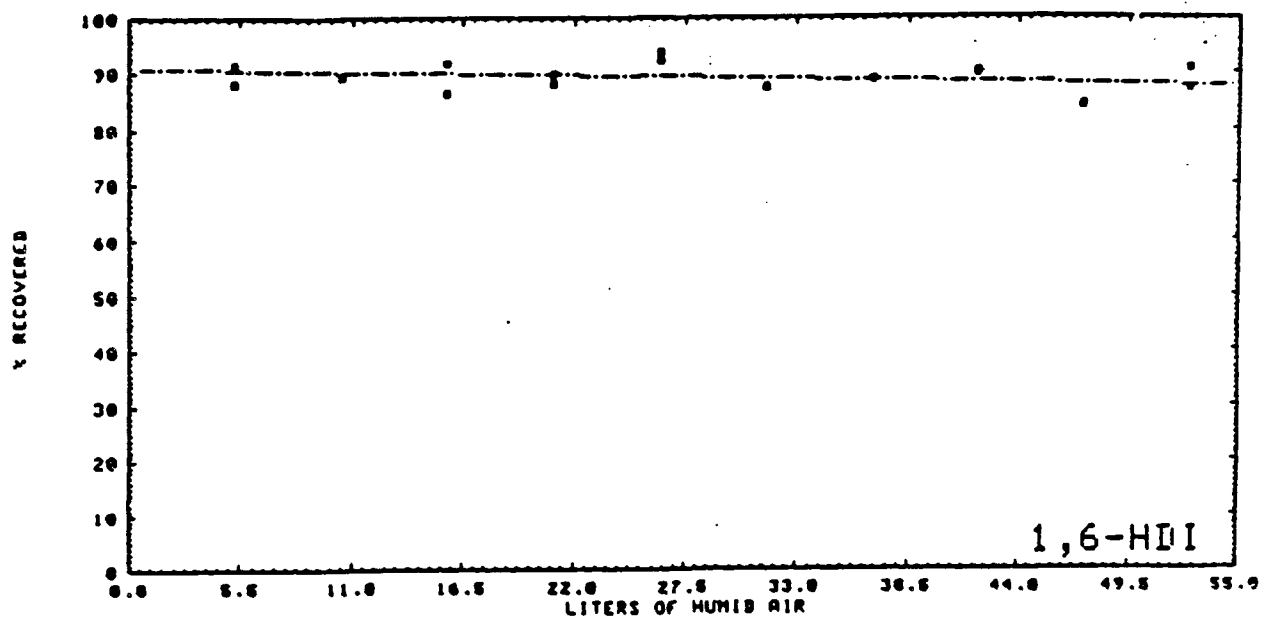


FIGURE 4.6.2. DETERMINATION OF MAXIMUM AIR VOLUME.

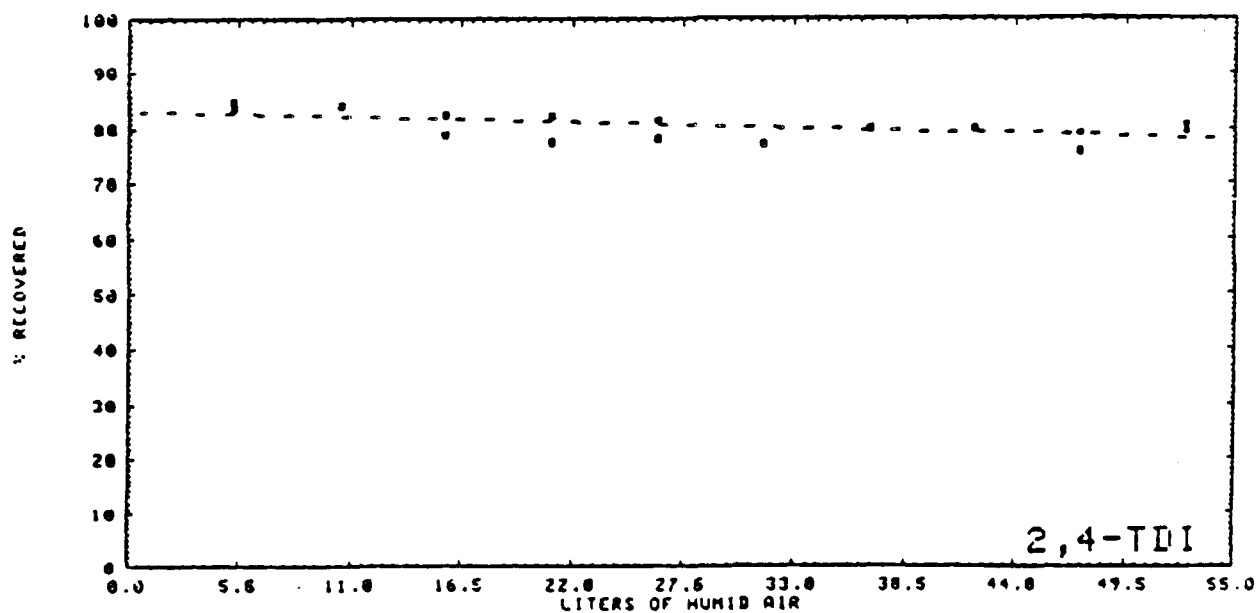


FIGURE 4.6.3. DETERMINATION OF MAXIMUM AIR VOLUME.

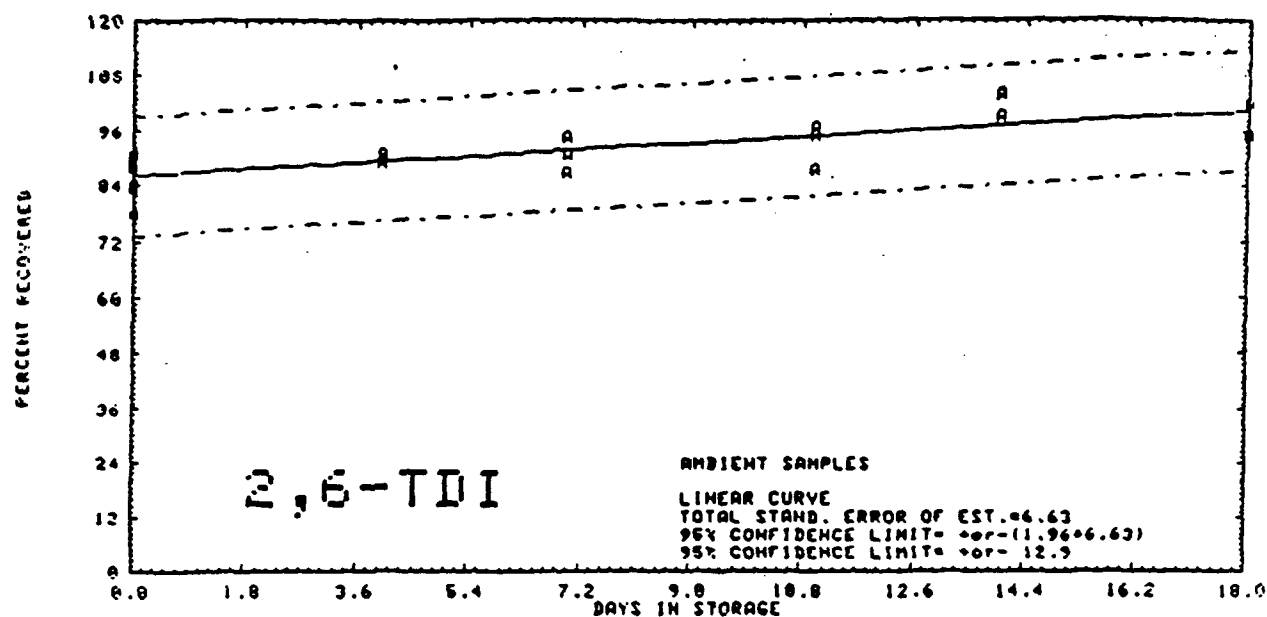


FIGURE 4.9.1. STORAGE TEST.

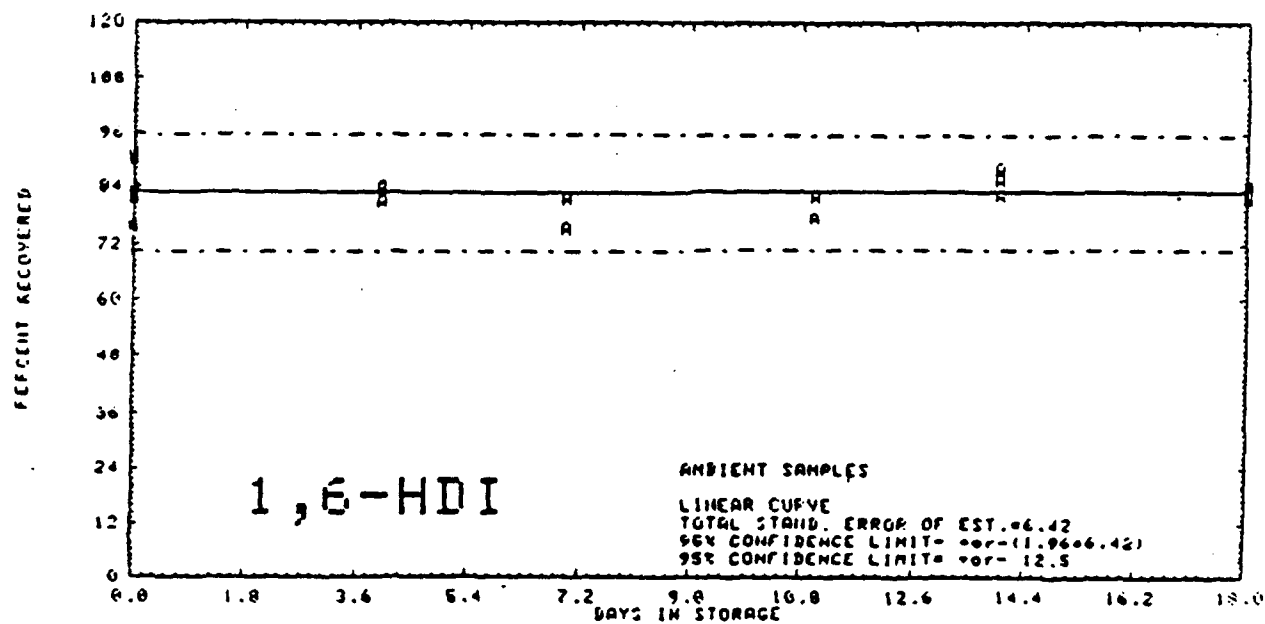


FIGURE 4.9.2. STORAGE TEST.

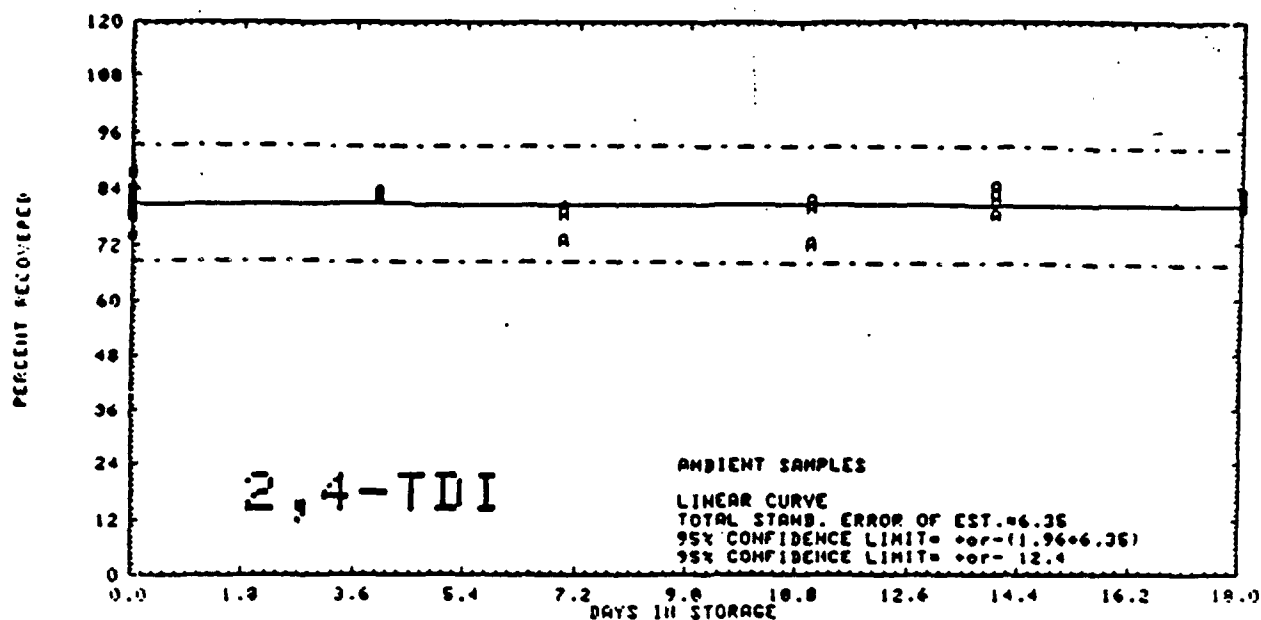


FIGURE 4.8.3. STORAGE TEST.

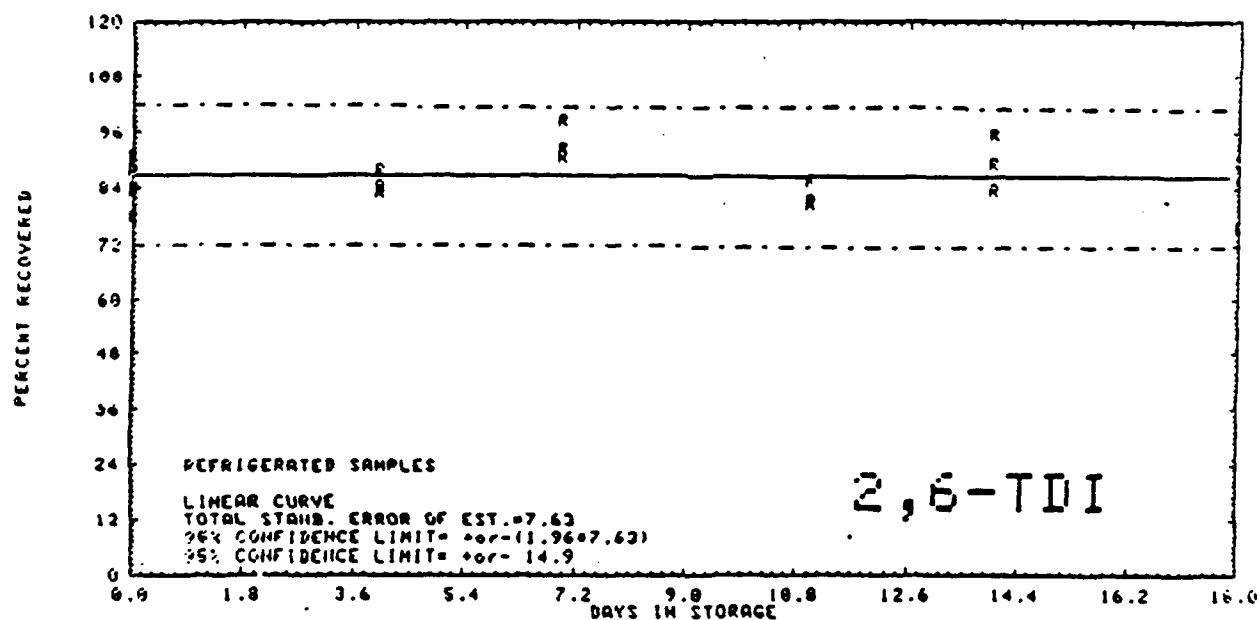


FIGURE 4.8.4. STORAGE TEST.

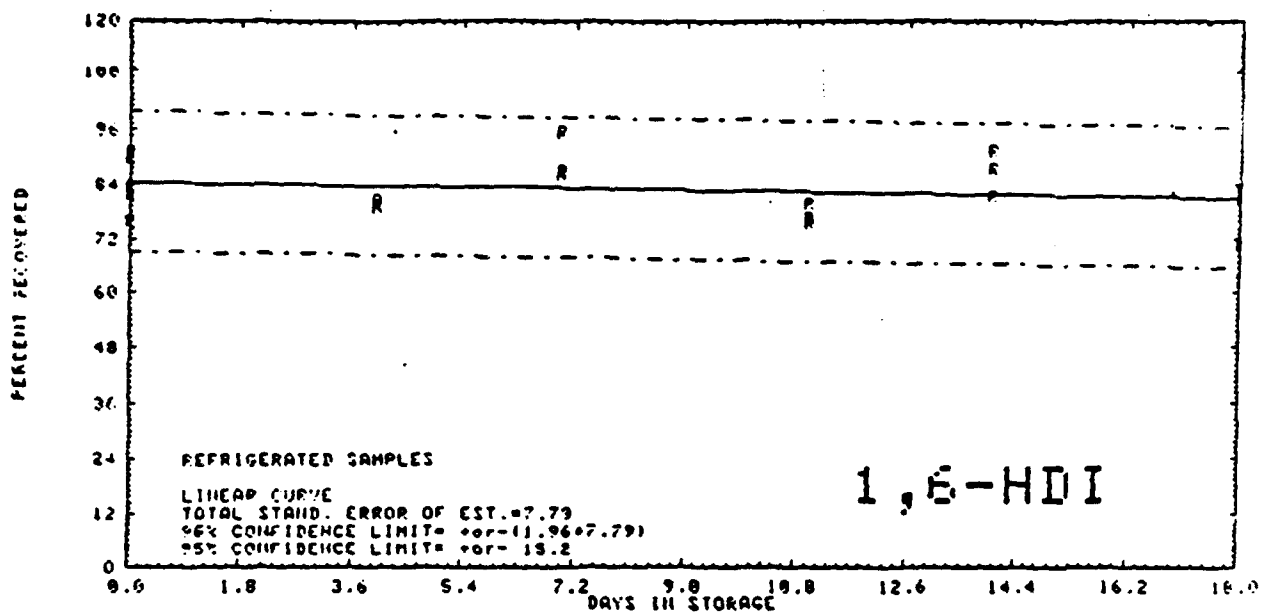


FIGURE 4.9.5. STORAGE TEST.

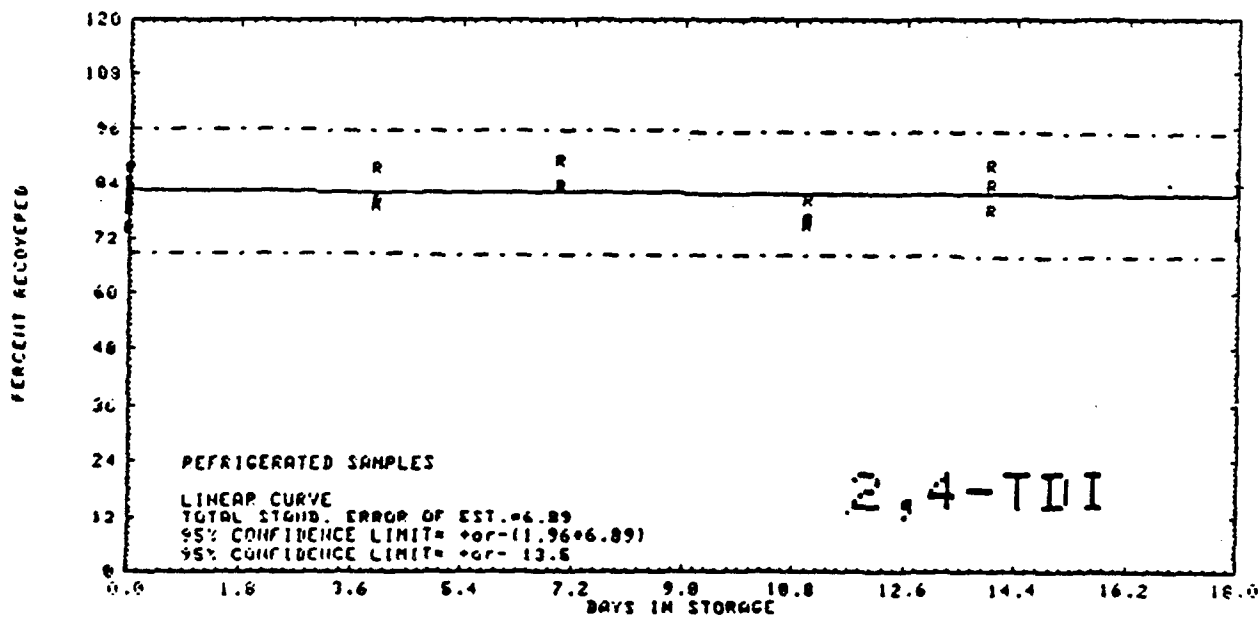


FIGURE 4.9.6. STORAGE TEST.

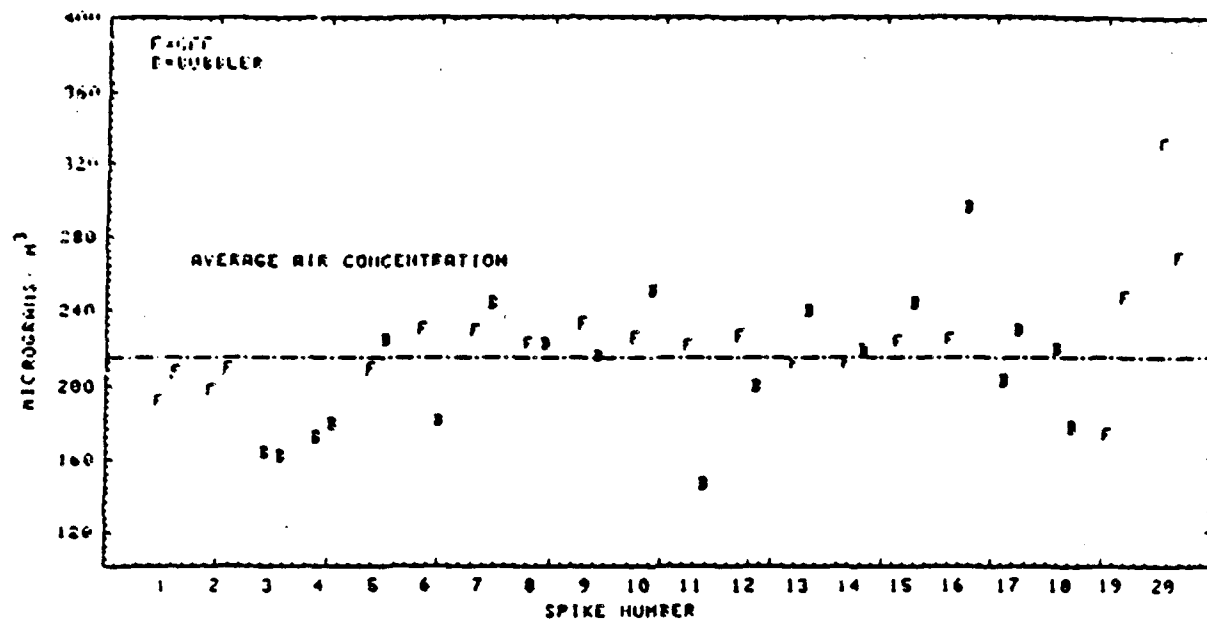


FIGURE 4.10. SIDE-BY-SIDE COMPARISON.

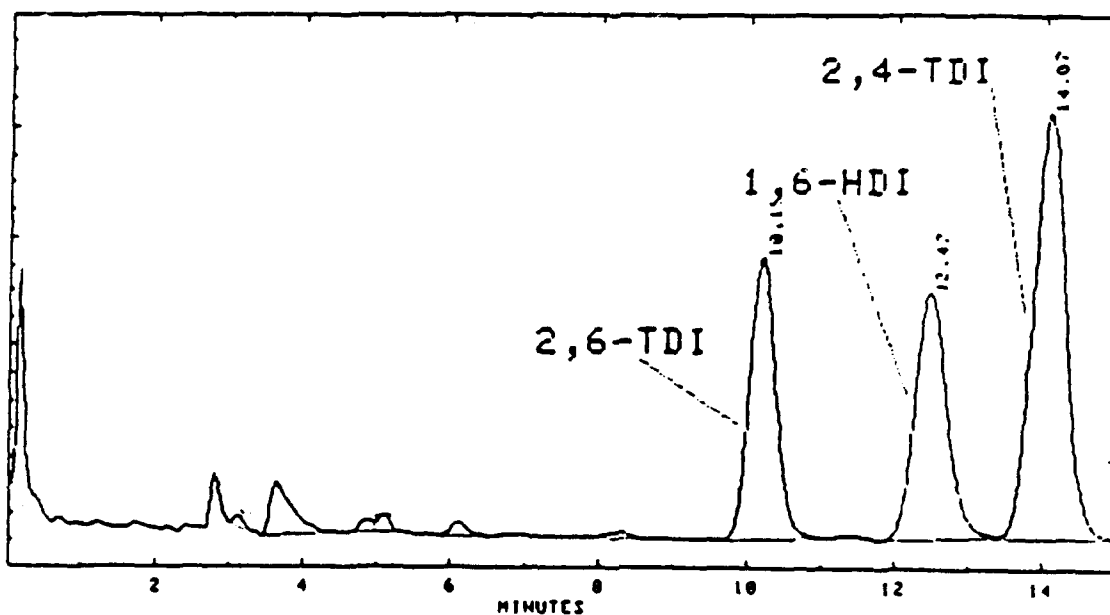


FIGURE 4.11. SEPARATION OF DIISOCYANATE DERIVATIVES AT 254 NM.

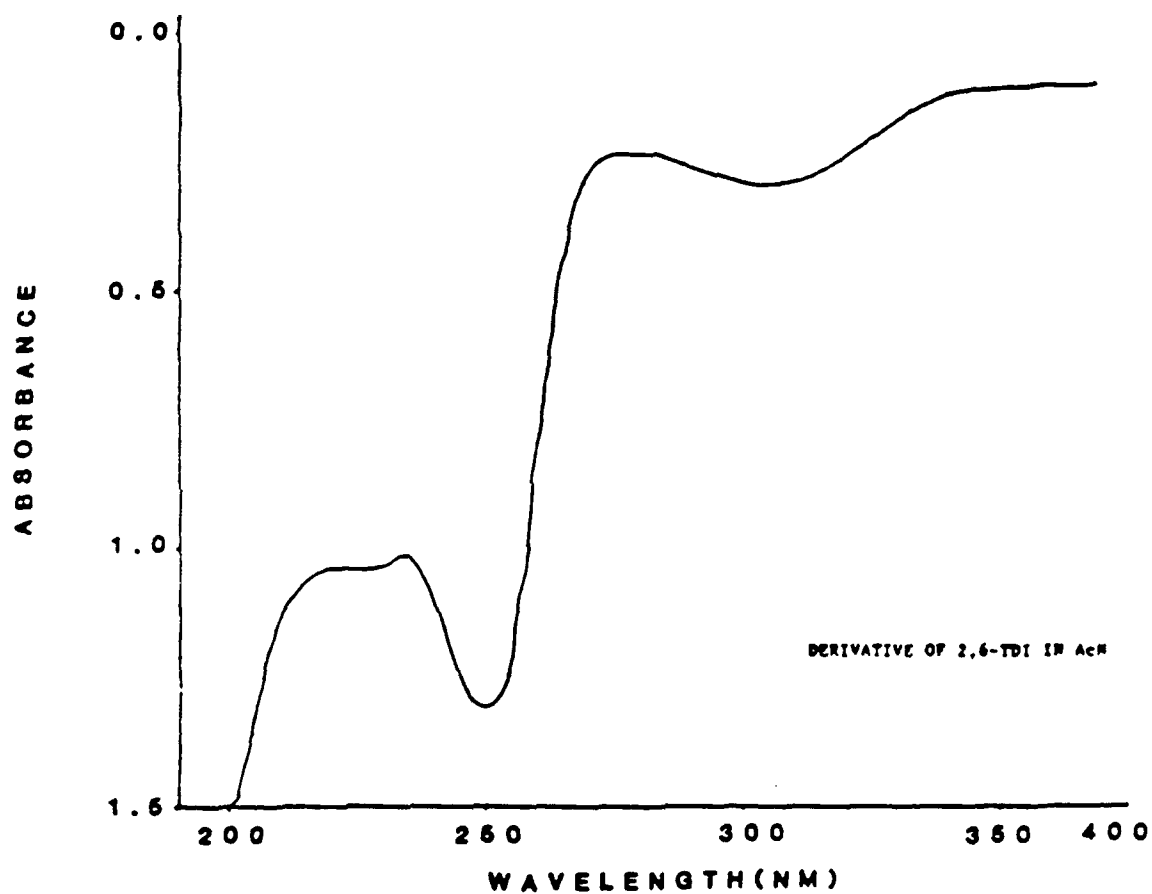


FIGURE 4.12.1.

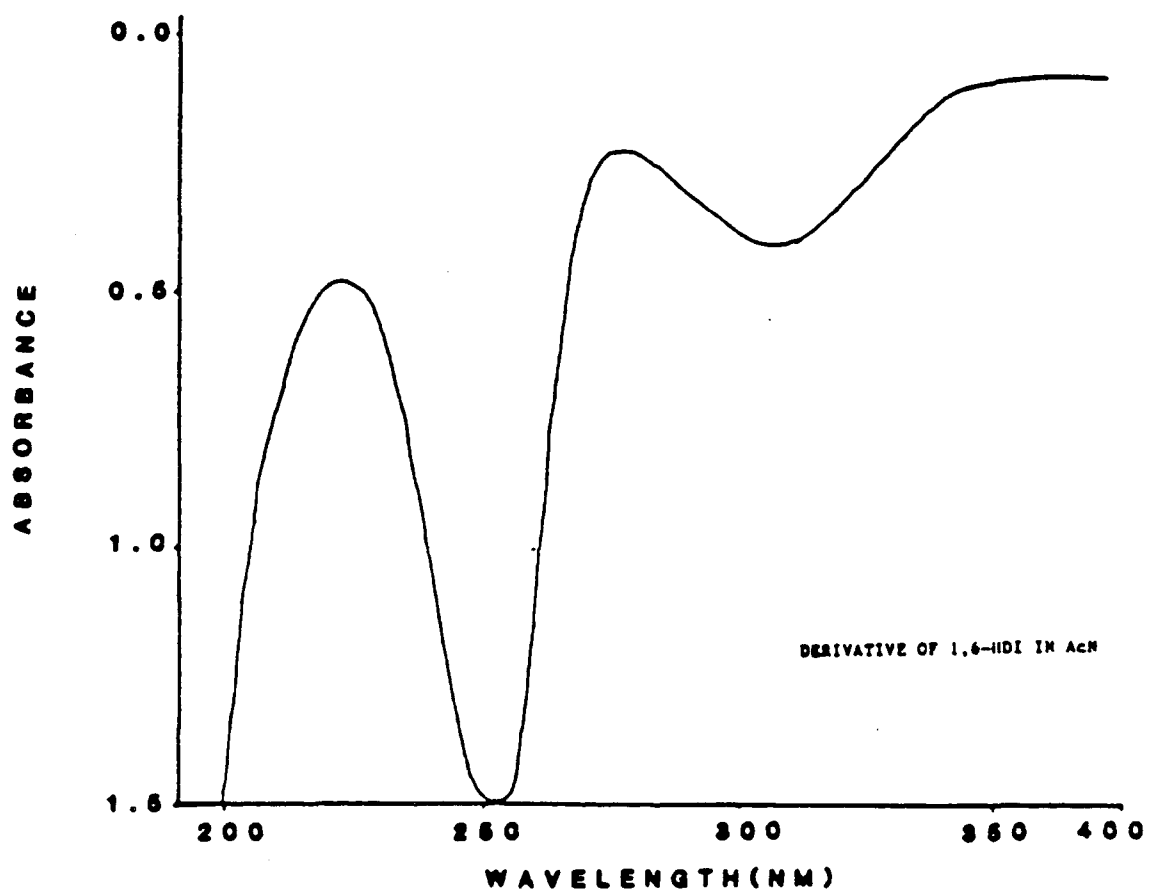


FIGURE 4.12.2.

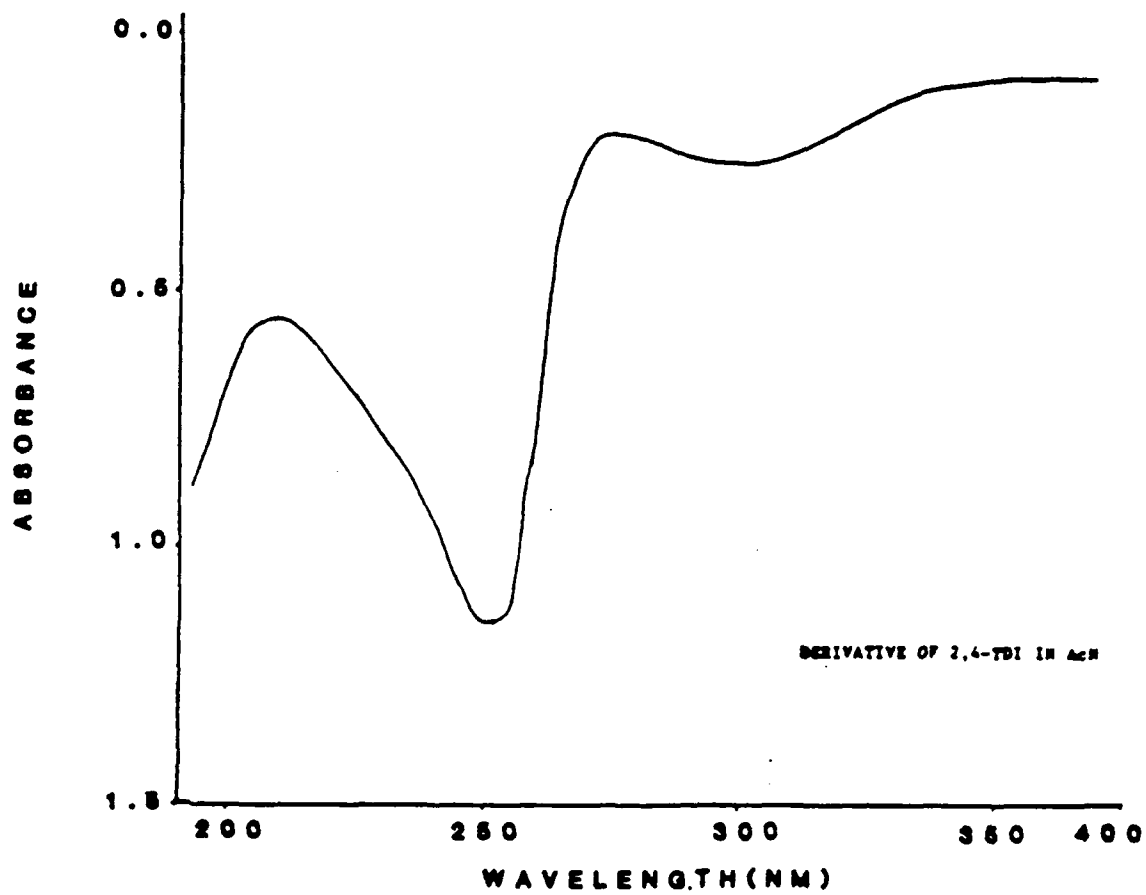


FIGURE 4.12.3.

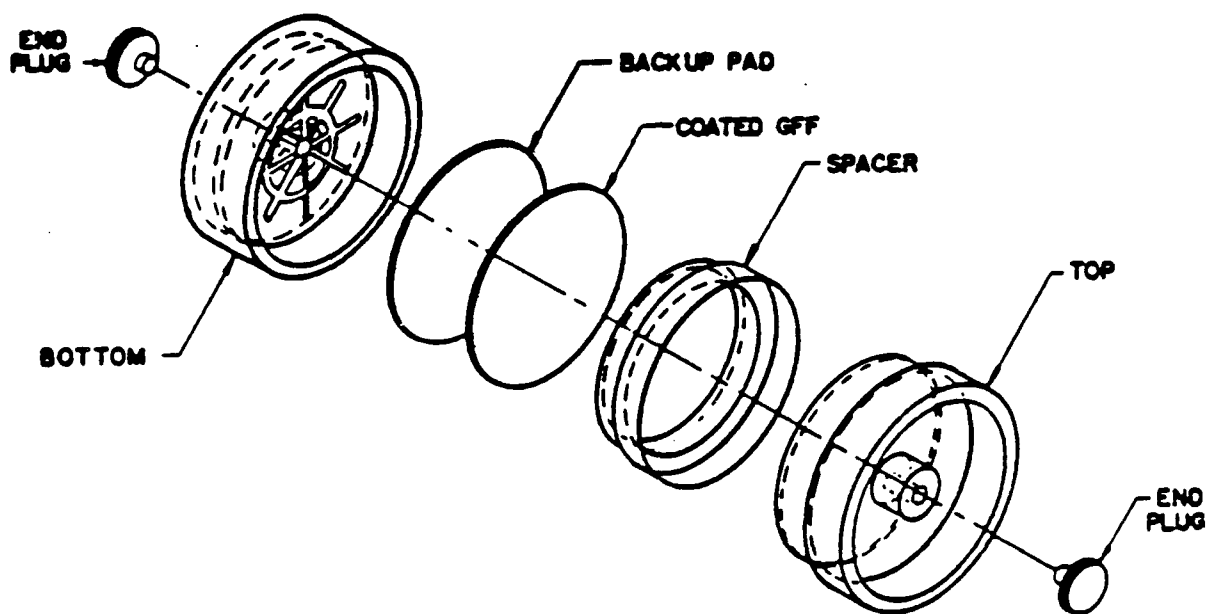


FIGURE 4.13.1. SAMPLE CASSETTE.

5. References

- 5.1. "Criteria for a Recommended Standard...Occupational Exposure to Toluene Diisocyanate", Department of Health, Education and Welfare, National Institute for Occupational Safety and Health: Cincinnati, OH, 1973; HMS 73-11022.
- 5.2. "Criteria for a Recommended Standard...Occupational Exposure to Diisocyanates"; Department of Health, Education and Welfare, National Institute for Occupational Safety and Health: Cincinnati, OH, 1978; DHEW (NIOSH) Publ. (U.S.), No. 78-215.
- 5.3. Kormos, L.H.; Sandridge, R.L.; Keller, Anal. Chem. 1981, 53, 1125.
- 5.4. Sango, C.; Zimerson, E. J. Liq. Chromatogr. 1980, 3, 971.
- 5.5. Hardy, H.L.; Walker, R.F. Analyst 1979, 104, 890.
- 5.6. Ellwood, P.A., Hardy, H.L.; Walker, R.F. Analyst 1981, 106, 85.
- 5.7. Goldberg, P.A.; Walker, R.F.; Ellwood, P.A.; Hardy, H.L. J. Chromatogr. 1981, 212, 93.
- 5.8. Hosein, H.R.; Farkes, S. Am. Ind. Hyg. Assoc. J. 1981, 42, 663.
- 5.9. Woolrich, P.F. Am. Ind. Hyg. Assoc. J. 1982, 43, 89.
- 5.10. Cummins, K., Diisocyanates, 2,4-TDI and MDI (Method 18, Organic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, Utah) unpublished (2-80).

APPENDIX C
OSHA RULING ON PAINT BOOTH EXHAUST GAS RECIRCULATION

[Unedited reproduction of correspondence and attached material.]

U.S. Department of Labor

Occupational Safety and Health Administration
Washington, D.C. 20210

Reply to the Attention of:



JAN 16 1990

Susan R. Wyatt, Chief
Chemicals and Petroleum Branch
Emission Standards Division
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

Dear Ms. Wyatt:

This is in response to your letter of October 31, 1989, concerning the Occupational Safety and Health Administration (OSHA) regulation at 29 CFR 1910.107(d)(9) which prohibits the recirculation of exhaust air from spray finishing operations. Please excuse the delay in response.

As you are aware, 29 CFR 1910.107 was adopted from the NFPA 33-1969, Standard for Spray Finishing Using Flammable and Combustible Materials. The NFPA-33 standard is explicitly a fire and explosion safety standard. Therefore, the OSHA standard at 29 CFR 1910.107 pertains to the prevention of workplace fire and explosion hazards and does not pertain to health considerations.

Although the NFPA has updated their standard since the 1969 edition, OSHA has not. As a result, the current NFPA 33-1985, Spray Application Using Flammable and Combustible Materials, reflects the most up to date state of the art concerning the prevention of fire and explosion hazards during spray finishing operations.

Under an OSHA policy for "de minimis violations", employers are encouraged to abide by the most current consensus standard applicable to their operations, rather than with the standard in affect at the time of the inspection when the employer's action provides equal or greater employee protection. De minimis violations are violations of existing OSHA standards which have no direct or immediate relationship to safety or health. Such violations of the OSHA standards result in no citation, no penalty and no required abatement. A copy of the OSHA policy for de minimis violations is enclosed.

JUN 15 1989

6. De Minimis Violations. De minimis violations are violations of standards which have no direct or immediate relationship to safety or health. Whenever de minimis conditions are found during an inspection, they shall be documented in the same way as any other violation but shall not be included on the citation.

- a. Explanation. The criteria for finding a de minimis violation are as follows:

- (1) An employer complies with the clear intent of the standard but deviates from its particular requirements in a manner that has no direct or

immediate relationship to employee safety or health. These deviations may involve distance specifications, construction material requirements, use of incorrect color, minor variations from recordkeeping, testing, or inspection regulations, or the like.

EXAMPLES: (a) 29 CFR 1910.27(b)(1)(ii) allows 12 inches as the maximum distance between ladder rungs. Where the rungs are 13 inches apart, the condition is de minimis.

(b) 29 CFR 1910.28(a)(3) requires guarding on all open sides of scaffolds. Where employees are tied off with safety belts in lieu of guarding, the intent of the standard is met; and the absence of guarding is de minimis.

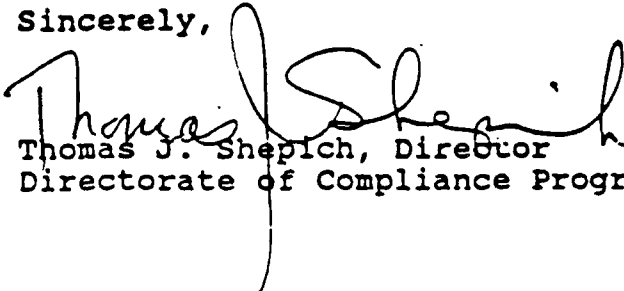
(c) 29 CFR 1910.217(e)(1)(ii) requires that mechanical power presses be inspected and tested at least weekly. If the machinery is seldom used, inspection and testing prior to each use is adequate to meet the intent of the standard.

- (2) An employer complies with a proposed standard or amendment or a consensus standard rather than with the standard in effect at the time of the inspection when the employer's action provides equal or greater employee protection.
- (3) An employer's workplace is at the "state of the art" which is technically beyond the requirements of the applicable standard and provides equivalent or more effective employee safety or health protection.
- b. Professional Judgment. Maximum professional discretion must be exercised in determining the point at which noncompliance with a standard constitutes a de minimis violation.
- c. Area Director Responsibilities. Area Directors shall ensure that the de minimis violation meets the criteria set out in B.6.a.

Employers who fully comply with the specifications and requirements of the NPPA 33-1989, concerning the recirculation of exhaust air to an occupied spray booth, would not be cited under 29 CFR 1910.107(d)(9) under the policy for de minimis violations. However, the quality of the respirable air in the booth must comply, at a minimum, with the requirements set forth by 29 CFR 1910.1000 which establishes permissible exposure limits (PEL's).

If we may be of further assistance, please contact us.

Sincerely,


Thomas J. Sheplich, Director
Directorate of Compliance Programs